Five- and Seven-Membered Metallacycles in [C,N,N′] and [C,N] Cycloplatinated Compounds

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The reactions of *cis*-[Pt(4-$C_6H_4Me)_2(\mu$-$SEt_2)]_2$ with ligands ArCH=$NCH_2CH_2NMe_2$ (Ar = 4-ClC_6H_4 (**1a**); 2-BrC_6H_4 (**1b**); 2,6-$Cl_2C_6H_3$ (**1c**); C_6F_5 (**1d**)) and ArCH=NCH_2(4-ClC_6H_4) (Ar = 4-ClC_6H_4 (**1e**); 2-BrC_6H_4 (**1f**); 2,6-$Cl_2C_6H_3$ (**1g**); C_6F_5 (**1h**)) were studied. Several types of compounds were formed including (i) [N,N′] coordination compounds (**2a**, **2c**, **2d**), (ii) [C,N,N′] platinum(IV) (**3b**, **3c**), [C,N,N′] platinum(II) (**4a**), and [C,N] platinum(II) (**4e**) cyclometalated compounds with a five-membered metallacycle, and (iii) [C,N,N′] platinum(II) (**5c**) and [C,N] platinum(II) (**5f**, **5g**) cyclometalated compounds with a seven-membered metallacycle. The reactions of the obtained cyclometalated compounds with triphenylphosphine were studied, and the new compounds were fully characterized including structure determinations for **4a**, **5c**, **5g**, and the phosphine derivative **7 g′**. The ease of formation of seven-membered metallacycles is discussed on the basis of the structure of the ligand (terdentate versus bidentate) and the C−X bond to be activated.

Introduction

Palladium and platinum cyclometalated compounds with nitrogen donor ligands attract a great deal of interest due to their numerous applications in several fields, such as organic and organometallic synthesis, the design of new metallomesogens, and biologically active compounds.[1] An interesting feature of platinum derivatives is that, in addition to square-planar platinum(II) compounds, octahedral platinum(IV) complexes may also be obtained; this fact has stimulated the development of electron-rich platinum precursors such as $[Pt_2Me_4(SMe_2)_2]$,[2] which are able to produce either platinum(II) or platinum(IV) compounds.

Several diarylplatinum(II) compounds have also been tested as metalating agents and shown to produce different types of reactions. A process involving intramolecular C−H activation and loss of 1 equiv of the corresponding arene has been reported for adequate N-donor ligands when *cis*-$[PtPh_2(dmso)_2]$,[3] *cis*-$[PtPh_2(SMe_2)_2]$,[4,5] *cis*-$[Pt(3,5\text{-}R_2C_6H_3)_2(dmso)_2]$ (R = Me, CF_3),[6] or *trans*-$[Pt(2,4,6\text{-}Me_3C_6H_2)_2(dmso)_2]$[7] is used. On the other hand, reactions involving intramolecular C−Br activation and elimination of 4,4′-bitolyl have been reported as a convenient method for the synthesis of [N,C,N] cyclometalated platinum(II) compounds[8] when substrate *cis*-[Pt(4-$C_6H_4Me)_2(\mu$-$SEt_2)]_2$ was used. Finally, processes leading to elimination of 1 equiv of benzene along with formal insertion of one phenyl ligand in the metallacycle have been reported upon reaction of *cis*-$[PtPh_2(SMe_2)_2]$ with N-donor ligands for which C−Br or C−Cl bond activation is possible.[4] The latter process leads to formation of seven-membered metallacycles (see method **a** in Scheme 1), and it is interesting to point out that this type of metallacycle has also been obtained in a process using *cis*-$[PtCl_2(dmso)_2]$ as metalating agent and involving intermolecular

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(1) (a) Ryabov, A. D. *Synthesis* **1985**, 233. (b) Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917. (c) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527. (d) Omae, I. *Coord. Chem. Rev.* **2004**, *248*, 995. (e) Espinet, P.; Esteruelas, M. A.; Oro, L. A.; Serrano, J. L.; Sola, E. *Coord. Chem. Rev.* **1992**, *117*, 215. (f) Navarro-Ranninger, C.; López-Solera, I.; Pérez, J. M.; Masaguer, J. R.; Alonso, C. *Appl. Organomet. Chem.* **1993**, *7*, 57. (g) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.

(2) (a) Anderson, C. M.; Crespo, M.; Jennings, M. C.; Lough, A. J.; Ferguson, G.; Puddephatt, R. J. *Organometallics* **1991**, *10*, 2672. (b) Crespo, M.; Martinez, M.; Sales, J.; Solans, X.; Font-Bardia, M. *Organometallics* **1992**, *11*, 1288. (c) Crespo, M.; Martinez, M.; Sales, J. *Organometallics* **1993**, *12*, 4297. (d) Crespo, M.; Solans, X.; Font-Bardia, M. *Organometallics* **1995**, *14*, 355. (e) Baar, C. R.; Jenkins, H. A.; Vittal, J. J.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 2805. (f) Baar, C. R.; Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 32.

(3) (a) Minghetti, G.; Stoccoro, S.; Cinellu, M. A.; Soro, B.; Zucca, A. *Organometallics* **2003**, *22*, 4770. (b) Zucca, A.; Doppiu, A.; Cinellu, M. A.; Stoccoro, S.; Minghetti, G.; Manassero, M. *Organometallics* **2002**, *21*, 783.

(4) (a) Crespo, M.; Font-Bardia, M.; Solans, X. *Organometallics* **2004**, *23*, 1708. (b) Font-Bardia, M.; Gallego, C.; Martinez, M.; Solans, X. *Organometallics* **2002**, *21*, 3305. (c) Gallego, C.; Martinez, M.; Safont, V. S. *Organometallics* **2007**, *26*, 527.

(5) Crespo, M.; Font-Bardia, M.; Solans, X. *J. Organomet. Chem.* **2006**, *691*, 1897.

(6) Yagyu, T.; Ohashi, J.; Maeda, M. *Organometallics* **2007**, *26*, 2383.

(7) Sarkar, B.; Schurr, T.; Hartenbach, I.; Schleid, T.; Fiedler, J.; Kaim, W. *J. Organomet. Chem.* **2008**, *693*, 1703.

(8) (a) Rodríguez, G.; Albrecht, M.; Schoenmaker, J.; Ford, A.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2002**, *124*, 5127. (b) Albrecht, M.; Rodríguez, G.; Schoenmaker, J.; van Koten, G. *Org. Lett.* **2000**, *2*, 3461. (c) Canty, A. J.; Patel, J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2000**, *599*, 195. (d) Slagt, M. Q.; Gebbink, R. J. M. K.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Dalton Trans.* **2002**, 2591.

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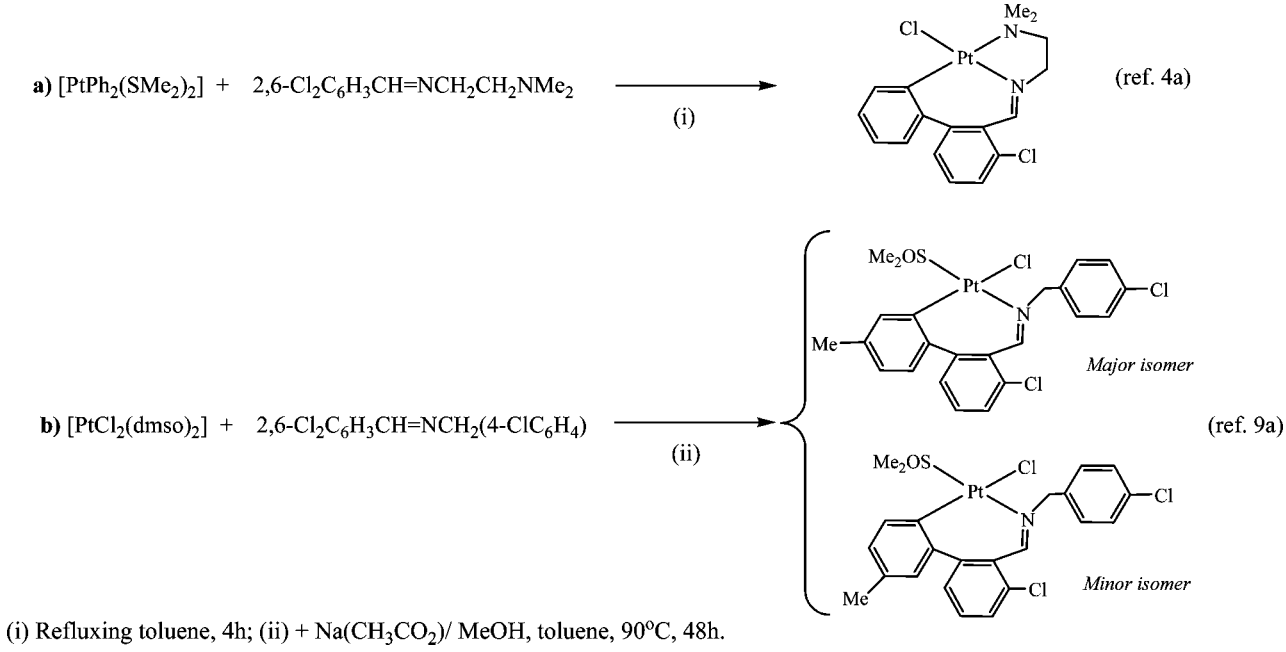
Scheme 1



(i) Refluxing toluene, 4h; (ii) + $Na(CH_3CO_2)$/ MeOH, toluene, 90°C, 48h.

activation of toluene used as a solvent,[9] as shown in method **b** in Scheme 1. These reactions involve formation of a C−C bond leading to a biaryl linkage, which is an important process in organic synthesis.[10]

In order to gain insight into the different processes that might take place when diarylplatinum compounds are used as metalating substrates, the study of the reactions of *cis*-[Pt(4-$C_6H_4Me)_2(\mu$-$SEt_2)]_2$ with imines of general formulas ArCH=$NCH_2CH_2NMe_2$ and ArCH=$NCH_2(4$-$ClC_6H_4)$ in which the aryl group Ar may contain either Br, Cl, H, or F in the *ortho* positions was envisaged. The aim of this work is to evaluate how both the nature of the *ortho* C−X bonds and the different structure of the ligands, containing either two or one nitrogen atoms, influence the obtained results. Dinuclear compound *cis*-$[Pt(4$-$C_6H_4Me)_2(\mu$-$SEt_2)]_2$, previously used as metalating agent as stated above,[8] was selected for this study since the presence of an electron-donor methyl substituent in the aryl ring facilitates the activation of the *ortho* C−X bonds[6] as well as the spectral characterization of the products by means of NOE interactions in which the methyl is involved. In addition, a comparison with the compounds arising from intermolecular activation of toluene[9] could be drawn, thus allowing for a better understanding of these processes.

Results and Discussion

Reactions with Ligands ArCH=$NCH_2CH_2NMe_2$ (Ar = 4-ClC_6H_4 (1a); 2-BrC_6H_4 (1b); 2,6-$Cl_2C_6H_3$ (1c); C_6F_5 (1d)). The reactions of *cis*-$[Pt(4$-$C_6H_4Me)_2(\mu$-$SEt_2)]_2$ with ligands **1a**, **1c**, or **1d** in toluene at room temperature produced compounds $[Pt(4$-$C_6H_4Me)_2(Me_2NCH_2CH_2NCHAr)]$ (**2a**, **2c**, **2d**) containing a bidentate [N,N′] ligand as yellow solids (see Scheme 2). $^1H-^1H$ NOESY experiments indicated an *E* conformation across the C=N bond since a cross-peak signal between the imine and the methylene protons was observed. *E* to *Z* isomerization in solution was followed by ^1H NMR spectroscopy at room temperature for compounds **2a** and **2c**, as shown in Scheme 3. For **2a**, after 96 h, the ratio of the isomers was *E*:*Z* = 1:1.9. For **2c**, the process was more complex since, in addition to *E*−*Z* isomerization, cyclometalated platinum(IV) compound $[PtCl(4$-$MeC_6H_4)_2\{2$-$ClC_6H_3CHNCH_2CH_2NMe_2\}]$ (**3c**) arising from intramolecular C−Cl oxidative addition and containing a terdentate [C,N,N′] ligand was formed. In this case, after 24 h, the ^1H NMR spectrum indicated disappearance of the *E* isomer and the presence of both the *Z* isomer and compound **3c** as the main product. After 120 h, conversion to compound **3c** was complete.

