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

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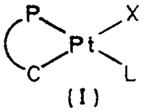
The complexes *trans*-$[PdCl_2L_2]$ $\{L = PBu^t(o\text{-tolyl})_2$ or $PBu^t{}_2(o\text{-tolyl})\}$ are shown to undergo internal metallation at the tolyl-methyl group very readily, to give complexes of the type $[Pd_2Cl_2(P\text{–}C)_2]$ $\{(P'\text{–}C) = CH_2C_6H_4PBu^t(o\text{-tolyl})$ and $(P''\text{–}C) = CH_2C_6H_4PBu_2{}^t\}$. The ligand $PBu^t{}_2(o\text{-tolyl})$ undergoes metallation more readily (in deuteriochloroform at *ca.* 35°) than $PBu^t(o\text{-tolyl})_2$. The chloride bridges of the binuclear complexes $[Pd_2Cl_2(P\text{–}C)_2]$ are replaced on treatment with silver carboxylates to give the compounds $[Pd_2X_2(P\text{–}C)_2]$ (X = OAc or OBz). These chloride bridges are split by various ligands (*e.g.* PPh_3, acetylacetonate, (−)-stilbenediamine *etc.*) to give mononuclear species.

EARLIER work [2] has shown that bulky tertiary phosphine ligands [*e.g.* PBu^tPh_2, $PBu^t{}_2Ph$, $PBu^tPr^n{}_2$, $PPh(o\text{-tolyl})_2$ *etc.*] promote internal metallation in complexes of the type *trans*-$[PtX_2L_2]$ (X = Cl, Br or I; L = tertiary phosphine) to give *trans*-$[PtX(P\text{–}C)L]$ [(I); (P–C) = internally metallated tertiary phosphine (L)]. However, internal metallation of the corresponding palladium(II) complexes *trans*-$[PdX_2L_2]$ could not be induced.[2] It has also been shown that the ligands $PBu^t(o\text{-tolyl})_2$ and $PBu^t{}_2(o\text{-tolyl})$ undergo internal metallation with platinum(II) very readily to give complexes of the types *trans*-$[PtCl(P\text{–}C)L]$ (I), *trans*-$[Pt(P\text{–}C)_2]$, *cis*-$[Pt(P'\text{–}C)_2]$, and $[Pt_2Cl_2(P\text{–}C)_2]$ with $(P'\text{–}C) = CH_2C_6H_4PBu^t(o\text{-tolyl})$ and $(P''\text{–}C) = CH_2C_6H_4PBu^t{}_2]$.[1] We now report that these two tertiary phosphines will undergo internal palladation very readily.

Addition of t-butyldi-*o*-tolylphosphine to a solution of sodium tetrachloropalladite(II) in methanol gives the yellow complex *trans*-$[PdCl_2\{PBu^t(o\text{-tolyl})_2\}_2]$ (Table 1). The assigned *trans*-configuration follows from the far-i.r. and ^1H n.m.r. data (Table 2). A molecular-weight determination in chloroform solution gives a low value (found 508, required 718). This low value is probably caused by partial dissociation of the bulky and rather poorly co-ordinating ligand $PBu^t(o\text{-tolyl})_2$ and/or internal metallation of the tertiary phosphine ligands. It is known that palladium(II) complexes containing bulky tertiary phosphines can dissociate to give binuclear species *e.g.* metathesis of *trans*-$[PdCl_2(PBu^t{}_2Ph)_2]$ with sodium iodide in acetone solution gives $[Pd_2I_4(PBu^t{}_2Ph)_2]$.[3]

When the yellow compound *trans*-$[PdCl_2\{PBu^t(o\text{-tolyl})_2\}_2]$ is heated at *ca.* 180°, the colour changes to cream. Similar behaviour is observed if the complex is boiled in dichloromethane–methanol solution, when an insoluble cream precipitate is formed after a few minutes. This cream compound is formulated as $[Pd_2Cl_2(P'\text{–}C)_2]$ [(II); X = Cl; $(P'\text{–}C) = CH_2C_6H_4PBu^t(o\text{-tolyl})$] on the basis of analytical and far-i.r. data (Tables 1 and 2). Similar values of ν(Pt–Cl) are obtained for the corresponding platinum(II) complex $[Pt_2Cl_2(P'\text{–}C)_2]$.[1] The configuration, (II), is confirmed by the bridge-splitting reactions of $[Pd_2Cl_2(P'\text{–}C)_2]$ (see later).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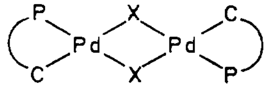
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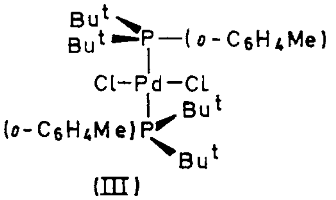
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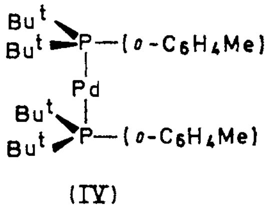
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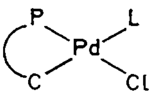
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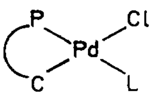
(VI)

Addition of a solution of sodium tetrachloropalladite(II) to a suspension of *trans*-$[PdCl_2\{PBu^t(o\text{-tolyl})_2\}_2]$ (1 molar equivalent) in methanol gives the red-brown complex $[Pd_2Cl_4\{PBu^t(o\text{-tolyl})_2\}_2]$. The far-i.r. spectrum of this compound (Table 2) shows typical values of ν(Pd–Cl) for complexes of this type.[4] On heating $[Pd_2Cl_4\{PBu^t(o\text{-tolyl})_2\}_2]$ at *ca.* 180° the colour changes to cream, presumably due to the formation of $[Pd_2Cl_2(P'\text{–}C)_2]$, with elimination of hydrogen chloride.

