Transition Metal–Carbon Bonds. Part XXX.[1] Internal Metallations of Platinum(II)-t-Butyldi-*o*-tolylphosphine and -Di-t-butyl-*o*-tolylphosphine Complexes †

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Platinum(II) complexes of the phosphines $PBu^t(o\text{-tolyl})_2$ and $PBu^t_2(o\text{-tolyl})$ have been prepared. The internally metallated compounds *trans*-$[PtCl(P\text{–}C)L]$ [$(P'\text{–}C) = CH_2C_6H_4PBu^t(o\text{-tolyl})$ or $(P''\text{–}C) = CH_2C_6H_4PBu^t_2$; $L = PBu^t(o\text{-tolyl})_2$ or $PBu^t_2(o\text{-tolyl})$] are very readily formed by treating Na_2PtCl_4 or *trans*-$[PtCl_2(PhCN)_2]$ with L. The metallation occurs at the tolyl-methyl of the ligand, L, in all cases. For complexes of the type $[PtX(P'\text{–}C)PBu^t(o\text{-tolyl})_2]$ ($X = Cl, NO_3$, or Me), metallation of the $PBu^t(o\text{-tolyl})_2$ ligand goes less readily to give the dimetallated complexes *cis*-$[Pt(P'\text{–}C)_2]$ or *trans*-$[Pt(P'\text{–}C)_2]$. The tendency to metallate increases in the order of anionic ligands $X = Cl < Me \simeq NO_3$. The compound *trans*-$[Pt(P''\text{–}C)_2]$ is prepared by heating $[PtMe(P''\text{–}C)PBu^t_2(o\text{-tolyl})]$. Bridged complexes of the type $[Pt_2Cl_2(P\text{–}C)_2]$ are readily prepared and the chloride bridges replaced on treatment with silver carboxylate to give the compounds $[Pt_2X_2(P\text{–}C)_2]$ ($X = OAc$ or OBz). The chloride bridges are also split by various ligands (*e.g.* pyridine, PPh_3, acetylacetonate, *etc*) giving monomeric species.

THE internal metallation of tertiary phosphine or phosphite ligands complexed to transition metals is a growing field of interest.[1-7] In a previous paper [1] we have shown that certain complexes of the type *trans*-$[PtX_2L_2]$ ($X =$ Cl, Br, or I; $L =$ tertiary phosphine) can undergo internal metallation to give the compounds *trans*-$[PtX(P\text{–}C)L]$ [$P\text{–}C =$ internally metallated tertiary phosphine (L)]. Two important factors which promote internal metallation in such complexes are (1) the presence of bulky substituents on the tertiary phosphine (*e.g.* PBu^tPh_2 or PBu^t_2Ph) and (2) the possibility of forming five-membered rings on metallation [*e.g.* with $PPh(o\text{-tolyl})_2$ by metallation of the tolyl-methyl group]. In order to investigate further the factors affecting these metallation reactions we have prepared platinum(II) complexes of $PBu^t(o\text{-tolyl})_2$ and $PBu^t_2(o\text{-tolyl})$. These two phosphines combine both the factors described above.

The phosphine $PBu^t(o\text{-tolyl})_2$ is prepared by adding t-butyldichlorophosphine to an excess of *ortho*-tolyllithium in ethereal solution. It is a white crystalline-air-stable solid (m.p. 88—89°). (Table 1). Similar

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† No reprints available.

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treatment of di-t-butylchlorophosphine gives PBu^t_2(*o*-tolyl) as a viscous air-sensitive liquid. These new tertiary phosphines are characterised as their methiodide salts (Table 1). The ^{1}H n.m.r. spectra of these four compounds show doublets for the t-butyl groups with ^3J(P–H) increasing from phosphorus(III) to phosphorus(V) (data in Table 2). Similar increases are found for tertiary methylphosphines and their methiodides.[8] The tolyl-methyl signal is split into a doublet with ^4J(P–H) of *ca.* 1·5 Hz for the compounds PBu^t_2(*o*-tolyl) and [PBu^t_2Me(*o*-tolyl)]I. However, this coupling is not apparent in the spectra of the PBu^t_2(*o*-tolyl)-platinum(II) complexes (see below).

Preparation and Reactions of the Complexes trans-[PtCl(P–C)L] [(P–C) = *internally metallated tertiary phosphine* (L); L = PBu^t(*o*-tolyl)$_2$ *or* PBu^t_2(*o*-tolyl)].—t-Butyldi-*o*-tolylphosphine (2·08 molar equiv.) slowly reacts with sodium tetrachloroplatinite(II) in methanol solution at 20° during 24 h to give a mixture of *trans*-[PtCl(P′–C)PBu^t(*o*-tolyl)$_2$] [(P′–C) = $CH_2C_6H_4PBu^t$(*o*-tolyl)], identified by its ^{1}H n.m.r. spectrum (Table 3), and *trans*-[$PtCl_2${PBu^t(*o*-tolyl)$_2$}$_2$]. The yellow crystalline complex *trans*-[$PtCl_2${PBu^t(*o*-tolyl)$_2$}$_2$] (Table 4), formed in low yield (28%) is identified by its i.r. and ^{1}H n.m.r. spectra (Table 3). The far-i.r. spectrum shows a strong band at 335 cm^{-1} due to ν(Pt–Cl) which is typical of mutually *trans* chlorine ligands.[9] The ^{1}H n.m.r. spectrum shows a triplet with $|^3J(P\text{–}H) + {}^5J(P\text{–}H)| =$ 14·8 Hz, indicating that the t-butylphosphine ligands are in mutually *trans*-positions.[1] The tolyl-methyl groups give a singlet at τ 7·70.

TABLE 1

Analytical and melting point data of PBu^t(*o*-tolyl)$_2$ and PBu^t_2(*o*-tolyl) and their methiodide derivatives [a]

Compound	% Yield	Analytical data [b] C	H	M.p.
PBu^t(*o*-tolyl)$_2$	63	79·5 (79·95)	8·4 (8·6)	88—89°
PBu^t_2(*o*-tolyl)	68			B.p. 84—94°/0·8 mm.
[PBu^tMe(*o*-tolyl)$_2$]I	72	55·25 (55·35)	6·4 (6·35)	199—201
[PBu^t_2Me(*o*-tolyl)]I	66	50·65 (50·8)	7·3 (7·45)	209—211 [c]

[a] All compounds are white. [b] Theoretical values in parentheses. [c] Decomposed.

A gas is evolved on heating *trans*-[$PtCl_2${PBu^t(*o*-tolyl)$_2$}$_2$] over the range 169—171°; the crystals turn white and eventually melt (225—227°) with decomposition. Probably the white crystals are the internally metallated compound [PtCl(P′–C){PBu^t(*o*-tolyl)$_2$}] (Table 4) and hydrogen chloride is evolved. The complex *trans*-[PtCl(P′–C)PBu^t(*o*-tolyl)$_2$] (Table 4) is obtained in high yield (*ca.* 90%) when a mixture of PBu^t(*o*-tolyl)$_2$ (2 molar equiv.) and Na_2PtCl_4 in n-propanol is heated under reflux for 10 min. We have also prepared this complex by heating *trans*-[$PtCl_2$(PhCN)$_2$] with PBu^t(*o*-tolyl)$_2$ in n-propanol, benzene, or chloroform solution. The configuration of the compound [PtCl(P′–C)PBu^t(*o*-tolyl)$_2$] (I; X = Cl) is shown by its ^{31}P n.m.r., ^{1}H n.m.r., and i.r. spectra (Tables 3 and 5). The ^{31}P n.m.r. spectrum (Table 5) shows an AB- (almost an AX-) pattern with accompanying ^{195}Pt satellites. The large value of ^2J(P–P) (409 Hz) shows that the two P nuclei are mutually in *trans*-positions.[1] The ^{1}H n.m.r. spectrum shows that the two t-butyl groups are non-equivalent and coupled to both ^{31}P nuclei: τ 8·49, ^3J(P–H) = 12·9 Hz and ^5J(P–H) = 1·7 Hz; τ 8·39, ^3J(P–H) = 12·8 Hz and ^5J(P–H) = 1·7 Hz. The *o*-tolyl methyls each give a singlet resonance and the methylene group, formed on metallation, gives a broad complex signal. The i.r. spectrum shows ν(Pt–Cl) at 270 cm^{-1} due to chlorine *trans* to carbon.

The chelate group $CH_2C_6H_4$ PBu^t(*o*-tolyl) has an asymmetric centre at the phosphorus atom.

