Biaryl formation in the synthesis of endo and exo-platinacycles†

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Abstract

The reactions of *cis*-[Pt_2(4-MeC_6H_4)4(μ-SEt_2)$_2$] with bifunctional ligands ArCH NCH_2(2-XC_6H_4) containing a C–X bond at the *ortho* positions of the benzyl ring (Ar = 4-ClC_6H_4, X = Br (**1d**); Ar = 2,4,6-$(CH_3)_3C_6H_2$, X = Br (**1e**); Ar = 2,4,6-$(CH_3)_3C_6H_2$, X = Cl (1f); Ar = 2-$CH_3C_6H_4$, X = Br (**1h**); Ar = 2,6-$F_2C_6H_3$, X = Br (**1i**)) in refluxing toluene were studied. Several types of platinum(II) cyclometallated compounds containing a biaryl linkage were obtained: i) *endo*-five-membered with a Pt–C(sp^2) bond (**2d**, **2h**), ii) *endo*-six-membered with a Pt–C(sp^3) bond (**2e**, **2f**), and iii) *exo*-five membered with a Pt–C(sp^2) bond (**2i**). The formed biaryl linkage involves the metallated ring for 2i and the non-metallated ring for the *endo*-metallacycles. The reaction of compounds **2** with PPh3 produced the corresponding phosphine derivatives, some of which (**3d**, **3e**, **3h** and **3i**) were characterized crystallographically. In addition, compound [PtBr{2-$CH_3C_6H_3C_6H_4$CH NCH_2(2-C_6H_4Br)}SEt_2] (**2c**) containing a seven-membered *endo*-metallacycle was also obtained and characterized crystallographically.

1. INTRODUCTION

C–C bond formation is one of the most important processes in organic synthesis. Palladium catalyzed cross-coupling reactions such as those initially reported by Heck,[1] Negishi,[2] and Suzuki,[3] are of great importance in the formation of new pharmaceuticals and bioactive compounds and this field is still being developed after 40 years.[4] It is becoming clear that in addition to Pd(0)/Pd(II) cycles, involvement of Pd(II)/Pd(IV) systems might play a decisive role, and that parallel studies with organoplatinumcompounds are often useful in providing more stable species.[5]

We have previously reported a process involving C–C coupling and formation of seven-membered platinum(II) metallacycles in the reactions of *cis*-[$Pt_2(4\text{-}MeC_6H_4)_4(\mu\text{-}SEt_2)_2$] with ligands $ArCH{=}NCH_2(4\text{-}ClC_6H_4)$ [Ar = 2-BrC_6H_4 (**1a**) or 2,6-$Cl_2C_6H_3$ (1b) shown in Scheme 1] or with the corresponding potentially terdentate ligands $ArCH{=}NCH_2CH_2NMe_2$. It has been shown that these reactions take place through initial intramolecular C–X (X = Br or Cl) bond activation to produce an *endo* cyclometallated platinum(IV) compound as intermediate.[6] In the final products **2a** and **2b** a biaryl linkage between a platinum-bound tolyl ligand and the benzylidene ring of the imine, as well as a sevenmembered metallacycle containing the imine functionality (*endo*-metallacycle) are formed. All related C–C coupling processes leading to either seven-[7] or five-membered[8] platinacycles also involve *endo*-metallacycles.

As part of a project aimed at analyzing the scope of the formation of biaryl linkages in the coordination sphere of platinum, we decided to study the behaviour in front of *cis*-[$Pt_2(4\text{-}MeC_6H_4)_4(m\text{-}SEt_2)_2$] of N-benzylidenebenzylamines for which formation of *exo*-metallacycles (in which the imine moiety is not included in the metallacycle) is favoured. The obtained results will disclose whether formation of a biaryl linkage is possible in this case or if the rigidity associated with *endo* metallacycles (containing the imine functionality) is required. The imines selected for this study contain a C–Br bond at one *ortho* position of the more flexible benzyl ring (**1c**, **1d**, **1e**, **1h** and **1i**), so that formation of *exo*-metallacycles is favoured, and different substituents at the benzylidene ring so that different types of metallacycles could be obtained as final products. In addition, we thought that for imines **1f**

and **1g**, in which the *ortho* positions of the benzylidene group are blocked with methyl substituents, the reaction could also be driven towards formation of an *exo*-metallacycle even by activation of stronger C–Cl or C–H bonds, instead of C–Br, at the *ortho* positions of the benzyl ring. A preliminary communication of part of this work involving imines **1e**, **1f** and **1g** and leading to unusual six-membered platinacycles has been already published.[9] The structures of all the N-benzylidenebenzylamines used in this work are shown in Chart 1 and compared with those previously studied.

2. RESULTS AND DISCUSSION

Initial work was carried out with bifunctional imine 2-$C_6H_4BrCH{=}NCH_2(2\text{-}BrC_6H_4)$ (**1c**) which contains bromo substituents on both benzylidene and benzyl rings. In the reaction with *cis*-$[Pt_2(4\text{-}MeC_6H_4)_4(\mu\text{-}SEt_2)_2]$ under the previously reported conditions,[6] only compound **2c** containing an *endo* seven-membered platinacycle could be isolated (see reaction (1)). Compound **2c** was characterised by usual techniques and its NMR parameters are similar to those reported for analogous seven-membered compounds.[6] The molecular structure confirms formation of a non-planar seven-membered metallacycle in which the imine functionality and two aryl rings tilted 53.5(2)° from each other are included. Bond lengths and angles are well within the range of values obtained for analogous compounds.[6] The obtained result indicates that intramolecular C–Br bond activation takes place selectively at the benzylidene ring which is consistent with the higher tendency to form *endo versus exo* metallacycles.[10]

Therefore, further work was planned using imines which contain a C–Br bond exclusively in the benzyl group, in order to drive the reaction towards formation of *exo*-platinacycles. It has been previously reported for the reactions of the compound *cis*-$[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with N-benzylidenebenzylamines that, in spite of the more favoured formation of *endo*-metallacycles, activation of a C–Br bond leading to an *exo*-cycle is preferred over activation of a C–H bond leading to an *endo*-cycle.[11]

As shown in Scheme 2, the reaction of *cis*-$[Pt_2(4\text{-}MeC_6H_4)_4(m\text{-}SEt_2)_2]$ with imine 4-$ClC_6{=}H_4CH\ NCH_2(2\text{-}BrC_6H_4)$ (**1d**) in refluxing toluene produced compound **2d**, which contains a fivemembered *endo*-platinacycle and a newly formed C–C bond. Formation of compound **2d** suggests a process consisting of activation of the C–Br bond leading to a platinum(IV) compound with a five-membered *exo*-metallacycle followed by C–C bond formation between the benzyl group of the imine ligand and one of the *para*-tolyl ligands leading to a biaryl linkage.The subsequent C–H activation does not take place at the biaryl system; instead, a C–H bond of the benzylidene group is activated to produce a five-membered *endo*-metallacycle with elimination of a toluene molecule. The reaction of compound **2d** with triphenylphosphine in a 1 : 1 ratio produced derivative **3d** which was characterized using one- (^1H, ^{31}P, ^{195}Pt) and two-dimensional ($\{^1H\text{-}^1H\}$-COSY and NOESY, $\{^1H\text{-}^{13}C\}$-gHSQC) NMR spectroscopy. The molecular structure shown in Fig. 1 confirmed formation of both a five-membered *endo*-metallacycle and an aryl–aryl bond between one of the *para*-tolyl ligands and the benzyl ring which are tilted 63.9(4)° from each other. The resulting biaryl linkage is pointing away from the platinum centre in order to avoid steric crowding in the

coordination sphere. No further reaction, such as cleavage of the metallacycle, took place when an excess of triphenylphosphine was used and, in agreement with previous results for analogous cyclometallated compounds, this result indicates high stability of the metallacycle.[12]

For previously studied reactions using cis-[PtCl2(dmso)2] as platinum precursor and imines such as 2,6-$C_6H_3Cl_2CH{=}NCH_2Ph$, it has been reported that arene solvents such as benzene, toluene or xylenes were involved as reagents in the biaryl formation.[7b,d] However, for the precursor *cis*-$[Pt_2(4\text{-}MeC_6H_4)_4(\mu\text{-}SEt_2)_2]$, it has been confirmed that the tolyl group involved in the biaryl formation arises exclusively from a tolyl ligand of the platinum precursor, while the other tolyl ligand is eliminated as toluene in the final cyclometallation step.[6] In order to confirm that this is also the case in the reaction of *cis*-$[Pt_2(4\text{-}MeC_6H_4)_4(\mu\text{-}SEt_2)_2]$ with imine **1d** here reported, the reaction was also carried out in benzene as solvent and it was confirmed that compound **2d** was exclusively formed.

