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^{31}P and ^{195}Pt NMR Studies of the Cluster Complexes [Pt$_3$(μ_2-CO)$_3$ (tertiary phosphine)$_3$]

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^{31}P and ^{195}Pt NMR data for the triangular clusters [Pt$_3$(μ_2-CO)$_3$(tertiary phosphine)$_3$] tertiary phosphine = PCy$_3$, PPr$^i_3$, PPr$^i_2$Ph, P(CH$_2$Ph)Ph$_2$, are reported. The nuclearity of the complexes in solution is readily identified via *^{31}P NMR using the multiplicity data in the ^{195}Pt satellites. The values $^1J(^{195}Pt,^{195}Pt)$ have been measured and fall in the range 1571–1619 Hz. It is suggested that the values $^2J(^{195}Pt,^{31}P)$ and $^3J(^{31}P,^{31}P)$ can be useful indicators for the presence of platinum–platinum bonds.*

Introduction

Many transitions of metal clusters have enjoyed increasing attention in recent times due to their value, as both models for heterogeneous catalysts [1] and actual catalysts in organic synthesis [2]. That the chemistry of platinum clusters has not been excepted is evidenced by a current review [3] describing synthetic pathways to these molecules. Specifically, several groups have drawn attention to the wide variety of structural possibilities obtainable for polynuclear platinum–phosphine carbonyl complexes. Thus, the structures of [Pt$_3$(μ_2-CO)$_3$[P(cyclohexyl)$_3$]$_3$] [4], [Pt$_3$(μ_2-CO)$_3$[P(cyclohexyl)$_3$]$_4$] [5], [Pt$_4$(μ_2-CO)$_5$(PMe$_2$Ph)$_4$] [6] and [Pt$_5$(μ_2-CO)$_5$(CO)(PPh$_3$)$_4$ [7] as well as those for the stacked triangles [Pt$_3$(CO)$_3$(μ_2-CO)$_3$]$^{2-}_n$, n = 2–5 [8], have been described. Although X-ray crystallography and IR spectroscopy are important structural methods in the solid state only the latter is currently available for the solution assignment.

Consequently, we thought it of value to investigate the potential for using ^{31}P and ^{195}Pt NMR spectroscopy in this area. These NMR probes can help in the identification of the number, type and relative orientation of these two nuclear spins and thus complement the IR measurements which concern themselves primarily with the C≡O ligands.

In addition, the analysis of these NMR spectra gives the one-bond coupling constant ^{1}J(^{195}Pt,^{195}Pt) for which there is only a sparse literature. A more thorough knowledge of this parameter could provide an empirical way of obtaining insight into the factors determining the nature of the metal–metal bond. For our initial studies we have chosen a relatively small cluster and report here our results for the triangular platinum complexes [Pt$_3$(μ_2-CO)$_3$(tertiary phosphine)$_3$].

Experimental

^{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 a) 36.43 and 101.27 MHz for ^{31}P and b) 19.34 and 53.77 MHz for ^{195}Pt. Typical pulse angles for both nuclei were 40–45° with acquisition times of ~0.7 and 0.2 sec, respectively, for ^{31}P and ^{195}Pt. Coupling constants are in Hz (±3) and chemical shifts in ppm (±0.1 for ^{31}P, ±0.5 for ^{195}Pt). Solvents and temperatures for the measurements are given in Table I. Spectral simulations were made using the programs NMRCAL and PANIC provided by the instrument manufacturer. IR spectra were measured using a Beckman IR 4250.

Preparation of the Complexes

Tricyclohexyl phosphine, as its CS$_2$ adduct, and triisopropyl phosphine were obtained from Strem Chemicals Inc. Diisopropylphenyl phosphine [10] and benzyldiphenyl phosphine [11] were prepared following literature methods as were *trans*-[PtHCl(PCy$_3$)$_2$] [12] and *trans*-[PtHCl(PPr$^i_3$)$_2$] [13]. [Pt(COD)$_2$] was purchased from Emser Werke, Zurich and [Pt$_3$(CO)$_3$(P(CH$_2$Ph)Ph$_2$)$_3$)] was prepared using the method of Chatt and Chine [14].

