Pergamon

PII: S0277-5387(97)00452-X

Polyhedron Vol. 17, No. 10, pp. 1651–1657, 1998

0277–5387/98 $19.00+0.00

Cyclometallated platinum compounds with N-benzylidenebenzylamines bearing trifluoromethyl groups. Crystal structure of [PtMe{3-(CF_3)C_6H_3CH=NCH_2Ph}(PPh_3)]

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(Received 11 September 1997; accepted 3 November 1997)

Abstract—The reaction of [$Pt_2Me_4(\mu$-$SMe_2)_2$] (**1**) with the imine 3-(CF_3)C_6H_4CH=NCH_2Ph (**2a**) yields the cyclometallated compound [PtMe{3-(CF_3)C_6H_3CH=NCH_2Ph}(SMe_2)] (**3a**) by selective metallation at the less hindered of the two *ortho* positions of the aryl ring followed by loss of methane. A similar reaction for imine 2-(CF_3)C_6H_4CH=NCH_2Ph (**2c**) yields the cyclometallated compound [PtMe{2-(CF_3)C_6H_3CH=NCH_2Ph}(SMe_2)] (**3c**). The reactions of these compounds with triphenylphosphine in (1 : 1) ratio produce compounds [PtMe{3-(CF_3)C_6H_3CH=NCH_2Ph}(PPh_3)] (**4a**) and [PtMe{2-(CF_3)C_6H_3CH=NCH_2Ph}(PPh_3)] (**4c**). The X-ray structure of **4a** is reported. An excess of triphenylphosphine produces metallacycle cleavage and [PtMe{3-(CF_3)C_6H_3CH=NCH_2Ph}(PPh_3)$_2$] (**5a**) is formed with the imine acting as a [C^-] unidentate ligand. Oxidative addition of methyl iodide to compounds **4a** and **4c** gives cyclometallated platinum(IV) complexes. Imines 3,5-(CF_3)$_2C_6H_3$CH=NCH_2Ph (**2b**) and 2-F-6-(CF_3)C_6H_3CH=NCH_2Ph (**2d**) fail to react with [$Pt_2Me_4(\mu$-$SMe_2)_2$] (**1**).

Keywords: selective metallation; N-benzylidenebenzylamine; trifluoromethyl.

There has been considerable interest in cyclometallated platinum(II) compounds due to their photochemical, photophysical and electrochemical properties [1]. The most convenient way to prepare cyclometallated compounds is the initial coordination of the heteroatom followed by metallation [2]. In particular, polyfunctional Schiff bases such as N-benzylidenebenzylamines, are suitable ligands to study these reactions, and the ease of such processes depends on the basicity of the N-donor atom and the nature of the substituents adjacent to the C-donor atom.

We are currently studying the influence of different substituents in the carbon atom adjacent to the metallation position on the formation of platinacycles from N-benzylidenebenzylamines. While metallation at the position adjacent to a small electron-withdrawing fluorine atom is favoured [3], electron-donating groups such as methyl or methoxy groups inhibit the metallation process [4]. For chlorinated N-benzylidenebenzylamines, metallation at a position adjacent to a chlorine atom has been achieved; however, metallation at the less hindered position is preferred for 3-ClC_6H_4CH=NCH_2Ph [5]. These results indicate a subtle balance between the favourable electron-withdrawing ability and the unfavourable size of the chlorine substituent.

We now report the results obtained for analogous imines bearing trifluoromethyl groups adjacent to the metallation positions such as 3-(CF_3)C_6H_4CH=NCH_2Ph (**2a**) and 3,5-(CF_3)$_2C_6H_4$CH=NCH_2Ph (**2b**). The trifluoromethyl group was chosen as a substituent because its approximate electronegativity (3.2) is similar to the electronegativities of chlorine (3.2) or flu-

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orine (4.0) [6] although it is considerably larger. A comparison of the stereo-electronic parameters of different substituents is presented in Table 1 [7].

Furthermore, the presence of CF_3 groups in the *ortho* positions of the aryl ring such as for ligands 2-$(CF_3)C_6H_4CH{=}NCH_2Ph$ (**2c**) and 2-F-6-$(CF_3)C_6H_3CH{=}NCH_2Ph$ (**2d**), may lead to activation of C(aliphatic)—F bonds upon reaction with the platinum substrate.

RESULTS AND DISCUSSION

The reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) with iminic ligands $ArCH{=}NCH_2Ph$ containing trifluoromethyl groups (**2a–2d**) were carried out in acetone and the results are shown in Scheme 1.

