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^{31}P Nuclear Magnetic Resonance Spectroscopic Studies on some Zerovalent Platinum Phosphine Complexes

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Data concerning the magnitude of the directly bonded platinum–phosphorus coupling constant, *J*(PtP), in platinum(0) phosphine complexes are comparatively rare. Malatesta *et al.* [1] found that [Pt(PPh$_3$)$_4$] dissociates in solution and this is also true for other four coordinate platinum(0) phosphine complexes which give rise to very reactive coordinatively unsaturated species [Pt(PR$_3$)$_3$] and [Pt(PR$_3$)$_2$]. The latter have only been isolated using very bulky phosphines [2–4]. The magnitude of *J*(PtP) for some [Pt(PR$_3$)$_4$] complexes has been determined by low temperature n.m.r. studies and the values are found to lie in the range 3740 Hz (R = Et) to 3780 Hz (R = *p*-tolyl) [5, 6]. The analogous phosphite complexes of zerovalent platinum do not undergo ligand dissociation at low temperature and as expected [7] the presence of the electron withdrawing substituents on phosphorus leads to larger values for *J*(PtP) *e.g.* [Pt(P(OEt)$_3$)$_4$] 5386 Hz; [Pt(P(OCH$_2$)$_3$CEt)$_4$] 5836 Hz; [Pt(P(OPh)$_3$)$_4$] 5798 Hz [8].

Previously we reported the synthesis of several fluorophosphine complexes of platinum(0), [Pt(PF$_3$)$_4$], [Pt(CF$_3$PF$_2$)$_4$] and [Pt(CF$_3$)$_2$PF)$_4$] [9, 10] which are stable with respect to ligand dissociation but the complexity of the ^{31}P n.m.r. spectra precluded accurate evaluation of coupling constants. Partial analyses of the n.m.r. spectra of several related nickel(0) fluorophosphine complexes have been accomplished [11], and a full analysis of [Pt(PF(OPh)$_2$)$_4$] has been reported (*J*(PtP) 5981 Hz) [12].

In order to facilitate evaluation of *J*(PtP) in [Pt(PF$_3$)$_4$] we have recorded its ^{31}P n.m.r. spectrum with simultaneous fluorine decoupling. The undecoupled ^{31}P n.m.r. spectrum (Fig. 1(a)) shows the complicated widely spaced 1-3-3-1 quartet pattern expected for the A part of an [X$_3$A]$_4$M spin system [X = fluorine, A = phosphorus and M = platinum] with platinum-195 satellites evident. The fluorine decoupled spectrum (Fig. 1(b)) simplifies to a single line with simple platinum satellites enabling *J*(PtP) to be accurately evaluated at 6480 Hz. The magnitude of *J*(PtP) is given by the expression [7]

$$J(\mathrm{PtP}) = \gamma_{\mathrm{P}}\gamma_{\mathrm{Pt}}\,\frac{h}{2\pi}\,\frac{256\pi^2}{9}\,\beta^2\,\frac{a^2(1-a^2)\alpha_{\mathrm{P}}^2}{n}\times\frac{|S_{\mathrm{P}}(0)|^2\,|S_{\mathrm{Pt}}(0)|^2}{{}^3\Delta E}$$

where γ_X is the magnetogyric ratio of nucleus X, $|S_X(0)|^2$ is the s-electron density of X evaluated at the nucleus, α_P^2 is the s-character of the phosphorus lone pair orbital, a^2 is the s-character of the metal hybrid orbital, n is the number of ligands and ΔE is an average triplet excitation energy. Changes in the magnitude of *J*(PtP) within a series of platinum-phosphine complexes are largely dependent on changes in $|S(0)|^2$ and α_P^2 [7].

