Reactions of Dihydridotetrakis(triphenylphosphine)ruthenium(II) with N, O, and S Ligands †

By **Ricardo Obeso Rosete, David J. Cole-Hamilton,** and **Geoffrey Wilkinson,*** Chemistry Department, Imperial College of Science and Technology, London SW7 2AY

The interaction of dihydridotetrakis(triphenylphosphine)ruthenium(II), $RuH_2(PPh_3)_4$, with the following compounds has been studied: 2,2′-bipyridyl, *o*-dicyanobenzene, 2-hydroxypyridine, 8-hydroxyquinoline, 2-aminopyridine, 2-mercaptopyridine, *o*-phenylenediamine, 2-aminothiophenol, 2-aminophenol, pyrocatechol, resorcinol, and hydroquinone.

The products have been characterised by i.r. and n.m.r. (^1H and ^{31}P) spectroscopy, and structures for new compounds proposed.

THE reactions of $RuH_2(PPh_3)_4$ with neutral donor ligands, such as N_2,[1] CO, pyridine,[2] nitriles,[1,3] dimethylformamide,[4] and tetrahydrofuran afford complexes in which a phosphine *trans* to a hydride is displaced. Weak monobasic acids, on the other hand, give either $RuHX(PPh_3)_3$ ($X = CH_2NO_2$[5] or RCO_2[6]), $RuHX(PPh_3)_2$ ($X = OPh$,[7] p-$MeC_6H_4SO_2$, or 1—5-η-cyclohexadienyl[8]), $RuH(PPh_3)_2L_3{}^+X^-$ [$L_3 = (H_2O)_2MeOH$,[9] PhH, PhMe, or PPh_3,[7] $X = BF_4$, PF_6, CF_3SO_3, or FSO_3] or, in the case of water, $RuH(OH)(PPh_3)_2(H_2O)$.[5] HCl gives $RuCl_2(PPh_3)_3$.

TABLE 1

^1H N.m.r. spectra of ruthenium complexes at 36 °C

		Hydride					
Complex	Solvent	δ	J_{HP_A} (Hz)	J_{HP_B} (Hz)	J_{HH} (Hz)	Ligand resonances	Phenyl resonances
$RuH_2(bipy)(PPh_3)_2$	C_6D_6	−13.8	28.0	28.0		8.6 (d), 6.8 (d), 6.2 (d)	6.8—8.0
$RuH_2\{(NC)_2C_6H_4\}(PPh_3)_3$	thf [a]	−9.0 −13.5	77.0 14.0	34.0 33.0	11.0		7.0—8.2
$RuH\{(O)NC_9H_6\}(PPh_3)_3$	C_6D_6	−16.2 [b]	24.0	24.0		6.3 (q), 5.7 (q)	6.4—8.2
$Ru\{(O)NC_9H_6\}_2(PPh_3)_2$	C_6D_6					5.8 (d)	6.6—7.8
$RuH\{(O)NC_5H_4\}(PPh_3)_3$	C_6D_6	−18.0	24.0	24.0		6.0 (d), 5.5 (s)	6.4—7.9
$Ru\{(O)NC_5H_4\}_2(PPh_3)_2$	C_6D_6					5.8 (d)	6.6—7.8
$RuH\{(HN)NC_5H_4\}(PPh_3)_3$	C_6D_6	−15.2	27.0	24.0		5.9 (t), 4.8 (d)	6.4—7.8
$Ru\{(HN)_2C_6H_4\}(PPh_3)_3$	CS_2						6.3—7.5
$Ru\{(HN)_2C_6H_4\}(CO)(PPh_3)_2$	C_6D_6						6.5—8.0
$Ru\{(H_2N)(O)C_6H_4\}_2(PPh_3)_2$	C_6D_6					7.9 (s), 5.1 (d), 4.0 (d), 3.5 (s)	5.8—7.7
$RuH\{o\text{-}(HO)(O)C_6H_4\}(PPh_3)_2\cdot 2C_6H_4(OH)_2$	$CDCl_3$	−11.4	34.0	34.0		4.9, [c] 4.5 [c]	6.4—7.5
$RuH\{m\text{-}(HO)(O)C_6H_4\}(PPh_3)_2$	thf	−10.8	33.0	33.0		7.7, [d] 6.3, [d] 6.2 [d]	6.6—7.6
$Ru_2H_2(O_2C_6H_4)_3(PPh_3)_4$	thf [a]	−7.5	27.0	27.0			6.9—7.9

[a] Obtained from a crude reaction solution. [b] Hydride resonance at 10 °C. [c] AA′BB′ type spectrum. [d] Complex multiplets.

TABLE 2

^{31}P n.m.r. spectra of ruthenium complexes in toluene at 36 °C

	Chemical shifts [a]		Coupling constants
Complex	P_A	P_B	J_{PP} (Hz)
$RuH_2(bipy)(PPh_3)_2$	62.0	62.0	
$RuH_2\{(NC)_2C_6H_4\}(PPh_3)_3$ [b]	47.1	24.3	27.0
$RuH\{(O)NC_9H_6\}(PPh_3)_3$	59.5	45.2	31.0
$Ru\{(O)NC_9H_6\}_2(PPh_3)_2$	44.3	44.3	
$RuH\{(O)NC_5H_4\}(PPh_3)_3$	67.2	44.7	29.1
$Ru\{(O)NC_5H_4\}_2(PPh_3)_2$	60.7	60.7	
$RuH\{(HN)NC_5H_4\}(PPh_3)_3$	67.3	44.9	26.0
$Ru\{(HN)_2C_6H_4\}(PPh_3)_3$	56.1	56.1	
$Ru\{(HN)_2C_6H_4\}(CO)(PPh_3)_2$	58.0	58.0	
$Ru\{(H_2N)(O)C_6H_4\}_2(PPh_3)_2$	52.3	52.3	

[a] P.p.m. to high frequency of external 85% H_3PO_4; for assignments see text and diagrams. [b] C_6H_6 as solvent.

