Bis[bis(diphenylphosphino)methane]platinum(II) Salts: Evidence for the Formation of a Five-co-ordinate Bis[bis(diphenylphosphino)methane]-halogenoplatinum(II) Cation

Martin C. Grossel
Department of Chemistry, Bedford and Royal Holloway New College, Egham, Surrey TW20 0EX
Roger P. Moulding
Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR
Kenneth R. Seddon and Fiona J. Walker
School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ

The salts $[Pt(dppm)_2]X_2$ (X = Cl, Br, I, PF_6, or BPh_4; dppm = $Ph_2PCH_2PPh_2$) have been studied in solution by ^1H, ^{31}P, and ^{195}Pt n.m.r. spectroscopy and by conductivity measurements. The halide salts are believed to form the five-co-ordinate cation $[Pt(dppm)_2X]^+$ in solution.

The salts $[Pt(dppm)_2]X_2$ (X = Cl, Br, I, or PF_6; dppm = $Ph_2PCH_2PPh_2$) were first reported in 1981,[1] and used as starting materials for the synthesis of $[Pt_2H(dppm\text{-}P)(\mu\text{-}dppm)_2]X$ and related complexes.[1] $[Pt(dppm)_2]^{2+}$ has also been deprotonated to give $[Pt^{II}(Ph_2PCHPPh_2)_2]$, the first homoleptic complex containing the chelated bis(diphenylphosphino)methanide ligand.[2,3] However, despite their utility as synthetic reagents, little is known of the nature of these salts. We report here the first spectroscopic study of these complexes, and provide evidence for the formation of five-co-ordinate adducts, $[Pt(dppm)_2X]^+$ (X = Cl, Br, or I) and $[Pt(dppm)_2(NCCH_3)]^{2+}$.

Experimental

General Procedures.—The complexes $[PtX_2(cod)]$ (X = Br or I, cod = cyclo-octa-1,5-diene)[4] were used to prepare $[PtX_2(dppm)]$ by an established route,[5] whereas $[PtCl_2(dppm)]$ was prepared from $K_2[PtCl_4]$ (Johnson Matthey) by a more recent method.[6] N.m.r. spectra were all recorded at ambient temperature using JEOL FX-90Q [^{195}Pt (19.16 MHz)], Bruker WH-90 [^{31}P (36.43 MHz)], Bruker WH-300 [^1H (300.13 MHz)], or Bruker WH-400 [^{195}Pt (85.62 MHz)] spectrometers. All chemical shifts are defined as positive to low field (high frequency) of the reference compound. Proton chemical shifts were measured relative to tetramethylsilane, phosphorus chemical shifts relative to trimethyl phosphate and solvent corrected, and platinum chemical shifts relative to a frequency of 21.4 MHz on an n.m.r. machine on which tetramethylsilane resonates at exactly 100.00 MHz [see Appendix (iii) of ref. 6].

Conductivity Measurements.—Conductivity measurements were made with a Phillips PW9506 digital conductivity meter. The cell, fitted with platinum electrodes, was calibrated with 1 mmol dm^{-3} aqueous potassium chloride solution. The solutions of platinum salts were studied in a concentration range of 10^{-5}—10^{-3} mol dm^{-3}, at 25 °C. The solvents used were purified by double distillation from phosphorus(V) oxide under dry dinitrogen. Typical background conductivities for ethanenitrile, nitromethane, and dichloromethane were 1.8, 1.5, and 1.4 μS cm^{-1}, respectively.

