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Synthesis, reactivity and crystal structures of platinum (II) and platinum (IV) cyclometallated compounds derived from 2- and 4-biphenylimines

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Abstract

The reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with ligands 4-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$ (**1a**) and 2-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$ (**1b**) carried out in acetone at room temperature produced compounds $[PtMe_2\{4\text{-}C_6H_5C_6H_4CHNCH_2CH_2NMe_2\}]$ (**2a**) and $[PtMe_2\{2\text{-}C_6H_5C_6H_4CHNCH_2CH_2NMe_2\}]$ (**2b**), respectively, in which the imines act as bidentate [N,N′] ligands. Cyclometallated [C,N,N′] compounds $[PtMe\{4\text{-}C_6H_5C_6H_3CHNCH_2CH_2NMe_2\}]$ (**3a**) and $[PtMe\{2\text{-}C_6H_5C_6H_3CHNCH_2CH_2NMe_2\}]$ (**3b**), were obtained by refluxing toluene solutions of compounds **2a** or **2b**. Reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with ligands 4-$C_6H_5C_6H_4CHNCH_2Ph$ (**1c**) and 2-$C_6H_5C_6H_4CHNCH_2Ph$ (**1d**) produced compounds $[PtMe\{4\text{-}C_6H_5C_6H_3CHNCH_2Ph\}SMe_2]$ (**5c**) and $[PtMe\{2\text{-}C_6H_5C_6H_3CHNCH_2Ph\}SMe_2]$ (**5d**) containing a [C,N] ligand, from which triphenylphosphine derivatives **6c** and **6d** were also prepared. In all cases, metallation took place to yield five-membered *endo*-metallacycles and formation of seven-membered or of *exo*-metallacycles was not observed. The reactions of **3a**, **3b**, **6c** and **6d** with methyl iodide were studied in acetone and gave the corresponding cyclometallated platinum (IV) compounds. All compounds were characterised by NMR spectroscopy and compounds **3b**, **4a**, **6c** and **6d** were also characterised crystallographically.

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

1. Introduction

Cyclometallated compounds 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]. The most widely studied examples are platinum and palladium compounds with nitrogen donors in which C–H activation takes place at phenyl *ortho* positions to produce five-membered metallacycles. Although metallation sites other than benzene ring carbon have been less explored, several examples of compounds containing a biphenyl cyclometallated moiety have been reported as shown in Chart 1. These include six-membered cycles derived from amines (structure A) [2] or imines (structure B) [3,4], as well as 10-membered rings derived from the latter through bis-insertion of alkynes [5]. Seven-membered platinacycles (structures C [6] and D [7]) containing the C=N group (*endo*-cycles) have been recently obtained in a process involving formal insertion of a phenyl ligand into a Pt–C bond. In addition, doubly cyclometallated compounds have also been reported (structures E [8] and F [9]). Apart from examples mentioned above which contain nitrogen donor ligands, five-membered platinacycles derived from the 2,2′-biphenyl dianion are also an interesting class of compounds [10].

Following our studies of imines containing aromatic groups such as benzene [11], thiophene [12], furane [13],

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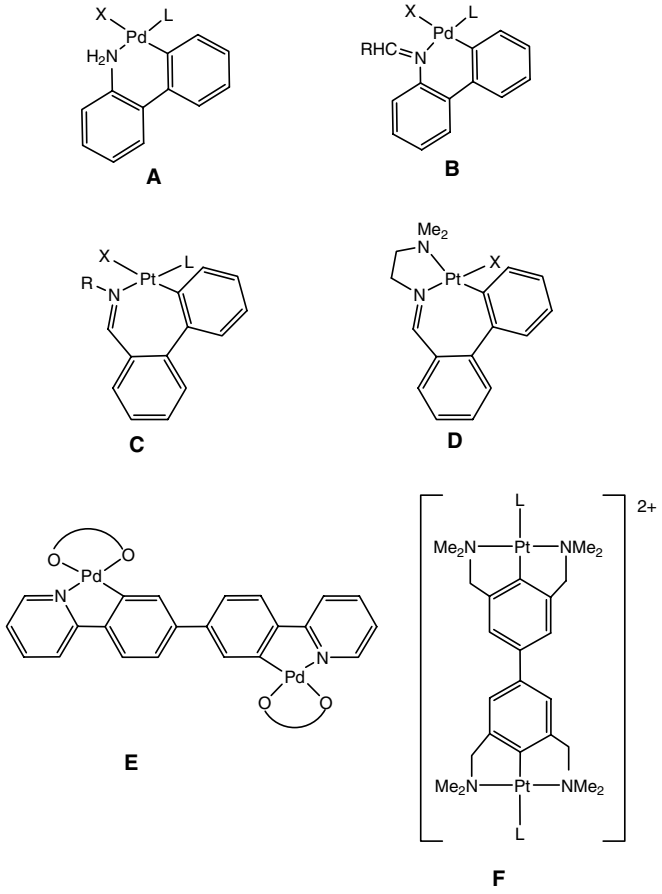


Chart 1. Several examples of compounds containing a biphenyl cyclometallated moiety.

naphthalene [14], phenanthrene- and anthracene [15], we now report the reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with imines derived from 2-biphenyl and 4-biphenylcarboxaldehydes. Ligands containing two (**1a** and **1b**) and one (**1c** and **1d**) nitrogen atoms have been studied since in some cases striking differences [12] have been observed in the preparation of cycloplatinated compounds from these two types of ligands. As shown in Chart 2, two non-equivalent metallation sites leading to either five- or seven-membered *endo*-metallacycles (containing the C=N group) are available for ligands derived from 2-biphenyl while ligands derived from 4-biphenyl can only produce five-membered metallacycles. Moreover, ligands derived from benzylamine (**1c** and **1d**) may lead to formation of *exo*-metallacycles although these are generally less prone to form than the most prevalent *endo*-cycles [16].

Additional interest arise from the fact that the resulting platinum (II) compounds are suitable substrates for studying the oxidative addition of alkyl halides [17] and therefore the influence in this process of the position (*ortho* or *para*) of the phenyl substituent can be evaluated.

2. Results and discussion

Ligands $4\text{-}C_6H_5C_6H_4CHNCH_2CH_2NMe_2$ (**1a**), $2\text{-}C_6H_5C_6H_4CHNCH_2CH_2NMe_2$ (**1b**), $4\text{-}C_6H_5C_6H_4CHNCH_2Ph$ (**1c**) and $2\text{-}C_6H_5C_6H_4CHNCH_2Ph$ (**1d**) were prepared from the condensation reactions of the corresponding aldehyde and *N*,*N*-dimethylethylenediamine or benzylamine carried out in toluene at room temperature. The resulting imines were characterised by ^1H NMR spectroscopy.

