Oxidation of Diphosphazane-bridged Derivatives of Diruthenium Nonacarbonyl by Silver(I) Salts in Protic Solvents: Synthesis, Structural Characterization and Protonation of the Adduct $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(O)\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) involving a Novel Mode of Co-ordination of Carbon Dioxide†

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Treatment of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) with $AgSbF_6$ in methanol, ethanol or tetrahydrofuran–water resulted in the formation of the solvento species $[Ru_2(CO)_5(R'OH)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][SbF_6]_2$ which is isolable for R′ = H but which spontaneously deprotonates to the alkoxycarbonyl-bridged derivative $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OR')\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]SbF_6$ for R′ = Me or Et. The aqua species $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][SbF_6]_2$ was readily deprotonated in consecutive steps by appropriate bases to afford respectively the hydroxycarbonyl-bridged species $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OH)\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]SbF_6$ and the adduct $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(O)\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ in which the carbon dioxide molecule adopts a novel bridging co-ordination mode; this deprotonation is reversible and treatment of the latter with $HBF_4\cdot OEt_2$ leads to stepwise regeneration of the aqua species. The co-ordinated water molecule in $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ was readily displaced by acids HA derived from conjugate bases with potential co-ordinating properties such as thiolate ions $R''S^-$ (R″ = H or Ph) or carboxylate ions $R'''CO_2^-$ (R‴ = H, Me, Ph or CF_3), to produce monocationic pentacarbonyl species of the type $[Ru_2A(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$; detection of an intermediate, presumably $[Ru_2(CO)_5(HA)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$, was possible for HA = HCO_2H and $MeCO_2H$. The sulfido derivatives $[Ru_2(SR'')(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ (R″ = H or Ph) rapidly decarbonylate in solution to afford the tetracarbonyl products $[Ru_2(\mu\text{-}SR'')(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ in which the sulfido group bridges the two ruthenium atoms. On the other hand the carboxylato derivatives $[Ru_2\{OC(O)R'''\}(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ (R‴ = H, Me, Ph or CF_3) are stable to decarbonylation in solution at room or elevated temperatures but can be decarbonylated to the carboxylato-bridged products $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R''')O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ by irradiation with ultraviolet light. The water molecule in $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ was also readily displaced by the conjugate bases of the above acids HA, but in contrast to that observed for the carboxylic acids $R'''CO_2H$ (R‴ = H, Me or Ph), reaction of the aqua species with the corresponding carboxylate ions $R'''CO_2^-$ led to direct formation of the carboxylato-bridged species $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R''')O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$. Possible mechanisms for the formation of the various products are discussed as are the structures of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2\cdot OCMe_2$, $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OEt)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$, $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$ and $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(O)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$, established X-ray crystallographically.

We have established previously that the highly unstable diruthenium nonacarbonyl $[Ru_2(CO)_9]$[1] can be stabilized by substitution of some of the carbonyl groups with the diphosphite-type ligands $(RO)_2PN(Et)P(OR)_2$ (R = Me or Pr^i)[2] and that the products so formed *viz.* $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) are sufficiently electron-rich to react with a wide range of electrophiles.[3–8] The redox behaviour of these compounds has been investigated electrochemically[9] and, in particular, it has been found that the one-electron oxidation of the tetramethoxydiphosphazane-bridged derivative **1** (R = Me) in weakly co-ordinating solvents such as acetone or benzonitrile is irreversible with the one-electron oxidized product reacting spontaneously with the solvent and with the product of this solvent attack being oxidized at a potential more cathodic than that of the parent species, thereby affording the dicationic solvento species $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ **2** (solv = Me_2CO or PhCN, R = Me). On the other hand, the one-electron oxidation of the tetraisopropoxydiphosphazane-bridged derivative **1** (R = Pr^i) in these solvents was found to be reversible on the time-scale of the experiment. However, further oxidation of the oxidized product $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ also proved to be irreversible with solvent attack on the resulting dication again leading to the formation of a dicationic solvento species, *viz.* **2** (solv = Me_2CO or PhCN, R = Pr^i). We have also established that the oxidation of **1** in non-protic solvents to the dicationic solvento species $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ **2** can be achieved chemically.[6,10] More specifically, it has been shown that oxidation by silver(I) salts occurs *via* the inner-sphere intermediate $[Ru_2(\mu\text{-}AgL)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ **3** (L = Me_2CO or PhCN) and that this silver(I) adduct degrades, with loss of elemental silver, to the one-electron oxidized product $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)\text{-}$

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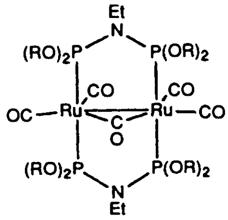
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



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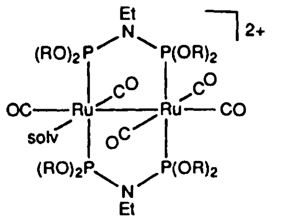

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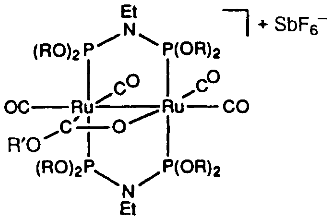

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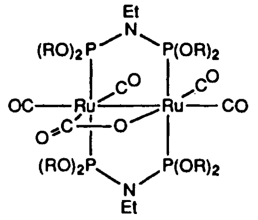

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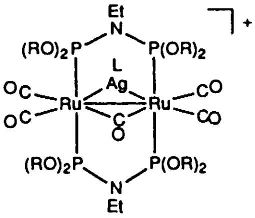


3

$P(OR)_2\}_2]^+$.[6] The latter, in turn, disproportionates in solution to the dication **2** and the neutral compound **1**.

The solvent molecules in dication **2** are weakly co-ordinating and are readily displaced by a wide range of neutral and anionic nucleophiles.[10] In particular, it was found[6] that co-ordinated acetone is readily and reversibly displaced by water, present in trace amounts in even pre-dried acetone, according to equilibrium (1). As a consequence, the SbF_6^- salts having solv = acetone could not be isolated free of the corresponding salts with solv = water.

$$\begin{array}{c}[Ru_2(CO)_5(Me_2CO)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}\\ \mathrm{Me_2CO}\ \Big\Updownarrow\ \mathrm{H_2O}\\ [Ru_2(CO)_5(H_2O)\{\mu\text{-}(RO)_2PN(Et)P(RO)_2\}_2]^{2+}\end{array} \qquad (1)$$

Protic solvents such as methanol and ethanol should also be weakly co-ordinating in complexes of the type **2** but furthermore should also be fairly acidic under these circumstances and very susceptible to deprotonation. The reactions of compound **1** with silver(I) salts in various solvents were thus extended to include various alcohols and water. The results of these investigations as well as those of the reactions of $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][SbF_6]_2$ (solv = acetone/water) with various alcohols, thiols and carboxylic acids are reported; some of them have been the subject of a preliminary communication.[11]

Results and Discussion

Oxidation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ *by* $AgSbF_6$ *in Methanol, Ethanol or Tetrahydrofuran–Water (Acetone–Water).*—Treatment of the diphosphazane-bridged diruthenium compounds **1** with a two-fold molar amount of silver(I) hexafluoroantimonate in methanol or ethanol led to the formation of products characterized as the alkoxycarbonyl-bridged derivatives $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OR')\}(CO)_4\{\mu\text{-}(RO)_2P(NEt)P(OR)_2\}_2]SbF_6$ **4** (R = Me or Pr^i, R′ = Me or Et). Their IR spectra exhibited peaks in the C–O stretching region characteristic of tetracarbonyl complexes of the type $[M_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{n+}$ (M = Fe or Ru, X = bridging ligand, n = 0–2) while their $^{31}P\text{-}\{^1H\}$ NMR spectra contained a set of resonances of AA′BB′ pattern indicating the non-equivalence of the phosphorus atoms and consistent with the presence of a non-symmetric bridging ligand. Although singlets were observed in the room-temperature $^{31}P\text{-}\{^1H\}$ NMR spectra of **4** (R = Me, R′ = Me or Et) measured in $[^2H_6]$acetone and of **4** (R = Pr^i, R′ = Me) measured in $CDCl_3$, AA′BB′ patterns of peaks were observed in the corresponding spectra of the two tetramethoxydiphosphazane derivatives measured at −40 °C. Some fluxional process involving the effective inversion of the alkoxycarbonyl group over the ruthenium–ruthenium edge would appear to be operative but no attempt was made to elucidate the actual mechanism.

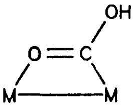
The formulation of these compounds as alkoxycarbonyl-bridged species was confirmed by crystal-structure determinations on **4** (R = R′ = Me) and **4** (R = Me, R′ = Et) (see below).

Significantly, these methoxy- and ethoxycarbonyl-bridged derivatives are also formed on addition of methanol or ethanol to the dicationic aqua species $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][SbF_6]_2$ (R = Me or Pr^i) (see below). Furthermore, their formation is reversible and treatment of **4** (R′ = Me or Et) with $HBF_4\cdot OEt_2$ in acetone led to formation of the dicationic solvento species **2** (solv = Me_2CO or H_2O). The alcohol adduct $[Ru_2(CO)_5(R'OH)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ (R′ = Me or Et) is presumed to be an intermediate in these reactions but attempts to detect it spectroscopically proved unsuccessful.

In contrast to the corresponding reactions involving methanol and ethanol that of the SbF_6^- salt of **2** (solv = H_2O, R = Pr^i) with an excess of *n*-propanol was incomplete, while furthermore no reaction was observed on treatment of the corresponding salts of **2**, (solv = H_2O) with phenol even when a vast excess of the latter was employed.

The oxidation of compound **1** with $AgSbF_6$ in aqueous media such as tetrahydrofuran(thf)–water or acetone–water differed from the oxidations described above in that a dicationic product in which the solvent molecule is co-ordinated in its protonated form, *viz.* $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][SbF_6]_2$, characterized by X-ray crystallography as well as by conventional methods, is produced. Consistent with the structure illustrated (Fig. 1) an AA′BB′ pattern of peaks, centred at δ 125.0, is observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum when R = Pr^i, while the IR spectrum of this species exhibits a pattern of peaks in the C–O stretching region characteristic of dicationic pentacarbonyl species of the type $[Ru_2(CO)_5L\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ (L = neutral ligand) together with a broad peak at *ca.* 3450 cm^{-1} which can be assigned to the O–H stretching vibration of the co-ordinated water. The ^1H NMR spectrum of this tetraisopropoxydiphosphazane-bridged derivative is also consistent with the presence of a co-ordinated water molecule. A broad peak at δ 3.15, the integral of which corresponds to two protons, was observed to collapse on addition of D_2O to the solution. The corresponding tetramethoxydiphosphazane-bridged product was insufficiently soluble in non-co-ordinating solvents such as dichloromethane for ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectral measurements, but its solid-state IR spectrum in the C–O stretching region is almost identical to that of its tetraisopropoxydiphosphazane-bridged analogue. Furthermore, a broad peak at 3520 cm^{-1} is readily assigned to the O–H stretching vibration of a co-ordinated water molecule.

