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## PREPARATION AND PROPERTIES OF SOME CATIONIC BINUCLEAR PLATINUM(I) COMPLEXES \*

MICHAEL P. BROWN \*, SUSAN J. FRANKLIN,

*Donnan Laboratories, Liverpool University, P.O. Box 147, Liverpool (U.K.)*

RICHARD J. PUDDEPHATT, MARY A. THOMSON,

*Department of Chemistry, University of Western Ontario, London N6A 5B7 (Canada)*

and KENNETH R. SEDDON

*Inorganic Chemistry Laboratory, Oxford University, Oxford (U.K.)*

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### Summary

Reaction of  $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$  with ligands, L, in the presence of  $[\text{PF}_6]^-$  gave stable cationic diplatinum(I) complexes  $[\text{Pt}_2\text{L}_2(\mu\text{-dppm})_2][\text{PF}_6]_2$  where L =  $\text{PMe}_2\text{Ph}$ ,  $\text{PMePh}_2$ ,  $\text{PPh}_3$ ,  $\text{NH}_3$ ,  $\text{C}_5\text{H}_5\text{N}$ . Reaction of  $[\text{Pt}_2(\text{NH}_3)_2(\mu\text{-dppm})_2][\text{PF}_6]_2$  with CO gave  $[\text{Pt}_2(\text{CO})_2(\mu\text{-dppm})_2][\text{PF}_6]_2$  and an unsymmetrical complex  $[\text{Pt}_2(\text{CO})(\text{C}_5\text{H}_5\text{N})(\mu\text{-dppm})_2][\text{PF}_6]_2$  was also prepared. The compounds were characterised by vibrational and  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy and the presence of direct platinum–platinum bonds is indicated.

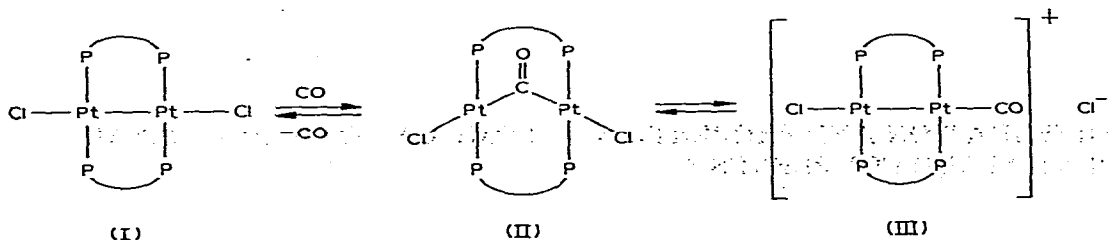
### Introduction

The ligand bis(diphenylphosphino)methane (dppm) commonly acts as a bridging ligand thus holding two metal atoms in close proximity [1–4]. This can lead to unusual properties, for example to the stabilisation of platinum(I) in the Pt–Pt bonded complex  $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$ , (I) [1,5]. Several small ligands have been shown to add to the Pt–Pt bond giving complexes  $[\text{Pt}_2\text{Cl}_2(\mu\text{-X})(\mu\text{-dppm})_2]$ , where X =  $\text{SO}_2$ , CO,  $\text{CH}_2$  (from  $\text{CH}_2\text{N}_2$ ) or  $\text{H}^+$ , thus weakening or completely breaking the Pt–Pt bond [6,7]. Carbon monoxide is unique in forming both a bridging carbonyl (II) and a cationic complex (III) in

\* Dedicated to Professor E.G. Rochow on the occasion of his 70th birthday.

which CO displaces a terminal chloride from I (Scheme 1) [5,8].

Scheme I.  $\text{P} \text{---} \text{P} = \text{dppm}$



A feature of these complexes is the wealth of information that can be derived from study of their NMR spectra. This is in part a fortunate consequence of the presence of  $^{195}\text{Pt}$  (natural abundance 33.8%) resulting in the formation of three different spin systems in binuclear platinum complexes [1,6,8,9]. It was thus of interest to extend the range of platinum(I) complexes which, like complex I, contain a direct platinum-platinum bond. In this paper we report how this has been achieved by displacement of chloride from complex I with some neutral  $\sigma$ -donor ligands, thus yielding cationic diplatinum(I) complexes.

## Experimental

The complex  $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$  was prepared as described previously [2]. Dimethylphenylphosphine and methyl-diphenylphosphine (Maybridge Chemical Co. Ltd.), triphenylphosphine and ammonium hexafluorophosphate (BDH Chemicals Ltd.) were used without further purification as was acetone- $d_6$  (Aldrich Chemical Company Inc.) used for NMR measurements. Complexes were dried on a vacuum line at  $10^{-3}$  Torr or better at room temperature. Infra-red spectra were measured as paraffin mulls. All new complexes had bands at 840 (vs, br) and 557 (s)  $\text{cm}^{-1}$  characteristic of  $[\text{PF}_6]^-$ .  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded as described earlier [1]. In this, as in previous publications, the convention of negative upfield shifts and positive downfield shifts with respect to the reference has been adopted. Simulation of spectra and refinement of coupling constants were carried out using the computer program LAOCN3 by A.A. Bothner-By and S. Castellano, Mellon Institute.