2.1. Cyclometallation in [C,N,N′] systems

The reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with potentially tridentate ligands **1a** and **1b** carried out in acetone at room temperature produced compounds $[PtMe_2\{4\text{-}C_6H_5C_6H_4\text{-}$

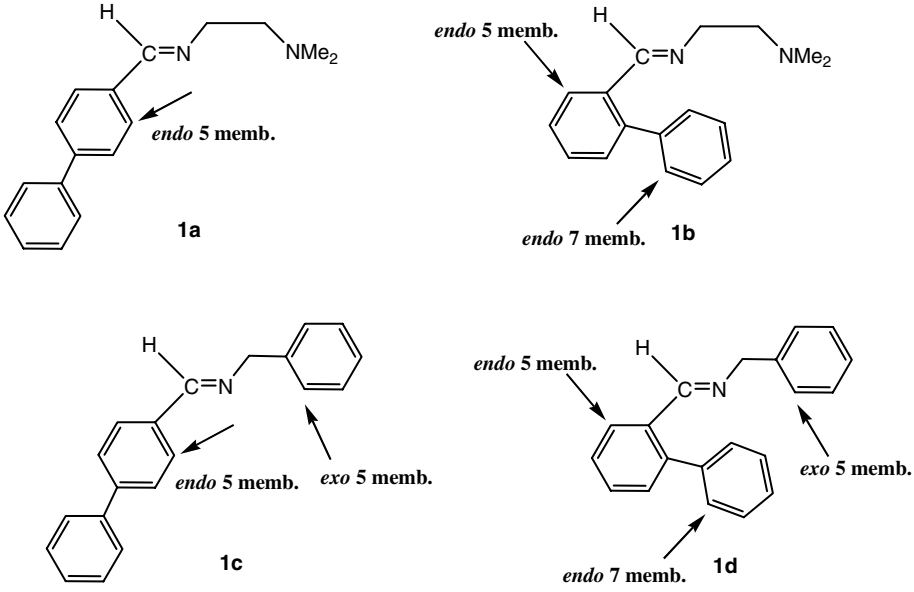
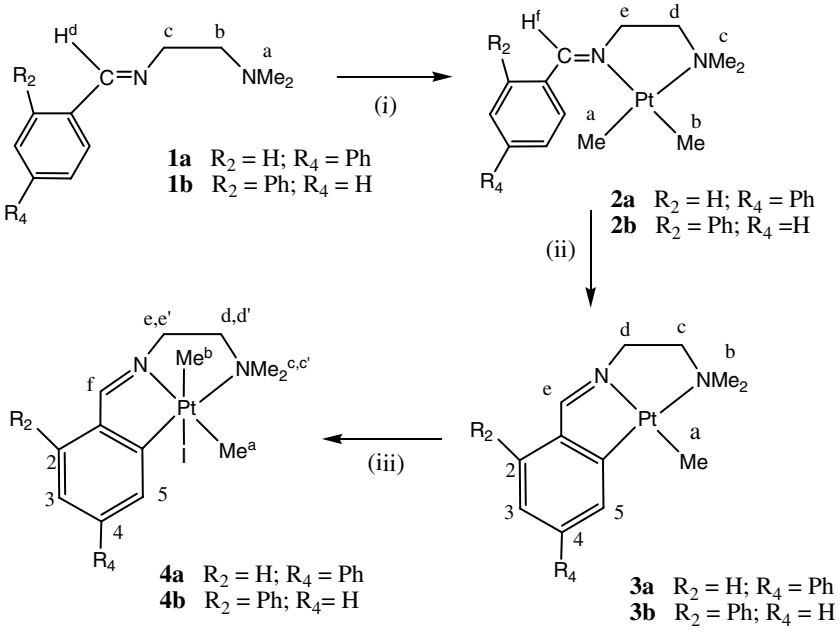


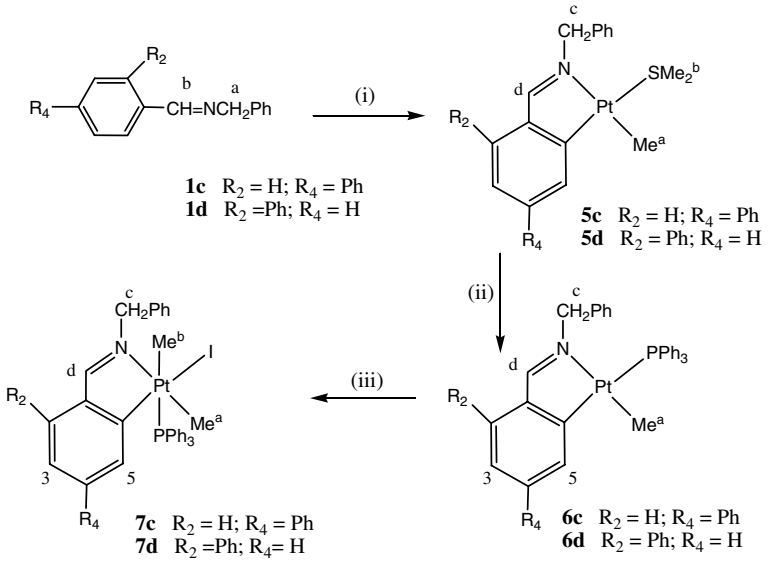
Chart 2. Possible metallation sites for ligands **1a**–**d** studied in this work.

$CHNCH_2CH_2NMe_2\}]$ (**2a**) and $[PtMe_2\{2\text{-}C_6H_5C_6H_4CHN\text{-}CH_2CH_2NMe_2\}]$ (**2b**), respectively in which the imines act as bidentate [N,N′] ligands. Compounds **2** were characterised by NMR spectroscopy and elemental analyses. In the ^1H NMR spectra, two distinct resonances appear in the methyl region, both coupled with ^{195}Pt. The one at higher field with a larger coupling to ^{195}Pt is assigned to the methyl *trans* to the NMe_2 moiety. This assignment was confirmed by a cross-peak between NMe_2 and Me^b observed in the 2D NOESY NMR spectra. In addition, the cross-peak between imine and methylene protons indicates an E conformation around the C=N bond. The coordination of the ligand through both nitrogen atoms is confirmed by the coupling of both amine and imine protons to platinum. The chemical shifts observed for ^{195}Pt are in the expected range [18] for a platinum(II) centre bound to two carbon and two nitrogen atoms see Scheme 1.

Intramolecular activation of C–H bonds followed by methane elimination as reported for analogous systems [11–15] was achieved when toluene solutions of compounds **2** were refluxed for 2 h. Work-up of the resulting solutions revealed in each case formation of a single isomer of a [C,N,N′] cycloplatinated compound as depicted in Scheme 2. Compounds **3** were characterised by NMR spectroscopy



Scheme 1. (i): $+[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, in acetone RT, 30 min; (ii): Refluxing toluene, 2 h; (iii): +MeI, acetone, 20 min.



Scheme 2. (i): $+[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, acetone RT, 16 h.; (ii): $+PPh_3$ (1:1), acetone, 2 h; (iii): +MeI, acetone, 10 min.

and elemental analyses. In the ^{1}H NMR spectra, the methyl ligand and the dimethylamino group are coupled to platinum and the values of the coupling constants are in the usual range for analogous compounds. In agreement with previous data, the J(H–Pt) values of the imine group increase from the coordination compounds **2** to the cyclometallated compounds **3**. In addition, the aromatic proton adjacent to the metallation site is also coupled to platinum [J(H–Pt) ca. 60 Hz]. The presence of resonances corresponding to 8 aromatic C–H confirms the metallation process. The values obtained for δ (^{195}Pt) are in each case shifted towards lower frequency when compared to the corresponding compound **2** which indicates a decrease in the electronic density of the platinum centre upon metallation.

As previously indicated, for ligand **1b** two non-equivalent metallation sites leading to either five- or seven-membered *endo*-metallacycles are available. However, all data suggest that formation of a five-membered platinacycle takes place exclusively. Therefore, this process is more favoured than the formation of a seven-membered metallacycle, although the latter has been obtained in stable cyclometallated compounds (see structure D of Chart 1 [7]). Seven-membered platinacycles display distinct spectral features derived from the formation of a non-planar metallacycle [7] which allow us to disregard formation of such species in the present case. Ultimate confirmation of formation of a five-membered metallacycle is obtained from crystallographic characterization for **3b** described below.

