Diphosphine Complexes of Iridium(I), Palladium(II), and Platinum(II)

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Diphosphines $Ph_2P[CH_2]_nPPh_2$ (n = 1—4) form novel *trans*-carbonyl complexes of Ir^I of stoicheiometry $[\{Ir(CO)Cl(diphosphine)\}_m]$ in which the diphosphine (n = 1,3, or 4) bridges the metal atoms. Contrary to a previous postulate, the complex of $Ph_2P[CH_2]_2PPh_2$ is $[Ir(CO)\{Ph_2P(CH_2)_2PPh_2\}_2][Ir(CO)_2Cl_2]$. The diphosphine complexes of Pd^{II} and Pt^{II}, some of which are described for the first time, are each of *cis* geometry. In each case $Ph_2P[CH_2]_2PPh_2$ chelates the metal and the complex is mononuclear, but $Ph_2P[CH_2]_4PPh_2$ bridges metal atoms of trinuclear complexes. The diphosphine $Ph_2P[CH_2]_3PPh_2$ chelates Pd^{II} but forms a bridged complex of Pt^{II}. Bridging by a diphosphine ligand occurs when the angle PMP which would be subtended by a chelating ligand exceeds 90°.

THE molecular weight and i.r. and ^{31}P n.m.r. spectra of $[Rh(CO)Cl\{Ph_2P(CH_2)_2PPh_2\}]$ showed that the complex is mononuclear, square planar, and that the diphosphine chelates the metal atoms.[1-4] The geometries of many complexes of similar stoicheiometry have been assumed to be analogous, even though, in many cases, molecular weights were not measured.[3] In an earlier paper from this laboratory the above complex was shown to be atypical of diphosphine complexes of Rh^I of similar stoicheiometry.[4] That the diphosphines $Ph_2P[CH_2]_nPPh_2$ (n = 1, 3, or 4), and related ligands, normally bridge rhodium atoms has been clearly demonstrated,[1,4] and also applies to homogeneous and polymer-supported catalyst systems.[5] A parallel study has shown that the similar ligands $Bu^t{}_2P[CH_2]_nPBu^t{}_2$ ($n \geqslant 9$) bridge rhodium(I) or palladium(II) atoms, but chelate iridium(I) or platinum(II) atoms in a *trans* manner.[6,7]

It is therefore of interest to know and compare the aggregations and geometries of related complexes of other platinum-group metals of the second and third transition series with diphosphines, $Ph_2P[CH_2]_nPPh_2$ [n = 1 (1), 2 (2), 3 (3), or 4 (4)] or *cis*-$Ph_2PCH{:}CHPPh_2$ (5), which are not capable of chelating *trans* positions in mononuclear complexes. I report the preparations of the novel complexes, and the vibrational spectra and aggregations of such complexes of Ir^I, Pd^{II}, and Pt^{II}. The complexes $[PdCl_2\{Ph_2P(CH_2)_nPPh_2\}]$ (n = 1—3) are mononuclear in the solid state.[8] The complex $[PtCl_2(Ph_2PCH_2PPh_2)]$ has been shown to be mononuclear, but the aggregations of the similar complexes of

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[1] J. T. Mague and J. P. Mitchener, *Inorg. Chem.*, 1969, **8**, 119.

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[3] W. Levason and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1972, **14**, 173.

[4] A. R. Sanger, *J.C.S. Chem. Comm.*, 1975, 893; *J.C.S. Dalton*, 1977, 120.

[5] A. R. Sanger, unpublished work.

[6] F. C. March, R. Mason, K. M. Thomas, and B. L. Shaw, *J.C.S. Chem. Comm.*, 1975, 584.

[7] A. Pryde, B. L. Shaw, and B. Weeks, *J.C.S. Dalton*, 1976, 322.

[8] W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, 1976, **15**, 2432.

(2) and (3) have not been previously determined.[9] Herein it will be demonstrated that platinum(II) complexes of (3) and (4) are each polynuclear. Indeed, it will be shown that (3) and (4) can form bridged complexes of Ir^{I}, Pd^{II}, and Pt^{II}, but that, for each metal, (2) always chelates the metal atom.

