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Journal of Organometallic Chemistry 483 (1994) 187–192

Journal of Organometallic Chemistry

Cyclometallated platinum(II) and platinum(IV) compounds of N-benzylidene-2-chlorobenzylamine. Crystal structure of [PtMe(PPh$_3$)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)]

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Received 7 March 1994

Abstract

The cyclometallated compound [PtMe(SMe$_2$)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] (**1**) undergoes a displacement reaction with PPh$_3$ to yield a cyclometallated platinum(II) compound [PtMe(PPh$_3$)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] (**2**), which has been characterized crystallographically. Complex **2** crystallizes in the monoclinic space group $C2/c$, with $a = 38.402(4)$ Å, $b = 7.993(3)$ Å, $c = 18.563(3)$ Å, $\beta = 101.34(3)°$ and $Z = 8$. The reaction of **1** with 1,2-bis(diphenylphosphino)ethane (dppe) yields [PtMe(dppe)-(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] (**3**) containing an unidentate C donor imine ligand and a chelating diphosphine. Oxidative addition of methyl iodide to **1** yields a cyclometallated platinum(IV) compound [PtMe$_2$I(SMe$_2$)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] (**4**), which undergoes a displacement reaction of SMe$_2$ by PPh$_3$ to yield [PtMe$_2$I(PPh$_3$)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] (**5**). Compound **5** can also be obtained by oxidative addition of methyl iodide to **2**. The stereochemistry of compounds **4** and **5** is discussed.

Keywords: Platinum; X-ray structure; Cyclometallated platinum(II), (IV); Imine; Oxidative addition

1. Introduction

The chemistry of cyclometallated complexes has attracted much attention due to their use in organic synthesis, catalysis, assymetric synthesis and photochemistry. Although cyclometallated organopalladium compounds have been studied more thoroughly, there are several classical examples of platinum complexes with *ortho*-metallated nitrogen donor ligands [1]. Recently, cyclometallated platinum complexes showing interesting photochemical, photophysical and electrochemical properties have been reported [2,3]. Furthermore, there is increasing interest in platinum(II) and platinum(IV) compounds containing bidentate (CN) [4,5], or terdentate (NCN) and (NNC) ligands [6,7], as well as in the investigation of formation of [C]$^-$ unidentate systems [8].

Cyclometallated platinum(II) compounds are good precursors both to cyclometallated platinum(IV) compounds through oxidative addition reactions and to platinum(II) C donor unidentate systems through metallocycle cleavage. In this paper, we report the behaviour of compound [PtMe(SMe$_2$)(C$_6$H$_4$CH=NCH$_2$-C$_6$H$_4$Cl-2)] in these reactions.

2. Results and discussion

Compound [PtMe(SMe$_2$)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] (**1**) [9] was obtained by reaction of [Pt$_2$Me$_4$(SMe$_2$)$_2$] with the bifunctional imine C$_6$H$_5$CH=NCH$_2$(C$_6$H$_4$Cl-2) as shown in Scheme 1.

Two different platinum(II) metallocycles, either with an endocyclic structure (containing the C=N group) or with an exocyclic structure, might be formed (see Fig. 1). Only one isomer was obtained and the more stable endocyclic structure was assumed for it.

The reaction of **1** with triphenylphosphine in acetone yielded [PtMe(PPh$_3$)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] (**2**) (see Scheme 1), which was characterized by analytical, spectroscopic and crystallographic methods. The ^{1}H NMR spectrum of compound **2** shows a methyl resonance as a doublet due to coupling with the phosphorus atom and with platinum satellites [^2J(H–Pt) = 82 Hz]. Both the imine and the benzyl protons appear coupled to platinum, showing that the imine is bound to platinum in a bidentate (CN) fashion. No coupling between the imine proton and the phosphorus atom is observed, and this is consistent with a mutual *cis* arrangement of the phosphorus and nitrogen atoms. In