Preparation of Bis[bis(diphenylphosphino)methane]platinum(II) Halides.—$[PtX_2(dppm)]$ (X = Cl, Br, or I) (0.5 g) was suspended in dichloromethane (50 cm^3) and dppm (1 mol equiv.; X = Cl, 0.295 g; X = Br, 0.259 g; X = I, 0.230 g) was added. The solution was shaken and gradually the suspension of $[PtX_2(dppm)]$ dissolved, the solution becoming darker in colour (X = Cl, pale green; X = Br, green; X = I, dark yellow-green). The solution was left to stand for *ca.* 2 h to ensure that the reaction was complete, then hexane (120 cm^3) was added. The precipitate which formed (X = Cl, white; X = Br, cream-white; X = I, yellow-cream) was collected by filtration, washed with diethyl ether (20 cm^3), and dried *in vacuo* (Found: C, 58.20; H, 4.30; Cl, 7.00. Calc. for $C_{50}H_{44}Cl_2P_4Pt$: C, 58.05; H, 4.30; Cl, 6.85%. Found: C, 52.90; H, 3.80; Br, 14.75. Calc. for $C_{50}H_{44}Br_2P_4Pt$: C, 53.45; H, 3.95; Br, 14.20%. Found: C, 48.70; H, 3.50; I, 22.10. Calc. for $C_{50}H_{44}I_2P_4Pt$: C, 49.30; H, 3.65; I, 20.85%).

Preparation of Bis[bis(diphenylphosphino)methane]platinum(II) Hexafluorophosphate.—$[Pt(dppm)_2]Cl_2$ (0.5 g, 0.48 mmol) was dissolved in dichloromethane (10 cm^3) and ammonium hexafluorophosphate (0.4 g, 2.44 mmol) in methanol (5 cm^3) was added. A white precipitate formed immediately, which was collected by filtration, and washed with dichloromethane (20 cm^3), methanol (20 cm^3), water (2 × 20 cm^3), and finally methanol (2 × 20 cm^3). The white solid was then dried *in vacuo* for 2 h (Found: C, 47.60; H, 3.60. Calc. for $C_{50}H_{44}F_{12}P_6Pt$: C, 47.90; H, 3.55%).

Preparation of Bis[bis(diphenylphosphino)methane]platinum(II) Tetraphenylborate.—$[Pt(dppm)_2]Cl_2$ (0.5 g, 0.48 mmol) was dissolved in dichloromethane (10 cm^3) and sodium tetraphenylborate (1.0 g, 2.92 mmol) in methanol (10 cm^3) was added. Precipitation of a white solid occurred at the interface of the two solutions, but on stirring a clear pale green solution was formed. Methanol (*ca.* 20 cm^3) was added and a white crystalline precipitate was formed. This was collected by filtration, washed with methanol (2 × 20 cm^3), and dried *in vacuo* for *ca.* 4 h (Found: C, 73.45; H, 5.40. Calc. for $C_{98}H_{84}B_2P_4Pt$: C, 73.45; H, 5.30%). This complex was kept out of strong sunlight since it discoloured, turning pale green.

Results and Discussion

N.M.R. Spectroscopic Studies.—The cation $[Pt(dppm)_2]^{2+}$ was prepared by a minor variation of an established synthetic route,[1] and the salts were isolated as pure products in high yield. All five salts $[Pt(dppm)_2]X_2$ (X = Cl, Br, I, PF_6, or BPh_4) were soluble in CD_3CN. All except the salt with X = PF_6 were soluble in CD_2Cl_2; all bar the salts with X = PF_6 or BPh_4 were soluble in $CDCl_3$. Proton and ^{31}P n.m.r. spectra were recorded using as many of the mentioned solvents as solubility would allow; ^{195}Pt n.m.r. spectra were recorded using CD_2Cl_2 or $CDCl_3$.

