# Complexes of Platinum and Palladium with Tertiary Dimethoxyphenylphosphines: Attempts to Effect *O*- or *C*-Metallation

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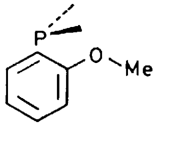
The new tertiary phosphines $PBu^t_2R$ and $PPh_2R$ (R = 2,3- or 2,6-dimethoxyphenyl) are described and characterized. The compound $PPh_2[C_6H_3(OMe)_2\text{-}2,6]$ reacts with $BBr_3$ followed by acetic anhydride to give $PPh_2[C_6H_3(OCOMe)_2\text{-}2,6]$. Conformational and steric effects of these new ligands are discussed and, as expected, bulky phosphines are demethylated more readily than less bulky ones on complex formation with platinum; 2,6-dimethoxyphenylphosphines lose one methyl group particularly easily on complex formation, 2,3-dimethoxyphenylphosphines less readily. Stable complexes of the type *cis*-$[Pt\{OC_6H_3(OMe)(PPh_2)\}_2]$ and *trans*-$[Pt\{OC_6H_3(OMe)(PBu^t_2)\}_2]$ have been prepared, where the ligand chelates through the phenoxo-oxygen and the phosphinophosphorus atoms. The dichelate *cis*-$[Pt\{OC_6H_3(OMe\text{-}6)(PPh_2\text{-}2)\}_2]$ is reduced by $Na[BH_4]$ to the hydride $[PtH\{OC_6H_3(OMe\text{-}3)(PPh_2\text{-}2)\}\{PPh_2[C_6H_3(OH\text{-}2)(OMe\text{-}6)]\}]$. Although several palladium complexes of the above ligands have been prepared, attempts to effect *O*-metallation have been unsuccessful, palladium metal being obtained. *O*-Metallation is favoured by a polar solvent, but in xylene $PPh_2[C_6H_3(OMe)_2\text{-}2,6]$ reacts with $[PtCl_2(NCPh)_2]$ to give the *C*-metallated complex $[Pt_2Cl_2\{CH_2OC_6H_3(OMe\text{-}3)(PPh_2\text{-}2)\}_2]$, several derivatives of which have been prepared. Attempts to effect di-*C*-metallation have been unsuccessful; on heating the complex *cis*-$[PtMe_2\{PPh_2[C_6H_3(OMe)_2\text{-}2,6]\}_2]$ methane is evolved but crystalline products have not been isolated. Hydrogen-1 n.m.r. and i.r. data are given.

We have reported that 2-methoxyphenylphosphines undergo *O*- or *C*-metallation with platinum(II) and that these metallations are promoted by steric effects.[1,2] Thus 2-methoxyphenyldi-t-butylphosphine, $PBu^t_2(C_6H_4OMe\text{-}2)$, is metallated much more readily than $PPh_2(C_6H_4OMe\text{-}2)$, and $PMe_2(C_6H_4OMe\text{-}2)$ could not be metallated. We also showed by n.m.r. spectroscopy that in solution $PBu^t_2(C_6H_4OMe\text{-}2)$ exists as two conformers (1) and (2), due to restricted rotation around the phosphorus–aryl bond. The two conformers (1) and (2) are present in similar amounts. When complexed to a metal halide such as platinum(II) dichloride, however, one would expect the configuration (3) to be very much preferred to (4) because of steric interaction with the chloride ligands. In these configurations one chloride ligand is *gauche* with respect to the two t-butyl groups and the other chloride is in close proximity to an *o*-hydrogen in (3) or an *o*-methoxy-group in (4). Only configuration (4) would lead to *O*-metallation. The less bulky $PPh_2(C_6H_4OMe\text{-}2)$ would presumably show similar effects although, at room temperature, n.m.r. spectroscopy does not show analogous conformers to (1) and (2). (We have not investigated low-temperature spectra.)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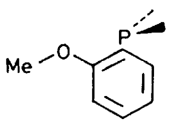
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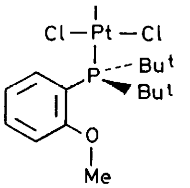
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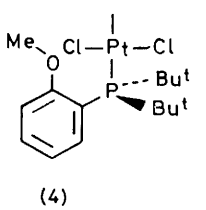
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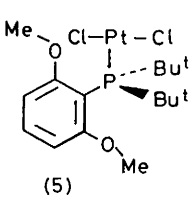
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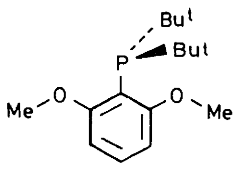
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We have now investigated the even more bulky 2,3- and 2,6-dimethoxyphenyl ligands $PBu^t_2R$ and $PPh_2R$ [$R = C_6H_3(OMe)_2\text{-}2,3$ or -2,6]. With the very bulky $PBu^t_2[C_6H_3(OMe)_2\text{-}2,6]$ complexed to $PtCl_2$ one would expect that one methoxy-group must be held in close proximity to a chlorine as shown in (5) and therefore that *O*-metallation (and also *C*-metallation) would occur more readily than with $PBu^t_2(C_6H_4OMe\text{-}2)$. (The greater bulk caused by the additional methoxy-group would also promote metallation.) Similarly $PPh_2[C_6H_3(OMe)_2\text{-}2,6]$ should be metallated more readily than $PPh_2(C_6H_4OMe\text{-}2)$. It was difficult to predict the behaviour of the 2,3-dimethoxyphenylphosphines but one would expect an increased steric interaction between the 2-methoxy-group and either the metal or the $PR_2$ group by a 'buttressing effect' of the 3-methoxy-group. It was also difficult to predict whether there would be significant electronic effects due to the additional methoxy-groups.

## RESULTS AND DISCUSSION

*Preparation of the Tertiary Phosphines.*—The new tertiary phosphines, $PBu^t_2R$ and $PPh_2R$ (R = 2,3- or 2,6-dimethoxyphenyl) were prepared by treating $PBu^t_2Cl$ or $PPh_2Cl$ with the appropriate organolithium reagent. 2,6-Dimethoxyphenyl-lithium was prepared by the reaction of n-butyl-lithium and *NNN'N'*-tetramethylethylenediamine (tmen) with 1,3-dimethoxybenzene. This preparation takes 30 min using tmen compared with *ca.* 72 h without tmen. However, the formation of 2,3-dimethoxyphenyl-lithium takes only 30 min even without using tmen. Steric effects possibly cause the metallation of 1,3-dimethoxybenzene to be slow. It was necessary to reflux chlorodi-t-butylphosphine with these sterically hindered organolithium reagents for several hours for complete reaction: chlorodiphenylphosphine required much less vigorous conditions.

