Synthesis and Reactivity of the Unsaturated Diruthenium Diphosphazane-bridged Species $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i)†

John S. Field, Raymond J. Haines,* Mark W. Stewart, Jörg Sundermeyer and Stephen F. Woollam
Unit of Metal Cluster Chemistry, Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg 3200, Republic of South Africa

Thermolysis of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$, $[Ru_2H_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ or $[Ru_2\{\mu\text{-}OC(O)\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) under appropriate reaction conditions affords the formally unsaturated species $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$, which have been established by X-ray crystallography for both R = Me and R = Pr^i to contain two complementary semi-bridging carbonyl groups as well as two terminal carbonyls. These compounds are highly labile and react under mild conditions with a range of small molecule nucleophiles and electrophiles including carbon monoxide, isonitriles, nitrosyl ions, alkynes, sulfur, hydrogen sulfide, dioxygen, sulfur dioxide, tin(II) chloride, dihydrogen, protons, halogens and carbon tetrachloride. The compound $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$, the product of the reaction involving dihydrogen and the tetraisopropoxydiphosphazane derivative and in which, as determined by X-ray crystallography, the hydrogens are situated equatorially and *trans* to each other on different ruthenium atoms, is also highly reactive, typically reductively eliminating dihydrogen in its reactions with nucleophiles including alkynes.

Considerable attention has been focused on the mechanism of activation of small molecule compounds by di- and poly-nuclear transition-metal complexes with the overall aim of producing systems which will model the chemisorption of small molecules on metal surfaces and/or which will homogeneously catalyse organic reactions not possible by mononuclear complexes.[1] A prime objective in the design of metal complexes which will function as homogeneous catalysts is the development of systems which readily give rise to formally co-ordinatively unsaturated species or which themselves are co-ordinatively unsaturated. Such systems will provide ready access of the substrate molecules to one or more metal atoms.[2] While the range of mononuclear co-ordinatively unsaturated species is extensive, that of dinuclear and metal cluster compounds is far more limited. Low-valent unsaturated dinuclear carbonyl and diphosphorus ligand-bridged carbonyl derivatives that have been reported include $[M_2(\mu\text{-}H)_2(CO)_8]^{2-}$ (M = Cr, Mo or W),[3] $[Re_2(\mu\text{-}H)_2(CO)_8]$,[4] $[Mn_2(\mu\text{-}H)_2(CO)_6\{\mu\text{-}(EtO)_2POP(OEt)_2\}]$,[5,6] $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)]$[6,7] and $[Mn_2(\mu\text{-}H)_2(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2]$,[8] all of which contain two bridging hydride ligands. The related bis(diphenylphosphino)methane-bridged dimanganese compound $[Mn_2(\mu\text{-}\eta^2\text{-}CO)_2(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2]$[9,10] is formally saturated if the bridging carbonyl group is considered as a four-electron donor (see below), but it can be converted into an unsaturated species through this carbonyl reverting to a two-electron donor. Co-ordinatively unsaturated complexes or species which readily afford co-ordinatively unsaturated derivatives are also valuable as precursors for the synthesis of generally inaccessible products.

We have shown previously that the diruthenium diphosphazane-bridged complexes $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **1** (R = Me, Et, Pr^i, *etc.*),[11] substituted derivatives of diruthenium nonacarbonyl, are electron rich and react readily with a wide range of electrophiles including protons,[12] metal salts,[13] halogens,[14] quinones,[15] tetracyanoquinodimethane and tetracyanoethylene[16] and nitrosyl ions.[17] On the other hand, more forceful conditions are required for the reaction of these pentacarbonyl species with nucleophilic agents such as isocyanides and alkynes. We have now established that under appropriate reaction conditions these compounds can be decarbonylated to the formally co-ordinatively unsaturated species $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$, which in contrast to the unsaturated dinuclear compounds described above do not contain an $M_2(\mu\text{-}H)_2$ core, and that these unsaturated species are susceptible to nucleophilic as well as electrophilic attack under mild conditions. The synthesis of these compounds and their reactivity towards various electrophilic and nucleophilic reagents are now described; some of the results have been the subject of a preliminary communication.[18]

Results and Discussion

Synthesis and Characterization of $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me *or* Pr^i).—The heating of a solution of the diphosphazane-bridged derivative of diruthenium nonacarbonyl, $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **1** (R = Pr^i) in toluene to between 80 and 90 °C resulted in a change in colour from yellow to pale red, but $^{31}P\text{-}\{^1H\}$ NMR and infrared spectral measurements indicated that if a reaction had taken place the product was present in very minute quantities. However, passage of argon through this heated solution resulted in the colour becoming intense purple and by monitoring this reaction by means of IR spectroscopy it was established that the parent pentacarbonyl derivative can be totally converted within 45 min into a new compound characterized as $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **2** (R = Pr^i), see Scheme 1.

