Interaction of Oximes with Dichlorotris(triphenylphosphine)-ruthenium(II) †

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Dichlorotris(triphenylphosphine)ruthenium(II), $RuCl_2(PPh_3)_3$, has been treated with (*a*) chelating oximes (α-di-oximes, α-carbonyloximes, α-imino-oximes, hydroxy-oximes, and pyridine oximes); and (*b*) simple oximes such as acetoxime, cyclohexanone oxime, *etc.*, both without and with added base. Thirty new compounds with oximes as neutral ligands or as uninegative anions have been characterised by infrared (i.r.) and ^1H and ^{31}P nuclear magnetic resonance (n.m.r.) spectra. All the compounds contain bound triphenylphosphine groups.

The interaction of $RuCl_2(PPh_3)_3$ with hydroxylamine in the presence of NaOH gives a compound $RuCl(NH_2O)(NH_2OH)(PPh_3)_2$, which is considered to have an η^2-hydroxylaminato-group.

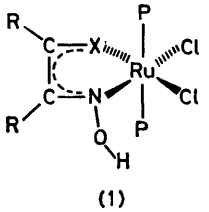
Although oxime complexes of most transition metals have been studied,[1] there are few known ruthenium–oxime compounds. Concurrent with our studies Cairns and James [2] have made dimethylglyoxime ($dmgH_2$) complexes, $[Ru(dmgH_2)_3]^{2+}$, $RuCl_2(Me_2SO)_2(dmgH_2)$, and $[RuCl(Me_2SO)(dmgH_2)_2]^+$ from $RuCl_2(Me_2SO)_4$.[2]

Interaction of chloronitrosylruthenium species with acetylacetone generates a species with a bidentate ketone oxime (hia = hydroxyiminoacetylacetonato), $Ru(acac)_2(hia)$,[3a] while ruthenium(II) violurato-complexes are also known.[3b]

RESULTS AND DISCUSSION

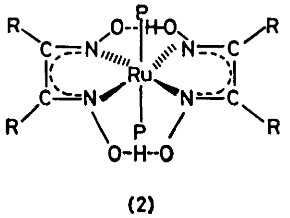
(*A*) *α-Dioximes.*—Refluxing $RuCl_2(PPh_3)_3$ with the α-dioximes (LH_2) dimethylglyoxime, nioxime, and benzil-α-dioxime in methanol gave diamagnetic, red to orange crystals of stoicheiometry $RuCl_2(LH_2)(PPh_3)_2$. The soluble benzil-α-dioxime complex was a non-conductor in nitromethane ($\Lambda_M < 10$), § and its ^{31}P n.m.r. spectrum showed that the phosphines were *trans* (singlet at 20.81 p.p.m.‡).

The analytical and spectroscopic data are consistent with the structure (1) with X = NOH. The reaction of $RuCl_2(LH_2)(PPh_3)_2$ with NaOH in the presence of an excess of oxime gave the yellow-orange complexes $Ru(LH)_2(PPh_3)_2$. Identical products were obtained by treating $RuCl_2(PPh_3)_3$ with two equivalents of oxime and NaOH, or by interacting $RuH_2(PPh_3)_4$ with oxime. The products were only slightly soluble, but the ^{31}P n.m.r. spectrum of $Ru(dmgH)_2(PPh_3)_2$ (singlet, 28.93 p.p.m.) showed that the phosphines were *trans*. The structure of these complexes is doubtless similar to that of $Rh^{III}Cl(dmgH)_2(PPh_3)$,[4] but with octahedral ruthenium(II) and hydrogen bonding between the two oxime groups as in (2).



(1)

(P=PPh$_3$, X=NOH, O, OH)

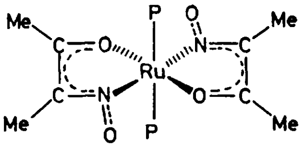


(2)

(*B*) *α-Carbonyl Oximes.*—On refluxing $RuCl_2(PPh_3)_3$ with butan-2,3-dione mono-oxime (bdoH) in methanol a brown crystalline complex precipitated. This had stoicheiometry $RuCl_2(bdoH)(PPh_3)_2$, was diamagnetic, and gave a non-conducting solution in nitromethane ($\Lambda_M < 10$). It was monomeric in dichloromethane and the ^{31}P n.m.r. spectrum (singlet 25.31 p.p.m.) showed that the phosphines were *trans*. The structure of this complex appeared to be similar to the complexes $RuCl_2(LH_2)(PPh_3)_2$ above as in (1) but with X = O.

Reaction of $RuCl_2(PPh_3)_3$ with bdoH in the presence of NaOH led to a deep red solution and a red precipitate. Recrystallisation of the red solid from acetone or thf (Sol) gave a complex of stoicheiometry $Ru(bdo)_2(PPh_3)_2{\cdot}2Sol$, while the red solution on cooling gave a red complex of stoicheiometry $Ru(bdo)_2(PPh_3)_4$. The ^{31}P n.m.r. spectrum of $Ru(bdo)_2(PPh_3)_2$ was a singlet at 45.9 p.p.m., suggesting a *cis* phosphine configuration. The spectrum of $Ru(bdo)_2(PPh_3)_4$ had an additional resonance due to free PPh_3 at −6.03 p.p.m. This suggests that it is best formulated as $Ru(bdo)_2(PPh_3)_2{\cdot}2PPh_3$ by analogy with the solvates. Reaction of $RuCl_2(bdoH)(PPh_3)_2$ with NaOH in the presence of bdoH led to a similar red complex of stoicheiometry $Ru(bdo)_2(PPh_3)_2$. This was evidently the *trans* isomer (^{31}P n.m.r., singlet at 33.5 p.p.m.).

