Reactivity of $Ph_2P(O)py$-2 with Platinum(II) Alkyl Derivatives − Building-up of a Chiral Phosphorus Atom through C,N-Cyclometallation

Giovanni Minghetti,*[a] Angelino Doppiu,[a] Sergio Stoccoro,[a] Antonio Zucca,[a] Maria Agostina Cinellu,[a] Mario Manassero,*[b] and Mirella Sansoni[b]

Keywords: Platinum / N ligands / Cyclometallation / Alkyl derivatives / Crystal structure

The reaction of $Ph_2P(O)py$-2 (HL) with methyl- and dimethylplatinum(II) derivatives afforded a series of six-membered *C,N*-cyclometallated species, [PtX(L′)(L)] (X=halide or Me; L′ = neutral ligand, e.g. SMe_2, $SOMe_2$, CO, PAr_3) arising from activation of one C(sp^2)–H bond of a phenyl substituent. The metallation entailed elimination of methane and caused the phosphorus atom to become chiral. The series includes the complex [Pt(Me)(CO)(L)] where the platinum atom is bonded to three different carbon atoms ($C_{sp}{}^3$, $C_{sp}{}^2$, C_{sp}). From the neutral species cationic derivatives $[Pt(L')(L'')(L)]^+$ (L′ = SMe_2, L′′ = CH_3CN; L′–L′′ = dppe; L′ = SMe_2 or $SOMe_2$, L′′ = H_2O) could be obtained. The new complexes were isolated and fully characterised by elemental analyses and spectroscopic techniques (IR, NMR, FAB-MS). The solid-state structures of $[PtCl(SMe_2)(L)]$, [PtCl(CO)(L)], $[Pt(Me)(SOMe_2)(L)]$, and $[Pt(SMe_2)(H_2O)(L)][BF_4]$ were determined by single-crystal X-ray diffraction.

Introduction

In recent years, coordination of pyridylphosphanes to typical soft acceptors such as Rh^I, Pd^{II}, or Pt^{II} has been extensively studied,[1] whereas much less investigated is the behaviour of the pyridylphosphane oxides.[2] In a previous paper we described the reactivity of palladium(II) and platinum(II) halides with the ligands $Ph_2P(O)CH(Me)py$-2 and $Ph_2P(O)CH_2py$-2.[3] We observed that they can act either as N-monodentate or N,O-*endo*-bidentate ligands to afford $[(HL)_2MX_2]$ or $[(HL)MX_2]$ adducts, respectively. In the case of $Ph_2P(O)py$-2, only a 1:1 species $[(HL)PdCl_2]$ was obtained; spectroscopic data are in agreement with a chelating behaviour to give a five-membered ring. In no case were the phenyl substituents involved; no C−H activation was observed to give cyclometallated species.

Now, following our interest in the reactivity of alkyl derivatives of platinum(II),[4] we report a study on the interaction of $Ph_2P(O)py$-2 with the methyl- and dimethylplatinum species *trans*-$[PtCl(Me)(SMe_2)_2]$, $[Pt(Me)_2(\mu\text{-}SMe_2)]_2$, *trans*-$[PtCl(Me)(SOMe_2)_2]$, and *cis*-$[Pt(Me)_2(SOMe_2)_2]$ to afford a series of six-membered *N,C*-cyclometallated derivatives.

Results and Discussion

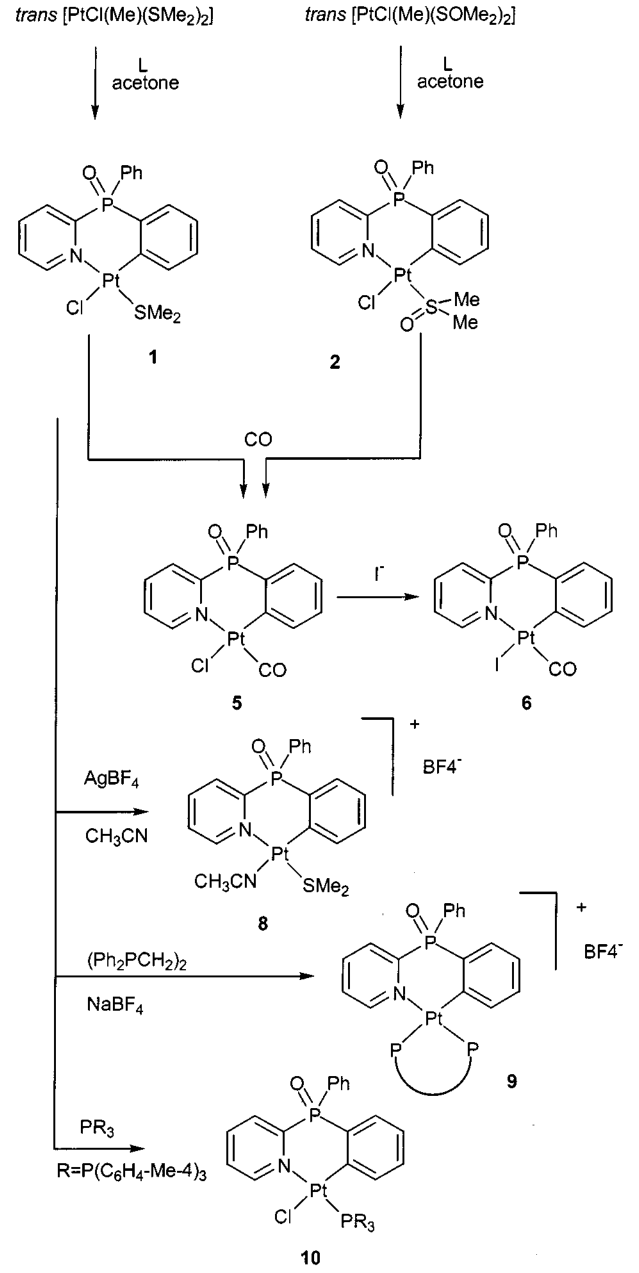
The N,O-ligand diphenyl(2-pyridyl)phosphane oxide (HL)[3] and the starting methyl- and dimethylplatinum complexes *trans*-$[PtCl(Me)(SMe_2)_2]$,[5] *trans*-$[PtCl(Me)(SOMe_2)_2]$,[6] $[Pt(Me)_2(\mu\text{-}SMe_2)]_2$,[5] and *cis*-$[Pt(Me)_2(SOMe_2)_2]$[6] were obtained as previously described. The reaction of the chloro(methyl) complexes with the ligand affords compounds $[PtCl(SMe_2)(L)]$ (**1**) and $[PtCl(SOMe_2)(L)]$ (**2**), respectively (see Scheme 1). Compounds **1** and **2** have been characterised by elemental analyses, conductivity measurements, FAB MS, IR, and ^1H-, and $^{31}P\{^1H\}$-NMR spectra. In the FAB MS spectra the molecular ions were observed at *m*/*z* = 570 and 586, respectively; in the IR spectra the absorption assigned to ν(P=O) is not significantly shifted with respect to the free ligand (1190 cm^{-1}), suggesting that the oxygen atom is not involved in the coordination to the platinum atom. In agreement, in the $^{31}P\{^1H\}$ NMR spectra, the resonances at $\delta = 31.15$ (compound **1**) and 31.65 (compound **2**) are only slightly deshielded compared to that of the ligand ($\delta = 22.0$). We have previously reported that in the adduct $[Pd(Cl)_2(HL)]$ (*N,O*-coordination) the ^{31}P resonance is strongly deshielded ($\delta = 60.5$).

