O- and *C*-Metallation of 2-Alkoxyphenylphosphines by Platinum(II) †

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The tertiary phosphines (L) PPh_2(2-methoxyphenyl), PBu^tMe(2-methoxyphenyl), PBu^t_2(2-methoxyphenyl), and PPh_2(2-ethoxyphenyl) were prepared. Complexes of these ligands and of PMe_2(2-methoxyphenyl) with platinum(II) halides are described. These complexes on heating are converted to *O*-metallated chelates, *e.g.* *trans*-[$PtCl_2${Ph_2P(2-methoxyphenyl)}$_2$] gives *cis*-[$Pt(Ph_2PC_6H_4O)_2$]. PMe_2(2-methoxyphenyl) is much more difficult to metallate but the complex [$PtI(Me_2PC_6H_4O)(Me_2PC_6H_4OMe)$] was prepared. *C*-Metallated derivatives containing six-membered chelate rings were prepared by heating the ligand or [$PtCl_2L_2$] with [$PtCl_2(RCN)_2$] in xylene. Metathesis and bridge splitting reactions are described. ^1H and ^{31}P N.m.r. and i.r. data are given and discussed.

LITTLE is known about complexes of 2-methoxyphenylphosphines with transition metals although we have shown that the 2-methoxy oxygen atom of a PMe_2-(2-methoxyphenyl) ligand causes a marked enhancement of the rates of oxidative addition reactions of *trans*-[IrClCO{PMe_2(2-methoxyphenyl)}$_2$] by a direct interaction with the metal (neighbouring group participation or the anchimeric effect).[1] One might also expect that the methoxy group of a 2-methoxyphenylphosphine ligand could interact chemically with the co-ordinated metal, *i.e.* reactions such as demethylation or metallation might occur. In this paper we describe the results of our studies on the interactions of platinum(II) with such phosphines.

RESULTS AND DISCUSSION

The tertiary phosphines, 2-ethoxyphenyl(diphenyl)phosphine, 2-methoxyphenyl(t-butyl)methylphosphine, and 2-methoxyphenyldi-t-butylphosphine are new and 2-methoxyphenyl(diphenyl)phosphine has been described only briefly.[2] They were prepared and characterized by standard methods (see Experimental section and Table 1 for details).

The complex *cis*-[$PtCl_2${PMe_2(2-methoxyphenyl)}$_2$] was prepared by treating an aqueous solution of dipotassium tetrachloroplatinate(II) with the phosphine. This complex was assigned the *cis*-configuration from its colour and from its far i.r. and ^1H n.m.r. spectra (see Tables 2 and 3). Metathesis with sodium iodide in acetone gave [PtI_2{PMe_2(2-methoxyphenyl)}$_2$] which had a *trans*-configuration (from ^1H n.m.r. data). Treatment of [$PtCl_2(Bu^tCN)_2$] with an 2-alkoxyphenyl(diphenyl)phosphine gave the pale yellow *trans*-[$PtCl_2L_2$]

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† No reprints available.

[1] E. M. Miller and B. L. Shaw, *J.C.S. Dalton*, 1974, 480.

[2] W. E. McEwen, V. L. Kyllingstad, D. N. Schulz, and Y-I. Yeh, *Phosphorus*, 1971, **1**, 145.

TABLE 1

Analytical, melting (boiling) point, and ^{1}H n.m.r. data for PPh_2(2-methoxyphenyl), PBu^tMe(2-methoxyphenyl), PBu^t_2(2-methoxyphenyl), PPh_2(2-ethoxyphenyl), and their quaternary phosphonium salts [a]

	Yield %	Analytical data (%) [b] C	H	M.p. (t/°C)	^{1}H N.m.r. data [c] τ(OMe)	τ(Bu^t)	τ(Me)	τ(–O–*CH*$_2$–Me)	τ(–O–CH$_2$–*Me*)	J(HH)	Notes
PPh_2(2-methoxyphenyl)	84			124—126	6·27						$CDCl_3$
PBu^tMe(2-methoxyphenyl)	60			(B.p.) 100—106° (0·6 mmHg)	6·42	9·03 (d) (11·5)	8·83 (d) (6·3)				Neat
PBu^t_2(2-methoxyphenyl)	80			104—109 (0·15 mmHg)	6·3	8·8 (d) (11·8)					Neat
PPh_2(2-ethoxyphenyl)	67			73—75				6·11 (q)	8·94 (t)	7·2	$CDCl_3$
$[PPh_2Me$(2-methoxyphenyl)$]I$	72	55·45 (55·4)	4·5 (4·65)	164—166	6·20		7·00 (d) (13·5)				$CDCl_3$
$[PBu^tMe_2$(2-methoxyphenyl)$]I$	60	44·5 (44·35)	6·25 (6·35)	230—240 [d]	6·03	8·63 (d) (22·5)	7·57 (d) (13·0)				$CDCl_3$
$[PBu^t_2Me$(2-methoxyphenyl)$]I$	75	48·5 (48·8)	7·2 (7·15)	>200 [d]	5·9	8·5 (d) (17·0)	7·55 (11·0)				$CDCl_3$
$[PPh_2Me$(2-ethoxyphenyl)$]I$	77	56·15 (56·25)	4·8 (4·95)	163—168			6·97 (d) (13·2)	5·90 (q)	8·97 (t)	7·2	$CDCl_3$

[a] All solid compounds are white. [b] Theoretical values in parentheses. [c] Spectra recorded at *ca.* 35 °C and 60 MHz. τ-Values ±0·2, J-values ±0·5 Hz; hydrogen–phosphorus coupling constants are given in parentheses. [d] With decomposition.