The i.r. spectra of these three complexes were virtually identical and suggested that the bdo ligand is bound through both N and ketonic oxygen atoms as in (3).



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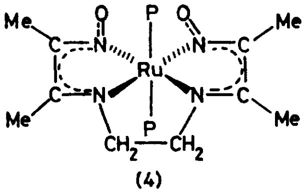

(4)

(*C*) *α-Imino-oximes.* On refluxing bdo_2enH_2 (en = ethylenediamine) and NaOH with $RuCl_2(PPh_3)_3$ in methanol, diamagnetic red crystals of stoicheiometry $Ru(bdo_2en)(PPh_3)_2$ were formed. The complex was monomeric and non-conducting in solution. The ^{31}P

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† No reprints available.

‡ Referenced to 85% external H_3PO_4.

§ Units of conductivity are Ω^{-1} cm^2 mol^{-1} throughout.

Analytical data for ruthenium complexes *

Compound	Colour	C	H	N	Cl	P
$RuCl_2(dmgH_2)(PPh_3)_2$	Red	59.1 (59.1)	4.8 (4.7)	3.5 (3.4)		
$RuCl_2(nioxH_2)(PPh_3)_2$	Red	61.1 (61.1)	4.8 (4.8)	2.9 (3.3)		
$RuCl_2(benziloxH)(PPh_3)_2$	Orange	64.0 (64.4)	4.4 (4.5)	3.0 (3.0)	6.5 (7.6)	6.0 (6.6)
$Ru(dmgH)_2(PPh_3)_2$	Orange	60.8 (61.7)	5.2 (5.1)	6.4 (6.5)	0 (0)	
$Ru(nioxH)_2(PPh_3)_2$	Orange	62.8 (63.4)	5.2 (5.2)	5.8 (6.1)	0 (0)	
$Ru(benziloxH)_2(PPh_3)_2$	Orange	68.8 (69.6)	4.8 (4.8)	5.1 (5.1)	0 (0)	5.3 (5.6)
$RuCl_2(bdoH)(PPh_3)_2$	Brown	58.6 (60.2)	4.6 (4.4)	1.8 (1.8)	8.2 (8.9)	
cis-$Ru(bdo)_2(PPh_3)_2\cdot 2thf$	Red	63.3 (63.4)	6 0 (6.0)	2.6 (2.9)	0 (0)	6.3 (6.4)
cis-$Ru(bdo)_2(PPh_3)_4$	Red	71 9 (71.4)	5 7 (5.6)	2.0 (2.1)	0 (0)	9.1 (9.1)
trans-$Ru(bdo)_2(PPh_3)_2$	Red	63.5 (63.8)	5.0 (5.3)	3.3 (3.4)	0 (0)	7.1 (7.5)
$Ru(bdo_2en)(PPh_3)_2$	Red	65.7 (65.0)	5.8 (5 4)	7 0 (6.6)	0 (0)	7.8 (7.3)
$RuCl_2(phayoxH_2)(PPh_3)_2$	Purple	64.3 (65.0)	4 7 (4.7)	1.5 (1.5)	5.7 (7.7)	6.3 (6.7)
$Ru(phayoxH)_2(PPh_3)_2$	Claret	69.4 (71.2)	5.0 (5.0)	2.5 (2.6)	0 (0)	6.2 (5.8)
$RuCl(saloxH)(saloxH_2)(PPh_3)$	Yellow-green	59.4 (59.9)	4.4 (4.5)	4.3 (4.4)	6.1 (5.5)	5.0 (4.8)
$Ru(saloxH)_2(PPh_3)_2\cdot saloxH_2$	Yellow	67.6 (66.2)	4.6 (4.6)	4.1 (4.1)	0 (0)	6.1 (6.0)
$[Ru(paoH)(pao)(PPh_3)_2]Cl$	Orange	63.6 (63 7)	4.7 (4.6)	6.0 (6.2)	3 9 (3.9)	6 2 (6.9)
$Ru(pao)_2(PPh_3)_2$	Orange	65.1 (66.3)	4.5 (4.8)	6.3 (6.4)	0 (0)	6.9 (7.1)
$RuCl_2(atoH)_2(PPh_3)_2$	Yellow	60.2 (59.9)	5.4 (5.2)	3.4 (3.3)		8.7 (7.4)
$RuCl_2(atoH)_2(PPh_3)_2\cdot 2CH_2Cl_2$	Yellow	51.6 (52.2)	4.7 (4 7)	2.6 (2.8)	20.3 (21.0)	5.4 (6.1)
$RuCl_2(cycloH)_2(PPh_3)_2$	Yellow	64.1 (63.9)	5.7 (5.8)	2.8 (3.1)	6.8 (7.9)	6.8 (6.9)
$RuCl_2(apoH)(PPh_3)_2$	Orange	64.1 (63.5)	4.7 (4.7)	1.7 (1.7)	8.2 (8.5)	7.2 (7.5)
$RuCl_2(n\text{-}butpoH)(PPh_3)_2$	Orange	65 6 (64.6)	5.2 (5.2)	1.6 (1.6)	8.2 (8.1)	6.7 (7.1)
$RuCl(ato)(PPh_3)_3$	Orange	68.6 (68.8)	5.2 (5.1)	1.4 (1.4)	3.9 (3.6)	9.1 (9.3)
$Ru(ato)_2(PPh_3)_2$	Orange	64.6 (65.5)	4.9 (5.5)	3.9 (3.6)	0 (0)	7.8 (8.1)
$RuClH(CO)(cycloH)(PPh_3)_2\cdot PPh_3$	Orange	69.5 (68.8)	5.5 (5 4)	1.5 (1.3)	2.3 (2.3)	8.9 (8.7)
$RuClH(CO)(apoH)(PPh_3)_2\cdot PPh_3$	Orange	68.7 (69.6)	5.0 (5.0)	1.4 (1.3)	3.1 (3 3)	8.4 (8.6)
$RuClH(CO)(n\text{-}butpoH)(PPh_3)_2\cdot PPh_3$	Yellow	69.3 (70.2)	5.2 (5.3)	1.2 (1.2)	3.0 (3.1)	8.6 (8.2)
$RuClH(CO)(apoH)(PPh_3)_2\cdot CH_2Cl_2$	Yellow	58.9 (60.7)	4.4 (4.6)	1.5 (1.5)	11.7 (11.7)	7.5 (6.8)
$RuCl_2(NH_2OH)_2(PPh_3)_2$	Yellow	58.1 (56.7)	4.9 (4.7)	3.7 (3.7)	9.6 (9.4)	8.2 (8.1)
$RuCl(\eta^2\text{-}NH_2O)(NH_2OH)(PPh_3)_2$	Orange	59.1 (59.9)	4.7 (4.8)	3.8 (3.9)	2.9 (4.9)	8.1 (8.5)