The ^1H NMR spectra allow a choice to be made between the two possible isomers having a Cl−Pt−C or a Cl−Pt−N *trans* arrangement; the H(6) proton of the pyridine ring is remarkably deshielded, as often observed for six-membered species with the chloride ligand *cis* to the nitrogen atom.[7] In addition, the very large value of $^3J_{Pt,H}$ relative to the methyl protons of SMe_2 in compound **1** supports the pres-

---

[a] Dipartimento di Chimica, Università di Sassari,
Via Vienna 2, 07100 Sassari, Italy
Fax: (internat.) + 39-079/212069
E-mail: mingh@ssmain.uniss.it
[b] Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, Centro CNR,
Via Venezian 21, 20133 Milano, Italy
E-mail: m.manassero@csmtbo.mi.cnr.it

1434−1948/02/0202−0431 $ 17.50+.50/0



Scheme 1

ence of a ligand (in a *trans* configuration) with low *trans* influence.[8]

The methyl groups of the coordinated SMe_2 ligand are diastereotopic; one of them resonates at rather high field ($\delta = 1.63$) with respect to the other one ($\delta = 2.49$) ($\Delta\delta = 0.86$). The shift at higher field of one of the resonances is likely related to the shielding effect of the phenyl ring. In an attempt to obtain more information on the structure of compound **1** in solution, an NOE difference experiment was carried out, but failed owing to interconversion of the methyl groups, due to either dissociation/association or partially hindered rotation of the Pt−S bond.

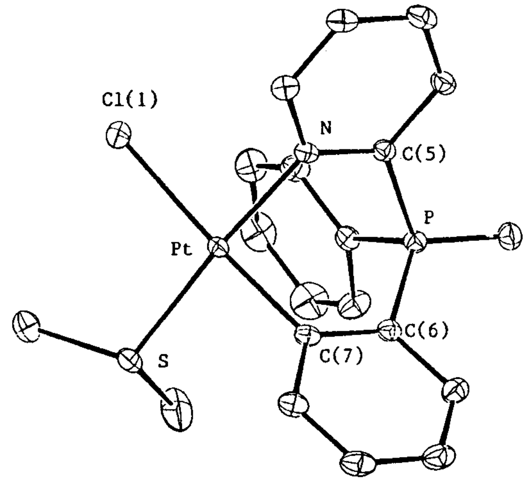


Figure 1. ORTEP view of compound **1**; thermal ellipsoids are drawn at the 30% probability level

Table 1. Selected bond lengths [Å] and angles [°] with e.s.d.s in parentheses

a) Compound **1**			
Pt−Cl(1)	2.400(1)	Pt−S	2.268(1)
Pt−N	2.046(2)	Pt−C(7)	2.003(2)
Cl(1)−Pt−S	97.01(2)	Cl(1)−Pt−N	87.78(5)
Cl(1)−Pt−C(7)	176.81(7)	S−Pt−N	175.20(5)
S−Pt−C(7)	85.92(6)	N−Pt−C(7)	89.29(8)
b) Compound **5**			
Pt−Cl	2.403(1)	Pt−N	2.069(3)
Pt−C(7)	2.028(3)	Pt−C(18)	1.897(4)
C(18)−O(2)	1.061(5)		
Cl−Pt−N	88.3(1)	Cl−Pt−C(7)	177.3(1)
Cl−Pt−C(18)	93.5(1)	N−Pt−C(7)	89.5(1)
N−Pt−C(18)	177.4(2)	C(7)−Pt−C(18)	88.8(2)

In the solid state, the nature of complex **1** was confirmed by X-ray diffraction. Suitable crystals were obtained by slow concentration of a $CHCl_3$ solution. The structure consists of the packing of $[PtCl(SMe_2)(L)]$ and $CHCl_3$ molecules in the molar ratio 1:1 with no unusual van der Waals contacts. An ORTEP view or the complex molecule is shown in Figure 1 and selected bond parameters are reported in Table 1.

The metal atom displays a square-planar coordination with a very slight square-pyramidal distortion, maximum distances from the best plane being −0.012(1) and +0.013(2) Å for Pt and C(7), respectively. The inner coordination sphere of the metal atom in the present compound is identical with that found in $[PtCl(SMe_2)(L^2)]$ (**13**) (HL^2= 6-*tert*-butyl-2,2′-bipyridine)[8] where the L^2 ligand is coordinated through a nitrogen atom and the C(3) atom of the substituted pyridine ring. Corresponding bond lengths involving the metal atom are all very similar in the two compounds, thus, Pt−Cl = 2.400(1) (here) and 2.395(2) Å (**13**); similarly, Pt−S = 2.268(1) and 2.263(2) Å, Pt−N = 2.046(2) and 2.042(4) Å, and Pt−C = 2.003(2) and 1.990(5) Å, respectively, here and in **13**.

The Pt−N−C(5)−P−C(6)−C(7) six-membered ring is in a boat conformation, with atoms N, C(5), C(6), and C(7) strictly coplanar, and atoms Pt and P lying 1.008(1) and 0.752(2) Å above that plane, respectively. The best plane of atoms N, C(5), C(6), and C(7) forms dihedral angles of 44.4(1)° with the Pt−N−C(7) plane and of 41.2(1)° with the C(5)−P−C(6) plane.

Compound **2** is similar to **1**, having the $SOMe_2$ ligand in place of SMe_2; the ^1H NMR spectra provide evidence for the same isomer as **1** and an *S*-bonded dimethyl sulfoxide.

Both compounds **1** and **2** reacted under mild conditions with carbon monoxide to give **5**; the stretching vibration of the terminal CO is observed at a rather high value, 2122 cm^{-1} (Nujol) typical of platinum(II) species. The chloride ligand in complex **5** could be easily replaced by iodide through exchange with LiI. A lowering of ν(CO) in complex **6** [PtI(CO)L] ($\Delta\nu = 28\ cm^{-1}$) is consistent with substitution of iodide in exchange for the more electronegative chloride.

An ORTEP view of the molecular structure of **5** is shown in Figure 2, and selected bond parameters are listed in Table 1. Crystals of this compound contain molecules of **5** and water molecules in the molar ratio 1:0.667. In **5**, the Pt^{II} atom is in the usual square-planar coordination. Bond lengths and angles involving the Pt−Cl−(N,C) moiety are all very similar to those already discussed for compound **1**. The Pt−CO bond length [1.897(4) Å] is in good agreement with those found in $[Pt_2(Me)_2(CO)_2(N,C^{\wedge}C,N\text{-terpy-2H})]$[9] [1.890 Å (average of two)] and in [Pt(COPh)(Me)-(CO)(PPh_3)][10] [1.897(7) Å]. The C−O distance [1.061(5) Å] is rather short.

From compound **1**, the ligand SMe_2 could be substituted by other neutral ligands such as $P(C_6H_4\text{-Me-4})_3$. In compound **10** the phosphane group is *trans* to the nitrogen atom as shown by the $^1J_{Pt,P}$ value of 4279 Hz.

