134. A ^{31}P-NMR. Study of Some Phosphite Complexes of Platinum(0)

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(16. III. 77)

Summary

^{31}P-NMR. spectra for a series of phosphite complexes of platinum(0) have been measured. Low temperature studies have revealed the existence in solution of the mixed complexes $Pt[PPh_3]_2[P(OPh_3)_3]_2$ and $Pt[PPh_3][P(OPh)_3]_3$ of which the former is isolable.

Introduction. – The chemistry of zero valent complexes of platinum remains an area of considerable interest. This stems, partially, from the usage of a number of these compounds as starting materials for the synthesis of new Pt(II) and Pt(0) complexes [1]. For those Pt(0) derivatives which contain phosphorus, ^{31}P-NMR. has played a useful role in the characterization of this type of complex. Thus, the complex $Pt[P(p\text{-}C_7H_7)_3]_3$ shows only a very broad ^{31}P resonance at room temperature but the typical triplet structure (main resonance plus ^{195}Pt satellites) at $\approx -90°$ [2]. In the presence of excess phosphine, at low temperature, the tetrakis compound $Pt[P(p\text{-}C_7H_7)_3]_4$ is formed [2]. Similar studies have helped to characterize the more reactive $Pt(PEt_3)_3$ and $Pt(PEt_3)_4$ derivatives [3].

In contrast to the *n*-alkyl and aryl phosphine analogs, tri-substituted alkyl and aryl phosphite derivatives of Pt(0) have been the subject of fewer studies. As part of a study involving the nickel triad, *Maier et al.* [4] determined the rate of exchange and activation parameters for the exchange of free triethyl phosphite with $Pt[P(OEt)_3]_4$ using ^{1}H-NMR. methods and *Bradley & Venanzi* [5] have extended those studies to a wider range of phosphite derivatives. In the latter work it was found that $Pt[P(OPh)_3]_4$ gave only a broad ^{31}P-NMR. signal at room temperature, whereas the signal for $Pt[P(OEt)_3]_4$ at this temperature was sharp. It seemed useful to us to investigate further the ^{31}P-NMR. characteristics of these systems and we report here some of our results.

Experimental Part. – All operations were carried out under nitrogen and the reaction mixtures stirred magnetically. Solvents were dried and degassed.

The phosphites were commercially available. $Pt[P(C_6H_5)_3]_4$ was prepared according to [1e] and $Na_2PtCl_4 \cdot 4H_2O$ obtained by evaporation of a 10% aqueous solution (*Johnson Matthey*). K_2PtCl_4 (*Johnson Matthey*) was used directly without further purification.

$^{31}P\{^1H\}$-NMR. spectra were measured as CH_2Cl_2 solutions, containing an external capillary of acetone-d_6 using a *Bruker*-HX-90 spectrometer operating at 36.43 MHz.

Since we encountered some difficulty in repeating the literature preparations for $Pt[P(OEt)_3]_4$ [6] and $Pt[P(OPh)_3]_4$ [7] we describe, below, the details for the preparation of some of the known complexes as well as that for $Pt[PPh_3]_2[P(OPh)_3]_2$.

Reaction of an aqueous K_2PtCl_4 solution with $P(OEt)_3$. – To a solution of 0.4 g KOH (7 mmol) and 2.5 g $P(OEt)_3$ (2.6 ml, 15 mmol) in 10 ml EtOH, maintained at 60°, was added dropwise a solution of 1.2 g K_2PtCl_4 (3 mmol) in 15 ml water. A white precipitate was formed which eventually disappeared. After 9 ml of the K_2PtCl_4 solution had been added, a clear pinkish brown solution remained in the reaction flask. The pinkish-brown color persisted after the dropwise addition of another 3 ml of the K_2PtCl_4 solution. The remaining K_2PtCl_4 solution was set aside and the reaction mixture maintained at 75° for 15 min. Filtration of the hot solution followed by cooling at -9° overnight gave white crystalline plates, which were filtered off, washed with 2 × 2 ml water to remove the red solid that precipitated with the product, then washed with $EtOH/H_2O$ 1:1 and finally pumped dry. Yield 0.35 g. The elemental analysis (see *Table 1*) is consistent with $[Pt\{P(OH)(OC_2H_5)_2\}_2\{P \cdot O \cdot (OC_2H_5)_2\}_2]$.