For imine 3-$(CF_3)C_6H_4CH{=}NCH_2Ph$ (**2a**), formation of cyclometallated compound $[PtMe\{3\text{-}(CF_3)C_6H_3CH{=}NCH_2Ph\}(SMe_2)]$ (**3a**) by *ortho*-metallation with loss of methane was achieved. As we have reported for analogous imines 3-$XC_6H_4CH{=}NCH_2Ph$ (X = Me, OMe, Cl), metallation occurred selectively at the less hindered of the two non-equivalent *ortho* positions of the benzal ring.

When imine 3,5-$(CF_3)_2C_6H_3CH{=}NCH_2Ph$ (**2b**) was exposed to **1** no reaction occurred. Previous results for analogous imines with different substituents in the carbon atoms adjacent to the metallation positions indicate that, although formation of platinacycles is achieved for F [3] or Cl [5] substituents, no reaction takes place for Me or MeO groups [4]. The failure to produce metallation can be related to an unfavourable combination of steric and electronic effects. For the highly electron-withdrawing trifluoromethyl group, steric effects alone account for the results observed.

The reaction of imine 2-$(CF_3)C_6H_4CH{=}NCH_2Ph$ (**2c**) with **1** produced compound $[PtMe\{2\text{-}(CF_3)C_6H_3CH{=}NCH_2Ph\}(SMe_2)]$ (**3c**) by C—H bond activation with loss of methane. Activation of the C(aliphatic)—F bond to yield a six-membered metallacycle was not observed.

In order to attempt the activation of a C(aliphatic)—F bond, imine 2-F-6-$(CF_3)C_6H_3CH{=}NCH_2Ph$ (**2d**) was tested. Activation of the C(aliphatic)—F bond was not observed upon reaction with **1**. This result is not unexpected since it has been reported that imine 2,6-$F_2C_6H_3CH{=}NCH_2Ph$ fails to react, and C—F activation is less likely for an aliphatic than for an aromatic carbon atom.

In contrast to the results observed for imines containing methyl or methoxy groups, coordination of the imine ligand to platinum through the nitrogen atom was not detected when the reaction of imines **2a–2d** with **1** was monitored by ^1H NMR spectroscopy. This result suggests that the metallation step is fast for **2a** and **2c**; for **2b** and **2d**, the electron-withdrawing ability of the CF_3 groups decreases the basicity of the nitrogen atom and prevents the formation of coordination compounds.

The reaction of compound **3a** with one equivalent of triphenylphosphine in acetone yielded the cyclometallated compound $[PtMe\{3\text{-}(CF_3)C_6H_3CH{=}NCH_2Ph\}(PPh_3)]$ (**4a**). When the reaction was carried out using a large excess of triphenylphosphine, the displacement of both the SMe_2 and the iminic nitrogen for two PPh_3 produced the cleavage of the metallacycle and the formation of compound $[PtMe\{3\text{-}(CF_3)C_6H_3CH{=}NCH_2Ph\}(PPh_3)_2]$ (**5a**). The formation of analogous compounds with the imine acting as a $[C^-]$ unidentate ligand has been previously reported for compounds containing a chlorine [5] or a fluorine [8] atom at C^5, and this has been attributed to unfavourable steric effects between the halogen atom and the methyl group. However, the result obtained for compound **3a** could only be explained on electronic grounds by assuming that a weaker Pt—N bond in *cis* may result from the electron-withdrawing ability of the CF_3 group.

The reaction of compound **3c** with triphenylphosphine in acetone yielded the cyclometallated compound $[PtMe\{2\text{-}(CF_3)C_6H_3CH{=}NCH_2Ph\}(PPh_3)]$ (**4c**) and, in this case, cleavage of the metallacycle was not observed even when a large excess of PPh_3 was used.

