

## $\pi$ -Arene and $\pi$ -Phenoxo Complexes of Ruthenium and Rhodium †

By David J. Cole-Hamilton, Robert J. Young, and Geoffrey Wilkinson,\* Inorganic Chemistry Laboratories, Imperial College of Science and Technology, London SW7 2AY

The action of fluoroboric acid on dihydridotetrakis(triphenylphosphine)ruthenium(II) or on acetatohydridotris(triphenylphosphine)ruthenium(II) in methanol produces the salt  $[\text{RuH}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{PPh}_3)_2][\text{BF}_4]$  in which the phenyl group of one triphenylphosphine molecule is  $\pi$ -bonded to the metal. In the presence of benzene or toluene, similar arene complexes,  $[\text{RuH}(\eta^6\text{-Ar})(\text{PPh}_3)_2][\text{BF}_4]$  are obtained.

The interaction of  $\text{RuH}_2(\text{PPh}_3)_4$  with phenol gives a neutral complex,  $\text{RuH}(\text{C}_6\text{H}_5\text{O})(\text{PPh}_3)_2$ , that may also be obtained with two additional molecules of phenol hydrogen bonded to the oxygen atom of the phenoxo-ligand. The  $\text{C}_6\text{H}_5\text{O}^-$  ligand can be considered to be bound as an  $\eta^6$ -phenoxo or probably more realistically as an  $\eta^5$ -oxacyclohexadienyl ligand. Re-investigation of the compounds obtained by action of phenol on methyl- or phenyl-tris(triphenylphosphine)rhodium(I) shows that these also are  $\pi$ -phenoxo-complexes.

An  $\eta^6$ -toluene-*p*-sulphonate is also described.

I.r.,  $^1\text{H}$ , and  $^{31}\text{P}$  n.m.r. spectra of the compounds are given.

PROTONATED methanolic solutions of hydrido-phosphine complexes of ruthenium, e.g.  $\text{RuH}_2(\text{PPh}_3)_4$  and  $\text{RuH}(\text{OAc})(\text{PPh}_3)_3$ , have been shown<sup>1</sup> to be catalysts for the homogeneous hydrogenation of alk-1-enes under mild conditions. However, the loss of catalytic activity arises<sup>2</sup> from the formation of inactive cationic complexes of ruthenium that contain the basic unit  $[\text{RuH}(\text{PPh}_3)_2]^+$ . The ruthenium atom in this unit has twelve *d* electrons in its outer shell and thus requires, from donors, an additional six electrons to achieve the stable eighteen-electron configuration. Thus the complexes<sup>2</sup>  $[\text{RuH}(\text{PPh}_3)_2(\text{MeOH})_n(\text{H}_2\text{O})_{3-n}][\text{BF}_4]$  ( $n = 0-3$ ) may be isolated when aqueous  $\text{HBF}_4$  is used. In the presence of an excess of triphenylphosphine, however,  $[\text{RuH}(\text{PPh}_3)_3][\text{BF}_4]$  is formed.<sup>2,3</sup> This complex cation, which was first prepared<sup>4</sup> as its  $[\text{PF}_6]$  salt by treatment of  $\text{RuH}_2(\text{PPh}_3)_4$  with  $[\text{CPh}_3][\text{PF}_6]$  in  $\text{CH}_2\text{Cl}_2$ , has been shown by  $^{31}\text{P}$  n.m.r. and X-ray crystallographic study<sup>3</sup> to contain a triphenylphosphine group co-ordinated to the metal atom *via* a  $\pi$ -bonded phenyl ring in accordance with the original suggestion.<sup>4</sup> Details of the work are now given; details of the X-ray crystallographic study are given separately.<sup>5</sup>

Although this type of  $\pi$ -co-ordination is unusual for an arylphosphine other similar complexes such as  $\text{M}(\text{CO})_3\text{P}(\text{o-tolyl})_3$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{or W}$ ),<sup>6</sup>  $\text{Cr}(\text{PPh}_3)_2$ ,<sup>7</sup> and  $\text{Mo}(\text{PMe}_2\text{Ph})_4$ <sup>8</sup> are known.

The apparent stability of the  $\text{RuH}(\text{PPh}_3)_2^+$  unit, which is isoelectronic with  $\text{Cr}(\text{CO})_3$ , and its similar ability to accommodate six-electron donors suggested the possibility of formation of other  $\pi$ -arene complexes.<sup>9</sup>

On account of the charge on the ruthenium atom, it also seemed probable that neutral  $\pi$ -bonded complexes might be formed if the protonating acid contained an aromatic ring, particularly if the negative charge of the

conjugate base could be delocalised into the aromatic ring, as is the case for the known  $(\eta^5\text{-C}_5\text{H}_5)\text{RuH}(\text{PR}_3)_2$ <sup>10</sup> and  $\text{RuH}(\text{PPh}_3)_2(\eta^6\text{-PhBPh}_3)$ .<sup>11</sup>

### RESULTS AND DISCUSSION

*Neutral Aromatic Donors.*—The reaction of  $\text{RuH}_2(\text{PPh}_3)_4$  with an excess of acid in methanol in the presence of an excess of  $\text{PPh}_3$  leads to a red solution which rapidly becomes pale yellow and precipitates the yellow complex  $[\text{RuH}(\text{PPh}_3)_3]^+\text{X}^-$  [ $\text{X} = \text{BF}_4$  (Ia),  $\text{MeC}_6\text{H}_4\text{SO}_3$  (Ib), or  $\text{CF}_3\text{SO}_3$  (Ic)]. Similarly, if a solution of  $\text{RuH}_2(\text{PPh}_3)_4$  in an aromatic solvent (benzene or toluene) is treated with an excess of aqueous fluoroboric acid, the aromatic layer immediately becomes deep red. The red colour is rapidly discharged to give a pale yellow solution from which yellow crystalline complexes analysing for  $[\text{RuH}(\text{PPh}_3)_2\text{Ar}][\text{BF}_4]$  [ $\text{Ar} = \text{PhH}$  (II) or  $\text{PhMe}$  (III)] may be isolated in high yield. All of these air-stable complexes are 1 : 1 electrolytes in acetone and are diamagnetic (sharp n.m.r. signals), indicating that the aromatic ring is  $\pi$ -bonded to the metal. This formulation is confirmed by their i.r. and n.m.r. spectra (see below). The similarity, based on observation of colour changes, between these reactions in aromatic solvents and the protonations of  $\text{RuH}_2(\text{PPh}_3)_4$  in methanol in the presence of an excess of triphenylphosphine,<sup>2</sup> is very marked, and it seems likely that a similar reaction mechanism is operating, such that the transient red colour arises from the presence of  $[\text{RuH}(\text{PPh}_3)_3][\text{BF}_4]$  which then rapidly dissociates  $\text{PPh}_3$  and co-ordinates the aromatic ring of the solvent to yield the observed product.

