Reactions of μ_3-Oxo-triruthenium Carboxylates with π-Acid Ligands †

By **Alwyn Spencer** and **Geoffrey Wilkinson,*** Inorganic Chemistry Laboratories, Imperial College, London SW7 2AY

The interactions of the oxo-centred ruthenium(III) acetate, $[Ru_3O(CO_2Me)_6(MeOH)_3]CO_2Me$ or species formed from it by reduction, with carbon monoxide, methyl isocyanide, sulphur dioxide, and nitric oxide have been studied. Only a monocarbonyl, *e.g.*, $Ru_3O(CO_2Me)_6(CO)(py)_2$ is formed and the six bridged carboxylate groups of the original oxo-centred species rearrange to give two bridged and four bidentate carboxylate groups. The complexes have been studied, where feasible, by i.r. and n.m.r. spectroscopy and their electrochemical behaviour investigated. The mean oxidation state for ruthenium of $2\frac{1}{3}$ (or II, II, III) in a trinuclear complex has been characterised. The complexes $Ru(CO)(CO_2Me)_2(PPh_3)_2$ and $Ru(MeNC)_2(CO_2Me)_2(PPh_3)_2$ are described; the former has one bidentate and one monodentate acetate and appears to be a non-rigid molecule. Bis- and tris-isocyanide complexes were obtained, with acetate and propionate respectively, and mononitrosyl and sulphur dioxide complexes were prepared.

AMONG the trinuclear oxo-centred carboxylates $[M_3O(CO_2R)_6L_3]^+$ (M^{III} = Cr, Mn, Fe, Co, Ru, Rh, or Ir, L = H_2O, MeOH, py, *etc.*) the ruthenium complexes are unique in undergoing reduction first by an electrochemically reversible one-electron step, and secondly by a two-electron reduction that involves loss of the central oxygen atom and which is reversed by oxygen.[1,2]

Reactions of the ruthenium complexes were made using the acetate, except where higher solubility in organic solvents was required, when the propionate or n-butyrate was used.

Interaction with Carbon Monoxide.—The reactions described here are summarised in the Scheme. The complex[1] $[Ru_3O(CO_2Me)_6(MeOH)_3]^+$ in methanol reacts only slowly with carbon monoxide (2 atm), but with the reduced forms, $Ru_3O(CO_2Me)_6(MeOH)_3$ and $Ru_3(CO_2Me)_6(MeOH)_3$, a purple complex $Ru_3O(CO_2Me)_6(CO)(MeOH)_2$ (*A*) is formed within a few minutes. Action of pyridine on the latter gives the blue $Ru_3O(CO_2Me)_6(CO)(py)_2$ (*B*). This species may also be obtained by action of CO on a refluxing methanol solution of $[Ru_3O(CO_2Me)_6(py)_3]^+$. Molecular weight determinations confirm the retention of the trinuclear structure. The n.m.r. spectrum of *A* in D_2O has methyl resonances at τ 7·68, 7·49, and 6·07, relative intensities 1 : 2 : 1. The τ 6·07 peak is due to MeOH; the complex *B* in $PhNO_2$ also has two similar methyl resonances (Table 1) showing two types of acetate group. In the i.r., both *A* and *B* have a single carbonyl (CO) stretch and carboxylate stretches (Table 1). The latter[3] also confirm the presence of two types of acetate, both bridges (*ca.* 1570 cm^{-1}) and bidentate (*ca.* 1600 cm^{-1}). However, since at present we are unable to correlate the acetate n.m.r. resonances with the type of carboxylate bonding, we cannot say whether these are four bridge and two bidentate groups or *vice versa*. However, from the reaction of *A* with triphenylphosphine (see later) we prefer the structure (I). This formulation (or indeed an alternative) requires the ruthenium atoms to have mean oxidation state $2\frac{2}{3}$ (or II, III, III) as observed previously[1] in Ru_3O-

---

† No reprints available.

[1] A. Spencer and G. Wilkinson, *J.C.S. Dalton*, 1972, 1570.

[2] S. Uemura, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 2565.

[3] *Cf.* 'Spectroscopic Properties of Inorganic and Organometallic Compounds,' Specialist Reports, Chemical Society, vols. 3—5.

SCHEME Interactions of oxoruthenium carboxylates with carbon monoxide. Complexes in parentheses were not isolated