The reaction of *cis*-$[Pt(4$-$C_6H_4Me)_2(\mu$-$SEt_2)]_2$ with ligand **1b** in toluene at room temperature produced compound $[PtBr(4$-$MeC_6H_4)_2\{C_6H_4CHNCH_2CH_2NMe_2\}]$ (**3b**) as a white solid, in an analogous process to that described for **3c**, which involves coordination of the ligand, followed by intramolecular oxidative addition of a C−Br bond. In this case, the corresponding coordination compound could not be isolated, or even detected in solution, and this fact is consistent with the higher reactivity of a C−Br versus C−Cl or C−H bond.[4a,11]

In an attempt to obtain cyclometalated platinum(II) compounds, coordination precursors **2a** and **2c** were treated in toluene under reflux for 6 h to produce, respectively, compounds $[Pt(4$-$MeC_6H_4)\{4$-$ClC_6H_3CHNCH_2CH_2NMe_2\}]$ (**4a**) and $[PtCl\{(MeC_6H_3)(ClC_6H_3CHNCH_2CH_2NMe_2\}]$ (**5c**). The proposed structures, shown in Scheme 2, contain a terdentate [C,N,N′] ligand. The former arises from intramolecular C−H bond activation and elimination of a toluene molecule to yield a five-membered metallacycle, while the latter is formed in a more complex process involving formation of a C−C bond between two aryl rings and formation of a seven-membered platinacycle.[4]

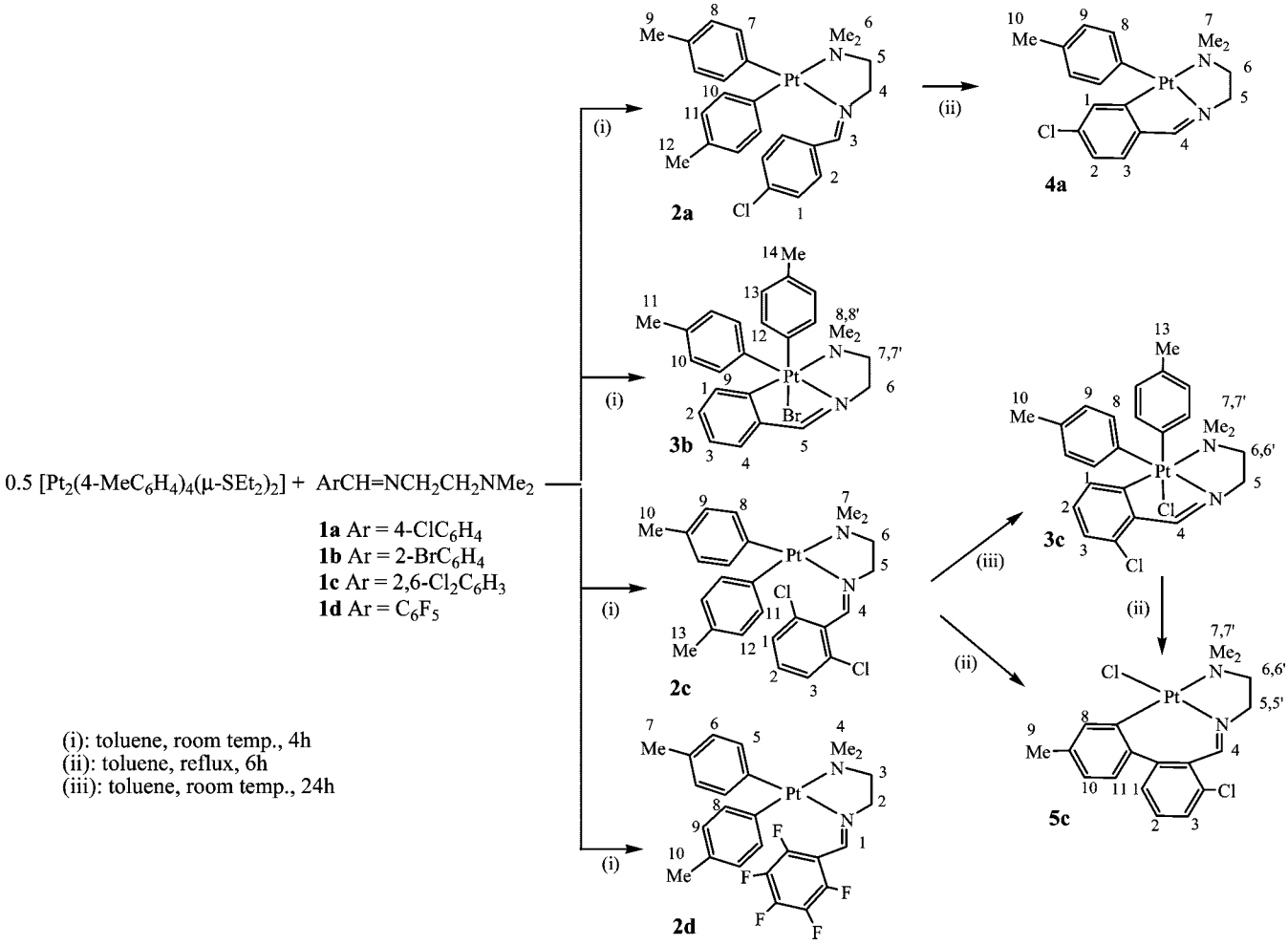
Under analogous conditions, no reaction was observed for ligand $C_6F_5CH=NCH_2CH_2NMe_2$ (**1d**), which can be related to the combined effects of the inertness of the C−F bond and the

(9) (a) Capapé, A.; Crespo, M.; Granell, J.; Vizcarro, A.; Zafrilla, J.; Font-Bardía, M.; Solans, X. *Chem. Commun.* **2006**, 4128. (b) Capapé, A.; Crespo, M.; Granell, J.; Font-Bardía, M.; Solans, X. *Dalton Trans.* **2007**, 2030.

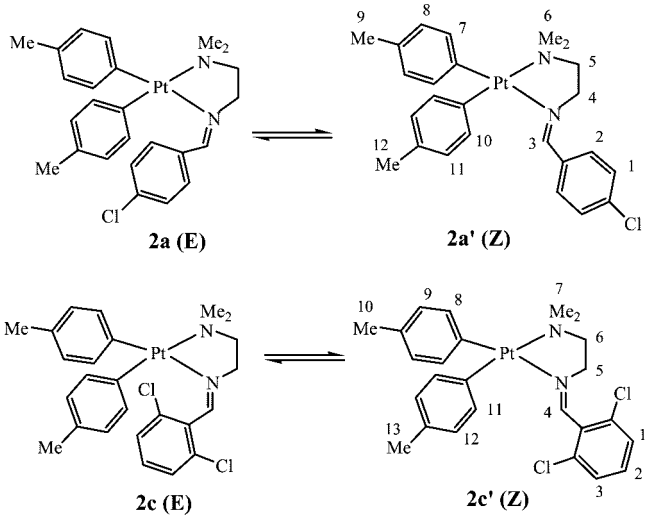
(10) (a) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442. (b) Bedford, R. B. *Chem. Commun.* **2003**, 1787. (c) Bedford, R. B.; Cazin, C. S. J.; Holder, D. *Coord. Chem. Rev.* **2004**, *248*, 2283. (d) Godula, K.; Sames, D. *Science* **2006**, *312*, 67.

(11) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

Scheme 2



Scheme 3



unfavorable steric effects of the tolyl groups. Although the C−F bond has been activated upon reaction of analogous ligands with platinum substrate $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$,[12] no reaction has been observed when *cis*-$[PtPh_2(SMe_2)_2]$ was used.[4a]

In order to prove whether the formation of platinum(IV) compounds is involved in the mechanism of formation of seven-membered metallacycles such as compound **5c**, the behavior of compound $[PtCl(4\text{-}MeC_6H_4)_2\{2\text{-}ClC_6H_3CHNCH_2CH_2NMe_2\}]$ (**3c**) in refluxing toluene was also studied. It was confirmed that compound **5c** can be obtained from compound **3c**, although along with some decomposition leading to metallic platinum and lower yields than for the direct synthesis from **2c**. Under the same reaction conditions, compound **3b** reacted very slowly, and concomitant decomposition processes prevented isolation of the corresponding seven-membered derivative.

The new compounds were characterized by elemental analyses, ESI mass spectra, and NMR spectroscopy, and compounds **4a** and **5c** were also characterized crystallographically. In most cases, $\{^1H-^1H\}$ COSY and NOESY NMR spectra were taken and allowed for a full assignment of the ^1H NMR signals.

For compounds **2**, the J(H−Pt) value for the imine is higher for the *E* (ca. 40−50 Hz) than for the Z (ca. 26 Hz) isomers, in agreement with the *trans* arrangement for the former.[5,13] The *ortho* hydrogen atoms in the tolyl ligands are also coupled to platinum, and the J(H−Pt) values are smaller for the group *trans* to the imine, in agreement with the higher *trans* influence of imine versus amine.

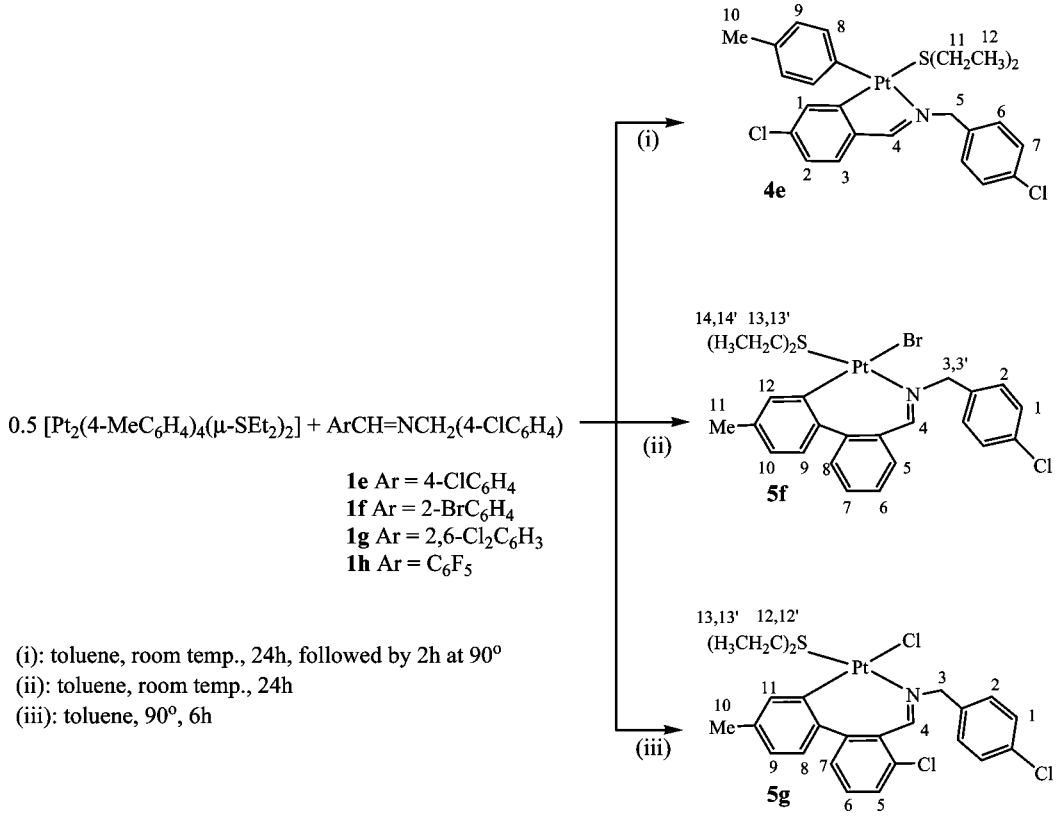
For octahedral platinum(IV) compounds **3**, distinct features are observed. As expected, the J(H−Pt) values observed for the imine and the tolyl *ortho* hydrogen atoms decrease when compared to related platinum(II) compounds.[14] As a result of

(12) (a) Anderson, C. M.; Crespo, M.; Ferguson, G.; Lough, A. J.; Puddephatt, R. J. *Organometallics* **1992**, *11*, 1177. (b) López, O.; Crespo, M.; Font-Bardia, M.; Solans, X. *Organometallics* **1997**, *16*, 1233.

(13) Crespo, M.; Font-Bardia, M.; Granell, J.; Martinez, M.; Solans, X. *Dalton Trans.* **2003**, 3763.

(14) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548.

