# Reactions of Diphosphazane-bridged Derivatives of Diruthenium Nonacarbonyl with Metal-containing Electrophiles: Formation of Solvento Species $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ (R = Me or Pr$^i$) and their Reactivity towards Various Nucleophiles†

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Reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr$^i$) with equimolar quantities of metal-containing electrophiles such as $[AuCl(PPh_3)]$, silver(I) salts, $[Cu(MeCN)_4]PF_6$ and $HgCl_2$ has afforded cationic products in which the metal substrates are co-ordinated either terminally as in $[Ru_2(\sigma\text{-}HgCl)(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ or in the bridging mode as in $[Ru_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and $[Ru_2(\mu\text{-}AgL_x)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (L = pyridine or MeCN, *x* = 1 or 2). The silver adducts readily rearrange in solution with the nature of the product(s) formed being dependent on the identity of the ligand L and/or the solvent employed. For non-protic weakly co-ordinating ligands such as acetonitrile, the silver-bridged cations disproportionate in solution to the parent compound $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ and the solvento species $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ thereby establishing that the formation of $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ by treatment of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ with a two-fold molar amount of silver(I) ions in non-protic weakly co-ordinating solvents occurs *via* an inner-sphere mechanism. In the case of the aqua and acetone solvento species $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ (solv = $H_2O$ or $Me_2CO$), both the solvent molecule and the carbonyl groups are labile with one or both being readily displaced by a wide range of neutral and ionic nucleophiles including carbon monoxide, isonitriles, nitriles, pyridine, 4,4′-bipyridine, dimethyl sulfide and tetrahydrothiophene, and halide, thiocyanate, benzenethiolate, trifluoroacetate, acetate and hydride ions. The crystal structures of $[Ru_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$, $[Ru_2(CO)_5(PhCN)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ and $[Ru_2(CO)_5(SC_4H_8)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ have been determined.

A feature of all dinuclear compounds containing an $M_2(\mu\text{-}R_2PYPR_2)_2$ (M = transition metal; R = Me, Ph, OMe, *etc.*; Y = $CH_2$, NEt, O, *etc.*) chromophore and to a lesser extent of those with an $M_2(\mu\text{-}R_2PYPR_2)$ core is that they are electron-rich and react readily with a wide range of electrophilic agents.[1] Thus $[Rh_2(CO)_3(\mu\text{-}dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) and $[Mn_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}H)(CO)_6(\mu\text{-}dppm)]$ are readily protonated to produce $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]^+$ [2] and $[Mn_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}H)_2(CO)_6(\mu\text{-}dppm)]^+$ [3] respectively while $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dmpm)_2]$ (dmpm = $Me_2PCH_2PMe_2$) is sufficiently electron-rich to react with diphenylacetylene affording $[Ru_2(\mu\text{-}\sigma^2\text{-}PhC{=}CPh)(CO)_4(\mu\text{-}dmpm)_2]$.[4]

We have established previously from cyclic voltammetric studies carried out in both acetone and benzonitrile that the diiron and diruthenium diphosphorus ligand-bridged derivatives $[M_2(\mu\text{-}CO)(CO)_4(\mu\text{-}R_2PYPR_2)_2]$ (M = Fe, Y = $CH_2$, R = Ph or Me; Y = NEt, R = OMe, OEt or OPr$^i$; M = Ru, Y = $CH_2$, R = Ph or Me; Y = NEt, R = OMe or OPr$^i$) are readily oxidised in either two one-electron steps or a single two-electron step to the dicationic solvento species $[M_2(CO)_5(solv)(\mu\text{-}R_2PYPR_2)_2]^{2+}$.[5] In particular it was observed that while the primary oxidation wave in the cyclic voltammogram of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ reflects an irreversible process those for the remainder of the compounds are reversible indicating that their one-electron oxidised products $[M_2(\mu\text{-}CO)(CO)_4(\mu\text{-}R_2PYPR_2)_2]^+$ are stable on the time-scale of the measurement. Further oxidation of the latter leads to the formation of dicationic products but apart from that involving $[Fe_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]^+$ in acetone these oxidation processes are irreversible with the dicationic oxidised species $[M_2(\mu\text{-}CO)(CO)_4(\mu\text{-}R_2PYPR_2)_2]^{2+}$ reacting spontaneously with the solvent to afford a product identified as the solvento species $[M_2(CO)_5(solv)(\mu\text{-}R_2PYPR_2)_2]^{2+}$. The primary oxidation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ was shown to be a two-electron process which is readily reconciled in terms of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ participating in some chemical process involving solvent attack and the product thereof being immediately oxidised to $[Ru_2(CO)_5(solv)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^{2+}$.

The solvento species $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ (R = Me or Pr$^i$) are potentially excellent precursors for the synthesis of a wide range of diphosphazane-bridged diruthenium compounds and thus their synthesis by chemical means was investigated. Silver (I) salts are very effective one-electron oxidants and as a consequence their

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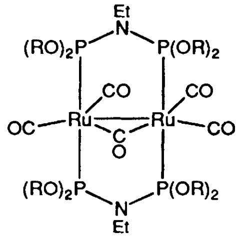
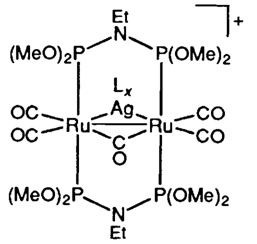
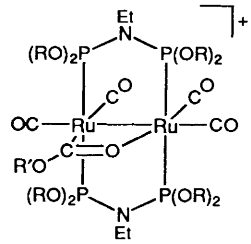
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



| | R |
|---|---|
| **1a** | Me |
| **1b** | Pr$^i$ |



| | L |
|---|---|
| **6a** | MeCN |
| **6b** | py |



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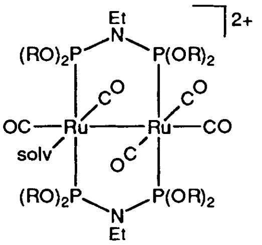

| | R | solv | | R | solv |
|---|---|---|---|---|---|
| **2a** | Me | Me$_2$CO | **4c** | Me | PhCN |
| **2b** | Pr$^i$ | Me$_2$CO | **4d** | Pr$^i$ | PhCN |
| **3a** | Me | H$_2$O | **5a** | Me | MeOH |
| **3b** | Pr$^i$ | H$_2$O | **5b** | Pr$^i$ | MeOH |
| **4a** | Me | MeCN | **5c** | Me | EtOH |
| **4b** | Pr$^i$ | MeCN | **5d** | Pr$^i$ | EtOH |

reactions, together with those of other metal-containing electrophiles, with $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ were studied. The results of this investigation as well as that of the reactivity of $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ with various nucleophiles is reported here; some of these results have been the subject of two preliminary communications.[6,7]

## Results and Discussion

*Reaction of* $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ *with Metal-containing Electrophiles.*—Not surprisingly the diruthenium diphosphazane-bridged derivatives $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **1** are sufficiently electron-rich to be susceptible to attack by silver(I) ions but significantly the final product resulting from this attack was found to be dependent on the nature of the ligand co-ordinated to the silver(I) ion as well as on the stoichiometry of the reaction. For instance, treatment of **1** with an equimolar amount of $AgSbF_6$ in acetone leads to the precipitation of elemental silver and the formation of a half-molar equivalent of products characterised as the dicationic acetone species $[Ru_2(CO)_5(Me_2CO)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ (as the $SbF_6^-$ salt). The acetone ligand in these species is labile, particularly that in the tetraisopropoxydiphosphazane-bridged acetone adduct **2b**, and is readily displaced by other ligands (see below) such that the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the latter, measured in $[^2H_6]$-acetone, revealed the presence of a second, minor product in solution, identified as the aqua species $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^{2+}$ **3b** and resulting from the presence of trace amounts of water in the $[^2H_6]$acetone. In fact crystallisation of **2b** (as the $SbF_6^-$ salt) from acetone–toluene gave two types of single crystals, those produced in minor quantities being established X-ray crystallographically to be $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^{2+}$ **3b** (as the $SbF_6^-$ salt),[8] even when 'rigorously' dried acetone was employed.* Apart from a weak singlet in the spectrum of **2b** and assigned to **3b** (see below), the above $^{31}P\text{-}\{^1H\}$ NMR spectra exhibited an AA'BB' pattern of peaks consistent with the asymmetric structure shown while the pattern of peaks observed in the C–O stretching region of the IR spectra of these acetone species is typical of compounds of the type $[Ru_2(CO)_5L\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{x+}$ (L = ligand). A peak of medium intensity at 1654 cm$^{-1}$ for **2a** and one at 1680 cm$^{-1}$ for **2b**, assigned to the C–O stretching mode of the co-ordinated acetone, was also observed in these IR spectra. Relevant spectroscopic data are summarised in Table 1.

In contrast to that established for the above reactions involving acetone as solvent, addition of an equimolar amount of $AgSbF_6$ to $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ **1a** in MeCN or of an equimolar amount of $[Ag(py)_4]SbF_6$ (py = pyridine) to **1a** in tetrahydrofuran (thf) was found to result in the formation of products characterised as $[Ru_2(\mu\text{-}AgL_x)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ ($x$ = 1 or 2, L = MeCN **6a** or py **6b**, both as $SbF_6^-$ salts). The IR spectra of these species were found to contain a peak in the C–O stretching region corresponding to a bridging carbonyl group, as well as peaks associated with terminal carbonyls while their $^{31}P\text{-}\{^1H\}$ NMR spectra exhibited doublets at δ 153.2 $[^2J(^{107,109}Ag\text{-}P) = 13.9$ Hz$]$ and at δ 150.2 $[^2J(^{107,109}Ag\text{-}P) = 13.6$ Hz$]$ respectively, indicative of a symmetrical structure with the silver(I) ion bridging the two ruthenium atoms. Significantly solid $[Ru_2\{\mu\text{-}Ag(MeCN)_x\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ was found to degrade to elemental silver and an intense purple, extremely oxygen-sensitive species, presumed to be the one-electron oxidation product $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$, on heating to 50–70 °C *in vacuo*. This compound was observed to disproportionate spontaneously to the solvento species $[Ru_2(CO)_5(solv)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$ and the parent complex **1a** on dissolution in weakly co-ordinating solvents such as acetone or benzonitrile. The silver–pyridine adduct $[Ru_2\{\mu\text{-}Ag(py)_x\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ is thermodynamically more stable than its silver–acetonitrile analogue but interestingly, while $[Ru_2\{\mu\text{-}Ag(MeCN)_x\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ slowly disproportionates to $[Ru_2(CO)_5(MeCN)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$ and **1a** in acetonitrile, the silver–pyridine adduct degrades solely back to **1a** on heating in pyridine.

Solvento species of the type $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][SbF_6]_2$ are also produced on reaction of compound **1** with an equimolar amount of $AgSbF_6$ in protic solvents such as methanol or ethanol. However, the solvent molecules in these complexes are readily deprotonated, with methanol and ethanol being sufficiently basic to spontaneously deprotonate the co-ordinated alcohol in $[Ru_2(CO)_5(R'OH)$-

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* The single crystals of the major component of the material rapidly lost solvent of crystallisation, producing a powder, such that a structure determination could not be effected.

