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TRANSITION METAL—CARBON BONDS

XLI*. INTERNAL METALLATION REACTIONS OF PALLADIUM(II)—*t*-BUTYLDIBENZYLPHOSPHINE AND —BENZYLDI-*t*-BUTYLPHOSPHINE COMPLEXES

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Summary

The complexes *trans*-$[PdCl_2L_2]$ {L = P-t-Bu (benzyl)$_2$ or P-t-Bu$_2$ (benzyl)} are shown to undergo internal metallation with difficulty to give complexes of the type $[Pd_2Cl_2(P—C)_2]$ {(P′—C) = $C_6H_4CH_2$P-t-Bu (benzyl) and (P″—C) = $C_6H_4CH_2$P-t-Bu$_2$}. The ligand P-t-Bu$_2$(benzyl) undergoes metallation more readily than P-t-Bu(benzyl)$_2$. The bridging chlorides of the binuclear complex $[Pd_2Cl_2(P''—C)_2]$ are replaced by bromide or iodide and the bridges may be split by various ligands to give mononuclear species.

Introduction

The internal metallation of *N,N*-dimethylbenzylamine by palladium goes particularly readily, e.g. on treating Na_2PdCl_4 with the amine in ethanol at 20°C the *o*-metallated complex $[Pd_2Cl_2\{Me_2NCH_2C_6H_4\}_2]$ is rapidly precipitated [2]. One might expect therefore that benzylphosphine ligands would be similarly metallated. However, although complexes of Mn, Fe, Ru, Rh, Ni, Pd or Pt with various tertiary benzylphosphines such as PMe_2(benzyl), PPh_2(benzyl), PPh(benzyl)$_2$ or P(benzyl)$_3$ are known their internal metallation has not been observed [3-5]. Indeed prolonged (24 h) heating of PMe_2(benzyl)—palladium(II) or —platinum(II) complexes in high boiling solvents such as 2-methoxyethanol or diglyme caused no metallation [4]. Earlier work has shown however that internal metallation of tertiary phosphine or tertiary arsine ligands is promoted by steric effects e.g. with ligands such as PR_2-t-Bu or PR-t-Bu$_2$, the R group is often readily metallated [6-8]. We have therefore prepared the new ligand

* For part XL see ref. 1.

TABLE 1

ANALYTICAL, MOLECULAR WEIGHT, AND MELTING POINT DATA FOR SOME PALLADIUM(II) COMPLEXES OF THE PHOSPHINES P-t-Bu(BENZYL)$_2$ AND P-t-Bu$_2$(BENZYL)

Compound[a]	Yield (%)	Colour	M.p. (°C)	Analytical data[b]			$M^{b,c}$
				C	H	X	
trans-[$PdCl_2L'_2$]	85	Yellow	258-261	58.7 (60.2)	6.4 (6.45)	9.65(9.9)	695(718)
trans-[$PdBr_2L'_2$]	87	Yellow	250-252	54.05(53.6)	5.85(5.75)	19.4 (19.8)	804(807)
trans-[$PdI_2L'_2$]	95	Orange	263-265	47.5 (48.0)	5.15(5.15)	29.45(28.2)	870(901)
[$Pd_2Cl_4L'_2$]	86	Red	210-213	48.45(48.3)	5.15(5.2)	15.75(15.8)	858(895)
[Pd_2Cl_2(P'—C)$_2$]	12	Cream	245-250[d]	52.6((52.6)	5.5 (5.4)	8.85(8.6)	813(822)
trans-[$PdCl_2L''_2$]	72	Yellow	242-245[d]	55.05(55.45)	7.5 (7.75)	10.8 (10.9)	655(650)
trans-[$PdBr_2L''_2$]	89	Yellow	278-280	48.4 (48.8)	6.55(6.8)	21.9 (21.65)	731(740)
trans-[$PdI_2L''_2$]	71	Brown	238-241	44.0 (43.25)	6.15(6.05)	33.25(30.45)	668(833)
[Pd_2Cl_2(P''—C)$_2$]	75	Cream	248-251[d]	47.7 (47.75)	6.5 (6.4)	9.45(9.4)	746(754)
[Pd_2Br_2(P''—C)$_2$]	80	Pale yellow	258-259	41.25(42.75)	5.6 (5.75)	20.55(18.95)	938(843)
[Pd_2I_2(P''—C)$_2$]	85	Yellow	286-291[d]	38.85(38.45)	5.2 (5.15)	27.75(27.05)	985(937)
[Pd(acac)(P''—C)]	94	White	160-161	54.5 (54.5)	7.05(7.1)	—	468(441)[e]