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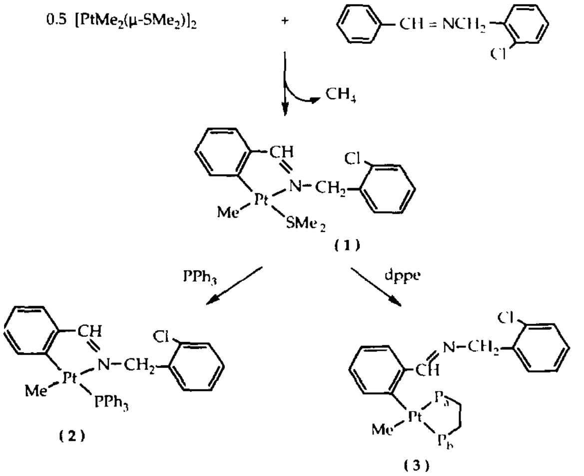


Scheme 1.

the ^{31}P NMR spectrum, a single resonance appears and the value of ^{1}J (P–Pt) is consistent with the presence of an aryl carbon atom *trans* to the phosphine.

Compound **2** was also characterized crystallographically (Table 1). The crystal structure is composed of discrete molecules separated by van der Waals distances. Crystallographic data are given in the Experimental Section, atomic coordinates in Table 2, and selected bond distances and angles are in Table 1. The structure is shown in Fig. 2, and confirms the features predicted from the spectroscopic studies. In particular, the C=N group is endo to the cycle and the methyl group is *trans* to the nitrogen atom.

The coordination sphere of platinum is planar and the platinum lies 0.024 Å above the plane. The metallocycle is planar and nearly coplanar with the coordination plane, the dihedral angle being 1.09°.

Table 1
Selected bond lengths (Å) and angles (°) with e.s.d. in parentheses for compound **2**

Bond lengths			
P–Pt	2.334(3)	C(4)–C(3)	1.434(15)
N–Pt	2.090(7)	C(5)–C(4)	1.290(15)
C(1)–Pt	2.010(12)	C(6)–C(5)	1.407(19)
C(2)–Pt	1.973(10)	C(7)–C(6)	1.522(15)
C(16)–P	1.740(11)	C(8)–C(7)	1.313(19)
C(22)–P	1.797(10)	C(10)–C(9)	1.558(12)
C(28)–P	1.794(10)	C(11)–C(10)	1.428(15)
C(11)–Cl	1.703(12)	C(15)–C(10)	1.350(16)
C(8)–N	1.307(14)	C(12)–C(11)	1.478(16)
C(9)–N	1.463(12)	C(13)–C(12)	1.385(20)
C(3)–C(2)	1.395(21)	C(14)–C(13)	1.418(16)
C(7)–C(2)	1.431(14)	C(15)–C(14)	1.367(13)
Bond angles			
N–Pt–P	105.7(3)	C(6)–C(7)–C(2)	121.5(10)
C(1)–Pt–P	89.3(5)	C(8)–C(7)–C(2)	113.9(11)
C(1)–Pt–N	165.0(6)	C(8)–C(7)–C(6)	124.1(9)
C(2)–Pt–P	174.9(5)	C(7)–C(8)–N	122.0(10)
C(2)–Pt–N	79.3(5)	C(10)–C(9)–N	109.0(8)
C(2)–Pt–C(1)	85.7(6)	C(11)–C(10)–C(9)	114.3(10)
C(16)–P–Pt	109.3(4)	C(15)–C(10)–C(9)	125.9(9)
C(22)–P–Pt	126.0(3)	C(15)–C(10)–C(11)	119.8(9)
C(22)–P–C(16)	99.2(5)	C(10)–C(11)–Cl	121.7(8)
C(28)–P–Pt	113.6(4)	C(12)–C(11)–Cl	125.6(9)
C(28)–P–C(16)	107.2(4)	C(12)–C(11)–C(10)	112.6(11)
C(28)–P–C(22)	99.5(5)	C(13)–C(12)–C(11)	125.6(11)
C(8)–N–Pt	110.8(8)	C(14)–C(13)–C(12)	117.3(11)
C(9)–N–Pt	127.1(7)	C(15)–C(14)–C(13)	117.0(12)
C(9)–N–C(8)	121.8(9)	C(14)–C(15)–C(10)	127.5(12)
C(3)–C(2)–Pt	141.8(11)	C(17)–C(16)–P	119.7(7)
C(7)–C(2)–Pt	114.0(10)	C(21)–C(16)–P	119.8(9)
C(7)–C(2)–C(3)	103.4(9)	C(23)–C(22)–P	125.3(7)
C(4)–C(3)–C(2)	141.1(12)	C(27)–C(22)–P	118.2(9)
C(5)–C(4)–C(3)	110.5(12)	C(29)–C(28)–P	128.3(9)
C(6)–C(5)–C(4)	122.3(12)	C(33)–C(28)–P	118.8(7)
C(7)–C(6)–C(5)	120.8(10)		