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

| Compound | $\nu(CO)^a/cm^{-1}$ | $^{31}P-\{^1H\}$ NMR $^b$ |
|---|---|---|
| $[Ru_2(CO)_5(Me_2CO)\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$ | 2098m, 2051vs, 2038vs, 1998s, 1654s $^c$ | 139.5 $^d$ |
| $[Ru_2(CO)_5(Me_2CO)\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ | 2099w, 2054(sh), 2033s, 1980m, 1680m $^c$ | 127.5 $^d$ |
| $[Ru_2(CO)_5(H_2O)\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$ | 2107w, 2062s, 2052s, 2031vs, 2005ms $^{c,e}$ | 136.0 $^d$ |
| $[Ru_2(CO)_5(H_2O)\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ $^f$ | 2097w, 2045(sh), 2034s, 1987m $^{c,g}$ | 125.0 $^{d,h}$ |
| $[Ru_2(CO)_5(MeCN)\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$ $^i$ | 2104w, 2060s, 2041s, 2011m $^j$ | 137.0 $^d$ |
| $[Ru_2(CO)_5(MeCN)\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ $^k$ | 2094w, 2053, 2031s, 2003m | 130.0 $^d$ |
| $[Ru_2(CO)_5(PhCN)\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$ | 2103w, 2059s, 2041s, 2012m $^l$ | 140.5 (s) $^m$ |
| $[Ru_2(CO)_5(PhCN)\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ | 2100w, 2043s, 2031s, 1993m $^{c,n}$ | 128.5 (s) $^o$ |
| $[Ru_2\{\mu-Ag(MeCN)_x\}(\mu-CO)(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ | 2036w, 1992vs, 1942s, 1723br s $^p$ | 153.2 (d, $^2J^{107,109}$Ag–P 13.9) |
| $[Ru_2\{\mu-Ag(NC_5H_5)_x\}(\mu-CO)(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ | 2029w(sh), 1987vs, 1951s, 1722br s $^p$ | 150.2 (d, $^2J^{107,109}$Ag–P 13.6) |
| $[Ru_2\{\mu-Au(PPh_3)\}(\mu-CO)(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ | 2049w, 1996vs, 1951s, 1735s | 146.8 (d, $^3J_{P-P}$ 8.2), $^g$<br>61.0 (q, $^3J_{P-P}$ 8.2) $^h$ |
| $[Ru_2\{\mu-Cu(MeCN)_2\}(\mu-CO)(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ $^q$ | 2047w, 1984vs, 1934s, 1751s $^r$ | 147.0 (s) $^h$ |
| $[Ru_2(\sigma-HgCl)(CO)_5\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ | 2095w, 2035vs, 2026vs(sh), 1984m | 143.8 $^{d,h}$ |
| $[Ru_2(\sigma-SbCl_2)(CO)_5\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]Sb_2Cl_7$ | 2088m, 2040s (sh), 2023vs, 1990s $^s$ | 136.4 $^{d,t}$ |
| $[Ru_2(CO)_6\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$ | 2052vs, 2042vs, 2013m, 1990m $^u$ | 134.0 (s) |
| $[Ru_2(CO)_5(CNC_6H_3Me_2-2,6)\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$ | 2106s, 2068vs, 2043vs, 2025s(sh) $^{s,v}$ | 137.1 $^d$ |
| $[Ru_2(CO)_5(SC_4H_8)\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ | 2097m, 2044s, 2031s, 1994ms | 120.2 $^{d,h}$ |
| $[Ru_2(CO)_5(SMe_2)\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ $^w$ | 2096w, 2046s, 2032s, 1994m | 121.2 $^{d,h}$ |
| $[Ru_2(CO)_5(py)\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ | 2086w, 2043s, 2023s, 1994m | 126.9 $^d$ |
| $[Ru_2(CO)_5(\sigma-4,4'-bipy)\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ $^x$ | 2086w, 2040s, 2020s, 1995m | 129.7 $^d$ |
| $[Ru_2(CO)_5(Et_2CO)\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ | 2091w, 2043s, 2023s, 1985m, 1650m $^c$ | n.m. |
| $[Ru_2(CO)_5(MeNO_2)\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ | 2094w, 2051s, 2030vs, 2006m $^c$ | n.m. |
| $[Ru_2(NCS)(CO)_5\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ | 2086w, 2032s, 2020(sh), 1973m | 144.7 $^d$ |

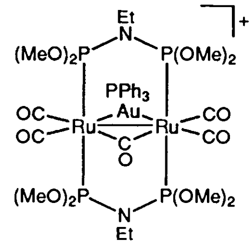
[a] Abbreviations: v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad; measured in $CH_2Cl_2$, unless otherwise stated. [b] Abbreviations: s = singlet, d = doublet, q = quintet; δ scale in ppm relative to 85% $H_3PO_4$; coupling constants in Hz; measured at room temperature in $[^2H_6]$acetone unless otherwise stated, n.m. = not measured. [c] Measured as a Nujol mull. [d] Centre of an AA′BB′ pattern. [e] ν(OH) 3518br $cm^{-1}$. [f] $^1H$ NMR: 3.62 (s, br, OH), δ scale in ppm relative to $SiMe_4$; measured at room temperature in $CD_2Cl_2$. [g] ν(OH) 3450br $cm^{-1}$. [h] Measured in $CD_2Cl_2$. [i] $^1H$ NMR: 2.75 (s, $CH_3CN$), measured in $[^2H_6]$acetone. [j] Measured in MeCN. [k] $^1H$ NMR: 2.83 (s, $CH_3CN$), measured in $[^2H_6]$acetone. [l] ν(CN) 2240 $cm^{-1}$. [m] $^{31}P-\{^1H\}$ NMR measured at −96 °C: δ 141.5, centre of an AA′BB′ pattern. [n] ν(CN) 2145 $cm^{-1}$. [o] $^{31}P-\{^1H\}$ NMR measured at −77 °C: δ133.8, centre of an AA′BB′ pattern. [p] Measured in thf. [q] $^1H$ NMR: 2.15 (s, $CH_3CN$), measured in $CD_2Cl_2$. [r] ν(CN) 2300 $cm^{-1}$. [s] Measured in 1,2-dichloroethane. [t] Measured in acetone. [u] Measured in $CDCl_3$. [v] ν(NC) 2161 $cm^{-1}$. [w] $^1H$ NMR: 2.62 [s, $S(CH_3)_2$], measured in $CD_2Cl_2$. [x] 4,4′-bipy = 4,4′-bipyridine.

$\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ **5** (R′ = Me or Et). As a consequence the only products that could be detected in the reactions of **1** with $AgSbF_6$ in methanol or ethanol were the alkoxycarbonyl-bridged derivatives $[Ru_2\{\mu-OC(OR')\}(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^+$ **7**. These latter reactions are the subject of previous publications.[8] Alkoxycarbonyl-bridged products are also obtained when silver acetate is employed as the oxidant and methanol or ethanol are used as solvent whereas for thf as solvent the treatment of **1** with an equimolar amount of this silver salt leads to the formation of a half-molar equivalent of a product characterised as the acetate-bridged derivative $[Ru_2\{\mu-OC(Me)O\}(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]O_2CMe$.[8]

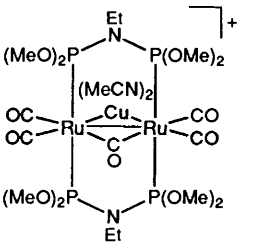
Compound **1** proved to be susceptible to attack by other metal-containing electrophiles. Thus treatment of **1a** with an equimolar amount of $[AuCl(PPh_3)]$ in thf under reflux afforded a cationic species $[Ru_2\{\mu-Au(PPh_3)\}(\mu-CO)(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ **8**, readily isolated as its hexafluoroantimonate salt by addition of $AgSbF_6$. The presence of both a doublet and a quintet in the $^{31}P-\{^1H\}$ NMR spectrum of this species and a peak corresponding to a bridging carbonyl group in its IR spectrum was interpreted in terms of a symmetrical structure and the $Au(PPh_3)$ moiety bridging the two ruthenium atoms. Reaction of **1a** with $[Cu(MeCN)_4]PF_6$ likewise gave a product of symmetrical structure *viz.* $[Ru_2\{\mu-Cu(MeCN)_2\}(\mu-CO)(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ **9** (as the $PF_6^-$ salt) on the basis of the spectroscopic evidence. In contrast, products of unsymmetrical structure were isolated from the reactions involving $HgCl_2$ and $SbCl_3$. In particular, treatment of **1a** with an equimolar amount of $HgCl_2$ in thf in the absence of light, followed by addition of $AgSbF_6$, afforded a compound of stoichiometry $[Ru_2(\sigma-HgCl)(CO)_5\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ **10** which, on the basis of the presence of an AA′BB′ pattern of peaks in its $^{31}P-\{^1H\}$ NMR spectrum and a set of peaks in the terminal carbonyl stretching region of its IR spectrum typical of compounds of the type $[Ru_2(CO)_5L\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^{x+}$, contains a terminally co-ordinated HgCl unit. The reaction of **1a** with $SbCl_3$ similarly gave a product, $[Ru_2(\sigma-SbCl_2)(CO)_5\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ **11** (as the $Sb_2Cl_7^-$ salt), in which the $SbCl_2$ group is also bonded terminally. Compound **10** is light sensitive and, if not kept in the dark, degrades relatively rapidly in $CH_2Cl_2$ to $[Ru_2Cl(CO)_5\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ **12** and the latter's decarbonylation product $[Ru_2(\mu-Cl)(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ **13**.[9] The parent compound **1a** also reacts spontaneously with $SnCl_4$ but the product could not be isolated pure and hence fully characterised.

It is thus apparent from the results described above that silver(I) salts are very effective for the two-electron oxidation of compound **1** and thereby provide an efficient method for the synthesis of the solvento species $[Ru_2(CO)_5(solv)\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$. Indeed addition of a two-fold molar equivalent amount of $AgSbF_6$ to **1** in acetone produces **2** (as the $SbF_6^-$ salt) in quantitative yield. Likewise treatment of **1** with a twice molar amount of $AgSbF_6$ in the aprotic weakly co-ordinating solvents acetonitrile or benzonitrile was found to lead to the formation of the organonitrile derivatives $[Ru_2(CO)_5(R'CN)\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ **4** (as the $SbF_6^-$ salts) (R′ = Me or Ph). The solid-state and solution IR spectra of these derivatives exhibit very similar band patterns in the C–O stretching region typical of species of the type $[Ru_2(CO)_5L\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^{x+}$ while peaks at 2237 and 2145 $cm^{-1}$ for R = Me and $Pr^i$ respectively, readily assigned to C–N stretching modes, were observed in the solid-state IR spectra of the benzonitrile derivatives.

The $^{31}P-\{^1H\}$ NMR spectra of the latter, *viz.* **4c** and **4d** measured in $[^2H_6]$acetone at low temperature (< −77 °C),



**8**



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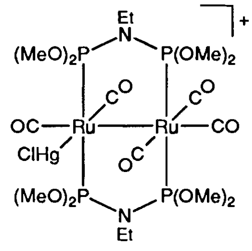

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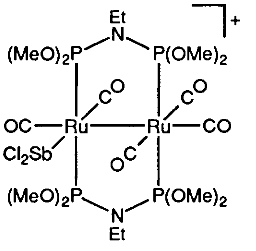

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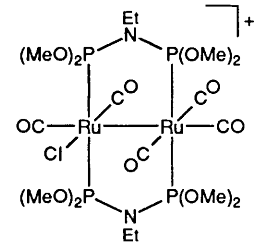

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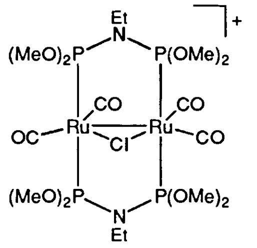


**13**

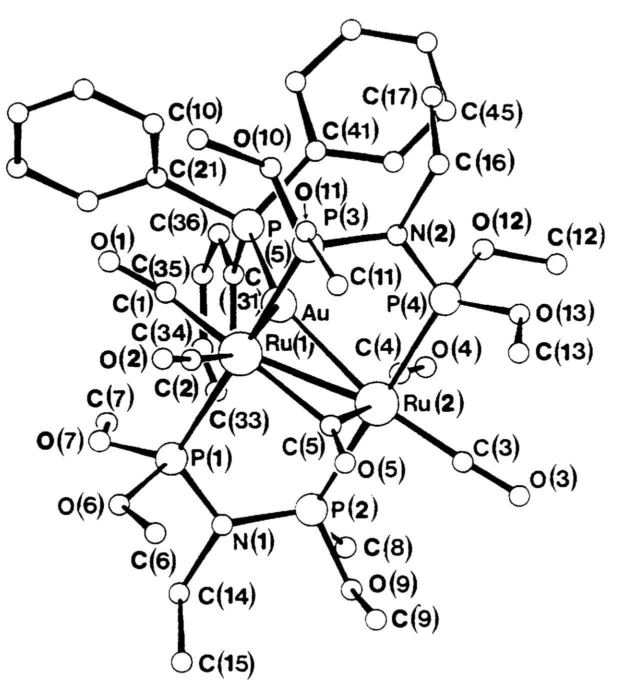


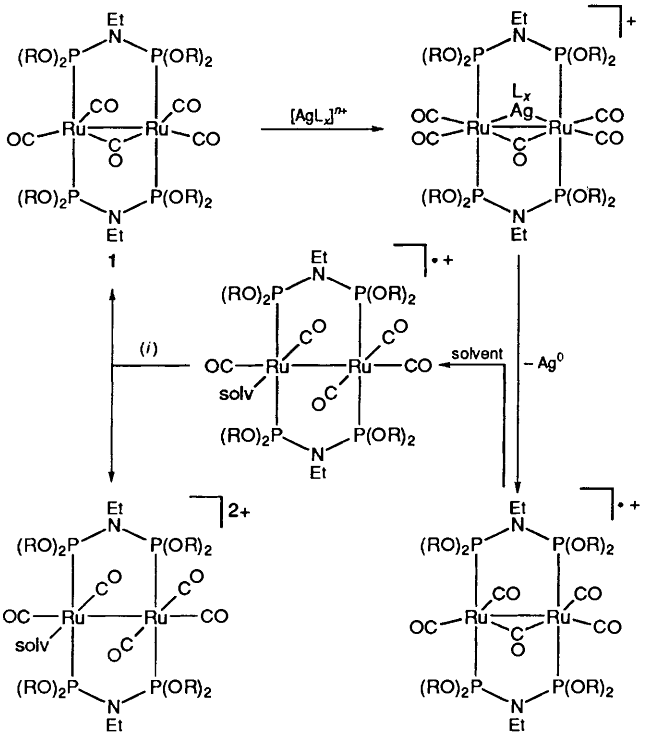
**Fig. 1** Perspective view of the cation of [Ru$_2${μ-Au(PPh$_3$)}(μ-CO)(CO)$_4${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]SbF$_6$