We also studied the demethylation of 2,6-dimethoxyphenyldiphenylphosphine. Refluxing in the presence of 45% aqueous hydrobromic acid caused incomplete

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[1] C. E. Jones, B. L. Shaw, and B. L. Turtle *J.C.S. Dalton*, 1974, 992.

[2] H. D. Empsall, B. L. Shaw, and B. L. Turtle, *J.C.S. Dalton*, 1976, 1500.

demethylation, and refluxing in concentrated hydriodic acid led to decomposition. However, boron tribromide at −78 °C,[3] followed by acetic anhydride at 20 °C, gave 2,6-diacetoxyphenyldiphenylphosphine in 65% yield. We were unable to isolate dihydroxyphenyldiphenylphosphine after the first stage of the reaction. Although we did not study this diacetoxyphosphine as a ligand, we report its preparations here since the use of $BBr_3$ to effect demethylation of methoxyphenylphosphines has not been reported before. All the new tertiary phosphines have been fully characterized as their corresponding methiodides (see Experimental section and Table 1). The more salient features of the $^1H$ n.m.r. spectra of the new tertiary phosphines (data in Table 1) are discussed below. The $^1H$ n.m.r. spectra of the tertiary t-butylphosphines $PBu^t{}_2R$ (R = 2,3- or 2,6-dimethoxyphenyl) and their corresponding phosphonium salts show doublets for the t-butyl groups with $^3J(PH)$ increasing from $P^{III}$ to $P^V$. The methoxy-groups of $PPh_2[C_6H_3(OMe)_2\text{-}2,6]$ resonate as a singlet, but for $PBu^t{}_2[C_6H_3(OMe)_2\text{-}2,6]$ they are non-equivalent and separated by *ca.* 0.05 p.p.m. The same phenomenon occurs with the two respective methiodide salts. As discussed above, the very bulky t-butyl groups cause restricted rotation around the phosphorus–aryl bond rendering the methoxy-groups non-equivalent, as in (6). In $PPh_2[C_6H_3(OMe)_2\text{-}2,6]$ the methoxy-groups are magnetically equivalent. The $^1H$ n.m.r. spectrum of 2,6-diacetoxyphenyldiphenylphosphine shows a singlet for the two equivalent acetoxy-groups as does its methiodide salt. The methyl resonances of the methiodide salts of the above phosphines are doublets, $^2J(PH)$ *ca.* 13.5 Hz for the aryldiphenylphosphines and 11—12 Hz for the aryldi-t-butylphosphines.

TABLE 1

Analytical, boiling (melting) point, and $^1H$ n.m.r. data for some new tertiary phosphines and their quaternary salts [a]

| Compound | Yield (%) | Analysis [b] (%) C | H | M.p. ($\theta_c$/°C) | $^1H$ N.m.r. (δ/p.p.m.) [c] OMe | Bu[t] [d] | P–Me [e] |
|---|---|---|---|---|---|---|---|
| $PPh_2[C_6H_3(OMe)_2\text{-}2,6]$ | 76 | | | 108—113 | 3.41(s) | | |
| $PPh_2[C_6H_3(OMe)_2\text{-}2,3]$ | 77 | | | 121—123 | 3.82(s), 3.70(s) | | |
| $PPh_2[C_6H_3(OCOMe)\text{-}2,6]$ [f] | | | | | | | |
| $[PMePh_2\{C_6H_3(OMe)_2\text{-}2,6\}]I$ | 88 | 54.5 (54.3) | 4.7 (4.8) | 184—185 | 3.66(s) | | 3.02(d) (13.6) |
| $[PMePh_2\{C_6H_3(OMe)_2\text{-}2,3\}]I$ | 89 | 54.15 (54.3) | 4.95 (4.8) | 158—162 | 3.98(s), 3.56(s) | | 3.04(d) (13.7) |
| $[PMePh_2\{C_6H_3(OCOMe)_2\text{-}2,6\}]I$ [g] | | | | | | | 3.20(d) (13.1) |
| $PBu^t{}_2[C_6H_3(OMe)_2\text{-}2,6]$ | 77 | | | 128—134 (0.35 mmHg) | 3.81(s), 3.75(s) | 1.17(d) (12.5) | |
| $PBu^t{}_2[C_6H_3(OMe)_2\text{-}2,3]$ | 64 | | | 120—122 [h] (0.15 mmHg) | 3.83(s) | 1.26(d) (11.8) | |
| $PMeBu^t{}_2[C_6H_3(OMe)_2\text{-}2,6]I$ | 77 | 48.5 (48.15) | 7.15 (7.15) | 188—191 | 4.02(s), 3.97(s) | 1.50(d) (16.8) | 2.40 (11.9) |
| $PMeBu^t{}_2[C_6H_3(OMe)_2\text{-}2,3]I$ | 83 | 48.4 (48.15) | 6.9 (7.15) | 185—188 | 4.15(s), 3.96(s) | 1.51(d) (16.2) | 2.38 (11.0) |

[a] All the compounds are colourless. [b] Calculated values are given in parentheses. [c] Recorded at *ca.* 35 °C and 60 MHz in deuteriochloroform solutions. δ ± 0.02 p.p.m., *J* ± 0.5 Hz. s = singlet; d = doublet. [d] Values of $^3J(PH)$ are given in parentheses. [e] Values of $^2J(PH)$ are given in parentheses. [f] $OCOCH_3$, δ 1.77(s) p.p.m. [g] $OCOCH_3$, δ 1.59(s) p.p.m. [h] Boiling point.