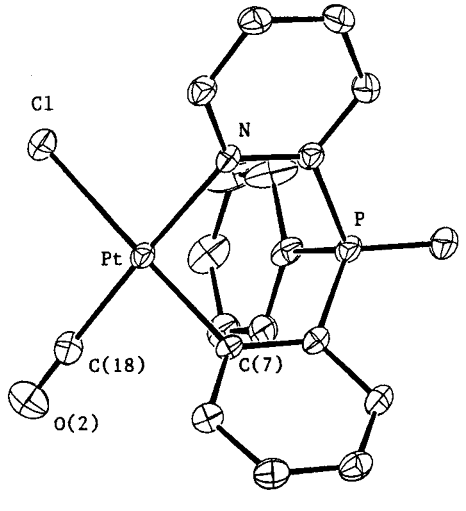
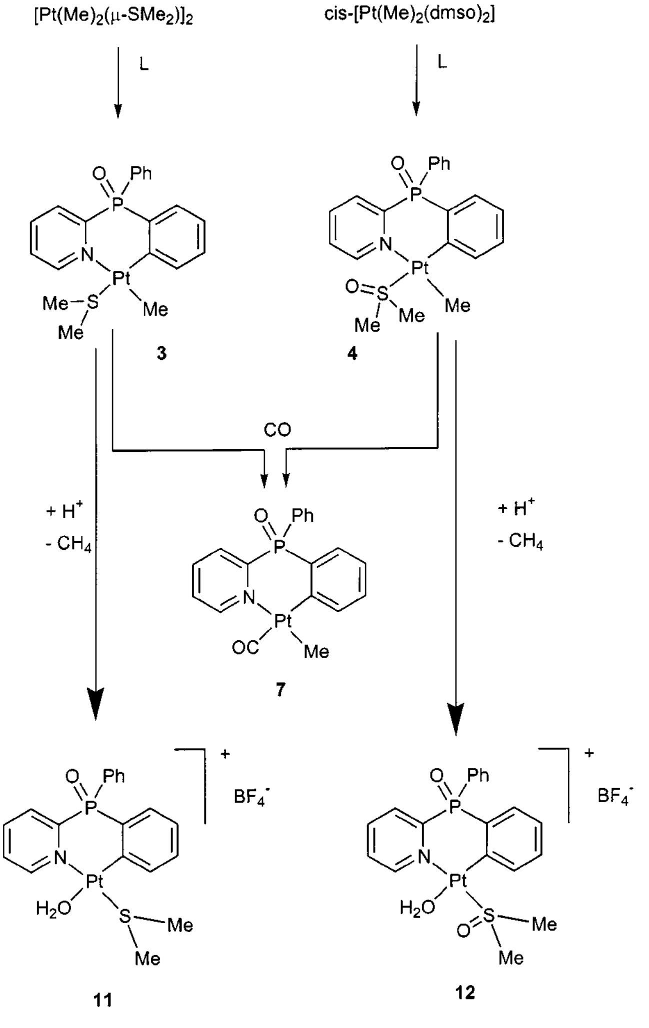


Figure 2. ORTEP view of compound **5**; thermal ellipsoids as in Figure 1

The chloride ion could be displaced by means of silver salts to give cationic species such as **8** {$[Pt(MeCN)(SMe_2)(L)][BF_4]$}, or by chelating ligands in the presence of a non-coordinating anion. Thus compound **9** {$[Pt(dppe)(L)][BF_4]$} could be easily isolated by reaction of **1** with dppe and $Na[BF_4]$ [dppe = 1,2-bis(diphenylphosphanyl)ethane]. In the cationic species **9**, in addition to the six-membered N,C-ring, a second five-membered ring was formed by chelation of dppe. The behaviour of the diphosphane is unambiguously shown by the $^{31}P\{^1H\}$ NMR spectrum. Noteworthy is the long-range coupling ($^4J_{P,P}$ = 9.2 Hz) between the ^{31}P nucleus in the C,N-cycle and the ^{31}P *trans* to the carbon atom. The molecular ion at *m*/*z* = 871 in the FAB mass spectrum confirms the nature of the cation.

The behaviour of the ligand HL towards the dimethyl derivatives $[Pt(Me)_2(\mu\text{-}SMe_2)]_2$ and *cis*-$[Pt(Me)_2(SOMe_2)_2]$ is similar to that observed in the case of the monoalkyl species. Indeed, metallation of a phenyl group occurs with loss of methane (Scheme 2) to give the six-membered *C,N*-metallated compounds **3** and **4**, respectively (Scheme 2).



Scheme 2

One isomer only was formed having the methyl group *trans* to the nitrogen atom (as shown by ^{1}H NMR spectra). The structure in solution for **3** and **4** were ascertained by means of ^{1}H NMR NOE difference spectra, which unambiguously show that in $CDCl_3$ solution the methyl group is coordinated *trans* to the pyridine ring. For example, in the case of **3**, irradiation of the coordinated methyl group at $\delta = 0.59$ enhanced the doublet ($\delta = 7.52$) of the H *ortho* to the C(sp^2)−Pt bond. At variance, irradiation of the singlet at $\delta = 1.80$ (SMe_2) revealed contacts with the coordinated methyl group ($\delta = 0.59$) and the H(6) proton of the substituted pyridine ring ($\delta = 8.76$). Contacts among the C_6H_5 protons (two multiplets at $\delta = 7.30$ and 7.64) and the methyl group of the coordinated dimethyl sulfide suggest that in the boat conformation of the six-membered cyclometallated ring they are spatially close.

The structure consists of the packing of molecules of **4** and water molecules in the molar ratio 1:0.25. The asymmetric unity of **4**·$0.25H_2O$ contains two crystallographically independent molecules of **4**. An ORTEP view of molecule A is shown in Figure 3. Selected bond parameters for both molecules are reported in Table 2. Corresponding bond lengths and angles in the two molecules are all very similar. Pt−N1 and Pt−S1 bond lengths (2.130 and 2.303 Å, respectively, average of two), are both elongated by the influence of the *trans*-carbon atoms. All other bond lengths and angles are normal.

Also, with these methyl species, carbon monoxide easily displaced the ligands SMe_2 or $SOMe_2$ from **3** and **4**, respectively, to afford the not trivial derivative **7** [Pt(Me)(CO)(L)] where three carbon ligands, C(sp^3), C(sp^2), C(sp) are assembled around the platinum center.

The CO ligand is coordinated *cis* to the pyridine ring as shown, inter alia, by ^{1}H NMR NOE difference spectra; irradiation of the singlet at $\delta = 0.76$ (CH_3−Pt) produced enhancement of the doublet at $\delta = 7.56$, assigned to the hydrogen atom *ortho* to the C(sp^2)−metal bond, proving that the coordinated methyl group is close in space to the metallated phenyl ring. In addition, the $^{2}J_{Pt,H}$ of the methyl protons (88.2 Hz) is consistent with a methyl group *trans* to a nitrogen atom.[4] Under mild conditions, no migration insertion to give an acyl group was observed.