As expected *J*(PtP) in [Pt(PF$_3$)$_4$] is larger than in [Pt(PR$_3$)$_4$] or [Pt(P(OR)$_3$)$_4$] because the strongly electronegative fluorine substituents increase the s-character of the phosphorus lone pair in PF$_3$

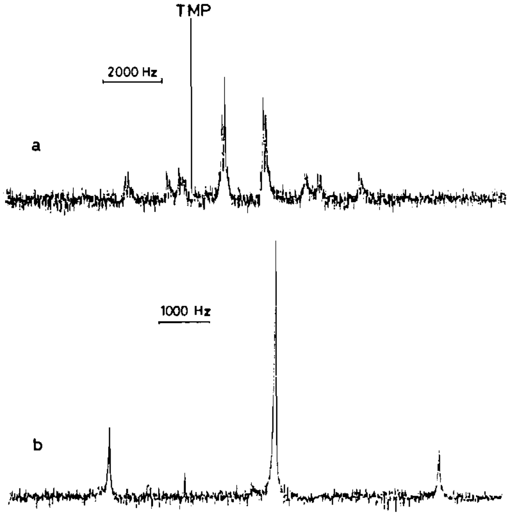


Fig. 1. Fluorine undecoupled (a) and decoupled (b) ^{31}P n.m.r. spectra of Pt(PF$_3$)$_4$.

TABLE I. $J(PH)^a$ in $[PR_3H]^+$ and $J(PtP)^a$ in $Pt(L)_4$ Complexes.

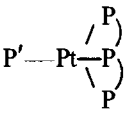
L	J(PH)	J(PtP)
PF_3	1191	6480
$P(OCH_2)_3CEt$	898^b	5836
$P(OPh)_3$	870	5798
$P(O\text{-}iPr)_3$	795	5395
$P(OEt)_3$	806	5386
$P(p\text{-tolyl})_3$	506^c	3780
PEt_3	457^d	3740

[a] In Hz. [b] Value refers to analogous –CMe compound. [c] Value refers to PPh_3 d value refers to PBu_3.

compared with the other phosphine ligands [7]. The value of J(PtP) in $[Pt(PF_3)_4]$ is expected to be the largest observable for this class of complexes. Recently Goodfellow *et al.* [12] have shown that J(PtP) in complexes of the type $[PtX_3(PR_3)]^-$ and $[PtX_5(PR_3)]^-$ (X = halogen) is also maximised when R = F.

McFarlane and White [13] established a linear relationship between J(PH) in protonated phosphine species $[PR_3H]^+$ and J(WP) in $[W(CO)_5(PR_3)]$ complexes (R = ethyl, aryl, OR). J(PH) reported recently 14] for $[PF_3H]^+$ is the largest known value and correlates well with J(WP) in $[W(CO)_5(PF_3)]$. In Table I and Fig. 1 we show analogous data for J(PH) and J(PtP) in $Pt(PR_3)_4$ complexes.

Meek *et al.* [15] have recently overcome the problem of ligand dissociation in a series of Pt(0) phosphine complexes of the type [Pt(triphos)P′], (A) (triphos = $CH_3(CH_2PPh_2)_3$; P′ = PPh_3, $P(p\text{-tolyl})_3$, PPh_2Me, PF_2NMe_2, $P(OPh_3)_3$, PF_3 and $P(OCH_2)_3CMe$). The magnitude of J(PtP) for the triphos ligand decreased steadily as the monodentate phosphine was changed from $P(p\text{-tolyl})_3$ to PF_3 [see Table II].



(A) (PPP = triphos)

The smaller values (2867–3098 Hz) of J(PtP) in (A) compared with the $[Pt(PR_3)_4]$ compounds discussed earlier reflects the smaller P–Pt–P bond angles (93–94°) resulting from the restrictions imposed by the triphos ligand. Accordingly the unique Pt–P′ bond in (A) should have a higher degree of s-character and as expected J(PtP′) in (A) are larger than in $[PtP'_4]$. An inverse relationship between J(PtP) and J(PtP′) in (A) was noted, the latter increas-

TABLE II. ^{31}P and ^{19}F n.m.r. Coupling Constant $Data^a$ on Pt(triphos)P′.

$Complex^b$	P′	$^1J(PtP)^c$	$^2J(PPtP')$	$^1J(PtP')^d$	$^2J(PtF)$	$^1J(PF)$	$^3J(PF)$	Σ electronegativity of substituent attached to P	Ref.
1	PPh_3	3096	51	5400	–	–	–	8.1	15
2	$P(p\text{-}C_6H_4CH_3)_3$	3098	51	5380	–	–	–	–	15
3	PPh_2Me	3075	51	5370	–	–	–	7.9	15
4	$P(OCH_2)_3CMe$	2990	68	6787	–	–	–	10.7	15
5	PF_2NMe_2	2893	83	8838	640	1111	43	11.0	15
6	$P(OPh)_3$	2883	87	9150	–	–	–	10.7	15
7	$PF_2(OPh)$	2875	88.1	9766	796	1244	47.6	11.6	This work
8	PF_3	2867	95.2	10200	895	1321	46.4	12.0	This work

[a] Hz. [b] The numbers refer to the points on the graphs shown in Figs. 2–4. [c] Coupling constant of the triphos ligand. [d] Coupling constant of the monodentate ligand.