The complex [PtCl(P′–C) PBu^t(*o*-tolyl)$_2$] is unaffected by treatment with dry hydrogen chloride in ether at 20°, for three days. Similar resistance to hydrogen chloride has been observed with related complexes,[1] although it has been reported that the platinum–carbon bond in [PtCl{CH(Me)$C_6H_4PPh_2$}{PPh_2(*o*-vinylphenyl)}] is cleaved by hydrogen chloride to give *cis*-[$PtCl_2${PPh_2(*o*-ethylphenyl)}{PPh_2(*o*-vinylphenyl)}].[10] Treatment of *trans*-[PtCl(P′–C)PBu^t(*o*-tolyl)$_2$] with silver nitrate gives the corresponding nitrato-complex, configuration (I; X = NO_3), as shown by the ^{1}H n.m.r. spectrum (Table 3) which is very similar to that of the chloro-complex. [PtCl(P′–C)PBu^t(*o*-tolyl)$_2$] also reacts with methyl-lithium to give [PtMe(P′–C)-PBu^t(*o*-tolyl)$_2$] configuration (II; X = Me), *i.e.* with *cis*-phosphines. The *cis*-configuration for the phosphines follows from the ^{1}H n.m.r. pattern of the platinum-bonded methyl which consists of a 1 : 1 : 1 : 1 quartet at τ 9·88 flanked by satellites due to coupling with platinum-195 with ^2J(Pt–H) = 68 Hz. This coupling constant is characteristic of a platinum(II) methyl in the *trans*-position to phosphorus, *e.g.* *cis*-[$PtMe_2$(PMe_2Ph)$_2$] has ^2J(Pt–H) = 67 Hz and *cis*-[$PtMe_2$($PMePh_2$)$_2$], ^2J(Pt–H) = 68 Hz.[11] The quartet is due to coupling to the ^{31}P-nuclei ^3J(P–H) = 6·0 and 7·4 Hz. The t-butyl groups each give a 1 : 1 doublet resonance.

trans-[PtCl(P′–C)PBu^t(*o*-tolyl)$_2$] is recovered unchanged after being heated in boiling 2-methoxyethanol for 20 h but on heating in decalin at *ca.* 190° for 6 days a very soluble white crystalline complex [$C_{36}H_{44}P_2Pt$] is formed in 39% yield. The complex is monomeric in chloroform and its ^{1}H n.m.r. pattern is very simple (Table 3) consisting of a doublet (relative intensity 3) at τ 9·06 [J(P–Bu^t) = 13·9 Hz] and a singlet (relative intensity 1) at τ 8·04 due to the *o*-tolyl methyls. A broad band at *ca.* τ 6·65 is assigned to the platinum-methylene protons. The *doublet* due to the two t-butyl

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TABLE 2

^{1}H n.m.r. data [a] of PBu^t(*o*-tolyl)$_2$ and PBu$^t_2$(*o*-tolyl) and their methiodide derivatives

Compound	τ(Bu^t)	^3J(P–H)	τ(tolyl-Me) [b]	τ(Me)	^{2}J(P–H)
PBu^t(*o*-tolyl)$_2$ [c]	8·77	13·0	7·60 br		
PBu$^t_2$(*o*-tolyl) [d]	8·82	11·6	7·40 dl [e]		
[PBu^{t}Me(*o*-tolyl)$_2$]I [f]	8·36	17·0	7·93 br	7·32	11·0
[PBu$^t_2$Me(*o*-tolyl)]I [f]	8·70	15·6	7·28 dl [g]	7·31	11·5

[a] Spectra recorded at *ca.* 35° and 60 MHz. τ-Values ±0·02, *J*-values ±0·5 Hz. [b] br = Broad; dl = doublet. [c] Recorded in benzene solution. [d] Recorded as a neat liquid. [e] ^4J (P–H) = 1·5 Hz. Recorded in CDCl$_3$ solution. [g] ^4J (P–H) = 1·3 Hz.

TABLE 3

^{1}H N.m.r.[a] and i.r. data of some internally metallated platinum(II) complexes of the phosphines PBu^t(*o*-tolyl)$_2$ and PBu$^t_2$(*o*-tolyl)

Compound [b]	τ(Bu^t) [c]	*J*(P–Bu^t)	τ(tolyl-Me)	τ(CH$_2$) [c]	ν(Pt–Cl) (cm^{-1})
trans-[PtCl$_2${PBu^t(*o*-tolyl)$_2$}$_2$]	8·38 tr	14·8 [d]	7·70		335
trans-[PtCl(P′–C)PBu^t(*o*-tolyl)$_2$]	8·49 dl [e]	12·9	8·07, 7·93	cx	270
	8·39 dl [e]	12·8	7·79		
trans-[PtNO$_3$(P′–C)PBu^t(*o*-tolyl)$_2$]	8·48 dl [f]	12·8	8·01, 7·93	*ca.* 7·4 br	
	8·44 dl [f]	12·7	7·87		
cis-[PtMe(P′–C)PBu^t(*o*-tolyl)$_2$] [g]	8·92 dl	12·6	8·45, 7·94	*ca.* 6·8 br	
	8·74 dl	13·0	7·49		
rac-cis-[Pt(P′–C)$_2$]	9·06 dl	13·9 [d]	8·04	*ca.* 6·65 br	
rac-trans-[Pt(P′–C)$_2$]	8·52 tr	14·0 [d]	8·05	cx	
trans-[PtCl(P″–C)PBu$^t_2$(*o*-tolyl)]	cx		6·96	nv	275
[PtMe(P″–C)PBu$^t_2$(*o*-tolyl)] [h]	cx		7·12	nv	
trans-[Pt(P″–C)$_2$]	8·64 tr	13·3 [d]		6·76 [i]	

[a] Spectra recorded at *ca.* 35° and 60 MHz in CDCl$_3$ solution. τ-Values ±0·02, *J*-values ±0·5 Hz. [b] (P′–C) = [CH$_2$C$_6$H$_4$PBu^t-(*o*-tolyl)]; (P″–C) = [CH$_2$C$_6$H$_4$PBu$^t_2$). [c] tr = Triplet; dl = doublet; cx = complex; br = broad; nv = not visible. [d] '*J*' = |^3J(P–H) + ^5J(P–H)|. [e] ^5J(P–H) = 1·7 Hz. [f] Bu^t signals are double doublets with ^5J(P–H) of *ca.* 2 Hz. [g] Platinum-methyl at τ 9·88 (1 : 1 : 1 : 1 quartet); ^2J(Pt–H) = 68 Hz; ^3J(P–H) *cis* and *trans* = 6·0 and 7·4 Hz. [h] Platinum-methyl at τ 9·86. [i] Triplet, ^3J(P–H) = 9·0 Hz.

TABLE 4

Analytical, molecular weight, and melting point data for some internally metallated platinum(II) complexes [a] of the phosphines PBu^t(*o*-tolyl)$_2$ and PBu$^t_2$(*o*-tolyl)

		Analytical data [c]				
Compound [b]	% Yield	C	H	Cl	*M* [c,d]	M.p.
trans-{PtCl$_2$[PBu^t(*o*-tolyl)$_2$]$_2$} [e]	28	53·8 (53·6)	5·8 (5·75)	8·95 (8·8)		169—171° [f] 225—227
trans-[PtCl(P′–C)PBu^t(*o*-tolyl)$_2$]	91	55·95 (56·1)	5·9 (5·9)	4·6 (4·6)	756 (770)	219—229 [f] *ca.* 300 [g]
trans-[PtNO$_3$(P′–C)PBu^t(*o*-tolyl)$_2$]	73	54·4 (54·25)	5·5 (5·7)			187—200
cis-[PtMe(P′–C)PBu^t(*o*-tolyl)$_2$]	92	59·3 (59·25)	6·55 (6·45)		729 (750)	175—186 [f] 255—266
rac-cis-[Pt(P′–C)$_2$]	39	58·9 (58·9)	5·95 (6·05)		720 (734)	239—244
rac-trans-[Pt(P′–C)$_2$]	60	58·6 (58·9)	5·9 (6·05)		710 (734)	261—263
trans-[PtCl(P″–C)PBu$^t_2$(*o*-tolyl)] [h]	65	50·25 (50·5)	6·75 (6·9)	6·5 (5·95)		190—195 [f] 320 [g]
(PtMe(P″–C)PBu$^t_2$(*o*-tolyl)]	64	54·1 (54·6)	7·5 (7·7)		668 (682)	195—200 [f,g]
trans-[Pt(P″–C)$_2$]	26	54·0 (54·15)	7·35 (7·25)			230—250 [i] 296—298 [g]

[a] All complexes are white except where indicated otherwise. [b] (P′–C) = [CH$_2$C$_6$H$_4$PBu^t(*o*-tolyl)]; (P″–C) = (CH$_2$C$_6$H$_4$PBu$^t_2$). [c] Theoretical values in parentheses. [d] Chloroform solution. [e] Compound is yellow. [f] Gas evolved. [g] Decomposed. [h] Compound contains 0·2 mol equiv. of CH$_2$Cl$_2$ per platinum atom. [i] Sublimed.

