Some Complexes of Platinum, Palladium, Nickel, and Cobalt formed from (2-Hydroxyphenyl)diphenylphosphine and (2-Hydroxyphenyl)di-t-butylphosphine †

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The new phosphines $PPh_2(C_6H_4OH\text{-}2)$ and $PBu^t_2(C_6H_4OH\text{-}2)$ are described. With $K_2[PtCl_4]$ or $Na_2[PdCl_4]$ $PPh_2(C_6H_4OH)$(L) gives impure complexes $[MCl_2L_2]$ (M = Pt or Pd) which readily lose hydrogen chloride to give $[M(OC_6H_4PPh_2)_2]$ (the palladium complex as a hydrate). With $Na[BH_4]$, *cis*-$[Pt(OC_6H_4PPh_2)_2]$ gives the hydride $[PtH(OC_6H_4PPh_2)L]$, and with methyl-lithium the derivative $[PtMe(OC_6H_4PPh_2)L]$. With acetic anhydride the platinum hydride gives the acetyl complex $[Pt(COMe)(OC_6H_4PPh_2)\{PPh_2(C_6H_4O_2CMe\text{-}2)\}]$. The phosphine $PPh_2(C_6H_4OH\text{-}2)$ with $[Pd_2(2\text{-methylallyl})_2(O_2CMe)_2]$ gives $[Pd(2\text{-methylallyl})(O_2CMe)L]$. The complexes $[M(OC_6H_4PBu^t_2)_2]$ (M = Pt, Pd, Ni, or Co) are readily prepared from $PBu^t_2(C_6H_4OH\text{-}2)$ (L′). The nickel complex is green but changes reversibly to an orange form on heating. The complex $[Pd(2\text{-methylallyl})(O_2CMe)L']$ has also been prepared and on heating gives the volatile and non-fluxional $[Pd(2\text{-methylallyl})(OC_6H_4PBu^t_2)]$. Hydrogen-1, ^{13}C, and ^{31}P n.m.r. and i.r. data are given.

TERTIARY 2-hydroxyphenylphosphines or their complexes with metals have not previously been described although we have prepared several complexes containing the chelate system (I; M = metal) by *O*-dealkylation of 2-alkoxyphenylphosphines (II).[1,2] Some of these complexes show interesting properties such as the reversible uptake of dioxygen,[3] co-ordinative unsaturation, and a high reactivity to small molecules:[3] a few are highly coloured. We have also shown that the

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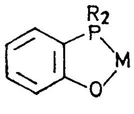
† No reprints available.

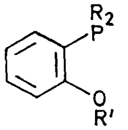
[1] C. E. Jones, B. L. Shaw, and B. L. Turtle, *J.C.S. Dalton*, 1974, 992.

[2] H. D. Empsall, E. M. Hyde, C. E. Jones, and B. L. Shaw, *J.C.S. Dalton*, 1974, 1980.

[3] R. Mason, K. M. Thomas, H. D. Empsall, S. R. Fletcher, P. N. Heys, E. M. Hyde, C. E. Jones, and B. L. Shaw, *J.C.S. Chem. Comm.*, 1974, 612.

2-methoxy-groups in *trans*-[Ir(CO)Cl{$PMe_2(C_6H_4OMe)$}$_2$] greatly increase the rate of the oxidative addition of


(I)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methyl iodide (neighbouring-group participation or intramolecular catalysis).[4]

It was therefore of interest to synthesise two tertiary 2-hydroxyphenylphosphines, *viz.* $PPh_2(C_6H_4OH\text{-}2)$ and $PBu^t_2(C_6H_4OH\text{-}2)$, and to study their complexes with metals. We anticipated that these hydroxy-ligands would readily lose a proton to give a chelate system of type (I), but we also hoped to prepare complexes in which the hydroxy-group was intact and in a suitable position for interaction with another ligand in a *cis* position (for example by hydrogen bonding).

TABLE 1

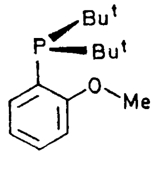
^1H N.m.r.[a] and i.r.[b] data for the phosphines $PPh_2(C_6H_4OH\text{-}2)$ and $PBu^t_2(C_6H_4OH\text{-}2)$ and their methiodide salts

Compound	δ(OH)	δ(Bu^t)	δ(Me)	ν(OH)
$PPh_2(C_6H_4OH\text{-}2)$	6.00(br)			3 220sbr
$PBu^t_2(C_6H_4OH\text{-}2)$	7.60(br)	1.20(d)(12.7)		3 240mbr
[$PMePh_2(C_6H_4OH\text{-}2)$]I	9.10(br)		2.78(d)(13.4)	3 025sbr
[$PMeBu^t_2(C_6H_4OH\text{-}2)$]I	9.64(br)	1.49(d)(16.1)	2.19(d)(11.0)	3 080vsbr

[a] Spectra were recorded at *ca.* 35 °C and 60 MHz in $CDCl_3$ solution; δ ±0.2 p.p.m., *J* ±0.5 Hz; d = doublet. ^2J(PH) Values are given in parentheses. [b] Spectra were recorded as Nujol mulls (cm^{-1}); m = medium, s = strong, and br = broad.

