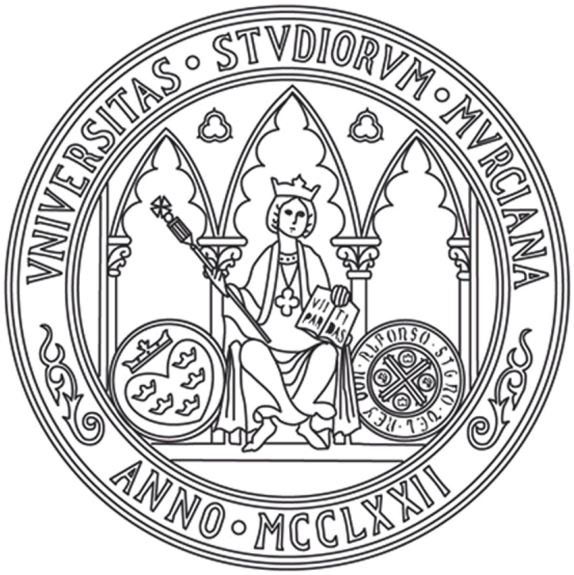

UNIVERSIDAD DE MURCIA

DEPARTAMENTO DE QUÍMICA INORGÁNICA

Synthesis, Characterization and Reactivity of Mono-, Di-, and Tripalladated *ortho*-Substituted Arenes

Síntesis, Caracterización y Reactividad de Arenos Mono-, Di- y Tripaladiados con Sustituyentes en *orto*

Dña. María José Fernández Rodríguez

2015

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Memoria presentada por Dª María José Fernández Rodríguez para optar al grado de Doctor por la Universidad de Murcia

Dado que la presente Tesis ha sido redactada en inglés, se incluye un resumen en castellano, con una extensión de más de 2000 palabras y encuadernado como parte de la Tesis, en cumplimiento del Artículo 18 del Reglamento de Doctorado de la Universidad de Murcia (“Redacción de la Tesis”).

UNIVERSIDAD DE
MURCIA

D. JOSÉ J. VICENTE SOLER, Catedrático de Universidad, y Dª ELOÍSA MARTÍNEZ VIVIENTE, Profesora Titular de Universidad, ambos del Departamento de Química Inorgánica de la Universidad de Murcia, AUTORIZAN:

La presentación de la Tesis Doctoral titulada **"SÍNTESIS, CARACTERIZACIÓN Y REACTIVIDAD DE ARENOS MONO-, DI- Y TRIPALADIADOS CON SUSTITUYENTES EN *ORTO*"**, realizada por Dña. MARÍA JOSÉ FERNÁNDEZ RODRÍGUEZ bajo su inmediata dirección y supervisión, y que presenta para la obtención del grado de Doctor por la Universidad de Murcia.

Murcia, 30 de septiembre de 2015

Fdo.: José J. Vicente Soler

Fdo.: Eloísa Martínez Viviente

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Deseo expresar mi más sincero agradecimiento a todas las personas que de alguna forma me han ayudado en la realización de esta Tesis Doctoral, especialmente:

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A la memoria de mi padre

ABBREVIATIONS

1D	one-dimensional
2D	two-dimensional
A	anion (OTf^- or ClO_4^-)
AcOH	acetic acid
app	apparent
APT	Attached Proton Test
aq	aqueous
Ar	aryl
B	base
Bn	benzyl
bpy	2,2'-bipyridyl
br	broad
^{t}Bu	*tert*-butyl
^{n}Bu	*n*-butyl
ca	*circa* (approximately)
cat	catalyst
calcd	calculated
COSY	Correlation Spectroscopy
Cp	cyclopentadienyl
d	doublet
dba	dibenzylideneacetone
dd	doublet of doublets
ddd	doublet of doublets of doublets
dec	decompose
DMF	dimethylformamide
DMSO	dimethylsulfoxide
dsept	doublet of septuplets
dt	doublet of triplets
e.g.	for example
equiv	equivalent
ESI	Electrospray Ionization
Et	ethyl
EXSY	Exchange Spectroscopy
HMBC	Heteronuclear Multiple Bond Correlation
HMQC	Heteronuclear Multiple Quantum Correlation
HR	high resolution
^{i}Pr	isopropyl
IR	infrared
L	neutral ligand (general), liter

m	multiplet (regarding NMR)
m	medium (regarding IR)
m	*meta*
Me	methyl
MS	Mass Spectrum / Mass Spectroscopy
Mp	melting point
MW	microwaves
m/z	mass/charge ratio
NMR	Nuclear Magnetic Resonance
N^N	chelate N-donor ligand (tmeda, bpy or tbbpy)
NOE	Nuclear Overhauser Effect
NOESY	Nuclear Overhauser Effect Spectroscopy
o	*ortho*
OTf	triflate (trifluoromethanesulfonate)
p	*para*
Ph	phenyl
phen	phenanthroline
ppm	parts per million
psi	pounds-force per square inch
PTA	1,3,5-triaza-7-phosphaadamantane
q	quadruplet
quint	quintuplet
R	alkyl group
rf	retardation factor
rt	room temperature
s	singlet (regarding NMR) / strong (regarding IR)
sept	septuplet
t	triplet
td	triplet of doublets
tbbpy	4,4'-di-*tert*-butyl-2,2'-bipiridyl
THF	tetrahydrofurane
tmeda	*N*,*N*,*N'*,*N'*-tetramethylethylenediamine
TMS	tetramethylsilane
TOF	time of life
To	tolyl (*p*-methylphenyl)
vs	*versus*
vt	virtual triplet
VT-NMR	variable temperature Nuclear Magnetic Resonance
w	weak
Xy	xylyl (2,6-dimethylphenyl)

RESUMEN EN CASTELLANO

Síntesis, Caracterización y Reactividad de Arenos Mono-, Di- y Tripaladiados con Sustituyentes en *orto*

Esta Tesis está dividida en nueve capítulos, siendo el primero de ellos una Introducción General. Los Capítulos II-VI describen el trabajo desarrollado por la autora en el Grupo de Química Organometálica de la Universidad de Murcia, dirigido por el Prof. José Vicente Soler, y el Capítulo VII describe el trabajo realizado durante una estancia de tres meses en la Universidad Técnica de Lisboa, en el grupo del Prof. Armando Pombeiro. Cada uno de estos capítulos, del II al VII, corresponde a una publicación científica (ya en prensa o en preparación) y por tanto siguen la estructura general del artículo correspondiente, incluyendo el Resumen (excepto para las publicaciones en preparación), la Introducción (que en algunos aspectos pueden solaparse entre sí o con la Introducción General) y las Referencias. La Parte Experimental, por el contrario, se ha unificado en el Capítulo VIII de esta Tesis. La numeración de los complejos también ha sido unificada, de forma que sea consecutiva en esta Tesis (ver Tabla en págs. xxiii-xxiv), y puede haber cambios adicionales con respecto a los artículos ya publicados, especialmente en lo referente a la incorporación de contenidos que se encontraban en el Material Suplementario. El Capítulo IX contiene las Conclusiones de la Tesis, que se incluyen también en este Resumen.

Los artículos ya publicados son:

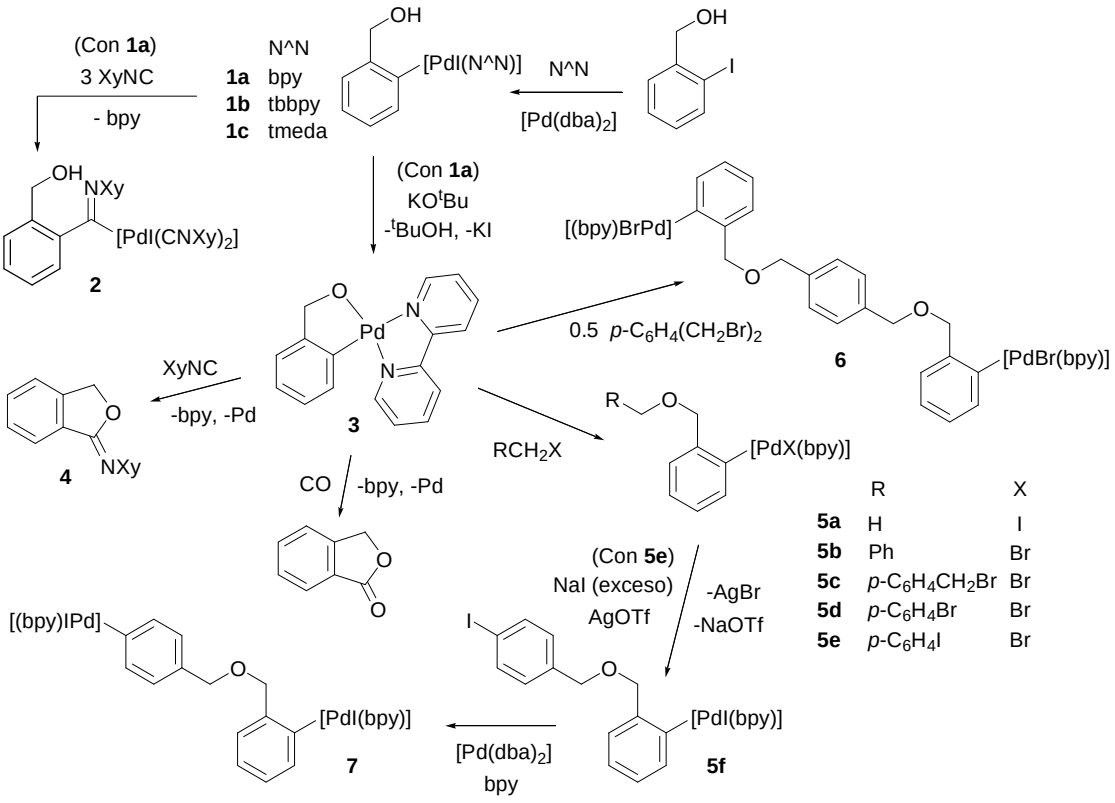
- J. Vicente, E. Martínez-Viviente, M.-J. Fernández-Rodríguez, *Organometallics* **2009**, 28, 5845-5847 (corresponde a parte del Capítulo IV)
- J. Lasri, M.-J. Fernández-Rodríguez, M. F. C. Guedes da Silva, P. Smoleński, M. N. Kopylovich, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *J. Organomet. Chem.* **2011**, 696, 3513-3520 (corresponde al Capítulo VII)
- M.-J. Fernández-Rodríguez, E. Martínez-Viviente, J. Vicente, P. G. Jones, *Organometallics* **2015**, 34, 2240-2254 (corresponde al Capítulo IV)
- M.-J. Fernández-Rodríguez, E. Martínez-Viviente, J. Vicente, P. G. Jones, *Organometallics* **2015**, 34, 3282-3291 (corresponde al Capítulo II)

En los siguientes párrafos se resumen los Capítulos II a VII de esta Tesis. Los cinco primeros (del II al VI) se enmarcan dentro de una línea de investigación que el Grupo de Química Organometálica de la Universidad de Murcia ha seguido con gran éxito, consistente en la síntesis de complejos de Pd(II) con ligandos arilo sustituidos en *orto*, y la investigación de su reactividad frente a moléculas orgánicas insaturadas. Con

frecuencia, se produce la inserción de dichas moléculas en el enlace aril-Pd, acompañada en ocasiones por su interacción con el sustituyente en *orto*, formando nuevos complejos (frecuentemente ciclopaladiados) o, tras reacciones de despaladación, moléculas orgánicas de interés. En los últimos años se ha intentado extender esta reactividad a arenos di- o tripaladiados, con sustituyentes en *orto* a cada átomo de Pd, con el objetivo de obtener novedosos complejos polinucleares o compuestos orgánicos policíclicos.

Capítulo II: Síntesis de aril complejos de Pd(II) derivados del alcohol bencílico; reactividad frente a haluros de alquilo y síntesis de aril complejos dinucleares de Pd(II).

El **Capítulo II** (*Esquema 1*) describe la síntesis, mediante reacciones de adición oxidante, de tres aril complejos de Pd(II), **1a-c**, derivados del alcohol bencílico, así como de un complejo ciclopaladiado, **3**, obtenido a partir de **1a** mediante un reacción de desprotonación. Por reacción de **3** con distintos haluros de alquilo primarios se han obtenido una serie de complejos, **5a-e**, resultado del ataque nucleófilo de **3** sobre el grupo alquilo del haluro, seguido de la coordinación del haluro al átomo de Pd y la apertura del anillo quelato. No existen precedentes para este tipo de reactividad en aril complejos de Pd. Se han preparado también dos novedosos complejos dinucleares, bien por reacción de **3** con un dihaluro de alquilo, o bien mediante una segunda reacción de adición oxidante sobre el aril complejo de Pd **5f**, obtenido a partir de **5e** mediante una reacción de intercambio de haluro. Los complejos **6** y **7** son los primeros ejemplos de complejos de bis(arilpaladio) en los que los grupos arilo tienen sustituyentes en *orto*. El Capítulo II también describe la reactividad de **1a** y **3** frente a XyNC, que da lugar, respectivamente, a la formación del complejo **2**, (resultado de una reacción de inserción en **1a**) o a la formación del imidato ciclado **4**, que no había sido descrito con anterioridad. Se describen las estructuras de difracción de rayos X de los complejos **1a**, **3**·H_2O y **5e**. Estos resultados han sido publicados en *Organometallics*, 2015, 34, 3282-3291.

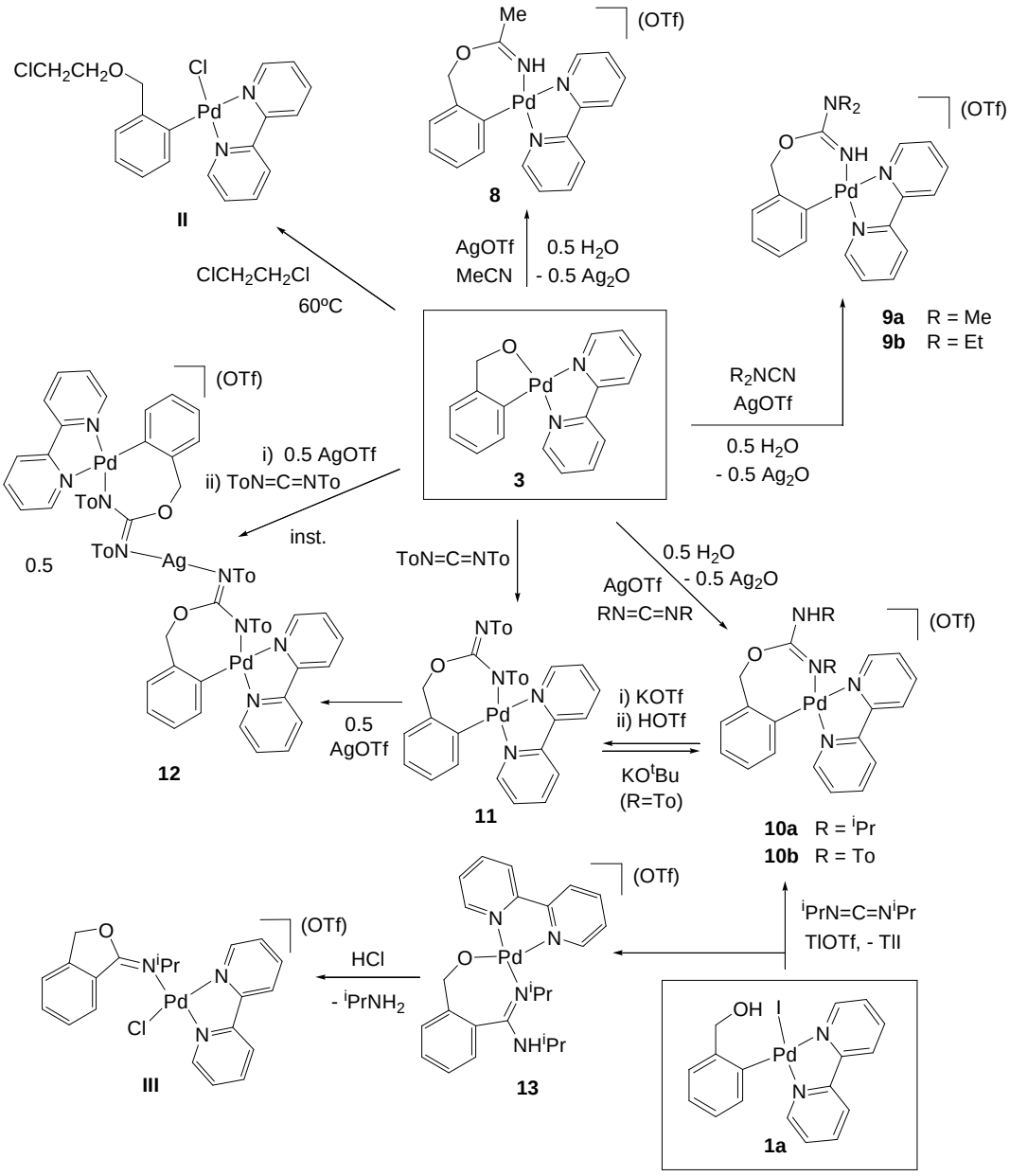


Esquema 1. Reacciones y compuestos descritos en el Capítulo II

Capítulo III: Reactividad de complejos de Pd(II) derivados del alcohol bencílico frente a nitrilos, cianamidas y carbodiimidas. Síntesis de un complejo mixto Pd_2Ag.

El **Capítulo III** (*Esquema 2*) describe la reactividad del complejo ciclopaladiado **3** frente a MeCN, R_2NCN (R = Me, Et) y RN=C=NR (R = To, ^{i}Pr), en presencia de AgOTf y agua residual, para formar los complejos **8**, **9a,b** y **10a,b**, que son el resultado de la inserción de las moléculas insaturadas en el enlace O-Pd de **3**, acompañada por la protonación de un átomo de N por parte del agua residual. Estas reacciones requieren la presencia de Ag, que probablemente forma *in situ* un complejo con las moléculas orgánicas, aumentando su carácter electrofílico y favoreciendo así el ataque nucléofilo del átomo de O del complejo **3**. No existen en la bibliografía precedentes de reacciones de este tipo, en las que el nucleófilo sea un complejo. Cuando el complejo **3** reacciona ToN=C=NTo en ausencia de AgOTf se forma el complejo neutro **11**, que es la base conjugada de **10b**. En condiciones adecuadas, la reacción de **3** con ToN=C=NTo y AgOTf también puede dar lugar a un complejo trinuclear de Pd_2Ag, **12** (**12** = [Ag(*N*-**11**)$_2$](OTf)). El Capítulo III también

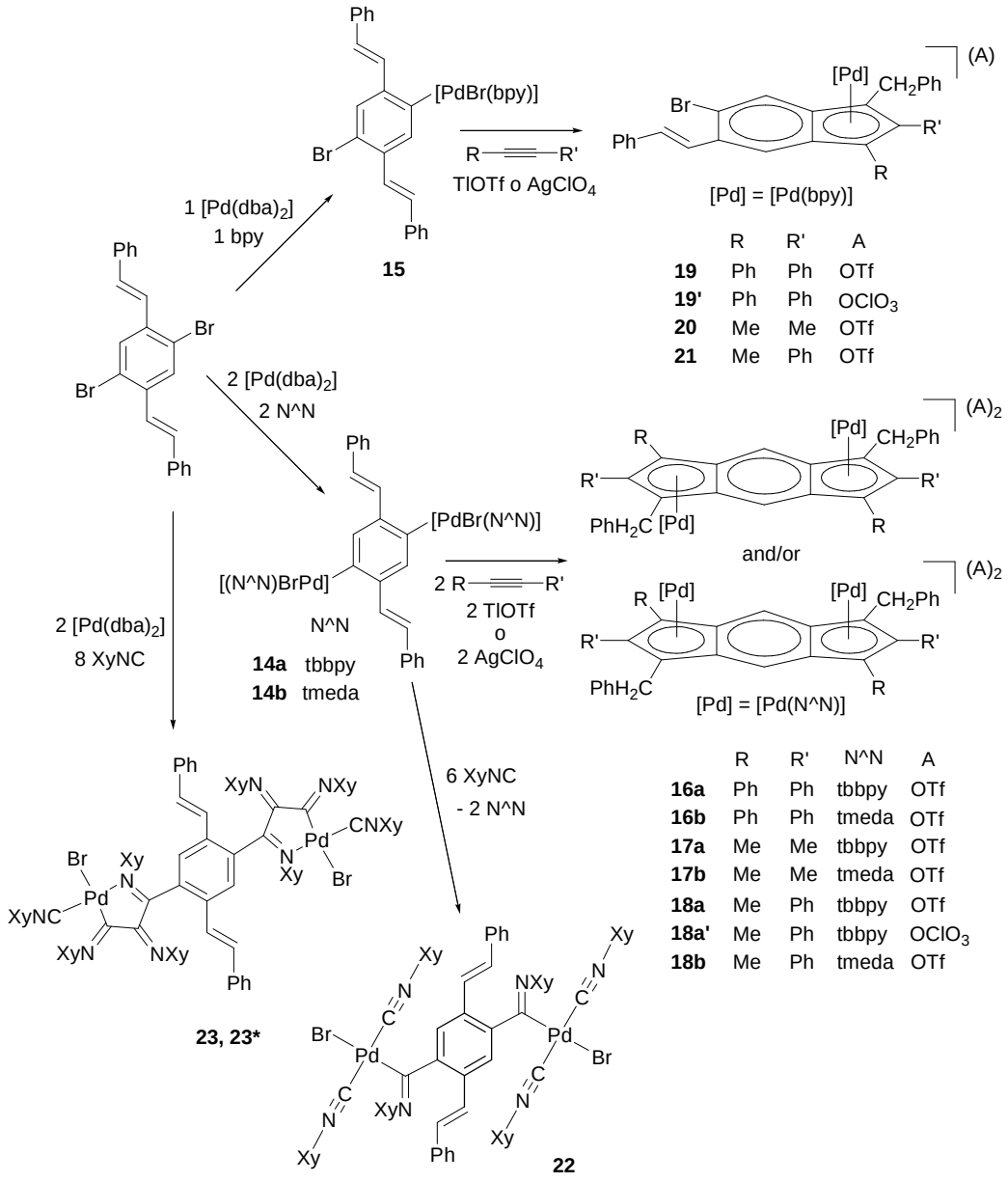
describe la reactividad del complejo **1a** frente a las mismas moléculas insaturadas, aunque en estas reacciones el único resultado positivo ha sido la obtención y caracterización del complejo **13**, que se forma debido a la inserción del $^{i}PrN=C=N^{i}Pr$ en el enlace aril-Pd de **1a**. Se describen las estructuras de difracción de rayos X de los complejos **9a**, **10a** y **12**$\cdot 2.5CHCl_3 \cdot 0.5Et_2O$, junto con las de los complejos **II** y **III**, que no han podido ser caracterizados. Estos resultados serán próximamente enviados para su publicación.



Esquema 2. Reacciones y compuestos descritos en el Capítulo III

Capítulo IV: Derivados mono- y dipaladiados de 2,5-diestirilbenceno. Reactividad frente a XyNC y alquinos. Síntesis de complejos con ligandos indacenodiilo.

El **Capítulo IV** (*Esquema 3*) describe la síntesis, mediante reacciones de adición oxidante, de derivados de 2,5-diestirilbenceno mono- (**15**) o dipaladiados (**14a**,**b**). Los complejos **14a**,**b** son los primeros derivados dipaladiados del benceno con sustituyentes alquenilo en el anillo aromático. Sus reacciones con PhC≡CPh, MeC≡CMe y PhC≡CMe, en presencia de TlOTf o $AgClO_4$, dan lugar a la formación de indacenodiilos dipaladiados, **16a**,**b**, **17a**,**b** y **18a**,**a'**,**b**, que son los primeros compuestos de este tipo en ser descritos. Reacciones similares con el complejo monopaladiado **15** resultan en la formación de complejos de indenilpaladio, **19**, **19'**, **20** y **21**. El Capítulo IV también describe la reactividad de los complejos **14a**,**b** frente a XyNC, que da lugar a la inserción de una molécula del isocianuro en cada enlace aril-Pd, y el desplazamiento de los ligandos tbbpy o tmeda, formando el complejo dinuclear **22**. Finalmente, la adición oxidante de *trans*,*trans*-2,5-diestiril-2,4-dibromobenceno a $[Pd(dba)_2]$ en presencia de XyNC resulta en la formación de una mezcla de dos estereoisómeros, **23**,**23***, en los que tres moléculas de isocianuro se insertan en ambos enlaces aril-Pd, coordinándose al Pd el átomo de N de una de ellas, de modo que se forman dos anillos quelato de cinco miembros. No se habían descrito anteriormente complejos dinucleares de Pd similares. Se describen las estructuras de difracción de rayos X de los complejos **16a**$\cdot 7CDCl_3$, **16b**$\cdot CH_2Cl_2$, **18a'**$\cdot 4CH_2Cl_2$, **19** y **21**. Estos resultados se han publicado en dos artículos en *Organometallics*: una comunicación (2009, 28, 5845-5847) y un artículo (2015, 34, 2240-2254).



	R	R'	A
19	Ph	Ph	OTf
19'	Ph	Ph	$OClO_3$
20	Me	Me	OTf
21	Me	Ph	OTf

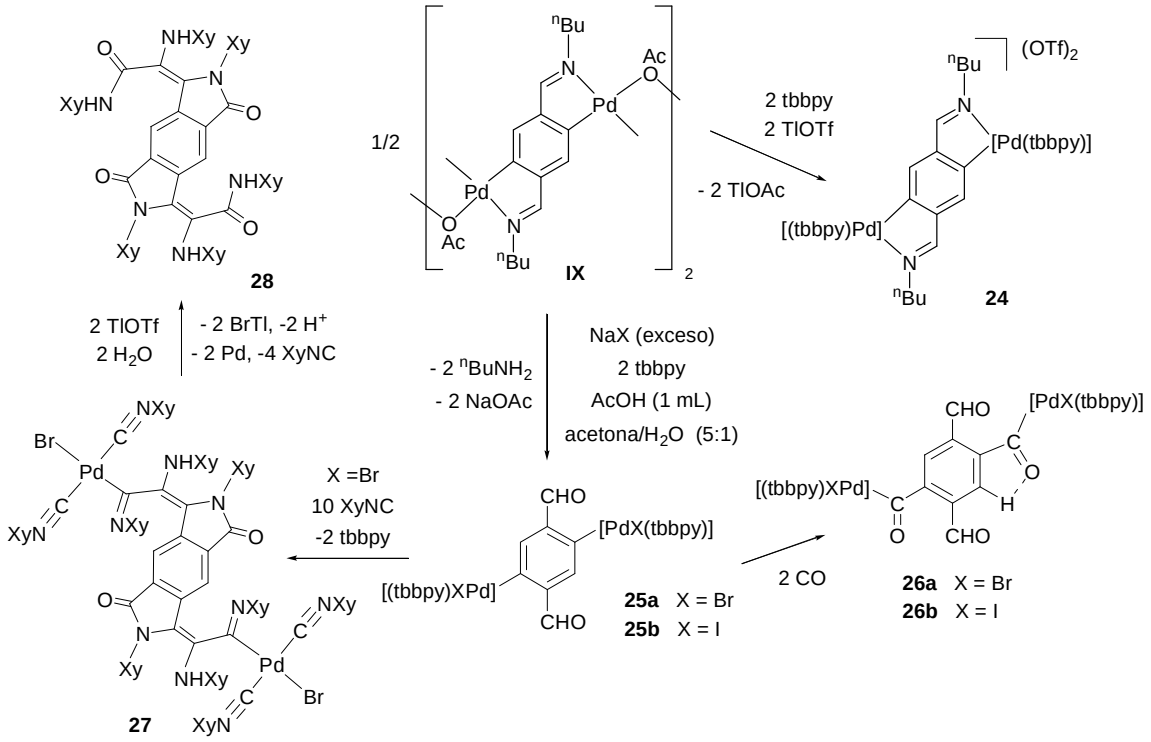
	R	R'	N^N	A
16a	Ph	Ph	tbbpy	OTf
16b	Ph	Ph	tmeda	OTf
17a	Me	Me	tbbpy	OTf
17b	Me	Me	tmeda	OTf
18a	Me	Ph	tbbpy	OTf
18a'	Me	Ph	tbbpy	$OClO_3$
18b	Me	Ph	tmeda	OTf

Esquema 3. Reacciones y compuestos descritos en el Capítulo IV

Capítulo V: Síntesis y reactividad de derivados dipaladiados del tereftaldehído.

El **Capítulo V** (*Esquema 4*) describe la síntesis de dos derivados dipaladiados del tereftaldehído, **25a**,**b**, por hidrólisis de una base de Schiff dipaladiada, **IX**. Se describe también un derivado dicatiónico de dicha base, el complejo **24**. Por reacción de los complejos **25a**,**b** con CO se forman dos nuevos complejos, **26a**,**b**, que son los primeros ejemplos de la inserción de CO en dos enlaces aril-metal en el mismo anillo aromático. La reacción de **25a** con XyNC da lugar al complejo **27**, que es el resultado de la tri-inserción del isocianuro en ambos enlaces aril-Pd, seguida por el ataque nucleófilo de uno de los isocianuros a cada uno del grupos formilo de **25a**, junto con

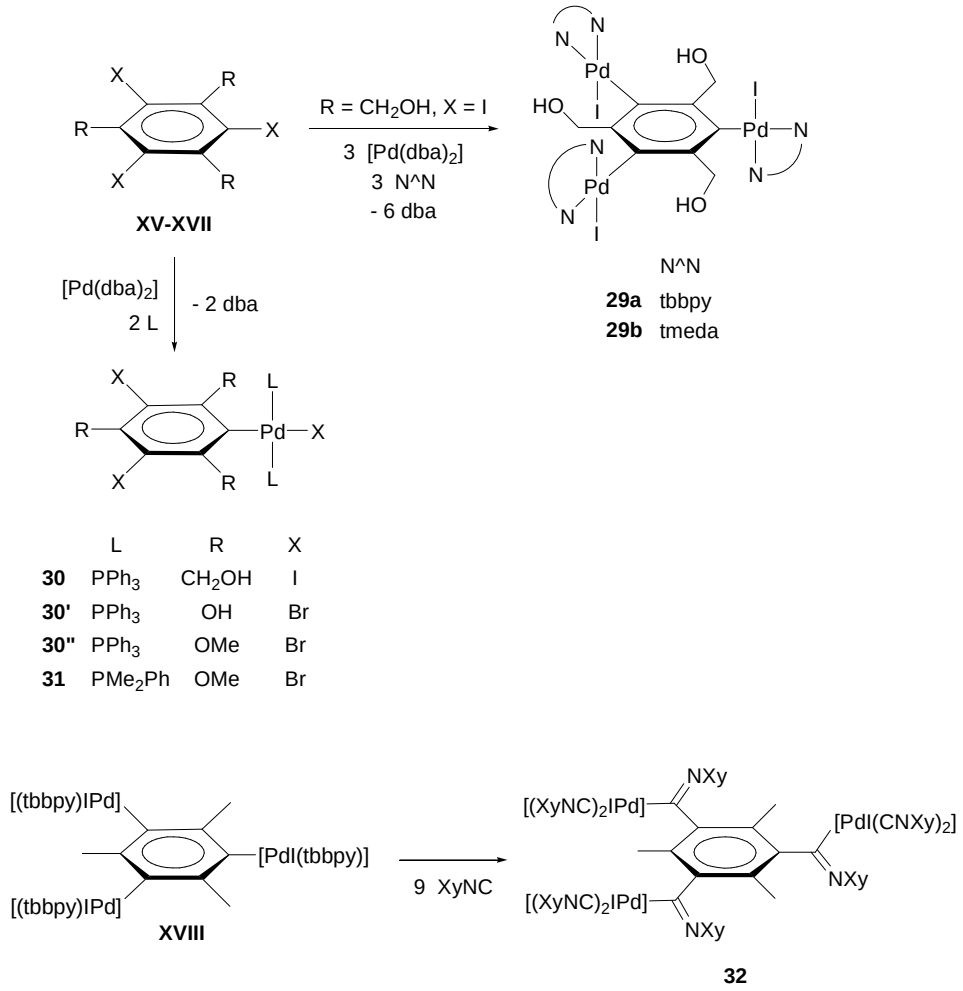
el desplazamiento del ligando tbbpy. El complejo **27** reacciona con TlOTf en presencia de agua residual para formar el compuesto orgánico **28**. Se describen las estructuras de difracción de rayos X de los complejos **24**·$4CHCl_3$, **27**·$2CH_2Cl_2$·3hexano y **28**·$2CDCl_3$.



Esquema 4. Reacciones y compuestos descritos en el Capítulo V

Capítulo VI: Síntesis de arenos mono- y tripaladiados 2,4,6-trisubstituidos. Triple inserción de XyNC en tres enlaces aril-Pd en un mismo areno.

El **Capítulo VI** (*Esquema 5*) describe la síntesis, mediante reacciones de adición oxidante, de arenos 2,4,6-trisubstituidos tripaladiados (**29a,b**) y monopaladiados (**30**, **30'**, **30"** y **31**). Por reacción con XyNC de un complejo trinuclear descrito con anterioridad (**XVIII**) se ha conseguido por primera vez la inserción de isocianuro en tres enlaces aril-Pd de un mismo anillo aromático, dando lugar al complejo **32**. Se describen las estructuras de difracción de rayos X de los complejos **30"** y **31**.

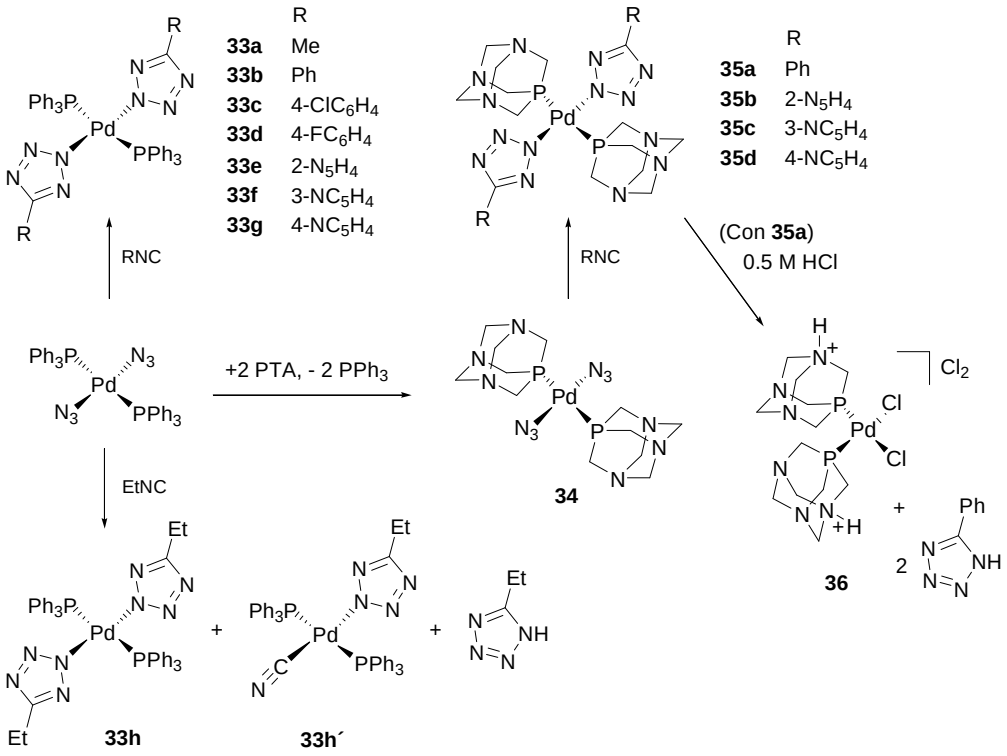


Esquema 5. Reacciones y compuestos descritos en el Capítulo VI

Capítulo VII: Síntesis mediante microondas de complejos bis(tetrazolato) de Pd(II) con PPh_3 y de complejos con PTA (1,3,5-triaza-7-fosfaadamantano) solubles en agua. El primer ejemplo de ruptura del enlace C-CN del propionitrilo por Pd(II).

El **Capítulo VII** (*Esquema 6*) describe la síntesis de una serie de complejos *trans*-bis(tetrazolato pentasustituido) de Pd(II), **33a-g** y **35a-d**, obtenidos por reacciones de cicloadición [2+3] de dos complejos de partida, (*trans*-$[Pd(N_3)_2(PPh_3)_2]$ y su derivado hidrosoluble con PTA, *trans*-$[Pd(N_3)_2(PTA)_2]$ **34**), con diferentes organonitrilos. La solubilidad en agua de la PTA permite la fácil liberación del tetrazolato coordinado en el complejo *trans*-$[Pd(N_4CPh)_2(PTA)_2]$ (**35a**), lo que constituye una ruta sintética muy conveniente para la síntesis de tetrazoles sustituidos. En la reacción de *trans*-$[Pd(N_3)_2(PPh_3)_2]$ con propionitrilo se obtiene una mezcla de dos complejos, el esperado *trans*-$[Pd(N_4CEt)_2(PPh_3)_2]$ (**33h**), más *trans*-$[Pd(CN)(N_4CEt)(PPh_3)_2]$ (**33h´**), que es el resultado de una inusual ruptura del enlace NC-C del propionitrilo, que se comporta así

como una fuente de ligando cianuro. En la reacción también se detecta la formación de 5-etil-1*H*-tetrazol, que debe proceder de la adición oxidante del nitrilo a Pd(II), seguida de una eliminación β de hidruro del ligando etilo, y una eliminación reductora del tetrazol. Estos resultados han sido publicados en *J. Organomet. Chem.*, 2011, 696, 3513-3520.



Esquema 6. Reacciones y compuestos descritos en el Capítulo VII

CONCLUSIONES

1. Se han preparado nuevos aril-complejos de Pd(II) (**1a-c**, ver Tabla en págs. xxiii-xxiv) mediante reacciones de adición oxidante del alcohol 2-iodobencílico a [Pd(dba)$_2$]. Por reacción de **1a** con XyNC o con KO^{t}Bu se han obtenido productos resultantes de una reacción de inserción (**2**) o de desprotonación (**3**), respectivamente. El complejo **3** cristaliza como pares de moléculas unidas mediante enlaces por puente de H a moléculas de cristalización.

2. El complejo **3** reacciona con CO o con XyNC formando, respectivamente, ftalida o el imidato cíclico *N*-(2,6-dimetilfenil)-2-benzofuran-1(*3H*)-imino (**4**), no descrito anteriormente.

3. El ataque nucleófilo de **3** sobre el grupo alquilo de haluros de alquilo primarios (RCH$_2$X) resulta en la apertura del anillo quelato y la formación de los complejos **5**,

con nuevos enlaces RCH_2-O y Pd-X. No existe precedente en la bibliografía de este tipo de reactividad en grupos arilo *C,O*-ciclometalados. Se han preparado dos complejos dinucleares de bis(arilpaladio), bien por reacción de **3** con *p*-$C_6H_4(CH_2Br)_2$ (complejo **6**) o por reacción de **5f** (R = *p*-C_6H_4I) con [Pd(dba)$_2$] (complejo **7**). Los complejos **6** y **7** son los primeros ejemplos de complejos de bis(arilpaladio) en los que los grupos arilo están sustituidos en *orto*.

4. El complejo **3** reacciona con acetonitrilo, cianamidas o carbodiimidas, en presencia de AgOTf y agua residual, para formar complejos iónicos (**8-10**) que son el resultado de la inserción de las moléculas orgánicas en el enlace O-Pd de **3**, y la protonación de uno de los átomos de N. Sugerimos que estas reacciones tienen lugar a través del ataque nucleófilo de **3** sobre el compuesto orgánico, activado previamente por coordinación a la Ag^+ (una observación sin precedentes). En ausencia de AgOTf el complejo **3** sólo reacciona limpiamente con ToN=C=NTo, formando un complejo neutro **11**, que es la base conjugada de **10b**. Los complejos **10b** y **11** pueden interconvertirse mediante reacciones de protonación y desprotonación.

5. Se ha aislado y caracterizado un complejo bis-quelato heterometálico del tipo Pd_2Ag (**12** = [Ag(*N*-**11**)$_2$](OTf)). Su novedosa estructura ha sido confirmada mediante cristalografía de rayos X.

6. Tan sólo en la reacción de **1a** con ^{i}PrN=C=N^{i}Pr en presencia de TlOTf (en lugar de AgOTf) ha sido posible obtener un complejo (**13**) resultado de la inserción de la carbodiimida en el enlace aril-Pd de **1a**. Por tanto, hemos constatado que la reactividad de los complejos **1a** y **3** frente a nitrilos, cianamidas y carbodiimidas difiere de la de los complejos de Pd(II) con ligandos *orto*-fenol (previamente descritos), para los que el grupo OH directamente enlazado al areno promueve reacciones limpias de inserción de las moléculas orgánicas en el enlace aril-Pd.

7. Hemos preparado derivados mono- (**15**) y di-paladiados (**14**) de bencenos con sustituyentes alquenilo en *orto*, mediante reacciones de adición oxidante de *trans,trans*-2,5-diestiril-2,4-dibromobenceno a uno o dos equivalentes [Pd(dba)$_2$]. En las reacciones de estos complejos con alquinos hemos obtenido complejos de Pd(II) con ligandos indenilo altamente sustituidos (**19-21**), así como indacenodiilos dipaladiados (**16-18**). Esta es la primera síntesis de este tipo de complejos dinucleares en la que el ligando se forma por mediación del metal. Los datos de

difracción de rayos X y RMN de ^{13}C sugieren que el modo de coordinación de los ligandos indenilo e indacenodiilo en los complejos **16-21** está desplazado hacia η^3.

8. La reactividad frente a XyNC de los complejos dipaladiados **14** ha resultado en la primera inserción simultánea de isocianuro en dos enlaces aril-Pd en el mismo anillo aromático, formando el complejo dinuclear monoinsertado **22**. La síntesis de los complejos **16-22** constituye el primer estudio de la reactividad de arenos dipaladiados frente a reactivos insaturados.

9. La adición oxidante de *trans*,*trans*-2,5-diestiril-1,4-dibromobenceno a $[Pd(dba)_2]$ en presencia de XyNC ha dado lugar a la formación de dos complejos dinucleares isómeros (**23**,**23***), en los que se han insertado tres moléculas de isocianuro en cada enlace aril-Pd. Ambos isómeros se encuentran en intercambio lento en disolución, según indica un espectro EXSY de ^1H.

10. Hemos preparado dos derivados dipaladiados del tereftaldehído (**25a,b**), por hidrólisis de una base de Schiff dipaladiada (**IX**), previamente descrita. Un derivado dinuclear dicatiónico de dicha base de Schiff (**24**) ha sido también caracterizado, incluyendo su estructura de difracción de rayos X.

11. La reacción de **25a,b** con CO resulta en la primera inserción de CO en dos enlaces aril-metal en el mismo ligando arilo, formando los complejos dinucleares **26a,b**. Los datos de RMN de estos complejos sugieren que una de las moléculas de CO insertadas forma un enlace por puente de H con el hidrógeno arílico situado en *orto*, mientras que lo mismo no ocurre con la otra molécula de CO.

12. La reacción de **25a** con XyNC da lugar a un complejo dinuclear de Pd(II) (**27**), que es el resultado de la inserción de tres moléculas de XyNC en los dos enlaces aril-Pd, seguida por la interacción de dos de los isocianuros insertados con los grupos formilo en *orto*. No se habían descrito anteriormente complejos dinucleares similares.

13. Mediante la hidrólisis del complejo **27**, promovida por Tl^+, se libera el ligando central formándose el heteropoliciclo **28**.

14. Hemos preparado dos arenos tripaladiados con formula general $C_6R_3[Pd]_3$ (**29a,b**) y cuatro complejos monopaladiados con fórmula general $C_6R_3X_2[Pd]$ (**30-31**), mediante reacciones de adición oxidante de 1,3,5-trihaloarenos 2,4,6-trisustituidos

($C_6R_3X_3$, R = CH_2OH, OH, OMe; X = Br, I) a [$Pd(dba)_2$] en presencia de ligandos auxiliares.

15. Hemos conseguido la primera inserción de XyNC en tres enlaces aril-Pd de un areno tripaladiado (**XVIII**), formándose un complejos trinuclear fluxional (**32**) que ha sido investigado mediante VT-RMN.

16. Los complejos di(azido) *trans*-[$Pd(N_3)_2(PPh_3)_2$] y el hidrosoluble [$Pd(N_3)_2(PTA)_2$] (**34**) son buenos productos de partida para la síntesis de una serie de complejos de Pd(II) *trans*-bis(tetrazolato-5-sustituido) (**33**,**35**), formados por reacciones de cicloadición [2+3] con nitrilos. Estas reacciones son fuertemente aceleradas por irradiación con microondas.

17. El propionitrilo reacciona con el complejo *trans*-[$Pd(N_4CEt)_2(PPh_3)_2$] (**33h**) sufriendo una inusual ruptura del enlace NC-C y comportándose como una fuente de ligando cianuro, para formar el complejo mixto ciano-tetrazolato **33h´** junto con 5-etil-1*H*-tetrazol. Esta reacción transcurre mediante una inusual adición oxidante del nitrilo a Pd(II), seguida por una eliminación β de hidruro en el ligando etilo y una eliminación reductora del tetrazol. Esta es la primera síntesis de un complejo mixto ciano-tetrazolato de Pd(II) por ruptura de un enlace C-C de un organonitrilo.

18. El estudio por difracción de rayos X del complejo **33b** muestra que la disposición *trans* de los dos ligandos tetrazolato es la más favorecida, en contraste con lo que se había publicado anteriormente. La estructura de rayos X también muestra que los ligandos tetrazolato se coordinan a través del N^2.

19. Aprovechando la solubilidad en agua del ligando PTA, se ha logrado la liberación del ligando tetrazolato de la esfera de coordinación de un complejo bis(tetrazolato) de Pd(II) (**35a**), lo que constituye un método sintético conveniente para la síntesis de tetrazoles sustituidos.

20. Los complejos descritos en esta Tesis han sido caracterizados mediante análisis elemental o espectroscopia de masas de alta resolución, así como por espectroscopia de IR y de RMN (experimentos 1D y 2D). Se han resuelto un total de 19 estructuras de difracción de rayos X.

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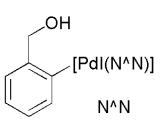
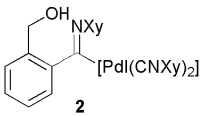


	N^N
1a	bpy
1b	tbbpy
1c	tmeda



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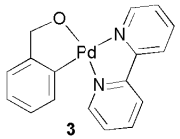

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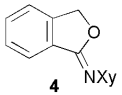

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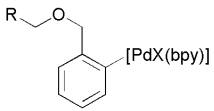
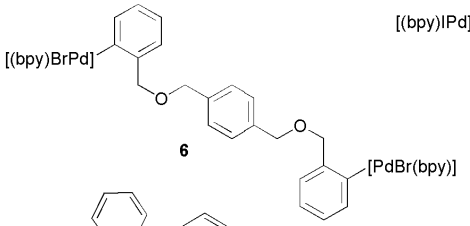


	R	X
5a	H	I
5b	Ph	Br
5c	*p*-$C_6H_4CH_2Br$	Br
5d	*p*-C_6H_4Br	Br
5e	*p*-C_6H_4I	Br
5f	*p*-C_6H_4I	I



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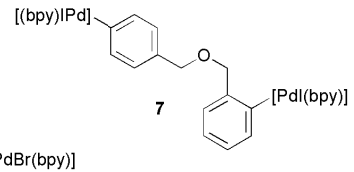

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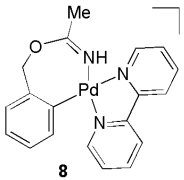

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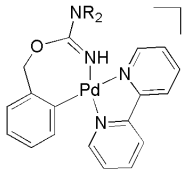
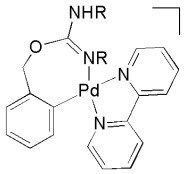
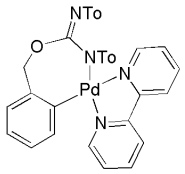


9a	R = Me
9b	R = Et



10a	R = ^{i}Pr
10b	R = To



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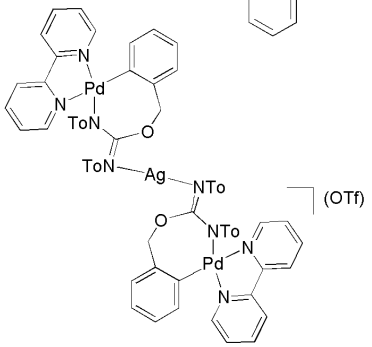

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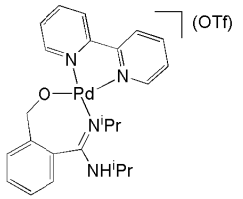

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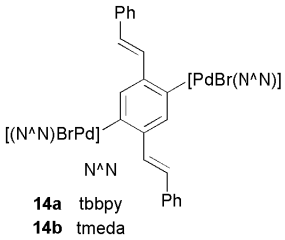
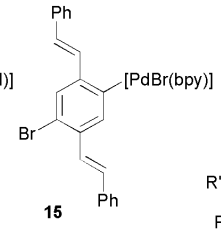


14a	tbbpy
14b	tmeda



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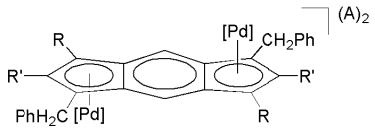

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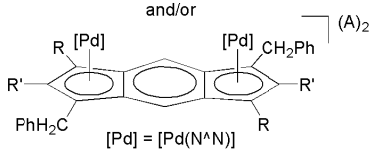
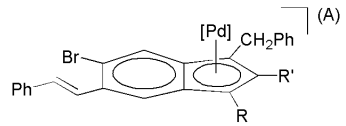


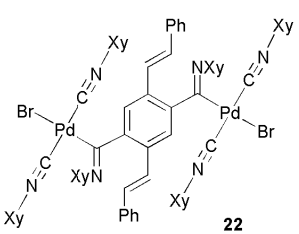
[Pd] = [Pd(N^N)]

	R	R'	N^N	A
16a	Ph	Ph	tbbpy	OTf
16b	Ph	Ph	tmeda	OTf
17a	Me	Me	tbbpy	OTf
17b	Me	Me	tmeda	OTf
18a	Me	Ph	tbbpy	OTf
18a'	Me	Ph	tbbpy	$OClO_3$
18b	Me	Ph	tmeda	OTf



[Pd] = [Pd(bpy)]

	R	R'	A
19	Ph	Ph	OTf
19'	Ph	Ph	$OClO_3$
20	Me	Me	OTf
21	Me	Ph	OTf



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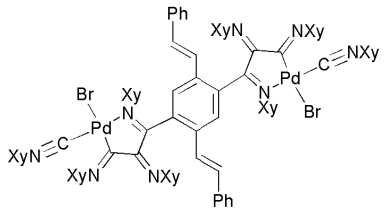
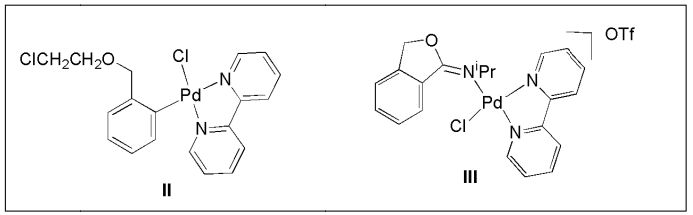


23, 23*



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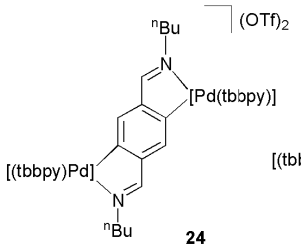

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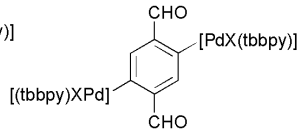
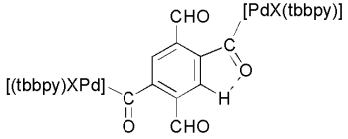
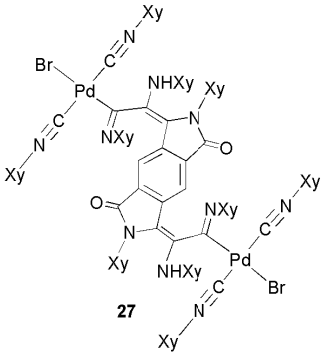


25a X = Br
25b X = I



26a X = Br
26b X = I



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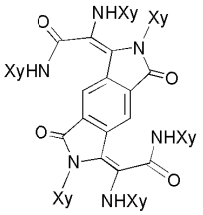

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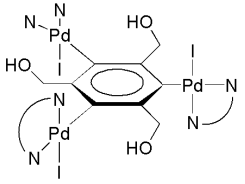
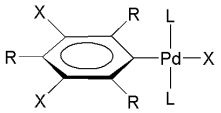
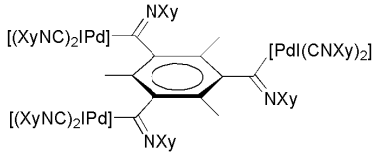


N^N
29a tbbpy
29b tmeda



	L	R	X
30	PPh_3	CH_2OH	I
30'	PPh_3	OH	Br
30"	PPh_3	OMe	Br
31	PMe_2Ph	OMe	Br



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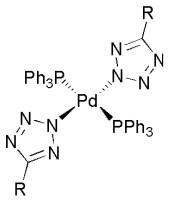
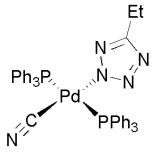
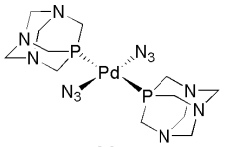


	R
33a	Me
33b	Ph
33c	4-ClC_6H_4
33d	4-FC_6H_4
33e	2-NC_5H_4
33f	3-NC_5H_4
33g	4-NC_5H_4
33h	Et



33h'



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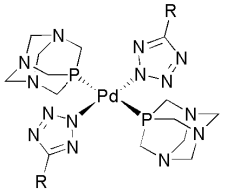
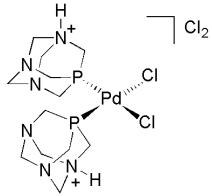


	R
35a	Ph
35b	2-NC_5H_4
35c	3-NC_5H_4
35d	4-NC_5H_4



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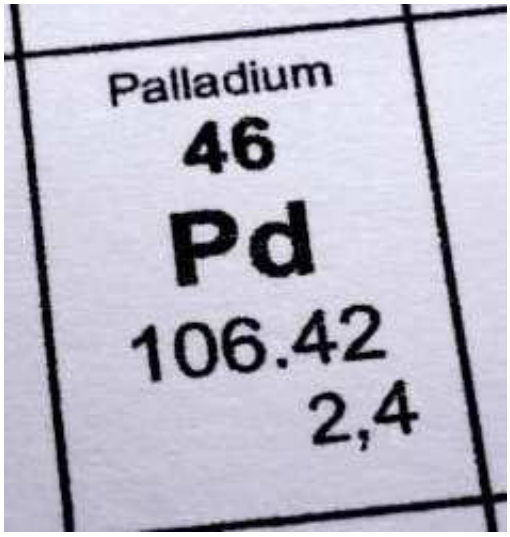
CHAPTER I

General Introduction



I.1 ORGANIZATION AND SUMMARY

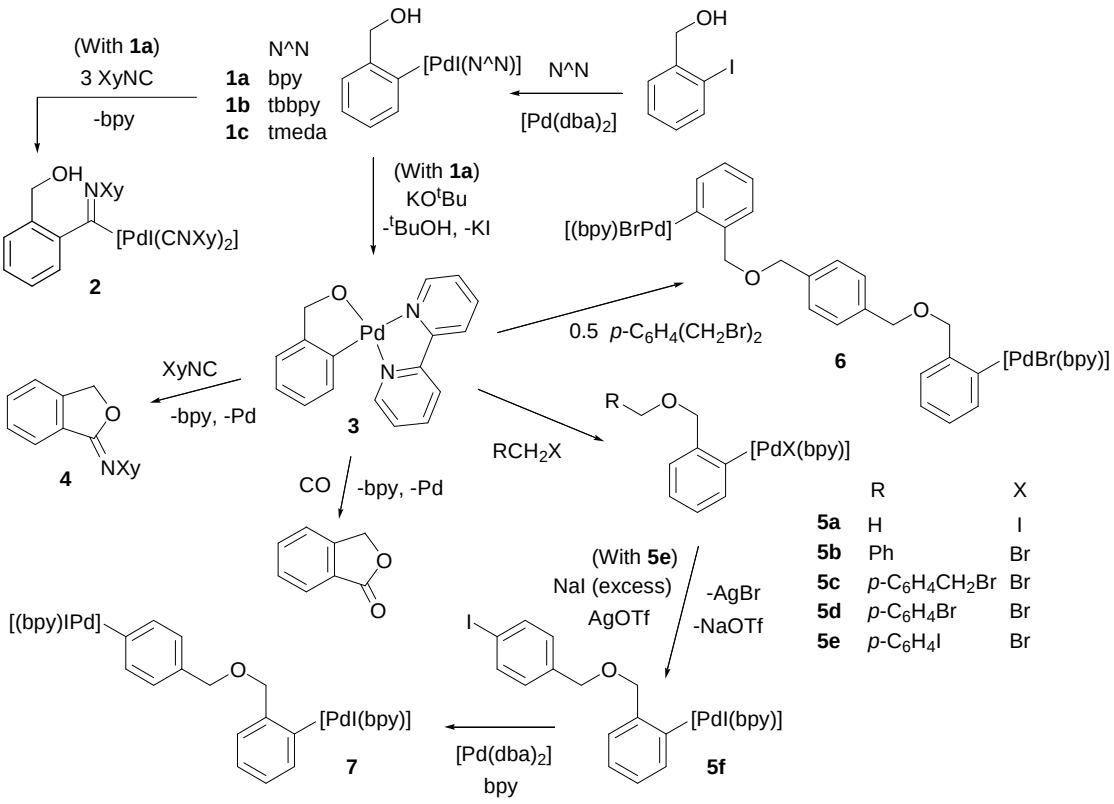
This Thesis is divided in nine chapters, being Chapter I this General Introduction. Chapters II-VI describe the chemistry developed by the author at the University of Murcia, in the group of Prof. José Vicente Soler, and Chapter VII describes the work done during a 3-month stay at the University of Lisbon, in the group of Prof. Armando Pombeiro. Each of these chapters corresponds to a scientific publication (already published, or in different stages of preparation), and thus they follow in general the structure of the corresponding paper, including the Abstract (except for publications in preparation), Introduction (which may sometimes overlap with each other, or with this General Introduction), and References, but not the Experimental Section, which has been unified in Chapter VIII. The numbering of the compounds has also been unified, to achieve a consecutive numbering, and there are some additional changes with respect to the original papers, especially involving the inclusion of parts of the Supplementary Material in the main text. Chapter IX contains the Conclusions of the Thesis.

A brief summary of Chapters II-VII is given in the following paragraphs:

Chapter II: Synthesis of Arylpalladium(II) Complexes Derived from Benzyl Alcohol, Reactivity toward Alkyl Halides, and Synthesis of Dinuclear Arylpalladium(II) Complexes.

Chapter II (*Scheme I.1*) describes the synthesis by oxidative addition reactions of three arylpalladium(II) complexes, **1a-c**, derived from benzyl alcohol, as well as a cyclopalladated complex, **3**, obtained by a deprotonation reaction on **1a**. By reaction of **3** with different primary alkyl halides a series of complexes, **5a-e**, were obtained, resulting from the nucleophilic attack of **3** at the alkyl group of the halide, followed by the coordination of the halide to the Pd atom and the opening of the chelate ring. There is no precedent for this type of reaction in an arylpalladium complex. Two novel bis(arylpalladium) complexes, **6** and **7**, have also been synthesized, either by reaction of **3** with an alkyl dihalide, or by a second oxidative addition reaction on the arylpalladium complex **5f**, obtained from **5e** by an halide exchange reaction. **6** and **7** are the first examples of bis(arylpalladium) complexes where the aryl groups are *ortho*-substituted. Chapter II also describes the reactivity of **1a** and **3** toward XyNC, resulting, respectively, in an insertion complex, **2**, or in the formation of the cyclic

imidate **4**, which had not been previously described. The X-ray structures of **1a**, **3**·H_2O, and **5e** are described. These results have been published in *Organometallics*, 2015, 34, 3282-3291.

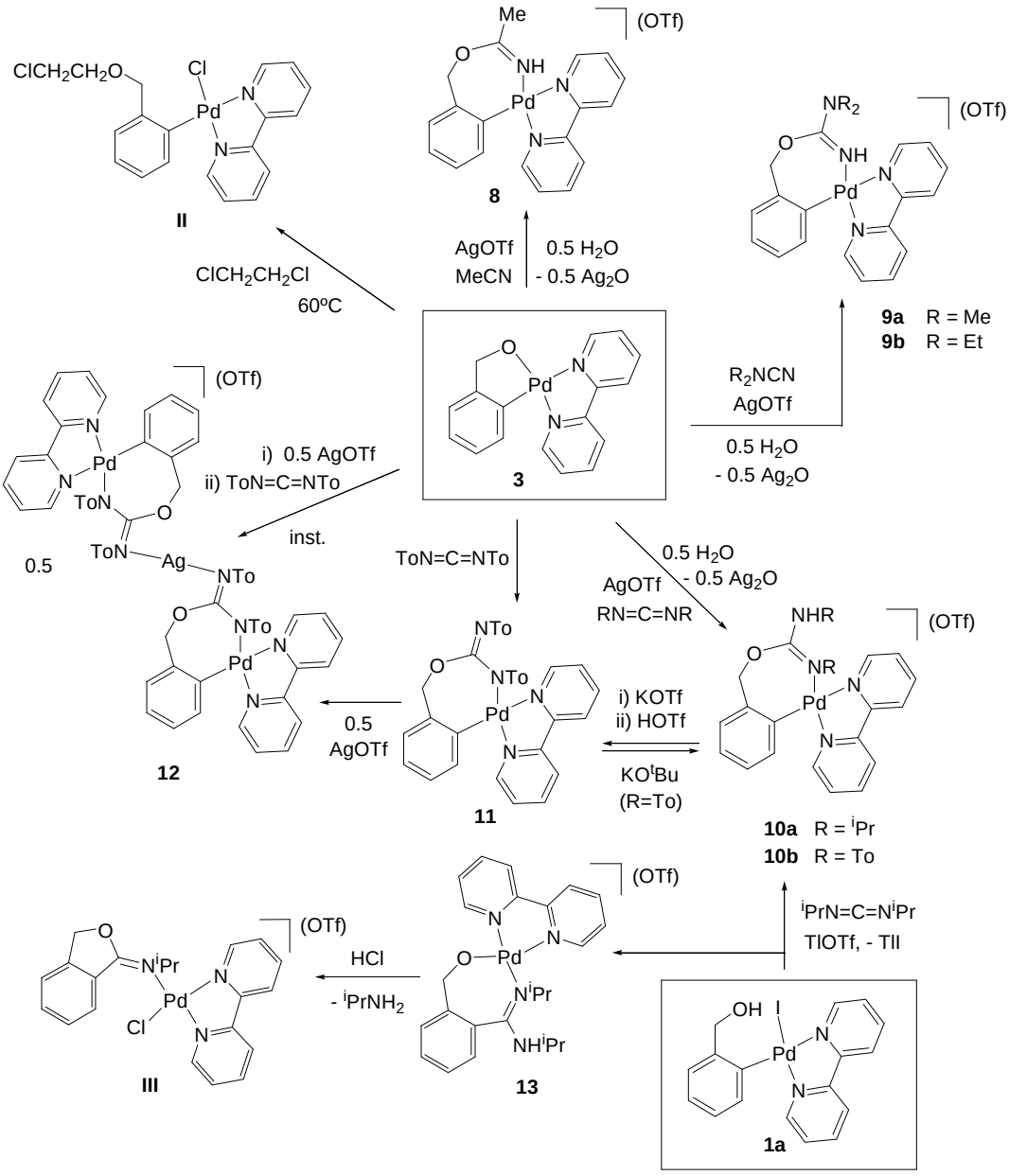


Scheme I.1 Reactions and compounds described in Chapter II

Chapter III: Reactivity toward Nitriles, Cyanamides, and Carbodiimides of Palladium Complexes Derived from Benzyl Alcohol. Synthesis of a Mixed Pd_2Ag Complex.

Chapter III (*Scheme I.2*) describes the reactivity of the cyclopalladated complex **3** toward MeCN, R_2NCN (R = Me, Et), and RN=C=NR (R = To, ^{i}Pr), in the presence of AgOTf and residual water, to form complexes **8**, **9a,b**, and **10a,b**, resulting from the insertion of the unsaturated molecules into the O-Pd bond of **3**, and the protonation of a N atom by the residual water. These reactions require the presence of Ag, which probably forms *in situ* a complex with the organic molecules, increasing their electrophilicity, and thus favoring the nucleophilic attack of the O atom of **3**. There is no precedent in the literature for reactions of this type, where the nucleophile is a complex. When complex **3** reacts with ToN=C=NTo in the absence of AgOTf the neutral complex **11** is formed, which is the conjugate base of **10b**.

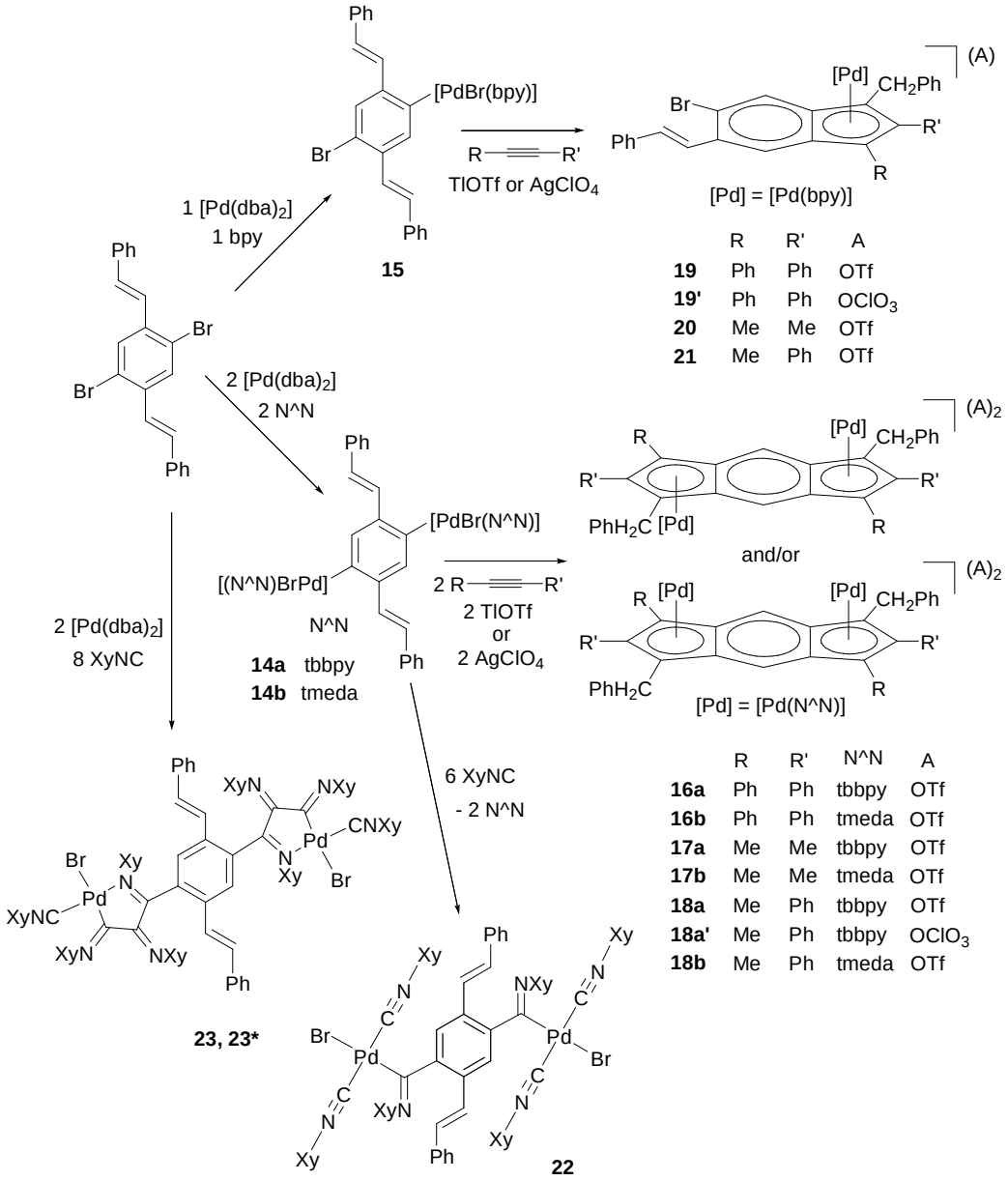
Under adequate conditions, the reaction of **3** with ToN=C=NTo and AgOTf can also yield the mixed-metal Pd_2Ag complex **12** (**12** = [Ag(*N*-**11**)$_2$](OTf)). Chapter III also describes the reactivity of complex **1a** toward the same unsaturated molecules, although these reactions have only given a positive result in the isolation of complex **13**, which is the result of the insertion of ^{i}PrN=C=N^{i}Pr into the aryl-Pd bond of **1a**. The X-ray structures of **9a**, **10a**, and **12**·2.5$CHCl_3$·0.5Et_2O, together with those of the non-characterized products **II** and **III**, are described. These results will be soon submitted for publication.



Scheme I.2 Reactions and compounds described in Chapter III

Chapter IV: Mono- and Dipalladated Derivatives of 2,5-Distyrylbenzene. Reactivity Toward XyNC and Alkynes. Synthesis of Complexes with Indacenediide Ligands.

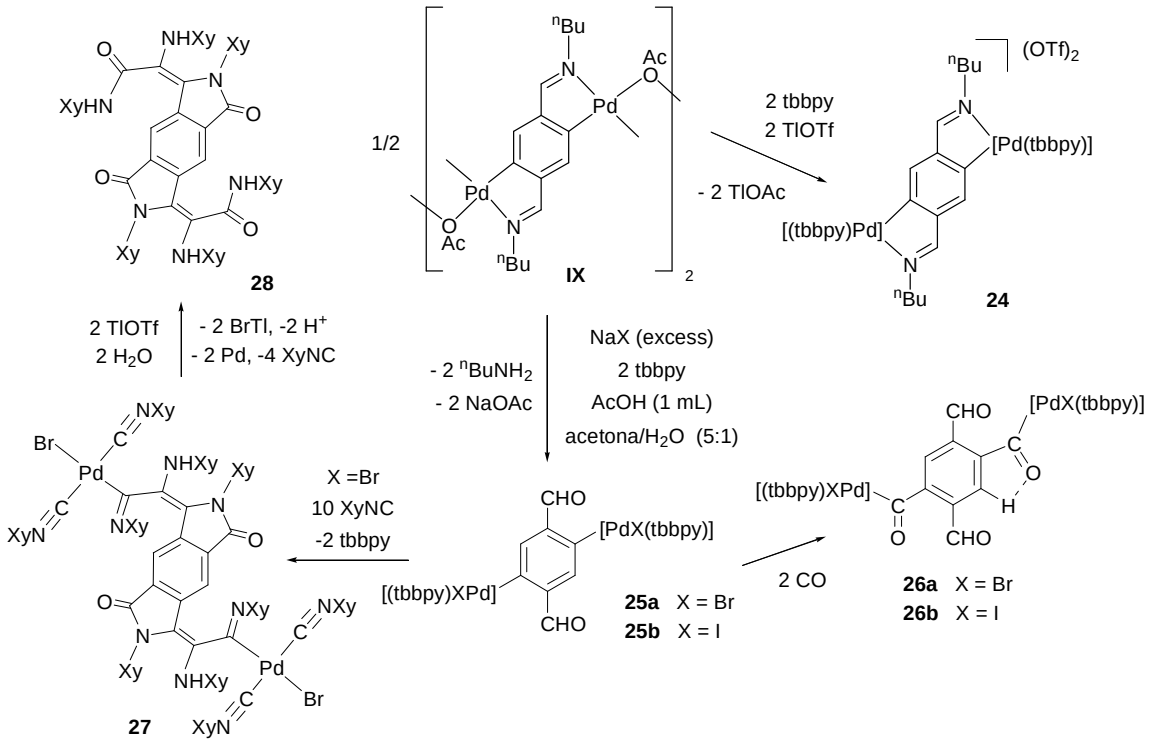
Chapter IV (*Scheme I.3*) describes the synthesis by oxidative addition reactions of one mono- (**15**) and two dipalladated (**14a**,**b**) derivatives of 2,5-distyrylbenzene. **14a**,**b** are the first dipalladated benzene derivatives with alkenyl groups on the aryl ring. Their reactions with PhC≡CPh, MeC≡CMe, and PhC≡CMe, in the presence of TlOTf or $AgClO_4$, gave the dipalladated indacenediide complexes **16a**,**b**, **17a**,**b**, and **18a**,**a'**,**b**, which are the first such compounds to be described. Similar reactions with the monopalladated complex **15** resulted in the indenylpalladium complexes **19**, **19'**, **20**, and **21**. Chapter IV also describes the reactivity of **14a**,**b** toward XyNC, resulting in the insertion of one molecule of the isocyanide into each aryl-Pd bond, and the displacement of the tbbpy or tmeda ligands, to yield the dinuclear complex **22**. Finally, the oxidative addition of *trans*,*trans*-2,5-distyryl-2,4-dibromobenzene to $[Pd(dba)_2]$ in the presence of XyNC results in a mixture of two stereoisomers, **23**,**23***, in which three isocyanide molecules are inserted into both aryl-Pd bonds, with the N atom of one of them coordinated to Pd, foming two five-membered chelate rings. No such dinuclear Pd complexes had been described before. The X-ray structures of **16a**·$7CDCl_3$, **16b**·CH_2Cl_2, **18a'**·$4CH_2Cl_2$, **19**, and **21** are described. These results have been published in two articles in *Organometallics*: a communication (2009, 28, 5845-5847) and a full paper (2015, 34, 2240-2254).



Scheme I.3 Reactions and compounds described in Chapter IV

Chapter V: Synthesis and Reactivity of Dipalladated Derivatives of Terephthalaldehyde.

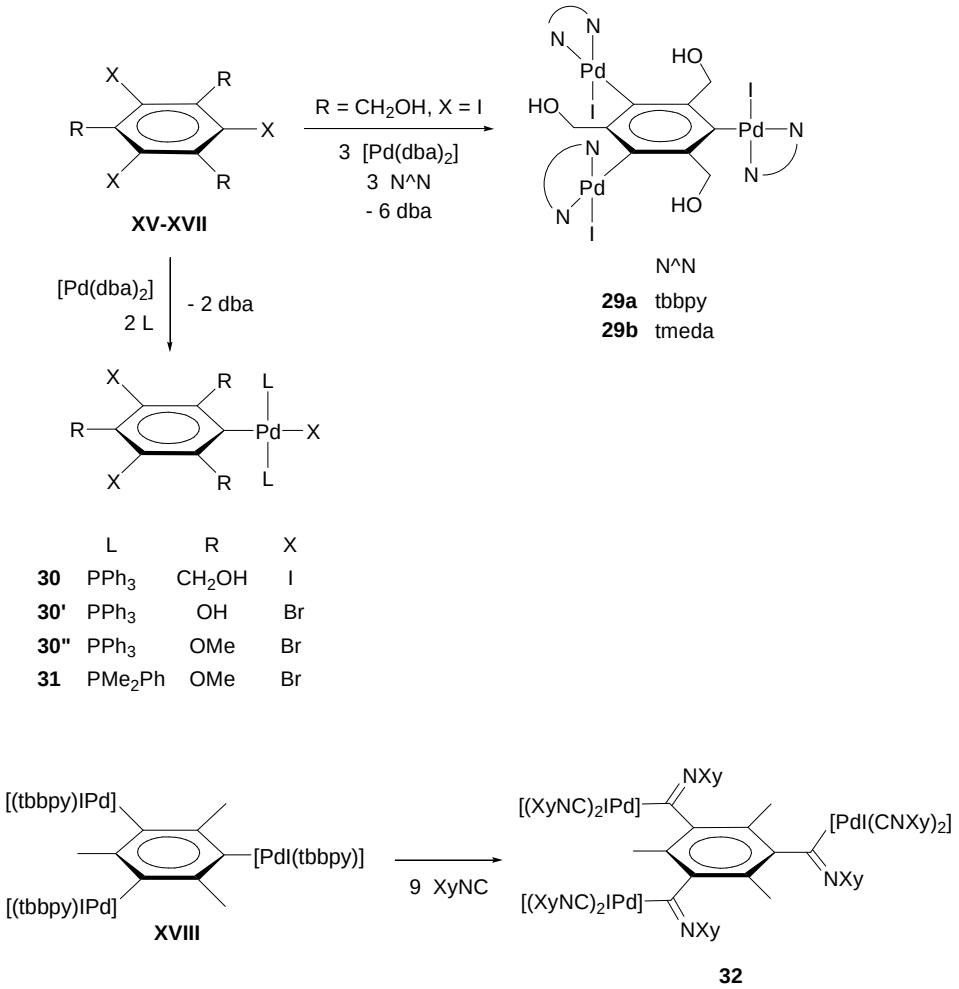
Chapter V (*Scheme I.4*) describes the synthesis of two dipalladated derivatives of terephthalaldehyde, **25a**,**b**, by hydrolysis of a dipalladated Schiff base, **IX**. A dicationic dinuclear derivative of the Schiff base, complex **24**, has also been obtained. By reaction of **25a**,**b** with CO two new complexes, **26a**,**b**, form, which are the first examples of a double insertion of CO into two separate aryl-metal bonds on the same aryl ring. The reaction of **25a** with XyNC yields complex **27**, which is the result from the triinsertion of the isocyanide into both aryl-Pd bonds, and the nucleophilic attack of one isocyanide to each formyl group of **25a**, plus the displacement of the tbbpy ligand. Complex **27** reacts with TlOTf in the presence of residual water to form the organic compound **28**. The X-ray structures of **24**·4$CHCl_3$, **27**·2CH_2Cl_2·3hexane, and **28**·2$CDCl_3$ are described.



Scheme I.4 Reactions and compounds described in Chapter V

Chapter VI: Synthesis of Mono- and Tripalladated 2,4,6-Trisubstituted Arenes. 3-Fold Insertion of XyNC into Three Aryl-Palladium Bonds on the Same Arene.

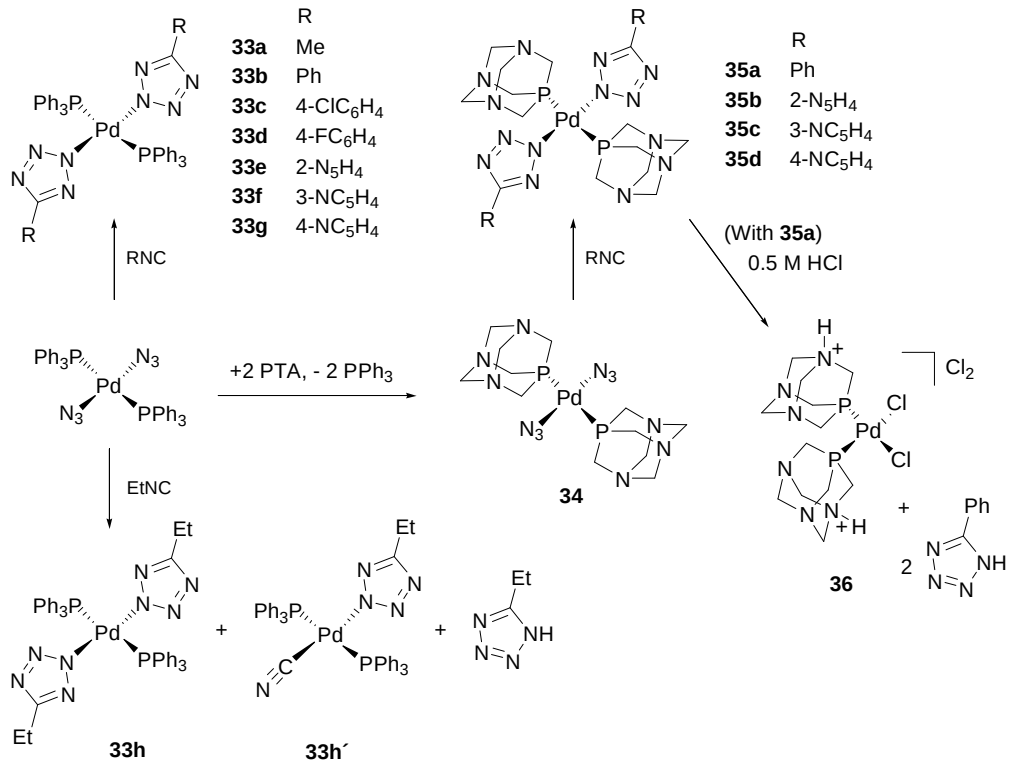
Chapter VI (*Scheme I.5*) describes the synthesis by oxidative addition reactions of two tripalladated (**29a,b**) and four monopalladated (**30**, **30'**, **30"**, and **31**) 2,4,6-trisubstituted arenes. By reaction of a previously described trinuclear complex, **XVIII**, with XyNC, the 3-fold insertion of the isocyanide into three aryl-Pd bonds on the same ring is achieved for the first time, forming complex **32**. The X-ray structures of **30"** and **31** are described.



Scheme I.5 Reactions and compounds described in Chapter VI

Chapter VII: Microwave Synthesis of Bis(tetrazolato)-Pd(II) Complexes with PPh_3 and Water-Soluble 1,3,5-Triaza-7-Phosphaadamantane (PTA). The First Example of C-CN Bond Cleavage of Propionitrile by a Pd(II) Center.

Chapter VII (*Scheme I.6*) describes the synthesis of a variety of *trans*-bis(5-substituted tetrazolato)-Pd(II) complexes, **33a-g** and **35a-d**, derived upon [2+3] cycloaddition reactions of different organonitriles with two di(azido) compounds, *trans*-$[Pd(N_3)_2(PPh_3)_2]$ and its hydrosoluble PTA derivative, *trans*-$[Pd(N_3)_2(PTA)_2]$ (**34**). The hydro-solubility of PTA allows the facile liberation of the coordinated tetrazolate from the coordination sphere of *trans*-$[Pd(N_4CPh)_2(PTA)_2]$ (**35a**), providing a convenient synthetic method for substituted tetrazoles. In the reaction of *trans*-$[Pd(N_3)_2(PPh_3)_2]$ with propionitrile a mixture of two complexes is obtained, the expected *trans*-$[Pd(N_4CEt)_2(PPh_3)_2]$ (**33h**), plus *trans*-$[Pd(CN)(N_4CEt)(PPh_3)_2]$ (**33h´**), which is the result of an unusual NC-C bond cleavage in the propionitrile, that behaves as a source of cyano ligand. 5-ethyl-1*H*-tetrazole is also formed in this reaction, which is suggested to proceed via an unusual oxidative addition of the nitrile to Pd(II), followed by a β-H-elimination from the ethyl ligand, and a reductive elimination of the tetrazole. These results have been published in *J. Organomet. Chem.*, 2011, 696, 3513-3520.



Scheme I.6 Reactions and compounds described in Chapter VII

I.2 ORGANOPALLADIUM CHEMISTRY

Organometallic Chemistry is the chemistry of compounds containing at least one carbon-metal bond. It is a broad field, spanning the boundaries of Organic and Inorganic Chemistry, and which has evolved at a dizzying pace in recent decades, to acquire a great prominence in modern Chemistry. Its relevance is evidenced by the publication of several international jounals and book series of high impact factor (*if*)[a] exclusively dedicated to this area, such as *Advances in Organometallic Chemistry* (first publication year, 1964; *if* 7.000), *Topics in Organometallic Chemistry* (1998, *if* 5.293), *Organometallics* (1982, *if* 4.126), *Journal of Organometallic Chemistry* (1963, *if* 2.173), and *Applied Organometallic Chemistry* (1987, *if* 2.248). In transition metal organometallic complexes, the bond between the organic ligand and the metal usually has a strong covalent character, very often with a π bond component involving the metal d orbitals. As a result, transition metals have a unique ability to activate organic compounds, and to catalyze the formation of new bonds. This is the main point of interest in Organometallic Chemistry, and the reason for its importance in Organic Synthesis.[1]

Within Organometallic Chemistry, Organopalladium Chemistry has emerged as a field of prime importance on its own.[2,3] Palladium organometallic complexes display simultaneously a wide-range reactivity and high stereo-, regio-, and chemo-selectivities. They are highly reactive, and yet stable enough to be used as recyclable reagents and intermediates in catalytic processes. Other late second-row transition metals, especially Rh and Ru, share these favorable characteristics, which seem to stem from: (i) relatively high electronegativity, (ii) moderately large atomic size (they are very “soft” elements), (iii) ready and simultaneous availability of both filled nonbonding and empty valence-shell orbitals, and (iv) ready and reversible availability of two oxidation states, separated by two electrons. Other favourable features from these metals, from a practical point of view, are: (v) the general lack of serious toxicity problems, (vi) the ease of handling, which often does not require rigorous exclusion of air and moisture, and (vii) the compatibility with sensitive funcional groups, which do not need to be protected.[3] Palladium is, additionally, one

[a] Impact factors given are for 2014

of the least expensive of the platinum group metals, and so its complexes have found application in almost all subdisciplines of modern Chemistry, from materials science to the synthesis of drug candidates and approved drugs. This progress is still on, without any end in sight.

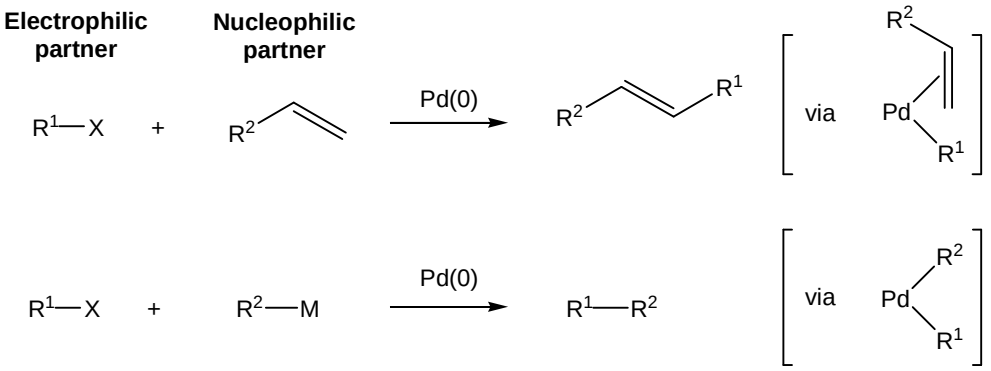
Probably the most relevant application of organopalladium complexes is their use as catalysts in carbon-carbon[4-15] and carbon-heteroatom[12,14,16-22] bond forming reactions, which have become essential tools in Organic Synthesis. A key feature in these reactions is the ability of palladium complexes to undergo oxidative addition (to Pd(0)) and reductive elimination (from Pd(II)) reactions which, coupled with other transformations (β-hydride eliminations, carbometalations, migratory insertions, nucleophilic substitutions), provide a powerful method to construct σ-bonds within substrates. In the next section we revise the most important so-called "Pd-catalyzed cross-coupling reactions".

I.3 Pd-CATALYZED CROSS-COUPLING REACTIONS

The transition-metal-catalyzed substitution of an aryl, vinyl or alkyl halide or pseudohalide by a nucleophile is generally refered to as a "cross-coupling reaction". The principle of these reactions is that the two molecules of interest are bonded to the metal, and thus they are brought very close to one another. Then they couple forming a new carbon-carbon[4-15] or carbon-heteroatom[12,14,16-22] (N, O, S) bond. Nowadays these reactions are key steps in virtually every synthesis of modern pharmaceuticals, agrochemicals, and otherwise biologically active compounds, as well as polymers or other fine chemicals, both in industrial settings and in laboratories, and it is difficult to imagine contemporary Organic Synthesis without them.[1,14,22,23] Among the numerous developed methodologies, Pd-catalyzed reactions[2,3,24] occupy a prominent position, as they fuction under mild conditions and with very high precision. Their imporance in modern Chemistry was recognized by the bestowal of the 2010 Nobel Prize in Chemistry to Richard F. Heck,[25] Ei-ichi Negishi[26] and Akira Suzuki[27] for their development of "Palladium-Catalyzed Cross-Couplings in Organic Synthesis". Pd-catalyzed carbon-carbon and carbon-heteroatom bond-forming reactions are discussed separately in the following sections.

I.3.1 Pd-Catalyzed Carbon-Carbon Bond Forming Reactions

Pd-catalyzed carbon-carbon bond forming reactions start with the oxidative addition of an organohalide (R^1X) or pseudohalide (e.g., X = OTf), to Pd(0), generating an organopalladium(II) complex, R^1PdX, where R^1 is the electrophilic coupling partner. This complex will then react with a nucleophile, R^2, which can be a free molecule (such as an alkene or CO), or part of an organometallic compound, (R^2M). R^2 will coordinate to Pd (via a ligand-displacement, usually followed by an insertion reaction, or via a transmetallation reaction), and then a carbon-carbon bond between R^1 and R^2 will form in the Pd coordination sphere. The resulting new molecule, R^1-R^2, will be eventually released from the Pd atom, and a new cycle will start. Two general examples are shown in *Scheme I.7*, and some important reactions are discussed in the following paragraphs.

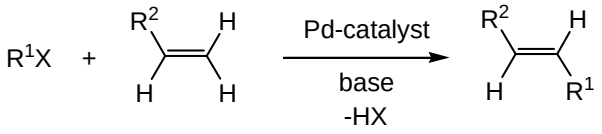


Scheme I.7 Pd-catalyzed carbon-carbon bond forming reactions

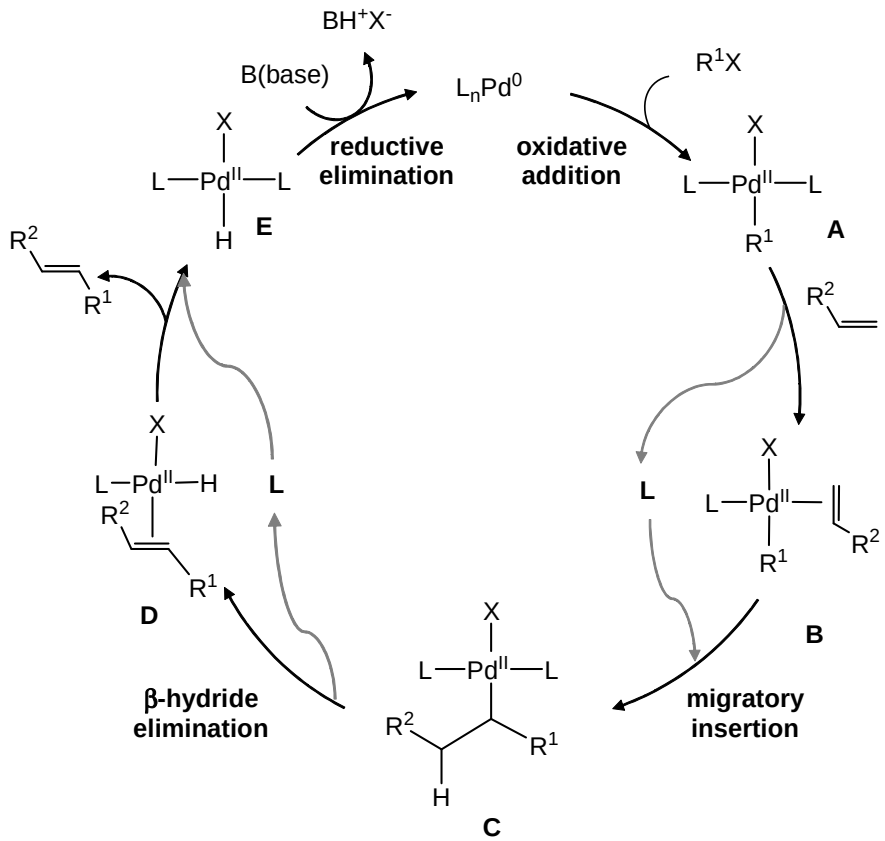
I.3.1.1 C-C Bond Forming Reactions with Olefins: The Heck Reaction

The Heck Reaction[7,25] consists in the Pd-catalyzed carbon-carbon coupling between aryl, benzyl, or vinyl halides or pseudohalides, and an activated alkene (usually with electron-withdrawing substituents), in the presence of a base. After some preliminary reports,[28] the standard version of the Heck Reaction was published in 1972,[29] and it was the first example of a carbon-carbon coupling reaction using a Pd(0)/Pd(II) catalytic cycle. It is sometimes referred to as the "Mizoroki-Heck Reaction", to acknowledge the early contributions of T. Mizoroki[30] in the development of this chemistry. The reaction is stereoselective toward the *E* isomer, and in its intramolecular version[31] it is widely used for the synthesis of carbocyles and heterocycles.[32] *Scheme I.8* shows the generally accepted mechanism. After the

oxidative addition of the organohalide R^1X to the Pd(0) catalyst, the olefin coordinates to the resulting Pd(II) organometallic species, **A**, forming a π-alkene complex, **B**. The *syn* migratory insertion of the olefin into the Pd-R^1 bond results in an alkyl complex, **C**, where the R^1 group is bonded to the less substituted carbon of the olefin. Compound **C** rapidly decomposes through a β-hydride elimination, forming again a π-alkene complex, **D**, where the olefin has adopted an sterically favored (*E*) geometry. The olefin is then released, resulting in the formation of a Pd(II) hydride, **E**, which through a base-assisted hydrogen halide elimination regenerates the catalytically active Pd(0) species.



R = aryl, vinyl
X = halide, triflate



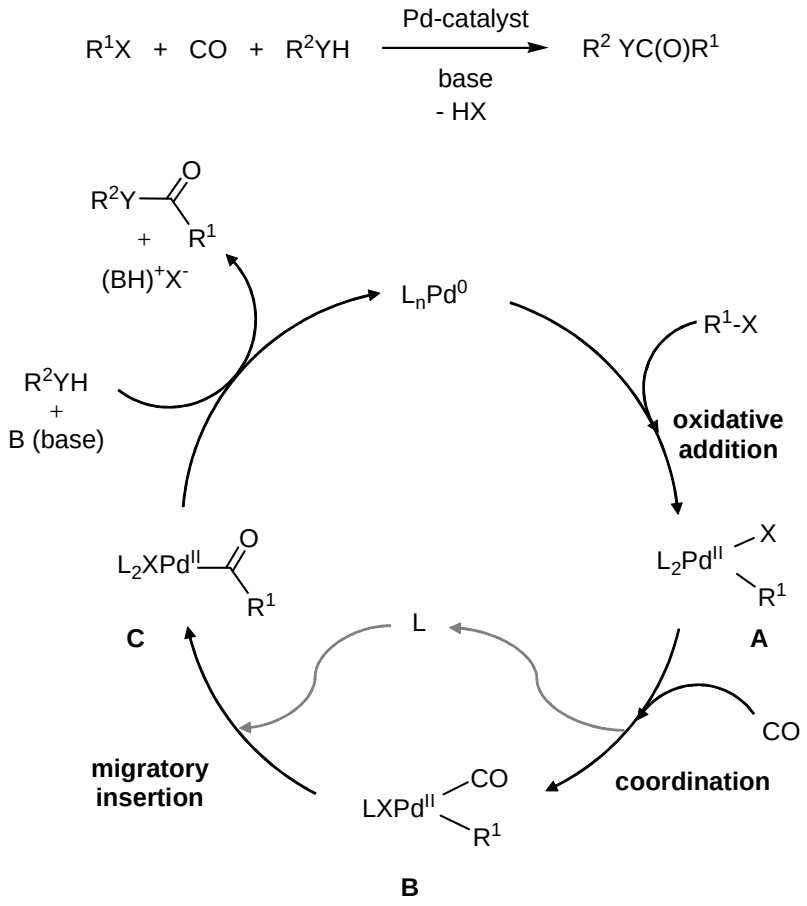
Scheme I.8 Generally accepted mechanism for the Heck Reaction

In 1975, Heck and Cassar reported an extension of the Heck reaction to 1-alkynes, catalyzed by a phosphine-Pd(0) complex in the presence of amines.[33] In the

same year Sonogashira and Hagihara developed their successful Pd(0)-CuI-catalyzed coupling of alkynes with organic halides, where the alkyne is activated through the formation of a Cu(I) acetylide, and which follows a different mechanism (see Section I.3.I.4 below).[4]

I.3.1.2 C-C Bond Forming Reactions with CO: The Heck Carbonylation

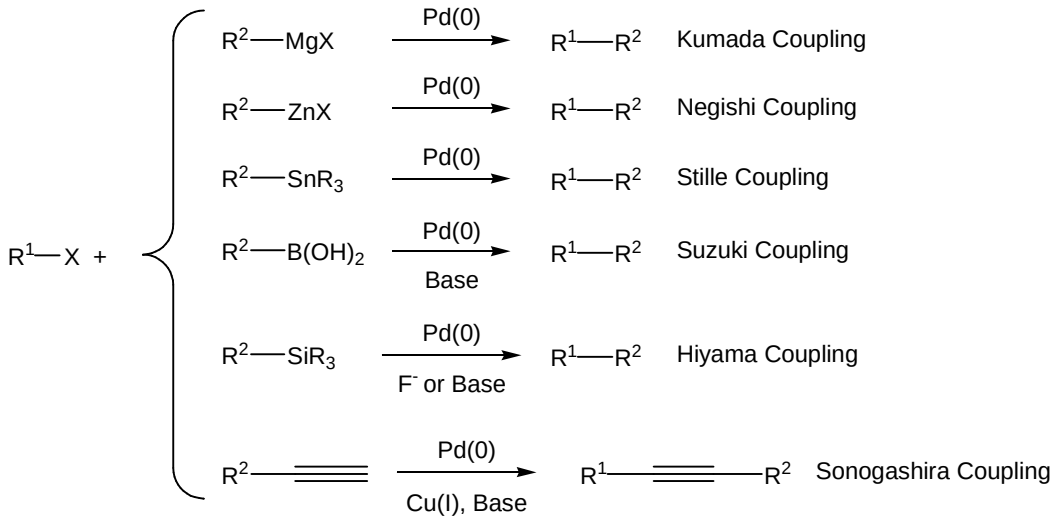
The Pd-catalyzed carbonylation of aryl and vinyl halides was first described more than 30 years ago by Richard Heck.[34] However, limitations in the conditions originally described[35] meant that this reaction achieved less prominence than the coupling reaction with alkenes described above. The so-called Heck Carbonylation[13] involved the reaction of aryl and vinyl halides with carbon monoxide to form acylpalladium intermediates, which were then converted by reaction with a nucleophile to products such as carboxylic acids, esters, amides, or aldehydes.[35] The addition of a base was necessary to react with the acid generated in the reaction, and to promote the formation of the Pd(0) catalyst. *Scheme I.9* shows the general mechanism for these reactions,[13] involving the oxidative addition of the organohalide to the Pd(0) catalyst, forming a Pd(II) organometallic complex, **A**. Coordination of a molecule of CO to the Pd atom results in an organo(carbonyl)palladium complex **B**.[36-39] These compounds are difficult to isolate, as they readily undergo migratory insertion to give an acyl derivative **C**,[40-57] which may further react with an internal or external nucleophile to form a carbonyl-containing organic product upon depalladation. The utility of this chemistry for the synthesis of carbonyl derivatives has led many researchers to attempt to expand the scope of the reaction beyond the originally described bromide, iodide, and triflate substrates, with conditions suited to large-scale application (particularly low-pressure). To a large degree, this has now been achieved.[35]



Scheme I.9 A general mechanism for the Heck Carbonylation

I.3.1.3 C-C Bond Forming Reactions with Organometallic Reagents

There is a quite long list of reactions involving the Pd-catalyzed coupling between organohalides or organotriflates with organometallic reagents. These reactions are usually named after their discoverers, being the most popular those using organotin (Stille), organoboron (Suzuki), and organozinc (Negishi) reagents, because of their stability and good functional group compatibility. An enduring objective in this field is the search for reactions that proceed under mild conditions, without toxic byproducts, and involving cheap and readily available starting materials. *Scheme I.10* summarizes the most important Pd-catalyzed carbon-carbon bond forming reactions with organometallic reagents, which are briefly described in the following paragraphs (the metal in the organometallic reagent and the year of discovery are given in brackets).



Scheme I.10 Pd-catalyzed carbon-carbon bond forming reactions with organometallic reagents

Kumada-Corriu Reaction (Mg, 1975):[9] The first version of this reaction was concurrently reported in 1972 by the Corriu[58] and Kumada[59] groups, and it described the coupling of Grignard reagents and organic halides, using Ni-containing catalysts. This was a truly ground-breaking discovery of a novel carbon-carbon bond forming process,[15] and it foreshadowed the development of the many other related processes that followed. With the introduction of Pd catalysts in 1975 by the Murahashi group,[60] the scope of the Kumada coupling reaction was further broadened.[61] Still, its major drawback is the poor functional group tolerance of Grignard reagents, while its major advantage is that many of these reagents are commercially available, or easily synthesized, and so they can be directly used without the need of transmetallation reactions to prepare other metal-containing reagents.

Sonogashira Reaction (Cu, 1975):[4] As described at the end of Section I.3.1.1, this reaction consists in the Pd-catalyzed cross-coupling between a terminal alkyne and a vinyl or aryl halide, using as cocatalyst a Cu(I) species that activates the alkyne through the formation of a Cu(I) acetylide. The presence of an amine base is also required. The reaction takes place under mild conditions, and it is compatible with a wide range of functional groups.

Negishi Reaction (Zn, 1977):[5,26] This reaction uses organozinc species, which may be obtained by oxidative addition of an organohalide to Zn(0), or may be generated *in situ* by transmetalation of Grignard or organolithium reagents with $ZnCl_2$. It was the first reaction that allowed the preparation of unsymmetrical

biaryls in good yield, and it has a broad scope (R^1 = alkenyl, aryl, allyl, benzyl, propargyl; R^2 = alkenyl, aryl, alkynyl, alkyl, benzyl, allyl).

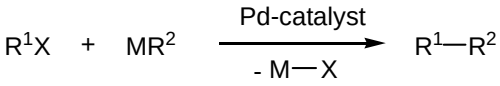
Stille Reaction (Sn, 1978):[6] This is a versatile carbon-carbon bond forming reaction between organostannanes and halides or pseudohalides, with very few limitations on the nature of the R^1, R^2 groups. Its major drawback is the toxicity of the tin compounds.

Suzuki-Miyaura Reaction (B, 1979):[8,27] The original Suzuki-Miyaura Reaction used organoboronic acids and halides (a base was needed to activate the acid), but later developments extended the scope of the reaction to (i) R groups other than aryls (alkyls, alkenyls, alkynyls), (ii) other organoboron reagents (trifluoroborates, organoboranes, or boronate esters), in place of boronic acids, and (iii) some pseudohalides (e.g. triflates), as coupling partners. Due to the stability, ease of preparation, and low toxicity of boronic acids, there is currently a widespread interest in applications of the Suzuki Coupling, with new improvements being constantly reported. This may soon lead to the same versatility in the Suzuki Reaction as in the Stille Reaction, without the drawback of using tin compounds.

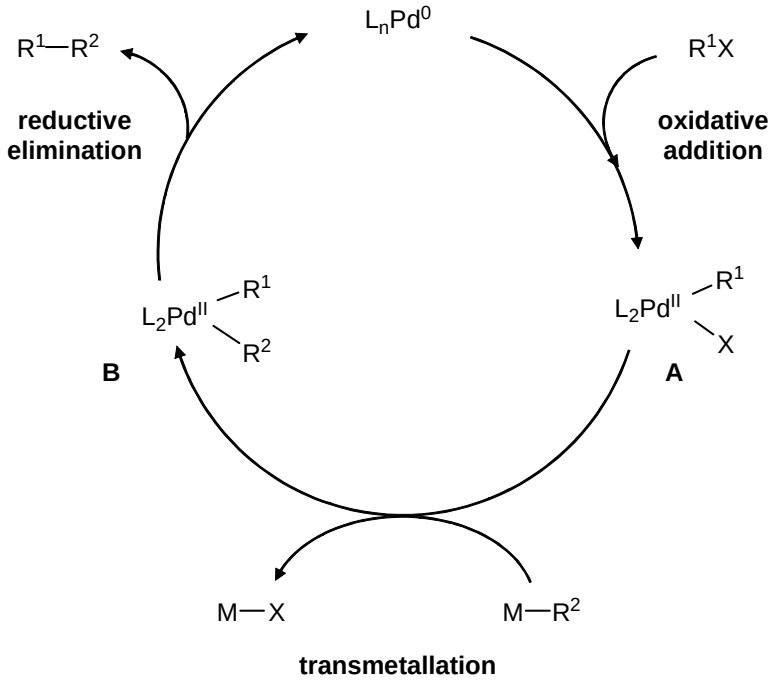
Hiyama Reaction (Si, 1988):[10] This is a Pd-catalyzed carbon-carbon bond forming reaction between aryl, alkenyl, or alkyl halides or pseudohalides, and organosilanes. Similarly to the Suzuki Reaction, it requires an activating agent, such as a fluoride ion or a base, to increase the polarization of the carbon-silicon bond. Organosilanes are stable and easily prepared compounds with low toxicity, and they are compatible with many functional groups. The Hiyama Reaction has become and interesting alternative to the Suzuki Reaction, with a comparable scope of conversions, although the broad commercial availability of boronic acids and boronates often makes the Suzuki Reaction the more convenient choice.

All the reactions described in the previous paragraphs follow the general mechanism depicted in *Scheme I.11*. The first step is again the oxidative addition of the organohalide R^1X to the Pd(0) catalyst, forming a Pd(II) organometallic complex, **A**. Then, the organic group R^2 is transferred to the Pd center by a transmetallation process. The resulting intermediate, **B**, undergoes a reductive elimination, forming

the organic product of interest, R^1-R^2, and regenerating the Pd(0) catalyst.



R = aryl, viny, alkyl, allyl, benzyl, etc.
X = halide, triflate



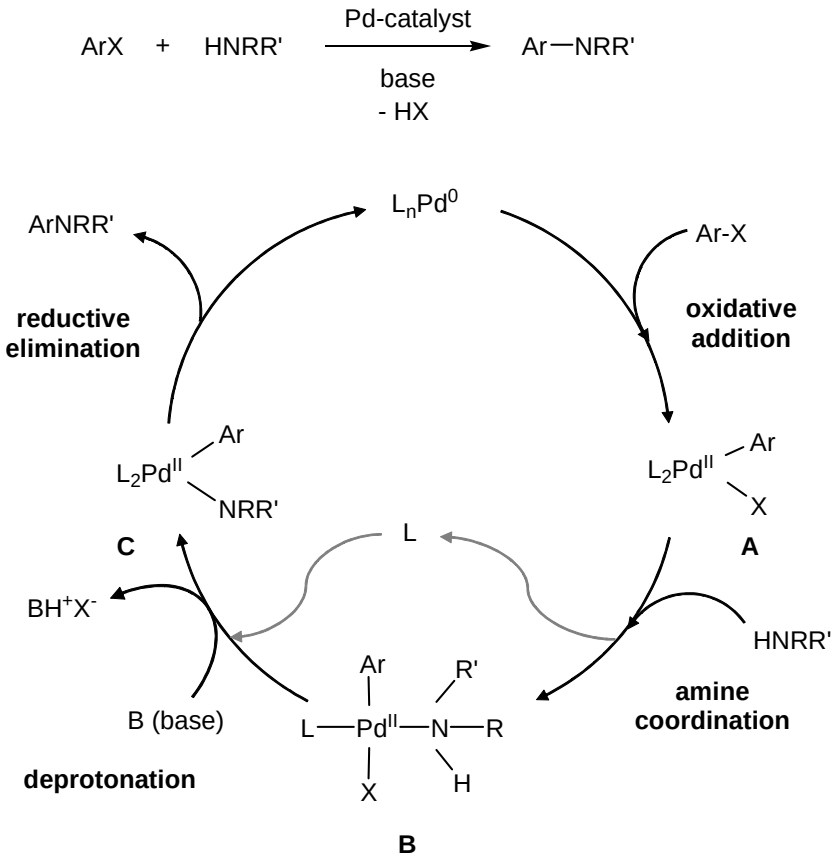
Scheme I.11 General mechanism for the Pd-catalyzed carbon-carbon bond forming reactions with organometallic reagents

I.3.2 Pd-Catalyzed Carbon-Heteroatom Bond Forming Reactions

A relatively recently success in Organometallic Catalysis is the discovery of reactions that form bonds between carbon and heteroatoms, such as N, O, S, Si, and B, via complexes of transition metals with amides, alcoxides, thiolates, silyl groups or boryl groups. These reactions are very important, as the functionality of many molecules, such as pharmaceuticals and conductive polymers, is often derived from the presence of heteroatoms (N, O, S) within the carbon skeleton. Heterocyclic compounds with C-N, C-O, and C-S bonds are found in almost all applications of Chemistry. Moreover, useful intermediates in synthesis often contain C-B or C-Si bonds that are later converted into C-C, C-O, or C-N bonds in the final products.[20]

The first example for the Pd-catalyzed formation of a carbon-nitrogen bond was reported by Migita,[62] and it used aryl bromides and tin amides, which are toxic and sensitive compounds. This work went unreferenced for a decade until John Hartwig started to investigate the mechanism of this reaction, discovering that it involved Ar-Pd(II) compounds and a transmetallation step (of the amine) from Sn to Pd, similarly to the Stille reaction.[63] Three months after Hartwig's paper was submitted, Stephen Buchwald submitted his first work on the same subject, extending the scope of the reaction by generating tin amines *in situ*.[64] Both authors began then an ongoing trend of independent, overlapping research, publishing methods for tin-free Pd-catalyzed aryl-amine couplings,[64,65] the use of bidentate phosphine ligands,[66] the extension of the reaction to aryl iodides, triflates,[65,67] and chlorides[68] and, a major breakthrough, the formation of aryl-oxygen bonds.[69] Several generations of catalyst systems have been developed, with each system allowing greater scope in terms of coupling partners and milder conditions, until nowadays virtually any amine can be coupled with a wide variety of aryls. Many reviews have been published by both authors, and the reaction is now known as the Hartwig-Buchwald Amination.[17,20] The general accepted mechanism for this reaction is depicted in *Scheme I.12*, and it is similar to those described above for the Pd-catalyzed carbon-carbon coupling reactions. The main difference is that after formation of the Pd(II) complex **A**, by oxidative addition of the aryl halide to the Pd(0) species, the free amine coordinates to **A** forming the amine complex **B**. This complex is deprotonated by the action of a base, losing the halide ligand in the form of (baseH)X, and forming the intermediate amido complex **C**. Finally, a reductive elimination on **C** forms the new amine, ArNRR', and regenerates the Pd(0) catalyst.

Alcohols can also be coupled with aryl halides to form the corresponding aryl ethers, under similar conditions to those of the the amination reaction.[16] Thiols and thiophenols can participate in these reactions as well, forming the corresponding arylthioethers.[19] Trifluoromethyl sulphides have also been used as a source of SCF_3 groups.[21]



Scheme I.12 General mechanism for the Hartwig-Buchwald Amination

I.4 ARYLPALLADIUM(II) COMPLEXES

Arylpalladium(II) complexes play a prominent role in Organopalladium Chemistry. They display an especially rich chemistry, as a consequence of the relative lability of the Pd-aryl bond, and they are often involved in some of the most important Pd-mediated processes, as shown in Section I.3. Consequently, there have been intensive studies on the synthesis of Pd(II) aryl complexes and on the study of their reactivity.

Our research group has been specially interested in the synthesis of *ortho*-substituted arylpalladium complexes,[44-49,51,53,54,56,57,70-87] and the investigation of their reactivity toward unsaturated organic molecules.[39,44-57,71,72,74,76-80,82,83,85-99] These molecules often insert into the aryl-Pd bond, forming new palladium complexes, and this reactivity may be affected by the group in *ortho*, as a consequence of electronic or steric effects. Very often new ligands and/or organic compounds are formed, involving *both* the insertion of the organic molecule into the carbon-palladium bond *and* its interaction with the group in *ortho* position.[39,47-50,53,54,57,71,72,74,77,80,82,83,86-88,90-

[96,98,99] Cyclopalladated compounds[100,101] (see Section I.4.1.1 below) are often involved in these reactions.[50,72,77,79,81,82,86,89]

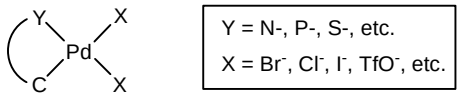
In this section we will revise the main methods for the synthesis of (*ortho*-substituted) arylpalladium(II) complexes, as well as some of the most representative insertion reactions with organic molecules, namely alkynes, carbon monoxide, and isocyanides.

I.4.1 Synthesis of *ortho*-Substituted Arylpalladium(II) Complexes

The most popular methods for the synthesis of *ortho*-substituted arylpalladium(II) complexes are: (i) direct cyclopalladation (*ortho*palladation), (ii) transmetallation, and (iii) oxidative addition reactions.

I.4.1.1 Orthopalladation Reactions

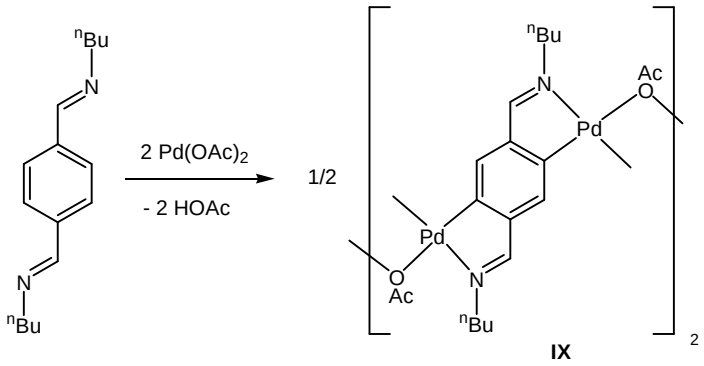
Cyclopalladated compounds contain a Pd-C σ-bond stabilized by the coordination to Pd of a heteroatom of the ligand (*Scheme I.13*). They have been extensively investigated[102] because they combine the reactivity of the Pd-C bond with a remarkable stability. Their electronic and steric properties can be modulated by changing (i) the size of the palladacycle (3- to 10-membered palladacyles are known), (ii) the nature of the carbon atom bonded to Pd (aromatic, aliphatic, vinylic…), (iii) the nature of the heteroatom bonded to Pd (N-, S-, P-, O-, etc.), (iv) the substituents on the heteroatom (or on other parts of the ligand), and (v) the rest of the ligands bonded to the Pd atom.[103]



Scheme I.13 Schematic representation of a palladacycle

Most frequently, palladacycles are *ortho*palladacycles, i.e., arylpalladium complexes where the Pd atom is bonded to the carbon atom in *ortho* to the substituent which is also coordinated to Pd. They are usually prepared by direct activation (by reaction with an electrophilic Pd(II) compound, such as $[Pd(OAc)_2]$, $PdCl_2$, or a $[PdCl_4]^{2-}$ salt) of a C-H bond in *ortho* to a funcional group containing a suitable donor atom. This reaction is known as orthopalladation.[104] The most common palladacycles are those derived from *N*-donor ligands, mainly imines and tertiary amines, and

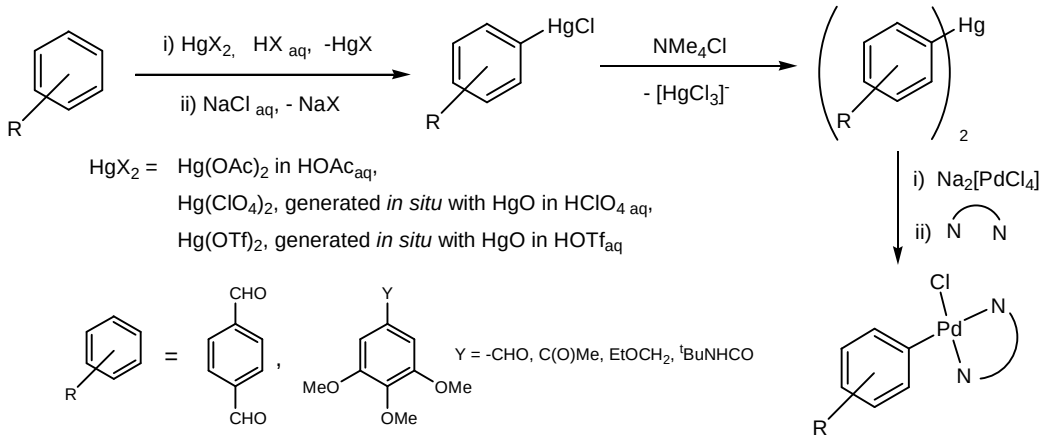
containing 5- or 6-membered rings.[103] *Scheme I.14* shows the orthopalladation of the diimine $C_6H_4(CH=N^nBu)_2$-1,4 with $[Pd(OAc)_2]$, forming the tetranuclear complex $[\{\mu$-*C1,C4,N,N"*-$C_6H_2\{C(H)=N(^nBu)\}_2$-2,5$\}\{Pd(\mu$-OAc$)\}]_2$ (**IX**),[105] which is the starting material of the chemistry described in Chapter V of this Thesis.



Scheme I.14 Orthopalladation of a diimine with $Pd(OAc)_2$[105]

I.4.1.2 Transmetallation Reactions

A transmetallation reaction[106] involves the transfer of a ligand from one metal to another. The general reaction involving organic ligands is: $M^1–R + M^2–R' \rightarrow M^1–R' + M^2–R$ (R, R' = alkyl, aryl, alkynyl, allyl, etc.). Organolithium and organomagnesium reagents are commonly used transmetallation reagents, but they are not compatible with many functional groups, such as proton acids, electrophilic groups, or good leaving groups. Organomercurials, in contrast, are very easy to prepare and handle, and they have been used in our research group for the synthesis of aryl derivatives of Pt,[107] Au,[108] Rh,[109] Sn,[110] Tl,[111] and Pd[71,72,112-115] (see *Scheme I.15* for an example).



Scheme I.15 Synthesis of arylpalladium complexes with 2-formyl-4,5,6-trimethoxyphenyl,[113] 2-acetyl-4,5,6-trimethoxyphenyl,[114] 2-ethoxy-4,5,6-trimethoxyphenyl,[71] 2-*tert*-butylcarbamoyl-4,5,6-trimethoxyphenyl,[72] and 2,5-diformyl[115] ligands, by transmetallation reactions involving organomercurials

Transmetallation reactions to Pd are a key step in Pd-catalyzed carbon-carbon bond forming reactions involving organometallic reagents, such as those described in Section I.3.1.3 (Kumada (M = Mg), Negishi (M = Zn), Stille (M = Sn), Suzuki (M = B), Hiyama (M = Si), and Sonogashira (M = Cu) reactions).

I.4.1.3 Oxidative Addition Reactions

In an oxidative addition reaction,[116] a compound A-B adds to a metallic complex [M]. As a result both fragments of the oxidant bond to the central atom of the complex, increasing both its oxidation state and its coordination number in two units:

$$[M] + A{-}B \rightleftharpoons A{-}[M]{-}B \qquad \textit{Eq. I.1}$$

The opposite reaction is the reductive elimination.[117] Both reactions are very common in the chemistry of transition metals, because of the availability of different and easily accessible oxidation states. The most important systems are.

$$[M(0)] \rightleftharpoons [M(II)] \qquad M = Ni, Pd, Pt \qquad \textit{Eq. I.2}$$

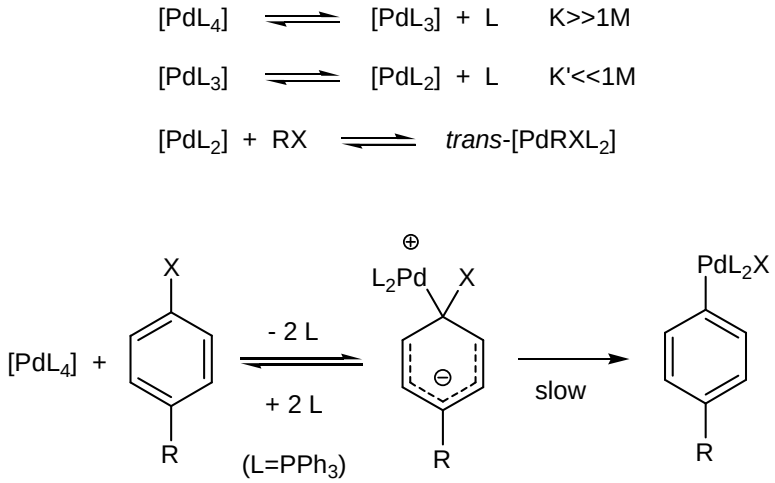
$$[M(I)] \rightleftharpoons [M(III)] \qquad M = Rh, Ir \qquad \textit{Eq. I.3}$$

Oxidative additions are common for coordinatively unsaturated, electron-rich metal centers, in low oxidation states (mainly 0 and +1). Good σ-donor ligands, such as R_3P, bpy, alkyl and hydride ligands, favour the reaction, while π-acceptors, such as CO and olefins, hinder, or even prevent it. A wide range of A-B oxidants can be used in these reactions. They can be polar electrophiles such as H-X, R-X, RCO-X, and RSO_2-X, non polar electrophiles such as X_2, H_2, R_3Si-H, RCO-H, R-H, and Ar-H, multiple bonds like in O_2 or carbonyls, and even strained hydrocarbons.[118]

When A, B, or both are organic groups, oxidative addition reactions are very useful for the synthesis of organometallic compounds, and they are involved in important catalytic and stoichiometric reactions in metal-mediated Organic Synthesis, as described in Section I.3 for Pd-catalyzed cross-coupling reactions. The most common reaction is the oxidative addition of an organic halide or pseudohalide, RX, where R is an organic group (alkyl, aryl, vinyl, benzyl, acyl, etc.) and X an anion such as bromide, iodide, acetate, or triflate (*Eq. I.4*). A major advantage of these reactions is that they allow the use of R groups containing reactive substituents such as carbonyls, amines, etc., which would be incompatible with organolithium or organomagnesium reagents.

$$[M^0] + R-X \rightleftharpoons R-[M^{II}]-X \qquad \textit{Eq. I.4}$$

A great number of reactions of organic halides or pseudohalides with Pd^0 compounds[119,120] have been described since the first reports by Fitton.[121] Considerable attention has been paid to phosphine complexes, especially $[Pd(PPh_3)_4]$.[70,122] These are easily prepared, and they are used in their stable chemical form, $[PdL_4]$, although it seems that in solution the dissociation of two phosphine ligands takes place, affording dicoordinated species, $[PdL_2]$, which are the real substrate of the oxidative addition (*Scheme I.16*).[123] The low rate constant of the second dissociation step often makes the concentration of $[PdL_2]$, which is the active catalyst, very low, and subsequently the overall kinetics is very slow. To avoid this problem, several methods have been developed to generate the $[PdL_2]$ moiety *in situ*. One of them is the reduction of $[Pd(OAc)_2]$ by phosphines, generally PPh_3.[120,124] Once the $[PdL_2]$ substrate is generated, it has been suggested that the oxidative addition takes place through a S_N2 mechanism, as described also in *Scheme I.16*.[125] Reactivity decreases in the sequence ArI > ArBr >> ArCl, in agreement with the cleavage of the C-X bond being the rate-determining step. The rate constant increases with the electron-withdrawing character of the R substituent (*p*-$NO_2C_6H_4Cl$ > *p*-NCC_6H_4Cl > *p*-$PhC(O)C_6H_4Cl$), which is consistent with a nucleophilic attack of the palladium on the aromatic carbon.

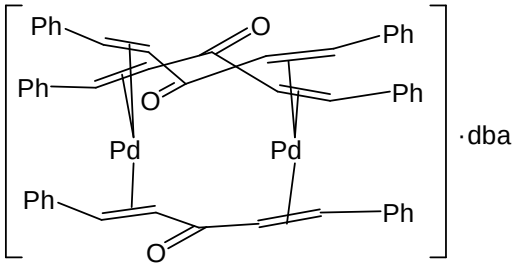


Scheme I.16 Proposed mechanism for the generation of the $[PdL_2]$ substrate (L = phosphine), and S_N2 mechanism for the oxidative addition of aryl halides to $[Pd(PPh_3)_2]$

This Thesis describes some oxidative addition reactions of aryl halides to a different Pd(0) compound, namely $[Pd_2(dba)_3]\cdot dba$ (dba=dibencylidenacetone). This molecule is formed by two Pd atoms bridged by three dba molecules, and it crystallizes

with a fourth dba molecule (*Scheme I.17*). For simplicity, it is often written as $[Pd(dba)_2]$. This Pd(0) substrate is used in the presence of auxiliary ligands L, usually phosphines, or chelate N-donors such as 2,2'-bipyridyl (bpy) or *N,N,N`,N'*-tetramethylethylenediamine (tmeda), to complete the coordination sphere of the Pd. The general reaction is shown in *Eq. I.5*.

$$[Pd^0(dba)_2] + 2\,L + Ar\text{-}X \longrightarrow [Pd^{II}ArXL_2] + 2\,dba \qquad \textit{Eq. I.5}$$



Scheme I.17 Structure of $[Pd(dba)_2]$

Because the dba is a labile ligand, it was initially thought that it would be easily displaced from the metallic center by the other ligands (L), affording $[PdL_2]$ in nearly quantitative yield.[126] It is now known, however, that $[Pd(dba)L_2]$ is generated instead, although it is in equilibrium with free dba and $[PdL_2]$, which is the active species that reacts with RX to give $[PdXRL_2]$. In fact, NMR and cyclic voltametry studies of the reaction of $[Pd(dba)_2]$ with PPh_3 show that the dba is a better ligand to $[Pd(PPh_3)_2]$ than PPh_3 itself, and that the concentration of free $[PdL_2]$ in a mixture of $[Pd(dba)_2]$ and PPh_3 can be lower than in $[Pd(PPh_3)_4]$ solutions.[127]

In any case, this method is being increasingly used[44,46,48,53,54,74-76,78-80,82-84,86,87,128] because it has important synthetic advantages. First of all, $[Pd(dba)_2]$ is easily prepared and it is air-stable, so that it can be handled and stored without any special precautions (in contrast, for example, with $[Pd(PPh_3)_4]$). As only two equivalents of phosphine are needed, expensive quiral phosphines can be used, and quiral catalysts can be generated *in situ*. Moreover, it is possible to prepare complexes with ligands other than phosphines, such as bpy, tmeda, or phen. Another important advantage of $[Pd(dba)_2]$ is that the by-product, dba, is easily separated from the products of the reaction.[118]

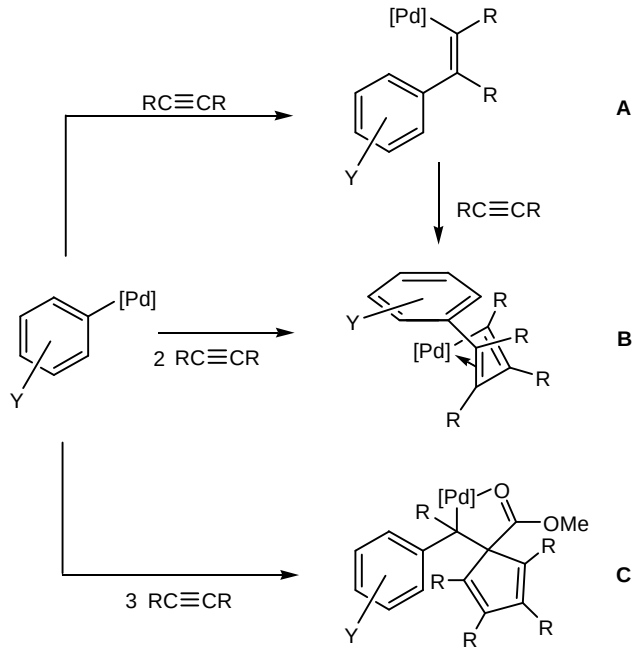
I.4.2 Reactivity of Arylpalladium(II) Complexes toward Unsaturated Organic Molecules: Insertion of Unsaturated Molecules into the Aryl-Pd Bond

An insertion reaction may be defined as the migration of a ligand from a metal center to an adjacent coordinated unsaturated molecule, resulting in the formation of a new complex.[129] The new ligand thus generated may eventually be released from the complex (e.g., via a reductive elimination reaction) so that new organic products are formed. Insertion reactions are thus basic steps in many transition metal-catalyzed organic syntheses and, in particular, in Pd-catalyzed reactions,[130] such as the Heck reaction (Section I.3.1.1), and the Heck carbonylation (Section I.3.1.2), where an alkene or a CO molecule is inserted into a carbon-palladium bond. Consequently, the investigation of stoichiometric insertion reactions may lead to a better understanding of the related catalytic cycles.

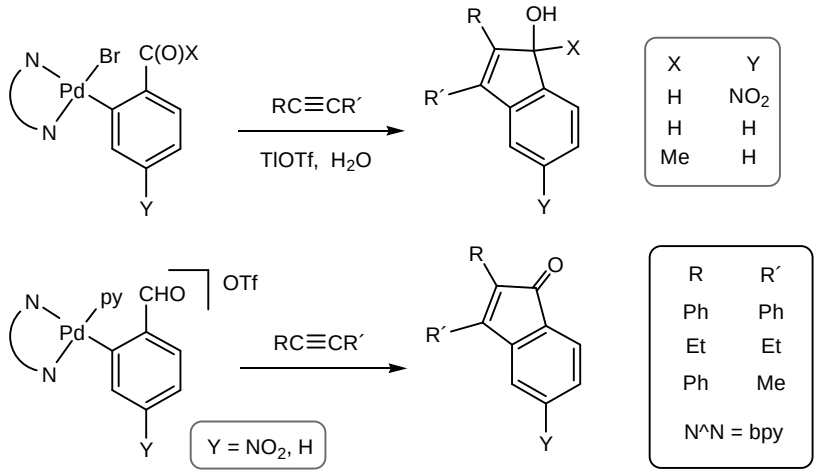
I.4.2.1 Insertion of Alkynes into Aryl-Pd Bonds

The first reports on the reactivity of palladium organometallic complexes with alkynes were due mainly to the group of Maitlis,[131] who studied the oligomerization of alkynes in the presence of Pd complexes. Later, the reactivity of many arylpalladium complexes toward alkynes was also investigated, mainly in the groups of Pfeffer,[37,132-140] Heck,[141-145] and Larock,[146,147] as well as ours.[38,39,45,47,48,51,53,55,56,71,72,77,78,80,84,86-88,90,91,96,99,148-150] Many of these reactions involved N-donor palladacycles.

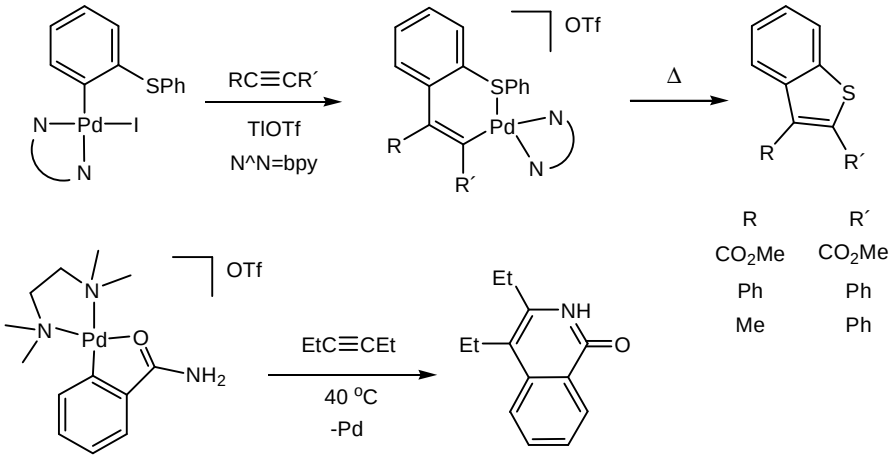
In the reactions of arylpalladium complexes with alkynes, the insertion of one, two, or three alkynes into the carbon-palladium bond has been described, giving in most cases products of the types **A**-**C**, represented in *Scheme I.18*. Vinylpalladium complexes (type **A**), are most frequently formed, while products of the type **B** or **C**[38,45,47,51,135,136,138,139,151-153] are less common. Through depalladation processes, some of these complexes give new organic products such as spirocycles,[71,72,88,139,149] indenols, indenones,[77,91,148] other carbocycles,[88,136,137,139,141,142,152,154] and heterocycles where the heteroatom is oxygen,[140,155149,164] sulphur,[53,134] or nitrogen.[48,80,86,132,138,140,141,143,150,151] In some cases, the palladation reaction and the insertion of the alkyne are part of a catalytic cycle.[144,146,147,156,157] *Schemes I.19-21* show some examples of stoichiometric and catalytic syntheses of organic molecules, where the insertion of an alkyne into an aryl-Pd bond is a key step of the process.