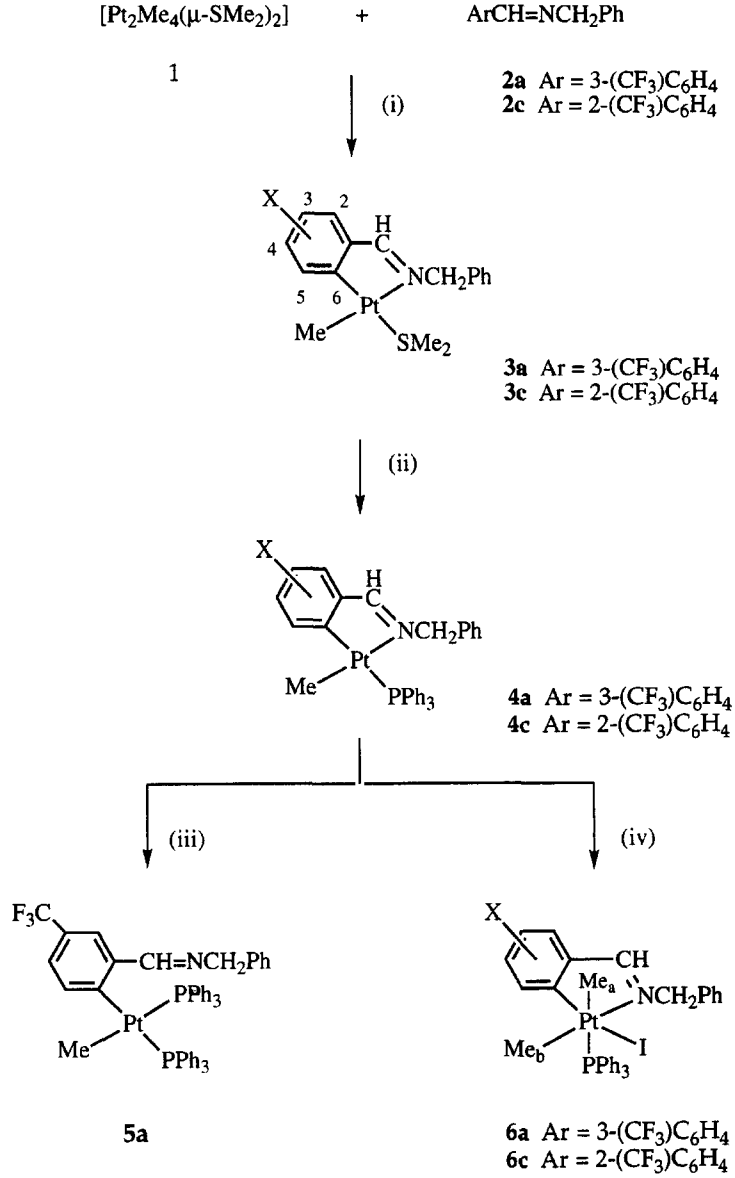
The reactions of **4a** and **4c** with methyl iodide were also studied. Oxidative addition of alkyl halides to square-planar platinum(II) complexes is well documented; in particular, studies concerning compounds $[PtMe_2(NN)]$ (where NN is a bidentate nitrogen donor ligand) have been reported and experimental evidence points to *trans* stereochemistry in the resulting platinum compounds [9,10]. This process is inhibited by the presence of highly electron-withdrawing groups, as in $[Pt(4\text{-}CF_3C_6H_4)_2(bipy)]$ or by steric hindrance as in $[Pt(2\text{-}MeC_6H_4)_2(bipy)$ [11]. In the latter case, the presence of the *ortho*-substituent may prevent attack at the platinum by blocking the coordination sites above and below the plane.

Upon addition of an excess of methyl iodide to

Table 1. Electronic and steric parameters for several substituents[a]

	σ_I	σ_R	E_S
F	0.50	−0.31	−0.46
Me	−0.05	−0.13	−1.24
OMe	0.27	−0.42	−0.55
Cl	0.46	−0.18	−0.97
CF_3	0.42	0.08	−2.4

[a] σ_I, σ_R, and E_S are inductive (*para*), mesomeric (*para*) and steric parameters, respectively, taken from Ref. [7]. H is taken as a standard, with a value 0. Positive σ values indicate electron-withdrawing groups, negative σ values indicate electron-donating groups and negative E_S values indicate unfavourable steric effects.



Scheme 1. (i) Acetone, room temperature, 16 h, C—CH_4 1 ; (ii) $+PPh_3$ (1 : 1), acetone, room temperature, 16 h ; (iii) $+PPh_3$ (5 : 1), acetone, room temperature, 16 h ; (iv) +HeI, acetone, room temperature, 2 h.

solutions of compounds **4** in acetone, the colour of the solution faded and compounds $[PtMe_2I\{(CF_3)C_6H_3CH{=}NCH_2Ph\}(PPh_3)]$ (**6**) were isolated. Thus, in this system, the presence of the electron-withdrawing group CF_3 does not prevent the oxidative addition; a similar result has been reported for fluorinated cyclometallated compounds [12]. Moreover, oxidative addition of methyl iodide takes place even when the bulky CF_3 group is in an *ortho* position of the aryl group as in **6c**.

Compounds **3a**, **3c**, **4a**, **4c**, **5a**, **6a** and **6c** were characterized by elemental analysis and ^1H and ^{19}F NMR spectra, together with ^{31}P NMR spectra for the phosphine derivatives. In the ^1H NMR spectra, the resonance for the methyl-platinum group, in all cases coupled to ^{195}Pt, appears as a singlet for compounds **3a** and **3c**, as a doublet due to coupling with one phosphorus atom for **4a** and **4c**, and as a doublet of doublets due to coupling with two non-equivalent phosphorus atoms for **5a**. For the latter compound, the coupling constant of the iminic hydrogen to platinum is much lower than that of cyclometallated compounds **3a** and **4a**. Two methyl-platinum resonances, coupled with ^{195}Pt and ^{31}P, appear for compounds **6**. The small value for the coupling constant of the axial methyl with platinum suggest a *trans* arrangement of

the axial methyl and the PPh_3, as previously observed for analogous compounds [13]. For all the compounds, the ^{19}F NMR spectra consist of a single resonance; the lack of platinum satellites for **3a** confirms that metallation occurred at position C^6. The ^{31}P NMR spectra consist of a single resonance for compounds **4** and **6**, and of a doublet of doublets for **5a**, in all cases with platinum satellites. Reduced coupling constants to platinum are observed for platinum(IV) compounds **6a** and **6c**.