RESULTS AND DISCUSSION

Preparation of the 2-Hydroxyphenylphosphines, $PPh_2(C_6H_4OH\text{-}2)$ *and* $PBu^t_2(C_6H_4OH\text{-}2)$.—3- or 4-Hydroxyphenylphosphines have been prepared by demethylation of the corresponding methoxyphenylphosphine using 48% hydrobromic acid or 57% hydriodic acid.[5-7] However, we find that similar treatment of $PPh_2(C_6H_4OMe\text{-}2)$ gives $PPh_2(C_6H_4OH\text{-}2)$ in low yield. Since the isopropoxy-group is more readily cleaved by acids than the methoxy-group,[8] we therefore treated $PPh_2(C_6H_4OPr^i\text{-}2)$ with 60% HBr and obtained the hydrobromide salt of the required phosphine. This hydrobromide salt was insoluble in aqueous sodium hydroxide but was converted into the required phosphine by dissolving it in acetone and adding sodium acetate until the solution was neutral. (2-Hydroxyphenyl)di-t-butylphosphine was prepared by demethylation of the corresponding 2-methoxyphenylphosphine [1] and subsequent treatment with aqueous sodium carbonate. Both these phosphines were characterised by their methiodide salts: details of the preparation and characterisation (i.r. and n.m.r. data) are in the Experimental section and Table 1. The ^{31}P n.m.r. spectrum of $PBu^t_2(C_6H_4OH\text{-}2)$ in C_6D_6 showed only one resonance [$\delta(H_3PO_4)$ −6.22 p.p.m.] and the ^{13}C n.m.r. spectrum (Table 2) in C_6D_6 also showed only one species. This contrasts with $PBu^t_2(C_6H_4OMe\text{-}2)$ where both the ^{31}P and ^{13}C n.m.r. spectra show two species, conformations (III) and (IV), to be present. (The ^{31}P data are given in footnote *b*, Table 2.) This difference probably arises because the methoxy-group is more bulky than hydroxy and rotation around the phosphorus–aryl bond is prevented, giving two conformations.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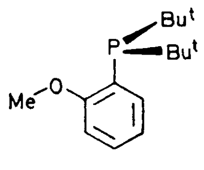
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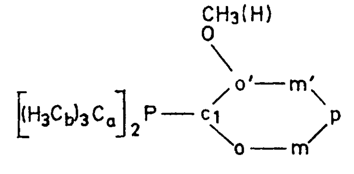
TABLE 2

^{13}C N.m.r. data[a] for $PBu^t_2(C_6H_4OH\text{-}2)$ and the two conformers of $PBu^t_2(C_6H_4OMe\text{-}2)$

$PBu^t_2(C_6H_4OH\text{-}2)$	$PBu^t_2(C_6H_4OMe\text{-}2)$		Assignment[c]
	Conformer 1	Conformer 2[b]	
30.2(d)(13)	30.7(d)(17)	30.7(d)(17)	b
32.2(d)(13)	32.2(d)(21)	32.5(d)(19)	a
	53.6(s)	55.4(s)	OCH_3
119.2(s)	110.3(s)	111.6(s)	m
131.5(s)	119.8(s)	135.8(s)	p
115.4(s)	120.1(d)(16)	130.6(d)(20)	m′
119.4(d)(11)	126.5(d)(38)	129.0(29)	c_1
134.3(s)	141.2(s)	143.7(s)	o
162.2(d)(20)	161.2(d)(6)	164.0(d)(19)	o′

[a] Spectra were recorded at ambient temperature and 22.62 MHz in C_6D_6 solution with all ^1H nuclei decoupled; δ ±0.1 p.p.m., *J* (in parentheses) ±1.5 Hz; $SiMe_4$ was used as internal standard. All the shifts are to low field and positive. [b] The resonances for conformer 2 were less intense than those of conformer 1. The ^{31}P n.m.r. spectrum (in $CDCl_3$) showed resonances at δ 55.09(s) and 10.32 p.p.m. in an intensity ratio of *ca.* 11 : 9. [c] The assignments are tentative. They were made by comparison with the ^{13}C spectra of $PBu^t_2[C_6H_3(OMe)_2\text{-}2,3]$ and $PBu^t_2[C_6H_3(OMe)_2\text{-}2,6]$ [12] and a literature source.[13] The various carbon atoms are labelled as follows:



Platinum, Palladium, Nickel, and Cobalt Complexes formed from $PR_2(C_6H_4OH\text{-}2)$ (R = Ph *or* Bu^t) *and* $PPh_2(C_6H_4OH\text{-}2)$.—Treatment of an ethanolic solution of $PPh_2(C_6H_4OH\text{-}2)$ (L) with an aqueous solution of

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

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

[6] O. Neunhoffer and L. Lamza, *Chem. Ber.*, 1961, **94**, 2519.

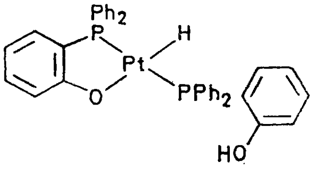
[7] L. Lamza, *J. prakt. Chem.*, 1964, **25**, 294.