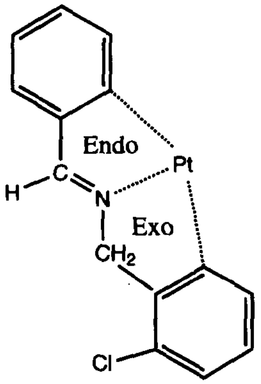


Fig. 1. Possible endo and exo structures of platinocycles.

The angles between adjacent atoms in the coordination sphere of platinum lie in the range 105.7(3)–79.3(5)°, the smallest angle corresponding to the metallocycle. The Pt–C(2) bond length (1.973(10) Å) is shorter than the platinum–aryl carbon bond length in a related platinum(IV) compound [9]. Pt–Me and Pt–N distances are similar to those reported for analogous platinum(II) compounds [10].

Even when the reaction was carried out using an excess of PPh_3, the metallocycle was not cleaved and compound **2** was obtained. This result is analogous to that reported for both platinum(IV) [9] and palladium (II) [11] five-membered metallocycles containing benzylidenebenzylamines. The results obtained in the reaction of cyclopalladated compounds with phosphines show that cleavage of the metal–nitrogen bond depends on the nature of the cycle and the basicity of the nitrogen atom, benzylidenebenzylamine cycles being among the most stable.

On the other hand, the reaction of **1** with the diphosphine 1,2-bis(diphenylphosphino)ethane (dppe) leads to $[PtMe(dppe)(C_6H_4CH{=}NCH_2C_6H_4Cl\text{-}2)]$ (**3**) with cleavage of the platinum–nitrogen bond. Compound **3** was characterized by elemental and spectroscopic analysis. In the ^{1}H NMR spectrum, the methyl

Table 2
Atomic coordinates ($\times 10^4$) for non-hydrogen atoms with e.s.d. in parentheses for compound **2**

	x	y	z
Pt	3629(1)	3449(1)	1805(1)
P	4060(1)	5315(5)	1552(1)
Cl	2881(1)	9044(6)	−70(2)
N	3143(2)	4405(14)	1247(4)
C(1)	4016(3)	2029(28)	2398(8)
C(2)	3300(3)	1726(22)	2050(5)
C(3)	3294(3)	116(22)	2353(5)
C(4)	3051(3)	−1174(18)	2478(5)
C(5)	2730(4)	−778(24)	2169(6)
C(6)	2649(3)	720(18)	1763(7)
C(7)	2935(3)	2032(18)	1728(5)
C(8)	2882(3)	3427(25)	1341(6)
C(9)	3081(3)	6027(14)	867(5)
C(10)	3148(3)	5826(18)	70(5)
C(11)	3056(3)	7277(17)	−385(6)
C(12)	3121(4)	7033(22)	−1136(7)
C(13)	3252(4)	5575(20)	−1399(7)
C(14)	3330(3)	4198(19)	−905(6)
C(15)	3283(3)	4449(21)	−202(5)
C(16)	4212(3)	6563(19)	2321(6)
C(17)	4452(3)	7907(18)	2277(6)
C(18)	4583(3)	8832(15)	2903(6)
C(19)	4478(3)	8471(29)	3520(6)
C(20)	4214(3)	7186(16)	3614(6)
C(21)	4104(3)	6185(22)	3009(6)
C(22)	3993(3)	6931(15)	859(5)
C(23)	3825(3)	8415(19)	903(5)
C(24)	3748(3)	9622(20)	396(8)
C(25)	3857(3)	9258(20)	−279(6)
C(26)	4035(3)	7816(17)	−397(7)
C(27)	4098(3)	6591(23)	186(6)
C(28)	4440(3)	4281(18)	1324(6)
C(29)	4790(3)	4852(17)	1440(7)
C(30)	5064(4)	3735(23)	1176(9)
C(31)	4991(4)	2368(26)	759(9)
C(32)	4648(4)	1673(28)	638(7)
C(33)	4386(3)	2670(19)	893(6)