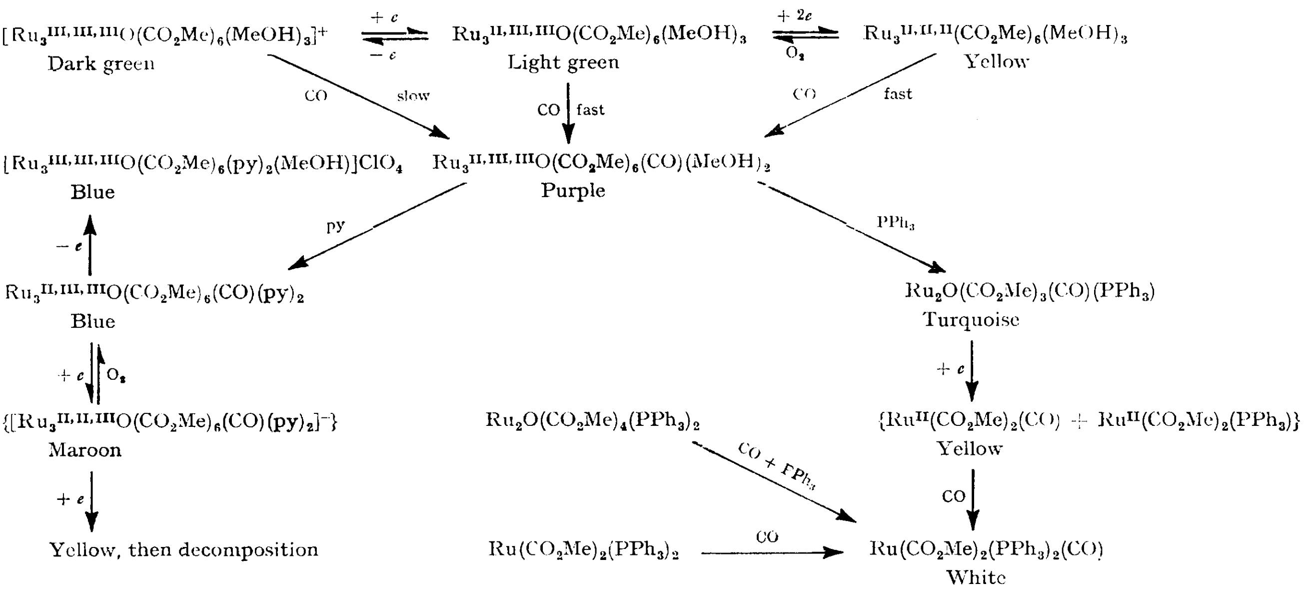


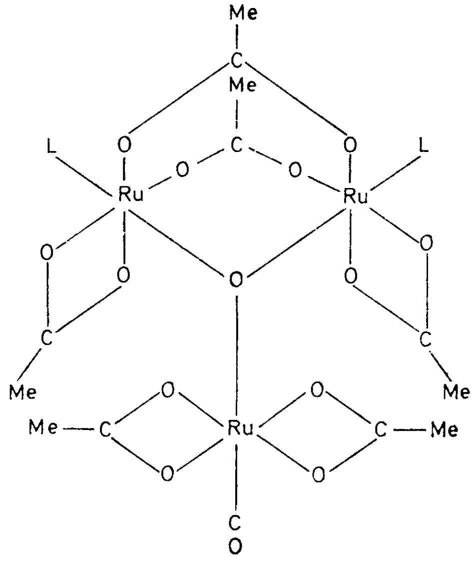
TABLE 1

Spectroscopic and magnetic data for ruthenium complexes

	Complex	N.m.r. [a]	I.r./cm^{-1} [d]		μ_{eff}/B.M.
A	$Ru_3O(CO_2Me)_6(CO)(MeOH)_2$	6·07 (1) [b] 7·49 (2) 7·68 (1)	1960s 1608s 1570m	ν CO ν CO_2	1·91
B	$Ru_3O(CO_2Me)_6(CO)(py)_2$	7·84 (2) [c] 8·24 (1)	1930s 1959s 1565m	ν CO ν CO_2	1·77
C	$Ru_2O(CO_2Me)_3(CO)PPh_3)$	1·56, 1·78br (5) 7·19 (2) 7·61 (1)	1945s 1592s 1545m	ν CO ν CO_2	1·75
D	$Ru_2O(CO_2Pr)_3(CO)(PPh_3)$	1·67, 1·96br (7·5) 7·03 (m) (2) 7·5 (t) (1) 8·37 (m) (3) 8·99 (t) (4·5)	1945 1592 1545	ν CO ν CO_2	
E	$Ru(CO_2Me)_2(CO)(PPh_3)_2$	1·50, 1·82br (5) 8·58br (1)	1938s 1610br	ν CO ν CO_2	
F	$Ru(CO_2Me)_2(MeNC)_2(PPh_3)_2$	1·50, 1·82br (5) 6·23 (MeNC) (1) 7·97 (1)	2135 1605	ν NC ν CO_2	
G	$Ru_3O(CO_2Me)_6(MeNC)_2(H_2O)$	4·86 (1) (MeNC) [b] 7·44 (3)	2160 1530	ν NC ν CO_2	
H	$Ru_3O(CO_2Me)_6(MeNC)_2(MeOH)$		2160 1525	ν NC ν CO_2	1·67
I	$Ru_3O(CO_2Et)_6(MeNC)_3$	4·44 (1) 6·98 (q) (1·3) 8·63 (t) (2)	2140 1520	ν NC ν CO_2	1·28
J	$Ru_3O(CO_2Me)_6(MeNC)_2(py)$		2120 1540	ν NC ν CO_2	1·38
K	$Ru_3O(CO_2Me)_6(MeOH)_2(MeO)(SO_2)$	6·37 (1) [b] 8·72 (2)	1555	ν CO_2	2·44
L	$[Ru_3O(CO_2Me)_6(py)_3(SO_2)]CO_2Me$		1545	ν CO_2	2·84
M	$Ru_3O(CO_2Me)_6(NO)(PPh_3)_2$		1550	ν CO_2	
N	$Ru_3O(CO_2Me)_6[P(OMe)_3]_3$	5·0 br (1·5) 7·33 br (1)	1540	ν CO_2	2·09

[a] τ Values relative to benzene external reference (τ 2·80), in $CDCl_3$ unless otherwise specified. [b] In D_2O. [c] In $PhNO_2$. [d] The CO_2 asymmetric stretches only are given; the symmetric ones lie *ca.* 1450 cm^{-1}.

