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Synthesis and ^{31}P and ^{195}Pt NMR characterisation of the first binuclear platinum(I) complex $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-Bu}^tCP)]$ containing a μ-parallel ligated phospha-alkyne

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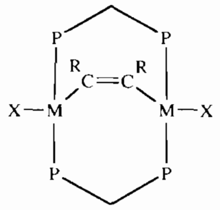
Abstract

The first example of a μ-parallel ligated phospha-alkyne is reported in the complex $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-Bu}^tCP)]$ whose structure has been elucidated by ^{31}P and ^{195}Pt NMR studies.

Introduction

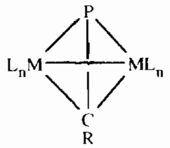
In recent years extensive work has been carried out on a variety of binuclear transition metal complexes of dppm [1]. The greatest interest has focussed on studies of $[MM'X_2(\mu\text{-dppm})_2]$ complexes $M=M'=Pd$, Pt or Rh; $M=Pd$, $M'=Pt$ [2–14]. In these complexes the addition of small molecules (e.g. CH_2, CO, CNR, C_2R_2, CS_2, H, S and SO_2) across the metal–metal bond have been thoroughly studied to give the so-called 'A-frame' complexes [15–33].

Of particular interest in connection with the work described in this paper concerns the interaction of these dinuclear complexes with alkynes, since the resulting products adopt a *cis*-dimetallated olefin μ-parallel bonding mode shown below as evidenced by NMR studies, single crystal X-ray diffraction studies [15, 22, 25] and rationalised by MO calculations [32] rather than the more common perpendicular bridging mode found in other systems.



(P⌒P = dppm)

Phospha-alkynes, RC≡P, are known to behave like alkynes in their coordination complexes of transition metals [34], but to date interactions with dimetallic centres have resulted in μ-perpendicular complexes of the type [35–38]



It was therefore of interest to investigate analogous reactions of $[M_2Cl_2(\mu\text{-dppm})_2]$ (M = Pt) with the phospha-alkyne Bu^{t}CP to see if it also undergoes a μ-parallel bonding mode in accord with the Hoffmans' predictions based on MO calculations [32].

Results and discussion

Treatment of a solution of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ in dichloromethane with an excess of Bu^{t}CP at ambient temperature afforded a high yield of the yellow microcrystalline complex $[Pt_2Cl_2(\mu\text{-dppm})_2(\text{Bu}^tCP)]$ (**1**) which was characterised by elemental analysis, IR spectroscopy and its structure suggested by $^{31}P\{^1H\}$ NMR and ^{195}Pt NMR spectroscopy (*vide infra*).

The $^{31}P\{^1H\}$ NMR spectra of **1** recorded at 32.4 and 145.8 MHz are shown in Figs. 1 and 2 and coupling constant data are listed in Table 1. Analysis of the $^{31}P\{^1H\}$ NMR spectrum recorded at 32.4 MHz was complicated by the overlapping of the low field ^{195}Pt satellites of the dppm resonance with that of the μ-Bu^{t}CP ligand, but the 145.8 MHz spectrum proved more amenable and observed and simulated resonances for P^A and P^B are shown using data listed in Table 1.

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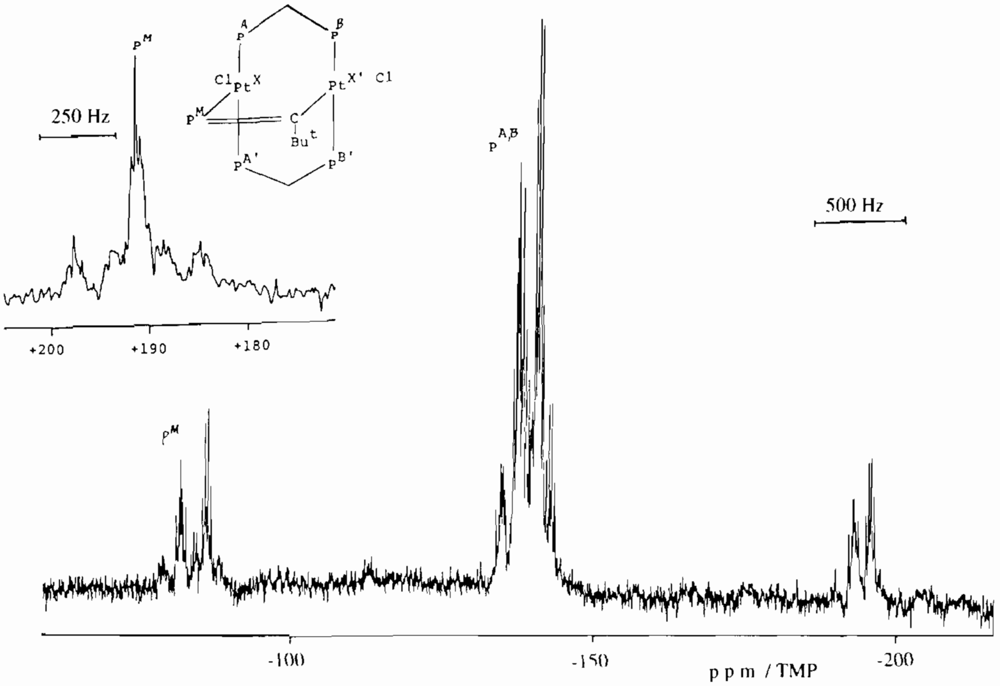