It was anticipated that the co-ordinated water molecules in the dicationic species **2** would be fairly acidic and that these species could be readily deprotonated by weak bases. Consistent with this, addition of a slight excess of pyridine or triethylamine to these aqua species afforded monocationic products characterized as the hydroxycarbonyl-bridged derivatives **4** (R′ = H); as observed for the related reactions involving the formation of the methoxy- and ethoxy-carbonyl-bridged derivatives, the intermediate in the formation of this hydroxycarbonyl-bridged species, *viz.* $[Ru_2(OH)(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$, could not be detected. The IR spectra of these complexes were almost identical to those of the corresponding alkoxycarbonyl-bridged derivatives **4**, while their $^{31}P\text{-}\{^1H\}$ NMR spectra contained a set of peaks of AA′BB′ pattern as expected for products in which an OC(OH) group bridges the two ruthenium atoms unsymmetrically; the co-ordination of this group in the form **A** rather than **B** is proposed on the basis of the structures established X-ray crystallographically for the methoxy- and ethoxy-carbonyl-bridged derivatives **4** (R = R′ = Me) and **4** (R = Me, R′ = Et) (see below).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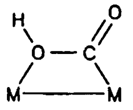
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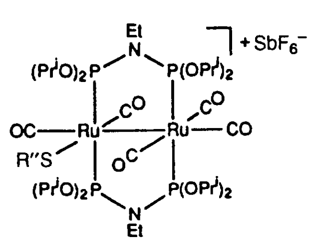
The hydroxycarbonyl derivatives **4** (R′ = H) can be deprotonated further provided stronger bases such as potassium hydroxide or an excess of triethylamine are employed. The neutral product obtained on deprotonation was characterized as the carbon dioxide adduct $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(O)\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **5** (R = Me or Pr^i) in which, as established X-ray crystallographically (see below), the carbon dioxide molecule bridges the two ruthenium atoms. Consistent with the structure established the $^{31}P\text{-}\{^1H\}$ NMR spectra of these compounds contain a set of peaks of AA′BB′ pattern while their IR spectra contain peaks in the C–O stretching region characteristic of species $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{n+}$ (X = bridging ligand) but of lower frequency than that observed for related monocationic derivatives.

Very significantly, the deprotonation of the aqua species **2** to the hydroxycarbonyl- and carbon dioxide-bridged products is reversible and reaction of **5** with $HBF_4{\cdot}OEt_2$ in dichloromethane was found to afford the hydroxycarbonyl-bridged species **4** (R′ = H) and the aqua species **2** in consecutive steps.

The two carbon dioxide adducts **5** (R = Me or Pr^i) are readily decarboxylated* under thermal conditions to produce the previously synthesised co-ordinatively unsaturated species $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (sb = semi-bridging, R = Me or Pr^i);[12] the rate of loss of CO_2 from the former (R = Me) prevented its isolation in a pure state but it was sufficiently stable at low temperatures to be observed and identified spectroscopically.

Reactions of the Aqua Species $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ *with Acids* HA *derived from Conjugate Bases with Potential Co-ordinating Properties.*—The reactions of the tetraisopropoxydiphosphazane-bridged aqua species **2** with weak acids such as hydrogen sulfide, thiophenol and carboxylic acids have been investigated in some detail. In particular it has been found that addition of this aqua species to a saturated solution of H_2S in acetone or to an equimolar amount of PhSH in the same solvent affords products identified spectroscopically as $[Ru_2(SR'')(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ **6** (R″ = H or Ph). The $^{31}P\text{-}\{^1H\}$ NMR spectra of these species contained a distinctive AA′BB′ pattern of peaks for R″ = Ph and a singlet for R″ = H while their solution IR spectra contained a band pattern in the C–O stretching region typical of species $[Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (X = monoanionic ligand). Significantly an intermediate,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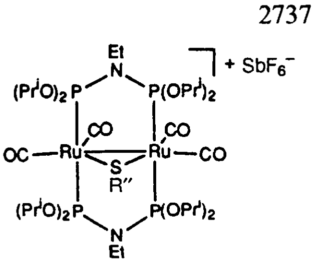
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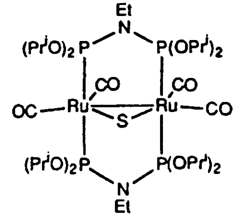
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presumably $[Ru_2(CO)_5(H_2S)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$, which exhibited an AA′BB′ pattern of peaks of chemical shift *ca.* δ 2.5 to high field of that of **6** (R″ = H) was detected in the reaction involving H_2S, but the ready displacement of the co-ordinated H_2S in this intermediate by water in the absence of an excess of H_2S prevented its isolation in a pure state. In contrast, the reaction involving thiophenol led directly to formation of the monocationic phenylsulfido species **6** (R″ = Ph); no thiophenol intermediate could be detected. The pentacarbonylsulfido derivatives readily decarbonylate in solution such that these species could also not be isolated in pure form. The products formed as a consequence of this decarbonylation were characterized as $[Ru_2(\mu\text{-}SR'')(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ **7** (R″ = H or Ph), containing a symmetrically bridging sulfido group. This structure is based on that established previously for $[Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ synthesised by reaction of **1** (R = Me) with PhSH in the presence of an excess of HPF_6.[3] The two ruthenium atoms in this compound are not only bridged by the phenylsulfido group and the two tetramethoxydiphosphazane ligands but are also linked by a formal metal–metal bond. The low-temperature $^{31}P\text{-}\{^1H\}$ NMR spectrum of **7** (R″ = Ph) and the room-temperature $^{31}P\text{-}\{^1H\}$ NMR spectrum of **7** (R″ = H) exhibited a set of peaks of AA′BB′ pattern consistent with the R″ group lying out of the RuSRu plane, but significantly it collapsed to a singlet at room temperature for R″ = Ph and at 55 °C for R″ = H resulting from the inversion of the R″ group at the sulfur atom.

The hydrogensulfido-bridged species **7** (R″ = H) is readily deprotonated by potassium hydroxide to afford the sulfur-bridged product $[Ru_2(\mu\text{-}S)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **8**, also synthesised by reaction of the dichloro compound $[Ru_2Cl_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ with sodium sulfide[13] or by reaction of the co-ordinatively unsaturated species $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ with S_8.[12] This deprotonation is reversible and treatment of the sulfur-bridged compound with HPF_6 produces **7** (R″ = H) in quantitative yield. A similar reversibility involving protonation of the sulfido-bridged dirhodium compound $[Rh_2(\mu\text{-}S)(CO)_2(\mu\text{-}dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) has been reported by Kubiak and Eisenberg.[14]

Addition of an excess of formic or acetic acid to a solution of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ in acetone resulted in the formation of products which exhibited respectively a singlet at δ 125.7 and an AA′BB′ pattern of peaks at δ 124.8 in their $^{31}P\text{-}\{^1H\}$ NMR spectra and which, on the basis of this spectroscopic evidence and of their deprotonation behaviour, are assumed to be the carboxylic acid co-ordinated derivatives $[Ru_2(CO)_5(R'''CO_2H)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ **9** (R‴ = H or Me). The co-ordinated carboxylic acid in these products is readily displaced by water in the absence of an excess of carboxylic acid such that they

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* Most readily achieved by passage of argon through a solution of these species in toluene at 60 °C for 30 min. Warming of crystals of these species under vacuum also leads to the ready formation of $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i).

Table 1 Infrared and $^{31}P\text{-}\{^1H\}$ nuclear magnetic resonance spectroscopic data

Compound	R	R′	R″	R‴	$\nu(CO)^a/cm^{-1}$	$^{31}P\text{-}\{^1H\}$ NMR[b,c]
$[Ru_2(CO)_5(H_2O)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][SbF_6]_2$						
	Me[d]				2105w, 2061s, 2050s, 2031s, 2005s[e]	Not measured
	Pr^i[f]				2097w, 2045(sh), 2034s, 1987m[e]	125.0[g,h]
$(Ru_2\{\mu\text{-}\eta^2\text{-}OC(OR')\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]SbF_6$						
	Me	H			2042s, 2012vs, 1986s, 1962m, 1600w[e]	151.0[h,i]
	Pr^i	H			2033s, 2000vs, 1973s, 1952m, 1600w[e]	135.5[h,j]
	Me	Me			2042s, 2014vs, 1987s, 1966m, 1608w[e]	150.5[h,i,k,l]
	Pr^i	Me			2033s, 2000vs, 1972s, 1951m, 1630w[e]	139.7[h,m]
	Me	Et			2041s, 2012vs, 1985s, 1965(sh), 1605w[e]	150.6[h,i,k,n]
	Pr^i	Et			2033s, 2000vs, 1973s, 1950m, 1600w[e]	135.5(s)[j]
$[Ru_2(SR'')(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]SbF_6$						
	Pr^i		H[o]		2082w, 2033s, 2020(sh), 1969w[e]	128.4(s)[j]
	Pr^i		Ph		2080w, 2031s, 2021(sh), 1970w[e]	125.6[h,j]
$[Ru_2(\mu\text{-}SR'')(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]SbF_6$						
	Pr^i		H		2030s, 2000vs, 1967s, 1946s[p]	136.2[h,j]
	Pr^i		Ph		2032m, 2001s, 1973m, 1951w[e]	130.0(s)[j]
$[Ru_2\{OC(OR''')\}(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]SbF_6$						
	Pr^i			H	2087w, 2032s, 2023s, 1972m, 1610m[p]	128.4[h,j]
	Pr^i			Me	2084w, 2031s, 2020s, 1968m, 1600m[p]	128.0[h,j]
	Pr^i			Ph	2086w, 2032s, 2018s, 1966m, 1600m[p]	128.6[h,j]
	Pr^i			CF_3[q]	2087w, 2038s, 2021s, 1974m, 1685m[p]	130.8[j,k]
$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R''')O\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]SbF_6$						
	Pr^i			H	Not measured	135.8(s)[j]
	Pr^i			Me	2030s, 2001vs, 1972s, 1947m, 1550m[p]	135.6(s)[j]
	Pr^i			Ph	2031s, 2001vs, 1972s, 1949m, 1534m[p]	134.2(s)[j]
	Pr^i			CF_3[r]	2031s, 2001vs, 1972s, 1949m, 1534m[p]	133.0(s)[i]
$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(O)\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$						
	Me				2017s, 1988vs, 1955s, 1936s, 1714m, 1600m[e]	149.6[h,j]
	Pr^i				2010s, 1972vs, 1940s, 1923s, 1710s, 1505m[s]	140.2[h,j,k]
$[Ru_2(\mu\text{-}S)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$						
	Pr^i				2000s, 1963vs, 1925s, 1920vs[s]	137.6(s)[t]

[a] Abbreviations: v = very, s = strong, m = medium, w = weak, sh = shoulder. [b] δ in ppm relative to H_3PO_4; measured at room temperature unless otherwise stated. [c] Abbreviation: s = singlet. [d] ν(OH): 3520 cm^{-1}, Nujol mull. [e] Measured in CH_2Cl_2. [f] ν(OH): 3450 cm^{-1}, Nujol mull. ^1H NMR: δ 3.15 (s, 2 H, H_2O) measured in CD_2Cl_2, δ in ppm relative to $SiMe_4$. [g] Measured in CD_2Cl_2. [h] Centre of AA′BB′ pattern of peaks. [i] Measured in $CDCl_3$. [j] Measured in $[^2H_6]$acetone. [k] Measured at −40 °C. [l] Room-temperature spectrum: δ 149.5(s). [m] Measured in CD_3OD. [n] Room-temperature spectrum: δ 149.6(s). [o] ^1H NMR: δ 0.63 [q, J_{P-H} 13.8 Hz, SH], measured in $CDCl_3$, δ in ppm relative to $SiMe_4$. [p] Measured in $CHCl_3$. [q] ^{19}F NMR: δ −70.4(s), measured in $[^2H_6]$acetone, δ in ppm relative to $CFCl_3$. [r] ^{19}F NMR: δ −70.3(s) measured in $[^2H_6]$acetone, δ relative to $CFCl_3$. [s] Measured in hexane. [t] Measured in C_6D_6.

could not be isolated in a pure state. Deprotonation of these species was readily effected by the addition of a weak base such as pyridine to afford the monocationic pentacarbonyl carboxylato derivative $[Ru_2\{OC(O)R'''\}(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ **10** (R‴ = H or Me). In contrast to that observed for both formic and acetic acid, reaction of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ with either benzoic or trifluoroacetic acid in acetone led directly to formation of a carboxylato derivative, *viz.* **10** (R‴ = Ph or CF_3). Each of these carboxylato pentacarbonyl derivatives exhibited an AA′BB′ pattern of peaks in its $^{31}P\text{-}\{^1H\}$ NMR spectrum and a band pattern in the C–O stretching region of its solution IR spectrum typical of pentacarbonyl species $[Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (X = monoanionic ligand). In addition each compound afforded a peak in its IR spectrum readily assigned to the C–O stretching vibration of a monoligated carboxylato group at 1610, 1600, 1600 and 1685 cm^{-1} for R‴ = H, Me, Ph and CF_3 respectively.

