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A comparative study of metallating agents in the synthesis of [C,N,N']-cycloplatinated compounds derived from biphenylimines

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Abstract

The reactions of ligands 4-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$ (**1a**) and 2-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$ (**1b**) in front of *cis*-[$PtCl_2(dmso)_2$] or *cis*-[$PtPh_2(SMe_2)_2$] produced compounds [$PtCl_2${4-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$}] (**2aCl**) and [$PtCl_2${2-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$}] (**2bCl**) or [$PtPh_2${4-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$}] (**2aPh**) and [$PtPh_2${2-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$}] (**2bPh**). From all these compounds, the corresponding cyclometallated [C,N,N'] platinum(II) compounds **3aCl**, **3bCl**, **3aPh** and **3bPh** were obtained although under milder conditions and with higher yields for the phenyl derivatives. The reaction of compounds **3aPh** and **3bPh** with methyl iodide gave cyclometallated [C,N,N'] platinum(IV) compounds **4aPh** and **4bPh** of formula [PtMePhI{$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}]. Compounds **3aCl** and **3bCl** containing a chloro ligand, although unreactive towards methyl iodide, undergo oxidative addition of chlorine to produce the corresponding platinum(IV) compounds [$PtCl_3${4-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**6aCl** and **6bCl**). All compounds were characterised by NMR spectroscopy and crystal structures of compounds **3bCl** and **6bCl** are also reported.

Keywords: Platinum; Imines; Biphenyl; Cyclometallation; Crystal structure

1. Introduction

Different synthetic strategies have been reported in the synthesis of [C,N,N'] cyclometallated compounds including the use of a variety of metallating substrates such as *cis*-[$PtCl_2(dmso)_2$] [1], [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] [2] and *cis*-[$PtPh_2(SMe_2)_2$] [3] among others. For all these systems, the labile sulfoxide or sulfide ligands are easily replaced by the two nitrogen atoms of the ligands leading to isolation of [N,N'] coordination compounds which are precursors for the cyclometallated derivatives. Different mechanisms may operate in each case for the actual C–H bond activation [4]. When [$PtCl_2(dmso)_2$] is used, electrophilic substitution on the aromatic carbon with release of HCl takes place while oxidative addition followed by reductive elimination of methane or benzene occurs for the other substrates.

In order to compare the ease of formation of both [N,N'] and [C,N,N'] platinum(II) compounds as well as the reactivity of the resulting compounds towards oxidative addition of alkyl halides, we now report the reactivity of ligands 4-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$ (**1a**) and 2-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$ (**1b**) containing 2- or 4-biphenyl groups in front of *cis*-[$PtCl_2(dmso)_2$] and *cis*-[$PtPh_2(SMe_2)_2$] in order to complete the results recently reported involving [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] as metallating substrate [5]. In addition, these ligands allow to consider the influence in these reactions of the phenyl substituent in 2- or 4-positions.

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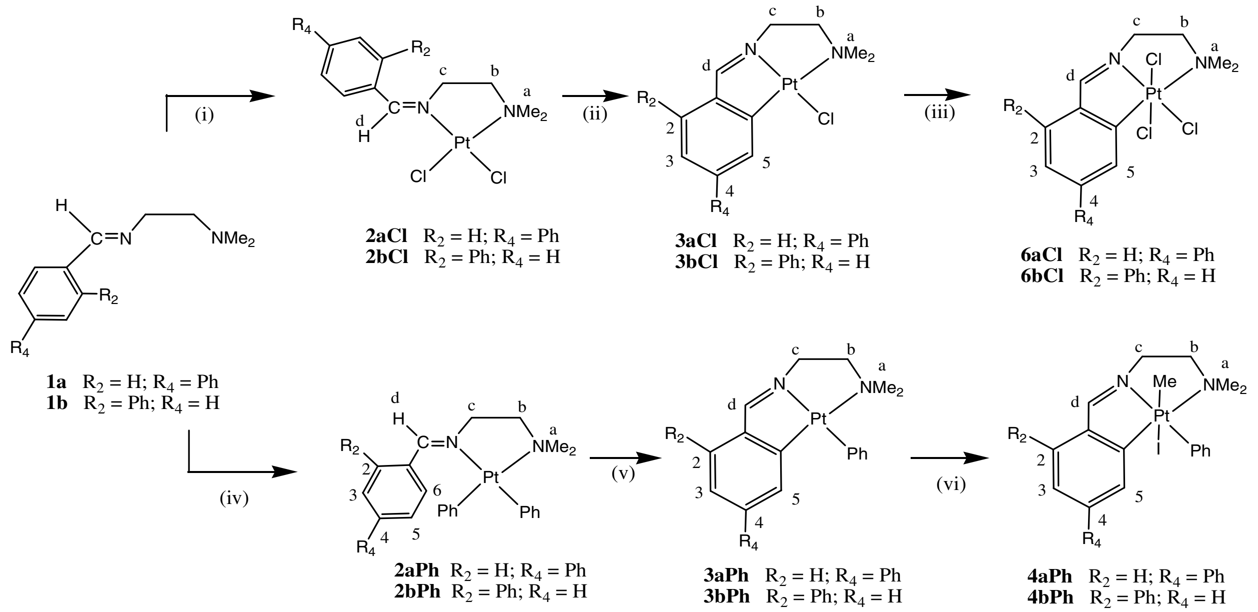
2. Results and discussion

2.1. *[N,N′] platinum compounds*

Ligands **1a** and **1b** were prepared as the *E* conformer following the reported procedure [5] and their reactions with *cis*-$[PtCl_2(dmso)_2]$ and *cis*-$[PtPh_2(SMe_2)_2]$ were studied. Previous work [6] indicated that dimethylsulfide is a worse leaving ligand than dimethylsulfoxide for platinum(II) and for this reason *cis*-$[PtCl_2(dmso)_2]$ was used as starting material. When equimolar amounts of this compound and ligand **1a** or **1b** were refluxed in methanol during 4 h, the corresponding compounds $[PtCl_2\{4\text{-}C_6H_5C_6H_4CHNCH_2CH_2NMe_2\}]$ (**2aCl**) and $[PtCl_2\{2\text{-}C_6H_5C_6H_4CHNCH_2CH_2NMe_2\}]$ (**2bCl**) were obtained in good yields (see Scheme 1). These compounds although scarcely soluble in most common solvents could be characterised by ^1H and ^{195}Pt NMR spectra. Evidence of coordination of both nitrogen atoms to platinum is obtained from the fact that both methylamine and imine protons are coupled to ^{195}Pt nucleus ($J(H\text{–}Pt) = 36.0$ and 59.0 Hz (**2aCl**) and 31.0 and 58.4 Hz (**2bCl**), respectively). As previously noticed for analogous systems [1f], a *Z* conformation around the C=N bond is adopted with the imine proton close to the platinum nucleus which is evidenced by the downfield shift of the imine signal ($\delta = 9.56$ (**2aCl**) and 9.64 (**2bCl**)). This fact suggests that coordination of a bidentate ligand to a $PtCl_2$ moiety produces a conformational change from the most stable *E* conformation of the free ligand to the *Z* and, consequently, *Z*–*E* isomerisation should precede the cyclometallation step as previously reported for analogous systems [1f]. Evidence of this isomerisation process was obtained when **2aCl** was refluxed in dichloromethane for 10 h since in the ^1H NMR spectrum of the final mixture new signals corresponding to the *E* isomer were observed, the ratio *E*:*Z* being 0.8:1. Under the same experimental conditions, isomerisation was not observed for the 2-biphenylderivative **2bCl** in agreement with the higher crowding in the platinum coordination sphere arising from the presence of a phenyl substituent in *ortho*.