The solid-state IR spectrum of this compound contained two bands in the C–O stretching region at 1864 and 1820 cm^{-1}, these frequencies being considerably lower than those associated with the terminal carbonyls of the parent species $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ but higher than

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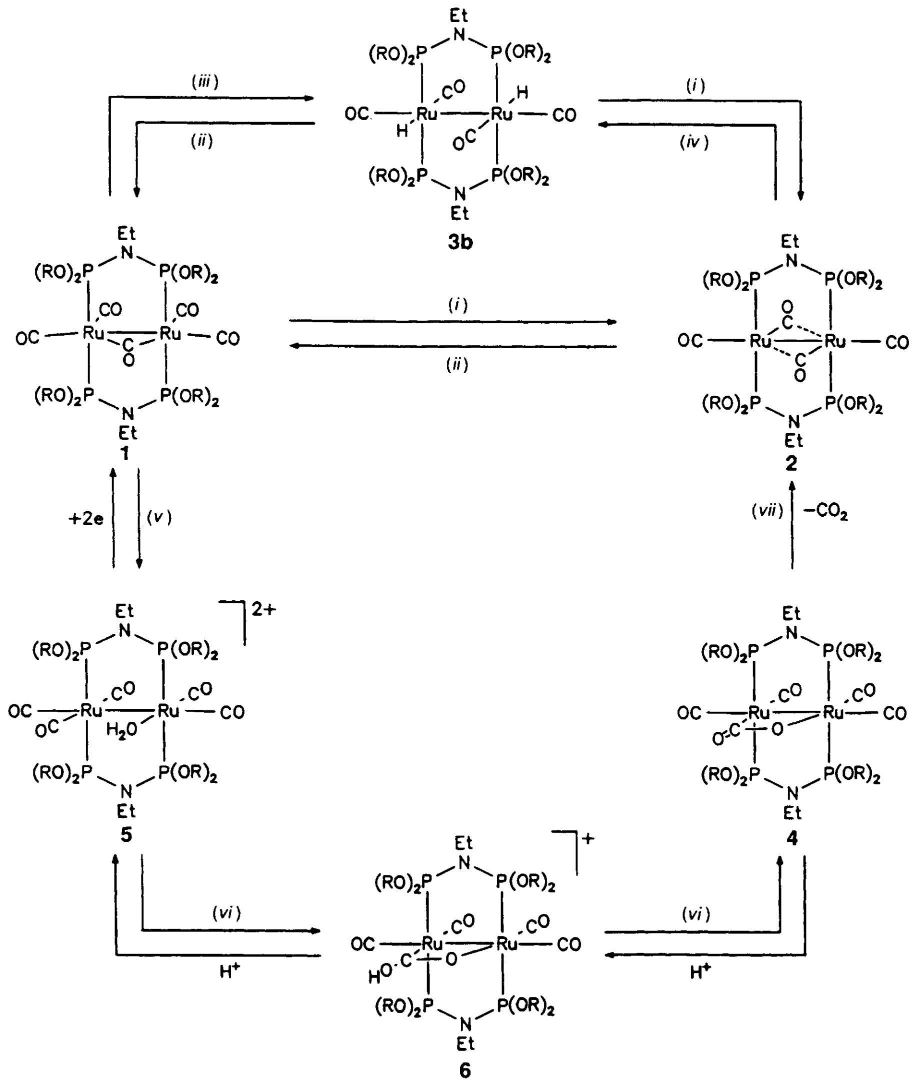
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1 Synthetic routes to $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **2** (R = Me or Pr^i) and $[Ru_2H_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **3** (R = Me or Pr^i). (*i*) 80 °C, argon–toluene or solid state; (*ii*) CO, room temperature, (r.t.) (*iii*) H_2, toluene, 80 °C; (*iv*) H_2, r.t.; (*v*) Ag^+, thf–water; (*vi*) base; (*vii*) toluene, 60 °C

that for the bridging carbonyl. The $^{31}P\text{-}\{^1H\}$ NMR spectrum, measured in C_6D_6, exhibited a singlet at δ 158.9 indicating the equivalence of the four phosphorus atoms, while the $^{13}C\text{-}\{^1H\}$ NMR spectrum revealed two downfield quintets at δ 203.5 and 220.2, readily assigned to the carbon atoms of the carbonyl ligands and interpreted in terms of the presence of two sets of non-equivalent carbonyl groups. These data are consistent with a product of symmetrical structure and containing at least one pair of semi-bridging carbonyls, as indeed subsequently confirmed X-ray crystallographically (see below).

The compound $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ was also prepared by a number of other methods. These included the passage of argon through a solution of $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **3** (R = Pr^i) readily synthesised by direct hydrogenation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ under appropriate reaction conditions (see below) in toluene at 80–90 °C, the pyrolysis of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ or $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ in the solid state at 80 °C under high vacuum or the decarboxylation of $[Ru_2\{\mu\text{-}OC(O)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **4** (R = Pr^i), synthesised by stepwise deprotonation of $[Ru_2(CO)_5(H_2O)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^{2+}$ **5** (R = Pr^i) and $[Ru_2\{\mu\text{-}OC(OH)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ **6** (R = Pr^i) in toluene at 60 °C.[13b,d] These methods are summarized in Scheme 1.

The analogous tetramethoxydiphosphazane-bridged derivative $[Ru_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ **2** (R = Me) can be synthesised similarly but its formation by passage of argon through a toluene solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ **1** (R = Me) at 80 °C is minimal with extensive decomposition occurring prior to it being produced in any substantial yield. However passage of argon through a solution of the carbon dioxide adduct $[Ru_2\{\mu\text{-}OC(O)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ **4** (R = Me) in toluene at room temperature afforded the corresponding unsaturated tetracarbonyl species in good yield.

Both tetracarbonyl compounds afford intensely coloured solutions with that of the tetraisopropoxydiphosphazane derivative being red-purple (λ_{max} = 553 nm, in acetonitrile) and that of the tetramethoxydiphosphazane species being blue-purple (λ_{max} = 500 nm, in acetonitrile). Interestingly, while single crystals of the latter are intense red, the crushed compound is intense blue. This dichroic behaviour is not observed for the tetraisopropoxydiphosphazane species, the crystals of which are deep purple.

