Effect of Chelate-ring Size on Spectroscopic and Chemical Properties of Methylplatinum(II) Complexes of the Ditertiary Phosphines $Ph_2P[CH_2]_nPPh_2$ (n = 1, 2, or 3)

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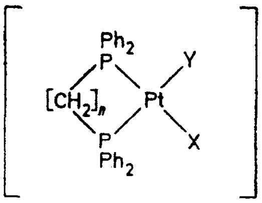
The ditertiary phosphines $Ph_2P[CH_2]_nPPh_2$ (n = 2 or 3, dppe and dppp respectively) displace cyclo-octa-1,5-diene (cod) from [PtMe(cod)Cl] to give monomeric complexes [PtMe(Cl)(dppe)] and [PtMe(Cl)(dppp)]. A similar reaction using $Ph_2PCH_2PPh_2$ (dppm) gives predominantly an oligomer [{PtMe(Cl)(dppm)}$_n$] containing bridging dppm groups, together with a small amount of monomeric [PtMe(Cl)(dppm)]. Molecular-weight measurements suggest that the oligomers [{PtMe(X)(dppm)}$_n$] (X = Cl or I) may be trimeric in solution (n = 3). Dimethyl complexes, [$PtMe_2$(diphosphine)], have been obtained from [$PtMe_2$(cod)] and dppe, dppp, or dppm. ^{31}P N.m.r. parameters and oxidative-addition reactions of the complexes with iodine or methyl iodide are very dependent on the ditertiary phosphine.

IN the course of work on the effect of stereochemistry on the sign of $J(P\text{-}Pt\text{-}CH_3)$,[1] we prepared the complex [1,2-bis(diphenylphosphino)ethane]chloro(methyl)-platinum(II), [PtMe(Cl)(dppe)], by displacement of cyclo-octa-1,5-diene (cod) from its complex [PtMe(cod)-Cl]. We now describe the chloro(methyl)- and dimethyl-platinum(II) complexes of 1,3-bis(diphenylphosphino)-propane (dppp) and bis(diphenylphosphino)methane (dppm) and examine the effects of varying chelate-ring size on spectroscopic properties and on oxidative-addition reactions. The platinum(II) complexes prepared in this work are assigned structures (I)—(IV) on the basis of data discussed below. Spectroscopic and analytical data are given in Tables 1 and 2 respectively.

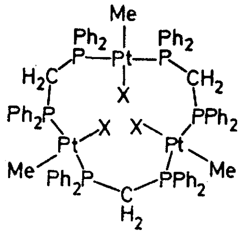


(I) X = Cl, Y = Me
(III) X = Y = Me
(IV) X = Y = Cl
(a) n = 1, (b) n = 2, (c) n = 3

RESULTS AND DISCUSSION

Preparation and Spectra.—The monomeric complexes [PtMe(Cl)(dppe)], (Ib), and [PtMe(Cl)(dppp)], (Ic), precipitated on addition of the appropriate ditertiary phosphine to a benzene solution of [PtMe(cod)Cl]. Their i.r. spectra showed a medium-intensity band due to ν(PtCl) at *ca.* 290 cm^{-1}. The methyl resonances in their ^1H n.m.r. spectra appeared as the expected doublet of doublets, arising from coupling with two inequivalent ^{31}P nuclei, together with satellites due to coupling with ^{195}Pt (33.6% abundance, $I = \frac{1}{2}$) (Table 1). The ^{31}P-{^1H} n.m.r. spectra of (Ib) and (Ic) in dichloromethane consisted of two 1 : 4 : 1 triplets arising from the two inequivalent ^{31}P nuclei coupled to ^{195}Pt, the values of J(Pt–P) being similar to those observed for *cis*-[PtMe(Cl)(PEt_3)$_2$].[2] In the case of the dppp complex, (Ic), further splitting due to P–P coupling was observed [^2J(P–P) 21 Hz].

When stoicheiometric amounts of [PtMe(cod)Cl] and dppm were heated under reflux in benzene a mixture of monomeric and oligomeric forms of [PtMe(Cl)(dppm)], (Ia) and (IIa), respectively, was obtained. Pure (IIa) could be obtained in solvated form by keeping a dichloromethane solution of the mixture at room temperature for several days, or by twice recrystallizing the mixture from dichloromethane–n-hexane or chloroform–n-hexane. When [PtMe(cod)Cl] and dppm were mixed in benzene at room temperature the product isolated by precipitation with n-hexane consisted almost entirely of oligomer, but on heating in benzene (Ia) was formed. Thus the oligomer (IIa) is the first product of reaction between [PtMe(cod)Cl] and dppm.



(IIa) X = Cl
(IIb) X = I

Samples containing (Ia) showed a medium-intensity band due to ν(PtCl) at 292 cm^{-1} similar to those observed for (Ib) and (Ic), and the methyl resonance pattern of (Ia) also resembled those of (Ib) and (Ic).

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[1] M. A. Bennett, R. Bramley, and I. B. Tomkins, *J.C.S. Dalton*, 1973, 166.

[2] F. H. Allen and A. Pidcock, *J. Chem. Soc. (A)*, 1968, 2700.