## Preparations

(i)  $[\text{Pt}_2(\text{MePh}_2\text{P})_2(\mu\text{-dppm})_2][\text{PF}_6]_2$ . The pale yellow  $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$  (0.34 g, 0.28 mmol) was suspended in methanol (10 ml) and methyl-diphenylphosphine (0.16 g, 0.80 mmol) in methanol (2 ml) was added with stirring. The  $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$  immediately dissolved to give a yellow solution. Ammonium hexafluorophosphate (0.40 g, 2.45 mmol) in methanol (3 ml) was then added slowly with stirring. At this stage the product partially precipitated as a yellow solid. After stirring for a further 10 min, the methanol was evaporated in a stream of nitrogen. The yellow residue was washed with water and with n-hexane to remove soluble ammonium salts and excess of methyl-diphenylphosphine, respectively. The yellow residue was finally washed with methanol

(5 ml) to give the crude product (0.45 g). This was dissolved in acetone, giving a deep orange solution, and was recrystallized by careful addition of n-hexane to give pure  $[\text{Pt}_2(\text{MePh}_2\text{P})_2(\mu\text{-dppm})_2][\text{PF}_6]_2$  (0.42 g, 82%). Anal. Found: C, 49.24; H, 3.96; F, 12.52; P, 13.51. Calcd.: C, 49.36; H, 3.81; F, 12.33; P, 13.40%.

(ii)  $[\text{Pt}_2(\text{Me}_2\text{PhP})_2(\mu\text{-dppm})_2][\text{PF}_6]_2$ . An identical method gave this complex (yellow crystals) in good yields. Anal. Found: C, 46.03; H, 4.33; F, 13.32. Calcd.: C, 45.95; H, 3.86; F, 13.21%.

(iii)  $[\text{Pt}_2(\text{Ph}_3\text{P})_2(\mu\text{-dppm})_2][\text{PF}_6]_2$ . To  $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$  (0.32 g, 0.26 mmol) in methanol (3 ml) was added triphenylphosphine (0.25 g, 0.95 mmol) in methanol (15 ml). Ammonium hexafluorophosphate (0.4 g, 2.45 mmol) in methanol (4 ml) was added to the clear yellow solution. The solvent was completely evaporated, the resulting solid was washed with water, dried and recrystallized from acetone and n-hexane to give the yellow  $[\text{Pt}_2(\text{Ph}_3\text{P})_2(\mu\text{-dppm})_2][\text{PF}_6]_2$  (0.47 g, 92%). Anal. Found: C, 52.80; H, 4.05; F, 11.58; P, 12.26. Calcd.: C, 52.34; H, 3.78; F, 11.55; P, 12.56%.

(iv)  $[\text{Pt}_2(\text{py})_2(\mu\text{-dppm})_2][\text{PF}_6]_2$ . To  $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$  (0.23 g, 0.19 mmol) in methanol (3 ml) was added pyridine (0.1 g, 1.26 mmol) in methanol (2 ml). After 10 min a clear pale yellow solution was obtained. The crude hexafluorophosphate (0.28 g) was obtained as in (iii) above and was recrystallized from dichloromethane and n-hexane to give the pale yellow  $[\text{Pt}_2(\text{py})_2(\mu\text{-dppm})_2][\text{PF}_6]_2$  (0.21 g, 70%). Anal. Found: C, 43.61; H, 3.25; F, 13.99; N, 1.67; P, 11.43. Calcd.: C, 44.84; H, 3.39; F, 14.19; N, 1.74; P, 11.56%.

(v)  $[\text{Pt}_2(\text{NH}_3)_2(\mu\text{-dppm})_2][\text{PF}_6]_2$ . Ammonia was bubbled through a suspension of  $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$  (0.54 g, 0.44 mmol) in methanol (30 ml). A pale yellow solution was immediately produced. After 10 min a large excess of solid ammonium hexafluorophosphate (~1.0 g, 6.1 mmol) was added and the passage of ammonia continued for a further 10 min. The solvent was evaporated completely and the pale yellow residue washed with water to give the crude product (0.71 g). Recrystallization from dichloromethane and n-hexane gave pure pale yellow  $[\text{Pt}_2(\text{NH}_3)_2(\mu\text{-dppm})_2][\text{PF}_6]_2$  (0.42 g, 65%). Anal. Found: C, 40.33; H, 3.31; F, 15.33; N, 1.96; P, 12.26. Calcd.: C, 40.50; H, 3.40; F, 15.37; N, 1.89; P, 12.53%. The infrared spectrum showed  $\nu(\text{NH}_3)$  at 3351, 3275 and 3183  $\text{cm}^{-1}$  and  $\delta(\text{NH}_3)$  at 1613  $\text{cm}^{-1}$ .

(vi)  $[\text{Pt}_2(\text{CO})_2(\mu\text{-dppm})_2][\text{PF}_6]_2$ . Carbon monoxide was passed through a solution of  $[\text{Pt}_2(\text{NH}_3)_2(\mu\text{-dppm})_2][\text{PF}_6]_2$  (0.75 g, 0.51 mmol) in dichloromethane (20 ml) when the solution quickly became somewhat deeper yellow in colour. After 1 h the supply of carbon monoxide was increased to completely evaporate the solvent and thus leave a yellow oil. This was redissolved in dichloromethane (5 ml) and crystallized by adding n-hexane to yield the crude product (0.67 g). An infrared spectrum showed the presence of weak N—H absorptions and thus indicated incomplete reaction. Hence dichloromethane (20 ml) was added to the product and treatment with carbon monoxide continued for a further hour. Partial crystallization occurred at this stage but further crystallization was achieved by addition of n-hexane to yield  $[\text{Pt}_2(\text{CO})_2(\mu\text{-dppm})_2][\text{PF}_6]_2$  as a white solid (0.51 g, 67%). Anal. Found: C, 41.25; H, 3.03; F, 15.32; P, 12.08. Calcd.: C, 41.50; H, 2.95; F, 15.15; P, 12.35%. The infrared spectrum shows  $\nu(\text{CO})$  2,105w (sharp), 2,085s, 2,075 (sh)  $\text{cm}^{-1}$ .

