



**UNIVERSIDAD DE MURCIA**

**ESCUELA INTERNACIONAL DE DOCTORADO**

**TESIS DOCTORAL**

**SYNTHESIS, PHOTOPHYSICAL PROPERTIES AND  
PHOTOCHEMICAL REACTIVITY OF CYCLOMETALATED  
PLATINUM(IV) COMPLEXES**

**SÍNTESIS, PROPIEDADES FOTOFÍSICAS Y  
REACTIVIDAD FOTOQUÍMICA DE COMPLEJOS  
CICLOMETALADOS DE PLATINO(IV)**

**D. Juan Carlos López López**

**2023**





**UNIVERSIDAD DE MURCIA**  
ESCUELA INTERNACIONAL DE DOCTORADO

TESIS DOCTORAL

SYNTHESIS, PHOTOPHYSICAL PROPERTIES AND  
PHOTOCHEMICAL REACTIVITY OF CYCLOMETALATED  
PLATINUM(IV) COMPLEXES

SÍNTESIS, PROPIEDADES FOTOFÍSICAS Y  
REACTIVIDAD FOTOQUÍMICA DE COMPLEJOS  
CICLOMETALADOS DE PLATINO(IV)

Autor: D. Juan Carlos López López

Director: D. Pablo González Herrero





**DECLARACIÓN DE AUTORÍA Y ORIGINALIDAD  
DE LA TESIS PRESENTADA EN MODALIDAD DE COMPENDIO O ARTÍCULOS PARA  
OBTENER EL TÍTULO DE DOCTOR**

*Aprobado por la Comisión General de Doctorado el 19-10-2022*

D./Dña. Juan Carlos López López

doctorando del Programa de Doctorado en

Química Básica y Aplicada

de la Escuela Internacional de Doctorado de la Universidad Murcia, como autor/a de la tesis presentada para la obtención del título de Doctor y titulada:

SYNTHESIS, PHOTOPHYSICAL PROPERTIES AND PHOTOCHEMICAL REACTIVITY OF  
CYCLOMETALATED PLATINUM(IV) COMPLEXES/SÍNTESIS, PROPIEDADES FOTOFÍSICAS Y  
REACTIVIDAD FOTOQUÍMICA DE COMPLEJOS CICLOMETALADOS DE PLATINO(IV)

y dirigida por,

D./Dña. Pablo González Herrero

**DECLARO QUE:**

La tesis es una obra original que no infringe los derechos de propiedad intelectual ni los derechos de propiedad industrial u otros, de acuerdo con el ordenamiento jurídico vigente, en particular, la Ley de Propiedad Intelectual (R.D. legislativo 1/1996, de 12 de abril, por el que se aprueba el texto refundido de la Ley de Propiedad Intelectual, modificado por la Ley 2/2019, de 1 de marzo, regularizando, aclarando y armonizando las disposiciones legales vigentes sobre la materia), en particular, las disposiciones referidas al derecho de cita, cuando se han utilizado sus resultados o publicaciones.

Además, al haber sido autorizada como compendio de publicaciones o, tal y como prevé el artículo 29.8 del reglamento, cuenta con:

- *La aceptación por escrito de los coautores de las publicaciones de que el doctorando las presente como parte de la tesis.*
- *En su caso, la renuncia por escrito de los coautores no doctores de dichos trabajos a presentarlos como parte de otras tesis doctorales en la Universidad de Murcia o en cualquier otra universidad.*

Del mismo modo, asumo ante la Universidad cualquier responsabilidad que pudiera derivarse de la autoría o falta de originalidad del contenido de la tesis presentada, en caso de plagio, de conformidad con el ordenamiento jurídico vigente.

En Murcia, a 28 de Septiembre de 2023

Fdo.: Juan Carlos López López

*Esta DECLARACIÓN DE AUTORÍA Y ORIGINALIDAD debe ser insertada en la primera página de la tesis presentada para la obtención del título de Doctor.*

Información básica sobre protección de sus datos personales aportados	
Responsable:	Universidad de Murcia. Avenida teniente Flomesta, 5. Edificio de la Convalecencia. 30003; Murcia. Delegado de Protección de Datos: dpd@um.es
Legitimación:	La Universidad de Murcia se encuentra legitimada para el tratamiento de sus datos por ser necesario para el cumplimiento de una obligación legal aplicable al responsable del tratamiento. art. 6.1.c) del Reglamento General de Protección de Datos
Finalidad:	Gestionar su declaración de autoría y originalidad
Destinatarios:	No se prevén comunicaciones de datos
Derechos:	Los interesados pueden ejercer sus derechos de acceso, rectificación, cancelación, oposición, limitación del tratamiento, olvido y portabilidad a través del procedimiento establecido a tal efecto en el Registro Electrónico o mediante la presentación de la correspondiente solicitud en las Oficinas de Asistencia en Materia de Registro de la Universidad de Murcia



## AGRADECIMIENTOS

Este espacio está dedicado a la expresión de mis mas sinceros agradecimientos hacia todas las personas que han influido de una manera u otra en este trabajo.

Primero me gustaría agradecer a mi tutor y director, el Dr. Pablo González Herrero, por haberme permitido trabajar con él y haberme guiado a lo largo de esta Tesis, haciéndola una experiencia verdaderamente enriquecedora. Él ha sido la persona que me ha formado profesionalmente como investigador y me ha enseñado no solo muchos conocimientos de química, si no de otros aspectos muy importantes en investigación como el rigor y la meticulosidad en el trabajo, haciéndome más perfeccionista y completo. Además, me gustaría destacar el buen trato y la involucración tanto personal como profesional que ha tenido hacia mí durante todos los años en los que hemos estado trabajando juntos.

También tengo que darle las gracias a todos mis compañeros de Tesis con los que he coincidido. Ellos están entre las personas con las que mas tiempo he compartido durante este período y siempre ha habido muy buen ambiente, compartiendo multitud de momentos diariamente y apoyándonos los unos a los otros en los momentos duros y compartiendo felicidad en los buenos, haciendo mucho más ameno este camino.

Agradecer a los miembros del Grupo de Química Organometálica con los que he trabajado por haberme hecho partícipe del mismo y haberme acogido como uno mas.

También agradecer al servicio de instrumentación de la Universidad de Murcia sus servicios, que han hecho posible esta investigación. En especial, me gustaría dar las gracias a la Dra. Delia Bautista Cerezo por su contribución en la resolución de todas las estructuras cristalinas que se incluyen en este trabajo y que han aportado un valor tan significativo a este trabajo de investigación.

Darle las gracias también al Dr. Thomas S. Teets por haberme acogido en su grupo de investigación para la realización de la estancia en la Universidad de Houston. El trato y atención de él y de los compañeros que tuve allí hacia mi desde que inicié todo el procedimiento hasta que regresé de Estados Unidos fue extraordinario.

Dar mi gratitud a todos mis amigos que han sido un apoyo constante durante mi vida y con los que he compartido momentos de toda índole, siendo una parte muy importante de mi persona y que siempre han tenido plena confianza en mi.

Para concluir, agradecer a mi familia todo, sin ellos no habría no sería la persona que soy de hoy en día. Ellos son las personas que me han influido desde que nací, me han apoyado siempre y me han aportado todos los recursos personales y materiales que necesitaba para poder seguir mi propio camino en la vida.

Muchas gracias a todos.

## ACKNOWLEDGEMENTS

This doctoral thesis was possible thanks to the funding provided by the following institutions:

**Ministerio de Economía y Competitividad/Agencia Estatal de Investigación/ERDF.** Grant No. CTQ2015-69568-P.

**Fundación Séneca-Agencia de Ciencia y Tecnología de la Región de Murcia.** Grant No. 19890/GERM/15.

**Ministerio de Ciencia, Innovación y Universidades/Agencia Estatal de Investigación/ERDF.** Grants No. PGC2018-100719-B-I00 and PID2021-122966NB-I00.

**Universidad de Murcia.** Predoctoral grant to J. C. López López.



## ORGANIZATION AND STRUCTURE

The present doctoral thesis is organized as a collection of articles. In compliance with the regulations established by the University of Murcia for this type of theses, the articles are preceded by a general introduction to the topic and a summary of the objectives and conclusions. In addition, a summary in Spanish of a minimum of 2000 words is included to comply with the requirement established for theses written in English.

The thesis comprises the following articles, which are included in chronological order with the corresponding Supporting or Supplementary Information:

### Article 1:

**Title:** Stereoselective Formation of Facial Tris-Cyclometalated Pt<sup>IV</sup> Complexes: Dual Phosphorescence from Heteroleptic Derivatives.

**Authors:** Juan Carlos López López, Delia Bautista Cerezo, Pablo González Herrero.

**Journal:** Chemistry, A European Journal.

**Year:** 2020.

**Volume:** 26.

**Pages:** 11307–11315.

**Complete reference:** J. C. López-López, D. Bautista, P. González-Herrero. *Chem. Eur. J.* **2020**, *26*, 11307–11315.

**DOI:** [10.1002/chem.202001164](https://doi.org/10.1002/chem.202001164)

### Article 2:

**Title:** Luminescent halido(aryl) Pt(IV) complexes obtained via oxidative addition of iodobenzene or diaryliodonium salts to bis-cyclometalated Pt(II) precursors.

**Authors:** Juan Carlos López López, Delia Bautista Cerezo, Pablo González Herrero.

**Journal:** Dalton Transactions.

**Year:** 2021.

**Volume:** 50.

**Pages:** 13294–13305.

**Complete reference:** J. C. López-López, D. Bautista, P. González-Herrero. *Dalton Trans.* **2021**, *50*, 13294–13305.

**DOI:** [10.1039/D1DT02349G](https://doi.org/10.1039/D1DT02349G)

### Article 3:

**Title:** Phosphorescent biaryl platinum(IV) complexes obtained through double metalation of dibenziodolium ions.

**Authors:** Juan Carlos López López, Delia Bautista Cerezo, Pablo González Herrero.

**Journal:** Chemical Communications.

**Year:** 2022.

**Volume:** 58.

**Pages:** 4532–4535.

**Complete reference:** J. C. López-López, D. Bautista, P. González-Herrero. *Chem. Commun.* **2022**, *58*, 4532–4535.

**DOI:** [10.1039/D2CC01018F](https://doi.org/10.1039/D2CC01018F)

#### Article 4:

**Title:** Photoinduced Reductive C–C and C–Heteroatom Couplings from Bis-cyclometalated Pt(IV) Alkynyl Complexes.

**Authors:** Juan Carlos López López, Delia Bautista Cerezo, Pablo González Herrero.

**Journal:** Inorganic Chemistry.

**Year:** 2023.

**Volume:** 62.

**Pages:** 14411–14421.

**Complete reference:** J. C. López-López, D. Bautista, P. González-Herrero. *Inorg. Chem.* **2023**, 62, 14411–14421.

DOI: [10.1021/acs.inorgchem.3c02162](https://doi.org/10.1021/acs.inorgchem.3c02162)

#### Author affiliations:

**Juan Carlos López López:** Departamento de Química Inorgánica, Universidad de Murcia, Campus de Espinardo, 19, 30100 Murcia (Spain). E-mail: [jc.lopezlopez@um.es](mailto:jc.lopezlopez@um.es)

**Pablo González Herrero:** Departamento de Química Inorgánica, Universidad de Murcia, Campus de Espinardo, 19, 30100 Murcia (Spain). E-mail: [pgh@um.es](mailto:pgh@um.es)

**Delia Bautista Cerezo:** Área Científica y Técnica de Investigación (ACTI), Universidad de Murcia, Campus de Espinardo, 21 30100 Murcia (Spain). E-mail: [dbc@um.es](mailto:dbc@um.es)

#### Contribution of the doctoral student:

The contribution of the doctoral student to each of the articles is the same and is detailed in the following points:

- Participation in the design of the synthetic and reactivity experiments and the execution of all of them in the laboratory.
- Measurements for the characterization of all the synthesized compounds by means of nuclear magnetic resonance spectroscopy and their interpretation.
- Spectroscopic measurements for the photophysical characterization of the compounds, including ultraviolet-visible absorption spectra, emission and excitation spectra, lifetimes and emission quantum yields, and interpretation of the obtained data.
- Extraction and writing up of all experimental data shown in the articles.
- Participation in the writing of the articles and in the literature review.

---

**TABLE OF CONTENTS**

<i>Abbreviations</i> .....	<i>iii</i>
<b>GENERAL INTRODUCTION</b> .....	<b>1</b>
Luminescent transition-metal complexes with heteroaromatic ligands.....	3
Electronic transitions and excited states.....	5
Luminescent platinum(IV) complexes with cyclometalated ligands.....	7
<i>Structural types and properties of cyclometalated platinum(IV) complexes</i> .....	9
Unsymmetrical [Pt(C <sup>^</sup> N) <sub>2</sub> X <sub>2</sub> ] complexes.....	10
C <sub>2</sub> -Symmetrical [Pt(C <sup>^</sup> N) <sub>2</sub> X <sub>2</sub> ] complexes.....	12
Unsymmetrical [Pt(C <sup>^</sup> N) <sub>2</sub> (R/Ar)X] complexes.....	13
C <sub>2</sub> -Symmetrical, tris-chelate [Pt(C <sup>^</sup> N) <sub>2</sub> (N <sup>^</sup> N)] <sup>2+</sup> or [Pt(C <sup>^</sup> N) <sub>2</sub> (L <sup>^</sup> X)] <sup>+</sup> complexes.....	16
Tris-cyclometalated complexes [Pt(C <sup>^</sup> N) <sub>3</sub> ] <sup>+</sup> .....	16
Complexes with terdentate ligands.....	18
Complexes with tetradentate ligands.....	20
References.....	21
<b>SUMMARY OF OBJECTIVES AND CONCLUSIONS</b> .....	<b>33</b>
OBJECTIVES.....	35
CONCLUSIONS.....	37
<b>RESUMEN EN CASTELLANO</b> .....	<b>41</b>
Introducción.....	43
ARTÍCULO 1. Formación estereoselectiva de complejos faciales tris-ciclometalados de Pt(IV): Fosforescencia dual de derivados heterolépticos.....	44
ARTÍCULO 2. Haluro(aril)-complejos luminiscentes de Pt(IV) obtenidos mediante adición oxidante de yodobenceno o sales de diarylyodonio a precursores bis-ciclometalados de Pt(II).....	46
ARTÍCULO 3. Biaril-complejos fosforescentes de platino(IV) obtenidos mediante doble metalación de iones dibenzoyodolio.....	47
ARTÍCULO 4. Acoplamiento reductores C-C y C-heteroátomo fotoinducidos en alquinil- complejos bis-ciclometalados de Pt(IV).....	50
<b>ARTICLES</b> .....	<b>53</b>



## Abbreviations

bpy	2,2'-bipyridine
Bppy	4-(dimesitylboranyl)-2-phenylpyridine
Bn	benzyl
Br-pbt	2-(4-bromophenyl)benzothiazole
Bu	n-Butyl
bzq	benzoquinoline
dFbpy	4,4'-difluoro-2,2'-bipyridine
dfppy	cyclometalated 2-(2,4-difluorophenyl)pyridine
dMeObpy	5,5'-dimethoxy-2,2'-bipyridine
DMSO	dimethyl sulfoxide
dppyH	monocyclometalated 2,6-diphenylpyridine
dtpyH	monocyclometalated 2,6-di( <i>p</i> -tolyl)pyridine
flpy	cyclometalated 2-(9,9-dimethylfluoren-2-yl)pyridine
F-mppy	cyclometalated 2-(4-fluorophenyl)-5-methylpyridine
HOMO	highest occupied molecular orbital
IC	internal conversion
IL	intraligand
ILCT	intraligand charge transfer
ISC	intersystem crossing
LC	ligand-centered
LECs	light-emitting electrochemical cells
LLCT	ligand-to-ligand charge-transfer
LMCT	ligand-to-metal charge-transfer
LUMO	lowest unoccupied molecular orbital
MC	metal-centered
MeOppy	cyclometalated 2-(4-methoxyphenyl)pyridine
MeO-mppy	cyclometalated 2-(4-methoxyphenyl)-5-methylpyridine
Ph-mppy	cyclometalated 2-(1,1'-biphenyl-4-yl)-5-methylpyridine
MLCT	metal-to-ligand charge-transfer
NIR	near infrared
npy	cyclometalated 2-(2-naphthyl)pyridine
OLEDs	organic light-emitting diodes
OTf	triflate or trifluoromethanesulfonate
oxd	cyclometalated 2-cyclohexyl-5-phenyl-1,3,4-oxadiazole
PBn <sub>3</sub>	tribenzylphosphine
pbt	cyclometalated 2-phenylbenzothiazole
piq	cyclometalated 1-phenylisoquinoline
PMMA	poly(methyl methacrylate)
PPr <sub>3</sub>	tripropylphosphine
ppy	cyclometalated 2-phenylpyridine
ppz	cyclometalated 1-phenylpyrazole
pq	cyclometalated 2-phenylquinoline

pypy	cyclometalated 2-(1-pyrenyl)pyridine
ROS	reactive oxygen species
SOC	spin-orbit coupling
thpy	cyclometalated 2-(2-thienyl)pyridine
tpy	cyclometalated 2-( <i>p</i> -tolyl)pyridine

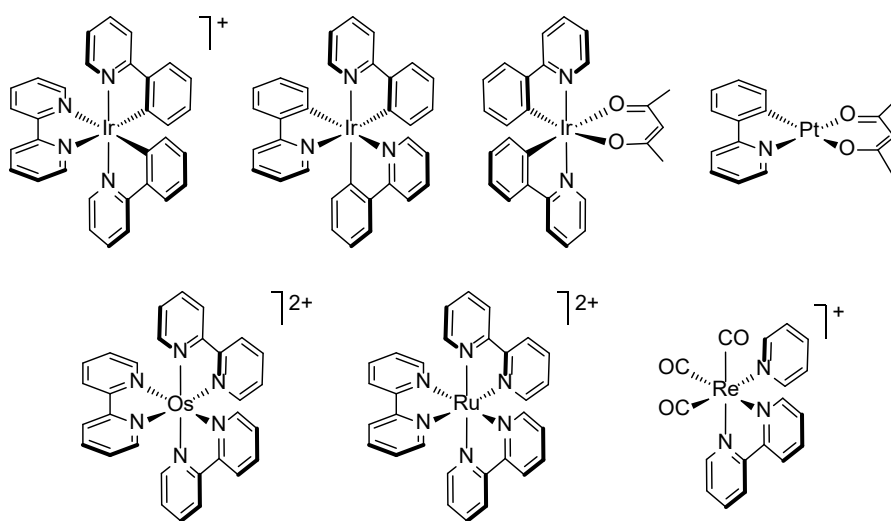
# **GENERAL INTRODUCTION**





## Luminescent transition-metal complexes with heteroaromatic ligands

Transition-metal complexes with chelating heteroaromatic ligands, such as 2,2'-bipyridines, cyclometalated 2-arylpyridines, and related compounds, have been intensively studied for their luminescence and other excited-state properties.<sup>1–6</sup> Most of the reported complexes with this kind of ligands have second- or third-row transition-metal ions with a  $d^6$  electronic configuration, mainly Ru(II),<sup>1,3,4,7</sup> Re(I),<sup>8</sup> Os(II)<sup>9–12</sup> and Ir(III),<sup>13–17</sup> or a  $d^8$  configuration, like Pt(II)<sup>18–30</sup> or Au(III).<sup>31–37</sup> Complexes of first-row transition metals have also been increasingly studied in recent years.<sup>38–42</sup> Archetypal luminescent complexes of the most frequently employed metal ions are shown in Figure 1.



**Figure 1.** Archetypal luminescent transition metal complexes with chelating heteroaromatic ligands.

The metal ion in these complexes induces a strong spin-orbit coupling (SOC) effect that results in a fast intersystem crossing between singlet and triplet excited states, leading to phosphorescent emissions that can reach high efficiencies and are usually characterized by lifetimes in the  $\mu\text{s}$  scale. These properties make this kind of complexes suitable for applications in the fields of electroluminescent materials for lighting and displays, photocatalysis for hydrogen production and organic synthesis, chemical and biological analysis and sensing, and chemotherapy for the treatment of cancer. Some of the most relevant specific applications are summarized below.

**Electroluminescent materials.** Many transition-metal complexes with heteroaromatic ligands have been tested as phosphorescent dopants for organic light-emitting diodes (OLEDs)<sup>43–50</sup> and light-emitting electrochemical cells (LECs),<sup>51</sup> most of which are Ir(III) and Pt(II) derivatives bearing cyclometalated 2-arylpyridines and related ligands. These devices are based on electroluminescence, *i.e.*, the emission of light as a consequence of the application of an external electrical voltage. Phosphorescent emitters are especially suited for this application because they are capable of collecting all the produced excitons, regardless of their spin multiplicity, to produce a phosphorescent emission from a triplet excited state.<sup>52</sup> The most sought-after characteristics that dopants need to meet are relatively short lifetimes (less than 1  $\mu\text{s}$ ), wide colour tunability and high stability.

**Photocatalysis.** The use of transition-metal complexes as photocatalysts has been a breakthrough in the context of the quest for alternative and sustainable methods for organic synthesis that can lead to novel transformations under mild conditions. Transition-metal complexes can function as photosensitizers that, upon excitation with light, are capable of performing or promoting different types of chemical transformations. Most frequently, the complexes in the excited state engage in bimolecular electron-transfer reactions with organic substrates (*photoredox catalysis*),<sup>53–59</sup> although they can also perform energy-transfer processes (*energy-transfer photocatalysis*).<sup>60–62</sup> A key feature of a photocatalyst is its excited-state lifetime. Longer lifetimes are beneficial for photocatalysis because bimolecular processes are governed by diffusion and the probability of the excited photocatalyst to engage in a reaction with the substrate is higher for longer lifetimes.<sup>63</sup>

A different emerging strategy that takes advantage of the excited-state properties of transition-metal complexes has been termed *Light-induced transition metal catalysis*,<sup>64</sup> which is based on the possibility that the organic substrate directly binds to the catalyst, forming a new complex that can produce useful transformations upon photoexcitation. Therefore, a single metal system performs the double function of light harvesting and promotion of a chemical transformation.

**Bioimaging.** Bioimaging or cell imaging techniques are based on the photoexcitation of luminescent compounds absorbed by biological tissues, which allows to visualize them by recording their emission.<sup>65–71</sup> They are used to label cell organelles and different types of molecular structures in living organisms, allowing an accurate monitoring of biological processes and facilitating their study. The requirements of the compounds employed for bioimaging are a relatively low molecular weight, the possibility to modulate their excitation and emission energies along the visible-near infrared spectrum, and the lack of cytotoxicity. Transition-metal complexes can meet these properties, which has made them widely used in this field. Moreover, their relatively long lifetimes are a key advantage with respect to fluorescent compounds because they allow to suppress the background fluorescence of biological tissues (*autofluorescence*) through time-resolved imaging techniques, resulting in increased sensitivity.<sup>68–71</sup>

**Chemosensors.** Chemosensors are systems that, in the presence of certain substances, give rise to some type of observable response. This change can be in properties such as their absorption, emission, or lifetime. The best-known chemosensors are those used for oxygen detection, usually referred to as *oxygen sensing*. It is based on the quenching of the luminescence and shortening of lifetimes by the presence of molecular oxygen through an energy-transfer mechanism. Many transition-metal complexes are suitable for this application.<sup>72,73</sup> In addition, transition-metal-based chemical sensors have been developed for pH determination and detection of a multitude of anions, cations, and biological substances such as amino acids and DNA.<sup>74,75</sup>

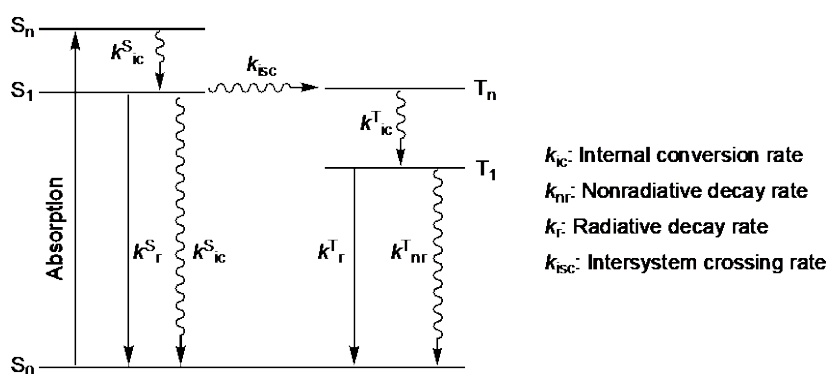
**Chemotherapeutic agents.** Based on the quenching of luminescence by molecular oxygen, transition-metal complexes have been employed as photosensitizers that mediate the transformation of triplet oxygen (non-reactive) into singlet oxygen (reactive), resulting in the formation of reactive oxygen species (ROS) that kill cancer cells.<sup>76</sup> This has allowed the development of *photodynamic therapy*, which employs light in combination with transition-metal-based photosensitizers to locally promote the generation of singlet oxygen in tumours, leading to a much more selective treatment that prevent unwanted side effects of classical drugs

due to accumulation in healthy tissues.<sup>77–79</sup> Thus, the employed complexes used are not toxic in dark conditions and only act in the irradiated area.