Compound **4a** was also characterized crystallographically. Suitable crystals of **4a** were grown in acetone solution. The crystal structure is composed of discrete molecules separated by van der Waals distances. The structure is shown in Fig. 1 and the molecular dimensions are listed in Table 2. The coordination sphere of platinum is square-planar. The metallacycle is approximately planar; the largest deviation from the mean plane determined by the five atoms is 0.059 Å for C(6). The metallacycle is nearly coplanar with the coordination plane, the dihedral angle being 8.16°. The angles between adjacent atoms in the coordination sphere of platinum lie in the range 78.93(13)–98.97(9)°, the smallest angles corresponding to the metallacycle. Bond lengths in the coordination sphere of platinum are in the range expected for cyclometallated platinum compounds [4,8,13].

The results reported in this paper for N-benzylidenebenzylamines bearing trifluoromethyl groups indicate that the bulk of the CF_3 substituent inhibits the metallation at the adjacent positions. Thus, in contrast to the result obtained for chlorine substituents, the electron-withdrawing ability of the CF_3 group does not overcome its unfavourable steric effect. However, oxidative addition of methyl iodide to the obtained cyclometallated compounds is not prevented by the bulk of the CF_3 group due to the nearly coplanar arrangement of the metallacycle and the coordination plane.

EXPERIMENTAL

^1H and ^{31}P-$\{^1H\}$ NMR spectra were recorded by using Varian Gemini 200 (^1H, 200 MHz), Bruker WP80SY (^{31}P, 32.4 MHz), and Varian XL 300FT (^{19}F, 282.2 MHz; ^{31}P, 121.4 MHz) spectrometers, and referenced to $SiMe_4$ (^1H), H_3PO_4 (^{31}P) and CCl_3F (^{19}F). δ values are given in ppm and J values in Hz. Mic-

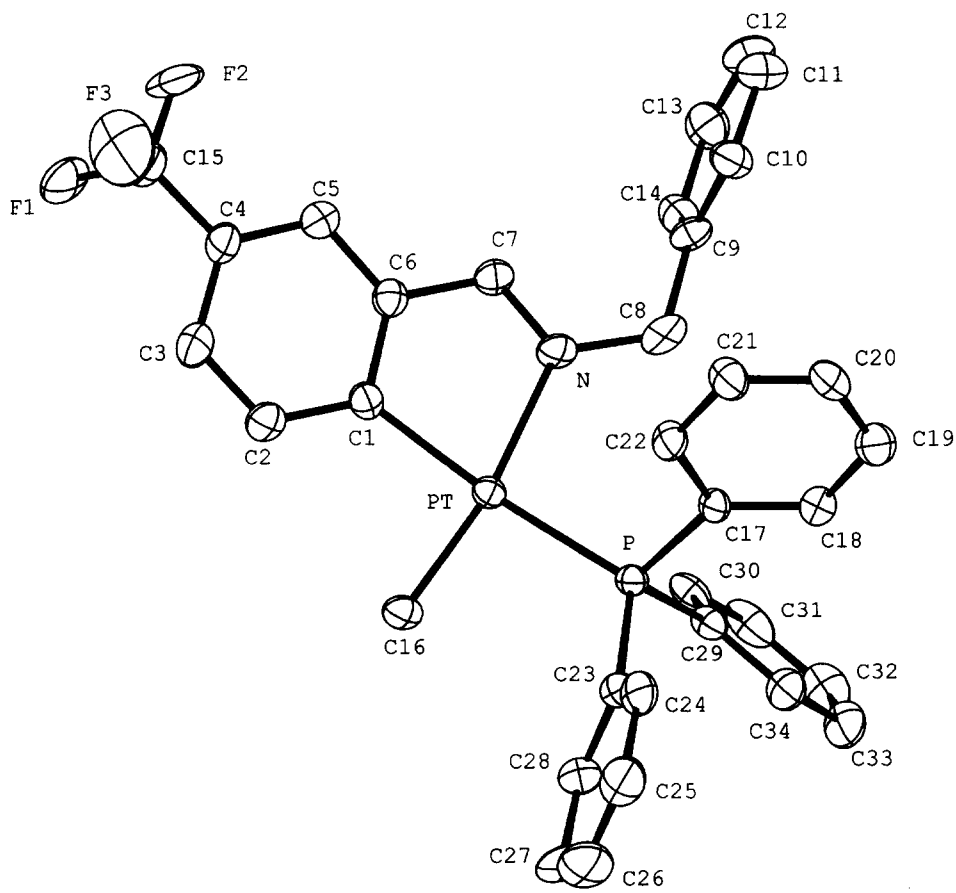


Fig. 1. Molecular structure of **4a**.