[8] 'Protective Groups in Organic Chemistry,' ed. J. F. W. McOmie, Plenum, London, 1973.

$K_2[PtCl_4]$ gave the yellow complex *trans*-$[PtCl_2L_2]$ which was purified by recrystallisation from dichloromethane–methanol. The microanalytical data give an approximate fit for a dichloromethane solvate (Table 3). Neither this complex nor the analogous palladium complex *cis*-$[PdCl_2L_2]$ (see Experimental section) could be isolated analytically pure, although highly crystalline; the microanalytical data for the palladium complex were particularly variable. We believe that this is due to the ease of ring closure of the complexes (see later) and the uptake of solvents (detected by ^1H n.m.r. spectroscopy). The stereochemical assignments *trans*-$[PtCl_2L_2]$ and *cis*-$[PdCl_2L_2]$ follow from the far-i.r. data (Table 4). A *cis* configuration for palladium is unusual and we cannot explain why it should be preferred to the *trans* configuration. The i.r. spectra showed bands due to ν(OH) at 3 495 and 3 200 cm^{-1} for the platinum complex and at 3 220 cm^{-1} for the palladium complex. The ^1H n.m.r. spectra showed signals due to the hydroxy-proton at δ 1.49 p.p.m. for the platinum, and δ 2.05 p.p.m. for the palladium, complex.

When a suspension of *trans*-$[PtCl_2L_2]$ was heated for 10 min in ethanol containing sodium acetate, the known complex *cis*-$[Pt(OC_6H_4PPh_2)_2]$ was formed readily. Similar treatment of *cis*-$[PdCl_2L_2]$ gave a yellow suspension. This was evaporated to dryness and extracted with dichloromethane, and then water. Dilution of the dichloromethane solution with light petroleum gave a bright yellow complex which we have formulated as $[Pd(OC_6H_4PPh_2)_2]\cdot H_2O$. The i.r. spectrum of the complex in Nujol showed bands at 3 410 and 3 300 cm^{-1} due to ν(OH) and a band at 1 685 cm^{-1}. An i.r. spectrum of 'wet' Nujol gave nearly identical bands. The analytical data (Table 3) fit the formulation and the ^1H n.m.r. spectrum (Table 4) had a signal at δ 1.65 p.p.m. due to hydroxy-protons.

We had hoped to prepare platinum(0) complexes of the type $[Pt(acetylene)L_2]$ with acetylenes containing polar groups such as hydroxy and to look for direct ligand–ligand interactions (*e.g.* hydrogen bonding). However, when *trans*-$[PtCl_2L_2]$ was treated with ethanolic hydrazine hydrate in the presence of an acetylene only *cis*-$[Pt(OC_6H_4PPh_2)_2]$ was isolated (and in good yield). We have however reduced *cis*-$[Pt(OC_6H_4PPh_2)_2]$ to a hydride by treatment with sodium tetrahydroborate in ethanol–benzene. The white complex $[PtH(OC_6H_4PPh_2)\{PPh_2(C_6H_4OH)\}]$ (V) was readily obtained. The i.r. spectrum showed a band at 2 200 cm^{-1} due to ν(PtH), and bands at 2 500 and 2 415 cm^{-1} due to ν(OH), *cf.* ν(OH) for $PPh_2(C_6H_4OH\text{-}2)$ is at 3 220 cm^{-1} (see above). For the same amount of complex, the bands due to ν(OH) are not concentration dependent in $CHCl_3$ solution so the interaction which causes them to be at such low frequencies is probably intramolecular. We suggest that the hydroxy-group is interacting with the metal, or possibly the hydride ligand. The complex is sparingly soluble in organic solvents. The 90-MHz ^1H n.m.r. spectrum showed a doublet of doublets at δ −19.22 p.p.m. due to the metal hydride coupled to two inequivalent phosphorus atoms (Table 5). A broad signal at δ 11.00 p.p.m. disappeared on adding D_2O to the n.m.r. solution and so it is assigned to the hydroxyl proton. The *trans* arrangement of phosphorus atoms follows from the large value of $^2J(PP)$ 388 Hz.



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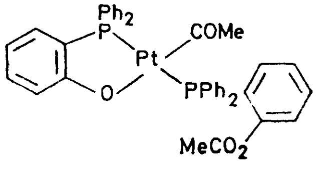


(VI)

This 2-hydroxyphenylphosphine hydride complex is sparingly soluble in organic solvents and in order to prepare a more soluble derivative we attempted to acetylate the hydroxy-group by treatment with acetic anhydride. However, an acetylplatinum complex, $[Pt(COMe)(OC_6H_4PPh_2)\{PPh_2(C_6H_4O_2CMe)\}]$ (VI), was formed in good yield (see Tables). The ^1H n.m.r. spectrum showed a signal due to the acetate methyl at δ 1.67 p.p.m. and a signal due to the metal-acetyl methyl at δ 1.32 p.p.m. with ^{195}Pt satellites. The i.r. spectrum had bands at 1 638 and 1 768 cm^{-1} due to the acetyl ν(CO) and acetate ν(CO) respectively. Benzene protons (solvate) were detected in the ^1H n.m.r. spectrum. A *trans* arrangement of the phosphorus nuclei is shown from the high value of $^2J(PP)$ 356 Hz. We treated $[PtCl(H)(PEt_3)_2]$ with acetic anhydride under the same conditions, but the hydride was recovered unchanged. Possibly, in the acetylation of $[PtH(OC_6H_4PPh_2)\{PPh_2(C_6H_4OH)\}]$, the hydroxy-group is acetylated and then intramolecular acyl transfer to the metal occurs.