Since few reactions of $RuH_2(PPh_3)_4$ with potentially bidentate ligands have been reported, we have studied some of these with substrates which are neutral or mono- or di-functional acids.

I.r. spectroscopic data for new compounds is given in the Experimental section and ^1H and ^{31}P n.m.r. data in Tables 1 and 2.

RESULTS AND DISCUSSION

Reactions of $RuH_2(PPh_3)_4$ *with Neutral potentially Bidentate Ligands.—2,2′-Bipyridyl.* $RuH_2(PPh_3)_4$ reacts smoothly with 2,2′-bipyridyl in toluene to give a green solution from which purple crystals of $RuH_2(bipy)(PPh_3)_2$ may be isolated on addition of petroleum. ^1H and ^{31}P n.m.r. spectra of this complex suggest that the two hydrides and the two phosphines are each equivalent. The ^{31}P n.m.r. chemical shift suggests that the phosphines are mutually *cis*, by comparison with known compounds [10,11] and with complexes (see below) which have three phosphines in a meridional arrangement. The compound thus has structure (I).

Reaction of the complex with chloroform gives a purple solution which rapidly deposits yellow-brown microcrystals of the known [12] $[Ru(\mu\text{-}Cl)(PPh_3)_2(bipy)]_2Cl_2$.

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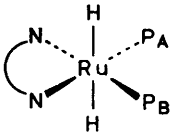
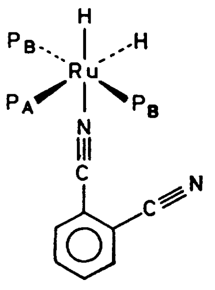
† No reprints available.

o-Dicyanobenzene. Although *o*-dicyanobenzene has two potential co-ordinating sites, their spatial distribution is such that it cannot form a chelate to one metal, but may act as a bridging ligand. The highly insoluble red product obtained from reaction of $RuH_2(PPh_3)_4$ with *o*-$C_6H_4(CN)_2$ has an analysis consistent with its formulation as $RuH_2(PPh_3)_3\{C_6H_4(CN)_2\}$. Although this compound is too insoluble for molecular-weight studies, a high-field ^1H n.m.r. spectrum of a supersaturated reaction solution shows a pattern very similar to that obtained from the hydrides of $RuH_2(PPh_3)_3(PhCN)$,[1] and hence suggests the structure (II). The presence of two ν(C≡N) absorptions in the i.r. spectrum, one of them with the same frequency as that for free *o*-$C_6H_4(CN)_2$ (2 222 cm^{-1}) also suggests that only one cyanide group is bound to the metal. This compound reacts with chloroform to give a highly insoluble yellow compound of formula $RuCl_2\{(NC)_2C_6H_4\}(PPh_3)_2$ which is presumably dimeric with bridging dicyanobenzene groups as two ν(Ru–Cl) at 330 and 315 cm^{-1} indicate terminal chlorine ligands.

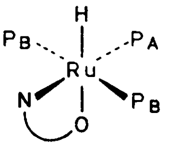


(I)



(II)

Reactions of $RuH_2(PPh_3)_4$ *with potentially Monofunctional Bidentate Acids.—2-Hydroxypyridine and 8-hydroxyquinoline.* $RuH_2(PPh_3)_4$ reacts with 2-hydroxypyridine or 8-hydroxyquinoline in tetrahydrofuran (thf) at room temperature to give products whose analyses are consistent with their formulation as $RuHX(PPh_3)_3$ (X = 2-OC_5H_4N or 8-OC_9H_6N). For X = 8-OC_9H_6N, ^1H and ^{31}P n.m.r. data suggest that the hydride is *cis* to three meridional phosphines. For X = 2-OC_5H_4N the hydride resonance is broad at 36 °C but sharpens to a quartet at 10 °C. This suggests that at higher temperatures some exchange process involving dissociation of phosphine is occurring. It is not possible unequivocally to decide whether the hydride is *trans* to either the co-ordinated oxygen (III) or nitrogen (IV) in either case, although the large difference in chemical shift of the unique phosphorus atom in the two complexes suggests that in one this atom is *trans* to nitrogen (III) whilst in the other it is *trans* to oxygen (IV). Since for $RuH(HNC_5H_4N)(PPh_3)_3$, derived from 2-aminopyridine (see later) the chemical shift of the unique phosphorus atom is almost identical to that of unique phosphorus atom in $RuH(OC_5H_4N)(PPh_3)_3$, we suggest that complexes $RuH(HNC_5H_4N)(PPh_3)_3$ and $RuH(OC_5H_4N)(PPh_3)_3$ have the unique phosphorus atom *trans* to the ring nitrogen atom as in (I) and (III). Then, $RuH(OC_9H_6N)(PPh_3)_3$ has structure (IV). For both $RuH(OC_9H_6N)(PPh_3)_3$ and $RuH(OC_5H_4N)(PPh_3)_3$, the presence in solution of another hydride [weak quartet at δ −12.3, ν(Ru–H) 2 045 cm^{-1}, X = OC_9H_6N; δ −14.1, ν(Ru–H) 1 975 cm^{-1}, X = OC_5H_4N] suggests that there is contamination by a second isomer (<20%).



