Electrophilic Attack on Diphosphazane-bridged Derivatives of Diruthenium Nonacarbonyl by Halogens. Crystal Structure of $[Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ †

John S. Field,[a] **Raymond J. Haines,***[a] **Eric Minshall,**[a] **Clifford N. Sampson,**[a] **Jörg Sundermeyer,**[a] **Stephen F. Woollam,**[a] **Christine C. Allen**[b] **and Jan C. A. Boeyens**[b]

[a] *Unit of Metal Cluster Chemistry, Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg 3200, Republic of South Africa*

[b] *Department of Chemistry, University of the Witwatersrand, P.O. Wits 2050, Republic of South Africa*

Treatment of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) with halogens results in the ready formation of $[Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (X = Cl, Br or I) with the halogen atom co-ordinating terminally. These pentacarbonyl species, isolated as their hexafluorophosphate salts, decarbonylate in solution, rapidly in the presence of trimethylamine *N*-oxide dihydrate but slowly in the absence of this decarbonylating agent, to produce the tetracarbonyl species $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ in which the halogen bridges the two ruthenium atoms. Substitution of the carbonyl groups in these tetracarbonyl species can be effected further by halide ions, either photochemically or by promoting the process using $Me_3NO{\cdot}2H_2O$ and thus reaction of $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ with chloride, bromide or iodide ions in the presence of $Me_3NO{\cdot}2H_2O$ readily affords $[Ru_2(\mu\text{-}X)X(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$. Significantly, treatment of $[Ru_2I(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]I_3$, or $[Ru_2I(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]PF_6$ in the presence of iodide ions, with an excess of $Me_3NO{\cdot}2H_2O$ leads solely to the neutral tetracarbonyl derivative $[Ru_2I_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$. On the basis of an X-ray crystallographic study on $[Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$, the tricarbonyl derivatives have structures related to that of $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ with an axial carbonyl group having been replaced by a halide ion.

Dinuclear diphosphorus ligand-bridged derivatives such as $[Mn_2(\mu\text{-}\eta^2\text{-}CO)(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2]$, $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(EtO)_2POP(OEt)_2\}_2]$, $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$ and $[Rh_2(CO)_3(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ are electron-rich and as such are susceptible to electrophilic attack.[1–8] Thus Deeming and co-workers[9] have established that $[Mn_2(\mu\text{-}\eta^2\text{-}CO)(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ is readily protonated to afford, in the presence of carbon monoxide, $[Mn_2(\mu\text{-}H)(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)_2]^+$ while Eisenberg and co-workers[7] have reported that $[Rh_2(CO)_3(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ is also readily protonated to give $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]^+$. Similarly, $[Mn_2(CO)_6\{\mu\text{-}(EtO)_2POP(OEt)_2\}_2]$ has been shown to react spontaneously with halogens with the nature of the product being dependent on the halogen employed, bromine affording neutral $[Mn_2Br_2(CO)_6\{\mu\text{-}(EtO)_2POP(OEt)_2\}_2]$ and iodine, ionic $[Mn_2(\mu\text{-}I)(CO)_6\{\mu\text{-}(EtO)_2POP(OEt)_2\}_2]^+$.[10] Likewise, we have established that the diiron diphosphazane-bridged derivative $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me, Pr^i or Ph) is also readily halogenated to produce $[Fe_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ which in turn readily decarbonylates to $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (X = Cl, Br or I).[11]

With the aim of developing a method for the synthesis of the dihydride $[Ru_2H_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **1** (R = Me or Pr^i), we have endeavoured to synthesize $[Ru_2X_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **2** (X = Cl, Br or I) by reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **3** with halogens, it being envisaged that reaction of a suitable hydridic agent with the neutral dihalide would afford the dihydrido species. The results of this investigation are reported here; some of these have been reported previously in a preliminary form.[12]

Results and Discussion

Synthetic Studies.—Both $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ **3**; R = Me[13] and $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **3**; R = Pr^i[13] were found to react spontaneously with chlorine, bromine and iodine to afford products, isolated as hexafluorophosphate salts and characterized as $[Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]PF_6$ **4** PF_6 (R = Me or Pr^i; X = Cl, Br or I). The iodo- and bromo-isopropoxydiphosphazane derivatives were found to decarbonylate in solution at a rate sufficient to prevent their isolation in a pure form and as a consequence they were identified by spectroscopic means only, but the corresponding chloro species is much more stable to loss of carbon monoxide and could be characterized fully. The methoxydiphosphazane derivatives were observed to be more stable to decarbonylation than their isopropoxydiphosphazane analogues however, with the chloro derivative being stable in dichloromethane for several weeks, such that all three of them could be fully characterized.

In all cases, these halogenopentacarbonyl derivatives were identified by their distinctive $^{31}P\text{-}\{^1H\}$ NMR spectra which exhibited AA′BB′ patterns of peaks and by the characteristic band patterns of the C–O stretching peaks in their solution IR spectra (Table 1). These spectroscopic features are consistent with structure **4a** illustrated, which is based on that established previously for $[Fe_2I(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ from an X-ray crystallographic study.[11] The two iron atoms in this cation are bridged by two methoxydiphosphazane ligands and are separated by a distance corresponding to a formal Fe–Fe bond. The cation adopts a staggered conformation to

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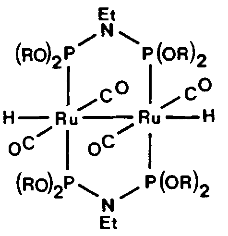
† Tricarbonyl-$1\kappa^2C,2\kappa C$-bis[μ-2-ethyl-1,1,3,3-tetraisopropoxydiphosphazane-$\kappa P^1:\kappa P^3$]-μ-iodo-iodo-$2\kappa I$-diruthenium (*Ru–Ru*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



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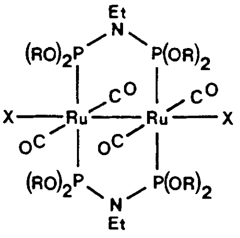

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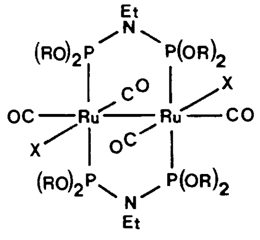

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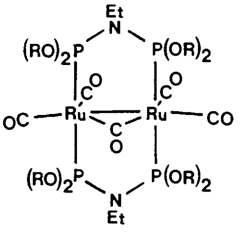

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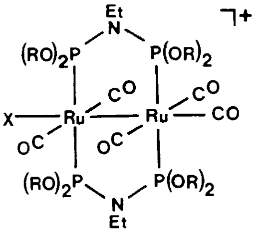

