Transition Metal–Carbon Bonds. Part XXXIII.[1] Internal Metallations of Secondary and Tertiary Carbon Atoms by Platinum(II) and Palladium(II) †

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The internally metallated complexes $[Pt_2Cl_2(P{-}C)_2]$ [$(P'{-}C) = CH(CH_3)C_6H_4PBu^t_2$ or $(P''{-}C) = C(CH_3)_2C_6H_4PBu^t_2$] are readily prepared by treating $[PtCl_2(PhCN)_2]$ with L[L′ = PBu^t_2(*o*-ethylphenyl) or L″ = PBu^t_2(*o*-isopropylphenyl)]. Treatment of Na_2PdCl_4 with L′ yields *trans*-$[PdCl_2L'_2]$, which on heating produces $[Pd_2Cl_2(P'{-}C)_2]$. The metallation occurs at the α-carbon atom of the ligand, L, in all cases. The chelate ligand (P′–C) contains an asymmetric carbon atom. The complexes $[M_2Cl_2(P{-}C)_2]$ (M = Pd or Pt) undergo bridge-splitting reactions with various ligands (*e.g.* pyridine, PPh_3, $PMeBu^tPh$, *etc.*) giving mononuclear species. Treatment of Na_2PdCl_4 with L″ gives $[Pd_2Cl_4L''_2]$ which does not undergo internal metallation. ^1H, ^{13}C, and ^{31}P N.m.r. data are given and discussed.

In recent years there has been a growing interest in the internal metallation of tertiary phosphine or phosphite ligands by transition metals.[2-9] In a previous paper[5] we have shown that bulky substituents on a tertiary phosphine ligand promote the metallation of secondary and even tertiary carbon atoms, such as when *trans*-$[PtCl_2(PhCN)_2]$ is treated with PBu^t_2(*o*-ethylphenyl) or PBu^t_2(*o*-isopropylphenyl).

The phosphines PBu^t_2R (R = *o*-ethylphenyl or *o*-isopropylphenyl) are prepared by addition of RLi in ethereal solution to di-t-butylchlorophosphine. Both

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† No reprints available.

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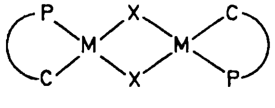
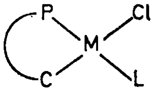
tertiary phosphines are viscous, air-sensitive liquids. These new tertiary phosphines are characterised as their methiodide salts (Table 1). The ^{1}H n.m.r. spectra of these phosphines and their methiodides show doublets for the t-butyl groups with ^3J(P–H) increasing from phosphorus(III) to phosphorus(V) (data in Table 1). Similar increases have been reported for ^2J(P–H) in tertiary methylphosphines and their methiodide salts.[10] The methylene group of PBu$^t_2$(*o*-ethylphenyl) appears as a quartet of doublets with ^3J(H–H) = 7·4 Hz and ^4J(P–H) *ca.* 2·2 Hz, and the methyl protons of the ethyl group appear as a triplet with ^3J(H–H) = 7·4 Hz. Its methiodide salt, [PBu$^t_2$Me(*o*-ethylphenyl)]I, shows no phosphorus–hydrogen coupling with the methylene protons. The ^{1}H n.m.r. spectrum of PBu$^t_2$(*o*-isopropylphenyl), however, shows unusually strong phosphorus–hydrogen coupling with the methine proton of the isopropyl group. The signal appears as two overlapping septets with ^3J(H–H) = 7·0 Hz, and the methyl protons of the isopropyl groups appear as a doublet with ^3J(H–H) = 7·0 Hz. Irradiation of the isopropyl methyl signal caused the methine proton signal to collapse to a doublet with ^4J(P–H) = 11·0 Hz. This abnormally high value of the phosphorus–hydrogen coupling constant may be due to the tertiary phosphine adopting a preferred conformation in which the methine proton is positioned close to the phosphorus atom. The close proximity of the proton to the phosphorus atom may then lead to ' through-space ' coupling. We could not detect phosphorus–hydrogen coupling in the methiodide salt, [PBu$^t_2$Me(*o*-isopropylphenyl)]I, possibly because the methine proton cannot now come close to the phosphorus atom. ' Through-space ' coupling has also been used to explain the unusually large phosphorus–fluorine coupling constants observed in triphenylphosphines containing trifluoromethyl groups in the *ortho*-positions on the phenyl rings.[11]

Internal Platination of Secondary Carbon Atoms.—Complexes containing internally metallated secondary carbon atoms have been prepared previously from olefinic tertiary phosphines by a variety of methods, *e.g.* nucleophilic attack,[12] electrophilic attack,[13,14] and by insertion of the olefin into a metal–hydrogen bond.[7,15] We have investigated the formation of such complexes by the metallation of bulky tertiary t-butyl phosphine ligands by platinum(II) and palladium(II).

When a mixture of PBu$^t_2$(*o*-ethylphenyl) (2 mol) and *trans*-[PtCl$_2$(PhCN)$_2$] (1 mol) in n-propanol is heated under reflux for 1·5 h a white precipitate is formed. By elemental analysis the complex is formulated as [C$_{16}$H$_{26}$ClPPt]$_n$ (Table 2). This compound is insoluble in organic solvents and the far-i.r. spectrum (Table 3) shows two bands due to ν(Pt–Cl) at 260 and 226 cm^{-1}. These data are consistent with the complex being a chlorine-bridged binuclear compound [Pt$_2$Cl$_2$(P′–C)$_2$] [(P′–C) = CH(CH$_3$)C$_6$H$_4$PBu$^t_2$]. We assign the sym-*trans*-configuration (I; M = Pt; X = Cl) to it by analogy with the complexes [Pt$_2$Cl$_2$(P–C)$_2$] [(P–C) = CH$_2$C$_6$H$_4$PBu$^t_2$ or CH$_2$C$_6$H$_4$PBu^t(*o*-tolyl)].[3] Similar treatment of PBu$^t_2$(*o*-tolyl) with *trans*-[PtCl$_2$(PhCN)$_2$], however, yielded [PtCl{CH$_2$C$_6$H$_4$PBu$^t_2$}{PBu$^t_2$(*o*-tolyl)}].[2] We were unable to isolate a complex of this type even on reducing the reaction time to 20 min, when [Pt$_2$Cl$_2$(P′–C)$_2$] was again formed, but in reduced yield (50%).



(I)



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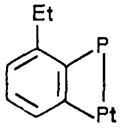

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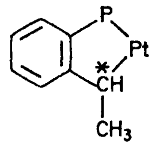

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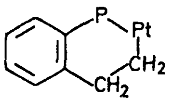

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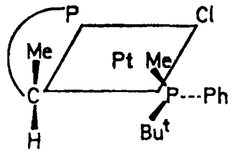

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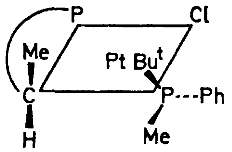

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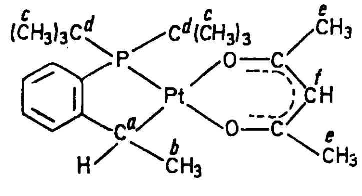

(VIII)

Treatment of a suspension of [Pt$_2$Cl$_2$(P′–C)$_2$] in acetone with silver nitrate gave the soluble white complex [Pt(NO$_3$)(P′–C)]$_n$ (n = 1 or 2). The ^{1}H n.m.r. spectrum (Table 3) shows two doublets due to non-equivalent t-butyl groups at τ 8·58 and 8·53, a doublet due to the methyl protons of the ethyl group at τ 8·58 with platinum-195 satellites [^3J(Pt–H) 45·1 Hz], and a quartet of doublets due to the methine proton at τ 5·57 with ^3J(P–H) 2·7 Hz and ^2J(Pt–H) 141·9 Hz. A molecular weight determination on this compound (Table 2) would indicate a mononuclear species with a bidentate nitrate group, but the value may be interpreted in terms of complete dissociation of a binuclear complex with