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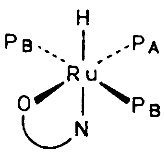

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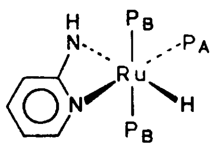
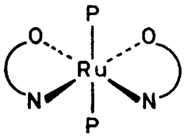


(V)

In the ^1H n.m.r. spectrum of $RuH(OC_5H_4N)(PPh_3)_3$ certain of the phenyl resonances appear in the region normally associated[7] with a π-interaction of the phenyl ring. For this species we do not believe that the oxopyridine group is π-bound to the metal, since such high-field shifts have previously been observed[13] in species containing the α-picolyl anion bound as a bridging ligand.

For both 2-$HO(C_5H_4N)$ and 8-$HO(C_9H_6N)$, if the reaction with $RuH_2(PPh_3)_4$ is carried out in refluxing toluene, both hydrides are replaced to give $RuX_2(PPh_3)_2$. Once again, ^{31}P n.m.r. data suggest different stereochemistries. For X = OC_9H_6N the phosphines are evidently mutually *trans* as in (VI) or (VII), whilst for X = OC_5H_4N they are equivalent and *cis*. The similarity of the chemical shift of the phosphorus atoms of this complex to that of the unique phosphorus atom in $RuH(OC_9H_6N)(PPh_3)_3$ strongly suggests that the phosphorus atoms are *trans* to oxygen as in (VIII) rather than nitrogen (IX). Molecular-weight studies on $RuH(OC_5H_4N)(PPh_3)_3$ confirm that it is a monomer and hence contains the four-membered chelate ring.



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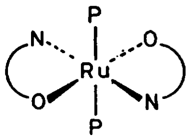

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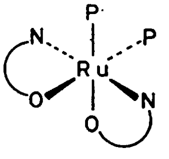

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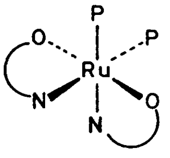


(IX)

2-Aminopyridine. Reaction of $RuH_2(PPh_3)_4$ with 2-$(H_2N)C_5H_4N$ in refluxing thf or toluene leads to $RuH(HNC_5H_4N)(PPh_3)_3$ but attempts to prepare $Ru(HNC_5H_4N)_2(PPh_3)_2$ by carrying out the reaction in higher boiling solvents lead to extensive decomposition. This is presumably because the NH_2 group is a substantially weaker acid than the OH group. As discussed above, $RuH(HNC_5H_4N)(PPh_3)_3$ has very similar spectroscopic properties to those of $RuH(OC_5H_4N)(PPh_3)_3$, except that the hydride resonance is a doublet of triplets at room temperature, and the complex has structure (V). A single ν(N–H) absorption at 3 412 cm^{-1} and the absence of a strong δ-NH_2 near 1 600 cm^{-1} confirm the presence of an imino, rather than an amino-group.

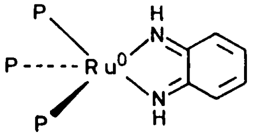
2-*Mercaptopyridine.* Reaction of $RuH_2(PPh_3)_4$ with $2\text{-}HSC_5H_4N$ in cold or refluxing thf gives the known $Ru(SC_5H_4N)_2(PPh_3)_2$ for which the crystal structure shows equivalent phosphorus atoms *trans* to nitrogen.[14,15] We have been unable to isolate any hydride-containing complex from this reaction presumably because of the high affinity of the soft sulphur atom for ruthenium.

Reactions of $RuH_2(PPh_3)_4$ *with potentially Dibasic Acids.*—(i) o-*Phenylenediamine.* In refluxing toluene, $RuH_2(PPh_3)_4$ and $o\text{-}(H_2N)_2C_6H_4$ give a green-purple dichroic solution from which dark-green crystals of $Ru\{(HN)_2C_6H_4\}(PPh_3)_3$ may be isolated. The same product is obtained from $RuCl_2(PPh_3)_3$ and $o\text{-}(H_2N)_2C_6H_4$ in presence of base when refluxed in a thf–water (1 : 2) mixture. Although the solid-state i.r. spectrum shows two ν(N–H) bands at 3 340 and 3 310 cm^{-1}, this appears as one broad absorption at 3 320 cm^{-1} in CS_2 solution. Absence of peaks near 1 620 cm^{-1} attributable to δ-NH_2 and the high value of $\nu C \overset{\cdots}{-} N$ [1 358 and 1 332 cm^{-1}; *cf.* 1 272 and 1 248 cm^{-1} for free $(H_2N)_2C_6H_4$] confirm that the ligand is, as commonly found,[16] present as a di-imine, rather than a diamine. The bonding in this compound can be viewed in several ways (X)—(XII), but we prefer the butadiene-like delocalised view (XII), since the complex then contains an 18-electron Ru^{II} metal atom. This view, with some rotation of the phenylenedi-imine moiety more readily explains the ^{31}P n.m.r. spectrum which shows a sharp singlet (equivalent phosphorus atoms) at all temperatures down to −80 °C. A dissociative exchange of PPh_3 groups is ruled out since addition of PPh_3 only gives rise to a new peak (from free PPh_3) and no broadening or shifting of the original resonance. This compound reacts with CO to give $Ru\{(HN)_2C_6H_4\}(CO)(PPh_3)_2$.