$(CO_3Me)_6(PPh_3)_3$ and $Ru_3O(CO_2Me)_6L_3$ (L = MeOH, py). By contrast with the complex $Ru_3^{II,III,III}O(CO_2Me)_6(H_2O)_3$ which is diamagnetic,[1] *A* and *B* are paramagnetic, μ_{eff} = 1·91 and 1·77 B.M. (297 K) respectively; this is discussed later. Electrochemical data (Table 2) is consistent with this, the polarograms of *A* and *B* in acetone with tetraethylammonium perchlorate (used throughout) as supporting electrolyte showing reduction waves in the region beyond −1·0 V (*vs.* S.C.E.) for $Ru_3^{II,III,III} \longrightarrow Ru_3^{II,II,II}$ but no waves in the region 0 to —0·3 V found for $Ru_3^{III,III,III} \longrightarrow Ru_3^{II,III,III}$. *A* shows two cathodic waves at —1·08 and *ca.* —1·60 V of equal height, the latter being partly obscured by a third much larger wave doubtless due to catalytic reduction of H^+ from co-ordinated methanol.[1] This wave does not occur for *B* and controlled potential coulometric reduction of *B* at —1·2 V using a mercury pool working electrode gave an *n* value of 0·95 and produced a maroon solution. This solution on exposure to air instantly reverted to the blue colour of *B*.



(I; L = MeOH or py)

TABLE 2

Electrochemical data [a]

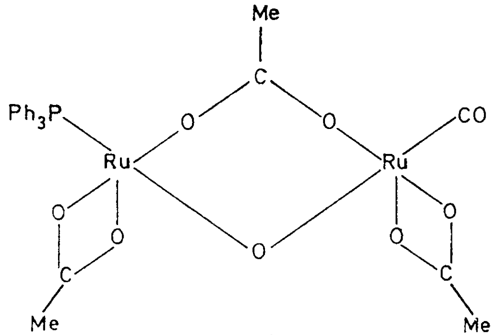
	Complex	Half-wave potential (V) (*n* Value)	
		Anodic [b]	Cathodic
A	$Ru_3O(CO_2Me)_6(CO)(MeOH)_2$	+0·62	−1·08; −1·60
B	$Ru_3O(CO_2Me)_6(CO)(py)_2$	+0·60	−1·08 (0·95); −1·69
C	$Ru_2O(CO_2Me)_3(CO)(PPh_3)$	+0·53	−0·76 (0·98)
D	$Ru_2O(CO_2Pr^n)_3(CO)(PPh_3)$	+0·51	−0·80 (0·995)
K	$Ru_3O(CO_2Me)_6(MeOH)_2(MeO)(SO_2)$ [c]		−0·14 (0·86)
L	$[Ru_3O(CO_2Me)_6(py)_3(SO_2)]CO_2Me$		−0·17 (1·08)

[a] In acetone, 0·1M in Et_4NClO_4. All potentials *vs.* external aqueous S.C.E., and obtained at D.M.E. unless otherwise stated. [b] At rotating platinum electrode. [c] In methanol.

The similarity in electrochemical behaviour of *A* and *B* indicates that for both the reduction occurs in two one-electron steps, (II, III, III) ⟶ (II, II, III) ⟶ (II, II, II). The intermediate (II, II, III) state was not observed previously.[1] Cyclic voltammograms (hanging mercury drop electrode) of the first waves for *A* and *B* show that both reduction and oxidation occur at the electrode but the ΔEp values indicate that even at low scan rates (40 mV s^{-1}) the reductions are not thermodynamically reversible. The $E_{\frac{3}{4}}$—$E_{\frac{1}{4}}$ separations in the polarograms are *ca.* 63 mV, slightly greater than the theoretical value for a thermodynamically reversible process (59 mV for $n = 1$ at 25°).

The reduced maroon solution from *B* has an oxidation wave at —0·99 V. The first reduction step is hence assigned as a simple slow one-electron transfer. Reduction of *B* at —2·0 V gives a golden-yellow solution and a very irregular current–time curve. As electrolysis continues this solution darkens and a dark precipitate forms. The cyclic voltammograms of the second waves of *A* and *B* show no well defined anodic portions although the cathodic half-cycles are normal. The polarographic waves are also markedly irreversible. We conclude that the reduction to the (II, II, II) state involves loss of the central oxygen atom, as observed previously[1] and that dissociation of the trimer to mononuclear species occurs as in the reduction of $Ru_3O(CO_2Me)_6(PPh_3)_3$.[4] The intermediate (II, II, III) complexes must be anionic, *i.e.*, $[Ru_3O(CO_2Me)_6(CO)L_2]^-$, L = MeOH, py; although a maroon solid, evidently the tetra-alkylammonium salt separates during electrolysis, attempts to collect the samples for analysis were unsuccessful.

The interaction of *A* in methanol at 25° with triphenylphosphine gives $Ru_2O(CO_2Me)_3(CO)(PPh_3)$, *C*, as a turquoise precipitate, and not the expected trinuclear substitution product. The complex can be easily prepared directly by action of CO on a refluxing methanol solution of $Ru_3O(CO_2Me)_6(PPh_3)_3$.[1] In the preparation from *A* the residual solution is blue and contains another species which we have not been able to isolate. Since the acetate had low solubility in acetone for electrochemical study, the butyrate *D* was also prepared. Analytical and spectroscopic data are consistent with the structure (II).



(II)

The n.m.r. spectrum of *C* (Table 1) shows two broad resonances for PPh_3 as in $Ru_3O(CO_2Me)_6(PPh_3)_3$[1] and two acetate resonances (2 : 1). The spectrum of *D* is similar except that the two types of butyrate lead to a more complex spectrum which can be assigned as follows: four proton multiplet, α-CH_2 groups of two inequivalent bidentate carboxylates; two proton triplet, α-CH_2 group of bridge carboxylate; six proton multiplet, three β-CH_2 groups; nine proton triplet, three CH_3 groups. The inequivalence of the ligands

[4] R. W. Mitchell, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 846.