The complex $[Pd_2Cl_2(P'\text{–}C)_2]$ is prepared in high yield (96—97%) by three methods (see Experimental) and in two of them a red-brown suspension of $[Pd_2Cl_4\{PBu^t(o\text{-tolyl})_2\}_2]$ is formed at an intermediate stage.

The ligand di-t-butyl-*o*-tolylphosphine undergoes internal metallation with palladium(II) even more readily than t-butyldi-*o*-tolylphosphine. Addition of $PBu^t{}_2(o\text{-tolyl})$ (2 molar equivalents) to a solution of Na_2PdCl_4 in methanol at −6° gives the complex *trans*-

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[1] Part XXX, A. J. Cheney and B. L. Shaw, *J.C.S. Dalton*, 1972, 754.

[2] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *Chem. Comm.*, 1970, 1176; *J. Chem. Soc.* (*A*), 1971, 3833.

[3] B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 2976.

[4] 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.

$[PdCl_2\{PBu^t_2(o\text{-tolyl})\}_2]$, identified by far-i.r. and ^1H n.m.r. data (Table 2). The complex is slightly impure (Table 1) and could not be isolated in the pure state because it undergoes internal metallation so readily. The ^1H n.m.r. spectrum in deuteriochloroform (Table 2) at *ca.* 35° shows that two species are present in solution. There are two triplets due to the t-butyl groups at τ 8·34 and 8·30 (intensity ratio *ca.* 3 : 1) and two singlets due to the tolyl-methyl protons at τ 6·62 and 6·76 (intensity ratio *ca.* 3 : 1). We suggest that these two species are conformers, formed because of restricted rotation about the Pd–P bonds. Molecular models suggest that the very bulky t-butyl groups prefer to be aligned as shown in the two conformers (III) and (IV). The *ortho*-tolyl groups further hinder rotation about the Pd–P bonds. The existence of two rotamers in solution is confirmed by the ^{31}P n.m.r. spectrum (recorded at −10° with all ^1H nuclei decoupled), which shows two singlets at −44·4 and −42·9 p.p.m. (relative to 85% H_3PO_4) of relative intensity ratio *ca.* 3 : 1 (as above).

TABLE 1

Analytical, molecular weight and melting point data for complexes of the types *trans*-$[PdCl_2L_2]$ [L′ = $PBu^t(o\text{-tolyl})_2$ and L″ = $PBu^t_2(o\text{-tolyl})$] and $[Pd_2X_2(P\text{–}C)_2]$ [X = Cl, OAc or OBz; (P′–C) = $CH_2C_6H_4PBu^t(o\text{-tolyl})$, (P″–C) = $CH_2C_6H_4PBu^t_2$]

Compound	% Yield	Colour	Analytical data [a] C	H	Cl	*M* [a, b]	M.p.
trans-$[PdCl_2L'_2]$	88	Yellow	59·85 (60·2)	6·45 (6·45)	10·55 (9·9)	508 (718)	180—185° [c] 320 decomp.
$[Pd_2Cl_4L'_2]$	85	Red-brown	47·85 (48·3)	5·05 (5·2)	16·2 (15·85)		180—190 [c] 300 decomp.
$[Pd_2Cl_2(P'\text{–}C)_2]$	96	Cream	52·7 (52·6)	5·55 (5·4)	8·5 (8·6)		320 decomp.
$[Pd_2(OAc)_2(P'\text{–}C)_2]$ [d]	77	Pale yellow	58·0 (57·9)	6·7 (6·55)			143—148 [e] 211—214
$[Pd_2(OBz)_2(P'\text{–}C)_2]$ [f]	88	Cream	63·9 (64·1)	6·7 (6·75)			127—130 [e]
$[Pd_2(OBz)_2(P'\text{–}C)_2]$	65	Cream	60·7 (60·4)	5·7 (5·5)		603 (994)	125—130
trans-$[PdCl_2L''_2]$	84	Yellow	54·35 (55·45)	7·6 (7·75)	11·35 (10·9)		125—130 [c] 280 decomp.
$[Pd_2Cl_2(P''\text{–}C)_2]$	90	Yellow	47·8 (47·75)	6·5 (6·4)	9·3 (9·4)		250 decomp.
$[Pd_2(OAc)_2(P''\text{–}C)_2]$	80	White	50·45 (50·95)	6·65 (6·8)		514 (801)	218—224 decomp.
$[Pd_2(OBz)_2(P''\text{–}C)_2]$	71	Pale yellow	56·5 (57·1)	6·15 (6·3)			195—210 decomp.

