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Regioselective activation of C–H bonds of naphthyl imines at platinum(II). Crystal structures of [PtMe{1-(2′-ClC₆H₄CH₂NCH)C₁₀H₆}PPh₃] and [PtMe{2-(2′-ClC₆H₄CH₂NCH)C₁₀H₆}PPh₃]

Margarita Crespo [a],*, Mercè Font-Bardía [b], Sonia Pérez [a], Xavier Solans [b]

[a] *Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Diagonal 647, E-08028 Barcelona, Spain*
[b] *Departament de Cristal.lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, E-08028 Barcelona, Spain*

Abstract

The reaction of [Pt₂Me₄(μ-SMe₂)₂] with ligands 1-(Me₂NCH₂CH₂NCH)C₁₀H₇ (**2a**) and 2-(Me₂NCH₂CH₂NCH)C₁₀H₇ (**2b**) carried out in acetone at room temperature produced compounds [PtMe₂{1-(Me₂NCH₂CH₂NCH)C₁₀H₇}] (**3a**) and [PtMe₂{1-(Me₂NCH₂CH₂NCH)C₁₀H₇}] (**3b**), respectively, in which the imines act as bidentate [N,N′] ligands. Cyclometallated [C,N,N′] compounds [PtMe{1-(Me₂NCH₂CH₂NCH)C₁₀H₆}] (**4a**) and [PtMe{2-(Me₂NCH₂CH₂NCH)C₁₀H₆}] (**4b**) were obtained by refluxing toluene solutions of compounds **3a** or **3b**. Reaction of [Pt₂Me₄(μ-SMe₂)₂] with ligands 1-(2′-ClC₆H₄CH₂NCH)C₁₀H₇ (**2c**) and 2-(2′-ClC₆H₄CH₂NCH)C₁₀H₇ (**2d**) produced straightforward metallation to yield [PtMe{1-(2′-ClC₆H₄CH₂NCH)C₁₀H₆}SMe₂] (**5c**) and [PtMe{2-(2′-ClC₆H₄CH₂NCH)C₁₀H₆}SMe₂] (**5d**) containing a [C,N] ligand. Triphenylphosphine derivatives [PtMe{1-(2′-ClC₆H₄CH₂NCH)C₁₀H₆}PPh₃] (**6c**) and [PtMe{2-(2′-ClC₆H₄CH₂NCH)C₁₀H₆}PPh₃] (**6d**) were also prepared. All compounds were characterised by NMR spectroscopies and **6c** and **6d** were also characterised crystallographically. For both [C,N,N′] and [C,N] systems, the metallation took place regioselectively at β-positions of the naphthyl group. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Platinum; Naphthyl imines; Cyclometallation; Crystal structures

1. Introduction

Cyclometallated platinum and palladium compounds have been studied extensively, particularly for benzene derivatives. Metallation sites other than benzene ring carbon have been less explored, although fused ring systems and heterocyclic compounds are attractive for regioselectivity studies due to the presence of non-equivalent positions.

Following our studies of imines derived from aromatic aldehydes [1], we now report the reactions of [Pt₂Me₄(μ-SMe₂)₂] with imines derived from 1- and 2-naphthaldehydes.

As shown in Scheme 1, naphthalenes with donor-bearing substituents at C(1) can be cyclometallated at the *ortho*-C(2) or the *peri*-C(8) positions. Palladium and platinum compounds cyclometallated at the peri position have been reported [2] including a bis-cyclo-platinated compound derived from 1-(dimethyl-lamino)naphthalene [3] and a binuclear dipalladated compound derived from 1,1′-bis(dimethylamino)-naphthalene [4]. For 1,1′-azonaphthalenes, it has been
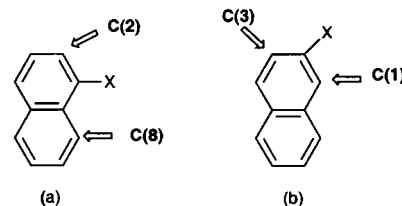
Scheme 1. Metallation sites for (a) 1-substituted naphthalenes and (b) 2-substituted naphthalenes.

* Corresponding author. Tel.: +34-93-4021273; fax: +34-93-4907725.
E-mail address: margarita.crespo@qi.ub.es (M. Crespo).
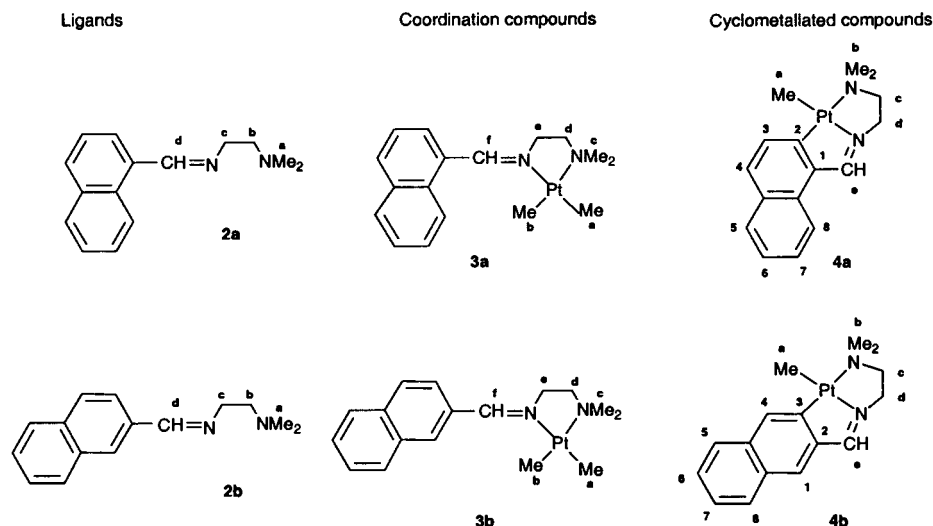
Scheme 2.

reported that metallation at both C(2) and C(8) yields, respectively, five- and six-membered metallacycles [5]. However, palladation of (1-naphthyl)ethylamine [6], *N*,*N*-dimethyl-1-(1-naphthyl)ethylamine [7] and imines derived from 1-naphthaldehyde [8] took place exclusively at the C(2) of the naphthyl to give five-membered metallacycles, which have been used as resolving agents for phosphines.