* Calculated values (%) are given in parentheses.

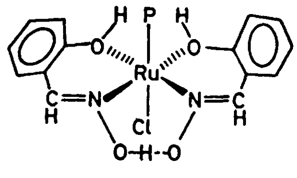
n.m.r. spectrum (singlet at 38.24 p.p.m.) does not conclusively determine the structure as this chemical shift is intermediate between those expected for *cis* and *trans* isomers, but the near equivalence of the methyls in the ^1H n.m.r. spectrum suggests that the phosphines are most likely *trans*, with the oxime bound through the N atoms as in (4).

(*D*) *Hydroxy-oximes*.—(1) *α-Acyloin oximes*. The reaction of α-benzoin oxime ($phayoxH_2$) with $RuCl_2(PPh_3)_3$ in methanol or benzene gave purple diamagnetic crystals of a compound $RuCl_2(phayoxH_2)(PPh_3)_2$, which was nonconducting in nitromethane and monomeric in dichloromethane. The PPh_3 groups were *trans* according to the ^{31}P n.m.r. spectrum (singlet at 25.44 p.p.m.). The i.r. spectrum suggests that the complex has a structure similar to that of the copper complex, $CuCl_2(phayoxH_2)$,[5] with *trans* phosphines, as in (1) but with X = OH. In the presence of NaOH, $RuCl_2(PPh_3)_3$ reacts with $phayoxH_2$ to give a claret-coloured solution and red crystals of stoicheiometry $Ru(phayoxH)_2(PPh_3)_2$.

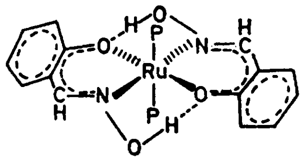
This compound is diamagnetic, monomeric in dichloromethane, and the phosphines are probably *cis* (^{31}P n.m.r., singlet at 44.11 p.p.m.), although the latter value is rather lower than expected for *cis* phosphines.[5]

The i.r. spectrum is consistent with the oxime ligands bound through the N atom and the hydroxyl group, with hydrogen bonding between oxime ligands.[6,7]

(2) *Salicylaldoxime*. Refluxing salicylaldoxime ($saloxH_2$) in methanol with $RuCl_2(PPh_3)_3$ gave a green solution from which precipitated a yellow-green solid of stoicheiometry $RuCl(saloxH)(saloxH_2)(PPh_3)$. This solid was diamagnetic, monomeric in dichloromethane, and non-conducting in nitromethane. The ^{31}P n.m.r. spectrum (singlets at 28.80 and 35.28 p.p.m.) suggested that the product was probably a mixture of isomers. Attempted separation by chromatography failed. The i.r. spectrum is consistent with the oximes bound through both the N atoms and hydroxyl groups, with hydrogen bonding between the oxime ligands as in (5).



(5)

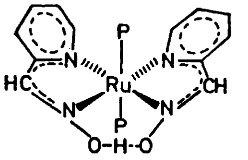


(6)

The reaction of $saloxH_2$ with $RuCl_2(PPh_3)_3$ in the presence of NaOH gave a yellow, virtually insoluble diamagnetic complex of stoicheiometry $Ru(saloxH)_2(PPh_3)_2\cdot(saloxH_2)$. The i.r. spectrum is consistent with a gross planar $M(saloxH)_2$ structure with stepped hydrogen bonds similar to the Ni and Cu complexes,[8–10] but having two additional phosphines giving octahedral co-ordination as in (6). A molecule of $saloxH_2$ appears to be trapped in the lattice.

(*E*) *Pyridine Oximes*.—The reaction of $RuCl_2(PPh_3)_3$ with 2-pyridinaldoxime (paoH) in methanol gave a red solution and an orange, diamagnetic crystalline product of stoicheiometry $[Ru(pao)(paoH)(PPh_3)_2]Cl$. The molecular weight was lower than expected in dichloromethane and the conductivity in nitromethane ($\Lambda_M = 80$) was typical of a 1 : 1 electrolyte. The absence of a ν(Ru–Cl) band in the i.r., and the singlet ^{31}P n.m.r. resonance (25.10 p.p.m.), suggests a planar M(paoH)(pao) arrangement as is well known [1,11] for Ni, Cu, and Pd, with *trans* phosphines as in (7).