2.2. Cyclometallation in [C,N] systems

The reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with ligands 4-$C_6H_5C_6H_4CHNCH_2Ph$ (**1c**) and 2-$C_6H_5C_6H_4CHNCH_2Ph$ (**1d**) were also studied. As depicted in Chart 2, for these ligands formation of *exo*-cyclic structures, in addition to five- or seven-membered *endo*-cycles is possible. The reactions of ligands **1c** and **1d** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ carried out in acetone at room temperature produced cyclometallated platinum compounds [PtMe{4-$C_6H_5C_6H_3CHNCH_2Ph$}SMe_2] (**5c**) and [PtMe{2-$C_6H_5C_6H_3CHNCH_2Ph$}SMe_2] (**5d**) in which the imines act as bidentate [C,N] ligands. The cyclometallation process, which occurs along with methane formation, takes place under milder conditions than those reported for ligands **1a** and **1b**. In both cases, metallation took place to yield the five-membered *endo*-metallacycles depicted in Scheme 2. Formation of seven-membered metallacycles (for **1d**) or of *exo*-metallacycles was not observed.

The reactions of compounds **5c** and **5d** with PPh_3 were also carried out and produced cyclometallated compounds [PtMe{4-$C_6H_5C_6H_3CHNCH_2Ph$}PPh_3] (**6c**) and [PtMe{2-$C_6H_5C_6H_3CHNCH_2Ph$}PPh_3] (**6d**), respectively, in which the phosphine replaces the SMe_2 ligand. Even with an excess of phosphine the metallacycles are not cleaved, which can be taken as an indication of the high stability of the formed *endo*-metallacycles [19]. It is interesting to note that steric crowding in the coordination sphere of platinum has been shown to favour the cleavage of metallacycles upon reaction with triphenylphosphine [20].

Compounds **5** and **6** were characterised by NMR spectroscopy and elemental analyses and compounds **6c** and **6d** were also characterised crystallographically. All spectral parameters are in good agreement with the results obtained for analogous aryl cyclometallated compounds. In the ^{1}H NMR spectra, the methyl ligand as well as the methylene and the imine groups are coupled to platinum; in addition for compounds **5** the dimethylsulfide is also coupled to ^{195}Pt while for compounds **6** the methyl group is also coupled to ^{31}P. The aromatic proton adjacent to the metallation site (H^5) appears as a singlet for **5c** and as a doublet for **5d**, in both cases coupled to platinum; in addition, H^5 is also coupled to ^{31}P in compounds **6**. J(P–Pt) values are in the range expected for a *trans* arrangement of the phosphine and a phenyl group [12]. The values obtained for δ(^{195}Pt) are shifted towards lower frequency as the ligand covalence increases from S-donor (compounds **5**) to P-donor (compounds **6**).

2.3. Oxidative addition reactions

Previous studies of the oxidative addition of alkyl halides to platinum (II) compounds indicate that nitrogen donor ligands impart high nucleophilicity to the metal centre, increasing its reactivity, which is, however, moderated by the presence of bulky ligands that might hinder or even inhibit the reaction [17]. In order to evaluate the effect of the phenyl substituent in the metallated ring as well as the effect of the bulky PPh_3 ligand the reactions of **3a**, **3b**, **6c** and **6d** with methyl iodide were studied in acetone. In all cases, the reactions proceed to yield the corresponding cyclometallated platinum (IV) compounds containing either a [C,N,N′] (**4a** and **4b**) or a [C,N] (**7c** and **7d**) ligand. The obtained compounds were characterized by elemental analyses and NMR spectroscopies and **4a** was also characterized crystallographically.

For **4b**, the ^{1}H NMR spectrum reveals the formation of a minor isomer (ca. 8% of the mixture) with spectral data very close to those observed for the major isomer which possibly arises from different orientations of the phenyl substituent. Previous studies indicated that the increased bulk of octahedral platinum (IV) versus square-planar platinum (II) centres led to conformational changes related to the steric requirements of the final compounds [21]. In the ^{1}H NMR spectra of **4a** and **4b**, both the dimethylamino and methylene groups are diastereotopic as a result of the chirality resulting from octahedral coordination around the platinum. In both ^{1}H and ^{13}C NMR spectra the couplings to ^{195}Pt observed for methyl and imine are considerably reduced when compared to those of the corresponding platinum (II) substrates, in agreement with the increase of the

oxidation state of the platinum centre. Consistently, the values obtained for $\delta(^{195}Pt)$ are shifted towards higher frequency when compared to those of compounds **3**.

For compounds **7c** and **7d,** a reduced coupling to platinum is observed for the axial methyl, which suggests a *trans* arrangement of the axial methyl and the PPh_3. The *J*(P–Pt) values, which are considerably reduced from those of the corresponding platinum (II) compounds, are in the range expected for platinum (IV) derivatives [12]. The results obtained indicate that the oxidative addition takes place with *trans* stereochemistry and is followed by isomerization of the resulting platinum (IV) compound in order to minimise the unfavourable steric effects of the bulky triphenylphosphine ligand.

2.4. Crystal structures

Suitable crystals of **3b**, **4a**, **6c** and **6d** were grown from acetone solutions. The crystal 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. 1–4.

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

*Compound **3b***			
Pt–C(1)	1.964(3)	Pt–C(18)	2.064(3)
Pt–N(1)	1.990(3)	Pt–N(2)	2.138(3)
N–C(13)	1.262(4)	N(1)–C(14)	1.432(4)
N(2)–C(15)	1.492(6)	C(1)–C(6)	1.403(4)
C(6)–C(13)	1.460(5)	C(14)–C(15)	1.444(5)
C(1)–Pt–N(1)	80.59(11)	C(1)–Pt–C(18)	97.95(14)
N(1)–Pt–N(2)	83.38(11)	C(18)–Pt–N(2)	98.06(13)
*Compound **4a***			
Pt–C(9)	2.002(6)	Pt–N(1)	2.067(5)
Pt–C(19)	2.076(6)	Pt–C(18)	2.082(8)
Pt–N(2)	2.268(6)	Pt–I	2.7947(11)
N(1)–C(13)	1.283(8)	N(1)–C(14)	1.450(9)
N(2)–C(15)	1.507(9)	C(9)–C(10)	1.430(7)
C(10)–C(13)	1.445(9)	C(14)–C(15)	1.524(11)
C(9)–Pt–N(1)	81.4(2)	C(9)–Pt–C(19)	98.4(3)
C(9)–Pt–C(18)	86.6(3)	N(1)–Pt–C(18)	91.1(3)
C(19)–Pt–C(18)	86.6(4)	N(1)–Pt–N(2)	80.0(2)
C(19)–Pt–N(2)	100.2(2)	C(18)–Pt–N(2)	94.7(3)
C(9)–Pt–I	87.81(17)	N(1)–Pt–I	91.83(15)
C(19)–Pt–I	90.5(3)	N(2)–Pt–I	92.19(16)
*Compound **6c***			
Pt–C(1)	2.059(4)	Pt–C(39)	2.062(4)
Pt–N	2.128(3)	Pt–P	2.3022(12)
N–C(13)	1.283(5)	N–C(14)	1.476(6)
C(1)–C(12)	1.395(5)	C(12)–C(13)	1.445(6)
C(1)–Pt–C(39)	90.60(16)	C(1)–Pt–N	78.89(15)
C(39)–Pt–P	86.35(13)	N–Pt–P	104.21(10)
*Compound **6d***			
Pt–C(9)	2.056(6)	Pt–C(39)	2.054(8)
Pt–N	2.134(5)	Pt–P	2.2979(17)
N–C(13)	1.292(7)	N–C(14)	1.474(7)
C(8)–C(9)	1.389(8)	C(8)–C(13)	1.477(8)
C(9)–Pt–C(39)	89.2(3)	C(9)–Pt–N	78.5(2)
C(39)–Pt–P	85.5(2)	N–Pt–P	107.23(14)

In all cases the structures deduced from NMR studies are confirmed. For **3b** and **4a**, 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 **3b**, a methyl ligand completes the square-planar coordination of the platinum atom, while for **4a** an octahedral coordination with the usual *fac*-PtC_3 arrangement [11] is displayed. For **6c** and **6d**, the ligand behaves as [C,N]-bidentate leading to a fused [5,6] bicyclic system containing a five-membered metallacycle; a methyl group, *trans* to the nitrogen atom, and a triphenylphosphine ligand complete the coordination around the platinum.