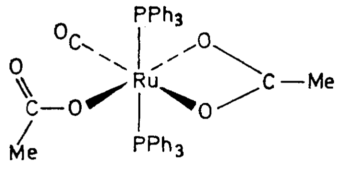
apparent in the α-CH_2 group decreases along the alkyl chain and is not observed in the γ position. The i.r. spectra of *C* and *D* have both bridge and chelate carboxylate bands as in *A* and *B*.

The structure (II) implies that (i), the inequivalence of the two bidentate carboxylates due to the asymmetry resulting from the presence of CO and PPh_3 groups does not appear in the n.m.r. of the acetate, which has only two bands; (ii), the resonances of the two bidentate acetate and the α-protons of the two bidentate n-butyrates occur at a lower field than the corresponding protons of the single bridge carboxylates. If we assume that this difference is valid also for *A* and *B* then structure (I) is preferred rather than any alternative with four bridge and two bidentate carboxylates; (iii), that the mean oxidation state of ruthenium is 2·5 or (II, III) and the magnetic moment for the dimer, 1·75 B.M. (297 K), corresponds to one unpaired electron per two Ru atoms. In the tetra-bridged carboxylates, $[Ru_2(CO_2R)_4]Cl$,[5] where ruthenium also is in the mean oxidation state 2·5, the magnetic moments (4—4·6 B.M. per dimer) correspond to a spin-free, three unpaired electron, system.

Electrochemical study confirms this oxidation state. The polarogram of *C* has a cathodic wave at $E_{\frac{1}{2}} = -0{\cdot}76$ V and controlled potential coulometric reduction of a stirred suspension gives $n = 0{\cdot}98$ per Ru_2 unit. *D* Shows similar behaviour (Table 2). The reduced solution is yellow and is not reoxidised to *C* by air, suggesting decomposition to monomeric species as with $Ru_3O(CO_2Me)_6(PPh_3)_3$.

If CO is passed through the yellow reduced solution, the complex $Ru(CO_2Me)_2(CO)(PPh_3)_2$, discussed below, separates as a white powder but the yield is low (*ca.* 30% based on Ru) as would be expected from the required redistribution of PPh_3.

An attempt to obtain *C* from the oxo-bridged dimer[4] $Ru^{III}{}_2O(CO_2Me)_4(PPh_3)_2$ by interaction with CO in methanol gave only $Ru(CO_2Me)_2(CO)(PPh_3)_2$, *E* Spectra (Table 1) do not distinguish between the possible isomers but to preserve the normal six-co-ordination characteristic for Ru^{II}, one carboxylate group must be monodentate. By analogy with the similar formimidoyl complex $Ru(CO_2Me)(HC{=}NR)(CO)(PPh_3)_2$ whose structure has been determined by *X*-ray diffraction,[6] structure (III) seems likely. The n.m.r. spectrum of *E*



(III)

in $CDCl_3$ over the temperature +60 to −60 °C shows only a single methyl resonance. This indicates that the molecule is non-rigid; the low solubility precludes study at lower temperatures where two methyl resonances might have been expected.

The formation of *E* involves a redistribution of PPh_3 and addition of an extra mole PPh_3 per mole $Ru_2O(CO_2Me)_4(PPh_3)_2$ gives an increased yield of the carbonyl. The carbonyl may also be readily obtained from $Ru(CO_2Me)_2(PPh_3)_2$[7] and CO in methanol; manometric determination of CO uptake in $CHCl_3$ solution confirms the monocarbonyl formulation.

It may be noted by contrast that $Ru(CO_2Me)_2(PPh_3)_2$ reacts with CH_3NC in methanol to give $Ru(CO_2Me)_2(MeNC)_2(PPh_3)_2$ (*F*) which has only two sharp methyl resonances at τ 6·23 (MeNC) and 7·97 (CO_2Me) respectively. The i.r. spectrum has the asymmetric carboxylate stretch at 1605 cm^{-1} consistent with monodentate acetate and the N–C stretch at 2135 cm^{-1}.

The $Ru_3{}^{II,III,III}$ carbonyl complexes undergo oxidation waves (Table 2) and controlled potential electrolysis of *B* at +0·8 V (Pt foil electrode) gave an *n* value of 0·96 V. A preparative scale electrolysis allowed isolation of the salt $[Ru_3O(CO_2Me)_6(py)_2(MeOH)]ClO_4$. The spectroscopic properties are those of the normal (III, III, III) oxo-centred species and the carbonyl has been lost. The oxidation is thus a method for obtaining bispyridine species. The (III, III, III) complexes do not show oxidation waves.

Interaction with Methyl Isocyanide.—The reduced acetate[1] $Ru_3(CO_2Me)_6(MeOH)_3$ in methanol reacts rapidly with CH_3NC to give a blue-green precipitate, which appears to be a mixture of $Ru_3O(CO_2Me)_6(MeNC)_2MeOH$ with some $Ru_3O(CO_2Me)_6(MeNC)_3$. Chromatography in water on Sephadex or recrystallisation from dichloromethane give the pure complexes $Ru_3O(CO_2Me)_6(MeNC)_2L$, L = H_2O (*G*) or MeOH (*H*) respectively. The trisisocyanide has not been obtained pure even on prolonged reaction with an excess of isocyanide. However, for the propionate, the trisisocyanide (*I*) only was obtained; this is the only case in which different products are found using a different carboxylate.