TABLE 1

Spectroscopic data

	^{1}H N.m.r.									^{31}P N.m.r.					
Compound	Solvent	$\delta(PtCH_3)$ ^{a} $\pm$0.1 p.p.m.	$\lvert ^{2}J(Pt-CH_3)\rvert$ $\pm$0.5 Hz	$\lvert ^{3}J(P-PtCH_3)\rvert$ $\pm$0.2 Hz	$\delta(P-CH_2)$ ^{a} (or $P-CH_3$) $\pm$0.01 p.p.m.	$\lvert ^{2}J(P-CH_2)\rvert$ (or $P-CH_3$) $\pm$0.2 Hz	$\lvert ^{3}J(Pt-P-CH_2)\rvert$ (or $Pt-P-CH_3$) $\pm$0.5 Hz	$\delta(C-CH_2-C)$ ^{a} $\pm$0.1 p.p.m.	Ref.^{b}	Solvent	δ_P ^{c} $\pm$0.5 p.p.m.	ΔP ^{d}	$\lvert ^{1}J(Pt-P)\rvert$ $\pm$10 Hz	Ref.^{b}	$\nu(Pt-Cl)$ ^{e} / cm^{-1}
$PMePh_2$										CH_2Cl_2	−28.1			^{r}	
$Ph_2P(CH_2)_3PPh_2$ (dppp)	$CDCl_3$				2.6	6.6			^{f}	$CHCl_3$	−17.3			^{f}	
$Ph_2P(CH_2)_2PPh_2$	$CDCl_3$				2.1	4.1			^{f}	$CHCl_3$	−12.5			^{f}	
(dppe)										C_6H_6	−14.3				
$Ph_2PCH_2PPh_2$ (dppm)	$CDCl_3$				2.8	0			^{f}	CH_2Cl_2	−23.0			^{f}	
cis-$[PtMe_2(PMePh_2)_2]$	$CDCl_3$	0.44	68	*g*	1.63	7.0	20		5	CH_2Cl_2	+6.4	+34.5	1 851		
$[PtMe_2(dppp)]$ (IIIc)	$CDCl_3$	0.57	69	*g*	2.31	*g*	*g*	1.69		CH_2Cl_2	+3.2	+20.5	1 790		
$[PtMe_2(dppe)]$ (IIIb)	C_6D_6	1.08	71	*g, h*	1.44	*g*	*g*		3	C_6H_6	+45.4	+59.7	1 794		
$[PtMe_2(dppm)]$ (IIIa)	C_6D_6	1.25	75	*g, h*	3.47	9.0	11.5			CH_2Cl_2	−40.4	−17.4	1 434		
	$CDCl_3$	0.99			4.33										
cis-$[PtMe(Cl)(PMePh_2)_2]$	$CDCl_3$	0.65	56	4.6, 7.3	1.93 ^{i} 1.58 ^{j}	9.6 ^{i} 10.1 ^{j}	14.4 ^{i} 47 ^{j}		5						
$[PtMe(Cl)(dppp)]$ (Ic) ^{k}	$CDCl_3$	0.50	55	5.0, 7.5	2.47	*g*	*g*	1.86		CH_2Cl_2	+3.0 ^{i} +5.1 ^{j}	+20.3 ^{i} +22.4 ^{j}	1 644 ^{i} 4 116 ^{j}		300
$[PtMe(I)(dppp)]$	$CDCl_3$	0.79	59	6.5, 6.5	2.51	*g*	*g*	1.92							
$[PtMe(Cl)(dppe)]$ (Ib)	CD_2Cl_2	0.51	53.5	3.5, 8.0		*g*	*g*		3	CH_2Cl_2	+43.4 ^{i} +42.0 ^{j}	+55.9 ^{i} +54.5 ^{j}	1 737 ^{i} 4 224 ^{j}		290
$[PtMe(Cl)(dppm)]$ (Ia)	CD_2Cl_2	0.80	62	2.8, 8.3											292
trans-$[PtMe(Cl)(PMePh_2)_2]$	$CDCl_3$	−0.04	81.0	6.8	2.21	7.2	28.7		5	CH_2Cl_2	+13.2	+41.3	3 028		
$[\{PtMe(Cl)(dppm)\}_n]$ (IIa) ^{l}	$CDCl_3$	0.51	88.0	6.5 ^{g}	4.13	*g*	*g*			CH_2Cl_2	+13.0	+36.0	3 042		
$[\{PtMe(I)(dppm)\}_n]$ (IIb) ^{l}	$CDCl_3$	0.66	85.0	6.5 ^{g}	4.57	*g*	*g*			CH_2Cl_2	+9.9	+32.9	2 934		
cis-$[PtCl_2(PMePh_2)_2]$										CH_2Cl_2	−1.2	+26.9	3 616 ^{r}		
$[PtCl_2(dppp)]$ (IVc)										CH_2Cl_2	−5.6	+11.7	3 420		312, 291
$[PtCl_2(dppe)]$ (IVb)										CH_2Cl_2	+45.3	+57.8	3 618		318, 295
$[PtCl_2(dppm)]$ (IVa)										CH_2Cl_2	−64.3	−41.3	3 078		305, 292
$[PtMe_3(I)(PMePh_2)_2]$ (Vb)	$CDCl_3$	0.77 ^{m} 1.21 ^{n}	69.2 ^{m} 58.4 ^{n}	7.0 ^{m,g,n}	2.17	8.0	10.0			CD_2Cl_2	−39.3 ^{o}	−16.3	1 126 ^{o}		
$[PtMe_3(I)(dppe)]$ (VIb)	$CDCl_3$	0.49 ^{m} 1.62 ^{n}	69.4 ^{m} 60.0 ^{n}	7.5 ^{g,p}	2.97	*g*	*g*			CD_2Cl_2	−1.0 ^{o}	+11.5	1 039 ^{o}		
$[PtMe_3(I)(dppm)]$ (VIa)	$CDCl_3$	0.85 ^{m} 1.67 ^{n}	71.0 ^{m} 63.0 ^{n}	8.0 ^{g}	H_A 5.78 ^{q} H_B 4.57	H_A 7.5, H_B 11.5	H_A 15, H_B <3			CD_2Cl_2	−64.0 ^{o}	−41	871 ^{o}		

[a] Downfield from $SiMe_4$. [b] Where previously run. [c] Downfield from external 85% H_3PO_4. [d] δ_P (complex) − δ_P (free ligand). [e] Nujol mull, CsI plates. [f] H. G. Horn and K. Sommer, *Spectrochim. Acta*, 1971, **A27**, 1049. [g] Complicated pattern. [h] 1 : 3.5 : 1 'triplet,' spacing, 7.5 Hz. [i] *trans* to CH_3. [j] *trans* to Cl. [k] $J(P-P)$ 21 Hz. [l] $^{2}J(P-CH_2P)$ 33 Hz. [m] *trans* to I. [n] *trans* to P. [o] Obtained by INDOR. [p] 1 : 3.2 : 1 'triplet,' spacing 7 Hz. [q] $\lvert J_{AB}\rvert$ 15 Hz. [r] S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 1133.