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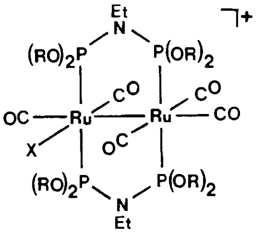

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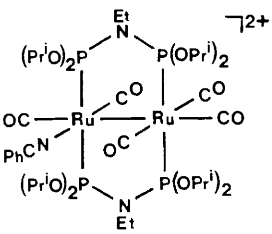

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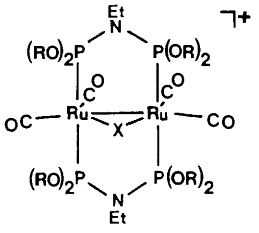

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Table 1 Infrared and $^{31}P-\{^{1}H\}$ nuclear magnetic resonance spectroscopic data

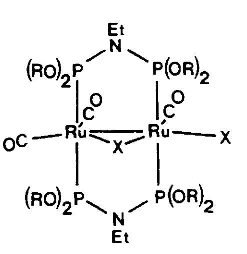
Compound X	R	Z	$\nu(CO)^{a}/cm^{-1}$	$^{31}P-\{^{1}H\}$ NMR^{b}
$[Ru_2X(CO)_5\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]Z$				
Cl	Me	PF_6	2080w, 2028s, 2015s, 1965m (br)^{c}	133.6^{d,e}
Br	Me	PF_6	2080w, 2029s, 2016s, 1965m (br)^{c}	137.0^{d,e}
I	Me	PF_6	2090w, 2048 (sh), 2023s (br), 1973m (br)^{c}	135.4^{d,f,g} 133.2^{d,f,h}
Cl	Pr^{i}	PF_6	2085w, 2035s, 2026 (sh), 2008ms, 1971m (br)^{c}	128.2^{d,e}
Br	Pr^{i}	Br	2080w, 2033s, 2025 (sh), 2005ms, 1968m (br)^{c}	126.6^{d,e}
I	Pr^{i}	I	2087w, 2023s, 2007 (sh), 1975m (br)^{c}	124.2^{d,f,g} 122.4^{d,f,h}
$[Ru_2(\mu-X)(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]Z$				
Cl	Me	PF_6	2047m, 2020s, 1985ms, 1968w^{c}	139.2 (s)^{e}
Br	Me	PF_6	2042m, 2020s, 1985ms, 1966w^{c}	143.7 (s)^{e}
I	Me	PF_6	2045m, 2019s, 1986ms, 1969w^{c}	141.3 (s)^{e}
Cl	Pr^{i}	PF_6	2040m, 2000s, 1972ms, 1950w^{c}	132.2 (s)^{e}
Br	Pr^{i}	PF_6	2037ms, 1999s, 1970ms, 1949m^{c}	134.5 (s)^{e}
I	Pr^{i}	PF_6	2038ms, 2000s, 1973ms, 1951m^{c}	131.0 (s)^{e}
$[Ru_2(\mu-X)X(CO)_3\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]$				
Cl	Me		2004s, 1995 (sh), 1949vs, 1916 (sh)^{i}	146.4^{d,e}
Br	Me		2007s, 1957vs^{i}	145.0^{d,e}
Br	Pr^{i}		2002 (sh), 1987s, 1933vs, 1907m^{i}	136.9^{d,j}
I	Pr^{i}		1989s, 1935vs, 1920 (sh)^{i}	136.5^{d,e}
$[Ru_2X_2(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]$				
I	Me		2015m, 1985s, 1950m^{c}	144.8 (s)^{j}
I	Pr^{i}		2021w, 1975s, 1938m^{i}	134.3 (s)^{j}
$[Ru_2X_2(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}-\{\mu-(Pr^{i}O)_2PN(Et)P(OPr^{i})_2\}]$				
I			2022w, 2007m, 1979vs, 1943m^{i}	139.8^{d,h,j} 139.3^{d,g,j}

[a] Abbreviations: v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad. [b] δ scale relative to H_3PO_4; s = singlet. [c] Measured in CH_2Cl_2. [d] Midpoint of AA′BB′ pattern. [e] Measured in CD_2Cl_2. [f] Measured in $CDCl_3$. [g] Major isomer. [h] Minor isomer. [i] Measured in hexane. [j] Measured in C_6D_6.

minimize steric repulsions but the extent of twisting about the iron–iron vector is small. Two isomeric forms of $[Ru_2X(CO)_5\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^{+}$ are possible with the halogen bonding axially, **4a**, as found in $[Fe_2I(CO)_5\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]^{+}$ [11] or equatorially, **4b**, as established for the benzonitrile ligand in $[Ru_2(CO)_5(PhCN)\{\mu-(Pr^{i}O)_2PN(Et)P(OPr^{i})_2\}_2]^{2+}$ **5**.[14] Significantly, in contrast to the rest of the pentacarbonyl derivatives, $[Ru_2I(CO)_5\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]PF_6$ were found to exhibit two sets of resonances each with a typical AA′BB′ pattern in their $^{31}P-\{^{1}H\}$ NMR spectra which is indicative of these compounds being present in both isomeric forms in solution at this temperature. The presence of a single set of resonances of AA′BB′ pattern in the room-temperature spectra of the other pentacarbonyl derivatives is consistent with these species occurring as a single isomer in solution, but whether the halogen is axially or equatorially disposed cannot be unequivocally established from the available spectroscopic data. However, the band patterns of the C–O stretching peaks in the solution IR spectra of the species more stable to decarbonylation are slightly different to those for the less-stable compounds, and with the isomer with an equatorially disposed halogen being expected to decarbonylate more readily to $[Ru_2(\mu-X)(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^{+}$ **6** (see below) than the isomer with an axially disposed halogen it is tempting to suggest that the less-stable species adopt the former conformation in solution while the more-stable derivatives adopt the latter conformation.

As described above, the pentacarbonyl compounds $[Ru_2X(CO)_5\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]PF_6$ **4**, PF_6 decarbonylate in solution with the rate of decarbonylation increasing slightly along the series X = Cl < Br < I, with the isopropoxydiphosphazane derivatives decarbonylating slightly more readily than their methoxydiphosphazane analogues and with the decarbonylation being accelerated in polar, co-ordinating solvents such as dimethyl sulphoxide and acetone or under thermal or photochemical conditions or by use of the decarbonylating agent trimethylamine *N*-oxide dihydrate.