*Anionic Aromatic Donors: the Phenoxide Ion.*—Although neutral complexes with  $\pi$ -bonded aromatic systems are known for many metals<sup>9</sup> including ruthenium, e.g.  $(\text{C}_6\text{H}_6\text{RuCl}_2)_2$ <sup>12,13</sup> and  $\text{C}_6\text{H}_6\text{RuCl}_2\text{L}$ ,<sup>13</sup> complexes in which the donor is a ring of an anionic moiety

† No reprints available.

<sup>1</sup> R. W. Mitchell, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 846.

<sup>2</sup> R. J. Young and G. Wilkinson, *J.C.S. Dalton*, 1976, 719.

<sup>3</sup> J. C. McConway, A. C. Skapski, L. Phillips, R. J. Young, and G. Wilkinson, *J.C.S. Chem. Comm.*, 1974, 327.

<sup>4</sup> J. R. Sanders, *J.C.S. Dalton*, 1973, 743.

<sup>5</sup> J. C. McConway and A. C. Skapski, *J. Organometallic Chem.*, in the press.

<sup>6</sup> J. A. Bowden and R. Colton, *Austral. J. Chem.*, 1971, 24, 2471.

<sup>7</sup> Ch. Elschenbrouch and F. Stohler, *J. Organometallic Chem.*, 1974, 67, C51.

<sup>8</sup> R. Mason, K. M. Thomas, and G. A. Heath, *J. Organometallic Chem.*, 1975, 90, 195.

<sup>9</sup> For references on arene complexes, see W. E. Silverthorn, *Adv. Organometallic Chem.*, 1975, 13, 47 and references therein.

<sup>10</sup> T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1971, 2376.

<sup>11</sup> J. J. Hough and E. Singleton, *J.C.S. Chem. Comm.*, 1972, 371.

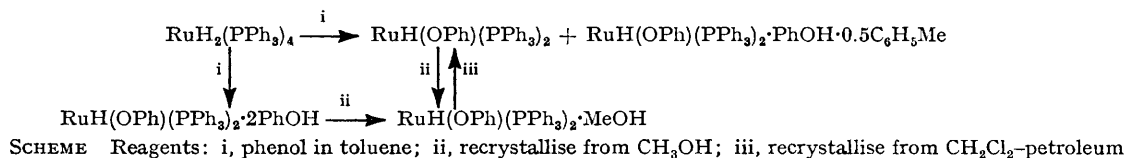
<sup>12</sup> M. A. Bennett and A. K. Smith, *J.C.S. Dalton*, 1974, 233.

<sup>13</sup> R. A. Zelonka and M. C. Baird, *Canad. J. Chem.*, 1972, 50, 3063.

(other than  $C_5H_5^-$ ,  $C_8H_8^{2-}$ , etc.) are comparatively rare, being confined largely to complexes in which  $BPh_4^-$  is bound to a metal through one ring, *viz.*  $RhL_2BPh_4$  ( $L =$  phosphite,<sup>14</sup> phosphine,<sup>15</sup> or olefin,<sup>15</sup> or  $L_2 =$  diene<sup>15</sup>),  $(\eta^5-C_5H_5)RuBPh_4$ ,<sup>16</sup> and  $RuH(PPh_3)_2BPh_4$ <sup>11</sup> and a few complexes of heterocyclic anionic ligands including: (phospholyl) $Mn(CO)_3$ ,<sup>17</sup> (pyrrolyl) $Mn(CO)_3$ ,<sup>18</sup> and azaferrocene.<sup>19</sup>

The most obvious potential anionic  $\pi$ -arene ligand is the phenoxide ion,  $C_6H_5O^-$ . Whether this ion will bind to the metal through oxygen, as in well known phenoxo-complexes such as  $W(OPh)_6$ ,<sup>20</sup> or will be  $\pi$ -bonded, will doubtless depend on the nature of the metal and its ligands but where a metal-ligand system can achieve an eighteen-electron configuration by addition of six-electrons,  $\pi$ -bonding may be a possibility.

When  $RuH_2(PPh_3)_4$  is treated with phenol different products may be isolated depending upon the conditions both of the reaction and of the recrystallisation procedure. Thus a large excess of phenol in toluene gives a pale yellow solution from which yellow crystals of stoichiometry  $RuH(OPh)(PPh_3)_2 \cdot 2PhOH$  (IV) may be



isolated on addition of petroleum. This compound, which may also be prepared by reaction of  $RuHCl(PPh_3)_3$  with an excess of phenol both in the presence or absence of base (triethylamine), may be recovered unchanged on recrystallisation from dichloromethane-petroleum. On crystallisation from methanol, the yellow crystals obtained analyse for  $RuH(OPh)(PPh_3)_2 \cdot MeOH$  (V). This complex may, in turn, be recrystallised from dichloromethane-petroleum to give  $RuH(OPh)(PPh_3)_2$  (VI) which is the main product, along with a small amount of  $RuH(OPh)(PPh_3)_2 \cdot PhOH \cdot 0.5C_6H_5CH_3$  (VII) from the reaction of  $RuH_2(PPh_3)_4$  with a small excess of phenol in toluene, as well as from the reaction of  $RuHCl(PPh_3)_3$  with sodium phenoxide. These interconversions are summarised in the Scheme.

The compound  $RuH(OPh)(PPh_3)_2$  does not react with carbon dioxide in boiling toluene but reacts with CO at room temperature to give  $Ru(CO)_3(PPh_3)_2$ <sup>21</sup> and with methanol to give (V).

All these complexes are diamagnetic (sharp n.m.r. signals) and non-conducting in dichloromethane which suggests that the phenoxide ion is  $\pi$ -bonded to the metal. This is confirmed not only by i.r. and n.m.r.

<sup>14</sup> L. M. Haines, *Inorg. Chem.*, 1971, **10**, 1685.

<sup>15</sup> R. R. Schrock and J. A. Osborn, *Inorg. Chem.*, 1970, **9**, 2339; P. W. Clark and G. E. Martwell, *J. Organometallic Chem.*, 1975, **102**, 387.

<sup>16</sup> R. J. Haines and A. L. Du Preez, *J. Amer. Chem. Soc.*, 1971, **93**, 2820; G. J. Kruger, A. L. Du Preez, and R. J. Haines, *J.C.S. Dalton*, 1974, 1302.

<sup>17</sup> F. Mathey, *J. Organometallic Chem.*, 1975, **93**, 377.

<sup>18</sup> K. K. Joshi and P. L. Pauson, *Proc. Chem. Soc.*, 1962, 326.

data discussed later, but by an X-ray structural study<sup>22</sup> of  $RuH(OPh)(PPh_3)_2 \cdot 2PhOH$ .