All four of the pendant carboxylato species **10** proved to be stable to decarbonylation in solution under thermal conditions but they could be readily converted in solution into products characterized as the tetracarbonyl carboxylato-bridged species $[Ru_2\{\mu\text{-}OC(R''')O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ **11** by irradiation with ultraviolet light. These complexes exhibit a singlet in their $^{31}P\text{-}\{^1H\}$ NMR spectra, confirming the symmetrical co-ordination of the bridging carboxylato group, as well as a four-line pattern in the C–O stretching region of their IR spectra, readily associated with species $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (X = anionic ligand). The frequencies of the C–O stretching vibration corresponding to the carboxy group of the pendant carboxylato ligands in **10** were observed to shift by *ca.* 60 cm^{-1} to lower values on adoption of a bridging co-ordination mode by the carboxylato ligands.

Significantly, irradiation of the pendant formato species **10** (R‴ = H) with untraviolet light produced the formato-bridged derivative **11** (R‴ = H) as well as the hydrido species $[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ in the ratio 2 : 1. The latter complex is presumed to have formed as a result of the decarboxylation of **10** (R‴ = H) under ultraviolet light. This observation is analogous to the previously established decarboxylation of $[Rh_2\{OC(O)H\}(CO)_3(\mu\text{-dppm})_2]^+$ in the presence of CO to $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]^+$.[15] Equally significantly, treatment of **11** (R‴ = H) in chloroform

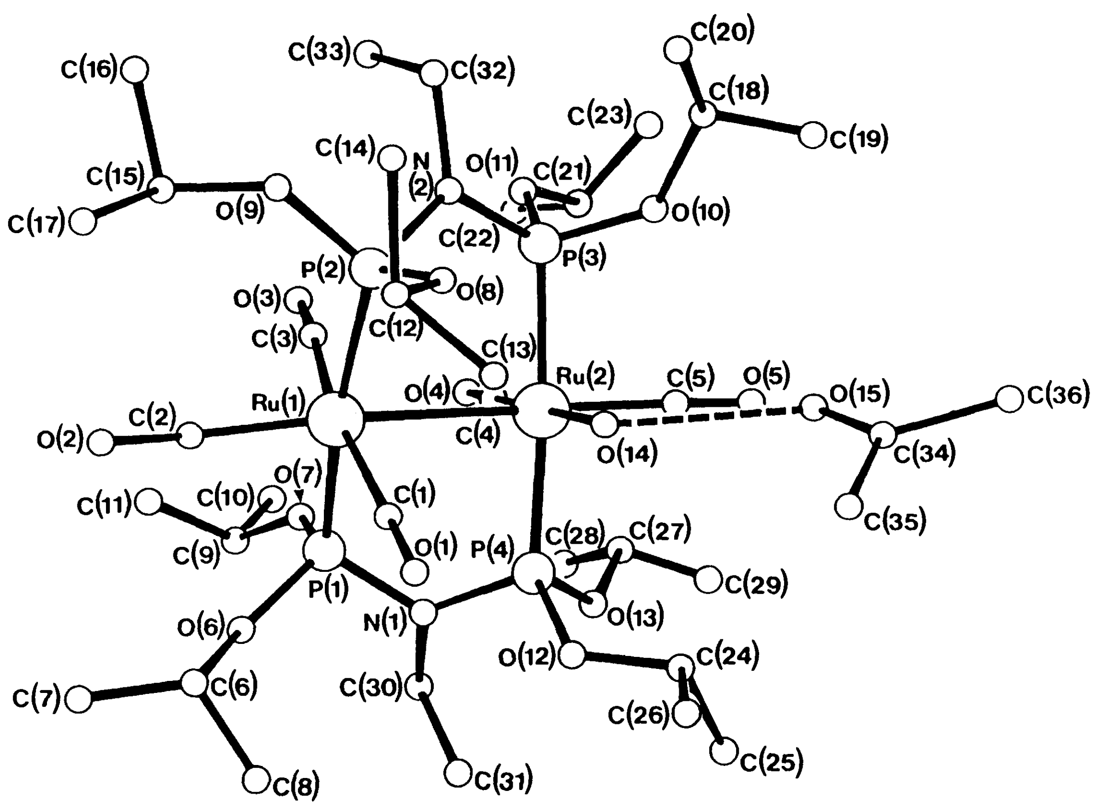
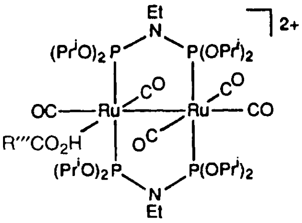


Fig. 1 Structure of the cation of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2\cdot OCMe_2$ showing the hydrogen bonding of the acetone solvent molecule to the co-ordinated water molecule



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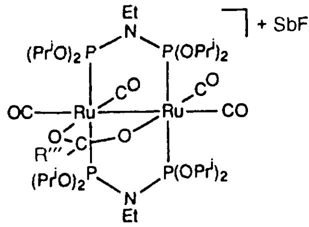

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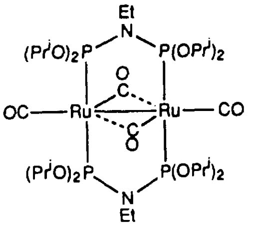

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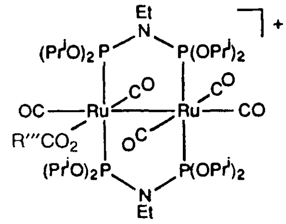


10

with a slight excess of aqueous KOH afforded $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **12** *via* a presumed CO_2 complex.

The acetato-bridged species **11** (R''' = Me) is isomeric with the methoxycarbonyl-bridged cation **4** (R = Pr^i, R' = Me) but significantly all attempts to convert one isomer into the other both thermally and photochemically proved unsuccessful.

Reactions of the Aqua Species $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ *with Hydroxide, Alkoxide, Mercaptide and Carboxylato Ions.*—The reactions of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ with hydroxide, alkoxide and phenylmercaptide ions followed pathways analogous to those of their conjugate acids, affording the hydroxycarbonyl **4** (R = Pr^i, R' = H), the alkoxycarbonyl **4** (R = Pr^i, R' = Me or Et) and the phenylmercaptide derivatives **6** (R'' = Ph) and **7** (R'' = Ph) respectively. Reaction with phenoxide ions did not lead to the formation of **4** (R = Pr^i, R' = Ph) but to the hydroxycarbonyl species **4** (R = Pr^i, R' = H) as a consequence of the phenoxide ions functioning as a base and deprotonating the aqua species. On the other hand formate, acetate and benzoate ions adopt different pathways to their conjugate acids on reaction with the aqua species. In particular, while the addition of formic, acetic and benzoic acids in acetone led to the eventual formation of the pentacarbonyl carboxylato derivatives **10** (R''' = H, Me or Ph) provided, as described above, base is subsequently added for R''' = H and Me, the corresponding reactions involving the conjugate bases of these acids afforded the tetracarbonyl carboxylato-bridged derivatives **11** (R''' = H, Me or Ph) respectively. In contrast, treatment of the aqua species with trifluoroacetate ions produced the stable pentacarbonyl trifluoroacetato derivative **10** (R''' = CF_3) which could only be decarbonylated to the corresponding tetracarbonyl trifluoroacetato-bridged derivative **11** (R''' = CF_3) by irradiation with ultraviolet light.

Crystal Structure of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2\cdot OCMe_2$.—The stereochemistry of the dication of this complex is illustrated in Fig. 1. Selected interatomic distances and angles are listed in Table 2. The two ruthenium atoms, each of which is approximately octahedral, are not only bridged by the two diphosphazane ligands, *trans* disposed with respect to each other, but are separated by a distance of 2.872(1) Å corresponding to a formal ruthenium–ruthenium bond. The water molecule occupies an equatorial

Table 2 Selected interatomic distances (Å) and angles (°) for $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2\cdot OCMe_2$

Ru(1)–Ru(2)	2.872(1)	Ru(1)–P(1)	2.333(3)
Ru(1)–P(2)	2.338(3)	Ru(2)–P(3)	2.349(3)
Ru(2)–P(4)	2.351(3)	Ru(2)–O(14)	2.202(7)
O(14) ⋯ O(15)	2.680(16)		
Ru(2)–Ru(1)–P(1)	88.0(1)	Ru(1)–Ru(2)–P(3)	89.4(1)
Ru(2)–Ru(1)–P(2)	84.5(1)	Ru(1)–Ru(2)–P(4)	87.9(1)
Ru(2)–Ru(1)–C(1)	83.1(3)	Ru(1)–Ru(2)–O(14)	89.2(2)
Ru(2)–Ru(1)–C(2)	176.3(3)	Ru(1)–Ru(2)–C(4)	87.0(3)
Ru(2)–Ru(1)–C(3)	87.9(3)	Ru(1)–Ru(2)–C(5)	177.3(3)
P(1)–Ru(1)–P(2)	172.4(1)	P(3)–Ru(2)–P(4)	176.2(1)
P(1)–Ru(1)–C(1)	87.4(3)	P(3)–Ru(2)–O(14)	89.0(2)
P(1)–Ru(1)–C(2)	88.6(3)	P(3)–Ru(2)–C(4)	90.8(3)
P(1)–Ru(1)–C(3)	90.6(3)	P(3)–Ru(2)–C(5)	90.7(3)
P(2)–Ru(1)–C(1)	92.8(3)	P(4)–Ru(2)–O(14)	93.5(2)
P(2)–Ru(1)–C(2)	98.9(3)	P(4)–Ru(2)–C(4)	86.5(3)
P(2)–Ru(1)–C(3)	88.0(3)	P(4)–Ru(2)–C(5)	92.2(3)
C(1)–Ru(1)–C(2)	95.2(5)	O(14)–Ru(2)–C(4)	176.3(3)
C(1)–Ru(1)–C(3)	170.8(4)	O(14)–Ru(2)–C(5)	88.1(4)
C(2)–Ru(1)–C(3)	93.7(5)	O(4)–Ru(2)–C(5)	95.6(5)

Table 3 Selected interatomic distances (Å) and angles (°) for $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OEt)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$

Ru(1)–Ru(2)	2.777(1)	Ru(1)–P(1)	2.325(3)
Ru(1)–P(2)	2.324(3)	Ru(2)–P(3)	2.306(3)
Ru(2)–P(4)	2.318(3)	Ru(2)–O(5)	2.140(8)
Ru(2)–C(5)	2.091(12)	C(5)–O(5)	1.268(14)
C(5)–O(6)	1.311(15)	O(6)–C(6)	1.56(2)
Ru(2)–Ru(1)–P(1)	89.6(1)	Ru(1)–Ru(2)–P(3)	91.6(1)
Ru(2)–Ru(1)–P(2)	90.6(1)	Ru(1)–Ru(2)–P(4)	90.7(1)
Ru(2)–Ru(1)–O(5)	71.2(3)	Ru(1)–Ru(2)–C(3)	94.9(3)
Ru(2)–Ru(1)–C(1)	170.6(3)	Ru(1)–Ru(2)–C(4)	162.7(4)
Ru(2)–Ru(1)–C(2)	93.4(4)	Ru(1)–Ru(2)–C(5)	66.4(3)
P(1)–Ru(1)–P(2)	176.0(1)	P(3)–Ru(2)–P(4)	174.9(1)
P(1)–Ru(1)–O(5)	85.8(2)	P(3)–Ru(2)–C(3)	88.5(4)
P(1)–Ru(1)–C(1)	90.4(4)	P(3)–Ru(2)–C(4)	88.5(4)
P(1)–Ru(1)–C(2)	92.5(4)	P(3)–Ru(2)–C(5)	89.5(3)
P(2)–Ru(1)–O(5)	90.5(2)	P(4)–Ru(2)–C(3)	86.8(4)
P(2)–Ru(1)–C(1)	88.7(4)	P(4)–Ru(2)–C(4)	90.6(4)
P(2)–Ru(1)–C(2)	91.5(4)	P(4)–Ru(2)–C(5)	95.6(3)
O(5)–Ru(1)–C(1)	99.4(4)	C(3)–Ru(2)–C(4)	102.3(6)
O(5)–Ru(1)–C(2)	164.5(4)	C(3)–Ru(2)–C(5)	161.2(5)
C(1)–Ru(1)–C(2)	96.1(5)	C(4)–Ru(2)–C(5)	96.3(5)
Ru(1)–O(5)–C(5)	103.3(7)	Ru(2)–C(5)–O(5)	118.0(8)
Ru(2)–C(5)–O(6)	124.5(9)	O(5)–C(5)–O(6)	117.5(11)

position similar to that found for the benzonitrile molecule in the related complex $[Ru_2(CO)_5(PhCN)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$.[10] The dication adopts a staggered conformation as reflected by P(1)–Ru(1)–Ru(2)–P(4) and P(2)–Ru(1)–Ru(2)–P(3) torsion angles of 26.2 and 27.8° respectively. An interesting feature of the structure is the presence of an acetone molecule hydrogen bonded to the co-ordinated water molecule; the hydrogen atoms of the water molecule were not located but an O(water) ⋯ O(acetone) distance of 2.680(16) Å is consistent with the two oxygen atoms being linked through a hydrogen bond. One other structurally characterized diruthenium compound containing co-ordinated water molecules, *viz.* $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}_4(H_2O)_2]$, has been reported previously[16] but the ruthenium atoms in this complex have formal oxidation states of +2.