Table 1. *Analytical Data for some of the Platinum Complexes*

Complex	Emp. Formula	M. p. (°C)	Analysis (%)	Calc. (Found)
			C	H
$[Pt\{P(OH)(OC_2H_5)_2\}_2\{P \cdot O \cdot (OC_2H_5)_2\}_2]$	$C_{16}H_{42}O_{12}P_4Pt$	92	25.78 (25.72)	5.68 (5.66)
$[Pt\{P(C_6H_5)_3\}_2\{P(OC_6H_5)_3\}_2]$	$C_{72}H_{60}O_6P_4Pt$	153	64.53 (64.52)	4.51 (4.52)
$[Pt\{P(OC_2H_5)_3\}_4]$	$C_{24}H_{60}O_{12}P_4Pt$	140 (dec)	33.54 (33.62)	7.03 (7.08)
$[Pt\{P(OCH_2)_3C \cdot C_2H_5\}_4]$	$C_{24}H_{44}O_{12}P_4Pt$	–	34.18 (34.07)	5.26 (5.30)
$[Pt\{P(OC_6H_5)_3\}_4]$	$C_{72}H_{60}O_{12}P_4Pt$	146–8	60.23 (60.58)	4.21 (4.19)

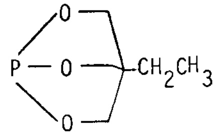
Preparation of $[Pt\{P(OC_2H_5)_3\}_4]$. To a boiling solution of 0.19 g KOH and 1.1 g $P(OEt)_3$ (6.5 mmol) in 20 ml EtOH was added dropwise a solution of 0.54 g $Na_2PtCl_4 \cdot 4H_2O$ (1.3 mmol) in 5 ml EtOH. A white precipitate formed. The reaction mixture was diluted with 11.5 ml water to give a clear colourless solution which was then filtered and left at −9° overnight. The white solid which separated was isolated at −9°, washed with $EtOH/H_2O$ 1:1 and pumped dry. Yield 0.24 g.

Preparation of $[Pt\{P(C_6H_5)_3\}_2\{P(OC_6H_5)_3\}_2]$. To a suspension of $[Pt\{P(C_6H_5)_3\}_4]$ (1.37 g, 1.1 mmol) in 10 ml of EtOH at 65° was added dropwise in the course of 3 min. 1.7 g (5.5 mmol) $P(OC_6H_5)_3$. The reaction mixture was further stirred for *ca.* 4 min, allowed to cool and filtered. The grey residue was washed with 3 × 10 ml of warm EtOH and pumped dry. The solid was then dissolved in 10 ml benzene, and the solution treated with activated charcoal. After filtration the resulting greenish filtrate was diluted with 20 ml hexane and then left at *ca.* 5° overnight. The greenish grey crystals isolated were washed with a mixture of 0.15 ml benzene and 1.5 ml hexane in three portions and pumped for 24 h under high vacuum. Yield 0.99 g.

Preparation of $[Pt\{P(OC_6H_5)_3\}_4]$. A suspension of 0.5 g $[Pt\{P(C_6H_5)_3\}_2\{P(OC_6H_5)_3\}_2]$ (0.38 mmol) and 0.46 g $P(OC_6H_5)_3$ (1.5 mmol) in 4 ml of EtOH was heated under reflux for 12 h. The white suspension which resulted was filtered hot and the solid washed with 3 ml hexane and pumped dry. Yield 0.1 g.

Preparation of $[Pt\{P(OCH_2)_3C \cdot C_2H_5\}_4]$. A suspension of 1.1 g $[Pt\{P(C_6H_5)_3\}_4]$ (0.9 mmol) and 0.9 g of the ligand I (6.3 mmol) in 10 ml of EtOH was heated under reflux for 36 h, and the resulting suspension filtered hot. The white solid residue was washed first with 2 × 2 ml EtOH, then 5 ml hexane and pumped dry. Yield 0.44 g.

Results and Discussion. – The phosphite complexes of Pt(0) may be prepared relatively easily starting from $Pt(PPh_3)_4$. Thus, a suspension of $Pt(PPh_3)_4$ and the caged phosphite I, when heated under reflux in ethanol afforded $Pt(I)_4$. In our hands the procedure described previously for the preparations of $Pt[P(OEt)_3]_4$ [6] and $Pt[P(OPh)_3]_4$ [7] led to unexpected results. The reduction of K_2PtCl_4 with KOH in $EtOH/H_2O$ in the presence of $P(OEt)_3$ afforded a white crystalline solid whose $^{31}P\{^1H\}$-NMR. spectrum showed a single resonance flanked by ^{195}Pt ($I = ^1/_2$) satellites. Since phosphites generally [8] show one-bond coupling to ^{195}Pt of the order of 4–7 kHz, the observed coupling of ~3.4 kHz suggested that the ligand had undergone significant modification. The microanalytical (see *Table 1*) data were consistent with the formulation $Pt[P(OH)(OEt)_2]_2[PO(OEt)_2]_2$, which, since this is a known compound [9], we have been able to confirm. The reaction of $Pt(PPh_3)_4$ with $P(OPh)_3$ in hot ethanol gave, after cooling and dilution with hexane, green-yellow crystals whose $^{31}P\{-^1H\}$-NMR. spectrum was very broad at RT. At $-50°$ the ^{31}P-NMR. spectrum showed an A_2X_2 pattern with accompanying ^{195}Pt satellites. These data (see *Table 2*) in combination with the microanalysis suggest that only two of the four phosphines have been displaced by $P(OPh)_3$ and therefore that the product is $Pt[PPh_3]_2[P(OPh)_3]_2$ (II). The tetrakis derivative, $Pt[P(OPh)_3]_4$, was subsequently obtained by prolonged heating of an ethanolic suspension of II containing $P(OPh)_3$.