[a] L' = P-t-Bu(benzyl)$_2$, L'' = P-t-Bu$_2$(benzyl); (P'—C) = [$C_6H_4CH_2$P-t-Bu(benzyl)], (P''—C) = [$C_6H_4CH_2$P-t-Bu$_2$]. [b] Calcd. values in parentheses. [c] Chloroform solution except where stated. [d] Decomposed. [e] Benzene solution.

TABLE 2

^{1}H NMR[a] AND IR[b] DATA FOR THE COMPLEXES *trans*-[$PdX_2L'_2$], *trans*-[$PdX_2L''_2$] AND [$Pd_2Cl_4L'_2$]

Compound	τ(t-Bu)	$\lvert^3J(P—H) + {}^5J(P—H)\rvert$	$\tau(CH_2)^c$	$\lvert^2J(P—H) + {}^4J(P—H)\rvert$	ν(Pd—Cl)
trans-[$PdCl_2L''_2$]	8.40t	13.3	6.27t	7.0	342
trans-[$PdBr_2L''_2$]	8.43t	13.4	6.75t	10.5	—
trans-[$PdCl_2L'_2$]	8.59t	14.0	6.35m	*d*	337s
trans-[$PdBr_2L'_2$]	8.59t	14.7	*e*	*e*	—
		$^3J(P—H)$			
[$Pd_2Cl_4L'_2$]	8.51d	16.0	*f*	*f*	354s, 337s

[a] Spectra recorded at ca. 35°C and 60 MHz in $CDCl_3$ solution. [b] Spectra recorded from Nujol mulls (cm^{-1}). [c] t = 1/2/1 triplet, m = multiplet (see text). [b] Resonance not susceptible to first-order analysis (see text). [e] Complex multiplet centred at τ 6.17, width 57 Hz. [f] Complex multiplet centred at τ 6.40, width 65 Hz.

P-t-Bu(benzyl)$_2$ and the previously described P-t-Bu$_2$(benzyl) [9] and studied their reactions with palladium(II).

Results and discussion

P-t-Bu(benzyl)$_2$ (L') was prepared by adding t-butyldichlorophosphine to an excess of benzylmagnesium chloride in THF solution. P-t-Bu$_2$(benzyl) [9] (L'') was similarly prepared from di-t-butylchlorophosphine and benzyllithium. For our work, the benzyllithium was prepared by the Gilman method from benzyl methyl ether, and not by the metallation of toluene, which gives about 10% of ring metallated and polymetallated arenes, unless sec-butyllithium is used as the metallating agent.

The action of dibenzyl-t-butylphosphine on sodium tetrachloropalladite(II) in methanol rapidly gave the bright yellow complex, *trans*-[PdCl$_2${P-t-Bu(benzyl)$_2$}$_2$]. The *trans*-configuration follows from the far IR and ^{1}H NMR data (Table 2). The ^{1}H NMR spectrum contains a triplet assigned to the t-butyl group. The methylene protons are non-equivalent and, as expected, give a complex multiplet which could not be interpreted by first order analysis. Molecular weight measurements of *trans*-[PdCl$_2${P-t-Bu(benzyl$_2$)}$_2$] correspond well with the theoretical value and show no evidence of dissociation of the bulky phosphine ligand. In the related and isomeric compound *trans*-[PdCl$_2${P-t-Bu(*o*-tolyl)$_2$}$_2$] a low molecular weight measurement was attributed to either partial dissociation of the bulky phosphine ligand and/or internal metallation [7].

Treatment of *trans*-[PdCl$_2${P-t-Bu(benzyl)$_2$}$_2$] with lithium bromide or sodium iodide in acetone at room temperature readily gives the complexes *trans*-[PdX$_2${P-t-Bu(benzyl)$_2$}$_2$] (X = Br, I).

Benzyldi-t-butylphosphine reacted with a methanolic solution of sodium tetrachloropalladite(II) to give the bright yellow complex *trans*-[PdCl$_2${P-t-Bu$_2$-(benzyl)}$_2$]. The configuration follows from the far IR and ^{1}H NMR data (Table 2). For this complex the methylene hydrogens are equivalent and give a 1/2/1 triplet pattern.