EXPERIMENTAL

Except where noted, dry solvents were used. The preparations of all the complexes were necessarily performed in an oxygen-free environment. The complexes $[Ir_2Cl_2(cod)_2]$ (cod = cyclo-octa-1,5-diene), $[Ir(CO)Cl(PPh_3)_2]$, $[(PdCl_2)_n]$, $PdCl_2\cdot2PhCN$, $Na_2[PdCl_4]$, and $K_2[PtCl_4]$ and the diphosphine ligands were obtained commercially (Alfa Products, or Strem Chemicals Inc.) or prepared by standard literature methods, and used without further treatment after satisfactory spectroscopic and elemental analyses.

Spectra were obtained using the following instruments: i.r. (Beckman IR 12); Raman (Beckman 700, with coherent argon and krypton lasers); $^{31}P-\{^1H\}$ n.m.r., solutions in $[^2H_8]$toluene or $[^2H_2]$dichloromethane (Varian HA100, with Fourier-transform capability: Digilab FTS/NMR-3 data system and pulse unit); mass (A.E.I. MS12). Analyses were by the analytical service of the Department of Chemistry, University of Alberta, Edmonton (C, H, and *M*) and Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany (C, H, Cl, and P). All the i.r. bands are reported in wavenumbers. Phosphorus-31 n.m.r. chemical shifts (δ) are reported in p.p.m. to low field of external 85% H_3PO_4; coupling constants are reported in Hz.

The five preparative methods employed are described below. Most complexes were prepared using more than one method Analytical and spectroscopic data are given in Tables 1, 2, and 4.

(1) *Preparative Methods.—Reaction of* $[M_2Cl_2(cod)_2]$ (M = Rh *or* Ir) *with carbon monoxide and a diphosphine.* Typically, under an atmosphere of CO, $[Ir_2Cl_2(cod)_2]$ (0.225 g, 0.670 mequiv.) was added to a stirred solution of $Ph_2P[CH_2]_4PPh_2$ (4) (0.285 g, 0.669 mmol) in benzene (12 cm^3). A golden-yellow solution formed from which $[IrCl(cod)\{Ph_2P(CH_2)_4PPh_2\}(C_6H_6)]$ precipitated as a yellow powder (5 min). The mixture was stirred (18 h) and the initial precipitate redissolved to form a yellow solution from which $[\{Ir(CO)Cl[Ph_2P(CH_2)_4PPh_2]\}_3]$ (0.374 g, 82%) was subsequently precipitated as white to pale yellow crystals. The crystals dried *in vacuo* to form a pale yellow powder. Dilution of the mother liquor with light petroleum (4 : 1) gave more of the same material.

The solvated complex initially isolated from the reaction (1 d) of $Ph_2PCH_2PPh_2$ (1) with an equivalent amount of $[Ir_2Cl_2(cod)_2]$ is yellow. The solvent of crystallization is readily lost *in vacuo* to give a much redder powder. Analytical results support formulation of the intermediate as an intimate mixture of $[\{Ir(CO)Cl(Ph_2PCH_2PPh_2)\}_2]$, analogous to the rhodium complex,[1,4] and $[Ir_2(CO)_2Cl_2(cod)(Ph_2PCH_2PPh_2)]$. Longer reaction periods were required to give the former complex in a pure state.

(2) *Reaction of* $[Ir(CO)Cl(PPh_3)_2]$ *with a diphosphine.* Typically, under an atmosphere of CO, $[Ir(CO)Cl(PPh_3)_2]$ (0.116 g, 0.149 mmol) and (4) (0.066 g, 0.155 mmol) were successively added to benzene (10 cm^3) to form a golden-yellow solution. The mixture was successively stirred (20 min) and then filtered to give, as a white powder which became pale yellow when dried, $[\{Ir(CO)Cl[Ph_2P(CH_2)_4PPh_2]\}_3]$.

(3) *Reaction of* $MCl_2\cdot2PhCN$ (M = Pd *or* Pt) *with a diphosphine.* Typically, addition of $Ph_2P[CH_2]_2PPh_2$ (2) (0.206 g, 0.518 mmol) to a solution of $PdCl_2\cdot2PhCN$ (0.195 g, 0.508 mmol) in benzene (25 cm^3) caused the golden-yellow solution to become paler. A pale precipitate subsequently formed. The mixture was successively stirred (1 h) and filtered to give, as a pale buff powder, $[PdCl_2\{Ph_2P(CH_2)_2PPh_2\}]$ (0.278 g, 95%). When the above type of experiment was repeated using dichloromethane as solvent some products contained solvent of crystallization which was not removed when the sample was dried *in vacuo* (25 °C).