Crystal Structures of $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OR')\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ (R′ = Me *or* Et).—A single-crystal X-ray diffraction study was initially undertaken on the methoxycarbonyl species **4** (R = R′ = Me). This revealed the gross features of the structure of the cation but, because of the poor quality of the crystal, the data could not be refined to an acceptably low value for the *R* factor. Better crystals of the ethoxycarbonyl derivative were grown and the single-crystal X-ray determination revealed the structure to be analogous to that of the former methoxycarbonyl species. The stereochemistry of the cation of **4** (R = Me, R′ = Et) is illustrated in Fig. 2 while selected interatomic distances and angles are listed in Table 3. The notable feature of this structure is the presence of a bridging ethoxycarbonyl group {OC(OEt)} giving rise to a four-membered Ru_2OC ring. The C(5)–O(5) distance [1.27(1) Å] is slightly shorter than C(5)–O(6) [1.31(2) Å], as expected with the former formally representing a double bond, but the difference is small which could reflect some delocalization over the whole ring system. The separation of 2.777(1) Å between the two ruthenium atoms, bridged by two *trans*-disposed diphosphazane ligands, represents a formal metal–metal bond and compares with the corresponding distance of 2.801(2) Å for **1** (R = Me).[2] The cation adopts a slightly staggered configuration as reflected by P(1)–Ru(1)–Ru(2)–P(4) and P(2)–Ru(1)–Ru(2)–P(3) torsion angles of 14.8 and 6.4° respectively. Significantly, only one other structurally characterized alkoxycarbonyl-bridged derivative has been reported previously, *viz.* $[Os_6(\mu_3\text{-}PH)H_3\{\mu\text{-}\eta^2\text{-}OC(OMe)\}(CO)_{19}]$.[17]

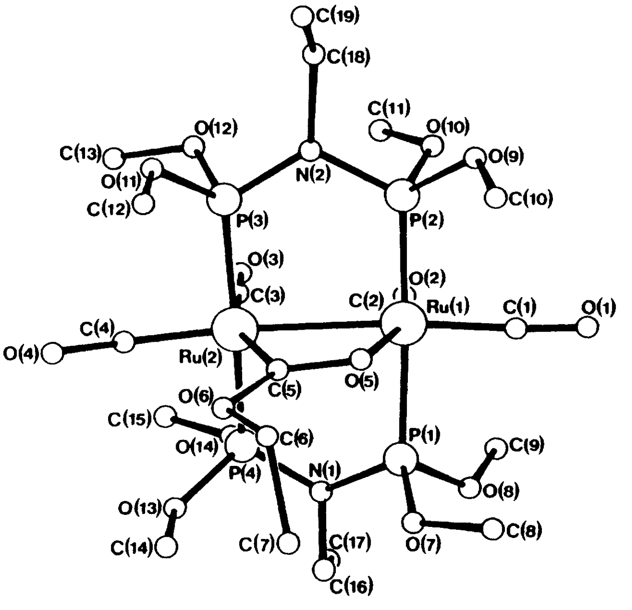


Fig. 2 Structure of the cation of $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OEt)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$

Crystal Structure of $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(O)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$.—The molecular structure of complex **5** (R = Pr^i) is illustrated in Fig. 3 while selected interatomic distances and angles are listed in Table 4. The two ruthenium atoms, separated by a distance of 2.800(1) Å corresponding to a formal ruthenium–ruthenium bond, are not only bridged by the two diphosphazane ligands mutually *trans* to each other but also by a carbon dioxide molecule co-ordinating to the rutheniums through its carbon and one oxygen atom. The C(33)–O(13) distance [1.29(3) Å] is longer than C(33)–O(14) [1.06(3) Å] with the latter formally representing a C–O double bond. These distances are comparable to those established for the nickel–carbon dioxide derivative $[Ni\{\eta^2\text{-}OC(O)\}\{P(C_6H_{11})_3\}_2]$ [1.22(2) and 1.17(2) Å] and the niobium species $[Nb(\eta\text{-}C_5H_4Me)_2(CH_2SiMe_3)(\eta^2\text{-}CO_2)]$ [1.283(8) and 1.216(8) Å] in which the carbon dioxide molecule similarly co-ordinates to the nickel[18] and the niobium[19] through its carbon and one oxygen atom. Similar to what is found for the methoxy-and ethoxy-carbonyl-bridged derivatives the molecule is essentially eclipsed as reflected by P(1)–Ru(1)–Ru(2)–P(4) and P(2)–Ru(1)–Ru(2)–P(3) torsion angles of 4.3 and 5.3° respectively.

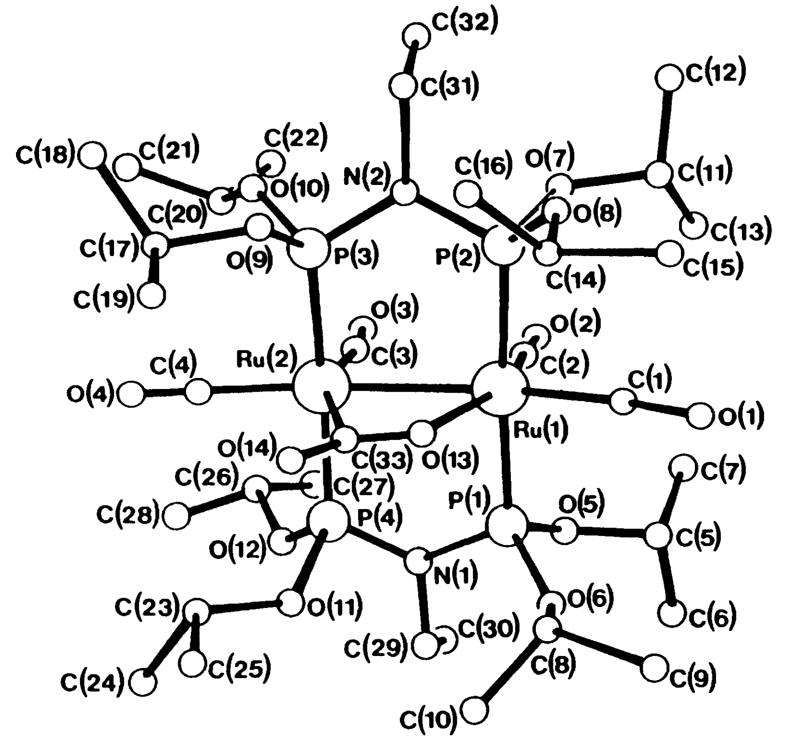


Fig. 3 Structure of $[Ru_2(\mu\text{-}\eta^2\text{-}OC(O))(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$

Table 4 Selected interatomic distances (Å) and angles (°) for $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(O)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$

Ru(1)–Ru(2)	2.800(1)	Ru(1)–P(1)	2.315(2)
Ru(1)–P(2)	2.326(2)	Ru(2)–P(3)	2.318(3)
Ru(2)–P(4)	2.318(2)	Ru(1)–O(13)	2.204(15)
Ru(2)–C(33)	2.05(2)	C(33)–O(13)	1.29(3)
C(33)–O(14)	1.06(3)		
Ru(2)–Ru(1)–P(1)	91.5(1)	Ru(1)–Ru(2)–P(3)	90.3(1)
Ru(2)–Ru(1)–P(2)	92.0(1)	Ru(1)–Ru(2)–P(4)	90.1(1)
Ru(2)–Ru(1)–O(13)	67.7(5)	Ru(1)–Ru(2)–C(3)	91.0(4)
Ru(2)–Ru(1)–C(1)	165.8(4)	Ru(1)–Ru(2)–C(4)	165.3(4)
Ru(2)–Ru(1)–C(2)	94.0(3)	Ru(1)–Ru(2)–C(33)	70.9(10)
P(1)–Ru(1)–P(2)	175.9(1)	P(3)–Ru(2)–P(4)	172.3(1)
P(1)–Ru(1)–O(13)	91.4(3)	P(3)–Ru(2)–C(3)	93.5(4)
P(1)–Ru(1)–C(1)	88.4(3)	P(3)–Ru(2)–C(4)	88.1(3)
P(1)–Ru(1)–C(2)	88.7(4)	P(3)–Ru(2)–C(33)	86.9(5)
P(2)–Ru(1)–O(13)	91.9(3)	P(4)–Ru(2)–C(3)	94.1(4)
P(2)–Ru(1)–C(1)	88.7(3)	P(4)–Ru(2)–C(4)	89.5(3)
P(2)–Ru(1)–C(2)	89.0(4)	P(4)–Ru(2)–C(33)	86.0(5)
O(13)–Ru(1)–C(1)	98.1(6)	C(3)–Ru(2)–C(4)	103.8(5)
O(13)–Ru(1)–C(2)	161.6(6)	C(3)–Ru(2)–C(33)	161.8(11)
C(1)–Ru(1)–C(2)	100.2(5)	C(4)–Ru(2)–C(33)	94.4(10)

Table 5 Selected interatomic distances (Å) and angles (°) for $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$

Ru(1)–Ru(2)	2.806(1)	Ru(1)–P(1)	2.335(2)
Ru(1)–P(2)	2.324(2)	Ru(2)–P(3)	2.336(2)
Ru(2)–P(4)	2.333(2)	Ru(2)–O(13)	2.140(5)
Ru(2)–O(14)	2.131(6)	C(33)–O(13)	1.236(10)
C(33)–O(14)	1.286(10)	O(33)–C(34)	1.497(15)
Ru(2)–Ru(1)–P(1)	89.6(1)	Ru(1)–Ru(2)–P(3)	89.5(1)
Ru(2)–Ru(1)–P(2)	90.6(1)	Ru(1)–Ru(2)–P(4)	90.6(1)
Ru(2)–Ru(1)–O(13)	81.4(1)	Ru(1)–Ru(2)–O(14)	81.3(2)
Ru(2)–Ru(1)–C(1)	173.4(2)	Ru(1)–Ru(2)–C(3)	90.8(3)
Ru(2)–Ru(1)–C(2)	89.7(4)	Ru(1)–Ru(2)–C(4)	173.4(3)
P(1)–Ru(1)–P(2)	177.6(1)	P(3)–Ru(2)–P(4)	176.3(1)
P(1)–Ru(1)–O(13)	88.9(2)	P(3)–Ru(2)–O(14)	88.6(2)
P(1)–Ru(1)–C(1)	88.7(2)	P(3)–Ru(2)–C(3)	92.7(3)
P(1)–Ru(1)–C(2)	91.7(3)	P(3)–Ru(2)–C(4)	88.7(3)
P(2)–Ru(1)–O(13)	88.8(2)	P(4)–Ru(2)–O(14)	87.8(2)
P(2)–Ru(1)–C(1)	90.8(2)	P(4)–Ru(2)–C(3)	90.9(3)
P(2)–Ru(1)–C(2)	90.7(3)	P(4)–Ru(2)–C(4)	90.8(3)
O(13)–Ru(1)–C(1)	92.1(3)	O(14)–Ru(2)–C(3)	172.0(3)
O(13)–Ru(1)–C(2)	171.1(3)	O(14)–Ru(2)–C(4)	92.4(3)
C(1)–Ru(1)–C(2)	96.8(3)	C(3)–Ru(2)–C(4)	95.6(4)

The mode of co-ordination adopted by the carbon dioxide in complex **5** (R = Pr^i) has not been reported previously, although a related one has been established for the CO_2 molecule in $[OsRh_2(\mu\text{-}H)_2(\mu_3\text{-}\eta^3\text{-}CO_2)(C_8H_{12})_2(PMe_2Ph)_3]$ which bridges three metal atoms through its carbon and both oxygen atoms.[20] Furthermore, it has been proposed that the complex $[CoK(Pr^n\text{-salen})(CO_2)(thf)]$ [Pr^n-salen = *N*,*N'*-ethylenebis(α-propylsalicylideneiminato(2−)] adopts a structure in solution whereby one of the oxygen atoms of the CO_2, co-ordinated to the cobalt through its carbon atom, is weakly bound to the potassium ion.[21] Also it can be assumed that the CO_2 molecule in the ditertiary phosphine-bridged dirhodium compound $[Rh_2(CO_2)(CO)_2(\mu\text{-dppm})_2]$, first reported by Kubiak *et al.*,[15] adopts this mode of co-ordination.