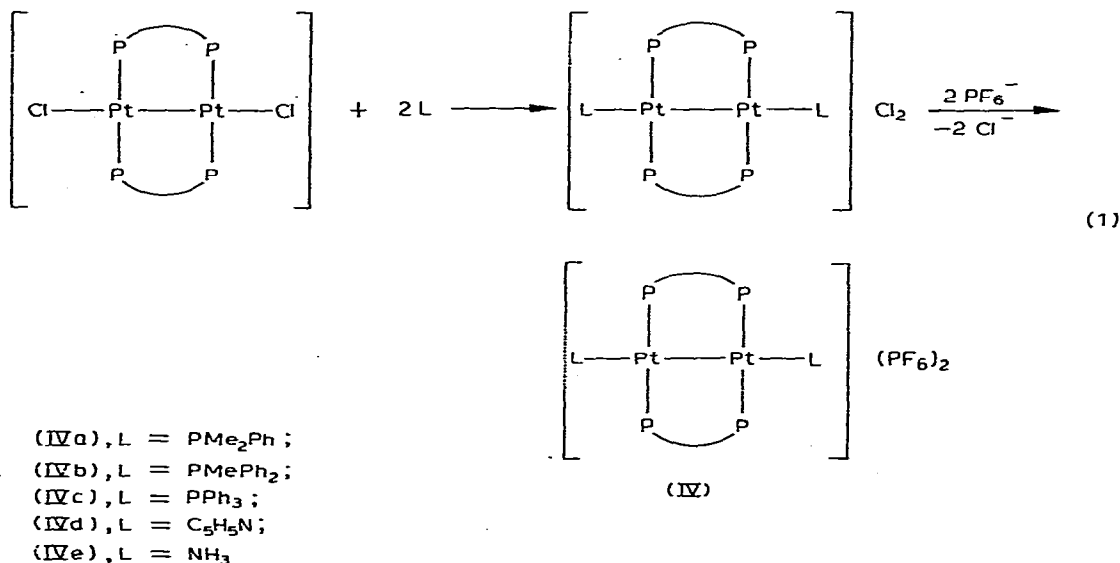
The solubility of this complex and of  $[\text{Pt}_2(\text{NH}_3)_2(\mu\text{-dppm})_2][\text{PF}_6]_2$  in dichloromethane appears to depend on the history of the sample and is greatly increased by the addition of a trace of methanol.

(vii)  $[\text{Pt}_2(\text{py})(\text{CO})(\mu\text{-dppm})_2][\text{PF}_6]_2$  (impure). Carbon monoxide was bubbled through a solution of  $[\text{Pt}_2(\text{py})_2(\mu\text{-dppm})_2][\text{PF}_6]_2$  (0.33 g, 0.21 mmol) in dichloromethane (10 ml) for 1 h. The solution was left under an atmosphere of carbon monoxide for 2 h after which time the solvent and displaced pyridine were removed in a stream of nitrogen. The residue was crystallised from dichloromethane and n-hexane to yield the impure product (0.30 g). Microanalysis gave: C, 43.07, H, 3.18; F, 14.57; N, 1.08; P, 11.68. Pure  $[\text{Pt}_2(\text{py})(\text{CO})(\mu\text{-dppm})_2][\text{PF}_6]_2$  calcd.: C, 43.24; H, 3.02; F, 14.66; N, 0.90; P, 11.95%. The infrared spectrum showed a single  $\nu(\text{CO})$  band at  $2062\text{ cm}^{-1}$  but also showed peaks characteristic of those of the starting material. The NMR spectra also indicated the presence of unchanged starting material (see Results).

## Results

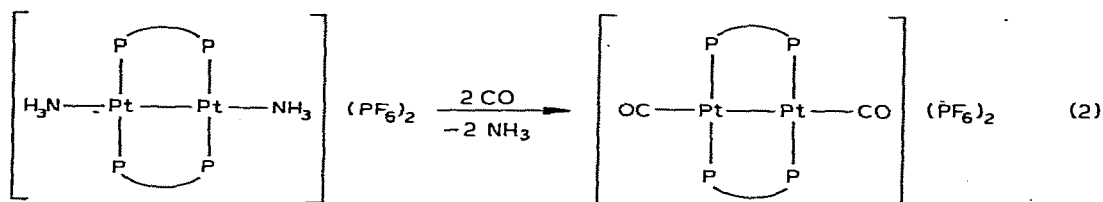
### Synthesis and properties of the complexes

In general the complexes were prepared by addition of the ligand L (in excess of 2 mol) to complex I (1 mol) in methanol, when a clear solution of  $[\text{Pt}_2\text{L}_2(\mu\text{-dppm})_2]\text{Cl}_2$  was obtained. This was followed by precipitation of the cation as the hexafluorophosphate salt (eq. 1,  $\text{P}^-\text{P} = \text{dppm}$ ).