Clearly other  $\pi$ - $C_6H_5O$  complexes should exist and synthetic studies are now in progress. However, Keim<sup>23</sup> reported that the complex  $Rh(OPh)(PPh_3)_3$  obtained by action of phenol on  $RhCH_3(PPh_3)_3$  or  $RhC_6H_5(PPh_3)_3$  slowly loses  $PPh_3$  when stirred under petroleum and gives  $Rh(OPh)(PPh_3)_2$  which 'is presumably dimeric and analogous to  $Rh_2(CO)_4Cl_2$ .' No evidence to support this assumption was given. Since the  $Rh(PPh_3)_2$  and  $RuH(PPh_3)_2$  moieties are isoelectronic it seemed most likely that the complex is monomeric with a  $\pi$ -bonded phenoxo-group.

Interaction of  $RhPh(PPh_3)_3$  with an excess of phenol in toluene leads, as reported, to a red solution from which red crystals analysing for  $Rh(OPh)(PPh_3)_2 \cdot 3PhOH \cdot C_6H_5CH_3$  (VIII) may be isolated along with a small amount of an amorphous orange solid (*ca.* 1%). The reaction of  $RhMe(PPh_3)_3$  in molten phenol (40–50 °C) leads to a red suspension which, on extraction of excess of phenol with petroleum and recrystallisation from toluene, also gives (VIII). The amorphous orange solid

is present in such small quantities that it could not be fully characterised but i.r. evidence indicates the presence of triphenylphosphine and O-bonded phenoxide indicating that it could be  $Rh(OPh)(PPh_3)_3$ .

When stirred under petroleum for 24 h (VIII) gives a pink solid and a clear solution. The pink solid may be recrystallised from toluene and is  $Rh(OPh)(PPh_3)_2 \cdot 2PhOH$  (IX), whilst the clear petroleum solution, on evaporation to dryness, affords a white sticky solid identified as phenol from its i.r. spectrum. The complex (IX) with its hydrogen-bonded phenol is evidently the analogue of  $RuH(OPh)(PPh_3)_2 \cdot 2PhOH$  above.

Although we cannot, of course, be sure that these rhodium complexes are the same as those obtained by Keim, their preparations are reproducible and they have similar colours and solubility properties to those reported. The complexes are non-conducting in dichloromethane and spectroscopic evidence unequivocally confirms the presence of  $\pi$ -bonded phenoxo-moieties. It is perhaps worth noting that the analytical figures for carbon and hydrogen do not differ greatly between the formulations proposed by Keim and those given here,

<sup>19</sup> R. E. King and M. B. Bisnette, *Inorg. Chem.*, 1964, **3**, 796; K. K. Joshi, P. L. Pauson, A. R. Qazi, and W. A. Stubbs, *J. Organometallic Chem.*, 1964, **1**, 471.

<sup>20</sup> H. Funk and W. Baumann, *Z. anorg. Chem.*, 1937, **231**, 264.

<sup>21</sup> J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1965, **87**, 4008.

<sup>22</sup> J. C. McConway and A. C. Skapski, personal communication.

<sup>23</sup> W. Keim, *J. Organometallic Chem.*, 1967, **8**, P25; *ibid.*, 1968, **14**, 179.

but there is a large difference in the phosphorus analyses.

Finally, the reaction between  $\text{RuH}_2(\text{PPh}_3)_4$  and an excess of toluene-*p*-sulphonic acid in tetrahydrofuran (thf) leads to an orange solution from which yellow crystals analysing for  $\text{RuH}(\text{MeC}_6\text{H}_4\text{SO}_3)(\text{PPh}_3)_2 \cdot \text{thf}$  separate on prolonged stirring. This complex is non-conducting in dichloromethane and i.r. and n.m.r.

whereas all triphenylphosphine-containing complexes have a single sharp peak at *ca.*  $1430\text{ cm}^{-1}$ , in all the complexes here reported, with the exception of (V), there are two peaks separated by *ca.*  $3\text{ cm}^{-1}$  in this region (see Table 1). The region  $480\text{--}550\text{ cm}^{-1}$  is also much more complicated for these complexes than for those which do not contain  $\pi$ -bonded phenyl rings, usually consisting of the characteristic six peaks shown

TABLE 1  
Infrared spectra

Complex	$\nu(\text{M-H})$ $\text{cm}^{-1}$	$\nu(\text{C}\cdots\text{C})$ of phenyl rings $\text{cm}^{-1}$		Other bands $\text{cm}^{-1}$
(Ia) $[\text{RuH}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{PPh}_3)_2][\text{BF}_4] \cdot \text{MeOH}$	2 035m	1 436s, 1 432s		
(Ib) $[\text{RuH}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{PPh}_3)_2][\text{MeC}_6\text{H}_4\text{SO}_3]$	2 030m	1 438s, 1 434s		
(Ic) $[\text{RuH}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{PPh}_3)_2][\text{CF}_3\text{SO}_3]$	2 025m	1 437s, 1 433s		
(II) $[\text{RuH}(\eta^6\text{-C}_6\text{H}_5)(\text{PPh}_3)_2][\text{BF}_4]$	2 000m	1 436s, 1 430s		
(III) $[\text{RuH}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{PPh}_3)_2][\text{BF}_4]$	2 015m	1 437sh, 1 432s		
	2 040w	1 437s, 1 432s		
(IV) $\text{RuH}(\eta^6\text{-PhO})(\text{PPh}_3)_2 \cdot 2\text{PhOH}$	1 973m, br	1 435s, 1 432s	3 120mv, br, <sup>a</sup> 1 520vs, br, <sup>b</sup> 1 332s, <sup>c</sup> 1 238m <sup>e</sup>	
(V) $\text{RuH}(\eta^6\text{-PhO})(\text{PPh}_3)_2 \cdot \text{MeOH}$	2 000m	1 430s	3 160w, br, <sup>a</sup> 2 050m, br, <sup>d</sup> 1 550vs, br, <sup>b</sup> 1 050m <sup>e</sup>	
(VI) $\text{RuH}(\eta^6\text{-PhO})(\text{PPh}_3)_2$	1 982m	1 435s, 1 430s	1 577vs <sup>b</sup>	
(VII) $\text{RuH}(\eta^6\text{-PhO})(\text{PPh}_3)_2 \cdot \text{PhOH} \cdot 0.5\text{C}_6\text{H}_5\text{Me}$	1 980m, br	1 435sh, 1 432s	3 120wbr, <sup>a</sup> 1 532s, <sup>b</sup> 1 350m, <sup>c</sup> 1 332m, <sup>e</sup> 1 245m <sup>e</sup>	
(VIII) $\text{Rh}(\eta^6\text{-PhO})(\text{PPh}_3)_2 \cdot 3\text{PhOH} \cdot \text{C}_6\text{H}_5\text{Me}$		1 435s, 1 432s	3 120wbr, <sup>a</sup> 1 525s, br, <sup>b</sup> 1 318m, <sup>c</sup> 1 275m <sup>e</sup>	
			1 245s <sup>c</sup>	
(IX) $\text{Rh}(\eta^6\text{-PhO})(\text{PPh}_3)_2 \cdot 2\text{PhOH}$		1 432sh, 1 430s	3 120w, br, <sup>a</sup> 1 530s, br, <sup>b</sup> 1 344m, <sup>c</sup> 1 329m, <sup>e</sup>	
			1 245m <sup>e</sup>	
$\text{RhPPh}_3\text{Oph}$		1 435s	1 250s, br <sup>e</sup>	

