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^{31}P and ^{195}Pt NMR Studies on the Triangular Cluster Complexes $[Pt_3(\mu\text{-}CO)_3(\text{tertiary phosphine})_4]$

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^{31}P and ^{195}Pt NMR data for the triangular clusters $[Pt_3(\mu\text{-}CO)_3L_4]$ (L = PEt_3, PMe_2Ph, $PMePh_2$, PEt_2Bu^t, $P(CH_2Ph)Ph_2$) are reported. The ^{31}P measurements show the presence of non-equivalent phosphines and the ^{195}Pt spectra identify the two different types of platinum. There are two markedly different $^1J(^{195}Pt, ^{195}Pt)$ coupling constants with ranges of 1808–1840 Hz (base to base) and 385–586 Hz (top to base), as well as different $^2J(^{195}Pt, ^{31}P)$ values, 411–459 Hz and 272–292 Hz. The two $^1J(^{195}Pt, ^{31}P)$ coupling constants also vary considerably and depend upon the number of coordinated phosphine ligands. These and the remaining NMR data suffice for purposes of proof of structure.

Introduction

There is an increasing interest in the chemistry of cluster complexes, due in part to their possible relation to metal surfaces [1]. X-ray crystallography has made a major contribution to the understanding of the structural aspects of cluster chemistry; however, the dynamic aspects of the solution properties are more suitable for study using NMR methods [2]. The chemistry of platinum carbonyl complexes has benefited from both of these methods. Solid state structures for several triangular 'Pt_3' units are known [3–5], as are those for several heteronuclear platinum clusters [6]. There are only a few reports concerned with the solution structures of such molecules, *e.g.*, the multinuclear study on the stacked triangles $[Pt_3(\mu\text{-}CO)_3]_n^{2-}$ [7]. We have recently shown [8] that the phosphine-containing triangular compounds $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ are especially amenable to NMR study and that both ^{31}P and ^{195}Pt methods potentially provide insight into the nature of the metal–ligand interactions. Specifically we noted that the values $^2J(^{195}Pt, ^{31}P)$ were relatively large, *i.e.* 413–488 Hz, and that the one-bond metal–metal coupling constant, $^1J(^{195}Pt, ^{195}Pt)$ (1571–1770 Hz) seemed reasonable for direct metal–metal bonds. A complete analysis of the various sub-spectra arising from the most abundant ^{195}Pt isotopomers was shown to be relatively simple.

To further our knowledge of the chemistry and physical properties of such small platinum clusters, we have extended our studies to the complexes $[Pt_3(\mu\text{-}CO)_3L_4]$ (L = tertiary phosphine).

This type of complex is more complicated spectroscopically, since it contains two different types of platinum. Despite their complexity, these molecules give interpretable spectra and we report here our ^{31}P and ^{195}Pt results.

Experimental

The ligands PEt_3 [9], $P(CH_2Ph)Ph_2$ [10] and PBu^tEt_2 [9, 11] were prepared according to the literature, whereas PMe_2Ph and $PMePh_2$ were purchased from Fluka AG, Buchs, Switzerland. *Cis*-$[PtCl_2(PMe_2Ph)_2]$ [12] and $[Pt_3(\mu\text{-}CO)_3(P(CH_2Ph)Ph_2)_3]$ [13] were prepared using standard methods and $[Pt(COD)_2]$ (COD = 1,5-cyclooctadiene) was purchased from Emser Werke, Zurich.

^{31}P and ^{195}Pt NMR spectra were measured as solutions in 10 mm tubes using Bruker HX-90 and WM-250 NMR spectrometers operating at 36.43 and 101.27 MHz for ^{31}P and 19.34 and 53.77 MHz for ^{195}Pt. Pulse angles were of the order of 45–50° for both nuclei, with acquisition times of ~0.7 and 0.2 sec, respectively. Spectral simulations were performed using the program PANIC provided by the manufacturer. IR spectra were measured using a Beckmann IR 4250 spectrometer.