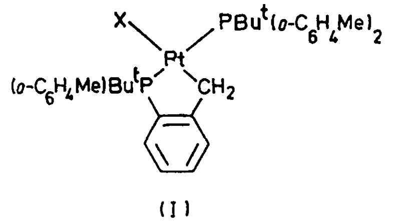
TABLE 5

^{31}P N.m.r.[a] data for complexes of the type [PtCl(P–C)L] [(P′–C) = CH$_2$C$_6$H$_4$PBu^t(*o*-tolyl) and (P″–C) = CH$_2$C$_6$H$_4$-PBu$^t_2$; L = tertiary phosphine]

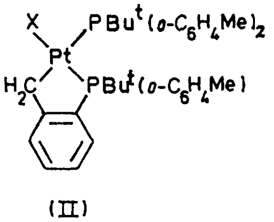
Unmetallated phosphine			Metallated phosphine			
L	δ	^1J(Pt–P)	(P–C)	δ	^1J(Pt–P)	^2J(P–P)
PBu^t(*o*-tolyl)$_2$	−31·1	2755	(P′–C)	−52·0	3262	409
PPh$_3$	−28·9	2847	(P″–C)	−74·8	3289	412·5

[a] Spectra recorded at 36·43 MHz in dichloromethane solution with all ^{1}H nuclei decoupled and C$_6$F$_6$ used to provide a ^{19}F field/frequency lock. Chemical shifts are given relative to 85% H$_3$PO$_4$ (±0·2 p.p.m.); *J*-values ±1 Hz.

groups indicates that both the phosphorus ligands are now equivalent and in mutually *cis*-positions, *i.e.* ^2J(P–P) is small. These data indicate that the second PBu^t(*o*-tolyl)$_2$ ligand has been metallated to give the complex *cis*-[Pt(P′–C)$_2$]. This has the racemic configuration (III) as shown by preliminary *X*-ray data.[12] Configuration (III) is probably the sterically favoured form since the very bulky t-butyl groups are on different sides of the PtP_2-plane [contrast with the *meso*-form (IV)]. The complex *cis*-[Pt(P′–C)$_2$] is also formed when a solution of *trans*-[Pt(NO_3)(P′–C)PBu^t(*o*-tolyl)$_2$] is heated in n-propanol at *ca.* 90° for 3 h. Possibly nitric acid or n-propyl nitrate, is also formed.



(I)



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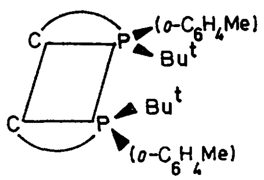

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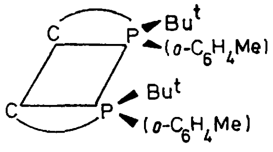

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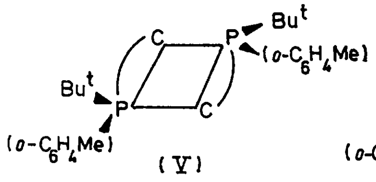
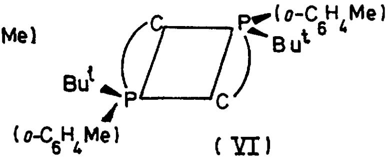


(V)



(VI)

The corresponding *trans*-isomer *rac-trans*-[Pt(P′–C)$_2$], configuration (V), is prepared by heating a solution of *cis*-[PtMe(P′–C)PBu^t(*o*-tolyl)$_2$] in 2-methoxyethanol for 90 min. It is less soluble in organic solvents than the *cis*-isomer and is monomeric in chloroform solution. The *trans*-configuration is confirmed by the ^1H n.m.r. spectrum (Table 3) which shows a triplet (relative intensity 3) at τ 8·52 with $|^3J(P\text{–}H) + {}^5J(P\text{–}H)| = 14{\cdot}0$ Hz. This indicates that the two phosphines are equivalent and in mutually *trans*-positions. The *o*-tolyl methyls appear as a singlet at τ 8·05 (relative intensity 1) and the platinum bonded methylene groups give a broad complex signal at lower field. An *X*-ray structural determination[12] confirms the *trans*-configuration and shows that the compound is the *rac*-isomer, configuration (V) and not the *meso*-isomer (VI). In this configuration (V), the t-butyl groups project towards the same side of the PtP_2-plane but they do not interact as much as they would in the *meso-cis*-isomer. Pyrolysis of [PtMe(P′–C)PBu^t(*o*-tolyl)$_2$] gives methane (identified by its i.r. spectrum) and *rac-trans*-[Pt(P′–C)$_2$] mixed with an unidentified substance. *trans*-[Pt(P′–C)$_2$] is unaffected by treatment with methyl iodide at 20° for three weeks, but with hydrogen chloride it gives *trans*-[PtCl(P′–C)PBu^t(*o*-tolyl)$_2$], *i.e.* with cleavage of one of the platinum–carbon bonds. In contrast, complexes of the type *cis*-[PtR_2L_2], *cis*-[$PtClRL_2$], or *trans*-[$PtClRL_2$] (R = alkyl, CH_2Ph, or aryl; L = tertiary phosphine or tertiary arsine) are readily attacked by hydrogen chloride to give [$PtCl_2L_2$],[11,13-15] although it has been shown that the rate of cleavage of the second platinum–carbon bond is much slower than that of the first.[16]

There are many examples of complexes containing internal transition-metal–carbon bonds[2] but relatively few have been reported to contain two internally metallated ligands per metal atom and very forcing conditions are generally required to make them. Complexes containing two internally metallated nitrogen-donor ligands have been reported for iron(II)[17] and rhodium(III)[18] and the palladium(II) complex *trans*-[Pd($C_6H_4CH_2NMe_2$)$_2$] was prepared *via* the lithio-derivative [$LiC_6H_4CH_2NMe_2$].[19] Complexes of the type *cis*-[M($CH_2C_6H_4PPh_2$)$_2$] [M = Ni^{II}, Pd^{II}, or Pt^{II}] have similarly been prepared *via* the potassium derivative [$KCH_2C_6H_4PPh_2$][7] and complexes of Ir^{III} and Rh^{III} containing two metallated phosphite ligands are formed under forcing conditions (boiling decalin).[3]

The ligand PBu^t_2(*o*-tolyl) shows significant differences from PBu^t(*o*-tolyl)$_2$ in the formation and properties of platinum(II) complexes. For example PBu^t_2(*o*-tolyl) does not react with sodium tetrachloroplatinite(II) in methanol at 20°, presumably because it is very sterically hindered. However, when a mixture of PBu^t_2(*o*-tolyl) (2·2 molar equiv.) and *trans*-[$PtCl_2$(PhCN)$_2$] in n-propanol is heated under reflux for 40 min, the white complex *trans*-[PtCl(P″–C) PBu^t_2(*o*-tolyl)] [(P″–C) = $CH_2C_6H_4PBu^t_2$] is obtained. The far-i.r. spectrum (Table 3) shows ν(Pt–Cl) at 275 cm^{-1} assigned to chlorine *trans* to carbon. The ^1H n.m.r. spectrum is very complex presumably due to the presence of rotational isomers but the relative intensities of the resonances for t-butyl : tolyl-methyl : aromatic are 35 : 3 : 8·3, close to the theoretical ratios 36 : 3 : 8. The ^1H n.m.r. spectrum of

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trans-[$PdCl_2\{PBu^t_2$(o-tolyl)$\}_2$] shows that rotational isomers are present.[20] When a mixture of PBu^t_2(*o*-tolyl) (2·2 mol per Pt atom) and *trans*-[$PtCl_2(PhCN)_2$] in n-propanol is heated under reflux for 2 h a mixture of *trans*-[PtCl(P″–C)PBu^t_2(*o*-tolyl)] and [Pt_2Cl_2(P″–C)$_2$] (see below) is formed in approximately equal amounts.