The results obtained for the reaction with imine **1d** indicated that biaryl formation may take place at the saturated arm of the N-benzylidenebenzylamine ligand, but, in spite of this, the final cyclometallation step produced an *endo*-metallacycle. In view of this result, imine 2,4,6-$(CH_3)_3C_6H_2CH{=}NCH_2(2\text{-}BrC_6H_4)$ (**1e**) was tested. The mesityl group was chosen in order to block the *ortho* positions of the benzylidene group and to drive the cyclometallation reaction towards the benzyl ring of the ligand. As shown in Scheme 2, C–C bond formation does indeed take place between the benzyl group of the imine ligand and one of the *para*-tolyl groups leading to a biaryl linkage. However, in contrast to previous results, the subsequent C–H bond activation does not take place at an aromatic site but instead an aliphatic C–H bond of the mesityl group is activated to produce a six-membered *endo*-metallacycle (compound **2e**). Due to the low stability of **2e**, the triphenylphosphine derivative **3e** was also prepared and fully characterised using one- and two-dimensional NMR techniques. As reported in a previouscommunication,[9] crystals of **3e**, just good enough for structure resolution, were obtained and the formation of an aryl–aryl bond and of a six-membered platinacycle was confirmed (Fig. 1). The resulting biaryl linkage is pointing away from the platinum centre and the two phenyl rings are tilted 66.3(4)◦ from each other. As for **3d**, the reaction with an excess of phosphine does not produce cleavage of the metallacycle.

Ligand 2,4,6-$(CH_3)_3C_6H_2CH{=}NCH_2(2\text{-}ClC_6H_4)$ (**1f**) was also tested and produced an analogous reaction to that reported for **1e** while ligand 2,4,6-$(CH_3)_3C_6H_2CH{=}NCH_2C_6H_5$ (**1g**) failed to react. These results confirm that intramolecular oxidative addition of the C–X bond (X = Br (**1e**) or Cl (**1f**)) to produce a platinum(IV) metallacycle is required for the process to take place, and the reaction does not proceed when there is not a C–X bond at the ortho positions of the benzyl group

as for **1g**. On the other hand, formation of a six-membered platinacycle through sp^3 C–H bond activation is remarkable, since a strong tendency to form five- *versus* six membered rings, as well as a preference for the activation of sp^2 over sp^3 C–H bonds, are generally observed in cyclometallation reactions.[13] In particular, platinacycles formed through aliphatic C–H bond activation are uncommon.[14] While activation of amethyl C–H bond of a mesityl group with formation of six membered metallacycles is well known at palladium,[15] such a process has not been observed in the reactions of imines **1d** or **1e** with platinum substrates *cis*-$[PtCl_2(dmso)_2]$[16] or *cis*-$[PtMe_2(\mu\text{-}SMe_2)]_2$,[11] which instead gave *exo*-metallacycles through activation of aromatic C–H or C–Cl bonds.

Our attention was then turned to imine 2-$(CH_3)C_6H_4CH{=}NCH_2(2\text{-}BrC_6H_4)$ (**1h**) which contains just one methyl group in the benzylidene group, so that competition between aromatic or aliphatic C–H bond activation can be addressed. In this case, upon reaction with cis-$[Pt_2(4\text{-}MeC_6H_4)_4(\mu\text{-}SEt_2)_2]$, compound **2h** was formed exclusively and the corresponding mono-phosphine derivative **3h** was also obtained and characterised. As for **3d**, the molecular structure (Fig. 1) confirms the formation of both a five membered *endo*-metallacycle and a biphenyl moiety (tilt angle: 52.0(2)◦). In this case, the biaryl linkage is pointing towards the bromo ligand as a result of the presence of a methyl substituent in the *ortho* position and the planarity of the metallacycle. As for imines **1d**–**1f**, the process consists of initial C–X (X = Br or Cl) bond activation, formation of a biaryl linkage and a final cyclometallation step which, in this case, takes place at the sp^2 C–H bond exclusively. It is therefore concluded that activation of an aromatic C–H bond is more favourable than that of an aliphatic C–H bond, and that activation of either of these bonds leading to an *endo*-metallacycle is more favourable than activation of an sp^2 C–H bond leading to an *exo*-metallacycle, which was not observed in these reactions.

Finally, the reaction of imine 2,6-$F_2C_6H_3CH{=}NCH_2(2\text{-}BrC_6H_4)$ (**1i**) with *cis*-$[Pt_2(4\text{-}MeC_6H_4)_4(\mu\text{-}SEt_2)_2]$ was tested with the aim that the fluorine atoms could efficiently block the cyclometallation at the benzylidene ring, and drive the reaction towards formation of an *exo*-metallacycle. Although C–F activation at platinum(II) has been reported for analogous systems, such a process is most favourable for polyfluorophenyl groups, and is not expected for the 2,6-difluoroaryl group.[17] Under the conditions reported for imines **1d**–**1h**, compound **2i** was obtained as a yellow oil, which could not be purified due to its low stability, along with moderate amounts of metallic platinum. Further reaction with triphenylphosphine led to the expected compound **3i**, containing an *exo*-five-membered metallacycle (shown in Scheme 2), along with formation of $[PtBr(4\text{-}CH_3C_6H_4)(PPh_3)_2]$ as a minor component. In order to confirm that the toluene solvent was not

involved in the reaction, and in an attempt to reduce the decomposition process—evidenced by formation of metallic platinum—the reaction was also carried out in benzene, a solvent with a lower boiling point. In this case, compound **3i** was also obtained and the yield was only slightly improved. Compound **3i** was characterised using one- and two-dimensional NMR techniques. A Z conformation of the imine bond, minimizing the steric effects around the platinum, is deduced based on the position and coupling of the imine resonance (δ = 9.79 [^{3}J(H–Pt) = 40.4 Hz]). The presence of an aromatic *AB* system, showing cross-peak signals with the methyl and the CH_2 resonances in the NOESY experiment, indicates that a five-membered ring is formed, leaving the *para*-tolyl ring unchanged. The molecular structure (Fig. 1) confirms the formation of both a five-membered *exo*-metallacycle and a biaryl linkage involving the metallated ring [tilt angle: 55.4(3)◦]. Bond lengths and angles are similar to those obtained for five-membered *endo*-metallacycles **3d** and **3h**. The sum of internal angles of the five-memberedmetallacycles is 530.7° which suggests a deviation fromplanarity, in contrast to the values obtained for the *endo*-cycles **3d** (539.4°) and **3h** (539.9°) which are close to 540◦, thus suggesting a planar arrangement.[16,18] The imine adopts a Z conformation which allows an intramolecular C(15)–H(15) · · · Br interaction [d(C · · · Br) = 3.289(6)Å] involving the imine group.