(4) *Reaction of* $PdCl_2$ *with a diphosphine.* Typically, a stirred suspension of $PdCl_2$ (0.064 5 g, 0.364 mmol) in a solution of $Ph_2P[CH_2]_3PPh_2$ (3) (0.151 g, 0.367 mmol) in acetone (15 cm^3) slowly formed a very pale solution and, as a white precipitate, $[PdCl_2\{Ph_2P(CH_2)_3PPh_2\}]$ (0.109 g, 51%).

(5) *Reaction of* $M_2[M'Cl_4]$ (M = Na *or* K; M′ = Pd *or* Pt) *with a diphosphine.* Typically, a solution of $Ph_2PCH{:}CHPPh_2$ (5) (0.220 g, 0.556 mmol) in dichloromethane (10 cm^3) and a solution of $K_2[PtCl_4]$ (0.230 g, 0.554 mmol) in water were intimately agitated (1 h). The aqueous layer slowly became colourless and the organic layer became yellow. A pale precipitate was subsequently formed. The aqueous layer was removed, and the organic layer and precipitate were washed with copious amounts of water. The organic layer was then filtered to give, as a white powder, $[\{PtCl_2(Ph_2PCH{:}CHPPh_2)\}_2]\cdot2H_2O$ (0.235 g, 57%).

Reactions of $K_2[PtCl_4]$ with other diphosphines were slower, requiring reaction periods of up to 1 d.

(6) *Reaction of* $[Ir(CO)\{Ph_2P(CH_2)_2PPh_2\}_2][Ir(CO)_2Cl_2]$ *with* $Na[BPh_4]$. A solution of $[Ir(CO)\{Ph_2P(CH_2)PPh_2\}_2][Ir(CO)_2Cl_2]$ (0.329 g, 0.252 mmol) in acetone (10 cm^3) in an atmosphere of dinitrogen reacted with $Na[BPh_4]$ (0.327 g, excess) to form a deep gold solution from which precipitated cream crystals of $[Ir(CO)\{Ph_2P(CH_2)_2PPh_2\}_2]$ $[BPh_4]$ (0.152 g, 45%) (Found: C, 68.6; H, 5.25; P, 8.95%; *M* 1 348. Calc. for $C_{77}H_{68}BIrOP_4$: C, 69.15; H, 5.15; P, 9.25%; *M* 1 337). Addition of methanol to the filtrate gave more of the same material. The complex exhibited a single carbonyl band in the i.r. spectrum (1 935s cm^{-1}). The conductivity (99 S cm^{-1}) of a solution (10^{-3} mol dm^{-3}) of the complex in acetone showed that the complex is a **1 : 1** electrolyte.

In order that confidence could be placed in assignments of bands in the far-i.r. spectra to metal–chlorine stretching modes, it was first necessary to examine the spectra of the ligands (1)—(5). A Nujol mull of each of these diphosphines exhibited three to five bands of low intensity in the relevant region (see Table 3). For complexes of Pd^{II} or Pt^{II} the relevant metal–chlorine bands were normally of sufficient strength to facilitate resolution and assignment. For some complexes of Ir^{I} the metal–chlorine bands were of similar intensity to, or superimposed upon, ligand bands. Careful comparison of complex and ligand spectra was therefore necessary before assignments could be made in these cases.

RESULTS AND DISCUSSION

Iridium Complexes.—Method (1) was normally the efficient preparative technique for the synthesis of

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[9] T. G. Appleton, M. A. Bennett, and I. B. Tomkins, *J.C.S. Dalton*, 1976, 439.