Table 2. Selected bond lengths (Å) and angles (°) for compound **4a** with estimated standard deviations in parentheses

Bond lengths			
Pt—C(1)	2.053(4)	N—C(7)	1.272(5)
Pt—C(16)	2.049(4)	N—C(8)	1.487(4)
Pt—N	2.148(3)	C(1)—C(6)	1.397(5)
Pt—P	2.2955(1)	C(4)—C(15)	1.491(6)
P—C(23)	1.822(3)	C(6)—C(7)	1.462(5)
P—C(29)	1.823(4)	C(8)—C(9)	1.488(5)
P—C(17)	1.828(3)	C(9)—C(10)	1.390(6)
Bond angles			
C(16)—Pt—C(1)	91.5(2)	C(23)—P—Pt	117.33(12)
C(16)—Pt—N	169.39(13)	C(29)—P—Pt	118.82(12)
C(1)—Pt—N	78.93(13)	C(17)—P—Pt	109.60(11)
C(16)—Pt—P	91.23(12)	C(7)—N—C(8)	120.3(2)
C(1)—Pt—P	170.04(10)	C(7)—N—Pt	113.5(2)
N—Pt—P	98.97(9)	C(8)—N—Pt	126.1(2)
N—C(7)—C(6)	118.3(3)	N—C(8)—C(9)	117.5(3)

roanalyses were performed by the Serveis Científico-Tècnics de la Universitat de Barcelona. Decomposition points were obtained with a Buchi 510 melting point instrument.

Preparation of the compounds

The complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) was prepared by the method reported in the literature [14]. Compounds **2** were prepared by the reaction of 5 mmol of the corresponding aldehyde with 0.53 g (5 mmol) of the benzylamine in 25 ml of ethanol. The mixture was refluxed for 2 h and the solvent was removed in a rotary evaporator to yield yellow oils or white solids [15].

3-$(CF_3)C_6H_4CH{=}NCH_2Ph$ (**2a**). Yield: 1.0 g (76%). ^1H NMR ($CDCl_3$), $\delta = 4.86$ [s, CH_2], {7.35 [m], 7.56 [d, 1H], 7.66 [d, 1H], 7.96 [d, 1H], 8.07 [s], aromatics}, 8.43 [s, CHN]. ^{19}F NMR (acetone-d^6), $\delta = -69.29$ [s, CF_3].

3,5-$(CF_3)_2C_6H_3CH{=}NCH_2Ph$ (**2b**). Yield: 1.4 g (85%). ^1H NMR ($CDCl_3$), $\delta = 4.89$ [s, CH_2], {7.33 [m], 7.92 [s, 1H], 8.24 [s, 2H], aromatics}, 8.46 [s, CHN]. ^{19}F NMR (acetone-d^6), $\delta = -69.61$ [s, CF_3].

2-$(CF_3)C_6H_4CH{=}NCH_2Ph$ (**2c**). Yield: 1.1 g (84%). ^1H NMR ($CDCl_3$), $\delta = 4.87$ [s, CH_2], {7.34 [m], 7.53 [t, 1H], 7.66 [d, 1H], 8.26 [d, 1H], aromatics}, 8.77 [s, CHN]. ^{19}F NMR (acetone-d^6), $\delta = -63.82$ [s, CF_3].

2-F-6-$(CF_3)C_6H_3CH{=}NCH_2Ph$ (**2d**). Yield: 1.3 g (93%). ^1H NMR ($CDCl_3$), $\delta = 4.91$ [s, CH_2], {7.34 [m], 7.50 [m]}, 8.61 [s, CHN]. ^{19}F NMR (acetone-d^6), $\delta = -64.64$ [s, CF_3], -119.07 [s, F].

Compounds **3** were prepared by reaction of 100 mg (0.17 mmol) of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) with 0.35 mmol of the corresponding imine in acetone (25 ml). The mixture was stirred for 16 h and the solvent was removed in a rotary evaporator. The residue was washed with hexane (3 × 5 ml) and recrystallized in acetone (2 ml)/hexane (10 ml) to yield yellow-orange solids, which were filtered and washed with hexane (3 × 5 ml).