Crystal Structures of $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me *or* Pr^i).—The molecular structure of the tetraisopropoxydiphosphazane derivative $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **2** (R = Pr^i) has been determined by X-ray

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

Compound	$\nu(CO)$ [a]/cm^{-1}	$^{31}P-\{^{1}H\}$ NMR [b]
$[Ru_2(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]$	1894s, 1788m [c]	166.8(s) [d]
$[Ru_2(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ [e]	1880s, 1782m [f]	158.9(s) [d]
$[Ru_2(\mu-CO)(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]$	1999s, 1960s, 1929s, 1913s, 1703ms [f]	160.5(s) [d]
$[Ru_2(\mu-CO)(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$	1989s, 1939s, 1906ms, 1885s, 1730m [f]	152.6(s) [d]
$[Ru_2(\mu-CO)(CO)_3(CNC_6H_3Me_2-2,6)\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]$ [g]	1967s, 1924vs, 1913vs, 1699s [h]	169.9(s, br) [i]
$[Ru_2(\mu-CO)(CO)_3(CNC_6H_3Me_2-2,6)\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ [j]	1923m, 1893s, 1879s, 1714m [h]	155.0(s) [d] 155.9 [i,k]
$[Ru_2(\mu-\sigma-C{=}CH_2)(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ [l]	1991s, 1947s, 1906s, 1890s [f]	148.8(s) [m]
$[Ru_2(\mu-\sigma^2-CH{=}CH)(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ [n]		146.1(s) [m]
$[Ru_2(\mu-\sigma-C{=}CHPh)(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ [o]	1992vs, 1949vs, 1918s, 1891vs [h]	147.0 [k,m]
$[Ru_2(\mu-\sigma-C{=}CHCO_2Me)(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ [p]	2000s, 1963vs, 1930ms, 1908s [f]	144.1 [k,q]
$[Ru_2(\mu-\sigma^2-CH{=}CCO_2Me)(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ [r]		148.0 [k,q]
$[Ru_2(\mu-\sigma^2-MeO_2CC{=}CCO_2Me)(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ [s]	2001s, 1967vs, 1940s, 1917s [f]	140.9(s) [m]
$[Ru_2(\mu-NO)(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ [t]	2034ms, 1998s, 1971ms, 1951m [u]	135.5(s) [q]
$[Ru_2(\mu-S)(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$	2000s, 1963vs, 1925s, 1920vs [h]	137.6(s) [d]
$[Ru_2(\mu-SH)H(CO)_3\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ [v]	1946s (br), 1889s (br), 1838m [h]	158.26 [k,w] 158.29 [x]
$[Ru_2(\mu-SO_2)(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$	2018vs, 1983vs, 1942s, 1927vs [h]	140.3(s) [d]
$[Ru_2(\mu-SnCl_2)(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]$	2012s, 1981vs, 1953m, 1936s [u]	157.3(s) [q]
$[Ru_2(\mu-SnCl_2)(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$	2006s, 1965vs, 1944s (sh), 1923ms [u]	144.0(s) [q]
$[Ru_2H_2(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]$ [y]	2000s, 1959s [h]	170.0(s) [d] 169.4(s)
$[Ru_2H_2(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ [z]	1997m, 1935s [h]	159.3(s) [d]
$[Ru_2H(\mu-CO)(CO)_3\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ *	2059s, 2007s, 1955s (br), 1757ms [u]	138.9(s) † 142.0 [k,‡]
$[Ru_2(\mu-I)(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$	2038ms, 2000s, 1973ms, 1951m [u]	131.0(s) [q]
$[Ru_2Cl_2(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]$	2012ms, 1976s, 1954w §	145.2 [m]
$[Ru_2Cl_2(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$	2001s, 1968s, 1942w §	135.2 [m]
$[Ru_2(\mu-Cl)Cl(CO)_3\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]$	2004s, 1995 (sh), 1949vs, 1916 (sh) [h]	146.4 [h,q]
$[Ru_2(\mu-Cl)Cl(CO)_3\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$	2000 (sh), 1984s, 1933vs, 1902 (sh) [h]	138.0 [d,k]
$[Ru_2(\mu-Br)Br(CO)_3\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$	2002 (sh), 1987s, 1933vs, 1907 (sh) [h]	136.9 [d,k]