Scheme 4



the lack of symmetry plane, the methyl and methylene groups of the coordinated ligand are nonequivalent. Resonances of the tolyl ligands were assigned on the basis of the 2D-NOESY experiment carried out for **3b**, in which the *ortho* hydrogen atoms of the equatorial tolyl display cross-peaks with both methyl groups of the dimethylamino moiety, while the axial tolyl with only one of them.

For platinum(II) derivatives **4a** and **5c**, both the imine and the aromatic hydrogen adjacent to the metalation site are coupled to platinum. The remarkably different J(H−Pt) values for the imine are consistent with the presence of a tolyl (**4a**, J(H−Pt) = 56.0 Hz) or a chloro (**5c**, J(H−Pt) = 147.7 Hz) ligand in a *trans* position. For **5c**, as reported for related compounds with a seven-membered metallacycle,[4] the methyl and methylene groups of the coordinated ligand are nonequivalent. The {^{1}H−^{13}C}-heterocorrelation spectra of **4a** and **5c** show respectively five and six cross-peaks in the aromatic region, which is consistent with the proposed structures. For both **2a** and **4a**, the position of the ^{195}Pt resonance within the range expected for a [C, C, N, N] set of ligands[15] confirms the proposed structures.

Reactions with Ligands ArCH=NCH$_2$(4-ClC$_6$H$_4$) (Ar = 4-ClC$_6$H$_4$ (1e); 2-BrC$_6$H$_4$ (1f); 2,6-Cl$_2$C$_6$H$_3$ (1g); C$_6$F$_5$ (1h)). In order to complete the present study, the reactions of *cis*-[Pt(4-C$_6$H$_4$Me)$_2$(μ-SEt$_2$)]$_2$ with ligands **1e**, **1f**, **1g**, and **1h** containing only one nitrogen were also studied (see Scheme 4). Previous work using *N*-benzylidenbenzylamines with other metalating agents such as [Pt$_2$Me$_4$(SMe$_2$)$_2$] indicate that, although coordination of the ligand is postulated as a previous step to the intramolecular C−X bond activation, the corresponding coordination compounds are not usually isolated.[2b,c,16]

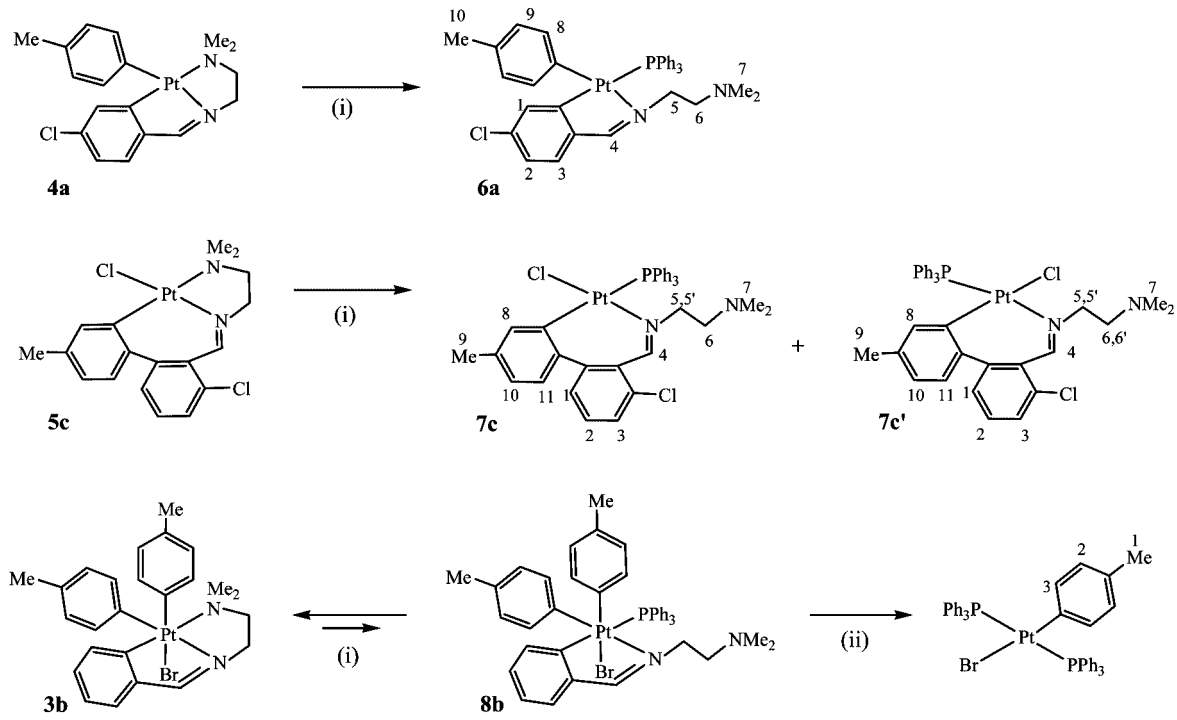
Initially, the reactions were carried out in toluene at room temperature for 24 h. Under these conditions, imine **1f** gave compound **5f**, which contains a seven-membered metallacycle, while imines **1e** and **1g** gave mixtures of compounds, which when submitted to more drastic conditions, evolved to compounds **4e** and **5g**, respectively. Compound **5g** was best obtained when the platinum substrate and imine **1g** were treated in toluene at 90 °C for 6 h. Compounds **4e**, **5f**, and **5g** contain a bidentate [C,N] ligand. Compound [Pt(4-MeC$_6$H$_4$){4-ClC$_6$H$_3$CHNCH$_2$(4-ClC$_6$H$_4$)}SEt$_2$] (**4e**), which contains a five-membered metallacycle, arises from intramolecular C−H bond activation with elimination of a molecule of toluene. Compounds [PtBr{(MeC$_6$H$_3$)C$_6$H$_4$CHNCH$_2$(4-ClC$_6$H$_4$)}SEt$_2$] (**5f**) and [PtCl{(MeC$_6$H$_3$)(ClC$_6$H$_3$)CHNCH$_2$(4-ClC$_6$H$_4$)}SEt$_2$] (**5g**) are formed in processes involving C−X (X = Br or Cl) oxidative addition, formation of a C−C bond between the metalated phenyl and a tolyl ligand, and elimination of one molecule of toluene. No reaction, other than decomposition and imine hydrolyses when more drastic conditions were used, was observed for ligand **1h**. As previously indicated for ligand **1d**, the lack of reactivity can be related to the low reactivity of the C−F bond;[17] in addition, the presence of only one nitrogen and the electron-withdrawing effect of the pentafluoro group prevent the formation of a coordination compound.

The new compounds were characterized by elemental analyses, ESI mass spectra, and NMR spectroscopy, and compounds **5g** was also characterized crystallographically.

In spite of the presence of a bidentate [C,N] ligand and a diethylsulfide in the coordination sphere of the compounds described in this section versus a tridentate [C,N,N′] in those

(15) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247.
(16) Crespo, M.; Solans, X.; Font-Bardia, M. *J. Organomet. Chem.* **1996**, *518*, 105.
(17) (a) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber. Recl.* **1997**, *130*, 145. (b) Bosque, R.; Clot, E.; Fantacci, S.; Maseras, F.; Eisenstein, O.; Perutz, R. N.; Renkema, K. B.; Caulton, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 12634.

Scheme 5



(i): + PPh_3 (1:1), acetone, room temp., 2h; (ii): + PPh_3 (2:1), acetone, room temp., 2h

described above, common features are observed for five-membered metallacycles (**4a** and **4e**) on one side and seven-membered metallacycles (**5c**, **5f**, and **5g**) on the other. As for **4a** and **5c**, both the imine and the aromatic hydrogen adjacent to the metalation site are coupled to platinum in compounds **4e**, **5f**, and **5g**. For **5f** and **5g**, the J(H−Pt) values for the imine are lower (ca. 120 Hz) than that observed for **5c** (J(H−Pt) = 147.7 Hz), in agreement with the presence of a diethylsulfide ligand in a *trans* position. For **5f** and **5g**, the methylene groups of the coordinated ligand are nonequivalent. The {^{1}H−^{13}C}-heterocorrelation spectra of **4j**, **5f**, and **5g** show respectively seven, nine, and eight cross-peaks in the aromatic region, which is consistent with the proposed structures.

Reactions with Triphenylphosphine. The reactions of compounds **3b**, **4a**, **4e**, **5c**, **5f**, and **5g** with triphenylphosphine were carried out in acetone at room temperature (see Schemes 5 and 6).

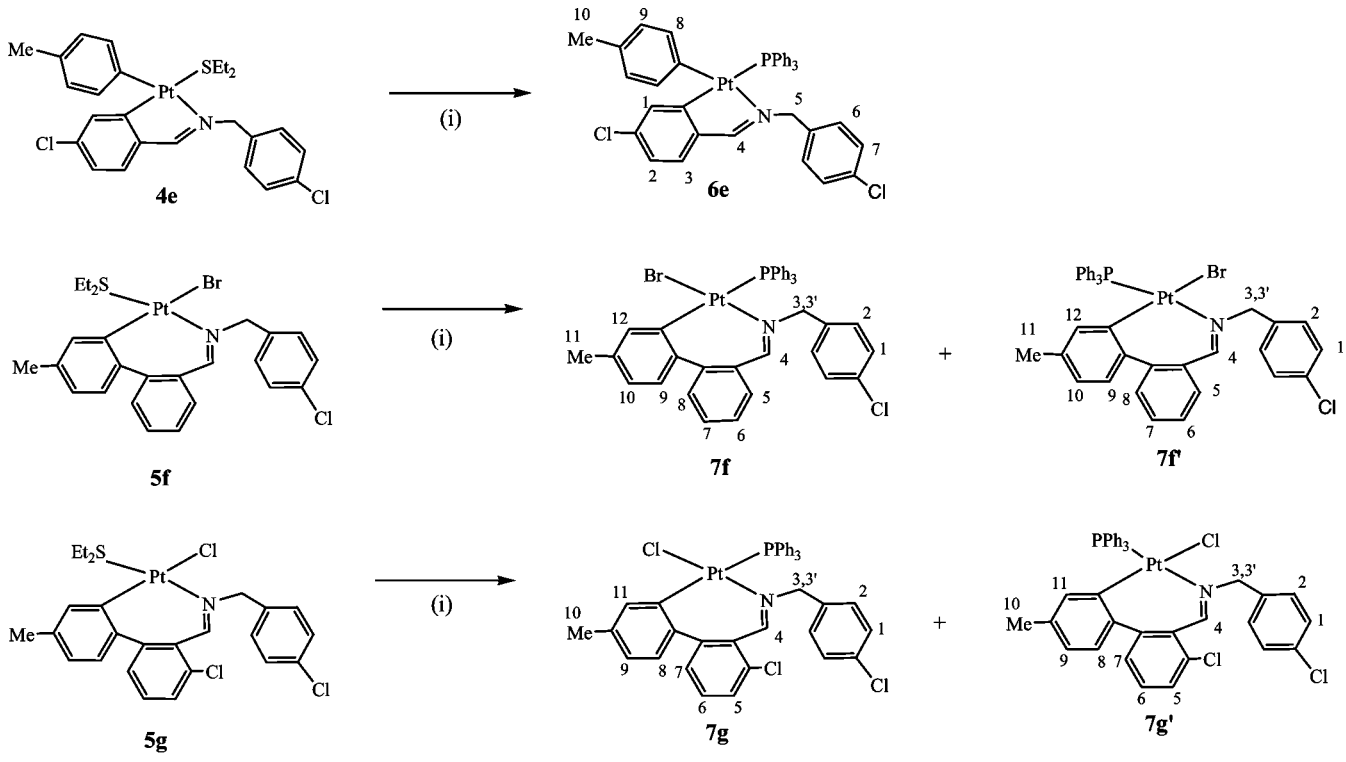
For compounds **4a** and **4e**, the PPh_3 replaces either the dimethylamino moiety or the diethylsulfide ligand in the coordination sphere of platinum to yield, respectively, compounds **6a** and **6e**. An analogous process was observed for compound **5c**; however, in this case, two isomers in a 1:1 ratio were formed as reaction products. This result arises from the fact that replacement of NMe_2 for PPh_3 yields compound **7c** with the PPh_3 *trans* to a tolyl group, and this compound isomerizes to **7c′**, in which the PPh_3 is *trans* to the imine, a more stable situation according to the *transphobia*[18] and the *trans-choice*[19] models. In agreement with the higher stability of isomer **7c′**, after 18 h in solution the ratio **7c′**:**7c** is 3:1. As for **5f** and **5g**, the SEt_2 ligand is *trans* to the N atom, in agreement with the *transphobia* and the *trans-choice* models, and the reactions with triphenylphosphine indicate that the entering ligand is initially placed *trans* to the metalated carbon to yield **7f** and **7g**, respectively, which later isomerize to the more stable **7f′** and **7g′**, in which the phosphine is *trans* to the N atom. For **5f**, the reaction produced initially isomer **7f** only, which later isomerizes in solution to **7f′**. The reaction of **5g** with triphenylphosphine was monitored by NMR spectroscopy, and it was observed that before the replacement of the SEt_2 ligand was complete, both isomers **7g** and **7g′** were formed. Within 4 h, the substitution process was complete and the ratio of isomers **7g**:**7g′** was 2.3:1.0; after 140 h in solution, the ratio was 0.7:1.0. Isomer **7g′** crystallized in dichloromethane−methanol. The obtained results suggest that although steric effects of the bulky triphenylphosphine might be responsible for the initial formation of compounds **7f** and **7g**, these isomerize to the more stable species according to the *transphobia* model.