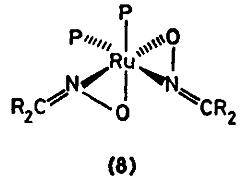
The reaction of $RuCl_2(PPh_3)_3$ with paoH and NaOH led to a virtually insoluble, orange diamagnetic complex $Ru(pao)_2(PPh_3)_2$, which is probably similar to the complexes $M(pao)_2 \cdot 2H_2O$ (M = Pt or Pd)[12,13] rather than the polymeric $Ni(pao)_2$.[14,15]



(7)

(*F*) *Simple Oximes*.—The reaction of $RuCl_2(PPh_3)_3$ with simple oximes (LH) in benzene gave yellow or orange diamagnetic complexes of stoicheiometry $RuCl_2(LH)_2(PPh_3)_2$ (acetoxime, cyclohexanone oxime) or $RuCl_2(LH)(PPh_3)_2$ (acetophenone oxime, n-butyl phenyl ketone oxime).

The compound $RuCl_2(atoH)_2(PPh_3)_2$ (ato = acetoxime) crystallises from ethanol or dichloromethane with two molecules of solvent but crystallisation from benzene gives a non-solvated product which has *trans* phosphines (^{31}P, singlet at 26.58 p.p.m.). The complexes with oximes having phenyl groups were five-co-ordinate; no reaction was observed with the more bulky t-butyl methyl ketone oxime. Hindered oximes give *ortho*-metalled palladium species;[16] however, metallation did not occur here. The oxime ligands in these complexes can be removed by reaction with pyridine to give $RuCl_2(py)_3(PPh_3)$. Reaction of oxime (LH) and NaOH with $RuCl_2(PPh_3)_3$ in t-butyl alcohol or benzene gave identical products $RuCl_2(LH)_n(PPh_3)_2$ ($n = 1$ or 2). Using a stoicheiometric amount of acetoxime and NaOH in methanol, orange diamagnetic crystals of stoicheiometry $RuCl(ato)(PPh_3)_3$ were obtained. This compound was non-conducting and monomeric in solution. The ^{31}P spectrum showed a triplet (75.55 p.p.m., J_{P-P} 24.8 Hz) and a doublet (41.65, 41.03 p.p.m., J_{P-P} 24.8 Hz) confirming the *mer* configuration of phosphines. Using an excess of acetoxime and NaOH in methanol, orange diamagnetic crystals of $Ru(ato)_2(PPh_3)_2$ were formed, which were non-conducting and monomeric in solution with *cis* phosphines (^{31}P, broadened singlet at 66.36 p.p.m.). The i.r. and ^1H n.m.r. spectra indicated that the oximes in these two complexes were bonded through both N and O as three-electron donors, as in (8).

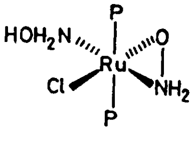


(8)

Reactions of $RuCl_2(PPh_3)_3$ with other oximes (LH), cyclohexanone oxime, acetophenone oxime, and n-butyl phenyl ketone oxime, in methanol led to the decarbonylation of methanol[17-19] and products of stoicheiometry $RuClH(CO)(LH)(PPh_3)_2 \cdot PPh_3$, which on recrystallisation from dichloromethane gave $RuClH(CO)(LH)(PPh_3)_2 \cdot CH_2Cl_2$. Reaction with the bulky t-butyl methyl ketone oxime led to the colourless products of decarbonylation, $RuClH(CO)(LH)(PPh_3)_2 \cdot Sol$ and $RuH_2(CO)(PPh_3)_3 \cdot Sol$ (Sol = MeOH or CH_2Cl_2), depending on the amount of NaOH present. The i.r. and n.m.r. spectra of the complexes $RuClH(CO)(LH)(PPh_3)_2 \cdot Sol$ show that the oxime is bound to the metal *via* the N atom only, and that one solvent molecule (or phosphine) is not bound to the metal but is weakly held in the lattice. The complex with n-butyl phenyl ketone oxime was most soluble, and was non-conducting in solution. The ^{31}P n.m.r. spectrum of these complexes had two resonances at *ca.* 55.7 and 35.0 p.p.m. due to uncoupled phosphines, whilst the complexes with free PPh_3 had a further resonance at *ca.* −6.0 p.p.m.

(*G*) *Hydroxylamine*.—The reaction of $RuCl_2(PPh_3)_3$ with hydroxylamine hydrochloride in the presence of two equivalents of NaOH gave an insoluble, diamagnetic, yellow complex of stoicheiometry $RuCl_2(NH_2OH)_2(PPh_3)_2$.

The i.r. spectrum suggests that the hydroxylamine ligands are bound *via* the nitrogen atoms as in other hydroxylamine complexes.[3] Reaction in the presence of an excess of NaOH, however, led to an insoluble, diamagnetic, orange product of stoicheiometry $RuCl(NH_2OH)(NH_2O)(PPh_3)_2$. The structure of this product probably has one hydroxylamine bound through its N atom and one η^2-hydroxylaminato-group bound through both its N and O atoms, as a three-electron donor, as in (9). Such an η^2-group was recently confirmed in a vanadium compound while this work was in progress.[20]



(9)

I.r. Spectra.—The chelating oxime complexes all had weak bands in the range 1 580—1 640 cm^{-1} due to $\nu(C=N)$, characteristic of oxime complexes co-ordinated through the N atom. The relative strength of the hydrogen bonds varies quite considerably. In the complex $RuCl_2(dmgH_2)(PPh_3)_2$ the sharp $\nu(O-H)$ bands at 3 440 and 3 380 cm^{-1} suggest little hydrogen bonding, but in the complex $Ru(dmgH)_2(PPh_3)_2$ the vicinal hydrogen bond is strong, and the absorption is obscured by $\nu(C-H)$ modes. The complexes $RuCl_2(phayoxH_2)(PPh_3)_2$, $Ru(phayoxH)_2(PPh_3)_2$, and $[Ru(pao)(paoH)(PPh_3)_2]Cl$ have broad bands at *ca.* 3 350—3 300 cm^{-1} which suggest weak hydrogen bonding. The complex $Ru(saloxH)_2(PPh_3)_2 \cdot saloxH_2$ has two sharp bands above 3 000 cm^{-1} at 3 650 and 3 255 cm^{-1}, assignable to non-hydrogen-bonded $\nu(O-H)$ and $\nu(NO-H)$ respectively. This suggests that two oximes are strongly bonded to the metal with strong hydrogen bonding between the two ligands as in (7), whilst the third oxime is weakly held in the lattice.