[Pt$_3$(CO)$_3$(PCy$_3$)$_3$]

A suspension of *trans*-[PtHCl(PCy$_3$)$_2$] (1.0 g, 1.3 mmol) in 50 ml ethanol was brought to a boil in a carbon monoxide atmosphere and treated immediately with 10 ml 0.1 *M* KOH. After refluxing for 1 h the dark suspension was filtered hot and the resulting brown powder recrystallized from toluene-ethanol to

TABLE I. ^{31}P and ^{195}Pt NMR Data[a] for the Complexes $[Pt_3(\mu_2\text{-}CO)_3(\text{tertiary phosphine})_3]$.

Phosphine	$\delta\,^{31}P$[b]	$\delta\,^{195}Pt$[c]	$^1J(^{195}Pt,^{195}Pt)$[d]	$^1J(^{195}Pt,^{31}P)$	$^2J(^{195}Pt,^{31}P)$[d]	$^3J(^{31}P,^{31}P)$[d]
PCy_3[e]	69.8	−4392	1571	4412	430	58
PPr^i_3[f]	81.6	−4530	1607	4422	419	56
PPr^i_2Ph[g]	76.7	−4450	1610	4605	453	57
$P(CH_2Ph)Ph_2$[h]	55.6	−4448	1619	4751	488	63
PBu^t_2Me[i]	68.4		1770	4724	413	51

[a] Chemical shifts are in ppm, coupling constants in Hz; ±3. [b] Relative to H_3PO_4 at room temperature. [c] Relative to Na_2PtCl_6 at room temperature. [d] This may be a sum if there is a coupling pathway *via* the carbonyl. [e] Cy = cyclohexyl; in toluene at room temperature. [f] In acetone at −10 °C. [g] Acetone/toluene at 273 K. [h] Methylene chloride at 273 K. [i] Data from ref. 9.

afford 0.57 g of product as a mono-toluene solvate (85% yield based on platinum).

$[Pt_3(CO)_3(PPr^i_3)_3]$

A suspension of *trans*-$[PtHCl(PPr^i_3)_2]$ (1.2 g, 2.3 mmol) in 20 ml ethanol was warmed under a CO atmosphere until the complex dissolved. Solid potassium hydroxide (1.0 g, 17.8 mmol) was then added and the reaction mixture refluxed for 2 h. After cooling to room temperature the resulting suspension was filtered to afford 0.67 g of product as a red powder (77% yield based on platinum).

$[Pt_3(CO)_3(PPr^i_2Ph)_3]$

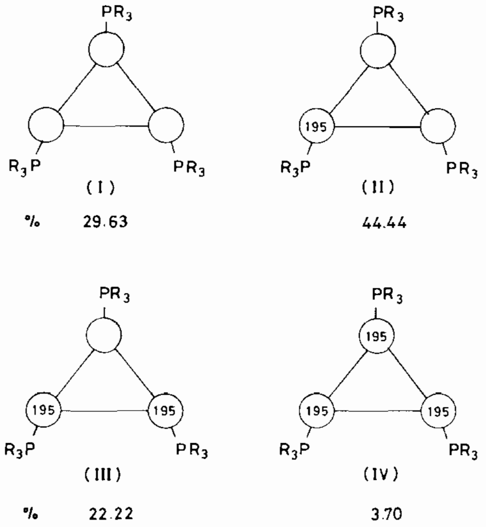
$[Pt(1,5\text{-cyclo-octadiene})_2]$ (0.83 g, 2.0 mmol) was added in small portions, over a 15 min period, to a saturated solution of ethylene in 15 ml of petroleum ether (30–60°) at 0 °C. PPr^i_2Ph (0.42 ml, 2.0 mmol) was then injected and the reaction mixture filtered to remove small quantities of insoluble impurities. The filtrate was then treated with carbon monoxide for 10 min and the reaction mixture brought to room temperature. Concentration of the solution gave an oil which was recrystallized from acetone-methanol to afford 0.52 g of product as red needles (62% yield based on platinum). In Table II are given some microanalytical data as well as CO IR stretching frequencies for the complexes.