In all cases the metallacycles are approximately planar as suggested by the sum of internal angles of the five-membered metallacycles which are in all cases close to 540° [22] and nearly coplanar with both the metallated phenyl and the mean coordination plane. Bond lengths and angles lie in the usual range for analogous compounds [11,14,20]. 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 80.59(11)° (**3b**), 81.4(2)° (**4a**), 78.89(15)° (**6c**) and 78.5(2)° (**6d**) and N(1)–Pt–N(2) of 83.38(11)° (**3b**) and 80.0(2)° (**4a**). Conversely, the largest angles correspond to N–Pt–P (104.21(10)° (**6c**) and 107.23(14)° (**6d**)) in agreement with the steric effects associated with the bulk of the triphenylphosphine.

An interesting feature for these compounds containing biphenyl fragments is the dihedral angle between both phenyl groups which are mainly related to steric effects, although packing effects cannot be disregarded. For analogous platinum (II) compounds containing a triphenylphosphine, the two phenyl rings are tilted 10.4(2)° (**6c**) or 49.9(3)° (**6d**) from each other; these values suggest that for the 2-biphenyl system in **6d** the phenyl substituent in the *ortho* position produces a larger congestion in the platinum coordination sphere which is minimised by rotation around the C–C bond. On the other hand, a comparison between the fairly similar values obtained for 2-biphenyl systems (43.5(2)° (**3b**) and 49.9(3)° (**6d**)) indicate that the bulky triphenylphosphine in **6d** is sufficiently far away as to have a significant effect in the position of the phenyl substituent. However, a comparison of the values obtained for 4-biphenyl systems (10.4(2)° (**6c**) and 40.4(2)° (**4a**)) suggest that the increased bulk of octahedral platinum (IV) versus square-planar platinum (II) centres may play a significant role in the relative position of the phenyl substituent.

Although stacked structures are common for platinum complexes, and they become increasingly favoured with increasing arene size [23], significant $\pi\cdots\pi$ interactions have not been found for these compounds derived from biphenyl systems.

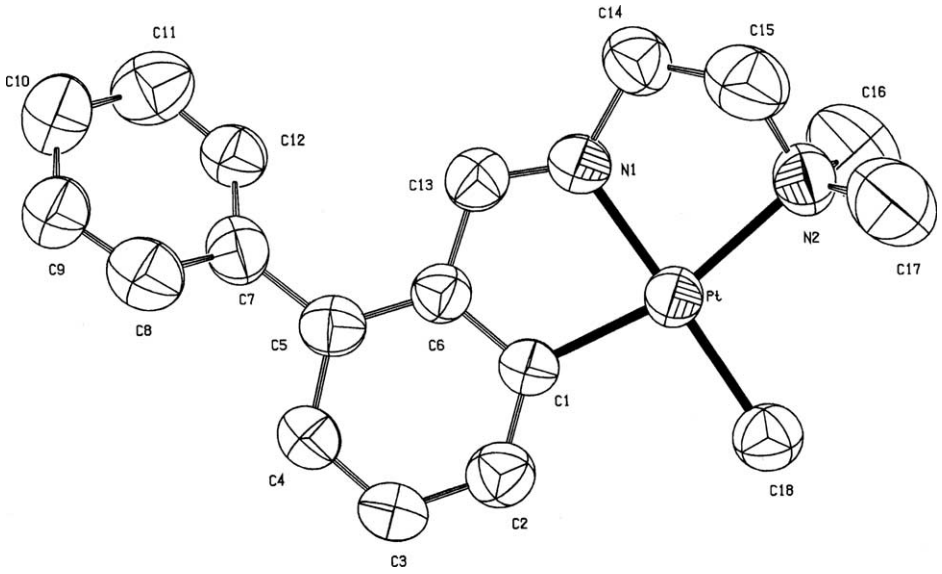


Fig. 1. Molecular structure of compound **3b**.

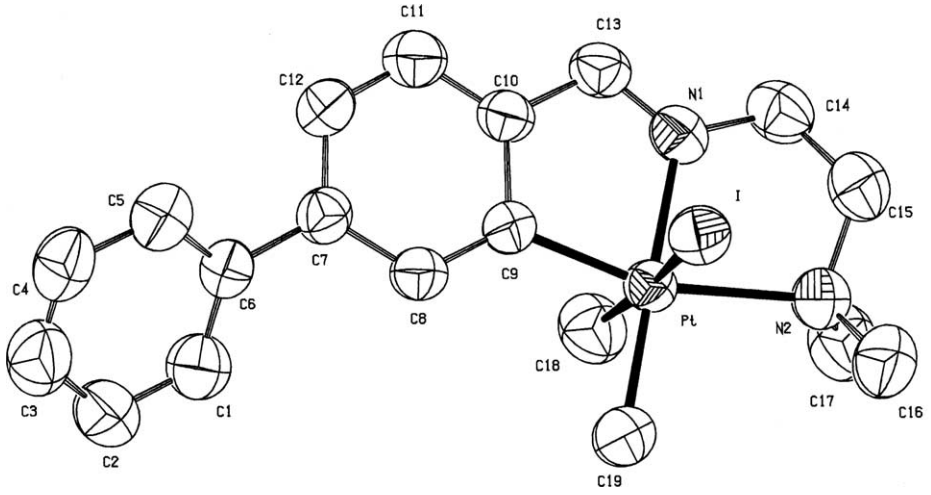


Fig. 2. Molecular structure of compound **4a**.

2.5. Conclusions

In spite of the fact that seven-membered metallacycles have been described [6,7], this type of compound could not be obtained from direct reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with ligands 2-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$ (**1b**) and 2-$C_6H_5C_6H_4CHNCH_2Ph$ (**1d**) derived from 2-biphenylcarboxaldehyde. Instead, these reactions led selectively to formation of the more favoured five-membered metallacycles. The obtained [C,N,N′] and [C,N] cyclometallated platinum (II) compounds along with their analogues derived from 4-biphenylcarboxaldehyde and in some cases the phosphine derivatives were fully characterized including crystal structures. Interestingly, an *ortho* phenyl substituent does not affect the stability of the five-membered metallacycle – since this is not cleaved upon reaction with triphenylphosphine – and does not inhibit the oxidative addition of methyl iodide. However, indication of the steric crowding comes from the fact that while the two phenyl groups are nearly coplanar in 4-biphenyl system **6c**, a larger dihedral angle is observed for 2-biphenyl systems **3b** and **6d** and even for platinum (IV) compound **4a** containing a 4-biphenyl system. In the latter cases, rotation around the C–C bond of the biphenyl systems tends to minimise the steric repulsion in the coordination sphere of platinum (II) (**3b**, **6d**) or platinum (IV) (**4a**).