The acetates *G* or *H* react slowly with pyridine in dichloromethane to give a turquoise solution from which $Ru_3O(CO_2Me)_6(MeNC)_2(py)$ (*J*) can be isolated; this complex was too insoluble for n.m.r. study. The complexes *G* and *H* show broad O–H bands in the i.r. at *ca.* 3400 and 3460 cm^{-1} respectively and there is no band *ca.* 1600 cm^{-1} so that this and the single methyl resonance in the n.m.r. indicate that only bridged acetate is present. The mean oxidation state is $2\frac{2}{3}$ but the solubility in acetone is too low for study and the polarogram in dimethylacetamide shows only an irregular cathodic wave at *ca.* −0·7 V. The complex *I* in dimethylacetamide showed a reduction wave at $E_{\frac{1}{2}} = -0{\cdot}71$ V and an oxidation wave at +0·1 V of heights 2 and 1 respectively. Controlled potential electrolysis

---

[5] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2285.

[6] D. F. Christian, G. R. Clark, W. R. Roper, J. M. Waters, and K. R. Whittle, *J.C.S. Chem. Comm.*, 1972, 458.

[7] J. D. Gilbert and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 1749.

at —1·0 V gave a yellow-green solution and an *n* value of 1·92, but the solution is not reoxidised to *I* by air. The *n* value does indicate that the complex is of the $Ru_3^{II,III,III}$ type. The cyclic voltammogram of the polarographic reduction wave shows no anodic portion and the overall behaviour is typical of the cases in which reduction to the (II) state is accompanied by loss of the central oxygen atom and break up of the Ru_3 unit in species of the type $Ru(CO_2R)_2(MeNC)nMeOH$.

Interaction with Sulphur Dioxide.—The interaction of $[Ru_3O(CO_2Me)_6(MeOH)_3]^+$ with SO_2 in methanol is very slow (24 h) at 25 °C. The light blue product contains no carbon and has stoicheiometry approximately $RuSH_4O_6$. If the reaction is stopped while the solution is still green, chromatography shows that several species are present. If $Ru_3(CO_2Me)_6(MeOH)_3$ is treated with SO_2, the light blue solutions are obtained quickly.

When SO_2 is slowly bubbled through $Ru_3O(CO_2Me)_6(MeOH)_3$ at 25° for 1 h, chromatography of the green solution shows only a single species to be present and this can be isolated as a dark green powder by addition of ether. The complex appears to be $Ru_3O(CO_2Me)_6(MeOH)_3(SO_2)$ (*K*) by analysis. The n.m.r. spectrum shows acetate and methanol resonances (Table 1). Addition of pyridine to the green solution and stirring under nitrogen for 12 h gives a blue precipitate, $[Ru_3O(CO_2Me)_6(py)_3(SO_2)]CO_2Me$ (*L*). Polarographic study of *K* and *L* (below) confirms that the oxidation state is (III, III, III) and *K* is hence best formulated as $Ru_3O(CO_2Me)_6(MeOH)_2(OMe)(SO_2)$ since there is no evidence for the presence of an anion.

Complex *K* is not soluble in acetone but in methanol there is a polarographic cathodic wave at $E_{\frac{1}{2}} = -0{\cdot}14$ V just before the wave due to catalytic hydrogen evolution. Electrolysis at —0·2 V gave an approximate *n* value of 0·86. For *L* in acetone, $E_{\frac{1}{2}} = -0{\cdot}17$ V and $n = 1{\cdot}08$. The reduced solution in both cases is yellow and slow reoxidation occurs in air. *L* Shows a further irregular wave beginning *ca.* —0·7 V, the diffusion current for which is about fifty times that of the one-electron wave; this is presumably a catalytic wave from reduction of the $Ru_3^{II,III,III}$ species.

In both *K* and *L* the Ru atoms are octahedral even without the SO_2. Further, the electronic absorption spectra of both complexes are very similar to those[1] of $Ru_3O(CO_2Me)_6(L)_3^+$ (L = MeOH, py). Excluding seven-co-ordination of Ru, which is unlikely, the only reasonable site for SO_2 co-ordination is to the central oxygen atom. It is well known that SO_2 forms weak complexes with various donors and the central oxygen atom could function in this way, particularly if some distortion out of the plane of the Ru atoms occurred. The i.r. spectra of *K* and *L* show four medium intensity bands *ca.* 1000 cm^{-1}; one band can be ascribed to the methyl rocking vibration of acetate. Since the sulphite ion in Na_2SO_3 has three bands in the region 950—1250 cm^{-1} the remaining three bands could be ascribed to a $Rh-OSO_2$ unit. There are no strong bands in the region *ca.* 1100 and 1300 cm^{-1} found in known complexes where SO_2 is directly *S*-bonded to ruthenium.[8]

Interaction with Nitric Oxide.—The interaction of $[Ru_3O(CO_2Me)_6(MeOH)_3]^+$ with NO is slow, but with the reduced forms, brown solutions are rapidly obtained. These contain several species and we have been unable to characterise them. Addition of PPh_3 yields a brown precipitate which appears to be $Ru_3O(CO_2Me)_6(PPh_3)_2(NO)$ *M*. It is too insoluble for determination of its molecular weight or n.m.r. spectrum; the polarogram in dimethylacetamide was uninstructive. A band in the i.r. at 1790 cm^{-1} is doubtless the NO stretch.

Interactions with Sulphur Compounds.—Since the oxygen atom can be clearly reinserted into $Ru_3(CO_2Me)_6L$ species by O_2 or aromatic *N*-oxides[1] attempts were made to synthesise an S-centred complex by interaction of the yellow (II, II, II) species with various sulphur compounds. These attempts failed and there is no reaction with S_8, Ph_3PS, or CS_2 at room temperature in methanol, while SH^-, PhSH, and propylene sulphide lead to decomposition. Interaction with carbonyl sulphide in methanol gave $Ru_3O(CO_2Me)_6(CO)(MeOH)_2$ identical with that described earlier and no evidence for sulphur incorporation; the oxygen is presumably obtained from methanol as in the reaction of the reduced species with PPh_3.[1]

Interaction with Trimethyl Phosphite.—Addition of $P(OMe)_3$ to $[Ru_3O(CO_2Me)_6(MeOH)_3]^+$ in methanol gives a light green precipitate of $Ru_3O(CO_2Me)_6\{P(OMe)_3\}_3$, *N*. The reaction is similar to that with triphenylphosphine[1] but is much faster.