TABLE 2

Melting-point, analytical, and spectral data for the palladium complexes

| Complex | Yield (%) | Colour | M.p.[a] ($\theta_c$/°C) | Analysis [b] (%) C | H | Halogen | $^1H$ N.m.r.[c] δ(OMe) | δ(Me) | ν(Pd–Cl) [d] |
|---|---|---|---|---|---|---|---|---|---|
| $L = PPh_2[C_6H_3(OMe)_2\text{-}2,6]$ | | | | | | | | | |
| *trans*-$[PdCl_2L_2]$ | 87 | Yellow | 298—300 | 58.65 (58.45) | 4.7 (4.6) | 8.65 (8.5) | 3.48 | | 360 |
| *trans*-$[PdI_2L_2]$ | 89 | Red | 205—210 | 47.8 (47.8) | 4.0 (3.8) | 25.35 (25.25) | 3.40 | | |
| *sym-trans*-$[Pd_2Cl_4L_2]$ | 80 | Red | 240—250 | 47.8 (48.05) | 3.85 (3.85) | 14.0 (14.2) | Too insoluble | | 350, 294, 258 |
| *trans*-$[PdCl_2(4Me\text{-}py)L]$ | 91 | Yellow | 172—176 | 52.95 (52.7) | 4.4 (4.4) | | 3.62 | 2.32 | 345 |
| $L' = PPh_2[C_6H_3(OMe)_2\text{-}2,3]$ | | | | | | | | | |
| *trans*-$[PdCl_2L'_2]$ | 92 | Yellow | 295—298 | 58.4 (58.4) | 4.6 (4.65) | 8.8 (8.6) | Too insoluble | | 359 |
| *trans*-$[PdI_2L'_2]$ | 89 | Orange | 201—205 | 47.6 (47.8) | 3.8 (3.8) | 25.1 (25.25) | $\begin{cases}3.73\\3.34\end{cases}$ | | |

[a] With decomposition. [b] Calculated values are given in parentheses. [c] In p.p.m.; recorded at 60 MHz and 35 °C in $CDCl_3$ solution. [d] As Nujol mulls ($cm^{-1}$); all the bands due to ν(Pd-Cl) were strong or very strong.

*Preparation of the Complexes.*—Although $PR_2(C_6H_4\text{-}OMe\text{-}2)$ (R = Ph or Bu[t]) undergo *O*- or *C*-metallation with platinum, we have been unsuccessful in effecting similar reactions with palladium, either the unmetallated species being obtained or decomposition occurring (giving palladium metal). The new palladium complexes *trans*-$[PdX_2L_2]$ $\{L = PPh_2[C_6H_3(OMe)_2\text{-}2,3]$ or $PPh_2[C_6H_3(OMe)_2\text{-}2,6]\}$ were made and characterized by standard methods (Table 2). On heating these complexes in 2-methoxyethanol, decomposition to palladium metal occurred and we were unable to isolate any metallated species. Nor were we able to isolate metallated species using lower-boiling solvents (ethanol or toluene). Either decomposition to metal occurred and/or the complex was recovered unchanged. These complexes also decomposed to palladium metal on heating with sodium iodide in 2-methoxyethanol. Also, treatment of $[PdCl_2(NCPh)_2]$ with $PPh_2[C_6H_3(OMe)_2\text{-}2,6]$ (1 : 1 proportion) in boiling xylene caused decomposition. In dichloromethane these two compounds reacted to give the very insoluble binuclear species $[Pd_2Cl_4L_2]$ which with 4-methylpyridine (4Me-py) gave the soluble mononuclear species $[PdCl_2(4Me\text{-}py)L]$ having mutually *trans* chloride ligands since only one i.r. absorption band due to ν(Pd–Cl) was present (at 345 $cm^{-1}$), a value characteristic of mutually *trans* chloride

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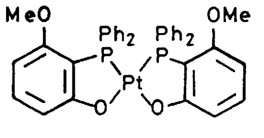
[3] E. Haslam, in ' Protective Groups in Organic Chemistry,' ed. J. F. W. McOmie, Plenum, London, 1973, p. 158.

ligands on $Pd^{II}$.[4] The $^{31}P$ n.m.r. spectrum ($CDCl_3$) showed only one resonance, a singlet at δ 12.1 p.p.m.; *i.e. cis* and *trans* isomers were not present in solution. Attempts to prepare palladium complexes with the tertiary di-t-butylphosphine ligands described above led to decomposition and the formation of palladium metal.

The platinum complexes of type *trans*-$[PtX_2L_2]$ {X = Cl or I; L = $PPh_2[C_6H_3(OMe)_2$-2,6] or $PPh_2$-$[C_6H_3(OMe)_2$-2,3]} were prepared and characterized by standard methods (see Experimental section and Table 3).

On heating $[PtCl_2\{PPh_2[C_6H_3(OMe)_2\text{-}2,6]\}_2]$ to 300 °C, methyl chloride was evolved (identified by its i.r. spectrum) and the very stable *cis*-bis[2-(diphenylphosphino)-3-methoxyphenoxo-*OP*]platinum(II), (7), was formed. A corresponding complex (8) was obtained with $[PtCl_2\{PPh_2[C_6H_3(OMe)_2\text{-}2,3]\}_2]$. These two complexes were too insoluble for n.m.r. studies but are assigned a *cis* stereochemistry by analogy with *cis*-bis[2-(diphenylphosphino)phenoxo]platinum(II).[1] They were also produced by heating $[PtX_2\{PPh_2[C_6H_3(OMe)_2\text{-}2,6]\}_2]$ or $[PtX_2\{PPh_2[C_6H_3(OMe)_2\text{-}2,3]\}_2]$ (X = Cl or I) in 2-methoxyethanol. As expected, complexes of $PPh_2[C_6H_3(OMe)_2$-2,6] were *O*-metallated much faster than corresponding complexes of $PPh_2(C_6H_4OMe$-2), *e.g.* the di-iodide was *O*-metallated completely in boiling acetone (25 h) whereas the di-iodide of $PPh_2(C_6H_4$-OMe-2) was recovered unchanged after this treatment. In contrast, $[PtI_2\{PPh_2[C_6H_3(OMe)_2\text{-}2,3]\}_2]$ required 50 h reflux in 2-methoxyethanol in order to effect *O*-metallation to (8).