Under the same conditions, compound **3b** led to nearly quantitative recovery of the initial compound. A new signal observed in the ^{1}H NMR spectra of the crude product is consistent with formation of compound **8b**, which was formed in a very small extension, indicating a high stability of the terdentate [C,N,N′] platinum(IV) compound. In an attempt to displace the reaction, a PPh_3:**3b** = 2:1 ratio was used; however under these conditions compound *trans*-[PtBr(4-$CH_3C_6H_4$)-(PPh_3)$_2$] was formed.

Phosphine derivatives were characterized by ^{1}H and ^{31}P NMR spectra; in order to achieve a full assignment {^{1}H−^{1}H} COSY and NOESY experiments were also carried out for **7c** and **7c′**. For compounds **6**, the imine proton is a singlet coupled to platinum and the J(H−Pt) values are very similar to those observed for the parent compounds **4**. The J(P−Pt) values (ca. 2200 Hz) indicate that the PPh_3 is *trans* to the aryl group rather

(18) Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, *21*, 4454.
(19) Cuevas, J. V.; García-Herbosa, G.; Miguel, D.; Muñoz, A. *Inorg. Chem. Commun.* **2002**, *5*, 340.

Scheme 6



than to the nitrogen atom.[20] Isomers **7** and **7′** show distinct features in both the ^{1}H and ^{31}P NMR spectra. The imine appears as a singlet with a coupling to platinum of ca. 140 Hz for compounds **7** and as a doublet—due to coupling with the phosphorus atom—with a reduced J(H−Pt) value (ca. 88 Hz) for compounds **7′**. These data as well as the different J(P−Pt) values observed in the ^{31}P NMR spectra (ca. 1860 Hz for compounds **7** and ca. 4300 Hz for compounds **7′**) are consistent with the position of the phosphine *trans* either to the metalated carbon or to the nitrogen atoms.[20]

For compounds **6** and **7**, the NMR spectra did not show the presence of compounds with two coordinated phosphine ligands, even when an excess of the phosphine was present. This fact suggests that both the five-membered and the seven-membered metallacycles are stable and not easily cleaved upon reaction with phosphines.

Crystal Structures. Suitable crystals of compounds **4a**, **5c**, **5g**, and **7g′** were grown from dichloromethane−methanol at room temperature.

The crystal structures are composed of discrete molecules separated by van der Waals distances. Compound **5c** crystallizes with one molecule of CH_2Cl_2. The structures are shown in Figures 1, 2, 3, and 4, and selected molecular dimensions are listed in Table 1. Compound **4a** displays disorder in the positions of atoms C(16) and C(17).

The molecular structures confirm the geometries predicted from spectroscopic data. Square-planar coordination of the platinum(II) is achieved with a terdentate [C,N,N′] and a tolyl (**4a**) or a chloro (**5c**) ligand, or with a bidentate [C,N], a chloro, and a diethylsulfide (**5g**) or a triphenylphosphine (**7g′**) ligand.

For **5c**, **5g**, and **7g′** the metallacycle consists of a nonplanar seven-membered system in which the imine functionality and

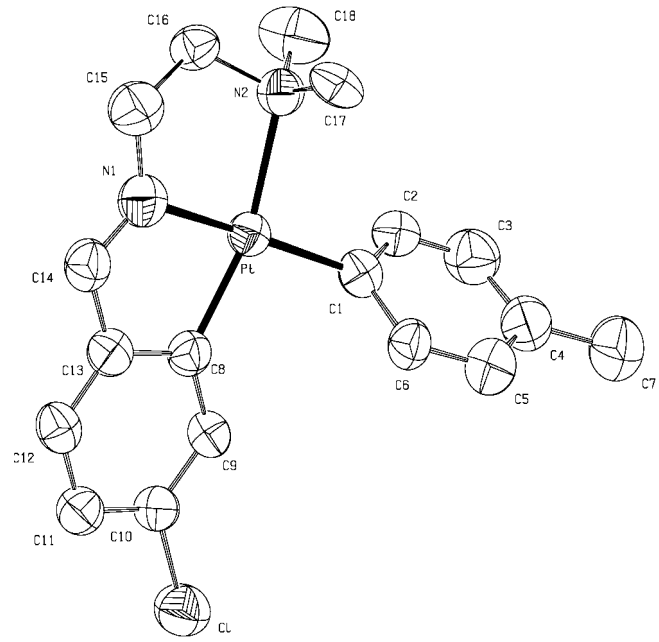


Figure 1. Molecular structure of compound **4a**.

two aryl rings tilted 50.6(2)° (**5c**), 55.2(2)° (**5g**), or 51.9(2)° (**7g′**) from each other are included. For **4a**, the five-membered metallacycle contains the imine functionality and the sum of internal angles is 540.0°, which suggest a planar arrangement for the *endo*-metallacycle.[21] The dihedral angle between the mean planes of the metallacycle and the coordination plane is 3.9(2)°, and the tolyl ligand is tilted from the coordination plane by 59.8(3)°.

(20) Pregosin, P. S.; Kunz, R. W. *In ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes;* Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1979.

(21) Klein, H. F.; Camadanli, S.; Beck, R.; Leukel, D.; Flörke, U. *Angew. Chem., Int. Ed.* **2005**, *44*, 975.

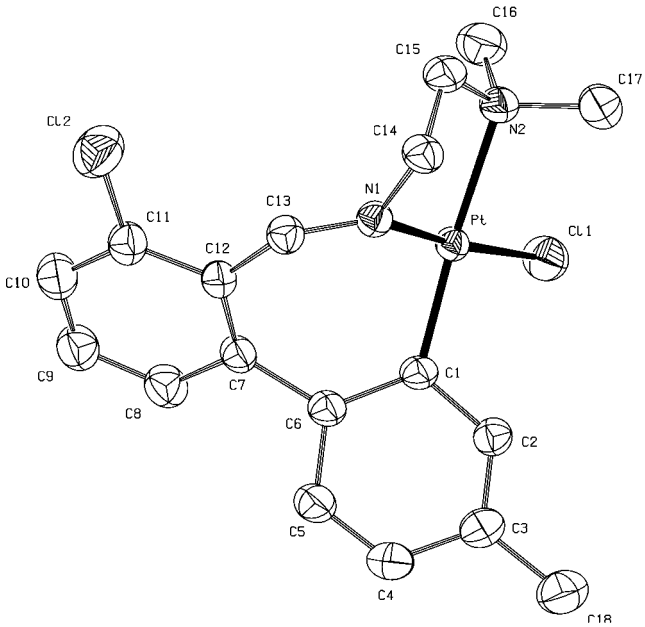


Figure 2. Molecular structure of compound **5c**.

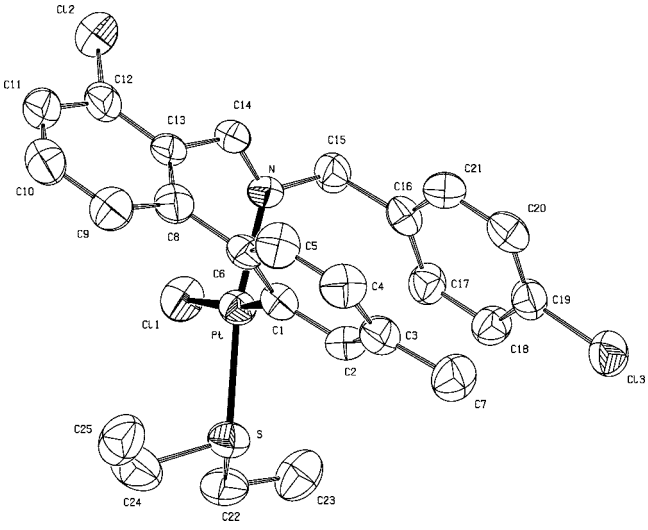


Figure 3. Molecular structure of compound **5g**.

Bond lengths and angles are well within the range of values obtained for analogous compounds. In particular, the Pt−C bonds are in the range of values found for other aryl complexes of platinum(II)[4,9] and the Pt−amine distances are larger (2.177 and 2.204 Å) than platinum−imine distances (1.959−2.082 Å), consistent with the weaker ligating ability of amines for platinum.[22] The Pt−Cl bond in **5c** (2.315 Å) is shorter than in **5g** (2.414 Å) and **7g′** (2.399 Å), in agreement with the presence of either a nitrogen or a carbon atom in a *trans* position. Most bond angles at platinum are close to the ideal value of 90°, and the smallest angles correspond to N(2)−Pt−N(1) (82.31(14)° for **5c** and 81.4(2)° for **4a**) and to the metallacycle (C(8)−Pt−N(1) = 81.3(2)° for **4a**, C(1)−Pt−N = 85.40(16)° for **5g**, and C(1)−Pt−N = 86.53(15) for **7g′**). For [C,N,N′] compounds, the metallacycle angle is larger for seven- than for five-membered metallacycles (92.90(15)° for **5c** versus 81.3(2)° for **4a**).

(22) Capapé, A.; Crespo, M.; Granell, J.; Font-Bardia, M.; Solans, X. *J. Organomet. Chem.* **2005**, *690*, 4309.

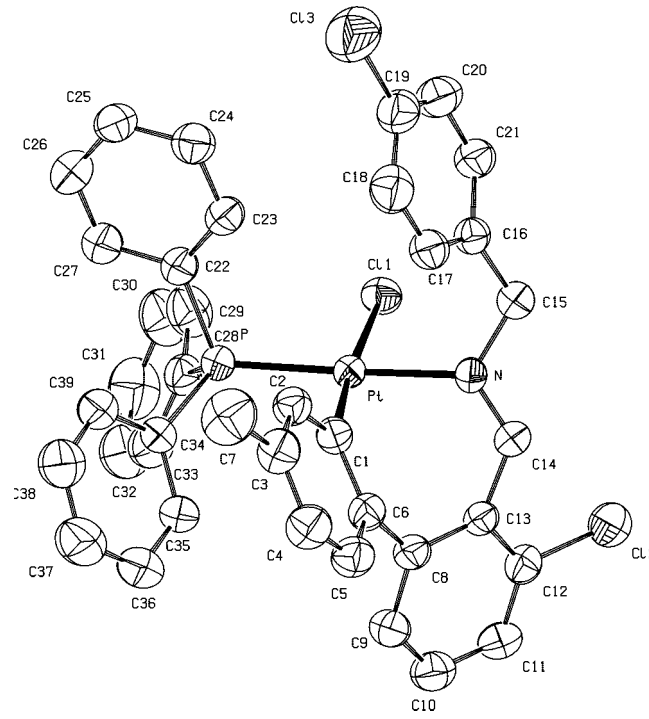


Figure 4. Molecular structure of compound **7g′**.

Conclusions

Previous work using *cis*-[Pt(4-$C_6H_4Me)_2(\mu$-$SEt_2)]_2$ as metalating agent involved oxidative addition to give a platinum(IV) compound, followed by reductive elimination of 4,4′-bitolyl, consistent with the expected instability of triarylplatinum(IV) systems.[8] However, this process or the also plausible aryl-halogen elimination[23] was not observed in the present study. In addition to [N,N′] coordination compounds (**2a**, **2c**, **2d**), cyclometalated compounds with a five-membered metallacycle (such as [C,N,N′] platinum(IV) (**3b**, **3c**) and platinum(II) (**4a**) as well as [C,N] platinum(II) (**4e**) complexes) or with a seven-membered metallacycle (such as [C,N,N′] platinum(II) (**5c**) and [C,N] platinum(II) (**5f**, **5g**) complexes) were obtained.[24] A general scheme showing the processes leading to such compounds is presented (Scheme 7) for potentially tridentate ligands. Analogous processes in which the diamine moiety is replaced by a SEt_2 ligand should take place for the bidentate ligand.