<sup>a</sup>  $\nu(\text{O-H})$  of hydrogen-bonded phenol or methanol. <sup>b</sup>  $\nu(\text{C-O})$  of  $\pi$ -bonded phenoxide. <sup>c</sup>  $\nu(\text{C-O})$  of hydrogen-bonded phenol. <sup>d</sup> Bands from hydrogen-bonded methanol. <sup>e</sup>  $\nu(\text{C-O})$  of O-bonded phenoxide.

TABLE 2  
 $^1\text{H}$  N.m.r. spectra of complexes ( $J$  in Hz)

Complex	Solvent	Hydride $\tau(J_{\text{PH}})$ *	$\pi$ -Bonded ring			$J_{om}$	$J_{op}$	$J_{pm}$	Other phenyl resonances $\tau$	Other resonances
			$\tau$ (intensity) *							
			<i>o</i>	<i>p</i>	<i>m</i>					
(Ia)	$\text{CDCl}_3$	18.7t (33)	5.68t, <sup>a</sup> (2)	2.88s (1)	4.60t (2)	6	0	6	2.5—2.8	
(Ib)	$\text{CDCl}_3$	18.5t (35)	5.70t (2)		4.62t (2)	6	0	6	2.5—3.0	7.82 <sup>b</sup>
(Ic)	$\text{CDCl}_3$	18.6t (33)	5.66t (2)		4.60t (2)	6	0	6	2.5—3.0	
(II)	$\text{CDCl}_3$	19.0t (36)		4.46s					2.0—3.0	
(III)	$\text{CDCl}_3$	19.4t (36)	5.4d (2)	3.6t (1)	4.7t (2)	6	0	6	2.5—3.0	7.80 <sup>c</sup>
	$\text{CD}_2\text{Cl}_2$	19.90t (36)	5.66d		4.49d	6			2.3—3.2	7.78s, <sup>d</sup> 6.42, <sup>m</sup> 8.30 <sup>m</sup>
(IV)	$\text{CDCl}_3$	20.05t (33)	5.45d (2)	5.35t (1)	4.95t (2)	<i>k</i>	0	<i>k</i>	2.0—3.0	1.13 <sup>e</sup> (30) <sup>f</sup>
(V)	$\text{CDCl}_3$	20.4t (36)		5.55d (3) <sup>d</sup>	4.85t (2)	<i>k</i>	0	<i>k</i>	2.3—3.0	6.40 <sup>g</sup>
(VI)	$\text{CDCl}_3$	20.4t (34)		5.6d (3) <sup>d</sup>	4.9 <sup>h</sup> (2)	<i>k</i>	0	<i>k</i>	2.4—3.2	
(VI)	$\text{C}_6\text{D}_6$	21.3t (34)	5.30d (2)	6.12t (1)	4.85 <sup>h</sup> (2)	7	0	5	1.9—3.2	
(VII)	$\text{CDCl}_3$	20.5t (32)		5.6d (3) <sup>d</sup>	5.0 <sup>h</sup> (2)	<i>k</i>	0	<i>k</i>	2.0—3.0	2.85 <sup>e</sup> (5), <sup>f</sup> 7.75 <sup>e</sup>
(VIII)	$\text{C}_6\text{D}_6$		4.55d (2)	5.60t (1)	5.05 <sup>h</sup> (2)	7	0	6	2.0—3.5	1.17 <sup>e</sup> (4), <sup>f</sup> 8.00 <sup>e</sup>
(IX)	$\text{C}_6\text{D}_6$		4.5d (2)	5.63t (1)	4.98 <sup>h</sup> (2)	7	0	6	2.3—3.5	-0.43 <sup>e</sup> (6) <sup>f</sup>

<sup>a</sup>  $J_{\text{PH}} = 6\text{ Hz}$ . <sup>b</sup> Me group of  $\text{MeC}_6\text{H}_4\text{SO}_3^-$ . <sup>c</sup> Me group of  $\text{PhCH}_3$ . <sup>d</sup> Both *o*- and *p*-protons. <sup>e</sup> Hydrogen-bonded OH proton of  $\text{PhOH}$ . <sup>f</sup> Width of peak at half-height. <sup>g</sup> Me group of  $\text{MeOH}$ . <sup>h</sup> Doublet of doublets. <sup>i</sup> These signals are best described in terms of a second-order AA'BB'C type spin system, see text. <sup>j</sup> Broad. <sup>m</sup> thf of solvation.

\* s = singlet, d = doublet, t = triplet.

evidence strongly indicate that it contains a  $\pi$ -bonded-toluene-*p*-sulphonato-group.

**Spectroscopic Data.**—*I.r. spectra.* All the complexes reported show peaks in the i.r. spectrum arising from co-ordinated triphenylphosphine ligands in addition to those assignable to the anion in the case of complexes  $[\text{RuH}(\text{PPh}_3)_3]\text{X}$  and  $[\text{RuH}(\text{Ar})(\text{PPh}_3)_2]\text{X}$ . In addition, all the ruthenium complexes have sharp absorptions in the region  $1960\text{--}2040\text{ cm}^{-1}$  which are attributable to  $\nu(\text{Ru-H})$ . The i.r. spectra of these complexes all have other features which do not occur in the spectra of complexes which do not contain a  $\pi$ -bonded ring. Thus,

in Figure 1. Although the extra peaks in the i.r. spectrum cannot be taken as proof that a complex contains a  $\pi$ -bonded ring, we have found them very useful as an indicator that  $\pi$ -interaction is occurring; for this reason their presence in the rhodium complexes (VII) and (VIII), but not in the orange amorphous solid, possibly  $\text{Rh}(\text{OPh})(\text{PPh}_3)_3$ , strongly indicates that the former contain a  $\pi$ -bonded ring system and the latter a normal phenoxo-group.