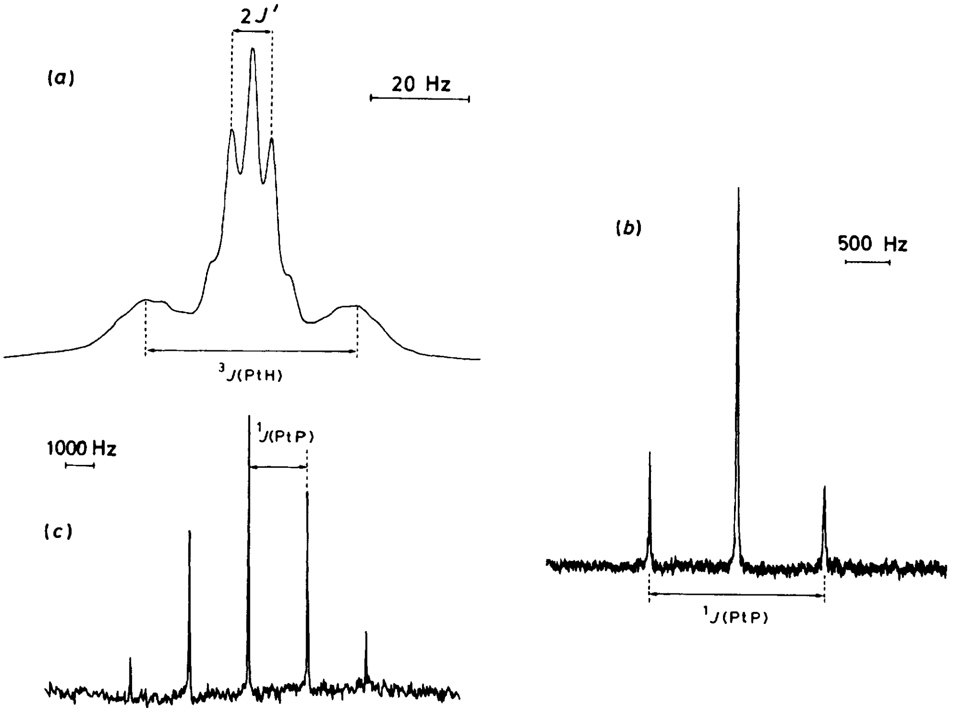


Figure 1. N.m.r. spectra of $[Pt(dppm)_2]Cl_2$ in CD_2Cl_2 solution: (*a*) ^1H, (*b*) $^{31}P-\{^1H\}$, and (*c*) $^{195}Pt-\{^1H\}$

Table 1. ^1H N.m.r. spectroscopic data[a] for $[Pt(dppm)_2]X_2$

		PCH$_2$P					
X	Solvent	δ(CH$_2$)[b,c]	Δ_1[c,d]	Δ_2[c,e]	Δ_3[c,f]	^2J(PH)/ Hz[g]	^3J(PtH)/ Hz
Cl	CD_2Cl_2	4.76			0.25	8.40	43
	$CDCl_3$	4.59	0.17			8.20	44
	CD_3CN	4.77		−0.01		8.40	45
Br	CD_2Cl_2	5.18			0.57	8.84	38
	$CDCl_3$	5.29	−0.11			8.72	43
	CD_3CN	5.25		−0.07		8.84	40
I	CD_2Cl_2	5.36			0.85	8.40	31
	$CDCl_3$	5.41	−0.05			8.40	36
	CD_3CN	5.44		−0.08		8.72	34
BPh_4	CD_2Cl_2	4.51			0.00	9.24	43
	CD_3CN	5.31		−0.80		9.74	57
PF_6	CD_3CN	5.36				9.74	57

[a] All spectra recorded at ambient temperatures at 300.13 MHz. [b] Measured relative to tetramethylsilane. [c] Units of p.p.m. [d] Defined in equation (1). [e] Defined in equation (2). [f] Defined in equation (3). [g] $^2J(PH) = 2J'$ if $^4J(PH) \sim 0$ Hz; see text and ref. 6.