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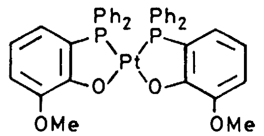

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TABLE 3

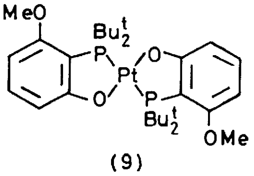
Melting-point, analytical, and spectral data for complexes of type $PtX_2L_2$ and *O*-metallated complexes

| | | | | Analysis (%) [a] | | | | ¹H N.m.r. [b] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Complex | Yield (%) | Colour | M.p. ($\theta_c$/°C) | C | H | Halogen | *M* [a] | δ(OMe) | Other assignments | $\tilde{\nu}$(Pt–Cl) [c] |
| L = $PPh_2[C_6H_3(OMe)_2$-2,6] | | | | | | | | | | |
| *trans*-$[PtCl_2L_2]$ | 96 | Yellow | 295—300 [d] | 52.65 (52.75) | 4.2 (4.2) | 7.8 (7.85) | | 3.35 | | 339 |
| *trans*-$[PtI_2L_2]$ | 93 | Orange | 185—194 [d] | 44.35 (43.9) | 3.55 (3.5) | 22.6 (23.2) | | 3.40 | | |
| *cis*-$[Pt\{OC_6H_3(OMe\text{-}3)(PPh_2\text{-}2)\}_2]$ (7) | 95 | White | 325 | 56.05 (56.35) | 4.1 (4.0) | | | | | |
| *trans*-$[PtH\{OC_6H_3(OMe\text{-}3)(PPh_2\text{-}2)\}$-$\{PPh_2[C_6H_3(OH\text{-}2)(OMe\text{-}6)]\}]$ | 77 | White | 152—154 [d] | 58.25 (57.9) | 4.3 (4.4) | | 830(851) | | δ(O–H) 10.54<br>δ(Pt–H) −20.0(t), $^2J$(P–H) 15, $^1J$(Pt–H) 1 180 | |
| *cis*-$[PtL_2Me_2]$ | 79 | White | 183—189 [e] | 57.7 (58.0) | 5.05 (5.1) | | 844(870) | | | |
| L′ = $PPh_2[C_6H_3(OMe)_2$-2,3] | | | | | | | | | | |
| *trans*-$[PtCl_2L'_2]$ | 98 | Yellow | 263—265 [d] | 52.75 (52.75) | 4.15 (4.20) | | | Too insoluble | | 346 |
| *trans*-$[PtI_2L'_2]\cdot CH_2Cl_2$ | 98 | Orange | 145—148 [d] | 42.2 (41.8) | 3.4 (3.4) | 21.55 (21.7) (I)<br>5.35 (6.0) (Cl) | | 3.79, 3.52 | | |
| *cis*-$[Pt\{OC_6H_3(OMe\text{-}6)(PPh_2\text{-}2)\}]$ (8) | 98 | White | 325 | 56.3 (56.35) | 3.95 (4.0) | | | | | |
| L = $PBu^t{}_2[C_6H_3(OMe)_2$-2,6] | | | | | | | | | | |
| *trans*-$[Pt\{OC_6H_3(OMe\text{-}3)(PBu^t{}_2\text{-}2)\}]$ (9) | 70 | White | 308—315 [f] | 49.1 (49.4) | 6.7 (6.65) | | 723(730) | 3.78 | δ(Bu$^t$) 1.51(t)<br>\|$^3J$(P–H) + $^5J$(P–H)\|15.0 | |
| L′ = $PBu^t{}_2[C_6H_3(OMe)_2$-2,3] | | | | | | | | | | |
| *trans*-$[Pt\{OC_6H_3(OMe\text{-}6)(PBu^t{}_2\text{-}2)\}]$ (10) | | White | 300—305 [f] | 50.1 (49.4) | 6.95 (6.65) | | | 3.71 | δ(Bu$^t$) 1.46(t)<br>\|$^3J$(P–H) + $^5J$(P–H)\|14.6 | |

[a] Calculated values are given in parentheses. [b] δ/p.p.m., *J*/Hz; recorded in $CDCl_3$ at 60 MHz and 35 °C. [c] As Nujol mulls (cm$^{-1}$). [d] Evolves gas on melting; white needles separate from the melt and these do not melt below 325 °C. [e] Evolves gas on melting and the solid product melts at 180—183 °C. [f] Decomposes without melting.

There was no reaction between $[PtCl_2(NCPh)_2]$ or $[PtCl_2(NCBu^t)_2]$ and the more bulky phosphines $PBu^t{}_2$-$[C_6H_3(OMe)_2$-2,3] and $PBu^t{}_2[C_6H_3(OMe)_2$-2,6] at ambient temperatures, but in boiling 2-methoxyethanol the very stable bis(chelate) *trans*-bis[2-(di-t-butylphosphino)-3-methoxyphenoxo-*OP*]platinum(II) (9) (from the 2,6-dimethoxy-derivative) or (10) (from the 2,3-dimethoxy-derivative) were formed (see Table 3 for characterizing data). The $^{31}P$ n.m.r. spectrum of (9) showed a singlet with satellites at δ 67.3 p.p.m. [$^1J$(Pt–P) 2 739 Hz]; similarly for (10), δ 62.3 p.p.m. [$^1J$(Pt–P) 2 800 Hz] (spectra recorded in $CDCl_3$).

Although the di-t-butylphosphine complex (9) was resistant to sodium tetrahydroborate, the diphenylphosphine complex (7) was reduced in high yield to the hydride (11). The bis(chelate) (7) was reformed when (11) was heated in benzene. The structure (11) follows from the analytical and spectroscopic data (Table 3) and also from the $^{31}P$ n.m.r. spectrum (in $CDCl_3$) which showed an AB pattern with satellites (due to $^{195}Pt$) at $\delta_A$ 37.15 p.p.m. [$^1J$(Pt–$P_A$) 2 951 Hz], and $\delta_B$ 24.7 p.p.m. [$^1J$(Pt–$P_B$) 2 976 and $^2J$($P_A$–$P_B$) 383 Hz].



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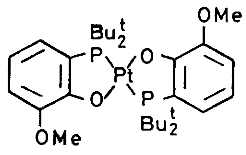

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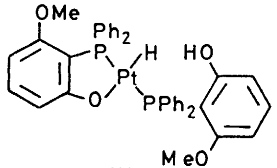

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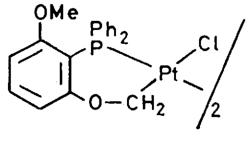

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We have reported previously[1] that in a non-polar solvent such as xylene the phosphines $PR_2(C_6H_4OMe$-2) (R = Ph or Bu$^t$) react with $[PtCl_2(NCPh)_2]$ and undergo *C*-metallation to give a six-membered chelate ring. We find that the phosphine $PPh_2[C_6H_3(OMe)_2$-2,6] with

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

$[PtCl_2(NCPh)_2]$ in xylene similarly gives $[Pt_2Cl_2\{CH_2OC_6H_3(OMe)(PPh_2)_2\}_2]$ (12). The formulation follows from the microanalytical and other data (Tables 4 and 5) and reactions. This chloride-bridged complex is very insoluble but it undergoes bridge-splitting reactions with 4Me-py, dimethylphenylphosphine, thallium(I) pentane-2,4-dionate, or silver(I) acetate to give more soluble mononuclear derivatives which are more amenable to study by n.m.r. spectroscopy and have been fully characterized by analytical and spectroscopic studies (see Tables 4 and 5). The product produced by treating the chloride-bridged dimer with 4Me-py was crystalline.