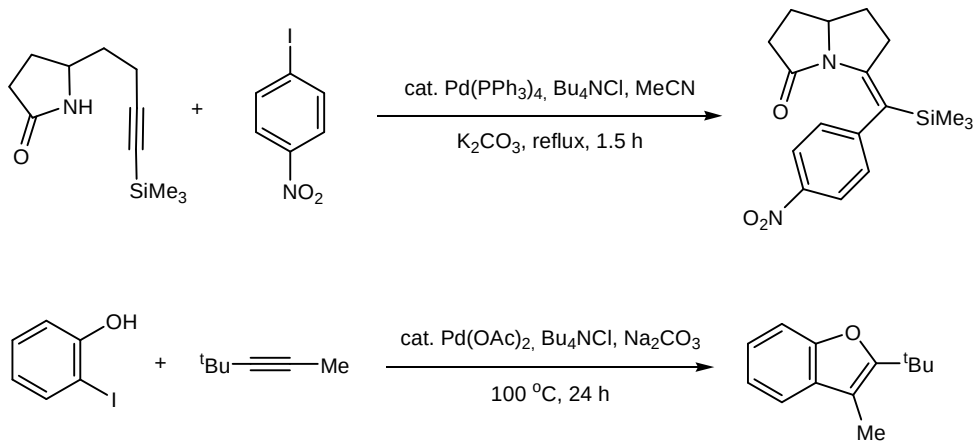
Scheme I.18 Insertion reactions of alkynes in arylpalladium(II) complexes



Scheme I.19 Reactivity of arylpalladium(II) complexes toward alkynes, resulting in the formation of indenols and indenones[77]



Scheme I.20 Reactivity of arylpalladium(II) complexes toward alkynes, resulting in the formation of S-[53] or N-[86]containing heterocycles



Scheme I.21 Pd-catalyzed ($[Pd(PPh_3)_4]$[157] or $[Pd(OAc)_2]$[147]) synthesis of organic molecules, involving the insertion of an alkyne into an aryl-Pd bond

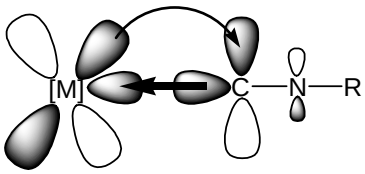
I.4.2.2 Insertion of CO and Isocyanides into Aryl-Pd Bonds

Isocyanides (or isonitriles) and carbon monoxide are isoelectronic compounds and thus their chemical behaviour as ligands has many similarities. For example, both tend to coordinate to metals in low oxidation states, such as Cr(0), Mo(0), W(0), Mn(0), Fe(0), Ni(0), or Pd(0).[158] However, there are also differences between them:[118,159]

- Unlike CO, isocyanides have a considerable dipolar moment, with the negative pole on the carbon, (μ_{CNPh} = 3.44 Debye, μ_{CO} = 0.1 Debye).
- It is not so common for isocyanides to act as bridging ligands as for CO, although there are some examples, such as $[(RNC)_3Co((\mu\text{-}CNR)_2)Co(CNR)_3]$ or $[Pd_2(\eta^5\text{-}C_5Ph_5)_2(\mu\text{-}XyNC)_2]$.[160]
- There is always a decrease in the $\nu(C\equiv O)$ stretching band upon coordination of CO to a metal, while the $\nu(C\equiv N)$ band of coordinated isonitriles may shift both to higher (most frequently), or lower frequencies with respect to the free ligand.
- Metallic isocyanides show a major tendency than carbonyls to exist in high oxidation states (M(II), M(III)). An example of this are the Pd(II) isocyanide complexes described in this Thesis.

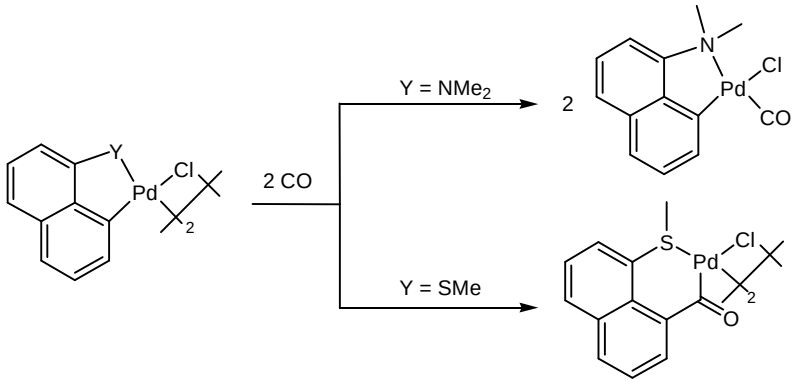
The latter two differences are a consequence of isocyanides being better σ-donors and weaker π acceptors than carbonyls.[161] The σ component of the M-CO or M-CNR bond corresponds to a transfer of electron density from the antibonding HOMO of the ligand (wih $sp\sigma^*$ symmetry), to empty d orbitals of the metal, whereas

the π bond component corresponds to a transfer of electron density from filled d metallic orbitals to the pπ* LUMO of the ligand (*Scheme I.22*). Thus, the σ component causes an increase (and the π component a decrease) in the C-O or C-N bond order. In metal carbonyls, the π component is always predominant, so that there is a decrease in the ν(C≡O) upon coordination. In contrast, for isocyanide complexes, the importance of the π component varies with the nature of the metal and the R group of the isocyanide, so that sometimes there is an increase, and sometimes a decrease, in the ν(C≡N) upon coordination.

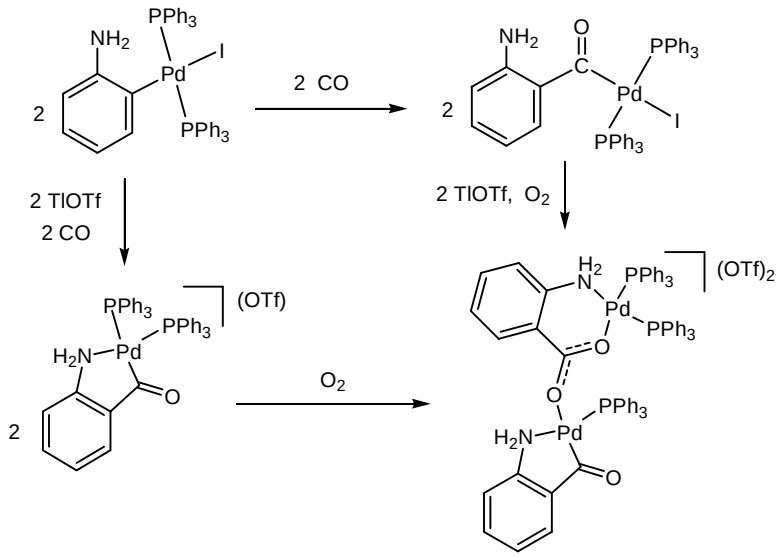


Scheme I.22 σ and π components of the M-CNR bond

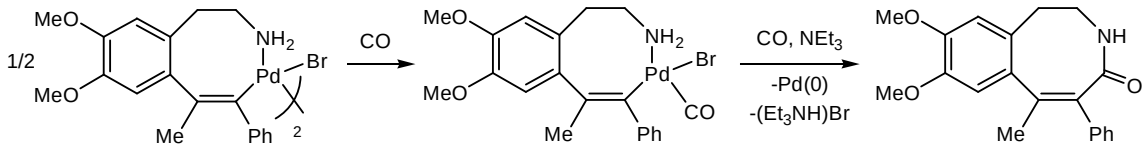
Organopalladium complexes react with CO to form acyl or aroyl complexes,[40-57,162] which may further react with an internal or external nucleophile to form a carbonyl-containing organic product upon depalladation,[48-50,96,98,100,163,164] and these reactions are a key step in Pd-catalyzed carbonilations,[13,34,35,42,165] as described in Section I.3.1.2. *Schemes I.23-25* show some interesting examples of the reactivity of Pd(II) organometallic complexes toward CO. Two of them (*Schemes I.24*[44] and *I.25*[39]) have been reported by our research group.



Scheme I.23 Influence of the donor atom in a palladacycle on the reactivity toward CO[41]

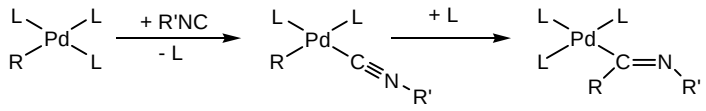


Scheme I.24 Insertion of CO into the C-Pd bond of an *ortho*-aminophenylpalladium complex, followed by an unexpected oxidation of the resulting *ortho*-aminobenzoyl ligand[44]

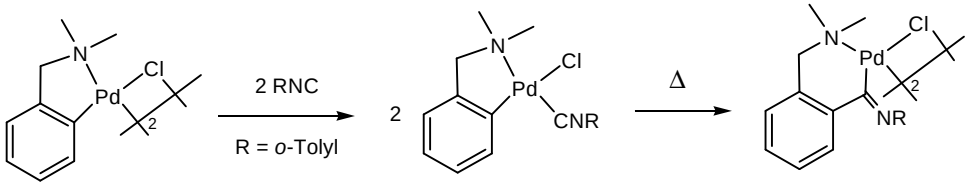


Scheme I.25
Isolation of a Pd(II) organocarbonyl intermediate in the synthesis of eight-membered lactams[39]

Isocyanides, in contrast, coordinate to Pd(II) to give stable compounds, which are more easily isolated than carbonyls.[166] In the case of organopalladium complexes, the coordination of the isocyanide to the metal is frequently followed by the insertion into the carbon-palladium bond, forming iminoacyl Pd complexes,[41,43,45-50,52-54,56,57,72,76,78-80,82,83,85-87,92-94,97,99,167-172] as generally shown in *Scheme I.26*. An example involving a cyclopalladated arylpalladium complex is shown in *Scheme I.27*.[170] An increase in the electrophilic character of the isocyanide favours the insertion reaction.[172]

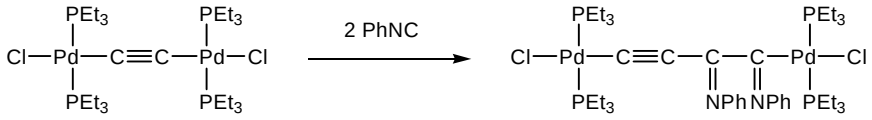


Scheme I.26 Proposed mechanism for the insertion of isocyanides into carbon-palladium bonds

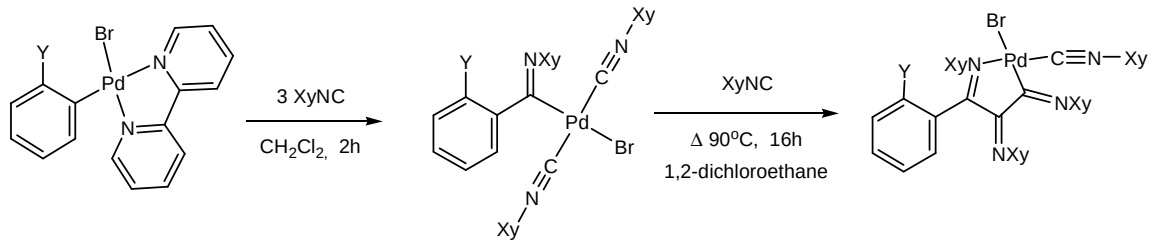


Scheme I.27 Coordination of an isocyanide to Pd(II), followed by insertion into the aryl-Pd bond[170]

While multiple insertions of CO into the carbon-palladium bond are virtually unknown, they are common with isocyanides.[53,76,93,167,171] Two examples are shown in *Scheme I.28*[171] and *I.29*.[93] The formation of oligomeric compounds, which implies a higher number of isocyanide insertions, has been observed in the palladium-catalyzed asymmetric helicoidal polymerization of isocyanides.[173]

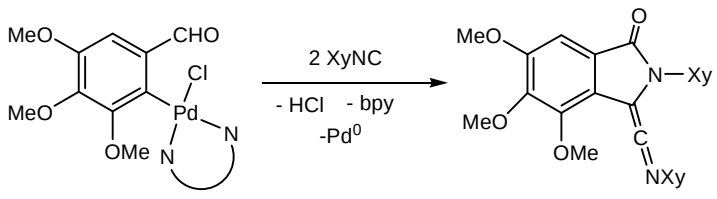


Scheme I.28 Selective diinsertion of isocyanide in a dinuclear palladium complex[171]



Scheme I.29
Mono- and triinsertion of XyNC into an aryl-palladium bond. The product resulting from the triinsertion is stabilized by the formation of a five-membered chelate[93]

The insertion reactions of isocyanides in organopalladium complexes were initially investigated to get insight into the mechanisms of Pd-mediated carbonylation reactions, as a consequence of the isoelectronic nature of isocyanides and CO. Nowadays, however, they have acquired interest on their own, as they are involved in many stoichiometric[47-50,72,92,163,168] and catalytic[174] syntheses of organic compounds. *Scheme I.30* shows the synthesis of a highly functionalized ketenimine by reaction of a 2,3,4-trimethoxy-6-formylphenylpalladium complex with XyNC.[72]



Scheme I.30 Obtention of a highly functionalized ketenimine by reaction of an arylpalladium complex with XyNC[72]

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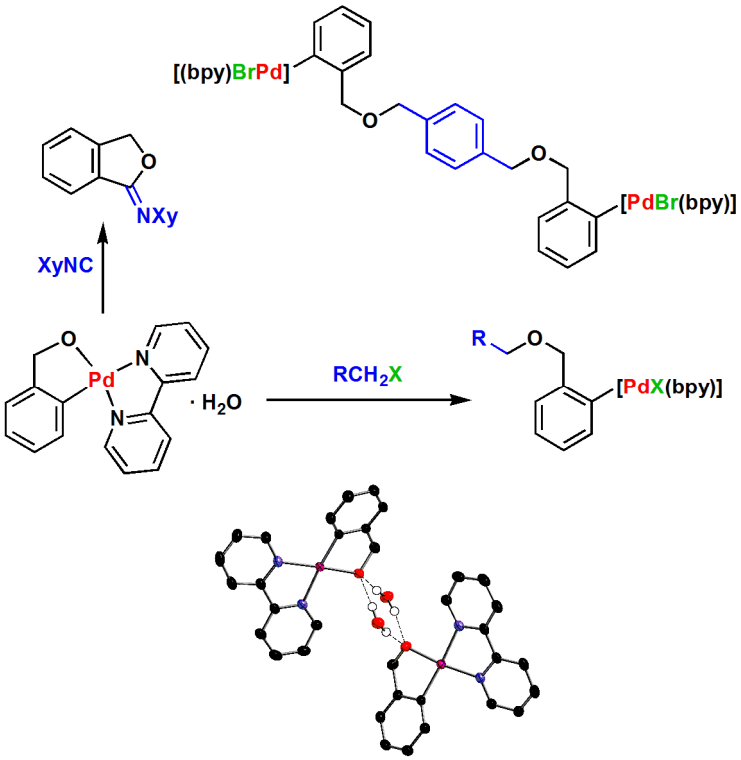
CHAPTER II

Synthesis of Arylpalladium(II) Complexes Derived from Benzyl Alcohol, Reactivity toward Alkyl Halides, and Synthesis of Dinuclear Arylpalladium(II) Complexes



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II.1 ABSTRACT

The arylpalladium complexes [PdI($C_6H_4CH_2OH$-2)(N^N)] (N^N = bpy = 2,2'-bipyridyl (**1a**), tbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine (**1b**), tmeda = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (**1c**)) were synthesized by oxidative addition of 2-iodobenzyl alcohol to one equivalent of "[$Pd(dba)_2$]" (dba = dibenzylideneacetone) in the presence of the N^N ligands. By reaction of **1a** with three equivalents of XyNC (Xy = 2,6-dimethylphenyl) the insertion complex *trans*-[PdI{C(=NXy)($C_6H_4CH_2OH$-2)}$(CNXy)_2$] (**2**) was formed. The reaction of **1a** with KO^tBu resulted in the formation of the chelate complex [Pd(κ^2-*C*,*O*-$C_6H_4CH_2O$-2)(bpy)] (**3**), which crystallizes as pairs of molecules bridged by hydrogen bonds to water of crystallization. Complex **3** reacts with XyNC forming the cyclic imidate *N*-(2,6-dimethylphenyl)-2-benzofuran-1(*3H*)-imine (**4**). By reaction of **3** with various primary alkyl halides RCH_2X, the complexes [PdX($C_6H_4CH_2OCH_2R$-2)(bpy)] (X = I, R = H (**5a**), X = Br, R = Ph (**5b**), *p*-$C_6H_4CH_2Br$ (**5c**), *p*-C_6H_4Br (**5d**), and *p*-C_6H_4I (**5e**)) were obtained. When the reaction of **3** with *p*-$C_6H_4(CH_2Br)_2$ was carried out in a 2:1 ratio, the dinuclear arylpalladium complex [{(bpy)BrPd($C_6H_4CH_2OCH_2$-2)}$_2$(C_6H_4-1,4)] (**6**) formed. An halide exchange reaction on **5e**, using AgOTf and an excess of NaI, afforded [PdI{$C_6H_4(CH_2OCH_2(C_6H_4I$-4))-2}(bpy)] (**5f**), which by oxidative addition to [$Pd(dba)_2$] in the presence of bpy formed another dinuclear arylpalladium complex, [(bpy)IPd($C_6H_4CH_2$-2)O($CH_2C_6H_4$-4)PdI(bpy)] (**7**). All the complexes have been extensively characterized by NMR spectroscopy. The crystal structures of **1a**, **3**·H_2O, and **5e** were determined by X-ray diffraction studies.

II.2 INTRODUCTION

Pd(II) aryl complexes have acquired a great relevance in Organometallic Chemistry, because of their involvement in carbon-carbon and carbon-heteroatom bond-forming reactions of great synthetic importance.[1] We have been especially interested in the synthesis of *ortho*-substituted arylpalladium complexes,[2-8] as the substituent in *ortho* position may participate in the reactions with unsaturated organic molecules, forming new ligands and/or organic compounds.[2-6,8-15] Very often, the *ortho*-substitution also results in the formation of cyclopalladated complexes.[2,3,6-8,10,12-15]

Within this line of research, our group has previously reported on the synthesis and reactivity of *ortho*-palladated phenol derivatives.[5,12-14,16] Their reactions with CO,

isocyanides, alkenes, alkynes, and allenes did not involve the interaction with the OH group in *ortho* position.[5,16] The electron-donating ability of this group, however, played a crucial role in the reactivity toward nitriles,[12,14] carbodiimides,[13,14] and isothiocyanates,[14] which afforded the first examples of the insertion of these molecules into a C-M bond of a late transition metal. In view of these results, we decided to extend our research to *ortho*-palladated hydroxymethylphenyl complexes, to investigate how the methylene link in the alcoholic substituent would affect the reactivity of the complexes. 2-Hydroxymethylphenyl palladium complexes with a dppf ligand (dppf = 1,1'-bis(diphenylphosphino)ferrocene) have been used as catalysts to build end-functionalized polyacetylenes.[17] There has also been a report on oxapalladacycles derived from 2-hydroxymethylbenzene[18] and their use as precatalysts in Heck and cross-coupling reactions.[19] However, the reactivity of these complexes toward unsaturated molecules has not been systematically investigated.

In this paper we report our first results with *ortho*-palladated hydroxymethylphenyl complexes, which involve the synthesis of a family of Pd complexes derived from benzyl alcohol, one of them a chelate complex resulting from the deprotonation of the alcohol. This chelate complex has shown an interesting chemistry toward alkyl halides, involving the nucleophilic attack of the coordinated oxygen on the alkyl group, and resulting in the opening of the chelate ring and the formation of new arylpalladium complexes with larger substituents on the aryl ring. We have found no precedent in the literature for this type of reactivity in a *C,O*-cyclometalated aryl group coordinated to a late transition metal. The reaction works very well for a variety of primary alkyl halides and can be a useful chemical tool to build ligands on a pre-existing complex.

Dinuclear Pd complexes have attracted considerable interest in the literature. There are examples where the two [Pd] moieties are attached to the same aryl ring,[19-24] as well as examples where the two Pd atoms are linked by other ligands.[8,23,25-33] These dinuclear complexes have in some cases been used as catalysts, e.g. for Heck,[28] Hartwig-Buchwald,[32] Hiyama,[33] and Suzuki-Miyaura reactions.[25,31] The presence of two Pd atoms can improve the efficiency and selectivity of a catalyst, promote reactions that are difficult to achieve with a mononuclear complex, and result in the formation of unexpected compounds.[30,31] The dinuclear complexes that we report in this paper are quite novel in that they are bis(arylpalladium) complexes, for which there are very few precedents in the literature.[8,23,26,29] Moreover, they are the first examples where the aryl

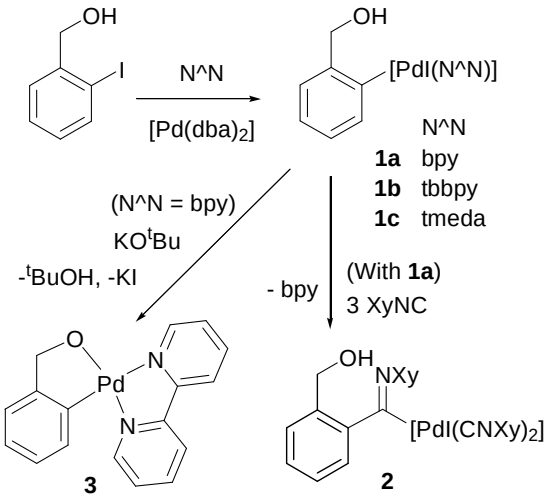
groups are *ortho*-substituted. Their reactivity in insertion[8] or coupling[26] reactions can afford interesting and novel compounds, and we plan to pursue this subject.

We also report in this paper the result of the reactions with XyNC of the complexes derived from benzyl alcohol, where a previously unknown cyclic imidate has been isolated and characterized. Five-membered cyclic imidates are expected to have potential bioactivities similar to those of their structurally similar isoindolin-1-one counterparts.[34]

II.3 RESULTS AND DISCUSSION

II.3.1 Synthesis of [PdI($C_6H_4CH_2OH$-2)(N^N)] (N^N = bpy (1a), tbbpy (1b), tmeda (1c))

Complexes **1a-c** were obtained by oxidative addition of 2-iodobenzyl alcohol to one equivalent of [Pd(dba)$_2$] in the presence of bpy, tbbpy, and tmeda (*Scheme II.1*). We have similarly prepared the related complex [PdI($C_6H_4CH_2OH$)-2}(PPh_3)$_2$] (**I**), which had already been prepared using [Pd(PPh_3)$_4$] as the oxidative addition substrate.[18] In the synthesis of **1b** (N^N = tbbpy) and **1c** (N^N = tmeda) the reactants were used in stoichiometric amounts, while in the synthesis of **1a** (N^N = bpy) and **I**, 50% excess alcohol was used to obtain either a better yield (**1a**) or a clean product (**I**). Complexes **1b,c** decompose in solution to form [PdI$_2$(N^N)] (N^N = tbbpy, tmeda), which are identified by their characteristic ^{1}H NMR resonances at 9.84 ppm (dd) for [PdI$_2$(tbbpy)] (which also has a characteristic red color) or 2.95 ppm (s) for [PdI$_2$(tmeda)]. Attempts to prepare complexes similar to **1a-c** with a Br ligand instead of I, starting from 2-bromobenzyl alcohol, were unsuccessful.



Scheme II.1 Synthesis of complexes **1**-**3**

II.3.2 Reactivity of [PdI($C_6H_4CH_2OH$-2)(bpy)] (1a)

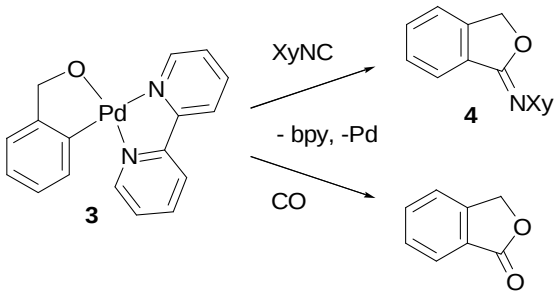
We have investigated the reactivity of complex **1a** toward unsaturated molecules such as alkynes, alkenes, nitriles, cyanamides, allenes, and carbon monoxide, with and without the addition of TlOTf, but we were not able to obtain clean insertion (C-Pd bond) or addition (O-H bond) products, in contrast to our previous observations with *ortho*-palladated phenol derivatives.[5,16] We had already proposed that the OH group directly bonded to the aryl ligand played a crucial role in the insertion reactions with nitriles,[12,14] carbodiimides,[13,14] and isothiocyanates,[14] via a resonance form that locates the negative charge on the *ipso* carbon (see *Scheme III.2* in Chapter III for an example).[12,14] It now seems that the methylene link is detrimental even in the reactions with other molecules such as alkynes, alkenes and CO, where the OH group did not seem to be involved.[5,16] We have been successful only in the reaction of **1a** with three equivalents of XyNC (Xy = 2,6-dimethylphenyl) which, when carried out in cold THF, instantaneously formed the insertion complex *trans*-[PdI{C(=NXy)($C_6H_4CH_2OH$-2)}$(CNXy)_2$] (**2**, *Scheme II.1*), which had to be isolated immediately to avoid decomposition. Complex **2** is the result of the insertion of one isocyanide molecule into the C-Pd bond and the displacement of the bpy ligand by two other molecules. The compound is stable in the solid state, but it decomposes in solution to form [$Pd_2I_2(CNXy)_4$], which is easily identified by its ^{1}H NMR resonance at 2.53 ppm. Pd complexes similar to **2**, with other functional groups in the aryl ring, have been previously prepared in a similar manner, mainly by our research group.[5,6,8,10,11,35] We have also described a few dinuclear analogues, prepared by oxidative addition[22] or by a double insertion reaction.[8,24]

The reaction of complex **1a** with KO^{t}Bu resulted in the abstraction of the alcoholic proton and the coordination of the oxygen to Pd, displacing the iodo ligand and forming the neutral chelate complex [Pd{κ^2-*C*,*O*-$C_6H_4(CH_2O)$-2}(bpy)] (**3**, *Scheme II.1*), which crystallizes as a dinuclear aqua-bridged species (see Section II.3.7 and *Figure II.2*).

II.3.3 Reactions of [Pd(κ^2-*C*,*O*-$C_6H_4CH_2O$-2)(bpy)] (3) with XyNC and CO

The reaction of **3** with XyNC resulted in the formation of *N*-(2,6-dimethylphenyl)-2-benzofuran-1(*3H*)-imine (**4**) (*Scheme II.2*), which was isolated as a yellowish oil and characterized by NMR spectroscopy and high resolution mass spectroscopy (see Chapter VIII, Experimental Section). The cyclic imidate **4** had not been described before,

although the related compound with a ^{t}Bu group instead of Xy had been prepared by reaction of a dimeric oxapalladacycle phosphine complex with ^{t}BuNC.[18] The synthesis of other five-membered imidates by Pd-catalyzed reaction of 2-bromobenzyl alcohol and several isocyanides (not XyNC)[36] or by other, unrelated methods[37] has also been reported. The reaction of **3** with CO resulted in the decomposition of the complex to give 1(*3H*)-isobenzofuranone (phthalide) (*Scheme II.2*). Both cyclic compounds reasonably form through a XyNC or CO insertion reaction into the C-Pd bond, followed by a C-O coupling reaction. A CO insertion into the O-Pd bond would also be possible.[38]

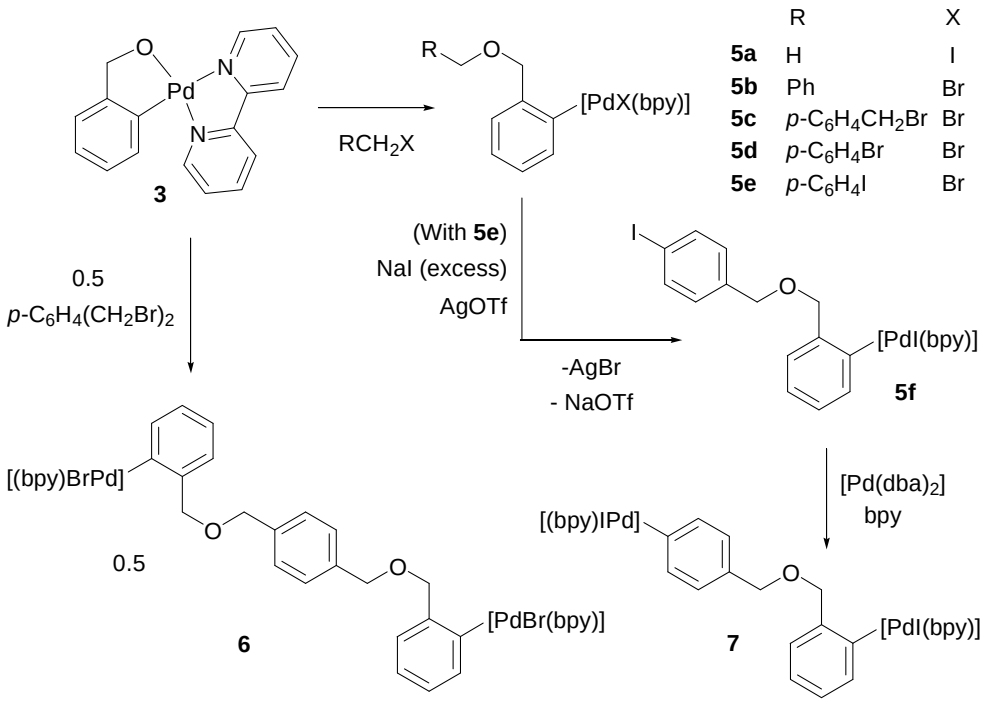


Scheme II.2 Synthesis of **4** and phthalide

II.3.4 Reactions of [Pd(κ^2-*C,O*-$C_6H_4CH_2O$-2)(bpy)] (3) with Alkyl Halides

By reaction of complex **3** with an excess of various primary alkyl halides of general formula RCH_2X (X = Br, I), the complexes [Pd$X(C_6H_4CH_2OCH_2R$-2)(bpy)] (X = I, R = H (**5a**), X = Br, R = Ph (**5b**), *p*-$C_6H_4CH_2Br$ (**5c**), *p*-C_6H_4Br (**5d**), and *p*-C_6H_4I (**5e**)) were obtained (*Scheme II.3*). These complexes result from the nucleophilic attack of the coordinated oxygen in **3** at the alkyl group of the halide, followed by the coordination of the halide to the Pd atom and the opening of the chelate ring. We have found no precedent for this type of reaction in an arylpalladium complex. A 5-fold excess of RCH_2X was enough for the synthesis of **5d,e** in good yield, while for **5a-c** a 10-fold excess was required (see Chapter VIII, Experimental Section).[a] Similar reactions with PhI or ^{i}PrI did not result in the formation of analogous complexes, suggesting that the success of the nucleophilic substitution requires a primary halide as substrate.

[a] A reviewer has suggested that a more polar solvent, such as acetone, could enhance the reactivity and decrease the amount of substrate required in these reactions.



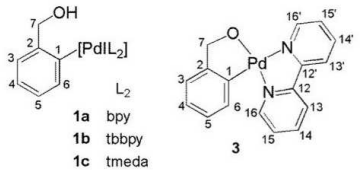
Scheme II.3 Synthesis of complexes **5a-f**, **6**, and **7**

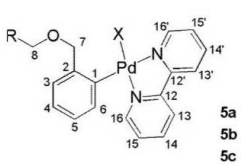
II.3.5 Synthesis of Dinuclear Palladium Complexes

When the reaction of **3** with *p*-$C_6H_4(CH_2Br)_2$ was carried out in a 2:1 ratio, we obtained the dinuclear Pd complex [{(bpy)BrPd($C_6H_4CH_2OCH_2$-2)}$_2$(C_6H_4-1,4)] (**6**, *Scheme II.3*), which is the result of the nucleophilic attack of **3** on both methylene groups of the dihalide.

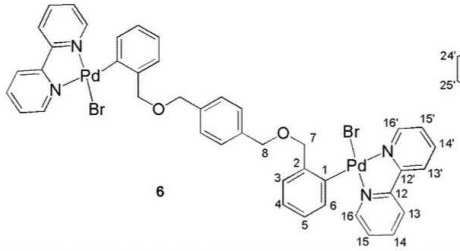
We also attempted to prepare a dinuclear complex by oxidative addition of the C-X bond in **5d** (X = Br) or **5e** (X = I) to [Pd(dba)$_2$] in the presence of bpy. However, with **5d** (X = Br) there was no oxidative addition, and with **5e** (X = I) we obtained a mixture of two complexes, probably as a consequence of the partial substitution by I of the Br ligand attached to Pd. We decided then to fully replace this Br ligand by I before the oxidative addition, by reaction of **5e** with AgOTf and a large excess of NaI, obtaining complex [PdI{C_6H_4(CH_2OCH_2(C_6H_4I-4))-2}(bpy)] (**5f**, *Scheme II.3*). By reaction of **5f** with [Pd(dba)$_2$] and bpy (1:1:1 ratio) we cleanly obtained the dinuclear Pd complex [(bpy)IPd($C_6H_4CH_2$-2)O($CH_2C_6H_4$-4)PdI(bpy)] (**7**, *Scheme II.3*). Similarly to **6**, complex **7** shows a bridging organic chain with two aryl-Pd bonds, although now only one of them is *ortho*-substituted. Bis(arylpalladium) complexes are not common in the literature.[8,23,26,29] Complexes **6** and **7** are the first examples with *ortho*-substituted aryl groups.

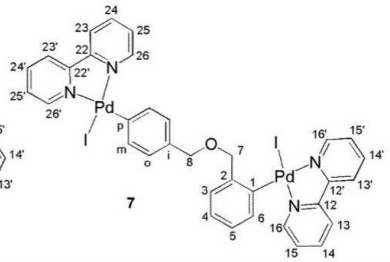
Table II.1 ^{13}C and ^{1}H NMR data ($CDCl_3$, r.t.) of complexes **1a-c**, **I**, **3**, **5a-f**, **6**, and **7**[(a)]





	R	X
5a	H	I
5b	Ph	Br
5c	*p*-$C_6H_4CH_2Br$	Br
5d	*p*-C_6H_4Br	Br
5e	*p*-C_6H_4I	Br
5f	*p*-C_6H_4I	I





	I[(b)] L_2=2 PPh_3		**1c** L_2=tmeda		**1b** L_2=tbbpy		**1a** L_2=bpy		**3**		**5a** R=H, X=I		**5b** R=Ph, X=Br		**5c** $C_6H_4CH_2Br$		**5d** *p*-C_6H_4Br		**5e** C_6H_4I, X=Br		**5f** C_6H_4I, X=I		**6**		**7**	
	Aryl ligand										**Aryl ligand(s)**															
	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C[(c)]	^{1}H[(c)]	^{13}C	^{1}H
C1	**158.6**		143.7		146.3		146.3		151.0		145.3		149.7		150.2		149.9		150.0		146.8		149.99, 149.96		148.8	
C2	144.4		145.0		144.8		145.4		**166.2**		142.2		141.9		141.8		141.6		141.7		142.0		142.05, 142.01		142.3	
CH3	128.6	6.41	128.4	7.11	128.6	7.20	128.8	7.11	119.1	7.04-6.97	127.1	7.24	128.1	7.30	128.1	7.30	128.1	7.23	128.1	7.23	128.0	7.23	128.08, 128.01	7.26, 7.21	128.6	7.21
CH4	123.8	6.62	123.7	6.93-	123.9	7.02-	124.3	6.93-	124.0		123.8	7.02-	123.9	7.05-	123.8	7.03-	123.9	7.04-	123.9	7.04-	123.7	7.01-	123.81, 123.77	7.06-6.98	123.4	6.96
CH5	125.9	6.47	126.2	6.84	126.6	6.93	126.8	6.89	123.6		126.3	6.95	126.7	6.98	126.8	6.99	126.8	6.98	126.8	6.98	126.7	6.95	126.75, 126.69		126.9	7.02
CH6	134.2	7.06	135.6	7.29	136.2	7.50	136.6	7.38	131.7	7.21	136.1	7.48	135.0	7.50	135.0	7.51	135.0	7.48	135.0	7.48	136.3	7.48	135.23, 135.20	7.53-7.49	136.3	7.59-7.53
CH_2-7	68.4	**4.16**	69.1	5.43 4.68	68.8	5.21 4.66	68.7	4.99 4.48	**78.4**	**5.21**	78.5	5.00 4.77	76.0	5.31 4.89	76.2	5.28 4.85	76.1	5.28 4.85	76.1	5.28 4.84	77.1	5.14 4.79	75.8, 75.6	5.20, 4.87 5.20, 4.80	77.6	5.22, 4.62
OH		**0.02**		3.00		2.89		2.66																		
											CH_2-8	72.6	4.56 4.52	72.0	4.53	71.8	4.52 4.46	71.9	4.51 4.46	71.9	4.49 4.44	72.4, 72.3	4.45-4.37	72.6	4.48, 4.40
											***i*-C**	139.2		139.7		138.2		139.0		139.0		137.76, 137.75		133.8	
											***o*-CH**	127.7	7.12-7.05	127.8	7.01	129.5	6.95	129.7	6.81	129.7	6.79	127.40, 127.35	**6.77**	126.5, 126.4	6.57, 6.42
											***m*-CH**	128.1		128.8	7.07	131.1	7.11	137.1	7.30	137.1	7.28			135.8, 135.6	7.03, 6.85
											***p*-C[(d)]**	127.1		136.6		120.8		92.5		92.5				143.9	

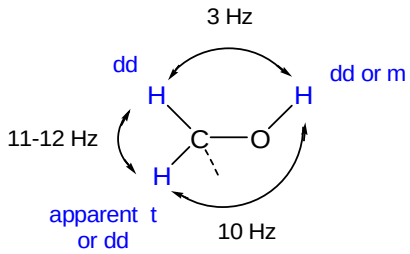
	tbbpy[(e)]		**bpy ligand**[(e)]																							
	1b		**1a**		**3**		**5a**		**5b**		**5c**		**5d**		**5e**		**5f**		**6**		**7**	
	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C[(f)]	^{1}H
C12	156.2		156.6		156.6		155.9		155.9		155.7		155.8		155.8		155.6		155.96, 155.93		155.7, 155.2	
C12'	154.0		154.4		153.4		153.9		153.7		153.7		153.6		153.6		153.6		153.79, 153,71		154.5, 153.9	
CH16	149.7	**7.33**	150.4	**7.33**	152.0	9.18	**150.6**	**7.53**	151.7	**7.69**	151.4	**7.62**	151.5	**7.62**	151.5	**7.62**	**150.5**	**7.44**	151.32, 151.30	**7.58-7.56**	**150.6, 150.0**	**7.48-7.36**
CH16'	**152.6**	9.46	**153.1**	9.46	149.9	9.03	**153.2**	**9.66**	150.9	9.43	150.7	9.39	150.8	9.39	150.8	9.40	**153.1**	**9.61**	150.58, 150.57	9.36-9.33	**153.0, 152.4**	**9.61, 9.57**
CH14[(g)]	163.6		139.6	7.94	138.1	8.03-7.96	138.7	7.98	138.4	7.88	138.4	7.85	138.4	7.89	138.4	7.89	138.4	7.89	138.74, 138.66	7.89, 7.78	138.89, 138.86	8.02-7.87
CH14'[(g)]	163.6		139.5	7.98	138.8			8.01	138.9	8.03	139.0	8.01	139.0	8.03	139.0	8.03	138.7	8.02	139.23, 139.16	8.04, 7.88	138.8, 138.5	
CH15	123.9	7.28	127.2	7.25	126.6	7.59-7.52	126.6	7.32	126.6	7.17	126.5	7.14	126.5	7.17	126.5	7.17	126.4	7.20	126.53, 126.49	7.17-7.11	126.4, 125.9	7.35, 7.11
CH15'	124.2	7.53	127.6	7.53	126.3		127.1	7.57	126.7	7.60	126.7	7.57	126.8	7.57	126.8	7.58	127.0	7.55	126.66, 126.62	7.57-7.48	126.94, 126.92	7.59-7.41
CH13	118.7	7.98	122.8	8.06-8.02	122.5	8.08-8.03	121.9	8.09-8.04	121.8	7.97	122.0	7.94	121.8	7.98	121.8	7.97	121.7	7.95	122.39, 122.32	8.00-7.97	122.9, 122.4	8.17-8.02
CH13'	118.2	7.97	122.4		121.1		121.6		121.3	8.03	121.6	8.01	121.5	8.03	121.5	8.03	121.6	8.02	121.91, 121.85	8.04, 7.99	122.0, 121.7	

(a) The data for complex **2** are not included in this Table because it is not an aryl palladium complex. The data for the ligands PPh_3 and tmeda are not included for lack of space and relevance. Neither are the ^{t}Bu groups of the tbbpy ligand, the Me group of **5a** and the CH_2Br group of **5c**. The data which are highlighted in bold are commented in the text. (b) Published in *Organometallics*, **2001**, 20, 2998, but ^{1}H data were measured in C_6D_6 and the ^{13}C data were not assigned. (c) The halves of the molecule in **6** are not equivalent (the NMR resonances are duplicated). The ^{1}H resonances are coincident (but not identical) except those of the aryl H3, one CH_2-7 proton, and H14,14' and 13' of the bpy ligand, which appear separated in the spectrum. (d) For **5b**, *p*-CH. (e) The two halves of the tbbpy and bpy ligands have been assigned based on NOE contacts between H16 and the aryl group. (f) It has not been possible to distinguish the resonances of the two different bpy ligands which are thus written together. (g) For **1a**, C14,14'

All the complexes reported in this paper were extensively studied by NMR spectroscopy (1D and 2D experiments), allowing an almost full assignment of the ^{1}H and ^{13}C resonances. To facilitate comparison, the data are collected in *Table II.1*. We also include the data of complex **I**, which had been reported but not fully assigned.[18]

II.3.6.1 NMR and IR Data of Complexes 1a-c, I, and 3

The methylenic protons of the CH_2OH groups are diastereotopic in complexes **1a-c**. Thus, they couple with each other and with the OH proton, as shown in *Scheme II.4*. In contrast, for the PPh_3 complex **I**, which has a symmetry plane, the two methylenic protons are equivalent, and they appear as a doublet coupled ($^{3}J_{HH}$ = 7 Hz) with the OH proton, which is a triplet. In the chelate complex **3** the methylenic protons are also equivalent (they appear as a singlet). This is an indication that the molecule has a symmetry plane in solution. Indeed, even in the solid state the molecule is almost planar, as shown by the X-ray structure (see Section II.3.7 and *Figure II.2*).



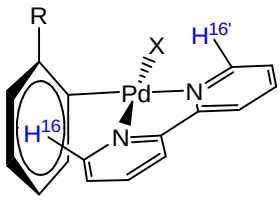
Scheme II.4 Coupling pattern within the CH_2OH group in complexes **1a-c**

The OH proton of **I** is strongly shifted to lower frequency (δ 0.02 ppm, almost coincident with the TMS), with respect to **1a** (δ 2.66 ppm), **1b** (δ 2.89 ppm), and **1c** (δ 3.00 ppm), as a consequence of the anisotropic effect of the PPh_3 ligands. Another peculiarity of complex **I** is the shift of the aryl *ipso* carbon to higher frequency (158.6 ppm) with respect to the complexes with N,N-donor ligands, **1a-c** (143.7–146.3 ppm). A similar trend has been observed previously by some of us for other arylpalladium complexes,[3,21] and cannot be explained in terms of simplistic resonance or induction effects, as ^{13}C chemical shifts are mainly determined by the paramagnetic contribution to the shielding constant.[39]

The aryl ^{13}C chemical shifts of the chelate complex **3** differ from those of the "open" complexes **1a-c**, **I**. Specially noteworthy is the large shift to higher frequency of C2

(166.2 ppm) with respect to the 144–145 ppm value in **1a-c**, **I**. The methylenic carbon is also shifted to higher frequencies (78.4 ppm in **3** with respect to 68–69 ppm in **1a-c**, **I**).

In the tbbpy (**1b**) and bpy (**1a**) ligands, the *ortho* hydrogen atoms of the pyridyl ring *cis* to the aryl group (H16 in our numbering system) are strongly shielded (δ 7.33 ppm for both complexes) with respect to those of the pyridyl ring *trans* to aryl (H16', δ 9.46 ppm for both). This is a common observation in arylpalladium complexes[3,21,24] and is a consequence of the anisotropic effect of the aryl group on the closest hydrogen of the bpy or tbbpy ligand. The aryl group is perpendicular to the [PdI(N^N)] plane, so that the H16 proton sits "on top" of the aryl ring, in the shielded zone (see *Scheme II.5*). For the chelate complex **3**, in contrast, this effect is not observed (δ = 9.03 ppm for H16' and 9.18 ppm for H16), because the aryl group is forced to be almost coplanar with the bpy ligand by the formation of the O-Pd bond.



Scheme II.5

Anisotropic effect of the aryl ligand on the H16 protons of a bpy ligand. The *ortho* substituent (R) usually hinders the rotation around the Ar-Pd bond. However, even when this rotation is allowed, e.g. in the complex [PdXPh(bpy)] (X = Br, I),[40] the Ar group still adopts a perpendicular disposition with respect to the [PdX(N^N)] plane, and the shielding of the H16 proton is observed

In the tmeda complex (**1c**) the presence of four ^{1}H and ^{13}C resonances for the Me groups of the tmeda indicates that the rotation around the Ar-Pd bond is hindered by the presence of the CH_2OH substituent in *ortho* position.[3]

A single ^{31}P resonance for the PPh_3 complex **I** (at 22.6 ppm, see Chapter VIII, Experimental Section) confirms the *trans* geometry of the complex. The aryl carbons C1, C2, and CH6, as well as the methylene carbon, appear as triplets because of the coupling with the two equivalent ^{31}P nuclei ($^{2}J_{CP}$ = 3 Hz for C1, $^{3}J_{CP}$ = 3 Hz for C2, $^{3}J_{CP}$ = 4 Hz for CH6 and $^{4}J_{CP}$ = 3 Hz for CH_2). Both ^{31}P nuclei are *magnetically non-equivalent*, so that the *ipso*, *ortho* and *meta* carbons of the phosphine phenyl rings appear as virtual triplets ($^{1}J_{CP}+^{3}J_{CP}$ = 46 Hz for *i*-C, $^{2}J_{CP}+^{4}J_{CP}$ = 12 Hz for *o*-CH, $^{3}J_{CP}+^{5}J_{CP}$ = 10 Hz for *m*-CH).

Finally, the IR spectra of complexes **1a-c** show the expected O-H bands at 3430, 3490 and 3305 cm^{-1}, respectively.

II.3.6.2 NMR Data of Complexes 5a-f, 6, and 7

In the complexes **5a-f**, **6**, and **7** the methylenic protons of the CH_2-7 group (the one closer to the [PdX(bpy)] moiety) are always diastereotopic, and they appear as an AB system with $^2J_{HH}$ = 11 Hz, similarly to **1a-c**. The methylenic protons of the RCH_2 group (CH_2-8) appear as an AB system for **5b,d,e,f** and **7** ($^2J_{HH}$ = 12 Hz and chemical shifts almost coincident around 4.5 ppm), and as a singlet at 4.53 pm for **5c**.[b] For the dinuclear complex **6** the two non-equivalent CH_2-8 groups appear as a multiplet at ca. 4.4 ppm.

In the complexes **5c-f** the two *ortho* protons and the two *meta* protons of the C_6H_4 moiety are each chemically (but not magnetically) equivalent, indicating that there is free rotation around the C_6H_4-CH_2 bond. These protons form an AA'BB' system (two doublets, with $^3J_{AB}$ = 8 Hz).

For the dinuclear complex **6** we expected that both halves of the molecule would be equivalent in solution, but this is not the case, as we observe two sets of ^1H and ^{13}C resonances that are almost coincident, with a few exceptions in the ^1H spectrum (see *Table II.1*, footnote c). The molecule seems to be too bulky to adopt a completely symmetric structure in solution. The four central C_6H_4 protons appear as a single sharp doublet with J = 4 Hz. Most probably these protons also form an AA'BB' system (as in **5c-f**), where now A and B are isochrones (but not equivalent, so that they are coupled with each other).

Complex **7** shows, as expected, two clearly separated sets of bpy resonances, as the two [PdI(bpy)] moieties are non-equivalent. The *p*-[PdI(bpy)] fragment hinders the rotation of the C_6H_4 group, so that now the two *ortho* protons and the two *meta* protons are not equivalent, and they form an ABMN system, i.e., four (slightly broad) doublets with $^3J_{AB} = {}^3J_{MN}$ = 8 Hz.

In the bpy ligand of complexes **5a-f**, **6**, and **7** the H16 protons are also strongly shielded (δ = 7.36–7.69 ppm) with respect to H16' (δ = 9.33–9.66 ppm), again as a consequence of the anisotropic effect of the aryl group on the H16 protons. It is also noteworthy that the H16' proton (the one close to the halo ligand) is slightly deshielded in the iodo complexes (**5a,f** and **7**, δ = 9.57–9.66 ppm) with respect to the bromo complexes (**5b-e** and **6**, δ = 9.33–9.43 ppm). The CH16' carbon is also deshielded in the

iodo complexes, with the result that it resonates at higher frequency (δ = 152.4–153.2 ppm) than the CH16 carbon (δ = 150.0–151.7 ppm), as opposed to the bromo complexes where δ(CH16) > δ(CH16'). The same tendency, δ(CH16') > δ(CH16), is observed in **1a** (for bpy) and **1b** (for tbbpy), which are also iodo complexes. For the quaternary carbons C12,12', we always observe that δ(C12) > δ(C12') (for C12, in the pyridyl ring *trans* to I, Br or O, δ = 156.6–155.2 ppm, while for C12', in the pyridyl ring *trans* to aryl, δ = 154.5–153.4 ppm).

II.3.6.3 NMR and IR Data of 2 and 4

The structure of the cyclic imidate **4** is confirmed by the $^{1}H,^{13}C$-HMBC spectrum, where the expected two- and three-bond $^{1}H,^{13}C$ correlations are observed. In the IR spectrum, the C=N band appears at 1693 cm^{-1}.

Finally, for complex **2**, resulting from the reaction of **1a** with XyNC, we have no ^{13}C NMR data, as the complex decomposes too rapidly in solution. In the ^{1}H NMR spectrum we observe the expected 1:2 methyl resonances corresponding, respectively, to the inserted and the two (equivalent) coordinated XyNC groups. These groups give characteristic IR bands at 2182 cm^{-1} for the coordinated C≡NXy groups, and at 1606 cm^{-1} for the inserted C=NXy group.

II.3.7 X-Ray Structure Determinations

The crystal structures of the complexes **1a** (*Figure II.1*, *Table II.3*), **3**·H_2O (*Figures II.2*, *II.3*, and *Table II.4*), and **5e** (*Figure II.4* and *Table II.5*), were determined by X-ray diffraction studies (see *Table II.2* for experimental details).[c] The three structures show somewhat distorted square planar coordination around the Pd atoms. Mean deviations from the best plane through Pd and the four donor atoms are 0.05 Å for **1a**, 0.08 Å for **3**·H_2O, and 0.04 Å for **5e**. For **3**·H_2O, the distortion arises from the steric pressure between the two ligands, which are forced to be approximately coplanar with a short

[b] The CH_2Br group in **6c**, not included in *Table II.1*, also appears as a singlet.

[c] Crystals were mounted in inert oil on glass fibres. Intensity data were recorded on various diffractometers of the firms Bruker or Oxford Diffraction using monochromated Mo *K*α or mirror-focused Cu *K*α radiation. Absorption corrections were based on multi-scans. Structures were refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen). Hydroxyl and water hydrogens were refined freely (but for **3**·H_2O with OH distance restraints). Methyls were refined as idealized rigid groups allowed to rotate but not tip. Other H atoms were included using a riding model starting from calculated positions.

contact H6···H26, 2.14 Å; N21 lies 0.34 Å out of the plane of Pd and the other three ligand donor atoms. The lesser distortion for the other two structures might be a consequence of the chelating nature of the bpy ligand. The Pd-C bond distances are very similar for the three complexes (2.003(2) Å for **1a**, 1.9968(17) Å for **3**·H_2O and 1.9903(19) Å for **5e**) and in the range expected for Pd-C bonds *trans* to a N-donor ligand.[3,21] The Pd-N bond distances follow the expected order of *trans* influence:[41] Pd-N *trans* to aryl (2.1364(16) Å in **1a**, 2.1039(15) Å in **3**·H_2O, and 2.1362(17) Å in **5e**) > Pd-N *trans* to I (2.0649(16) Å in **1a**) > Pd-N *trans* to Br (2.0563(17) Å in **5e**) > Pd-N *trans* to O (2.0379(15) Å in **3**·H_2O). From the three Pd-N bond distances *trans* to aryl we can observe that in the chelate complex **3**·H_2O the *trans* influence of the aryl ligand is lower than for **1a** and **5e**.

The five-membered chelate ring in **3**·H_2O displays an approximate envelope conformation, whereby the Pd atom lies 0.55 Å out of the plane of the other four atoms (mean deviation 0.08 Å); the aryl ring is forced to an angle of only 26º with the plane defined by the bpy fragment, as opposed to the almost perpendicular disposition in **1a** (88º) and **5e** (87º). Within the chelate ring, the O-Pd bond distance is 1.9916(12) Å, slightly shorter than the O-Pd distance (2.048(3) Å) found in a related 2-hydroxymethylphenyl chelate complex that is a dimer with a PPh_3 ligand *trans* to O and two Pd-O bridges.[18] The C-O bond distance in **3**·H_2O (1.419(2) Å) is slightly shorter than the C-O bond distances in **1a** (1.423(2) Å) and **5e** (1.432(2) and 1.423(2) Å), and the Ar-CH_2 bond distances are similar (all in the range 1.498–1.505 Å), indicating that the formation of the chelate ring does not involve a weakening of the bonds within the ring.

The packing of **1a** involves O–H···I hydrogen bonds that connect the molecules via the *n* glide planes. The chelate complex **3**·H_2O (*Figure II.2*) crystallizes with two molecules of water, both lying with the oxygen atom on a crystallographic 2-fold axis, which are hydrogen-bonded to the oxygen in the chelate ring, forming dimeric units (**3**·H_2O)$_2$ bridged by two water molecules. The central ring belongs to the graph set $R_4^2(8)$. The (**3**·H_2O)$_2$ dimers are further connected by three-center interactions H23···O1W,O2W to form ribbons of molecules parallel to the short *b* axis (*Figure II.3*).

Table II.2 X-ray crystallographic data for compounds **1a**, **3·H$_2$O**, and **5e**

	1a	**3**·H$_2$O	**5e**
Formula	$C_{17}H_{15}IN_2OPd$	$C_{17}H_{16}N_2O_2Pd$	$C_{24}H_{20}BrIN_2OPd$
M_r	496.61	386.72	665.63
T (K)	100(2)	133(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	C2/c	$P2_1/c$
cell constants			
a (Å)	9.2580(2)	25.7969(16)	9.3227(3)
b(Å)	16.3219(4)	7.2646(4)	13.4757(4)
c (Å)	10.7044(3)	16.8495(11)	17.8619(5)
α (deg)	90	90	90
β (deg)	97.977(3)	109.801(3)	92.273(3)
γ (deg)	90	90	90
V (Å^3), Z	1601.87(7), 4	2971.0(3), 8	2242.22(12), 4
ρ (calcd) (Mg m^{-3})	2.059	1.729	1.972
abs. coef. (mm^{-1})	3.088	1.257	4.005
F(000)	952	1552	1280
cryst size (mm)	0.25 × 0.20 × 0.10	0.33 × 0.20 × 0.12	0.40 × 0.20 × 0.15
θ range (deg)	2.29 - 30.84	1.68 - 30.51	2.28 - 30.89
index ranges	$-12 \le h \le 13$ $-23 \le k \le 23$ $-15 \le l \le 15$	$-36 \le h \le 36$ $-10 \le k \le 10$ $-24 \le l \le 24$	$-12 \le h \le 13$ $-19 \le k \le 18$ $-25 \le l \le 25$
reflections collected	41363	33977	62095
independent reflections	4754	4528	6729
R_{int}	0.0280	0.0246	0.0380
abs corr	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
transmissions	1.000 - 0.654	0.864 - 0.700	1.000 - 0.418
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	4754 / 0 / 203	4528 / 1 / 208	6729 / 0 / 271
goodness-of-fit on F^2	1.093	1.090	1.082
Final R indices ($I>2\sigma(I)$)			
$R1$	0.0192	0.0225	0.0229
$wR2$	0.0409	0.0522	0.0471
R indices (all data)			
$R1$	0.0239	0.0308	0.0304
$wR2$	0.0429	0.0569	0.0496
largest diff peak (e Å^{-3})	1.20	1.14	0.61
largest diff hole (e Å^{-3})	-0.58	-0.43	-0.67

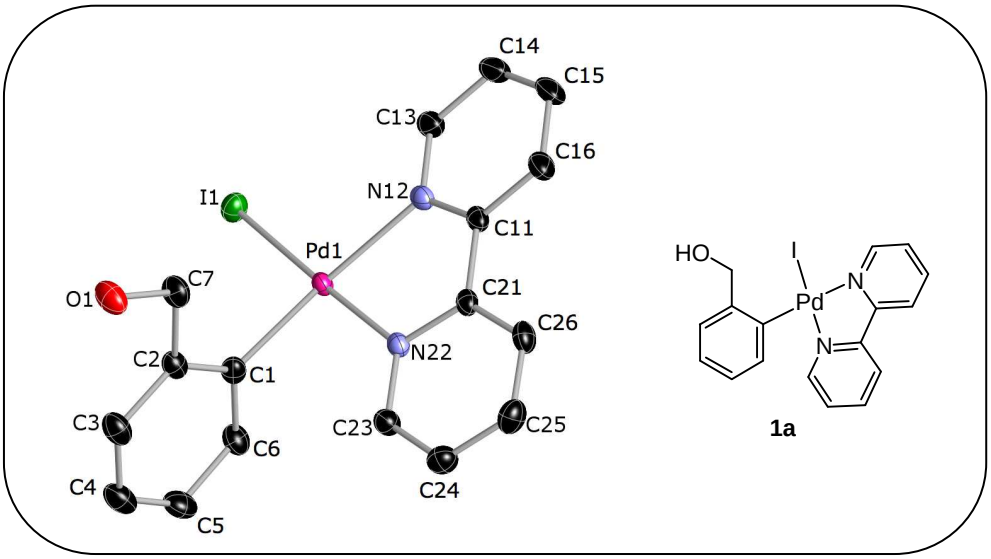


Figure II.1 Thermal ellipsoid plot (50% probability level) of **1a**

Table II.3 Selected bond lengths (Å) and angles (deg) of **1a**

Pd(1)-C(1)	2.003(2)	C(1)-Pd(1)-N(22)	93.36(7)
Pd(1)-N(12)	2.1364(16)	C(1)-Pd(1)-I(1)	88.53(5)
Pd(1)-N(22)	2.0649(16)	N(12)-Pd(1)-N(22)	78.80(6)
Pd(1)-I(1)	2.5810(2)	N(12)-Pd(1)-I(1)	99.48(5)
C(7)-O(1)	1.423(2)	C(1)-Pd(1)-N(12)	171.18(7)
C(2)-C(7)	1.505(3)	N(22)-Pd(1)-I(1)	177.02(5)
C(1)-C(2)	1.399(3)	C(2)-C(7)-O(1)	110.69(17)
		C(1)-C(2)-C(7)	119.46(18)
		C(2)-C(1)-Pd(1)	119.08(15)

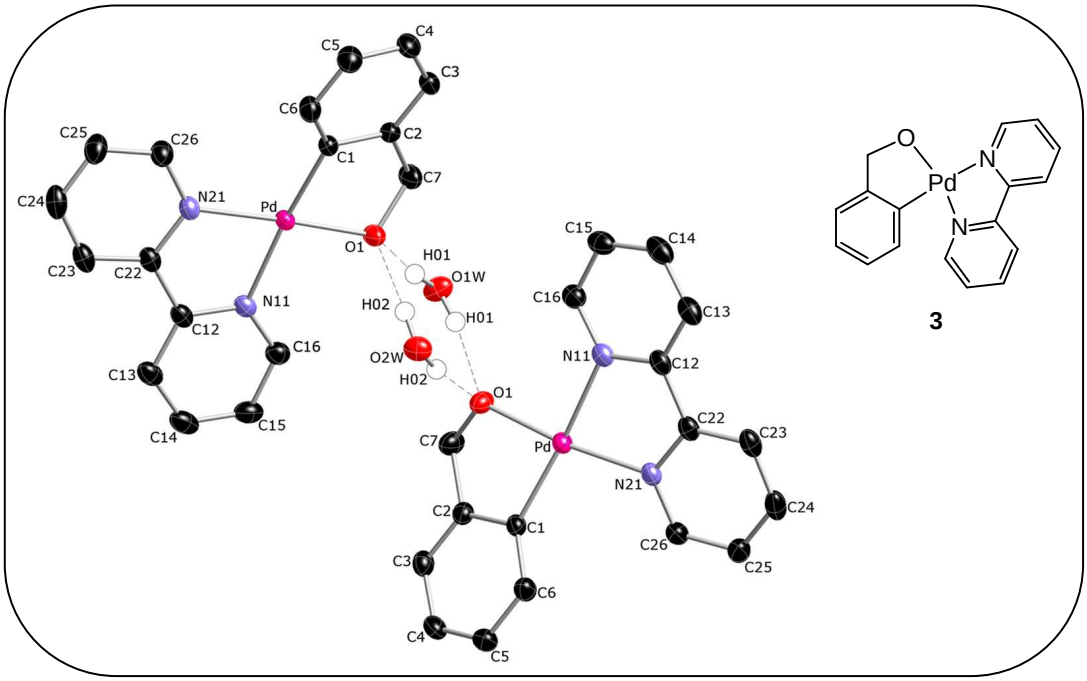


Figure II.2 Thermal ellipsoid plot (30% probability level) of **3**·H_2O. Two adjacent molecules of **3** are connected by two water molecules, each of which lies on a 2-fold axis

Table II.4 Selected bond lengths (Å) and angles (deg) of **3**·H_2O

Pd-O(1)	1.9916(12)	C(1)-Pd-N(21)	103.50(6)
Pd-C(1)	1.9968(17)	O(1)-Pd-C(1)	82.54(6)
Pd-N(21)	2.0379(15)	O(1)-Pd-N(11)	95.34(6)
Pd-N(11)	2.1039(15)	N(21)-Pd-N(11)	79.21(6)
C(7)-O(1)	1.419(2)	C(1)-Pd-N(11)	173.15(6)
C(2)-C(7)	1.498(3)	O(1)-Pd-N(21)	172.22(6)
C(1)-C(2)	1.409(2)	C(7)-O(1)-Pd	111.32(10)
		O(1)-C(7)-C(2)	109.73(15)
		C(1)-C(2)-C(7)	115.65(15)
		C(2)-C(1)-Pd	111.49(12)

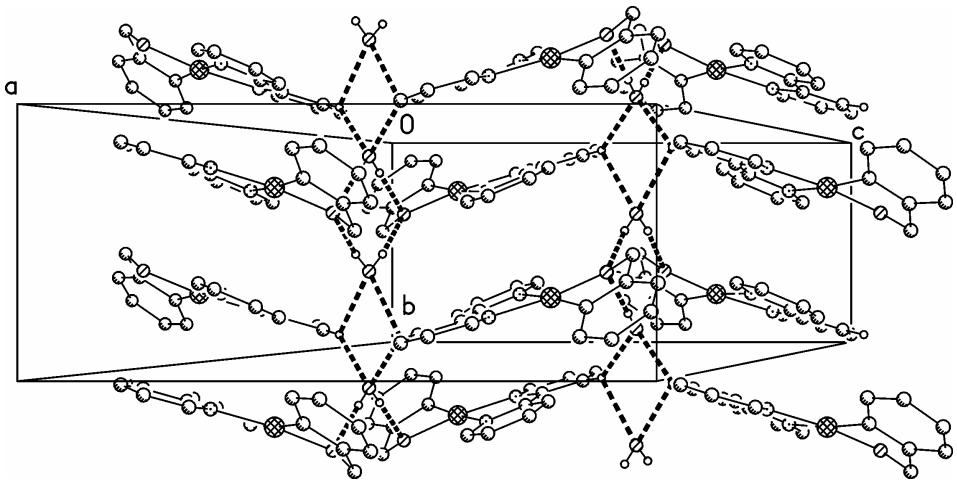


Figure II.3 Packing diagram of **3**·H_2O viewed perpendicular to the *bc* plane. Hydrogen bonds O–H···O and C–H···O are drawn as dashed bonds. Adjacent chains of molecules overlap in this view direction, but are not connected

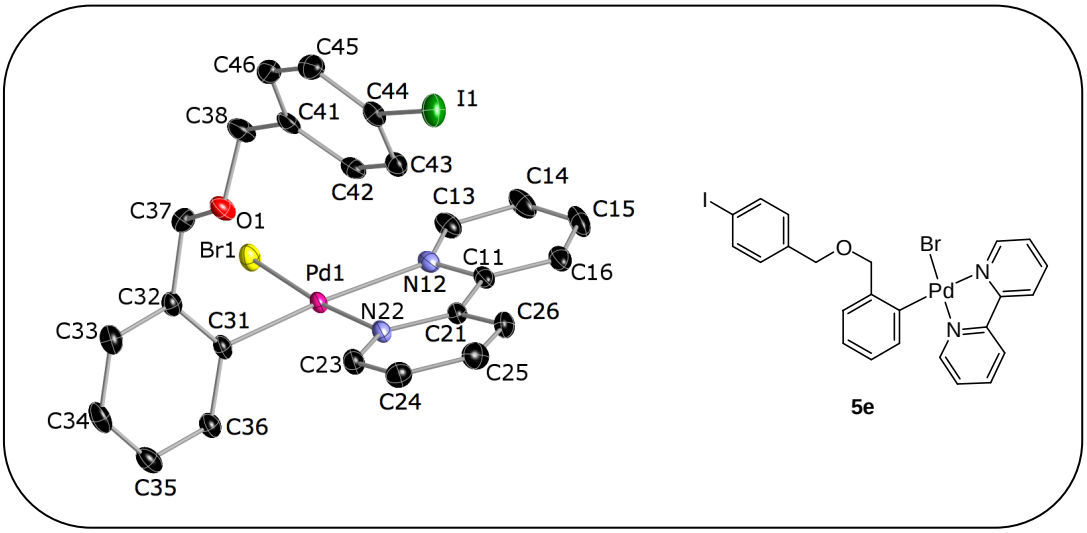


Figure II.4 Thermal ellipsoid plot (50% probability level) of **5e**

Table II.5 Selected bond lengths (Å) and angles (deg) of **5e**

Pd(1)-C(31)	1.9903(19)	C(31)-Pd(1)-N(22)	93.59(7)
Pd(1)-N(22)	2.0563(17)	C(31)-Pd(1)-Br(1)	90.12(6)
Pd(1)-N(12)	2.1362(17)	N(12)-Pd(1)-Br(1)	97.49(5)
Pd(1)-Br(1)	2.4226(3)	N(22)-Pd(1)-N(12)	78.86(7)
C(44)-I(1)	2.097(2)	C(31)-Pd(1)-N(12)	172.34(7)
C(37)-O(1)	1.432(2)	N(22)-Pd(1)-Br(1)	174.97(5)
C(38)-O(1)	1.423(2)	C(32)-C(37)-O(1)	108.19(16)
C(31)-C(32)	1.398(3)	C(37)-O(1)-C(38)	110.84(15)
C(32)-C(37)	1.498(3)	O(1)-C(38)-C(41)	108.10(16)
C(38)-C(41)	1.501(3)		

II.4 CONCLUSIONS

We have synthesized new aryl Pd complexes derived from benzyl alcohol, one of them a chelate complex resulting from the deprotonation of the alcohol. The reactivity of these complexes toward XyNC has resulted in an insertion complex and a cyclic imidate. The chelate complex reacts with primary alkyl halides via a nucleophilic attack of the coordinated oxygen on the alkyl group, resulting in the opening of the chelate ring and the formation of new arylpalladium complexes with larger substituents on the aryl ring. Two novel dinuclear bis(arylpalladium) complexes have been prepared, either by reaction with an alkyl dihalide or by a secondary oxidative addition in one of the new complexes.

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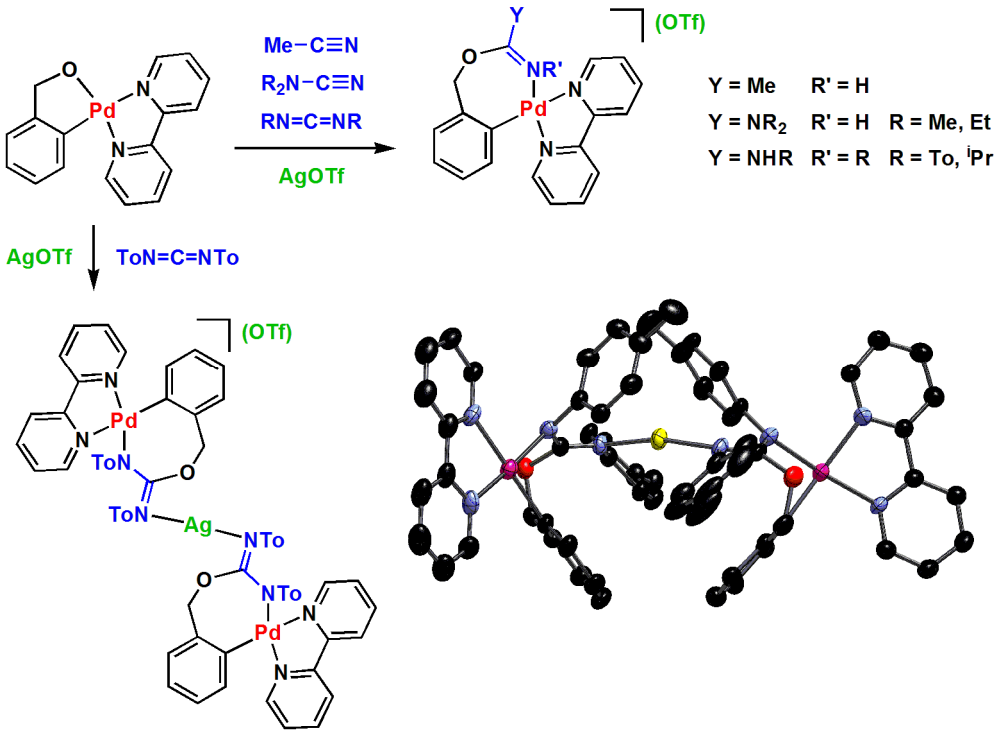
CHAPTER III

Reactivity toward Nitriles, Cyanamides, and Carbodiimides of Palladium Complexes Derived from Benzyl Alcohol. Synthesis of a Mixed Pd_2Ag Complex



The results of this Chapter will soon be submitted for publication

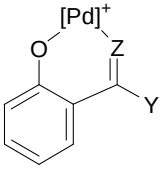
III.1 ABSTRACT

The chelate complex [Pd(κ^2-*C*,*O*-$C_6H_4CH_2O$-2)(bpy)] (**3**) reacts with acetonitrile, cyanamides or carbodiimides, in the presence of AgOTf (1:5:1 molar ratio) and residual water, to form complexes [Pd{κ^2-*C*,*N*-C_6H_4{$CH_2OC(=NX)Y$}-2}(bpy)](OTf), where X = H, Y = Me (**8**), NMe_2 (**9a**), NEt_2 (**9b**), X = R, Y = NHR (R = ^{i}Pr (**10a**), To (**10b**)), as a result of the insertion of the unsaturated reagent into the O-Pd bond of **3**, and the protonation of one of the N atoms. In the absence of AgOTf the reaction of **3** with ToN=C=NTo (To = *p*-Tolyl) results in the formation of the neutral complex [Pd{κ^2-*C*,*N*-C_6H_4{$CH_2OC(=NTo)NTo$}-2}(bpy)] (**11**). Complexes **10b** and **11** can be interconverted by deprotonation (**10b** + KO^tBu) or protonation (**11** + KOTf + HOTf) reactions. When the reaction of **3** with ToN=C=NTo in the presence of AgOTf is carried out in a 1:1:1 stoichiometric ratio, or for a short period of time, a mixture of **10b** and a mixed heterometallic Ag_2Pd complex **12** is obtained (**12 =** [Ag(*N*-**11**)$_2$](OTf)). Complex **12** is the major product when the AgOTf is added before the carbodiimide, and the reaction is stopped immediately. **12** can also be obtained by reaction of **11** with 0.5 equivalents of AgOTf. When complex [PdI($C_6H_4CH_2OH$-2)(bpy)] (**1a**) reacts with ^{i}PrN=C=N^{i}Pr in the presence of TlOTf, instead of AgOTf, a ca. 1:1 mixture of **10a** and [Pd{κ^2-*O*,*N*-OCH_2{C_6H_4{$C(=NH^iPr)N^iPr$}-2}}(bpy)](OTf) (**13**) forms. Complex **13** is the result of the insertion of the carbodiimide into the C-Pd bond. Complexes **8-13** have been extensively characterized by NMR spectroscopy, and the crystal structures of **9a**·0.19H_2O, **10a**, and **12**·2.5$CHCl_3$·0.5Et_2O have been determined by X-ray diffraction studies.

III.2 INTRODUCTION

The importance of Pd(II) aryl complexes in Organometallic Chemistry derives mainly from their involvement in carbon-carbon and carbon-heteroatom bond-forming reactions.[1] Their reactivity with unsaturated molecules often results in the insertion of these molecules into the aryl-Pd bonds, forming new ligands or, after decomposition reactions, organic compounds.[2] A valuable synthetic tool that we have extensively explored is the incorporation of a substituent at the *ortho* position of the aryl group,[3-7] as this substituent can become involved in the reactivity with the Pd center and the organic substrate in many interesting ways.[3-6,8-12] Very often, the *ortho*-substitution also results in the formation of cyclopalladated complexes.[3,4,7,9-12]

Following this line of research, our group has previously investigated the reactivity of *ortho*-palladated phenol derivatives.[6,10-13] Their reactions with CO, isocyanides, alkenes, alkynes, and allenes did not involve the OH group in the *ortho* position.[6,13] In contrast, the electron-donating ability of this group played a crucial role in the reactivity toward nitriles,[10,12] carbodiimides,[11,12] cyanamides,[12] and isothiocyanates,[12] which afforded the first examples of the insertion[10-12] of these molecules into a C-M bond of a late transition metal. These insertion reactions occurred together with the deprotonation and coordination of the hydroxyl oxygen to Pd, forming six-membered chelate rings (*Chart III.1*).[10-12] With carbodiimides,[11] the addition of the O-H group to one of the C=N bonds of the substrate, together with the coordination of the other N to the Pd atom, was an alternative reaction to the insertion.[11]



Y	Z
R	NH
NHR	NR
NR_2	NH
NHR	S

[Pd] = [Pd(N^N)]

N^N = bpy, tmeda

Chart III.1
Insertion complexes obtained in the reaction of *ortho*-palladated phenol derivatives with nitriles,[10,12] carbodiimides,[11,12] cyanamides,[12] and isothiocyanates.[12]

We have recently extended this research to *ortho*-palladated hydroxymethylphenyl complexes,[14] where the methylene link in the alcoholic substituent might significantly influence the reactivity toward unsaturated molecules. There are very few reports of 2-hydroxymethylphenyl palladium complexes[15] or oxapalladacycles derived from them.[16] These compounds have been used as precatalysts in Heck and cross-coupling reactions,[17] but their reactivity toward unsaturated molecules had not been investigated. In our recent work (see Chapter II of this Thesis),[14] we synthesized the complex [PdI($C_6H_4CH_2OH$-2)(bpy)] (**1a**) and investigated its reactivity toward alkynes, alkenes, nitriles, cyanamides, allenes, and carbon monoxide, which did not result in clean insertion (C-Pd bond) or addition (O-H bond) reactions.[14] Only the reaction of **1a** with XyNC gave a clean insertion product, *trans*-[PdI{C(=NXy)$C_6H_4CH_2OH$-2}$(CNXy)_2$] (**2**).[14] By deprotonation of **1a** we prepared the chelate complex [Pd{κ^2-*C,O*-$C_6H_4(CH_2O)$-2}(bpy)] (**3**), which displayed an interesting reactivity toward primary alkyl halides, via a nucleophilic attack of the coordinated oxygen at the alkyl group of the halide.[14] We describe now the

reactivity of **3** toward acetonitrile, cyanamides and carbodiimides, in the presence of AgOTf. These reactions have yielded novel complexes containing a [Pd{κ^2-*C*,*N*-C_6H_4{$CH_2OC(=NX)Y$}-2}] chelate ring, resulting from insertion reactions of the C≡N or C=N bonds into the O-Pd bonds of **3**. We have found no precedent for such a chelate structure with any metal. The Ag^+ cations play a key role in these reactions, which is also an unprecedented observation. An insertion reaction of a carbodiimide into the aryl-Pd bond of **1a** is also described, as is a mixed-metal Pd_2Ag complex, which has been characterized by X-ray crystallography. Other heterometallic Pd_2Ag[18] or Pd_2Ag_2[19] complexes have been described in the literature, but their structures differ greatly from the one reported in this work.

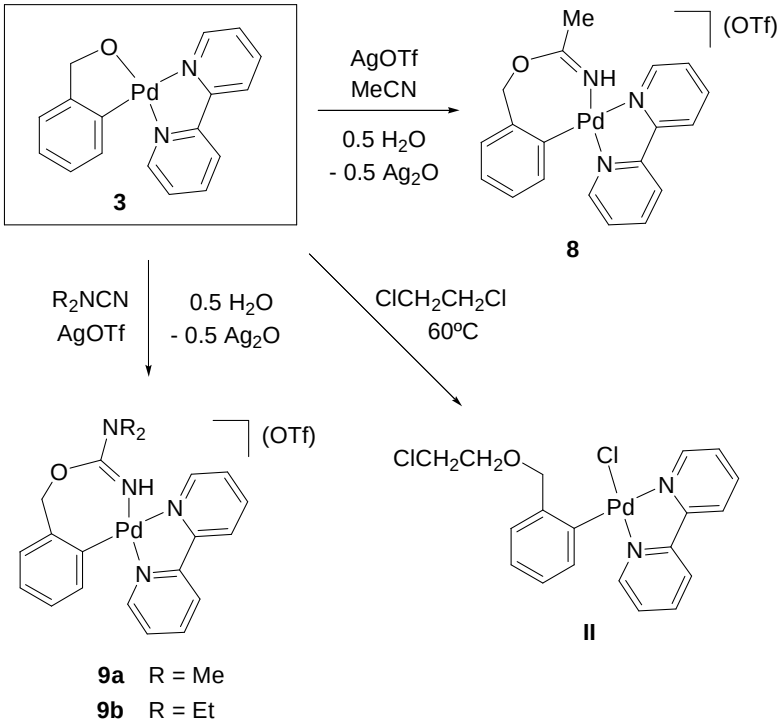
III.3 RESULTS AND DISCUSSION

III.3.1 Reactions with Nitriles and Cyanamides

The chelate complex [Pd{κ^2-*C*,*O*-$C_6H_4CH_2O$-2}(bpy)] (**3**) reacts with acetonitrile and AgOTf (1:5:1 molar ratio, CH_2Cl_2), in the presence of residual water, to form [Pd{κ^2-*C*,*N*-C_6H_4{$CH_2OC(=NH)Me$}-2}(bpy)](OTf) (**8**, *Scheme III.1*), the result of the insertion of the nitrile into the O-Pd bond of **3**, and the protonation of the N by the residual water. Complex **3** reacts similarly with the cyanamides R_2N-C≡N (R = Me, Et) and AgOTf to form [Pd{κ^2-*C*,*N*-C_6H_4{$CH_2OC(=NH)NR_2$}-2}(bpy)](OTf) (R = Me (**9a**), Et (**9b**), *Scheme III.1*). The presence of Ag^+ is a requirement in these reactions (otherwise there is no reaction or, with TlOTf, mixtures of compounds are obtained), probably because it forms *in situ* a complex with the ligands, increasing the electrophilicity of the unsaturated carbon atom, and thus favoring the nucleophilic attack of the O atom of **3**. This influence of added Ag^+ on the reactivity of an arylpalladium complex toward unsaturated molecules is unprecedented. Although nucleophilic reactions at coordinated nitriles have been thoroughly investigated,[20] this is the first nucleophilic attack of a complex at an (initially) uncoordinated nitrile or cyanamide. Seven-membered C_3-Pd-N=C-O chelate rings as those in **8** and **9a,b** have not been described before for any metal.

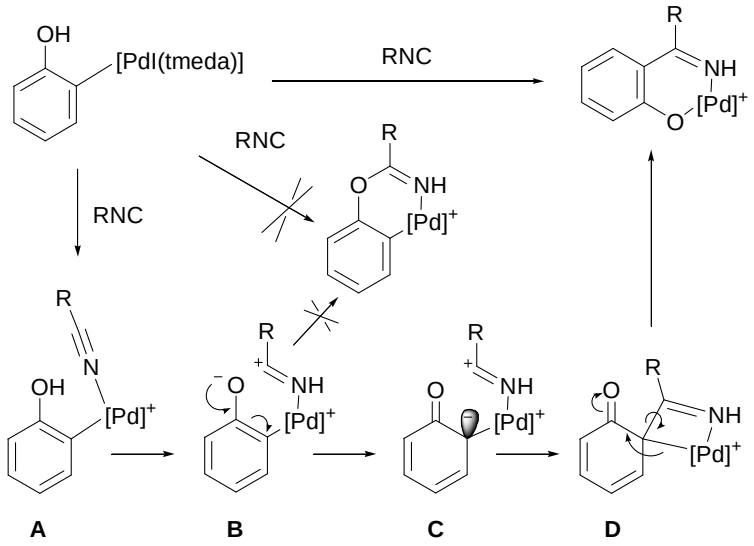
We have not been able to achieve the insertion of nitriles or cyanamides into the C-Pd bond of complexes **1a** or **3**. This negative result contrasts with the successful insertion reactions that we observed with the related complexes [PdI(C_6H_4Y-2)(tmeda)] (Y = OH, NH_2, N^N = tmeda, bpy, tbbpy), and a wide variety of nitriles[10,12] and cyanamides.[12] In those reactions (see *Scheme III.2* for an example), we proposed that the electron-donating

OH or NH_2 group in *ortho* position would play a key role in the mechanism, via delocalization of a negative charge on the aryl *ipso* carbon, so that this carbon would be the one attacking the nitrile (previously coordinated to the Pd atom). The aryl-Pd bond would then break and a new O-Pd (or N-Pd) bond form, resulting in the insertion of the nitrile or cyanamide into the aryl-Pd bond, and the formation of a six-membered chelate ring.[10,12] That mechanistic proposal is now supported by the failure of these insertion reactions with the complexes **1a** and **3**, for which the CH_2 link between the OH function and the aryl ring prevents the delocalization of electron density.



Scheme III.1 Synthesis of complexes **8**, **9a,b**, and **II**

In one of our attempts to react complex **3** with nitriles, we used 1,2-dichloroethane as solvent and heated to 60ºC. We obtained then the complex [PdCl{C_6H_4($CH_2OCH_2CH_2Cl$)-2}(bpy)] (**II**), which is the result of the nucleophilic attack of the oxygen in **3** at a CH_2 group of the 1,2-dichloroethane solvent. Complex **II** has been characterized by X-ray diffraction studies (see Section III.3.4), but we have not been able to purify and fully characterize it. We have described similar reactions of **3** with alkyl halides (bromides and iodides) in a previous paper (see Chapter II of this Thesis).[14]



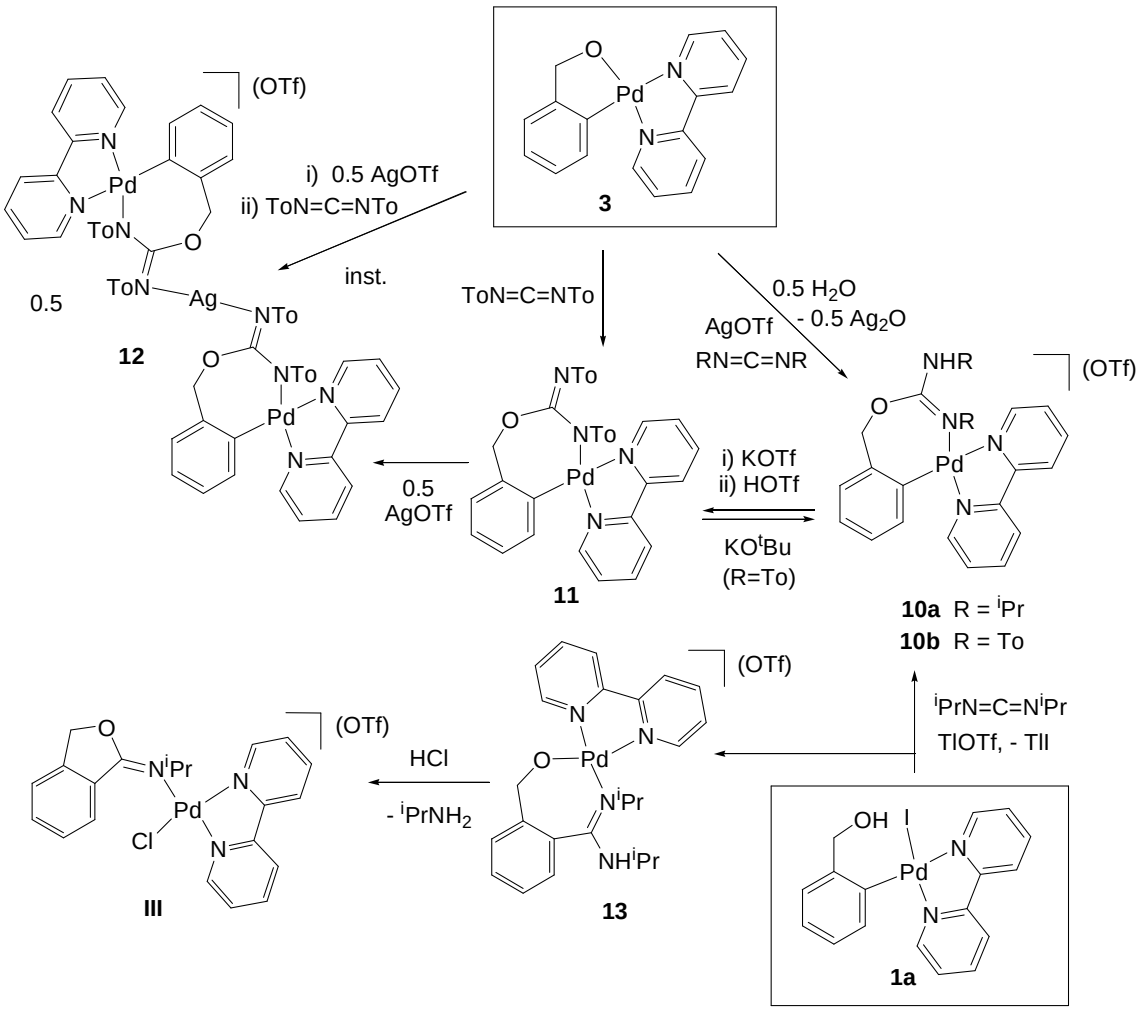
[Pd] = [Pd(tmeda)]

Scheme III.2
Proposed mechanism for the insertion of nitriles into the aryl-Pd bond of $[PdI(C_6H_4OH\text{-}2)(tmeda)]$[10,12]

III.3.2 Reactions with Carbodiimides

Complex **3** reacts with the carbodiimides RN=C=NR (R = ^{i}Pr, To) and AgOTf (1:5:1 molar ratio, CH_2Cl_2) in the presence of residual water, to form [Pd{κ^2-*C,N*-C_6H_4{$CH_2OC(=NR)NHR$}-2}(bpy)](OTf) (R = ^{i}Pr (**10a**), To (**10b**), *Scheme III.3*) which, similarly to **8** and **9a,b**, are the result of the insertion of the organic products into the O-Pd bond of **3**.

When these reactions were performed in the absence of AgOTf, however, the results differed for the two carbodiimides investigated. With ^{i}PrN=C=N^{i}Pr there was no reaction, whereas with ToN=C=NTo the reaction in the absence of AgOTf resulted in the formation of [Pd{κ^2-*C,N*-C_6H_4{$CH_2OC(=NTo)NTo$}-2}(bpy)] (**11**, *Scheme III.3*), which is the conjugate base of **10b**. These results suggest that the 1,3-di-*p*-tolylcarbodiimide is the only reactant investigated in this work that is electrophilic enough to undergo nucleophilic attack by the O atom in **3**, without being previously activated by the coordination to Ag. Complex **11** has a characteristic red color, and it forms after only 5 min in the reaction with either one equivalent or excess of the carbodiimide. It is partially soluble in Et_2O.



Scheme III.3 Reactions of complexes **1a** and **3** with carbodiimides

By deprotonation of the ionic complex **10b** with KO^{t}Bu, it is possible to obtain the neutral complex **11** and, vice versa, by reaction of **11** with KOTf and HOTf complex **10b** is obtained. In this reaction it is necessary to add the KOTf first and then the HOTf after a few minutes, as otherwise a different product forms, which could not be characterized. Thus, the K^+ ion seems to stabilize the reaction intermediate, probably by coordinating to the O atom. The deprotonation of the ionic complex **10a** (R = ^{i}Pr) with KO^{t}Bu gives a red neutral complex similar to **11**, but it reprotonates very easily, so that it could not be characterized. Clearly, the To groups in **11** play a very important role in the stability of this complex, most probably through resonance effects.

Curiously, when the reaction of **3** with AgOTf and a 5-fold excess of ToN=C=NTo was stopped after only 2 hours, or when it was performed in a ca. 1:1:1 stoichiometric ratio, a mixture of **10b** and a different product formed. This product was identified by X-ray crystallography (see Section III.3.4 and *Figure III.4*) as an ionic mixed-metal

trinuclear complex consisting of two molecules of **11** coordinated through *N* to one atom of Ag (complex **12** = [Ag(*N*-**11**)$_2$](OTf), *Scheme III.3*). The structure of **12** differs greatly from other heterometallic Pd_2Ag[18] or Pd_2Ag_2[19] complexes found in the literature, and it is thus unprecedented. With ^{i}PrN=C=N^{i}Pr we did not observe a similar reactivity. The formation of complex **12** is favored by a shorter reaction time and a smaller amount of carbodiimide, and we have also observed that it is strongly influenced by the order of addition of the reactants. Thus, in the reactions of **3** with one equivalent of ToN=C=NTo and AgOTf, if the carbodiimide is added first and then the AgOTf, the major product is **10b** (even if the reaction is stopped immediately), although it forms together with a variable amount of **12**. In contrast, if AgOTf is added first, followed by one equivalent of ToN=C=NTo, and the reaction is stopped immediately, the trinuclear complex **12** is the major product, with only ca. 20% of **10b** (this amount increases if a longer reaction time is allowed). Complex **12** can then be separated from **10b** by exploiting differences in solubility (see Chapter VIII, Experimental Section). From these observations we suggest that the trinuclear complex **12** forms by the nucleophilic attack of **3** on a [Ag(ToN=C=NTo)$_2$]$^+$ intermediate, and then it reacts with residual water, losing the Ag atom and forming two molecules of **10b**. This "decomposition" to **10b** would be favored by an excess of carbodiimide, which would coordinate to the Ag facilitating the rupture of **12** (in an overnight reaction with a 5-fold excess of ToN=C=NTo, only **10b** is detected, while the same reaction with only one equivalent of ToN=C=NTo gives a mixture of **10b** and **12** in ca. 1:0.8 ratio). In contrast, when the carbodiimide is added *before* the AgOTf, it would immediately react with **3**, forming, presumably, first the neutral complex **11** and then, upon addition of the AgOTf, the ionic complex **10b**, so that **12** would only be a minor product. We have tried to obtain complex **12** by reaction of **11** with 0.5 equivalents of AgOTf and, after 2 hours in CH_2Cl_2, the major product of this reaction was indeed the trinuclear complex **12**, together with ca. 20% of **10b**. Thus, it seems that complex **11** can be transformed in the presence of AgOTf to both **10b** or **12**, and the favored product is determined by the reaction conditions.

Complexes **10a,b** also form in the reaction of the 2-hydroxymethylphenyl Pd complex [PdI($C_6H_4CH_2OH$-2)(bpy)] (**1a**) with the corresponding carbodiimides and AgOTf, but with a lower yield and purity. When complex **1a** reacts with ^{i}PrN=C=N^{i}Pr in the presence of TlOTf, instead of AgOTf, a ca. 1:1 mixture of two complexes forms: one is again **10a** (which is now the result of the addition of the OH group to the carbodiimide and the coordination of one of the N atoms to Pd) and the other is [Pd{κ^2-*O*,*N*-

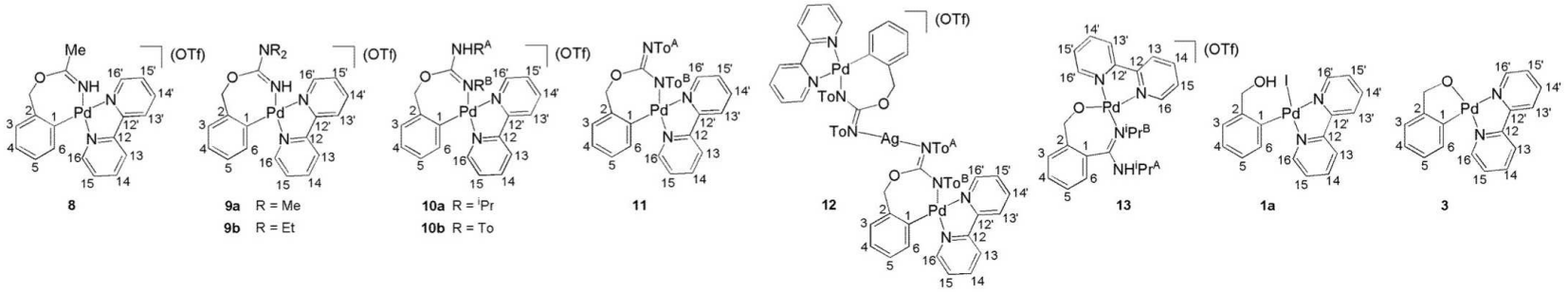
$OCH_2\{C_6H_4\{C(=N^iPr)NH^iPr\}\text{-}2\}\}(bpy)](OTf)$ (**13**, *Scheme III.3*), which is the result of the insertion of the carbodiimide into the C-Pd bond. We have not been able to obtain complex **13** independently of **10a**, even by varying the amount of carbodiimide or the reaction time, but we have been able to separate it from **10a** by preparative TLC on alumina (see Chapter VIII, Experimental Section). Additionally, from a $CDCl_3$ solution of **13** we obtained single crystals, the X-ray structure of which showed them to be the unexpected complex **III**, apparently formed by reaction of **13** with the residual HCl of the deuterated solvent (the attack of HCl on **13** would promote the intramolecular attack of the O on the C=N group of the inserted carbodiimide, the breaking of the C-N and Pd-N bonds and the formation of a new Pd-N bond). Unfortunately, in spite of our much effort we have not been able to reproduce the synthesis of this complex, but we include the X-ray data in Section III.3.4. Finally, the reaction of **1a** with ToN=C=NTo and TlOTf, instead of AgOTf, resulted in the formation of a complex that is probably an insertion product similar to **13** but that was not pure enough to be characterized. The (relatively) cleaner reactivity of the carbodiimides with **1a** and TlOTf, compared to the similar reactions with acetonitrile and cyanamides, which gave intractable mixtures, is probably attributable to a combination of electronic and steric effects. The greater steric hindrance in the carbodiimides, together with their appreciable dipole moments, would favor one (or two) major reaction pathways while hindering other secondary reactions.

III.3.3 NMR and IR Data

All the complexes reported in this paper have been extensively studied by NMR spectroscopy (1D and 2D experiments), allowing an almost full assignment of the ^1H and ^{13}C resonances. To facilitate comparison, the data are collected in *Table III.1*. For the same reason, we include in this Table the data of complexes **1a** and **3**[14] (Chapter II).

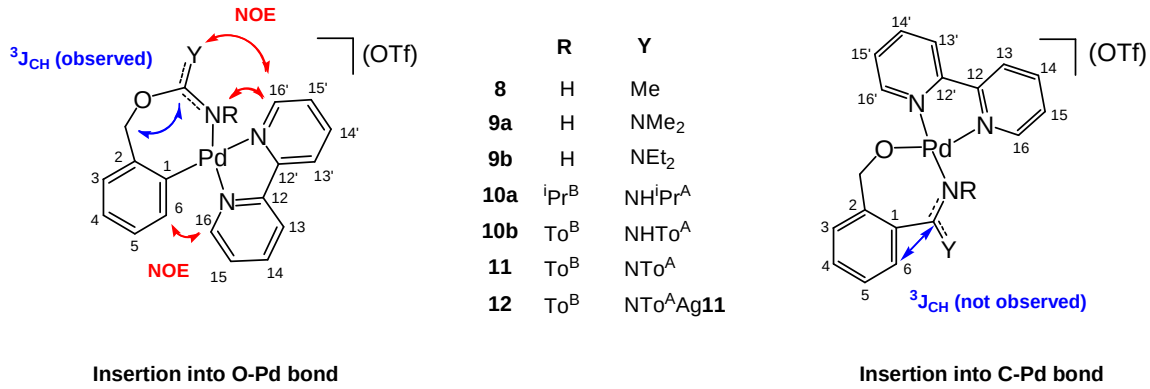
For the complexes **8-12** the insertion of the organic molecules (MeC≡N, R_2N-C≡N, or RN=C=NR) into the O-Pd bond, and not the C-Pd bond, is confirmed by the $^1H,^{13}C$-HMBC spectrum, where the three-bond correlation between the inserted C=N carbon and the methylenic CH_2O protons is always observed, while no correlation is observed between the C=N carbon and the aryl H6 proton, as would be the case for an insertion into the C-Pd bond (*Scheme III.4*). The halves of the bpy ligand in these complexes have been assigned based on NOE contacts between H16 and H6 of the aryl group, and between H16' and the protons which are close in space (see also *Scheme III.4*).

Table III.1 ^{13}C and ^{1}H NMR data ($CDCl_3$, r.t.) of complexes **8-13, 1a,**[14] and **3**[14] (a)



	8		**9a** (R=Me)		**9b** (R=Et)		**10b** (R=To)		**11**		**12**		**10a** (R=^{i}Pr)		**13**		**1a**		**3**	
Aryl ligand	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C[(b)]	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H
C1	152.0		153.1		153.0		153.7		149.6		150.0		153.6		**134.2**		146.3		151.0	
C2	139.4		139.3		139.1		137.9		140.7		138.9		138.3		**146.0**		145.4		**166.2**	
CH3	127.6	7.15-	127.6	7.16-	127.4	7.14-	127.9	7.22-	124.9	6.70	126.6	6.66	127.4	7.03	130.8	7.43	128.8	7.11	119.1	7.04-
CH4	125.4	7.11	125.1	7.10	125.0	7.12	125.6	7.18	123.5	6.93	124.1	7.17	124.7	7.07	131.3	7.40	124.3	6.93-	124.0	6.97
CH5	130.6	7.29	130.3	7.29-	130.2	7.29-	131.2	7.44	126.9	7.03	127.2	7.36	129.8	7.26	127.9	7.32	126.8	6.89	123.6	
CH6	134.7	7.22	134.9	7.26	134.9	7.26	134.2	7.50	136.2	7.70	136.1	7.84	134.4	7.39	128.0	7.55	136.6	7.38	131.7	7.21
CH_2	72.2	6.60 5.05	73.2	6.62 5.10	73.1	6.66 5.11	74.2	7.22 5.27	71.2	5.02 4.73 (br)	72.9	4.88 4.19	74.3	6.65 5.12	69.9	4.57 3.84	68.7	4.99 4.48	**78.4**	**5.21**
C=NH/ NH	175.1	**8.45**	161.3	4.81	160.2	4.76	156.5	6.49	155.7		162.2		156.3	5.57	162.0	6.39				
					To^{A}	***i*-C**	133.4		147.9		143.6	6.8	45.4	3.89	48.9	3.55	**CH^{A}**	**^{i}Pr^{A}**		
						***o*-CH**	123.9	6.85	122.7	7.00-6.95	[(c)]	**6.85 (br)**								
						***m*-CH**	129.9	7.09	129.0	(br)	**129.7 (br)**	[(c)]	23.7	1.28	25.2	1.04	**Me^{A}** [(e)]			
						***p*-C**	136.2		129.0		132.5		23.1	1.14	23.1	1.40				
					To^{B}	***i*-C**	141.8		146.4		146.4		51.0	3.78	50.7	4.25	**CH^{B}**	**^{i}Pr^{B}**		
						***o*-CH**	125.9	7.29	124.6	7.9 [(d)]	124.2	6.13								
						***m*-CH**	131.3	7.20	128.9	6.85	128.7	7.00	26.0	1.55	24.9	1.65	**Me^{B}** [(e)]			
						***p*-C**	137.4		129.5		131.3		22.0	0.70	22.4	1.54				
Bpy[(f)]																				
C12	157.0		157.0		157.0		156.9		155.2		156.5		156.9		154.8		156.6		156.6	
C12'	152.6		153.1		153.2		153.4		153.1		153.7		153.1		155.7		154.4		153.4	
CH16	151.9	8.37	151.6	8.32	151.6	8.32	151.6	8.31	152.1	8.45	152.4	8.35	151.7	8.52	152.2	8.52	**150.4**	**7.33**	152.0	9.18
CH16'	151.0	8.89	149.1	8.65	148.9	8.58	149.3	8.61	149.3	8.39	149.0	8.13	150.8	8.68	148.1	8.85	**153.1**	9.46	149.9	9.03
CH14	140.1	8.07	140.3	8.14	140.3	8.15	141.0	8.18	138.8	7.96	139.8	8.10	140.3	8.16	140.1	8.00	139.6	7.94	138.1	8.03-
CH14'	140.1	8.11	140.5	8.08	140.6	8.13		8.14	139.1	7.91	139.9	8.00	140.4	8.15	140.6	8.08	139.5	7.98	138.8	7.96
CH15	126.7	7.43	126.7	7.39	126.7	7.39	126.9	7.39	126.7	7.39	126.8	7.36	126.9	7.44	128.4	7.71	127.2	7.25	126.6	7.59-
CH15'	128.3	7.82	127.9	7.79	127.7	7.78	127.5	7.69	127.0	-7.30	126.9	7.31	128.2	7.82	126.1	7.55	127.6	7.53	126.3	7.52
CH13	123.0	8.25	123.8	8.42	123.9	8.44	124.5	8.54	122.1	8.06	123.4	8.33	123.5	8.40	122.8	8.04	122.8	8.06-	122.5	8.08-
CH13'	122.1	8.17	123.0	8.35	123.2	8.39	123.8	8.50	121.6	8.02	122.7	8.28	122.7	8.35	122.4	8.08	122.4	8.02	121.1	8.03

(a) The data for the Me groups of **8**, **9a**, **10b**, **11**, **12** and the Et groups of **9b** are not included in the tables for lack of space. The data highlighted in bold are commented in the text. (b) Measured at 213K. (c) The To^{A} group in **12** is fluxional: for the *o*-CH the ^{13}C resonance is not observed and the ^{1}H resonance is broad; for the *m*-CH the ^{13}C resonance is broad and the ^{1}H resonance is not observed. (d) This resonance appears in a multiplet together with the resonances of H13,13',14,14'. (e) For each Me group the corresponding ^{13}C and ^{1}H resonances are in the same line. (f) The two halves of the bpy ligands have been assigned based on NOE contacts between H16 and the aryl group

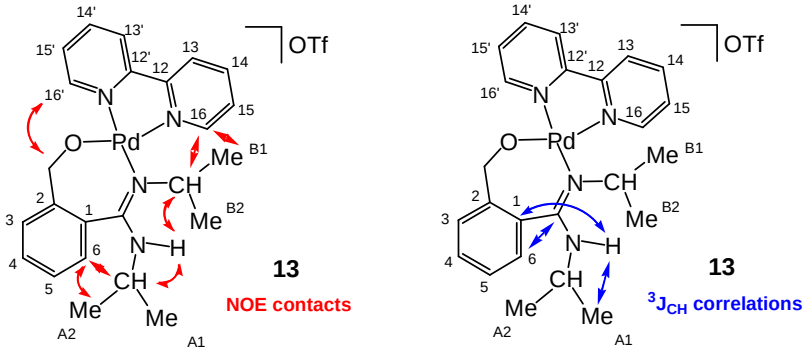


	R	Y
8	H	Me
9a	H	NMe_2
9b	H	NEt_2
10a	$^iPr^B$	NH^iPr^A
10b	To^B	$NHTo^A$
11	To^B	NTo^A
12	To^B	NTo^AAg**11**

Scheme III.4

In blue: expected $^3J(^{13}C\text{-}^1H)$ correlations in the complexes resulting from the insertion of the organic molecules (MeC≡N, $R_2NC{\equiv}N$, or RN=C=NR) into the O-Pd bond (left) or C-Pd bond (right) of **3**. Only the $^3J_{CH}$ coupling between the C=N carbon and the methylenic protons is observed, indicating insertion into the O-Pd bond. In red: assignment of the halves of the bpy ligand in **8-12**, based on selective NOE contacts

In complex **13**, in contrast, the insertion of the carbodiimide into the C-Pd bond is confirmed by the $^1H,^{13}C$-HMBC and ^1H-NOESY experiments (see *Scheme III.5*). The halves of the bpy ligand are assigned based on the NOE contacts, as well. Complex **13** is not an arylpalladium complex and this is reflected in the chemical shifts of the aryl carbons, which differ from those of **8-12**, especially for C1 (δ 134 ppm for **13** and 149.6-153.7 ppm for **8-12**) and C2 (δ 146 ppm for **13** and 137.9-140.7 ppm for **8-12**).



Scheme III.5

Observed NOE contacts between different groups in complex **13** (left), and observed $^3J(^{13}C,^1H)$ correlations in the $^1H,^{13}C$-HMBC spectrum (right), both confirming the insertion of the carbodiimide into the C-Pd bond, as well as the position of the proton on the uncoordinated nitrogen

The two ^{i}Pr groups in **10a** and **13**, as well as the two To groups in **10b**, **11**, and **12**, (labeled A and B) are assigned based on NOE data. The two Me groups within each ^{i}Pr are always diastereotopic (inequivalent), as are the methylenic protons of all the

complexes (**8-13**). The methinic proton of $^{i}Pr^{A}$ resonates as a doublet of septets ($^{3}J_{HH}$ = 7 Hz, $^{3}J_{HH}$ = 6 Hz for **10a**, and $^{3}J_{HH}$ = 9 Hz, $^{3}J_{HH}$ = 6 Hz for **13**), because of the coupling with the six methyl protons and the NH proton, which appears as a doublet ($^{3}J_{HH}$ = 7 Hz for **10a**, and $^{3}J_{HH}$ = 9 Hz for **13**). This coupling pattern confirms the position of the NH proton in **10a** and **13** on the N that is not coordinated to Pd, as also revealed by the NMR data (^{1}H-NOESY and ^{1}H,^{13}C-HMBC) of **10a,b** and **13** (see *Scheme III.5* for **13**), and by the X-ray data of **10a** (see *Figure III.3*). This position is similar to that observed in the related complexes resulting from the reaction with carbodiimides of *ortho*-palladated phenol derivatives.[11,12]

The C=NH proton in complex **8** resonates at much higher frequency (δ 8.45 ppm) than in **9a,b** (δ 4.81 and 4.76 ppm), for which the partial release of the lone pair from the NR_2 group results in resonance form with a negative charge on the NH, an effect that is lacking in **8**. This electronic delocalization along the R_2N-C=NH bonds is confirmed by the X-ray diffraction study of **9a** (see Section III.3.4). For the complexes derived from carbodiimides, the three NHR chemical shifts are not very different: δ 5.57 ppm for **10a**, 6.49 ppm for **10b** and 6.39 ppm for **13**.

The neutral complex **11** shows a fluxional behavior within the chelate ring, which results in the broadening of one of the methylenic ^{1}H resonances, and also of the ^{1}H resonances of the more external tolyl group (To^{A}). These resonances sharpen at low temperature (213 K), but the ^{1}H chemical shifts do not change significantly, so that the values at room temperature are given in *Table III.1* and in the Experimental Section (Chapter VIII). The ^{13}C NMR data, however, are given for 213 K, because at room temperature the S/N ratio of some resonances is too low.

In the mixed trinuclear Pd_2Ag complex **12**, the halves of the molecule are equivalent in solution (not in the solid state, see Section III.3.4), as only one set of ^{1}H and ^{13}C NMR resonances is observed. This is in contrast to what we have recently observed for another "dimeric" complex, $[C_6H_4\{CH_2OCH_2(C_6H_4\{PdBr(bpy)\}\text{-}2)\}_2\text{-}1,4]$ (**6**, Chapter II), where the halves of the molecule were not equivalent.[14] The chelate nature of the Pd moieties in **12**, as well as the linear geometry of the Ag bridge, seem to favor the symmetry of this complex in solution. The tolyl group To^{A} in **12** again shows strongly broadened ^{1}H and ^{13}C resonances, indicating that the rotation around the To-N bond is hindered by the steric crowding in the molecule. Curiously, in the ^{1}H spectrum the resonance of the *o*-CH^{A} group is very broad and the resonance of the *m*-CH^{A} group is not observed, while in

the ^{13}C spectrum the opposite is observed: *m*-CH^A broad and *o*-CH^A not observed.[a] This different behavior in the ^{1}H and ^{13}C spectra can be explained by the frequency dependence of the NMR timescale. The To groups A and B are distinguished because To^A shows NOE contacts with H3,4 of the aryl group, as expected from the X-ray structure (see *Figure III.1*).

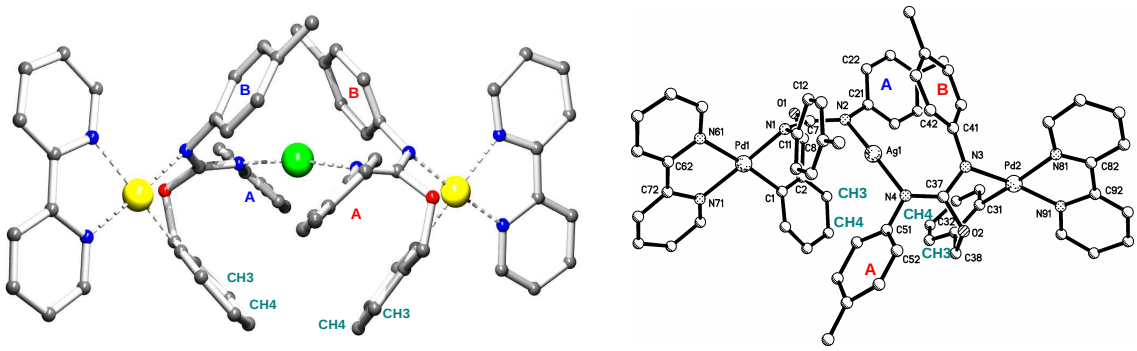


Figure III.1

X-ray structure of **12**, showing the proximity in space of the *o*-H of To^A with the protons H3,4 of the aryl group

Within the bpy ligand, we observe that for the arylpalladium complexes **8-12**, δ(C12) > δ(C12') (for C12, in the pyridyl ring *trans* to N, δ = 157.0-155.2 ppm, while for C12', in the pyridyl ring *trans* to aryl, δ = 153.7-152.6 ppm). We had already observed in a previous paper, including complexes **1a** and **3** (see Chapter II),[14] that δ(C12) (*trans* to I, Br, O, 156.6-155.2 ppm) > δ(C12') (*trans* to aryl, 154.5-153.4 ppm). Combining now all the data it is clear that δ(C12) (*trans* to I, Br ,O, N, 157.0-155.2 ppm) is always larger than δ(C12') (*trans* to aryl, 154.5-152.6 ppm). For complex **13**, the C12,12' ^{13}C chemical shifts are: δ(C12) = 154.8 ppm (*trans* to O); δ C(12') = 155.7 ppm (*trans* to N).

For all the complexes, **8-13**, δ(CH16) (152.4-151.6 ppm) is also larger than δ(CH16') (151.0-148.1 ppm), although the difference is smaller than for C12,12'. In the iodo complex **1a** however, this tendency is reversed (δ(CH16), 150.4 ppm < δ(CH16'), 153.1 ppm), as we had already noted in our previous paper (Chapter II).[14]

The chemical shifts of the *ortho* hydrogen atoms of both pyridyl rings, H16 and H16', are rather similar for **8-12** (H16, δ 8.31-8.52 ppm; H16', δ 8.13-8.89 ppm). Usually, in arylpalladium complexes the protons H16 (in the ring *cis* to the aryl group)

[a] This resonances have been assigned based on ^{1}H,^{13}C correlation and ^{1}H NOE data. The chemical shifts are similar to those of the related complex **11**.

are strongly shielded with respect to H16', as a consequence of the anisotropic effect of the aryl group (see *Scheme II.5*, in Chapter II).[4,14,21,22] Thus, for **1a,** δ(H16) = 7.33 ppm and δ(H16') = 9.46 ppm. The chelate nature of complexes **8-12**, which forces the orientation of the aryl ring toward the plane of the bpy ligand, would explain the absence of this effect (similarly to what is observed for the cycled complex **3**,[14] where δ(H16) = 9.18 ppm and δ(H16') = 9.03 ppm).

The IR bands of the C=N bonds in **8**, **9a,b**, **10a,b** and **13** all appear in the range 1599-1635 cm^{-1}. For complex **11**, where the C=N bond is uncoordinated, the corresponding IR band appears at higher frequency, 1660 cm^{-1}. In the related complex **12** (**12 =** [Ag(*N*-**11**)$_2$](OTf)), however, the coordination of the C=N bond to Ag shifts the IR band again to lower frequency, 1600 cm^{-1}. The IR bands of the N-H bonds in **8**, **9a,b**, **10a,b**, and **13** are observed in the range 3213-3401 cm^{-1}.

III.3.4 X-Ray Structure Determinations

The crystal structures of the complexes **9a**·0.19H_2O (*Figure III.2*, *Table III.3*), **10a** (*Figure III.3*, *Table III.4*), and **12**·2.5$CHCl_3$·0.5Et_2O (*Figure III.4*; only one of the two independent cations is shown, and *Table III.5*), have been determined by X-ray diffraction studies, as well as the crystal structures of the uncharacterized complexes **II** (*Figure III.5*, *Table III.6*) and **III** (*Figure III.6*, *Table III.7*). *Table III.2* contains experimental details on all the structures.[b]

The structures of **9a**·0.19H_2O, **10a**, and **12**·2.5$CHCl_3$·0.5Et_2O show somewhat distorted square planar coordination around the Pd atoms. Mean deviations from the best plane through Pd and the four donor atoms are 0.01 Å for **9a**, 0.02 Å for **10a**, and 0.03 (Pd1), 0.14 (Pd2), 0.04 (Pd1'), and 0.01 (Pd2') Å for **12**. The PdN2C2 chelate rings are all essentially planar and also coplanar with the Pd coordination planes (maximum interplanar angle 8°). The seven-membered rings in **9a** and **10a** have similar conformations, with the five atoms, Pd, N1, O1, C7, and C8 approximately coplanar, and C1 and C2 lying out of the plane to the same side. For **12**, however, all four seven-

[b] Crystals were mounted in inert oil on glass fibres. Intensity data were recorded on various Bruker or Oxford Diffraction diffractometers using either monochromated Mo *K*α or mirror-focused Cu *K*α radiation. Absorption corrections were based on multi-scans. NH hydrogens were refined freely; other hydrogen atoms were included using either rigid methyl groups or a riding model. Structures were refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany).

membered rings have a different form in which C1, C2, N1, and C7 are coplanar, with Pd, O1, and C8 lying out of the plane to the same side.

The Pd-C bond distances for **9a** and **10a** are 1.981(3) Å and 1.9716(15) Å, respectively, both in the range expected for aryl ligands *trans* to N (ca. 1.97-2.00 Å).[4,11,14,21] The two Pd-C bond distances for **12** are slightly longer, 2.014(7) Å for Pd(1)-C(1) and 2.009 Å for Pd(2)-C(31). The Pd-N(*trans* to aryl) bond distances are very similar for the three complexes (between 2.115(5) and 2.118(2) Å), and they are longer than the Pd-N(*trans* to N) bond distances (in the range 2.026(2)-2.070(5) Å), as expected for the stronger *trans* influence of the aryl ligand with respect to N-donor ligands.

The X-ray diffraction study of **12** (*Figure III.4*) confirms the structure proposed for this compound, consisting of two molecules of **11** coordinated via nitrogen to a silver atom. The two Ag-N bond lengths are 2.121(5) and 2.128(4) Å, similar to other Ag-N bond distances reported in the literature for compounds with a N-Ag-N moiety.[23] The N(2)-Ag(1)-N(4) angle of 167.5(2)º departs significantly from linearity, but is still close to those found in the literature (between 168 and 179º).[23]

For the three structures we can suggest electronic delocalization along the N-C-N group: the "single" bonds Me_2N(2)-C(8) (1.343(4) Å, **9a**), ^{i}PrN(2)-C(8) (1.346(2) Å, **10a**), and ToN(1)-C(7), ToN(3)-C(37) (1.341(8) and 1.322(10) Å, **12**) are much shorter than the C-N bonds (Me-N, ^{i}Pr-N and To-N) in the same complexes, which measure between 1.415(10) and 1.494(2) Å. The corresponding "double" bonds C(8)=N(1) (1.305(4) Å, **9a**; 1.3054(18) Å, **10a**), and C(7)=N(2), C(37)=N(4) (1.292(8), and 1.310(9) Å, **12**) are longer than the mean value in imines (1.279 Å).[24] This C=N bond lengthening can be attributed to both the electronic delocalization along the N-C-N bonds, and the coordination of the iminic nitrogen to Pd (in **9a**, **10a**) or Ag (in **12**) (although it is interesting to note that the coordination of N(1) and N(3) to Pd in **12** does not cause a significant lengthening of the corresponding C-N single bonds (1.341(8) and 1.322(10) Å) with respect to the values for the (uncoordinated) C(8)-N(2) bonds in **9a** (1.343(4) Å) and **10a** (1.346(2) Å)). Our group has previously observed a similar electronic delocalization along the N-C-N bonds for complexes resulting from the insertion of carbodiimides and cyanamides into the C-Pd bond, or the addition of carbodiimides to the O-H bond, of *ortho*-palladated phenol derivatives.[12] It is also interesting to note that in the trinuclear complex **12** the electronic delocalization in one of the N-C=N moieties is much greater than in the other (bond lengths in N(1)-C(7)=N(2) are 1.292(8) and

1.341(8) Å, while for N(3)-C(37)-N(4) the two bond lengths are more similar, 1.310(9) and 1.322(10) Å.

The structure of **10a** shows a classical hydrogen bond between the NH proton of the complex and an oxygen atom of the triflate, with an O(3)···H-N(2) distance of 2.22(2) Å.

The X-ray structure of **II** shows a distorted square planar coordination around the Pd atom, with a mean deviation from the best plane through Pd and the four donor atoms of 0.02 Å. The Pd-C(1) bond distance of 1.981(3) Å is in the range expected for Pd-C bonds *trans* to a N-donor ligand (ca. 1.97-2.00 Å).[4,11,14,21] The Pd-N(11) (2.121(3) Å) and Pd-N(21) (2.059(3) Å) bond lengths follow the expected order of *trans* influence: Pd-N *trans* to aryl > Pd-N *trans* to Cl. The Pd-Cl(1) bond length of 2.2977(9) Å is in the range found for other aryl palladium complexes with bpy and a chloro ligand (ca. 2.28-2.31 Å).[25] The C(9)-Cl(2) bond distance of 1.795(6) Å is close to the reported value of 1.790 Å for CH_2-Cl bonds.[24]

The structure of **III** shows a distorted square planar coordination around the Pd atom, with a mean deviation from the best plane through Pd and the four donor atoms of 0.04 Å. The three Pd-N bond distances are very similar, Pd-N(1), 2.0373(11) Å; Pd-N(21), 2.0338(11) Å; and Pd-N(11), 2.0210(11) Å, and shorter than the Pd-N bond distances for N-donor ligands *trans* to aryl described so far in this Thesis (between 2.1039(15) and 2.1364(16) Å).[14] The Pd-Cl bond length of 2.2914(4) Å is very similar to that of **II** (2.2977(9) Å) and in the range found for other aryl palladium complexes with bpy and a chloro ligand (ca. 2.28-2.31 Å).[25] The coordination of the iminic nitrogen to Pd leads to a slight lengthening of the C=N bond (1.2890(17) Å) with respect to the mean value in imines (1.279 Å).[24]

Table III.2 X-ray crystallographic data for compounds **9a**·0.19H_2O, **10a**, **12**·2.5$CHCl_3$·0.5Et_2O, **II**, and **III** [(c)]

	9a·0.19H_2O	**10a**	**12**·2.5$CHCl_3$·0.5Et_2O	**II**	**III**
Formula	$C_{21}H_{20.38}F_3N_4O_{4.19}PdS$	$C_{25}H_{29}F_3N_4O_4PdS$	$C_{69.5}H_{63.5}AgCl_{7.5}F_3N_8O_{5.5}Pd_2S$	$C_{19}H_{18}Cl_2N_2OPd$	$C_{22}H_{21}ClF_3N_3O_4PdS$
M_r	591.29	644.98	1774.39	467.65	622.33
T (K)	100(2)	103(2)	103(2)	133(2)	100(2)
λ (Å)	1.54184	0.71073	1.54184	0.71073	0.71073
cryst syst	triclinic	orthorhombic	triclinic	monoclinic	triclinic
space group	*P(-1)*	*Pbca*	*P(-1)*	*$P2_1/n$*	*P(-1)*
cell constants					
a (Å)	7.5154(2)	7.9720(2)	12.8921(7) Å	9.132(2) Å	8.0300(4) Å
b(Å)	9.8002(3)	17.9802(5)	17.7080(10) Å	11.578(2) Å	9.1108(4) Å
c (Å)	15.6928(5)	36.9522(10)	33.077(2) Å	17.024(3) Å	16.7796(8) Å
α (deg)	93.082(3)	90	84.739(5)	90	96.350(4)
β (deg)	93.631(3)	90	86.381(5)	91.879(8)	98.048(4)
γ (deg)	101.326(3)	90	79.154(5)	90	107.239(4)
V (Å^3), Z	1128.44(6), 2	5296.7(2), 8	7376.9(7), 4	1798.9(6), 4	1145.78(9), 2
ρ (calcd) (Mg m^{-3})	1.740	1.618	1.598	1.727	1.804
abs. coef. (mm^{-1})	8.070	0.840	9.284	1.338	1.079
F(000)	594	2624	3560	936	624
cryst size (mm)	0.25 x 0.15 x 0.03	0.28 x 0.25 x 0.06	0.10 x 0.08 x 0.05	0.40 x 0.23 x 0.20	0.40 x 0.25 x 0.08
θ range (deg)	4.61 75.70	2.78 30.51	3.49 76.49	2.13 30.54	2.37 30.99
index ranges	$-9 \le h \le 9$ $-12 \le k \le 10$ $-19 \le l \le 19$	$-11 \le h \le 9$ $-25 \le k \le 25$ $-52 \le l \le 52$	$-16 \le h \le 16$ $-19 \le k \le 22$ $-41 \le l \le 41$	$-13 \le h \le 12$ $0 \le k \le 16$ $0 \le l \le 24$	$-11 \le h \le 11$ $-13 \le k \le 13$ $-24 \le l \le 24$
reflections collected	45759	140731	135416	5343	43722
independent reflections	4664	8074	30575	5452	7294
R_{int}	0.0643	0.0512	0.0837	0.0000	0.0293
abs corr	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
transmissions	1.00000 0.24636	1.00000 0.92996	1.00000 0.88379	0.8622 0.7557	1.00000 0.83340
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	4664 / 79 / 346	8074 / 0 / 351	30575 / 943 / 1836	5452 / 0 / 227	7294 / 116 / 351
goodness-of-fit on F^2	1.071	1.019	1.056	1.086	1.050
Final R indices (I>2σ(I))					
R1	0.0363	0.0254	0.0652	0.0341	0.0209
wR2	0.0976	0.0599	0.1679	0.0827	0.0517
R indices (all data)					
R1	0.0369	0.0420	0.0965	0.0395	0.0254
wR2	0.0981	0.0619	0.1841	0.0851	0.0524
largest diff peak (e Å^{-3})	0.776	0.447	2.639	1.270	0.771
largest diff hole (e Å^{-3})	1.402	0.701	-1.586	-0.802	-0.838

(c) *Exceptions and special features*: For all disordered groups, appropriate restraints were employed to improve refinement stability, but the dimensions of disordered groups should always be interpreted with caution. For **9a**: The triflate ion is disordered over two positions. A difference peak of ca. 2.3 e A^{-3} was tentatively interpreted as a partially occupied water site. It is impossibly close to O3 and therefore was assigned the same occupation factor as the minor triflate component, with which it does not collide. Water H were not located. For **12**: The asymmetric unit contains two molecules of the Pd/Ag complex, two triflates, five chloroforms and one ether. One of the triflates and two of the chloroforms are disordered. The ether has high U values. For **II**: The crystal was non-merohedrally twinned by 180° rotation about the a axis. The structure was refined using the 'HKLF 5' method, which involves different reflection classes for non-overlapped and overlapped reflections. Because of the special handling of twinned crystals (e.g. all equivalents are merged during the untwining process), the numbers of reflections should be treated with caution. The scale factor refined to 0.495(1). For **III**: The triflate anion is disordered "head-to-toe".

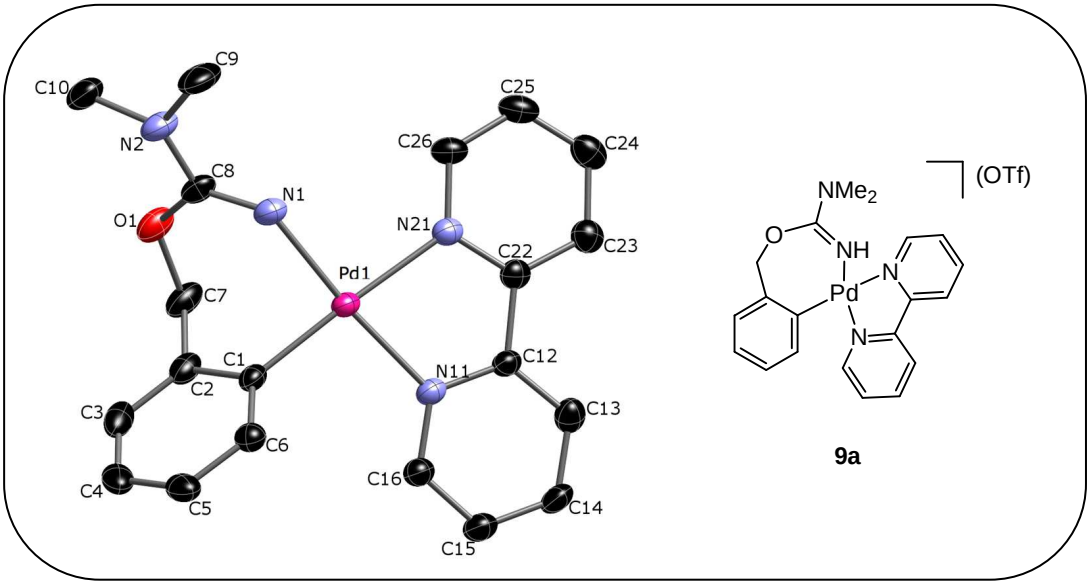


Figure III.2 Thermal ellipsoid plot (50% probability level) of **9a**·0.19H_2O. Only the cation is shown

Table III.3 Selected bond lengths (Å) and angles (deg) of **9a**·0.19H_2O.