TABLE 2

Analytical and melting point data for complexes of the type $[PtX_2L_2]$ and *O*-metallated complexes

Complex	% Yield	Colour	M.p. (t/°C)	Analytical data C	H	Halogen
L = PMe_2(2-methoxyphenyl)						
cis-$[PtCl_2L_2]$	80	White	217—220 [a]	35·65 (35·9)	4·2 (4·35)	12·05 (11·75)
trans-$[PtI_2L_2]$	72	Yellow	194—197 [a]	27·9 (27·55)	3·35 (3·35)	
[PtI(P–O)L]	63	White	237—245 [a]	31·6 (31·75)	3·55 (3·6)	19·8 (19·75)
L = PPh_2(2-methoxyphenyl)						
trans-$[PtCl_2L_2]$	95	Yellow	258—260 [a,b]	53·4 (53·65)	3·95 (4·05)	8·55 (8·35)
trans-$[PtI_2L_2]$	88	Orange	208—220 [a,b]	44·6 (44·2)	3·4 (3·3)	
cis-$[Pt(P–O)_2]$	98	White	>315	57·7 (57·7)	3·8 (3·75)	
[PtI(P–O)L]	74	Yellow	>315	49·75 (49·8)	3·55 (3·5)	14·35 (14·2)
cis-$[PtMe_2L_2],C_6H_6$	85	White	127—143 [a]	61·6 (62·0)	5·3 (5·45)	
L = PPh_2(2-ethoxyphenyl)						
trans-$[PtCl_2L_2]$	89	Yellow	252—257 [a,b]	54·45 (54·7)	4·3 (4·35)	8·3 (8·1)
trans-$[PtI_2L_2]$	86	Orange	254—258 [a,b]	45·7 (45·25)	3·75 (3·6)	
L = PBu^tMe(2-methoxyphenyl)						
meso-trans-$[PtCl_2L_2]$	40	Yellow	210—215 [a]	41·85 (42·0)	5·65 (5·6)	10·4 (10·35)
rac-trans-$[PtCl_2L_2]$	24	Yellow	184—186 [a]	41·8 (42·0)	5·6 (5·6)	10·15 (10·35)
trans-$[PtI_2L_2]$	91	Orange	203—205 [a]	34·05 (33·15)	4·5 (4·4)	
cis-$[Pt(P–O)_2]$	33	White	sublimes >230	45·05 (45·15)	5·3 (5·5)	
L = PBu^t_2(2-methoxyphenyl)						
trans-$[PtCl_2L_2]$	70	Yellow	200—210 [a]	47·0 (46·75)	6·55 (6·55)	
trans-$[Pt(P–O)_2]$	80	Yellow	sublimes >300	50·1 (50·2)	6·75 (6·6)	
$[PtCl(P–O)(PBu^t_2C_6H_4OH)]$	73	Yellow	decomp.	47·5 (4·76)	6·45 (6·4)	

[a] Evolves gas on melting. [b] White plates separate from melt and these do not melt below 315°.

TABLE 3

^{1}H N.m.r. [a] and i.r. [b] data for complexes of the type $[PtX_2L_2]$ and *O*-metallated complexes

Complex	τ(OMe)	τ(Bu^t)	^3J(PH) + ^5J(PH)	τ(Me)	^2J(PH) + ^6J(PH)	^3J(PH)	ν(PtCl)
L = PMe_2(2-methoxyphenyl)							
cis-$[PtCl_2L_2]$	6·14			8·18 (d)	11·3	34·5	313, 330
trans-$[PtI_2L_2]$	6·15			7·85 (t)	7·3	24·5	
[PtI(P–O)L]	6·05			7·71 (d)	11·5	34·7	
				8·80 (d)	12·1	41·5	
L = PPh_2(2-methoxyphenyl)							
trans-$[PtCl_2L_2]$	6·22						336
trans-$[PtI_2L_2]$	6·35						
cis-$[PtMe_2L_2],C_6H_6$ [c]	6·81						
L = PBu^tMe(2-methoxyphenyl)							
meso-trans-$[PtCl_2L_2]$	6·10	8·62 (t)	14·7	8·19 (t)	6·8	23·4	334
rac-trans-$[PtCl_2L_2]$	6·09	8·62 (t)	14·2	8·17 (t)	6·9	23·0	334
trans-$[PtI_2L_2]$	6·15	8·46 (t)	14·0	7·81 (t)	7·0	25·3	
L = PBu^t_2(2-methoxyphenyl)							
trans-$[PtCl_2L_2]$	6·1	8·35 (t)	14·0				330
trans-$[Pt(P–O)_2]$		8·45 (t)	14·5				
$[PtCl(P–O)(PBu^t_2C_6H_4OH)]$		8·35 (t)	14·5				335
		8·40 (t)	14·0				
L = PPh_2(2-ethoxyphenyl)							
trans-$[PtCl_2L_2]$	τ(O*CH*$_2$CH$_3$) 6·10 (q), τ(OCH$_2$*CH*$_3$) 8·89 (t), ^3J(HH) 7·0 Hz; ν(PtCl) 346 cm^{-1}						
trans-$[PtI_2L_2]$	τ(O*CH*$_2$CH$_3$) 6·16 (q), τ(OCH$_2$*CH*$_3$) 8·87 (t), ^3J(HH) 7·0 Hz						

[a] Spectra at 35 °C and 60 MHz in $CDCl_3$ solution, τ-values ±0·2, J-values ±0·5 Hz. [b] Spectra recorded as Nujol mulls (cm^{-1}). [c] τ(Me) 9·76 (q) ^2J(PtH) 70·2 Hz, complex pattern due to coupling with phosphorus.

L = PPh_2(2-methoxyphenyl) or PPh_2(2-ethoxyphenyl) (Table 2). These were assigned a *trans*-configuration from their yellow colour and from the occurrence of only one i.r. absorption band due to ν(Pt–Cl). The values 336 and 346 cm^{-1} are typical of chlorine *trans* to chlorine in platinum(II) complexes.[3] Treatment of aqueous K_2PtCl_4 solution with t-butyl(methyl)-(2-methoxyphenyl)phosphine gave a yellow solid which was separated into two isomers by fractional crystallization from dichloromethane–methanol. ^1H N.m.r. data (Table 3) showed both these to have the *trans*-configuration. Single crystal *X*-ray diffraction studies showed that the molecular symmetry in the first-crop crystals was C_i and were therefore of the *meso*-isomer (1). The molecular symmetry in the second-crop crystals was C_2 and these were therefore of the *rac*-isomer (2).* *trans*-Dichlorobis(di-t-butyl-2-methoxyphenylphosphine)platinum(II) was prepared from $PtCl_2(PhCN)_2$ by treatment with PBu^t_2(2-methoxyphenyl).