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TABLE 1

Analytical, boiling (melting) point, conductivity, and ^1H n.m.r. data for PBu^t_2(*o*-ethylphenyl) and PBu^t_2(*o*-isopropylphenyl) and their quaternary phosphonium salts[a]

		Analytical data (%)[b]				^1H n.m.r. data[d]				
	Yield %	C	H	M.p.	Λ_M (Ω cm^2 mol^{-1})[c]	$\tau(Bu^t)$	$\tau(-C_6H_4CH_nMe_{3-n})$	$\tau(-C_6H_4CH_n-Me_{3-n})$	^3J(H–H)	Notes
PBu^t_2(*o*-ethylphenyl)	72			B.p. 116—118°, 0·95 mmHg		8·78 (11·7)(d)	6·85(2·2)(qd)	8·79(t)	7·4	Neat
PBu^t_2(*o*-isopropylphenyl)	56			B.p. 120—125°, 0·85 mmHg		8·79 (11·9)(d)	5·51(11·0)(dse)[e]	8·78(d)	7·0	Neat
[PBu^t_2Me(*o*-ethylphenyl)]I	87	52·2 (52·05)	7·5 (7·7)	189—192°	100	8·36 (15·9)(d)	6·98 (<0·3)(q)	8·61(t)	7·6	In $CDCl_3$[f]
[PBu^t_2Me(*o*-isopropylphenyl)]I	76	53·4 (53·2)	7·9 (7·95)	257—268	76	8·35 (17·1)(d)	6·08 (<0·3)(se)[e]	8·64(d)	6·9	In $CDCl_3$[g]
[PBu^t_2H(*o*-ethylphenyl)]BPh_4		83·7 (84·2)	8·35 (8·5)	159—160	80	8·90 (17·6)(d)	7·50(<0·3) (q)	8·82(t)	7·4	In $CDCl_3$
[PBu^t_2H(*o*-isopropylphenyl)]BPh_4		84·35 (84·25)	8·7 (8·6)	182—185	90	8·82 (17·5)(d)	n.v.	8·69(d)	6·7	In $CDCl_3$

[a] All compounds are white. [b] Theoretical values in parentheses. [c] Recorded in acetone solution at 23°. [d] Spectra recorded at *ca.* 35° and 60 MHz. τ-Values ±0·02, *J*-values ±0·5 Hz; d, doublet; t, triplet; q, quartet; qd, quartet of doublets; se, septet; dse, doublet of septets; n.v. = not visible; hydrogen–phosphorus coupling constants are given in parentheses. [e] Outer lines of septet not visible. [f] τ(P–*Me*) 7·27; ^2J(P–CH$_3$) 11·5 Hz. [g] τ(P–*Me*) 7·35; ^2J(P–CH$_3$) 12·3 Hz.

TABLE 2

Analytical, molecular weight, and melting point data for complexes of the type $[Pt_2X_2\{CH(CH_3)C_6H_4PBu^t_2\}_2]$ X = Cl or NO_3) and the products obtained from the bridge-splitting reactions of the complex $[Pt_2Cl_2\{CH(CH_3)C_6H_4PBu^t_2\}_2]$

		Analytical data (%)[c]				
Compound[a,b]	% Yield	C	H	Cl	*M*[c,d]	M.p./°C
$[Pt_2Cl_2(P'-C)_2]$	82	40·0 (40·05)	5·7 (5·45)	7·5 (7·4)		295[e]
$[Pt_2(NO_3)_2(P'-C)_2]$[f]	85	38·2 (37·95)	5·35 (5·2)		518 (1013)	179—183
$[PtCl(py)(P'-C)]$[g]	87	45·3 (45·1)	5·45 (5·6)	6·35 (6·35)	551 (559)	290—295[e]
$[PtCl(PPh_3)(P'-C)]$	85	55·0 (55·0)	5·6 (5·55)	4·8 (4·75)		290—295[h]
$[PtCl(PMe_2Ph)(P'-C)]$	74	46·65 (46·65)	6·1 (6·05)	5·75 (5·75)	617 (618)	165—168
$[PtCl(AsMe_2Ph)(P'-C)]$	83	43·6 (43·55)	5·85 (5·65)	5·5 (5·35)	671 (662)	158—162
$[PtCl(PMeBu^tPh)(P'-C)]$[i]	87	48·8 (49·1)	6·4 (6·55)	5·15 (5·35)		204—210
$[Pt(sten)(P'-C)]Cl$[j]	94	52·25 (52·05)	6·05 (6·1)	5·3 (5·1)		235—250
$[Pt(acac)(P'-C)]$	68	46·6 (46·45)	6·5 (6·1)		535 (544)	125—128

[a] All complexes are white. [b] (P′–C) = $[CH(CH_3)C_6H_4PBu^t_2]$; py = pyridine; sten = (−)-stilbenediamine; (acac) = acetylacetonate. [c] Theoretical values in parentheses. [d] Chloroform solution. [e] With decomposition. [f] N = 2·8 (2·75)%. [g] N = 2·6 (2·5)%. [h] Gas evolved. [i] Compound is a mixture of diastereoisomers. [j] N = 4·15 (4·05)%.

TABLE 3

^1H N.m.r.[a] and i.r. data for some internally metallated platinum(II) complexes of the type $[Pt_2X_2\{CH(CH_3)C_6H_4PBu^t_2\}_2]$ (X = Cl or NO_3), and the products obtained from the bridge-splitting reactions of the complex $[Pt_2Cl_2\{CH(CH_3)C_6H_4PBu^t_2\}_2]$

			C*H*(CH$_3$)				CH(C*H*$_3$)			
Compound[b]	$\tau(Bu^t)$[c]	*J*(P–Bu^t)	τ(CH)[c]	^3J(H–H)	^3J(P–H)	^2J(Pt–H)	τ(Me)[c]	^3J(H–H)	^3J(Pt–H)[c]	ν(Pt–Cl)
$[Pt_2Cl_2(P'-C)_2]$										260s, 226m
$[Pt_2(NO_3)_2(P'-C)_2]$	8·58(d) 8·53(d)	15·0 15·0	5·57(qd)	7·3	2·7	141·9	8·58(d)	7·3	45·1	
$[PtCl(py)(P'-C)]$	8·49(d) 8·40(d)	14·1 14·3	6·65(qd)	7·3	1·9	105·3	9·01(d)	7·3	n.v.	262vs
$[PtCl(PPh_3)(P'-C)]$	8·49(d) 8·35(d)	13·4 13·6	n.v.				n.v.			279vs
$[PtCl(PMe_2Ph)(P'-C)]$[d,e]	8·57(d) 8·46(d)	13·4 13·8	6·83(dq)	7·3	9·6	69·4	8·77(dd)	7·2	n.v. ^4J(P–H) = 2·8	255vs
$[PtCl(AsMe_2Ph)(P'-C)]$[f]	8·52(d) 8·45(d)	14·3 14·5	6·54(q)	7·3	<0·5	70·0	8·69(d)	7·2	n.v.	259vs
$[PtCl(PMeBu^tPh)(P'-C)]$[g]	8·65(d) 8·54(d)	14·4 13·6	6·86(cx)			n.v.	9·19(dd) *ca.* 8·84(dd)	7·4	n.v. ^4J(P–H) 2·4 ^4J(P–H) 2·2	262s,vbr
$[Pt(acac)(P'-C)]$[d,h]	8·64(d) 8·57(d)	13·6 13·8	6·25(qd)	7·2	2·2	121·6	8·64(d)	7·2	42·1	