Pd(1)-C(1)	1.981(3)	C(1)-Pd(1)-N(1)	87.22(11)
Pd(1)-N(1)	2.026(2)	C(1)-Pd(1)-N(11)	97.84(10)
Pd(1)-N(11)	2.051(2)	N(1)-Pd(1)-N(21)	95.85(10)
Pd(1)-N(21)	2.118(2)	N(11)-Pd(1)-N(21)	79.20(10)
O(1)-C(7)	1.462(4)	N(1)-Pd(1)-N(11)	174.20(9)
O(1)-C(8)	1.334(4)	C(1)-Pd(1)-N(21)	176.21(9)
C(8)-N(1)	1.305(4)	C(7)-O(1)-C(8)	120.0(2)
C(8)-N(2)	1.343(4)	O(1)-C(8)-N(1)	124.7(3)
C(9)-N(2)	1.450(4)	O(1)-C(8)-N(2)	112.2(3)
C(10)-N(2)	1.462(4)	N(1)-C(8)-N(2)	123.1(3)
		C(8)-N(1)-Pd(1)	136.3(2)

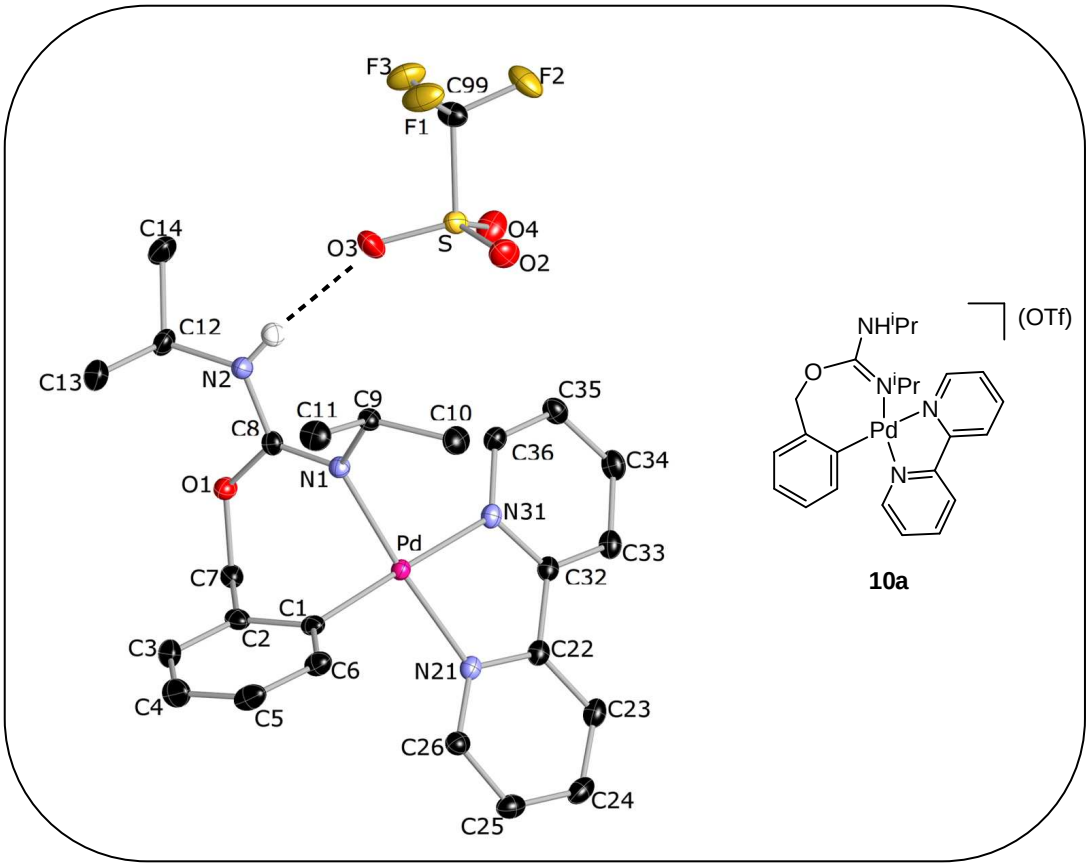


Figure III.3 Thermal ellipsoid plot (50% probability level) of **10a**

Table III.4 Selected bond lengths (Å) and angles (deg) of **10a**

Pd-C(1)	1.9716(15)	C(1)-Pd-N(1)	84.69(6)
Pd-N(1)	2.0313(13)	C(1)-Pd-N(21)	98.38(6)
Pd-N(21)	2.0331(13)	N(1)-Pd-N(31)	97.75(5)
Pd-N(31)	2.1157(12)	N(21)-Pd-N(31)	79.53(5)
O(1)-C(7)	1.4567(19)	N(1)-Pd-N(21)	175.14(5)
O(1)-C(8)	1.3350(19)	C(1)-Pd-N(31)	174.44(6)
C(8)-N(1)	1.3054(18)	C(7)-O(1)-C(8)	123.79(12)
C(8)-N(2)	1.346(2)	O(1)-C(8)-N(1)	125.21(14)
C(9)-N(1)	1.494(2)	O(1)-C(8)-N(2)	111.20(13)
C(12)-N(2)	1.4658(19)	N(1)-C(8)-N(2)	123.58(16)
		C(8)-N(1)-Pd	125.84(12)

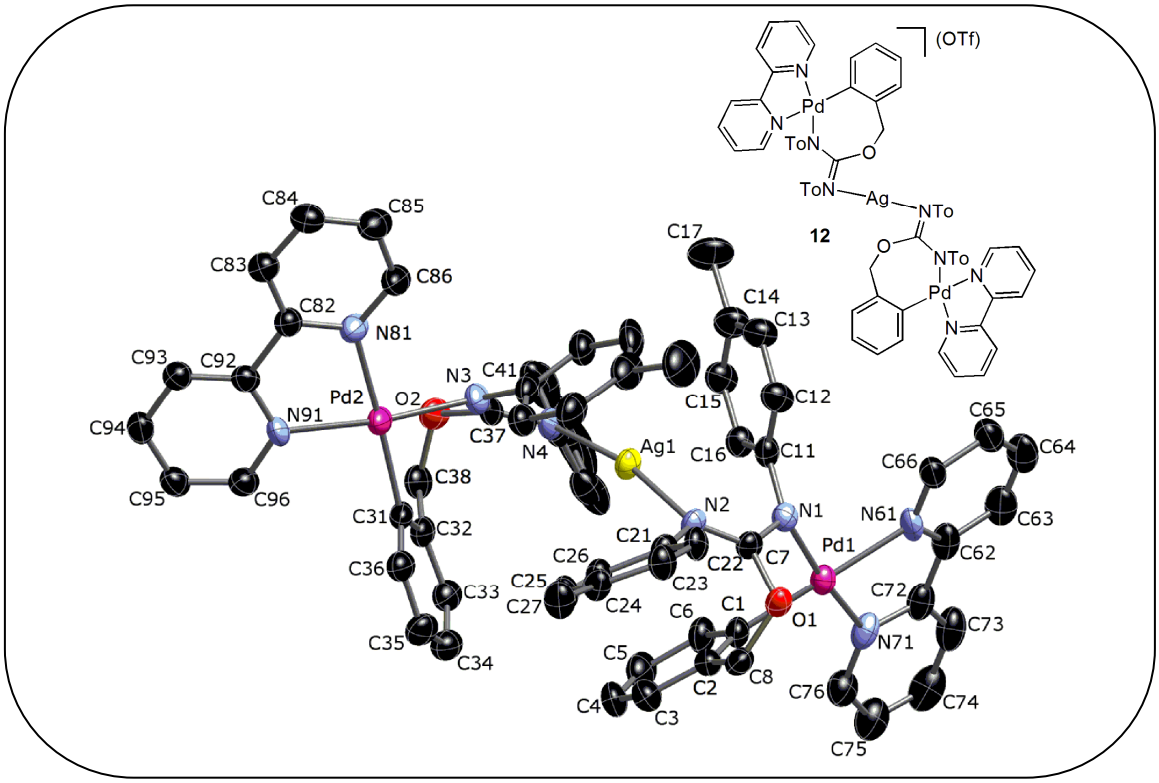


Figure III.4 Thermal ellipsoid plot (50% probability level) of **12**·2.5$CHCl_3$·0.5Et_2O. Only one of the two independent cations is shown

Table III.5 Selected bond lengths (Å) and angles (deg) of **12**·2.5$CHCl_3$·0.5Et_2O

Ag(1)-N(4)	2.121(5)	N(4)-Ag(1)-N(2)	167.5(2)
Ag(1)-N(2)	2.128(4)	C(1)-Pd(1)-N(1)	88.7(2)
Pd(1)-C(1)	2.014(7)	C(1)-Pd(1)-N(71)	96.5(3)
Pd(1)-N(1)	2.044(5)	N(1)-Pd(1)-N(61)	95.7(2)
Pd(1)-N(71)	2.070(5)	N(71)-Pd(1)-N(61)	78.5(2)
Pd(1)-N(61)	2.115(5)	N(1)-Pd(1)-N(71)	171.9(2)
Pd(2)-C(31)	2.009(6)	C(1)-Pd(1)-N(61)	173.1(2)
Pd(2)-N(91)	2.045(5)	C(31)-Pd(2)-N(91)	97.9(2)
Pd(2)-N(3)	2.054(6)	C(31)-Pd(2)-N(3)	86.4(3)
Pd(2)-N(81)	2.117(6)	N(91)-Pd(2)-N(81)	79.7(2)
O(1)-C(8)	1.439(8)	N(3)-Pd(2)-N(81)	97.5(2)
O(1)-C(7)	1.368(7)	N(91)-Pd(2)-N(3)	168.8(2)
N(1)-C(7)	1.341(8)	C(31)-Pd(2)-N(81)	171.3(3)
N(1)-C(11)	1.422(8)	C(7)-O(1)-C(8)	112.9(4)
N(2)-C(7))	1.292(8)	O(1)-C(7)-N(1)	111.4(5)
N(2)-C(21)	1.418(8)	O(1)-C(7)-N(2)	122.1(6)
O(2)-C(38)	1.456(9)	N(1)-C(7)-N(2)	126.4(6)
O(2)-C(37)	1.390(7)	C(7)-N(1)-Pd(1)	117.3(4)
N(3)-C(37)	1.322(10)	C(37)-O(2)-C(38)	112.0(5)
N(3)-C(41)	1.416(8)	O(2)-C(37)-N(3)	112.2(6)
N(4)-C(37)	1.310(9)	O(2)-C(37)-N(4)	119.7(7)
N(4)-C(51)	1.415(10)	N(3)-C(37)-N(4)	128.1(6)
		C(37)-N(3)-Pd(2)	112.6(4)

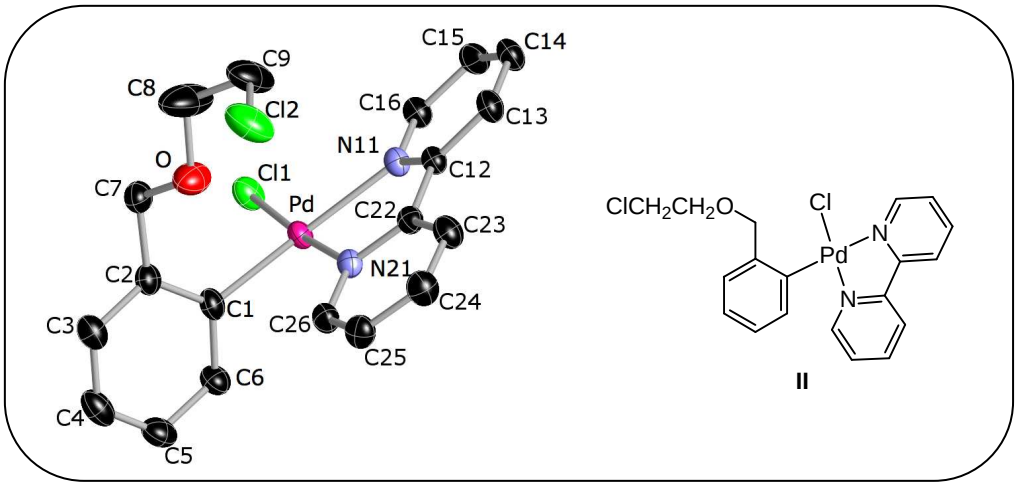


Figure III.5 Thermal ellipsoid plot (50% probability level) of **II**

Table III.6 Selected bond lengths (Å) and angles (deg) of **II**

Pd-C(1)	1.981(3)	C(1)-Pd-N(21)	93.77(12)
Pd-N(11)	2.121(3)	C(1)-Pd-Cl(1)	89.76(10)
Pd-N(21)	2.059(3)	N(11)-Pd-N(21)	78.97(11)
Pd-Cl(1)	2.2977(9)	N(11)-Pd-Cl(1)	97.36(8)
C(1)-C(2)	1.411(5)	N(11)-Pd-C(1)	172.28(12)
C(2)-C(7)	1.497(5)	N(21)-Pd-Cl(1)	175.54(8)
C(7)-O	1.424(4)	C(2)-C(7)-O	108.9(3)
O-C(8)	1.417(6)	C(7)-O-C(8)	110.7(4)
C(8)-C(9)	1.456(7)	O-C(8)-C(9)	111.2(5)
C(9)-Cl(2)	1.795(6)	C(8)-C(9)-Cl(2)	111.4(5)

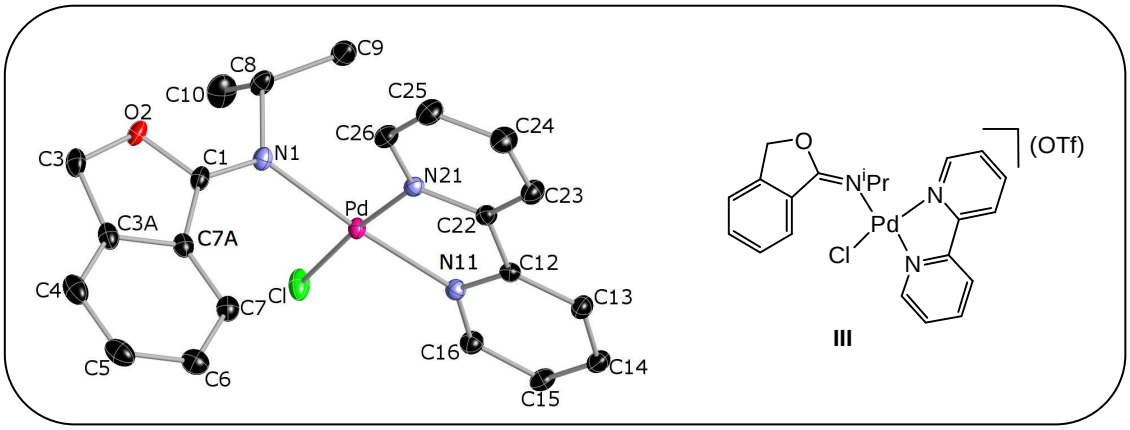


Figure III.6 Thermal ellipsoid plot (50% probability level) of **III**

Table III.7 Selected bond lengths (Å) and angles (deg) of **III**

Pd-N(1)	2.0373(11)	N(1)-Pd-N(21)	96.50(4)
Pd-N(11)	2.0210(11)	N(1)-Pd-Cl	88.17(3)
Pd-N(21)	2.0338(11)	N(11)-Pd-N(21)	80.66(4)
Pd-Cl	2.2914(4)	N(11)-Pd-Cl	94.78(3)
N(1)-C(1)	1.2890(17)	N(11)-Pd-N(1)	175.39(5)
C(1)-C(7A)	1.4633(19)	N(21)-Pd-Cl	175.05(3)
C(1)-O(2)	1.3517(16)	Pd-N(1)-C(1)	124.05(10)
O(2)-C(3)	1.4571(16)	Pd-N(1)-C(8)	118.57(8)
C(3)-C(3A)	1.496(2)	N(1)-C(1)-O(2)	119.96(12)
		N(1)-C(1)-C(7A)	130.51(12)
		C(1)-O(2)-C(3)	110.44(11)
		O(2)-C(3)-C(3A)	103.91(11)

III.4 CONCLUSIONS

We have investigated the reactivity of two Pd complexes derived from benzyl alcohol (one of them a κ^2-*C*,*O* chelate) toward nitriles, cyanamides and carbodiimides. With the chelate complex we have obtained novel neutral or ionic complexes containing a seven-membered κ^2-*C*,*N* chelate ring, resulting from the insertion of the organic molecules into the O-Pd bond. The presence of AgOTf was necessary for most of these reactions, an unprecedented observation. A novel heterometallic bis-chelate Pd_2Ag complex has also been synthesized. Starting from the non-chelate complex, we have achieved the insertion of a carbodiimide into the aryl-Pd bond. All the new compounds have been extensively characterized by NMR spectroscopy, and three of them, including the mixed-metal complex, by X-ray crystallography.

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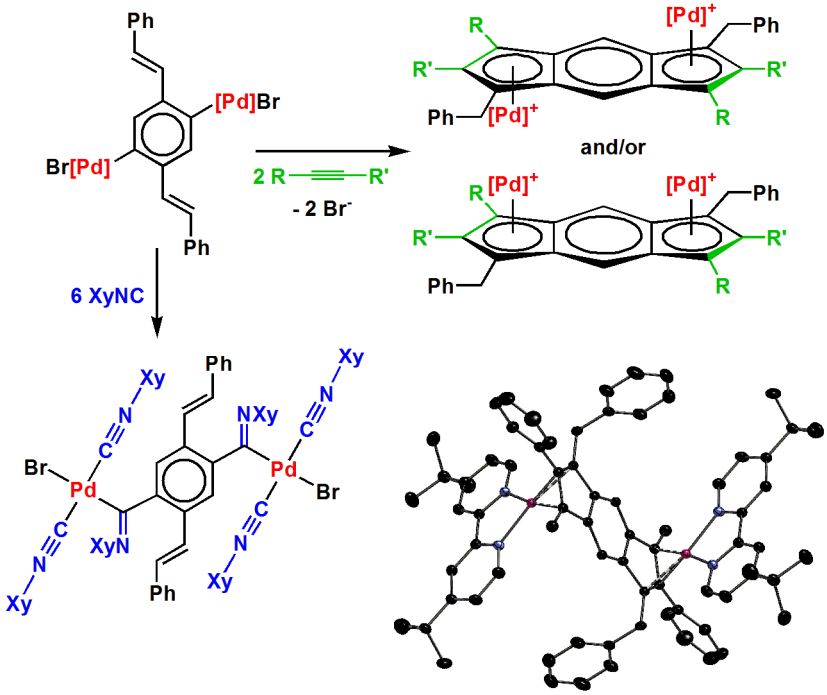
CHAPTER IV

Mono- and Dipalladated Derivatives of 2,5-Distyrylbenzene. Reactivity toward XyNC and Alkynes. Synthesis of Complexes with Indacenediide Ligands



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IV.1 ABSTRACT

The dinuclear complexes [C_6H_2{PdBr(N^N)}$_2$-1,4-((*E*)-CH=CHPh)$_2$-2,5] (N^N = tbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine (**14a**), tmeda = *N,N,N',N'*-tetramethylethylene-diamine (**14b**)) have been synthesized by oxidative addition of *trans,trans*-2,5-distyryl-1,4-dibromobenzene to two equivalents of "[Pd(dba)$_2$]" ([Pd_2(dba)$_3$]·dba; dba = dibenzylideneacetone) in the presence of the N^N ligands. A similar reaction with N^N = bpy = 2,2'-bipyridine afforded the mononuclear complex [PdBr{C_6H_2(Br-4){((*E*)-CH=CHPh)$_2$-2,5}}(bpy)] (**15**). The reaction of **14a,b** with PhC≡CPh, MeC≡CMe, and PhC≡CMe in the presence of TlOTf or $AgClO_4$ gave the dipalladated indacenediide complexes [(μ-η,η-$C_{12}H_2Bn_2$-1,5-R_4-2,3,6,7){Pd(N^N)}$_2$](OTf)$_2$ (Bn = benzyl, R = Ph, N^N = tbbpy (**16a**), tmeda (**16b**); R = Me, N^N = tbbpy (**17a**), tmeda (**17b**)) and [(μ-η,η-$C_{12}H_2Bn_2$-1,5-Ph_2-2,6-Me_2-3,7){Pd(N^N)}$_2$](A)$_2$ (N^N = tbbpy, A = OTf (**18a**), ClO_4 (**18a'**); N^N = tmeda, A = OTf (**18b**)). The reactions of **15** with the same alkynes afforded the indenyl complexes [Pd(η-C_9H_2Bn-1-R_2-2,3-((*E*)-CH=CHPh)-5-Br-6)(bpy)](A) (R = Ph, A = OTf (**19**), ClO_4 (**19'**); R = Me, A = OTf (**20**)) and [Pd(η-C_9H_2Bn-1-Ph-2-Me-3-((*E*)-CH=CHPh)-5-Br-6)(bpy)]OTf (**21**). By reaction of either **14a** or **14b** with XyNC (Xy = 2,6-dimethylphenyl), the dinuclear complex [C_6H_2{C(=NXy)(*trans*-PdBr(CNXy)$_2$)}$_2$-1,4-((*E*)-CH=CHPh)$_2$-2,5] (**22**) was obtained, while the oxidative addition of *trans,trans*-2,5-distyryl-1,4-dibromobenzene to [Pd(dba)$_2$] in the presence of eight equivalents of XyNC afforded the dinuclear complexes [C_6H_2{C(=NXy){C(=NXy)}$_2${PdBr(CNXy)}}$_2$-1,4-((*E*)-CH=CHPh)$_2$-2,5] (**23**,**23***) as a mixture of isomers (1:0.3 ratio) which are in slow exchange in solution, as shown by an EXSY spectrum. The crystal structures of *anti*-**16a**·7$CDCl_3$, *syn*-**16b**·CH_2Cl_2, *anti*-**18a'**·4CH_2Cl_2, **19**, and **21** have been determined by X-ray diffraction studies.

IV.2 INTRODUCTION

Pd(II) aryl complexes are a subject of great interest because of their participation in carbon-carbon and carbon-heteroatom bond-forming reactions.[1,2] Our group has been particularly interested in the synthesis of *ortho*-substituted arylpalladium complexes[3-20] and the investigation of their reactivity toward unsaturated organic molecules.[3,5,7-33] Very often new ligands and/or organic compounds are formed, involving both the insertion of the organic molecule into the carbon-palladium bond and its interaction with the group in an *ortho* position.[3,4,8,10,13-18,20-27,29,31,33] We are now exploring the extension of this

chemistry to complexes with two[34-37] or three[35,37] Pd atoms around a benzene ring, each of them *ortho* to an organic group. The reactions of such complexes with unsaturated organic molecules could lead to novel polynuclear Pd complexes and/or new organic polycyclic compounds that are otherwise difficult to prepare.

In this article we report our results on mono- and dipalladated derivatives of 2,5-distyrylbenzene and their reactivity toward several alkynes and xylyl isocyanide (XyNC). Although there have been previous reports on dipalladated *ortho*-substituted aryl complexes, these refer, with some exceptions,[19,34-38] to dipalladacycles with N-[34,39] or P-donor[40] groups, which afford chelates. We report here the first dipalladated benzene derivatives with alkenyl groups at the *ortho* position of the aryl ring, and describe their reactions with alkynes and XyNC. This is the first study of the reactivity of dipalladated arene derivatives with unsaturated reagents. Some of these results have been reported in a preliminary communication.[36] It is well-known that arylpalladium complexes react with alkynes to give mono-, di-, and triinserted derivatives[7,11,19,20,32,41,42] or, after depalladation, organic compounds[43] such as spirocycles,[3,4,21,23,42,44-46] benzofulvenes,[21] indenols,[8,10,23,45,47] indenones,[10,23,47] carbocycles,[42,44,48,49] and oxygen-,[13,50,51] sulfur-,[18,45,52] or nitrogen-containing[4,14,15,31,33,48,50,53] heterocycles. Sometimes these reactions are part of catalytic cycles yielding interesting organic compounds.[2,54-56]

We have previously prepared highly functionalized indenylpalladium complexes by reaction of 2-styrylbenzene Pd(II) complexes with alkynes.[22,24] Similarly, we have preliminarily reported the synthesis of the first Pd(II) complex with an indacenediide ligand.[36] Homo- or heterobimetallated symmetric (*syn*) and antisymmetric (*anti*) indacenediide complexes have been described with Fe,[57-65] Co,[59,60,63,66] Ni,[59,64,67] Ru,[63,64,67,68] Rh,[62,63,67,69-74] Ir,[70,71] Mn,[64,67,73] and Ge.[75] Shortly after our first communication[36] this type of complex was postulated as intermediate in the Pd-catalyzed cross-coupling of bromostilbene with a diarylalkyne to form *s*-indacenes.[76,a] We now describe a series of dipalladated indacenediides, together with some mononuclear indenylpalladium complexes. The procedure represents the first synthesis of such dinuclear complexes through metal-mediated building of the ligand, as these are usually prepared by reaction of indacenes with metal salts[57] or complexes.[60-66,68,69,71-73,75] Five of

[a] *s*-Indacenes and *as*-indacenes differ in the relative orientation of the three fused rings (our complexes are all *s*-indacenediide complexes). This nomenclature should not be confused with the *syn* and *anti* isomers of bimetallated indacenediide complexes, which differ in the relative orientation of the two metallic moieties (*syn*: both in the same side of the ligand; *anti*: one in each side of the ligand).

these complexes (three dinuclear and two mononuclear compounds) have been characterized by X-ray diffraction studies.

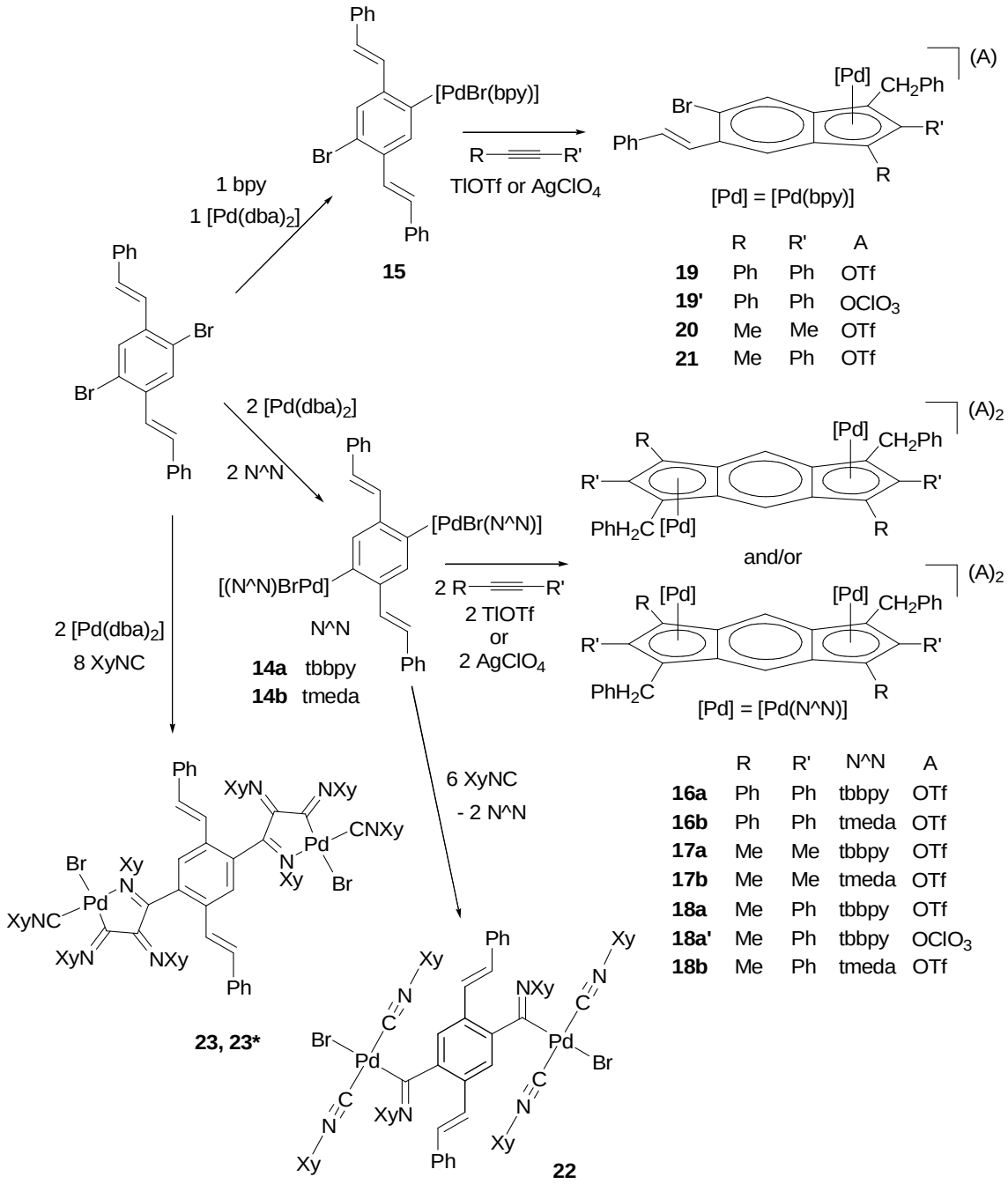
The reactivity toward XyNC of the mixture of *trans*,*trans*-2,5-distyryl-1,4-dibromobenzene and "[Pd(dba)$_2$]" ([Pd$_2$(dba)$_3$]·dba; dba = dibenzylideneacetone) and also of the dipalladated derivatives [C$_6$H$_2${PdBr(N^N)}$_2$-1,4-((*E*)-CH=CHPh)$_2$-2,5] (N^N = tbbpy, tmeda) has been investigated as well, resulting in the tri- and monoinsertion (respectively) of the isocyanide into C–Pd bonds. Although the insertion reactions of isocyanides into Ar–Pd bonds have been extensively investigated,[4,9,11-20,25-27,30,33,77,78] this is the first report of the simultaneous insertion of isocyanide into two aryl-Pd bonds on the same benzene ring of a complex.

IV.3 RESULTS AND DISCUSSION

IV.3.1 Synthesis of [C$_6$H$_2${PdBr(N^N)}$_2$-1,4-((*E*)-CH=CHPh)$_2$-2,5] (N^N = tbbpy (1a), tmeda (1b))

The dinuclear complexes **14a,b** were obtained by oxidative addition of *trans*,*trans*-2,5-distyryl-1,4-dibromobenzene[79] to two equivalents of [Pd(dba)$_2$] in the presence of tbbpy or tmeda (*Scheme IV.1*). Complexes **14a,b** are the first dipalladated benzene derivatives with alkenyl groups on the aryl ring, although the synthesis of **14b** was reported in a preliminary communication.[36] The dinuclear complexes **14a,b** form together with small amounts of the more soluble monopalladated derivatives [PdBr{C$_6$H$_2$(Br-4){((*E*)-CH=CHPh)$_2$-2,5}}(N^N)] (less than 15%), from which they can be easily separated (see Chapter VIII, Experimental Section). In order to minimize the formation of the monopalladated complexes, the oxidative additions were carried out with a 15% excess of [Pd(dba)$_2$] and the N^N ligands tbbpy and tmeda. When bpy was used as the N^N chelating ligand, the result of the reaction was different, as the major product turned out to be the monopalladated complex [PdBr{C$_6$H$_2$(Br-4){((*E*)-CH=CHPh)$_2$-2,5}(bpy)] (**15,** *Scheme IV.1*), together with only a very small amount (ca. 10%) of the expected dinuclear complex [C$_6$H$_2${PdBr(bpy)}$_2$-1,4-((*E*)-CH=CHPh)$_2$-2,5]. Our group has already encountered difficulties in synthesizing polynuclear complexes with bpy as an auxiliary ligand,[35] most probably caused by the lower solubility of bpy complexes in comparison to tmeda and tbbpy analogues. Even when different stoichiometries were used in the oxidative addition with bpy, the crude product was always a mixture of the mononuclear species **15** with small amounts of the dinuclear

complex and the starting dialkene. We finally established that the best option for the isolation of **15** was to use a 1:1.5:1.5 dialkene:[$Pd(dba)_2$]:bpy ratio and to purify the complex by solubility difference, first removing the less soluble dinuclear derivative, which was precipitated with CH_2Cl_2/Et_2O (15 mL/5 mL), and then separating **15** from the more soluble starting dialkene by precipitation of **15** with acetone/Et_2O (2 mL/20 mL) (see Chapter VIII, Experimental Section).

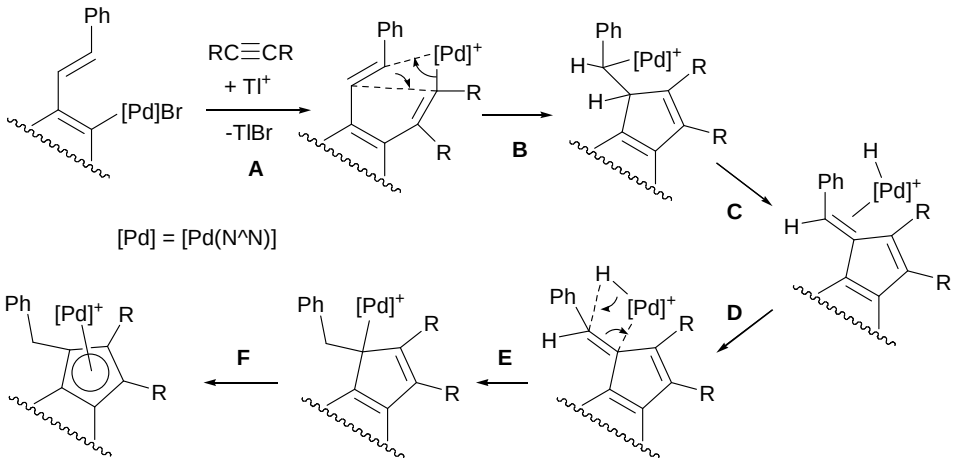


Scheme IV.1 Synthesis of complexes **14-23**

IV.3.2 Synthesis of Indacenediide Complexes

The reaction of **14a,b** with two equivalents of the alkynes PhC≡CPh, MeC≡CMe, and PhC≡CMe in the presence of TlOTf or $AgClO_4$ afforded the dipalladated μ_2-η,η-*s*-indacenediide complexes **16-18** (*Scheme IV.1*), which are the first indacenediide Pd(II) complexes to be described (the synthesis of **16b** was preliminarily reported).[36] For the complexes with tbbpy, the reactions were cleaner in THF than in CH_2Cl_2. In contrast, with tmeda, the reactions in THF afforded mixtures of compounds, so that CH_2Cl_2 was the preferred solvent. All of the reactions were performed with an excess of the alkyne, and the purification of all the products required crystallization (see Chapter VIII, Experimental Section). For some of them the elemental analysis was too low in carbon, most probably because of combustion problems of the triflate anion, a problem already encountered by some of us.[24] These substances were additionally characterized by high-resolution mass spectroscopy (see Chapter VIII, Experimental Section). We explored the possibility of using $AgClO_4$ instead of TlOTf as the Br-withdrawing agent, but the reactions did not improve. However, in one case (complex **18a'**) we obtained single crystals of the indacenediide complex, suitable for X-ray analysis (*Figure IV.8*), and thus this complex has been characterized as well. The reactions with the alkyne $MeO_2CC{\equiv}CCO_2Me$ yielded untractable mixtures.

Scheme IV.2 shows the mechanism that we have proposed for these reactions.[36] The first step (**A**) would be the insertion of the alkyne into the aryl C-Pd bond, followed by addition of the C–Pd bond to the alkenyl group in an *ortho* position (step **B**). A β-hydride elimination (**C**) and readdition (**D**,**E**) would give a σ,σ-indacenediide complex, which would isomerize to the more stable η:η derivative (**F**).



Scheme IV.2 Proposed mechanism for the formation of the indacenediide complexes

IV.3.3 Synthesis of Indenyl Complexes

As mentioned above, the oxidative addition of *trans*,*trans*-2,5-distyryl-1,4-dibromobenzene to [Pd(dba)$_2$] in the presence of bpy does not give a dinuclear complex similar to **14a,b** but the monopalladated analogue **15**. We decided nonetheless to investigate the reactivity of **15** with the same alkynes used toward **14a,b**, to check if the additional styryl and Br substituents would interfere in the formation of indenylpalladium complexes similar to those described before by some of us.[22,24] We were successful in preparing the new highly substituted indenylpalladium complexes **19-21** (*Scheme IV.1*), a result that confirms the potential of our synthetic route. The use of $AgClO_4$ instead of TlOTf in these reactions was successful only with the alkyne PhC≡CPh, affording complex **19'**, while for the other two alkynes the complexes obtained were too insoluble to be purified. The elemental analyses of two of the OTf complexes were again too low in carbon, and thus they were additionally characterized by high-resolution mass spectroscopy.

IV.3.4 Steroselectivity of the Reactions with Alkynes

Complexes **16-18** can form as two stereoisomers, symmetric (*syn*) or antisymmetric (*anti*) (*Scheme IV.1*), depending on the relative orientation of the two [Pd] moieties with respect to the indacenediide ligand, which can only be distinguished by X-ray crystallography. Both geometries have been described in the literature for other homonuclear bimetallic indacenediide complexes.[59-61,66,68,71,72] We have observed that the stereoselectivity of our reactions and (when characterized) the geometry of the resulting products depend on the nature of the alkyne, the N^N ligand, and the reaction conditions. Thus, with PhC≡CPh the reactions (THF or CH_2Cl_2, room temperature) were always stereoselective although, surprisingly, the opposite isomers were obtained with tbbpy (*anti*-**16a**) and tmeda (*syn*-**16b**),[36] as shown by X-ray diffraction studies (see Section IV.3.8). With the less voluminous alkynes MeC≡CMe and the unsymmetric MeC≡CPh, we usually obtained mixtures of the two stereoisomers, although the stereoselectivity could be enhanced by increasing the excess of alkyne and (for tbbpy in THF) the temperature (THF was not a suitable solvent for the reactions with tmeda, as commented above). Thus, the reaction of **14a** (tbbpy complex) with MeC≡CPh and TlOTf in THF at 60ºC afforded **18a** as a single isomer, while in a similar reaction with **14b** (tmeda complex), in CH_2Cl_2 at room temperature, complex **18b** formed together with a minor isomer, which was removed upon crystallization. No single crystals of **18a,b**, suitable for

X-ray analysis, could be obtained, but the X-ray data of the perchlorate homologue of **18a** (formed as a major isomer at room temperature in CH_2Cl_2) showed it to be the *anti*-**18a'** isomer. With the less voluminous alkyne MeC≡CMe, the tbbpy complex **17a** could be obtained regioselectively in THF at 60°C, by doubling the amount of alkyne (from ×8 to ×16) with respect to **16a**. However, for the analogous tmeda complex **17b** the reaction in CH_2Cl_2 at room temperature afforded a mixture of the two stereoisomers, even when the amount of alkyne was increased to ×32. These isomers were present in a ratio of ca. 1:3.5 after recrystallization. All of our attempts to obtain suitable single crystals of **17a,b** also failed. In conclusion, the stereoselectivity of these reactions with alkynes to form indacenediide complexes increases with the size of the alkyne, the temperature and the excess of alkyne. We cannot predict the geometry of the resulting complexes, but the three structures solved show that in the tbbpy complexes the *anti* isomers are favored, probably for steric reasons. The NMR data in solution do not allow a distinction between *syn* and *anti* isomers.

IV.3.5 Regioselectivity of the Reactions with Alkynes

With the unsymmetric alkyne MeC≡CPh the formation of the complexes **18a**,**a'**,**b** and **21** always occurs regioselectively, with the Ph group in position 2 of the indenyl or indacenediide ligand, next to the benzyl group. These structures have been confirmed by X-ray diffraction data for complexes **18a'** and **21**, and by NMR data for all of them. According to the mechanism proposed in *Scheme IV.2*, the regioselectivity must be determined in the alkyne insertion step and in this case it seems to be attributable to steric effects. The preference of a CMe moiety over a CPh moiety to be attached to the carbon atom in an alkyne insertion reaction into a C-Pd bond has been observed before,[23,24,55] although non-regioselective reactions have also been reported.[56]

IV.3.6 Reactions with Isocyanides

We have also investigated the reactivity toward isocyanides (^{t}BuNC and XyNC) of the mixture *trans*,*trans*-2,5-distyryl-1,4-dibromobenzene plus [Pd(dba)$_2$], and also of the dipalladated derivatives **14a**,**b**. While the reactions with ^{t}BuNC afforded mixtures of compounds, with XyNC we were able to isolate the dinuclear complexes **22** and **23**,**23*** (*Scheme IV.1*), resulting, respectively, from the mono- and triinsertion of the isocyanide into C–Pd bonds.

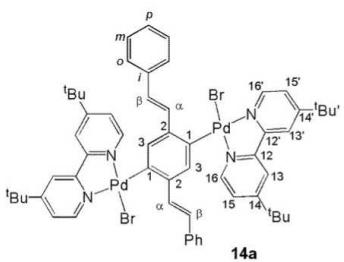
Complex **22** forms in the reactions of both **14a** and **14b** with a stoichiometric amount of XyNC (although an excess can also be used with the same result), and it is formed by the insertion of one isocyanide molecule into each C-Pd bond, and the displacement of each of the N^N ligands by two other molecules of isocyanide. The compound is stable in the solid state but it slowly decomposes in solution to form $[Pd_2Br_2(CNXy)_4]$, which is easily identified by its ^1H NMR resonance at 2.52 ppm. Mononuclear analogues to **22** have been previously prepared by insertion reactions of XyNC into C–Pd bonds of arylpalladium complexes.[9,13,15,17,18,25,26,78] Three dinuclear complexes with a similar pattern around the Pd atoms have also been reported by our group: one of them was obtained by oxidative addition, instead of insertion into an already formed complex,[19] and in the other two compounds the Pd atoms were not on the same aryl ring.[18] Thus, this is the first report of the simultaneous insertion of isocyanide into two aryl-Pd bonds on the same benzene ring of a complex.

The triinserted complexes **23** and **23*** form as a mixture of isomers (1:0.3 ratio) by oxidative addition of *trans*,*trans*-2,5-distyryl-1,4-dibromobenzene to $[Pd(dba)_2]$ in the presence of eight equivalents of XyNC. Both complexes have the same empirical formula and atom connectivities, as confirmed by the elemental analysis and NMR ^1H-^{13}C correlations, but different NMR spectra. Consequently, they must be stereoisomers that probably differ in the mutual orientation, *E* or *Z*, of the iminoacyl groups. They are always present in the same ratio, even if the reaction conditions (excess of XyNC and temperature) are changed. The structure of one of them was confirmed by X-ray analysis, but the data were not of adequate quality to be reported, because of disorder effects. It was not possible to obtain **23**,**23*** by reaction of **22** with XyNC, even at high temperature. Only a few mononuclear analogues of **23** and **23*** have been reported, mainly by our research group,[26,80] but no such dinuclear complex had been prepared until now.

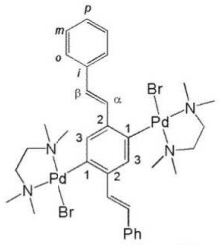
IV.3.7 NMR Data

All the complexes reported in this paper have been extensively studied by NMR (1D and 2D experiments), allowing an almost full assignment of the ^1H and ^{13}C resonances. To facilitate comparison, the data are collected in *Table IV.1* (for **14a,b** and **15**), *Table IV.2* (for **22, 23** and **23***), and *Table IV.3* (for complexes **16-21**). These Tables also contain some comments on the assignment process and on the chemical shifts.

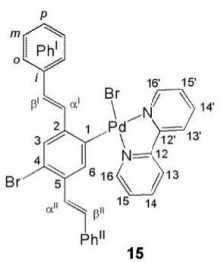
Table IV.1 ^{13}C and ^{1}H NMR data (ppm, $CDCl_3$, r.t.) of the 2,5-distyrylbenzene complexes **14a**, **14b**, **15**



14a



14b



15

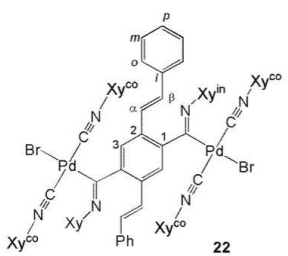
	^{13}C-NMR data. 2,5-distyrylbenzene																	^{13}C-NMR data. N^N (tbbpy, bpy, tmeda) [a]						
	Aryl						CH=CH-Ph											C12'	CH16'	C14'	CH15'	CH13'	C'	^{t}Bu'
	C1	C2	CH3				=CHα	=CHβ	*i*-C	*o*-CH	*m*-CH	*p*-CH						C12	CH16	C14	CH15	CH13	C	^{t}Bu'
14a	146.4	140.0	132.2				133.9	125.7	139.3	128.4	128.4	126.3						154.1	150.3	163.4	123.6	117.8	35.7	30.7
																		155.7	151.9	162.8	124.9	118.4	35.6	30.4
	Aryl						CH=CH-Ph^I						CH=CH-Ph^{II}					C12'	CH16'	CH14'	CH15'	CH13'		
	C1	C2	CH3	C4	C5	CH6	=CHα^I	=CHβ^I	*i*-C	*o*-CH	*m*-CH	*p*-CH	=CHα^{II}	=CHβ^{II}	*i*-C	*o*-CH	*m*-CH	*p*-CH	C12	CH16	CH14	CH15	CH13		
15	150.4	143.2	129.2	121.5	133.8	133.3	132.2	127.3	138.2	126.9	128.6	127.9	127.7	130.4	137.8	126.9	128.9	127.8	153.8	151.1	139.2	127.0	121.5		
																			156.2	151.4	138.9	127.1	122.2		
	Aryl						CH=CH-Ph											CH$_2$		Me				
	C1	C2	CH3				=CHα	=CHβ	*i*-C	*o*-CH	*m*-CH	*p*-CH												
14b	142.9	140.2	131.7				134.4	125.6	139.5	126.4	128.8	126.5						62.8, 58.5		51.9, 49.9, 49.4, 47.9				

	^{1}H-NMR data. 2,5-distyrylbenzene																	^{1}H-NMR data. N^N (tbbpy, bpy, tmeda) [a]						
	Aryl						CH=CH-Ph											H16'		H15'	H13'		^{t}Bu'	
		H3					Hα	Hβ		*o*-H	*m*-H	*p*-H						H16		H15	H13		^{t}Bu'	
14a		7.70					8.18	7.25		7.46	7.19	7.06						9.36		7.55	7.94		1.44	
																		7.66 [b]		7.33	7.89		1.34	
	Aryl						CH=CH-Ph^I						CH=CH-Ph^{II}					H16'	H14'	H15'	H13'			
		H3		H6			Hα^I	Hβ^I		*o*-H	*m*-H	*p*-H	Hα^{II}	Hβ^{II}		*o*-H	*m*-H	*p*-H	H16	H14	H15	H13			
15		7.73		7.93			8.15	7.14		7.47	~7.2	~7.1	7.42	7.10		7.51	~7.3	~7.2	9.52	~8.05	7.63	~8.05			
																		7.77 [b]	7.96	~7.3				
	Aryl						CH=CH-Ph											CH$_2$		Me				
		H3					Hα	Hβ		*o*-H	*m*-H	*p*-H												
14b		7.26					8.26	7.48		7.62	7.35	7.20						2.86-2.6, 2.6-2.4		2.72, 2.69, 2.47, 2.12				

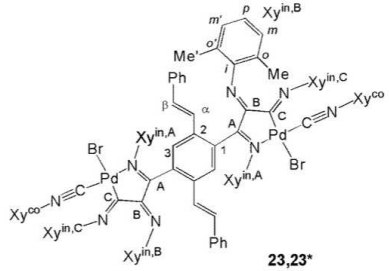
(a) The two halves of the tbbpy and bpy ligands have been assigned based on NOE contacts between H16 and Hα (for **14a**) and between H16 and both H6 and Hα^I (for **15**). H16 is close in the space to Hα (in **14a**) and Hα^I (in **15**) because the N^N ligand lies in a plane perpendicular to the plane of the distyrylbenzene group. For **14a** the expected NOE contact between H16 and H3 cannot be seen because both resonances are very close in the ^{1}H spectrum, so that in the NOESY spectrum the cross-peak lies on the diagonal.

(b) The H16 protons of **14a** and **15** are shielded with respect to H16' as a consequence of the anisotropic effect of the central aromatic ring.

Table IV.2 ^{13}C and ^{1}H NMR data (ppm, $CDCl_3$, r.t.) of the complexes **22**, **23, 23***



22



23,23*

	^{13}C-NMR data. 2,5-distyrylbenzene[a]									^{13}C-NMR data. XyNC (inserted)							^{13}C-NMR data. XyNC (coordinated)					
	C1	**C2**	**CH3**	**=CHα**	**=CHβ**	***i*-C**	***o*-CH**	***m*-CH**	***p*-CH**		**C=N**	***i*-C**	***o*-C**	***m*-CH**	***p*-CH**	**Me**	**C≡N**	***i*-C**	***o*-C**	***m*-CH**	***p*-CH**	**Me**
22	144.2	131.2	127.1	126.6	131.0	137.2	126.9	128.7	128.0		176.2	150.3	127.0	128.6	123.9	19.6	143.3	125.5	136.0	128.2	130.3	18.9
23	131.9	134.8	126.3	123.7	134.1	136.2	127.3	129.1	129.1	XyNC^{A}	174.8[b]	143.4	131.5	127.6	127.4	20.8	138.3	126.6	134.9	127.7	129.5	18.7
													127.9	128.8		18.3						
										XyNC^{B}	174.8 & 167.7	147.8	122.0	128.0	124.3	19.1						
													127.2	128.2		18.9						
										XyNC^{C}		151.0	125.3	128.4	124.3	20.0						
													127.7	127.2		17.7						
23*	131.8	134.2	125.8	123.9	133.6	136.3	127.4	129.0	129.1	XyNC^{a}	174.5[b]	143.3	131.1	127.5	127.4	20.5	(c)	126.6	134.9	127.7	129.5	18.7
													127.8	128.9		18.9						
										XyNC^{b}	174.9 & 169.1	147.6	121.7	128.0	124.3	19.3						
													128.1	128.1		18.6						
										XyNC^{c}		150.8	125.0	128.4	124.3	20.4						
													128.0	127.5		17.8						
	^{1}H-NMR data. 2,5-distyrylbenzene									^{1}H-NMR data. XyNC (inserted)							^{1}H-NMR data. XyNC (coordinated)					
			H3	**Hα**	**Hβ**		***o*-H**	***m*-H**	***p*-H**				***m*-H**	***p*-H**	**Me**					***m*-H**	***p*-H**	**Me**
22			8.12	8.24	6.95		7.31	~7.2	~7.2				~7.0		2.33					~7.0	~7.2	2.22
23 (**23***)[d]			7.32 (7.39)[d]	7.25 (7.07)[d]	6.67 (6.78)[d]		~7.49	~7.25	~7.25	XyNC^{A}			7.21	~7.10	2.77 (2.75)[d]					~6.93	~7.10	2.13
													~6.9		1.66 (2.04)[d]							
										XyNC^{B}			6.98	~6.85	2.33 (2.34)[d]							
													~6.9		2.06 (1.69)[d]							
										XyNC^{C}			~6.85	~6.37	2.26 (2.48)[d]							
													~6.37		1.15 (1.11)[d]							

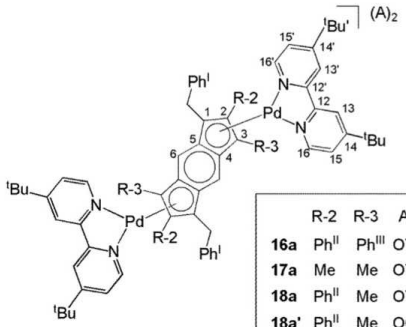
(a) Some ^{13}C resonances of the 2,5-distyrylbenzene group change significantly in **22**,**23**,**23*** with respect to **14a**,**14b**,**15**. Thus, the carbons C1 and C2 are shifted to lower frequencies in **22**,**23**,**23*** and the relative positions of the ethylene carbons CH^{α} and CH^{β} are exchanged, with δ($CH\alpha$) < δ ($CH\beta$) in **22**,**23**,**23*** while the opposite is observed in **14a**,**14b**,**15** δ($CH\alpha$) > δ ($CH\beta$). A similar effect is not observed for the protons Hα and Hβ, although Hβ is shielded in **22**,**23**,**23*** (and Hα in **23**,**23***) with respect to the resonances observed in **14a**,**14b**,**15**.

(b) The imine carbon of the $^{a}C{=}N\text{-}Xy^{in,A}$ group can be assigned based on the correlation with the H3 proton in the $^{1}H,^{13}C$-HMBC experiment. The other two C=N-Xy resonances cannot be distinguished, because they do not correlate with any ^{1}H resonance.

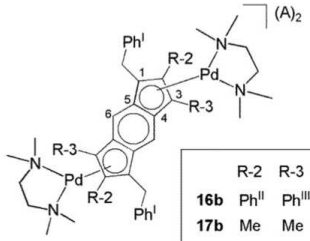
(c) Too weak to be observed

(d) The assigned resonances of the minor isomer **23*** are included in the table in brackets and in grey.

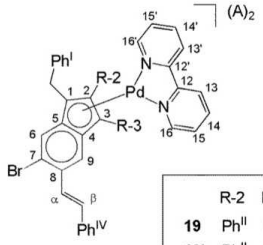
Table IV.3 ^{13}C and ^{1}H NMR data (ppm, $CDCl_3$, r.t.) of the indenyl and indacenediide complexes **16-21** [a]



	R-2	R-3	A
16a	Ph^{II}	Ph^{III}	OTf
17a	Me	Me	OTf
18a	Ph^{II}	Me	OTf
18a'	Ph^{II}	Me	$OClO_3$



	R-2	R-3	A
16b	Ph^{II}	Ph^{III}	OTf
17b	Me	Me	OTf
18b	Ph^{II}	Me	OTf



	R-2	R-3	A
19	Ph^{II}	Ph^{III}	OTf
19'	Ph^{II}	Ph^{III}	$OClO_3$
20	Me	Me	OTf
21	Ph^{II}	Me	OTf

	^{13}C-NMR data. Indacenediide Ligand																						^{13}C-NMR data. tbbpy [b]						
	"core"									CH_2Ph^I					R-2 [c]				R-3 [c]				C12'	CH16'	C14'	CH15'	CH13'	C	^tBu
	C1	C2	C3	C4	C5		CH6			*i*-C	*o*-CH	*m*-CH	*p*-CH	CH_2	*i*-C	*o*-CH	*m*-CH	*p*-CH	*i*-C	*o*-CH	*m*-CH	*p*-CH	C12	CH16	C14	CH15	CH13		
16a	95.8	129.7	93.3	133.5	136.1		107.3			135.9	129.0	128.2	126.1	30.1	131.8	131.1 & 128.8		128.5	129.5	130.3	129.7	129.8	152.3	154.8	165.5	127.1	119.8	36.1	30.6 & 30.5
																							153.9	151.3	165.2	123.9	119.2	35.9	
17a	91.8	126.1	91.9	137.4	136.1		105.7			135.9	128.7	128.9	126.8	30.8	2-Me: 13.2 [d]				3-Me: 10.4 [d]				152.5 & 152.6	154.3 & 153.5	164.6	125.6 & 125.5	118.7	35.8 & 35.7	30.5
18a	93.1	129.1	94.0	136.2	135.0		105.9			136.1	129.3	128.3	126.3	30.4	131.5	130.9	128.8	128.7	3-Me: 11.3				152.3	154.3	165.3	126.3	119.5	36.0 & 35.9	30.6
																							153.4	151.5	165.2	124.7	119.3		

	^{13}C-NMR data. Indenyl Ligand																									^{13}C-NMR data. bpy [b]				
	"core"									CH=CH-Ph^{IV}						CH_2Ph^I					R-2 [c]				R-3 [c]				C12'	CH16'	C14'	CH15'	CH13'
	C1	C2	C3	C4	C5	C7	C8	CH6	CH9	$=CH^{\alpha}$	$=CH^{\beta}$	*i*-C	*o*-CH	*m*-CH	*p*-CH	*i*-C	*o*-CH	*m*-CH	*p*-CH	CH_2	*i*-C	*o*-CH	*m*-CH	*p*-CH	*i*-C	*o*-CH	*m*-CH	*p*-CH	C12	CH16	C14	CH15	CH13
19'	93.1	131.2	94.1	134.2	136.0	124.1	137.5	122.8	114.7	127.6	132.1	136.8	127.1	129.1	128.7	134.4	128.7	129.0	127.4	31.2	130.8	131.0	129.1	129.2	129.7	129.9	129.7	130.0	153.8	152.3	142.2	128.3	125.7
																													154.0	151.4	141.8	127.2	125.1
20	90.1	127.6	91.3	137.6	137.4	124.1	136.1	120.3	113.6	127.0	131.8	137.0	127.1	129.0	128.5	134.5	128.3	129.4	127.7	31.4	2-Me: 13.2 [d]				3-Me: 10.8 [d]				153.7 & 153.5	152.1 & 151.7	141.6	128.0	124.9 & 124.9
21	90.5	132.1	92.8	136.9	136.4	124.7	136.9	121.3	114.2	127.0	132.2	137.0	127.1	129.1	128.6	134.7	128.5	129.1	127.5	31.4	130.5	130.7	129.2	129.5	3-Me: 11.4				154.0	151.8	142.0	127.8	125.5
																													153.6	151.4	141.9	128.0	125.4

	^{13}C-NMR data. Indacenediide Ligand							^{13}C-NMR data. tmeda	
	"core"							CH_2	Me
	C1	C2	C3	C4	C5		CH6		
								i-C	*o*-CH	*m*-CH	*p*-CH	CH_2	*i*-C	*o*-CH	*m*-CH	*p*-CH	*i*-C	*o*-CH	*m*-CH	*p*-CH		
16b	91.4	132.5	92.1	133.9	137.9		108.4	135.7	129.3	128.9	127.2	31.4	132.1	131.0 & 129.2		129.1	130.7	129.5	129.2	129.4	63.5, 61.7	53.9, 53.2, 52.3, 49.2
17b [e]	89.0	126.6	89.2	138.6	137.3		104.2	135.3	128.5	129.0	127.1	31.2	2-Me: 13.2 [d]				3-Me: 10.6 [d]				61.62, 61.59	52.5, 52.2, 52.0, 51.5
18b	88.5	132.4	91.4	138.3	136.7		105.6	135.7	128.9	128.7	126.9	31.1	131.6	130.5	129.3	126.9	3-Me: 11.3				61.9, 61.8	52.8, 52.3, 52.2, 51.7

Table IV.3 (continuation)

	^{1}H-RMN data. Indacenediide Ligand													^{1}H-RMN data. tbbpy [b]				
	"core"		Bn				R-2 [c]		R-3 [c]			H16'	H13'		H15'	^{t}Bu'
	CH		*o*-H	*m*-H	*p*-H	CH_2 (AB syst)	*o*-H	*m,p*-H	*o*-H	*m*-H	*p*-H	H16	H13		H15	^{t}Bu
16a	7.45		6.99-6.96	6.80-6.77		4.30, 3.78	7.22-7.13		7.60	7.42-7.37	7.45-7.42	9.10	8.09		8.23	1.50
												7.00 [f]	8.00		7.06	1.39
17a[b]	7.08		7.38	7.31	7.23	4.22, 3.32	2-Me: 2.28 [d]		3-Me: 1.67 [d]			8.84 & 8.64	7.89		7.83 & 7.78	1.35 & 1.33
18a	7.29		7.08-7.05	6.93-6.90		4.13, 3.51	7.37-7.33	7.30-7.27	3-Me: 1.70			8.89	8.05		7.97	1.47
												8.20	8.02		7.61	1.46
18a'	7.27		7.06-7.03	6.94-6.88		4.09, 3.50	7.36-7.32	7.30-7.27	3-Me: 1.72			8.89	8.06		8.00	1.47
												8.19	8.03		7.59	1.46

	^{1}H-RMN data. Indenyl Ligand															^{1}H-RMN data. bpy [b]			
	"core"		CH=CH-Ph					Bn				R-2 [c]		R-3 [c]			H16'	H13'	H14'	H15'
	H9	H6	CH^{10}	CH^{11}	*o*-H	*m*-H	*p*-H	*o*-H	*m*-H	*p*-H	CH_2 (AB syst)	*o*-H	*m,p*-H	*o*-H	*m*-H	*p*-H	H16	H13	H14	H15
19'	7.58	7.52	7.34	7.01	7.57-7.51	7.36	7.34-7.27	6.99-6.95	7.18-7.13		3.80, 3.76	7.26-7.20	7.34-7.27	7.57-7.51	7.38	7.57-7.51	8.73	8.75	8.36	7.86
																	7.50 [f]	8.64	8.15	7.25
19	7.58	7.51	7.34	7.01	7.56-7.51	7.36	7.34-7.27	6.98-6.95	7.19-7.14		3.79, 3.73	7.26-7.20	7.34-7.27	7.56-7.51	7.38	7.56-7.51	8.69	8.88	8.39	7.84
																	7.49 [f]	8.77	8.16	7.24
20	7.33	7.19	7.31	7.12	7.54	7.38-7.30	7.28-7.24	7.38-7.30			3.90, 3.53	2-Me: 2.42 [d]		3-Me: 1.82 [d]			8.53 & 8.49	8.61 & 8.59	8.25 & 8.32	7.74 & 7.71
21	7.42	7.31	7.33	7.14	7.55-7.52	7.35	7.30-7.28	7.00-6.98	7.22-7.19		3.72, 3.53	7.39 (br s)		3-Me: 1.76			8.59	8.77	8.33	7.74
																	8.41	8.72	8.25	7.69

	^{1}H-RMN data. Indacenediide Ligand									^{1}H-RMN data. tmeda	
	"core"	Bn			R-2 [c]		R-3 [c]			CH_2	Me
	CH	*o*-H	*m,p*-H	CH_2 (AB syst)	*m*-H	*o,p*-H	*o*-H	*m*-H	*p*-H		
16b	7.09	7.10	7.3-7.2	3.60, 3.32	7.45-7.35		7.07	7.19	7.45-7.35	3.45-3.38, 3.15-3.08 3.06-2.98, 2.62-2.56	3.03, 3.02, 2.50, 2.27
17b[g]	6.63	7.3-7.2		3.66, 3.24	2-Me: 2.35 [d]		3-Me: 1.41 [d]			3.23-3.16, 2.7-2.6	2.88, 2.80, 2.72, 2.61
17b[h]	6.28	7.3-7.2		3.45, 3.28	2-Me: 2.42 [d]		3-Me: 1.42 [d]			3.23-3.16, 2.7-2.6	2.67, 2.66, 2.49, 1.99
18b	6.90	6.97-6.95	7.15-7.13	3.54, 3.29	7.49-7.45	7.45-7.40	3-Me: 1.36			3.35-3.24, 2.78-2.70	3.00, 2.90, 2.82, 2.53

(a) Two numbers separated by "&" indicate that it has not been possible to assign the separate resonances.

(b) The two halves of the tbbpy and bpy ligands have been assigned based on NOE contacts between H16' and ^{1}H resonances of the benzyl and R-2 groups, and between H16 and ^{1}H resonances of the R-3 group. For complexes **17a** and **20** the NOE contacts were not selective, and the distinction between the two halves of the N^N ligands was not possible.

(c) The assignment of the R-2 and R-3 groups is derived from the ^{1}H,^{13}C-HMBC spectra, and confirmed by the ^{1}H,^{1}H-NOESY spectra. For example, the two Me groups of **17a** and **20** show selective NOE contacts: Me-2 with the o-H's and the CH_2 of the benzyl group, and Me-3 with CH-6 (for **17a**) or CH-9 (for **20**).

(d) The Me-2 groups are always deshielded (in ^{1}H and ^{13}C spectra) with respect to Me-3 groups, due (at least for the ^{1}H spectra) to the anisotropic effect of the benzyl group. (The variations in the ^{13}C chemical shifts are usually influenced by more factors, involving the paramagnetic contributions to the NMR shielding constant)

(f) The H16 protons of **16a**, **19** and **19'** are shielded with respect to H16' due to the anisotropic effect of the Ph-3 ring. For the complexes lacking a Ph group in position 3 (**17a**, **18a**, **18a'**, **20**, **21**), H16 and H16' resonate at more similar frequencies.

For **17b**: (e) ^{13}C data for the major isomer (g) Major isomer (h) Minor isomer

IV.3.7.1 NMR Data of 14a,b, 22, 23, and 23*

The dinuclear complexes containing the 2,5-distyrylbenzene moiety (**14a**,**b**, **22**, **23,** and **23***) show a single set of ^{1}H and ^{13}C NMR resonances for the halves of the molecule. We suggest that **14a,b**, **22,** and **23** contain an inversion center in solution (confirmed for **23** by low-quality X-ray analysis data, see *Figure IV.4*), while the minor isomer **23*** would possess a C_2 axis. The separate resonances of **23** and **23***, in a 1:0.3 ratio, are clearly observed in the APT spectrum of the mixture (*Figure IV.1*).

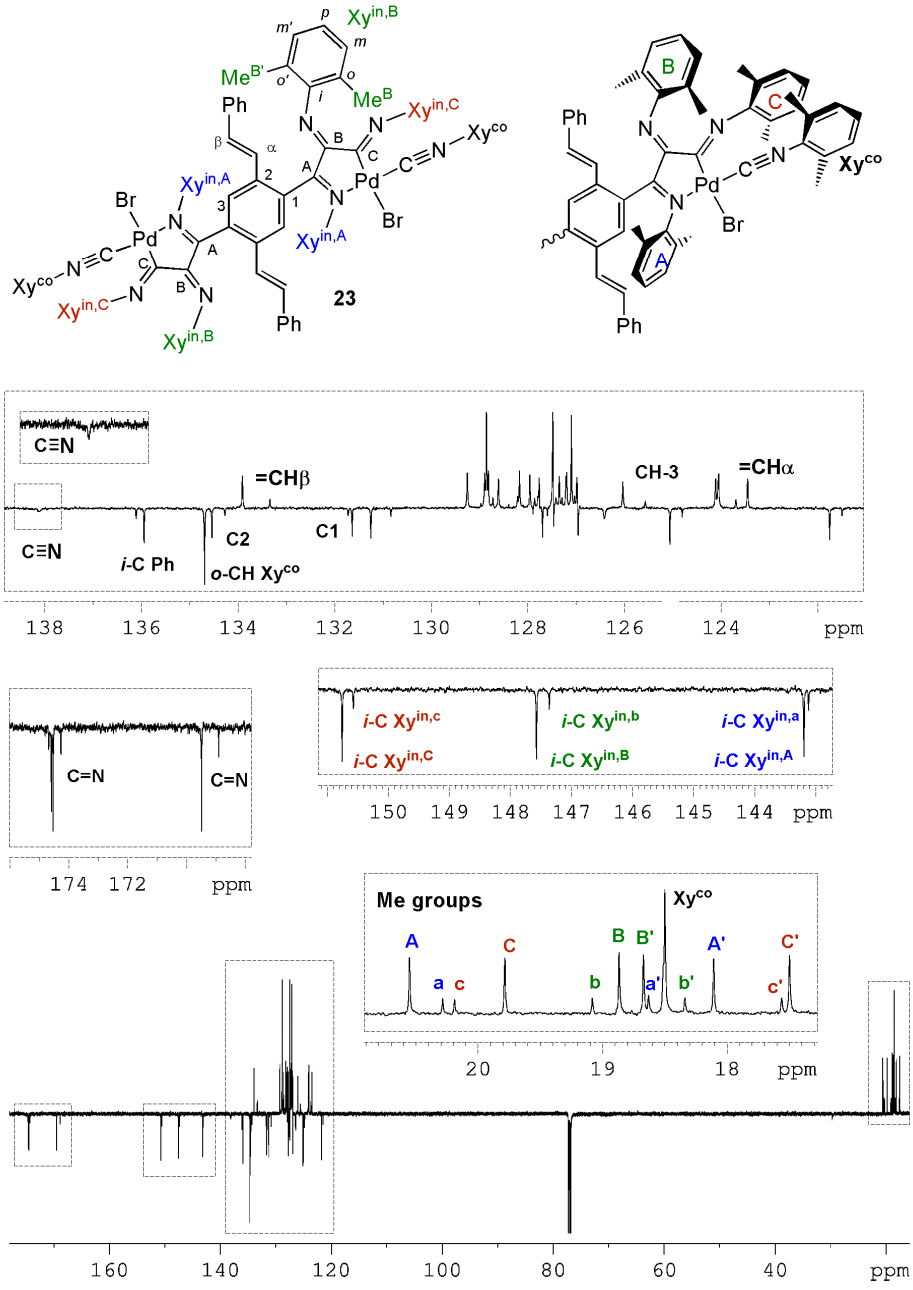


Figure IV.1 APT spectrum (150 MHz, $CDCl_3$) of complexes **23** and **23*** with expansions. The separate resonances for both complexes can be clearly observed in ca. 1:0.3 ratio. The Xy resonances of the major isomer (**23**) are labeled in capital letters, while those of the minor isomer (**23***) are labeled in small-case letters. Only a weak C≡N resonance is observed, which is assigned to the major isomer **23**

IV.3.7.1.1 Assignment of the NMR Resonances of 23 and 23*

From the three inserted XyNC groups in **23** and **23*** only the imine ^{13}C resonance of $XyNC^{in,A}$ (for **23**) and $XyNC^{in,a}$ (for **23***) can be assigned, based on the correlation with the corresponding H3 proton of the central aryl ring ($^{1}H,^{13}C$ HMBC spectrum, *Figure IV.2*). The other two C=NXy ^{13}C imine resonances cannot be distinguished because they do not correlate with any ^{1}H resonances.

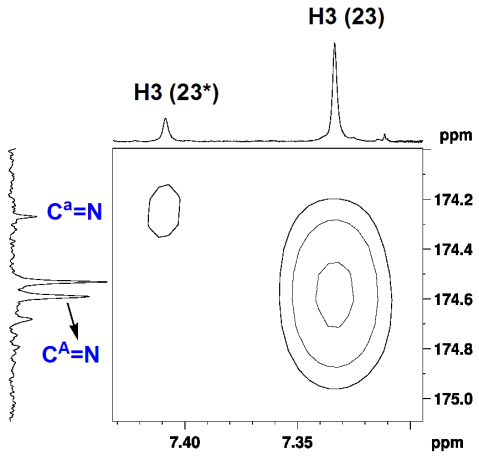


Figure IV.2 Section of the $^{1}H,^{13}C$ HMBC spectrum of **23** and **23*** showing the $^{3}J_{CH}$ correlations between the imine carbons of $XyNC^{in,A}$ (for **23**) and $XyNC^{in,a}$ (for **23***) with the corresponding H3 proton of the central aryl ring

Figure IV.3 shows another section of the $^{1}H,^{13}C$ HMBC spectrum of **23** and **23***, where the $^{3}J_{CH}$ couplings between the *ipso* carbons and the methyl protons within each of the three inserted XyNC groups in **23** ($XyNC^{in,A}$, $XyNC^{in,B}$, and $XyNC^{in,C}$) and **23*** ($XyNC^{in,a}$, $XyNC^{in,b}$, and $XyNC^{in,c}$) can be clearly seen.

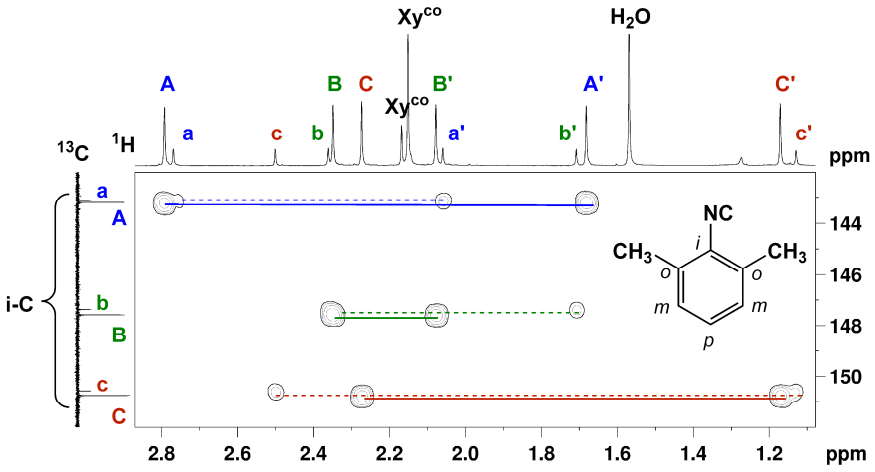


Figure IV.3 Section of the $^{1}H,^{13}C$ HMBC spectrum of **23** and **23*** showing the $^{3}J_{CH}$ correlations between the *ipso* carbons and the methyl protons within each of the inserted XyNC groups. The Me resonances of the major isomer (**23**) are labeled in capital letters, while those of the minor isomer (**23***) are labeled in small-case letters

The distinction between the three inserted XyNC groups is based on selective NOE contacts found between the Me resonances of these groups and the protons Hα, Hβ, H3 and *o*-H of the central 2,5-distyrylbenzene moiety. The relevant section of the ^{1}H NOESY spectrum is shown in *Figure IV.4* together with an X-ray structure of **23** which was not of adequate quality to be reported, because of disorder effects. The NOE cross-peaks are surrounded by orange rectangles, and corresponding orange arrows have been drawn in the structure. We can make the following observations:

i) **XyNC^{in,B}** is assigned by the NOE between Me$^{B'}$ and an o-H of the Ph group.

ii) **XyNC^{in,C}** shows a weak NOE between Me^{C} and both Hα and *o*-H Ph. However, the assignment of this group is based mainly on the strong NOE between Me^{C} and Me$^{A'}$, shown with a pink arrow in the structure in *Figure IV.3* and which can be observed in *Figure IV.4* (^{1}H EXSY spectrum of **23** and **23***), surrounded by a pink rectangle.

iii) The assignment of **XyNC^{in,A}** is confirmed by the NOE between Me^{A} and both Hβ and H3 (*Figure IV.4*).

iv) For the minor isomer **23*** the ^{1}H resonances are assigned from the exchange cross-peaks between the Me groups of **23** and **23*** (^{1}H EXSY in *Figure IV.4*).

v) **Me^{A}** would be shifted to higher frequency because it sits *on* the plane of the central aryl ring and the styrene groups, and thus it is deshielded by their anisotropic effect. **Me$^{A'}$,** on the contrary, would be shielded because it sits *over* the styrene group, where the anisotropic effect is negative. **Me$^{C'}$** would be strongly shielded by the ring current of XyNC^{in,B}.

vi) No NOE cross-peaks are observed between XyNC^{co} and XyNC^{in,C}, although a Me^{co}/Me^{C} cross-peak could be obscured by the diagonal

vii) A strong NOE is observed between H3 and Hβ, showing that in solution the orientation of the styrene groups is the same as in the solid state.

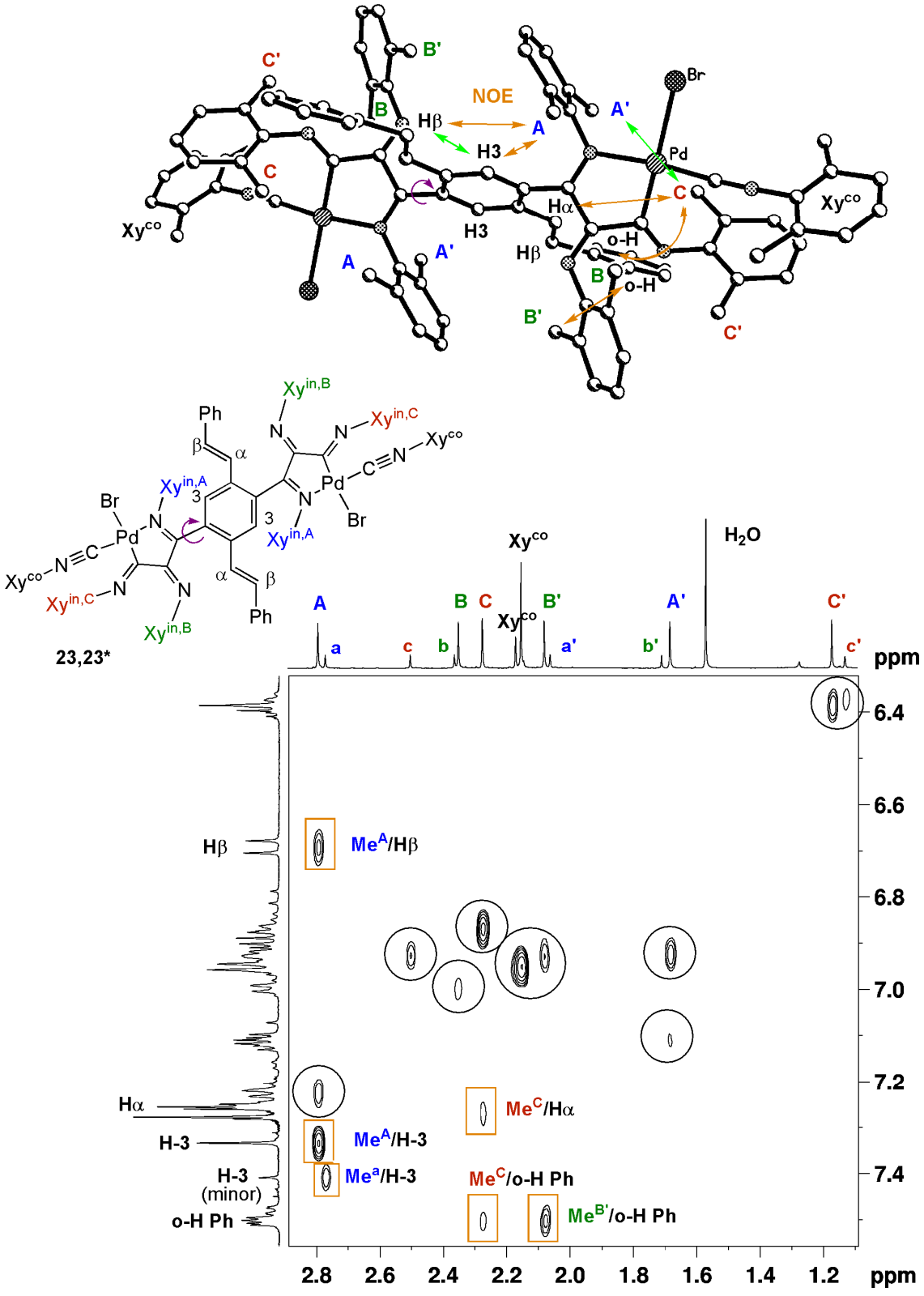


Figure IV.4 Section of the ^{1}H NOESY spectrum of **23** and **23***. The NOE cross-peaks between some of the Me groups and the protons Hα, Hβ, H3 and *o*-H Ph of the central 2,5-distyrylbenzene group are surrounded by orange rectangles and indicated by orange arrows in the X-ray structure. These NOE contacts allow the assignment of the three inserted XyNC groups. The (non-relevant) NOE cross-peaks within each Xy group (between the Me groups and the *m*-H's) are surrounded by black circles

IV.3.7.1.2 Dynamic Behavior of 22, 23 and 23*

The inserted XyNC groups in **22**, **23** and **23*** behave differently, as a single Me resonance is observed for **22** (indicating free rotation around the N-Xy bond), while for **23** and **23*** each of the inserted XyNC groups affords two separate Me resonances (as well as two separate *o*-C and *m*-CH resonances), indicating hindered rotation around the N-Xy bond caused by the larger steric hindrance within the molecule. In contrast, the coordinated XyNC groups afford single Me, *o*-C, and *m*-CH resonances in each complex, because of free rotation around the N-Xy bond (and the equivalence of the two CNXy groups on each Pd in complex **22**).

The ^{1}H NOESY/EXSY spectrum of **23** and **23*** affords more insight into the dynamic behavior of these complexes in solution. A section of the Me region of the spectrum is shown in *Figure IV.5*. Exchange cross peaks can be observed between the Me resonances of the major (**23**) and minor (**23***) isomers, revealing a slow exchange process that interconverts both stereoisomers. This equilibrium explains why both isomers are always present in solution in the same ratio, even when crystals of the major isomer are dissolved. Additionally, the EXSY spectrum shows that the rotation around the N-Xy bonds of two of the inserted isocyanides in the major isomer ($XyNC^{in,B}$ and $XyNC^{in,C}$) is indeed taking place, although very slowly, while for the third group ($XyNC^{in,A}$) no rotation is observed, probably because of the steric hindrance caused by the Br ligand. The same behavior is found for the minor isomer, **23***. Interestingly, each of the Me groups of $XyNC^{in,A}$ exchanges with *both* Me groups in the minor isomer ($XyNC^{in,a}$), meaning that during the interconversion between stereoisomers the N-Xy bond of this isocyanide can indeed rotate.

It is also interesting to observe that some of the Me resonances of **23** and **23*** are almost coincident (Me^{A}/Me^{a}, Me^{B}/Me^{b}, $Me^{C'}/Me^{c'}$ and those of the coordinated XyNC), while others are quite separated in ppm ($Me^{A'}/Me^{a'}$, $Me^{B'}/Me^{b'}$ and Me^{C}/Me^{c}), meaning that their magnetic environment is quite different in both isomers. We suggest that the interconversion between both stereoisomers takes place via rotation around the C-C bond between the central ring and one of the $[C(=NXy)\{C(=NXy)\}_2\{PdBr(CNXy)\}]$ moieties, as shown by the circular arrow in *Figure IV.4*. The Me groups which would be more affected in their chemical shifts by the rotation would be those directed toward the inner part of the molecule, which are indeed $Me^{A'}$, $Me^{B'}$ and Me^{C}.

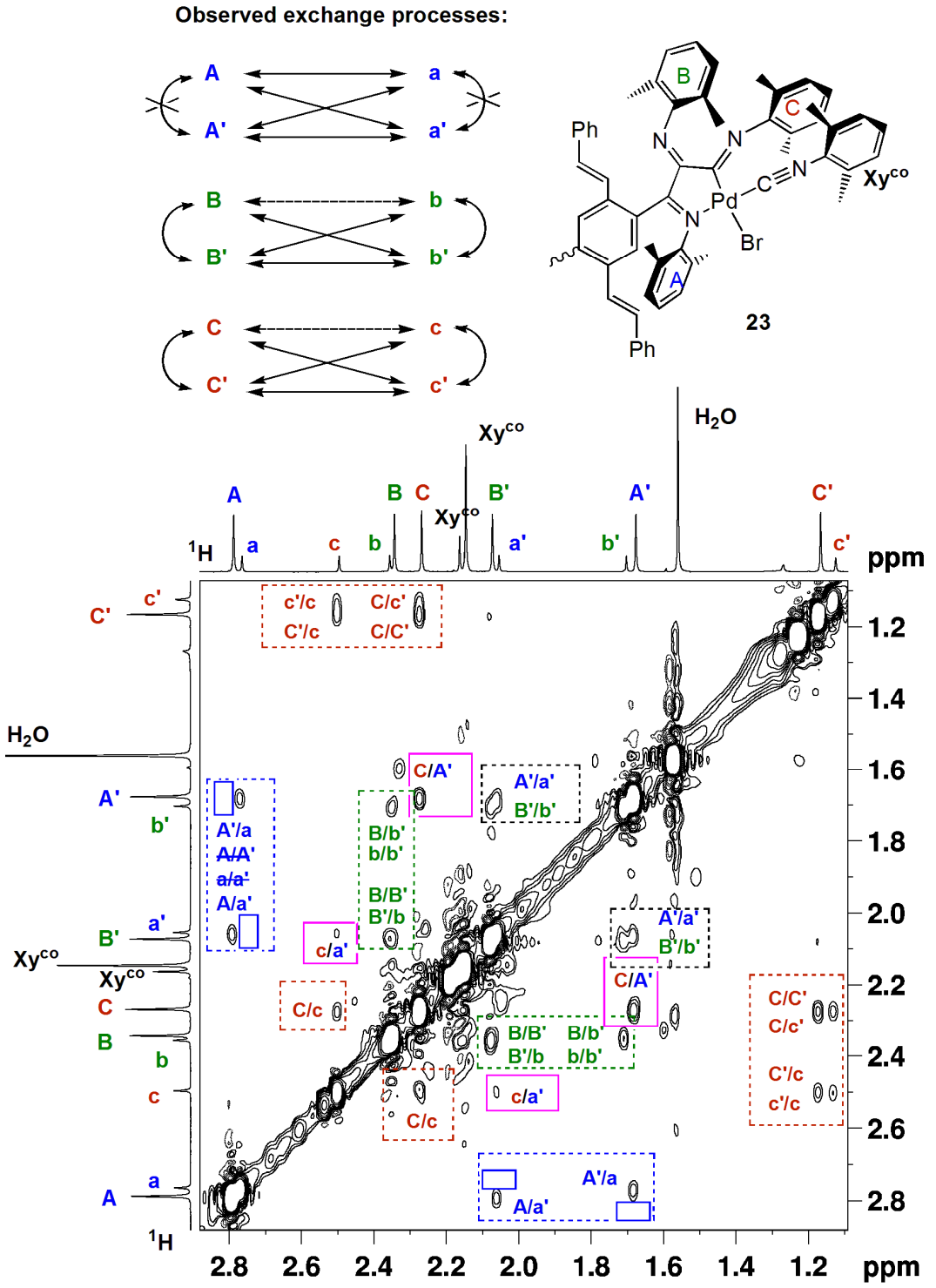


Figure IV.5. Section of the ^{1}H NOESY/EXSY spectrum of **23** and **23***, showing the Me region. The Me resonances of the major isomer (**23**) are labeled in capital letters, while those of the minor isomer (**23***) are labeled in lower-case letters. The exchange cross-peaks are surrounded by dotted rectangles. No cross-peaks are observed between $Me^{A}/Me^{A'}$ or between $Me^{a}/Me^{a'}$ (empty blue rectangles). The observed exchange processes are summarized in the arrow diagram. The dotted arrows represent presumed exchange cross-peaks ($Me^{A}/Me^{a'}$, Me^{B}/Me^{b}, and $Me^{C'}/Me^{c'}$) which cannot be observed because of their coincidence with the diagonal. The pink rectangles surround NOE cross-peaks found between Me^{C} and $Me^{A'}$, as well as between Me^{c} and Me^{a}. These NOE cross-peaks have the same sign as the diagonal and exchange cross-peaks because of the size of the molecule (slow-motion regime).

IV.3.7.2 NMR data of the Indacenediide and Indenyl Complexes 16-21

For the dinuclear indacenediide complexes **16-18** (with the exception of **17b**) a single set of ^{1}H and ^{13}C NMR resonances is observed. This is in agreement with the reactions being regio- and stereoselective, and with the presence of an inversion center (for the *anti* isomers) or a C_2 symmetry axis (for the *syn* isomers) in the resulting complexes. The NMR data do not allow a distinction between *syn* and *anti* isomers, and thus these can only be identified when X-ray diffraction data are available. Interestingly, the phase-sensitive ^{1}H-NOESY experiments have revealed a slow exchange process between the halves of the tbbpy and bpy ligands in all of the indenyl and indacenediide complexes, while for tmeda this behavior has only been observed for **17b**. This dynamic process might involve the coordination of the counteranion (OTf^- or ClO_4^-) to the Pd atom, leading to a five-coordinate intermediate, followed by dissociation of one of the N atoms which, after rotation around the remaining Pd-N bond and recoordination, would result in the exchange of the halves of the chelate ligands. Such exchange processes involving bpy ligands have been observed before, and a similar mechanism involving different counteranions was proposed.[81] We consider a partial dissociation of the ligands more plausible than a rearrangement within the five-coordinate intermediate, because of the steric hindrance around the Pd atoms. In the tmeda complex **17b** the exchange is selective between the opposed Me groups of the tmeda,[b] an indication that the process does not involve rotations and N-inversion processes within the ligand. Surprisingly, no slow exchange was observed for the tmeda complexes **16b** and **18b**. This different behavior could be explained by the lower electron-withdrawing ability of the tmeda ligand and the presence of Ph groups in the coordination sphere of the Pd in these two complexes, which could hinder the coordination of the anion and thus the exchange process. In the neutral 2,5-distyrylbenzene complexes **14a,b** and **15** no exchange between the halves of the N^N ligands was observed either, supporting the involvement of the counterions in this process.

The **hapticity of indenyl ligands** in solution can be assessed spectroscopically by the difference in the ^{13}C chemical shifts of the ring junction carbons with respect to those of NaInd, $\Delta\delta(C_{junc})$.[82-84] Large negative values of $\Delta\delta(C_{junc})$ in the range of -30 to -45 ppm (shift to lower frequencies) indicate an η^5 coordination of the indenyl ligand,[84,85] while

[b] Considering the plane defined by the N^1-CH_2-CH_2-N^2 groups, the Me group which points "up" on N^1 exchanges only with the Me group which points "down" on N^2, and vice versa.

positive values of $\Delta\delta(C_{junc})$ above +20 ppm indicate an η^3 coordination.[84,86] Intermediate values, from ca. -25 to +10 ppm, are indicative of increasingly slipped η^5-indenyl ligands.[83-85,87] For our indenyl complexes **19-21**, $\Delta\delta(C_{junc})$ is +4.4 ppm for **19'**, +6.8 ppm for **20**, and +6.0 ppm for **21**,[c] indicating that the indenyl ligands are significantly slipped toward an η^3 coordination. These values are similar to those found for our previous Pd indenyl complexes,[22,24] for which $\Delta\delta(C_{junc})$ was in the range +2.2 to +6.7 ppm.

A large negative difference in chemical shift between the central and terminal "allylic carbons" ($\Delta\delta_{13C} = \delta_{C(1,3)} - \delta_{C(2)}$) has also been proposed as an indication of a strong allyl-ene distortion in indenyl complexes.[88] These $\Delta\delta_{13C}$ values are in the range −36.9 to −40.5 ppm for **19-21**, also supporting an η^3 coordination. These solution data are in agreement with the degree of ring slippage observed in the X-ray structures of **19** and **21** (see Section IV.3.8).

The same ^{13}C NMR criteria can be applied to assess the **hapticity of indacenediyl complexes**.[36,72] In our complexes **16-18**, the ring junction carbons C(4,5) all resonate at higher frequencies (in the range 133.5-138.6 ppm) in comparison to those in the *s*-indacenediide anion (127.8 ppm),[89] affording $\Delta\delta(C_{junc})$ values of +5.7 to +10.8 ppm. The ($\Delta\delta_{13C} = \delta_{C(1,3)} - \delta_{C(2)}$) values are in the range −34.3 ppm (for **17a**) to −42.5 ppm (for **18b**). Both sets of data suggest a significantly slipped η^3,η^3 coordination mode for the ligands in solution, similar to that observed in the solid-state X-ray structures of **16a**,**b** and **18a'** (see next Section).

IV.3.8 X-Ray Structure Determinations

The crystal structures of the indacenediide complexes *anti*-**16a**·7$CDCl_3$ *(Figure IV.6*), *syn*-**16b**·CH_2Cl_2 (*Figure IV.7*) and *anti*-**18a'**·4CH_2Cl_2 (*Figure IV.8*), and the indenyl complexes **19** (*Figure IV.9*) and **21** (*Figure IV.10*) have been determined by X-ray diffraction studies (see also *Tables IV.4-10*).[d]

[c] We have used the chemical shift of the ring junction carbons in NaInd (130.7 ppm), as reported by Cadierno et al. in *Coord. Chem. Rev*. **1999**, *195*, 147, because our free indenyls have not been characterized. The addition of substituents to the indenyl moiety might affect the chemical shifts of the bridgehead carbons, but we think that the general trend is still valid.

[d] Crystals were mounted in inert oil on glass fibres. Intensity data were recorded on various diffractometers of the firms Bruker or Oxford Diffraction using wither monochromated Mo *K*α or mirror-focused Cu *K*α radiation. Absorption corrections were based on multi-scans. Structures were refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany). Me groups were refined as idealized rigid groups allowed to rotate but not tip; other H's were included using a riding model starting from calculated positions.

Table IV.4 X-ray crystallographic data for compounds **16a**·7$CDCl_3$, **16b**·CH_2Cl_2, **18a'**·4CH_2Cl_2, **19**, and **21** [(a)]

	16a·7$CDCl_3$	**16b**·CH_2Cl_2	**18a'**·4CH_2Cl_2	**19**	**21**
Formula	$C_{95}H_{84}D_7Cl_{21}F_6N_4O_6Pd_2S_2$	$C_{65}H_{70}Cl_2F_6N_4O_6Pd_2S_2$	$C_{80}H_{88}Cl_{10}N_4O_8Pd_2$	$C_{47}H_{34}BrF_3N_2O_3PdS$	$C_{42}H_{324}BrF_3N_2O_3PdS$
M_r	2527.13	1465.07	1800.84	950.13	888.07
T (K)	133(2)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	1.54184	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/c$
cell constants					
a (Å)	14.4062(12)	13.6279(6)	14.9171(2)	12.8550(4)	14.0869(3)
b(Å)	19.8994(16)	13.8070(6)	22.1678(3)	24.6545(7)	14.8008(2)
c (Å)	22.0291(18)	19.2244(10)	13.1545(3)	13.0448(6)	18.4244(3)
α (deg)	64.271(4)	93.796(4)	90	90	90
β (deg)	74.026(4)	103.789(4)	108.661(2)	98.382(5)	108.439(3)
γ (deg)	88.309(4)	112.947(4)	90	90	90
V (Å^3), Z	5439.8(8), 2	3183.4(3), 2	4121.24(12), 2	4090.2(3), 4	3644.25(11), 4
ρ (calcd) (Mg m^{-3})	1.543	1.528	1.451	1.543	1.619
abs. coef. (mm^{-1})	0.947	6.547	0.816	1.540	1.722
F(000)	2544	1496	1844	1912	1784
cryst size (mm)	0.4 × 0.2 × 0.05	0.2 × 0.2 × 0.1	0.4 × 0.2 × 0.1	0.40 × 0.25 × 0.05	0.35 × 0.20 × 0.20
θ range (deg)	1.07-27.52	3.53-75.96	2.34-30.03	2.24-26.37	2.33-30.03
	$-18 \le h \le 18$	$-17 \le h \le 17$	$-20 \le h \le 20$	$-16 \le h \le 16$	$-19 \le h \le 19$
index ranges	$-25 \le k \le 25$	$-17 \le k \le 17$	$-31 \le k \le 31$	$-30 \le k \le 30$	$-20 \le k \le 20$
	$-28 \le l \le 28$	$-19 \le l \le 24$	$-18 \le l \le 18$	$-16 \le l \le 16$	$-25 \le l \le 25$
reflections collected	76772	51588	203781	101330	227869
independent reflections	24845	13164	11989	8359	10599
R_{int}	0.0667	0.0392	0.0303	0.0668	0.0346
abs corr	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	Gaussian (face-indexed)	semi-empirical from equivalents
transmissions	0.954-0.789	1.000-0.503	1.000-0.920	0.868-0.597	1.000-0.890
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	24845/1823/1237	13164/447/875	11989/86/510	8359/0/523	10599/0/480
goodness-of-fit on F^2	1.035	1.049	1.085	0.904	1.051
Final R indices (I>2σ(I))					
R1	0.0746	0.0395	0.0328	0.0305	0.0316
wR2	0.1766	0.1113	0.0902	0.0688	0.0803
R indices (all data)					
R1	0.1287	0.0413	0.0417	0.0497	0.0383
wR2	0.2010	0.1130	0.0929	0.0707	0.0845
largest diff peak (e Å^{-3})	2.666	0.825	0.794	1.008	2.234
largest diff hole (e Å^{-3})	-2.824	-1.373	-1.563	-0.415	-1.149

(a) Special features: For **16a·7CDCl$_3$**, the Bu group at C27, the Ph ring at C51, the OTf at S2' and the $CDCl_3$ molecule at C106 are all disordered over two positions; C107 and C108 represent alternative orientations of the same $CDCl_3$ molecule. For **16b·CH$_2$Cl$_2$**, one OTf and the CH_2Cl_2 molecule are disordered over two positions. For **18a'·4CH$_2$Cl$_2$**, the ClO_4 anion and one CH_2Cl_2 are slightly disordered (minor components 9%, 18% respectively). Suitable restraints were employed to improve the refinement of disordered groups, but their dimensions should be interpreted with caution.

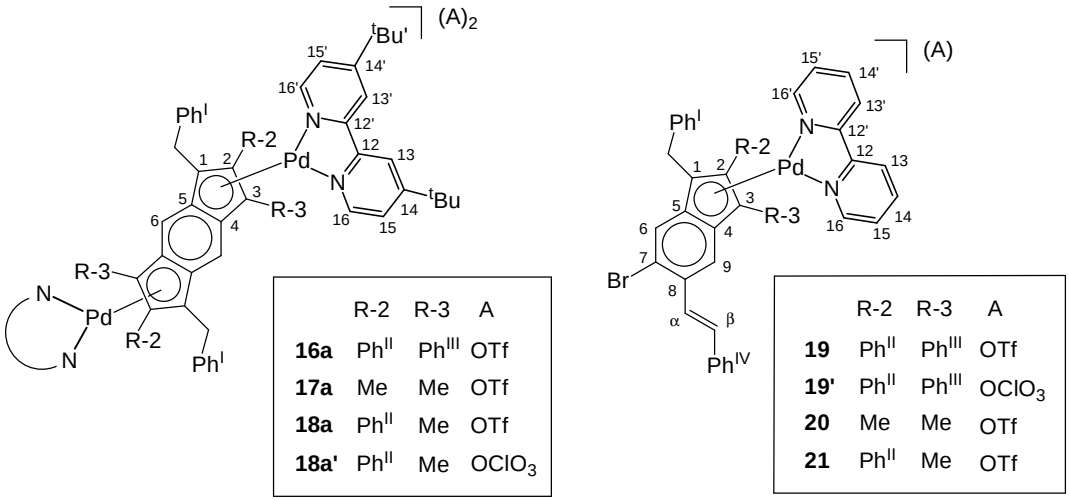
The indacenediide complex with tmeda, *syn*-**16b**·CH_2Cl_2 (*Figure IV.7*), shows a synfacial coordination of the two [Pd(tmeda)] moieties, with approximate C_2 symmetry (although some of the ring orientations depart from this ideal symmetry).[36] In contrast, both tbbpy complexes, *anti*-**16a**·7$CDCl_3$ (two molecules on inversion centers, *Figure IV.6*) and *anti*-**18a**'·4CH_2Cl_2 (one molecule on an inversion center, *Figure IV.8*) show *anti* geometries, with the two [Pd(tbbpy)] moieties on opposite sides of the indacenediide plane. Maybe the larger volume of the tbbpy ligand plays a role in the *anti* steric preference observed with this ligand. Crystallographic investigations of other homonuclear bimetallic indacenediide complexes have revealed both *syn*[60,61,66,71,72] and *anti*[59,68,71] geometries. In the complex *syn*-**16b** (*Figure IV.7*),[36] the steric interaction between the two [Pd(tmeda)] moieties is diminished by a significant deviation from planarity of the indacenediide ligand, which loses part of its aromaticity upon coordination, (the atoms C1-7 and C10 are fairly coplanar, with a mean deviation of 0.04 Å, but the atoms C8,9,11,12 lie 0.39, 0.23, 0.45, and 0.26 Å, respectively, out of the plane, all to the same side). Similar deviations have been found in other *syn* indacenediide complexes,[66,71,72] while in the *anti* isomers the ligand usually retains its planarity.[68,71] Indeed, in our complexes *anti*-**16a** and *anti*-**18a'** the indacenediide is reasonably planar (mean deviations all 0.03 Å excluding C2 and its symmetry-equivalent). For all three indacenediide complexes, *anti*-**16a**·7$CDCl_3$, *syn*-**16b**·CH_2Cl_2 and *anti*-**18a'**·4CH_2Cl_2, the bond distances between the ring junction carbons (C4 and C5 in our general numbering system; see *Chart IV.1*)[e] and the terminal "allylic carbons" (C1 and C3 in *Chart IV.1*) are significantly longer (1.473(4)–1.492(8) Å) than the other C-C bond distances within the indacenediide "core" (1.383(8)–1.447(8) Å). This feature is thus independent of the binding mode and probably reflects the different resonance forms contributing to the structure.

The degree of ring slippage from η^5 to η^3 in indenyl complexes can be related to three parameters, according to Taylor and Marder:[84,85,87] the **slip parameter (Δ)**, which is the difference in the average bond lengths of the metal to the indenyl ring junction carbons (C4, C5 in our numbering system; see *Chart IV.1*), and to the adjacent carbon atoms of the five-membered ring (C1, C3), the **hinge angle (HA)**, which is the angle between normals to the least squares planes defined by C1, C2, C3 and by C1, C5, C4,

[e] The numbering system used in the X-ray structures of *anti*-**16a**·7$CDCl_3$, *syn*-**16b**·CH_2Cl_2 and *anti*-**18a'**·4CH_2Cl_2 differs, in part because of crystallographic symmetry within the molecules. In *Chart IV.1* we propose a common numbering system for the discussion of crystallographic (and NMR) data.

C3 (i.e., the bending of the indenyl ligand at C1, C3), and the **fold angle (FA)**, which is the angle between normals to the least squares planes defined by C1, C2, C3 and by the six benzenoid carbons of the indenyl ligand (i.e., the bending of the indenyl ligand at the junction carbons). Other parameters (slip angle and slip distortion)[f] have been suggested by other authors.[90] In general, indenyl complexes considered to be ideally or only slightly distorted η^5 show values of Δ less than ca. 0.15 Å and HA, FA less than ca. 8-9º.[83-85,91-93] Stronger slip-fold distortions lead to values of Δ up to 0.50 Å and HA, FA up to 16-17º.[83-85,87,93,94] Complexes considered to be η^3 show values of Δ between 0.7 and 0.8 Å and HA, FA above 20º.[86,92,95] These parameters can also be applied to indacenediide complexes.[36] *Table IV.5* shows the Δ, HA, and FA values for both Pd-C5 rings in *anti*-**16a**, *syn*-**16b** and *anti*-**18a'**, and also for the indenyl complexes **19** and **21**, together with those of our previously reported indenylpalladium complexes: [Pd{η-C_9H-Bn-1-$(Ph)_2$-2,3-$(OMe)_3$-5,6,7}(tmeda)]OTf (**IV**),[22] [Pd{η-C_9H_2-Bn-1-Ph-3-$(OMe)_3$-5,6,7}(tmeda)]OTf (**V**),[22] [Pd{η-C_9H_2Bn-1-(Ac)-2-$(OMe)_3$-5,6,7}-(tmeda)]OTf (**VI**),[24] [Pd{η-C_9H_5Bn-1-Ph-3}(tmeda)]OTf (**VII**),[24] and [Pd{η-C_9H_4Bn-1-Ph-2-Me-3}(bpy)]OTf (**VIII**).[24] We have slightly modified the definition of the fold angle FA as the angle between the least squares planes defined by C1, C5, C4, C3 and by the six benzenoid carbons. We think that this is a better indication of the bending at C4, C5, considering the non-planarity of the five-membered ring. Indeed, some authors had already noticed that the FA as previously defined is not necessarily a good indication of η^3-slippage for indenyl groups: in some [Pd_2(μ-η^3-indenyl)$_2$(isocyanide)$_2$] complexes, a clear η^3-allyl-ene bonding mode of the indenyl groups was found, while the distortion of the indenyl groups from planarity was very small (FA =10º),[96] and in a dicarbonyl (η^3-indenyl)(η^5-indenyl)vanadium(II) complex a Δ value of 0.50 Å was accompanied by a small FA of 12º, for the η^3-indenyl group.[97] The values shown in *Table IV.5* indicate that the hapticity of both our indacenediide and indenyl ligands is intermediate between η^3 and η^5, the Δ values found for *anti*-**16a** and *syn*-**16b** being among the largest reported for any dinuclear indacenediide complex.[59-61,63,66,68,71,72]

[f] The slip angle or angle slip is the angle between the normal to the plane of the five-membered ring and the centroid-metal vector. The slip distortion is the length of the slip vector, which is the vector connecting the projection of the five-membered ring centroid and the projection of the metal atom on the plane



	R-2	R-3	A
16a	Ph^{II}	Ph^{III}	OTf
17a	Me	Me	OTf
18a	Ph^{II}	Me	OTf
18a'	Ph^{II}	Me	$OClO_3$

	R-2	R-3	A
19	Ph^{II}	Ph^{III}	OTf
19'	Ph^{II}	Ph^{III}	$OClO_3$
20	Me	Me	OTf
21	Ph^{II}	Me	OTf

Chart IV.1
Numbering system used in the crystallographic X-ray data discussion

Table IV.5
Ring slippage parameters, **Δ**, **HA**, and **FA**, obtained from crystallographic X-ray data for the indacenediide complexes *anti*-**16a**·7$CDCl_3$, *syn*-**16b**·CH_2Cl_2, and *anti*-**18a'**·4CH_2Cl_2 and the indenyl complexes **19**, **21**, and **IV-VIII**

Compound		**Δ** (Å)[a]	**HA** (deg)[b]	**FA** (deg)	**Reference**
anti-**16a**	Pd1	0.35	15	5	this work
	Pd2	0.35	15	5	
syn-**16b**	Pd1	0.36	15	6	this work
	Pd2	0.38	17	8	
anti-**18a'**	Pd1 and Pd2	0.27	14	5	this work
19		0.37	15	5	this work
21		0.42	17	1	this work
IV		0.35	13	7	[22]
V		0.39	12	10	[22]
VI		0.36	15	11	[24]
VII		0.41	15	18	[24]
VIII		0.42	16	15	[24]

[a] **Δ** = average d[M-C1, C3] − average d[M-C4, C5]. [b] **HA** (hinge angle) is the angle defined by [C1, C2, C3] and [C1, C5, C4, C3]. [c] **FA** (fold angle) is the angle defined by the six benzenoid carbons and [C1, C5, C4, C3]. The numbering system is shown in *Chart IV.1*. Note that for various reasons (crystallographic symmetry, more than one Pd atom in the asymmetric unit) the crystallographic numbering may differ from that in *Chart IV.1*.

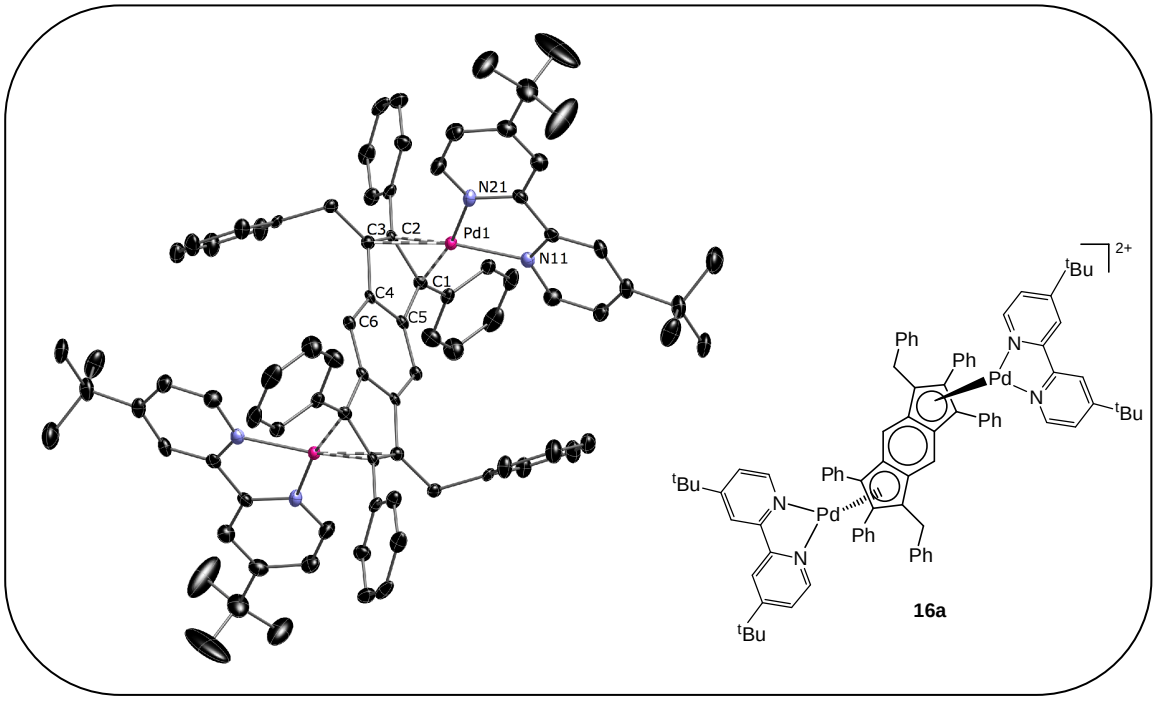


Figure IV.6
Thermal ellipsoid plot (50% probability level) of *anti*-**16a**·7$CDCl_3$. Only the cation is shown

Table IV.6 Selected bond lengths (Å) and angles (deg) of *anti*-**16a**·7$CDCl_3$

Pd(1)–C(1)	2.208(6)	C(1)-Pd(1)-C(2)	37.9(2)
Pd(1)-C(2)	2.180(5)	C(1)-Pd(1)-C(3)	63.4(2)
Pd(1)-C(3)	2.193(6)	C(2)-Pd(1)-C(3)	38.5(2)
Pd(1)-C(4)	2.549(5)	N(11)-Pd(1)-N(21)	78.91(19)
Pd(1)-C(5)	2.560(5)	N(11)-Pd(1)-C(1)	109.9(2)
Pd(1)-N(11)	2.070(5)	N(11)-Pd(1)-C(2)	141.0(2)
Pd(1)-N(21)	2.076(5)	N(11)-Pd(1)-C(3)	168.6(2)
Pd(2)-C(1')	2.189(6)	N(21)-Pd(1)-C(1)	170.5(2)
Pd(2)-C(2')	2.185(6)	N(21)-Pd(1)-C(2)	132.6(2)
Pd(2)-C(3')	2.188(6)	N(21)-Pd(1)-C(3)	108.4(2)
Pd(2)-C(4')	2.532(5)	C(1')-Pd(2)-C(2')	38.6(2)
Pd(2)-C(5')	2.535(5)	C(1')-Pd(2)-C(3')	63.6(2)
Pd(2)-N(11')	2.080(5)	C(2')-Pd(2)-C(3')	37.9(2)
Pd(2)-N(21')	2.086(5)	N(11')-Pd(2)-N(21')	78.83(19)
		N(11')-Pd(2)-C(1')	108.5(2)
		N(11')-Pd(2)-C(2')	141.3(2)
		N(11')-Pd(2)-C(3')	166.3(2)
		N(21')-Pd(2)-C(1')	171.1(2)
		N(21')-Pd(2)-C(2')	132.5(2)
		N(21')-Pd(2)-C(3')	110.2(2)

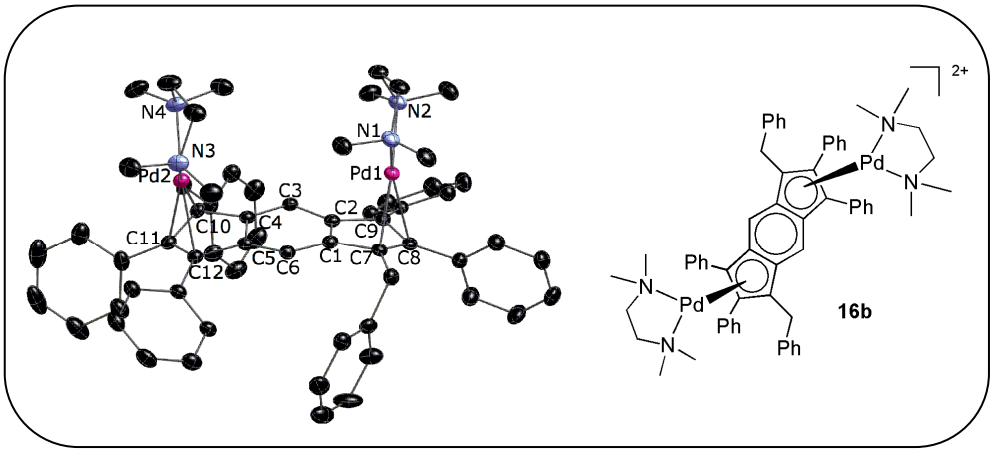


Figure IV.7

Thermal ellipsoid plot (30% probability level) of *syn*-**16b**·CH_2Cl_2. Only the cation is shown

Table IV.7 Selected bond lengths (Å) and angles (deg) of *syn*-**16b**·CH_2Cl_2

Pd(1)-C(7)	2.220(3)	C(7)-Pd(1)-C(8)	37.82(10)
Pd(1)-C(8)	2.187(2)	C(7)-Pd(1)-C(9)	63.14(9)
Pd(1)-C(9)	2.199(2)	C(8)-Pd(1)-C(9)	38.42(9)
Pd(1)-C(1)	2.597(3)	N(1)-Pd(1)-N(2)	84.11(9)
Pd(1)-C(2)	2.541(2)	N(1)-Pd(1)-C(7)	106.65(9)
Pd(1)-N(1)	2.140(2)	N(1)-Pd(1)-C(8)	136.34(10)
Pd(1)-N(2)	2.129(2)	N(1)-Pd(1)-C(9)	168.11(10)
Pd(2)-C(10)	2.221(2)	N(2)-Pd(1)-C(7)	168.12(9)
Pd(2)-C(11)	2.186(2)	N(2)-Pd(1)-C(8)	134.91(10)
Pd(2)-C(12)	2.195(2)	N(2)-Pd(1)-C(9)	105.58(10)
Pd(2)-C(4)	2.626(3)	C(10)-Pd(2)-C(11)	37.75(10)
Pd(2)-C(5)	2.558(3)	C(10)-Pd(2)-C(12)	63.16(9)
Pd(2)-N(3)	2.136(2)	C(11)-Pd(2)-C(12)	38.33(9)
Pd(2)-N(4)	2.146(2)	N(3)-Pd(2)-N(4)	83.96(9)
		N(3)-Pd(2)-C(10)	166.35(10)
		N(3)-Pd(2)-C(11)	137.35(10)
		N(3)-Pd(2)-C(12)	105.88(9)
		N(4)-Pd(2)-C(10)	106.12(9)
		N(4)-Pd(2)-C(11)	135.27(10)
		N(4)-Pd(2)-C(12)	168.28(10)

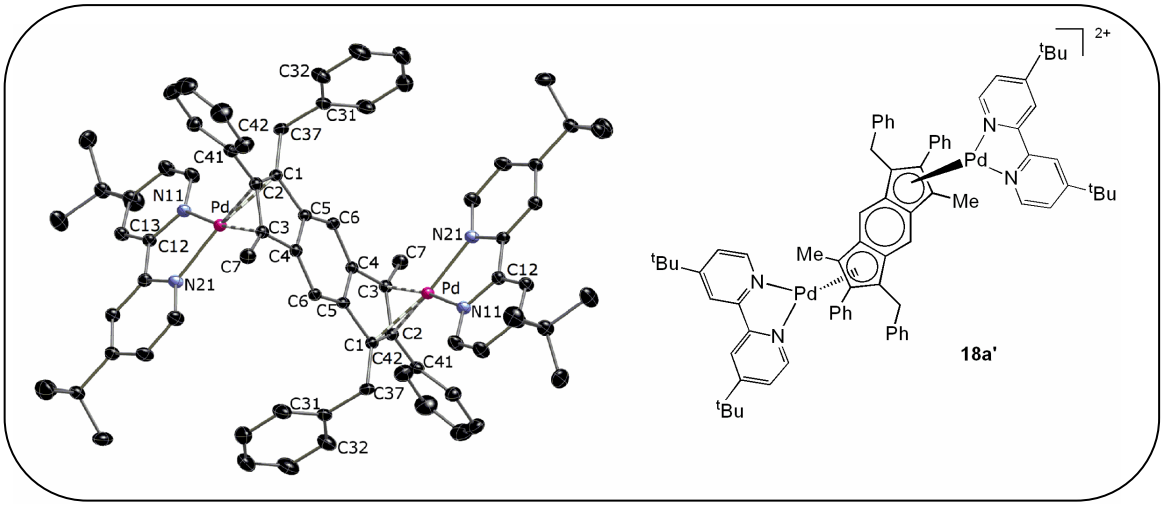


Figure IV.8
Thermal ellipsoid plot (50% probability level) of *anti*-**18a'**·$4CH_2Cl_2$. Only the cation is shown

Table IV.8 Selected bond lengths (Å) and angles (deg) of *anti*-**18a'**·$4CH_2Cl_2$

Pd-C(1)	2.1861(17)	C(1)-Pd-C(2)	38.06(6)
Pd-C(2)	2.2200(17)	C(1)-Pd-C(3)	63.28(6)
Pd-C(3)	2.2161(16)	C(2)-Pd-C(3)	37.57(6)
Pd-C(4)	2.4690(17)	N(11)-Pd-N(21)	78.65(6)
Pd-C(5)	2.4658(17)	N(11)-Pd-C(1)	109.61(6)
Pd-N(11)	2.0724(14)	N(11)-Pd-C(2)	135.47(6)
Pd-N(21)	2.0751(15)	N(11)-Pd-C(3)	172.61(6)
		N(21)-Pd-C(1)	169.32(6)
		N(21)-Pd-C(2)	138.89(6)
		N(21)-Pd-C(3)	108.65(6)

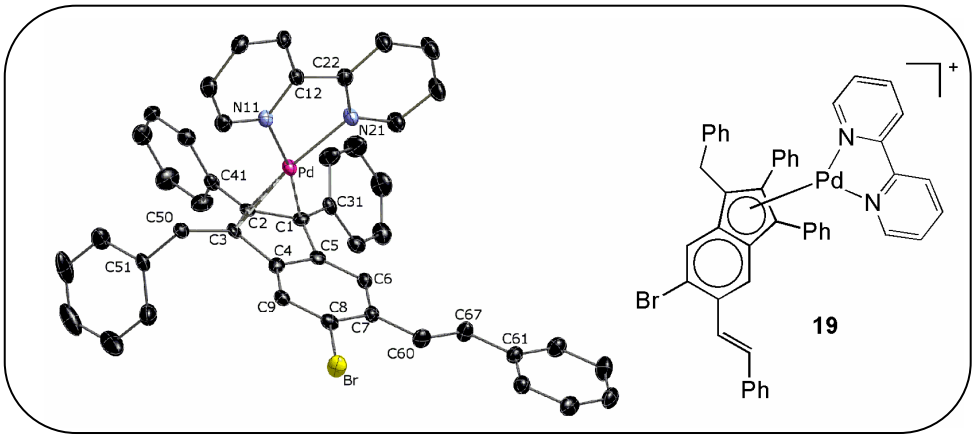


Figure IV.9

Thermal ellipsoid plot (50% probability level) of **19**. Only the cation is shown

Table IV.9 Selected bond lengths (Å) and angles (deg) of **19**

Pd-C(1)	2.209(2)	C(1)-Pd-C(2)	37.96(9)
Pd-C(2)	2.172(3)	C(2)-Pd-C(3)	38.32(10)
Pd-C(3)	2.205(3)	C(1)-Pd-C(3)	63.15(10)
Pd-C(4)	2.581(3)	N(21)-Pd-C(1)	109.07(9)
Pd-C(5)	2.568(3)	N(21)-Pd-C(2)	138.56(10)
Pd-N(11)	2.094(2)	N(21)-Pd-C(3)	170.18(9)
Pd-N(21)	2.071(2)	N(11)-Pd-C(3)	109.67(9)
		N(11)-Pd-C(2)	132.40(9)
		N(11)-Pd-C(1)	170.33(9)

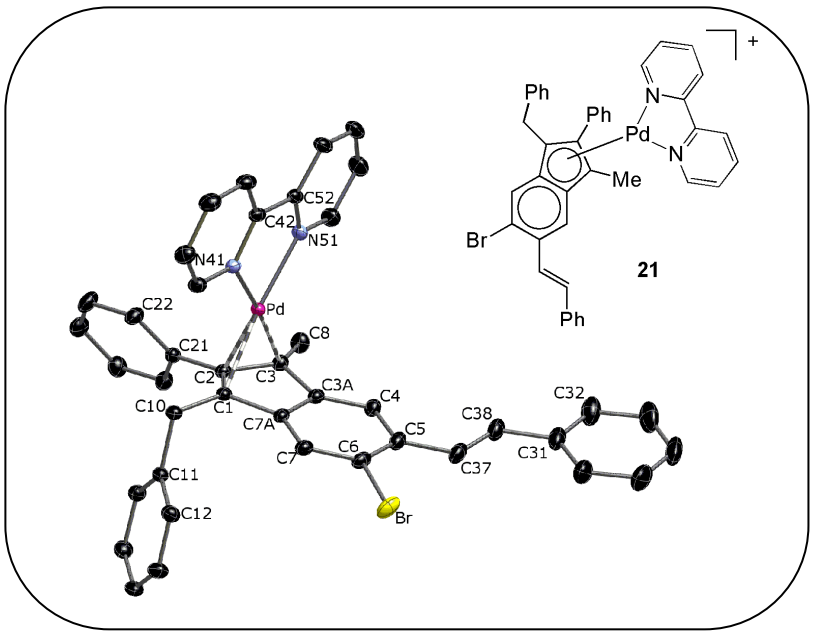


Figure IV.10

Thermal ellipsoid plot (50% probability level) of **21**. Only the cation is shown

Table IV.10 Selected bond lengths (Å) and angles (deg) of **21**

Pd-C(1)	2.1884(19)	C(1)-Pd-C(2)	38.62(7)
Pd-C(2)	2.1609(19)	C(2)-Pd-C(3)	38.00(7)
Pd-C(3)	2.229(2)	C(1)-Pd-C(3)	63.11(7)
Pd-C(3A)	2.632(32)	N(41)-Pd-N(51)	78.35(7)
Pd-C(7A)	2.6174(19)	N(41)-Pd-C(1)	110.10(7)
Pd-N(41)	2.1040(17)	N(41)-Pd-C(2)	137.19(70)
Pd-N(51)	2.0836(17)	N(41)-Pd-C(3)	173.13(7)
		N(51)-Pd-C(1)	171.01(7)
		N(51)-Pd-C(2)	136.05(7)
		N(51)-Pd-C(3)	108.37(7)

IV.4 CONCLUSIONS

We have prepared mono- and dipalladated benzene derivatives with alkenyl groups at the *ortho* position. In their reactions with alkynes we have obtained highly substituted indenylpalladium complexes and dipalladated indacenediides. This is the first synthesis of such dinuclear indacenediide complexes through metal-mediated building of the ligand. The stereo- and regioselectivity of the reactions have been discussed and the complexes have been extensively characterized by 2D-NMR and X-ray diffraction studies, which indicate that the hapticity of the indenyl and indacenediide ligands is intermediate between η^3 and η^5. The reactivity toward XyNC of the dipalladated benzene derivatives has resulted in the simultaneous insertion of the isocyanide into both aryl-Pd bonds, forming a monoinserted dinuclear complex. A related triinserted dinuclear complex has been obtained as well, by reaction of XyNC with *trans*,*trans*-2,5-distyryl-1,4-dibromobenzene and [Pd(dba)$_2$]. This complex forms as a mixture of two isomers which are in slow exchange in solution, as shown by an EXSY spectrum.

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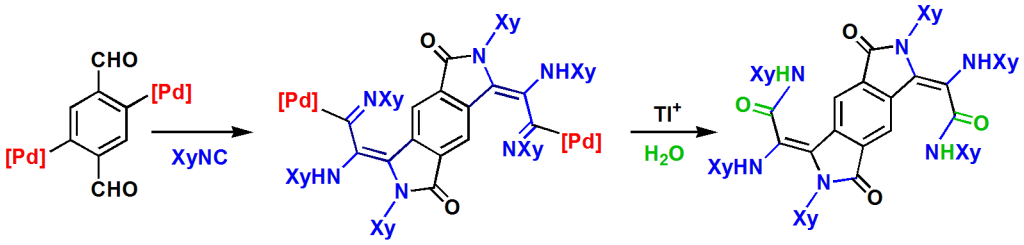
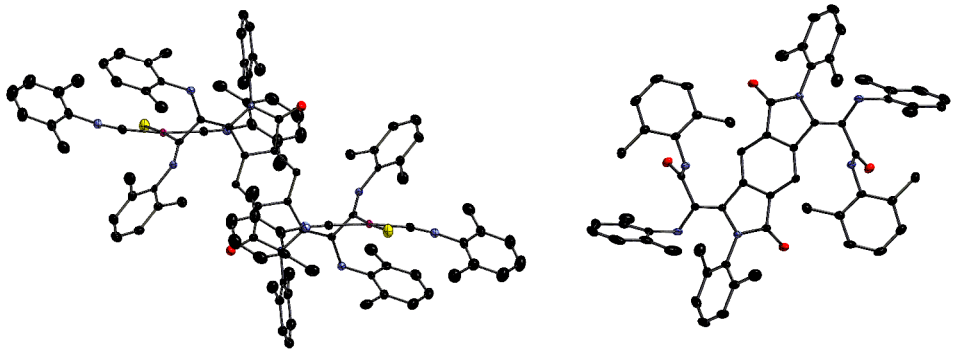
CHAPTER V

Synthesis and Reactivity of Dipalladated Derivatives of Terephthalaldehyde





The results of this Chapter will soon be submitted for publication

V.1 INTRODUCTION

We have already described in this Thesis (see Chapter I, General Introduction, and the Introductions to the Chapters II-IV) the importance of arypalladium complexes in Organometallic Chemistry, and how our group has been specially interested in the synthesis of *ortho*-substituted arylpalladium complexes and the investigation of their reactivity toward unsaturated organic molecules. These molecules may insert into the aryl-Pd bond and interact with the group in *ortho* position, resulting in the formation of novel ligands and/or organic compounds. Our group is now interested in the extension of this chemistry to polypalladated arenes,[1-6] which could provide interesting structures and pave the way to the synthesis of organic polycyclic compounds that are otherwise difficult to prepare.

Although there have been previous reports on dipalladated *ortho*-substituted aryl complexes, these refer, with some exceptions[1-8] to dipalladacycles with N-donor groups[8-11] (see *Chart V.1*). Our group[8,12] has also been involved in this research, and it has reported the first "akimbo" complexes,[5] where the two donor atoms are on the same substituent and thus the two palladacycles are fused:

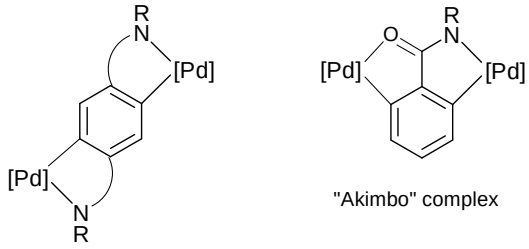


Chart V.1 "Traditional" dipalladacycles and "akimbo" complexes

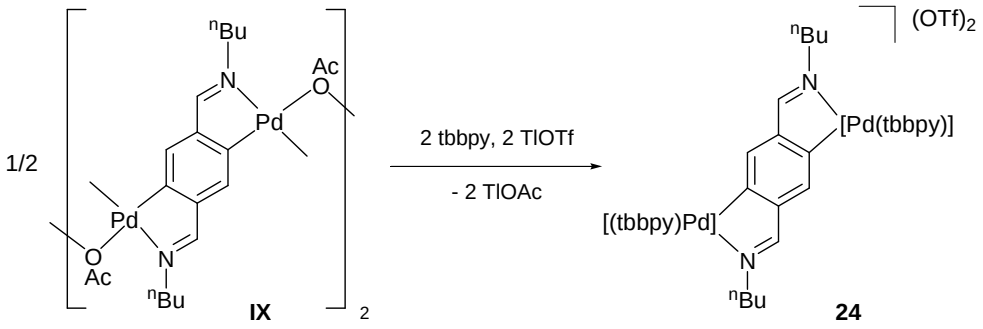
In the previous Chapter we have described the synthesis and reactivity of dipalladated derivatives of 2,5-distyrylbenzene.[2,6] In the present Chapter we will describe the synthesis of dipalladated derivatives of terephthalaldehyde (by hydrolysis of a "traditional" N-donor dipalladacycle) and their reactivity toward CO and XyNC. We have already commented on the importance of the insertion reactions of CO and isocyanides into the C-Pd bond of arylpalladium complexes (see Section I.3.2.2 in Chapter I, General Introduction). The reactions we describe now are quite novel in that they represent the first double insertion of CO into two separate aryl-metal bonds on the same aryl ring, as well as a double 3-fold insertion of XyNC which, together with an

interaction with the formyl groups in *ortho* position, results in the formation of a dinuclear Pd(II) complex with a benzodipyrrole-1,5-dione core. The central ligand can be liberated from this complex by reaction with TlOTf.

V.2 RESULTS AND DISCUSSION

V.2.1 Synthesis and Reactivity

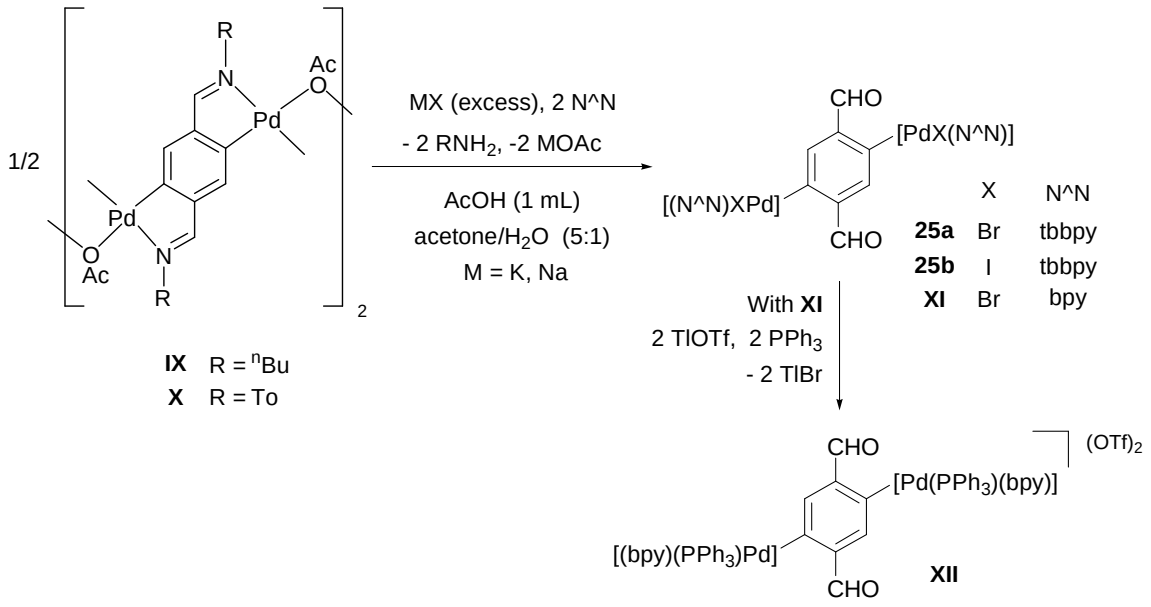
The tetranuclear complex [{μ-*C1,C4,N,N"*-C_6H_2{C(H)=N(^{n}Bu)}$_2$-2,5}{Pd(μ-OAc)}]$_2$ (**IX**) had been previously prepared in our research group by palladation of the diimine $C_6H_4(CH=N^nBu)_2$-1,4 with [Pd(OAc)$_2$].[12] Complex **IX** is soluble in common solvents, in contrast to the similarly prepared complex with To instead of ^{n}Bu.[8] The reaction of **IX** with tbbpy and TlOTf results in the formation of the dicationic complex [{μ-*C1,C4,N,N"*-C_6H_2{C(H)=N(^{n}Bu)}$_2$-2,5}{Pd(tbbpy)}$_2$] (**24**, *Scheme V.1*). Complexes **IX** and **24** are of interest because they contain an aryl ligand capable of binding to two different metal centers simultaneously, in a tetradentate fashion, resulting in two independent palladacycles on the same aryl ring. Such complexes are still relatively rare in the literature, although some examples can be found, involving mainly N-donor groups.[8-11] The examples most closely related to our work are the dipalladated Schiff bases reported by Vila and co-workers, prepared by palladation or oxidative addition reactions, followed by ligand-exchange.[10,11] These dinuclear square-planar palladium(II) complexes with two blocked *cis*-coordination sites can be very useful as building blocks in Supramolecular Chemistry.[11,13]



Scheme V.1. Synthesis of complex **24**

The hydrolysis of **IX** by reaction with acetic acid in a 5:1 acetone/water mixture, and in the presence of two equivalents of tbbpy, and an excess of NaX (X = Br, I), yields the dipalladated terephthalaldehyde derivatives [C_6H_2{PdX(tbbpy)}$_2$-1,4-(CHO)$_2$-2,5] (X = Br (**25a**), X = I (**25b**), *Scheme V.2*). There is a close precedent for this reaction in the

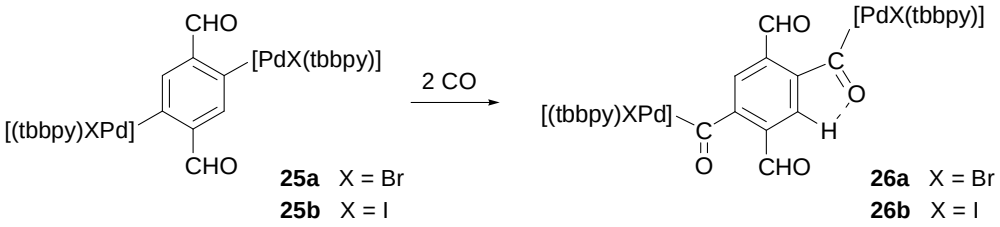
synthesis of the related complex with bpy, $[C_6H_2\{PdBr(bpy)\}_2$-1,4-$(CHO)_2$-2,5] (**XI**, see also *Scheme V.2*), by hydrolysis of an analogue to **IX** with To instead of ^{n}Bu (complex **X**).[8] However, in that reaction the insolubility of complex **XI** prevented complete purification, a problem which is common in polynuclear complexes containing bpy as an auxiliary ligand.[1,6] Nonetheless, a more soluble derivative, $[C_6H_2\{Pd(PPh_3)(bpy)\}_2$-1,4-$(CHO)_2$-2,5] (**XII**, *Scheme V.2*), was prepared by reaction of **XI** with PPh_3 and KOTf. Complex **XII** was partially characterized, although no ^{13}C NMR data could be obtained.[8] Complexes **25a,b**, in contrast, are soluble in common solvents and have been fully characterized. The reaction of **IX** with tmeda instead of tbbpy, and either NaBr or NaI, has given mixtures of compounds which could not be separated. **25a,b**, **XI**, and **XII** are the only known examples of dipalladated phthalaldehydes. Mono-, di- and tripalladated derivatives of benzenetricarboxaldehyde have also been reported by our group.[3]



Scheme V.2 Synthesis of complexes **25a,b**, and related complexes **XI**, **XII**

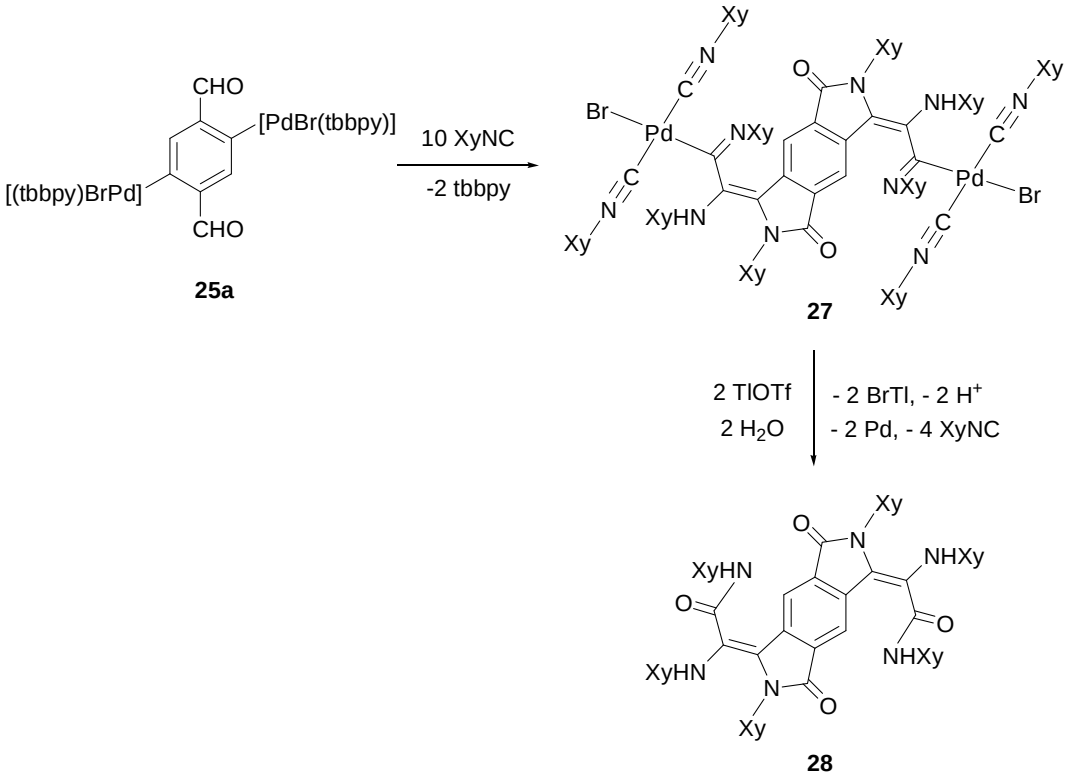
By reaction of **25a,b** with CO we have obtained the complexes **26a,b**, resulting from the insertion of CO into both aryl-Pd bonds (*Scheme V.3*). This is the first double insertion of CO into two separate aryl-metal bonds on the same aryl ligand. The NMR data (see Section V.3) of these complexes suggest that one of the inserted CO groups forms a hydrogen bond with the aryl hydrogen, while, surprisingly, the same does not happen with the other inserted CO. The insertion of the CO molecules is confirmed by the IR spectra (see Section V.3). However, and curiously, the mass spectra of **25a** and **26a** both show the same main peak, at m/z 961.13, corresponding to the loss of the Br ligand (for **25a**) plus two CO fragments (for **26a**). The same happens for **25b** and **26b**,

which show the main peak at m/z 1008.12, corresponding to the loss of the I ligand (for **26a**) plus two CO fragments (for **26b**). The syntheses of **26a,b** are best carried out in distilled THF (and heating to 60ºC for several hours). If CH_2Cl_2 or 1,2-dichloroethane are used as solvent instead of THF, compounds **26a,b** also form but together with some impurities. A reaction time of only 20 minutes results in an incomplete reaction.