$[Pt_3(\mu\text{-}CO)_3(PMe_2Ph)_4]$

A suspension of 3 g (5.5 mmol) *cis*-$[PtCl_2(PMe_2Ph)_2]$ in methanol (60 ml) was treated with 1 ml of hydrazine hydrate and then boiled for 10 min. The resulting yellow solution was saturated with carbon monoxide, after which 1 g of potassium hydroxide in 5 ml water was added. The mixture was kept at 60° for 30 min and then boiled for five minutes. The dark red solution, on standing for 2 days

TABLE I. IR and Microanalytical Data for $[Pt_3(\mu\text{-}CO)_3L_4]$.

L	Carbonyl stretching vibrations (Nujol)	Microanalyses; Calc. (Found)		
		C	H	P
PEt_3	1808w, 1760vs, 1745sh			
PMe_2Ph	1825w, 1772vs, 1750vs	34.40 (34.27)	3.63 (3.47)	10.14 (9.96)
$PMePh_2$	1840w, 1792vs, 1772vs	44.93 (43.82)	3.57 (3.45)	8.43 (7.70)
PBu^tEt_2*	1822w, 1760sb, 1752sh			
$P(CH_2Ph)Ph_2$	1835wb, 1785sh, 1765sb	53.47 (53.70)	3.86 (4.19)	6.98 (6.93)

*No satisfactory analytical data could be obtained; however, the structure of the complex is clear from its solution NMR properties.

under carbon monoxide precipitates $[Pt_3(\mu\text{-}CO)_3(PMe_2Ph)_4]$ as violet plates (1.23 g, 54%).

$[Pt_3(\mu\text{-}CO)_3(PEt_3)_4]$

$[Pt(COD)_2]$ (0.42 g; 0.10 mmol) was dissolved in 15 ml petroleum ether (30–60 °C) under ethylene at 0 °C. Addition of PEt_3 (0.3 ml; 2.0 mmol) gave a pale-yellow solution which was saturated with carbon monoxide and then allowed to stand for 0.5 h. Removal of solvent *i.v.* gave an oily red residue which was extracted with boiling methanol. On cooling $[Pt_3(\mu\text{-}CO)_3(PEt_3)_4]$ crystallized as red plates (0.12 g; 32%).

$[Pt_3(\mu\text{-}CO)_3(PMePh_2)_4]$

$[Pt(COD)_2]$ (0.42 g; 1.0 mmol) was dissolved in 15 ml of petroleum ether (30–60 °C) at 0 °C. Addition of $PMePh_2$ (0.3 ml; 1.6 mmol), followed by saturation with carbon monoxide and standing for 0.5 h, resulted in the deposition of a red-brown powder. Removal of the solvent *i.v.* and extraction of the residue with hot toluene (70 °C) afforded the product as red crystals after precipitation with methanol (0.22 g; 45%).

$[Pt_3(\mu\text{-}CO)_3(PBu^tEt_2)_4]$ and $[Pt_3(\mu\text{-}CO)_3(PBu^t\text{-}Et_2)_3]$

The procedure described for the $PMePh_2$ complex was followed except that the extraction was performed with 3 ml of hot acetone from which the product crystallized as red needles. From $[Pt(COD)_2]$ (0.42 g; 1.0 mmol) and PBu^tEt_2 (1.1 mmol) 0.11 g (26%) of tetrakis phosphine cluster were obtained. Crystallization of the residue from toluene/methanol in a nitrogen atmosphere gave the tris phosphine cluster $[Pt_3(\mu\text{-}CO)_3(PBu^tEt_2)_3]$ (0.17 g; 46%).

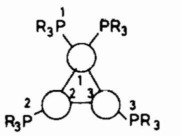
$[Pt_3(\mu\text{-}CO)_3(P(CH_2Ph)Ph_2)_4]$

Solid $[Pt_3(\mu\text{-}CO)_3(P(CH_2Ph)Ph_2)_3]$ (0.20 g; 0.13 mmol) was added to solid $P(CH_2Ph)Ph_2$ (0.05 g; (0.18 mmol) and the mixture extracted with 5 ml ether. Addition of petroleum ether precipitated the product as a red powder (0.11 g; 48%).

Some microanalytical and IR data for the complexes are given in Table I.