[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) = $[CH(CH_3)C_6H_4PBu^t_2]$. All mononuclear complexes have the *trans*-configuration. [c] d = Doublet; dd = doublet of doublets; qd = quartet of doublets; dq = doublet of quartets; q = quartet; cx = complex; nv = not visible. [d] Spectra recorded at ambient temperature and 90 MHz in $CDCl_3$ solution. τ-Values ±0·01, *J*-values ±0·2 Hz. [e] PMe_2Ph-methyls at τ 8·17(dd); ^2J(P–H) 9·1 Hz; ^4J(P–H) 2·3 Hz; ^3J(Pt–H) not visible; and τ 8·11 (dd); ^2J(P–H) 9·4 Hz; ^4J(P–H) 2·4 Hz. [f] $AsMe_2Ph$-methyls at τ 8·27(d); ^4J(P–H) 1·5 Hz; ^3J(Pt–H) not visible; and τ 8·23(d); ^4J(P–H) 1·5 Hz. [g] Mixture of two diastereoisomers. The $PMeBu^tPh$-methyls appear as two sets of doublets of doublets. One doublet of the higher field set is obscured and the lower field set is centred at τ 8·01; ^2J(P–H) 8·3 Hz; ^4J(P–H) 2·4 Hz. $PMeBu^tPh$-t-butyl groups at τ 8·42(d); ^3J(P–H) 13·7 Hz; and τ 8·37(d); ^3J(P–H) 14·5 Hz. [h] acac-Methyls at τ 8·18 and 8·05; central proton at τ 4·60, ^4J(Pt–H) *ca.* 4 Hz. Irradiation of the methyl doublet at τ 8·64 caused collapse of Pt–*CH*–CH$_3$ resonance to a broad singlet. Irradiation of the higher field platinum satellite of the methyl doublet caused collapse of the lower field platinum satellite of the Pt–*CH*–CH$_3$ resonance showing, that ^2J(Pt–H) and ^3J(Pt–H) are opposite in sign.

bridging nitrate groups. The i.r. spectrum does not, however, distinguish between the two possible structures.

There are three possible positions of metallation on PBu^t_2(*o*-ethylphenyl), by which four-, five-, or six-membered rings may be formed [configurations (III), (IV), and (V) respectively]. Metallation of the CH_2 group, producing configuration (IV), generates an asymmetric carbon atom. In order to establish the position of metallation the complex $[Pt_2Cl_2(P'{-}C)_2]$ was treated with a racemic mixture of PBu^tMePh to give the complex $[PtCl(P'{-}C)(PBu^tMePh)]$. The ^{31}P n.m.r. spectrum of the complex (Table 4) showed two overlapping AB patterns, with their respective platinum-195 satellites, of approximately equal intensities. This result is consistent with there being a mixture of two diastereoisomeric species (VI) and (VII) in solution. The large values of ^2J(P–P) of 396·1 and 399·8 Hz show that the phosphorus nuclei are in mutually *trans*-positions. To explain this observation, the metallated ligand must contain an asymmetric centre, and thus be of configuration (IV). The ^1H n.m.r. spectrum (Table 4), although complex, supports the presence of two diastereoisomers in solution. Additional evidence for configuration (IV) was obtained by synthesis of [Pt(acac)(P′–C)] (VIII) by treatment of a suspension of $[Pt_2Cl_2(P'{-}C)_2]$ in benzene with thallous acetylacetonate. The ^{13}C n.m.r. spectrum of this compound was recorded with all protons decoupled and peak assignments made (Table 5). With off-resonance proton decoupling C_a appeared as a doublet, due to coupling with the adjacent proton, and C_b appeared as a quartet, although the outer lines were not properly resolved, due to coupling with the three adjacent protons. If the metallated ligand had been of configuration (III) a triplet and quartet would have been observed, or if configuration (V) two triplets. The ^1H n.m.r. spectrum (Table 3) is completely consistent with the assigned structure; an interesting feature is the large value of ^2J(Pt–H) of 121·6 Hz for the platinum-bonded methine proton. Double resonance experiments showed the methine proton to be coupled with the adjacent methyl group, and the platinum-195-hydrogen coupling to these two groups to be of opposite sign (see Table 3). This observation is consistent with the results reported for the complex $[(C_2H_5)_3PtCl]_4$, in which the values for $^2J(^{195}Pt{-}CH_2)$ and $^3J(^{195}Pt{-}CH_3)$ were found to be of opposite sign.[16]

TABLE 4

^{31}P N.m.r. data [a] for complexes of the type [PtCl(P–C)L][(P′–C) = $CH(CH_3)C_6H_4PBu^t_2$ and (P″–C) = $C(CH_3)_2C_6H_4P\ Bu^t_2$; L = tertiary phosphine]

Unmetallated phosphine			Metallated phosphine			
L	δ	^1J(Pt–P) [b]	(P–C)	δ	^1J(Pt–P) [b]	^2J(P–P)
PMe_2Ph	+0·4	2991·3	(P′–C)	−73·0	3279·3	414·0
$PMeBu^tPh$ [c]	−20·7	2978·6	(P′–C)	−70·7	3383·7	396·1
	−15·3	3020·8		−69·7	3382·1	399·8
PPh_3	−31·2	n.v.	(P″–C)	−71·3	n.v.	391·4

[a] Spectra recorded at ambient temperature and 36·43 MHz in dichloromethane solution with all ^1H nuclei decoupled and C_6F_6 used to provide a ^{19}F field/frequency lock. Chemical shifts are given relative to 85% H_3PO_4 (±0·2 p.p.m.) in the sense that increasing field is positive; *J*-values ±0·2 Hz. [b] n.v. = Not visible. [c] Mixture of two diastereoisomers.

Bridge-splitting Reactions of the Complex $[Pt_2Cl_2(P'{-}C)_2]$.—Halogen-bridged binuclear complexes of platinum(II) undergo bridge-splitting reactions with a variety of ligands to give mononuclear compounds.[2,3,17,18] Treatment of a suspension of $[Pt_2Cl_2(P'{-}C)_2]$ in benzene with dimethylphenylphosphine gives a clear colourless solution from which *trans*-$[PtCl(P'{-}C)PMe_2Ph]$, configuration (II; L = PMe_2Ph; M = Pt) (Table 2), can be isolated. The ^1H n.m.r. spectrum at 90 MHz (Table 3) shows two doublets for the non-equivalent t-butyl groups at τ 8·57 and 8·46. As there is no plane of symmetry through the molecule the methyl groups of the dimethylphenylphosphine are non-equivalent and coupled to both ^{31}P nuclei, appearing as double-doublets at τ 8·17 [^2J(P–H) 9·1; ^4J(P–H) 2·3 Hz] and τ 8·11 [^2J(P–H) 9·4; ^4J(P–H) 2·4 Hz]. The methine proton appears as a doublet of quartets at τ 6·83 with an unusually large value of ^3J(P–H) 9·6 Hz, the value of ^3J(P–H) for other compounds containing the chelate group $[\overline{PtCH(CH_3)C_6H_4P}Bu^t_2]$ being in the range 0—2·7 Hz. This large value is presumably due to coupling

TABLE 5

^{13}C N.m.r. data * for the complex $[Pt(acac)\{CH(CH_3)C_6H_4PBu^t_2\}]$ (VIII)

	δ	*J*(Pt–C)	*J*(P–C)
C_a †	20·6(dl)	785	
C_b †	25·9(q)	46	
C_c	30·1	26	
C_d	36·6	44	30
C_e	28·2		
C_f	100·8		

* Spectra recorded at ambient temperature and 22·62 MHz in dichloromethane solution with all ^1H nuclei decoupled and C_6F_6 used to provide a ^{19}F field/frequency lock. Chemical shifts are given relative to tetramethylsilane (±0·3 p.p.m.) in the sense that increasing frequency is positive; *J*-values ±2 Hz. † Multiplicity recorded with off-resonance proton decoupling.