[a] Theoretical values in parentheses. [b] Chloroform solution. [c] Colour changes to cream. [d] Compound contains 0·5 mol of cyclohexane per g. atom palladium. [e] Gas evolves. [f] Complex contains one mol of cyclohexane per g. atom palladium.

TABLE 2

^1H N.m.r. [a] and i.r. [b] data for complexes of the types *trans*-$[PdCl_2L_2]$ [L′ = $PBu^t(o\text{-tolyl})_2$ and L″ = PBu^t_2 (*o*-tolyl)] and $[Pd_2X_2(P\text{–}C)_2]$ [X = Cl, OAc or OBz; (P′–C) = $CH_2C_6H_4PBu^t(o\text{-tolyl})$ and (P″–C) = $CH_2C_6H_4PBu^t_2$]

Compound	τ(Bu^t)	*J*(P–Bu^t)	τ(tolyl-Me)	τ(CH_2) [c]	^3J(P–H)	ν(Pd–Cl)
trans-$[PdCl_2L'_2]$	8·36	14·8 [d]	7·64			350s
$[Pd_2Cl_4L'_2]$ [e]						350s, 305m, 266s
$[Pd_2Cl_2(P'\text{–}C)_2]$ [e]						283s, 244m
$[Pd_2(OAc)_2(P'\text{–}C)_2]$	8·54	15·2	8·13, 7·62 [g]	6·66br		
$[Pd_2(OBz)_2(P'\text{–}C)_2]$ [h]	8·51	15·1	7·48	6·48d	4·0	
trans-$[PdCl_2L''_2]$ [i]	8·34	13·8 [d]	6·62			345s
	8·30	13·8 [d]	6·76			
$[Pd_2Cl_2(P''\text{–}C)_2]$	8·51	14·2		6·42d	5·0	280s, 238m
$[Pd_2(OAc)_2(P''\text{–}C)_2]$ [j]	8·55	14·1		6·52d	4·5	
$[Pd_2(OBz)_2(P''\text{–}C)_2]$	8·52	14·2		6·44d	4·5	

[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; d = doublet. [d] '*J*' = $|^3J(P\text{–}H) + {}^5J(P\text{–}H)|$. [e] Too insoluble to record spectrum. [f] Signal at τ 8·58 due to 0·5 mol of cyclohexane per g. atom palladium. [g] One of these signals due to the acetate-methyl. [h] Signal at τ 8·57 due to 1 mol of cyclohexane per g. atom palladium. [i] The two sets of signals are in the intensity ratio of *ca.* 3 : 1 for τ (Bu^t) 8·34 : 8·30. [j] τ (acetate-methyl) 7·96.

The complexes *trans*-$[MX_2(PHBu^t_2)_2]$ (M = Pd^{II}; X = Br or I: M = Pt^{II}; X = Cl, Br or I) also give two conformers in solution, as shown by ^1H n.m.r. spectroscopy.[5] The ^1H n.m.r. spectrum of *trans*-$[PdCl_2(PHBu^t_2)_2]$ shows that two conformers are present at 0° but at *ca.* 30° only one set of resonances is observed, presumably because of an increased speed of rotation about the Pd–P bonds.

The ^1H n.m.r. spectrum of *trans*-$[PdCl_2\{PBu^t_2(o\text{-tolyl})\}_2]$ in deuteriochloroform at *ca.* 35: changes with time and after 85 min the spectrum is consistent with that of an equimolar mixture of $[Pd_2Cl_2(P''\text{–}C)_2]$ [(P″–C) = $CH_2C_6H_4PBu^t_2$] and $[PHBu^t_2(o\text{-tolyl})]Cl$. The resonances are assigned by comparison with the

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[5] A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *J. Chem. Soc. (A)*, 1971, 1826.

^1H n.m.r. spectra of authentic samples of $[Pd_2Cl_2(P''-C)_2]$ (Table 2) and $[PHBu^t_2(o\text{-tolyl})]Cl$. $[PHBu^t_2(o\text{-tolyl})]Cl$ is obtained by treating $PBu^t_2(o\text{-tolyl})$ with hydrogen chloride and the ^1H n.m.r. spectrum shows a doublet at τ 8·40 $[^3J(P-H) = 16{\cdot}4$ Hz$]$ due to the t-butyl groups and a singlet at τ 7·13 due to the tolyl-methyl group. The two components of the deuteriochloroform solution described above are isolated and identified (see Experimental section). Thus *trans*-$[PdCl_2\{PBu^t_2(o\text{-tolyl})\}_2]$ undergoes internal metallation ~~very readily to give $[Pd_2Cl_2(P''-C)_2]$ with elimination~~ of $PBu^t_2(o\text{-tolyl})$ and hydrogen chloride.

A similar ^1H n.m.r. study of the complex *trans*-$[PdCl_2\{PBu^t(o\text{-tolyl})_2\}_2]$ shows that the rate of internal metallation is much slower. After 5 h the solution still contained *ca.* 30% of *trans*-$[PdCl_2\{PBu^t(o\text{-tolyl})_2\}_2]$ as indicated by the relative intensities of the tolyl-methyl signals of the starting material and the phosphonium salt $[PHBu^t(o\text{-tolyl})_2]Cl$. The internally metallated product $[Pd_2Cl_2(P'-C)_2]$ is very insoluble and precipitates out of solution; only very weak signals due to the residual complex in solution could be detected in the ^1H n.m.r. spectrum.