Since *cis*-$[Pt(OC_6H_4PPh_2)_2]$ was readily ring-opened by $Na[BH_4]$, we attempted to effect a similar reaction with methyl-lithium. Thus, when a suspension of the *O*-metallated complex in dry benzene was treated with an excess of LiMe in diethyl ether a colourless solution was formed. This was hydrolysed with water to give a sparingly soluble methylplatinum complex, $[PtMe(OC_6H_4PPh_2)\{PPh_2(C_6H_4OH)\}]\cdot C_6H_6$. Benzene protons were detected in the ^1H n.m.r. spectrum (Table 5). There is also a sharp signal at δ 1.42 p.p.m. due to the hydroxy-proton (*cf.* δ 11.0 p.p.m. for that of the hydride complex). The platinum–methyl protons appeared as a doublet of doublets due to ^{31}P coupling of two inequivalent phosphorus nuclei, with sidebands due to ^{195}Pt coupling. The i.r. spectrum showed weak bands at 2 670 and 2 540 cm^{-1} attributed to ν(OH).

Complex (V) is isomeric with a hypothetical platinum(0) species $[Pt\{PPh_2(C_6H_4OH\text{-}2)_2\}]$, *i.e.* $[PtL_2]$ and we attempted to make acetylene complexes of the type $[Pt(acetylene)L_2]$ by heating this hydride with acetylenes in solvents such as ethanol or benzene. However, no acetylene complex could be detected; instead

TABLE 3

Analytical, melting point, and yield data for complexes of $PPh_2(C_6H_4OH\text{-}2)$ and $PBu^t_2(C_6H_4OH\text{-}2)$; calculated values are given in parentheses

	Complex	Yield (%)	M.p. (θ_c/°C)	Analysis (%)		
				C	H	Cl
(*a*)	L = $PPh_2(C_6H_4OH)$					
	trans-$[PtCl_2L_2]\cdot 1.5CH_2Cl_2$ [a]	100	160—170 [b]	46.65 (47.5)	3.55 (3.4)	19.9 (18.7)
	cis-$[PdCl_2L_2]$ [a]	100	178—180 [b]		see text	
	$[Pd(OC_6H_4PPh_2)_2]\cdot H_2O$	100	310	63.9 (63.7)	4.5 (4.45)	
						M ($CHCl_3$)
	[Pd(2-methylallyl)(O_2CMe)L]	68	205—210	58.15 (57.8)	5.05 (5.05)	498 (499)
(*b*)	L′ = $PBu^t_2(C_6H_4OH)$					
	trans-$[Ni(OC_6H_4PBu^t_2)_2]$	51	210 [c]	62.95 (63.05)	8.1 (8.3)	542 (533)
	trans-$[Pd(OC_6H_4PBu^t_2)_2]$	100	240 [c]	57.7 (57.9)	7.5 (7.65)	
	$[Co(OC_6H_4PBu^t_2)_2]$	45	210 [c]	63.5 (63.05)	8.45 (8.3)	529 (534)
	[Pd(2-methylallyl)(O_2CMe)L′]	79	110 [d]	52.45 (52.35)	7.2 (7.25)	454 (459)
	[Pd(2-methylallyl)($OC_6H_4PBu^t_2$)]	100	174—176 [e]	54.25 (54.2)	7.3 (7.35)	405 (399)

[a] Analyses were variable due to the ease of ring closure and uptake of solvents. [b] Evolves gas. [c] Sublimes without melting. [d] Resolidified at 140 °C with sublimation, remelted at 174—176 °C, decomposed at 200 °C. [e] Sublimes at 130 °C.

TABLE 4

^{1}H N.m.r.[a] and i.r.[b] data for some platinum(II) and palladium(II) complexes of $PPh_2(C_6H_4OH\text{-}2)$, (L)

Complex	^{1}H N.m.r. (p.p.m.)		I.r. (cm^{-1})
	δ(OH)	other resonances	
trans-$[PtCl_2L_2]$	1.49(br)		ν(OH) 3 495mbr, 3 200sbr ν(PtCl) 341s
cis-$[PdCl_2L_2]$	2.05(br)		ν(OH) 3 220sbr ν(PdCl) 308s, 282m
$[Pd(OC_6H_4PPh_2)_2]\cdot H_2O$	1.65		ν(OH) 3 410mbr, 3 300(sh), 1 685mbr
[Pd(2-methylallyl)(O_2CMe)L] [c] (VII)	10.60(br)	Acetate Me: 2.05 2-methylallyl protons: H_a 4.62 d[J(PH) 6.0 Hz], H_b 3.58 d[J(PH) 9.0 Hz], H_c,H_d 2.86(br), H_e 1.97	ν(OH) 2 740sbr, 1 950sbr ν(CO) 1 759w, 1 712vs

[a] Spectra were recorded at 90 MHz and ambient temperatures in $CDCl_3$ unless stated otherwise; br = broad, d = doublet. [b] As Nujol or hexachlorobutadiene mulls; m = medium, s = strong, w = weak, sh = shoulder, br = broad. [c] At 60 MHz.