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, ^{31}P

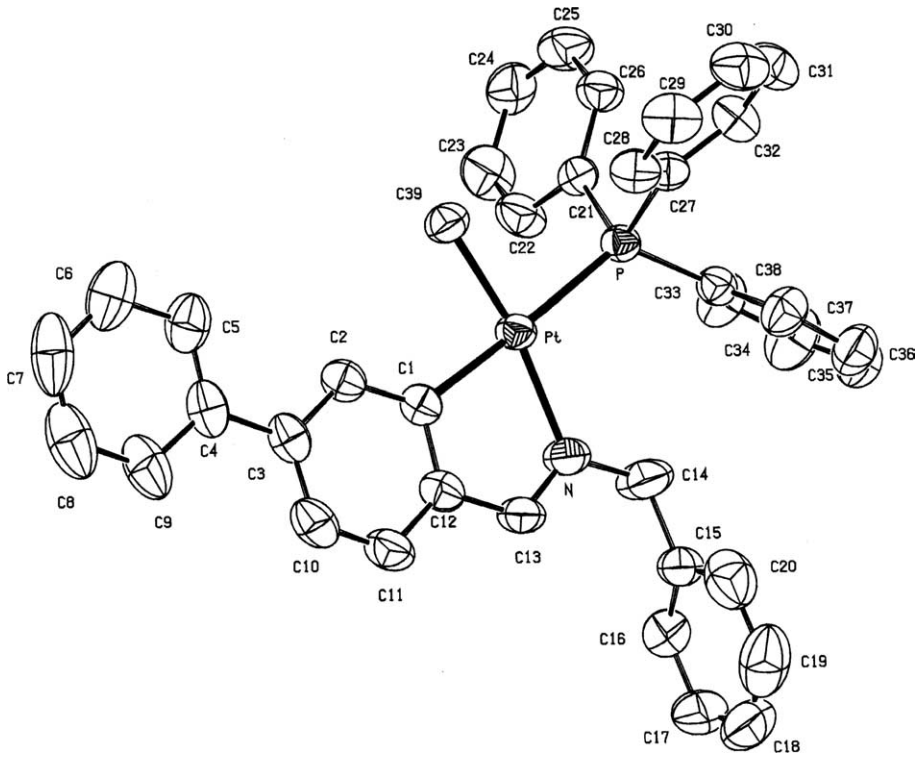


Fig. 3. Molecular structure of compound **6c**.

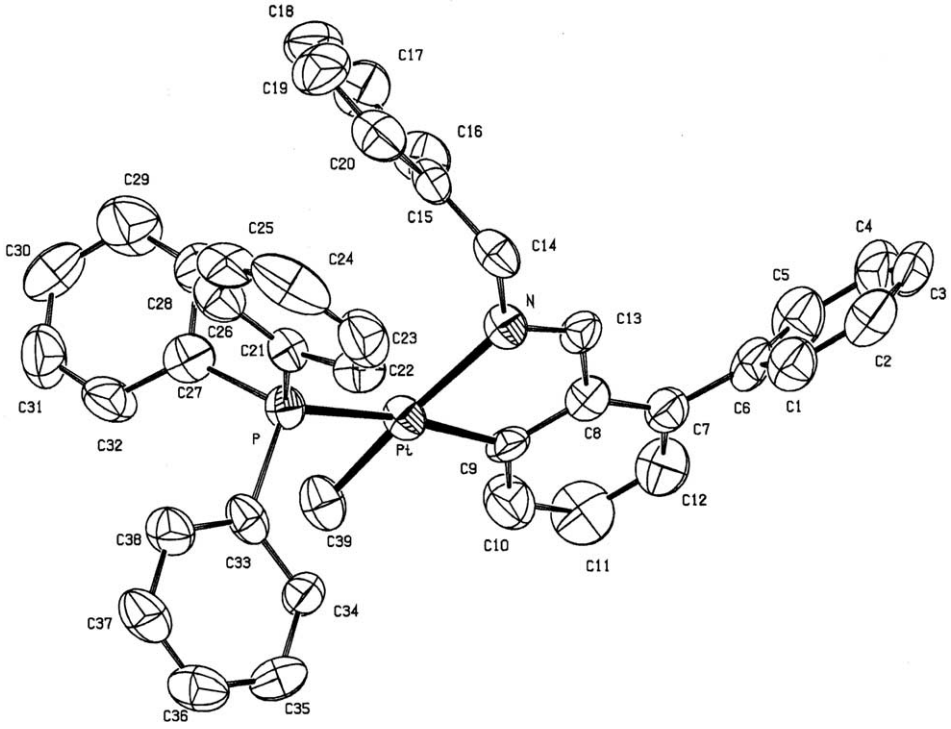


Fig. 4. Molecular structure of compound **6d**.

and ^{195}Pt NMR spectra were recorded by using Varian Gemini 200 (^{1}H, 200 MHz), Bruker 250 (^{31}P, 101.2 MHz;^{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), 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. Microanalyses were performed by the Servei de Recursos Científics i Tècnics de la Universitat Rovira i Virgili de Tarragona.

3.2. Preparation of the compounds

Compound $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ was prepared as reported [24].

3.2.1. Synthetic procedure for the ligands

Compounds **1** were prepared by the reaction of 0.24 g of *N*,*N*-dimethylethylenediamine or 0.29 g of *N*-benzylamine (2.7×10^{-3} mol) with an equimolar amount (0.5 g) of the corresponding aldehyde in toluene (20 mL). The mixture was stirred for 1 h and dried over Na_2SO_4. The solvent was removed in a rotary evaporator to yield yellow oils (**1a**, **1b** and **1d**) or a white solid (**1c**). 4-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$ (**1a**). Yield 0.6 g (87%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.33$ [s, H^a]; 2.66 [t, $^3J(H^b–H^c) = 7.0$, H^b]; 3.77 [t, $^3J(H^c–H^b) = 7.0$, H^c]; {7.18 [t, $^3J(H–H) = 7.0$, 1H], 7.44 [t, $^3J(H–H) = 7.0$, 2H], 7.63 [m, 4H], 7.80 [d, $^3J(H–H) = 8.0$, 2H], aromatics}; 8.35 [s, H^d]. 2-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$ (**1b**). Yield 0.58 g (84%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.27$ [s, H^a]; 2.61 [t, $^3J(H^b–H^c) = 7.0$, H^b]; 3.63 [t, $^3J(H^c–H^b) = 7.0$, H^c]; {7.18 [t, $^3J(H–H) = 7.0$, 1H], 7.34–7.48 [m, 7H], 8.07 [dd, $J(H–H) = 7.0$; 2.0, 1H], aromatics}; 8.26 [s, H^d]. 4-$C_6H_5C_6H_4CHNCH_2Ph$ (**1c**). Yield 0.67 g (90%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.85$ [s, H^a]; {7.37 [m, 5H], 7.46 [t, $^3J(H–H) = 7.0$, 3H], 7.63 [d, $^3J(H–H) = 7.0$, 2H], 7.65 [d, $^3J(H–H) = 8.0$, 2H], 7.86 [d, $J(H–H) = 8.0$, 2H], aromatics}; 8.44 [s, H^d]. 2-$C_6H_5C_6H_4CHNCH_2Ph$ (**1d**). Yield 0.60 g (81%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.71$ [s, H^a]; {7.32–7.48 [m, 13H], 8.16 [dd, $J(H–H) = 7.0$; 2.0, 1H], aromatics}; 8.36 [s, H^d].