The internally metallated complex $[Pd_2Cl_2(P''-C)_2]$ [configuration (II), X = Cl] is prepared by treating *trans*-$[PdCl_2\{PBu^t_2(o\text{-tolyl})\}_2]$ with sodium tetrachloropalladite(II) (0·96 molar equivalents) in boiling ethanol solution for 5 min. The far-i.r. spectrum shows ν(Pd–Cl) at 280 and 238 cm^{-1} and the ^1H n.m.r. spectrum (Table 2) shows the palladium-methylene protons as a doublet with $^3J(P-Pd-H) = 5{\cdot}0$ Hz.

Treatment of a suspension of $[Pd_2Cl_2(P'-C)_2]$ in acetone with silver acetate or silver benzoate gives the bridged complexes $[Pd_2X_2(P'-C)_2]$, [(II), X = OAc or OBz]. These complexes take up cyclohexane of solvation in the same ratios as found for the corresponding platinum(II) complexes[1] *i.e.* 0·5 mol of cyclohexane per palladium atom (X = OAc) and 1 mol per palladium atom (X = OBz) as shown by analytical and ^1H n.m.r. data (Tables 1 and 2). The complex $[Pd_2(OBz)_2(P'-C)_2]$ is obtained unsolvated after recrystallisation from ether and drying *in vacuo* at *ca.* 0·05 mmHg, 20° for several hours. The complexes $[Pd_2X_2(P''-C)_2]$ (II; X = OAc or OBz) are prepared in a similar manner but they do not take up cyclohexane of solvation. The ~~configuration (II) follows from the ^1H n.m.r. spectra~~ (Table 2). The palladium-methylene protons give a doublet with $^3J(P-Pd-H) = 4{\cdot}5$ Hz.

Molecular weight determinations of these carboxylato-complexes give low values indicating dissociation in solution and palladium metal is deposited after a few days.

TABLE 3

Analytical, molecular weight and melting point data for complexes formed by bridge-splitting reactions of the compounds $[Pd_2Cl_2(P-C)_2]$ $[(P'-C) = CH_2C_6H_4PBu^t(o\text{-tolyl})$; $(P''-C) = CH_2C_6H_4PBu^t_2]$

Compound [a,b]	% Yield	Analytical data [c] C	H	Cl	*M* [c,d]	M.p.
cis- and *trans*-[PdCl(P′–C)py]	79	56·1 (56·3)	5·45 (5·55)	7·35 (7·2)		165°[e] 290[f]
trans-[PdCl(P′–C)PPh$_3$] [h]	84	67·0 (67·0)	5·8 (5·75)	4·5 (4·7)	717 (753)	95—100[g] 230—235[f]
[Pd(acac)(P′–C)]	70	57·8 (58·2)	6·05 (6·15)		467 (475)	206—209
[PdCl(P′–C){(–)-(α)-pen}] [i]	91	55·1 (55·35)	5·9 (5·95)	11·9 (12·3)	510 (575)	101—108[g] 300[f]
[Pd(P′–C){(–)-stien}]Cl	92	61·1 (61·55)	6·05 (6·15)	6·0 (5·7)		180—186
trans-[PdCl(P″–C)PPh$_3$]	95	61·7 (62·0)	6·25 (6·15)	5·4 (5·55)	644 (640)	232—238[e] 310[f]
[Pd(acac)(P″–C)]	63	54·9 (54·75)	7·1 (7·1)		427 (439)	166—171

[a] ~~All complexes are~~ white. [b] ~~py~~ = Pyridine; ~~acac = acetylacetonato; (–)-α-pen = (–)-(α)-phenylethylamine; (–)-stien =~~ (–)-stilbenediamine. [c] Theoretical values in parentheses. [d] Chloroform solution. [e] Crystals undergo a change. [f] Decomposed. [g] Gas evolved. [h] Compound contains 1 mol of C_6H_6 per g. atom palladium. [i] Compound contains 0·5 mol of CH_2Cl_2 per g. atom palladium.

Bridge-Splitting Reactions of the Complexes $[Pd_2Cl_2(P-C)_2]$ $[(P'-C) = CH_2C_6H_4PBu^t(o\text{-}tolyl)$ *and* $(P''-C) = CH_2C_6H_4PBu^t_2]$.—The chloride bridges of these binuclear compounds are readily cleaved by various ligands to give mononuclear complexes. The corresponding platinum(II) complexes and other halogen-bridged binuclear platinum(II) and palladium(II) complexes undergo similar bridge-splitting reactions.[1,6-8] The reactions of $[Pd_2Cl_2(P'-C)_2]$ are summarized in the Scheme. Analytical data are in Table 3 and the ^1H n.m.r. and i.r. data in Table 4.