Although discussed so far in this paper as $[Pt(dppm)_2]X_2$, as in the literature,[1,2] the halide salts could be conceivably formulated as $[Pt(dppm\text{-}P)_2X_2]$ (**1**), $[Pt(dppm\text{-}PP')(dppm\text{-}P)X]X$ (**2**), $[Pt(dppm\text{-}PP')_2X_2]$ (**3**), $[Pt(dppm\text{-}PP')_2X]X$ (**4**), or $[Pt(dppm\text{-}PP')_2]X_2$ (**5**). For both the salts $[Pt(dppm)_2][PF_6]_2$ and $[Pt(dppm)_2][BPh_4]_2$, only formulation (**5**) is reasonable. The ^1H, ^{31}P, and ^{195}Pt n.m.r. spectra of $[Pt(dppm)_2]Cl_2$ in CD_2Cl_2 are illustrated in Figure 1, and similar profiles were observed for this salt in $CDCl_3$ and CD_3CN, and for the other four salts in all the solvents studied. Consideration of Figure 1 clearly reveals the complexes to contain a $Pt(dppm\text{-}PP')_2$ skeleton, in which all four phosphorus atoms and all four methylenic protons are equivalent. Thus, formulations (**1**) and (**2**) can be immediately eliminated. Each of the spectra will now be considered in more detail.

The proton n.m.r. data for the five salts are summarized in Table 1. The methylenic protons are coupled to platinum to give a 1:4:1 triplet {separation $\frac{1}{2}[^3J(PtH)]$}, each line of which is further split into a quintet of separation $\frac{1}{2}[^2J(PH) + {}^4J(PH)]$, defined as the apparent coupling constant J', due to virtual coupling with the neighbouring phosphorus atoms. If it is assumed that $^4J(PH) \sim 0$ Hz, then $^2J(PH) = 2J'$. The values of $^2J(PH)$ and $^3J(PtH)$ in Table 1 are comparable with, but smaller than, those reported elsewhere for $[PtX_2(dppm)]$ [X = Cl, Br, or I; $^3J(PtH) = 68$—71, $^2J(PH) = 10.8$—11.1 Hz].[6] The most striking feature of the ^1H n.m.r. data, however, is its strong dependency both upon solvent and upon anion. Parameters Δ_1, Δ_2, and Δ_3 were defined according to equations (1)—(3) to highlight these important differences; Δ_1 is a

$$\Delta_1 = \delta(CD_2Cl_2) - \delta(CDCl_3) \qquad (1)$$

$$\Delta_2 = \delta(CD_2Cl_2) - \delta(CD_3CN) \qquad (2)$$

$$\Delta_3 = \delta(X,CD_2Cl_2) - \delta(BPh_4,CD_2Cl_2) \qquad (3)$$

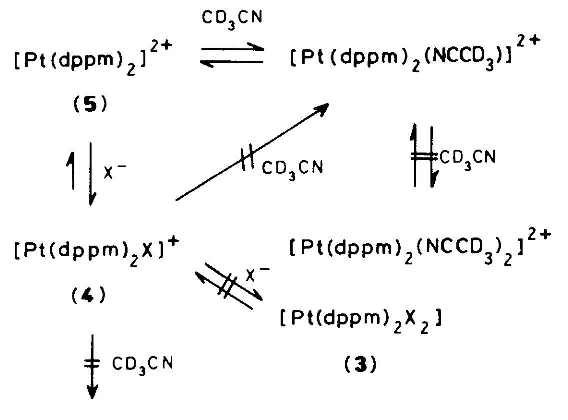
measure of the effect of changing solvent from CD_2Cl_2 to $CDCl_3$ for a given anion, Δ_2 is a measure of the effect of changing solvent from CD_2Cl_2 to CD_3CN for a given anion, and Δ_3 is a measure of the effect of changing the anion in the same solvent (CD_2Cl_2). The parameter Δ_1 is small, but encompasses a range of 0.28 p.p.m. {*cf.* for $[PtX_2(dppm)]$, the range of Δ_1 is 0.04 p.p.m.}; Δ_2 is between −0.01 and −0.08 p.p.m. for the halide salts, but a huge −0.8 p.p.m. for the tetraphenylborate salt. Moreover, Δ_3 is between 0.25 and 0.85 p.p.m. for the halide salts. These results cannot be rationalized if structure (**5**), implicit in formulating the salts as $[Pt(dppm)_2]X_2$,[1,2] is the predominant form of the complex in solution.