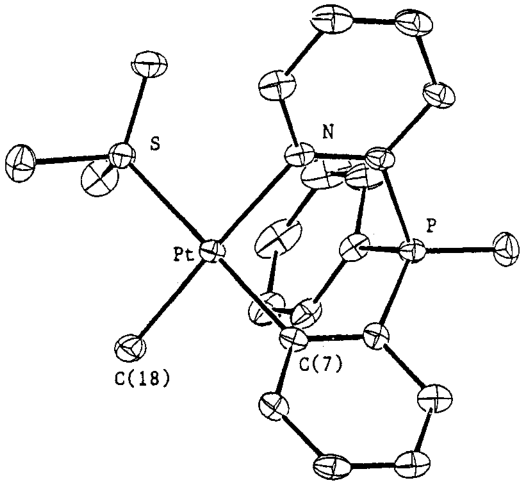


Figure 3. ORTEP view of compound **4**; thermal ellipsoids as in Figure 1

Table 2. Selected bond lengths [Å] and angles [°] with e.s.d.s in parentheses

a) Compound **4**

	Molecule A	Molecule B
Pt−S	2.305(2)	2.300(2)
Pt−N	2.139(5)	2.121(6)
Pt−C(7)	2.040(6)	2.032(6)
Pt−C(18)	2.074(8)	2.088(8)
S−Pt−N	90.8(1)	89.8(2)
S−Pt−C(7)	175.3(2)	176.9(2)
S−Pt−C(18)	91.4(2)	92.9(2)
N−Pt−C(7)	90.8(2)	88.7(2)
N−Pt−C(18)	177.7(2)	177.3(2)
C(7)−Pt−C(18)	87.0(3)	88.7(3)

b) Compound **11**

Pt−S	2.273(1)	Pt−O(2)	2.133(2)
Pt−N	2.036(3)	Pt−C(7)	1.986(3)
S−Pt−O(2)	91.2(1)	S−Pt−N	178.2(1)
S−Pt−C(7)	89.1(1)	O(2)−Pt−N	88.6(1)
O(2)−Pt−C(7)	177.9(1)	N−Pt−C(7)	91.2(1)

A remarkable result was obtained by reaction of compounds **3** and **4** with the complex acid [H_3O]-18-crown-6-[BF_4] (Scheme 2). We have preferred this acid because it is solid, easily obtainable, and can be weighted accurately so that an excess can be avoided. This excess could potentially also attack the Pt−C(sp^2) bond, destroying the cyclometallated ring. Indeed, the Pt−C(sp^3) bond is cleaved selectively with elimination of methane. In the resulting cationic derivatives, **11** and **12**, the fourth position in the coordination sphere of the platinum atom is filled by a molecule of water *trans* to the carbon atom. The isomerization observed is likely due to the remarkable difference of the lability production action (*trans* effect) between the C- and N-ligands.

Crystals of **11** suitable for X-ray diffraction were isolated from a dichloromethane solution. The structure of **11** consists of the packing of [$Pt(OH_2)(SMe_2)(L)]^+$ cations and [$BF_4]^-$ anions in the molar ratio 1:1. An ORTEP view of the cation in **11** is shown in Figure 4. Selected bond lengths and angles are listed in Table 2. The Pt−S, Pt−N, and Pt−C7 distances, 2.273(1), 2.036(3), and 1.986(3) Å, respectively, are very close to the corresponding distances already discussed for compound **1** [2.268(1), 2.046(2), and 2.003(2) Å, respectively]. The Pt−O2 bond length [2.133(2) Å] is significantly shorter than the Pt−OH_2 distance [2.186(2) Å] found in cation [$Pt\{C_6H_3(CH_2NMe_2)_2$-2,6$\}(OH_2)]^+$,[11] which to the best of our knowledge, is a rare example of a cyclometallated aqua complex of Pt^{II} for which a crystal structure determination has been reported.

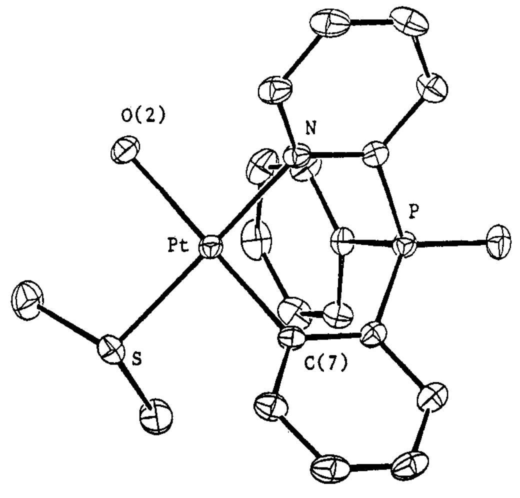


Figure 4. ORTEP view of the cation in compound **11**; thermal ellipsoids as in Figure 1

The hydrogen atoms of the coordinated water molecule are both involved in interionic hydrogen bonds, one towards the O1 phosphane oxide atom of a neighbouring cation [O2····O1 = 2.573(3) Å] and the other towards a fluorine atom of the $[BF_4]^-$ anion [O2····F1 = 2.719(4) Å], as shown in Figure 5.

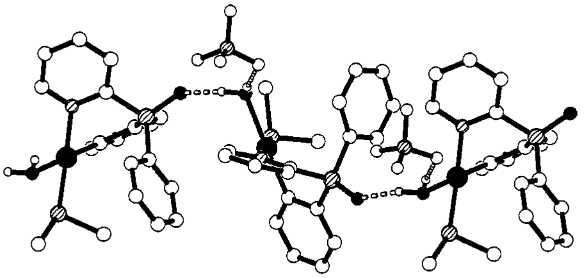


Figure 5. A view of the hydrogen-bonding network in the crystal packing of compound **11**

Conclusion

In a previous paper, we reported on the reactivity of some (2-pyridyl)phosphane oxides with platinum and palladium halides. At variance with the behaviour shown in the reaction with mono- and dimethyl derivatives, no involvement of the phenyl substituents was observed; only 1:1 or 1:2 (Pt/LH) adducts were obtained. It seems, therefore, that metallation is easier, at least in the case of platinum, when methane rather than hydrogen chloride elimination is involved. This points to methyl or methyl halide derivatives as suitable starting materials to achieve activation of $C(sp^2)-H$ bonds. It is worth underlining the fact that in this case, metallation entailed the building-up of a stereogenic centre, the phosphorus atom, inside the *C,N*-metallated ring. The behaviour of analogous intermediates of palladium(II) is currently under investigation.

Experimental Section

General: The ligand HL and the platinum complexes *trans*-$[PtCl(Me)(SMe_2)_2]$, $[Pt(Me)_2(\mu\text{-}SMe_2)]_2$, *trans*-$[PtCl(Me)(SOMe_2)_2]$, and *cis*-$[Pt(Me)_2(SOMe_2)_2]$, were obtained as previously described.[5−6] $[H_3O]$-18-Crown-6-$[BF_4]$ was synthesised as reported elsewhere.[12] All solvents were distilled and dried according to established methods. Elemental analyses were performed with a Perkin−Elmer Elemental Analyzer 240B by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari). Infrared spectra were recorded with a Perkin−Elmer 983 spectrophotometer; the values are given in cm^{-1}. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 299.9 and 121.4 MHz, respectively. Chemical shifts are given in ppm relative to internal TMS (^1H) or external H_3PO_4 (^{31}P). Mass spectra were obtained with a VG 7070EQ instrument operating under FAB conditions with 3-nitrobenzyl alcohol as supporting matrix.