**Table 2** Selected interatomic distances (Å) and angles (°) for [Ru$_2${μ-Au(PPh$_3$)}(μ-CO)(CO)$_4${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]SbF$_6$

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 2.883(1) | Au–Ru(1) | 2.749(1) |
| Au–Ru(2) | 2.741(1) | Ru(1)–P(1) | 2.331(3) |
| Ru(1)–P(3) | 2.321(3) | Ru(2)–P(2) | 2.328(3) |
| Ru(2)–P(4) | 2.320(3) | Au–P(5) | 2.328(3) |
| Ru(1)–C(5) | 2.091(1) | Ru(2)–C(5) | 2.09(1) |
| Ru(1)–Au–Ru(2) | 63.3(1) | Ru(1)–Au–P(5) | 145.1(1) |
| Ru(2)–Au–P(5) | 151.5(1) | Au–Ru(1)–Ru(2) | 58.2(1) |
| Au–Ru(1)–P(1) | 93.9(1) | Au–Ru(1)–P(3) | 85.0(1) |
| Au–Ru(1)–C(1) | 63.6(4) | Au–Ru(1)–C(2) | 160.5(4) |
| Au–Ru(1)–C(5) | 104.5(3) | Ru(2)–Ru(1)–P(1) | 91.0(1) |
| Ru(2)–Ru(1)–P(3) | 90.2(1) | Ru(2)–Ru(1)–C(1) | 121.5(2) |
| Ru(2)–Ru(1)–C(2) | 140.4(4) | Ru(2)–Ru(1)–C(5) | 46.3(3) |
| P(1)–Ru(1)–P(3) | 177.6(1) | P(1)–Ru(1)–C(1) | 86.8(3) |
| P(1)–Ru(1)–C(2) | 91.8(4) | P(1)–Ru(1)–C(5) | 89.4(3) |
| P(3)–Ru(1)–C(1) | 90.8(3) | P(3)–Ru(1)–C(2) | 88.6(4) |
| P(3)–Ru(1)–C(5) | 92.9(3) | C(1)–Ru(1)–C(2) | 98.1(5) |
| C(1)–Ru(1)–C(5) | 167.2(5) | C(2)–Ru(1)–C(5) | 94.3(5) |
| Au–Ru(2)–Ru(1) | 58.4(1) | Au–Ru(2)–P(2) | 93.3(1) |
| Au–Ru(2)–P(4) | 86.3(1) | Au–Ru(2)–C(3) | 161.6(4) |
| Au–Ru(2)–C(4) | 61.7(3) | Au–Ru(2)–C(5) | 104.7(3) |
| Ru(1)–Ru(2)–P(2) | 90.4(1) | Ru(1)–Ru(2)–P(4) | 90.9(1) |
| Ru(1)–Ru(2)–C(3) | 139.4(4) | Ru(1)–Ru(2)–C(4) | 120.0(3) |
| Ru(1)–Ru(2)–C(5) | 46.3(3) | P(2)–Ru(2)–P(4) | 178.2(1) |
| P(2)–Ru(2)–C(3) | 91.4(4) | P(2)–Ru(2)–C(4) | 88.8(3) |
| P(2)–Ru(2)–C(5) | 89.2(3) | P(4)–Ru(2)–C(3) | 88.5(4) |
| P(4)–Ru(2)–C(4) | 89.5(3) | P(4)–Ru(2)–C(5) | 92.6(3) |
| C(3)–Ru(2)–C(4) | 100.6(5) | C(3)–Ru(2)–C(5) | 93.1(5) |
| C(4)–Ru(2)–C(5) | 166.1(5) | | |

were found to contain an AA′BB′ pattern of peaks consistent with the structure established X-ray crystallographically (see below). However, a sharp singlet is observed in the corresponding room-temperature spectra. Sharp singlets are also observed in the room-temperature $^{31}$P-{$^{1}$H} NMR spectra of these benzonitrile species measured in benzonitrile, acetonitrile and dichloromethane. In contrast an AA′BB′ pattern of peaks is observed in the room-temperature as well as the low-temperature $^{31}$P-{$^{1}$H} NMR spectra of the acetonitrile derivatives **4a** and **4b** in both [$^{2}$H$_6$]acetone and acetonitrile. Furthermore, addition of an excess of benzonitrile to deuteriated acetonitrile solutions of these two acetonitrile species did not lead to a collapse of the AA′BB′ set of peaks. These results are interpreted in terms of the benzonitrile derivatives being involved in some fluxional process, with these complexes not exchanging their co-ordinated nitriles with free nitrile ligands and with the fluxional process occurring *via* an intra- and not an inter-molecular mechanism. The benzonitrile ligand in **4d** has been established X-ray crystallographically (see below) to co-ordinate equatorially and a possible mechanism would involve the migration of the benzonitrile ligand from an equatorial site on one of the ruthenium atoms to an adjacent equatorial site on the other ruthenium atom. The apparent non-fluxionality of the acetonitrile species may be explained in terms of the less bulky acetonitrile ligand co-ordinating axially, as established X-ray crystallographically for the iodo group in [Fe$_2$I(CO)$_5${μ-(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}$_2$]$^+$,[9a,10] and with exchange being considerably more restricted in this situation.

Treatment of **1b** with a twice molar amount of AgSbF$_6$ in thf was found not to lead to the formation of a thf solvento species but to the aqua derivative **3b**, formed as a consequence of the trace amounts of water, still present in the thf in spite of rigorous drying procedures being employed, preferentially co-ordinating to the diruthenium chromophore. The aqua compound was likewise formed when dichloromethane was used as solvent, it not being possible to produce sufficiently dry dichloromethane to inhibit the formation of this compound. Dissolution of this aqua species in pre-dried acetone was shown to lead, according to the spectroscopic evidence, to the partial displacement of the water by the acetone, while addition of water to this acetone solution was found to result in an immediate increase in the amount of aqua species in solution relative to that of the acetone derivative, **2b**. It is thus apparent that the acetone and water ligands are readily



**Scheme 1** Proposed pathway for the reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ with silver(I) salts. (*i*) Disproportionation

displaced from their respective complexes but that the equilibrium (1) is such that the aqua species is present in

$$\underset{\mathbf{2b}}{[Ru_2(CO)_5(Me_2CO)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^{2+}} + H_2O \rightleftharpoons \underset{\mathbf{3b}}{[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^{2+}} + Me_2CO \quad (1)$$

significant quantities even in conventionally dried acetone. As described above the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the acetone species measured in $[^2H_6]$acetone exhibits a singlet assigned to **3b** as well as an AA'BB' pattern of peaks attributed to **2b**. Addition of water to this acetone solution leads to an increase in intensity of the singlet relative to that of the set of peaks of AA'BB' pattern with the former being effectively the sole peak when a sufficient quantity of water has been added. On the other hand the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **2b**, measured in dichloromethane, exhibits solely an AA'BB' pattern of peaks. These latter results are interpreted in terms of the aqua species being involved in some fluxional process in acetone.

The reaction of the tetramethoxydiphosphazane-bridged parent species, **1a**, likewise affords an aqua adduct *viz.* **3a** as the sole product, on treatment with a two-fold molar amount of $AgSbF_6$ in thf. Similarly, solvento products were also obtained when the parent compound **1b** was oxidised by a two-fold molar quantity of $AgSbF_6$ in the solvents diethyl ketone and nitromethane. In both cases, to a lesser extent for the diethyl ketone product and to a greater extent for the nitromethane species, the co-ordinated solvent was displaced by water such that neither could be isolated totally pure.

*Crystal Structure of* $[Ru_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$.—The structure of the cation of $[Ru_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$ is illustrated in Fig. 1. The cation is symmetrical with the two ruthenium atoms, separated by a distance of 2.883(1) Å, being bridged by a carbonyl and an Au(PPh$_3$) moiety as well as by the two diphosphazane ligands. The co-ordination at each ruthenium atom is completed by two terminal carbonyls. The two ruthenium atoms, the bridging carbonyl, the four terminal carbonyls and the gold and phosphorus atoms of the Au(PPh$_3$) moiety are essentially coplanar and lie in a plane which is essentially orthogonal to a plane defined by the two rutheniums and the four phosphorus atoms of the diphosphazane ligands. An interesting feature of the structure is the close approach of two of the carbonyl groups, CO(1) and CO(4), to the gold atom [Au–C(1) 2.57(1), Ru(1)–C(1) 1.95; Au–C(4) 2.50(1), Ru(2)–C(4) 1.94(1) Å]. This structural feature which has been observed previously for a number of other heteronuclear metal clusters containing gold, silver or copper fragments[11] could be interpreted in terms of these groups functioning as semi-bridging carbonyls, consistent with which are the Ru(1)–C(1)–O(1) and Ru(2)–C(4)–O(4) bond angles of 165(1) and 164(1)° respectively. However, the Ru(2)–Ru(1)–C(1) and Ru(1)–Ru(2)–C(4) bond angles of 121.5(2) and 120.0(3)° respectively, are considerably greater than the corresponding bond angles for $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ [93.8(5) and 94.0(5)°][12] which could be interpreted in terms of the gold atom repelling rather than attracting the carbonyl groups in question as has been suggested for the silver atom in $[Ru_3\{\mu\text{-}AgOC(O)CF_3\}(CO)_8(\mu\text{-}dppm)_2]$ in order to account for certain structural features.[13] On the other hand the insertion of a gold(I) ion across the two ruthenium atoms in $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ would be expected to lead to an increase in these bond angles. Selected interatomic distances and angles are summarised in Table 2.

*Mechanism of Oxidation of* $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ *by Silver*(I) *Salts*.—A mechanism for the formation of the solvento species $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ by oxidation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ in weak donor solvents by silver(I) salts is summarised in Scheme 1. The initial step in the reaction pathway involves the insertion of the solvated silver(I) ions across the ruthenium–ruthenium edge in **1** to afford $[Ru_2(\mu\text{-}AgL_x)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$; the proposed structure of this species is based on spectroscopic evidence and the structure established X-ray crystallographically for $[Ru_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$. The second step involves electron transfer from the diruthenium fragment to the silver and the loss of silver from the silver adduct as the free metal. Although it was not possible to characterise the product of this latter process it was presumed to be $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ on the basis that cyclic voltammetric studies have revealed that compound **1** is readily oxidised electrochemically to $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and that for R = Pr$^i$ this oxidation is fully reversible on the time-scale of the measurement.[5] Furthermore, oxidation of $[Fe_2(cp)_2(\mu\text{-}CO)_2(\mu\text{-}dppm)]$ (cp = cyclopentadienyl) by silver(I) ions has been shown to afford $[Fe_2(cp)_2(\mu\text{-}CO)_2(\mu\text{-}dppm)]^+$, fully characterised as the tetrafluoroborate, tetraphenylborate and hexafluoroantimonate salts.[14] As noted above, the violet species presumed to be $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$, readily disproportionates in weakly co-ordinating solvents to $[Ru_2(CO)_5(solv)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^{2+}$ and **1a**, with $[Ru_2(CO)_5(solv)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ being a possible intermediate in this disproportionation process. The results of this study provide unequivocal evidence that the one-electron oxidation of compound **1**, and presumably related dinuclear compounds bridged by diphosphorus ligands, by silver(I) salts occurs *via* an inner-sphere mechanism. Silver(I) salts are used extensively as one-electron oxidants in inorganic and organometallic chemistry while a wide range of compounds formed by addition of silver(I) complexes across a metal–metal bond in dinuclear and metal cluster derivatives or across a face of a metal cluster have been reported.[3,11,13,15-23] However, this is the first detailed study to provide tangible evidence that one-electron oxidation of polynuclear derivatives by silver(I) salts