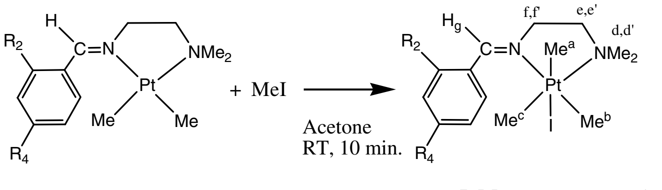
On the other hand, dialkylsulfide ligands have been reported to be readily displaced from diarylplatinum(II) complexes [7] and accordingly, the reactions of ligands **1a** or **1b** with *cis*-$[PtPh_2(SMe_2)_2]$ proceed under milder conditions than those reported for *cis*-$[PtCl_2(dmso)_2]$. The reactions carried out in acetone at room temperature produced compounds $[PtPh_2\{4\text{-}C_6H_5C_6H_4CHNCH_2CH_2NMe_2\}]$ (**2aPh**) and $[PtPh_2\{2\text{-}C_6H_5C_6H_4CHNCH_2CH_2NMe_2\}]$ (**2bPh**) in good yields. The obtained compounds are soluble in most common solvents and were characterised by ^1H, ^{13}C and ^{195}Pt NMR spectroscopies. In addition 2D-NOESY and ^1H–^{13}C gHSQC (**2aPh**) NMR spectra were also taken. As for compounds above, dimethylamine protons are coupled to platinum, and in agreement with the higher *trans* influence of phenyl versus chloro ligand, the $J(H\text{–}Pt)$ values are in this case smaller. 2D-NOESY experiments suggest an *E* conformation across the C=N bond which is the most favoured conformation of the free ligands as well as the adequate arrangement for producing cyclometallation at the biphenyl group. Although this result suggests that steric crowding in the coordination sphere of the platinum(II) centre is not too severe, isomerisation to the less congested *Z* form takes place in solution at room temperature. This process occurred



Scheme 1. (i) +*cis*-$[PtCl_2(dmso)_2]$, MeOH, reflux, 4 h; (ii) +$Na(CH_3COO)$, MeOH, reflux, 12 h; (iii) +Cl_2 in CH_3CN, RT, 10 min; (iv) +*cis*-$[PtPh_2(SMe_2)_2]$, acetone, RT, 30 min; (v) toluene, reflux, 6h; (vi) MeI, acetone, RT, 30 min.

faster and in a larger extension for the 2-biphenyl derivative **2bPh** since after 4 h the ratio *Z*:*E* was 2:1 while for **2aPh** after 48 h the ratio *Z*:*E* was 0.8:1. In both cases, the *E* to *Z* isomerisation is evidenced by a decrease in *J*(H–Pt) value of the imine proton from 46.4 (**2aPh**) or 43.4 Hz (**2bPh**) to 24.0 and 27.2 Hz, respectively. Such an isomerisation has not been observed previously for compounds such as $[PtPh_2\{C_6H_5CHNCH_2CH_2NMe_2\}]$ [3] or methyl derivatives $[PtMe_2\{C_6H_5C_6H_4CHNCH_2CH_2NMe_2\}]$ [5] which suggests that the combined effect of two phenyl ligands and a dangling biphenyl group in **2aPh** and **2bPh** increases the steric bulk in the coordination sphere which is minimised by conformational changes.

Analyses of the δ (^{195}Pt) values show that those obtained for **2aPh** and **2bPh** are very close to the previously reported for analogous [PtMe$_2$(*NN'*)] compounds [5], that is in the range expected for a platinum(II) centre coordinated to two nitrogen and two carbon atoms [8]. However, when C donor ligands (methyl or phenyl) are replaced by chloro ligands as in **2aCl** and **2bCl**, the ^{195}Pt resonance is downfield shifted. In order to gain more insight into the chemistry of these compounds as well as to evaluate whether δ (^{195}Pt) values can be taken as a measure of the reactivity at the platinum centre, the reactions of compounds **2aCl**, **2bCl**, **2aPh** and **2bPh** with methyl iodide were studied along with those of methyl analogues $[PtMe_2\{4\text{-}C_6H_5C_6H_4CHNCH_2CH_2NMe_2\}]$ (**2aMe**) and $[PtMe_2\{2\text{-}C_6H_5C_6H_4CHNCH_2CH_2NMe_2\}]$ (**2bMe**) previously described. As shown in Reaction (1), compounds **2aMe** and **2bMe** reacted with methyl iodide under very mild conditions to produce an oxidative addition process leading to platinum(IV) compounds **5aMe** and **5bMe** which were characterised by NMR spectroscopy and analytical data. Under the same conditions or even using longer reaction times up to 48 h, compounds **2aCl** and **2bCl** were recovered unaltered; their lower tendency to experiment an oxidative addition process can be related to their lower electronic density at the platinum(II) centre evidenced by their δ (^{195}Pt) values. Unfortunately, the reactions of **2aPh** and **2bPh** with methyl iodide did not produce clear results leading to some decomposition process evidenced by formation of metallic platinum and aldehyde. When these reactions were monitored by ^1H NMR spectroscopy, in the early stages of the reaction, resonances that could be tentatively assigned to platinum(IV) derivatives were observed [9] although overlapped with those corresponding to the platinum(II) precursors. After a short time, these signals disappear to give a complex mixture in which only the corresponding cation $C_6H_5C_6H_4CHNCH_2CH_2NMe_3^+$ could be identified by a peak at 267 in the FAB-mass spectra. These results suggest that, according to the ^{195}Pt NMR results, the electronic density at the metal centre for diphenylplatinum(II) compounds is high enough as to allow for oxidative addition to take place, however, the steric crowding resulting from the presence of two phenyl ligands and a biphenyl moiety along with the increased bulk of octahedral versus square-planar platinum centre [10] led to decomposition of the resulting compounds



2aMe $R_2 = H; R_4 = Ph$
2bMe $R_2 = Ph; R_4 = H$
5aMe $R_2 = H; R_4 = Ph$
5bMe $R_2 = Ph; R_4 = H$

(1)

2.2. Cyclometallated [*C*,*N*,*N'*] platinum compounds

Compounds **2** containing the imine ligand coordinated through both nitrogen atoms to platinum(II) might be precursors of cyclometallated [*C*,*N*,*N'*] platinum(II) compounds. Intramolecular C–H bond activation may lead to formation of five-membered metallacycles and, in the case of compounds derived from ligand **1b**, formation of a seven-membered metallacycle, as shown in Fig. 1, can also be considered.

The most widely used conditions for converting compounds analogous to **2aCl** and **2bCl** into cycloplatinated derivatives are refluxing for several hours in either toluene or in a donor solvent such as methanol or ethanol, in some cases in the presence of an external base which favours the formal elimination of HCl [1]. Following the conditions used in the preparation of $[PtCl(C_6H_4CHNCH_2CH_2NMe_2)]$ [1f], **2aCl** was treated with an equimolar amount of sodium acetate in refluxing methanol during 12 h to produce $[PtCl\{4\text{-}C_6H_5C_6H_3CHNCH_2CH_2NMe_2\}]$ (**3aCl**) while formation of $[PtCl\{2\text{-}C_6H_5C_6H_3CHNCH_2CH_2NMe_2\}]$ (**3bCl**) from **2bCl** under the same conditions required a reaction time of 48 h and careful control of the temperature in order to avoid formation of metallic platinum. In both cases, the yield obtained for metallation at the biphenyl group is slightly lower than that obtained for the phenyl derivative $[PtCl(C_6H_4CHNCH_2CH_2NMe_2)]$ [1f]. The process requires an initial step in which *Z* to *E* imine isomerisation brings the aryl ring closer to platinum followed by the actual intramolecular C–H bond activation which in both cases lead to five-membered metallacycles.

Compounds **3aCl** and **3bCl** depicted in the scheme were characterised by ^1H, ^{13}C and ^{195}Pt NMR spectra and

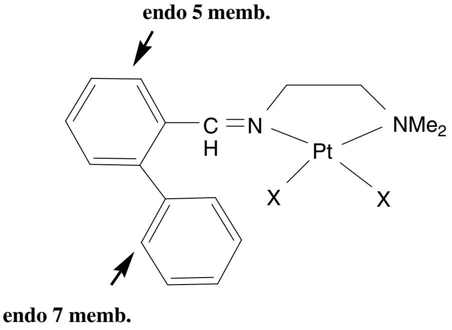


Fig. 1. Metallation sites for compounds derived from ligand **1b**.

elemental analyses, and **3bCl** was also characterised crystallographically. The ^3J(H–Pt) value for the methylamine proton decreases from **2aCl** or **2bCl** to the corresponding cyclometallated derivatives **3aCl** and **3bCl** as a result of the higher *trans* influence of aryl versus chloro ligands. Conversely, an increase in the coupling constant of the imine proton to platinum is observed upon cyclometallation. In addition, the coupling to platinum of the aromatic proton adjacent to the metallation site (H^5) and the presence of signals corresponding to eight $C_{aromatic}$–H atoms in the ^{13}C NMR spectra confirm that metallation took place.