TABLE 2

Analytical data, molecular weights, and melting points [a]

Complex	M.p. (θ_c/°C)[a]	Analysis [b] (%) C	H	Hal	P	M [b,c]
[PtMe(Cl)(dppp)]·0.5C_6H_6(Ic) [d]	205 (decomp.)	54.2 (53.4)	4.7 (4.6)	5.2 (5.1)	8.7 (9.9)	696 (658) [e]
[PtMe(Cl)(dppm)]·0.3CH_2Cl_2 (IIa)	230 (decomp.)	46.9 (48.0)	4.1 (3.9)	9.2 (9.0)	9.3 (9.4)	1 819 (1 890) [f]
[PtMe(Cl)(dppm)]·0.1$CHCl_3$ (IIa)	N.m.	47.0 (48.6)	4.35 (4.3)	7.5 (7.2)	9.0 (9.6)	1 746 (1 890) [f]
[PtMe(I)(dppm)] (IIb) [g]	205 (decomp.)	44.2 (43.2)	4.1 (3.5)	17.6 (17.6)	8.5 (8.6)	1 660 (2 164) [f]
[$PtMe_2$(dppm)]·0.5C_6H_6 (IIIa) [d]	157—159 (decomp.)	55.0 (55.5)	5.0 (4.8)		9.3 (9.6)	691 (609) [h,e]
[$PtMe_2$(dppp)]·0.5C_6H_6 (IIIc) [d]	217—221	56.7 (56.8)	5.7 (5.2)		9.2 (8.7)	675 (637) [e]
[$PtCl_2$(dppm)] (IVa)	N.m.	47.2 (46.1)	3.8 (3.4)	11.0 (10.9)	9.3 (9.5)	760 (650) [i]
[$PtCl_2$(dppe)] (IVb)	>300 (decomp.)	47.4 (47.0)	3.5 (3.6)	10.6 (10.7)	8.9 (9.3)	
[$PtCl_2$(dppp)] (IVc)	N.m.	47.6 (47.8)	4.1 (3.8)	12.6 (10.5) [j]	8.5 (9.15)	
[$PtMe_3$(I)(dppm)] (VIIa) [g]	182 (decomp.)	46.4 (44.6)	4.8 (4.1)	16.2 (16.9)	8.1 (8.25)	795 (751)
[$PtMe_3$(I)(dppe)] (VIb)	237—239 (decomp.)	45.9 (45.5)	4.4 (4.3)	16.3 (16.6)	8.3 (9.1)	779 (765)
[PtMe(I)(dppp)]	227 (decomp.)	44.5 (44.9)	4.2 (3.9)	16.9 (16.9)	7.9 (8.3)	733 (749)

[a] N.m. = Not measured. [b] Calculated values are given in parentheses. [c] Determined osmometrically in $CHCl_3$ at 25 °C, except where stated. [d] Presence of C_6H_6 of solvation indicated by a sharp singlet in the aromatic region of the ^1H n.m.r. spectra at δ 7.37 p.p.m. ($CHCl_3$ in $CDCl_3$ appears at δ 7.27 p.p.m.). [e] Calculated for the unsolvated complex. [f] Calculated for unsolvated trimer. [g] Presence of *ca.* 0.5 mol C_6H_{14} confirmed by resonances at δ *ca.* 0.9 and *ca.* 1.3 p.p.m. in the ^1H n.m.r. spectrum. [h] Determined osmometrically in C_6H_6 at 25 °C. [i] Determined osmometrically in $CHCl_3$ at 37 °C. [j] The high Cl analysis may be due to residual occluded $CHCl_3$.

Molecular-weight measurements on a solution of (IIa) in chloroform at 25 °C (Experimental section) are in reasonable agreement with a trimeric formulation containing bridging dppm groups. No band due to ν(PtCl) could be located in the i.r. spectrum above 200 cm^{-1}. The corresponding iodo-complex (IIb), obtained by metathesis with sodium iodide in hot acetone, appears to be similar, though its molecular weight in chloroform was somewhat lower than expected. The presence of higher oligomers cannot be excluded, but we think the trimer is probably the predominant species in solution and we assume this formulation in subsequent discussion. The ^{31}P–{^1H} n.m.r. spectrum of (IIa) consisted of a 1 : 4 : 1 triplet of closely spaced triplets, the values of δ_P and ^1J(Pt-P) being very similar to those of *trans*-[PtMe(Cl)($PMePh_2)_2$] (Table 1), consistent with the postulated *trans* arrangement of phosphorus atoms with respect to platinum. The lines of the ^{195}Pt satellite triplets were of unequal but comparable intensity, whereas in the central triplet the centre line was considerably more intense than the outer lines. The spectrum must be a weighted sum of the spectra expected for the different ^{31}P environments in the various isotopic isomers. Thus, for a trimer, there may be zero to three ^{195}Pt nuclei, and in all but the first case there will be a number of distinct ^{31}P environments. Each of the resulting spin systems is too complex for detailed analysis to be carried out. The Pt-CH_3 resonance of (IIa) (Figure 1) consisted of a complex central absorption together with *ca.* 1 : 2 : 1 triplet satellite resonances. Broad-band ^{31}P irradiation caused this pattern to collapse to sharp 1 : 4 : 1 singlets, indicating that the complexity arises from ^{31}P coupling [^2J(P-C-P) 33 Hz], not from long-range coupling to other ^{195}Pt nuclei. The ^1H spectrum, like the ^{31}P n.m.r. spectrum, will be a weighted sum of the spectra corresponding to distinct methyl environments in the various isotopic isomers, each of which constitutes a very complex spin system, so that detailed analysis is impossible.

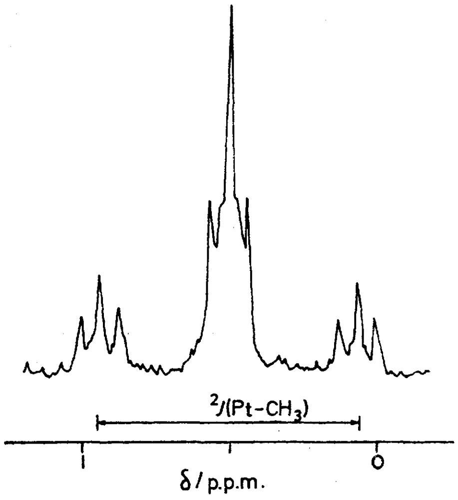

FIGURE 1 Methyl resonance pattern of [{PtMe(Cl)(dppm)}$_n$]

All the complexes (IIIa)—(IIIc) were prepared by reaction of stoicheiometric amounts of the ditertiary phosphine with [$PtMe_2$(cod)]. The complex [$PtMe_2$(dppm)], (IIIa), is monomeric in chloroform. In agreement with Hooton,[3] the ^1H n.m.r. spectrum of [$PtMe_2$ (dppe)], (IIIb), in the Pt-CH_3 region consisted of a 1 : 3.5 : 1 'triplet' with ^{195}Pt satellites. The spectra of (IIIa) and [$PtMe_2$(dppp)], (IIIc), are basically similar to this, and to the spectra of *cis*-[$PtMe_2(PR_3)_2$] (PR_3 =

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[3] K. A. Hooton, *J. Chem. Soc.* (*A*), 1970, 1896.