Results and Discussion

Isotopomers and Subspectra

In contrast to the NMR spectroscopy for clusters of other transition metals, spectra derived from polynuclear platinum complexes are complicated by the presence of a mixture of isotopomers. These arise from the differing isotopic distributions of ^{195}Pt, I = 1/2, natural abundance = 33.7%.

To properly analyse the ^{31}P and ^{195}Pt spectra for these molecules we will need a clear picture of the spin systems which we will encounter. For a triangle of metals with three tertiary terminal phosphines and three bridging carbonyls we can write the isotopomers I–IV, which are given together with their relative abundances.



(The carbonyls are omitted for clarity)

The open circles represent non-NMR active nuclei whereas the 195 symbol indicates the presence of ^{195}Pt. The most abundant species is that containing a single ^{195}Pt and this isotopomer, (II), affords an AA'_2X spin system using the labels A = ^{31}P, X = ^{195}Pt. The next most abundant is I which is an A_3 type, followed by III, an AA′A″XX′ system, in turn followed by IV which can be symbolized as AA′A″XX′X″. For IV the combination of low natural abundance and spectral complexity results in only very weak signals which need not concern us*. Since the ^{31}P spectrum of I is only a single line we need only involve ourselves with II and III. The ^{31}P and ^{195}Pt spectra for these two spin systems are, by definition, not suitable for a first order analysis. Fortunately, access to both an ample

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*There is no additional information to be obtained from this isotopomer other than that relating to possible isotope effects.

TABLE II. IR and Microanalytical Data for the Complexes $\{Pt_3(\mu_2\text{-}CO)_3(\text{tertiary phosphine})_3\}$.

Tertiary Phosphine	Carbonyl Stretching Frequencies	Microanalytical Data: Calcd. (found) C	H	P
PCy_3[a]	1840w, 1770vs, 1737w	45.32 (45.42)	6.61 (6.71)	6.15 (6.20)
PPr^i_3[a]	1838w, 1770vs[b], 1738sh	31.33 (31.40)	5.52 (5.66)	8.08 (7.97)
PPr^i_2Ph[a][b]	1865w, 1800s, 1785s, 1760sh [a] 1863w, 1805s, 1798sh, 1788s, 1764vw [b]	37.41 (37.54)	4.59 (4.54)	7.42 (7.69)
$P(CH_2Ph)Ph_2$	1855w, 1795s, 1788s, 1760sh, 1750sh	48.10 (48.17)	3.43 (3.31)	6.20 (6.40)

[a] Nujol. [b] Hexane.

NMR literature [15] and spectral simulation computer programs permits a ready analysis, allowing a certain input due to experience. For example, in II, we expect that there will be a splitting in both the ^{31}P and ^{195}Pt spectra due to the ~4 KHz large $^1J(^{195}Pt,^{31}P)$ coupling [16]. This has the effect of reducing the spin system to a pseudo first order AM_2X type, for which we may estimate $^1J(^{195}Pt,^{31}P)$ and $^2J(^{195}Pt,^{31}P)$ (from either the ^{31}P or ^{195}Pt spectra) and $^3J(^{31}P,^{31}P)$ (from the ^{31}P spectrum). In III we make a similar approximation and consider that the ^{31}P spin *not* on ^{195}Pt (and therefore whose resonance frequency is several KHz from the remaining ^{31}P lines) will give a pseudo first order splitting of the remaining AA'XX' sub-system. The analysis of this simple second-order four spin grouping is straightforward [15] and will yield $^1J(^{195}Pt,^{195}Pt)$. The results which we obtain from these approximations can then be used as input for the computer program in order to refine the data.

