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Multinuclear NMR Studies of $[Pt(alkyl)(PR_3)_3]^+$ Complexes

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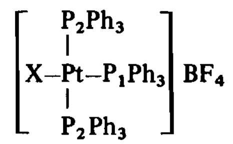
As part of our program [1, 2] involving the synthesis and study of new platinum–alkyl complexes containing phosphine ligands we have prepared the cationic complexes $[PtX(PPh_3)_3]BF_4$, X = CH_3, CH_2CH_3, CH_2CF_3, CH_2Ph, CH_2CN, CH_2CH_2CN, $CH_2CH_2CH_2CN$, o-$CH_2C_6H_4CN$, CH_2NO_2, CH_2COCH_3. During the characterization of these molecules we noticed some interesting aspects of their ^{31}P NMR properties, and in particular, the values $^1J(^{195}Pt, ^{31}P)$.



$$\left[\begin{array}{c} P_2Ph_3 \\ | \\ X\text{–}Pt\text{–}P_1Ph_3 \\ | \\ P_2Ph_3 \end{array}\right] BF_4$$

The absolute magnitudes of the two one-bond coupling constants (see Table I) do not differ markedly from literature expectations (less than 2000 Hz for PPh_3 *trans* to C and 2500–3000 Hz for PPh_3 *trans* to PPh_3) [3]; however, it is interesting to note that the changes in $^1J(^{195}Pt, ^{31}P_2)$ are as large (up to 400 Hz) as those for $^1J(^{195}Pt, ^{31}P_1)$. Further, for the complexes *1–5, 7, 9, 10,* there is roughly an inverse correlation of these two one-bond coupling constants. The variance of $^1J(^{195}Pt, ^{31}P_2)$ is surprising in that the *trans* ligand (another phosphine) is constant throughout the series. Moreover, there was no obvious reason for the change in $^1J(^{195}Pt, ^{31}P_1)$, as the relative size and electronic characteristics for these carbon ligands do not vary enormously, *e.g.*, CH_3 and CH_2CH_3. Nevertheless, there are changes in the one-bond coupling approaching 10–15% for P_2 and ~ 20% for P_1. It is conceivable that the nitrile nitrogen was somehow coordinated, however, this seemed unlikely based on our previous solid state studies [4]†; on the other hand, the possibility of a deviation from square planar geometry could not be excluded as we had previously shown that the complex cation $[PtCl(PMe_3)_3]Cl$ [5] is significantly tetrahedrally distorted. Since PMe_2Ph is sterically larger than PMe_3 perhaps this type of intramolecular twist might prove significant.

We were successful in growing crystals suitable for X-ray diffraction of $[Pt(CH_2CN)(PMe_2Ph)_3]PF_6$ *via* slow evaporation of a $CDCl_3$ solution at 5 °C, and show in Fig. 1 an ORTEP diagram of the molecule with some relevant bond angles and bond distances. A full description of the structure will appear separately.

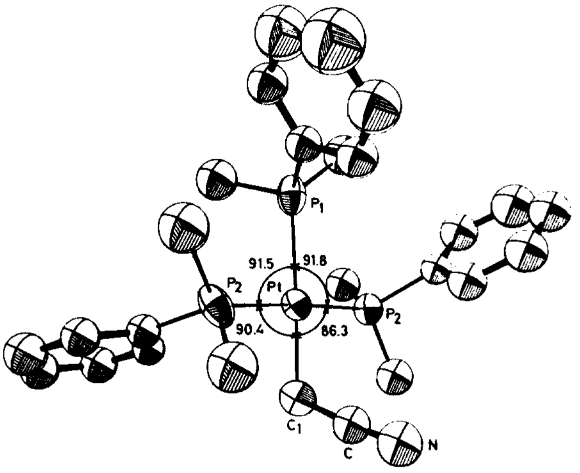


Fig. 1. Perspective view of the ionic complex $[Pt(CH_2CN)(PMe_2Ph)_3]PF_6$.

Although the cation $[Pt(CH_2CN)(PMe_2Ph)]^+$ has several interesting features, there is absolutely nothing unusual about the observed square planar coordination geometry. The bond angles deviate only slightly from the 90° norm and there is no evidence for a significant tetrahedral distortion. The bond distances, on the other hand, are of interest in that they represent extremes for the phosphorus–platinum and phosphorus–carbon bonds in platinum (II) complexes. The value of 2.395(5) Å for the Pt–P bond represents the longest bond of this type yet observed, whereas the value of 2.023(16) Å for the Pt–C bond is one of the shortest ever observed for an sp^3 carbon bound to platinum. Some representative bond distances for other platinum phosphine complexes are given in Table II.

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†Complexes *6* and *8* are geometrically capable of forming pseudo 5- and 6-membered rings *via* association of the nitrile π-bond with the metal.