Crystal Structure of $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$.—Single crystals, suitable for an X-ray diffraction study, were more readily obtained for the hexafluorophosphate salt rather than the hexafluoroantimonate salt **11** (R‴ = Me). This compound was synthesised directly by treatment of **1** (R = Pr^i) with a twice molar amount of silver acetate in thf or acetone followed by addition of an excess of NH_4PF_6.[22] The structure of the cation is illustrated in Fig. 4 and confirms the presence of a bridging acetato group. Selected interatomic distances and angles are listed in Table 5. The two ruthenium atoms, which have approximate octahedral geometries with the angles subtended at these atoms ranging from 81.3(2) to 96.8(4)°, are bridged by two tetraisopropoxydiphosphazane ligands in a *trans* arrangement as well as by the acetate group. The cation is slightly staggered as reflected by

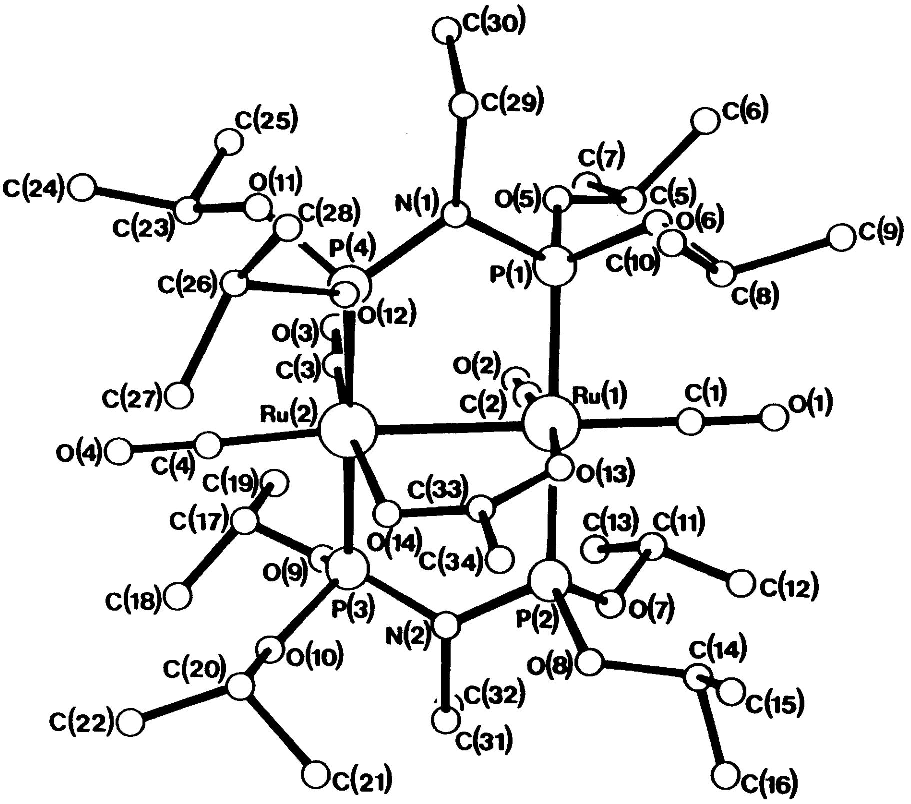


Fig. 4 Structure of the cation of $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$

P(1)–Ru(1)–Ru(2)–P(4) and P(2)–Ru(1)–Ru(2)–P(3) torsion angles of 17.3 and 13.8° respectively. The structure of this species is totally analogous to that established previously for $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_4(\mu\text{-}dppm)_2]PF_6$[23] with the ruthenium–ruthenium separation for the former [2.806(1) Å] being very slightly less than that for the latter [2.841(1) Å].

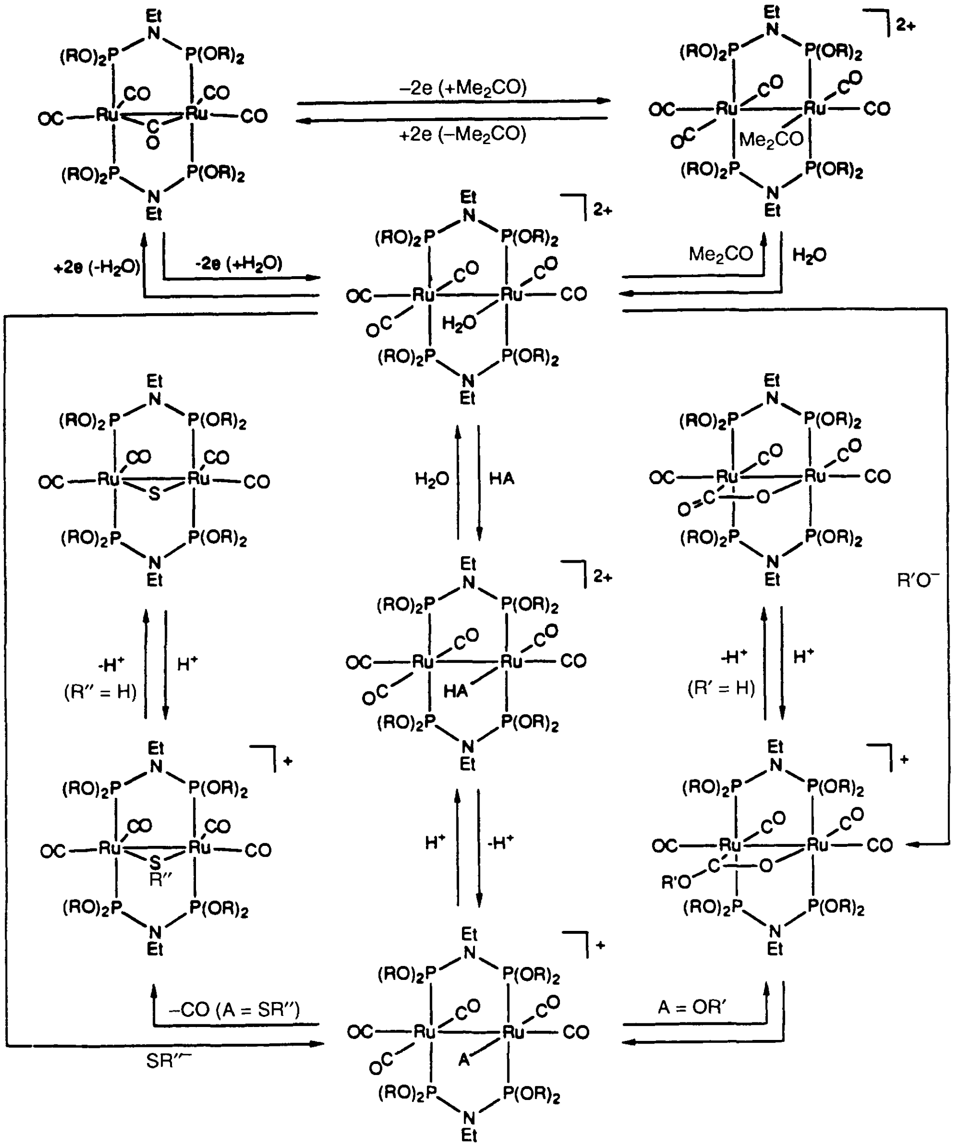
Mechanism of Reaction.—In proposing mechanisms for the formation of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$, $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OR')\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$, $[Ru_2A(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ [A = SR″ or OC(O)R‴], $[Ru_2(\mu\text{-}SR'')(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R''')O\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (R′ = H, Me or Et; R″ = H or Ph; R‴ = H, Me or CF_3) in the reactions of $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ with R′OH, R″SH or R‴CO_2H or with $R'O^-$, $R''S^-$ or $R'''CO_2^-$ a number of observations were taken into consideration:

(*i*) Dissolution of the $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][SbF_6]_2$ in acetone results in partial displacement of the co-ordinated water such that the cationic species **2** (solv = H_2O or Me_2CO) are present in equilibrium.

(*ii*) As described earlier in the text, treatment of the species **2** (solv = H_2O) in acetone with methanol or ethanol results in rapid formation of the alkoxycarbonyl-bridged species **4** (R′ = Me or Et) which, on protonation in acetone containing trace amounts of water, reaffords **2** (solv = Me_2CO/H_2O). These results are interpreted in terms of the alcohol species **2** (solv = R′OH, R′ = Me or Et) being an intermediate in these reactions, that this intermediate spontaneously deprotonates in alcohol in the absence of an excess of acid to a second intermediate $[Ru_2(OR')(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and that in acetone the co-ordinated alcohol in the former intermediate is readily displaced by the solvent. The alkoxide intermediate spontaneously rearranges in solution for R′ = Me or Et with the alkoxide group migrating from the metal to the carbon atom of an adjacent carbonyl ligand to afford the alkoxycarbonyl-bridged product **4**. The formation of the latter in the reaction of **1** with $AgSbF_6$ in alcohol is assumed to involve the same pathway with the two-electron oxidation leading initially to **2** (solv = R′OH). Likewise, the formation of the hydroxycarbonyl-bridged species **4** (R′ = H) and subsequently the carbon dioxide adduct **5** involves an analogous pathway except that water is not sufficiently basic to deprotonate the co-ordinated H_2O in **2** (solv = H_2O) and the addition of a base such as pyridine is required to promote the reaction. These reactions are summarized in Scheme 1.

(*iii*) Treatment of $[Ru_2(CO)_5(solv)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ (solv = Me_2CO/H_2O) with the carboxylic acids R‴CO_2H (R‴ = H, Me, Ph or CF_3) results in the formation of the carboxylato pentacarbonyl species **10** provided base is added for R = H or Me; irradiation with ultraviolet light was necessary to effect decarbonylation of these species to afford the carboxylato-bridged species **11**. On the other hand as described above, addition of the carboxylate ions $R'''CO_2^-$ (R‴ = H, Me or Ph) leads directly to the tetracarbonyl species **11**; these latter reactions were monitored by means of $^{31}P\text{-}\{^1H\}$ NMR and IR spectroscopy and significantly the pentacarbonyl species **10** could not be detected as an intermediate. It is apparent that different pathways are being followed and it is proposed that in the case of the carboxylic acids attack occurs at the metal co-ordinated to the solvent leading to displacement of the solvent molecule and formation of a pentacarbonyl product. However for the carboxylate ions $R'''CO_2^-$ (R‴ = H, Me or Ph) the results are not inconsistent with the initial attack occurring at a carbonyl group co-ordinated to the solvent-free ruthenium, resulting in displacement of a carbonyl group as well as the solvent molecule. These reactions are summarized in Scheme 2.