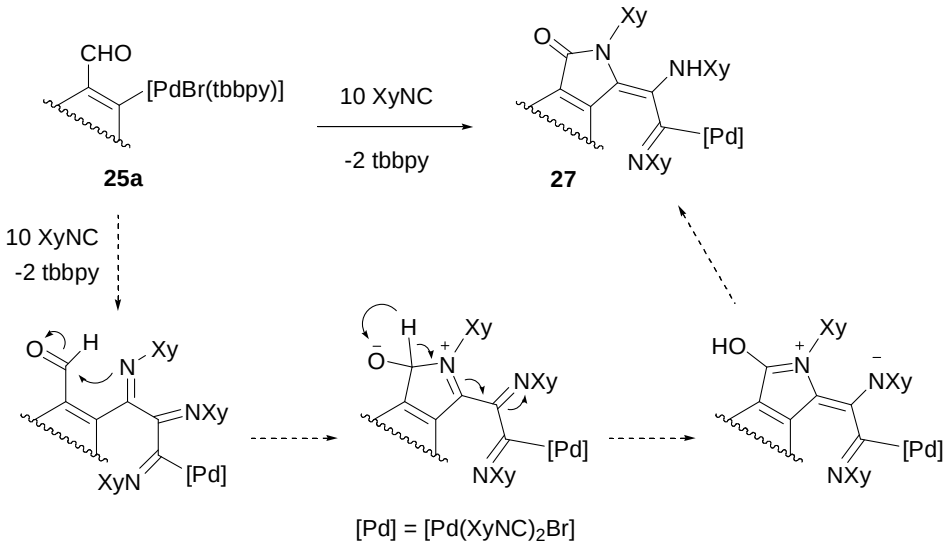


Scheme V.3. Synthesis of complexes **26a,b**

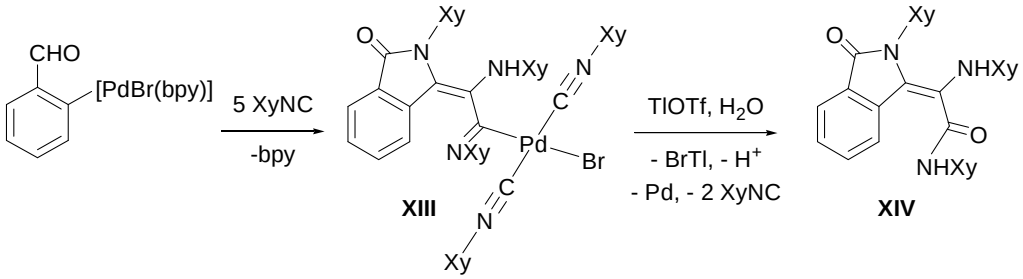
In the reaction of **25a** (X = Br) with an excess (2-fold) of XyNC in acetone the dinuclear complex **27** precipitates as a red solid (*Scheme V.4*). This complex is the result of the insertion of three molecules of the isocyanide into each aryl-Pd bond and the nucleophilic attack of one isocyanide to each formyl group, followed by an intramolecular proton migration (*Scheme V.5*). The tbbpy ligands on the Pd atoms are displaced by two other XyNC molecules which, as usual, adopt a *trans* disposition. We haven't found in the literature molecules with a structure related to complex **27**. The only precedent for this reaction is the synthesis of the mononuclear complex **XIII** (*Scheme V.6*), containing an isoindolinone moiety, which was prepared by some of us by reaction of an *ortho*-formyl arylpalladium complex with XyNC.[14] Similar reactions with **26b** (X = I), or with ^{t}BuNC instead of XyNC, result in mixture of compounds. Complex **27** decomposes slowly in solution to give $[PdBr_2(XyNC)_4]$, which is easily identified by its ^{1}H NMR resonance at 2.52 ppm.



Scheme V.4. Synthesis of compounds **27** and **28**



Scheme V.5 Mechanism for the formation of complex **27**



Scheme V.6 Synthesis of compounds **XIII** and **XIV**

Finally, the reaction of **27** with TlOTf in 1,2-dichloroethane, at 70ºC, results in the decomposition of the complex yielding the organic compound **28**, containing a benzodipyrrole-1,5-dione core with two alkylidene substituents in positions 2,6. This reaction is promoted by the precipitation of TlBr, which would favor the displacement of both [PdBr(XyNC)$_2$] moieties by hydroxyl groups from residual water molecules. A tautomeric equilibrium would then result in the formation of the amide functions in **27**. We can find a mononuclear parallel for this reaction in the formation of the organic compound **XIV**, by reaction of **XIII** with TlOTf (*Scheme V.5*), reported by some of us.[14] In that reaction compound **XIII** formed together with its tautomeric form, in a 2:3 ratio, and both could be separated by differences in solubility.[14] The structures of both **27** and **28** have been confirmed by X-ray crystallography (see Section V.4).

V.2.2 NMR and IR Data

Compounds **25-28** have been extensively studied by NMR spectroscopy (1D and 2D experiments), allowing an almost full assignment of the ^{1}H and ^{13}C resonances. Complex **24** is an exception, as it shows a fluxional behavior at room temperature, resulting in broad ^{1}H resonances for the tbbpy ligand. This dynamic process might involve the coordination to the OTf anion to the Pd atom, leading to a five-coordinate intermediate in which dissociation of one of the N atoms, followed by rotation around the remaining Pd-N bond, and recoordination, would result in the exchange of the halves of the tbbpy ligand. We have described a similar process for the bpy and tbbpy complexes **16-21** in Chapter IV.[6] Complex **24** shows the expected IR bands for the imine C=N bond (1614 cm^{-1}) and the S=O bond of the OTf anion (1030, 1280 cm^{-1}).

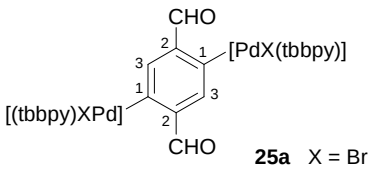
For the tbbpy complexes **25a,b** and **26a,b**, as usual, the H16 protons are shielded (δ = 7.78-7.38 ppm) with respect to H16' (δ = 9.53-9.24 ppm), as a consequence of the anisotropic effect of the aryl group on the H16 protons (see *Scheme II.4*, in Chapter II).

Complexes **25a,b** show the expected IR bands for the formyl C=O bonds at 1672 and 1662 cm^{-1}, respectively. For the complexes **26a,b**, resulting from the insertion of CO into both aryl-Pd bonds of **25a,b**, we observe a broad band at 1682 cm^{-1} (for **26a**) or two bands, at 1662 and 1678 cm^{-1} (for **26b**) confirming the presence of additional C=O bonds within these molecules.

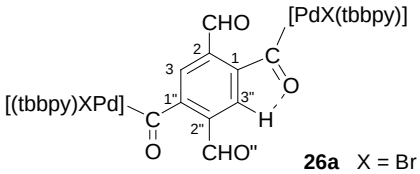
The ^{1}H and ^{13}C NMR spectra of **25a,b** and **26a,b**, show the expected resonances for the formyl groups (see *Table V.1*), but for **26a,b** we have not been able to observe the ^{13}C resonances of the inserted CO groups, even when using long relaxation delays between scans of up to 10 s (to allow for the longer relaxation times usually associated to quaternary carbons).

As shown in *Table V.1*, complexes **25a,b** show a single set of ^{1}H and ^{13}C NMR resonances for the halves of the molecule, an indication that they possess an inversion center in solution. We expected that complexes **26a,b** would show a similar symmetry, but, surprisingly, we observed two well-separated ^{1}H and ^{13}C NMR resonances for the two CH groups of the aryl ring (CH3 and CH3"), and only for them (*Table V.1*). We think that the inequivalence of the two CH groups can be explained by the formation of a hydrogen bond between one of the inserted CO groups and the adjacent aryl proton, while the same would not happen for the other CO group, as a result of steric or electronic reasons. The aryl hydrogen involved in the hydrogen bond (H3") would be shifted to higher frequencies (data in red in *Table V.1*) with respect to **25a,b**, while the other aryl hydrogen would resonate at a similar frequency to **25a,b** (data in blue). The ^{13}C resonances of CH3 and CH3" would also be affected, but the chemical shifts of the other aryl carbons (C1,1",C2,2") and of the formyl groups, CHO, CHO", would be very similar, resulting in single resonances (indeed, the APT spectrum of **26b**, when processed without window function,[a] shows a significant broadening of the ^{13}C resonances of the CHO/CHO", C1/C1" and C2/C2" carbons, and not of those of the tbbpy ligand).

*Table V.1. Selected ^{1}H and ^{13}C NMR data (ppm) for **25a,b** and **26a,b**.*



25a X = Br
25b X = I



26a X = Br
26b X = I

	25a		**25b**			**26a**		**26b**	
	^{13}C	**^{1}H**	**^{13}C**	**^{1}H**		**^{13}C**	**^{1}H**	**^{13}C**	**^{1}H**
C1	152.6		149.2		**C1**	168.3		165.7	
C2	143.9		143.6		**C2**	138.7		138.9	
CH	135.8	8.12	136.6	8.11	**CH3"**	144.6	8.48	146.5	8.48
					CH3	128.5	8.14	128.3	8.14
CHO	197.4	11.10	197.8	11.03	**CHO**	196.3	11.01	196.8	10.95

[a] Using the command ft instead of ef, or using the command ef with lb=0 (for Bruker software)

As we were not able to observe the ^{13}C NMR resonances of the inserted CO groups in **26a,b**, we decided to carry out the reaction of **25a** with ^{13}CO, in order to confirm by ^{13}C NMR the presence of these inserted CO groups.[b] The APT spectra of the product showed the presence of two very weak resonances at 240.5 and 237.0 ppm (*Figure V.1*), confirming the presence of two non-equivalent inserted CO groups. But, surprisingly, the CHO resonance was the most strongly affected by the introduction of ^{13}CO, suggesting an unexpected exchange process between the inserted CO and the formyl group. In the ^{1}H NMR spectrum (box in *Figure V.1*), the formyl resonance was also strongly affected, showing strong ^{13}C satellites.

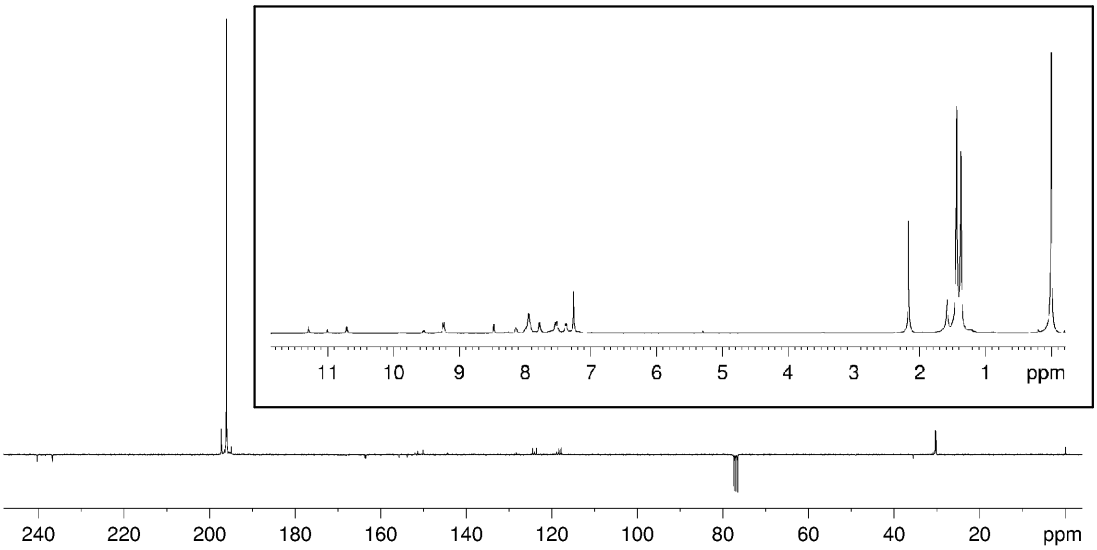


Figure V.1
^{1}H (300 MHz) and APT (75.6 MHz) spectra of the reaction of **25a** with ^{13}CO

The IR spectrum of complex **27** shows the expected bands for the N-H bond (3376 cm^{-1}), the C≡N bonds of the coordinated isocyanides (2182 cm^{-1}), the carbonyl C=O bonds (1682 cm^{-1}), and the C=N bond of the inserted isocyanide (1614 cm^{-1}). For the organic compound **28** we observe an N-H band at 3369 cm^{-1}, and a broad C=O band at 1674 cm^{-1}. Both **27** and **28** posses an inversion center in solution, so that the halves of the molecules are equivalent, and only a set of ^{1}H and ^{13}C NMR resonances is observed. The NMR data also indicate that there is free rotation around all the N-Xy bonds, making both Me groups on each ring equivalent. For complex **27**, the two XyNC ligands on each Pd are also equivalent, confirming the *trans* geometry proposed for this complex.

[b] ^{13}CO was bubbled for 3 min through a solution of **25a** (60.0 mg, 0.0576 mmol) in THF (10mL) under N_2. The mixture was then heated to 60ºC for 24h, and then it was stirred at rt for another 24 h. Workup as in the reaction with ^{12}CO (see Chapter VIII, Experimental Section), yielded 19 mg of a pink solid.

V.2.3 X-Ray Structure Determinations

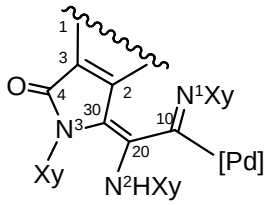
The crystal structures of **24**·4$CHCl_3$ *(Figure V.2*), **27**·2CH_2Cl_2·3hexane (*Figure V.3*) and **28**·2$CDCl_3$ (*Figure V.4*) have been determined by X-ray diffraction studies (see also *Tables V.2-5*).[c]

The structure of **24**·4$CHCl_3$ (*Figure V.2* and *Table V.3*), in which the complex displays crystallographic inversion symmetry, confirms the doubly chelating nature of the diimine ligand. The chelate ring is to a good approximation planar, with a mean deviation of 0.014 Å. The coordination of the iminic nitrogen to Pd leads to a slight lengthening of the C=N bond (1.291(7) Å) with respect to the mean value in imines (1.279 Å).[15] The coordination around the Pd atoms is square planar, but is markedly distorted to avoid a close contact between H3 and H26 (for which the observed distance is 2.12 Å); the atoms Pd, N11, N21 and N1 are coplanar (mean deviation 0.04 Å) but C2 lies 0.64 Å outside the plane thus defined. The Pd-C bond distance in **24**·4$CHCl_3$ is 2.002(5) Å, similar to the values reported by us for other aryl palladium complexes with the aryl ligand *trans* to bpy or tbbpy (between ca. 1.97 and 2.00 Å).[3,16,17] Because there is no significant difference in *trans* influence between the Br and tbbpy ligands, the Pd-C bond distance in **24**·4$CHCl_3$ (2.002(5) Å) is similar to that found for complexes **30"** (2.012(3) Å) and **31** (2.004(2) Å) (see Chapter VI), where the aryl ligand is *trans* to Br. This similarity has been observed before.[17] The three Pd-N bond distances in **24**·4$CHCl_3$ follow the expected order of *trans* influence: Pd-N *trans* to aryl (2.160(4) Å) > Pd-N *trans* to N (2.039(5) Å and 2.058(5) Å).

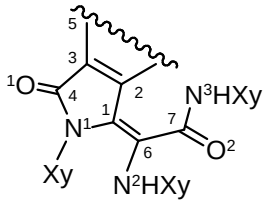
The structure of complex **27** is confirmed by its X-ray diffraction study (*Figure V.3*); like **24**, it displays crystallographic inversion symmetry. Unfortunately the large amount of included solvent leads to data with poorer resolution than one would expect at low temperature. The structure is closely related to the structure of the mononuclear analogue **XIII**, also drawn in the Figure.[18] *Table V.4* shows, for comparison, the bond

[c] Crystals were mounted in inert oil on glass fibers. Intensity data were recorded on a Bruker SMART 1000 CCD (**24, 27**),or a Bruker APEX-2 diffractometer (**28**) using monochromated Mo *K*α radiation. Absorption corrections were based on multi-scans. The NH hydrogens, where present, were refined freely but with distance restraints. Other hydrogen atoms were included using rigid methyl groups or a riding model. Structures were refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany). *Special features and exceptions*: In structure **24**, both chloroform molecules, the triflate anion and one *t*-butyl group are disordered. The dataset for **27** was of limited resolution because of the large amount of solvent. For **28** no absorption correction was applied; the $CDCl_3$ molecule was disordered.

distances and angles for both complexes, **27**·2CH_2Cl_2·3hexane and **XIII**·CH_2Cl_2[18] Similarly, the structure of **28** (*Figure V.4*) is closely related to the structure of the 3-alkylidene-2,3-dihydroisoindolinone **XIV**,[14] and *Table V.5* shows, for comparison, the bond distances and angles for both compounds, **28**·2$CDCl_3$ and **XIV**·0.5Et_2O.[14] *Chart V.1* shows the numbering system used in this work for the complexes **27** and **XIII**, as well as for the organic compounds **28** and **XIV**.[d]



27 and **XIII**



28 and **XIV**

Chart V.1 Numbering system used in the X-ray data discussion of **27** and **28**

The Pd atom in **27**·2CH_2Cl_2·3hexane shows square planar coordination to a reasonable approximation, with a mean deviation from the best plane through Pd and the four donor atoms of 0.07 Å. The Pd-C(10) bond distance of the iminoacyl ligand is 2.041(7) Å, similar to that of **XIII**·CH_2Cl_2 (2.031(3) Å),[18] and considerably longer than the Pd-C bond distances in the aryl palladium complexes reported in this Thesis (between 1.9903(19) and 2.012(3) Å). Pd-C bond distances in iminoacyl ligands vary considerable depending on the influence of the *trans* ligand.[18,19] The Pd-C bond distances of the isocyanide ligands, Pd-C(40) and Pd-C(50), are slightly shorter in **27**·2CH_2Cl_2·3hexane (both 1.969(8) Å) than in **XIII**·CH_2Cl_2 (1.986(3) and 1.999(3) Å) and similar to the values found in other Pd complexes with two mutually *trans* XyNC ligands (ca. 1.96-1.99 Å in those reported by us).[18-20] Finally, the Pd-Br bond distances of 2.5338(10) Å for **27**·2CH_2Cl_2·3hexane and 2.5288(4) Å for **XIII**·CH_2Cl_2,[18] are similar to those observed in other complexes where the Br ligand is *trans* to an iminoacyl ligand.[18,21]

The data in *Tables V.4* and *V.5* suggest for the four compounds, **27**·2CH_2Cl_2·3hexane, **XIII**·CH_2Cl_2, **28**·2$CDCl_3$, and **XIV**·0.5Et_2O, a delocalization of π electron density along the N-C(4)=O bonds within the five-membered ring (*Chart V.1*). This suggestion is based on the short N-C(4) bond distance (ca. 1.38 Å), compared with

[d] The original numbering in the X-ray diffraction studies of compounds **XIII**·CH_2Cl_2 and **XIV**·0.5Et_2O was different from the numbering used here for **27**·2CH_2Cl_2·3hexane and **28**·2$CDCl_3$. To facilitate comparison, in this work we have changed the numberings in **XIII**·CH_2Cl_2 and **XIV**·0.5Et_2O to make them compatible with those of **27**·2CH_2Cl_2·3hexane and **28**·2$CDCl_3$.

the ca. 1.43-1.44 Å value for the N(3)-C(30) (**27** and **XIII**) or N(1)-C(1) (**28** and **XIV**) bonds, within the same ring. The angles around the N atoms within the five-membered ring (N(3) or N(1)) also support this suggestion, as their values are ca. 112º (for C(4)-N(3)-C(30) or C(4)-N(1)-C(1)), 118-121º (for C(4)-N(3)-C(31) or C(4)-N(1)-C(11)), and 127-129º (for C(30)-N(3)-C(31) or C(1)-N(1)-C(11)).

We also find a delocalization of π electron density along the N(2)-C=C bonds, (N(2)-C(20)-C(30) for **27** and **XIII**, and N(2)-C(6)-C(1) for **28** and **XIV**). This suggestion is based again on the short N(2)-C(20) or N(2)-C(6) bond lengths of ca. 1.37-1.39 Å, which are intermediate between the values for the double bonds N(1)=C(10) (in **27** and **XIII**; 1.261(9) and 1.267(3) Å, respectively) and the single bonds N(2)-C(21) (ca. 1.42-1.43 Å for the four compounds). The wide C-N(2)-C(21) angles (between ca. 125 and 129º), and the short C=C bonds (C(30)-C(20) or C(1)-C(6), all ca. 1.36 Å), compared with the adjacent C(30)-C(2) (**27** and **XIII**) or C(1)-C(2) (**28** and **XIV**) bonds (ca. 1.46-1.47 Å), also support this suggestion.

The delocalization of π electron density is also reflected in the almost planar arrangement of the atoms in the heterocyclic core, O(1), the carbons of the aliphatic chain and N(2). Thus, for **27** and **XIII** the atoms C(1)-C(2)-C(3)-C(4)-O-N(3)-C(31)-C(30)-C(20)-C(10)-N(2)-C(21) are almost coplanar (mean deviation 0.07 Å for **27**), as are (to a lower degree), for **28** and **XIV** the atoms C(5)-C(3)-C(2)-C(4)-O(1)-N(1)-C(31)-C(1)-C(6)-C(7)-N(2)-C(21) (the mean deviation is larger, 0.17 Å for **28**).

In the organic compounds, **28**·2$CDCl_3$·and **XIV**·0.5Et_2O, we also find a delocalization of electron density over the bonds N(3)-C(7)-O(2), as shown by the coplanarity of the group of atoms C(31)-N(3)-C(7)-O(2)-C(6), with mean deviations of 0.02 Å for **28** and 0.01 Å for **XIV**.[14] The angle between this plane and the major plane described in the previous paragraph is 89.5º for **28**. The N(3)-C(7) bond lengths (1.3540(19) Å for **28** and 1.358(3) Å for **XIV**) are even shorter than the N(1)-C(4) (1.3799(19) Å for **28** and 1.379(3) Å for **XIV**) and N(2)-C(6) bond lengths (1.3721(19) Å for **28** and 1.371(3) Å for **XIV**). The carbonyl C=O bond lengths (C(7)-O(2), 1.2195(19) Å (**28**) and 1.224(2) Å (**XIV**); C(4)-O(1), 1.2252(19) Å (**28**) and 1.234(2) Å (**XIV**)) are as expected for C_{sp2}=O amides.[15]

Table V.2 X-ray crystallographic data for compounds **24**·4$CHCl_3$, **27**·2CH_2Cl_2·2hexane, and **28**·2$CDCl_3$

	24·4$CHCl_3$	**27**·2CH_2Cl_2·2hexane	**28**·2$CDCl_3$
Formula	$C_{58}H_{74}Cl_{12}F_6N_6O_6Pd_2S_2$	$C_{118}H_{140}Br_2Cl_4N_{10}O_2Pd_2$	$C_{64}H_{60}D_2Cl_6N_6O_4$
M_r	1767.55	2244.82	1193.91
T (K)	133(2)	133(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
cryst syst	Triclinic	Monoclinic	Triclinic
space group	P(-1)	$P2_1/n$	P(-1)
cell constants			
a (Å)	11.9565(7)	16.1438(19)	8.7235(8)
b(Å)	12.5085(8)	19.885(2)	12.5281(12)
c (Å)	13.4126(8)	18.120(2)	14.1188(14)
α (deg)	105.376(3)	90	101.419(4)
β (deg)	94.960(3)	103.313(3)	94.655(4)
γ (deg)	102.884(3)	90	99.974(4)
V (Å^3), Z	1862.7(2), 1	5660.5(11), 2	1478.9(2), 1
ρ (calcd) (Mg m^{-3})	1.576	1.317	1.340
abs. coef. (mm^{-1})	1.034	1.171	0.344
F(000)	894	2328	622
cryst size (mm)	0.40 x 0.30 x 0.15	0.40 x 0.30 x 0.15	0.25 x 0.15 x 0.13
θ range (deg)	1.59 -30.03	1.52 -25.53	2.39 -30.51
	$-16 \le h \le 16$	$-19 \le h \le 19$	$-12 \le h \le 12$
index ranges	$-17 \le k \le 17$	$-24 \le k \le 24$	$-17 \le k \le 17$
	$-18 \le l \le 18$	$-21 \le l \le 21$	$-20 \le l \le 20$
reflections collected	37843	47241	37642
independent reflections	10792	10450	9012
R_{int}	0.0329	0.1178	0.0268
abs corr	Semi-empirical from equivalents	Semi-empirical from equivalents	None
transmissions	0.8604 - 0.7421	0.8439 - 0.5900	0.9566 - 0.9189
refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
no. of data/restraints/params	10792 / 331 / 547	10450 / 927 / 620	9012 / 40 / 388
goodness-of-fit on F^2	1.232	1.067	1.029
Final R indices (I>2σ(I))			
R1	0.0685	0.0821	0.0527
wR2	0.1841	0.1823	0.1345
R indices (all data)			
R1	0.0806	0.1424	0.0686
wR2	0.1889	0.2065	0.1463
largest diff peak (e Å^{-3})	1.450	1.327	0.856
largest diff hole (e Å^{-3})	-1.428	-1.180	-0.756

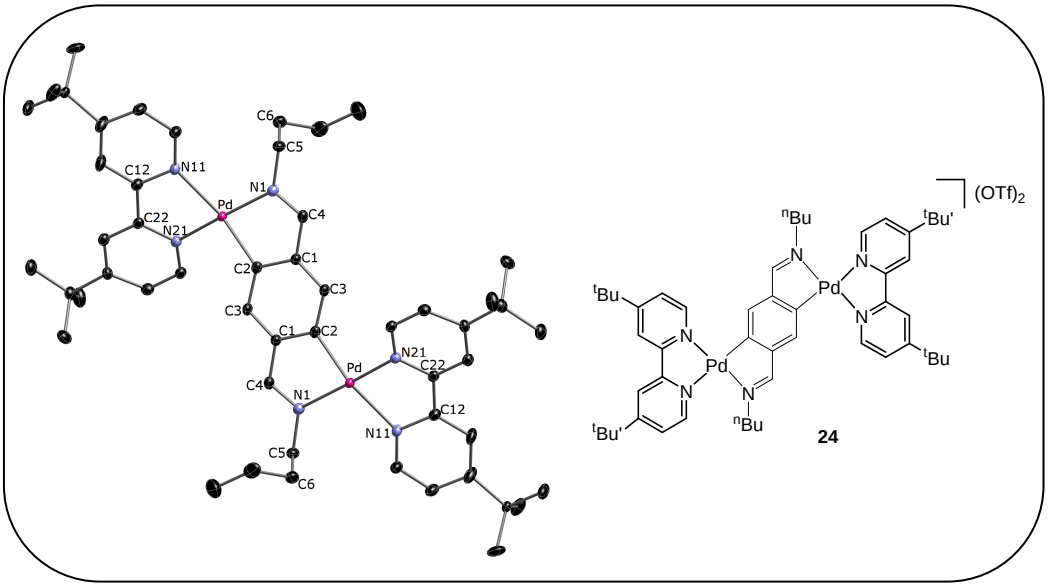


Figure V.2
Thermal ellipsoid plot (50% probability level) of **24**·4$CHCl_3$. Only the cation is shown

Table V.3 Selected bond lengths (Å) and angles (deg) of **24**·4$CHCl_3$

Pd-C(2)	2.002(5)	C(2)-Pd-N(1)	80.3(2)
Pd-N(1)	2.058(5)	C(2)-Pd-N(21)	98.5(2)
Pd-N(21)	2.039(5)	N(21)-Pd-N(11)	78.14(17)
Pd-N(11)	2.160(4)	N(1)-Pd-N(11)	104.84(17)
C(1)-C(2)	1.428(7)	N(21)-Pd-N(1)	172.26(19)
C(1)-C(4)	1.428(7)	C(2)-Pd-N(11)	165.77(19)
N(1)-C(4)	1.291(7)	C(4)-C(1)-C(2)	114.1(5)
		C(1)-C(2)-Pd	113.1(4)
		N(1)-C(4)-C(1)	117.8(5)
		C(4)-N(1)-Pd	114.6(4)

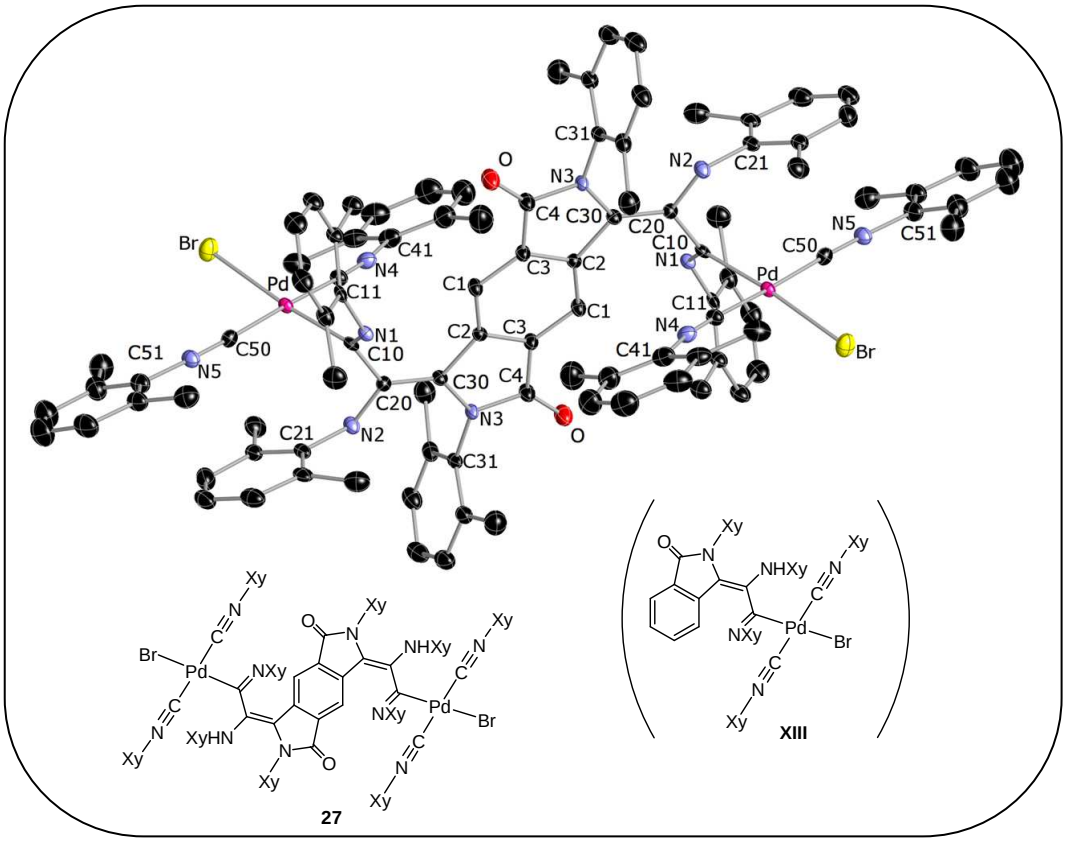


Figure V.3

Thermal ellipsoid plot (50% probability level) of **27**·$2CH_2Cl_2$·3hexane

Table V.4

Comparison of selected bond lengths (Å) and angles (deg) of **27**·$2CH_2Cl_2$·3hexane and **XIII**·CH_2Cl_2

	27	**XIII**		**27**	**XIII**
Pd-C(40)	1.969(8)	1.999(3)	C(40)-Pd-C(10)	89.8(3)	90.64(11)
Pd-C(50)	1.969(8)	1.986(3)	C(50)-Pd-C(10)	92.5(3)	93.09(11)
Pd-C(10)	2.041(7)	2.031(3)	C(40)-Pd-Br	88.5(2)	88.30(8)
Pd-Br	2.5338(10)	2.5288(4)	C(50)-Pd-Br	89.7(2)	88.25(9)
N(1)-C(10)	1.261(9)	1.267(3)	C(40)-Pd-C(50)	174.0(3)	173.50(12)
N(2)-C(20)	1.389(9)	1.378(3)	C(10)-Pd-Br	174.9(2)	176.82(7)
N(3)-C(30)	1.428(9)	1.439(3)	C(20)-C(10)-Pd	114.1(5)	112.93(17)
C(2)-C(30)	1.471(10)	1.476(4)	C(30)-C(20)-C(10)	123.2(6)	123.0(2)
N(1)-C(11)	1.428(9)	1.413(4)	C(20)-C(30)-N(3)	125.4(6)	123.6(2)
N(2)-C(21)	1.421(10)	1.426(3)	C(10)-N(1)-C(11)	127.2(6)	127.9(3)
N(3)-C(31)	1.437(10)	1.440(3)	C(20)-N(2)-C(21)	125.3(6)	125.8(2)
C(10)-C(20)	1.475(10)	1.503(4)	C(4)-N(3)-C(30)	112.6(6)	112.3(2)
C(20)-C(30)	1.364(10)	1.368(4)	C(4)-N(3)-C(31)	117.9(6)	119.7(2)
O-C(4)	1.217(9)	1.220(3)	C(30)-N(3)-C(31)	129.5(6)	127.9(2)
N(3)-C(4)	1.388(10)	1.384(4)	N(4)-C(40)-Pd	175.1(7)	171.9(3)
N(4)-C(40)	1.159(9)	1.151(4)	C(40)-N(4)-C(41)	168.0(8)	173.7(3)
N(5)-C(50)	1.167(9)	1.150(4)	N(5)-C(50)-Pd	169.2(7)	169.3(3)
N(4)-C(41)	1.414(10)	1.408(4)	C(50)-N(5)-C(51)	171.0(8)	174.5(3(
N(5)-C(51)	1.404(10)	1.410(3)			

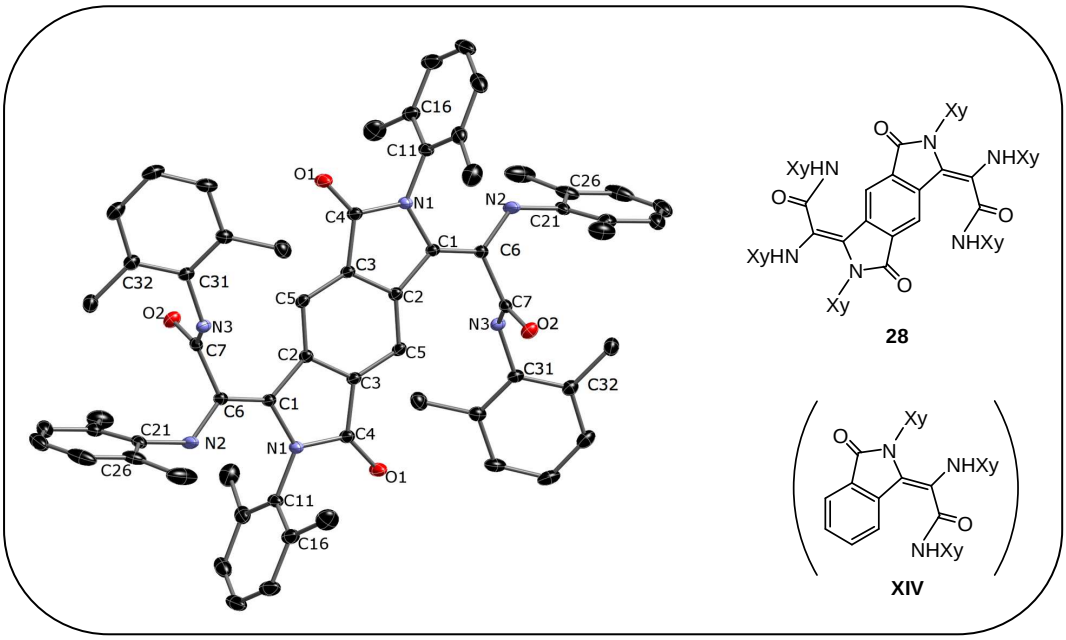


Figure V.4
Thermal ellipsoid plot (50% probability level) of **28**·2$CDCl_3$

Table V.5 Selected bond lengths (Å) and angles (deg) of **28**·2$CDCl_3$. and **XIV**·0.5Et_2O

	28	**II**		**28**	**XIV**
C(1)-C(6)	1.357(2)	1.357(3)	C(6)-C(1)-N(1)	125.80(13)	125.57(19)
C(1)-N(1)	1.4270(18)	1.438(2)	C(6)-C(1)-C(2)	128.67(13)	129.02(19)
C(1)-C(2)	1.4621(19)	1.465(3)	N(1)-C(1)-C(2)	105.35(12)	105.17(17)
C(4)-O(1)	1.2252(19)	1.234(2)	C(5)-C(2)-C(3)	118.98(13)	118.83(19)
C(4)-N(1)	1.3799(19)	1.379(3)	C(5)-C(2)-C(1)	133.20(13)	133.56(19)
C(4)-C(3)	1.467(2)	1.458(3)	C(3)-C(2)-C(1)	107.81(12)	107.60(18)
C(6)-N(2)	1.3721(19)	1.372(3)	C(5)-C(3)-C(2)	124.62(13)	121.9(2)
C(6)-C(7)	1.522(2)	1.519(3)	C(5)-C(3)-C(4)	126.67(13)	128.7(2)
C(7)-O(2)	1.2195(19)	1.224(2)	C(2)-C(3)-C(4)	108.70(13)	109.34(18)
C(7)-N(3)	1.3540(19)	1.358(3)	O(1)-C(4)-N(1)	125.13(14)	124.1(2)
C(11)-N(1)	1.4334(18)	1.442(3)	O(1)-C(4)-C(3)	128.96(14)	129.88(19)
C(21)-N(2)	1.419(2)	1.432(3)	N(1)-C(4)-C(3)	105.88(12)	106.00(17)
C(31)-N(3)	1.4397(19)	1.445(3)	C(1)-C(6)-N(2)	124.75(14)	123.67(19)
			C(1)-C(6)-C(7)	118.67(12)	118.38(18)
			N(2)-C(6)-C(7)	116.50(13)	117.83(18)
			O(2)-C(7)-N(3)	123.66(14)	123.43(19)
			O(2)-C(7)-C(6)	120.29(13)	119.80(18)
			N(3)-C(7)-C(6)	116.04(13)	116.73(18)
			C(4)-N(1)-C(1)	112.18(12)	111.79(17)
			C(4)-N(1)-C(11)	120.43(12)	120.86(17)
			C(1)-N(1)-C(11)	127.29(12)	126.79(16)
			C(6)-N(2)-C(21)	125.75(14)	128.62(19)
			C(7)-N(3)-C(31)	122.54(13)	123.47(18)

V.3 CONCLUSIONS

We have prepared two dipalladated derivatives of terephthalaldehyde by hydrolysis of a previously described dipalladated Schiff base. A dicationic dinuclear derivative of the Schiff base has also been characterized, including an X-ray diffraction structure. The reactivity of the dinuclear terephthalaldehyde complexes towards CO and XyNC has been investigated. Thus, the first double insertion of CO into two separate aryl-metal bonds on the same aryl ligand has been achieved. In the resulting complexes the two inserted CO groups are inequivalent, as one of them seems to form a hydrogen bond with the adjacent aryl proton, while the same would not happen for the other CO group. These insertion reactions have been investigated with the help of ^{13}CO, whereby an unexpected exchange process between the inserted CO and the formyl group in *ortho* position was evidenced. In the reactions with XyNC we have isolated a novel dinuclear Pd(II) complex, resulting from a double 3-fold insertion of XyNC into the aryl-Pd bonds, followed by the interaction of two of the inserted isocyanide molecules with the formyl groups in *ortho*. This complex has been characterized by X-ray crystallography. By a Tl^+-promoted hydrolysis of the complex the central ligand can be released, and the resulting polycyclic heterocycle has also been characterized by X-ray crystallography.

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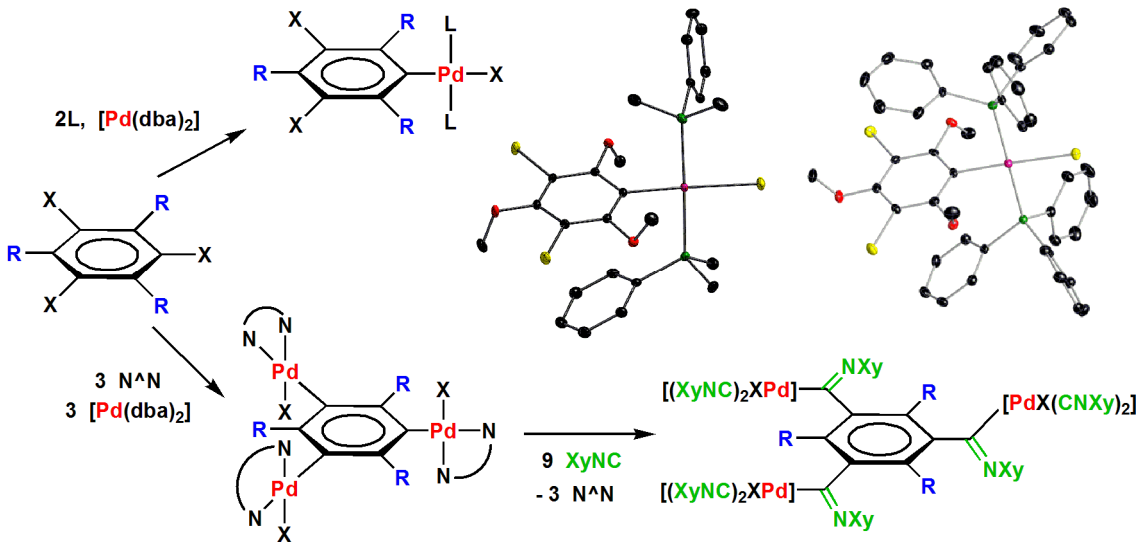
CHAPTER VI

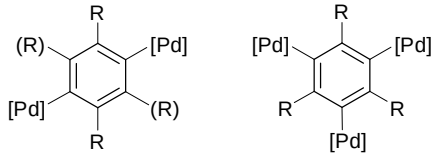
Synthesis of Mono- and Tripalladated 2,4,6-Trisubstituted Arenes. 3-Fold Insertion of XyNC into Three Aryl-Palladium Bonds on the Same Arene



The results of this Chapter will soon be submitted for publication

VI.1 INTRODUCTION

Our group is interested in the synthesis of polypalladated benzene derivatives with functionalized organic substituents *ortho* to each Pd atom (*Chart VI.1*),[1-6] as an extension of our successful chemistry with (mononuclear) *ortho*-substituted arylpalladium complexes, and their reactivity with unsaturated organic molecules (see Chapter I, General Introduction, and the Introductions to the Chapters II-IV). These molecules may insert into the aryl-Pd bonds and interact with the groups in *ortho* position, providing interesting polynuclear organometallic complexes and organic polycyclic compounds.



(A) **(B)**

Chart VI.1 Di- (**A**) and tri-(**B**) palladated *ortho*-substituted arenes

Several groups, including ours,[2,6,7] have reported on dipalladated *ortho*-substituted aryl complexes of type (**A**) (*Chart VI.1*), usually dipalladacycles with N-donor groups.[7,8] Chapters IV and V of this Thesis describe the synthesis and reactivity of dipalladated derivatives of 2,5-distyrylbenzene[2,6] and terephthalaldehyde, respectively. In this Chapter our aim was to prepare tripalladated derivatives of type (**B**), i.e. with general formula $C_6R_3[Pd]_3$ (*Chart VI.1*).

Although the synthesis and applications of polymetalated derivatives of benzene ($C_6R_{6-n}M_n$, n = 3–6) are well-documented, most of them involve representative elements. The element best studied is Hg(II), for which examples with three[17], four,[18-20] five[19,21,22] and six [9] metal atoms around a benzene ring have been reported. Hexalithiobenzene has also been described, and shown to possess excellent thermodynamic stability.[10] There are also many reports on 1,3,5-trilithiobenzene[11,12] (the use of which to prepare trimetalated Mg, Hg and Sn derivatives has also been described[11]), and symmetrically 2,4,6-trisubstituted derivatives thereof.[13] 1,3,5-tris(trimethylstannyl)benzene[14] has been obtained by several routes[20,24,27,28] and it has been used in coordination,[15] transmetallation,[12,16] and C–C bond forming reactions.[17] 1,3,5-Tris(trimethylgermyl)benzene[18] and hexakis(trimethylgermyl)benzene[19] have also been reported.

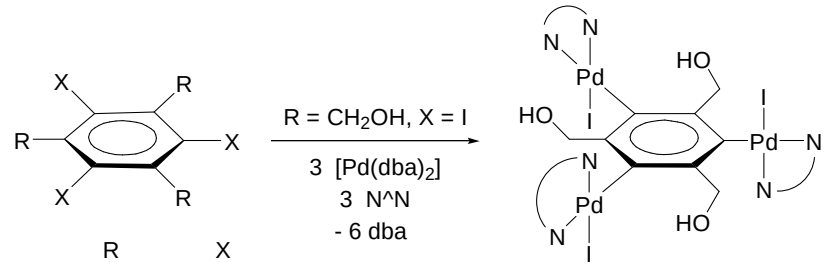
As regards transition metal derivatives, research has been conducted on metal clusters with face-capping arene ligands $\mu^3,\eta^2,\eta^2,\eta^2$ coordinated to three metal atoms such as Co,[20] Ru,[35,36] Rh,[21] and Os.[35,38,39] An unusual $\mu^3,\eta^1,\eta^1,\eta^1$ coordination mode has been described as well.[22] These compounds have been proposed as models for benzene adsorption at a 3-fold site on the surface of a close-packed metal lattice.[23] Very recently, a similar situation has been described for Pd in a μ^3-tripalladium sandwich complex,[24] and there are also reports on Pd3 to Pd5 sheets between polycyclic aromatic hydrocarbon ligands.[25] However, there has been very little research on σ-bonded polymetalated derivatives of benzene with transition metals. Until recently the only examples were 1,3,5-$C_6H_3[Mn(CO)_5]_3$,[26] 1,3,5-$C_6H_3[Fe(\eta^5\text{-Cp})(CO)_2]_3$,[26,27] and 1,3,5-$C_6H_3[Fe(\eta^5\text{-}C_5H_4Me)(CO)_2]_3$,[28] prepared in two steps involving the reaction of Na[M] ([M] = $[Mn(CO)_5]$, $[Fe(\eta^5\text{-Cp})(CO)_2]$ or $[Fe(\eta^5\text{-}C_5H_4Me)(CO)_2]$), with 1,3,5-$C_6H_3(COCl)_3$, and subsequent decarbonylation of the resulting 1,3,5-$C_6H_3[C(O)M]_3$ triacyl complexes. The two first complexes were later prepared by reaction of 1,3,5-triiodobenzene with three equivalents of $[KMn(CO)_5]$ or $[Fe(\eta^5\text{-Cp})(CO)_2]ZnCl$, respectively.[29] In 2001 our group published the first tripalladated benzene derivative, prepared by oxidative addition of 1,3,5-triiodomesitylene to three equivalents of $[Pd(dba)_2]$ in the presence of chelating N-donor ligands.[1] Shortly after that, another group reported the first 3-fold cyclopalladation of a single benzene ring, 1,3,5-tris(di-2-pyridylamino)benzene.[30] In 2009 we published a report on mono-, di-, and tripalladated 1,3,5-benzenetricarboxaldehyde complexes[3] and in 2011 we reported a Pd_3Tl derivative prepared by reaction of a trinuclear Pd complex of type **B** (R = Me)[1] with TlOTf (see *Scheme VI.4* in this Chapter).[4] Since then there have been no further reports on the subject, in spite of its potential interest for the Pd-mediated synthesis of organic polycyclic compounds and in the field of metallodendrimers.[31]

We have tried to extend this chemistry to tripalladated derivatives of type (**B**) (*Chart VI.1*), with R = CH_2OH, OH, and OMe. These R groups were chosen with the aim of expanding the chemistry developed with the related mononuclear complexes, C_6H_4(R-2)[Pd], in Chapters II and III of this Thesis (R = CH_2OH),[32] or in previous publications of our group (R = OH).[33,34] The group R = OMe was chosen (with no success) when the synthesis of a tripalladated derivative with R = OH failed (see Section VI.2.1). We have nonetheless been successful in the synthesis of two tripalladated complexes with R = CH_2OH and, although the investigation of its reactivity towards unsaturated molecules

has not given positive results yet, we have achieved a 3-fold insertion of XyNC into the aryl-Pd bonds of the trinuclear derivative with R = Me.

VI.2 RESULTS AND DISCUSSION

VI.2.1 Oxidative Addition Reactions



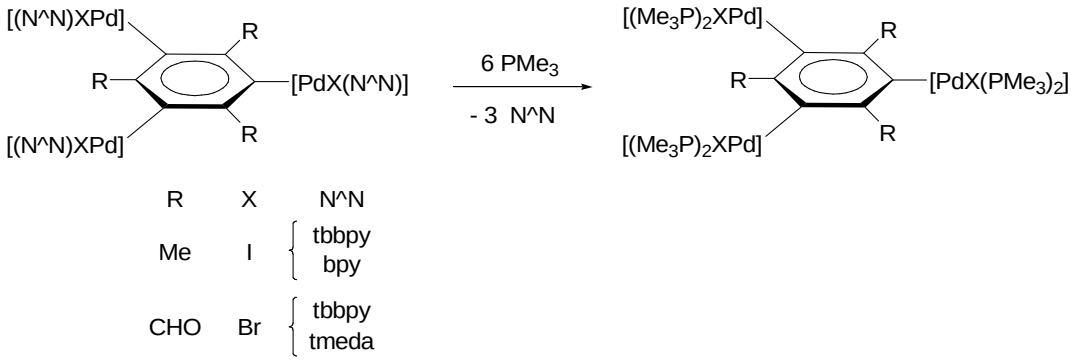
	R	X
XV	CH_2OH	I
XVI	OH	I
XVI'	OH	Br
XVII	OMe	I
XVII'	OMe	Br

Scheme VI.1 Synthesis of complexes **29a,b**

The trisubstituted trihaloarene 1,3,5-$C_6(CH_2OH)_3I_3$ (**XV**, *Scheme VI.1*) has been prepared according to a literature procedure[35,a] (see Chapter VIII, Experimental Section). By oxidative addition of **XV** to three equivalents of $[Pd(dba)_2]$, in the presence of tbbpy or tmeda, the trinuclear arylpalladium complexes $[\{PdI(N\hat{}N)\}_3(\mu_3\text{-}C1,C3,C5\text{-}C_6(CH_2OH)_3\text{-}2,4,6\}]$ (N^N = tbbpy (**29a**), N^N = tmeda (**29b**), *Scheme VI.1*) have been obtained. A similar reaction with bpy resulted in an insoluble product which we could not characterize (low solubility is often a drawback when using bpy as an auxiliary ligand in polynuclear arylpalladium complexes).[1,3,6] Complex **29a** was obtained with higher purity when using a 20% excess of $[Pd(dba)_2]$ and tbbpy, while for **29b** a stoichiometric amount of the reactants was sufficient. Both reactions have to be conducted carefully, under N_2 and in distilled toluene, to avoid the formation of $[PdI_2(N\hat{}N)]$ (N^N = tbbpy, tmeda). These undesired byproducts are identified by their characteristic NMR resonances at 9.84 ppm (dd) or 2.95 ppm (s), respectively, as well as by the red color of the tbbpy complex. Once they are formed in the reaction they are very difficult to separate from **29a,b**. Complexes $[Pd(C_6H_4CH_2OH\text{-}2)I(N\hat{}N)]$ (N^N = bpy (**1a**), tbbpy (**1b**), and tmeda (**1c**), Chapter II)[32] are mononuclear analogues to **29a,b** with a single CH_2OH substituent on the arene.

[a]The tribrominated analogue, 1,3,5-$C_6(CH_2OH)_3Br_3$, is also known (Bruns, D.; Miura, H.; Stanger, A.; Vollhardt, K. P. C.; *Organic Letters* **2003**, 5, 549), but we have not investigated its chemistry in this work.

As already mentioned in the Introduction to this Chapter, our research group has similarly prepared other tripalladated benzene derivatives, with R = Me, X = I, N^N = tbbpy, bpy,[1] and R = CHO, X = Br, N^N = tmeda, tbbpy.[3] Starting from them it was possible to synthesize complexes of general formula [{PdX(PMe_3)$_2$}$_3$(μ_3-*C1,C3,C5*-C_6R_3-2,4,6}] (R = Me, X = I; R = CHO; X = Br, *Scheme VI.2*), by displacement of the N^N ligands with an excess of PMe_3. A similar reaction with **29a** or **29b** also results in the formation of the corresponding PMe_3 complex, [{PdI(PMe_3)$_2$}$_3$(μ_3-*C1,C3,C5*-$C_6(CH_2OH)_3$-2,4,6}], but this product could not be sufficiently purified for a full characterization.



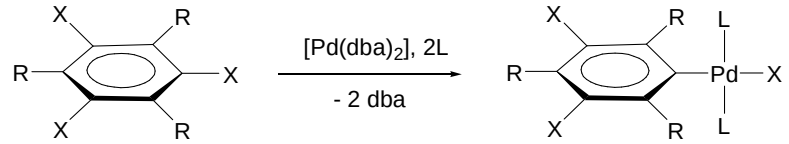
Scheme VI.2 Synthesis of trinuclear PMe_3 complexes starting from complexes with N^N ligands

The use of substoichiometric amounts of [Pd(dba)$_2$] and tmeda/tbbpy in the synthesis of **29a,b** results in the formation of the same trinuclear complexes, although with a lower yield and purity. This behavior is similar to that observed with the arene 1,3,5-$C_6Me_3I_3$.[1] In contrast, with 1,3,5-$C_6(CHO)_3Br_3$,[3] the electron-withdrawing nature of the CHO groups allowed a selectivity in the number of oxidative additions undergone by the arene, and thus mono- ([Pd{$C_6(CH_2OH)_3$-2,4,6-Br_2-3,5}Br(N^N)]) and dinuclear ([{PdBr(N^N)}$_2$(μ_2-*C1,C3*-$C_6(CH_2OH)_3$-2,4,6-Br-5)]) palladium complexes could be isolated.

To further expand our chemistry on tripalladated trisubstituted arenes we have synthesized the trihaloarenes 1,3,5-$C_6R_3X_3$ (R = OH, X = I (**XVI**),[36] R = OH, X = Br (**XVI'**),[37] R = OMe, X = I (**XVII**),[38] R = OMe, X = Br (**XVII'**)[39], *Scheme VI.1*). Unfortunately, their reactions with [Pd(dba)]$_2$ in the presence of tmeda or tbbpy have resulted in mixtures of compounds (with a predominance of [PdX_2(N^N)]). It would seem that the presence of an O atom directly bonded to the arene is highly detrimental for the success of multiple oxidative addition reactions. In contrast, the oxidative addition of

2-iodophenol[33,40] or 2-iodoanisole[41] to [Pd(dba)$_2$] in the presence of different N^N ligands (bpy, tbbpy, tmeda, phen), to form complexes [Pd(C_6H_4OR-2)I(N^N)] (R = H, Me, N^N = bpy, tbbpy, tmeda, phen), is a facile reaction.

We have also investigated the oxidative addition reactions of the trihaloarenes **XV-XVII** to [Pd(dba)$_2$] in the presence of phosphine ligands. In our previous experience with 1,3,5-$C_6Me_3I_3$[1] and 1,3,5-$C_6(CHO)_3Br_3$,[3] the oxidative additions in the presence of PPh_3 afforded only mononuclear complexes of general formula *trans*-[Pd{C_6R_3-2,4,6-X_2-3,5}X(PPh_3)$_2$] (R = Me, X = I; R = CHO, X = Br), while the reactions with the more basic and less sterically demanding PMe_2Ph allowed the synthesis of mono- (*trans*-[Pd{C_6R_3-2,4,6-X_2-3,5}X(PMe_2Ph)$_2$]) and dinuclear ([{*trans*-PdX(PMe_2Ph)$_2$}$_2$(μ_2-*C1,C3*-C_6R_3-2,4,6-X-5)]) complexes (R = Me, X = I; R = CHO, X = Br). In our present work, we have been able to synthesize the mononuclear complexes *trans*-[Pd{C_6R_3-2,4,6-X_2-3,5}X(PPh_3)$_2$] (R = CH_2OH, X = I (**30**), R = OH, X = Br (**30'**), R = OMe, X = Br (**30"**), *Scheme VI.3*), by reaction of **XV**, **XVI'** and **XVII'** with [Pd(dba)$_2$] in the presence of PPh_3.



	R	X
XV	CH_2OH	I
XVI	OH	I
XVI'	OH	Br
XVII	OMe	I
XVII'	OMe	Br

	L	R	X
30	PPh_3	CH_2OH	I
30'	PPh_3	OH	Br
30"	PPh_3	OMe	Br
31	PMe_2Ph	OMe	Br

Scheme VI.3 Synthesis of complexes **30**, **30'**, **30"**, and **31**

In these reactions with PPh_3, the conditions have to be carefully adjusted to obtain pure products. Thus, in the reaction with 1,3,5-$C_6(CH_2OH)_3I_3$ (**XV**) a 3-fold excess of PPh_3 was necessary (ratio **XV**:[Pd(dba)$_2$]: PPh_3 1:1:6), and the reaction was finished at 0ºC in only 15 min. Other reactant ratios (1:1:2, 1:1:4 or 1:3:6) resulted in the formation of undesired products, together with **30**. With 1,3,5-$C_6(OH)_3Br_3$ (**XVI'**) we always obtained a mixture of **30'** with [$PdBr_2(PPh_3)_2$], which is identified by its ^{31}P resonance at 25 ppm (in $CDCl_3$). Different reactant proportions or reaction times only resulted in a different ratio of the two products, but not in the formation of pure **30'**. The reaction temperature had to be kept low (0ºC or room temperature), because heating resulted in

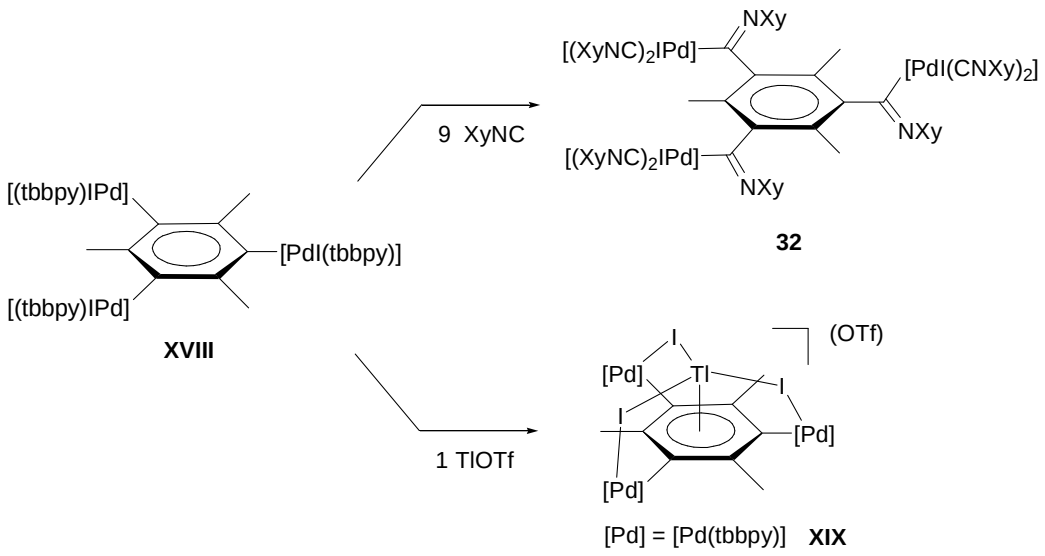
the formation of mostly $OPPh_3$. We finally established that the best conditions for this reaction were using a 2-fold excess of PPh_3 (ratio **XVI'**:[$Pd(dba)_2$]: PPh_3 1:1:4), and leaving the reaction at room temperature overnight. The ratio **30'**:[$PdBr_2(PPh_3)_2$] in the crude product was thus ca. 3:1, and **30'** could be purified by washing with cold $CHCl_3$, in which **30'** is less soluble than [$PdBr_2(PPh_3)_2$] (see Chapter VIII, Experimental Section). With the arene 1,3,5-$C_6(OMe)_3Br_3$ (**XVII'**), the clean synthesis of complex **30"** required an excess of the arene (ratio **XVII'**:[$Pd(dba)_2$]:PPh_3 2:1:2) and high temperature (110ºC, 45 min), as otherwise mixtures of compounds were obtained. These different reactions conditions required for the synthesis of **30, 30'** and **30"** are in contrast with our previously reported syntheses of *trans*-[Pd{C_6R_3-2,4,6-X_2-3,5}X(PPh_3)$_2$] (R = Me, X = I;[1] R = CHO, X = Br[3]), which proceeded cleanly when using a stoichiometric 1:1:2 ratio (arene:[$Pd(dba)_2$]:PPh_3). The analogous PPh_3 complexes with monosubstituted arenes, *trans*-[Pd{C_6H_4R-2}X(PPh_3)$_2$] (R = CH_2OH, X = Br,[42] I[32,43]; R = OH, X = I[40] (not Br), and R = OMe, X = I[44] (not Br)), are known and have also been prepared by oxidative addition reactions (*trans*-[Pd{$C_6H_4CH_2OH$-2}Br(PPh_3)$_2$] is a commercial catalyst for the low pressure carbonylation of arylmethyl halides leading to phenylacetic acids[45]). The reactions of the tri-iodo arenes 1,3,5-$C_6(OR)_3I_3$ (R = H (**XVI**), Me (**XVII**)) with [$Pd(dba)_2$] and PPh_3 resulted in mixtures of compounds, and they were not further pursued after the characterization of the bromo complexes **30'** and **30"** was finally achieved.

The oxidative addition reactions of the trihaloarenes **XV-XVII** to [$Pd(dba)_2$] in the presence of PMe_2Ph have only given a positive result with 1,3,5-$C_6(OMe)_3Br_3$ (**XVII'**), which formed the mononuclear complex *trans*-[Pd{$C_6(OMe)_3$-2,4,6-Br_2-3,5}Br(PMe_2Ph)$_2$]) (**31,** *Scheme VI.3*), even when the ratio **XVII'**:[$Pd(dba)_2$]:PMe_2Ph was 1:2:4 (the adequate ratio for the synthesis of a dinuclear complex). Heating the reaction or using a larger excess of [$Pd(dba)_2$] and PMe_2Ph did not result in the formation of a dinuclear complex, either. When the stoichiometric ratio **XVII'**: [$Pd(dba)_2$]:PMe_2Ph was 1:1:2, the mononuclear complex **31** was also obtained, although in a lower yield and less pure. Preliminary reactions with the tri-iodo analogue, 1,3,5-$C_6(OMe)_3I_3$ (**XVII**), and [$Pd(dba)_2$] and PPh_2Me did not give a better result and were thus abandoned. Similar reactions with 1,3,5-$C_6(CH_2OH)_3I_3$ (**XV**), under different conditions and stoichiometric **XV**:[$Pd(dba)_2$]:PPh_2Me ratios resulted in mixtures of mono- and dinuclear complexes (plus other products), which could not be separated or characterized. Finally the reactions of 1,3,5-$C_6(OH)_3I_3$ (**XVI**) and 1,3,5-$C_6(OH)_3Br_3$ (**XVI'**) with [$Pd(dba)_2$] and PPh_2Me

resulted in mixtures of $[PdX_2(PMe_2Ph)_2]$ (X = Br, I) and other, unidentified, products. The analogue complexes to **31** with a single substituent on the arene, *trans*-$[Pd\{C_6H_4R\text{-}2\}X(PMe_2Ph)_2]$, R = CH_2OH, OH, OMe; X = Br, I) have not been described.

VI.2.2 Reactivity of the Tripalladated 2,4,6-Trisubstituted Arenes

We have investigated the reactivity of the tripalladated complexes **29a,b** toward carbon monoxide, xylyl isocyanide and several nitriles, with and without the presence of TlOTf, but we have always obtained mixtures of compounds which we could not characterize. As described in Chapter II, the mononuclear analogue $[PdI\{C_6H_4CH_2OH\text{-}2\}(bpy)]$ (**1a**),[32] has not given good results in insertion reactions either, except with XyNC, which formed the unstable product *trans*-$[PdI\{C(=NXy)(C_6H_4CH_2OH\text{-}2)\}(CNXy)_2]$ (**2**).[32] Although this reactivity toward XyNC could not be reproduced with the trinuclear complexes **29a,b**, we have been successful in achieving a 3-fold XyNC insertion, in three separate C-Pd bonds on the same aryl ring, starting from the related complex $[\{PdI(tbbpy)\}_3(\mu_3\text{-}C1,C3,C5\text{-}C_6Me_3\text{-}2,4,6\}]$ (**XVIII**),[1] with Me substituents instead of CH_2OH. Thus, complex **XVIII** reacts with 9 molecules of XyNC to form the trinuclear complex $[C_6\{C(=NXy)(trans\text{-}PdI(CNXy)_2)\}_3\text{-}1,3,5\text{-}Me_3\text{-}2,4,6]$ (**32**, *Scheme VI.4*), resulting from the insertion of one XyNC molecule into each aryl-Pd bond of **XVIII**, and the displacement of each tbbpy ligand by two other XyNC molecules. Although mono-[32,33,40,46,47] and dinuclear[5,6,47] analogues to **32** have been reported in the literature, mainly by our research group, this is the first such 3-fold insertion on the same aryl ring.



Scheme VI.4 Reactivity of **XVIII** toward TlOTf and XyNC

We have previously reported that complex **XVIII** reacts with TlOTf to form an adduct of stoichiometry **XVIII**·Tl (Complex **XIX**, *Scheme VI.4*),[4] containing Tl(I)-I and Tl(I)-η^6-mesitylene bonds, and existing in the solid state as a 2:1 mixture of the monomer and an I-bridged dimer. Complexes **29a,b**, in contrast, react with TlOTf under different conditions to form mixture of compounds.

VI.2.3 NMR and IR Data

Compounds **29**-**31** have been extensively studied by NMR spectroscopy (1D and 2D experiments), allowing an almost full assignment of the ^{1}H and ^{13}C resonances. To facilitate comparison, the data are collected in *Table VI.1*, together with the numbering system used in the following discussion.

The trinuclear complexes **29a,b** show in their NMR spectra a 2:1 pattern for all ^{1}H and ^{13}C resonances. This observation is consistent with the structure depicted for these complexes in *Scheme VI.1* and *Table VI.1*, where two of the I atoms lie on one side of the aryl plane, while the third I atom points to the other side. The rotation around the Pd-aryl bonds would be hindered (a usual feature in *ortho*-substituted arylpalladium complexes),[7,48,49] and the molecule would possess a symmetry plane perpendicular to the aryl plane, and containing the carbon atoms C1 and C4 (C_s symmetry). Thus, the methylenic protons within the two equivalent CH_2OH substituents in positions 2 would be diastereotopic, forming an ABX system with the OH proton. In contrast, the methylenic protons of the CH_2OH substituent in position 4 would be enantiotopic, forming an A_2X system. For the tmeda complex **29b**, the four Me groups of the two equivalent tmeda ligands in positions 3 would be inequivalent, resulting in four Me resonances corresponding to two Me groups each. In contrast, for the tmeda ligand in position 1, the symmetry plane would render the two Me groups on each N equivalent, resulting in two Me resonances corresponding to two Me groups each. Thus, complex **29b** shows six ^{1}H and ^{13}C methyl resonances of similar intensity, corresponding each of them to two Me groups.

The mononuclear complexes **30,30',30",31** all have a *trans* geometry for the two phosphine ligands, confirmed by the presence of a single ^{31}P NMR resonance. The ^{31}P chemical shift, as usual,[3] is negative for the PMe_2Ph ligands (-5.6 ppm), and above 20 ppm for the PPh_3 ligands (21.1 ppm for **30**, 24.9 ppm for **30'** and 23.8 ppm for **30"**). Most of the aryl carbons appear as triplets because of the coupling with the two

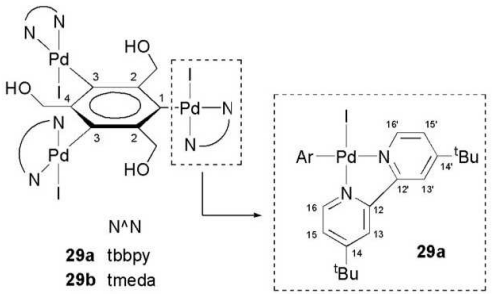
equivalent ^{31}P nuclei, while the *ipso*, *ortho* and *meta* carbons of the phosphine phenyl ring (and the Me carbons in the PMe_2Ph ligands) resonate as virtual triplets as a consequence of the magnetic non-equivalence of the two ^{31}P nuclei. These phosphine complexes have a C_{2v} symmetry, with a C_2 axis along the Ar-Pd-X bond, which renders two of the three R substituents equivalent. Additionally, there is a symmetry plane on the aryl ring and thus, for **30**, all the methylenic protons are enantiotopic, forming two A_2X systems in a 2:1 ratio.

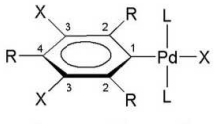
In the trinuclear complexes **29a,b** the aryl carbon atoms bonded to Pd (C1 and C3), resonate at higher frequencies (between 152.2 and 147.5 ppm) than the carbon atoms C2 and C4, bonded to CH_2OH (144.1-142.7 ppm). In the mononuclear complex **30**, with CH_2OH groups as well, the C1 chemical shift is even higher (169.0 ppm) as it is usually the case when comparing PPh_3 and N^N complexes containing the same aryl ligand.[3,32,48] The C3 carbons in **30** are bonded to I and shifted to lower frequencies (106.0 ppm). For the mononuclear complexes with OH (**30'**) or OMe groups (**30",31**), the aryl carbons at higher frequencies are C2,C4, bonded to the OR substituents (δ 146.7 and 149.9 ppm for **30'** and 151.9-157.3 ppm for **30"**,**31**). The C3 carbons, bonded to Br, appear at low frequencies (88.3 ppm for **30'** and ca. 107 ppm for **30",31**), and the *ipso* carbon C1 resonates at 140.6 ppm for **30"**, 137.7 pm for **31** and, unexpectedly low, 118.5 ppm, for **30'**. This low C1 chemical shift in **30'** is in contrast with the usual shift to higher frequencies of aryl carbons directly bonded to Pd[50] and it is difficult to explain (^{13}C chemical shifts in organometallic complexes depend mostly on the paramagnetic contribution to the shielding constant).[50]

In the tbbpy complex **29a**, as usual, the H16 protons are shielded (δ = 7.93, 7.76 ppm) with respect to H16' (δ = 9.45, 9.30 ppm), as a consequence of the anisotropic effect of the aryl group on the H16 protons.

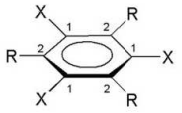
The OH protons in **30** are shifted to lower frequency (1.17 and 1.94 ppm) with respect to the OH protons in **29a,b** (2.83-3.63 ppm), probably as a consequence of the anisotropic effect of the Ph groups of the PPh_3 ligands.

Table VI.1 ^{13}C and ^{1}H NMR data (ppm, $CDCl_3$, r.t.) of complexes **29a,b**, **30, 30', 30"**, and **31**. Reference ^{13}C-NMR data of the trihaloarenes 1,3,5-$C_6R_3X_3$, are included in the box





	L	R	X
30	PPh_3	CH_2OH	I
30'	PPh_3	OH	Br
30"	PPh_3	OMe	Br
31	PMe_2Ph	OMe	Br



R	X	C1	C2	
CH_2OH	I	106.4	145.8	(d^6-DMSO)
OH	Br	91.1	151.7	(d^6-acetone)
OMe	Br	110.7	156.2	(d^6-acetone)

		29a (N^N = tbbpy)		**29b** (N^N = tmeda)	
		^{13}C	^{1}H	^{13}C	^{1}H
C1		152.2 (1C)		148.6 (1C)	
C2		143.5 (2C)		144.1 (2C)	
C3		151.9 (2C)		147.5 (2C)	
C4		143.9 (1C)		142.7 (1C)	
R-2	CH_2	72.4 (2C)	5.88, 5.79 (2H, *ABX*)	71.3 (2C)	6.01, 5.98 (2H, *ABX*)
	OR		3.11 (2H, AB*X*)		3.57 (2H, AB*X*)
R-4	CH_2	69.5 (1C)	5.74 (2H, A_2X)	70.8 (1C)	5.64 (2H, A_2X)
	OR		2.83 (1H, A_2X)		3.63 (1H, A_2X)

	tbbpy				**tmeda**	
	2C	**1C**	**2H**	**1H**		
C14	162.7	162.6			**tmeda-3 CH_2**	2.92-2.45 (12H)
C14'	162.9	162.9			62.9, 58.6 (2C)	
C12	156.1	155.1			**tmeda-1 CH_2**	
C12'	154.0	154.7			63.0, 58.7 (1C)	
CH16	150.9	152.5	7.93	7.76	**tmeda-3 Me**	
CH16'	152.4	151.7	9.45	9.30	51.9 (2C)	2.49 (6H)
CH15	122.8	124.6	7.31	7.51	50.4 (2C)	2.38 (6H)
CH15'	123.8	123.3	7.45	7.41	50.8 (2C)	2.73 (6H)
CH13	118.5	118.0	7.90	7.92	49.4 (2C)	2.71 (6H)
CH13'	117.9 (3C)		7.91	7.87	**tmeda-1 Me**	
C*Me*$_3$	30.5(6C)	30.5(3C)	1.40(18H)	1.41(9H)	51.3 (2C)	2.23 (6H)
C*Me*$_3$'	30.5(6C)	30.5(3C)	1.39(18H)	1.39(9H)	49.9 (2C)	2.69 (6H)
C*Me*$_3$	35.6	35.6				
C*Me*$_3$'	35.5	35.5				

		30 (L = PPh_3)		**30'** (L = PPh_3)		**30"** (L = PPh_3)		**31** (L = PMe_2Ph)	
		^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H
C1		169.0 (1C, t)		118.5 (1C, t)		140.6 (1C, t)		136.7 (1C, t)	
C2		145.1 (2C, t)		149.9 (2C, t)		155.9 (2C, t)		157.3 (2C, t)	
C3		106.0 (2C, s)		88.3 (2C, s)		107.6 (2C, s)		107.9 (2C, t)	
C4		141.9 (1C, t)		146.7 (1C, t)		152.3 (1C, t)		151.9 (1C, t)	
R-2	CH_2	74.1 (2C, t)	4.96 (4H, d)						
	OR		1.17 (2H, t)		5.27 (2H)	60.1 (2C)	3.75 (6H)	60.2 (2C)	3.89 (6H)
R-4	CH_2	76.6 (1C, s)	4.94 (2H, d)						
	OR		1.94 (1H, t)		5.10 (1H)	60.6 (1C)	3.56 (3H)	60.7 (1C)	3.66 (3H)
		PPh_3		**PPh_3**		**PPh_3**		**PMe_2Ph**	
***i*-C**		131.2 (6C,vt)		131.0 (6C,vt)		131.6 (6C,vt)		134.8 (2C,vt)	
***o*-CH**		135.0 (12C,br)	7.7-7.4 (12H)	134.7 (12C,vt)	7.8-7.6 (12H)	135.2 (12C,br)	8.0-7.5 (12H)	131.2 (4C,vt)	7.6-7.5 (4H)
***m*-CH**		128.2 (12C,vt)	7.3-7.2 (12H)	128.1 (12C,vt)	7.4-7.2 (18H)	127.9 (12C,br)	7.5-7.2 (18H)	128.1 (4C,vt)	7.32-7.27 (6H)
***p*-C**		130.8 (6C,s)	7.4-7.3 (6H)	130.5 (6C,s)		130.4 (6C,br)		129.7 (2C,s)	
Me								14.7 (4C,vt)	1.69 (12H,vt)
^{31}P		21.1 (^{31}P)		24.9 (^{31}P)		23.8 (^{31}P)		-5.6 (^{31}P)	

(a) Within the tmeda-1, the CH_2 group at 63.0 ppm is next to the Me groups at 51.3 ppm, and the CH_2 group at 58.7 ppm is close to the Me groups at 49.9 ppm. Within the tmedas-3, the CH_2 groups at 62.9 ppm are close to the Me groups at 51.9 and 50.4 ppm, and the CH_2 groups at 58.6 ppm are close to the Me groups at 50.8 and 49.4 ppm

The trinuclear complex **32** (*Figure VI.1*), resulting from the reaction of **XVIII** with XyNC, is not included in *Table VI.1* because it is not an arylpalladium complex. Its ^{1}H NMR spectrum shows a fluxional behavior at room temperature, which makes the three Me^{Ar} groups equivalent (affording a single ^{1}H resonance at 3.05 ppm, corresponding to 9 protons), and also *all* the Me^{Xy} groups of the isocyanides (inserted and coordinated), affording a single ^{1}H resonance at 2.25 ppm, corresponding to 54 protons. Thus, at room temperature there is a rapid exchange of *all* the XyNC groups within the molecule. When the temperature is decreased to 243 K, the dynamic process is slow on the NMR timescale and we observe two ^{1}H Me^{Ar} resonances at 3.18 ppm (3H) and 3.01 ppm (6H), indicating that only two of the Me^{Ar} groups are now equivalent. In the Me^{Xy} region we observe five resonances at 2.33 ppm (6H), 2.28 ppm (24H), 2.22 ppm (6H), 2.18 ppm (12H), and 2.08 ppm (6H). We can explain these signals assuming that at low temperature the molecules possess a symmetry plane perpendicular to the aryl plane (*Cs* symmetry), making the two C(=NXy)[PdI(XyNC)$_2$] moieties in position 3 equivalent. Within each [PdI(XyNC)$_2$] fragment, the two XyNC groups in *trans* would also be equivalent, and within each Xy group a free rotation around the N-Xy bonds would make the two Me groups equivalent as well. Thus, a single ^{1}H resonance corresponding to 24 protons would be observed for the two equivalent [PdI(XyNC)$_2$] fragments in position 3, and another ^{1}H resonance corresponding to 12 protons would be observed for the third [PdI(XyNC)$_2$] moiety in position 1. As for the inserted C(=NXy) groups, we observe three ^{1}H resonances, integrating for 6 protons each. Two of them would correspond to the two equivalent C(=NXy) groups in positions 3, for which the rotation around the N-Xy would be hindered, resulting in two inequivalent Me resonances (corresponding to 6H each). In contrast, for the third C(=NXy) group, in position 1, the rotation around the N-Xy bond would be allowed, so that the two Me groups would be equivalent, resulting in a single Me resonance (integrating for 6H as well).

The complexes with hydroxyl groups, **29a,b**, **30**, and **30'**, show characteristic IR bands between 3451 and 2492 cm^{-1}, corresponding to the O-H bonds. Complex **32** gives an IR bands at 1630 cm^{-1} for the inserted C=NXy groups, and another at 2174 cm^{-1} for the coordinated C≡NXy groups.

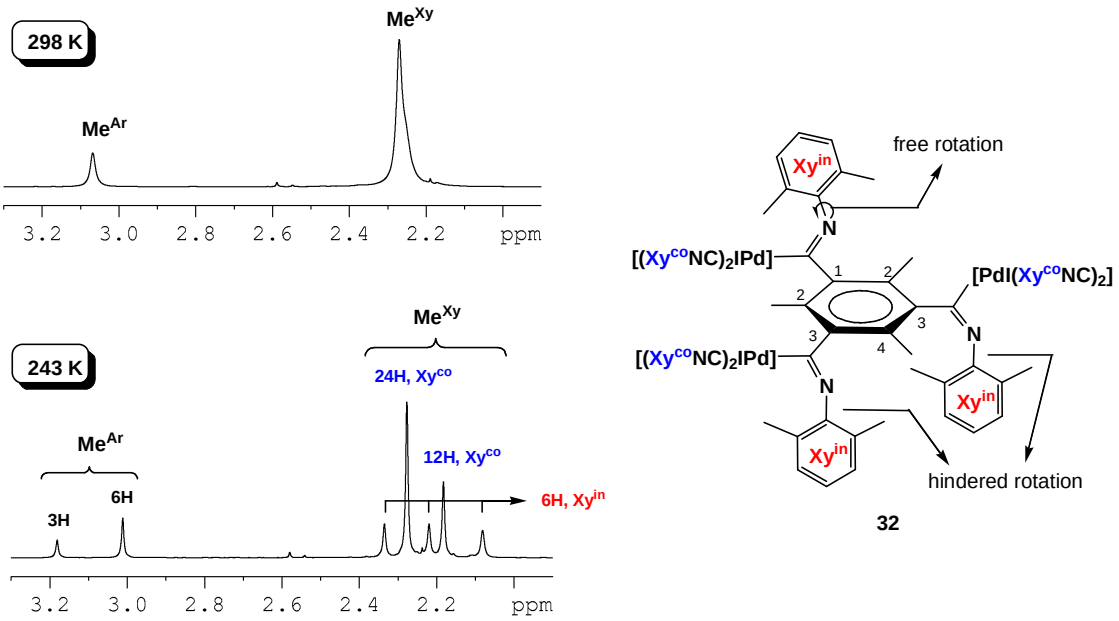


Figure VI.1 Section of the ^{1}H NMR spectra of complex **32** at 298 K (up) and 243 K (down), showing the Me region. Me^{Ar} represents the Me groups bonded to the arene, and Me^{Xy} the Me groups of the XyNC ligands.

VI.2.4 X-Ray Structure Determinations

The crystal structures of **30”** (*Figure VI.2*) and **31** (*Figure VI.3*) have been determined by X-ray diffraction studies (see also *Tables VI.2-3*).[b] Compound **30”** crystallizes with two independent molecules in the asymmetric unit, which are essentially similar, with an r.m.s. deviation of 0.27 Å. Both structures show slightly distorted square planar coordination around the Pd atoms. Mean deviations from the best plane through Pd and the four donor atoms are 0.06, 0.06 Å for **30”** and 0.01 Å for **31**. The Pd-C bond distances are 2.012(3), 2.100(3) Å for **30”** and 2.004(2) Å for **31**, in the range expected for Pd-C bonds *trans* to a Br ligand (between 1.991(2) Å and 2.033(4) Å in our previous reports).[3,47,48,51] The Pd-Br bond distances are almost identical in both complexes (2.4915(5), 2.4968(5) Å for **30”** and 2.4958(3) Å for **31**), and similar to those found in other *trans* aryl-Pd(II) phosphine complexes with Br ligands prepared in our group (between 2.5462(5) Å and 2.4865(2) Å).[3,47,48,51] The two, mutually *trans*, Pd-P bond distances (2.3340(9), 2.3280(9) and 2.3267(9), 2.3288(9)Å in **30”** and 2.3205(6), 2.3210(6) Å in **31**), are also similar to the reported values in those papers (between 2.3142(11) Å and 2.3426(4) Å).[3,47,48,51]

[b] Crystals were mounted in inert oil on glass fibers. Intensity data were recorded on a Bruker SMART 1000 CCD (**30”**) or an Oxford Diffraction Xcalibur diffractometer (**31**) using monochromated Mo *K*α radiation. Absorption corrections were based on multi-scans. Hydrogen atoms were included using rigid methyl groups or a riding model. Structures were refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany).

Table VI.2 X-ray crystallographic data for compounds **30”** and **31** [(a)]

	30”	**31**
Formula	$C_{45}H_{39}Br_3O_3P_2Pd$	$C_{25}H_{31}Br_3O_3P_2Pd$
M_r	1035.83	787.57
T (K)	133(2)	100(2)
λ (Å)	0.71073	0.71073
cryst syst	Monoclinic	Monoclinic
space group	$P2_1$	$P2_1/c$
cell constants		
a (Å)	10.8767(12)	14.8070(3)
b(Å)	22.461(2)	12.5410(3)
c (Å)	17.017(2)	17.5117(4)
α (deg)	90	90
β (deg)	96.801(4)	114.594(3)
γ (deg)	90	90
V (Å^3), Z	4128.0(8), 4	2956.81(11), 4
ρ (calcd) (Mg m^{-3})	1.667	1.769
abs. coef. (mm^{-1})	3.471	4.814
F(000)	2056	1544
cryst size (mm)	0.30 x 0.15 x 0.07	0.4 x 0.4 x 0.2
θ range (deg)	1.21 -30.51	2.56 -32.03
	$-15 \le h \le 15$	$-22 \le h \le 22$
index ranges	$-32 \le k \le 32$	$-17 \le k \le 17$
	$-24 \le l \le 24$	$-26 \le l \le 26$
reflections collected	86739	89518
independent reflections	25102	9942
R_{int}	0.0496	0.0362
abs corr	Semi-empirical from equivalents	Semi-empirical from equivalents
transmissions	0.7932 - 0.5845	1.00000 - 0.32514
refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
no. of data/restraints/params	25102 / 1 / 346	9942 / 0 / 314
goodness-of-fit on F^2	0.997	1.090
Final R indices ($I>2\sigma(I)$)		
$R1$	0.0336	0.0339
$wR2$	0.0581	0.0592
R indices (all data)		
$R1$	0.0541	0.0448
$wR2$	0.0638	0.0615
largest diff peak (e Å^{-3})	0.905	1.373
largest diff hole (e Å^{-3})	-0.555	-0.799

(a) *Special features*: Compound **30”** is achiral, but nonetheless crystallizes in a chiral (Sohncke) space group. The Flack parameter refined to 0.003(3)

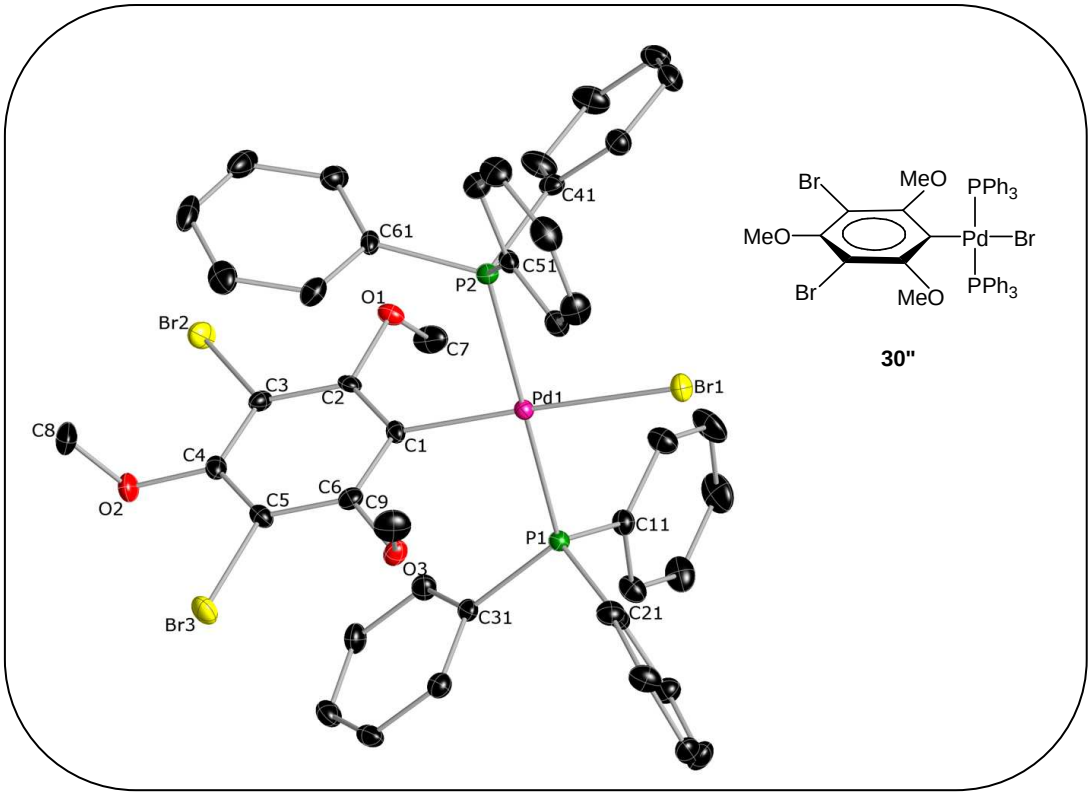


Figure VI.2 Thermal ellipsoid plot (50% probability level) of **30”**

Table VI.3 Selected bond lengths (Å) and angles (deg) of **30”**

Pd(1)-C(1)	2.012(3)	C(1)-Pd(1)-P(1)	88.55(9)
Pd(1)-P(1)	2.3340(9)	C(1)-Pd(1)-P(2)	90.25(9)
Pd(1)-P(2)	2.3280(9)	P(2)-Pd(1)-Br(1)	89.92(2)
Pd(1)-Br(1)	2.4915(5)	P(1)-Pd(1)-Br(1)	91.56(2)
		P(1)-Pd(1)-P(2)	175.66(3)
		C(1)-Pd(1)-Br(1)	176.13(9)

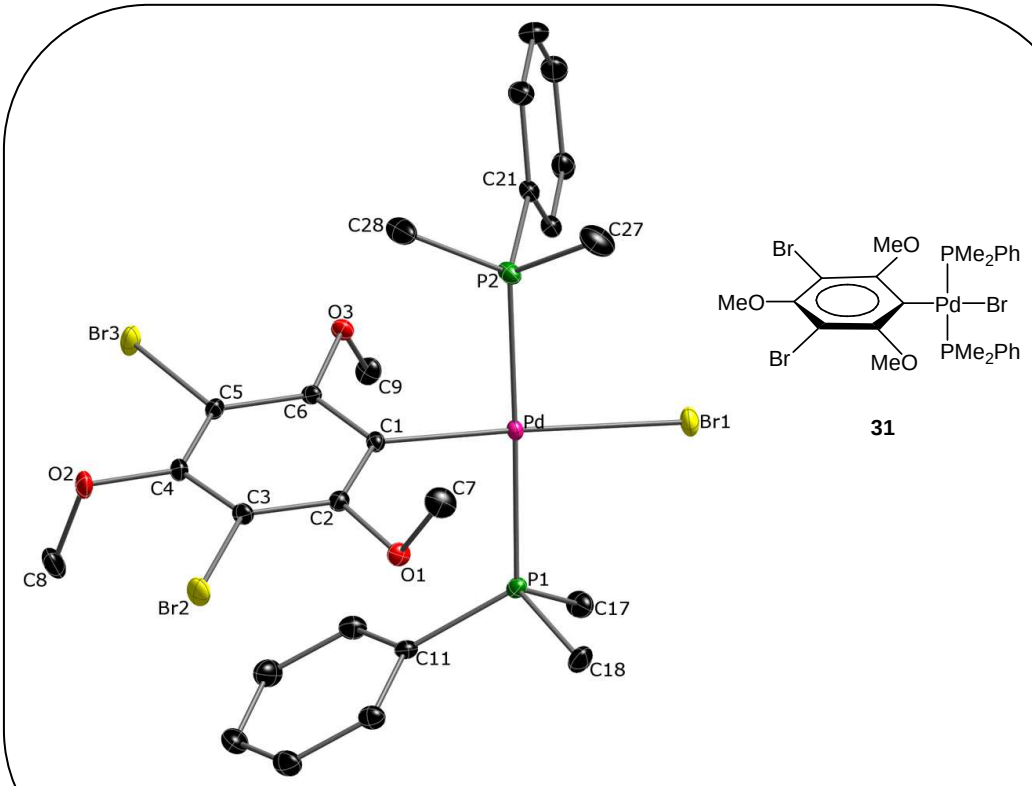


Figure VI.3 Thermal ellipsoid plot (50% probability level) of **31**

Table VI.4 Selected bond lengths (Å) and angles (deg) of **31**

Pd-C(1)	2.004(2)	C(1)-Pd-P(1)	87.98(6)
Pd-P(1)	2.3205(6)	C(1)-Pd-P(2)	90.58(6)
Pd-P(2)	2.3210(6)	P(2)-Pd-Br(1)	91.062(17)
Pd-Br(1)	2.4958(3)	P(1)-Pd-Br(1)	90.373(16)
		P(1)-Pd-P(2)	178.54(2)
		C(1)-Pd-Br(1)	177.78(6)

VI.3 CONCLUSIONS

We have prepared two tripalladated arene derivatives of general formula $C_6R_3[Pd]_3$ (R = CH_2OH) and four monopalladated derivatives of general formula $C_6R_3X_2[Pd]$, (R = CH_2OH, OH, OMe), by oxidative addition reactions of the corresponding 2,4,6-trihaloarenes $C_6R_3X_3$ (X = Br, I) to $[Pd(dba)_2]$ in the presence of tbbpy, tmeda, PPh_3, or PMe_2Ph. Two of the mononuclear complexes have been characterized by X-ray crystallography. The first insertion of XyNC into three aryl-Pd bonds of a tripalladated arene has been achieved, resulting in a fluxional trinuclear complex that has been investigated by VT-NMR.

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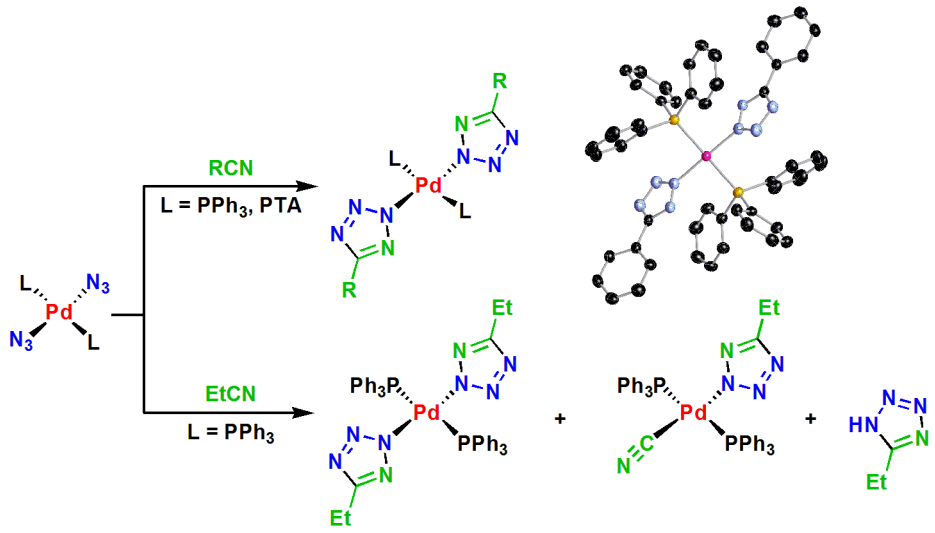
CHAPTER VII

Microwave Synthesis of Bis(tetrazolato)-Pd(II) Complexes with PPh_3 and Water-Soluble 1,3,5-Triaza-7-Phosphaadamantane (PTA). The First Example of C-CN Bond Cleavage of Propionitrile by a Pd(II) Centre



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VII.1 ABSTRACT

[2+3] Cycloaddition reactions of the di(azido)-Pd(II) complex *trans*-[Pd(N_3)$_2$(PPh_3)$_2$] with an organonitrile RCN, under heating for 12 h, give the bis(tetrazolato) complexes *trans*-[Pd(N_4CR)$_2$(PPh_3)$_2$] (**33**) [R = Me (**33a**), Ph (**33b**), 4-ClC_6H_4 (**33c**), 4-FC_6H_4 (**33d**), 2-NC_5H_4 (**33e**), 3-NC_5H_4 (**33f**), 4-NC_5H_4 (**33g**)]. The reaction of *trans*-[Pd(N_3)$_2$(PPh_3)$_2$] with propionitrile also affords, apart from *trans*-[Pd(N_4CEt)$_2$(PPh_3)$_2$] (**33h**), the unexpected mixed cyano-tetrazolato complex *trans*-[Pd(CN)(N_4CEt)(PPh_3)$_2$] (**33h´**) which is derived from the reaction of the bis(tetrazolato) **33h** with propionitrile, with concomitant formation of 5-ethyl-1*H*-tetrazole, *via* a suggested unusual oxidative addition of the nitrile to Pd(II). The [2+3] cycloadditions of [Pd(N_3)$_2$(PTA)$_2$] (**34**) (PTA =1,3,5-triaza-7-phosphaadamantane) with RCN, under heating for 12 h, give the bis(tetrazolato) complexes *trans*-[Pd(N_4CR)$_2$(PTA)$_2$] (**35**) [R = Ph (**35a**), 2-NC_5H_4 (**35b**), 3-NC_5H_4 (**35c**), 4-NC_5H_4 (**35d**)]. All these reactions are greatly accelerated by microwave irradiation (1 h, 125 °C, 300 W). Taking advantage of the hydro-solubility of PTA, a simple liberation of 5-phenyl-1*H*-tetrazole from the coordination sphere of *trans*-[Pd(N_4CPh)$_2$(PTA)$_2$] (**35a**) was achieved. The complexes were characterized by IR, ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopies, ESI$^+$-MS, elemental analyses and, for **33b**, also by X-ray structure analysis. Weak agostic interactions between the CH groups of the triphenylphosphines and the palladium(II) centre were found.

VII.2 INTRODUCTION

Tetrazoles constitute an important class of compounds with applications in areas of coordination chemistry, materials science and medicinal chemistry.[1-4] They can be synthesized by [2+3] cycloaddition of an organonitrile with an azide, but only a few activated nitriles are known to undergo this reaction in an *inter*molecular fashion.[5] When the azide and the nitrile moieties are in the same molecule, the rate of cycloaddition can be greatly enhanced and polycyclic fused tetrazoles can be synthesized *via intra*molecular [2+3] cycloaddition.[6] The cycloaddition can also be promoted by using fluorous tin or trimethylsilyl azide,[7] a strong Lewis acid[8] or a strong acidic media.[9] Sharpless *et al*.[10] improved the synthetic method by using a zinc salt as the Lewis acid and performing the reaction in aqueous medium. Amantini *et al*.[11] efficiently

synthesized tetrazoles by reaction of trimethylsilyl azide with a nitrile using tetrabutylammonium fluoride as catalyst. The use of nanocrystalline ZnO as an heterogeneous catalyst,[12] and microwave irradiation[13] to shorten the reaction time have also been reported. Phthalonitrile and terephthalonitrile react with azides in the presence of a metal chloride to give mono-tetrazoles.[14]

Moreover, the formation of substituted tetrazoles can be achieved by using an azide coordinated to a transition metal and free organonitriles,[15] isocyanides[16a] or isothiocyanates.[16b] For example, we have shown[17] that the di(azido) complexes of the type *cis*-$[Pt(N_3)_2(PPh_3)_2]$ can react with nitriles NCR to give the bis(tetrazolato) compounds *trans*-$[Pt(N_4CR)_2(PPh_3)_2]$ from which the tetrazoles can be liberated. Very recently, we have reported that [2+3] cycloaddition of *cis*-$[Pt(N_3)_2(PPh_3)_2]$ with 4-cyanobenzaldehyde furnishes a (formylphenyl)tetrazolate complex that reacts with 2-dimethylaminoethylamine to give the corresponding Schiff base derivative, the latter undergoing hydrolysis in the presence of a metal salt, while the reactions of di(azido) complexes with dicyanobenzenes give (cyanophenyl)tetrazolate complexes.[18] In addition, the reactions of bis(tetrazolato)-Pt(II) compounds with propionitrile furnish mono- or dicyano-complexes, *via* an unusual oxidative addition involving NC-C bond cleavage of one or two propionitrile molecules, respectively.[17a-c] On the other hand, in Organometallic Chemistry, activation of carbon-carbon bonds has been a popular topic and a few examples of NC-C bond cleavage in organonitriles by group 10 transition metal complexes are known[19] when the metals are in zero oxidation state. Moreover, the first example of C-C cleavage by oxidative addition of the C-CN bond to a Rh(I) centre has been recently reported.[20]

Concerning the Pd(II)-assisted [2+3] cycloadditions of azides to organonitriles, Beck and co-workers[21] have investigated the reaction of benzonitrile with $[Pd(N_3)_2(PPh_3)_2]$, by the traditional heating method, leading to *cis*-$[Pd(N_4CPh)_2(PPh_3)_2]$ and the structure of the cycloadduct was confirmed by X-ray diffraction analysis. In this case, both 5-phenyltetrazolato ligands are coordinated to Pd by the N^2 atom. On the other hand, the crystal structure of the related complex *cis*-$[Pd(N_4CMe)_2(PMe_2Ph)_2]$ demonstrates that both tetrazolato rings are N^1-bonded.[22]

The coordination chemistry of the aqua-soluble phosphine 1,3,5-triaza-7-phosphaadamantane (PTA) and derived species has received an increased interest in

recent years, in view of the good solubility of their complexes in water, thus making possible their efficient application in aqueous phase catalysis, as water-soluble antitumor agents and photoluminescent materials.[23] Four- and five-coordinated diazido-platinum(II) complexes *cis*-[$Pt(N_3)_2(PTA)_2$] and [$Pt(N_3)_2(PTA)_3$] were obtained by us,[17a] in reaction of *cis*-[$Pt(N_3)_2(PPh_3)_2$] with stoichiometric amounts of PTA. [2+3] Cycloadditions with organonitriles NCR give the bis(tetrazolato) *trans*-[$Pt(N_4CR)_2(PTA)_2$] species,[17a] from which the tetrazoles can be liberated and also conveniently isolated in a pure form on account, on one hand, of the high water solubility of the concomitantly formed PTA-platinum complex and, on the other hand, of the water insolubility of the tetrazole which spontaneously precipitates out from the solution. In this way, the 5-substituted tetrazoles were obtained and isolated as solids by an easy single-pot process upon simple treatment of the respective tetrazolato complexes with aqueous diluted HCl. However, the generality of this rather convenient preparative method was not established.

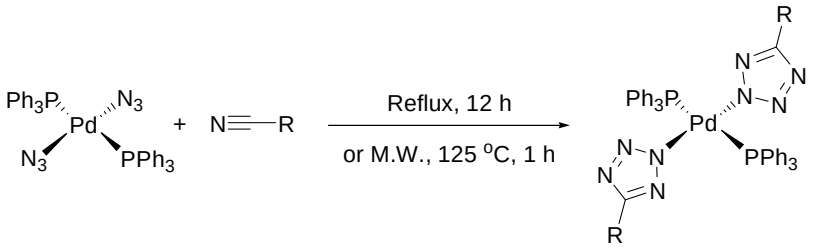
Thus, the aims of the current work are: i) to extend the number of *trans* tetrazolato-Pd(II) complexes synthesized by [2+3] cycloaddition of a nitrile with an azide coordinated to a palladium(II) metal centre using PPh_3 and hydrosoluble PTA ligands; ii) to check if the mentioned reaction of azido-Pd(II) species with propionitrile as a starting material involves carbon-carbon bond cleavage similarly to that observed for the tetrazolato-Pt(II) complexes; iii) to investigate the effect of focused microwave irradiation (M.W.), since M.W. is an alternative way to the traditional refluxing method with the possible advantages[24] of increasing the selectivity and reducing the reaction time.

VII.3 RESULTS AND DISCUSSION

VII.3.1 Complexes with PPh_3

Treatment of the di(azido)-Pd(II) complex *trans*-[$Pd(N_3)_2(PPh_3)_2$] with an organonitrile RCN, under heating for 12 h, gives the corresponding bis(tetrazolato) compounds *trans*-[$Pd(N_4CR)_2(PPh_3)_2$] (**33**) [R = Me (**33a**), Ph (**33b**), 4-ClC_6H_4 (**33c**), 4-FC_6H_4 (**33d**), 2-NC_5H_4 (**33e**), 3-NC_5H_4 (**33f**), 4-NC_5H_4 (**33g**)], isolated as white or yellow crystalline solids in moderate yields (*ca*. 65-54%) (*Scheme VII.1*). When using a liquid organonitrile (acetonitrile and benzonitrile), this behaves also as the solvent

whereas, in the case of solid nitriles dimethylformamide (DMF) is the solvent used. The reactions are undertaken either in solvent refluxing conditions (for 12 h) by conventional heating or under focused microwave (M.W.) irradiation (1 h, 125 °C, 300 W). The latter method greatly accelerates the reactions, leading only in 1 h to yields that are comparable to those obtained after 12 h under conventional heating. The tetrazolato-Pd(II) complexes are formed *via* [2+3] cycloaddition of the organonitriles with the ligated azides.

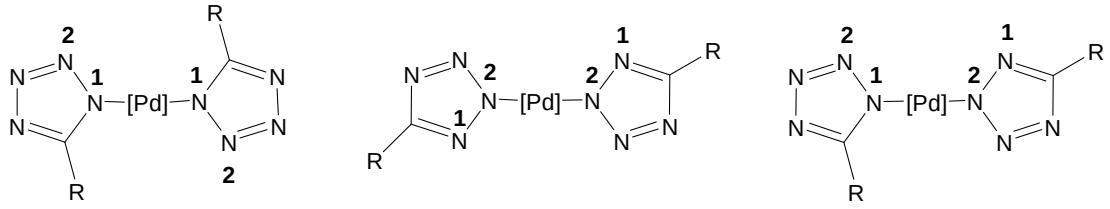


	R
33a	Me
33b	Ph
33c	4-ClC_6H_4
33d	4-FC_6H_4
33e	2-NC_5H_4
33f	3-NC_5H_4
33g	4-NC_5H_4

Scheme VII.1 Synthesis of complexes **33a-g**

The obtained complexes **33a-g** were characterized by elemental analyses, IR and ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ spectroscopies, and ESI^{+}-MS. Their IR spectra do not show the typical azide band at *ca*. 2036 cm^{-1} and display a new strong band within the 1615–1638 cm^{-1} range due to the tetrazole ring, in agreement with the literature.[17] No band assigned to N-H stretching or bending was observed, in contrast to typical bands of triphenylphosphine ligands at *ca*. 1436 cm^{-1} and 693 cm^{-1}, which are also displayed by the starting complex *trans*-$[Pd(N_3)_2(PPh_3)_2]$. The $^{13}C\{^{1}H\}$ NMR spectra of complexes **33** show the characteristic signal in the 151-164 ppm range due to the carbon of the tetrazolato ring.

Moreover, the NMR spectra of **33** often display more than one peak for each particular type of atoms, what can be accounted for by linkage isomerism due to the possible ambidentate behaviour of the tetrazolate ligand which, in principle, can bind to the metal through either the N^1 or the N^2 atom leading to the possibility of existence of several isomers (N^1N^1, N^2N^2 and N^1N^2 combinations), in addition to *cis*- and *trans*-isomers[17c] (*Scheme VII.2*). However, N^2N^2-coordinated is sterically favourable and is that established in the solid state by X-ray diffraction (see below).



Scheme VII.2 Isomers due to the ambidentate behaviour of the tetrazolate ligand

For instance, the ^{1}H NMR spectrum of *cis*/*trans*-[Pd($N_4CMe)_2(PPh_3)_2$] (**33a**) shows four signals for the methyl protons at δ 1.88, 2.01, 2.21, and 2.24, whereas in the $^{13}C\{^{1}H\}$ NMR spectrum four resonances for the methyl carbon are detected at δ 9.93, 9.95, 10.60, and 10.69, suggesting the presence of four isomers in solution. In the $^{31}P\{^{1}H\}$ NMR spectrum, also four signals were observed at δ 17.65, 18.08, 23.02, and 29.19. Those four isomers concern **33a** obtained under M.W. irradiation (1 h, 125 °C, 300 W). Nevertheless, the $^{31}P\{^{1}H\}$ NMR spectrum of **33a** synthesized by conventional heating methods (reflux, 12 h) shows only three signals at δ 17.65, 23.02, and 29.19, probably due to the conversion of the *cis* isomer ($^{31}P\{^{1}H\}$ NMR δ 18.08) into the thermodynamically more stable *trans* form.

In our previous work,[17c] we found that the 5-phenyltetrazolato-Pt(II) complex *trans*-[Pt($N_4CPh)_2(PPh_3)_2$] exhibits one signal at δ 17.11 ($J_{Pt\text{-}P}$ = 2720 Hz) in the $^{31}P\{^{1}H\}$ NMR spectrum, due to the presence of only one isomer in solution. Moreover, the single *trans* isomer was prepared by both conventional heating methods and under M.W. irradiation. However, the $^{31}P\{^{1}H\}$ NMR spectrum of the analogous Pd(II) complex [Pd($N_4CPh)_2(PPh_3)_2$] (**33b**) prepared under M.W. irradiation (1 h, 125 °C, 300 W) shows three resonances at δ 18.40, 22.82, and 29.25. When **33b** is prepared under solvent refluxing conditions (12 h), only one signal at δ 18.40 is observed in its $^{31}P\{^{1}H\}$ NMR spectrum. This is indicative that in this case the possible *cis*/*trans* isomers (with different coordination modes) can also convert into the thermodynamically more stable *trans* one, and in order to avoid steric congestion, both the bulky phenyl-tetrazolato rings are conceivably coordinated to the metal centre only by the N^2 atom.[17c]

The single crystal X-ray diffraction analysis of **33b** confirms the proposed structure (crystal data and details of data collection are given in *Table VII.1*). The structure (*Figure VII.1*) clearly displays the N^2N^2-coordination mode of the tetrazolato ligands. The metal lies on a crystallographic inversion point in a slightly distorted square-planar geometry

with the two tetrazolato rings in mutually *trans* position. The tetrazole rings are essentially planar and their phenyl moieties are twisted out of the N_4C plane with a dihedral angle of 16.43º. Moreover, the phenyl substituents attached to the tetrazolato rings are oriented in the opposite direction (*anti* orientation), while the phosphine groups take a staggered conformation. The Pd−N bond distance (1.9953(15) Å) is comparable with those found (*ca*. 2.08 Å) in other bis-tetrazolato Pd(II) complexes,[21,22] and is somewhat shorter than the sum of the metal and nitrogen covalent radii (1.39 + 0.68 Å) suggesting a partial π-character in this bond. The Pd–P bond distance (2.3469(4) Å) is also shorter than the metal and phosphorus covalent radii (1.39 + 1.05 Å), what is commonly found in mutually *trans*-phosphines.

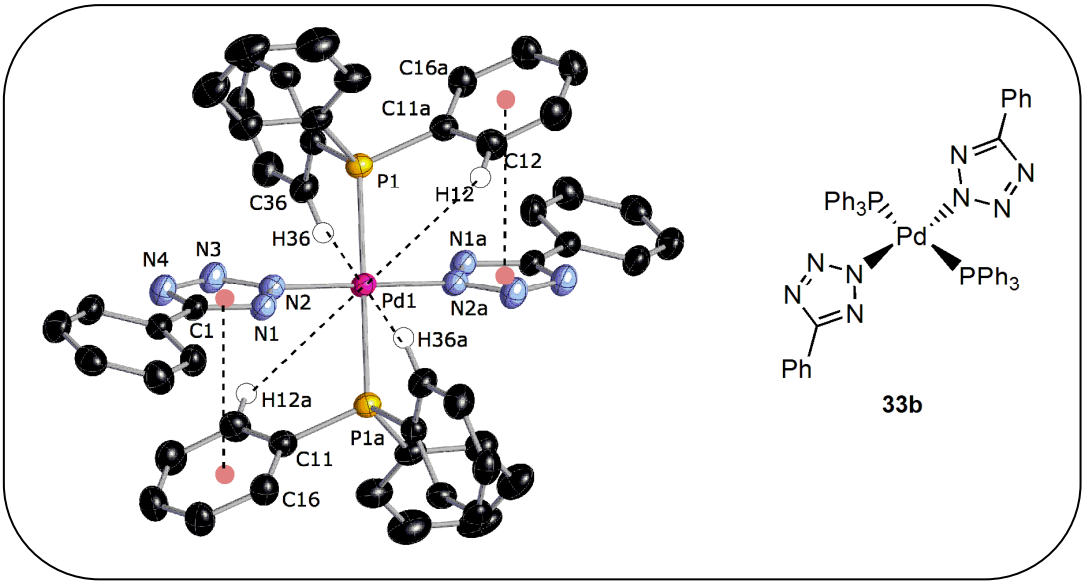


Figure VII.1

Thermal ellipsoid plot, drawn at the 50% probability level, of the *trans* 5-phenyltetrazolato Pd(II) complex **33b** with atomic numbering scheme. Selected bond lengths (Å) and angles (°): Pd1−P1 2.3469(4), Pd1−N2 1.9953(15), P1−Pd1−N2 91.49(4), N2−Pd1−P1a 88.50(4). π···π and agostic interactions (shown as dashed lines): *centroid*···*centroid* 3.6536(12) Å; *d*(H12···Pd1) 3.40 Å, ∠(C12–H12···Pd1) 107.09 º; *d*(H36···Pd1) 2.93 Å, ∠(C36–H36···Pd1) 119.51 º. Hydrogen atoms not involved in fundamental interactions are omitted for clarity. Symmetry code to generate equivalent atoms: a) −x,1−y,1−z

The complex molecule conformation is stabilized by intramolecular π···π interaction involving the tetrazole ring and the phosphine C11 > C16 phenyls (*centroid*···*centroid* distance of 3.6536(12) Å). Moreover, reasonably strong intramolecular agostic interactions were also found, involving the metal and aromatic phosphine hydrogens (H12···Pd1 3.40 Å, C12–H12···Pd1 107.09º; H36···Pd1 2.93 Å, C36–H36···Pd1 119.51º). Therefore, the above considered square-planar geometry

around the Pd(II) centre in **33b** can be envisaged as a distorted octahedron if the longer agostic Pd1···H interactions are taken into consideration.

Table VII.1 X-ray crystallographic data for *trans*-[$Pd(N_4CPh)_2(PPh_3)_2$] (**33b**) [(a)]

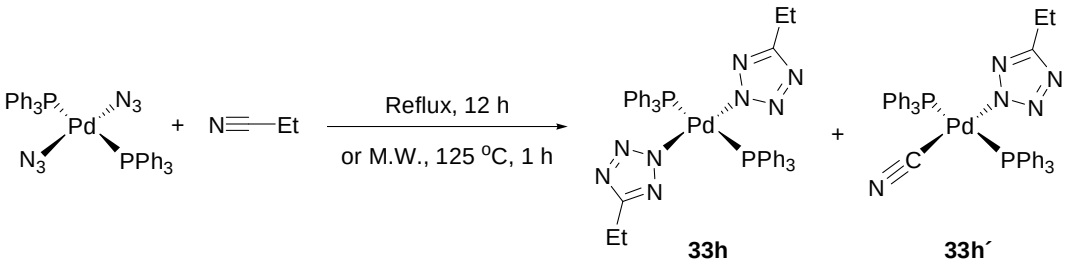
Formula	$C_{50}H_{40}N_8P_2Pd$	Mr	921.24
λ (Å)	0.71073		
cryst syst	Triclinic	space group	P -1
a (Å)	8.7688(3)	α (deg)	68.890(2)
b (Å)	11.7142(4)	β (deg)	76.809(3)
c (Å)	11.7416(4)	γ (deg)	72.483(2)
V (Å^3), Z	1063.20(7), 1		
ρ_{calcd} (mg/m^3)	1.439	μ(Mo Kα) (mm^{-1})	0.558
no. of collected reflns	25117	no. of unique reflns	6886
R_{int}	0.0403	Final *R*1 [(b)], *wR*2 [(c)] ($I \geq 2\sigma$)	0.0373, 0.0821
GOF on F^2	1.049		

[(a)] Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer using graphite monochromated Mo-Kα radiation. Data were collected at 150 K, using omega scans of 0.5º per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all the observed reflections. Absorption corrections were applied using SADABS.[25] Structures were solved by direct methods by using the SHELXS–97 package[26] and refined with SHELXL–97.[26] Calculations were performed with the WinGX System-Version 1.80.03.[27] All hydrogens were inserted in calculated positions. Least square refinement with anisotropic thermal motion parameters for all the non–hydrogen atoms and isotropic for the remaining were employed.

[(b)] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

[(c)] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$

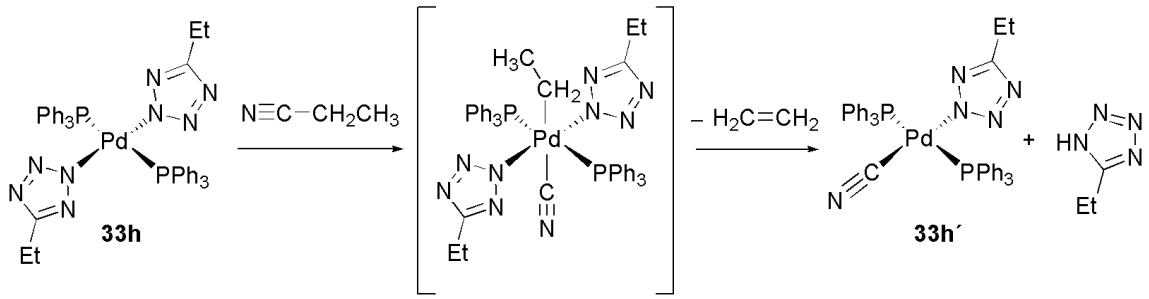
Similarly to the case of platinum(II) complexes,[17c] the reaction of propionitrile with *trans*-[$Pd(N_3)_2(PPh_3)_2$], by refluxing for 12 h or under M.W. irradiation (1 h, 125 °C, 300 W), gives not only the expected *trans*-[$Pd(N_4CEt)_2(PPh_3)_2$] (**33h**), but also the cyano-complex *trans*-[$Pd(CN)(N_4CEt)(PPh_3)_2$] (**33h´**) (*Scheme VII.3*).



Scheme VII.3 Synthesis of **33h** and **33h´**

The formation of **33h´** is believed to proceed *via* the bis(tetrazolato) compound **33h**, propionitrile being the precursor of the cyanide ligand. The initial formation of complex **33h** *via* the [2+3] cycloaddition of the propionitrile (as observed with the other nitriles) with a ligated azide is kinetically driven and such a complex, upon prolonged reaction time, converts into the thermodynamically more stable cyano-complex **33h´**.

A possible pathway for the unexpected conversion of **33h** into the corresponding cyano-complex **33h´** is proposed in *Scheme VII.4*. It involves an oxidative addition of propionitrile (which thus undergoes NC-C bond cleavage[17c,19,20]) to Pd(II) to give a cyano-ethyl-Pd(IV) intermediate, followed by β-elimination from the ethyl ligand to form ethylene,[a] and reductive elimination of 5-ethyl-1*H*-tetrazole, which could be isolated and characterized by IR, ^{1}H and ^{13}C{^{1}H} NMR spectroscopies and ESI^{+}-MS.



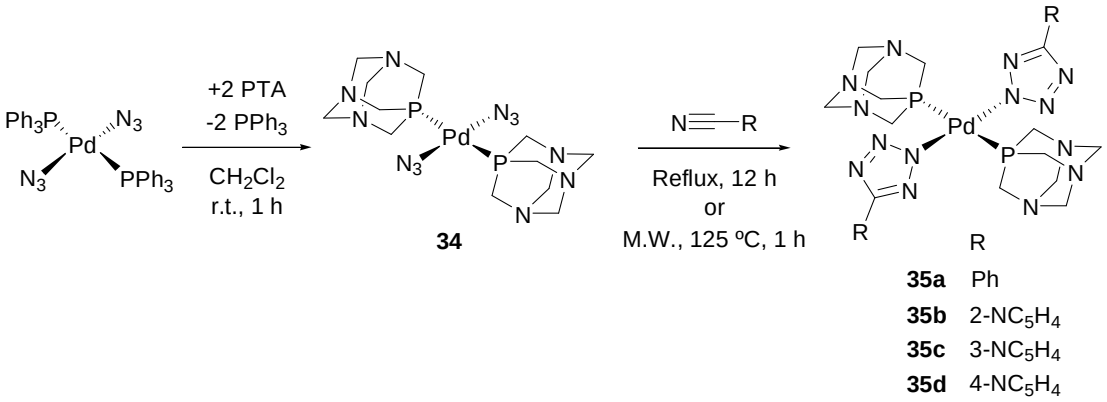
Scheme VII.4 Synthesis of **33h´** and 5-ethyl-1*H*-tetrazole

Complex **33h´** cannot be isolated in a pure form, by thermal heating or under M.W. irradiation, and a mixture of **33h** and **33h´** was obtained. The mixture has been characterized by IR and ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopies, and ESI^{+}-MS. The IR spectrum of the mixture shows a strong band at 1630 cm^{-1} due to the tetrazole rings, and a band at 2139 cm^{-1} is assigned to ν(CN) of the cyano ligand (complex **33h´**). The ^{13}C{^{1}H} NMR resonances at 126.9 and 166.5 ppm confirm the presence of cyano and tetrazolato ligands, respectively.[17] The ^{31}P{^{1}H} NMR spectrum of the reaction mixture shows two resonances at δ 23.0 and 30.2 (3:1 relative intensities).

[a] Ethylene cannot be detected in solution by NMR on account of its too low amount relatively to that of the propionitrile solvent bearing the interfering strong propyl NMR resonances. However, the formation of ethylene is corroborated by the stoichiometry of the reaction (*Scheme VII.4*).

VII.3.2 Complexes with PTA

As mentioned above, PTA can be an alternative and useful phosphine for further applications in aqua-systems. Hence, we decided to synthesize analogous complexes with PTA instead of PPh_3, and to carry out the liberation of ligated tetrazole in aqueous medium. The reaction of stoichiometric quantities of PTA and *trans*-$[Pd(N_3)_2(PPh_3)_2]$ (Pd:PTA = 1:2) in CH_2Cl_2 at room temperature leads to the precipitation of $[Pd(N_3)_2(PTA)_2]$ (**34)** as an yellow microcrystalline solid in 60% yield (*Scheme VII.5*). Complex **34** is stable in the solid state and in solution. The bis(tetrazolato) complexes *trans*-$[Pd(N_4CR)_2(PTA)_2]$ (**35**) [R = Ph (**35a**), 2-NC_5H_4 (**35b**), 3-NC_5H_4 (**35c**) or 4-NC_5H_4 (**35d**)] were synthesized by reaction of $[Pt(N_3)_2(PTA)_2]$ (**34**) with the appropriate organonitrile NCR, and the reaction is accelerated by M.W. (125 ºC, 1 h, 300 W). They were isolated in moderate yields (*ca.* 50-55%) as yellow powders (*Scheme VII.5*). The tetrazolato-Pd(II) complexes **35a-d** are formed *via* [2+3] cycloaddition of the organonitriles with the ligated azides and they are stable in the solid state. Complex **35a** is soluble in middle polar solvents, such as $CHCl_3$ and CH_2Cl_2, sparingly soluble in polar ones such as H_2O, MeOH, MeCN and Me_2SO, while compounds **35b-d** are insoluble in common organic solvents and water.

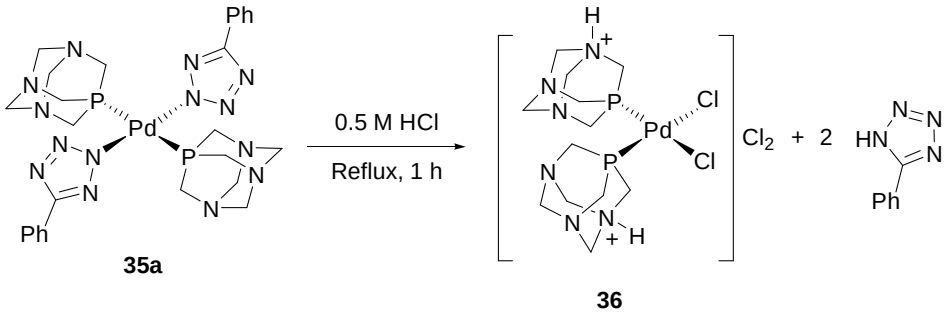


Scheme VII.5 Synthesis of **34** and **35**

Compounds **34** and **35** have been characterized by elemental analyses, IR and NMR spectroscopies. The IR spectrum of **34** exhibits the typical azide band (2037 cm^{-1}). The $^{13}C\{^1H\}$ NMR spectrum of **35a** shows the characteristic signal at 165 ppm due to the tetrazolato ring carbon. The ^1H NMR spectra of **34** and **35a** at room temperature show two types of methylene protons. One of them, P-CH_2-N, occurs as a broad singlet at δ

4.35 and 4.20, respectively. The second type, N-CH_2-N, displays for **34** and **35a** an AB spin system centred at δ 4.47 and 4.44 (J_{AB} = 13 and 15 Hz), respectively, assigned to the N-CH_{ax}-N and the N-CH_{eq}-N protons.[23] The $^{31}P\{^1H\}$ NMR spectra of **34** and **35a** display singlets at -30.2 and -47.3 ppm, respectively.

Liberation of the ligated tetrazole from the coordination sphere of the bis(tetrazolato)-Pd(II) complex *trans*-[Pd($N_4CPh)_2$($PTA)_2$] (**35a**) was achieved by treatment with aqueous HCl, similarly to the previously described[17a] reaction of the platinum compounds *trans*-[Pt($N_4CR)_2$($PTA)_2$] (R = Ph, 4-ClC_6H_4, or 3-NC_5H_4) with diluted HCl (*Scheme VII.6*). The method is simple and convenient in terms of providing an easy separation of the tetrazole products. It involves refluxing a suspension of **35a** in aqueous 0.5 M HCl for 1 h. The precipitate formed during the reaction was separated by filtration and the white solid was then extracted with chloroform, and shown (by IR and NMR spectroscopies) to be the corresponding 5-phenyl-1*H*-tetrazole (yield *ca.* 50%).[17a] The remaining white-yellow precipitate is completely insoluble in chloroform, which, by IR (KBr) and elemental analysis, was shown to be [$PdCl_2$($PTA\text{-}H)_2$]Cl_2 (**36**) (PTA-H = *N*-protonated PTA cation). Its insolubility in most solvents precluded NMR analysis, but it is deprotonated by base (NaOH) to give the expected known [$PdCl_2$($PTA)_2$],[28] as proved by $^{31}P\{^1H\}$NMR in a D_2O solution with NaOH.



Scheme VII.6 Synthesis of **36** and 5-phenyl-1*H*-tetrazole

VII.4 CONCLUSIONS

In this work we have shown that the di(azido) compounds *trans*-[Pd$(N_3)_2(PPh_3)_2$] and the hydrosoluble [Pd$(N_3)_2(PTA)_2$] (**34**) are good starting materials for a variety of *trans* bis(5-substituted tetrazolato)-Pd(II) complexes derived upon [2+3] cycloadditions with nitriles. We have also found that propionitrile, on reaction with *trans*-[Pd$(N_4CEt)_2(PPh_3)_2$] (**33h**), undergoes an unusual NC-C bond cleavage behaving as a source of a cyano ligand to give *trans*-[Pd(CN)$(N_4CEt)(PPh_3)_2$] (**33h´)** and 5-ethyl-1*H*-tetrazole, *via* a suggested unusual oxidative addition of this nitrile to Pd(II) followed by β-H-elimination from the derived ethyl ligand and reductive elimination of the tetrazole. This provides, to our knowledge, the first example of synthesis of a mixed cyano-tetrazolato Pd(II) complex, which is obtained by C-C bond cleavage of an organonitrile.

The *trans* arrangement of the two tetrazolato ligands appears to be the most favourable one, in contrast to the previous reports,[21,22,29] as clearly established by X-ray diffraction analysis. Different linkage isomers, on account of the ambidentate character of the tetrazolato ligand that can coordinate by either the N^1 or the N^2 mode, have been spectroscopically detected in solution, but the resolved crystal structure of complex **33b** shows that, in the solid state, the mode of tetrazolato binding is through the N^2-atom. The multifunctionality of the tetrazolato and of the cyano-tetrazolato complexes provides a potential convenient entry to polynuclear assemblies which deserves to be explored.

Taking advantage of the hydro-solubility of PTA, a simple liberation of the ligated tetrazolate from the coordination sphere of *trans*-[Pd$(N_4CPh)_2(PTA)_2$] was achieved, similarly to related Pt(II) complexes, what constitutes a convenient metal-mediated synthetic method for substituted tetrazoles.

Finally, microwave irradiation promotes the [2+3] cycloaddition of organonitriles with azide, resulting in a pronounced shortening of the reaction time relatively to the conventional heating.

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CHAPTER VIII

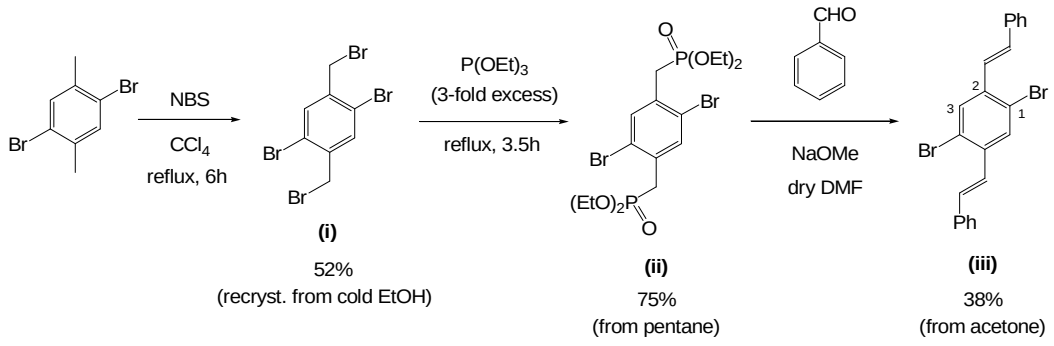
Experimental Section

VIII.1 GENERAL CONSIDERATIONS AND CHARACTERIZATION TECHNIQUES

VIII.1.1 Relating Compounds 1-32

Complexes **1-32** have been prepared at the *Inorganic Chemistry Department of the University of Murcia*. Unless otherwise stated, all experiments have been conducted under a N_2 atmosphere using Schlenk techniques. Toluene, THF, CH_2Cl_2, hexane, and Et_2O were degassed and dried using a Pure Solv MD-5 solvent purification system from Innovative Technology, Inc. All other solvents have been obtained from commercial sources and used without further purification. Chromatographic separations were achieved by preparative thin layer chromatography using silica gel 60A. For colorless compounds ca. 5% of silica gel $60GF_{254}$ was added and the bands were located with the help of a 254/365 nm lamp. The following paragraphs describe the synthesis of some of the starting materials. All other reagents have been obtained from commercial sources and used without further purification.

- **[Pd(dba)$_2$]** was prepared according to literature procedures.[1]
- ***trans,trans*-2,5-Distyryl-1,4-dibromobenzene** (Chapter IV) was prepared according to the procedure reported by Blum and Zimmerman[2] (*Scheme VIII.1*). As the authors do not report NMR data of the intermediate and final compounds, these data are included in the Scheme, together with the observed colors.[3]



(**i**): ^{1}H-NMR: δ 7.66 (s, 2H, CH), 4.51 (s, 4H, CH_2). White crystals

(**ii**): ^{1}H-NMR: δ 7.64 (d, 2H, CH, $^4J_{HH}$ = 2 Hz), 4.07 (quint, 8H, OCH_2, $^3J_{HH}$ = 7 Hz), 3.33 (d, 4H, PCH_2, $^3J_{PH}$ = 21 Hz), 1.28 (t, 12H, CH_3, $^3J_{HH}$ = 7 Hz); ^{31}P-NMR: δ 24.6 (s). White crystals.

(**iii**): ^{1}H-NMR: δ 7.88 (s, 2H, CH-3), 7.55 (d, 4H, CH Ph), 7.4–7.25 (several m, 8H, Ph and CH=CH), 7.06 (d, 2H, CH=CH, $^3J_{HH}$ = 16 Hz). Yellow crystals.