TABLE 4

Analytical data, melting points, % yields, and colours for the *C*-metallated derivatives and for $[Pt_2Cl_4\{PMe_2(2\text{-methoxyphenyl})\}_2]$

Complex [a]	% Yield	Colour	M.p. (*t*/°C)	Analytical data [b]			
				C	H	Halogen	*M* [c]
L = PMe_2(2-methoxyphenyl)							
$[Pt_2Cl_4L_2]$	54	Yellow	214—218	25·2 (24·9)	3·05 (3·0)	16·35 (16·35)	
L = PPh_2(2-methoxyphenyl)							
$[Pt_2Cl_2(P{-}O{-}C)_2]$	90	White	265—300	44·65 (43·75)	3·2 (3·1)	6·5 (6·8)	
[Pt(acac)(P–O–C)]	76	White	218—235	49·4 (49·35)	4·15 (3·9)		
[PtCl(py)(P–O–C)]	89	White	120—122	47·65 (47·95)	3·35 (3·5)	6·0 (5·9)	617 (601)
[PtCl(P–O–C)L]	79	White	265—267	55·75 (56·05)	4·0 (4·1)	4·8 (4·35)	
[PtI(P–O–C)L]	92	Cream	257—259	49·6, 49·45 (50·4)	3·76 (3·65) 3·75	13·6 (14·0)	
L = PPh_2(2-ethoxyphenyl)							
$[Pt_2Cl_2(P{-}O{-}C)_2]$	71	White	268—270	44·65 (44·85)	3·5 (3·4)	7·1 (6·6)	
[Pt(acac)(P–O–C)]	81	Cream	199—205	49·85 (50·1)	4·2 (4·2)		
[PtCl(P–O–C)(py)],$\frac{1}{2}CH_2Cl_2$	73	White	167—177	46·15 (45·6) 46·55	3·6 (3·6) 3·65	11·0 (10·55)	
L = PBu^tMe(2-methoxyphenyl]							
$[Pt_2Cl_2(P{-}O{-}C)_2]$	71	Cream	200—225	32·8 (32·8)	4·1 (4·15)	8·65 (8·05)	871 (878)
$[Pt_2I_2(P{-}O{-}C)_2]$	90	Brown	228—238	27·05 (27·15)	3·55 (3·4)	23·65 (23·9)	
$[Pt(dibz)(P{-}O{-}C)_2]$	92	Yellow	187—192	51·3 (51·65)	4·6 (4·65)		

[a] dibz = Dibenzoylmethanate, P–O–C = *C*-metallated ligand. [b] Theoretical values in parentheses. [c] Molecular weights were determined osmometrically in chloroform at 30 °C, theoretical values in parentheses.

TABLE 5

^1H N.m.r.[a] and i.r.[b] data for the *C*-metallated derivatives and for $[Pt_2Cl_4\{PMe_2(2\text{-methoxyphenyl}\}_2]$

Complex	τ(OMe)	τ(Bu^t)	$^3J(PH)$ + $^5J(PH)$	τ(Me)	$^2J(PH)$ + $^4J(PH)$	$^3J(PtH)$	τ(CH_2)	$^3J(PH)$	$^2J(PtH)$	ν(PtCl)
L = PMe_2(2-methoxyphenyl)										
$[Pt_2Cl_4L_2]$	6·00			8·15 (d)	12·6	37·2				348, 343, 323, 312, 257
L = PPh_2(2-methoxyphenyl)										
$[Pt_2Cl_2(P{-}O{-}C)_2]$										273, 247
[Pt(acac)(P–O–C)] [c,d]							8·18 (d)	3·8	81·6	
[PtCl(P–O–C)(py)] [e]							5·07 (d) 5·48 (d)	5·4 4·4	79·2 79·8	291
[PtCl(P–O–C)L] [c]	6·49						5·65 (dd)	6·9 7·8	70·8	283
[PtI(P–O–C)L]	6·53						5·70 (dd)	*ca.* 8	66·0	
L = PBu^tMe(2-methoxyphenyl)										
$[Pt_2Cl_2(P{-}O{-}C)_2]$		8·76 (d,br)	15·5	8·20 (d,br)	9·5	52·0	4·99 (cx)		93·6	282, 271sh, 232sh, 219
$[Pt_2I_2(P{-}O{-}C)_2]$		8·76 (d,br)	15·5	8·10 (d,br)	10·0	54·5	4·90 (cx)		90·0	
[Pt(dibz)(P–O–C)] [f]		8·67 (d)	15·0	8·09 (d)	10·0	54·0				
L = PPh_2(2-ethoxyphenyl)										
$[Pt_2Cl_2(P{-}O{-}C)_2]$										268, 262, 246, 217
[Pt(acac)(P–O–C)] [c]	τ(C*H*CH_3) 4·84 (dq) *J*(HH) 6·0, ^3J(PH) 3·6, ^2J(PtH) 92·0 Hz τ(CHCH_3) 8·54 (dd), *J*(HH) 6·0, ^4J(PH) *ca.* 0·5, ^3J(PtH) 37·5 Hz acac group τ(Me) 8·04, ^4J(PtH) 3·4, τ(Me) 8·38; τ(CH) 4·66, ^3J(PtH) 4·4 Hz									
[PtCl(P–O–C)(py)] [e]	τ(C*H*CH_3) 4·26 (dq), *J*(HH) 6·5, ^4J(PH) 1·2 and 5·07 (dq) *J*(HH) 6·8, ^3J(PH) 1·0 Hz τ(CHCH_3) 8·36 (dd) ^3J(HH) 6·5, ^4J(PH) *ca.* 0·5, ^3J(PtH) 34·0 Hz and τ8·65 (dd) ^3J(HH) 6·5, ^4J(PH) *ca.* 0·5, ^3J(PtH) 48·4 Hz									

[a] Recorded at 60 MHz and 35 °C in $CDCl_3$ solution unless stated otherwise. τ-values ±0·2 *J*-values ±0·5 Hz, br = broad, dd = doublet of doublets, dq = doublet of quartets, cx = complex. [b] As Nujol mulls (cm^{-1}). [c] At 90 MHz and ambient temperature τ-values ±0·1, *J*-values ±0·2 Hz. [d] acac group τ(Me) 8·02 and 8·32 τ(C–H) 4·62 ^4J(PtH) 4·4 Hz. [e] Mixture of two isomers. [f] τ(C*H*) 3·31, ^4J(PtH) 4·3 Hz.