The products of the decarbonylation process were characterized as the halogeno-bridged derivatives $[Ru_2(\mu-X)(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]PF_6$ **6**, PF_6 (R = Me or Pr^{i}; X = Cl, Br or I) of proposed structure illustrated. This structure is based on that established previously for $[Fe_2(\mu-Br)(CO)_4\{\mu-(PhO)_2-$



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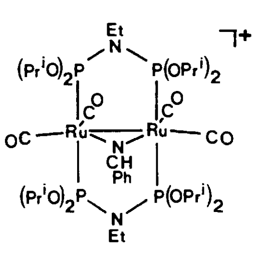

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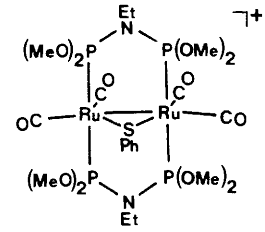

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$PN(Et)P(OPh)_2\}_2]PF_6$ [11] in which the two iron atoms are not only bridged by the two diphosphazane ligands as well as by the bromo group but are also linked by a formal iron–iron bond. In contrast to $[Fe_2I(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ this cationic species adopts an eclipsed conformation. The IR spectra of the $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]PF_6$ derivatives exhibit a four-line pattern in the C–O stretching region characteristic of species of the type $[M(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{n+}$ (M = Fe or Ru, X = bridging ligand) while the $^{31}P\text{-}\{^1H\}$ NMR spectra contain a single resonance indicating the equivalence of the phosphorus atoms and consistent with structure **6**.

An earlier investigation of the reactivity of the halogeno-bridged diiron species $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (R = Me, Pr^i or Ph; X = Cl, Br or I) towards halide ions X^-, which had as one of its objectives the synthesis of $[Fe_2X_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$, established that these species were inert to halide-ion attack for R = Pr^i or Ph but were involved in a Michaelis–Arbuzov type rearrangement to afford $[Fe_2(\mu\text{-}X)\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$ for R = Me.[11] The susceptibility of the diruthenium species $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ **6** (R = Me or Pr^i; X = Cl, Br or I) to halide-ion attack has now also been investigated and indeed these species have been found to react with halide ions with the nature of the product being dependent on the reaction conditions and the halide ion employed. No Michaelis–Arbuzov type rearrangement products were observed to be formed however. In the case of bromide and chloride ions the final product was shown to result from the substitution of a carbonyl group by the halide ions and was characterized as $[Ru_2(\mu\text{-}X)X(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **7** (R = Me or Pr^i, X = Cl or Br). Synthesis of these neutral tricarbonyl derivatives is achieved much more readily by heating or irradiating solutions of $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X$ in tetrahydrofuran (thf) with ultraviolet light, by eluting a solution of the latter through a silica column or by treating $[Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X$ or $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X$ in acetone with an excess of trimethylamine *N*-oxide dihydrate.

The iodo-bridged species $[Ru_2(\mu\text{-}I)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ was found to be inert to iodide-ion attack in the absence of $Me_3NO{\cdot}2H_2O$ but in the presence thereof readily afforded the neutral tricarbonyl species $[Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **7**; X = I, (R = Me or Pr^i). Significantly, treatment of the pentacarbonyl species $[Ru_2I(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ with iodide ions in the presence of excess of $Me_3NO{\cdot}2H_2O$ was found to lead to the formation of a product characterized as the neutral tetracarbonyl diiodo species $[Ru_2I_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **2**; X = I. In contrast to $[Ru_2Cl_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ which rearranges in polar solvents to $[Ru_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]Cl$,[15] $[Ru_2I_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ is stable in both polar and non-polar solvents and cannot be decarbonylated to $[Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **7**; X = I even by treatment with an excess of both $Me_3NO{\cdot}2H_2O$ and iodide ions.

The $^{31}P\text{-}\{^1H\}$ NMR spectra of the tricarbonyl species $[Ru_2(\mu\text{-}X)X(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i; X = Cl, Br or I) were found to contain a set of resonances of AA′BB′ pattern consistent with the presence of a single isomer in solution and with the solid-state structure (see below) being retained in solution. On the other hand, a singlet was observed in the $^{31}P\text{-}\{^1H\}$ NMR spectra of $[Ru_2I_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) which is indicative of a symmetrical structure and the compound occurring as either the axial,axial isomer **2a**; X = I or the equatorial,equatorial isomer **2b**; X = I. The band pattern of the peaks in the C–O stretching region of the IR spectrum of $[Ru_2I_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ is substantially different to that for $[Ru_2Cl_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ which is interpreted in terms of these compounds occurring in different isomeric forms. A crystallographic investigation has shown that the dichloro compound occurs as the axial,axial isomer **2a**; X = Cl[15] and on this basis it is proposed that $[Ru_2I_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ is present as the equatorial,equatorial isomer **2b**; X = I. The mixed-ligand diiodo species $[Ru_2I_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}]$ was also synthesised and significantly its $^{31}P\text{-}\{^1H\}$ NMR spectrum was found to exhibit two sets of peaks of AA′BB′ pattern which is indicative of this compound occurring as both the axial,axial and the equatorial,equatorial isomer in solution.

Crystallographic Study.—With the object of establishing the structure of the tricarbonyl species $[Ru_2(\mu\text{-}X)X(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$, a crystal-structure determination was carried out on $[Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. The molecular geometry of this compound is related to those of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ **3**; R = Me[13] and $[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]PF_6$ [11] and is illustrated in Fig. 1. The two ruthenium atoms are not only linked through two bridging diphosphazane ligands, *trans* disposed with respect to each other, but through a bridging iodine atom as well. The ruthenium–ruthenium distance of 2.794(1) Å corresponds to a formal bond and compares with corresponding distances of 2.801(2), 2.714(1) and 2.796(1) Å for $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ **3**; R = Me,[13] $[Ru_2\{\mu\text{-}\sigma\text{-}N(CHPh)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **8**[16] and $[Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ **9**[14] respectively. The three carbonyl groups and the second iodine atom co-ordinate terminally with the latter and one of the carbonyls occupying axial sites and the other two carbonyls being located equatorially as illustrated. Together with the two ruthenium atoms and the bridging iodine these terminal carbonyls and iodine atom are essentially coplanar lying in the plane that is orthogonal to one containing the two ruthenium and the four phosphorus atoms. The equatorial carbonyl co-ordinated to the ruthenium atom that has the axial carbonyl bonded to it is disordered with the crystallographic refinement favouring neither of two discrete alternative positions for the oxygen atom such that two conformations must be assumed to occur with