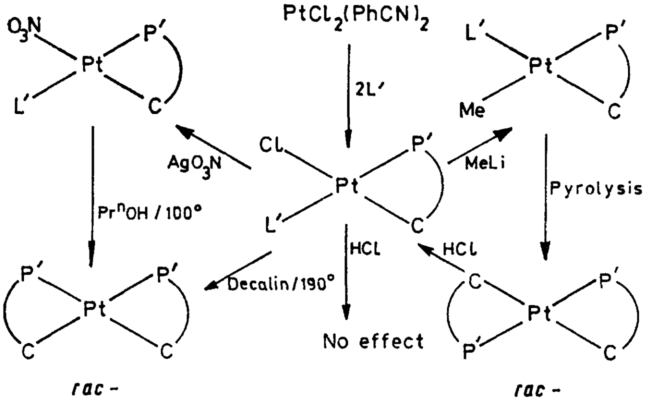
Treatment of *trans*-[PtCl(P″–C)PBu^t_2(*o*-tolyl)] with an excess of methyl-lithium gives the white monomeric complex [PtMe(P″–C)PBu^t_2(*o*-tolyl)] (Table 4). The ^1H n.m.r. spectrum (Table 3) of this compound again shows a complex signal due to the t-butyl groups and the platinum-methyl also gives a complex signal at τ 9·86. This compound is less soluble than the corresponding PBu^t(*o*-tolyl)$_2$ complex and ^2J(Pt–H) of the platinum-methyl could not be measured so we cannot determine the stereochemistry. When [PtMe(P″–C)PBu^t_2-*o*-tolyl)] is heated under reflux in n-propanol for 2 h, the complex *trans*-[Pt(P″–C)$_2$] is obtained in low yield (26%). The ^1H n.m.r. spectrum of this complex is very simple (Table 3). The t-butyl groups give a triplet at τ 8·64 with $|^3J(P\text{–}H) + {}^5J(P\text{–}H)| = 13{\cdot}3$ Hz which shows that the two phosphorus ligands are equivalent and in mutually *trans*-positions. The platinum-methylene protons give a triplet at τ 6·76 with ^3J(P–H) = 9·0 Hz.

TABLE 6

Analytical, molecular weight, and melting point data for complexes of the type [Pt_2X_2(P–C)$_2$], [X = Cl, acetate or benzoate; (P′–C) = $CH_2C_6H_4PBu^t$(*o*-tolyl) and (P″–C) = $CH_2C_6H_4PBu^t_2$]

Compound	% Yield	Colour [a]	Analytical data [b] C	H	Cl	*M* [b,c]	M.p.
[Pt_2Cl_2(P′–C)$_2$]	91	w	43·25 (43·25)	4·7 (4·65)	7·3 (7·1)		290° [d]
[$Pt_2(OAc)_2$(P′–C)$_2$] [e]	65	cm	49·1 (48·85)	5·6 (5·5)			160—165 [f] 205—210 [d]
[$Pt_2(OBz)_2$(P′–C)$_2$] [g]	78	w	55·5 (55·6)	5·8 (5·85)		801 (1340)	150—160 [f] 170—178 [d]
[Pt_2Cl_2(P″–C)$_2$]	92	w	38·6 (38·7)	5·15 (5·2)	7·35 (7·6)		315—325 [d]
[$Pt_2(OAc)_2$(P″–C)$_2$]	60	cm	41·45 (41·75)	5·7 (5·55)		727 (979)	250—255 [d]
[$Pt_2(OBz)_2$(P″–C)$_2$]	55	cm	47·95 (47·9)	5·2 (5·3)			200 [d]

[a] cm = Cream; w = white. [b] Theoretical values given in parentheses. [c] Chloroform solution. [d] Decomposed. [e] Complex contains 0·5 mol. of cyclohexane per platinum atom. [f] Gas evolved. [g] Complex contains 1 mol. of cyclohexane per platinum atom.



SCHEME 1

Some platinum(II) complexes of t-butyldi-*o*-tolylphosphine (L′) (P′–C) = asymmetric chelate ligand $CH_2C_6H_4PBu^t$(*o*-tolyl)

Scheme 1 summarises the more important reactions of internally metallated compounds with two phosphorus donor ligands which have been described above.

Preparation of Complexes of the Type [Pt_2X_2(P–C)$_2$] [X = Cl, OAc *or* OBz; (P′–C) = $CH_2C_6H_4PBu^t$(*o*-tolyl); (P″–C) = $CH_2C_6H_4PBu^t_2$].—When an equimolar mixture of PBu^t(*o*-toly)$_2$ and *trans*-[$PtCl_2(PhCN)_2$] is heated in 2-methoxyethanol under reflux for 10 min a white precipitate is formed of formulation [$C_{18}H_{22}$Cl-PPt]$_n$ (Table 6). This is insoluble in organic solvents and the far-i.r. spectrum (Table 7) shows two bands due to ν(Pt–Cl) at 275 and 244 cm^{-1}. These data are consistent with the compound being a chlorine-bridged binuclear compound [Pt_2Cl_2(P′–C)$_2$], we assign the *sym-trans*-configuration (VII; X = Cl) to it by analogy with complexes of the type [$M_2X_4L_2$][21], [M_2X_2\{diene(OMe)\}$_2$][22], or [M_2X_2(N–C)$_2$][2] [M = Pd or Pt; X = Cl, Br, or I; L = tertiary phosphine or tertiary arsine; diene(OMe) = 2-methoxycyclo-oct-5-enyl, *etc.*, (N–C) = C_6H_4N=NPh or $C_6H_4CH_2NMe_2$]. The complex [Pt_2Cl_2(P′–C)$_2$] is also formed by heating a mixture of [PtCl(P′–C)PBu^t(*o*-tolyl)$_2$] and platinum(II) chloride in xylene at 130—150° for 1 h.

Many examples of complexes of the type [Pt_2Cl_2-(N–C)$_2$] [(N–C) = ring-closed nitrogen-donor ligand] are known [2] but the complex [Pt_2Cl_2(P′–C)$_2$] is the first compound of this type to be reported. The tertiary phosphine PBu^t_2(*o*-tolyl) undergoes a similar reaction with *trans*-[$PtCl_2(PhCN)_2$] in boiling 2-methoxyethanol to give the complex [Pt_2Cl_2(P″–C)$_2$] (Table 5). The far-i.r. spectrum (Table 7) shows two bands due to bridging chlorines at 280 and 238 cm^{-1}. Treatment of a suspension of [Pt_2Cl_2(P′–C)$_2$] in acetone with silver acetate or silver benzoate gives the corresponding acetato- or benzoato-bridged binuclear complexes [Pt_2X_2(P′–C)$_2$] (X = OAc or OBz). These complexes are soluble in organic solvents and an interesting feature is that they take up saturated hydrocarbons into the crystal lattice when they are recrystallised from a mixture of dichloromethane–hydrocarbon. The ^1H n.m.r. spectrum (Table 7) of [$Pt_2(OAc)_2$(P′–C)$_2$], which has been re-

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[20] A. J. Cheney and B. L. Shaw, unpublished results.

[21] G. Booth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 1.

[22] J. Chatt, M. L. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2496.

crystallised from dichloromethane–light petroleum (b.p. 40—60°), shows a doublet due to the t-butyl protons at τ 8·59, two singlets at τ 8·19 and 8·12 due to the tolyl-methyl and the acetate-methyl groups and a broad complex signal at τ 6·75 due to the platinum-methylene protons. There is an additional broad signal at *ca.* τ 9 which we assign to the hydrocarbon protons. When the complex $[Pt_2(OAc)_2(P'{-}C)_2]$ is recrystallised from dichloromethane–cyclohexane, the ^1H n.m.r. spectrum (Table 7) shows a singlet due to cyclohexane at τ 8·55 which integrates to give a ratio of 0·5 mol equiv. of cyclohexane per platinum atom; this formulation is confirmed by the analytical data (Table 6). When the complex is heated in the solid state, a vigorous evolution of gas is observed (160—165°) which is presumably due to release of the cyclohexane. A white crystalline solid remains which decomposes at 205—210°. The corresponding benzoate, $[Pt_2(OBz)_2(P'{-}C)_2]$, takes up 1 mol. equiv. of cyclohexane per platinum atom, as is shown in its ^1H n.m.r. spectrum (Table 7). The trapped cyclohexane is released on heating (150—160°) but the trapped molecules are retained by both complexes when they are set aside under reduced pressure (*ca.* 0·05 mmHg) for several days. The complexes $[Pt_2X_2(P''{-}C)_2]$ (X = OAc or OBz) are similarly prepared from $[Pt_2Cl_2(P''{-}C)_2]$ but they do not take up cyclohexane of solvation. The ^1H n.m.r. spectrum (Table 7) of the acetate shows a doublet at τ 8·55 with $^3J(P{-}H) = 14{\cdot}1$ Hz and the platinum-methylene protons give a doublet at τ 6·52 with $^3J(P{-}H) = 4{\cdot}5$ Hz. The compound $[Pt_2(OBz)_2(P''{-}C)_2]$ shows a broad complex signal for the t-butyl protons which is possibly due to restricted rotation.

