Protonation of Diphosphazane Ligand-bridged Derivatives of Diruthenium Nonacarbonyl by Protic Acids with Co-ordinating and Non-co-ordinating Conjugate Bases†

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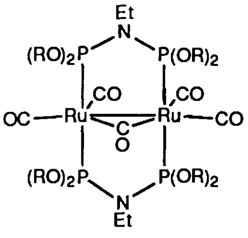
Protonation of the diphosphazane ligand-bridged derivatives $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) by HBF_4 or HPF_6 leads to the formation of the cationic hydrido products $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ in which the hydride ligand is co-ordinated terminally. On the other hand, protonation of these species with strong protic acids HA having conjugate bases A^- with co-ordinating properties [$A^- = Cl^-, Br^-, NO_3^-, FB(O)OH^-$ or $CF_3CO_2^-$] gives rise to products of the type $[Ru_2A(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and/or $[Ru_2(\mu\text{-}A)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$. Weak acids HA ($A^- = SPh^-$ or HCO_3^-) also afford these types of products but the presence of a strong acid such as HPF_6 is necessary. The structures of two of the products $[Ru_2\{\mu\text{-}OB(F)OH\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]BF_4$ and $[Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ have been established by X-ray crystallography and are discussed as is the fluxional behaviour of the hydrido species $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$.

The protonation of electron-rich dinuclear metal complexes is a recognized procedure for the synthesis of dinuclear metal hydride complexes. For instance, treatment of the dirhodium species $[Rh_2(CO)_3(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ with toluene-*p*-sulfonic acid or hexafluorophosphoric acid etherate has been shown to lead to the formation of the hydrido-bridged product $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]A$ (A^- = $p\text{-}MeC_6H_4SO_3^-$ or PF_6^-).[1] Provided the parent compounds are sufficiently electron-rich, diprotonation may be effected to afford, in these cases, dihydride products as observed, for example, in the protonation of $[Pt_2(\mu\text{-}R_2PCH_2PR_2)_3(PPh_3)_n]$ ($n = 0$, R = Et; $n = 1$, R = Me; $n = 2$, R = OEt) by NH_4PF_6 which afforded $[Pt_2H_2(\mu\text{-}R_2PCH_2PR_2)_3]^{2+}$.[2] The protonation of dinuclear metal hydrides may lead, however, to products resulting from the loss of dihydrogen and thus reaction of the neutral diiridium tetrahydride $[Ir_2H_4(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ with $HBF_4{\cdot}Et_2O$ produces the cationic trihydride $[Ir_2(\mu\text{-}H)_2H(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]^+$ which can be protonated further to the dicationic tetrahydride $[Ir_2(\mu\text{-}H)_2H_2(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]^{2+}$.[3] Use of hydrogen halides to protonate dinuclear metal hydrides can result in the accompanying co-ordination of the halide ion and reaction of $[Rh_2(\mu\text{-}H)_2(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ with HCl and HBr, for instance, gives $[Rh_2Cl_2(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ and $[Rh_2Br_2(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ and $[Rh_2(\mu\text{-}H)Br_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_2]Br$ respectively.[4] Other examples of the synthesis of dinuclear metal hydrides by protonation of dinuclear metal complexes are provided by those protonation reactions involving $[Fe_2(cp)_2(\mu\text{-}CO)_2(CO)_2]$ (cp = $\eta\text{-}C_5H_5$),[5–8] $[Mn_2(\mu\text{-}\eta^2\text{-}CO)(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2]$,[9–12] $[Rh_2(cp)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)]$[13] and $[MPt(\mu\text{-}PPh_2)(cp)(CO)_3(PPh_3)]$ (M = Mo or W).[14]

We have shown previously that the highly unstable diruthenium nonacarbonyl, $[Ru_2(CO)_9]$,[15] can be stabilized by substitution of the carbonyl groups by the diphosphazane ligands $(RO)_2PN(Et)P(OR)_2$ (R = Me, Et or Pr^i)[16] and that the products obtained *viz.* $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **1** are electron rich and susceptible to electrophilic attack.[17–25] We now report the behaviour of these compounds to protic attack and how the nature of the product is dependent on the co-ordination properties of the conjugate base of the acid employed. Some of these results have been communicated previously.[26,27]



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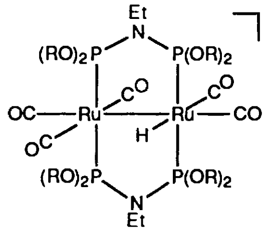

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Results and Discussion

Synthetic Studies.—(*i*) *Protonation by acids* HA *with non-co-ordinating conjugate bases* A^-. Treatment of the diruthenium species $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) **1** with the protic acids $HBF_4{\cdot}Et_2O$ in diethyl ether or aqueous HPF_6 in CH_2Cl_2, both acids containing conjugate bases with very weak ligating properties, was shown to lead to the formation of either white (PF_6^-) or pale yellow (BF_4^-) crystalline products which after recrystallization were characterized as the hydride derivatives $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]A$ (A^- = BF_4^- or PF_6^-) **2** A. The solid-state and solution IR spectra of these compounds were found to exhibit similar band patterns in the C–O stretching region with the frequencies of the constituent peaks corresponding to those of terminal carbonyls only. This observation can only be interpreted in terms of the hydride ligand in these species co-ordinating terminally as shown.

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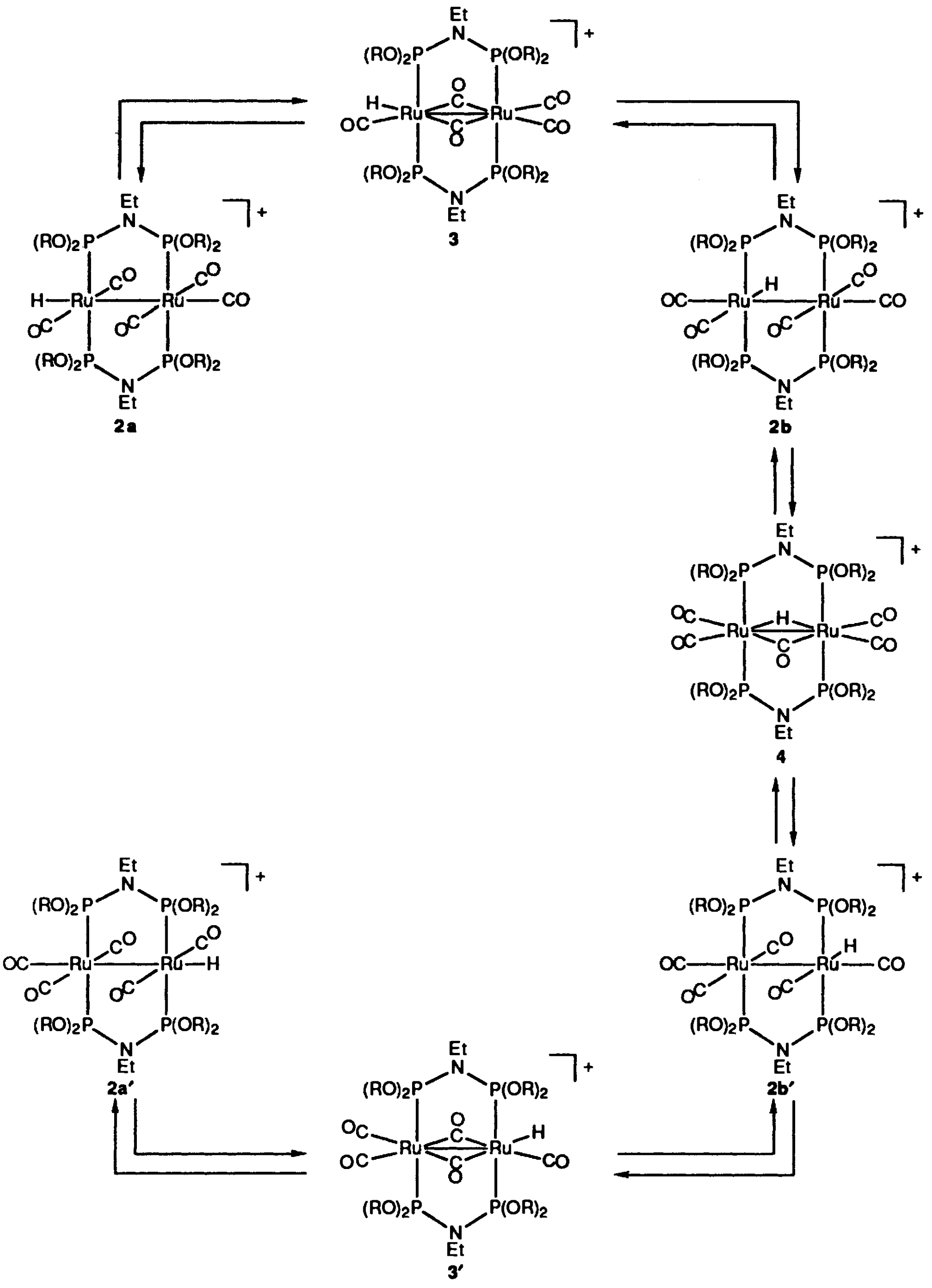
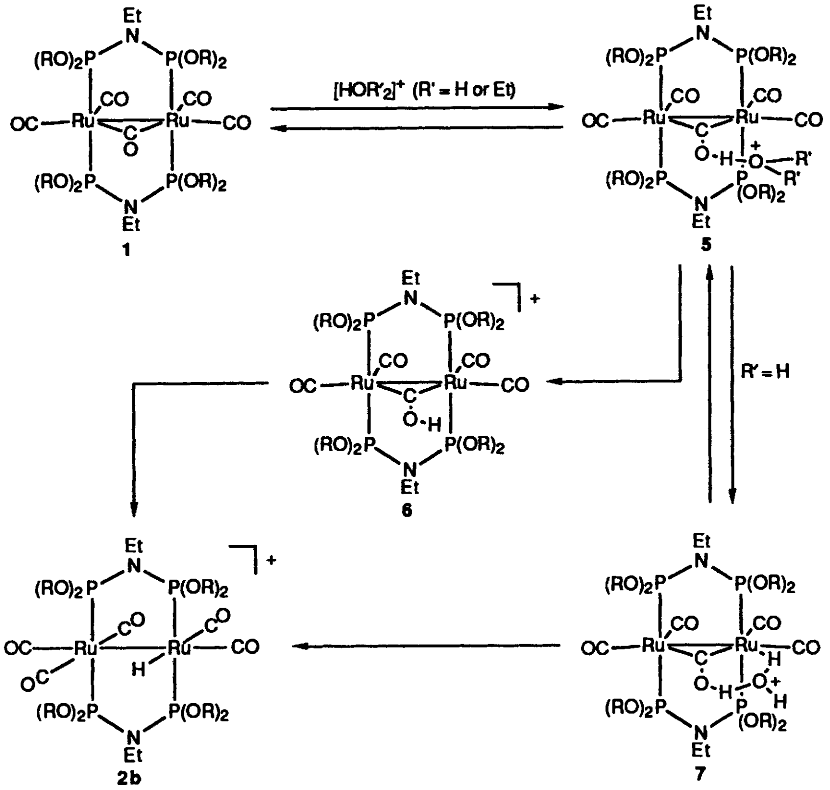
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