DISCUSSION

The previous[1] and present work shows that the $Ru_3O(CO_2R)_6$ unit enjoys considerable stability to reduction and to reaction with various ligands even though reorganisation of the carboxylate groups occurs as in the carbonyl species. In the numerous species now known all four possible oxidation states from $Ru_3^{II,II,II}$ to $Ru_3^{III,III,III}$ have been obtained. With donor ligands such as H_2O, MeOH, py, *etc.*, all three sites on ruthenium in the air stable species $[Ru_3O(CO_2R)_6L]^+$ can be occupied. The magnetic moments[1] of these complexes at room temperature are close to that expected for one unpaired electron per Ru_3O unit, indicating maximum spin pairing; in the Ru_3O unit, the Ru–O π-bonding is presumably maximised. With weakly π-acid ligands, Ph_3P and $(MeO)_3P$, the stable oxidation state is now (II, III, III), which is not surprising in view of the ease of reduction (III, III, III) $\longrightarrow$ (II, III, III) ($E_{\frac{1}{2}}$ *ca.* —0·1 to —0·2 V) and all three ligand sites are occupied. Although methyl isocyanide is a better π-acid than R_3P, again two or three ligand sites may be occupied in (II, III, III) complexes. However, no evidence for the formation of dicarbonyl species was obtained with CO and even with one CO present, there is a profound change in structure of the (II, III, III) complex. It seems likely that the reason for this is

---

[8] L. H. Vogt, jun., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, 1965, **4**, 1157.

that the π-bonding requirements of CO so reduce the electron density that π-bonding in the Ru_3O unit cannot survive in the same form as in the species with six carboxylate bridges. There is also a marked effect on the magnetism, for the (II, III, III) state the moments rising from near diamagnetic to *ca.* 2 B.M. per Ru_3O unit in the carbonyl. The Ru–O bond *trans* to CO could be expected to be longer than the other two and lead to the formation of bidentate carboxylate groups. It is noteworthy that on electrolytic oxidation, where CO is lost, the trinuclear six-bridged structure is re-formed. The complete loss of the trinuclear structure on reaction of the carbonyl complex with triphenylphosphine reflects the further reduction of electron density in the Ru_3O unit.

In reactions of π-bonding ligands with the (II, II, II) species without the central oxygen, the product is the oxo-centred (II, III, III) complex, as first noted[1] for PPh_3. The (II, II, II) forms must therefore be capable of abstracting oxygen from the solvent. The high electrolysis currents observed on attempted electrochemical reduction of, *e.g.*, $Ru_3O(CO_2Me)_6(CO)(py)_2$, which must be catalytic in origin, may well arise from the initial reduction product being reoxidised by the acetone solvent.

TABLE 3

Analytical data for ruthenium complexes

	Complex	Found (Required) C	H	N	P	S	M[a]
A	$Ru_3O(CO_2Me)_6(CO)(MeOH)_2$	23·3 (23·5)	3·3 (3·4)				
B	$Ru_3O(CO_2Me)_6(CO)(py)_2$[b]	32·6 (32·1)	3·4 (3·3)	3·2 (3·3)			823 (861)
C	$Ru_2O(CO_2Me)_3(CO)(PPh_3)$[c]	43·3 (43·7)	3·7 (3·5)		5·0 (4·5)		641 (687)
D	$Ru_2O(CO_2Pr)_3(CO)(PPh_3)$	48·4 (48·2)	4·7 (4·7)		4·2 (4·0)		861 (771)
E	$Ru(CO_2Me)_2(CO)(PPh_3)_2$	63·7 (63·7)	4·9 (4·7)		7·4 (8·0)		
F	$Ru(CO_2Me)_2(MeNC)_2(PPh_3)_2$	63·7 (63·9)	4·9 (5·1)	3·3 (3·4)	8·1 (7·5)		
	$[Ru_3O(CO_2Me)_6(py)_2(MeOH)]ClO_4$	28·8 (28·6)	3·5 (3·3)	2·8 (2·9)			
G	$Ru_3O(CO_2Me)_6(MeNC)_2(H_2O)$	24·4 (24·7)	3·3 (3·4)	3·9 (3·6)			628 (776)
H	$Ru_3O(CO_2Me)_6(MeNC)_2(MeOH)$	25·6 (25·8)	3·5 (3·6)	3·8 (3·5)			
I	$Ru_3O(CO_2Et)_6(MeNC)_3$	32·9 (32·6)	4·6 (4·5)	4·6 (4·8)			931 (893)
J	$Ru_3O(CO_2Me)_6(MeNC)_2(py)$	29·9 (30·1)	3·9 (3·5)	4·7 (5·0)			
K	$Ru_3O(CO_2Me)_6(MeOH)_2(MeO)SO_2$	21·1 (21·5)	3·8 (3·6)			3·6 (3·8)	
L	$[Ru_3O(CO_2Me)_6(py)_3(SO_2)CO_2Me$	33·4 (33·6)	3·7 (3·5)	4·3 (4·0)		3·2 (3·1)	
M	$Ru_3O(CO_2Me)_6(NO)(PPh_3)_2$	46·1 (46·8)	3·9 (3·9)	1·5 (1·1)	5·0 (5·0)		
N	$Ru_3O(CO_2Me)_6[(MeO)_3P]_3$	24·0 (24·0)	4·3 (4·3)		9·0 (8·9)		994 (1048)

[a] Chloroform solution. [b] *C*-Methyl determination 10·7 (10·4) %. [c] Ru determination 29·5 (29·7). *C*-Methyl determination 6·4 (6·6) %.