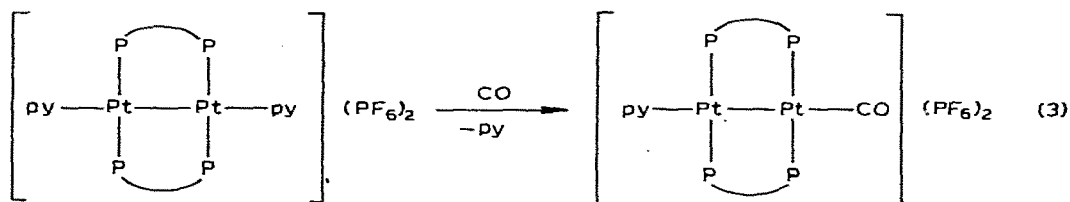


The complex IVf with L = CO could not be prepared in pure form in this way but was prepared instead by displacement of ammonia by CO from IVe (equation 2,  $\text{P}^-\text{P} = \text{dppm}$ )

Displacement of pyridine from IVd by CO (equation 3) was less readily achieved and resulted in the formation of the mixed complex  $[\text{Pt}_2(\text{py})(\text{CO})(\mu\text{-dppm})_2][\text{PF}_6]_2$  (V) contaminated with unchanged starting material.



(IV f)



(V)

The complexes were all air-stable yellow or white solids which were soluble in chlorinated solvents such as dichloromethane and also in acetone. Generally they were thermally more stable than I and were less reactive. Thus I reacts slowly with chlorinated solvent [1] but complexes IV were stable for weeks or months under these conditions. Reactivity with unsaturated molecules was also less than for I and complex IVa, for example, did not react with carbon monoxide or sulphur dioxide whereas I readily adds these molecules across the Pt—Pt bond [5,8]. The Pt—Pt bond in IVa also did not appear to undergo protonation unlike that in I.

#### Characterisation of the complexes

The complexes, with the exception of V, gave satisfactory elemental analyses and were further characterized by vibrational and by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra.

**Vibrational spectra.** The infrared spectra all showed bands (840 and 557  $\text{cm}^{-1}$ ) characteristic of  $\text{PF}_6^-$  ions. The ammonia complex (IVe) gave typical bands due to  $\nu(\text{NH}_3)$  at 3351, 3275 and 3183  $\text{cm}^{-1}$  as sharp well resolved peaks. The carbonyl complex IVf gave a strong  $\nu(\text{CO})$  band at 2085  $\text{cm}^{-1}$  but also present was a weak sharp peak at 2105  $\text{cm}^{-1}$  and a shoulder (at 2075  $\text{cm}^{-1}$ ) on the strong peak could just be resolved. The interpretation of these peaks is not clear since a  $\text{OCPtPtCO}$  unit would be expected to give either one or two  $\nu(\text{CO})$  bands depending on the symmetry of the molecule. By analogy with I, which has an approximately linear  $\text{ClPtPtCl}$  unit and only one infrared active Pt—Cl stretching vibration despite a  $38.5^\circ$  twist in the molecule [5], only one similarly active  $\nu(\text{CO})$  band was expected. It would appear that an X-ray structure determination is required to settle the question of the geometry of the  $\text{OCPtPtCO}$  unit. The infrared spectrum of  $[\text{Pt}_2(\text{py})(\text{CO})(\mu\text{-dppm})_2][\text{PF}_6]_2$  (V) showed as expected a single  $\nu(\text{CO})$  band (at 2060  $\text{cm}^{-1}$ ).

Unfortunately, several of the complexes IV fluoresced and failed to give satisfactory Raman spectra. Only the pyridine complex IVd gave a satisfactory spectrum and showed  $\nu(\text{Pt—Pt})$  at 140  $\text{cm}^{-1}$ . The value may be compared with  $\nu(\text{Pt—Pt})$  frequencies of 150  $\text{cm}^{-1}$  for I, 118  $\text{cm}^{-1}$  and 106  $\text{cm}^{-1}$  for the corre-

TABLE 1  
 $^1\text{H}$  NMR DATA <sup>a</sup> OF  $[\text{Pt}_2\text{L}_2(\mu\text{-dppm})_2][\text{PF}_6]_2$  COMPLEXES

Complex	L	$\text{CH}_2$ resonance of $\mu\text{-dppm}$ ligands			$\text{CH}_3$ resonance of phosphine ligand		
		$\delta$ (ppm)	$^3J(\text{Pt-H})$ (Hz)	$^2J(\text{P-H})$ (Hz)	$\delta$ (ppm)	$^3J(\text{Pt-H})$ (Hz)	$^2J(\text{P-H})$ (Hz)
IVa <sup>b</sup>	$\text{Me}_2\text{PhP}$	5.71	53.0		0.69 1.04	28.5 30.5	3.7 3.7
IVb <sup>b</sup>	$\text{MePh}_2\text{P}$	5.67	53.0		1.16	30.0 [ $^4J(\text{Pt-H})$ 13.3]	3.5
IVc <sup>c</sup>	$\text{Ph}_3\text{P}$	5.56	$56.0 \pm 3.0$ <sup>c</sup>				
IVd <sup>b</sup>	$\text{C}_5\text{H}_5\text{N}$	5.28	56.2	4.5			
IVe <sup>d</sup>	$\text{NH}_3$	4.98	58.0	4.8			
IVf	$\text{CO}$	5.80	62.0	5.4			

<sup>a</sup> At 60 MHz and 35°C in  $(\text{CD}_3)_2\text{CO}$ . Chemical shifts from internal TMS. <sup>b</sup> Also recorded at 220 MHz.