Fig 1. $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2Cl_2(\mu\text{-dppm})_2(Bu^tCP)]$ (**1**) at 32.4 MHz.

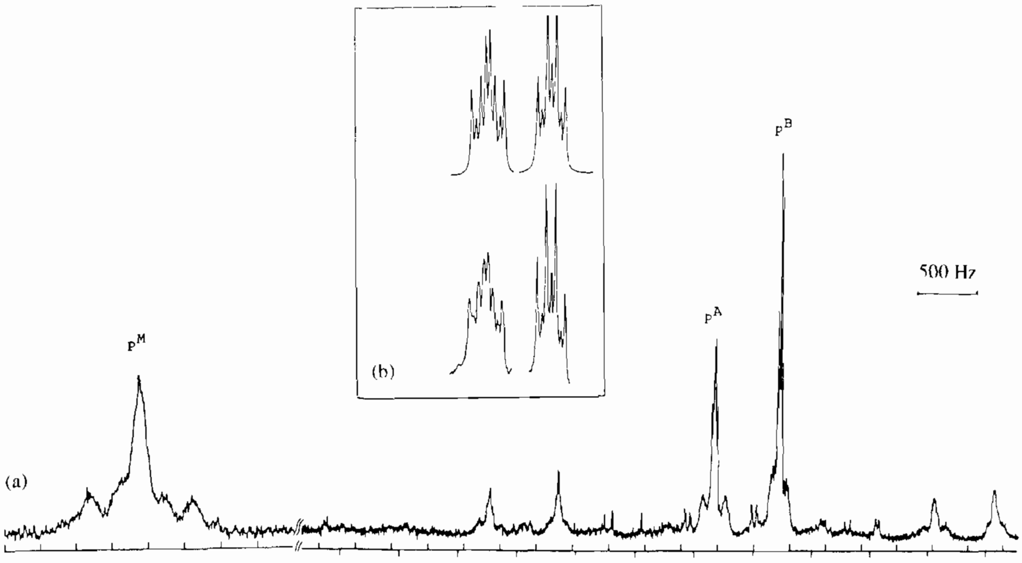
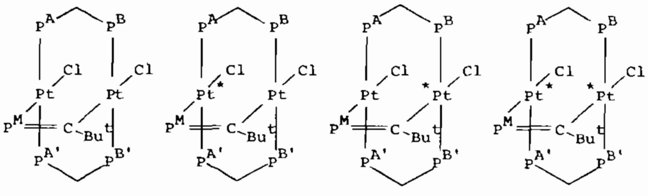


Fig. 2. (a) $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2Cl_2(\mu\text{-dppm})_2(Bu^t\text{-CP})]$ (**1**) at 145.8 MHz (b) Simulated (top) and experimental $^{31}P\{^1H\}$ NMR spectra for the A and B spectra of the central [AA'BB'M] resonance.



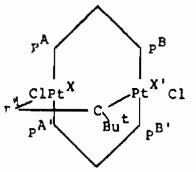
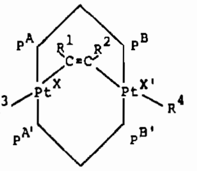
(i) = 44.4% (ii) = 44.4% (iii) = 11.2%

(Pt* = ^{195}Pt) (P⌒P = dppm)

Data for related μ-alkyne diplatinum complexes are listed for comparison. No change was observed in the $^{31}P\{^1H\}$ NMR spectrum of **1** over the temperature range −60 to 30 °C.