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with the ^{31}P nucleus of the dimethylphenylphosphine ligand rather than that of the chelate group. The methyl group adjoining the metallated carbon atom appears as a double doublet at τ 8·77 [^3J(H–H) 7·2; ^4J(P–H) 2·8 Hz]. The *trans*-configuration is confirmed by the ^{31}P n.m.r. spectrum (Table 5) which shows that ^2J(P–P) is large (414·0 Hz) and characteristic of mutually *trans*-phosphorus nuclei. Additionally, the far-i.r. spectrum (Table 3) shows a strong band at 255 cm^{-1} due to ν(Pt–Cl) for chlorine *trans* to carbon.[3,19]

Similar bridge-splitting reactions with pyridine, dimethylphenylarsine, or triphenylphosphine gave the complexes [PtCl(P′–C)L], configuration (II; L = py, $AsMe_2Ph$, or PPh_3; M = Pt). These complexes were assigned the *trans*-configuration from their far-i.r. spectra, the values of ν(Pt–Cl) (Table 3) being in the range 259—279 cm^{-1}; characteristic of chlorine *trans* to carbon.

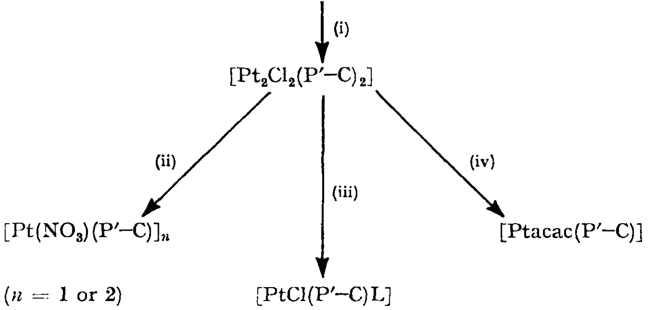
TABLE 6

Analytical, molecular weight, melting point, and spectroscopic data for complexes of the type $[Pt_2X_2\{C(CH_3)_2C_6H_4PBu^t_2\}_2]$, (X = Cl or I), and the products obtained from the bridge-splitting reactions of the complex $[Pt_2Cl_2\{C(CH_3)_2C_6H_4PBu^t_2\}_2]$

			Analytical data (%)[b]					¹H N.m.r. data [d]					
										Methyl groups			
Compound [a]	Colour	% Yield	C	H	Cl	M [b,c]	M.p.	τ(Bu^t)	J(P–Bu^t)	τ(Me)	^4J(P–H)	^3J(Pt–H)	ν(Pt–Cl)/cm^{-1}
$[Pt_2Cl_2(P''\text{–}C)_2]$	White	61	41·9 (41·35)	5·75 (5·7)	7·25 (7·2)	973 (988)	305—314° [e]	8·50(d)	14·8	8·38(s)		40·1	283s, 246vs
$[Pt_2I_2(P''\text{–}C)_2]$ [f]	Light yellow	96	35·0 (34·9)	4·75 (4·8)			307—308 [e]	8·46(d)	14·1	8·13(s)		45·2	
[PtCl(py)(P″–C)]	White	70	46·3 (46·1)	6·1 (5·8)	6·4 (6·2)		290—310 [e]	8·44(d)	14·2	8·64(s)		45·1	247vs
$[PtCl(PPh_3)(P''\text{–}C)]$	White	92	55·3 (55·6)	5·65 (5·75)	4·9 (4·7)	721 (756)	217—223 [g]	8·41(d)	13·7	8·44(d)	3·9	55·0	255vs
$[PtCl(PMe_2Ph)(P''\text{–}C)]$ [h]	White	84	47·55 (47·5)	6·2 (6·2)	5·6 (5·6)	640 (632)	177—180	8·46(d)	14·0	8·30(d)	4·0	58·3	247vs
$[PtCl(AsMe_2Ph)(P''\text{–}C)]$ [i]	White	87	44·2 (44·4)	5·9 (5·8)	5·05 (5·25)		158—165 [g]	8·47(d)	14·1	8·33(s)		50·6	249vs
[Pt(acac)(P″–C)] [j]	White	61	47·2 (47·4)	6·25 (6·35)		565 (558)	173—175	8·56(d)	13·9	8·53(s)		34·9	

[a] (P″–C) = $[C(CH_3)_2C_6H_4PBu\text{-}_2]$; py = pyridine; acac = acetylacetonate. [b] Theoretical values in parentheses. [c] Chloroform solution. [d] Spectra recorded at *ca.* 35° and 60 MHz in $CDCl_3$ solution. τ-Values ±0·02, *J*-values ±0·5 Hz. [e] With decomposition. [f] Iodine analysis: 21·4 (21·7)%. [g] Decomposes to $[Pt_2Cl_2(P''\text{–}C)_2]$. [h] PMe_2Ph-methyls at τ 8·06 (dd), ^4J(P–H) 2·3 Hz, ^2J(P–H) 8·5 Hz, ^3J(Pt–H) 25·3 Hz. [i] $AsMe_2Ph$-methyls at τ 8·22 (d), ^4J(P–H) 1·4 Hz, ^4J(Pt–H) not visible. [j] acac-Methyls at τ 8·16 and 8·03; central proton at τ 4·61, ^4J(Pt–H) 3·8 Hz.

As discussed earlier, the chelating group (P′–C), *i.e.* $[CH(CH_3)C_6H_4PBu^t_2]$, contains an asymmetric carbon atom and we have attempted to resolve its platinum complex. Treatment of $[Pt_2Cl_2(P'\text{–}C)_2]$ with the optically active amine (—)-stilbenediamine (sten) gives [Pt(P′–C)(sten)]Cl. This complex, however, was found to be of low solubility and we were unable to resolve it. Scheme 1 summarises the reactions of $[Pt_2Cl_2(P'\text{–}C)_2]$.



SCHEME 1

Some reactions of $[Pt_2Cl_2(P'\text{–}C)_2]$[(P′–C) = $CH(CH_3)C_6H_4PBu^t_2$] (i) n-propanol, 100°; (ii) $AgNO_3$; (iii) L = py, PPh_3, PMe_2Ph, $AsMe_2Ph$, or $PMeBu^tPh$; (iv) thallous acetylacetonate

Several workers have reported the preparation of platinum complexes containing two internally metallated tertiary phosphine ligands.[3,9,12] As mentioned earlier, we were unable to isolate the complex [PtCl(P′–C)-$\{PBu^t_2$(*o*-ethylphenyl)$\}$] by treating *trans*-$[PtCl_2(PhCN)_2]$ with PBu^t_2(*o*-ethylphenyl), and thus could not proceed to prepare $[Pt(P'\text{–}C)_2]$. An alternative method of preparation of $[Pt(P'\text{–}C)_2]$, by treating $[Pt(NO_3)(P'\text{–}C)]_n$ (*n* = 1 or 2) with PBu^t_2(*o*-ethylphenyl), was attempted, as the nitrate group has been shown previously to promote internal metallation.[3] A solution of $[Pt(NO_3)(P'\text{–}C)]_n$ (*n* = 1 or 2) in 2-methoxyethanol was heated under reflux with PBu^t_2(*o*-ethylphenyl) for 6 h, but only impure starting material could be isolated. The inability to form the complexes $[Pt(P'\text{–}C)_2]$ and [PtCl-(P′–C)$\{PBu^t_2$(*o*-ethylphenyl)$\}$] may be due to an increase in steric hindrance caused by the methyl group attached to the metallated carbon atom.

