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Insertion of Allenes into the Pd–C bond of Ortho-Palladated Primary Arylamines of Biological Relevance: Phenethylamine, Phentermine, (L)-Phenylalanine Methyl Ester and (L)-Tryptophan Methyl Ester. Synthesis of 3-Benzazepines and Their Salts

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ABSTRACT: The previously reported ortho-metalated complexes $[Pd(C,N\text{-}ArCH_2CRR'NH_2\text{-}2)(\mu\text{-}X)]_2$ derived from phenethylamine (Ar = C_6H_4, R = R' = H, X = Br), phentermine (Ar = C_6H_4, R = R' = Me, X = Cl), (L)-phenylalanine methyl ester (Ar = C_6H_4, R = H, R' = CO_2Me, X = Cl, Br)) and (L)-tryptophan methyl ester (Ar = C_8H_5N, R = H, R' = CO_2Me, X = Cl) react with various allenes to give: (1) the corresponding η^3-allyl complexes derived from the insertion of one molecule of the allene into the Pd–C bond, which formation has been studied by DFT using a model complex, or (2) Pd(0) and the benzazepinium salts resulting from the decomposition of the above η^3-allyl complexes containing an exocyclic double bond, which subsequently react with a base to afford the corresponding benzazepines. The regiochemistry of these decomposition reactions has been studied and compared with that described for similar processes involving five-membered palladacycles. The crystal structures of the salts of some benzazepines and one isoquinoline, derived from a five-membered palladacycle, have been determined by X-ray diffraction studies.

INTRODUCTION

Allenes insert into the Pd–C_{aryl} bonds to give η^3-allyl-complexes in which a new bond forms between the previously metalated carbon and the central carbon of the allene moiety.[1-3] These insertion reactions have been widely investigated because they are the key step in the palladium-catalyzed coupling reactions of 1,2-dienes and aryl halides to afford carbo- and heterocycles.[1,4-6] We report here a study on the reactivity towards allenes of six-membered palladacycles derived from amines of biological relevance as phenethylamine, phentermine, (L)-phenylalanine methyl ester and (L)-tryptophan methyl ester, which functionalization was also an objective of the work. There are just a few examples of insertion reactions of allenes into the Pd–C_{aryl} bond of stable $\kappa^2(C,N)$-palladacycles.[3,7] These include mainly five-membered cyclometalated complexes derived from α-tetralone ketimine,[8] benzo[*h*]quinoline, 2-phenylpyridine,[9,10] *N*,*N*-dimethylbenzylamine, *N*,*N*-dimethylnaphthylamine, and

N,*N*-dimethylpropargylamines,[11] although there are two examples containing six-membered derivatives of 2-benzylpyridine and *N*-phenyl-*N*-(2-pyridyl)-amine.[9,10] As the later amine is bonded to Pd through the pyridine group, our study represents the first devoted to the reactivity of six-membered cyclopalladated amines toward allenes. There is a study on a seven-membered palladacycle derived from (2-ethynylphenyl)-*N*,*N*-dimethylmethanamine.[11] Therefore, we also report here the first insertion reactions of allenes into the Pd–C of orthopalladated primary amines.

η^3-Allyl-complexes and, in appropriate conditions, the corresponding tetrahydro-3-benzazepines, resulting from C–N coupling processes, have been isolated. These heterocycles are comprised in natural alkaloids[12-14] with great potential as drugs. Thus, some tetrahydro 3-benzazepines have been used as antileukemic agents[12,15] and some others show high affinity and selectivity for dopamine (D_1, D_3 or D_5),[16-18] serotonine,[19] or *N*-methyl-(D)-aspartate (NMDA)[20,21] receptors. Because of this last activity, 3-benzazepines can be used as antihypertensive[16,22] and antipsycotic[18,23] agents and in the treatment of Alzheimer's disease,[24] obesity,[19,25] or tobacco addiction syndrome.[26]

Most commonly employed synthesis of tetrahydro-3-benzazepines involve intramolecular cyclization of highly *N*-functionalized phenethylamines *via* radical mechanisms,[27] condensation reactions,[21] electrophilic aromatic substitutions,[16,23,25,28] or Heck-type coupling processes.[25,29,30]

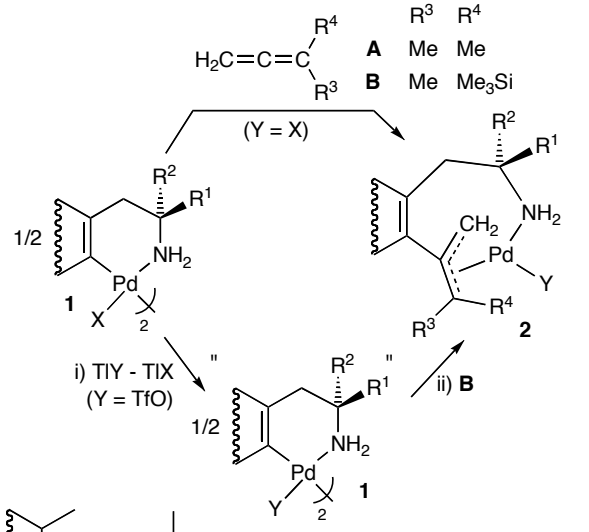
In this paper, we describe (1) the insertion reactions of symmetrical and non-symmetrical allenes into the Pd–C bond of palladacycles derived from phenethylamine, phentermine, (L)-phenylalanine methyl ester and (L)-tryptophan methyl ester, which lead to the synthesis of the corresponding η^3-allyl-complexes of Pd(II), (2) the decomposition reactions of these η^3-allyl complexes to give tetrahydro-3-benzazepine derivatives, and (3) the steric and electronic factors that affect the regiochemistry of the decomposition reactions.

RESULTS AND DISCUSSION

Synthesis and structure of η^3-allyl-complexes. The reaction of the previously reported palladacycles

derived from phenethylamine (**1a, 1b**)[31,32] phentermine (**1d**),[33] (L)-phenylalanine methyl ester (**1i**)[32,34] or (L)-tryptophan methyl ester (**1g**)[33] with two equiv of 1,1-dimethylallene (**A**) or 1-methyl-1-(trimethylsilyl)allene (**B**) at room temperature led to the formation of the corresponding complexes **2** (Scheme 1).

Scheme 1. Synthesis of Complexes Derived from the Reaction of Palladacycles **1** with 1,1-Dimethylallene or 1-Methyl-1-(trimethylsilyl)allene

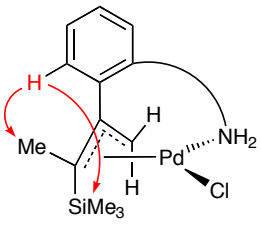


	X/Y	R^1	R^2	R^3	R^4	
1a	Cl	H	H	Me	Me_3Si	**2a**
1b	Br	H	H	Me	Me	**2b**
1c	TfO	H	H	Me	Me_3Si	**2c**
1d	Cl	Me	Me	Me	Me	**2d**
				Me	Me_3Si	**2e**
1e	Br	CO_2Me	H	Me	Me	**2f**
1f	TfO	CO_2Me	H	Me	Me_3Si	**2g**
1g	Cl	CO_2Me	H	Me	Me	**2h**
				Me	Me_3Si	**2i**

The reaction of **1e** with allene **B** afforded a solid, which elemental analysis and reactivity did not correspond with the expected η^3-allyl complex. However, using the corresponding triflato complex **1f**, prepared *in situ* from **1i** and TlTfO (see Supporting Information), complex **2g** was isolated (Scheme 1). This method was also applied to synthesize **2c** from **1b** (via **1c** and **B**).

All complexes **2**, except **2a** and **2e**, were insoluble in CH_2Cl_2, $CHCl_3$ and acetone, and insoluble or unstable in DMSO, which precluded their characterization by ^1H and ^{13}C NMR. Nevertheless, their elemental analyses were in agreement with the formulae shown in Schemes 1 and 2.

Chart 1. Proposed Structure for Complex **2e**

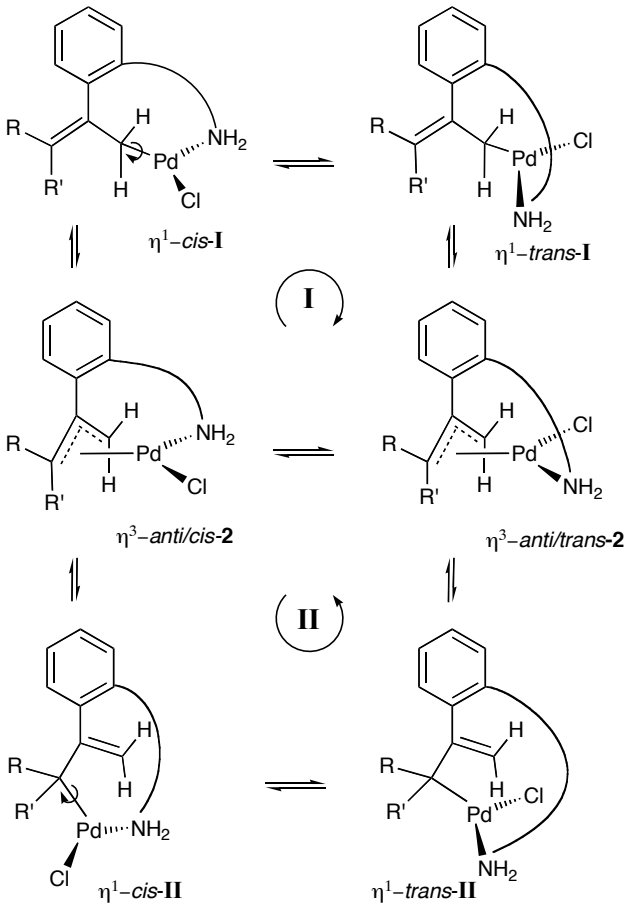


The ^1H and ^{13}C NMR spectra of complexes **2a** and **2e** in $CDCl_3$ at room temperature showed a unique set of signals. In the case of **2e**, the signals could be partially asigned with the help of APT and HMQC techniques. We propose in solution the structure shown in Chart 1 for these complexes because the chemical shift of the amine protons (2.64–3.20 ppm) are in the range of all complexes we have prepared containing *C,N*-chelating ligands derived from the studied amines (2.50–3.10 ppm) and is far away from that of the free amines (ca. 1.20 ppm), ruling out a dinuclear structure in which the amine was not coordinated. In addition, all the crystal structures of cyclopalladated primary amines show the NH_2 coordination in the solid state.[32,34-36] Finally, similar structures have been proposed for isolated η^3-allyl complexes derived from cyclopalladated tertiary benzylamines, (dimethylamino)methyl ferrocenes, dimethylanilines or alkylpyridines on the basis of NMR[37] and X-ray diffraction studies.[38] Furthermore, a NOESY 2D experiment of the complex **2e** showed cross peaks between the resonance corresponding to the H^6 aromatic proton and both substituents (Me and $SiMe_3$) of the allene. These data suggest a trans position of the NH_2 group with respect to the Me/Me_3Si groups, which was supported by a DFT study (see Supporting Information) that showed this geometry being slightly more stable than the cis isomer. This must be also the geometry of the rest of complexes derived from the allene **B**, given the structure of their decompositon products (see below). For the same reason and on steric grounds we assume an anti

arrangement of the aryl and Me_3Si groups. The ^1H NMR spectrum of complex **2a** was not easy to interpret, because the $CH_2CH_2NH_2$ and allyl CH_2 protons appear as broad and overlapped signals in the 2.53–3.97 region.

In order to elucidate the nature of the process that broadens the signals corresponding to the phentermine and the allylic fragments in complex **2e**, its ^1H NMR was recorded at variable temperature (CD_2Cl_2, from –40 to 25 ºC; $CDCl_3$, from 25 to 60 ºC). Unfortunately, broad signals, which chemical shifts slightly changed, were observed at all temperatures. However, from –40 ºC to 60 ºC, both protons of the CH_2 group of the allylic moiety appeared as two separated singlets, which indicated that an anti/syn isomerization does not take place. Probably, a low activation energy of the trans to cis isomerization through an η^3-η^1-η^3 mechanism (Scheme 2), as well as the inherent fluxionality of the non-rigid palladacycle, was responsible for the broadening of the CH_2 signals. In fact, the isomerization of *cis*-**2e** to *trans*-**2e** has a calculated activation energy of 12.2 Kcal/mol (see Supporting Information)

Scheme 2. Proposed Mechanism for cis/trans Isomerization for η^3-Allyl Complexes **2** through η^1-Allyl Intermediates (**I** or **II**)



DFT Study of the Insertion Reaction of Allenes into the Pd–C Bond of Palladacycles. In order to elucidate if there were kinetics reasons which favored the formation of one of the isomers (η^3-*anti*/*cis*-**2** or η^3-*anti*/*trans*-**2**), we studied in detail the insertion reaction of 1,1-dimethylallene (**A**) into the Pd–C_{aryl} bond of six-membered palladacycles through DFT calculations, using the complex [Pd(*C*,*N*-$C_6H_4CH_2CH_2NH_2$-2)(μ-Cl)]$_2$ (**1a**) as a model. In agreement with the accepted mechanism for insertion reactions, this process was likely to happen in two steps: (1) coordination of the allene to the metal center and (2) subsequent insertion of the coordinated allene into the Pd–C bond to afford a η^3-allyl complex.

The allene could coordinate to the palladium atom in a η^2-mode through (1) the C=CH_2 double bond or (2) the C=CMe_2 one. Each possibility generated two isomers, as the remaining non-coordinated double bond could be located on each side of the metal coordination plane (Figure 1). Coordination of the allene trans to the aryl group was not considered, as only cis coordination is relevant for the

insertion process (that is, if coordination of the allene took place trans to the aryl group, the complex should isomerizate to the cis form before the insertion reaction).