The trends in Δ_1, Δ_2, and Δ_3 can be understood

Table 2. Phosphorus-31 and ^{195}Pt n.m.r. spectroscopic data[a] for $[Pt(dppm)_2]X_2$

		^{31}P		^{195}Pt	
X	Solvent	δ(P)/ p.p.m.[b]	^1J(PtP)/ Hz	δ(Pt)/ p.p.m.[c,d]	^1J(PtP)/ Hz
Cl	CD_2Cl_2	−39.3	2 048.3		
	$CDCl_3$	−38.2	2 048.2	338	2 048
	CD_3CN	−41.9	2 048.3		
Br	CD_2Cl_2	−53.0	2 170.4		
	$CDCl_3$	−51.9	2 148.4	340	2 155
	CD_3CN	−53.3	2 163.0		
I	CD_2Cl_2	−61.0	2 179.0	314[e]	2 194
	$CDCl_3$	−56.2	2 187.5		
	CD_3CN	−63.0	2 193.6		
BPh_4	CD_2Cl_2	−45.5	1 961.7	161[e]	1 968
	CD_3CN	−42.6	2 015.4		
PF_6	CD_3CN	−38.5	2 016.6		

[a] All spectra recorded at ambient temperatures. [b] Measured at 36.43 MHz relative to trimethyl phosphate. [c] Measured relative to a frequency of 21.4 MHz upon a hypothetical n.m.r. machine upon which tetramethylsilane resonates at exactly 100.00 MHz. [d] Recorded at 19.16 MHz, unless otherwise stated. [e] Measured at 85.62 MHz.



Scheme. The postulated reactions of $[Pt(dppm)_2]^{2+}$ with CD_3CN and X^- (X = Cl, Br, or I)

if it is assumed that a solution of $[Pt(dppm)_2][BPh_4]_2$ in CD_2Cl_2 contains a complex of structure (5), the cation being 'naked' $[Pt(dppm)_2]^{2+}$. The large value of Δ_2 will be induced if $[Pt(dppm)_2]^{2+}$ reacts with CD_3CN to give either five-co-ordinate $[Pt(dppm)_2(NCCD_3)]^{2+}$ or six-co-ordinate $[Pt(dppm)_2(NCCD_3)_2]^{2+}$, and this is supported by the similarity in spectral parameters for solutions of $[Pt(dppm)_2][BPh_4]_2$ and $[Pt(dppm)_2][PF_6]_2$ in CD_3CN. However, the large values of Δ_3 for the halide salts show that the platinum containing species in CD_2Cl_2 *cannot* be $[Pt(dppm)_2]^{2+}$ and, furthermore, as Δ_3 is dependent on X, the complex probably contains co-ordinated X. Moreover, as Δ_2 for the halide salts is small, co-ordinated halide is not displaced by CD_3CN, nor supplemented by it. These conclusions are summarized in the Scheme. Upon the n.m.r. data alone, it is not possible to deduce whether the predominant solution species is (3) or (4), however.

The ^{31}P and ^{195}Pt data (Table 2) reinforce the conclusions summarized in the Scheme, but again do not distinguish between the five- or six-co-ordinate structures for the platinum complex.

Table 3. Molar conductivity data for $[Pt(dppm)_2]X_2$

	CH_3CN		CH_3NO_2		CH_2Cl_2	
X	$(\Lambda_m)_0$[a]	Λ_m[a,b]	$(\Lambda_m)_0$[a]	Λ_m[a,b]	$(\Lambda_m)_0$[a]	Λ_m[a,b]
Cl	188	116	86	78	41	31
Br	156	132	84		53	40
I	156	130	82	79	60	47
PF_6	337	283	200	184		
BPh_4	238	206	108	108		

[a] Units of S cm^2 mol^{-1}. [b] Measured at 10^{-3} mol dm^{-3}.