Results

Any nuclear magnetic resonance study of polynuclear platinum complexes is complicated by the relative distributions of ^{195}Pt, I = ½ (natural abundance = 33.7%). For the complexes $[Pt_3(\mu\text{-}CO)_3L_4]$ these are:



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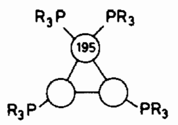
(I)



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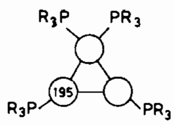
(II)



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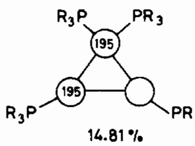

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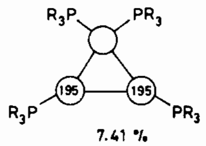

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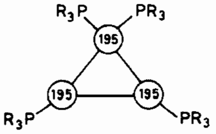
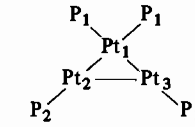


3.71%
(VI)

TABLE II. NMR Data[a] for the Cluster Complexes.

[$Pt_3(\mu\text{-}CO)_3L_4$]



L	δP_1	δP_2	δPt_1	δPt_2	$^1J(Pt_1Pt_2)$	$^1J(Pt_2Pt_3)$	$^1J(Pt_1P_1)$	$^1J(Pt_2P_2)$	$^2J(Pt_1P_2)$	$^2J(Pt_2P_1)$	$^2J(Pt_2P_3)$	$^3J(P_2,P_3)$	$^3J(P_1,P_2)$
PEt_3[b]	33.7	60.8	−3908	−3883	586	1830	3621	4463	445	272	411	65	21
PMe_2Ph[c,d]	8.8	35.6	−3760	−3949	507	1840	3611	4643	487	292	427	55	21
$PMePh_2$[f]	24.5	49.8	−3828	−3970			3651	4614	519	282	453	68	21
PEt_2Bu^t[e]	47.0	82.5	−3836	−3758	385	1808	3741	4317	440	270	459	70	25
$P(CH_2Ph)Ph_2$[g]	43.8	60.0	−3855	−4066			3615	4849	455	272	435	60	20
[$Pt_3(\mu\text{-}CO)_3(PEt_2Bu^t)_3$][h]	73.8		−4445		1595		4430		435			59	

[a] Chemical shifts are in ppm (H_3PO_4 for ^{31}P; Na_2PtCl_6 for ^{195}Pt). For ^{195}Pt, the frequency difference was divided by 53.77; coupling constants are in Hz. [b] Toluene, 220 K. [c] ^{31}P in toluene/acetone. [d] ^{195}Pt in CH_2Cl_2/C_6D_6 at 197 K. [e] CH_2Cl_2/C_6D_6, 203 K. [f] CH_2Cl_2/toluene, 179 K. [g] CH_2Cl_2/Freon 11, 203 K. [h] CH_2Cl_2/C_6D_6.