TABLE 4

Analytical and melting-point data for the *C*-metallated derivatives

| Complex | Yield (%) | Colour | M.p. ($\theta_C$/°C) | Analysis (%) |  |  | *M* |
|---|---|---|---|---|---|---|---|
|  |  |  |  | C | H | Halogen |  |
| $[Pt_2Cl_2\{CH_2OC_6H_3(OMe-3)(PPh_2-2)\}_2]$ | 59 | White | 290—295 [b] | 43.55 (43.55) | 3.35 (3.3) | 6.45 (6.4) |  |
| $[PtCl(4Me-py)\{CH_2OC_6H_3(OMe-3)-(PPh_2-2)\}]$ | 79 | White | 119—203 | 48.5 (48.5) | 3.85 (3.9) |  | 669 (645) |
| $[PtCl\{CH_2OC_6H_3(OMe-3)(PPh_2-2)\}-(PMe_2Ph)]$ | 76 | White | 148—156 | 49.0 (48.75) | 4.5 (4.25) |  |  |
| $[Pt(pd)\{CH_2OC_6H_3(OMe-3)(PPh_2-2)\}]$ | 71 | White | 198—205 [b] | 48.75 (48.8) | 3.95 (4.1) |  | 599 (616) |
| $[Pt_2(O_2CMe)_2\{CH_2OC_6H_3(OMe-3)-(PPh_2-2)\}]$ | 73 | Cream | 255—263 | 45.55 (45.9) | 3.8 (3.7) |  |  |
| $[PtCl\{CH_2OC_6H_3(OMe-3)(PPh_2-2)\}-\{PPh_2[C_6H_3(OMe)_2-2,6]\}]$ | 77 | White | 238—243 [c] | 54.95 (55.05) | 4.3 (4.25) | 4.3 (4.05) |  |
| $[PtI\{CH_2OC_6H_3(OMe-3)(PPh_2-2)\}-\{PPh_2[C_6H_3(OMe)_2-2,6]\}]$ | 82 | Cream | 208—210 [c] | 49.25 (49.75) | 3.75 (3.85) | 13.8 (13.15) | 923 (966) |

[a] Calculated values are given in parentheses. [b] Decomposes without melting. [c] Microcrystals separate from the melt and decompose at >325 °C.

TABLE 5

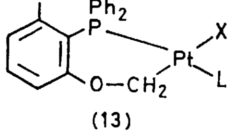
Spectral data for the *C*-metallated derivatives

| Complex | $^1H_2$ N.m.r.[a] |  |  |  |  | $\nu$(Pt–Cl) [b] |
|---|---|---|---|---|---|---|
|  | δ(OMe) | $\delta(CH_2)$ | $^3J$(Pt–H) | $^2J$(Pt–H) | Other assignments |  |
| $[Pt_2Cl_2\{CH_2OC_6H_3(OMe-3)(PPh_2-2)\}_2]$ (13) |  |  |  |  |  | 271, 241 |
| $[PtCl(4Me-py)\{CH_2OC_6H_3(OMe-3)(PPh_2-2)\}]$ [c] | 3.07 | 4.91(d) | 5.5 | 76.0 | δ(N–Me) 2.15 | 293 |
| $[PtCl\{CH_2OC_6H_3(OMe-3)(PPh_2-2)\}(PMe_2Ph)]$ | 3.12 | 4.33(t) | *ca.* 8.8 | 70.8 | δ(P-Me) 0.85(d), $^2J$(P–H) 6.45, $^3J$(Pt–H) 30.7 | 284 |
| $[Pt(pd)\{CH_2OC_6H_3(OMe-3)(PPh_2-2)\}]$ | 3.15 | 4.85(d) | 3.95 | 79.2 | δ(Me) 1.94 and 1.56, δ(C–H) 5.28 |  |
| $[Pt_2(O_2CMe)_2\{CH_2OC_6H_3(OMe-3)(PPh_2-2)\}]$ | 3.12 | 4.89(d) |  |  | δ(Me) 1.39 |  |
| $[PtCl\{CH_2OC_6H_3(OMe-3)(PPh_2-2)\}-\{PPh_2[C_6H_3(OMe)-2,6]\}]$ | 3.22 [d]<br>3.09 | 4.29(t) | *ca.* 4.5 [e] | 73 |  | 283 |
| $[PtI\{CH_2OC_6H_3(OMe-3)(PPh_2-2)\}-\{PPh_2[C_6H_3(OMe)_2-2,6]\}]$ | 3.26 [d]<br>3.02 | 4.28(t) | *ca.* 4.5 [e] | 67 |  |  |

[a] In $CDCl_3$ solution at 90 MHz and ambient temperature; δ/p.p.m., *J*/Hz. [b] In $cm^{-1}$; Nujol mulls. [c] A minor component was also present in solution (see text). [d] Corresponding to two OMe groups; *i.e.* probably of the unmetallated ligand. [e] The methylene resonance pattern is possibly second order due to strong P–P coupling.

In solution the $^1H$ n.m.r. spectrum showed a major component (data in Table 5) but there were also very weak resonances at δ 4.5 and 2.35 p.p.m., possibly due to $CH_2$ and $CH_3C_5H_4N$ respectively of another component. The mononuclear pentane-2,4-dionate showed a singlet $^{31}P$ n.m.r. resonance with satellites at δ −0.3 p.p.m. [$^1J$(Pt-P) 4 524 Hz].