[a] Abbreviations: v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad. [b] δ scale in ppm relative to H_3PO_4; measured at room temperature unless otherwise stated. Abbreviations: s = singlet, t = triplet, qnt = quintet. [c] Measured in thf. [d] Measured in C_6D_6. [e] $^{13}C-\{^{1}H\}$ NMR: δ 203.5 (qnt, $|^2J_{PC} + {}^3J_{P'C}|$ 10.5) and 220.2 (qnt, $|^2J_{PC} + {}^3J_{P'C}|$ 9.2 Hz) (*C*O); measured in C_6D_6; δ scale in ppm relative to $SiMe_4$. [f] Measured in cyclohexane. [g] ν(CN) 2077s cm^{-1}, measured in hexane. [h] Measured in hexane. [i] Measured at −80 °C in $[^2H_8]$toluene. [j] ν(CN) 2071 cm^{-1}, measured in hexane. [k] Centre of an AA′BB′ pattern. [l] $^{13}C-\{^{1}H\}$ NMR: δ 131.9 (qnt, $^3J_{PC}$ 4.1, $C{=}CH_2$), 203.8 (qnt, $|^2J_{PC} + {}^3J_{P'C}|$ 10.3, CO), 210.7 (qnt, $|^2J_{PC} + {}^3J_{P'C}|$ 6.0, CO) and 232.7 (qnt, $^2J_{PC}$ 16.4 Hz, $C{=}CH_2$), measured in $CDCl_3$. ^1H NMR: δ 6.34 (q, $^4J_{PH}$ 2.4 Hz, $C{=}CH_2$), measured in $CDCl_3$. [m] Measured in $CDCl_3$. [n] ^1H NMR: δ 7.02 (s), measured in $CDCl_3$. [o] $^{13}C-\{^{1}H\}$ NMR: δ 145.4 (qnt, $^3J_{PC}$ 4.5, $C{=}CHPh$), 202.2 (t, $^2J_{PC}$ 17.1, CO), 204.8 (t, $^2J_{PC}$ 17.1, CO), 210.1 (t, $^2J_{PC}$ 13.4, CO), 211.4 (t, $^2J_{PC}$ 10.4, CO) and 234.4 (qnt, $^2J_{PC}$ 15.9 Hz, $C{=}CHPh$), measured in C_6D_6. ^1H NMR: δ 8.19 (qnt, $^4J_{PH}$ 2.4 Hz, $C{=}CHPh$). [p] ^1H NMR: 7.35 (qnt, $|^4J_{PH} + {}^5J_{P'H}|$ 2.4 Hz, $C{=}CHCO_2Me$), measured in $CDCl_3$. [q] Measured in CD_2Cl_2. [r] ^1H NMR: δ 9.12 (qnt, $|^3J_{PH} + {}^4J_{P'H}|$ 1.9 Hz, $CH{=}CCO_2Me$), measured in $CDCl_3$. [s] $^{13}C-\{^{1}H\}$ NMR: δ 152.0 (qnt, $|^2J_{PC} + {}^3J_{P'C}|$ 3.6, $MeO_2CC{=}CCO_2Me$), 197.2 (qnt, $|^2J_{PC} + {}^3J_{P'C}|$ 9.0, CO) and 209.3 (qnt, $|^2J_{PC} + {}^3J_{P'C}|$ 7.1 Hz, CO), measured in $CDCl_3$. [t] ν(NO) 1545s cm^{-1}, measured in CH_2Cl_2. [u] Measured in CH_2Cl_2. [v] ^1H NMR: δ −1.67 (qnt, $^3J_{PH}$ 13.8, SH) and −10.03 (t, br, $^2J_{PH}$ 17.8 Hz, RuH). [w] Measured at −32 °C in $[^2H_8]$toluene. Major set of peaks. [x] Centre of multiplet; minor set of peaks. [y] ^1H NMR: δ −8.50 (qnt, $|^2J_{PH} + {}^3J_{P'H}|$ 10.8) and −8.69 (qnt, $|^2J_{PH} + {}^3J_{P'H}|$ 10.7 Hz), measured in C_6D_6. ν(RuH) 1869w cm^{-1} measured in hexane. [z] ^1H NMR: δ −8.39 (qnt, $|^2J_{PH} + {}^3J_{P'H}|$ 11.1 Hz), measured in C_6D_6. ν(RuH) 1886w cm^{-1}, measured in hexane. * ^1H NMR: δ −9.69 (qnt, $|^2J_{PH} + {}^3J_{P'H}|$ 14.7 Hz), measured in $(CD_3)_2CO$. † Measured in $(CD_3)_2CO$. ‡ Measured at −80 °C in $(CD_3)_2CO$. § Measured in CCl_4.

crystallography and is illustrated in Fig. 1. The Ru_2P_4 skeletal framework is similar to that for the parent pentacarbonyl derivative[11] with the two bridging diphosphazane ligands being *trans* disposed with respect to each other other and with the two ruthenium atoms being separated by a distance of 2.763(1) Å which is slightly less than that for $[Ru_2(\mu-CO)(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]$ **1** (R = Me) [2.801(2) Å].[11] The molecule contains a crystallographic centre of symmetry which is located midway between the ruthenium atoms. It adopts a near-eclipsed configuration as revealed by the P(1)–Ru–Ru′–P(2′) torsion angle of 4.75(8)°. The salient feature of the structure is the presence of two complementary semi-bridging carbonyl groups as well as two terminal carbonyls which are essentially collinear with the Ru–Ru vector [Ru′–Ru–C(1) 175.2(2)°]. The Ru–C–O bond angle for the semi-bridging carbonyls is 153.5(9)° while the Ru–C(2) and Ru′–C(2) distances are 1.926(9) and 2.434(9) Å respectively.

The molecular structure of $[Ru_2(CO)_4\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]$ **2** (R = Me) has also been established by X-ray crystallography and is illustrated in Fig. 2. It is totally analogous to that of the isopropoxydiphosphazane derivative with corresponding interatomic distances and angles being almost identical. The Ru–Ru distance of 2.729(1) Å is 0.034 Å shorter than that for the isopropoxydiphosphazane derivative and 0.072 Å shorter than that for the parent carbonyl.[11]