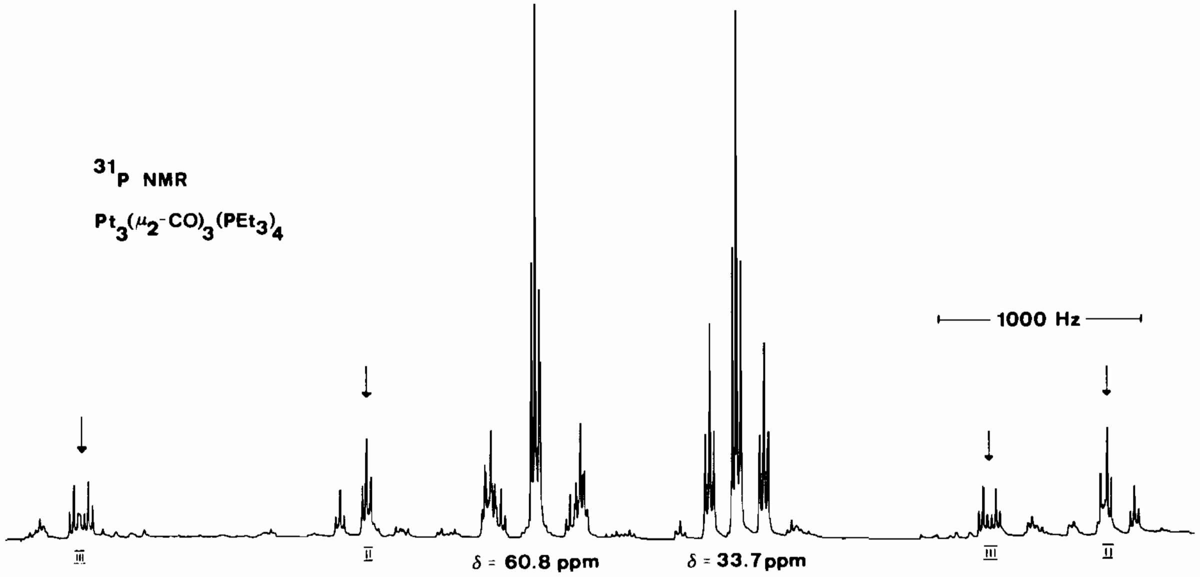


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of [$Pt_3(\mu\text{-}CO)_3(PEt_3)_4$]. II and III are found *via* the ^{195}Pt satellites, marked with arrows.

where the symbol 195 indicates the presence of a ^{195}Pt atom.

Before attempting to analyse our NMR spectra we can simplify the interpretation by recognizing that I gives a relatively simple* A_2X_2 ^{31}P spectrum and no metal spectrum, whereas VI due to its low abundance can be ignored**. Consequently we must concern ourselves with only four potentially complex spin systems. *We shall refer to the unique Pt and to its two coordinated tertiary phosphines as Pt_1 and P_1, respectively, whereas the remaining metals and phosphines will be Pt_2 and Pt_3 with P_2 and P_3, respectively.* For II, assuming that the two phosphorus types are sufficiently separated, we have an A_2M_2X system ($X = {}^{195}$Pt). This should show a ^{31}P spectrum similar to I, with the addition of a one-bond interaction to P_1 and two-bond couplings to P_2 and P_3. In species of type III we encounter our first strongly coupled spin system. The spins P_2 and P_3 are no longer magnetically equivalent and we have a spectrum of A_2MNX type. This magnetic non-equivalence of P_2 and P_3 is also present in IV and V (A_2MNXY and $A_2MM'XX'$, respectively), with the result that these NMR spectra for P_2, P_3, Pt_2 and Pt_3 will be considerably more complex than for P_1 and Pt_1. Nevertheless, II and III should be readily recognizable in the ^{31}P spectra since the ^{195}Pt satellites could appear as pseudo first-order multiplets.

^{31}*P NMR*

The $^{31}P\{^1H\}$ spectrum for $[Pt_3(\mu\text{-}CO)_3(PEt_3)_4]$ is shown in Fig. 1. The most intense features are the two triplets at δ = 60.8 and 33.7 from I, which show that four ^{31}P spins are present and therefore that the cluster contains different metal atoms and consequently cannot be a symmetrical cluster *e.g.* $[Pt_3(\mu\text{-}CO)_3(PEt_3)_3]$. Inspection of the ^{195}Pt satellite spectra shows the presence of II and III and allows the calculation of preliminary values of $^1J(^{195}Pt_1, {}^{31}P_1)$, $^1J(^{195}Pt_2, {}^{31}P_2)$, $^2J(^{195}Pt_1, {}^{31}P_2)$, $^2J(^{195}Pt_2, {}^{31}P_1)$, $^2J(^{195}Pt_2, {}^{31}P_3)$, $^3J(^{31}P_1, {}^{31}P_2)$ and $^3J(^{31}P_2, {}^{31}P_3)$. Refinement of these coupling constants gave the data shown in Table II.

The following points are worthy of note:

1) The two one-bond Pt–P coupling constants differ markedly with $^1J(^{195}Pt_1, {}^{31}P_1)$ (3611–3741 Hz) being smaller than $^1J(^{195}Pt_2, {}^{31}P_2)$ (4317–4849 Hz) thereby allowing the assignment of the ^{31}P spectra.