O-Metallation.—S- and Se-Metallation reactions of mixed phosphorus or arsenic S- or Se-donor chelating

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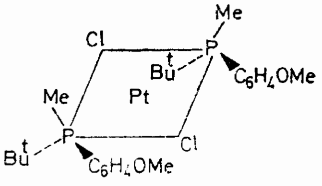
* The space group and cell dimensions of both sets of crystals were determined (W. S. McDonald and K. H. P. O'Flynn, unpublished results).

[3] 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.

ligands have been observed in nickel, palladium, and platinum complexes.[4-6] Since the oxygen of a 2-methoxyphenyldimethylarsine ligand has been shown by *X*-ray diffraction to co-ordinate to rhodium(III) in trichlorobis(*o*-methoxyphenyldimethylarsine)rhodium(III)[7] we anticipated that a similar interaction could occur in complexes of 2-methoxyphenylphosphines with platinum(II). Such an interaction could promote loss of the methyl group as methyl halide as with the methylthio- and methylseleno-ligands mentioned above. Thus we found that on heating the yellow [PtCl$_2${PPh$_2$(2-methoxyphenyl)}$_2$] to 270 °C, chloromethane was lost (as shown by the i.r. spectrum of the evolved gas) and the extremely stable white *cis*-bis{*o*-(diphenylphosphino)phenoxy}platinum(II) (3) was formed. The *cis*-configuration follows from the large value of ^1J(PtP), 3530 Hz, $\delta = -19·3$ p.p.m. The same compound was obtained on heating [PtX$_2${PPh$_2$(2-methoxyphenyl)}$_2$] (X = Cl or I) or [PtX$_2${PPh$_2$(2-ethoxyphenyl)}$_2$] (X = Cl or I) in boiling 2-methoxyethanol (b.p. 124°). The iodides were found to demethylate faster than the chlorides, *e.g.* [PtCl$_2${PPh$_2$(2-methoxyphenyl)}$_2$] gave a 68% yield after 30 h reflux whereas the iodide gave an 88% yield after 2 h. Added halide ion increased the rate of dealkylation only slightly, *e.g.* in the presence of a 20-fold excess of lithium chloride [PtCl$_2${PPh$_2$(2-methoxyphenyl)}$_2$] gave a 91% yield after 24 h and [PtI$_2${PPh$_2$(2-methoxyphenyl)}$_2$] in the presence of sodium iodide (20-fold excess) 98% yield after 1·5 h.



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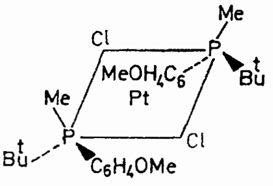

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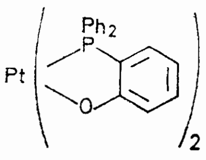

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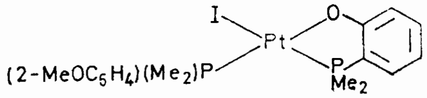
The ethoxy complex [PtX$_2${PPh$_2$(2-ethoxyphenyl)}$_2$] dealkylated more slowly than the methoxy complex. The dimethyl-2-methoxyphenylphosphine complex *cis*-[PtCl$_2${PMe$_2$(2-methoxyphenyl)}$_2$] on melting did not appear to demethylate and even after heating with a large excess of sodium iodide under reflux in 2-methoxyethanol for 24 h only one of the methoxy methyl groups had been lost, giving (4). This *cis*-configuration follows from the ^{31}P n.m.r. data with ^2J(PP) only 14·7 Hz, $\delta_1 = -7·5$ p.p.m., ^1J(PtP) 3538 Hz and $\delta_2 = 33·2$ p.p.m., ^1J(PtP) 3261 Hz. When the orange [PtI$_2${PBu^{t}Me(2-methoxyphenyl)}$_2$] was heated with sodium iodide (20-fold excess) in 2-methoxyethanol for 4 days, the stable bis-chelate complex *cis*-[Pt{PBu^{t}Me(OC$_6$H$_4$)}$_2$] was isolated in low yield (33%). The white needles could be sublimed at 280° to give prisms. The *cis*-configuration was assigned on the basis of the ^{1}H n.m.r. (Table) and ^{31}P n.m.r. data with $\delta_{H_3PO_4} = -21·9$ and a large value of J(PtP), 3486 Hz. The ^{31}P n.m.r. spectrum indicated that only one isomer was present.

On heating *trans*-[PtCl$_2${PBu$^t_2$(2-methoxyphenyl)}$_2$] *in vacuo* at 200 °C methyl chloride was evolved and the very stable bis-chelate complex *trans*-[Pt{PBu$^t_2$(OC$_6$H$_4$)}$_2$] (5) formed. The *trans*-configuration follows from the ^{1}H n.m.r. data (Table 3). This bis-chelate complex was also slowly formed on heating the dichloro-complex in refluxing 2-methoxyethanol for 30 h (50% yield). In the presence of sodium iodide (20-fold excess) demethylation was a little faster (80% yield after 30 h reflux). This di-chelate complex is thermally stable and sublimes without decomposition when heated above 230°.