TABLE 1

Diphosphine complexes of Ir^{I}

Complex	Preparation [a]	Solvent	Yield (%)	Colour	Analysis (%) [b] C	H	Cl	P	M [b,c]	I.r. bands (cm^{-1}) [d] ν(Ir–Cl) [e]	ν(C–O) [f]
$[\{Ir(CO)Cl(Ph_2PCH_2PPh_2)\}_2]$	1	C_6H_6	65	Orange-red	48.1 (48.7)	3.50 (3.45)	5.00 (5.55)	9.35 (9.65)	1 245 (1 282)	283	1 960 (2000)
$[Ir(CO)\{Ph_2P(CH_2)_2PPh_2\}_2][Ir(CO)_2Cl_2]$ [g]	1	C_6H_6	79	Yellow	48.95 (49.35)	3.90 (3.60)	5.90 (5.30)	9.80 (9.25)	1 234 (1 338)	304 (366)	(1 935) 1 963, 2 051
$[\{Ir(CO)Cl[Ph_2P(CH_2)_3PPh_2]\}_2]$	1	C_6H_6	54	Pale yellow	50.4 (50.25)	4.05 (3.90)	5.25 (5.30)	8.90 (9.25)	1 341 (1 338)	(290) 308	1 952 (2 003)
$[\{Ir(CO)Cl[Ph_2P(CH_2)_4PPh_2]\}_3]$	1, 2	C_6H_6, CH_2Cl_2	87	Pale yellow	51.7 (51.0)	4.25 (4.15)	4.75 (5.20)	8.85 (9.05)	1 858 (2 049)	307	1 951 (2 000)
$[Ir(CO)(Ph_2PCH{:}CHPPh_2)_2][Ir(CO)_2Cl_2]$	1	C_6H_6, CH_2Cl_2	83	Orange	49.95 (49.5)	3.40 (3.30)	5.45 (5.30)	9.15 (9.30)	1 368 (1 334)	304 (335)	(1 933) 1 963, 2 052

[a] See Experimental section. [b] Calculated values are given in parentheses. [c] By osmometry in CH_2Br_2. [d] Values in parentheses are shoulders. [e] Nujol mulls. [f] Pellets, 0.3% in KBr. [g] *cf.* ref. 12.

TABLE 2

Diphosphine complexes of Pd^{II} and Pt^{II}

Complex	Preparation [a]	Solvent	Yield (%)	Colour	Analysis (%) [b] C	H	Cl	P	M [b,c]	M–Cl Bands (cm^{-1}) [d] I.r. [e]	Raman [f]
$[PdCl_2\{Ph_2P(CH_2)_2PPh_2\}]$ [g]	3	C_6H_6	95	Pale buff	54.7 (54.25)	4.20 (4.20)	12.0 (12.3)	10.4 (10.25)	579 (576)	493, 314	285, 307
$[PdCl_2\{Ph_2P(CH_2)_3PPh_2\}]$	3, 4	C_6H_6, Me_2CO	51	White	55.15 (55.0)	4.40 (4.45)	12.05 (12.05)	10.5 (10.5)	*h*	290, 306	285, 305
$[\{PdCl_2[Ph_2P(CH_2)_4PPh_2]\}_3]$	3	C_6H_6	78	Cream	55.4 (55.7)	4.60 (4.65)	10.45 (11.75)	9 .20 (10.25)	*h*	292, 307	284, 300
$[\{PdCl_2[Ph_2P(CH_2)_4PPh_2]\}_3]\cdot 3H_2O$	5	CH_2Cl_2	66	Pale yellow	53.85 (54.1)	4.50 (4.85)	11.1 (11.4)	9.20 (9.95)	1 918 (1 865)	292, 310	286, 310
$[\{PdCl_2(Ph_2PCH{:}CHPPh_2)\}_2]$	3	C_6H_6	75	Pale yellow	54.0 (54.45)	3.85 (3.85)	12.5 (12.35)	10.55 (10.8)	799 *h* (574)	(291) (304)	272, 280 (298)
$[PtCl_2(Ph_2PCH_2PPh_2)]$		*i*							Monomer *i*	292, 305 *i*	
$[PtCl_2\{Ph_2P(CH_2)_2PPh_2\}]$ [g,i,j]	5	CH_2Cl_2 [k]	86	White	46.6 (47.0)	3.70 (3.65)	10.6 (10.65)	8.95 (9.35)	*h*	281, 314	
$[PtCl_2\{Ph_2P(CH_2)_2PPh_2\}]\cdot H_2O$ [g,i,j]	5	CH_2Cl_2	64	Pale flesh	45.65 (45.75)	3.55 (3.85)	10.95 (10.4)	9.25 (9.10)	*h*	(292) 316	292, 315
$[\{PtCl_2[Ph_2P(CH_2)_3PPh_2]\}_2]\cdot 2H_2O$ [i]	5	CH_2Cl_2	60	White	46.75 (45.55)	3.80 (4.05)	10.2 (10.2)	8.55 (8.90)	*h*	291, 311	(273) 282 (308)
$[\{PtCl_2[Ph_2P(CH_2)_4PPh_2]\}_3]$	5	CH_2Cl_2	65	White	48.35 (48.55)	4.05 (4.10)	10.75 (10.25)	9.20 (8.95)	2 285 (2 078)	291, 313	292, 313
$[\{PtCl_2(Ph_2PCH{:}CHPPh_2)\}_2]\cdot 2H_2O$	5	CH_2Cl_2	98	White	45.55 (45.9)	3.55 (3.55)	10.95 (10.4)	9.15 (9.10)	*h*	(302) 309	275, 284 (306)