Table 2 Fractional atomic coordinates (× 10^4) for non-hydrogen atoms of $[Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	5 000	7 714(1)	5 000	C(6)	7 446(19)	10 659(15)	3 528(13)
Ru(2)	6 396(1)	7 133(1)	3 845(1)	C(7)	5 567(15)	8 030(13)	1 301(11)
I(1)	3 184(1)	3 030(1)	7 960(1)	C(8)	5 444(20)	7 018(17)	947(14)
I(2)	2 214(1)	1 515(1)	126(1)	C(9)	5 073(24)	8 799(21)	718(17)
O(1)	3 304(8)	8 097(7)	6 090(6)	C(10)	4 523(16)	10 661(14)	5 254(12)
O(2)	4 097(15)	6 434(13)	3 850(10)	C(11)	5 649(22)	11 184(21)	5 648(16)
O(2*)	3 379(14)	6 214(11)	3 883(9)	C(12)	3 479(20)	11 405(18)	5 035(15)
O(3)	4 969(11)	5 702(10)	2 652(8)	C(13)	1 980(14)	8 513(13)	3 998(10)
C(1)	3 999(14)	8 063(12)	5 755(10)	C(14)	981(16)	8 969(14)	4 363(12)
C(2)	4 113(19)	6 826(17)	4 293(14)	C(15)	1 617(20)	8 241(18)	3 065(13)
C(3)	5 536(13)	6 279(12)	3 117(9)	C(16)	9 482(13)	6 346(12)	5 084(9)
P(1)	5 656(3)	8 450(3)	2 939(2)	C(17)	9 752(18)	6 561(16)	5 991(12)
P(2)	4 259(3)	9 099(3)	4 175(2)	C(18)	10 521(16)	5 968(15)	4 771(12)
P(3)	7 171(3)	5 774(3)	4 704(2)	C(19)	7 047(14)	4 143(13)	3 665(10)
P(4)	5 805(3)	6 458(3)	5 950(2)	C(20)	8 194(19)	3 583(18)	3 863(15)
N(1)	4 542(10)	9 133(9)	3 197(7)	C(21)	6 033(18)	3 497(18)	3 354(14)
N(2)	6 832(10)	5 714(9)	5 666(7)	C(22)	6 031(18)	7 119(15)	7 559(12)
O(4)	6 509(9)	9 299(8)	2 660(6)	C(23)	6 528(25)	6 418(21)	8 226(18)
O(5)	5 022(8)	8 085(7)	2 031(6)	C(24)	6 339(22)	8 233(18)	7 727(16)
O(6)	4 733(9)	10 223(8)	4 480(6)	C(25)	3 709(14)	5 460(13)	5 604(10)
O(7)	2 878(9)	9 296(8)	4 068(6)	C(26)	3 685(19)	4 459(16)	5 507(13)
O(8)	8 551(9)	5 587(7)	4 882(6)	C(27)	3 023(16)	5 527(15)	6 633(11)
O(9)	6 794(9)	4 642(8)	4 403(6)	C(28)	3 853(16)	9 863(13)	2 581(11)
O(10)	6 530(9)	6 844(8)	6 811(7)	C(29)	4 422(19)	10 889(17)	2 497(14)
O(11)	4 930(9)	5 705(8)	6 296(6)	C(30)	7 464(15)	4 947(13)	6 277(11)
C(4)	7 639(15)	9 643(13)	3 092(11)	C(31)	6 819(22)	3 933(18)	6 321(15)
C(5)	8 415(18)	9 760(16)	2 428(13)				

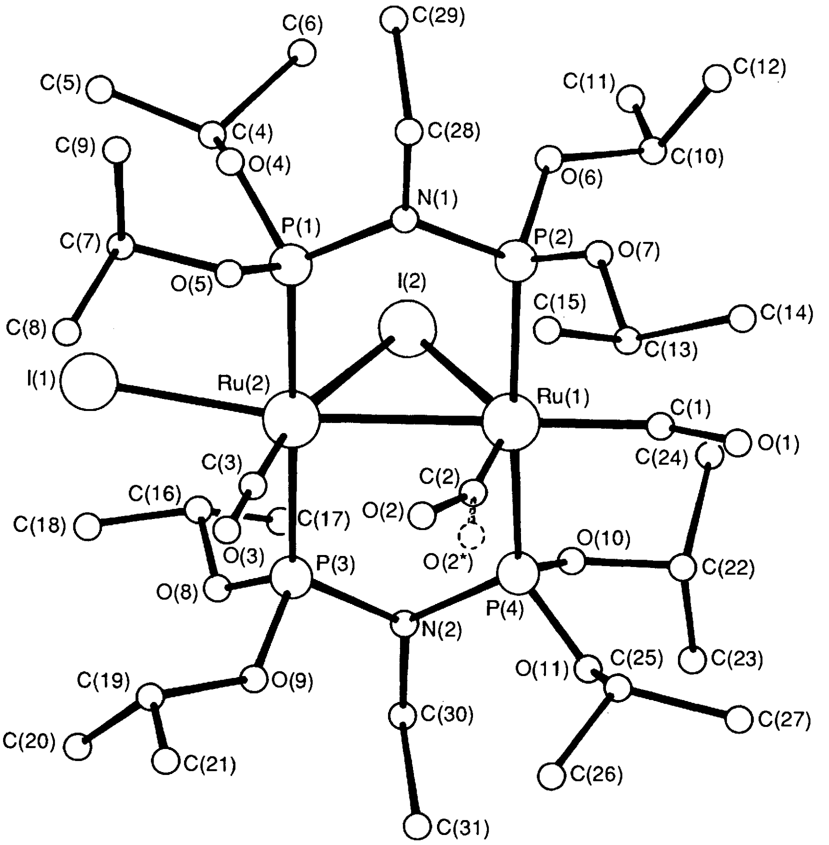


Fig. 1 Molecular structure of $[Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ showing the atom labelling scheme

equal probability in the crystal. Alternative positions for the carbon of this carbonyl were not resolved but its comparatively refined thermal parameter is consistent with two closely spaced alternative positions. Significantly, the disposition of this equatorial carbonyl is such that it could be considered as semi-bridging on the basis that the ratio of the Ru(2)–C(2) distance [2.89(2) Å] to the Ru(1)–C(2) distance [1.82(2) Å] is less than 1.6:1, the value that is taken for practical purposes to be the boundary between terminal and semi-bridging carbonyl groups.[17] Moreover, one of the two positions for the oxygen atom of this carbonyl group allows for a weak interaction between this oxygen and the second ruthenium atom [Ru(1)–C(2)–O(2) 144(3)°, Ru(2)–O(2) 2.81(2) Å]. Another striking structural feature is the different orientations of the two equatorial carbonyl groups. A comparison of the two angles Ru(2)–Ru(1)–C(2) [74.4(7)°] and Ru(1)–Ru(2)–C(3) [107.2(5)°] reveals that while CO(2) is drawn towards Ru(2), CO(3) points outward. On the basis of the relative sizes of a carbonyl group and an iodine atom the opposite would have been expected. The net result of the different orientations of these two carbonyl groups is a more regular arrangement around Ru(2) compared to that of Ru(1).