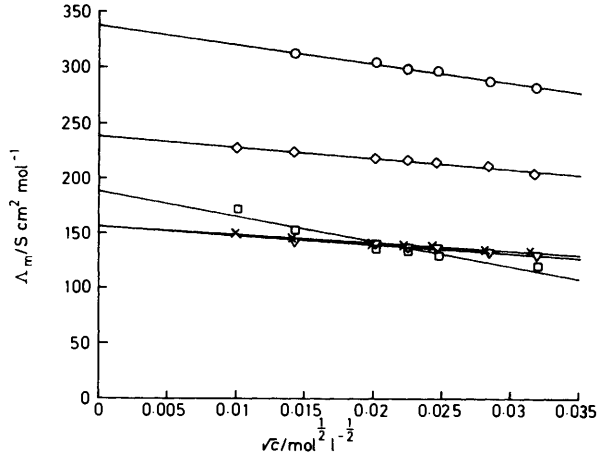


Figure 2. The molar conductivity, Λ_m, of solutions of $[Pt(dppm)_2]X_2$ plotted as a function of $\sqrt{c}$ for X = Cl (□), Br (×), I (▽), PF_6 (○), and BPh_4 (◇). The straight lines were fitted to the experimental data by a conventional least-squares linear regression procedure

Conductivity Measurements.—The conductivities, κ, of solutions of the salts $[Pt(dppm)_2]X_2$ (X = Cl, Br, I, PF_6, or BPh_4) in ethanenitrile, nitromethane, and dichloromethane were measured at 25 °C. Their molar conductivities, Λ_m, were calculated from equation (4),[7] where c is the molar

$$\Lambda_m = \kappa/c \tag{4}$$

concentration. A common form of the Onsager limiting law [equation (5), where $(\Lambda_m)_0$ is the limiting molar conductivity

$$\Lambda_m = (\Lambda_m)_0 - \alpha\sqrt{c} \tag{5}$$

and α is the Onsager coefficient] was used to fit the experimental data by a conventional least-squares linear regression procedure, and the data for ethanenitrile are illustrated in Figure 2. All the plots are catabatic. Similar fits were obtained in nitromethane and dichloromethane, and the extrapolated and interpolated values for $(\Lambda_m)_0$ and Λ_m (10^{-3} mol dm^{-3}) are detailed in Table 3.

Geary[7] and Walton[8] have suggested that typical values of Λ_m (10^{-3} mol dm^{-3}) in ethanenitrile for 1:1 electrolytes lie in the range 120—160 S cm^2 mol^{-1}, and values for 1:2 electrolytes in the range 220—300 S cm^2 mol^{-1}. Examination of Figure 2 and Table 3 reveals that, as anticipated above, the salt $[Pt(dppm)_2][PF_6]_2$ is unambiguously a 1:2 electrolyte, but that the value of Λ_m (10^{-3} mol dm^{-3}) for $[Pt(dppm)_2][BPh_4]$ lies a little below the normal range. It is widely recognized[7] that tetraphenylborate salts show a significantly lower conductivity than hexafluorophosphate salts. In ethanenitrile, the limiting ionic conductivity, λ_0, for PF_6^- is 103 S cm^2 mol^{-1}, whereas for BPh_4^- it is 58 S cm^2 mol^{-1}.[9] Thus, the limiting molar conductivity of $[Pt(dppm)_2][BPh_4]_2$ should be *ca.* 90 S cm^2 mol^{-1} lower than that of $[Pt(dppm)_2][PF_6]_2$ if both are 1:2 electrolytes: the empirical difference is 99 S cm^2 mol^{-1}. The halide salts $[Pt(dppm)_2]X_2$, however, show values of Λ_m (10^{-3} mol dm^{-3}) which are characteristic of 1:1 electrolytes, clearly favouring structure (**4**) over either (**5**) or (**3**). Similar behaviour is found in nitromethane, in which 1:1 electrolytes normally have values of Λ_m (10^{-3} mol dm^{-3}) in the range 75—95 S cm^2 mol^{-1} and 1:2 electrolytes lie in the range 150—180 S cm^2 mol^{-1}.[7,10] The slight deviation from perfect linearity in the case of the chloride salt (see Figure 2) might indicate that some dissociation occurs in very dilute solution.