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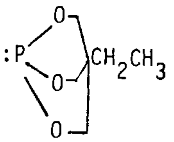
The ^{31}P-NMR. data for the complexes $Pt[P(OR)_3]_4$ are shown in *Table 2*. For the straight chain alkyl derivatives, as well as the caged phosphite I, the RT. ^{31}P-NMR. spectra showed the expected triplet with reasonably narrow linewidths; however, for the isopropyl, phenyl and mixed phosphine-phosphite derivatives the RT. spectra revealed only very broad resonances. For these latter molecules satisfactory spectra were obtained at $-50°$. The dissociation of a phosphine ligand at RT. to afford tris-complexes of Pt(0) is well documented [2] [3]. As the temperature of the sample is lowered, the equilibrium shown in the equation is shifted

$$Pt(PR_3)_4 \rightleftarrows Pt(PR_3)_3 + PR_3 \ (R = \text{alkyl, aryl or alkoxy})$$

to the left. In the case of the straight chain phosphite derivatives, warming the sample tube has been shown to produce similar results [4] [5].

Addition of 1 mol of $P(OPh)_3$ to an NMR. tube containing a CH_2Cl_2 solution of II produces a new ^{31}P-NMR. spectrum of the type AX_3. Although we have not been able to isolate this derivative, its NMR. parameters are consistent with the structure $Pt[PPh_3][P(OPh)_3]_3$. The complex $Pt[PPh_3][P(O\text{-}p\text{-}ClC_6H_4)_3]_3$ has been mentioned in an earlier study [1]. Addition of further $P(OPh)_3$ resulted in the appearance of the resonance characteristic of free phosphite. Warming of this sample to RT. followed by re-cooling to $-50°$ produced no further changes in the ^{31}P-NMR. spectrum. Addition of 1 mol of phosphite to $Pt(PPh_3)_3$ afforded a solution containing primarily II.

Table 2. *NMR. Data for the Platinum Phosphite Complexes, Pt* [*P*(*OR*)$_3$]$_4$[a])

R =		δ^{31}P[b])	$\Delta\delta$	^1J(Pt, P)(Hz)
1 Et		127.5	−11.5	5386
2 *n*-Pr		127.4	−11.6	5371
3 *i*-Pr[d])		127.1	−10.5	5395
4 *n*-Bu[e])		127.2	−11.8	5388
5 		92.1	− 0.9	5836
6 Ph[d])		97.9	−30.2	5798
	PPh$_3$	12.2	+17.8	3430
7 Pt[PPh$_3$][P(OPh)$_3$]$_3$[f])	P(OPh)$_3$	98.8	−29.4	6033
	PPh$_3$	13.5	+19.1	3433
8 Pt[PPh$_3$]$_2$[P(OPh)$_3$]$_2$	P(OPh)$_3$	98.9	−29.3	6480
9 Pt[P(C$_2$H$_5$)$_3$]$_4$[g])		−17		3740
10 Pt[P(p-C$_7$H$_7$)$_3$]$_4$[h])		11	+19	3780
11 PtCl$_2$[P(OPh)$_3$]$_2$		67.5	−60.7	5695
12 PtI$_2$[P(OPh)$_3$]$_2$		59.2	−69.0	5520

[a]) Measured as CH$_2$Cl$_2$ solutions.
[b]) Relative to external H$_3$PO$_4$, ± 0.1 ppm.
[c]) A negative sign indicates an upfield shift.
[d]) Measured at −50°
[e]) Pure complex not isolated free from impurities.
[f]) Generated in solution by the addition of P(OPh)$_3$ to **8**.
[g]) Data from [3].
[h]) Data from [2].