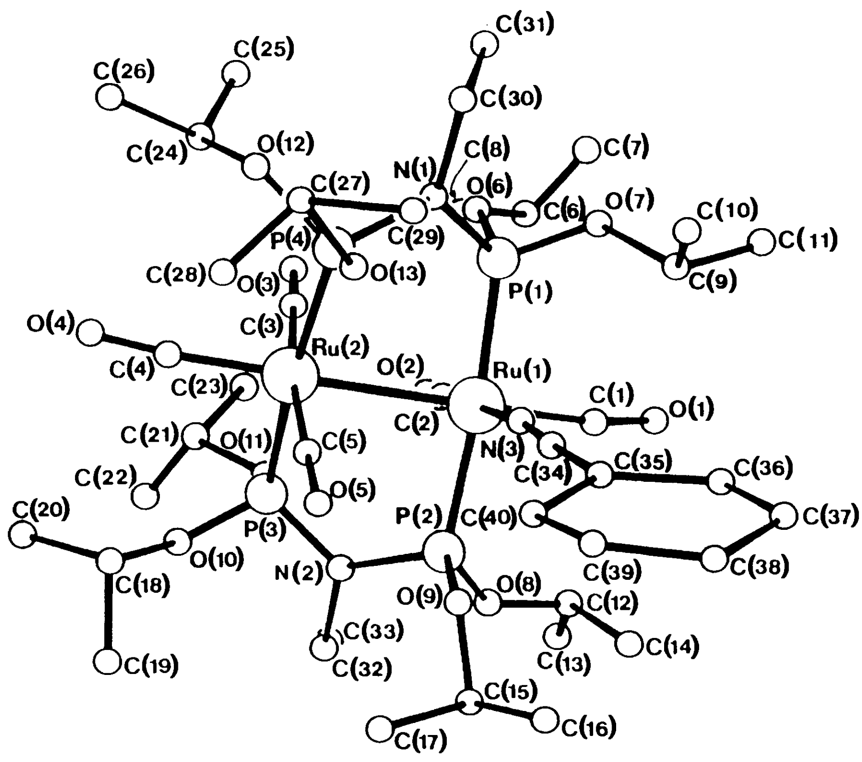


Fig. 2 Perspective view of the cation of $[Ru_2(CO)_5(PhCN)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$

Table 3 Selected interatomic distances (Å) and angles (°) for $[Ru_2(CO)_5(PhCN)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$

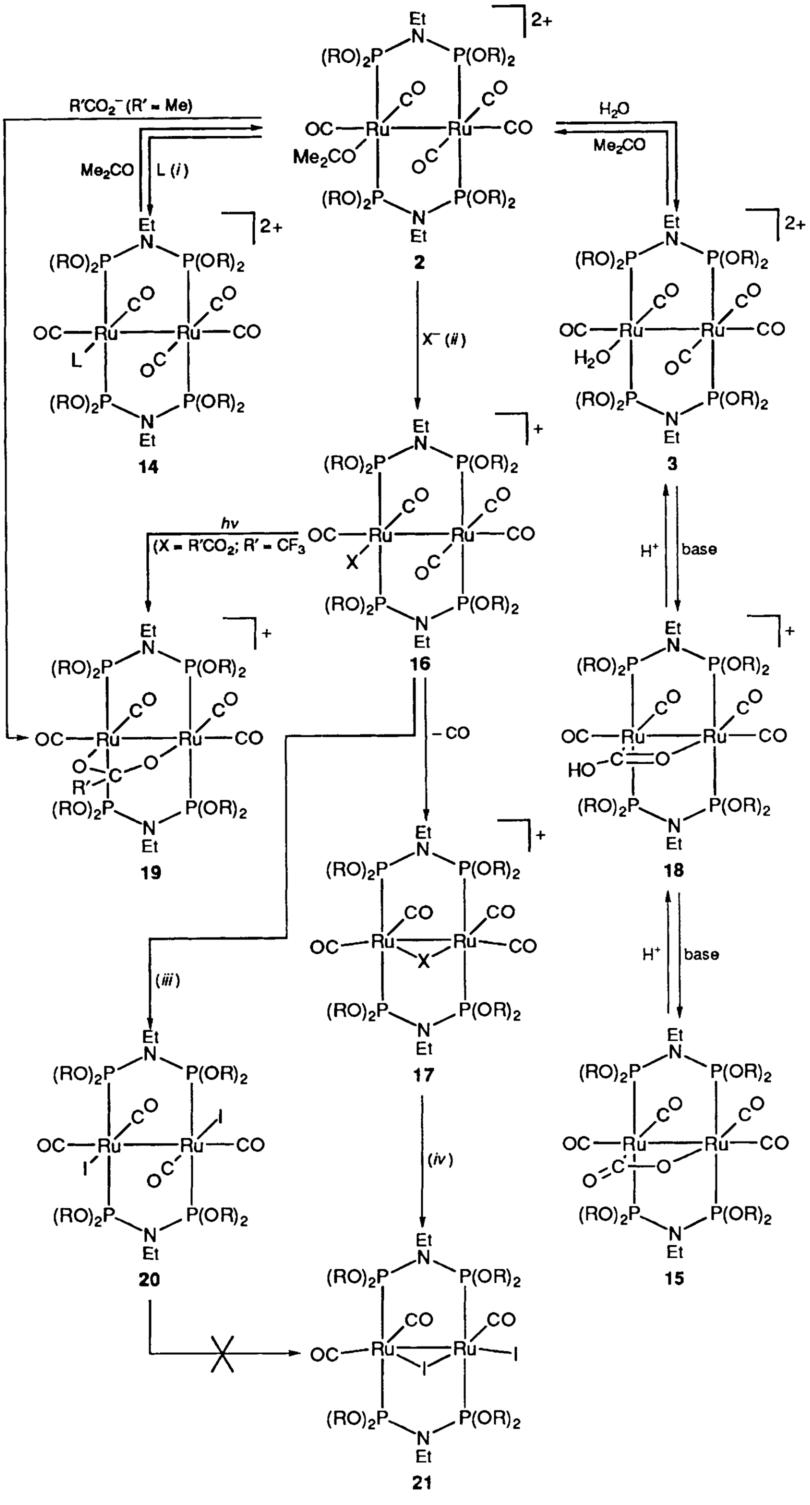
| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 2.887(3) | Ru(1)–P(1) | 2.350(7) |
| Ru(1)–P(2) | 2.360(7) | Ru(2)–P(3) | 2.349(7) |
| Ru(2)–P(4) | 2.336(7) | Ru(1)–N(3) | 2.08(2) |
| N(3)–C(34) | 1.15(3) | C(34)–C(35) | 1.38(4) |
| Ru(2)–Ru(1)–P(1) | 86.9(2) | Ru(2)–Ru(1)–P(2) | 87.1(2) |
| Ru(2)–Ru(1)–N(3) | 92.6(6) | Ru(2)–Ru(1)–C(1) | 174.1(9) |
| Ru(2)–Ru(1)–C(2) | 86.4(8) | P(1)–Ru(1)–P(2) | 173.4(2) |
| P(1)–Ru(1)–N(3) | 88.4(6) | P(1)–Ru(1)–C(1) | 89.4(10) |
| P(1)–Ru(1)–C(2) | 93.0(8) | P(2)–Ru(1)–N(3) | 89.1(6) |
| P(2)–Ru(1)–C(1) | 96.8(10) | P(2)–Ru(1)–C(2) | 89.4(8) |
| N(3)–Ru(1)–C(1) | 91.9(11) | N(3)–Ru(1)–C(2) | 178.2(10) |
| C(1)–Ru(1)–C(2) | 89.2(13) | Ru(1)–Ru(2)–P(3) | 87.0(2) |
| Ru(1)–Ru(2)–P(4) | 88.4(2) | Ru(1)–Ru(2)–C(3) | 87.2(8) |
| Ru(1)–Ru(2)–C(4) | 178.8(9) | Ru(1)–Ru(2)–C(5) | 85.0(8) |
| P(3)–Ru(2)–P(4) | 175.4(3) | P(3)–Ru(2)–C(3) | 90.4(8) |
| P(3)–Ru(2)–C(4) | 93.5(9) | P(3)–Ru(2)–C(5) | 91.1(8) |
| P(4)–Ru(2)–C(3) | 89.0(8) | P(4)–Ru(2)–C(4) | 91.1(9) |
| P(4)–Ru(2)–C(5) | 88.9(8) | C(3)–Ru(2)–C(4) | 91.7(12) |
| C(3)–Ru(2)–C(5) | 172.0(11) | C(4)–Ru(2)–C(5) | 96.0(12) |
| Ru(1)–N(3)–C(34) | 171(2) | N(3)–C(34)–C(35) | 177(3) |

occurs *via* inner-sphere intermediates in which the silver has added across an edge or a face of the metal atom framework. Furthermore, apart from an investigation of the reactions of AgY salts with $[Fe_2(cp)_2(CO)_{4-n}(CNMe)_n]$ complexes by Manning and coworkers,[24] this is the first to establish that the nature of the final product of this type of reaction can be very dependent on the nature of the ligand co-ordinated to the silver.

*Crystal Structure of* $[Ru_2(CO)_5(PhCN)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$.—The structure of cation **4d** is illustrated in Fig. 2. The two ruthenium atoms, each of which is approximately octahedral, are not only linked through the two bridging tetraisopropoxydiphosphazane ligands, *trans* disposed with respect to each other, but also by a formal ruthenium–ruthenium bond [Ru(1)–Ru(2), 2.887(3) Å]. The benzonitrile ligand is co-ordinated essentially linearly [Ru(1)–N(3)–C(34) 171(2)°] at an equatorial site with the co-ordination at each ruthenium being completed by terminal carbonyl groups. The cation adopts an essentially 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 28.4 and 31.0° respectively. Selected interatomic distances and angles are summarised in Table 3.

*Reactions of the Solvento Species* $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ *with Nucleophiles.*—The strength of the bond between nitriles and transition metals in organometallic compounds containing organonitrile ligands is, in general, relatively weak such that these ligands are readily displaced by other donor ligands under mild conditions. For instance the cationic iron complexes $[Fe(cp)(CO)_2(R'CN)]^+$ (R′ = Me, Et, Ph, *etc*), produced by oxidative cleavage of $[Fe_2(cp)_2(\mu\text{-}CO)_2(CO)_2]$ in the presence of an excess of the organonitrile R′CN, react with Group 15 donor ligands $ER''_3$ as well as with anionic nucleophiles $X^-$, affording complexes of the type $[Fe(cp)(CO)_2(ER''_3)]^+$ and $[Fe(cp)X(CO)_2]$ in high yield respectively.[25] Likewise the triosmium species $[Os_3(CO)_{12-n}(MeCN)_n]$ and the more unstable triruthenium species $[Ru_3(CO)_{12-n}(MeCN)_n]$ (*n* = 1 or 2), react readily with a wide range of nucleophiles and in fact are utilised extensively as precursors for the synthesis of triosmium or triruthenium products.[26–28] Attempts to displace the co-ordinated nitrile ligand in $[Ru_2(CO)_5(R'CN)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][SbF_6]_2$ (R′ = Me or Ph) with neutral and anionic donor ligands were not particularly successful however indicating that the co-ordinated nitrile ligands in these complexes are fairly strongly bound. The acetone ligand in $[Ru_2(CO)_5(Me_2CO)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ (**2a** and **2b**) can be expected to be less strongly bound than the organonitrile ligand in the corresponding nitrile species and thus the acetone species were employed as precursors for further study.