The $^{31}P\{^1H\}$ NMR spectrum of **1** results from the three non-equivalent phosphorus nuclei (P^A, P^B and P^M), and therefore consists of three super-imposed spectra which arise from the structures shown below, which reflect the fact that ^{195}Pt ($I = 1/2$) occurs in 33.8%

TABLE 1. $^{31}P\{^1H\}$ NMR data for **1** and related diplatinum complexes

Compound		$\delta P^{A\,a}$	$\delta P^{B\,a}$	$^1J(Pt^XP^A)^b$ $=^1J(Pt^XP^{A'})$	$^3J(Pt^XP^B)^b$ $=^3J(Pt^XP^{B'})$	$^1J(Pt^XP^B)^b$ $=^1J(Pt^XP^{B'})$	$^3J(Pt^{X'}P^A)^b$ $=^3J(Pt^XP^{A'})$	$^2J(P^AP^B)^b$ $=^2J(P^{A'}P^{B'})$	Ref.
	(1)	+3.2	-0.4^c $+332^d$	3605^e 420^f	+122.1	3557	+180.6	$22\ 1^g$ $22\ 5^h$ 6.8^i 14.8^j	this work
	$R^1=R^2=CF_3$ $R^3=H$ $R^4=Me_2CO$	+11.88	−0.15	3110	90	3055	100	20	24
	$R^1=R^2=CF_3$ $R^3=H$ $R^4=Cl$	+11.3	+0.06	3232	50	3193	70	25	24
	$R^1=CF_3$ $R^2=H$ $R^3=R^4=CCCF_3$	+0 9	−0.206	3020	100	3250	100	17	24

[a] In ppm relative to 85% H_3PO_4. [b] In Hz. [c] δP^B. [d] δP^M. [e] $^1J(Pt^XP^A)={}^1J(Pt^{X'}P^{A'})$. [f] $^1J(Pt^XP^M)$. [g] $^2J(P^AP^B)={}^2J(P^{A'}P^{B'})$. [h] $^2J(P^AP^M)={}^2J(P^{A'}P^M)$. [i] $^4J(P^AP^{B'})={}^4J(P^BP^{A'})$. [j] $^3J(P^BP^M)={}^3J(P^{B'}P^M)$. P^P = dppm.

abundance. The three spin systems are thus [AA'BB'M] for (i), [AA'BB'MX] for (ii) and [AA'BB'MXX'] for (iii), ($A=B=M$, ^{31}P $I=1/2$ 100%; $X={}^{195}Pt$ $I=1/2$ 33.8%), from which the coupling constants given in Table 1 were obtained.

The $^{195}Pt\{^1H\}$ NMR spectrum (Fig. 3) though much poorer resolved than the $^{31}P\{^1H\}$ NMR spectra shows the expected two non-equivalent Pt nuclei both appearing as 'triplets' but only the latter showing the extra $J(PtP^M)$ coupling (420 Hz).

The NMR data thus confirm the presence of an η^2-ligated phospha-alkyne adopting the same μ-parallel ligating behaviour as in alkyne diplatinum complexes. This bonding type for the phospha-alkyne is in fact peculiar to the dinuclear platinum systems since in related work affording the dirhodium complex $[Rh_2Cl_2(\mu\text{-dppm})_2(Bu^tCP)]$ the phospha-alkyne adopts a different ligating mode in which the two metal atoms are chemically identical both in solution and in the solid state as shown below [39].

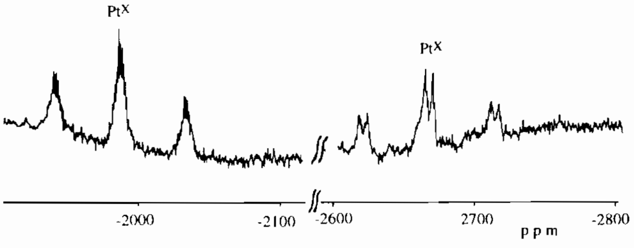
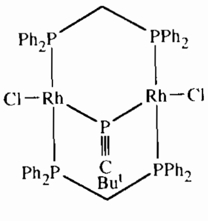


Fig. 3. ^{195}Pt NMR spectrum of $[Pt_2Cl_2(\mu\text{-dppm})_2(Bu^tCP)]$.