It has been established previously that the chromium, molybdenum and tungsten bis(cyclopentadienyl)hexacarbonyl derivatives $[M_2(\eta-C_5R'_5)_2(CO)_6]$ (M = Cr, Mo or W; R′ = H or Me) can be readily decarbonylated under thermal conditions to afford the corresponding tetracarbonyl derivatives $[M_2(\eta-C_5R'_5)_2(CO)_4]$ which on the basis of the effective atomic number rule are predicted to have metal–metal triple bonds.[19–23] Consistent with this prediction, a difference of *ca.* 0.8 Å was observed between the molybdenum–molybdenum distance for $[Mo_2(\eta-C_5H_5)_2(CO)_6]$ and that for $[Mo_2(\eta-C_5H_5)_2(CO)_4]$.[24] Short chromium–chromium distances corresponding to a Cr–Cr triple bond were also established by X-ray crystallography for $[Cr_2(\eta-C_5Me_5)_2(CO)_4]$[25] and $[Cr_2(\eta-C_5H_5)_2(CO)_4]$.[26] Applying a similar rationale to $[Ru_2(\mu-CO)(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]$, the loss of a single carbonyl group from this species would be expected to lead to the formation of a product with a ruthenium–ruthenium double bond, with the ruthenium–ruthenium distance for the latter being appreciably less than

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

Atom	X/a	Y/b	Z/c
Ru	4590(1)	95(1)	837(1)
P(1)	5590(1)	−795(2)	1896(1)
P(2)	3511(1)	814(2)	−162(1)
O(1)	3702(4)	603(9)	2629(5)
O(2)	5477(4)	2663(6)	563(5)
O(3)	5996(3)	187(5)	2767(4)
O(4)	5408(3)	−2043(5)	2610(4)
O(5)	2825(3)	−232(5)	−382(4)
O(6)	3035(3)	2027(5)	255(4)
N	3627(3)	1271(6)	8639(4)
C(1)	4042(4)	370(9)	1974(6)
C(2)	5207(5)	1586(10)	449(7)
C(3)	5594(5)	623(8)	3622(6)
C(4)	6069(7)	103(14)	4569(9)
C(5)	5541(9)	2167(10)	3536(10)
C(6)	4836(5)	−3075(7)	2299(6)
C(7)	5248(7)	−4442(10)	2333(10)
C(8)	4260(7)	−3035(12)	3030(11)
C(9)	2432(4)	−827(8)	439(6)
C(10)	2638(7)	−2364(9)	471(10)
C(11)	1565(6)	−652(14)	124(11)
C(12)	3397(5)	3173(7)	859(6)
C(13)	2814(6)	3593(10)	1580(7)
C(14)	3559(7)	4280(9)	100(9)
C(15)	2975(5)	1993(9)	8002(6)
C(16)	2359(5)	1051(12)	7479(8)

Table 3 Selected interatomic distances (Å) and angles (°) for $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$

Ru–P(1)	2.314(2)	Ru–P(2)	2.315(2)
Ru–C(1)	1.884(9)	Ru–C(2)	1.926(9)
Ru–Ru′	2.763(1)	Ru′–C(2)	2.434(9)
P(1)–Ru–P(2)	174.1(1)	P(1)–Ru–C(1)	89.1(2)
P(2)–Ru–C(1)	87.8(2)	P(1)–Ru–C(2)	92.7(2)
P(2)–Ru–C(2)	93.2(2)	C(1)–Ru–C(2)	116.3(4)
Ru′–Ru–P(1)	92.5(2)	Ru′–Ru–P(2)	90.9(2)
Ru′–Ru–C(1)	175.2(2)	Ru′–Ru–C(2)	59.4(2)
Ru′–C(2)–Ru	77.8(2)		

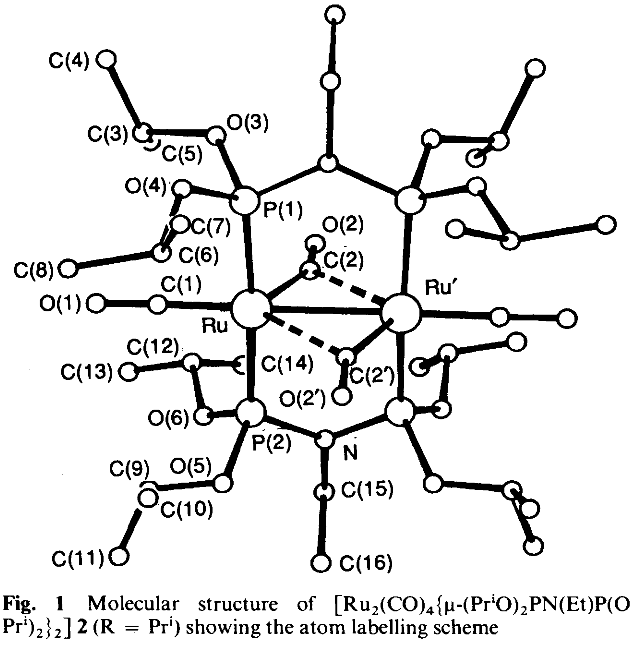


Fig. 1 Molecular structure of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **2** (R = Pr^i) showing the atom labelling scheme

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

Atom	X/a	Y/b	Z/c
Ru	540(1)	1391(1)	4867(1)
P(1)	1772(2)	2765(1)	7129(1)
P(2)	−940(2)	292(1)	2697(1)
N	−2059(5)	−1644(4)	2062(4)
O(1)	2227(9)	4188(7)	4356(6)
O(2)	3007(5)	−704(5)	4064(4)
O(3)	3565(4)	4048(4)	7524(4)
O(4)	759(4)	3939(4)	8186(3)
O(5)	−2256(4)	1193(4)	2374(3)
O(6)	137(4)	325(4)	1498(3)
C(1)	1550(8)	3131(7)	4566(5)
C(2)	1815(7)	−208(6)	4445(5)
C(3)	4950(7)	3669(9)	6743(7)
C(4)	233(10)	5160(8)	7966(7)
C(5)	−3388(8)	1856(8)	3358(6)
C(6)	1522(7)	−380(9)	1245(5)
C(7)	−2972(8)	−2479(7)	619(5)
C(8)	−4779(8)	−2283(9)	492(7)