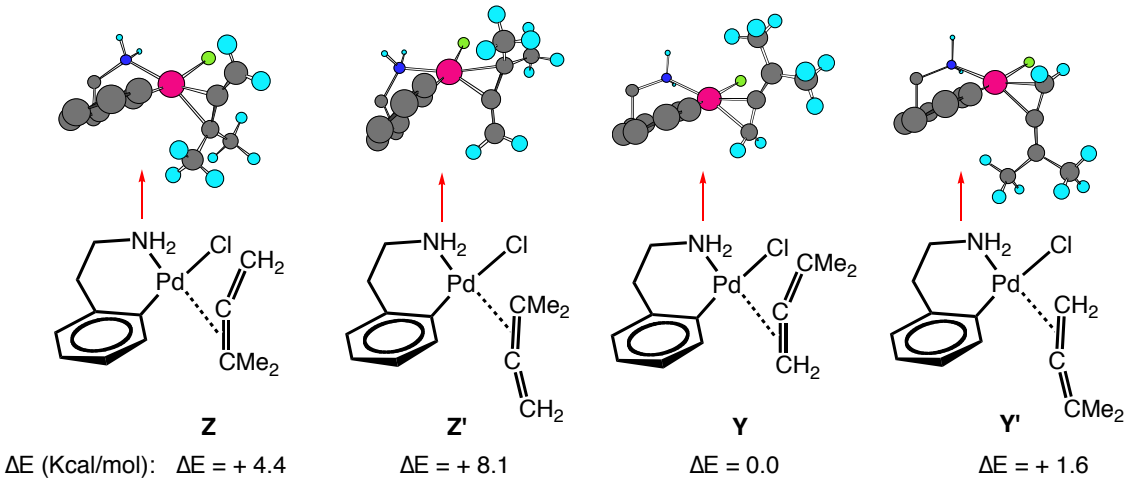


Figure 1. Relative energies of η^2-allene-complexes compared to **Y** and view of their optimized structures. Most hydrogen atoms are omitted for clarity.

The two isomers where the allene was coordinated through the C=CH_2 bond (**Y** and **Y'**) were more stable (2.8–8.1 Kcal/mol) than those where the allene was coordinated through the C=CMe_2 bond (**Z** and **Z'**), probably due to sterical effects.[39] Nevertheless, the four coordination isomers could easily interconvert through energetically accessible transition states. For example, the conversion process **Z**→**Y'** had a barrier of 13.9 Kcal/mol (see Supporting Information, **TSi**).

When the insertion step was studied from complex **Y** two possible pathways were found, which afforded two slightly different η^3-allyl complexes, *trans*-**2j** and *trans*-**2k**. These η^3-allyl-complexes had slightly different energies due to small conformation changes in the aliphatic chain (the NH_2 group of both η^3-allyl-complexes was located trans to the CH_2 group of the allyl moiety: N–Pd–CH_2 157º, N–Pd–CMe_2 = 107º). There was a single-stage pathway, through the transition state **TSz** (Figure 2), which afforded directly the η^3-allyl-complex *trans*-**2k**. The energy barrier to reach this transition state was high (36.8 Kcal/mol). In this process, the phenyl ring migrated to the central carbon of the coordinated

allene, forming a new bond and simultaneously, the palladium atom approached the non-coordinated double bond. The other pathway consisted in a three-stages pathway, in which, first, **Y** was transformed into the isomer **Y'** through the rotation of the η^2-alkene–palladium bond (transition state **TSy**, activation energy = 13.7 Kcal/mol; Figure 2). Then, **Y'** reached the transition state **TSx** (activation energy = 12.9 Kcal/mol) to give an intermediate alkylvinyl-complex **X** (similar to intermediate **I** or **II** proposed in Scheme 2), where the central carbon of the allene moiety was bound to the aromatic carbon, and the phenyl ring was η^2-coordinated to the palladium atom. Finally, the vinyl complex **X** led easily to the formation of the η^3-allyl-complex *trans*-**2j** through the transition state **TSw** (activation energy = 0.4 Kcal/mol).

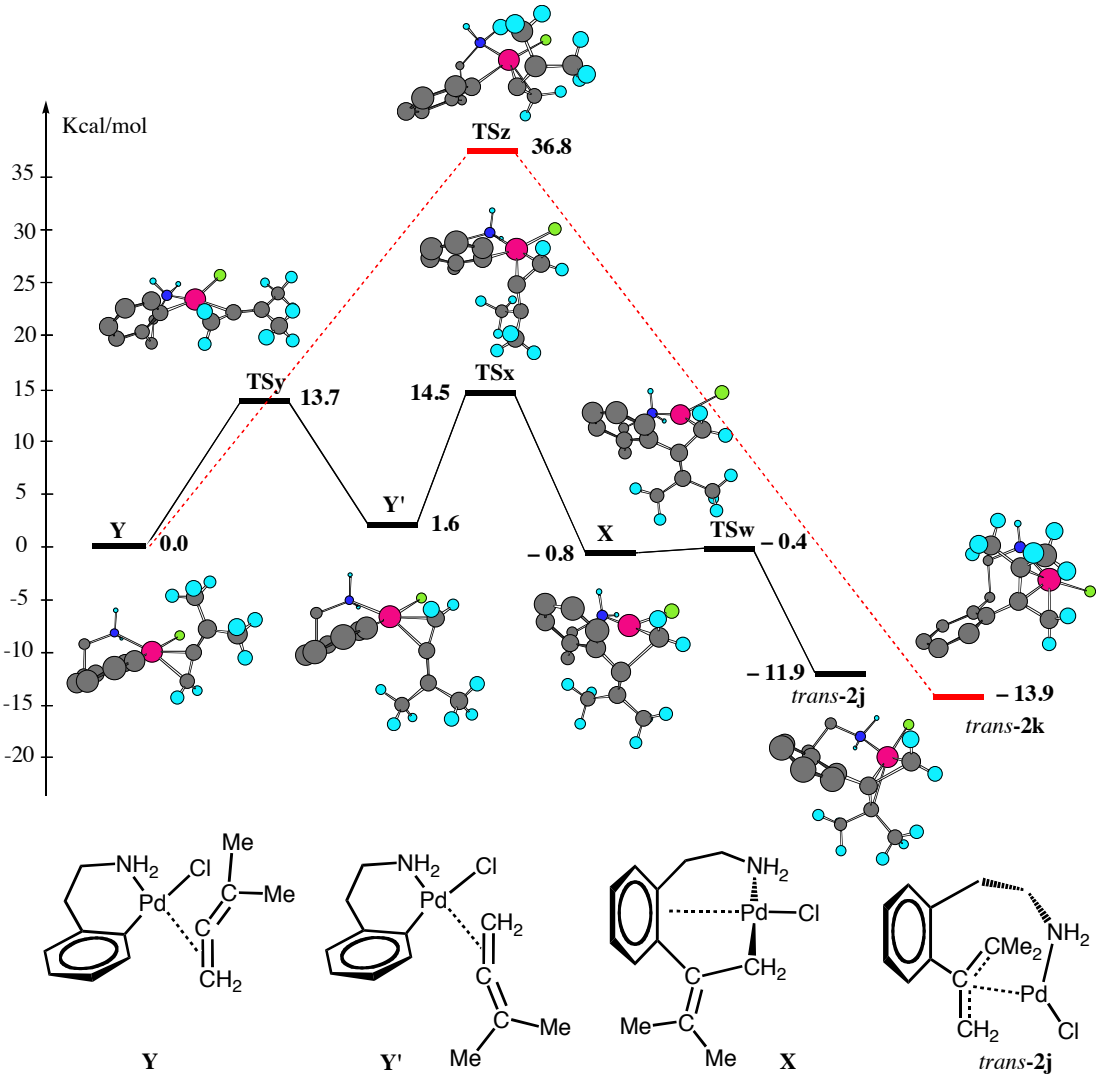


Figure 2. Calculated Energy Profile for the Insertion of 1,1-Dimethylallene into the Pd–C Bond of Palladacycle **1a**

According to these calculations, we propose that the insertion process of the coordinated ligand takes place through the pathway where an intermediate alkylvinyl-complex **X** is involved. This mechanism is similar to that proposed by Lin et al. for the insertion reactions of allenes in palladium aryl complexes $[PdI(Ph)(PPh_3)]_2$ and [PdI(Ph)(dppe)].[40]

When the calculations for the insertion reaction were carried out using isomer **Z** as precursor, a similar pathway involving three stages was found (Figure 3). In this case, the energy barrier to reach **TSy'** was 8.6 Kcal/mol, slightly lower than that found in the case of complex **Y** to get to **TSy** (13.7 Kcal/mol), because of the higher energy of complex **Z** compared to **Y** and the similar energies of both transition states. The intermediate **X'** was 5.7 Kcal/mol less stable than **X**, probably due to the higher steric hindrance of CMe_2 group compared to CH_2 group, which rendered more difficult the coordination of the aromatic ring to the palladium atom (distance Pd–C_{Ar} in **X** and **X'**: 2.357 and 2.403 Å, respectively). In the obtained η^3-allyl-complex *cis*-**2j**, the NH_2 group was located trans to the CMe_2 group (N–Pd–CMe_2 = 158º, N–Pd–CH_2 = 103º). Complex *cis*-**2j** was 4 Kcal/mol more stable than η^3-allyl-complex *trans*-**2j**. This difference could be explained by the greater steric hindrance between the CMe_2 group and the aliphatic chain of the amine in complex *trans*-**2j** compared to that in complex *cis*-**2j**.

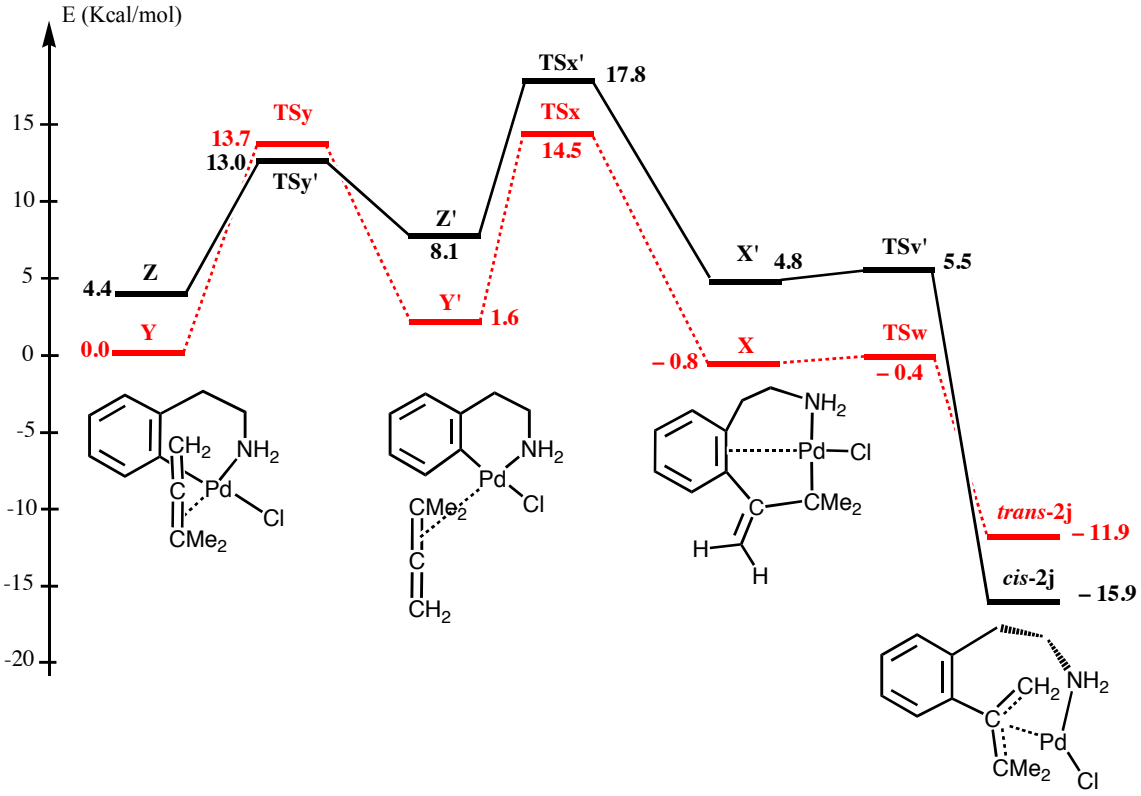


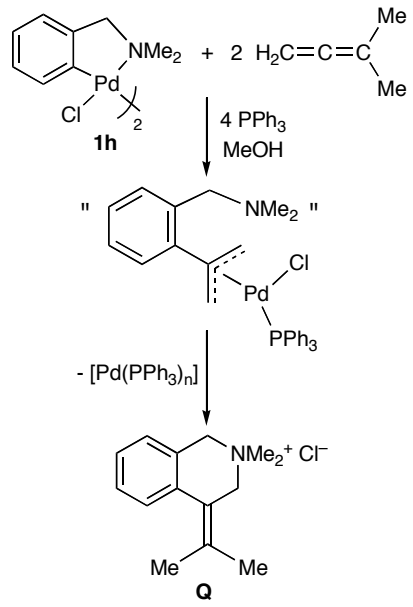
Figure 3. Comparison of Energy Profiles for Both Types of η^3-Allyl-Complexes. Only Species **Z**, **Z'**, **X'** and *cis*-**2j** are Depicted in the Figure.

According to these data, we concluded that coordination of the allene to Pd(II) through the least substituted double bond (intermediates **Y** and **Y'**) led to *trans*-**2j** and coordination of the allene through the most substituted double bond (**Z** and **Z'**) led to *cis*-**2j**. Unfortunately, the calculations described here did not permit us to distinguish which η^3-allyl-complex was preferentially formed (cis or trans). Neither the stability of both complexes, nor the activation energies involved in the reaction pathways that render them were significantly different. That is, there were neither thermodynamic nor kinetic reasons which substantially favoured the formation of one isomer, in agreement with the proposed equilibrium in solution shown in Scheme 2.

Synthesis of 3-Benzazepinium Salts. Pfeffer et al. have reported the stoichiometric synthesis of *N*-

hererocycles from allenes and palladacycles containing functionalized pyridines, tertiary anilines or *N*,*N*-dimethyl amines.[10,11] For instance, the reaction of [Pd(*C*,*N*-$C_6H_4CH_2NMe_2$-2)(μ-Cl)]$_2$ (**1h**; Scheme 3) with 1,1-dimethylallene in the presence of PPh_3 affords the isoquinolinium salt **Q**.[11] It was proposed that this reactions occurred through (1) formation of an η^3-allyl complex, in which the NMe_2 group was not coordinated to the metal and (2) nucleophilic attack of the free amino group to the less hindered external carbons of the allylic moiety.