PPh_3,[4] $PMePh_2$,[5] or PMe_3 [6]), though in the cases of the dppp and $PMePh_2$ complexes the central line of each triplet appeared as a closely spaced doublet. As recently pointed out,[6] such systems cannot be analyzed on the basis of $[AX_3]_2$ or $A_3XX'A'_3$.

The dichloro-complexes (IVa)—(IVc) were prepared by reaction of the appropriate ditertiary phosphine with a suspension of anhydrous platinum(II) chloride in various organic solvents. Only $[PtCl_2(dppm)]$, (IVa), was sufficiently soluble for an osmometric molecular-weight determination, which showed the complex to be monomeric. The far-i.r. spectra of (IVa)—(IVc) showed two strong bands assignable to ν(PtCl) modes in the vicinity of 300 cm^{-1} (Table 1), consistent with the presence of a *cis*-$PtCl_2$ group.

As expected, the ^{31}P–$\{^1H\}$ spectra of the [Pt(diphosphine)X_2] complexes each showed a central peak with ^{195}Pt satellites. For the dimethyls, the order of $|^1J(\text{Pt-P})|$ in Hz is dppm (1 434) $\ll$ dppe (1 794) $\sim$ dppp (1 790) $<$ $2PMePh_2$ (1 851), while for the dichlorides the corresponding order is dppm(3 098) $<$ dppp(3 420) $<$ $2PMePh_2$(3 616) $\sim$ dppe(3 618). The lower value of ^1J(Pt-P) for the dimethyls is probably a consequence of the lower *trans* influence of Cl relative to Me,[7] and in both series the value for the dppm complex is considerably less than that for the complexes of the other tertiary phosphines. Platinum–phosphorus coupling constants are usually considered to be dominated by the Fermi-contact term,[7,8] *i.e.* equation (1) where α_X^2 is the *s*

$$|^1J(\text{Pt-P})| \propto \alpha_{Pt}^2\alpha_P^2[S_{Pt(6s)}(0)][S_{P(3s)}(0)](\Delta E)^{-1} \quad (1)$$

character of the relevant bonding orbital of X, $S_{X(ns)}(0)$ is the density of the *ns* orbital at the X nucleus, and ΔE is a mean singlet–triplet excitation energy. The differences between coupling constants are probably largely determined by variations in α_{Pt}^2 and α_P^2, which in turn will be strongly affected by variations in the angles P-Pt-P and Pt-P-CH_2; since the groups immediately adjacent to phosphorus in the various phosphines we have used are similar, changes in electronic effects must be relatively small. We suggest that the low values of ^1J(Pt-P) for the dppm complexes are associated with strain in the chelate ring, in particular with distortions in the angles P-Pt-P and Pt-P-CH_2. According to recent *X*-ray studies, these angles are 73 and 96° respectively in $[PtPh_2(dppm)]$,[9] and 73 and 95° respectively in $[Pd(dppm)(SCN)_2]$,[10] values which can be compared with normal values of 85 and 108° respectively for $[Pt(C_6H_9)(CH_2COPh)(dppe)]$ [11] and [Pd(NCS)-(dppe)(SCN)],[10] and values of 89 and 114° respectively for $[Pd(NCS)_2(dppe)]$.[10] It should again be pointed out that $|^1J(\text{Pt-P})|$ for the mutually *trans*-phosphorus atoms in $[\{PtMe(Cl)(dppm)\}_n]$, (IIa), where there is no severe angle strain, is very similar to $|^1J(\text{Pt-P})|$ in *trans*-$[PtMe(Cl)(PMePh_2)_2]$. Braterman *et al.*[9] also independently noted the anomalously low value (1 391.8 Hz) * of $|^1J(\text{Pt-P})|$ in $[PtPh_2(dppm)]$ compared with the values for $[PtPh_2(dppe)]$ and *cis*-$[PtPh_2(PPh_3)_2]$, and have associated this with distortions in bond angles at platinum and phosphorus. In our dimethyl complexes a small but definite trend in the opposite direction to ^1J(Pt-P) was found for $^2J(\text{Pt-C}H_3)$, *viz.* dppm(75) $>$ dppe(71) $>$ dppp(69) $>$ $2PMePh_2$(68). This may reflect the effect of the angle C-Pt-C on the Pt 6*s* character of the Pt-CH_3 bonds, tending to increase as the angle P-Pt-P decreases.

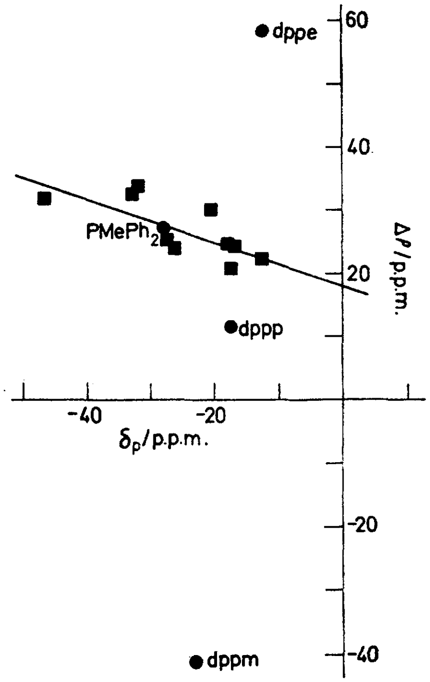

FIGURE 2 Plot of chemical shift, δ_P, of free phosphine against $\Delta P = \delta_P(\text{complex}) - \delta_P(\text{free phosphine})$ for *cis*-$[PtCl_2L_2]$ complexes

The ^{31}P chemical shifts for the ditertiary phosphine complexes are also anomalous. If a downfield chemical shift δ_P is defined as positive, and if ΔP is defined by equation (2), then, empirically, ΔP is related linearly to

$$\Delta P = \delta_P(\text{complex}) - \delta_P(\text{ligand}) \quad (2)$$

δ_P for the free ligand.[12] Figure 2 shows the least-

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* Not 1 491.8 Hz as reported in ref. 9 (K. W. Muir, personal communication).

[4] E. O. Greaves, R. Bruce, and P. M. Maitlis, *Chem. Comm.*, 1967, 860.

[5] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2801.