All the chlorine-containing complexes except [Ru(pao)(paoH)$(PPh_3)_2$]Cl have bands in the ν(Ru–Cl) region, 250—330 cm^{-1}.

There are two ν(N–O) bands[19,21,22] in the range 1 190—1 260 and 1 071—1 110 cm^{-1} for strongly hydrogen-bonded species such as $Ru(dmgH)_2(PPh_3)_2$, whilst in weakly hydrogen-bonded species with neutral oxime ligands the ν(N–O) absorption occurs at *ca.* 1 150 and 1 020 cm^{-1}. These absorptions were observed for all the complexes, but unequivocal assignment was often difficult due to the presence of triphenylphosphine bands. The complexes with simple oximes had similar bands for ν(N–O) and ν(Ru–Cl). The bands due to ν(C=N) were weak and occurred at *ca.* 1 625 (aliphatic oximes) and *ca.* 1 670 cm^{-1} (aromatic oximes). This band moved to *ca.* 1 615 cm^{-1} on removal of the proton in $Ru(ato)_2(PPh_3)_2$. The bands due to ν(O–H) were sharp, indicating little hydrogen bonding. The complexes RuClH(CO)(LH)$(PPh_3)_2$ contained two bands at *ca.* 1 930 and *ca.* 1 895 cm^{-1}, which were due to ν(CO) and ν(Ru–H) respectively.

^{1}H *N.M.R. Spectra.*—The spectra of these compounds were often poor due to solubility problems. However, all the spectra observed had resonances due to triphenylphosphine at *ca.* 7.2 p.p.m. The alkyl substituents of the oxime ligands were observed in all cases; however, the hydroxyl resonances were often obscured by phenyl resonances due to the upfield shift on co-ordination. The complexes RuClH(CO)(LH)$(PPh_3)_2$·PPh_3 were not soluble enough in benzene or acetone for the hydride resonance to be observed, but in deuteriochloroform resonances at 5.28 p.p.m. were clearly due to the formation of $CDHCl_2$ by reaction.

EXPERIMENTAL

Microanalyses were by Butterworth Microanalytical Consultancy Ltd., and by Imperial College Laboratories. Spectrometers: Perkin-Elmer R12 (^{1}H); Varian XL-100 (^{31}P, Fourier-transform); Perkin-Elmer PE457, 257 (i.r.). Molecular weights were determined oxmometrically using a Perkin-Elmer–Hitachi osmometer in CH_2Cl_2. All i.r. spectra reported below were taken in Nujol mulls and n.m.r. spectra in $CDCl_3$.

All preparations were carried out under oxygen-free argon or nitrogen. All solvents were dried, distilled, and degassed before use. The compounds decompose between 170—200 °C without melting.

(1) *Dichloro(dimethylglyoxime)bis(triphenylphosphine)ruthenium*(II).—$RuCl_2(PPh_3)_3$ (0.1 g, 1.04 mmol) was added to a suspension of dimethylglyoxime (0.2 g, 1.73 mmol) in methanol (30 ml) and the suspension refluxed (2 h). The resulting red *precipitate* was washed with methanol, thf, and ether, and dried *in vacuo*; yield 70% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 3 440s, 3 393(sh), (O–H); 1 610w, 1 552w, 1 514w, (C=N); 1 152w, 1 027s (N–O); and 232s cm^{-1} (Ru–Cl).

(2) *Dichloro(cyclohexane-*1,2-*dione dioxime)bis(triphenylphosphine)ruthenium*(II).—As in (1) but using nioxime gave the *complex* as a red microcrystalline solid, yield 70% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 3 435s, 3 377s (O–H); 1 582w, 1 569w, 1 534w (C=N); 1 153w, 1 005s (N–O); and 323s cm^{-1} (Ru–Cl).

(3) *(Benzil-α-dioxime)dichlorobis(triphenylphosphine)ruthenium*(II).—As in (1) but using benzil-α-dioxime gave the *complex* as an orange microcrystalline solid, yield 81% based on $RuCl_2(PPh_3)_3$; *M* 911 (936); $\nu_{max.}$ 3 635s, 3 502(sh) (O–H); 1 616w, 1 580w, 1 557m, 1 539w (C=N); 1 153w, 1 020s (N–O); and 312 cm^{-1} (Ru–Cl). δ_H 6.1 (m, 2H, CH); 7.3 (m, 15 H, PPh_3); 7.55 (m, 3 H, CH); and 10.6 (br s, 1 H, OH).

(4) *Bis(dimethylgloximato)bis(triphenylphosphine)ruthenium*(II).—To a solution of $dmgH_2$ (0.24 g, 2.08 mmol) and NaOH (0.08 g, 2.08 mmol) in methanol (30 ml) was added $RuCl_2(PPh_3)_3$ (1.0 g, 1.04 mmol) and the mixture refluxed (10 h). The solid was collected, washed with water and methanol, and recrystallised from hot thf (300 ml) to give orange *microcrystals*, yield 80% based on $RuCl_2(PPh_3)_3$. The same complex was also obtained using commercial Na_2dmg, by reaction of $RuCl_2(dmgH_2)(PPh_3)_2$ with a solution containing $dmgH_2$ and NaOH in methanol, and finally by direct reaction of $dmgH_2$ with $RuH_2(PPh_3)_4$ in benzene; $\nu_{max.}$ 1 640w, 1 581w, 1 570w, 1510w (C=N); 1 224s, 1 081m cm^{-1} (N–O).