Scheme 1

The room-temperature ^1H NMR spectra of these species exhibit a well resolved quintet in the region $\delta = -7.0$ to -8.5, readily assigned to the hydride ligand, with the chemical shift thereof, although being dependent on the solvent, the counter ion and the bridging diphosphazane ligand, being consistent with the hydride ligand co-ordinating terminally. However, the room-temperature (30 °C) $^{31}P\text{-}\{^1H\}$ NMR spectra of these compounds contain a relatively sharp singlet corresponding to the diphosphazane ligands which is inconsistent with a terminally bonded hydride unless the latter is rapidly exchanging co-ordination sites leading to the apparent equivalence of the phosphorus atoms. A variable-temperature $^{31}P\text{-}\{^1H\}$ NMR spectroscopic study of $[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]BF_4$ in deuteriated acetone revealed that a decrease in the temperature of the solution to 0 °C resulted in some broadening of the singlet observed at room temperature and the appearance of a set of sharp peaks of much weaker intensity than the singlet and spanning a narrow frequency range while a further decrease in temperature to −30 °C led to appreciable broadening of the singlet and an apparent increase in intensity of the AA′BB′ pattern of peaks. Further decreases in temperature to −60 and −90 °C respectively resulted initially in the collapse of the singlet and subsequently in the formation of a second set of peaks of AA′BB′ pattern. This set of peaks was much more intense and spanned a much greater frequency range than the first set, with the latter appearing to continue to increase in intensity from −30 to −90 °C albeit by a limited amount. A singlet was again observed on raising the temperature of the solution to 30 °C. Similar variable-temperature $^{31}P\text{-}\{^1H\}$ NMR spectral behaviour was observed for $[Ru_2H(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$. These results are reconciled as follows. First, the presence of two sets of peaks of AA′BB′ pattern in the −90 °C spectrum is explained in terms of the occurrence of two isomers, **2a** and **2b**, in solution

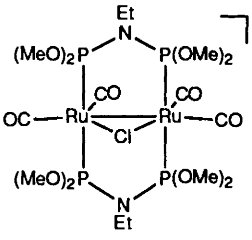


Scheme 2

at low temperature with the one being considerably more abundant than the other (see Scheme 1). Secondly, the existence of a singlet in the room-temperature spectrum and the variable-temperature NMR behaviour observed for it is interpreted in terms of one of two explanations. The one is that the cationic hydride occurs essentially as a single isomer, **2b**, in solution at room temperature and that the terminal hydrogen atom in this species rapidly migrates to the other ruthenium atom *via* $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ **4** as intermediate to give its mirror image **2b'**, thereby giving rise to the apparent equivalence of the phosphorus atoms. A decrease in the temperature of the solution results in the formation of a second isomer in solution in small but increasing quantities as well as to a decrease in the rate of exchange of the hydrogen atom between the two ruthenium atoms in the major isomer with this decrease leading eventually to the presence of the second AA'BB' pattern of peaks in the spectrum. The alternative explanation is that $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ exists to a small extent as isomer **2a** as well as isomer **2b** in solution at room temperature and that the hydrogen atom migrates rapidly around the two ruthenium atoms in a plane perpendicular to that defined by the two ruthenium and the four phosphorus atoms by the merry-go-round process illustrated in Scheme 1; the Scheme only depicts half of the actual process. The variable-temperature NMR behaviour is reconciled in terms of the rate of exchange between an axial and an equatorial isomer being less than that between an equatorial isomer, **2b**, and its mirror image, **2b'**. Significantly, the hydride-bridged carbonyl-bridged species $[M_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4(\mu\text{-}R'_2PYPR'_2)_2]^+$, structurally analogous to intermediate **4**, is the isomeric form of the product isolated from the protonation reactions of $[M_2(\mu\text{-}CO)(CO)_4(\mu\text{-}R'_2PYPR'_2)_2]$ [M = Fe, Y = CH_2, R' = Me or Ph; M = Fe, Y = N(Et), R' = OMe, OEt, OPr^i or OPh; M = Ru, Y = CH_2, R' = Me or Ph][26,28] while, although species of the type $[M_2H(\mu\text{-}CO)_2(CO)_3(\mu\text{-}R'_2PYPR'_2)_2]^+$ (*cf.* **3**) are unknown, the diiridium species $[Ir_2(\mu\text{-}H)_2H(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]^+$ and $[Ir_2(\mu\text{-}H)_2H_2(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]^{2+}$, obtained by protonation of $[Ir_2H_4(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]$, are structurally related to **3**.[3]

The protonation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ is reversible but in contrast to that observed for $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$,[26] a strong base such as $NaBH_4$ is required to deprotonate the cationic hydrido species.

It has been reported previously that protonation of $[M_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ (M = Fe, Ru or Os) at low temperature under anhydrous conditions affords the O-protonated products $[M_3(\mu\text{-}H)(\mu\text{-}COH)(CO)_{10}]$ which, at slightly higher temperatures, rearrange to the dihydride $[M_3(\mu\text{-}H)H(CO)_{11}]$ and subsequently to $[M_3(CO)_{12}]$ in the case of the iron and ruthenium hydrides.[29–31] Likewise, the O-protonated product $[Fe_4(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}COH)(CO)_{12}]$, proposed as an intermediate in the proton-induced reduction of carbon monoxide in $[Fe_4(CO)_{13}]^{2-}$,[32] has been shown to be formed on protonation of $[Fe_4H(CO)_{13}]^-$ at 90 °C.[33] Significantly, the addition of $HBF_4\cdot Et_2O$ to an anhydrous pale yellow solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ in diethyl ether was found to lead initially to the spontaneous formation of a red solution which rapidly decolourised with formation of a pale yellow solution from which the pale yellow crystalline hydride $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]BF_4$ separated quantitatively. An apparent intermediate in the formation of the hydride could also be detected by monitoring the protonation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ with $HBF_4\cdot Et_2O$ in tetrahydrofuran (thf) at −60 °C by means of $^{31}P\text{-}\{^1H\}$ NMR spectroscopy; a singlet at δ 138.9, observed in the early stages of the addition of the $HBF_4\cdot Et_2O$, was found to disappear with the appearance of the broad singlet (at δ 143.7) resulting from the formation of $[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]BF_4$. On the basis of the above studies, it is assumed that the site of the initial attack of the protonated etherate on $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ is at the oxygen of the bridging carbonyl group and that the red colour and the singlet at δ 138.9 in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the monitored reaction arises from the formation of the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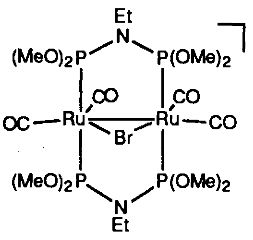
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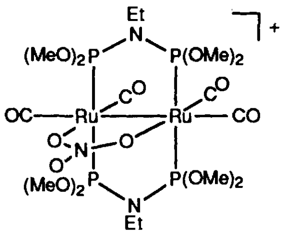
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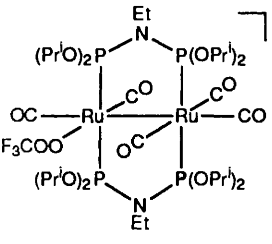
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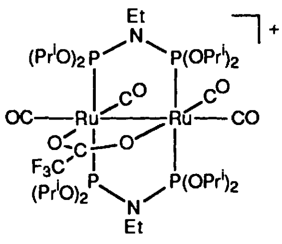
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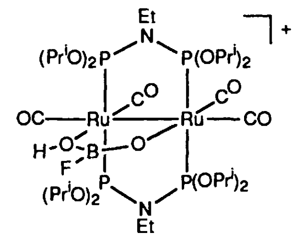
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O-protonated product $[Ru_2(\mu\text{-COH})(CO)_4\{\mu\text{-(RO)}_2PN(Et)P(OR)_2\}_2]^+$ **6**. Johnson and Gladfelter[34] have recently shown that one of the major products of the reaction of the related bis(dimethylphosphino)methane-bridged derivative $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-}Me_2PCH_2PMe_2\}_2]$ with methyl trifluoromethanesulfonate is the methoxymethylidyne-bridged cationic species $[Ru_2(\mu\text{-COMe})(CO)_4\{\mu\text{-}Me_2PCH_2PMe_2\}_2]^+$ resulting from the direct methylation of the oxygen of the bridging carbonyl of the parent compound.