Compounds [PtPh{4-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**3aPh**) and [PtPh{2-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**3bPh**) were obtained after refluxing a toluene solution of **2aPh** or **2bPh**, respectively, during 6 h. Although some decomposition took place, as evidenced by formation of metallic platinum, the cyclometallated compounds were isolated in good yield in a process involving intramolecular activation of a $C_{aromatic}$–H bond along with elimination of benzene [3]. As for compounds described above in both cases five-membered metallacycles are formed leading to a [*C*,*N*,*N′*] cyclometallated compounds. Compounds **3aPh** and **3bPh** (see Scheme 1) were characterised by elemental analyses and NMR spectra (^{1}H, ^{13}C, ^{195}Pt and gHSQC). The coupling constant of the imine proton to platinum increases slightly from compounds **2aPh** and **2bPh** (*E* conformers) to the corresponding cyclometallated compounds as a result of the formation of a metallacycle. The presence of nine cross-peak signals in the aromatic region of the ^{1}H–^{13}C heterocorrelation spectra supports the proposed structures. Metallation of the dichloro compounds produces a large upfield shift of the ^{195}Pt resonance (ca. 1200 ppm) as a result of replacing a chloro ligand for an aryl group. However, the analogous process at the diphenyl compounds produces only a moderate upfield shift (ca. 160 ppm) since in this case there is no change in the donor atoms set at the coordination sphere of platinum.

The reactivity with methyl iodide was also tested for all the obtained cyclometallated platinum(II) compounds and striking differences were obtained between compounds containing a chloro or a phenyl ligand in spite of the fact that δ (^{195}Pt) values are in the same range for these two types of compounds. Compounds **3aCl** and **3bCl** were recovered unaltered after treating their acetone solutions with a large excess of methyl iodide during 48 h. On the other hand, both **3aPh** and **3bPh** reacted with methyl iodide to produce an oxidative addition process leading to cyclometallated platinum(IV) compounds [PtMePhI{4-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**4aPh**) and [PtMePhI{2-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**4bPh**) which were characterised by NMR spectroscopy, FAB mass spectra and analytical data. In particular 2D-NOESY experiments in which the methyl-platinum resonance show a cross-peak with only one of the two diastereotopic NMe_2 resonances support the proposed structure (see Scheme 1) in which the methyl ligand is in an axial position [11]. This is the expected geometry assuming that the oxidative addition of methyl iodide takes place in *trans* and that no further isomerisation of the resulting platinum(IV) compound occurs [12]. The *J*(H–Pt) value for the methylplatinum and the dimethylamino groups are in the range expected for a platinum(IV) compound and the δ (^{195}Pt) values appear downfield shifted when compared to the platinum(II) precursors. The easy formation of [*C*,*N*,*N′*] platinum(IV) compounds from **3aPh** and **3bPh** is a similar result to that previously reported for the methyl analogues [PtMe{$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] [5]. The success of this reaction compared with the poor results obtained for the [*N*,*N′*] coordination compounds **2aPh** and **2bPh** can be related to the higher stability imparted by the terdentate coordination of the ligand in **3aPh** and **3bPh**.

Finally, a new cyclometallated platinum(IV) compound [$PtCl_3${2-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**6bCl**), formally arising from chlorine addition to **3bCl** was obtained unexpectedly in an attempt to crystallise **2bCl** directly from equimolar amounts of *cis*-[$PtCl_2(dmso)_2$] and **1b** mixed in dichloromethane. The structure resolution (see below) of the crystals obtained after slow evaporation along one week reveals the formation of platinum(IV) compound **6bCl**. Although oxidative addition reactions have been extensively performed on square-planar organoplatinum species containing nitrogen ligands [12], relatively few examples of cyclometallated platinum(IV) compounds obtained by halogen addition have been reported [13]. On the other hand, several platinum(IV) cyclometallated compounds with a *fac*-$PtCl_3$ arrangement have been obtained through deoxygenation of coordinated dimethylsulfoxide [6]. In agreement with those results, formation of **6bCl** in dichloromethane could arise from oxidation of platinum(II) to platinum(IV) along with reduction of dmso to SMe_2. However, attempts to obtain compound **6bCl** in a preparative scale from *cis*-[$PtCl_2(dmso)_2$] and **1b** in dichloromethane were unsuccessful since only compound **2bCl** and a small amount of 2-biphenylcarboxaldehyde were detected in the ^{1}H NMR spectra of the resulting mixture.

The reactions of **3aCl** and **3bCl** with chlorine in acetonitrile were carried out following the procedure reported in the literature [13a] and, as depicted in the scheme, yielded compounds **6aCl** and **6bCl**. These were characterised by ^{1}H NMR and ES-Mass spectra. For both compounds, the *J*(H–Pt) value obtained for the imine proton (ca. 100 Hz) is smaller than that observed for the platinum(II) precursors (ca. 140 Hz) in agreement with the higher oxidation state of the platinum centre. The ^{1}H NMR of **6bCl** was coincident with that of the crystals obtained but, although it is confirmed that oxidative addition of chlorine to compounds **3aCl** and **3bCl** is possible, the mechanism of the unexpected formation of crystals of **6bCl** remains unclear.

2.3. Crystal structures

Suitable crystals of **3bCl** and **6bCl** were grown in acetone and dichloromethane, respectively. The crystal

Table 1
Selected bond lengths (Å) and angles (°) with estimated standard deviations

Compound ***3bCl***			
Pt–C(1)	2.009(6)	Pt–Cl	2.302(2)
Pt–N(1)	1.967(6)	Pt–N(2)	2.168(7)
N(1)–C(13)	1.292(8)	N(1)–C(14)	1.441(10)
N(2)–C(15)	1.486(12)	C(1)–C(6)	1.425(9)
C(6)–C(13)	1.436(10)	C(14)–C(15)	1.373(12)
C(1)–Pt–N(1)	81.1(3)	C(1)–Pt–Cl	98.8(2)
N(1)–Pt–N(2)	83.5(2)	Cl–Pt–N(2)	96.66(18)
Compound ***6bCl***			
Pt–N(1)	1.982(5)	Pt–C(11)	2.039(7)
Pt–N(2)	2.300(6)	Pt–Cl(3)	2.314(2)
Pt–Cl(1)	2.324(2)	Pt–Cl(2)	2.329(2)
N(1)–C(13)	1.243(8)	N(1)–C(14)	1.500(8)
N(2)–C(16)	1.395(16)	N(2)–C(17)	1.489(10)
N(2)–C(15)	1.604(12)	C(11)–C(12)	1.407(9)
C(12)–C(13)	1.455(9)		
N(1)–Pt–C(11)	80.2(2)	N(1)–Pt–N(2)	83.5(2)
N(1)–Pt–Cl(3)	90.08(17)	C(11)–Pt–Cl(3)	87.30(18)
N(2)–Pt–Cl(3)	92.2(2)	C(11)–Pt–Cl(1)	99.76(19)
N(2)–Pt–Cl(1)	96.58(16)	Cl(3)–Pt–Cl(1)	91.61(9)
N(1)–Pt–Cl(2)	88.69(16)	C(11)–Pt–Cl(2)	88.53(18)
N(2)–Pt–Cl(2)	91.6(2)	Cl(1)–Pt–Cl(2)	89.61(9)

structures are composed of discrete molecules separated by van der Waals interactions. Selected bond lengths and angles are given in Table 1 and molecular views are shown in Figs. 2 and 3.

In both cases the structures deduced from NMR studies are confirmed. For **3bCl** and **6bCl**, the ligand behaves as $[C,N,N']$-tridentate and three fused [6,5,5] ring systems containing a five-membered *endo* metallacycle are formed. For **3bCl**, a chloro ligand completes the square-planar coordination of the platinum atom, while for **6bCl** an octahedral coordination with the tridentate ligand in a meridional arrangement is displayed.

In both cases the metallacycles are approximately planar and nearly coplanar with both the metallated phenyl and the mean coordination plane. Bond lengths and angles are very similar for **3bCl** and **6bCl**, in agreement with a previous comparison between platinum(II) and platinum(IV) analogues [13a], and to those reported for [PtMe{2-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] [5]. Most bond angles at platinum are close to the ideal value of 90°, and the smallest angles correspond to those involving the ligand: "bite" angles C(phenyl)–Pt–N of 81.1(3)° (**3bCl**) and 80.2(2)° (**6bCl**) and N(1)–Pt–N(2) of 83.5(2)° (**3bCl** and **6bCl**).