TABLE 7

^1H N.m.r.[a] and i.r.[b] data for complexes of the type $[Pt_2X_2(P{-}C)_2]$, [X = Cl, acetate, or benzoate; $(P'{-}C) = CH_2C_6H_4PBu^t$(*o*-tolyl) and $(P''{-}C) = CH_2C_6H_4PBu^t{}_2$]

Compound	$\tau(Bu^t)$ [c]	$^3J(P{-}H)$	τ(tolyl-Me) [c]	$\tau(CH_2)$ [c]	$\nu(Pt{-}Cl)$
$[Pt_2Cl_2(P'{-}C)_2]$ [d]					275s, 244m
$[Pt_2(OAc)_2(P'{-}C)_2]$ [e]	8·59	15·0	8·19, 8·12 [f]	6·75 br	
$[Pt_2(OBz)_2(P'{-}C)_2]$ [g]	8·53	15·0	7·75 br	*h*	
$[Pt_2Cl_2(P''{-}C)_2]$ [d]					280s, 238m
$[Pt_2(OAc)_2(P''{-}C)_2]$	8·55	14·1	7·95 [i]	6·52 dl [j]	
$[Pt_2(OBz)_2(P''{-}C)_2]$	*h*			*ca.* 6·6 br	

[a] Spectra recorded at *ca.* 35° and 60 MHz in $CDCl_3$ solution. τ-Values ±0·02, *J*-values ±0·5 Hz. [b] Spectra recorded from Nujol mulls (cm.$^{-1}$). [c] br = Broad; dl = doublet. [d] Too insoluble to record spectrum. [e] Signal observed at τ 8·55 due to 0·5 mol equiv. of cyclohexane per platinum atom. [f] One of these signals due to the acetate-methyl. [g] Signal at τ 8·57 due to 1 mol equiv. of cyclohexane per platinum atom. [h] Broad complex signal. [i] Acetate-methyl signal. [j] $^3J(P{-}H) = 4{\cdot}5$ Hz.

TABLE 8

Analytical, molecular weight, and melting point data for compounds [a] obtained from some bridge-splitting reactions of the complexes $[(Pt_2Cl_2(P{-}C)_2]$. [$(P'{-}C) = CH_2C_6H_4\,PBu^t$(*o*-tolyl) and $(P''{-}C) = CH_2C_6H_4PBu^t{}_2$]

Compound [b]	% Yield	Analytical data [c] C	H	Cl	M [c,d]	M.p.
cis- and *trans*-$[PtCl(P'{-}C)py]$ [f]	74	50·4 (50·55)	4·9 (4·7)	5·9 (5·75)	566 (579)	181—183°
trans-$[PtCl(P'{-}C)PPh_3]$	73 [g]	56·35 (56·7)	4·95 (4·9)	4·9 (4·65)	753 (762)	243—247
cis-$[PtCl(P'{-}C)PPh_3]$	73 [g]	56·15 (56·7)	4·7 (4·9)	4·9 (4·65)		221—225 [h]
cis-$[PtMe(P'{-}C)PPh_3]$	86	59·9 (59·9)	5·4 (5·45)		732 (742)	218—221 [i]
$[Pt(P'{-}C)\{(-)\text{-stien}\}]Cl$	74	53·55 (53·95)	5·4 (5·4)	5·7 (5·0)		224—229 [e]
$[Pt(acac)(P'{-}C)]$	67	48·95 (49·05)	5·1 (5·2)		565 (564)	205—207 [e]
trans-$[PtCl(P''{-}C)PPh_3]$	74	55·45 (55·45)	5·25 (5·4)	4·9 (4·85)	722 (728)	242—255
$[Pt(acac)(P''{-}C)]$	54	45·6 (45·3)	5·95 (5·9)		525 (535)	160—166

[a] All compounds are white. [b] py = Pyridine; acac = acetylacetonate; (—)-stien = (—)-stilbenediamine. [c] Theoretical values in parentheses. [d] Chloroform solution. [e] Decomposed. [f] Compound contained 0·5 mol equiv. of C_6H_6 per platinum atom. [g] Combined yield of *cis*- and *trans*-isomers. [h] Isomerised to the *trans*-complex. [i] Gas evolved.

Bridge-splitting Reactions of the Complexes $[Pt_2Cl_2(P{-}C)_2]$, $[(P'{-}C) = CH_2C_6H_4PBu^t$(*o*-tolyl) *or* $(P''{-}C) = CH_2C_6H_4PBu^t{}_2]$.—Halogen-bridged platinum(II) binuclear complexes undergo bridge-splitting reactions with a variety of ligands to give mononuclear compounds.[2,21,23] When pyridine is added to a suspension of $[Pt_2Cl_2(P'{-}C)_2]$ in chloroform, a clear colourless solution is obtained from which a mixture of *cis*- and *trans*-$[PtCl(P'{-}C)py]$ (Table 8) can be isolated. The ^1H n.m.r. spectrum of the mixture (Table 9) shows that in chloroform the ratio of isomers is 4 : 1 but we cannot assign the signals to each isomer. The predominant isomer shows a doublet at τ 8·75 (Bu^t), a singlet at τ 7·69 (tolyl-Me), and an apparent doublet due to the platinum-methylene protons at τ 6·25 with platinum-195 satellites [$^2J(Pt{-}H) = 98$ Hz]. The other isomer shows a similar spectrum but the methylene signal is not observed. We could not separate the two isomers by fractional crystallisation.

Addition of triphenylphosphine to a suspension of $[Pt_2Cl_2(P'{-}C)_2]$ in benzene also gives a mixture of isomers but these can be separated by fractional crystallisation. The more-soluble complex, *trans*-$[PtCl(P'{-}C)PPh_3]$, configuration (VIII; L = PPh_3; X = Cl) (Table 8), shows a strong band in the far-i.r. spectrum (Table 9) at 281 cm^{-1} due to ν(Pt–Cl) for chlorine *trans* to carbon.[11] The ^1H n.m.r. spectrum (Table 9) shows a double-doublet at τ 8·38 with $^3J(P{-}H) = 13{\cdot}3$ Hz and $^5J(P{-}H)$

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[23] B. Crociani, P. Uguagliati, T. Boschi, and U. Belluco, *J. Chem. Soc.* (*A*), 1968, 2869.

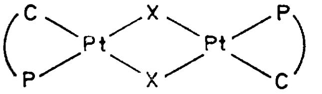
TABLE 9

^{1}H N.m.r.[a] and i.r. data of compounds obtained from some bridge-splitting reactions of the complexes $[Pt_2Cl_2(P-C)_2]$, [(P′–C) = $CH_2C_6H_4PBu^t$(*o*-tolyl) and (P″–C) = $CH_2C_6H_4PBu^t_2$]

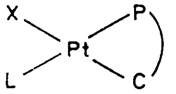
Compound [b]	τ(Bu^t)	^3J(P–H)	τ(tolyl-Me)	τ(CH_2) [c]	*J* [d]	ν(Pt–Cl) (cm^{-1})
cis- and *trans*-	8·75	15·0	7·69	6·25 dl	2 = ^3J(P–H)	288
[PtCl(P′–C)py] [e]	8·40	15·0	7·63		98 = ^2J(Pt–H)	
trans-[PtCl(P′–C)PPh_3]	8·38[f]	13·3	7·65	*ca.* 7·3 cx		281
cis-[PtCl(P′–C)PPh_3]	8·77	15·0	7·66	6·35 dl	9 = ‘ *J* ’	292
cis-[PtMe(P′–C)PPh_3] [g]	8·84	14·0	7·80	*ca.* 6·7 cx		
[Pt(P′–C) (—)-stien]Cl	8·45	15·1	7·60	nv		
	8·44	15·3				
[Pt(P′–C)acac] [h]	8·53	15·0	7·66	6·44 br	109·5 = ^2J(Pt–H)	
trans-[PtCl(P″–C)PPh_3]	8·46	13·7		7·38 dl	5·6 = ‘ *J* ’ 90 = ^2J(Pt–H)	276
[Pt(acac)(P″–C)] [i]	8·60	13·9		6·50 dl	2·0 = ^3J(P–H) 112 = ^2J(Pt–H)	

[a] Spectra recorded at *ca.* 35° and 60 MHz in $CDCl_3$ solution. τ-Values ±0·02, *J*-values ±0·5 Hz. [b] py = Pyridine; acac = acetylacetonate; (—)-stien = (—)-stilbenediamine. [c] br = Broad; dl = doublet; cx = complex signal; nv = not visible. [d] ‘ *J* ’ = separation of the apparent doublet. [e] Ratio of isomers (80 : 20) for the signals τ 8·75 : 8·40. [f] Signal is a double-doublet, ^5J(P–H) = 1·3 Hz. [g] Pt–Me at τ 9·62 (1 : 1 : 1 : 1 quartet); ^2J(Pt–H) = 68·7 Hz, ^3J(P–H) *cis* and *trans* = 6·3 and 8·0 Hz. [h] acac-methyl signals at τ 8·30 and 8·07; central proton at τ 4·77, ^4J(Pt–H) = 4·0 Hz. [i] acac-methyl signals at τ 8·20 and 8·06; central proton at τ 4·62, ^4J(Pt–H) *ca.* 4 Hz.