It is more difficult to replace the chloride ligands by bromide or iodide in *trans*-[PdCl$_2${P-t-Bu$_2$(benzyl)}$_2$] than in the less-hindered complex *trans*-[PdCl$_2$-{P-t-Bu(benzyl)$_2$}$_2$]. Thus, although *trans*-[PdBr$_2${P-t-Bu$_2$(benzyl)}$_2$] is obtained in high yield (89%) by reaction of the dichloride with lithium bromide in refluxing ethyl methyl ketone after 1$\frac{1}{2}$ h, a similar treatment in acetone is incomplete after 22 h at reflux temperature. Similarly, when *trans*-[PdCl$_2${P-t-Bu$_2$-(benzyl)}$_2$] is treated with sodium iodide in acetone under reflux, little substitution takes place during 1 h. However, in the higher-boiling solvent 2-methoxyethanol, *trans*-[PdI$_2${P-t-Bu$_2$(benzyl)}$_2$] is produced after 20 min at reflux temperature, together with traces of a white (unidentified) product. The apparently low molecular weight for this complex (Table 1) suggested some dissociation of the very bulky phosphine ligand.

Formation of binuclear compounds and internal metallation

We find that the internal metallation of benzylphosphine ligands by palladium occurs only under vigorous conditions and differs strikingly from the ease with which such metallations are achieved with the isomeric palladium com-

TABLE 3

^{1}H NMR[a] AND IR[b] DATA FOR SOME INTERNALLY METALLATED PALLADIUM(II) COMPLEXES OF THE PHOSPHINES P-t-Bu$_2$(BENZYL) AND P-t-Bu(BENZYL)$_2$.

Compound[c]	τ(t-Bu)[d]	^3J(P—H)	τ(CH$_2$)	^2J(P—H)	ν(Pd—Cl)
[Pd$_2$Cl$_2$(P″—C)$_2$]	8.56d	14.0	6.76d	10.0	280m, 252s
[Pd$_2$Br$_2$(P″—C)$_2$]	8.62d	14.2	6.78d	10.7	—
[Pd$_2$I$_2$(P″—C)$_2$]	8.56d	14.3	6.66d	10.7	—
[Pdacac(P″—C)][e]	8.60d	10.0	6.85d	7.5	—
trans-[PdCl(P″—C)PPh$_3$]	8.55d	13.2	6.60d	9.6	284s
[Pd$_2$Cl$_2$(P′IC)$_2$]	8.62d	15.0	*f*	*f*	275s

[a] Spectra recorded at ca. 35°C and 60 MHz in $CDCl_3$ solution. [b] Spectra recorded from Nujol mulls (cm^{-1}). [c] (P″—C) = [$CH_2C_6H_4PBu^t_2$], (P′—C) = [$CH_2C_6H_4PBu^t$(benzyl)]. [d] d = 1/1 doublet. [e] τ Me(acac) 7.90, 8.10; τ H(acac) 4.52. [f] Complex multiplet centred at τ 6.46, width 78 Hz.

plexes of the *o*-tolylphosphines, P-t-Bu(*o*-tolyl)$_2$ and P-t-Bu$_2$(*o*-tolyl) [7]. Thus *trans*-[PdCl$_2${P-t-Bu(benzyl)$_2$}$_2$] was recovered unchanged after heating in refluxing 2-methoxyethanol for 1 day. However, we have shown that sodium acetate promotes internal metallation [10] and a refluxing 2-methoxyethanol solution of the complex in the presence of sodium acetate gradually becomes paler and after 1 day a cream-coloured precipitate may be isolated in low yield. This compound is formulated as [Pd$_2$Cl$_2$(P′—C)$_2$] [I, X = Cl; (P′—C) = $C_6H_4CH_2$P-t-Bu(benzyl)] on the basis of analytical, molecular weight and far IR data (Tables 1 and 3). The comparative slowness of this internal metallation reaction is shown by the recovery of *trans*-[PdCl$_2${P-t-Bu(benzyl)$_2$}$_2$] both after 4 h at reflux temperature in 2-methoxyethanol in the presence of excess sodium acetate, or after 20 h at reflux temperature in ethanol in the presence of an equimolar amount of triethylamine; no internally metallated product could be isolated in either case.