TABLE I. NMR Spectral Data for $[PtXL_3]^{+}$.[a]

Complex	X	$\delta(P_1)$; $^1J(Pt, P_1)$[c] P_1 *trans* to X	$\delta(P_2)$; $^1J(Pt, P_2)$[c] P_2 *cis* to X	$^2J(P, P)$	$\delta(C)$; $^1J(Pt, C)$[d] C bonded to Pt	$\delta(H)$; $^2J(Pt, H)$[f] Methylene Group
L = PPh_3						
1	$-CH_3$	20.2; 1919	28.4; 2931	19	11.1; 440	0.28; 56.7[g]
2	$-CH_2CH_3$	18.7; 1674	25.7; 3140	19	18.5; 454	1.21; h
3	$-CH_2CF_3$[b]	15.4; 2068	18.4; 2780	22		1.85; h
4	$-CH_2C_6H_5$	18.3; 1795	22.7; 3000	19		2.65; 62.0
5	$-CH_2CN$	15.8; 2218	21.3; 2718	20	−0.7; 470[e]	1.38; 71.0
6	$-CH_2CH_2CN$	17.2; 1830	23.3; 2896	22		1.23; h
7	$-CH_2CH_2CH_2CN$	18.6; 1778	24.6; 3018	21		0.62; h
8	*o*-$CH_2C_6H_4CN$	18.3; 1865	21.9; 2850	21		2.83; 65.0
9	$-CH_2NO_2$	14.3; 2094	19.7; 2754	22	65.9; 673	4.38; 48.3
10	$-CH_2COCH_3$	18.0; 1850	22.9; 2918	22		
11	$-CF_3$[b]	11.0; 1824	20.2; 2824	23		
12	−H	23.1; 2219	22.5; 2821	19		g
13	−Cl	12.1; 3647	22.9; 2487	19		
L = PPh_2Me						
14	$-CH_3$	1.5; 1882	10.0; 2778	21	6.4; 457	0.23; 55.6[i]
15	$-CH_2CN$	−3.7; 2176	4.8; 2590	24	−0.4; 483	1.12; 73.0[i]
L = $PPhMe_2$						
16	$-CH_3$	−13.1; 1831	−5.7; 2682	24	0.2; 456	0.58; 57.4[gi]
17	$-CH_2CN$	−15.7; 2156	−7.1; 2501	24	−7.1; 462	1.59; 74.5[i]
18	$-CF_3$[b]	−23.2; 1859	−6.6; 2586	18		
19	−H	−11.2; 1956	−11.2; 2531	21		g

[a] All data refer to CD_2Cl_2 solutions at room temperature. The counterion is BF_4^- for complexes *1–13, 18* and PF_6^- for *14–17, 19.* [b] ^{19}F NMR data. Chemical shifts are in ppm referred to external $CFCl_3$. *3*: δ(F) −47.0, $^3J(Pt, F)$ 106, $^4J(P, F)$ 11.3 (*trans*) and <2 (*cis*), $^2J(H, F)$ 13.0 Hz; *11*: δ(F) −14.0, $^2J(Pf, F)$ 541, $^3J(P, F)$ 56 (*trans*) and 19.5 Hz (*cis*); *18*: see ref. 4. [c] Chemical shifts are in ppm referred to external H_3PO_4 62.5% and are correct to ± 0.1 ppm; coupling constants are correct to ±3 Hz (spectrum width 6024 Hz, 4096 points). [d] Chemical shifts are in ppm referred to internal TMS and are correct to ±0.1 ppm; coupling constants are correct to ± 3 Hz (spectrum width 6024 Hz, 8192 points). $^2J(C, P_1)$ for *1*: 71; *2*: 71; *5*: 77; *9*: 88; *14*: 74; *15*: 76; *16*: 75; *17*: 75 Hz. [e] J ± 6 Hz. [f] Chemical shifts are in ppm referred to internal TMS. $^3J(P_1, H)$ and $^3J(P_2, H)$ for *1*: 5.8, 8.0; *4*: 6.5, 9.8; *5*: 7.2, 9.0; *8*: 5.0, 9.0; *9*: 3.3, 9.0; *14*: 6.0, 7.9; *15*: 7.7, 9.0; *16*: 6.3, 7.9; *17*: 7.4, 8.8 Hz. [g] ^1H NMR data for $[Pt(CH_3)(PPh_3)_3]FSO_3$ in acetone: see ref. 17; *12*: see ref. 18; *16* in $CDCl_3$: see ref. 14; *19*: see ref. 16. [h] Unresolved multiplet. [i] The following data refer to the phosphine methyls. $\delta(P_1\text{-}CH_3)$ in ppm, $[^2J(P, H) + {}^4J(P, H)]$ and $^3J(Pt, H)$ in Hz for *14*: 1.8, 6.4, 31.5; *15*: 1.93, 6.3, 29.6; *16*: 1.66, 6.9; 30.2; *17*: 1.74, 6.9, 28.3. $\delta(P_2-CH_3)$ in ppm, $^2J(P_2, H)$ and $^3J(Pt, H)$ in Hz for *14*: 1.37, 8.0, 19.2; *15*: 1.66, 8.6, 23.0; *16*: 1.25, 8.3, 18.3; *17*: 1.36, 9.1, 22.5.

It seems reasonable that the large *trans* influence of the carbon ligand [6] is partly responsible for the very long platinum–phosphorus bond. Further, steric crowding of the three tertiary phosphine ligands might also lead to bond lengthening, although the remaining platinum–phosphorus distances of 2.339(4) Å and 2.302(5) Å are not unusually long. It would be of interest to have structural data for a PPh_3 complex.

