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Formation and cleavage of platinacycles containing a fluorinated imine. Crystal structure of [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)PPh_3]

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Abstract

The reaction of [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] with the ligand 3,4,5-$C_6H_2F_3CH{=}NCH_2C_6H_5$ (**L**) yielded the cyclometallated platinum(II) compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)SMe_2] (**1**), in which the imine acts as a [C,N]-bidentate ligand. Compounds [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)DMSO] (**2**) (DMSO = dimethyl sulfoxide) and [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)PPh_3] (**3**) were obtained from a displacement reaction of SMe_2 for DMSO or PPh_3, respectively. Oxidative addition of methyl iodide to compounds **1**–**3** produced, respectively, [$PtMe_2I$(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)SMe_2] (**4a**/**4b**) as two isomers, [{$PtMe_2I$(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)}$_2$] (**5**) and [$PtMe_2I$(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)PPh_3] (**6**). Platinum(II) metallacycles can be cleaved upon reaction with an excess of PPh_3 or with the diphosphine dppe to yield, respectively, compounds [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)$(PPh_3)_2$] (**7**) and [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)dppe] (**8**) in which the imine acts as a monodentate [C] ligand. Analogous compounds could not be obtained for platinum(IV) since in this case neither PPh_3 nor dppe can cleave the metallacycle. The reaction of **4a**/**4b** with dppe produced [{$PtMe_2I$(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)}$_2$dppe] (**11**), a binuclear compound in which the diphosphine bridges two platinum(IV) moieties with the imine acting as a [C,N]-bidentate ligand. All compounds were characterised by analytical and spectroscopic techniques and compound **3** was also characterised crystallographically.

Keywords: Platinum; Cyclometallation; Imine; Fluorine; Phosphine; Crystal structures

1. Introduction

Cyclometallated complexes of the Group 10 elements have generated considerable interest due to their numerous applications and interesting properties. Previous results showed that the reactions with phosphines could be taken as a criterion for the stability of metallacycles [1]. Moreover, it has been shown that steric crowding in the co-ordination sphere of the metal favoured the cleavage of metallacycles upon reaction with triphenylphosphine. In particular, the presence of a fluorine [2–4] or a chlorine [5,6] atom in the position adjacent to the M–C(aryl) bond seems to be decisive. On the other hand, both palladium(II) [7] and platinum(II) [6,8,9] metallacycles are cleaved easily with diphosphines such as 1,2-bis(diphenylphosphino)-ethane, which can be explained by the chelating nature of this ligand. Nevertheless, examples in which the formation of either compounds containing a bridging diphosphine [10] or ionic compounds with a chelate diphosphine [11] is favoured over cleavage of the metallacycles have also been reported.

In this paper we report new cyclometallated platinum compounds containing the imine 3,4,5-$C_6H_2F_3CH{=}NCH_2C_6H_5$ and their reactions with phosphines in order to analyse the factors governing the cleavage of the formed metallacycles.

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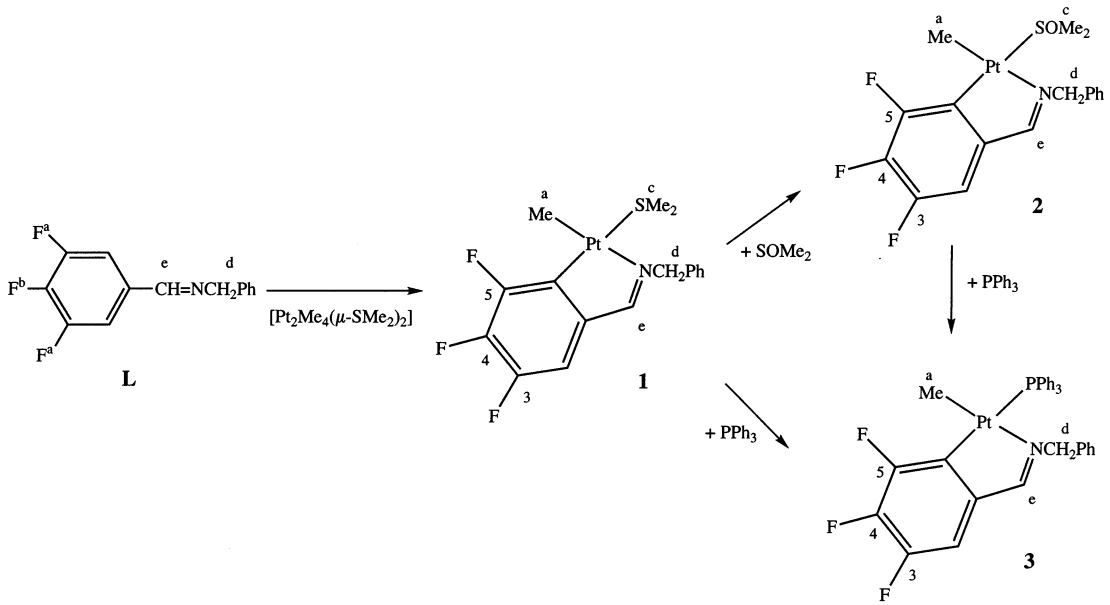
2. Results and discussion

The reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with ligand 3,4,5-$C_6H_2F_3CH{=}NCH_2C_6H_5$ (**L**) yielded the cyclometallated platinum(II) compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2$-C_6H_5) SMe_2] (**1**) by *ortho* metallation with loss of methane, as reported for analogous systems [3,4]. Compound **1** reacted with an excess of dimethylsulfoxide (DMSO) or with PPh_3 in a 1:1 molar ratio to yield respectively compounds [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2$-C_6H_5)DMSO] (**2**) and [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2$-C_6H_5)PPh_3] (**3**) which result from a displacement reaction of SMe_2 for DMSO or PPh_3. The reaction of compound **2** with PPh_3 gave compound **3** which indicates the lability order $SMe_2 > DMSO > PPh_3$ for these platinum(II) compounds. Compounds **1**–**3**, shown in Scheme 1, were characterised by elemental analysis and NMR spectroscopies. In the ^1H NMR spectra, the methyl group bound to platinum is coupled to the fluorine atom in position five of the aryl ring, thus revealing a through-space interaction; additional coupling to the phosphorous atom is observed for compound **3**. The methyl, the imine and the methylene hydrogens are coupled to ^{195}Pt and the values of the coupling constants are characteristic of this kind of cyclometallated platinum(II) compounds. For compound **2**, the $J(H{-}Pt)$ value of the protons of DMSO [12] and the $\delta(^{195}Pt)$ value [13] indicate that DMSO is S-bonded to platinum; this is further confirmed by a strong band at 1110 cm^{-1} in the IR spectrum. A process involving oxidative cycloplatination and sulfur deoxygenation has been reported in the reaction between (*E*)-2-methyl-1-phenylbutan-1-one oxime and *cis*-$[PtCl_2(DMSO)_2]$ in refluxing methanol [14]; however, compound **2** was recovered unchanged when treated under such conditions. The presence of the PPh_3 ligand in **3** is confirmed by ^{31}P NMR spectroscopy and the value of the coupling constant to platinum ($J(P{-}Pt) = 2631$ Hz) is in the expected range for a phosphine with a fluorinated aryl group in *trans*. In the ^{19}F NMR spectra, three distinct resonances appear in the aromatic region and the values of the coupling constants are in the range expected for analogous compounds [15].