<sup>c</sup> Weaker than usual spectrum. <sup>d</sup> Broad peak at  $\delta = 2.60$  may be  $\text{NH}_3$  resonance.

sponding bromide and iodide derivatives [1], and  $157\text{ cm}^{-1}$  for complex III [8].

<sup>1</sup>H and <sup>31</sup>P NMR spectra. The <sup>1</sup>H NMR spectra (Table 1) of complexes IV all contained resonances with a 1 : 8 : 17 : 8 : 1 intensity pattern due to the  $\text{CH}_2$  protons of the dppm ligands which are coupled to <sup>195</sup>Pt nuclei, proving that the ligands are bridging between two platinum atoms. Such spectra have been discussed previously [1,6,8]. In some cases coupling to <sup>31</sup>P was also observed. Thus for the complexes IVd, IVe and IVf, each peak appeared as a 1 : 4 : 6 : 4 : 1 quintet with individual peaks separated by approximately 5 Hz. The  $\text{CH}_2$  protons and four phosphorus atoms should give an  $\text{A}_2\text{A}'_2\text{X}_2\text{X}'_2$  spin system, and the quintet pattern is expected if the *trans*-coupling  $^2J(\text{P-P})$  is considerably larger than other couplings. This is the case as will be shown later.

The <sup>1</sup>H NMR spectra in the region of the methylphosphorus peaks for compounds IVa and IVb are of interest. The complex IVa gave two distinct methylphosphorus resonances (Fig. 1) while the complex IVb gave only one such peak. These observations suggest that the two methyl groups of each  $\text{PMe}_2\text{Ph}$  ligand of IVa are non-equivalent and hence that there is no plane of symmetry containing the Pt-P bonds. A plane of symmetry would be expected if the  $\text{Pt}_2\text{P}_6$  grouping were planar and if there was free-rotation about the Pt-P $\text{Me}_2\text{Ph}$  bonds. Asymmetry would be induced if there were a twist in the  $\text{Pt}_2(\text{dppm})_2$  unit as found in  $[\text{Pt}_2(\text{dppm})_2\text{Cl}_2]$  and the twisted structure was rigid on the NMR time scale, or if there was a high barrier to rotation about the Pt-P $\text{Me}_2\text{Ph}$  bond and the  $\text{PMe}_2\text{Ph}$  substituents were locked in an asymmetric arrangement due to steric interactions with the phenyl substituents of the  $\mu\text{-dppm}$  groups. At 50°C the NMR signals broadened but did not coalesce indicating a fairly high activation energy to any fluxional process.

The <sup>31</sup>P NMR spectra of complexes IVd-IVf were very similar in appearance to that of I and were analysed in the same way [1]. The magnitude of the coupling constants  $^3J(\text{Pt-P})$  and  $^3J(\text{P-P})$  indicate strong Pt-Pt bonding in the complexes (Table 2) [9]. However, the magnitude of the coupling  $^1J(\text{Pt-Pt})$  is