[6] R. J. Goodfellow, M. J. Hardy, and B. F. Taylor, *J.C.S. Dalton*, 1973, 2450.

[7] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, **10**, 335.

[8] A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 1707.

[9] P. S. Braterman, R. J. Cross, L. Manojlović-Muir, K. W. Muir, and G. B. Young, *J. Organometallic Chem.*, 1975, **84**, C40.

[10] G. J. Palenik, M. Mathew, W. L. Steffen, and G. Beran, *J. Amer. Chem. Soc.*, 1975, **97**, 1059.

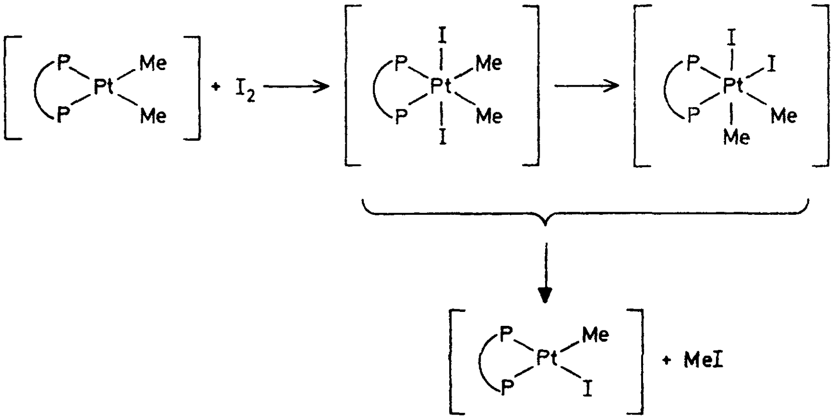
[11] G. B. Robertson and P. O. Whimp, unpublished work.

[12] B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 881.

squares plot and the points which give rise to it for the series *cis*-[$PtCl_2L_2$] ($\Delta P = 0.326\delta_P + 0.183$; our sign convention is different from that used by Mann *et al.*[12]). Points representing [$PtCl_2$(diphosphine)] have been added. While the point corresponding to *cis*-[$PtCl_2(PMePh_2)_2$] is very close to the line, that for (IVc) is significantly below the line, *i.e.* the chemical shift is further upfield than expected, and (IVb) shows a larger deviation in the opposite direction, *i.e.* the chemical shift is further downfield than expected. The point corresponding to (IVa) is very much below the line *i.e.* the chemical shift is much further upfield than would be expected, and ΔP is actually of opposite sign to that for all the other phosphines. Since the basis of the empirical relation itself is unknown, deviations from it cannot be accounted for in detail. They are presumably associated with the reduction of the angles P-Pt-P and P-C-P from their normal values in the small chelate rings, but it is remarkable that the sign of this strain effect should be opposite for dppe and dppm. A similar anomaly in the case of a four-membered chelate ring has been noted in the complexes [$M(CO)_4\{NEt(PF_2)_2\}$] (M = Mo or W), the ^{31}P nuclei of which are more shielded than those of the free ligand.[13]

Although there are as yet insufficient data to allow a similar empirical relation between δ_P and ΔP to be deduced for complexes *cis*-[$PtMe_2L_2$], the results for the [$PtMe_2$(diphosphine)] complexes parallel those for [$PtCl_2$(diphosphine)]; ΔP (δ_P) values for $2PMePh_2$, dppp, dppe, and dppm in [$PtMe_2L_2$] are respectively 34.5 (−28.1), 20.5 (−17.3), 59.7 (−12.5), and −17.4 (−23.0). Although δ_P for dppm is between the values for $PMePh_2$ and dppp, ΔP for dppm is of opposite sign. As with the dichloride, ΔP for dppe is of the usual sign but larger in magnitude than would be expected.

It is of interest that only [PtMe(X)(dppm)] (X = Cl or I) of the complexes studied show any tendency to oligomerize. We ascribe this behaviour to two factors: (*a*) relief of strain in the four-membered chelate dppm ring; and (*b*) attainment of the preferred geometry for [$PtMe(X)(PR_3)_2$] (X = Cl, Br, or I) complexes, *i.e.* that in which X is *trans* to methyl. In contrast, [$PtMe_2(PR_3)_2$] complexes are exclusively *cis*, while *cis*-[$Pt(PR_3)_2X_2$] complexes are favoured in terms of enthalpy over their *trans* isomers. Several complexes containing bridging dppm are known, *e.g.* [$Mo_2(CO)_4X_4(\mu$-dppm)(dppm)$_2$] (X = Cl or Br),[14] [$Ir_2(CO)_4Cl_2(\mu$-dppm)],[15] and [$Fe_2(CO)_7(\mu$-dppm)].[16] The bridging capability of dppe is better established,[17-19] but this probably only reflects the greater effort devoted to the co-ordination chemistry of this ligand.



SCHEME

Oxidative-addition Reactions.—(a) *Iodination*. Hooton [3] found that complex (IIIb), on reaction with one equivalent of iodine in acetone at 50 °C, gave 26% [PtI_2(dppe)]; the other product was presumably [PtMe(I)(dppe)] together with unchanged (IIIa). Addition of one equivalent of iodine to (IIIb) in dichloromethane at room temperature gave a transient brown colour, suggesting that the expected platinum(IV) adduct had been formed, but the solution rapidly turned colourless. N.m.r. examination showed the product to be [PtMe(I)(dppe)], presumably formed by an oxidative-addition–reductive-elimination sequence (Scheme). Iodination of (IIIa) gave predominantly a mixture of the two expected platinum(IV) isomers, as shown by ^1H n.m.r. spectroscopy, but attempted recrystallization at room temperature gave only (IIb), possibly contaminated with some [PtI_2(dppm)]. ^1H N.m.r. examination of the initial product from (IIIc) and iodine showed peaks corresponding to [PtMe(I)(dppp)] and peaks presumably arising from platinum(IV) species, but on standing for several hours the orange colour of the solution faded

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[15] W. Hieber and R. Kummer, *Chem. Ber.*, 1967, **100**, 148.

[16] F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 4422.

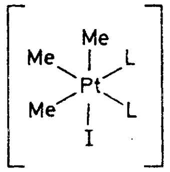
[17] R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1967, 94.

[18] K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, 1967, **6**, 294.