2-*Aminothiophenol and* 2-*aminophenol.* Both $2\text{-}(H_2N)C_6H_4XH$ (X = O or S) react with $RuH_2(PPh_3)_4$ to give $Ru\{(H_2N)C_6H_4X\}_2(PPh_3)_2$ which, for X = S, has previously been reported.[17] Both have two ν(N–H) absorptions in solution and a strong absorption near 1 600 cm^{-1} attributed to δ-NH_2. The ^{31}P n.m.r. spectra show temperature-invariant singlets in the region expected for *cis*-phosphines which do not split when coupling to any hydrido-ligands is introduced. These thus have either structure (XIII) or (XIV) (X = O or S).

The ^{31}P chemical shift for X = O suggests that in this compound P is *trans* to N (XIV).

Pyrocatechol and resorcinol. Both pyrocatechol and resorcinol react with $RuH_2(PPh_3)_4$ to give yellow crystalline complexes, the analyses for which are consistent with their formulation as $RuH(OC_6H_4OH)(PPh_3)_2 \cdot n[(OH)_2C_6H_4]$ (*n* = 2 and 0 respectively). The i.r. spectra of the two complexes are similar with ν(C=O) near 1 500 cm^{-1} and ν(C–O) between 1 200 and 1 300 cm^{-1}, the compound derived from pyrocatechol shows a more complex spectrum in the latter region. For both complexes ν(OH) is broad (the more so for the compound derived from pyrocatechol). For the resorcinol compound this suggests intermolecular hydrogen bonding since intramolecular hydrogen bonding is unlikely on steric grounds. For the pyrocatechol compound however the hydrogen bonding is probably similar to that found [7]



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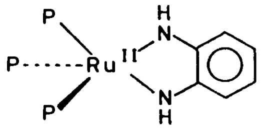

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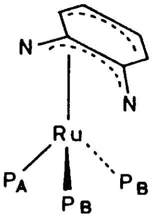

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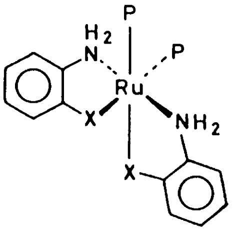

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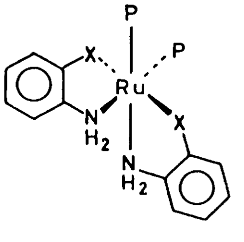

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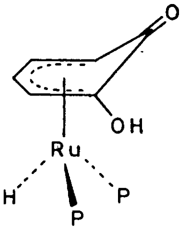

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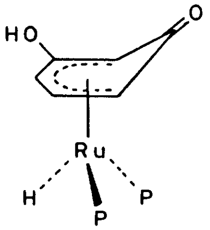


(XVI)

in $RuH(OPh)(PPh_3)_2{\cdot}2PhOH$, which is formed from $RuH_2(PPh_3)_4$ and an excess of phenol.

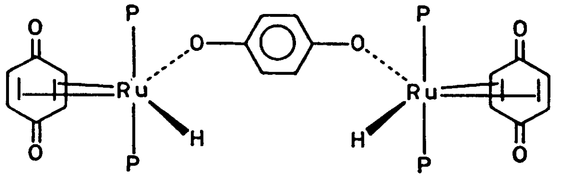
Splitting of the peak near 1 430 cm^{-1}, as well as the characteristic six-line pattern near 530 cm^{-1} previously observed[7] for complexes containing π-bonded phenoxo-rings strongly suggest that in these complexes the phenyl rings of the pyrocatechol or resorcinol are π-bonded to the metal. The ν(Ru–H) absorptions appear as sharp peaks of medium intensity near 2 000 cm^{-1}.

Confirmation that the phenolic rings are π-bonded to the metal comes from the ^1H n.m.r. spectra which, in each case show resonances from the (OC_6H_4OH) rings shifted to substantially higher field than could be expected for the *O*-bonded ligands. For the complex derived from pyrocatechol, a typical AA'BB' type spectrum is observed, whereas for the resorcinol derivative a more complex pattern, which we have not attempted to analyse, is seen. In both cases the hydride resonates as a triplet near δ −11.

The complexes thus have structures (XV) and (XVI) which are similar to the structure of the complex obtained from reaction of $RuH_2(PPh_3)_4$ with 1 mol equiv. of phenol. We have omitted the hydrogen-bonded pyrocatechol molecules, but the lack of any sharp ν(O–H) absorption suggests that all five acidic hydrogen atoms are involved in hydrogen bonding.

If the reaction with pyrocatechol is carried out under different conditions, several other products may be obtained, but the reproducibility of these reactions is not good. We have not characterised any of these other products.