The non-metallated binuclear complex [Pd$_2$Cl$_4${P-t-Bu(benzyl)$_2$}$_2$] is obtained either by treatment of Na_2PdCl_4 with one molar equivalent of t-butyldibenzylphosphine, or from equimolar mixtures of Na_2PdCl_4 and *trans*-[PdCl$_2$-{P-t-Bu(benzyl)$_2$}$_2$]. The far IR spectrum of [Pd$_2$Cl$_4${P-t-Bu(benzyl)$_2$}$_2$] (Table 2) shows typical values of ν(Pd—Cl) for complexes of this type while the ^{1}H NMR spectrum (Table 2) shows a 1/1 doublet for the t-butyl resonance as expected. Treatment of *trans*-[PdCl$_2${P-t-Bu(benzyl)$_2$}$_2$] with chloride solution slowly gave the same complex, [Pd$_2$Cl$_4${P-t-Bu(benzyl)$_2$}$_2$].

A red solution of [Pd$_2$Cl$_4${P-t-Bu(benzyl)$_2$}$_2$] in 2-methoxyethanol appeared unchanged after 16 h at reflux temperature. However, subsequent addition of sodium acetate to this refluxing solution caused the deposition of a palladium mirror and, after a further 25 h at reflux temperature, a low-yield (15%) of [Pd$_2$Cl$_2$(P′—C)$_2$] was isolated. The slowness of this internal metallation reaction again contrasts with the behaviour of the corresponding *o*-tolyl complex [Pd$_2$Cl$_4${P-t-Bu(*o*-tolyl)$_2$}$_2$] which rapidly gives the cream complex [Pd$_2$Cl$_2${$CH_2C_6H_4$P-t-Bu(*o*-tolyl)}$_2$] [7].

The ligand di-t-butylbenzylphosphine undergoes internal metallation with palladium(II) more readily than does t-butyldibenzylphosphine especially in the presence of sodium acetate. Thus when the yellow complex, *trans*-[PdCl$_2$-

(P-t-Bu_2benzyl)$_2$], was heated in 2-methoxyethanol under reflux for 5 days the cream-coloured complex [Pd_2Cl_2(P″—C)$_2$] (I, X = Cl; (P″—C) = $C_6H_4CH_2$P-t-Bu_2) was isolated in 64% yield. The formulation is based upon analytical, molecular weight and far IR data (Tables 1 and 3). When P-t-Bu_2(benzyl) is metallated there is a marked shift of the ^{31}P NMR resonance to low field, from δ = —33.8 (free ligand) to δ = —102.1{[Pd_2Cl_2(P″—C)$_2$]} relative to 85% H_3PO_4. This is possibly because on metallation the methylene protons are forced to point at the t-Bu groups. This will cause the C—P—C angle to increase and give a marked low-field shift. When *trans*-[$PdCl_2${P-t-Bu_2(benzyl)$_2$}] together with an excess of sodium acetate was heated to reflux temperature in 2-methoxyethanol the colour of the mixture rapidly lightened and after 1½ h [Pd_2Cl_2(P″—C)$_2$] was isolated in 75% yield.

Triethylamine will also promote the internal metallation reaction of *trans*-[$PdCl_2${P-t-Bu_2(benzyl)}$_2$]. Thus when the dichloride is boiled in dekalin in the presence of triethylamine [Pd_2Cl_2(P″—C)$_2$] is formed in 64% yield, although under similar conditions (15 h), refluxing dekalin) in the absence of triethylamine the starting material, *trans*-[$PdCl_2${P-t-Bu_2(benzyl)}$_2$] is recovered unchanged. The complex, *trans*-[$PdCl_2${P-t-Bu_2(benzyl)}$_2$] is also stable in refluxing chloroform (5 h) and is recovered unchanged from either refluxing n-propanol (6½ h) or after shorter periods (4 h) in refluxing 2-methoxyethanol. This contrasts with the behaviour of the isomeric *o*-tolyl phosphine complex, *trans*-[$PdCl_2${P-t-Bu_2(*o*-tolyl)}$_2$], which undergoes rapid internal metallation in deuteriochloroform even at 35°C [4].