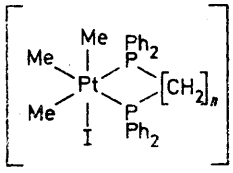
[19] P. M. Treichel, K. W. Barnett, and R. L. Shubkin, *J. Organometallic Chem.*, 1967, **7**, 449.

and the n.m.r. spectrum then showed a mixture of [PtMe(I)(dppp)] and methyl iodide to be present. The ease with which this reductive elimination occurs may be due in part to the severe steric interactions which must exist between the phenyl groups attached to phosphorus and the axial ligands, especially the large iodo-groups.

(b) *Addition of methyl iodide*. Methyl iodide adds oxidatively to *cis*-[$PtMe_2(PMe_2Ph)_2$] to give *fac*-[$PtMe_3(I)(PMe_2Ph)_2$], (Va).[5] Similar reactions occurred with *cis*-[$PtMe_2(PMePh_2)_2$], (IIIa), and (IIIb) to give the platinum(IV) complexes [$PtMe_3(I)(PMePh_2)_2$], (Vb), [$PtMe_3(I)(dppm)$], (VIa), and [$PtMe_3(I)(dppe)$], (VIb) respectively. In the case of (IIIc), the platinum(II) complex [PtMe(I)(dppp)] was isolated instead of the expected adduct [$PtMe_3I(dppp)$], (VIc). In contrast, complexes (VIa) and (VIb) are stable indefinitely in solution. Complex (Vb) slowly decomposes in solution giving *trans*-[$PtMe(I)(PMePh_2)_2$]. The greater tendency of the presumed intermediate (VIc) to eliminate ethane compared with its analogues (VIa) and (VIb) may be associated with larger steric interactions between the P-bound phenyl groups and the axial ligands in (VIc). After submission of this paper, other workers [20] reported on (VIb) and its stability towards reductive-elimination.



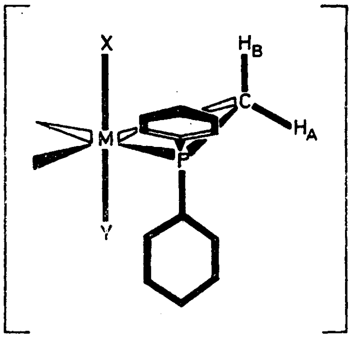
(Va) L = PMe_2Ph
(Vb) L = $PMePh_2$



(VIa) *n* = 1
(VIb) *n* = 2
(VIc) *n* = 3

The ^1H n.m.r. spectra of (Vb), (VIa), and (VIb) are characterized by a high-field Pt-CH_3 resonance corresponding to the methyl group *trans* to I, consisting of a triplet (coupling to two equivalent ^{31}P) with satellites from coupling to ^{195}Pt, and a complicated pattern further downfield corresponding to the two Me groups *trans* to P. The P-CH_3 groups in (Vb) showed a doublet (with satellites) indicating that the phosphines are mutually *cis*. The methylene group in (VIa) represents the AB part of an ($ABX_2 + \frac{1}{2}ABMX_2$) pattern, since the two protons are non-equivalent by virtue of the different groups above and below the (Pt-P_2) plane, and couple appreciably to the two P atoms (X) and to $^{195}Pt(M)$. Analysis of the spectrum with the aid of ^{31}P decoupling gave the coupling constants in Table 1. For the low-field 'A' proton, accidental equality of $|J_{AB}|$, $2|^2J(P\text{-}C\text{-}H_A)|$, and $|^3J(Pt\text{-}P\text{-}C\text{-}H_A)|$ gives rise to a theoretical 1 : 6 : 11 : 12 : 11 : 6 : 1 multiplet, if the small intensity distortion arising from the proximity of the B proton is ignored; $|^2J(P\text{-}C\text{-}H_B)|$ is larger for the high-field 'B' proton, but $|^3J(Pt\text{-}P\text{-}C\text{-}H_B)|$ could not be resolved. It has been shown [21,22] that $|^3J(Pt\text{-}N\text{-}C\text{-}H)|$ shows a Karplus-type angular dependence relation with the dihedral angle ϕ between the planes Pt-N-C and N-C-H, *i.e.* $|^3J(Pt\text{-}Q\text{-}C\text{-}H)| \approx k\cos^2\phi$ where Q = N. Assuming an analogous relation where Q = P, the difference in couplings between ^{195}Pt and H_A and H_B suggests that values of ϕ are different for H_A and H_B. This could arise from a puckering of the four-membered chelate ring to reduce steric interactions as in (A). If the puckering is such that the C atom of the methylene group bends towards the group X, the dihedral angle ϕ_A would increase from the original 120° and ϕ_B would decrease, causing $\cos^2\phi_A$ to be greater than $\cos^2\phi_B$, and hence $|^3J(Pt\text{-}P\text{-}H_A)| > |^3J(Pt\text{-}P\text{-}H_B)|$, as observed. The result of this puckering would be to bend the phenyl groups away from X and toward Y. If it is assumed that the Ph groups interact more severely with iodide than with a Me group, then, with X = I and Y = Me, H_A, the low-field proton with the larger coupling to ^{195}Pt, corresponds to the proton on the same side of the ring as the Me group.

The ^{31}P n.m.r. spectra of (Vb), (VIa), and (VIb) were obtained by INDOR, using the high-field methyl resonance in each case (corresponding to the Me group *trans* to I^-). The results are in Table 2. The same order of $|^1J(Pt\text{-}P)|$ was observed as for [$PtMe_2L_2$], *i.e.* dppm $\ll$ dppe $<$ $2PMePh_2$. The ratios $J(Pt^{IV}\text{-}P) : J(Pt^{II}\text{-}P)$ are 0.607, 0.578, and 0.608 : 1 respectively, *i.e.* very similar to those obtained for *cis*- and *trans*-[$Pt(PBu^n_3)_2X_4$] and [$Pt(PBu^n_3)_2X_2$] (X = halide).[3] Clearly, distortions due to chelate-ring strain have a similar effect on coupling constants in octahedral complexes of Pt^{IV} as in square-planar complexes of Pt^{II}. The value of J(Pt-P) in (VIa), is, incidentally, the lowest yet recorded.



(A)

The Pt-CH_3 coupling constants *trans* to phosphorus follow the same order as for [$PtMe_2L_2$], dppm > dppe > $2PMePh_2$. The chemical shifts of (Vb), (VIa), and (VIb) follow the same trends as previously noted for [$PtMe_2L_2$] and [$PtCl_2L_2$]. Although ΔP for (VIa) has the same sign as for (Vb), the upfield shift is much

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[21] L. E. Erickson, J. W. McDonald, J. K. Howie, and R. P. Clow, *J. Amer. Chem. Soc.*, 1968, **90**, 6371.