The reaction pathway shown in Scheme 3 is proposed for the formation of compound **2i**. Initial C–Br bond activation produces a platinum(**IV**) derivative (intermediate **A**) and is followed by reductive elimination with formation of an aryl–aryl bond (intermediate **B**). Assuming that C–F activation is not favoured, the final cyclometallation step could lead to either *exo*-five-or *exo*-seven-membered platinacycles through aromatic C–H bond activation (at positions indicated in Scheme 3 as ***a*** and ***b***, respectively). The results reported here reveal that the first option is the most favoured and this can be related to the higher stability generally reported for five-membered metallacycles.[13] In contrast, as reported in this work (compound **2d**) and elsewhere[6] formation of a seven-membered metallacycle is favoured when the imine moiety is included in the metallacycle (*endo*-cycles). Therefore, the presence of the imine bond is decisive in the formation of seven membered platinacycles.

On the other hand, formation of [PtBr(4-$CH_3C_6H_4$)(PPh_3)$_2$]—arising from intermediate **B**—along with **3i** in the reaction with PPh_3 can be taken as an indication that the final cyclometallation step is slower than for the *endo*-metallacycles (**2d**, **2e**, **2f** and **2h**). In addition, formation of metallic platinum could indicate a lower stability for **2i** compared to the *endo*-metallacycles. However, the reaction of **3i** with an excess of PPh_3 does not produce cleavage of the metallacycle, as for the more stable *endo*-metallacycles **3d** and **3e**.

3. CONCLUSION

The results reported here indicate that intramolecular C–X (X = Br or Cl) bond activation at the saturated arm of Nbenzylidene-benzylamines may promote, upon reaction with *cis*-[$Pt_2(4\text{-}MeC_6H_4)_4(\mu\text{-}SEt_2)_2$], the formation of a biaryl linkage between one of the tolyl ligands and the benzyl group of the imine ligand. In contrast to initially reported reactions,[6–8] the biaryl linkage is not necessarily involved in the subsequent metalation which leads to either *endo*-five (**2d**, **2h**), *endo*-six- (**2e**, **2f**) or *exo*-five (**2i**) membered platinacycles.

The proposed reaction path outlined for **2i** in Scheme 3 can be considered a general route for all the reactions reported here. The mechanism consists of: i) initial C–X (X = Br, Cl) bond activation to produce a platinum(IV) derivative **A**, ii) reductive elimination with formation of an aryl–aryl bond leading to intermediate **B**, iii) a final cyclometallation step with elimination of a toluene molecule arising from the tolyl ligand. The results here presented confirm that formation of intermediate **A** is required, since when there is not a C–X bond available for intramolecular oxidative addition the reaction fails, as observed for **1g**. In addition, formation of intermediate **B** allows cyclometallation at either the benzylidene (**1d**, **1e**, **1f** and **1h**) or the benzyl (**1i**) arms of the bifunctional imine. In addition, the following trends in reactivity could be deduced: Activation of an aromatic C–H bond is more favoured than that of an aliphatic C–H bond as shown for imine **1h**, and activation of either of these bonds leading to an *endo*-metallacycle is more favoured than activation of a sp^2 C–H bond leading to an *exo*-metallacycle, which was only achieved for imine **1i** in which two fluorine atoms block efficiently the *ortho* positions of the benzylidene ring. These results can be related to the higher stability of the *endo versus exo*-metallacycles (the so-called *endo* effect) which allows to overcome the low tendency to form six membered rings and to activate a sp^3 C–H bond as shown for imines **1e** and **1f**.

In summary, platinum-mediated C–C coupling between a coordinated *para*-tolyl group and the saturated arm of a Nbenzylidene-benzylamine can be achieved. In addition, the process here reported produces several novel types of platinum(II) cyclometallated compounds containing a biaryl linkage: i) *endo*-five membered with a Pt–C(sp^2) bond (**2d**–**2h**), ii) *endo*-six-membered with a Pt–C(sp^3) bond (**2e**–**2f**), and iii) *exo*-five membered with

247 a Pt–C(sp^2) bond (**2i**). As a whole, the results here presented expand the scope of a sequential
248 intramolecular process in which biaryl formation and cycloplatination take place in one pot
249 *via* a platinum(IV) intermediate.
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4. EXPERIMENTAL SECTION

General

Microanalyses were performed at the Serveis Cientifico-Tècnics (Universitat de Barcelona). Electrospray mass spectra were performed at the Servei d'Espectrometria de Masses (Universitat de Barcelona) 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; ^{19}F, 282.4 MHz), Mercury-400 (^{1}H, 400 MHz; ^{1}H-^{1}H-NOESY; ^{1}H-^{1}H-COSY; ^{1}H-^{13}C-gHSQC; ^{19}F, 376.5MHz) and Varian Inova DMX-500 (^{13}C) spectrometers, and referenced to SiMe4 (^{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.

Preparation of the compounds

cis-[Pt_2(4-MeC_6H_4)$_4$(μ-SEt_2)$_2$][19] and ligands **1c**, **1e**, **1f** and **1g**[10,11,16,20] were prepared as reported elsewhere.

Ligand 4-ClC_6H_4CH NCH_2(2-BrC_6H_4) (1d). This ligand was prepared from 0.30 g (1.35 mmol) of 2-bromobenzylamine hydrochloride which was treated with 75 mg of KOH in water. The mixture was extracted with diethyl ether, and the resulting organic layer was treated with sodium sulphate, filtered and evaporated to dryness. A solution of 0.19 g (1.35 mmol) of 4-chlorobenzaldehyde in 20 mL of ethanol was added to the residue and the resulting mixture was heated under reflux for 2 hours. The solvent was removed *in vacuo* to produce a white solid. Yield 300 mg (72%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.37 [s, 1H, CHN]; 7.73 [d, ^3J(H–H) = 6.8, 2H, H^1 or H^2]; 7.57 [dd, J(H–H) = 7.6, 1.0, 1H, H^3]; 7.42 [m, H^6]; 7.39 [d, ^3J(H–H) = 6.8, 2H, H^1 or H^2]; 7.30 [td, ^3J(H–H) = 7.6, 1.2, 1H, H^4 or H^5];

7.14 [td, ^{3}J(H–H) = 7.6, 1.2, 1H, H^{4} or H^{5}]; 4.88 [s, 2H, CH^{2}]. **ESI-MS**, *m/z*: 309.98 $[M+H]^{+}$.

Ligand 2-MeC_6H_4CH NCH_2(2-BrC_6H_4) (1h). This ligand was prepared from *ortho*-tolualdehyde following the same procedure as for **1d**. Yield 250 mg (64.2%). **^{1}HNMR** (400 MHz, $CDCl_3$): δ = 8.75 [s, 1H, CHN]; 7.95 [dd, ^{3}J(H–H) = 7.6, 4J(H–H) = 1.2, 1H]; 7.57 [dd, ^{3}J(H–H) = 8.0, ^{4}J(H–H) = 1.2, 1H]; 7.45 [dd, ^{3}J(H–H) = 7.6, ^{4}J(H–H) = 1.6, 1H]; 7.31 [m, 2H], 7.26 [m, 1H,]; 7.19 [d, ^{3}J(H–H) = 7.6, 1H]; 7.13 [td, ^{3}J(H–H) = 7.6, ^{4}J(H–H) = 1.6, 1H]; 4.90 [s, 2H, CH2]; 2.53 [s, 3H, CH_3]. **ESI-MS**, m/z: 290.04 $[M+H]^{+}$.

Ligand 2,6-$F_2C_6H_3CH$ NCH_2(2-BrC_6H_4) (1i). This ligand was prepared from 2,6-difluorobenzaldehyde following the same procedure as for **1d**. Yield 320 mg (76.4%). **^{1}H NMR** (400 MHz, CDCl3): δ = 8.63 [s, 1H, CHN]; 7.57 [dd, ^{3}J(H–H) = 8.0, ^{4}J(H–H) = 1.2, 1H, H^{3} or H^{6}]; 7.46 [dd, ^{3}J(H–H) = 7.6, ^{4}J(H–H) = 1.6, 1H, H^{3} or H^{6}]; 7.36 [t, ^{3}J(H–H) = 7.2, 1H, H^{2}]; 7.32 [td, ^{3}J(H–H) = 7.6, ^{4}J(H–H) = 1.6, 1H, H^{4} or H^{5}]; 7.14 [td, ^{3}J(H–H) = 7.6, ^{4}J(H–H) = 1.6, 1H, H^{4} or H^{5}]; 6.96 [t, ^{3}J(H–F) = ^{3}J(H–H) = 8.8, 2H, H^{1}]; 4.95 [s, 2H, CH_2]. **^{19}F NMR** (376.5 MHz, $CDCl_3$): d = -113.58 [t, ^{3}J(H–F) = 7.5]; **ESI-MS**, m/z: 312.02 $[M+H]^{+}$.