(5) *Bis(cyclohexane-*1,2-*dione dioximato)bis(triphenylphosphine)ruthenium*(II).—As in (4) but using nioxime gave the *complex* as an orange powder, which was, however, not soluble enough to allow crystallisation; yield 80% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 1 620w, 1 518w, 1 569w (C=N); 1 218s, 1 080m cm^{-1} (N–O).

(6) *Bis(benzil-α-dioximato)bis(triphenylphosphine)ruthenium*(II).—As in (4) but using benzil-α-dioxime gave the *complex* as an orange powder, yield 54% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 1 620w, 1 595w, 1 585w, 1 570w (C=N); 1 262s, 1 083m cm^{-1} (N–O).

(7) *(Butane-*2,3-*dione mono-oxime)dichlorobis(triphenylphosphine)ruthenium*(II).—$RuCl_2(PPh_3)_3$ (1.0 g, 1.04 mmol) was added to a solution of butane-2,3-dione mono-oxime (bdoH) (0.4 g, 4.1 mmol) in methanol (30 ml) and the mixture refluxed (16 h). After cooling the brown crystalline complex was collected, washed with methanol and ether, and dried *in vacuo*, yield 60% based on $RuCl_2(PPh_3)_3$; *M* 739 (Calculated, 769); $\nu_{max.}$ 1 625w, 1 582w, 1 569w, 1 508w (C=N) 1 080—1 065(br) (N–O), 259s (Ru–Cl). δ_H 0.90 (s, 3 H, Me); 1.77 (s, 3 H, Me); 7.30—7.80 (m, 30 H, PPh_3); and 12.39 (s, 1 H, OH).

(8) cis-*[Bis(butane-*2,3-*dione mono-oximato)]bis(triphenylphosphine)ruthenium*(II).—To a solution of butane-2,3-dione mono-oxime (0.21 g, 2.08 mmol) and NaOH (0.08 g, 2.08 mmol) in methanol (30 ml) was added $RuCl_2(PPh_3)_3$ (1.0 g, 1.04 mmol) and the mixture refluxed (7 h). A pale red precipitate was collected. Evaporation of the deep red filtrate to low volume yielded the red microcrystalline *complex* $Ru(bdo)_2(PPh_3)_4$, yield 15% based on $RuCl_2(PPh_3)_3$. The pale red precipitate was recrystallised from thf to yield red crystals of $Ru(bdo)_2(PPh_3)_2(thf)_2$, yield 50% based on $RuCl_2(PPh_3)_3$. The same complex was formed by recrystallisation of $Ru(bdo)_2(PPh_3)_4$ from thf. The i.r. spectra of these two complexes were virtually identical; $\nu_{max.}$ 1 580w, 1 569w, 1 518w (C=N); 1 263s cm^{-1} (N–O); δ_H 1.27 (s, 3 H, Me); 1.93 (s, 3 H, Me); and 7.09 (br s, 15 H, PPh_3): the ^{1}H n.m.r. spectrum of $Ru(bdo)_2(PPh_3)_4$ had two further resonance at δ 7.21(s) and 7.36(s), which are due to free triphenylphosphine.

(9) trans-*[Bis(butane-*2,3-*dione mono-oximato)]bis(triphenylphosphine)ruthenium*(II).—To a solution of butane-

2,3-dione mono-oxime (bdoH) (0.06 g, 0.6 mmol) and NaOH (0.002 5 g, 0.6 mmol) in methanol (30 ml) was added $RuCl_2(bdoH)(PPh_3)_2$ (0.3 g, 0.4 mmol) and the mixture refluxed until a little $RuCl_2(bdoH)(PPh_3)_2$ dissolved. The red solution was concentrated and cooled to give red *crystals* of *trans*-$Ru(bdo)_2(PPh_3)_2$; $\nu_{max.}$ 1 580w, 1 569w, 1 502w (C=N); 1 263s cm^{-1} (N–O); δ_H 0.84 (s, 3 H, Me); 1.27 (s, 3 H, Me); and 7.25 (br s, 15 H, PPh_3).

(10) *[N,N'-Ethylenebis(butane-2,3-dione-2-oxime-3-iminato)]bis(triphenylphosphine)ruthenium*(II).—To a solution of bdo_2enH_2 (0.32 g, 1.04 mmol) and NaOH (0.08 g, 2.1 mmol) in methanol (30 ml) was added $RuCl_2(PPh_3)_3$ (1.0 g, 1.04 mmol) and the mixture refluxed until all the $RuCl_2(PPh_3)_3$ had reacted (*ca.* 1 h). The dark red solution was cooled, filtered to remove NaCl, and then evaporated, to low volume to yield red crystals of the *complex*, which were recrystallised from hot thf; yield 40% based on $RuCl_2(PPh_3)_3$; *M* 793 (Calculated, 849); $\nu_{max.}$ 1 635w, 1 583w, 1 569w (C=N); 1 260s, 1 130s cm^{-1} (N–O); δ_H 1.08 (s, 3 H, Me); 1.17 (s, 3 H, Me); 3.70 (s, 2 H, CH_2); and 7.24 (br s, 15 H, PPh_3).