Five-membered rings are the most commonly formed in cyclometalation reactions due to their high stability. The seven-membered rings are novel examples of a recently reported process[4] involving formal aryl insertion into the metallacycle with reductive elimination of an arene molecule in a process in which a C−C bond is formed. The results here reported support that formation of seven-membered metallacycles may arise from both C−Br and C−Cl intramolecular activation in both potentially terdentate or bidentate ligands. For ligand **1c**, the corresponding platinum(IV) compound **3c** was shown to be an intermediate in the formation of compound **5c**. On the basis of the observation that **5f** and **5g** were easily formed, we may conclude that the process is more facile for bidentate than for tridentate ligands. Assuming that a vacant site in the coordination

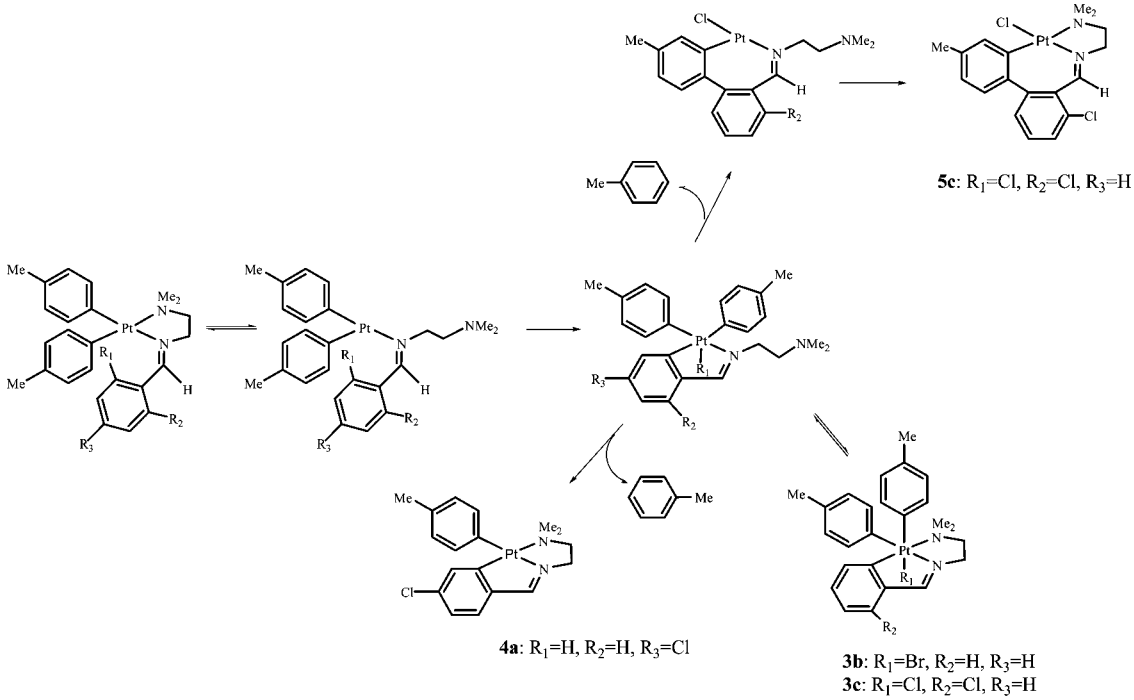
(23) (a) Vigalok, A. *Chem.−Eur. J.* **2008**, *14*, 5102. (b) Yahav-Levi, A.; Goldberg, I.; Vigalok, A.; Vedernikov, A. N. *J. Am. Chem. Soc.* **2008**, *130*, 724.

(24) In order to rule out the possibility that the tolyl groups in the products could arise from the toluene used as a solvent, the syntheses of **4a** and **5f** were also carried out successfully in benzene.

Table 1. Selected Bond Lengths (Å) and Angles (deg.) for Compounds 4a, 5c, 5g, and 7g′ with Estimated Standard Deviations

compound **4a**		compound **5c**		compound **5g**		compound **7g′**	
Pt−C(8)	1.976(5)	Pt−C(1)	1.978(4)	Pt−C(1)	2.004(4)	Pt−C(1)	2.017(4)
Pt−C(1)	2.026(6)	Pt−Cl(1)	2.315(3)	Pt−Cl(1)	2.4144(14)	Pt−Cl(1)	2.3993(12)
Pt−N(2)	2.177(5)	Pt−N(2)	2.204(3)	Pt−N	2.031(3)	Pt−N	2.082(3)
Pt−N(1)	2.014(5)	Pt−N(1)	1.959(4)	Pt−S	2.2719(14)	Pt−P	2.2417(11)
C(8)−Pt−C(1)	97.6(2)	C(1)−Pt−Cl(1)	92.46(12)	C(1)−Pt−N	85.40(16)	C(1)−Pt−N	86.53(15)
C(8)−Pt−N(1)	81.3(2)	Cl(1)−Pt−N(2)	92.55(11)	C(1)−Pt−S	88.33(13)	C(1)−Pt−P	92.69(12)
C(1)−Pt−N(2)	99.7(2)	C(1)−Pt−N(1)	92.90(15)	N−Pt−Cl(1)	88.95(11)	N−Pt−Cl(1)	87.71(9)
N(2)−Pt−N(1)	81.4(2)	N(2)−Pt−N(1)	82.31(14)	S−Pt−Cl(1)	97.77(5)	P−Pt−Cl(1)	93.07(4)

Scheme 7



sphere of platinum is required for the process leading to compounds **5**, the higher lability of the SEt_2 should favor the process. Conversely, the failure to transform easily **3b** into a seven-membered metallacycle can be related to the low tendency of the chelate dinitrogen ligand to dissociate. This is also evidenced from the fact that compound **3b** is reluctant to react with PPh_3. When an excess of phosphine was used, the reaction yielded compound *trans*-[$PtBr(4\text{-}CH_3C_6H_4)(PPh_3)_2$], which is analogous to that reported for a reductive elimination process taking place from octahedral platinum(IV) compound [$PtPh_2Br(C_6H_4CH{=}NCH_2Ph)SMe_2$].[4b]

For both potentially tridentate or bidentate ligands, seven-membered metallacycles were not formed from intramolecular C−H or C−F bond activation. The former gave five-membered metallacycles with loss of 1 equiv of toluene, while the stronger C−F bond could not be activated.

The methyl substituent in the tolyl group remains *para* to the platinum in coordination compounds **2** or in cyclometalated platinum(IV) or platinum(II) compounds (**3** and **4**, respectively). However, for compounds **5** the methyl group is now *para* to the formed C−C bond and *meta* to the platinum center. This is evidenced from the ^{1}H NMR spectra of compound **5**, in which a singlet coupled to platinum (J(H−Pt) ca. 53 Hz) was observed and further confirmed in the molecular structures of compounds **5c**, **5g**, and **7g′**. It is interesting to point out that the same position of the methyl substituent has been observed in the major isomer formed in the process described in Scheme 1b for intermolecular toluene activation. The position of the methyl group is consistent with a process involving C−C coupling between the carbon atoms bound to platinum of the metalated aryl ring and the *para*-tolyl ligand, as expected for a biaryl reductive elimination from a platinum(IV) compound.

Experimental Section

General Procedures. Microanalyses were performed by the Servei de Recursos Científics i Tècnics de la Universitat Rovira i Virgili (Tarragona). Mass spectra were performed at the Servei d'Espectrometria de Masses (Universitat de Barcelona). Electrospray mass spectra were carried out in a LC/MSD-TOF spectrometer using H_2O-CH_3CN (1:1) to introduce the sample. NMR spectra were performed at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona using Bruker DRX-250 (^{195}Pt, 54 MHz), Varian Unity 300 (^{1}H, 300 MHz; ^{31}P{^{1}H}, 121.4 MHz), Mercury-400 (^{1}H, 400 MHz; ^{1}H−^{1}H-NOESY, ^{1}H−^{1}H-COSY, ^{1}H−^{13}C-gHSQC), and Varian Inova DMX-500 (^{1}H, 500 MHz; ^{1}H−^{1}H-NOESY, ^{1}H−^{1}H-COSY, ^{1}H−^{13}C-gHSQC) spectrometers, and referenced to $SiMe_4$ (^{1}H, ^{13}C), H_3PO_4 (^{31}P), and H_2PtCl_6 in D_2O (^{195}Pt). δ values are given in ppm and J values in Hz. Abbreviations used: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad; NMR labeling is as shown in Schemes 2−6.

Preparation of the Compounds. *cis*-[$Pt(4\text{-}C_6H_4Me)_2(\mu\text{-}SEt_2)]_2$[25] and ligands **1a**−**1j**[2a,b,9,26] were prepared as reported elsewhere.

(25) Steele, B. R.; Vrieze, K. *Trans. Met. Chem.* **1977**, *2*, 140.
(26) Crespo, M.; Martín, R.; Calvet, T.; Font-Bardía, M.; Solans, X. *Polyhedron* **2008**, *27*, 2603.

Compound [Pt(4-MeC$_6$H$_4$)$_2${4-ClC$_6$H$_4$CHNCH$_2$CH$_2$NMe$_2$}] (**2a**) was obtained from 45 mg (0.22 mmol) of imine **1a** and 100 mg (0.11 mmol) of compound [Pt$_2$(4-MeC$_6$H$_4$)$_2$(μ-SEt$_2$)$_2$] in toluene. The mixture was stirred for 4 h at room temperature. The solvent was removed in a rotary evaporator, and the residue was treated with ether. The solid was filtered and dried *in vacuo*. Yield: 87 mg (67%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.74 [s, ^3J(Pt−H^3) = 42.4, 1H, H^3]; 7.88 [d, ^3J(H^1−H^2) = 8.5, 2H, H^1]; 7.30 [d, ^3J(Pt−H^7) = 68.8, ^3J(H^7−H^8) = 7.92, 2H, H^7]; 6.89 [d, ^3J(H^1−H^2) = 8.5, 2H, H^2]; 6.75 [d, ^3J(H^7−H^8) = 7.5, 2H, H^8]; 6.73 [d, ^3J(H^{10}−H^{11}) = 8.0, ^3J(Pt−H^{10}) = 73.4, 2H, H^{10}]; 6.22 [d, ^3J(H^{10}−H^{11}) = 7.5, 2H, H^{11}]; 4.15 [m, ^3J(H^4−H^5) = 5.4, 2H, H^4]; 2.76 [m, ^3J(H^4−H^5) = 5.4, 2H, H^5]; 2.64 [s, ^3J(Pt−H^6) = 18.3, 6H, H^6]; 2.19 [s, 3H, H^9], 1.93 [s, 3H, H^{12}]. ^{195}Pt NMR (54 MHz, CDCl$_3$): δ −3438.14. ESI-MS, *m/z*: 588.18 [M + H]$^+$, 496.11 [M − C$_7$H$_7$]$^+$. Anal. Found (calc for C$_{25}$H$_{29}$ClN$_2$Pt): C: 51.1 (51.06); H: 5.2 (4.97); N: 4.5 (4.76). After standing in solution for 48 h, compound **2a′** was formed: ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.43 [s, ^3J(Pt−H^3) = 26.0, 1H, H^3]; 7.40 [d, ^3J(H^7−H^8) = 8.5, 2H, H^7]; 7.31 [d, ^3J(H^1−H^2) = 8.7, 2H, H^2]; 7.29 [d, ^3J(H^7−H^8) = 8.2, 2H, H^8]; 7.20 [d, ^3J(H^{10}−H^{11}) = 8.0, 2H, H^{10}]; 6.75 [d, ^3J(H^1−H^2) = 8.7, 2H, H^1]; 6.71 [d, ^3J(H^{10}−H^{11}) = 8.1, 2H, H^{11}]; 3.97 [m, 2H, H^4]; 2.75 [m, 2H, H^5]; 2.63 [s, br, 6H, H^6]; 2.17 [s, 3H, H^9], 2.13 [s, br, 3H, H^{12}].