EXPERIMENTAL

Ruthenium trichloride hydrate was obtained from Johnson Matthey Ltd., other reagents were AnalaR grade. Ruthenium carboxylates used as starting materials were prepared as previously described.[1,4] Elemental analyses (Table 3) were by the Microanalytical Laboratory, Imperial College, and molecular weights were obtained using a Hitachi–Perkin-Elmer 115 instrument. N.m.r. spectra were recorded on Perkin-Elmer R 12A (60 MHz) and R 14 (100 MHz) instruments and i.r. spectra on a Perkin-Elmer 457 spectrometer. Magnetic measurements were obtained using the Evans' modification of the Gouy balance. Electrochemical studies utilised tetraethylammonium perchlorate (recrystallised three times from water) as supporting electrolyte. The cell configuration was as previously described,[1] except for the difference in supporting electrolyte. A Beckman Electroscan TM 30 was used for polarographic and coulometric studies, and a Chemical Electronics TA 70/2A potentiostat for preparative electrolyses. Cyclic voltammograms were obtained with an instrument designed by the authors. This utilised a Hewlett–Packard 3310A function generator to provide the triangular wave, and a conventional potentiostat based on three Analog Devices 148A operational amplifiers. Triggering from the anodic or cathodic points of the triangular wave was by a field-effect transistor biased (indirectly) from the function generator synchronisation output. Recording was by a Telequipment DM 64 storage oscilloscope, and a Polaroid–Land CR 9 camera.

A Warburg apparatus (Townson and Mercer Ltd.) was used to measure carbon monoxide uptake.

Carbonylbis(methanol)hexa-acetato-μ_3*-oxo-triruthenium*(II, III, III), *A*.—Crude oxotriruthenium(III) acetate (0·5 g) in methanol (10 ml) was reduced under hydrogen pressure (2 atm) in the presence of Adams' catalyst[1] to give the yellow species $Ru_3(CO_2Me)_6(MeOH)_3$ (2—3 h). The hydrogen was released, and the pressure bottle was flushed three times with carbon monoxide (2 atm). The solution was then stirred under 2 atm carbon monoxide for 30 min to give a deep purple solution. This was concentrated and chromatographed on Sephadex LH 20 in methanol. The purple band was concentrated, filtered, and an excess of ether added. The complex separated as a purple precipitate on chilling at −30°. This was collected, washed with ether, and dried *in vacuo*. Prolonged exposure to vacuum causes some loss of methanol from the complex. Yield 0·37 g (80%).

Carbonylbis(pyridine)hexa-acetato-μ_3*-oxo-triruthenium*(II, III, III), *B*.—Crude oxotriruthenium(III) acetate (0·5 g) was converted to the purple carbonyl complex as above. After reaction with carbon monoxide, the solution was filtered, pyridine (1 ml) added, and the solution heated on a steam-bath, with constant shaking for 5 min. The solution becomes blue in colour, and affords a precipitate. After cooling to room temperature, the blue *complex* was collected, washed with methanol and ether, and dried *in vacuo*. Yield 0·34 g (67%).

Carbonyl(triphenylphosphine)triacetato-μ*-oxo-diruthenium-*(II, III), *C*.—Crude oxotriruthenium(III) acetate (0·5 g) was converted to the purple carbonyl complex as above. After reaction with carbon monoxide, the solution was filtered and triphenylphosphine (0·32 g) was added, and the solution was stirred under nitrogen for 4 h. The solution became blue and gave a turquoise *precipitate*. This was collected, washed with methanol and ether, and dried *in vacuo*. Yield 0·23 g (55%).

Carbonyl(triphenylphosphine)tri-n-butyrato-μ-oxo-diruthenium(II, III), *D*.—This was prepared by the above method from the crude n-butyrate [1] (1 g). Yield 0·6 g (85%).

Diacetatobis(triphenylphosphine)carbonylruthenium(II), *E*. —(a) *From μ-oxo-bis[diacetatotriphenylphosphineruthenium* (III)]. The complex (0·5 g) and triphenylphosphine (0·27 g) were stirred in methanol (5 ml) and carbon monoxide was passed for 1 h. The resulting white precipitate was collected, washed with methanol and ether, and dried *in vacuo*. Yield 0·29 g (73%).

(b) *From diacetatobis(triphenylphosphine)ruthenium*(II).[4] The complex (0·3 g) was stirred in methanol (10 ml) and carbon monoxide was passed for 1 h. The resulting white *precipitate* was treated as in (a). Yield 0·25 g (79%).

Diacetatobis(triphenylphosphine)bis(methyl isocyanato)ruthenium(II), *F*.—Diacetatobis(triphenylphosphine)ruthenium(II) (0·3 g), and methyl isocyanide (0·05 g) in methanol (10 ml) were stirred under nitrogen for 15 min. The resulting pale cream precipitate was collected, washed with methanol and ether, and dried *in vacuo*. Yield 0·19 g (60%).