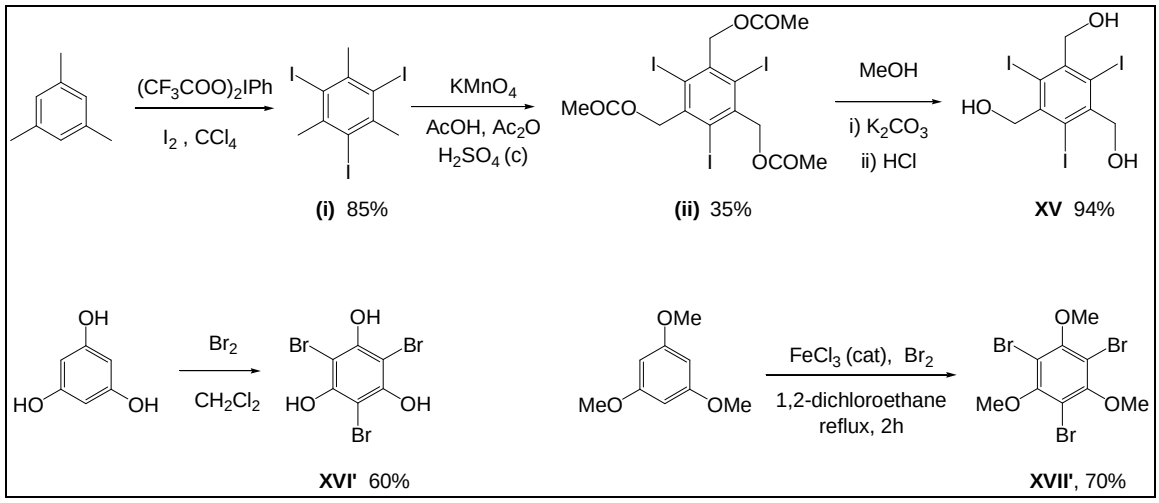
Scheme VIII.1 Synthesis of *trans,trans*-2,5-distyryl-1,4-dibromobenzene

- **TlOTf** was prepared by the reaction of Tl_2CO_3 and triflic acid (1:2) in water and recrystallized from acetone/Et_2O. **AgOTf** was obtained from TCI, and **$AgClO_4$** (anhydrous) from Alfa Aesar.

- **[{μ-*C1,C4,N,N"*-C_6H_2{C(H)=N(^{n}Bu)}$_2$-2,5}{Pd(μ-OAc)}]$_2$** (**IX**) (Chapter V) had been previously prepared in our research group by palladation of the diimine $C_6H_4(CH=N^nBu)_2$-1,4 (generated in situ) with $[Pd(OAc)_2]$.[4] The experimental data for this compound can be found in a PhD Thesis[4] but they have not been otherwise published yet. For this reason we reproduce them in Section VIII.2.

- **1,3,5-Triiodo-2,4,6-trihydroxymethylbenzene** (**XV**)[5]
  Tribromophloroglucinol (**XVI'**)[6]
  2,4,6-Tribromo-1,3,5-trimethoxybenzene (**XVII'**)[7]

  These trisubstituted trihaloarenes (Chapter VI) were prepared according to literature procedures (*Scheme VIII.2*):[5-7]



Scheme VIII.2 Synthesis of trisubstituted trihaloarenes[5-7]

For the characterization of compounds **1-32**, the following equipment and techniques have been used:

Elemental analyses: C, H, N, and S elemental analyses were carried out with a Carlo Erba 1106 microanalyzer.

Melting points: Melting points were determined on a Reichert apparatus and are uncorrected.

Conductivity: Molar conductivities were measured for ca. 5×10^{-4} M solutions in acetone, using a CRISON micro CM 2200 conductivity meter. In these conditions, W. J. Geary[8] gives the following reference values:

Electrolyte	Λ_M ($\Omega^{-1}cm^2mol^{-1}$)
1:1	100-140
2:1	160-200
3:1	270

Mass spectra: High resolution ESI mass spectra were recorded on an Agilent 6220 Accurate-Mass TOF LC/MS spectrometer

IR spectra: Infrared spectra were recorded in the range 4000-200 cm^{-1} on a Perkin Elmer Spectrum 100 spectrophotometer using Nujol mulls (bands at 2960-2840, 1455 and 1370 cm^{-1}) between polyethylene sheets (bands at 728 and 718 cm^{-1}).

NMR spectra: NMR spectra were recorded on Bruker Avance 200, 300, 400, or 600 spectrometers at 298 K unless otherwise indicated. Chemical shifts are referred to internal TMS (^1H and ^{13}C) or 85% H_3PO_4 (^{31}P). The ^1H and ^{13}C resonances were assigned with the help of 2D experiments (^1H-COSY, ^1H-NOESY, ^1H,^{13}C-HMQC, ^1H,^{13}C-HMBC).

X-ray diffractions structures: All the X-ray diffraction structures have been solved by Prof. Dr. Peter G. Jones at the Institute for Inorganic and Analytic Chemistry of the Technical University of Braunschweig. Details for each structure are given in the corresponding Chapters.

VIII.1.2 Relating Complexes 33-36

Complexes **33-36** have been prepared at *Centro de Química Estrutural of the Instituto Superior Técnico, University of Lisbon (Portugal).* Solvents were purchased from Aldrich and dried by usual procedures. *Trans*-$[Pd(N_3)_2(PPh_3)_2]$[9] and PTA (1,3,5-triaza-7-phosphaadamantane)[10] were prepared according to published procedures.

For the characterization of compounds **33-36**, the following equipment and techniques have been used:

Elemental analyses: C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico of Lisbon (Portugal) by using a Perkin Elmer PE 2400 Series II microanalyzer.

Mass spectra: Electrospray mass spectra were carried out with a Varian 500-MS LC Ion Trap Mass Spectrometer equipped with an electrospray (ESI) ion source. The solutions in methanol were continuously introduced into the mass spectrometer

source with a syringe pump at a flow rate of 10 μL/min. The drying gas temperature was maintained at 350 °C and N_2 was used as nebulizer gas at a pressure of 35 psi. Scanning was performed from *m/z* = 50 to 1500.

Microwave irradiation experiments: Microwave irradiation experiments were undertaken in a focused microwave CEM Discover reactor (10 mL, 13 mm diameter, 300 W) fitted with a rotational system and an IR detector of temperature.

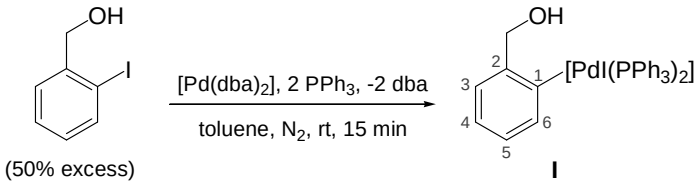
IR spectra: Infrared spectra were recorded in the range 4000-400 cm^{-1} on a Bio-Rad FTS 3000MX instrument in KBr pellets.

NMR spectra: NMR spectra were measured on Bruker Avance II 300 and 400 MHz spectrometers at ambient temperature unless otherwise indicated. ^{1}H, ^{13}C and ^{31}P chemical shifts (δ) are expressed in ppm relative to TMS (^{1}H and ^{13}C) or 85% H_3PO_4 (^{31}P).

X-ray diffractions structures: The X-ray diffraction structure of complex **33b** has been solved by Prof. Dr. M. Fátima C. Guedes da Silva at the Instituto Superior Técnico of the Technical University of Lisbon. Details for the structure are given in Chapter VII.

VIII.2 SYNTHESIS AND CHARACTERIZATION OF SECONDARY PRODUCTS

Synthesis of *trans*-[PdI{$C_6H_4(CH_2OH)$-2}(PPh_3)$_2$] (I)[11]

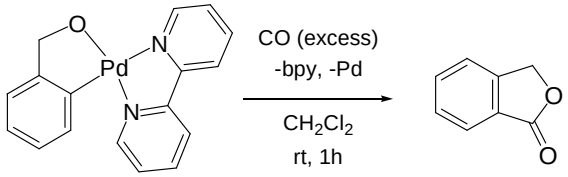


I

2-Iodobenzyl alcohol (183 mg, 0.782 mmol) was added to a suspension of [Pd(dba)$_2$] (300 mg, 0.521 mmol) and PPh_3 (273 mg, 1.04 mmol) in dry degassed toluene (20 mL) under N_2. The resulting brownish suspension was stirred for 15 min at room temperature and then concentrated in vacuo. The residue was extracted with CH_2Cl_2 (20 mL) and the extract was filtered over Celite. The resulting yellow solution was evaporated to dryness and Et_2O (20 mL) was added forming a pale pink suspension which was filtered off, washed with Et_2O (3x5 mL), and dried in vacuo to

give **I** as an orange solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 256 mg (56.8%). Mp: 142 ^oC. IR (cm^{-1}): ν(OH): 3566. ^1H NMR (400 MHz, $CDCl_3$): 7.49-7.42 (m, 12H, *o*-CH PPh_3), 7.37-7.31 (m, 6H, *p*-CH PPh_3), 7.28-7.22 (m, 12H, *m*-CH PPh_3), 7.08-7.04 (m, 1H, H6 aryl), 6.62 (t, $^3J_{HH}$ = 7, 1H, H4 aryl), 6.47 (t, $^3J_{HH}$ = 7, 1H, H5 aryl), 6.41 (d, $^3J_{HH}$ = 7, 1H, H3 aryl), 4.16 (d, $^3J_{HH}$ = 7, 2H, CH_2), 0.02 (t, $^3J_{HH}$ = 7, 1H, OH). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): 158.6 (t, $^2J_{CP}$ = 3, 2C, C1 aryl), 144.4 (t, $^3J_{CP}$ = 3, 1C, C2 aryl), 135.1 (vt, $^2J_{CP}$ + $^4J_{CP}$ = 12, 4C, *o*-CH PPh_3), 134.2 (t, $^3J_{CP}$ = 4, 2C, CH6 aryl), 132.0 (vt, $^1J_{CP}$ + $^3J_{CP}$ = 46, 2C, *i*-C PPh_3), 130.2 (s, 6C, *p*-CH PPh_3), 128.6 (s, 1C, CH3 aryl), 128.1 (vt, $^3J_{CP}$ + $^5J_{CP}$ = 10, 4C, *m*-CH PPh_3), 125.9 (s, CH5 aryl), 123.8 (s, CH4 aryl), 68.4 (t, $^4J_{CP}$ = 3, CH_2). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): 22.6 (s). Anal. Calcd for $C_{43}H_{37}IOP_2Pd$: C, 59.70; H, 4.31. Found: C, 59.35; H, 4.47.

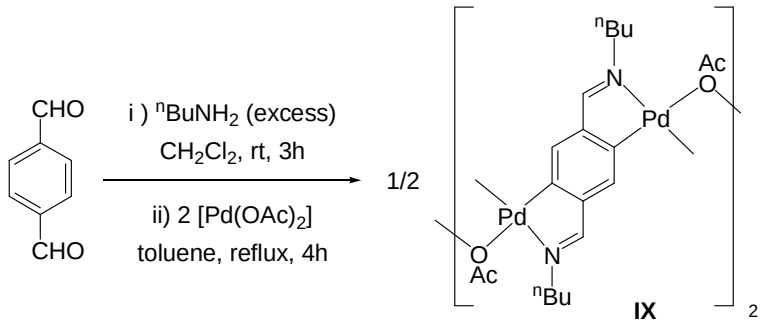
Reaction of 3 with CO to give phthalide



3

CO was bubbled for 5 min through a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL), whereby extensive decomposition was observed. The mixture was stirred for 1 h in a CO atmosphere. It was then filtered over $MgSO_4$, and the resulting yellow solution was evaporated to dryness, whereby a reddish color appeared in the residue. This residue was extracted with cold Et_2O (10 mL), and the resulting yellowish solution was filtered over Celite and then dried in vacuo to give a solid (45 mg), which is shown by ^1H NMR spectroscopy to be a clean mixture of 1(*3H*)-isobenzofuranone (phthalide) and bpy in a 1:1 ratio. ^1H NMR (400 MHz, $CDCl_3$): 8.69 (d, $^3J_{HH}$ = 5, 2H, bpy), 8.40 (d, $^3J_{HH}$ = 8, 2H, bpy), 7.94 (d, $^3J_{HH}$ = 8, 1H, phthalide), 7.83 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 2H, bpy), 7.69 (td, $^3J_{HH}$ = 7, $^4J_{HH}$ = 1, 1H, phthalide), 7.54 (td, $^3J_{HH}$ = 7, $^4J_{HH}$ = 1, 1H, phthalide), 7.50 (dt, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1, 1H, phthalide), 7.32 (ddd, $^3J_{HH}$ = 8, $^4J_{HH}$ = 5, $^4J_{HH}$ = 1, 2H, bpy), 5.33 (s, 2H, phthalide).

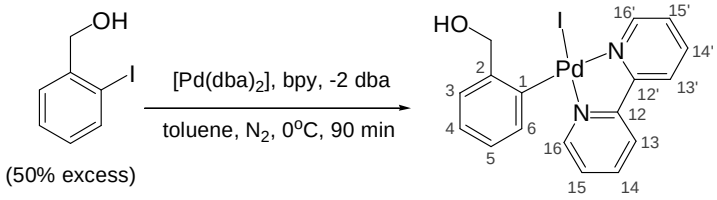
Synthesis of [{μ-*C1,C4,N,N"*-C_6H_2{C(H)=N(^{n}Bu)}$_2$-2,5}{Pd(μ-OAc)}]$_2$ (IX)[4]



A solution of ^{n}BuNH$_2$ (1.00 g, 7.45 mmol) and terephthalaldehyde (250 mg, 1.86 mmol) in CH_2Cl_2 (3 mL) was stirred for 1.5 h. The solvent and the excess amine were then evaporated in vacuo, leaving a yellow oil to which [Pd(OAc)]$_2$ (877 mg, 3.91 mmol) and toluene (60 mL) were added. The mixture was refluxed for 4 h in a CaH_2-containing Soxhlet, and then it was concentrated in vacuo. The residue was extracted with CH_2Cl_2 (60 mL) and the extract was filtered over Celite. The resulting red solution was concentrated in vacuo to ca. 3 mL. Et_2O (25 mL) was added forming an orange suspension which was filtered off, washed with Et_2O (3x10 mL), and dried in vacuo to give **IX** as an orange solid, which is soluble in CH_2Cl_2 and acetone. For a complete purification the solid was dried in an oven at 70ºC for 24 h and then in a desiccator over P_2O_5 for 5 days. Yield: 826 mg (77%). Mp: 240 ^{o}C (dec). IR (cm^{-1}): ν(C=O): 1576; ν(C=N): 1556. ^{1}H NMR (300 MHz, $CDCl_3$): 7.62 (s, 2H, HC=N), 6.48 (s, 2H, aryl), 3.75-3.55 and 3.25-3.05 (m, 2H, CH_2 nBu), 2.19 and 2.00 (s, 3H, $MeCO_2$), 1.95-1.65 (m, 4H, CH_2 nBu), 1.50-1.15 (m, 4H, CH_2 nBu), 0.93 (t, $^3J_{HH}$ = 7 Hz, 6H, Me nBu). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): 181.2 and 179.7 (Me*C*O$_2$), 172.6 (C=N), 152.0 and 145.3 (aryl C), 129.9 (aryl CH), 59.7, 31.7, and 19.8 (CH_2 nBu), 24.5 and 24.3 (*Me*CO$_2$), 13.6 (Me nBu). Anal. Calcd for $C_{20}H_{28}N_2O_4Pd_2$: C, 41.90; H, 4.93; N, 4.89. Found: C, 42.17; H, 5.00, N, 4.88.

VIII.3 SYNTHESIS AND CHARACTERIZATION OF THE MAIN PRODUCTS

[PdI($C_6H_4CH_2OH$-2)(bpy)] (1a)



1a

2-Iodobenzyl alcohol (183 mg, 0.782 mmol) was added to a suspension of [Pd(dba)$_2$] (300 mg, 0.521 mmol) and bpy (81.4 mg, 0.521 mmol) in dry degassed toluene (20 mL) under N_2. The resulting mixture was stirred in an ice bath for ca. 90 min until the dark red color of [Pd(dba)$_2$] was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the orange solution was evaporated to dryness. Et_2O (20 mL) was added, and the resulting pale pink suspension was filtered off, washed with Et_2O (3×5 mL), and dried in vacuo to give **1a** as a pale reddish solid. Yield: 124 mg (48%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, CD_2Cl_2): 9.46 (ddd, 1H, $^3J_{HH}$ = 5, $^4J_{HH}$ = 2, $^5J_{HH}$ = 1, H16' bpy), 8.06-8.02 (m, 2H, H13,13' bpy), 7.98 (td, 1H, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, H14' bpy), 7.94 (td, 1H, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, H14 bpy), 7.53 (dd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 5, $^4J_{HH}$ = 2, 1H, H15' bpy), 7.39-7.36 (m, 1H, H6 aryl), 7.33 (ddd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 2, $^5J_{HH}$ = 1, H16 bpy), 7.27-7.23 (m, 1H, H15 bpy), 7.13-7.10 (m, 1H, H3 aryl), 6.93-6.89 (m, 2H, H5,H4 aryl), 4.99 (dd, $^2J_{HH}$ = 12, $^3J_{HH}$ = 3, 1H, CH_2), 4.48 (dd, $^2J_{HH}$ = 12, $^3J_{HH}$ = 10, 1H, CH_2), 2.66 (dd, $^3J_{HH}$ = 10, $^3J_{HH}$ = 3, 1H, OH).

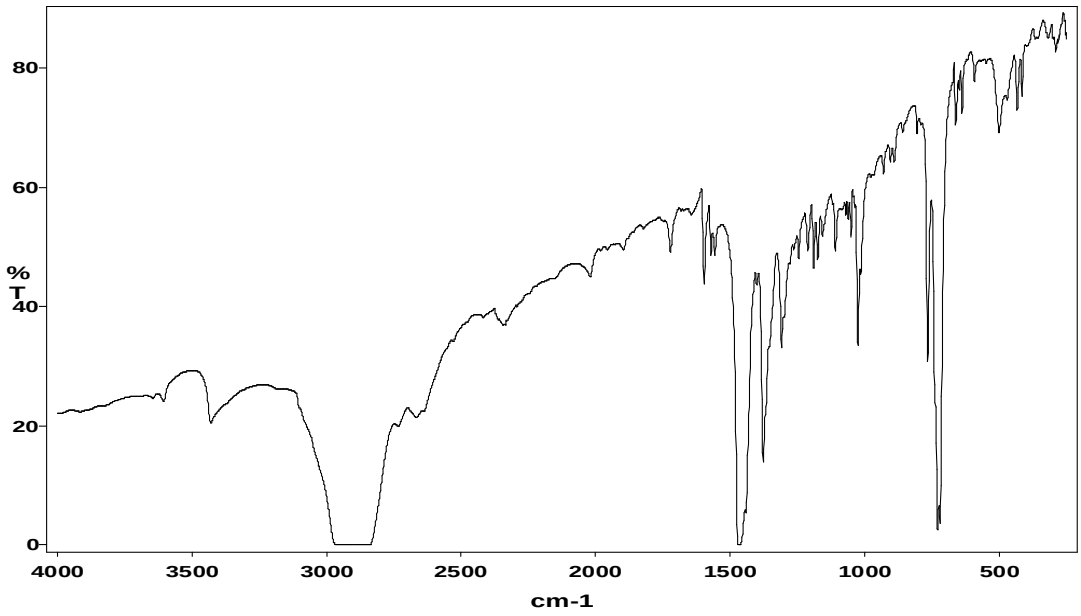
^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2): 156.6 (C12 bpy), 154.4 (C12' bpy), 153.1 (CH16' bpy), 150.4 (CH16 bpy), 146.3 (C1 aryl), 145.4 (C2 aryl), 139.6 (CH14 bpy), 139.5 (CH14' bpy), 136.6 (CH6 aryl), 128.8 (CH3 aryl), 127.6 (CH15' bpy), 127.2 (CH15 bpy), 126.8 (CH5 aryl), 124.3 (CH4 aryl), 122.8 (CH13 bpy), 122.4 (CH13' bpy), 68.7 (CH_2).

IR (cm^{-1}): ν(O-H): 3430. **Melting point:** 229 °C (dec).

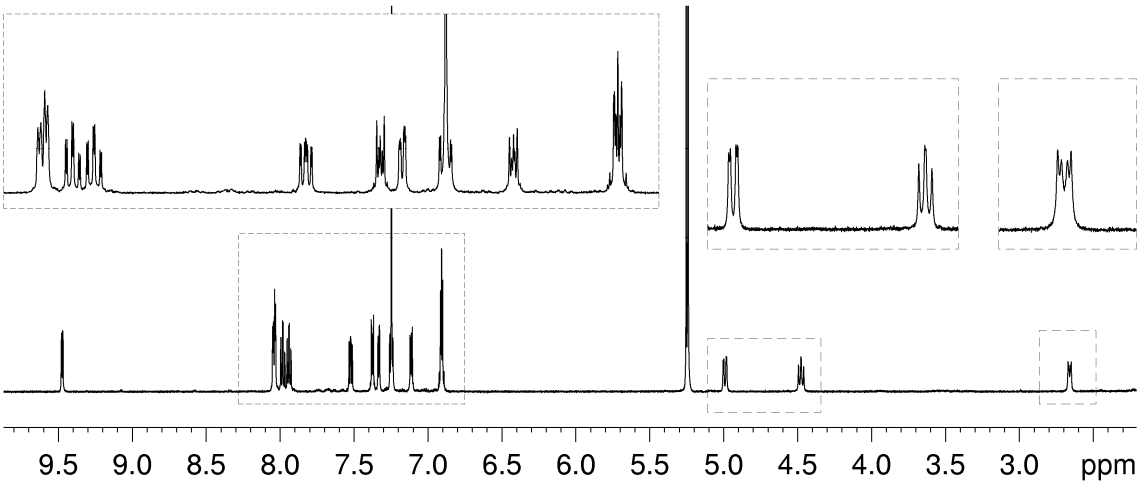
Elemental analysis (%):	C, 40.98	H, 3.06	N, 5.70
Calcd for $C_{17}H_{15}IN_2OPd$:	C, 41.11	H, 3.04	N, 5.64

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

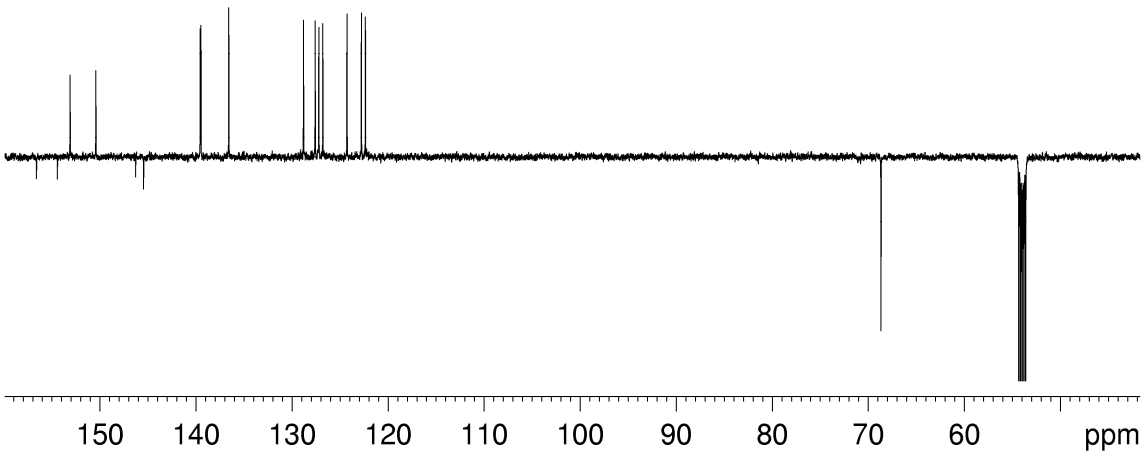
X-ray crystallography: Single crystals of **1a** were grown by liquid diffusion of Et_2O into a solution of **1a** in CH_2Cl_2.



IR spectrum of 1a

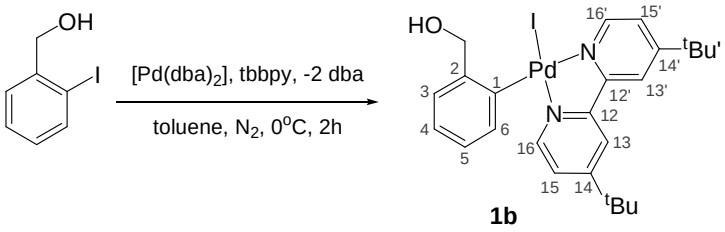


^{1}H-RMN spectrum (600 MHz) of 1a



APT spectrum (150.9 MHz) of 1a

[PdI($C_6H_4CH_2OH$-2)(tbbpy)] (1b)



2-Iodobenzyl alcohol (122 mg, 0.521 mmol) was added to a suspension of [$Pd(dba)_2$] (300 mg, 0.521 mmol) and tbbpy (140 mg, 0.521 mmol) in dry degassed toluene (20 mL) under N_2. The resulting mixture was stirred in an ice bath for 2 h until the dark red color of [$Pd(dba)_2$] was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the orange solution was evaporated to dryness. Warm hexane (20 mL) was added, and the resulting yellow suspension was filtered off, washed with warm hexane (3×5 mL), and dried in vacuo to give **1b** as a pale yellow solid. Yield: 133 mg (42%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 9.46 (d, $^3J_{HH}$ = 6, 1H, H16' tbbpy), 7.98 (s, 1H, H13 tbbpy), 7.97 (s, 1H, H13' tbbpy), 7.53 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 1H, H15' tbbpy), 7.50 (dd, $^3J_{HH}$ = 7, $^4J_{HH}$ = 2, 1H, H6 aryl), 7.33 (d, $^3J_{HH}$ = 6, 1H, H16 tbbpy), 7.28 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15 tbbpy), 7.20 (dd, $^3J_{HH}$ = 7, $^4J_{HH}$ = 2, 1H, H3 aryl), 7.02-6.93 (m, 2H, H5,H4 aryl), 5.21 (dd, $^3J_{HH}$ = 12, $^4J_{HH}$ = 3, 1H, CH_2), 4.66 (app t, J_{HH} = 10, 1H, CH_2), 2.92-2.86 (m, 1H, OH), 1.43 (s, 9H, ^{t}Bu' tbbpy), 1.38 (s, 9H, ^{t}Bu tbbpy).

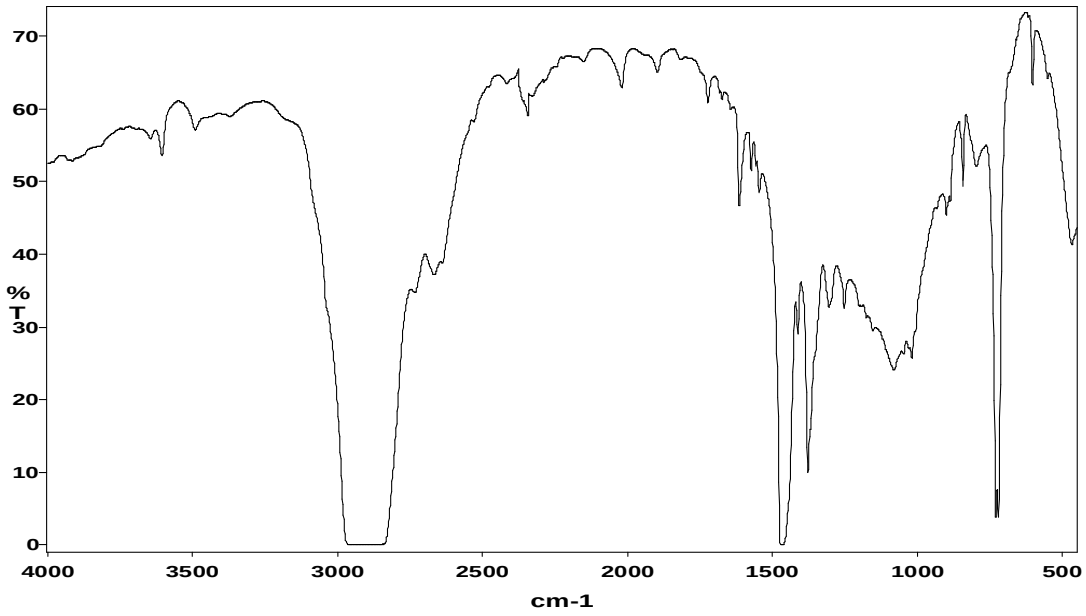
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 163.62 (C14 tbbpy), 163.58 (C14' tbbpy), 156.2 (C12 tbbpy), 154.0 (C12' tbbpy), 152.6 (CH16' tbbpy), 149.7 (CH16 tbbpy), 146.3 (C1 aryl), 144.8 (C2 aryl), 136.2 (CH6 aryl), 128.6 (CH3 aryl), 126.6 (CH5 aryl), 124.2 (CH15' tbbpy), 123.93 (CH4 aryl), 123.91 (CH15 tbbpy), 118.7 (CH13 tbbpy), 118.2 (CH13' tbbpy), 68.8 (CH_2), 35.74 (*C*Me_3 tbbpy), 35.70 (*C*Me_3' tbbpy), 30.6 (C*Me*$_3$' tbbpy), 30.5 (C*Me*$_3$ tbbpy).

IR (cm^{-1}): ν(O-H): 3490.

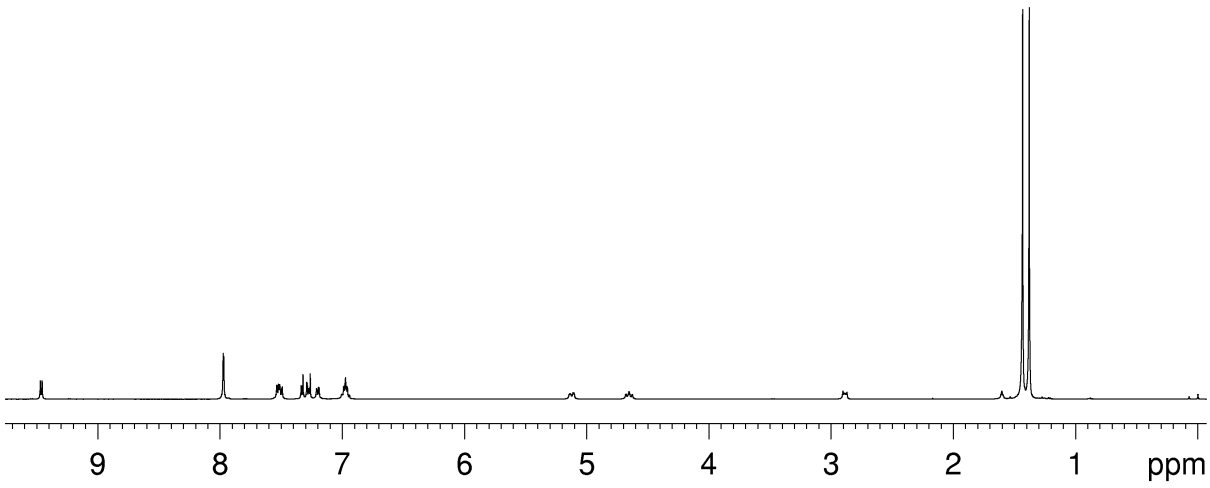
Elemental analysis (%):	C, 49.43	H, 5.11	N, 4.68
Calcd for $C_{25}H_{31}IN_2OPd$:	C, 49.32	H, 5.13	N, 4.60

Melting point: 217 °C (dec).

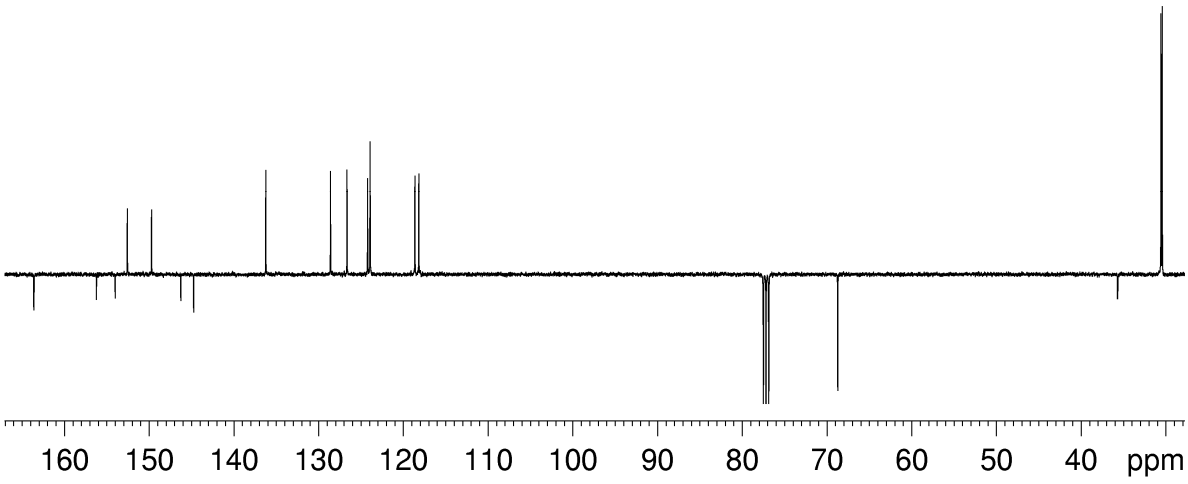
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, acetone, and Et_2O (partially). Insoluble in hexane.



IR spectrum of 1b

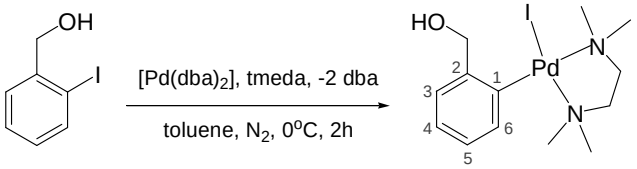


^{1}H-RMN spectrum (400 MHz) of 1b



APT spectrum (100.6 MHz) of 1b

[PdI($C_6H_4CH_2OH$-2)(tmeda)] (1c)



1c

2-Iodobenzyl alcohol (122 mg, 0.521 mmol) was added to a suspension of [Pd(dba)$_2$] (300 mg, 0.521 mmol) and tmeda (78.2 μL, 0.521 mmol) in dry degassed toluene (20 mL) under N_2. The resulting mixture was stirred in an ice bath for 4 h until the dark red color of [Pd(dba)$_2$] was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the reddish solution was evaporated to dryness. Et_2O (20 mL) was added, and the resulting pale pink suspension was filtered off, washed with Et_2O (3×5 mL), and dried in vacuo to give **1c** as an orange solid. Yield: 140 mg (59%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 7.29 (dd, $^3J_{HH}$ = 7, $^4J_{HH}$ = 2, 1H, H6 aryl), 7.11 (dd, $^3J_{HH}$ = 7, $^4J_{HH}$ = 2, 1H, H3 aryl), 6.93-6.84 (m, 2H, H5,H4 aryl), 5.43 (dd, $^3J_{HH}$ = 11, $^4J_{HH}$ = 3, 1H, CH_2), 4.68 (app t, J_{HH} = 11, 1H, CH_2), 3.00 (dd, $^3J_{HH}$ = 10, $^3J_{HH}$ = 3, 1H, OH), 2.95-2.86 (m, 1H, CH_2 tmeda), 2.75-2.45 (several m, 3H, CH_2 tmeda), 2.72, 2.69, 2.48, and 2.12 (s, 3H, Me tmeda).

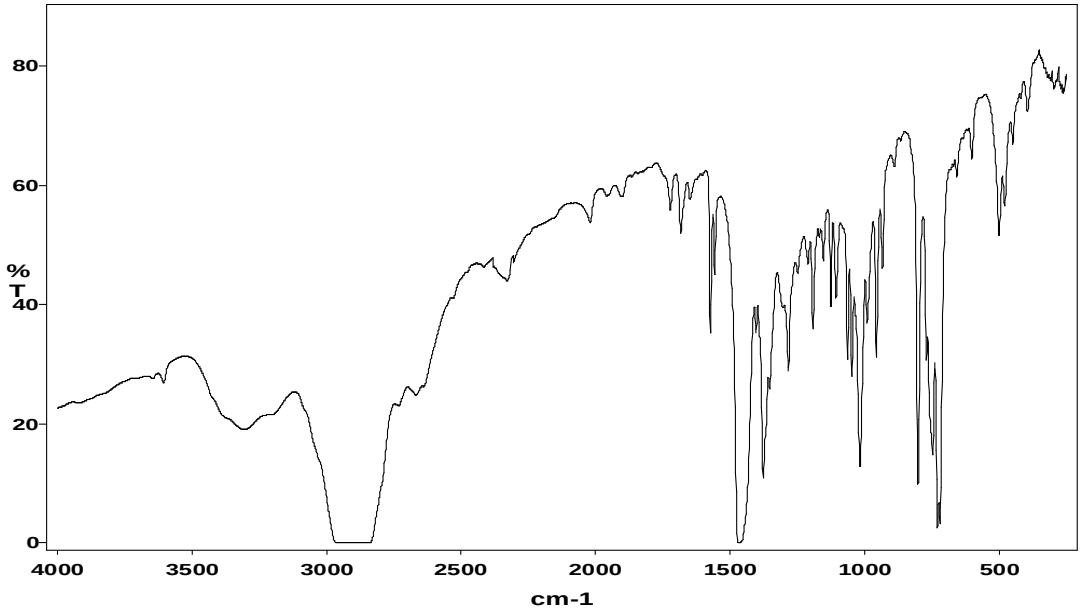
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 145.0 (C2 aryl), 143.7 (C1 aryl), 135.6 (CH6 aryl), 128.4 (CH3 aryl), 126.2 (CH5 aryl), 123.7 (CH4 aryl), 69.1 (CH_2), 62.4 (CH_2 tmeda), 58.5 (CH_2 tmeda), 51.2 and 50.7 (Me tmeda), 49.0 (2C, Me tmeda).

IR (cm^{-1}): ν(O-H): 3305.

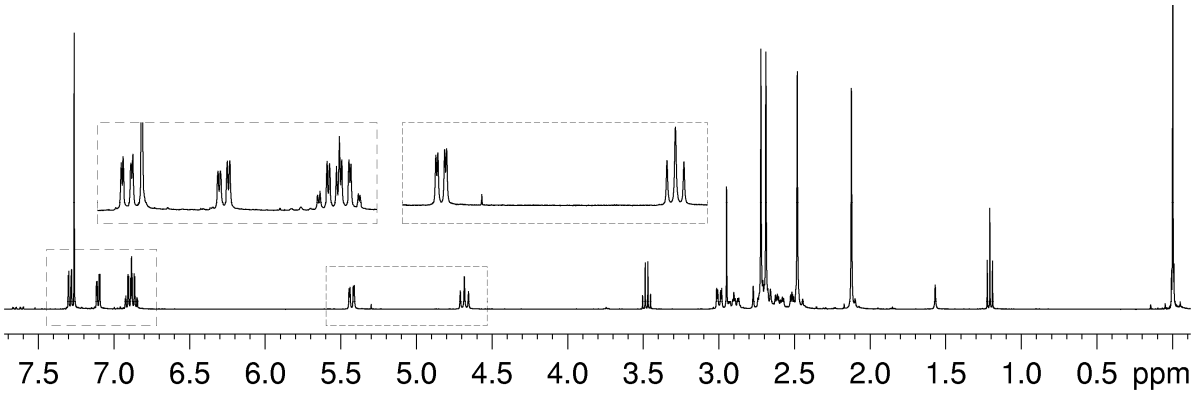
Elemental analysis (%):	C, 34.54	H, 5.02	N, 5.94
Calcd for $C_{25}H_{31}IN_2OPd$:	C, 34.19	H, 5.08	N, 6.13

Melting point: 105 °C.

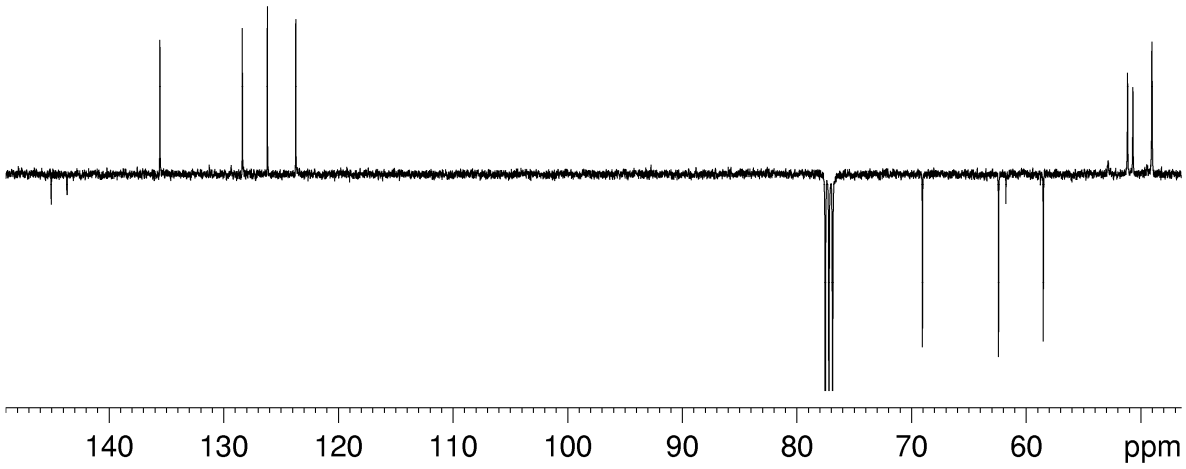
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 1c

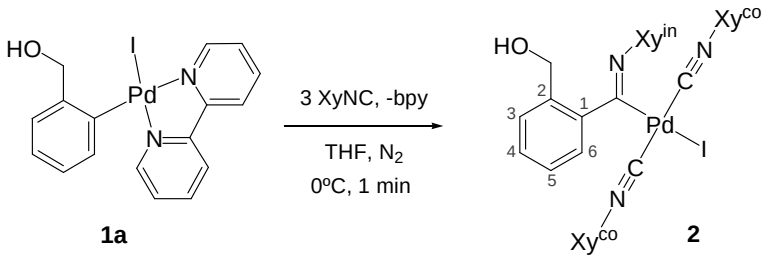


^{1}H-RMN spectrum (400 MHz) of 1c



APT spectrum (100.6 MHz) of 1c

***trans*-[PdI{C(=NXy)($C_6H_4CH_2OH$-2)}$(CNXy)_2$] (2)**



1a **2**

XyNC (159 mg, 1.21 mmol) was added to a solution of **1a** (200 mg, 0.403 mmol) in dry degassed THF (20 mL), under N_2 and in an ice bath. The solvent was immediately evaporated in vacuo, and Et_2O (20 mL) was added under N_2, forming a yellow suspension, which was filtered off, washed with Et_2O (3×5 mL), and dried in vacuo to give **2** as a yellow solid. Yield: 147 mg (50%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (300 MHz, $CDCl_3$): 8.56 (d, $^3J_{HH}$ = 8, 1H, aryl), 7.56-7.48 (m, 1H, aryl), 7.41-7.37 (m, 2H, aryl), 7.26-7.18 (m, 2H, Xy^{co}), 7.06 (d, $^3J_{HH}$ = 8, 4H, Xy^{co}), 6.95 (br s, 3H, Xy^{in}), 5.12 (t, $^3J_{HH}$ = 7, 1H, OH), 4.70 (d, $^3J_{HH}$ = 7, 2H, CH_2), 2.192 (s, 6H, Me Xy^{in}), 2.186 (s, 12H, Me Xy^{co}).

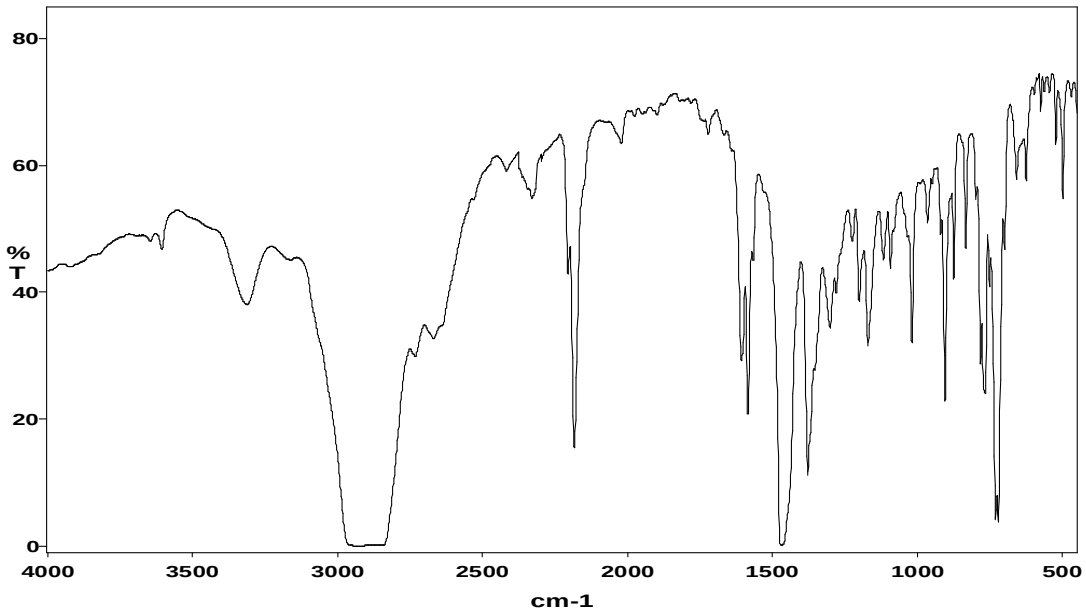
^{13}C{^{1}H} NMR: No ^{13}C NMR data are available because the complex decomposes rapidly in solution.

IR (cm^{-1}): ν(O-H): 3311, ν(C≡N): 2182, ν(C=N): 1606.

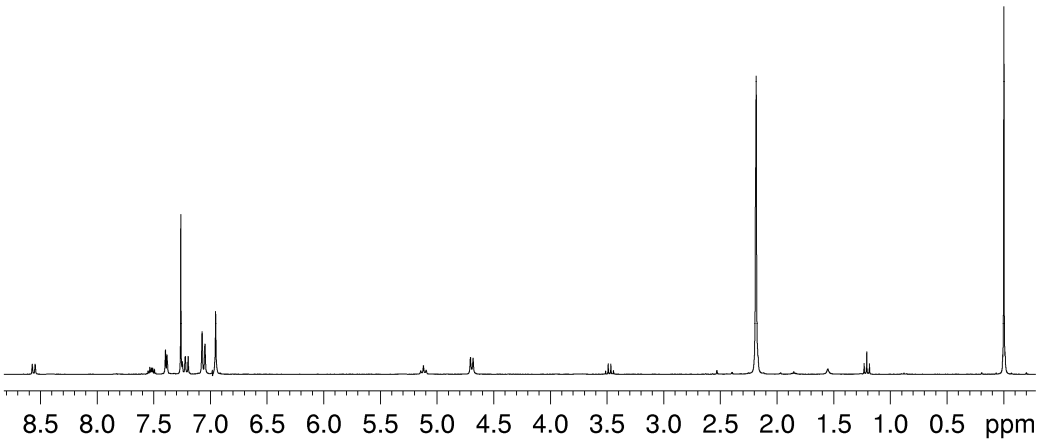
Elemental analysis (%):	C, 55.57	H, 4.80	N, 5.64
Calcd for $C_{34}H_{34}IN_3OPd$:	C, 55.64	H, 4.67	N, 5.72

Melting point: 130 ^{o}C.

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

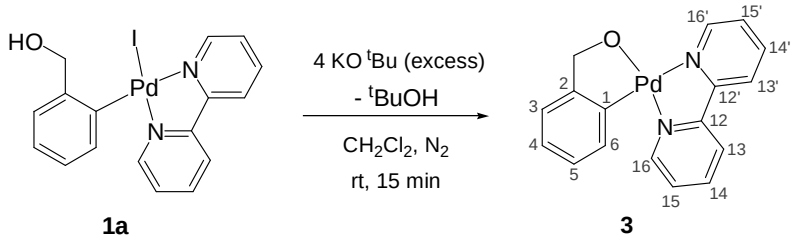


IR spectrum of 2



^{1}H-RMN spectrum (300 MHz) of 2

[Pd(κ^2-*C*,*O*-$C_6H_4CH_2O$-2)(bpy)] (3)



KO^tBu (361 mg, 3.22 mmol) was added to a solution of **1a** (400 mg, 0.805 mmol) in CH_2Cl_2 (20 mL) under N_2, whereby the color changed from reddish to yellow. The mixture was stirred for 15 min at room temperature and then filtered over Celite. The resulting yellow solution was evaporated to dryness, and Et_2O (20 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **3** as a yellow solid. Yield: 227 mg (77%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, CD_2Cl_2): 9.18 (d, $^3J_{HH}$ = 5, 1H, H16 bpy), 9.03 (ddd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, $^5J_{HH}$ = 1, 1H, H16' bpy), 8.08-7.96 (m, 4H, H13,13',14,14' bpy), 7.59-7.52 (m, 2H, H15,15' bpy), 7.23-7.19 (m, 1H, H6 aryl), 7.04-6.97 (m, 3H, H3,4,5 aryl), 5.21 (s, 2H, CH_2).

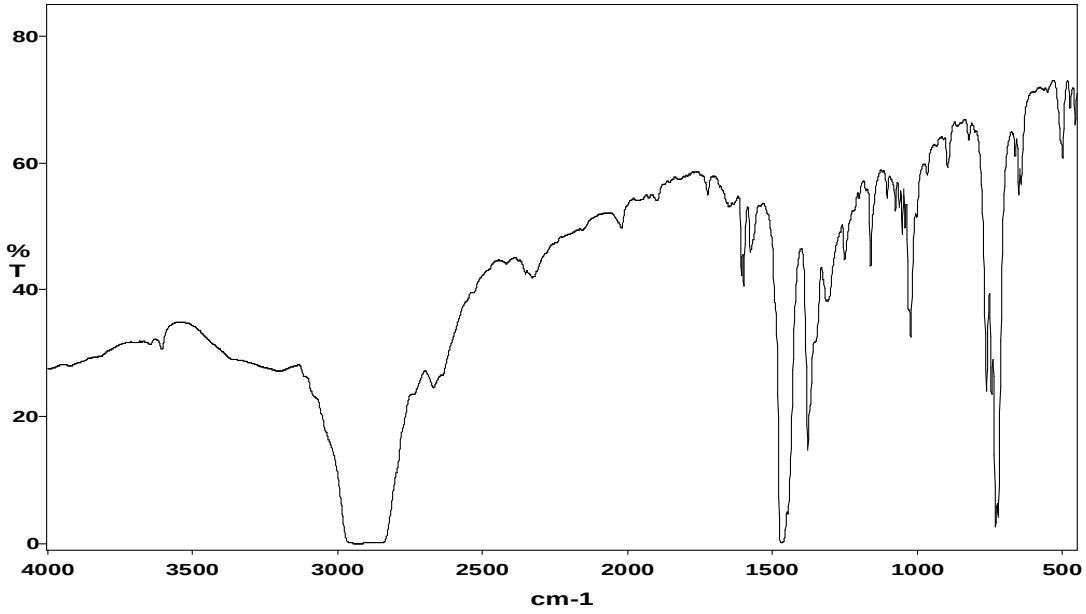
^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): 166.2 (C2 aryl), 156.6 (C12 bpy), 153.4 (C12' bpy), 152.0 (CH16 bpy), 151.0 (C1 aryl), 149.9 (CH16' bpy), 138.8 (CH14' bpy), 138.1 (CH14 bpy), 131.7 (CH6), 126.6 (CH15 bpy), 126.3 (CH15' bpy), 124.0 (CH4 aryl), 123.6 (CH5 aryl), 122.5 (CH13 bpy), 121.1 (CH13' bpy), 119.1 (CH3 aryl), 78.4 (CH_2).

Elemental analysis (%):	C, 55.12	H, 3.74	N, 7.43
Calcd for $C_{17}H_{14}N_2OPd$:	C, 55.37	H, 3.83	N, 7.60

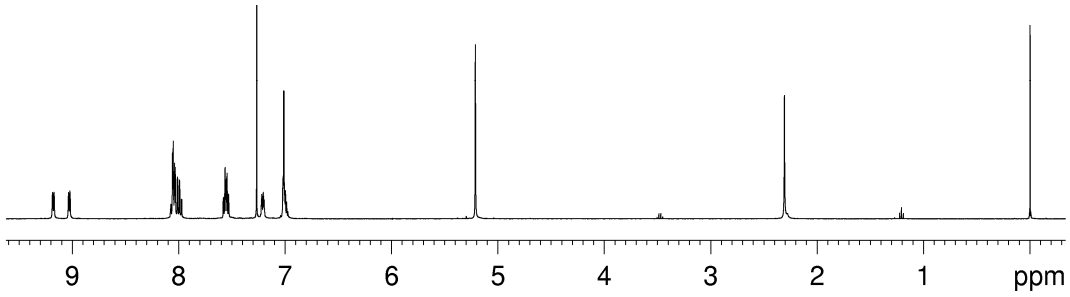
Melting point: 129 ^{o}C (dec).

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

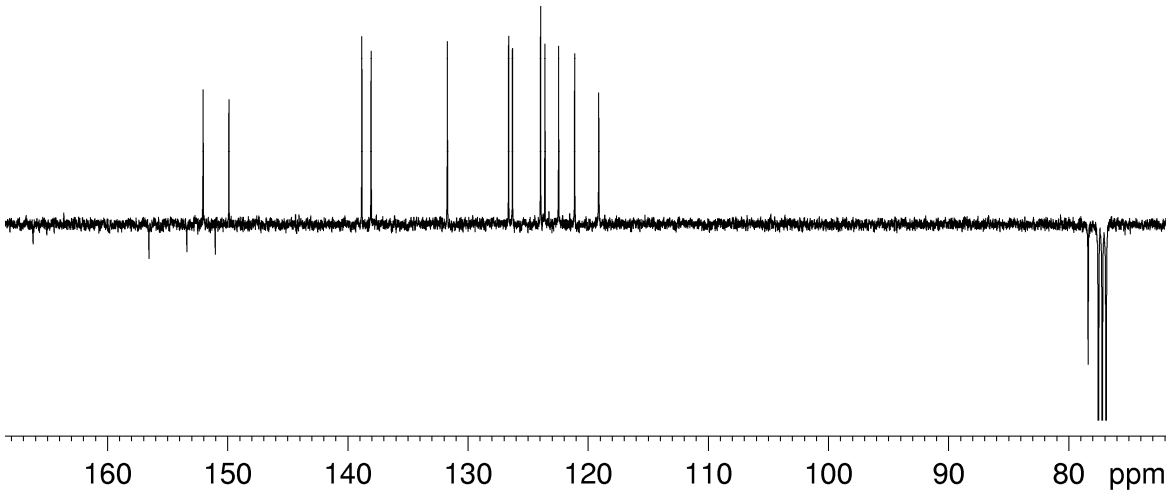
X-ray crystallography: Single crystals of **3**·H_2O were grown by liquid diffusion of hexane into a solution of **3** in CH_2Cl_2.



IR spectrum of 3

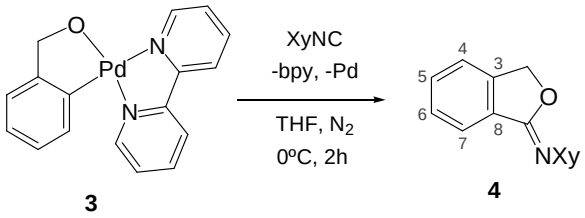


^{1}H-RMN spectrum (400 MHz) of 3



APT spectrum (100.6 MHz) of 3

***N*-(2,6-dimethylphenyl)-2-benzofuran-1(3H)imine (4)**



3 **4**

XyNC (35.6 mg, 0.271 mmol) was added to a solution of **3** (100 mg, 0.271 mmol) in THF (20 mL) under N_2. The mixture was stirred for 2 h in an ice bath, whereby the color changed from yellow to black. It was then filtered over $MgSO_4$, and the resulting yellow solution was evaporated to dryness, leaving a yellow oil. This oil was washed with cold hexane (10 mL), to eliminate the bpy ligand, and then dried in vacuo to give **4** as a yellow oil. Yield: 29.0 mg (45%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (d, $^{3}J_{HH}$ = 7, 1H, H7), 7.59 (t, $^{3}J_{HH}$ = 7, 1H, H5), 7.53 (t, $^{3}J_{HH}$ = 7, 1H, H6), 7.41 (d, $^{3}J_{HH}$ = 7, 1H, H4), 7.05 (d, $^{3}J_{HH}$ = 7, 2H, *m*-H Xy), 6.93 (t, $^{3}J_{HH}$ = 7, 1H, *p*-H Xy), 5.31 (s, 2H, CH_2), 2.16 (s, 6H, Me Xy).

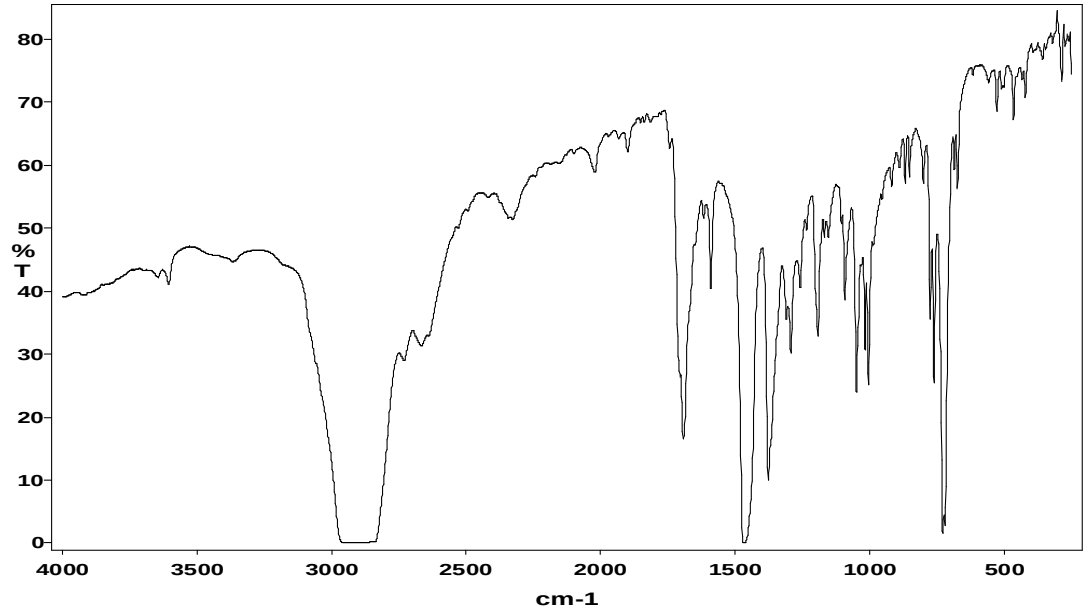
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 158.1 (C=N), 145.4 (*i*-C Xy), 143.9 (C3), 132.1 (CH5), 129.9 (C8), 128.9 (CH6), 128.4 (2C, *o*-C Xy), 127.8 (2C, *m*-CH Xy), 124.4 (CH7), 123.3 (*p*-CH Xy), 121.7 (CH4), 72.6 (CH_2), 18.5 (2C, Me Xy).

IR (cm^{-1}): ν(C=N): 1693.

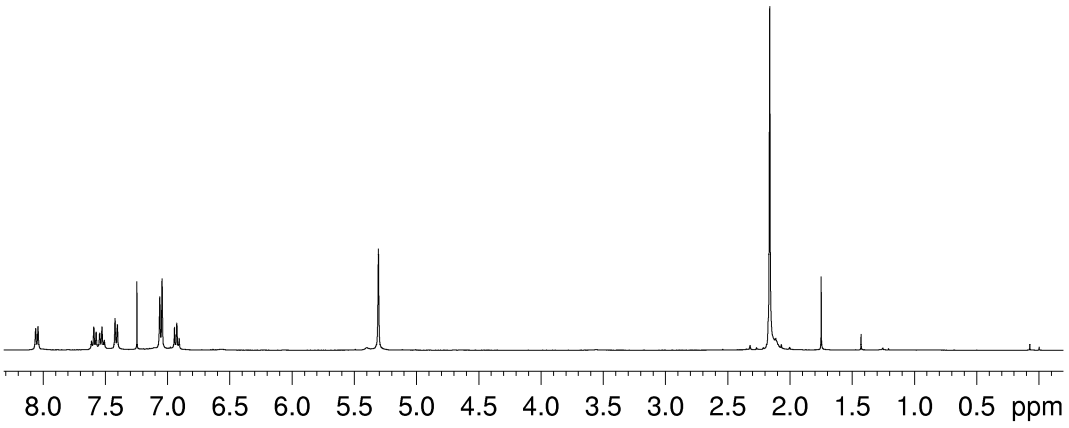
Exact Mass: HR ESI+ TOF MS: calcd for $C_{16}H_{15}NO$ m/z 238.1226, found 238.1226, Δ = 0. 0.00 ppm.

Calculated:	**238.1226 (100)**	239.1259 (17.89)	240.1289 (1.71)
Found:	**238.1226 (100)**	239.1251 (18.99)	240.1280 (1.76)

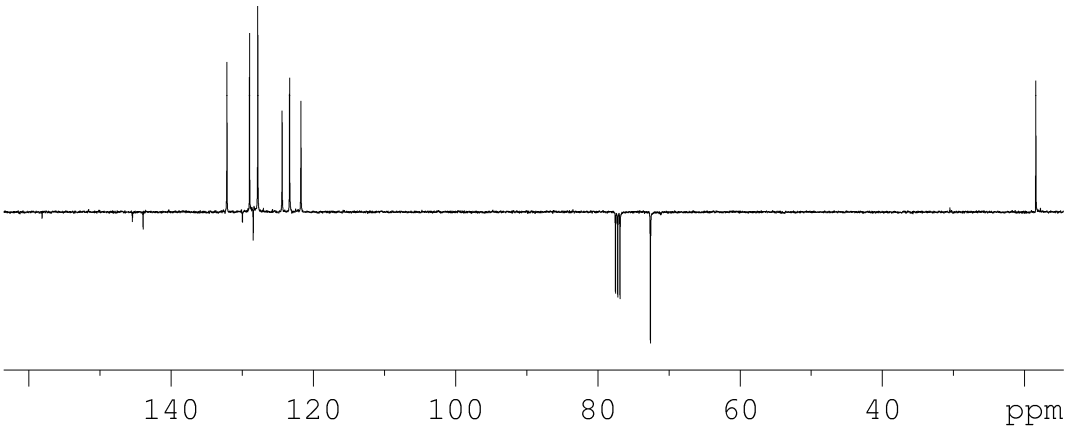
Solubility: Soluble in Et_2O, CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in hexane.



IR spectrum of 4

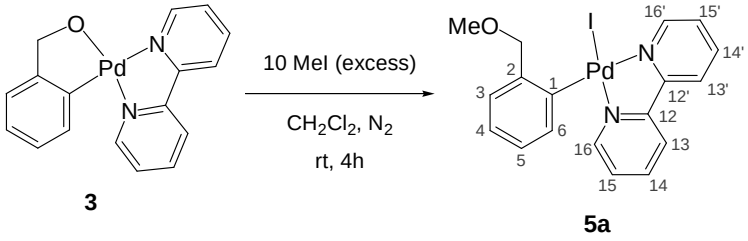


^{1}H-RMN spectrum (400 MHz) of 4



APT spectrum (100.6 MHz) of 4

[PdI($C_6H_4CH_2OMe$-2)(bpy)] (5a)



3 **5a**

MeI (169 μL, 2.71 mmol) was added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred in the dark for 4 h at room temperature, whereby the yellow color darkened. It was then filtered over Celite, and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **5a** as a yellow solid. Yield: 101 mg (73%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

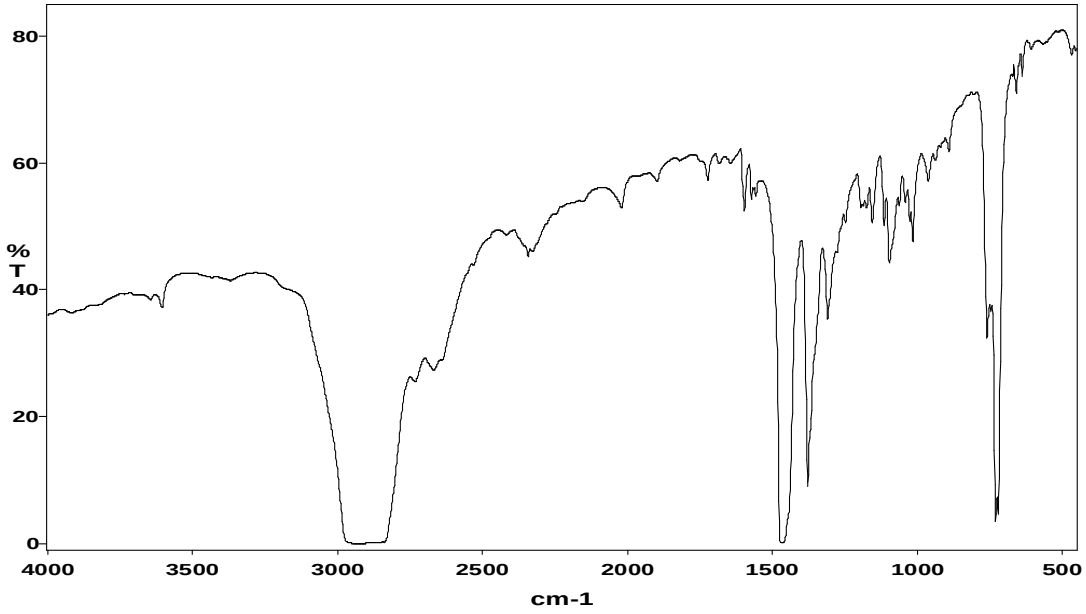
^{1}H NMR (400 MHz, $CDCl_3$): 9.66 (ddd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 2, $^5J_{HH}$ = 1, 1H, H16' bpy), 8.09-8.04 (m, 2H, H13,13' bpy), 8.01 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14' bpy), 7.98 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14 bpy), 7.57 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H15' bpy), 7.53 (ddd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, $^5J_{HH}$ = 1, 1H, H16 bpy), 7.50-7.45 (m, 1H, H6 aryl), 7.32 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 6, $^4J_{HH}$ = 1, 1H, H15 bpy), 7.26-7.22 (m, 1H, H3 aryl), 7.02-6.95 (m, 2H, H4,5 aryl), 5.00 and 4.77 (AB system, $^2J_{HH}$ = 11, 2H, CH_2), 3.32 (s, 3H, Me).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 155.9 (C12 bpy), 153.9 (C12' bpy), 153.2 (CH16' bpy), 150.6 (CH16 bpy), 145.3 (C1 aryl), 142.2 (C2 aryl)), 138.74 (CH14' bpy), 138.69 (CH14 bpy), 136.1 (CH6 aryl)), 127.08 (CH3 aryl)), 127.05 (CH15' bpy), 126.6 (CH15 bpy), 126.3 (CH5 aryl)), 123.8 (CH4 aryl)), 121.9 (CH13 bpy), 121.6 (CH13' bpy), 78.5 (CH_2), 58.5 (Me).

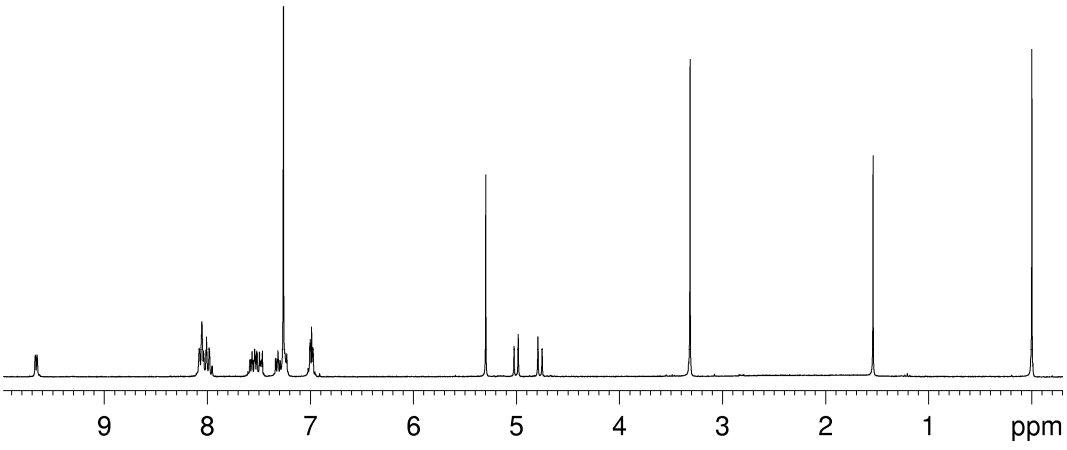
Elemental analysis (%):	C, 41.97	H, 3.23	N, 5.53
Calcd for $C_{18}H_{17}IN_2OPd$:	C, 42.34	H, 3.36	N, 5.49

Melting point: 202 ^{o}C.

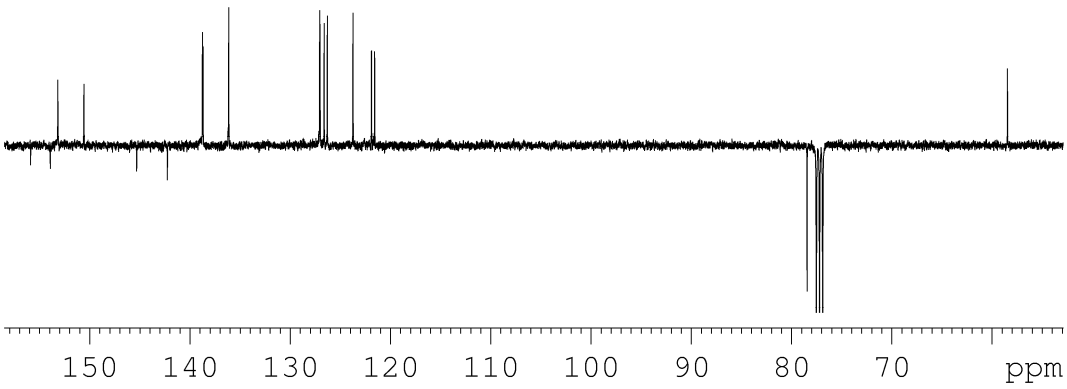
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 5a

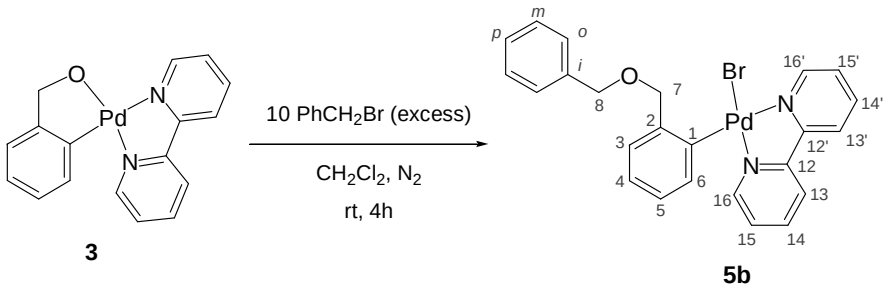


^{1}H-RMN spectrum (400 MHz) of 5a



APT spectrum (100.6 MHz) of 5a

[PdBr($C_6H_4CH_2OCH_2Ph$-2)(bpy)] (5b)



$PhCH_2Br$ (322 μL, 2.71 mmol) was added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred for 4 h at room temperature with no significant change in color. It was then filtered over Celite, and the resulting yellow solution was evaporated in vacuo to dryness. Cold Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with cold Et_2O (3×5 mL), and dried in vacuo to give **5b** as a pale yellow solid. Yield: 122 mg (83%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

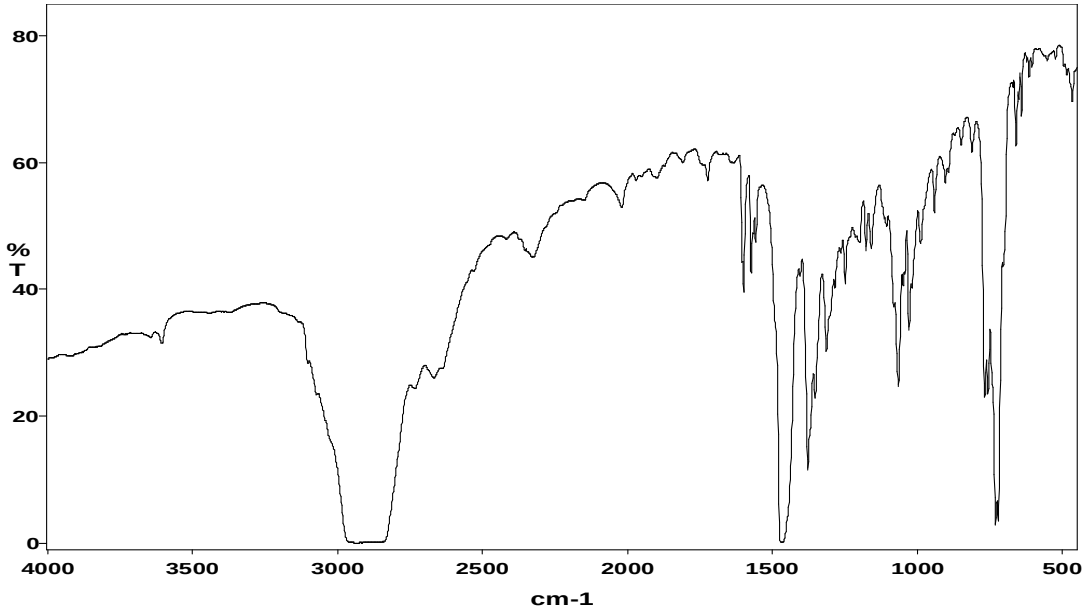
^{1}H NMR (400 MHz, $CDCl_3$): 9.43 (ddd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, $^5J_{HH}$ = 1, 1H, H16' bpy), 8.06-7.99 (m, 2H, H14',13' bpy), 7.97 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 7.88 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14 bpy), 7.69 (ddd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, $^5J_{HH}$ = 2, 1H, H16 bpy), 7.62-7.57 (m, 1H, H15' bpy), 7.53-7.47 (m, 1H, H6 aryl), 7.32-7.27 (m, 1H, H3 aryl), 7.17 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 6, $^4J_{HH}$ = 1, 1H, H15 bpy), 7.12-7.05 (m, 5H, Ph), 7.05-6.98 (m, 2H, H4,5 aryl), 5.31 and 4.89 (AB system, $^2J_{HH}$ = 11, 2H, CH_2-7), 4.56 and 4.52 (AB system, $^2J_{HH}$ = 12, 2H, CH_2-8).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 155.9 (C12 bpy), 153.7 (C12' bpy), 151.7 (CH16 bpy), 150.9 (CH16' bpy), 149.7 (C1 aryl), 141.9 (C2 aryl), 139.2 (*i*-C Ph), 138.9 (CH14' bpy), 138.4 (CH14 bpy), 135.0 (CH6 aryl), 128.13 (CH3 aryl), 128.12 (2C, *m*-CH Ph), 127.7 (2C, *o*-CH Ph), 127.1 (*p*-CH Ph), 126.74 (CH15' bpy), 126.71 (CH5 aryl), 126.6 (CH15 bpy), 123.9 (CH4 aryl), 121.8 (CH13 bpy), 121.3 (CH13' bpy), 76.0 (CH_2-7), 72.6 (CH_2-8).

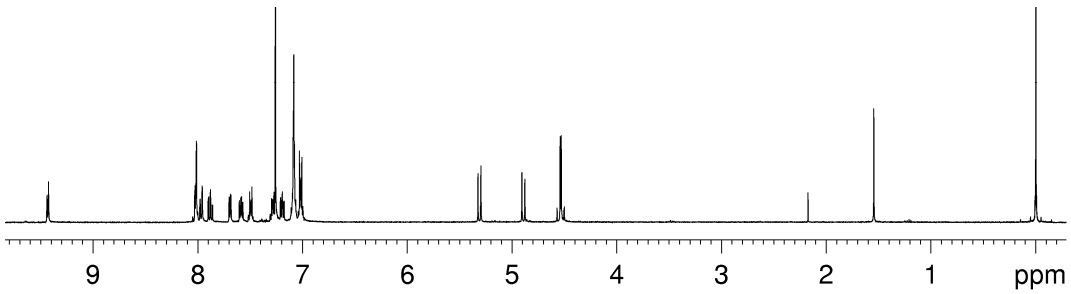
Elemental analysis (%):	C, 53.65	H, 4.04	N, 5.42
Calcd for $C_{24}H_{21}BrN_2OPd$:	C, 53.40	H, 3.92	N, 5.19

Melting point: 171 °C.

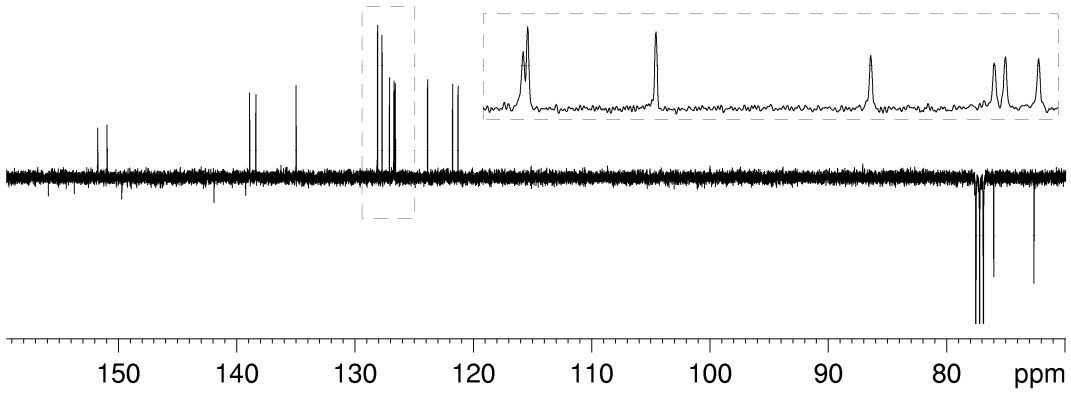
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Partially soluble in Et_2O. Insoluble in hexane.



IR spectrum of 5b

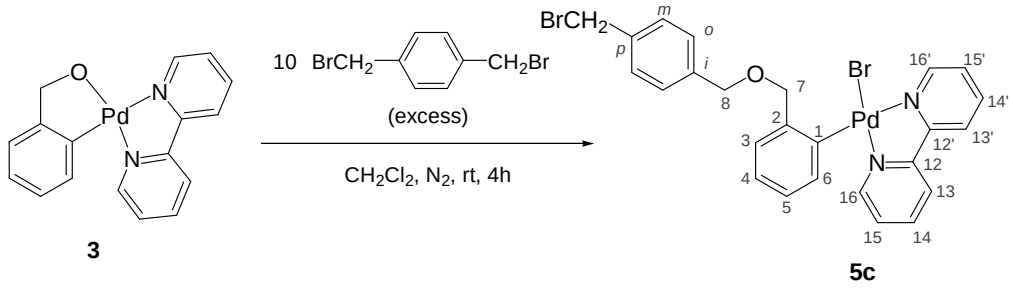


^{1}H-RMN spectrum (400 MHz) of 5b



APT spectrum (100.6 MHz) of 5b

[PdBr{$C_6H_4(CH_2OCH_2(C_6H_4CH_2Br$-4))-2}(bpy)] (5c)



p-Xylylene dibromide (715 mg, 2.71 mmol) was added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred for 4 h at room temperature, whereby the color changed from yellow to orange. It was then filtered over Celite, and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **5c** as a yellow solid. Yield: 104 mg (61%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

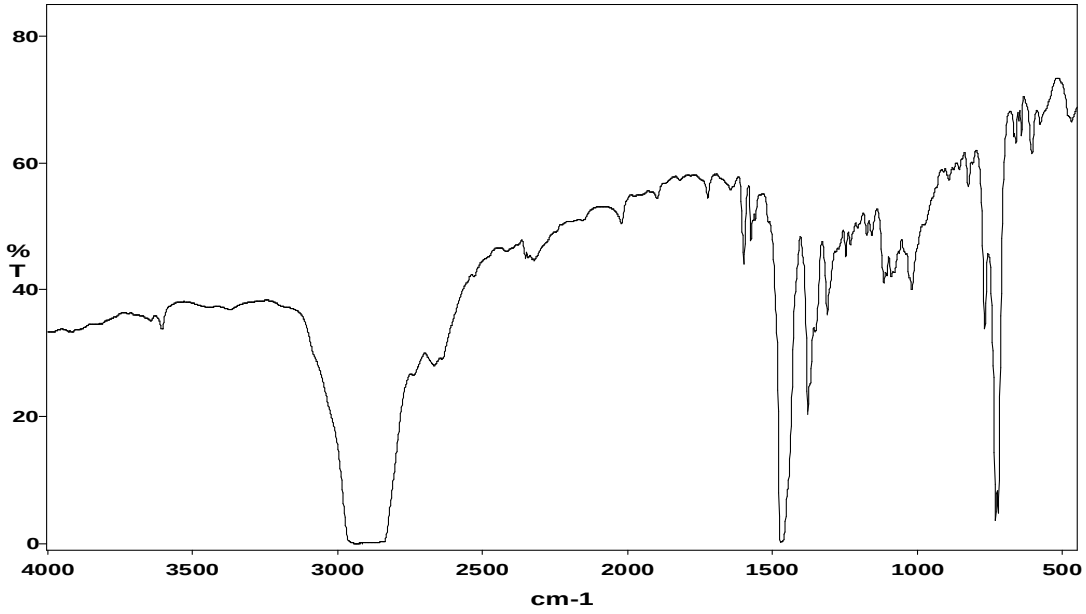
^{1}H NMR (400 MHz, $CDCl_3$): 9.39 (ddd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, $^5J_{HH}$ = 1, 1H, H16' bpy), 8.03-7.99 (m, 2H, H14',13' bpy), 7.94 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 7.85 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14 bpy), 7.62 (ddd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 2, $^5J_{HH}$ = 1, 1H, H16 bpy), 7.59-7.54 (m, 1H, H15' bpy), 7.53-7.48 (m, 1H, H6 aryl), 7.32-7.27 (m, 1H, H3 aryl), 7.14 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H15 bpy), 7.07 (A part of AB system, $^3J_{HH}$ = 8, 2H, *m*-H C_6H_4), 7.01 (B part of AB system, $^3J_{HH}$ = 8, 2H, *o*-H C_6H_4), 7.03-6.99 (m, 2H, H4,5 aryl), 5.28 and 4.85 (AB system, $^2J_{HH}$ = 11, 2H, CH_2-7), 4.53 (s, 2H, CH_2-8), 4.41 (s, 2H, CH_2Br).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 155.7 (C12 bpy), 153.7 (C12' bpy), 151.4 (CH16 bpy), 150.7 (CH16' bpy), 150.2 (C1 aryl), 141.8 (C2 aryl), 139.7 (*i*-C $C_6H_4CH_2Br$), 139.0 (CH14' bpy), 138.5 (CH14 bpy), 136.3 (*p*-C $C_6H_4CH_2Br$), 135.0 (CH6 aryl), 128.8 (2C, *m*-CH $C_6H_4CH_2Br$), 128.1 (CH3 aryl), 127.8 (2C, *o*-CH $C_6H_4CH_2Br$), 126.8 (CH5 aryl), 126.7 (CH15' bpy), 126.5 (CH15 bpy), 123.8 (CH4 aryl), 122.0 (CH13 bpy), 121.6 (CH13' bpy), 76.2 (CH_2-7), 72.0 (CH_2-8), 34.0 (CH_2Br).

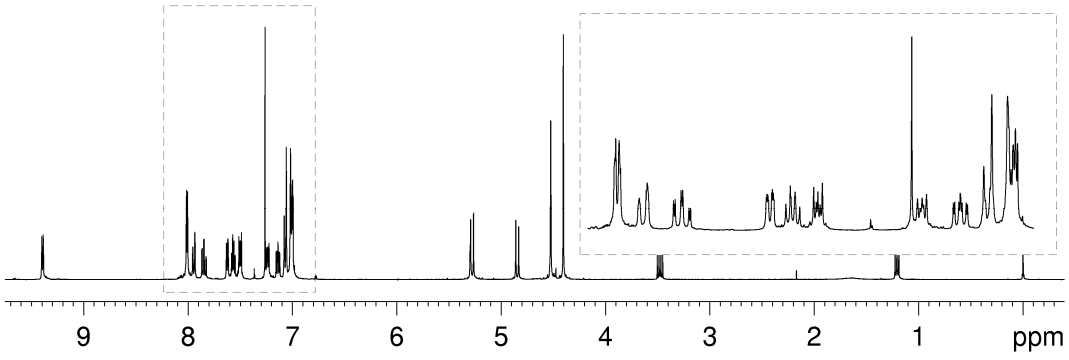
Elemental analysis (%):	C, 47.47	H, 3.78	N, 4.30
Calcd for $C_{25}H_{22}Br_2N_2OPd$:	C, 47.46	H, 3.50	N, 4.43

Melting point: 103 ^{o}C (dec).

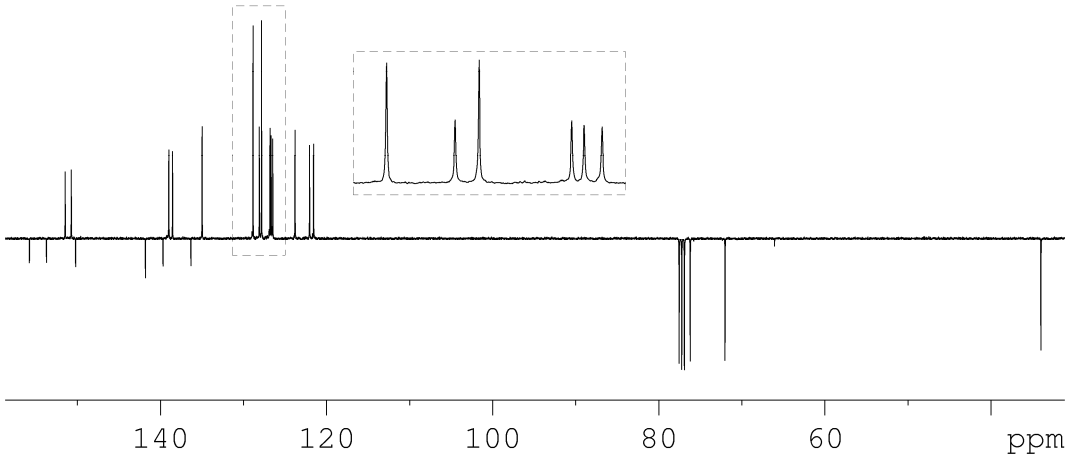
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 5c

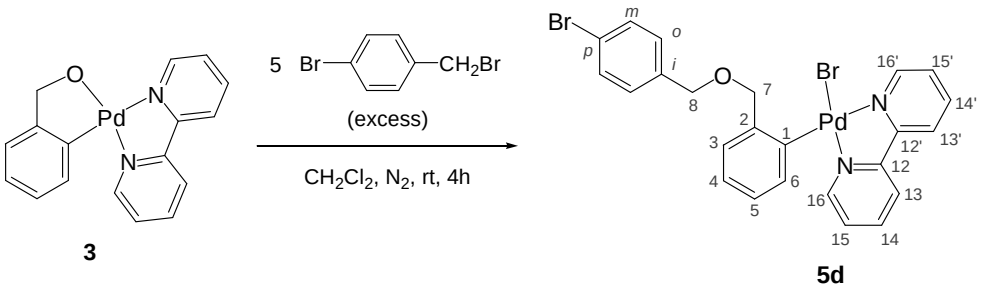


^{1}H-RMN spectrum (400 MHz) of 5c



APT spectrum (100.6 MHz) of 5c

[PdBr{$C_6H_4(CH_2OCH_2(C_6H_4Br$-4))-2}(bpy)] (5d)



3 **5d**

4-Bromobenzyl bromide (340 mg, 1.36 mmol) was added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred for 4 h at room temperature, whereby the color changed from yellow to orange. It was then filtered over Celite, and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **5d** as a yellow solid. Yield: 145 mg (87%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

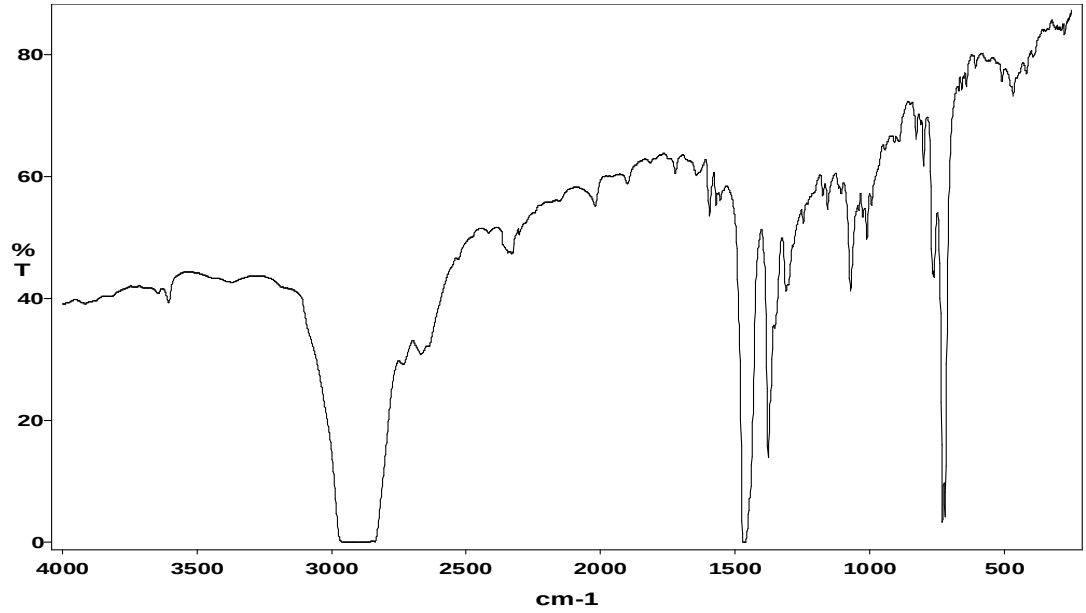
^{1}H NMR (300 MHz, $CDCl_3$): 9.39 (d, $^3J_{HH}$ = 5, 1H, H16' bpy), 8.05-8.01 (m, 2H, H13',14' bpy), 7.98 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 7.89 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14 bpy), 7.62 (d, $^3J_{HH}$ = 6, 1H, H16 bpy), 7.61-7.53 (m, 1H, H15' bpy), 7.51-7.46 (m, 1H, H6 aryl), 7.26-7.21 (m, 1H, H3 aryl), 7.17 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 6, $^4J_{HH}$ = 1, 1H, H15 bpy), 7.11 (A part of AB system, $^3J_{HH}$ = 8, 2H, *m*-H C_6H_4Br), 7.04-6.98 (m, 2H, H4,5 aryl), 6.95 (B part of AB system, $^3J_{HH}$ = 8, 2H, *o*-H C_6H_4Br), 5.28 and 4.85 (AB system, $^2J_{HH}$ = 11, 2H, CH_2-7), 4.52 and 4.46 (AB system, $^2J_{HH}$ = 12, 2H, CH_2-8).

^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): 155.8 (C12 bpy), 153.6 (C12' bpy), 151.5 (CH16 bpy), 150.8 (CH16' bpy), 149.9 (C1 aryl), 141.6 (C2 aryl), 139.0 (CH14' bpy), 138.4 (CH14 bpy), 138.2 (*i*-C C_6H_4Br), 135.0 (CH6 aryl), 131.1 (2C, *m*-CH C_6H_4Br), 129.5 (2C, *o*-CH C_6H_4Br), 128.1 (CH3 aryl), 126.82 (CH5 aryl), 126.76 (CH15' bpy), 126.5 (CH15 bpy), 123.9 (CH4 aryl), 121.8 (CH13 bpy), 121.5 (CH13' bpy), 120.8 (*p*-C C_6H_4Br), 76.1 (CH_2-7), 71.8 (CH_2-8).

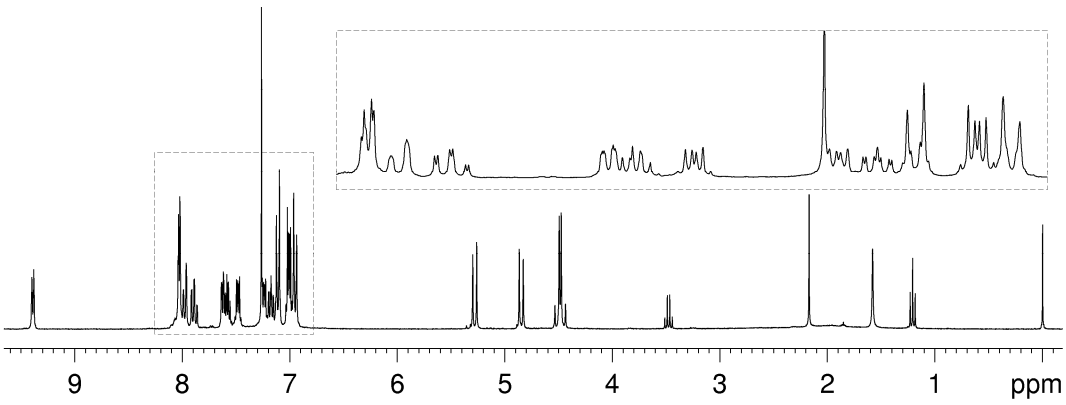
Elemental analysis (%):	C, 46.51	H, 3.23	N, 4.36
Calcd for $C_{24}H_{20}Br_2N_2OPd$:	C, 46.59	H, 3.26	N, 4.53

Melting point: 185 ºC.

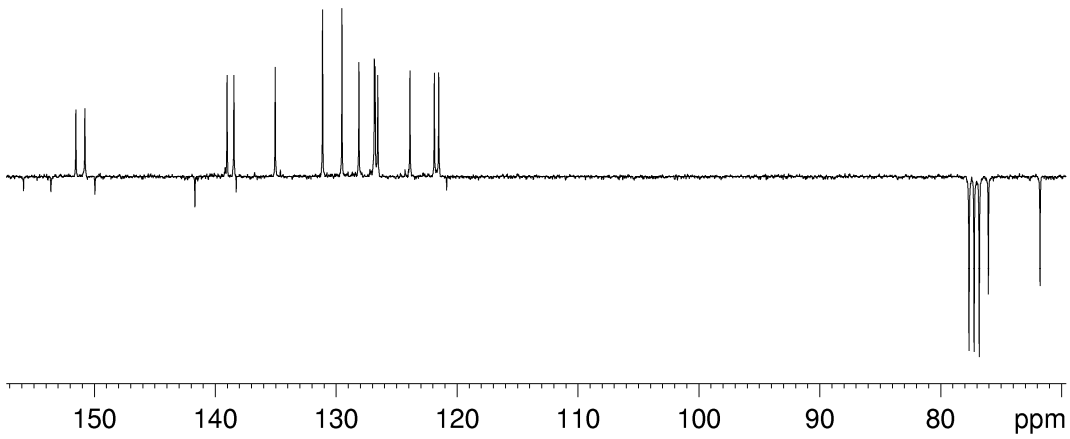
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 5d

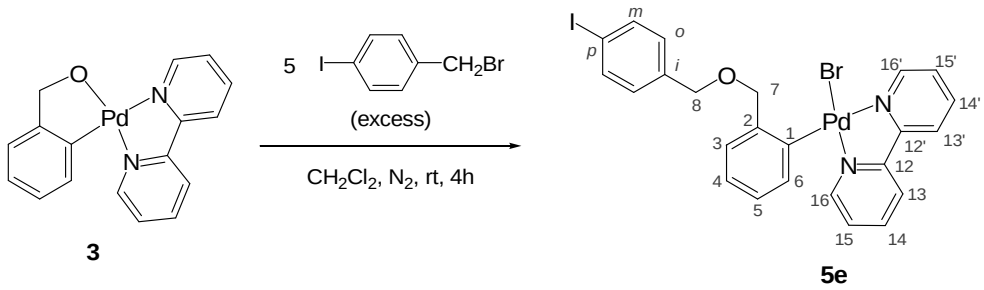


^{1}H-RMN spectrum (300 MHz) of 5d



APT spectrum (75.4 MHz) of 5d

[PdBr{$C_6H_4(CH_2OCH_2(C_6H_4I\text{-}4))\text{-}2$}(bpy)] (5e)



4-Iodobenzyl bromide (404 mg, 1.36 mmol) was added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred for 4 h at room temperature with no significant change in color. It was then filtered over Celite, and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **5e** as a pale yellow solid. Yield: 167 mg (93%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 9.40 (d, $^3J_{HH}$ = 5, 1H, H16' bpy), 8.05-8.01 (m, 2H, H13',14' bpy), 7.97 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 7.89 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14 bpy), 7.62 (d, $^3J_{HH}$ = 6, 1H, H16 bpy), 7.58 (td, $^3J_{HH}$ = 5, $^4J_{HH}$ = 3, 1H, H15' bpy), 7.51-7.46 (m, 1H, H6 aryl), 7.30 (A part of AB system, $^3J_{HH}$ = 8, 2H, *m*-H C_6H_4I), 7.25-7.20 (m, 1H, H3 aryl), 7.17 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 6, $^4J_{HH}$ = 1, 1H, H15 bpy), 7.04-6.98 (m, 2H, H4,5 aryl), 6.81 (B part of AB system, $^3J_{HH}$ = 8, 2H, *o*-H C_6H_4I), 4.84 and 5.28 (AB system, $^2J_{HH}$ = 11, 2H, CH_2-7), 4.51 and 4.46 (AB system, $^2J_{HH}$ = 12, 2H, CH_2-8).

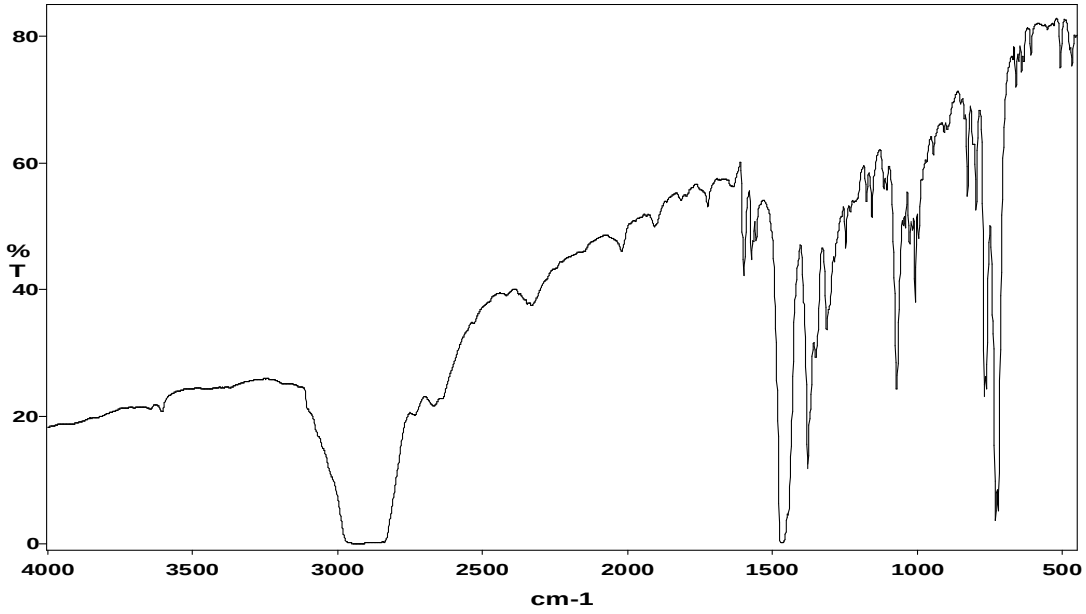
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 155.8 (C12 bpy), 153.6 (C12' bpy), 151.5 (CH16 bpy), 150.8 (CH16' bpy), 150.0 (C1 aryl), 141.7 (C2 aryl), 138.99 (CH14' bpy), 138.96 (*i*-C C_6H_4I), 138.4 (CH14 bpy), 137.1 (2C, *m*-CH C_6H_4I), 135.0 (CH6 aryl), 129.7 (2C, *o*-CH C_6H_4I), 128.1 (CH3 aryl), 126.83 (CH5 aryl), 126.76 (CH15' bpy), 126.5 (CH15 bpy), 123.9 (CH4 aryl), 121.8 (CH13 bpy), 121.5 (CH13' bpy), 92.5 (*p*-C C_6H_4I), 76.1 (CH_2-7), 71.9 (CH_2-8).

Elemental analysis (%):	C, 43.41	H, 3.03	N, 4.42
Calcd for $C_{24}H_{20}BrIN_2OPd$:	C, 43.30	H, 3.03	N, 4.21

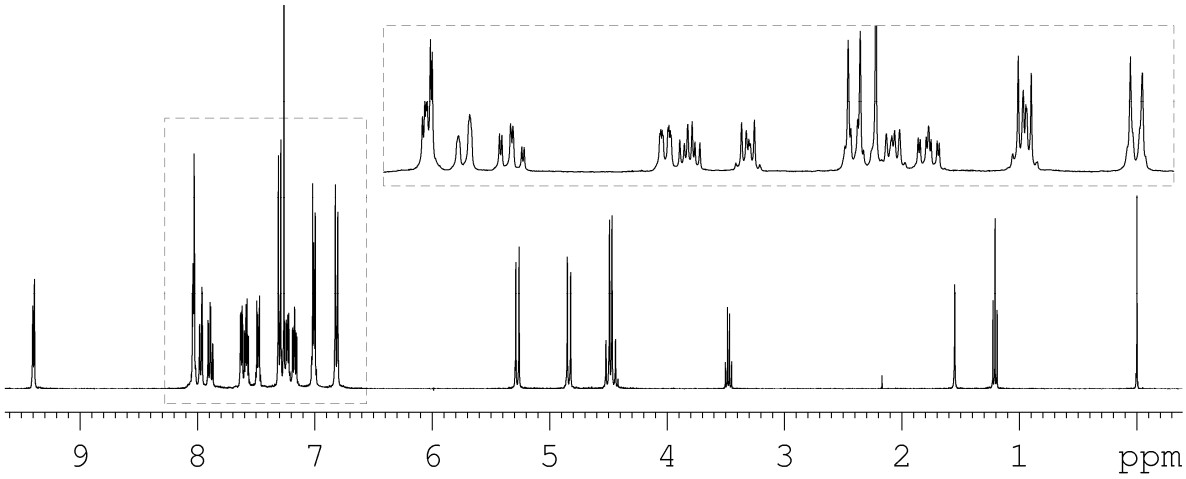
Melting point: 173 ºC.

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

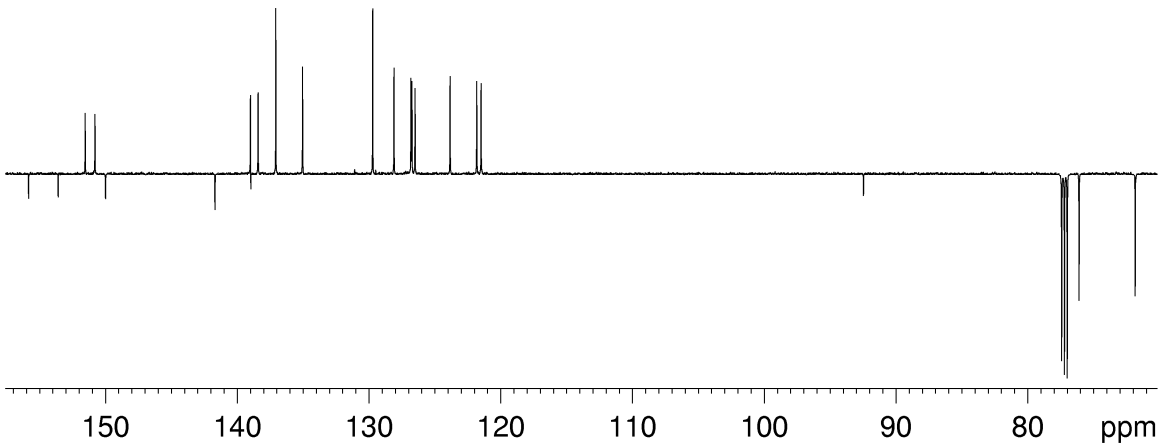
X-ray crystallography: Single crystals of **5e** were grown by liquid diffusion of Et_2O into a solution of **5e** in CH_2Cl_2.



IR spectrum of 5e

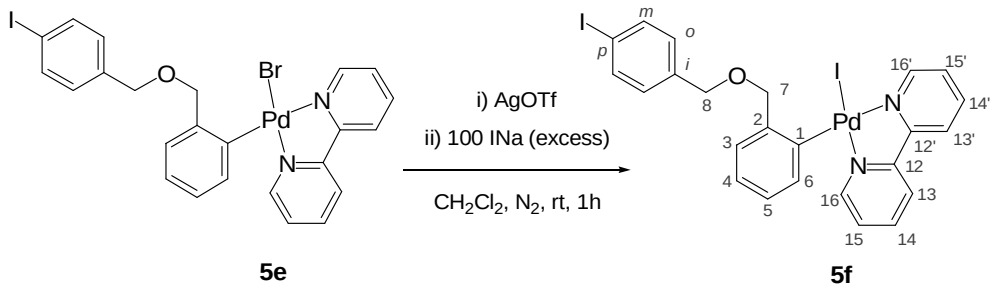


^{1}H-RMN spectrum (400 MHz) of 5e



APT spectrum (100.6 MHz) of 5e

[PdI{$C_6H_4(CH_2OCH_2(C_6H_4I\text{-}4))\text{-}2$}(bpy)] (5f)



5e **5f**

AgOTf (38.5 mg, 0.150 mmol) and an excess of NaI (2250 mg, 15.0 mmol) were added to a solution of **5e** (100 mg, 0.150 mmol) in CH_2Cl_2 (20 mL) under N_2. A suspension formed immediately, which was stirred for 1 h at room temperature. It was then filtered over $MgSO_4$, and the resulting orange solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (25 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **5f** as an orange solid. Yield: 51.0 mg (48%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

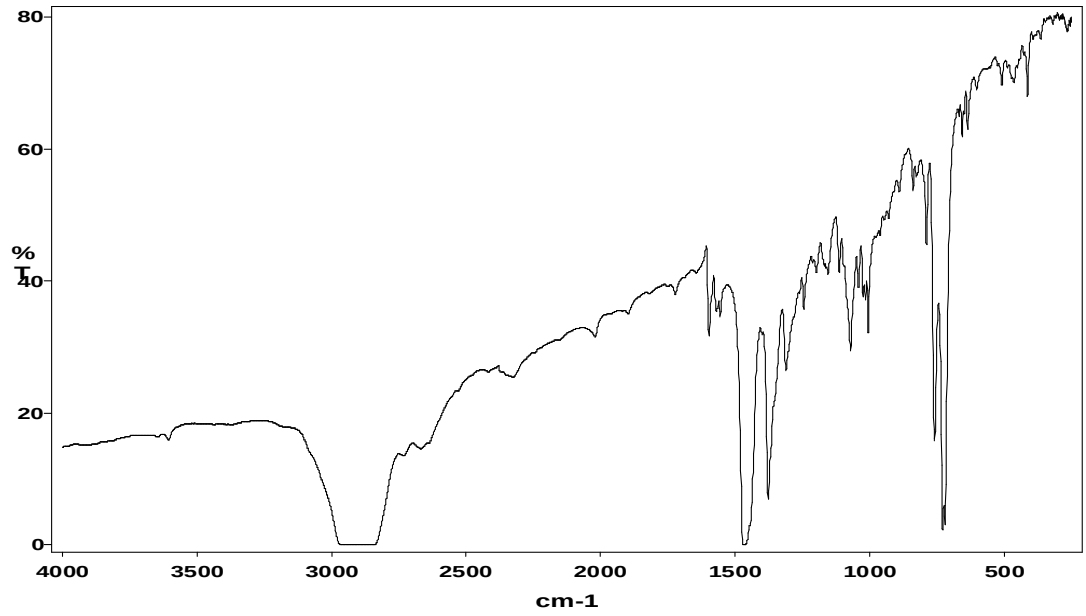
^{1}H NMR (300 MHz, $CDCl_3$): 9.61 (ddd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, $^5J_{HH}$ = 2, 1H, H16' bpy), 8.04-8.00 (m, 2H, H13',14' bpy), 7.97-7.85 (m, 2H, H13,14 bpy), 7.58-7.52 (m, 1H, H15' bpy), 7.50-7.42 (m, 2H, H6 aryl, H16 bpy), 7.28 (A part of AB system, $^3J_{HH}$ = 8, 2H, *m*-H C_6H_4I), 7.25-7.17 (m, 2H, H3 aryl, H15 bpy), 7.01-6.95 (m, 2H, H4,H5 aryl), 6.79 (B part of AB system, $^3J_{HH}$ = 8, 2H, *o*-H C_6H_4I), 5.14 and 4.79 (AB system, $^2J_{HH}$ = 11, 2H, CH_2-7), 4.49 and 4.44 (AB system, $^2J_{HH}$ = 12, 2H, CH_2-8).

^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): 155.6 (C12 bpy), 153.6 (C12' bpy), 153.1 (CH16' bpy), 150.5 (CH16 bpy), 146.8 (C1 aryl), 142.0 (C2 aryl), 139.0 (*i*-C C_6H_4I), 138.7 (CH14' bpy), 138.4 (CH14 bpy), 137.1 (2C, *m*-CH C_6H_4I), 136.3 (CH6 aryl), 129.7 (2C, *o*-CH C_6H_4I), 128.0 (CH3 aryl), 127.0 (CH15' bpy), 126.7 (CH5 aryl), 126.4 (CH15 bpy), 123.7 (CH4 aryl), 121.7 (CH13 bpy), 121.6 (CH13' bpy), 92.5 (*p*-C C_6H_4I), 77.1 (CH_2-7), 71.9 (CH_2-8).

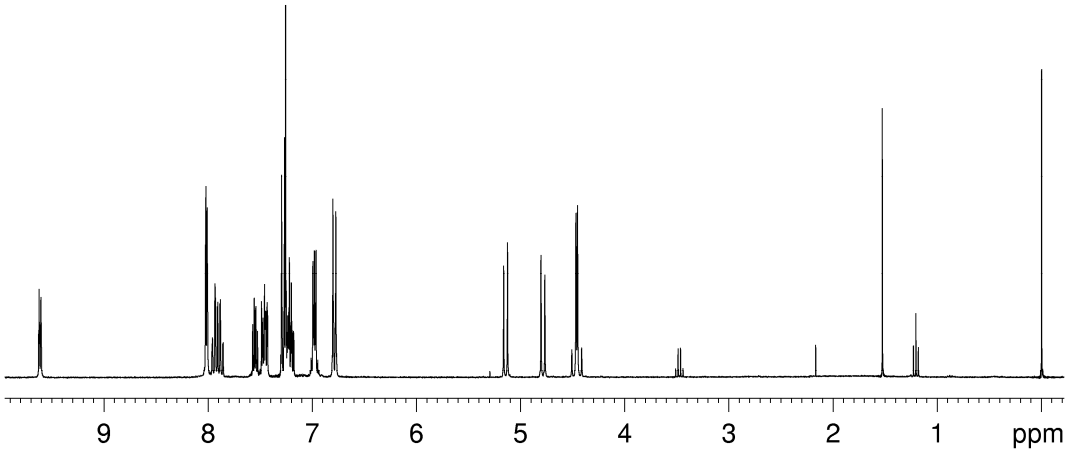
Elemental analysis (%):	C, 40.20	H, 2.68	N, 4.00
Calcd for $C_{24}H_{20}I_2N_2OPd$:	C, 40.45	H, 2.83	N, 3.93

Melting point: 145 ºC.

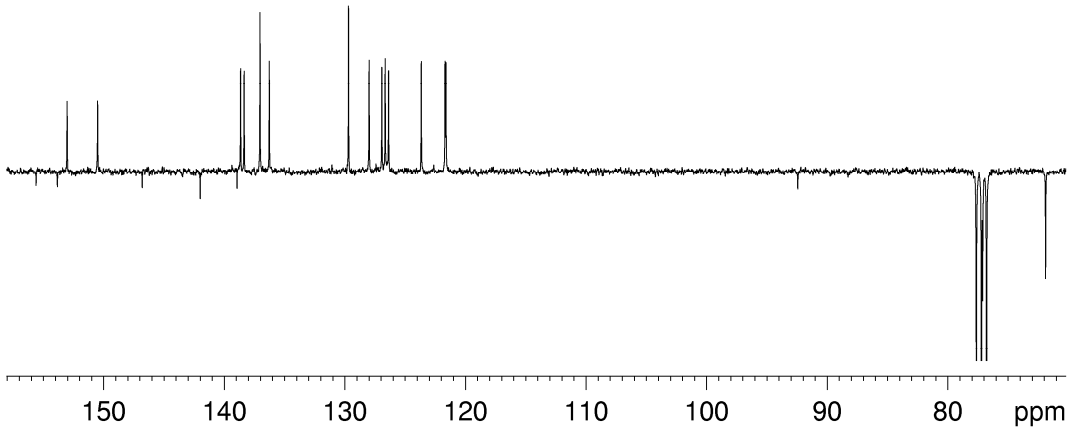
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 5f

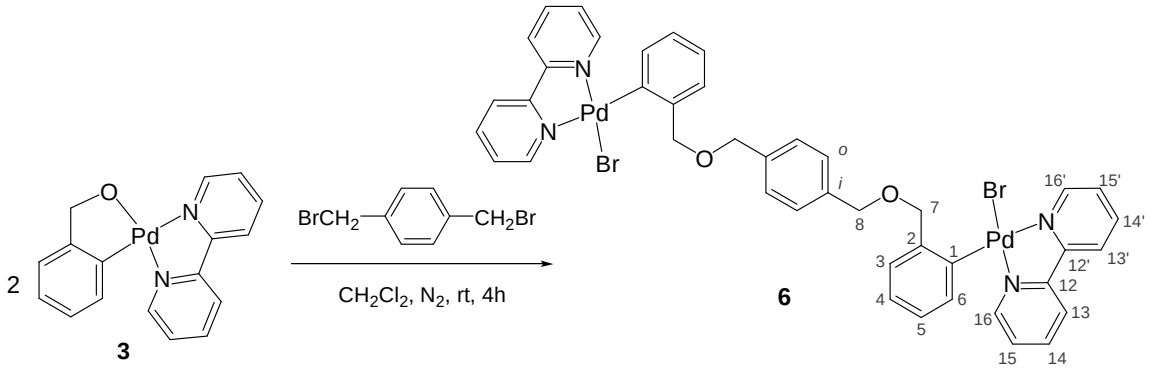


^{1}H-RMN spectrum (300 MHz) of 5f



APT spectrum (75.4 MHz) of 5f

[{(bpy)BrPd($C_6H_4CH_2OCH_2$-2)}$_2$(C_6H_4-1,4)] (6)



p-Xylylene dibromide (35.9 mg, 0.136 mmol) was added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred for 4 h at room temperature with no significant change in color. It was then filtered over Celite, and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **6** as a yellow solid. Yield: 115 mg (85%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

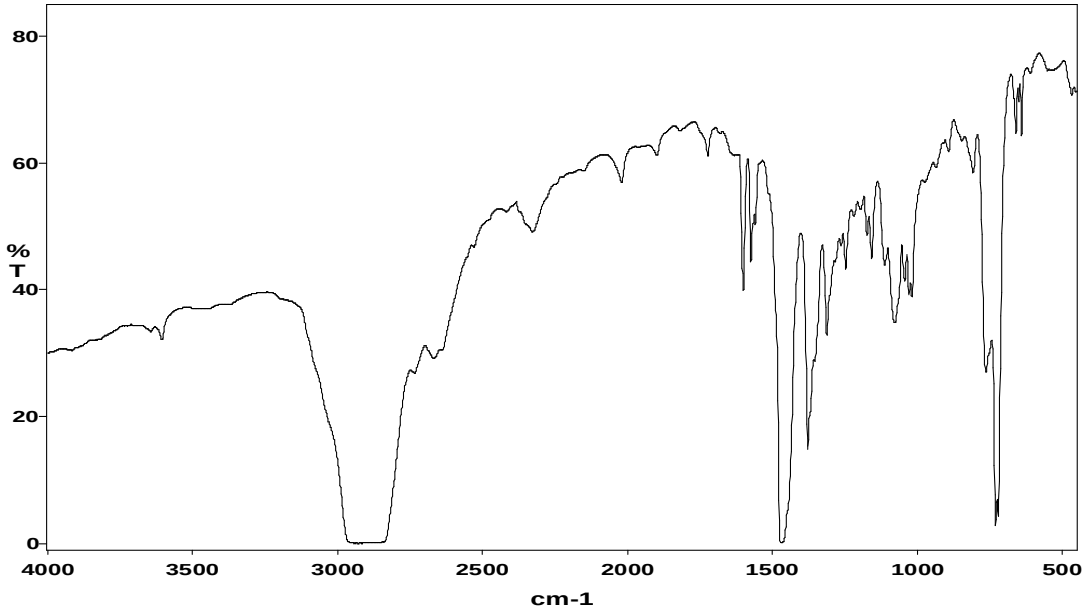
^{1}H NMR (400 MHz, $CDCl_3$): 9.36-9.33 (m, 2H, H16',16' bpy), 8.06-8.03 (m, 2H, H14',13' bpy), 8.00-7.97 (m, 3H, H13',13,13 bpy), 7.89 and 7.88 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14,14' bpy), 7.78 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14 bpy), 7.58-7.53 (m, 3H, H16,16,15' bpy), 7.53-7.48 (m, 3H, H6,6 aryl and H15' bpy), 7.28-7.24 (m, 1H, H3 aryl), 7.23-7.19 (m, 1H, H3 aryl), 7.17-7.11 (m, 2H, H15,15 bpy), 7.06-6.98 (m, 4H, H5,5,4,4), 6.77 (d, $^3J_{HH}$ = 4, 4H, C_6H_4), 5.20 and 4.87 (AB system, $^2J_{HH}$ = 11, 2H, CH_2-7), 5.20 and 4.80 (AB system, $^2J_{HH}$ = 11, 2H, CH_2-7), 4.45-4.37 (m, 4H, CH_2-8, CH_2-8).

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 155.96 and 155.93 (C12 bpy), 153.79 and 153.71 (C12' bpy), 151.32 and 151.30 (CH16 bpy), 150.58 and 150.57 (CH16' bpy), 149.99 and 149.96 (C1 aryl), 142.05 and 142.01 (C2 aryl), 139.23 and 139.16 (CH14' bpy), 138.74 and 138.66 (CH14 bpy), 137.76 and 137.75 (*i*-C C_6H_4), 135.23 and 135.20 (CH6 aryl), 128.08 and 128.01 (CH3 aryl), 127.40 and 127.35 (2C, CH C_6H_4), 126.75 and 126.69 (CH5 aryl), 126.66 and 126.62 (CH15' bpy), 126.53 and 126.49 (CH15 bpy), 123.81 and 123.77 (CH4 aryl), 122.39 and 122.32 (CH13 bpy), 121.91 and 121.85 (CH13' bpy), 75.78 and 75.63 (CH_2-7), 72.41 and 72.30 (CH_2-8).

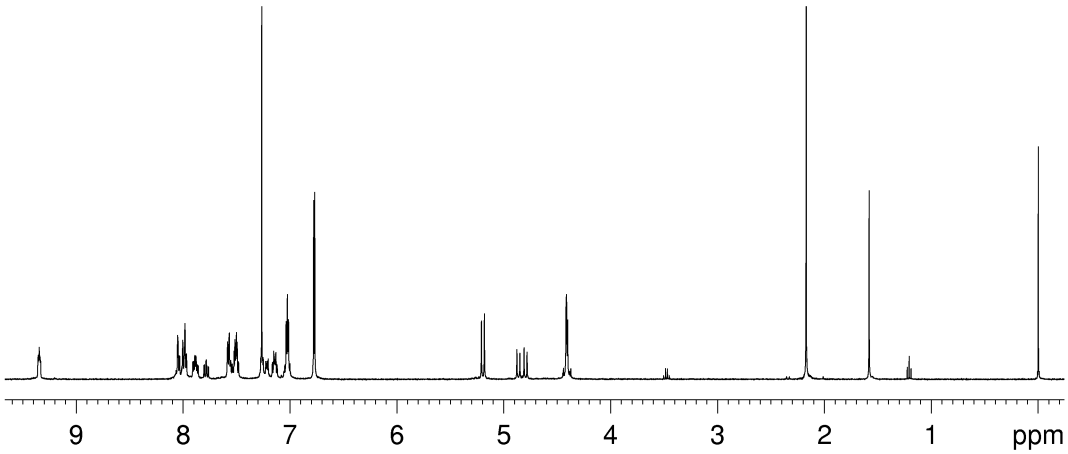
Elemental analysis (%):	C, 50.03	H, 3.50	N, 5.62
Calcd for $C_{42}H_{36}Br_2N_4O_2Pd_2$:	C, 50.37	H, 3.62	N, 5.59

Melting point: 137 ºC.

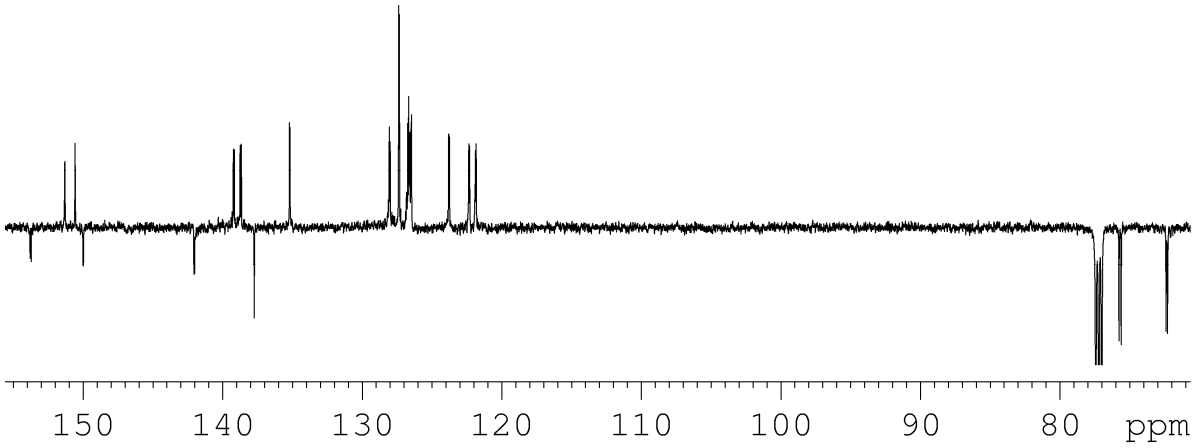
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 6

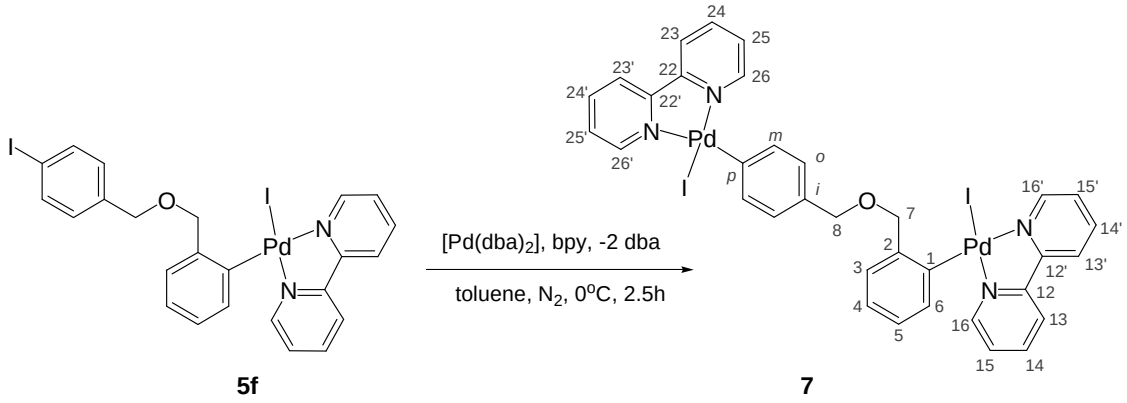


^{1}H-RMN spectrum (400 MHz) of 6



APT spectrum (150.9 MHz) of 6

[(bpy)IPd($C_6H_4CH_2$-2)O($CH_2C_6H_4$-4)PdI(bpy)] (7)



5f **7**

5f (71.0 mg, 0.100 mmol) was added to a suspension of [$Pd(dba)_2$] (57.6 mg, 0.100 mmol) and bpy (15.6 mg, 0.100 mmol) in dry degassed toluene (20 mL) under N_2. The resulting mixture was stirred in an ice bath for ca. 2.5 h until the dark red color of [$Pd(dba)_2$] was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the orange solution was evaporated to dryness. Et_2O (20 mL) was added and the resulting orange suspension was filtered off, washed with Et_2O (3x5 mL), and dried in vacuo to give **7** as an orange solid. Yield: 55.0 mg (56%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

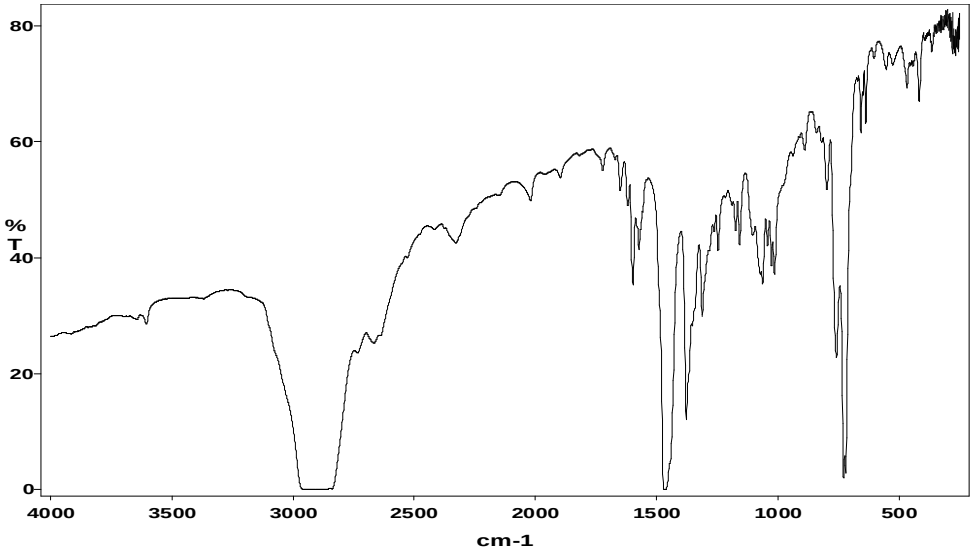
^{1}H NMR (300 MHz, $CDCl_3$): 9.61 and 9.57 (ddd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 2, $^5J_{HH}$ = 1, 1H, H16',26' bpy), 8.17-8.02 (several m, 4H, H13,13',23,23' bpy), 8.02-7.92 (several m, 4H, H14',24' and H14 or H24 bpy), 7.87 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H24 or H14 bpy), 7.59-7.53 (m, 2H, H6 aryl and H15' or 25' bpy), 7.48-7.36 (m, 3H, H16,26, H25'or 15' bpy), 7.35 (ddd, $^3J_{HH}$ = 7, $^3J_{HH}$ = 6, $^4J_{HH}$ = 1, 1H, H15 or 25 bpy), 7.21 (dd, $^3J_{HH}$ = 7, $^4J_{HH}$ = 2, 1H, H3 aryl), 7.11 (ddd, $^3J_{HH}$ = 7, $^3J_{HH}$ = 6, $^4J_{HH}$ = 1, 1H, H25 or 15 bpy), 7.02 (td, $^3J_{HH}$ = 7, $^4J_{HH}$ = 2, 1H, H5 aryl), 6.96 (td, $^3J_{HH}$ = 7, $^4J_{HH}$ = 1, 1H, H4 aryl), 7.03 and 6.85 (br, A part of AB system, 1H, $^3J_{HH}$ = 8, *m*-H C_6H_4[Pd]), 6.57 and 6.42 (br, B part of AB system, 1H, $^3J_{HH}$ = 8, *o*-H C_6H_4[Pd]), 5.22 and 4.62 (AB system, $^2J_{HH}$ = 11, 2H, CH_2-7), 4.48 and 4.40 (AB system, $^2J_{HH}$ = 11, 2H, CH_2-8).

^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): 155.7 and 155.2 (C12,22 bpy), 154.5 and 153.9 (C12',22' bpy), 153.0 and 152.4 (C16',26' bpy), 150.6 and 150.0 (CH16,26 bpy), 148.8 (C1 aryl), 143.9 (*p*-C C_6H_4[Pd]), 142.3 (C2 aryl), 138.89, 138.86, 138.8, and 138.5 (CH14,14',24,24' bpy), 136.3 (CH6 aryl), 135.8 and 135.6 (*m*-CH C_6H_4[Pd]), 133.8 (*i*-C C_6H_4[Pd]), 128.6 (CH3 aryl), 126.94, 126.92, and 126.86 (CH15',25' and CH5 bpy), 126.5 and 126.4 (*o*-CH C_6H_4[Pd]), 126.4 and 125.9 (CH15,25 bpy), 123.4 (CH4 aryl), 122.9, 122.4, 122.0, and 121.7 (CH13,13',23,23' bpy), 77.6 (CH_2-7), 72.6 (CH_2-8).

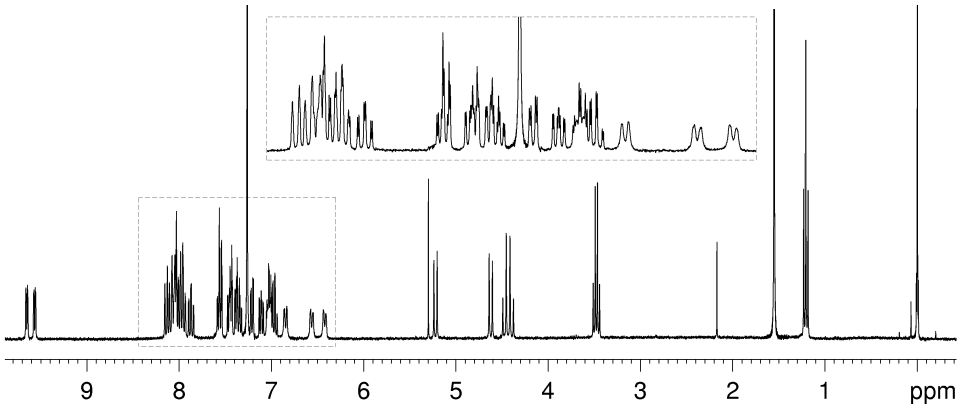
Elemental analysis (%):	C, 41.80	H, 3.23	N, 5.53
Calcd for $C_{34}H_{28}I_2N_4OPd_2$:	C, 41.87	H, 2.89	N, 5.74

Melting point: 153 ºC.

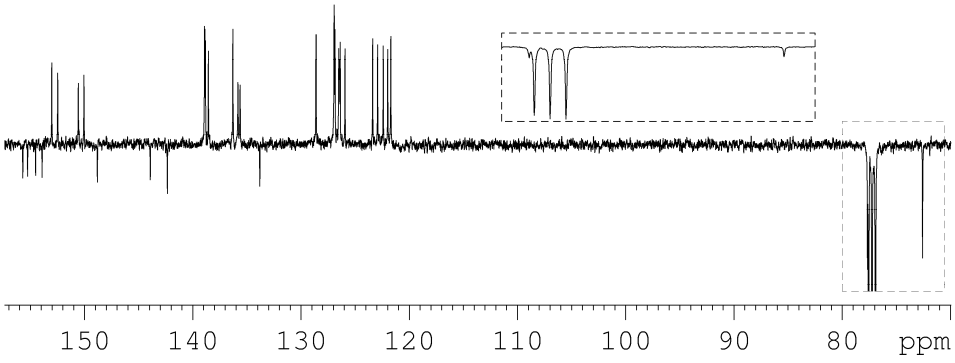
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 7

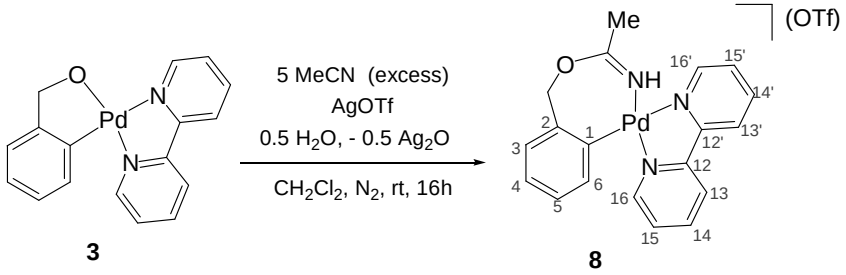


^{1}H-RMN spectrum (300 MHz) of 7



APT spectrum (75.4 MHz) of 7

[Pd{κ^2-*C*,*N*-C_6H_4{$CH_2OC(=NH)Me$}-2}(bpy)](OTf) (8)



Acetonitrile (71.0 μL, 1.36 mmol) and AgOTf (69.6 mg, 0.271 mmol) were added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred in the dark for 16 h at room temperature (the color darkened and a precipitate formed). It was then filtered over Celite, and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **8** as a yellow solid. Yield: 85 mg (56%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 8.89 (ddd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 2, $^5J_{HH}$ = 1, 1H, H16' bpy), 8.45 (br s, 1H, NH), 8.37 (ddd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, $^5J_{HH}$ = 1, 1H, H16 bpy), 8.25 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 8.17 (d, $^3J_{HH}$ = 8, 1H, H13' bpy), 8.11 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14' bpy), 8.07 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14 bpy), 7.82 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H15' bpy), 7.43 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 6, $^4J_{HH}$ = 1, 1H, H15 bpy), 7.31-7.27 (m, 1H, H5 aryl), 7.22 (d, $^3J_{HH}$ = 7, 1H, H6 aryl), 7.15-7.11 (m, 2H, H3,4 aryl), 6.60 and 5.05 (AB system, $^2J_{HH}$ = 11, 2H, CH_2), 2.30 (s, 3H, Me).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 175.1 (C=NH), 157.0 (C12 bpy), 152.6 (C12' bpy), 152.0 (C1 aryl), 151.9 (CH16 bpy), 151.0 (CH16' bpy), 140.09 and 140.06 (CH14,14' bpy), 139.4 (C2 aryl), 134.7 (CH6 aryl), 130.6 (CH5 aryl), 128.3 (CH15' bpy), 127.6 (CH3 aryl), 126.7 (CH15 bpy), 125.4 (CH4 aryl), 123.0 (CH13 bpy), 122.1 (CH13' bpy), 121.0 (q, $^1J_{CF}$ = 320, OTf), 72.2 (CH_2), 23.6 (Me).