Internal Platination of Tertiary Carbon Atoms.—Although many internal metallation reactions have been reported, we are the only workers to have reported the metallation of a tertiary carbon atom.[5] This work is now described more fully.

When a mixture of PBu^t_2(*o*-isopropylphenyl) (2 mol) and *trans*-$[PtCl_2(PhCN)_2]$ (1 mol) is heated under reflux in n-propanol for 4·5 h a white precipitate is formed of formulation $[C_{17}H_{28}ClPPt]_n$ (Table 6). The far-i.r. spectrum (Table 6) showed the complex to contain chlorine bridges and a molecular weight determination (Table 6) showed it to be binuclear. The complex was found to be fairly soluble and the ^1H n.m.r. spectrum (Table 6) showed a doublet for the t-butyl groups at τ 8·50 and the methyl groups appeared as a singlet with platinum-195 satellites [^3J(Pt–H) = 40·1 Hz] at τ 8·38, coincident with one of the peaks of the t-butyl doublet.

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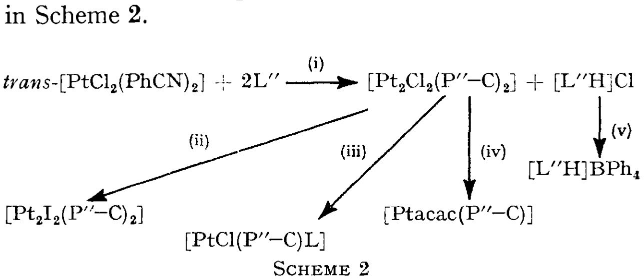
[19] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2801.

These data are consistent with the compound being $[Pt_2Cl_2(P''{-}C)_2][(P''{-}C) = C(CH_3)_2C_6H_4PBu^t_2]$, to which we also assign the *sym-trans*-configuration (I; X = Cl; M = Pt). Addition of a methanolic solution of sodium tetraphenylborate to the mother-liquor gives $[PBu^t_2$(*o*-isopropylphenyl)H]BPh_4. This product presumably arises by the hydrogen chloride produced in the metallation reaction protonating the excess of free phosphine forming $[PBu^t_2$(*o*-isopropylphenyl)H]$^+$, which is then precipitated from solution as the tetraphenylborate salt.

Metathesis of this metallated bridged-complex with sodium iodide in boiling n-propanol yields the complex $[Pt_2I_2(P''{-}C)_2]$ configuration (I; X = I; M = Pt). The ^1H n.m.r. spectrum (Table 6) shows a doublet for the t-butyl groups at τ 8·46 and a clearly defined singlet for the methyl groups at τ 8·13 [^3J(Pt–H) 45·2 Hz].

Bridge-splitting Reactions of the Complex $[Pt_2Cl_2(P''{-}C)_2]$.—Addition of triphenylphosphine to a suspension of $[Pt_2Cl_2(P''{-}C)_2]$ in benzene gives a white mononuclear complex showing a band at 255 cm^{-1} in the far-i.r. spectrum (Table 6) due to chlorine *trans* to carbon. The complex is formulated as *trans*-$[PtCl(P''{-}C)PPh_3]$, configuration (II; M = Pt; L = PPh_3). The configuration is confirmed by the ^1H n.m.r. spectrum (Table 6) which shows a doublet at τ 8·41 due to the t-butyl groups; the methyl groups attached to the metallated carbon atom appear as a doublet with ^{195}Pt satellites at τ 8·44 with ^4J(P–H) 3·9 and ^3J(Pt–H) 55·0 Hz. Further confirmation of the *trans*-configuration is obtained from the ^{31}P n.m.r. spectrum (Table 5) which shows that ^2J(P–P) is large (391·4 Hz) and characteristic of mutually *trans*-phosphorus ligand atoms. Similar treatment of $[Pt_2Cl_2(P''{-}C)_2]$ with pyridine, dimethylphenylphosphine, or dimethylphenylarsine yields the complexes *trans*-$[PtCl(P''{-}C)L]$, configuration (II; M = Pt; L = py, PMe_2Ph, or $AsMe_2Ph$). The *trans*-configuration of these complexes is verified by their ^1H n.m.r. and far-i.r. spectra (Table 6). Thallous acetylacetonate reacts with a suspension of $[Pt_2Cl_2(P''{-}C)_2]$ in benzene to give the complex [Pt(acac)(P''–C)] as very soluble white prisms. The ^1H n.m.r. spectrum (Table 6) confirms the assigned structure. The reactions of $[Pt_2Cl_2(P''{-}C)_2]$ have been summarised in Scheme 2.



SCHEME 2

Some reactions of $[Pt_2Cl_2(P''{-}C)_2][(P''{-}C) = C(CH_3)_2C_6H_4PBu^t_2]$ (i) n-propanol, 100° [(L'' = PBu^t_2(*o*-isopropylphenyl)]; (ii) NaI; (iii) L = py, PPh_3, PMe_2Ph, or $AsMe_2Ph$; (iv) thallous acetylacetonate; (v) $NaBPh_4$

Comparison of Platinum–Chlorine Stretching Frequencies trans *to Primary, Secondary, and Tertiary Carbon Atoms*.—The synthesis of a series of complexes of the type *trans*-[PtCl(P–C)L][(P–C) = $CH_2C_6H_4PBu^t_2$, $CH(CH_3)C_6H_4PBu^t_2$, $C(CH_3)_2C_6H_4PBu^t_2$; L = neutral ligand] has enabled us to make a comparison of the values of ν(Pt–Cl), where the chlorine atom is in the *trans*-position to a primary, secondary, or tertiary carbon atom (Table 7). It can be seen that the values of ν(Pt–Cl) decrease in the order of the *trans*-carbon atom 1° > 2° > 3°. The effect may be largely electronic since on going from a primary carbon atom through to a tertiary carbon atom the +*I* effect increases, and one would expect the *trans*-bond weakening effect also to increase and cause a lowering in the frequency of the platinum–chlorine stretch.

TABLE 7

Values of ν(Pt–Cl) for the complexes *trans*-[PtCl(P–C)L], configuration [II; (P'''–C) = $CH_2C_6H_4PBu^t_2$; (P'–C) = $CH(CH_3)C_6H_4PBu^t_2$; (P''–C) = $C(CH_3)_2C_6H_4PBu^t_2$)] in cm^{-1}

	Metallated Ligand		
L	(P'''–C)	(P'–C)	(P''–C)
py	271	262	247
PPh_3	276	279	255
$AsMe_2Ph$	280	259	249
PMe_2Ph		255	247

Palladium Complexes of PBu^t_2(*o-ethylphenyl*) *and* PBu^t_2(*o-isopropylphenyl*).—Addition of PBu^t_2(*o*-ethylphenyl) to a solution of sodium tetrachloropalladite(II) in methanol–ethanol yields the yellow complex *trans*-$[PdCl_2\{PBu^t_2$(*o*-ethylphenyl)$\}_2]$ (Table 8). The assigned *trans*-configuration follows from its far-i.r. and ^1H n.m.r. spectra (Table 8). Satisfactory analytical data were obtained for the complex, but on recrystallization internal metallation readily occurs. The ^1H n.m.r. spectrum in deuteriochloroform (Table 8) at *ca.* 35° shows that two species are present in solution. There are two triplets due to the t-butyl groups at τ 8·35 and 8·30 (intensity ratio *ca.* 2·5 : 1). A similar result has been obtained previously for the complex *trans*-$[PdCl_2\{PBu^t_2$(*o*-tolyl)$\}_2]$.[20] On the basis of ^1H and ^{31}P n.m.r. data it was postulated that the complex exists as two rotamers in solution, due to restricted rotation about the Pd–P bonds. It is likely that a similar phenomenon is occurring with *trans*-$[PdCl_2\{PBu^t_2$(*o*-ethylphenyl)$\}_2]$.