Naphthalenes with donor groups at C(2) could, in principle, be metallated at two non-equivalent positions, as shown in Scheme 1. Previous reports indicate that the preferred metallation site is the less hindered C(3) position [9].

2. Results and discussion

Ligands 1-$(Me_2NCH_2CH_2NCH)C_{10}H_7$ (**2a**), 2-$(Me_2NCH_2CH_2NCH)C_{10}H_7$ (**2b**), 1-$(2'$-$ClC_6H_4CH_2$-$NCH)C_{10}H_7$ (**2c**) and 2-$(2'$-$ClC_6H_4CH_2NCH)C_{10}H_7$ (**2d**) were prepared from the condensation reactions of the corresponding aldehyde and *N*,*N*-dimethylethylenediamine or 2-chlorobenzylamine carried out in toluene at room temperature. The resulting imines were characterised by ^{1}H- and ^{13}C-NMR spectra.

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

The reactions of $[Pt_2Me_4(\mu$-$SMe_2)_2]$ (**1**) with potentially terdentate ligands 1-$(Me_2NCH_2CH_2NCH)C_{10}H_7$ (**2a**) and 2-$(Me_2NCH_2CH_2NCH)C_{10}H_7$ (**2b**) carried out in acetone at room temperature produced compounds $[PtMe_2\{1$-$(Me_2NCH_2CH_2NCH)C_{10}H_7\}]$ (**3a**) and $[PtMe_2\{1$-$(Me_2NCH_2CH_2NCH)C_{10}H_7\}]$ (**3b**), respectively, in which the imines act as bidentate [N,N′] ligands. Compound **3** was characterised by NMR spec-

troscopies, elemental analyses and FAB-mass spectra. In the ^{1}H-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 was assigned to the methyl *trans* to the NMe$_2$ moiety. The coordination of the ligand through both nitrogen atoms is confirmed by the coupling of both amine and imine protons to platinum. ^{13}C-NMR and FABMS spectra were consistent with the structures depicted in Scheme 2. The chemical shifts observed for ^{195}Pt were in the expected range [10] for a platinum(II) centre bound to two-carbon and two-nitrogen atoms.

Compound $[PtMe_2\{2$-$(Me_2NCH_2CH_2NCH)C_{10}H_7\}]$ (**3b**) in acetone solution at room temperature within 16 h produced the cyclometallated compound $[PtMe\{2$-$(Me_2NCH_2CH_2NCH)C_{10}H_6\}]$ (**4b**) in which the imine acted as a [C,N,N′] ligand. This process consisted of intramolecular activation of a C–H bond of the aryl group followed by methane elimination as reported for analogous systems [1]. In marked contrast, compound $[PtMe_2\{1$-$(Me_2NCH_2CH_2NCH)C_{10}H_7\}]$ (**3a**) is stable in acetone solution at room temperature for several days, which indicates a lower tendency to cyclometallate.

Cyclometallated compound $[PtMe\{1$-$(Me_2NCH_2$-$CH_2NCH)C_{10}H_6\}]$ (**4a**) could be obtained by refluxing a toluene solution of compound **3a** for 2 h and this method could also be used to obtain **4b** from **3b**.

Compound **4** was characterised by NMR spectroscopies, elemental analyses and FABMS. In both cases, the reaction yielded regioselectively one single isomer as depicted in Scheme 2. Assignment of the aromatic regions of **4a** and **4b** was performed with the aid of ^{1}H–^{1}H correlation spectroscopy (COSY). All spectral parameters for compound **4** are in good agreement with the results obtained for analogous aryl cyclometallated compounds. The values obtained for $\delta(^{195}$Pt) are in

each case shifted towards higher fields when compared with the corresponding compound **3**, which indicates a decrease in the electronic density of the platinum centre upon metallation.

As reported in the literature for analogous systems [8], the metallation site for **4a** is C(2), while for **4b**, two singlets in the aromatic region, assigned to H^1 and H^4, confirm that the metallation site is C(3). Therefore, for both naphthyl systems under study, metallation took place selectively at β-positions to yield four fused ring systems containing a five-membered metallacycle. Even though in both cases, substitution at β-position was thermodynamically favoured [11], the factors involved in the regioselectivity of the process were not entirely the same as for ligands **2a** and **2b**. In the former case, the only α-position available for metallation should lead to a less favoured six-membered metallacycle [12], while for **2b** metallation at C(1) would lead to steric repulsions between the methyl group and H(8) [9].

2.2. Cyclometallation in [C,N] systems

The reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) with ligands 1-(2′-ClC$_6$H$_4$CH$_2$NCH)C$_{10}$H$_7$ (**2c**) and 2-(2′-ClC$_6$H$_4$-CH$_2$NCH)C$_{10}$H$_7$ (**2d**) were also studied. As depicted in Scheme 3, four different metallation sites are now available leading to platinum metallacycles with either an *endo*-cyclic (containing the C=N group) or an *exo*-cyclic structure.