[a] See Experimental section. [b] Calculated values are given in parentheses. [c] By osmometry in CH_2Br_2. [d] Values in parentheses are shoulders. [e] Nujol mulls. [f] Solid state. [g] See also refs. 14 and 15. [h] Very low solubility in appropriate solvents. [i] See ref. 9. [j] See also ref. 16. [k] Precipitate washed with copious amounts of ethanol and then diethyl ether.

TABLE 3

Infrared spectra of ligands (240—300 cm^{-1})

Ligand						
$Ph_2PCH_2PPh_2$	254w			305w	325m	329m
$Ph_2P[CH_2]_2PPh_2$	256w		291m	305w–m		329m
$Ph_2P[CH_2]_3PPh_2$	256m—w			305vw		328m
$Ph_2P[CH_2]_4PPh_2$	253m—w			305w—m		329m
cis-$Ph_2PCH{:}CHPPh_2$	255w	283vw	290vw	305w		328m
$Ph_2As[CH_2]AsPh_2$	256w—m		290w	308w		329s

complexes of Ir^{I} [*e.g.* equation (1)]. The synthesis

$$[Ir_2Cl_2(cod)_2] + 2Ph_2P[CH_2]_3PPh_2 + 2CO \longrightarrow 2\,cod + [\{Ir(CO)Cl[Ph_2P(CH_2)_3PPh_2]\}_2] \quad (1)$$

described by equation (1) is in fact complex and occurs slowly in at least three steps. The initial precipitate contained no carbonyl ligand, and appeared to be the solvated complex $[\{IrCl(cod)(diphosphine)\}_n]$. This complex subsequently redissolved to form an unidentified carbonyl complex, which then reacted further to give the reported products as white or pale yellow solvated complexes. Benzene of crystallization was lost *in vacuo* to give pale yellow or yellow unsolvated products. In each case the diphosphine complexes of Ir^{I} are very soluble in halogenated solvents and their molecular weights can be readily determined. None of the iridium complexes described herein is mononuclear; no complex analogous to $[Rh(CO)Cl\{Ph_2P(CH_2)_2PPh_2\}]$ was detected.[1,2,4]

When the diphosphine is (2) or (5) the complex product in each case is binuclear, containing three carbonyl ligands per di-iridium complex molecule (t.g.a.), and is a 1 : 1 electrolyte in solution (*ca.* 10^{-3} mol dm^{-3}) in acetone (κ 120 and 109 S cm^{-1} respectively).