3.2.2. Synthetic procedure for the platinum (II) compounds

Compounds **2** were obtained by adding a solution of 88 mg (3.49×10^{-4} mol) of the corresponding imine in acetone (10 mL) to a solution of 100 mg (1.74×10^{-4} mol) of compound $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ in acetone (10 mL). The mixture was stirred for 30 min at room temperature. Compounds **2a** and **2b** were obtained upon removal of the acetone in a rotary evaporator. The yellow solids were washed with ether (3×2 mL) and dried in vacuo. [$PtMe_2${4-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$}] (**2a**). Yield 120 mg (72%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.27$ [s, $^2J(Pt–H) = 90.0$, Me^a]; 0.63 [s, $^2J(Pt–H) = 84.0$, Me^b]; 2.69 [m, H^d]; 2.84 [s, $^3J(H–Pt) = 22.0$, H^c]; 4.07 [m, H^e]; {7.44 [m, 3H], 7.63 [m, 4H], 8.36 [d, $J(H–H) = 8.0$, 2H], aromatics}; 9.00 [s, $^3J(Pt–H) = 46.0$, H^f]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3461.5$ [s]. Anal. Calc. for $C_{19}H_{26}N_2Pt$: C, 47.79; H, 5.49; N, 5.87. Found: C, 47.3; H, 5.8 N, 5.6%. [$PtMe_2${2-$C_6H_5C_6H_4CHNCH_2CH_2NMe_2$}] (**2b**). Yield 127 mg (76%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.19$ [s, $^2J(Pt–H) = 88.8$, Me^a]; 0.61 [s, $^2J(Pt–H) = 84.0$, Me^b]; 2.65 [m, $J(H–H) = 5.0$, H^d], 2.84 [s, $^3J(H–Pt) = 20.8$, H^c]; 3.89 [m, $^3J(H–H) = 5.0$, H^e]; {7.36–7.44 [m, 7H], 7.54 [m, 2H], aromatics}; 8.69 [s, $^3J(Pt–H) = 44.4$, H^f]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3463.0$ [s]. Anal. Calc. for $C_{19}H_{26}N_2Pt \cdot 2H_2O$: C, 44.44; H, 5.89; N, 5.45. Found: C, 45.0; H, 5.6; N, 5.5%.

Compounds **3** were obtained by refluxing during 2 h a toluene solution (20 mL) containing 100 mg of the corresponding compound **2**. The solvent was concentrated in a rotary evaporator to a small volume (2–3 mL) and orange crystals of **3b** were formed. **3a** was obtained as an orange solid when toluene was totally removed and the residue was washed with ether (3×2 mL). [$PtMe${4-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**3a**). Yield 65 mg (67%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.02$ [s, $^2J(Pt–H) = 78.8$, Me^a]; 2.85 [s, $^3J(H–Pt) = 20.0$, H^b]; {3.17 [t, $^3J(H–H) = 6.0$], 4.06 [t, $^3J(H–H) = 6.0$], $H^{c,d}$}; 7.17 [dd, $J(H–H) = 7.6$; 2.0, 1H, H^2 or H^3]; 7.31 [d, $^3J(H–H) = 7.6$, 1H, H^2 or H^3]; 7.40 [t, $^3J(H–H) = 7.6$, 2H, Ph^{meta}]; 7.49 [t, $^3J(H–H) = 7.2$, 1H, Ph^{para}]; 7.63 [d, $^3J(H–H) = 8.0$, 2H, Ph^{ortho}]; 7.84 [d, $J(H–H) = 2.0$, $^3J(H–Pt) = 58.8$, 1H, H^5]; 8.60 [s, $^3J(Pt–H) = 58.8$, H^e]. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -12.25$ [Me^a]; 48.96 [C^b]; {52.27 [$^2J(C–Pt) = 30.2$], 68.12, C^c, C^d}; {121.55, 127.32, 127.62 [2C, $J(C–Pt) = 59.2$], 128.18, 128.68 [2C], 132.57 [$J(C–Pt) = 101.2$], aromatic C–H}; 167.44 [$^2J(Pt–C) = 94.7$, C^e]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3625.9$ [s]. Anal. Calc. for $C_{18}H_{22}N_2Pt$: C, 46.85; H, 4.80; N, 6.07. Found: C, 47.4; H, 5.0; N, 5.9%. [$PtMe${2-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**3b**). Yield 57 mg (59%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.99$ [s, $^2J(Pt–H) = 78.8$, Me^a]; 2.83 [s, $^3J(H–Pt) = 19.6$, H^b]; {3.12 [t, $^3J(H–H) = 6.0$], 3.97 [t, $^3J(H–H) = 6.0$], $H^{c,d}$}; 6.87 [dd, $^3J(H–H) = 7.6$; 1.2, 1H, H^3]; 7.23 [t, $^3J(H–H) = 7.6$, 1H, H^4]; 7.34 [t, $^3J(H–H) = 7.6$, 2H, Ph^{meta}]; 7.38 [d, $^3J(H–H) = 8.0$, 2H, Ph^{ortho}]; 7.39 [t, $^3J(H–H) = 7.6$, 1H]; 7.60 [d, $^3J(H–H) = 7.6$, $^3J(H–Pt) = 63.6$, 1H, H^5]; 8.59 [s, $^3J(Pt–H) = 61.6$, H^e]. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -12.25$ [$^1J(C–Pt) = 791.8$, Me^a]; 49.23 [C^b]; {52.94 [$^2J(C–Pt) = 30$], 68.33, C^c, C^d}; {124.20, 127.48, 128.61 [2C], 130.03 [2C], 131.80 [1C, $^3J(C–Pt) = 73.6$, C^3], 133.35 [1C, $^2J(C–Pt) = 90.3$, C^2], aromatic C–H}; {142.37, 143.46, 143.59, 148.16, aromatic C}; 167.41 [$^2J(Pt–C) = 93.6$, C^e]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3609.4$ [s]. Anal. Calc. for $C_{18}H_{22}N_2Pt$: C, 46.85; H, 4.80; N, 6.07. Found: C, 46.8; H, 4.8; N, 6.1%.

Compounds **5c** and **5d** were obtained by adding a solution of 94 mg (3.5×10^{-4} mol) of the corresponding imine in acetone (10 mL) to a solution of 100 mg (1.74×10^{-4} mol) of compound $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ in acetone (10 mL). The mixture was stirred for 16 h at room temperature and compounds **5** were obtained as orange (**5c**) or yellow (**5d**) solids upon removal of the acetone in a rotary evaporator. The products were washed with hexane (3×2 mL) and dried in vacuo. [$PtMe${4-$C_6H_5C_6H_4CHNCH_2Ph$}SMe_2] (**5c**). Yield 110 mg (58%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.06$ [s, $^2J(Pt–H) = 82.4$,

Me^{a}]; 2.02 [s, ^{3}J(H–Pt) = 26.4, H^{b}]; 5.22 [s, ^{3}J(Pt–H) = 12.8, H^{c}], {7.33 [m, 5H], 7.43 [m, 4H], 7.66 [m, 3H], 7.99 [s, ^{3}J(H–Pt) = 62.4, H^{5}], aromatics}; 8.62 [s, ^{3}J(H–Pt) = 54.4, H^{d}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3633.2$ [s]. Anal. Calc. for $C_{23}H_{25}NPtS$: C, 50.91; H, 4.64; N, 2.58. Found: C, 51.4; H, 4.7; N, 2.7%. [PtMe{2-$C_6H_5C_6H_4CHNCH_2Ph$}SMe_2] (**5d**). Yield 100 mg (53%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.01$ [s, ^{2}J(Pt–H) = 80.2, Me^{a}]; 1.99 [s, ^{3}J(H–Pt) = 26.6, H^{b}]; 5.14 [s, ^{3}J(Pt–H) = 13.8, H^{c}], {7.01 [d, ^{3}J(H–H) = 8.0, 1H], 7.29–7.40 [m, 11H], 7.75 [d, ^{3}J(H–H) = 7, ^{3}J(H–Pt) = 62.8, 1H, H^{5}], aromatics}; 8.67 [s, ^{3}J(H–Pt) = 56.4, H^{d}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3972.9$ [s]. Anal. Calc. for $C_{23}H_{25}NPtS$: C, 50.91; H, 4.64; N, 2.58. Found: C, 50.5; H, 4.8; N, 2.8%.