^{31}P NMR

In Fig. 1 we show the $^{31}P\{^1H\}$ spectrum for $[Pt_3(\mu_2\text{-}CO)_3(PCy_3)_3]$. The large signal, in the center of the spectrum, stems as expected from I. Proceeding, the most intense signals in the ^{195}Pt satellites show considerable first order character and indeed this doublet of triplets may be assigned to the A resonance of II. These signals arise from the large one-bond metal–phosphorus coupling further split by the two equivalent A' ^{31}P atoms. The A' lines appear

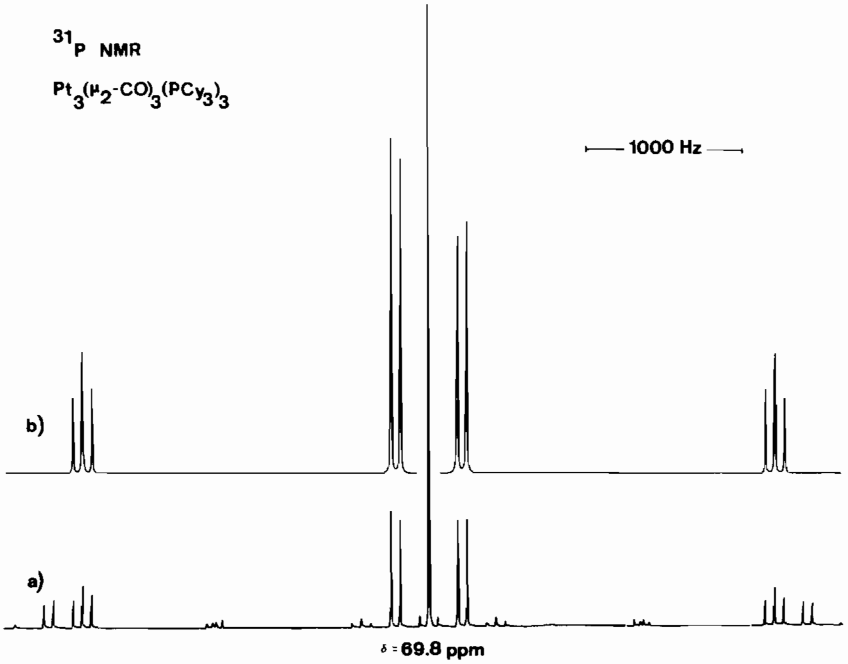

Fig. 1. (a) ^{31}P NMR spectrum of $[Pt_3(\mu_2\text{-}CO)_3(PCy_3)_3]$ in toluene at RT. Note the weak triplet of triplets, in the center of the spectrum. (b) Simulated ^{31}P spectrum for II with PCy_3 as phosphine.

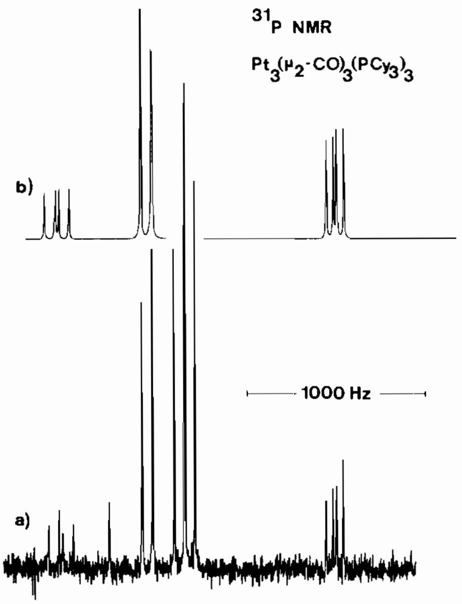

Fig. 2. (a) Low field ^{195}Pt satellites in the ^{31}P spectrum of $[Pt_3(\mu_2\text{-}CO)_3(PCy_3)_3]$. (b) Simulated ^{31}P spectrum for III with PCy$_3$ as phosphine. The 10 resonances from the high field satellites have been omitted for clarity.

as a doublet of doublets, symmetrically disposed about the singlet from I at the center of the spectrum, and stem from a single two-bond metal phosphorus and one three-bond phosphorus–phosphorus interaction. From this preliminary analysis we have all of the coupling constants except $^1J(^{195}Pt, ^{195}Pt)$ and are in a position to simulate the ^{31}P spectrum of this isotopomer, as shown in Fig. 1.