(*iv*) Reaction of species **2** (solv = Me_2CO/H_2O) with alkoxide or hydroxide ions results in direct formation of the hydroxy- or alkoxy-carbonyl-bridged species **4** (R′ = H, Me or Et) whereas, as described earlier, reaction of **2** (R = Pr^i) with PhS^- ions as well as with PhSH or H_2S gives the pentacarbonylsulfido species

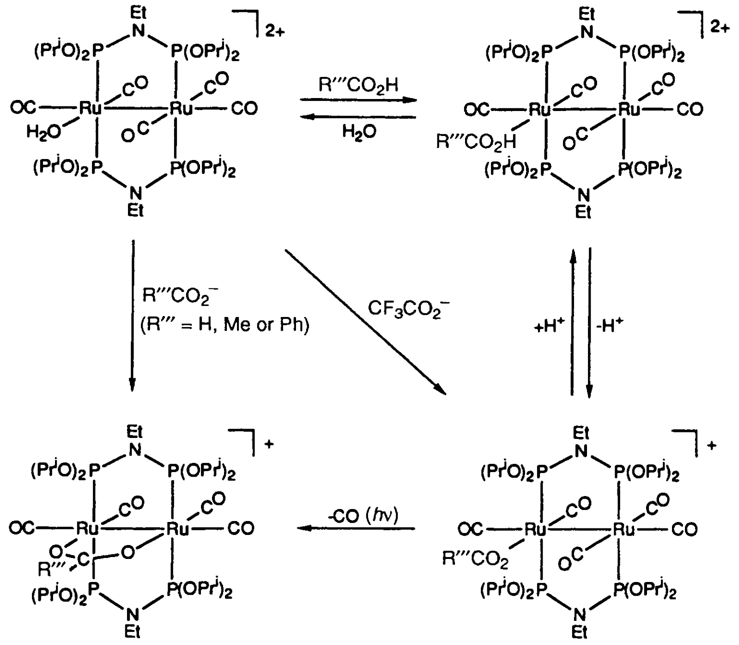


Scheme 1 Reactions of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ with HA and A^- (A = OR′ or SR″; R′ = H, Me, Et or Pr^i; R″ = H or Ph)

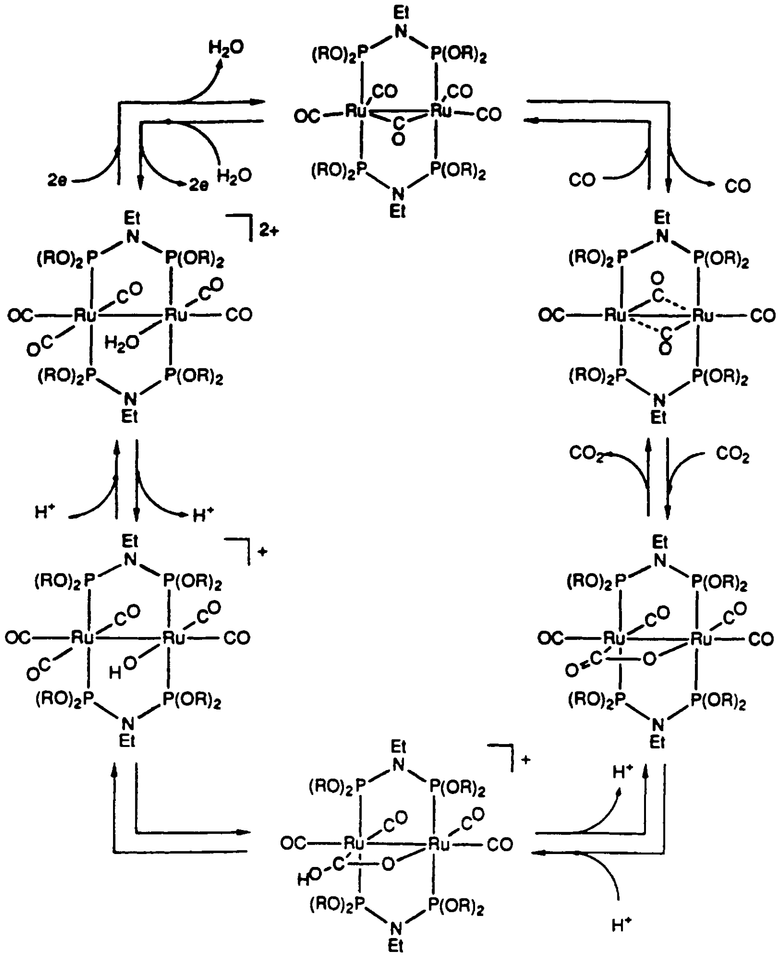
6 (R″ = H or Ph) which readily decarbonylate in solution to **7**. It is apparent that for the more polarizable sulfur ligands the site of attack is the ruthenium atom to which the solvent is co-ordinated, resulting in spontaneous replacement of the solvent molecule by the incoming ligand. A similar reaction pathway could be envisaged for hydroxide and alkoxide ions, particularly as it has been concluded that the formation of the hydroxy- and alkoxy-carbonyl-bridged species from **2** (solv = H_2O) and **2** (solv = R′OH) respectively occurs *via* hydroxy- or alkoxy-pentacarbonyl intermediates. Nevertheless it is proposed that the initial site of attack of the solvento species for the harder hydroxide and alkoxide ions is the carbon atom of a carbonyl group bonded to the solvent-free ruthenium.

Hydroxide and alkoxide ion attack on co-ordinated carbonyl groups is well documented and Darensbourg *et al.*[24] for instance have established that whereas the reaction of the Group VI metal carbonyls $[M(CO)_6]$ (M = Cr, Mo or W) with hydrogensulfide ions affords the species $[M(SH)(CO)_5]^-$ the corresponding reaction involving hydroxide ions affords the anionic hydride $[MH(CO)_5]^-$ *via* the metallocarboxylic acid species $[M\{C(O)OH\}(CO)_5]^-$ as intermediate. Likewise, the reactions of hydroxide and methoxide ions with $[Ru_3(CO)_{12}]$ have been shown to produce the hydroxy- and methoxy-carbonyl species $[Ru_3\{C(O)OH\}(CO)_{11}]^-$ and $[Ru_3\{C(O)OMe\}(CO)_{11}]^-$ respectively;[25] the hydroxycarbonyl species readily loses carbon dioxide to afford the anionic hydride $[Ru_3H(CO)_{11}]^-$,[26] a species which has received considerable attention as a homogeneous catalyst for the water-gas shift reaction.[27]

Scheme 3 represents a catalytic cycle for the electrochemical reduction of CO_2 to CO and H_2O in acidic media utilizing complex **1** as catalyst and most significantly the majority of the intermediates in this cycle have been identified and characterized in this study. Furthermore as reported earlier in the text, we have shown that the parent pentacarbonyl species can be oxidized, both chemically and electrochemically, to the solvento species **2** and most important have established that this redox process is chemically reversible.[9] The completion of the catalytic cycle requires, however, the displacement of a carbonyl ligand from the neutral pentacarbonyl by a carbon dioxide molecule. Our recent studies have shown that **1** (R = Pr^i) can in fact be reversibly decarbonylated under appropriate reaction conditions to the formally unsaturated compound **12** in almost quantitative yield.[12] This compound is extremely labile, reacting with a wide range of nucleo- and electro-philes, but proved to be inert to attack by CO_2 even though one of the methods of its synthesis involves decarboxylation of the CO_2 derivative **5** (R = Pr^i). It is envisaged that the more electron-



Scheme 2 Reactions of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^{2+}$ with $R'''CO_2H$ and $R'''CO_2^-$ (R''' = H, Me, Ph or CF_3)



Scheme 3 A possible catalytic cycle involving $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) for the reduction of carbon dioxide in acidic media to carbon monoxide and water

rich diruthenium compounds $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}R_2PCH_2PR_2)_2]$ (R = Me, C_6H_{11}, Ph, *etc.*) containing more basic ditertiary phosphines would be far more susceptible to attack by carbon dioxide and studies in this area are continuing.

Experimental

The neutral pentacarbonyls **1** (R = Me or Pr^i) were synthesised according to a literature method.[2b] All reactions and manipulations were carried out under nitrogen by Schlenk-tube

Table 6 Crystal data and details of refinement

Compound	$[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2\cdot OCMe_2$	$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OEt)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$	$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(O)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$	$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$
M	1572.792	1081.298	1040.927	1200.925
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$Pbca$	$P1$
a/Å	12.181(2)	11.491(8)	16.858(8)	10.516(1)
b/Å	28.389(2)	15.698(4)	17.993(2)	11.995(1)
c/Å	22.901(2)	21.542(7)	31.602(5)	13.055(1)
α/°	90	90	90	108.15(1)
β/°	99.55(1)	103.09(4)	90	112.65(1)
γ/°	90	90	90	100.75(1)
U/Å^3	6434.28	3785.20	9586.12	1353.11
Z	4	4	8	1
D_c/g cm^{-3}	1.62	1.89	1.44	1.47
F(000)	3128	2128	4304	616
μ/cm^{-1}	14.82	17.40	8.07	7.70
Crystal size/mm	0.46 × 0.15 × 0.15	0.38 × 0.12 × 0.12	0.77 × 0.46 × 0.27	0.23 × 0.19 × 0.08
Total data measured (maximum 2θ/46°)	9457	5653	7307	3952
No. of unique reflections	7742	4658	5786	3928
No. of observed reflections [$F_o > 3\sigma(F_o)$]	5994	3771	4602	3886
No. of parameters	642	338	496	395
ρ_{max}/e Å^{-3}	2.22*	1.66*	0.85	0.60
Maximum least-squares shift-to-error ratio	0.32	0.05	0.07	0.12
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.0091	0.0067	0.0094	0.0019
Final R	0.0661	0.0703	0.0613	0.0403
Final R'	0.0728	0.0755	0.0762	0.0465

* Close to metal atoms; otherwise featureless.

techniques. The photochemical reactions utilized a home-built reactor based on a Philips HPW 125W Blacklight Blue lamp. Solvents were purified and dried using standard literature procedures. Infrared spectra were recorded on a Perkin Elmer 457 spectrophotometer, $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectra on a Varian FT80A and a Gemini 200 instrument respectively; spectroscopic data are summarized in Table 1.

Syntheses.—$[Ru_2(CO)_5(H_2O)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][SbF_6]_2$. A solution of a two-fold molar amount of $AgSbF_6$ (0.20 g, 0.58 mmol) in thf (2 cm^3) containing 1% water was added dropwise to a stirred solution of complex **1** (R = Me) (0.23 g, 0.29 mmol) or **1** (R = Pr^i) (0.30 g, 0.29 mmol) in thf (*ca.* 10 cm^3) and the mixture stirred for 1 h, during which time silver metal separated. The solution was filtered and the volume of the filtrate reduced under reduced pressure to *ca.* 2 cm^3. Crystallization was effected by addition of diethyl ether. Yield: 80–90% (Found: C, 15.5; H, 2.8; N, 2.2. Calc. for $C_{17}H_{36}F_{12}N_2O_{14}P_4Ru_2Sb_2$: C, 15.8; H, 2.8; N, 2.2. Found: C, 26.4; H, 4.4; N, 1.8. Calc. for $C_{33}H_{68}F_{12}N_2O_{14}P_4Ru_2Sb_2$: C, 26.2; H, 4.5; N, 1.8%).

$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OH)\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]SbF_6$. A solution of a slight excess of pyridine (0.015 g, 0.20 mmol) in thf (1 cm^3) was added to a stirred solution of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$ (0.15 g, 0.12 mmol) or $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ (0.15 g, 0.10 mmol) in thf (*ca.* 5 cm^3). The solvent was removed under reduced pressure and the residue was washed with water (3 × 5 cm^3) and dried. Crystallization was effected from acetone–diethyl ether. Yield: 70–80% (Found: C, 31.3; H, 5.3; N, 2.4. Calc. for $C_{33}H_{67}F_6N_2O_{14}P_4Ru_2Sb$: C, 31.0; H, 5.3; N, 2.2%).