Table 3
Summary of crystallographic data for compound **2**

Formula	$C_{33}H_{29}NClPPt$
FW	701.12
Crystallographic system	Monoclinic
Space group	$C2/c$
a (Å)	38.402(4)
b (Å)	7.999(3)
c (Å)	18.563(3)
β (°)	101.34(3)
V (Å^3)	5591(4)
D (expt) (g cm^{-3})	1.665
Z	8
F(000)	2752.0
Crystal size (mm^3)	0.1 × 0.1 × 0.2
μ (Mo K$_\alpha$) (cm^{-1})	54.55
λ (Mo K$_\alpha$) (Å)	0.71069
T (K)	298
No. of reflections collected	4312
R	0.033
R_w	0.033

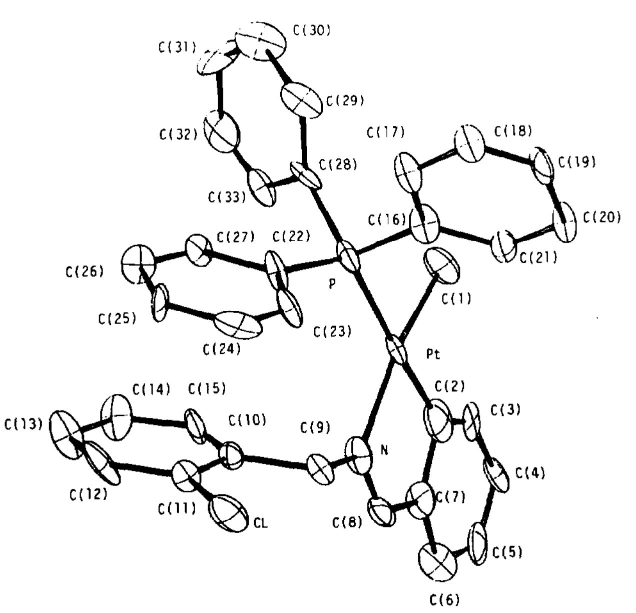


Fig. 2. View of the structure of compound 2.

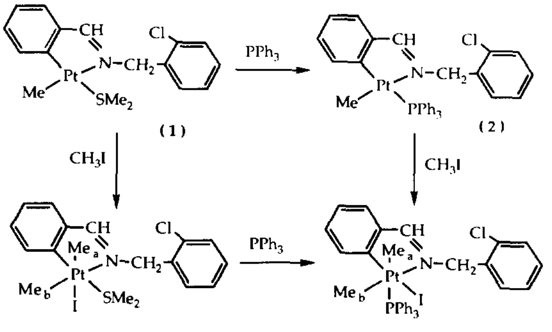
resonance is coupled with both phosphorus atoms and shows platinum satellites, while the imine and benzyl protons are not coupled with ^{195}Pt. This is a result of the cleavage of the metallocycle. The imine ligand is unidentate through the aryl carbon and the square-planar coordination of platinum(II) is achieved with the methyl group and the bidentate diphosphine. In the ^{31}P NMR spectrum, two resonances due to the non-equivalent phosphorus atoms appear. Both are coupled with ^{195}Pt, and ^{1}J(P–Pt) values (1757 and 1841 Hz) are consistent with the presence of carbon atoms *trans* to the phosphorus. No coupling between phosphorus atoms was observed.

Analogous compounds containing chelating dppe and unidentate C-donor imine ligands have been reported for palladium [12].

The easy cleavage of the metallocycle by dppe can be explained by the chelating nature of this ligand and the affinity of platinum(II) for phosphorus ligands, so that SMe_2 is readily replaced.

In an attempt to obtain a bis-cyclometallated compound $[Pt(C_6H_4CHNCH_2C_6H_4Cl\text{-}2)_2]$, the reaction of **1** with an excess of imine was carried out. However, under these experimental conditions, no reaction was observed and compound **1** was recovered. This is not unexpected, since SMe_2 is a better ligand for platinum (II) than nitrogen donors. Even bidentate nitrogen donors such as 2,2′-bipyridine fail to react with compound **1**.