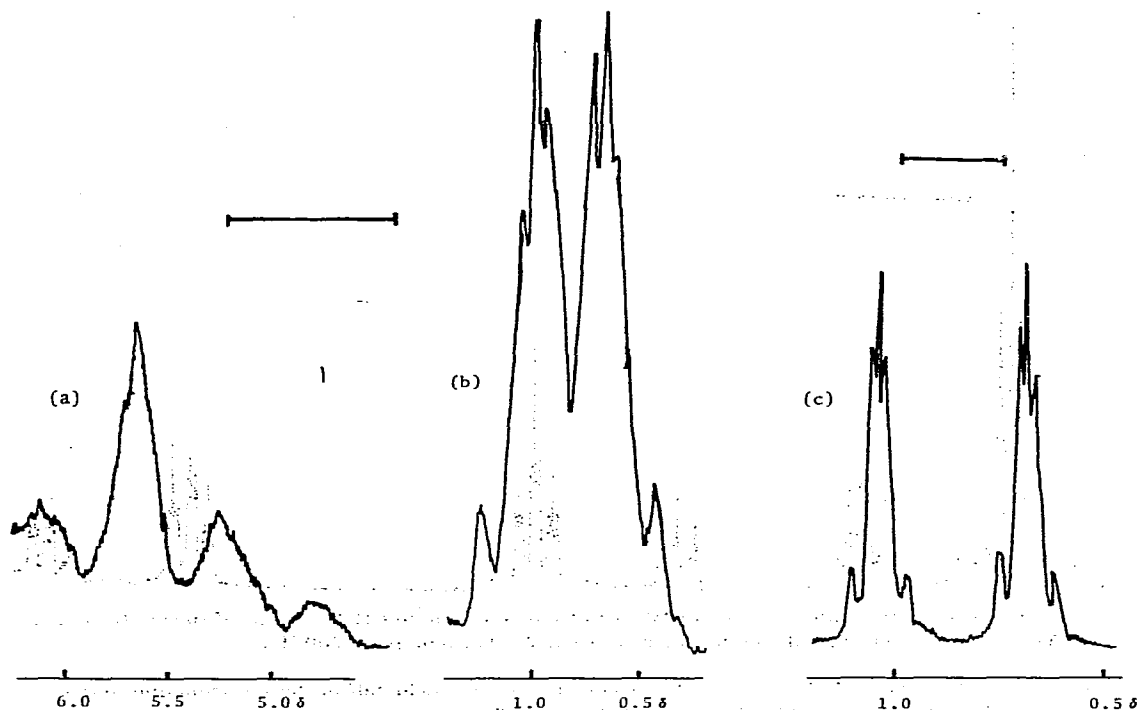


Fig. 1. The  $^1\text{H}$  NMR spectrum of IVa. (a)  $\text{CH}_2\text{P}_2$  resonance at 60 MHz (the low-field peak was obscured), bar represents 50 Hz; (b)  $\text{CH}_3\text{P}$  resonances at 60 MHz; (c)  $\text{CH}_3\text{P}$  resonances at 220 MHz, bar represents 50 Hz.

TABLE 2

DATA FROM THE  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR SPECTRA <sup>a</sup> OF THE COMPLEXES  $[\text{Pt}_2(\mu\text{-dppm})_2\text{L}_2]^{2+}$

Complex	L	$\delta$ (ppm) <sup>b</sup>	$^1J(\text{Pt}-\text{P})$	$^2J(\text{Pt}-\text{P})$	$^2J(\text{P}-\text{P})$ <sup>c</sup>	$^3J(\text{P}-\text{P})$ <sup>d</sup>	$^1J(\text{Pt}-\text{Pt})$
IVa	$\text{Me}_2\text{PhP}$	-7.61 <sup>e</sup>	2840	100 <sup>f</sup>	48	22	
		-13.36 <sup>g</sup>	1938	650	24	4	
IVb	$\text{McPh}_2\text{P}$	-7.31 <sup>e</sup>	2870	-120	50	20	
		-9.37 <sup>h</sup>	1914	750	22	5	
IVc	$\text{Ph}_3\text{P}$	-8.27 <sup>e</sup>	2800				
		14.15 <sup>i</sup>	1680				
IVd	$\text{C}_5\text{H}_5\text{N}$	0.90	2828	-113	58	30	4940
IVe	$\text{NH}_3$	-0.15	2833	-124	62	28	5860
IVf	$\text{CO}$	-9.88	2390	-96	46	33	4810
V	$\text{CO}/\text{C}_5\text{H}_5\text{N}$	0.58 <sup>j</sup>	2762	90 <sup>k</sup>	46	36	
		-8.35 <sup>l</sup>	2508	120 <sup>f</sup>			

<sup>a</sup> Solvent acetone- $d_6$ . <sup>b</sup> From trimethyl phosphate as reference. The *trans* coupling  $^2J(\text{P}-\text{P})$  [ $J(\text{AA}')$  in Fig. 3] was large but could not be determined accurately. A magnitude of 500 Hz was found to be satisfactory in simulation of spectra. <sup>c</sup>  $J(\text{AA}')$  in Fig. 3; <sup>d</sup>  $J(\text{AA}')$  in Fig. 3. <sup>e</sup> For dppm ligand. <sup>f</sup> Sign probably negative; <sup>g</sup> For  $\text{PMe}_2\text{Ph}$  ligand,  $^3J(\text{P}-\text{P})$ ,  $J(\text{MM}')$  in Fig. 3, 195 Hz. <sup>h</sup> For  $\text{PMePh}_2$  ligand. <sup>i</sup> For  $\text{PPh}_3$  ligand. <sup>j</sup> Assigned as phosphorus atoms adjacent to  $\text{C}_5\text{H}_5\text{N}$ . <sup>k</sup> Approximate value, sign not determined but presumably negatively. <sup>l</sup> Phosphorus atoms adjacent to  $\text{CO}$ .