Scheme 3. Synthesis of Isoquinolinium Salt from 1,1-Dimethylallene and Orto-metalated *N*,*N*-Dimethylbenzylamine

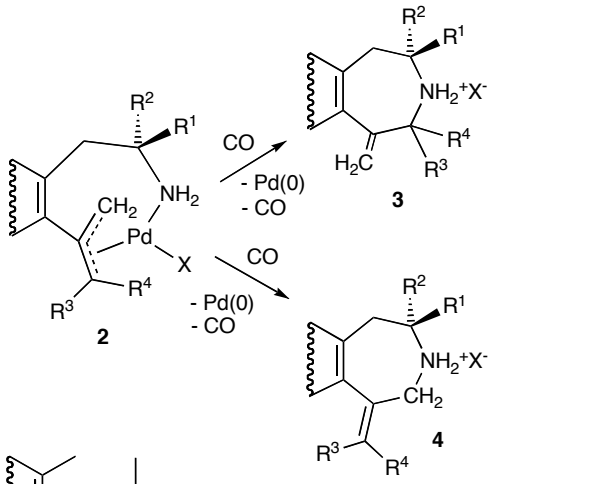


We tried a similar method to decompose the η^3-allyl-complexes derived of our six-membered palladacycles. However, when complex **2d** was reacted with PPh_3 (molar ratio Pd:PPh_3 = 1:1) in CH_2Cl_2 at room temperature for 1 h, depalladation took place, but no pure organic compound could be isolated from the reaction mixture. The ^1H and ^{31}P NMR spectra of this mixture indicated the presence of the expected benzazepinium salt **3b** (Scheme 4) along with $OPPh_3$ and traces of [Pd(PPh_3)]$_4$. Alternatively, we tested two other methods to synthesize the *N*-heterocyclic derivatives.

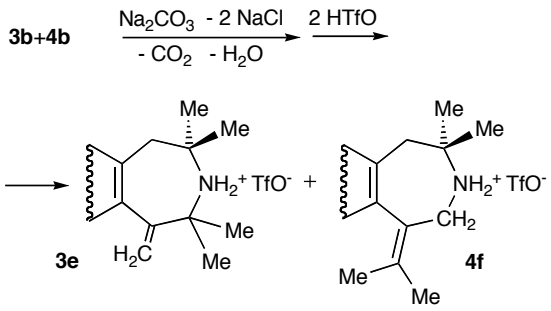
Method A. When a suspension of an η^3-allyl-complex in $CHCl_3$ was stirred under a CO atmosphere at

room temperature, decomposition to metallic palladium and formation of a benzazepinium salt **3** or **4** took place (Scheme 4). When **2d** was used, a 5:1 mixture of the regioisomeric benzazepinium chlorides **3b** and **4b** was obtained, which could not be separated. However, when this mixture was treated with Na_2CO_3 and then with HOTf the pure triflate **3e** could be isolated (Scheme 4).

Scheme 4. Synthesis of Tetrahydro-3-Benzazepinium Salts. Method A



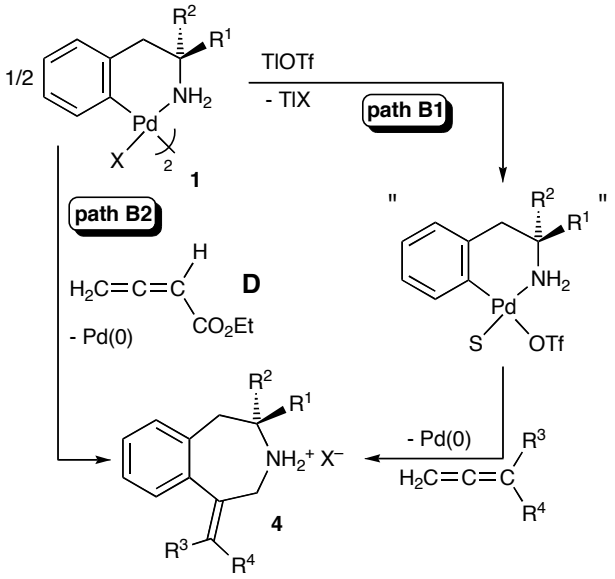
	X	R^1	R^2	R^3	R^4	
2b	Br	H	H	Me	Me	**3a**
2c	TfO	H	H	Me	Me_3Si	**4a**
2d	Cl	Me	Me	Me	Me	**3b+4b**
2e	Cl	Me	Me	Me	Me_3Si	**4c**
2f	Br	CO_2Me	H	Me	Me	**3c**
2g	TfO	CO_2Me	H	Me	Me_3Si	**4d**
2h	Cl	CO_2Me	H	Me	Me	**3d**
2i	Cl	CO_2Me	H	Me	Me_3Si	**4e**



Method B. This method was designed to obtain some benzazepinium salts at room temperature from complexes **1** without isolation ot the η^3-allyl-complex or the need of using CO. Two routes were

succesfully attempted: Path B1 involved *in situ* formation of the corresponding triflato complex (Scheme 5) from **1d** or **1i**, which reacted with allenes $H_2C=C=C(R^3)R^4$ (R^3 = Me, R^4 = Me_3Si (**B**), R^3 = R^4 = Ph (**C**), R^3 = H, R^4 = CO_2Et (**D**)), to give **4g**, **4h** or **4i**, respectively. In this way, **4g** was obtained from **1d** in 60% yield, exceeding the global 34% yield of the two-steps method used to obtain **4c**. The second route, Path B2, involved the reaction of complexes **1** with an allene containing electron-withdrawing substituents, as **D**, which afforded a benzazepinium salt, probably through an unstable η^3-allyl-complex intermediate. Thus, the palladacycle **1b** or **1d** reacted with **D** to give metallic palladium and the salt **4j** or **4k**, respectively.

Scheme 5. Synthesis of Tetrahydro-3-Benzazepinium Salts. Method B

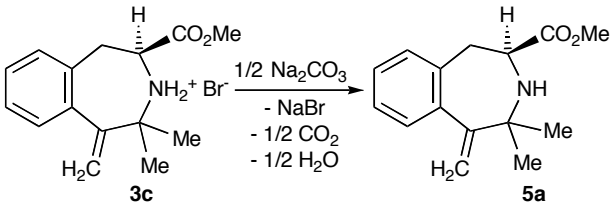


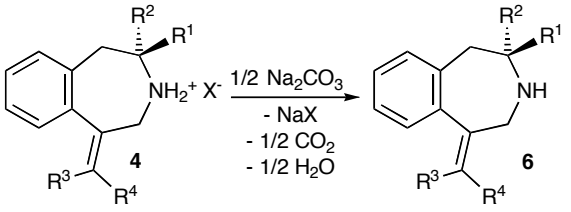
	X	R^1	R^2
1b	Br	H	H
1d	Cl	Me	Me
1i	Cl	CO_2Me	H

	X	R^1	R^2	R^3	R^4
4g	OTf	Me	Me	Me	$SiMe_3$
4h	OTf	Me	Me	Ph	Ph
4i	OTf	CO_2Me	H	H	CO_2Et
4j	Br	H	H	H	CO_2Et
4k	Cl	Me	Me	H	CO_2Et

Reactivity of Tetrahydro-3-benzazepinium Salts. Some 3-benzazepinium salts were reacted with Na_2CO_3 to afford the corresponding benzazepines **5** or **6** (Scheme 6).

Scheme 6. Synthesis of Tetrahydro-3-Benzazepines

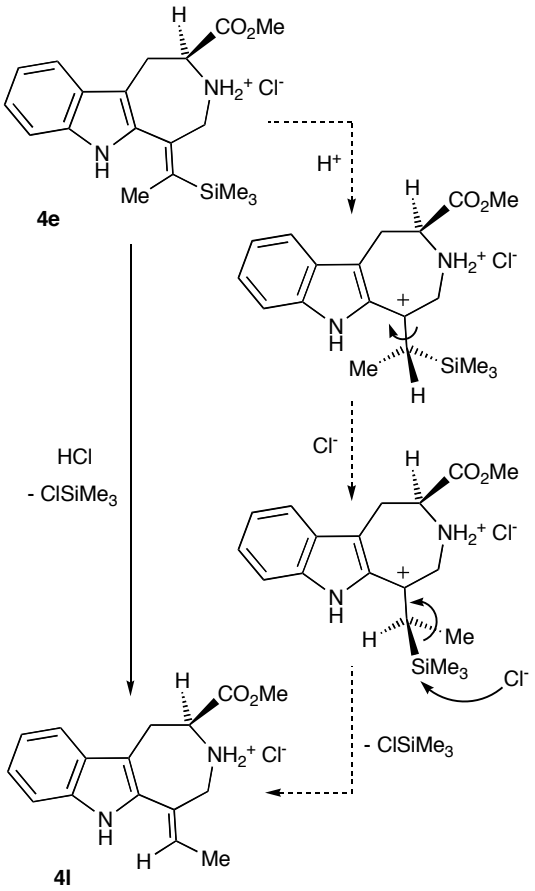




	X	R^1	R^2	R^3	R^4	
4g	TfO	CO_2Me	H	Me	Me_3Si	**6a**
4i	TfO	CO_2Me	H	H	CO_2Et	**6b**
4j	Br	H	H	H	CO_2Et	**6c**
4k	Cl	Me	Me	H	CO_2Et	**6d**

When **4e** was dissolved in a saturated solution of HCl in CH_2Cl_2 (Scheme 7), quantitative formation of **4l**, a $MeCH{=}C{=}CH_2$ (**E**) derivative, was obtained. The process involves the replacement of the $SiMe_3$ group by a hydrogen atom and the isomerization of the exocyclic double bond to give the *E* isomer, which minimizes the steric hindrance between the bulkiest substituent of the exocyclic double bond (Me) and the indol group. A possible mechanism for this reaction would involve: (1) protonation of the double bond and generation of a carbocation, which would be stabilizated by the β effect of the silicon atom and by resonance with the aromatic system, (2) rotation around the C–C σ-bond to minimize the steric hindrance, and (3) nucleophilic attack of chloride at the silicon atom, and the restoration of the double bond character (Scheme 7). Similar desilylation reactions are well documented.[41]

Scheme 7. Proposed Mecanism for the Desilylation of **4e** to Give Compound **4l**

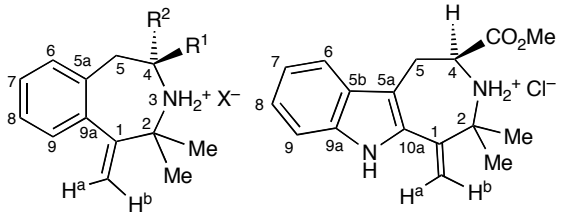


None of the 3-benzazepinium salts or 3-benzazepines reported in this work has been described previously, although similar compounds containing exocyclic double bonds are known. They were mainly prepared by: (1) insertion reactions of allenes into the Pd–C bond of *N*-palladacycles containing tertiary amines, *N*,*N*-disubstituted anilines or pyridines;[8,9] (2) palladium catalyzed coupling reactions of allenes and 2-haloaryl-alkylamines or imines;[5,6,10,11] (3) intramolecular Heck-coupling reactions;[25,29,42] and (4) palladium-catalyzed intramolecular coupling of aryl halides and alkynes.[14,24,43] Our derivatives are the first obtained from primary amines.

Structure of benzazepines and benzazepinium salts. All the tetrahydro 3-benzazepines and benzazepinium salts have been characterized by IR and NMR spectroscopies and by elemental analysis (solid compounds) or exact mass (liquid products). Additionally, the crystal structures of compounds **3a**, **3e**, **4a**, **4c**·CH_2Cl_2 and **4h** have been determined by X ray diffraction studies (see Supporting Information).

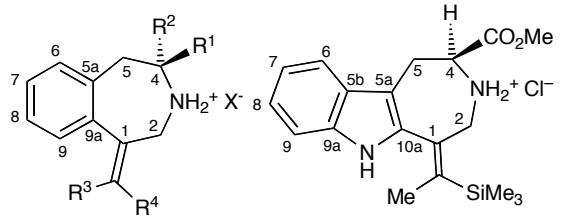
In the ^{1}H NMR spectra the $=CH_2$ protons appear as two singlets between 4.99–5.72 ppm. The most shielded proton (4.99–5.38 ppm) is the one nearest to the aromatic ring (H^a), which shows a NOE interaction with H9 (see Chart 2 for the numbering scheme). As observed in the crystal structures of **3a** and **3b**, the $=CH_2$ and the aryl groups are not coplanar, which allows the H^a proton to be shielded by the aryl ring. Contrarily, in compound **3d**, H^a is deshielded with respect to H^b (5.58 *vs* 5.51 ppm, respectively). In this case, both protons can be easily distinguished by a NOE effect with the indol NH group (H^a) or with one of the two methyl groups of the inserted allene (H^b).

Chart 2. Numbering Schemes for Representative 3-Benzazepine Derivatives (Compounds **3** and **4**)



	X	R^1	R^2
3a	Br	H	H
3b	Cl	Me	Me
3c	Br	CO_2Me	H

3d



	X	R^1	R^2	R^3	R^4
4a	OTf	H	H	Me	$SiMe_3$
4c	Cl	Me	Me	Me	$SiMe_3$
4d	OTf	CO_2Me	H	Me	$SiMe_3$
4k	Cl	Me	Me	H	CO_2Et

4e

Although two isomers were possible for the 3-benzazepines and 3-benzazepinium salts resulting from the insertion of 1-methyl-1-(trimethylsilyl)allene and ethyl buta-2,3-dienoate, only products with *Z* stereochemistry were isolated. This has been established in solution (**4g**, **4e**, **4l**, **6a)** or in the solid state by X ray diffraction studies (**4a** and **4c**). Based of these data and because this is the expected geometry from the anti isomers of the η^3-allyl-complexes **2** (Scheme 2), we assume the same geometry for the

rest.

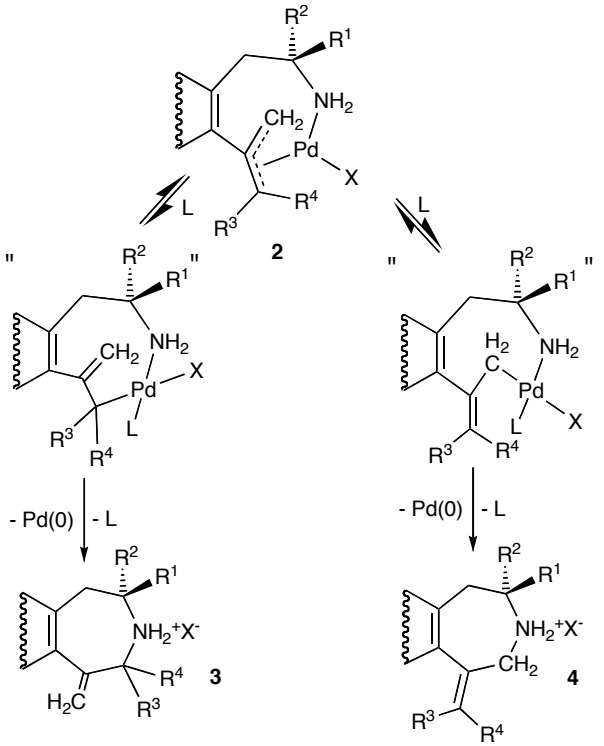
The crystal structures of benzazepinium salts show that the azepane ring adopts a chair (**3e**, **4a**, **4c**), a boat (**4h**) or both (**3a**) conformations. The bond lengths and angles are in the expected intervals and they are comparable to those found for other 3-benzazepines containing an exocyclic double bond (see details in the Supporting Information).[43,44] In all cases, the organic cations are associated with the anions forming dimers (**4h**), zigzag (**4a**, **4c**·CH_2Cl_2) or double chains (**3a**, **3e)** through classical N–H···O, N–H···Cl, N–H···Br or non-classical C–H···Cl, C–H···O hydrogen bond interactions. Additionally, the chains of **4c**·CH_2Cl_2 are associated through non-classical hydrogen interaction C–H···Cl with the crystallization solvent to give layers (see Supporting Information).