[22] T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 1971, **10**, 1717.

larger, and only for (VIb) is a downfield shift on coordination observed.

EXPERIMENTAL

The ditertiary phosphines were used as supplied by Strem Chemicals Incorporated. Platinum complexes were prepared from anhydrous platinum(II) chloride (Johnson, Matthey Ltd.). AnalaR grade solvents were dried over molecular sieves (B.D.H., 4A) before use. The complexes were heated at 60 °C (10^{-3} mmHg) * for 1 h before being submitted for analysis.

Analyses and osmometric molecular-weight measurements (model 301A Mechrolab) were by the Microanalytical Laboratories of the Research School of Chemistry and the John Curtin School of Medical Research, Australian National University (Miss B. Stevenson and Dr. J. Fildes and their associates). Melting points were determined on samples in capillaries and are corrected. Analytical data, molecular weights, and m.p.s are in Table 2. Both analytical and spectroscopic data showed the presence of residual occluded solvent in most of the samples which could not be completely removed by prolonged pumping. The degree of solvation was variable and the formulations for (Ic), (IIa), (IIb), (IIIa), and (IIIc) are those in best agreement with the analytical and ^1H n.m.r. data for these complexes. The presence of small quantities of occluded solvent in an involatile complex will lead to errors in molecular-weight determinations based on the lowering of vapour pressure of a solvent which is different from that present in the complex. Thus the observed molecular weights of (Ic), (IIb), (IIIc), and (VIa) must be regarded as approximate, though the agreement with the calculated values is generally satisfactory and within the usual error limits of osmometric molecular-weight determinations.† In the cases of (IIa) and (IIb), some dissociation of the oligomers may be occurring in solution. Unfortunately the complexes (Ic), (IIb), (IIIc), and (VIa) were not sufficiently soluble in the solvation solvent for purposes of osmometry.

^1H N.m.r. spectra were obtained on JEOL MH-100 and Varian HA-100 spectrometers. INDOR and heteronuclear-decoupling experiments were made on the latter instrument with a double-tuned transmitter coil.[1] After recrystallization, some of the complexes (see Table 2) contained occluded *n*-hexane which could not be completely removed *in vacuo*, and which interfered with the study of the Pt-CH_3 resonances. These complexes were dissolved in chloroform or dichloromethane, the solutions were evaporated to dryness under reduced pressure, and the residual solid was then dissolved in $CDCl_3$. Direct ^{31}P n.m.r. spectra were obtained with ^1H decoupling on a JEOL C60-HL spectrometer, with external 85% H_3PO_4 as reference, using a CAT program on a PDP8-1 computer to accumulate scans. Calculated spectra were obtained using a program written for the PDP-11 computer in the Research School of Chemistry. I.r. spectra were recorded on a Perkin-Elmer model 457 spectrophotometer on Nujol mulls using CsI windows.

[1,3-Bis(diphenylphosphino)propane]chloro(methyl)-platinum(II), [PtMe(Cl)(dppp)] (Ic).—To a solution of [PtMe(cod)Cl] (0.44 g, 1.24 mmol) in benzene (6 cm^3) was added a solution of dppp (0.51 g, 1.24 mmol) in benzene (10 cm^3). Colourless crystals slowly formed. After 1 h, they were filtered off, washed with n-hexane, n-pentane, and dried *in vacuo*, to give the *complex* (0.54 g, 61%). A further 0.15 g (7%) was obtained by adding n-hexane to the filtrate.

[Bis(diphenylphosphino)methane]chloro(methyl)platinum(II), [PtMe(Cl)(dppm)] (*Oligomer–Monomer Mixture*).—To a solution of [PtMe(cod)Cl] (0.16 g, 0.45 mmol) in benzene (20 cm^3) was added dppm (0.173 g, 0.45 mmol) and the mixture was stirred under reflux for 45 min. After cooling, the white insoluble *product* was collected by vacuum filtration and washed with cold benzene (2 × 3 cm^3). The molecular weight of the product (25 °C, $CHCl_3$) was 1 034 (*cf.* monomer, 630; trimer, 1 890), and remained unchanged over 4 h. The ^1H n.m.r. spectrum in CD_2Cl_2 showed the ratio of oligomer, (IIa), to monomer, (Ia), to be *ca.* 2 : 1, but after 2—3 d in solution all the monomer was converted into oligomer. The same product mixture was obtained on titrating a benzene solution of [$PtMe_2$(dppm)], (IIIa), with the stoicheiometric amount of a standard solution of HCl in diethyl ether. The oligomer was recrystallized from dichloromethane–n-pentane or chloroform–n-hexane to give dichloromethane or chloroform solvates.

Reaction of [PtMe(cod)Cl] *and dppm in Benzene at Room Temperature*.—Bis(diphenylphosphino)methane (0.46 g, 1.2 mmol) in benzene (10 cm^3) was added dropwise to a solution of [PtMe(cod)Cl] in benzene (10 cm^3). The stirred solution remained only slightly cloudy. After *ca.* 5 min the colourless *product* was precipitated with n-hexane. Its n.m.r. spectrum showed that it was exclusively oligomeric [PtMe(Cl)(dppm)], (IIa) (0.71 g, 95%). No ν(PtCl) band due to the monomer was observed near 292 cm^{-1} in the i.r. spectrum. A suspension of this product (0.089 g) in benzene (10 cm^3) was heated under reflux for 3 h. The solution was filtered hot from undissolved (IIa) and benzene was evaporated from the warmed filtrate under reduced pressure. The residue (0.04 g) was shown by its ^1H n.m.r. and far-i.r. spectra [ν(PtCl) at 292 cm^{-1}] to be monomeric (Ia).

[Bis(diphenylphosphino)methane]iodo(methyl)platinum(II) *Oligomer*, [{PtMe(I)(dppm)}$_n$], (IIb).—The complex (IIa) (0.1 g) and sodium iodide (0.16 g, *ca.* five-fold excess) were heated under reflux for 2 h in acetone (50 cm^3). Acetone was then evaporated under reduced pressure, and the residue was extracted with dichloromethane to give a pale yellow solution. Evaporation to dryness gave a pale yellow *solid* which was recrystallized from dichloromethane–n-hexane to give the hexane solvate, (IIb).