A measure of the ready displacement of acetone from **2b** is that acetone solutions of this species always contain some



**Scheme 2** Reaction pathways for the reactions of [Ru$_2$(CO)$_5$(Me$_2$CO){μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$]$^{2+}$ with neutral nucleophiles L and anionic nucleophiles X$^-$; (*i*) L = CO, MeCN, PhCN, Me$_2$S, SC$_4$H$_8$, H$_2$O, py or 4,4′-bipy; (*ii*) X = Cl, Br, I, SCN, SPh or CF$_3$CO$_2$; (*iii*) X = I; I$^-$ (equimolar) followed by Me$_3$NO·2H$_2$O (excess). (*iv*) X = I; Me$_3$NO·2H$_2$O (excess) followed by I$^-$ (excess)

[Ru$_2$(CO)$_5$(H$_2$O){μ-(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}]$^{2+}$ **3b** even when, as described above, the acetone is rigorously dried. The acetone ligand in **2**, and likewise the aqua ligand in **3**, was found to be readily displaced by a wide range of nucleophiles, in some cases reversibly, affording products of the type [Ru$_2$(CO)$_5$L{μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$]$^{2+}$ upon reaction with the corresponding nucleophiles L; CO (R = Me **14a**), CNC$_6$H$_3$Me$_2$-2,6 (R = Me **14b**), SC$_4$H$_8$ (R = Pr$^i$ **14c**), SMe$_2$ (R = Pr$^i$ **14d**), py (R = Pr$^i$ **14e**), 4,4′-bipy (R = Pr$^i$ **14f**), Et$_2$CO (R = Pr$^i$ **14g**), MeNO$_2$ (R = Pr$^i$ **14h**), MeCN **4a** or **4b** or PhCN **4c** or **4d**. While the displacement by carbon monoxide was incomplete and the probable product, [Ru$_2$(CO)$_6${μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$]$^{2+}$, could only be detected spectroscopically, the products from the reactions involving the other nucleophiles could be isolated in high yield. The solution and solid-state IR spectra of all of the products isolated, apart from that formed in the carbon monoxide reaction, exhibit very similar band patterns in the C–O stretching region typical of species of the type [Ru$_2$(CO)$_5$L{μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$]$^{x+}$ while the $^{31}$P-{$^1$H} NMR spectra of these species were found to contain an AA′BB′ pattern of peaks consistent with the asymmetric structure proposed and indeed established X-ray crystallographically for $[Ru_2(CO)_5(PhCN)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ (see above) and $[Ru_2(CO)_5(SC_4H_8)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ (see below). It is presumed that the ligands L are co-ordinated equatorially as indeed established for PhCN and $SC_4H_8$ in their respective products. *o*-Xylyl isocyanide also readily displaces the acetone ($H_2O$) molecule from **2a** (**3a**) but the product $[Ru_2(CO)_5(CNC_6H_3Me_2\text{-}2,6)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$ could not be isolated totally pure even though satisfactory analytical results were obtained. It proved to be light sensitive in solution and, in acetone, slowly, but incompletely, degraded to a new product believed to be the acetone–xylyl isocyanide substituted derivative $[Ru_2(CO)_4(CNC_6H_3Me_2\text{-}2,6)(Me_2CO)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$ on the basis of its analytical and spectroscopic data.

We have shown previously, as described above, that the solvento species $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ are readily deprotonated when the co-ordinated solvent is a protic solvent of the type R′OH (R′ = H, Me, Et, *etc*) and in particular to $[Ru_2\{\mu\text{-}OC(OR')\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and, in the case of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$, to $[Ru_2\{\mu\text{-}OC(O)\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **15**.[8] As a consequence a competing reaction in the above nucleophilic substitution reactions is the deprotonation of **3**, present in the acetone solution, by the ligand L functioning as a base. The extent of this deprotonation was found to be dependent not only on the amount of water present but also on the relative nucleophilic and basic strengths of the ligand. Thus, while the reaction of **2b**/**3b** with tetrahydrothiophene in acetone afforded solely $[Ru_2(CO)_5(SC_4H_8)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$, the corresponding reaction involving pyridine produced $[Ru_2(CO)_5(py)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ and $[Ru_2\{\mu\text{-}OC(OH)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]SbF_6$ in approximately equal amounts and that involving triethylamine gave primarily $[Ru_2\{\mu\text{-}OC(OH)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ together with a small amount of $[Ru_2\{\mu\text{-}OC(O)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$.

Anionic ligands $X^-$ also readily displace the acetone from **2** affording either cationic products of the type $[Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ **16** or, for those ligands which are capable of effecting further substitution and of adopting a bridging co-ordination mode, of the type $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ **17**. However, those anionic ligands with moderate to strong basic properties were again found to effect the deprotonation of **3** present in the acetone solution. In particular while halide and trifluoroacetate ions gave the pentacarbonyl $[Ru_2X(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ and/or tetracarbonyl $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ species on reaction with **2b**/**3b**, acetate, benzenethiolate and thiocyanate ions afforded a small amount of $[Ru_2\{\mu\text{-}OC(OH)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ as well as $[Ru_2\{\mu\text{-}OC(Me)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$, $[Ru_2(\sigma\text{-}SPh)(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+/[Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ or $[Ru_2(\sigma\text{-}SCN)(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ respectively and alkoxide and hydroxide ions produced solely $[Ru_2\{\mu\text{-}OC(OH)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ **18** (R = $Pr^i$) or $[Ru_2\{\mu\text{-}OC(O)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **15** (R = $Pr^i$).

Significantly, while treatment of **2b**/**3b** with acetate ions afforded a tetracarbonyl product *viz*. $[Ru_2\{\mu\text{-}OC(Me)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ **19** (R = $Pr^i$, R′ = Me), the corresponding reaction involving trifluoroacetate ions gave solely the pentacarbonyl species $[Ru_2\{\sigma\text{-}OC(O)CF_3\}(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ **16** (R = $Pr^i$, X = $CF_3CO_2$). Furthermore, $[Ru_2\{\sigma\text{-}OC(O)Me\}(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ **16** (R = $Pr^i$, X = $MeCO_2$) could not be detected in the formation of **19** (R = $Pr^i$, R′ = Me) in spite of this pentacarbonyl derivative, which can be synthesised by an alternative procedure, being relatively stable to decarbonylation and requiring irradiation with ultraviolet light for its conversion. These reactions and those involving alkoxide and hydroxide ions described above are reported in more detail elsewhere.[8]

The decarbonylation of $[Ru_2I(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ **16** (R = $Pr^i$, X = I) to $[Ru_2(\mu\text{-}I)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ **17** (R = $Pr^i$, X = I) is relatively slow but can be accelerated by the addition of a slight excess of trimethylamine *N*-oxide dihydrate. Interestingly, addition of an equimolar amount of iodide ions to **16** (R = $Pr^i$, X = I) prior to the addition of an excess of $Me_3NO{\cdot}2H_2O$ resulted in the formation of the neutral diiodide $[Ru_2I_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **20** (R = $Pr^i$). On the other hand treatment of the ionic tetracarbonyl species **17** (R = $Pr^i$, X = I) with an equimolar amount of iodide ions and trimethylamine *N*-oxide dihydrate gave the tricarbonyl derivative $[Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **21** (R = $Pr^i$). These results have been reported previously.[9]

The acetone/water solvento species mixture is also, not surprisingly, susceptible to hydride ion attack affording not only **18** (R = $Pr^i$) and **15** (R = $Pr^i$) but also the parent complex **1b**, with the latter being formed *via* $[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$.[29]

The salient spectroscopic features of the pentacarbonyl species $[Ru_2X(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ (X = Cl, Br, I, SCN, SPh or $CF_3CO_2$) are the distinctive band patterns in the C–O stretching region of their IR spectra and the AA′BB′ pattern of peaks in the $^{31}P\text{-}\{H\}$ NMR spectra. Likewise those for the tetracarbonyl species $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ (X = Cl, Br, I, SPh or $MeCO_2$) are again the distinctive band patterns in the C–O stretching region of their IR spectra and the presence of a singlet in their $^{31}P\text{-}\{^1H\}$ NMR spectra.

The reactions of $[Ru_2(CO)_5(Me_2CO)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ with various nucleophiles are summarised in Scheme 2.

*Crystal Structure of* $[Ru_2(CO)_5(SC_4H_8)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2{\cdot}CH_2Cl_2$.—The structure of the dication of $[Ru_2(CO)_5(SC_4H_8)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ is illustrated in Fig. 3. It is very similar to that of $[Ru_2(CO)_5(PhCN)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^{2+}$ with the two ruthenium atoms being separated by a distance of 2.926(2) Å and being bridged by the two diphosphazane ligands, with the tetrahydrothiophene ligand being co-ordinated equatorially and with the cation adopting an essentially staggered conformation as reflected by the P(1)–Ru(1)–Ru(2)–P(4) and P(2)–Ru(1)–Ru(2)–P(3) torsion angles of 26.6 and 30.5° respectively. The tetrahydrothiophene ring, which is slightly puckered as reflected by the small deviations of the constituent atoms from their least squares plane [S −0.06, C(34) 0.10, C(35) −0.20, C(36) 0.20, C(37) −0.09 Å], is bent away from the $Ru_2P_4$ chromophore, the sulfur being positioned at a distance of 0.77(1) Å from the plane defined by Ru(1), C(34) and C(35). Selected interatomic distances and angles are summarised in Table 4.

## Experimental

The neutral pentacarbonyls $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ were synthesised according to a literature procedure.[12] All reactions and manipulations were carried out under an atmosphere of nitrogen by Schlenk techniques. The solvents acetone, benzonitrile, acetonitrile, thf and dichloromethane were purified and dried according to the procedures described in ref. 5. IR spectra were recorded on a Perkin-Elmer 457 spectrometer. $^{31}P\text{-}\{^1H\}$ NMR spectra were measured on a Varian FT80A spectrometer while $^1H$ NMR spectra were obtained on a Varian Gemini 200 instrument. Appropriate spectroscopic data are summarised in Table 1.

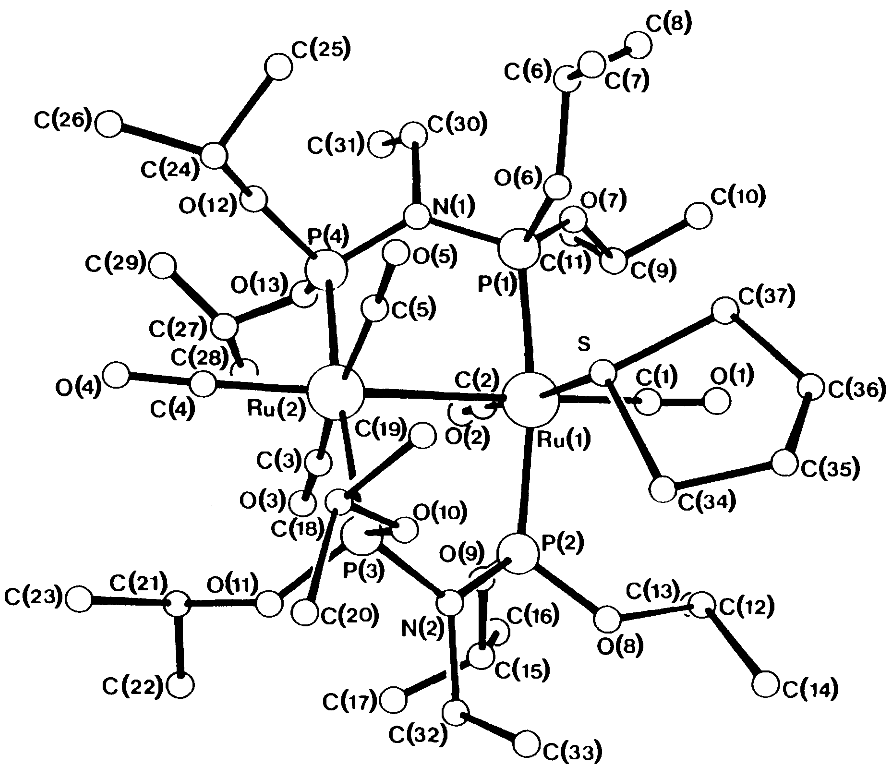


Fig. 3 Perspective view of the cation of $[Ru_2(CO)_5(SC_4H_8)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2\cdot CH_2Cl_2$

Table 4 Selected interatomic distances (Å) and angles (°) for $[Ru_2(CO)_5(SC_4H_8)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2\cdot CH_2Cl_2$

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 2.926(2) | Ru(1)–P(1) | 2.355(6) |
| Ru(1)–P(2) | 2.365(7) | Ru(2)–P(3) | 2.362(6) |
| Ru(2)–P(4) | 2.332(5) | Ru(1)–S | 2.482(5) |
| S–C(34) | 1.88(2) | S–C(37) | 1.82(2) |
| C(34)–C(35) | 1.54(4) | C(35)–C(36) | 1.40(5) |
| C(36)–C(37) | 1.53(4) | | |
| Ru(2)–Ru(1)–P(1) | 86.4(1) | Ru(2)–Ru(1)–P(2) | 85.1(1) |
| Ru(2)–Ru(1)–S | 92.3(1) | Ru(2)–Ru(1)–C(1) | 179.3(6) |
| Ru(2)–Ru(1)–C(2) | 86.1(7) | P(1)–Ru(2)–P(2) | 170.3(2) |
| P(1)–Ru(1)–S | 90.4(2) | P(1)–Ru(1)–C(1) | 93.1(7) |
| P(1)–Ru(1)–C(2) | 87.1(7) | P(2)–Ru(1)–S | 94.7(2) |
| P(2)–Ru(1)–C(1) | 95.3(7) | P(2)–Ru(1)–C(2) | 87.6(7) |
| S–Ru(1)–C(1) | 88.2(7) | S–Ru(1)–C(2) | 177.1(8) |
| C(1)–Ru(1)–C(2) | 93.4(9) | Ru(1)–Ru(2)–P(3) | 87.4(1) |
| Ru(1)–Ru(2)–P(4) | 88.0(1) | Ru(1)–Ru(2)–C(3) | 88.3(6) |
| Ru(1)–Ru(2)–C(4) | 177.8(6) | Ru(1)–Ru(2)–C(5) | 88.5(7) |
| P(3)–Ru(2)–P(4) | 175.2(2) | P(3)–Ru(2)–C(3) | 86.8(6) |
| P(3)–Ru(2)–C(4) | 94.7(6) | P(3)–Ru(2)–C(5) | 92.4(6) |
| P(4)–Ru(2)–C(3) | 91.8(6) | P(4)–Ru(2)–C(4) | 89.9(6) |
| P(4)–Ru(2)–C(5) | 88.5(6) | C(3)–Ru(2)–C(4) | 92.2(9) |
| C(3)–Ru(2)–C(5) | 173.9(9) | C(4)–Ru(2)–C(5) | 94.0(9) |
| Ru(1)–S–C(34) | 113.6(7) | Ru(1)–S–C(37) | 110.1(7) |
| C(34)–S–C(37) | 95.1(9) | | |

*Syntheses*.—$[Ru_2\{\mu\text{-}Cu(MeCN)_2\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$.—Solid $[Cu(MeCN)_4]PF_6$ (0.14 g, 0.4 mmol) was added to a solution of **1a** (0.32 g, 0.4 mmol) in thf (30 cm$^3$) at 50 °C. After 20 min the reaction mixture was evaporated to dryness and the residue crystallised from MeCN–toluene (1 : 5). Yield: *ca.* 80% (yellow plates) (Found: C, 22.8; H, 3.5; N, 5.2. Calc. for $C_{21}H_{40}CuF_6N_4O_{13}P_5Ru_2$: C, 23.1; H, 3.7; N, 5.1%).