Metathesis of the binuclear metallated complex [Pd_2Cl_2(P″—C)$_2$] with lithium bromide or sodium iodide in acetone at room temperature yield the complexes [Pd_2X_2(P″—C)$_2$] (X = Br, I; configuration I). See Tables for analytical and spectroscopic data.

(I)

Treatment of a suspension of [Pd_2Cl_2(P″—C)$_2$] in benzene with thallous acetylacetonate gave the complex [Pd(P″—C)acac] as very soluble white needles (Table 1). The ^{1}H NMR spectrum (Table 3) is consistent with the assigned structure.

Attempts were made to split the chlorine bridges of [Pd_2Cl_2(P″—C)$_2$] using P-t-Bu_2(benzyl). For example, a suspension of [Pd_2Cl_2(P″—C)$_2$] was treated with P-t-Bu_2(benzyl) in refluxing benzene for 5 min, but only unreacted starting material could be recovered. Treatment of a solution of the complex in refluxing dichloromethane with P-t-Bu_2(benzyl) for 75 min also gave only unreacted starting material. Similar attempts to prepare complexes of the type *trans*-[PdCl(P—C)L] [where L = P-t-Bu_2(*o*-tolyl), P-t-Bu(*o*-tolyl)$_2$] have not been successful. The analogous platinum complexes are all known [11] and the inability to form the palladium complexes may be due to greater crowding about the metal atom in the Pd case.

Factors affecting intramolecular metal—carbon bond formation have previously been discussed [6,12]. In accordance with the dependence on steric hindrance which was observed, we find that the more bulky P-t-Bu_2(benzyl) is

more readily metallated than is P-t-Bu(benzyl)$_2$. Work on amine complexes of palladium, in which the primary and secondary amines Ph_3CNH_2 and $Ph_3CN(H)$-Me have been metallated [13], supports earlier inferences that steric hindrance is a contributory factor in the internal metallation of amines as well as in that of phosphines.

Thus we find that palladium complexes of the benzylphosphines P-t-Bu$_2$ (benzyl) and P-t-Bu(benzyl)$_2$ do not undergo internal metallation under the mild conditions which are sufficient for the analogous *o*-tolyl phosphines P-t-Bu$_2$-(*o*-tolyl) and P-t-Bu(*o*-tolyl)$_2$. Since a 5-membered ring is formed in each case we suggest that the differences are largely electronic and not steric. Interestingly the methyl group of 8-methylquinoline is metallated by platinum but 2-phenylpyridine gives only pyridinium salts [14].

Experimental

Melting points were determined on a Köfler hot-stage apparatus and are corrected. All operations involving free tertiary phosphines, organolithium or Grignard reagents, or heating under reflux were carried out under argon. Percentage yields, melting points analytical and molecular weight data are given in the Tables.

Molecular weights were determined on a Hitachi—Perkin Elmer 115 apparatus in chloroform at 30°C. IR spectra were recorded on a Perkin—Elmer 257 spectrometer (4000-250 cm^{-1}) and on Grubb—Parsons DB3/DN2 or DM4 spectrometers (400-200 cm^{-1}).

^1H NMR spectra were recorded on a Perkin—Elmer R12 60 MHz spectrometer at ca. 34°C. ^{31}P NMR spectra were recorded in CH_2Cl_2 solution on a Bruker Spectrospin HFX spectrometer at ambient temperatures and 36.43 MHz with all ^1H nuclei decoupled.

t-Butyldibenzylphosphine

An ethereal solution of benzylmagnesium chloride was made from magnesium (30 g, 1.25 g.atom) and benzyl chloride (126 g, 1 mol) in ether (1 l). The volume of ether was reduced to about 250 ml and THF (250 ml) was added. The mixture was cooled to —60°C and t-butyldichlorophosphine (50.1 g, 0.32 mol) in THF (120 ml) was added dropwise during 1.5 h. The mixture was stirred for a further 4 h while it warmed to room temperature. The THF was distilled off and ether (800 ml) was added to the cooled residue. The mixture was hydrolysed with an aqueous solution of ammonium chloride (1 l) and the ether layer was siphoned off and dried ($MgSO_4$). Ether was removed at atmosphere pressure and the residue was distilled to give white crystals of t-butyldibenzylphosphine (66.9 g, 80%), b.p. 173°C/3 mmHg, m.p. 74°C. ^1H NMR (C_6H_6 solution). τ(t-Bu) = 9.06d, ^3J(P—H) = 11.0 Hz; $\tau(CH_2)$ = 7.29d, ^2J = 2.2 Hz.