Methanolbis(pyridine)hexa-μ-acetato-μ_3-oxo-triruthenium-(III, III, III) *Perchlorate*.—Carbonylbis(pyridine)hexa-μ-acetato-μ_3-oxo-triruthenium(II, III, III) (0·2 g) was suspended in acetone (50 ml), 0·1 M in $NaClO_4$, in a conventional 'H'-cell.[1] The suspension was stirred vigorously and oxidised at a platinum-foil electrode (total surface area, 22·5 cm^2) at +0·1 V *vs.* external aqueous S.C.E. for 16 h. There is no colour change, but the starting material gradually dissolves as the oxidation proceeds. After oxidation, the solvent was removed, and the residue was dissolved in methanol (10 ml). The solution was filtered, and a large excess of ether was added to induce precipitation. The *complex* was collected, washed with water and ether, and dried *in vacuo*. Yield 0·08 g (38%).

Methanolbis(methyl isocyanide)hexa-μ-acetato-μ_3-oxo-triruthenium(II, III, III), *H*.—Crude oxotriruthenium(III) acetate (0·5 g) in methanol (10 ml) was reduced under hydrogen pressure to $Ru_3(CO_2Me)_6(MeOH)_3$ as previously described.[1] The hydrogen was released and the solution was flushed with nitrogen for 5 min. Methyl isocyanide (0·5 ml) in methanol (3 ml) was added under nitrogen, and the solution was stirred under nitrogen for 6 h. The dark green *precipitate* which formed was collected, washed well with methanol and ether, and dried *in vacuo*. Yield 0·37 g (79%).

Aquobis(methyl isocyanide)hexa-μ-acetato-μ_3-oxo-triruthenium(II, III, III), *G*.—The methanol complex was prepared as above. This was dissolved in water (10 ml) and chromatographed on Sephadex G 10 column (35 × 4·5 cm). The dark green band was collected and concentrated to give a precipitate of the aquo adduct. This was recrystallised from dichloromethane ether to give the pure *complex* as a dark green powder. This was collected, washed with ether, a little water, and ether again, and dried *in vacuo*. Yield 0·34 g (74%).

Pyridinebis(methyl isocyanide)hexa-μ-acetato-μ_3-oxo-triruthenium(II, III, III), *J*.—The methanolbis(methyl isocyanide)complex (0·3 g) was dissolved in dichloromethane (20 ml). Pyridine (0·5 ml) was added, and the solution was stirred under nitrogen for 24 h. The resulting blue-green solution was concentrated, filtered, and ether (*ca.* 1 vol.) was added. On chilling the solution at −30 °C for 2 h, the *complex* separated as a green powder. This was collected, washed with ether, and dried *in vacuo*. Yield 0·18 g (56%).

Tris(methyl isocyanide)hexa-μ-propionato-μ_3-oxo-triruthenium(II, III, III), *I*.—This reaction was carried out as for the preparation of the methanolbis(methyl isocyanide) complex, using crude oxotriruthenium(III) propionate (0·5 g) as starting material. After the reaction, the solution was chilled at −30 °C for 2 h. The resulting green precipitate was recrystallised from dichloromethane–ether, from which the pure *complex* separates on chilling at −30 °C. This was collected, washed with ether, and dried *in vacuo*. Yield 0·36 g (68%).

(Sulphur dioxide)bis(methanol)methoxohexa-μ-acetato-μ_3-oxo-triruthenium(III, III, III), *K*.—Crude oxotriruthenium(III) acetate (0·5 g) in methanol (10 ml) was reduced under hydrogen to the intermediate reduced form $Ru_3O(CO_2Me)_6(MeOH)_3$ as previously described.[1] Nitrogen was then passed through the stirred solution to remove hydrogen (5 min), and then a slow stream of sulphur dioxide was passed for 1 h. The solution was then concentrated and chromatographed on a Sephadex LH 20 column (35 × 4·5 cm) in methanol. The main blue-green band was concentrated, filtered, and an excess of ether was added. The *complex* separated as a blue powder on chilling at −30 °C. This was collected, washed with ether, and dried *in vacuo*. Yield 0·18 g (38%).

(Sulphur dioxide)tris(pyridine)hexa-μ-acetato-μ_3-oxo-triruthenium(III, III, III) *Acetate*, *L*.—Crude oxotriruthenium(III) acetate (0·5 g) was converted to the SO_2 complex as above. After passage of sulphur dioxide for 1 h, the solution was swept with nitrogen for 5 min. Pyridine (4 ml) was then added, and the solution was stirred overnight (16 h). The product separated as a blue *precipitate*, which was collected, washed with ether, and dried *in vacuo*. Yield 0·2 g (32%).

Tris(trimethylphosphite)hexa-μ-acetate-μ_3-oxo-triruthenium-(II, III, III), *N*.—To crude oxotriruthenium(III) acetate (0·5 g) in methanol (10 ml) was added trimethyl phosphite (0·5 ml) and the solution was stirred under nitrogen for 1 h. After chilling the solution at −30 °C for 2 h, the green precipitate of the *complex* was collected, washed with methanol and ether, and dried *in vacuo*. Yield 0·37 g (59%).

Nitrosylbis(triphenylphosphinehexa-μ-acetato-μ_3-oxo-triruthenium, *M*.—Crude oxotriruthenium(III) acetate (0·5 g) in methanol (20 ml) was reduced under hydrogen to $Ru_3(CO_2Me)_6(MeOH)_3$. Nitrogen was passed through the reduced solution (with stirring) for 5 min, and then nitric oxide was passed for 30 min. The solution was filtered, triphenylphosphine (0·79 g) was added, and the solution was stirred under nitrogen for 24 h. After chilling at −30 °C for 3 h, the brown *complex* was collected, washed with methanol and ether, and dried *in vacuo*. Yield 0·38 g (52%).

We are indebted to Dr. B. Wozniak for preliminary work on these reactions, and we thank Johnson Matthey Limited for the loan of ruthenium trichloride and Albright and Wilson for gifts of triphenylphosphine.

[3/2002 *Received*, 1*st October*, 1973]