The reaction of compound **1** with methyl iodide was also carried out. Oxidative addition of alkyl halides to platinum(II) substrates is well documented [13]. In particular, several studies concerning compounds $[PtMe_2(NN)]$ (where NN is a bidentate nitrogen donor)



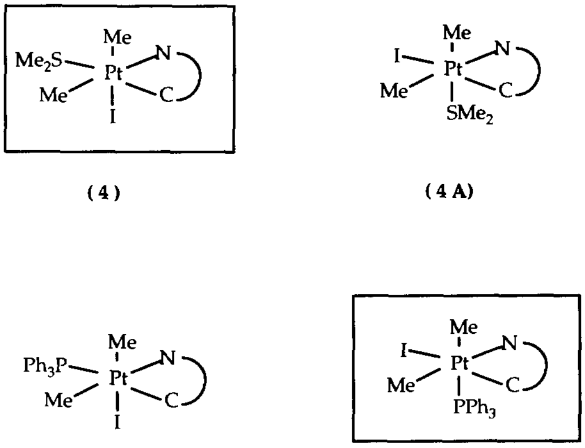
Scheme 2.

have been reported, and experimental evidence points to *trans*-stereochemistry in the resulting platinum(IV) compounds [14]. Studies on cyclometallated platinum (II) compounds have also been reported to yield platinum(IV) compounds [3,15] or, more unexpectedly, an arenonium platinum(II) complex [16]. Canty has reported the reaction of [PtMe$_2${(pz)$_3$CH}] (pz = pyrazol-1-yl) with CH$_3$I which induces cyclometallation of a pyrazol-1-yl group under oxidative addition conditions [8].

The reaction of compound **1** with CH$_3$I in acetone yields [PtMe$_2$I(SMe$_2$)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] **4**, for which the stereochemistry shown in Scheme 2 is proposed.

Two methyl-platinum resonances coupled with ^{195}Pt appear at δ 1.22 (^2J(H-Pt) = 71 Hz) and 1.44 (^2J(H-Pt) = 68 Hz). From the ^2J(H-Pt) coupling constants a *fac*-PtC$_3$ structure is deduced. The resonance at lower field with a smaller coupling constant is assigned to the methyl *trans* to nitrogen. As shown in Table 4, a decrease in J(H-Pt) for both methyl and imine groups is observed upon oxidation from platinum(II) to platinum(IV). It is not possible to deduce whether the axial methyl is *trans* to I or to SMe$_2$ (structures **4** and **4A** in Fig. 3), since similar ^2J(H-Pt) are expected in either case. However, the former is more likely, since it is assumed that oxidative addition of CH$_3$I to platinum(II) substrates occurs with a *trans* stereochemistry.

Compound **4** reacts with PPh$_3$ to yield [PtMe$_2$I(PPh$_3$)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] (**5**); for this compound, two methyl-platinum resonances appear at δ 1.21 (^2J(H-Pt) = 61Hz) and 1.53 (^2J(H-Pt) = 67 Hz), both coupled with the phosphorus atoms. The decrease in the coupling constant of the axial methyl with platinum suggests a *trans* arrangement of the axial methyl and the PPh$_3$. As already described for platinum(IV) analogues [9,17], and assuming structure **4** for the dimethylsulfide derivative, isomerization takes place during the displacement reaction of SMe$_2$ by PPh$_3$. However, previous isomerization of **4** to **4A** followed by a displacement reaction cannot be ruled out.



(4) (4A)

(5B) (5)

Fig. 3. Two possible isomers for compounds 4 and 5.

The oxidative addition of methyl iodide to compound **2** in acetone produces [PtMe$_2$I(PPh$_3$)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] (**5**), for which the same stereochemistry is deduced from spectral parameters. If the oxidative addition of CH$_3$I to **2** occurs with *trans* stereochemistry, as expected for a platinum(II) substrate [14], isomer (**5B**) (see Fig. 3) would be produced initially and *trans*-to-*cis* isomerization would finally yield compound **5**. *Trans* addition followed by isomerization to a *cis* configuration has been reported in the oxidative addition of alkyl halides to homoleptic cycloplatinated complexes [3].