Compound [PtBr{2-$CH_3C_6H_3C_6H_4CH$=NCH_2(2-C_6H_4Br)}-SEt_2] (2c). This compound was obtained from76mg (0.21 mmol) of imine 1c and 100 mg (0.11 mmol) of compound *cis*-[Pt_2(4-MeC_6H_4)$_4$(μ-SEt_2)$_2$] in 20 mL of toluene. The mixture was heated for 4 hours under refluxing conditions. Insoluble materials were filtered off, the solvent was removed in a rotary evaporator and the residue was recrystallised in CH_2Cl_2/CH_3OH to yield white crystals. Yield: 90 mg (58%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.70 [d, ^{3}J(H–Pt) =

119.6, ^{4}J(H–H) = 1.6, 1H, CHN]; 7.99 [dd, ^{3}J(H–H) = 7.2, ^{4}J(H–H) = 1.6, 1H, H^{7}]; 7.48–7.45 [m, 1H]; 7.41–7.35 [m, 3H]; 7.30 [dd, ^{3}J(H–H) = 8.0; ^{4}J(H–H) = 1.2, 2H]; 7.23 [td, ^{3}J(H–H) = 7.6, ^{4}J(H–H) = 1.6, 1H]; 6.81 [d, ^{3}J(H–H) = 7.6, 1H, H^{3}]; 6.71 [dd, ^{3}J(H–H) = 7.6, ^{4}J(H–H) = 1.2, 1H, H^{2}]; 5.96 [d, ^{3}J(H–Pt) = 55.2, ^{4}J(H–H) = 1.0, 1H, H^{1}]; 5.76 [dd, ^{2}J(H–H) = 12.4; ^{4}J(H–H) = 2.0, 1H, CH_2N]; 4.99 [d, ^{2}J(H–H) = 12.4, ^{3}J(H–Pt) = 57.6, 1H, CH_2N]; {3.01 [s, br, 1H]; 2.66 [s, br, 2H]; 2.38 [s, br, 1H], SCH_2}; 2.08 [s, 3H, CH_3]; 1.19 [s, br., 3H, $SCCH_3$]; 0.92 [s, br., 3H, $SCCH_3$]. **ESI-MS**, m/z: 648.55 $[M\text{-}Br]^{+}$. **Anal.** calc. for $C_{25}H_{27}Br_2NSPt$: C: 41.22; H: 3.73; N: 1.92; S: 4.40%. Found: C: 41.3; H: 3.9; N: 2.2; S: 4.3%.

Compound [PtBr{4-ClC_6H_3CH=$NCH_2C_6H_4$(4-$CH_3C_6H_4$)}-SEt_2] (2d). This compound was obtained from 66 mg (0.21 mmol) of imine **1d** and 100 mg (0.11 mmol) of compound *cis*-[Pt_2(4-MeC_6H_4)4(μ-SEt_2)2] in 20 mL of toluene. The mixture was heated for 4 hours under refluxing conditions. The solvent was removed in a rotary evaporator to yield a red oil which could not be purified due to its low stability. The reaction was also carried out using benzene as a solvent and the same product was obtained. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.73 [s, 1H, CHN]; 5.40 [s, ^{3}J(H–H) = 22.2, 2H, NCH_2]; 3.36 [m, 2H, SCH_2]; 2.98 [m, 2H, SCH_2]; 2.38 [s, 3H, CH_3]; 1.38 [t, J(H–H) = 8.0, 6H, SCH_2CH_3].

Compound [PtBr{4-ClC_6H_3CH=$NCH_2C_6H_4$(4-$CH_3C_6H_4$)}-PPh_3] (3d). This compound was obtained from 66 mg (0.21 mmol) of imine **1d** and 100 mg (0.11 mmol) of compound *cis*-[Pt_2(4-MeC_6H_4)4(μ-SEt_2)2] in 20 mL of toluene. The mixture was heated for 4 hours under refluxing conditions. The solvent was removed in a rotary evaporator and a solution of 56 mg of PPh3 (0.21 mmol) in 20 mL of acetone was added to the residue. After stirring at room temperature for 2 hours, the solvent was removed and the residue was recrystallised in dichloromethane/methanol to produce a yellow solid. Yield: 126 mg (69%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.91 [d, ^{4}J(H–P) = 9.6, ^{3}J(H–Pt) = 92, 1H, CHN]; 7.75–

7.71 [m, 6H, PPh_3 ^{ortho}]; 7.56–7.53 [m, 1H, H^9]; 7.44–7.42 [m, 3H, $H^{6,7,8}$]; 7.37 [td, ^3J(H–H) = 8.0, ^4J(H–H) = 2.0, 9H, PPh_3 $^{meta, para}$]; {7.22 [^3J(H–H) = 8.0]; 7.19 [^3J(H–H) = 8.0], 4H, *AB* system, $H^{4,5}$}; 7.03 [d, ^3J(H–H) = 8.0, 1H, H^3]; 6.85 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 2.0, 1H, H^2]; 6.36 [t, ^4J(H–H) = 2, ^{3}J(H–Pt) = 55.6, 1H, H^1]; 5.52 [br. s, ^3J(H-Pt) *ca*. 20 Hz, 2H, CH_2]; 2.38 [s, 3H, CH_3]. **^{13}C NMR** (125.9 MHz, $CDCl_3$): δ = 177.24 [s, ^2J(C–Pt) = 84.6, CHN]; 148.38 [d, ^2J(C–P) = 5.8, ^1J(C–Pt) = 1103.4, C–Pt]; singlets at 144.96, 142.30, 137.68, 137.02, 130.53, 129.49 [aromatic carbon atoms]; 136.05 [d, ^3J(C–P) = 5.7, ^2J(C–Pt) = 96.0, C^1]; 135.35 [d, ^2J(C–P) = 11.3, PPh_3, C^{ortho}]; singlets at 130.88; 130.86; 130.39; 130.04 [$C^{6,7,8,9}$]; singlets at 129.18, 129.84 [$C^{4,5}$]; 128.55 [s, C^3]; 127.95 [d, ^3J(C–P) = 10.5, PPh_3, C^{meta}]; 127.72 [d, ^4J(C–P) = 2.5, PPh_3, C^{para}]; 122.93 [s, C^2]; 59.99 [s, ^2J(C–Pt) = 35.0, CH_2]; 21.21 [s, CH_3]. **^{31}P NMR** (121.4 MHz, $CDCl_3$): d = 20.50 [s, ^1J(P–Pt) = 4107.7]. **^{195}Pt NMR** (54 MHz, $CDCl_3$): d = -4243.0 [d, ^1J(P–Pt) = 4131.5]. **ESI-MS**, m/z: 776.17 $[M\text{-}Br]^+$. *Anal.* calc. for $C_{39}H_{32}BrClNPPt\cdot H_2O$: C: 53.58; H: 3.92; N: 1.60%. Found: C: 53.3; H: 3.6; N: 1.7%.