t-Butyldibenzylmethylphosphonium iodide

Iodomethane (1.4 ml, 20.5 mmol) was added to a solution of t-butyldibenzylmethylphosphine (0.56 g, 2.05 mmol) in acetone (20 ml). White needles of the product (0.49 g) were formed almost immediately (60%) m.p. 278°C. (Found: C, 55.55; H, 6.35. $C_{19}H_{26}IP$ calcd.: C, 55.35; H, 6.35%). Molar conductivity in ca. 10^{-3} *M* nitrobenzene solution of 22°C was 36.5 $cm^2\ \Omega^{-1}$.

trans-Dichlorobis(t-butyldibenzylphosphine)palladium(II)

A mixture of sodium chloropalladite (1.8 g, 6.0 mmol) and t-butyldibenzylphosphine (3.4 g, 12.6 mmol) in methanol (50 ml) and benzene (10 ml) was shaken at room temperature for 1 h. The precipitate was washed with water and recrystallised from dichloromethane/methanol to give yellow prisms of the product (3.65 g).

trans-Dibromobis(t-butyldibenzylphosphine)palladium(II)

A mixture of *trans*-dichlorobis(t-butyldibenzylphosphine)palladium(II) (0.18 g, 0.25 mmol) and lithium bromide (0.39 g, 4.44 mmol) in acetone (35 ml) was set aside at room temperature for 24 h. Acetone was evaporated under reduced pressure and the residue was washed with water to give the product (0.16 g).

trans-Di-iodobis(t-butyldibenzylphosphine)palladium(II)

The compound was prepared in a similar manner from the dichloro-complex and an excess of sodium iodide.

sym-Di-μ-chlorodichlorobis(t-butyldibenzylphosphine)dipalladium(II)

A suspension of t-butyldibenzylphosphine (0.27 g, 1.0 mmol) in benzene (1 ml) and n-propanol (10 ml) was added to a solution of sodium tetrachloropalladite(II) (0.37 g, 1.0 mmol) in methanol (4 ml) and the mixture was heated to reflux for 16 h. The resultant red solution was filtered to remove a trace of black material. Solvent was removed under reduced pressure and the residue was washed with water to give the product as prisms (0.38 g, 86%) from dichloromethane/methanol.

sym-Di-μ-chlorobis-[o-(benzyl-t-butylphosphinomethyl)phenyl]dipalladium(II)

A mixture of *trans*-dichlorobis(t-butyldibenzylphosphine)palladium(II) (1.54 g, 1.88 mmol) and sodium acetate (2.78 g, 32.3 mmol) was heated under reflux in 2-methoxyethanol (35 ml) for 24 h. On cooling a cream-coloured solid separated, together with much brown material. This mixture was recrystallised three times from dichloromethane/methanol to give the product (0.27 g).

Action of sodium acetate on sym-di-μ-chlorodichlorobis(t-butyldibenzylphosphine)dipalladium(II)

sym-trans-Di-μ-chlorodichlorobis(t-butyldibenzylphosphine)dipalladium(II) was prepared in situ from *trans*-dichlorobis(t-butyldibenzylphosphine)palladium(II) (0.72 g, 1.00 mmol) and sodium tetrachloropalladite(II) (0.29 g, 1.00 mmol) in 2-methoxyethanol (35 ml). The mixture was heated under reflux for 16 h with no apparent change. Sodium acetate (1.14 g, 13.90 mmol) was added and the mixture was heated under reflux for 23 h. A palladium mirror was formed. The metal was separated and the mixture, now pale pink, was heated under reflux for a further 2 h. On being cooled, the solution deposited white crystals of *sym-trans*-di-μ-chlorobis-[*o*-(benzyl-t-butylphosphinomethyl)-phenyl]dipalladium(II) (0.12 g, 15%).

trans-Dichlorobis(benzyldi-t-butylphosphine)palladium(II)

Benzyldi-t-butylphosphine (4.5 ml, 19 mmol) was added to a solution of sodium tetrachloropalladite (3.12 g, 8.53 mmol) in methanol (50 ml) and the mixture was shaken at room temperature for 3 h. The yellow precipitate was filtered off and washed with water and then a little ethanol. Recrystallisation from dichloromethane/methanol gave bright-yellow prisms of the product (4.55 g).