trans-[PtCl$_2${PBu$^t_2$(2-methoxyphenyl)}$_2$] shows strong i.r. absorption bands at 1250 cm^{-1} and 800 cm^{-1} attributed to the C–O–CH$_3$ grouping; these bands were absent from the i.r. absorption spectrum of *trans*-[Pt{PBu$^t_2$(OC$_6$H$_4$)}$_2$]. When treated with an excess of dry hydrogen chloride in ether–chloroform one of the chelate rings was opened to give the *o*-hydroxyphenylphosphine complex [PtCl(PBu$^t_2$C$_6$H$_4$O){PBu$^t_2$-(2-hydroxyphenyl)}] (6). The constitution of this



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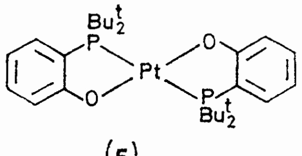

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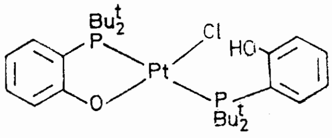

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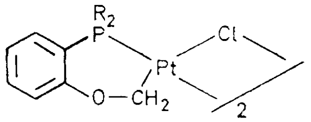
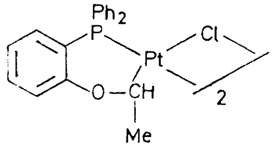
complex follows from the analytical, i.r., and ^{1}H n.m.r. data (Tables). Although we could not detect the OH proton in the ^{1}H n.m.r. spectrum (presumably it was duried under the other resonances) the i.r. spectrum showed a band at 3160 cm^{-1} (broad) due to OH and a strong band at 335 cm^{-1} {ν(PtCl)}. When treated with a methanolic solution of sodium hydroxide $[\mathrm{PtCl\{PBu^t_2(C_6H_4O)\}\{PBu^t_2(C_6H_4OH)\}}]$ readily reverted to *trans*-$[\mathrm{Pt\{PBu_2(C_6H_4O)\}_2}]$. The white $[\mathrm{Pt(Ph_2PC_6H_4O)_2}]$ dissolved in a $\mathrm{CHCl_3}$–HCl–$\mathrm{Et_2O}$ mixture to give a yellow solution but on the addition of methanol it was recovered unchanged. Possibly ring-opening had occurred in the yellow solution but we were unable to isolate a ring-opened species.

C-*Metallation of* 2-*Methoxyphenylphosphines*.—As described above compounds of the type $[\mathrm{PtX_2L_2}]$ (X = halogen, L = 2-methoxyphenylphosphine) when heated, especially in a polar solvent, undergo *O*-metallation (*i.e.* demethylation). In contrast, we find that several of these phosphines when heated in a non-polar solvent with $[\mathrm{PtCl_2(PhCN)_2}]$ in the ratio P : Pt of 1 : 1 undergo *C*-metallation with evolution of hydrogen chloride. Thus heating a mixture of $\mathrm{PPh_2}$(2-methoxyphenyl) and $[\mathrm{PtCl_2(PhCN)_2}]$ in xylene for 1·5 h gave the very insoluble chlorine-bridged *C*-metallated complex (7) (R = Ph). This formulation follows from the analytical data, from the occurrence of two bands due to ν(PtCl) (bridging) at 273 and 247 cm^{-1} and from the bridge-splitting reactions (see below). $\mathrm{PPh_2}$(2-ethoxyphenyl) underwent a similar reaction with $[\mathrm{PtCl_2(PhCN)_2}]$ although less readily to give (8), containing a metallated secondary carbon atom. $\mathrm{PBu^tMe}$(2-methoxyphenyl) similarly gave a bridged complex $[\mathrm{Pt_2Cl_2(MeBu^tPC_6H_4OCH_2)_2}]$ of this type. The ^{1}H n.m.r. spectrum (Table 5) showed a broad doublet at τ 8·76 due to the t-butyl resonance and a broad doublet at τ 8·20 with ^{195}Pt satellites due to the phosphine methyls. The broadness of the resonances was possibly due to the presence of *rac*- and *meso*-isomers. The methylene resonance centred at τ 4·99 was complex. Metathesis with sodium iodide gave the corresponding iodide mixture, $[\mathrm{Pt_2I_2(MeBu^tPC_6H_4OCH_2)_2}]$.



(7)

$\mathrm{R_2 = Ph_2}$ or $\mathrm{Me.Bu^t}$



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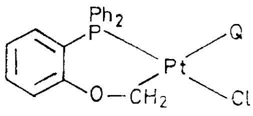

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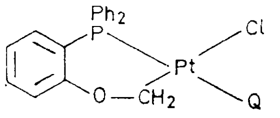

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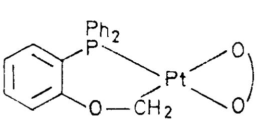
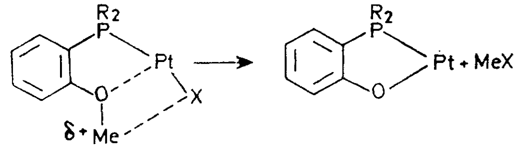


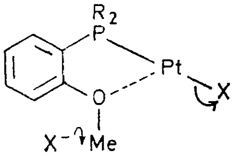
(11)

These *C*-metallated compounds are unusual in that they appear to be the first examples of internal metallation with formation of a six-membered ring and in that the carbon atom metallated is bonded to oxygen. We have been unable to make the analogous complex from $\mathrm{PMe_2}$(2-methoxyphenyl) for a mixture of $[\mathrm{PtCl_2(PhCN)_2}]$ and $[\mathrm{PtCl_2\{PMe_2(2\text{-}methoxyphenyl)\}_2}]$ when heated in xylene gave metallic platinum and in refluxing toluene (1·5 h) the bright yellow chlorine bridged unmetallated $[\mathrm{Pt_2Cl_4(Me_2PC_6H_4OMe)_2}]$ (see Tables for data confirming this formulation).