Compound **3** was also characterised crystallographically. Suitable crystals were grown from acetone solution. The crystal structure is composed of discrete molecules separated by van der Waals interactions. A view of the molecule is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. As expected from spectroscopic characterisation, the methyl group is *trans* to the nitrogen atom, the C=N group is *endo* to the cycle and the imine adopts an (*E*)-configuration, the torsion angle C(6)–C(7)–N–C(8) being $-173.99(4)°$. The platinum atom displays a tetrahedral distorted planar co-ordination and the following displacements (Å) are observed from the least-squares plane of the co-ordination sphere: Pt, -0.0264; P, 0.1658; N, -0.1785; C(1), 0.2074; C(15), -0.1683. The metallacycle is approximately planar; the largest deviation from the mean plane determined by the five atoms is -0.0628 Å for C(1). The dihedral angle between the metallacycle and the co-ordination plane is larger (10.24°) than those reported for [PtMe(2,3,4-$C_6HF_3CH{=}NCH_2C_6H_5$)PPh_3] (4.6°) [3] and [PtMe-(2,3,4-$C_6HF_3CH{=}NCH_2CH_2NMe_2$)] (0.28°) [4]. A larger deviation from coplanarity reduces the steric interaction between the methyl group and the fluorine substituent



Scheme 1.

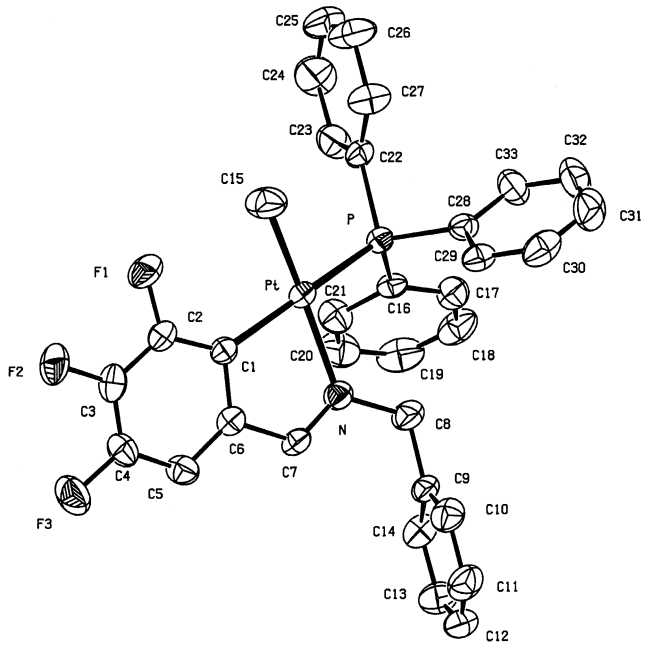


Fig. 1. Molecular structure of compound **3**.

Table 1
Selected bond lengths (Å) and bond angles (°)

Bond lengths			
Pt–C(15)	2.053(6)	Pt–C(1)	2.064(5)
Pt–N	2.144(4)	Pt–P	2.2815(12)
P–C(28)	1.816(5)	Pt–C(16)	1.824(5)
P–C(22)	1.833(5)	F(1)–C(2)	1.360(6)
F(2)–C(3)	1.344(6)	F(3)–C(4)	1.354(6)
N–C(7)	1.279(6)	N–C(8)	1.489(7)
C(1)–C(2)	1.384(7)	C(1)–C(6)	1.409(7)
C(2)–C(3)	1.379(7)	C(3)–C(4)	1.360(8)
C(4)–C(5)	1.366(8)	C(5)–C(6)	1.388(7)
C(6)–C(7)	1.451(7)	C(8)–C(9)	1.498(7)
C(13)–C(12)	1.349(9)	C(13)–C(14)	1.373(8)
C(12)–C(11)	1.359(9)	C(11)–C(10)	1.387(8)
C(10)–C(9)	1.368(8)	C(9)–C(14)	1.366(8)
Bond angles			
C(15)–Pt–C(1)	94.8(2)	C(15)–Pt–N	169.3(2)
C(1)–Pt–N	79.08(17)	C(15)–Pt–P	90.58(18)
C(1)–Pt–P	167.76(13)	N–Pt–P	97.17(11)
C(28)–P–C(16)	106.5(2)	C(28)–P–C(22)	101.6(2)
C(16)–P–C(22)	101.7(2)	C(28)–P–Pt	117.48(16)
C(16)–P–Pt	110.25(15)	C(22)–P–Pt	117.67(17)
C(7)–N–C(8)	119.3(4)	C(7)–N–Pt	113.6(3)
C(8)–N–Pt	126.6(3)	C(2)–C(1)–C(6)	112.3(4)
C(2)–C(1)–Pt	135.0(4)	C(6)–C(1)–Pt	112.3(3)
C(3)–C(2)–C(1)	124.3(5)	C(4)–C(3)–C(2)	120.2(5)
C(3)–C(4)–C(5)	119.9(5)	C(4)–C(5)–C(6)	118.2(5)
C(5)–C(6)–C(1)	125.0(5)	C(5)–C(6)–C(7)	119.1(4)
C(1)–C(6)–C(7)	115.8(4)	N–C(7)–C(6)	118.3(4)
N–C(8)–C(9)	116.4(4)		