The rate of formation of the cationic hydride $[Ru_2H(CO)_5\{\mu\text{-(RO)}_2PN(Et)P(OR)_2\}_2]^+$ in these protonation reactions was found to be markedly increased by the addition of water to the reaction mixture. This increase can be readily explained in terms of Scheme 2, with the water catalysing the proton transfer from the oxygen of the bridging carbonyl to the ruthenium atom *via* the six-membered transition state **7**.

(*ii*) *Protonation by acids* HA *with co-ordinating conjugate bases* A^-. Reaction of the tetramethoxydiphosphazane parent complex $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-(MeO)}_2PN(Et)P(OMe)_2\}_2]$ with the hydrogen halides HCl and HBr in diethyl ether was found not to afford the hydride $[Ru_2H(CO)_5\{\mu\text{-(MeO)}_2PN(Et)P(OMe)_2\}_2]^+$ but to lead instead to the formation and the separation of products characterized as $[Ru_2(\mu\text{-Cl})(CO)_4\{\mu\text{-(MeO)}_2PN(Et)P(OMe)_2\}_2]Cl$ **8** Cl and $[Ru_2(\mu\text{-Br})(CO)_4\{\mu\text{-(MeO)}_2PN(Et)P(OMe)_2\}_2]Br$ **9** Br respectively. These compounds, in which the two ruthenium atoms are bridged by a halogeno group as well as by two diphosphazane ligands, have been synthesized previously by direct reaction of $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-(MeO)}_2PN(Et)P(OMe)_2\}_2]$ with the appropriate halogen.[20,22]

$$[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-(RO)}_2PN(Et)P(OR)_2\}_2] + R''CO_2H \rightleftharpoons [Ru_2H(CO)_5\{\mu\text{-(RO)}_2PN(Et)P(OR)_2\}_2]^+ + R''CO_2^-$$

Scheme 3 R = Me or Pr^i; R'' = H, Me or Ph

A related nitrato-bridged cationic species, $[Ru_2\{\mu\text{-ON(O)O}\}(CO)_4\{\mu\text{-(MeO)}_2PN(Et)P(OMe)_2\}_2]^+$ **10**, was found to be formed on treatment of $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-(MeO)}_2PN(Et)P(OMe)_2\}_2]$ with nitric acid in 1,2-dimethoxyethane (dme). This species, which was isolated and characterized as the hexafluorophosphate salt, afforded a singlet in its $^{31}P\text{-}\{^1H\}$ NMR spectrum, consistent with the symmetrical structure shown. Sulfuric and phosphoric acids were also shown to react with the neutral parent complexes $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-(RO)}_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) but in these cases the product was established to be the protonated species $[Ru_2H(CO)_5\{\mu\text{-(RO)}_2PN(Et)P(OR)_2\}_2]A$ **2** A ($A^- = HSO_4^-$ or $H_2PO_4^-$) which were readily converted to the hexafluorophosphate salts.

The parent compounds $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-(RO)}_2PN(Et)P(OR)_2\}_2]$ are also susceptible to attack by carboxylic acids, but the nature of the product is dependent on the strength of the carboxylic acid. For instance, reaction of $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ with trifluoroacetic acid afforded a product, characterized as the hexafluorophosphate salt, as the pentacarbonyl species $[Ru_2\{\sigma\text{-OC(O)CF}_3\}(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ **11** in which the trifluoroacetato group is terminally bonded to one of the ruthenium atoms on the basis of the presence of an AA'BB' pattern of peaks in its $^{31}P\text{-}\{^1H\}$ NMR spectrum. The site of co-ordination of the latter, *viz.* axial or equatorial, could not be established from the spectroscopic data however. The hexafluorophosphate salt of this pentacarbonyl species could be readily converted to the tetracarbonyl derivative $[Ru_2\{\mu\text{-OC(CF}_3)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$ **12** PF_6 by decarbonylation under photochemical conditions. The trifluoroacetato group adopts a bridging co-ordination mode in this species as established from the presence of a single singlet in its $^{31}P\text{-}\{^1H\}$ NMR spectrum. With the weaker carboxylic acids $R''CO_2H$ on the other hand, where R'' = H, Me or Ph, the hydride $[Ru_2H(CO)_5\{\mu\text{-(RO)}_2PN(Et)P(OR)_2\}_2]^+$ was shown to be in equilibrium with the parent species $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-(RO)}_2PN(Et)P(OR)_2\}_2]$ according to Scheme 3. This equilibrium can be shifted to the right by using an excess of the carboxylic acid but attempts to isolate the protonated species as the carboxylate salt led to its deprotonation by the carboxylate anion and the formation of the parent derivative $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-(RO)}_2PN(Et)P(OR)_2\}_2]$. Significantly, the presumably more basic diruthenium complex $[Ru_2(\mu\text{-H})_4(\eta\text{-}C_5Me_5)_2]$ reacts with formic, acetic and benzoic acids, as well as with trifluoroacetic acid, to afford a carboxylato-bridged product *viz.* $[Ru_2(\mu\text{-H})_2\{\mu\text{-OC(R')O}\}_2(\eta\text{-}C_5Me_5)_2]$ (R' = H, Me, Ph or CF_3).[35]

Treatment of a diethyl ether solution of $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ with a batch of tetrafluoroboric acid diethyl etherate, which was subsequently established to be impure, resulted in the separation from solution of a most unexpected product. Instead of the anticipated hydride $[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$, a product characterized by X-ray crystallography, as well as by conventional methods, as the fluoroborato derivative $[Ru_2\{\mu\text{-OB(F)OH}\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]BF_4$ **13** BF_4 was found to be formed. A more controlled method of synthesis of this compound has now been developed and involves the addition of small amounts of water to a solution of $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ and excess $HBF_4\cdot Et_2O$ in a thf–

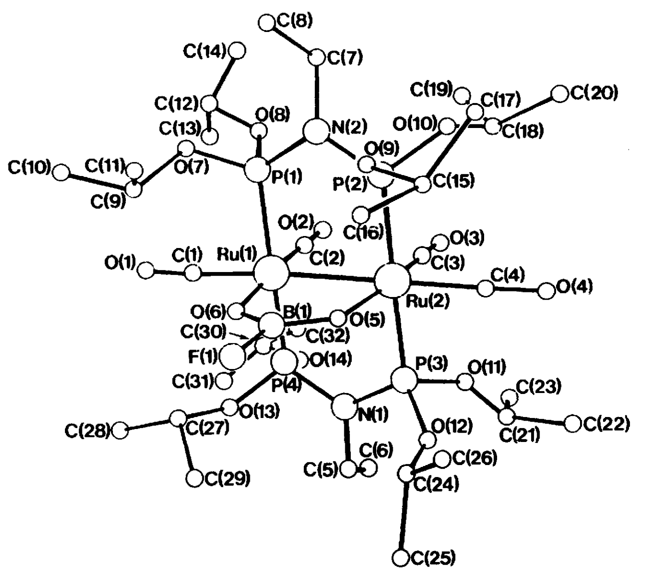


Fig. 1 Stereochemistry of $[Ru_2\{\mu\text{-}OB(F)OH\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ showing the atom labelling scheme

diethyl mixture and allowing the solution to stand for at least 5 d, preferably 2–3 weeks, in a glass vessel. In this context it is relevant that reaction of $[Rh_2(cp)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)]$ with an impure sample of $AgPF_6$ has been shown to afford $[Rh_2(cp)_2(\mu\text{-}AgOPF_2O)(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)]$ containing a difluorophosphate ion co-ordinated to the bridging silver atom[36] while Maitlis and co-workers[37] have reported that $[Rh_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}OPF_2O)_3]PF_6$ can be generated by partial solvolysis of the hexafluorophosphate ion in $[Rh(\eta\text{-}C_5Me_5)(Me_2SO)_3][PF_6]_2$.

The stereochemistry of the cation of $[Ru_2\{\mu\text{-}OB(F)OH\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]BF_4$ is illustrated in Fig. 1. The two ruthenium atoms, which are separated by a distance of 2.814 Å, corresponding to a formal ruthenium–ruthenium bond, are bridged by a novel OB(F)OH group as well as by two tetraisopropoxydiphosphazane ligands. The two ruthenium atoms, the four carbonyls and the oxygen, boron and fluorine atoms of the OB(F)OH group lie in a plane which is orthogonal to a plane containing the two ruthenium and four phosphorus atoms. Significantly, the planar geometry of the OB(F)O fragment in this species is in contrast to the puckered configuration established for the acetate group in $[Ru_2\{\mu\text{-}OC(Me)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$,[38] as reflected by the P(1)–Ru(1)–Ru(2)–P(2) and P(4)–Ru(1)–Ru(2)–P(3) torsion angles of 5.5 and 3.7° respectively in the former, compared with corresponding torsion angles of 17.3 and 13.9° for the latter. The hydrogen of the OB(F)OH group could not be detected by X-ray crystallography but its site of co-ordination could be inferred from the NMR spectroscopic data. In particular, the $^{31}P\text{-}\{^1H\}$ NMR spectrum of this species was shown to exhibit a singlet corresponding to the phosphorus atoms of the diphosphazane ligands which is consistent with this hydrogen, identified by means of ^1H NMR spectroscopy, bridging the two oxygen atoms of the fluoroborato group. Two alternative sites of co-ordination cannot be summarily eliminated however. Terminal bonding of the hydrogen to one of the oxygen atoms of the fluoroborato group is one possibility, but a rapid exchange of the hydrogen between the two oxygen atoms has to be assumed to explain the $^{31}P\text{-}\{^1H\}$ NMR spectral data. This could involve either an intra- or an inter-molecular mechanism. Alternatively, the hydrogen may be bonded directly to the fluorine atom, but to reconcile the presence of a singlet corresponding to the fluorine atom in the fluoroborato group in the ^{19}F NMR spectrum of this compound, a rapid reversible dissociation of the hydrogen from the fluorine would have to be invoked.