When treated with $PPh_2[C_6H_3(OMe)_2-2,6]$ (1 mol per Pt atom), complex (12) gave a single product identified as $\{13;\ X = Cl,\ L = PPh_2[C_6H_4(OMe)_2-2,6]\}$ (see Tables for characterizing data). The $^{31}P$ n.m.r. spectrum showed an AB pattern with satellites and a large value for $^2J$(P–P) (439 Hz), characteristic of mutually *trans*-bonded P nuclei[5] {$\delta(P_A)$ 19.45 p.p.m. [$^1J(Pt-P_A)$ 3 142 Hz], $\delta(P_B)$ 8.15 p.p.m. [$^1J(Pt-P_B)$ 3 166 Hz]}. Metathesis gave the corresponding iodide (X = I). When heated to 250 °C the chloride (13; X = Cl) evolved MeCl (identified by its i.r. spectrum). The product was a red oil which could not be induced to crystallize, but we tentatively suggest it contained a species with both a *C*- and an *O*-metallated ligand. (The $^1H$ n.m.r. spectrum in $CDCl_3$ showed two OMe resonances at δ 3.24 and 2.85 p.p.m.) It has previously been shown that *C*-metallation of a co-ordinated phosphine often occurs readily if the group lost is methyl (as methane).[6,7] We therefore synthesized the dimethyl complex *cis*-$[PtMe_2\{PPh_2[C_6H_3(OMe)_2-2,6]\}_2]$ from the corresponding



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dichloride and methyl-lithium. The $^1H$ n.m.r. spectrum showed a complex signal at δ 1.34 p.p.m. corresponding to the two methyl groups [$^2J$(PtH) 70.2 Hz]. Pyrolysis of this complex at 200 °C gave methane (from its i.r.

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

[6] A. J. Cheney, W. S. McDonald, K. O'Flynn, B. L. Shaw, and B. L. Turtle, *J.C.S. Chem. Comm.*, 1973, 128.

[7] J. M. Duff, B. E. Mann, B. L. Shaw, and B. L. Turtle, *J.C.S. Dalton*, 1974, 139.

spectrum) and a red oil. No solid material could be isolated from this oil but the $^1$H n.m.r. spectrum was identical to that of the pyrolysis product of [PtCl{CH$_2$OC$_6$H$_3$(OMe)(PPh$_2$)}{PPh$_2$[C$_6$H$_3$(OMe)$_2$-2,6]}] (see above) and therefore possibly contained *O*- and *C*-metallated species.

## EXPERIMENTAL

Operations involving organolithium reagents or free tertiary phosphines were carried out under argon. Melting points are corrected. Molecular weights were measured osmometrically in chloroform solution.

2,6-*Dimethoxyphenyl-lithium*.—A mixture of n-butyllithium (0.15 mol) in hexane (68 cm$^3$) and dry diethyl ether (70 cm$^3$) was added to a well stirred mixture of 1,3-dimethoxybenzene (22.1 g, 0.16 mol) and *NNN′N′*-tetramethylethylenediamine (tmen) (17.4 g, 0.15 mol) in dry diethyl ether (200 cm$^3$) at room temperature over 1 h; the mixture was stirred for 4 h after the addition, producing a dense white suspension of the *product* which was used *in situ*.

2,3-*Dimethoxyphenyl-lithium*.—A mixture of LiBu$^n$ (0.10 mol) in hexane (48.8 cm$^3$) and dry diethyl ether (50 cm$^3$) was added to a stirred solution of 1,2-dimethoxybenzene (16.6 g, 0.12 mol) in dry diethyl ether (50 cm$^3$) over 15 min at *ca.* 0 °C. The mixture was stirred for 30 min after addition, allowing the temperature to rise to room temperature, giving the *product* as a dense white suspension which was used *in situ*.

2,6-*Dimethoxyphenyldiphenylphosphine*.—A solution of chlorodiphenylphosphine (31.5 g, 0.15 mol) in dry diethyl ether (50 cm$^3$) was added to a well stirred suspension of Li[C$_6$H$_3$(OMe)$_2$-2,6] (0.150 mol) in hexane (20 cm$^3$) and dry diethyl ether (250 cm$^3$) over 20 min at room temperature. The mixture was stirred for 19 h then hydrolyzed with degassed water (200 cm$^3$). Extraction with benzene gave the *product* (35.9 g, 0.11 mol, 76%) as white prisms from ethanol. 2,3-*Dimethoxyphenyldiphenylphosphine* was prepared similarly (24.9 g, 0.077 mol, 77%).

2,6-*Dimethoxyphenyl*(*methyl*)*diphenylphosphonium Iodide*.—Methyl iodide (1.0 cm$^3$) was added to a solution of PPh$_2$[C$_6$H$_3$(OMe)$_2$-2,6] (0.203 g, 0.600 mmol) in acetonitrile (5 cm$^3$). Addition of diethyl ether (2 cm$^3$) caused crystallization of the *product* (0.245 g, 0.528 mmol, 88%) as white plates. 2,3-*Dimethoxyphenyl*(*methyl*)*diphenylphosphonium iodide*, 2,6-*diacetoxyphenyl*(*methyl*)*diphenylphosphonium iodide*, 2,6-*dimethoxyphenyl*(*methyl*)*di-t-butylphosphonium iodide*, and 2,3-*dimethoxyphenyl*(*methyl*)*di-t-butylphosphonium iodide* were prepared similarly.

2,6-*Dimethoxyphenyldi-t-butylphosphine*.—A solution of chlorodi-t-butylphosphine (19.7 g, 0.11 mol) in dry diethyl ether (100 cm$^3$) was added to a well stirred suspension of Li[C$_6$H$_3$(OMe)$_2$-2,6] (0.24 mol) in hexane (90 cm$^3$) and dry diethyl ether (100 cm$^3$) over 1 h at room temperature and then heated under reflux for 16 h. The mixture was cooled, hydrolyzed with water (200 cm), and extracted with diethyl ether. Fractional distillation under reduced pressure gave the *product* (23.7 g, 0.084 mol, 77%) as white prisms. 2,3-*Dimethoxyphenyldi-t-butylphosphine* was prepared similarly (17.9 g, 0.063 mol, 64%) as white prisms.