2) The two-bond coupling constants involving Pt_2 with P_1 (270–292 Hz) and P_3 (411–459 Hz) are quite different.

3) The three-bond coupling between the phosphorus atoms also vary: $^3J(P_2, P_3)$ being 55–70 Hz and $^3J(P_1, P_2)$ being 21–25 Hz.

4) All of the coupling constants involving only Pt_2, P_2 and P_3 are similar to those found in the $[Pt_3(\mu\text{-}CO)_3L_3]$ complexes [8].

^{195}*Pt NMR*

The $^{195}Pt\{^1H\}$ spectra show the two types of platinum environment, although the chemical shift differences are not especially large, *e.g.* for the PEt_3 complex the ^{195}Pt resonances are separated by only 25 ppm; indeed in several compounds resonances overlap. In some cases Pt_1 resonates at higher field, but the reverse is also observed. These chemical shifts are at the low-field end of the range observed for other Pt(0) complexes [14].

The two metal–metal coupling constants differ by more than 1200 Hz with $^1J(^{195}Pt_1, {}^{195}Pt_2)$ = 385–586 Hz and $^1J(^{195}Pt_2, {}^{195}Pt_3)$ = 1808–1840 Hz, with the latter being close to the 1571–1770 Hz range found in the $[Pt_3(\mu\text{-}CO)_3P_3]$ analogs. The Pt_1 signals of $[Pt_3(\mu\text{-}CO)_3(PMe_2Ph)_4]$ are shown in Fig. 2. This spectrum is essentially the sum of the spectra of II and IV and it is noteworthy in that $^1J(^{195}Pt, {}^{195}Pt)$ is similar to $^2J(^{195}Pt, {}^{31}P)$ thereby creating pseudo quartet structure for IV.

Discussion

From the spectroscopic results it is clear that the addition of a fourth phosphine to $[Pt_3(\mu\text{-}CO)_3L_3]$, as shown in the equation,

$$[Pt_3(\mu\text{-}CO)_3L_3] + L \rightarrow [Pt_3(\mu\text{-}CO)_3L_4]$$

causes changes in the electronic structure of the cluster. These seem to be mainly localized at Pt_1 since the NMR parameters for Pt_2 and P_2 resemble those of the tris phosphine precursor. The most obvious changes concern the two one-bond coupling constants $^1J(^{195}Pt_1, {}^{31}P_1)$ and $^1J(^{195}Pt_1, {}^{195}Pt_2)$, both of which decrease when the fourth phosphine coordinates. Since there is a known correlation between $^1J(^{195}Pt, {}^{31}P)$ and Pt–P bond lengths [15], it is tempting to seek a connection between our data and the solid state structural information. Comparison of the structures of $[Pt_3(\mu\text{-}CO)_3(P(cyclohexyl)_3)_3]$, VII, [5] and $[Pt_3(\mu\text{-}CO)_3(P(cyclohexyl)_3)_4]$, VIII, [4] shows that a) the Pt_1–P_1 bond length in VIII is longer than that in VII (an average of 2.350 Å as opposed to an average of 2.275 Å) and b) the Pt_1–Pt_2 bond in VIII is longer than that in VII (2.725 Å vs. 2.654 Å). Although VIII cannot be obtained in solution, presumably because of the steric bulk of the $P(cyclohexyl)_3$ ligand, we believe that our data for the complexes of the other

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*The ^{31}P chemical shifts are sufficiently separated so as not to observe A_2B_2 character.

**There is no information lost since IV and V provide the two types of one-bond metal–metal coupling constants, assuming no isotope effects.