The reactions of ligands **2c** and **2d** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) carried out in acetone at room temperature produced cyclometallated platinum compounds [PtMe{1-(2′-ClC$_6$H$_4$CH$_2$NCH)C$_{10}$H$_6$}SMe$_2$] (**5c**) and [PtMe{2-(2′-ClC$_6$H$_4$CH$_2$NCH)C$_{10}$H$_6$}SMe$_2$] (**5d**) in which the imines act as a bidentate [C,N] ligands.

The cyclometallation process, which occurs along with methane formation, takes place under milder conditions than those reported for ligands **2a** and **2b**. Previous results indicate that coordination of the imine ligand to platinum is a preceding step to the cyclometallation process but for imines containing only a single nitrogen, such intermediates could only be de-

tected when the metallation step is hindered by bulky groups [13].

In both cases, metallation took place exclusively at β-positions of the naphthalene to yield regioselectively the *endo*-metallacycles depicted in Scheme 4. Formation of *exo*-metallacycles was not observed in spite of the fact that this process could be achieved by activation of a weaker C–Cl bond. This result suggests the reactivity order: C–H (*endo*) > C–Cl (*exo*) as reported previously for phenyl systems [1b,1c]. Even though four metallation sites are available for ligands **2c** and **2d**, the results obtained are analogous in terms of selectivity to those reported above for the terdentate ligands.

The reactions of compounds **5c** and **5d** with PPh$_3$ were also carried out and produced cyclometallated compounds [PtMe{1-(2′-ClC$_6$H$_4$CH$_2$NCH)C$_{10}$H$_6$}PPh$_3$] (**6c**) and [PtMe{2-(2′-ClC$_6$H$_4$CH$_2$NCH)C$_{10}$H$_6$}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.

Compounds **5** and **6** were characterised by NMR spectroscopy and elemental analyses and compound **6** was also characterised crystallographically. All spectral parameters are in good agreement with the results obtained for analogous aryl cyclometallated compounds. In particular, J(P–Pt) values are in the same range as obtained for [PtMe{2-ClC$_6$H$_4$CH$_2$NCHC$_6$-H$_4$}PPh$_3$] [14] as expected from the similar *trans* influence of naphthyl and phenyl groups. The values obtained for δ(^{195}Pt) are shifted towards higher fields as the ligand covalency increases from N-donor (compound **4**) to S-donor (compound **5**) to P-donor (compound **6**).

2.3. Crystal structures of compounds 6c and 6d

Suitable crystals were grown from dichloromethane solutions, which were layered with hexane. The crystal structures are composed of discrete molecules separated by van der Waals interactions. Selected bond lengths

Scheme 3. Possible metallation sites for (i) ligands **2c** and **2d**.

Ligands   Cyclometallated compounds
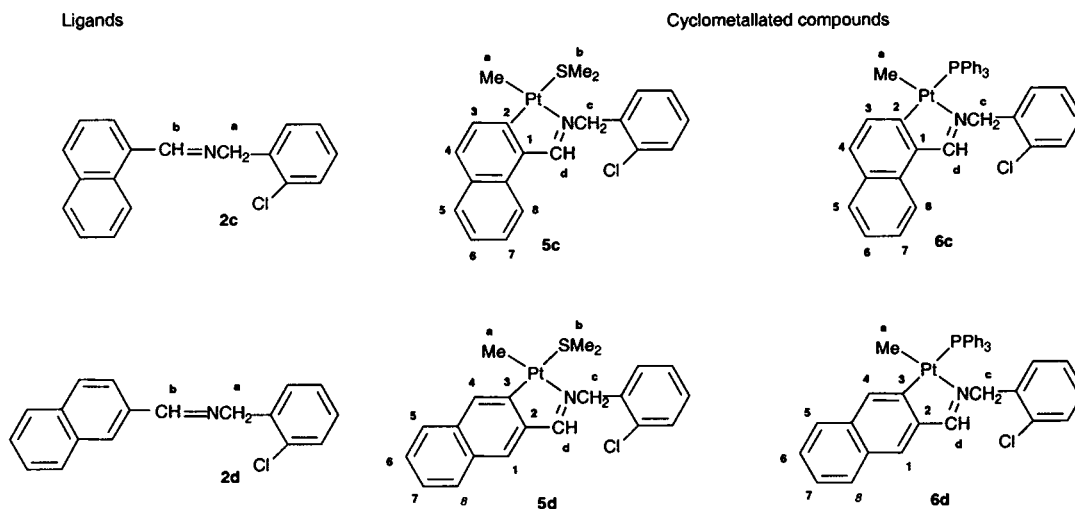
Scheme 4.

and angles are given in Table 1 (**6c**) and Table 2 (**6d**), and molecular views are shown in Fig. 1 (**6c**) and Fig. 2 (**6d**).

Both structures show that metallation took place at a β-position of the naphthyl group to yield a three-fused [6,6,5] ring system containing a five-membered *endo*-metallacycle. The methyl group, *trans* to the nitrogen atom, and the triphenylphosphine ligand complete a tetrahedral distorted planar coordination around the platinum. The metallacycles are approximately planar; the largest deviation from the mean plane determined by the five atoms is 0.0172 Å for C(11) (**6c**) and 0.0197 Å for N (**6d**). In each case, the metallacycle is nearly coplanar with the mean coordination plane, the dihedral angles being 3.02 (**6c**) and 2.80° (**6d**). Bond lengths and angles lie in the usual range for analogous compounds [1,14,15]. The 'bite' angles C(naphthyl)–Pt–N of 79.18 (**6c**) and 79.67° (**6d**) are characteristic of cyclometallated platinum(II) compounds [16].