Compound [PtBr{$CH_2C_6H_2(CH_3)_2CH{=}NCH_2C_6H_4(4\text{-}CH_3C_6H_4)$}$SEt_2$] (2e). This compound was obtained from 68 mg (0.21 mmol) of imine **1e** using the same procedure as for **2d**. A yellow oil which could not be purified due to its low stability was obtained. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.23 [s, br., 1H, CHN]; {7.39 [m, 3H]; 7.23 [m, 1H]; 7.14 [m, 4H]; 6.72 [s, 1H, H^1 or H^2]; 6.57 [s, 1H, H^1 or H^2], aromatics}; 5.56 [s, ^3J(H–Pt) = 27.2, 2H, NCH_2]; 3.10 [m, 2H, SCH_2]; 2.70 [m, 2H, SCH_2]; 2.35 [s, 3H, CH_3 ^{c}]; 2.32 [m, 2H, CH_2Pt]; {2.18 [s, 3H]; 1.92 [s, 3H], CH_3 ^{a,b}}; 1.24 [t, ^3J(H–H) = 7.2, 6H, SCH_2CH_3].

Compound [PtBr{$CH_2C_6H_2(CH_3)_2CH{=}NCH_2C_6H_4(4\text{-}CH_3C_6H_4)$}$PPh_3$] (3e). This compound was obtained from 68 mg (0.21 mmol) of imine **1e** using the same procedure

as for **3d**. After partial removal of the solvent, yellow crystals were formed. Yield: 97 mg (54%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.30 [br. m, 1H, CHN]; 7.57–7.52 [m, 6H, PPh_3 ^{ortho}]; 7.49–7.47 [m, 2H]; 7.40–7.31 [m, 11H, PPh_3 $^{meta,\ para}$ + 2H]; {7.16 [^{3}J(H–H) = 8.0]; 7.13 [^{3}J(H–H) = 8.0], 4H, AB system, $H^{3,4}$}; 6.51 [s, 1H, H^{2}]; 5.67 [d, ^{4}J(H–H) = 2.0, ^{3}J(H–Pt) = 32.0, 2H, CH_2N]; 5.62 [s, 1H, H^{1}]; 2.35 [s, 3H,CH_3 ^{c}]; 2.06 [d, ^{4}J(H–P) = 4.0, ^{3}J(H–Pt) = 96.0, CH_2Pt]; 2.02 [s, 3H, CH_3 ^{b}]; 1.92 [s, 3H, CH_3 ^{a}]. **^{13}C NMR** (125.9 MHz, $CDCl_3$): δ = 160.27 [s, CHN]; singlets at 145.10, 142.99, 141.63, 138.22, 137.84, 136.95, 133.11, 130.97, 130.49 [aromatic carbon atoms]; 134.86 [d, ^{2}J(C–P) = 11.0, PPh_3, C^{ortho}]; 130.16 [d, 4J(C–P) = 2.0, PPh_3, C^{para}]; 129.15 [s, $C^{3,4}$]; 127.75 [d, ^{3}J(C–P) = 11.0, PPh3, C^{meta}]; singlets at 130.06; 129.95; 128.04; 127.42 [$C^{5,6,7,8}$]; 126.80 [s, C^{2}]; 125.37 [s, C^{1}]; 63.77 [s, NCH_2]; 21.36 [s, CH_3 ^{b}]; 21.07 [s, CH_3^{c}]; 18.40 [CH_3^{a}]; 14.70 [d, ^{1}J(C–P) = 4.0, J(C–Pt) = 630.0, CH_2Pt]. **^{31}P NMR** (121.4 MHz, $CDCl_3$): δ = 19.09 [s, J(P–Pt) = 4484.5]. **^{195}Pt NMR** (54 MHz, $CDCl_3$): δ = -4266.3 [d, J(P–Pt) = 4474.0]. **HR-ESI-MS**, m/z: 783.2458, calculated for $C_{42}H_{39}NPPt$ [M-Br] 783.2462; 824.2721, calculated for $C_{44}H_{42}N_2PPt$ [M-Br+CH_3CN] 824.2727. **Anal.** calc for $C_{42}H_{39}BrNPPt\cdot CH_2Cl_2$: C: 54.44; H: 4.35; N: 1.48%. Found: C: 54.2; H: 4.2; N: 1.6%.

Compound [PtCl{$CH_2C_6H_2(CH_3)_2CH{=}NCH_2C_6H_4(4\text{-}CH_3\text{-}C_6H_4)$}$PPh_3$] (3f). This compound was obtained as yellow crystals from 58 mg (0.21 mmol) of imine **1f** using the same procedure as for **3d**. Yield: 110 mg (63%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.26 [s, br., m, 1H, CHN]; 7.58–7.53 [m, 6H]; 7.46 [m, 2H]; 7.40–7.30 [m, 11H]; 7.14 [m, 4H]; 6.52 [s, 1H, H^{2}]; 5.71 [s, 1H, H^{1}]; 5.59 [d, ^{4}J(H–H) = 2.0, 2H, CH_2N]; 2.35 [s, 3H, CH_3^{c}]; 2.05 [d, ^{4}J(H–P) = 4.0, CH_2Pt]; 2.04 [s, 3H, CH_3^{b}]; 1.93 [s, 3H, CH_3 ^{a}]. **^{31}P NMR** (121.4 MHz, $CDCl_3$): δ = 18.54 [s, J(P–Pt) = 4482.1]. **ESI-MS**, m/z: 783.26 $[M–Cl]^{+}$. **Anal**. calc. for $C_{42}H_{39}ClNPPt$: C: 61.57; H: 4.80; N: 1.71%. Found: C: 61.3; H: 5.3; N: 2.0%.

Compound [PtBr{2-$CH_3C_6H_3CH$=$NCH_2C_6H_4$(4-$CH_3C_6H_4$)}-SEt_2] (2h). This compound was obtained from 62 mg (0.21 mmol) of imine **1h** using the same procedure as for **2d** using toluene as a solvent. An orange oil which could not be purified due to its low stability was obtained. **^{1}HNMR** (400 MHz, $CDCl_3$): δ = 8.05 [s, ^3J(H–Pt) = 124.8, 1H, CHN]; {7.64 [m, 1H]; 7.43 [d, ^3J(H–H) = 7.8, 1H]; 7.33 [m, 2H]; 7.26 [m, 4H], 7.17 [t, ^3J(H–H) = 7.2, 1H]; 7.04 [t, ^3J(H–H) = 7.8, 1H], 6.77 [d, ^3J(H–H) = 7.8, 1H], aromatics}; 5.45 [s, ^3J(H–Pt) = 27.3, 2H, NCH_2]; 3.38 [m, 2H, SCH_2]; 2.95 [m, 2H, SCH_2]; 2.38 [s, 3H, CH_3]; 2.29 [s, 3H, CH_3]; 1.36 [t, ^3J(H–H) = 7.5, 6H, SCH_2CH_3].

Compound [PtBr{2-$CH_3C_6H_3CH$=$NCH_2C_6H_4$(4-$CH_3C_6H_4$)}-PPh_3] (3h). This compound was obtained from 62 mg (0.21 mmol) of imine **1h** using the same procedure as for **3d**. After partial removal of the solvent, yellow crystals were formed. Yield: 135 mg (75%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.30 [d, ^4J(H–P) = 9.6, ^3J(H–Pt) = 94, 1H, CHN]; 7.77–7.72 [m, 6H, PPh_3 ^{ortho}]; 7.64 [dd, ^3J(H–H) = 6.8, ^4J(H–H) = 2.4, 1H]; 7.40–7.34 [m, 12H, $PPh_3$$^{meta,\ para}$ + 3H]; {7.27 [^3J(H–H) = 8.4]; 7.21 [^3J(H–H) = 8.4], 4H, **AB** system, $H^{4,5}$}; 6.60 [d, ^3J(H–H) = 7.2, 1H, H^3]; 6.42 [t, ^3J(H–H) = 7.6, 1H, H^2]; 6.33 [dd, ^3J(H–H) = 7.6, ^4J(H–P) = 3.2, 1H, H^1]; 5.58 [d, ^4J(H–P) = 3.6, ^3J(H–Pt) = 15.0, 2H, CH_2]; 2.38 [s, 3H, CH_3]; 2.30 [s, 3H, Me]. **^{31}PNMR**(121.4MHz, $CDCl_3$): δ = 22.85 [s, J(P–Pt) = 4169.7]. **ESI-MS**, m/z: 755.21, [M-Br]. **Anal.** calc. for $C_{40}H_{35}BrNPPt$: C: 57.49; H: 4.22; N: 1.68%. Found: C: 57.8; H: 4.4; N: 1.7%.