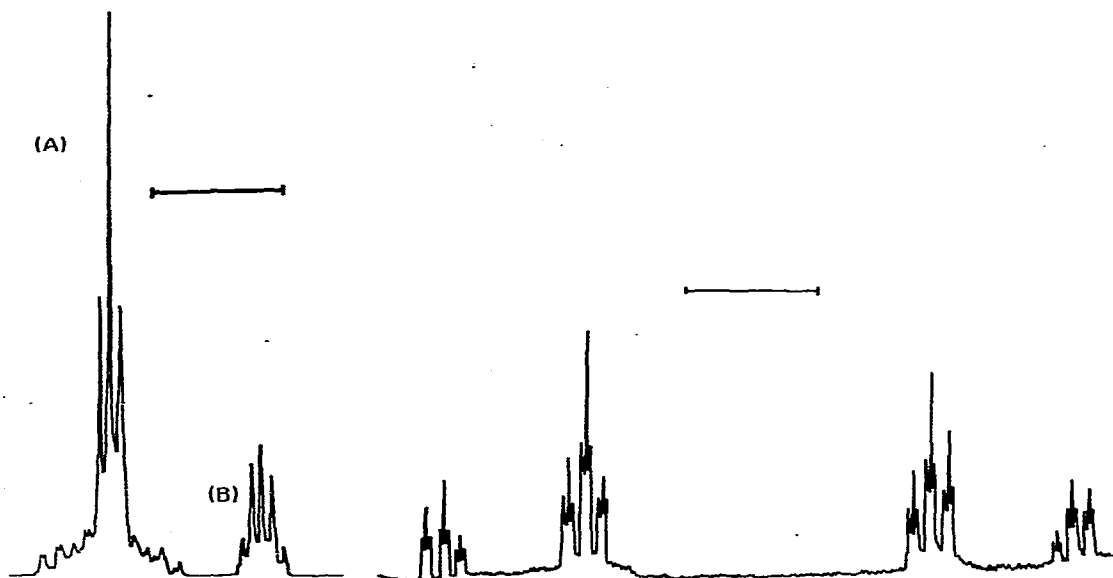


Fig. 2a. The  $^{31}\text{P}\text{--}\{^1\text{H}\}$  NMR spectrum of IVa. (A) Resonance due to  $\text{CH}_2\text{P}_2$  groups of species (i), Fig. 3 and (B) resonance due to  $\text{PMe}_2\text{Ph}$  groups of species (i). The bar represents 200 Hz.

Fig. 2b. The  $^{31}\text{P}\text{--}\{^1\text{H}\}$  NMR spectrum of IVa showing the high field half of the spectrum due to the  $\text{PMe}_2\text{Ph}$  groups of species (ii), Fig. 3. The bar represents 200 Hz.

considerably lower than that found by other workers [10] for complex (I) ( $^1J(\text{Pt}\text{--}\text{Pt}) = 8197$  Hz). This decrease cannot be ascribed entirely to the *trans*-influence of the ligands  $\text{NH}_3$ ,  $\text{C}_5\text{H}_5\text{N}$  and  $\text{CO}$ . Nevertheless, within the series of cationic complexes IV, the magnitude of  $^1J(\text{Pt}\text{--}\text{Pt})$  for  $\text{L} = \text{NH}_3 > \text{C}_5\text{H}_5\text{N} > \text{CO}$  is the reverse of the *trans*-influence series.

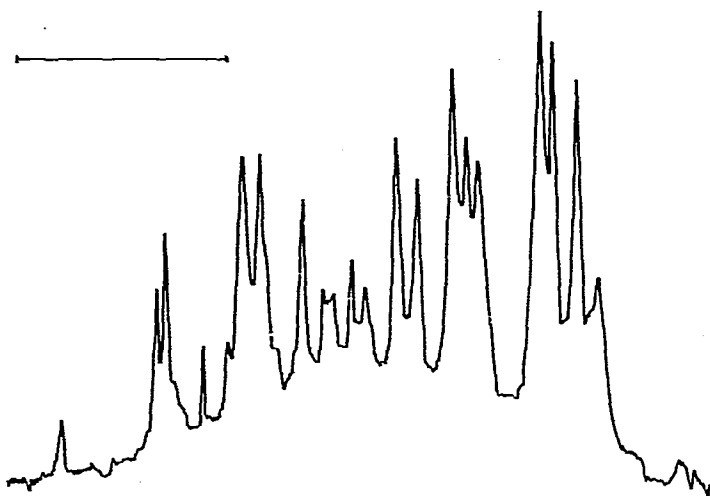


Fig. 2c. The  $^{31}\text{P}\text{--}\{^1\text{H}\}$  NMR spectrum of IVa showing the low field  $^{195}\text{Pt}$  satellites due to the  $\text{CH}_2\text{P}_2$  groups (AA' nuclei) of species (ii), Fig. 3. The bar represents 50 Hz.



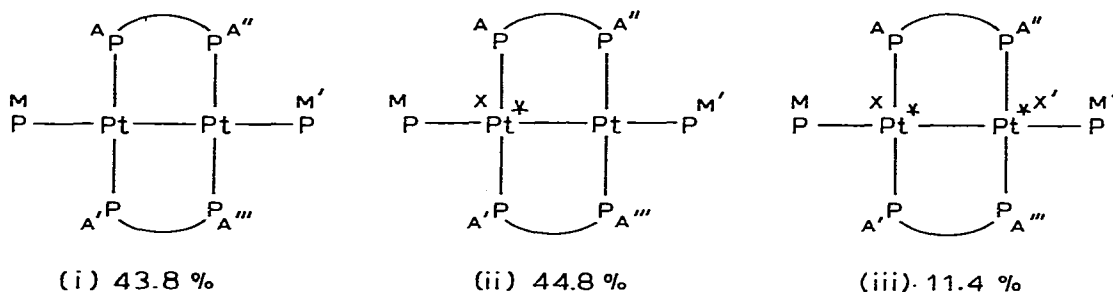
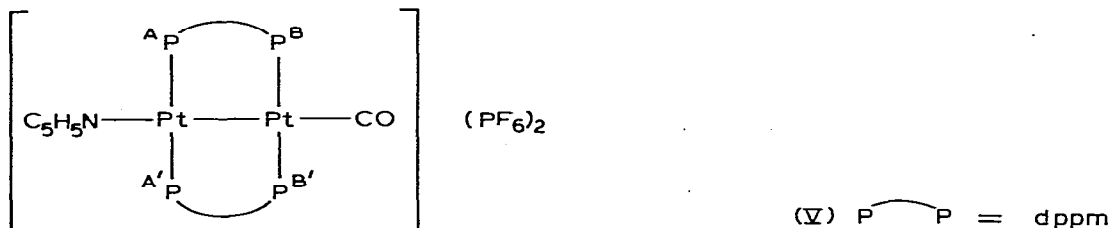


Fig. 3. Spin systems arising from presence of naturally occurring  $^{195}\text{Pt}$  in complex (IVa) [ $\text{P} = \text{PMe}_2\text{Ph}$ ,  $\text{P}^* = \text{dppm}$ ,  $\text{Pt}^* = ^{195}\text{Pt}$ ].