In conclusion, for both [*C,N,N'*] and [*C,N*] systems, the C–H bond at the β-position of the naphthyl group is activated selectively, even in the presence of a weaker C–Cl bond.

3. Experimental

3.1. General

^{1}H-, ^{13}C-, ^{31}P- and ^{195}Pt-NMR spectra were recorded by using Varian Gemini 200 (^{1}H, 200 MHz; ^{13}C, 50 MHz), Varian XL300FT (^{13}C, 75.4 MHz), Varian 500 (^{1}H and ^{1}H–^{1}H COSY, 500 MHz), and Bruker 250 (^{13}C, 62.5 MHz; ^{31}P, 101.2 MHz; ^{195}Pt, 54 MHz) spectrometers, and referenced to SiMe$_4$ (^{1}H, ^{13}C), H$_3$PO$_4$ (^{31}P) and H$_2$PtCl$_6$ in D$_2$O (^{195}Pt). δ-Values are given in

Table 1
Selected bond lengths (Å) and angles (°) for compound **6c** with estimated S.D.

Bond lengths			
Pt–C(19)	2.035(4)	Pt–C(1)	2.045(4)
Pt–N	2.116(3)	Pt–P	2.2818(9)
N–C(11)	1.293(5)	N–C(12)	1.478(6)
C(1)–C(10)	1.403(6)	C(1)–C(2)	1.403(6)
C(2)–C(3)	1.376(6)	C(3)–C(4)	1.393(9)
C(4)–C(9)	1.404(8)	C(4)–C(5)	1.420(6)
C(5)–C(6)	1.373(11)	C(6)–C(7)	1.389(13)
C(7)–C(8)	1.372(8)	C(8)–C(9)	1.410(8)
C(9)–C(10)	1.451(6)	C(10)–C(11)	1.426(7)
C(12)–C(13)	1.505(6)		

Bond angles			
C(19)–Pt–C(1)	91.27(18)	C(19)–Pt–N	169.73(16)
C(1)–Pt–N	79.18(16)	C(19)–Pt–P	90.86(13)
C(1)–Pt–P	176.62(11)	N–Pt–P	98.85(10)

Table 2
Selected bond lengths (Å) and angles (°) for compound **6d** with estimated S.D.

Bond lengths			
Pt–C(37)	2.057(4)	Pt–C(3)	2.052(4)
Pt–N	2.125(3)	Pt–P	2.3015(10)
N–C(1)	1.275(6)	N–C(12)	1.469(5)
C(1)–C(2)	1.447(5)	C(2)–C(7)	1.366(6)
C(2)–C(3)	1.441(5)	C(3)–C(4)	1.370(5)
C(4)–C(5)	1.416(6)	C(5)–C(11)	1.416(6)
C(5)–C(6)	1.424(6)	C(6)–C(7)	1.409(6)
C(6)–C(8)	1.410(7)	C(8)–C(9)	1.371(8)
C(9)–C(10)	1.398(10)	C(10)–C(11)	1.358(8)
C(12)–C(13)	1.501(6)		

| Bond angles			
C(3)–Pt–C(37)	90.06(18)	C(3)–Pt–N	79.67(13)
C(37)–Pt–N	169.01(18)	C(3)–Pt–P	176.05(10)
C(37)–Pt–P	86.40(16)	N–Pt–P	103.97(10)
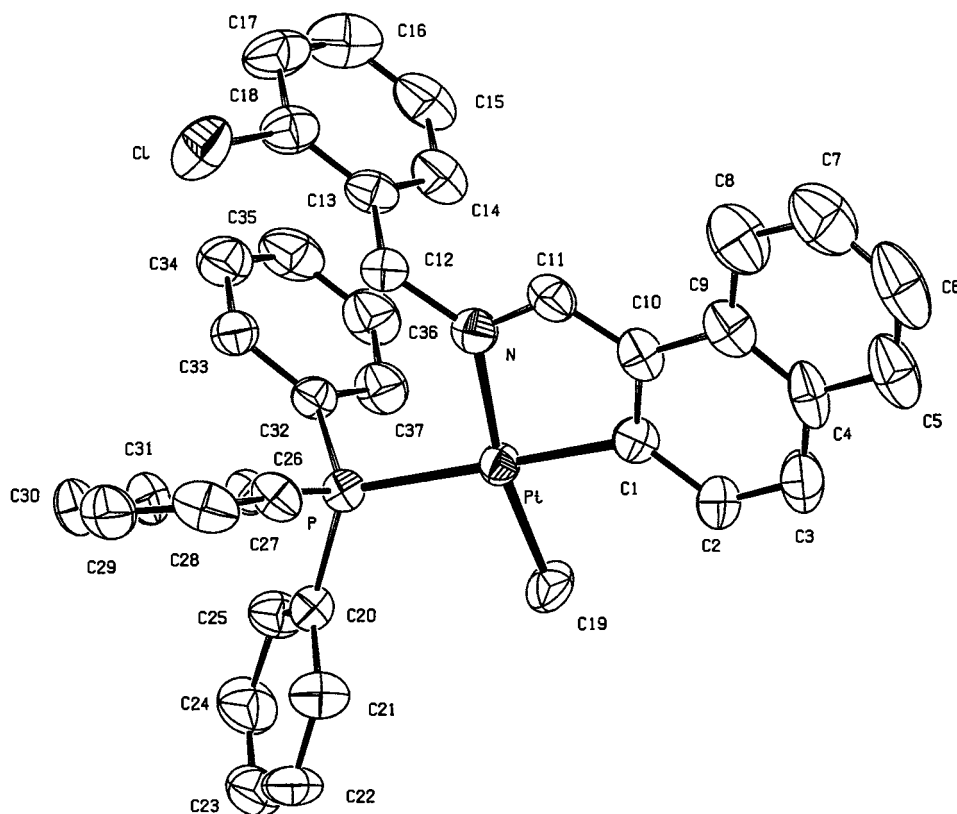
Fig. 1. Molecular structure of compound **6c**.