= 1·3 Hz. A similar coupling of ^5J(P–H) with the phosphorus nuclei in *trans*-positions has already been described for the complex *trans*-[PtCl(P′–C)PBu^t(*o*-tolyl)$_2$] (Table 3). The far-i.r. spectrum (Table 9) of the complex *cis*[PtCl(P′–C)PPh_3], configuration (IX; X = Cl; L = PPh_3) shows a strong band at 292 cm^{-1}, characteristic of ν(Pt–Cl) for chlorine *trans* to phosphorus.[11] The ^{1}H n.m.r. spectrum (Table 9) is consistent with the assigned structure and comparison of the τ-values of the platinum-methylene protons for the two isomers shows that methylene *trans* to chlorine (*ca.* τ 7·3) is at higher field than the methylene *trans*- to phosphorus (τ 6·35). Similar shifts have been found for the τ-values of the platinum-methyl groups in the complexes *cis*- and *trans*-[Pt(ClMeL_2] (L = PMe_2Ph or $PMePh_2$).[11] When the complex *cis*-[PtCl(P′–C)PPh_3] configuration (IX) is heated, it melts at 221—225° but isomerises to the *trans*-isomer which resolidifies and then remelts at 243—247°. A similar thermal isomerisation is found for the complexes *cis*-[PtClMeL_2] (L = PMe_2Ph or $PMePh_2$), which also give the corresponding *trans*-isomers on melting.[11]



(VII)



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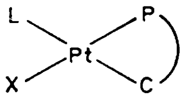


(IX)

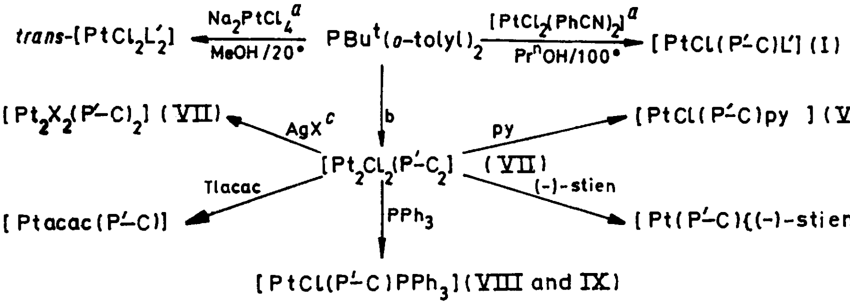
Addition of an excess of methyl-lithium to the complex *trans*-[PtCl(P′–C)PPh_3] gives the compound *cis*-[PtMe(P′–C)PPh_3] (Table 8). The assigned *cis*-configuration (IX; X = Me; L = PPh_3) follows from the ^{1}H n.m.r. spectrum (Table 9) of the platinum-bonded methyl which gives a 1 : 1 : 1 : 1 quartet at 9·62 due to coupling with the *cis*- and *trans*-phosphorus nuclei. The platinum-195 satellites have ^2J(Pt–H) = 68·7 Hz, a value characteristic of *cis*-dimethylplatinum(II) complexes.[11,15] This methylplatinum(II) complex is very stable and is recovered unchanged after being heated under reflux in 2-methoxyethanol solution for 24 h.

As discussed earlier, the chelating group (P′–C), *i.e.* [$CH_2C_6H_4PBu^t$(*o*-tolyl)] contains an asymmetric phosphorus atom and we have attempted to resolve some of its complexes. Treatment of $[Pt_2Cl_2(P'-C)_2]$ with the optically active amine, (—)-stilbenediamine gives [Pt(P′–C) (—)-stien]Cl. The ^{1}H n.m.r. spectrum (Table 9) suggests that this salt is an approximately 1 : 1 mixture of diasterioisomers since the two t-butyl doublets, at τ 8·45 and τ 8·44 are found. We have been unable to achieve separation of this mixture by fractional crystallisation.

Thallous acetylacetonate reacts with a suspension of $[Pt_2Cl_2(P'-C)_2]$ in benzene to give the complex [Pt(acac)(P′–C)] (Table 8) as very soluble white needles. The ^{1}H n.m.r. spectrum (Table 9) is completely consistent with the assigned structure; a feature is the large value of ^2J(Pt–H) of 109·5 Hz for the platinum-bonded methylene protons. For convenience the reactions of $[Pt_2Cl_2(P'-C)_2]$ have been summarised in Scheme 2.

The di-t-butyl-*o*-tolylphosphine derivative $[Pt_2Cl_2(P''-C)_2]$ also undergoes bridge-splitting reactions. With triphenylphosphine, the complex *trans*-[PtCl(P″–C)PPh_3] (Table 8) is formed: no *cis*-isomer could be detected, probably because of the steric requirements of these bulky phosphines. The configuration is confirmed by the i.r. and ^{1}H n.m.r. spectra (Table 9) which are similar to those of the corresponding PBu^t(*o*-tolyl)$_2$ derivative. The *trans*-configuration is further confirmed by the ^{31}P n.m.r. spectrum (Table 5) which shows that ^2J(P–P) is large (412·5 Hz) and characteristic of mutually *trans* phosphorus nuclei. The compound $[Pt_2Cl_2(P''-C)_2]$ is converted by thallous acetylacetonate to the mononuclear complex [Pt(acac)(P″–C)]. The ^{1}H n.m.r. spectrum (Table 9) is very similar to that of the corresponding PBu^t(*o*-tolyl)$_2$ derivative, [Pt(acac)(P′–C)], although the platinum-methylene group shows a less complex signal. It gives a doublet with ^{195}Pt satellites at τ 6·50 with ^3J(P–H) = 2·0 Hz and ^2J(Pt–H) = 112 Hz.

Factors Affecting Metallation.—The ligands PBu^t(*o*-tolyl)$_2$ and PBu$^t_2$(*o*-tolyl) metallated by platinum much faster than other tertiary phosphine ligands, previously described. This is presumably because (1) they are extremely bulky and (2) they form 5-membered rings on metallation. These two ligands are also unusual in that they will also form complexes of the type [Pt$_2$Cl$_2$(P–C)$_2$] (P–C) = (P′–C) or (P″–C) on treating [PtCl$_2$(PhCN)$_2$] with the tertiary phosphine (1 mol equiv. per Pt atom) in boiling 2-methoxyethanol. Binuclear complexes of this type are not obtained directly by treating the tertiary phosphines PBu$^t_2$Ph, or PPh(*o*-tolyl)$_2$ with [PtCl$_2$(PhCN)$_2$].[1]



SCHEME 2

Some reactions of [Pt$_2$Cl$_2$(P′–C)] [(P′–C) = CH$_2$C$_6$H$_4$PBu^t(*o*-tolyl)]

[a] 2 mol equiv. PBu^t(*o*-tolyl)$_2$ per Pt atom. [b] 1 mol equiv. PBu^t(*o*-tolyl)$_2$ per Pt atom. [c] X = OAc or OBz.

As mentioned above the complexes [PtX(P′–C)PBu^t(*o*-tolyl)$_2$] (X = Cl, NO$_3$, or Me) undergo a second internal metallation to give *cis*-[Pt(P′–C)$_2$] or *trans*-[Pt(P′–C)$_2$]. The tendency to undergo the second metallation increases in the order of anionic ligand X = Cl > Me ≃ NO$_3$. The nitrato-complexes possibly metallate faster than the chloro-complexes because nitrate is a better leaving group than chloride.[24] It has been shown previously that transition-metal-methyls can be readily eliminated as methane with internal metallation of a triphenylphosphine ligand in complexes of rhodium(I) [25] and manganese(I).[6] We also find that a methyl group bound to platinum promotes internal metallation.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and are corrected. All reactions involving free tertiary phosphines or heating under reflux in 2-methoxyethanol solution were carried out under nitrogen. Percentage yields, m.p.s, analytical and molecular-weight data are given in Tables 1, 4, 6, and 8.

*t-Butyldi-*o*-tolylphosphine.*— t-Butyldichlorophosphine [26] (27·5 g, 0·173 mol) in ether (250 ml) was added dropwise during 1 h to a well-stirred ethereal solution of *o*-tolyl-lithium (0·6 mol) at *ca.* –20°. The mixture was stirred at 20° for 1 h and then heated under reflux for 30 min. After hydrolysis of the mixture with water, the ether was removed by distillation and the residue gave the required *product* (29·6 g) as prisms from methanol.

*Di-t-butyl-*o*-tolylphosphine.*—A solution of *o*-tolyl-lithium (0·31 mol) in ether (250 ml) was added dropwise with stirring during 1 h to a solution of di-t-butylchlorophosphine [26] (37·6 g, 0·208 mol) in ether (100 ml) at 20°. The mixture was heated under reflux for 2 h and then hydrolysed with water. The ether was removed by distillation and fractional distillation of the residue gave the *product* (33·3 g) as a colourless liquid.