Hydroquinone. Warming of $RuH_2(PPh_3)_4$ with an excess of hydroquinone in tetrahydrofuran leads to a pale yellow, highly insoluble compound the analysis for which is consistent with its formulation as $Ru_2H_2(O_2C_6H_4)_3(PPh_3)_4$. Apart from a sharp ν(Ru–H) peak at 1 960 cm^{-1}, the i.r. spectrum shows the presence of both ν(C=O) (1 520 cm^{-1}) and ν(C–O) (1 296 cm^{-1}). Another peak at 1 565 cm^{-1} may also arise from ν(C=O), but is more likely ν(C=C) of a co-ordinated quinone moiety. No ν(O–H) absorption is observable above 3 000 cm^{-1}. The insolubility of this complex has prevented a full spectroscopic characterisation, but a ^1H n.m.r. spectrum of a reaction solution shows a weak hydride resonance (broad triplet at δ −7.5) apart from the broadened quartet at δ −10.5 from unchanged $RuH_2(PPh_3)_4$. The limited data available suggest that *p*-benzoquinone is co-ordinated both as the dianion and as the neutral molecule, so that we tentatively propose structure (XVII) or an isomer thereof.



(XVII)

EXPERIMENTAL

The microanalyses reported were carried out by Imperial College, Butterworth Microanalytical Consultancy Limited, and Pascher Mikroanalytisches Laboratorium (Bonn). I.r. spectra were recorded in Nujol mulls between KBr or CsI plates on Perkin-Elmer 457 and 597 grating spectrophotometers. N.m.r. spectra were measured on Perkin-Elmer R12 and R32 (^1H) and Varian Associates XL-100-12 (^{31}P) spectrometers, the latter operating in the Fourier transform mode with noise proton decoupling. Melting points were measured on an Electrothermal melting-point apparatus in tubes sealed under argon and are uncorrected. Molecular weights were measured cryoscopically in benzene under argon.

The reactions were carried out under an inert atmosphere (Ar) and all solvents were thoroughly degassed and dried before use. Petroleum had boiling range 40—60 °C. Other reagents were S.L.R. grade and were used without further purification.

$RuH_2(PPh_3)_4$ was synthesised by a published method.[3] Analytical data for new compounds are collected in Table 3.

cis-2,2′-*Bipyridyldihydridobis*(*triphenylphosphine*)-*ruthenium*(II).—$RuH_2(PPh_3)_4$ (1 g) and 2,2′-bipyridine (0.3 g) were stirred in toluene (60 ml) at 100 °C for 1 h. Petroleum (30 ml) was added to the filtered dark green solution. The purple crystals which formed on cooling (−15 °C) were collected, washed with petroleum, and dried

TABLE 3

Analytical data for ruthenium complexes

Complex	Colour	M.p. (θc/°C)	Found (%)					Required (%)				
			C	H	N	P	Other	C	H	N	P	Other
$RuH_2(bipy)(PPh_3)_2$	Purple	217d	70.0	5.4	3.8	7.5		70.5	5.1	3.6	7.9	
$RuH_2\{(NC)_2C_6H_4\}(PPh_3)_3$	Red	170d	73.5	5.2	2.4	9.1		73.1	5.0	2.7	9.1	
$[RuCl_2\{(NC)_2C_6H_4\}(PPh_3)_2]_2$	Yellow	280d	63.0	4.1	3.3	7.2	Cl, 9.1	64.1	4.1	3.4	7.5	Cl, 8.6
$RuH\{(O)NC_9H_6\}(PPh_3)_3$	Orange	125d	73.5	5.2	1.6	8.7		73.2	5.0	1.4	9.0	
$Ru\{(O)NC_9H_6\}_2(PPh_3)_2$	Red	275d	70.1	4.7	3.0	6.5		70.9	4.6	3.1	6.8	
$RuH\{(O)NC_5H_4\}(PPh_3)_3$	Yellow	245d	72.1	5.3	1.5	9.4		72.1	5.1	1.4	9.5	
$Ru\{(O)NC_5H_4\}_2(PPh_3)_2$	Yellow	275d	68.0	4.5	3.7	7.4		67.9	4.7	3.4	7.6	
$RuH\{(HN)NC_5H_4\}(PPh_3)_3$	Yellow	225d	72.5	5.3	2.8	9.7		72.2	5.2	2.8	9.5	
$Ru\{(HN)_2C_6H_4\}(PPh_3)_3$	Dark green	231d	73.0	5.5	2.7	10.0		72.5	5.1	2.8	9.4	
$Ru\{(HN)_2C_6H_4\}(CO)(PPh_3)_2$	Purple	225d	68.3	4.8	3.7	8.4		68.0	4.7	3.7	8.2	
$Ru\{(H_2N)(O)C_6H_4\}_2(PPh_3)_2$	Yellow-green	145—148	68.6	5.3	3.0	7.3		68.5	5.0	3.3	7.4	
$RuH\{o\text{-}(HO)(O)C_6H_4\}(PPh_3)_2{\cdot}2C_6H_4(OH)_2$	Yellow	135d	67.2	5.1		6.1	O, 10.7	67.9	5.0		6.5	O, 10.1
$RuH\{m\text{-}(HO)(O)C_6H_4\}(PPh_3)_2$	Yellow	170d	68.5	5.3		8.2		68.6	4.9		8.4	
$Ru_2H_2(O_2C_6H_4)_3(PPh_3)_4$	Yellow	165d	68.0	5.5		7.7	O, 5.9	68.5	4.7		7.8	O, 6.1

in vacuo, yield *ca.* 80%; i.r. 3 040m, 1 900m, 1 580m, 1 475s, 1 430vs, 1 305w, 1 255m, 1 180m, 1 080m, 1 065m,sh, 1 025w, 1 000w, 765m,sh, 745vs, 720m, 695vs, 680sh, 535sh, 530s, 510vs, 495sh, 445m,sh, and 420m cm^{-1}.