$[Ru_2\{\mu\text{-}Ag(MeCN)_x\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$. A solution of $AgSbF_6$ (0.05 g, 0.14 mmol) in acetonitrile (*ca.* 3 cm$^3$) was added dropwise to a stirred solution of **1a** (0.12 g, 0.15 mmol) in acetonitrile (*ca.* 5 cm$^3$) with exclusion of light. The stirring was continued for 30 min and the solution concentrated to *ca.* 2 cm$^3$. The product was precipitated by addition of diethyl ether (*ca.* 10 cm$^3$) as a yellow thermally- and light-sensitive solid which was only stable in the presence of trace amounts of free acetonitrile. Because of the variable acetonitrile content of the product satisfactory microanalysis could not be obtained and identification was by spectroscopic means only.

$[Ru_2\{\mu\text{-}Ag(py)_x\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$. Silver hexafluoroantimonate (0.05 g, 0.14 mmol) was dissolved in pyridine (1 cm$^3$) and the excess pyridine removed under reduced pressure at 80 °C. The silver–pyridine complex was dissolved in acetone (*ca.* 5 cm$^3$) and the solution cooled to −80 °C. Solid **1a** (0.12 g, 0.15 mmol) was added to this solution with exclusion of light. The reaction mixture was allowed to warm to room temperature and was stirred for a further 1 h. The solution was concentrated to *ca.* 2 cm$^3$ and the product precipitated by addition of diethyl ether (*ca.* 10 cm$^3$). The product which is thermally and light-sensitive was only stable in the presence of trace amounts of pyridine. As a consequence it could not be isolated analytically pure and it was identified by spectroscopic means only.

$[Ru_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$. A solution of $[AuCl(PPh_3)]$ (0.21 g, 0.42 mmol) and **1a** in thf (50 cm$^3$) was refluxed for 25 min during which time the reaction mixture turned dark orange. An equimolar amount of $AgSbF_6$ (0.14 g, 0.4 mmol) in thf (10 cm$^3$) was added to the reaction mixture and the solution evaporated to dryness. The residue was extracted with $CH_2Cl_2$ (2 × 300 cm$^3$) and the combined extracts were filtered through a glass fibre frit and concentrated under reduced pressure to *ca.* 20 cm$^3$. The product was obtained by addition of ethanol (10 cm$^3$) and allowing crystallisation to occur at −10 °C. Yield: 75%

**Table 5** Crystal data and details of refinement[a]

| Compound | [Ru$_2${μ-Au(PPh$_3$)}(μ-CO)(CO)$_4${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]SbF$_6$ | [Ru$_2$(CO)$_5$(PhCN){μ-(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}$_2$] [SbF$_6$]$_2$ | [Ru$_2$(CO)$_5$(SC$_4$H$_8$){μ-(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}$_2$] [SbF$_6$]$_2$·CH$_2$Cl$_2$ |
|---|---|---|---|
| $M$ | 1497.02 | 1599.51 | 1669.49 |
| Crystal system | Monoclinic | Orthorhombic | Orthorhombic |
| Space group | $P2_1/c$ | $P2_12_12$ | $Pna2_1$ |
| $a$/Å | 13.481(2) | 22.710(5) | 27.167(2) |
| $b$/Å | 20.723(3) | 23.695(5) | 14.629(2) |
| $c$/Å | 18.440(3) | 12.256(3) | 16.704(2) |
| β/° | 90.90(1) | 90 | 90 |
| $U$/Å$^3$ | 5074.66 | 6594.9 | 6638.9 |
| $D_c$/g cm$^{-3}$ | 1.957 | 1.611 | 1.670 |
| $F$(000) | 2894 | 3176 | 3248 |
| μ(Mo-Kα)/cm$^{-1}$ | 42.17 | 13.12 | 16.33 |
| Crystal size/mm | 0.36 × 0.15 × 0.15 | 0.50 × 0.23 × 0.16 | 0.46 × 0.31 × 0.19 |
| Total data measured | 8278 | 5104 | 3821 |
| No. of unique reflections | 7933 | 4617 | 3304 |
| No. of observed reflections [$I > 3\sigma(I)$] | 7933[b] | 3877 | 2788 |
| No. of parameters | 386 | 436 | 349 |
| $\rho_{max}$/e Å$^{-3}$ | 1.86 | 0.88 | 0.64 |
| Max. least-squares absolute shift-to-error ratio | 0.11 | 1.32 | 0.28 |
| Weighting scheme parameter $g$ in $w = 1/[\sigma^2(F) + gF^2]$ | Unit weights | 0.006 | 0.001 |
| Final $R$[c] | 0.0618 | 0.0663 | 0.0580 |
| Final $R'$[d] | 0.0618 | 0.0722[e] | 0.0658 |

[a] Details in common: $Z = 4$, $2\theta_{max} = 46°$, semiempirical absorption correction. [b] All reflections were used in the refinement. [c] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [d] $R' = \Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}|F_o|$. [e] Refinement in the other hand gives slightly higher $R$ factors.

(yellow-green plates) (Found: C, 28.4; H, 3.1; N, 1.9. $C_{35}H_{49}AuF_6N_2O_{13}P_5Ru_2Sb$ requires C, 28.1; H, 3.3; N, 1.9%).

[Ru$_2$(σ-HgCl)(CO)$_5${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]SbF$_6$. A slight excess of solid HgCl$_2$ (0.12 g, 0.45 mmol) was added to a solution of **1a** (0.32 g, 0.40 mmol) in thf (20 cm$^3$) at −10 °C. The solution was stirred for 1 h with exclusion of light resulting in the separation of a beige precipitate which redissolved on addition of dichloromethane (30 cm$^3$). The reaction mixture was treated with a solution of AgSbF$_6$ (0.14 g, 0.40 mmol) in thf (10 cm$^3$) to effect the precipitation of AgCl. The solvent was reduced under reduced pressure, the residue extracted with CH$_2$Cl$_2$ (2 × 15 cm$^3$) and the combined extracts filtered. The solution was concentrated and the product precipitated by addition of *n*-hexane (*ca.* 20 cm$^3$) as a light-sensitive rose coloured solid. Yield: 70% (Found: C, 16.4; H, 2.7; N, 2.4. $C_{17}H_{34}ClF_6HgN_2O_{13}P_4Ru_2Sb$ requires C, 16.0; H, 2.7; N, 2.4%).

[Ru$_2$(σ-SbCl$_2$)(CO)$_5${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]Sb$_2$Cl$_7$. Solid SbCl$_3$ (0.29 g, 1.0 mmol) was added to a solution of **1a** (0.28 g, 0.35 mmol) in 1,2-dichloroethane (30 cm$^3$). The yellow solution became orange within 2 min. After 1 h at room temperature the volume of the solution was reduced to 10 cm$^3$ and acetonitrile (10 cm$^3$) and then diethyl ether added until the mixture became turbid. The product was allowed to separate at 4 °C. Yield: 55% (orange microcrystalline solid) (Found: C, 13.7; H, 2.3; N, 1.9. $C_{17}H_{34}Cl_9N_2O_{13}P_4Ru_2Sb_3$ requires C, 13.7; H, 2.3; N, 1.9%).

[Ru$_2$(CO)$_5$(Me$_2$CO){μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$][SbF$_6$]$_2$ (R = Me *or* Pr$^i$). A solution of a twice molar amount of AgSbF$_6$ (0.17 g, 0.50 mmol) in acetone (3 cm$^3$) was added dropwise to a stirred solution of **1a** (0.20 g, 0.25 mmol) or **1b** (0.25 g, 0.25 mmol) in acetone (10 cm$^3$) and the solution stirred for a further 1 h. The orange solution turned pale yellow and a black precipitate of silver metal separated. The suspension was filtered through a glass fibre frit and the volume of the filtrate concentrated under reduced pressure to 5 cm$^3$. For R = Me, the product was precipitated from the filtrate by the addition of diethyl ether (5 cm$^3$) and was crystallised from acetone–diethyl ether. For R = Pr$^i$, toluene (2 cm$^3$) was added to the filtrate and the solution kept at −10 °C to effect the crystallisation of the product. Yields: 90 and 70% respectively (Found: C, 18.2; H, 3.0; N, 2.2. $C_{20}H_{40}F_{12}N_2O_{13}P_4Ru_2Sb_2$ requires C, 18.2; H, 3.0; N, 2.1. Found: C, 27.8; H, 4.4; N, 2.0. $C_{36}H_{72}F_{12}N_2O_{13}P_4Ru_2Sb_2$ requires C, 27.8; H, 4.6; N, 1.8%).

[Ru$_2$(CO)$_5$(H$_2$O){μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$][SbF$_6$]$_2$ (R = Me *or* Pr$^i$). 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 **1a** (0.23 g, 0.29 mmol) or **1b** (0.30 g, 0.29 mmol) in thf (*ca.* 10 cm$^3$) and the mixture stirred for a further 1 h, during which time silver metal separated. The solution was filtered and the volume of the filtrate was reduced under reduced pressure to *ca.* 2 cm$^3$. Crystallisation was effected by addition of diethyl ether. Yield: 80–90% (Found: C, 15.5; H, 2.8; N, 2.2. $C_{17}H_{36}F_{12}N_2O_{14}P_4Ru_2Sb_2$ requires C, 15.8; H, 2.8; N, 2.2. Found: C, 26.4; H, 4.4; N, 1.8. $C_{33}H_{68}F_{12}N_2O_{14}P_4Ru_2Sb_2$ requires C, 26.2; H, 4.5; N, 1.8%).

[Ru$_2$(CO)$_5$(MeCN){μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$][SbF$_6$]$_2$ (R = Me *or* Pr$^i$). A solution of a two-fold molar amount of AgSbF$_6$ (0.10 g, 0.29 mmol) in acetonitrile (3 cm$^3$) was added dropwise to a stirred solution of **1a** (0.12 g, 0.15 mmol) or **1b** (0.15 g, 0.15 mmol) in acetonitrile (5 cm$^3$) and the solution stirred for a further 1 h during which time a precipitate of silver metal separated. The pale yellow solution was filtered through a glass fibre frit and the volume of the filtrate concentrated under reduced pressure to *ca.* 3 cm$^3$. Toluene (5 cm$^3$) was added and the solution kept at −10 °C to effect the separation of the product in crystalline form. Yield: 80–90% (Found: C, 17.8; H, 2.8; N, 3.3. $C_{19}H_{37}F_{12}N_3O_{13}P_4Ru_2Sb_2$ requires C, 17.4; H, 2.8; N, 3.2. Found: C, 27.8; H, 4.7; N, 2.9. $C_{36}H_{69}F_{12}N_3O_{13}P_4Ru_2Sb_2$ requires C, 27.3; H, 4.5; N, 2.7%).