Regioselectivity of the decomposition reactions of the η^3-allyl-complexes containing primary arylalkylamines. The chloro- or bromo-η^3-allyl-complexes derived from the insertion of **A** or **B** decomposed only when they were reacted with a ligand such as CO or PPh_3 or dissolved in a coordinating solvent, such as DMSO. For instance, a solution of **2e** in CH_2Cl_2 or $CHCl_3$ was stable for days, while the complex decomposed in DMSO or when its $CHCl_3$ solution was stirred in the presence of CO.

Larock et al.[5] proposed that the palladium-catalyzed formation of medium-ring nitrogen heterocycles from allenes and aryl iodides bearing amine fuctionalities occurred through oxidative addition of the aryl iodide to Pd(0) and insertion of the allene into the Pd–C bond to give a η^3-allyl-complexes followed by intramolecular nucleophilic substitution. In this last step, the amine functionality is assumed to attack one of the two extremes of the coordinated allylic moiety. A similar mechanism was proposed by Pfeffer et al. for the stoichiometric synthesis of *N*-hererocycles from allenes and palladacycles containing functionalized pyridines, tertiary anilines or *N*,*N*-dimethyl amines (see above; Scheme 3).[10,11] However, in our case, decoordination of the NH_2 group is very unlikely taking into account the great strength of the Pd–N bond. We consider more probable that the formation of the 3-benzazepinium salts from the η^3-allyl-complexes occurs in two steps: (1) conversion of η^3-allyl-**2** to η^1-allyl-**2**, induced by

coordination of the added ligand L (CO, DMSO) and (2) a reductive elimination reaction to give **3** or **4** through a C–N coupling (Scheme 8).

Scheme 8. Proposed Mechanism for the Decomposition of the η^3-Allyl Derivatives **2** in Presence of CO



In order to support this proposal, reactions of compounds **2d** and **2e** and 4-picoline (pic) were investigated. We could not isolate any complex from these reactions at room temperature because complex **2d** did not react with pic (1:2, CH_2Cl_2) and when pic was added to a pale yellow solution of complex **2e** in CH_2Cl_2, a bright yellow solution initially formed, but attempts to precipitate a solid from the reaction mixture led to the recovery of **2e**. The ^{1}H NMR spectrum of the **2e** + pic (1:2.5) solution in $CDCl_3$ showed a unique set of signals, some of which were rather broad, different from those observed in the starting materials. The existence of an unique set of signal for the pic, in spite of using a slight excess of the ligand, proves the existence of an equilibrium between free picoline and the coordination complex. At 55 ºC, the ^{1}H NMR spectrum of this sample showed sharper signals and the protons of the CH_2 group and the Me of the CMe_2 fragment are diastereotopic. This is compatible with our proposal

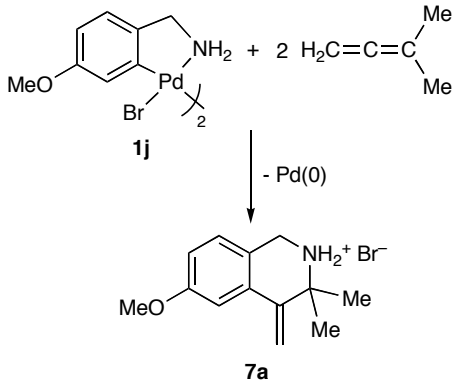
that assumes that the NH_2 group remains coordinated to Pd(II). Unfortunately, the signals of the NH_2 group were not observed at this temperature. A NOESY 2D experiment for the sample **2e** + 2.5pic showed a cross peak between the resonance corresponding to the H^6 aromatic proton and the Me substituent of the allene, but not with the $SiMe_3$ group as it happened with the starting η^3-allyl complex **2e**, which is compatible with the proposed η^3-allyl to η^1-allyl change. No longer NMR experiments could be performed because the sample started to decompose after several minutes, to give the 3-benzazepinum salt **4c**. The molar conductivity of the mixture of **2e** + 2.5pic in 1,2-dichloroethane (1.3 x 10^{-3} mol L^{-1}) at room temperature was practically zero which proves that pic has not replaced the chloro ligand. Although all these data does not conclusively prove that the **2e**+2.5pic reaction affords an η^1-allyl complex they suggest such possibility. Correspondingly, similar compounds could be intermediates in the formation of benzazepinum salts from the η^3-allyl complexes (Scheme 8). The role of the ligand L in this proposal, when CO or PPh_3 was not used (Method B, Scheme 5), could be played by the solvent (THF) or the allene (**D**).

From the results obtained (Schemes 4 and 5), it can be concluded that the C–NH_2 coupling takes places with the carbon bonded to the most electron-releasing or less voluminous substituents of the allyl ligand, leaving the most electron-withdrawing or the largest groups bonded to the exocyclic carbon. Thus, in the reaction with the allene **A** ($R^3 = R^4 = Me$) the carbon involved in the C–NH_2 coupling is the Me_2C carbon, affording 3-benzazepinium salts **3**, containing the exocyclic $=CH_2$ group. Correspondingly, with the allene **B** ($R^3 = Me$, $R^4 = SiMe_3$), for steric reasons, and with the other allenes, because of the electron-withdrawing nature of R^3 and R^4 (**C**, $R^3 = R^4 = Ph$; **D**, $R^3 = H$, $R^4 = CO_2Et$), the carbon implicated in the coupling process is the CH_2, giving salts **4**, with the exocyclic $=CR^3R^4$ group. A reasonable explanation for these electronic effects is that the reduction of the metal is favored in the η^1-allyl isomer in which the carbon bonded to Pd is the most electron-rich. Consequently, the cyclization occurs after the resulting carbocation attacks the amine nitrogen. The influence of steric hindrance associated to the amine moiety is reflected in the reaction involving the palladacycle **1d**. The α,α-

disubstitution in the aliphatic chain may slightly favor the formation of the η^1-allyl complex with the CH_2 group bonded to the metal, which explains the obtention of a small amount of the benzazepine **4b**.

We have also carried out the reaction of 1,1-dimethylallene with the five-membered palladacycle derived from a primary arylalkylamine $[Pd(C,N\text{-}C_6H_3CH_2NH_2\text{-}2,OMe\text{-}5)(\mu\text{-}Br)]_2$ (**1j**; Scheme 9). Under the usual experimental conditions (molar ratio allene:palladium = 1:1, CH_2Cl_2 and nitrogen atmosphere), salt **7a** was obtained. As the reaction follows the same regiochemistry that complexes **2** obtained from the same allene, a similar mechanism can be suggested. Consequently, the different regiochemistry with respect to that reported by Pfeffer et al.[11] in the synthesis of the isoquinolinium salt **Q** (Scheme 3), is not caused by the different number of members of the cycle but by the nature of the amine, primary or tertiary, respectively.

Scheme 9. Synthesis of the Isoquinolinium Salt from 1,1-Dimethylallene and Five-Memberd Palladacycle **1j**



The crystal structure of the isoquinolinium salt **7a** has been determined by X ray diffraction studies (see Supporting Information). The six-membered azacycle shows an envelope conformation. The exocyclic C=CH_2 double bond is not coplanar with the aromatic ring, with a torsion angle C(9)–C(4)–C(4A)–C(5) of 21.9º, notably lower than that observed for 3-benzazepinium rings. The organic cations are associated through hydrogen bonds with the bromide anions, giving single chains (see Supporting Information).

CONCLUSION

Ortho-metalated primary arylalkylamines react with 1,1-dimethylallene and 1-methyl-1-(trimethylsilyl)allene to give the corresponding η^3-allyl-complexes of Pd(II). These η^3-allyl-complexes decompose in the presence of auxiliary ligands (CO, PR_3, DMSO, THF) to give metallic palladium and tetrahydro-3-benzazepinium salts with an exocyclic double bond. The decomposition reactions of some η^3-allyl-complexes occur spontaneously when cationic palladacycles and polar solvents are used, or when the allene contains electron-withdrawing groups. The C–NH_2 coupling takes places with the carbon bonded to the most electron-releasing or less voluminous substituents of the allyl ligand, leaving the most electron-withdrawing or the largest groups bonded to the exocyclic carbon. The strength of the Pd–NH_2 bond, in the palladacycles under study, may induce the formation of a η^1-allyl complex, by contrast to the nucleophilic substitution reported for η^3-allyl complexes arising from palladacycles contining tertiary amines. This change in the mechanism might be responsible of the different regiochemisry observed in decomposition process of the complexes arising from 1,1-dimethylallene.

EXPERIMENTAL SECTION

General procedures. Infrared spectra were recorded on a Perkin Elmer 16F-PC-FT spectrometer. Mass spectra and exact masses were recorded on an AUTOSPEC 5000 VG mass spectrometer. C, H, N and S analyses, conductance measurements, and melting point determinations were carried out as described elsewhere.[36] NMR spectra were recorded in Bruker Avance 300 or 400 spectrometers, using $CDCl_3$ solutions unless otherwise stated. Chemical shifts are referenced to TMS (^1H and ^{13}C). Signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra were assigned with the help of APT, HMQC and HMBC techniques.

1,1-Diphenylallene (**C**)[45] and the ortho-metalated complexes $[Pd_2(C,N\text{-}C_6H_4CH_2CH_2NH_2\text{-}2)_2(\mu\text{-}X)_2]$ (X = Cl, **1a**; Br, **1b**),[32] $[Pd_2(C,N\text{-}C_6H_4CH_2CMe_2NH_2\text{-}2)_2(\mu\text{-}Cl)_2]$ (**1d**),[33] (*S*,*S*)-$[Pd_2\{C,N\text{-}C_6H_4CH_2CH(CO_2Me)NH_2\text{-}2\}_2(\mu\text{-}X)_2]$ (X = Cl, **1i**; Br, **1e**),[32] (*S*,*S*)-$[Pd_2\{C,N\text{-}C_8H_5N(CH_2CH(CO_2Me)NH_2\text{-}2\}_2(\mu\text{-}Cl)_2]$ (**1g**),[33] and $[Pd_2(C,N\text{-}C_6H_3CH_2NH_2\text{-}2,OMe\text{-}5)_2(\mu\text{-}Br)_2]$ (**1j**)[31] were prepared as previously reported. 1,1-Dimethylallene (**A**; Fluka), 1-methyl-1-(trimethylsilyl)allene (**B**; Aldrich), ethyl 1,2-butadienoate (**D**; Aldrich), HTfO (HSO_3CF_3) (Fluka), Na_2CO_3 (Aldrich) and $Pd(OAc)_2$ (Johnson Matthey) were used as received. TlTfO was prepared by reaction of Tl_2CO_3 and HO_3SCF_3 (1:2) in water, and recrystallized from acetone/Et_2O. Chart 2 gives the numbering schemes for the organic compounds. Synthesis and data of **3b**, **3c**, **4b**, **4d, 4f**, **4i**, **4j**, and **4k** are included along with those of **3e**, **5a**, **3e**, **6a**, **3e**, **6b**, **6c**, and **6d**, respectively.

Synthesis of 2a. 1-Methyl-1-(trimethylsilyl)allene (170 μL, 1.022 mmol) was added to a suspension of palladacycle **1a** (250 mg, 0.477 mmol) in dry CH_2Cl_2 (15 mL) under N_2 atmosphere, and the mixture was stirred for 3 h. The resulting solution was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 mL, and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give complex **2a** as a colorless solid. Yield: 270 mg, 0.695 mmol, 73%. Dec pt: 194 ºC. Anal. Calcd for $C_{15}H_{24}ClNPdSi$ (388.320): C, 46.39; H, 6.23; N, 3.61. Found: C, 46.24; H, 6.16; N, 3.54. IR (cm^{-1}): ν(NH) 3446 br, 3313 w, 3218 m. ^1H NMR (400.91 MHz):

δ 0.31 (br s, 9 H, $SiMe_3$), 1.23 (br s, 3 H, Me), 2.53 (br s, 1 H), 2.64 (br s, 1 H), 2.97 (br s, 2 H), 3.16 (br s, 1 H), 3.48 (m, 1 H), 3.65 (m, 1 H), 3.97 (m, 1 H), 6.95 (d, 1 H, Ar, $^3J_{HH}$ = 6.8 Hz), 7.15 (m, 3 H, Ar).

Synthesis of 2b. 1,1-Dimethylallene (70 μL, 0.706 mmol) was added to a suspension of palladacycle **1b** (200 mg, 0.326 mmol) in dry CH_2Cl_2 (15 mL) under N_2 atmosphere, and the mixture was stirred for 4 h. The resulting suspension was filtered, and the solid was washed with CH_2Cl_2 (2 x 3 mL) and air-dried to give a first crop of complex **2b** (171 mg) as a yellow solid. A solid precipitated in the mother liquors. The suspension was filtered, and the solid was washed with Et_2O (5 mL) and air-dried to give a second crop of complex **2b** (30 mg) as a yellow solid. Yield: 201 mg, 0.536 mmol, 82%. Dec pt: 168 ºC. Anal. Calcd for $C_{13}H_{18}BrNPd$ (374.603): C, 41.68; H, 4.84; N, 3.74. Found: C, 41.32; H, 4.81; N, 3-68. IR (cm^{-1}): ν(NH) 3219 m. Complex **2b** was insoluble in CH_2Cl_2, $CHCl_3$, acetone and DMSO, which prevented us from measuring its NMR spectra.