Compounds **6c** and **6d** were obtained by adding 24 mg (0.9×10^{-4} mol) of PPh_3 to a solution of 50 mg (0.9×10^{-4} mol) of the corresponding compound **5** in acetone (10 mL). The mixture was stirred for 1 h at room temperature and the acetone was removed in a rotary evaporator. The yellow solids were washed with hexane (3×2 mL) and ether (3×2 mL) and dried in vacuo. [PtMe{4-$C_6H_5C_6H_4CHNCH_2Ph$}PPh_3] (**6c**). Yield 40 mg (58%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.87$ [d, ^{2}J(Pt–H) = 82.4, ^{3}J(P–H) = 7.4, Me^{a}]; 4.29 [s, ^{3}J(Pt–H) = 10.0, H^{c}], {6.81–6.86 [m, 1H], 7.17–7.20 [m, 1H], 7.34–7.44 [m, 15H], 7.64–7.74 [m, 10H], 8.13 [d, ^{4}J(H–P) = 7.0, ^{3}J(H–Pt) = 48.6, H^{5}], aromatics}; 8.33 [s, ^{3}J(H–Pt) = 55.2, H^{d}]. ^{31}P NMR (101.2 MHz, $CDCl_3$): $\delta = 30.13$ [s, ^{1}J(Pt–P) = 2189.0]. ^{195}Pt NMR (54 MHz, acetone-d^{6}): $\delta = -4248.5$ [s, ^{1}J(Pt–P) = 2196.0]. Anal. Calc. for $C_{39}H_{34}NPPt \cdot 2H_2O$: C, 60.15; H, 4.92; N, 1.80. Found: C, 59.8; H, 4.7; N, 2.0%. [PtMe{2-$C_6H_5C_6H_4CHNCH_2$-Ph}PPh_3] (**6d**). Yield 40 mg (58%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.82$ [d, ^{2}J(Pt–H) = 82.0, ^{3}J(P–H) = 7.0, Me^{a}]; 4.25 [s, ^{3}J(Pt–H) = 10.2, H^{c}], {6.70–6.75 [m, 1H], 7.07–7.10 [m, 1H], 7.30–7.34 [m, 15H], 7.59–7.68 [m, 10H], 7.94 [dd, ^{3}J(H–H) = 6, ^{4}J(H–P) = 5.0, ^{3}J(H–Pt) = 50.8, H^{5}], aromatics}; 8.46 [s, ^{3}J(H–Pt) = 57.4, H^{d}]. ^{31}P NMR (101.2 MHz, $CDCl_3$): $\delta = 29.87$ [s, ^{1}J(Pt–P) = 2168.0]. ^{195}Pt NMR (54 MHz, acetone-d^{6}): $\delta = -4245.5$ [s, ^{1}J(Pt–P) = 2164.0]. Anal. Calc. for $C_{39}H_{34}NPPt \cdot H_2O$: C, 61.57; H, 4.6; N, 2.0. Found: C, 61.1; H, 4.6; N, 2.0%.

3.2.3. Synthetic procedure for the platinum (IV) compounds

An excess of methyl iodide (0.5 mL) was added to a solution of 20 mg of compound **3a** in acetone and the mixture was stirred at room temperature. After 15 min, the solution colour changed from red to yellow. The solvent was removed and the residue was washed with hexane to yield **4a** as a light yellow solid which was dried in vacuo. [$PtMe_2I${4-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**4a**). Yield 18 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.84$ [s, ^{2}J(Pt–H) = 71.6, Me^{b}]; 1.30 [s, ^{2}J(Pt–H) = 64.8, Me^{a}]; {2.58 [s, ^{3}J(H–Pt) = 15.2], 3.22 [s, ^{3}J(H–Pt) = 11.2], Me^{c}}; {3.02 [ddd, J(H–H) = 12.0; 5.0; 3.0, 1H], 4.23 [td, J(H–H) = 12.0; 5.0, 1H], H$^{d,d\prime}$} {4.05 [ddd, J(H–H) = 12.0; 4.0; 2.0, 1H], 4.13 [m, 1H], H$^{e,e\prime}$}; 7.26 [dd, J(H–H) = 8.0; 1.6, 1H, H^{2}]; 7.35 [t, ^{3}J(H–H) = 7.2, 1H, Ph^{para}]; 7.41 [d, ^{3}J(H–H) = 7.6; 1H, H^{3}]; 7.43 [t, ^{3}J(H–H) = 7.6; 2H, Ph^{meta}]; 7.53 [d, J(H–H) = 1.6, ^{3}J(H–Pt) = 46.4, 1H, H^{5}]; 7.66 [d, ^{3}J(H–H) = 7.2, 2H, Ph^{ortho}]; 8.42 [s, ^{3}J(Pt–H) = 48.0, H^{f}]. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -5.49$ [^{1}J(C–Pt) = 622.7, Me^{a}]; 9.57 [^{1}J(C–Pt) = 662.2, Me^{b}]; {47.32, 53.46, C$^{c,c\prime}$}; 51.96 [^{2}J(C–Pt) = 15.2, C^{e}]; 67.85 [C^{d}]; 122.87 [C^{2}]; 127.79 [2C, Ph^{meta}]; 128.01 [Ph^{para}]; 128.87 [2C, Ph^{ortho}]; 129.71 [^{2}J(C–Pt) = 47.1, C^{5}]; 129.77 [^{4}J(C–Pt) = 34.6, C^{3}]; 167.92 [^{2}J(Pt–C) = 52.3, C^{e}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -2653.72$ [s]. Anal. Calc. for $C_{19}H_{25}IN_2Pt$: C, 37.82; H, 4.17; N, 4.64. Found: C, 37.5; H, 4.2; N, 4.3%. Compounds **4b**, **7c** and **7d** were obtained following the same procedure from **3b**, **6c** and **6d**, respectively. [$PtMe_2I${2-$C_6H_5C_6H_3CHNCH_2CH_2NMe_2$}] (**4b**). Yield 18 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer, $\delta = 0.85$ [s, ^{2}J(Pt–H) = 71.6, Me^{b}]; 1.26 [s, ^{2}J(Pt–H) = 64.0, Me^{a}]; {2.57 [s, ^{3}J(H–Pt) = 15.2], 3.21 [s, ^{3}J(H–Pt) = 10.8], Me^{c}}; {2.99 [m, 1H], 3.97 [m, 1H], 4.08 [m, 1H], 4.18 [td, J(H–H) = 12.0; 5.0, 1H], H$^{d,d\prime,e,e\prime}$}; {6.96 [dd, J(H–H) = 7.0; 1.2, 1H], 7.27–7.32 [m, 2H], 7.38–7.43 [m, 5H], aromatics}; 8.41 [s, ^{3}J(Pt–H) = 49.2, H^{f}]. minor isomer, $\delta = 0.68$ [s, ^{2}J(Pt–H) = 74.4, Me^{b}]; 1.06 [s, ^{2}J(Pt–H) = 62.8, Me^{a}]; {2.57 [s, ^{3}J(H–Pt) = 15.2], 2.97 [s, ^{3}J(H–Pt) = 9.0], Me^{c}}; 7.00 [d, J(H–H) = 7.2; 1H]; 8.46 [s, ^{3}J(Pt–H) = 49.6, H^{f}]. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -5.26$ [^{1}J(C–Pt) = 620.6, Me^{a}]; 9.67 [^{1}J(C–Pt) = 665.1, Me^{b}]; {47.27, 53.46, C$^{c,c\prime}$}; 52.30 [^{2}J(C–Pt) = 15.0, C^{e}]; 67.73 [C^{d}]; {125.30, 127.79, 128.52 [2C], 129.90 [2C], 130.36 [J(C–Pt) = 40.9], 132.41 [J(C–Pt) = 58.5], aromatics C–H}; {139.55, 140.62, 143.24, 144.37, aromatic C}; 168.02 [^{2}J(Pt–C) = 50.0, C^{e}]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -2662.9$ [s]. Anal. Calc. for $C_{19}H_{25}IN_2Pt$: C, 37.82; H, 4.17; N, 4.64. Found: C, 38.1; H, 4.4; N, 4.6%. [$PtMe_2I${4-$C_6H_5C_6H_4CHNCH_2Ph$}PPh_3] (**7c**). Yield 20 mg (84%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.27$ [d, ^{2}J(Pt–H) = 59.8, ^{3}J(P–H) = 7.6, Me^{b}]; 1.64 [d, ^{2}J(Pt–H) = 70.2, ^{3}J(P–H) = 7.8, Me^{a}]; {4.70 [d], 5.55 [d], ^{3}J(H–H) = 17.0, H^{c}}, {6.69 [s, ^{3}J(H–Pt) = 46.6, 1H, H^{5}], 6.88–6.91 [m, 1H], 7.20–7.47 [m, 26H], aromatics}; 7.71 [d, J(H–P) = 1.6, ^{3}J(H–Pt) = 48.2, H^{d}]. ^{31}P NMR (101.2 MHz, $CDCl_3$): $\delta = -9.20$ [s, ^{1}J(Pt–P) = 1009.7]. Anal. Calc. for $C_{40}H_{37}INPPt \cdot 2H_2O$: C, 52.18; H, 4.49; N, 1.52. Found: C, 52.6; H, 4.7; N, 1.5%. [$PtMe_2I${2-$C_6H_5C_6H_4CHNCH_2Ph$}PPh_3] (**7d**). Yield 18 mg (75%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.25$ [d, ^{2}J(Pt–H) = 60.4, ^{3}J(P–H) = 7.6, Me^{b}]; 1.56 [d, ^{2}J(Pt–H) = 69.6, ^{3}J(P–H) = 7.8, Me^{a}]; {4.79 [d], 5.53 [d], ^{3}J(H–H) = 16.4, H^{c}}, {6.61 [m, 1H], 6.83–6.85 [m, 2H], 6.92–6.95 [m, 3H], 7.18–7.45 [m, 22H], aromatics}; 7.80 [d, J(H–P) = 1.6, ^{3}J(H–Pt) = 49.6, H^{d}]. ^{31}P NMR (101.2 MHz, $CDCl_3$): $\delta = -8.96$ [s, ^{1}J(Pt–P) = 991.4]. Anal. Calc. for $C_{40}H_{37}INPPt \cdot 2H_2O$: C, 52.18; H, 4.49; N, 1.52. Found: C, 52.6; H, 4.7; N, 1.6%.