General Procedures: The compounds **1−4** were synthesised according to the following procedure. The relevant starting complex (ca. 0.1 g) and a stoichiometric amount of the ligand were dissolved in anhydrous acetone (ca. 30 mL). The solution was heated at reflux for 24 h under nitrogen, it was then concentrated to dryness. The solid was dissolved in dichloromethane (20 mL) and the resulting solution was filtered through Celite and concentrated to a small volume. Dropwise addition of *n*-hexane afforded a white crystalline solid, which was filtered off and collected. − Compound **5** was obtained in almost quantitative yield by carbonylation (p_{CO} = 1 bar) of a dichloromethane solution (5 mL) of either **1** or **2** (ca. 0.1 g) for 24 h at room temperature. Compound **7** was obtained from either **3** or **4** in quantitative yield, according to a similar procedure, but with shorter reaction time (6 h). − Compounds **11** and **12** were prepared in ca. 80% yield according to the following procedure. The relevant starting complex **1** or **2** (ca. 0.100 g), was dissolved in dichloromethane (5 mL) and a stoichiometric amount of the complex acid $[H_3O]$-18-crown-6-$[BF_4]$ was added. The solution was kept unstirred for 8 h. The white crystals that formed were washed with dichloromethane and collected.

$[PtCl(SMe_2)(L)]$ (1): Yield 85%, m.p. 234−236 °C (dec.). $C_{19}H_{19}ClNOPSPt$ (570.9): calcd. C 39.96, H 3.36, N 2.45; found C 39.65, H 3.12, N 2.33. IR (Nujol): $\tilde{\nu}$ = 1583 m, 1559 m, 1196s, 692s, 545 vs, 502s, 306s, 279 s. ^1H NMR ($CDCl_3$): δ = 9.23 [dd, 1 H, $^3J_{Pt,H} \approx 49$, $^3J_{H,H} = 5.6$, $^4J_{H,H} \approx 1$ Hz, H(6)], 8.57 (1 H, td, $^3J_{H,H} = 6.1$ Hz), 8.1 (m, 2 H), 7.7−7.1 (m, 9 H), 2.49 (s, 3 H, $^3J_{Pt,H} = 53.7$ Hz, SMe), 1.63 (s, 3 H, $^3J_{Pt,H} = 57.4$ Hz, SMe). ^{31}P NMR ($CDCl_3$): δ = 31.15 (1 P, s, $^3J_{Pt,P} = 395.2$ Hz). FAB$^+$: *m*/*z* = 570 [M$^+$], 535 [M − Cl], 508 [M − SMe_2], 473 [M − Cl − SMe_2].

$[PtCl(SOMe_2)(L)]$ (2): Yield 89%, m.p. 242 °C (dec.). $C_{19}H_{19}ClNO_2PSPt$ (586.9): calcd. C 38.88, H 3.27, N 2.39; found C 39.06, H 3.42, N 2.35. IR (Nujol): $\tilde{\nu}$ = 1587 m, 1562 m, 1196s, 693s, 542 vs, 501s, 295 s. ^1H NMR ($CDCl_3$): δ = 9.11 [dd, 1 H, $^3J_{Pt,H} \approx 45$, $^3J_{H,H} = 5.6$, $^4J_{H,H} \approx 1$ Hz, H(6)], 8.62 (1 H, td, $^3J_{H,H} = 6.1$ Hz), 8.2−7.1 (m, 11 H), 3.40 (s, 3 H, $^3J_{Pt,H} = 23.4$ Hz, OSMe), 2.55 (s, 3 H, $^3J_{Pt,H} = 26.0$ Hz, OSMe). ^{31}P NMR ($CDCl_3$): δ = 31.65 (1 P, s, $^3J_{Pt,P} = 383.0$ Hz). FAB$^+$: *m*/*z* = 586 [M$^+$], 551 [M − Cl], 508 [M − $SOMe_2$], 473 [M − Cl − $SOMe_2$].

$[Pt(Me)(SMe_2)(L)]$ (3): Yield 87%, m.p. 155−160 °C. $C_{20}H_{22}NOPSPt$ (550.5): calcd. C, 43.63, H 4.04, N 2.54; found C 43.46, H 3.84, N 2.33. IR (Nujol): $\tilde{\nu}$ = 1582 m, 1562 m, 1164s, 691s, 544 vs, 494 m. ^1H NMR ($CDCl_3$): δ = 8.76 [dd, 1 H, $^3J_{Pt,H} \approx$ 20, $^3J_{H,H} = 5.3$, $^4J_{H,H}$ ca. 1 Hz, H(6)], 8.63 (1 H, td, $^3J_{H,H}$ = 6.3 Hz), 8.2−7.1 (m, 11 H), 1.80 [6 H, br. s, $S(Me)_2$], 0.59 (s, 3 H,

$^{2}J_{\mathrm{Pt,H}}$ = 83.5 Hz, Pt-Me). ^{31}P NMR ($CDCl_3$): δ = 27.41 (1 P, s, $^{3}J_{\mathrm{Pt,P}}$ = 351.7 Hz). FAB$^+$: *m*/*z* = 550 [M$^+$], 535 [M − Me], 488 [M − SMe_2], 473 [M − Me − SMe_2].

[Pt(Me)($SOMe_2$)(L)] (4): Yield 90%, m.p. 183−185 °C. $C_{20}H_{22}NO_2PSPt$ (566.5): calcd. C, 42.40, H 3.92, N 2.47; found C 42.19, H 3.72, N 2.36. IR (Nujol): ṽ = 1584 m, 1562 m, 1191s, 689s, 540 vs, 504 m. ^{1}H NMR ($CDCl_3$): δ = 8.89 [d, 1 H, $^{3}J_{\mathrm{Pt,H}}$ ≈ 18.1, $^{3}J_{\mathrm{H,H}}$ = 5.3, $^{4}J_{\mathrm{H,H}}$ ≈ 1 Hz, H(6)], 8.62 (t, 1 H, $^{3}J_{\mathrm{H,H}}$ = 6.8 Hz), 8.2−7.2 (m, 11 H), 2.99 (s, 3 H, $^{3}J_{\mathrm{Pt,H}}$ = 17.3 Hz, OSMe), 2.11 (s, 3 H, $^{3}J_{\mathrm{Pt,H}}$ = 16.1 Hz, OSMe), 0.30 (s, 3 H, $^{2}J_{\mathrm{Pt,H}}$ = 83.2 Hz, Pt-Me). ^{31}P NMR ($CDCl_3$): δ = 28.10 (1 P, s, $^{3}J_{\mathrm{Pt,P}}$ = 346.4 Hz). FAB$^+$: *m*/*z* = 566 [M$^+$], 551 [M − Me], 488 [M − $SOMe_2$], 473 [M − Me − $SOMe_2$].