Mechanism of Reaction.—In proposing a mechanism for the formation of $[Ru_2A(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and/or $[Ru_2(\mu\text{-}A)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ in the reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ with the acid HA, a number of observations were taken into consideration.

(*i*) The formation of the hydride $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ by protonation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ requires a strong acid with the conjugate bases of the weaker acids deprotonating the hydride under appropriate reaction conditions. Thus the extent of protonation of the neutral pentacarbonyl derivative by acetic acid is limited even when an excess of the acid is employed (see above) while treatment of the protonated species with sodium acetate in methanol produces $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ in quantitative yield.

(*ii*) The hydride $[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ as well as the neutral pentacarbonyl $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ affords the trifluoroacetato product $[Ru_2\{\sigma\text{-}OC(O)CF_3\}(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ on treatment with trifluoroacetic acid.

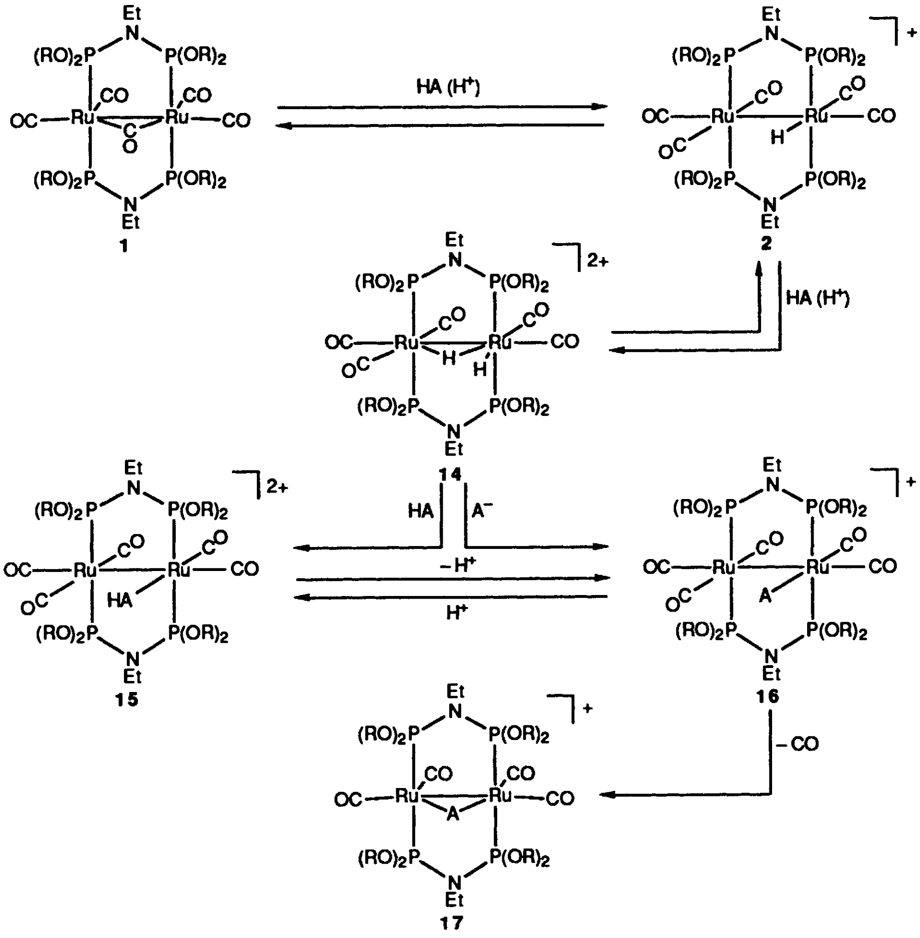
(*iii*) Reaction of $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ with anionic ligands X^- such as halide or nitrate ions does not lead to the formation of $[Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and/or $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ unless, in certain cases, a strong acid such as HBF_4 is present.

(*iv*) The formation of $[Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and/or $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ only occurs for those protonation reactions involving strong acids and, in particular, for those reactions in which the acid is sufficiently strong presumably to protonate $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ to a diprotonated product $[Ru_2H_2(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ and in which the conjugate base X^- is sufficiently nucleophilic to substitute H_2 in this species.

(*v*) It has been established previously that reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ with silver(I) ions in acetone affords the acetone solvento species $[Ru_2(CO)_5(Me_2CO)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ [19] which on treatment with carboxylic acids $R'CO_2H$ produces sequentially $[Ru_2(CO)_5\{\sigma\text{-}O(H)C(O)R'\}(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ and $[Ru_2\{\sigma\text{-}OC(O)R'\}(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$.[38] Significantly, although this species could be decarbonylated to $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R')O\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$, photolytic conditions were necessary, whereas reaction of the acetone solvento species with carboxylate anions[38] or reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ with silver carboxylate in acetone[39] leads directly to the formation of the bridged carboxylato species under non-photolytic conditions. On the other hand, both benzenethiol and its conjugate base afford the bridged sulfido species $[Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ on reaction with $[Ru_2(CO)_5(Me_2CO)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ under non-photolytic conditions.[38]

(*vi*) A product, presumably the diprotonated species $[Ru_2H_2(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ (see below) could be detected spectroscopically in the reactions of $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ with strong acids such as $HBF_4\cdot Et_2O$ but it was only found to exist in appreciable quantities in the presence of an excess of these acids and all attempts to isolate it led instead to the isolation of the monoprotonated species. More significantly, the known stable solvento species $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ (solv = MeCN, PhCN, Me_2CO, thf, or H_2O)[19] could not be detected in any of these reactions irrespective of the solvent employed and the amount of acid utilized. On this basis, it is concluded that the solvento species is not an intermediate in the formation of $[Ru_2A(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and/or $[Ru_2(\mu\text{-}A)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$.

(*vii*) Products of the type $[Ru_2(\mu\text{-}A)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ in which the Ru_2A moiety occurs as a five-

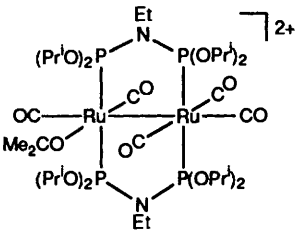


Scheme 4

membered dimetallocyclic ring have only been obtained for conjugate bases of the type $\mathrm{D}\cdots\mathrm{Y(Z)}\cdots\mathrm{D}$ (D = donor atom, Y = linking atom) where the bonding over the DYD fragment is delocalized and the conjugate base itself is planar. Thus products of this type have been isolated where the conjugate base is $\mathrm{NO_3^-}$, $\mathrm{CF_3CO_2^-}$ or $\mathrm{FB(O)OH^-}$ but not in the case of $\mathrm{HSO_4^-}$ or $\mathrm{H_2PO_4^-}$.

Formally, the formation of $[\mathrm{Ru_2A(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ from $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]$ involves the addition of the electrophile $\mathrm{A^+}$ such that in a formal sense the acid HA exhibits a type of umpolung behaviour. The presence of protons is obviously necessary for this addition to occur and a reaction pathway which will account for the formation of $[\mathrm{Ru_2(\mu\text{-}A)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ as well as $[\mathrm{Ru_2A(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ in the reactions of $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]$ with acids of formula HA is that presented in Scheme 4. The first step in the Scheme involves the protonation of the parent complex to produce the monoprotonated species $[\mathrm{Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ while the second involves further protonation to afford a diprotonated intermediate, possibly $[\mathrm{Ru_2H_2(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^{2+}$ or $[\mathrm{Ru_2(\mu\text{-}H)H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^{2+}$ **14**; Scheme 4 illustrates only one possibility for this intermediate. The proposed formation of a diprotonated intermediate is consistent with the formation of $[\mathrm{Ru(cp)(\eta^2\text{-}H_2)(PPh_3)(CNBu^t)}]\mathrm{PF_6}$, containing an $\eta^2\text{-}\mathrm{H_2}$ ligand, in the reaction of $[\mathrm{Ru(cp)H(PPh_3)(CNBu^t)}]$ with $\mathrm{HPF_6}$[40] and the observation that hydrogen is liberated on reaction of $[\mathrm{Rh_2(\mu\text{-}H)_2(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2}]$ with hydrogen chloride to afford $[\mathrm{Rh_2Cl_2(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2}]$, as described above. The third step in Scheme 4 involves the nucleophilic substitution of dihydrogen, by HA or its conjugate base $\mathrm{A^-}$ to give $[\mathrm{Ru_2(CO)_5(HA)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^{2+}$ **15** or $[\mathrm{Ru_2A(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ **16** respectively. Although $\mathrm{A^-}$ is undoubtedly a stronger nucleophile than its conjugate acid, HA, for weak acids the concentration of the latter in solution will be considerably greater than that of its conjugate base $\mathrm{A^-}$ such that possible attack of the diprotonated intermediate by HA cannot summarily be dismissed. Indeed it has recently been established that acetic acid will displace acetone from the solvento species $[\mathrm{Ru_2(CO)_5(Me_2CO)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]^{2+}$ **18** to afford $[\mathrm{Ru_2(CO)_5(\sigma\text{-}MeCO_2H)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]^{2+}$ **19** which is readily and reversibly deprotonated to $[\mathrm{Ru_2\{\sigma\text{-}OC(O)Me\}(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]^+$ **20**.[41] The final step in Scheme 4 is the decarbonylation of $[\mathrm{Ru_2A(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ **16** to afford, in the appropriate reactions, the bridged tetracarbonyl $[\mathrm{Ru_2(\mu\text{-}A)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ **17**.