Although the magnitude of ^1J(Pt,P) has been shown to provide useful structural information for complexes of Pt(II) [10], relatively little is known about this parameter for Pt(0). The complexes Pt[P(*p*-C$_7$H$_7$)$_3$]$_4$ [2] and Pt[P(C$_2$H$_5$)$_3$]$_4$ [3] show ^1J(Pt,P) couplings of 3780 and 3740 Hz respectively. These values are qualitatively similar in magnitude to the analogous bis-*cis* phosphinedichloro derivatives. Similarly there is only a relatively small difference between PtCl$_2$[P(OPh)$_3$]$_2$ (^1J(Pt,P) = 5,695 Hz) and Pt[P(OPh)$_3$]$_4$ (^1J(Pt,P) = 5,798 Hz); however, substitution of phosphite for phosphine (*e.g.* entries 7 and 8, *Table 2*) results in an increase in ^1J(Pt,P) for the phosphite and a decrease in ^1J(Pt,P) for the phosphine relative to Pt[P(*p*-C$_7$H$_7$)$_3$]$_4$ and Pt[PPh$_2$-(CH$_2$)$_3$PPh$_2$]$_2$ [11] (3780 and 3644 Hz respectively). It is tempting to ascribe these changes in coupling constant to some form of rehybridization of the platinum-phosphorus bond stemming from the differing σ and π-bonding capabilities of the two ligands in question; however, in view of the fact that the relative changes in ^1J(Pt,P) are of the order of 10% or less this type of hypothesis requires additional support before it can be seriously considered. We do note that in a recent report [11] concerning the molecules Pt[CH$_3$C(CH$_2$PPh$_2$)$_3$]X, the values ^1J(Pt,P) for the phosphite (X = P(OPh)$_3$) and the triphenyl phosphine (X = PPh$_3$) are 9,150 and 5,400 Hz respectively. These marked increases have been accounted for via a rehybridization argument.

For the open chain alkyl phosphites the one bond couplings fall in the narrow range 5371–5395 Hz. It is interesting that the isopropyl derivative is included in this grouping since its ^{31}P-NMR. spectrum is broad and featureless at RT. *Bradley & Venanzi* [5] have measured a significant difference in the activation parameters between $Pt[P(OEt)_3]_4$ and $Pt[P(O\text{-}i Pr)_3]_4$ ($\Delta H^{\pm} = 25.9$ kcal/mol^{-1}, $\Delta S = 21$ e.u. and $\Delta H = 14.7$ kcal/mol^{-1}, $\Delta S = 4.5$ e.u., respectively) for ligand dissociation. It would seem therefore, that the ground state properties of these complexes, as measured *via* ^{31}P-NMR., do not reflect the factors which influence the dissociation of phosphite ligands in these molecules. The value ^1J(Pt, P) for the caged complex, $Pt(I)_4$, is somewhat larger (5836 Hz) than the analogous alkyl derivatives. This might stem from the special nature of this ligand [12].

The coordination chemical shifts, $\Delta\delta$, for the phosphite complexes are given in *Table 2.* For all the phosphites coordination to Pt(0) produces an upfield shift while the reverse is true for PPh_3. It is interesting that the magnitude of $\Delta\delta$ for the $P(OPh)_3$ derivatives is a) considerably smaller for Pt(0) than for Pt(II) and b) essentially unchanged for entries 6–8. Similarly, there is little variance in the phosphine resonance position of 7, 8 and 10. The explanation for the changes in both chemical shift and coupling constant must await further knowledge of the NMR. characteristics of these systems.

We wish to thank the *Swiss National Science Foundation* for support.

REFERENCES

[1] *L. Malatesta & C. Cariello*, J. chem. Soc. 1958, 2323; b) *H. Kurusowa*, J. Organomet. Chemistry *112*, 369 (1976); c) *R. A. Schunn*, Inorg. Chemistry *15*, 208 (1976); d) *F. Faraone & S. Sergi*, J. organomet. Chemistry *112*, 201 (1976); *R. Ugo, F. Cariati & G. La Monica*, Inorg. Synth. XI, 105 (1968).

[2] *C. A. Tolman, W. C. Seidel & D. H. Gerlach*, J. Amer. chem. Soc. *94*, 2669 (1972).

[3] *D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson & E. L. Muetterties*, J. Amer. chem. Soc. *93*, 3543 (1971).

[4] *M. Meier, F. Basolo & R. G. Pearson*, Inorg. Chemistry *8*, 795 (1969).

[5] *J. S. Bradley*, D. Phil Thesis, Oxford 1971.

[6] *M. Meier & F. Basolo*, Inorg. Synth. *13*, 115 (1972).

[7] *J. J. Levison & S. D. Robinson*, Inorg. Synth. *13*, 109 (1972).

[8] *N. Ahmad, E. Ainscough, T. A. James & S. D. Robinson*, J. chem. Soc. Dalton 1973, 1148.

[9] *F. H. Allen, A. Pidcock & C. Waterhouse*, J. chem. Soc. Dalton 1970, 2087.

[10] *A. Pidcock, R. E. Richards & L. M. Venanzi*, J. chem. Soc. Dalton, 1966, 1707; b) *S. O. Grim, R. L. Keiter & W. McFarlane*, Inorg. Chemistry *6*, 1133 (1967).

[11] *J. Chatt, R. Mason & D. W. Meek*, J. Amer. chem. Soc. *97*, 3826 (1975).

[12] *J. G. Verkade*, Coord. chem. Rev. *9*, 1 (1972/73).