Compound [PtBr{C_6H_3(4-$CH_3C_6H_4$)CH_2N=CH(2,6-C_6H_3-F_2)}SEt_2] (2i). This compound was obtained from 66 mg (0.21 mmol) of imine **1i** using the same procedure as for **2d** in toluene. In this case, a moderate amount of metallic platinum was filtered off prior to solvent removal. A yellow oil which could not be purified due to its low stability was obtained. An analogous result was obtained when the reaction was carried out in benzene. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.71 [s, 1H, CHN]; 5.21 [s, ^3J(H–Pt) = 30.0, 2H, NCH_2];

3.28 [m, 2H, SCH_2]; 2.85 [m, 2H, SCH_2]; 2.41 [s, 3H, CH_3]; 1.39 [t, ^3J(H–H) = 7.5, 6H, SCH_2CH_3]. **^{19}F NMR** (282.4 MHz, $CDCl_3$): δ = -107.54 [t, ^3J(H–F) = 8.5].

Compound [PtBr{C_6H_3(4-$CH_3C_6H_4$)CH_2N CH(2,6-C_6H_3-F_2)}PPh_3] (3i). This compound was obtained from 66 mg (0.21 mmol) of imine **1i** using the same procedure as for **2d**. In this case, a moderate amount of metallic platinum was filtered off prior to solvent removal. Recrystallisation in CH_2Cl_2/MeOH mixtures led to [PtBr(4-$CH_3C_6H_4$)$(PPh_3)_2$] (*ca*. 10 mg) which was filtered off; further crystallisation produced a white-yellow solid (**3i**). Yield: 61 mg (33%). When the reaction was carried out in benzene the yield was 72 mg (39%). **^{1}HNMR** (400 MHz, $CDCl_3$): δ = 9.79 [d, ^4J(H–P) = 6.0, ^3J(H–Pt) = 40.4, 1H, CHN]; 7.87–7.45 [m, 6H, PPh_3^{ortho}]; 7.44–7.38 [m, 10H, $PPh_3^{meta,\ para}$ + $1H^{Ar}$]; {7.14 [^{3}J(H–H) = 8.0]; 7.08 [^{3}J(H–H) = 8.0], 4H, AB system, $H^{6,7}$}; 6.90 [t, ^{3}J(H–F) = 8.4, 2H, H^1]; 6.80 [d, ^{3}J(H–H) = 7.2, 1H]; 6.54 [m, 1H]; 6.45 [t, ^{3}J(H–H) = 7.6, 1H, H^2]; 4.97 [s, ^{3}J(H–Pt) = 25.0, 2H, CH_2]; 2.32 [s, 3H, CH_3]. **gHSQC-{^{1}H,^{13}C} NMR** (^{1}H: 400 MHz, $CDCl_3$): d (^{13}C) = 160.73 [CHN]; {136.31; 133.65; 125.53; 125.05, $C^{2,3,4,5}$};135.54 [PPh_3, C^{ortho}]; 130.59 [PPh_3, C^{meta}]; {128.51; 128.93, $C^{6,7}$}; 127.91 [PPh_3, C^{para}]; 111.99 [C^1]; 66.83 [CH_2]; 20.89 [CH_3]. **^{19}F NMR** (376.5 MHz, $CDCl_3$): δ = -106.34 [t, ^3J(H–F) = 8.4]. **^{31}P NMR** (121.4 MHz, $CDCl_3$): δ = 20.35 [s, ^1J(P–Pt) = 4285.3]. **^{195}Pt NMR** (54 MHz, $CDCl_3$): δ = -4045.6 [d, ^1J(P–Pt) = 4303.3]. ESI-MS, m/z: 777.18 [M-Br]+. **Anal.** calc. $C_{39}H_{31}BrF_2NPPt\cdot CH_2Cl_2$: C: 50.97; H: 3.53; N: 1.49%. Found: C: 50.8; H: 3.5; N: 1.1%.

X-ray structure analysis

Prismatic crystals were selected and mounted on a MAR345 diffractometer with an image plate detector. Intensities were collected with graphite monochromatized Mo Kα radiation. The structures were solved by direct methods using SHELXS computer program[21] and refined by the full-matrix least-squares method, with the SHELXL97 computer program

using 6984 (**2c**), 27088 (**3d**), 16366 (**3e**), 16162 (**3h**) and 16933 (**3i**) reflections (very negative intensities were not assumed). The function minimized was $\sum w \mid |Fo|^2 - |Fc|^2 \mid^2$, where $w = [\sigma^2(I) + (0.0447\ P)2 + 0.2738\ P]-1$ (**2c**), $w = [\sigma^2(I) + (0.0717\ P)^2 + 1.3414\ P]-1$ (**3d**), $w = [\sigma^2(I) + (0.0995\ P)^2 + 2.9343\ P]^{-1}$ (**3e**), $w = [\sigma^2(I) + (0.0592\ P)^2 + 0.2478\ P]^{-1}$ (**3h**) or $w = [\sigma^2(I) + (0.0810\ P)^2 + 2.0463\ P]^{-1}$ (**3i**) and $P = (|Fo|^2 + 2|Fc|^2)/3$. f, f' and f'' were taken from International Tables of X-ray crystallography.[22] All hydrogen atoms were computed and refined using a riding model with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom to which they are linked. Further details are given in Table 2.

ACKNOWLEDGEMENTS

We thank the Ministerio de Ciencia y Tecnología (project CTQ2009-11501) for financial support.

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Table 1 Selected bond lengths (Å) and angles (deg.) for compounds **2c, 3d, 3e, 3h** and **3i** with estimated standard deviations

Compound **2c**		Compound **3d**		Compound **3e**		Compound **3h**		Compound **3i**	
Pt–C(1)	1.994(4)	Pt(1)–C(20)	2.071(6)	Pt–C(22)	1.988(6)	Pt–C(1)	2.048(3)	Pt–C(1)	2.041(5)
Pt–S	2.2746(14)	Pt(1)–P(1)	2.2427(16)	Pt–P	2.1801(16)	Pt–P	2.2477(11)	Pt–P	2.2386(16)
Pt–N(1)	2.025(3)	Pt–N(1)	2.090(5)	Pt–N	2.055(4)	Pt–N	2.094(3)	Pt–N(1)	2.055(4)
Pt–Br(1)	2.5732(12)	Pt–Br(1)	2.5021(11)	Pt–Br	2.4417(10)	Pt–Br	2.4994(10)	Pt–Br	2.5017(13)
C(1)–Pt–N(1)	86.22(15)	C(20)–Pt(1)–N(1)	80.1(2)	C(22)–Pt–N	86.8(2)	C(1)–Pt–N	80.68(12)	C(1)–Pt–N(1)	81.4(2)
C(1)–Pt–S	88.60(11)	C(20)–Pt(1)–P(1)	95.53(16)	C(22)–Pt–P	90.32(17)	C(1)–Pt–P	95.15(10)	C(1)–Pt–P	96.14(16)
N(1)–Pt–Br(1)	90.09(11)	N(1)–Pt–Br(1)	93.27(15)	N–Pt–Br	87.73(13)	N–Pt–Br	90.63(8)	N(1)–Pt–Br	87.53(12)
S–Pt–Br(1)	95.09(4)	P(1)–Pt(1)–Br(1)	91.65(5)	P–Pt–Br	95.11(5)	P–Pt–Br	93.51(4)	P–Pt–Br	93.16(5)

Table 2. Crystallographic and refinement data for compounds **2c, 3d, 3e, 3h** and **3i**