Further information on the phenoxides arises from the position of  $\nu(\text{C-O})$  in the complexes. Thus the complexes (IV)—(IX) have a strong broad absorption in the

region 1 580—1 600  $\text{cm}^{-1}$ . In comparison,  $\nu(\text{C-O})$  for complexes of O-bonded phenoxide usually occur in the region 1 200—1 300  $\text{cm}^{-1}$ , as is the case for alkali-metal

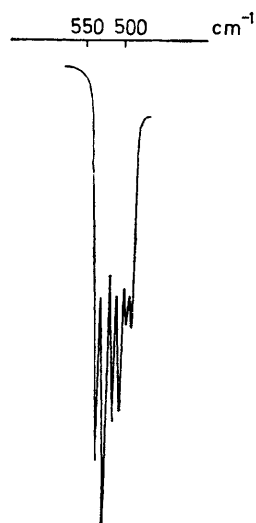


FIGURE 1 I.r. spectrum of  $[\text{RuH}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{PPh}_3)_2][\text{BF}_4]$  in the 470—530  $\text{cm}^{-1}$  region

phenoxides (1 270), thallium phenoxide (1 260) and phenol (1 240) itself; in contrast in cyclohexanone

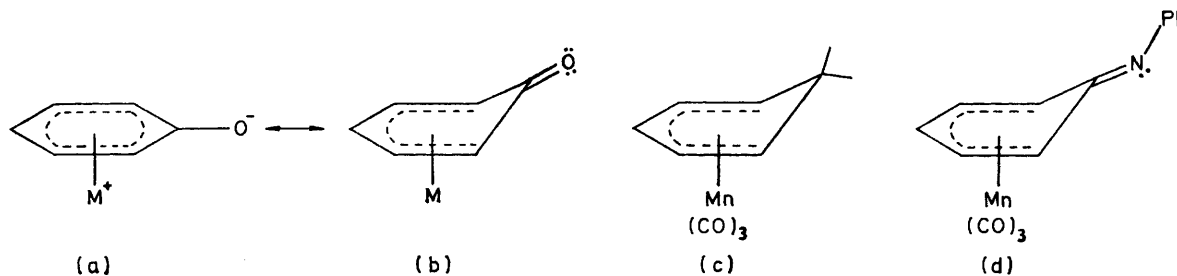


FIGURE 2 Resonance hybrids for  $\pi$ -complexing of phenoxo-group: (a) as phenoxide ion, (b) as cyclohexadienonyl, (c) tricarbonyl- $\eta^5$ -cyclohexadienylmanganese, and (d) tricarbonyl(phenylimino- $\eta$ -cyclohexadienyl)manganese

$\nu(\text{C-O})$  is at 1 720  $\text{cm}^{-1}$  and this shifts to lower wavenumbers on conjugation (1 680  $\text{cm}^{-1}$  in cyclohex-2-enone and 1 650  $\text{cm}^{-1}$  in benzoquinone).<sup>24</sup> This indicates that the C-O bond of the phenoxo-moiety has substantial double-bond character and this is best explained in terms of a large contribution from resonance structure (b) in Figure 2. This view is supported by the crystal structure of (V),<sup>22</sup> in which the C-O bond length of the  $\pi$ -bonded phenoxo-moiety (1.277 Å) is between that for a normal phenolic C-O bond (1.35—1.37 Å) and that for a C=O double-bond (1.22 Å in benzoquinone). The X-ray structure also shows the  $\pi$ -bonded ring to have a boat conformation although the *para* carbon atom is considerably less above the plane of the *ortho* and *meta* carbon atoms than is the carbon atom bound to oxygen. The latter is 0.185 Å and the oxygen atom 0.409 Å above the plane of the ring. The complexes may be compared

<sup>24</sup> 'I.r. Spectra of Selected Chemical Compounds,' Heydon and Son Ltd., London, 1961; 'Aldrich Library of Infrared Spectra,' C. J. Pouchet, Aldrich Chemical Co. Ltd.

with  $\eta$ -cyclohexadienyls, *e.g.*  $\eta\text{-C}_6\text{H}_7\text{Mn}(\text{CO})_3$ <sup>25</sup> [Figure 2(c)] and tricarbonyl(phenylimino- $\eta$ -cyclohexadienyl)-manganese<sup>26</sup> [Figure 2(d)]; the  $\text{C}_6$  ring in the latter probably has a boat conformation with the N atom on C<sup>1</sup> well above the plane of C<sup>2,3,5,6</sup>. We can thus describe the complexes as of 2-6- $\eta$ -cyclohexadienonyl (or 2-6- $\eta$ -oxa-cyclohexadienyl) although for convenience we use the alternative description  $\eta^6$ -phenoxo with a positive charge on the metal.

Compounds (IV), (VII), (VIII), and (IX) also show extra absorptions compared with (VI) in the region 1 250—1 350  $\text{cm}^{-1}$  [ $\nu(\text{C-O})$ ], as well as broad absorptions above 3000  $\text{cm}^{-1}$  [ $\nu(\text{O-H})$ ], indicative of strongly hydrogen-bonded phenol molecules in the complexes. Since the position of  $\nu(\text{C-O})$  for the  $\pi$ -bonded phenoxide is sensitive to the number of molecules hydrogen-bonded in the complex and since the oxygen atom in this group is the most likely position for the highest negative-charge density, it seems probable that the hydrogen-bonded molecules are bound to this oxygen atom as in Figure 3. This is confirmed by the X-ray crystal structure determination.<sup>22</sup> Note that in  $\text{RuH}(\eta^6\text{-PhO})(\text{PPh}_3)_2$  the C-O stretch is higher (at 1 577  $\text{cm}^{-1}$ ) than in the other Ru or Rh complexes in which the oxygen is hydrogen-bonded to phenol.

Finally, although (V) does not have the double-peak

above 1 430  $\text{cm}^{-1}$  its chemistry indicates that it does contain a  $\pi$ -bonded phenoxo-ring and this is confirmed by its proton n.m.r. spectrum.

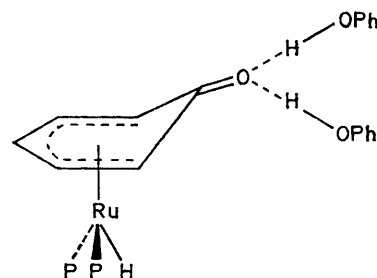


FIGURE 3 Structure of  $\text{RuH}(\text{OPh})(\text{PPh}_3)_2 \cdot 2\text{PhOH}$

*N.m.r. Spectra.*—All the  $^1\text{H}$  n.m.r. spectra show, in addition to the normal resonances arising from the

<sup>25</sup> G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 3807.