On refluxing a solution of *trans*-$[PdCl_2\{PBu^t_2$(*o*-ethylphenyl)$\}_2]$ in n-propanol the colour of the solution rapidly changes from yellow to red, before becoming pale yellow. After 4 min under reflux pale yellow prisms begin to precipitate from the pale yellow solution. The far-i.r. spectrum of this complex (Table 8) shows two bands due to ν(Pd–Cl) at 283 and 246 cm^{-1}, and the complex is formulated as $[Pd_2Cl_2(P'{-}C)_2]$, configuration (I; M = Pd; X = Cl), by analogy with the corresponding platinum complex. Addition of a methanolic solution of sodium tetraphenylborate to the mother-liquor gave a white precipitate of $[PBu^t_2$(*o*-ethylphenyl)H]BPh_4 (Table 1). From the above observations it

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[20] A. J. Cheney and B. L. Shaw, *J.C.S. Dalton*, 1972, 860.

would seem likely that the mechanism of the metallation reaction involves initial dissociation of PBu^t_2(*o*-ethylphenyl) to form $[Pd_2Cl_4\{PBu^t_2(o\text{-ethylphenyl})\}_2]$ (indicated by the transient red colour of the solution) followed by internal metallation with elimination of hydrogen chloride, and subsequent protonation of the dissociated phosphine.

Addition of dimethylphenylphosphine to a suspension of $[Pd_2Cl_2(P'\text{–}C)_2]$ in benzene gives a soluble white complex which shows a band due to ν(Pd–Cl) at 265 cm^{-1} characteristic of chlorine *trans* to carbon.[18] This compound is formulated as *trans*-$[PdCl(P'\text{–}C)(PMe_2Ph)]$, configuration (II; M = Pd; L = PMe_2Ph) (Table 8). This formulation is confirmed by the ^1H n.m.r. spectrum (Table 8) which shows two doublets for the non-equivalent t-butyl groups at τ 8·57 and 8·43, a quartet of doublets for the methine proton at τ 6·64 [^3J(H–H) 7·2; ^3J(P–H) 3·3 Hz], and two triplets for the non-equivalent methyl groups of the dimethylphenylphosphine at τ 8·23 and 8·09 (|^2J(P–H) + ^4J(P–H)| 4·1 Hz). Similar treatment of $[Pd_2Cl_2(P'\text{–}C)_2]$ with triphenylphosphine gave the insoluble complex *trans*-$[PdCl(P'\text{–}C)\text{-}PPh_3]$ configuration (II; M = Pd; L = PPh_3) as shown by the low value of ν(Pd–Cl) of 279 cm^{-1} (Table 8).

Treatment of $[Pd_2Cl_2(P'\text{–}C)_2]$ with thallous acetylacetonate gives the very soluble complex [Pd(acac)-(P′–C)]. The ^1H n.m.r. spectrum (Table 8) is consistent with this formulation. The reactions of $[Pd_2Cl_2(P'\text{–}C)_2]$ are summarised in Scheme 3.

Addition of PBu^t_2(*o*-isopropylphenyl) (2 mol) to a solution of sodium tetrachloropalladite(II) in methanol–ethanol did not yield the complex *trans*-$[PdCl_2\{PBu^t_2(o\text{-isopropylphenyl})\}_2]$, but gave instead the complex $[Pd_2Cl_4\{PBu^t_2(o\text{-isopropylphenyl})\}_2]$. The far-i.r. spectrum (Table 8) shows typical values of ν(Pd–Cl) (256, 297, and 347 cm^{-1}) for complexes of this type.[21] Due to the low solubility of this complex it was only possible to detect the t-butyl doublet at τ 8·30 [^3J(P–H) 15·1 Hz] in the ^1H n.m.r. spectrum.

TABLE 8

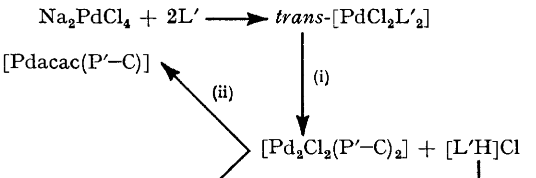
Analytical, molecular weight, melting point, and spectroscopic data for the complexes *trans*-$[PdCl_2L'_2]$ [L′ = PBu^t_2-(*o*-ethylphenyl)] and $[Pd_2Cl_4L''_2]$[L″=PBu^t_2(*o*-isopropylphenyl)] and for the complex $[Pd_2Cl_2\{CH(CH_3)C_6H_4PBu^t_2\}_2]$ and the products of its bridge-splitting reactions

	%		Analytical data (%) [b]					¹H n.m.r. data [d]								
Compound [a]	Yield	Colour	C	H	Cl	M [b,c]	M.p.	τ(But)	J(P–But)	τ(CH)	³J(H–H)	³J(P–H)	τ(Me)	³J(H–H)	ν(Pd–Cl)/cm⁻¹
trans-$[PdCl_2L'_2]$	82	Yellow	56·6 (56·7)	7·85 (8·05)	10·35 (10·45)		122—125° [e] 305—308 [f]	8·35(t) 8·30(t)	13·8 [g] 13·6 [g]	6·01(q)	7·3	<0·5	8·50(t)	7·3	343s
$[Pd_2Cl_2(P'\text{–}C)_2]$	95	Light yellow	48·9 (49·1)	6·75 (6·7)	8·8 (9·05)		305—310 [f]				Insoluble				283s, 246s
$[PdCl(PMe_2Ph)(P'\text{–}C)]$ [h]	76	White	53·95 (54·45)	7·15 (7·05)	6·95 (6·7)	521 (529)	160—169	8·57(d) 8·43(d)	13·8 14·1	6·64(qd)	7·2	3·3	8·82(dd) [i]	7·3	265s
$[PdCl(PPh_3)(P'\text{–}C)]$	82	White	62·5 (62·5)	6·4 (6·35)	5·5 (5·45)		232—235 [f]				Insoluble				279s
[Pd(acac)(P′–C)] [j]	58	White	55·45 (55·45)	7·35 (7·3)		443 (455)	129—132	8·59(d) 8·53(d)	14·0 14·1	6·09(qd)	7·3	3·9	8·61(d)	7·7	
$[Pd_2Cl_4L''_2]$	59	Rust	46·0 (46·25)	6·55 (6·6)	16·25 (16·05)		185—190 [f]	8·30(d)	15·1						256vs, 297s, 347vs

[a] (P′–C) = $[CH(CH_3)C_6H_4PBu^t_2]$. [b] Calculated values in parentheses. [c] In chloroform solution. [d] Spectra recorded at *ca.* 35° and 60 MHz in $CDCl_3$ solution. τ-Values ±0·02, *J*-values ±0·5 Hz. [e] Decomposes to $[Pd_2Cl_3(P'\text{–}C)_2]$. [f] With decomposition. [g] *J*(P–But) = |^3J(P–H) + ^5J(P–H)|. [h] PMe_2Ph-methyls at τ 8·23(t); |^2J(P–H) + ^4J(P–H)| = 4·1 Hz. τ 8·09(t); |^2J(P–H) + ^4J(P–H)| = 4·1 Hz. [i] ^3J(P–H) 2·3 Hz. [j] acac-methyls at τ 8·11 and 7·98; central proton at τ 4·67.