Mechanism of Halogenation.—The products of the halogenation reactions of $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]$ (R = Me or $\mathrm{Pr^i}$) as well as those resulting from their stepwise decarbonylation, together with the pathways in their formation, are summarized in Scheme 1. The formation of the cationic halogenopentacarbonyl species $[\mathrm{Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ (X = Cl, Br or I) can be explained in terms of one of two mechanistic pathways as proposed previously for the formation of $[\mathrm{Fe_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$.[11] One involves electrophilic attack by the halogen molecule at one or both ruthenium centres followed by heterolytic cleavage of the halogen–halogen bond leading to the loss of a halide ion and the formation of the cationic product. The second involves a one-electron oxidation of the parent pentacarbonyl to produce $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ followed by attack by halogen radicals on the latter to give $[\mathrm{Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$, the halogen radicals being derived from $\mathrm{X_2}^-$.

Table 3 Interatomic distances (Å) for $[\mathrm{Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]$

I(1)–Ru(2)	2.732(1)	I(2)–Ru(1)	2.724(1)
I(2)–Ru(2)	2.767(1)	Ru(1)–Ru(2)	2.794(1)
Ru(1)–P(2)	2.325(4)	Ru(1)–P(4)	2.333(4)
Ru(2)–P(1)	2.327(4)	Ru(2)–P(3)	2.339(4)
Ru(1)–C(1)	1.89(2)	Ru(1)–C(2)	1.82(2)
Ru(2)–C(3)	1.79(2)	P(1)–O(4)	1.61(1)
P(1)–O(5)	1.60(1)	P(1)–N(1)	1.68(1)
P(2)–O(6)	1.62(1)	P(2)–O(7)	1.60(1)
P(2)–N(1)	1.68(1)	O(1)–C(1)	1.05(2)
P(3)–O(8)	1.59(1)	P(3)–O(9)	1.60(1)
P(3)–N(2)	1.68(1)	P(4)–O(10)	1.58(1)
P(4)–O(11)	1.59(1)	P(4)–N(2)	1.66(1)
O(2)–C(2)	0.88(2)	O(2*)–C(2)	1.27(3)
O(3)–C(3)	1.18(2)	O(4)–C(4)	1.44(2)
O(5)–C(7)	1.44(2)	O(6)–C(10)	1.45(2)
O(7)–C(13)	1.45(2)	O(8)–C(16)	1.46(2)
O(9)–C(19)	1.44(2)	O(10)–C(22)	1.48(2)
O(11)–C(25)	1.47(2)	N(1)–C(28)	1.50(2)
N(2)–C(30)	1.51(2)	C(4)–C(5)	1.53(2)
C(4)–C(6)	1.54(2)	C(7)–C(8)	1.44(3)
C(7)–C(9)	1.43(3)	C(10)–C(11)	1.51(3)
C(10)–C(12)	1.55(3)	C(13)–C(14)	1.51(2)
C(13)–C(15)	1.54(3)	C(16)–C(17)	1.48(2)
C(16)–C(18)	1.47(2)	C(19)–C(20)	1.50(2)
C(19)–C(21)	1.46(2)	C(22)–C(23)	1.46(3)
C(22)–C(24)	1.52(3)	C(25)–C(26)	1.46(2)
C(25)–C(27)	1.54(2)	C(28)–C(29)	1.51(2)
C(30)–C(31)	1.53(3)		

The formation of the halogen-bridged tetracarbonyl species $[\mathrm{Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ is presumed to result from the decarbonylation of the equatorial isomer of $[\mathrm{Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ *viz.* **4b**, while the former is in turn presumed to be the intermediate in the formation of $[\mathrm{Ru_2(\mu\text{-}X)X(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]$; the C–O stretching vibrations for $[\mathrm{Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]^+$ occur at a higher frequency than the corresponding vibrations for $[\mathrm{Ru_2X_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]$ and on this basis the ionic tetracarbonyl derivative is assumed to decarbonylate more easily than the neutral tetracarbonyl species.

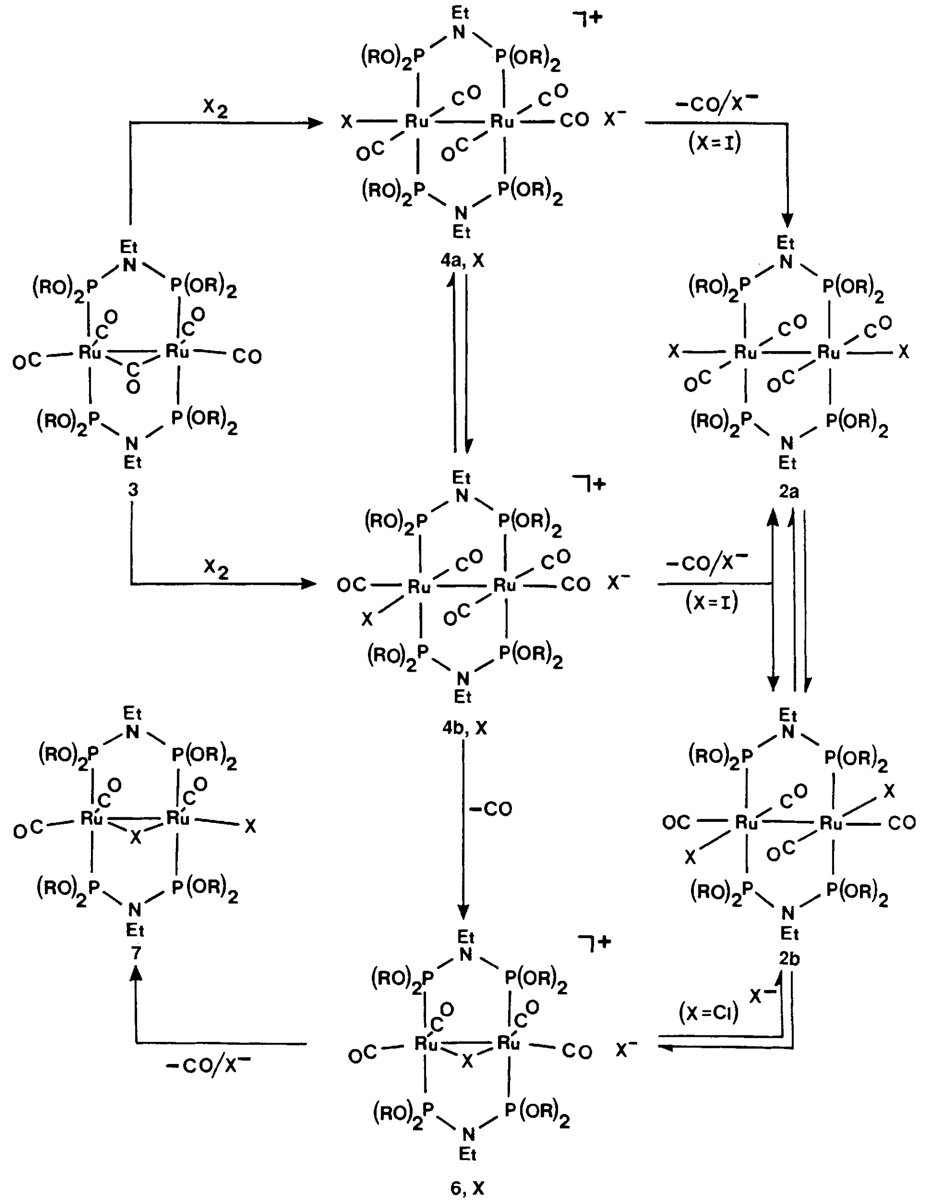
On the basis of earlier investigations[18–24] it had been widely recognized that the halogenation of dinuclear metal carbonyl derivatives containing a formal metal–metal bond involves the cleavage of this bond and the formation of neutral mononuclear halogenated products.[25] The results of this study provide further evidence[10,11,26–30] however that halogenation of this type of compound leads to the formation of ionic halogenated products and that the neutral species are products in a secondary process.