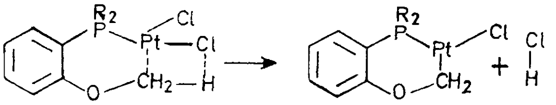
When pyridine was added to a suspension of $[\mathrm{Pt_2Cl_2\{Ph_2PC_6H_4OCH_2\}_2}]$ in deuteriochloroform a clear colourless solution was obtained. The ^{1}H n.m.r. spectrum indicated that a mixture was present in solution since methylene resonances occurred at τ 5·02 and 5·48 in approximate intensity ratios of 4 : 1. These resonances were doublets with satellites due to platinum-195 splitting. The two isomers (9) and (10) were probably present in solution (Q = py). The solid crystalline product was probably only one of these isomers and showed one band due to ν(PtCl) but we could not definitely assign its stereochemistry. Similarly $[\mathrm{Pt_2Cl_2(Ph_2PC_6H_4OCHMe)_2}]$ when treated with pyridine gave a mixture of isomers in approximate ratio of 3 : 1 (see Table 5). Treatment of $[\mathrm{Pt_2Cl_2(PPh_2C_6H_4OCH_2)_2}]$ with $\mathrm{Ph_2PC_6H_4OMe}$ gave only one isomer (Table 5), ν(PtCl) 283 cm^{-1}. The ^{31}P n.m.r. spectrum showed this to have configuration (10) with ^{2}J(PP) 437 Hz, $\delta_1 = -25{\cdot}1$ p.p.m., ^{1}J(PtP) 3177 Hz and $\delta_2 = -8{\cdot}3$ p.p.m., ^{1}J(PtP) 3178 Hz. We cannot explain these large values for ^{1}J(PtP). Metathesis with sodium iodide in acetone gave the corresponding iodide (Tables 4 and 5). When heated with sodium iodide under reflux for 3 days in 2-methoxyethanol the monochloride $[\mathrm{PtCl(Ph_2PC_6H_4OCH_2)(Ph_2PC_6H_4OMe)}]$ gave a mixture of the corresponding mono-iodide and $[\mathrm{Pt(Ph_2PC_6H_4O)_2}]$. When treated with thallous acetylacetonate a suspension of the binuclear chlorine bridged $[\mathrm{Pt_2Cl_2(Ph_2PC_6H_4OCH_2)_2}]$ (7) in benzene readily gave the soluble mononuclear acetylacetonate $[\mathrm{Pt(acac)(Ph_2PC_6H_4OCH_2)}]$ (11). The corresponding chlorine-bridged complex from $\mathrm{Ph_2PC_6H_4OCH_2Me}$ was also converted into the acetylacetonate (see Table 5 for the ^{1}H n.m.r. data). $[\mathrm{Pt_2Cl_2\{Bu^tMePC_6H_4OCH_2\}_2}]$ was similarly converted to a benzoylacetophenate although the resonance due to the methylene protons was complex and not analysed.

Factors Affecting O- *or* C-*Metallation*.—*O*-Metallation was observed for compounds of the type $[PtX_2(R_2PC_6H_4OR')_2]$ {R = Ph or Bu^t and Me (with difficulty), R′ = Me or Et} either on very strong heating or on heating in a high boiling alcohol (2-methoxyethanol, b.p. 124°). Iodides metallated faster than chlorides but since added halide ion had very little affect on the rate we suggest that demethylation (de-ethylation) occurs *via* a four-centre transition state rather than with external attack by halide ion such as occurs in the demethylation of anisole by hydriodic acid. We found that boiling a suspension of *trans*-$[PtI_2\{Ph_2P(2\text{-methoxyphenyl})\}_2]$ in xylene (b.p. *ca.* 135°) even after 3 days caused demethylation of only one phosphine, giving $[PtI\{Ph_2P(C_6H_4O)\}\{Ph_2P(2\text{-methoxyphenyl})\}]$. Possibly therefore demethylation is favoured by a polar solvent and involves a polar transition state.





C-Metallation was observed when the tertiary 2-alkoxyphenylphosphine and $[PtCl_2(RCN)_2]$, in 1 : 1 mole ratio, were heated in a non-polar solvent such as xylene. It seems unlikely that *C*-metallation could involve an oxidative addition reaction with a platinum(IV) intermediate since platinum(II) with only one tertiary phosphine ligand is likely to have very little nucleophilic character. We tentatively suggest that in *C*-metallation a four centre intermediate is involved and the metal acts essentially as an electrophile.



It has been shown that *C*-metallation by platinum(II) can be promoted if the leaving group is methyl.[8] We therefore synthesised the dimethyl complex *cis*-$[PtMe_2\{Ph_2P(2\text{-methoxyphenyl})\}_2]$ from the corresponding dichloride and methyl-lithium. Although methane was evolved from this complex on pyrolysis (200 °C, 5 min) no solid material could be isolated from the resultant red oil.

EXPERIMENTAL

M.p.s were recorded on a Kofler hot-stage apparatus and are corrected. All reactions involving free tertiary phosphines or heating under reflux in 2-methoxyethanol or xylene were carried out under argon. Percentage yields, m.p.s, and analytical and molecular-weight data are given in the Tables.

The ligands *diphenyl*(2-*methoxyphenyl*)*phosphine* and *diphenyl*(2-*ethoxyphenyl*)*phosphine* were prepared by a general method.[9] They were obtained as prisms from benzene–ethanol and needles from ethanol respectively.

t-Butyl(2-*methoxyphenyl*)*methylphosphine*.— t-Butyl(methyl)chlorophosphine (38·1 g, 0·275 mol) in ether (100 ml) was added dropwise during 40 min to a well stirred solution of 2-methoxyphenylmagnesium bromide (0·413 mol) in ether (200 ml) at 0 °C. The mixture was heated under reflux for 1 h and then hydrolysed with water. Isolation by distillation gave the *product* (33·0 g) as a colourless liquid.

Di-t-butyl(2-*methoxyphenyl*)*phosphine*.—A solution of di-t-butylchlorophosphine (101·7 g, 0·564 mol) in diethyl ether (100 ml) was added to a well stirred solution of 2-methoxyphenyl-lithium (1·24 mol) in diethyl ether (500 ml) at 20°. The resultant mixture was refluxed for 6 h, cooled, hydrolysed with water, and the product worked up in ether in the usual way.