	Compound **2c**	Compound **3d**	Compound **3e**	Compound **3h**	Compound **3i**
Formula	$C_{25}H_{27}Br_2NPtS$	$C_{39}H_{32}BrClNPPt$	$C_{42}H_{39}BrNPPt{\cdot}H_2O$	$C_{40}H_{35}BrNPPt$	$C_{39}H_{31}BrF_2NPPt{\cdot}0.5\ CH_2Cl_2{\cdot}H_2O$
Fw	728.45	856.08	881.73	835.66	918.10
Temp, K	293(2)	173(2)	293(2)	173(2)	173(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	$P2_1/c$	P-1	P-1	P-1
a, Å	10.039(4)	21.026(8)	12.032(5)	9.683(5)	9.508(4)
b, Å	10.075(6)	7.879(5)	12.230(4)	9.885(4)	11.237(4)
c, Å	12.819(5)	21.075(8)	12.715(3)	17.635(7)	18.529(6)
α, deg	90.85(2)	90	81.08(2)	85.59(2)	81.01(3)
β, deg	103.59(3)	108.56(2)	72.52(2)	82.01(2)	82.46(2)
γ, deg	90.42(3)	90	79.01(2)	82.75(2)	76.34(3)
V, Å3; Z	1260.0 (10); 2	3310(3); 4	1742.3(10); 2	1655.2(13); 2	1890.8(12);2
d (calcd), Mg/m3	1.920	1.718	1.681	1.677	1.613
Abs coeff, mm−1	8.834	5.605	5.254	5.523	4.920
F(000)	696	1672	872	820	898
Rflns coll./unique	13491/6984 [*R*(int) = 0.0435]	27088/9183 [*R*(int) = 0.0748]	16366/8758 [*R*(int) = 0.0627]	16162/8611 [*R*(int) = 0.0446]	16933/9453 [*R*(int) = 0.0587]
Data/restraint/parameters	6984/0/272	9183/1/399	8758/2/435	8611/2/400	9453/1/453
GOF on *F*2	1.129	1.090	1.087	1.125	1.080
$R1(I>2\sigma(I))$	0.0310	0.0563	0.0550	0.0344	0.0520
w*R*2 (all data)	0.0934	0.1659	0.1579	0.0927	0.1526
Peak and hole, e.Å^{-3}	1.250 and −1.040	2.829 and −0.909	1.802 and −2.558	2.138 and −1.164	2.114 and −1.466

Figures Captions

Scheme 1. Previously reported formation of seven-membered platina cycles (ref. 6).

Scheme 2. Synthetic method (i): + 0.5 $[Pt_2(4\text{-}MeC_6H_4)_4(m\text{-}SEt_2)_2]$ in refluxing toluene or benzene for 4h; (ii): + PPh_3 (1 : 1) in acetone at RT for 2 h.

Figure 1. Molecular structures of compounds showing 50% probability ellipsoids: (a): **2c**; (b): **3d**; (c): **3e**; (d): **3h** and (e): **3i**.

Scheme 3 Proposed reaction pathway for the formation of **2i** and phosphine derivatives (i): Intramolecular C–Br bond activation; (ii): Reductive elimination with formation of an aryl–aryl bond; (iii): Cyclometallation at the **a** position; (iv): Reaction with PPh3.

546 **Scheme 1**

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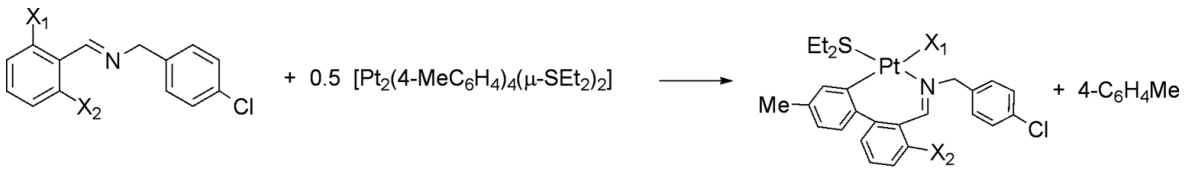

1a X_1 = Br; X_2 = H
1b X_1 = X_2 = Cl

2a X_1 = Br; X_2 = H
2b X_1 = X_2 = Cl

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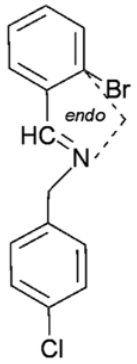
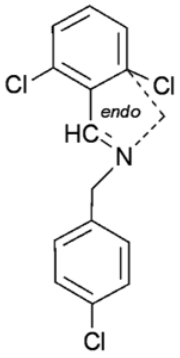
Chart 1

a) Previously studied ligands (ref 6) leading to *endo*-metallacycles

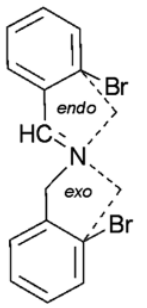


1a

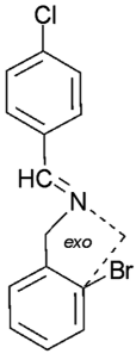


1b

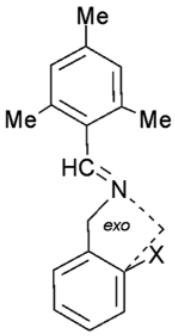
b) Ligands under study in the present work aimed at formation of *exo*-metallacycles[a]



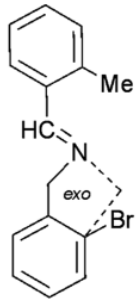
1c



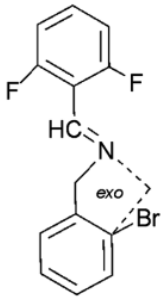
1d



1e X = Br
1f X = Cl
1g X = H



1h



1i

[a] Part of the work involving imine **1e**, **1f**, and **1g** has been published in a preliminary communication (ref.9)