*t-Butylmethyldi-*o*-tolylphosphonium Iodide.*—Iodomethane (0·5 ml) was added to a solution of t-butyldi-*o*-tolylphosphine (0·20 g) in acetone (5 ml) and the mixture was set aside for 2 h. Isolation gave the *product* (0·22 g) as prisms.

*Di-t-butylmethyl-*o*-tolylphosphonium Iodide.*—This was prepared in a similar manner to give the *product* as prisms.

trans-*Dichlorobis-*(t-*butyldi-o-tolylphosphine*)*platinum*(II).—t-Butyldi-*o*-tolylphosphine (0·28 g, 2·08 mol equiv. per platinum atom) in ether (5 ml) was added to sodium tetrachloroplatinite(II) (0·219 g) in methanol (10 ml) and the mixture was set aside at 20° in the dark for 24 h. Isolation gave the required *product* (0·062 g) as yellow prisms from dichloromethane–light petroleum (b.p. 40—60°). Addition of light petroleum to the mother-liquor gave the white crystalline complex *trans*-[PtCl{CH$_2$C$_6$H$_4$PBu^t(*o*-tolyl)}{PBu^t(*o*-tolyl)$_2$}], identified by its i.r. and ^{1}H n.m.r. spectra.

trans-*Chloro-*[o-(*t-butyl-*o*-tolylphosphino*)*benzyl*](*t-butyldi-*o*-tolylphosphine*)*platinum*(II), [PtCl{CH$_2$C$_6$H$_4$PBu^t(*o*-tolyl)}{PBu^t(*o*-tolyl)$_2$}].—A mixture of *trans*-dichlorobis(benzonitrile)platinum(II) (2·36 g) and t-butyldi-*o*-tolylphosphine (2·8 g, 2·07 mol equiv. per platinum atom) in n-propanol (50 ml) was heated under reflux for 20 min to give a clear pale yellow solution. The solvent was removed under reduced pressure to give the *product* (3·52 g) as prisms from dichloromethane–methanol. The required *product* was also obtained if the reaction was carried out in benzene or chloroform, and a similar reaction with sodium tetrachloroplatinite(II) and t-butyldi-*o*-tolylphosphine in n-propanol gave the required *product*.

trans-*Nitrato-*[o-(*t-butyl-*o*-tolylphosphino*)*benzyl*][*t-butyldi-*o*-tolylphosphine*)*platinum*(II), [PtNO$_3${CH$_2$C$_6$H$_4$PBu^t(*o*-tolyl)}{PBu^t(*o*-tolyl)$_2$}].—A solution of silver nitrate (0·093 g) in aqueous acetone (5 ml) was added to a solution of *trans*-chloro[*o*-(t-butyl-*o*-tolylphosphino)benzyl](t-butyldi-*o*-tolylphosphine)platinum(II) (0·365 g) in acetone (25 ml). The mixture was shaken in the dark for 2 h and the resulting precipitate of silver chloride was filtered off. The filtrate

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was evaporated to dryness under reduced pressure to give the *product* (0·29 g) as prisms from dichloromethane–methanol.

cis-*Methyl-*[o-(t-*butyl-*o-*tolylphosphino*)*benzyl*] (*t-butyldi-*o-*tolylphosphine*)*platinum*(II), $[PtMe\{CH_2C_6H_4PBu^t(o\text{-tolyl})\}\{PBu^t(o\text{-tolyl})_2\}]$.—An ethereal solution of methyl-lithium (2 molar equiv.) was added to a finely powdered suspension of *trans*-chloro-[*o*-(t-butyl-*o*-tolylphosphino)benzyl](t-butyldi-*o*-tolylphosphine)platinum(II) (0·89 g) in benzene (15 ml). After 1 h, isolation gave the *product* (0·79 g) as prisms from dichloromethane–methanol.

rac-cis-*Bis-*[o-(*t-butyl-*o-*tolylphosphino*)*benzyl*]*platinum*(II), $[Pt\{CH_2C_6H_4PBu^t(o\text{-tolyl})\}_2]$.—A solution of *trans*-chloro[*o*-(t-butyl-*o*-tolylphosphino)benzyl](t-butyldi-*o*-tolylphosphine)platinum(II) (0·40 g) in decalin (20 ml) was heated under reflux for 6 days. The solvent was removed under pressure (oil-pump) and the residue was extracted with boiling, light petroleum (b.p. 60—80°; 10 ml) which on cooling gave the required *product* (0·149 g) as prisms. The *product* was also obtained by heating a solution of *trans*-nitrato-[o-(t-butyl-*o*-tolylphosphino)benzyl](t-butyldi-o-tolylphosphine)platinum(II) in n-propanol at 90° for 3 h. The required complex was identified by its ^1H n.m.r. spectrum.

rac-trans-*Bis-*[*o*-(t-butyl-*o*-tolylphosphino)benzyl]platinum(II), $[PtCH_2C_6H_4PBu^t(o\text{-tolyl})_2]$.—A solution of *cis*-methyl-[*o*-(t-butyl-*o*-tolylphosphino)benzyl](t-butyldi-*o*-tolylphosphine)platinum(II) (0·50 g) in 2-methoxyethanol (35 ml) was heated under reflux for 90 min. The solvent was then removed under reduced pressure and the residue was washed with methanol to give the *product* (0·30 g) as prisms from dichloromethane–methanol.

Action of Hydrogen Chloride on rac-trans-*Bis-*[o-(*t-butyl-*o-*tolylphosphino*)*benzyl*]*platinum*(II).—To a solution of the complex (0·1 g) in benzene (10 ml) was added an ethereal solution of hydrogen chloride (1 molar equiv.). After 1 h, isolation gave *trans*-chloro-[*o*-(t-butyl-*o*-tolylphosphino)-benzyl](t-butyldi-*o*-tolylphosphine)platinum(II) (0·065 g) as prisms from benzene–light petroleum (b.p. 80—100°).

Pyrolysis of cis-*Methyl-*[o-(*t-butyl-*o-*tolylphosphino*)-*benzyl*](*t-butyldi-*o-*tolylphosphine*)*platinum*(II).—The complex (0·15 g) was heated in an evacuated flask (5 ml) at 210—215° for 5 min. The gas evolved was collected in an evacuated gas-cell and identified as methane from its i.r. spectrum. The ^1H n.m.r. spectrum of the residue showed it to be a mixture of *rac-trans*-bis-[*o*-(t-butyl-*o*-tolylphosphino)-benzyl]platinum(II) and an unidentified substance.

trans-*Chloro-*[o-(*di-t-butylphosphino*)*benzyl*][*di-t-butyl*(o-*tolyl*)*phosphine*]*platinum*(II), $[PtCl(CH_2C_6H_4PBu^t{}_2)\{PBu^t{}_2(o\text{-tolyl})\}]$.—Di-t-butyl-*o*-tolylphosphine (1·86 g, 2·2 mol equiv. per platinum atom) was added to suspension of *trans*-dichlorobis(benzonitrile)platinum(II) (1·70 g) in n-propanol (40 ml). The mixture was heated under reflux for 40 min and the solvent was then removed under reduced pressure to give the *product* (1·65 g) as prisms from dichloromethane–methanol.

Methyl-[o-(*di-t-butylphosphino*)*benzyl*][*di-t-butyl*(o-*tolyl*)-*phosphine*]*platinum*(II), $[PtMe(CH_2C_6H_4PBu^t{}_2)\{PBu^t{}_2(o\text{-tolyl})\}]$.—An ethereal solution of methyl-lithium (2 mol equiv. per platinum atom) was added to a finely powdered suspension of *trans*-chloro-[*o*-(di-t-butylphosphino)benzyl]-[di-t-butyl(*o*-tolyl)phosphine]platinum(II) (0·5 g) in benzene (10 ml). After 1 h, the mixture was heated under reflux for 5 min. Isolation gave the required *product* (0·31 g) as prisms from dichloromethane–methanol.

trans-*Bis-*[o-(di-t-butylphosphino)benzyl]platinum(II), $[Pt(CH_2C_6H_4PBu^t{}_2)_2]$.—A suspension of methyl-[*o*-(di-t-butylphosphino)benzyl][di-t-butyl(*o*-tolyl)phosphine]platinum(II) (0·223 g) in n-propanol (10 ml) was heated under reflux for 2 h to give a pale yellow solution. The solvent was removed under reduced pressure and the residue was washed with light petroleum (b.p. 40—60°), leaving the *product* (0·057 g) which formed prisms from dichloromethane–methanol.

sym-trans-*Di-μ-chloro-bis-*[o-(*t-butyl-*o-*tolylphosphino*)-*benzyl*]*diplatinum*(II), $[Pt_2Cl_2CH_2C_6H_4PBu^t(o\text{-tolyl})_2]$.—*Method* 1. A mixture of *trans*-dichlorobis(benzonitrile)-platinum(II) (1·652 g) and t-butyldi-*o*-tolylphosphine (0·945 g, 1 mol equiv. per platinum atom) in 2-methoxyethanol (70 ml) was heated under reflux for 10 min. During this period, the suspension dissolved to give a clear pale yellow solution and then a white crystalline solid was deposited. The solid was filtered off and washed with methanol and then benzene to give the *product* (1·67 g) as microcrystals. A similar reaction with sodium tetrachloroplatinite(II) and t-butyldi-*o*-tolylphosphine also gave the required *product*.