Reactions involving Weak Acids HA.—On the basis of the proposed mechanism it was anticipated that a procedure could be developed for the synthesis of a wide range of species of the type $[\mathrm{Ru_2A(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ and/or $[\mathrm{Ru_2(\mu\text{-}A)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ which involved the addition of weak acids HA or their conjugate bases $\mathrm{A^-}$ to $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]$ in the presence of a strong acid; the weak acid HA would have to be sufficiently nucleophilic to displace dihydrogen from the diprotonated species $[\mathrm{Ru_2H_2(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^{2+}$ for this procedure to be effective. Indeed, although benzenethiol is unreactive towards $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]$ at room temperature, it readily affords $[\mathrm{Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ **21** on reaction with the neutral



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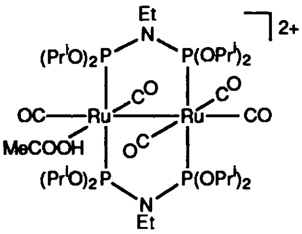

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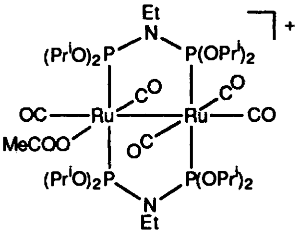

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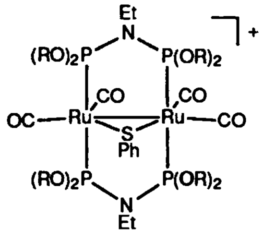

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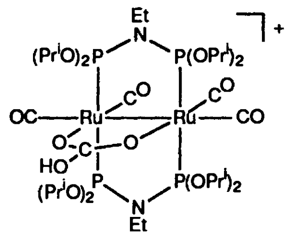

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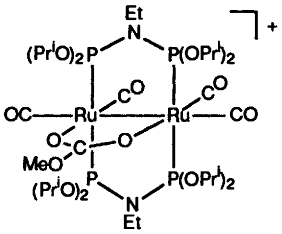

23

parent pentacarbonyl derivative in the presence of HPF$_6$. The stereochemistry of the cation of the tetramethoxydiphosphazane sulfido-bridged species, $[Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ **21** PF$_6$ (R = Me), which was characterized by X-ray crystallography as well as by conventional methods, is illustrated in Fig. 2. The structure is very similar to that of its parent[16] with the two ruthenium atoms being bridged by a SPh group as well as by two diphosphazane ligands and with the ruthenium–ruthenium distance of 2.796(1) Å corresponding to a formal ruthenium–ruthenium bond; the plane defined by the two ruthenium and the four phosphorus atoms is essentially orthogonal to the plane defined by the two rutheniums and the sulfur of the benzenethiolate group (dihedral angle = 84.6°). Two of the carbonyl groups are almost collinear with the Ru–Ru vector while the other two are essentially orthogonal to it. The phenyl group lies out of the Ru$_2$S plane with the vector defined by the sulfur and the adjacent carbon of the phenyl group subtending an angle of 44.1° with this plane. Consistent with this disposition of the phenyl group, a well resolved AA′BB′ pattern of peaks centred at δ 140.1 is observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of this compound, measured at −20 °C; this set of resonances collapses into a singlet at δ 138.1 at a temperature of 55 °C, resulting from inversion at the sulfur atom.

The reaction of H$_2$S with $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ in the presence of hexafluorophosphoric acid was also investigated but in this case no reaction was observed. It is assumed that the more basic H$_2$S (compared with PhSH) is protonated and in this form will not displace the dihydrogen from the diprotonated intermediate.

Carbon dioxide is also unreactive towards $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$, or for that matter towards $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$, both in the presence of water as well as under anhydrous conditions, but significantly, in the presence of a strong acid such as HPF$_6$ and under partially aqueous conditions, it has been shown to react with $[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ to afford a product believed to be the hydrogencarbonato-bridged derivative $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OH)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$ **22** PF$_6$ [ν(C–O): 2034s, 2004vs, 1984s and 1966m (sh) cm^{-1} measured in CH$_2$Cl$_2$]. Attempts to obtain crystals of this species by use of solvent mixtures such as acetone–diethyl ether or CH$_2$Cl$_2$–hexane always led to the separation of oils and thus its identity could not be established directly. However, yellow crystals of a derivative thereof could be obtained by crystallization of these oils from methanol–water. These were characterized as the methyl carbonato-bridged derivative $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OMe)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$ **23** PF$_6$ resulting presumably from the reaction of the hydrogencarbonato-bridged derivative with methanol.

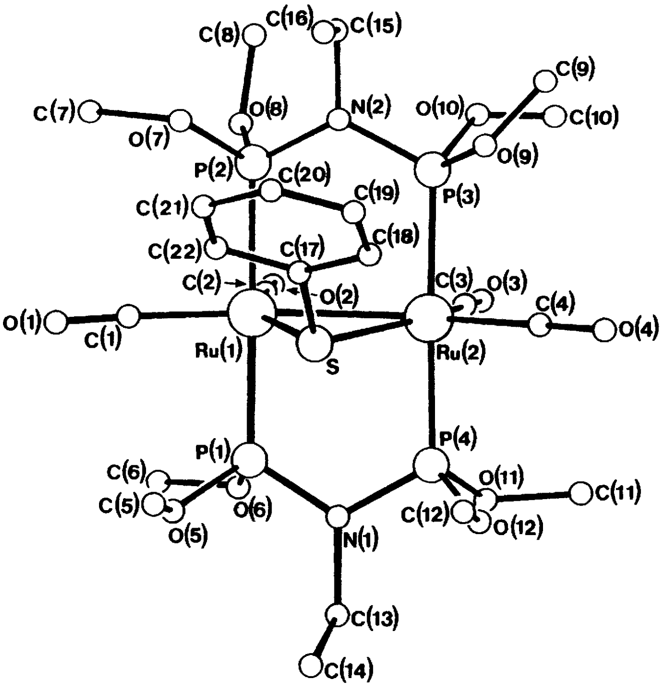

Fig. 2 Stereochemistry of $[Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ showing the atom labelling scheme

Methanol and benzoic acid proved unreactive towards $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ or $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ in the presence of HPF$_6$ whereas addition of methanol to $[Ru_2(CO)_5(solvent)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ has been shown to afford $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(OMe)\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ [18] while the corresponding reactions involving PhCO$_2$H and PhCO$_2^-$ have been established to give as final products, $[Ru_2\{\sigma\text{-}OC(O)Ph\}(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Ph)O\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ respectively.[38] It is thus concluded that, under the conditions of the reaction, MeOH and PhCO$_2$H occur in their protonated forms or alternatively are not sufficiently nucleophilic to displace H$_2$ from $[Ru_2H_2(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$.

The use of acids to catalyse reactions related to those described above and, in particular, the addition of acetylenes to metal complexes has been reported recently. Thus Higgins and Shaw[42] have shown that the addition of acetylenes HC≡CR (R = H, Ph or *p*-MeC$_6$H$_4$) to the dipalladium compounds $[Pd_2X_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ (X = Cl, Br or I) is promoted by traces of HBF$_4$ while Kashef and Richards[43] have established that reaction of *trans*-$[MoH_4(Ph_2PC_2H_4PPh_2)_2]$ with RCO$_2$C≡CH (R = Me or Et) affords the carboxylato-σ-alkenyl complexes $[MoH_2\{CH{=}CHC(OR)O\}(Ph_2PC_2H_4PPh_2)_2]BF_4$ in the presence of HBF$_4$.