[PtCl(CO)(L)] (5): M.p. 221−223 °C. $C_{18}H_{13}ClNO_2PPt$ (536.8): calcd. C 40.27, H 2.44, N 2.61; found C 40.42, H 2.57, N 2.80. IR (Nujol): ṽ = 2122 vs, 1588 m, 1564 m, 1190 s, 689 s, 542 v s, 496 s, 303 s, 295 s. ^{1}H NMR ($CDCl_3$): δ = 9.09 [dd, 1 H, $^{3}J_{\mathrm{Pt,H}}$ = 39.8, $^{3}J_{\mathrm{H,H}}$ = 5.6, $^{4}J_{\mathrm{H,H}}$ ≈ 1 Hz, H(6)], 8.69 (t, $^{3}J_{\mathrm{H,H}}$ = 5.9 Hz, 1 H), 8.2 (m, 2 H), 7.8−7.2 (m, 9 H). ^{31}P NMR ($CDCl_3$): δ = 31.27 (1 P, s, $^{3}J_{\mathrm{Pt,P}}$ = 322.7 Hz). FAB$^+$: *m*/*z* = 536 [M$^+$], 501 [M − Cl], 473 [M − Cl − CO].

[PtI(CO)(L)] (6): Compound **5** (0.034 g, 0.063 mmol) was dissolved in acetone (5 mL), LiI (0.025 g, 0.19 mmol) was added and the solution stirred for 1.5 h; then it was concentrated to dryness, the solid was dissolved with dichloromethane (10 mL) and the resulting solution was filtered, concentrated to small volume, and *n*-hexane (10 mL) added. The cream-yellow solid was filtered and collected. Yield 0.038 g (95%), m.p. 234−235 °C. $C_{18}H_{13}INO_2PPt$ (628.3): calcd. C 34.41, H 2.10, N 2.23; found C 34.21, H 1.91, N 2.37. IR (Nujol): ṽ = 2094 vs, 1588 m, 1562 m, 1210 s, 692 s, 542 vs, 501 s. ^{1}H NMR ($CDCl_3$): δ = 9.41 [d, 1 H, $^{3}J_{\mathrm{Pt,H}}$ = 43.0, $^{3}J_{\mathrm{H,H}}$ = 5.4 Hz, H(6)], 8.70 (t, $^{3}J_{\mathrm{H,H}}$ = 6.3 Hz, 1 H), 8.25 (m, 1 H), 8.15 (t, $^{3}J_{\mathrm{H,H}}$ = 7.8 Hz, 1 H), 7.8−7.2 (m, 9 H). ^{31}P NMR ($CDCl_3$): δ = 30.77 (1 P, s, $^{3}J_{\mathrm{Pt,P}}$ = 319.7 Hz). FAB$^+$: *m*/*z* = 628 [M$^+$], 501 [M − I], 473 [M − I − CO].

[Pt(Me)(CO)(L)] (7): M.p. 195−197 °C (dec.). $C_{19}H_{16}NO_2PPt$ (516.4): calcd. C 44.19, H 3.13, N 2.71; found C 43.98, H 2.91, N 2.71. IR (Nujol): ṽ = 2051 vs, 1585 m, 1562 m, 1202 s, 693 s, 541 vs, 494 s. ^{1}H NMR ($CDCl_3$): δ = 8.86 [dd, 1 H, $^{3}J_{\mathrm{Pt,H}}$ = 23.0, $^{3}J_{\mathrm{H,H}}$ = 5.4, $^{4}J_{\mathrm{H,H}}$ ≈ 1 Hz, H(6)], 8.73 (t, 1 H, $^{3}J_{\mathrm{H,H}}$ = 6.3 Hz), 8.22−8.02 (m, 2 H), 7.7−7.2 (m, 9 H), 0.76 (s, 3 H, $^{2}J_{\mathrm{Pt,H}}$ = 88.2 Hz, Me−Pt). ^{31}P NMR ($CDCl_3$): δ = 28.90 (1 P, s, $^{3}J_{\mathrm{Pt,P}}$ = 292.2 Hz). FAB$^+$: *m*/*z* = 516 [M$^+$], 501 [M − Me], 473 [M − Me − CO].

[Pt(MeCN)(SMe_2)(L)][BF_4] (8): Compound **1** (0.100 g, 0.175 mmol) was dissolved in dichloromethane (10 mL), $AgBF_4$

Table 3. Crystallographic data

	1·$CHCl_3$	**5**·0·67H_2O
Empirical formula	$C_{20}H_{20}Cl_4NOPPtS$	$C_{18}H_{14\cdot33}ClNO_{2.67}PPt$
M	690.33	548.84
Colour	colourless	pale yellow
Crystal system	monoclinic	trigonal
Space group	*C*2/*c* (no.15)	*R*$\bar{3}$ (no.148)
a [Å]	33.159(4)	33.736(5)
b [Å]	8.261(1)	33.736(5)
c [Å]	17.350(3)	8.645(1)
α [°]	90	90
β [°]	101.00(1)	90
γ [°]	90	120
V [Å^3]	4665.3(1.4)	8520.9(1.9)
Z	8	18
F(000)	2656	4692
D_c [g cm^{-3}]	1.966	1.925
T [K]	223	223
Crystal dimensions [mm]	0.31 × 0.39 × 0.48	0.11 × 0.14 × 0.45
μ(Mo-K_α) [cm^{-1}]	67.1	77.2
Min.−max. transmiss. factors	0.63−1.00	0.56−1.00
Scan mode	ω	ω
Frame width [°]	0.30	0.30
Time per frame [s]	20	25
No. of frames	2450	1321
Detector−sample distance [cm]	5.00	5.00
θ range [°]	3−26	3−26
Reciprocal space explored	full sphere	hemisphere
No. of reflections: total/independent	27531/5675	19256/4696
R_{int}	0.025	0.053
Final R_2, R_{2w} indices[a] (F^2, all reflections)	0.029, 0.043	0.043, 0.063
Conventional R_1 index [$I > 2\sigma(I)$]	0.016	0.028
Reflections with $I > 2\sigma(I)$	4809	3430
No. of variables	262	235
Goodness of fit[b]	0.94	0.97

[a] $R_2 = [\Sigma(|F_o^2 - kF_c^2|)/\Sigma F_o^2]$, $R_{2w}=[\Sigma w(F_o^2 - kF_c^2)^2/w(F_o^2)^2]^{1/2}$. [b] $[\Sigma w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (PF_o^2)^2]^{1/2}$, N_o is the number of observations, N_v the number of variables, and *P* the ignorance factor (= 0.03 for **1**·$CHCl_3$ and 0.04 for **5**·0.67H_2O).

(0.035 g, 0.180 mmol), dissolved in acetonitrile (5 mL) was added. The mixture was stirred in the absence of light for 0.5 h, then it was filtered through Celite and concentrated to about 3 mL; diethyl ether (20 mL) was added dropwise, the resulting crystalline solid was filtered off and washed with diethyl ether (3 × 5 mL). Yield 0.110 g (0.166 mmol, 95%), m.p. 198−201 °C. $C_{21}H_{22}BF_4N_2OPSPt$ (663.3): calcd. C 38.02, H 3.35, N 4.22; found C 38.02, H 3.11, N 4.09. IR (Nujol): ṽ = 2334 and 2303 m, 1588 m, 1562 m, 1205 s, 1055 vs, 696 s, 543 vs, 505 s. ^1H NMR ([D$_6$]acetone): δ = 9.24 [d, 1 H, $^3J_{Pt,H}$ = 47.8, $^3J_{H,H}$ = 5.9 Hz, H(6)], 8.60 (t, $^3J_{H,H}$ = 7.1 Hz, 1 H), 8.48 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H), 8.04−7.10 (m, 10 H), 2.59 (s, 3 H, $^3J_{Pt,H}$ = 53.2 Hz, SMe), 2.55 (s, 3 H, MeCN), 1.76 (s, 3 H, $^3J_{Pt,H}$ = 61.0 Hz, SMe). ^{31}P NMR ($CDCl_3$): δ = 30.27 (1 P, s, $^3J_{Pt,P}$ = 384.5 Hz). FAB$^+$: *m*/*z* = 576 [M$^+$], 535 [M − MeCN], 473 [M − MeCN − SMe_2].