$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OMe)\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]SbF_6$. A solution of a two-fold molar amount of $AgSbF_6$ (0.10 g, 0.29 mmol) in methanol (1 cm^3) was added dropwise to a stirred suspension of complex **1** (R = Me) (0.12 g, 0.14 mmol) or **1** (R = Pr^i) (0.15 g, 0.14 mmol) in methanol (*ca.* 5 cm^3) and the mixture stirred for 2 h during which time silver separated. The pale yellow solution was filtered and toluene was added to the filtrate to effect the separation of the product in crystalline form. Yield: 70–80% (Found: C, 20.1; H, 3.4; N, 2.7. Calc. for $C_{18}H_{37}F_6N_2O_{14}P_4Ru_2Sb$: C, 20.2; H, 3.5; N, 2.6. Found: C, 31.8; H, 5.4; N, 2.2. Calc. for $C_{34}H_{69}F_6N_2O_{14}P_4Ru_2Sb$: C, 31.6; H, 5.4; N, 2.2%).

$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OEt)\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]SbF_6$. A solution of a two-fold molar amount of $AgSbF_6$ (0.10 g, 0.29 mmol) in ethanol (1 cm^3) was added dropwise to a stirred suspension of **1** (R = Me) (0.12 g, 0.14 mmol) or **1** (R = Pr^i) (0.15 g, 0.14 mmol) in ethanol (*ca.* 5 cm^3) and the mixture stirred for 2 h during which time silver separated. The pale yellow solution was filtered, toluene (*ca.* 3 cm^3) was added to the filtrate and the solution kept at −10 °C to effect the separation of the product in crystalline form. Yield: 70–80% (Found: C, 21.3; H, 3.7; N, 2.7. Calc. for $C_{19}H_{39}F_6N_2O_{14}P_4Ru_2Sb$: C, 21.1; H, 3.6; N, 2.6. Found: C, 31.3; H, 5.3; N, 2.3. Calc. for $C_{35}H_{71}F_6N_2O_{14}P_4Ru_2Sb$: C, 32.2; H, 5.4; N, 2.1%).

$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(O)\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$. An excess of an aqueous solution (*ca.* 3 cm^3) of potassium hydroxide (0.03 g, 0.54 mmol) was added to a solution of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$ (0.175 g, 0.13 mmol) or $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ (0.20 g, 0.13 mmol) in dichloromethane (*ca.* 3 cm^3) and the two-layered mixture vigorously stirred for 30 min. The dichloromethane layer was separated from the aqueous layer and the solvent removed under reduced pressure. The yellow residue was extracted with hexane (5 × 3 cm^3) and

Table 7 Fractional coordinates (× 10^4) for $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2{\cdot}OCMe_2$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	3 015(1)	8 318(1)	1 683(1)
Ru(2)	5 337(1)	8 111(1)	1 680(1)
P(1)	3 540(2)	8 955(1)	2 463(1)
P(2)	2 736(2)	7 645(1)	918(1)
P(3)	4 897(2)	7 184(1)	1 322(1)
P(4)	5 694(2)	9 030(1)	2 082(1)
O(1)	3 343(7)	9 299(4)	843(4)
O(2)	579(8)	8 613(4)	1 731(5)
O(3)	3 044(8)	7 315(4)	2 552(4)
O(4)	5 507(7)	7 702(4)	2 932(3)
O(5)	7 796(8)	7 922(4)	1 605(5)
O(6)	2 711(6)	9 456(3)	2 536(4)
O(7)	3 631(7)	8 652(4)	3 080(3)
O(8)	2 987(6)	7 884(3)	303(3)
O(9)	1 570(5)	7 355(3)	726(3)
O(10)	5 602(9)	7 077(6)	813(5)
O(11)	5 067(8)	6 665(3)	1 771(4)
O(12)	5 738(6)	9 547(3)	1 642(3)
O(13)	6 864(6)	9 117(3)	2 514(3)
O(14)	5 124(6)	8 418(3)	759(3)
N(1)	4 767(7)	9 279(4)	2 487(4)
N(2)	3 570(7)	7 069(3)	1 036(4)
C(1)	3 246(9)	8 941(5)	1 147(5)
C(2)	1 471(10)	8 507(4)	1 708(6)
C(3)	3 043(8)	7 686(5)	2 240(5)
C(4)	5 419(8)	7 857(5)	2 458(5)
C(5)	6 886(10)	7 986(4)	1 641(5)
C(6)	2 001(14)	9 838(7)	2 032(9)
C(7)	917(17)	9 928(8)	2 283(10)
C(8)	2 724(20)	10 290(9)	1 918(13)
C(9)	3 137(19)	8 718(9)	3 582(8)
C(10)	3 879(26)	8 350(14)	4 065(10)
C(11)	2 042(18)	8 661(17)	3 539(11)
C(12)	2 182(13)	8 137(8)	−169(6)
C(13)	2 795(20)	8 605(8)	−481(7)
C(14)	1 632(23)	7 721(11)	−576(9)
C(15)	581(12)	7 350(7)	1 011(8)
C(16)	160(19)	6 696(11)	979(12)
C(17)	−261(14)	7 738(13)	669(10)
C(18)	5 778(21)	6 695(11)	401(9)
C(19)	6 979(15)	6 672(8)	364(10)
C(20)	5 057(29)	6 788(15)	−165(9)
C(21)	6 105(14)	6 503(6)	2 151(8)
C(22)	5 845(20)	6 351(7)	2 733(9)
C(23)	6 593(25)	6 042(13)	1 900(15)
C(24)	6 598(10)	9 605(5)	1 267(5)
C(25)	7 495(14)	10 023(7)	1 593(8)
C(26)	6 047(13)	9 896(6)	708(6)
C(27)	7 566(10)	8 689(6)	2 875(6)
C(28)	7 343(19)	8 695(8)	3 509(7)
C(29)	8 742(12)	8 865(8)	2 848(9)
C(30)	5 146(13)	9 683(7)	3 013(8)
C(31)	5 596(16)	10 227(8)	2 825(10)
C(32)	3 188(12)	6 458(6)	847(8)
C(33)	2 750(17)	6 156(9)	1 449(11)
Sb(1)	5 343(1)	2 001(1)	2 074(1)
F(1)	6 673(10)	2 388(5)	2 066(7)
F(2)	4 108(10)	1 573(5)	2 119(6)
F(3)	6 083(15)	1 763(8)	2 815(5)
F(4)	4 863(14)	2 243(6)	1 390(7)
F(5)	5 923(11)	1 367(4)	1 750(5)
F(6)	4 769(10)	2 593(5)	2 457(6)
Sb(2A)	0	0	0
F(7)	645(14)	9 360(9)	476(7)
F(8)	26(16)	10 513(10)	632(8)
F(9)	1 444(12)	10 234(8)	−72(8)
Sb(2B)	5 000	0	5 000
F(10)	9 236(14)	4 432(8)	301(9)
F(11)	9 109(15)	5 513(8)	240(9)
F(12)	10 913(12)	5 054(6)	708(5)
O(15)	3 158(9)	1 687(4)	−172(5)
C(34)	3 004(12)	1 453(6)	282(7)
C(35)	3 736(16)	1 003(8)	580(8)
C(36)	2 097(20)	1 661(10)	582(10)

Table 8 Fractional coordinates (× 10^4) for $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OEt)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	6 776(1)	1 024(1)	1 718(1)
Ru(2)	8 536(1)	1 995(1)	2 501(1)
P(1)	7 948(3)	949(2)	970(1)
P(2)	5 540(2)	1 181(2)	2 428(1)
P(3)	7 286(3)	2 316(2)	3 168(2)
P(4)	9 901(3)	1 611(3)	1 907(2)
O(1)	4 680(9)	175(7)	795(5)
O(2)	7 755(9)	−627(6)	2 330(5)
O(3)	9 484(9)	507(7)	3 380(5)
O(4)	10 120(11)	3 483(9)	3 073(6)
O(5)	6 512(7)	2 333(5)	1 445(4)
O(6)	7 613(9)	3 495(6)	1 643(5)
O(7)	7 628(8)	1 664(6)	420(4)
O(8)	7 816(10)	163(7)	512(5)
O(9)	4 169(7)	1 373(6)	2 114(4)
O(10)	5 270(8)	344(6)	2 795(4)
O(11)	7 143(9)	3 269(6)	3 377(5)
O(12)	7 694(7)	1 944(6)	3 873(4)
O(13)	10 827(8)	2 289(9)	1 783(5)
O(14)	10 872(8)	908(7)	2 229(4)
N(1)	9 394(8)	1 144(6)	1 210(4)
N(2)	5 888(8)	1 943(6)	2 991(5)
C(1)	5 428(12)	518(9)	1 106(7)
C(2)	7 376(10)	11(8)	2 093(6)
C(3)	9 164(10)	1 074(8)	3 059(6)
C(4)	9 529(13)	2 927(9)	2 867(7)
C(5)	7 430(11)	2 698(8)	1 776(6)
C(6)	6 672(17)	3 986(12)	1 130(10)
C(7)	7 202(25)	4 020(18)	553(14)
C(8)	6 467(15)	1 652(11)	−8(9)
C(9)	7 688(14)	−720(11)	688(8)
C(10)	3 841(14)	2 026(10)	1 630(8)
C(11)	6 125(15)	13(11)	3 352(8)
C(12)	6 786(14)	3 943(10)	2 915(8)
C(13)	8 820(14)	2 221(10)	4 299(8)
C(14)	10 339(19)	3 086(13)	1 420(11)
C(15)	11 796(15)	1 065(11)	2 814(9)
C(16)	10 199(12)	1 045(9)	749(7)
C(17)	10 961(15)	209(11)	882(8)
C(18)	5 038(13)	2 090(9)	3 409(8)
C(19)	4 325(17)	2 892(12)	3 270(9)
Sb	2 704(1)	3 257(1)	−152(1)
F(1)	3 803(10)	2 378(8)	−62(9)
F(2)	1 581(13)	4 063(8)	−268(10)
F(3)	3 471(21)	3 711(16)	587(9)
F(4)	1 884(13)	2 758(9)	−914(5)
F(5)	3 551(15)	3 945(8)	−618(9)
F(6)	1 809(13)	2 535(9)	239(7)

the product isolated in crystalline form by cooling the combined extracts to −25 °C. Yield: 30–40% (Found: C, 37.7; H, 6.3; N, 3.3. Calc. for $C_{33}H_{66}N_2O_{14}P_4Ru_2$: C, 38.1; H, 6.4; N, 2.7%).