TABLE 5

^{1}H N.m.r.[a] and i.r.[b] data for some *O*-metallated platinum(II) complexes

Complex	^{1}H N.m.r. (δ/p.p.m., J/Hz)	I.r. (cm^{-1})
$[PtH(OC_6H_4PPh_2)\{PPh_2(C_6H_4OH)\}]$ [c]	δ(OH) 11.00(br) δ(PtH) −19.22(44) [^{2}J(PH) 13.43, ^{2}J(P′H) 17.09, ^{1}J(PtH) 1 205]	ν(OH) 2 500mbr, 2 415mbr ν(PtH) 2 220m
$[Pt(COMe)(OC_6H_4PPh_2)\text{-}\{PPh_2(C_6H_4O_2CMe)\}]\cdot C_6H_6$	δ(PtCOMe) 1.32 [^{3}J(PtH) 8.68] δ(O·OCMe) 1.67, δ(C_6H_6) 7.31	(PtCOMe) 1 638s ν(CO) (O_2CMe) 1 768s ν(CO)
$[PtMe(OC_6H_4PPh_2)\text{-}\{PPh_2(C_6H_4OH)\}]\cdot C_6H_6$ [c]	δ(OH) 1.42, δ(C_6H_6) 7.31 δ(PtMe) 0.74(dd) [^{3}J(PH) 3.5, ^{3}J(P′H) 7.0, ^{2}J(PtH) 52.4]	ν(OH) 2 540w, 2 670w

[a] Spectra were recorded at 60 MHz and 35 °C unless stated otherwise. [b] Nujol mulls. [c] Spectra were recorded at 90 MHz and ambient temperatures in $CDCl_3$ solution; δ ±0.1 p.p.m., J ±0.2 Hz.

TABLE 6

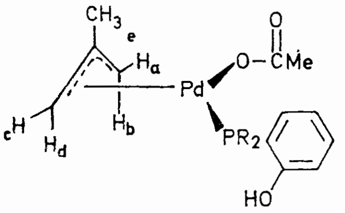
^{1}H N.m.r.[a] and i.r.[b] data for nickel(II) and palladium(II) complexes of $PBu^t_2(C_6H_4OH\text{-}2)$, (L′)

Complex	^{1}H N.m.r. (δ/p.p.m., J/Hz)		I.r. (cm^{-1})
	δ (Bu^t) [^{3}J(PH)]	other protons	
trans-$[Ni(OC_6H_4PBu^t_2)_2]$	1.60(t) [13.8]		
trans-$[Pd(OC_6H_4PBu^t_2)_2]$	1.51(t) [14.3]		
[Pd(2-methylallyl)(O_2CMe)L′] (VII)	1.27(d) [14.3]	acetate Me: 2.05 hydroxy H: 12.47(br)	ν(OH) 2 450sbr, 1 910sbr
	1.38(d) [14.3]	2-methylallyl protons: H_a 4.55(dd) [J(PH) 5.4, ^{4}J(HH) 2.2], H_b 3.54(d) [J(PH) 8.5 Hz), H_c 3.61(br), H_d 2.46(br), H_e 1.99(br)	ν(CO) 1 760w, 1 705s
[Pd(2-methylallyl)($OC_6H_4PBu^t_2$)] (VIII)	1.37(d) (14.3) 1.29(d) (14.0)	H_a 4.28(dd) [J(PH) 5.5, ^{4}J(HH) 3.0], H_b 3.48 d[J(PH) 8.5], H_c 3.41(br), H_d 2.38(br), H_e 1.97	

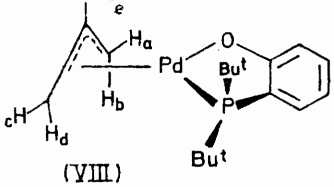
[a] Spectra were recorded at 60 MHz and 35 °C in $CDCl_3$ solution; d = doublet, dd = double doublet, t = triplet, br = broad.
[b] As hexachlorobutadiene mulls; s = strong, br = broad, w = weak.

the bis-chelated species $[Pt(OC_6H_4PPh_2)_2]$ was produced in high yield.