As reported for analogous compounds [5], the dihedral angle between both phenyl groups of the metallated 2-biphenyl fragments suggests that the phenyl substituent in the *ortho* position produces a congestion in the platinum coordination sphere which is minimised by rotation around the C–C bond. The obtained values 41.0(4)° (**3bCl**) and 49.7(4)° (**6bCl**) are in the same range than those previously reported for [PtMe{2-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (43.5(2)°) and [PtMe{2-$C_6H_5C_6H_4CHNCH_2Ph$}PPh_3] (49.9(3)°).

2.4. Conclusions

The presence of methyl or phenyl groups *trans* to the labile ligand in the metallating substrate favours the bidentate $[N,N']$ coordination as well as the metallation process leading to $[C,N,N']$ systems, which occurred in milder conditions and with higher yields than when *cis*-[$PtCl_2(dmso)_2$] was used as substrate. The smaller steric requirements of methyl or phenyl versus chloro ligands allows for a *E* conformation of the imine ligand in the $[N,N']$ compounds and this is the adequate arrangement for further metallation. In addition the methyl and phenyl groups increase the nucle-

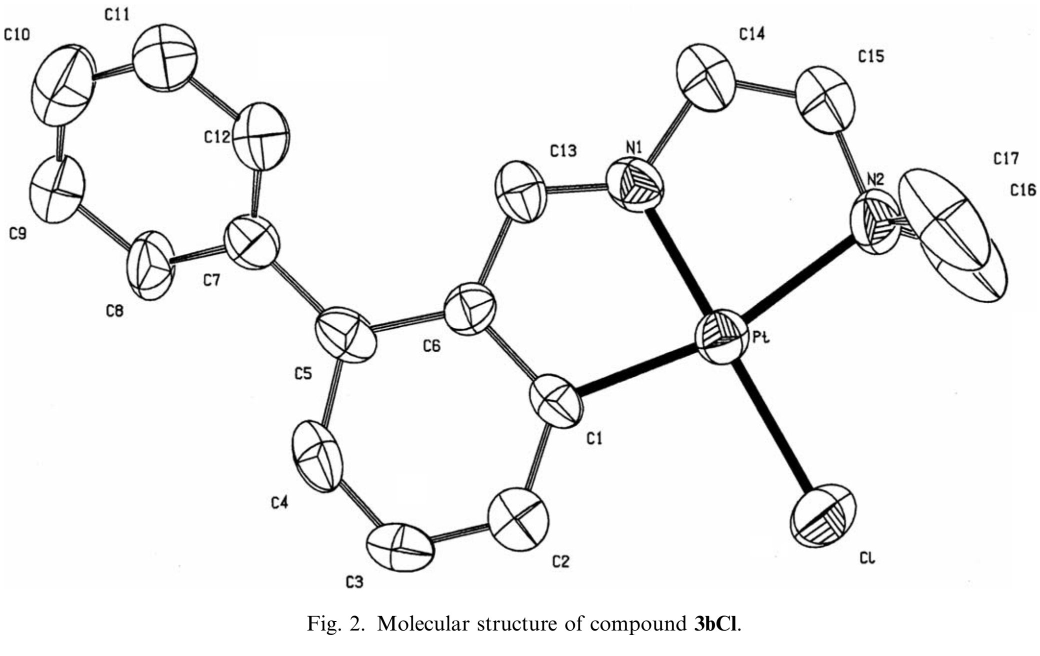


Fig. 2. Molecular structure of compound **3bCl**.

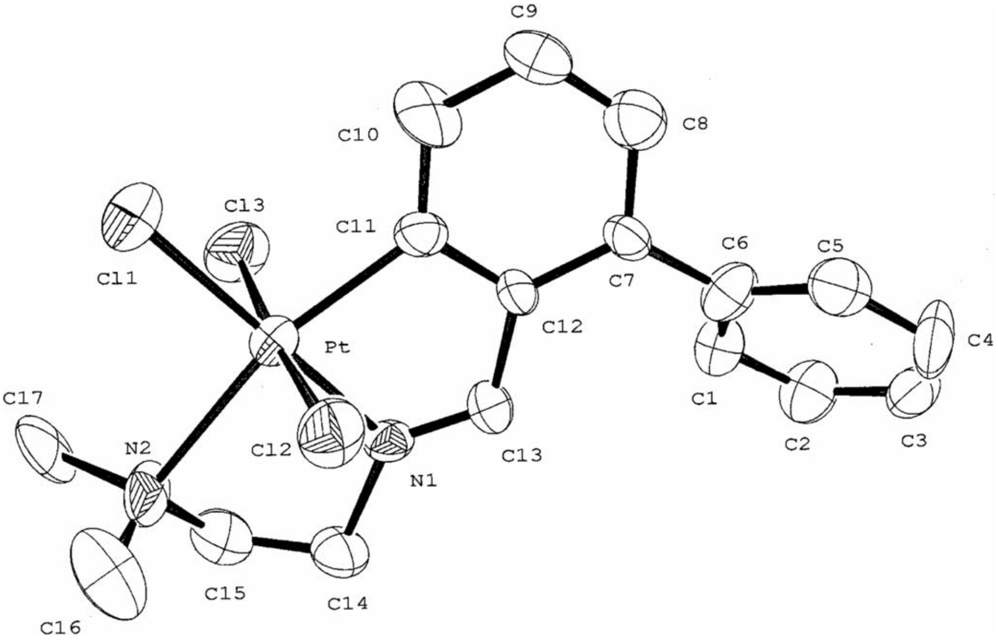


Fig. 3. Molecular structure of compound **6bCl**.

ophilicity of the platinum centre allowing for the synthesis of [*C*,*N*,*N′*] cyclometallated platinum(IV) compounds via oxidative addition of methyl iodide. Platinum(II) compounds **3aCl** and **3bCl** containing a chloro ligand, although unreactive towards methyl iodide, undergo oxidative addition of chlorine to produce the corresponding platinum(IV) compounds.

Slight differences are observed in the behaviour of compounds derived from ligands **1a** or **1b**. For instance, for compounds **2bCl** and **2bPh** the presence of a phenyl substituent in an *ortho* position favours the *Z* isomer compared to analogous compounds **2aCl** and **2aPh**. In addition, formation of compound **3bCl** is much slower than that of the corresponding compound **3aCl** indicating that the presence of a phenyl substituent in an *ortho* position hinders the process.

3. Experimental

3.1. General

NMR spectra were performed at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona. ^{1}H, ^{13}C and ^{195}Pt NMR spectra were recorded by using Varian Gemini 200 (^{1}H, 200 MHz), Bruker 250 (^{195}Pt, 54 MHz), Mercury 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{1}H–^{1}H NOESY; ^{1}H–^{13}C gHSQC) and Varian 500 (^{1}H and ^{1}H–^{1}H COSY, 500 MHz) spectrometers, and referenced to $SiMe_4$ (^{1}H, ^{13}C) and H_2PtCl_6 in D_2O (^{195}Pt). δ values are given in ppm and *J* values in Hz. Mass spectra (FAB or ESI) were performed at the Servei d'Espectrometria de Masses de la Universitat de Barcelona using a VG-Quattro spectrometer. Microanalyses were performed by the Servei de Recursos Científics i Tècnics de la Universitat Rovira i Virgili (Tarragona).

3.2. Preparation of the compounds

Compounds *cis*-[$PtCl_2(dmso)_2$] [14], *cis*-[$PtPh_2(SMe_2)_2$] [15], 4-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$ (**1a**) and 2-C_6H_5-$C_6H_4CHNCH_2CH_2NMe_2$ (**1b**) [5] were prepared as reported.

3.2.1. Synthetic procedure for the [*N*,*N′*] platinum(II) compounds

Compound [$PtCl_2\{4\text{-}C_6H_5C_6H_4CHNCH_2CH_2NMe_2\}$] (**2aCl**) was obtained from 100 mg (2.37×10^{-4} mol) of *cis*-[$PtCl_2(dmso)_2$] and the equimolar amount (59.8 mg) of **1a** after refluxing the mixture in methanol during 4 h. On cooling, a white solid is formed. Yield: 90 mg (73%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.69$ [t, ^2J(H–H) = 6.0, H^b]; 3.14 [s, ^3J(Pt–H) = 36.0, Me^a]; 4.07 [t, ^2J(H–H) = 6.0, H^c]; {7.46–7.62 [m, 6H], 7.72 [d, ^3J(H–H) = 8.0, 2H], 7.82 [t, ^3J(H–H) = 8.0, 1H], aromatics}; 9.56 [s, ^3J(Pt–H) = 59.0, H^d]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -2210.0$ [s]. ESI-MS: 483 [M − Cl]. Anal. Found: C, 38.0; H, 3.9; N, 5.1. Calc. for $C_{17}H_{20}Cl_2N_2Pt \cdot H_2O$: C, 38.06; H, 4.13; N, 5.22%. After refluxing a dichloromethane solution during 10 h, isomer *E* is formed. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.68$ [t, ^2J(H–H) = 6.0, H^b]; 3.17 [s, Me^a]; 4.24 [t, ^2J(H–H) = 6.0, H^c]; 8.76 [s, H^d].