trans-Dibromobis(benzyldi-t-butylphosphine)palladium(II)

A mixture of *trans*-dichlorobis(benzyldi-t-butylphosphine)palladium(II) (0.45 g, 0.69 mmol) and lithium bromide (0.16 g, 1.84 mmol) in ethyl methyl ketone (30 ml) was heated under reflux for 1¼ h. The solvent was evaporated under reduced pressure and the residue was washed with water to give the product (0.45 g).

trans-Di-iodobis(benzyldi-t-butylphosphine)palladium(II)

A mixture of *trans*-dichlorobis(benzyldi-t-butylphosphine)palladium(II) (0.65 g, 1.00 mmol) and sodium iodide (1.0 g, 6.67 mmol) in 2-methoxyethanol (75 ml) was heated under reflux for 20 min. The mixture was filtered hot and the residue was washed with water and then dissolved in excess dichloromethane. Light petroleum (b.p. 40-60°C) was added to precipitate traces of white material (m.p. 198-200°C). The solvents were removed under reduced pressure and the residue was recrystallised from dichloromethane/light petroleum (b.p. 40-60°C) to give the product (0.59 g).

sym-Di-μ-chlorobis-[o-(di-t-butylphosphinomethyl)phenyl]dipalladium(II)

A mixture of *trans*-dichlorobis(benzyldi-t-butylphosphine)palladium(II) (0.38 g, 0.58 mmol) and sodium acetate (1.69 g, 20 mmol) was suspended in 2-methoxyethanol (15 ml) and heated under reflux for 30 min to give a pale yellow solution. Water (50 ml) was added and the precipitated solid was filtered off and recrystallised from dichloromethane/light petroleum (b.p. 80-100°C) to give pale yellow prisms of the product (0.33 g).

sym-Di-μ-bromobis-[o-(di-t-butylphosphinomethyl)phenyl]dipalladium(II)

sym-Di-μ-chlorobis-[*o*-di-t-butylphosphinomethyl)phenyl]dipalladium(II), (0.31 g, 0.42 mmol) and lithium bromide (0.40 g, 4.60 mmol) in acetone (30 ml) were set aside at room temperature for 20 h. The solvent was evaporated under reduced pressure and the residue was washed with water to leave the product (0.28 g).

sym-Di-μ-iodobis-[o-(di-t-butylphosphinomethyl)phenyl]dipalladium(II)

The compound was prepared similarly using sodium iodide.

Acetylacetonate-[o-(di-t-butylphosphinomethyl)phenyl]palladium(II)

A mixture of *sym*-di-μ-chlorobis-[*o*-(di-t-butylphosphinomethyl)phenyl]-dipalladium(II) (0.32 g, 0.42 mmol) and thallous acetylacetonate (0.25 g, 0.85 mmol) was shaken in benzene (25 ml) at room temperature for 2½ h. Thallous chloride was filtered off and the benzene solution was evaporated to give a

yellow oil which was crystallised from methanol to give white prisms of the product (0.34 g).

Action of triethylamine on trans-dichlorobis(benzyldi-t-butylphosphine)palladium(II) in refluxing dekalin

trans-Dichlorobis(benzyldi-t-butylphosphine)palladium(II) (0.35 g, 0.54 mmol) and triethylamine (150 μl, 1.08 mmol) were heated in refluxing dekalin for 17 h. Crystals of triethylamine hydrochloride sublimed around the neck of the flask. The solvent was removed under reduced pressure and the residue was recrystallised from dichloromethane/methanol to give pale yellow crystals of *sym*-di-μ-chlorobis-[*o*-(di-t-butylphosphinomethyl)phenyl]dipalladium(II) (0.13 g, 64%).

sym-Di-μ-chlorobis-[o-(di-t-butylphosphinomethyl)phenyl]dipalladium(II)

trans-Dichlorobis(benzyldi-t-butylphosphine)palladium(II) (0.40 g, 0.62 mmol) was heated in boiling 2-methoxyethanol (30 ml) for 5 days. The solvent (30 ml) for 5 days. The solvent was removed under reduced pressure and the residue was recrystallised from dichloromethane/methanol to give the product (0.16 g, 64%) identified by its IR spectrum.

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