Treatment of $[Pd_2Cl_2(P'-C)_2]$ with pyridine gives a mixture of *cis*- and *trans*-[PdCl(P′–C)(py)] [configurations (V) and (VI); L = py] which readily dissociate in solution. The ^1H n.m.r. spectrum (Table 4) is recorded in the presence of an excess of pyridine and shows the existence of two isomers. This is confirmed by the far-i.r. spectrum. Addition of PPh$_3$ to $[Pd_2Cl_2(P'-C)_2]$

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

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

[8] B. Crociani, T. Boschi, R. Pietropaolo, and U. Belluco, *J. Chem. Soc.* (*A*), 1970, 531.

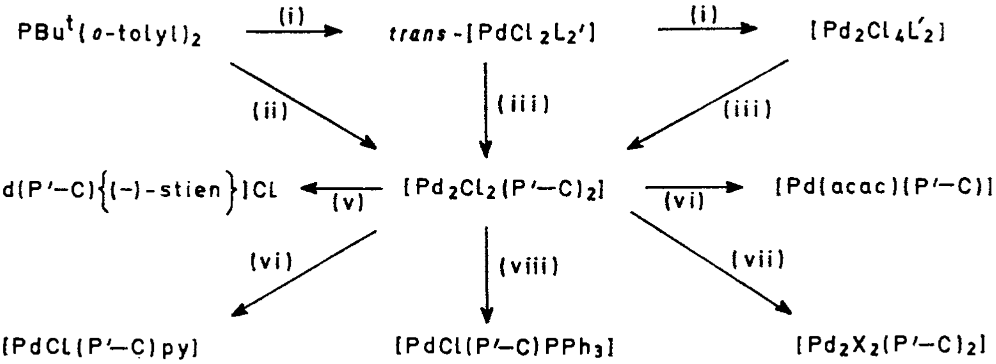
gives only *trans*-[PdCl(P′–C)PPh$_3$] [configuration (VI); L = PPh$_3$] as shown by the low value[8] of ν(Pd–Cl) at 273 cm^{-1}. The ^{31}P n.m.r. spectrum gives a large value of |^2J(P–P)| (400·5 Hz) (Table 5) which confirms the *trans*-assignment.[9] The ^{1}H n.m.r. spectrum shows a broad signal for the methylene group because the two protons are non-equivalent and coupled with two different ^{31}P nuclei. Thallous acetylacetonate also cleaves the chloride bridges to give the complex [Pd(acac)(P′–C)] and the structure follows from the ^{1}H n.m.r. spectrum (Table 4).

TABLE 4

^{1}H N.m.r. [a] and i.r. data for complexes formed by bridge-splitting reactions of the compounds [Pd$_2$Cl$_2$(P–C)$_2$] [(P′–C) = CH$_2$C$_6$H$_4$PBu^t(*o*-tolyl); (P″–C) = CH$_2$C$_6$H$_4$PBu$^t_2$]

Compound [b]	τ (Bu^t)	^3J(P–H)	τ (tolyl-Me)	τ (CH$_2$) [c]	^3J(P–H)	ν(Pd–Cl) cm^{-1}
cis- and *trans*-[PdCl(P′–C)py] [d]	8·68	15·2	7·62	nv		293, 282
	8·41	15·0	7·58			
trans-[PdCl(P′–C)PPh$_3$]	8·38	14·0	7·58	7·20br		273
[Pd(acac)(P′–C)] [e]	8·51	15·5	7·44	6·56d	3·5	
trans-[PdCl(P′–C){(–)-α-pen}]	8·50	15·0	7·67	nv		274
	8·47	15·0	7·65			
[Pd(P′–C){(–)-stien}]Cl	8·42	15·5	7·54	6·52cx		
	8·39	15·8				
trans-[PdCl(P″–C)PPh$_3$]	8·46	14·0		7·38q	3·0 7·2	268
[Pd(acac)(P″–C)] [f]	8·57	13·8		6·63d	4·0	

[a] Spectra recorded at *ca.* 34° and 60 MHz in CDCl$_3$ solution. τ-Values ±0·02, *J*-values ±0·5 Hz. [b] py = Pyridine; acac = acetylacetonato; (–)-(α)-pen = (–)-phenylethylamine; (–)-stien = (–)-stilbenediamine. [c] nv = Not visible, br = broad, d = doublet, cx = complex signal, q = 1 : 1 : 1 : 1 quartet. [d] Spectrum recorded with an excess of pyridine present and the ratio of isomers was *ca.* (55 : 45) for the signals τ 8·68 : 8·41. [e] acac group: τ (Me) 8·23 and 8·02, τ (C–H) 4·83. [f] acac group: τ (Me) 8·11 and 8·0, τ (C–H) 4·70.