2,6-*Diacetoxyphenyldiphenylphosphine*.—A solution of boron tribromide (8.76 g, 34.45 mmol) in toluene (100 cm$^3$) was added to a well stirred suspension of PPh$_2$[C$_6$H$_3$(OMe)$_2$-2,6] (3.36 g, 10.43 mmol) in toluene (200 cm$^3$) over 1 h at *ca.* −78 °C. The mixture was then stirred for another 2 h, allowing it to warm up to room temperature. Hydrolysis with aqueous sodium acetate solution and evaporation of the toluene under reduced pressure gave a yellow oil. Acetic anhydride (20 cm$^3$) was added to the oil and the resulting mixture was stirred for 30 min. Water (50 cm$^3$) was then added giving the *product* (2.66 g, 7.05 mmol, 65%) as white prisms.

trans-*Dichlorobis*(2,6-*dimethoxyphenyldiphenylphosphine*)-*palladium*(II).—A solution of bis(benzonitrile)dichloropalladium(II) (0.38 g, 1.00 mmol) in dichloromethane (5 cm$^3$) was treated with PPh$_2$[C$_6$H$_3$(OMe)$_2$-2,6] (0.71 g, 2.20 mmol) and the resulting solution diluted with methanol to give the *product* (0.71 g, 0.87 mmol, 87%) as yellow plates. trans-*Dichlorobis*(2,3-*dimethoxyphenyldiphenylphosphine*)*palladium*(II) was prepared similarly (0.82 g, 0.99 mmol, 99%) as yellow plates.

trans-*Bis*(2,6-*dimethoxyphenyldiphenylphosphine*)*di-iodopalladium*(II).—A solution of *trans*-[PtCl$_2${PPh$_2$[C$_6$H$_3$(OMe)$_2$-2,6]}$_2$] (0.25 g, 0.50 mmol) in acetone (15 cm$^3$) was treated with NaI (0.70 g, 5.00 mmol). Isolation after 1 h gave the *product* (0.28 g, 0.28 mmol, 89%) as needles. trans-*Bis*(2,3-*dimethoxyphenyldiphenylphosphine*)*di-iodopalladium*(II) was prepared similarly (0.27 g, 0.27 mmol, 89%) as prisms from dichloromethane–methanol.

*Di-μ-chloro-bis*[*chloro*(2,6-*dimethoxyphenyldiphenylphosphine*)*palladium*(II)].—A solution of [PdCl$_2$(NCPh)$_2$] (0.13 g, 0.33 mmol) in dichloromethane (15 cm$^3$) was treated with PPh$_2$[C$_6$H$_3$(OMe)$_2$-2,6] (0.11 g, 0.33 mmol). Isolation gave the *product* (0.13 g, 0.13 mmol, 80% as needles from dichloromethane–methanol.

trans-*Dichloro*(2,6-*dimethoxyphenyldiphenylphosphine*)(4-*methylpyridine*)*palladium*(II).—A solution of [Pd$_2$Cl$_2${PPh$_2$[C$_6$H$_3$(OMe)$_2$-2,6]}$_2$] (0.07 g, 0.07 mmol) was treated with 4-methylpyridine (0.01 g, 0.14 mmol). Isolation gave the *product* (0.07 g, 0.13 mmol, 91%) as needles from dichloromethane–light petroleum (b.p. 40—60 °C).

trans-*Dichlorobis*(2,6-*dimethoxyphenyldiphenylphosphine*)-*platinum*(II).—A solution of bis(benzonitrile)dichloroplatinum(II) (0.472 g, 1.00 mmol) in dichloromethane was treated with PPh$_2$[C$_6$H$_3$(OMe)$_2$-2,6] (0.711 g, 2.2 mmol) and the resulting solution diluted with methanol to give the *product* (0.871 g, 0.962 mmol, 96%) as pale yellow plates. trans-*Dichlorobis*(2,3-*dimethoxyphenyldiphenylphosphine*)*platinum*(II) was prepared similarly (1.82 g, 2.00 mmol, 98%).

(2,6-*Dimethoxyphenyldiphenylphosphine*)*di-iodoplatinum*(II).—A solution of [PtCl$_2$(NCPh)$_2$] (0.193 g, 0.408 mmol) in acetone (25 cm$^3$) was treated with NaI (0.61 g, 4.08 mmol). After 10 min, PPh$_2$[C$_6$H$_3$(OMe)$_2$-2,6] (0.292 g, 0.900 mmol) was added. Isolation and recrystallization gave the *product* (0.415 g, 0.382 mmol, 93%) from dichloromethane–methanol.

*Bis*(2,3-*Dimethoxyphenyldiphenylphosphine*)*di-iodoplatinum*(II).—A solution of *trans*-[PtCl$_2${PPh$_2$[C$_6$H$_3$(OMe)$_2$-2,3]}$_2$] (0.261 g, 0.237 mmol) in acetone (20 cm$^3$) and NaI (0.355 g, 2.37 mmol) were heated under reflux for 3 h. Isolation and recrystallization gave the *product* (0.252 g, 0.231 mmol, 98%).

cis-*Bis*[2-(*diphenylphosphino*)-3-*methoxyphenoxo*-OP]-*platinum*(II).—*Method* (1). A suspension of [PtCl$_2${PPh$_2$[C$_6$H$_3$(OMe)$_2$-2,6]}$_2$] (0.546 g, 0.600 mmol) and NaI (0.302 g, 3.00 mmol) was heated under reflux in 2-methoxyethanol (20 cm$^3$) for 0.5 h. Isolation gave the *product* (0.464 g, 0.574 mmol, 95%) as white needles.

*Method* (2). A suspension of [PtI$_2${PPh$_2$[C$_6$H$_3$(OMe)$_2$-2,6]}$_2$] (0.126 g, 0.116 mmol) in acetone (20 cm$^3$) was heated under reflux for 3 h. Isolation gave the *product* (0.071 g, 0.088 mmol, 76%) as needles.

cis-*Bis*[2-(*diphenylphosphino*)-6-*methoxyphenoxo*-OP]*platinum*(II).—A suspension of $[PtCl_2\{PPh_2[C_6H_3(OMe)_2\text{-}2,3]\}$ (0.780 g, 0.858 mmol) and NaI (0.307 g, 8.58 mmol) was heated under reflux in 2-methoxyethanol (25 cm$^3$) for 187 h. Isolation gave the *product* (0.704 g, 0.856 mmol, 98%) as white needles.

trans-*Bis*[2-(*di-t-butylphosphino*)-3-*methoxyphenoxo*-OP]*platinum*(II).—A solution of $[PtCl_2(NCPh)_2]$ (0.751 g, 1.59 mmol) in 2-methoxyethanol (30 cm$^3$) was treated with $PPh_2[C_6H_3(OMe)_2\text{-}2,6]$ (0.985 g, 3.50 mmol) and the resulting solution heated under reflux for 5 h. Isolation gave the *product* (0.813 g, 1.12 mmol, 70%) as white needles from dichloromethane–light petroleum (b.p. 60—80 °C).

trans-*Bis*[2-(*di-t-butylphosphino*)-6-*methoxyphenoxo*-OP]*platinum*(II).—A solution of $[PtCl_2(NCPh)_2]$ (0.305 g, 0.650 mmol) in 2-methoxyethanol (20 cm$^3$) was treated with $PBu^t{}_2[C_6H_3(OMe)_2\text{-}2,3]$ (0.403 g, 1.430 mmol) and the mixture heated under reflux for 23 h. Isolation gave the *product* (0.204 g, 0.302 mmol, 43%) as white prisms from dichloromethane–light petroleum (b.p. 60—80 °C).