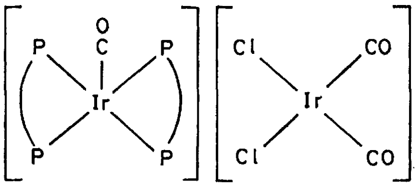
TABLE 4

Phosphorus-31 n.m.r. spectra

Complex	δ_P [a]/p.p.m.	^1J(Pt–P)/ Hz
$[Ir(CO)\{Ph_2P(CH_2)_2PPh_2\}_2][Ir(CO)_2Cl_2]$	+28.5	
$[\{Ir(CO)Cl[Ph_2P(CH_2)_3PPh_2]\}_2]$	−4.6	
$[\{Ir(CO)Cl[Ph_2P(CH_2)_4PPh_2]\}_3]$	+1.7	
$[Ir(CO)(Ph_2PCH{:}CHPPh_2)_2][Ir(CO)_2Cl_2]$	+35.4	
$[PdCl_2\{Ph_2P(CH_2)_2PPh_2\}]$	+68.3	
$[PdCl_2\{Ph_2P(CH_2)_3PPh_2\}]$	+12.9	
$[\{PdCl_2[Ph_2P(CH_2)_4PPh_2]\}_3]$	+32.8	
$[\{PdCl_2(Ph_2PCH{:}CHPPh_2)\}_2]$	+75.5	
$[PtCl_2(Ph_2PCH_2PPh_2)]$ [b]	−64.3	3 078
$[PtCl_2\{Ph_2P(CH_2)_2PPh_2\}]$ [b]	+45.3	3 618
$[\{PtCl_2[Ph_2P(CH_2)_3PPh_2]\}_2]$ [b]	−5.6	3 420
$[\{PtCl_2[Ph_2P(CH_2)_4PPh_2]\}_3]$	+13.4	N.o.[c]
$[\{PtCl_2(Ph_2PCH{:}CHPPh_2)\}_2]$	+9.4	N.o.[c]

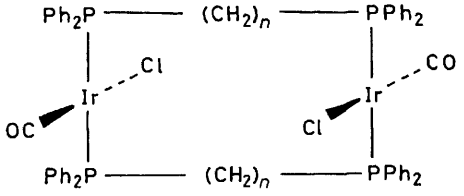
[a] Downfield from 85% H_3PO_4. [b] See ref. 9. [c] The signal-to-noise ratio for this sample precluded determination of ^1J(Pt–P).

The anion $[Ir(CO)_2Cl_2]^-$ was identified by comparison of carbonyl bands in the i.r. spectrum with those of an authentic sample.[10] This ion should also exhibit two i.r.-active metal–chlorine stretching modes.[11] Only one band was clearly observed in each case (304 cm^{-1}), but a *shoulder* (335—336 cm^{-1}) was observed close to a stronger band of the diphosphine ligand (328—329 cm^{-1}). The analogous rhodium anion, $[Rh(CO)_2Cl_2]^-$, exhibits two bands at 293 and 323 cm^{-1}.[4] The cation $[Ir(CO)(diphosphine)_2]^+$ is characterized in each case by a single sharp resonance in the ^{31}P-{^1H} n.m.r. spectrum [diphosphine = (2), δ_P 28.5 p.p.m.; (5), δ_P 35.4 p.p.m.], and a band (1935 cm^{-1}) in the i.r. spectrum of these complexes or of $[Ir(CO)\{Ph_2P(CH_2)_2PPh_2\}_2][BPh_4]$. The binuclear complexes are therefore of the structure (A). The analytical and i.r. spectroscopic data for the complex postulated [12] to be $[Ir(CO)_2\{Ph_2P(CH_2)_2PPh_2\}]Cl$ indicate that it is instead the complex described herein (A).[13]



(A)

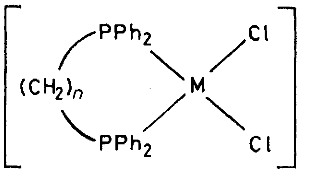
The product of the reaction of (1) or (3) with $[Ir_2Cl_2(cod)_2]$ is binuclear, and the reaction with (4) gave a trinuclear complex (Table 1). The i.r. spectrum of a Nujol mull of each complex showed a strong carbonyl band (1 950—1 960 cm^{-1}) and a very weak band (*ca.* 2 000 cm^{-1}). Metal–chlorine bands were observed at 283—308 cm^{-1}. These ligands were therefore terminal. The elemental and thermogravimetric analyses showed that each of these complexes contains one carbonyl ligand per iridium atom. The ^{31}P-{^1H} n.m.r. spectra each showed a sharp singlet, indicating that in each case the phosphorus atoms are chemically equivalent at room temperature. These data show that these complexes are diphosphine bridged (B).