Method 2. A suspension of finely ground *trans*-[chloro-{*o*-(t-butyl-*o*-tolylphosphino)benzyl} (t-butyldi-*o*-tolylphosphine)platinum(II)] (0·965 g) and platinum(II) chloride (0·28 g, 1 mol equiv.) was heated in xylene (10 ml) at 130—150° for 1 h. The resultant white solid was filtered off and washed with light petroleum (b.p. 60—80°) and then benzene to give the *product* (1·17 g), identified by its i.r. spectrum.

sym-trans-*Di-μ-chloro-bis-*[o-(*di-t-butylphosphino*)*benzyl*]-*platinum*(II), $[Pt_2Cl_2(CH_2C_6H_4PBu^t{}_2)_2]$.—Di-t-butyl-*o*-tolylphosphine (1·51 g, 1·08 mol equiv. per platinum atom) was added to a suspension of *trans*-dichlorobis(benzonitrile)-platinum(II) (2·80 g) in 2-methoxyethanol (35 ml) and the mixture was heated under reflux for 30 min. A white precipitate was formed which was filtered off and washed with benzene (15 ml) to give the required *product* (2·57 g).

sym-trans-*Di-μ-acetato-bis-*[o-(*t-butyl-*o-*tolylphosphino*)-*benzyl*]*diplatinum*(II), $[Pt_2(OAc)_2\{CH_2C_6H_4PBu^t(o\text{-tolyl}\}_2]$.—A suspension of di-μ-chloro-bis-[*o*-(t-butyl-*o*-tolylphosphino)-benzyl]diplatinum(II) (0·3 g) and silver acetate (0·11 g, 1·1 mol equiv. per platinum atom) in acetone was shaken in the dark overnight. The solution was filtered and the solvent was removed under reduced pressure to give the *product* (0·221 g) as prisms from dichloromethane–cyclohexane.

sym-trans-*Di-μ-acetato-bis*[o-(*di-t-butylphosphino*)*benzyl*]-*diplatinum*(II), $[Pt_2(OAc)_2(CH_2C_6H_4PBu^t{}_2)_2]$.—This compound was prepared in a similar manner to give *product* as prisms from dichloromethane–cyclohexane.

sym-trans-*Di-μ-benzoato-bis-*[o-(*t-butyl-*o-*tolylphosphino*)-*benzyl*]*diplatinum*(II), $[Pt_2(OBz)_2CH_2C_6H_4PBu^t(o\text{-tolyl})_2]$.—A suspension of di-μ-chloro-bis[o-(t-butyl-*o*-tolylphosphino)-benzyl]diplatinum(II) (0·35 g) and silver benzoate (0·175 g, 1·1 mol equiv. per platinum atom) in acetone (40 ml) was shaken in the dark overnight. The solution was filtered and the solvent was removed under reduced pressure to form the *product* (0·366 g) as plates from dichloromethane–cyclohexane.

sym-trans-*Di-μ-benzoato-bis-*[o-(*di-t-butylphosphino*)-*benzyl*]*diplatinum*(II), $[Pt_2(OBz)_2(CH_2C_6H_4PBu^t{}_2)_2]$.—This compound was prepared in a similar manner to give the *product* as prisms from dichloromethane–light petroleum (b.p. 40—60°).

cis- and trans-*Chloro-*[o-(*t-butyl-*o-*tolylphosphino*)*benzyl*]-*pyridineplatinum*(II), $[PtCl\{CH_2C_6H_4PBu^t(o\text{-tolyl})\}py]$.—

Pyridine (*ca.* 2 mol equiv. per platinum atom) was added to a suspension of di-μ-chloro-bis-[*o*-(t-butyl-*o*-tolylphosphino)-benzyldiplatinum(II) (0·2 g) in chloroform (10 ml). The mixture was set aside for 1 h and isolation gave a mixture of the *cis*- and *trans-product* (0·154 g) as prisms from benzene–n-hexane.

cis- and trans-*Chloro*[o-(*t-butyl*-o-*tolylphosphino*)*benzyl*]-*triphenylphosphineplatinum*(II), $[\mathrm{PtCl}\{\mathrm{CH_2C_6H_4PBu^t}(o\text{-tolyl})\}\mathrm{PPh_3}]$.—Triphenylphosphine (0·11 g, 1·05 mol equiv. per platinum atom) was added to a suspension of di-μ-chloro-bis-[*o*-(t-butyl-*o*-tolylphosphino)benzyl]diplatinum(II) (0·20 g) in benzene (10 ml). The mixture was warmed at *ca.* 60° for 2 min to give a clear colourless solution. Isolation gave the *cis-product* (0·06 g) as prisms from dichloromethane–methanol. The mother-liquor was set aside for 12 h to give the *trans-product* (0·16 g) as prisms.

cis-*Methyl*-[o-(*t-butyl*-o-*tolylphosphino*)*benzyl*]*triphenylphosphineplatinum*(II), $[\mathrm{PtMe}\{\mathrm{CH_2C_6H_4PBu^t}(o\text{-tolyl})\}\mathrm{PPh_3}]$.—An ethereal solution of methyl-lithium (2 mol equiv. per platinum atom) was added to a suspension of *trans*-chloro[*o*-(t-butyl-*o*-tolylphosphino)benzyl]triphenylphosphineplatinum(II) (0·60 g) in benzene (10 ml) and the mixture was set aside for 1 h. Isolation gave the *product* (0·50 g) as prisms from dichloromethane–methanol.

[o-(t-*Butyl*-o-*tolylphosphino*)*benzyl*]{(−)-*stilbenediamine*}-*platinum*(II) *Chloride*, $[\mathrm{Pt}\{\mathrm{CH_2C_6H_4PBu^t}(o\text{-tolyl})\}\{-(\text{-stien}\}]\mathrm{Cl}$.— Di-μ-chloro-bis[*o*-(t-butyl-*o*-tolylphosphino)-benzyl]diplatinum(II) (0·40 g) was suspended in dichloromethane (15 ml) and (−)-stilbenediamine (0·175 g) was added. After 3 h, isolation gave the *product* (0·42 g) as needles from dichloromethane–light petroleum (b.p. 40—60°).

Acetylacetonato-[o-(*t-butyl*-o-*tolylphosphino*)*benzyl*]*platinum*(II), $[\mathrm{Pt(acac)}\{\mathrm{CH_2C_6H_4PBu^t}(o\text{-tolyl})\}]$.—Thallous acetylacetonate (0·126 g, 1·05 mol equiv. per platinum atom) was added to a suspension of di-μ-chloro-bis-[*o*-(t-butyl-*o*-tolylphosphino)benzyl]diplatinum(II) (0·20 g) in benzene (15 ml). The mixture was shaken for 2 h and then the precipitate of thallous chloride was filtered off. Isolation gave the product (0·15 g) as needles from light petroleum (b.p. 80—100°).

Acetylacetonato-[o-(*di-t-butylphosphino*)*benzyl*]*platinum*(II), $[\mathrm{Pt(acac)(CH_2C_6H_4PBu^t{}_2)}]$.—This compound was prepared in a similar manner to give the *product* as prisms from light petroleum (b.p. 60—80°).

trans-*Chloro*-[o-(*di-t-butylphosphino*)*benzyl*]*triphenylphosphineplatinum*(II) $[\mathrm{PtCl(CH_2C_6H_4PBu^t{}_2)PPh_3}]$.—Triphenylphosphine (0·15 g, 1·15 mol equiv. per platinum atom) was added to a suspension of di-μ-chloro-bis-[*o*-(di-t-butylphosphino)benzyl]diplatinum(II) (0·233 g) in benzene (10 ml). The mixture was warmed at *ca.* 60° for 2 min to give a clear colourless solution. Isolation gave the *product* (0·27 g) as prisms from dichloromethane–light petroleum (b.p. 40—60°).

Nuclear Magnetic Resonance Spectra.—^{1}H N.m.r. spectra were recorded at *ca.* 35° and 60 MHz on a Perkin-Elmer R12A spectrometer. ^{31}P N.m.r. spectra were recorded on a Bruker Spectrospin HFX spectrometer at ambient temperatures and 36·43 MHz.

Infrared Spectra.—These spectra were recorded on a Perkin-Elmer 457 spectrometer (4000—250 cm^{-1}) and a Grubb–Parsons D.B. 3/D.N.2 spectrometer (500—200 cm^{-1}).

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