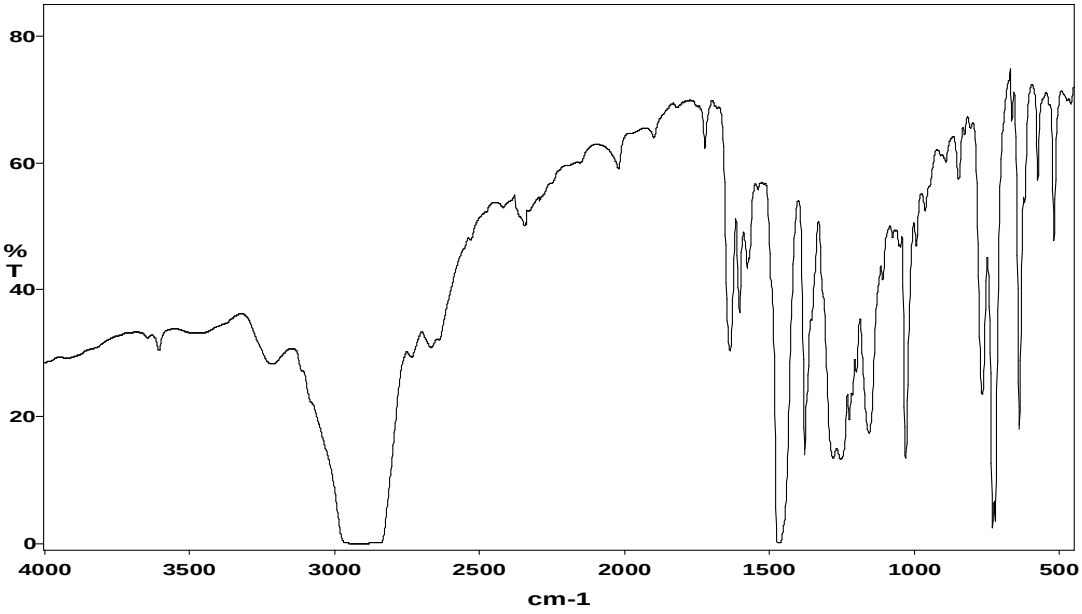
IR (cm^{-1}): ν(S=O) 1029, 1279; ν(C=N): 1635; ν(NH) 3213.

Elemental analysis (%):	C, 42.58	H, 2.92	N, 7.19	S, 5.42
Calcd for $C_{20}H_{18}F_3N_3O_4PdS$:	C, 42.91	H, 3.24	N, 7.51	S, 5.73

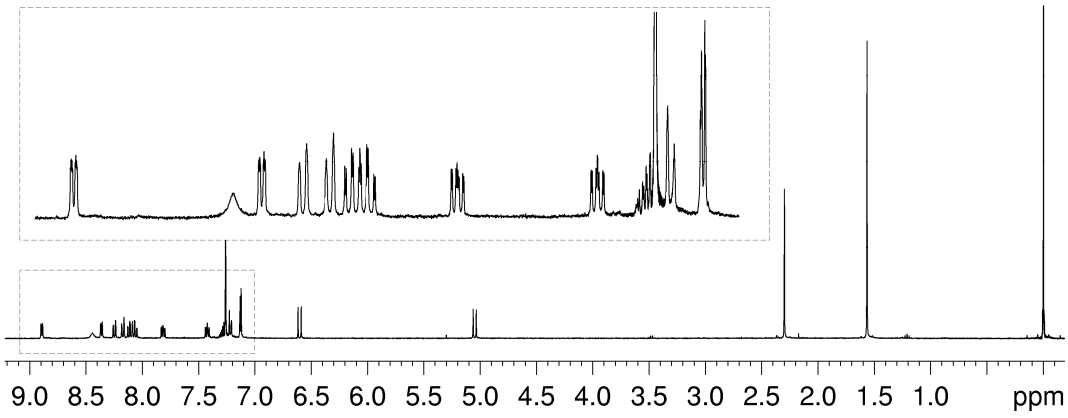
Melting point: 99 ºC.

Conductivity: Λ_M (acetone): 115 $\Omega^{-1}cm^2mol^{-1}$.

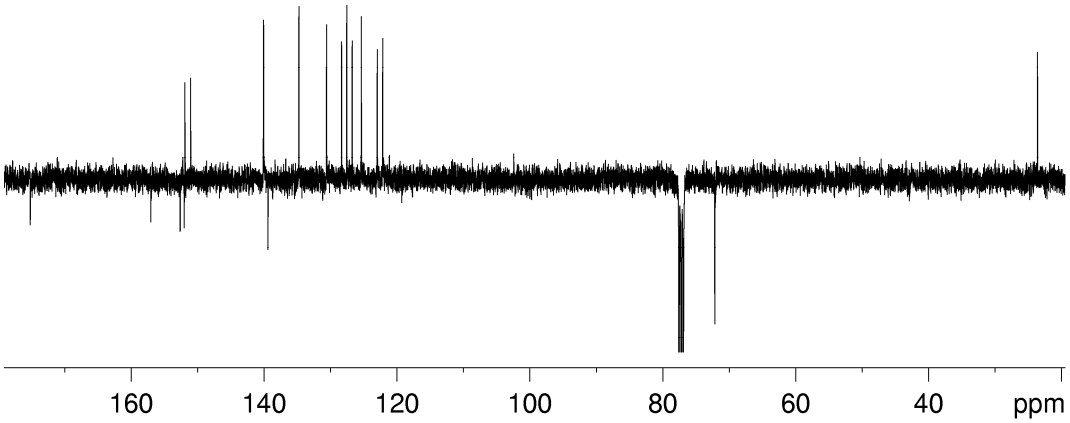
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 8

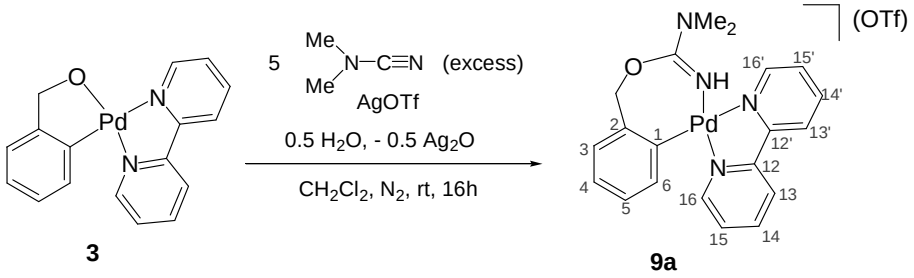


^{1}H-RMN spectrum (400 MHz) of 8



APT spectrum (100.6 MHz) of 8

[Pd{κ^2-*C,N*-C_6H_4{$CH_2OC(=NH)NMe_2$}-2}(bpy)](OTf) (9a)



Dimethylcyanamide (110 μL, 1.36 mmol) and AgOTf (69.6 mg, 0.271 mmol) were added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred in the dark for 16 h at room temperature (the color darkened and a precipitate formed). It was then filtered over Celite, and the resulting pale yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **9a** as a pale yellow solid. Yield: 91 mg (57%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 8.65 (ddd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 2, $^5J_{HH}$ = 1,1H, H16' bpy), 8.42 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 8.35 (d, $^3J_{HH}$ = 8, 1H, H13' bpy), 8.32 (ddd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, $^5J_{HH}$ = 1, 1H, H16 bpy), 8.14 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14 bpy), 8.08 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14' bpy), 7.79 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H15' bpy), 7.39 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 6, $^4J_{HH}$ = 1, 1H, H15 bpy), 7.29-7.26 (m, 2H, H5,6 aryl), 7.16-7.10 (m, 2H, H3,4 aryl), 6.62 and 5.10 (AB system, $^2J_{HH}$ = 11, 2H, CH_2), 4.81 (s, 1H, NH), 3.00 (s, 6H, Me).

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 161.3 (C=NH), 157.0 (C12 bpy), 153.13 and 153.11 (C12' bpy and C1 aryl), 151.6 (CH16 bpy), 149.1 (CH16' bpy), 140.5 (CH14' bpy), 140.3 (CH14 bpy), 139.3 (C2 aryl), 134.9 (CH6 aryl), 130.3 (CH5 aryl), 127.9 (CH15' bpy), 127.6 (CH3 aryl), 126.7 (CH15 bpy), 125.1 (CH4 aryl), 123.8 (CH13 bpy), 123.0 (CH13' bpy), 121.0 (q, $^1J_{CF}$ = 320, OTf), 73.2 (CH_2), 38.0 (Me).

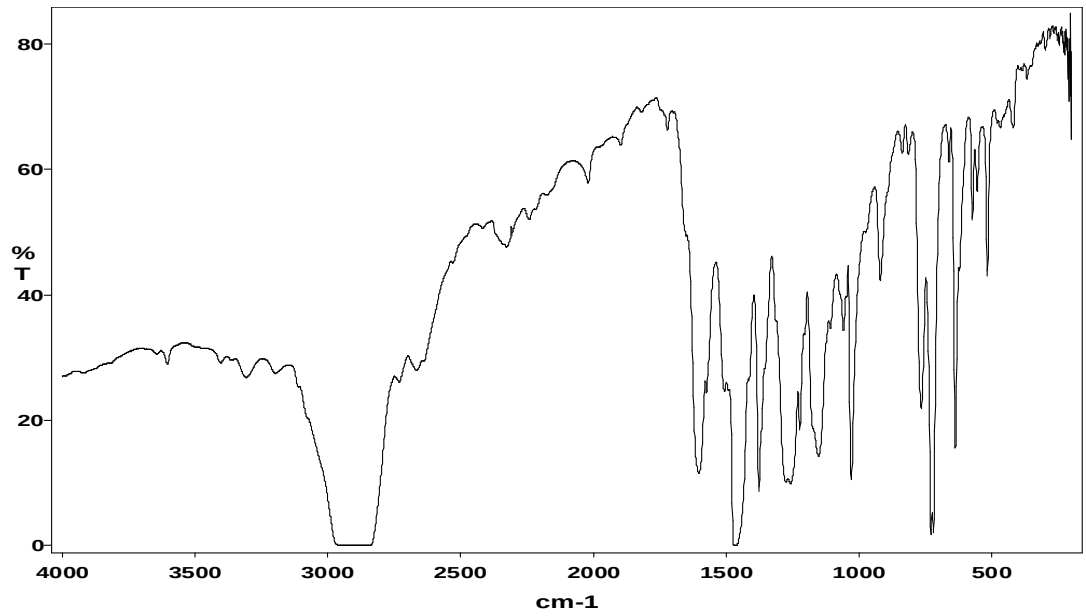
IR (cm^{-1}): ν(S=O): 1029, 1275; ν(C=N): 1602; ν(NH): 3306.

Elemental analysis (%):	C, 42.81	H, 3.60	N, 9.43	S, 5.12
Calcd for $C_{21}H_{21}F_3N_4O_4PdS$:	C, 42.83	H, 3.59	N, 9.51	S, 5.44

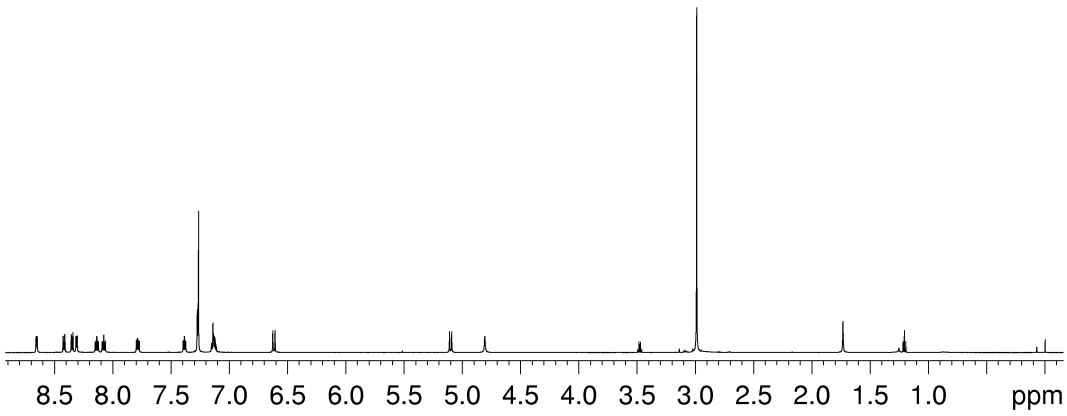
Melting point: 182 °C (dec). **Conductivity:** Λ_M (acetone): 125 $\Omega^{-1}cm^2mol^{-1}$.

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

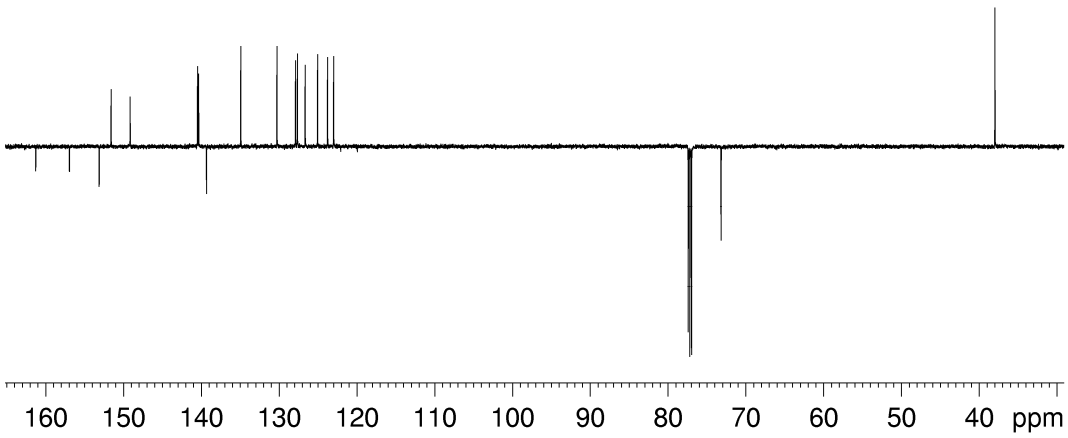
X-ray crystallography: Single crystals of **9a** were grown by liquid diffusion of Et_2O into a solution of **9a** in CH_2Cl_2.



IR spectrum of 9a

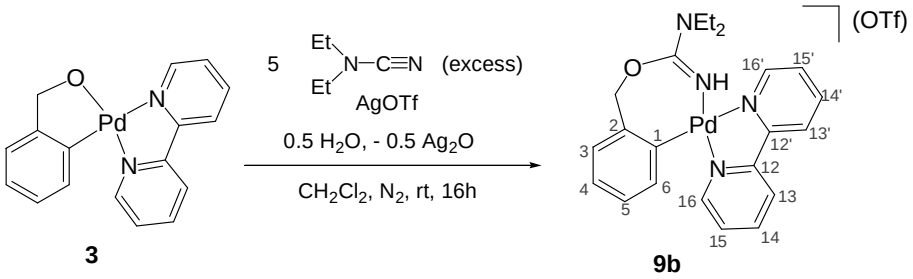


^{1}H-RMN spectrum (600 MHz) of 9a



APT spectrum (150.9 MHz) of 9a

[Pd{κ^2-*C*,*N*-C_6H_4{$CH_2OC(=NH)NEt_2$}-2}(bpy)](OTf) (9b)



Diethylcyanamide (158 μL, 1.36 mmol) and AgOTf (69.6 mg, 0.271 mmol) were added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred in the dark for 16 h at room temperature (the color darkened and a precipitate formed). It was then filtered over Celite, and the resulting pale yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **9b** as a pale yellow solid. Yield: 100 mg (54%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 8.58 (dd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H16' bpy), 8.44 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 8.39 (d, $^3J_{HH}$ = 8, 1H, H13' bpy), 8.32 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 1, 1H, H16 bpy), 8.15 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1, 1H, H14 bpy), 8.13 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1, 1H, H14' bpy), 7.78 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H15' bpy), 7.39 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 6, $^4J_{HH}$ = 1, 1H, H15 bpy), 7.29-7.26 (m, 2H, H5,6 aryl), 7.14-7.12 (m, 2H, H3,4 aryl), 6.66 and 5.11 (AB system, $^2J_{HH}$ = 11, 2H, CH_2O), 4.76 (s, 1H, NH), 3.33 (m, 4H, CH_2CH_3), 1.13 (t, $^3J_{HH}$ = 7, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 160.2 (C=NH), 157.0 (C12 bpy), 153.2 (C12' bpy), 153.0 (C1 aryl), 151.6 (CH16 bpy), 148.9 (CH16' bpy), 140.6 (CH14' bpy), 140.3 (CH14 bpy), 139.1 (C2 aryl), 134.9 (CH6 aryl), 130.2 (CH5 aryl), 127.7 (CH15' bpy), 127.4 (CH3 aryl), 126.7 (CH15 bpy), 125.0 (CH4 aryl), 123.9 (CH13 bpy), 123.2 (CH13' bpy), 121.0 (q, $^1J_{CF}$ = 321, OTf), 73.1 (CH_2O), 43.3 (CH_2CH_3), 13.6 (CH_2CH_3).

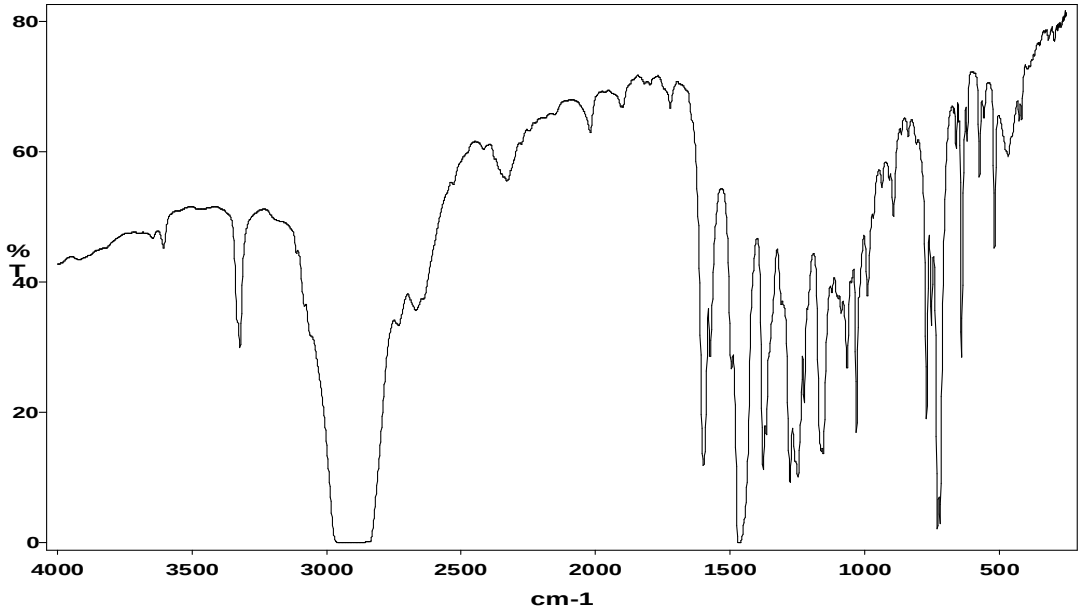
IR (cm^{-1}): ν(S=O): 1030, 1277; ν(C=N): 1599; ν(NH): 3321.

Elemental analysis (%):	C, 44.95	H, 4.22	N, 8.85	S, 4.89
Calcd for $C_{23}H_{25}F_3N_4O_4PdS$:	C, 44.78	H, 4.08	N, 9.08	S, 5.20

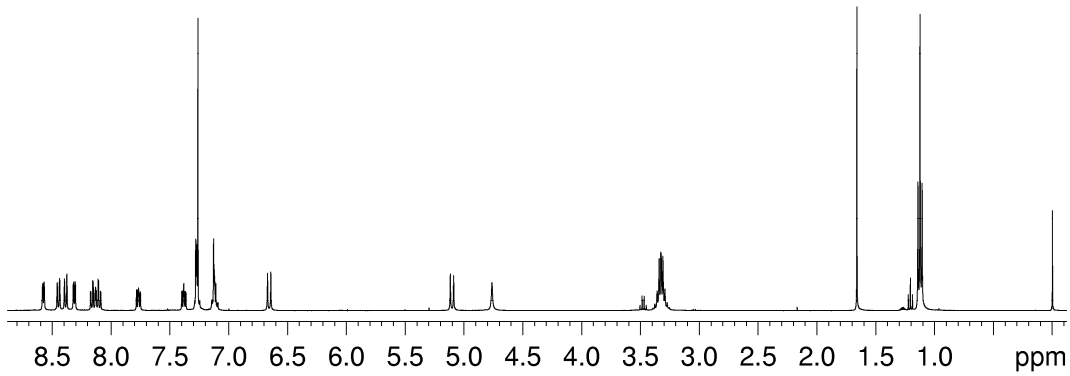
Melting point: 104 °C.

Conductivity: Λ_M (acetone): 123 $\Omega^{-1}cm^2mol^{-1}$.

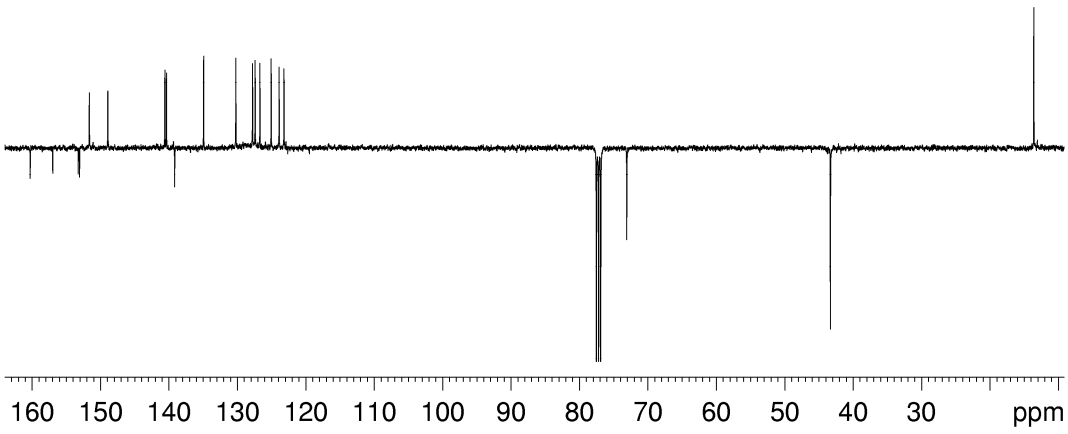
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 9b

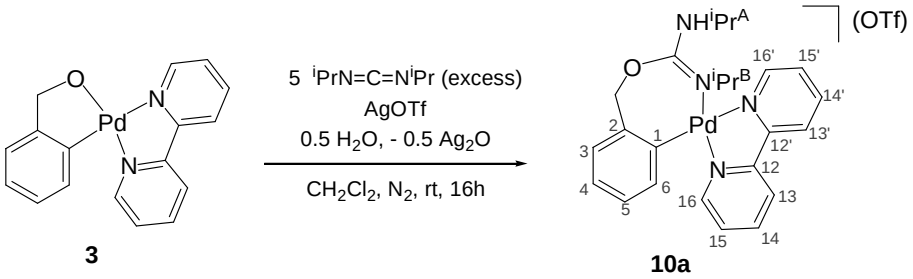


^{1}H-RMN spectrum (400 MHz) of 9b



APT spectrum (100.6 MHz) of 9b

[Pd{κ^2-*C*,*N*-C_6H_4{$CH_2OC(=N^iPr)NH^iPr$}-2}(bpy)](OTf) (10a)



1,3-Diisopropylcarbodiimide (213 μL, 1.36 mmol) and AgOTf (69.6 mg, 0.271 mmol) were added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred in the dark for 16 h at room temperature. It was then filtered over Celite, and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **10a** as a pale yellow solid. Yield: 104 mg (60%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 8.68 (dd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H16' bpy), 8.52 (dd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H16 bpy), 8.40 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 8.35 (d, $^3J_{HH}$ = 8, 1H, H13' bpy), 8.16 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14 bpy), 8.15 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14' bpy), 7.82 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H15' bpy), 7.44 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H15 bpy), 7.39 (dd, $^3J_{HH}$ = 7, $^4J_{HH}$ = 1, 1H, H6 aryl), 7.26 (td, $^3J_{HH}$ = 7, $^4J_{HH}$ = 2, 1H, H5 aryl), 7.07 (td, $^3J_{HH}$ = 7, $^4J_{HH}$ = 1, 1H, H4 aryl), 7.03 (dd, $^3J_{HH}$ = 7, $^4J_{HH}$ = 2, 1H, H3 aryl), 6.65 (A part of AB system, $^2J_{HH}$ = 11, 1H, CH_2), 5.57 (d, $^3J_{HH}$ = 7, 1H, NH), 5.12 (B part of AB system, $^2J_{HH}$ = 11, 1H, CH_2), 3.89 (dsept, $^3J_{HH}$ = 7, $^3J_{HH}$ = 6, 1H, CH $^iPr^A$), 3.78 (sept, $^3J_{HH}$ = 6, 1H, CH $^iPr^B$), 1.55 (d, $^3J_{HH}$ = 6, 3H, Me $^iPr^B$), 1.28 (d, $^3J_{HH}$ = 6, 3H, Me $^iPr^A$), 1.14 (d, $^3J_{HH}$ = 6, 3H, Me $^iPr^A$), 0.70 (d, $^3J_{HH}$ = 6, 3H, Me of $^iPr^B$).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 156.9 (C12 bpy), 156.3 (C=N), 153.6 (C1 aryl), 153.1 (C12' bpy), 151.7 (CH16 bpy), 150.8 (CH16' bpy), 140.4 (CH14' bpy), 140.3 (CH14 bpy), 138.3 (C2 aryl), 134.4 (CH6 aryl), 129.8 (CH5 aryl), 128.2 (CH15' bpy), 127.4 (CH3 aryl), 126.9 (CH15 bpy), 124.7 (CH4 aryl), 123.5 (CH13 bpy), 122.7 (CH13' bpy), 121.1 (q, $^1J_{CF}$ = 320, OTf), 74.3 (CH_2), 51.0 (CH $^iPr^B$), 45.4 (CH $^iPr^A$), 26.0 (Me $^iPr^B$), 23.7 (Me $^iPr^A$), 23.1 (Me $^iPr^A$), 22.0 (1C, Me $^iPr^B$).

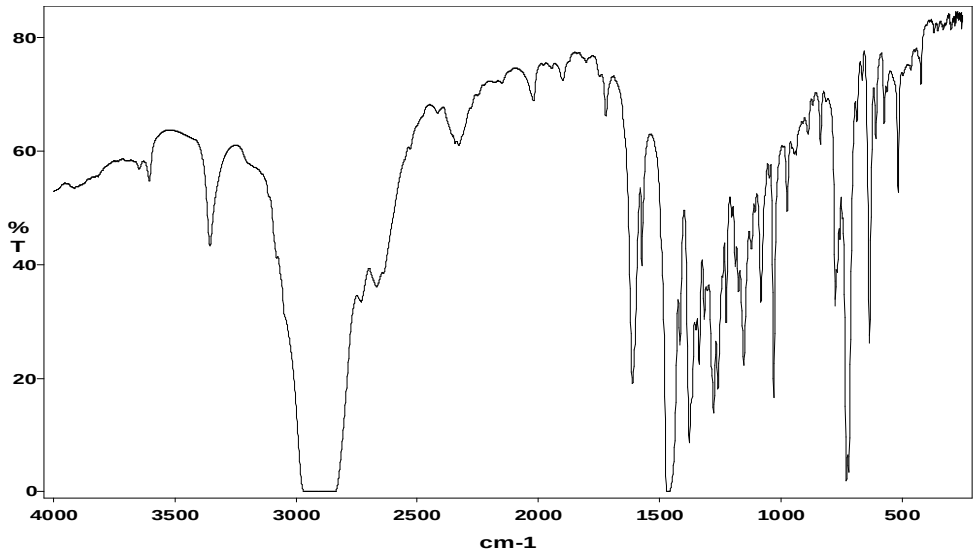
IR (cm^{-1}): ν(S=O): 1028, 1276; ν(C=N): 1611; ν(NH): 3354.

Elemental analysis (%):	C, 46.67	H, 4.40	N, 8.37	S, 4.59
Calcd for $C_{25}H_{29}F_3N_4O_4PdS$:	C, 46.55	H, 4.53	N, 8.69	S, 4.97

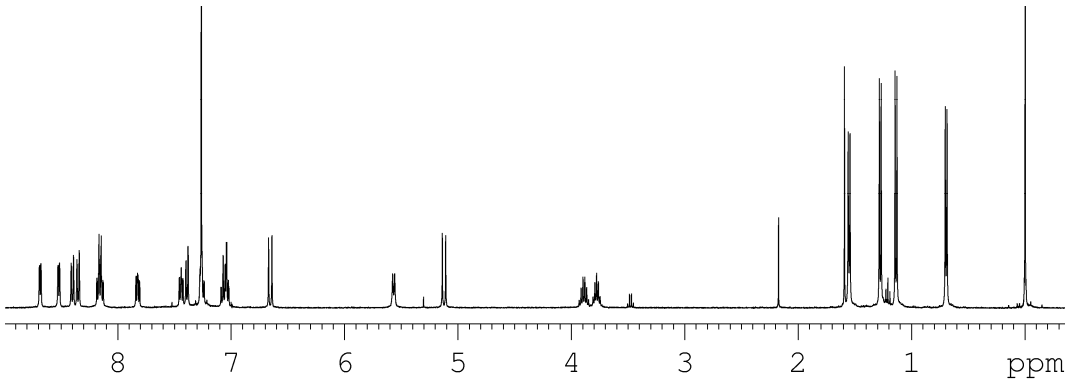
Melting point: 195 °C. **Conductivity:** Λ_M (acetone): 140 $\Omega^{-1}cm^2mol^{-1}$.

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

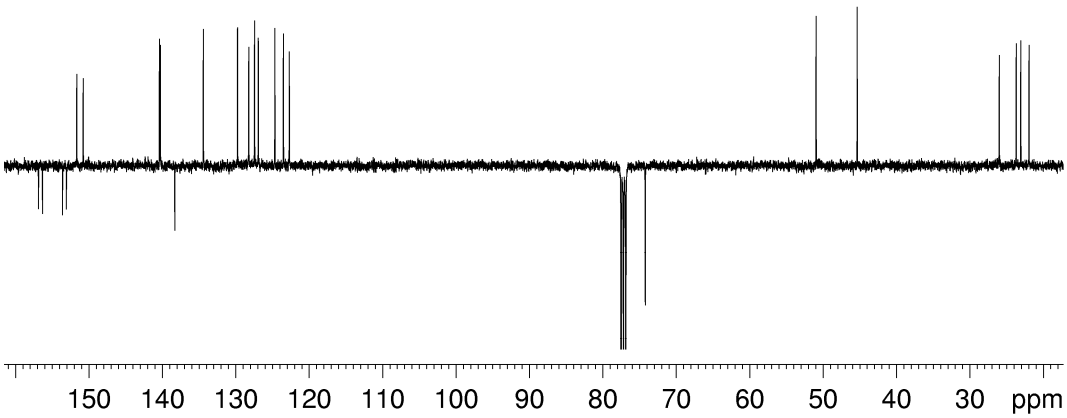
X-ray crystallography: Single crystals of **10a** were grown by liquid diffusion of Et_2O into a solution of **10a** in CH_2Cl_2.



IR spectrum of 10a

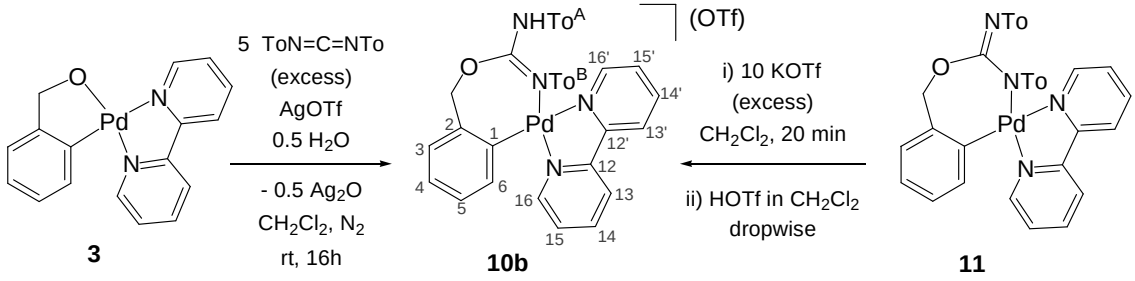


^{1}H-RMN spectrum (400 MHz) of 10a



APT spectrum (100.6 MHz) of 10a

[Pd{κ^2-*C*,*N*-C_6H_4{$CH_2OC(=NTo)NHTo$}-2}(bpy)](OTf) (10b)



Starting from 3: 1,3-Di-*p*-tolylcarbodiimide (302 mg, 1.36 mmol) and AgOTf (69.6 mg, 0.271 mmol) were added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred in the dark for 16 h at room temperature. It was then filtered over Celite, and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **10b** as a yellow solid. Yield: 128 mg (64%).

Starting from 11: KOTf (190 mg, 1.01 mmol) was added to a solution of **11** (60 mg, 0.101 mmol) in commercial CH_2Cl_2 (20 mL) and in an open flask. The mixture was stirred for 20 min at room temperature, with no change in the yellow color. Then a solution of HOTf in commercial CH_2Cl_2 (15.0 mg, 0.100 mmol, in 2 mL) was added dropwise (whereupon the color changed from yellow to red). After the addition the mixture was filtered over Celite, and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **10b** as a yellow solid. Yield: 46.2 mg (62%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 8.61 (d, $^3J_{HH}$ = 5, 1H, H16' bpy), 8.54 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 8.50 (d, $^3J_{HH}$ = 8, 1H, H13' bpy), 8.31 (d, $^3J_{HH}$ = 5, 1H, H16 bpy), 8.18 (t, $^3J_{HH}$ = 8, 1H, H14 bpy), 8.14 (t, $^3J_{HH}$ = 8, 1H, H14' bpy), 7.69 (dd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 5, 1H, H15' bpy), 7.50 (d, $^3J_{HH}$ = 7, 1H, H6 aryl), 7.44 (td, $^3J_{HH}$ = 7, $^4J_{HH}$ = 2,1H, H5 aryl), 7.39 (dd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 5, 1H, H15 bpy), 7.29 (part A of AB system, $^3J_{HH}$ = 8, 2H, *o*-H To^B), 7.22 (part A of AB system, $^2J_{HH}$ = 11, 1H, CH_2), 7.20 (part B of AB system, $^3J_{HH}$ = 8, 2H, *m* -H To^B), 7.22-7.18 (m, 2, H3,4 aryl), 7.09 (part A of AB system, $^3J_{HH}$ = 8, 2H, *m*-H To^A), 6.85 (part B of AB system, $^3J_{HH}$ = 8, 2H, *o*-H To^A), 6.49 (s, 1H, NH), 5.27 (part B of AB system, $^2J_{HH}$ = 11, 1H, CH_2), 2.31 (s, 3H, Me To^A), 2.29 (s, 3H, Me To^B).

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 156.9 (C12 bpy), 156.5 (C=N), 153.7 (C1 aryl), 153.4 (C12' bpy), 151.6 (CH16 bpy), 149.3 (CH16' bpy), 141.8 (*i*-C To^B), 141.0 (2C, CH14,14' bpy), 137.9 (C2 aryl), 137.4 (*p*-C To^B), 136.2 (*p*-C To^A), 134.2 (CH6

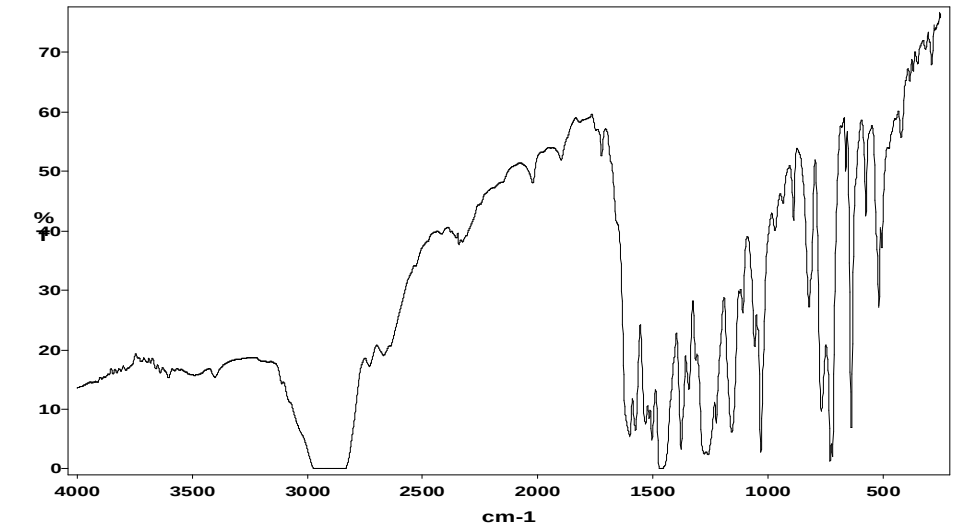
aryl), 133.4 (*i*-C To^A), 131.3 (2C, *m*-CH To^B), 131.2 (CH5 aryl), 129.9 (2C, *m*-CH To^A), 127.9 (CH3 aryl), 127.5 (CH15' bpy), 126.9 (CH15 bpy), 125.9 (2C, *o*-CH To^B), 125.6 (CH4 aryl), 124.5 (CH13 bpy), 123.9 (2C, *o*-CH To^A), 123.8 (CH13' bpy), 74.2 (CH_2), 21.14 (Me To^B), 21.11 (Me To^A). The OTf carbon is not observed.

IR (cm^{-1}): ν(S=O): 1030, 1259; ν(C=N): 1600; ν(NH): 3401.

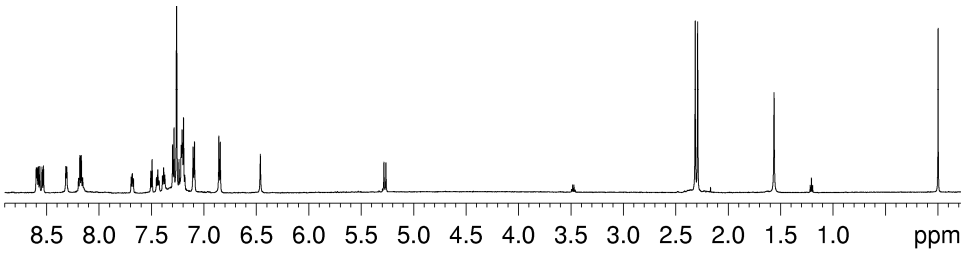
Elemental analysis (%):	C, 53.12	H, 3.64	N, 7.52	S, 4.09
Calcd for $C_{33}H_{29}F_3N_4O_4PdS$:	C, 53.48	H, 3.94	N, 7.56	S, 4.33

Melting point: 182 °C. **Conductivity:** Λ_M (acetone): 125 $\Omega^{-1}cm^2mol^{-1}$.

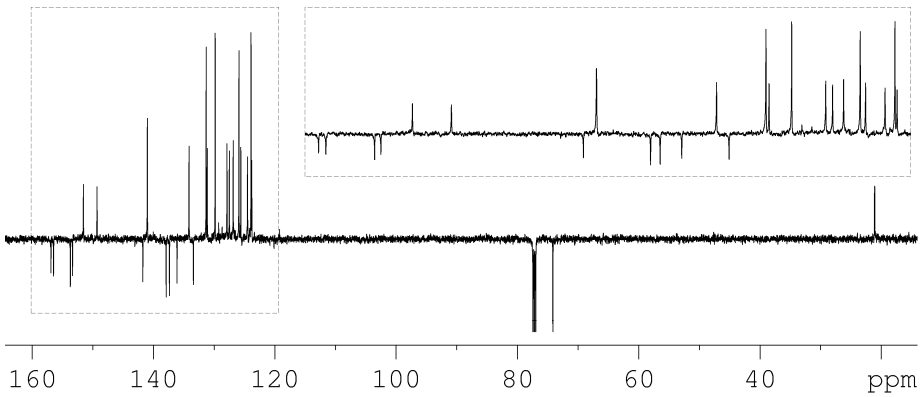
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 10b

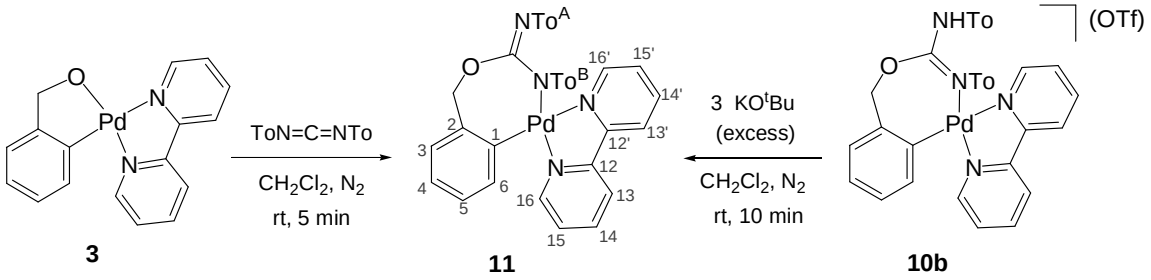


^{1}H-RMN spectrum (600 MHz) of 10b



APT spectrum (150.9 MHz) of 10b

[Pd{κ^2-*C*,*N*-C_6H_4{$CH_2OC(=NTo)NTo$}-2}(bpy)] (11)



Starting from 3: 1,3-Di-*p*-tolylcarbodiimide (60 mg, 0.27 mmol) was added to a solution of **3** (100 mg, 0.27 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred for 5 min at room temperature, with a change in color from yellow to red. It was then filtered over Celite, and the resulting red solution was evaporated to dryness in vacuo. Cold Et_2O (15 mL) was added to precipitate a solid, which was filtered off, washed with cold Et_2O (3×5 mL), and dried in vacuo to give **11** as a red solid. Yield: 130 mg (81%).

Starting from 10b: KO^{t}Bu (27 mg, 0.24 mmol) was added to a solution of **10b** (60 mg, 0.08 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred for 10 min at room temperature, with a change in color from yellow to red. Work-up as in the previous reaction gave **11** as a red solid. Yield: 38 mg, 80 %.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 8.45 (d, $^3J_{HH}$ = 5, 1H, H16 bpy), 8.39 (d, $^3J_{HH}$ = 5, 1H, H16' bpy), 8.06 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 8.02 (d, $^3J_{HH}$ = 8, 1H, H13' bpy), 7.96 (t, $^3J_{HH}$ = 8, 1H, H14 bpy), 7.91 (t, $^3J_{HH}$ = 8, 1H, H14' bpy), 7.9 (A part of AB system, $^3J_{HH}$ = 8, 2H, *o*-H To^B), 7.70 (d, $^3J_{HH}$ = 7, 1H, H6 aryl), 7.39-7.30 (m, 2H, H15,15' bpy), 7.03 (t, $^3J_{HH}$ = 7, 1H, H5 aryl), 7.00-6.95 (br m, 4H, *o,m*-H To^A), 6.93 (t, $^3J_{HH}$ = 7, 1H, H4 aryl), 6.85 (B part of AB system, $^3J_{HH}$ = 8, 2H, *m*-H To^B), 6.70 (d, $^3J_{HH}$ = 7, 1H, H3), 5.02 and 4.73 (br) (AB system, $^2J_{HH}$ = 14, 2H, CH_2), 2.27 (s, 3H, Me To^A), 2.16 (s, 3H, Me To^B), 1.54 (s, 2H, H_2O).

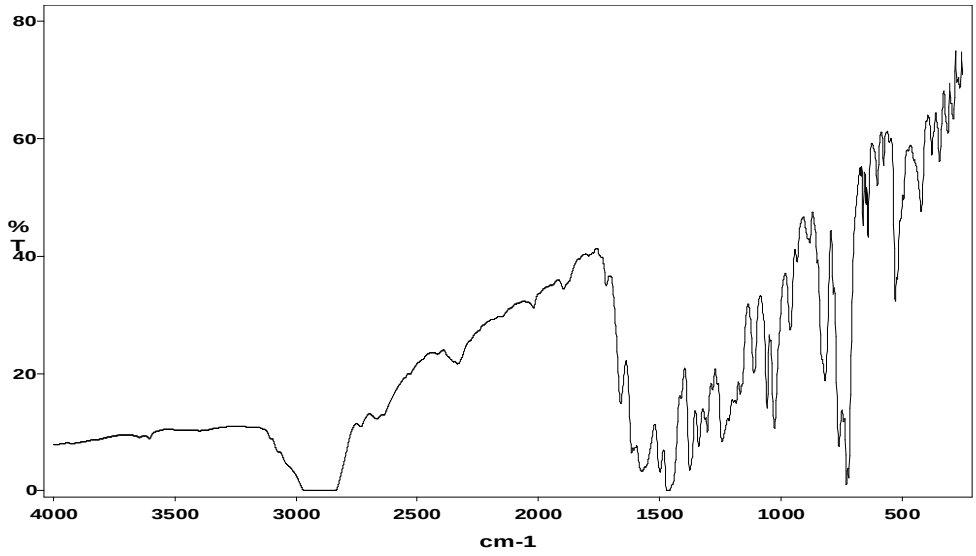
^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 213K): 155.7 (C=N), 155.2 (C12 bpy), 153.1 (C12' bpy), 152.1 (CH16 bpy), 149.6 (C1 aryl), 149.3 (CH16' bpy), 147.9 (*i*-C To^A), 146.4 (i-C To^B), 140.7 (C2 aryl), 139.1 (CH14' bpy), 138.8 (CH14 bpy), 136.2 (CH6 aryl), 129.5 (p-C To^B), 128.97 (2C, *m*-CH To^A), 128.92 (*p*-C To^A), 128.91 (2C, *m*-CH To^B), 127.0 (CH15' bpy), 126.9 (CH5 aryl), 126.7 (CH15 bpy), 124.9 (CH3 aryl), 124.6 (2C, *o*-CH To^B), 123.5 (CH4 aryl), 122.7 (2C, *o*-CH To^A), 122.1 (CH13 bpy), 121.6 (CH13' bpy), 71.2 (CH_2), 21.1 (Me To^A), 21.0 (Me To^B).

IR (cm^{-1}): ν(C=N): 1660.

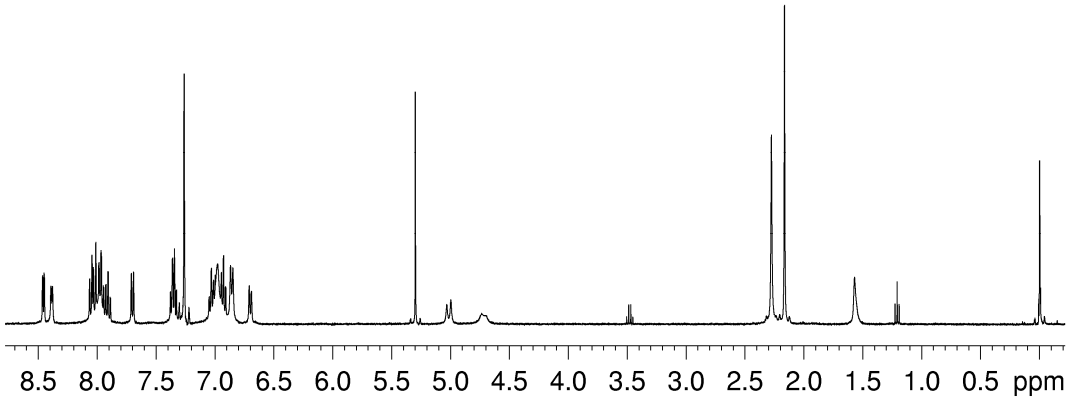
Elemental analysis (%):	C, 63.25	H, 4.68	N, 9.27
Calcd for $C_{32}H_{30}N_4O_2Pd$ (**11**·H_2O):	C, 63.11	H, 4.96	N, 9.20

Melting point: 96 ^{o}C.

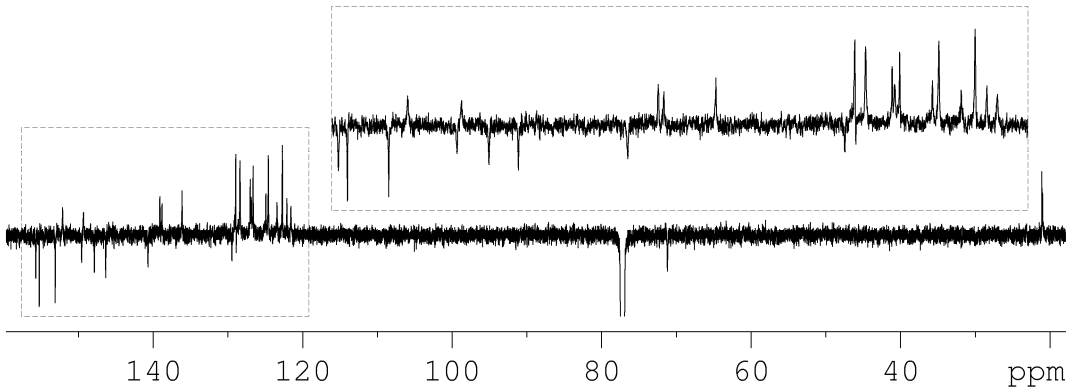
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Partially soluble in Et_2O. Insoluble in hexane.



IR spectrum of 11

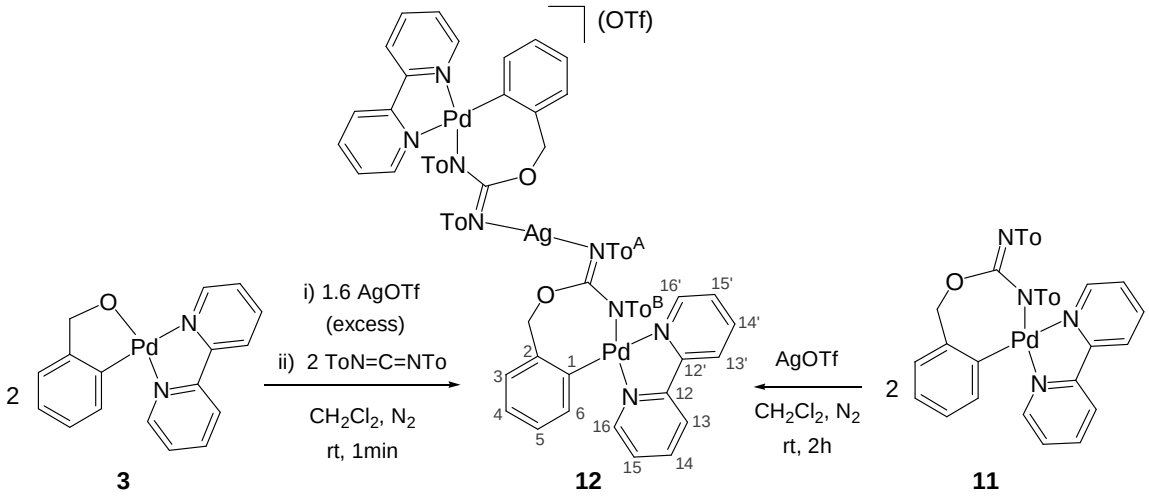


^{1}H-RMN spectrum (400 MHz) of 11



APT spectrum (100.6 MHz) of 11 at 213 K

[Ag(*N*-11)$_2$](OTf) (12)



Starting from 3: AgOTf (57 mg, 0.22 mmol) was added to a solution of **3**[12] (100 mg, 0.27 mmol) in CH_2Cl_2 (20 mL) under N_2, followed by 1,3-di-*p*-tolylcarbodiimide (60 mg, 0.27 mmol). The solvent was immediately evaporated in vacuo and Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give a mixture of **12** and **10b** in ca. 1:0.2 ratio. Yield, 192 mg. This solid was dissolved in CH_2Cl_2 (20 mL) and the resulting solution was filtered over Celite. The yellow solution was then concentrated in vacuo to a volume of ca. 1 mL. A small amount of Et_2O (7 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give pure **12** as a yellow solid. Yield: 124 mg (64%).

Starting from 11: AgOTf (13 mg, 0.05 mmol) was added to a solution of **11** (60 mg, 0.10 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred for 2 h at room temperature, with a change in color from red to yellow. It was then filtered over Celite, and the resulting yellow solution was evaporated to dryness in vacuo. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, washed with Et_2O (3×5 mL), and dried in vacuo to give a mixture of **12** and **10b** in ca. 1:0.2 ratio. Yield: 71 mg. This solid was dissolved in CH_2Cl_2 (20 mL) and the resulting solution was filtered over Celite. The yellow solution was then concentrated in vacuo to a volume of ca. 0.5 mL. A small amount of Et_2O (3 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give pure **12** as a yellow solid. Yield: 38 mg (53%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 8.35 (d, $^3J_{HH}$ = 5, 2H, H16 bpy), 8.33 (d, $^3J_{HH}$ = 8, 2H, H13 bpy), 8.28 (d, $^3J_{HH}$ = 8, 2H, H13’ bpy), 8.13 (d, $^3J_{HH}$ = 5, 2H, H16’ bpy), 8.10

(td, $^{3}J_{HH}$ = 8, $^{4}J_{HH}$ = 1, 2H, H14 bpy), 8.00 (td, $^{3}J_{HH}$ = 8, $^{4}J_{HH}$ = 1, 2H, H14' bpy), 7.84 (d, $^{3}J_{HH}$ = 7, 2H, H6 aryl), 7.39-7.33 (m, 4H, H15 bpy, H5 aryl), 7.33-7.30 (m, 1H, H15' bpy), 7.17 (t, $^{3}J_{HH}$ = 7, 2H, H4 aryl), 7.00 (A part of AB system, $^{3}J_{HH}$ = 7, 4H, *m*-H To^{B}), 6.95-6.75 (br, 4H, *o*-H To^{A}), 6.66 (d, $^{3}J_{HH}$ = 7, 2H, H3 aryl), 6.13 (B part of AB system br, $^{3}J_{HH}$ = 7, 4H, *o*-H To^{B}), 4.88 and 4.19 (AB system, $^{2}J_{HH}$ = 12, 2H, CH_2), 2.37 (s, 6H, Me To^{B}), 2.04 (s, 6H, Me To^{A}). The *m*-H To^{A} protons are not observed.

$^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): 162.2 (2C, C=N), 156.5 (2C, C12 bpy), 153.7 (2C, C12' bpy), 152.4 (2C, CH16 bpy), 150.0 (2C, C1 aryl), 149.0 (2C, CH16' bpy), 146.4 (2C, *i*-C To^{B}), 143.6 (2C, *i*-C To^{A}), 139.9 (2C, CH14' bpy), 139.8 (2C, CH14 bpy), 138.9 (2C, C2 aryl), 136.1 (2C, CH6 aryl), 132.5 (2C, *p*-C To^{A}), 131.3 (2C, *p*-C To^{B}), 129.7 (4C, br, *m*-CH To^{A}), 128.7 (4C, *m*-CH To^{B}), 127.2 (2C, CH5 aryl), 126.9 (2C, CH15' bpy), 126.8 (2C, CH15 bpy), 126.6 (2C, CH3 aryl), 124.2 (4C, *o*-CH To^{B}), 124.1 (2C, CH4 aryl), 123.4 (2C, CH13 bpy), 122.7 (2C, CH13' bpy), 119.9 (q, $^{1}J_{CF}$ = 321, OTf), 72.9 (2C, CH_2), 21.2 (2C, Me To^{B}), 21.0 (2C, Me To^{A}). The *o*-CH To^{A} and OTf carbons are not observed.

IR (cm^{-1}): ν(S=O): 1030, 1272; ν(C=N): 1600.

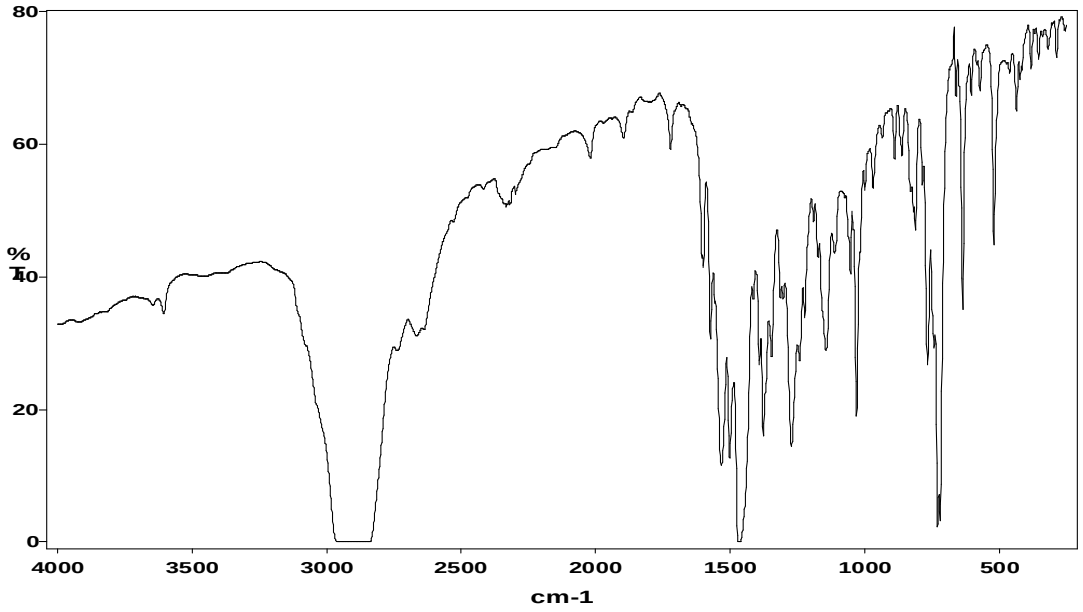
Elemental analysis (%):	C, 54.11	H, 3.81	N, 7.86	S, 2.07
Calcd for $C_{65}H_{56}AgF_3N_8O_5Pd_2S$:	C, 54.25	H, 3.92	N, 7.79	S, 2.23

Melting point: 159 ^{o}C.

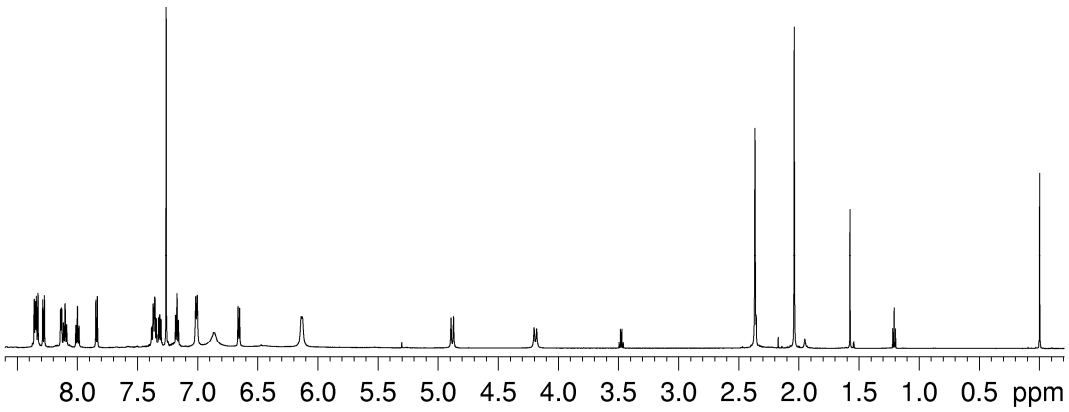
Conductivity: Λ_M (acetone): 148 $\Omega^{-1}cm^{2}mol^{-1}$.

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

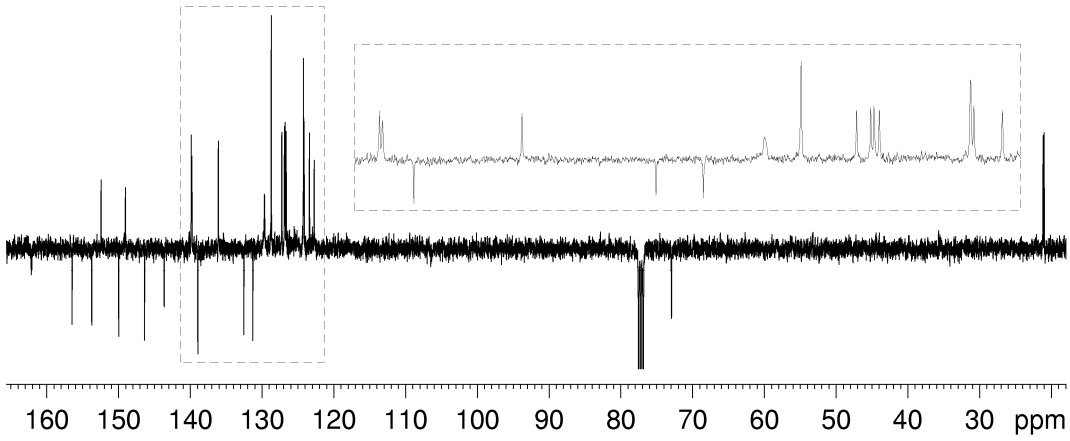
X-ray crystallography: Single crystals of **12** $2.5CHCl_3 \cdot 0.5Et_2O$ were grown by liquid diffusion of Et_2O into a solution of **12** in $CHCl_3$.



IR spectrum of 12

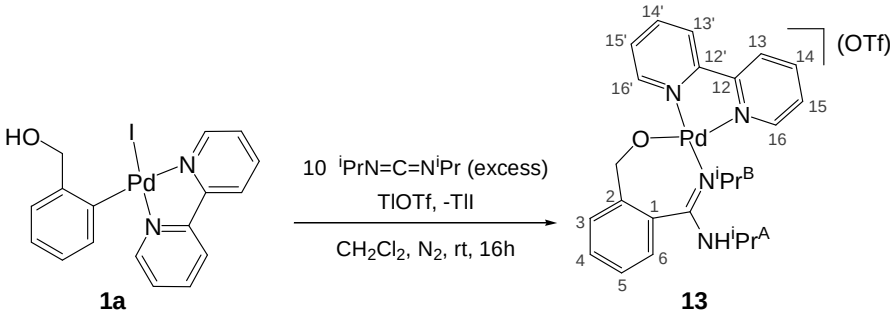


^{1}H-RMN spectrum (600 MHz) of 12



APT spectrum (100.6 MHz) of 12

[Pd{κ^2-*O,N*-OCH$_2${C$_6$H$_4${C(=N^{i}Pr)NH^{i}Pr}-2}}(bpy)](OTf) (13)



1,3-Diisopropylcarbodiimide (252 mg, 2.0 mmol) and TlOTf (70 mg, 0.20 mmol) were added to a solution of **1a** (100 mg, 0.20 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred for 16 h at room temperature. It was then filtered over Celite and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give a mixture of **10a** and **13** in a 1:1.3 ratio. Yield: 97 mg. The products were separated by preparative TLC on alumina using acetone as eluent. The band with Rf = 0.48 was collected, and the product was extracted with acetone (30 mL). Evaporation of the acetone and addition of Et_2O (15 mL) resulted in the formation of a precipitate, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **13** as a yellow solid. Yield: 54 mg (31%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 8.85 (d, $^3J_{HH}$ = 5, 1H, H16' bpy), 8.52 (d, $^3J_{HH}$ = 5, 1H, H16 bpy), 8.10-8.06 (m, 2H, H13',14' bpy), 8.04 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 8.00 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1, 1H, H14 bpy), 7.71 (td, $^3J_{HH}$ = 6, $^4J_{HH}$ = 1, 1H, H15 bpy), 7.57-7.53 (m, 2H, H15' bpy, H6 aryl), 7.43 (d, $^3J_{HH}$ = 8, 1H, H3 aryl), 7.40 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1, 1H, H4 aryl), 7.32 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1, 1H, H5 aryl), 6.39 (d, $^3J_{HH}$ = 9, 1H, NH), 4.57 and 3.84 (AB system, $^2J_{HH}$ = 10, 2H, CH_2), 4.25 (sept, $^3J_{HH}$ = 6, 1H, CH ^{i}Pr^B), 3.55 (dsept, $^3J_{HH}$ = 9, $^3J_{HH}$ = 6, 1H, CH ^{i}Pr^A), 1.65 and 1.54 (d, $^3J_{HH}$ = 6, 3H, Me ^{i}Pr^B), 1.40 and 1.04 (d, $^3J_{HH}$ = 6, 3H, Me ^{i}Pr^A).

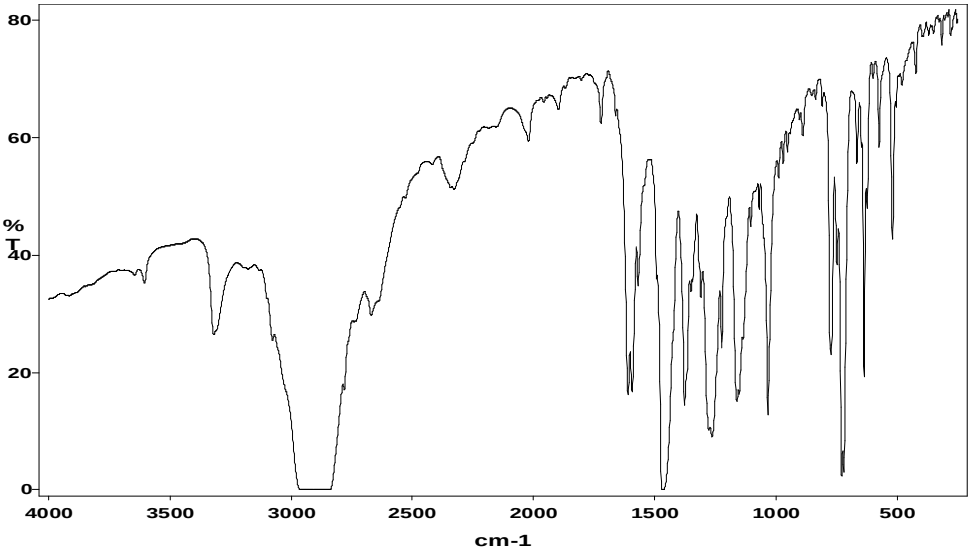
^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 162.0 (C=N), 155.7 (C12' bpy), 154.8 (C12 bpy), 152.2 (CH16 bpy), 148.1 (CH16' bpy), 146.0 (C2 aryl), 140.6 (CH14' bpy), 140.1 (CH14 bpy), 134.2 (C1 aryl), 131.3 (CH4 aryl), 130.8 (CH3 aryl), 128.4 (CH15 bpy), 128.0 (CH6 aryl), 127.9 (CH5 aryl), 126.1 (CH15' bpy), 122.8 (CH13 bpy), 122.4 (CH13' bpy), 121.2 (q, $^1J_{CF}$ = 321, OTf), 69.9 (CH_2), 50.7 (CH ^{i}Pr^B), 48.9 (CH ^{i}Pr^A), 25.2 (Me ^{i}Pr^A), 24.9 (Me ^{i}Pr^B), 23.1 (Me ^{i}Pr^A), 22.4 (1C, Me ^{i}Pr^B).

IR (cm^{-1}): ν(S=O): 1032, 1262; ν(C=N): 1609; ν(NH): 3318.

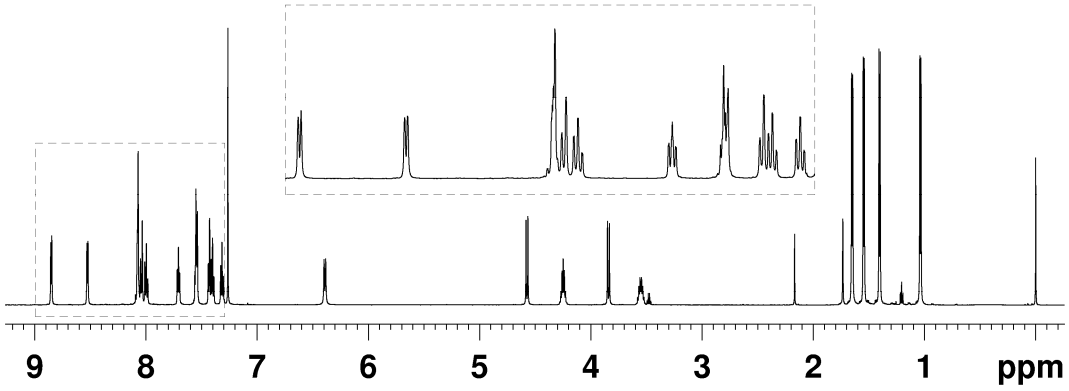
Elemental analysis (%):	C, 46.38	H, 4.80	N, 8.54	S, 4.98
Calcd for $C_{25}H_{29}F_3N_4O_4PdS$:	C, 46.55	H, 4.53	N, 8.69	S, 4.97

Melting point: 177 ^{o}C. **Conductivity:** Λ_M (acetone): 122 $\Omega^{-1}cm^2mol^{-1}$.

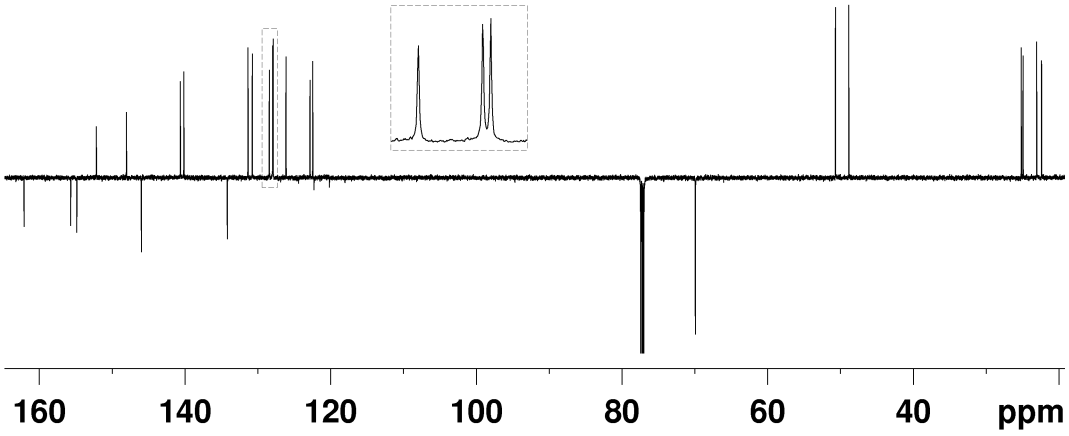
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 13

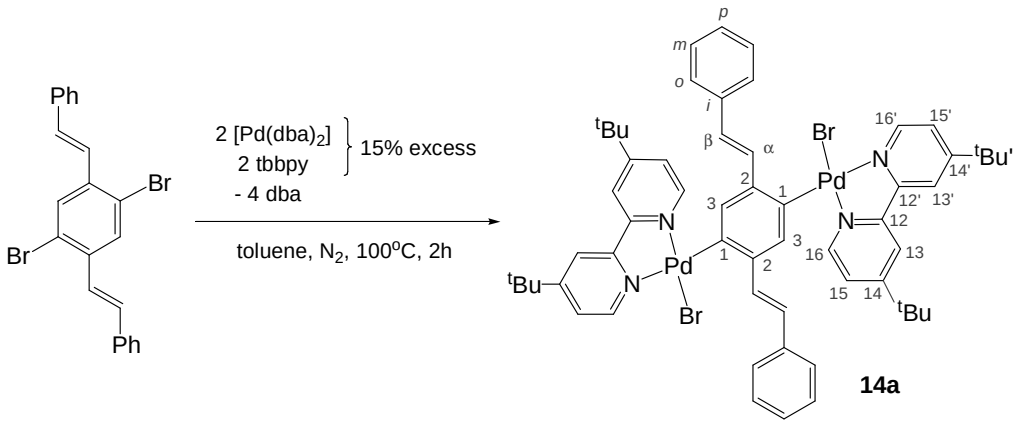


^{1}H-RMN spectrum (600 MHz) of 13



APT spectrum (150.9 MHz) of 13

[C_6H_2{PdBr(tbbpy)}$_2$-1,4-((*E*)-CH=CHPh)$_2$-2,5] (14a)



trans,trans-2,5-Distyryl-1,4-dibromobenzene (200 mg, 0.45 mmol) was added to a suspension of [$Pd(dba)_2$] (605 mg, 1.05 mmol) and tbbpy (282 mg, 1.05 mmol) in dry degassed toluene (15 mL) under N_2. The resulting mixture was stirred at 100ºC for 2 h until the dark red color of [$Pd(dba)_2$] was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the resulting yellow solution was evaporated to dryness. Et_2O (15 mL) was added, and the resulting yellow suspension was filtered off and washed with Et_2O (3x5 mL). *To eliminate traces of a mononuclear complex*, this solid was placed in a flask and a small amount (5 mL) of CH_2Cl_2 was added. The resulting suspension was stirred for 5 min, affording a yellow precipitate that was filtered off, washed with CH_2Cl_2 (2 mL) and Et_2O (3×5 mL), and dried in vacuo to give **14a** as a yellow solid. Yield: 278 mg (52%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

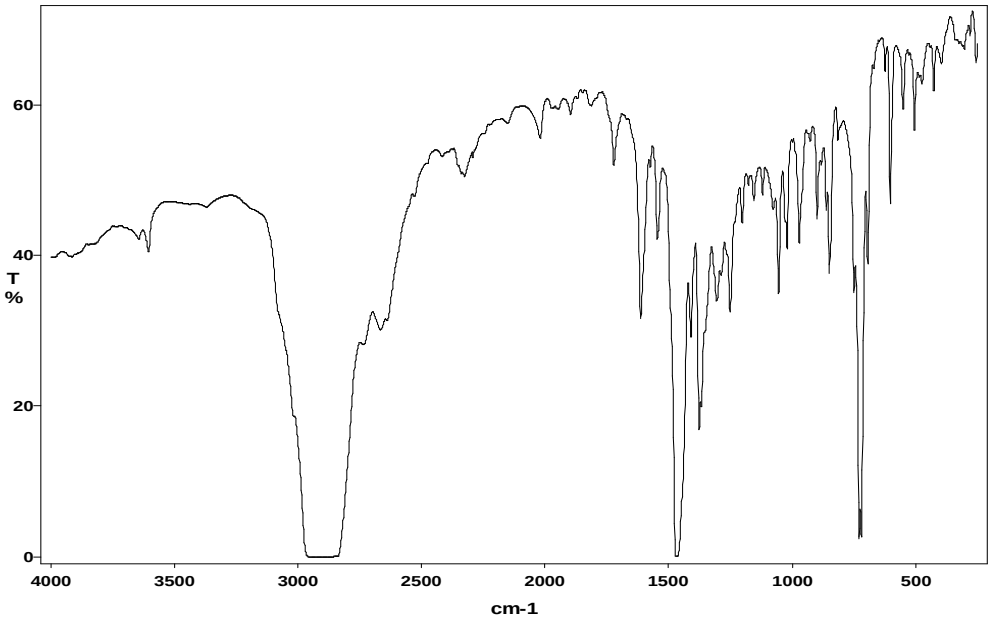
^{1}H NMR (400 MHz, $CDCl_3$): 9.36 (d, $^3J_{HH}$ = 6, 2H, H16' tbbpy), 8.18 (d, $^3J_{HH}$ = 16, 2H, Hα), 7.94 (d, $^3J_{HH}$ = 2, 2H, H13' tbbpy), 7.89 (d, $^3J_{HH}$ = 2, 2H, H13 tbbpy), 7.70 (s, 2H, H3 aryl), 7.66 (d, $^3J_{HH}$ = 6, 2H, H16 tbbpy), 7.55 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15' tbbpy), 7.46 (d, $^3J_{HH}$ = 7, 4H, *o*-H Ph), 7.33 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15 tbbpy), 7.25 (d, $^3J_{HH}$ = 16, 2H, Hβ), 7.19 (t, $^3J_{HH}$ = 8, 4H, *m*-H Ph), 7.06 (t, $^3J_{HH}$ = 7, 2H, *p*-H Ph), 1,44 (s, 18H, ^{t}Bu' tbbpy), 1.34 (s, 18H, ^{t}Bu tbbpy).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 163.4 (2C, C14' tbbpy), 162.8 (2C, C14 tbbpy), 155.7 (2C, C12 tbbpy), 154.1 (2C, C12' tbbpy), 151.9 (2C, CH16 tbbpy), 150.3 (2C, CH16' tbbpy), 146.4 (2C, C1 aryl), 140.0 (2C, C2 aryl), 139.3 (2C, *i*-C Ph), 133.9 (2C, =CHα), 132.2 (2C, CH3 aryl), 128.4 (4C, *m*-CH Ph), 128.4 (4C, *o*-CH Ph), 126.3 (2C, *p*-CH Ph), 125.7 (2C, =CHβ), 124.9 (2C, CH15 tbbpy), 123.6 (2C, CH15' tbbpy), 118.4 (2C, CH13 tbbpy), 117.8 (2C, CH13' tbbpy), 35.7 (2C, *C*Me_3' tbbpy), 35.6 (2C, *C*Me_3 tbbpy), 30.7 (6C, C*Me*$_3$' tbbpy), 30.4 (6C, C*Me*$_3$ tbbpy).

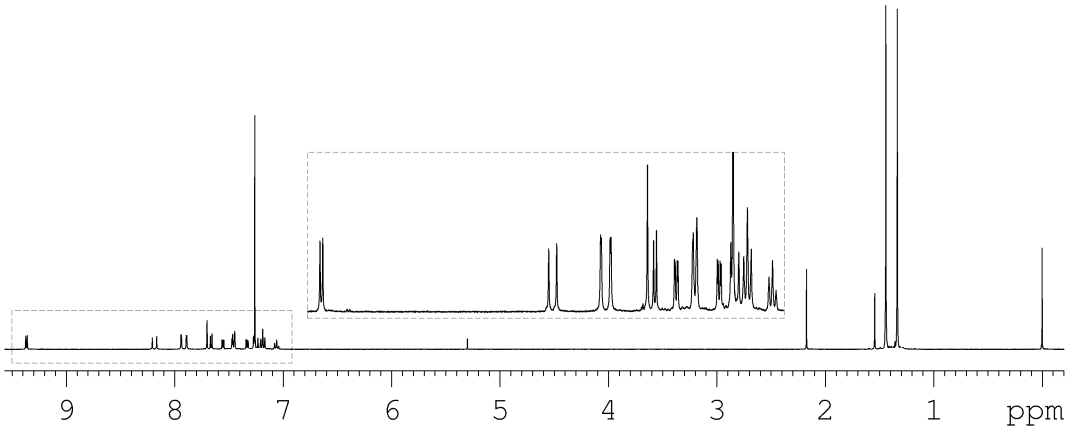
Elemental analysis (%):	C, 58.93	H, 5.42	N, 4.73
Calcd for $C_{58}H_{64}Br_2N_4Pd_2$:	C, 58.55	H, 5.42	N, 4.71

Melting point: 293 ^{o}C (dec).

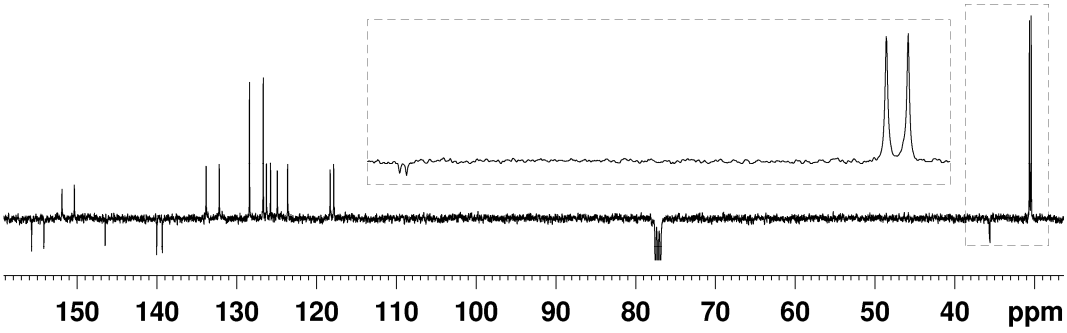
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 14a

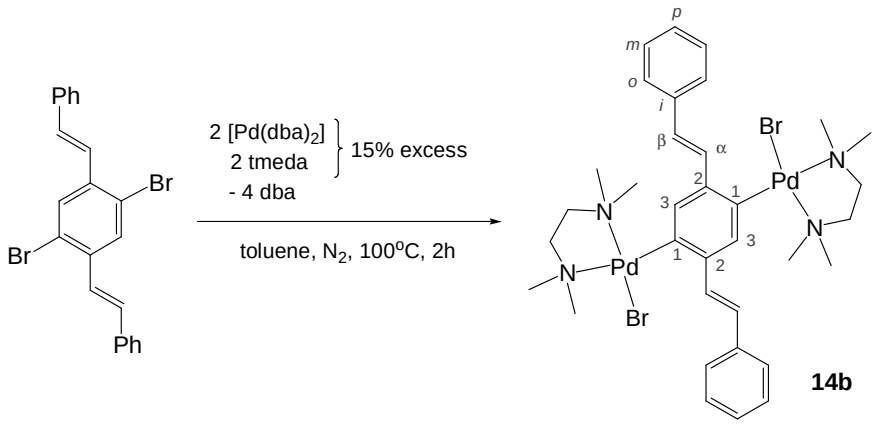


^{1}H-RMN spectrum (400 MHz) of 14a



APT spectrum (100.6 MHz) of 14a

[C_6H_2{PdBr(tmeda)}$_2$-1,4-((*E*)-CH=CHPh)$_2$-2,5] (14b)



14b

trans,trans-2,5-Distyryl-1,4-dibromobenzene (200 mg, 0.45 mmol) was added to a suspension of [$Pd(dba)_2$] (605 mg, 1.05 mmol) and tmeda (158 μL, 1.05 mmol) in dry degassed toluene (15 mL) under N_2. The resulting mixture was stirred at 100ºC for 2 h until the dark red color of [$Pd(dba)_2$] was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the resulting yellow solution was evaporated to dryness. Et_2O (15 mL) was added to precipitate a yellow solid, which was filtered off and washed with Et_2O (3×5 mL). *To eliminate traces of a mononuclear complex*, this solid was placed in a flask and a small amount (5 mL) of CH_2Cl_2 was added. The resulting suspension was stirred for 5 min, affording a yellow precipitate that was filtered off, washed with CH_2Cl_2 (2 mL) and Et_2O (3×5 mL), and dried in vacuo to give **14b** as a yellow solid. Yield: 195 mg (49%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

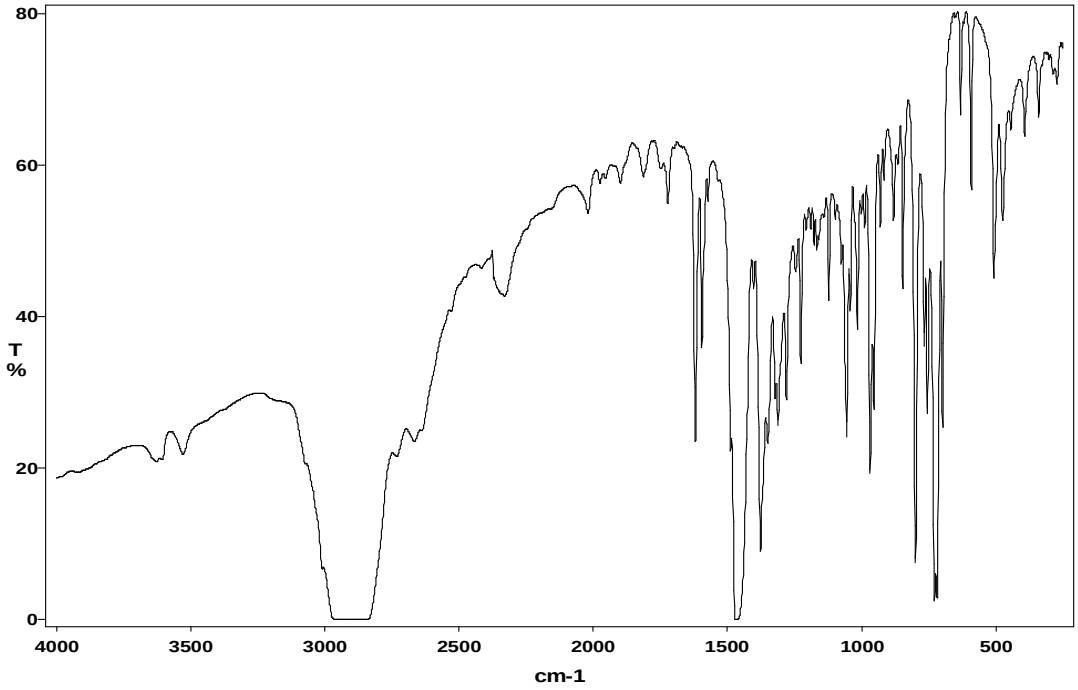
^{1}H NMR (400 MHz, $CDCl_3$): 8.26 (d, $^3J_{HH}$ = 16, 2H, Hα), 7.62 (d, $^3J_{HH}$ = 8, 4H, *o*-H Ph), 7.48 (d, $^3J_{HH}$ = 16, 2H, Hβ), 7.35 (t, $^3J_{HH}$ = 8, 4H, *m*-H Ph), 7.26 (s, 2H, H3 aryl), 7.20 (t, $^3J_{HH}$ = 7.0, 2H, *p*-H Ph), 2.86-2.6 (m, 4H, CH_2 tmeda), 2.72 and 2.69 (s, 6H, Me tmeda), 2.6-2.4 (m, 4H, CH_2 tmeda), 2.47 and 2.12 (s, 6H, Me tmeda).

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 142.9 (2C, C1 aryl), 140.2 (2C, C2 aryl), 139.5 (2C, *i*-C Ph), 134.4 (2C, =CHα), 131.7 (2C, CH3 aryl), 128.8 (4C, *m*-CH Ph), 126.5 (2C, *p*-CH Ph), 126.4 (4C, *o*-CH Ph), 125.6 (2C, =CHβ), 62.8 and 58.5 (2C, CH_2 tmeda), 51.9, 49.9, 49.4, and 47.9 (2C, Me tmeda).

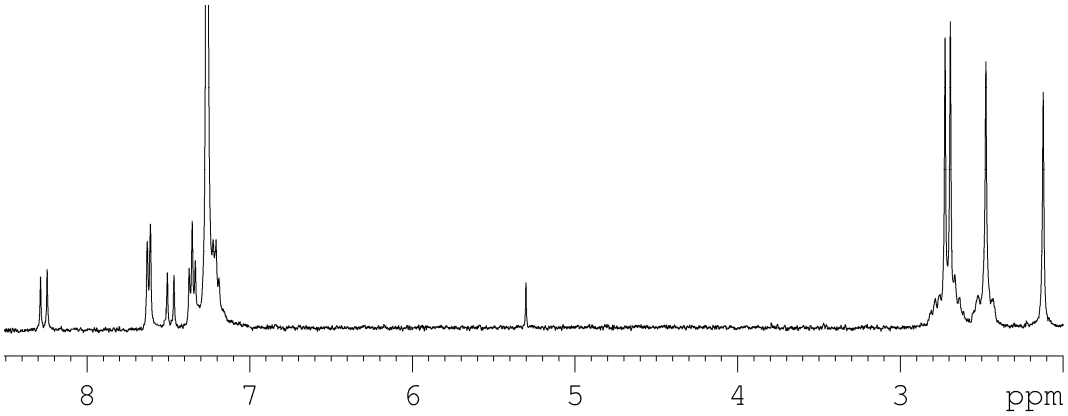
Elemental analysis (%):	C, 45.85	H, 5.50	N, 6.35
Calcd for $C_{34}H_{48}Br_2N_4Pd_2$:	C, 46.12	H, 5.46	N, 6.33

Melting point: 215 ºC (dec).

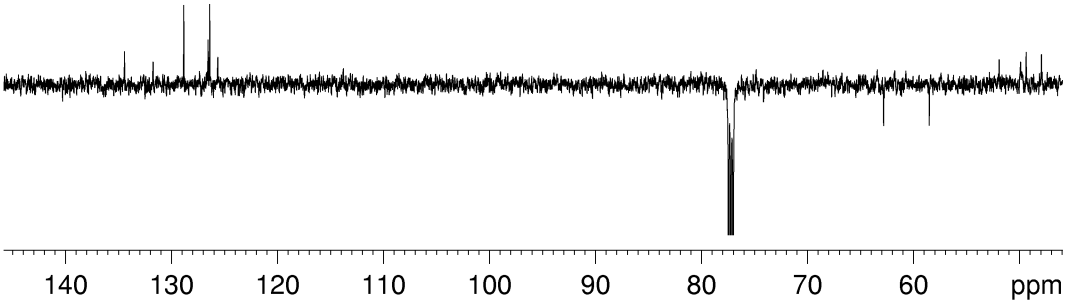
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 14b

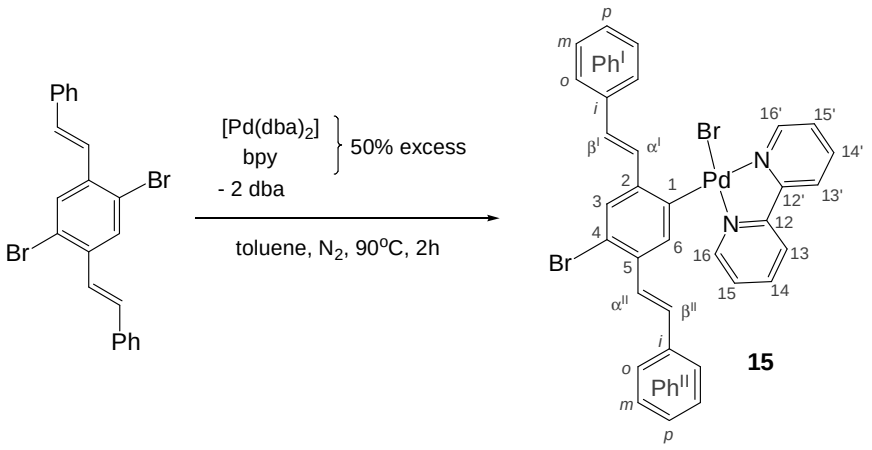


^{1}H NMR spectrum (400 MHz) of 14b



APT spectrum (150.9 MHz) of 14b

[PdBr{C_6H_2(Br-4){((*E*)-CH=CHPh)$_2$-2,5}}(bpy)] (15)



trans,*trans*-2,5-Distyryl-1,4-dibromobenzene (200 mg, 0.45 mmol) was added to a suspension of [Pd(dba)$_2$] (389 mg, 0.67 mmol) and bpy (105 mg, 0.67 mmol) in dry degassed toluene (15 mL) under N_2. The resulting mixture was stirred at 90ºC for 2 h until the dark red color of [Pd(dba)$_2$] was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over anhydrous $MgSO_4$, and the resulting yellow solution was evaporated to dryness. *To eliminate traces of a dinuclear complex*, a mixture of CH_2Cl_2/Et_2O (15 mL:5 mL) was added and the resulting suspension was stirred for 5 min and again filtered over anhydrous $MgSO_4$. *To eliminate traces of the starting arene*, the resulting yellow solution was evaporated to dryness and a mixture of acetone/Et_2O (2 mL:20 mL) was added, affording a yellow precipitate that was filtered off, washed with Et_2O (3×5 mL) and dried in vacuo to give **15** as a yellow solid. Yield: 141 mg, 45 %.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 9.52 (d, $^3J_{HH}$ = 5, 1H, H16' bpy), 8.15 (d, $^3J_{HH}$ = 16, 1H, Hα^I), 8.07-8.04 (m, 3H, H14',13,13' bpy), 7.96 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 2, 1H, H14 bpy), 7.93 (s, 1H, H6 aryl), 7.77 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 1, 1H, H16 bpy), 7.73 (s, 1H, H3 aryl), 7.63 (td, $^3J_{HH}$ = 5, $^4J_{HH}$ = 3, 1H, H15' bpy), 7.51 (d, $^3J_{HH}$ = 7, 2H, *o*-H Ph^{II}), 7.47 (d, $^3J_{HH}$ = 7, 2H, *o*-H Ph^I), 7.42 (d, $^3J_{HH}$ = 16, 1H, Hα^{II}), 7.36-7.3 (m, 3H, *m*-H Ph^{II}, H15 bpy), 7.25-7.2 (m, 3H, *p*-H Ph^{II}, *m*-H Ph^I), 7.18-7.14 (m, 1H, *p*-H Ph^I), 7.14 (d, $^3J_{HH}$ = 16, 1H, Hβ^I), 7.10 (d, $^3J_{HH}$ = 16, 1H, Hβ^{II}).

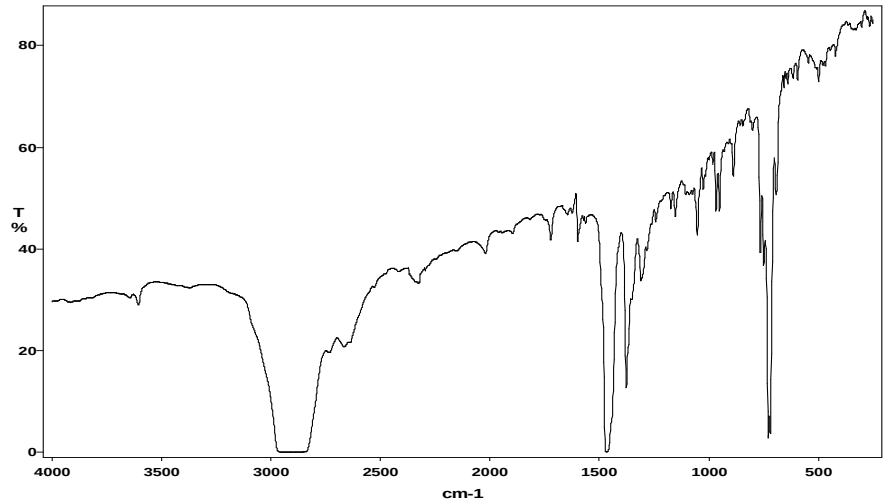
^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 156.2 (1C, C12 bpy), 153.8 (1C, C12' bpy), 151.4 (1C, CH16 bpy), 151.1 (1C, CH16' bpy), 150.4 (1C, C1 aryl), 143.2 (1C, C2 aryl), 139.2 (1C, CH14' bpy), 138.9 (1C, CH14 bpy), 138.2 (1C, *i*-C Ph^I), 137.8 (1C, *i*-C Ph^{II}), 133.8 (1C, C5 aryl), 133.3 (1C, CH6 aryl), 132.2 (1C, =CHα^I), 130.4 (1C, =CHβ^{II}),

129.2 (1C, CH3 aryl), 128.9 (2C, *m*-CH Ph^{II}), 128.6 (2C, *m*-CH Ph^{I}), 127.9 (1C, *p*-CH Ph^{I}), 127.8 (1C, *p*-CH Ph^{II}), 127.7 (1C, =CHα^{II}), 127.3 (1C, =CHβ^{I}), 127.1 (1C, CH15 bpy), 127.0 (1C, CH15' bpy), 126.9 (2C, *o*-CH Ph^{I}), 126.9 (2C, *o*-CH Ph^{II}), 122.2 (1C, CH13 bpy), 121.5 (1C, CH13' bpy), 121.5 (1C, C4 aryl).

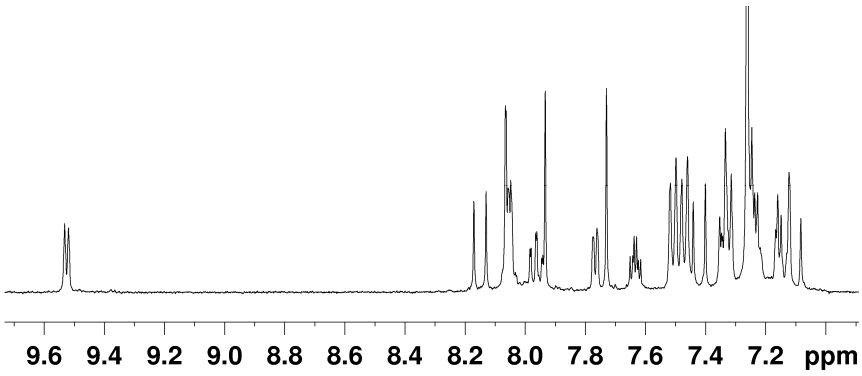
Elemental analysis (%):	C, 54.96	H, 3.10	N, 4.13
Calcd for $C_{32}H_{24}Br_2N_2Pd$:	C, 54.69	H, 3.44	N, 3.99

Melting point: 111 ^{o}C.

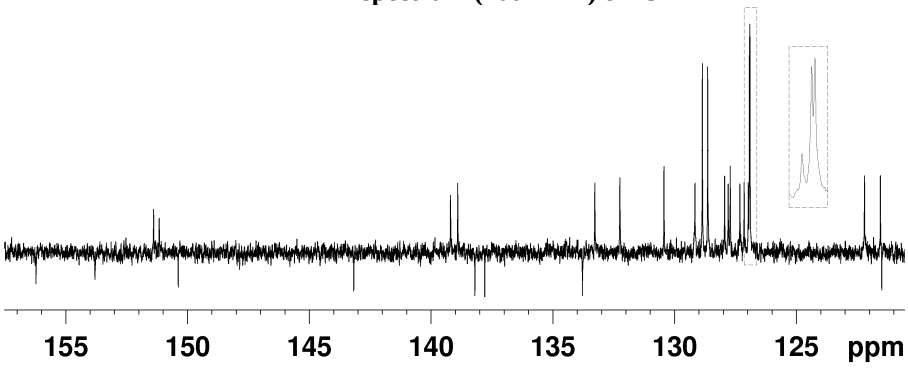
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 15

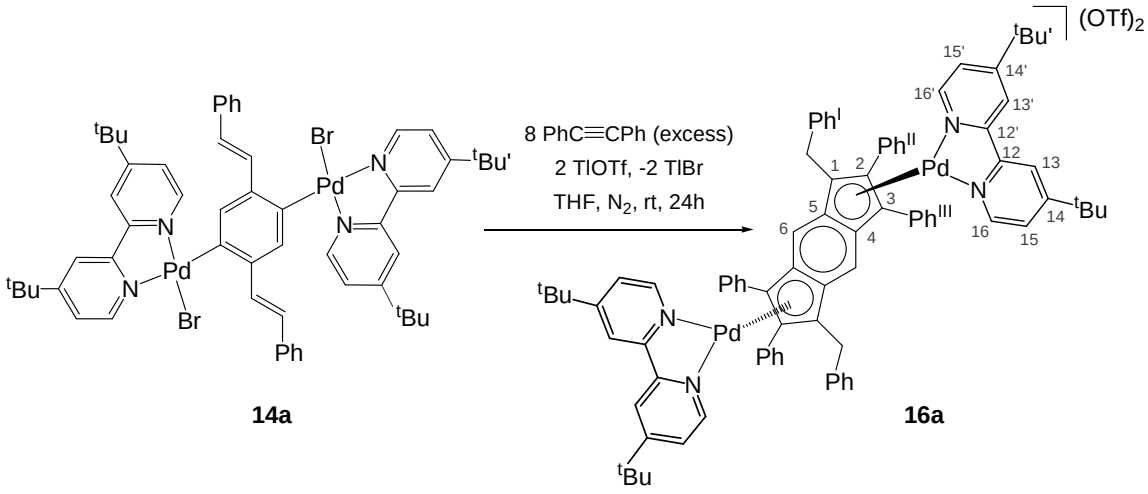


^{1}H NMR spectrum (400 MHz) of 15



APT spectrum (150.9 MHz) of 15

[(μ-η,η-$C_{12}H_2Bn_2$-1,5-Ph_4-2,3,6,7){Pd(tbbpy)}$_2$](OTf)$_2$ (16a)



PhC≡CPh (114 mg, 0.64 mmol) was added to a suspension of **14a** (100 mg, 0.08 mmol) and TlOTf (56 mg, 0.16 mmol) in THF (15 mL) under N_2. The mixture was stirred for 24 h at room temperature (color changed from yellow to brown) and filtered over Celite. The resulting brownish solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a brownish solid which was filtered off and thoroughly washed with Et_2O (3×5 mL). Yield: 110 mg. This solid was divided into four parts, and each of them was purified by crystallization from 2 mL CH_2Cl_2 / 8 mL Et_2O, yielding brown crystals of pure **16a**. Yield: 59 mg (44%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 9.10 (d, $^3J_{HH}$ = 6, 2H, H16' tbbpy), 8.23 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15' tbbpy), 8.09 (s, 2H, H13' tbbpy), 8.00 (s, 2H, H13 tbbpy), 7.60 (d, $^3J_{HH}$ = 7, 4H, *o*-H Ph^{III}), 7.45 (s, 2H, H6), 7.45-7.42 (m, 2H, *p*-H Ph^{III}),7.42-7.37 (m, 4H, *m*-H Ph^{III}), 7.22-7.13 (m, 10H, Ph^{II}), 7.06 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15 tbbpy), 7.00 (d, $^3J_{HH}$ = 6, 2H, H16 tbbpy), 6.99-6.96 (m, 4H, *o*-H Ph^{I}), 6.80-6.77 (m, 6H, *m*,*p*-H Ph^{I}), 4.30 and 3.78 (AB system, $^2J_{HH}$ = 14, 4H, C*H*$_2$Ph^{I}), 1.50 (s, 18H, ^{t}Bu' tbbpy), 1.39 (s, 18H, ^{t}Bu tbbpy).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 165.5 (2C, C14' tbbpy), 165.2 (2C, C14 tbbpy), 154.8 (2C, CH16' tbbpy), 153.9 (2C, C12 tbbpy), 152.3 (2C, C12' tbbpy), 151.3 (2C, CH16 tbbpy), 136.1 (2C, C5), 135.9 (2C, *i*-C Ph^{I}), 133.5 (2C, C4), 131.8 (2C, *i*-C Ph^{II}), 131.1 (4C, CH Ph^{II}), 130.3 (4C, *o*-CH Ph^{III}), 129.8 (2C, *p*-CH Ph^{III}), 129.7 (4C, *m*-CH Ph^{III}), 129.7 (2C, C2), 129.5 (2C, *i*-C Ph^{III}), 129.0 (4C, *o*-CH Ph^{I}), 128.8 (4C, CH Ph^{II}), 128.5 (2C, *p*-CH Ph^{II}), 128.2 (4C, *m*-CH Ph^{I}), 127.1 (2C, CH15' tbbpy), 126.1 (2C, *p*-CH Ph^{I}), 123.9 (2C, CH15 tbbpy), 119.8 (2C, CH13' tbbpy), 119.2 (2C, CH13 tbbpy), 107.3 (2C, CH6), 95.8 (2C, C1), 93.3 (2C, C3), 36.1 (2C, *C*Me$_3$' tbbpy), 35.9 (2C, *C*Me$_3$ tbbpy), 30.6 (6C, C*Me$_3$*' tbbpy), 30.5 (6C, C*Me$_3$* tbbpy), 30.1 (2C, *C*H$_2$Ph^{I}).

IR (cm^{-1}): ν(S=O): 1030, 1256, 1270.

Elemental analysis (%):	C, 61.82;	H, 4.83;	N, 3.15;	S, 3.62
Calcd for $C_{88}H_{84}F_6N_4O_6Pd_2S_2$:	C, 62.74;	H, 5.03;	N, 3.33;	S, 3.81

With respect to the deviation of the C percentage see discussion in Chapter IV.

Exact Mass: HR ESI+ TOF MS: calcd for [**16a**-OTf]$^+$ ($C_{87}H_{84}F_3N_4O_3Pd_2S$) m/z 1535.4324, found 1535.4322, Δ = 0.13 ppm.

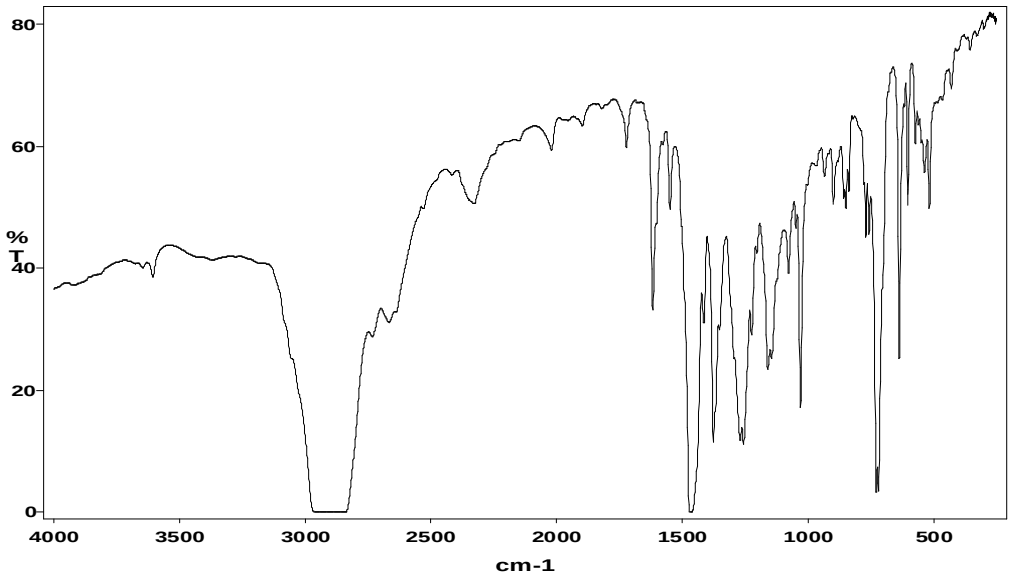
Calculated:	1532.4324 (67.79)	1533.4324 (83.86)	1534.4329 (87.85)	**1535.4324 (100)**	1536.4337 (82.22)	1537.4332 (79.49)	1538.4347 (52.73)
Found:	1532.4334 (66.04)	1533.4329 (82.68)	1534.4330 (87.42)	**1535.4322 (100)**	1536.4341 (82.49)	1537.4333 (79.81)	1538.4359 (53.02)

Melting point: 295 ^oC.

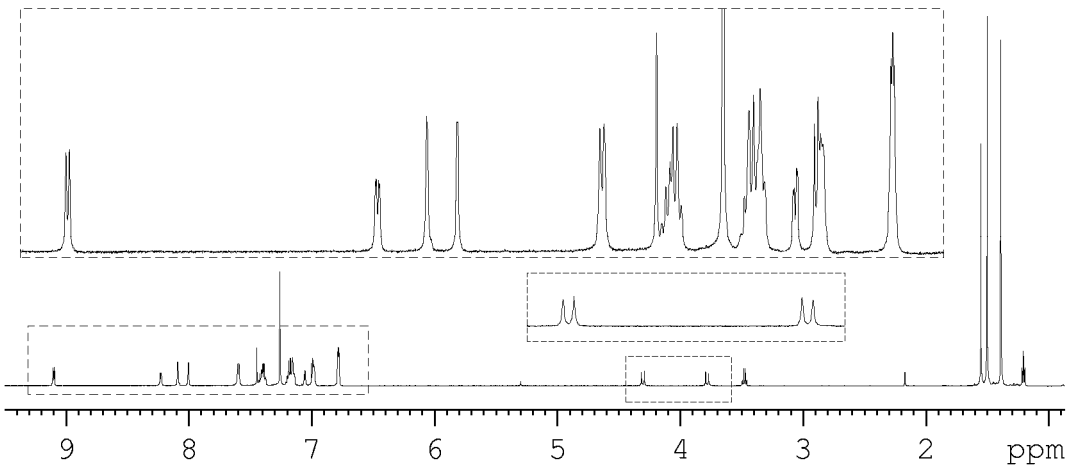
Conductivity: Λ_M (acetone): 255 $\Omega^{-1}cm^2mol^{-1}$.

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

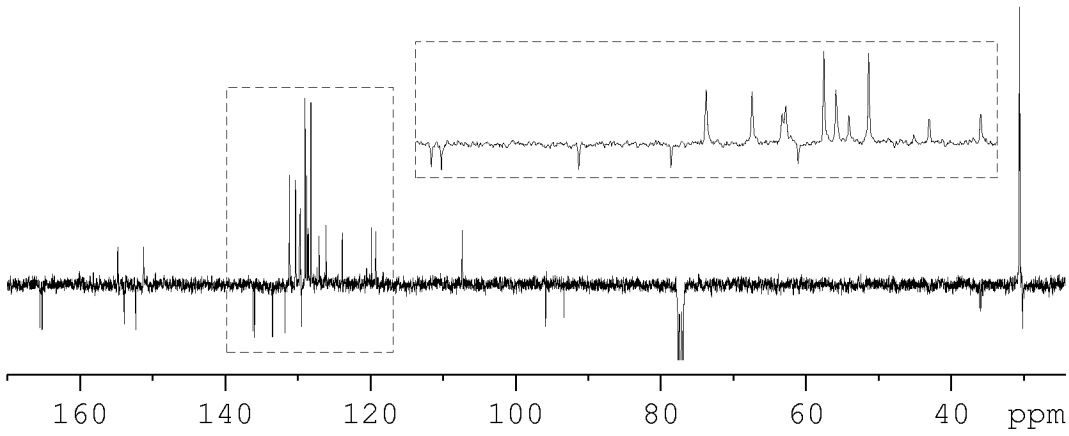
X-ray crystallography: Single crystals of *anti*-**16a**·$7CDCl_3$ were grown by slow evaporation of a $CDCl_3$ solution of **16a**.



IR spectrum of 16a

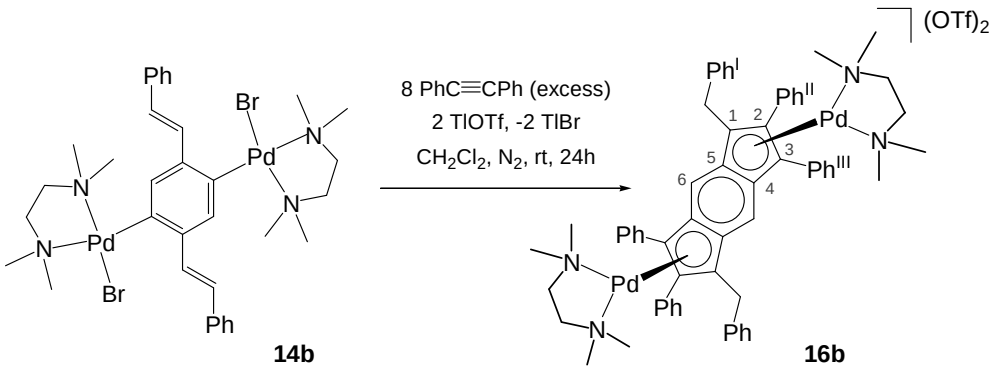


^{1}H NMR spectrum (600 MHz) of 16a



APT spectrum (100.6 MHz) of 16a

[(μ-η,η-$C_{12}H_2Bn_2$-1,5-Ph_4-2,3,6,7){Pd(tmeda)}$_2$](OTf)$_2$ (16b)



PhC≡CPh (96 mg, 0.54 mmol) was added to a suspension of **14b** (60 mg, 0.067 mmol) and TlOTf (47 mg, 0.13 mmol) in CH_2Cl_2 (15 mL) under N_2. The mixture was stirred for 24 h at room temperature (color changed from yellow to dark green) and filtered over Celite. The resulting greenish solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a greenish solid which was filtered off and thoroughly washed with Et_2O (3×5 mL). Yield: 68 mg. This solid was divided into four parts, and each of them was purified by crystallization from 2 mL CH_2Cl_2 / 8 mL Et_2O, yielding green crystals of pure **16b**·CH_2Cl_2. Yield: 47 mg (48%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 7.45-7.35 (m, 12H, Ph^{II}, *p*-H Ph^{III}), 7.3-7.2 (m, 6H, *m*,*p*-H Ph^{I}), 7.19 (t, $^3J_{HH}$ = 8, 4H, *m*-H Ph^{III}), 7.10 (d, $^3J_{HH}$ = 7, 4H, *o*-H Ph^{I}), 7.09 (s, 2H, H6), 7.07 (d, $^3J_{HH}$ = 8, 4H, *o*-H Ph^{III}), 3.60 and 3.32 (AB system, $^2J_{HH}$ = 15, 4H, C*H*$_2Ph^{I}$), 3.45-3.38, 3.15-3.08, 3.06-2.98, and 2.62-2.56 (m, 2H, CH_2 tmeda), 3.03, 3.02, 2.50, and 2.27 (s, 6H, Me tmeda).

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 137.9 (2C, C5), 135.7 (2C, *i*-C Ph^{I}), 133.9 (2C, C4), 132.5 (2C, C2), 132.1 (2C, *i*-C Ph^{II}), 131.0 (4C, CH Ph^{II}), 130.7 (2C, *i*-C Ph^{III}), 129.5 (4C, *o*-CH Ph^{III}), 129.4 (2C, *p*-CH Ph^{III}), 129.3 (4C, *o*-CH Ph^{I}), 129.2 (4C, *m*-CH Ph^{III}), 129.2 (4C, CH Ph^{II}), 129.1 (2C, *p*-CH Ph^{II}), 128.9 (4C, *m*-CH Ph^{I}), 127.2 (2C, *p*-CH Ph^{I}), 108.4 (2C, CH6), 92.1 (2C, C3), 91.4 (2C, C1), 63.5 and 61.7 (2C, CH_2 tmeda), 53.9, 53.2, 52.3 and 49.2 (2C, Me tmeda), 31.4 (2C, *C*H_2Ph^{I}).

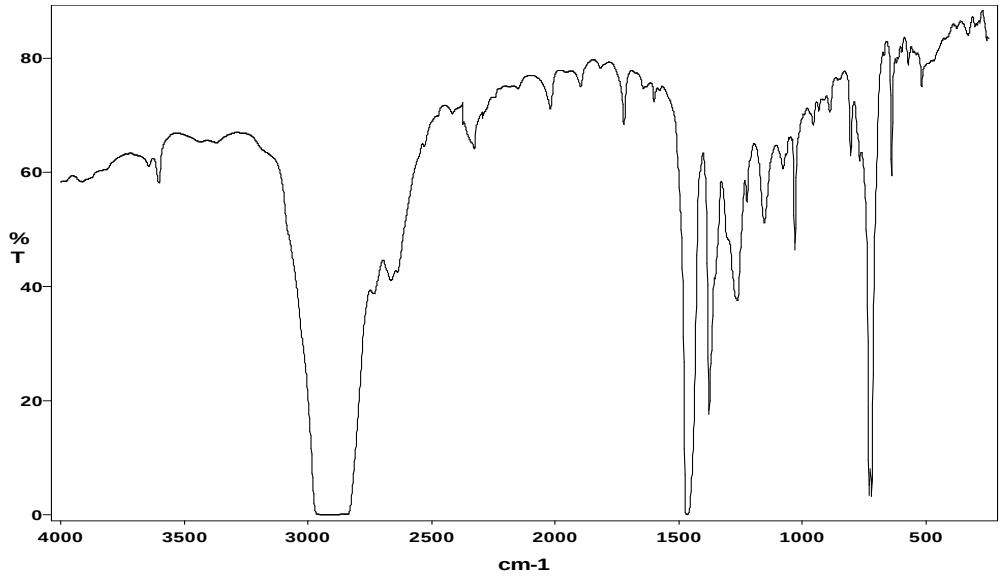
IR (cm^{-1}): ν(S=O): 1030, 1261.

Elemental analysis (%):	C, 53.38	H, 5.08	N, 3.82	S, 4.38
Calcd for $C_{65}H_{70}Cl_2F_6N_4O_6Pd_2S_2$:	C, 53.28	H, 4.82	N, 3.82	S, 4.38

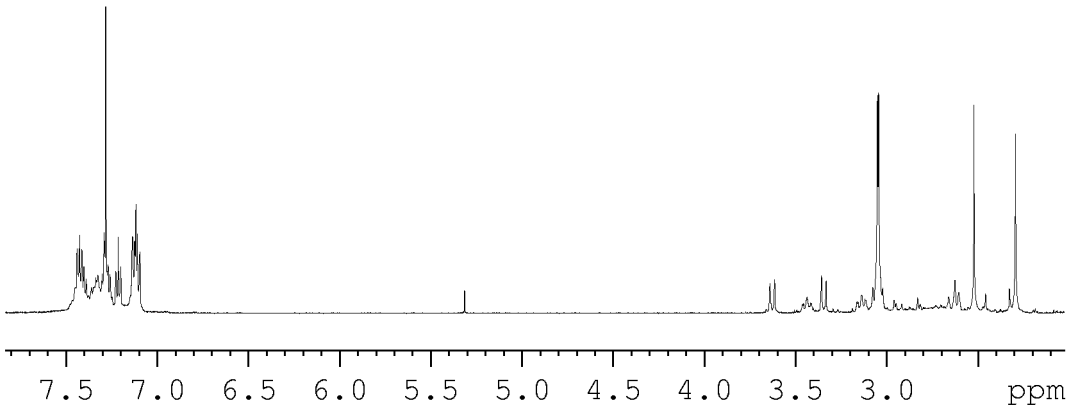
Melting point: 199 °C. **Conductivity:** Λ_M (acetone): 222 $\Omega^{-1}cm^2mol^{-1}$.

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

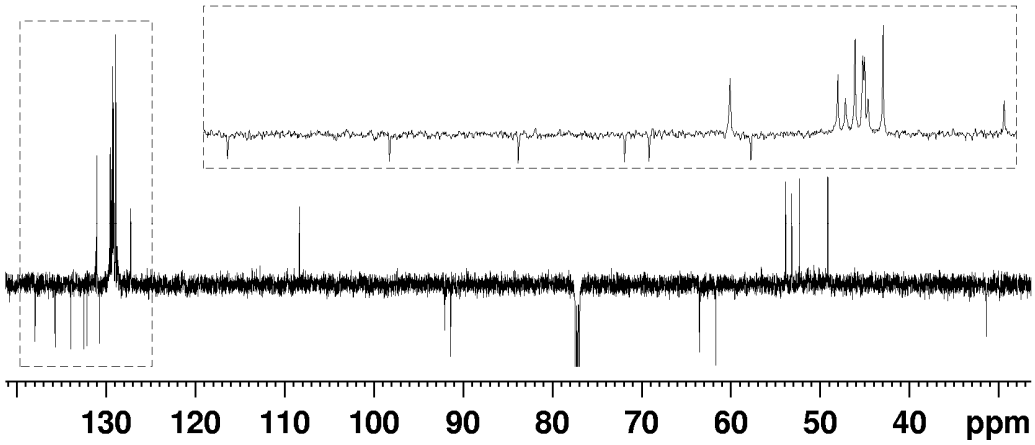
X-ray crystallography: Single crystals of *syn*-**16b**·CH_2Cl_2 were grown by liquid diffusion of Et_2O into a solution of **16b** in CH_2Cl_2.



IR spectrum of 16b

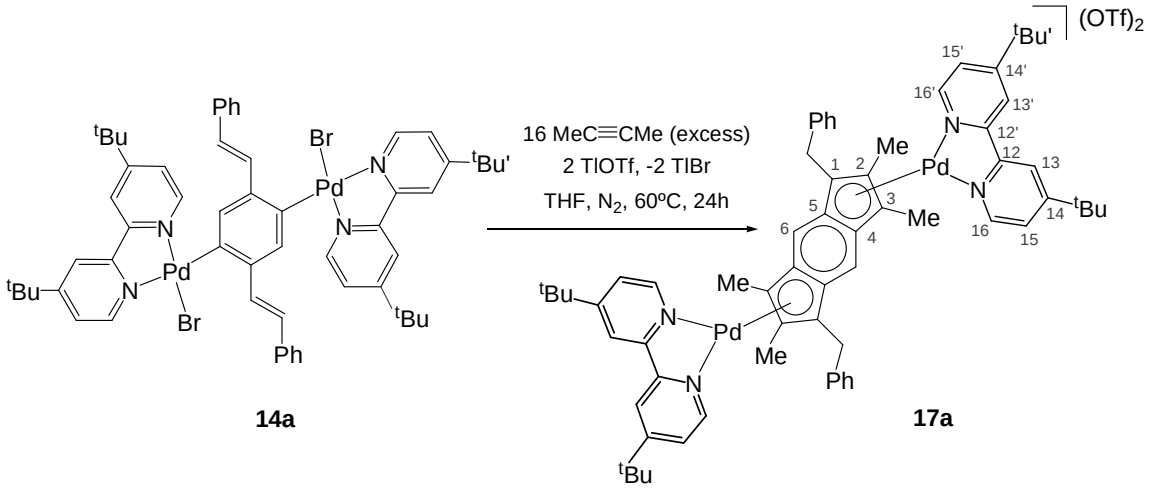


^{1}H NMR spectrum (600 MHz) of 16b



APT spectrum (150.9 MHz) of 16b

[(μ-η,η-$C_{12}H_2Bn_2$-1,5-Me_4-2,3,6,7){Pd(tbbpy)}$_2$](OTf)$_2$ (17a)



14a **17a**

MeC≡CMe (96 μL, 1.28 mmol) was added to a suspension of **14a** (100 mg, 0.08 mmol) and TlOTf (56 mg, 0.16 mmol) in THF (15 mL) under N_2. The mixture was stirred for 24 h at 60ºC (color changed from yellow to brown) and filtered over Celite. The resulting brownish solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a brownish solid which was filtered off and thoroughly washed with Et_2O (3×5 mL). Yield: 63 mg. This solid was divided into four parts, and each of them was purified by crystallization from 2 mL CH_2Cl_2 / 8 mL Et_2O, yielding brown crystals of pure **17a**. Yield: 44 mg (38%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 8.84 and 8.64 (d, $^3J_{HH}$ = 6, 2H, H16',16 tbbpy), 7.89 (m, 4H, H13',H13 tbbpy), 7.83 and 7.78 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15',H15 tbbpy), 7.38 (d, 4H, $^3J_{HH}$ = 7, *o*-H Ph), 7.31 (t, 4H, $^3J_{HH}$ = 7, *m*-H Ph), 7.23 (t, 2H, $^3J_{HH}$ = 7, *p*-H Ph), 7.08 (s, 2H, H6), 4.22 and 3.32 (AB system, $^2J_{HH}$ = 15, 4H, CH_2Ph), 2.28 (s, 6H, Me-2), 1.67 (s, 6H, Me-3), 1.35 and 1.33 (s, 18H, ^{t}Bu tbbpy).

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 164.6 (4C, C14',14 tbbpy), 154.3 and 153.5 (2C, CH16',16 tbbpy), 152.6 and 152.5 (2C, C12',12 tbbpy), 137.4 (2C, C4), 136.1 (2C, C5), 135.9 (2C, *i*-C Ph), 128.9 (4C, *m*-CH Ph), 128.7 (4C, *o*-CH Bn), 126.8 (2C, *p*-CH Ph), 126.1 (2C, C2), 125.6 and 125.5 (2C, CH15',15 tbbpy), 118.7 (4C, CH13',13 tbbpy), 105.7 (2C, CH6), 91.9 (2C, C3), 91.8 (2C, C1), 35.8 and 35.7 (2C, *C*Me_3 tbbpy), 30.8 (2C, *C*H_2Ph), 30.5 (12C, C*Me*$_3$ tbbpy), 13.2 (2C, Me-2), 10.4 (2C, Me-3).

IR (cm^{-1}): ν(S=O): 1030, 1260, 1274.

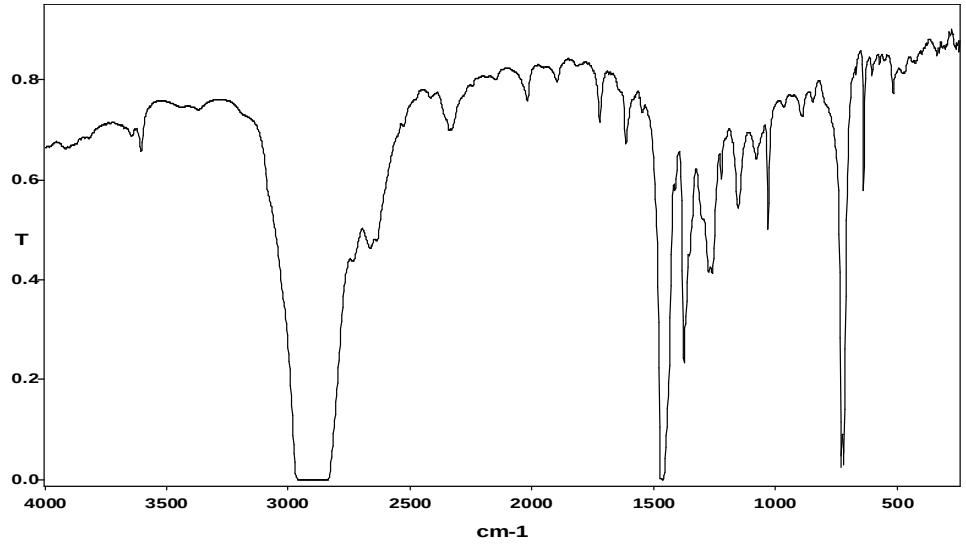
Elemental analysis (%):	C, 55.71	H, 5.31	N, 4.20	S, 4.18
Calcd for $C_{68}H_{76}F_6N_4O_6Pd_2S_2$:	C, 56.86	H, 5.33	N, 3.90	S, 4.46

With respect to the deviation of the C percentage see discussion in Chapter IV.

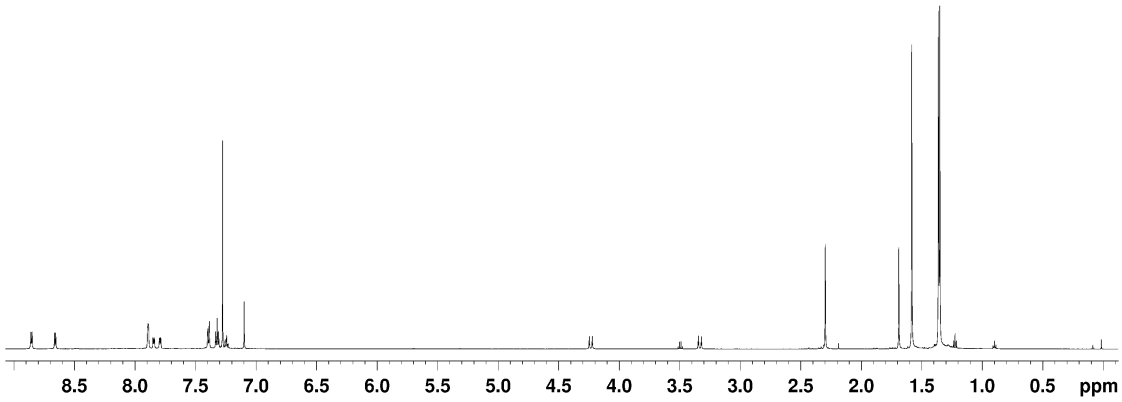
Exact Mass: HR ESI+ TOF MS: calcd for [**17a**-OTf]$^+$ ($C_{67}H_{76}F_3N_4O_3Pd_2S$) m/z 1287.3690, found 1287.3692, Δ = 0.15 ppm.

Melting point: 233 ^{o}C. **Conductivity:** Λ_M (acetone): 252 $\Omega^{-1}cm^2mol^{-1}$.

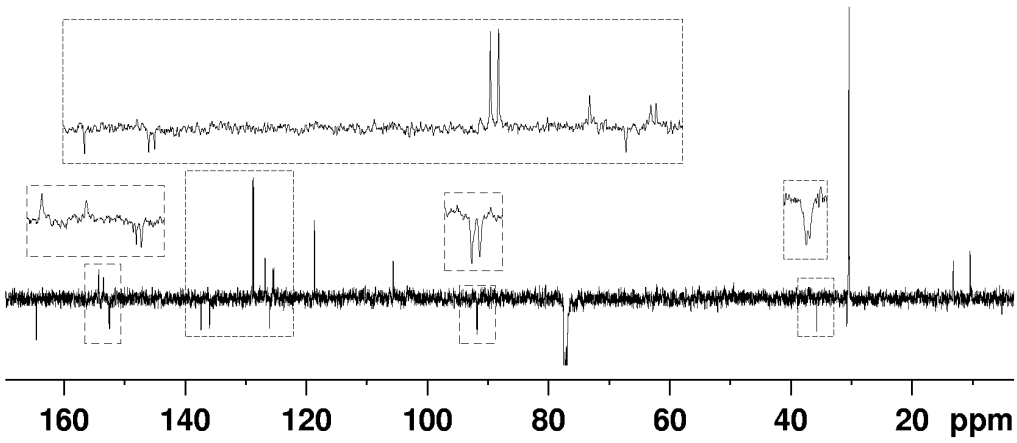
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 17a

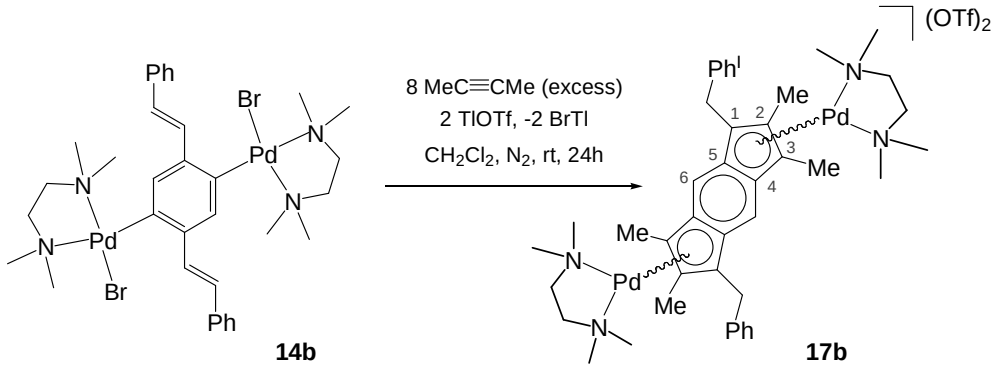


^{1}H NMR spectrum (600 MHz) of 17a



APT spectrum (150.9 MHz) of 17a

[(μ-η,η-$C_{12}H_2Bn_2$-1,5-Me_4-2,3,6,7){Pd(tmeda)}$_2$](OTf)$_2$ (17b)



MeC≡CMe (42 μL, 0.54 mmol) was added to a suspension of **14b** (60 mg, 0.067 mmol) and TlOTf (47 mg, 0.13 mmol) in CH_2Cl_2 (15 mL) under N_2. The mixture was stirred for 24 h at room temperature (color changed from yellow to greenish) and filtered over Celite. The resulting greenish solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a greenish solid which was filtered off and thoroughly washed with Et_2O (3×5 mL). Yield: 48 mg. This solid was divided into four parts, and each of them was purified by crystallization from 2 mL CH_2Cl_2 / 8 mL Et_2O, yielding green crystals of pure **17b**, as a mixture of *syn* and *anti* isomers. Yield: 28 mg (37%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): Major isomer, 7.30-7.26 (m, 4H, *m*-H Ph), 7.25-7.21 (m, 6H, *o*,*p*-H Ph), 6.63 (s, 2H, H6), 3.66 and 3.24 (AB system, $^2J_{HH}$ = 15, 4H, C*H*$_2$Ph), 3.23-3.16 and 2.7-2.6 (m, 4H, CH_2 tmeda), 2.88, 2.80, 2.72 and 2.61 (s, 6H, Me tmeda), 2.35 (s, 6H, Me-2), 1.41 (s, 6H, Me-3). Minor isomer, 7.33-7.19 (several m, 10H, Ph), 6.28 (s, 2H, H6), 3.45 and 3.28 (AB system, $^2J_{HH}$ = 15, 4H, C*H*$_2$Ph), 3.23-3.16 and 2.7-2.6 (several m, 8H, CH_2 tmeda), 2.67, 2.66, 2.49, and 1.99 (s, 6H, Me tmeda), 2.42 (s, 6H, Me-2), 1.42 (s, 6H, Me-3).