Compound [$PtCl_2\{2\text{-}C_6H_5C_6H_4CHNCH_2CH_2NMe_2\}$] (**2bCl**) was prepared following the same procedure than for **2aCl** from **1b**. Yield: 90 mg (73%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.11$ [t, ^2J(H–H) = 6.0, H^b]; 2.91 [s, ^3J(Pt–H) = 33.0, Me^a]; 3.28 [t, ^2J(H–H) = 6.0, H^c];

{7.30 [dd, ^{3}J(H–H) = 8.0, ^{4}J(H–H) = 2, 2H], 7.41–7.62 [m, 7H], aromatics}; 9.64 [s, ^{3}J(Pt–H) = 58.4, H^{d}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -2299.0$ [s]. ESI-MS: 483 [M − Cl]. Anal. Found: C, 38.2; H, 4.0; N, 5.1. Calc. for $C_{17}H_{20}Cl_{2}N_{2}Pt \cdot H_{2}O$: C, 38.06; H, 4.13; N, 5.22%.

Compound [$PtPh_2${4-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$}] (**2aPh**) was obtained from 100 mg (2.11×10^{-4} mol) of *cis*-[$PtPh_2(dmso)_2$] and the equimolar amount (53.3 mg) of **1a** after stirring the mixture in acetone at room temperature during 30 min. The solvent was removed in a rotary evaporator and the residue was treated with ether to yield a yellow solid. Yield: 90 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.66$ [s, ^{3}J(H–Pt) = 21.2, H^{a}]; 2.78 [m, H^{b}]; 4.19 [t, ^{2}J(H–H) = 6.0, H^{c}]; {6.32 [t, ^{3}J(H–H) = 7.2, 1H], 6.39 [t, ^{3}J(H–H) = 7.2, 2H], 6.80 [t, ^{3}J(H–H) = 7.2, 1H], 6.93 [t, ^{3}J(H–H) = 7.2, 1H], 6.94 [d, ^{3}J(H–H) = 8.0, 2H], 7.16 [d, ^{3}J(H–H) = 8.0, 2H], 7.35 [d, ^{3}J(H–H) = 8.0, 2H], 7.40 [t, ^{3}J(H–H) = 7.4, 2H], 7.46 [d, ^{3}J(H–H) = 7.6, 2H], 7.47 [t, ^{3}J(H–H) = 7.6, 2H], 8.07 [d, ^{3}J(H–H) = 8.0, 2H, H^{2,6}], aromatics}; 8.79 [s, ^{3}J(Pt–H) = 46.4, H^{d}]. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 50.16$ [C^{a}], 65.49 [C^{c}], 66.40 [C^{b}], {121.03, 121.25, 125.65 [2C], 126.19 [2C], 126.73 [2C], 127.28 [2C], 127.95, 128.96 [2C], 130.40 [2C], 138.33 [2C], 138.69 [2C], C$_{Ar}$–H}, {131.56, 135.62, 140.78, 143.89, 147.91, C$_{Ar}$}, 164.93 [C^{d}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3436.0$ [s]. After standing in solution during 48 h, isomer *Z* is formed: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.64$ [s, H^{a}]; 2.76 [m, H^{b}]; 4.07 [t, ^{2}J(H–H) = 6.0, H^{c}]; {6.90 [t, ^{3}J(H–H) = 7.0, 1H], 7.36 [t, ^{3}J(H–H) = 7.0, 2H], 7.58 [d, ^{3}J(H–H) = 8.0, 2H], 7.64 [d, ^{3}J(H–H) = 8.0, 2H, H^{2,6}], aromatics}; 8.42 [s, ^{3}J(Pt–H) = 24.0, H^{d}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3398.4$ [s]. Anal. Found: C, 57.6; H, 5.5; N, 4.4. Calc. for $C_{29}H_{30}N_{2}Pt$: C, 57.89; H, 5.02; N, 4.66%.

Compound [$PtPh_2${2-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$}] (**2bPh**) was obtained as a light yellow solid following the same procedure than for **2aPh** from **1b**. Yield: 90 mg (71%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.65$ [s, ^{3}J(H–Pt) = 21.2, H^{a}]; 2.70 [m, H^{b}]; 4.00 [t, ^{2}J(H–H) = 6.0, H^{c}]; {6.25 [t, ^{3}J(H–H) = 7.2, 1H], 6.39 [t, ^{3}J(H–H) = 7.2, 2H], 6.80 [d, ^{3}J(H–H) = 7.4, 1H], 6.92 [t, ^{3}J(H–H) = 7.6, 2H], 7.06 [t, ^{3}J(H–H) = 7.6, 3H], 7.22 [d, ^{3}J(H–H) = 7.0, 1H], 7.39–7.49 [m, 8H], 8.83 [d, ^{3}J(H–H) = 7.6, 1H], aromatics}; 8.51 [s, ^{3}J(Pt–H) = 43.4, H^{d}]. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 50.01$ [C^{a}], 64.74 [C^{c}], 66.08 [C^{b}], {120.86, 121.17, 126.69 [2C], 126.99 [2C], 127.46 [2C], 127.96 [1C], 128.48 [2C], 128.64, 128.97, 129.93, 130.81, 138.22 [2C], 138.70 [2C], C$_{Ar}$–H}, {139.99, 140.90, 141.66, 148.35, C$_{Ar}$}, 165.22 [C^{d}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3436.1$ [s]. After standing in solution during 4 h, isomer *Z* is formed: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.48$ [s, ^{3}J(H–Pt) = 16.8, H^{a}]; 2.53 [t, ^{2}J(H–H) = 6.0, H^{b}]; 3.43 [t, ^{2}J(H–H) = 6.0, H^{c}]; {6.65 [t, ^{3}J(H–H) = 7.2, 1H], 6.71 [t, ^{3}J(H–H) = 7.6, 2H], 6.74 [t, ^{3}J(H–H) = 7.2, 1H], 6.88 [t, ^{3}J(H–H) = 7.6, 2H], 7.34–7.59 [m], aromatics}; 8.39 [s, ^{3}J(Pt–H) = 27.2, H^{d}]. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 49.20$ [C^{a}], 54.02 [C^{c}], 64.51 [C^{b}], {121.31, 121.41, 125.54, 126.73 [2C], 126.78 [2C], 128.64 [1C], 129.16 [2C], 129.26 [2C], 129.74, 130.48, 130.64, 138.26 [2C], 138.29 [2C], C$_{Ar}$–H}, {139.46, 141.29, 146.85, C$_{Ar}$}, 166.65 [C^{d}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3434.5$ [s]. Anal. Found: C, 58.0; H, 5.6; N, 4.4. Calc. for $C_{29}H_{30}N_{2}Pt$: C, 57.89; H, 5.02; N, 4.66%.

3.2.2. Synthetic procedure for the [C,N,N′] platinum(II) compounds

Compound [PtCl{4-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**3aCl**) was prepared from 60 mg (1.16×10^{-4} mol) of **2aCl** and the equimolar amount of $Na(CH_3COO)$ (9 mg) after refluxing the mixture in methanol during 12 h. The reaction mixture was cooled, filtered to remove unreacted materials and concentrated to half volume. The obtained crystals were recrystallised in dichloromethane-methanol to yield red crystals. Yield: 25 mg (45%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.92$ [s, ^{3}J(H–Pt) = 14.0, H^{a}]; 3.12 [t, ^{2}J(H–H) = 6.0, H^{b}]; 4.04 [td, ^{2}J(H–H) = 6.0, ^{4}J(H–H) = 1.0, ^{3}J(H–Pt) = 35.0, H^{c}]; {7.23 [dd, ^{3}J(H–H) = 8.0, ^{4}J(H–H) = 2, 1H, H^{3}], 7.30 [d, ^{3}J(H–H) = 8.0, 1H, H^{2}], 7.33 [t, ^{3}J(H–H) = 7.2, 1H, R_4^{para}], 7.41 [t, ^{3}J(H–H) = 7.2, 2H, R_4^{meta}], 7.66 [dd, ^{3}J(H–H) = 8.0, ^{4}J(H–H) = 2, 2H, R_4^{ortho}], 7.99 [d, ^{4}J(H–H) = 2.0, J(H–Pt) = 44.0, 1H, H^{5}], aromatics}; 8.24 [t, ^{4}J(H–H) = 1.0, ^{3}J(Pt–H) = 141.0, H^{d}]. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 48.90$ [C^{a}], 54.55 [C^{c}], 66.36 [C^{b}], {122.65, 127.65 [2C], 127.81, 128.20, 128.79 [2C], 132.99, C$_{Ar}$–H}, {141.50, 142.90, 144.55, 148.24, C$_{Ar}$}, 171.70 [^{2}J(C–Pt) = 112, C^{d}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3473.5$ [s]. Anal. Found: C, 43.1; H, 4.4; N, 5.6. Calc. for $C_{17}H_{19}ClN_{2}Pt$: C, 42.37; H, 3.97; N, 5.81%.