Synthesis of 2c. TlTfO (231 mg, 0.653 mmol) was added to a suspension of palladacycle **1b** (200 mg, 0.326 mmol) in CH_2Cl_2 (40 mL). The resulting suspension was stirred for 12 h and filtered through a plug of Celite to remove the TlBr formed. The solvent was removed, the residue was dissolved in CH_2Cl_2 (15 mL) under N_2 atmosphere, 1-methyl-1-(trimethylsilyl)allene (120 μL, 0.721 mmol) was added, and the mixture was stirred for 5 h. The resulting suspension was filtered, and the solid was washed with CH_2Cl_2 (2 x 5 mL) and air-dried to give a first crop of complex **2c** (260 mg, 0.517 mmol) as an off-white solid. The filtrate was concentrated to ca. 4 mL, and Et_2O (20 mL) was added. The resulting suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give a second crop of complex **2c** as a pale yellow solid (55 mg, 0.109 mmol). Yield: 315 mg, 0.627 mmol, 96%. Mp: 201 ºC dec. Anal. Calcd for $C_{16}H_{24}F_3NO_3PdSSi$ (501.932): C, 38.29; H, 4.82; N, 2.79; S, 6.39. Found: C, 38.67; H, 4.97; N, 3.02; S, 3.53.[46] IR (cm^{-1}): ν(NH) 3255 w; ν(SO) 1279 s, 1030 s; ν(CF_3) 1160 m. Complex **2c** was insoluble in CH_2Cl_2, $CHCl_3$ and acetone, and unstable in DMSO, which prevented us from measuring its NMR spectra.

Synthesis of 2d·1/2H_2O. 1,1-Dimethylallene (80 μL, 0.806 mmol) was added to a solution of

palladacycle **1d** (220 mg, 0.379 mmol) in dry CH_2Cl_2 (15 mL) under N_2 atmosphere, and the mixture was stirred for 12 h. The resulting suspension was filtered, and the solid was washed with CH_2Cl_2 (5 mL) and Et_2O (2 x 5 mL) and air-dried to give complex **2d**·1/2H_2O as a colourless solid. Yield: 264 mg, 0.719 mmol, 95%. Dec pt: 169 ºC. Anal. Calcd for $C_{15}H_{22}ClNPd$·1/2H_2O (367.208): C, 49.06; H, 6.31; N, 3.81. Found: C, 49.19; H, 6.40; N, 3.79. IR (cm^{-1}): ν(H_2O) 3452 br w; ν(NH) 3303 m, 3212 m, 3138 m. Complex **2d**·1/2H_2O was insoluble in CH_2Cl_2, $CHCl_3$, acetone and DMSO, which prevented us from measuring its NMR spectra.

Synthesis of 2e. 1-Methyl-1-(trimethylsilyl)allene (86 μL, 0.516 mmol) was added to a solution of palladacycle **1d** (150 mg, 0.258 mmol) in dry CH_2Cl_2 (15 mL) under N_2 atmosphere, and the resulting solution was stirred for 5 h. The solvent was evaporated to ca. 2 mL, and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give complex **2e** as a colourless solid. Yield: 194 mg, 0.466 mmol, 91%. Dec pt: 187 ºC. Anal. Calcd for $C_{17}H_{28}ClNSiPd$ (416.374): C, 49.04; H, 6.78; N, 3.36. Found: C, 49.12; H, 6.86; N, 3.66. IR (cm^{-1}): ν(NH) 3288 w, 3224 w. ^{1}H NMR (400.91 MHz): δ 0.37 (s, 9 H, $SiMe_3$), 1.07 (br s, 3 H, Me), 1.27 (br s, 3 H, Me, CMe_2), 1.31 (br s, 3 H, Me, CMe_2), 2.64–3.20 (m, 4 H, CH_2 + NH_2), 3.31 (br s, 1 H, CH_2=C), 3.70 (br s, 1 H, CH_2=C), 7.27 (br s, 3 H, C_6H_4), 7.80 (br s, 1 H, C_6H_4). ^{13}C NMR (100.81 MHz): δ 1.7 (s, $SiMe_3$), 21.1 (s, Me), 29.8 (br s, C*Me*$_2$), 45.4 (br s, CH_2), 54.4 (s, *C*Me_2), 58.6 (br s, *C*H_2=C), 87.5 (br s, *C*(Me)$SiMe_3$=C), 127.9 (s, CH), 130.7 (s, CH), 131.8 (s, CH), 133.7 (s, C), 137.1 (s, C), 139.4 (s, C).

Synthesis of 2f. 1,1-Dimethylallene (65 μL, 0.655 mmol) was added to a solution of palladacycle **1e** (200 mg, 0.274 mmol) in dry CH_2Cl_2 (15 mL) under N_2 atmosphere. The mixture was stirred for 12 h and filtered through a plug of Celite. The filtrate was concentrated to ca. 1 mL, and Et_2O (25 mL) was added. The resulting suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give complex **2f** as a yellow solid. Yield: 189 mg, 0.437 mmol, 79%. Mp: 172 ºC dec. Anal. Calcd for $C_{15}H_{20}BrNO_2Pd$ (432.639): C, 41.64; H, 4.66; N, 3.24. Found: C, 41.73; H, 4.85; N, 3.54. IR (cm^{-1}): ν(NH) 3390 br, 3200 br; ν(CO) 1737 s. Complex **2f** was insoluble in CH_2Cl_2, $CHCl_3$, acetone

and DMSO, which prevented us from measuring its NMR spectra.

Synthesis of 2g. TlTfO (222 mg, 0.628 mmol) was added to a solution of palladacycle **1i** (200 mg, 0.312 mmol) in acetone (10 mL). The resulting suspension was stirred for 30 min and filtered through a plug of Celite to remove the TlCl formed. The solvent was removed, the residue was dissolved in dry CH_2Cl_2 (10 mL) under N_2 atmosphere, and 1-methyl-1-(trimethylsilyl)allene (115 μL, 0.691 mmol) was added. The resulting yellow solution was stirred for 12 h, and filtered through a plug of Celite. The filtrate was concentrated to ca. 1 mL, and Et_2O (15 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to afford complex **2g** as a yellow solid. Yield: 222 mg, 0.396 mmol, 64%. Mp: 170 ºC dec. Anal. Calcd for $C_{18}H_{26}F_3NO_5PdSSi$ (559.968): C, 38.61; H, 4.68; N, 2.50; S, 5.73. Found: C, 38.68; H, 4.67; N, 2.74; S, 3.62.[46] IR (cm^{-1}): ν(NH) 3239 w; ν(CO) 1741 s; ν(SO) 1283 s, 1029 s; $\nu(CF_3)$ 1163 s. Complex **2g** was insoluble in CH_2Cl_2, $CHCl_3$ and acetone, and unestable in DMSO, which prevented us from measuring its NMR spectra.

Synthesis of 2h·1/2H$_2$O. 1,1-Dimethylallene (100 μL, 1.010 mmol) was added to a suspension of palladacycle **1g** (300 mg, 0.374 mmol) in dry CH_2Cl_2 (10 mL) under N_2 atmosphere, and the mixture was stirred for 12 h. The resulting suspension was filtered, and the solid was washed with CH_2Cl_2 (2 x 5 mL) and air-dried to give complex **2h**·1/2H_2O as a dark orange solid. Yield: 247 mg, 0.566 mmol, 76%. Dec pt: 190 ºC. Anal. Calcd for $C_{17}H_{21}ClN_2O_2Pd$·1/2H_2O (436.227): C, 46.81; H, 5.08; N, 6.42. Found: C, 46.34; H, 5.19; N, 6.22. IR (cm^{-1}): ν(NH) 3220 br; ν(CO) 1732 s. Complex **2h**·1/2H_2O was insoluble in CH_2Cl_2, $CHCl_3$, acetone and DMSO, which prevented us from measuring its NMR spectra.

Synthesis of 2i. 1-Methyl-1-(trimethylsilyl)allene (64 μL, 0.384 mmol) was added to a suspension of palladacycle **1g** (150 mg, 0.187 mmol) in dry CH_2Cl_2 (10 mL) under N_2 atmosphere, and the mixture was stirred for 6 h. The resulting suspension was filtered, and the solid was washed with CH_2Cl_2 (2 x 5 mL) and air-dried to give complex **2i** contaminated with traces of metallic palladium, as a grey solid. Yield: 110 mg, 0.226 mmol, 60%. Dec pt: 198 ºC. Anal. Calcd for $C_{19}H_{27}ClN_2O_2PdSi$ (485.388): C, 47.01; H, 5.61; N, 5.77. Found: C, 45.70; H, 5.52; N, 5.59. IR (cm^{-1}): ν(NH) 3228 br; ν(CO) 1741 s.

Complex **2i** was insoluble in CH_2Cl_2, $CHCl_3$ and acetone, and unestable in DMSO, which prevented us from purifying it and measuring its NMR spectra.

Synthesis of 1-Methylen-2,2-dimethyl-2,3,4,5-tetrahydro-benzo[*d*]azepinium Bromide (3a). A suspension of the η^3-allyl-complex **2b** (150 mg, 0.400 mmol) in $CHCl_3$ (15 mL) was stirred under CO atmosphere for 5 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 mL, and *n*-pentane (20 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to afford compound **3a** as a colorless solid. Yield: 59 mg, 0.22 mmol, 55%. Mp: 170 ºC. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 20 (5.2 x 10^{-4} M). Anal. Calcd for $C_{13}H_{18}BrN$ (268.203): C, 58.22; H, 6.76; N, 5.22. Found: C, 57.86; H, 7.03; N, 5.31. ^{1}H NMR (400.91 MHz): δ 1.67 (br s, 6 H, CMe_2), 3.14 (br s, 2 H, CH_2Ar), 3.39 (br s, 2 H, CH_2N), 5.36 (s, 1 H, CH_2=C), 5.72 (s, 1 H, CH_2=C), 7.09–7.17 (m, 2 H, H6 + H9), 7.22–7.32 (m, 2 H, H7 + H8), 9.32 (br s, 2 H, NH_2). ^{13}C{^{1}H} NMR (100.81 MHz): δ 25.1 (br s, C*Me*$_2$), 31.8 (s, CH_2Ar), 41.5 (s, CH_2N), 59.1 (s, *C*Me$_2$), 119.8 (s, *C*H$_2$=C), 127.8 (s, CH, C7), 128.65 (s, CH, C6 or C8), 128.68 (s, CH, C6 or C8), 129.6 (s, CH, C9), 134.9 (s, C5a), 140.3 (s, C9a), 149.3 (s, CH$_2$=*C*). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **3a** in CH_2Cl_2.

Synthesis of (*S*)-1-Methylen-2,2-dimethyl-4-(methoxycarbonyl)-2,3,4,5-tetrahydro-indolo[2,1-*d*]azepinium Chloride Monohydrate (3d·H$_2$O). A suspension of the η^3-allyl-complex **2h**·1/2H$_2$O (205 mg, 0.470 mmol) in $CHCl_3$ (15 mL) was stirred under CO atmosphere for 12 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL, and Et_2O (20 mL) was added. The resulting suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to afford compound **3d**·H$_2$O as a pale yellow solid. Yield: 144 mg, 0.425 mmol, 90%. Mp: 172–174 ºC. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 12 (4.9 x 10^{-4} M). Anal. Calcd for $C_{17}H_{21}ClN_2O_2$·H$_2$O (338.835): C, 60.26; H, 6.84; N, 8.27. Found: C, 59.85; H, 6.86; N, 8.07. IR (cm^{-1}): ν(NH) 3388 br, 3186 br; ν(CO) 1749 s. ^{1}H NMR (400.91 MHz): δ 1.72 (s, 3 H, Me, CMe_2),

1.87 (s, 3 H, Me, CMe_2), 1.92 (br s, partially obscured by the signal corresponding to the Me group, H_2O), 3.46 (dd, 1 H, CH_2, $^2J_{HH}$ = 16.8, $^3J_{HH}$ = 3.2 Hz), 3.66 (dd, 1 H, CH_2, $^2J_{HH}$ = 16.4, $^3J_{HH}$ = 10.8 Hz), 3.77 (s, 3 H, MeO), 4.39 (dd, 1 H, C*H*CO_2Me, $^3J_{HH}$ = 10.4, $^3J_{HH}$ = 3.2 Hz), 5.51 (s, 1 H, CH_2=C), 5.58 (s, 1 H, CH_2=C), 7.09 (td, 1 H, H7, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 0.8 Hz), 7.18 (td, 1 H, H8, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 0.8 Hz), 7.37 (d, 1 H, H9, $^3J_{HH}$ = 8.0 Hz), 7.46 (d, 1 H, H6, $^3J_{HH}$ = 8.0 Hz), 8.73 (s, 1 H, NH indole). The resonance corresponding to the NH_2 group was not observed. $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 25.2 (s, Me, CMe_2), 25.3 (s, CH_2Ar), 28.0 (s, Me, CMe_2), 53.6 (s, MeO), 56.6 (s, *C*HCO_2Me), 64.3 (s, *C*Me_2), 108.1 (s, C5a), 111.3 (s, CH, C9), 117.6 (s, *C*H_2=C), 118.4 (s, CH, C6), 120.1 (s, CH, C7), 123.3 (s, CH, C8), 127.7 (s, C5b), 132.0 (s, C10a), 135.9 (s, C9a), 141.4 (s, CH_2=*C*), 169.0 (s, CO).

Synthesis of 1-Methylen-2,2,4,4-tetramethyl-2,3,4,5-tetrahydro-benzo[*d*]azepinium Triflate (3e). A suspension of the η^3-allyl-complex **2d**·1/2H_2O (200 mg, 0.545 mmol) in $CHCl_3$ (15 mL) was stirred under CO atmosphere for 5 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL, and n-pentane (20 mL) was added. The suspension was filtered, and the white solid was washed with n-pentane (2 x 5 mL) and air-dried (75 mg). The ^1H NMR of this solid proved it to be a mixture 5:1 of the regioisomers **3b** and **4b**, which could not be separated neither by fractional crystallization nor by chromatography. The ^1H NMR data of both isomers were extracted from the spectrum of the mixture. **3b**: ^1H NMR (400.91 MHz): δ 1.62 (br s, 6 H, C*Me*$_2$$CH_2$), 1.79 (br s, 6 H, Me_2C=), 2.86 (br s, 2 H, CH_2Ar), 5.20 (s, 1 H, CH_2=C), 5.51 (s, 1 H, CH_2=C), 7.06–7.33 (m, 4 H, Ar), 8.95 (br s, 2 H, NH_2). **4b**: ^1H NMR (400.91 MHz): δ 1.15 (br s, 3 H, Me, C*Me*$_2$$CH_2$), 1.71 (s, 3 H, Me, Me_2C=), 1.74 (br s, 3 H, Me, C*Me*$_2$$CH_2$), 2.08 (s, 3 H, Me, Me_2C=), 2.45 (br d, 1 H, CH_2, $^2J_{HH}$ = 14.8 Hz), 3.34 (br d, 1 H, CH_2, $^2J_{HH}$ = 14.8 Hz), 3.39 (br d, 1 H, CH_2, $^2J_{HH}$ = 13.2 Hz), 4.16 (br d, 1 H, CH_2, $^2J_{HH}$ = 13.2 Hz), 7.06–7.33 (m, 4 H, Ar), 9.60 (br s, 2 H, NH_2). The signals corresponding to the aromatic protons of both isomers were overlapped.