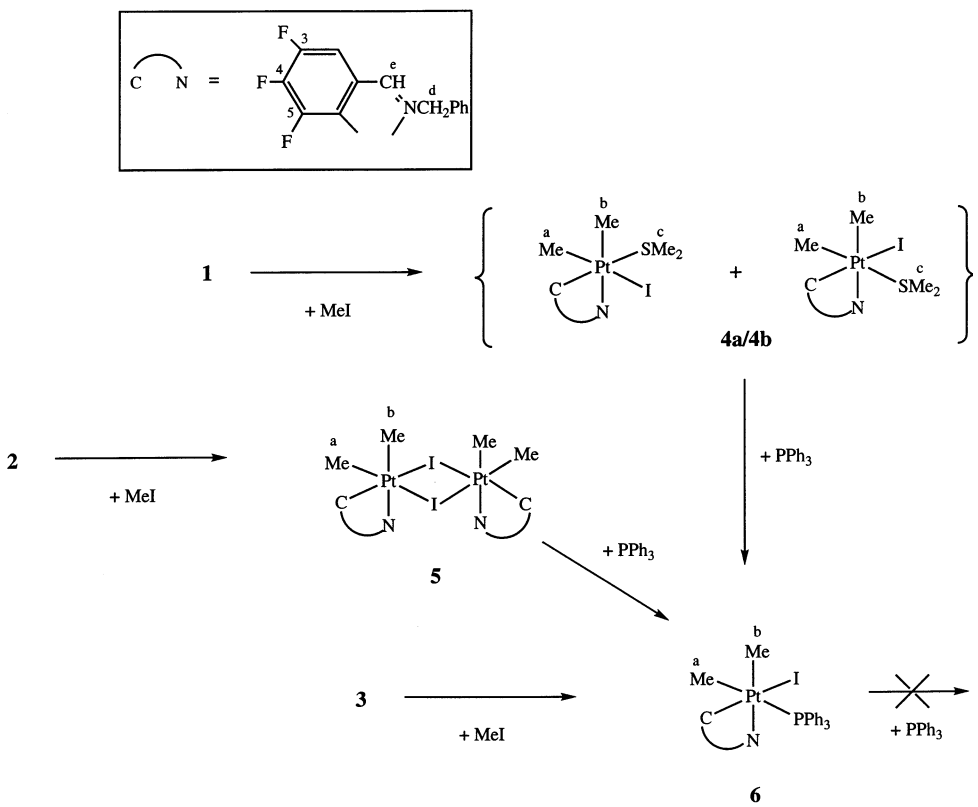
in a position adjacent to the Pt–C(aryl) bond. Nevertheless, the distance C(15)···F(1) of 2.929 Å can be taken as an indication of a short contact between the methyl group and the fluorine, which are close enough for the van der Waals radii to overlap. The coupling between the methyl protons and ^{19}F in the NMR spectrum implies that this interaction persists in solution. Bond lengths and angles are well within the range of values obtained for analogous compounds [3,4,16]. The 'bite' angle C(1)–Pt–N of 79.08(17) is characteristic of cyclometallated platinum(II) complexes [17].

Oxidative addition of methyl iodide to compound **1** carried out in $CDCl_3$ at NMR scale produced a mixture of two isomers of platinum(IV) compound $[PtMe_2I(3,4,5\text{-}C_6HF_3CH{=}NCH_2C_6H_5)SMe_2]$ (**4a**/**4b**) in nearly equal amounts together with a very small amount (less than 5% of the reaction mixture) of compound **5** (see below). The spectral parameters for compounds **4** are in good agreement with those reported in the literature for analogous compounds [18] and are assigned to the isomers depicted in Scheme 2, which differ only in having a SMe_2 or an I *trans* to the axial methyl. For both isomers only the equatorial methyl is coupled to the fluorine at position five of the aryl ring. Oxidative addition of methyl iodide to compound **2** gave compound **5** as a pale yellow solid which was characterised by NMR and FAB spectroscopies. Of the two methyl resonances—both coupled to platinum—the one at lower field is assigned to the equatorial methyl which is also coupled to the fluorine atom F^5. The absence of coordinated S– or O–DMSO in the ^1H and IR spectra points to an iodide bridged platinum(IV) dimer, a structure that is confirmed by FAB mass spectrometry. Moreover, since resonances due to SMe_2 are not observed, the formation of dimethylsulfide from DMSO within the co-ordination sphere of platinum as described in the literature for analogous systems[14] can be ruled out. The low affinity of the DMSO ligand for platinum(IV) has already been shown in the reaction of *cis*-$[PtMe_2(DMSO)_2]$ with methyl iodide which yields the platinum(IV) tetramer $[\{PtMe_3(\mu_3\text{-}I)\}_4]$ [19]. The $\delta(^{195}Pt)$ value obtained for **5** (-2700 ppm) is similar to that reported in the literature for the tetramer (-2769 ppm) [20]. Oxidative addition of methyl iodide to compound **3** produced cyclometallated platinum(IV) compound $[PtMe_2I(3,4,5\text{-}C_6HF_3CH{=}NCH_2C_6H_5)(PPh_3)]$ (**6**) which was characterised by elemental analyses and NMR spectra. Two methyl resonances appear at $\delta = 1.38$ ($^2J(Pt–H) = 60$ Hz) and $\delta = 2.20$ ($^2J(Pt–H) = 69$ Hz) both coupled to ^{195}Pt and ^{31}P ($^3J(P–H) = 8$ Hz). The small value of the coupling constant of the axial methyl with platinum suggest a *trans* arrangement of this group and the PPh_3 ligand, as reported previously for analogous compounds [8]. The equatorial methyl is also coupled to the fluorine atom at position five of the aryl ring. The $J(P–Pt)$ value is in the range expected for platinum(IV) compounds, which is considerably reduced compared to that of the platinum(II) compound. Alternatively, compound **6** could be prepared upon reaction of com-