SCHEME

(i) Na$_2$PdCl$_4$–MeOH, 20°. (ii) Na$_2$PdCl$_4$–n-propanol, 100°. (iii) n-propanol, 100°. (iv) Thallium acetylacetonate. (v) (–)-Stilbenediamine. (vi) Pyridine. (vii) AgX. (viii) Triphenylphosphine

The chelating group (P′–C) *i.e.* [CH$_2$C$_6$H$_4$PBu^t-(*o*-tolyl)] contains an asymmetric phosphorus atom and we have attempted to resolve some of its complexes by treating [Pd$_2$Cl$_2$(P′–C)$_2$] with optically active amines. The ^{1}H n.m.r. spectra of the complexes *trans*-[PdCl-(P′–C){(–)-α-phenylethylamine}] and [Pd(P′–C){(–)-stilbenediamine}]Cl (Table 3) suggest that 1 : 1 mixtures of diastereoisomers are formed as both complexes give two sets of t-butyl doublets. However we have been unable to separate the mixtures by fractional crystallisation. The assigned *trans*-configuration (VI, L = amine) of [PdCl(P′–C){(–)-(α)-phenylethylamine}] follows from the low value of ν(Pd–Cl) (274 cm^{-1}), typical of chlorine *trans* to carbon.[8]

The compound [Pd$_2$Cl$_2$(P″–C)$_2$] undergoes bridge-splitting reactions with triphenylphosphine or thallous

TABLE 5

^{31}P N.m.r. data [a] for complexes of the type [PdCl(P–C)PPh$_3$] [(P′–C) = CH$_2$C$_6$H$_4$PBu^t(*o*-tolyl) and (P″–C) = CH$_2$C$_6$H$_4$PBu$^t_2$]

Unmetallated phosphine		Metallated phosphine		
	δ	P–C	δ	^2J(P–P)
PPh$_3$	–25·3	(P′–C)	–58·8	400·5
PPh$_3$	–25·4	(P″–C)	–85·9	381·8

[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 ± 0·2 Hz.

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[9] S. O. Grim and R. L. Keiter, *Inorg. Chim. Acta*, 1970, **4**, 56.

acetylacetonate. The ^{31}P n.m.r. spectrum of the complex $[PdCl(P''-C)PPh_3]$ (Table 5) shows that the phosphorus nuclei are in mutually *trans*-positions *i.e.* $|^2J(P-P)| = 381{\cdot}8$ Hz and the low value of $\nu(Pd-Cl)$ at 268 cm^{-1} corresponds with chlorine *trans* to carbon. The ^1H n.m.r. spectrum shows that the methylene group gives a 1 : 1 : 1 : 1 quartet due to coupling with the two ^{31}P nuclei. The ^1H n.m.r. spectrum of the complex $[Pd(acac)(P''-C)]$ (Table 4) is very similar to that of the complex $[Pt(acac)(P''-C)]$.

The ligands $PBu^t(o\text{-tolyl})_2$ and $PBu^t{}_2(o\text{-tolyl})$ undergo internal metallation reactions more readily with palladium(II) than with platinum(II), *e.g.* *trans*-$[PdCl_2\{PBu^t{}_2(o\text{-tolyl})\}_2]$ undergoes internal metallation in deuteriochloroform solution at *ca.* 35° to give $[Pd_2Cl_2(P''-C)_2]$ whereas the reaction of $PBu^t{}_2(o\text{-tolyl})$ (2 molar equivalents) with *trans*-$[PtCl_2(PhCN)_2]$ requires boiling n-propanol to give *trans*-$[PtCl(P''-C)PBu^t{}_2(o\text{-tolyl})]$ and after *ca.* 3 h some of the binuclear complex $[Pt_2Cl_2(P''-C)_2]$ is formed.

Complexes of the type *trans*-$[PdCl(P-C)L]$ $L = PBu^t(o\text{-tolyl})_2$ or $PBu^t{}_2(o\text{-tolyl})]$ could not be detected. It is significant that the complex *trans*-$[PdCl(CH_2Ph)(PPh_3)_2]$ readily dissociates in solution to give the binuclear compound $[Pd_2Cl_2(CH_2Ph)_2(PPh_3)_2]$.[10] However, complexes of the type $[PdX(P-C)L]$ [X = Cl or Br; L = aryl phosphite have been prepared but no binuclear compounds were reported.[11]

$PBu^t{}_2(o\text{-tolyl})$ is more bulky than $PBu^t(o\text{-tolyl})_2$ and undergoes internal metallation more readily with palladium(II). The effect of bulky tertiary phosphine ligands in promoting such internal metallation reactions has been discussed previously.[2]

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are corrected. All reactions involving tertiary phosphines and methyl-lithium were carried out under nitrogen. Yields, melting points, analytical and molecular weight data are given in Tables 1 and 3.

trans-*Dichlorobis(t-butyldi-*o*-tolylphosphine)palladium*(II).—t-Butyldi-*o*-tolylphosphine (2·20 g, 8·1 mmol) in ethanol (35 ml) was added to sodium tetrachloropalladite(II) (3·84 mmol) in methanol (30 ml). After 30 min, the *product* (2·41 g) was isolated as prisms.

sym-trans-*Di-μ-chloro-dichlorobis(t-butyldi-*o*-tolylphosphine)dipalladium*(II).—A solution of sodium tetrachloropalladite(II) (0·10 g, 0·273 mmol) in methanol (2 ml) was added to a suspension of *trans*-dichlorobis(t-butyldi-*o*-tolylphosphine)palladium(II) (0·20 g, 0·28 mmol) in acetone. The mixture was set aside for 1 h at 20° and isolation gave the *product* (0·21 g) as plates from dichloromethane–light petroleum (b.p. 40—60°).

sym-trans-*Di-μ-chloro-bis*[o-(*t-butyl-*o*-tolylphosphino*)-*benzyl*]*dipalladium*(II), $[Pd_2Cl_2\{CH_2C_6H_4PBu^t(o\text{-tolyl})\}_2]$.—*Method* 1: A suspension of *trans*-dichlorobis(t-butyldi-*o*-tolylphosphine)palladium(II) in n-propanol (25 ml) was heated under reflux for 3 min. The resulting solid was filtered off to give the *product* (0·33 g) as micro-prisms.