We also studied the action of this hydroxyphosphine, L, on $[Pd_2(C_6H_4Me\text{-}2)_2(O_2CMe)_2]$. When a benzene solution of this 2-methylallyl complex was treated with the hydroxyphosphine, L, in benzene, the pale yellow complex $[Pd(2\text{-methylallyl})(O_2CMe)L]$ (VII) was isolated (see Tables for characterising data). The ^{1}H n.m.r. spectrum of this complex showed a signal at δ 10.60 p.p.m. due to the hydroxyl proton. The i.r. spectrum had strong broad bands at 2 740 and 1 950 cm^{-1} due to ν(OH). These data indicate some interaction between the hydroxyl group and the palladium ion or even the acetate carbonyl. The assignment of the ^{1}H n.m.r. spectrum of the 2-methylallyl-proton region was made by comparison with the previously analysed spectrum of $[Pd(2\text{-methylallyl})Cl(PPh_3)]$.[9]



(VII)



(VIII)

(2-Hydroxyphenyl)di-t-butylphosphine.—When $[PtCl_2(NCBu^t)_2]$ was treated with $PBu^t_2(C_6H_4OH\text{-}2)$ (2 mol) (L′) in boiling ethanol the known *trans*-$[Pt(OC_6H_4PBu^t_2)_2]$ [1] was formed. The conversion took only 20 min, whereas formation of the complex by heating $[PtCl_2\{PBu^t_2(C_6H_4OH\text{-}2)\}_2]$ in 2-methoxyethanol took 24 h. The analogous nickel and palladium complexes were similarly prepared (see Table 3). The ^{1}H n.m.r. and i.r. spectra of the nickel and palladium complexes are very similar to those of the platinum complex. The complex *trans*-$[Ni(OC_6H_4PBu^t_2)_2]$ is unusual in that it is green both in the solid state and in solution and shows no paramagnetic shift or signal broadening in the ^{1}H n.m.r. spectrum. Square-planar nickel(II) complexes are usually red, yellow, or brown and diamagnetic, whereas tetrahedral nickel(II) complexes are usually blue or green and paramagnetic. However, *trans*-$[Ni(OC_6H_4PBu^t_2)_2]$, as well as showing no paramagnetic shift in the ^{1}H n.m.r. spectrum, shows only one signal in its ^{31}P n.m.r. spectrum at δ 46.1 p.p.m. The nickel ion has a room-temperature magnetic moment (Gouy method) of 1.3 B.M. after the usual correction for diamagnetism (*cf.* 2.8—4.0 B.M. in paramagnetic complexes).[*] On heating, the complex sublimes at 210 °C (1 atm) to give orange prisms, which became pale green again on cooling. Possibly the green form is a slightly distorted square-planar complex which changes to a more strictly square-planar form at higher temperatures.

Treatment of cobalt(II) chloride in boiling propan-2-ol with L (2 mol) readily gave the orange paramagnetic complex $[Co(OC_6H_4PBu^t_2)_2]$ (analytical data, Table 3). The i.r. spectrum of this complex is very similar to that of the platinum, palladium, and nickel analogues. The complex sublimes unchanged when heated to 180 °C under high vacuum. The cobalt ion has a room-temperature magnetic moment of 2.2 B.M. Square-planar complexes of Co^{II} are not common, but those known are all low spin, with magnetic moments of 2.2—2.7 B.M. The analogous square d^7 complexes $[M(OC_6H_4PBu^t_2)_2]$ (M = Ir or Rh) have been described. The rhodium and iridium complexes both react with NO to give the nitrosyl complexes $[M(NO)(OC_6H_4PBu^t_2)_2]$.[3] However, $[Co(OC_6H_4PBu^t_2)_2]$ was recovered unchanged when NO was bubbled through its benzene solution for 0.5 h. Possibly the smaller ionic radius of Co^{II} compared to Rh^{II} and Ir^{II} leads to excessive steric hindrance about the metal ion, so that even small molecules like NO cannot be accommodated in the co-ordination sphere.

Treatment of $[Pd_2(2\text{-methylallyl})_2(O_2CMe)_2]$ with L′ in benzene gave $[Pd(2\text{-methylallyl})(O_2CMe)L']$ (VII) (see Table 3 for analytical data). The i.r. spectrum of the complex (hexachlorobutadiene mull) showed strong broad bands at 2 450 and 1 910 cm^{-1} due to ν(OH), and in benzene solution the spectrum showed bands at 2 500 and 1 920 cm^{-1} which did not shift in more dilute solutions. The ^{1}H n.m.r. spectrum (Table 6) showed a hydroxy-proton signal at δ 12.47 p.p.m. The phosphine t-butyl groups are magnetically non-equivalent and give rise to two doublets in the ^{1}H n.m.r. spectrum.

When $[Pd(2\text{-methylallyl})(O_2CMe)L']$ was heated under high vacuum (0.005 mmHg) at 130 °C it gave a white sublimate. The ^{1}H n.m.r. and i.r. spectra of the sublimate showed that no hydroxy or acetate groups are present. The analytical data (Table 3) support the formulation $[Pd(C_3H_4Me\text{-}2)(OC_6H_4PBu^t_2)]$, (VIII). This thermally stable complex is a novel example of a neutral palladium–methylallyl complex containing a bidentate tertiary phosphine ligand. The ^{1}H n.m.r. spectrum of the complex was recorded in C_6D_6 within the range 30—100 °C and showed that no $\pi \rightarrow \sigma \rightarrow \pi$ interconversion of the 2-methylallyl group occurs. It is well known that π-allylpalladium complexes of the type $[\{Pd(allyl)Cl\}_2]$ undergo many types of rapid exchange processes at room temperature in the presence of unidentate tertiary phosphines.[9,10]

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[*] 1 B.M. ≈ 9.27×10^{-24} A m^2; 1 atm = 101 325 Pa; 1 mmHg ≈ 13.6 × 9.8 Pa.