ppm and *J* values in Hz. Microanalyses and mass spectra (FAB, 3-nitrobenzyl alcohol matrix) were performed by the Serveis Científico-Tècnics de la Universitat de Barcelona.

3.2. Preparation of the compounds

Compound $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) was prepared as reported [17].

3.2.1. Synthetic procedure for the ligands

Compound **2** was prepared by the reaction of 0.46 g of *N,N*-dimethylethylenediamine or 0.74 g of 2-chlorobenzylamine (5.2×10^{-3} mol) with an equimolar amount (0.8 g) of the corresponding naphthaldehyde 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 (**2a**) or white solids (**2b**, **2c** and **2d**). 1-$(Me_2NCH_2CH_2NCH)C_{10}H_7$ (**2a**). Yield 0.9 g (76%). ^{1}H-NMR (200 MHz, CDCl$_3$): $\delta = 2.32$ [s, H^a]; 2.71 [t, ^3J(H^b–H^c) = 7, H^b]; 3.84 [td, ^3J(H^c–H^b) = 7, H^c]; {7.44–7.56 [m, 3H], 7.81–7.88 [m, 3H], 8.84 [d, *J*(H–H) = 8, 1H], aromatics}; 8.92 [s, 1H, H^d]. ^{13}C-NMR (50 MHz, CDCl$_3$): $\delta = 45.90$ [s, C^a]; {60.21; 60.77, C^b, C^c}, {124.16 [1C], 125.15 [1C], 125.91 [1C], 126.98 [1C], 128.52 [2C], 130.86 [1C], aromatics}; 161.24 [s, C^d]. 2-$(Me_2NCH_2CH_2NCH)C_{10}H_7$ (**2b**). Yield
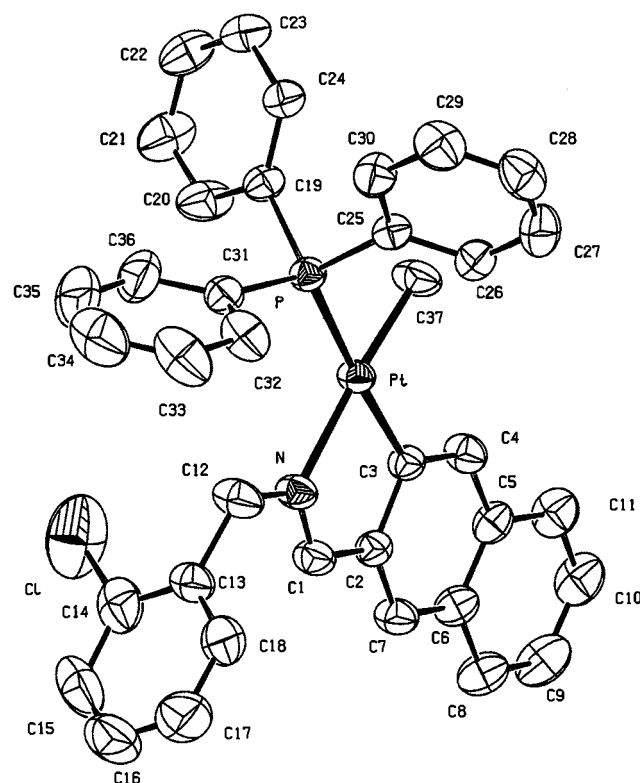
Fig. 2. Molecular structure of compound **6d**.

0.9 g (76%). ^{1}H-NMR (200 MHz, CDCl$_3$): $\delta = 2.32$ [s, H^a]; 2.68 [t, ^3J(H^b–H^c) = 7, H^b]; 3.79 [td, ^3J(H^c–H^b) = 7, H^c]; {7.81–8.00 [m, 6H]; 8.28 [s, 1H], aromatics}; 8.43 [s, 1H, H^d]. ^{13}C-NMR (50 MHz, CDCl$_3$): $\delta = 45.93$ [s, C^a]; {60.03; 60.19, C^n, C^c}, {123.79 [1C], 126.32 [1C], 127.00 [1C], 127.76 [1C], 128.33 [1C], 128.50 [1C], 129.76 [1C], aromatics}; 161.82 [s, C^d]. 1-(2′-ClC$_6$H$_4$CH$_2$NCH)C$_{10}$H$_7$ (**2c**). Yield 1.2 g (82%). ^{1}H-NMR (200 MHz, CDCl$_3$): $\delta = 5.03$ [s, H^a]; {7.24 [m, 1H], 7.49–7.64 [m, 5H], 7.87–7.98 [m, 4H], 8.97 [d, J(HH) = 8, 1H], aromatics}; 9.07 [s, H^d]. ^{13}C-NMR (50 MHz, CDCl$_3$): $\delta = 62.99$ [s, C^a]; {124.26, 125.17, 126.00, 126.86, 127.19, 128.14, 128.57, 129.08, 129.23, 129.63, 131.19, C–H aromatics}; {132.75, 133.30, 133.74, 137.07, 140.46, aromatics}; 162.60 [s, C^b]. 2-(2′-ClC$_6$H$_4$CH$_2$NCH)C$_{10}$H$_7$ (**2d**). Yield 1.2 g (82%). ^{1}H-NMR (200 MHz, CDCl$_3$): $\delta = 4.97$ [s, C^a]; {7.29 [m, 2H], 7.39 [d, J(HH) = 2, 1H], 7.46–7.57 [m, 3H], 7.84–7.93 [m, 3H], 8.01 [s, 1H], 8.06 [d, J(HH) = 2, 1H], aromatics}; 8.57 [s, H^b]. ^{13}C-NMR (50 MHz, CDCl$_3$): $\delta = 61.97$ [s, C^a]; {123.75, 126.41, 126.84, 127.15, 127.79, 128.15, 128.43, 128.55, 129.21, 129.64, 130.18, C–H aromatics}; {132.98, 133.32, 133.64, 134.70, 136.95, aromatics}; 162.85 [s, C^b].