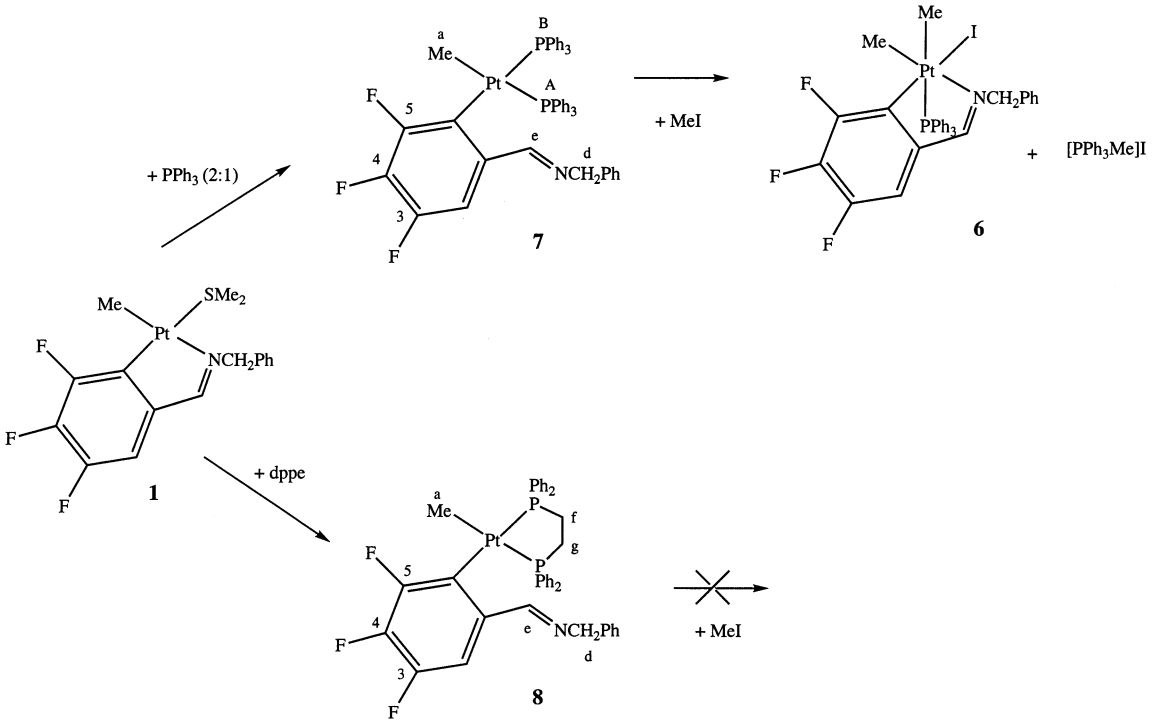
pounds **4a**/**4b** or **5** obtained in situ in acetone with the equivalent amount of triphenylphosphine and all preparative methods lead to the same stereoisomer in which the bulky triphenylphosphine is in an axial position. The lability order $DMSO > SMe_2 > PPh_3$ is deduced for platinum(IV) compounds.

Cleavage of the metallacycle in platinum(II) compounds was achieved upon reaction of compound **1** with two equivalents of PPh_3 or with one equivalent of the bidentate phosphine 1,2-bis(diphenylphosphino)ethane (dppe) to yield, respectively, compounds [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)(PPh_3)$_2$] (**7**) and [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)dppe] (**8**) (see Scheme 3) which were obtained as white solids and characterised by elemental analyses and NMR spectroscopies. In both cases, the methyl resonance is coupled to two non-equivalent phosphorus atoms and the value of the coupling constants with ^{195}Pt are reduced (^2J(Pt–H) = 65 Hz (**7**) or 67 Hz (**8**)) when compared to that of cyclometallated compound **3** (83 Hz). Moreover, the imine proton is not coupled to ^{195}Pt and the ^{31}P NMR spectra show two sets of resonances due to two non-equivalent phosphorus atoms, both coupled to platinum. These results indicate that two phosphorus atoms are present in the co-ordination sphere of platinum(II) and therefore the imine is acting as a monodentate ligand through the aryl carbon. As observed previously for analogous compounds [3,4], the ^3J(Pt–F^5) values are much larger (412 Hz (**7**) and 385 Hz (**8**)) than those obtained for cyclometallated compounds **1** (140 Hz), **2** (98 Hz) and **3** (87 Hz). The large value of the coupling constant may arise from a perpendicular orientation of the aryl group to the co-ordination plane [21]. The methyl group consistently does not couple with the fluorine in position five of the aryl ring.

In spite of the easy cleavage of the metallacycle reported above for platinum(II) compounds, cyclometallated platinum(IV) compound **6** did not react further with triphenylphosphine even when large excesses were used. Other attempts to obtain triphenylphosphine platinum(IV) derivatives in which the imine acts as a monodentate [C] ligand were also unsuccessful. For instance, the reaction of platinum(II) compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)(PPh_3)$_2$] (**7**) with methyl iodide gave a mixture of cyclometallated platinum(IV) compound **6**, characterised as above, and the phosphonium salt [PPh_3Me]I, for which ^{1}H and ^{31}P NMR data are consistent with the values given in the literature [22]. In this process, oxidative addition of methyl iodide took place along with co-ordination of the dangling imine nitrogen to platinum and dissociation of the phosphine, which gave the phosphonium salt. This result can be related to the higher affinity of platinum(IV) for nitrogen than for phosphorus donor ligands due to its harder nature.



Scheme 2.



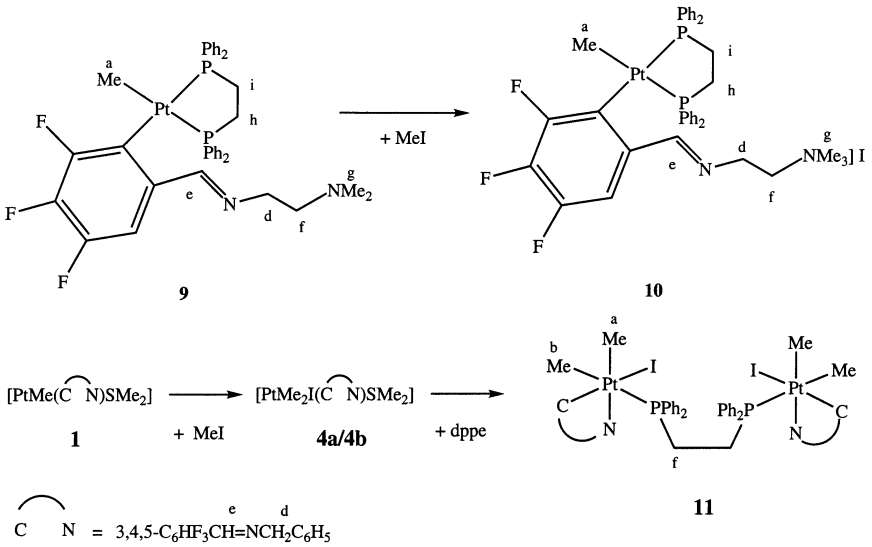
Scheme 3.