Reaction of $RuH_2(bipy)(PPh_3)_2$ *with Chloroform.*—*cis*-$RuH_2(bipy)(PPh_3)_2$ (0.15 g) was stirred in $CHCl_3$ (5 ml) for 2 h. The light brown precipitate was washed with $CHCl_3$ and dried *in vacuo*. It was identified as $[Ru(\mu\text{-}Cl)(PPh_3)_2(bipy)]_2Cl_2$ by comparison with an authentic sample; yield *ca.* 90%; i.r. 3 040m, 1 595m, 1 583m, 1 570w, 1 480vs, 1 430vs, 1 415s, 1 330m, 1 305w, 1 265m, 1 188w, 1 155m, 1 085m, 1 065w, 1 025w, 995w, 965w, 840w, 772m, 762m, 745vs, 738vs, 730m, 695vs, 690vs, 660w, 528m, 510vs, 490vs, 455w, 430m, and 403m cm^{-1}.

o-*Dicyanobenzene(dihydrido)tris(triphenylphosphine)ruthenium*(II).—$RuH_2(PPh_3)_4$ (0.5 g) in thf (10 ml) was mixed with $o\text{-}C_6H_4(CN)_2$ (0.25 g) in thf (5 ml). The resulting red solution was stirred for 30 min after which petroleum (15 ml) was added and the solution cooled to −15 °C. The dark red crystals were collected, washed with Et_2O, and dried *in vacuo*; yield *ca.* 90%; i.r. 3 050m, 2 222w, 2 175vs, 1 930m, 1 892m, 1 582m, 1 568w, 1 475s, 1 430vs, 1 180m, 1 083m, 1 068m, 1 025w, 998w, 770m, 740s, 695vs, 533m, 515vs, 500s, 450m, 432m, and 410m cm^{-1}.

*Bis-*μ*-*o*-dicyanobenzene-bis[dichlorobis(triphenylphosphine)ruthenium*(II)].—$RuH_2\{(NC)_2C_6H_4\}(PPh_3)_3$ (0.2 g) was stirred in chloroform (10 ml) for 5 h. The yellow precipitate formed was collected, washed with chloroform and dried *in vacuo*; yield *ca.* 95%; i.r. 3 050m, 2 252w, 2 225vs, 1 582w, 1 570w, 1 482s, 1 435vs, 1 222w, 1 089m, 780m, 760m, 740m, 715m, 698vs, 684m, 580w, 554w, 538m, 528vs, 520vs, 495m, 480w, 460w, 450w, 330w, and 315w cm^{-1}.

Hydrido(8-hydroxyquinolinato)tris(triphenylphosphine)ruthenium(II).—$RuH_2(PPh_3)_4$ (0.11 g) and $C_9H_6N(OH)$ (0.015 g) were stirred in thf (5 ml) for 12 h. Petroleum (20 ml) was added to the orange solution and the orange crystals which formed on cooling (−15 °C) were collected, washed with diethyl ether, and dried *in vacuo*; yield *ca.* 80%; i.r. 3 045s, 2 045m, 1 585m, 1 560s, 1 490m, 1 480s, 1 450vs, 1 435sh, 1 430s, 1 350m, 1 323s, 1 165w, 1 080sh, 1 065m, 910w, 812m, 800w, 772m, 745s, 732s, 697vs, 690sh, 535m, 520sh, 512vs, 495m, 485m, 472w, 420w, and 400w cm^{-1}.

Bis(8-hydroxyquinolinato)bis(triphenylphosphine)ruthenium(II).—$RuH_2(PPh_3)_4$ (0.2 g) and $C_9H_6N(OH)$ (0.06 g) were refluxed in toluene (10 ml) for 1 h. The hot red solution was filtered and treated with petroleum (10 ml) before cooling to −15 °C. The red crystals so formed were collected, washed with diethyl ether, and dried *in vacuo*; yield *ca.* 80%; i.r. 3 050s, 1 590m, 1 580m, 1 560vs, 1 495vs, 1 480s, 1 435vs, 1 428vs, 1 370vs, 1 318vs, 1 285s, 1 220m, 1 210w, 1 190m, 1 170m, 1 105m, 1 090m, 1 028m, 918m, 848w, 820s, 812s, 800m, 785m, 775s, 745s, 735vs, 725sh, 705sh, 692vs, 620w, 585w, 530vs, 520vs, 510sh, 505m, 500m, 485m, 465m, 460sh, 435m, 425m, and 410m cm^{-1}.

Hydrido(2-hydroxypyridinato)tris(triphenylphosphine)ruthenium(II).—$RuH_2(PPh_3)_4$ (0.2 g) and $C_5H_4N(OH)$ (0.03 g) were stirred in thf (10 ml) for 10 h. The yellow solution was filtered, petroleum (30 ml) was added to it and the solution cooled to −15 °C. The yellow crystals were collected, washed with diethyl ether, and dried *in vacuo*; yield *ca.* 90%; *M* 912; (requires 983); i.r. 3 050m, 2 010w, 1 975w, 1 595vs, 1 585m, 1 570w, 1 540w, 1 480vs, 1 470vs, 1 435vs, 1 430vs, 1 350m, 1 280m, 1 242w, 1 080m, 1 026w, 1 000m, 847w, 775m, 750sh, 740s, 730m, 692vs, 680m, 580w, 539m, 532m, 515vs, 507vs, 495s, 482m, 458sh, 445m, 420m, and 405m cm^{-1}.