3.2.2. Synthetic procedure for the platinum compounds

Compound **3** was obtained by adding a solution of 90 mg (3.9 × 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$_2$Me$_4$(μ-SMe$_2$)$_2$] (**1**) in acetone (10 ml). The mixture was stirred for 30 min at room temperature and allowed to settle. Crystals of **3a** were formed readily while **3b** was obtained upon removal of the acetone in a rotary evaporator. The orange-yellow solids were washed with ether (3 × 2 ml) and dried in vacuum.

3.2.2.1. [PtMe$_2${1-(Me$_2$NCH$_2$CH$_2$NCH)C$_{10}$H$_7$}] (3a).
Yield 110 mg (70%). ^{1}H-NMR (200 MHz, CDCl$_3$): $\delta = -0.08$ [s, ^2J(Pt–H) = 89, Me^a]; 0.57 [s, ^2J(Pt–H) = 84, Me^b]; 2.78 [m, H^d]; 2.87 [s, ^3J(H–Pt) = 21, H^c]; 4.22 [t, J(H–H) = 6, H^e]; {7.55–7.68 [m, 3H], 7.96–8.09 [m, 3H], 8.80 [d, J(H–H) = 7, 1H], aromatics}; 9.68 [s, ^3J(Pt–H) = 44, H^f]. ^{13}C-NMR (62.5 MHz, CDCl$_3$): $\delta = -25.02$ [J(Pt–C) = 803, Me^a]; −18.66 [J(Pt–C) = 828, Me^b]; 49.36 [C^c]; {65.25, 65.81, C^d, C^e}; {122.56, 125.35, 126.16, 126.86, 127.19, 128.96, 131.12, 130.58, 131.45, 133.14, aromatics}; 160.61 [J(Pt–C) = 23, C^f]. ^{195}Pt-NMR (54 MHz, CDCl$_3$): $\delta = -3437$ [s]. FAB(+)-MS, m/z: 435 [M–Me], 419 [M–2Me]. Anal. Found: C, 44.9; H, 5.4; N, 6.2. Calc. for C$_{17}$H$_{24}$N$_2$Pt: C, 45.23; H, 5.36; N, 6.20%.

3.2.2.2. [PtMe$_2${2-(Me$_2$NCH$_2$CH$_2$NCH)C$_{10}$H$_7$}] (3b).
Yield 120 mg (76%). ^{1}H-NMR (200 MHz, CDCl$_3$): $\delta = 0.23$ [s, ^2J(Pt–H) = 90, Me^a]; 0.64 [s, ^2J(Pt–H) = 85,

Me^b]; 2.72 [t, J(H–H) = 5, H^d]; 2.85 [s, ^3J(H–Pt) = 21, H^c]; 4.10 [t, J(H–H) = 5, H^e]; {7.52 [m, 2H], 7.80 [m, 2H], 7.95 [d, J(H–H) = 8, 1H], 8.47 [s, H^1], 8.65 [d, J(H–H) = 8, 1H], aromatics}; 9.12 [s, ^3J(Pt–H) = 45, H^f]. ^{13}C-NMR (75 MHz, CDCl$_3$): $\delta = -24.77$ [J(Pt–C) = 810, Me^a]; −18.84 [J(Pt–C) = 832, Me^b]; 49.51 [C^c]; {65.46, 66.10, C^d, C^e}; {125.18, 126.53, 127.49, 127.55, 128.05, 128.72, 130.80, 131.85, 132.64, 134.74, aromatics}; 161.97 [J(Pt–C) = 20, C^f]. ^{195}Pt-NMR (54 MHz, CDCl$_3$): $\delta = -3565$ [s]. FAB(+)-MS, m/z: 451 [M], 435 [M–Me], 419 [M–2Me]. Anal. Found: C, 45.0; H, 5.3; N, 5.7. Calc. for C$_{17}$H$_{24}$N$_2$Pt: C, 45.23; H, 5.36; N, 6.20%.

Compounds **4a** and **4b** were obtained by refluxing during 2 h a toluene solution (20 ml) containing 100 mg of the corresponding compound **3**. The solvent was removed in a rotary evaporator and the red residue was washed with ether (3 × 2 ml) to yield red (**4a**) or orange (**4b**) solids, which were dried in vacuum.