[Bis(diphenylphosphino)methane]dimethylplatinum(II), [$PtMe_2$(dppm)] (IIIa).—The complex [$PtMe_2$(cod)] (0.1 g, 0.3 mmol) and dppm (0.116 g, 0.3 mmol) were heated under reflux in benzene (40 cm^3) for 45 min. The volume was reduced to *ca.* 5 cm^3, and the benzene *solvate* crystallized on addition of n-hexane (20 cm^3) (0.148 g, 81%).

[1,2-Bis(diphenylphosphino)ethane]dimethylplatinum(II), [$PtMe_2$(dppe)], (IIIb).—A solution of [$PtMe_2$(cod)] (0.89 g, 2.67 mmol) in benzene (5 cm^3) was treated dropwise with dppe (1.07 g, 2.7 mmol) dissolved in benzene (10 cm^3). A white solid immediately precipitated. Benzene was removed from the suspension under reduced pressure until the

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

† We are indebted to a referee for showing that osmometric molecular-weight measurements on a stable complex in chloroform containing up to 5% v/v dichloromethane lead to increasingly high apparent molecular weights as the proportion of the more volatile dichloromethane is increased. The values were *ca.* 6% high for chloroform containing 0.2% and 0.5% v/v dichloromethane. In all our complexes, the proportion of foreign solvent introduced into the chloroform was 0.5% v/v or less.

volume was *ca.* 5 cm^3. The solid was then filtered off, washed with benzene (5 cm^3), then with pentane. After two recrystallizations from acetone, the *product* (1.23 g, 71%) was identical (m.p. and n.m.r. spectra) with that reported by Hooton.[3]

[1,3-*Bis(diphenylphosphino)propane*]*dimethylplatinum*(II), $[PtMe_2(dppp)]$ (IIIc).—A mixture of $[PtMe_2(cod)]$ (0.29 g, 0.88 mmol) and dppp (0.371 g, 0.90 mmol) in benzene (7 cm^3) was allowed to stand for 5 min. White crystals formed, and more were precipitated on addition of n-heptane. The white *complex* was filtered off, washed with n-pentane, and dried *in vacuo*.

[*Bis(diphenylphosphino)methane*]*dichloroplatinum*(II), $[PtCl_2(dppm)]$ (IVa).—Anhydrous platinum(II) chloride (0.25 g, 0.94 mmol) and dppm (0.38 g, 0.99 mmol) were heated under reflux in chloroform–benzene (1 : 1, 50 cm^3) for 4 h. The solution was filtered while hot and the residue was washed with hot chloroform (3 × 5 cm^3). The solvent was removed under reduced pressure, and the white benzene *solvate* was washed with n-hexane, centrifuged, and dried *in vacuo* (0.55 g, 90%).

[1,2-*Bis(diphenylphosphino)ethane*]*dichloroplatinum*(II), $[PtCl_2(dppe)]$ (IVb).—A suspension of anhydrous platinum(II) chloride (2.42 g, 9.1 mmol) and dppe (3.64 g, 9.0 mmol) in 2-methoxyethanol (100 cm^3) was stirred and heated under reflux for 2 h. The volume was reduced to 20 cm^3 under reduced pressure and the resulting solid, containing complex (IVb) contaminated with platinum metal, was filtered off. This residue was extracted with acetone in a Soxhlet extractor, the volume was concentrated to 50 cm^3, and the resulting white *complex* was filtered off and washed with acetone; yield 4.2 g (70%).

[1,3-*Bis(diphenylphosphino)propane*]*dichloroplatinum*(II), $[PtCl_2(dppp)]$ (IVc).—Anhydrous platinum(II) chloride (0.2 g, 0.75 mmol) and dppp (0.31 g, 0.75 mmol) were heated under reflux in chloroform (40 cm^3) for 3 h. The *product* was precipitated from the hot solution on addition of n-hexane. The product remained solvated with both chloroform and hexane, even after prolonged heating *in vacuo*.

Reactions of Complexes $[PtMe_2$(diphosphine)] *with Iodine*.—These were carried out similarly on complexes (III). The procedure is illustrated using the dppe complex, (IIIb). A solution of (IIIb) (0.083 g, 0.13 mmol) in dichloromethane (5 cm^3) was treated with a solution of iodine (0.034 g, 0.133 mmol) in dichloromethane (10 cm^3). The solution initially turned brown but this lightened over a few minutes to yellow, then to colourless. The solution was evaporated to dryness under reduced pressure without heating. N.m.r. examination of the residue showed it to be [PtMe(I)(dppe)], by comparison with a sample prepared by a metathetical reaction from (Ib) [PtMe(Cl)(dppe)].[23]

With (IIIa) the initial product obtained as above appeared to be a mixture of isomers $[PtMe_2I_2(dppm)]$. However, attempted recrystallization from chloroform–*n*-hexane gave (IIa), contaminated with some $[PtI_2(dppm)]$. Similarly, with (IIIc), the initial product contained Pt^{IV}, but on standing in solution [PtMe(I)(dppp)][similar spectrum to that of sample obtained from (IIIc) and MeI] was obtained.

Reactions of Complexes $[PtMe_2$(*diphosphine*)] *with Methyl Iodide*.—These reactions were all carried out in the same way. The dimethyl complex (*ca.* 0.1 g) in dichloromethane (5 cm^3) was treated with methyl iodide (0.5 cm^3). The solution was allowed to stand overnight, then evaporated to dryness under reduced pressure without heating. The product was recrystallized from dichloromethane–n-hexane. The product $[PtMe_3(I)(PMePh_2)_2]$, (Vb), derived from $[PtMe_2(PMePh_2)_2]$, was sufficiently stable for its ^1H n.m.r. spectrum to be obtained, but it decomposed in solution to give *trans*-$[PtMe(I)(PMePh_2)_2]$ and satisfactory analyses for the platinum(IV) compound were not obtained. The complexes $[PtMe_3(I)(dppm)]$, (VIa), and $[PtMe_3(I)(dppe)]$, (VIb), were isolated in yields of 66 and 62% respectively. Reaction of methyl iodide with (IIIc) gave [PtMe(I)(dppp)] (60%).

We thank Mr. C. Arandjelović and Mr. K. Kinealy for running direct ^{31}P n.m.r. spectra, and Dr. R. Bramley and Mr. C. Henman for ^{31}P-decoupled ^1H and INDOR spectra.

[4/698 *Received, 5th April*, 1974]

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[23] T. G. Appleton and M. A. Bennett, unpublished work.