The probability of the halide salts forming a non-conducting solution containing six-co-ordinate (**3**) will be at its highest in dichloromethane, which has a very low dielectric constant. However, the values of the limiting molar conductivities in dichloromethane (Table 3) show that, even in dichloromethane, the halide salts are best formulated as (**4**).

The possibility that (**4**) might be an intimate ion pair, rather than a covalent five-co-ordinate complex monocation, cannot be entirely eliminated, but the constancy of Δ_2 for the halide salts and the linearity of the Λ_m *versus* $\sqrt{c}$ plots would appear to argue against such a possibility.

Conclusions

The combined evidence of the n.m.r. and conductivity studies demonstrates that $[Pt(dppm)_2]X_2$ ($X = PF_6$ or BPh_4) dissolves in both chlorinated hydrocarbons and ethanenitrile as a 1:2 electrolyte, but that the cation present in the ethanenitrile solution is probably $[Pt(dppm)_2(NCCH_3)]^{2+}$. The halide salts dissolved in all the solvents studied as $[Pt(dppm)_2X]X$ (X = Cl, Br, or I), and the co-ordinated halide could not be displaced with ethanenitrile. Moreover, $[Pt(dppm)_2X]^+$ does not form the six-co-ordinate ion $[Pt(dppm)_2X(NCCH_3)]^+$ in ethanenitrile; nor does it form $[Pt(dppm)_2X_2]$ in dichloromethane. Thus, given the rarity of five-co-ordinate platinum(II) complexes,[11] $[Pt(dppm)_2X]^+$ possesses a remarkable stability.

Acknowledgements

We wish to thank the S.E.R.C. for the award of two studentships (to R. P. M. and F. J. W.). We are also extremely grateful to Dr. G. Hawkes and Mr. M. Buckingham (ULIRS WH-400 N.M.R. Service, Queen Mary College, University of London) and Mr. D. Parkinson (JEOL FX-90Q, Bedford and Royal Holloway New College, University of London) for their assistance with recording multinuclear n.m.r. spectra, and to Dr. O. Wernberg for invaluable discussions and a preprint of ref. 11.

References

1 M. P. Brown, J. R. Fisher, R. H. Hill, R. J. Puddephatt, and K. R. Seddon, *Inorg. Chem.*, 1981, **20**, 3516.
2 M. P. Brown, A. Yavari, Lj. Manojlović-Muir, K. W. Muir, R. P. Moulding, and K. R. Seddon, *J. Organomet. Chem.*, 1982, **236**, C33.
3 M. P. Brown, A. Yavari, Lj. Manojlović-Muir, K. W. Muir, R. P. Moulding, and K. R. Seddon, unpublished work.
4 F. A. Cotton, *Inorg. Synth.*, 1972, **13**, 48.
5 M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1977, 951.
6 M. C. Grossel, J. R. Batson, R. P. Moulding, and K. R. Seddon, *J. Organomet. Chem.*, 1986, **304**, 391.
7 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
8 R. A. Walton, *Qt. Rev., Chem. Soc.*, 1965, **19**, 126.
9 A. C. Harkness and H. M. Daggett, jun., *Can. J. Chem.*, 1965, **43**, 1215.
10 J. F. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, 1965, **87**, 2529.
11 O. Wernberg, *J. Chem. Soc., Dalton Trans.*, 1986, 725.

Received 5*th March* 1986; *Paper* 6/443