<sup>26</sup> P. L. Pauson and J. A. Segal, *J.C.S. Dalton*, 1975, 1677.

phenyl groups of the triphenylphosphine ligands and sharp resonances from any methyl groups in the molecule [(Ib), (III), (V), (VII), and (VIII)], weaker resonances in the region  $\tau$  4.5–6.2. The spectra of the ruthenium complexes also contain signals to high field (*ca.*  $\tau$  20) which are attributable to the hydridic proton. These high-field signals are all split into triplets ( $J$  *ca.* 35 Hz), indicating that, in each case, the hydride is coupled to two equivalent phosphorus atoms. For (I), the triplet is further split into a doublet ( $J = 5.8$  Hz) due to coupling between the hydride and the phosphorus atom of the  $\pi$ -bonded phosphine moiety. Confirmation of this arises from analysis of the  $^1\text{H}$ -decoupled  $^{31}\text{P}$  n.m.r. spectrum, which consists of a doublet at +48.91 p.p.m. (relative intensity 2,  $J_{\text{PP}} = 0.8$  Hz) and a triplet (relative intensity 1,  $J_{\text{PP}} = 0.8$  Hz) at  $-5.77$  p.p.m. to high frequency of external  $\text{H}_3\text{PO}_4$ . When the  $^{31}\text{P}$  spectrum is observed with only partial decoupling of the protons (in the phenyl region), each line of the spectrum is further split into a doublet, the high-frequency doublet with  $J_{\text{PH}} = 33.3$  Hz and the triplet with  $J_{\text{PH}} = 5.8$  Hz. Thus, it is clear that the small splitting observed in the hydride resonance of the proton spectrum arises from coupling to the unique phosphorus atom which gives rise to the triplet at  $-5.7$  p.p.m. in the  $^{31}\text{P}$  n.m.r. spectrum, and the contention that this is the phosphorus atom of the  $\pi$ -bound phosphine ligand is strongly supported by the relative intensity (1) and chemical shift (close to free  $\text{PPh}_3$ ;  $-6.34$  p.p.m.) of the signal arising from it in the  $^{31}\text{P}$  spectrum.<sup>3,4</sup>

The weak resonances in the region  $\tau$  4.5–6.2 unequivocally confirm that all these complexes (I)–(IX) contain a  $\pi$ -bonded phenyl ring system since it is well known that bonding of this kind produces shifts of the proton resonances to higher fields and this is thought to be due to a combination of three factors; the withdrawal of  $\pi$ -electron density from the ring by the metal, the quenching of the ring currents by interaction with the metal, and the magnetic anisotropy of the rest of the metal complex.<sup>27</sup>

In some of the complexes, (I), (III), (VIII), (IX), the *ortho*-, *meta*-, and *para*-protons are sufficiently differently affected by the metal to give rise to separate signals and the spectra may be interpreted on a first-order basis, assuming that there is only coupling between protons, or protons and phosphorus atoms, attached to adjacent carbon atoms. Qualitatively, similar spectra are obtained from  $(\eta^6\text{-Bu}^t\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_3$ <sup>28</sup> and from  $\eta^5$ -cyclohexadienyl complexes of several metals although the latter show further coupling to the methylene protons in the ring as well as, for  $(\eta^5\text{-C}_6\text{H}_7)\text{Mn}(\text{CO})_3$ , some long-range couplings.<sup>25,29</sup>

For the ruthenium phenoxo-complexes in  $\text{CDCl}_3$ , however, the *ortho*- and *para*-protons seem to be approximately equally shielded and second-order spectra (see Figure 4a) are obtained. A similar spectrum has

<sup>27</sup> D. A. Brown and F. J. Hughes, *J. Chem. Soc. (A)*, 1968, 1519.

<sup>28</sup> W. R. Jackson, W. B. Jennings, S. C. Rennison, and R. Spratt, *J. Chem. Soc. (B)*, 1969, 1214.

been reported for  $(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_3$  in decalin (ref. 28, Figure 2c).

In benzene, however, the resonance of the *para*-proton in (VI) is shifted to significantly higher field and a pseudo-first-order spectrum again results (Figure 4b). The origin of this effect is not clear but presumably reflects preferential solvation of one part of the molecule.

In the  $^1\text{H}$  n.m.r. spectrum of  $\text{RuH}(\text{MeC}_6\text{H}_4\text{SO}_3)_2(\text{PPh}_3)_2 \cdot \text{thf}$ , the two sets of protons on the ring each give rise to a doublet although in one of these lines are considerably broadened. Since the signal arising from the methyl group on the ring is also broad, we assign the broader doublet ( $\tau$  5.66) to the protons *ortho* to the methyl group, and the broadening to a small

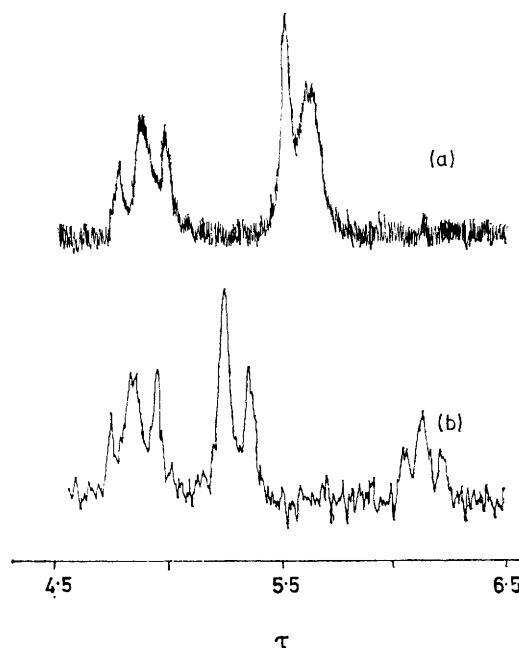


FIGURE 4 Part of the  $^1\text{H}$  n.m.r. spectrum of  $\text{RuH}(\text{OPh})(\text{PPh}_3)_2$  in (a)  $\text{CDCl}_3$  and (b)  $\text{C}_6\text{D}_6$ .

coupling between these protons and those of the methyl group.

For the ruthenium complexes, it is apparent that the chemical shifts of the *ortho*- and *meta*-protons of the  $\pi$ -bonded ring are not much affected by the charge on the ring but that the resonance arising from the *para*-proton is at higher field in the phenoxo-complexes than in the cationic complexes. The reason for this is not apparent but it is not thought to arise from different preferred conformations of the  $\pi$ -bonded ring with respect to the rest of the molecule as, at least in the solid state, the substituted carbon atom eclipses the Ru-H bond for both (Ia) and (IV).<sup>5,22</sup>

For the rhodium complexes, however, the amounts of shielding of the  $\pi$ -bonded ring protons are different from those in the ruthenium complexes and this probably does arise from the different stereochemistry of the

<sup>29</sup> D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4458.

phosphine groups, caused by the absence of the hydride ligand.