This solid was dissolved in $CHCl_3$, Na_2CO_3 (300 mg, 2.83 mmol) was added, and the mixture was stirred for 2 h. The suspension was filtered, the filtrate was concentrated to ca. 1 mL, *n*-pentane (30 mL)

was added, and the resulting suspension was filtered. The solvent was removed from the filtrate, the residue was dissolved in CH_2Cl_2 (10 mL), and HTfO (100 μL, 1.146 mmol) was added. The solution was stirred for 15 min, the solvent was concentrated to ca. 2 mL, and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to afford the salt **3e** (55 mg) as a colorless solid. The mother liquors were concentrated to ca. 1 mL, and *n*-pentane (20 mL) was added. The suspension was filtered, and the colorless solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give a mixture of regioisomers **3e** and **4f** (35 mg, 0.096 mmol). **3e**: Yield: 55 mg, 0.150 mmol, 28%. Mp: 215 ºC. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 140 (4.9 x 10^{-4} M). $C_{16}H_{22}F_3NO_3S$ (365.414): C, 52.59; H, 6.07; N, 3.83; S, 8.77. Found: C, 52.43; H, 6.21; N, 3.93; S, 8.49. IR (cm^{-1}): ν(NH) 3104 s; ν(SO) 1288 s, 1030 s; ν(CF_3) 1156 s. ^{1}H NMR (300.1 MHz): δ 1.49 (s, 6 H, C*Me*$_2$CH$_2$), 1.64 (s, 6 H, CMe$_2$C=), 2.94 (br s, 2 H, CH$_2$Ar), 5.28 (s, 1 H, CH$_2$=C), 5.59 (s, 1 H, CH$_2$=C), 7.10–7.13 (m, 1 H, H6), 7.16–7.20 (m, 1 H, H9), 7.29–7.35 (m, 2 H, H7 + H8). The NH_2 group appeared as a broad singlet, partially obscured by the signal corresponding to H7 + H8. ^{13}C{^{1}H} NMR (75.45 MHz): δ 27.4 (br s, C*Me*$_2$CH$_2$ + C*Me*$_2$C=), 43.8 (s, CH$_2$Ar), 61.3 (s, *C*Me$_2$CH$_2$), 62.8 (s, *C*Me$_2$C=), 118.3 (s, *C*H$_2$=C), 119.9 (q, CF_3, $^1J_{CF}$ = 318.8 Hz), 128.3 (s, CH, C8), 128.9 (s, CH, C7), 129.6 (s, CH, C9), 129.7 (s, CH, C6), 132.9 (s, C5a), 139.7 (s, C9a), 149.4 (s, CH$_2$=*C*). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-hexane into a solution of **3e** in acetone. **4f**: The data corresponding to **4f** were extracted from the spectrum of the mixture. ^{1}H NMR (400.91 MHz): δ 1.17 (br s, 3 H, Me, C*Me*$_2$CH$_2$), 1.27 (br s, 3 H, Me, C*Me*$_2$CH$_2$), 1.70 (s, 3 H, Me, Me$_2$C=), 2.05 (s, 3 H, Me, Me$_2$C=), 2.47 (br d, 1 H, CH$_2$, $^2J_{HH}$ = 12.8 Hz), 3.36 (br m, 2 H, 1 H of CH$_2$Ar + 1 H of CH$_2$C=), 4.18 (br d, 1 H, CH$_2$, $^2J_{HH}$ = 11.2 Hz), 8.98 (br s, 2 H, NH_2). The signals corresponding to aromatic protons were overlapped with the ones from the isomer **3e**.

Synthesis of (*Z*)-1-(1-(trimethylsilyl)ethyliden)-2,3,4,5-tetrahydro-benzo[*d*]azepinium Triflate (4a). A suspension of the η^3-allyl-complex **2c** (200 mg, 0.398 mmol) in THF (10 mL) was stirred under CO atmosphere for 48 h. Decomposition to metallic palladium was observed. The suspension was

filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL, and Et_2O (10 mL) was added. The resulting suspension was filtered through a plug of Celite, the solvent was removed from the filtrate, *n*-pentane (15 mL) was added, and the mixture was vigorously stirred in an ice bath. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give crude **4a** as a pale yellow solid. Yield: 54 mg, 0.137 mmol, 37%. Crude **4a** (25 mg, 0.063 mmol) was dissolved in CH_2Cl_2 (1 mL) and *n*-pentane (20 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give analytically pure **4a** (16 mg, 0.040 mmol, recrystallization yield: 64%). Mp: 181 ºC. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 140 (5.2 x 10^{-4} M). Anal. Calcd for $C_{16}H_{24}F_3NO_3SSi$ (395.512): C, 48.59; H, 6.12; N, 3.54; S, 8.11. Found: C, 48.72; H, 6.31; N, 3.58; S, 7.61. IR (cm^{-1}): ν(SO) 1299 s, 1028 s; $\nu(CF_3)$ 1235 s. ^{1}H NMR (400.91 MHz): δ 0.31 (s, 9 H, $SiMe_3$), 1.70 (s, 3 H, Me), 2.87 (br s, 1 H, CH_2), 3.02 (br s, 1 H, CH_2), 3.18 (br s, 1 H, CH_2), 3.47 (br s, 1 H, CH_2), 3.65 (br s, 1 H, CH_2C=), 4.27 (br s, 1 H, CH_2C=), 6.18 (br s, 2 H, NH_2), 7.03–7.06 (m, 1 H, H9), 7.18–7.21 (m, 1 H, H6), 7.23–7.26 (m, 2 H, H7 + H8). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 0.11 (s, $SiMe_3$), 20.9 (s, *Me*C=C), 32.7 (s, CH_2Ar), 46.2 (s, CH_2N), 50.6 (s, *C*H_2C=), 120.0 (q, CF_3, $^1J_{CF}$ = 318.8 Hz), 127.1 (s, CH, C8), 128.0 (s, CH, C7), 129.5 (s, CH, C6), 139.5 (s, CH, C9), 135.6 (s, C5a), 140.2 (s, MeC=*C*), 141.2 (s, C9a), 144.9 (s, Me*C*=C). Single crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a solution of **4a** in acetone.

Synthesis of (*Z*)-1-(1-(Trimethylsilyl)ethyliden)-4,4-dimethyl-2,3,4,5-tetrahydro-benzo[*d*]azepinium Chloride (4c). A solution of the η^3-allyl-complex **2e** (130 mg, 0.313 mmol) in $CHCl_3$ (15 mL) was stirred under CO atmosphere for 12 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL, and *n*-pentane (30 mL) was added. The resulting suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give compound **4c** as a colorless solid. Yield: 30 mg, 0.097 mmol, 37%. Mp: 172 ºC. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 4 (5.5 x 10^{-4} M). Anal. Calcd for $C_{17}H_{28}ClNSi$ (309.949): C, 65.88; H, 9.11; N, 4.52. Found: C, 65.41; H, 9.14; N, 4.10. ^{1}H NMR (300.1 MHz): δ 0.23 (s, 9 H,

$SiMe_3$), 1.21 (br s, 3 H, Me, CMe_2), 1.55 (br s, partially obscured by the signal corresponding to MeC=C, 3 H, Me, CMe_2), 1.57 (s, 3 H, MeC=C), 2.35 (br d, 1 H, CH_2Ar, $^2J_{HH}$ = 13.5 Hz), 3.02 (br d, 1 H, CH_2Ar, $^2J_{HH}$ = 13.5 Hz), 3.66 (br d, 1 H, CH_2C=, $^2J_{HH}$ = 12.6 Hz), 3.92 (br d, 1 H, CH_2C=, $^2J_{HH}$ = 13.5 Hz), 7.06–7.16 (m, 2 H, H6 + H9), 7.16–7.27 (m, 2 H, H7 + H8), 8.80 (br s, 1 H, NH_2), 9.70 (br s, 1 H, NH_2). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ –0.03 (s, $SiMe_3$), 20.3 (s, *Me*C=C), 24.2 (s, Me, CMe_2), 25.6 (s, Me, CMe_2), 44.1 (s, CH_2Ar), 44.2 (s, *C*H_2C=), 56.6 (s, *C*Me_2), 127.4 (s, CH, C8), 128.0 (s, CH, C7), 129.4 (s, CH, C6), 130.5 (s, CH, C9), 132.8 (s, C5a), 138.3 (s, C9a), 138.7 (s, Me*C*=C), 140.0 (s, MeC=*C*). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **4c** in CH_2Cl_2.

Synthesis of (*Z*)-(*S*)-1-(1-(Trimethylsilyl)ethyliden)-4-(methoxycarbonyl)-2,3,4,5-tetrahydro-indolo[2,1-*d*]azepinium Chloride (4e). A suspension of the η^3-allyl-complex **2i** (155 mg, 0.319 mmol) in $CHCl_3$ (15 mL) was stirred under CO atmosphere for 7 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL, and Et_2O (30 mL) was added. The resulting suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give a first crop of compound **4e** (67 mg) as a pale yellow solid. The mother liquors were concentrated to ca. 2 mL, and *n*-pentane (30 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give a second crop of compound **4e** (26 mg). Yield: 93 mg, 0.245 mmol, 77%. Mp: 185 ºC dec. The insolubility of complex **4e** in acetone prevented us from measuring its conductivity. Anal. Calcd for $C_{19}H_{27}ClN_2O_2Si$ (378.968): C, 60.22; H, 7.18; N, 7.39. Found: C, 59.84; H, 7.45; N, 7.43. IR (cm^{-1}): ν(NH) 3234 m; ν(CO) 1755 s. ^1H NMR (300.1 MHz): δ 0.40 (s, 9 H, $SiMe_3$), 2.05 (s, 3 H, MeC=C), 3.60 (m, partially obscured by the signal corresponding to the OMe group, 2 H, CH_2Ar), 3.65 (s, 3 H, MeO), 4.24 (d, 1 H, CH_2C=, $^2J_{HH}$ = 12.0 Hz), 4.38 (d, 1 H, CH_2C=, $^2J_{HH}$ = 12.0 Hz), 4.60 (br s, 1 H, C*H*CO_2Me), 7.11 (t, 1 H, H7, $^3J_{HH}$ = 7.5 Hz), 7.18 (t, 1 H, H8, $^3J_{HH}$ = 7.2 Hz), 7.33 (d, 1 H, H9, $^3J_{HH}$ = 7.8 Hz), 7.47 (d, 1 H, H6, $^3J_{HH}$ = 7.8 Hz), 8.16 (s, 1 H, NH indole), 9.81 (br s, 1 H, NH_2), 10.82 (br s, 1 H, NH_2). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ

0.5 (s, $SiMe_3$), 21.5 (s, *Me*C=C), 24.0 (s, CH_2Ar), 48.6 (s, *C*H_2C=), 53.1 (s, MeO), 57.1 (s, *C*HCO_2Me), 108.9 (s, C5a), 111.0 (s, CH, C9), 118.2 (s, CH, C6), 120.0 (s, CH, C7), 122.8 (s, CH, C8), 127.3 (s, C5b), 130.9 (s, Me*C*=C), 135.0 (s, C10a), 137.3 (s, C9a), 147.9 (s, MeC=*C*), 168.6 (s, CO).

Synthesis of (*Z*)-1-(1-(Trimethylsilyl)ethyliden)-4,4-dimethyl-2,3,4,5-tetrahydro-benzo[d]azepinium Triflate (4g). TlTfO (122 mg, 0.345 mmol) was added to a solution of palladacycle **1d** (100 mg, 0.172 mmol) in acetone (15 mL). The suspension was stirred for 30 min and filtered through a plug of Celite to remove the TlCl formed. The solvent was removed from the filtrate, the residue was dissolved in dry THF (15 mL) under N_2 atmosphere, 1-trimethylsilyl-1,2-butadiene (58 μL, 0.348 mmol) was added, and the mixture was stirred for 12 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, the solvent was removed from the filtrate, and Et_2O (2 mL) and *n*-pentane (20 mL) were added. The resulting suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give crude **4g** as a colorless solid. Yield: 88 mg, 0.208 mmol, 60%. Crude **4g** (75 mg, 0.177 mmol) was dissolved in CH_2Cl_2 (1 mL) and *n*-pentane (15 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give analytically pure **4g** (68 mg, 0.160 mmol, recrystallization yield: 90%). Mp: 184 ºC. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 143 (4.8 x 10^{-4} M). Anal. Calcd for $C_{18}H_{28}F_3NO_3SSi$ (423.565): C, 51.04; H, 6.66; N, 3.31, S, 7.57. Found: C, 51.01; H, 6.99; N, 3.22; 7.40. IR (cm^{-1}): ν(SO) 1263 s, 1030 s. ^{1}H NMR (300.1 MHz): δ 0.21 (s, 9 H, $SiMe_3$), 1.21 (br s, 3 H, Me, CMe_2), 1.43 (br s, 3 H, Me, CMe_2), 1.58 (s, 3 H, MeC=C), 2.42 (br s, 1 H, CH_2Ar), 3.00 (br s, 1 H, CH_2Ar), 3.80 (br s, 1 H, CH_2C=), 4.00 (br s, 1 H, CH_2C=), 7.01–7.06 (m, 2 H, H6 + H9), 7.16–7.24 (m, 2 H, H7 + H8), 7.60 (br s, 1 H, NH_2). The resonance corresponding to the NH_2 group was not observed. ^{13}C{^{1}H} NMR (75.45 MHz): δ –0.21 (s, $SiMe_3$), 20.3 (s, *Me*C=C), 43.9 (s, CH_2Ar), 45.6 (s, *C*H_2C=), 57.7 (s, *C*Me_2), 127.8 (s, CH, C8), 128.3 (s, CH, C7), 129.7 (s, CH, C6), 130.5 (s, CH, C9), 132.5 (s, C5a), 138.2 (s, C9a), 139.0 (s, Me*C*=C), 140.7 (s, MeC=*C*). The ^{13}C NMR resonances corresponding to C*Me*$_2$ and CF_3 were not observed.