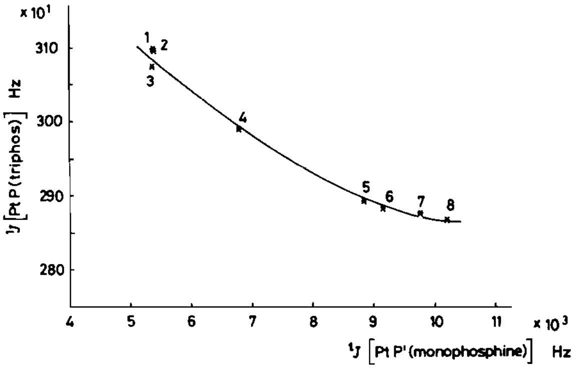


Fig. 2. Plot of ^{1}J[PtP(triphos)] against ^1J[PtP'(monophosphine)] in complexes Pt(triphos)(P').

ing in magnitude as more electronegative substituents are attached to phosphorus.

In view of our results on [Pt(PF$_3$)$_4$] the magnitude of J(PtP) in [Pt(triphos)(PF$_3$)] is of interest but the complex was to insoluble to observe the PF$_3$ ^{31}P resonance directly. The highest J(PtP') value recorded by Meek [15] was for P' = P(OPh)$_3$ = 9150 Hz and an extrapolated value (~9500 Hz) was assigned to the PF$_3$ complex based on a plot of J(PtP) *versus* J(PtP') which was said to be linear.

In order to extend this work we have synthesised a number of additional platinum(0) complexes of type (A) where P' = PF(CF$_3$)$_2$; PPhCl$_2$; PF$_2$(OPh); PCl$_3$ and PF$_2$CHCl$_2$ by displacement of PPh$_2$Me from [Pt(triphos)(PPh$_2$Me)].

$$\mathrm{Pt(triphos)(PPh_2Me)} \xrightarrow{P'} \mathrm{Pt(triphos)P'} + \mathrm{PPh_2Me}$$

[P' = PF(CF$_3$)$_2$; PPhCl$_2$; PF$_2$(OPh), PCl$_3$; PF$_2$CHCl$_2$]

Although the new complexes were all obtained in good yield by this route as evidenced by microanalytical data and infra-red spectroscopy their insolubilities precluded a detailed n.m.r. study. The complex [Pt(triphos)(PF$_2$OPh)] was however soluble enough to obtain a satisfactory ^{31}P n.m.r. spectrum exhibiting the expected 1-2-1 triplet of quartets at low field for the PF$_2$OPh ligand (coupling to fluorine and triphos P's) with ^{195}Pt satellites and a high field triphos resonance appearing as a doublet of triplets (coupling to PF$_2$OPh) with platinum satellites. [see Table II for data).

The value of J(PtP') for [Pt(triphos)(PF$_2$OPh)] is 9766 Hz which is the largest so far recorded in this series of complexes and suggests that J(PtP') in the analogous PF$_3$ complex was underestimated by Meek *et al.* Inclusion of the new data [Table II] show that the originally suggested linear plot of J(PtP) *versus* J(PtP') in (A) is better represented by a smooth curve [Fig. 2] and extrapolation suggests a value of J(PtPF$_3$) of *ca.* 10,200 Hz. Support comes from consideration of the variation of J(PtP') in [Pt(triphos)P'] as a function of the electronegativity of the substituents attached to phosphorus [Table [II] and [Fig. 3] which has not been discussed explicitly by Meek *et al.* Similar observations have been made by us and others on other transition metal–phosphine systems [7, 16].