Since the resonances arising from the *ortho*-, *meta*-, and *para*-protons of the  $\pi$ -bonded rings in these complexes are often well separated and since the complexes here reported are relatively easy to prepare, these kinds of complex have potential as n.m.r. shift reagents for aromatic rings. It has otherwise proved difficult to find reagents which separate aromatic resonances reasonably well, the only reported compounds that will do this being cyclodextrins.<sup>30</sup>

For those complexes whose i.r. spectra indicate the presence of hydrogen-bonded phenol molecules (IV), (VII), (VIII), and (IX), broad resonances to low field ( $-0.43$  to  $+2.85$ ) appear in their  $^1\text{H}$  n.m.r. spectra. These presumably arise from the hydrogen-bonded H atoms of the phenol molecules, and the fact that for the different complexes they resonate at different positions but that their chemical shifts do not appear to be very concentration dependent indicates that the hydrogen bonds are not broken in solution.

Finally, since, for (VIII) there is a possibility that, rather than the phenoxide being  $\pi$ -bonded to the metal, the complex has an ionic structure with a  $\pi$ -bonded toluene ligand, it should be pointed out that the chemical shift of the methyl protons in this complex ( $\tau$  8.0) is identical to that of free toluene in  $\text{C}_6\text{D}_6$  and that addition of free toluene to a solution of this complex in  $\text{C}_6\text{D}_6$  only increases the intensity of this signal. Further confirmation that it is the phenoxide that is  $\pi$ -bonded to the rhodium atom arises from the non-conductance of the complex in  $\text{CH}_2\text{Cl}_2$ .

#### EXPERIMENTAL

Microanalyses by Imperial College and Butterworth Microanalytical Consultancy Limited.

I.r. spectra were obtained using a Perkin-Elmer 457 instrument and n.m.r. spectra using Perkin-Elmer R12 (60 Hz) and Varian XL-100 spectrometers. Conductivity measurements were made using a Mullard E7566/3 Conductivity Bridge. M.p.s were measured using a Köfler hot-stage microscope or Electrothermal melting point apparatus (in capillaries) and are uncorrected.

The petroleum used had b.p.  $60$ – $80$  °C unless otherwise specified and all operations were carried out in dry degassed solvents in an inert atmosphere ( $\text{N}_2$  or argon).

Analytical data for the compounds are given in Table 3.

*Hydrido*( $\eta^6$ -phenyldiphenylphosphine)*bis*(triphenylphosphine)ruthenium(II) Tetrafluoroborate, (Ia).—Suspensions of  $\text{RuH}(\text{CO}_2\text{Me})(\text{PPh}_3)_3$ ,<sup>1</sup>  $\text{RuH}_2(\text{PPh}_3)_4$ ,<sup>31</sup> or  $\text{Ru}(\text{CO}_2\text{Me})_2(\text{PPh}_3)_2$ <sup>1</sup> in methanol under Ar,  $\text{N}_2$ , or  $\text{H}_2$  all react with large excesses of  $\text{HBF}_4(\text{aq})$  and  $\text{PPh}_3$  to yield  $[\text{RuH}(\eta^6\text{-Ph-PPh}_2)(\text{PPh}_3)_2][\text{BF}_4]$ .  $\text{RuH}(\text{CO}_2\text{Me})(\text{PPh}_3)_3$  (0.5 g, 0.53 mmol) and  $\text{PPh}_3$  (0.5 g, 1.91 mmol) were added to 42% (aq.)  $\text{HBF}_4$  (5  $\text{cm}^3$ ) in methanol (50  $\text{cm}^3$ ), which had been purged with hydrogen for ca. 5 min. The suspension was heated to reflux with rapid stirring and then allowed to cool under  $\text{H}_2$ . The precipitated pale yellow crystalline complex was collected under  $\text{N}_2$ , washed with degassed methanol and ether, and dried *in vacuo*. The complex as isolated contains one methanol of solvation (0.35–0.40 g, 66–75%).

TABLE 3  
Analytical data (%) for complexes

Complex	Required			Found			$\Lambda/\Omega^{-1}\text{cm}^2\text{mol}^{-1}$
	C	H	P	C	H	P	
(Ia)	65.5	5.0	9.2	65.7	5.1	9.9	112
(Ib)	69.0	5.0	8.8	68.1	4.8	8.3	
(Ic)	63.6	4.5	9.0	63.2	4.7	8.2	
(II)	63.1	4.6	7.9	62.6	4.8	7.2	122
(III)	64.2	4.7	7.6	64.1	4.9	7.6	120
a	65.0	5.3	7.2	65.6	6.0	7.4	None
(IV)	71.5	5.3	6.8	71.9	5.6	6.9	None
(V)	68.7	5.3	8.3	69.4	5.4	7.7	None
(VI)	70.1	5.1	8.6	70.9	5.3	6.4	None
(VII)	72.2	5.4	7.2	73.8	5.7	7.9	None
(VIII)	73.6	5.7	5.7	73.8	6.0	5.8	None
(IX)	71.5	5.3	6.8	71.3	5.4	6.7	None

a  $\eta^6$ -toluene-*p*-sulphonate complex: S found 4.5%, required 3.7%.

*Hydrido*( $\eta^6$ -phenyldiphenylphosphine)*bis*(triphenylphosphine)ruthenium(II) Toluene-*p*-sulphonate, (Ib).— $\text{RuH}(\text{CO}_2\text{Me})(\text{PPh}_3)_3$  (0.5 g, 0.53 mmol) and  $\text{PPh}_3$  (0.5 g, 1.91 mmol) were treated with toluene-*p*-sulphonic acid monohydrate (1.9 g, 10 mmol) in methanol (50  $\text{cm}^3$ ), which had been purged with  $\text{H}_2$  for ca. 5 min. The suspension was heated to reflux and then allowed to cool under  $\text{H}_2$ . The solution was reduced to 20  $\text{cm}^3$  by pumping and cooled to  $-20$  °C for 12 h. The precipitated yellow complex was collected under  $\text{N}_2$ , washed with  $\text{N}_2$ -purged methanol and diethyl ether, and dried *in vacuo*. The complex appeared to contain methanol of solvation (0.19 g, ca. 33%).

*Hydrido*( $\eta^6$ -phenyldiphenylphosphine)*bis*(triphenylphosphine)ruthenium(II) Trifluoromethanesulphonate, (Ic), was similarly prepared from  $\text{CF}_3\text{SO}_3\text{H}$ , added dropwise with caution.