The synthesis of platinum(IV) cyclometallated compounds containing N-benzylidenebenzylamines by intramolecular oxidative addition of C(aryl)-X bonds (X = F, Cl or Br) to platinum(II) substrates has been

Table 4
Selected ^{1}H NMR data [a]

	Me *trans* to N δ(H)[^2J(HPt)][^3J(HP)]	Me *trans* to X δ(H)[^2J(HPt)][^3J J(HP)]	CH=N δ(H)[^3J(HPt)]
[PtMe(SMe$_2$)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] (**1**)	0.91 [80]		8.81 [53]
[PtMe(PPh$_3$)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] (**2**)	0.77 [82] [8]		8.50 [55]
[PtMe(dppe)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] (**3**)		0.49 [71] [7]	8.94
[PtMe$_2$I(SMe$_2$)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] (**4**)	1.44 [68]	1.22 [71]	8.15 [45]
[PtMe$_2$I(PPh$_3$)(C$_6$H$_4$CH=NCH$_2$C$_6$H$_4$Cl-2)] (**5**)	1.53 [67] [8]	1.21 [61] [8]	7.80 [46]

[a] δ in ppm, J in Hz.

reported elsewhere [9,17]. The stereochemistry of the triphenylphosphine derivative $[PtMe_2Cl(PPh_3)(C_6H_3ClCH{=}NCH_2C_6H_5)]$, analogous to **5**, was assigned unambiguously by a crystal structure determination [9]. The geometry is probably determined by steric factors in order to minimise unfavourable interaction between the aryl rings in the phosphine and the dangling benzyl group in the imine. For dimethylsulfide derivatives, there is no such effect and structure **4** was assumed. Further experimental evidence for the stereochemistry of such compounds was obtained from ^{19}F NMR parameters for $[PtMe_2F(SMe_2)(C_6F_4CH{=}NCH_2C_6H_5)]$ and $[PtMe_2F(PPh_3)(C_6F_4CH{=}NCH_2C_6H_5)]$. The values of ^1J(F–Pt) are sensitive to the substituents in *trans* position and confirm structures **4** and **5**, respectively, for these compounds [17].

Here we report alternative procedures to prepare these compounds by intermolecular oxidative addition of methyl iodide to cyclometallated platinum(II) precursors. Experimental evidence points to the same stereochemistry of the final product, irrespective of the synthetic route.

3. Experimental

^{1}H and ^{31}P-{^{1}H} NMR spectra were recorded by using Varian Gemini 200 (200 MHz) and Bruker WP80SY (32.4 MHz) spectrometers, respectively, and referenced to $SiMe_4$ and H_3PO_4, respectively. δ values are given in ppm and J values in Hz. Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (CSIC).

3.1. Preparation of the compounds

Compound **1** was prepared as described elsewhere [9]. Compound **2** was prepared by reaction of 50 mg of compound **1** with the equimolecular amount of PPh_3 in acetone. The mixture was stirred at room temperature for 2 h. On addition of hexane, yellow crystals were formed, and they were collected by filtration, washed with hexane and dried in vacuo. Suitable crystals for crystallographic analysis were grown by slow evaporation from an acetonehexane solution.

Compound **3** was prepared by an analogous procedure and was obtained as a white powder.

2: $[PtMe(PPh_3)(C_6H_4CH{=}NCH_2C_6H_4Cl)]$. Yield 59.0 mg (84%), m.p. 177°C (d). Anal. calc. for $C_{33}H_{29}ClNPPt$: C, 56.53; H, 4.17; N, 2.00%. Found: C, 56.28; H, 4.15; N, 1.92%. ^{1}H NMR (acetone-*d*6): δ 0.77 (d, ^2J(HPt) = 82, ^3J(HP) = 8, Me), 4.43 (s, ^3J(HPt) = 10, CH_2), 8.50(s, ^3J(HPt) = 55, CHN), {6.95 (m), 7.45 (m), 7.70 (m), 7.65 (m), aromatics}. ^{31}P NMR (acetone): δ 30.50 (^1J(PPt) = 2175).

3: $[PtMe(Ph_2PCH_2CH_2PPh_2)(C_6H_4CH{=}NCH_2C_6H_4Cl)]$. Yield 75.0 mg (90%), m.p. 153°C(d). Anal. calc. for $C_{41}H_{38}ClNP_2Pt$: C, 58.81; H, 4.57; N, 1.67%. Found: C, 58.42; H, 4.59; N, 1.44%. ^{1}H NMR (acetone-d_6): δ 0.49 (t, ^2J(HPt) = 71, ^3J(HP) = 7, Me), 2.40 (m, CH_2P), (4.40 (d), 4.50 (d), ^2J(HH) = 14, AB pattern, CH_2), 8.94 (s, CHN), {7.10 (m), 7.50 (m), aromatics}. ^{31}P NMR (acetone): δ 42.64 (s, ^1J(PPt) = 1757), 44.44 (s, ^1J(PPt) = 1841).