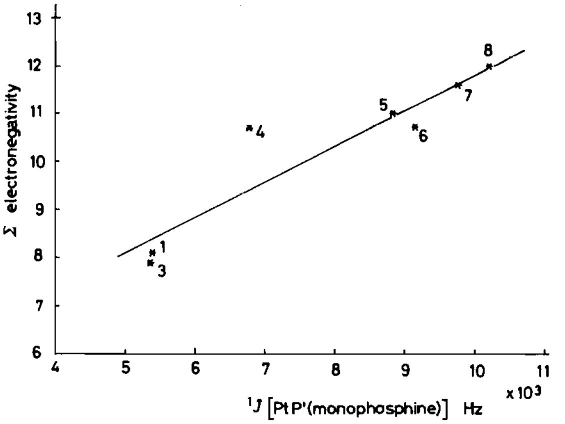


Fig. 3. Plot of ^1J(PtP') against Σ electronegativity of atoms or groups attached to phosphorus in phosphine complexes of the type Pt(triphos)(P').

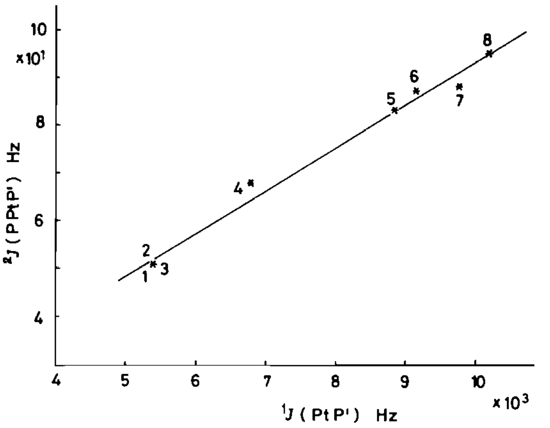


Fig. 4. Plot of ^{2}J(PPtP') against ^{1}J(PtP') in complexes Pt-(triphos)(P').

In related studies we have established a correlation between J(PM) and J(PMP') in suitable transition metal phosphine complexes. Systems studied include [W(CO)$_4$(PF$_2$R)$_2$] [17–18], [Rh(h^5-C$_5$H$_5$)(PF$_2$R)$_2$] and [Rh(h^5-C$_9$H$_7$)(PF$_2$R)$_2$] [17, 20], and [RhCl$_n$(PPh$_3$)$_2$P'] (n = 1, 3) [20]. Inspection of the data in Table II show that J(PPtP') in [Pt(triphos)P'] increases in magnitude as J(PtP'). The data are plotted in Fig. 4 to give a good straight line and inclusion of $J(\mathrm{PPtP'})$ for [Pt(triphos)($\mathrm{PF_3}$)] gives a value of $J(\mathrm{PtP'}) \approx 10{,}200$ Hz in accord with other extrapolated data.

Experimental

Reactions were carried out under an atmosphere of dry nitrogen gas or *in vacuo* in sealed pyrex glass tubes. $^{31}\mathrm{P}$ n.m.r. spectra were recorded on a Jeol PFT 100 Fourier Transform spectrometer operating at 40.49 MHz using 8 mm spinning tubes. Infra-red spectra in the 4000–250 $\mathrm{cm^{-1}}$ range were recorded on a Perkin-Elmer 457 spectrometer. Elemental analyses were carried out by Mr and Mrs A. G. Olney of this laboratory.

Preparation of [Pt(triphos)(PR$_3$)] Complexes

$\mathrm{PR_3 = PF_2OPh}$

A mixture of [Pt(triphos)($\mathrm{PMePh_2}$)] (0.300 g, 0.294 mmol), $\mathrm{PF_2OPh}$ (0.054 g, 0.330 mmol) and benzene (10 $\mathrm{cm^3}$) was sealed off in an ampoule and shaken at room temperature for several hours. After removal of volatiles the residue was washed with hexane (15 $\mathrm{cm^3}$) and dried *in vacuo* to give the slightly yellow solid complex *Phenoxydifluorophosphine-1,1,1-tris(diphenylphosphinomethyl)ethane platinum(0)* (0.225 g, 0.229 mmol; 78%); m.p. 95 °C (dec.) [Found: C, 57.6; H, 4.9. $\mathrm{C_{47}H_{44}F_2OP_4Pt}$ requires C, 57.49; H, 4.51%]. I.r. spectrum: 3560vw, 3060w, 1585m,br, 1310w, 1220m, 1190m,br, 1160m, 1090m, 1030m, 1000w, 890s,br, 790s, 770w, 750m, 740s, 725m, 700s, 620w, 580w, 520s, 500vw, 485w $\mathrm{cm^{-1}}$ (Nujol mull).