Experimental

All manipulations were carried out under an atmosphere of dry dinitrogen or argon, and all reactions were handled by high-vacuum and Schlenk tube techniques. Solvents were dried by standard methods and freshly distilled under dinitrogen before use unless otherwise stated.

IR spectra were recorded on a Perkin-Elmer 457 spectrometer (4000–250 cm^{-1}) or Perkin-Elmer 1430 spectrometer (4000–200 cm^{-1}).

Elemental analyses were carried out by Mrs A.G. Olney of this School.

$^{31}P\{^1H\}$ NMR spectra were obtained using either Bruker WP80 (32.4 MHz) or Bruker WM360 (145.8 MHz) spectrometers both operating in the FT mode. Trimethyl phosphite $P(OMe)_3$ (TMP) was used as an external standard and chemical shifts were converted relative to 85% H_3PO_4 by using the relationship $\delta p(P(OMe)_3) = +141$ ppm. ^{195}Pt NMR spectra were recorded on a WM360 spectrometer (77.1 MHz) and referenced to K_2PtCl_4.

Preparation of [$Pt_2Cl_2(\mu$-dppm$)_2$]

[$Pt_2Cl_2(\mu$-dppm$)_2$] was prepared by a variation of synthetic routes reported elsewhere [40, 41] involving either (a) or (b).

(a) Reaction of [$Pt(PPh_3)_4$] with [$PtCl_2(SEt_2)_2$] and dppm

To a solution of [$Pt(PPh_3)_4$] (0.920 g, 0.739 mmol) (slight excess) in dry benzene (30 cm^3) was added dppm (0.517 g, 1.344 mmol) under dinitrogen. [$PtCl_2(SEt_2)_2$] (0.30 g, 0.672 mmol) was added and the mixture was refluxed under dinitrogen for 1 h. The mixture was left to cool to room temperature and the yellow product was filtered off, washed with benzene (10 cm^3), and dried *in vacuo* for 3 h to give the yellow microcrystalline complex [$Pt_2Cl_2(\mu$-dppm$)_2$] (0.560 g, 67%). *Anal.* Found: C, 48.2; H, 3.4. Calc. for $C_{50}H_{44}P_4Cl_2Pt_2$: C, 48.83; H, 3.61%. The $^{31}P\{^1H\}$ NMR and IR spectra are similar to those described in the literature.

(b) Reaction of [$Pt(PPh_3)_4$] with [$PtCl_2(COD)$] and dppm

[$Pt(PPh_3)_4$] (1.254 g, 1.008 mmol) and dppm (0.704 g, 1.832 mmol) in dry benzene (30 cm^3) were refluxed with [$PtCl_2(COD)$] (0.343 g, 0.916 mmol) to afford [$Pt_2Cl_2(\mu$-dppm$)_2$] (0.45 g, 40%), identical with the above sample.

Preparation of [$Pt_2Cl_2(\mu$-dppm$)_2(Bu^tCP)$] (1)

To a solution of [$Pt_2Cl_2(\mu$-dppm$)_2$] (0.40 g, 0.325 mmol) in dry dichloromethane (15 cm^3) was added Bu^tCP (0.050 g, 0.50 mmol) in dichloromethane (5 cm^3). The mixture was stirred for 1 h at room temperature during which time its colour changed from yellow to orange. The volatile materials were removed under reduced pressure and the yellow solid washed several times with a mixture of dichloromethane and petroleum ether (60–80 °C) (1:1). The product was dried *in vacuo* to give the yellow microcrystalline complex [1,2-dichloro-di-μ-{bis(diphenylphosphino)-methane-*P,P'*}{μ-2,2-dimethylpropylidynephosphine-(*P*, *C*)}diplatinum(I) (Pt^1, Pt^2) (0.37 g, 85%). *Anal.* Found: C, 48.95; H, 4.0. Calc. for $C_{55}H_{53}P_5Cl_2Pt_2$: C, 49.67; H, 4.02%. IR spectrum (KBr): 3050w, 2958m, 2905w, 2830w, 1573w, 1560m, 1483s, 1455sh, 1450vw, 14w, vs, 1382w, 1358m, 1332w, 1310w, 1261vs, 1223vw, 1192m, 1160vw, 1146sh, 1101vs, 1025vs, br, 1008sh, 990sh, 830w, br, 803vs, 790sh, 775s, 756sh, 742vs, 722s, 700vs, 678sh, 625w, 600sh, 503vs, 473s, 423w, 40m, 387s, 362w, 347w cm^{-1}.

Acknowledgements

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