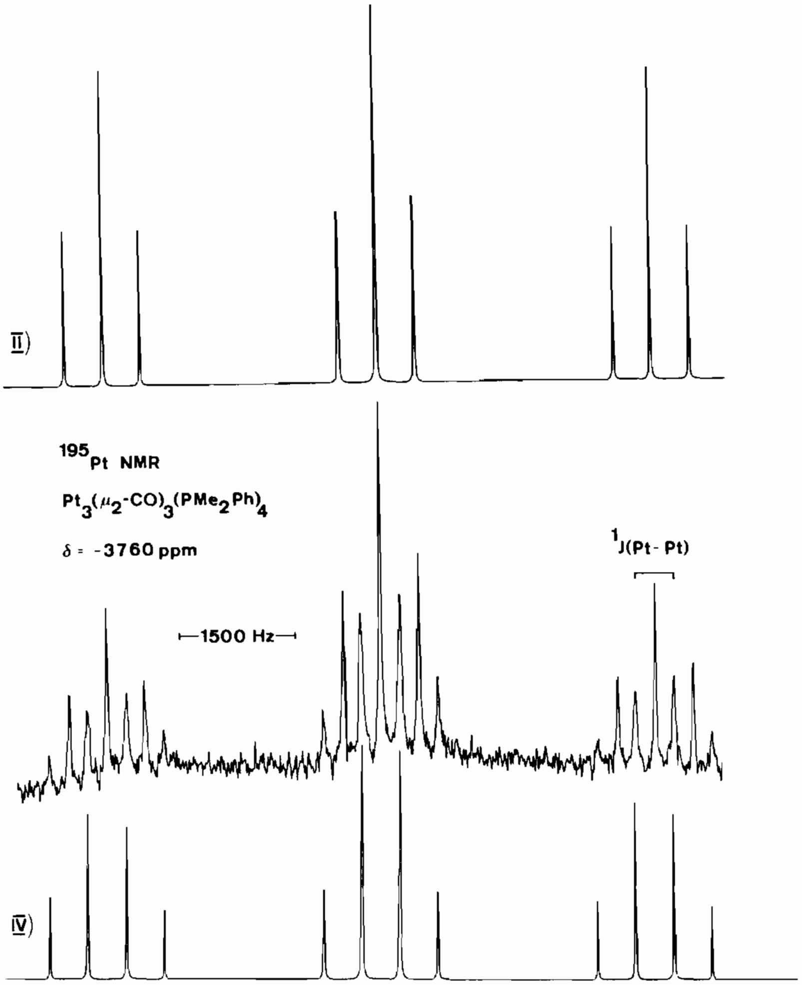

Fig. 2. $^{195}Pt\{^1H\}$ spectrum for Pt_1 (middle) in $[Pt_3(\mu\text{-}CO)_3(PMe_2Ph)_4]$ along with the simulations for II (above) and IV (below).

phosphine ligands reflect the connection between one-bond coupling constants $^1J(^{195}Pt, ^{195}Pt)$ and bond lengths l(Pt,Pt). This correlation is unusual in that, to date, there appears to be no general relationship between these two physical parameters in the dozen or so complexes for which data are available [14, 16].

The magnitude of $^1J(^{195}Pt, ^{195}Pt)$ also deserves some comment. For the complexes where this one bond interaction is ≫1 KHz, one normally finds short metal–metal separations; however, a small $^1J(^{195}Pt, ^{195}Pt)$ need not imply a longer distance. Thus for $[Pt_2Cl_2(CO)_2(PPh_3)_2]$ $^1J(^{195}Pt, ^{195}Pt)$ = 760 and l(Pt, Pt) = 2.584(2) Å [16] while in the cationic bridging hydride complex $[(PEt_3)_2Pt(\mu\text{-}H)_2Pt(C_6H_5)(PEt_3)_2]^+$; $^1J(^{195}Pt, ^{195}Pt)$ = 796 Hz and l(Pt, Pt) = 2.819 Å [17]. Further, our $^1J(^{195}Pt_1, ^{195}Pt_2)$ values (385–586 Hz) are smaller than the above, although the separation of these metals is not large. Clearly, we are still in the learning stage where such coupling constants are concerned.

We note in passing that for $[Pt(PEt_3)_4]$, $^1J(^{195}Pt, ^{31}P)$ = 3740 Hz, whereas for $[Pt(PEt_3)_3]$, $^1J(^{195}Pt, ^{31}P)$ = 4220 Hz [18], and suggest that the observed changes in $^1J(^{195}Pt, ^{31}P)$ in going from $[Pt_3(\mu\text{-}CO)_3P_3]$ to $[Pt_3(\mu\text{-}CO)_3L_4]$ may be related to the simple expansion of the coordination number of the platinum.