3.2.2.3. [PtMe{1-(Me$_2$NCH$_2$CH$_2$NCH)C$_{10}$H$_6$}] (4a).
Yield 75 mg (78%). ^{1}H-NMR (500 MHz, acetone-d_6): $\delta = 0.96$ [s, ^2J(Pt–H) = 79, Me^a]; 2.80 [s, ^3J(H–Pt) = 20, H^b]; {3.23 [t, J(H–H) = 6], 4.23 [t, J(H–H) = 6], H^c, H^d}; {7.11 [t, J(H–H) = 8], 7.19 [t, J(H–H) = 8], H^6, H^7}; {7.48 [d, J(H–H) = 8.5, J(H–Pt) = 17], 7.62 [d, J(H–H) = 8.5, J(H–Pt) = 59], H^3, H^4}, {7.57 [d, J(H–H) = 8], 7.93 [d, J(H–H) = 8], H^5, H^8}; 9.59 [s, ^3J(Pt–H) = 64, H^e]. ^{13}C-NMR (62.5 MHz, CDCl$_3$): $\delta = -10.91$ [J(Pt–C) = 792, Me^a]; 48.66 [C^b]; {52.50 [s, J(C–Pt) = 31], 67.85 [s], C^c, C^d}; {121.24, 122.76, 126.41, 129.14, 131.20 [J(C–Pt) = 68], 132.58 [J(C–Pt) = 89], C^3–C^8}; {130.34, 133.01, 143.00, 148.05 [J(C–Pt) = 1155], aromatics}; 164.32 [J(Pt–C) = 100, C^e]. ^{195}Pt-NMR (54 MHz, CDCl$_3$): $\delta = -3590$ [s]. FAB(+)-MS, m/z: 435 [M], 419 [M–Me]. Anal. Found: C, 44.7; H, 4.9; N, 5.9. Calc. for C$_{16}$H$_{20}$N$_2$Pt: C, 44.13; H, 4.63; N, 6.43%.

3.2.2.4. [PtMe{2-(Me$_2$NCH$_2$CH$_2$NCH)C$_{10}$H$_6$}] (4b).
Yield 80 mg (83%). ^{1}H-NMR (500 MHz, acetone-d_6): $\delta = 0.85$ [s, ^2J(Pt–H) = 80, Me^a]; 2.80 [s, ^3J(H–Pt) = 21, H^b]; {3.18 [t, J(H–H) = 6], 4.19 [t, J(H–H) = 6], H^c, H^d}; {7.08 [t, J(H–H) = 8], 7.20 [t, J(H–H) = 8], H^6, H^7}; {7.49 [d, J(H–H) = 8], 7.55 [d, J(H–H) = 8], H^5, H^8], 7.63 [s, H^1], 7.67 [s, J(H–Pt) = 7, H^4]; 8.90 [s, ^3J(Pt–H) = 60, H^e]. ^{13}C-NMR (75.4 MHz, CDCl$_3$): $\delta = -12.97$ [J(Pt–C) = 793, Me^a]; 48.79 [C^b]; {52.30 [J(C–Pt) = 29], 67.75 [s], C^c, C^d}; {123.54, 126.89, 127.13, 128.37 [J(C–Pt) = 38], 128.79, 131.40 [J(C–Pt) = 99], C^1, C^4–C^8}; {130.45, 134.48, 135.97, 151.09, aromatics}; 167.06 [J(Pt–C) = 89, C^e]. ^{195}Pt-NMR (54 MHz, CDCl$_3$): $\delta = -3880$ [s]. FAB(+)-MS, m/z: 435 [M], 419 [M–Me]. Anal. Found: C, 43.7; H, 4.6; N, 6.0. Calc. for C$_{16}$H$_{20}$N$_2$Pt: C, 44.13; H, 4.63; N, 6.43%.

Table 3
Crystallographic and refinement data parameters for compounds **6c** and **6d**

	Compound **6c**	Compound **6d**
Empirical formula	$C_{37}H_{31}ClNPPt$	$C_{37}H_{31}ClNPPt$
f_w	751.14	751.14
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71069
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a (Å)	10.1280(10)	12.2470(10)
b (Å)	12.7320(10)	12.5220(10)
c (Å)	13.1070(10)	12.9140(10)
α (°)	113.58(2)	108.8310(10)
β (°)	98.3750(10)	106.3750(10)
γ (°)	91.36(2)	110.4720(10)
V (Å^3); Z	1522.1(2); 2	1572.6(2); 2
d_{Calc} (Mg m^{-3})	1.639	1.586
Absorption coefficient (mm^{-1})	4.777	4.623
$F(000)$	740	740
Reflections collected/unique	8746/6140 ($R_{int} = 0.0283$)	13 280/8116 ($R_{int} = 0.0211$)
Data/restraints/ parameters	6140/0/390	8116/0/483
GOF on F^2	1.105	1.106
R_1 ($I > 2\sigma(I)$)	0.0299	0.0323
wR_2 (all data)	0.0826	0.0821
Peak and hole (e Å^{-3})	0.694 and −0.797	0.679 and −0.597

Compounds **5c** and **5d** were obtained by adding a solution of 97 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 $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) in acetone (10 ml). The mixture was stirred for 16 h at room temperature and allowed to settle. Yellow crystals of **5d** were formed readily while **5c** was obtained as an orange solid upon removal of the acetone in a rotary evaporator. The products were washed with hexane (3×2 ml) and dried in vacuum.