We have suggested earlier that $[Pd_2Cl_4\{PBu^t_2(o\text{-ethylphenyl})\}_2]$ may be an intermediate in the internal palladation of PBu^t_2(*o*-ethylphenyl), and Cheney and Shaw[20] have shown $[Pd_2Cl_4\{PBu^t(o\text{-tolyl})_2\}_2]$ to be a precursor of $[Pd_2Cl_2(P\text{–}C)_2]$ [(P–C) = $CH_2C_6H_4PBu^t$(*o*-tolyl)], thus it may be expected that $[Pd_2Cl_4L''_2]$ [L″ = PBu^t_2(*o*-isopropylphenyl)] would lead to $[Pd_2Cl_2(P''\text{–}C)_2]$ [(P″–C) = $C(CH_3)_2C_6H_4PBu^t_2$]. Refluxing a suspension of $[Pd_2Cl_4L''_2]$ in n-propanol, however, led to decomposition with deposition of palladium metal.

Thus the ligands PBu^t_2(*o*-ethylphenyl) and PBu^t_2(*o*-isopropylphenyl) are readily metallated by platinum and PBu^t_2(*o*-ethylphenyl) by palladium to give five-membered rings. As shown previously[3,4,20] the metallation is undoubtedly promoted by steric effects, so that even a tertiary carbon atom can be metallated. The metallation of $[Pt_2Cl_2(P''\text{–}C)_2]$ was not reversed even on contact with dry hydrogen chloride (in $CHCl_3$–Et_2O) for 3 weeks at 20° suggesting that the chelate system is very stable thermodynamically.



SCHEME 3

Reactions of some PBu^t_2(*o*-ethylphenyl) (L′) complexes of palladium

(i) n-propanol, 100°; (ii) thallous acetylacetonate; (iii) L = PMe_2Ph or PPh_3; (iv) $NaBPh_4$

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and are corrected. All operations involving free tertiary phosphines or heating under reflux in n-propanol solution

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[21] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc.* (*A*), 1970, 545 and references therein.

were carried out under argon. Percentage yields, m.p.s, analytical and molecular-weight data are given in the Tables.

*Di-t-butyl-*o*-ethylphenylphosphine*.—A solution of *o*-ethylphenyl-lithium (0·16 mol) in diethyl ether (250 ml) was added dropwise to a solution of di-t-butylchlorophosphine (19·9 g, 0·11 mol) in diethyl ether (100 ml) at *ca.* 0° over 1·5 h. The mixture was then heated under reflux for 3 h and then hydrolysed with water. Separation and fractional distillation under reduced pressure gave the *product* (19·8 g) as a colourless liquid.

*Di-t-butyl-*o*-isopropylphenylphosphine*.—A solution of *o*-isopropylphenyl-lithium (0·12 mol) in diethyl ether (200 ml) was added dropwise to a solution of di-t-butylchlorophosphine (10·2 g, 0·06 mol) in diethyl ether (100 ml) over 1·5 h. The mixture was then heated under reflux for 18 h and then hydrolysed with water. Separation and fractional distillation under reduced pressure gave the *product* (8·3 g) as a colourless liquid.

*Di-t-butylmethyl-*o*-ethylphenylphosphonium Iodide*.—Iodomethane (5 ml) was added to a solution of di-t-butyl-*o*-ethylphenylphosphine (0·69 g) in acetone (10 ml). The mixture was set aside overnight. Isolation gave the *product* (0·99 g) as prisms.

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

sym-trans-*Di-μ-chloro-bis{1-[*o*-(di-t-butylphosphino)-phenyl]ethyl}diplatinum*(II), $[Pt_2Cl_2\{CH(CH_3)C_6H_4PBu^t_2\}_2]$.—Di-t-butyl-*o*-ethylphenylphosphine (0·63 g, 2·51 mmol) was added to a suspension of *trans*-dichlorobis(benzonitrile)-platinum(II) (0·54 g, 1·14 mmol) in n-propanol (30 ml) and the mixture was heated under reflux for 1·5 h. A white precipitate was formed which was filtered off and washed with methanol to give the *product* as prisms (0·45 g).

sym-trans-*Di-μ-nitrato-bis{1-[*o*-(di-t-butylphosphino)-phenyl]ethyl}diplatinum*(II), $[Pt_2(NO_3)_2\{CH(CH_3)C_6H_4PBu^t_2\}_2]$.—A solution of silver nitrate (0·18 g, 1·07 mmol) in water (1 ml)–acetone (24 ml) was added to a suspension of di-μ-chloro-bis{1-[*o*-(di-t-butylphosphino)phenyl]ethyl}diplatinum(II) (0·37 g, 0·39 mmol) in acetone (25 ml) and the mixture was shaken in the dark for 5 h. The solution was filtered and the solvent was removed under reduced pressure to give the *product* (0·33 g) as prisms from dichloromethane–light petroleum (b.p. 60—80°).

trans-*Chloro-{1-[*o*-(di-t-butylphosphino)phenyl]ethyl}-pyridineplatinum*(II), $[PtCl\{CH(CH_3)C_6H_4PBu^t_2\}py]$.—Pyridine (99 μl, 1·22 mmol) was added to a suspension of di-μ-chloro-bis{1-[*o*-(di-t-butylphosphino)phenyl]ethyl}diplatinum(II) (0·47 g, 0·49 mmol) in benzene (10 ml). The mixture was heated to boiling point to give a clear colourless solution. Isolation gave the *product* (0·28 g) as prisms from dichloromethane–methanol.

The following complexes were prepared in a similar way and obtained as prisms from dichloromethane–methanol. trans-*Chloro-{1-[*o*-(di-t-butylphosphino)phenyl]ethyl}triphenylphosphineplatinum*(II), $[PtCl\{CH(CH_3)C_6H_4PBu^t_2\}PPh_3]$. trans-*Chloro-{1-[*o*(di-t-butylphosphino)phenyl]ethyl}-dimethylphenylphosphineplatinum*(II), $[PtCl\{CH(CH_3)C_6H_4PBu^t_2\}PMe_2Ph]$. trans-*Chloro-{1-[*o*-(di-t-butylphosphino)-phenyl]ethyl}dimethylphenylarsineplatinum*(II), $[PtCl\{CH(CH_3)C_6H_4PBu^t_2\}AsMe_2Ph]$. rac-trans-*Chloro-{1-[*o*-(di-t-butylphosphino)phenyl]ethyl}methyl-t-butylphenylphosphine-platinum*(II), $[PtCl\{CH(CH_3)C_6H_4PBu^t_2\}PMeBu^tPh]$.

*{1-[*o*-(Di-t-butylphosphino)phenyl]ethyl}{(−)-(stilbenediamine)}platinum*(II) *Chloride*, $[Pt\{CH(CH_3)C_6H_4PBu^t_2\}\{(-)\text{-sten}\}]Cl$.—A solution of (−)-stilbenediamine (0·19 g, 0·88 mmol) in benzene (5 ml) was added to a suspension of di-μ-chloro-bis-{1-[*o*-(di-t-butylphosphino)phenyl]ethyl}diplatinum(II) (0·40 g, 0·42 mmol) in benzene (10 ml). The mixture was heated to boiling point to give a clear colourless solution, which on cooling gave the *product* (0·55 g) as prisms.