## Electronic transitions and excited states

Upon absorption of light by a transition-metal complex, a series of electronic transitions can occur that are often represented using a Jabłoński diagram (Figure 2). Transitions to different singlet excited states ( $S_n$ ) from the ground state ( $S_0$ ) are produced depending on the energy of the absorbed light. Then, an internal conversion (IC) to the lowest singlet excited state ( $S_1$ ) occurs through vibrational relaxation. From this state, three different processes can occur: light emission (fluorescence), nonradiative relaxation (internal conversion) to the ground state, or intersystem crossing (ISC) to a triplet excited state ( $T_n$ ). Within the triplet manifold, internal conversion to the lowest triplet excited state ( $T_1$ ) occurs, from which light emission (phosphorescence) or nonradiative relaxation to the ground state can take place.<sup>80</sup> All transitions between electronic states are characterized by a rate constant.

Transitions between singlet and triplet states are forbidden by the spin selection rule. However, they can occur if there is a strong spin-orbit coupling (SOC). Transition metals and other heavy atoms typically induce a strong SOC, and therefore ISC from the  $S_1$  state to the triplet manifold and from the  $T_1$  state to the singlet ground state can be very effective, implying that the emissions from complexes of transition metal ions are usually phosphorescence.



**Figure 2.** Jabłoński diagram showing the electronic transitions can occur upon irradiation of a transition-metal complex.

Emission lifetimes ( $\tau$ ) and quantum yields ( $\Phi$ ) are the most important parameters to characterize the observed luminescence. They can be defined in terms of the radiative and nonradiative rate constants.<sup>80</sup> For a phosphorescent compound, assuming that the efficiency or intersystem crossing is unity:

$$\tau = \frac{1}{k_r^T + k_{nr}^T}$$

$$\Phi_P = \frac{k_r^T}{k_r^T + k_{nr}^T} = k_r^T \cdot \tau$$

High quantum yields are usually necessary for many applications of luminescent compounds. Therefore, increasing the radiative constant and/or reducing the nonradiative one is often sought. Lifetimes are often in the microsecond ( $\mu s$ ) range for transition-metal complexes, but they can

vary depending on the metal orbital involvement in the excited state. Thus, if the participation of metal orbitals is high, the SOC effects induced by the metal are stronger and faster transitions between the triplet emitting state and the singlet ground state are observed, meaning shorter lifetimes.

States of different nature are possible in transition-metal complexes bearing heteroaromatic ligands depending on the involved molecular orbitals.<sup>5,81,82</sup> The most common are the following:

**Metal-to-ligand charge-transfer (MLCT) states.** These states originate from electronic promotions from occupied  $d\pi$  orbitals of the metal to unoccupied  $\pi^*$  orbitals of the heteroaromatic ligand. Due to the intrinsic rigidity of the heteroaromatic ligands, they produce little geometrical distortions with respect to the ground state and can lead to efficient luminescence.

**Ligand-centred (LC) states.** These states originate from electronic promotions within the heteroaromatic ligand, usually  $\pi$ - $\pi^*$  transitions. They are often termed *intraligand* (IL) states or, if the  $\pi$  and  $\pi^*$  orbitals are distributed over different parts of the ligand, *intraligand charge-transfer* (ILCT). Most commonly, they cause little geometrical distortions with respect to the ground state because of the rigidity of the ligand, and therefore can produce intense luminescence.

**Metal-centred (MC) or d-d states.** These states arise from electronic transitions from occupied to unoccupied metal orbitals. In late transition-metal complexes, they are usually geometrically distorted with respect to the ground state or have a dissociative character because they involve the filling of  $d\sigma^*$  orbitals, which are strongly antibonding along the metal–ligand  $\sigma$  bonds. As a result, they usually produce nonradiative deactivation and can also lead to photoreactivity.

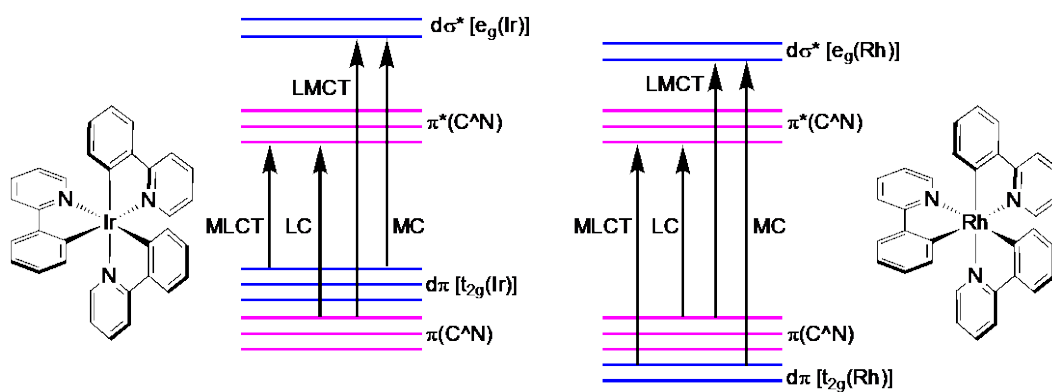
**Ligand-to-metal charge-transfer (LMCT) states.** These states arise from promotions from occupied  $\pi$  orbitals of the heteroaromatic ligand to unoccupied metal  $d\sigma^*$  orbitals. In late transition-metal complexes, they can lead to geometrical distortions or ligand dissociation. They can also trigger the reduction of the metal.

**Ligand-to-ligand charge-transfer (LLCT) states.** These states arise from promotions from occupied orbitals of one ligand (heteroaromatic or not) to unoccupied  $\pi^*$  orbitals of a heteroaromatic ligand. They can lead to significant geometrical distortions. In some cases, they have been found to produce luminescence,<sup>83–85</sup> but in others they are not emissive.<sup>86,87</sup>

It is important to note that excited states of transition-metal complexes often have a mixed character. Most commonly, LC and MLCT states mix through configuration interaction, leading to LC/MLCT admixtures with variable proportions of LC and MLCT character.<sup>88</sup> A higher proportion of MLCT character in  $^3\text{LC/MLCT}$  states leads to faster radiative and nonradiative decay rates and shorter emission lifetimes, because the stronger SOC effects induced by the metal facilitate transitions between states of different spin multiplicities. Conversely, states of predominantly  $^3\text{LC}$  character involve little participation of metal orbitals and can have very long lifetimes.

As an illustration of the possible electronic transitions in transition-metal complexes with chelating heteroaromatic ligands, a simplified representation is provided in Figure 3 for facial tris-cyclometalated Ir(III) and Rh(III) complexes with 2-phenylpyridine. These two complexes are luminescent, but the nature of their emitting state is different. For the Ir(III) complex, the

lowest-energy triplet excited state is  $^3\text{MLCT}$ , while for the Rh(III) complex it is  $^3\text{LC}$  because the occupied metal orbitals are lower in energy for second-row transition-metal ions.<sup>89</sup>



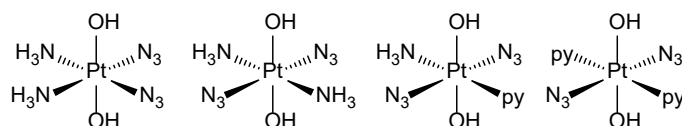
**Figure 3.** Qualitative energy diagrams showing the ordering of frontier molecular orbitals and possible electronic transitions of complexes [Ir(ppy)<sub>3</sub>] and [Rh(ppy)<sub>3</sub>].

Depending on the electronic properties of the heteroaromatic ligand, the frontier orbital energies and the nature of the emitting state can be different. In general, for late transition-metal complexes containing cyclometalated 2-arylpyridines, bipyridines or related ligands,  $^3\text{LC}$ ,  $^3\text{MLCT}$  or  $^3\text{LC/MLCT}$  admixtures are most commonly the lowest triplet excited states and, hence, the emitting states. In certain cases,  $^3\text{LMCT}$  or  $^3\text{MC}$  states can exist at higher energies and provide deactivation pathways via thermal population from the lowest excited state.<sup>90</sup>

The strategies to modulate emission quantum yields of  $^3\text{LC/MLCT}$  emitters are varied. Generally, increasing the MLCT character increases  $k_r$  to a higher degree than  $k_{nr}$ , leading to increased quantum yields.<sup>88</sup> This can be achieved by introducing stronger  $\pi$  donor ligands, which raise the energy of the occupied metal  $d\pi$  orbitals and their participation in the excited state. When there are thermally accessible  $^3\text{LMCT}$  or  $^3\text{MC}$  states, a way to reduce  $k_{nr}$  is to raise the energy of these states using ligands that induce a stronger ligand field, thereby raising the energy of  $d\sigma^*$  orbitals. This can be achieved by using strong  $\sigma$  donor ligands, e.g., metalated aryls or carbene ligands.<sup>91–97</sup> An additional strategy to reduce  $k_{nr}$  is to increase the energy of the emitting state with respect to the ground state, which reduces the nonradiative deactivation due to vibrational coupling between these states (Energy Gap Law).<sup>98–100</sup>

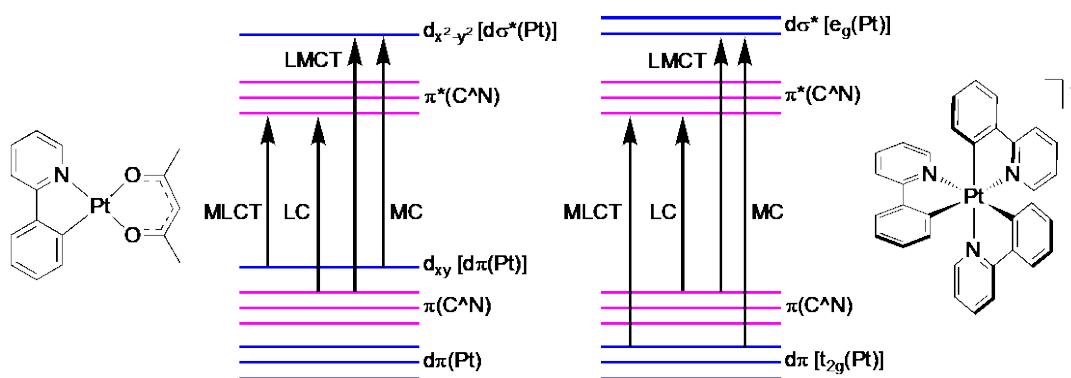
## Luminescent platinum(IV) complexes with cyclometalated ligands

Traditionally, the major interest in Pt(IV) complexes has been connected to their involvement in oxidative addition/reductive elimination processes that are crucial in many catalytic cycles, and therefore they have been regarded as models for mechanistic studies.<sup>101–110</sup> The most outstanding application of their excited-state properties has been the development of photoactivatable prodrugs for the treatment of cancer,<sup>111–118</sup> which take advantage of the existence of low-lying LMCT excited states due to the highly electrophilic character of the Pt(IV) ion. Thus, whereas Pt(IV) complexes are inactive against cancer cells, population of LMCT states through light irradiation triggers their reduction to Pt(II) species, which are cytotoxic, allowing a localized treatment on the irradiated area that entails fewer side effects.<sup>119,120</sup> Some examples of photoactivatable Pt(IV) prodrugs are shown in Figure 4.<sup>116,121,122</sup>



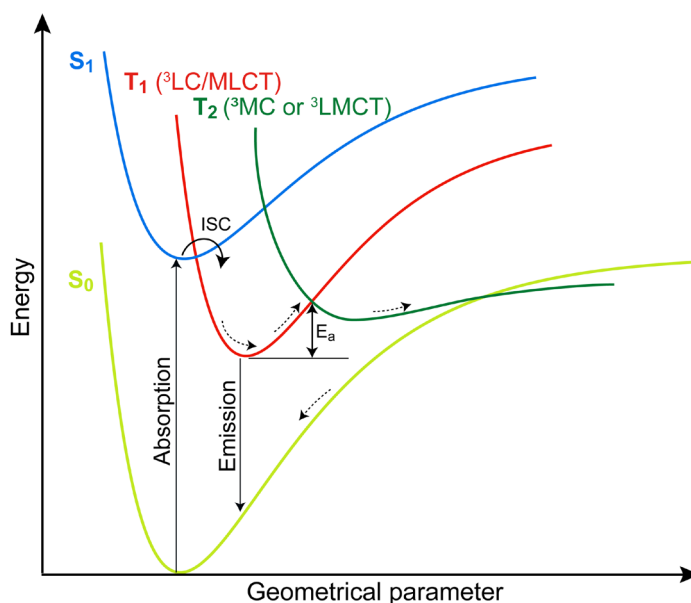
**Figure 4.** Examples of Pt(IV) complexes studied as photoactivatable Pt(IV) prodrugs.

The luminescence of Pt(IV) complexes received very little attention until very recently, with studies carried out by the Organometallic Chemistry Group of the University of Murcia.<sup>123</sup> This is in sharp contrast with the extensive studies on luminescent complexes of other  $d^6$  metal ions, such as Ru(II),<sup>1,3,4,7</sup> Os(II)<sup>9–12</sup> and Ir(III),<sup>13–17</sup> or on Pt(II) complexes,<sup>18–30</sup> and is possibly attributable to synthetic difficulties and the strong focus on Pt(II). Most of the reported luminescent Pt(IV) complexes contain cyclometalated 2-arylpyridine ligands.<sup>90,123–133</sup> They can achieve highly efficient phosphorescent emissions from  $^3\text{LC}$  excited states with very little MLCT character, featuring by very long lifetimes, which make them promising as photosensitizers or photocatalysts. These properties are drastically different to those of cyclometalated Pt(II) complexes, which can be understood by looking at the simplified orbital energy diagrams represented in Figure 5. In Pt(II) complexes, the  $d_{xy}$  orbital is often the highest occupied molecular orbital (HOMO), and therefore the emitting state can be predominantly  $^3\text{MLCT}$ , although mixed  $^3\text{LC}/\text{MLCT}$  emitting states with variable proportions of LC and MLCT character are possible.<sup>128,133</sup> In contrast, in Pt(IV) complexes the occupied metal  $d\pi$  orbitals are very low in energy and the HOMO is a  $\pi$  orbital of the cyclometalated ligand, leading to an essentially  $^3\text{LC}$  emitting state with very little participation of metal orbitals. This implies that the SOC effects induced by the metal are drastically diminished with respect to those in Pt(II) complexes, resulting in much longer emission lifetimes.



**Figure 5.** Qualitative energy diagrams showing the ordering of frontier molecular orbitals and possible electronic transitions of cyclometalated Pt(II) and Pt(IV) complexes.

Another difference between cyclometalated Pt(II) and Pt(IV) complexes is the type of deactivating excited states that can be thermally accessible from the emitting state and may lead to nonradiative decay. In Pt(II) complexes, there can be low-lying  $^3\text{MC}$  states, whereas in Pt(IV) there can be  $^3\text{LMCT}$  states (Figure 6). In both cases, the emission properties are improved by increasing the energy of unoccupied  $d\sigma^*$  orbitals, which can be done using strong  $\sigma$  donor ligands that provide a large ligand-field splitting.<sup>127,128</sup> This leads to a higher energy of  $^3\text{MC}$  or  $^3\text{LMCT}$  states, requiring a higher activation energy to populate them.

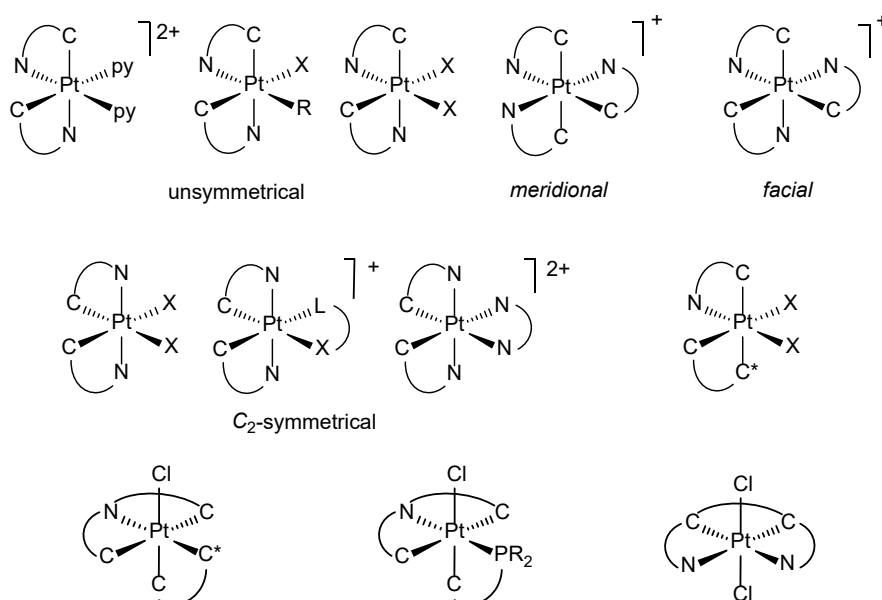


**Figure 6.** Potential energy curves of the states involved in the absorption and emission of Pt(II) or Pt(IV) complexes with chelating heteroaromatic ligands and non-radiative deactivation by thermal population of  $^3MC$  or  $^3LMCT$  states.

## Structural types and properties of cyclometalated platinum(IV) complexes

Pt(IV) complexes require at least two strong  $\sigma$  donor atoms to get a significant emission quantum yield. Since the metalated aryl of cyclometalated 2-arylpyridines is a strong  $\sigma$  donor, two of these ligands may suffice to attain the necessary ligand-field splitting.<sup>128</sup> Thus, many of the reported luminescent Pt(IV) complexes present at least two cyclometalated ligands. Bis-cyclometalated and tris-cyclometalated Pt(IV) complexes with 2-arylpyridines can exhibit efficient luminescence from  $^3LC$  states with a very small but critical participation of metal  $d\pi$  orbitals that provides some MLCT character. This MLCT character allows the intersystem crossing between the singlet and the triplet states to take place due to the spin-orbit coupling induced by the metal and can be modulated by varying the  $\pi$  donor ability of the cyclometalated or ancillary ligands, which affects the energy of occupied metal  $d\pi$  orbitals. The emission energies of cyclometalated Pt(IV) complexes can be tuned by varying the electronic properties of the 2-arylpyridine ligands and is generally determined by the energy gap between its  $\pi$  and  $\pi^*$  orbitals.

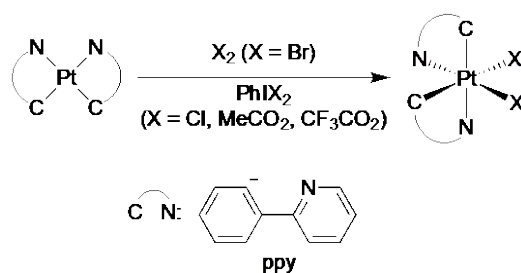
A compilation of the main structural types of luminescent cyclometalated Pt(IV) complexes with at least two metalated carbon atoms from heteroaromatic ligands, which were reported before the first article of the present thesis, is shown in Figure 7. Although most of them bear bidentate cyclometalated 2-arylpyridines, complexes with cyclometalated aryl-N-heterocyclic carbenes or with terdentate or tetradentate heteroaromatic ligands are also known.



**Figure 7.** Reported classes of cyclometalated Pt(IV) complexes with at least two metalated carbon atoms from heteroaromatic ligands before the first publication of the present thesis. C<sup>^</sup>N = cyclometalated 2-arylpyridine; X = halide; R: alkyl, C<sub>6</sub>F<sub>5</sub>; N<sup>^</sup>N = diamine or aromatic  $\alpha$ -diimine; L<sup>^</sup>X: monoanionic chelating ligand; C<sup>^</sup>C\* = cyclometalated aryl-N-heterocyclic carbene; C<sup>^</sup>PR<sub>2</sub> = cyclometalated benzyl- or alkylphosphine; C<sup>^</sup>N<sup>^</sup>C = dimetalated 2,6-diarylpyridine; C<sup>^</sup>N<sup>^</sup>N = 6-aryl-2,2'-bipyridine; N<sup>^</sup>C<sup>^</sup>C<sup>^</sup>N = tetradentate heteroaromatic ligand.

### Unsymmetrical [Pt(C<sup>^</sup>N)<sub>2</sub>X<sub>2</sub>] complexes

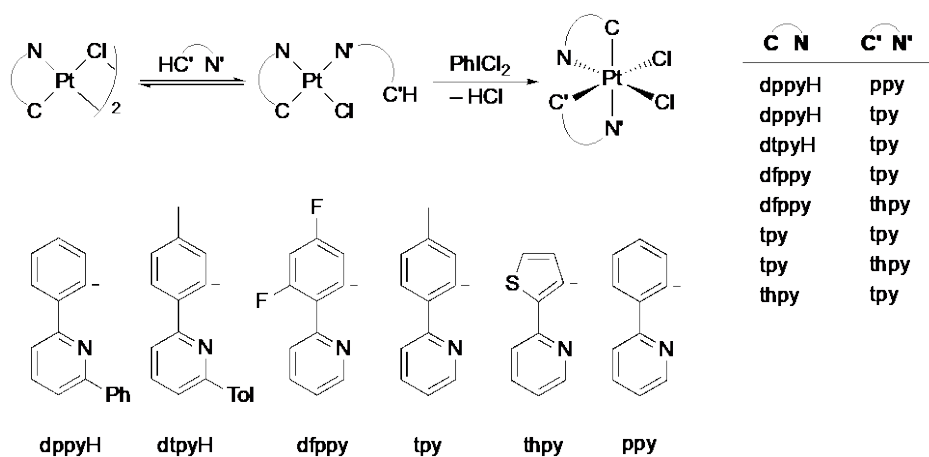
Pt(IV) complexes of the type [Pt(C<sup>^</sup>N)<sub>2</sub>X<sub>2</sub>], where C<sup>^</sup>N = cyclometalated 2-arylpyridine; X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> or MeCO<sub>2</sub><sup>-</sup>, can be obtained by oxidation of *cis*-[Pt(C<sup>^</sup>N)<sub>2</sub>] with the hypervalent iodine reagents PhIX<sub>2</sub> or X<sub>2</sub>,<sup>128,134,135</sup> resulting in complexes with an unsymmetrical arrangement of cyclometalated ligands (Scheme 1).



**Scheme 1.** Synthesis of unsymmetrical bis-cyclometalated complexes [Pt(ppy)<sub>2</sub>X<sub>2</sub>] from *cis*-[Pt(C<sup>^</sup>N)<sub>2</sub>] precursors.

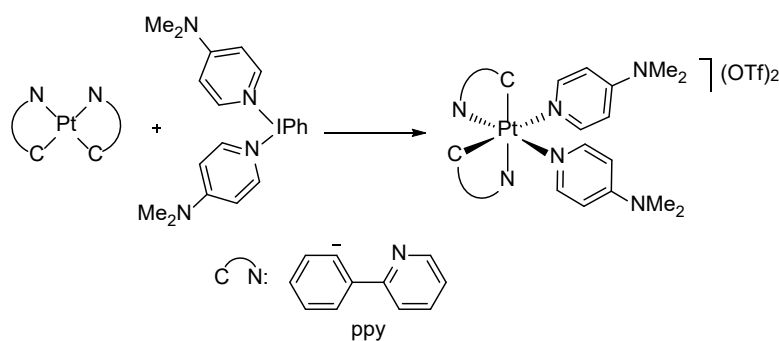
Complexes of this class with two different or equal cyclometalated 2-arylpyridines have also been synthesized through the oxidation of Pt(II) complexes *cis*-N,N-[Pt(C<sup>^</sup>N)(N<sup>^</sup>C'H)Cl] with PhICl<sub>2</sub>, which promotes the electrophilic metalation of the pendant aryl group of the coordinated N<sup>^</sup>C'H ligand (Scheme 3).<sup>133</sup>





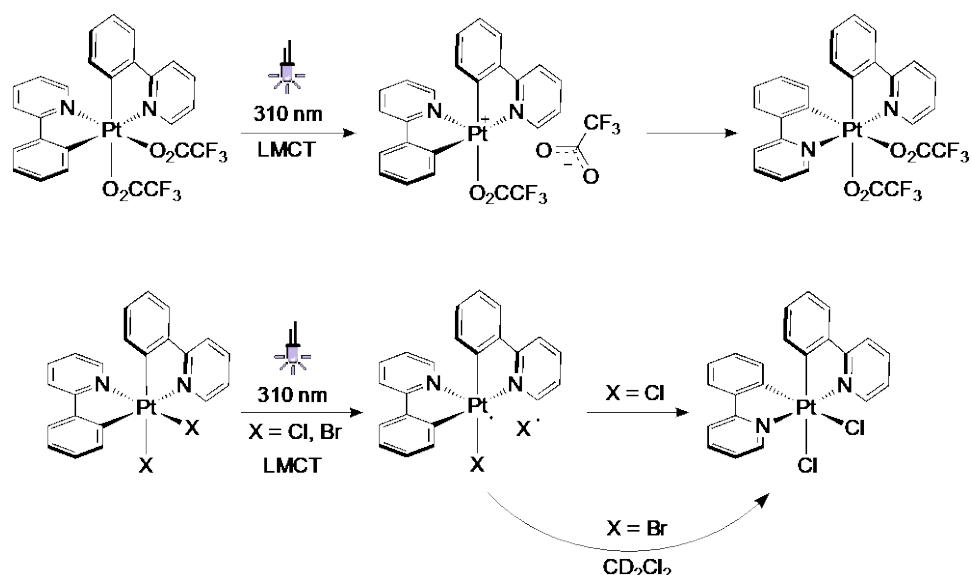
**Scheme 2.** Synthesis of unsymmetrical bis-cyclometalated Pt(IV) dihalido complexes.