To obtain the metal–metal coupling we assume (see above) that the A″ of the AA′A″XX′ for III can be separated as an 'M' spin (indeed the presence of a weak triplet of triplets in the center of the spectrum, coming from the two metal–phosphorus splittings over two-bonds, and the two phosphorus–phosphorus couplings across three bond supports this supposition) after which the extraction of the metal–metal coupling follows from the remaining AA′XX′ subspectrum (see Fig. 2). This 20 line sub-spectrum appears in both the ^{31}P and ^{195}Pt spectra and thus both forms of spectroscopy yield $^1J(^{195}Pt,^{195}Pt)$.

We should like to emphasize that the nuclearity of this symmetrical cluster is defined by the ^{31}P fine structure on the ^{195}Pt satellite signals of isomer II. Each of the A′ phosphorus atoms resides on a non-active platinum and therefore the multiplicity of the A satellite permits a direct count of the remaining metals. A compilation of the ^{31}P chemical shifts and coupling constants is shown in Table I. From an empirical viewpoint it is worth noting that the ^{31}P resonances all appear at relatively low field. This is expected for PCy$_3$ and PPr$^i_3$ but somewhat unexpected for P(CH$_2$Ph)Ph$_2$ [17], *e.g.* $\delta\,^{31}$P for *cis* and *trans*-$[PtCl_2(P(CH_2Ph)Ph_2)_2]$ = 15.6 and 9.7 ppm, respectively. The magnitudes of the coupling constants involving ^{31}P are also of some interest. Although the values $^1J(^{195}Pt,^{31}P)$ of 4412–4751 Hz are only slightly larger than those found for other platinum(0) complexes [16], $^2J(^{195}Pt,^{31}P)$ of 419–488 Hz, and $^3J(^{31}P,^{31}P)$, of 56–63 Hz, are rather large. Brown *et al.* [18] have suggested that $^3J(^{31}P,^{31}P)$ may have diagnostic value for determining the presence of a platinum–platinum bond and report values between 26 and 43 Hz for compounds containing the $Pt_2(\mu\text{-dppm})_2$ unit, dppm = bis(diphenylphosphino)-methane. We feel that the values $^2J(^{195}Pt,^{31}P)$ will prove an equally valid indicator.

^{195}Pt NMR

The $^{195}Pt\{^1H\}$ spectra of the triangular clusters (see Fig. 3) show strong signals from II and III, and only weak (often not observed) lines from IV. The six line doublet of triplets for II (see Fig. 3(II)) is comprehensible assuming a first order analysis; and, the 20 signals derived from III (Fig. 3(III)) can be shown, with computer assistance, to be the analogous to those discussed above in the ^{31}P section. Once again the twenty resonances in two groups of ten contain the metal–metal coupling information. In contrast to the ^{31}P spectrum, the nuclearity of the cluster is not directly obvious since a number of the signals from II–IV overlap. The platinum chemical shifts for these complexes can be seen to be ~4400 ppm to high field of Na$_2$PtCl$_6$. There is no obvious correlation of this parameter with formal oxidation number of the metal as *cis*-$[PtCl_2(PR_3)_2]$ complexes have very similar resonance frequencies [19].

The analysis of the multiplets in both the ^{195}Pt and ^{31}P spectra give $^1J(^{195}Pt,^{195}Pt)$. These values fall in the narrow range 1571–1619 Hz and, as for $\delta\,^{195}$Pt, are not very sensitive to the tertiary phosphine. A slightly larger value, 1770 Hz, has been reported for $[Pt_3(\mu_2\text{-}CO)_3(PBu^t_2Me)_3]$ [9], and it seems safe to conclude that ~1500–1800 Hz is typical for this type of phosphine cluster. In a study of the ^{195}Pt spectra of the stacked triangles $[Pt_n(CO)_{2n}]^{2-}$, (n = 3, 6, 9, 12, 15) averaged one-bond values of 822 and 750 Hz were found for the molecules having n = 9 and 12 [20].