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

Ru(1)–P(1)	2.304(1)	Ru–P(2)	2.296(1)
Ru–C(1)	1.843(5)	Ru–C(2)	1.900(5)
Ru–Ru′	2.729(1)	Ru′–C(2)	2.327(5)
P(1)–Ru–P(2)	171.5(0)	P(1)–Ru–C(1)	90.7(2)
P(2)–Ru–C(1)	86.5(2)	P(1)–Ru–C(2)	93.8(1)
P(2)–Ru–C(2)	94.7(1)	C(1)–Ru–C(2)	113.9(3)
Ru′–Ru–P(1)	90.9(1)	Ru′–Ru–P(2)	93.3(1)
Ru′–Ru–C(1)	170.9(2)	Ru′–Ru–C(2)	57.0(2)
Ru′–C(2)–Ru	79.7(2)		

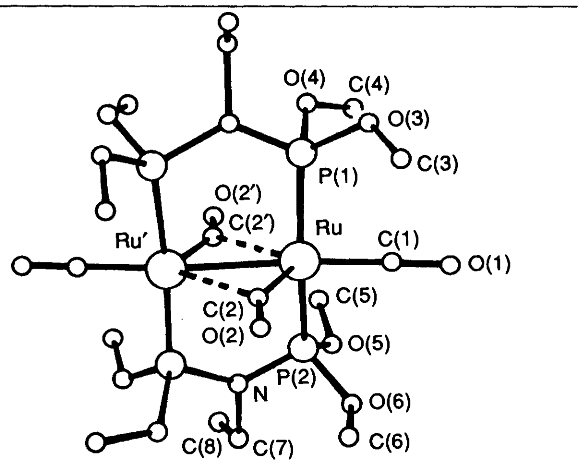
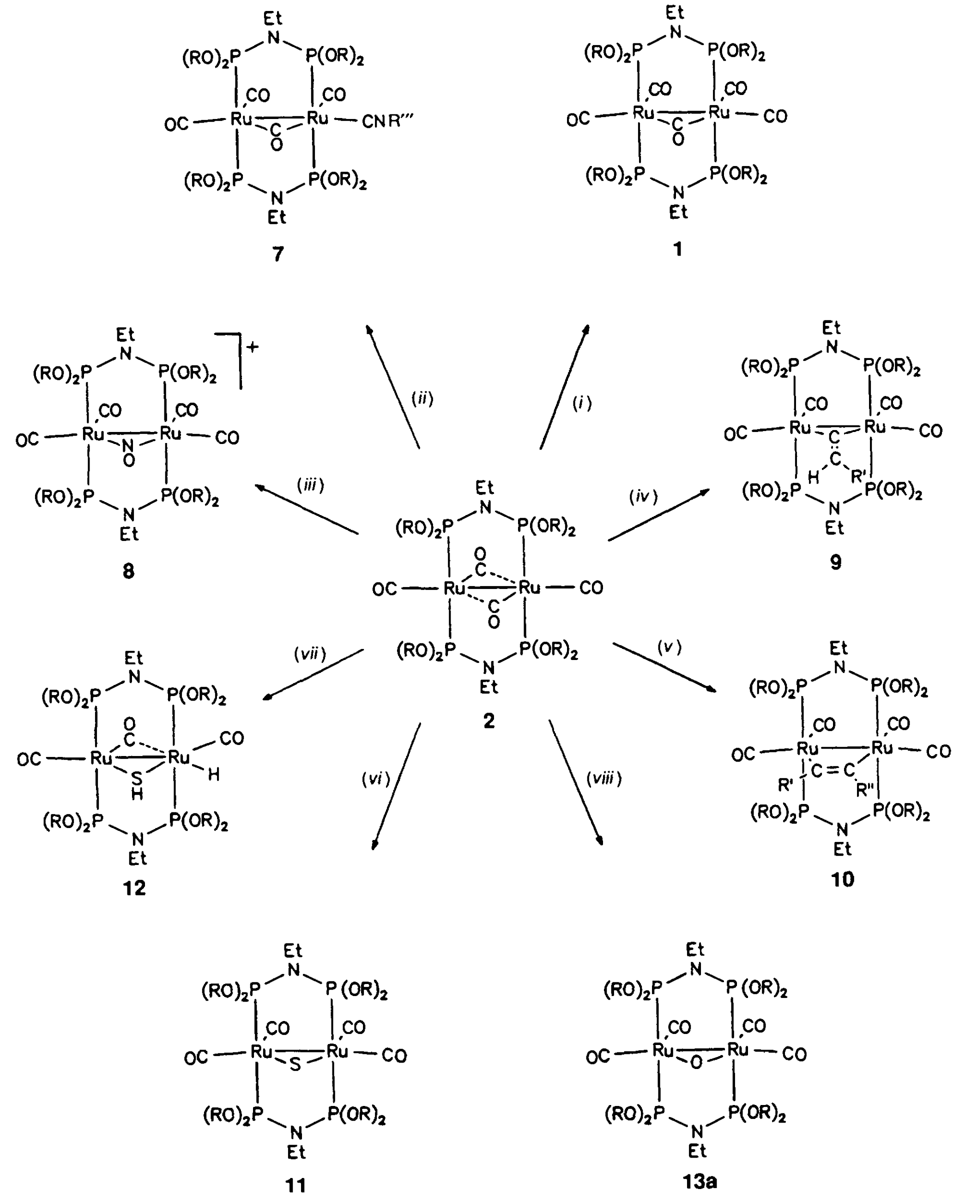