(B)

A binuclear dicarbonyl complex with ideal C_{2h} symmetry (B) should display one i.r.-active and one Raman-active carbonyl-stretching band (B_u and A_g respectively).[11] Any divergence from ideal symmetry will render each of these bands both i.r. and Raman active. The shoulder (*ca.* 2 000 cm^{-1}) in the i.r. spectrum of VII ($n = 3$) may be a solid-state effect. Alternatively, this band may be tentatively assigned as the 'symmetric' carbonyl-stretching mode, which would indicate that each binuclear complex deviates from ideal C_{2h} symmetry.* Attempts to obtain proof of this assignment by investigating the Raman spectra of these complexes were unsuccessful. In each case strong fluorescence occurred and some decomposition of the material in the laser beam was noticed.

Palladium and Platinum Complexes.—A series of complexes of Pd^0, Pd^{II}, Pt^0, and Pt^{II} with diphosphines (1)—(3) and (5) has been described.[3,8,9,14-16] However, in many cases the molecular weight in solution and far-i.r. and Raman spectroscopic data have not been reported. The crystal structures of the dichloropalladium complexes of (1)—(3) (C) have recently been determined.[8] Each is mononuclear, but the local geometry about palladium varies greatly with change in chelate-ring size.[8] The complex $[PtCl_2(Ph_2PCH_2PPh_2)]$ is mononuclear in solution;[9] the related complexes of diphosphines (2)[9,15] and (3)[9] have been described as insufficiently soluble to permit determination of their molecular weights.



(C) M = Pd or Pt

The complex '$[PdCl_2\{Ph_2P(CH_2)_2PPh_2\}]$', which is mononuclear in the solid state,[8] has previously been described as white [14] or pale yellow,[15] and insufficiently soluble to determine the molecular weight.[15] Although it is of low solubility, I have shown that the complex is also mononuclear (Table 2) in CH_2Br_2 solution. The metal–chlorine stretching bands ($A_1 + B_1$) in the i.r. (293 and 314 cm^{-1}) and Raman spectra (285 and 307 cm^{-1}) have similar values, and agree well with literature values for the i.r. spectra (288 and 311 cm^{-1}),[15] as expected for a square-planar chelated complex (C). The complexes $[PdCl_2\{Ph_2P(CH_2)_3PPh_2\}]$ and $[PtCl_2\{Ph_2P(CH_2)_2PPh_2\}]$, which have also been described as white [9,16] or yellow,[14,15] are not sufficiently soluble to permit determination of molecular weights in solution. However, the very strong similarity of the i.r., Raman, and mass spectra with those of $[PdCl_2\{Ph_2P(CH_2)_2PPh_2\}]$ (see Table 2) leads to the conclusion that these complexes are of similar structure. The complex

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* A referee comments that the separation (40—50 cm^{-1}) between the two bands is surprisingly large for the assignments tentatively postulated. For similar complexes of Rh^I the A_g mode is 26—36 cm^{-1} higher than the B_u mode.[4]

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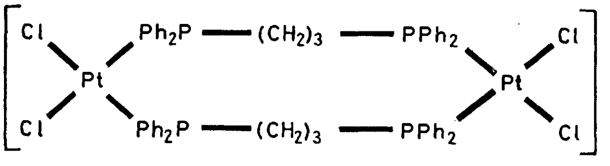
$[PtCl_2\{Ph_2P(CH_2)_2PPh_2\}]$ described herein is the monohydrate. The presence of water of crystallization is confirmed by sharp bands close to 1 625 and 3 475 cm^{-1} in the i.r. spectrum of each hydrate reported herein.

The complex $[\{PtCl_2[Ph_2P(CH_2)_3PPh_2]\}_n]$ shows i.r. bands similar to those of the above complexes, indicating that *cis* geometry about platinum is retained. However, the dissimilarity of the Raman and mass spectra of this complex or $[\{MCl_2(Ph_2PCH{:}CHPPh_2)\}_n]$ (M = Pd or Pt) from the spectra of the above complexes indicates that the structures of these complexes are different. The relatively greater intensities of binuclear ions (*e.g.* $[(PtCl_2)_2\{Ph_2P(CH_2)_3PPh_2\}]^+$) in the mass spectra of these complexes indicate a binuclear structure (D).



(D)

The complexes $[\{MCl_2[Ph_2P(CH_2)_4PPh_2]\}_3]$ (M = Pd or Pt) are each trinuclear in solution in dibromomethane. The i.r. and Raman spectra are consistent with *cis* geometry about the central metal atoms. These complexes are therefore trinuclear analogues of (D). The mass spectra of these complexes were very complicated, precluding unambiguous assignments.