Boag *et al.* [9] have compiled existing one-bond platinum–platinum coupling constants and suggest that there is little from these values which can be related to the metal–metal bond. Since this observation we have reported platinum–platinum coupling constants for the mono and di-hydrido-bridged dimers $[Pt_2H_2(C_6H_5)(PEt_3)_4]PF_6$, 366 Hz, [21] and $[Pt_2H_3(PPh_3)_4]BF_4$, 325 Hz [22], respectively; and Brown *et al.* [23] have found $J(^{195}Pt,^{195}Pt)$ = 332 Hz for $[Pt_2Me_3(Ph_2PCH_2PPh_2)_2]PF_6$. Further, Lallemand and co-workers [24] give $^2J(^{195}Pt,^{195}Pt)$ values of 190, 390 and 880 Hz for $[Pt_2(\mu\text{-}X,Y)Cl_2(PBu^n_3)_2]$,

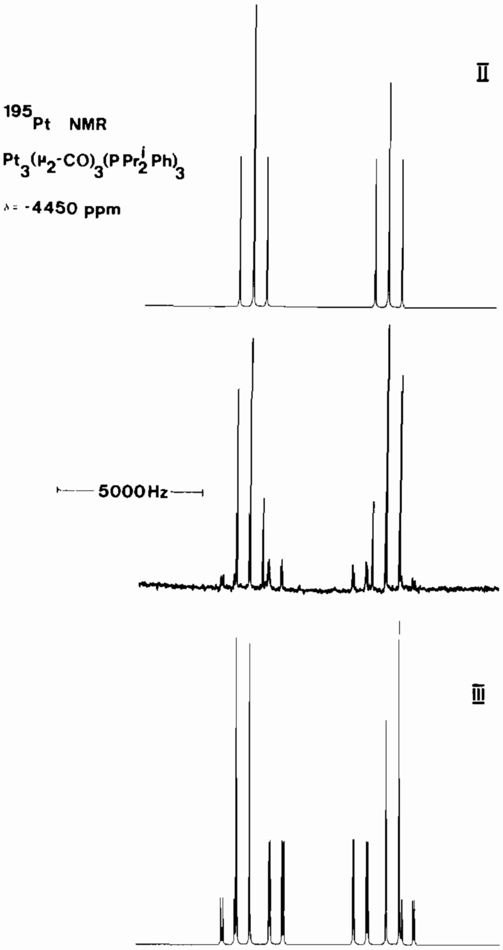

Fig. 3. ^{195}Pt NMR spectrum (center) of $[Pt_3(\mu_2\text{-}CO)_3(PPr^i_2Ph)_3]$ in acetone/toluene at 273 K. The simulated ^{195}Pt spectra for II and III are shown above and below, respectively.

X,Y = Cl, Cl; Cl, SCH_2Ph; and SCH_2Ph, SCH_2Ph; respectively, in good agreement with the value of 380 Hz found earlier by Kiffer *et al.* [25] for $[Pt_2(\mu I_2)I_2(PBu^n_3)_2]$. There seems, therefore, reason to believe that $^2J(^{195}Pt,^{195}Pt)$ will be <1 KHz. Interestingly, Lallemand and co-workers [24] find that $^2J(^{195}Pt,^{195}Pt)$ is negative, and Boag [9] gives $^1J(^{195}Pt,^{195}Pt)$ as positive. Returning to our clusters, it is conceivable that the 1571–1619 Hz values are a sum derived from a larger positive one-bond coupling and a negative two-bond coupling (through the carbonyl); however, the data for several platinum clusters which have very small $^1J(^{195}Pt,^{195}Pt)$ values, notably $[Pt_3(\mu L)_3L_3]$, L = $CNBu^t$, of 188 Hz [9] remain puzzling.

Obviously, the differing bridging ligands play an important role in determining $^1J(^{195}Pt,^{195}Pt)$ and further studies will be required before a comprehensive picture can emerge.

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