Diphenylmethyl(2-*methoxyphenyl*)*phosphonium Iodide*.—Iodomethane (0·5 ml) was added to a solution of diphenyl-2-methoxyphenylphosphine (5·00 g, 17·2 mmol) in acetonitrile (20 ml). After ½ h, the solution was evaporated to dryness and the resultant oil crystallized from acetone to give the *product* (5·34 g) as micro-crystals.

Diphenylmethyl(2-*ethoxyphenyl*)*phosphonium iodide*, *t-butyldimethyl*(2-*methoxyphenyl*)*phosphonium iodide*, and *di-t-butylmethyl*(2-*methoxyphenyl*)*phosphonium iodide* were prepared similarly.

trans-*Dichlorobis*{*diphenyl*(2-*methoxyphenyl*)*phosphine*}-*platinum*(II).—A solution of dichlorobis(trimethylacetonitrile)platinum(II) (1·30 g, 3·00 mmol) in dichloromethane (20 ml) was treated with diphenyl(2-methoxyphenyl)phosphine (1·78 g, 6·04 mmol) and the resulting solution diluted with methanol to give the *product* (2·40 g) as plates.

trans-*Dichlorobis*{*diphenyl*(2-*ethoxyphenyl*)*phosphine*}-*platinum*(II); cis-*Dichlorobis*{*dimethyl*(2-*methoxyphenyl*)-*phosphine*}*platinum*(II).—These were prepared in a similar manner as plates from dichloromethane–methanol and prisms from dichloromethane–light petroleum (b.p. 60—80°) respectively.

meso-trans- *and* rac-trans-*Dichlorobis*{*t-butyl*(*methyl*)-(2-*methoxyphenyl*)*phosphine*}*platinum*(II).—A solution of dipotassium tetrachloroplatinate(II) (1·470 g, 3·50 mmol) in water (50 ml) was treated with t-butyl(methyl)(2-methoxyphenyl)phosphine (1·546 g, 7·35 mmol) in ethanol (10 ml). A yellow solid separated after 1 h *via* a transient pink one. Extraction with dichloromethane and dilution with methanol at 20° gave the *meso-trans* isomer (0·965 g) as plates. The mother liquors later deposited the *rac-trans* isomer (0·567 g) as needles.

trans-*Dichlorobis*{*di-t-butyl*(2-*methoxyphenyl*)*phosphine*}-*platinum*(II).— Di-t-butyl(2-methoxyphenyl)phosphine (0·60 g) was added to a solution of dichlorobis(benzonitrile)-platinum(II) (0·48 g) in dichloromethane (10 ml). Methanol (*ca.* 15 ml) was added to the resultant mixture after 15 min and most of the dichloromethane slowly removed under reduced pressure to give the required product as yellow microprisms.

Di-iodobis{*diphenyl*(2-*methoxyphenyl*)*phosphine*}*platinum*(II).—A solution of dichlorobis(trimethylacetonitrile)platinum(II) (0·20 g, 0·463 mmol) in acetone (15 ml) was treated with sodium iodide (0·610 g, 4·63 mmol). After 10

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

[9] A. E. Senear, W. Valient, and J. Wirth, *J. Org. Chem.*, 1960, **25**, 2001.

min, diphenyl(2-methoxyphenyl)phosphine (0·295 g, 1·02 mmol) was added. Isolation and recrystallization from dichloromethane–methanol gave the *product* (0·491 g) as prisms.

Di-iodobis{diphenyl(2-ethoxyphenyl)phosphine}platinum(II); *and Di-iodobis{t-butyl(methyl)(2-methoxyphenyl)phosphine}platinum*(II).—These were prepared in a similar manner as prisms and needles respectively.

Di-iodobis{dimethyl(2-methoxyphenyl)phosphine}platinum(II).—A suspension of *cis*-dichlorobis{dimethyl(2-methoxyphenyl)phosphine}platinum(II) (0·800 g, 1·33 mmol) in acetone (30 ml) was heated with sodium iodide (1·99 g, 13·3 mmol) for 10 min. Isolation and recrystallization from dichloromethane–methanol gave the *product* (0·748 g) as prisms.

cis-*Bis{2-(diphenylphosphino)phenoxy}platinum*(II).—*Method* 1. A suspension of dichlorobis{diphenyl(2-methoxyphenyl)phosphine}platinum(II) (0·140 g, 0·136 mmol) and sodium iodide (0·409 g, 2·72 mmol) was heated under reflux in 2-methoxyethanol (20 ml) for 1·5 h. Isolation gave the *product* (0·100 g) as needles from dichloromethane–methanol.

Method 2. An identical product was similarly obtained from dichlorobis{diphenyl(2-ethoxyphenyl)phosphine}platinum(II) but with a reaction time of 3 days.

Method 3. Dichlorobis{diphenyl(2-methoxyphenyl)-phosphine}platinum(II) was heated to 270 °C under high vacuum. The evolved gas was collected and identified as chloromethane by its i.r. spectrum. Recrystallization of the residue from dichloromethane–methanol gave the required product (85% yield).

trans-*Bis{2-(di-t-butylphosphino)phenoxy}platinum*(II).—A mixture of the dichloride (0·25 g) and sodium iodide (0·55 g) in 2-methoxyethanol (25 ml) was heated under reflux for 30 h. The mixture was cooled giving the required product as yellow prisms which could be sublimed at 200 °C, 0·01 mmHg.

Chloro{2-(di-t-butylphosphino)phenoxy}{di-t-butyl(2-hydroxyphenyl)phosphine}platinum(II).—A solution of *trans*-bis{2-(di-t-butylphosphino)phenoxy}platinum(II) (0·10 g, 0·16 mmol) in deuteriochloroform (0·5 ml) was treated with an excess of a solution of hydrogen chloride in ether (1·7 M, 0·48 mmol). The solvent was removed under reduced pressure giving the required complex as yellow prisms.

cis-*Bis{2-[t-butyl(methyl)phosphino]phenoxy}platinum*(II).—A mixture of di-iodobis{t-butyl(methyl)(2-methoxyphenyl)phosphine}platinum(II) (1·12 g, 1·29 mmol) and sodium iodide (2 g) was heated in refluxing 2-methoxyethanol (20 ml) for 4 days. Isolation by evaporation and extraction with dichloromethane, followed by dilution with methanol gave the required product (0·25 g) as long white needles.