We have not been successful in obtaining $^1J(^{195}Pt, ^{195}Pt)$ data for the $PMePh_2$ and $P(CH_2Ph)Ph_2$ complexes. For the PEt_3 complex sharp spectra are observed at about 220 K, whereas for the PEt_2Bu^t, PMe_2Ph and PPh_3* analogs lower temperatures are required, with the latter showing sharp features only at 163 K. Curiously, the $PMePh_2$ and $P(CH_2Ph)Ph_2$

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*R. Roulet, unpublished results.

analogs reveal two phases of dynamic behavior. The ^{31}P NMR resonances sharpen in the region around 200 K, but become broader again as the temperature is lowered. Solvent freezing occurs below 163° before a static situation is reached. The spectral quality was insufficient for a complete interpretation, due to the line broadening associated with the lower activation energy process. In view of the sharp spectra obtainable with the PEt_3 and PPh_3 complexes we suspect that slow rotation about the Pt–P bonds, with the consequent development of rotational isomers, may be associated with the second process. The presence of such rotational isomers in the $[Pt_3(\mu\text{-}CO)_3P_4]$ complexes presumably derives from the local crowding at Pt_1.

The inability to generate the complex with $P(cyclohexyl)_3$ in solution, along with the observation that the PBu^tEt_2 derivative has a lower exchange activation energy, suggests the importance of steric effects. This topic will be discussed separately [19].

References

1 E. L. Muetterties, *Bull. Soc. Chim. Belg., 84,* 959 (1975).

2 S. Aime and L. Milone, 'Progress in NMR Spectroscopy', Pergamon Press, 1977, vol. 11, p. 183.

3 J. C. Calabrese, L. F. Dahl, P. Chini, G. Longoni and S. Martinengo, *J. Am. Chem. Soc., 96,* 2614 (1974). See also ref. 7.

4 A. Albinati, G. Carturan and A. Musco, *Imorg. Chim. Acta, 16,* L3 (1976).

5 A. Albinati, *Inorg. Chim. Acta, 22,* L31 (1977).

6 P. Braunstein, J. Dehand and J. F. Nennig, *J. Organomet. Chem., 92,* 117 (1975).

7 C. Brown, B. T. Heaton, A. D. C. Towl, A. Fumagalli and C. Longoni, *J. Organomet. Chem., 181,* 233 (1979).

8 A. Moor, P. S. Pregosin and L. M. Venanzi, *Inorg. Chim. Acta, 48,* 153 (1981).

9 Houben-Weyl, 'Methoden der Org. Chemie', Georg Thieme Verlag, Stuttgart, 1963, 4th Ed. XII/1 p. 33.

10 *Ibid.,* p. 52.

11 Th. Weil, B. Prijs and H. Erlenmeyer, *Helv. Chim. Acta,* 1413 (1952).

12 S. O. Grim, R. L. Keiter and W. McFarlane, *Inorg. Chem., 6,* 1133 (1967).

13 J. Chatt and P. Chini, *J. Chem. Soc. A,* 1538 (1970).

14 P. S. Pregosin, to appear in *Coord. Chem. Revs.,* 1982.

15 G. G. Mather, A. Pidcock and G. N. Rapsey, *J. Chem. Soc. Dalton,* 2095 (1973).

16 N. M. Boag, J. Browning, C. Crocker, P. L. Goggin, R. J. Goodfellow, M. Murray and J. L. Spencer, *J. Chem. Res. S,* 228 (1978); *J. Chem. Res. M,* 2962 (1978).

17 F. Bachechi, G. Bracher, D. M. Grove, B. Kellenberger, P. S. Pregosin, L. M. Venanzi and L. Zambonelli, unpublished results.

18 D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson and E. L. Muetterties, *J. Am. Chem. Soc., 93,* 3543 (1971).

19 A. Moor, P. S. Pregosin and L. M. Venanzi, unpublished results.