TABLE 5

Structures of diphosphine complexes of Rh^{I}, Ir^{I}, Pd^{II}, and Pt^{II}

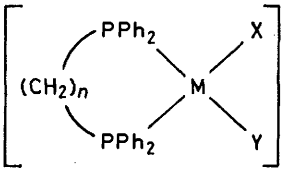
	L				
	$Ph_2P[CH_2]_nPPh_2$				
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$Ph_2PCH{:}CHPPh_2$
$[\{Rh(CO)ClL_m\}]$	binuclear *trans*	chelated *cis*	binuclear *trans*	binuclear *trans*	ionic $[RhL_2][Rh(CO)_2Cl_2]$
$[\{Ir(CO)ClL\}_m]$ [a]	binuclear *trans*	ionic $[Ir(CO)L_2][Ir(CO)_2Cl_2]$	binuclear *trans*	trinuclear *trans*	ionic $[Ir(CO)L_2][Ir(CO)_2Cl_2]$
$[\{PdCl_2L\}_m]$	mononuclear [b] *cis*	mononuclear [b] *cis*	mononuclear [b] *cis*	trinuclear *cis*	binuclear [c] *cis*
$[\{PtCl_2L\}_m]$	mononuclear [d] *cis*	mononuclear [c] *cis*	binuclear [c] *cis*	trinuclear *cis*	binuclear [c] *cis*

[a] Ionic complexes have stoicheiometry $Ir_2(CO)_3Cl_2L_2$. [b] Ref. 8. [c] Tentative assignment on the basis of i.r., Raman, and mass spectra. [d] Ref. 9.

The anion $[PtCl_4]^-$ exhibits [17] Raman-active bands at 164, 304, and 335 cm^{-1}, and a strong i.r. band (doublet) at 325 cm^{-1}, and is therefore not present in any of the above complexes.

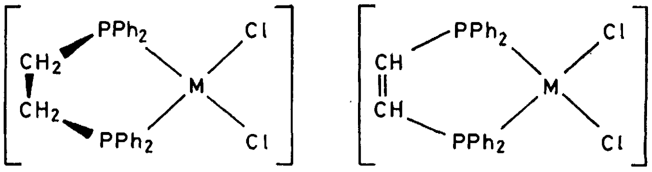
Chelating or Bridging Character.—The question arises as to the cause of the difference in character of apparently similar diphosphine ligands. It is suggested that the factors which determine whether or not the ligand is chelating or bridging are (*i*) the nature of the central metal atom, and (*ii*) the angle PMP which a diphosphine would subtend at the metal if it were chelating (E).

The crystal structures of $[PdCl_2\{Ph_2P(CH_2)_nPPh_2\}]$ ($n = 1 - 3$) and some related complexes have been determined.[8,18] The angle PPdP is *ca.* 73° for $n = 1$, 85° for $n = 2$, and 90° for $n = 3$.[8,18] The systems $n = 1$ and 3 are also constrained to adopt structures in which various bonds are eclipsed,[8] slightly increasing strain in these systems. This is reflected in the bond lengths (Pd–P).[8] The ^{31}P n.m.r. chemical shifts and coupling constants [^1J(Pt–P)] for these complexes, as well as for complexes of Pt^{II} with (1)—(3),[9] also vary greatly.



(E) M=Rh or Ir,X=Cl,Y=CO
M=Pd or Pt,X=Y=Cl

The diphosphine (4), with four methylene groups bridging the phosphorus atoms, is expected to subtend an angle PPdP greater than 90°. Similarly the more rigid, unsaturated, diphosphine (5) is expected to subtend a much larger angle at palladium than the flexible saturated diphosphine (2) (F). As a consequence, extra strain is introduced into a structure of the type shown in (C) and such a structure is thereby marginally destabilized relative to a structure of the type (D).



(F)

The behaviour of these ligands when complexed with Pt^{II} shows, as expected, a similar trend to that shown by the palladium complexes (see Tables 2 and 5). Only diphosphine (3) apparently differs in behaviour. The molecular aggregations and structures of the diphosphine

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complexes of Rh^I, Ir^I, Pd^{II}, and Pt^{II} discussed are summarized in Table 5.

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