Compound [Pt(4-MeC$_6$H$_4$)$_2${2,6-Cl$_2$C$_6$H$_3$CHNCH$_2$CH$_2$NMe$_2$}] (**2c**) was obtained using the same procedure as that described above from 57 mg (0.23 mmol) of imine **1c** and 104 mg (0.11 mmol) of compound [Pt$_2$(4-MeC$_6$H$_4$)$_2$(μ-SEt$_2$)$_2$]. Yield: 97 mg (71%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.69 [s, br, ^3J(Pt−H^4) = 53.5, 1H, H^4]; 7.24 [d, ^3J(H^8−H^9) = 7.9, ^3J(Pt−H^8) = 59.3, 2H, H^8]; 6.90 [s, 3H, H^{1,2,3}]; 6.74 [d, ^3J(H^{11}−H^{12}) = 7.9, 2H, H^{11}]; 6.68 [d, ^3J(H^8−H^9) = 7.4, 2H, H^9]; 6.16 [d, ^3J(H^{11}−H^{12}) =7.4, 2H, H^{12}]; 4.17 [td, ^3J(H^5−H^6) = 5.6, ^4J(H^4−H^5) = 1.5, 2H, H^5]; 2.79 [d, ^3J(H^5−H^6) =5.5, 2H, H^6]; 2.62 [s, br, 6H, H^7]; 2.13 [s, 3H, H^{10}], 1.91 [s, 3H, H^{13}]. ^{13}C NMR (^{1}H−^{13}C-gHSQC, 400 MHz, CDCl$_3$): δ 160.2 [C^4]; 137.8 [C^8]; 137.2 [C^{11}]; 130.4 [C^2]; 128.1 [C^9]; 127.7 [C^{1,3}]; 126.8 [C^{12}]; 64.5 [C^5]; 65.4 [C^6]; 49.5 [C^7]; 21.0 [C^{10}]; 20.6 [C^{13}]. ESI-MS, *m/z*: 639.14 [M + NH$_4$]$^+$, 622.14 [M + H]$^+$, 530.07 [M − C$_7$H$_7$]$^+$. Anal. Found (calc for C$_{25}$H$_{28}$Cl$_2$N$_2$Pt·CH$_2$Cl$_2$): C: 44.7 (44.14); H: 4.2 (4.27); N: 4.0 (3.96). After standing in solution for a few hours, compound **2c′** was formed: ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.36 [t, ^4J(H^4−H^5) = 2.2, ^3J(Pt−H^4) = 26.8, 1H, H^4]; {7.31 [d, ^3J(H−H) = 7.6, 2H]; 7.26 [d, ^3J(H−H) = 7.9, 2H]; 6.97 [d, ^3J(H−H) = 7.9, 2H]; 6.96 [d, ^3J(H−H) = 7.9, 2H]; 6.77 [dd, ^3J(H−H) = 8.6, ^4J(H−H) = 0.7, 1H]; 6.72 [dd, ^3J(H−H) = 8.2, ^4J(H−H) = 0.5, 1H]; H^{1,3,8,9,11,12}}; 4.34−4.32 [m, 2H, H^5]; 3.64−3.60 [m, 2H, H^6]; 2.63 [s, ^3J(Pt−H^7) = 19.3, 6H, H^7]; 2.18 [s, 3H, H^{10}], 2.13 [s, 3H, H^{13}].

Compound [Pt(4-MeC$_6$H$_4$)$_2${C$_6$F$_5$CHNCH$_2$CH$_2$NMe$_2$}] (**2d**) was obtained using the same procedure as that described above from 59 mg (0.22 mmol) of imine **1d** and 101 mg (0.11 mmol) of compound [Pt$_2$(4-MeC$_6$H$_4$)$_2$(μ-SEt$_2$)$_2$]. Yield: 95 mg (67%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.67 [s, ^3J(Pt−H^1) = 48.4, 1H, H^1]; 7.19 [d, ^3J(H^5−H^6) = 7.9,^3J(Pt−H^5) = 71.0, 2H, H^5]; 6.81 [d, ^3J(H^8−H^9) = 7.9,^3J(Pt−H^8) = 76.8, 2H, H^8]; 6.7 [d, ^3J(H^5−H^6) = 7.5, 2H, H^6]; 6.35 [d, ^3J(H^8−H^9) = 7.6, 2H, H^9]; 4.09 [td, ^3J(H^2−H^3) = 5.1, ^4J(H^1−H^2) = 1.5, 2H, H^2]; 2.75 [m, 2H, H^3]; 2.61 [s, ^3J(Pt−H^4) = 18.7, 6H, H^4]; 2.14 [s, 3H, H^7], 1.99 [s, 3H, H^{10}]. ^{13}C NMR (^{1}H−^{13}C-gHSQC, 400 MHz, CDCl$_3$): δ 152.1 [C^1]; 137.5 [C^5]; 137.4 [C^8]; 127.5 [C^6]; 126.8 [C^9]; 65.4 [C^3]; 64.6 [C^2]; 49.5 [C^4]; 20.8 [C^7]; 20.4 [C^{10}]. ESI-MS, *m/z*: 661.18 [M + NH$_4$]$^+$, 644.18 [M + H]$^+$, 552.10 [M − C$_7$H$_7$]$^+$. Anal. Found (calc for C$_{25}$H$_{25}$F$_5$N$_2$Pt): C: 46.3 (46.66); H: 4.1 (3.92); N: 4.1 (4.35).

Compound [PtBr(4-MeC$_6$H$_4$)$_2${C$_6$H$_4$CHNCH$_2$CH$_2$NMe$_2$}] (**3b**) was obtained using the same procedure as that described above from 57 mg (0.22 mmol) of imine **1b** and 102 mg (0.11 mmol) of compound [Pt$_2$(4-MeC$_6$H$_4$)$_2$(μ-SEt$_2$)$_2$]. Yield: 90 mg (65%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.59 [s, ^3J(Pt−H^5) = 45.6, 1H, H^5]; 7.56 [d, ^3J(H^9−H^{10}) = 7.6,^3J(Pt−H^9) = 33.8, 2H, H^9]; 7.35 [dd, ^3J(H^3−H^4) = 7.5,^4J(H^2−H^4) = 1.5, 1H, H^4]; 7.33 [d, ^3J(H^1−H^2) = 8.0, 1H, H^1]; 7.09 [td, ^3J(H^2−H^{1,3}) = 7.7,^4J(H^2−H^4) = 1.6, 1H, H^2]; 7.00 [td, ^3J(H^3−H^{2,4}) = 7.4,^4J(H^1−H^3) = 1.0, 1H, H^3]; 6.94 [d, ^3J(H^9−H^{10}) = 7.7, 2H, H^{10}]; 6.63 [m, ^3J(Pt−H) = 20.4, 4H, H^{12,13}]; 4.40−4.33 [m, 1H, H^7]; 4.31−4.23 [m, 2H, H^6]; 2.97 [s, ^3J(Pt−H^8) = 10.4, 3H, H^8]; 2.81−2.79 [m, 1H, H$^{7\prime}$]; 2.47 [s, ^3J(Pt−H$^{8\prime}$) = 14.8, 3H, H$^{8\prime}$]; 2.34 [s, 3H, H^{11}]; 2.14 [s, 3H, H^{14}]. ^{13}C NMR (^{1}H−^{13}C-gHSQC, 400 MHz, CDCl$_3$): δ 170.0 [C^5]; 137.2 [C^9]; 133.8 [C^{12}]; 132.3 [C^1]; 132.2 [C^2]; 129.9 [C^4]; 127.8 [C^{10}]; 127.7 [C^{13}]; 124.3 [C^3]; 65.8 [C^7]; 52.4 [C^6]; 50.6 [C^8]; 48.1 [C$^{8\prime}$]; 20.7 [C^{11}]; 20.3 [C^{14}]. ESI-MS, *m/z*: 650.14 [M + NH$_4$]$^+$, 633.12 [M + H]$^+$, 552.20 [M − Br]$^+$. Anal. Found (calc for C$_{25}$H$_{29}$BrN$_2$Pt): C: 47.1 (47.47); H: 4.5 (4.62); N: 4.5 (4.43).

Compound [PtCl(4-MeC$_6$H$_4$)$_2${2-ClC$_6$H$_3$CHNCH$_2$CH$_2$NMe$_2$}] (**3c**) was obtained when a solution of compound **2c** was stirred in CH$_2$Cl$_2$ at room temperature for 24 h. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.04 [d, ^4J(H^4−H^5) = 1.7, ^3J(Pt−H^4) = 46.6, 1H, H^4]; 7.47 [d, ^3J(H^8−H^9) = 7.8,^3J(Pt−H^8) = 33.7, 2H, H^8]; 7.32 [dd, ^3J(H^2−H^3) = 6.9,^4J(H^1−H^3) = 0.7, 1H, H^3]; 7.21 [dd, ^3J(H^1−H^2) = 7.5, 1H, H^1]; 7.02 [t, ^3J(H^2−H^{1,3}) = 7.8, 1H, H^2]; 6.95 [d, ^3J(H^8−H^9) = 8.3, 2H, H^9]; 6.72 [d, ^3J(H^{11}−H^{12}) = 8.3, 2H, H^{11}]; 6.65 [d, ^3J(H^{11}−H^{12}) = 8.3, 2H, H^{12}]; 4.46−4.39 [m, 1H, H^6]; 4.32−4.23 [m, 2H, H^5]; 2.83 [s, ^3J(Pt−H^7) = 11.2, 3H, H^7]; 2.79−2.75 [m, 1H, H$^{6\prime}$]; 2.52 [s, ^3J(Pt−H$^{7\prime}$) = 16.2, 3H, H$^{7\prime}$]; 2.33 [s, 3H, H^{10}], 2.16 [s, 3H, H^{13}].

Compound [Pt(4-MeC$_6$H$_4$){4-ClC$_6$H$_3$CHNCH$_2$CH$_2$NMe$_2$}] (**4a**) was obtained from 50 mg (0.09 mmol) of compound **2a** after reaction in toluene at 90 °C for 6 h. The solvent was removed and the residue was treated with ether to produce a solid, which was filtered and dried *in vacuo*. Yield: 26 mg (62%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.45 [d, ^4J(H^4−H^5) = 1.4, ^3J(Pt−H^4) = 56.0, 1H, H^4]; 7.40 [d, ^3J(H^8−H^9) = 7.8,^3J(Pt−H^8) = 57.2, 2H, H^8]; 7.16 [d, ^3J(H^2−H^3) = 8.1, 1H, H^3]; 7.08 [d, ^3J(Pt−H^1) = 69.4, ^3J(H^1−H^2) = 2.1, 1H, H^1]; 6.96 [d, ^3J(H^8−H^9) = 7.5, 2H, H^9]; 6.93 [dd, ^3J(H^2−H^3) = 8.0,^4J(H^1−H^2) = 2.1, 1H, H^2]; 4.03 [td, ^3J(H^5−H^6) = 6.0, ^4J(H^4−H^5) = 1.3, 2H, H^5]; 3.18 [t, ^3J(H^5−H^6) = 6.0, 2H, H^6]; 2.76 [s, ^3J(Pt−H^7) = 20.9, 6H, H^7]; 2.30 [s, 3H, H^{10}]. ^{13}C NMR (^{1}H−^{13}C-gHSQC, 500 MHz, CDCl$_3$): δ 168.5 [C^4]; 137.0 [C^8]; 135.7 [C^1]; 129.0 [C^3]; 128.0 [C^9]; 122.5 [C^2]; 67.1 [C^6]; 52.3 [C^5]; 49.0 [C^7]; 20.8 [C^{10}]. ^{195}Pt NMR (54 MHz, CDCl$_3$): δ −3580.76. ESI-MS, *m/z*: 899.15 [2M − C$_7$H$_7$]$^+$, 496.11 [M + H]$^+$, 404.05 [M − C$_7$H$_7$]$^+$. Anal. Found (calc for C$_{18}$H$_{21}$ClN$_2$Pt): C: 43.9 (43.60); H: 4.3 (4.27); N: 5.3 (5.65).