Experimental

The neutral pentacarbonyls $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN\text{-}$

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

Compound	ν(CO)/cm^{-1} [a]	$^{31}P\text{-}\{^1H\}$ NMR [b,c]
$[Ru_2H(CO)_5(\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]BF_4$ [d]	2080w, 2108vs, 2131s, 1971m(br) [e]	144.4(s) [f]
$[Ru_2H(CO)_5(\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ [g]	2079w, 2036vs, 2016vs, 1985s [h]	150.7(s) [i]
$[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]BF_4$ [j]	2066w, 2030s, 2000vs, 1994(sh), 1974m [k]	143.7(s) [f] 145.5 [e] 147.9 [f,l,m]
$[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$ [n]	2064w, 2031s, 2000vs, 1995(sh), 1975m [h]	140.0(s) [i]
$[Ru_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]Cl$	2047m, 2020s, 1985ms, 1968w [h]	139.2(s) [i]
$[Ru_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]Br$	2042m, 2020s, 1985ms, 1966w [h]	143.7(s) [i]
$[Ru_2\{\mu\text{-}ON(O)O\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$	2051m, 2030vs, 1998s, 1983(sh) [h]	147.9(s) [f]
$[Ru_2(\sigma\text{-}OC(O)CF_3\}(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$ [o]	2091w, 2040vs, 2026vs, 1980m(br) [h]	130.8 [l]
$[Ru_2\{\mu\text{-}OC(CF_3)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$ [p]	2039s, 2010vs, 1982vs, 1958s [h]	138.1(s) [f]
$[Ru_2\{\mu\text{-}OB(F)OH\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]BF_4$ [q]	2032s, 2002vs, 1975vs, 1950m [h]	136.6(s) [i]
$[Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$	2040s, 2013vs, 1985vs, 1966m [h]	140.1 [i,l,r]
$[Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$	2032ms, 2001s, 1973ms, 1951m [h]	129.9(s) [s]
$[Ru_2\{\mu\text{-}OC(OH)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$	2034s, 2004vs, 1984s, 1966(sh) [h]	
$[Ru_2\{\mu\text{-}OC(OMe)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$	2037s, 2003vs, 1984s, 1964m [h]	130.9(s) [s]

[a] Abbreviations: v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad. [b] δ relative to H_3PO_4; measured at room temperature (*ca.* 30 °C) unless otherwise stated. [c] Abbreviations: s = singlet, qnt = quintet. [d] ^1H NMR $[(CD_3)_2CO]$: δ −8.02 [qnt, $^2J(PH)$ 10.1 Hz, RuH], δ relative to $SiMe_4$. [e] In acetone. [f] In $[^2H_6]$acetone. [g] ^1H NMR $[(CD_3)_2SO]$: δ −8.02 [qnt, $^2J(PH)$ 10.1 Hz, RuH]. [h] In CH_2Cl_2. [i] In CD_2Cl_2. [j] ^1H NMR $[(CD_3)_2CO]$: δ −7.40 [qnt, $^2J(PH)$ 10.4 Hz, RuH]. [k] In thf. [l] Centre of an AA′BB′ pattern of peaks. [m] At −90 °C. [n] ^1H NMR (CD_2Cl_2): δ − 7.57 [qnt, $^2J(PH)$ 10.4 Hz, RuH]. [o] ^{19}F NMR $[(CD_3)_2CO]$: δ −70.4 (s, 3F) and −69.4 [d, 6F, $^1J(PF)$ 707.5 Hz], δ relative to $CFCl_3$. [p] ^{19}F NMR: δ − 70.3 (s, 3F) and −69.5 [d, 6F, $^1J(PF)$ 707.3 Hz]. [q] ^{19}F NMR: δ −152.2 (s, 1F) and −152.3 (s, 4F). [r] At −20 °C. [s] In $CDCl_3$.

$(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) were synthesised according to a literature method.[16] All reactions and operations were carried out under an atmosphere of nitrogen. The IR and NMR spectra were recorded on a Perkin-Elmer model 457 spectrophotometer and on a Varian FT80A instrument respectively. Light petroleum refers to that fraction of b.p. 60–80 °C.

Syntheses.—$[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]BF_4$. An excess of $HBF_4\cdot Et_2O$ (0.5 g, 54% solution in diethyl ether, 3 mmol) in diethyl ether (3 cm^3) was added to a stirred solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.51 g, 0.5 mmol) in diethyl ether (150 cm^3) at room temperature. The solution immediately turned red and within 2 min light yellow, and a pale yellow microcrystalline solid separated. This was isolated after 2 h, washed with diethyl ether and crystallized from acetone–diethyl ether. Pale yellow crystals; yield 80% (Found: C, 35.3; H, 6.1; N, 2.5. $C_{33}H_{67}BF_4N_2O_{13}P_4Ru_2$ requires C, 35.6; H, 6.0; N, 2.5%).

$[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]PF_6$ (R = Me *or* Pr^i). An excess of HPF_6 (2 cm^3, 60% solution in H_2O) in water (15 cm^3) was added to a stirred solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (0.80 g, 1.0 mmol) or $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (1.025 g, 1 mmol) in CH_2Cl_2 at room temperature and the resultant two-phase mixture stirred vigorously for 1 h. The mixture initially turned red but after a few seconds adopted a yellow colour. The organic layer was separated and the aqueous layer washed with CH_2Cl_2 (30 cm^3). The CH_2Cl_2 solutions were combined and evaporated to dryness and the residue crystallized from acetone–diethyl ether. White crystals; yield 90% (Found: C, 21.8; H, 3.7; N, 2.8. $C_{17}H_{35}F_6N_2O_{13}P_5Ru_2$ requires C, 21.6; H, 3.7; N, 2.9%. Found: C, 33.8; H, 5.6; N, 2.6. $C_{33}H_{67}F_6N_2O_{13}P_5Ru_2$ requires C, 33.8; H, 5.6; N, 2.4%).

$[Ru_2\{\mu\text{-}ON(O)O\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$. An excess of HNO_3 (*ca.* 0.2 g, 65% solution in H_2O) was added to a solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (0.40 g, 0.5 mmol) in 1,2-dimethoxyethane (40 cm^3) at −40 °C and the solution stirred for 6 h. The solution turned orange, then pale yellow and, on warming to room temperature, yellow-green. The solvent was removed under reduced pressure and the residue extracted with methanol (40 cm^3) containing excess NH_4PF_6 (*ca.* 1.5 g). This solution was in turn evaporated to dryness and the residue washed with two aliquots (30 cm^3) of water and crystallized from acetone–diethyl ether. Light yellow crystals; yield 75% (Found: C, 20.3; H, 3.6; N, 4.3. $C_{16}H_{34}F_6N_3O_{15}P_5Ru_2$ requires C, 19.6; H, 3.5; N, 4.3%).

$[Ru_2\{\sigma\text{-}OC(O)CF_3\}(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$. A solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.41 g, 0.4 mmol) in CF_3CO_2H (10 cm^3) at room temperature was stirred for 15 min. The solution instantaneously adopted a pale yellow colour and a gas was evolved. The excess CF_3CO_2H was removed under reduced pressure and the residue washed with diethyl ether and dissolved in acetone (60 cm^3) containing excess NH_4PF_6 (1 g). This solution was in turn evaporated to dryness and the residue washed with three aliquots of water (40 cm^3) and crystallized from ethanol–water (4:1). White crystals; yield 85% (Found: C, 32.9; H, 5.2; N, 2.2. $C_{35}H_{66}F_9N_2O_{15}P_5Ru_2$ requires C, 33.1; H, 5.2; N, 2.2%).

$[Ru_2\{\mu\text{-}OC(CF_3)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$. A solution of $[Ru_2\{\sigma\text{-}OC(O)CF_3\}(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$ (0.25 g, 0.2 mmol) in thf (40 cm^3) was irradiated with ultraviolet light through Pyrex glass for 25 min during which time the colourless solution turned yellow. The solvent was removed under reduced pressure and the residue crystallized from ethanol. Yellow crystals; yield 95% (Found: C, 32.9; H, 5.2; N, 2.2. $C_{34}H_{66}F_9N_2O_{14}P_5Ru_2$ requires C, 32.9; H, 5.3; N, 2.3%).

$[Ru_2\{\mu\text{-}OB(F)OH\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]BF_4$. An excess of $HBF_4\cdot Et_2O$ (1.0 g, 54% solution in diethyl ether, 6 mmol) in diethyl ether (6 cm^3) was added to a solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.51 g, 0.5 mmol) in thf–diethyl ether (1:1, 150 cm^3) at room temperature containing trace amounts of water and the solution allowed to stand for 2–3 weeks in a glass flask. Yellow crystals of the product slowly separated from solution. Yield: 10% (Found: C, 34.2; H, 5.7; N, 2.9. $C_{32}H_{67}B_2F_5N_2O_{14}P_4Ru_2$ requires C, 33.5; H, 5.8; N, 2.5%).

$[Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]PF_6$ (R = Me *or* Pr^i). An excess of $HBF_4\cdot Et_2O$ (0.5 g, 54% solution in diethyl ether, 3 mmol) in diethyl ether (3 cm^3) was added to a solution of PhSH (*ca.* 0.2 g) and $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (0.40 g, 0.5 mmol) or $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.51 g, 0.5 mmol) in thf (40 cm^3) at room temperature and the resultant solution stirred for 6 h. The solvent was removed under reduced pressure and the oily residue dissolved in methanol (60 cm^3) containing