Method 2: an equimolar mixture of *trans*-dichlorobis-(t-butyldi-*o*-tolylphosphine)palladium(II) (1·335 g) and sodium tetrachloropalladite(II) (0·67 g) in methanol (10 ml) was heated at *ca.* 50° for 2 min to give a red-brown suspension. n-Propanol (30 ml) was then added to the mixture which was heated under reflux for 5 min to give the insoluble *product* (1·49 g).

Method 3: A solution of t-butyldi-*o*-tolylphosphine (0·273 g, 1 mmol) in n-propanol (10 ml) was added to sodium tetrachloropalladite(II) (0·365 g 1 mmol) in methanol (4 ml) and the mixture was heated under reflux for 3 min to give the required *product* (0·397 g).

trans-*Dichlorobis(di-t-butyl-*o*-tolylphosphine)palladium*(II).—Di-t-butyl-*o*-tolylphosphine (2·02 g, 0·855 mmol) was added to a solution of sodium tetrachloropalladite (1·52 g, 0·415 mmol) in methanol (20 ml). The mixture was set aside at −6° for 45 min. Isolation gave the slightly impure *product* (2·25 g) as prisms.

sym-trans-*Di-μ-chloro-bis*[o-(*di-t-butylphosphino*)*benzyl*]-*dipalladium*(II), $[Pd_2Cl_2(CH_2C_6H_4PBu^t{}_1)_2]$.—A solution of sodium tetrachloropalladite(II) (0·117 g, 0·329 mmol) in methanol (5 ml) was added to a suspension of *trans*-dichlorobis[di-t-butyl(*o*-tolyl)phosphine]palladium(II) (0·217 g, 0·320 mmol) in ethanol (15 ml) and the mixture was boiled for 5 min. Isolation gave the *product* (0·225 g) as prisms from dichloromethane–methanol.

*Internal Metallation of Dichlorobis(di-t-butyl-*o*-tolylphosphine)palladium*(II) *in Deuteriochloroform Solution.*—The internal metallation of the complex was followed by re-recording the ^1H n.m.r. spectrum of the solution at intervals. The temperature remained at *ca.* 35° throughout the experiment. When the metallation was completed, yellow prisms were filtered off from the solution and shown to be *sym-trans*-di-μ-chloro-[*o*-(di-t-butylphosphino)benzyl]dipalladium(II) from the i.r. spectrum. The deuteriochloroform filtrate was evaporated under reduced pressure and the residue was dissolved in methanol. Addition of an excess of sodium tetraphenylborate to the methanol solution gave *hydrido-di-t-butyl-*o*-tolylphosphine tetraphenylborate* as needles, m.p. 156—159°. The compound was identified by analytical data (Found: C, 84·15; H, 8·55. $C_{39}H_{46}BPCl$ requires C, 84·15, H, 8·35) and comparison of its i.r. spectrum with a genuine sample, prepared by the addition of hydrogen chloride (1 molar equivalent) and an excess of sodium tetraphenylborate to di-t-butyl-*o*-tolylphosphine.

sym-trans-*Di-μ-acetato-bis*[o-(*t-butyl-*o*-tolylphosphino*)-*benzyl*]*dipalladium*(II), $[Pd_2(OAc)_2\{CH_2C_6H_4PBu^t(o\text{-tolyl})\}_2]$.—A suspension of *sym-trans*-di-μ-chloro-bis[*o*-(t-butyl-*o*-tolylphosphino)benzyl]dipalladium(II) (0·41 g, 0·50 mmol) and silver acetate (0·18 g, 1·06 mmol) in acetone (50 ml) was shaken in the dark for 12 h. The mixture was filtered and the filtrate was evaporated under reduced pressure to give the *product* (0·36 g) as prisms from dichloromethane–cyclohexane. The complex contained one mole of cyclohexane per mole of product.

The following three compounds were prepared in a similar manner using silver acetate or silver benzoate and the appropriate chloro-bridged dimer. Solvents used for recrystallisation are given in parentheses: sym-trans-*Di-μ-benzoato-bis*[o-(*t-butyl-*o*-tolylphosphino*)*benzyl*]*dipalladium*(II), $[Pd_2(OBz)_2\{CH_2C_6H_4PBu^t(o\text{-tolyl})\}_2]$—(prisms

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[10] P. Fitton, J. E. McKeon, and B. C. Ream, *Chem. Comm.*, 1969, 370.