$[PtMe\{3\text{-}(CF_3)C_6H_3CH{=}NCH_2Ph\}(SMe_2)]$ (**3a**). Yield: 138 mg (74%) m.p. 115–118°C (d). Anal: calc. for $C_{18}H_{20}F_3NSPt$: C, 40.45; H, 3.77; N, 2.62. Found: C, 40.85; H, 3.93; N, 2.66. ^1H NMR (acetone-d^6), $\delta = 0.89$ [s, ^2J(HPt) = 83, Me], 1.97 [s, ^3J(HPt) = 27, SMe_2], 5.26 [s, ^3J(HPt) = 12, CH_2], {7.31 [m], 7.75 [m], aromatics}, 8.98 [s, ^3J(HPt) = 56, CHN]. ^{19}F NMR (acetone-d^6), $\delta = -63.96$ [s, CF_3].

$[PtMe\{2\text{-}(CF_3)C_6H_3CH{=}NCH_2Ph\}(SMe_2)]$ (**3c**). Yield: 140 mg (75%) m.p. 123–127°C (d). Anal: calc. for $C_{18}H_{20}F_3NSPt$: C, 40.45; H, 3.77; N, 2.62. Found: C, 40.85; H, 3.77; N, 2.62. ^1H NMR (acetone-d^6), $\delta = 0.89$ [s, ^2J(HPt) = 83, Me], 1.98 [s, ^3J(HPt) = 27, SMe_2], 5.38 [s, ^3J(HPt) = 10, CH_2], {7.32 [m], 7.90 [d, J(HPt) = 61, J(HH) = 8, 1H], aromatics}, 9.15 [s, ^3J(HPt) = 54, CHN]. ^{19}F NMR (acetone-d^6), $\delta = -59.97$ [s, ^5J(FPt) = 7, CF_3].

Compounds **4** were prepared by reaction of 50 mg (94 mmol) of the corresponding compound **3** with 25 mg (95 mmol) of PPh_3 in acetone (10 ml). The mixture was stirred at room temperature for 16 h. On addition of hexane (15 ml), yellow crystals were formed, and they were collected by filtration, washed with hexane (3 × 5 ml) and dried *in vacuo*.

$[PtMe\{3\text{-}(CF_3)C_6H_3CH{=}NCH_2Ph\}(PPh_3)]$ (**4a**). Yield: 50 mg (73%) m.p. 148°C (d). Anal: calc. for $C_{34}H_{29}F_3NPPt$: C, 55.59; H, 3.98; N, 1.91. Found: C, 55.72; H, 4.13; N, 2.12. ^1H NMR (acetone-d^6), $\delta = 0.74$ [d, ^2J(HPt) = 83, ^3J(HP) = 7, Me], 4.41 [s, ^3J(HPt) = 10, CH_2], {6.9 [m], 7.2 [m], 7.45 [m], 7.68 [m], aromatics}, 8.71 [s, ^3J(HPt) = 55, CHN]. ^{19}F

NMR (acetone-d^6), $\delta = -64.03$ [s, CF_3]. ^{31}P NMR (acetone), $\delta = 29.33$ [s, ^1J(PPt) = 2237].

[PtMe{2-(CF$_3$)C$_6$H$_3$CH=NCH$_2$Ph}(PPh$_3$)] (**4c**). Yield: 55 mg (80%) m.p. 145°C (d). Anal: calc. for $C_{34}H_{29}F_3NPPt$: C, 55.59; H, 3.98; N, 1.91. Found: C, 55.59; H, 4.01; N, 1.97. ^{1}H NMR (acetone-d^6), $\delta = 0.70$ [d, ^2J(HPt) = 82, ^3J(HP) = 7, Me], 4.47 [s, ^3J(HPt) = 9, CH_2], {6.8 [d, 2H], 7.21 [m], 7.43 [m], 7.61 [m], 8.05 [m, 1H], aromatics}, 8.83 [s, ^3J(HPt) = 58, CHN]. ^{19}F NMR (acetone-d^6), $\delta = -59.55$ [s, CF_3]. ^{31}P NMR (acetone), $\delta = 29.05$ [s, ^1J(PPt) = 2236].

Compound **5a** was prepared by reaction of 50 mg (94 mmol) of the corresponding compound **3a** with 120 mg (0.458 mol) of PPh_3 in acetone (10 ml). Within 1 h, the colour of the solution faded and a white precipitate was formed. After addition of hexane (10 ml), the white solid was collected by filtration, washed with hexane (3 × 5 ml) and dried *in vacuo*.