Experimental

The neutral pentacarbonyls $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]$ (R = Me or $\mathrm{Pr^i}$) were synthesised according to a literature method.[13] 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; data are

Table 4 Interatomic angles (°) for $[\mathrm{Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]$

Ru(1)–I(2)–Ru(2)	61.2(1)	I(2)–Ru(1)–Ru(2)	60.2(1)	Ru(1)–P(4)–O(11)	118.0(4)	Ru(1)–P(4)–N(2)	116.6(4)
I(2)–Ru(1)–P(2)	89.8(1)	I(2)–Ru(1)–P(4)	87.4(1)	O(10)–P(4)–O(11)	98.5(5)	O(10)–P(4)–N(2)	98.3(6)
I(2)–Ru(1)–C(1)	122.7(5)	I(2)–Ru(1)–C(2)	134.5(7)	O(11)–P(4)–N(2)	105.5(6)	P(1)–N(1)–P(2)	120.6(7)
Ru(2)–Ru(1)–P(2)	91.2(1)	Ru(2)–Ru(1)–P(4)	92.5(1)	P(1)–N(1)–C(28)	120(1)	P(2)–N(1)–C(28)	119(1)
Ru(2)–Ru(1)–C(1)	177.2(5)	Ru(2)–Ru(1)–C(2)	74.4(7)	P(3)–N(2)–P(4)	122(1)	P(3)–N(2)–C(30)	119(1)
P(2)–Ru(1)–P(4)	173.5(1)	P(2)–Ru(1)–C(1)	89.0(5)	P(4)–N(2)–C(30)	120(1)	P(1)–O(4)–C(4)	129(1)
P(2)–Ru(1)–C(2)	91.5(6)	P(4)–Ru(1)–C(1)	87.5(5)	P(1)–O(5)–C(7)	126(1)	P(2)–O(6)–C(10)	122(1)
C(1)–Ru(1)–C(2)	102.8(8)	P(4)–Ru(1)–C(2)	94.6(6)	P(2)–O(7)–C(13)	126(1)	P(3)–O(8)–C(16)	128(1)
I(1)–Ru(2)–Ru(1)	163.6(1)	I(1)–Ru(2)–I(2)	105.0(1)	P(3)–O(9)–C(19)	126(1)	P(4)–O(10)–C(22)	126(1)
I(1)–Ru(2)–P(3)	90.6(1)	I(1)–Ru(2)–P(1)	87.2(1)	P(4)–O(11)–C(25)	127(1)	Ru(1)–C(1)–O(1)	165(1)
I(2)–Ru(2)–Ru(1)	58.7(1)	I(1)–Ru(2)–C(3)	89.1(5)	Ru(1)–C(2)–O(2)	144(3)	Ru(1)–C(2)–O(2*)	171(2)
I(2)–Ru(2)–P(3)	89.7(1)	I(2)–Ru(2)–P(1)	92.2(1)	Ru(2)–C(3)–O(3)	178(2)	O(4)–C(4)–C(5)	106(1)
P(1)–Ru(2)–P(3)	177.4(1)	I(2)–Ru(2)–C(3)	165.8(5)	O(4)–C(4)–C(6)	108(1)	C(5)–C(4)–C(6)	113(2)
P(3)–Ru(2)–C(3)	91.6(5)	P(1)–Ru(2)–C(3)	87.0(5)	O(5)–C(7)–C(8)	111(2)	O(5)–C(7)–C(9)	109(2)
Ru(1)–Ru(2)–P(3)	90.6(1)	Ru(1)–Ru(2)–P(1)	91.9(1)	C(8)–C(7)–C(9)	113(2)	O(6)–C(10)–C(11)	107(2)
Ru(1)–Ru(2)–C(3)	107.2(5)	Ru(2)–P(1)–O(4)	121.1(4)	O(6)–C(10)–C(12)	107(2)	C(11)–C(10)–C(12)	113(2)
Ru(2)–P(1)–O(5)	114.7(4)	Ru(2)–P(1)–N(1)	116.6(4)	O(7)–C(13)–C(14)	106(1)	O(7)–C(13)–C(15)	108(2)
O(4)–P(1)–O(5)	98.5(5)	O(4)–P(1)–N(1)	103.8(5)	C(14)–C(13)–C(15)	113(1)	O(8)–C(16)–C(17)	112(1)
O(5)–P(1)–N(1)	98.4(5)	Ru(1)–P(2)–O(6)	117.7(4)	O(8)–C(16)–C(18)	108(1)	C(17)–C(16)–C(18)	112(2)
Ru(1)–P(2)–O(7)	116.4(4)	Ru(1)–Ru(2)–N(1)	117.0(4)	O(9)–C(19)–C(20)	111(2)	O(9)–C(19)–C(21)	106(2)
O(6)–P(2)–O(7)	99.4(5)	O(6)–P(2)–N(1)	98.8(5)	C(20)–C(19)–C(21)	114(2)	O(10)–C(22)–C(23)	108(2)
O(7)–P(2)–N(1)	104.8(5)	Ru(2)–P(3)–O(8)	119.4(4)	O(10)–C(22)–C(24)	106(2)	C(23)–C(22)–C(24)	115(2)
Ru(2)–P(3)–O(9)	118.0(4)	Ru(2)–P(3)–N(2)	117.5(4)	O(11)–C(25)–C(26)	109(1)	O(11)–C(25)–C(27)	104(1)
O(8)–P(3)–O(9)	96.9(5)	O(8)–P(3)–N(2)	102.7(5)	C(26)–C(25)–C(27)	115(2)	N(1)–C(28)–C(29)	116(2)
O(9)–P(3)–N(2)	98.3(6)	Ru(1)–P(4)–O(10)	116.4(4)	N(2)–C(30)–C(31)	115(2)		



Scheme 1

summarized in Table 1. Light petroleum refers to that fraction of b.p. 60–80 °C.