$[Ru_2(SR'')(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ (R″ = H *or* Ph). Solid $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ (0.20 g, 0.13 mmol) was added to a stirred saturated solution of hydrogen sulfide in acetone (*ca.* 5 cm^3) or to a stirred solution of an equimolar amount of thiophenol (0.14 g, 0.13 mmol) in acetone (*ca.* 5 cm^3). The solvent was removed under reduced pressure and the residue washed with

Table 9 Fractional coordinates (× 10^4) for $[Ru_2\{\mu-\eta^2-OC(O)\}(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	528(1)	7 976(1)	3 941(1)	C(7)	133(13)	5 132(11)	4 398(7)
Ru(2)	−604(1)	8 684(1)	3 434(1)	C(8)	−624(8)	7 441(6)	4 928(4)
P(1)	−357(2)	7 039(1)	4 112(1)	C(9)	−1 485(11)	7 493(11)	5 022(5)
P(2)	1 490(1)	8 854(1)	3 774(1)	C(10)	−218(12)	7 159(13)	5 325(5)
P(3)	275(2)	9 649(2)	3 306(1)	C(11)	2 898(7)	8 172(7)	3 754(5)
P(4)	−1 546(1)	7 815(1)	3 635(1)	C(12)	2 927(8)	7 374(9)	3 699(7)
O(1)	1 533(6)	7 439(7)	4 660(4)	C(13)	3 630(9)	8 517(9)	3 531(8)
O(2)	1 138(6)	7 000(5)	3 222(3)	C(14)	1 557(8)	9 554(7)	4 532(4)
O(3)	−71(7)	7 784(6)	2 659(3)	C(15)	1 489(12)	10 368(8)	4 501(5)
O(4)	−1 891(5)	9 626(5)	3 072(4)	C(16)	2 189(14)	9 352(11)	4 904(5)
O(5)	−73(4)	6 216(3)	3 990(2)	C(17)	−493(8)	10 911(8)	3 544(7)
O(6)	−540(4)	6 898(3)	4 601(2)	C(18)	−337(19)	11 556(12)	3 348(10)
O(7)	2 259(4)	8 538(3)	3 538(2)	C(19)	−793(16)	11 145(15)	3 970(10)
O(8)	1 949(4)	9 263(4)	4 151(2)	C(20)	−36(9)	9 802(9)	2 474(5)
O(9)	153(5)	390(4)	3 581(4)	C(21)	535(11)	9 386(15)	2 152(9)
O(10)	313(6)	10 006(6)	2 871(3)	C(22)	−428(12)	10 521(12)	2 314(7)
O(11)	−2 164(5)	8 059(4)	4 005(2)	C(23)	−2 733(7)	8 667(6)	3 975(4)
O(12)	−2 171(4)	7 532(4)	3 290(3)	C(24)	−3 608(10)	8 357(14)	3 854(7)
O(13)	−173(9)	8 799(7)	4 297(5)	C(25)	−2 771(13)	8 991(9)	4 447(6)
O(14)	−987(20)	9 398(15)	4 274(9)	C(26)	−2 102(8)	7 583(8)	2 839(4)
N(1)	−1 233(5)	7 028(4)	3 865(3)	C(27)	−2 936(11)	7 807(13)	2 693(6)
N(2)	1 235(4)	9 513(4)	3 434(3)	C(28)	−1 787(15)	6 830(12)	2 663(6)
C(1)	1 192(7)	7 640(6)	4 397(4)	C(29)	−1 829(8)	6 446(6)	3 993(5)
C(2)	921(8)	7 360(6)	3 487(4)	C(30)	−1 838(13)	5 798(8)	3 676(7)
C(3)	−261(7)	8 123(7)	2 945(4)	C(31)	1 852(7)	10 123(6)	3 336(5)
C(4)	−1 416(5)	9 293(5)	3 222(4)	C(32)	2 306(9)	9 970(9)	2 944(5)
C(5)	495(7)	5 793(6)	4 238(4)	C(33)	−689(16)	9 082(16)	4 039(5)
C(6)	1 167(10)	5 607(9)	3 964(7)				

Table 10 Fractional coordinates (× 10^4) for $[Ru_2\{\mu-\eta^2-OC(Me)O\}(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	0	0	0	C(11)	−3050(10)	664(8)	−2169(8)
Ru(2)	−198(1)	−2428(1)	−191(1)	C(12)	−3001(15)	1657(12)	−2621(12)
P(1)	1321(3)	779(2)	2129(2)	C(13)	−4607(14)	−137(12)	−2586(12)
P(2)	−1223(3)	−755(2)	−2121(2)	C(14)	339(12)	668(10)	−2736(10)
P(3)	−2000(3)	−3241(2)	−2235(2)	C(15)	2035(18)	981(15)	−2284(15)
P(4)	1714(3)	−1616(2)	1807(2)	C(16)	−474(15)	527(12)	−4056(12)
O(1)	527(10)	2707(7)	267(9)	C(17)	−4277(13)	−4777(10)	−2275(10)
O(2)	−2899(7)	−367(7)	26(7)	C(18)	−4816(14)	−6077(12)	−3377(12)
O(3)	−2404(8)	−2488(7)	727(8)	C(19)	−5494(19)	−4447(15)	−2005(15)
O(4)	−310(12)	−5078(7)	−560(9)	C(20)	−536(12)	−4570(10)	−3139(10)
O(5)	455(6)	1113(5)	2880(5)	C(21)	−130(21)	−3967(18)	−3883(17)
O(6)	2655(6)	2096(5)	2810(5)	C(22)	−812(16)	−5982(13)	−3596(13)
O(7)	−2385(8)	−179(7)	−2729(6)	C(23)	435(12)	−3291(10)	2491(10)
O(8)	−194(7)	−570(5)	−2742(5)	C(24)	1039(17)	−4306(14)	2738(13)
O(9)	−3667(6)	−3796(6)	−2556(6)	C(25)	−155(19)	−2706(15)	3302(16)
O(10)	−1912(8)	−4442(6)	−3167(6)	C(26)	4011(15)	−2453(12)	2004(12)
O(11)	1677(9)	−2351(8)	2639(7)	C(27)	3693(24)	−3347(20)	796(20)
O(12)	3300(7)	−1515(6)	1899(6)	C(28)	5755(28)	−1446(23)	2840(22)
O(13)	1988(6)	−22(5)	−84(5)	C(29)	3213(10)	428(8)	4048(8)
O(14)	1428(6)	−2102(5)	−761(5)	C(30)	2587(13)	514(11)	4916(11)
N(1)	2072(9)	−139(7)	2734(7)	C(31)	−3074(13)	−2814(10)	−4325(10)
N(2)	−2151(12)	−2322(9)	−2944(8)	C(32)	−4686(21)	−2966(16)	−4739(17)
C(1)	371(9)	1713(8)	171(7)	C(33)	2246(9)	−991(7)	−459(7)
C(2)	−1764(9)	−237(7)	35(8)	C(34)	3586(14)	−862(11)	−629(11)
C(3)	−1582(10)	−2477(8)	368(8)	P(5)	−3696(4)	−6457(3)	494(3)
C(4)	−215(10)	−4094(9)	−429(8)	F(1)	7187(23)	4757(15)	523(16)
C(5)	−222(12)	2074(10)	2893(10)	F(2)	7189(16)	4065(12)	1934(10)
C(6)	918(15)	3350(12)	4031(12)	F(3)	5394(12)	2956(11)	−979(9)
C(7)	−1615(17)	1586(14)	2976(14)	F(4)	5432(24)	2391(18)	472(15)
C(8)	3675(9)	2476(8)	2372(8)	F(5)	7282(22)	2764(20)	408(13)
C(9)	4153(14)	3884(2)	2854(11)	F(6)	5185(20)	4133(20)	611(16)
C(10)	4972(15)	2014(2)	2820(12)				

water (3 × 5 cm^3) and dried thoroughly. The decarbonylation of the products **6** (R″ = H or Ph) in solution prevented their isolation in a pure state for full characterization and thus they were identified by spectroscopic means only.

$[Ru_2(\mu-SR'')(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ (R″ = H *or* Ph). A solution of complex **6** (R″ = H) (0.15 g, 0.12 mmol) or **6** (R″ = Ph) (0.20 g, 0.15 mmol) in acetone (*ca.* 5 cm^3) was stirred at room temperature for 15 h. The product was obtained in crystalline form by addition of diethyl ether (*ca.* 3 cm^3) and allowing the solution to stand at −20 °C. Yield: 80–90% (Found: C, 30.6; H, 4.9; N, 2.4. Calc. for $C_{32}H_{67}F_6N_2O_{12}P_4Ru_2SSb$: C, 30.6; H, 5.2; N, 2.2. Found: C, 33.9; H, 5.9; N, 2.2. Calc. for $C_{38}H_{71}F_6N_2O_{12}P_4Ru_2SSb$: C, 34.0; H, 5.3; N, 2.1%).

$[Ru_2(\mu\text{-}S)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. An excess of an aqueous solution (*ca.* 3 cm^3) of potassium hydroxide (0.03 g, 0.54 mmol) was added to a solution of complex **6** (R'' = H) (0.10 g, 0.08 mmol) in dichloromethane (*ca.* 3 cm^3) and the two-layered mixture was vigorously stirred for 30 min. The dichloromethane layer was separated from the aqueous layer and the solvent removed under reduced pressure. The yellow residue was extracted with toluene (5 × 3 cm^3) and the combined extracts were concentrated under reduced pressure to *ca.* 2 cm^3. Crystallization of the product was effected by addition of methanol. Yield: 80% (Found: C, 38.1; H, 4.4; N, 2.7. Calc. for $C_{32}H_{66}N_2O_{12}P_4Ru_2S$: C, 37.4; H, 4.4; N, 2.7%).

$[Ru_2\{OC(O)R'''\}(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ (R''' = H, Me, Ph *or* CF_3). An excess of HCO_2H (0.05 g, 1.09 mmol), $MeCO_2H$ (0.05 g, 0.83 mmol), $PhCO_2H$ (0.07 g, 0.60 mmol) or CF_3CO_2H (0.05 g, 0.44 mmol) was added to a solution of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ (0.15 g, 0.10 mmol) in acetone (*ca.* 5 cm^3) and stirred at room temperature for 1 h for R''' = H, Me or CF_3 or for 2 d for R''' = Ph. An excess of pyridine (0.03 g, 0.40 mmol) was added and the solvent removed under reduced pressure. The residue was washed in turn with warm water (3 × 5 cm^3) and diethyl ether (3 × 5 cm^3), dried and crystallized from chloroform–hexane. Yield: 60–80% (Found: C, 31.4; H, 5.1; N, 2.5. Calc. for $C_{34}H_{67}F_6N_2O_{15}P_4Ru_2Sb$: C, 31.3; H, 5.2; N, 2.1. Found: C, 30.9; H, 4.9; N, 2.4. Calc. for $C_{35}H_{69}F_6N_2O_{15}P_4Ru_2Sb$: C, 31.9; H, 5.3; N, 2.1. Found: C, 36.6; H, 5.2; N, 2.1. Calc. for $C_{40}H_{71}F_6N_2O_{15}P_4Ru_2Sb$: C, 34.8; H, 5.2; N, 2.0. Found: C, 31.0; H, 4.8; N, 2.1. Calc. for $C_{35}H_{66}F_9N_2O_{15}P_4Ru_2Sb$: C, 30.6; H, 4.9; N, 2.0%).

$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R''')O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ (R''' = H, Me, Ph *or* CF_3). (*i*) A solution of the complex **10** (R''' = H) (0.15 g, 0.11 mmol), **10** (R''' = Me) (0.20 g, 0.15 mmol), **10** (R''' = Ph) (0.15 g, 0.11 mmol) or **10** (R''' = CF_3) (0.15 g, 0.11 mmol) in acetone (*ca.* 100 cm^3) was irradiated with ultraviolet light through Pyrex glass for 10 min during which time the colourless solution turned yellow. The solvent was removed under reduced pressure and the residue crystallized from chloroform–diethyl ether. Yield: 80–90%. (Found: C, 31.0; H, 4.9; N, 2.3. Calc. for $C_{34}H_{69}F_6N_2O_{14}P_4Ru_2Sb$: C, 31.6; H, 5.4; N, 2.2. Found: C, 34.6; H, 4.9; N, 2.3. Calc. for $C_{39}H_{71}F_6N_2O_{14}P_4Ru_2Sb$: C, 34.6; H, 5.3; N, 2.1. Found: C, 30.3; H, 4.9; N, 1.9. Calc. for $C_{34}H_{66}F_9N_2O_{14}P_4Ru_2Sb$: C, 30.3; H, 5.0; N, 2.1%).

(*ii*) An equimolar amount of solid sodium formate (0.12 g, 0.17 mmol), sodium acetate (0.14 g, 0.17 mmol) or sodium benzoate (0.24 g, 0.17 mmol) was added to a solution of **2** (solv = H_2O) (0.25 g, 0.17 mmol) in acetone (*ca.* 5 cm^3) and the mixture stirred for 1 h. The solvent was removed under reduced pressure and the residue washed with water (3 × 5 cm^3), dried and crystallized from chloroform–diethyl ether. Yield: 60–70%.

X-*Ray Crystallography*.—Cell dimensions and intensity data were recorded as previously described using a CAD4 diffractometer.[28] The structures were solved and developed *via* the heavy-atom method and refined by full-matrix least squares using the program SHELX 76.[29] Absorption corrections were applied using the ψ-scan semiempirical method. The non-hydrogen atoms of each structure were refined anisotropically except for the carbon atoms of $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OEt)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ and $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$ and the acetone solvent molecule atoms of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2\cdot OCMe_2$. Hydrogen atoms were not located. Crystal data and experimental details are given in Table 6. Final fractional atomic coordinates are given in Tables 7–10.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond distances and angles.

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