(11) *(Benzoin-α-oxime)dichlorobis(triphenylphosphine)ruthenium*(II).—To a solution of benzoin-α-oxime (0.3 g, 1.32 mmol) in benzene (30 ml) was added $RuCl_2(PPh_3)_3$ (0.5 g, 0.52 mmol) and the mixture refluxed (16 h). The purple solution was filtered and concentrated to give purple crystals of the *complex*, which were recrystallised from dichloromethane–ethanol, yield 66% based on $RuCl_2(PPh_3)_3$; *M*, 948 (Calculated 923); $\nu_{max.}$ 3 350(br) (O–H), 1 610w, 1 570 (C=N); 1 178m, 1 090s (N–O); 296w, 276w cm^{-1} (Ru–Cl); δ_H 6.33 (m, 2 H, CH); 6.41 (m, 1 H, CH); 7.08 (s, 15 H, PPh_3); 7.49 (m, 3 H, CH); and 7.95 (m, 2 H, OH).

(12) *Bis(benzoin-α-oximato)bis(triphenylphosphine)ruthenium*(II).—As in (11) but in the presence of NaOH (0.4 g, 1.04 mmol) and in methanol (30 ml) gave a claret-coloured solution and claret-coloured *crystals*; yield 58% based on $RuCl_2(PPh_3)_3$; *M*, 1 023 (Calculated 1 077); $\nu_{max.}$ 3 350 (O–H), 1 640w, 1 535w (C=N); 1 260m, 1 085s cm^{-1} (N–O): δ_H 6.66 (m, 2 H, CH); 7.16 (s, 15 H, PPh_3); and 7.54 (m, 3 H, CH).

(13) *Chloro(salicylaldoximato)salicylaldoxime(triphenylphosphine)ruthenium*(II).—$RuCl_2(PPh_3)_3$ (0.5 g, 0.52 mmol) was added to a solution of salicylaldoxime (0.3 g, 2.19 mmol) in methanol (30 ml), and the mixture refluxed (16 h). The green solution was filtered, and then concentrated to give a yellow-green powder, which was recrystallised from benzene to give a darker green powder; yield 51% based on $RuCl_2(PPh_3)_3$; *M*, 668 (Calculated 672); $\nu_{max.}$ 3 300(br), 3 150(br) (O–H); 1 598s, 1 530w (C=N); 1 270m, 1 090s (N–O); and 298 cm^{-1} (Ru–Cl); δ_H 3.37 (s, 1 H, CH); 7.26 (s, 15 H, PPh_3); 7.58 (m, 2 H, CH); and 7.72 (m, 2 H, CH).

(14) *Bis(salicylaldoximato)bis(triphenylphosphine)ruthenium*(II)*–Salicylaldoxime* (1 : 1).—As in (13) but in the presence of NaOH (0.04 g, 1.04 mmol) precipitated a pale yellow solid, which was collected, washed with methanol (30 ml) and ether (30 ml), and dried *in vacuo*; yield 44% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 3 650(sh), 3 255(sh) (O–H); 1 615s, 1 600s, 1 528m (C=N); 1 255w, 1 092s cm^{-1} (N–O).

(15) *Pyridine-2-aldoximato(pyridine-2-aldoxime)bis(triphenylphosphine)ruthenium*(II) *Chloride*.—$RuCl_2(PPh_3)_3$ (0.5 g, 0.52 mmol) was added to a solution of pyridine-2-aldoxime (0.2 g, 1.64 mmol) in methanol (30 ml) and the mixture refluxed to give orange crystals of the *complex*, which was recrystallised from dichloromethane–ethanol; yield 75% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 3 350(br) (O–H); 1 600s, 1 570m (C=N); 1 230m, 1 088s cm^{-1} (N–O); δ_H 6.82 (m, 2 H, CH); 7.20 (s, 30 H, PPh_3); 7.60 (m, 8 H, CH); and 9.60 (s, 1 H, OH).

(16) *Bis(pyridine-2-aldoximato)bis(triphenylphosphine)ruthenium*(II).—As in (15) but in the presence of NaOH (0.04 g, 1.04 mmol) precipitated orange crystals of the *complex*, which were collected, washed with ether, and dried *in vacuo*; yield 62% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 3 530(br) (O–H); 1 600s, 1 570m (C=N); 1 230m, 1 088s cm^{-1} (N–O).

(17) *Bis(acetoxime)dichlorobis(triphenylphosphine)ruthenium*(II).—$RuCl_2(PPh_3)_3$ (0.5 g, 0.52 mmol) was added to a solution of acetoxime (0.08 g, 1.04 mmol) in benzene (30 cm^3) and the mixture refluxed (16 h) to precipitate a yellow powder, which was collected, and washed with methanol and ether. Recrystallisation from dichloromethane or thf produced a bis-solvate, but recrystallisation from hot benzene gave the non-solvated form; yield 65% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 3 220(sh) (O–H); 1 628 (C=N); 1 182s, 1 085s (N–O); 330, 302 cm^{-1} (Ru–Cl).

(18) *Dichlorobis(cyclohexanone oxime)bis(triphenylphosphine)ruthenium*(II).—As in (17) but using cyclohexanone oxime (0.12 g, 1.04 mmol); recrystallisation from CH_2Cl_2 or thf gave the non-solvated form; yield 65% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 3 220(sh) (O–H); 1 623 (C=N); 1 185s, 1 185s (N–O); 330w, 300w cm^{-1} (Ru–Cl).

(19) *(Acetophenone oxime)dichlorobis(triphenylphosphine)ruthenium*(II).—As in (17) but using acetophenone oxime (0.14 g, 1.04 mmol) gave the non-solvated form, yield 80% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 3 325(sh) (O–H); 1 670w, 1 570w (C=N); 1 182s, 1 085s (N–O); 302 cm^{-1} (Ru–Cl).

(20) *Dichloro(n-butyl phenyl ketone oxime)bis(triphenylphosphine)ruthenium*(II).—As in (17) but using n-butyl phenyl ketone oxime (1.85 g, 1.04 mmol) gave the non-solvated form, yield 54% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 3 320(sh) (O–H); 1 670w, 1 570w (C=N); 1 182s, 1 088s (N–O); 302 cm^{-1} (Ru–Cl).