Compound [PtCl{2-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**3bCl**) was similarly obtained from 60 mg (1.16×10^{-4} mol) of **2bCl** and the equimolar amount of $Na(CH_3COO)$ (9 mg) after heating at 65 °C the mixture in methanol during 48 h. Yield: 20 mg (36%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.90$ [s, ^{3}J(H–Pt) = 14.2, H^{a}]; 3.08 [t, ^{2}J(H–H) = 6.0, H^{b}]; 4.03 [td, ^{2}J(H–H) = 6.0, ^{4}J(H–H) = 1.2, ^{3}J(H–Pt) = 34.8, H^{c}]; {6.94 [dd, ^{3}J(H–H) = 7.6, ^{4}J(H–H) = 1.2, 1H, H^{3}], 7.30 [t, ^{3}J(H–H) = 7.6, 1H, H^{4} or R_2^{para}], 7.33 [dd, ^{3}J(H–H) = 8.0, 1.6, 2H, R_2^{ortho}], 7.38–7.42 [m, 3H, R_2^{meta} + H^{4} or R_2^{para}], 7.75 [dd, ^{3}J(H–H) = 7.6, ^{4}J(H–H) = 1, J(H–Pt) = 44.4, 1H, H^{5}], aromatics}; 8.35 [t, ^{4}J(H–H) = 1.2, ^{3}J(Pt–H) = 143.4, H^{d}]. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 48.82$ [C^{a}], 54.82 [C^{c}], 66.31 [C^{b}], {125.03, 127.64, 128.56 [2C], 129.55 [2C], 132.53, 133.79, C$_{Ar}$–H}, {141.20, 142.91, C$_{Ar}$}, 171.87 [C^{d}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3476.0$ [s]. Anal. Found: C, 42.6; H, 3.6; N, 5.5. Calc. for $C_{17}H_{19}ClN_{2}Pt$: C, 42.37; H, 3.97; N, 5.81%.

Compound [PtPh{4-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**3aPh**) was prepared from 60 mg (1.00×10^{-4} mol) of **2aPh** after refluxing in toluene during 6 h. The solution was filtered to remove a metallic residue. The solvent was removed and the residue was treated with ether to produce a red-brick solid. Yield: 40 mg (77%). ^{1}H NMR (400 MHz,

$CDCl_3$): $\delta = 2.78$ [s, ^{3}J(H–Pt) = 20.4, H^{a}]; 3.19 [t, ^{2}J(H–H) = 6.0, H^{b}]; 4.05 [t, ^{2}J(H–H) = 6.0, H^{c}]; {6.94 [t, ^{3}J(H–H) = 7.2, 1H, Ph^{para} or R_4^{para}], 7.09 [t, ^{3}J(H–H) = 7.6, 2H, Ph^{meta} or R_4^{meta}], 7.16 [dd, J(H–H) = 7.6; 1.6, 1H, H^{2} or H^{3}], 7.24 [t, ^{3}J(H–H) = 7.2, 1H, Ph^{para} or R_4^{para}], 7.31 [dd, ^{3}J(H–H) = 8.0, ^{4}J(H–H) = 2.0, 1H, H^{2} or H^{3}], 7.32 [t, ^{3}J(H–H) = 7.2, 2H, Ph^{meta} or R_4^{meta}], 7.36 [d, ^{4}J(H–H) = 1.6, 1H, H^{5}], 7.45 [dd, J(H–H) = 8.0; 1.6, 2H, R_4^{ortho}], 7.59 [d, ^{3}J(H–H) = 8.0, ^{3}J(H–Pt) = 55.2, 2H, Ph^{ortho}], aromatics}; 8.48 [s, ^{3}J(Pt–H) = 56.0, H^{d}]. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 49.45$ [C^{a}], 52.75 [^{2}J(C–Pt) = 29.0, C^{c}], 67.74 [C^{b}], {121.86 [C^{2} or C^{3}], 122.01 [Ph^{para} or R_4^{para}], 127.28 [J(C–Pt) = 70.6, 2C, Ph^{meta} or R_4^{meta}], 127.37 [Ph^{para} or R_4^{para}], 127.58 [2C, R_4^{ortho}], 128.65 [2C, Ph^{meta} or R_4^{meta}], 128.78 [J(C–Pt) = 45.8, C^{2} or C^{3}], 135.35 [^{2}J(C–Pt) = 106.9, C^{5}], 138.00 [^{2}J(C–Pt) = 24.9, 2C, Ph^{ortho}], C_{Ar}–H}, {141.94, 143.96, 144.39, 149.24, 153.42, C_{Ar}}, 169.51 [^{2}J(C–Pt) = 95.9, C^{d}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3600.3$ [s]. Anal. Found: C, 52.5; H, 5.1; N, 5.4. Calc. for $C_{23}H_{24}N_2Pt$: C, 52.76; H, 4.62; N, 5.35%.

Compound [PtPh{2-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**3bPh**) was obtained as a golden solid following the same procedure from **2bPh**. Yield: 35 mg (67%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.76$ [s, ^{3}J(H–Pt) = 20.4, H^{a}]; 3.15 [t, ^{2}J(H–H) = 6.0, H^{b}]; 3.96 [t, ^{2}J(H–H) = 6.0, H^{c}]; {6.97 [t, ^{3}J(H–H) = 7.2, 1H, Ph^{para} or R_2^{para}], 7.07 [dd, ^{3}J(H–H) = 7.2; 2, 2H], 7.11 [t, J(H–H) = 7.4, 2H, Ph^{meta} or R_2^{meta}], 7.32–7.42 [m, 5H], 7.60 [d, ^{3}J(H–H) = 7.0, J(H–Pt) = 59.2, 2H, Ph^{ortho}], aromatics}; 8.47 [s, ^{3}J(Pt–H) = 57.6, H^{d}]. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 49.41$ [C^{a}], 53.14 [^{2}J(C–Pt) = 28.5, C^{c}], 67.61 [C^{b}], {121.96 [Ph^{para} or R_2^{para}], 124.26, 127.33 [J(C–Pt) = 70.5, 2C, Ph^{meta} or R_2^{meta}], 127.34, 128.37 [2C], 129.73 [2C], 132.22 [J(C–Pt) = 76.8], 136.13 [^{2}J(C–Pt) = 97.7], 138.02 [^{2}J(C–Pt) = 25.4, 2C, Ph^{ortho}], C_{Ar}–H}, {141.77, 143.68, 144.10, 146.98, 154.87, C_{Ar}}, 169.36 [^{2}J(C–Pt) = 94.5, C^{d}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3599.7$ [s]. Anal. Found: C, 52.0; H, 5.1; N, 5.1. Calc. for $C_{23}H_{24}N_2Pt$: C, 52.76; H, 4.62; N, 5.35%.