In the absence of a significant geometric distortion we returned to electronic effects as the primary source of the changes in the NMR coupling constants. Since the complexes *1* and *5* (and *14* and *15* as well as *16* and *17*) were available in sufficient quantity we measured their ^{13}C NMR spectra in the hope of learning something of the effect of phosphine on the *trans* carbon ligand. Clark and co-workers [7, 8] have shown that $^1J(^{195}Pt, ^{13}C)$ is markedly dependent on the *trans* ligand in a wide variety of neutral and cationic complexes. Since $^1J(^{195}Pt, ^{31}P)$ in the three pairs of complexes *1* and *5, 14* and *15* and *16* and *17* varies by approximately 300 Hz, some significant change in $^1J(^{195}Pt, ^{13}C)$ might be expected. Unfortunately, there are only trivial changes in this coupling with the values falling in the range 440–483 Hz. For a given phosphine the change is less than 5%. We cannot exclude the possibility that this negative result stems from two opposing effects (a decrease in $^1J(^{195}Pt, ^{13}C)$ due to a weaker σ-bond for the CH_2CN ligand, which is compensated by an increase in $^1J(^{195}Pt, ^{13}C)$ due to the presence of the electron withdrawing cyano group on carbon [9]), however, the result remains inconclusive.

To summarize, we join with Ball *et al.* [10] in repeating our previous comment [11], that although phosphorus chemical shifts and one-bond platinum–

TABLE II. Representative Pt–P Distances in Pt(II) Complexes as a Function of the *trans* Ligand.

Compound	Bond Length, Pt–P, Å
cis-[$PtCl_2(PEt_3)(P(OPh)_3)$]	2.182[a]
cis-[$PtCl_2(PMe_3)_2$]	2.248[b]
trans-[$PtCl(CH_2CN)(PPh_3)_2$]	2.309[c]
[$Pt(C_3H_5)(P(cyclohexyl)_3)_2$]$^+$	2.330[d]
[$PtH(PPh_3)(P(cyclohexyl)_3)_2$]$^+$	2.359[e]
trans-[$PtI_2(P(cyclohexyl)_3)_2$]	2.371[f]
[$Pt(CH_2CN)(PMe_2Ph)_3$]$^+$	2.395[g]
[$PtCl(PMe_3)_3$]$^+$	2.242[h]
	2.337

[a] A. M. Caldwell, L. M. Muir and K. W. Meier, *J. Chem. Soc. Dalton*, 2265 (1977). Pt–P for PEt_3. [b] G. G. Messmer, E. L. Amma and J. A. Ibers, *Inorg. Chem.*, *6*, 725 (1967). [c] Ref. 4. [d] J. D. Smith and J. D. Oliver, *Inorg. Chem.*, *17*, 2585 (1978). [e] H. C. Clark, N. J. Dymarski and J. D. Oliver, *J. Organometal. Chem.*, *154*, C40 (1978). [f] P. B. Hitchcock, B. Jacobson and A. Pidcock, *J. Chem. Soc. Dalton*, 2038 (1977). [g] P. S. Pregosin and M. Parvez, unpublished results. Pt–P for PMe_2Ph *trans* to CH_2CN. [h] Ref. 5. P *trans* to Cl and P *trans* to P, respectively.

phosphorus coupling constants are a qualitative help to the chemist, a quantitative interpretation should be made with caution.

Experimental

The following cationic complexes were prepared according to literature methods: *1, 13* [12], *5* [1]; *8* [2]; *12* [13]; *16* [14]; *18* [15]; *19* [16]. A typical procedure is given for the preparation of the new [$PtR(PPh_3)_3$]BF_4 complexes: a solution of $AgBF_4$ (one equivalent) in acetone (5 ml) was added to a solution of *cis*- or *trans*-$PtXRL_2$ (*ca.* 0.4 g) in dichloromethane. Silver halogenide was filtered off and PPh_3 (one equivalent) was added to the filtrate. The solution was reduced to a small volume and diethylether added. The white precipitate formed was recrystallised from CH_2Cl_2/C_6H_6 giving [$PtR(PPh_3)_3$]-BF_4 in almost quantitative yield. In the case of *10*, the complex was dissolved in CH_2Cl_2 and the solution was passed through a short Florisil column before recrystallisation. All complexes gave satisfactorily elemental analyses. IR data: $\nu(BF_4)$ 1055–1060 cm^{-1}, vs, broad for *1–12;* $\nu(CN)$ 2214 m for *5*, 2216 m for *6*, 2245 w for *7*, 2220 for *8*, 2211 m for *15*, 2210 m for *17*; $\nu(NO_2)$ 1520s, 1365 m for *9*; $\nu(CO)$ 1686 m for *10;* $\nu(PtH)$ see ref. 17 for *12* and ref. 16 for *19*. Unambiguous assignment of the $\nu(Pt-C)$ of these complexes could not be made as other absorptions are present in the 500–600 cm^{-1} IR and Raman regions.

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