[Ru$_2$(CO)$_5$(PhCN){μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$][SbF$_6$]$_2$ (R = Me *or* Pr$^i$). A solution of a two-fold molar amount of AgSbF$_6$ (0.10 g, 0.29 mmol) in benzonitrile (3 cm$^3$) was added dropwise to a stirred solution of **1a** (0.12 g, 0.15 mmol) or **1b** (0.15 g, 0.15 mmol) in benzonitrile (5 cm$^3$) and the solution stirred for a further 1 h. The products were isolated in the same way as that described above for the analogous acetonitrile species. Yield: 80–90% (Found: C, 21.9; H, 2.9; N, 3.2. $C_{24}H_{39}F_{12}N_3O_{13}P_4Ru_2Sb_2$ requires C, 21.0; H, 2.9; N, 3.0.

**Table 6** Fractional coordinates ( × $10^4$) for $[Ru_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| Au | 1796(1) | 902(1) | 2197(1) |
| Ru(1) | 1145(1) | 1239(1) | 3479(1) |
| Ru(2) | 440(1) | 88(1) | 2673(1) |
| P(1) | −234(2) | 1820(2) | 2877(2) |
| P(2) | −946(2) | 649(2) | 2052(2) |
| P(3) | 2562(2) | 689(2) | 4059(2) |
| P(4) | 1828(2) | −485(2) | 3258(2) |
| P(5) | 2861(2) | 1177(2) | 1377(2) |
| N(1) | −1129(7) | 1401(5) | 2334(5) |
| N(2) | 2703(7) | −78(5) | 3837(5) |
| O(1) | 2411(7) | 2331(5) | 2966(5) |
| O(2) | 1102(7) | 1892(5) | 4939(6) |
| O(3) | −816(8) | −1098(5) | 2841(6) |
| O(4) | 930(7) | −315(4) | 1166(5) |
| O(5) | −331(6) | 363(4) | 4121(4) |
| O(6) | −831(7) | 2258(4) | 3373(5) |
| O(7) | 4(6) | 2417(4) | 2388(5) |
| O(8) | −949(6) | 760(4) | 1199(5) |
| O(9) | −2029(7) | 323(5) | 2001(5) |
| O(10) | 3612(7) | 977(4) | 3945(5) |
| O(11) | 2769(6) | 693(4) | 4945(5) |
| O(12) | 2478(6) | −814(4) | 2728(4) |
| O(13) | 1601(6) | −1114(4) | 3709(5) |
| C(1) | 1987(9) | 1867(6) | 3085(6) |
| C(2) | 1083(9) | 1648(6) | 4367(7) |
| C(3) | −347(9) | −631(6) | 2769(7) |
| C(4) | 843(8) | −91(6) | 1731(6) |
| C(5) | 177(8) | 492(5) | 3659(6) |
| C(6) | −1232(12) | 1964(9) | 3986(8) |
| C(7) | 253(12) | 2349(7) | 1663(7) |
| C(8) | −1468(12) | 367(8) | 602(7) |
| C(9) | −2423(12) | 117(10) | 2656(9) |
| C(10) | 4015(12) | 1579(8) | 4319(9) |
| C(11) | 2054(11) | 422(8) | 5368(7) |
| C(12) | 2271(15) | −1436(7) | 2388(11) |
| C(13) | 1092(12) | −1097(6) | 4347(7) |
| C(14) | −2025(11) | 1772(7) | 1930(8) |
| C(15) | −2948(11) | 1754(10) | 2307(11) |
| C(16) | 3632(12) | −443(8) | 4213(9) |
| C(17) | 4523(13) | −392(10) | 3803(11) |
| C(21) | 3520(8) | 1929(5) | 1632(6) |
| C(22) | 4245(10) | 1952(7) | 2246(7) |
| C(23) | 4718(11) | 2530(7) | 2501(8) |
| C(24) | 4415(13) | 3073(9) | 2135(10) |
| C(25) | 3693(14) | 3078(9) | 1529(10) |
| C(26) | 3213(11) | 2499(7) | 1254(8) |
| C(31) | 2205(9) | 1297(6) | 438(6) |
| C(32) | 1176(10) | 1310(6) | 303(7) |
| C(33) | 649(11) | 1448(7) | −407(8) |
| C(34) | 1219(11) | 1553(7) | −969(8) |
| C(35) | 2217(11) | 1549(7) | −835(8) |
| C(36) | 2743(10) | 1417(6) | −137(7) |
| C(41) | 3838(8) | 598(5) | 1302(6) |
| C(42) | 4759(9) | 765(7) | 1099(7) |
| C(43) | 5449(11) | 297(7) | 1002(8) |
| C(44) | 5259(12) | −351(8) | 1120(9) |
| C(45) | 4351(11) | −516(8) | 1338(8) |
| C(46) | 3661(11) | −53(7) | 1433(7) |
| Sb | 6452(1) | 2304(1) | −108(1) |
| F(1) | 6511(7) | 1512(5) | 339(6) |
| F(2) | 7793(7) | 2444(5) | 301(5) |
| F(3) | 6412(8) | 3112(5) | −555(7) |
| F(4) | 5120(7) | 2140(6) | −533(7) |
| F(5) | 684(9) | 1972(5) | −930(6) |
| F(6) | 6024(12) | 2670(7) | 678(7) |

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

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| Ru(1) | −1 564(1) | −1 803(1) | −8 820(1) |
| Ru(2) | −1 524(1) | −1 571(1) | −6 508(1) |
| P(1) | −2 077(2) | −947(2) | −9 005(3) |
| P(2) | −1 089(2) | −2 665(2) | −8 424(3) |
| P(3) | −649(2) | −2 099(2) | −6 464(3) |
| P(4) | −2 394(2) | −1 055(2) | −6 705(4) |
| O(1) | −1 456(7) | −1 864(7) | −11 305(13) |
| O(2) | −391(6) | −1 257(6) | −9 032(10) |
| O(3) | −851(6) | −508(6) | −7 036(11) |
| O(4) | −1 546(8) | −1 316(8) | −4 080(16) |
| O(5) | −2 266(7) | −2 640(7) | −6 235(13) |
| O(6) | −1 684(6) | −393(5) | −9 140(10) |
| O(7) | −2 505(6) | −880(6) | −10 006(12) |
| O(8) | −631(6) | −2 924(6) | −9 221(11) |
| O(9) | −1 568(6) | −3 108(5) | −8 196(10) |
| O(10) | −464(6) | −2 377(5) | −5 356(10) |
| O(11) | −56(5) | −1 762(5) | −6 755(9) |
| O(12) | −2 502(6) | −584(6) | −5 863(12) |
| O(13) | −2 971(7) | −1 439(6) | −6 564(12) |
| N(1) | −2 515(6) | −759(7) | −7 958(12) |
| N(2) | −622(6) | −2 640(6) | −7 349(11) |
| N(3) | −2 371(6) | −2 212(6) | −8 698(12) |
| C(1) | −1 558(9) | −1 880(8) | −10 378(16) |
| C(2) | −834(7) | −1 453(7) | −8 897(14) |
| C(3) | −1 080(8) | −893(8) | −6 867(14) |
| C(4) | −1 496(9) | −1 402(8) | −4 994(15) |
| C(5) | −1 998(8) | −2 259(8) | −6 363(14) |
| C(6) | −1 339(10) | −249(9) | −10 112(18) |
| C(7) | −1 731(16) | 107(15) | −10 882(28) |
| C(8) | −821(12) | 59(12) | −9 715(22) |
| C(9) | −2 859(11) | −1 349(10) | −10 619(20) |
| C(10) | −3 446(13) | −1 366(11) | −10 200(21) |
| C(11) | −2 855(14) | −1 149(13) | −11 761(24) |
| C(12) | −618(16) | −2 992(15) | −10 419(28) |
| C(13) | 14(15) | −3 130(14) | −10 654(25) |
| C(14) | −1 073(23) | −3 394(21) | −10 843(44) |
| C(15) | −1 516(12) | −3 741(11) | −8 163(20) |
| C(16) | −2 000(18) | −3 963(18) | −8 695(33) |
| C(17) | −1 487(27) | −3 902(27) | −6 831(50) |
| C(18) | −818(10) | −2 565(10) | −4 419(18) |
| C(19) | −765(21) | −3 203(20) | −4 288(41) |
| C(20) | −530(14) | −2 250(13) | −3 455(26) |
| C(21) | 234(10) | −1 370(10) | −6 042(20) |
| C(22) | 675(12) | −1 648(12) | −5 361(22) |
| C(23) | 516(13) | −937(12) | −6 840(23) |
| C(24) | −2 094(14) | −173(13) | −5 324(25) |
| C(25) | −2 132(30) | 333(27) | −5 990(55) |
| C(26) | −2 452(19) | −43(19) | −4 208(34) |
| C(27) | −3 463(12) | −1 350(11) | −5 854(21) |
| C(28) | −3 422(26) | −1 674(22) | −5 073(49) |
| C(29) | −4 054(25) | −1 516(22) | −6 494(46) |
| C(30) | −3 036(10) | −401(10) | −8 122(19) |
| C(31) | −2 956(18) | 141(18) | −8 629(32) |
| C(32) | −173(10) | −3 116(11) | −7 265(19) |
| C(33) | 441(13) | −2 938(13) | −7 715(25) |
| C(34) | −2 779(8) | −2 502(8) | −8 684(14) |
| C(35) | −3 273(8) | −2 842(8) | −8 726(16) |
| C(36) | −3 572(12) | −2 952(12) | −9 707(23) |
| C(37) | −4 072(12) | −3 298(12) | −9 687(23) |
| C(38) | −4 224(13) | −3 532(13) | −8 802(27) |
| C(39) | −4 015(14) | −3 417(14) | −7 819(26) |
| C(40) | −3 479(12) | −3 074(12) | −7 704(21) |
| Sb(1) | −2 598(1) | −3 002(1) | −2 703(2) |
| F(1) | −2 404(10) | −2 736(13) | −1 322(21) |
| F(2) | −3 006(12) | −3 616(10) | −2 070(19) |
| F(3) | −3 209(9) | −2 502(11) | −2 605(27) |
| F(4) | −2 029(19) | −3 522(14) | −2 594(37) |
| F(5) | −2 137(11) | −2 462(9) | −3 342(19) |
| F(6) | −2 808(10) | −3 248(10) | −4 016(19) |
| Sb(2) | −1 000 | 0 | −3 500(2) |
| F(7) | −9 429(19) | −443(25) | −3 474(50) |
| F(8) | −10 257(26) | −466(24) | −2 447(56) |
| F(9) | −10 462(22) | −346(25) | −4 591(35) |
| Sb(3) | −5 000 | 0 | −1 326(8) |
| F(10) | −4 603(79) | −499(52) | −3 02(132) |
| F(11) | −5 649(27) | −205(22) | −997(89) |
| F(12) | −5 360(26) | −165(32) | −2 421(41) |

**Table 8** Fractional coordinates ( × $10^4$) for $[\mathrm{Ru_2(CO)_5(SC_4H_8)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}][\mathrm{SbF_6}]_2\cdot\mathrm{CH_2Cl_2}$