Syntheses.—$[\mathrm{Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]\mathrm{PF_6}$ (R = Me *or* $\mathrm{Pr^i}$; X = Cl, Br *or* I). A twice molar amount of iodine or bromine in hexane (*ca.* 25 cm^3) or chlorine in $\mathrm{CCl_4}$ (*ca.* 5 cm^3) was added dropwise over a period of 15 min to a stirred solution of $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2}]$ (0.20 g, 0.25 mmol) or $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]$ (0.26 g, 0.25 mmol) in hexane (*ca.* 100 cm^3) and the solution stirred for 30 min at room temperature. The product, which separated from solution and was identified as $[\mathrm{Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]\mathrm{X}$, was washed with light petroleum and dissolved in acetone (*ca.* 25 cm^3). The salt $\mathrm{NH_4PF_6}$ (0.08 g, 0.05 mmol) in acetone (*ca.* 5 cm^3) was added to this solution followed by water (*ca.* 30 cm^3). The acetone was removed under reduced pressure resulting in the separation of the required compound from solution. Crystallization was effected in the dark from ethanol–water. Yield 40–50% (Found: C, 20.6; H, 3.6; N, 2.9. $\mathrm{C_{17}H_{34}ClF_6N_2O_{13}P_5Ru_2}$ requires C, 20.8; H, 3.5; N, 2.9. Found: C, 19.7; H, 3.4; N, 2.9. $\mathrm{C_{17}H_{34}BrF_6N_2O_{13}P_5Ru_2}$ requires C, 19.9; H, 3.3; N, 2.7. Found: C, 19.1; H, 3.4; I, 12.1; N, 2.8; P, 14.2. $\mathrm{C_{17}H_{34}F_6IN_2O_{13}P_5Ru_2}$ requires C, 19.0; H, 3.2; I, 11.9; N, 2.6; P, 14.5. Found: C, 32.8; H, 5.6; N, 2.4. $\mathrm{C_{33}H_{66}ClF_6N_2O_{13}P_5Ru_2}$ requires C, 32.9; H, 5.5; N, 2.3%). The decarbonylation of $[\mathrm{Ru_2X(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]^+$ (X = Br or I) in solution prevented their isolation in a pure state and they were thus identified by spectroscopic means only.

$[\mathrm{Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]\mathrm{PF_6}$ (R = Me *or* $\mathrm{Pr^i}$; X = Cl, Br *or* I). (*i*) A solution of $[\mathrm{Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]\mathrm{PF_6}$ (R = Me, X = Cl, Br or I; R = $\mathrm{Pr^i}$, X = Cl) (*ca.* 0.2 mmol) or $[\mathrm{Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]\mathrm{X}_x$ (R = $\mathrm{Pr^i}$, X = Br or I, x = 1 or 3) (*ca.* 0.2 mmol) in acetone (*ca.* 30 cm^3) was stirred for 2 (R = $\mathrm{Pr^i}$, X = Br or I), 7 (R = $\mathrm{Pr^i}$, X = Cl; R = Me, X = Br or I) or 10 d (R = Me, X = Cl) at room temperature. The solvent was removed under reduced pressure and the residue crystallized from ethanol–water. Yield 70–80%.

(*ii*) A twice molar amount of chlorine in $\mathrm{CCl_4}$ (*ca.* 10 cm^3) or bromine in $\mathrm{CH_2Cl_2}$ (*ca.* 15 cm^3) was added dropwise to a stirred solution of $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]$

(0.26 g, 0.25 mmol) and trimethylamine *N*-oxide dihydrate (0.25 mmol) in $\mathrm{CH_2Cl_2}$ (*ca.* 25 $\mathrm{cm^3}$) and the solution stirred for 2 h for the bromination or for 3 h for the chlorination. The solvent was removed under reduced pressure and the oily residue, identified as $[\mathrm{Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]X}$, was washed with light petroleum. The residue was dissolved in acetone (*ca.* 25 $\mathrm{cm^3}$) and $\mathrm{NH_4PF_6}$ (0.08 g, 0.5 mmol) in acetone (*ca.* 5 $\mathrm{cm^3}$) was added followed by water (*ca.* 30 $\mathrm{cm^3}$). The acetone was removed under reduced pressure leading to the separation of the required compound from solution. Crystallization was effected from ethanol–water. Yield 60–70% (Found: C, 19.9; H, 3.4; Cl, 3.6; N, 2.9; P, 16.0. $\mathrm{C_{16}H_{34}ClF_6N_2O_{12}P_5Ru_2}$ requires C, 20.2; H, 3.6; Cl, 3.7; N, 2.9; P, 16.3. Found: C, 19.4; H, 3.1; Br, 7.8; N, 2.9; P, 15.6. $\mathrm{C_{16}H_{34}BrF_6N_2O_{12}P_5Ru_2}$ requires C, 19.3; H, 3.4; Br, 8.0; N, 2.8; P, 15.6. Found: C, 18.3; H, 3.4; N, 3.0. $\mathrm{C_{16}H_{34}F_6IN_2O_{12}P_5Ru_2}$ requires C, 18.4; H, 3.3; N, 2.7. Found: C, 33.5; H, 5.8; N, 2.4. $\mathrm{C_{32}H_{66}ClF_6N_2O_{12}P_5Ru_2}$ requires C, 33.7; H, 5.6; N, 2.4. Found: C, 31.1; H, 5.6; N, 2.3. $\mathrm{C_{32}H_{66}BrF_6N_2O_{12}P_5Ru_2}$ requires C, 31.5; H, 5.4; N, 2.3. Found: C, 30.0; H, 5.4; I, 9.9; N, 2.3; P, 12.0. $\mathrm{C_{32}H_{66}F_6IN_2O_{12}P_5Ru_2}$ requires C, 30.3; H, 5.2; I, 10.0; N, 2.2; P, 12.1%).