$\mathrm{PR_3 = PF(CF_3)_2}$

The product was obtained as light-yellow solid, washed with hexane and dried *in vacuo* (0.264 g, 0.262 mmol; 89%); m.p. 153 °C (dec) (Found: C, 51.9; H, 4.4. $\mathrm{C_{43}H_{39}F_7P_4Pt}$ requires: C, 51.25; H, 3.9%). I.r. spectrum: 3540vw, 3025w, 1590w, 1570w, 1340vw, 1310w, 1280vw, 1200m,sh, 1190s, 1170s, 1155m,sh, 1140s, 1125m, 1095m, 1075m, 1050vw, 1030w, 1005w, 965vw,br, 890w,br, 835w,br, 800vw, 770m,sh, 740s, 735m, 700s, 690m,sh, 635vw, 590m, 580m, 520s, 500m,sh, 490m, 450vw, 410w,br $\mathrm{cm^{-1}}$ (Nujol mull).

$\mathrm{Pr_3 = PF(CF_3)_2}$

The product was isolated as pale-yellow solid, washed with hexane and dried *in vacuo*. Yield: 0.28 g, 0.288 mmol; 94%; m.p. 122 °C (dec.). (Found: C, 55.5; H, 4.9. $\mathrm{C_{42}H_{40}Cl_2F_2P_4Pt}$ requires: C, 51.86, H, 4.14%). I.r. spectrum: 3540vw, 3050w, 1590vw, 1575vw, 1310w,br, 1160vw,br, 1100s, 1075vw, 1030m, 1005m, 970w,br, 890m,br, 845w,br, 830m,br, 745s, 730m,sh, 700s, 680w,sh, 620vw,br, 570m, 525s, 505m, 495m, 460, 425w,br, 315w,br $\mathrm{cm^{-1}}$ (Nujol mull).

Reaction of Pt(triphos)$\mathrm{PPh_2Me}$ with $\mathrm{PCl_3}$ and $\mathrm{PPhCl_2}$

Pt(triphos)$\mathrm{PPh_2Me}$ (0.300 g, 0.294 mmol) in benzene (10 $\mathrm{cm^3}$) was placed in a Schlenk tube. $\mathrm{PCl_3}$ (0.045 g, 0.33 mmol) was distilled in and the mixture was stirred at room temperature. The initially yellow solution became colourless. After stirring overnight, the solvent was removed, giving a white solid, which was formulated as impure *trichlorophosphine-1,1,1-tris(diphenylphosphinomethyl)-ethane-platinum(0)*, which was washed with hexane (10 $\mathrm{cm^3}$) and dried *in vacuo*. Yield: 0.24 g, 0.25 mmol; 85%; m.p. 193 °C (dec.). A satisfactory analysis could not be obtained. (Found: C, 55.3; H, 4.8. $\mathrm{C_{41}H_{39}\text{-}Cl_3P_4Pt}$ requires: C, 51.45; H, 4.1%). I.r. spectrum: 3540vw, 3050w, 1590w, 1580vw, 1315w,br, 1190w,br, 1170w,br, 1120m,sh, 1100s, 1075vw,br, 1060w, 1030m, 1000m, 930w, 895s, 850vw,sh, 840w, 820w, 800w, 755s, 740s, 730m, 700s, 615m, 590vw, 575m, 540w, 525s, 505m, 490m, 460m, 445vw,sh, 420w $\mathrm{cm^{-1}}$ (Nujol mull).

$\mathrm{PR_3 = PPhCl_2}$

This product was obtained as pale-yellow solid using the above procedure, but a satisfactory analysis was not obtained. Yield: 0.23 g, 0.231 mmol; m.p. 118 °C (dec.) (Found: C, 52.0; H, 4.4 $\mathrm{C_{47}H_{44}Cl_2\text{-}P_4Pt}$ requires: C, 56.52; H, 4.44). I.r. spectrum: 3550vw, 3050w, 1585vw, 1575vw,sh, 1335vw,br, 1310m, 1275vw, 1190w,br, 1160w, 1120m,sh, 1100s, 1075vw, 1060vw, 1030m, 1000m, 965w,br, 940vw,br, 895m, 845, 820vw, 800vw, 750s, 730m, 700s, 615vw, 570w, 525s, 505w,sh, 490w, 460w $\mathrm{cm^{-1}}$ (Nujol mull).

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