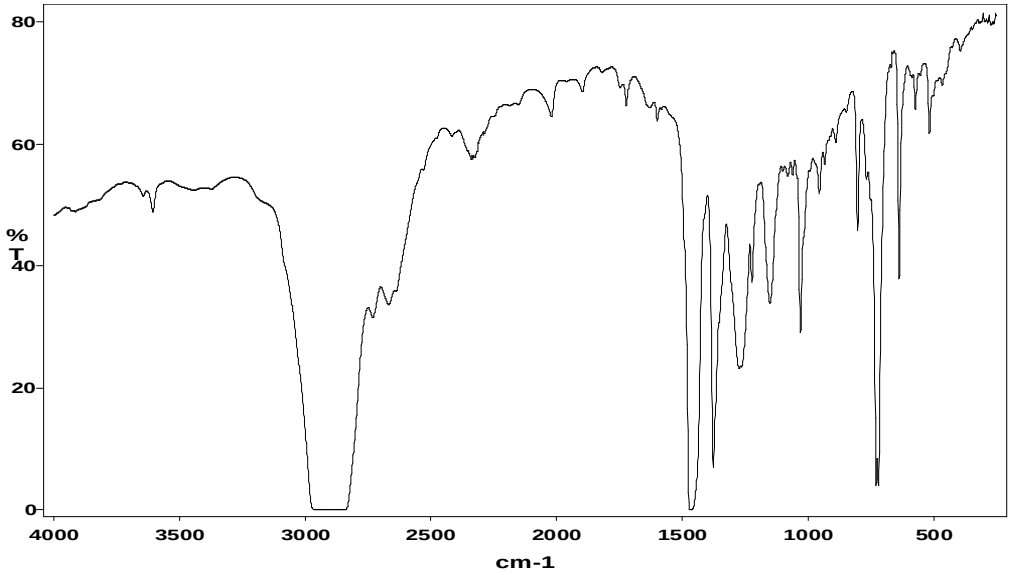
^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): Major isomer, 138.6 (2C, C4), 137.3 (2C, C5), 135.3 (2C, *i*-C Ph), 129.0 (4C, *m*-CH Ph), 128.5 (4C, *o*-CH Ph), 127.1 (2C, *p*-CH Ph), 126.6 (2C, C2), 104.2 (2C, CH6), 89.2 (2C, C3), 89.0 (2C, C1), 61.62 and 61.59 (2C, CH_2 tmeda), 52.5, 52.2, 52.0, and 51.5 (2C, Me tmeda), 31.2 (2C, *C*H_2Ph), 13.2 (2C, Me-2), 10.6 (2C, Me-3).

IR (cm^{-1}): ν(S=O): 1030, 1262, 1273.

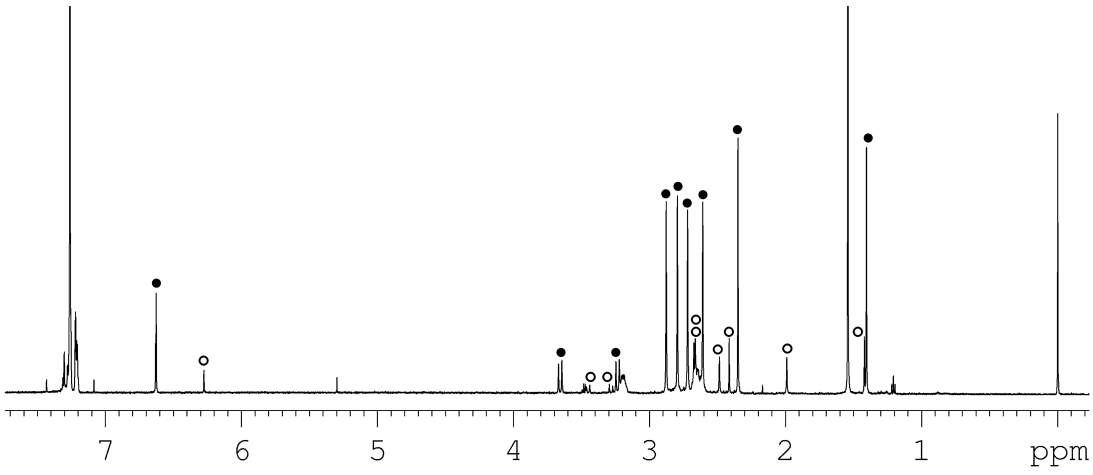
Elemental analysis (%):	C, 46.33	H, 4.99	N, 4.55	S, 5.24
Calcd for $C_{44}H_{60}F_6N_4O_6Pd_2S_2$:	C, 46.69	H, 5.34	N, 4.95	S, 5.66

Melting point: 175 °C. **Conductivity:** Λ_M (acetone): 217 $\Omega^{-1}cm^2mol^{-1}$.

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

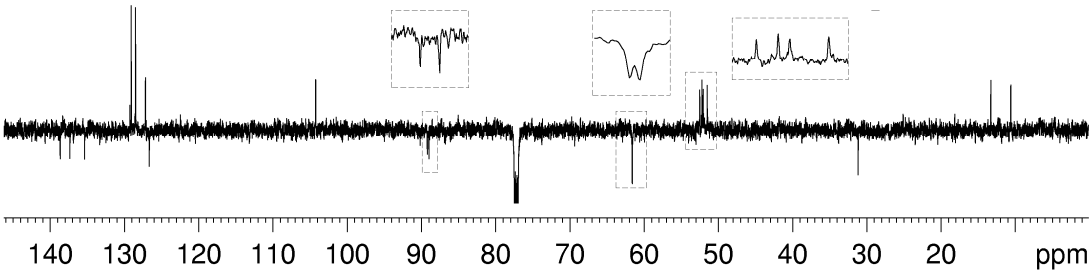


IR spectrum of 17b



^{1}H NMR spectrum (600 MHz) of 17b (*syn*+*anti* isomers)

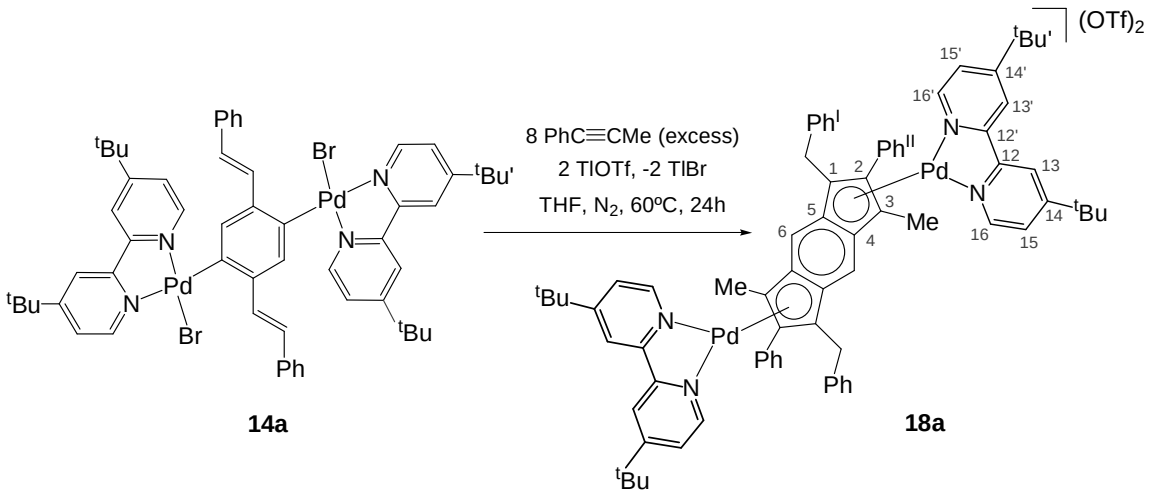
The resonances of the two isomers are distinguished by the symbols ●/○



APT spectrum (150.9 MHz) of 17b (*syn*+*anti* isomers)

(Only the resonances of the major isomer are observed)

[(μ-η,η-$C_{12}H_2Bn_2$-1,5-Ph_2-2,6-Me_2-3,7){Pd(tbbpy)}$_2$](OTf)$_2$ (18a)



PhC≡CMe (80 μL, 0.64 mmol) was added to a suspension of **14a** (100 mg, 0.08 mmol) and TlOTf (56 mg, 0.16 mmol) in THF (15 mL) under N_2. The mixture was stirred for 24 h at 60ºC (color changed from yellow to brownish) and filtered over Celite. The resulting brownish solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a brownish solid which was filtered off and thoroughly washed with Et_2O (3×5 mL). Yield: 72 mg. This solid was divided into four parts, and each of them was purified by crystallization from 2 mL CH_2Cl_2 / 8 mL Et_2O, yielding brown crystals of pure **18a**. Yield: 36 mg (29%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 8.89 (d, $^3J_{HH}$ = 6, 2H, H16' tbbpy), 8.20 (d, $^3J_{HH}$ = 6, 2H, H16 tbbpy), 8.05 (s, 2H, H13' tbbpy), 8.02 (s, 2H, H13 tbbpy), 7.97 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15' tbbpy), 7.61 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15 tbbpy), 7.37-7-33 (m, 4H, *o*-H Ph^{II}), 7.30-7.27 (m, 6H, *m*,*p*-H Ph^{II}), 7.29 (s, 2H, H6), 7.08-7.05 (m, 4H, *o*-H Ph^{I}), 6.93-6.90 (m, 6H, *m*,*p*-H Ph^{I}), 4.13 and 3.51 (AB system, $^2J_{HH}$ = 14, 4H, CH_2Ph^{I}), 1.70 (s, 6H, Me-3), 1.47 (s, 18H, ^{t}Bu' tbbpy), 1.46 (s, 18H, ^{t}Bu tbbpy).

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 165.3 (2C, C14' tbbpy), 165.2 (2C, C14 tbbpy), 154.3 (2C, CH16' tbbpy), 153.4 (2C, C12 tbbpy), 152.3 (2C, C12' tbbpy), 151.5 (2C, CH16 tbbpy), 136.2 (2C, C4), 136.1 (2C, *i*-C Ph^{I}), 135.0 (2C, C5), 131.5 (2C, *i*-C Ph^{II}), 130.9 (4C, *o*-CH Ph^{II}), 129.3 (4C, *o*-CH Ph^{I}), 129.1 (2C, C2), 128.8 (4C, *m*-CH Ph^{II}), 128.7 (2C, *p*-CH Ph^{II}), 128.3 (4C, *m*-CH Ph^{I}), 126.3 (4C, CH15' tbbpy, *p*-CH Ph^{I}, 124.7 (2C, CH15 tbbpy), 119.5 (2C, CH13' tbbpy), 119.3 (2C, CH13 tbbpy), 105.9 (2C, CH6), 94.0 (2C, C3), 93.1 (2C, C1), 36.0 (2C, *C*Me$_3$' tbbpy), 35.9 (2C, *C*Me$_3$ tbbpy), 30.6 (12C, C*Me$_3$* tbbpy), 30.4 (2C, *C*H$_2$Ph^{I}), 11.3 (2C, Me-3).

IR (cm^{-1}): ν(S=O): 1030, 1270.

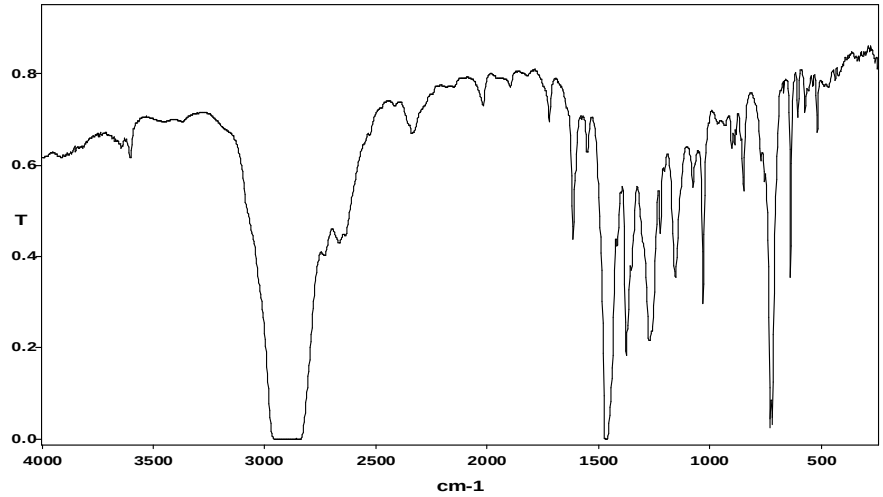
Elemental analysis (%):	C, 59.40	H, 5.34	N, 3.59	S, 3.85
Calcd for $C_{78}H_{80}F_6N_4O_6Pd_2S_2$:	C, 60.03	H, 5.17	N, 3.59	S, 4.11

With respect to the deviation of the C percentage see discussion in Chapter IV.

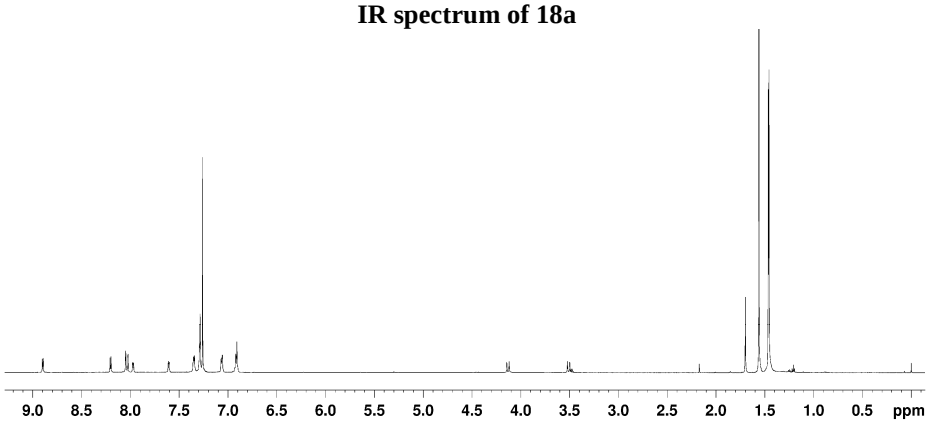
Exact Mass: HR ESI+ TOF MS: calcd for [**18a**-OTf]$^+$ ($C_{77}H_{80}F_3N_4O_3Pd_2S$) m/z 1411.4007, found 1411.3983, Δ = 1.7 ppm.

Melting point: 212 ^{o}C. **Conductivity:** Λ_M (acetone): 231 $\Omega^{-1}cm^2mol^{-1}$.

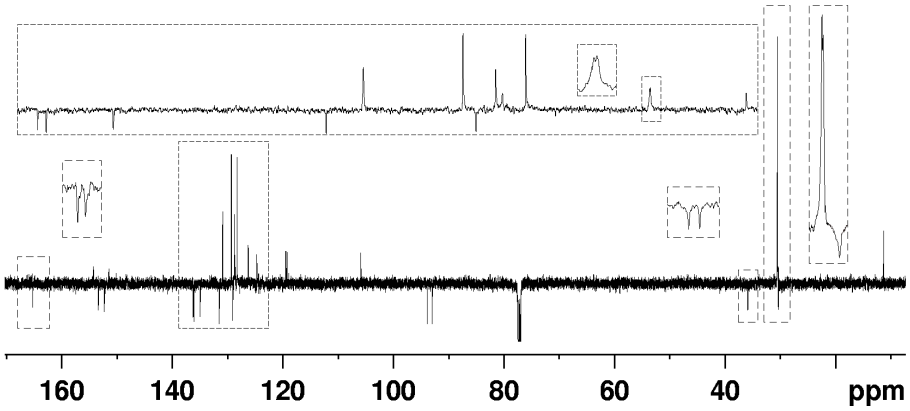
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 18a

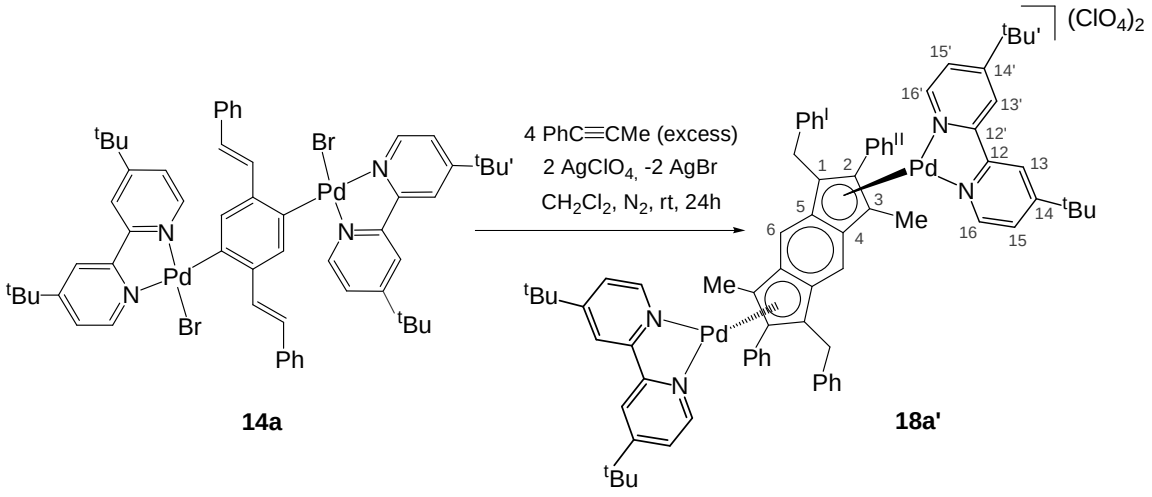


^{1}H NMR spectrum (600 MHz) of 18a



APT spectrum (150.9 MHz) of 18a

[(μ-η,η-$C_{12}H_2Bn_2$-1,5-Ph_2-2,6-Me_2-3,7){Pd(tbbpy)}$_2$](ClO_4)$_2$ (18a')



PhC≡CMe (40 μL, 0.32 mmol) was added to a suspension of **14a** (100 mg, 0.08 mmol) and $AgClO_4$ (33 mg, 0.16 mmol) in CH_2Cl_2 (15 mL) under N_2. The mixture was stirred for 24 h at room temperature (color changed from yellow to brownish) and filtered over Celite. The resulting brownish solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a brownish solid which was filtered off and thoroughly washed with Et_2O (3×5 mL). Yield: 90 mg. This solid was divided into four parts and each of them was purified by crystallization from 2 mL CH_2Cl_2 / 8 mL Et_2O, yielding brown crystals of pure **18a'**. Yield: 39 mg (33%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 8.89 (d, $^3J_{HH}$ = 6, 2H, H16' tbbpy), 8.19 (d, $^3J_{HH}$ = 6, 2H, H16 tbbpy), 8.06 (d, $^3J_{HH}$ = 2, 2H, H13' tbbpy), 8.03 (d, $^3J_{HH}$ = 2, 2H, H13 tbbpy), 8.00 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15' tbbpy), 7.59 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15 tbbpy), 7.36-7-32 (m, 4H, *o*-H Ph^{II}), 7.30-7.27 (m, 6H, *m*,*p*-H Ph^{II}), 7.27 (s, 2H, H6), 7.06-7.03 (m, 4H, *o*-H Ph^{I}), 6.94-6.88 (m, 6H, *m*,*p*-H Ph^{I}), 4.09 and 3.50 (AB system, $^2J_{HH}$ = 14, 4H, C*H*$_2$Ph^{I}), 1.72 (s, 6H, Me-3), 1.47 (s, 18H, ^{t}Bu' tbbpy), 1.46 (s, 18H, ^{t}Bu tbbpy).

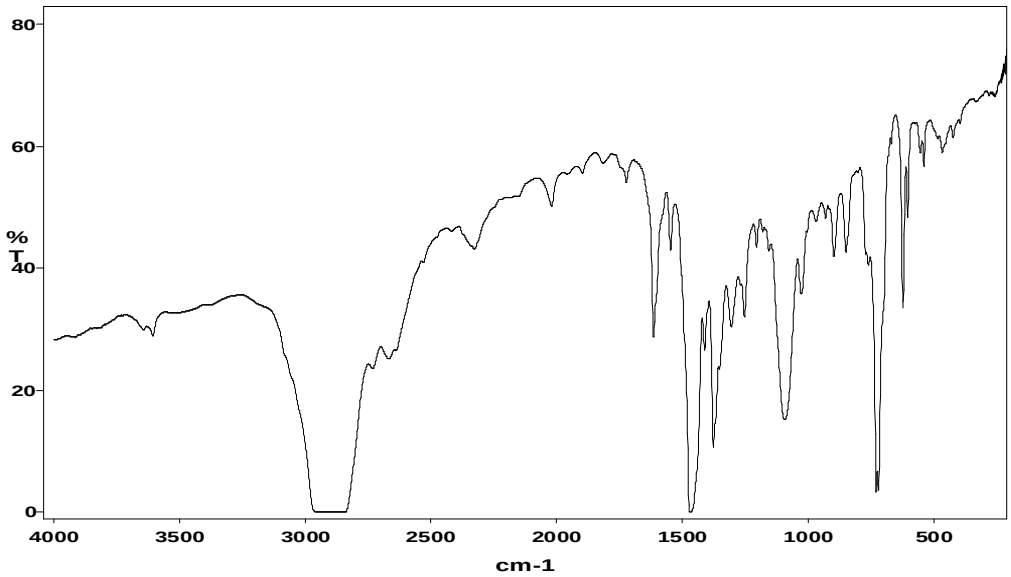
IR (cm^{-1}): ν(Cl−O): 623, 1093.

Elemental analysis (%):	C, 62.42	H, 5.71	N, 3.81
Calcd for $C_{76}H_{80}Cl_2N_4O_8Pd_2$:	C, 62.47	H, 5.52	N, 3.83

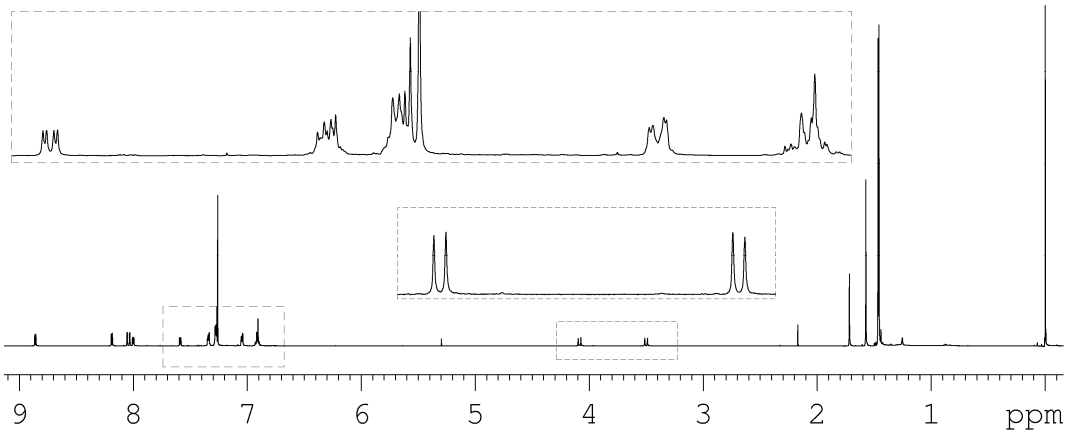
Melting point: 286 ^{o}C. **Conductivity:** Λ_M (acetone): 257 $\Omega^{-1}cm^2mol^{-1}$.

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

X-ray crystallography: Single crystals of *anti*-**18a'**·$8CH_2Cl_2$ were grown by liquid diffusion of Et_2O into a solution of **18a'** in CH_2Cl_2.

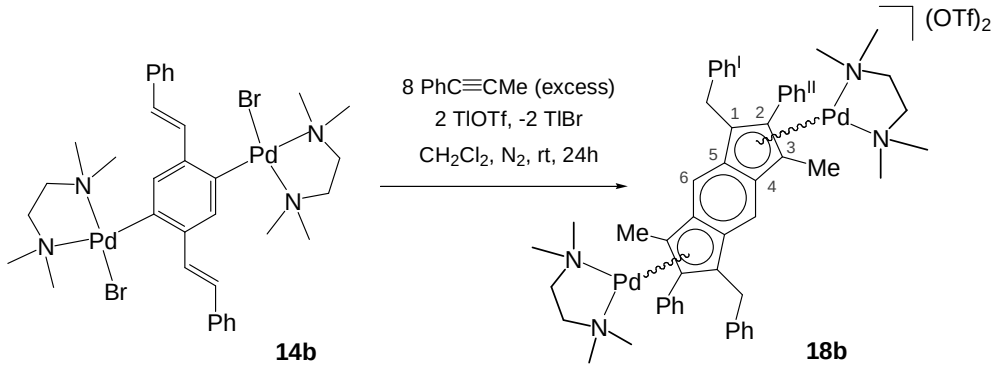


IR spectrum of 18a'



^{1}H NMR spectrum (600 MHz) of 18a'

[(μ-η,η-$C_{12}H_2Bn_2$-1,5-Ph_2-2,6-Me_2-3,7){Pd(tmeda)}$_2$](OTf)$_2$ (18b)



PhC≡CMe (68 μL, 0.54 mmol) was added to a suspension of **14b** (60 mg, 0.067 mmol) and TlOTf (47 mg, 0.13 mmol) in CH_2Cl_2 (15 mL) under N_2. The mixture was stirred for 24 h at room temperature (color changed from yellow to greenish) and filtered over Celite. The resulting greenish solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a greenish solid which was filtered off and thoroughly washed with Et_2O (3×5 mL). Yield: 63 mg. This solid was divided into four parts, and each of them was purified by crystallization from 2 mL CH_2Cl_2 / 8 mL Et_2O, yielding green crystals of pure **18b**. Yield: 38 mg (45%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 7.49-7.45 (m, 4H, *m*-H Ph^{II}), 7.45-7.40 (m, 6H, *o*,*p*-H Ph^{II}), 7.15-7.13 (m, 6H, *p*,*m*-H Ph^{I}), 6.97-6.95 (m, 4H, *o*-H Ph^{I}), 6.90 (s, 2H, H6), 3.54 and 3.29 (AB system, $^2J_{HH}$ = 15, 4H, C*H*$_2$$Ph^{I}$), 3.35-3.24 (m, 4H, CH_2 tmeda), 3.00, 2.90, 2.82, and 2.53 (s, 6H, Me tmeda), 2.78-2.70 (m, 4H, CH_2 tmeda), 1.36 (s, 6H, Me-3).

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 138.3 (2C, C4), 136.7 (2C, C5), 135.7 (2C, *i*-C Ph^{I}), 132.4 (2C, C2), 131.6 (2C, *i*-C Ph^{II}), 130.5 (4C, *o*-CH Ph^{II}), 129.3 (4C, *m*-CH Ph^{II}), 129.1 (2C, *p*-CH Ph^{II}), 128.9 (4C, *o*-CH Ph^{I}), 128.7 (4C, *m*-CH Ph^{I}), 126.9 (2C, *p*-CH Ph^{II}), 105.6 (2C, CH6), 91.4 (2C, C3), 88.5 (2C, C1), 61.9 and 61.8 (2C, CH_2 tmeda), 52.8, 52.3, 52.2, and 51.7 (2C, Me tmeda), 31.1 (2C, *C*$H_2$$Ph^{I}$), 11.3 (2C, Me-3).

IR (cm^{-1}): ν(S=O): 1029, 1264.

Elemental analysis (%):	C, 50.32	H, 4.93	N, 4.61	S, 4.95
Calcd for $C_{54}H_{64}F_6N_4O_6Pd_2S_2$:	C, 51.64	H, 5.14	N, 4.46	S, 5.11

With respect to the deviation of the C percentage see discussion in Chapter IV.

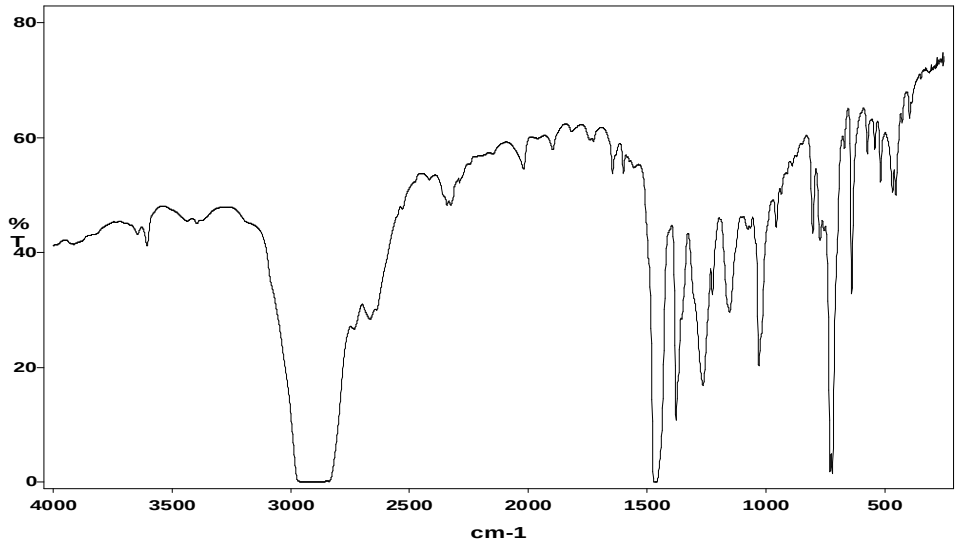
Exact Mass: HR ESI+ TOF MS: calcd for [**18b**-OTf]$^+$ ($C_{53}H_{64}F_3N_4O_3Pd_2S$) m/z 1107.2746, found 1107.2753, Δ = 0.6 ppm.

Calculated:	1104.2751 (72.36)	1105.2746 (84.75)	1106.2753 (83.61)	**1107.2746 (100)**	1108.2763 (68.38)	1109.2750 (75.92)	1110.2771 (37.53)
Found:	1104.2757 (70.49	1105.2750 (82.63)	1106.2757 (82.66)	**1107.2753 (100)**	1108.2767 (67.80)	1109.2756 (76.27)	1110.2776 (35.92)

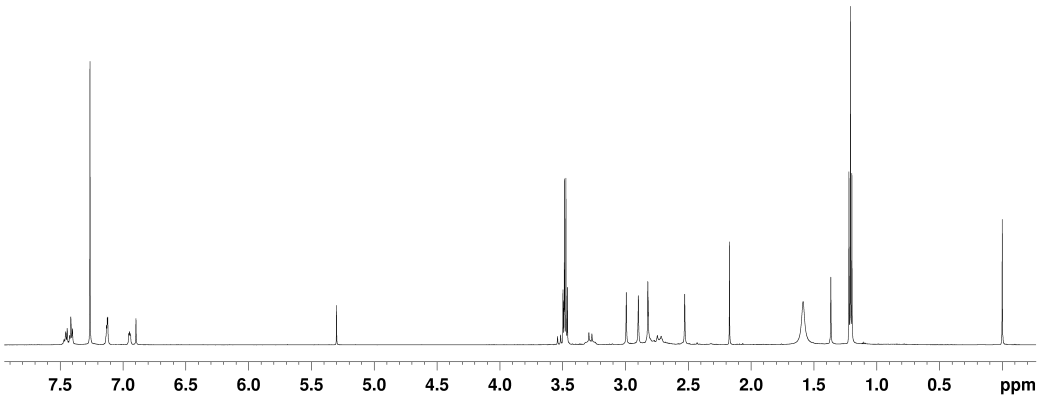
Melting point: 185 ^{o}C.

Conductivity: Λ_M (acetone): 237 $\Omega^{-1}cm^2mol^{-1}$.

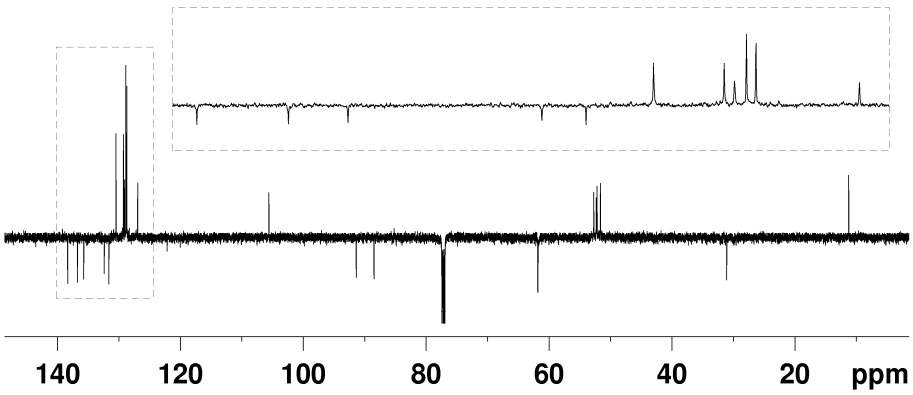
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 18b

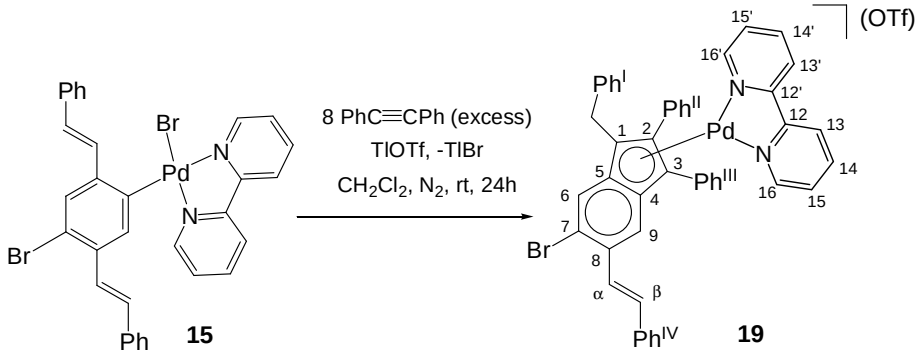


^{1}H NMR spectrum (600 MHz) of 18b



APT spectrum (150.9 MHz) of 18b

[Pd(η-C_9H_2Bn-1-Ph_2-2,3-(*E*-CH=CHPh)-5-Br-6)(bpy)](OTf) (19)



PhC≡CPh (157 mg, 0.88 mmol) was added to a suspension of **15** (80 mg, 0.11 mmol) and TlOTf (39 mg, 0.11 mmol) in CH_2Cl_2 (15 mL) under N_2. The mixture was stirred for 24 h at room temperature (color changed from yellow to brown) and filtered over Celite. The resulting brownish solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a brownish solid which was filtered off, thoroughly washed with Et_2O (3×5 mL) and dried in vacuo to give **19** as a brown solid. Yield: 73 mg (70%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 8.88 (d, $^3J_{HH}$ = 8, 1H, H13' bpy), 8.77 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 8.69 (d, $^3J_{HH}$ = 5, 1H, H16' bpy), 8.39 (t, $^3J_{HH}$ = 8, 1H, H14' bpy), 8.16 (t, $^3J_{HH}$ = 8, 1H, H14 bpy), 7.84 (t, $^3J_{HH}$ = 6, 1H, H15' bpy), 7.58 (s, 1H, H9), 7.56-7.51 (m, 5H, *o,p*-H Ph^{III}, *o*-H Ph^{IV}), 7.51 (s, 1H, H6), 7.49 (d, $^3J_{HH}$ = 5, 1H, H16 bpy), 7.38 (t, $^3J_{HH}$ = 8, 2H, *m*-H Ph^{III}), 7.36 (t, $^3J_{HH}$ = 8, 2H, *m*-H Ph^{IV}), 7.34 (d, $^3J_{HH}$ = 16, 1H, Hα), 7.34-7.27 (m, 4H, *m,p*-H Ph^{II}, *p*-H Ph^{IV}), 7.26-7.20 (m, 3H, H15 bpy, *o*-H Ph^{II}), 7.19-7.14 (m, 3H, *m,p*-H Ph^{I}), 7.01 (d, $^3J_{HH}$ = 16, 1H, Hβ), 6.98-6.95 (m, 2H, *o*-H Ph^{I}), 3.79 and 3.73 (AB system, $^2J_{HH}$ = 14, 2H, C$H_2$$Ph^{I}$).

IR (cm^{-1}): ν(S=O): 1030, 1264.

Elemental analysis (%):	C, 58.90	H, 3.65	N, 2.92	S, 3.36
Calcd for $C_{47}H_{34}BrF_3N_2O_3SPd$:	C, 59.41	H, 3.61	N, 2.95	S, 3.37

With respect to the deviation of the C percentage see discussion in Chapter IV.

Exact Mass: HR ESI+ TOF MS: calcd for [**19**-OTf]$^+$ ($C_{46}H_{34}BrN_2Pd$) m/z 801.0944, found 801.0944, Δ = 0.00 ppm.

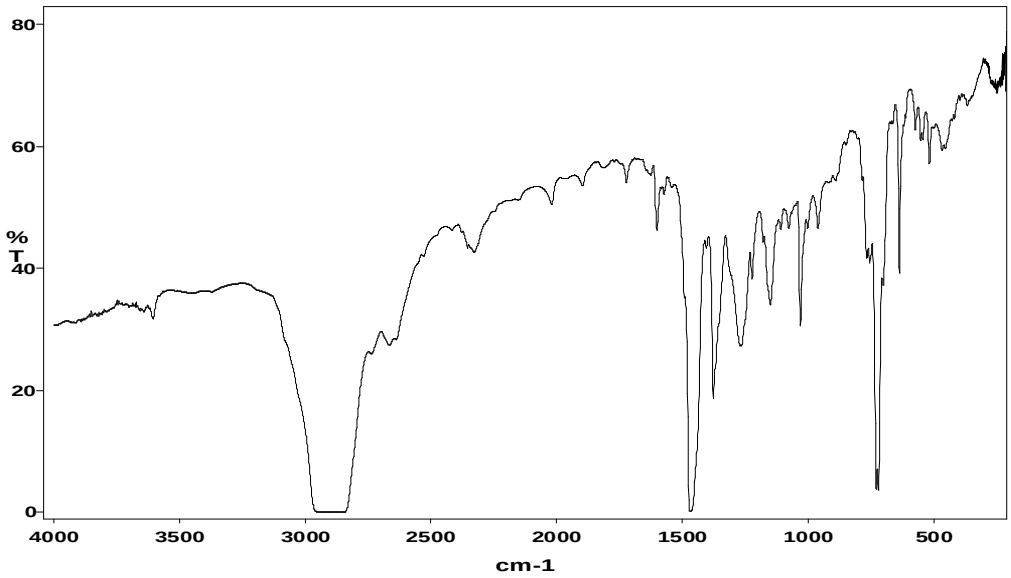
Calculated:	798.0961 (41.09)	799.095 (73.56)	800.0956 (63.69)	**801.0944 (100)**	802.097 (44.05)	803.0945 (64.43)	804.0971 (29.11)
Found:	798.0959 (38.81)	799.0952 (72.23)	800.0954 (62.72)	**801.0944 (100)**	802.0966 (42.74)	803.0947 (63.72)	804.0966 (27.07)

Melting point: 186 °C.

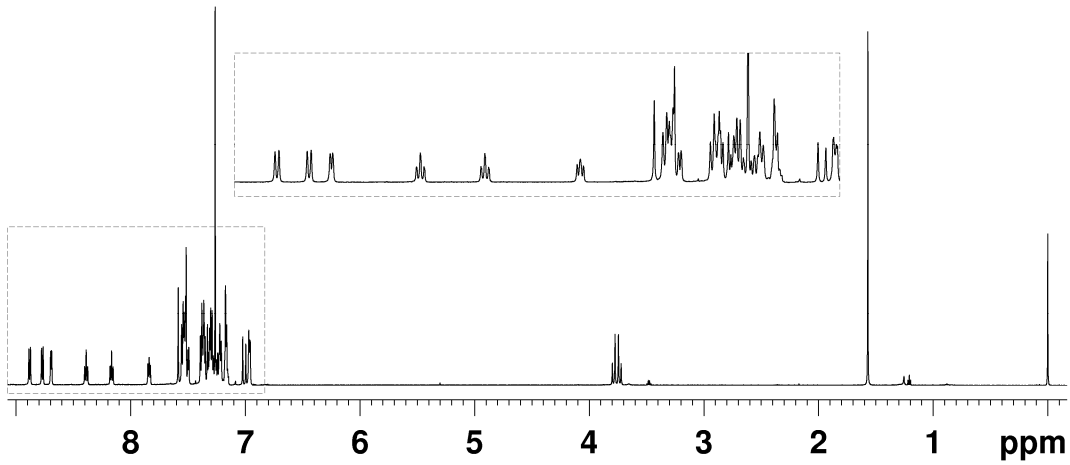
Conductivity: Λ_M (acetone): 150 $\Omega^{-1}cm^2mol^{-1}$.

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

X-ray crystallography: Single crystals of **19** were grown by liquid diffusion of Et_2O into a solution of **19** in CH_2Cl_2.

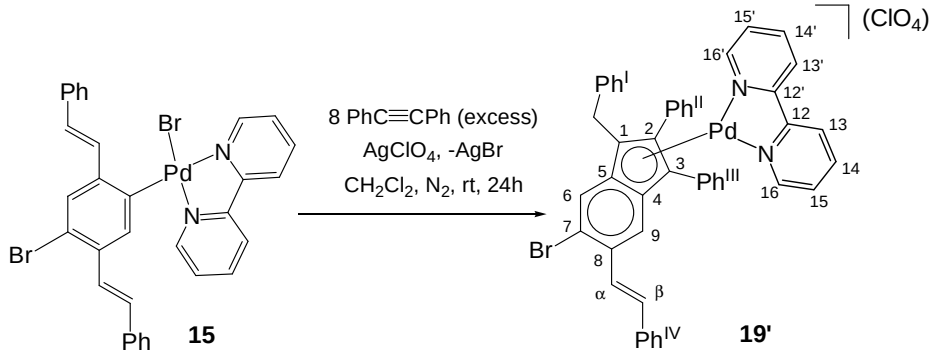


IR spectrum of 19



^{1}H NMR spectrum (600 MHz) of 19

[Pd(η-C_9H_2Bn-1-Ph_2-2,3-(*E*-CH=CHPh)-5-Br-6)(bpy)](ClO_4) (19')



PhC≡CPh (157 mg, 0.88 mmol) was added to a suspension of **15** (80 mg, 0.11 mmol) and $AgClO_4$ (23 mg, 0.11 mmol) in CH_2Cl_2 (15 mL) under N_2. The mixture was stirred for 24 h at room temperature (color changed from yellow to brown) and filtered over Celite. The resulting brownish solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a brownish solid which was filtered off, thoroughly washed with Et_2O (3×5 mL) and dried in vacuo to give **19'** as a brown solid. Yield: 58 mg (58%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 8.75 (d, $^3J_{HH}$ = 8, 1H, H13' bpy), 8.73 (d, $^3J_{HH}$ = 5, 1H, H16' bpy), 8.64 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 8.36 (t, $^3J_{HH}$ = 8, 1H, H14' bpy), 8.15 (t, $^3J_{HH}$ = 8, 1H, H14 bpy), 7.86 (t, $^3J_{HH}$ = 6, 1H, H15' bpy), 7.58 (s, 1H, H9), 7.57-7.51 (m, 5H, *o,p*-H Ph^{III}, *o*-H Ph^{IV}), 7.52 (s, 1H, H6), 7.50 (d, $^3J_{HH}$ = 5, 1H, H16 bpy), 7.38 (t, $^3J_{HH}$ = 8, 2H, *m*-H Ph^{III}), 7.36 (t, $^3J_{HH}$ = 8, 2H, *m*-H Ph^{IV}), 7.34 (d, $^3J_{HH}$ = 16, 1H, Hα), 7.34-7.27 (m, 4H, *m,p*-H Ph^{II}, *p*-H Ph^{IV}), 7.26-7.20 (m, 3H, H15 bpy, *o*-H Ph^{II}), 7.18-7.13 (m, 3H, *m,p*-H Ph^{I}), 7.01 (d, $^3J_{HH}$ = 16, 1H, Hβ), 6.99-6.95 (m, 2H, *o*-H Ph^{I}), 3.80 and 3.76 (AB system, $^2J_{HH}$ = 14, 2H, C*H*$_2$$Ph^{I}$).

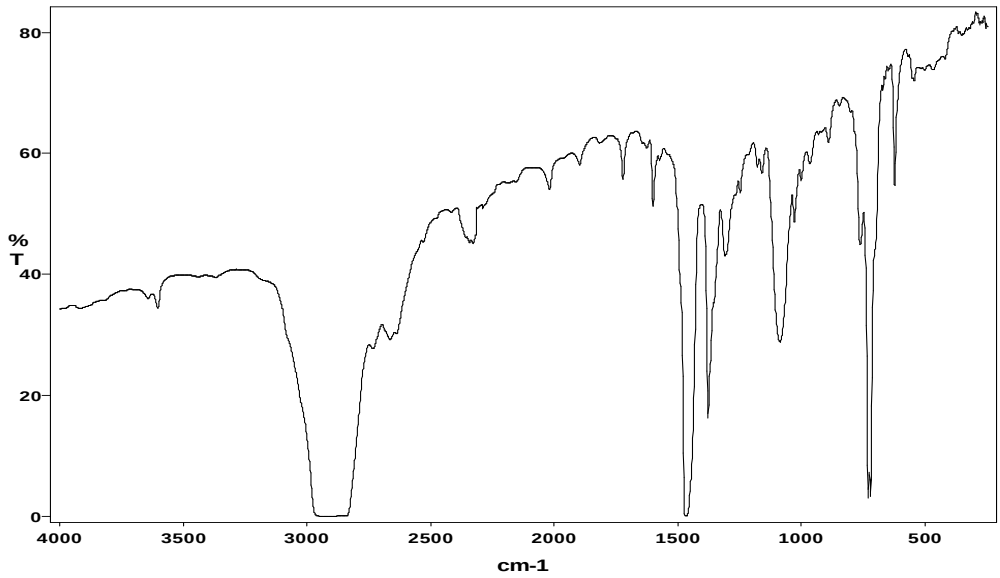
^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 154.0 (1C, C12 bpy), 153.8 (1C, C12' bpy), 152.3 (1C, CH16' bpy), 151.4 (1C, CH16 bpy), 142.2 (1C, CH14' bpy), 141.8 (1C, CH14 bpy), 137.5 (1C, C8), 136.8 (1C, *i*-C Ph^{IV}), 136.0 (1C, C5), 134.4 (1C, *i*-C Ph^{I}), 134.2 (1C, C4), 132.1 (1C, =CHβ), 131.2 (1C, C2), 131.0 (2C, *o*-CH Ph^{II}), 130.8 (1C, *i*-C Ph^{II}), 130.0 (1C, *p*-CH Ph^{III}), 129.9 (2C, *o*-CH Ph^{III}), 129.7 (2C, *m*-CH Ph^{III}), 129.7 (1C, *i*-C Ph^{III}), 129.2 (1C, *p*-CH Ph^{II}), 129.15 and 129.09 (4C, *m*-CH Ph^{I},Ph^{IV}), 129.0 (2C, *m*-CH Ph^{I}), 128.7 (1C, *p*-CH Ph^{IV}), 128.7 (2C, *o*-CH Ph^{I}), 128.3 (1C, CH15' bpy), 127.6 (1C, =CHα), 127.4 (1C, *p*-CH Ph^{I}), 127.2 (1C, CH15 bpy), 127.1 (2C, *o*-CH Ph^{IV}), 125.7 (1C, CH13' bpy), 125.1 (1C, CH13 bpy), 124.1 (1C, C7), 122.8 (1C, CH6), 114.7 (1C, CH9), 94.1 (1C, C3), 93.1 (1C, C1), 31.2 (1C, *C*$H_2$$Ph^{I}$).

IR (cm^{-1}): ν(Cl−O): 622, 1087.

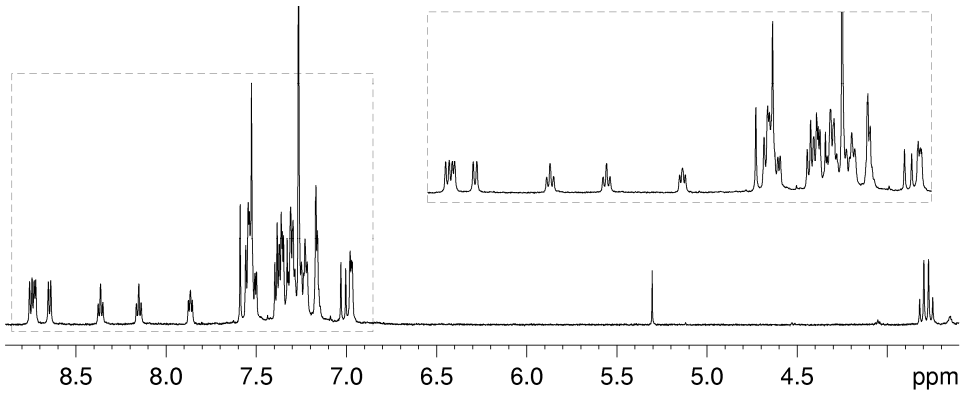
Elemental analysis (%):	C, 61.73	H, 3.77	N, 3.15
Calcd for $C_{46}H_{34}BrClN_2O_4Pd$:	C, 61.35	H, 3.81	N, 3.11

Melting point: 194 ^{o}C. **Conductivity:** Λ_M (acetone): 144 $\Omega^{-1}cm^2mol^{-1}$.

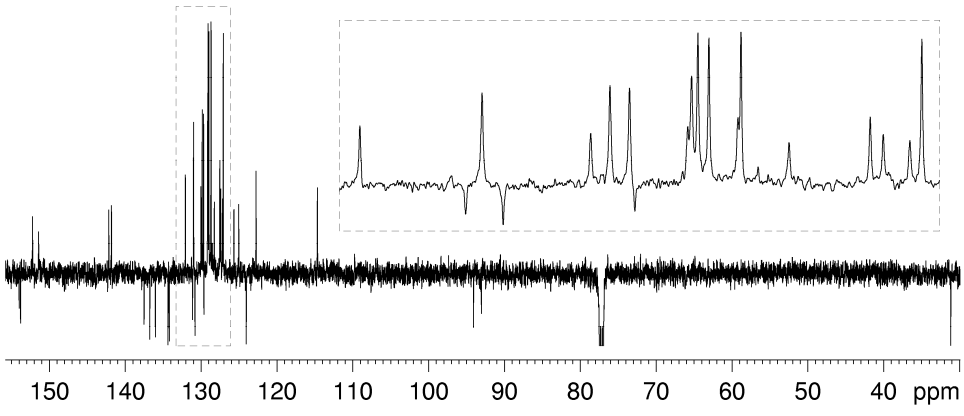
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 19'

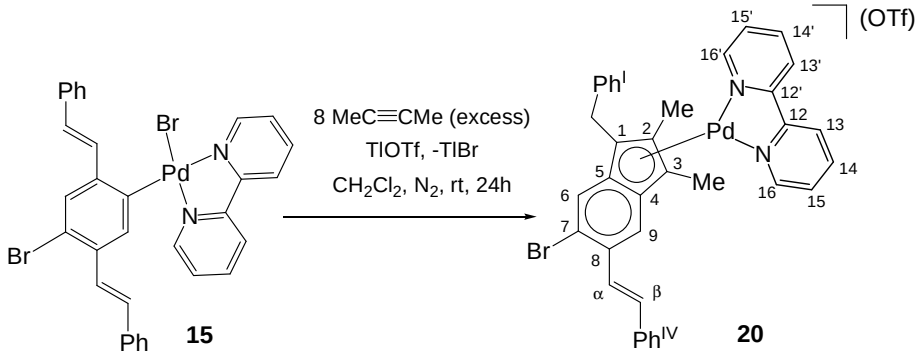


^{1}H NMR spectrum (600 MHz) of 19'



APT spectrum (150.9 MHz) of 19'

[Pd(η-C_9H_2Bn-1-Me_2-2,3-(*E*-CH=CHPh)-5-Br-6)(bpy)](OTf) (20)



MeC≡CMe (69 μL, 0.88 mmol) was added to a suspension of **15** (80 mg, 0.11 mmol) and TlOTf (39 mg, 0.11 mmol) in CH_2Cl_2 (15 mL) under N_2. The mixture was stirred for 24 h at room temperature (color changed from yellow to brown) and filtered over Celite. The resulting brownish solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a brownish solid which was filtered off, thoroughly washed with Et_2O (3×5 mL) and dried in vacuo to give **20** as a reddish brown solid. Yield: 45 mg (50%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 8.61 and 8.59 (d, $^3J_{HH}$ = 8, 1H, H13,13' bpy), 8.53 and 8.49 (d, $^3J_{HH}$ = 5, 1H, H16,16' bpy), 8.25 and 8.32 (t, $^3J_{HH}$ = 8, 1H, H14,14' bpy), 7.74 and 7.71 (t, $^3J_{HH}$ = 6, 1H, H15,15' bpy), 7.54 (d, $^3J_{HH}$ = 8, 2H, *o*-H Ph^{IV}), 7.38-7.30 (m, 7H, Ph^I, *m*-H Ph^{IV}), 7.33 (s, 1H, H9), 7.31 (d, $^3J_{HH}$ = 16, 1H, Hα), 7.28-7.24 (m, 1H, *p*-H Ph^{IV}), 7.19 (s, 1H, H6), 7.12 (d, $^3J_{HH}$ = 16, 1H, Hβ), 3.90 and 3.53 (AB system, $^2J_{HH}$ = 14, 2H, CH_2Ph^I), 2.42 (s, 3H, Me-2), 1.82 (s, 3H, Me-3).

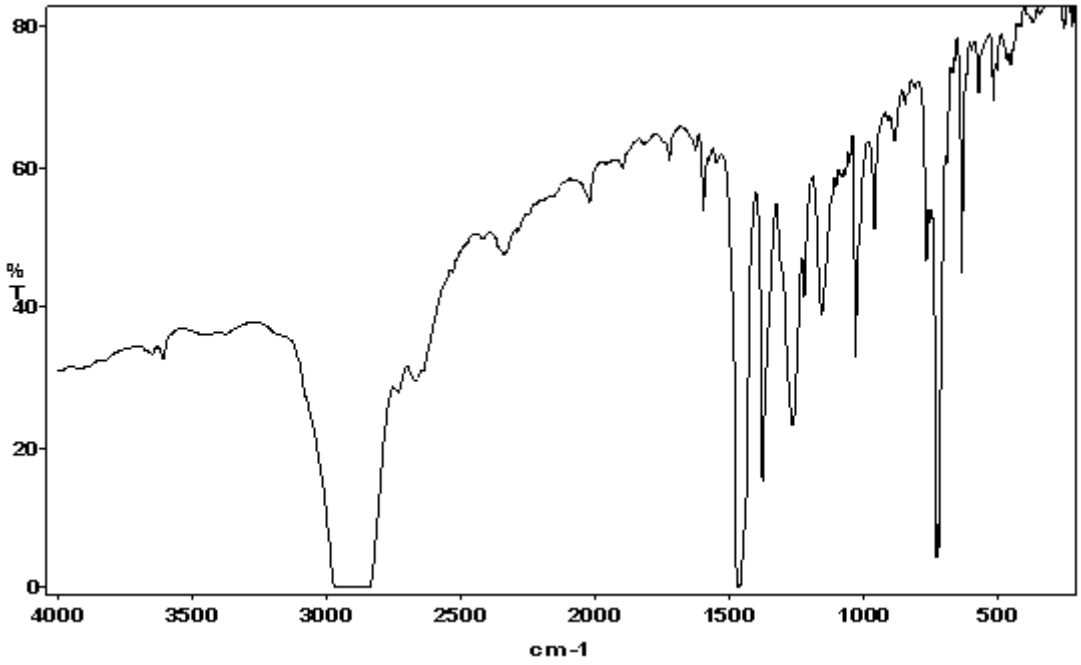
^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 153.7 and 153.5 (1C, C12,12' bpy), 152.1 and 151.7 (1C, CH16,16' bpy), 141.6 (2C, CH14,14' bpy), 137.6 (1C, C4), 137.4 (1C, C5), 137.0 (1C, *i*-C Ph^{IV}), 136.1 (1C, C8), 134.5 (1C, *i*-C Ph^I), 131.8 (1C, =CHβ), 129.4 (2C, *m*-CH Ph^I), 129.0 (2C, *m*-CH Ph^{IV}), 128.5 (1C, *p*-CH Ph^{IV}), 128.3 (2C, *o*-CH Ph^I), 128.0 and 127.7 (1C, CH15,15' bpy), 127.7 (1C, *p*-CH Ph^I), 127.6 (1C, C2), 127.1 (2C, *o*-CH Ph^{IV}), 127.0 (1C, =CHα), 124.93 and 124.87 (1C, CH13,13' bpy), 124.1 (1C, C7), 120.3 (1C, CH6), 113.6 (1C, CH9), 91.3 (1C, C3), 90.1 (1C, C1), 31.4 (1C, CH_2Ph^I), 13.2 (1C, Me-2), 10.8 (1C, Me-3).

IR (cm^{-1}): ν(S=O): 1029, 1263.

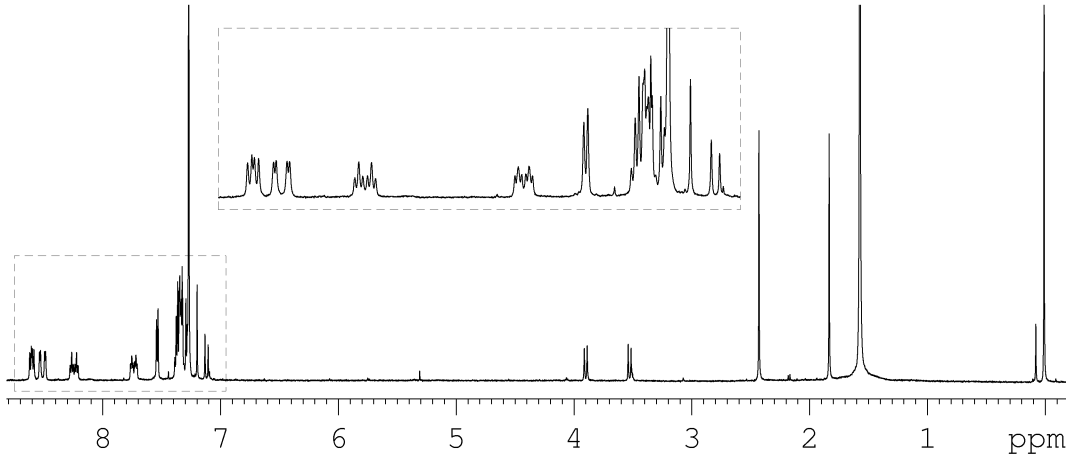
Elemental analysis (%):	C, 53.52	H, 3.94	N, 3.48	S, 3.59
Calcd for $C_{37}H_{30}BrF_3N_2O_3PdS$:	C, 53.80	H, 3.66	N, 3.39	S, 3.88

Melting point: 208 °C. **Conductivity:** Λ_M (acetone): 154 $\Omega^{-1}cm^2mol^{-1}$.

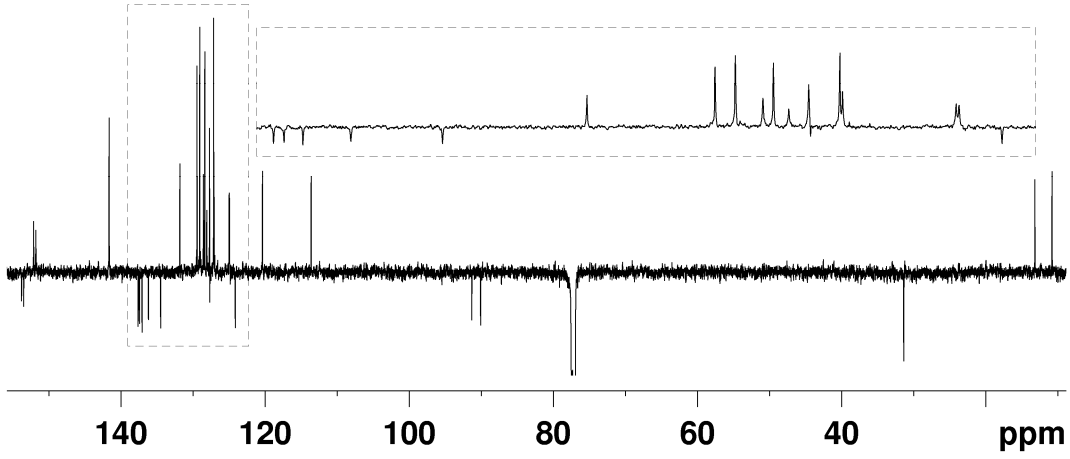
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 20

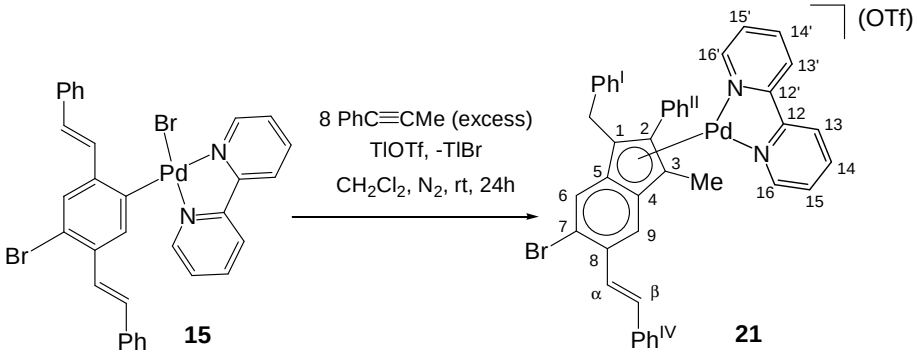


^{1}H NMR spectrum (600 MHz) of 20



APT spectrum (150.9 MHz) of 20

[Pd(η-C_9H_2Bn-1-Ph-2-Me-3-(*E*-CH=CHPh)-5-Br-6)(bpy)](OTf) (21)



PhC≡CMe (110 μL, 0.88 mmol) was added to a suspension of **15** (80 mg, 0.11 mmol) and TlOTf (39 mg, 0.11 mmol) in CH_2Cl_2 (15 mL) under N_2. The mixture was stirred for 24 h at room temperature (color changed from yellow to brown) and filtered over Celite. The resulting brownish solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a brownish solid which was filtered off, thoroughly washed with Et_2O (3×5 mL) and dried in vacuo to give **21** as a brown solid. Yield: 79 mg (81%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 8.77 (d, $^3J_{HH}$ = 8, 1H, H13' bpy), 8.72 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 8.59 (dd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H16' bpy), 8.41 (d, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H16 bpy), 8.33 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1, 1H, H14' bpy), 8.25 (td, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1, 1H, H14 bpy), 7.74 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H15' bpy), 7.69 (ddd, $^3J_{HH}$ = 8, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H15 bpy), 7.55-7.52 (m, 2H, *o*-H Ph^{IV}), 7.42 (s, 1H, H9), 7.39 (s, 5H, Ph^{II}), 7.35 (t, $^3J_{HH}$ = 8, 2H, *m*-H Ph^{IV}), 7.33 (d, $^3J_{HH}$ = 16, 1H, =CHα), 7.31 (s, 1H, H6), 7.30-7.28 (m, 1H, *p*-H Ph^{IV}), 7.22-7.19 (m, 3H, *m,p*-H Ph^{I}), 7.14 (d, $^3J_{HH}$ = 16, 1H, =CHβ), 7.00-6.98 (m, 2H, *o*-H Ph^{I}), 3.72 and 3.53 (AB system, $^2J_{HH}$ = 14, 2H, CH_2Ph^{I}), 1.76 (s, 3H, Me-3).

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 154.0 (1C, C12' bpy), 153.6 (1C, C12 bpy), 151.8 (1C, CH16' bpy), 151.4 (1C, CH16 bpy), 142.0 (1C, CH14' bpy), 141.9 (1C, CH14 bpy), 137.0 (1C, *i*-C Ph^{IV}), 136.9 (1C, C4), 136.9 (1C, C8), 136.4 (1C, C5), 134.7 (1C, *i*-C Ph^{I}), 132.2 (1C, =CHβ), 132.1 (1C, C2), 130.7 (2C, *o*-CH Ph^{II}), 130.5 (1C, *i*-C Ph^{II}), 129.5 (1C, *p*-CH Ph^{II}), 129.2 (2C, *m*-CH Ph^{II}), 129.1 (4C, *m*-CH Ph^{I},Ph^{IV}), 128.6 (1C, *p*-CH Ph^{IV}), 128.5 (2C, *o*-CH Ph^{I}), 128.0 (1C, CH15 bpy), 127.8 (1C, CH15' bpy), 127.5 (1C, *p*-CH Ph^{I}), 127.1 (2C, *o*-CH Ph^{IV}), 127.0 (1C, =CHα), 125.5 (1C, CH13' bpy), 125.4 (1C, CH13 bpy), 124.7 (1C, C7), 121.3 (1C, CH6), 114.2 (1C, CH9), 92.8 (1C, C3), 90.5 (1C, C1), 31.4 (1C, *C*H_2Ph^{I}), 11.4 (1C, Me-3).

IR (cm^{-1}): ν(S=O): 1030, 1258, 1274.

Elemental analysis (%):	C, 55.79	H, 3.26	N, 3.26	S, 3.52
Calcd for $C_{42}H_{32}BrF_3N_2O_3PdS$:	C, 56.80	H, 3.63	N, 3.15	S, 3.61

With respect to the deviation of the C percentage see discussion in Chapter IV.

Exact Mass: HR ESI+ TOF MS: calcd for [**21**-OTf]$^+$ ($C_{41}H_{32}BrN_2Pd$) m/z 739.0785, found 739.0773, Δ = 1.6 ppm.

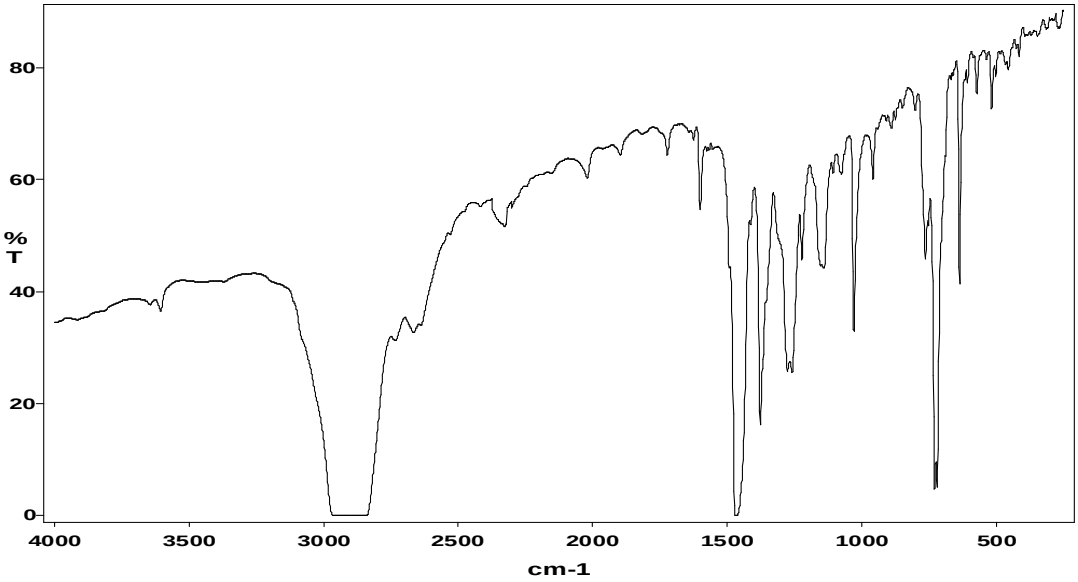
Calculated:	736.0804 (41.51)	737.0792 (73.82)	738.0798 (61.83)	**739.0785 (100)**	740.0813 (40.07)	741.0786 (64.35)	742.0813 (26.57)
Found:	736.0784 (44.29)	737.0776 (75.18)	738.0781 (65.08)	**739.0773 (100)**	740.0794 (44.17)	741.0770 (68.12)	742.0794 (29.84)

Melting point: 192 ^{o}C.

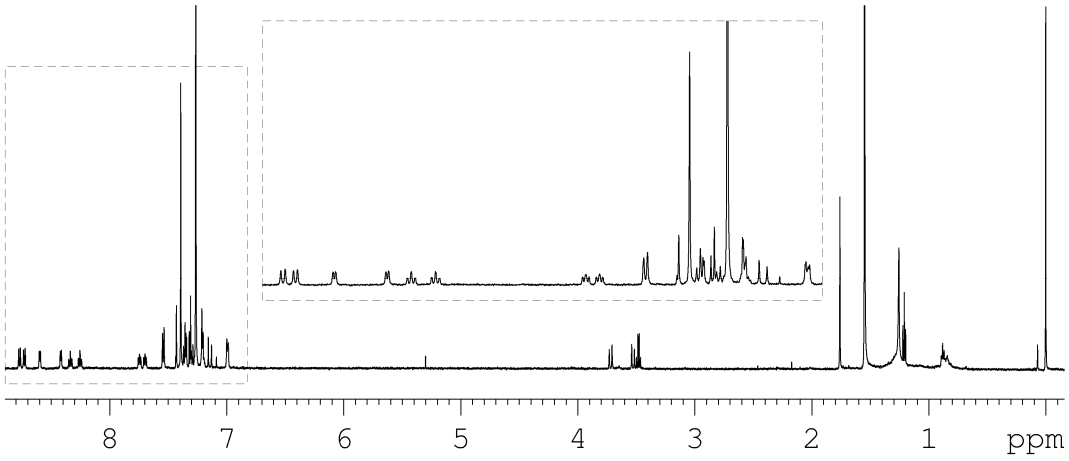
Conductivity: Λ_M (acetone): 165 $\Omega^{-1}cm^2mol^{-1}$.

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

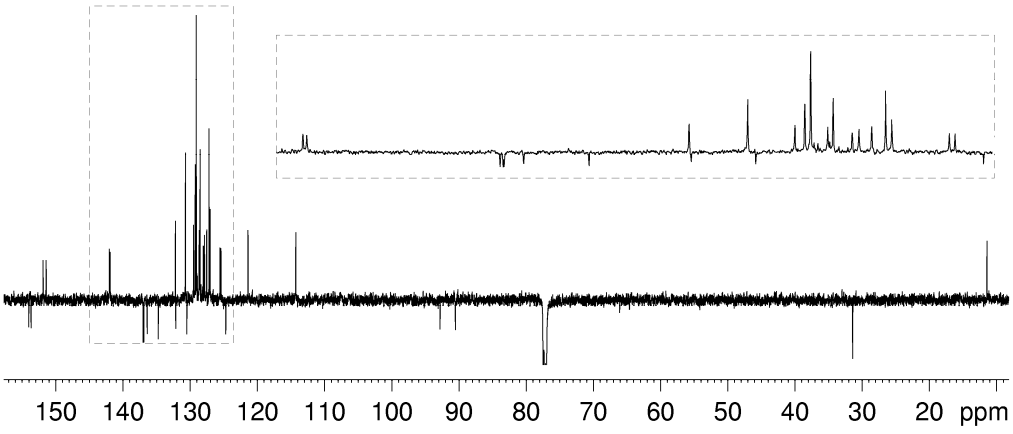
X-ray crystallography: Single crystals of **21** were grown by liquid diffusion of Et_2O into a solution of **21** in CH_2Cl_2.



IR spectrum of 21

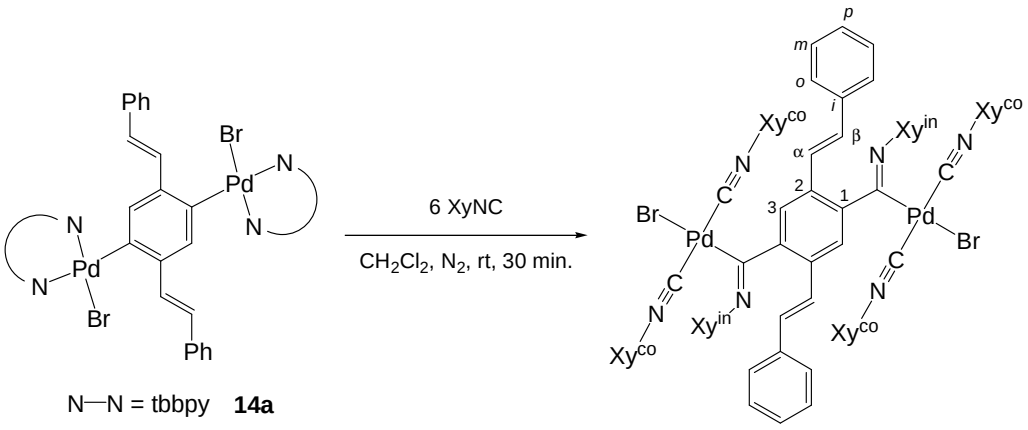


^{1}H NMR spectrum (600 MHz) of 21



APT spectrum (150.9 MHz) of 21

[C_6H_2{C(=NXy)(*trans*-PdBr(CNXy)$_2$)}$_2$-1,4-(*E*-CH=CHPh)$_2$-2,5] (22)



N—N = tbbpy **14a**

N—N = tmeda **14b**

22

XyNC (89 mg, 0.68 mmol) was added to a solution of **14a** (131 mg, 0.11 mmol) or **14b** (100 mg, 0.11 mmol) in CH_2Cl_2 under N_2, and the resulting mixture was stirred at room temperature for 30 min. Evaporation of the solvent in vacuo and addition of Et_2O (15 mL) yielded a solid, which was filtered off, washed with Et_2O (3×5 mL), and dried in vacuo to give **22** as a yellow solid. Yield: 120 mg (76%) from **14a** and 112 mg (71%) from **14b**.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 8.24 (d, $^3J_{HH}$ = 16, 2H, Hα), 8.12 (s, 2H, H3 aryl), 7.34-7.29 (m, 4H, *o*-H Ph), 7.26-7.14 (m, 10H, *m*,*p*-H Ph, *p*-H Xy^{co}), 7.03-6.92 (m, 16H, *m*-H Xy^{co,in}, *p*-H Xy^{in}, H5), 2.33 (s, 12H, Me Xy^{in}), 2.22 (s, 24H, Me Xy^{co}).

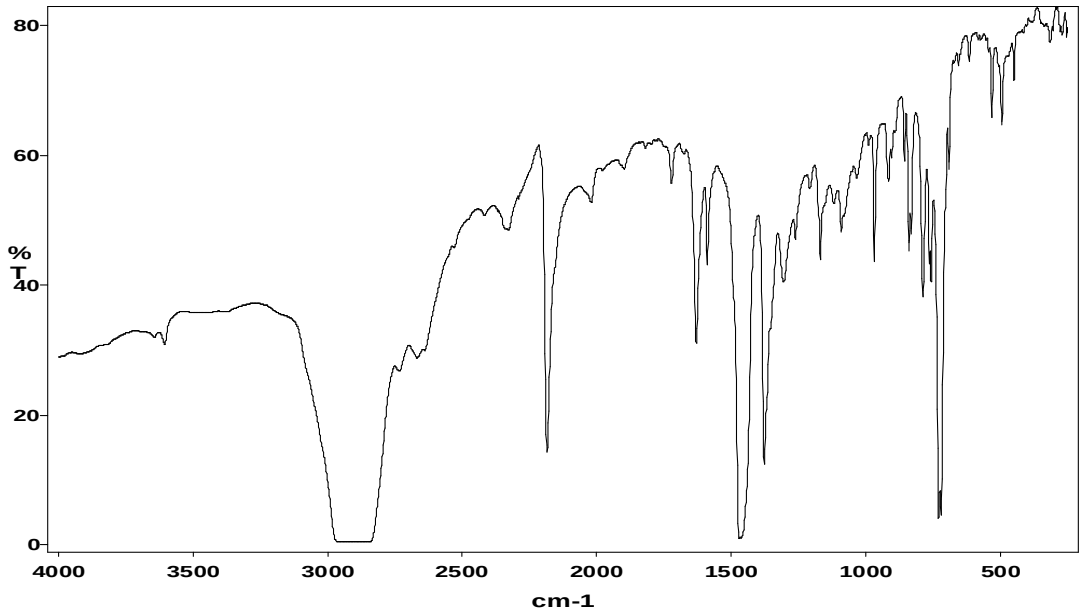
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 176.2 (2C, C=N), 150.3 (2C, *i*-C Xy^{in}), 144.2 (2C, C1 aryl), 143.3 (4C, C≡N), 137.2 (2C, *i*-C Ph), 136.0 (8C, *o*-C Xy^{co}), 131.2 (2C, C2 aryl), 131.0 (2C, =CHβ), 130.3 (4C, *p*-CH Xy^{co}), 128.7 (4C, *m*-CH Ph), 128.6 (4C, *m*-CH Xy^{in}), 128.2 (8C, *m*-CH Xy^{co}), 128.0 (2C, *p*-CH Ph), 127.1 (2C, CH3 aryl), 127.0 (4C, *o*-C Xy^{in}), 126.9 (4C, *o*-CH Ph), 126.6 (2C, =CHα), 125.5 (br, 4C, *i*-C Xy^{co}), 123.9 (2C, *p*-CH Xy^{in}), 19.6 (4C, Me Xy^{in}), 18.9 (8C, Me Xy^{co}).

IR (cm^{-1}): ν(C≡N): 2184, ν(C=N): 1629.

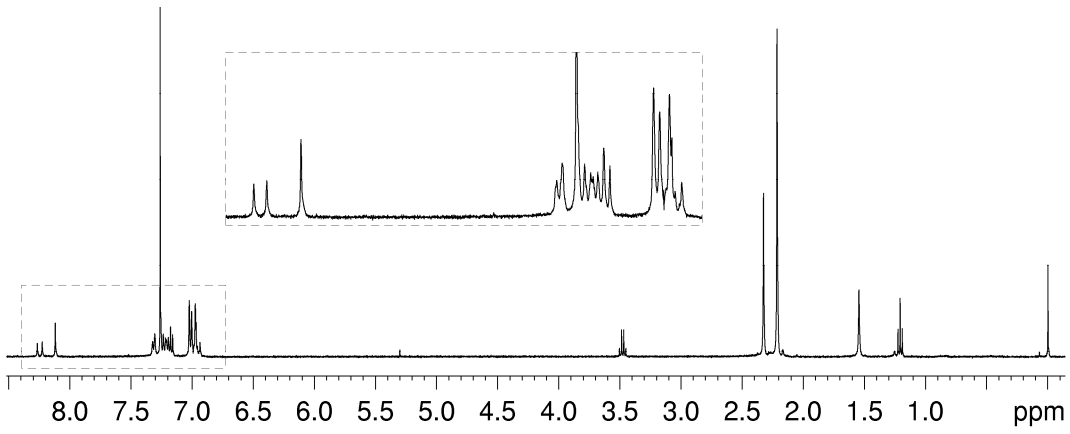
Elemental analysis (%):	C, 63.25	H, 5.12	N, 5.93
Calcd for $C_{76}H_{70}Br_2N_6Pd_2$:	C, 63.39	H, 4.90	N, 5.84

Melting point: 226 ^{o}C (dec).

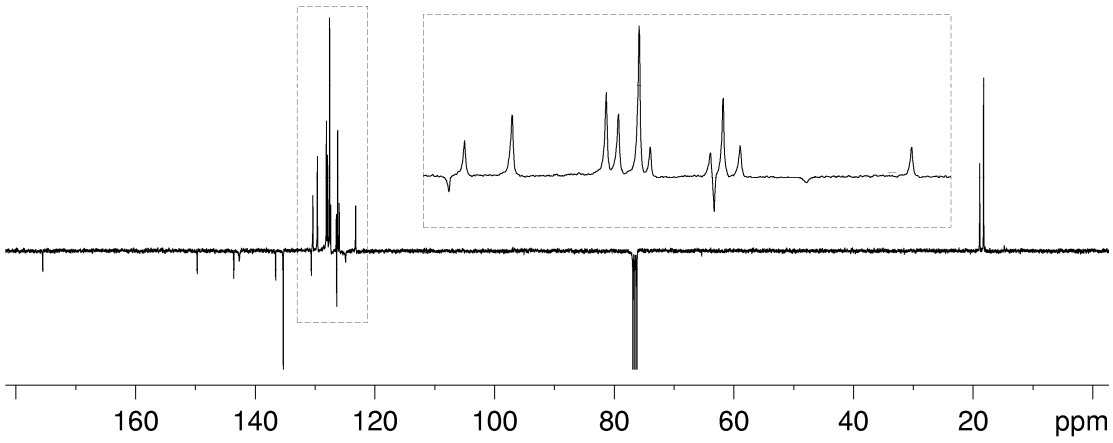
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 22

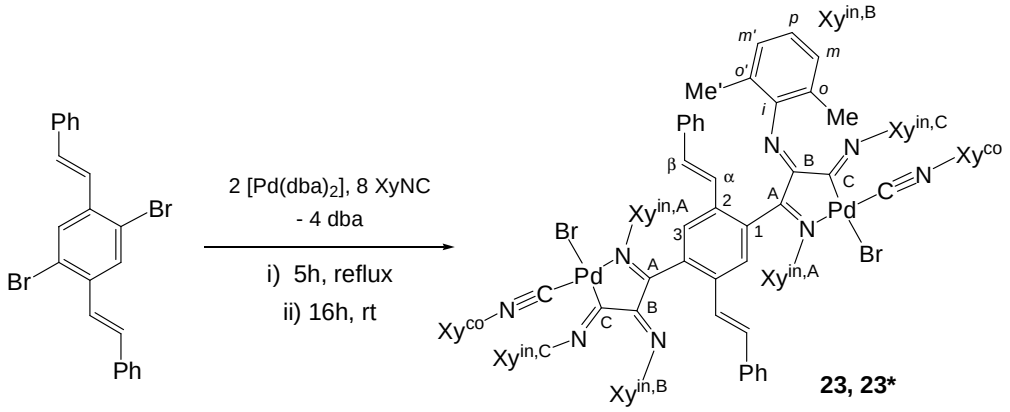


^{1}H NMR spectrum (400 MHz) of 22



APT spectrum (100.6 MHz) of 22

[C_6H_2{C(=NXy){C(=NXy)}$_2${PdBr(CNXy)}}$_2$-1,4-(*E*-CH=CHPh)$_2$-2,5] (23, 23*)



trans,*trans*-2,5-Distyryl-1,4-dibromobenzene (200 mg, 0.45 mmol) was added to a suspension of [$Pd(dba)_2$] (518 mg, 0.90 mmol) and XyNC (472 mg, 3.60 mmol) in dry degassed toluene (15 mL) under N_2. The resulting mixture was refluxed for 5 h and then stirred at room temperature for 16 h. No significant color change was observed. The mixture was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over anhydrous $MgSO_4$, and the resulting dark red solution was concentrated in vacuo to a volume of ca. 5 mL. Addition of Et_2O (15 mL) yielded a solid, which was filtered off, washed with Et_2O (3×5 mL) and dried in vacuo to give **23,23*** as a red solid. Yield: 322 mg (43%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): Major isomer (**23**), 7.50-7.47 (m, 4H, *o*-H Ph), 7.32 (s, 2H, H3 aryl), 7.25 (d, $^3J_{HH}$ = 16, 2H, Hα), 7.25-7.22 (m, 6H, *m,p*-H Ph), 7.21 (d, $^3J_{HH}$ = 7, 2H, *m*-H $Xy^{in,A}$), 7.12-7.07 (m, 4H, *p*-H Xy^{co}, *p*-H $Xy^{in,A}$), 6.98 (d, $^3J_{HH}$ = 7, 2H, *m*-H $Xy^{in,B}$), 6.95-6.84 (m, 12H, *m*-H^{co}, *m'*-H $Xy^{in,B}$, *m'*-H $Xy^{in,A}$, *m*-H $Xy^{in,C}$, *p*-H $Xy^{in,B}$), 6.67 (d, $^3J_{HH}$ = 16, 2H, Hβ), 6.40-6.34 (m, 4H, *m'*-H $Xy^{in,C}$, *p*-H $Xy^{in,C}$), 2.77 (s, 6H, Me $Xy^{in,A}$), 2.33 (s, 6H, Me $Xy^{in,B}$), 2.26 (s, 6H, Me $Xy^{in,C}$), 2.13 (s, 12H, Me Xy^{co}), 2.06 (s, 6H, Me' $Xy^{in,B}$), 1.66 (s, 6H, Me' $Xy^{in,A}$), 1.15 (s, 6H, Me' $Xy^{in,C}$). Minor isomer (**23***, only some resonances), 7.39 (s, 2H, H3 aryl), 7.07 (d, $^3J_{HH}$ = 16, 2H, Hα), 6.78 (d, $^3J_{HH}$ = 16, 2H, Hβ), 2.75 (s, 6H, Me $Xy^{in,a}$), 2.48 (s, 6H, Me $Xy^{in,c}$), 2.34 (s, 6H, Me $Xy^{in,b}$), 2.15 (s, 12H, Me Xy^{co}), 2.04 (s, 6H, Me' $Xy^{in,a}$), 1.69 (s, 6H, Me' $Xy^{in,b}$), 1.11 (s, 6H, Me' $Xy^{in,c}$).

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): Major isomer (**23**), 174.81 (2C, C^A=N), 174.75 (2C, C=N), 169.7 (2C, C=N), 151.0 (2C, *i*-C $Xy^{in,C}$), 147.8 (2C, *i*-C $Xy^{in,B}$), 143.4 (2C, *i*-C $Xy^{in,A}$), 138.3 (br, 2C, C≡N), 136.2 (2C, *i*-C Ph), 134.90 (4C, *o*-C Xy^{co}), 134.8 (2C, C2 aryl), 134.1 (2C, =CHβ), 131.93 (2C, C1 aryl), 131.5 (2C, *o*-C $Xy^{in,A}$), 129.5 (2C, *p*-CH Xy^{co}), 129.11 (2C, *p*-CH Ph), 129.08 (4C, *m*-CH Ph), 128.8 (2C, *m'*-CH

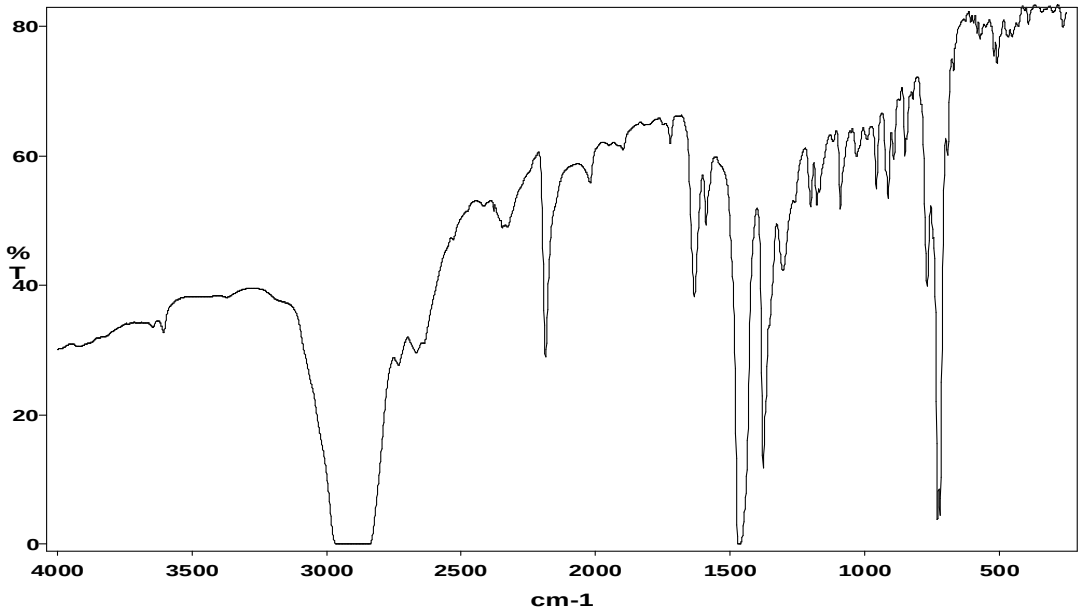
$Xy^{in,A}$), 128.39 (2C, *m*-CH $Xy^{in,C}$), 128.2 (2C, *m'*-CH $Xy^{in,B}$), 127.99 (2C, *m*-CH $Xy^{in,B}$), 127.9 (2C, *o'*-C $Xy^{in,A}$), 127.70 (4C, *m*-CH Xy^{co}), 127.68 (2C, *o'*-C $Xy^{in,C}$), 127.6 (2C, *m*-CH $Xy^{in,A}$), 127.43 (2C, *p*-CH $Xy^{in,A}$), 127.32 (4C, *o*-CH Ph), 127.21 (2C, *m'*-CH $Xy^{in,C}$), 127.18 (2C, *o'*-C $Xy^{in,B}$), 126.6 (2C, *i*-C $Xy^{in,D}$), 126.25 (2C, CH3 aryl), 125.3 (2C, *o*-C $Xy^{in,C}$), 124.33 (2C, *p*-CH $Xy^{in,B}$), 124.27 (2C, *p*-CH $Xy^{in,C}$), 123.67 (2C, =CHα), 122.0 (2C, *o*-C $Xy^{in,B}$), 20.8 (2C, Me $Xy^{in,A}$), 20.0 (2C, Me $Xy^{in,C}$), 19.1 (2C, Me $Xy^{in,B}$), 18.89 (2C, Me' $Xy^{in,B}$), 18.72 (4C, Me Xy^{co}), 18.3 (2C, Me' $Xy^{in,A}$), 17.7 (2C, Me' $Xy^{in,C}$). Minor isomer (**23***), 174.9 (2C, C=N), 174.5 (2C, C^{a}=N), 169.1 (2C, C=N), 150.8 (2C, *i*-C $Xy^{in,c}$), 147.6 (2C, *i*-C $Xy^{in,b}$), 143.3 (2C, *i*-C $Xy^{in,a}$), 136.3 (2C, *i*-C Ph), 134.91 (4C, *o*-C Xy^{co}), 134.5 (2C, C2 aryl), 133.6 (2C, =CHβ), 131.85 (2C, C1 aryl), 131.1 (2C, *o*-C $Xy^{in,a}$), 129.5 (2C, *p*-CH Xy^{co}), 129.11 (2C, *p*-CH Ph), 129.04 (4C, *m*-CH Ph), 128.9 (2C, *m'*-CH $Xy^{in,A}$), 128.43 (2C, *m*-CH $Xy^{in,C}$), 128.11 (2C, *o'*-C $Xy^{in,B}$), 128.08 (2C, *m'*-CH $Xy^{in,b}$), 128.01 (2C, *m*-CH $Xy^{in,b}$), 127.97 (2C, *o'*-C $Xy^{in,c}$), 127.8 (2C, *o'*-C $Xy^{in,a}$), 127.70 (4C, *m*-CH Xy^{co}), 127.5 (2C, *m*-CH $Xy^{in,a}$), 127.43 (2C, *p*-CH $Xy^{in,a}$),127.42 (4C, *o*-CH Ph), 127.25 (2C, *m'*-CH $Xy^{in,c}$), 126.6 (2C, *i*-C Xy^{co}), 125.79 (2C, CH3 aryl), 125.0 (2C, *o*-C $Xy^{in,c}$), 124.33 (2C, *p*-CH $Xy^{in,b}$), 124.27 (2C, *p*-CH $Xy^{in,c}$), 123.91 (2C, =CHα), 121.7 (2C, *o*-C $Xy^{in,b}$), 20.5 (2C, Me $Xy^{in,a}$), 20.4 (2C, Me $Xy^{in,c}$), 19.3 (2C, Me $Xy^{in,b}$), 18.85 (2C, Me' $Xy^{in,a}$), 18.73 (4C, Me Xy^{co}), 18.6 (2C, Me' $Xy^{in,b}$), 17.8 (2C, Me' $Xy^{in,c}$). The C≡N resonance of the minor isomer is too weak to be observed.

IR (cm^{-1}): ν(C≡N): 2186, ν(C=N): 1632 (br).

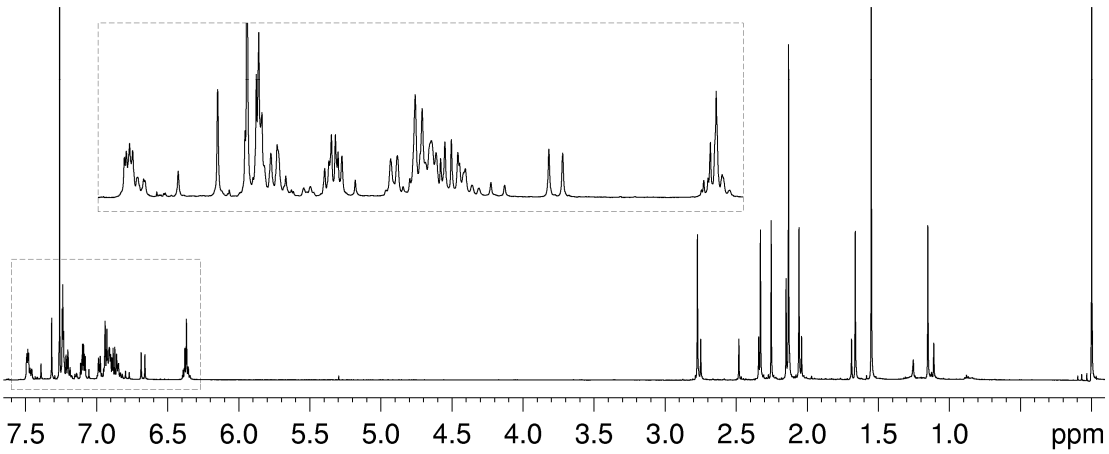
Elemental analysis (%):	C, 66.06	H, 5.33	N, 6.53
Calcd for $C_{94}H_{88}Br_2N_8Pd_2$:	C, 66.32	H, 5.21	N, 6.58

Melting point: 233 °C.

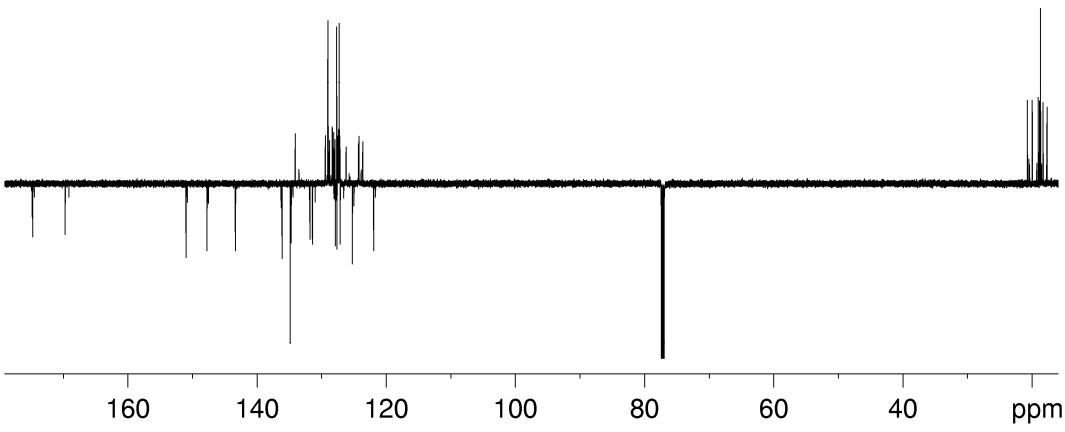
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 23,23*

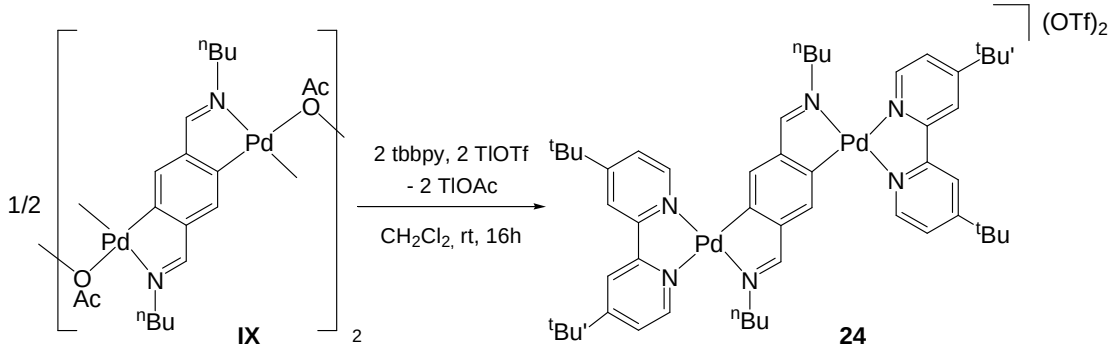


^{1}H NMR spectrum (600 MHz) of 23,23*



APT spectrum (150.9 MHz) of 23,23*

[{μ-*C1,C4,N,N”*-C_6H_2{C(H)=N(^{n}Bu)}$_2$-2,5}{Pd(tbbpy)}$_2$](OTf)$_2$ (24)



TlOTf (123 mg, 0.349 mmol) and tbbpy (93 mg, 0.349 mmol) were added to a solution of **IX** (100 mg, 0.0872 mmol) in CH_2Cl_2. The mixture was stirred for 16 h at room temperature (color changed from reddish to yellow). Then, it was filtered over Celite, and the resulting yellow solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a solid, which was filtered off, washed with Et_2O (3×5 mL), and dried in vacuo to give **24** as a yellow solid. Yield: 206 mg (92%)

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 9.08 (br s, 2H, tbbpy), 8.74 (s, 2H, HC=N), 8.57 (br s, 2H, tbbpy), 8.20-7.95 (br m, 6H, tbbpy), 7.69 (br s, 2H, tbbpy), 7.49 (s, 2H, H3 aryl), 3.92 (q, $^3J_{HH}$ = 7, 4H, CH_2 ^{n}Bu), 1.83 (quint, $^3J_{HH}$ = 7, 4H, CH_2 ^{n}Bu), 1.52 (m, 4H, CH_2 ^{n}Bu), 1.49 (s, 36H, ^{t}Bu tbbpy), 0.96 (t, $^3J_{HH}$ = 7, 6H, CH_3 ^{n}Bu).

IR (cm^{-1}): ν(C=N): 1614, ν(S=O): 1030, 1280.

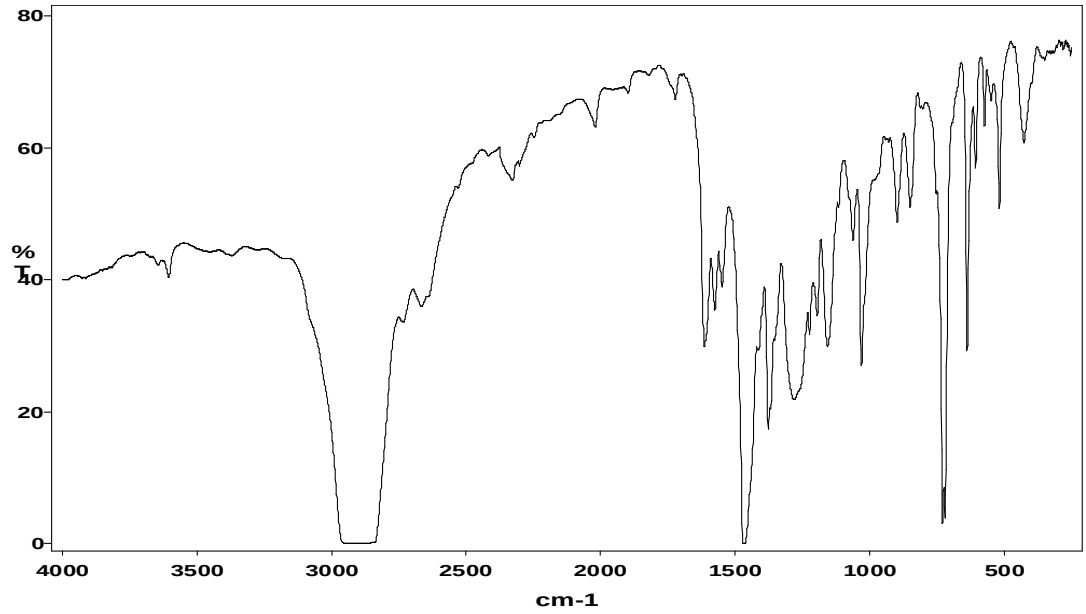
Elemental analysis (%):	C, 50.03	H, 5.58	N, 6.17	S, 4.73
Calcd for $C_{54}H_{70}F_6N_6O_6Pd_2S_2$:	C, 50.17	H, 5.22	N, 6.45	S, 4.72

Melting point: 204 ^{o}C.

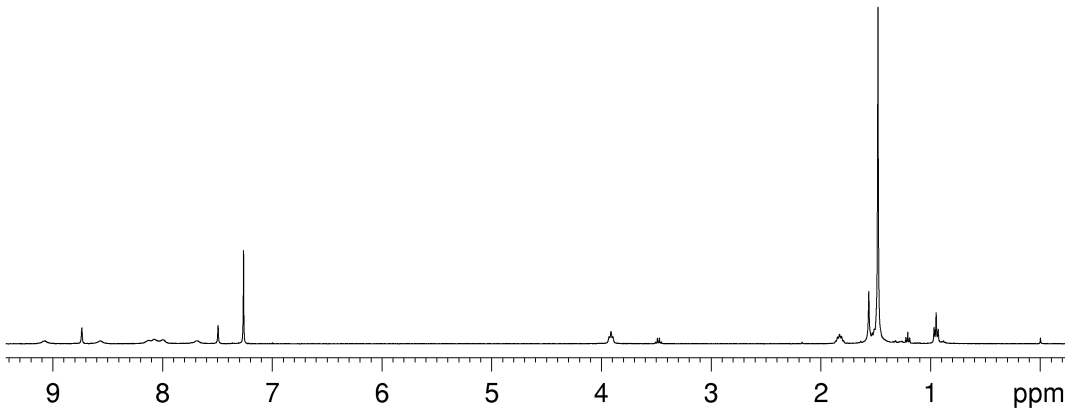
Conductivity: Λ_M (acetone): 143 $\Omega^{-1}cm^2mol^{-1}$.

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

X-ray crystallography: Single crystals of **24**·4$CHCl_3$ were grown by liquid diffusion of Et_2O into a solution of **24** in $CHCl_3$.

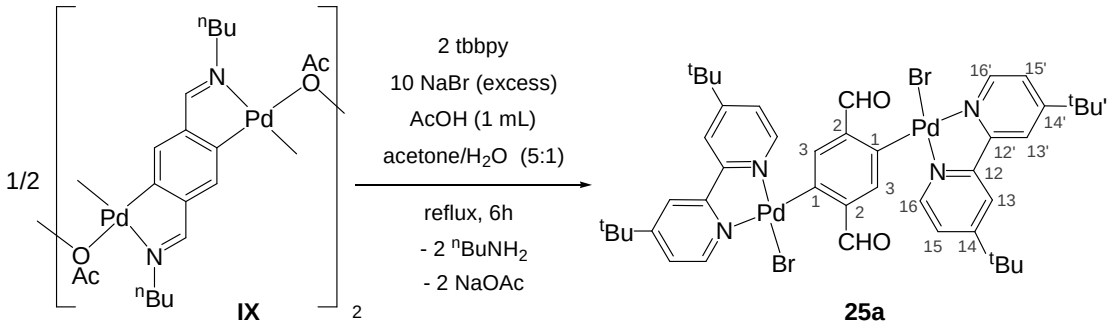


IR spectrum of 24



^{1}H NMR spectrum (400 MHz) of 24

[C_6H_2{PdBr(tbbpy)}$_2$-1,4-(CHO)$_2$-2,5] (25a)



Complex **IX** (500 mg, 0.436 mmol), NaBr (897 mg, 8.72 mmol), and AcOH (1 mL) were added to a solution of tbbpy (467 mg, 1.74 mmol) in a 72 mL mixture of acetone and water (5:1), and the resulting suspension was refluxed for 6 h. A solid formed, which was filtered off, washed with water (3×10 mL), and a small amount of acetone (2 mL). The solid was then redissolved in CH_2Cl_2 (20 mL), stirred with $MgSO_4$ for 30 min and then filtered over additional $MgSO_4$, yielding a yellow solution, which was evaporated to dryness. Et_2O (20 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **25a** as a yellow solid. Yield: 852 mg (94%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 11.10 (s, 2H, CHO), 9.31 (d, $^3J_{HH}$ = 6, 2H, H16' tbbpy), 8.12 (s, 2H, H3 aryl), 8.00 (d, $^4J_{HH}$ = 2, 2H, H13' tbbpy), 7.98 (d, $^4J_{HH}$ = 2, 2H, H13 tbbpy), 7.57 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15' tbbpy), 7.55 (d, $^3J_{HH}$ = 6, 2H, H16 tbbpy), 7.33 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15 tbbpy), 1.45 (s, 18H, ^{t}Bu' tbbpy), 1.38 (s, 18H, ^{t}Bu tbbpy).

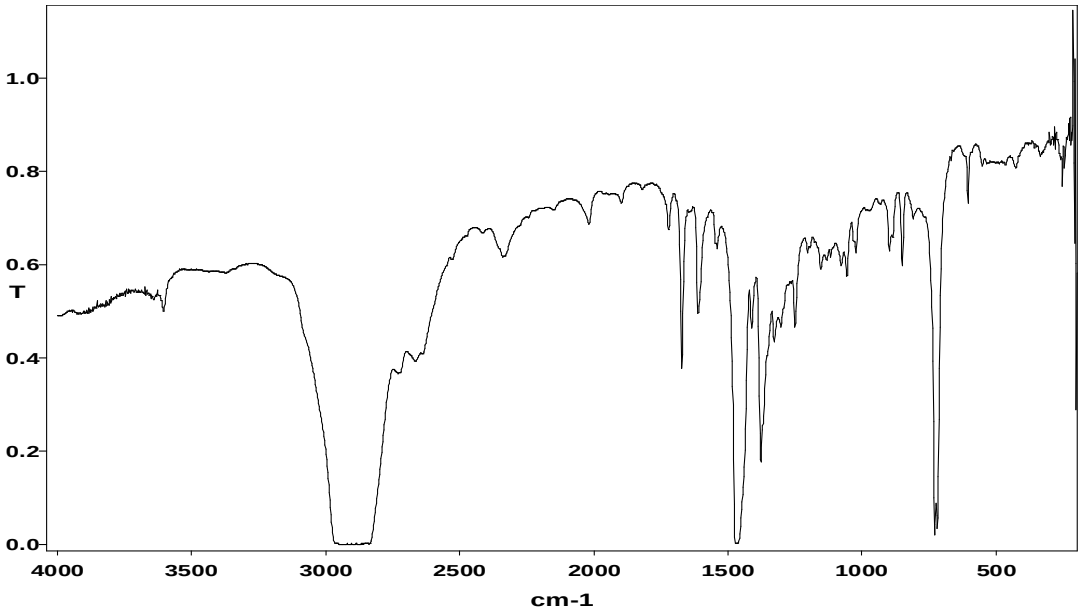
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 197.4 (2C, CHO), 163.9 (2C, C14' tbbpy), 163.7 (2C, C14 tbbpy), 156.1 (2C, C12 tbbpy), 154.1 (2C, C12' tbbpy), 152.6 (2C, C1 aryl), 151.3 (2C, CH16 tbbpy), 150.4 (2C, CH16' tbbpy), 143.9 (2C, C2 aryl), 135.8 (2C, CH3 aryl), 124.8 (2C, CH15 tbbpy), 124.0 (2C, CH15' tbbpy) 118.7 (2C, CH13 tbbpy), 118.2 (2C, CH13' tbbpy), 35.7 (4C, *C*Me$_3$ and C*Me*$_3$' tbbpy), 30.6 (6C, C*Me*$_3$' tbbpy), 30.4 (6C, C*Me*$_3$ tbbpy).

IR (cm^{-1}): ν(C=O): 1672.

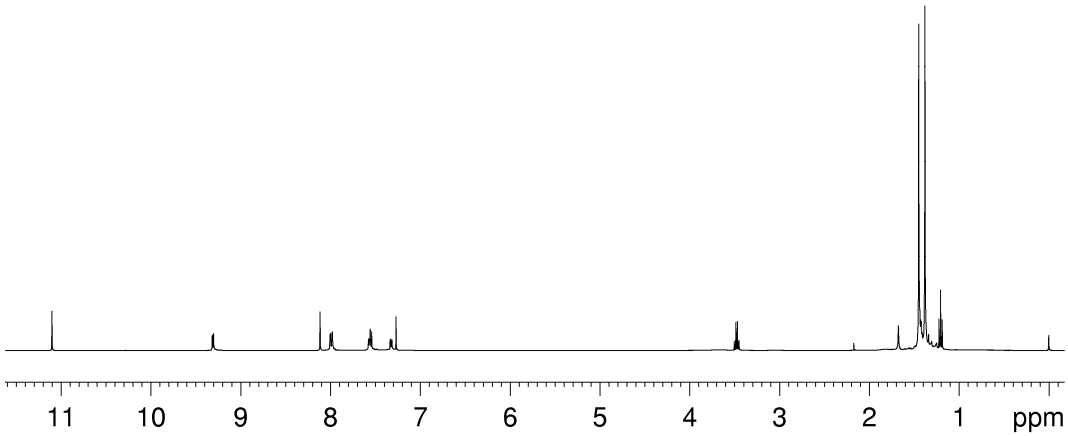
Elemental analysis (%):	C, 50.82	H, 4.79	N, 5.36
Calcd for $C_{44}H_{52}Br_2N_4O_2Pd_2$:	C, 50.74	H, 5.03	N, 5.38

Melting point: 262 ^{o}C.

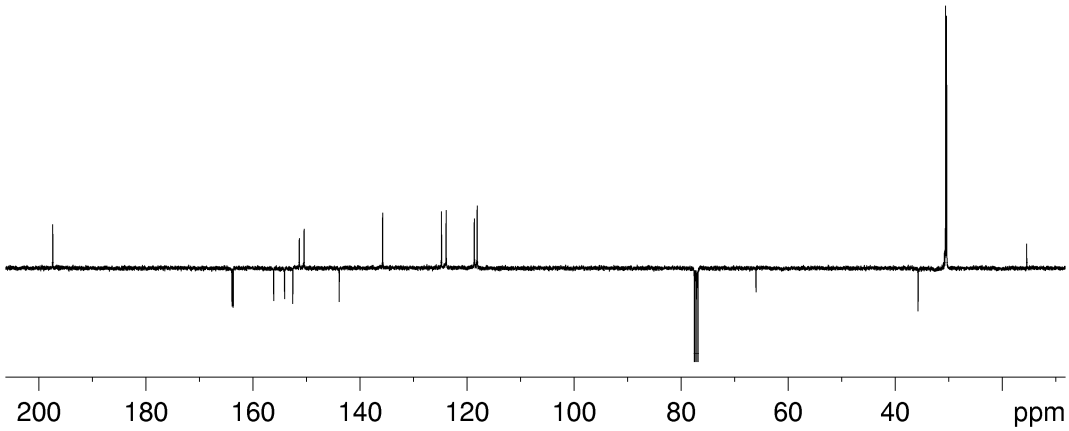
Solubility: Soluble in CH_2Cl_2 and $CHCl_3$. Low solubility in acetone. Insoluble in Et_2O and hexane.



IR spectrum of 25a

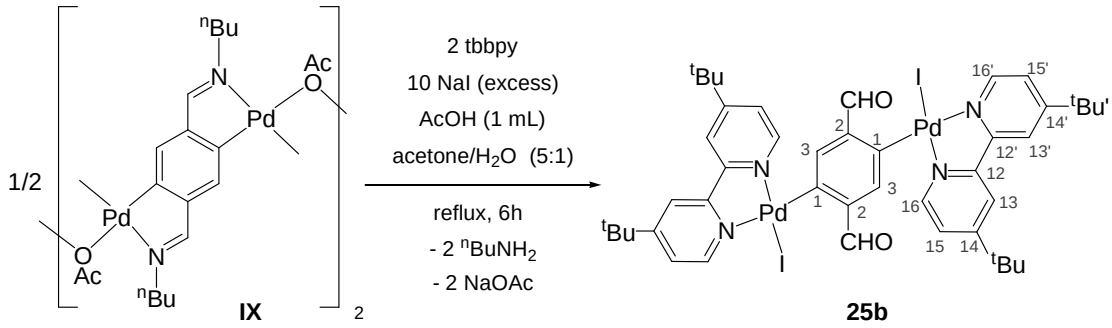


^{1}H NMR spectrum (400 MHz) of 25a



APT spectrum (100.6 MHz) of 25a

[C_6H_2{PdI(tbbpy)}$_2$-1,4-$(CHO)_2$-2,5] (25b)



Complex **IX** (500 mg, 0.44 mmol), NaI (1319 mg, 8.8 mmol) and AcOH (1 mL) were added to a solution of tbbpy (472 mg, 1.76 mmol) in a 72 mL mixture of acetone and water (5:1), and the resulting suspension was refluxed for 6 h. A solid formed, which was filtered off and washed with water (3×10 mL) and a small amount of acetone (2 mL). The solid was then redissolved in CH_2Cl_2 (20 mL), stirred with $MgSO_4$ for 30 min and then filtered over additional $MgSO_4$, yielding a yellow solution which was evaporated to dryness. Et_2O (20 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **25b** as a yellow solid. Yield: 879 mg (89%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 11.03 (s, 2H, CHO), 9.53 (d, $^3J_{HH}$ = 6, 2H, H16' tbbpy), 8.11 (s, 2H, H3 aryl), 7.99 (br s, 2H, H13' tbbpy), 7.95 (br s, 2H, H13 tbbpy), 7.54 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15' tbbpy) 7.38 (s, 4H, H15,16 tbbpy), 1.45 (s, 18H, ^{t}Bu' tbbpy), 1.39 (s, 18H, ^{t}Bu tbbpy).

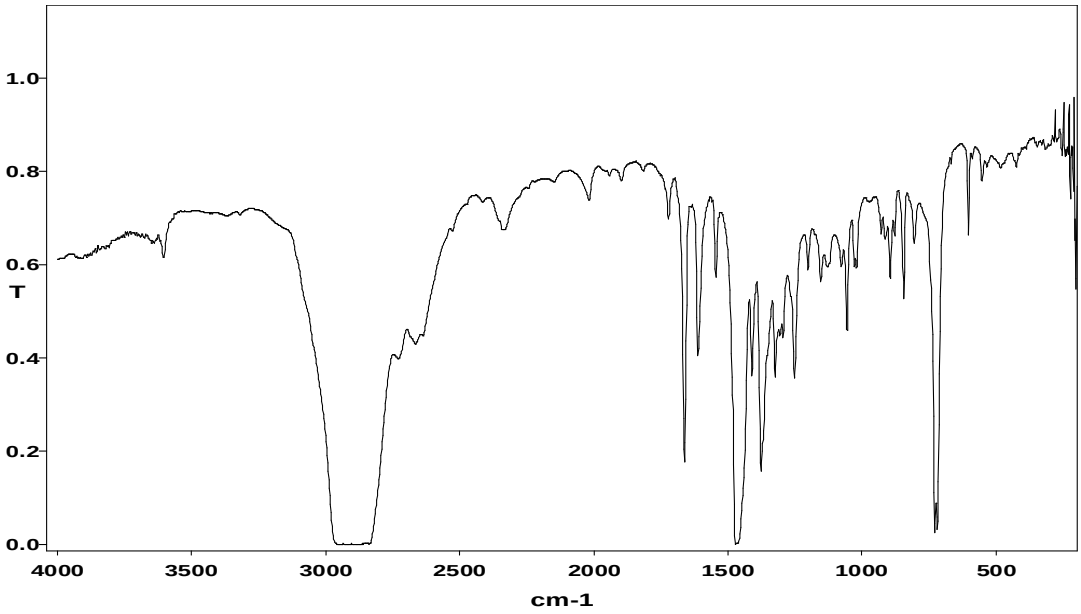
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 197.8 (2C, CHO), 163.42 and 163.37 (2C, C14,14' tbbpy), 155.7 (2C, C12 tbbpy), 154.1 (2C, C12' tbbpy) 152.6 (2C, CH16' tbbpy), 150.2 (2C, CH16 tbbpy), 149.2 (2C, C1 aryl), 143.6 (2C, C2 aryl), 136.6 (2C, CH3 aryl), 124.6 (2C, CH15 tbbpy), 124.0 (2C, CH15' tbbpy), 118.4 (2C, CH13 tbbpy), 118.1 (2C, CH13' tbbpy), 35.54 and 35.51 (2C, *C*Me$_3$ tbbpy), 30.4 (6C, C*Me*$_3$' tbbpy), 30.2 (6C, C*Me*$_3$ tbbpy).

IR (cm^{-1}): ν(C=O): 1662.

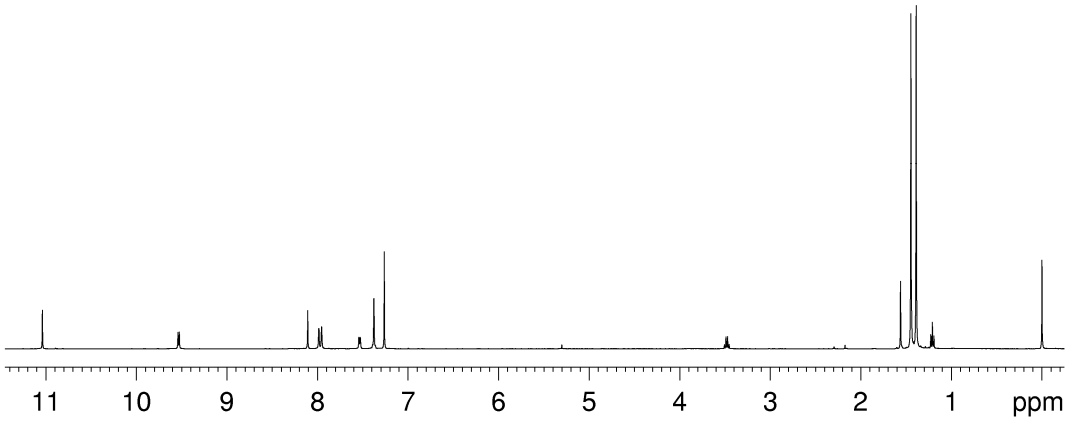
Melting point: 217 ^{o}C (dec).

Elemental analysis (%):	C, 46.59	H, 4.64	N, 5.03
Calcd for $C_{44}H_{52}I_2N_4O_2Pd_2$:	C, 46.54	H, 4.62	N, 4.93

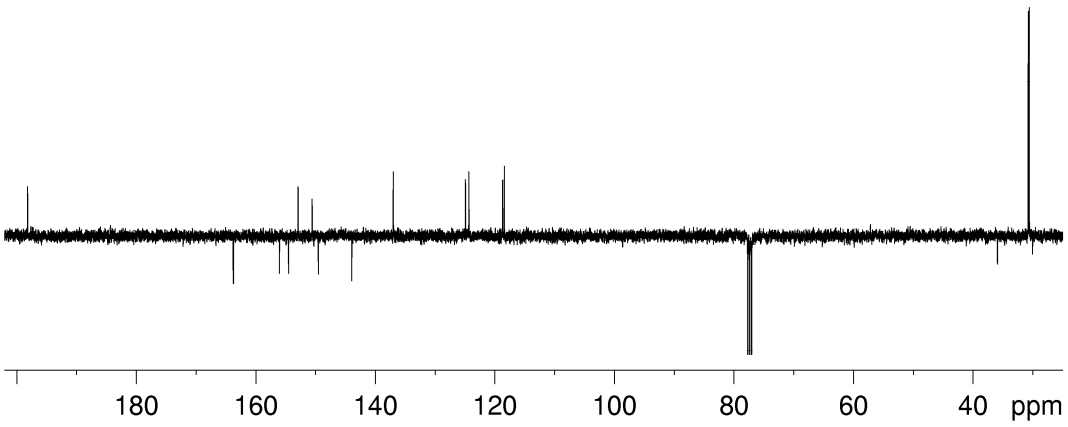
Solubility: Soluble in CH_2Cl_2 and $CHCl_3$. Low solubility in acetone. Insoluble in Et_2O and hexane.



IR spectrum of 25b

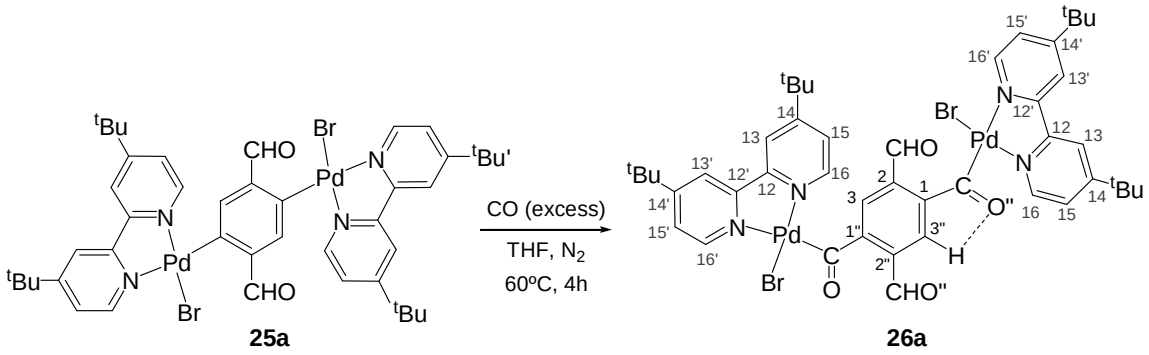


^{1}H NMR spectrum (400 MHz) of 25b



APT spectrum (100.6 MHz) of 25b

$[C_6H_2\{C(O)\{PdBr(tbbpy)\}\}_2$-1,4-$(CHO)_2$-2,5] (26a)



25a **26a**

CO was bubbled for 30 min through a solution of **25a** (100 mg, 0.08896 mmol) in THF (20 mL) under N_2, whereby the yellow color darkened. The mixture was then heated to 60°C for 4 h, in a CO atmosphere (whereby the color changed to red), and then filtered over $MgSO_4$, yielding a red solution which was evaporated to dryness. Et_2O (20 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **26a** as a pink solid. Yield: 72 mg (68%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 11.01 (s, 2H, CHO,CHO"), 9.24 (d, $^3J_{HH}$ = 6, 2H, H16' tbbpy), 8.48 (s, 1H, H3" aryl), 8.14 (s, 1H, H3 aryl), 7.96 (d, $^4J_{HH}$ = 2, 2H, H13' tbbpy), 7.95 (d, $^4J_{HH}$ = 2, 2H, H13 tbbpy), 7.78 (d, $^3J_{HH}$ = 6, 2H, H16 tbbpy), 7.53 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15' tbbpy), 7.38 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15 tbbpy), 1.44 (s, 18H, ^{t}Bu' tbbpy), 1.38 (s, 18H, ^{t}Bu tbbpy).

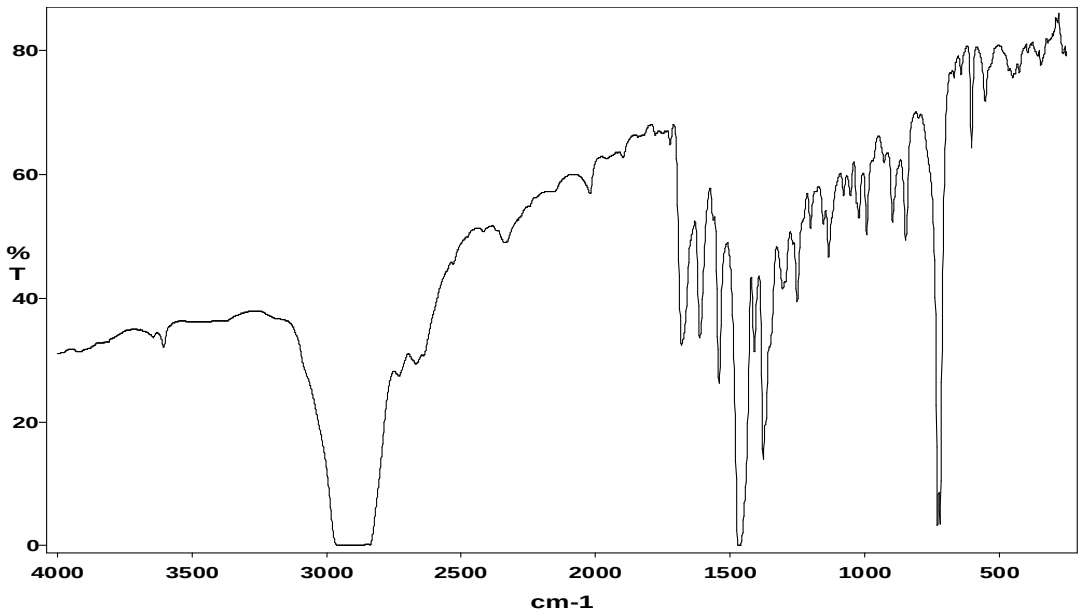
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 196.3 (2C, CHO,CHO"), 168.3 (2C, C1,1" aryl), 163.9 (2C, C14' tbbpy), 163.7 (2C, C14 tbbpy), 155.9 (2C, C12 tbbpy), 154.1 (2C, C12' tbbpy) 151.6 (2C, CH16 tbbpy), 150.3 (2C, CH16' tbbpy), 144.6 (1C, CH3" aryl), 138.7 (2C, C2,2" aryl), 128.5 (1C, CH3 aryl), 124.7 (2C, CH15 tbbpy), 123.9 (2C, CH15' tbbpy), 118.6 (2C, CH13 tbbpy) 118.1 (2C, CH13' tbbpy), 35.7 (4C, *C*Me_3 and *C*Me_3' tbbpy), 30.6 (6C, C*Me*$_3$' tbbpy), 30.4 (6C, C*Me*$_3$ tbbpy).

IR (cm^{-1}): ν(C=O): 1682 (br).

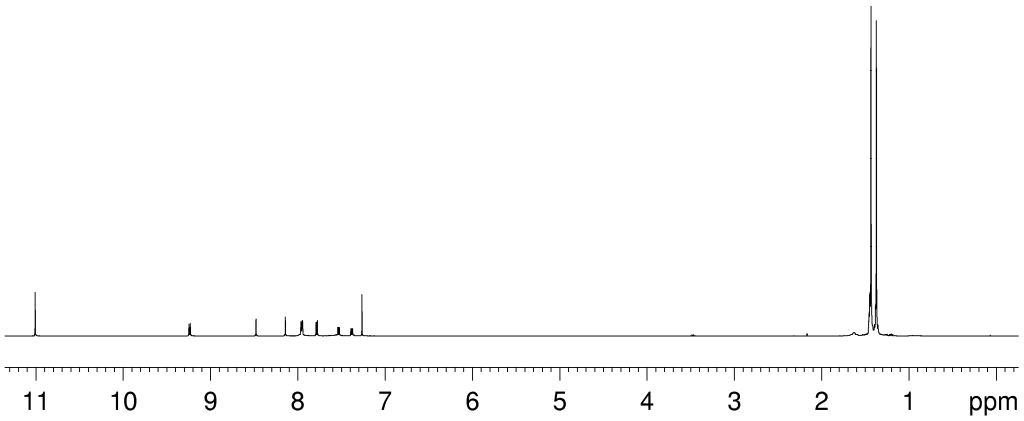
Melting point: 223°C (dec).

Elemental analysis (%):	C, 50.34	H, 4.78	N, 5.10
Calcd for $C_{46}H_{52}Br_2N_4O_4Pd_2$:	C, 50.12	H, 4.52	N, 4.93

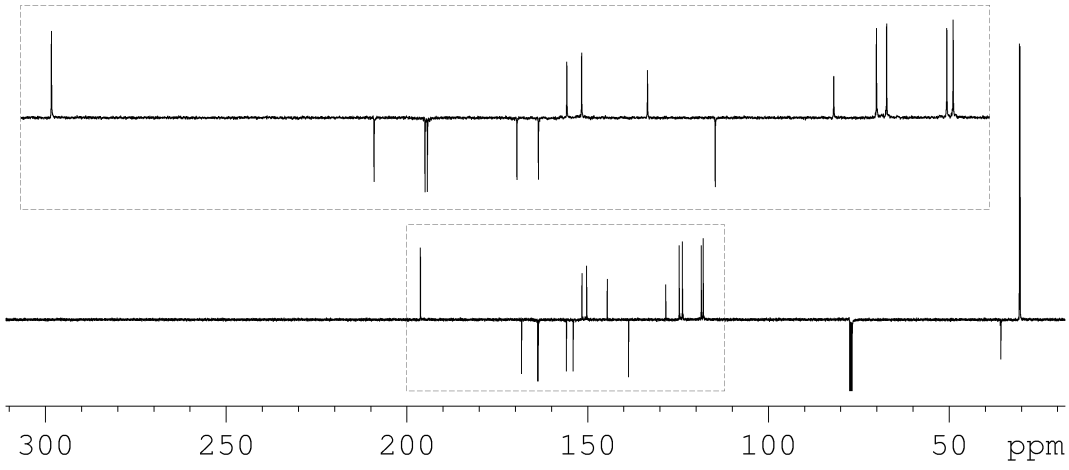
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 26a

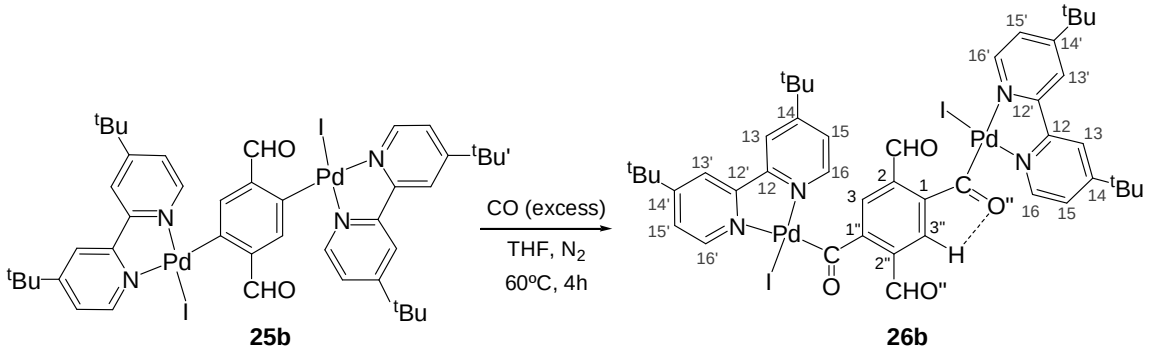


^{1}H NMR spectrum (400 MHz) of 26a



APT spectrum (100.6 MHz) of 26a

$[C_6H_2\{C(O)\{PdI(tbbpy)\}\}_2$-1,4-$(CHO)_2$-2,5] (26b)



25b **26b**

CO was bubbled for 30 min through a solution of **25b** (100 mg, 0.088 mmol) in THF (20 mL) under N_2, whereby the yellow color darkened. The mixture was then heated to 60°C for 4 h, in a CO atmosphere, and then filtered over $MgSO_4$, yielding a pink solution which was evaporated to dryness. Et_2O (20 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried in vacuo to give **26b** as a pink solid. Yield: 76 mg (73%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 10.95 (s, 2H, CHO,CHO"), 9.46 (d, $^3J_{HH}$ = 6, 2H, H16' tbbpy), 8.48 (s, 1H, H3" aryl), 8.14 (s, 1H, H3 aryl), 7.96 (d, $^4J_{HH}$ = 2, 2H, H13' tbbpy), 7.95 (d, $^4J_{HH}$ = 2, 2H, H13 tbbpy), 7.64 (d, $^3J_{HH}$ = 6, 2H, H16 tbbpy), 7.50 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15' tbbpy), 7.43 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15 tbbpy), 1.43 (s, 18H, ^{t}Bu' tbbpy), 1.38 (s, 18H, ^{t}Bu tbbpy).

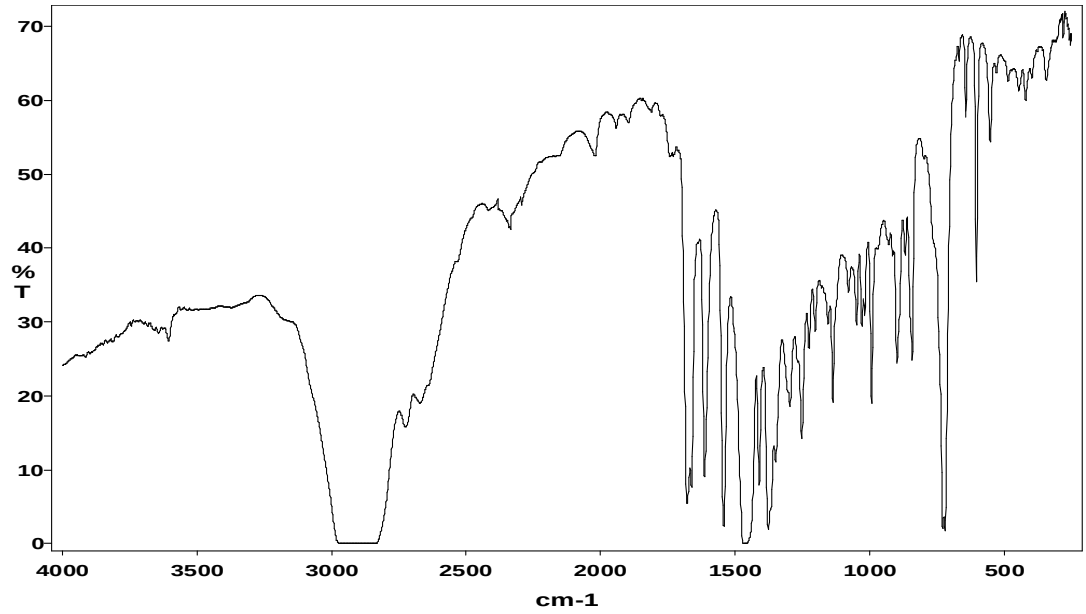
^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 196.8 (2C, CHO,CHO"), 165.8 (2C, C1,1" aryl), 163.7 (2C, C14 tbbpy), 163.6 (2C, C14' tbbpy), 155.8 (2C, C12 tbbpy), 154.4 (2C, C12' tbbpy) 152.7 (2C, CH16' tbbpy), 150.6 (2C, CH16 tbbpy), 146.5 (1C, CH3" aryl), 138.9 (2C, C2,2" aryl), 128.3 (1C, CH3 aryl), 124.7 (2C, CH15 tbbpy), 124.1 (2C, CH15' tbbpy), 118.5 (2C, CH13 tbbpy) 118.2 (2C, CH13' tbbpy), 35.8 (2C, *C*Me_3 tbbpy), 35.7 (2C, *C*Me_3' tbbpy), 30.6 (6C, C*Me*$_3$' tbbpy), 30.5 (6C, C*Me*$_3$ tbbpy).