A cationic unsymmetrical bis-cyclometalated Pt(IV) complex with a pyridine-derived ligand instead of anionic ligands has been also synthesized using a hypervalent iodine reagent, as represented in Scheme 3.<sup>136</sup> The photophysical properties of this compound have not been explored.



**Scheme 3.** Synthesis of an unsymmetrical Pt(IV) complex containing two pyridine-derived ligands.

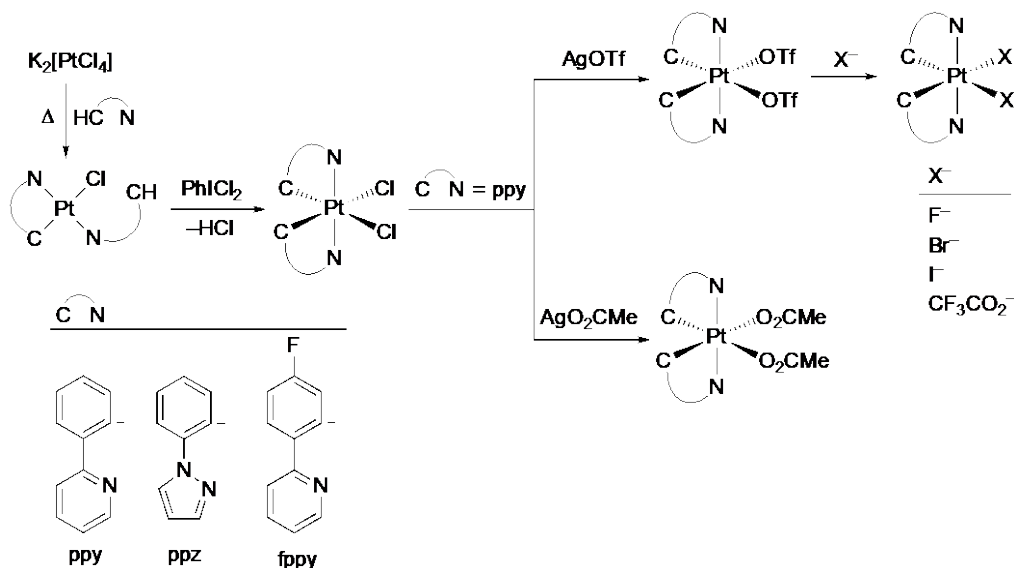
Unsymmetrical bis-cyclometalated Pt(IV) complexes do not emit in solution at room temperature but are emissive at low temperatures from <sup>3</sup>LC excited states.<sup>128,133</sup> This behaviour is attributable to the population <sup>3</sup>LMCT states, which are relatively low in energy because in these complexes  $d\sigma^*(Pt)$  orbitals have low energies and can become the LUMO. <sup>3</sup>LMCT states in Pt(IV) have dissociative character and can promote photochemical reactions. This was demonstrated for several halido and carboxylato derivatives bearing ppy as the cyclometalated ligand, which showed photochemical reactivity upon irradiation with UV light, resulting in isomerization to the more stable  $C_2$ -symmetrical geometry, or even halide exchange in  $CH_2Cl_2$  (Scheme 4).<sup>128</sup> A heterolytic Pt–O bond dissociation was postulated for the trifluoroacetate complex, whereas homolytic Pt–X bond dissociations were postulated for the chlorido and bromido complexes, which would result in radical species. The halogen-exchange process was explained by a halogen abstraction reaction of a Pt(III) intermediate with  $CD_2Cl_2$ . The irradiation of the diacetate derivative led to a mixture of unidentified compounds that was not investigated.



**Scheme 4.** Proposed pathways for the isomerization and halide-exchange reactions of unsymmetrical complexes [Pt(ppy)<sub>2</sub>X<sub>2</sub>].

### C<sub>2</sub>-Symmetrical [Pt(C<sup>^</sup>N)<sub>2</sub>X<sub>2</sub>] complexes

The oxidation of *trans*-N,N-[Pt(C<sup>^</sup>N)(N<sup>^</sup>CH)Cl] with PhICl<sub>2</sub> has been also studied, resulting in the cyclometalation of the coordinated N<sup>^</sup>CH ligand to produce C<sub>2</sub>-symmetrical complexes [Pt(C<sup>^</sup>N)<sub>2</sub>Cl<sub>2</sub>] (Scheme 5).<sup>123,125,126,137</sup> The abstraction of the chlorido ligands using silver acetate or triflate led to the corresponding [Pt(C<sup>^</sup>N)<sub>2</sub>X<sub>2</sub>] complexes.<sup>128</sup> The labile triflate ligand could be easily substituted by trifluoroacetate or halides.



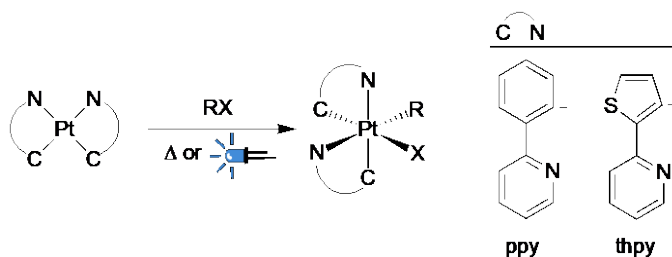
**Scheme 5.** Synthesis of C<sub>2</sub>-symmetrical bis-cyclometalated complexes [Pt(C<sup>^</sup>N)<sub>2</sub>X<sub>2</sub>].

The C<sub>2</sub>-symmetrical complexes [Pt(C<sup>^</sup>N)<sub>2</sub>X<sub>2</sub>] with X = MeCO<sub>2</sub><sup>-</sup>, CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup> as ancillary ligands showed significant luminescence in deaerated CH<sub>2</sub>Cl<sub>2</sub> solutions at 298 K from a <sup>3</sup>LC excited state with a small MLCT contribution.<sup>128</sup> The fluoro complex showed a high quantum yield (Φ = 0.398), but the rest of derivatives showed significantly weaker emissions (Φ = 0.0034–0.114). Along the halide series, the quantum yields decrease in the sequence F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> and the iodo complex is not emissive. This is explained by the existence of <sup>3</sup>LMCT [p(X)

$\rightarrow d\sigma^*$ ] and  $^3LLCT [p(X) \rightarrow \pi^*(ppy)]$  excited states, whose energies decrease as the energy of the halide lone pairs increase (for heavier halides), resulting in increased thermal accessibility and nonradiative deactivation. A similar effect was found for the acetato and trifluoroacetato complexes, the latter showing a somewhat higher quantum yield. The exceptionally high quantum yield of the fluoride complex was explained by the higher MLCT character of its emitting state, which leads to a much higher radiative rate constant with respect to the rest of complexes. In turn, this higher MLCT character was explained by the more effective  $d\pi(\text{Pt})-p(\text{F})$  orbital overlap, resulting in an enhanced  $\pi$  donation from the fluorido ligand.

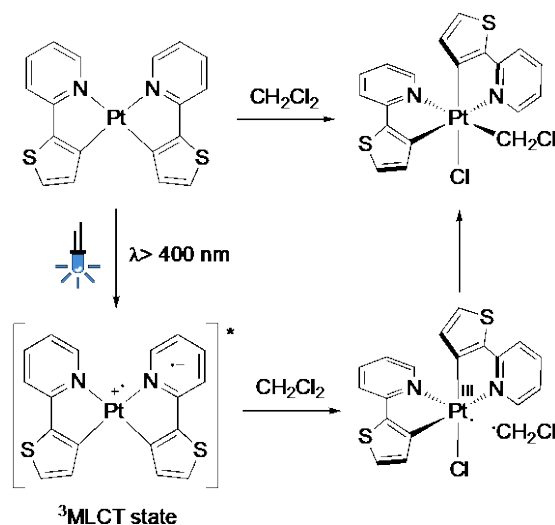
### Unsymmetrical $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{R}/\text{Ar})\text{X}]$ complexes

These complexes present an unsymmetrical arrangement of cyclometalated 2-arylpyridines, a metalated alkyl (R) or aryl (Ar) group, and a halido or other anionic ligand (X). Complexes of this type were obtained through photochemical oxidative addition of halocarbon solvents to *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$  complexes.<sup>124</sup> Extended series were prepared by thermal or photochemical oxidative addition of alkyl halides (Scheme 6).<sup>138</sup>



**Scheme 6.** Thermal or photochemical oxidative additions of alkyl halides to *cis*- $[\text{Pt}(\text{ppy})_2]$ . R = alkyl; X = Cl, Br.

The proposed mechanism for the photochemical oxidative addition of alkyl halides to *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$  complexes involves the reduction of the alkyl halide by the  $^3MLCT$  state of the complex, resulting in halogen abstraction to form a pentacoordinate Pt(III) intermediate and an alkyl radical. Combination of these two species results in the Pt(IV) complex (Scheme 7).<sup>138,139</sup> Additional radical steps can propagate the reaction. It is important to note that oxidative additions of aryl halides to *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$  complexes were not achieved.<sup>138</sup>



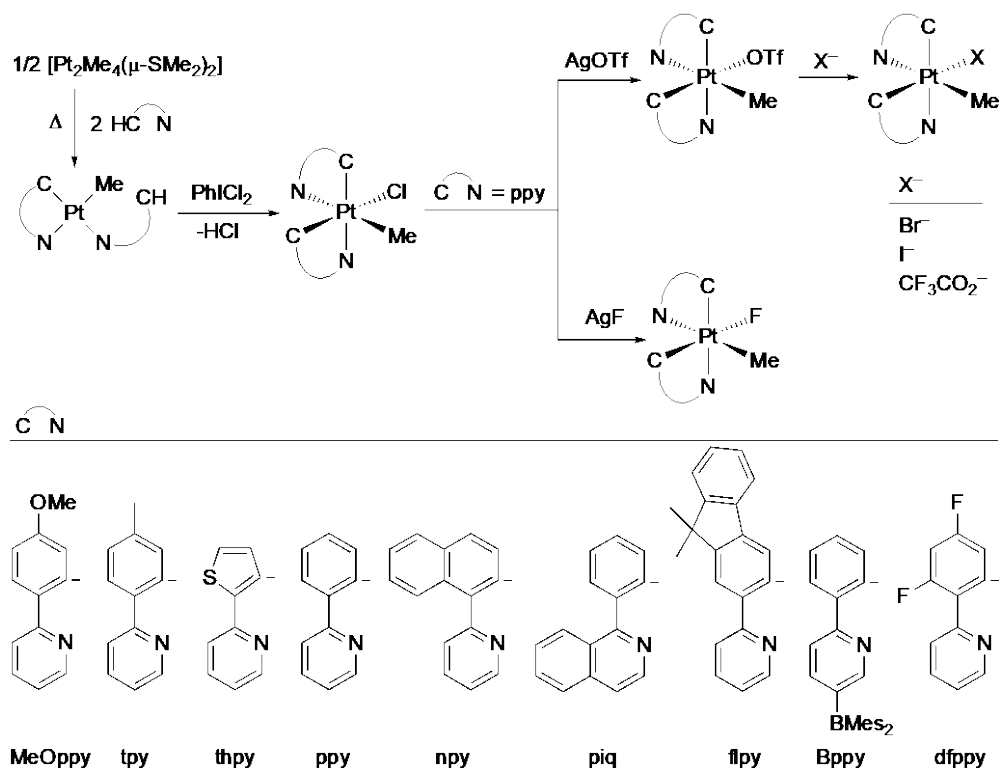
**Scheme 7.** Proposed mechanism for the photooxidative addition of  $\text{CH}_2\text{Cl}_2$  to *cis*- $[\text{Pt}(\text{thpy})_2]$ .

The complexes  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{R})\text{Cl}]$ , with  $\text{C}^{\wedge}\text{N}$  = cyclometalated 2-phenylpyridine or 2-(2-thienyl)pyridine and  $\text{R} = \text{CH}_2\text{Cl}$  or  $\text{CHCl}_2$ , presented phosphorescent emissions in solution at room temperature, with quantum yields in the range 0.05–0.15 and lifetimes in the range 100–270  $\mu\text{s}$ , which were ascribed to a  $^3\text{LC}$  excited state.<sup>124</sup> They are regarded as the first luminescent organometallic Pt(IV) complexes.

Complexes  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{Me})\text{Cl}]$  were synthesized by members of the Organometallic Chemistry Group of the University of Murcia through a high-yield method starting from  $[\text{Pt}_2(\text{Me})_4(\mu\text{-SMe}_2)_2]$  (Scheme 8).<sup>127</sup> The reaction with 2-arylpyridines gave complexes of the type  $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{Me})(\text{N}^{\wedge}\text{CH})]$ , which reacted with  $\text{PhICl}_2$  to give the Pt(IV) complexes  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{Me})\text{Cl}]$ , featuring an unsymmetrical arrangement of cyclometalated 2-arylpyridine ligands. Substitution of the chlorido ligand by triflate, carboxylato or other halido ligands was carried out for the 2-phenylpyridine derivative using silver salts.<sup>128</sup>

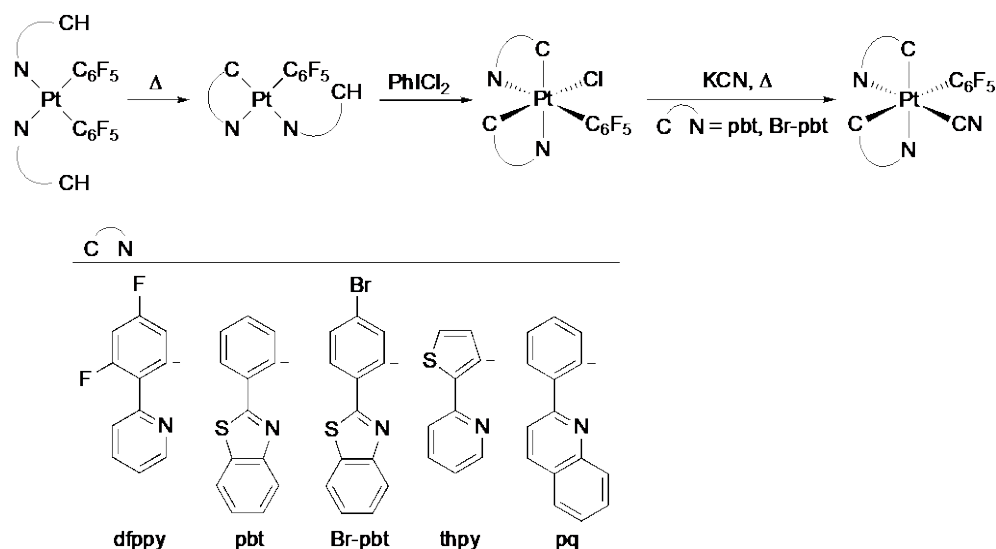
These bis-cyclometalated halido(methyl) Pt(IV) complexes can achieve very efficient phosphorescent emissions from  $^3\text{LC}$  states with a small MLCT contribution. The methyl group is a strong  $\sigma$  donor, which raises the energy of  $d\sigma^*(\text{Pt})$  orbitals and, hence, that of  $^3\text{LMCT}$  states, thereby drastically reducing nonradiative deactivation. The quantum yields in solution are in the range 0.04–0.81. The derivative with 5-(dimesitylboranyl)-2-phenylpyridine (Bppy) presented the highest quantum yield ever found for a Pt(IV) complex in fluid solution at room temperature ( $\Phi = 0.81$ ).

Among the  $[\text{Pt}(\text{ppy})_2(\text{Me})\text{X}]$  series, it was found that the fluoro complex showed the highest radiative rate constant ( $k_r$ ), which was attributed to an effective  $\pi$  donation from the fluoro ligand and increased MLCT character of its emitting state due to the greater participation of the metal  $d\pi$  orbitals.<sup>128</sup>



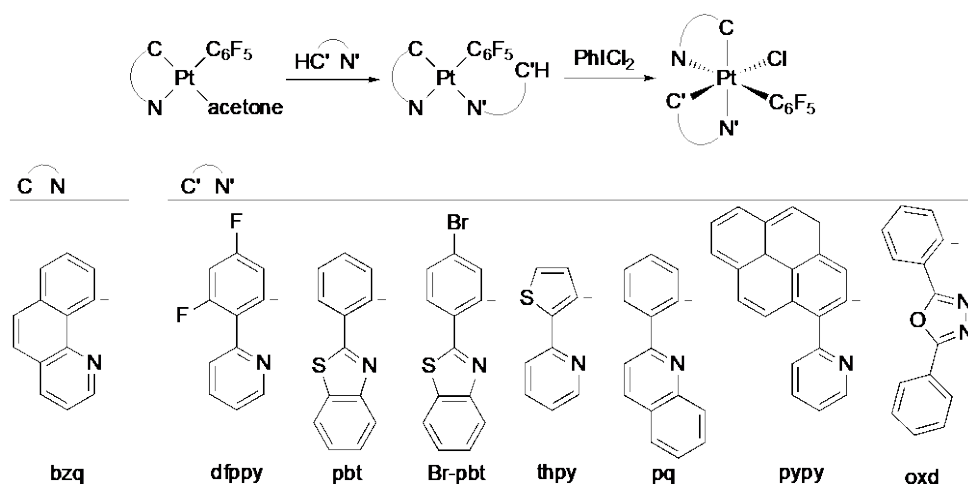
**Scheme 8.** Synthesis of bis-cyclometalated unsymmetrical  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{Me})\text{X}]$  complexes.

Pentafluorophenyl complexes  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{C}_6\text{F}_5)\text{X}]$  were the only bis-cyclometalated Pt(IV) aryl complexes reported before the present thesis was started.<sup>130,131</sup> Two different synthetic methodologies were employed. The first series was prepared from complexes of the type  $[\text{Pt}(\text{N}^{\wedge}\text{CH})_2(\text{C}_6\text{F}_5)_2]$ , which undergo metalation of one of the coordinated  $\text{N}^{\wedge}\text{CH}$  ligands upon heating to give complexes  $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{C}_6\text{F}_5)(\text{N}^{\wedge}\text{CH})]$ . Then, metalation of the remaining  $\text{N}^{\wedge}\text{CH}$  ligand is achieved upon oxidation with  $\text{PhICl}_2$  in dichloromethane, yielding complexes  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{C}_6\text{F}_5)\text{Cl}]$  (Scheme 9).<sup>130</sup>



**Scheme 9.** Synthesis of bis-cyclometalated Pt(IV) pentafluorophenyl complexes.

A second series of pentafluorophenyl Pt(IV) complexes bearing two different cyclometalated ligands was prepared from  $[\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)(\text{acetone})]$  (bzq = cyclometalated benzoquinoline), which reacted with diverse 2-arylpiperidines and related heteroaromatic ligands to give  $[\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)(\text{N}^{\wedge}\text{C}'\text{H})]$  derivatives. Oxidation with  $\text{PhICl}_2$  led to the cyclometalation of the  $\text{N}^{\wedge}\text{CH}$  ligand to produce complexes  $[\text{Pt}(\text{bzq})(\text{C}'^{\wedge}\text{N}')(\text{C}_6\text{F}_5)\text{Cl}]$  (Scheme 10).<sup>131</sup>



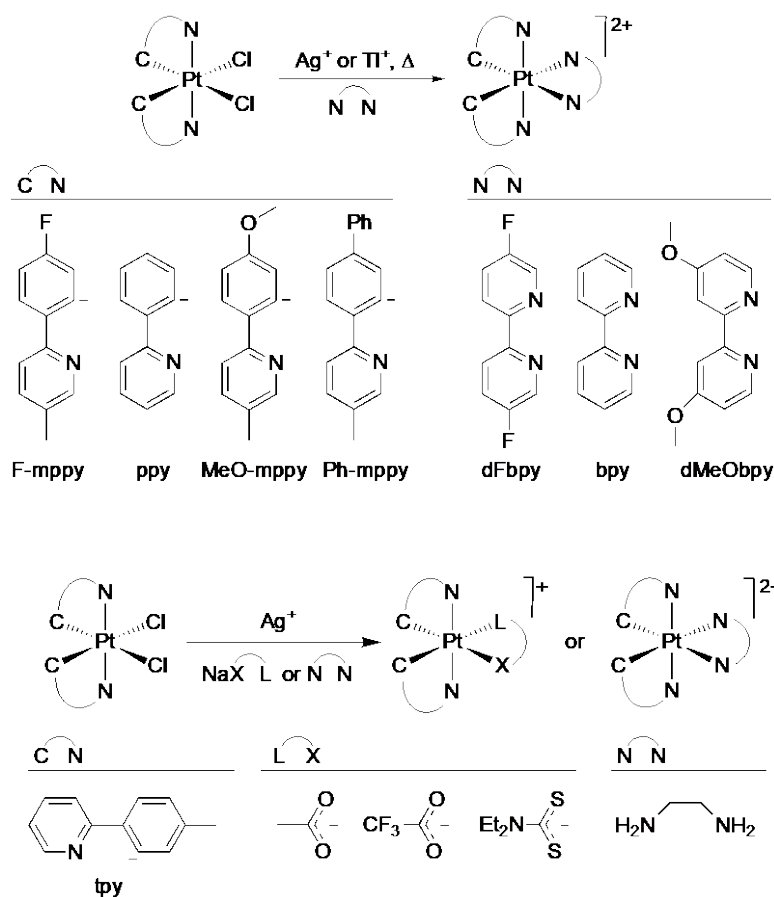
**Scheme 10.** Synthesis of pentafluorophenyl Pt(IV) complexes bearing two different cyclometalated ligands.

The  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{C}_6\text{F}_5)\text{Cl}]$  and  $[\text{Pt}(\text{bzq})(\text{C}'^{\wedge}\text{N}')(\text{C}_6\text{F}_5)\text{Cl}]$  complexes display phosphorescent emissions in fluid solution and solid matrices at room temperature from  $^3\text{LC}$  excited states, but

quantum yields were only measured in solid matrices, reaching up to 0.18 for the first series and 0.85 for the second series.

### $C_2$ -Symmetrical, tris-chelate $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^{2+}$ or $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{L}^{\wedge}\text{X})]^+$ complexes

The abstraction of the chlorido ligands in  $C_2$ -symmetrical complexes  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2\text{Cl}_2]$  using  $\text{Ag}(\text{I})$  or  $\text{Tl}(\text{I})$  salts in the presence of bidentate ligands has allowed the synthesis of  $C_2$ -symmetrical, cationic tris-chelate complexes of the types  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^{2+}$  or  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{L}^{\wedge}\text{X})]^+$ , where  $\text{N}^{\wedge}\text{N}$  can be an aromatic  $\alpha$ -diimine, such as 2,2'-bipyridine and substituted derivatives,<sup>125</sup> or an aliphatic diamine,<sup>140</sup> whereas  $\text{L}^{\wedge}\text{X}$  is a carboxylato or dithiocarbamato ligand<sup>140</sup> (Scheme 11).



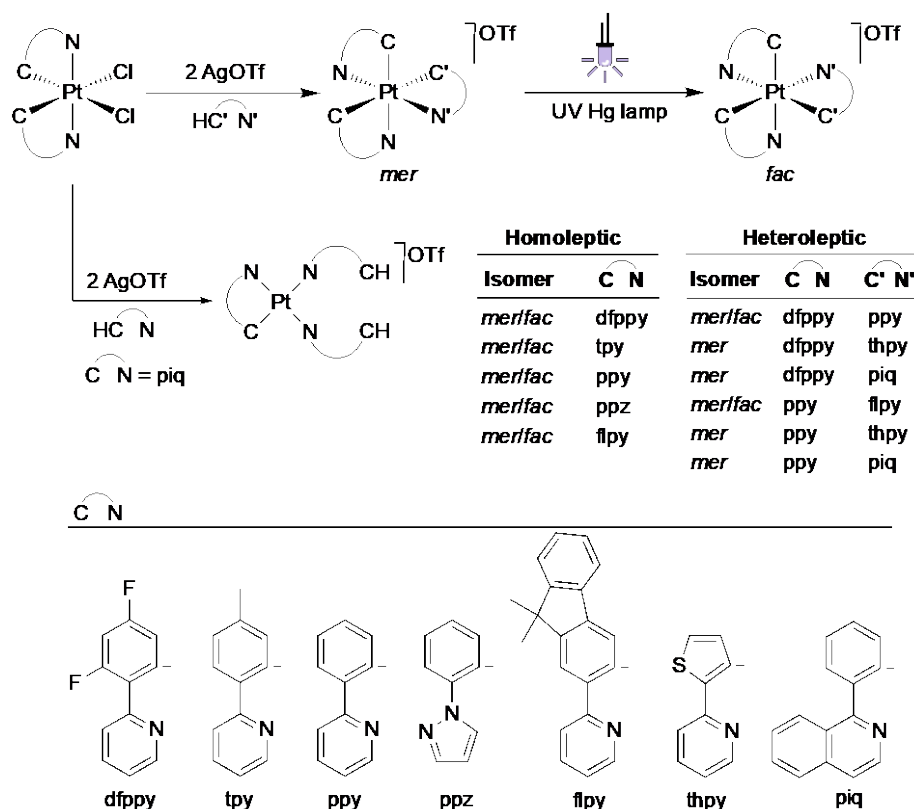
**Scheme 11.** Synthesis of complexes of the types  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^{2+}$  and  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{L}^{\wedge}\text{X})]^+$ .