Scheme 2

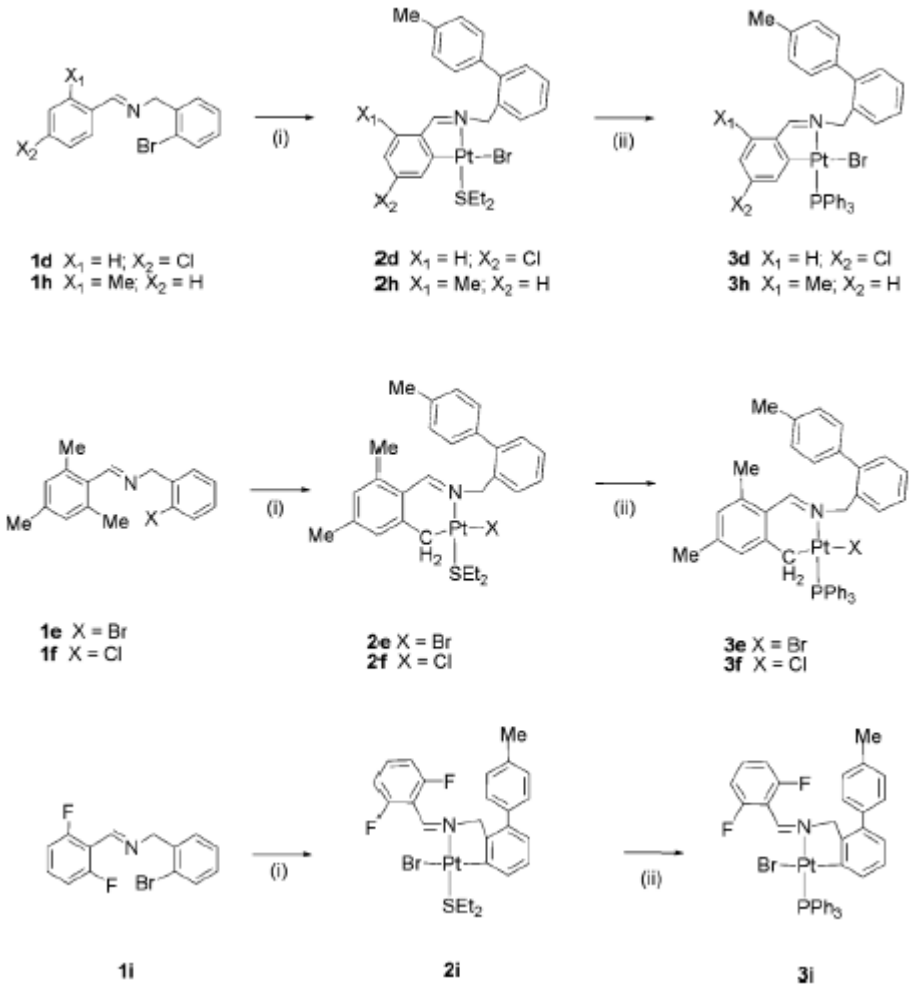
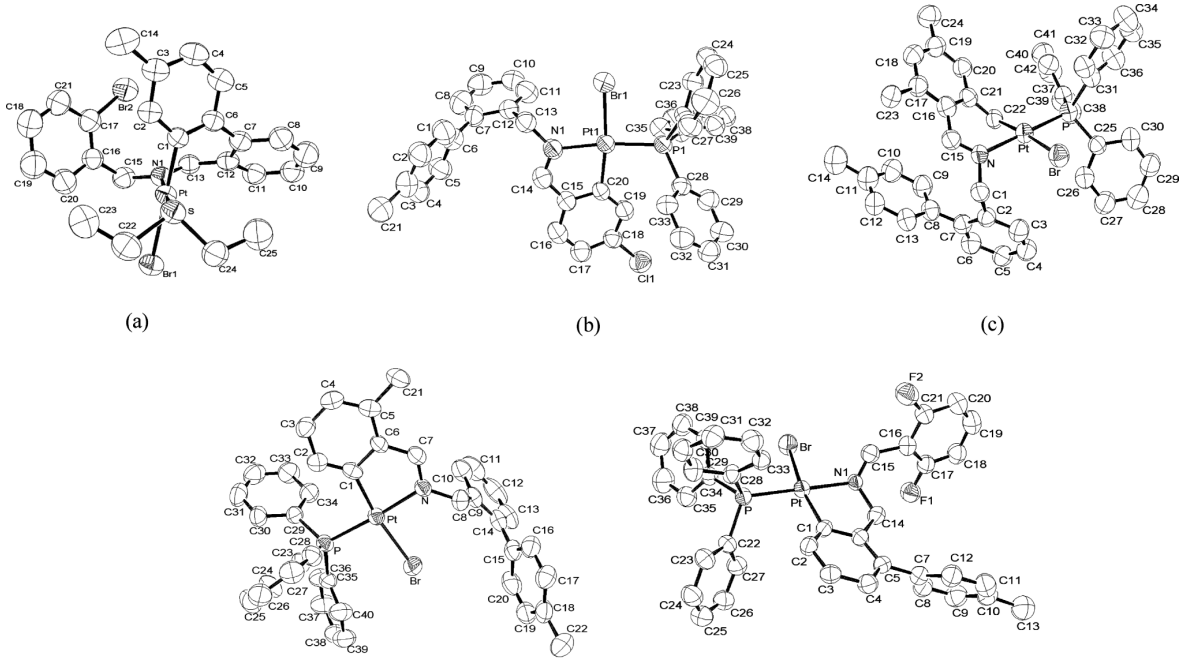
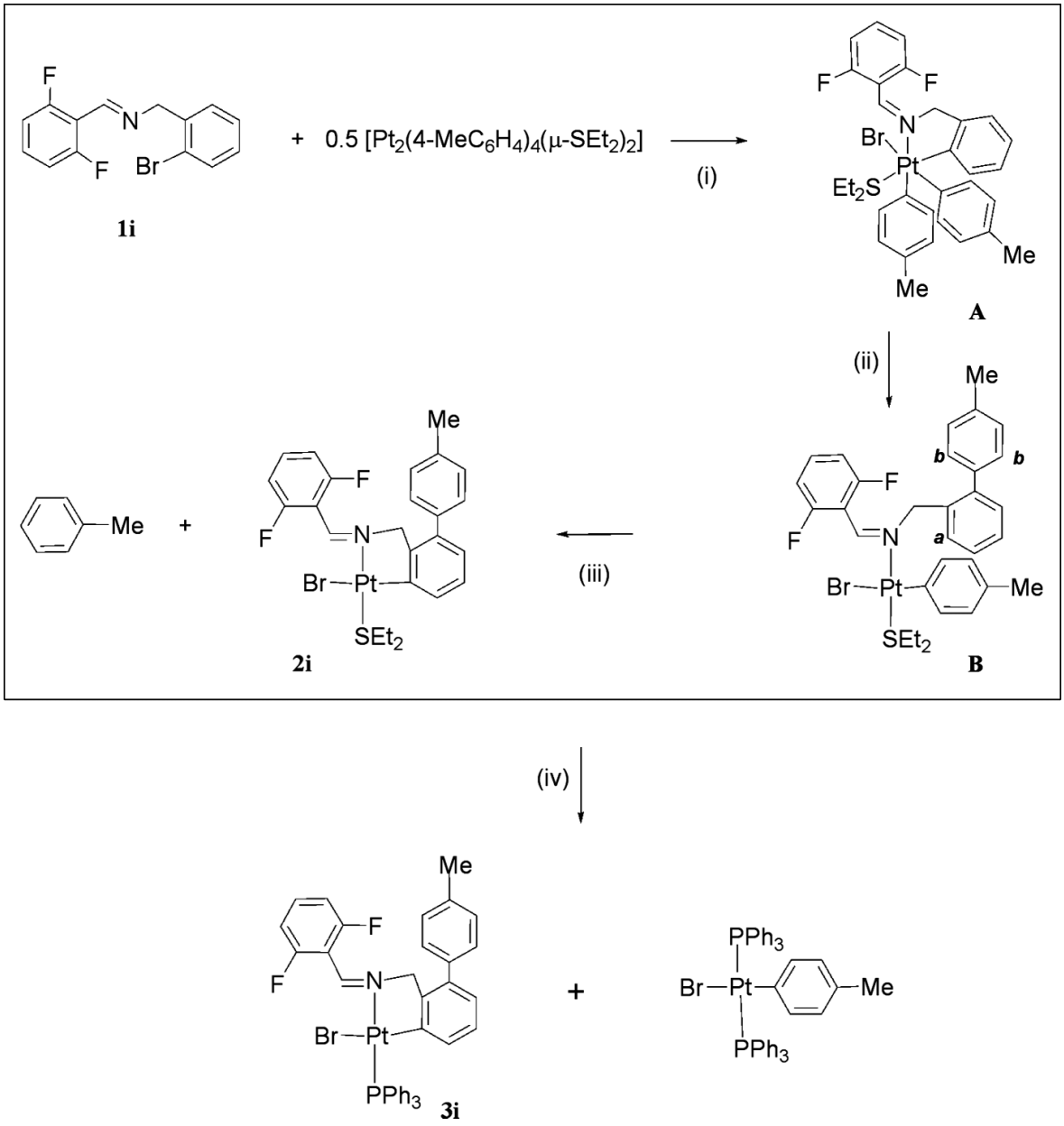

Me
X1
X2
N
Br
(i)
Pt
SEt2
(ii)
PPh3
1d X1 = H; X2 = Cl
1h X1 = Me; X2 = H
2d X1 = H; X2 = Cl
2h X1 = Me; X2 = H
3d X1 = H; X2 = Cl
3h X1 = Me; X2 = H
1e X = Br
1f X = Cl
2e X = Br
2f X = Cl
3e X = Br
3f X = Cl
F
1i
2i
3i

Figure 1



588 **Scheme 3**



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