Bis(2-hydroxypyridinato)bis(triphenylphosphine)ruthenium(II).—$RuH_2(PPh_3)_4$ (0.5 g) and $C_5H_4N(OH)$ (0.1 g) were refluxed in toluene (10 ml) for 1 h. Petroleum (7 ml) was added to the filtered brown-orange solution at room temperature to give brown-orange crystals. These were collected, washed with diethyl ether, and dried *in vacuo*; yield *ca.* 65%; i.r. 3 060m, 1 600vs, 1 570w, 1 548w, 1 480vs, 1 470vs, 1 441vs, 1 435vs, 1 350s, 1 290s, 1 250w, 1 192w, 1 185w, 1 150w, 1 145w, 1 100s, 1 090s, 1 030w, 1 015m, 1 000w, 858w, 840w, 770m, 755m, 743m, 732s, 695vs, 620w, 600m, 545s, 525vs, 515sh, 500m, 458w, 438w, and 422m cm^{-1}.

2-Aminopyridinato(hydrido)tris(triphenylphosphine)ruthenium(II).—$RuH_2(PPh_3)_4$ (0.4 g) and $C_5H_4N(NH_2)$ (0.1 g) were refluxed in thf (15 ml) for 5 h. Petroleum (85 ml) was added and the solution was filtered after 2 h. The yellow solution was kept at −20 °C for 10 days. The yellow-brown solid was collected and recrystallised by dissolution in hot toluene (10 ml) and addition of petroleum (30 ml). After 7 days at −15 °C the yellow crystals were collected, washed with petroleum, and dried *in vacuo*; yield *ca.* 60%; i.r. 3 412w, 3 050m, 1 930s, 1 605s, 1 588m, 1 490s, 1 480s, 1 450s, 1 432vs, 1 296s, 1 288m, 1 185w, 1 150w, 1 090s, 1 030w, 1 000w, 855w, 750s, 740s, 700vs, 682m,5 52m, 545m, 524vs, 518sh, 501m, 460m, 445w, and 405m cm^{-1}.

Bis(2-mercaptopyridinato)bis(triphenylphosphine)ruthenium(II).—$RuH_2(PPh_3)_4$ (0.2 g) in thf (5 ml) was mixed with $C_5H_4N(SH)$ (0.04 g) in thf (5 ml). The dark orange solution was stirred for 1 h, petroleum (30 ml) was added. After 5 h the filtered solution was cooled to −15 °C. The orange crystals were collected, washed with diethyl ether, and dried *in vacuo*; yield *ca.* 65%; i.r. 3 050m, 1 585sh, 1 572s, 1 545m, 1 477s, 1 436vs, 1 428vs, 1 418s, 1 260m, 1 250m, 1 134m, 1 081m, 1 065sh, 760m, 745vs, 735m, 729m, 707sh, 695vs, 680sh, 532s, 520vs, 512s, 492s, 465w, 430sh, and 410m cm^{-1}.

(o*-Benzoquinone di-imine)tris(triphenylphosphine)ruthenium*(II).—*Method* (*a*) $RuH_2(PPh_3)_4$ (2 g) and $o\text{-}C_6H_4(NH_2)_2$ (0.2 g) were refluxed in toluene (50 ml) for 3 h. After cooling, petroleum (35 ml) was added to the filtered dark green solution. The dark green crystals which formed within 12 h at room temperature were washed with diethyl ether and dried *in vacuo*. On concentrating the residual solution to 15 ml and adding petroleum (10 ml) more crystals were collected; yield *ca.* 80%.

Method (*b*). $RuCl_2(PPh_3)_3$ (0.5 g) and $o\text{-}C_6H_4(NH_2)_2$ (0.06 g) were refluxed in a mixture of water (10 ml) and thf (5 ml) with $BuNH_2$ (2 ml) for 3 h. The oily dark green precipitate was collected, dried *in vacuo*, and recrystallised from toluene–petroleum; yield *ca.* 80%; i.r. 3 340w, 3 310w, 3 050m, 1 585w, 1 570w, 1 490w, 1 479s, 1 430vs, 1 358m, 1 332m, 1 225w, 1 185w, 1 080m, 1 025w, 996w, 742vs, 725w, 705sh, 695vs, 680sh, 560m, 540s, 516vs, 506s, 498s, 460m, 446w, and 415m cm^{-1}.

(o*-Benzoquinone di-imine)carbonylbis(triphenylphosphine)ruthenium*(II).—$Ru\{(HN)_2C_6H_4\}(PPh_3)_3$ (0.3 g) was dissolved in toluene (20 ml) and CO was bubbled through the solution for 5 h. The dark purple solution formed was evaporated to 3 ml and kept at −15 °C for 5 days. The purple crystals were collected, washed with diethyl ether, and dried *in vacuo*; yield *ca.* 75%; i.r. 3 358w, 3 330w, 3 055m, 1 892vs, 1 850w, 1 582w, 1 568w, 1 477vs, 1 432vs, 1 364m, 1 350m, 1 330w, 1 315s, 1 220w, 1 185m, 1 157w, 1 142w, 1 085m, 995w, 754m, 745m, 731vs, 702sh, 693vs, 615w, 572m, 560w, 550w, 530vs, 520vs, 502s, 480m, 455m, 443w, and 415w cm^{-1}.