[PtMe{3-(CF$_3$)C$_6$H$_3$CH=NCH$_2$Ph}(PPh$_3$)$_2$] (**5a**). Yield: 80 mg (86%) m.p. 178°C (d). Anal: calc. for $C_{52}H_{44}F_3NP_2Pt$: C, 62.65; H, 4.45; N, 1.40. Found: C, 62.68; H, 4.62; N, 1.39. ^{1}H NMR (acetone-d^6), $\delta = 0.29$ [dd, ^2J(HPt) = 67, $^3J(HP_a)$ = 8, $^3J(HP_b)$ = 6, Me], {4.74 [d], 4.88 [d], ^2J(HH) = 13, *AB* pattern, CH_2], {6.5 [m], 6.7 [m], 7.2 [m], aromatics}, 9.52 [s, ^4J(HPt) = 10, CHN]. ^{19}F NMR (acetone-d^6), $\delta = -63.92$ [s, CF_3]. ^{31}P NMR (acetone), $\delta = 25.84$ [d, ^1J(PPt) = 1949, ^2J(PP) = 14], 26.18 [d, ^1J(PPt) = 1916, ^2J(PP) = 14].

Compounds **6** were prepared by reaction of 50 mg (68 mmol) of the corresponding compound **4** with an excess of methyl iodide (0.1 ml) in 10 ml of acetone. The mixture was stirred at room temperature for 2 h. On addition of hexane (15 ml), light yellow crystals were formed, and they were collected by filtration, washed with hexane (3 × 5 ml) and dried *in vacuo*.

[PtMe$_2$I{3-(CF$_3$)C$_6$H$_3$CH=NCH$_2$Ph}(PPh$_3$)] (**6a**). Yield: 50 mg (84%). Anal: calc. for $C_{35}H_{32}F_3INPPt$: C, 47.96; H, 3.68; N, 1.60. Found: C, 48.7; H, 4.0; N, 1.7. ^{1}H NMR (acetone-d^6), $\delta = 1.10$ [d, ^2J(HPt) = 60, ^3J(HP) = 8, Me$_a$], 1.59 [d, ^2J(HPt) = 70, ^3J(HP) = 8, Me$_a$], {4.74 [m], 5.65 [m], J(HH) = 16, *AB* system}, {6.7 [d, J(HH) = 8, J(HPt) = 43, 1H], 7.2 [m, 2H], 7.3 [m], 7.5 [m], aromatics}, 8.31 [s, ^3J(HPt) = 49, CHN]. ^{19}F NMR (acetone-d^6), $\delta = -65.18$ [s, CF_3]. ^{31}P NMR (acetone), $\delta = -9.63$ [s, ^1J(PPt) = 1021].

[PtMe$_2$I{2-(CF$_3$)C$_6$H$_3$CH=NCH$_2$Ph}(PPh$_3$)] (**6c**). Yield: 45 mg (75%). Anal: calc. for $C_{35}H_{32}F_3INPPt$: C, 47.96; H, 3.68; N, 1.60. Found: C, 47.9; H, 3.8; N, 1.7. ^{1}H NMR (acetone-d^6), $\delta = 1.08$ [d, ^2J(HPt) = 60, ^3J(HP) = 8, Me$_a$], 1.58 [d, ^2J(HPt) = 70, ^3J(HP) = 8, Me$_a$], {4.93 [m], 5.72 [m], J(HH) = 16, *AB* system}, {7.4 [m], 7.5 [m], aromatics}, 8.31 [s, ^3J(HPt) = 50, CHN]. ^{19}F NMR (acetone-d^6), $\delta = -61.02$ [s, CF_3]. ^{31}P NMR (acetone), $\delta = -9.85$ [s, ^1J(PPt) = 1015].

X-ray structure analysis, data collection

A prismatic crystal of **4a** was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centreing of 25 reflections ($12° < \theta < 21°$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo–K_α radiation, using $\omega/2\theta$ scan-technique. 8435 reflections were measured in the range $2.38° < \theta < 29.96°$, and 7202 were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control, significant intensity decay was not observed. Lorentz-polarization and absorption corrections were made. Further details are given in Table 3.

Table 3. Crystallographic data and details of the refinements for compound **4a**

Formula	$C_{34}H_{29}F_3NPPt$
FW	734.64
Crystal system, Space group	triclinic, $P\bar{1}$
a, b, c (Å)	9.102(5), 12.162(2), 14.726(5)
α, β, γ (°)	108.90(2), 104.17(4), 98.31(3)
V (Å^3)	1450.1(10)
D_{calc} (g cm^{-3})	1.682
Z	2
F(000)	720
Crystal size (mm^3)	0.1 × 0.1 × 0.2
μ (Mo–K_α)	54.14
λ (Mo–K_α) (Å)	0.71069
Temperature (K)	293(2)
Reflections collected	8435
R	0.0297
$wR(F^2)$	0.0707
Refined parameters	469
Max. shift/esd	6.6
Max. and min. diff. peaks (e Å^{-3})	0.385 and −0.222