IR (cm^{-1}): ν(C=O): 1662, 1678.

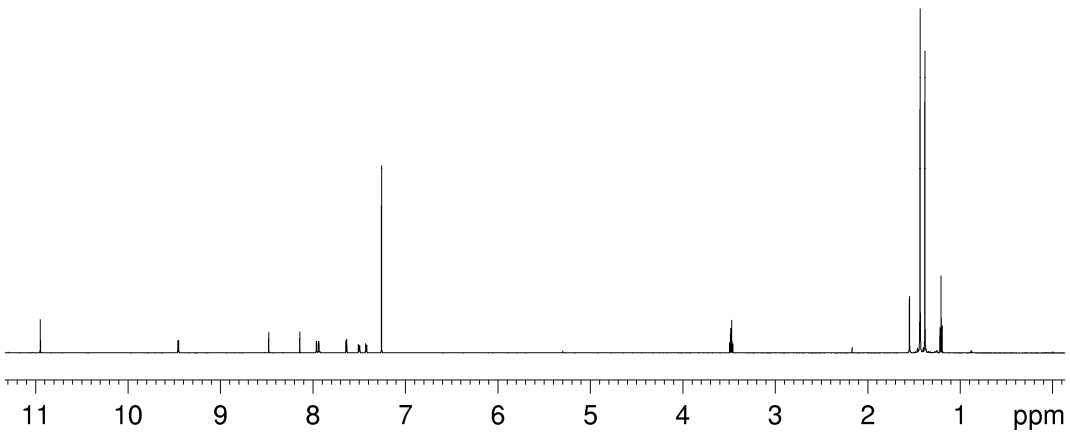
Melting point: 258 °C (dec).

Elemental analysis (%):	C, 46.69	H, 4.67	N, 4.67
Calcd for $C_{46}H_{52}I_2N_4O_4Pd_2$:	C, 46.37	H, 4.40	N, 4.70

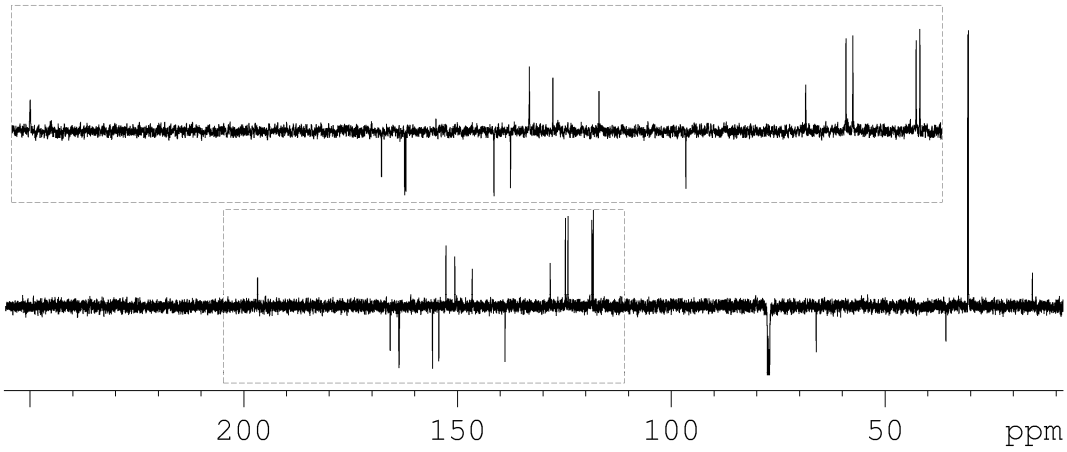
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 26b

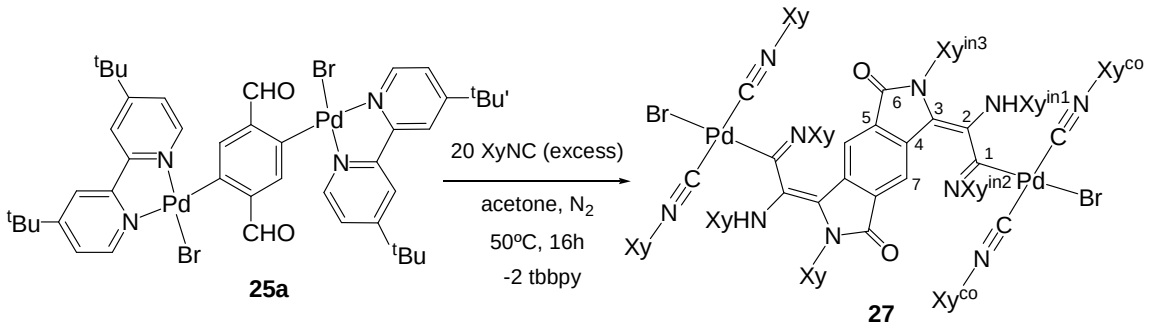


^{1}H NMR spectrum (600 MHz) of 26b



APT spectrum (150.9 MHz) of 26b

2,3,6,7-Tetrahydrobenzo[1,2-*c*:4,5-*c'*]dipyrrole-1,5-dione-2,6-dixylyl-3,7-bis{=C(NHXy)-C(=NXy)-[PdBr(CNXy)$_2$]} (27)



25a (300 mg, 0.29 mmol) was added to a solution of XyNC (760 mg, 5.8 mmol) in acetone under N_2, and the resulting mixture was stirred at 50ºC for 16h. A red solid formed, which was filtered off, washed with a small amount of acetone (2×3 mL), and dried in vacuo to give **27** as a red solid. Yield: 226 mg (43%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 8.91 (s, 2H, H7), 7.18-7.08 (m, 10H, *p*-H Xy^{in3}, *p*-H Xy^{co}, *m*-H Xy^{in3}), 6.91 (d, $^3J_{HH}$ = 8, 8H, *m*-H Xy^{co}), 6.84 (d, $^3J_{HH}$ = 8, 4H, *m*-H Xy^{in2}), 6.83 (d, $^3J_{HH}$ = 8, 4H, *m*-H Xy^{in1}), 6.64 (t, $^3J_{HH}$ = 8, 2H, *p*-H Xy^{in2}), 6.60 (t, $^3J_{HH}$ = 8, 2H, *p*-H Xy^{in1}), 5.57 (s, 2H, NH), 2.62 (s, 12H, Me Xy^{in1}), 2.49 (s, 12H, Me Xy^{in2}), 2.20 (s, 12H, Me Xy^{in3}), 2.06 (s, 24H, Me Xy^{co}).

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 167.4 (2C, C=N), 165.8 (2C, C=O), 149.1 (2C, *i*-C Xy^{in1}), 142.8 (2C, C≡N), 138.8 (2C, C2), 138.7 (2C, *i*-C Xy^{in2}), 137.2 (2C, *i*-C Xy^{in3}), 137.0 (4C, *o*-C Xy^{in3}), 136.0 (8C, *o*-C Xy^{co}), 134.57 (4C, *o*-C Xy^{in2}), 134.59 and 130.2 (2C, C4 and C5), 130.0 (4C, *p*-CH Xy^{co}), 129.7 (2C, *p*-CH Xy^{in3}), 129.5 (4C, *o*-C Xy^{in1}), 129.29 (4C, *m*-CH Xy^{in1}), 129.26 (4C, *m*-CH Xy^{in3}), 128.9 (4C, *m*-CH Xy^{in2}), 128.0 (8C, *m*-CH Xy^{co}), 125.9 (2C, *p*-CH Xy^{in2}), 125.6 (4C, *i*-C Xy^{co}), 124.6 (2C, *p*-CH Xy^{in1}), 119.4 (2C, CH7), 112.2 (2C, C3), 21.5 (4C, Me Xy^{in1}), 20.6 (4C, Me Xy^{in2}), 19.1 (8C, Me Xy^{co}), 18.3 (4C, Me Xy^{in3}).

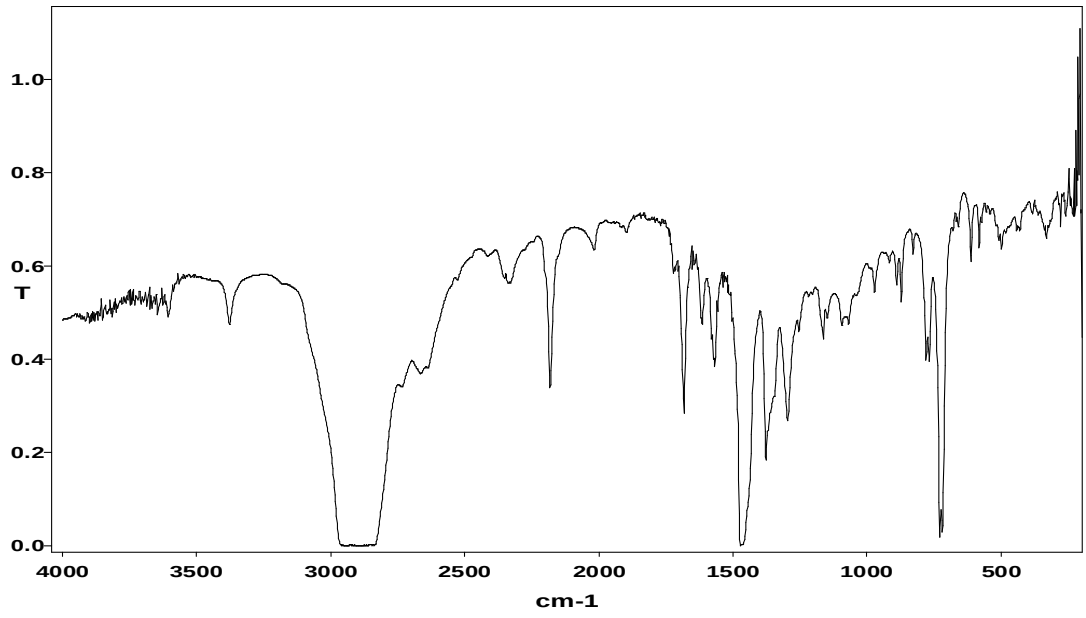
IR (cm^{-1}): ν(N-H): 3376, ν(C≡N): 2182, ν(C=O): 1682, ν(C=N): 1614

Melting point: 217 ^{o}C.

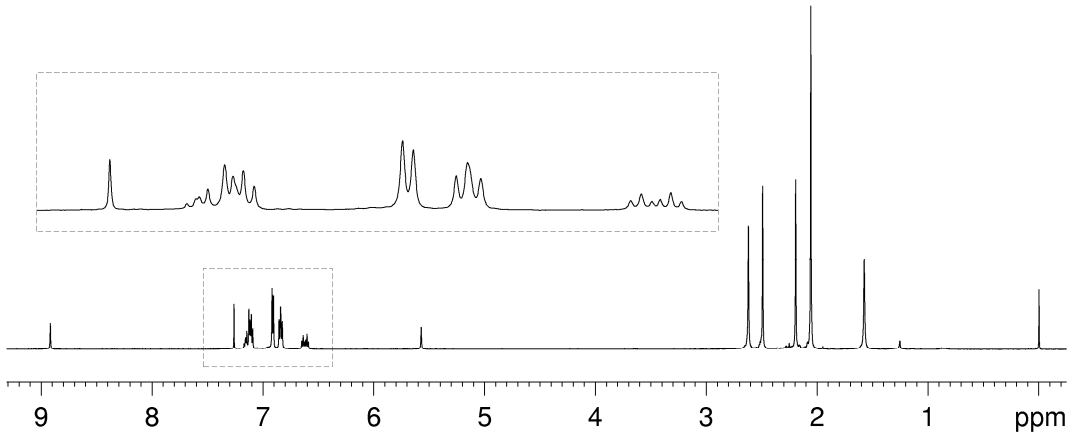
Elemental analysis (%):	C, 64.80	H, 5.22	N, 7.71
Calcd for $C_{98}H_{94}Br_2N_{10}O_2Pd_2$:	C, 64.53	H, 5.06	N, 7.78

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

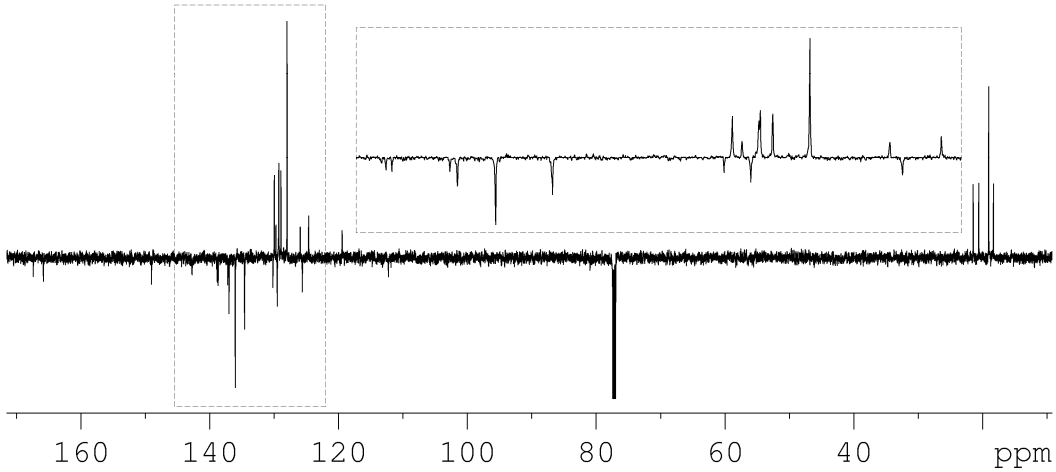
X-ray crystallography: Single crystals of **27**·2CH_2Cl_2·2hexane were grown by liquid diffusion of hexane into a solution of **27** in CH_2Cl_2.



IR spectrum of 27

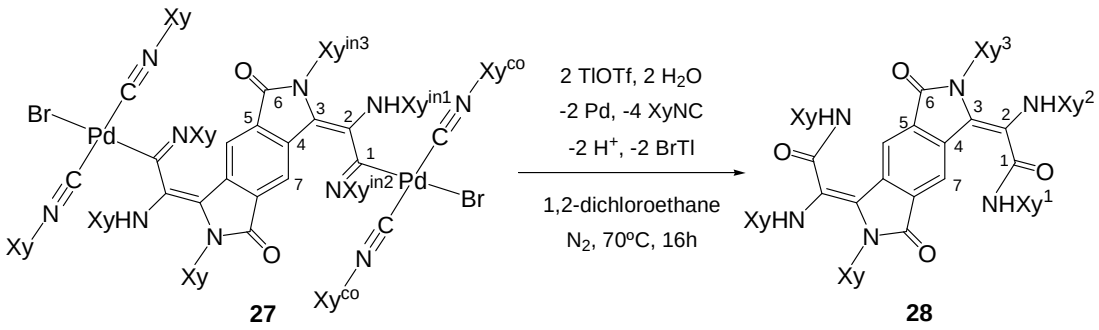


^{1}H NMR spectrum (600 MHz) of 27



APT spectrum (150.9 MHz) of 27

2,3,6,7-Tetrahydrobenzo[1,2-*c*:4,5-*c'*]dipyrrole-1,5-dione-2,6-dixylyl-3,7-bis{=C (NHXy)-C(O)NHXy} (28)



27 **28**

TlOTf (97.6 mg, 0.276 mmol) was added to a solution of **27** (250 mg, 0.138 mmol) in 1,2-dichloroethane (20 mL) under N_2, whereby the color changed from red to black. The mixture was heated to 70ºC for 16 h, and then it was filtered over $MgSO_4$, yielding a yellow solution which was concentrated in vacuo to a volume of ca. 2 mL. A small amount of Et_2O (ca. 5 mL) was added slowly until a yellow solid started to precipitate. The mixture was left in an ice bath for 24h and then it was filtered over Celite, yielding again a yellow solution which was evaporated in vacuo to dryness. Hexane (15 mL) was added to precipitate a solid, which was filtered off, washed with hexane (3×5 mL) and a small amount of cold Et_2O (1 mL), and dried in vacuo to give **28** as a yellow solid. Yield: 25 mg (56%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 8.34 (s, 2H, H7), 7.25-7.17 (m, 6H, *m,p*-H Xy^3), 7.06-7.00 (m, 2H, *p*-H Xy^1), 7.00-6.92 (m, 10H, *m*-H Xy^1, *m,p*-H Xy^2), 6.89 (s, 2H, NH^1), 5.12 (s, 2H, NH^2), 2.22 (s, 12H, Me Xy^3), 2.21 (s, 12H, Me Xy^2), 1.70 (s, 12H, Me Xy^1).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 164.8 (2C, CO^6), 161.7 (2C, CO^1), 137.6 (4C, *o*-C Xy^3), 137.2 (2C, *i*-C Xy^2), 135.8 (2C, *i*-C Xy^3), 135.6 (4C, *o*-C Xy^2), 135.2 (4C, *o*-C Xy^1), 133.4 (2C, C4 or C5), 132.5 (2C, *i*-C Xy^I), 130.7 (2C, C5 or C4), 130.0 (2C, *p*-CH Xy^3), 129.3 (4C, *m*-CH Xy^2), 129.2 (4C, *m*-CH Xy^3), 128.7 (4C, *m*-CH Xy^1), 127.7 (2C, *p*-CH Xy^1), 127.4 (2C, C2), 126.9 (2C, *p*-CH Xy^2), 118.2 (2C, CH7), 113.4 (2C, C3), 18.9 (4C, Me Xy^2), 18.4 (4C, Me Xy^3), 18.1 (4C, Me Xy^2).

IR (cm^{-1}): ν(N-H): 3369, ν(C=O): 1674 (br)

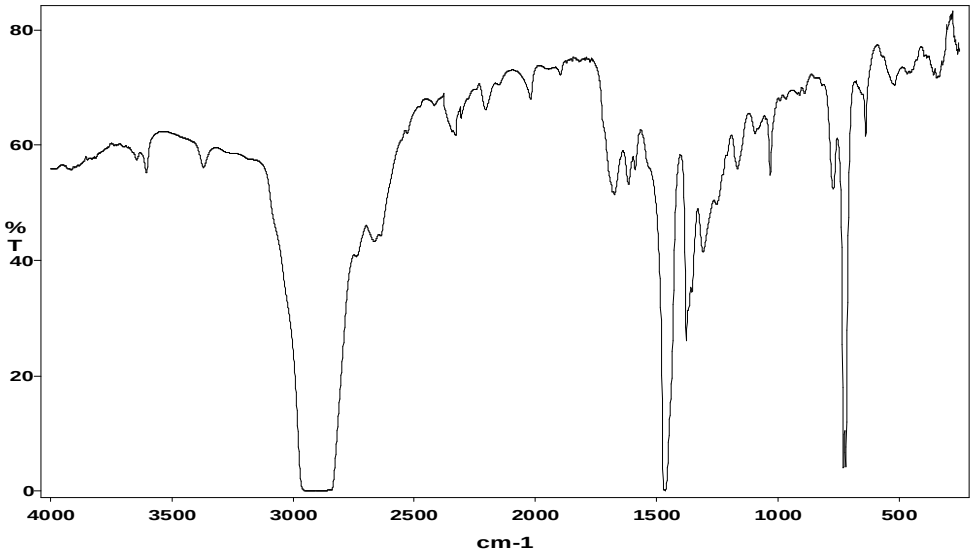
Exact Mass: HR ESI+ TOF MS: calcd for **28**+H^+ ($C_{62}H_{61}N_6O_4$) m/z 953.4749, found 953.4758, Δ = 0. 99 ppm.

Calculated:	**953.4749 (100)**	954.4781 (70.01)	955.4812 (25.03)	956.4842 (6.06)	957.4872 (1.12)
Found:	**953.4758 (100)**	954.4789 (68.53)	955.4815 (22.15)	956.4835 (5.14)	957.491 (1.17)

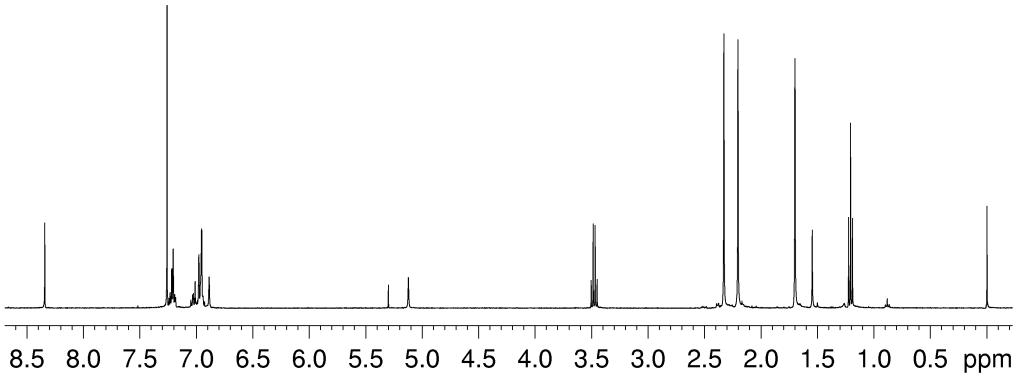
Melting point: 217 ^{o}C

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Partially soluble in Et_2O and insoluble in hexane.

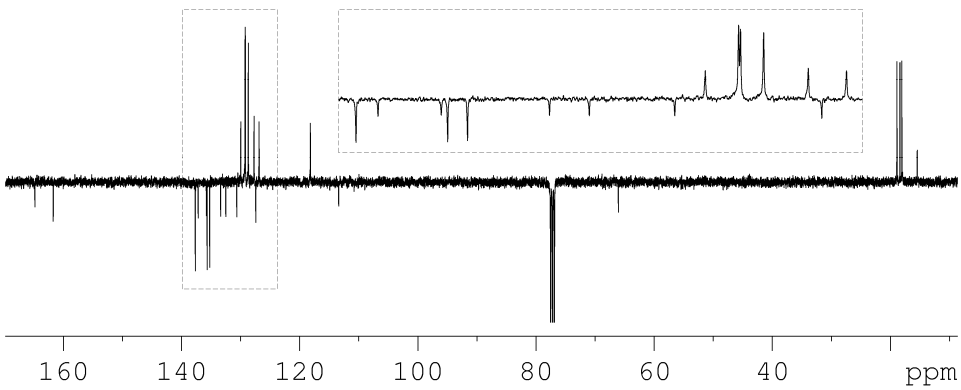
X-ray crystallography: Single crystals of **28**·2$CDCl_3$·were grown by slow evaporation of a solution of **28** in $CDCl_3$.



IR spectrum of 28

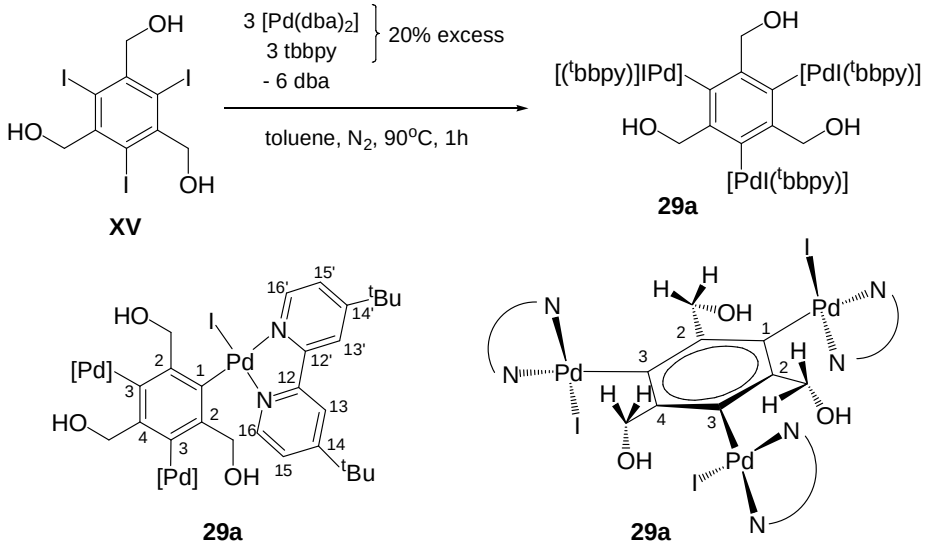


^{1}H NMR spectrum (400 MHz) of 28



APT spectrum (100.6 MHz) of 28

[{PdI(tbbpy)}$_3$(μ_3-*C1,C3,C5*-C$_6$(CH$_2$OH)$_3$-2,4,6}] (29a)



1,3,5-triiodo-2,4,6-trihydroxymethylbenzene (**XV**) (76 mg, 0.14 mmol) was added to a suspension of [Pd(dba)$_2$] (300 mg, 0.52 mmol) and tbbpy (140 mg, 0.52 mmol) in dry degassed toluene (15 mL) under N_2. The resulting mixture was stirred at 90ºC for 1 h until the dark red color of [Pd(dba)$_2$] was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the resulting orange solution was evaporated to dryness. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, washed with Et_2O (3×5 mL), and dried in vacuo to give **29a** as a yellow solid. Yield: 445 mg, 62%.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 9.45 (d, $^3J_{HH}$ = 6, 2H, H16' tbbpy), 9.30 (d, $^3J_{HH}$ = 6, 1H, H16' tbbpy), 7.93 (d, $^3J_{HH}$ = 6, 2H, H16 tbbpy), 7.92 (s, 1H, H13 tbbpy), 7.91 (s, 2H, H13' tbbpy), 7.90 (s, 2H, H13 tbbpy), 7.87 (s, 1H, H13' tbbpy), 7.76 (d, $^3J_{HH}$ = 6, 1H, H16 tbbpy), 7.51 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 1H, H15 tbbpy), 7.45 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15' tbbpy), 7.41 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 1H, H15' tbbpy), 7.31 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15 tbbpy), 5.88 (A part of ABX system, $^3J_{AX}$ = 12, $^2J_{AB}$ = 11, 2H, *CH$_2$*OH-2), 5.79 (B part of ABX system, $^3J_{BX}$ = 1, $^2J_{AB}$ = 11, 2H, *CH$_2$*OH-2), 5.74 (d, $^3J_{HH}$ = 6, 2H, *CH$_2$*OH-4), 3.11 (X part of ABX system, $^3J_{AX}$ = 12, $^3J_{BX}$ = 1, 2H, CH$_2$*OH*-2), 2.83 (t, $^3J_{HH}$ = 6, 1H, CH$_2$*OH*-4), 1.41 (s, 9H, ^{t}Bu tbbpy), 1.40 (s, 18H, ^{t}Bu tbbpy), 1.39 (s, 18H, ^{t}Bu' tbbpy), 1.39 (s, 9H, ^{t}Bu' tbbpy).

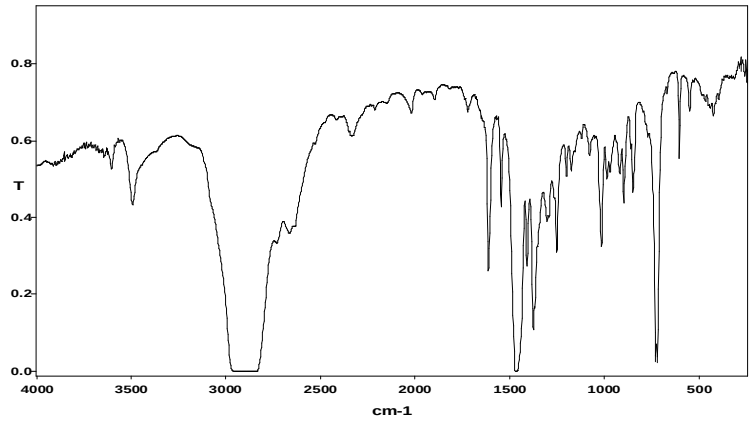
^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 162.94 (2C, C14' tbbpy), 162.90 (1C, C14' tbbpy), 162.7 (2C, C14 tbbpy), 162.6 (1C, C14 tbbpy), 156.1 (2C, C12 tbbpy), 155.1 (1C, C12 tbbpy), 154.7 (1C, C12' tbbpy), 154.0 (2C, C12' tbbpy), 152.5 (1C, CH16 tbbpy), 152.4 (2C, CH16' tbbpy), 152.2 (1C, C1 aryl), 151.9 (2C, C3 aryl), 151.7 (1C,

CH16' tbbpy), 150.9 (2C, CH16 tbbpy), 143,9 (1C, C4 aryl), 143.5 (2C, C2 aryl), 124.6 (1C, CH15 tbbpy), 123.8 (2C, CH15' tbbpy), 123.3 (1C, CH15' tbbpy), 122.8 (2C, CH15 tbbpy), 118.5 (2C, CH13 tbbpy), 118.0 (1C, CH13 tbbpy), 117.9 (3C, CH13' tbbpy), 71.3 (2C, CH_2-2), 70.8 (1C, CH_2-4), 35.6 (1C, *C*Me_3 tbbpy), 35.6 (2C, *C*Me_3 tbbpy), 35.5 (2C, *C*Me_3' tbbpy), 35.5 (1C, *C*Me_3' tbbpy), 30.57 and 30.54 (3C, C*Me*$_3$ and C*Me*$_3$' tbbpy), 30.56 and 30.53 (6C, C*Me*$_3$ and C*Me*$_3$' tbbpy).

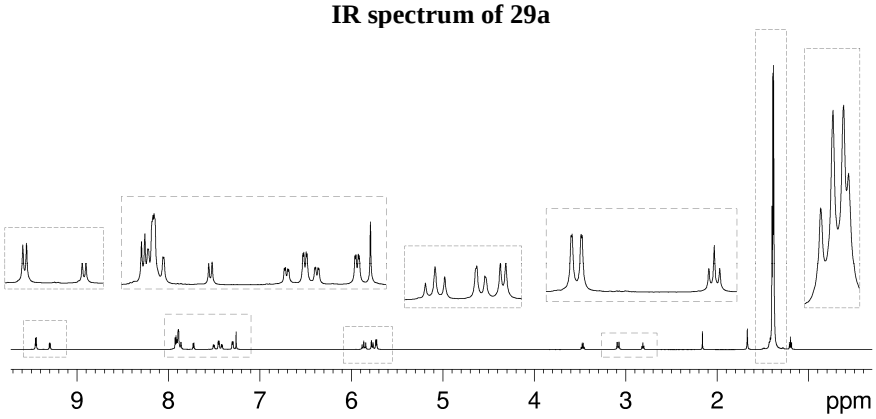
IR (cm^{-1}): ν(O-H): 3492. **Melting point:** 219 ^oC (dec).

Elemental analysis (%):	C, 45.21	H, 4.74	N, 5.01
Calcd for $C_{63}H_{81}I_3N_6O_3Pd_3$:	C, 45.30	H, 4.89	N, 5.03

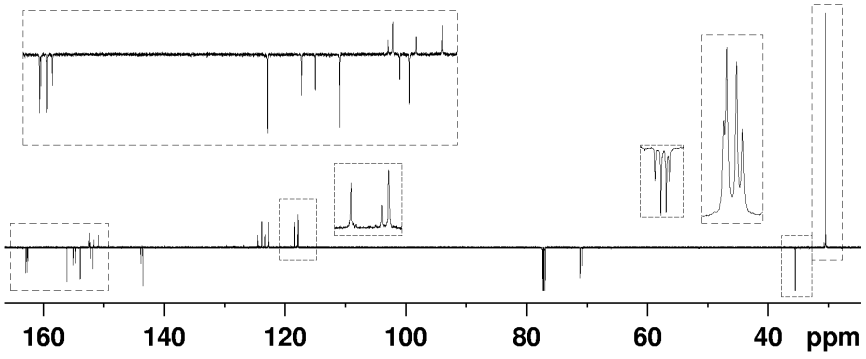
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 29a

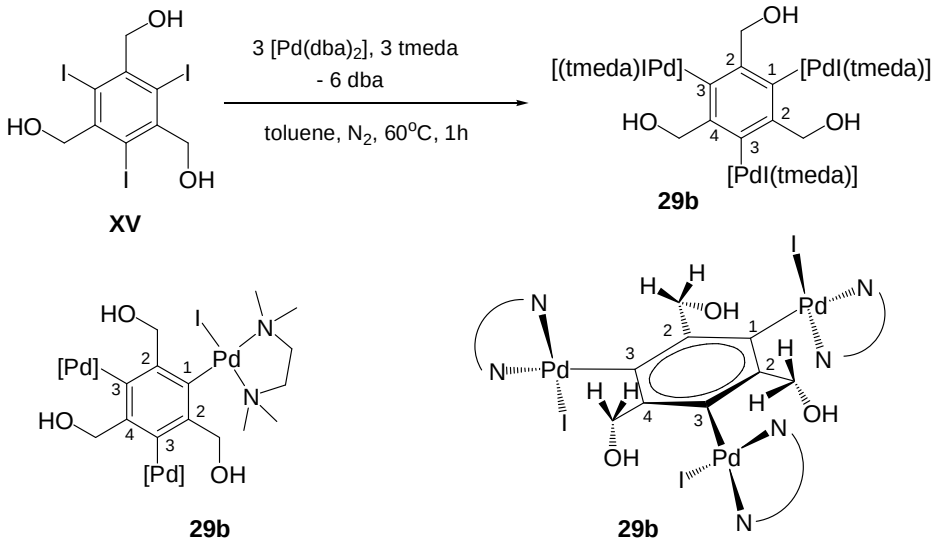


^{1}H NMR spectrum (600 MHz) of 29a



APT spectrum (150.9 MHz) of 29a

[{PdI(tmeda)}$_3$(μ_3-*C1,C3,C5*-C$_6$(CH$_2$OH)$_3$-2,4,6}] (29b)



1,3,5-triiodo-2,4,6-trihydroxymethylbenzene (**XV**) (93 mg, 0.17 mmol) was added to a suspension of [Pd(dba)$_2$] (300 mg, 0.52 mmol) and tmeda (78 μL, 0.52 mmol) in dry degassed toluene (15 mL) under N_2. The resulting mixture was stirred at 60ºC for 1 h until the dark red color of [Pd(dba)$_2$] was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the resulting yellow solution was evaporated to dryness. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, washed with Et_2O (3×5 mL), and dried in vacuo to give **29b** as a yellow solid. Yield: 124 mg, 60%.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

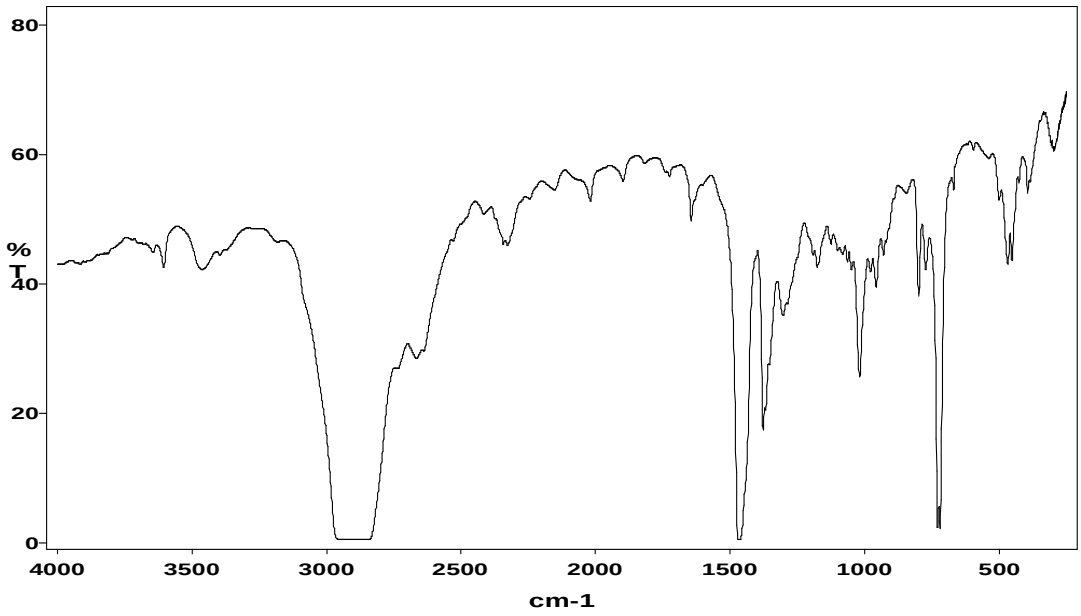
^{1}H NMR (600 MHz, $CDCl_3$): 6.01 (A part of ABX system, $^2J_{AB}$ = 11, $^3J_{AX}$ = 11, 2H, *CH*$_2$OH-2), 5.98 (B part of ABX system, $^2J_{AB}$ = 11, $^3J_{BX}$ = 3, 2H, *CH*$_2$OH-2), 5.64 (d, $^3J_{HH}$ = 6, 2H, *CH*$_2$OH-4), 3.63 (t, $^3J_{HH}$ = 6, 1H, CH$_2$*OH*-4), 3.57 (X part of ABX system, $^3J_{AX}$ = 11, $^3J_{BX}$ = 3, 2H, CH$_2$*OH*-2), 2.92-2.85 (m, 2H, CH$_2$ tmeda), 2.75-2.45 (several m, 10H, CH$_2$ tmeda), 2.73, 2.71, 2.69, 2.49, 2.38 and 2.23 (s, 6H, Me tmeda).

^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2): 148.6 (1C, C1 aryl), 147.5 (2C, C3 aryl), 144.1 (2C, C2 aryl), 142.7 (1C, C4 aryl), 72.4 (2C, CH$_2$OH-2), 69.5 (1C, CH$_2$OH-4), 63.0 (1C, CH$_2$ tmeda), 62.9 (2C, CH$_2$ tmeda), 58.65 (1C, CH$_2$ tmeda), 58.61 (2C, CH$_2$ tmeda), 51.9, 51.3, 50.8, 50.4, 49.9 and 49.4 (2C, Me tmeda).

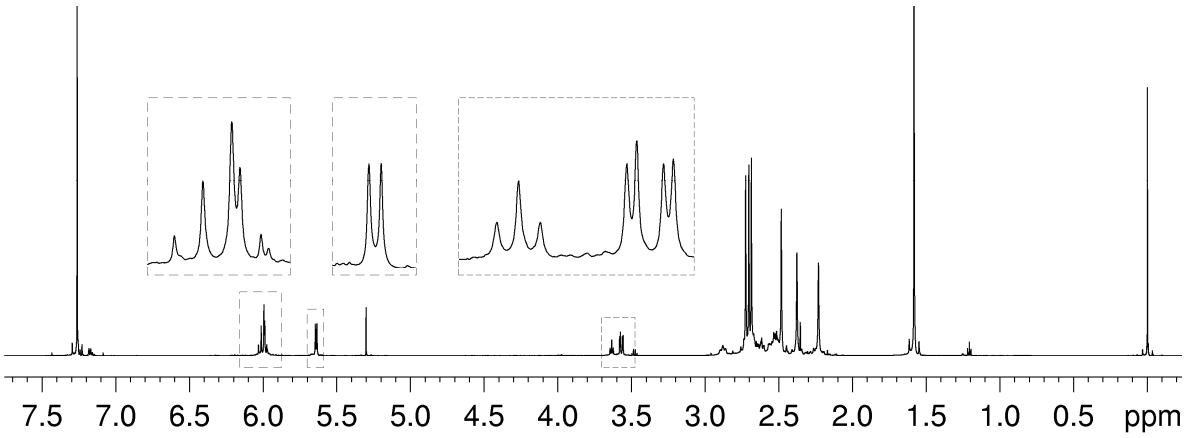
IR (cm^{-1}): ν(O-H): 3465. **Melting point:** 197 ºC.

Elemental analysis (%):	C, 27.07	H, 4.57	N, 6.63
Calcd for $C_{27}H_{57}I_3N_6O_3Pd_3$:	C, 26.72	H, 4.73	N, 6.92

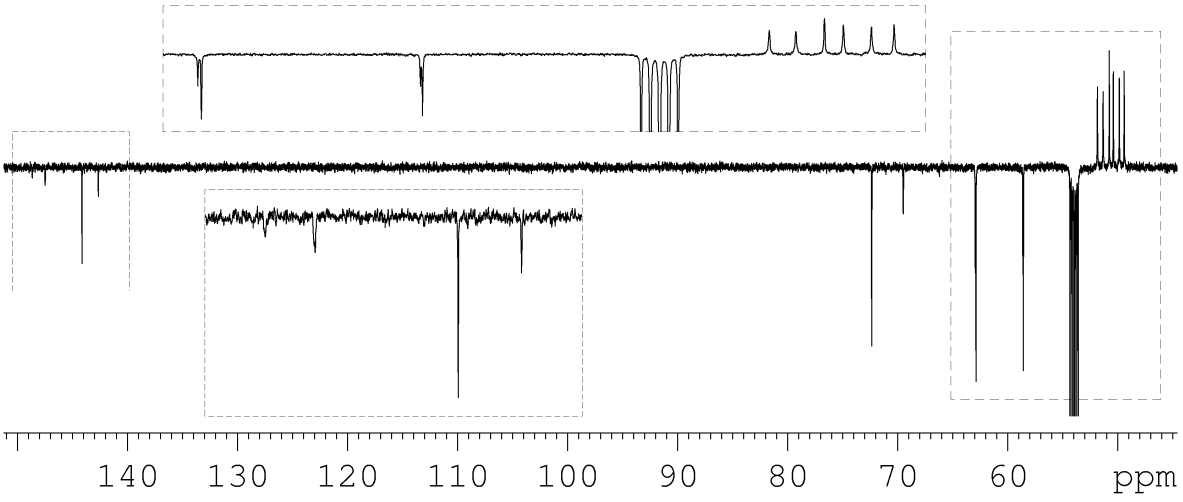
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 29b

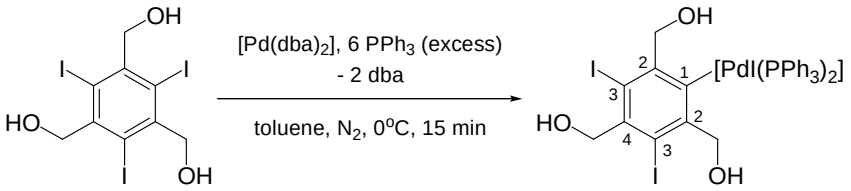


^{1}H NMR spectrum (600 MHz) of 29b



APT spectrum (150.9 MHz, CD_2Cl_2) of 29b

***trans*-[Pd{$C_6(CH_2OH)_3$-2,4,6-I_2-3,5}I($PMe_2Ph)_2$] (30)**



XV **30**

PPh_3 (268 mg, 1.02 mmol) was added to a suspension of [Pd(dba)$_2$] (100 mg, 0.17 mmol) and 1,3,5-triiodo-2,4,6-trihydroxymethylbenzene (**XV**) (93 mg, 0.17 mmol) in dry degassed toluene (15 mL) under N_2, whereby the dark red color of [Pd(dba)$_2$] immediately disappeared. The mixture was stirred in an ice bath for 15 min and then the solvent was evaporated in vacuo and the residue extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the resulting yellow solution was evaporated to dryness. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, washed with Et_2O (3×5 mL), and dried in vacuo to give **30** as a pale pink solid. Yield: 94 mg, 47%.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (400 MHz, $CDCl_3$): 7.66-7.42 (br s, 12H, *o*-H PPh_3), 7.42-7.33 (m, 6H, *p*-H PPh_3), 7.33-7.24 (m, 12H, *m*-H PPh_3), 4.96 (d, $^3J_{HH}$ = 7, 4H, *CH*$_2$OH-2), 4.94 (d, $^3J_{HH}$ = 7, 2H, *CH*$_2$OH-4), 1.94 (t, $^3J_{HH}$ = 7, 1H, CH$_2$*OH*-4), 1.17 (t, $^3J_{HH}$ = 7, 2H, CH$_2$*OH*-2).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 169.0 (t, $^3J_{PC}$ = 1, 1C, C1 aryl), 145.1 (t, $^3J_{PC}$ = 3, 2C, C2 aryl), 141.9 (t, $^3J_{PC}$ = 1, 1C, C4 aryl), 135.0 (br, 12C, *o*-CH PPh_3), 131.2 (vt, $^1J_{CP}$ + $^3J_{CP}$ = 47, 6C, *i*-C PPh_3), 130.8 (s, 6C, *p*-CH PPh_3), 128.2 (vt, $^3J_{CP}$ + $^5J_{CP}$ = 10, 12C, *m*-CH PPh_3), 106.0 (s, 2C, C3 aryl), 76.6 (s, 1C, CH_2OH-4), 74.1 (t, $^4J_{PC}$ = 1, 2C, CH_2OH-2).

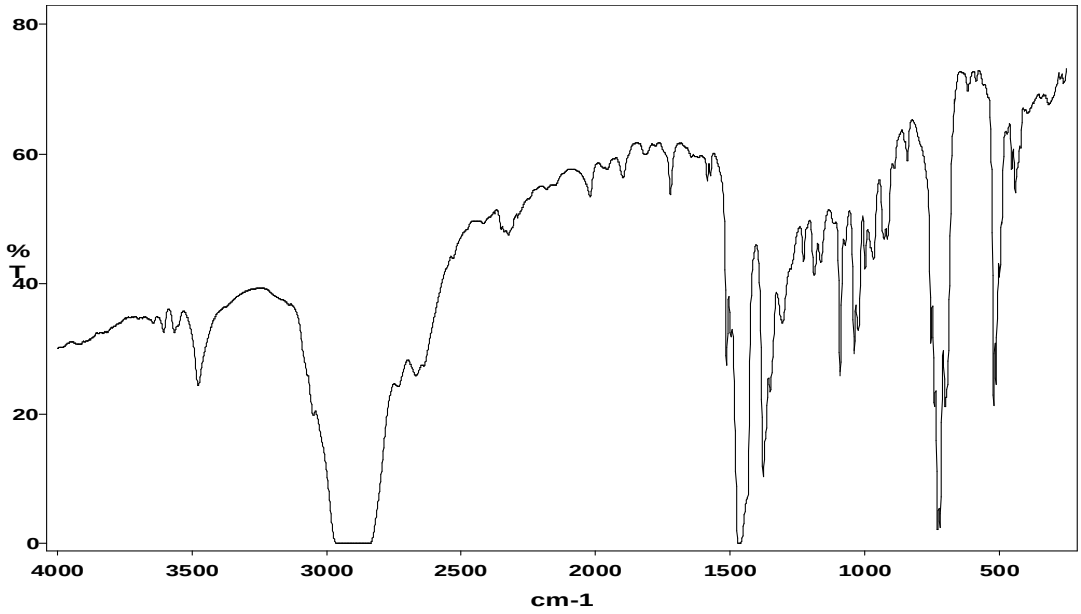
^{31}P{^{1}H}-NMR (161.9 MHz, $CDCl_3$): 21.1 (s).

IR (cm^{-1}): ν(O-H): 3476.

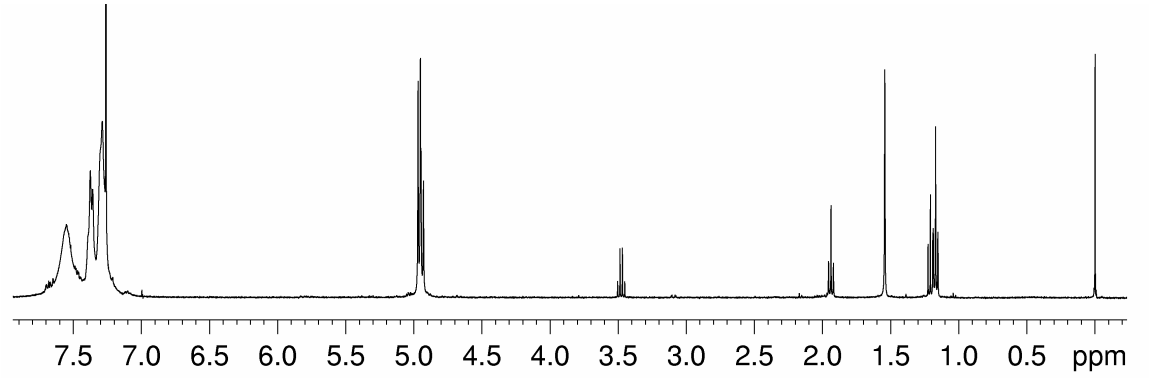
Elemental analysis (%):	C, 45.57	H, 3.37
Calcd for $C_{45}H_{39}I_3O_3P_2Pd$:	C, 45.93	H, 3.34

Melting point: 241 °C.

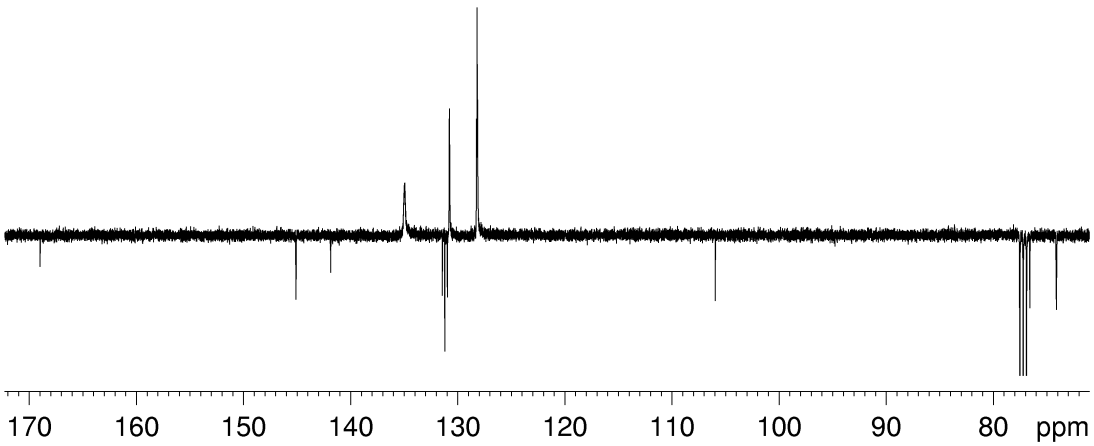
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



IR spectrum of 30

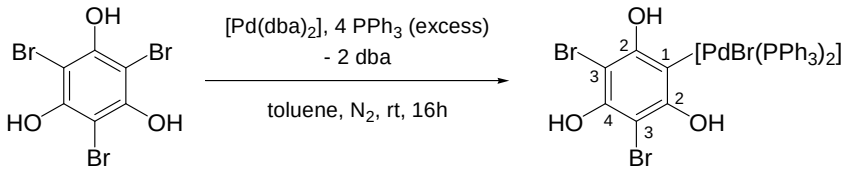


^{1}H NMR spectrum (400 MHz) of 30



APT spectrum (100.6 MHz) of 30

***trans*-[Pd{$C_6(OH)_3$-2,4,6-Br_2-3,5}$Br(PPh_3)_2$] (30')**



XVI' **30'**

PPh_3 (294 mg, 1.12 mmol) was added to a suspension of [$Pd(dba)_2$] (161 mg, 0.28 mmol) and 1,3,5-tribromophloroglucinol (**XVI'**) (100 mg, 0.28 mmol) in dry degassed toluene (15 mL) under N_2. The mixture was stirred at room temperature for 16 h, whereby the color changed from reddish to yellow. Then the solvent was evaporated in vacuo and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the resulting yellow solution was evaporated to dryness. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, washed with a small amount of cold $CHCl_3$ (3×2 mL) (to dissolve the [$PdBr_2(PPh_3)_2$] formed in the reaction), and dried in vacuo to give **30'** as a white solid. Yield: 100 mg, 36%.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (300 MHz, $CDCl_3$): 7.75-7.6 (m, 12H, *o*-H PPh_3), 7.4-7.2 (m, 18H, *p,m*-H PPh_3), 5.27 (s, 2H, OH-2), 5.10 (s, 1H, OH-4).

^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): 149.9 (t, $^3J_{CP}$ = 3, 2C, C2 aryl), 146.7 (t, $^5J_{CP}$ = 1, 1C, C4 aryl), 134.7 (vt, $^2J_{CP}$ + $^4J_{CP}$ = 13, 12C, *o*-CH PPh_3), 131.0 (vt, $^1J_{CP}$ + $^3J_{CP}$ = 48, 6C, *i*-C PPh_3), 130.5 (s, 6C, *p*-CH PPh_3), 128.1 (vt, $^3J_{CP}$ + $^5J_{CP}$ = 10, 12C, *m*-CH PPh_3), 118.5 (t, $^2J_{CP}$ = 5, 1C, C1 aryl), 88.3 (s, 2C, C3 aryl).

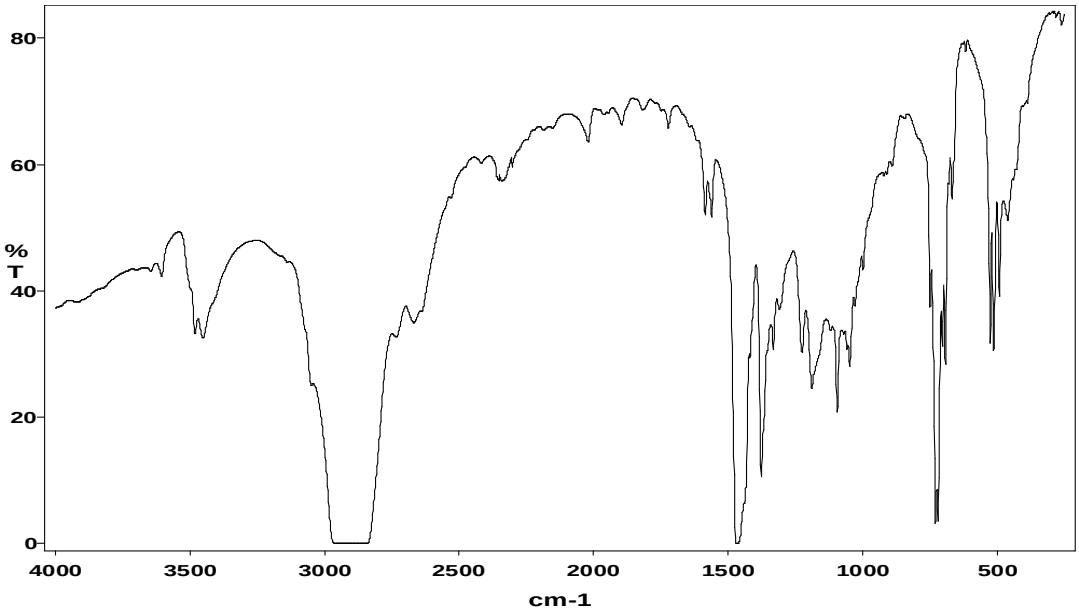
^{31}P{^{1}H}-NMR (121.4 MHz, $CDCl_3$): 24.9 (s).

IR (cm^{-1}): ν(O-H): 3451, 3480.

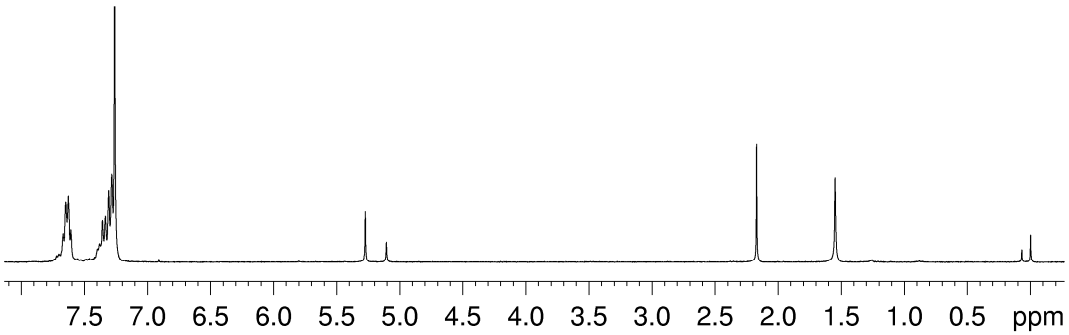
Elemental analysis (%):	C, 50.78	H, 3.68
Calcd for $C_{42}H_{33}Br_3O_3P_2Pd$:	C, 50.76	H, 3.35

Melting point: 174 °C.

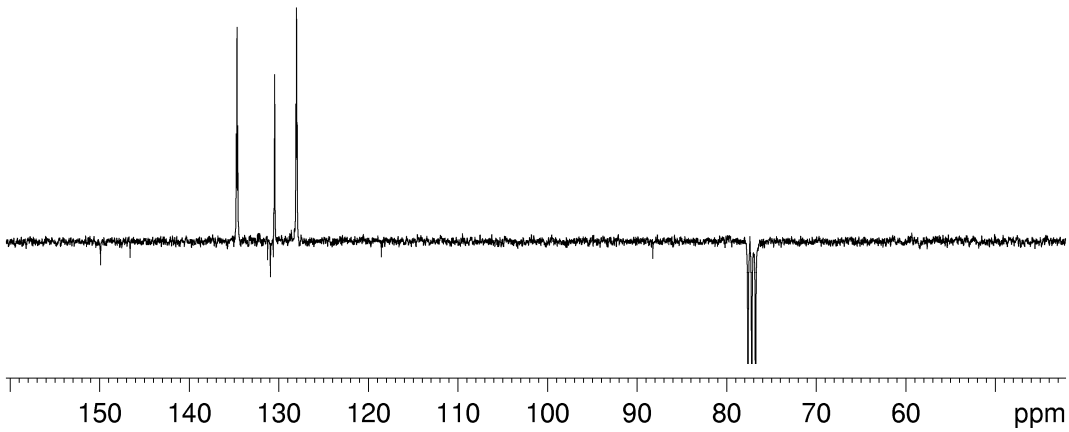
Solubility: Soluble in acetone. Low solubility in CH_2Cl_2 and $CHCl_3$. Insoluble in Et_2O and hexane.



IR spectrum of 30'

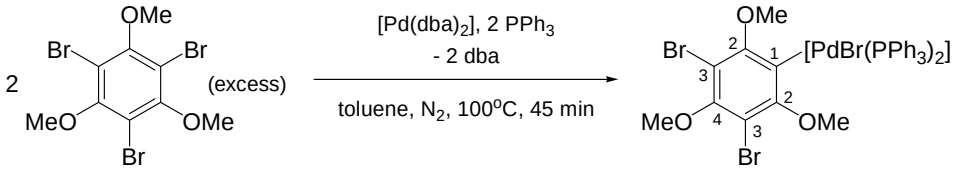


^{1}H NMR spectrum (300 MHz) of 30'



APT spectrum (75.4 MHz) of 30'

***trans*-[Pd{C$_6$(OMe)$_3$-2,4,6-Br$_2$-3,5}Br(PPh$_3$)$_2$] (30")**



XVII' **30"**

PPh_3 (89 mg, 0.34 mmol) was added to a suspension of $[Pd(dba)_2]$ (100 mg, 0.17 mmol) and 1,3,5-tribromo-2,4,6-trimethoxybenzene (**XVII'**) (138 mg, 0.34 mmol) in dry degassed toluene (15 mL) under N_2, whereby the dark red color of $[Pd(dba)_2]$ immediately disappeared. The mixture was stirred at 100ºC for 45 min, and then the solvent was evaporated in vacuo and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the resulting yellow solution was evaporated to dryness. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, washed with Et_2O (3×5 mL), and dried in vacuo to give **30"** as a white solid. Yield: 62 mg, 35%.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (300 MHz, $CDCl_3$): 8.0-7.5 (br, 12H, *o*-H PPh_3), 7.5-7.2 (br, 18H, *p,m*-H PPh_3), 3.75 (s, 6H, OMe-2), 3.56 (s, 3H, OMe-4).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 155.9 (t, $^3J_{CP}$ = 3, 2C, C2 aryl), 152.3 (t, $^5J_{CP}$ = 1, 1C, C4 aryl), 140.6 (t, $^2J_{CP}$ = 5, 1C, C1 aryl), 135.2 (br, 12C, *o*-CH PPh_3), 131.6 (vt, $^1J_{CP}$ + $^3J_{CP}$ = 48, 6C, *i*-C PPh_3), 130.4 (br, 6C, *p*-CH PPh_3), 127.9 (br, 12C, *m*-CH PPh_3), 107.6 (s, 2C, C3 aryl), 60.6 (s, 1C, OMe-4), 60.1 (s, 2C, OMe-2).

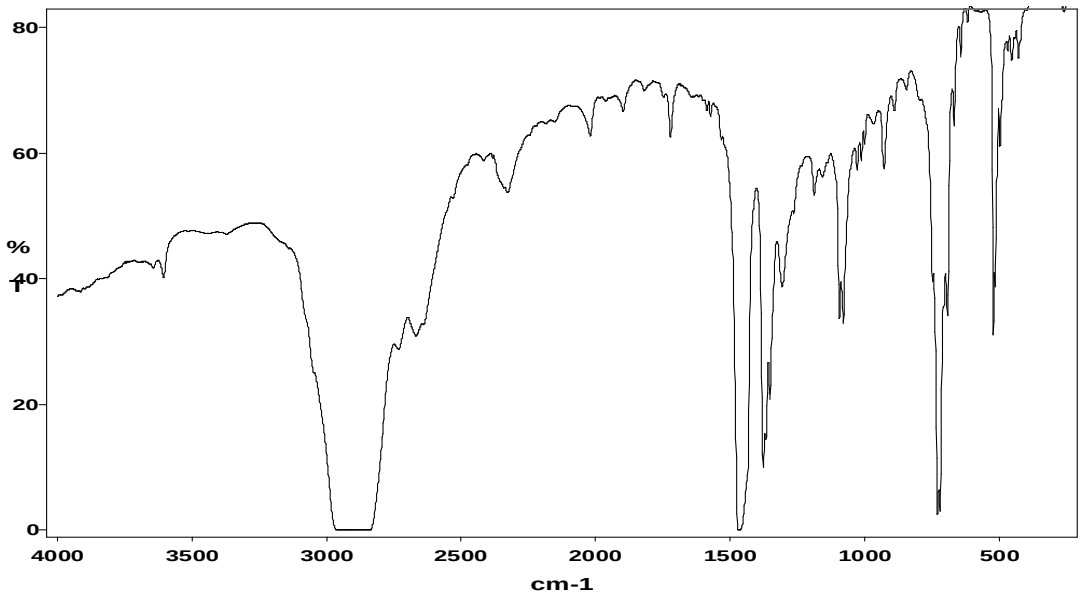
^{31}P{^{1}H}-NMR (161.9 MHz, $CDCl_3$): 23.8 (s).

Elemental analysis (%):	C, 52.20	H, 3.90
Calcd for $C_{45}H_{39}Br_3O_3P_2Pd$:	C, 52.18	H, 3.79

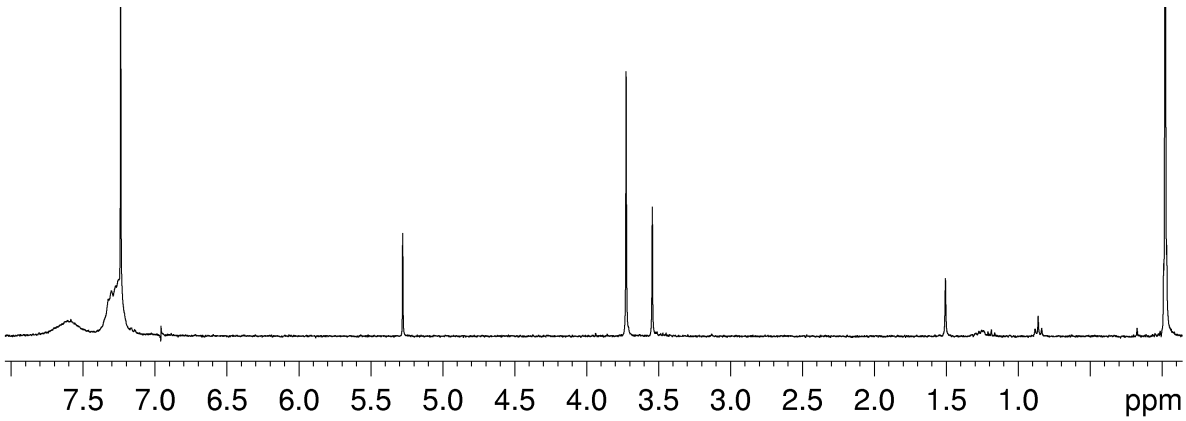
Melting point: 240 °C.

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.

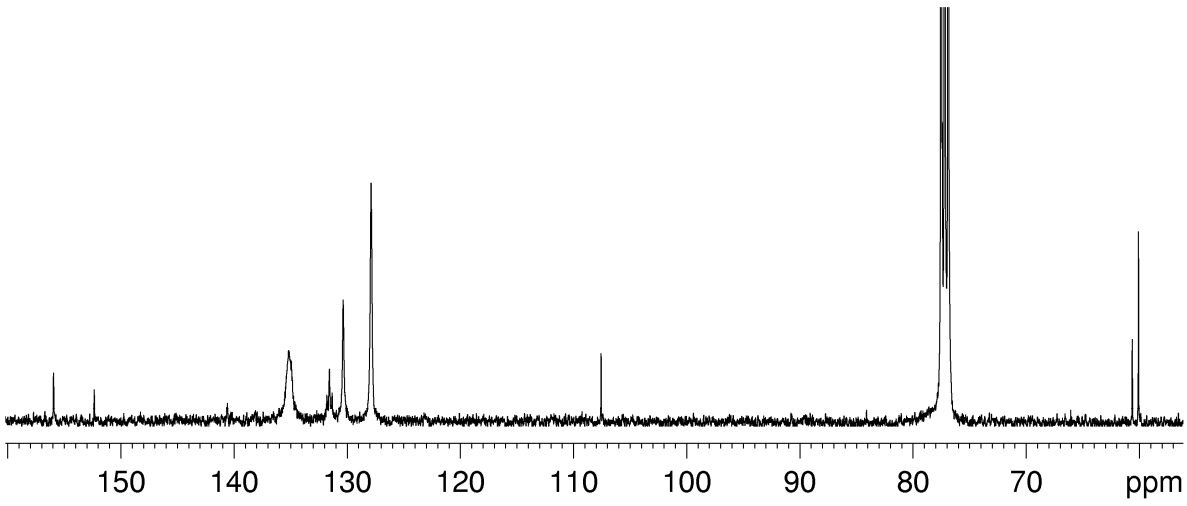
X-ray crystallography: Single crystals of **30"** were grown by liquid diffusion of Et_2O into a solution of **30"** in $CDCl_3$.



IR spectrum of 30”

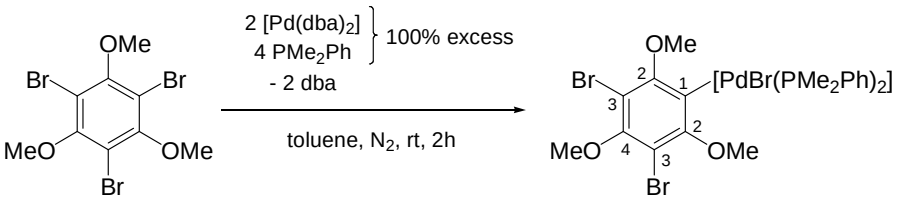


^{1}H NMR spectrum (300 MHz) of 30”



APT spectrum (100.6 MHz) of 30”

***trans*-[Pd{$C_6(OMe)_3$-2,4,6-Br_2-3,5}Br($PMe_2Ph)_2$] (31)**



XVII' **31**

PMe_2Ph (148 μL, 1.04 mmol) was added to a suspension of [$Pd(dba)_2$] (300 mg, 0.52 mmol) and 1,3,5-tribromo-2,4,6-trimethoxybenzene (**XVII'**) (105 mg, 0.26 mmol) in dry degassed toluene (15 mL) under N_2. The mixture was stirred at room temperature for 2 h, whereby the color changed from reddish to yellow. Then the solvent was evaporated in vacuo and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the resulting orange solution was evaporated to dryness. Et_2O (15 mL) and hexane (10 mL) were added to precipitate a solid, which was filtered off, washed with hexane (3×5 mL), and dried in vacuo to give **31** as a white solid. Yield: 131 mg, 64%.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$): 7.58-7.53 (m, 4H, *o*-H, PMe_2*Ph*), 7.32-7.27 (m, 6H, *p,m*-H, PMe_2*Ph*), 3.89 (s, 6H, OMe-2), 3.66 (s, 3H, OMe-4), 1.69 (vt, 12H, P*Me*$_2$Ph, $^{2}J_{PH}$ + $^{4}J_{PH}$ = 7).

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 157.3 (t, $^{3}J_{PC}$ = 3, 2C, C2 aryl), 151.9 (t, $^{5}J_{PC}$ = 2, 1C, C4 aryl), 136.7 (t, $^{2}J_{PC}$ = 6, 1C, C1 aryl), 134.8 (vt, $^{1}J_{CP}$ + $^{3}J_{CP}$ = 47, 2C, *i*-C PMe_2*Ph*), 131.2 (vt, $^{2}J_{CP}$ + $^{4}J_{CP}$ = 11, 4C, *o*-CH PMe_2*Ph*), 129.7 (s, 2C, *p*-CH PMe_2*Ph*), 128.1 (vt, $^{3}J_{CP}$ + $^{5}J_{CP}$ = 10, 4C, *m*-CH PMe_2*Ph*), 107.9 (t, $^{4}J_{PC}$ = 1, 2C, C3 aryl), 60.7 (s, 1C, OMe-4), 60.2 (s, 2C, OMe-2), 14.7 (vt, $^{1}J_{CP}$ + $^{3}J_{CP}$ = 321, 4C, P*Me*$_2$Ph).

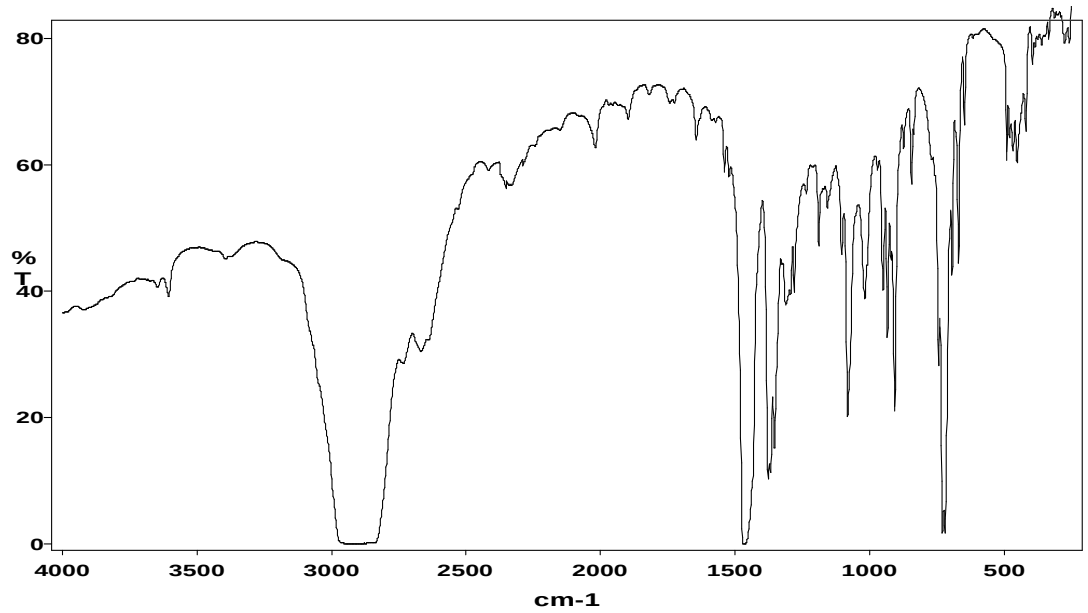
^{31}P{^{1}H}-NMR (121.4 MHz, $CDCl_3$): -5.6 (s).

Elemental analysis (%):	C, 38.32	H, 3.72
Calcd for $C_{25}H_{31}Br_3O_3P_2Pd$:	C, 38.12	H, 3.97

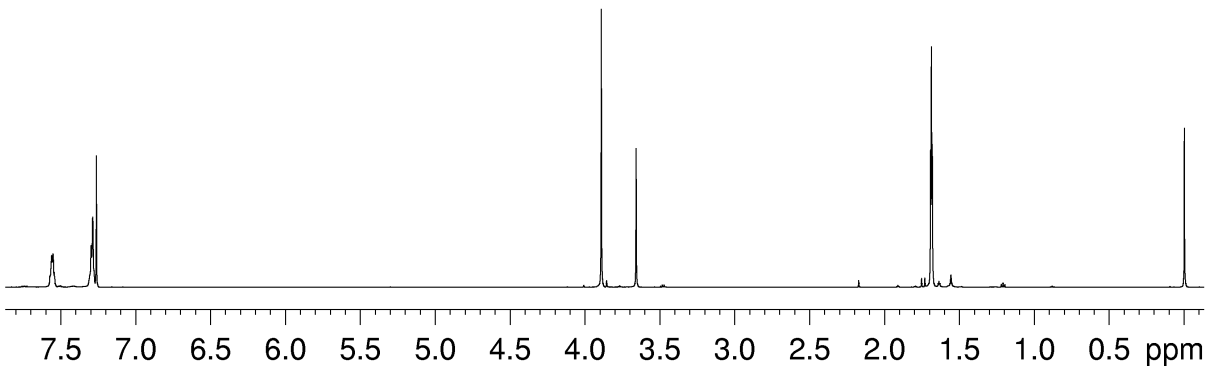
Melting point: 159 ^{o}C.

Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Partially soluble in Et_2O. Insoluble in hexane.

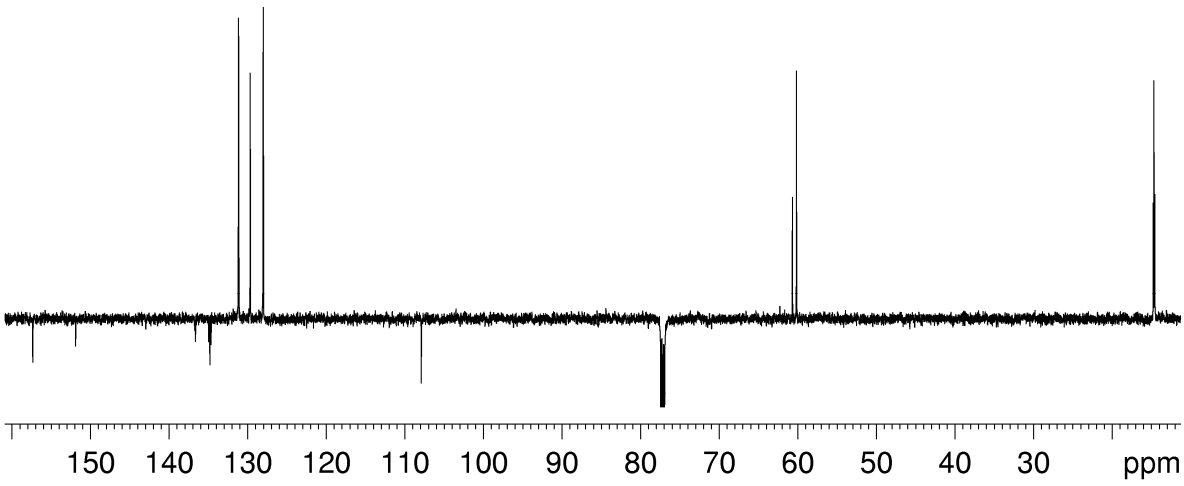
X-ray crystallography: Single crystals of **31** were grown by liquid diffusion of hexane into a solution of **31** in Et_2O.



IR spectrum of 31

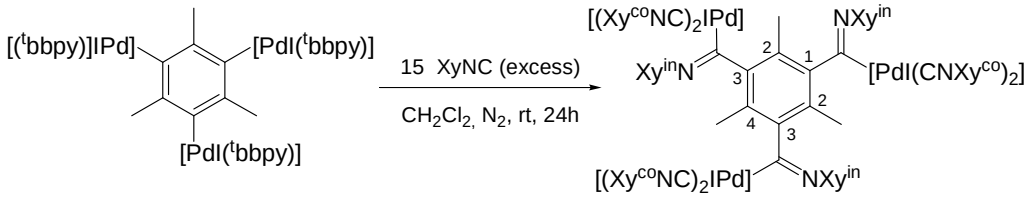


^{1}H NMR spectrum (600 MHz) of 31



APT spectrum (150.9 MHz) of 31

[C_6{C(=NXy)(*trans*-PdI(CNXy)$_2$)}$_3$-1,3,5-Me$_3$-2,4,6] (32)



XVIII **32**

XyNC (97 mg, 0.74 mmol) was added to a solution of complex **XVIII** (80 mg, 0.049 mmol) in CH_2Cl_2 (15 mL) under N_2, and the resulting mixture was stirred at room temperature for 24h. It was then filtered over Celite and the resulting yellow solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a solid, which was filtered off, washed with Et_2O (3×5 mL), and dried in vacuo to give **32** as a yellow solid. Yield: 62 mg, 62%.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (600 MHz, $CDCl_3$, **298K**): 7.11-7.06 (m, 6H, *p*-H Xy^{co}), 6.98-6.94 (m, 12H, *m*-H Xy^{co}), 6.81-6.75 (m, 9H, *p,m*-H Xy^{in}), 3.05 (s, 9H, Me), 2.25 (s, 54H, Me Xy).

^{1}H NMR (600 MHz, $CDCl_3$, **243K**): 7.16 (t, $^3J_{HH}$ = 7, 4H, *p*-H Xy^{co}-3), 7.11 (t, $^3J_{HH}$ = 7, 2H, *p*-H Xy^{co}-1), 7.02 (d, $^3J_{HH}$ = 7, 8H, *m*-H Xy^{co}-3), 6.97 (d, $^3J_{HH}$ = 7, 4H, *m*-H Xy^{co}-1), 6.87-6.79 (m, 9H, *p,m*-H Xy^{in}), 3.18 (s, 3H, Me-4), 3.01 (s, 6H, Me-2), 2.33 (s, 6H, Me Xy^{in}), 2.28 (s, 24H, Me Xy^{co}-3), 2.22 (s, 6H, Me Xy^{in}), 2.18 (s, 12H, Me Xy^{co}-1), 2.08 (s, 6H, Me Xy^{in}).

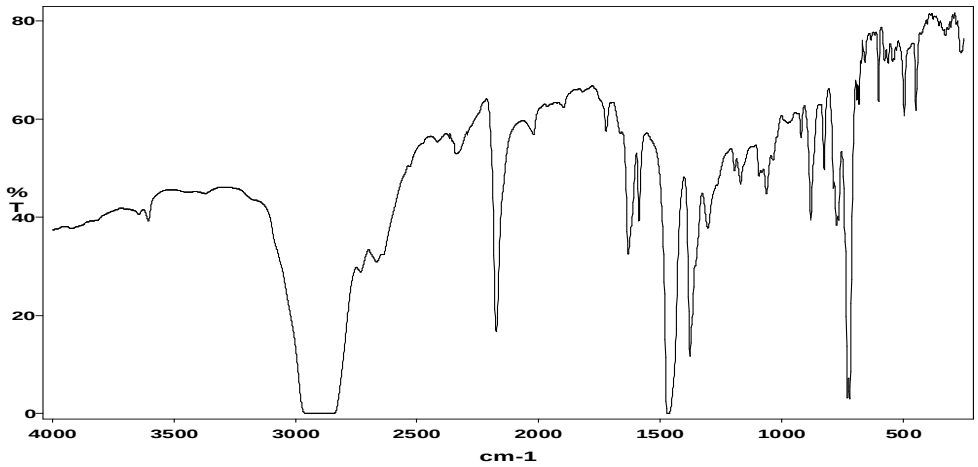
^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, **243K**): 178.2 (1C, C=N-1), 178.0 (2C, C=N-3), 150.5 (1C, *i*-C Xy^{in}-1), 150.2 (2C, *i*-C Xy^{in}-3), 146.3 (2C, C≡N-1), 145.6 (4C, C≡N-3), 142.9 (2C, C2 aryl), 142.7 (1C, C4 aryl), 135.5 (8C, *o*-C Xy^{co}-3), 135.3 (4C, *o*-C Xy^{co}-1), 130.0 (4C, *p*-CH Xy^{co}-3), 129.9 (2C, *p*-CH Xy^{co}-1), 128.13 (12C, *m*-CH Xy^{co}-3 + Xy^{in}), 128.09 (2C, *m*-CH Xy^{in}), 127.9 (4C, *m*-CH Xy^{co}-1), 127.54, 127.52, and 127.46 (2C each, *o*-C Xy^{in}), 126.3 (2C, C3 aryl), 126.2 (1C, C1 aryl), 125.2 (2C, *i*-C Xy^{co}-1), 125.0 (4C, *i*-C Xy^{co}-3), 123.85 (1C, *p*-CH Xy^{in}-1), 123.78 (2C, *p*-CH Xy^{in}-3), 21.3 (2C, Me-2), 20.7 (1C, Me-4), 20.1, 20.0 and 19.5 (2C each, Me Xy^{in}), 19.4 (8C, Me Xy^{co}-3), 18.8 (4C, Me Xy^{co}-1).

IR (cm^{-1}): ν(C≡N): 2174, ν(C=N): 1630.

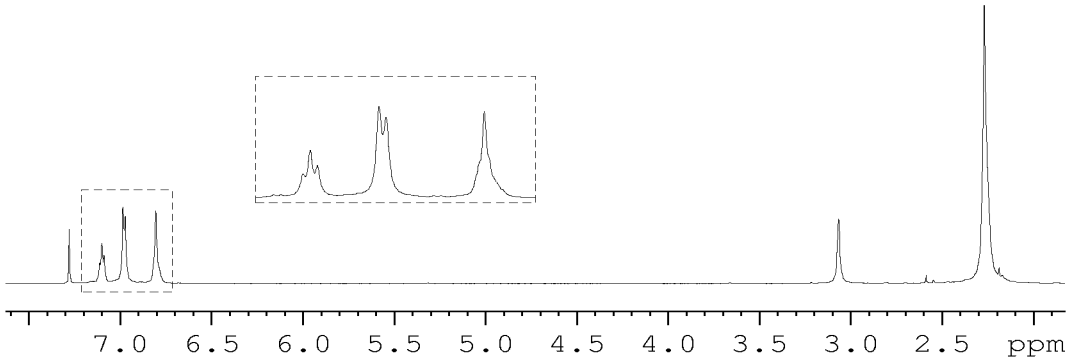
Elemental analysis (%):	C, 53.76	H, 4.56	N, 6.29
Calcd for $C_{90}H_{90}I_3N_9Pd_3$:	C, 54.11	H, 4.54	N, 6.31

Melting point: 229 ^{o}C (dec).

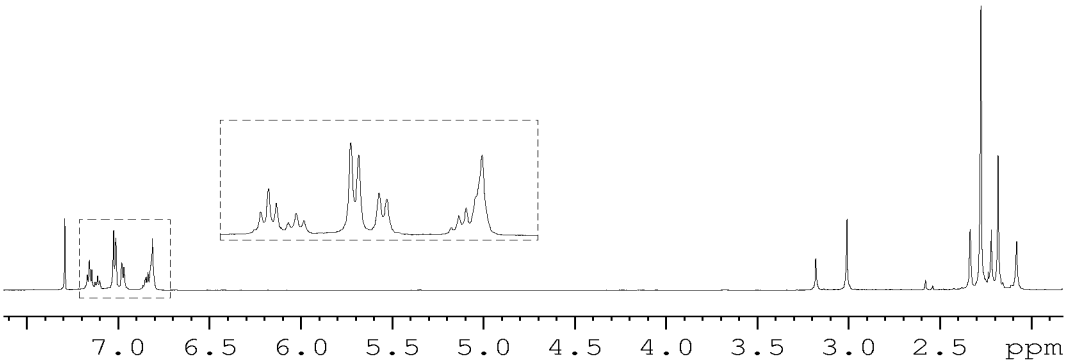
Solubility: Soluble in CH_2Cl_2, $CHCl_3$, and acetone. Insoluble in Et_2O and hexane.



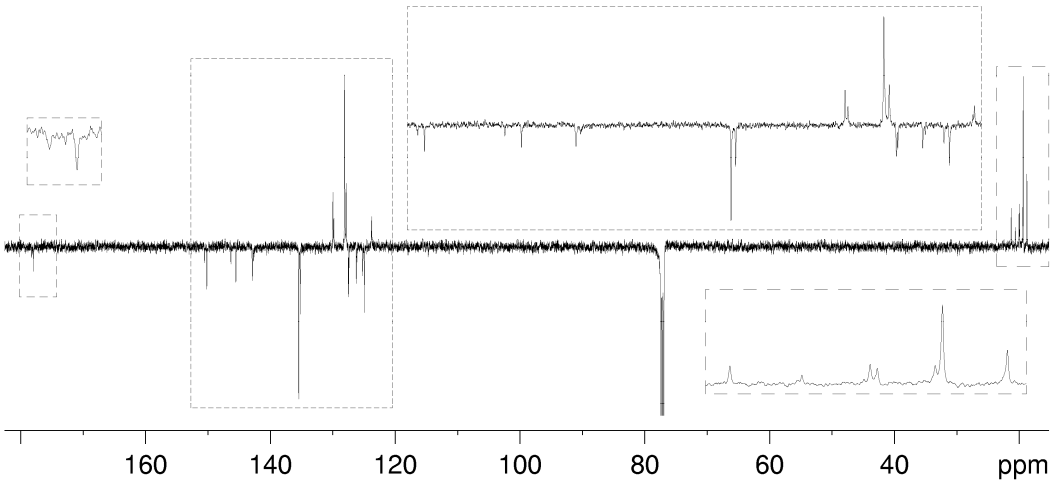
IR spectrum of 32 (298K)



^{1}H NMR spectrum (600 MHz, 298K) of 32

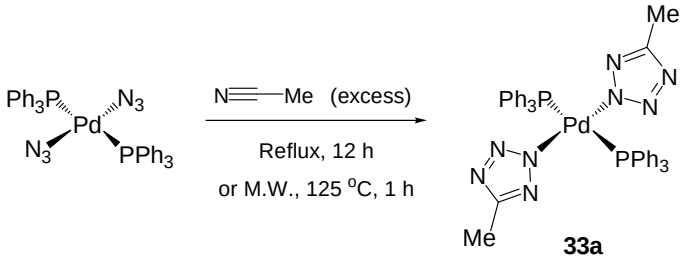


^{1}H NMR spectrum (600 MHz, 243K) of 32



APT spectrum (150.9 MHz, 243K) of 32

***trans*-[Pd(N$_4$CMe)$_2$(PPh$_3$)$_2$] (33a)**



33a

This complex was prepared by two different methods:

(i) By refluxing: A solution of *trans*-[Pd(N$_3$)$_2$(PPh$_3$)$_2$] (20.0 mg, 0.028 mmol) in acetonitrile (4 mL) was refluxed for 12 h, whereupon the solvent was removed in vacuo. The residue was washed with Et$_2$O to obtain a white crystalline solid. Recrystallization from a CHCl$_3$/Et$_2$O mixture gave the complex **33a** as a white solid. Yield: 60%.

(ii) By focused microwave irradiation: Identical amounts of the reagents described above were added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under irradiation for 1 h at 125 ºC. The solvent was then removed in vacuo and the resulting solid residue was treated in a manner similar to that described above to obtain **33a** as a white crystalline solid**.** Yield: 58%.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (CDCl$_3$): 1.88, 2.01, 2.21, and 2.24 (s, 6H, Me), 7.30-7.72 (m, 30H, aromatic).

^{13}C{^{1}H} NMR (CDCl$_3$): 9.93, 9.95, 10.60, and 10.69 (Me), 125.44-135.64 (C$_{aromatic}$), 151.44, 156.74, 157.01, and 161.27 (C=N).

^{31}P{^{1}H} NMR (CDCl$_3$): 17.65, *18.08*, 23.02 and 29.19 (the signal in *italic* was not observed when the complex was prepared under refluxing conditions).

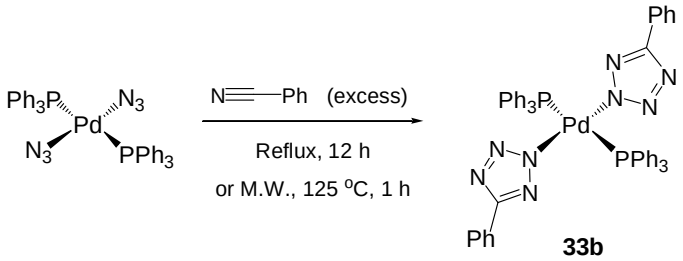
IR (cm^{-1}, KBr): 693 and 1436 (PPh$_3$), 1630 (C=N)

Elemental analysis (%):	C, 60.51	H, 4.31	N, 14.30
Calcd for $C_{40}H_{36}N_8P_2Pd$:	C, 60.27	H, 4.55	N, 14.06

Solubility: Soluble in CH$_2$Cl$_2$, CHCl$_3$, and acetone. Insoluble in Et$_2$O and hexane.

ESI$^+$-MS: *m*/*z* 798 [M+1]$^+$

***trans*-[Pd(N$_4$CPh)$_2$(PPh$_3$)$_2$] (33b)**



33b

This complex was prepared by two different methods:

(i) By refluxing: A solution of *trans*-[Pd(N$_3$)$_2$(PPh$_3$)$_2$] (20.0 mg, 0.028 mmol) in benzonitrile (4 mL) was refluxed for 12 h, whereupon the solvent was removed in vacuo. The residue was washed with Et$_2$O to obtain a white crystalline solid. Recrystallization from a CHCl$_3$/Et$_2$O mixture gave the complex **33b** as a white solid. Yield: 58%.

(ii) By focused microwave irradiation: Identical amounts of the reagents described above were added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under irradiation for 1 h at 125 ºC. The solvent was then removed in vacuo and the resulting solid residue was treated in a manner similar to that described above to obtain **33b** as a white crystalline solid**.** Yield: 62%.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (CDCl$_3$): 7.21–7.59 (m, 40H, aromatic).

^{13}C{^{1}H} NMR (CDCl$_3$): 126.24–135.52 (C$_{aromatic}$), 164.54 (C=N).

^{31}P{^{1}H} NMR (CDCl$_3$): *18.40*, 22.82, and 29.25 (only the signal in *italic* was observed when the complex was obtained under refluxing conditions).

IR (cm^{-1}, KBr): 693 and 1437 (PPh$_3$), 1638 (C=N)

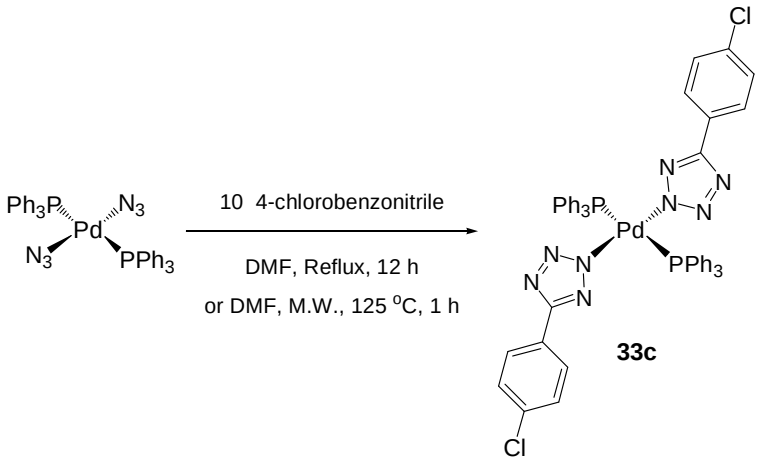
Elemental analysis (%):	C, 65.56	H, 4.19	N, 11.93
Calcd for C$_{50}$H$_{40}$N$_8$P$_2$Pd:	C, 65.19	H, 4.38	N, 12.16

Solubility: Soluble in CH$_2$Cl$_2$, CHCl$_3$, and acetone. Insoluble in Et$_2$O and hexane.

ESI$^+$-MS: *m*/*z* 922 [M+1]$^+$.

X-ray crystallography: Single crystals of **33b** were grown by slow evaporation of a CHCl$_3$ solution of the product.

***trans*-[Pd(N$_4$C(4-ClC$_6$H$_4$))$_2$(PPh$_3$)$_2$] (33c)**



This complex was prepared by two different methods:

(i) By refluxing: To a 4 mL solution of *trans*-[Pd(N$_3$)$_2$(PPh$_3$)$_2$] (20.0 mg, 0.028 mmol) in DMF was added 4-chlorobenzonitrile (0.280 mmol). The resulting mixture was refluxed for 12 h. The solution became turbid as the product started to precipitate. The mixture was cooled and the solid was filtered off, washed several times with 5 mL portions of Et$_2$O, and dried in vacuo to give **33c** as a white solid. Yield: 55%

(ii) By focused microwave irradiation: Complex **33c** was also prepared by dissolving the above mentioned amounts of the reagents in DMF (4 mL) and irradiating the solution with focused microwave for 1 h at 125 ºC. A white precipitate formed which was washed several times with Et$_2$O and dried in vacuo to give **33c** as a white solid. Yield: 58%.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (CDCl$_3$): 7.19–7.79 (m, 38H, aromatic).

^{13}C{^{1}H} NMR (CDCl$_3$): 127.39–135.63 (C$_{aromatic}$). The signal of the imine moiety (C=N) could not be observed even after more scans and/or by using DMSO-*d*$_6$ as solvent.

^{31}P{^{1}H} NMR (CDCl$_3$): 18.53, 20.05, 22.91, and 29.23 (only one signal of ^{31}P{^{1}H} NMR in DMSO-*d*$_6$ at δ 25.65 was observed when the complex was obtained under refluxing conditions).

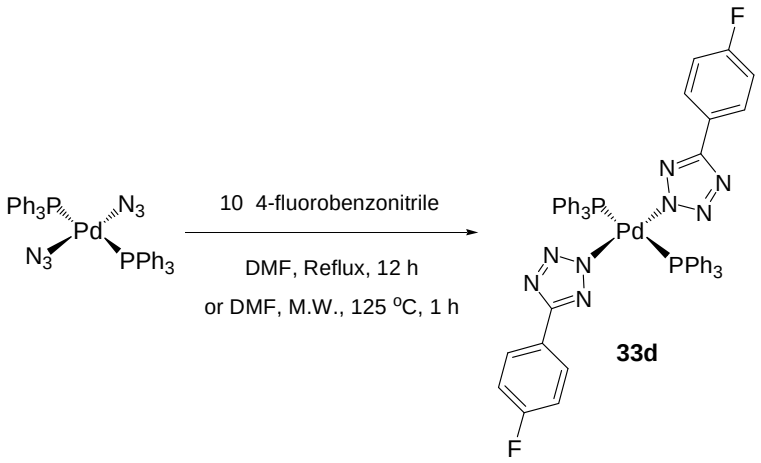
IR (cm^{-1}, KBr): 691 and 1438 (PPh$_3$), 1630 (C=N)

Elemental analysis (%):	C, 60.41	H, 3.71	N, 11.50
Calcd for $C_{50}H_{38}Cl_2N_8P_2Pd$:	C, 60.65	H, 3.87	N, 11.32

Solubility: Soluble in CH$_2$Cl$_2$, CHCl$_3$, and acetone. Insoluble in Et$_2$O and hexane.

ESI$^+$-MS: *m*/*z* 991 [M+1]$^+$.

***trans*-[Pd(N$_4$C(4-FC$_6$H$_4$))$_2$(PPh$_3$)$_2$] (33d)**



This complex can be prepared by two different methods:

(i) By refluxing: To a 4 mL solution of *trans*-[Pd(N$_3$)$_2$(PPh$_3$)$_2$] (20.0 mg, 0.028 mmol) in DMF was added 4-fluorobenzonitrile (0.280 mmol). The resulting mixture was refluxed for 12 h. The solution became turbid as the product started to precipitate. The mixture was cooled and the solid was filtered off, washed several times with 5 mL portions of Et$_2$O, and dried in vacuo to give **33d** as a white solid. Yield: 54%

(ii) By focused microwave irradiation: Complex **33d** was also prepared by dissolving the above mentioned amounts of the reagents in DMF (4 mL) and irradiating the solution with focused microwave for 1 h at 125 ºC. A white precipitate formed which was washed several times with Et$_2$O and dried in vacuo to give **33d** as a white solid. Yield: 56%.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (CDCl$_3$): 7.26–7.71 (m, 38H, aromatic).

^{13}C{^{1}H} NMR (CDCl$_3$): 129.17–133.71 (C$_{aromatic}$), 161.11, 161.83, and 162.41 (C=N).

^{31}P{^{1}H} NMR (DMSO-d$_6$): 25.50.

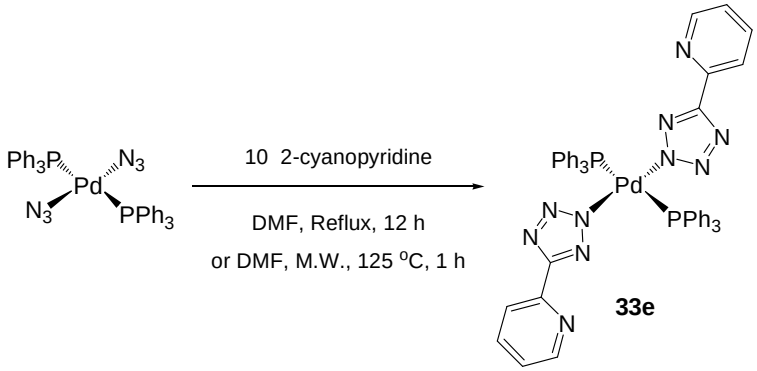
IR (cm^{-1}, KBr): 694 and 1451 (PPh$_3$), 1615 (C=N)

Elemental analysis (%):	C, 62.41	H, 4.21	N, 11.49
Calcd for $C_{50}H_{38}F_2N_8P_2Pd$:	C, 62.74	H, 4.00	N, 11.71

Solubility: Soluble in CH$_2$Cl$_2$, CHCl$_3$, and acetone. Insoluble in Et$_2$O and hexane.

ESI$^+$-MS: *m*/*z* 958 [M+1]$^+$

***trans*-[Pd($N_4C(2\text{-}NC_5H_4)$)$_2$(PPh_3)$_2$] (33e)**



This complex can be prepared by two different methods:

(i) By refluxing: To a 4 mL solution of *trans*-[Pd(N_3)$_2$(PPh_3)$_2$] (20.0 mg, 0.028 mmol) in DMF was added 2-cyanopyridine (0.280 mmol). The resulting mixture was refluxed for 12 h. The solution became turbid as the product started to precipitate. The mixture was cooled and the solid was filtered off, washed several times with 5 mL portions of Et_2O, and dried in vacuo to give **33e** as a white solid. Yield: 60%

(ii) By focused microwave irradiation: Complex **33e** was also prepared by dissolving the above mentioned amounts of the reagents in DMF (4 mL) and irradiating the solution with focused microwave for 1 h at 125 ºC. A white precipitate formed which was washed several times with Et_2O and dried in vacuo to give **33e** as a white solid. Yield: 62%.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR ($CDCl_3$): 7.34–7.75 (m, 38H, aromatic).

^{13}C{^{1}H} NMR ($CDCl_3$): This spectrum was not possible to obtain due to the very poor solubility of **33e** in common solvents ($CDCl_3$, MeOD-d_4 or DMSO-d_6).

^{31}P{^{1}H} NMR ($CDCl_3$): 23.50

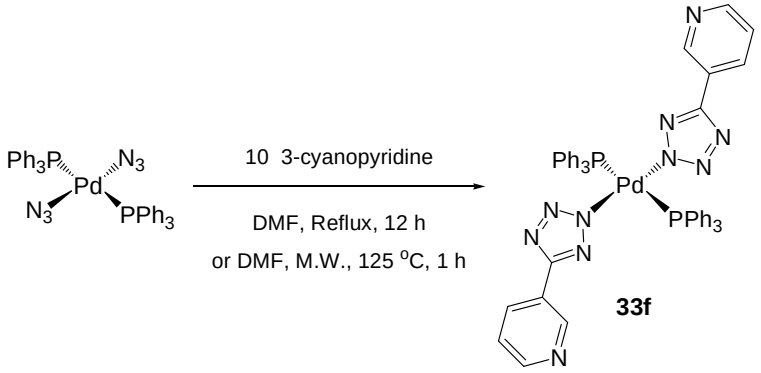
IR (cm^{-1}, KBr): 719 and 1450 (PPh_3), 1619 (C=N)

Elemental analysis (%):	C, 62.33	H, 4.44	N, 15.45
Calcd for $C_{48}H_{38}N_{10}P_2Pd$:	C, 62.44	H, 4.15	N, 15.17

Solubility: Only slightly soluble in $CHCl_3$, MeOH or DMSO. Insoluble in Et_2O and hexane.

ESI$^+$-MS: *m*/*z* 924 $[M+1]^+$

***trans*-[Pd(N$_4$C(3-NC$_5$H$_4$))$_2$(PPh$_3$)$_2$] (33f)**



This complex can be prepared by two different methods:

(i) By refluxing: To a 4 mL solution of *trans*-[Pd(N$_3$)$_2$(PPh$_3$)$_2$] (20.0 mg, 0.028 mmol) in DMF was added 3-cyanopyridine (0.280 mmol). The resulting mixture was refluxed for 12 h. The solution became turbid as the product started to precipitate. The mixture was cooled and the solid was filtered off, washed several times with 5 mL portions of Et$_2$O, and dried in vacuo to give **33f** as a white solid. Yield: 61%

(ii) By focused microwave irradiation: Complex **33f** was also prepared by dissolving the above mentioned amounts of the reagents in DMF (4 mL) and irradiating the solution with focused microwave for 1 h at 125 ºC. A white precipitate formed which was washed several times with Et$_2$O and dried in vacuo to give **33f** as a white solid. Yield: 60%.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (CDCl$_3$): 7.44–7.72 (m, 38H, aromatic).

^{13}C{^{1}H} NMR (CDCl$_3$): 128.40–134.02 (C$_{aromatic}$). The signal of the imine moiety (C=N) could not be observed even after more scans.

^{31}P{^{1}H} NMR (CDCl$_3$): 29.25.

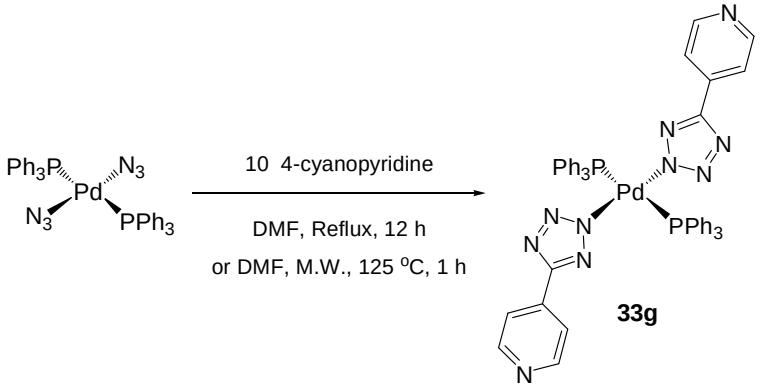
IR (cm^{-1}, KBr): 693 and 1436 (PPh$_3$), 1630 (C=N)

Elemental analysis (%):	C, 62.38	H, 4.55	N, 15.37
Calcd for C$_{48}$H$_{38}$N$_{10}$P$_2$Pd:	C, 62.44	H, 4.15	N, 15.17

Solubility: Soluble in CHCl$_3$, CH$_2$Cl$_2$ and acetone. Insoluble in Et$_2$O and hexane.

ESI$^+$-MS: *m*/*z* 924 [M+1]$^+$

***trans*-[Pd($N_4C(4\text{-}NC_5H_4)$)$_2$(PPh_3)$_2$] (33g)**



This complex can be prepared by two different methods:

(i) By refluxing: To a 4 mL solution of *trans*-[Pd(N_3)$_2$(PPh_3)$_2$] (20.0 mg, 0.028 mmol) in DMF was added 4-cyanopyridine (0.280 mmol). The resulting mixture was refluxed for 12 h. The solution became turbid as the product started to precipitate. The mixture was cooled and the solid was filtered off, washed several times with 5 mL portions of Et_2O, and dried in vacuo to give **33g** as a white solid. Yield: 63%

(ii) By focused microwave irradiation: Complex **33g** was also prepared by dissolving the above mentioned amounts of the reagents in DMF (4 mL) and irradiating the solution with focused microwave for 1 h at 125 ºC. A white precipitate formed which was washed several times with Et_2O and dried in vacuo to give **33g** as a white solid. Yield: 65%.

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR ($CDCl_3$): 7.19–7.67 (m, 38H, aromatic).

^{13}C{^{1}H} NMR ($CDCl_3$): 120.80–150.15 ($C_{aromatic}$), 161.67, 161.87, 162.09, and 162.50 (C=N).

^{31}P{^{1}H} NMR ($CDCl_3$): 18.96, *24.22*, 26.34, and 29.41 (only the signal in *italic* was observed when the complex was obtained under refluxing conditions).

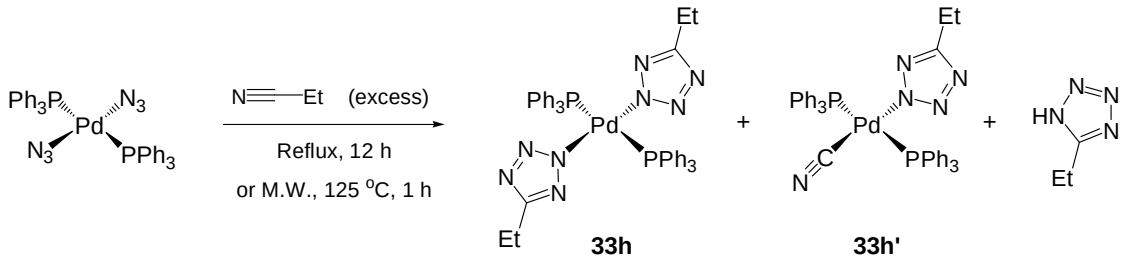
IR (cm^{-1}, KBr): 694 and 1436 (PPh_3), 1619 (C=N)

Elemental analysis (%):	C, 62.41	H, 4.20	N, 15.27
Calcd for $C_{48}H_{38}N_{10}P_2Pd$:	C, 62.44	H, 4.15	N, 15.17

Solubility: Soluble in $CHCl_3$, CH_2Cl_2 and acetone. Insoluble in Et_2O and hexane.

ESI$^+$-MS: *m*/*z* 924 $[M+1]^+$

***trans*-[Pd(N$_4$CEt)$_2$(PPh$_3$)$_2$] (33h) + *trans*-[Pd(CN)(N$_4$CEt)(PPh$_3$)$_2$] (33h´) + 5-ethyl-1*H*-tetrazole**



A solution of *trans*-[Pd(N$_3$)$_2$(PPh$_3$)$_2$] (20.0 mg, 0.028 mmol) in propionitrile (4 mL) was refluxed for 12 h or irradiated under M.W. (1 h, 125 ºC, 300 W) whereupon the solvent was removed *in vacuo*. The white solid (**33h** and **33h´**) was filtered off and washed with Et$_2$O for several times. The mother liquor was evaporated to dryness and the resulting compound was identified as 5-ethyl-1*H*-tetrazole.

Data for *trans*-[Pd(N$_4$CEt)$_2$(PPh$_3$)$_2$] (33h) + *trans*-[Pd(CN)(N$_4$CEt)(PPh$_3$)$_2$] (33h´):

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR ($CDCl_3$): 0.84-1.33 (m, 9H, CH_3), 2.18-2.37 (m, 6H, CH_2), 7.35–7.69 (m, 60H, aromatic).

^{13}C{^{1}H} NMR ($CDCl_3$): 10.87, 12.41, and 12.55 (CH_3), 18.64 and 18.78 (CH_2), 126.97 (C≡N), 127.59–134.39 ($C_{aromatic}$), 166.53 (C=N).

^{31}P{^{1}H} NMR ($CDCl_3$): 23.0 and 30.2.

IR (cm^{-1}, KBr): 2139 (C≡N), 1630 (C=N)

Solubility: Soluble in $CHCl_3$, CH_2Cl_2 and acetone. Insoluble in Et_2O and hexane.

ESI$^+$-MS: *m*/*z* 825 $[M+1]^+$ (**33h**) and 755 $[M+1]^+$ (**33h´**).

Data for 5-ethyl-1*H*-tetrazole:

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR ($CDCl_3$): 1.30 (t, J_{HH} = 7.6 Hz, 3H, CH_3), 2.87 (q, J_{HH} = 7.6 Hz, 2H, CH_2).

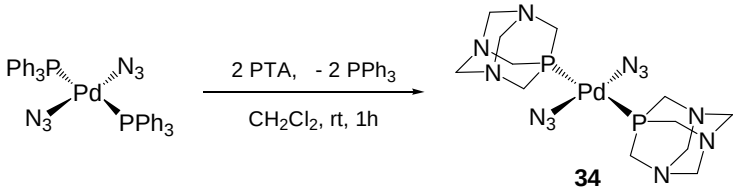
^{13}C{^{1}H} NMR ($CDCl_3$): 14.16 (CH_3), 19.33 (CH_2), 159.86 (C=N)

IR (cm^{-1}, KBr): 1638 (C=N)

ESI$^+$-MS: *m*/*z* 99 $[M+1]^+$

Solubility: Soluble in $CHCl_3$, CH_2Cl_2, acetone and Et_2O.

$[Pd(N_3)_2(PTA)_2]\cdot CH_2Cl_2$ ($34\cdot CH_2Cl_2$)



To a solution of *trans*-$[Pd(N_3)_2(PPh_3)_2]$ (200.0 mg, 0.28 mmol) in CH_2Cl_2 (25 mL), PTA (88.0 mg, 0.56 mmol) was added. The mixture was stirred for *ca.* 1 h under N_2 at room temperature. The yellow precipitate was separated from the brown solution by filtration, washed with $CHCl_3$ (3 x 10 mL) and dried in vacuo to afford complex **34**$\cdot CH_2Cl_2$ as a yellow microcrystalline solid. Yield: 85 mg (60%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (DMSO-d_6): 5.75 (s, CH_2Cl_2, 2H), 4.53 H^A and 4.41 H^B (J_{AB} = 13.0 Hz, NCH^AH^BN, 12H), 4.35 (s, PCH_2N, 12H).

^{13}C{^{1}H} NMR (DMSO-d_6): 72.6 (s, N-CH_2-N, PTA), 55.8 (s, CH_2Cl_2), 52.3 (br s, P-CH_2-N, PTA).

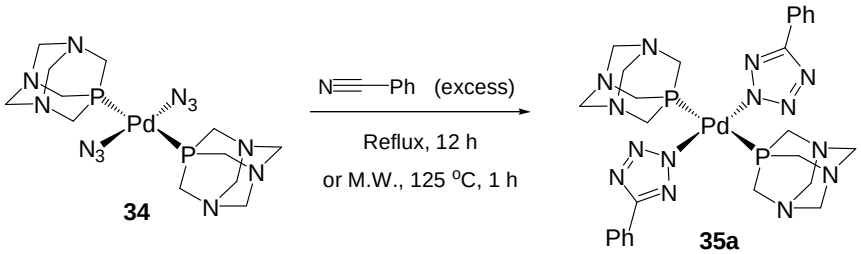
^{31}P{^{1}H} NMR (DMSO-d_6): -30.2 (s).

IR (cm^{-1}, KBr): 2930 (s br) ν(CH), 2037 (s br) ν(N_3), 1278 (m), 1242 (s), 1099 (m), 1014 (s), 972 (s), 943 (s), 904 (m), 805 (m), 741 (m), 582 (m) (PTA) cm^{-1}.

Elemental analysis (%):	C, 26.00	H, 29.11	N, 4.45
Calcd for $C_{13}H_{26}Cl_2N_{12}P_2Pd$ (**34**$\cdot CH_2Cl_2$):	C, 26.48	H, 28.50	N, 4.44

Solubility: Soluble in H_2O and DMSO, slightly soluble in MeOH and CH_2Cl_2, and insoluble in C_6H_6.

***trans*-[Pd(N$_4$CPh)$_2$(PTA)$_2$]·PhCN (35a·PhCN)**



A mixture of [Pd(N$_3$)$_2$(PTA)$_2$]·CH$_2$Cl$_2$ (**34**·CH$_2$Cl$_2$) (59.0 mg, 0.10 mmol) and benzonitrile (5 mL, 48.5 mmol) was added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under irradiation for 1 h at 125 ºC (the same product was obtained when the mixture of reagents was refluxed for 12 h). After reaction, the excess of benzonitrile was removed in vacuo and the resulting residue was washed repeatedly with 10 mL portions of Et$_2$O. Recrystallization from a CH$_2$Cl$_2$/Et$_2$O mixture afforded complex **35a**·PhCN as a yellow microcrystalline solid. Yield: 45 mg (55%).

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^{1}H NMR (CDCl$_3$): 8.18-7.45 (m, 2Ph + PhCN, 15H), 4.48 H^A and 4.40 H^B (J_{AB} = 15.0 Hz, NCH^{A}H^{B}N, 12H), 4.20 (s, PCH$_2$N, 12H).

^{13}C{^{1}H} NMR (CDCl$_3$,): 165.0 (s, N$_4$C), 126.4-135.0 (C$_{aromatic}$), 73.1 (s, N-CH$_2$-N, PTA), 50.9 (br s, P-CH$_2$-N, PTA).

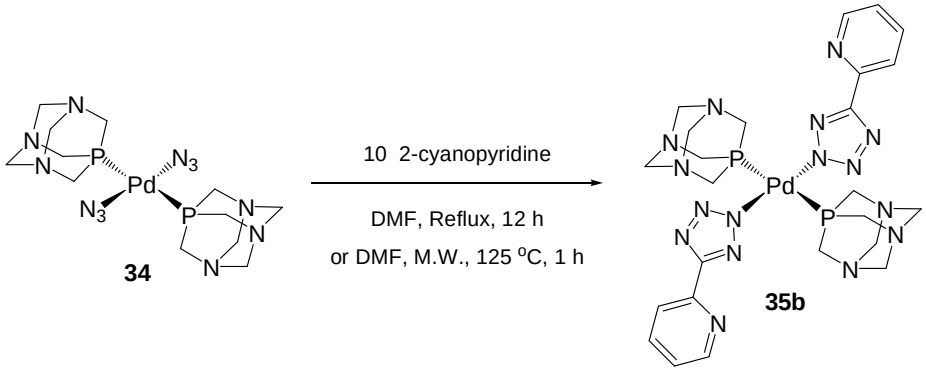
^{31}P{^{1}H} NMR (CDCl$_3$):- 47.3 (s).

IR (cm^{-1}, KBr): 2931 (m br), 2230 (w), 1629 (m), 1443 (m), 1384 (m), 1369 (w), 1285 (m), 1245 (m), 1101 (m), 1013 (s), 975 (s), 945 (s), 800 (m), 741 (m), 580 (m).

Elemental analysis (%):	C, 48.38	H, 24.76	N, 4.50
Calcd for C$_{33}$H$_{39}$N$_{15}$P$_2$Pd (**35a**·PhCN):	C, 48.68	H, 25.81	N, 4.83

Solubility: Soluble in DMSO, CHCl$_3$, and CH$_2$Cl$_2$, sparingly soluble in H$_2$O, and insoluble in Et$_2$O and C$_6$H$_6$.

***trans*-[Pd($N_4C(2\text{-}NC_5H_4)$)$_2$(PTA)$_2$] (35b)**



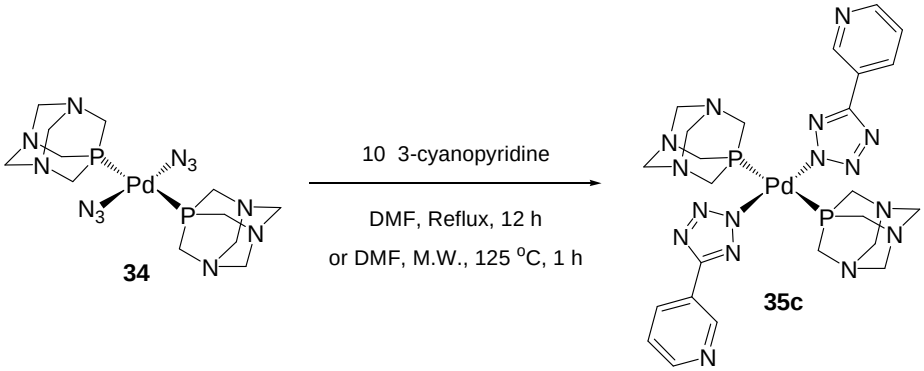
A mixture of [Pd(N_3)$_2$(PTA)$_2$]·CH_2Cl_2 (**34**·CH_2Cl_2) (59.0 mg, 0.10 mmol) and 2-cyanopyridine (104 mg, 1.0 mmol) in DMF (5 mL) was added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under irradiation for 1 h at 125 ºC (the same products were obtained when the mixture of reagents in DMF was refluxed for 12 h). After reaction, the solvent was removed in vacuo and the resulting residue was washed repeatedly with 10 mL portions of EtOH and Et_2O affording complex **35b** as a yellow microcrystalline solid. Yield: 39 mg (55%).

IR (cm^{-1}, KBr): 2933 (m br), 1671 (m), 1619 (m), 1449 (m), 1421 (m), 1284 (m), 1168 (m), 1010 (s), 974 (s), 945 (s), 808 (m), 580 (m).

Elemental analysis (%):	C, 40.50	H, 4.50	N, 30.11
Calcd for $C_{24}H_{32}N_{16}P_2Pd$:	C, 40.43	H, 4.52	N, 31.43

Solubility: Insoluble in common organic solvents and water.

***trans*-[Pd(N$_4$C(3-NC$_5$H$_4$))$_2$(PTA)$_2$] (35c)**



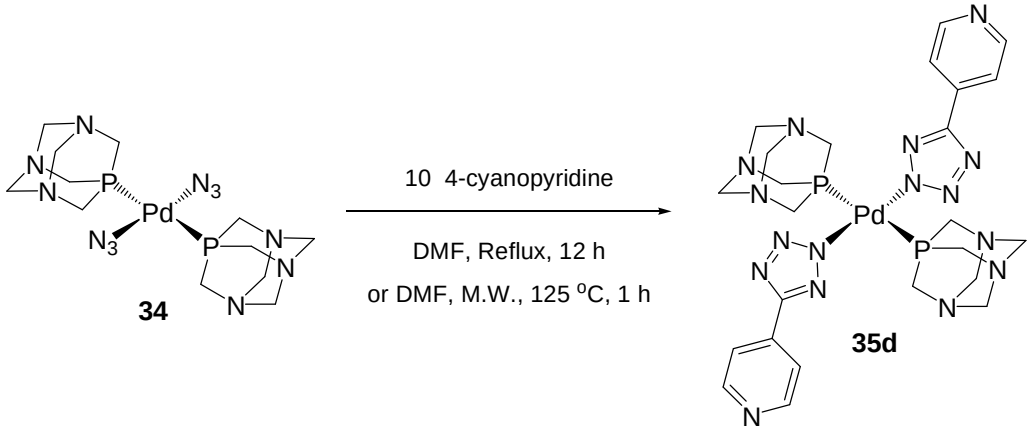
A mixture of [Pd(N$_3$)$_2$(PTA)$_2$]·CH$_2$Cl$_2$ (**34**·CH$_2$Cl$_2$) (59.0 mg, 0.10 mmol) and 3-cyanopyridine (104 mg, 1.0 mmol) in DMF (5 mL) was added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under irradiation for 1 h at 125 ºC (the same products were obtained when the mixture of reagents in DMF was refluxed for 12 h). After reaction, the solvent was removed in vacuo and the resulting residue was washed repeatedly with 10 mL portions of EtOH and Et$_2$O affording complex **35c** as a yellow microcrystalline solid. Yield: 36 mg (50%).

IR (cm^{-1}, KBr): 2933 (m br), 1634 (m), 1423 (m), 1284 (m), 1241 (m), 1097 (m), 1011 (s), 974 (s), 945 (s), 807 (m), 580 (m) cm^{-1}.

Elemental analysis (%):	C, 40.98	H, 4.48	N, 32.00
Calcd for C$_{24}$H$_{32}$N$_{16}$P$_2$Pd:	C, 40.43	H, 4.52	N, 31.43

Solubility: Insoluble in common organic solvents and water.

***trans*-[Pd($N_4C(4\text{-}NC_5H_4)$)$_2$(PTA)$_2$] (35d)**



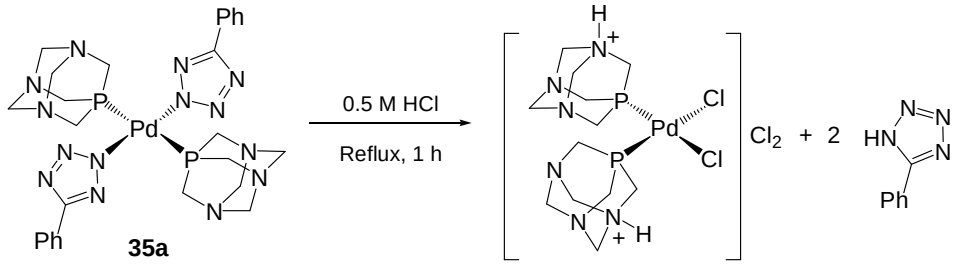
A mixture of [Pd(N_3)$_2$(PTA)$_2$]·CH_2Cl_2 (**34**·CH_2Cl_2) (59.0 mg, 0.10 mmol) and 4-cyanopyridine (104 mg, 1.0 mmol) in DMF (5 mL) was added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under irradiation for 1 h at 125 ºC (the same products were obtained when the mixture of reagents in DMF was refluxed for 12 h). After reaction, the solvent was removed in vacuo and the resulting residue was washed repeatedly with 10 mL portions of EtOH and Et_2O affording complex **35d** as a yellow microcrystalline solid. Yield: 37 mg (52%).

IR (cm^{-1}, KBr): 2936 (m br), 1671 (w), 1622 (m), 1446 (m), 1420 (m), 1283 (m), 1242 (m), 1097 (m), 1036 (m), 1011 (s), 973 (s), 944 (s), 803 (m), 700 (m), 580 (m).

Elemental analysis (%):	C, 40.40	H, 4.50	N, 31.00
Calcd for $C_{24}H_{32}N_{16}P_2Pd$:	C, 40.43	H, 4.52	N, 31.43

Solubility: Insoluble in common organic solvents and water.

$[PdCl_2(PTA\text{-}H)_2]Cl_2$ (36) (Liberation of 5-phenyl-1*H*-tetrazole from 35a)



35a **36**

A yellow suspension of *trans*-$[Pd(N_4CPh)_2(PTA)_2]\cdot PhCN$ (**35a**·PhCN) (40.7 mg, 0.05 mmol), in aqueous 0.5 M HCl (10 mL) was refluxed for 1 h. The white precipitate formed during the reaction was separated by filtration and extracted with $CHCl_3$. The extract was shown (by IR and NMR spectroscopies) to contain the corresponding 5-phenyl-1*H*-tetrazole.[13] The remaining white-yellow precipitate (insoluble in $CHCl_3$) was shown, by IR (KBr) and elemental analysis, to be $[PdCl_2(PTA\text{-}H)_2]Cl_2$ (**36**) (PTA-H = *N*-protonated PTA cation). The insolubility of **36** in common solvents precluded direct NMR analysis, but, upon addition of a diluted NaOH solution in D_2O (in an NMR tube), the $^{31}P\{^1H\}$NMR spectrum exhibits the expected signal of the known deprotonated complex $[PdCl_2(PTA)_2]$.[14] Additionally, its ESI^+-MS spectrum showed the expected (for the deprotonated complex) isotopic pattern centred at m/z 491 ($[M + 1]^+$).

Data for 36:

IR (cm^{-1}, KBr): 2925 (m br), 1443 (m), 1418 (m), 1365 (w), 1286 (m), 1241 (m), 1103 (m), 1014 (s), 973 (s), 898 (m), 810 (m), 740 (m), 575 (m).

Elemental analysis (%):	C, 25.60	H, 4.71	N, 14.55
Calcd for $C_{12}H_{26}Cl_4N_6P_2Pd$:	C, 25.53	H, 4.64	N, 14.89

Solubility: Insoluble in common organic solvents and water.

Data for 5-phenyl-1*H*-tetrazole:

NMR data. δ(ppm) (multiplicity, J[Hz], integral, assignment):

^1H NMR ($CDCl_3$): 7.43–8.16 (m, 5H, aromatic).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): 126.34–133.93 ($C_{aromatic}$), 158.49 (C=N).

IR (cm^{-1}, KBr): 1636 (C=N) **ESI^+-MS**: *m*/*z* 145 $[M\text{-}H]^-$

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CHAPTER IX

Conclusions

1. New aryl Pd(II) complexes (**1a-c**, see the General Compound Chart in pp xxiii-xxiv), have been synthesized by oxidative addition reactions of 2-iodobenzyl alcohol to [Pd(dba)$_2$]. By reaction of **1a** with XyNC or with KO^{t}Bu the product of an insertion (**2**), or deprotonation (**3**) reaction, respectively, has been obtained. Complex **3** crystallizes as pairs of molecules bridged by hydrogen bonds to water of crystallization.

2. Complex **3** reacts with CO or XyNC forming, respectively, phthalide or the cyclic imidate *N*-(2,6-dimethylphenyl)-2-benzofuran-1(*3H*)-imine (**4**), which had not been previously described.

3. The nucleophilic attack of **3** at the alkyl group of primary alkyl halides (RCH$_2$X) results in the opening of the chelate ring and the formation of complexes **5**, with new RCH$_2$-O and Pd-X bonds. There is no precedent in the literature for this type of reactivity in a *C,O*-cyclometalated aryl group. Two novel dinuclear bis(arylpalladium) complexes have been prepared, either by reaction of **3** with *p*-C$_6$H$_4$(CH$_2$Br)$_2$ (complex **6**) or by reaction of **5f** (R = *p*-C$_6$H$_4$I) with [Pd(dba)$_2$] (complex **7**). **6** and **7** are the first examples of bis(arylpalladium) complexes where the aryl groups are *ortho*-substituted.

4. Complex **3** reacts with acetonitrile, cyanamides, or carbodiimides, in the presence of AgOTf and residual water, to form ionic complexes (**8-10**) resulting from the insertion of the organic molecules into the O-Pd bond of **3**, and the protonation of one of the N atoms. These reactions are suggested to proceed via a nucleophilic attack of **3** on the organic molecule, previously activated by the coordination to Ag$^+$ (an unprecedented observation). In the absence of AgOTf complex **3** only reacts cleanly with ToN=C=NTo, forming a neutral complex **11**, which is the conjugate base of **10b**. Complexes **10b** and **11** can be interconverted by deprotonation or protonation reactions.

5. An heterometallic bis-chelate Pd$_2$Ag complex (**12 =** [Ag(*N*-**11**)$_2$](OTf)) has been isolated and characterized. Its novel structure has been confirmed by X-ray crystallography.

6. Only in the reaction of **1a** with ^{i}PrN=C=N^{i}Pr in the presence of TlOTf (instead of AgOTf) a complex (**13**) resulting from the insertion of the carbodiimide into the

aryl-Pd bond of **1a** could be isolated. Thus, the reactivity of **1a** and **3** toward nitriles, cyanamides, and carbodiimides has been shown to differ from that previously described for *ortho*-phenol Pd(II) complexes, for which the OH group directly bonded to the arene promoted clean insertion reactions of the organic molecules into the aryl-Pd bond.

7. We have prepared mono- (**15**) and di-palladated (**14**) benzene derivatives with alkenyl groups at the *ortho* position, by oxidative addition of *trans,trans*-2,5-distyryl-2,4-dibromobenzene to one or two equivalents of $[Pd(dba)_2]$. In their reactions with alkynes we have obtained highly substituted indenylpalladium complexes (**19-21**) and dipalladated indacenediides (**16-18**). This is the first synthesis of this type of dinuclear complexes through metal-mediated building of the ligand. X-ray and ^{13}C NMR data both suggest a significantly slipped η^3 coordination mode for the indenyl and indacenediyl ligands in **16-21**.

8. The reactivity toward XyNC of the dipalladated benzene derivatives **14** has resulted in the first reported simultaneous insertion of isocyanide into two aryl-Pd bonds on the same benzene ring, forming the monoinserted dinuclear complex **22**. The synthesis of complexes **16-22** is the first study of the reactivity of dipalladated arene derivatives with unsaturated reagents.

9. The oxidative addition of *trans,trans*-2,5-distyryl-1,4-dibromobenzene to $[Pd(dba)_2]$ in the presence of XyNC has afforded a mixture of two isomeric dinuclear complexes (**23**,**23***) with three isocyanide molecules inserted into each aryl-Pd bond. Both isomers are in slow exchange in solution, as shown by a ^1H-EXSY NMR spectrum.

10. We have prepared two dipalladated derivatives of terephthalaldehyde (**25a,b**), by hydrolysis of a previously described dipalladated Schiff base (**IX**). A dicationic dinuclear derivative (**24**) of the Schiff base has also been characterized, including an X-ray diffraction structure.

11. The reaction of **25a,b** with CO results in the first insertion of CO into two separate aryl-metal bonds on the same aryl ligand, forming the dinuclear complexes **26a,b**. The NMR data of these complexes suggest that one of the inserted CO groups forms a hydrogen bond with the aryl hydrogen in *ortho* position, while the other does not.

12. The reaction of **25a** with XyNC yields a novel dinuclear Pd(II) complex (**27**), resulting from a double 3-fold insertion of XyNC into the aryl-Pd bonds, followed by the interaction of two of the inserted isocyanide molecules with the formyl groups in *ortho* position. No similar dinuclear complex had been described before.

13. By a Tl^{+}-promoted hydrolysis of **27** the central ligand can be released, yielding the heteropolycycle **28**.

14. We have prepared two tripalladated arene derivatives of general formula $C_6R_3[Pd]_3$ (**29a,b**) and four monopalladated complexes of general formula $C_6R_3X_2[Pd]$ (**30-31**), by oxidative addition reactions of 2,4,6-trisubstituted-1,3,5-haloarenes ($C_6R_3X_3$, R = CH_2OH, OH, OMe; X = Br, I) to $[Pd(dba)_2]$ in the presence of auxiliary ligands.

15. The first insertion of XyNC into three aryl-Pd bonds of a tripalladated arene (**XVIII**) has been achieved, resulting in a fluxional trinuclear complex (**32**) that has been investigated by VT-NMR.

16. The di(azido) compounds *trans*-$[Pd(N_3)_2(PPh_3)_2]$ and the hydrosoluble $[Pd(N_3)_2(PTA)_2]$ (**34**) are good starting materials for a variety of *trans*-bis(5-substituted tetrazolato)-Pd(II) complexes (**33**, **35**) derived upon [2+3] cycloadditions with nitriles. These reactions are greatly accelerated by microwave irradiation.

17. Propionitrile, on reaction with *trans*-$[Pd(N_4CEt)_2(PPh_3)_2]$ (**33h**), undergoes an unusual NC-C bond cleavage behaving as a source of a cyano ligand to give a mixed cyano-tetrazolato complex (**33h´**) and 5-ethyl-1*H*-tetrazole. This reaction proceeds via an unusual oxidative addition of the nitrile to Pd(II), followed by β-H-elimination from the derived ethyl ligand and reductive elimination of the tetrazole. This is the first synthesis of a mixed cyano-tetrazolato Pd(II) complex obtained by C-C bond cleavage of an organonitrile.

18. An X-ray diffraction study of **33b** shows that the *trans* arrangement of the two tetrazolato ligands appears to be the most favourable one, in contrast to previous reports. The X-ray structure also shows that the mode of tetrazolato binding is through the N^2-atom.

19. Taking advantage of the hydrosolubility of PTA, a simple liberation of the ligated tetrazolate from the coordination sphere of a bis(tetrazolato) Pd(II) complex (**35a**)

was achieved. This is a convenient metal-mediated synthetic method for substituted tetrazoles.

20. The complexes in this Thesis have been characterized by elemental analyses or high resolution mass spectroscopy, as well as IR and NMR (1D and 2D) spectroscopy. A total of 19 X-ray crystal structures have been solved.