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* | Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|---|---|---|---|
| Ru(1) | 759(1) | 7 345(1) | 1 405 | C(17) | −682(14) | 8 808(24) | 3 383(22) |
| Ru(2) | 1 289(1) | 8 535(1) | 2 517(1) | C(18) | 1 691(12) | 6 697(20) | 4 258(20) |
| P(1) | 1 376(2) | 7 707(3) | 468(3) | C(19) | 1 992(12) | 5 890(19) | 3 974(17) |
| P(2) | 166(3) | 7 230(3) | 2 436(4) | C(20) | 1 503(22) | 6 660(37) | 5 125(38) |
| P(3) | 936(3) | 7 675(3) | 3 568(3) | C(21) | 881(12) | 9 084(18) | 4 595(18) |
| P(4) | 1 588(2) | 9 330(3) | 1 410(3) | C(22) | 378(15) | 9 335(23) | 4 955(24) |
| S(1) | 1 230(2) | 5 979(3) | 1 839(4) | C(23) | 1 331(15) | 9 178(24) | 5 238(23) |
| O(1) | 229(7) | 6 090(11) | 251(10) | C(24) | 2 533(10) | 9 430(15) | 1 917(14) |
| O(2) | 249(6) | 9 034(9) | 807(9) | C(25) | 2 840(12) | 8 878(19) | 1 362(18) |
| O(3) | 390(7) | 9 768(10) | 2 600(9) | C(26) | 2 802(14) | 10 312(24) | 2 219(20) |
| O(4) | 1 856(7) | 9 877(10) | 3 574(10) | C(27) | 1 217(10) | 11 075(16) | 1 594(14) |
| O(5) | 2 169(7) | 7 224(10) | 2 353(8) | C(28) | 699(14) | 11 458(19) | 1 420(22) |
| O(6) | 1 793(6) | 6 982(10) | 505(9) | C(29) | 1 619(12) | 11 685(19) | 1 505(19) |
| O(7) | 1 233(8) | 7 755(11) | −440(10) | C(30) | 1 897(10) | 9 169(16) | −130(15) |
| O(8) | −179(6) | 6 347(10) | 2 532(9) | C(31) | 1 755(12) | 10 002(20) | −479(17) |
| O(9) | −214(7) | 8 049(10) | 2 306(9) | C(32) | 32(12) | 6 957(19) | 4 051(18) |
| O(10) | 1 217(6) | 6 740(9) | 3 818(9) | C(33) | 167(13) | 5 925(21) | 4 314(21) |
| O(11) | 881(6) | 8 164(9) | 4 398(8) | C(34) | 874(9) | 5 199(13) | 2 521(14) |
| O(12) | 2 117(5) | 9 809(8) | 1 504(8) | C(35) | 901(13) | 4 268(21) | 2 088(20) |
| O(13) | 1 272(5) | 10 175(8) | 1 144(7) | C(36) | 936(14) | 4 371(23) | 1 255(22) |
| N(1) | 1 615(6) | 8 754(9) | 562(8) | C(37) | 1 273(9) | 5 161(13) | 1 022(12) |
| N(2) | 386(8) | 7 254(10) | 3 358(9) | Sb(1) | 3 178(1) | 8 260(1) | 4 163(1) |
| C(1) | 427(9) | 6 609(13) | 698(12) | Sb(2) | 983(1) | 2 438(2) | 4 094(2) |
| C(2) | 439(9) | 8 387(14) | 1 072(12) | F(1) | 471(9) | 2 277(14) | 4 819(14) |
| C(3) | 721(8) | 9 283(12) | 2 568(12) | F(2) | 914(13) | 3 641(24) | 4 103(26) |
| C(4) | 1 647(9) | 9 328(13) | 3 208(11) | F(3) | 970(13) | 1 239(24) | 3 860(21) |
| C(5) | 1 814(10) | 7 705(13) | 2 398(12) | F(4) | 1 407(18) | 2 635(26) | 3 322(30) |
| C(6) | 2 255(12) | 6 873(19) | 34(18) | F(5) | 557(15) | 2 520(18) | 3 282(24) |
| C(7) | 2 526(14) | 6 119(25) | 537(23) | F(6) | 1 399(20) | 2 408(29) | 4 928(36) |
| C(8) | 2 205(14) | 6 685(22) | −771(23) | F(7) | 2 458(9) | 3 476(15) | 8 790(13) |
| C(9) | 769(11) | 7 715(16) | −823(17) | F(8) | 1 207(11) | 3 014(19) | 9 559(17) |
| C(10) | 817(18) | 6 982(30) | −1 417(31) | F(9) | 2 012(10) | 3 496(17) | 10 191(17) |
| C(11) | 713(15) | 8 624(24) | −1 285(23) | F(10) | 1 595(12) | 3 298(20) | 8 152(20) |
| C(12) | −369(10) | 5 746(15) | 1 889(15) | F(11) | 1 921(12) | 2 098(22) | 9 289(23) |
| C(13) | −730(15) | 6 235(24) | 1 457(25) | F(12) | 1 765(12) | 4 531(22) | 9 094(22) |
| C(14) | −589(14) | 4 959(22) | 2 322(20) | C(38) | 2 458(25) | 3 296(40) | 2 236(36) |
| C(15) | −703(12) | 8 200(18) | 2 600(17) | Cl(1) | 3 081(9) | 2 937(16) | 2 164(16) |
| C(16) | −996(17) | 8 584(26) | 1 908(26) | Cl(2) | 2 504(12) | 4 469(22) | 2 407(21) |

Found: C, 32.1; H, 4.5; N, 2.7. $\mathrm{C_{40}H_{71}F_{12}N_3O_{13}P_4Ru_2Sb_2}$ requires C, 30.6; H, 4.5; N, 2.6%).

$[\mathrm{Ru_2(CO)_5(Et_2CO)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}][\mathrm{SbF_6}]_2$. A solution of a two-fold molar amount of a solution of $\mathrm{AgSbF_6}$ (0.10 g, 0.29 mmol) in diethyl ketone (3 $\mathrm{cm^3}$) was added to a solution of **1b** (0.15 g, 0.145 mmol) in diethyl ketone (5 $\mathrm{cm^3}$) and the resultant solution stirred for 90 min during which time silver metal separated. The solution was filtered and the volume of the filtrate was reduced under vacuum to *ca.* 1 $\mathrm{cm^3}$. Diethyl ether (5 $\mathrm{cm^3}$) was added and the solution was kept at −10 °C to effect the crystallisation of the product. Yield: 45% (Found: C, 27.9; H, 4.9; N, 1.9. $\mathrm{C_{38}H_{76}F_{12}N_2O_{13}P_4Ru_2Sb_2}$ requires C, 28.8; H, 4.9; N, 1.8%).

$[\mathrm{Ru_2(CO)_5(MeNO_2)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}][\mathrm{SbF_6}]_2$. A solution of a two-fold molar amount of $\mathrm{AgSbF_6}$ (0.10 g, 0.29 mmol) in nitromethane (3 $\mathrm{cm^3}$) was added to a solution of **1b** (0.15 g, 0.145 mmol) in nitromethane (5 $\mathrm{cm^3}$) and the resultant solution stirred for 90 min. The product was isolated as for the diethyl ketone derivative. Yield: 50% (Found: C, 27.3; H, 4.3; N, 2.8. $\mathrm{C_{34}H_{69}F_{12}N_3O_{14}P_4Ru_2Sb_2}$ requires C, 26.2; H, 4.5; N, 2.7%).

$[\mathrm{Ru_2(CO)_5(CNC_6H_3Me_2\text{-}2,6)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2}][\mathrm{SbF_6}]_2$. A solution of 2,6-dimethylphenyl isocyanide (0.06 g, 0.45 mmol) and **2a** (0.53 g, 0.40 mmol) in acetone (40 $\mathrm{cm^3}$) at room temperature was stirred for 48 h. Addition of *n*-hexane (*ca.* 40 $\mathrm{cm^3}$) resulted in the separation of unreacted starting material as a white precipitate (0.38 g) which was recovered by filtration. The volume of the filtrate was reduced to *ca.* 40 $\mathrm{cm^3}$ and kept at −10 °C to afford the product as a pale yellow microcrystalline solid. Yield: 20% (Found: C, 22.4; H, 3.5; N, 2.7. $\mathrm{C_{28}H_{49}F_{12}N_3O_{13}P_4Ru_2Sb_2}$ requires C, 22.3; H, 3.1; N, 3.0%).

$[\mathrm{Ru_2(CO)_5(SC_4H_8)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}][\mathrm{SbF_6}]_2$ and $[\mathrm{Ru_2(CO)_5(SMe_2)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}][\mathrm{SbF_6}]_2$. A solution of a slight excess of tetrahydrothiophene (0.01 g, 0.10 mmol) or dimethyl sulfide (0.01 g, 0.14 mmol) in acetone (2 $\mathrm{cm^3}$) was added to a solution of **2b** (0.15 g, 0.09 mmol) in acetone (5 $\mathrm{cm^3}$). White crystals of the product were obtained by addition of diethyl ether (10 $\mathrm{cm^3}$) to this solution. Yield: 90–95% (Found: C, 27.8; H, 4.7; N, 1.8. $\mathrm{C_{37}H_{74}F_{12}N_2O_{13}P_4Ru_2SSb_2}$ requires C, 28.0; H, 4.7; N, 1.8. Found: C, 27.9; H, 4.5; N, 2.0. $\mathrm{C_{35}H_{72}F_{12}N_2O_{13}P_4Ru_2SSb_2}$ requires C, 28.0; H, 4.7; N, 1.8%).

$[\mathrm{Ru_2(CO)_5(py)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}][\mathrm{SbF_6}]_2$. A solution of an equimolar amount of pyridine (0.015 g, 0.20 mmol) in acetone (2 $\mathrm{cm^3}$) was added to a solution of **2b** (0.20 g, 0.20 mmol) in acetone (5 $\mathrm{cm^3}$). The solvent was removed under reduced pressure and the residue washed with cold chloroform (3 x 5 $\mathrm{cm^3}$, 0 °C). The remaining white residue was extracted into dichloromethane (3 $\mathrm{cm^3}$) and the extract filtered. Diethyl ether (5 $\mathrm{cm^3}$) was added to the filtrate and the mixture allowed to stand at −10 °C to effect the separation of the product in crystalline form. Yield: 35% (Found: C, 28.7; H, 4.4; N, 2.9. $\mathrm{C_{38}H_{71}F_{12}N_3O_{13}P_4Ru_2Sb_2}$ requires C, 29.0; H, 4.6; N, 2.7%).

$[\mathrm{Ru_2(CO)_5(\sigma\text{-}4,4'\text{-}bipy)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}][\mathrm{SbF_6}]_2$. A solution of an equimolar amount of 4,4′-bipyridine (0.031 g, 0.20 mmol) in acetone (2 $\mathrm{cm^3}$) was added to a solution of **2b** (0.20 g, 0.20 mmol) in acetone (5 $cm^3$). The solvent was removed under reduced pressure and the residue washed with cold chloroform (3 × 5 $cm^3$, 0 °C). The white residue which remained was extracted with dichloromethane (3 $cm^3$) and the solution filtered. The product was obtained in low yield as an impure white microcrystalline material by addition of diethyl ether (5 $cm^3$) to this filtrate and allowing the solution to stand at −10 °C. Because of its impure state it was identified by spectroscopic means only.

*Reaction of* $[Ru_2(CO)_5(Me_2CO)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$—$[Ru_2(CO)_5(H_2O)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$ *with Carbon Monoxide.*—Carbon monoxide was passed slowly through a solution of **2a** (0.5 mmol) in acetone (10 $cm^3$) for 6 h in the absence of light. Monitoring of this reaction by means of IR spectroscopy indicated 25% conversion of **2a** to a product presumed to be $[Ru_2(CO)_6\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]_2$ but owing to its instability to decarbonylation the latter could not be isolated.

*Reactions of* $[Ru_2(CO)_5(Me_2CO)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$.—*With halide, benzenethiolate, trifluoroacetate and acetate ions.* A solution of an equimolar amount of $NEt_4Cl$, $NEt_4Br$, $NBu^nI$, NaSPh, $Na(O_2CCF_3)$ or $Na(O_2CMe)$ in acetone (5 $cm^3$) was added to a stirred solution of **2b** (0.20 g, 0.20 mmol) in acetone (5 $cm^3$) and the solution stirred for a further 30 min. The product was identified as $[Ru_2X(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ [X = Cl, Br, I, SPh or $OC(O)CF_3$] and/or $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ [X = Cl, Br, I, SPh or OC(O)Me] by spectroscopic means only.[8,9]

*With thiocyanate ions.* Solid NaSCN (0.04 g, 0.5 mmol) was added to a solution of **2b** (0.40 g, 0.40 mmol) in acetone (40 $cm^3$) and the solution stirred for 15 min. Two products were found to be formed in the reaction *viz.* $[Ru_2\{\mu\text{-}OC(OH)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ and $[Ru_2(SCN)(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ but because of the difficulty in effecting their separation they were identified by spectroscopic means only.

*X-Ray Crystallography.*—Cell dimensions and intensity data were recorded as previously described using a CAD4 diffractometer.[8b] The structures were solved and developed *via* Patterson and Fourier methods using the programs SHELX 86[30] and SHELX 76.[30] Hydrogen atoms were not located in any of the structures. Thermal parameters for $[Ru_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]$ were as follows: anisotropic for the Au, Ru, P and methyl C atoms and isotropic for the remaining atoms. The Ru, P, F and Sb atoms of $[Ru_2(CO)_5(PhCN)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2$ were refined anisotropically and the remaining atoms isotropically; very high thermal parameters for the F atoms suggest that the anions are rotationally disordered. The Ru, P, S and Sb atoms of $[Ru_2(CO)_5(SC_4H_8)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]_2\cdot CH_2Cl_2$ were refined anisotropically and the remaining atoms isotropically; again high thermal parameters for the F atoms suggest that the $SbF_6$ anions are disordered, the same being true for the dichloromethane solvent molecule. Full-matrix least-squares methods were used to refine the structures using the program SHELX 76.[30] Neutral atomic scattering factors corrected for anomalous dispersion were taken from ref. 31. Crystal data and experimental details are given in Table 5. Final fractional coordinates are given in Tables 6–8.

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

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