Structure solution and refinement

The structure was solved by direct methods, using SHELXS Computer Program [16], and refined by the full-matrix least-squares method, with the SHELX93 computer program [17] using 8435 reflections. The function minimized was $\Sigma w\|F_o|^2-|F_c|^2|^2$, where $w=[\sigma^2(I)+(0.0462P)^2]^{-1}$ and $P=(|F_o|^2+2|F_c|^2)/3$.f, f' and f'' were taken from International Tables of X-Ray Crystallography [18]. Fluorine atoms of CF_3 groups were located in disorder positions. An occupancy factor of 0.5 was assigned according to the height of Fourier synthesis. 19 hydrogen atoms were located from a difference synthesis and 10 hydrogen atoms were computed and refined with an overall isotropic temperature factor using a riding model. The final R factors, the number of refined parameters, and the maximum and minimum peaks in the final difference synthesis are given in Table 3.

Acknowledgments—We acknowledge financial support from the DGICYT (Dirección General de Investigación Científica y Técnica, Ministerio de Educación y Ciencia, Spain, PB 96-0164 project) and from the Generalitat de Catalunya (1995-SGR-0044 project).

REFERENCES

1. (a) Maestri, M., Deuschel-Cornioley, C. and von Zelewsky, A., *Coord. Chem. Rev.*, 1991, **111,** 117; (b) Minghetti, G., Pilo, M. I., Sanna, G., Seeber, R., Stoccoro, S. and Laschi, F., *J. Organomet. Chem.*, 1993, **452,** 257; (c) von Zelewsky, A., Suckling, A. P. and Stoeckli-Evans, H., *Inorg. Chem.*, 1993, **32,** 4585; (d) Mdleleni, M. M., Bridgewater, J. S., Watts, R. J. and Ford, P. C., *Inorg. Chem.*, 1995, **34,** 2334; (e) Kvam, P. I., Puzyk, M. V., Balashev, K. P. and Songstad, J., *Acta Chemica Scandinavica*, 1995, **49,** 335; (f) Gianini, M., Forster, A., Haag, P., von Zelewsky, A. and Stoeckli-Evans, H., *Inorg. Chem.*, 1996, **35,** 4889; (g) Jolliet, P., Gianini, M., von Zelewsky, A., Bernardinelli, G. and Stoeckli-Evans, H., *Inorg. Chem.*, 1996, **35,** 4883.
2. (a) Ryabov, A. D., *Chem. Rev.*, 1990, **90,** 403; (b) Omae, I., *Coord. Chem. Rev.*, 1988, **83,** 137.
3. Crespo, M., Martinez, M. and Sales, J., *Organometallics*, 1993, **12,** 4297.
4. Crespo, M., Solans, X. and Font-Bardía, M., *J. Organomet. Chem.*, 1996, **509,** 29.
5. Crespo, M., Solans, X. and Font-Bardía, M., *J. Organomet. Chem.*, 1996, **518,** 105.
6. Nyholm, R. S., *Quart. Rev.*, 1970, **24,** 1.
7. March, J., in *Advanced Organic Chemistry*, J. Wiley, New York, 1985, pp. 242–250.
8. Crespo, M., Solans, X. and Font-Bardía, M., *Organometallics*, 1995, **14,** 355.
9. (a) Scott, J. D. and Puddephatt, R. J., *Organometallics*, 1985, **4,** 1221; (b) Scott, J. D. and Puddephatt, R. J., *Organometallics*, 1986, **5,** 1538; (c) Crespo, M. and Puddephatt, R. J., *Organometallics*, 1987, **6,** 2548.
10. Crespo, M., *Polyhedron*, 1996, **15**(12), 1981.
11. Jawad, J. K. and Puddephatt, R. J., *J. Chem. Soc., Dalton Trans.*, 1977, 1466.
12. López, O., Crespo, M., Font-Bardía, M. and Solans, X., *Organometallics*, 1997, **16,** 1233.
13. Crespo, M., Solans, X. and Font-Bardía, M., *J. Organomet. Chem.*, 1994, **483,** 187.
14. Scott, J. D. and Puddephatt, R. J., *Organometallics*, 1983, **2,** 1643.
15. Bigelow, L. A. and Ealough, H., in *Organic Syntheses*, Vol. 1, ed. A. H. Blatt, J. Wiley. New York, 1944, Collect.
16. Sheldrick, G. M., *Acta Cryst.*, 1990, **A46,** 467.
17. Sheldrick, G. M., SHELX 93. *A computer program for crystal structure refinement.* University of Gottingen, Germany, 1993.
18. *International Tables of X-Ray Crystallography*, Vol. IV, Kynoch, Birmingham, 1974, pp. 99–100 and 149.