[9] J. Powell and B. L. Shaw, *J. Chem. Soc. (A)*, 1967, 1839.

[10] K. Vrieze, H. C. Volger, and P. W. N. M. van Leeuwen, *Inorg. Chim. Acta Rev.*, 1969, **3**, 109.

EXPERIMENTAL

The general techniques and instruments used were the same as those described previously.[11]

(2-Isopropoxyphenyl)diphenylphosphine.—n-Butyl-lithium (0.725 mol) in hexane (380 cm^3) was added over 0.5 h to a mixture of isopropyl phenyl ether (97.8 g, 0.725 mol) and *NNN'N'*-tetramethylethylenediamine (84.4 g, 0.725 mol). The mixture was stirred for 20 h. The cloudy suspension was cooled to 0 °C and chlorodiphenylphosphine (146 g, 0.659 mol) in diethyl ether (300 cm^3) was added over 1.5 h. The mixture was heated under reflux for 5 h, then cooled to 0 °C and hydrolysed with water (500 cm^3). The ether layer was separated and the ether removed under reduced pressure. Fractional distillation of the residue gave the *product* (149 g) as a viscous liquid, yield 70%, b.p. 170 °C (0.2 mmHg).

(2-Isopropoxyphenyl)methyldiphenylphosphonium Iodide.—Iodomethane (0.5 cm^3) was added to a solution of the phosphine (5.00 g) in acetonitrile (20 cm^3). The mixture was put aside for 30 min and the required product isolated as microcrystals by evaporation and recrystallisation from acetone, yield 54%, m.p. 136—140 °C (Found: C, 57.05; H, 5.25. $\mathrm{C_{22}H_{24}IOP}$ requires C, 57.15; H, 5.25%).

2-(Hydroxyphenyl)diphenylphosphine.—A mixture of $\mathrm{PPh_2(C_6H_4OPr^i\text{-}2)}$ (68.6 g, 0.214 mol) and hydrobromic acid (60%, 250 cm^3) was heated under reflux for 1 h. Addition of water (250 cm^3) to the resulting solution gave a fine white solid. This was filtered off, dissolved in acetone (100 cm^3), and neutralised with sodium acetate. The required *product* was precipitated with water and recrystallised from light petroleum (b.p. 60—80 °C, 200 cm^3), yield 38.7 g (75%).

(2-Hydroxyphenyl)di-t-butylphosphine.—Hydriodic acid (55%, 40 cm^3) was decolourised by adding hypophosphorous acid (2 cm^3) and warming. (2-Methoxyphenyl)di-t-butylphosphine (7.12 g, 28.3 mmol) was added and the mixture was boiled for 2 h then cooled to 0 °C. A saturated solution of sodium carbonate was carefully added until the solution was neutral. Extraction of the mixture with diethyl ether (2 × 50 cm^3) followed by fractional distillation of the ether layer gave the *product* (3.03 g), b.p. 115—120 °C (1.5 mmHg), which later solidified.

Also prepared by the above method were *(2-hydroxyphenyl)methyldiphenylphosphonium iodide*, m.p. 208—210 °C (with sublimation) (Found: C, 53.9; H, 4.4. $\mathrm{C_{19}H_{18}IOP}$ requires C, 54.3; H, 4.3%) and *(2-hydroxyphenyl)methyldi-t-butylphosphonium iodide*, m.p. 222—228 °C (Found: C, 47.25; H, 6.75. $\mathrm{C_{15}H_{25}IOP}$ requires C, 47.4; H, 6.9%).

trans-*Dichlorobis[(2-hydroxyphenyl)diphenylphosphine]platinum*(II).—A solution of dipotassium tetrachloroplatinate(II) (0.71 g, 1.71 mmol of Pt) in water (15 cm^3) was slowly added to a solution of (2-hydroxyphenyl)diphenylphosphine (1.00 g, 3.59 mmol) in boiling ethanol. The resulting yellow solid was filtered off to give the *product* (1.46 g) as yellow needles.

cis-*Dichlorobis[(2-hydroxyphenyl)diphenylphosphine]palladium*(II).—(2-Hydroxyphenyl)diphenylphosphine (0.614 g, 2.20 mmol) was added to a solution of bis(benzonitrile)dichloropalladium(II) (0.384 g, 1.00 mmol) in dichloromethane (15 cm^3). Addition of light petroleum (b.p. 60—80 °C) to the solution gave the *product* (0.736 g) as yellow needles.

cis-*Bis[2-(diphenylphosphino)phenoxo]platinum*(II).—A mixture of $\mathrm{[PtCl_2\{PPh_2(C_6H_4OH\text{-}2)\}_2]}$ (0.767 g, 0.935 mmol) and sodium acetate (0.485 g, 3.74 mmol) in ethanol was boiled for 10 min to give a white suspension. This was filtered off and washed with water to give the product (0.629 g) as needles, yield 90%.

Bis[2-(diphenylphosphino)phenoxo]palladium(II) *hydrate* was prepared similarly as yellow needles.