Fig. 2 Molecular structure of $[Ru_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ **2** (R = Me) showing the atom labelling scheme

that of the parent. However, as noted above, the ruthenium–ruthenium distance for $[Ru_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ is only marginally shorter (0.072 Å) than that for $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$. A structural feature which is common to both $[M_2(\eta\text{-}C_5R'_5)_2(CO)_4]$ and $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ is the presence of semi-bridging carbonyls. However, while all four carbonyl groups in the former adopt this mode of co-ordination, only two of the carbonyls in the latter are semi-bridging. Furthermore, those for $[M_2(\eta\text{-}C_5R'_5)_2(CO)_4]$ are linear[24–26] whereas, as described above, the semi-bridging carbonyls in **2** are bent. Not surprisingly, in view of the unusual nature of their linear semi-bridging carbonyl groups, the Group VI dimers, as well as the ditertiary phosphine-bridged dimanganese compound, $[Mn_2(CO)_5(\mu\text{-}Ph_2PCH_2PPh_2)_2]$,[9] also found to contain a



Scheme 2 (*i*) CO in toluene; (*ii*) $R'''NC$ ($R''' = C_6H_3Me_2$-2,6) in toluene; (*iii*) $[NO][SbF_6]$ in CH_2Cl_2; (*iv*) $R'C{\equiv}CH$ in toluene; (*v*) $R'C{\equiv}CR''$ ($R'' = R'$ or H) in toluene; (*vi*) S_8 in toluene; (*vii*) H_2S in toluene; (*viii*) O_2 or air in toluene. All reactions at r.t.

linear semi-bridging carbonyl,[10] have received considerable attention theoretically.[24,27-29] Early studies were interpreted in terms of the presence of these carbonyl groups being associated with these compounds being formally unsaturated and with the carbonyls functioning as four-electron donors.[24] Subsequent studies have established that linear semi-bridging carbonyls are in fact π acceptors and not π donors however,[27,28] while more recently it has been reported that the presence of these carbonyls is as a consequence of steric crowding and that their appearance signifies strong metal–metal bonding.[29] By extending this latter interpretation it is concluded that the ruthenium–ruthenium bond in $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ is weak and certainly does not have a formal bond order of two, consistent with the bond distance data. At the same time these diruthenium species are formally unsaturated in terms of the effective atomic number rule and certainly, on the basis of their intense purple colours, have low-lying lowest unoccupied molecular orbitals (LUMOs), but further theoretical studies are required before any real understanding of their electron distribution can be obtained. Significantly, Casey *et al.*[30] have recently reported the synthesis and structure of a related dirhenium tetracarbonyl species, *viz.* $[Re_2(\eta\text{-}C_5Me_5)_2(CO)_4]$, formally a decarbonylation product of $[Re_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)(CO)_4]$, and established that, similarly to the diruthenium compounds, it contains a complementary pair of semi-bridging carbonyls as well as two terminal carbonyls but, in contrast to the former, its rhenium–rhenium distance of 2.723(1) Å is appreciably shorter (0.234 Å) than that for $[Re_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)(CO)_4]$,[31] consistent with the presence of a double bond.

Reactivity of $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ ($R =$ Me *or* Pr^i).—As described above, $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **2** ($R =$ Me or Pr^i) are formally unsaturated and thus not surprisingly react readily, and in most cases spontaneously, with a wide range of small molecule electrophiles, nucleophiles and radical sources. Treatment of these species with carbon monoxide at room temperature, for instance, leads to the immediate formation of the parent pentacarbonyl species $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **1**[11] in quantitative yield. Likewise, reaction with 2,6-dimethylphenyl isocyanide, in toluene at room temperature, led to the rapid formation of the addition product $[Ru_2(\mu\text{-}CO)(CO)_3(CNC_6H_3Me_2\text{-}2,6)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **7** ($R =$ Me or Pr^i), see Scheme 2, in very high yield. The presence of a peak corresponding to a bridging carbonyl group in the infrared spectra of these compounds is indicative of the isonitrile having co-ordinated terminally, but whether it adopts an axial or an equatorial site cannot be established unequivocally. However, the band patterns of the terminal CO stretching peaks in these spectra are similar to those for compounds of the type $[Ru_2(\mu\text{-}X)X(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (X = Cl, Br or I) in which, as established by X-ray crystallography for $[Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$, the terminal halide co-ordinates axially.[14] A similar disposition is thus assumed for the isonitrile in **7**. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of $[Ru_2(\mu\text{-}CO)(CO)_3(CNC_6H_3Me_2\text{-}2,6)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ exhibits a sharp singlet at room temperature but an AA′BB′ pattern of peaks at −80 °C. On the other hand, a singlet is observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of $[Ru_2(\mu\text{-}CO)(CO)_3(CNC_6H_3Me_2\text{-}2,6)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ at both room and low (−80 °C) temperatures. These data are interpreted in terms of both compounds occurring as a single isomer in solution but being involved in some fluxional process, presumably an exchange of the carbonyl groups and the isonitrile ligand between the two ruthenium atoms.