Compound [PtCl{(MeC$_6$H$_3$)(ClC$_6$H$_3$CHNCH$_2$CH$_2$NMe$_2$}] (**5c**) was obtained from 100 mg (0.16 mmol) of compound **2c** after reaction in refluxing toluene for 6 h. The solvent was removed and the residue was treated with ether to produce a yellow solid, which was filtered and dried *in vacuo*. Yield: 58 mg (68%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 9.22 [s, ^3J(Pt−H^4) = 147.7, 1H, H^4]; 7.49 [t, ^3J(H^2−H^{1,3}) = 7.5, 1H, H^2]; 7.44 [s, br, ^3J(Pt−H^8) = 53.4, 1H, H^8]; 7.35 [dd, ^3J(H^{1,3}−H^2) = 8.1, ^3J(H^1−H^3) = 0.9, 2H, H^{1,3}]; 6.87 [d, ^3J(H^{10}−H^{11}) = 7.8, 1H, H^{11}]; 6.80 [dd, ^3J(H^8−H^9) = 8.0, ^4J(H^8−H^{10}) = 1.3, 1H, H^{10}]; 4.52 [m, ^2J(H^5−H$^{5\prime}$) = 11.9, ^3J(H^5−H$^{6\prime}$) = 3.9, ^4J(H^4−H^5) = 1.2, 1H, H^5]; 3.97 [dd, ^2J(H^5−H$^{5\prime}$) = 11.7, ^3J(H$^{5\prime}$−H^6) = 3.8, ^3J(Pt−H$^{5\prime}$) = 59.9, 1H, H$^{5\prime}$]; 3.08 [s, 3H, H^7]; 2.73 [s, 3H, H$^{7\prime}$]; 2.73 [m, 1H, H^6]; 2.60 [td, ^2J(H^6−H$^{6\prime}$) = 12.9,^3J(H^5−H$^{6\prime}$) = 4.0, 1H, H$^{6\prime}$]; 2.31 [s, 3H, H^9]. ^{13}C NMR (^{1}H−^{13}C-gHSQC, 500 MHz, CDCl$_3$): δ 162.7 [C^4]; 139.7 [C^8]; 132.4 [C^1]; 132.1 [C^2]; 129.1 [C^{11}]; 127.3 [C^3]; 124.8 [C^{10}]; 66.9 [C^5]; 65.13 [C^6]; 50.5 [C$^{7\prime}$]; 47.8 [C^7]; 21.0 [C^9]. ESI-MS, *m/z*: 530.07 [M + H]$^+$. Anal. Found (calc for C$_{18}$H$_{20}$Cl$_2$N$_2$Pt): C: 41.5 (40.76); H: 3.7 (3.80); N: 5.3 (5.28).

Compound [Pt(4-MeC$_6$H$_4$){4-ClC$_6$H$_3$CHNCH$_2$(4-ClC$_6$H$_4$)}SEt$_2$] (**4e**) was obtained from 70 mg (0.26 mmol) of imine **1e** and 124 mg (0.13 mmol) of compound [Pt$_2$(4-MeC$_6$H$_4$)$_2$(μ-SEt$_2$)$_2$] in toluene.

The mixture was stirred for 24 h at room temperature and then was heated at 90 °C for 2 h to complete the reaction. The solvent was removed in a rotary evaporator and the residue was treated with ether. The yellow solid was filtered and dried *in vacuo*. Yield: 115 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 [s, ^3J(Pt−H^4) = 52.0, 1H, H^4]; 7.34 [d, ^3J(H^6−H^7) = 8.5, 1H, H^7]; 7.30−7.26 [m, 3H, H^{3,6,8}]; 7.00 [dd, ^3J(H^2−H^3) = 8.0, ^4J(H^1−H^2) = 2.1, 1H, H^2]; 6.87 [d, ^3J(H^8−H^9) = 7.4, 2H, H^9]; 6.81 [d, ^3J(Pt−H^1) = 54.4, ^4J(H^1−H^2) = 2.1, 1H, H^1]; 5.12 [s, 2H, H^5]; 2.31 [m, ^3J(H^{11}−H^{12}) = 7.4, 4H, H^{11}]; 2.27 [s, 3H, H^{10}]; 1.06 [t, ^3J(H^{11}−H^{12}) = 7.4, 6H, H^{12}]. ^{13}C NMR (^{1}H−^{13}C-gHSQC, 400 MHz, $CDCl_3$): δ 176.4 [C^4]; 136.3 [C^3]; 136.3 [C^6]; 136.1 [C^1]; 129.1 [C^8]; 128.8 [C^7]; 128.8 [C^9]; 123.7 [C^2]; 61.8 [C^5]; 28.7 [C^{11}]; 20.8 [C^{10}]; 13.0 [C^{12}]. ESI-MS, *m/z*: 548.03 [M − SEt_2]$^+$. Anal. Found (calc for $C_{25}H_{27}Cl_2NPtS$): C: 46.7 (46.95); H: 4.2 (4.26); N: 2.4 (2.19); S: 3.8 (5.01).

Compound [PtBr{$(MeC_6H_3)C_6H_4CHNCH_2(4\text{-}ClC_6H_4)$}$SEt_2$] (**5f**) was obtained from 68 mg (0.22 mmol) of imine **1e** and 100 mg (0.11 mmol) of compound [$Pt_2(4\text{-}MeC_6H_4)_2(\mu\text{-}SEt_2)_2$] in toluene. The mixture was stirred for 24 h at room temperature. The solvent was removed in a rotary evaporator and the residue was treated with ether. The yellow solid was filtered and dried *in vacuo*. Yield: 98 mg (65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 [s, ^3J(Pt−H^4) = 119.4, 1H, H^4]; 7.50−7.46 [m, 1H, H^7]; 7.38−7.34 [m, 3H, H^{5,6,8}]; 7.20 [d, ^3J(H^1−H^2) = 8.4, 1H, H^1]; 7.15 [d, ^3J(H^1−H^2) = 8.3, 1H, H^2]; 6.82 [d, ^3J(H^9−H^{10}) = 7.6, 1H, H^9]; 6.71 [d, ^3J(H^9−H^{10}) = 7.3, 1H, H^{10}]; 6.22 [s, ^3J(Pt−H^{12}) = 54.4, 1H, H^{12}]; 5.73 [dd, ^2J(H^3−H$^{3\prime}$) = 12.7,^4J(H^3−H^4) = 1.5, 1H, H^3]; 4.88 [d, ^2J(H^3−H$^{3\prime}$) = 12.8, ^3J(Pt−H$^{3\prime}$) = 56.9, 1H, H$^{3\prime}$]; 3.03 [s, br, 1H, H$^{13\prime}$]; 2.66 [s, br, 2H, H^{13}]; 2.36 [s, br, 1H, H$^{13\prime\prime}$]; 2.16 [s, 3H, H^{11}]; 1.59 [s, br, 3H, H^{14}]; 0.96 [s, br, 3H, H$^{14\prime}$]. ^{13}C NMR (^{1}H−^{13}C-gHSQC, 400 MHz, $CDCl_3$): δ 165.68 [C^4]; 136.6 [C^{12}]; 131.6 [C^1]; 131.0 [C^7]; 130.2 [C^5]; 128.8 [C^8]; 128.6 [C^2]; 127.9 [C^9]; 126.3 [C^6]; 124.3 [C^{10}]; 68.3 [C^3]; 20.9 [C^{11}]. ESI-MS, *m/z*: 603.12 [M − Br]$^+$. Anal. Found (calc for $C_{25}H_{27}BrClNPtS$): C: 43.7 (43.90); H: 3.8 (3.98); N: 2.1 (2.05). S: 4.0 (4.69).

Compound [PtCl{$(MeC_6H_3)(ClC_6H_3)CHNCH_2(4\text{-}ClC_6H_4)$}$SEt_2$] (**5g**) was obtained as a yellow solid from 66 mg (0.22 mmol) of imine **1g** and 101 mg (0.11 mmol) of compound [$Pt_2(4\text{-}MeC_6H_4)_2(\mu\text{-}SEt_2)_2$] using an analogous procedure to that for **5f** in toluene at 90 °C for 6 h. Yield: 126 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 [d, ^3J(Pt−H^4) = 120.4, ^4J(H^3−H^4) = 1.2, 1H, H^4]; 7.41 [t, ^3J(H^6−H^{5,7}) = 7.7, 1H, H^6]; 7.37 [dd, ^3J(H^5−H^6) = 8.0, ^4J(H^5−H^7) = 1.5, 1H, H^5]; 7.24 [dd, ^3J(H^6−H^7) = 7.3, ^4J(H^5−H^7) = 1.5, 1H, H^7]; 7.20 [d, ^3J(H^1−H^2) = 8.4, 1H, H^1]; 7.12 [d, ^3J(H^1−H^2) = 8.4, 1H, H^2]; 6.82 [d, ^3J(H^8−H^9) = 7.7, 1H, H^8]; 6.70 [dd, ^3J(H^8−H^9) = 7.7, ^4J(H^9−H^{11}) = 1.11, 1H, H^9]; 6.27 [s, ^3J(Pt−H^{11}) = 53.0, 1H, H^{11}]; 5.57 [dd, ^2J(H^3−H$^{3\prime}$) = 13.0,^4J(H^3−H^4) = 1.8, 1H, H^3]; 4.95 [d, ^2J(H^3−H$^{3\prime}$) = 12.9,^3J(Pt−H$^{3\prime}$) = 54.6, 1H, H$^{3\prime}$]; 3.04 [s, br, 1H, H$^{12\prime}$]; 2.62 [s, br, 2H, H^{12}]; 2.38 [s, br, 1H, H$^{12\prime\prime}$]; 2.15 [s, 3H, H^{10}]; 1.26 [s, br, 1H, H^{13}]; 0.93 [s, br, 2H, H$^{13\prime}$]. ^{13}C NMR (^{1}H−^{13}C-gHSQC, 400 MHz, $CDCl_3$): δ 163.7 [C^4]; 137.2 [C^{11}]; 131.8 [C^2]; 131.8 [C^6]; 128.9 [C^1]; 128.9 [C^7]; 128.0 [C^8]; 127.4 [C^5]; 124.4 [C^9]; 67.6 [C^3]; 21.0 [C^{10}]; 12.5 [C^{13}]; 12.5 [C$^{13\prime}$]. ESI-MS, *m/z*: 601.03 [M − SEt_2 + NH_4]$^+$. Anal. Found (calc for $C_{25}H_{26}Cl_3NPtS$): C: 44.9 (44.55); H: 3.6 (3.89); N: 2.2 (2.08). S: 3.7 (4.76).

Compound [Pt(4-MeC_6H_4){4-$ClC_6H_3CHNCH_2CH_2NMe_2$}PPh_3] (**6a**) was prepared from 25 mg (0.05 mmol) of compound **4a** and 13 mg (0.05 mmol) of triphenylphosphine, which were dissolved in 30 mL of acetone and allowed to react at room temperature for 2 h. The solvent was removed and the residue was washed with ether and dried *in vacuo*. Yield: 15 mg (39%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 [s, ^3J(Pt−H^4) = 51.0, 1H, H^4]; 7.56−7.49 [m, 6H, PPh_3]; 7.37−7.23 [m, 9H, PPh_3]; 6.99 [m, 2H, H^{1,3}]; 6.92 [d, ^3J(H^8−H^9) = 7.2, 2H, H^8]; 6.87 [dd, ^3J(H^2−H^3) = 5.8,^4J(H^1−H^2) = 2.1, 1H, H^2]; 6.43 [d, ^3J(H^8−H^9) = 7.6, 2H, H^9]; 3.12 [t, ^3J(H^5−H^6) = 6.0, 2H, H^5]; 2.09 [s, 3H, H^{10}]; 1.89 [m, 8H, H^{6,7}]. ^{31}P NMR (121 MHz, $CDCl_3$): δ 28.06 [s, ^1J(Pt−P) = 2197.8].

Compound [Pt(4-MeC_6H_4){4-$ClC_6H_3CHNCH_2$(4-ClC_6H_4)}PPh_3] (**6e**) was prepared from 40 mg (0.06 mmol) of compound **4e** and 17 mg (0.06 mol) of triphenylphosphine using an analogous procedure to that for **6a**. Yield: 39 mg (80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 [s, ^3J(Pt−H^4) = 50.4, 1H, H^4]; {7.49−7.42 [m, 6H]; 7.36−7.30 [m, 6H]; 7.24−7.19 [m, 7H] PPh_3, H^8, H^9}; 7.14 [d, ^3J(H^6−H^7) = 8.4, 2H, H^7]; 6.99 [dd, ^3J(H^2−H^3) = 7.9, ^4J(H^1−H^2) = 2.1, 1H, H^2]; 6.89 [m, 1H, H^1]; 6.68 [d, ^3J(H^6−H^7) = 8.4, 2H, H^6]; 6.43 [d, ^3J(H^2−H^3) = 7.7, 1H, H^3]; 4.08 [s, br, 2H, H^5]; 2.09 [s, br, 3H, H^{10}]. ^{31}P NMR (121 MHz, $CDCl_3$): δ 27.59 [s, ^1J(Pt−P) = 2200.6]. ESI-MS, *m/z*: 811.14 [M + H]$^+$.