The reported complexes of the types  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^{2+}$  and  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{L}^{\wedge}\text{X})]^+$  show phosphorescence in solution at 298 K with very low quantum yields, arising from  $^3\text{LC}$  states involving the 2-arylpyridine ligands. These low efficiencies are possibly attributable to the presence of low-lying deactivating states of  $^3\text{LMCT}$  character that can be thermally populated.

### Tris-cyclometalated complexes $[\text{Pt}(\text{C}^{\wedge}\text{N})_3]^+$

Members of the Organometallic Chemistry Group of the University of Murcia showed that homoleptic and heteroleptic tris-cyclometalated complexes could be prepared by treatment of  $C_2$ -symmetrical complexes  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2\text{Cl}_2]$  with silver triflate and an excess of a 2-arylpyridine ligand, which can be equal ( $\text{N}^{\wedge}\text{CH}$ ) or different ( $\text{N}^{\wedge}\text{C}^{\wedge}\text{H}$ ) to that of the metal precursor. The silver

ions perform the abstraction of the chlorido ligands, facilitating the coordination of the  $N^{\wedge}CH$  or  $N^{\wedge}C'H$  ligand and its subsequent metalation to afford cationic complexes with a meridional (*mer*) geometry,  $mer-[Pt(C^{\wedge}N)_3]^+$  or  $mer-[Pt(C^{\wedge}N)_2(C^{\wedge}N')]^+$  (Scheme 12).<sup>123,126,129</sup> The formation of these complexes required long reaction times (3-4 days) and high temperatures (dichloroethane at 90 °C or 1,2-dichlorobenzene at 120 °C), and were successful only when the  $C^{\wedge}N$  ligands in the  $[Pt(C^{\wedge}N)_2Cl_2]$  precursors feature a relatively high energy for the  $\pi-\pi^*$  transition. In contrast, when the ligands in these precursors had a low energy for the  $\pi-\pi^*$  transition, as is the case of 2-(2-thienyl)pyridine (thpy) or 1-phenylisoquinoline (piq), reduction to Pt(II) species took place under the employed conditions.



**Scheme 12.** Reported syntheses of homoleptic and heteroleptic tris-cyclometalated Pt(IV) complexes.

The *mer* complexes could be transformed into their facial (*fac*) isomers,  $fac-[Pt(C^{\wedge}N)_3]^+$  or  $fac-[Pt(C^{\wedge}N)_2(C^{\wedge}N')]^+$ , upon irradiation of diluted MeCN solutions with a medium-pressure UV Hg lamp in a photoreactor (Scheme 12).<sup>123,126,129</sup> However, these photoisomerizations afforded low yields of the *fac* complexes and were only successful when all of the cyclometalated ligands had a relatively high energy for the  $\pi-\pi^*$  transition. In contrast, attempts to photoisomerize the heteroleptic complexes  $mer-[Pt(C^{\wedge}N)_2(thpy)]^+$  or  $mer-[Pt(C^{\wedge}N)_2(piq)]^+$  led to mixtures of unidentified complexes.<sup>126</sup> Before the present Thesis, the only heteroleptic tris-cyclometalated Pt(IV) complexes with a *fac* geometry were  $fac-[Pt(dfppy)_2(ppy)]^+$ <sup>126</sup> and  $fac-[Pt(ppy)_2(flpy)]^+$ .<sup>129</sup>

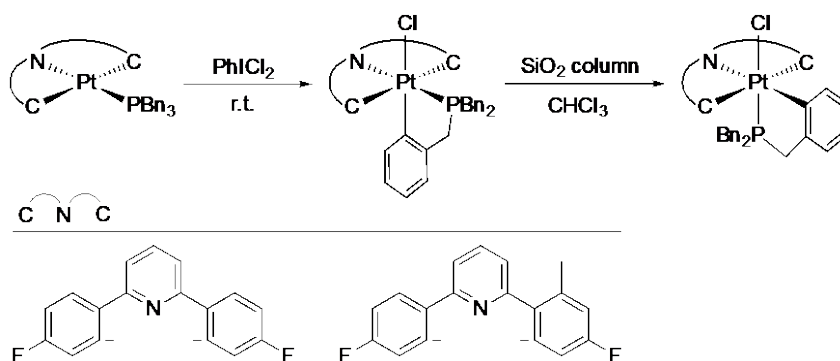
The observed photoreactivity of the *mer* isomers is due to the presence of low-lying, dissociative  $^3LMCT$  states that can be thermally populated from  $^3LC$  states.<sup>123</sup> In contrast, the *fac* isomers were highly photostable and were capable of producing highly efficient phosphorescent emissions in deaerated solutions at 298 K ( $\Phi = 0.01-0.49$ ), arising from  $^3LC$  states with very little

$^3\text{MLCT}$  character. These emissions were characterized by high energies (in the blue region) and long lifetimes (up to 319  $\mu\text{s}$ ), making these complexes promising as photosensitizers, photocatalysts or sensors. These high efficiencies are possible because the *fac* geometry leads to a large ligand-field splitting, resulting higher energies of the deactivating  $^3\text{LMCT}$  states, which become inaccessible from the lowest triplet state.

The heteroleptic tris-cyclometalated complexes with a *mer* geometry,  $\text{mer-}[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{thpy})]^+$  and  $\text{mer-}[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{piq})]^+$ , showed weak phosphorescent emissions in the yellow or orange colour regions in fluid solution at 298 K ( $\Phi = 0.020\text{--}0.072$ ), arising from  $^3\text{LC}$  states involving the thpy or piq ligand, respectively.<sup>126</sup> These emissions are possible because the emitting states lie at relatively low energies and the thermal population of the reactive  $^3\text{LMCT}$  states is less effective as compared to homoleptic *mer* complexes bearing ligands with high energies for the  $\pi\text{--}\pi^*$  transition. Therefore, before the present Thesis, these were the only tris-cyclometalated Pt(IV) complexes showing relatively low emission energies, and neither homoleptic nor heteroleptic *fac* complexes bearing thpy or piq as the cyclometalated ligands had been synthesized.

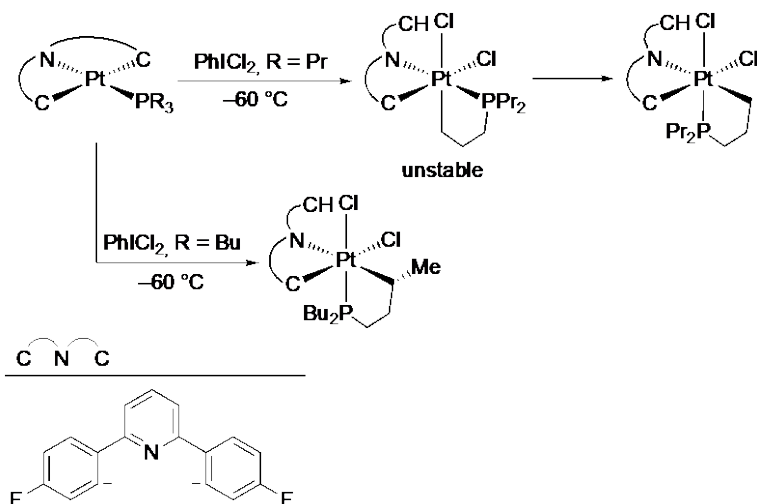
### Complexes with terdentate ligands

Pt(IV) complexes with terdentate dicyclopalladated 2,6-diarylpyridines ( $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$ ) have been obtained through the oxidation of Pt(II) complexes of the type  $[\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})(\text{PR}_3)]$  [ $\text{R} = \text{benzyl (Bn)}^{141}$ ,  $n\text{-propyl (Pr)}^{142}$  or  $n\text{-butyl (Bu)}^{143}$ ] with  $\text{PhICl}_2$ . When  $\text{R} = \text{Bn}$ , the electrophilic metalation of the pendant phenyl ring occurs, leading to the complex  $[\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})(\text{C}^{\wedge}\text{PBn}_2)\text{Cl}]$  (Scheme 13). For  $\text{R} = \text{Pr}$ , the oxidation with  $\text{PhICl}_2$  was carried out at  $-60\text{ }^\circ\text{C}$ , resulting in the metalation of the methyl group of one of the propyl chains, with concomitant demetalation of an aryl ring of the  $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$  ligand (Scheme 14). When the same reaction is carried out in chloroform with  $\text{R} = \text{Bu}$ , it is possible to obtain a similar complex as minor product where the alkyl chain is metalated by the third carbon (Scheme 14). Photophysical studies of these Pt(IV) complexes have not been carried out.



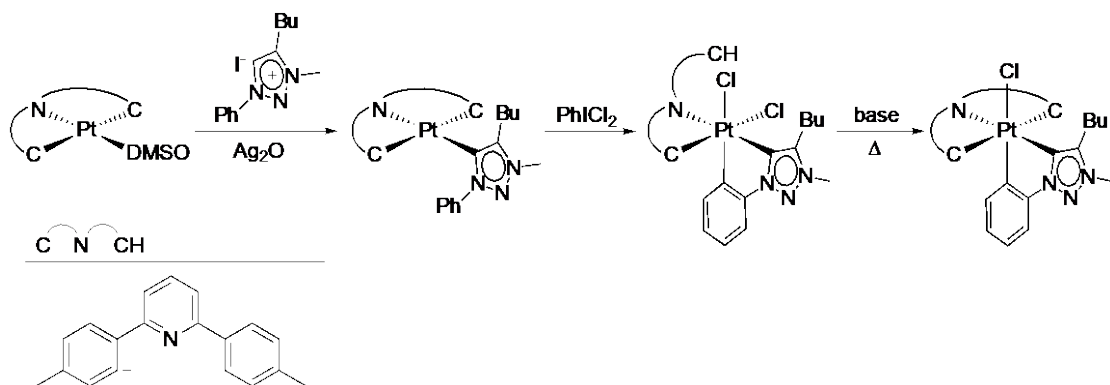
**Scheme 13.** Pt(IV) complexes containing dimetalated terdentate  $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$  ligands.





**Scheme 14.** Pt(IV) complexes containing dimetalated terdentate  $C^N^C$  ligands.

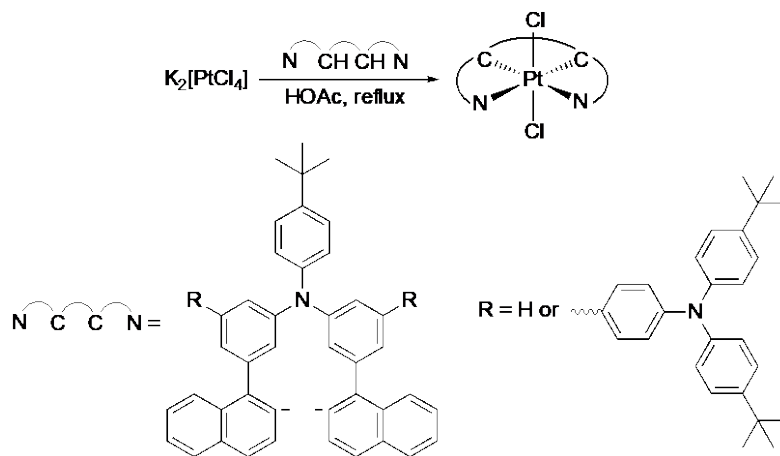
Recently, members of the Organometallic Chemistry Group of the University of Murcia developed a synthetic route to a Pt(IV) complex with one dimetalated terdentate  $C^N^C$  ligand and one cyclometalated aryl-N-heterocyclic carbene ( $C^*C^*$ ) (Scheme 15).<sup>132</sup> The synthesis implied the transmetalation of 4-butyl-3-methyl-1-phenyl-1*H*-1,2,3-triazol-5-ylidene ( $C^*CH$ ) to Pt(II) through the reaction between  $[Pt(C^N^C)(DMSO)]$ , where  $C^N^C$  = dicyclopentadienyl 2,6-di(*p*-tolyl)pyridine, DMSO = dimethyl sulfoxide, and the silver carbene to give  $[Pt(C^N^C)(C^*CH)]$ . Upon oxidation with  $PhICl_2$ , the electrophilic metalation of the pendant phenyl group of the  $C^*CH$  ligand was achieved, but demetalation of one of the *p*-tolyl groups of the  $C^N^C$  ligand occurred concomitantly to give  $[Pt(C^N^*CH)(C^*C)Cl_2]$ . By heating this complex in the presence of a base, the complex  $[Pt(C^N^C)(C^*C)Cl]$  was obtained. These two Pt(IV) complexes showed phosphorescent emissions from  $^3LC$  excited states involving the  $C^N^*CH$  or  $C^N^C$  ligand. The emission quantum yield of  $[Pt(C^N^*CH)(C^*C)Cl_2]$  in fluid solution at 298 K was found to be higher than that of  $[Pt(ppy)_2Cl_2]$  ( $C_2$ -symmetrical isomer), which has an analogous structure, presumably because the stronger  $\sigma$  donating ability of the carbene moiety compared with the pyridine group of *ppy* induces a stronger ligand-field splitting, raising the energy of deactivating  $^3LMCT$  states and decreasing nonradiative deactivation. However, the complex  $[Pt(C^N^C)(C^*C)Cl]$  presented a weak emission in fluid solution, which was attributed to the mutually trans arrangement of metalated carbon atoms.



**Scheme 15.** Synthesis of Pt(IV) complexes bearing an aryl-N-heterocyclic carbene and a bi- or terdentate 2,6-diarylpdridine.

## Complexes with tetradentate ligands

Pt(IV) complexes with a tetradentate heteroaromatic ligand have been reported, which were obtained as unexpected oxidation products from the reactions between  $K_2PtCl_4$  and the ligand precursor in acetic acid at reflux temperature (Scheme 16).<sup>144</sup> Luminescence studies showed red or NIR emissions in solution or solid state, respectively, which were attributed to  $^3LC/MLCT$  states. Quantum yields were not reported.



**Scheme 16.** Synthesis of bis-cyclometalated Pt(IV) complexes with a tetradentate ligand.

## References

- (1) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. Ru(II) Polypyridine Complexes: Photophysics, Photochemistry, Electrochemistry, and Chemiluminescence. *Coord. Chem. Rev.* **1988**, *84*, 85–277.
- (2) Demas, J. N.; DeGraff, B. A. Design and Applications of Highly Luminescent Transition Metal Complexes. *Anal. Chem.* **1991**, *63*, 829A–837A.
- (3) Baranoff, E.; Collin, J.-P.; Flamigni, L.; Sauvage, J.-P. From Ruthenium(II) to Iridium(III): 15 Years of Triads Based on Bis-terpyridine Complexes. *Chem. Soc. Rev.* **2004**, *33*, 147–155.
- (4) Balzani, V.; Juris, A. Photochemistry and Photophysics of Ru(II) Polypyridine Complexes in the Bologna Group. From Early Studies to Recent Developments. *Coord. Chem. Rev.* **2001**, *211*, 97–115.
- (5) Yam, V. W. W.; Wong, K. M. C. Luminescent Metal Complexes of  $d^6$ ,  $d^8$  and  $d^{10}$  Transition Metal Centres. *Chem. Commun.* **2011**, *47*, 11579–11592.
- (6) Lee, L. C.; Lo, K. K. Luminescent and Photofunctional Transition Metal Complexes: From Molecular Design to Diagnostic and Therapeutic Applications. *J. Am. Chem. Soc.* **2022**, *144*, 14420–14440.
- (7) Campagna, S.; Puntoriero, F.; Nastatsi, F.; Bergamini, G.; Balzani, V. Photochemistry and Photophysics of Coordination Compounds: Ruthenium. *Top. Curr. Chem.* **2007**, *280*, 117–214.
- (8) Kirgan, R. A.; Sullivan, B. P.; Rillema, D. P. Photochemistry and Photophysics of Coordination Compounds: Rhenium. *Top. Curr. Chem.* **2007**, *281*, 45–100.
- (9) Kumaresan, D.; Shankar, K.; Vaidya, S.; Schmehl, R. H. Photochemistry and Photophysics of Coordination Compounds: Osmium. *Top. Curr. Chem.* **2007**, *281*, 101–142.
- (10) Carlson, B.; Phelan, G. D.; Kaminsky, W.; Dalton, L.; Jiang, X.; Liu, S.; Jen, A. K. Y. Divalent Osmium Complexes: Synthesis, Characterization, Strong Red Phosphorescence, and Electrophosphorescence. *J. Am. Chem. Soc.* **2002**, *124*, 14162–14172.
- (11) Chen, Y. L.; Li, S. W.; Chi, Y.; Cheng, Y. M.; Pu, S. C.; Yeh, Y. S.; Chou, P. T. Switching Luminescent Properties in Osmium-Based Beta-Diketonate Complexes. *Chem. Phys. Chem.* **2005**, *6*, 2012–2017.
- (12) Chou, P. T.; Chi, Y. Osmium- and Ruthenium-Based Phosphorescent Materials: Design, Photophysics, and Utilization in OLED Fabrication. *Eur. J. Inorg. Chem.* **2006**, 3319–3332.
- (13) Flamigni, L.; Barbieri, A.; Sabatini, C.; Ventura, B.; Barigelletti, F. Photochemistry and Photophysics of Coordination Compounds: Iridium. *Top. Curr. Chem.* **2007**, *281*, 143–203.

- (14) Deaton, J. C.; Castellano, F. N. Archetypal Iridium(III) Compounds for Optoelectronic and Photonic Applications. In *Iridium(III) in Optoelectronic and Photonics Applications*; Zysman-Colman, E., Ed.; John Wiley & Sons: Chichester, UK, 2017; pp 1–69.
- (15) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. Synthesis and Characterization of Phosphorescent Cyclometalated Iridium Complexes. *Inorg. Chem.* **2001**, *40*, 1704–1711.
- (16) You, Y.; Park, S. Y. Phosphorescent Iridium(III) Complexes: Toward High Phosphorescence Quantum Efficiency through Ligand Control. *Dalton Trans.* **2009**, 1267–1282.
- (17) Mills, I. N.; Porras, J. A.; Bernhard, S. Judicious Design of Cationic, Cyclometalated Ir(III) Complexes for Photochemical Energy Conversion and Optoelectronics. *Acc. Chem. Res.* **2018**, *51*, 352–364.
- (18) Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P. I.; Tsyba, I.; Bau, R.; Thompson, M. E. Synthesis and Characterization of Phosphorescent Cyclometalated Platinum Complexes. *Inorg. Chem.* **2002**, *41*, 3055–3066.
- (19) Huo, S.; Carroll, J.; Vezzu, D. A. K. Design, Synthesis, and Applications of Highly Phosphorescent Cyclometalated Platinum Complexes. *Asian. J. Org. Chem.* **2015**, *4*, 1210–1245.
- (20) Williams, J. A. G.; Develay, S.; Rochester, D. L.; Murphy, L. Optimising the Luminescence of Platinum(II) Complexes and Their Application in Organic Light Emitting Devices (OLEDs). *Coord. Chem. Rev.* **2008**, *252*, 2596–2611.
- (21) Yam, V. W.; Tang, R. P.; Wong, K. M.; Lu, X. Syntheses, Electronic Absorption, Emission, and Ion-Binding Studies of Platinum(II) C<sup>N</sup>C and Terpyridyl Complexes Containing Crown Ether Pendants. *Chem. Eur. J.* **2002**, *8*, 4066–4076.
- (22) Ma, B.; Li, J.; Djurovich, P. I.; Yousufuddin, M.; Bau, R.; Thompson, M. E. Synthetic Control of Pt···Pt Separation and Photophysics of Binuclear Platinum Complexes. *J. Am. Chem. Soc.* **2005**, *127*, 28–29.
- (23) Vezzu, D. A. K.; Deaton, J. C.; Jones, J. S.; Bartolotti, L.; Harris, C. F.; Marchetti, A. P.; Kondakova, M.; Pike, R. D.; Huo, S. Highly Luminescent Tetradentate Bis-Cyclometalated Platinum Complexes: Design, Synthesis, Structure, Photophysics, and Electroluminescence Application. *Inorg. Chem.* **2010**, *49*, 5107–5119.
- (24) Kui, S. C. F.; Chui, S. S.-Y.; Che, C.-M.; Zhu, N. Structures, Photoluminescence, and Reversible Vapoluminescence Properties of Neutral Platinum(II) Complexes Containing Extended  $\pi$ -Conjugated Cyclometalated Ligands. *J. Am. Chem. Soc.* **2006**, *128*, 8297–8309.
- (25) Farley, S. J.; Rochester, D. L.; Thompson, A. L.; Howard, J. A. K.; Williams, J. A. G. Controlling Emission Energy, Self-Quenching, and Excimer Formation in

- Highly Luminescent N<sup>^</sup>C<sup>^</sup>N-Coordinated Platinum(II) Complexes. *Inorg. Chem.* **2005**, *44*, 9690–9703.
- (26) Williams, J. A. G. Photochemistry and Photophysics of Coordination Compounds: Platinum. *Top. Curr. Chem.* **2007**, *281*, 205–268.
- (27) Wong, K. M.-C.; Yam, V. W.-W. Luminescence Platinum(II) Terpyridyl Complexes - From Fundamental Studies to Sensory Functions. *Coord. Chem. Rev.* **2007**, *251*, 2477–2488.
- (28) Berenguer, J. R.; Lalinde, E.; Torroba, J. Synthesis, Characterization and Photophysics of a New Series of Anionic C,N,C Cyclometalated Platinum Complexes. *Inorg. Chem.* **2007**, *46*, 9919–9930.
- (29) Atoini, Y.; Prasetyanto, E. A.; Chen, P.; Silvestrini, S.; Harrowfield, J.; De Cola, L. Luminescence of Amphiphilic Pt<sup>II</sup> Complexes Controlled by Confinement. *Chem. Eur. J.* **2018**, *24*, 12054–12060.
- (30) Díez, Á.; Forniés, J.; Larraz, C.; Lalinde, E.; López, J. A.; Martín, A.; Moreno, M. T.; Sicilia, V. Structural and Luminescence Studies on  $\pi \cdots \pi$  and Pt $\cdots$ Pt Interactions in Mixed Chloro-Isocyanide Cyclometalated Platinum(II) Complexes. *Inorg. Chem.* **2010**, *49*, 3239–3251.
- (31) Bronner, C.; Wenger, O. S. Luminescent Cyclometalated Gold(III) Complexes. *Dalton Trans.* **2011**, *40*, 12409–12420.
- (32) Au, V. K.-M.; Wong, K. M.-C.; Zhu, N.; Yam, V. W.-W. Luminescent Cyclometalated Dialkynylgold(III) Complexes of 2-Phenylpyridine-Type Derivatives with Readily Tunable Emission Properties. *Chem. Eur. J.* **2011**, *17*, 130–142.
- (33) To, W. P.; Tong, G. S.; Lu, W.; Ma, C.; Liu, J.; Chow, A. L.; Che, C. M. Luminescent Organogold(III) Complexes with Long-Lived Triplet Excited States for Light-Induced Oxidative C-H Bond Functionalization and Hydrogen Production. *Angew. Chem. Int. Ed.* **2012**, *51*, 2654–2657.
- (34) Tang, M.-C.; Lee, C.-H.; Ng, M.; Wong, Y.-C.; Chan, M.-Y.; Yam, V. W.-W. Highly Emissive Fused Heterocyclic Alkynylgold(III) Complexes for Multiple Color Emission Spanning from Green to Red for Solution-Processable Organic Light-Emitting Devices. *Angew. Chem. Int. Ed.* **2018**, *57*, 5463–5466.
- (35) Bachmann, M.; Fessler, R.; Blacque, O.; Venkatesan, K. Towards Blue Emitting Monocyclometalated Gold(III) Complexes – Synthesis, Characterization and Photophysical Investigations. *Dalton Trans.* **2019**, *48*, 7320–7330.
- (36) Kumar, R.; Nevado, C. Cyclometalated Gold(III) Complexes: Synthesis, Reactivity, and Physicochemical Properties. *Angew. Chem., Int. Ed.* **2017**, *56*, 1994–2015.
- (37) Fernandez-Cestau, J.; Bertrand, B.; Pintus, A.; Bochmann, M. Synthesis, Structures, and Properties of Luminescent (C<sup>^</sup>N<sup>^</sup>C)Gold(III) Alkyl Complexes:

- Correlation between Photoemission Energies and C-H Acidity. *Organometallics* **2017**, *36*, 3304–3312.
- (38) Liu, Y.; Kjær, K. S.; Fredin, L. A.; Chábera, P.; Harlang, T.; Canton, S. E.; Lidin, S.; Zhang, J.; Lomoth, R.; Bergquist, K. E.; Persson, P.; Wärnmark, K.; Sundström, V. A Heteroleptic Ferrous Complex with Mesoionic Bis(1,2,3-triazol-5-ylidene) Ligands: Taming the MLCT Excited State of Iron(II). *Chem. Eur. J.* **2015**, *21*, 3628–3639.
- (39) Pal, A. K.; Li, C.; Hanan, G. S.; Zysman-Colman, E. Blue-Emissive Cobalt(III) Complexes and Their Use in the Photocatalytic Trifluoromethylation of Polycyclic Aromatic Hydrocarbons. *Angew. Chem., Int. Ed.* **2018**, *57*, 8027–8031.
- (40) Chábera, P.; Kjaer, K. S.; Prakash, O.; Honarfar, A.; Liu, Y.; Fredin, L. A.; Harlang, T. C. B.; Lidin, S.; Uhlig, J.; Sundström, V.; Lomoth, R.; Persson, P.; Wärnmark, K. Fe<sup>II</sup> Hexa N-Heterocyclic Carbene Complex with a 528 ps Metal-to-Ligand Charge-Transfer Excited-State Lifetime. *J. Phys. Chem. Lett.* **2018**, *9*, 459–463.
- (41) Wenger, O. S. Photoactive Complexes with Earth-Abundant Metals. *J. Am. Chem. Soc.* **2018**, *140*, 13522–13533.
- (42) Wenger, O. S. Is Iron the New Ruthenium? *Chem. Eur. J.* **2019**, *25*, 6043–6052.
- (43) Thompson, M. E.; Djurovich, P. E.; Barlow, S.; Marder, S. Organometallic Complexes for Optoelectronic Applications. In *Comprehensive Organometallic Chemistry III*; Robert, H. C., Mingos, D. M. P., Eds.; Elsevier: Oxford, 2007; pp 101–194.
- (44) Kalinowski, J.; Fattori, V.; Cocchi, M.; Williams, J. A. G. Light-Emitting Devices Based on Organometallic Platinum Complexes as Emitters. *Coord. Chem. Rev.* **2011**, *255*, 2401–2425.
- (45) Chou, P. T.; Chi, Y. Phosphorescent Dyes for Organic Light-Emitting Diodes. *Chem. Eur. J.* **2007**, *13*, 380–395.
- (46) Fu, H.; Cheng, Y.-M.; Chou, P.-T.; Chi, Y. Feeling Blue? Blue Phosphors for OLEDs. *Mater. Today* **2011**, *14*, 472–479.
- (47) Longhi, E.; De Cola, L. Iridium(III) Complexes for OLED Application. In *Iridium(III) in Optoelectronic and Photonics Applications*; John Wiley & Sons, Ltd: Chichester, UK, 2017; pp 205–274.
- (48) Fleetham, T.; Li, G.; Li, J. Phosphorescent Pt(II) and Pd(II) Complexes for Efficient, High-Color-Quality, and Stable OLEDs. *Adv. Mater.* **2017**, *29*, 1–16.
- (49) Tang, M. C.; Chan, A. K. W.; Chan, M. Y.; Yam, V. W. W. Platinum and Gold Complexes for OLEDs. *Top. Curr. Chem.* **2016**, *374*, 1–43.
- (50) Xiao, L.; Chen, Z.; Qu, B.; Luo, J.; Kong, S.; Gong, Q.; Kido, J. Recent Progresses on Materials for Electrophosphorescent Organic Light-Emitting Devices. *Adv. Mater.* **2011**, *23*, 926–952.

- (51) Costa, R. D.; Ortí, E.; Bolink, H. J.; Monti, F.; Accorsi, G.; Armaroli, N. Luminescent Ionic Transition-Metal Complexes for Light-Emitting Electrochemical Cells. *Angew. Chem., Int. Ed.* **2012**, *51*, 8178–8211.
- (52) Yersin, H. Highly Efficient OLEDs with Phosphorescent Materials; Yersin, H., Ed.; Wiley, 2008.
- (53) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113*, 5322–5363.
- (54) Narayanam, J. M. R.; Stephenson, C. R. J. Visible Light Photoredox Catalysis: Applications in Organic Synthesis. *Chem. Soc. Rev.* **2011**, *40*, 102–113.
- (55) McAtee, R. C.; McClain, E. J.; Stephenson, C. R. J. Illuminating Photoredox Catalysis. *Trends Chem.* **2019**, *1*, 111–125.
- (56) Kim, H.; Lee, C. Visible-Light-Induced Photocatalytic Reductive Transformations of Organohalides. *Angew. Chem., Int. Ed.* **2012**, *51*, 12303–12306.
- (57) Schultz, D. M.; Yoon, T. P. Solar Synthesis: Prospects in Visible Light Photocatalysis. *Science* **2014**, *343*, 1239176.
- (58) Arias-Rotondo, D. M.; McCusker, J. K. The Photophysics of Photoredox Catalysis: A Roadmap for Catalyst Design. *Chem. Soc. Rev.* **2016**, *45*, 5803–5820.
- (59) Shon, J. H.; Teets, T. S. Photocatalysis with Transition Metal Based Photosensitizers. *Comments Inorg. Chem.* **2020**, *40*, 53–85.
- (60) Strieth-Kalthoff, F.; James, M. J.; Teders, M.; Pitzer, L.; Glorius, F. Energy Transfer Catalysis Mediated by Visible Light: Principles, Applications, Directions. *Chem. Soc. Rev.* **2018**, *47*, 7190–7202.
- (61) Strieth-Kalthoff, F.; Glorius, F. Triplet Energy Transfer Photocatalysis: Unlocking the Next Level. *Chem* **2020**, *6*, 1888–1903.
- (62) To, W. P.; Zou, T.; Sun, R. W. Y.; Che, C. M. Light-Induced Catalytic and Cytotoxic Properties of Phosphorescent Transition Metal Compounds with a  $d^8$  Electronic Configuration. *Philos. Trans. R. Soc., A* **2013**, *371*:20120126.
- (63) Vlček, A. The Life and Times of Excited States of Organometallic and Coordination Compounds. *Coord. Chem. Rev.* **2000**, *200–202*, 933–978.
- (64) Cheung, K. P. S.; Sarkar, S.; Gevorgyan, V. Visible Light-Induced Transition Metal Catalysis. *Chem. Rev.* **2022**, *122*, 1543–1625.
- (65) Zhang, K. Y.; Yu, Q.; Wei, H.; Liu, S.; Zhao, Q.; Huang, W. Long-Lived Emissive Probes for Time-Resolved Photoluminescence Bioimaging and Biosensing. *Chem. Rev.* **2018**, *118*, 1770–1839.
- (66) Lo, K. K. W. Luminescent Rhenium(I) and Iridium(III) Polypyridine Complexes as Biological Probes, Imaging Reagents, and Photocytotoxic Agents. *Acc. Chem. Res.* **2015**, *48*, 2985–2995.

- (67) Yip, A. M.-H.; Lo, K. K.-W. Luminescent Rhenium(I), Ruthenium(II), and Iridium(III) Polypyridine Complexes Containing a Poly(Ethylene Glycol) Pendant or Bioorthogonal Reaction Group as Biological Probes and Photocytotoxic Agents. *Coord. Chem. Rev.* **2018**, *361*, 138–163.
- (68) Baggaley, E.; Weinstein, J. A.; Williams, J. A. G. Lighting the Way to See inside the Live Cell with Luminescent Transition Metal Complexes. *Coord. Chem. Rev.* **2012**, *256*, 1762–1785.
- (69) Baggaley, E.; Cao, D.-K.; Sykes, D.; Botchway, S. W.; Weinstein, J. A.; Ward, M. D. Combined Two-Photon Excitation and d→f Energy Transfer in a Water-Soluble Ir<sup>III</sup>/Eu<sup>III</sup> Dyad: Two Luminescence Components from One Molecule for Cellular Imaging. *Chem. Eur. J.* **2014**, *20*, 8898–8903.
- (70) Baggaley, E.; Botchway, S. W.; Haycock, J. W.; Morris, H.; Sazanovich, I. V.; Williams, J. A. G.; Weinstein, J. A. Long-Lived Metal Complexes Open up Microsecond Lifetime Imaging Microscopy under Multiphoton Excitation: From FLIM to PLIM and Beyond. *Chem. Sci.* **2014**, *5*, 879–886.
- (71) Baggaley, E.; Gill, M. R.; Green, N. H.; Turton, D.; Sazanovich, I. V.; Botchway, S. W.; Smythe, C.; Haycock, J. W.; Weinstein, J. A.; Thomas, J. A. Dinuclear Ruthenium(II) Complexes as Two-Photon, Time-Resolved Emission Microscopy Probes for Cellular DNA. *Angew. Chem., Int. Ed. Engl.* **2014**, *53*, 3367–3371.
- (72) Carraway, E. R.; Demas, J. N.; DeGraff, B. A.; Bacon, J. R. Photophysics and Photochemistry of Oxygen Sensors Based on Luminescent Transition-Metal Complexes. *Anal. Chem.* **1991**, *63*, 337–342.
- (73) Ashen-Garry, D.; Selke, M. Singlet Oxygen Generation by Cyclometalated Complexes and Applications. *Photochem. Photobiol.* **2014**, *90*, 257–274.
- (74) Zhao, Q.; Li, F.; Huang, C. Phosphorescent Chemosensors Based on Heavy-Metal Complexes. *Chem. Soc. Rev.* **2010**, *39*, 3007–3030.
- (75) Ma, D.-L.; Ma, V. P.-Y.; Chan, D. S.-H.; Leung, K.-H.; He, H.-Z.; Leung, C.-H. Recent Advances in Luminescent Heavy Metal Complexes for Sensing. *Coord. Chem. Rev.* **2012**, *256*, 3087–3113.
- (76) Ruggi, A.; van Leeuwen, F. W. B.; Velders, A. H. Interaction of Dioxygen with the Electronic Excited State of Ir(III) and Ru(II) Complexes: Principles and Biomedical Applications. *Coord. Chem. Rev.* **2011**, *255*, 2542–2554.
- (77) Pham, T. C.; Nguyen, V.-N.; Choi, Y.; Lee, S.; Yoon, J. Recent Strategies to Develop Innovative Photosensitizers for Enhanced Photodynamic Therapy. *Chem. Rev.* **2021**, *121*, 13454–13619.
- (78) Monro, S.; Colón, K. L.; Yin, H.; Roque, J.; Konda, P.; Gujar, S.; Thummel, R. P.; Lilje, L.; Cameron, C. G.; McFarland, S. A. Transition Metal Complexes and Photodynamic Therapy from a Tumor-Centered Approach: Challenges, Opportunities, and Highlights from the Development of TLD1433. *Chem. Rev.* **2019**, *119*, 797–828.



- (79) Lincoln, R.; Kohler, L.; Monro, S.; Yin, H.; Stephenson, M.; Zong, R.; Chouai, A.; Dorsey, C.; Hennigar, R.; Thummel, R. P.; McFarland, S. A. Exploitation of Long-Lived  $^3\text{IL}$  Excited States for Metal-Organic Photodynamic Therapy: Verification in a Metastatic Melanoma Model. *J. Am. Chem. Soc.* **2013**, *135*, 17161–17175.
- (80) Bernard Valeur. *Molecular Fluorescence: Principles and Applications*; Wiley-VCH, 2001.
- (81) Balzani, V.; Bergamini, G.; Campagna, S.; Puntoriero, F. Photochemistry and Photophysics of Coordination Compounds: Overview and General Concepts. *Top. Curr. Chem.* **2007**, *280*, 1–36.
- (82) Crosby, G. A. Spectroscopic Investigations of Excited States of Transition-Metal Complexes. *Acc. Chem. Res.* **1975**, *8*, 231–238.
- (83) Yang, J.; Kersi, D. K.; Giles, L. J.; Stein, B. W.; Feng, C.; Tichnell, C. R.; Shultz, D. A.; Kirk, M. L. Ligand Control of Donor-Acceptor Excited-State Lifetimes. *Inorg. Chem.* **2014**, *53*, 4791–4793.
- (84) Zhao, N.; Wu, Y. H.; Wen, H. M.; Zhang, X.; Chen, Z. N. Conversion from ILCT to LLCT/MLCT Excited State by Heavy Metal Ion Binding in Iridium(III) Complexes with Functionalized 2,2'-Bipyridyl Ligands. *Organometallics* **2009**, *28*, 5603–5611.
- (85) Langdon-Jones, E. E.; Hallett, A. J.; Routledge, J. D.; Crole, D. A.; Ward, B. D.; Platts, J. A.; Pope, S. J. A. Using Substituted Cyclometalated Quinoxaline Ligands to Finely Tune the Luminescence Properties of Iridium(III) Complexes. *Inorg. Chem.* **2013**, *52*, 448–456.
- (86) Schmidt, R.; Badger, R. M.; Wright, A. C.; Whitlock, R. F. Ligand-Ligand Charge-Transfer Excited States of Os(II) Complexes. *J. Phys. Chem.* **1989**, *93*, 4511–4522.
- (87) Kunkely, H.; Vogler, A. Photoreactivity of (2,9-Dimethyl-1,10-Phenanthroline) Copper(I) Borohydride. *Inorg. Chem. Commun.* **2002**, *5*, 239–241.
- (88) Yersin, H.; Rausch, A. F.; Czerwieńiec, R.; Hofbeck, T.; Fischer, T. The Triplet State of Organo-Transition Metal Compounds. Triplet Harvesting and Singlet Harvesting for Efficient OLEDs. *Coord. Chem. Rev.* **2011**, *255*, 2622–2652.
- (89) Colombo, M. G.; Brunold, T. C.; Riedener, T.; Giidel, H. U.; Fortsch, M.; Biirgi, H.-B. Facial Tris Cyclometalated  $\text{Rh}^{3+}$  and  $\text{Ir}^{3+}$  Complexes: Their Synthesis, Structure, and Optical Spectroscopic Properties. *Inorg. Chem.* **1994**, *33*, 545–550.
- (90) Parker, R. R.; Sarju, J. P.; Whitwood, A. C.; Williams, J. A. G.; Lynam, J. M.; Bruce, D. W. Synthesis, Mesomorphism, and Photophysics of 2,5-Bis(dodecyloxyphenyl)pyridine Complexes of Platinum(IV). *Chem. Eur. J.* **2018**, *24*, 19010–19023.
- (91) Uesugi, H.; Tsukuda, T.; Takao, K.; Tsubomura, T. Highly Emissive Platinum(II) Complexes Bearing Carbene and Cyclometalated Ligands. *Dalton Trans.* **2013**, *42*, 7396–7403.

- (92) Visbal, R.; Gimeno, M. C. N-Heterocyclic Carbene Metal Complexes: Photoluminescence and Applications. *Chem. Soc. Rev.* **2014**, *43*, 3551–3574.
- (93) Elie, M.; Renaud, J. L.; Gaillard, S. N-Heterocyclic Carbene Transition Metal Complexes in Light Emitting Devices. *Polyhedron* **2018**, *140*, 158–168.
- (94) Soellner, J.; Tenne, M.; Wagenblast, G.; Strassner, T. Phosphorescent Platinum(II) Complexes with Mesoionic 1H-1,2,3-Triazolylidene Ligands. *Chem. Eur. J.* **2016**, *22*, 9914–9918.
- (95) Na, H.; Cañada, L. M.; Wen, Z.; I-Chia Wu, J.; Teets, T. S. Mixed-Carbene Cyclometalated Iridium Complexes with Saturated Blue Luminescence. *Chem. Sci.* **2019**, *10*, 6254–6260.
- (96) Martínez-Junquera, M.; Lalinde, E.; Moreno, M. T.; Alfaro-Arnedo, E.; López, I. P.; Larráyo, I. M.; Pichel, J. G. Luminescent Cyclometalated Platinum(II) Complexes with Acyclic Diaminocarbene Ligands: Structural, Photophysical and Biological Properties. *Dalton Trans.* **2021**, *50*, 4539–4554.
- (97) Na, H.; Teets, T. S. Highly Luminescent Cyclometalated Iridium Complexes Generated by Nucleophilic Addition to Coordinated Isocyanides. *J. Am. Chem. Soc.* **2018**, *140*, 6353–6360.
- (98) Wilson, J. S.; Chawdhury, N.; Al-Mandhary, M. R. A.; Younus, M.; Khan, M. S.; Raithby, P. R.; Köhler, A.; Friend, R. H. The Energy Gap Law for Triplet States in Pt-Containing Conjugated Polymers and Monomers. *J. Am. Chem. Soc.* **2001**, *123*, 9412–9417.
- (99) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. Application of the Energy Gap Law to Excited-State Decay of Osmium(II)-Polypyridine Complexes: Calculation of Relative Nonradiative Decay Rates from Emission Spectral Profiles. *J. Phys. Chem.* **1986**, *90*, 3722–3734.
- (100) Englman, R.; Jortner, J. The Energy Gap Law for Radiationless Transitions in Large Molecules. *Mol. Phys.* **1970**, *18*, 285–287.
- (101) Jensen, M. P.; Wick, D. D.; Reinartz, S.; White, P. S.; Templeton, J. L.; Goldberg, K. I. Reductive Elimination/Oxidative Addition of Carbon-Hydrogen Bonds at Pt(IV)/Pt(II) Centers: Mechanistic Studies of the Solution Thermolyses of  $\text{TpMe}_2\text{Pt}(\text{CH}_3)_2\text{H}$ . *J. Am. Chem. Soc.* **2003**, *125*, 8614–8624.
- (102) Young, G. B.; Whitesides, G. M. Oxidative Addition and Reductive Elimination Reactions Involving Platinum Metallacycles. *J. Am. Chem. Soc.* **1978**, *100*, 5808–5815.
- (103) Niroomand Hosseini, F.; Nabavizadeh, S. M.; Shoara, R.; Dadkhah Aseman, M.; Abu-Omar, M. M. Selectivity in Competitive  $\text{Csp}^2\text{-Csp}^3$  versus  $\text{Csp}^3\text{-Csp}^3$  Reductive Eliminations at Pt(IV) Complexes: Experimental and Computational Approaches. *Organometallics* **2021**, *40*, 2051–2063.

- (104) Aseman, M. D.; Nabavizadeh, S. M.; Niroomand Hosseini, F.; Wu, G.; Abu-Omar, M. M. Carbon-Oxygen Bond Forming Reductive Elimination from Cycloplatinated(IV) Complexes. *Organometallics* **2018**, *37*, 87–98.
- (105) Crosby, S. H.; Thomas, H. R.; Clarkson, G. J.; Rourke, J. P. Concerted Reductive Coupling of an Alkyl Chloride at Pt(IV). *Chem. Commun.* **2012**, *48*, 5775–5777.
- (106) Ruan, J.; Wang, D.; Vedernikov, A. N. CH<sub>3</sub>-X Reductive Elimination Reactivity of Pt<sup>IV</sup>Me Complexes Supported by a Sulfonated CNN Pincer Ligand (X = OH, CF<sub>3</sub>CO<sub>2</sub>, PhNMe<sub>2</sub><sup>+</sup>). *Organometallics* **2020**, *39*, 142–152.
- (107) Williams, B. S.; Goldberg, K. I. Studies of Reductive Elimination Reactions to Form Carbon-Oxygen Bonds from Pt(IV) Complexes. *J. Am. Chem. Soc.* **2001**, *123*, 2576–2587.
- (108) Ríos, P.; Rodríguez, A.; Conejero, S. Enhancing the Catalytic Properties of Well-Defined Electrophilic Platinum Complexes. *Chem. Commun.* **2020**, *56*, 5333–5349.
- (109) Chianese, A. R.; Lee, S. J.; Gagné, M. R. Electrophilic Activation of Alkenes by Platinum(II): So Much More than a Slow Version of Palladium(II). *Angew. Chem., Int. Ed.* **2007**, *46*, 4042–4059.
- (110) Baar, C. R.; Jenkins, H. A.; Vittal, J. J.; Yap, G. P. A.; Puddephatt, R. J. Stereoselectivity in Organometallic Reactions: Oxidative Addition of Alkyl Halides to Platinum(II). *Organometallics* **1998**, *17*, 2805–2818.
- (111) Imberti, C.; Zhang, P.; Huang, H.; Sadler, P. J. New Designs for Phototherapeutic Transition Metal Complexes. *Angew. Chem.* **2020**, *132*, 61–73.
- (112) Shi, H.; Imberti, C.; Sadler, P. J. Diazido Platinum(IV) Complexes for Photoactivated Anticancer Chemotherapy. *Inorg. Chem. Front.* **2019**, *6*, 1623–1638.
- (113) Lee, V. E. Y.; Chin, C. F.; Ang, W. H. Design and Investigation of Photoactivatable Platinum(IV) Prodrug Complexes of Cisplatin. *Dalton Trans.* **2019**, *48*, 7388–7393.
- (114) Smith, N. A.; Sadler, P. J. Photoactivatable Metal Complexes: From Theory to Applications in Biotechnology and Medicine. *Philos. Trans. R. Soc., A* **2013**, *371*:20120519.
- (115) Berners-Price, S. J. Activating Platinum Anticancer Complexes with Visible Light. *Angew. Chem., Int. Ed. Engl.* **2011**, *50*, 804–805.
- (116) Farrer, N. J.; Woods, J. A.; Salassa, L.; Zhao, Y.; Robinson, K. S.; Clarkson, G.; Mackay, F. S.; Sadler, P. J. A Potent Trans-Diimine Platinum Anticancer Complex Photoactivated by Visible Light. *Angew. Chem., Int. Ed. Engl.* **2010**, *49*, 8905–8908.

- (117) Ruggiero, E.; Alonso-De Castro, S.; Habtemariam, A.; Salassa, L. The Photochemistry of Transition Metal Complexes and Its Application in Biology and Medicine. *Struct. Bonding* **2015**, *165*, 69–108.
- (118) Salassa, L.; Phillips, H. I. A.; Sadler, P. J. Decomposition Pathways for the Photoactivated Anticancer Complex *cis,trans,cis*-[Pt(N<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]: Insights from DFT Calculations. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10311–10316.
- (119) Hall, M. D.; Mellor, H. R.; Callaghan, R.; Hambley, T. W. Basis for Design and Development of Platinum(IV) Anticancer Complexes. *J. Med. Chem.* **2007**, *50*, 3403–3411.
- (120) Zhao, Y.; Farrer, N. J.; Li, H.; Butler, J. S.; McQuitty, R. J.; Habtemariam, A.; Wang, F.; Sadler, P. J. De Novo Generation of Singlet Oxygen and Ammine Ligands by Photoactivation of a Platinum Anticancer Complex. *Angew. Chem., Int. Ed.* **2013**, *52*, 13633–13637.
- (121) Berners-Price, S. J. Activating Platinum Anticancer Complexes with Visible Light. *Angew. Chem., Int. Ed. Engl.* **2011**, *50*, 804–805.
- (122) Westendorf, A. F.; Bodtke, A.; Bednarski, P. J. Studies on the Photoactivation of Two Cytotoxic *trans,trans,trans*-Diazidodiaminodihydroxo-Pt(IV) Complexes. *Dalton Trans.* **2011**, *40*, 5342–5351.
- (123) Juliá, F.; Bautista, D.; Fernández-Hernández, J. M.; González-Herrero, P. Homoleptic Tris-Cyclometalated Platinum(IV) Complexes: A New Class of Long-Lived, Highly Efficient <sup>3</sup>LC Emitters. *Chem. Sci.* **2014**, *5*, 1875–1880.
- (124) Chassot, L.; Von Zelewsky, A.; Sandrini, D.; Maestri, M.; Balzani, V. Photochemical Preparation of Luminescent Platinum(IV) Complexes via Oxidative Addition on Luminescent Platinum(II) Complexes. *J. Am. Chem. Soc.* **1986**, *108*, 6084–6085.
- (125) Jenkins, D. M.; Bernhard, S. Synthesis and Characterization of Luminescent Bis-Cyclometalated Platinum(IV) Complexes. *Inorg. Chem.* **2010**, *49*, 11297–11308.
- (126) Juliá, F.; Aullón, G.; Bautista, D.; González-Herrero, P. Exploring Excited-State Tunability in Luminescent Tris-Cyclometalated Platinum(IV) Complexes: Synthesis of Heteroleptic Derivatives and Computational Calculations. *Chem. Eur. J.* **2014**, *20*, 17346–17359.
- (127) Juliá, F.; Bautista, D.; González-Herrero, P. Developing Strongly Luminescent Platinum(IV) Complexes: Facile Synthesis of Bis-Cyclometalated Neutral Emitters. *Chem. Commun.* **2016**, *52*, 1657–1660.
- (128) Juliá, F.; García-Legaz, M.-D.; Bautista, D.; González-Herrero, P. Influence of Ancillary Ligands and Isomerism on the Luminescence of Bis-Cyclometalated Platinum(IV) Complexes. *Inorg. Chem.* **2016**, *55*, 7647–7660.
- (129) Juliá, F.; González-Herrero, P. Spotlight on the Ligand: Luminescent Cyclometalated Pt(IV) Complexes Containing a Fluorenyl Moiety. *Dalton Trans.* **2016**, *45*, 10599–10608.