*Acetylacetonato-{1-[*o*-(di-t-butylphosphino)phenyl]ethyl}-platinum*(II), $[Pt(acac)\{CH(CH_3)C_6H_4PBu^t_2\}]$.—Thallous acetylacetonate (0·13 g, 0·42 mmol) was dissolved in benzene (40 ml) and added to a suspension of di-μ-chloro-bis{1-[*o*-(di-t-butylphosphino)phenyl]ethyl}diplatinum(II) (0·18 g, 0·19 mmol) in benzene (20 ml). The mixture was shaken overnight in the dark and the resultant precipitate of thallous chloride then filtered off. Isolation gave the *product* (0·14 g) as prisms from dichloromethane–light petroleum (b.p. 60—80°).

sym-trans-*Di-μ-chloro-bis-{1-[*o*-(di-t-butylphosphino)-phenyl]-1-methylethyl}diplatinum*(II), $[Pt_2Cl_2\{C(CH_3)_2C_6H_4PBu^t_2\}_2]$.—Di-t-butyl-*o*-isopropylphenylphosphine (0·73 g, 2·76 mmol) was added to a suspension of *trans*-dichlorobis-(benzonitrile)platinum(II) (0·59 g, 1·25 mmol) in n-propanol (30 ml) and the mixture was heated under reflux for 4·5 h. A white precipitate was formed, which was filtered off and washed with methanol to give the *product* as prisms (0·38 g). Addition of an excess of sodium tetraphenylborate to the mother-liquor gave *hydrido-di-t-butyl-*o*-isopropylphenylphosphine tetraphenylborate* as prisms (0·21 g, 28%). The compound was identified by analytical data (Found: C, 84·35; H, 8·7. $C_{41}H_{50}BP$ requires C, 84·25; H, 8·6%) and by its i.r. and n.m.r. spectra (Table 2).

sym-trans-*Di-μ-iodo-bis-{1-[*o*-(di-t-butylphosphino)-phenyl]-1-methylethyl}diplatinum*(II), $[Pt_2I_2\{C(CH_3)_2C_6H_4PBu^t_2\}_2]$.—A suspension of *sym-trans*-di-μ-chloro-bis-{1-[*o*-(di-t-butylphosphino)phenyl]-1-methylethyl}diplatinum(II) (0·28 g, 0·28 mmol) and sodium iodide (0·5 g, 3·33 mmol) was refluxed in n-propanol (25 ml) for 3·25 h. The *product* was obtained as microneedles (0·32 g) by filtration, followed by washing with water and methanol.

trans-*Chloro-{1-[*o*-(di-t-butylphosphino)phenyl]-1-methylethyl}triphenylphosphineplatinum*(II), $[PtCl\{C(CH_3)_2C_6H_4PBu^t_2\}PPh_3]$.—A solution of triphenylphosphine (0·12 g, 0·46 mmol) in benzene (5 ml) was added to a suspension of *sym-trans*-di-μ-chloro-bis-{1-[*o*-(di-t-butylphosphino)-phenyl]-1-methylethyldiplatinum(II) (0·21 g, 0·21 mmol) in benzene (10 ml). The mixture was heated to boiling to give a clear colourless solution. Isolation gave the *product* (0·29 g) as prisms from dichloromethane–methanol.

The following three complexes were prepared in a similar manner and recrystallized from dichloromethane–methanol. trans-*Chloro-{1-[*o*-(di-t-butylphosphino)phenyl]-1-methylethyl}pyridineplatinum*(II), $[PtCl\{C(CH_3)_2C_6H_4PBu^t_2\}py]$. trans-*Chloro-{1-[*o*-(di-t-butylphosphino)phenyl]-1-methylethyl}dimethylphenylphosphineplatinum*(II), $[PtCl\{C(CH_3)_2C_6H_4PBu^t_2\}PMe_2Ph]$. trans-*Chloro-{1-[*o*-(di-t-butylphosphino)phenyl]-1-methylethyl}dimethylphenylarsineplatinum*(II), $[PtCl\{C(CH_3)_2C_6H_4PBu^t_2\}AsMe_2Ph]$.

*Acetylacetonato-{1-[*o*-(di-t-butylphosphino)phenyl]-1-methylethyl}platinum*(II), $[Pt(acac)\{C(CH_3)_2C_6H_4PBu^t_2\}]$.—A solution of thallous acetylacetonate (0·15 g, 0·48 mmol) in benzene (25 ml) was added to a suspension of *sym-trans*-di-μ-chloro-bis-{1-[*o*-(di-t-butylphosphino)phenyl]-1-methylethyl}diplatinum(II) (0·22 g, 0·22 mmol) in benzene (10 ml). The mixture was shaken overnight in the dark and then the precipitate of thallous chloride was filtered off.

Isolation gave the *product* (0·15 g) as prisms from dichloromethane–light petroleum (b.p. 60—80°).

trans-*Dichlorobis-(di-t-butyl-*o*-ethylphenylphosphine)palladium*(II).—Di-t-butyl-*o*-ethylphenylphosphine (0·69 g, 2·75 mmol) was added to a solution of sodium tetrachloropalladite(II) (0·45 g, 1·25 mmol) in methanol (5 ml) and ethanol (10 ml), and the mixture was set aside for 1 h. Isolation gave the *product* (0·7 g) as prisms.

sym-trans-*Di-μ-chloro-bis-*{1-[o-*(di-t-butylphosphino)-phenyl*]*ethyl*}dipalladium(II), [$Pd_2Cl_2\{CH(CH_3)C_6H_4PBu^t{}_2\}_2$].—A suspension of *trans*-dichlorobis(di-t-butyl-*o*-ethylphenylphosphine)palladium(II) (1·09 g, 1·61 mmol) in n-propanol (40 ml) was refluxed for 20 min. The resulting pale yellow precipitate was filtered off and washed with methanol to give the *product* as prisms (0·70 g). Addition of an excess of sodium tetraphenylborate to the mother liquor gave *hydrido-di-t-butyl-*o*-ethylphenylphosphonium tetraphenylborate* (0·48 g) as prisms (Tables 1 and 2).

trans-*Chloro-*{1-[o-*(di-t-butylphosphino)phenyl*]*ethyl*}*dimethylphenylphosphinepalladium*(II), [$PdCl\{CH(CH_3)C_6H_4\text{-}PBu^t{}_2\}PMe_2Ph$].—Dimethylphenylphosphine (103 μl, 0·71 mmol) was added to a suspension of di-μ-chloro-bis-{1-[*o*-(di-t-butylphosphino)phenyl]ethyl}dipalladium(II) (0·25 g, 0·32 mmol) in benzene (15 ml). The mixture was heated to boiling point to give a clear pale yellow solution. Isolation gave the *product* (0·26 g) as prisms from dichloromethane–light petroleum (b.p. 60—80°).

trans-*Chloro-*{1-[o-*(di-t-butylphosphino)phenyl*]*ethyl*}*triphenylphosphinepalladium*(II), [$PdCl\{CH(CH_3)C_6H_4PBu^t{}_2\}\text{-}PPh_3$], was prepared similarly as prisms.

Acetylacetonato-{1-[o-*(di-t-butylphosphino)phenyl*]*ethyl*}-*palladium*(II), [$Pd(acac)\{CH(CH_3)C_6H_4PBu^t{}_2\}$].—Thallous acetylacetonate (0·35 g, 1·16 mmol) was dissolved in benzene (40 ml) and added to a suspension of di-μ-chloro-bis-{1-[*o*-(di-t-butylphosphino)phenyl]ethyl}dipalladium(II) (0·41 g, 0·53 mmol) in benzene (20 ml). The mixture was shaken in the dark for 22 h and then the precipitate of thallous chloride was filtered off. Isolation gave the *product* (0·28 g) as prisms from dichloromethane–light petroleum (b.p. 60—80°).

sym-trans-*Di-μ-chloro-dichlorobis(di-t-butyl-*o*-isopropylphenylphosphine)dipalladium*(II).— Di-t-butyl-*o*-isopropylphenylphosphine (1·17 g, 4·42 mmol) was added to a solution of sodium tetrachloropalladite(II) (0·6 g, 2·01 mmol) in methanol (5 ml) and ethanol (5 ml), and the mixture set aside for 3 h. Isolation gave the *product* (0·52 g) as prisms.

Nuclear Magnetic Resonance Spectra.—^1H n.m.r. spectra were recorded at *ca.* 35° and 60 MHz on a Perkin-Elmer R12 A spectrometer. ^{13}C and ^{31}P n.m.r. spectra were recorded on a Bruker Spectrospin HFX spectrometer at ambient temperatures and at 22·62 and 36·43 MHz respectively.

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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