3.2.3. Synthetic procedure for the platinum(IV) compounds

Compound [PtMePhI{4-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**4aPh**) was obtained adding an excess of methyl iodide (0.5 mL) to a solution of 25 mg of compound **3aPh** in acetone and stirring the mixture at room temperature. After 30 min, the solution colour changed from orange to yellow. The solvent was removed and the residue was washed with ether. Yield: 25 mg (79%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.23$ [s, ^{2}J(Pt–H) = 68.8, Me^{a}]; 2.72 [s, ^{3}J(H–Pt) = 15.2, Me^{b}]; 3.17 [s, ^{3}J(H–Pt) = 11.2, Me^{c}]; {3.08 [dt, J(H–H) = 12.0; 4.0, 1H], 4.10 [d, J(H–H) = 12.0, 1H], 4.25 [dd, J(H–H) = 12.0; 4.0, 1H], 4.37 [td, J(H–H) = 12.0; 4.0, 1H], H$^{d,d',e,e'}$}; {7.08 [d, J(H–H) = 7.2, 1H]; 7.13 [t, ^{3}J(H–H) = 8.0, 2H]; 7.32 [t, ^{3}J(H–H) = 8.0, 2H]; 7.39 [t, ^{3}J(H–H) = 7.2; 2H]; 7.44 [d, J(H–H) = 8.0, 1H]; 7.57 [dd, ^{3}J(H–H) = 7.2; 1.2 2H]; 7.61 [d, J(H–H) = 1.2, 1H], 7.88 [d, J(H–H) = 7.0, J(H–Pt) = 35.0, 2H, Ph^{ortho}], aromatics}; 8.43 [s, ^{3}J(Pt–H) = 47.6, H^{d}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -2344.8$ [s]. FAB-MS: 538 [M − I], 523 [M − I − Me], 446 [M − I − Me − Ph]. Anal. Found: C, 43.8; H, 4.2; N, 4.6. Calc. for $C_{24}H_{27}IN_2Pt$: C, 43.32; H, 4.09; N, 4.21%.

Compound [PtMePhI{2-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**4bPh**) was obtained from **3bPh** using the method described above for **4aPh**. Yield: 25 mg (79%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.23$ [s, ^{2}J(Pt–H) = 68.4, Me^{a}]; 2.68 [s, ^{3}J(H–Pt) = 14.0, Me^{b}]; 3.16 [s, ^{3}J(H–Pt) = 10.0, Me^{c}]; {3.03 [m, 1H], 4.00 [d, J(H–H) = 11.0, 1H], 4.15 [m, 1H], 4.28 [td, J(H–H) = 11.0; 4.0, 1H], H$^{d,d',e,e'}$}; {6.99 [d, J(H–H) = 7.6, 1H]; 7.09–7.13 [m, 3H]; 7.23 [t, ^{3}J(H–H) = 7.6, 1H]; 7.32 [d, ^{3}J(H–H) = 8.0, 1H]; 7.40–7.47 [m, 5H]; 7.87 [d, J(H–H) = 6.4, J(H–Pt) = 35.0, 2H], aromatics}; 8.40 [s, ^{3}J(Pt–H) = 48.8, H^{d}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -2354.8$ [s]. FAB-MS: 665 [M], 538 [M − I], 523 [M − I − Me], 446 [M − I − Me − Ph]. Anal. Found: C, 42.2; H, 4.1; N, 4.3. Calc. for $C_{24}H_{27}IN_2Pt \cdot H_2O$: C, 42.17; H, 4.28; N, 4.10%.

Compound [$PtMe_3I${2-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$}] (**5aMe**) was obtained as a white solid using an analogous procedure to that described above from 30 mg (6.3×10^{-5} mol) of **2aMe** and a reaction time of 10 min. Yield: 25 mg (64%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = {0.85 [s, ^{2}J(Pt–H) = 71.0], 1.05 [s, ^{3}J(H–Pt) = 73.0], 1.24 [s, ^{2}J(Pt–H) = 71.0], Me^{a}, Me^{b}, Me^{c}}; {2.47 [s, ^{3}J(H–Pt) = 14.5], 3.23 [s, ^{3}J(H–Pt) = 11.0], Me$^{d,d'}$}; 2.70 [ddd, J(H–H) = 13.0; 4.0; 3.0, 1H], 3.47 [td, J(H–H) = 13.0; 3.0, 1H], 3.93 [tt, J(H–H) = 13.0; 3.0, 1H], 4.09 [dt, J(H–H) = 13.0; 4.0, 1H], H$^{e,e',f,f'}$}; {7.36 [t, J(H–H) = 7.0, 1H, R_4^{para}]; 7.44 [t, J(H–H) = 7.0, 2H]; 7.61 [d, J(H–H) = 7.0, 2H], 7.66 [d, J(H–H) = 8.0, 2H], 7.92 [d, J(H–H) = 8.0, 2H], aromatics}; 8.89 [s, ^{3}J(Pt–H) = 32.0, H^{g}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -2560.9$ [s]. Anal. Found: C, 36.9; H, 5.0; N, 4.2. Calc. for $C_{20}H_{29}IN_2Pt \cdot 2H_2O$: C, 36.64; H, 5.07; N, 4.27%.

Compound [$PtMe_3I${2-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$}] (**5bMe**) was obtained as a white solid using the same procedure than for **5aMe** from 20 mg (4.2×10^{-5} mol) of **2bMe**. Yield: 15 mg (58%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = {1.01 [s, ^{2}J(Pt–H) = 71.2], 1.08 [s, ^{3}J(H–Pt) = 72.8], 1.27 [s, ^{2}J(Pt–H) = 72.0], Me^{a}, Me^{b}, Me^{c}}; {2.49 [s, ^{3}J(H–Pt) = 14.4], 3.24 [s, ^{3}J(H–Pt) = 10.8], Me$^{d,d'}$}; 2.68 [ddd, J(H–H) = 12.0; 6.0; 3.0, 1H], 3.42 [ddd, J(H–H) = 12.0; 9.0; 3.0, 1H], 3.74 [ddt, J(H–H) = 9.0; 6.0; 3.0, 1H], 4.10 [m, 1H], H$^{e,e',f,f'}$}; {7.42 [d, J(H–H) = 8.0, 1H]; 7.43–7.48 [m, 4H]; 7.52 [d, 2H], 7.54 [t, J(H–H) = 8.0, 1H], 8.20 [d, J(H–H) = 8.0, 1H], aromatics}; 8.49 [s, ^{3}J(Pt–H) = 33.2, H^{g}]. ^{13}C NMR (100 MHz, $CDCl_3$): δ = {−5.56 [^{1}J(C–Pt) = 681.5], −4.90 [^{1}J(C–Pt) = 659.4], 9.59 [^{1}J(C–Pt) = 735.6], Me^{a}, Me^{b}, Me^{c}}; {46.87, 54.50, Me^{d}, Me^{e}}; {62.95, 63.21, C^{f}, C^{g}}; {126.96, 128.34, 128.82 [2C], 129.23, 129.97 [2C], 130.63, 131.38, C_{Ar}–H}, {131.86, 139.29, 141.87, C_{Ar}}, 170.45 [C^{d}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -2566.3$ [s]. Anal. Found: C, 38.3; H, 4.7; N, 4.4. Calc. for $C_{20}H_{29}IN_2Pt$: C, 38.78; H, 4.72; N, 4.52%.

Compound [$PtCl_3\{4\text{-}C_6H_5C_6H_3CHNCH_2CH_2NMe_2\}$] (**6aCl**) was obtained treating a solution of 10 mg of compound **3aCl** in acetonitrile (10 mL) with 10 mL of acetonitrile saturated with chlorine. The colour of the solution faded readily and the mixture was stirred during 10 min. The solvent was removed to produce a light yellow solid. Yield: 8 mg (70%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.94$ [s, 3H, Me^a]; 3.06 [s, 3H, Me^a]; {3.20 [m], 3.76 [m], 4.09 [m], 5.27 [m], H^b, H^c}; {7.39–7.51 [m, 4H], 7.61–7.69 [m, 3H], 7.80 [s, 1H], aromatics}; 8.39 [s, ^3J(Pt–H) = 100.8, H^d]. ESI-MS: 516 [M − Cl], 483 [M − 2Cl]. Anal. Found: C, 36.6; H, 3.8; N, 5.3. Calc. for $C_{17}H_{19}Cl_3N_2Pt$: C, 36.93; H, 3.46; N, 5.07%.

Compound [$PtCl_3\{2\text{-}C_6H_5C_6H_3CHNCH_2CH_2NMe_2\}$] (**6bCl**) was crystallised from a equimolar mixture of *cis*-[$PtCl_2(dmso)_2$] and **1b** in dichloromethane. Alternatively, compound **6bCl** was prepared as described for **6aCl**. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.92$ [s, 3H, Me^a]; 3.01 [s, 3H, Me^a]; {3.26 [m, 1H], 3.67 [m, 1H], 3.97 [m, 1H], 5.18 [m, 1H], H^b, H^c}; {7.31 [d, J(H–H) = 7.6, 1H], 7.42–7.52 [m, 6H], 7.60 [dd, J(H–H) = 8; 1, 1H], aromatics}; 8.21 [s, ^3J(Pt–H) = 102.8, H^d]. ESI-MS: 483 [M − 2Cl]. Anal. Found: C, 36.1; H, 4.5; N, 5.4. Calc. for $C_{17}H_{19}Cl_3N_2Pt$: C, 36.93; H, 3.46; N, 5.07%.