Bis(2-aminophenoxo)bis(triphenylphosphine)ruthenium(II).—$RuH_2(PPh_3)_4$ (0.6 g) and *o*-$C_6H_4(OH)(NH_2)$ (0.12 g) were refluxed in toluene (20 ml) for 1 h. The filtered yellow-green solution was allowed to crystallise at room temperature. The yellow-green compound was collected, washed with MeOH to remove excess 2-aminophenol, and dried *in vacuo*. After 24 h more crystals were collected from the mother-liquors and the yield increased by cooling or concentrating the remaining solution; yield *ca*. 75%; i.r. 3 280m, 3 270m, 3 242m, 3 050m, 1 600s, 1 580m, 1 550w, 1 482vs, 1 448s, 1 433m, 1 315vs, 1 305vs, 1 294m, 1 260w, 1 190w, 1 145w, 1 110w, 1 087w, 1 060m, 1 043w, 998w, 927w, 870w, 753s, 746s, 731m, 723w, 695vs, 618w, 537s, 522s, 508s, 495m, 460w, 435m, and 415w cm^{-1}.

Bis(2-aminothiophenoxo)bis(triphenylphosphine)ruthenium(II).—$C_6H_4(NH_2)(SH)$ (0.5 ml) was added to $RuH_2(PPh_3)_4$ (0.5 g) in thf (10 ml). The solution was stirred for 1 h. The yellow crystalline precipitate was collected, washed with diethyl ether, and dried *in vacuo*. From the mother-liquors more crystals were formed by adding petroleum (50 ml) and cooling to −15 °C for 24 h; yield *ca*. 70%; i.r. 3 272s, 3 230s, 3 045m, 1 583s, 1 540w, 1 478s, 1 430vs, 1 310w, 1 290w, 1 262w, 1 200sh, 1 190w, 1 152w, 1 080sh, 1 075s, 1 030w, 993w, 858w, 755m, 737vs, 695vs, 679m, 563w, 535s, 518vs, 508s, 495m, 461m, and 415m cm^{-1}.

Hydrido(2—6-η-pyrocatecholato)bis(triphenylphosphine)ruthenium(II)*-Pyrocatechol* (1/2).—$RuH_2(PPh_3)_4$ (0.25 g) and *o*-$C_6H_4(OH)_2$ (0.06 g) were stirred in toluene (7.5 ml) at 100 °C for 2.5 h. The solvent was evaporated and the solid residue dissolved in chloroform (3 ml). Petroleum (5 ml) was added to the solution. After the filtered solution had been cooled at −15 °C for 24 h, yellow crystals were formed, collected, washed with petroleum, and dried *in vacuo*; yield *ca*. 70%; i.r. 3 380m,br, 3 060w, 2 000w, 1 620m, 1 605m, 1 574w, 1 540m, 1 510sh, 1 500vs, 1 480sh, 1 470vs, 1 435sh, 1 432vs, 1 335m, 1 275s, 1 255vs, 1 238vs, 1 215sh, 1 188m, 1 090s, 1 070w, 1 030w, 1 017sh, 1 000w, 890vw, 875w, 850w, 835w, 770sh, 760vs, 748vs, 735sh, 700vs, 685sh, 635w, 618w, 580w, 538s, 528vs, 515s, 505sh, 495sh, 481w, 465w, 450w, 440w, and 425w cm^{-1}.

Hydrido(2—6-η-resorcinolato)bis(triphenylphosphine)ruthenium(II).—$RuH_2(PPh_3)_4$ (0.32 g) and *m*-$C_6H_4(OH)_2$ (0.1 g) were refluxed in thf (5 ml) for 15 min. Petroleum (2 ml) was added to the hot yellow solution and, after filtering, the solution was cooled to −15 °C for 24 h. The pale yellow crystals were collected, washed with methanol, and dried *in vacuo*; yield, *ca*. 75%; i.r. 3 240m,br, 3 050m, 2 060m, 1 588w, 1 575w, 1 500sh,br, 1 480s, 1 440sh, 1 433vs, 1 335m,br, 1 310m, 1 253m, 1 183s, 1 140m, 1 090s, 1 045s, 1 025w, 998w, 970w, 872w, 848w, 767sh, 750m, 738s, 693vs, 657w, 645w, 620w, 555m, 538vs, 528vs, 518vs, 500s, 491m, 465sh, 450m, 440m, and 422w cm^{-1}.

μ-Hydroquinonato-bis[(2—3,5—6-η-p-benzoquinone)hydridobis(triphenylphosphine)ruthenium(II)].— $RuH_2(PPh_3)_4$ (0.35 g) and *p*-$C_6H_4(OH)_2$ (0.1 g) were refluxed in thf (5 ml) for 15 min. The yellow crystalline precipitate was washed with thf and dried *in vacuo*; yield *ca*. 85%; i.r. 3 050m, 1 960s, 1 590w, 1 565m, 1 520m, 1 487sh, 1 482s, 1 478s, 1 435vs, 1 296m, 1 138w, 1 090s, 1 065s, 1 030w, 1 000w, 870w, 835w, 793s, 755sh, 745vs, 738vs, 700vs, 694vs, 680w, 627m, 617m, 603m, 540s, 537vs, 518s, 512s, 501m, 492s, 465m, 457m, 433w, 423w, and 380s cm^{-1}.

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