[2-(*Diphenylphosphino*)-3-*methoxyphenoxo*-OP]*hydrido*-(2-*hydroxy*-6-*methoxyphenyldiphenylphosphine*)*platinum*(II).—A suspension of *cis*-$[Pt\{OC_6H_3(OMe\text{-}3)(PPh_2\text{-}2)\}_2]$ (0.265 g, 0.312 mmol) in benzene and a solution of sodium tetrahydroborate (0.119 g, 3.12 mmol) in ethanol (20 cm$^3$) were heated under reflux for 2 h. Isolation gave the *product* (0.205 g, 0.239 mmol, 77%) as white prisms.

cis-*Bis*(2,6-*dimethoxyphenyldiphenylphosphine*)*dimethylplatinum*(II).—A solution of methyl-lithium (2.85 mmol) in diethyl ether (3.1 cm$^3$) was added to a stirred suspension of $[PtCl_2\{PPh_2[C_6H_3(OMe)_2\text{-}2,6]\}_2]$ (0.260 g, 0.285 mmol) and the mixture stirred for 2 h. Isolation gave the *product* (0.195 g, 0.225 mmol, 79%) as white prisms from benzene–n-heptane.

*Di-μ-chloro-bis*[{[2-(*diphenylphosphino*)-3-*methoxyphenoxy*]*methyl*}*platinum*(II)].—A solution of $[PtCl_2(NCPh)_2]$ (0.970 g, 2.05 mmol) and $PPh_2[C_6H_3(OMe)_2\text{-}2,6]$ (0.664 g, 2.05 mmol) in xylene (150 ml) was heated under reflux for 2 h and then filtered over charcoal. Evaporation of the filtrate gave the *product* (0.699 g, 1.23 mmol, 60%) as white microcrystals.

{[2-(*Diphenylphosphino*)-3-*methoxyphenoxy*]*methyl*-CP}-*pentane*-2,4-*dionatoplatinum*(II).—A suspension of $[Pt_2Cl_2\{CH_2OC_6H_3(OMe\text{-}3)(PPh_2\text{-}2)\}_2]$ (0.205 g, 0.186 mmol) and thallium(I) pentane-2,4-dionate (0.128 g, 0.39 mmol) in benzene (50 cm$^3$) was shaken for 16 h. Isolation gave the *product* (0.159 g, 0.266 mmol, 71%) as white prisms from benzene–light petroleum (b.p. 30—40 °C).

*Chloro*{[2-(*diphenylphosphino*)-3-*methoxyphenoxy*]*methyl*-CP}(4-*methylpyridine*)*platinum*(II).—A suspension of $[Pt_2Cl_2\{CH_2OC_6H_3(OMe\text{-}3)(PPh_2\text{-}2)\}_2]$ (0.135 g, 0.122 mmol) in dichloromethane (5 cm$^3$) was treated dropwise with 4-methylpyridine until dissolution occurred. Dilution with light petroleum (b.p. 60—80 °C) gave the *product* (0.124 g, 0.192 mmol) as white needles.

*Chloro*(*dimethylphenylphosphine*){[2-(*diphenylphosphino*)-3-*methoxyphenoxy*]*methyl*-CP}*platinum*(II).—A suspension of $[Pt_2Cl_2\{CH_2OC_6H_3(OMe\text{-}3)(PPh_2\text{-}2)\}_2]$ (0.175 g, 0.158 mmol) in dichloromethane (25 m$^3$) was treated with dimethylphenylphosphine (45.5 μl, 0.316 mmol) and heated under reflux for 5 min. Evaporation of the solvent gave the *product* (0.158 g, 0.230 mmol, 76%) as white needles from dichloromethane–methanol.

*Di-μ-acetato-bis*[{[2-(*diphenylphosphino*)-3-*methoxyphenoxy*]*methyl*}*platinum*(II)].—A suspension of $[Pt_2Cl_2\{CH_2OC_6H_3(OMe\text{-}3)(PPh_2\text{-}2)\}_2]$ (0.203 g, 0.184 mmol) in acetone (40 cm$^3$) and silver(I) acetate (0.071 g, 0.435 mmol) were shaken in the dark for 42 h. Isolation gave the *product* (0.154 g, 0.134 mmol, 73%) as pale yellow plates from dichloromethane–methanol.

*Chloro*(2,6-*dimethoxyphenyldiphenylphosphine*){[2-(*diphenylphosphino*)-3-*methoxyphenoxy*]*methyl*-CP}*platinum*(II).—A suspension of $[Pt_2Cl_2\{CH_2OC_6H_3(OMe\text{-}3)(PPh_2\text{-}2)\}_2]$ (0.311 g, 0.282 mmol) in dichloromethane (25 cm$^3$) and $PPh_2[C_6H_3(OMe)_2\text{-}2,6]$ (0.182 g, 0.564 mmol) were heated under reflux for 0.5 h. Cooling gave the *product* (0.378 g, 0.433 mmol, 77%) from dichloromethane–cyclohexane.

(2,6-*Dimethoxyphenyldiphenylphosphine*){[2-(*diphenylphosphino*)-3-*methoxyphenoxy*]*methyl*-CP}*iodoplatinum*(II).—A solution of $[PtCl\{CH_2OC_6H_3(OMe\text{-}3)(PPh_2\text{-}2)\}\{PPh_2[C_6H_3(OMe)_2\text{-}2,6]\}]$ (0.118 g, 1.30 mmol) in acetone (25 cm$^3$) and NaI (0.195 g, 1.30 mmol) were heated under reflux for 0.5 h. Isolation gave the *product* (0.134 g, 0.187 mmol, 82%) as cream plates.

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