Compound [PtCl{$(MeC_6H_4)(ClC_6H_3)CHNCH_2CH_2NMe_2$}$PPh_3$] (**7c/7c′**) was prepared from 40 mg (0.08 mmol) of compound **5c** and 20 mg (0.08 mol) of triphenylphosphine using an analogous procedure to that for **6a**. Yield: 27 mg (42%). ^{1}H NMR (300 MHz, $CDCl_3$): **7c**: δ 8.26 [s, ^3J(Pt−H^4) = 140.0, 1H, H^4]; 7.65−7.59 [m, 6H, H^{ar}]; 7.50−7.32 [m, 15H, H^{ar}]; 6.96 [dd, ^3J(H^{10}−H^{11}) = 7.6, ^4J(H^8−H^{10}) = 2.5, 1H, H^{10}]; 6.78 [d, ^3J(H^{10}−H^{11}) = 7.8, 1H, H^{11}]; 3.18 [m, 1H, H^5]; 3.03 [m, 1H, H$^{5\prime}$]; 2.45 [m, 2H, H^6]; 2.31 [s, 3H, H^9]; 1.78 [m, 6H, H^7]. **7c′**: δ 8.63 [s, ^3J(Pt−H^4) = 84.7, ^3J(P−H^4) = 11.25, 1H, H^4]; 7.42−7.17 [m, 17H, H^{ar}]; 7.11 [dd, ^3J(H^1−H^2) = 7.6, ^4J(H^1−H^3) = 0.9, 1H, H^1]; 6.70 [d, ^3J(H^{10}−H^{11}) = 7.7, 1H, H^{11}]; 6.47 [dd, ^3J(H^{10}−H^{11}) = 7.6, ^4J(H^8−H^{10}) = 0.9, 1H, H^{10}]; 6.40 [s, 1H, H^8]; 4.77 [m, 1H, H^5]; 3.95 [m, 1H, H$^{5\prime}$]; 2.93 [m, 2H, H^6]; 2.77 [m, 2H, H$^{6\prime}$]; 2.08 [s, 3H, H^7]; 1.76 [m, 6H, H^9]. ^{31}P NMR (121 MHz, $CDCl_3$) **7c**: δ 18.64 [s, ^1J(Pt−P) = 1866.5]. **7c′**: δ 15.19 [s, ^1J(Pt−P) = 4305.1].

Compound [PtBr{$(MeC_6H_3)(C_6H_4)CHNCH_2(4\text{-}ClC_6H_4)$}$PPh_3$] (**7f/7f′**) was prepared from 40 mg (0.06 mmol) of compound **5f** and 17 mg (0.06 mol) of triphenylphosphine using an analogous procedure to that for **6a**. Yield: 35 mg (68%). **7f**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 [s, ^3J(Pt−H^4) = 140.9, 1H, H^4]; {7.66−7.56 [m, 8H] PPh_3, H^{ar}}; 7.54−7.52 [m, 1H, H^7]; {7.42−7.36 [m, 10H] PPh_3, H^{ar}}; 7.13 [d, ^3J(H^1−H^2) = 8.3, 1H, H^2]; 7.06 [d, ^3J(H−H) = 7.4, 1H, H^{ar}]; 6.85 [dd, ^3J(H^9−H^{10}) = 7.6, ^4J(H^{10}−H^{12}) = 2.5, 1H, H^{10}]; 6.72 [d, ^3J(H^1−H^2) = 8.4, 2H, H^1]; 6.67 [s, ^3J(H−H) = 8.9, 1H, H^{ar}]; 4.21 [d, ^2J(H^3−H$^{3\prime}$) = 13.3, 1H, H^3]; 4.13 [d, ^2J(H^3−H$^{3\prime}$) = 13.4, 1H, H$^{3\prime}$]; 2.18 [s, br, 3H, H^{11}]. ^{31}P NMR (121 MHz, $CDCl_3$): δ 17.76 [s, ^1J(Pt−P) = 1862.2]. **7f′**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 [d, ^3J(Pt−H^4) = 87.7, ^4J(P−H^4) = 11.1, ^4J(H^3−H^4) = 1.5, 1H, H^4]; {7.44−7.36 [m, 2H]; 7.31−7.27 [m, 9H]; 7.16−7.21 [m, 10H]; PPh_3, H^{ar}}; 6.61 [d, ^3J(H^9−H^{10}) = 7.7, 1H, H^9]; 6.39 [d, ^3J(H^9−H^{10}) = 7.4, 1H, H^{10}]; 5.84 [d, ^3J(H^3−H$^{3\prime}$) = 12.4, 1H, H^3]; 5.52 [s, ^3J(Pt−H^{12}) = 59.5, 1H, H^{12}]; 4.88 [dd, ^3J(Pt−H^3) = 48.5, ^3J(H^3−H$^{3\prime}$) = 12.3,^4J(P−H$^{3\prime}$) = 5.2, 1H, H$^{3\prime}$]; 1.65 [s, br, 3H, H^{11}]. ESI-MS, *m/z*: 775.16 [M − Br]$^+$.

Compound [PtCl{$(MeC_6H_3)(ClC_6H_3)CHNCH_2$(4-$ClC_6H_4$)}$PPh_3$] (**7g/7g′**) was prepared from 40 mg (0.06 mmol) of compound **5g** and 17 mg (0.06 mol) of triphenylphosphine using an analogous procedure to that for **6a**. Yield: 23 mg (46%). **7g**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.48 [d, ^3J(Pt−H^4) = 138.9, ^4J(H^3−H^4) = 1.0, 1H, H^4]; {7.70−7.63 [m, 8H]; 7.48−7.44 [m, 4H]; 7.40−7.43 [m, 6H]; PPh_3, H^{ar}}; 7.12 [d, ^3J(H^1−H^2) = 8.4, 2H, H^1]; 6.86 [dd, ^3J(H−H) = 7.8, ^4J(H−H) = 2.3, 1H, H^{ar}]; 6.71−6.67 [m, 2H, H^{ar}]; 6.69 [d, ^3J(H^1−H^2) = 8.4, 2H, H^2]; 4.18 [d, ^3J(H^3−H$^{3\prime}$) = 13.5, ^3J(Pt−H$^{3\prime}$) = 66.97, 1H, H$^{3\prime}$]; 3.95 [dd, ^3J(H^3−H$^{3\prime}$)= 13.2,^4J(H^3−H^4) = 1.2, 1H, H^3]; 2.19 [s, br, 3H, H^{10}]. ^{31}P NMR (121 MHz, $CDCl_3$): δ 18.54 [s, ^1J(Pt−P) = 1856.5]. **7g′**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74 [dd, ^3J(Pt−H^4) = 87.1, ^4J(P−H^4) = 11.1, ^4J(H^3−H^4) = 1.6, 1H, H^4]; {7.41 [dd, ^3J(H−H) = 8.1, ^4J(H−H) = 1.3, 1H]; 7.37−7.26 [m, 14H]; 7.22−7.17 [m, 6H]; 7.11 [dd, ^3J(H−H) = 7.5, ^4J(H−H) = 1.2, 1H]; PPh_3, H^{ar}}; 6.60 [d, ^3J(H^8−H^9) = 7.6, 1H, H^8]; 6.38 [dd, ^3J(H^8−H^9) = 7.6,^4J(H^9−H^{11}) = 1.1, 1H, H^9]; 5.72 [d, ^3J(H^3−H$^{3\prime}$) = 12.2, 1H, H^3]; 5.55 [s, ^3J(Pt−H^{11}) = 54.5, 1H, H^{11}]; 4.93 [dd, ^3J(Pt−H$^{3\prime}$) =

Table 2. Crystallographic and Refinement Data for Compounds 4a, 5c, 5g, and 7g′

	compound **4a**	compound **5c**	compound **5g**	compound **7g′**
formula	$C_{18}H_{21}ClN_2Pt$	$C_{18}H_{20}Cl_2N_2Pt \cdot CH_2Cl_2$	$C_{25}H_{26}Cl_3NPtS$	$C_{39}H_{31}Cl_3NPPt$
fw	495.91	615.28	673.97	846.06
temp, K	293(2)	293(2)	293(2)	293(2)
wavelength, Å	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/a$
a, Å	10.683(4)	8.043(8)	10.998(5)	11.748(4)
b, Å	14.836(6)	11.709(2)	8.346(3)	15.925(4)
c, Å	15.174(6)	11.828(6)	27.121(10)	18.487(4)
α, deg	90	90.50(3)	90	90
β, deg	114.29(10)	109.26(6)	91.43(2)	97.46(2)
γ, deg	90	91.57(4)	90	90
V, Å^3; *Z*	1732.1(12); 4	1051.0(12); 2	2488.6(17); 4	3429.4(16); 4
d(calcd), Mg/m^3	1.902	1.944	1.799	1.639
abs coeff, mm^{-1}	8.253	7.190	6.058	4.401
F(000)	952	592	1312	1664
rflns coll./unique	3829/3829 [*R*(int) = 0.0562]	6114/6114 [*R*(int) = 0.0399]	23 534/7270	31 396/9622
data/restraint/params	3829/0/221	6114/2/236	7270/1/280	9622/2/ 407
GOF on F^2	1.118	1.075	1.115	1.146
R_1 ($I > 2\sigma(I)$)	0.0462	0.0360	0.0399	0.0374
wR_2 (all data)	0.1259	0.0866	0.1074	0.0859
peak and hole, e Å^{-3}	0.756 and −0.646	0.947 and −0.829	0.744 and −0.579	0.510 and −0.614

58.6, $^3J(H^3-H^{3\prime}) = 12.9$,$^4J(P-H^{3\prime}) = 5.3$, 1H, $H^{3\prime}$]; 1.64 [s, br, 3H, H^{10}]. ^{31}P NMR (121 MHz, $CDCl_3$): δ 14.82 [s, $^1J(Pt-P) = 4363.5$]. ESI-MS, *m/z*: 850.14 [M − Cl + CH_3CN]$^+$, 809.12 [M − Cl]$^+$.

Preparation of compound [PtBr(4-MeC_6H_4)$_2${$C_6H_4CHNCH_2$-CH_2NMe_2}PPh_3] (**8b**) was attempted from 54 mg (0.09 mmol) of compound **3b** and 25 mg (0.09 mol) of triphenylphosphine using an analogous procedure to that for **6a**. According to the ^{1}H NMR (300 MHz, $CDCl_3$) of the crude reaction mixture, the main product was starting material **3b**; a new imine resonance was observed (δ 8.37 [d, $^3J(Pt-H) = 40.30$, $^4J(P-H) = 8.40$, 1H, H]) and assigned to **8b**. Addition of a further equivalent of PPh_3 in order to facilitate the reaction resulted in formation of compound *trans*-[PtBr(4-$CH_3C_6H_4$)(PPh_3)$_2$]: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56−7.50 [m, 15H, PPh_3]; 7.34−7.20 [m, 15H, PPh_3]; 6.47 [d, $^3J(Pt-H^3) = 56.1$, $^3J(H^2-H^3) = 8.0$, 2H, H^3]; 5.95 [d, $^3J(H^2-H^3) = 7.7$, 2H, H^2]; 1.94 [s, 3H, H^1]. ^{31}P NMR (121 MHz, $CDCl_3$): δ 24.48 [s, $^1J(Pt-P) = 3141.8$]. ESI-MS: 907.16 [M + NH_4]$^+$, 851.23 [M − Br+CH_3CN]$^+$, 810.20 [M − Br]$^+$.

X-Ray Structure Analysis. Prismatic crystals were selected and mounted on an Enraf-Nonius CAD4 four-circle (**5c**) or on a MAR345 (**4a**, **5g**, and **7g′**) diffractometer with an image plate detector. Intensities were collected with graphite-monochromatized Mo Kα radiation. The structures were solved by direct methods using the SHELXS computer program[27] and refined by the full-matrix least-squares method with the SHELXL97 computer program using 3829 (**4a**), 6114 (**5c**), 23 524 (**5g**), and 31 396 (**7g′**) reflections (very negative intensities were not assumed). **5c**, **5g**, and **7g′** were refined with a rigid model restraint for some distances around the platinum center. Further details are given in Table 2.

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Supporting Information Available: X-ray crystallographic data in CIF format for the structure determinations of **4a**, **5c**, **5g**, and **7g′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Sheldrick, G. M. *SHELXS97, A Computer Program for Crystal Structure Determination*; University of Göttingen: Germany, 1997.