Table 2 Fractional atomic coordinates (× 10^4) for non-hydrogen atoms of [Ru$_2${μ-OB(F)OH}(CO)$_4${μ-(Pr^{i}O)$_2$PN(Et)P(OPr^i)$_2$}$_2$]BF$_4$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	3 045(1)	1 548(1)	280(1)	C(8)	2 874(8)	5 319(13)	1 694(8)
Ru(2)	1 787(1)	2 107(1)	−121(1)	C(9)	4 068(6)	3 785(10)	441(7)
P(1)	3 175(1)	2 848(2)	1 154(1)	C(10)	4 805(8)	3 831(13)	772(9)
P(2)	1 921(1)	3 511(2)	652(1)	C(11)	3 850(7)	4 800(12)	154(8)
P(3)	1 658(1)	826(2)	−991(1)	C(12)	3 889(7)	2 472(12)	2 470(9)
P(4)	2 932(1)	175(2)	−525(1)	C(13)	4 047(12)	1 387(19)	2 584(13)
F(1)	2 937(3)	3 597(5)	−1 524(4)	C(14)	3 652(16)	2 830(25)	3 137(18)
O(1)	4 464(3)	1 147(7)	554(5)	C(15)	1 512(6)	5 011(11)	−261(7)
O(2)	2 765(4)	205(7)	1 516(4)	C(16)	1 887(10)	5 513(18)	−792(12)
O(3)	1 413(4)	663(7)	1 019(4)	C(17)	1 179(10)	5 788(16)	167(11)
O(4)	420(3)	2 678(8)	−543(6)	C(18)	965(5)	3 089(9)	1 500(6)
O(5)	2 184(3)	3 016(4)	−926(3)	C(19)	1 290(8)	2 772(12)	2 199(9)
O(6)	3 168(3)	2 538(5)	−623(3)	C(20)	374(10)	3 720(16)	1 583(10)
O(7)	3 764(3)	3 566(5)	1 120(4)	C(21)	663(11)	−493(19)	−1 114(12)
O(8)	3 307(3)	2 448(5)	1 979(3)	C(22)	−14(13)	30(23)	−1 345(14)
O(9)	1 983(4)	4 552(5)	231(3)	C(23)	563(12)	−1 365(20)	−582(14)
O(10)	1 363(3)	3 804(5)	1 125(4)	C(24)	1 503(7)	1 696(12)	−2 305(9)
O(11)	1 094(5)	111(8)	−794(8)	C(25)	1 537(9)	1 165(15)	−3 071(10)
O(12)	1 377(6)	1 108(7)	−1 797(4)	C(26)	1 239(8)	2 764(13)	−2 460(9)
O(13)	3 478(3)	−13(5)	−1 048(3)	C(27)	3 824(5)	749(8)	−1 412(5)
O(14)	2 944(4)	−892(5)	−136(4)	C(28)	4 464(7)	362(12)	−1 435(8)
N(1)	2 270(3)	77(6)	−1 102(4)	C(29)	3 495(6)	978(11)	−2 158(7)
N(2)	2 556(3)	3 582(6)	1 266(4)	C(30)	3 428(7)	−1 384(12)	271(8)
B(1)	2 751(4)	3 011(7)	−991(5)	C(31)	3 154(12)	−2 093(18)	789(13)
C(1)	3 923(5)	1 277(8)	439(5)	C(32)	3 887(10)	−1 789(17)	−167(12)
C(2)	2 865(4)	702(7)	1 044(5)	B(2)	9 635(3)	1 611(6)	3 238(4)
C(3)	1 576(5)	1 242(8)	603(5)	F(2)	9 498(3)	2 168(6)	2 611(4)
C(4)	947(5)	2 511(8)	−421(5)	F(3)	9 109(3)	1 098(6)	3 392(4)
C(5)	2 233(5)	−689(9)	−1 722(6)	F(4)	10 105(3)	945(6)	3 135(4)
C(6)	2 102(7)	−1 747(12)	−1 464(8)	F(5)	9 826(3)	2 235(6)	3 814(4)
C(7)	2 579(5)	4 369(9)	1 875(6)				

Table 3 Selected interatomic distances (Å) and angles (°) for [Ru$_2${μ-OB(F)OH}(CO)$_4${μ-(Pr^{i}O)$_2$PN(Et)P(OPr^i)$_2$}$_2$]BF$_4$

Ru(1)–Ru(2)	2.814(2)	Ru(1)–P(1)	2.354(2)
Ru(1)–P(4)	2.345(2)	Ru(2)–P(2)	2.345(2)
Ru(2)–P(3)	2.330(2)	Ru(1)–O(6)	2.149(6)
Ru(2)–O(5)	2.146(6)	Ru(1)–C(1)	1.905(10)
Ru(1)–C(2)	1.866(9)	Ru(2)–C(3)	1.845(10)
Ru(2)–C(4)	1.901(10)	B(1)–O(5)	1.229(11)
B(1)–O(6)	1.235(11)	B(1)–F(1)	1.340(11)
P(1)–N(2)	1.675(8)	P(2)–N(2)	1.672(8)
P(3)–N(1)	1.675(8)	P(4)–N(1)	1.682(7)
C(1)–O(1)	1.166(12)	C(2)–O(2)	1.125(11)
C(3)–O(3)	1.161(12)	C(4)–O(4)	1.147(12)
Ru(2)–Ru(1)–P(1)	91.4(1)	Ru(2)–Ru(1)–P(4)	90.6(1)
Ru(2)–Ru(1)–O(6)	80.0(2)	Ru(2)–Ru(1)–C(1)	172.2(3)
Ru(2)–Ru(1)–C(2)	95.1(3)	P(1)–Ru(1)–P(4)	176.0(1)
P(1)–Ru(1)–O(6)	93.0(2)	P(1)–Ru(1)–C(1)	89.5(3)
P(1)–Ru(1)–C(2)	87.6(3)	P(4)–Ru(1)–O(6)	90.7(2)
P(4)–Ru(1)–C(1)	89.1(3)	P(4)–Ru(1)–C(2)	88.8(3)
O(6)–Ru(1)–C(1)	92.1(3)	O(6)–Ru(1)–C(2)	175.1(3)
C(1)–Ru(1)–C(2)	92.7(4)	Ru(1)–Ru(2)–P(2)	90.1(1)
Ru(1)–Ru(2)–P(3)	91.5(1)	Ru(1)–Ru(2)–O(5)	83.9(2)
Ru(1)–Ru(2)–C(3)	86.9(3)	Ru(1)–Ru(2)–C(4)	177.9(3)
P(2)–Ru(2)–P(3)	174.0(1)	P(2)–Ru(2)–O(5)	85.9(2)
P(2)–Ru(2)–C(3)	95.3(3)	P(2)–Ru(2)–C(4)	90.0(3)
P(3)–Ru(2)–O(5)	85.9(2)	P(3)–Ru(2)–C(3)	90.5(3)
P(3)–Ru(2)–C(4)	90.0(3)	O(5)–Ru(2)–C(3)	170.7(4)
O(5)–Ru(2)–C(4)	94.1(3)	C(3)–Ru(2)–C(4)	95.2(4)
P(1)–N(2)–P(2)	118.8(5)	P(3)–N(1)–P(4)	119.7(4)
O(5)–B(1)–O(6)	127.9(8)	O(5)–B(1)–F(1)	115.9(8)
O(6)–B(1)–F(1)	116.3(8)		

excess NH_4PF_6 (*ca.* 1 g). This solution was in turn evaporated to dryness and the residue washed with two aliquots of water (2 × 30 cm^3). The oily material remaining was retreated with an excess of NH_4PF_6 in methanol as above and the oily product eventually isolated was crystallized from acetone–ethanol. Orange crystals; yield 50% (Found: C, 25.7; H, 3.8; N, 2.7. $C_{22}H_{39}F_6N_2O_{12}P_5Ru_2S$ requires C, 25.7; H, 3.8; N, 2.7%).

[Ru$_2${μ-OC(OH)O}(CO)$_4${μ-(Pr^{i}O)$_2$PN(Et)P(OPr^i)$_2$}$_2$]PF$_6$ *and* [Ru$_2${μ-OC(OMe)O}(CO)$_4${μ-(Pr^{i}O)$_2$PN(Et)P(OPr^i)$_2$}$_2$]PF$_6$. (*i*) An excess of aqueous HPF_6 (2 cm^3, 60%) was added to a solution of [Ru$_2$(μ-CO)(CO)$_4${μ-(Pr^{i}O)$_2$PN(Et)P(OPr^i)$_2$}$_2$] (0.51 g, 0.5 mmol) in 1,2-dichloroethane and the mixture was refluxed for 8 h while a stream of carbon dioxide was passed through it. The solvents were removed under reduced pressure to afford an oily residue. Attempts to crystallize this residue from acetone–diethyl ether or CH_2Cl_2–hexane led to the separation of [Ru$_2${μ-OC(OH)O}(CO)$_4${μ-(Pr^{i}O)$_2$PN(Et)P(OPr^i)$_2$}$_2$]PF$_6$ (see text) as an impure oil. Crystallization of this oil from methanol–water resulted in the separation of yellow crystals of [Ru$_2${μ-OC(OMe)O}(CO)$_4${μ-(Pr^{i}O)$_2$PN(Et)P(OPr^i)$_2$}$_2$]PF$_6$; yield 30%.

(*ii*) An excess of aqueous HPF_6 (2 cm^3, 60%) was added to a solution of [Ru$_2$(μ-CO)(CO)$_4${μ-Pr^{i}O)$_2$PN(Et)P(OPr^i)$_2$}$_2$] (0.51 g, 0.5 mmol) in 1,2-dichloroethane–methanol (3:2, 100 cm^3) and the mixture was refluxed for 8 h while a stream of carbon dioxide was passed through it. The solvents were removed under reduced pressure and the oily residue crystallized from methanol–water. Yellow crystals; yield 40% (Found: C, 33.8; H, 5.7; N, 2.5. $C_{34}H_{69}F_6N_2O_{15}P_5Ru_2$ requires C, 33.6; H, 5.7; N, 2.3%).

Crystal Structure Determination of [Ru$_2${μ-OB(F)OH}(CO)$_4${μ-(Pr^{i}O)$_2$PN(Et)P(OPr^i)$_2$}$_2$]BF$_4$.—*Crystal data.* $C_{32}H_{67}B_2F_5N_2O_{14}P_4Ru_2$, $M = 1146.1$, monoclinic, space group $P2_1/n$ (alt. $P2_1/c$, no. 14), $a = 21.376(5)$, $b = 13.339(3)$, $c = 18.260(4)$ Å, $\beta = 95.88(3)°$, $U = 5179$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), $Z = 4$, $D_c = 1.47$ g cm^{-3}, $F(000)$ 2800. Yellow air-stable needle 0.16 × 0.12 × 0.49 mm, μ(Mo-Kα) 7.70 cm^{-1}.