The  $^{31}\text{P}$  NMR spectrum of IVa is extremely complex (Fig. 2). Thus the spectrum contains superimposed spectra due to the spin systems shown in Fig. 3.

The spectrum for (i) showed a triplet in the A spectrum and a quintet in the M spectrum (Fig. 2a) in each case giving "virtual coupling". This spectrum arises since the *cis*-coupling  $^2J(\text{AM})$  and  $^3J(\text{AM}')$  are considerably less than the couplings such as  $^3J(\text{MM}')$  and  $^2J(\text{AA}')$  [11]. In each case the spacings of the triplet or quintet are equal to  $1/2[{}^2J(\text{AM}) + {}^3J(\text{AM}')]$ . Spectra due to species (ii) are particularly complex. The different effective chemical shifts of M and M' due to the different couplings  $^1J(\text{MX})$  and  $^2J(\text{M}'\text{X})$  lead to their appearance in the  $^{31}\text{P}$  spectrum as an "AB" quartet on either side to the central resonance due to (i), with further coupling due to the phosphorus atoms of the dppm ligands. One set of satellite spectra due to the  $\text{PMe}_2\text{Ph}$  ligands of species (ii) is shown in Fig. 2b. Analysis of this then gave the couplings  $^1J(\text{MX})$ ,  $^2J(\text{M}'\text{X})$  and  $^3J(\text{MM}')$ . Refinement of these couplings was achieved by simulation of the  $^{31}\text{P}$  NMR spectra. Peaks due to the  $\text{MM}'$  phosphorus atoms of species (iii) appeared as a doublet of quintets with the doublet separation equal to  $^1J(\text{MX}) + ^2J(\text{MX}')$  showing that these couplings have the same sign. Since  $^1J(\text{Pt}-\text{P})$  is always positive [12], the coupling  $^2J(\text{Pt}-\text{Pt}-\text{PMe}_2\text{Ph})$  is also positive in this complex. The peaks due to the dppm phosphorus atoms (Fig. 2c) in species (ii) were particularly complex. However, the couplings  $^1J(\text{AX})$  and  $^2J(\text{A}''\text{X})$  could be calculated from the centre of the sets of outer and inner satellites respectively, and a reasonable simulation of the spectrum was achieved by refining the couplings  $J(\text{AA}''')$  and  $J(\text{AA}''')$ . Couplings are given in Table 2. The weak satellites due to species (iii) could not be located so that the magnitude of  $^1J(\text{Pt}-\text{Pt})$  could not be measured.

In the unsymmetrical complex V, the non-equivalent phosphorus atoms give an  $\text{AA}'\text{BB}'$  spectrum and analysis was similar to that described previously for the complex  $[\text{Pt}_2\text{Cl}(\text{CO})(\mu\text{-dppm})_2][\text{PF}_6]_2$  [8]. Couplings are given in Table 2.



## Discussion

In view of the fact that oxidation state one is not commonly observed for platinum, the previously reported neutral complex  $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$  (I) and the related dibromide and di-iodide were of interest as new examples of this. The ease of preparation and stability of the related cationic complexes  $[\text{Pt}_2\text{L}_2(\mu\text{-dppm})_2]^{2+}$  (IV), where L may be organophosphine,  $\text{NH}_3$ , py or CO, now reported indicate that many further examples of platinum(I) can be obtained. Whilst, to some extent at least, these complexes are stabilized by the two  $\mu\text{-dppm}$  ligands, it seems likely that platinum(I) is more accessible than perhaps was previously thought likely.

A direct Pt—Pt bond may be expected from the formulation of these complexes as  $[\text{Pt}_2\text{L}_2(\mu\text{-dppm})_2]^{2+}$  since if this were not so, an unpaired electron would be present on each Pt atom. Formation of a Pt—Pt bond gives a square planar environment electronically similar to that for  $\text{Pt}^{\text{II}}$ . Judging from the value of  $\nu(\text{Pt—Pt})$  for (IVd), the Pt—Pt bond strength in IV is probably similar to that in the neutral complex I and confirmation is obtained from the magnitudes of the long range coupling constants  $^2J(\text{Pt—P})$  and  $^3J(\text{P—P})$  whose significance has been discussed elsewhere [9]. However, the magnitude of the direct coupling constant  $^1J(\text{Pt—Pt})$  is much smaller for IVd—IVf, the only cationic complexes for which the coupling constant could be measured, than for I. Thus it appears that  $^1J(\text{Pt—Pt})$  is not a satisfactory criterion of bond strength even between the closely related structural types IV and I. This is not particularly surprising since previous workers have found that there is a poor correlation between  $^1J(\text{Pt—Pt})$  and the Pt—Pt bond distance [10] and our results tend to confirm this.

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