Synthesis of 1-(Diphenylmethylen)-4,4-dimethyl-2,3,4,5-tetrahydro-benzo[*d*]azepinium Triflate

(4h). TlTfO (171 mg, 0.483 mmol) was added to a solution of palladacycle **1d** (140 mg, 0.241 mmol) in acetone (15 mL). The suspension was stirred for 30 min and filtered through a plug of Celite to remove the TlCl formed. The solvent was removed from the filtrate, the residue was suspended in dry THF (15 mL) under N_2 atmosphere, 1,1-diphenylallene (120 mg, 0.624 mmol) was added, and the mixture was stirred for 12 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL, and Et_2O (20 mL) was added. The resulting suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give crude compound **4h** as an orange solid. Yield: 144 mg, 0.294 mmol, 61%. Crude **4h** was dissolved in CH_2Cl_2 (15 mL), and the resulting solution was filtered trough a plug of Celite. The filtrate was concentrated to ca. 2 mL, and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give analytically pure **4h** as a yellow solid (66 mg, 0.135 mmol, recrystallization yield: 28%). Mp: 256 ºC. Anal. Calcd for $C_{26}H_{26}F_3NO_3S$ (489.526): C, 63.79; H, 5.35; N, 2.86; S, 6.55. Found: C, 63.15; H, 5.56; N, 2.88; S, 6.05. IR (cm^{-1}): ν(NH) 3370 w; ν(SO) 1288 s, 1028 s; $\nu(CF_3)$ 1249 s. ^{1}H NMR (400.91 MHz): δ 1.34 (s, 6 H, CMe_2), 3.02 (br s, 2 H, CH_2Ar), 3.96 (s, 2 H, CH_2C=), 6.75–6.78 (m, 2 H, *o*-H, Ph), 6.87 (dd, 1 H, H9, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 0.8 Hz), 6.99–7.05 (m, 4 H, H8 + *p*-H of Ph + *m*-H of Ph), 7.13 (dd, 1 H, H6, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 0.8 Hz), 7.18 (td, 1 H, H7, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.2 Hz), 7.24–7.27 (m, 2 H, *o*-H, Ph), 7.32–7.35 (m, 1 H, *p*-H, Ph), 7.38–7.42 (m, 2 H, *m*-H, Ph). The resonance corresponding to the NH_2 group was obscured by the aromatic protons. $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 43.8 (s, CH_2C=), 44.4 (s, CH_2Ar), 57.4 (s, CMe_2), 119.8 (q, CF_3, $^1J_{CF}$ = 318.9 Hz), 127.2 (s, *p*-CH, Ph), 127.6 (s, *m*-CH, Ph), 128.1 (s, *p*-CH, Ph), 128.3 (s, CH, C8), 128.4 (s, CH, C7), 128.5 (s, Ph_2C=*C*), 128.9 (s, *m*-CH, Ph), 129.3 (s, *o*-CH, Ph), 129.6 (s, CH, C6), 129.8 (s, *o*-CH, Ph), 131.7 (s, CH, C9), 133.5 (s, C5a), 138.1 (s, C9a), 139.9 (s, *i*-C, Ph), 140.8 (s, *i*-C, Ph). The $^{13}C\{^1H\}$ NMR resonances corresponding to CMe_2 and Ph_2C=C were not observed. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a solution of **4h** in CH_3Cl.

Synthesis of (*Z*)-(*S*)-1-(Ethyliden)-4-(methoxycarbonyl)-2,3,4,5-tetrahydro-indolo[2,1-*d*]azepinium Chloride Monohydrate (4l·H_2O). The salt **4e** (30 mg, 0.079 mmol) was dissolved in a HCl-saturated solution of $CHCl_3$ (15 mL). The mixture was stirred for 12 h, upon which time a solid precipitated. The suspension was filtered, and the solid was washed with a 1:5 mixture of $CHCl_3$ and Et_2O (6 mL), then with Et_2O (5 mL), and air-dried to afford compound **4l**·H_2O as a pale yellow solid. Yield: 20 mg, 0.062 mmol, 78%. Mp: 224 ºC dec. The insolubility of complex **4l**·H_2O in acetone prevented us from measuring its conductivity. Anal. Calcd for $C_{16}H_{19}ClN_2O_2 \cdot H_2O$ (324.808): C, 59.17; H, 6.52; N, 8.62. Found: C, 58.75; H, 6.44; N, 8.77. IR (cm^{-1}): ν(NH) 3248 br; ν(CO) 1745 s. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 1.91 (d, 3 H, Me, $^3J_{HH}$ = 6.9 Hz), 3.35, 3.50 (AB part of an ABM system, 2 H, CH_2Ar, $^2J_{AB}$ = 16.6, $^3J_{BM}$ = 9.1, $^3J_{AM}$ = 2.9 Hz), 3.70 (s, 3 H, MeO), 4.14 (br s, 2 H, CH_2C=), 4.48 (br s, 1 H, C*H*CO_2Me), 5.44 (br s, H_2O), 6.35 (q, 1 H, CH=C, $^3J_{HH}$ = 6.9 Hz), 6.99 (t, 1 H, H7, $^3J_{HH}$ = 7.2 Hz), 7.09 (t, 1 H, H8, $^3J_{HH}$ = 7.2 Hz), 7.30 (d, H, H9, $^3J_{HH}$ = 7.8 Hz), 7.47 (d, 1 H, H6, $^3J_{HH}$ = 7.5 Hz), 9.47 (br s, 1 H, NH_2), 10.38 (br s, 1 H, NH_2), 11.27 (s, 1 H, NH, indole). ^{13}C{^{1}H} NMR (DMSO-d_6, 100.81 MHz): δ 13.6 (s, Me), 22.8 (s, CH_2Ar), 42.1 (s, *C*H_2C=), 53.1 (s, MeO), 58.7 (s, *C*HCO_2Me), 107.1 (s, C5a), 110.9 (s, CH, C9), 117.8 (s, CH, C6), 118.0 (s, CH, C7), 122.1 (s, CH, C8), 124.2 (s, CH=*C*), 127.3 (s, *C*H=C), 127.6 (s, C5b), 135.1 (s, C10a), 135.7 (s, C9a), 169.0 (s, CO).

Synthesis of (*S*)-1-Methylen-3,3-dimethyl-4-(methoxycarbonyl)-2,3,4,5-tetrahydro-benzo[*d*]azepine (5a). A suspension of the η^3-allyl-complex **2f** (150 mg, 0.346 mmol) in $CHCl_3$ (15 mL) was stirred under CO atmosphere for 12 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, the solvent was removed from the filtrate, and the oily residue was vacuum-dried to give compound **3c**. ^{1}H NMR (300.10 MHz): δ 1.64 (br s, 3 H, Me, CMe_2), 1.92 (br s, 3 H, Me, CMe_2), 3.26, 3.36 (AB part of an ABX system, 2 H, CH_2Ar, $^2J_{AB}$ = 14.1, $^3J_{AX}$ = 6.3, $^3J_{BX}$ = 2.7 Hz), 3.83 (br s, 3 H, MeO), 4.33 (br m, 1 H, C*H*CO_2Me), 5.33 (s, 1 H, CH_2=C), 5.67 (s, 1 H, CH_2=C), 7.12–7.21 (m, 2 H, Ar), 7.27–7.33 (m, 2 H, Ar). The signal corresponding to the resonance of NH_2 group is not observed.

The oily residue was dissolved in $CHCl_3$ (15 mL), Na_2CO_3 (100 mg, 0.943 mmol) was added, and the mixture was stirred for 3 h. The suspension was filtered, the solvent was removed from the filtrate, and *n*-pentane (30 mL) was added. The suspension was filtered through a plug of Celite, the solvent was removed from the filtrate, and the residue was vacuum-dried to afford compound **5a** as a pale yellow oil. Yield: 51 mg, 0.21 mmol, 60%. Anal. Calcd for $C_{13}H_{18}BrN$ (268.203): C, 58.22; H, 6.76; N, 5.22. Found: C, 57.86; H, 7.03; N, 5.31. IR (cm^{-1}): ν(NH) 3287 m, 3227 m; ν(CO) 1739 vs. EI-HRMS: exact mass calcd. for $C_{15}H_{19}NO_2$ 245.1416; found 245.1419; Δ = 0.0003. ^{1}H NMR (400.91 MHz): δ 1.30 (s, 3 H, Me, CMe_2), 1.39 (br s, 3 H, Me, CMe_2), 1.85 (br s, 1 H, NH), 2.93 (dd, 1 H, CH_2Ar, $^2J_{HH}$ = 14.2, $^3J_{HH}$ = 4.4 Hz), 3.21 (dd, 1 H, CH_2Ar, $^2J_{HH}$ = 14.2, $^3J_{AM}$ = 6.4 Hz), 3.72 (s, 3 H, MeO), 3.97 (dd, 1 H, C*H*CO_2Me, $^3J_{HH}$ = 6.4, $^3J_{HH}$ = 4.8 Hz), 4.99 (s, 1 H, CH_2=C), 5.24 (s, 1 H, CH_2=C), 7.01–7.03 (m, 1 H, H6), 7.14–7.26 (m, 1 H, H9), 7.23 (m, 2 H, H7 + H8). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 25.6 (s, Me, CMe_2), 32.3 (s, Me, CMe_2), 52.0 (s, MeO), 54.1 (s, *C*Me_2), 54.2 (s, *C*HCO_2Me), 112.6 (s, *C*H_2=C), 127.0 (s, CH, C8), 127.8 (s, CH, C7), 128.29 (s, CH, C6), 128.3 (s, CH, C9), 134.1 (s, C5a), 142.1 (s, C9a), 160.2 (s, CH_2=*C*), 173.7 (s, CO). The ^{13}C NMR resonance corresponding to CH_2Ar was not observed.

Synthesis of (*Z*)-(*S*)-1-(1-(Trimethylsilyl)ethyliden)-4-(carbomethoxy)-2,3,4,5-tetrahydro-benzo[d]azepine (6a). A solution of the η^3-allyl-complex **2g** (190 mg, 0.339 mmol) in acetone (15 mL) was stirred under CO atmosphere for 12 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, the solvent was removed from the filtrate, and the residue was vacuum-dried to give compound **4d** as a waxy solid (101 mg). ^{1}H NMR (200.13 MHz): δ 0.24 (s, 9 H, $SiMe_3$), 1.62 (s, 3 H, MeC=C), 3.17, 3.35 (AB part of an ABX system, 2 H, CH_2Ar, $^2J_{AB}$ = 14.6, $^3J_{AX}$ = 6.3 Hz), 3.66 (br s, 3 H, MeO), 4.10 (br s, 2 H, C*H*CO_2Me or CH_2C=), 4.51 (br s, 1 H, C*H*CO_2Me or CH_2C=), 6.96 (m, 1 H, Ar), 7.13–7.24 (m, 3 H, Ar), 8.20 (br s, 2 H, NH_2).

The waxy solid was dissolved in acetone (15 mL), Na_2CO_3 (100 mg, 0.94 mmol) was added, and the mixture was stirred for 6 h. The suspension was filtered through a plug of Celite, the solvent was

removed from the filtrate, and *n*-pentane (30 mL) was added. The mixture was filtered through a plug of Celite, the solvent was removed from the filtrate, and the residue was vacuum-dried to give compound **6a** as a colorless liquid. Yield: 62 mg, 0.204 mmol, 60%. Anal. Calcd for $C_{18}H_{28}F_3NO_3SSi$ (423.565): C, 51.04; H, 6.66; N, 3.31, S, 7.57. Found: C, 51.01; H, 6.99; N, 3.22; S, 7.40. IR (cm^{-1}): ν(CO) 1742 m. EI-HRMS: exact mass calcd for $C_{17}H_{25}NO_2Si$ 303.1655; found 303.1646; Δ = 0.0009. ^{1}H NMR (400.91 MHz): δ 0.26 (s, 9 H, $SiMe_3$), 1.62 (s, 3 H, MeC=C), 1.88 (s, 1 H, NH), 3.02 (br s, 2 H, CH_2Ar), 3.48 (br s, 1 H, C*H*CO_2Me or CH_2C=), 3.65 (br s, 1 H, C*H*CO_2Me or CH_2C=), 3.74 (s, 3 H, MeO), 3.85 (br s, 1 H, C*H*CO_2Me or CH_2C=), 7.03 (dd, 1 H, H9, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 2.8 Hz), 7.15–7.25 (m, 3 H, H6 + H7 + H8). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 0.3 (s, $SiMe_3$), 20.2 (s, *Me*C=C), 29.6 (s, CH_2Ar), 49.8 (s, *C*H_2C=), 52.0 (s, MeO), 126.4 (s, CH, C7 or C8), 126.9 (s, CH, C7 or C8), 128.9 (s, CH, C6), 129.0 (s, CH, C9), 151.5 (s, MeC=*C*), 173.6 (s, CO). The ^{13}C NMR resonances corresponding to *C*HCO_2Me, C5a, C9a and Me*C*=C were not observed.

Synthesis of (*Z*)-(*S*)-1-((Ethoxycarbonyl)methylen)-4-(carbomethoxy)-2,3,4,5-tetrahydro-benzo[*d*]azepine (6b). TlTfO (221 mg, 0.625 mmol) was added to a solution of palladacycle **1i** (200 mg, 0.312 mmol) in acetone (15 mL). The suspension was stirred for 30 min and filtered through a plug of Celite to remove the TlCl formed. The solvent was removed from the filtrate, the residue was suspended in dry CH_2Cl_2 (15 mL) under N_2 atmosphere, ethyl 2,3-butadienoate (80 μL, 0.654 mmol) was added, and the mixture was stirred for 24 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, the solvent was removed from the filtrate, and the oily residue was vacuum-dried to give compound **4i**. ^{1}H NMR (400.91 MHz): δ 1.32 (t, 3 H, *Me*CH_2, $^3J_{HH}$ = 7.2 Hz), 3.39 (m, 2 H, CH_2Ar), 3.86 (s, 3 H, MeO), 4.23 (q, 2 H, CH_2O, $^3J_{HH}$ = 7.2 Hz), 4.54 (br t, 1 H, C*H*CO_2Me, $^4J_{HH}$ = 6.0 Hz), 4.79 (br s, 2 H, CH_2C=), 6.17 (s, 1 H, CH=C), 7.15–7.38 (m, 4 H, Ar). The resonance corresponding to the resonance of NH_2 group is not observed.