- (130) Giménez, N.; Lara, R.; Moreno, M. T.; Lalinde, E. Facile Approaches to Phosphorescent Bis(Cyclometalated) Pentafluorophenyl Pt(IV) Complexes: Photophysics and Computational Studies. *Chem. Eur. J.* **2017**, *23*, 5758–5771.
- (131) Giménez, N.; Lalinde, E.; Lara, R.; Moreno, M. T. Design of Luminescent, Heteroleptic, Cyclometalated Pt(II) and Pt(IV) Complexes: Photophysics and Effects of the Cyclometalated Ligands. *Chem. Eur. J.* **2019**, *25*, 5514–5526.
- (132) Vivancos, Á.; Bautista, D.; González-Herrero, P. Luminescent Platinum(IV) Complexes Bearing Cyclometalated 1,2,3-Triazolylidene and Bi- or Terdentate 2,6-Diarylpyridine Ligands. *Chem. Eur. J.* **2019**, *25*, 6014–6025.
- (133) Vivancos, Á.; Poveda, D.; Muñoz, A.; Moreno, J.; Bautista, D.; González-Herrero, P. Selective Synthesis, Reactivity and Luminescence of Unsymmetrical Bis-Cyclometalated Pt(IV) Complexes. *Dalton Trans.* **2019**, *48*, 14367–14382.
- (134) Whitfield, S. R.; Sanford, M. S. Reactions of Platinum(II) Complexes with Chloride-Based Oxidants: Routes to Pt(III) and Pt(IV) Products. *Organometallics* **2008**, *27*, 1683–1689.
- (135) Whitfield, S. R.; Sanford, M. S. New Oxidation Reactions of Palladium and Platinum: Synthetic and Mechanistic Investigations, The University of Michigan, 2008.
- (136) Corbo, R.; Georgiou, D. C.; Wilson, D. J. D.; Dutton, J. L. Reactions of [PhI(Pyridine)<sub>2</sub>]<sup>2+</sup> with Model Pd and Pt II/IV Redox Couples. *Inorg. Chem.* **2014**, *53*, 1690–1698.
- (137) Newman, C. P.; Casey-Green, K.; Clarkson, G. J.; Cave, G. W. V.; Errington, W.; Rourke, J. P. Cyclometallated Platinum(II) Complexes: Oxidation to, and C–H Activation by, Platinum(IV). *Dalton Trans.* **2007**, 3170–3182.
- (138) von Zelewsky, A.; Suckling, A. P.; Stoeckli-Evans, H. Thermal and Photochemical Oxidative Addition of Alkyl Halides to the Cyclometalated Complex *cis*-Bis[2-(2-thienyl)pyridine]platinum(II). *Inorg. Chem.* **1993**, *32*, 4585–4593.
- (139) Sandrini, D.; Maestri, M.; Balzani, V.; Chassot, L.; Von Zelewsky, A. Photochemistry of the Orthometalated *cis*-Bis[2-(2-thienyl)pyridine]platinum(II) Complex in Halocarbon Solvents. *J. Am. Chem. Soc.* **1987**, *109*, 7720–7724.
- (140) Katlenok, E. A.; Balashev, K. P. Complexes of Rh(III), Ir(III), and Pt(IV) with Metallated 2-(*n*-Tolyl)Pyridine, Ethylenediamine, Acetate, and Diethyldithiocarbamate Ligands. *Russ. J. Gen. Chem.* **2014**, *84*, 927–933.
- (141) Shaw, P. A.; Clarkson, G. J.; Rourke, J. P. Reversible C–C Bond Formation at a Triply Cyclometallated Platinum(IV) Centre. *Chem. Sci.* **2017**, *8*, 5547–5558.
- (142) Shaw, P. A.; Phillips, J. M.; Clarkson, G. J.; Rourke, J. P. Trapping Five-Coordinate Platinum(IV) Intermediates. *Dalton Trans.* **2016**, *45*, 11397–11406.
- (143) Shaw, P. A.; Phillips, J. M.; Newman, C. P.; Clarkson, G. J.; Rourke, J. P. Intramolecular Transcyclometallation: The Exchange of an Aryl–Pt Bond for an

Alkyl–Pt Bond via an Agostic Intermediate. *Chem. Commun.* **2015**, *51*, 8365–8368.

- (144) Zhang, Y.; Meng, F.; You, C.; Yang, S.; Xiong, L.; Xiong, W.; Zhu, W.; Wang, Y.; Pei, Y.; Su, S. Efficient Near-Infrared Emitting Tetradentate Bis-Cyclometalated Platinum (IV) Complexes for Solution-Processed Polymer Light-Emitting Diodes. *Dyes Pigm.* **2017**, *142*, 457–464.

## **SUMMARY OF OBJECTIVES AND CONCLUSIONS**





## OBJECTIVES

Transition-metal complexes with chelating heteroaromatic ligands, such as 2,2'-bipyridines, cyclometalated 2-arylpyridines and related compounds, have been intensively studied for their luminescence and other excited-state properties, which make them suitable for many light-based applications, such as the development of electroluminescent materials for lighting and displays, probes for cell imaging, chemical and biological sensors, photosensitizers for singlet oxygen generation and photodynamic therapy, and photocatalysts for organic synthesis. During the last decades, metal ions with a  $d^6$  electronic configuration, such as Re(I), Ru(II), Os(II) and Ir(III), or a  $d^8$  configuration, such as Pt(II) and Au(III), have become the most employed for the development of this kind of complexes. In contrast, before the present thesis was started, only a few series of luminescent Pt(IV) complexes with chelating heteroaromatic ligands had been described, and there were important challenges regarding synthetic methodologies and excited-state tunability.

Among the previously reported luminescent Pt(IV) complexes, cationic tris-cyclometalated derivatives with a facial geometry,  $fac-[Pt(C^{\wedge}N)_3]^+$ , where  $C^{\wedge}N$  is a cyclometalated 2-arylpyridine or a related bidentate ligand, stood out as a unique class of complexes showing an exceptional photostability and highly efficient and long-lived phosphorescent emissions from essentially ligand-centred triplet excited states ( $^3LC$ ) with very little metal-to-ligand charge-transfer (MLCT) character, making them promising as photosensitizers, photocatalysts or sensors. However, the developed synthetic methodology presented important disadvantages, requiring long heating times for a ligand substitution step and a *mer-to-fac* photoisomerization step that resulted in low yields. In addition, this methodology was not suitable for the introduction of 2-arylpyridines of a low energy for the  $\pi-\pi^*$  transition, precluding tunability to achieve emissions in the orange or red regions of the visible spectrum.

Other previous studies had shown that the neutral bis-cyclometalated complexes with an unsymmetrical arrangement of  $C^{\wedge}N$  ligands,  $[Pt(C^{\wedge}N)_2(Me)X]$  and  $[Pt(C^{\wedge}N)_2(C_6F_5)Cl]$ , or  $C_2$ -symmetrical complexes of the type  $[Pt(C^{\wedge}N)_2X_2]$ , could attain significant emission efficiencies. The introduction of fluoride as the anionic X ligand in  $[Pt(C^{\wedge}N)_2(Me)X]$  and  $C_2$ -symmetrical  $[Pt(C^{\wedge}N)_2X_2]$  complexes allowed the modulation of their luminescence by increasing the MLCT contribution to the emitting state, leading to enhanced efficiencies, whereas the use of heavier halides in  $C_2$ -symmetrical  $[Pt(C^{\wedge}N)_2X_2]$  complexes led to weaker emissions due to the presence of low-lying deactivating ligand-to-metal or ligand-to-ligand charge-transfer excited states ( $^3LMCT$  or  $^3LLCT$ ) involving electronic promotions from the lone pairs of the halide to  $d\sigma^*(Pt)$  or  $\pi^*(C^{\wedge}N)$  orbitals, respectively. In addition, bis-cyclometalated  $[Pt(C^{\wedge}N)_2X_2]$  complexes with an unsymmetrical arrangement of  $C^{\wedge}N$  ligands had been demonstrated as photoreactive species that underwent isomerizations to the  $C_2$ -symmetrical isomers upon irradiation with UV light, attributable to dissociative  $^3LMCT$  states.

Based on the above precedents, the present thesis has focused on the development of alternative synthetic methods to obtain strongly luminescent Pt(IV) complexes that would allow the introduction of cyclometalated ligands of different energies for the  $\pi-\pi^*$  transition and ancillary ligands with different  $\sigma$  and  $\pi$  donor capabilities that would allow to modulate their luminescence. Another focus of the present work has been the synthesis and the study of the

photochemical reactivity of Pt(IV) complexes that could lead to reductive couplings with potential interest for the development of photochemical catalysed processes. To achieve these goals, the synthesis of different photoluminescent or photoreactive systems based on cyclometalated Pt(IV) complexes has been pursued by performing oxidative addition reactions on bis-cyclometalated Pt(II) complexes of the type *cis*-[Pt(C<sup>^</sup>N)<sub>2</sub>], and an exhaustive evaluation of the photophysical properties and photochemical reactivity of the resulting Pt(IV) complexes has been carried out. The specific objectives can be summarized in the following points:

1. Development of a convenient procedure for the direct synthesis of homoleptic and heteroleptic *fac*-[Pt(C<sup>^</sup>N)<sub>3</sub>]<sup>+</sup> complexes bearing 2-arylpyridine ligands of varying energies for the  $\pi$ - $\pi^*$  transition and study of their luminescence. This was attempted by performing oxidative additions of 2-(2-pyridyl)arenediazonium salts to *cis*-[Pt(C<sup>^</sup>N)<sub>2</sub>] complexes.

2. Synthesis of new bis-cyclometalated Pt(IV) complexes of the type [Pt(C<sup>^</sup>N)<sub>2</sub>(Ar)X] and study their luminescence. We targeted this type of complexes because they could offer the possibility to modulate the MLCT admixture into the emitting state by variation of the halido ligand (X) or the aryl group (Ar). More specifically, we sought to evaluate the effects of the introduction of fluoride by comparing the emission characteristics of two analogous series of fluoro and chlorido derivatives, and also employed two aryl ligands of different electronic properties (Ar = Ph, *t*-BuPh) to examine their effect. Although complexes [Pt(C<sup>^</sup>N)<sub>2</sub>(Ar)Cl] were previously reported, all of them contained the C<sub>6</sub>F<sub>5</sub> group as the aryl ligand and variations of the halide had not been investigated. To synthesize the target complexes, the oxidative addition of aryl halides or diaryliodonium salts to *cis*-[Pt(C<sup>^</sup>N)<sub>2</sub>] complexes were envisaged.

3. Synthesis of neutral tris-chelate Pt(IV) complexes of the type [Pt(C<sup>^</sup>N)<sub>2</sub>(C<sup>^</sup>C)], bearing two cyclometalated 2-arylpyridine ligands and one dimetalated biaryl, and study of their luminescence. Dimetalated biaryl ligands are strong  $\sigma$  donors that can lead to large ligand-field splittings and, as such, they have been pursued for the development of brightly luminescent complexes. However, the number of metal complexes with these ligands is small, possibly because of synthetic difficulties. We expected biaryl ligands to be suitable for the development of highly efficient Pt(IV) phosphorescent emitters, not only because of their strong  $\sigma$  donor character, but also because they have some  $\pi$  donor character, which would allow to modulate the MLCT admixture into the emitting state. Besides, the introduction of biaryl ligands would allow the synthesis of neutral emitters with a robust, tris-chelate structure, which are much better suited for applications as dopants for organic light-emitting devices. To synthesize this kind of complexes, we explored the oxidative addition of dibenzoiodonium ions (cyclic diaryliodoniums) to *cis*-[Pt(C<sup>^</sup>N)<sub>2</sub>] complexes.

4. Study of the photochemical reactivity of bis-cyclometalated complexes featuring an unsymmetrical {Pt(C<sup>^</sup>N)<sub>2</sub>} subunit. Based on the few precedents of photoreactive bis-cyclometalated Pt(IV) complexes, we hypothesized that the combination of an unsymmetrical arrangement of C<sup>^</sup>N ligands, which often entails low energies of  $d\sigma^*$  orbitals, with the introduction of an alkynyl ligand, having  $\pi$  orbitals at relatively high energies, would result in low-lying <sup>3</sup>LMCT or <sup>3</sup>LLCT excited states that could trigger photochemical reactivity. To obtain the alkynyl complexes, we envisaged a synthetic route involving the oxidative addition of hypervalent iodine reagents PhI(O<sub>2</sub>CR)<sub>2</sub> to a *cis*-[Pt(C<sup>^</sup>N)<sub>2</sub>] precursor to give unsymmetrical bis-

cyclometalated dicarboxylato complexes  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{O}_2\text{CR})_2]$ , and the subsequent substitution of one of the carboxylato ligands for an aryl acetylide.

## CONCLUSIONS

The main conclusions are linked to the objectives and can be summarized as follows:

**1.1.** The reactions between 2-(2-pyridyl)- or 2-(1-isoquinolyl)benzenediazonium salts and *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$  precursors, with  $\text{C}^{\wedge}\text{N}$  = cyclometalated 2-(*p*-tolyl)pyridine (tpy), 2-phenylquinoline (pq), 2-(2-thienyl)pyridine (thpy) or 1-phenylisoquinoline (piq), resulted in the formation of labile diazenide intermediates that undergo photochemical or thermal extrusion of  $\text{N}_2$ , resulting in homo- or heteroleptic tris-cyclometalated Pt(IV) complexes with a facial geometry, *fac*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_3]^+$  or *fac*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{C}^{\wedge}\text{N}')^+]$ . This reaction constitutes a stereoselective procedure for the synthesis of facial tris-cyclometalated Pt(IV) complexes and, at the same time, allows the introduction of 2-arylpyridines of low  $\pi$ - $\pi^*$  transition energies, such as thpy and piq.

**1.2.** Complexes *fac*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_3]^+$  and *fac*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{C}^{\wedge}\text{N}')^+]$  exhibit phosphorescent emissions from  $^3\text{LC}$  excited states in fluid solution at 298 K, which, in the cases of the heteroleptic derivatives, involve the ligand with the lowest energy for the  $\pi$ - $\pi^*$  transition. In rigid media at 298 K or 77 K, the heteroleptic complexes bearing the piq ligand show fluorescent and dual phosphorescent emissions from a  $^1\text{LC}(\text{piq})$  excited state and two  $^3\text{LC}$  excited states involving piq and the other cyclometalated ligand. The fact that a secondary phosphorescence can be observed can be explained by a slow internal conversion within the triplet manifold due to weak electronic coupling and poor vibrational relaxation. Therefore, heteroleptic *fac*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{C}^{\wedge}\text{N}')^+]$  complexes have been demonstrated as suitable for the development of multi-emissive materials with potential application in white light-emitting devices.

**2.1.** Bis-cyclometalated iodido(phenyl) complexes  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{Ph})\text{I}]$ , with  $\text{C}^{\wedge}\text{N}$  = cyclometalated 4-(*tert*-butyl)-2-phenylpyridine (bppy), 2-(*p*-tolyl)pyridine (tpy), 2-(2-thienyl)pyridine (thpy), or 1-phenylisoquinoline (piq), were obtained through the oxidative addition of iodobenzene to the respective *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$  complexes in MeCN solution under irradiation with blue light. These reactions are the first examples of intermolecular oxidative additions of a non-chelating aryl halide to Pt(II) precursors resulting in stable aryl Pt(IV) complexes.

**2.2.** The reactions of *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$  ( $\text{C}^{\wedge}\text{N}$  = bppy, tpy, thpy, piq) with diaryliodoniums  $\text{Ar}_2\text{I}^+$  (Ar = Ph, *t*-BuPh) in MeCN afforded intermediates of the type  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{Ar})(\text{NCMe})]^+$ , which were converted to  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{Ar})\text{X}]$  (X = Cl, I) upon addition of iodide or chloride salts. The fluoride homologues were obtained via halide exchange from the iodido complexes using AgF.

**2.3.** The series of complexes  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{Ar})\text{X}]$ , with X = F or Cl, Ar = Ph, *t*-Bu, were shown to reach high emission quantum yields of up to 0.51 in solution and 0.81 in PMMA films at 298 K. The fluoro derivatives consistently showed shorter emission lifetimes and higher radiative and nonradiative rate constants, demonstrating a higher proportion of MLCT character mixed into the essentially  $^3\text{LC}$  emitting state. A computational study showed a higher metal orbital participation in the excited state for the fluoro complexes, which can be ascribed to a stronger  $\pi$  donation from the metalated aryl of the cyclometalated ligand trans to the fluoride. The fluoro

ligand is therefore a suitable ancillary ligand to modulate emission lifetimes. In contrast, the stronger  $\pi$  donation from the *t*-BuPh aryl group with respect to the unsubstituted Ph group did not have an influence on the observed emission characteristics.

**3.1.** A synthetic route has been developed to obtain the first family of neutral, tris-chelate Pt(IV) complexes of the type  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{C}^{\wedge}\text{C})]$ , with  $\text{C}^{\wedge}\text{N}$  = cyclometalated 2-phenylpyridine (ppy), 2-(*p*-tolyl)pyridine (tpy) or 2-(2-thienyl)pyridine, and  $\text{C}^{\wedge}\text{C}$  = dimetalated 4,4'-di-*tert*-butylbiphenyl (dbbph), biphenyl (bph) or 4,4'-difluorobiphenyl (dFbph). The method is based on the reaction between dibenzoiolium ions and *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$  complexes under thermal or photochemical conditions. It involves the formation of the cationic intermediate  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{C}^{\wedge}\text{C}-\text{I}-\kappa^2\text{C},\text{I})]^+$ , bearing a singly metalated 2-(2-iodoaryl)aryl ligand ( $\text{C}^{\wedge}\text{C}-\text{I}$ ) resulting from the oxidative addition of the iolium ion to *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$ , followed by a reductive metalation of the C–I bond, which is performed by a second equivalent of the *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$  complex.

**3.2.** The  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{C}^{\wedge}\text{C})]$  complexes can produce phosphorescent emissions arising from  $^3\text{LC}(\text{C}^{\wedge}\text{N})$  excited states, reaching significant quantum yields in a fluid solution or rigid matrix at 298 K. The combined analysis of emission data and computational results indicate that the  $^3\text{LC}(\text{C}^{\wedge}\text{C})$  states are poorly emissive and can exert a detrimental effect on the observed luminescence via thermal equilibration with emitting  $^3\text{LC}(\text{C}^{\wedge}\text{N})$  states when both types of states have similar energies. For this reason, these systems are better suited to produce efficient emissions when the  $\text{C}^{\wedge}\text{N}$  ligand has a relatively low energy for the  $\pi-\pi^*$  transition, as exemplified by the thpy complexes. In addition, the electron donating ability of the biaryl ligand has been shown to affect the MLCT admixture into the  $^3\text{LC}(\text{C}^{\wedge}\text{N})$  state, allowing to control radiative rates. Therefore, these complexes are suitable for use as low-energy emitters and their luminescence can be modulated by varying both the arylpyridine and biaryl ligands.

**4.1.** The reactions between *cis*- $[\text{Pt}(\text{tpy})_2]$  and hypervalent iodine reagents  $\text{PhI}(\text{O}_2\text{CR})_2$  (R = Me,  $\text{CF}_3$ ) produced unsymmetrical bis-cyclometalated dicarboxylato complexes  $[\text{Pt}(\text{tpy})_2(\text{O}_2\text{CR})_2]$ , which, upon treatment with 4-methoxyphenylacetylene, phenylacetylene, 4-(trifluoromethyl)phenylacetylene or 3,5-difluorophenylacetylene in the presence of a base, afforded complexes *mer*- $[\text{Pt}(\text{tpy})_2(\text{O}_2\text{CR})(\text{CCAr})]$ , featuring a *mer* arrangement of metalated carbon atoms. In the cases of the trifluoroacetato derivatives, a *mer-to-fac* isomerization took place upon irradiation with UV light (LED source with  $\lambda_{\text{max}} = 365$  nm). In contrast, the complexes containing an acetato ligand gave a mixture of photoproducts that result from four different processes: (i) reduction to *cis*- $[\text{Pt}(\text{tpy})_2]$ ; (ii) isomerization to the *fac* geometry; (iii) reductive annulations between one of the tpy ligands and the  $\text{C}_\alpha$  and  $\text{C}_\beta$  atoms of the alkynyl to give benzoquinolizinium derivatives, or (iv) C–O couplings between the acetato ligand and one tpy to give 5-methyl-(2-pyridyl)phenyl acetate.

**4.2.** Irradiation of *fac*- $[\text{Pt}(\text{tpy})_2(\text{O}_2\text{CCF}_3)(\text{CCAr})]$  using a medium-pressure Hg UV lamp produced a reductive C–C coupling involving the alkynyl  $\text{C}_\alpha$  atom and one of the tpy ligands to give Pt(II) derivatives with a pyridoisindolium fragment, except for the methoxyphenylacetylde derivative, which was found to be photostable.

**4.3.** Based on TDDFT studies, it is postulated that the reduction to *cis*- $[\text{Pt}(\text{tpy})_2]$ , isomerization or reductive C–O coupling reactions from the *mer* complexes occur through the thermal population of  $^3\text{LMCT}$   $[\pi(\text{alkynyl}) \rightarrow \text{d}\sigma^*]$  states, while annulation reactions to give

benzoquinolizinium derivatives is possibly a consequence of the thermal population of  $^3\text{LLCT}$  [ $\pi(\text{alkynyl}) \rightarrow \pi^*(\text{tpy})$ ] states. The photoreactivity of the *fac* complexes is possibly attributable to photoreactive pentacoordinate intermediates.



## **RESUMEN EN CASTELLANO**





## Introducción

Los complejos de metales de transición con ligandos heteroaromáticos quelato, tales como 2,2'-bipiridinas, 2-arilpiridinas ciclometaladas y compuestos relacionados, han sido estudiados intensamente debido a su luminiscencia y otras propiedades de estado excitado, que los hacen adecuados para muchas aplicaciones basadas en la interacción entre la luz y la materia, como el desarrollo de materiales electroluminiscentes para iluminación y pantallas, sondas para análisis de tejidos biológicos por imagen, sensores químicos y biológicos, fotosensibilizadores para la generación de oxígeno singlete y terapia fotodinámica, y fotocatalizadores para síntesis orgánica. Durante las últimas décadas, los iones metálicos con una configuración electrónica  $d^6$ , como Re(I), Ru(II), Os(II) e Ir(III), o una configuración  $d^8$ , como Pt(II) y Au(III), se han convertido en los más empleados para el desarrollo de este tipo de complejos. En cambio, antes de que se iniciara la presente tesis, solo se habían descrito unas pocas series de complejos luminiscentes de Pt(IV) con ligandos heteroaromáticos quelato, y existían importantes desafíos para mejorar los métodos sintéticos y las posibilidades de modulación de los estados excitados.

Entre los complejos luminiscentes Pt(IV) previamente descritos, destacan los derivados tris-ciclometalados catiónicos con geometría facial,  $fac$ -[Pt(C<sup>^</sup>N)<sub>3</sub>]<sup>+</sup>, donde C<sup>^</sup>N es una 2-arilpiridina ciclometalada o un ligando bidentado relacionado, los cuales constituyen una clase única de complejos que muestran una excepcional fotoestabilidad y emisiones fosforescentes altamente eficientes y de larga duración desde estados excitados triplete esencialmente centrados en los ligandos ciclometalados (<sup>3</sup>LC) con muy poco carácter de transferencia de carga metal-ligando (MLCT), lo que los hace prometedores como fotosensibilizadores, fotocatalizadores o sensores. Sin embargo, la metodología sintética desarrollada en trabajos previos presenta desventajas importantes, requiriendo largos tiempos de calentamiento para una etapa de sustitución de ligandos y una etapa de fotoisomerización *mer-fac* que da bajos rendimientos. Además, esta metodología no es adecuada para la introducción de 2-arilpiridinas que poseen una baja energía para la transición  $\pi$ - $\pi^*$ , impidiendo la modulación del estado excitado para lograr emisiones en las regiones naranja o roja del espectro visible.