Compound **4** was obtained from the reaction of 50 mg of compound **1** with an excess of methyliodide (0.5 ml) in acetone at room temperature. After 2 h, acetone was removed on a rotary evaporator to yield an oily residue which, upon repeated treatment with hexane gave a white solid which was collected by filtration and dried in vacuo.

Compound **5** was obtained by an analogous procedure starting from 50 mg of compound **2** as a yellow solid, which was recrystallized from acetone hexane. Alternatively, compound **5** can be obtained from the reaction of compound **4** with the equimolecular amount of PPh_3 in acetone solution.

4: $[PtMe_2I(SMe_2)(C_6H_4CH{=}NCH_2C_6H_4Cl)]$. Yield 50.0 mg (78%), m.p. 88°C (d). Anal. calc. for $C_{18}H_{23}ClINPtS$: C, 33.63; H, 3.61; N, 2.18%. Found: C, 33.15; H, 3.35; N, 2.04%. ^{1}H NMR (acetone-d_6): δ 1.22 (s, ^2J(HPt) = 71, Me_a), 1.44 (s, ^2J(HPt) = 68, Me_b), {5.45, 5.70 (m, AB quartet, ^2J(HH) = 17, CH_2)}, 8.15 (s, ^3J(HPt) = 45, CHN), {7.10 (m), 7.40 (m), 7.70 (m), 7.65 (m), aromatics}.

5: $[PtMe_2I(PPh_3)(C_6H_4CH{=}NCH_2C_6H_4Cl)]$. Yield (from **2**) 50.0 mg (83%), m.p. 125°C (d). Anal. calc. for $C_{34}H_{32}ClINPtS$: C, 48.44; H, 3.83; N 1.66%. Found: C, 48.46; H, 3.93; N, 1.31%. ^{1}H NMR (acetone-d_6): δ 1.21 (d, ^2J(HPt) = 61, ^3J(HP) = 8, Me_a), 1.53 (d, ^2J(HPt) = 67, ^3J(HP) = 8, Me_b), {4.66, 5.75 (m, AB quartet, ^2J(HH) = 17, CH_2)}, 7.80 (s, ^3J(HPt) = 46, CHN), {6.45 (m), 6.90 (m), 7.32 (m), 7.46 (m), aromatics}. ^{31}P NMR (acetone): $\delta = -10.1$ (s, ^1J(PPt) = 1015).

3.2. X-Ray structure analysis

3.2.1. Data collection

A prismatic crystal ($0.1 \times 0.1 \times 0.2$ mm^3) was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections ($12° \le \theta \le 21°$) and refined by the least squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using the ω–2θ scan technique. A total of 4312 reflections were measured in the range $2° \le \theta \le 30°$, 2819 of which were assumed as observed applying the condition $I \ge 2.5\ \sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls and significant intensity decay was not observed. Lorentz polarization and absorption corrections were made.

3.2.2. *Structure solution and refinement*

The structure was solved by Patterson synthesis, using the SHELXS computer program [18] and refined by the full-matrix least-squares method, with the SHELX76 computer program [19]. The function minimized was $\Sigma w[|F_o| - |F_c|]^2$, where $w = \sigma^{-2}(F_o)$. f, f', and f'' were taken from International Tables of X-ray Crystallography [20]. All H atoms were computed and refined with an overall isotropic temperature factor, using a riding model. The final R factor was 0.033 ($R_w = 0.033$) for all observed reflections. The number of refined parameters was 335. The maximum shift/e.s.d. = 0.05; maximum and minimum peaks in the final difference synthesis were 0.6 and −0.6 e $Å^{-3}$, respectively.

Supplementary material. Tables of structure factors, thermal parameters, and a complete list of bond distances and angles are available from the authors on request. All data except structure factors have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgements

We thank Johnson Matthey Ltd for a generous loan of $K_2[PtCl_4]$ and the DGICYT (Ministerio de Educación y Ciencia of Spain, PB 93-0804 project) for financial support.

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