Intensity data were collected on a Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation

Table 4 Fractional atomic coordinates (× 10^4) for non-hydrogen atoms of $[Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	804(1)	3428(1)	3297(1)
Ru(2)	52(1)	1331(1)	2610(1)
P(1)	2328(2)	2938(1)	4441(1)
P(2)	−788(2)	3941(2)	2176(1)
P(3)	−1536(2)	1800(2)	1474(1)
P(4)	1627(2)	780(1)	3709(1)
S	2143(1)	2567(1)	2479(1)
O(1)	2317(7)	5690(4)	3864(4)
O(2)	−1622(6)	3288(5)	4249(4)
O(3)	−2411(5)	809(5)	3516(4)
O(4)	−124(7)	−781(4)	1660(4)
O(5)	3918(4)	3661(3)	4757(3)
O(6)	1749(5)	2993(3)	5270(3)
O(7)	−258(6)	4937(4)	1725(3)
O(8)	−2161(5)	4218(4)	2513(3)
O(9)	−1309(7)	1269(4)	627(3)
O(10)	−3247(7)	1455(7)	1409(6)
O(11)	840(5)	52(3)	4283(3)
O(12)	2724(5)	40(3)	3498(3)
N(1)	2697(5)	1721(4)	4410(3)
N(2)	−1418(6)	3076(4)	1324(3)
C(1)	1751(7)	4869(5)	3630(4)
C(2)	−712(8)	3347(5)	3897(4)
C(3)	−1508(8)	990(5)	3158(4)
C(4)	−11(7)	15(6)	2002(4)
C(5)	4883(7)	3891(5)	4195(4)
C(6)	1753(10)	3925(8)	5750(6)
C(7)	−51(10)	6010(8)	2061(6)
C(8)	−3542(11)	4365(8)	2026(7)
C(9)	−2198(18)	856(13)	−142(11)
C(10)	−4004(19)	560(16)	1407(12)
C(11)	151(10)	−1027(7)	4017(6)
C(12)	3651(9)	263(7)	2919(5)
C(13)	3722(7)	1386(5)	5156(4)
C(14)	5302(9)	1544(7)	5075(5)
C(15)	−2107(8)	3441(5)	518(4)
C(16)	−991(9)	3552(7)	−62(6)
C(17)	2315(6)	3001(4)	1498(3)
C(18)	2175(8)	2248(6)	837(5)
C(19)	2576(10)	2550(7)	104(6)
C(20)	3133(9)	3635(7)	64(5)
C(21)	3208(8)	4325(6)	684(5)
C(22)	2805(7)	4046(5)	1426(4)
P(5)	5343(3)	7569(2)	2092(2)
F(1)	3916(14)	7810(17)	2009(13)
F(2)	5979(14)	8434(9)	2799(7)
F(3)	6763(12)	7359(13)	2011(9)
F(4)	4755(20)	6703(13)	1432(11)
F(5)	5451(32)	6841(15)	2722(12)
F(6)	5445(25)	8295(16)	1451(10)

Table 5 Selected interatomic distances (Å) and angles (°) for $[Ru_2\{\mu\text{-}SPh)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$

Ru(1)–Ru(2)	2.796(1)	Ru(1)–P(1)	2.316(2)
Ru(1)–P(2)	2.335(2)	Ru(2)–P(3)	2.326(2)
Ru(2)–P(4)	2.323(2)	Ru(1)–S	2.380(2)
Ru(2)–S	2.387(1)	Ru(1)–C(1)	1.923(6)
Ru(1)–C(2)	1.899(8)	Ru(2)–C(3)	1.895(8)
Ru(2)–C(4)	1.909(7)	P(1)–N(1)	1.661(5)
P(2)–N(2)	1.690(5)	P(3)–N(2)	1.669(6)
P(4)–N(1)	1.673(4)	C(1)–O(1)	1.114(8)
C(2)–O(2)	1.131(10)	C(3)–O(3)	1.140(10)
C(4)–O(4)	1.122(9)		
Ru(2)–Ru(1)–P(1)	90.4(0)	Ru(2)–Ru(1)–P(2)	90.5(0)
P(1)–Ru(1)–P(2)	177.9(1)	Ru(2)–Ru(1)–S	54.2(0)
P(1)–Ru(1)–S	87.0(1)	P(2)–Ru(1)–S	95.1(1)
Ru(2)–Ru(1)–C(1)	164.8(2)	P(1)–Ru(1)–C(1)	88.5(2)
P(2)–Ru(1)–C(1)	91.1(2)	S–Ru(1)–C(1)	110.6(2)
Ru(2)–Ru(1)–C(2)	95.5(2)	P(1)–Ru(1)–C(2)	88.6(2)
P(2)–Ru(1)–C(2)	89.4(2)	S–Ru(1)–C(2)	149.3(2)
C(1)–Ru(1)–C(2)	99.6(3)	Ru(1)–Ru(2)–P(3)	90.0(1)
Ru(1)–Ru(2)–P(4)	91.9(0)	P(3)–Ru(2)–P(4)	177.1(1)
Ru(1)–Ru(2)–S	54.0(0)	P(3)–Ru(2)–S	95.0(1)
P(4)–Ru(2)–S	86.2(1)	Ru(1)–Ru(2)–C(3)	94.4(2)
P(3)–Ru(2)–C(3)	91.7(2)	P(4)–Ru(2)–C(3)	88.7(2)
S–Ru(2)–C(3)	147.7(2)	Ru(1)–Ru(2)–C(4)	164.0(2)
P(3)–Ru(2)–C(4)	89.0(2)	P(4)–Ru(2)–C(4)	88.2(2)
S–Ru(2)–C(4)	110.1(2)	C(3)–Ru(2)–C(4)	101.5(3)
Ru(1)–P(1)–N(1)	118.6(2)	Ru(1)–P(2)–N(2)	117.9(2)
Ru(2)–P(3)–N(2)	118.3(2)	Ru(2)–P(4)–N(1)	116.9(2)
Ru(1)–S–Ru(2)	71.8(0)	P(1)–N(1)–P(4)	120.1(3)
P(2)–N(2)–P(3)	116.3(3)		

(λ 0.710 69 Å). Diffraction intensities were measured in the range 3 ⩽ θ ⩽ 25° using the ω–2θ scan technique (ω scan width = 0.87 + 0.35 tan θ, ω scan speed 1.3–6.8° min^{-1}), with background counts made for half the total scan time on each side of the peak. Three standard reflections, measured every hour, showed no decrease in intensity during data collection. Empirical absorption corrections were made using the ψ-scan method. Of the 7095 unique reflections measured (merging *R* = 0.032 after absorption corrections), 5172 were classed as observed [$I > 3\sigma(I)$] and these were used for the solution and the refinement of the structure.

The ruthenium and phosphorus atoms were located from a Patterson map using the program SHELX 76[44] while the positions of the remaining non-hydrogen atoms were obtained from Fourier syntheses. The ruthenium, phosphorus and fluorine (cation) atoms were assigned anisotropic thermal parameters and all the remaining atoms, hydrogens excluded, isotropic thermal parameters (the BF_4 anion was treated as an idealized rigid group). The weighting scheme $w = 3.6/[\sigma^2(F_o) + 0.04F_o^2]$ with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analysis. A final full-matrix least-squares refinement gave final *R* and *R'* values of 0.076 and 0.097 (338 parameters) respectively. A final difference map was essentially featureless with maximum residual electron density of 1.5 e $Å^{-3}$ in the vicinity of the disordered BF_4^- anions. Scattering factors with corrections for anomalous dispersions were taken from ref. 45. Fractional atomic coordinates and selected interatomic distances and angles are given in Tables 2 and 3 respectively.

Crystal Structure Determination of $[Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$.—*Crystal data.* $C_{22}H_{39}F_6N_2O_{12}P_5Ru_2S$, *M* = 1028.7, triclinic, space group $P\bar{1}$, *a* = 9.424(1), *b* = 12.899(1), *c* = 16.628(2) Å, α = 93.386(9), β = 102.118(8), γ = 99.135(9)°, *U* = 1924 $Å^3$, λ = 0.710 69 Å, *Z* = 2, D_c = 1.76 g cm^{-3}, *F*(000) 1028. Yellow air-stable rectangular block 0.20 × 0.23 × 0.47 mm, μ(Mo-Kα) 11.04 cm^{-1}.

The experimental conditions for the intensity data collection were the same as those described above. Of the 5603 unique reflections measured (merging *R* = 0.010 after absorption corrections), 4692 were classified as observed [$I > 3\sigma(I)$] and these were used for the solution and the refinement of the structure.

The ruthenium atoms were located from a Patterson map using the program SHELX 86[46] while the positions of the remaining non-hydrogen atoms were obtained from Fourier syntheses. The ruthenium, sulfur, phosphorus, fluorine, oxygen and nitrogen atoms were assigned anisotropic thermal parameters and the remaining carbon atoms isotropic thermal parameters. A final full-matrix least-squares refinement gave final R and R' values of 0.053 and 0.076 (342 parameters) respectively. A final difference map was essentially featureless with maximum residual electron density of 1.1 e Å^{-3}. Fractional atomic coordinates and selected interatomic distances and angles are given in Tables 4 and 5 respectively.

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

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