3.2.2.5.   [PtMe{1-(2′-ClC₆H₄CH₂NCH)C₁₀H₆}SMe₂]
(5c). Yield 150 mg (78%). ^{1}H-NMR (200 MHz, acetone-d_6): $\delta = 1.03$ [s, $^2J(Pt–H) = 82$, Me^a]; 2.05 [s, $^3J(H–Pt) = 27$, H^b]; 5.35 [s, $^3J(Pt–H) = 13$, H^c], {7.29–7.50 [m, 6H], 7.76–7.93 [m, 3H], 8.25 [d, $J(H–H) = 8$, 1H], aromatics}; 9.82 [s, $^3J(H–Pt) = 59$, H^d]. ^{195}Pt-NMR (54 MHz, acetone-d_6): $\delta = -3986$ [s]. Anal. Found: C, 44.1; H, 4.1; N, 2.4. Calc. for $C_{21}H_{22}ClNPtS·H_2O$: C, 44.33; H, 4.25; N, 2.46%.

3.2.2.6.   [PtMe{2-(2′-ClC₆H₄CH₂NCH)C₁₀H₆}SMe₂]
(5d). Yield 150 mg (78%). ^{1}H-NMR (200 MHz, acetone-d_6): $\delta = 0.98$ [s, $^2J(Pt–H) = 83$, Me^a]; 2.08 [s, $^3J(H–Pt) = 27$, H^b]; 5.33 [s, $^3J(Pt–H) = 13$, H^c], {7.41–7.51 [m, 3H], 7.41–7.51 [m, 3H], 7.76[m, 2H], 8.03 [d,

$J(H–H) = 8$, 2H], aromatics}; 9.02 [s, $^3J(H–Pt) = 54$, H^d]. ^{195}Pt-NMR (54 MHz, acetone-d_6): $\delta = -3971$ [s]. Anal. Found: C, 45.9; H, 4.1; N, 2.6. Calc. for $C_{21}H_{22}ClNPtS$: C, 45.87; H, 4.03; N, 2.55%.

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 vacuum.

3.2.2.7.   [PtMe{1-(2′-ClC₆H₄CH₂NCH)C₁₀H₆}PPh₃]
(6c). Yield 50 mg (72%). ^{1}H-NMR (200 MHz, acetone-d_6): $\delta = 0.85$ [d, $^2J(Pt–H) = 82$, $^3J(P–H) = 8$, Me^a]; 4.56 [s, H^c], {7.20 [m, 4H], 7.39 [m, 11H], 7.60 [m, 6H], 7.81–8.11 [m, 4H], aromatics}; 9.60 [s, $^3J(H–Pt) = 58$, H^d]. ^{31}P-NMR (101.2 MHz, acetone-d_6): $\delta = 31.21$ [s, $J(Pt–P) = 2164$]. ^{195}Pt-NMR (54 MHz, acetone-d_6): $\delta = -4280$ [s, $J(Pt–P) = 2164$]. Anal. Found: C, 58.8; H, 4.2; N, 1.7. Calc. for $C_{37}H_{31}ClNPPt$: C, 59.16; H, 4.16; N, 1.86%.

3.2.2.8.   [PtMe{2-(2′-ClC₆H₄CH₂NCH)C₁₀H₆}PPh₃]
(6d). Yield 45 mg (65%). ^{1}H-NMR (200 MHz, acetone-d_6): $\delta = 0.81$ [d, $^2J(Pt–H) = 84$, $^3J(P–H) = 8$, Me^a]; 4.48 [s, H^c], {7.24–7.44 [m, 15H], 7.65–7.77 [m, 8H], 8.03 [m, 2H], aromatics}; 8.65 [s, $^3J(H–Pt) = 52$, H^d]. ^{31}P-NMR (101.2 MHz, acetone-d_6): $\delta = 31.70$ [s, $J(Pt–P) = 2200$]. ^{195}Pt-NMR (54 MHz, acetone-d_6): $\delta = -4255$ [s, $J(Pt–P) = 2222$]. Anal. Found: C, 56.5; H, 4.2; N, 1.8. Calc. for $C_{37}H_{31}ClNPPt·2H_2O$: C, 56.45; H, 4.48; N, 1.78%.

3.3. X-ray structure analysis

3.3.1. Data collection
Prismatic crystals were selected and mounted on an MAR345 diffractometer with an image plate detector. Unit cell parameters were determined from automatic centring of 8859 (**6c**) or 11 785 (**6d**) reflections (3° < θ < 31°) and refined by least-squares method. Intensities were collected with graphite monochromatised Mo–K$_\alpha$ radiation. For **6c**, 8746 reflections were measured in the range 2.88° < θ < 31.57°, 6140 of which were non-equivalent by symmetry ($R_{int} = 0.028$) and 5547 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. For **6d**, 13 280 reflections were measured in the range 2.89° < θ < 31.58°, 8116 of which were non-equivalent by symmetry ($R_{int} = 0.021$) and 7121 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 3.

3.3.2. Structure solution and refinement

The structures were solved by direct methods, using SHELXS-97 computer program [18], and refined by the full-matrix least-squares method, with the SHELXL-97 computer program [18] using 6140 (**6c**) or 8116 (**6d**) reflections (very negative intensities were not assumed). The function minimised was $\Sigma w ||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0459P)^2 + 1.5256P]^{-1}$ (**6c**) and $w = [\sigma^2(I) + (0.0312P)^2 + 3.4280P]^{-1}$ (**6d**) and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' And f'' were taken from the International Tables of X-ray Crystallography [19]. Five (**6c**) or 28 (**6d**) hydrogen atoms were located from a difference synthesis and refined with an overall isotropic temperature factor and 26 (**6c**) or three (**6d**) hydrogen atoms 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 3.

4. Supplementary material

The crystallographic data of compounds **6c** and **6d** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 166196 and 166195. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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