( $\eta^6$ -Benzene)hydridobis(triphenylphosphine)ruthenium(II) Tetrafluoroborate, (II).— $\text{RuH}_2(\text{PPh}_3)_4$  (0.5 g, 0.43 mmol) was added to benzene (10  $\text{cm}^3$ ) which had been purged with argon for ca. 10 min. The suspension was treated with argon-purged  $\text{HBF}_4$  (ca. 40% aq.) (5  $\text{cm}^3$ ). The resulting suspension was heated to reflux with rapid stirring to give, initially, an intense red solution. The red colour rapidly changed (ca. 30 s) to pale yellow. When set aside the reaction mixture separated into a yellow benzene layer and a colourless aqueous layer. The organic layer was separated and reduced to approximately half volume by pumping. The yellow crystalline solid which precipitated was collected under argon, washed with argon-purged ether, and dried *in vacuo*. Water was strongly held by the product and only removed slowly *in vacuo* at elevated temperature (ca. 60 °C) (yield 0.25 g, ca. 74%).

*Hydrido*( $\eta^6$ -toluene)*bis*(triphenylphosphine)ruthenium(II) Tetrafluoroborate, (III).—This compound was similarly prepared from toluene (yield ca. 70%).

*Hydrido*( $\eta^6$ -phenoxo)*bis*(triphenylphosphine)ruthenium(II)-Phenol (1/2), (IV).—(a) An excess of phenol (0.07 g) was dissolved in degassed toluene (15  $\text{cm}^3$ ) and  $\text{RuH}_2(\text{PPh}_3)_4$  (0.26 g) was added. The resulting dark yellow solution was warmed to 100 °C for 20 min during which time the colour became paler. The pale yellow solution was evaporated to dryness and the resulting pale yellow solid was recrystallised from toluene (2  $\text{cm}^3$ ) as yellow needles (yield ca. 70%). The compound could be recrystallised unchanged from dichloromethane-petroleum (60–80 °C), m.p. 165–166 °C.

<sup>30</sup> D. D. McNicol, *Tetrahedron Letters*, 1975, **38**, 3325.

<sup>31</sup> R. O. Harris, N. K. Hota, L. Sadavoy, and M. C. Yuen, *J. Organometallic Chem.*, 1975, **54**, 259.

(b)  $\text{RuHCl}(\text{PPh}_3)_3$  (0.5 g) and phenol (1.0 g) were suspended in  $\text{N}_2$ -purged toluene (20  $\text{cm}^3$ ) and an excess of triethylamine (2  $\text{cm}^3$ ) was added. After 2 h under reflux the orange solution was reduced to one-third volume and cooled to  $-20^\circ\text{C}$ . The yellow crystals of the *complex* were collected and washed with degassed ether.

(c) This reaction was carried out in a similar way to that described in (b) except 2 g of phenol was used and no  $\text{Et}_3\text{N}$  was added.

*Hydrido*( $\eta^6$ -phenoxo)*bis*(triphenylphosphine)*ruthenium*(II)-*Methanol* (1/1), (V).—The complex (IV) (0.1 g) was recrystallised from methanol (2  $\text{cm}^3$ ) to give yellow crystals in essentially quantitative yield. This complex was also obtained from recrystallisation of (VI) from methanol.

*Hydrido*( $\eta^6$ -phenoxo)*bis*(triphenylphosphine)*ruthenium*(II), (VI), and *Hydrido*( $\eta^6$ -phenoxo)*bis*(triphenylphosphine)-*ruthenium*(II)-*Phenol-Toluene* (1/1/0.5), (VII).—(a)  $\text{RuH}_2(\text{PPh}_3)_4$  (1.12 g) was dissolved in degassed toluene (20  $\text{cm}^3$ ) and phenol (0.11 g) was added. The solution was heated to  $100^\circ\text{C}$  with stirring for 1 h. The resulting orange solution was evaporated to half volume and allowed to crystallise. The yellow micro-crystals of the *complex* (VI) were filtered off and washed with petroleum before being dried *in vacuo* (decomp. ca.  $160^\circ\text{C}$ ). Degassed petroleum (1  $\text{cm}^3$ ) was added to the filtrate and the tar so formed redissolved by warming. On cooling, the yellow solution deposited yellow crystals of the complex (VII) which were recrystallised from toluene.

(b) Compound (VI) was also obtained by recrystallisation of (V) from  $\text{CH}_2\text{Cl}_2$ -petroleum.

( $\eta^6$ -Phenoxo)*bis*(triphenylphosphine)*rhodium*(I)-*Phenol-Toluene* (1/3/1).—(a) The complex  $^{23}\text{RhMe}(\text{PPh}_3)_3$  (0.5 g) was treated with phenol (1.0 g) under argon. The mixture was warmed ( $40$ – $50^\circ\text{C}$ ) to melt the phenol, when vigorous gas evolution was observed. The red suspension was stirred for 90 min at  $40$ – $50^\circ\text{C}$  and extracted with petroleum

( $4 \times 10 \text{ cm}^3$ ). The residual red solid was recrystallised from toluene (3  $\text{cm}^3$ ) as red needles which were washed with toluene ( $2 \times 2 \text{ cm}^3$ ) and petroleum ( $2 \times 2 \text{ cm}^3$ ) before being dried *in vacuo*.

(b) The compound  $^{23}\text{RhPh}(\text{PPh}_3)_3$  (0.95 g) and phenol (1.01 g) were added to degassed toluene (10  $\text{cm}^3$ ). The suspension was warmed to  $100^\circ\text{C}$  for 1 h and the resulting red solution was filtered whilst hot. On addition of ether (5  $\text{cm}^3$ ) a small amount of an orange flocculant precipitate was observed. The filtered red solution was allowed to crystallize at room temperature to give red crystals of the *complex* which were washed with toluene ( $2 \times 1 \text{ cm}^3$ ) before being dried *in vacuo* (yield ca. 70%), m.p.  $83$ – $85^\circ\text{C}$ .

( $\eta^6$ -Phenoxo)*bis*(triphenylphosphine)*rhodium*(I)-*Phenol* (1/2), (IX).—The complex (VIII) (0.3 g) was stirred under petroleum (10  $\text{cm}^3$ ) for 24 h. The salmon pink solid was collected from the clear solution and recrystallised from toluene (3  $\text{cm}^3$ ) to give red crystals, m.p.  $112$ – $114^\circ\text{C}$ . Evaporation of the petroleum to dryness afforded a white sticky solid whose i.r. spectrum was superimposable upon that of phenol.

*Hydrido*( $\eta^6$ -toluene-*p*-sulphonato)*bis*(triphenylphosphine)-*ruthenium*(II)-*Tetrahydrofuran* (1/1).— $\text{RuH}_2(\text{PPh}_3)_4$  (0.34 g) was dissolved in degassed tetrahydrofuran (15  $\text{cm}^3$ ) under argon and a two-molar excess of toluene-*p*-sulphonic acid monohydrate was (0.1 g) added. The orange solution was stirred at room temperature for 4 h during which time a yellow crystalline solid was deposited. This was filtered off and washed with tetrahydrofuran (5  $\text{cm}^3$ ) before being dried *in vacuo* (yield ca. 50%).

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