[Pt(dppe)(L)] [BF$_4$] (9): Compound **1** (0.051 g, 0.089 mmol) was dissolved in acetone (5 mL); $NaBF_4$ (0.011 g, 0.10 mmol) and dppe [1,2-bis(diphenylphosphanyl)ethane, 0.038 g, 0.095 mmol] were added. The solution was stirred for 6 h; it was then filtered and concentrated to a small volume; addition of *n*-hexane caused the precipitation of a white crystalline solid that was filtered off and collected. Yield 0.085 g (quantitative), m.p. 210 °C (dec.). $C_{43}H_{37}BF_4NOP_3Pt$ (958.6): calcd. C, 53.87, H 3.90, N 1.46; found C 53.73, H 3.67, N 1.28. IR (Nujol): ṽ = 1584 m, 1562 m, 1210 s, 1063 vs, 697 s, 534 vs, 491 s. ^1H NMR ([D$_6$]acetone): δ = 9.17 [1 H, br. s, $^3J_{Pt,H}$ = 37.6 Hz, H(6)], 8.70−6.70 (m, 32 H), 3.0−2.1 (m, 4 H, CH_2). ^{31}P NMR ([D$_6$]acetone): δ = 48.64 (1 P, d, $^4J_{P,P}$ = 9.2, $^1J_{Pt,P}$ = 1782 Hz), 33.12 (1 P, s, $^1J_{Pt,P}$ = 3737 Hz), 32.55 (1 P, d, $^4J_{P,P}$ = 9.2, $^3J_{Pt,P}$ = 277.0 Hz). FAB$^+$: *m*/*z* = 871 [M$^+$].

[PtCl[P(C$_6$H$_4$-Me-4)$_3$](L)] (10): Compound **1** (0.046 g, 0.081 mmol) was dissolved in dichloromethane (5 mL); P(C_6H_4-Me-4)$_3$ (0.025 g, 0.082 mmol) was added. The solution was stirred for 8 h, and then concentrated to a small volume. Addition of *n*-hexane caused the precipitation of a white crystalline solid that was filtered off and collected. Yield 0.065 g (quantitative), m.p. 195−196 °C. $C_{38}H_{34}ClNOP_2Pt$ (813.2): calcd. C 56.12, H 4.22, N 1.82; found C 55.95, H 3.99, N 1.97. IR (Nujol): ṽ = 1596 m, 1584 m, 1188 s, 694 s, 544 vs, 528 s, 512 m, 274m. ^1H NMR ($CDCl_3$): δ = 9.46 [1 H, br. s, $^3J_{Pt,H}$ = 31.7 Hz, H(6)], 8.56 (t, $^3J_{H,H}$ = 6.8 Hz, 1 H), 8.1−6.4 (m, 23 H), 2.33 (s, 9 H, Me). ^{31}P NMR ($CDCl_3$): δ = 31.00 (1 P, s, $^3J_{Pt,P}$ = 361.6 Hz), 10.10 (1 P, s, $^1J_{Pt,P}$ = 4279 Hz). FAB$^+$: *m*/*z* = 812 [M$^+$], 777 [M − Cl].

[Pt(H$_2$O)(SMe$_2$)(L)] [BF$_4$] (11): M.p. 204−206 °C (dec.). $C_{19}H_{21}BF_4NO_2PPtS$ (640.3): calcd. C 35.63, H 3.31, N 2.19; found C 34.43, H 3.11, N 2.11. IR (Nujol): ṽ = 3345 m, 1587 m, 1095

Table 4. Crystallographic data

	4·0·25H$_2$O	**11**
Empirical formula	$C_{20}H_{22.5}NO_{2.25}PPtS$	$C_{19}H_{21}BF_4NO_2PPtS$
M	571.04	640.32
Colour	colourless	colourless
Crystal system	monoclinic	monoclinic
Space group	*P*21/*c* (no.14)	*P*21/*n* (no.14)
a [Å]	17.326(2)	10.619(1)
b [Å]	14.451(1)	16.094(2)
c [Å]	16.925(2)	13.342(2)
α [°]	90	90
β [°]	99.45(1)	105.66(1)
γ [°]	90	90
V [Å^3]	4180.1(8)	2195.5(5)
Z	8	4
F(000)	2212	1232
D_c [g cm^{-3}]	1.815	1.937
T [K]	223	223
Crystal dimensions [mm]	0.11 × 0.17 × 0.23	0.17 × 0.17 × 0.28
μ(Mo-K_α) [cm^{-1}]	69.7	66.6
Min.−max. transmission factors	0.49−1.00	0.68−1.00
Scan mode	ω	ω
Frame width [°]	0.30	0.30
Time per frame [s]	30	25
No. of frames	1850	2450
Detector−sample distance [cm]	5.00	5.00
θ range [°]	3−26	3−26
Reciprocal space explored	full sphere	full sphere
No. of reflections: total/independent	39932/10552	27660/5624
R_{int}	0.071	0.035
Final R_2, R_{2w} indices[a] (F^2, all reflections)	0.090, 0.106	0.033, 0.054
Conventional R_1 index [$I > 2\sigma(I)$]	0.044	0.022
Reflections with $I > 2\sigma(I)$	6537	4656
No. of variables	478	271
Goodness of fit[b]	0.96	0.95

[a] $R_2 = [\Sigma(|F_o^2 - kF_c^2|)/\Sigma F_o^2]$, $R_{2w} = [\Sigma w(F_o^2 - kF_c^2)^2/w(F_o^2)^2]^{1/2}$. [b] $[\Sigma w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (PF_o^2)^2]^{1/2}$, N_o is the number of observations, N_v the number of variables, and *P* the ignorance factor (= 0.06 for **4**·0.25H$_2$O and 0.04 for **11**).

vs, 696 s, 543 vs, 505 s. ^{1}H NMR ([D$_3$]acetonitrile): δ = 8.94 [d, 1 H, $^3J_{\mathrm{Pt,H}}$ = 41.7, $^3J_{\mathrm{H,H}}$ = 5.4 Hz, H(6)], 8.60−7.20 (m, 12 H), 2.41 (s, 3 H, $^3J_{\mathrm{Pt,H}}$ = 55.2 Hz, SMe), 1.63 (s, 3 H, $^3J_{\mathrm{Pt,H}}$ = 61.3 Hz, SMe). ^{31}P NMR ([D$_3$]acetonitrile): δ = 30.69 (1 P, s, $^3J_{\mathrm{Pt,P}}$ = 388.3 Hz).