The oily residue was dissolved in CH_2Cl_2 (15 mL), Na_2CO_3 (200 mg, 1.88 mmol) was added, and the mixture was stirred for 3 h. The suspension was filtered through a plug of Celite, the filtrate was

concentrated ca. 1 mL, and *n*-pentane (20 mL) was added. A small amount of solid precipitated, which was separated by filtration. The solvent was removed from the filtrate, and the residue was vacuum-dried to give the benzazepine **6b** as a pale yellow oil. Yield: 47 mg, 0.163 mmol, 26%. IR (cm^{-1}): ν(NH) 3368 m; ν(CO) 1712 br. EI-HRMS: exact mass calcd for $C_{16}H_{19}NO_4$ 289.1314; found 289.1304; Δ = 0.001. ^{1}H NMR (300.1 MHz): δ 1.24 (t, 3 H, *Me*CH_2, $^3J_{HH}$ = 7.2 Hz), 1.96 (br s, 1 H, NH), 3.01 (m, 2 H, CH_2Ar), 3.67 (s, 3 H, MeO), 3.74 (m, 1 H, C*H*CO_2Me), 4.13 (q, 2 H, CH_2O, $^3J_{HH}$ = 7.2 Hz), 4.15 (dd, partially obscured by the signal corresponding to the CH_2O group, 1 H, CH_2C=, $^2J_{HH}$ = 20.1, $^4J_{HH}$ = 2.4 Hz), 4.28 (dd, 1 H, CH_2C=, $^2J_{HH}$ = 20.1, $^4J_{HH}$ = 2.4 Hz), 5.84 (t, 1 H, CH=C, $^4J_{HH}$ = 2.4 Hz), 7.03–7.06 (m, 1 H, H6), 7.19–7.28 (m, 3 H, H7 + H8 + H9). ^{13}C{^{1}H} NMR (50.30 MHz): δ 14.3 (s, *Me*CH_2), 35.3 (s, CH_2Ar), 46.6 (s, *C*H_2C=), 52.1 (s, MeO), 58.1 (s, *C*HCO_2Me), 60.0 (s, CH_2O), 117.3 (s, *C*H=C), 127.7 (s, CH), 127.8 (s, CH), 128.6 (s, CH, C6), 129.4 (s, CH), 135.1 (s, C5a), 140.1 (s, C9a), 164.8 (s, CH=*C*), 166.1 (s, *C*O_2Et), 173.3 (s, *C*O_2Me).

Synthesis of (*Z*)-1-((Ethoxycarbonyl)methylen)-2,3,4,5-tetrahydro-benzo[*d*]azepine (6c). Ethyl 1,2-butadienoate (80 μL, 0.654 mmol) was added to a suspension of palladacycle **1b** (192 mg, 0.313 mmol) in dry CH_2Cl_2 (10 mL) under N_2 atmosphere, and the resulting yellow solution was stirred for 7 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL, and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give crude compound **4j** as a grey solid (characterized by ^{1}H NMR). To this solid, $CHCl_3$ (15 mL) and Na_2CO_3 (200 mg, 1.88 mmol) were added, and the mixture was stirred for 12 h. The suspension was filtered, the solvent was removed from the filtrate, and *n*-pentane (30 mL) was added. The suspension was filtered through a plug of Celite, the solvent was removed from the filtrate, and the residue was vacuum-dried to afford compound **6c** as a colorless liquid (69 mg, 0.298 mmol, 48%). **Characterization of 4j.** It was not possible to obtain a correct elemental analysis of **4j** because it was contaminated with traces of colloidal palladium. ^{1}H NMR (300.1 MHz): δ 1.32 (t, 3 H, *Me*CH_2, $^3J_{HH}$ = 7.2 Hz), 3.17 ("t", 2 H, CH_2Ar, $^3J_{HH}$ = 5.4 Hz),

3.53 (“t”, 2 H, CH_2N, $^3J_{HH}$ = 5.4 Hz), 4.22 (q, 2 H, CH_2O, $^3J_{HH}$ = 7.2 Hz), 4.57 (s, 2 H, CH_2C=), 6.14 (s, 1 H, CH=C), 7.22 (d, 1 H, H6, $^3J_{HH}$ = 6.6 Hz), 7.27–7.39 (m, 3 H, H7 + H8 + H9), 8.61 (br s, 2 H, NH_2). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 14.1 (s, *Me*CH_2), 30.0 (s, CH_2Ar), 44.8 (s, CH_2N), 45.0 (s, *C*H_2C=), 60.8 (s, CH_2O), 122.8 (s, *C*H=C), 128.0 (s, CH), 128.3 (s, CH), 129.5 (s, CH, C6), 130.2 (s, CH), 134.7 (s, C5a), 138.1 (s, C9a), 149.8 (s, CH=*C*), 165.1 (s, CO). **Characterization of 6c.** IR (cm^{-1}): ν(NH) 3418 br; ν(CO) 1721 s. EI-HRMS: exact mass calcd for $C_{14}H_{17}NO_2$ 231.1259; found 231.1254; Δ = 0.0005. ^1H NMR (400.91 MHz): δ 1.31 (t, 3 H, *Me*CH_2, $^3J_{HH}$ = 6.8 Hz), 1.67 (br s, 1 H, NH), 2.81 (t, 2 H, CH_2Ar, $^3J_{HH}$ = 6.4 Hz), 3.03 (t, 2 H, CH_2N, $^3J_{HH}$ = 6.4 Hz), 4.16 (d, 2 H, CH_2C=, $^4J_{HH}$ = 2.0 Hz), 4.20 (q, 2 H, CH_2O, $^3J_{HH}$ = 6.8 Hz), 5.89 (t, 1 H, CH=C, $^4J_{HH}$ = 2.4 Hz), 7.13 (dd, 1 H, H6, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 0.4 Hz), 7.24–7.33 (m, 3 H, H7 + H8 + H9). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 14.2 (s, *Me*CH_2), 34.1 (s, CH_2Ar), 46.3 (s, CH_2N), 48.5 (s, *C*H_2C=), 59.9 (s, CH_2O), 117.1 (s, *C*H=C), 127.0 (s, CH, C8), 127.5 (s, CH, C7), 128.3 (s, CH, C6), 129.3 (s, CH, C9), 137.5 (s, C5a), 140.5 (s, C9a), 166.1 (s, CO), 166.3 (s, CH=*C*).

Synthesis of (*Z*)-1-((Ethoxycarbonyl)methylen)-4,4-dimethyl-2,3,4,5-tetrahydro-benzo[*d*]azepine (6d). Ethyl 1,2-butadienoate (90 μL, 0.736 mmol) was added to a solution of palladacycle **1d** (200 mg, 0.345 mmol) in dry CH_2Cl_2 (15 mL) under N_2 atmosphere, and the resulting yellow solution was stirred for 12 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL, and Et_2O (20 mL) was added. The suspension was filtered, the filtrate was concentrated to ca. 1 mL, and *n*-pentane (30 mL) was added. The resulting suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give the salt **4k** as a pale yellow solid (109.0 mg, 0.368 mmol, 53%). The solvent from the mother liquors was removed, and the residue was vacuum-dried to afford the 3-benzazepine **6d** as a colorless liquid (73.0 mg, 0.281 mmol, 41%). **Characterization of 4k.** It was not possible to obtain a correct elemental analysis of **4k** due to its hygroscopic character. ^1H NMR (400.91 MHz): δ 1.31 (t, 3 H, *Me*CH_2, $^3J_{HH}$ = 6.8 Hz), 1.50 (s, 6 H, CMe_2), 2.72 (s, 2 H, CH_2Ar), 4.21 (q, 2 H, CH_2O, $^3J_{HH}$ = 6.8 Hz), 4.51 (br s, 2 H,

CH_2C=), 6.00 (t, 1 H, CH=C, $^4J_{HH}$ = 2.4 Hz), 7.08–7.10 (m, 1 H, H6), 7.37–7.39 (m, 2 H, H8 + H7 or H9), 7.44–7.64 (m, 1 H, H7 or H9), 9.62 (br s, 2 H, NH_2). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 14.2 (s, *Me*CH_2), 24.5 (s, C*Me*$_2$), 42.3 (s, *C*H_2C=), 43.2 (s, CH_2Ar), 58.2 (s, *C*Me_2), 60.4 (s, CH_2O), 120.6 (s, *C*H=C), 128.8 (s, CH, C8), 129.7 (s, CH, C6), 129.8 (s, CH, C7 or C9), 130.9 (s, CH, C7 or C9), 132.4 (s, C5a), 137.3 (s, C9a), 152.4 (s, CH=*C*), 165.3 (s, CO). **Characterization of 6d.** IR (cm^{-1}): ν(NH) 3402 w; ν(CO) 1712 vs. EI-HRMS: exact mass calcd for $C_{16}H_{21}NO_2$ 259.1572; found 259.1568; Δ = 0.0004. ^1H NMR (400.91 MHz): δ 1.12 (s, 6 H, CMe_2), 1.31 (t, 3 H, *Me*CH_2, $^3J_{HH}$ = 6.4 Hz), 2.62 (s, 2 H, CH_2Ar), 4.20 (q, 2 H, CH_2O, $^3J_{HH}$ = 6.8 Hz), 4.24 (d, 2 H, CH_2C=, $^4J_{HH}$ = 2.4 Hz), 5.90 (t, 1 H, CH=C, $^4J_{HH}$ = 2.4 Hz), 7.07 (dd, 1 H, H6, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.6 Hz), 7.25–7.32 (m, 2 H, H7 + H8), 7.35 (dd, 1 H, H9, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.6 Hz). The resonance corresponding to NH was not observed. $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 14.3 (s, *Me*CH_2), 27.3 (s, C*Me*$_2$), 44.8 (s, *C*H_2C=), 45.0 (s, CH_2Ar), 52.1 (s, *C*Me_2), 59.9 (s, CH_2O), 116.8 (s, *C*H=C), 127.1 (s, CH, C8), 127.9 (s, CH, C9), 129.2 (s, CH, C7), 129.4 (s, CH, C6), 136.9 (s, C5a), 139.3 (s, C9a), 166.2 (s, CO), 166.6 (s, CH=*C*).

Synthesis of 3,3-Dimethyl-4-methylen-6-methoxy-1,2,3,4-tetrahydroisoquinolinium bromide (7a). 1,1-Dimethylallene (76 μL, 0.766 mmol) was added to a suspension of palladacycle [$Pd_2\{\kappa^2(C,N)$-$C_6H_3CH_2NH_2$-2,OMe-5$\}_2(\mu$-Br$)_2$] (**1j**; 240 mg, 0.372 mmol) in dry CH_2Cl_2 (15 mL) under N_2 atmosphere, and the mixture was stirred for 12 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 mL, and Et_2O (20 mL) was added. The resulting suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give crude compound **7a** as a pale yellow solid. Yield: 152 mg, 0.634 mmol, 85%. An analytically pure sample of **7a** was obtained by recrystallization from CH_2Cl_2/Et_2O (108 mg, 0.451 mmol, recrystallization yield: 71%). Mp: 186 ºC. Λ_M (Ω^{-1} cm^2 mol^{-1}): 14 (4.9 x 10^{-4} M). Anal. Calcd for $C_{13}H_{18}BrNO$ (284.202): C, 54.94; H, 6.38; N, 4.93. Found: C, 54.39; H, 6.39; N, 4.89. IR (cm^{-1}): $\delta(NH_2)$ 1609 s, 1576 s. ^1H NMR (400.91 MHz): δ 1.75 (s, 6 H, CMe_2), 3.81 (s, 3 H, MeO), 4.39 (s, 2 H,

CH_2Ar), 5.37 (s, 1 H, CH_2=C), 5.77 (s, 1 H, CH_2=C), 6.88 (dd, 1 H, H7, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 2.4 Hz), 7.08–7.11 (m, 2 H, H5 + H8), 9.00 (br s, 2 H, NH_2). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 24.6 (s, CMe_2), 40.3 (s, CH_2Ar), 55.3 (s, MeO), 57.1 (s, *C*Me_2), 109.6 (s, CH, C5), 111.9 (s, *C*H_2=C), 115.6 (s, CH, C7), 118.5 (s, C8a), 127.8 (s, CH, C8), 131.5 (s, C4a), 142.2 (s, CH_2=*C*), 159.4 (s, C6). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **7a** in $CHCl_3$.

Single Crystal X-ray Structure Determinations. Relevant crystallographic data and details of the refinements for the structures of compounds **3a**, **3e**, **4a**, **4c**·CH_2Cl_2, **4h** and **7a** are given in Table 1 and 2 in the Supporting Information. *Data Collection*. Crystals suitable for X-ray diffraction were mounted in inert oil on a glass fiber and transferred to a Bruker SMART diffractometer. Data were recorded at 100(2) K, using graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å) and ω-scan mode. Multiscan absorption corrections were applied for complexes **3a**, **3e**, **4a**, **4h**, and **7a**. *Structure Solution and Refinements*. Crystal Structures were solved by the direct method and all non hydrogen atoms refined anisotropically on F^2 using the program SHELXL-97.[47] Hydrogen atoms were refined as follows: Compounds **3a** and **4c**·CH_2Cl_2: NH_2, free with SADI; methyl, rigid group; all others, riding. Compounds **3e**, **4a** and **4h**: NH_2, free; methyl, rigid group; all others, riding. Compound **7a**: NH_2, free with DFIX; methyl, rigid group; all others, riding. Special features: Compound **3a**: absolute structure (Flack) parameter[48] –0.013(5). Compound **4a**: the triflate anion is disordered over two positions with a ca. 85:15 occupancy distribution. Compound **7a**: Flack parameter 0.014(10).

Computational details. Density funtional calculations were carried out using the Gaussian 03 package.[49] The hybrid density functional BP86[50] was applied, employing SDD basis set[51] to describe the Cl and Pd atoms and 6-31G* for N, C and H.[52] After geometry optimizations, analytical frequency calculations were carried out to determine the nature of the stationary points found and confirm they were minima or transition states.

ASSOCIATED CONTENT

Supporting Information Available: Complete set of cartesian coordinates for all computed structures; energy profiles for the isomerizations of **Z** into **Y'** and *cis*-**2e** into *trans*-**2e**; details (including symmetry operators) of hydrogen bondings and CIF files for compounds **3a**, **3e**, **4a**, **4c**·CH_2Cl_2, **4h** and **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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