$[\mathrm{Ru_2(\mu\text{-}X)X(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]$ (R = Me *or* $\mathrm{Pr^i}$; X = Cl, Br *or* I). (*i*) A solution of $[\mathrm{Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X}$ (R = Me, X = Cl or Br; R = $\mathrm{Pr^i}$, X = Cl) (0.3 mmol) or $[\mathrm{Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]X}$ (X = Cl or Br) (0.3 mmol) (or $[\mathrm{Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]PF_6}$ (X = Cl or Br) (0.3 mmol) or $[\mathrm{Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]PF_6}$ (X = Cl, Br or I) (0.3 mmol) together with an excess of the appropriate tetraethylammonium halide salt) in acetone (*ca.* 50 $\mathrm{cm^3}$) was treated with solid trimethylamine *N*-oxide dihydrate (0.6 mmol) and stirred for 3–4 h at room temperature. The volatiles were removed under reduced pressure and the residue extracted with warm light petroleum (3 × 30 $\mathrm{cm^3}$, 45 °C). The combined extracts were evaporated to dryness and the crude product was crystallized from ethanol. Yield 55–75%.

(*ii*) A solution of $[\mathrm{Ru_2X(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X}$ (R = Me, X = Cl or Br; R = $\mathrm{Pr^i}$, X = Cl) (0.4 mmol) or $[\mathrm{Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]X}$ (X = Cl, Br or I) (0.4 mmol) in thf (*ca.* 100 $\mathrm{cm^3}$) was irradiated with ultraviolet light through Pyrex glass using a 125 W high-pressure mercury lamp at a temperature of ambient or 50 °C for 1–5 h. The solvent was removed under reduced pressure and the residue extracted with warm light petroleum (3 × 20 $\mathrm{cm^3}$, 45 °C). The combined extracts were evaporated to dryness and the crude product was crystallized from ethanol or hexane. Yield 40–50%. The crude $[\mathrm{Ru_2(\mu\text{-}X)X(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]$ could also be purified by means of chromatography using a silica gel column (neutral) and eluting first with light petroleum and secondly with light petroleum–$\mathrm{CH_2Cl_2}$ (8:1) (Found: C, 22.0; H, 4.2; N, 3.3. $\mathrm{C_{15}H_{34}Cl_2N_2O_{11}P_4Ru_2}$ requires C, 22.1; H, 4.2; N, 3.4. Found: C, 20.3; H, 3.8; N, 3.3. $\mathrm{C_{15}H_{34}Br_2N_2O_{11}P_4Ru_2}$ requires C, 19.9; H, 3.8; N, 3.1. Found: C, 33.1; H, 6.0; N, 2.6. $\mathrm{C_{31}H_{66}Br_2N_2O_{11}P_4Ru_2}$ requires C, 33.0; H, 5.9; N, 2.5. Found: C, 30.8; H, 5.5; N, 2.4. $\mathrm{C_{31}H_{66}I_2N_2O_{11}P_4Ru_2}$ requires C, 30.4; H, 5.4; N, 2.3%).

$[\mathrm{Ru_2I_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}]$ (R = Me *or* $\mathrm{Pr^i}$) *and* $[\mathrm{Ru_2I_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}}]$. A twice molar amount of iodine in acetone (*ca.* 15 $\mathrm{cm^3}$) was added dropwise to a stirred solution of $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2}]$ (0.20 g, 0.25 mmol) or $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]$ (0.26 g, 0.25 mmol) or $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}}]$ (0.23 g, 0.25 mmol) and trimethylamine *N*-oxide dihydrate (0.75 mmol) in acetone (*ca.* 15 $\mathrm{cm^3}$) and the solution stirred for 60 min. The solvent was removed under reduced pressure, the residue extracted with toluene (*ca.* 10 $\mathrm{cm^3}$) and the extract filtered. The filtrate was concentrated to a volume of approximately 3 $\mathrm{cm^3}$ and the product crystallized by addition of ethanol (*ca.* 10 $\mathrm{cm^3}$) and allowing the solution to stand at 0 °C. Yield 80–90% (Found: C, 19.2; H, 3.3; I, 26.4; N, 3.3; P, 12.7. $\mathrm{C_{16}H_{34}I_2N_2O_{12}P_4Ru_2}$ requires C, 18.7; H, 3.3; I, 24.7; N, 2.7; P, 12.1. Found: C, 30.3; H, 5.3; I, 21.0; N, 2.1; P, 10.2. $\mathrm{C_{32}H_{66}I_2N_2O_{12}P_4Ru_2}$ requires C, 30.2; H, 5.6; I, 21.2; N, 2.3; P, 10.4. Found: C, 25.6; H, 4.5; N, 2.6. $\mathrm{C_{24}H_{50}I_2N_2O_{12}P_4Ru_2}$ requires C, 25.3; H, 4.4; N, 2.5%).

Crystal Structure Determination of $[\mathrm{Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]$.—*Crystal data.* $\mathrm{C_{31}H_{66}I_2N_2O_{11}P_4Ru_2}$, $M = 1222.7$, orange crystal of dimensions 0.05 × 0.12 × 0.42 mm grown from ethanol, monoclinic, space group *Pn*, $a = 11.557(4)$, $b = 13.095(3)$, $c = 16.263(4)$ Å, $\beta = 100.43(2)°$, $U = 2420.5$ Å^3, $Z = 2$, $D_c = 1.68$ g cm^{-3}, μ(Mo-Kα) = 19.1 cm^{-1}, $F(000) = 1216$.

Intensity data were collected on a Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å). A least-squares fit of high-angle reflections ($\theta > 12°$) was used to obtain accurate cell constants. Diffraction intensities were measured in the range $3 \leqslant 2\theta \leqslant 25°$ using the ω–2θ scan technique, 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 4139 unique reflections measured, 3896 were classed as observed [$I > 3\sigma(I)$] and used for the solution and refinement of the structure.

The ruthenium and iodine atoms were located using the direct methods routine of the program SHELX 76.[31] Subsequent Fourier syntheses gave the positions of the remaining non-H atoms. Hydrogen atoms were placed in calculated positions using the known geometry of the groups involved.[31] The ruthenium and iodine atoms were assigned anisotropic thermal parameters and all the remaining atoms isotropic thermal parameters. A final refinement using unit weights converged at $R = 0.046$ (298 parameters) the largest peak in the subsequent Fourier difference map being 1.2 e Å^{-3}. Fractional atomic coordinates for the non-H atoms are listed in Table 2 and interatomic distances and angles in Tables 3 and 4 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Acknowledgements

The authors express their sincere thanks to the Foundation for Research Development and the Universities of Natal and the Witwatersrand for financial support, Johnson Matthey plc for the loan of ruthenium salts and Dr. P. H. van Rooyen of the National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria for the intensity data collection.

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Received 19*th March* 1991; *Paper* 1/01336J