[Pt(H$_2$O)(SOMe$_2$)(L)] [BF$_4$] (12): M.p. 212−216 °C (dec.). $C_{19}H_{21}BF_4NO_3PPtS$ (656.3): calcd. C 34.76, H 3.23, N 2.13; found C 34.53, H 3.01, N 2.16. IR (Nujol): ṽ = 3345 m, 1588 m, 1562 m, 1176 s, 1090 vs, 695 s, 543 vs, 505 s. ^{1}H NMR ([D$_3$]acetonitrile): δ = 8.93 [d, 1 H, $^3J_{\mathrm{Pt,H}}$ = 45.6, $^3J_{\mathrm{H,H}}$ = 5.7 Hz, H(6)], 8.60−7.20 (m, 12 H), 3.09 (s, 3 H, $^3J_{\mathrm{Pt,H}}$ = 24.5 Hz, OSMe), 2.47 (s, 3 H, $^3J_{\mathrm{Pt,H}}$ = 32.0 Hz, OSMe). ^{31}P NMR ([D$_3$]acetonitrile): δ = 30.00 (1 P, s, $^3J_{\mathrm{Pt,P}}$ = 384.5 Hz). FAB$^+$: *m*/*z* = 551 [M − H$_2$O], 473 [M − H$_2$O − SOMe$_2$].

X-ray Data Collection and Structure Determinations: Crystal data and other experimental details are summarized in Tables 3 and 4. The diffraction experiments were carried out with a Bruker SMART CCD area-detector diffractometer at 223 K using Mo-K_α radiation (λ = 0.71073 Å) with a graphite crystal monochromator in the incident beam. Cell parameters and orientation matrices were obtained from the least-squares refinement of 124 (for **1**·CHCl$_3$), 123 (for **5**·0.67H$_2$O), 59 (for **4**·0.25H$_2$O), and 112 (for **11**) reflections measured in three different sets of 15 frames each, in the range 3° < θ < 23°. At the end of data collections the first 50 frames, containing 417, 334, 335, and 267 reflections (for **1**·CHCl$_3$, **5**·0.67H$_2$O, **4**·0.25H$_2$O, and **11**, respectively) were recollected to have a monitoring of crystal decay, which was not observed, so no time-decay correction was needed. The collected frames were processed with the software SAINT,[13] and an empirical absorption correction was applied (SADABS)[14] to the collected reflections. Scattering factors and anomalous dispersion corrections were taken from ref.[15] The calculations were performed with a Pentium III PC using the Personal Structure Determination Package,[16] and the physical constants tabulated therein. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares, using all reflections and minimizing the function $\Sigma w(F_o^2 - k|F_c|^2)^2$ (refinement on F^2). Anisotropic thermal factors were refined for all the non-hydrogen atoms. The hydrogen atoms of the coordinated water molecule in **11** were detected in the final Fourier maps and not refined. The hydrogen atoms of the clathrate water molecules in **5**·0.67H$_2$O and **4**·0.25H$_2$O were neglected. All the other hydrogen atoms were placed in their ideal positions (C−H = 0.97 Å; B = 1.10 times that of the carbon atom to which they are attached) and not refined. The final Fourier maps show maximum residuals of 1.0(2) e/Å^3 at 0.76 Å from Pt for **1**·CHCl$_3$, 1.8(3) e/Å^3 at 0.91 Å from Pt for **5**·0.67H$_2$O, 3.0(7) e/Å^3 at 0.83 Å from Pt(A) for **4**·0.25H$_2$O, and 1.0(2) e/Å^3 at 0.89 Å from Pt for **11**. The atomic coordinates of the structure models have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-164381 (**1**·CHCl$_3$), -164382 (**5**·0.67 H$_2$O), -164383 (**4**·0.25 H$_2$O), -164384 **11**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Financial support from Università di Sassari and RAS (Regione Autonoma della Sardegna) is gratefully acknowledged.

---

[1] [1a] G. R. Newkome, *Chem. Rev.* **1993**, *93*, 2067−2089. [1b] Z. Z. Zhang, H. Cheng, *Coord. Chem. Rev.* **1996**, *147*, 1−39. [1c] P. Espinet, K. Soulantica, *Coord. Chem. Rev.* **1999**, *193*, 499−556 and references cited therein.

[2] [2a] F. E. Wood, M. M: Olmstead, J. P. Farr, A. J. Balch, *Inorg. Chim. Acta* **1985**, *97*, 77−83. [2b] J. A. Casares, P. Espinet, J. M. Martìnez-Illarduya, Y. S. Lin, *Organometallics* **1997**, *16*, 770−779. [2c] J. P. Damiano, V. Munyejabo, M. Postel, *Polyhedron* **1995**, *14*, 1229−1234. [2d] P. Guillame, M. Postel, *Inorg. Chim. Acta* **1995**, *233*, 109−112. [2e] Z. Zhang, X. Wsng, Z. Xi, R. Wanf, H. Wang, *Jiegou Huaxue* **1989**, *8*, 107. [2f] C. Abu-Gnim, I. Amer, *J. Organomet. Chem.* **1996**, *516*, 235−243. [2g] J. A. Casares, P. Espinet, J. M. Martìn-Alvarez, G. Espino, M. Pérez-Manrique, F. Vattier, *Eur. J. Inorg. Chem.* **2001**, 289−296.

[3] G. Minghetti, S. Stoccoro, M. A. Cinellu, A. Zucca, M. Manassero, M. Sansoni, *J. Chem. Soc., Dalton Trans.* **1998**, 4119−4126.

[4] A. Doppiu, M. A. Cinellu, G. Minghetti, S. Stoccoro, A. Zucca, M. Manassero, M. Sansoni, *Eur. J. Inorg. Chem.* **2000**, 2555−2563.

[5] J. D Scott, R. J. Puddephatt, *Organometallics* **1983**, *2*, 1643−1648.

[6] C. Eaborn, K. Kundu, A. J. Pidcock, *J. Chem. Soc., Dalton Trans.* **1981**, 933.

[7] e. g.: G. Minghetti, A. Zucca, S. Stoccoro, M. A. Cinellu, M. Manassero, M. Sansoni, *J. Organomet. Chem.* **1994**, *481*, 195−204.

[8] G. Minghetti, A. Doppiu, A. Zucca, S. Stoccoro, M. A. Cinellu, M. Manassero, M. Sansoni, *Chem. Heterocycl. Compd. (N. Y.)* **1999**, *35*, 992−1000.

[9] A. Doppiu, G. Minghetti, M. A. Cinellu, S. Stoccoro, A. Zucca, M. Manassero, *Organometallics* **2001**, *20*, 1148−1152.

[10] J. T. Chen, T. M. Huang, M. C. Cheng, Y. Wang, *Organometallics* **1990**, *9*, 539−541.

[11] M. Schmulling, D. M. Grove, G. van Koten, R. van Eldik, N. Veldman, A. L. Spek, *Organometallics* **1996**, *15*, 1384−1391

[12] R. Cheenevert, A. Rodrigue, M. Pigeon-Gosselin, R. Savoie, *Can. J. Chem.* **1982**, *60*, 853.

[13] *SAINT, Reference manual*, Siemens Energy and Automation, Madison, WI, **1994−1996**.

[14] G. M. Sheldrick, *SADABS, Empirical Absorption Correction Program*, University of Göttingen, **1997**.

[15] *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, **1974**, vol.4.

[16] [16a] B. A. Frenz, *Comput. Phys.* **1988**, *2*, 42. [16b] B. A. Frenz, *Crystallographic Computing 5*, Oxford University Press, Oxford, U. K., **1991**, chapter 11, p. 126.

Received June 4, 2001
[I01203]