Iodo{2-(diphenylphosphino)phenoxy}{diphenyl(2-methoxyphenyl)phosphine}platinum(II).—A suspension of *trans*-di-iodobis[diphenyl(2-methoxyphenyl)phosphine]platinum(II) (0·30 g, 0·29 mmol) in xylene (20 ml) was heated under reflux for 41 h. The mixture was then cooled and the required product (0·19 g) filtered off as prisms.

Iodo{2-(dimethylphosphino)phenoxy}{dimethyl(2-methoxyphenyl)phosphine}platinum(II).—A suspension of dichlorobis[dimethyl(2-methoxyphenyl)phosphine]platinum(II) (0·301 g, 0·500 mmol) and sodium iodide (0·750 g, 5·00 mmol) in 2-methoxyethanol (15 ml) was heated under reflux for 23 h. Isolation gave the *product* (0·201 g) as needles from 2-methoxyethanol.

Di-μ-chloro-bis{2-(diphenylphosphino)phenoxymethyl(P)}diplatinum(II).—A solution of dichlorobis(benzonitrile)platinum(II) (0·995 g, 2·10 mmol) and diphenyl(2-methoxyphenyl)phosphine (0·585 g, 2·00 mmol) in xylene (200 ml) was heated under reflux for 1·5 h and then charcoal filtered. Evaporation of the filtrate gave the product (0·988 g) as microcrystals.

Di-μ-chloro-bis{1-[o-(diphenylphosphino)phenoxy]ethyl(P)}-diplatinum(II); *Di-μ-chloro-bis{2-(t-butylmethylphosphino)-phenoxymethyl}diplatinum*(II).—These two compounds were prepared similarly as microcrystals and prisms respectively.

Di-μ-chloro-dichlorobis{dimethyl(2-methoxyphenyl)phosphine}diplatinum(II).—This was prepared similarly using toluene as solvent and formed needles.

Acetylacetonato{2-(diphenylphosphino)phenoxymethyl(P)}-platinum(II).—A suspension of di-μ-chloro-bis{2-(diphenylphosphino)phenoxymethyl}diplatinum(II) (0·209 g, 0·20 mmol) and thallous acetylacetonate (0·127 g, 0·42 mmol) in benzene (20 ml) was shaken for 20 h. Isolation gave the *product* (0·177 g) as needles from benzene–cyclohexane.

Acetylacetonato{1-[o-(diphenylphosphino)phenoxy]-ethyl(P)}platinum(II).—This was prepared similarly as microcrystals.

Benzoylacetophenato{2-(t-butylmethylphosphino)phenoxymethyl(P)}platinum(II).—This was also prepared similarly as prisms from benzene–n-heptane by using thallous benzoylacetophenate.

Di-μ-iodo-bis{2-(t-butylmethylphosphino)phenoxymethyl}-diplatinum(II).—A suspension of di-μ-chloro-bis{2-(t-butylmethylphosphino)phenoxymethyl}diplatinum(II) (0·200 g, 0·228 mmol) and sodium iodide (0·342 g, 2·28 mmol) in acetone (10 ml) was heated under reflux for ½ h. Isolation gave the *product* (0·190 g) as prisms from dichloromethane–methanol.

Chloro{2-(diphenylphosphino)phenoxymethyl}pyridine-platinum(II).—A suspension of di-μ-chloro-bis{2-(diphenylphosphino)phenoxymethyl}diplatinum(II) (0·073 g, 0·07 mmol) in deuteriochloroform (0·5 ml) was treated with pyridine dropwise until dissolution occurred. Dilution with light petroleum (b.p. 60—80 °C) gave the *product* (0·075 g) as needles.

Chloro{1-[o-(diphenylphosphino)phenoxy]ethyl(P)}pyridineplatinum(II).—This was prepared similarly as plates from deuteriochloroform–methanol.

Chloro{2-(diphenylphosphino)phenoxymethyl}{diphenyl-(2-methoxyphenyl)phosphine}platinum(II).—A mixture of di-μ-chloro-bis{2-(diphenylphosphino)phenoxymethyl}di-platinum(II) (0·351 g, 0·336 mmol) and diphenyl(2-methoxyphenyl)phosphine (0·216 g, 0·738 mmol) in acetone (10 ml) was heated for 5 min. On cooling, the *product* (0·429 g) separated as prisms.

Iodo{2-(diphenylphosphino)phenoxymethyl}{diphenyl(2-methoxyphenyl)phosphine}platinum(II).—A suspension of chloro{2-(diphenylphosphino)phenoxymethyl}{diphenyl-(2-methoxyphenyl)phosphine}platinum(II) in acetone (10 ml) was treated with sodium iodide (0·157 g, 1·10 mmol). Isolation in the usual way gave the *product* (0·092 g) as prisms from dichloromethane–methanol.

cis-*Dimethyl{diphenyl(2-methoxyphenyl)phosphine}platinum*(II).—Methyl-lithium (10 mmol) in ether (5 ml) was added to a suspension of dichlorobis{diphenyl(2-methoxyphenyl)phosphine}platinum(II) (0·43 g, 0·5 mmol) in benzene (20 ml). After the addition of water the product was isolated from the organic layer and formed needles (0·40 g) from benzene–n-heptane.

N.M.R. Spectra.—^1H Spectra were measured at 60 MHz and 35 °C on a Perkin-Elmer R 12 spectrometer. ^{31}P Spectra were measured at 36·43 MHz and *ca.* 30 °C on a Bruker HFX spectrometer using a deuterium (CD_3COCD_3) lock and 'random noise' decoupling of protons. The chemical shifts were measured with respect to a 10% v/v $P(OMe)_3$ solution in CH_2Cl_2 and are quoted with respect to 85% H_3PO_4 which was found to be 141 p.p.m. to high field of $P(OMe)_3$. Shifts to high field of 85% H_3PO_4 are positive and to low field negative.

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