On the other hand, compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)dppe] (**8**) did not react with methyl iodide even after 48 h when evidence of decomposition was observed. For the purpose of comparison, the reaction with methyl iodide was also tested for compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2CH_2NMe_2$)(dppe)] (**9**) obtained from [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2CH_2NMe_2$)] [4] in which the terdentate imine 3,4,5-$C_6HF_3CH{=}NCH_2CH_2NMe_2$ acts as a monodentate [C] ligand. The reaction of compound **9** with methyl iodide is shown in reaction 1 and produced the ionic compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2CH_2NMe_3$)(dppe)]I (**10**) resulting from methylation of the amine group. NMR data are similar to those obtained for **9** except for the fact that the amine protons are shifted towards higher fields ($\delta = 3.43$ ppm) and integrate nine hydrogen atoms. An analogous process in which methyl iodide is added to the dangling NMe_2 moiety but not to the platinum centre has been described for compound [PtMe(3-$C_6H_3ClCH{=}NCH_2CH_2NMe_2$)(dppe)] [6].

In view of these results, the reaction of compounds **4a**/**4b**—obtained in situ from **1**—with dppe in the ratio 2:1 was also tested. A yellow non-electrolyte solid was obtained and was characterised as binuclear platinum(IV) compound [{$PtMe_2I$(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)}$_2$(dppe)] (**11**) by NMR and FAB Mass spectra. Compound **11** could not be isolated in a pure form due to decomposition processes during attempted crystallisation in several solvents. In the ^{1}H NMR spectrum two methyl resonances appear at $\delta = 1.05$ (^2J(Pt–H) = 59 Hz) and $\delta = 1.83$ (^2J(Pt–H) = 69 Hz) both coupled to ^{195}Pt and to one phosphorus atom (J(Pt–P) ca. 7–8 Hz), and the equatorial methyl also coupled to the fluorine atom at position five of the aryl ring. As in compound **6**, these values suggest a *trans* arrangement of the axial methyl and the phosphorus atom and a *fac*-PtC_3 stereochemistry. The imine proton is also coupled to ^{195}Pt (^{3}J(Pt–H) = 47 Hz) indicating that the metallacycle has not been cleaved. Two resonances appear in the ^{31}P NMR spectrum at $\delta = -10.4$ (J(Pt–P) = 1049 Hz) and $\delta = -10.9$ (J(Pt–P) = 1048 Hz); these values are characteristic of phosphines bound to platinum(IV) and *trans* to a methyl group [9], and can only be assigned to two different conformations of compound **11**. When larger amounts of diphosphine were used the main products are compound **11** and free diphosphine or its oxide. No evidence of formation of compounds containing chelate diphosphine was observed in the ^{1}H or in the ^{31}P NMR; the formation of such compounds requires dissociation of either nitrogen or iodide, and it is likely that such processes are not favoured for platinum(IV) compounds.

In conclusion, while platinum(II) metallacycles derived from imine 3,4,5-$C_6H_2F_3CH{=}NCH_2C_6H_5$ can be opened up using a diphosphine or an excess of a monodentate phosphine, platinum(IV) metallacycles are much more resistant to cleavage. Moreover, oxidative addition to platinum(II) compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)(PPh_3)$_2$] (**7**) in which the imine acts as a [C] ligand favours the co-ordination of the

imine nitrogen to yield a [C,N] platinum(IV) cyclometallated compound. These results could be explained by the higher affinity of platinum(IV) for nitrogen donor ligands when compared to the softer platinum(II).



3. Experimental

^{1}H, ^{19}F, $^{31}P-\{^{1}H\}$ and ^{195}Pt NMR spectra were recorded by using Varian Gemini 200 (^{1}H, 200MHz), Varian 300 (^{19}F, 282.2 MHz; ^{195}Pt, 64.2 MHz) and Bruker 250 (^{31}P, 101.25 MHz) spectrometers, and referenced to $SiMe_4$ (^{1}H), CCl_3F (^{19}F), H_3PO_4 (^{31}P) and H_2PtCl_6 (^{195}Pt). δ values are given in ppm and J values in Hz. IR spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer. Conductivity measurements were carried out to a Crison 2000 equipment. Microanalyses and FAB mass spectra were performed by the Serveis Científico-Tècnics de la Universitat de Barcelona.

3.1. Preparation of the compounds

Compounds $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ [23] and [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2CH_2NMe_2$)] [4] were prepared as reported.

The ligand 3,4,5-$C_6H_2F_3CH{=}NCH_2C_6H_5$ (**L**) was prepared by the reaction of 0.5 g (3.1×10^{-3} mol) of the corresponding aldehyde with an equimolecular amount (0.33 g) of benzylamine in refluxing ethanol. The mixture was refluxed for 2 h, and the solvent was removed in a rotary evaporator to yield a yellow oil. Yield 0.65 g (83%). ^{1}H NMR ($CDCl_3$): $\delta = 4.82$ [s, H^d]; 7.42 [m, aromatics]; 8.24 [s, H^e]. ^{19}F NMR ($CDCl_3$): $\delta = -140.09$ [dd, $J(F^a-F^b) = 20$, $J(F^a-H) = 8$, F^a]; -163.14 [tt, $J(F^a-F^b) = 20$, $J(F^b-H) = 6$, F^b].

Compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)SMe_2] (**1**) was obtained by the reaction of 100 mg (1.74×10^{-4} mol) of compound $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with 87.6 mg (3.52×10^{-4} mol) of the ligand 3,4,5-$C_6H_2F_3CH{=}NCH_2C_6H_5$ in acetone (20 ml). After continuous stirring during 16 h, the solvent was removed in a rotary evaporator and the resulting orange solid was washed with hexane (2×10 mL) and dried under vacuum. Yield 140 mg (77%). ^{1}H NMR (acetone-d^6): $\delta = 1.13$ [d, $^{2}J(Pt-H) = 80$, $J(F-H) = 6$, Me^a]; 1.90 [s, $^{3}J(Pt-H) = 36$, Me^c]; 5.19 [s, $^{3}J(Pt-H) = 13$, H^d]; {7.28–7.38 [m], aromatics}; 8.96 [s, $^{3}J(Pt-H) = 56$, H^e]. ^{19}F NMR (acetone-d^6): $\delta = -122.61$ [dt, $J(Pt-F^5) = 140$, $J(F^5-F^4) = 23$, $J(F^5-F^3) = J(F^5-H) = 5$, F^5]; -146.95 [m, F^3]; -159.89 [ddd, $J(Pt-F^4) = 100$, $J(F^4-F^5) = 24$, $J(F^4-F^3) = 20$, $J(F^4-H) = 7$, F^4]. *Anal.* Found: C, 39.4; H, 3.6; N, 2.9. Calc. for $C_{17}H_{18}F_3NSPt$: C, 39.23; H, 3.49; N, 2.69%.

Compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)-DMSO] (**2**) was obtained by adding two drops of DMSO to 50 mg (9.6×10^{-5} mol) of compound **1** in dichloromethane (20 ml). After continuous stirring during 1 h, the solvent was removed in a rotary evaporator and the oily residue was washed with diethylether (3×5 ml). The obtained yellow solid was dried in vacuum. Yield 35 mg (68%). ^{1}H NMR ($CDCl_3$): $\delta = 0.95$ [d, $^{2}J(Pt-H) = 80$, $J(F-H) = 6$, Me^a]; 2.78 [s, $^{3}J(Pt-H) = 20$, Me^c], 5.28 [s, $^{3}J(Pt-H) = 5$, H^d]; {7.14 [m, 1H]; 7.30–7.41 [m, 5H], aromatics}; 8.62 [s, $^{3}J(Pt-H^e) = 62$, H^e]. ^{19}F NMR ($CDCl_3$): $\delta = -120.91$ [dt, $J(Pt-F^5) = 98$, $J(F^5-F^4) = 22$, $J(F^5-F^3) = J(F^5-H) = 7$, F^5]; -142.97 [dt, $J(F^3-F^4) = 18$, $J(F^3-F^5) = J(F^3-H) = 7$, F^3]; -156.46 [m, $J(Pt-F^4) = 43$, $J(F^4-F^5) = 22$, $J(F^4-F^3) = 18$, $J(F^4-H) = 6$, F^4]. ^{195}Pt NMR ($CDCl_3$): $\delta = -3982$ [s]. IR (KBr): 1110 cm^{-1} (ν(SO)). FAB(+) MS (NBA, m/z): 521 ($[M-Me]^+$); 443 ($[M-Me-SOMe_2]^+$). *Anal.* Found: C, 37.6; H, 3.4; N, 2.6. Calc. for $C_{17}H_{18}F_3NOPtS$: C, 38.06; H, 3.38; N, 2.61%.

Compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)-PPh_3] (**3**) was obtained from the reaction of 50 mg (9.6×10^{-5} mol) of compound **1** with the equimolecular amount (25 mg) of PPh_3 in acetone (20 ml). After continuous stirring during 2 h, the solvent was removed in a rotary evaporator and the resulting yellow solid was washed with hexane (2×5 ml), and diethylether (2×5 ml) and dried under vacuum. Yield 55 mg (80%). ^{1}H NMR (acetone-d^6): $\delta=0.97$ [dd, ^2J(Pt–H) = 83, ^3J(P–H) = 9, J(F–H) = 6, Me^a]; 4.22 [s, ^3J(Pt–H) = 8, H^d]; {6.79 [m, 1H]; 7.40 [m], 7.64 [m], aromatics}; 8.63 [s, ^3J(Pt–H^e) = 55, H^e]. ^{19}F NMR (acetone-d^6): $\delta=-122.62$ [m, J(Pt–F^5) = 87, J(F^5–F^4) = 24, J(P–F^5) = J(F^5–F^3) = J(F^5–H) = 7, F^5]; -146.01 [m, F^3]; -159.80 [m, F^4]. ^{31}P NMR (acetone-d^6): $\delta=29.79$ [dd, J(Pt–P) = 2631, J(P–F^5) = 10, J(P–F^4) = 7]. *Anal.* Found: C, 54.7; H, 3.8; N, 2.0. Calc. for $C_{33}H_{27}F_3NPPt$: C, 55.00; H, 3.78; N, 1.94%.

Compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)-$(PPh_3)_2$] (**7**) was obtained as a white solid by an analogous procedure using 100 mg (1.9×10^{-4} mol) of PPh_3. Yield 80 mg (85%). ^{1}H NMR (acetone-d^6): $\delta=$ 0.27 [dd, ^2J(Pt–H) = 65, ^3J(P^A–H) = 8, ^3J(P^B–H) = 7, Me^a]; {4.74 [d], 4.87 [d], J(H–H) = 13, AB pattern, H^d}; 7.13–7.24 [m, aromatics]; 9.40 [s, H^e]. ^{19}F NMR (acetone-d^6): $\delta=-113.96$ [ddd, J(Pt–F^5) = 412, J(F^5–F^4) = 30, J(P–F^5) = 15, J(F^5–F^3) = 3, F^5]; -148.54 [m, F^3]; -164.33 [ddt, J(F^5–F^4) = 30, J(F^4–F^3) = 19, J(P–F^4) = J(F^4–H) = 7, F^4]. ^{31}P NMR (acetone-d^6): $\delta=25.38$ [d, J(Pt–P^A) = 1908, J(P^A–P^B) = 15, P^A]; 26.01 [td, J(Pt–P^A) = 2311, J(P^B–P^A) = J(P^B–F^5) = 15, J(P^B–F^4) = 8, P^B]. *Anal.* Found: C, 61.9; H, 4.3; N, 1.4. Calc. for $C_{51}H_{42}F_3NP_2Pt$: C, 62.32; H, 4.31; N, 1.44%.

Compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)-(dppe)] (**8**) was obtained as a white solid by an analogous procedure using 38 mg (9.5×10^{-5} mol) of dppe. Yield 70 mg (85%). ^{1}H NMR (acetone-d^6): $\delta=$ 0.48 [t, ^2J(Pt–H) = 67, ^3J(P^A–H) = ^3J(P^B–H) = 6, Me^a]; 2.44 [m, H^{f,g}]; 4.36 [s, H^d]; {7.12–7.32 [m], 7.45–7.55 [m], 7.70–7.79 [m], 7.89–7.98 [m], aromatics}; 8.65 [s, H^e]. ^{19}F NMR ($CDCl_3$): $\delta=-114.20$ [dd, J(Pt–F^5) = 385, J(F^5–F^4) = 27, J(P–F^5) = 11, F^5]; -147.38 [m, F^3]; -163.92 [ddt, J(F^5–F^4) = 29, J(F^4–F^3) = 20, J(P–F^4) = J(F^4–H) = 8, F^4]. ^{31}P NMR (acetone-d^6): $\delta=46.58$ [s, J(Pt–P^A) = 1718, P^A]; 47.36 [m, J(Pt–P^B) = 2287, P^B]. *Anal.* Found: C, 57.4; H, 4.4; N, 1.6. Calc. for $C_{41}H_{36}F_3NP_2Pt$: C, 57.48; H, 4.24; N, 1.63%.

Compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2CH_2$-NMe_2)(dppe)] (**9**) was obtained as a white solid by an analogous procedure from 50 mg (1.14×10^{-4} mol) of the compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2CH_2$-NMe_2)] and 45 mg of dppe. Yield 80 mg (84%). ^{1}H NMR (acetone-d^6): $\delta=0.46$ [t, ^2J(Pt–H) = 68, ^3J(P^A–H) = ^3J(P^B–H) = 7, Me^a]; 2.15 [s, Me^g]; {2.20–2.45 [m], 3.26 [t, J(H–H) = 7, H^{d,f,h,i}} 7.14–7.76 [m, aromatics]; 8.52 [s, H^e]. ^{19}F NMR ($CDCl_3$): $\delta=-109.17$ [dd, J(Pt–F^5) = 390, J(F^5–F^4) = 30, J(P–F^5) = 16, F^5]; -144.31 [m, F^3]; -161.64 [m, F^4]. ^{31}P NMR (acetone-d^6): $\delta=46.37$ [s, J(Pt–P^A) = 1718, P^A]; 47.27 [dd, J(Pt–P^B) = 2274, J(P^B–F^5) = 16, J(P^B–F^4) = 8, P^B]. $\Lambda_M=2.3\ \Omega^{-1}\ cm^2\ mol^{-1}$ (10^{-3} M in acetone). *Anal.* Found: C, 53.9; H, 4.7; N, 3.2. Calc. for $C_{38}H_{39}F_3N_2P_2Pt$: C, 54.48; H, 4.69; N, 3.34%.

Compound [PtMe$_2$I(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)-(SMe_2)] (**4a**/**4b**) was obtained from 20 mg of compound **1** (3.84×10^{-5} mol) and 10 μL of methyl iodide in 0.7 ml of $CDCl_3$ in a 5 mm NMR tube and was characterised by NMR spectra. ^{1}H NMR ($CDCl_3$): $\delta=$ {0.81 [s, ^2J(Pt–H) = 68], 1.46 [s, ^2J(Pt–H) = 70], Me^a}; {1.72 [d, ^2J(Pt–H) = 68, J(F–H) = 6], 2.10 [d, ^2J(Pt–H) = 68, J(F–H) = 7], Me^b}; 2.21 [s, ^3J(Pt–H) = 15, Me^c]; 5.25–5-50 [m, H^d]; {8.12 [s, ^3J(Pt–H) = 47], 8.30 [s, ^3J(Pt–H) = 42], H^e}.

Compound [{PtMe$_2$I(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)}$_2$] (**5**) was obtained as a pale yellow solid from the reaction of an excess of methyl iodide (0.1 ml) with 50 mg (9.3×10^{-5} mol) of compound **2** carried out in acetone (20 ml). The mixture was stirred for 3 h, and the solvent was removed under vacuum. The residue was washed with diethylether (3×5 ml) and dried under vacuum. Yield 35 mg (63%). ^{1}H NMR ($CDCl_3$): $\delta=1.27$ [s, ^2J(Pt–H) = 75, Me^a]; 2.94 [d, ^2J(Pt–H) = 69, J(F–H) = 8, Me^b]; {5.63 [d], 5.92 [d], J(H–H) = 16, AB pattern, H^d}; {7.01 [m, 1H]; 7.37–7.57 [m, 5H], aromatics}; 8.05 [s, ^3J(Pt–H^d) = 45, H^e]. ^{19}F NMR ($CDCl_3$): $\delta=-127.90$ [dt, J(F^5–F^4) = 21, J(F^5–F^3) = J(F^5–H) = 8, F^5]; -142.59 [m, F^3]; -153.64 [td, J(F^4–F^3) = J(F^4–F^5) = 20, J(F^4–H) = 7, F^4]. ^{195}Pt NMR ($CDCl_3$): -2700 [s]. FAB(+) MS (NBA, m/z): 1200 ($[M]^+$); 1073 ($[M-I]^+$); 1043 ($[M-I-2Me]^+$); 1028 ($[M-I-3Me]^+$); 779 ($[M-I-3Me-L]^+$). *Anal.* Found: C, 31.8; H, 2.5; N, 2.3. Calc. for $C_{32}H_{30}F_6I_2N_2Pt_2$: C, 32.01; H, 2.52; N, 2.33%.

Compound [PtMe$_2$I(3,4,5-$C_6HF_3CH{=}NCH_2C_6H_5$)-(PPh_3)] (**6**) was obtained as a white solid by an analogous procedure from 50 mg (6.9×10^{-5} mol) of compound **3**. Yield 50 mg (83%). ^{1}H NMR ($CDCl_3$): $\delta=1.38$ [d, ^2J(Pt–H) = 60, ^3J(P–H) = 8, Me^a]; 2.20 [t, ^2J(Pt–H) = 69, ^3J(P–H) = J(F–H) = 8, Me^b]; {4.58 [d], 5.52 [d], J(H–H) = 17, *AB* pattern, H^d}; {6.86 [m, 4H]; 7.31–7.58 [m], 7.64 [m], aromatics}; 7.69 [s, ^3J(Pt–H^d) = 44, H^e]. ^{19}F NMR ($CDCl_3$): $\delta=-127.35$ [dt, J(F^5–F^4) = 21, J(F^5–F^3) = J(F^5–H) = 7, F^5]; -144.57 [m, F^3]; -153.62 [td, J(F^4–F^3) = J(F^4–F^5) = 21, J(F^4–H) = 6, F^4]. ^{31}P NMR ($CDCl_3$): $\delta=-11.32$ [s, J(Pt–P) = 1001]. *Anal.* Found: C, 47.2; H, 3.5; N, 1.6. Calc. for $C_{34}H_{30}F_3INPPt$: C, 47.34; H, 3.51; N, 1.62%.