[11] E. W. Ainscough and S. D. Robinson, *Chem. Comm.*, 1971, 130.

from dichloromethane–cyclohexane); sym-trans-*di-μ-acetato-bis*[o-(*di-t-butylphosphino*)*benzyl*]*dipalladium*(II), [$Pd_2(OAc)_2(CH_2C_6H_4PBu^t{}_2)_2$]—(prisms from dichloromethane–cyclohexane); sym-trans-*di-μ-benzoato-bis*[o-(*di-t-butylphosphino*)*benzyl*]*dipalladium*(II), [$Pd_2(OBz)_2(CH_2C_6H_4PBu^t{}_2)_2$]—(prisms from dichloromethane–n-hexane).

cis- and trans-*Chloro*[o-(*t-butyl*-o-*tolylphosphino*)*benzyl*]*pyridinepalladium*(II), [$PdCl\{CH_2C_6H_4PBu^t(o\text{-tolyl})\}$pyridine].—Pyridine (15 μl, 1·5 mol per g. atom palladium) was added to a suspension of *sym-trans*-di-μ-chloro-bis[*o*-(t-butyl-*o*-tolylphosphino)benzyl]dipalladium(II) (0·051 g) in dichloromethane (10 ml). After 5 min, light petroleum (b.p. 40—60°) was added to the colourless clear solution to give a mixture of the *cis*- and *trans*-isomers as the *product* (0·048 g) in the form of prisms.

trans-*Chloro*[o-(*t-butyl*-o-*tolylphosphino*)*benzyl*]*triphenylphosphinepalladium*(II), [$PdCl\{CH_2C_6H_4PBu^t(o\text{-tolyl})\}PPh_3$].—Triphenylphosphine (0·334 g, 1·05 mol per g. atom palladium) was added to a suspension of *sym-trans*-di-μ-chloro-bis[*o*-(t-butyl-*o*-tolylphosphino)benzyl]dipalladium(II) (0·50 g) in benzene (25 ml). The mixture was heated at *ca.* 50° for 1 min to give a clear pale yellow solution. Isolation gave the *product* (0·768 g) as prisms from benzene–light petroleum (b.p. 80—100°).

Acetylacetonato[o-(*t-butyl*-o-*tolylphosphino*)*benzyl*]*palladium*(II), [$Pd(acac)\{CH_2C_6H_4PBu^t(o\text{-tolyl})\}$].—A mixture of *sym-trans*-μ-dichloro[*o*-(t-butyl-*o*-tolylphosphino)benzyl]dipalladium(II) (0·106 g) and thallous acetylacetonate (0·08 g, 1·02 mol per g. atom palladium) was shaken for 30 min. The solution was filtered and evaporated under reduced pressure to give the *product* (0·085 g) as prisms from light petroleum (b.p. 80—100°).

Chloro[o-(*t-butyl*-o-*tolylphosphino*)*benzyl*][(−)-*α-phenylethylamine*]*palladium*(II), [$PdCl\{CH_2C_6H_4PBu^t(o\text{-tolyl})\}\{(-)\text{-}\alpha\text{-phenylethylamine}\}$].—A suspension of *sym-trans*-di-μ-chloro-bis[*o*-(t-butyl-*o*-tolylphosphino)benzyl]dipalladium(II) (0·30 g) in dichloromethane (10 ml) was treated with (−)-α-phenylethylamine (0·11 g, 1·25 mol per g. atom palladium). After 1 h, isolation gave the *product* (0·346 g) from dichloromethane–n-hexane.

[o-(*t-Butyl*-o-*tolylphosphino*)*benzyl*][(−)-*stilbenediamine*]*palladium*(II) *chloride*, [$Pd\{CH_2C_6H_4PBu^t(o\text{-tolyl})\}\{(-)\text{-stilbenediamine}\}$]Cl.—This was prepared in a similar manner to give the *product* as needles from dichloromethane–light petroleum (b.p. 40—60°).

trans-*Chloro*-[o-(*di-t-butylphosphino*)*benzyl*]*triphenylphosphinepalladium*(II), [$PdCl(CH_2C_6H_4PBu^t{}_2)PPh_3$].—Triphenylphosphine (0·145 g, 1·25 mol per g. atom palladium) was added to a suspension of *sym-trans*-di-μ-chloro-bis[*o*-(di-t-butylphosphino)benzyl]dipalladium(II) (0·165 g) in dichloromethane (5 ml) to give a clear colourless solution. Isolation gave the *product* (0·265 g) as prisms from dichloromethane–methanol.

Acetylacetonato[o-(*di-t-butylphosphino*)*benzyl*]*palladium*(II), [$Pd(acac)(CH_2C_6H_4PBu^t{}_2)$].—Thallous acetylacetonate (0·264 g, 1·1 mol per g. atom palladium) was added to *sym-trans*-di-μ-chloro-[*o*-(di-t-butylphosphino)benzyl]dipalladium(II) (0·30 g) in benzene (40 ml) and the mixture was shaken for 5 h. Isolation gave the *product* (0·22 g) as prisms from light petroleum (b.p. 60—80°).

N.M.R. Spectra.—^{1}H n.m.r. spectra were recorded at *ca.* 35° and 60 MHz on a Perkin-Elmer R 12A spectrometer. ^{31}P N.m.r. spectra were recorded at ambient temperatures and 36·43 MHz on a Bruker Spectrospin HFX spectrometer.

I.r. Spectra.—These were recorded on a Perkin-Elmer model 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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