Otros estudios previos han demostrado que los complejos bis-ciclometalados neutros con una disposición no simétrica de ligandos C<sup>^</sup>N, [Pt(C<sup>^</sup>N)<sub>2</sub>(Me)X] y [Pt(C<sup>^</sup>N)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)Cl], o complejos de simetría  $C_2$  del tipo [Pt(C<sup>^</sup>N)<sub>2</sub>X<sub>2</sub>], pueden alcanzar eficiencias de emisión significativas. La introducción del fluoruro como ligando aniónico X en los complejos [Pt(C<sup>^</sup>N)<sub>2</sub>(Me)X] y [Pt(C<sup>^</sup>N)<sub>2</sub>X<sub>2</sub>] de simetría  $C_2$  permite la modulación de su luminiscencia al aumentar la contribución MLCT al estado emisor, lo que conduce a una mayor eficiencia, mientras que el uso de haluros más pesados en los complejos [Pt(C<sup>^</sup>N)<sub>2</sub>X<sub>2</sub>] de simetría  $C_2$  conduce a emisiones más débiles debido a la presencia de estados excitados de transferencia de carga ligando-metal o ligando-ligando (<sup>3</sup>LMCT o <sup>3</sup>LLCT) que involucran promociones electrónicas desde los pares solitarios de los orbitales de los haluros a orbitales  $d\sigma^*(Pt)$  o  $\pi^*(C^{\wedge}N)$ , respectivamente. Además, se ha demostrado que los complejos bis-ciclometalados [Pt(C<sup>^</sup>N)<sub>2</sub>X<sub>2</sub>] con una disposición no simétrica de ligandos C<sup>^</sup>N son especies fotorreactivas que sufren isomerizaciones a los isómeros de simetría  $C_2$  al irradiarlos con luz UV, causadas por estados disociativos <sup>3</sup>LMCT.

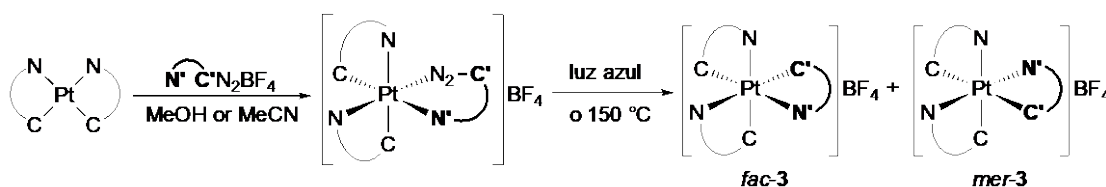
Sobre la base de los precedentes anteriores, la presente tesis se ha centrado en el desarrollo de métodos sintéticos alternativos para obtener complejos Pt(IV) fuertemente luminiscentes que

permitan la introducción de ligandos ciclometalados de diferentes energías para la transición  $\pi$ - $\pi^*$  y ligandos auxiliares con diferentes capacidades dadoras  $\sigma$  y  $\pi$ , que facilitarían la modulación de su luminiscencia. Otro objetivo del presente trabajo ha sido la síntesis y el estudio de la reactividad fotoquímica de complejos de Pt(IV) que podría conducir a acoplamientos reductores con potencial interés para el desarrollo de procesos catalíticos fotoquímicos. Para lograr estos objetivos, se ha perseguido la síntesis de complejos fotoluminiscentes o fotorreactivos mediante reacciones de adición oxidante sobre complejos bis-ciclometalados de Pt(II) del tipo *cis*-[Pt(C<sup>^</sup>N)<sub>2</sub>], y se ha llevado a cabo una evaluación exhaustiva de las propiedades fotofísicas y la reactividad fotoquímica de los complejos de Pt(IV) resultantes. A continuación, se presentan los objetivos y los resultados de cada uno de los artículos que conforman esta tesis.

## ARTÍCULO 1. Formación estereoselectiva de complejos faciales tris-ciclometalados de Pt(IV): Fosforescencia dual de derivados heterolépticos

El primer artículo tiene por objetivo el desarrollo de un procedimiento adecuado para la síntesis directa de complejos homolépticos y heterolépticos *fac*-[Pt(C<sup>^</sup>N)<sub>3</sub>]<sup>+</sup> con ligandos 2-arilpiridina que posean energías variables para la transición  $\pi$ - $\pi^*$  y el estudio de su luminiscencia. Esto se intentó mediante reacciones de adición oxidante de sales de 2-(2-piridil)bencenodiazonio a complejos *cis*-[Pt(C<sup>^</sup>N)<sub>2</sub>].

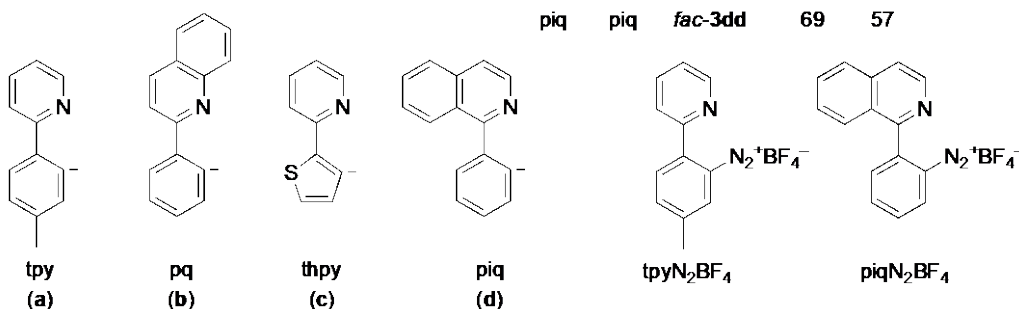
Así, las reacciones de sales de 2-(2-piridil)- o 2-(1-isoquinolinil)bencenodiazonio con los complejos *cis*-[Pt(C<sup>^</sup>N)<sub>2</sub>], donde C<sup>^</sup>N = 2-(*p*-tolil)piridina (tpy), 2-fenilquinolina (pq), 2-(2-tienil)piridina (thpy) o 1-fenilsioquinolina (piq), en metanol o acetonitrilo, dieron lugar a la formación de intermedios diazenuro que son relativamente lábiles y pueden sufrir la extrusión fotoquímica de N<sub>2</sub> por irradiación con luz azul para dar complejos de tris-ciclometalados Pt(IV) homo- o heterolépticos, que se formaron como mezclas de isómeros meridionales y faciales *mer/fac*-[Pt(C<sup>^</sup>N)<sub>3</sub>]<sup>+</sup> o *mer/fac*-[Pt(C<sup>^</sup>N)<sub>2</sub>(C<sup>^</sup>N')]<sup>+</sup> (Esquema 1) en distintas proporciones. El complejo diazenuro intermedio se pudo aislar puro en uno de los casos y se pudo determinar la estructura cristalina de la sal de tetrafenilborato, lo que reveló que la disposición de los ligandos es la adecuada para dar una geometría facial después de la eliminación de N<sub>2</sub>. El hecho de que se obtuvieran mezclas de isómeros se atribuyó a la posible descoordinación del grupo piridilo del ligando diazenuro antes o durante la fotoeliminación de N<sub>2</sub> en disolución, produciendo radicales N<sup>^</sup>C<sup>·</sup>. Por ello, se comprobó la posibilidad de llevar a cabo la extrusión de N<sub>2</sub> térmicamente en estado sólido mediante un análisis termogravimétrico de uno de los diazenuros, el cual mostró la pérdida de masa equivalente a una molécula de N<sub>2</sub> a 151.7 °C. Sobre la base de este análisis, se llevó a cabo el calentamiento en estado sólido a 150 °C, obteniéndose únicamente el isómero facial. Empleando esta metodología se llevó a cabo la síntesis de los diferentes complejos *fac*-[Pt(C<sup>^</sup>N)<sub>3</sub>]<sup>+</sup> o *fac*-[Pt(C<sup>^</sup>N)<sub>2</sub>(C<sup>^</sup>N')]<sup>+</sup> expuestos en el Esquema 1 con rendimientos del 37 al 69%. Esta reacción constituye un procedimiento estereoselectivo para la síntesis de complejos tris-ciclometalados de Pt(IV) con una geometría facial y, al mismo tiempo, permite la introducción de 2-arilpiridinas de bajas energías para la transición  $\pi$ - $\pi^*$ , como thpy y piq.

**Método fotoquímico:**

C	N	C'	N'	Productos	proporción <i>fac:mer</i>
tpy	tpy			<i>fac/mer-3aa</i>	1:2
thpy	tpy			<i>fac/mer-3ca</i>	7.3:1
thpy	piq			<i>fac/mer-3cd</i>	4:1
piq	piq			<i>fac-3dd</i>	—

**Método térmico:**

				Rendimiento (%)		
C	N	C'	N'	Producto	MeOH	MeCN
tpy	tpy			<i>fac-3aa</i>	60	33
tpy	piq			<i>fac-3ad</i>	62	43
pq	tpy			<i>fac-3ba</i>	38	47
pq	piq			<i>fac-3bd</i>	43	53
thpy	tpy			<i>fac-3ca</i>	42	39
thpy	piq			<i>fac-3cd</i>	37	37
piq	tpy			<i>fac-3da</i>	41	33
piq	piq			<i>fac-3dd</i>	69	57



**Esquema 1.** Reacciones de complejos *cis*-[Pt(C^N)<sub>2</sub>] con sales de 2-(2-piridil)- o 2-(1-isoquinolinil)bencenodiazonio.

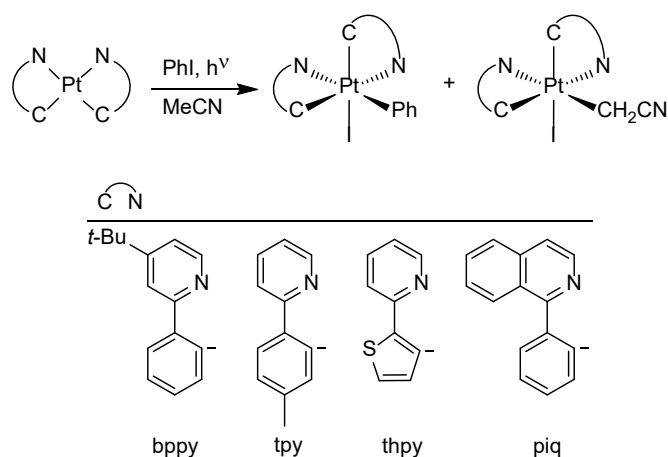
Los complejos *fac*-[Pt(C^N)<sub>3</sub>]<sup>+</sup> y *fac*-[Pt(C^N)<sub>2</sub>(C'^N')]<sup>+</sup> presentan emisiones fosforescentes desde estados excitados <sup>3</sup>LC en disolución a 298 K, matrices de poli(metilmacrilato) (PMMA) a 298 K y en butironitrilo a 77 K. En los casos de los derivados heterolépticos, el estado emisor implica al ligando con la energía más baja para la transición π-π\*. Los rendimientos cuánticos alcanzan 0.20 en disolución a 298 K y 0.46 en PMMA. Los complejos heterolépticos *fac*-[Pt(tpy)<sub>2</sub>(piq)]<sup>+</sup>, *fac*-[Pt(piq)<sub>2</sub>(tpy)]<sup>+</sup> y *fac*-[Pt(pq)<sub>2</sub>(piq)]<sup>+</sup> muestran emisiones fluorescentes y fosforescentes duales desde un estado excitado <sup>1</sup>LC(piq) y dos estados excitados <sup>3</sup>LC que involucran el ligando piq y el otro ligando ciclotalado. El hecho de que se pueda observar una fosforescencia secundaria puede explicarse por una conversión interna lenta dentro del sistema triplete debido a un acoplamiento electrónico débil a través de los orbitales dπ del metal y una relajación vibracional deficiente.

Mediante este trabajo, se ha conseguido un método sintético eficiente y directo para obtener complejos tris-ciclotalados de Pt(IV) con una geometría facial que pueden contener todo tipo de ligandos 2-arilpiridina, incluyendo aquellos con bajas energías para la transición π-π\*, ampliando las posibilidades de modulación de su luminiscencia. Además, se demuestra que estos complejos pueden dar lugar a emisiones múltiples que los pueden hacer aptos para su uso en aplicaciones de emisión de luz blanca.

## ARTÍCULO 2. Haluro(aril)-complejos luminiscentes de Pt(IV) obtenidos mediante adición oxidante de yodobenceno o sales de diarylodonio a precursores bis-ciclometalados de Pt(II)

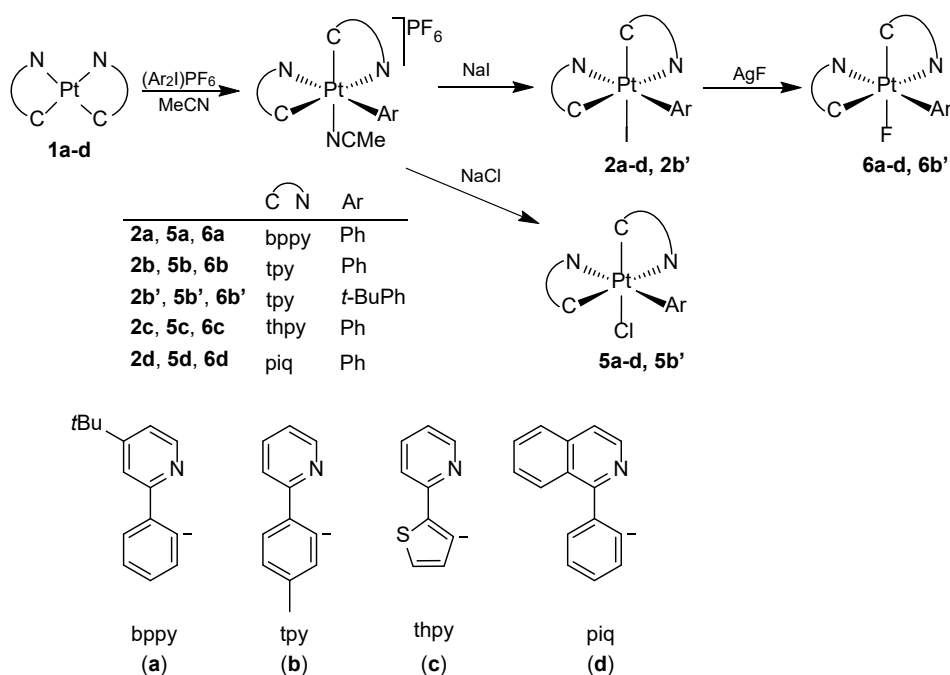
El objeto de este artículo es la síntesis y estudio de la luminiscencia de nuevos complejos bis-ciclometalados de Pt(IV) del tipo  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{Ar})\text{X}]$ , con una disposición no simétrica de ligandos  $\text{C}^{\wedge}\text{N}$ . Este tipo de complejos ofrecían la posibilidad de modular la mezcla MLCT en el estado emisor mediante la variación del ligando haluro (X) o el grupo arilo (Ar). Más específicamente, buscamos evaluar los efectos de la introducción de fluoruro comparando las características de emisión de dos series análogas de derivados de fluoruro y cloruro, y también empleamos dos ligandos de arilo de diferentes propiedades electrónicas (Ar = Ph, *t*-BuPh) para examinar su efecto. Aunque otros autores han descrito previamente complejos del tipo  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{Ar})\text{X}]$ , todos ellos contienen el grupo  $\text{C}_6\text{F}_5$  como ligando arilo y los posibles efectos de las variaciones del haluro no han sido investigados. Para sintetizar los complejos objetivo, nos planteamos llevar a cabo la adición oxidante de haluros de arilo o sales de diarylodonio a los complejos *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$ .

Para la obtención de los complejos de Pt(IV), se utilizaron como precursores los complejos de Pt(II) *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$ , con  $\text{C}^{\wedge}\text{N}$  = 4-(*terc*-butil)-2-fenilpiridina (bppy), 2-(*p*-tolil)piridina (tpy), 2-(2-tienil)piridina (thpy) y 1-fenilisoquinolina (piq) ciclometalada. Inicialmente, se intentaron las reacciones fotoquímicas de estos precursores con PhI mediante irradiación con luz azul en acetonitrilo, obteniéndose mezclas de  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{Ph})\text{I}]$  y  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{CH}_2\text{CN})\text{I}]$  en distintas proporciones (Esquema 2). La formación de los complejos de cianometilo se explica por un mecanismo radicalario, que conlleva un paso de abstracción de átomo de hidrógeno del disolvente. Las formaciones de los complejos  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{Ph})\text{I}]$  mediante estas reacciones constituyen los primeros ejemplos de adiciones oxidantes intermoleculares de un haluro de arilo no quelatante a precursores de Pt(II) que dan lugar a aril-complejos de Pt(IV) estables.



**Esquema 2.** Reacciones de *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$  con PhI en acetonitrilo.

Debido a que las reacciones anteriores dieron mezclas de complejos, se intentó el uso de sales de diarylodonio  $\text{Ar}_2\text{I}^+$  (Ar = Ph, *t*-BuPh), las cuales produjeron los complejos deseados por reacción con *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$  y posterior tratamiento de los complejos catiónicos intermedios con sales de cloruro o yoduro. Los derivados con fluoruro se obtuvieron por sustitución del ligando yoduro por fluoruro usando  $\text{AgF}$  (Esquema 3).



**Esquema 3.** Síntesis de complejos  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{Ar})\text{X}]$  a partir de reacciones de *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$  con sales de diariliodonio.

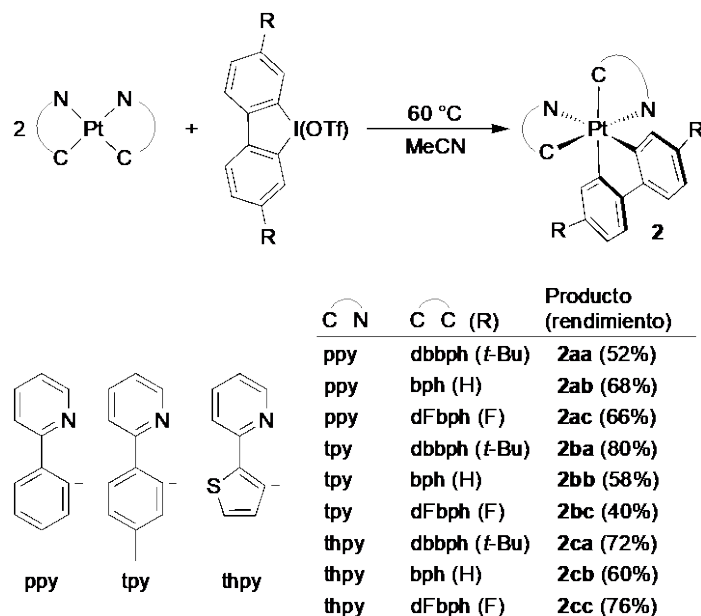
Se estudió la luminiscencia de la serie de cloruro- y fluoruro-complejos para determinar los efectos del haluro y del ligando arilo. Todos ellos producen fosforescencia eficiente desde estados  $^3\text{LC}$ , con rendimientos cuánticos hasta de 0.51 en disolución de  $\text{CH}_2\text{Cl}_2$  y de 0.88 en PMMA a 298 K. Los derivados del fluoruro mostraron tiempos de vida de emisión más cortos y constantes radiativas y no radiativas más altas, demostrando una mayor proporción de carácter MLCT en el estado  $^3\text{LC}$ . El estudio computacional mostró una mayor participación de los orbitales del metal en el estado excitado para los complejos de fluoruro, que puede atribuirse a una dación  $\pi$  más fuerte del arilo metalado trans al fluoruro debido a la menor influencia trans del fluoruro y una distancia Pt–C más corta. El ligando fluoruro es, por lo tanto, un ligando auxiliar adecuado para modular los tiempos de vida de emisión. En cambio, la dación  $\pi$  más fuerte del grupo *t*-BuPh con respecto al grupo Ph no sustituido no tuvo una influencia en las características de emisión observadas. No obstante, el grupo *t*-BuPh sí que produce a una disminución de la constante no radiativa en disolución, que probablemente se debe al efecto protector que proporciona el grupo *t*-Bu, que reduce la desactivación por colisiones con las moléculas de disolvente.

### ARTÍCULO 3. Biaril-complejos fosforescentes de platino(IV) obtenidos mediante doble metalación de iones dibenzoyodolio

Para este artículo nos propusimos como objetivo la síntesis de complejos tris-quelato neutros de Pt(IV) del tipo  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{C}^{\wedge}\text{C})]$ , que contienen dos ligandos 2-arilpiridina ciclometalados y un biarilo dimetalado, y el estudio de su luminiscencia. Los ligandos biarilo dimetalados son fuertes dadores  $\sigma$  que pueden conducir a grandes desdoblamientos del campo de los ligandos y, como tales, se han empleado para el desarrollo de complejos fuertemente luminiscentes. Sin embargo, los complejos con estos ligandos son escasos, posiblemente debido a dificultades sintéticas. Esperábamos que los ligandos biarilo fueran adecuados para el desarrollo de emisores

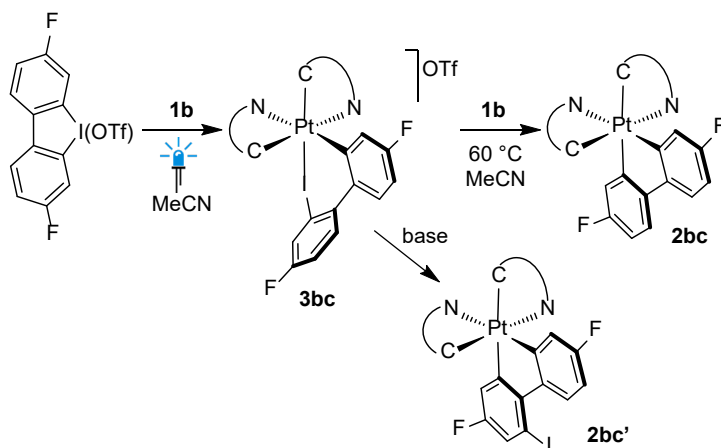
fosforescentes de Pt(IV) altamente eficientes, no solo por su fuerte carácter dador  $\sigma$ , sino también porque tienen cierto carácter dador  $\pi$ , lo que permitiría modular la mezcla MLCT en el estado emisor. Además, la introducción de ligandos biarilo permitiría la síntesis de emisores neutros con una robusta estructura tris-quelato, que son mucho más convenientes para su aplicación como dopantes para dispositivos orgánicos emisores de luz.

Se llevó a cabo la síntesis de nueve complejos de fórmula general  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{C}^{\wedge}\text{C})]$ , donde  $\text{C}^{\wedge}\text{N}$  = 2-fenilpiridina (ppy), 2-(*p*-tolil)piridina (tpy) o 2-(2-tienil)piridina ciclometalada, y  $\text{C}^{\wedge}\text{C}$  = 4,4'-di-*tert*-butilbifenilo (dbbph), bifenilo (bph) o 4,4'-difluorobifenilo (dFbph) dimetalado. El método se basa en la reacción entre los correspondientes complejos *cis*- $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$  y los triflatos de dibenzoyodolio (diariliodonios cíclicos) en condiciones térmicas (60 °C), el cual requiere una proporción molar 2:1 entre el precursor de Pt(II) y la sal de dibenzoyodolio (Esquema 4).



**Esquema 4.** Síntesis de complejos  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{C}^{\wedge}\text{C})]$ .

Con objeto de esclarecer el proceso mediante el que se forman estos complejos, se estudió la reacción de *cis*- $[\text{Pt}(\text{tpy})_2]$  con triflato de 3,7-difluorodibenzo-5-yodolio en condiciones fotoquímicas (irradiación con luz de 454 nm), que permitió aislar el intermedio catiónico  $[\text{Pt}(\text{tpy})_2(\text{dFbphI-}\kappa^2\text{C,I})\text{OTf}]$  (Esquema 5). A su vez, se comprobó que este intermedio puede sufrir la metalación reductora del enlace C–I por reacción con una segunda molécula de *cis*- $[\text{Pt}(\text{tpy})_2]$  a 60 °C, que proporciona los electrones necesarios, formándose el complejo  $[\text{Pt}(\text{tpy})_2(\text{dFbph})]$ . También pudimos comprobar que el intermedio  $[\text{Pt}(\text{tpy})_2(\text{dFbphI-}\kappa^2\text{C,I})\text{OTf}]$  puede sufrir la metalación electrofílica del enlace C–H orto del grupo 4-fluoro-2-yodofenilo en presencia de una base, produciendo el complejo  $[\text{Pt}(\text{tpy})_2(\text{dFbphI-}\kappa^2\text{C,C})]$ .



**Esquema 5.** Formación y reactividad del intermedio  $[\text{Pt}(\text{tpy})_2(\text{dFbphI-}\kappa^2\text{C,I})]\text{OTf}$ .