Table 2
Crystallographic and refinement data for compounds **3b**, **4a**, **6c** and **6d**

	Compound **3b**	Compound **4a**	Compound **6c**	Compound **6d**
Formula	$C_{18}H_{22}N_2Pt$	$C_{19}H_{25}IN_2Pt$	$C_{39}H_{34}NPPt$	$C_{39}H_{34}NPPt$
Fw	461.47	603.40	742.73	742.73
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Orthorhombic, *Pbca*	Monoclinic, $P2_1/n$	Triclinic $P\bar{1}$	Monoclinic, $P2_1/c$
a (Å)	11.212(4)	7.886(4)	12.215(6)	8.708(12)
b (Å)	25.578(2)	17.270(7)	12.488(5)	20.364(4)
c (Å)	11.121(4)	15.105(6)	12.746(5)	17.473(9)
α (°)	90	90	99.52(2)	90
β (°)	90	101.95(2)	115.15(2)	90.57(7)
γ (°)	90	90	106.78(3)	90
V (Å^3); Z	3189.3(16); 8	2012.6(15); 4	1589.2(12); 2	3098(5); 4
d (calcd) (Mg/m^3)	1.922	1.991	1.552	1.592
Absorption coefficient (mm^{-1})	8.794	8.507	4.493	4.609
$F(000)$	1776	1136	736	1472
Number of refections collected/unique (R_{int})	22,949/4503 (0.0241)	18,925/5640 (0.0460)	18,008/9327 (0.0284)	9021/9021 (0.0310)
Data/restraints/parameters	4503/0/190	5640/0/209	9327/0/380	9021/0/423
Goodness-of-fit F^2	0.975	1.224	1.208	0.850
$R_1(I > 2\sigma(I))$	0.0341	0.0473	0.0358	0.0363
wR_2 (all data)	0.1105	0.0932	0.0790	0.0862
Peak and hole (e Å^{-3})	0.895 and −0.702	0.869 and −0.663	0.881 and −0.768	0.771 and −0.847

3.3. X-ray structure analysis

3.3.1. Data collection

Crystals of **3b**, **4a**, **6c** and **6d** were obtained from slow evaporation of acetone solution. Prismatic crystals were selected and mounted on an MAR345 diffractometer with an image plate detector (**3b**, **4a** and **6c**) or on a Enraf-Nonius diffractometer (**6d**). Unit cell parameters were determined from 117 (**3b**), 97 (**4a**), 108 (**6c**) reflections ($3° < \theta < 31°$) or from automatic centering of 25 reflections ($12° < \theta < 21°$) (**6d**) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation. For **3b**, 22,949 reflections were measured in the range $3.52° < \theta < 33.46°$; 4503 of which were non-equivalent by symmetry ($R_{int} = 0.024$). For **4a**, 18,925 reflections were measured in the range $3.60° < \theta < 33.17°$; 5640 of which were non-equivalent by symmetry ($R_{int} = 0.046$). For **6c**, 18,008 reflections were measured in the range $3.49° < \theta < 33.23°$; 9327 of which were non-equivalent by symmetry ($R_{int} = 0.028$). For **6d**, 9021 reflections were measured in the range $2.00° < \theta < 29.97°$. 3211 (**3b**), 5189 (**4a**), 8387 (**6c**) and 4113 (**6d**) reflections 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 structures were solved by Patterson synthesis (**3b**) or direct methods (**4a**, **6c** and **6d**), using SHELXS-97 computer program [25], and refined by the full-matrix least-squares method, with the SHELXL-97 computer program [25] using 22,949 (**3b**), 18,925 (**4a**), 9327 (**6c**) and 9021 (**6d**) reflections (very negative intensities were not assumed). The function minimised was $\sum w \ |F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.1530P)^2]^{-1}$ (**3b**), $w = [\sigma^2(I) + (0.0187P)^2 + 7.0257P]^{-1}$ (**4a**), $w = [\sigma^2(I) + (0.0143P)^2 + 3.0417P]^{-1}$ (**6c**) and $w = [\sigma^2(I) + (0.0269P)^2]^{-1}$ (**6d**) and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f''were taken from International Tables of X-ray Crystallography [26]. For **6d**, 11 H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. Twenty three hydrogen atoms (**6d**) and all H atoms (**3b**, **4a** and **6c**) were 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. Further details are given in Table 2.

4. Supplementary material

The crystallographic data of compounds **3b**, **4a**, **6c** and **6d** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 278492, 278493, 278490 and 278491.

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