(21) *Acetoximato(chloro)tris(triphenylphosphine)ruthenium*(II).—$RuCl_2(PPh_3)_3$ (0.5 g, 0.52 mmol) was added to a solution of acetoxime (0.04 g, 0.52 mmol) and NaOH (0.02 g, 0.52 mmol) in methanol (30 ml), and the mixture was refluxed (16 h). The orange precipitate was collected, washed with methanol and ether, then recrystallised from dichloromethane–ethanol to give orange *crystals*, yield 60% based on $RuCl_2(PPh_3)_3$, *M* 945 (Calculated 944); $\nu_{max.}$ 1 615 (C=N); 1 270m, 1 080s (N–O); 305 cm^{-1} (Ru–Cl); δ_H 1.42 (s, 3 H, Me); 1.72 (s, 3 H, Me); and 7.14 (br s, 45 H, PPh_3).

(22) *Bis(acetoximato)bis(triphenylphosphine)ruthenium*(II).—As in (21) but using acetoxime (0.08 g, 1.04 mmol) and NaOH (0.04 g, 1.04 mmol) gave orange *crystals*, yield 65% based on $RuCl_2(PPh_3)_3$; *M* 817 (Calculated 769); $\nu_{max.}$ 1 620w (C=N); 1 265m, 1 080s cm^{-1} (N–O). δ_H 1.13 (s, 3 H, Me); 1.72 (s, 3 H, Me); and 7.17 (br s, 15 H, PPh_3).

(23) *Carbonylchloro(cyclohexanone oxime)hydridobis(triphenylphosphine)ruthenium*(II).—As in (21) but using cyclohexanone oxime (0.12 g, 1.04 mmol) gave an orange powder, which was collected, washed with methanol and ether, and dried *in vacuo*. This powder has one phosphine of crystallisation, yield 76% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 3 350w (O–H); 1 932s (C=O); 1 895s (Ru–H), 1 665w, 1 615w (C=N); 1 185s, 1 075s (N–O); 320w cm^{-1} (Ru–Cl); δ_H 1.50 (br, 10 H, CH_2); 5.28 (s, 1 H, $CDHCl_2$); 7.16 (br s, 30 H, PPh_3); and 7.70 (br, 1 H, OH).

(24) *(Acetophenone oxime)(carbonyl)chlorohydridobis(triphenylphosphine)ruthenium*(II).—As in (21) but using aceto-

phenone oxime (0.14 g, 1.04 mmol) gave an orange powder, which was collected, washed with methanol and ether, and then dried *in vacuo*. The unrecrystallised product contains one phosphine of crystallisation, yield 80% based on $RuCl_2(PPh_3)_3$. Recrystallisation from dichloromethane gave the dichloromethane solvate, yield 70% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 3 312(sh) (O–H); 1 922s (C≡O); 1 895w (Ru–H); 1 670w, 1 570w (C=N); 1 185s, 1 075s (N–O); 313w cm^{-1} (Ru–Cl); δ_H 1.16 (s, 3 H, Me); 5.28 (s, 1 H, $CDHCl_2$); 7.28 (br s, 30 H, PPh_3); 7.65 (m, 5 H, CH); and 9.60 (br, 1 H, OH).

(25) *Carbonylchloro(hydrido)(n-butyl phenyl ketone oxime)bis(triphenylphosphine)ruthenium*(II).—As in (21) but using n-butyl phenyl ketone oxime (1.85 g, 1.04 mmol) gave a yellow powder of the triphenylphosphine solvate, which was washed with methanol and ether, then dried *in vacuo*; yield 80% based on $RuCl_2(PPh_3)_3$. Recrystallisation from dichloromethane–ethanol gave the dichloromethane solvate as yellow crystals, yield 65% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 3 315(sh) (O–H); 1 936s (C≡O); 1 899w (Ru–H); 1 670w, 1 570w (C=N); 1 184s, 1 089s, (N–O); 320w cm^{-1} (Ru–Cl); δ_H 0.73 (m), 0.99 (m, 3 H, Me); 1.22 (m, 2 H, CH_2); 1.52 (m, 4 H, CH_2); 5.28 (s, 1 H, $CDHCl_2$); 7.28 (s, 30 H, PPh_3); 7.40 (m, 5 H, CH); and 8.52 (br, 1 H, OH).

(26) *Dichlorobis(hydroxylamine)bis(triphenylphosphine)ruthenium*(II).—$RuCl_2(PPh_3)_3$ (0.5 g, 0.52 mmol) was added to a solution of hydroxylamine hydrochloride (0.07 g, 1.04 mmol) and NaOH (0.04 g, 1.04 mmol) in methanol. This was refluxed (16h), and the yellow precipitate was washed with methanol and ether, and dried *in vacuo*; yield 85% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 3 250(br) (O–H,N–H); 1 280s 1 210s (N–O); 720m cm^{-1} (Ru–Cl).

(27) *Chloro(η^2-hydroxylaminato)(hydroxylamine)bis(triphenylphosphine)ruthenium*(II).—As in (26) but using NaOH (0.08 g, 2.08 mmol) gave an orange powder, yield 75% based on $RuCl_2(PPh_3)_3$; $\nu_{max.}$ 3 250(br) (O–H,N–H); 1 280s, 1 210s (N–O); 305w cm^{-1} (Ru–Cl).

We thank the S.R.C. for Studentships (to A. R. M. and J. R. T.), Johnson, Matthey Ltd. for the loan of ruthenium, and Albright and Wilson Ltd. for gifts of triphenylphosphine.

[9/114 *Received, 24th January, 1979*]

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