Compound [PtMe(3,4,5-$C_6HF_3CH{=}NCH_2CH_2$-NMe_3)(dppe)]I (**10**) was obtained as a yellow solid from the reaction of an excess of methyl iodide (0.1 ml) with 35 mg (4.18×10^{-5} mol) of compound **9** carried out in acetone. The mixture was stirred for 3 h, and the

solvent was removed under vacuum. Yield 35 mg (85%). ^{1}H NMR (acetone-d^6): $\delta = 0.43$ [t, ^2J(Pt–H) = 69, $^3J(P^A–H) = {}^3J(P^B–H) = 7$, Me[a]; 3.43 [s, Me[g]; {3.60–3.90 [m], H [d,f,h,i]}; 7.13–7.84 [m, aromatics]; 8.53 [s, H[e]. ^{19}F NMR ($CDCl_3$): $\delta = -108.75$ [ddd, J(Pt–F[5]) = 390, $J(F^5–F^4) = 30$, $J(P–F^5) = 15$, $J(F^5–F^3) = 4$, F[5]; –143.75 [m, F[3]; –160.30 [m, F[4]. ^{31}P NMR (acetone-d^6): $\delta = 47.28$ [s, $J(Pt–P^A) = 1711$, P[A]; 47.39 [dd, $J(Pt–P^B) = 2293$, $J(P^B–F^5) = 15$, $J(P^B–F^4) = 8$, P[B]. $\Lambda_M = 103\ \Omega^{-1}\ cm^2\ mol^{-1}$ (10^{-3} M in acetone). *Anal.* Found: C, 46.0; H, 4.5; N, 2.7. Calc. for $C_{39}H_{42}F_3IN_2P_2Pt{\cdot}2H_2O$: C, 46.12; H, 4.56; N, 2.76%.

[{$PtMe_2I(3,4,5\text{-}C_6HF_3CH{=}NCH_2C_6H_5)$}$_2$dppe] (**11**) was obtained using the following procedure: 50 mg (9.6×10^{-5} mol) of compound **1** was treated with an excess of methyl iodide (0.1 ml) in acetone (20 ml) with continuous stirring for 30 min. The solvent was removed in a rotary evaporator and the residue was treated with 19 mg (4.7×10^{-5} mol) of dppe in acetone (20 ml). The mixture was stirred for 1 h and the solvent was removed under vacuum. The residue was washed with hexane (3×5 ml) and the resulting white solid was dried under vacuum. Yield 63 mg (82%). ^{1}H NMR (acetone-d^6): $\delta = 1.05$ [d, ^2J(Pt–H) = 59, ^3J(P–H) = 8, Me[a]; 1.83 [t, ^2J(Pt–H) = 69, J(P–H) = J(F–H) = 7, Me[b]; 2.43 [m, H[f]; {4.27 [d], 5.47 [d], J(H–H) = 15, AB pattern, H[d]}; 7.18–7.35 [m, aromatics]; 8.04 [s, ^3J(Pt–H[e]) = 47, H[e]. ^{19}F NMR (acetone-d^6): $\delta = -128.07$ [m, F[5]; –144.03 [m, F[3]; –153.92 [m, F[4]. ^{31}P NMR (acetone-d^6): $\delta = -10.4$ [s, J(Pt–P) = 1049]; –10.9 [s, J(Pt–P) = 1048]. $\Lambda_M = 3\ \Omega^{-1}\ cm^2\ mol^{-1}$ (10^{-3} M in acetone). FAB(+) MS (NBA, m/z): 1471 ($[M-I]^+$); 1456 ($[M-I-Me]^+$); 1441 ($[M-I-2Me]^+$); 1344 ($[M-2I]^+$); 1299 ($[M-2I-3Me]^+$); 1192 ($[M-I-2Me-L]^+$); 1179 ($[M-I-3Me-L]^+$).

Table 2
Crystallographic details

Formula	$C_{33}H_{27}F_3NPPt$
F_w	720.62
Temperature (K)	293(2)
Wavelength, Å	0.71069
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.0350(10)
b (Å)	11.2170(10)
c (Å)	14.2390(10)
α (°)	90.63
β (°)	105.299(10)
γ (°)	92.62
V (Å^3)	1390.1(2)
Z	2
D_{calc} (Mg m^{-3})	1.722
Absorption coefficient (mm^{-1})	5.148
F(000)	704
θ Range for data collection (°)	2.37–24.95
No. of reflections collected/unique	7346/4108 [$R_{int} = 0.0219$]
No. of data/restraints/parameters	4108/0/432
Goodness-of-fit on F^2	1.076
$R_1(I>2\sigma(I))$	0.0259
wR_2 (all data)	0.0668
Largest difference peak and hole (e Å^{-3})	0.710, –0.642

3.2. X-ray structure analysis: data collection

A prismatic crystal ($0.1 \times 0.1 \times 0.2$ mm) was selected and mounted on a MAR345 diffractometer with an image plate detector. Unit cell parameters were determined from automatic centring of 6890 reflections ($3 < \theta < 31°$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation. 7346 reflections were measured in the range $2.37 < \theta < 24.95°$, 4108 of which were non-equivalent by symmetry (R_{int} (on I) = 0.021). A total of 3820 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz polarisation and absorption corrections were made.

3.3. Structure solution and refinement

The structure was solved by direct methods, using SHELXS computer program [24], and refined by the full-matrix least-squares method, with the SHELXL-97 computer program [25] using 4108 reflections (very negative intensities were not assumed). The function minimised was $\Sigma\, w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0374P)^2 + 3.1998P]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from the International Tables of X-ray Crystallography [24]. 20 H were located from a difference synthesis and refined with an overall isotropic temperature factor and 7 H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom to which they are linked. Further details are given in Table 2.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Centre, CCDC No. 167426. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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