[2-(Diphenylphosphino)phenoxo]hydrido[(2-hydroxyphenyl)diphenylphosphine]platinum(II), (V).—*Method* (a). A suspension of $\mathrm{[PtCl_2\{PPh_2(C_6H_4OH\text{-}2)\}_2]}$ (0.500 g, 0.61 mmol) in benzene (15 cm^3) and ethanol (15 cm^3) was warmed with sodium tetrahydroborate (0.369 g, 9.8 mmol) for 5 min giving a colourless solution. Addition of water to the solution and recrystallisation of the precipitate from benzene–n-heptane gave the product (0.378 g) as prisms, yield 76%.

Method (b). A suspension of *cis*-$\mathrm{[Pt(OC_6H_4PPh_2)_2]}$ (0.58 g, 0.76 mmol) in benzene (20 cm^3) and ethanol (20 cm^3) was warmed with $\mathrm{Na[BH_4]}$ (0.47 g) for 5 min to give a colourless solution. Addition of water to the solution and recrystallisation of the precipitate from benzene–n-heptane gave the *product* (0.43 g) as white prisms.

[(2-Acetoxyphenyl)diphenylphosphine]acetyl[2-(diphenylphosphino)phenoxo]platinum(II)*–Benzene* (1/1), (VI).—A mixture of complex (V) (0.10 g, 0.013 mmol) and acetic anhydride (1 cm^3) with a drop of pyridine was boiled for 2 min. Hydrolysis of the solution with water and recrystallisation of the precipitate from benzene–n-heptane gave the *product* (0.074 g) as cream needles.

[2-(Diphenylphosphino)phenoxo][(2-hydroxyphenyl)diphenylphosphine]methylplatinum(II)*–Benzene* (1/1).—A solution of methyl-lithium (4 mmol) in diethyl ether (3.4 cm^3) was added to a suspension of *cis*-$\mathrm{[Pt(OC_6H_4PPh_2)_2]}$ (0.63 g, 0.84 mmol) in dry benzene (20 cm^3). After 0.5 h, the solution was hydrolysed with water and the precipitate filtered off to give the *product* (0.38 g) as white microcrystals.

trans-*Bis[2-(di-t-butylphosphino)phenoxo]platinum*(II).—A mixture of dichlorobis(trimethylacetonitrile)platinum(II) (0.864 g, 2.00 mmol) and $\mathrm{PBu^t_2(C_6H_4OH\text{-}2)}$ (1.00 g, 4.19 mmol) in ethanol (15 cm^3) was boiled for 20 min. On cooling, a pale yellow solid was filtered off (1.24 g).

trans-*Bis[2-(di-t-butylphosphino)phenoxo]palladium*(II).—A solution of disodium tetrachloropalladate(II) (0.389 g, 1.32 mmol) in methanol (10 cm^3) was treated with $\mathrm{PBu^t_2(C_6H_4OH\text{-}2)}$ (0.694 g, 2.91 mmol) at room temperature. After 5 min, a yellow precipitate was filtered off and washed with water to give the *product* (0.770 g) as prisms. The product could be sublimed at 250 °C (0.03 mmHg).

trans-*Bis[2-(di-t-butylphosphino)phenoxo]nickel*(II).—A mixture of nickel(II) acetate (0.306 g, 1.73 mmol) and $\mathrm{PBu^t_2(C_6H_4OH\text{-}2)}$ (0.906 g, 3.81 mmol) in ethanol (30 cm^3) was boiled for 2 min to give a green solid. Isolation of this gave the *product* (0.471 g) as prisms. trans-*Bis[2-(di-t-butylphosphino)phenoxo]cobalt*(II) was prepared similarly from cobalt(II) chloride to give the *product* as orange prisms which sublimed at 180 °C (0.02 mmHg).

Acetato[(2-hydroxyphenyl)diphenylphosphine](2-methylallyl)palladium(II).—A solution of di-μ-acetato-bis[(2-methylallyl)palladium(II)] (0.175 g, 0.396 mmol) in benzene (5 cm^3) was treated with $\mathrm{PPh_2(C_6H_4OH\text{-}2)}$ (0.227 g, 0.815 mmol) and the resulting solution was stirred for 5 min.

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[11] H. D. Empsall, E. M. Hyde, and B. L. Shaw, *J.C.S. Dalton*, 1975, 1690.

[12] H. D. Empsall and P. N. Heys, unpublished work.

[13] 'Carbon-13 N.M.R. Spectroscopy,' ed. J. B. Stothers, Academic Press, New York, 1972.

Addition of n-heptane then gave the *product* (0.270 g) as pale yellow needles. *Acetato*[(*2-hydroxyphenyl*)*di-t-butylphosphine*](*2-methylallyl*)*palladium*(II) was prepared similarly as white prisms from light petroleum (b.p. 60—80 °C).

[2-(*Di-t-butylphosphino*)*phenoxo*](*2-methylallyl*)*palladium*(II).—The complex [Pd(2-methylallyl)(O_2CMe){$PBu^t{}_2$-(C_6H_4OH-2)}] (0.220 g, 0.480 mmol) was heated to 130 °C under high vacuum (0.005 mmHg). The white sublimate was collected, yield 0.193 g.

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