3.3. X-ray structure analysis

3.3.1. Data collection

Crystals of **3bCl** and **6bCl** were obtained from slow evaporation of acetone and dichloromethane solutions, respectively. Prismatic crystals were selected and mounted on an MAR345 diffractometer with an image plate detector. Unit cell parameters were determined from 288 (**3bCl**) or 148 (**6bCl**) reflections ($3° < \theta < 31°$) and refined by least-squares method. Intensities were collected with graphite monochromatised Mo Kα radiation. For **3bCl**, 3695 reflections were measured in the range $3.49° < \theta < 31.92°$ and 3020 were assumed as observed applying the condition $I > 2\sigma(I)$. For **6bCl**, 18,706 reflections were measured in the range $3.48° < \theta < 31.82°$, 5421 were non-equivalent by symmetry and 4077 were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz polarisation and absorption corrections were made. Further details are given in Table 2.

3.3.2. Structure solution and refinement

The structure was solved by direct methods (**3bCl**) or Patterson synthesis (**6bCl**), using SHELXS97 computer program [16], and refined by the full-matrix least-squares method, with the SHELXL97 computer program [16] using 3695 (**3bCl**) or 5421 (**6bCl**) reflections (very negative intensities were not assumed). The function minimised was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0428P)^2 + 9.6383P]^{-1}$ (**3bCl**) or $w = [\sigma^2(I) + (0.0220P)^2 + 7.7968P]^{-1}$ (**6bCl**) and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f′ and f″ were taken from International Tables of X-ray Crystallography [17]. For **3bCl**, 18H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor and 1H was computed and refined, using a riding model, with an isotropic factor equal to 1.2 times the equivalent temperature factor of the atom to which they are linked. For **6bCl**, all hydrogen atoms were computed and refined. Further details are given in Table 2.

Table 2
Crystallographic and refinement data for compounds **3bCl** and **6bCl**

	Compound **3bCl**	Compound **6bCl**
Formula	$C_{17}H_{19}ClN_2Pt$	$C_{17}H_{19}Cl_3N_2Pt$
Formula weight	481.88	552.78
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Orthorhombic, *Pcab*	Monoclinic, $P2_1/c$
a (Å)	11.102(5)	7.042(5)
b (Å)	11.224(3)	12.916(6)
c (Å)	25.986(9)	20.119(9)
α (°)	90	90
β (°)	90	101.56(3)
γ (°)	90	90
V (Å^3); Z	3238 (2); 8	1792.8(17); 4
d_{calcd} (Mg/m^3)	1.977	2.048
Absolute coefficient (mm^{-1})	8.826	8.273
F(000)	1840	1056
Number of reflections collected/unique (R_{int})	3695/3695 (0.0414)	18,706/5421 (0.0428)
Data/restraints/parameters	3695/0/182	5421/2/208
Goodness-of-fit on F^2	1.192	1.113
$R_1[I > 2\sigma(I)]$	0.0530	0.0429
wR_2 (all data)	0.1252	0.1021
Peak and hole (e Å^{-3})	0.630 and −0.625	0.620 and −0.843

4. Supplementary material

The crystallographic data of compounds **3bCl** and **6bCl** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 291025 and 291026, respectively.

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References

[1] (a) P.R.R. Ranatunge-Bandarage, B.H. Robinson, J. Simpson, Organometallics 13 (1994) 500;
(b) Y.J. Wu, L. Ding, H.X. Wang, Y.H. Liu, H.Z. Yuan, X.A. Mao, J. Organomet. Chem. 535 (1997) 49;
(c) L. Ding, D.P. Zou, Y.J. Wu, Polyhedron 17 (1998) 2511;
(d) A.D. Ryabov, I.M. Panyashkina, V.A. Polyakov, A. Fisher, Organometallics 21 (2002) 1633;
(e) S. Pérez, C. López, A. Caubet, X. Solans, M. Font-Bardía, New J. Chem. 27 (2003) 975;
(f) M. Crespo, M. Font-Bardía, J. Granell, M. Martínez, X. Solans, J. Chem. Soc., Dalton Trans. (2003) 3763;
(g) A. Capapé, M. Crespo, J. Granell, M. Font-Bardia, X. Solans, J. Organomet. Chem. 690 (2005) 4309.

[2] (a) C.R. Baar, H.A. Jenkins, J.J. Vittal, G.P.A. Yap, R.J. Puddephatt, Organometallics 17 (1998) 2805;
(b) C.R. Baar, G.S. Hill, J.J. Vittal, R.J. Puddephatt, Organometallics 17 (1998) 32;
(c) C.M. Anderson, M. Crespo, M.C. Jennings, A.J. Lough, G. Ferguson, R.J. Puddephatt, Organometallics 10 (1991) 2672.
[3] M. Crespo, M. Font-Bardia, X. Solans, Organometallics 23 (2004) 1708.
[4] A.D. Ryabov, Chem. Rev. 90 (1990) 403.
[5] M. Crespo, M. Font-Bardia, X. Solans, J. Organomet. Chem. 691 (2006) 444.
[6] (a) A.D. Ryabov, G.M. Kazankov, I.M. Panyashkina, O.V. Grozovsky, O.G. Dyachenko, V.A. Polyakov, L.G. Kuz'mina, J. Chem. Soc., Dalton Trans. (1997) 4385;
(b) L. Alexandrova, O.G. D'yachenko, G.M. Kazankov, V.A. Polyakov, P.V. Samuleev, E. Sansores, A.D. Ryabov, J. Am. Chem. Soc. 122 (2000) 5189.
[7] (a) R. Romeo, L. Monsù Scolaro, M.R. Plutino, A. Romeo, F. Nicoló, A. Del Zotto, Eur. J. Inorg. Chem. (2002) 629;
(b) M.A. Casado Lacabra, A.J. Canty, M. Lutz, J. Patel, A.L. Spek, H. Sun, G. van Koten, Inorg. Chim. Acta 327 (2002) 15.
[8] P.S. Pregosin, Coord. Chem. Rev. 44 (1982) 247.
[9] Resonances assigned to platinum(IV) compounds in the ^{1}H NMR spectra in $CDCl_3$ at 200 MHz (δ in ppm, J in Hz) for (a) the reaction of **2aPh** with MeI: $\delta = 1.80$ [Me], 3.25 [J(H–Pt) = 12.8, NMe], 8.99 [J(H–Pt) = 35.6, CHN]; (b) the reaction of **2bPh** with MeI: $\delta = 1.76$ [J(H–Pt) = 72.0, Me], 3.23 [J(H–Pt) = 12.8, NMe], 8.59 [J(H–Pt) = 34.0, CHN].
[10] F. Zhang, M.C. Jennings, R.J. Puddephatt, Organometallics 23 (2004) 1396.
[11] R. Bosque, M. Crespo, E. Evangelio, M. Font-Bardia, X. Solans, J. Organomet. Chem. 690 (2005) 2062.
[12] L.M. Rendina, R.J. Puddephatt, Chem. Rev. 97 (1997) 1735.
[13] (a) S. Chattopadhyay, C. Sinha, P. Basu, A. Chakravorty, Organometallics 10 (1991) 1135;
(b) M. Ghedini, D. Pucci, A. Crispini, G. Barberio, Organometallics 18 (1999) 2116;
(c) G. van Koten, Pure Appl. Chem. 62 (1990) 1155.
[14] J.H. Price, A.N. Williamson, R.F. Schramm, B.B. Wayland, Inorg. Chem. 11 (1972) 1280.
[15] (a) D. Song, S. Wang, J. Organomet. Chem. 648 (2002) 302;
(b) M. Rashidi, Z. Fakhroeian, R.J. Puddephatt, J. Organomet. Chem. 406 (1990) 261.
[16] G.M. Sheldrick, SHELXS97. A Computer Program for Crystal Structure Determination, University of Göttingen, Germany, 1997.
[17] International Tables of X-ray Crystallography, vol. IV, Kynoch Press, Birmingham, UK, 1974, pp. 99–100, 149.