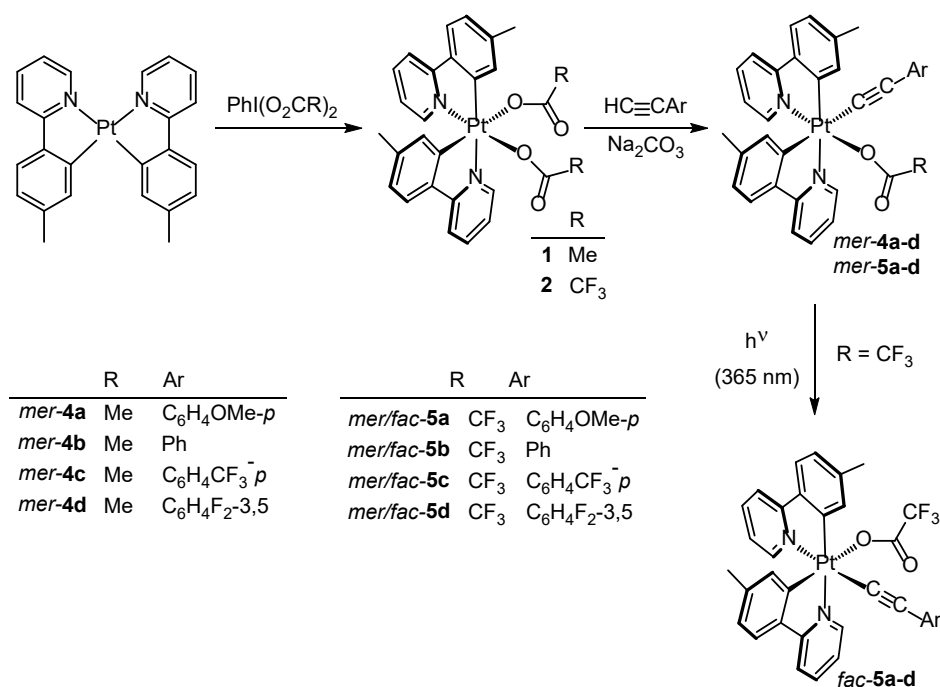
Los complejos  $[\text{Pt}(\text{C}^{\wedge}\text{N})_2(\text{C}^{\wedge}\text{C})]$  pueden producir emisiones fosforescentes derivadas de estados excitados  $^3\text{LC}(\text{C}^{\wedge}\text{N})$ , alcanzando rendimientos cuánticos significativos en disolución de  $\text{CH}_2\text{Cl}_2$  (hasta 0.21) o matriz rígida de PMMA (hasta 0.59) a 298 K. Sin embargo, el complejo  $[\text{Pt}(\text{ppy})_2(\text{dbbph})]$  presenta una emisión dual débil, procedente de un  $^3\text{LC}$  que involucra el ligando biarilo y otro que involucra un ligando ppy. Debido a que en este caso el estado  $^3\text{LC}(\text{dbbph})$  tiene menor energía que el estado  $^3\text{LC}(\text{ppy})$ , según la regla de Kasha debería observarse únicamente emisión desde el primero. La emisión dual observada indica que el estado  $^3\text{LC}(\text{ppy})$  es mucho mejor emisor y su desactivación radiativa es mucho más eficaz que la del estado  $^3\text{LC}(\text{dbbph})$ . Para el resto de los derivados con ppy y aquellos con tpy, se observa únicamente la emisión desde el estado  $^3\text{LC}(\text{C}^{\wedge}\text{N})$ , aumentando los rendimientos cuánticos en la secuencia  $\text{dbbph} > \text{bph} > \text{dFbph}$ , es decir, conforme aumenta la energía del estado  $^3\text{LC}(\text{C}^{\wedge}\text{C})$ . Esto indica que existe una equilibración térmica entre los estados  $^3\text{LC}(\text{C}^{\wedge}\text{N})$  y  $^3\text{LC}(\text{C}^{\wedge}\text{C})$  en los derivados de ppy y tpy, que es tanto más perjudicial para la emisión cuanto más próximos en energía se encuentran estos estados. En cambio, se observó la tendencia inversa para los derivados con thpy. Esto se debe a que el estado  $^3\text{LC}(\text{thpy})$  tiene una energía mucho menor que los estados  $^3\text{LC}(\text{C}^{\wedge}\text{C})$  y no se ve afectado por la equilibración térmica, mientras que se produce una mayor contribución MLCT en el estado emisor en la secuencia  $\text{dFbph} > \text{bph} > \text{dbbph}$ , debido a la mayor capacidad dadora  $\pi$  de los bifenilos con sustituyentes menos retiradores, alcanzándose rendimientos cuánticos de hasta 0.21 en disolución y 0.59 en PMMA para el complejo  $[\text{Pt}(\text{thpy})_2(\text{dbbph})]$ , siendo mejores emisores que los correspondientes complejos tris-ciclometalados con ligandos thpy. La interpretación de la luminiscencia de estos complejos se apoyó con estudios computacionales.

En resumen, se ha logrado sintetizar la primera serie de complejos luminiscentes neutros de Pt(IV) con una estructura tris-quelato mediante una doble metalación de iones dibenzoyodolío. Estos complejos son especialmente adecuados para el desarrollo de emisores de baja energía, como lo ejemplifican los complejos de thpy. Además, se ha demostrado que la capacidad electrodonadora del ligando biarilo afecta la mezcla MLCT en el estado  $^3\text{LC}(\text{C}^{\wedge}\text{N})$ . Por lo tanto, la luminiscencia de estos complejos puede ser modulada variando tanto los ligandos 2-arilpiridina como los ligandos biarilo.

## ARTÍCULO 4. Acoplamientos reductores C-C y C-heteroátomo fotoinducidos en alquinil-complejos bis-ciclometalados de Pt(IV)

La reactividad fotoquímica de los complejos de metales de transición ha adquirido una gran importancia debido a su aplicación en el desarrollo de procesos fotoquímicos catalíticos y su uso en terapia fotodinámica. Los complejos de Pt(IV) pueden presentar estados  $^3\text{LMCT}$  de baja energía que, al poblarse, pueden provocar la disociación de ligandos o la reducción del centro metálico, ya que involucran transiciones electrónicas a orbitales  $d\sigma^*$  fundamentalmente localizados sobre el metal. Además, se conoce la reactividad fotoquímica debida al poblamiento de estados  $^3\text{LMCT}$  de baja energía en complejos bis-ciclometalados de Pt(IV) que presentan una disposición no simétrica de los ligandos ciclometalados. Para este artículo, nos planteamos el estudio de la reactividad fotoquímica de complejos bis-ciclometalados con una subunidad  $\{\text{Pt}(\text{C}^{\wedge}\text{N})_2\}$  no simétrica y un ligando alquinilo, que presenta orbitales  $\pi$  ocupados de alta energía desde los que podrían producirse transiciones de transferencia de carga hacia orbitales  $d\sigma^*$  (LMCT) o  $\pi^*$  de los ligandos ciclometalados (LLCT), generando estados  $^3\text{LMCT}$  o  $^3\text{LLCT}$  que podrían conducir a reactividad fotoquímica.

Para la síntesis de los alquínulos bis-ciclometalados de Pt(IV), primero se obtuvieron los dicarboxilatos  $[\text{Pt}(\text{tpy})_2(\text{O}_2\text{CR})_2]$  ( $\text{R} = \text{Me}, \text{CF}_3$ ) mediante la adición oxidante de reactivos de yodo hipervalente  $\text{PhI}(\text{O}_2\text{CR})_2$  al precursor *cis*- $[\text{Pt}(\text{tpy})_2]$  y se hicieron reaccionar con los alquínulos 4-metoxifenilacetileno, fenilacetileno, 4-(trifluorometil)fenilacetileno o 3,5-difluorofenilacetileno en presencia de una base, lográndose la sustitución selectiva del ligando carboxilato trans al carbono metalado de uno de los ligandos tpy por un alquinilo para dar complejos *mer*- $[\text{Pt}(\text{tpy})_2(\text{O}_2\text{CR})(\text{CCAr})]$ , que presentan una disposición meridional de carbonos metalados (Esquema 6).

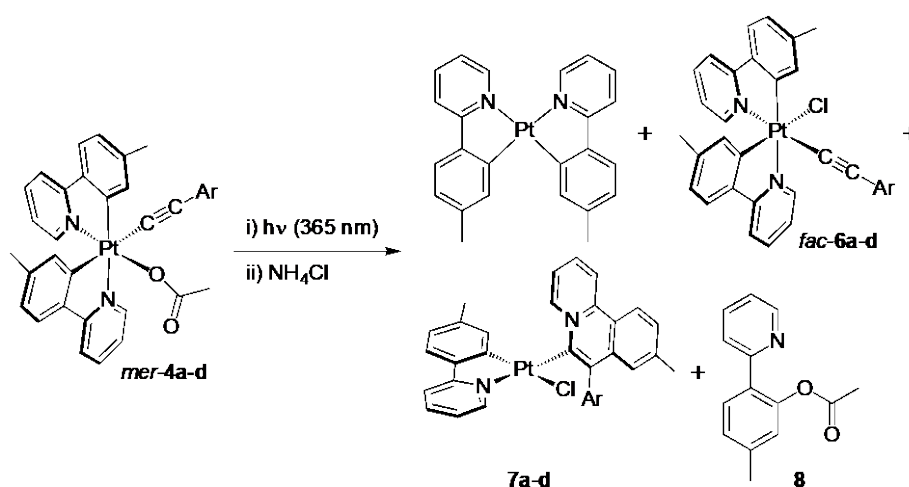


**Esquema 6.** Síntesis de alquínulos bis-ciclometalados de Pt(IV).

En los casos de los derivados de trifluoroacetato *mer*- $[\text{Pt}(\text{tpy})_2(\text{O}_2\text{CCF}_3)(\text{CCAr})]$ , la irradiación con luz UV (fuente LED con  $\lambda_{\text{max}} = 365 \text{ nm}$ ) condujo a la isomerización a la geometría



facial (*fac*) (Esquema 6). En cambio, los complejos que contienen el ligando acetato produjeron una mezcla de fotoproductos que resultan de cuatro procesos diferentes: (i) reducción a *cis*-[Pt(*tpy*)<sub>2</sub>]; (ii) anulaciones reductoras entre uno de los ligandos *tpy* y los átomos C<sub>α</sub> y C<sub>β</sub> del alquinilo para dar derivados de benzoquinolizino, (iii) isomerización a la geometría *fac*, o (iv) acoplamiento C–O entre el ligando acetato y un ligando *tpy* para dar acetato de 5-metil-(2-piridil)fenilo. Estas mezclas de productos fueron tratadas con NH<sub>4</sub>Cl para reemplazar el ligando acetato por cloruro y fueron analizadas por RMN de <sup>1</sup>H para identificar los productos y determinar las proporciones en que se forman (Esquema 7). También pudieron separarse los productos mayoritarios mediante cromatografía, cuyos rendimientos se dan en el Esquema 7. Los procesos de reducción a *cis*-[Pt(*tpy*)<sub>2</sub>] y de anulación para dar derivados de benzoquinolizino están más favorecidos para los alquinilos más dadores, mientras que los otros se favorecen para los alquinilos menos dadores.

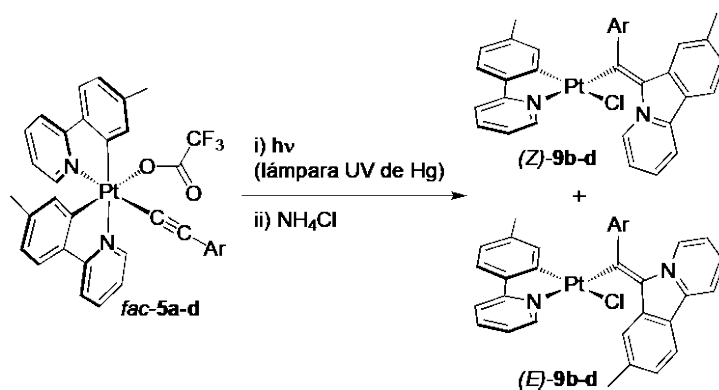


Complejo irradiado	Ar	Fuente LED de 365 nm				Lámpara UV de Hg	
		Proporciones en el crudo/rendimiento (%)				Rendimiento (%)	
		<i>cis</i> -[Pt( <i>tpy</i> ) <sub>2</sub> ]	<i>fac</i> -6a-d	7a-d	8	7a-d	8
<i>mer</i> -4a	C <sub>6</sub> H <sub>4</sub> OMe- <i>p</i>	52/22	18/13	30/22	0/0	22	0
<i>mer</i> -4b	Ph	7/-*	26/13	33/24	33/23	17	-*
<i>mer</i> -4c	C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub> - <i>p</i>	2/-*	39/21	5/-*	51/37	-*	48
<i>mer</i> -4d	C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> -3,5	7/-*	40/20	2/-*	51/36	-*	46

\*No se pudo separar.

Esquema 7. Reactividad fotoquímica de los complejos *mer*-[Pt(*tpy*)<sub>2</sub>(O<sub>2</sub>CMe)(CCAr)].

Los complejos *fac*-[Pt(*tpy*)<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)(CCAr)] fueron sometidos a irradiación con luz UV en un fotorreactor equipado con una lámpara de Hg de media presión. El complejo con metoxifenilacetiluro no reaccionó, mientras que los demás produjeron complejos de Pt(II) que resultan de un acoplamiento C–C entre el átomo C<sub>α</sub> del alquinilo y el carbono metalado de uno de los ligandos *tpy*, formando un ligando con un fragmento piridoisindolio, que se obtuvieron como mezclas de isómeros *Z/E* (Esquema 8).



Precursor	Ar	Producto (rendimiento)	proporción Z/E	
			Crudo	Aislado
fac-5a	C <sub>6</sub> H <sub>4</sub> OMe- <i>p</i>	—	—	—
fac-5b	Ph	(E/Z)-9b (25%)	1/0.7	1/0.4
fac-5c	C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub> - <i>p</i>	(E/Z)-9c (28%)	1/0.6	1/0.2
fac-5d	C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> -3,5	(E/Z)-9d (10%)	1/0.8	1/0.5

**Esquema 8.** Reactividad fotoquímica de los complejos *fac*-[Pt(tpy)<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)(CCAr)].

Sobre la base de las proporciones obtenidas de fotoproductos, las propiedades electrónicas de los ligandos carboxilato y alquinilo, y cálculos de TDDFT, postulamos que los procesos de reducción a *cis*-[Pt(tpy)<sub>2</sub>], isomerización o acoplamiento C–O de los complejos *mer*-[Pt(tpy)<sub>2</sub>(O<sub>2</sub>CR)(CCAr)] ocurren a través de la población térmica de estados excitados <sup>3</sup>LMCT [ $\pi(\text{alquinilo}) \rightarrow d\sigma^*$ ], mientras que las reacciones de anulación para dar derivados de benzoquinolinizino son posiblemente una consecuencia de la población térmica estados <sup>3</sup>LLCT [ $\pi(\text{alquinilo}) \rightarrow \pi^*(\text{tpy})$ ]. La fotorreactividad de los complejos *fac*-[Pt(tpy)<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)(CCAr)] es posiblemente atribuible a intermedios pentacoordinados fotorreactivos que presentan estados <sup>3</sup>LMCT de baja energía.

Con este trabajo se demuestra que se pueden inducir fotoquímicamente acoplamientos C–C y C–heteroátomo desde complejos bis-ciclometalados de Pt(IV), obteniendo un conocimiento importante sobre el comportamiento de los estados excitados reactivos que podría ser aplicado para el desarrollo de nuevos procesos de síntesis.

## **ARTICLES**



Article 1: *Chem. Eur. J.* **2020**, 26, 11307 – 11315

**Journal:** Chemistry - A European Journal

**Title:** Stereoselective Formation of Facial Tris-Cyclometalated Pt<sup>IV</sup> Complexes: Dual Phosphorescence from Heteroleptic Derivatives

**Authors:** Juan Carlos López López<sup>[a]</sup>, Delia Bautista Cerezo<sup>[b]</sup> and Pablo González Herrero<sup>\*[a]</sup>

**Affiliations:** [a] Departamento de Química Inorgánica, Universidad de Murcia, Campus de Espinardo, 19, 30100 Murcia (Spain) e-mail: pgh@um.es; jc.lopezlopez@um.es

[b] Dr. D. Bautista ACTI, Universidad de Murcia, Campus de Espinardo, 21 30100 Murcia (Spain) e-mail: dbc@um.es

\*Corresponding author

**URL:** <https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/chem.202001164>

**DOI:** 10.1002/chem.202001164

**Abstract:** A stereoselective synthetic route to homo- and heteroleptic facial tris-cyclometalated Pt<sup>IV</sup> complexes is reported, involving the oxidative addition of 2-(2-pyridyl)- or 2-(1-isoquinoliny)benzenediazonium salts to cis-[Pt(C<sup>^</sup>N)<sub>2</sub>] precursors, with C<sup>^</sup>N=cyclometalated 2-(p-tolyl)pyridine (tpy), 2-phenylquinoline (pq), 2-(2-thienyl)pyridine or 1-phenylisoquinoline (piq), to produce labile diazenide intermediates that undergo photochemical or thermal elimination of N<sub>2</sub>. The method allows the preparation of derivatives bearing cyclometalated ligands of low p–p\* transition energies. The new complexes exhibit phosphorescence in fluid solution at room temperature arising from triplet ligand-centered (<sup>3</sup>LC) excited states, which, in the cases of the heteroleptic derivatives, involve the ligand with the lowest p–p\* gap. The heteroleptic piq derivatives exhibit fluorescence and dual phosphorescence from different ligand-centered excited states in rigid media, demonstrating the potential of cyclometalated Pt<sup>IV</sup> complexes as multi-emissive materials.



**Journal:** Dalton Transactions

**Title:** Luminescent halido(aryl) Pt(IV) complexes obtained via oxidative addition of iodobenzene or diaryliodonium salts to bis-cyclometalated Pt(II) precursors

**Authors:** Juan Carlos López López<sup>[a]</sup>, Delia Bautista Cerezo<sup>[b]</sup> and Pablo González Herrero<sup>\*[a]</sup>

**Affiliations:** [a] Departamento de Química Inorgánica, Universidad de Murcia, Campus de Espinardo, 19, 30100 Murcia (Spain) e-mail: pgh@um.es

[b] Dr. D. Bautista ACTI, Universidad de Murcia, Campus de Espinardo, 21 30100 Murcia (Spain)

\*Corresponding author

**URL:** <https://pubs.rsc.org/en/content/articlelanding/2021/DT/D1DT02349G>

**DOI:** 10.1039/D1DT02349G

**Abstract:** The synthesis of bis-cyclometalated halido(aryl) Pt(IV) complexes [PtX(Ar)(C<sup>^</sup>N)<sub>2</sub>], with C<sup>^</sup>N = cyclometalated 4-(*tert*-butyl)-2-phenylpyridine (bppy), 2-(*p*-tolyl)pyridine (tpy), 2-(2-thienyl)pyridine (thpy), or 1-phenylisoquinoline (piq), X = I, Cl, or F, and Ar = Ph (for all C<sup>^</sup>N ligands) or *t*-BuPh (for C<sup>^</sup>N = tpy), and the photophysical properties of the chlorido and fluorido series is reported. The oxidative addition of iodobenzene to *cis*-[Pt(C<sup>^</sup>N)<sub>2</sub>] precursors is demonstrated to occur in MeCN under irradiation with visible light to give complexes [PtI(Ph)(C<sup>^</sup>N)<sub>2</sub>], presumably involving radical species that also produce the activation of the solvent to give cyanomethyl complexes [PtI(CH<sub>2</sub>CN)(C<sup>^</sup>N)<sub>2</sub>]. The introduction of an aryl ligand can also be achieved by reacting *cis*-[Pt(C<sup>^</sup>N)<sub>2</sub>] with (Ar<sub>2</sub>I)PF<sub>6</sub> (Ar = Ph, *t*-BuPh), which affords cationic intermediates of the type [Pt(Ar)(C<sup>^</sup>N)<sub>2</sub>(NCMe)]<sup>+</sup>. The subsequent addition of an iodide or chloride salt gives the corresponding iodido- or chlorido(aryl) complexes. The fluorido(aryl) derivatives can be obtained from the iodido complexes by halide exchange using AgF. The chlorido- and fluorido(aryl) complexes display intense phosphorescence in deaerated CH<sub>2</sub>Cl<sub>2</sub> solution and poly(methyl methacrylate) (PMMA) films at 298 K from triplet excited states primarily localized on the cyclometalated ligands (<sup>3</sup>LC) with a small MLCT admixture. Compared with the chlorido complexes, the fluorido derivatives consistently present significantly shorter emission lifetimes and higher radiative and nonradiative rate constants due to a greater MLCT contribution to the emissive state. In contrast, the introduction of the *t*-BuPh group did not induce significant changes in radiative rates with respect to the phenyl complexes.





Article 3: *Chem. Commun.* **2022**, 58, 4532–4535

**Journal:** Chemical Communications

**Title:** Phosphorescent biaryl platinum(IV) complexes obtained through double metalation of dibenziodolium ions

**Authors:** Juan Carlos López López<sup>[a]</sup>, Delia Bautista Cerezo<sup>[b]</sup> and Pablo González Herrero<sup>\*[a]</sup>

**Affiliations:** [a] Departamento de Química Inorgánica, Universidad de Murcia, Campus de Espinardo, 19, 30100 Murcia (Spain) e-mail: pgh@um.es

[b] Dr. D. Bautista ACTI, Universidad de Murcia, Campus de Espinardo, 21 30100 Murcia (Spain)

\*Corresponding author

**URL:** <https://pubs.rsc.org/en/content/articlelanding/2022/cc/d2cc01018f#!divCitation>

**DOI:** 10.1039/D2CC01018F

**Abstract:** The first series of neutral, tris-chelate, phosphorescent Pt(IV) complexes is reported, which combine two cyclometalated 2-arylpyridine ligands and a dimetalated biaryl. The introduction of biaryl ligands is achieved under mild conditions through the oxidative addition of dibenziodolium ions to Pt(II) precursors to give Pt(IV) intermediates with a singly metalated 2-(2-iodoaryl)aryl ligand, followed by the reductive metalation of the C–I bond. The modulation of emission characteristics *via* derivatization of both types of ligands is demonstrated.



Article 4: *Inorg. Chem.* **2023**, 62, 14411–14421

**Journal:** Inorganic Chemistry

**Title:** Photoinduced Reductive C–C and C–Heteroatom Couplings from Bis-cyclometalated Pt(IV) Alkynyl Complexes

**Authors:** Juan Carlos López López<sup>[a]</sup>, Delia Bautista Cerezo<sup>[b]</sup> and Pablo González Herrero<sup>\*[a]</sup>

**Affiliations:** [a] Departamento de Química Inorgánica, Universidad de Murcia, Campus de Espinardo, 19, 30100 Murcia (Spain) e-mail: pgh@um.es

[b] Dr. D. Bautista ACTI, Universidad de Murcia, Campus de Espinardo, 21 30100 Murcia (Spain)

\*Corresponding author

**URL:** <https://pubs.acs.org/doi/epdf/10.1021/acs.inorgchem.3c02162>

**DOI:** 10.1021/acs.inorgchem.3c02162

**Abstract:** Unsymmetrical dicarboxylato complexes [Pt-(tpy)<sub>2</sub>(O<sub>2</sub>CR)<sub>2</sub>] [tpy = cyclometalated 2-(p-tolyl)pyridine, R = Me, CF<sub>3</sub>] react with the terminal alkynes 4-methoxyphenylacetylene, phenylacetylene, 4-(trifluoromethyl)phenylacetylene or 3,5-difluoro-phenylacetylene in the presence of a base to produce complexes *mer*-[Pt(tpy)<sub>2</sub>(O<sub>2</sub>CR)(CCAr)], in which the metalated carbon atoms are in a meridional arrangement. Irradiation of the trifluoroacetato derivatives with a 365 nm LED source leads to isomerization to the facial complexes, which can be converted to chloride derivatives upon reaction with NH<sub>4</sub>Cl. In contrast, irradiation of the acetato derivatives leads to four different processes, namely, reduction to *cis*-[Pt(tpy)<sub>2</sub>], annulations involving one of the tpy ligands and the C $\alpha$  and C $\beta$  atoms of the alkynyl to give benzoquinolizinium derivatives, isomerization to the facial geometry, or C–O couplings between the acetato ligand and one tpy. The first two processes are favored by the presence of electron-donating groups on the alkynyl, whereas electron-withdrawing groups favor the last two. Irradiation of complexes *fac*-[Pt(tpy)<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)(CCAr)] with a medium-pressure Hg UV lamp leads to a reductive C–C coupling involving the alkynyl C $\alpha$  atom and one of the tpy ligands to give pyridoisindolium derivatives, except for the methoxyphenylacetylde derivative, which is photostable. On the basis of TDDFT calculations, the photoreactivity of the *mer* complexes is attributed to <sup>3</sup>LLCT [ $\pi$ (alkynyl)  $\rightarrow$   $\pi^*$ (tpy)] excited states for annulations or <sup>3</sup>LMCT [ $\pi$ (alkynyl)  $\rightarrow$  d $\sigma^*$ ] excited states for the rest of the processes, which are accessible through thermal population from <sup>3</sup>LC(tpy) states. The C–C couplings from the *fac* complexes are attributed to photoreactive pentacoordinate intermediates.