The reaction of the isopropoxydiphosphazane-bridged derivative $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ with nitrosyl ions has also been investigated and shown readily to produce the nitrosyl-bridged product $[Ru_2(\mu\text{-}NO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ **8** (R = Pr^i) in high yield. The same species is also formed in the corresponding reaction involving $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ and will be reported separately.[17]

The compounds $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **2** (R = Me or Pr^i) also react readily with alkynes at room temperature affording vinylidene-bridged products of the type $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CHR')(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **9** (R = Me or Pr^i; R′ = H, Me, Ph or CO_2Me) and/or alkenediyl derivatives of formula $[Ru_2(\mu\text{-}\sigma^2\text{-}R'C{=}CR'')(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **10** (R = Me or Pr^i; R′ = H, Me or CO_2Me; R″ = H or CO_2Me), the nature and relative yields of the products being dependent on the alkyne and the bridging diphosphazane ligand. For instance, while the reaction of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ with phenylacetylene affords the phenylvinylidene derivative $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CHPh)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ as the sole product, the corresponding reaction involving the sterically less bulky ethyne affords the alkenediyl species $[Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CH)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ as well as the vinylidene derivative $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CH_2)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ although the former is only produced in low yield. On the other hand, the reaction of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ with the internal alkyne $MeO_2CC{\equiv}CCO_2Me$ gives solely the alkenediyl product $[Ru_2(\mu\text{-}\sigma^2\text{-}MeO_2CC{=}CCO_2Me)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. In contrast to that observed for the tetraisopropoxydiphosphazane-bridged unsaturated system, the reaction of $[Ru_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ with ethyne afforded the alkenediyl-bridged species $[Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CH)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ as the major product with the vinylidene-bridged compound $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CH_2)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ only being produced in low yield. The relative yields of the vinylidene- and alkenediyl-bridged isomers formed in the reactions of $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ with various alkynes are basically the same as those for related reactions involving the pentacarbonyl species $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **1**. However, while very mild conditions are required for those reactions in which $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ is the precursor, far more forcing conditions are required for the reactions involving $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$. The latter have been reported elsewhere[32] and thus further details of the products of the reactions of the tetracarbonyl species with various alkynes will not be given.

Treatment of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ with borohydride ions in acetone was found to lead to the slow formation of a neutral product characterized as the dihydridic species $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (see below). Although the latter may have been produced as a result of the abstraction of a proton from the solvent by the expected anionic product, $[Ru_2H(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^-$, its slow rate of formation is more indicative of it arising from the reaction of the unsaturated neutral tetracarbonyl species with slowly produced dihydrogen.

Significantly, $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ was observed to not only react with sulfur in toluene at room temperature but to do so spontaneously affording the sulfido-bridged product $[Ru_2(\mu\text{-}S)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **11** (R = Pr^i). This compound, which exhibits a singlet in its $^{31}P\text{-}\{^1H\}$ NMR spectrum and a pattern of peaks in the C–O stretching region of its IR spectrum typical of compounds of the type $[Ru_2(\mu\text{-}L)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$, has been synthesised previously by treatment of the solvento species $[Ru_2(CO)_5(Me_2CO)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^{2+}$ with H_2S followed by stepwise deprotonation of the hydrogen sulfide product $[Ru_2(CO)_5(H_2S)\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^{2+}$ with an appropriate base.[13] It was assumed that the reaction of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ with hydrogen sulfide at room temperature would also afford the sulfido-bridged compound $[Ru_2(\mu\text{-}S)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ but the product isolated from this reaction was characterized as $[Ru_2(\mu\text{-}SH)H(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **12** (R = Pr^i). An X-ray crystallographic determination on this compound revealed the presence of a bridging sulfur atom, but as a result of disorder the exact positions of the hydrogensulfido group and the carbonyl and hydrido ligands could not be established. However, the frequencies and the pattern of the peaks in the C–O stretching region in the IR spectrum are very similar to those for $[Ru_2(\mu\text{-}I)H(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ which is interpreted in terms of the former having a structure closely related to that of the latter; this species has been established crystallographically to adopt a structure in which the iodo group bridges the two ruthenium atoms, the hydrogen is co-ordinated terminally and one of the carbonyl groups is semi-bridging.[33] The room-temperature ^1H NMR spectrum of the thiolate-bridged compound exhibits a broad triplet at δ −10.03, assigned to a terminal hydride ligand, and a quintet at δ −1.67, assigned to the hydride of the bridging hydrogensulfido group, while its $^{31}P\text{-}\{^1H\}$ NMR spectrum, measured in $[^2H_8]$toluene, exhibits a broad resonance at δ 158.5 at room temperature and two overlapping sets of peaks at −32 °C, with the major set having an AA′BB′ pattern. This observation is interpreted in terms of this compound occurring in two isomeric forms in solution, with the two isomers rapidly interconverting at room temperature through a process which results in the phosphorus atoms being equivalent on the NMR time-scale.

Not surprisingly, in view of its reactivity towards sulfur, $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ also reacts spontaneously with oxygen affording, as well as $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **1** (R = Pr^i),* two other products on the basis of the spectroscopic data; two singlets (approximate ratio 1 : 2) at δ 135.4 and 135.9 (measured in C_6D_6), as well as the singlet assigned to **1** (R = Pr^i), were observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the reaction mixture indicative of these products having symmetrical geometries. Significantly, the same two species are formed on exposure of a solution of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ to air. A partial separation of these two hexane-soluble products was possible by fractional precipitation from methanol but attempts to isolate them in a pure state proved unsuccessful. The band patterns of the C–O stretching peaks in the IR spectra of both products are typical of those associated with compounds of the

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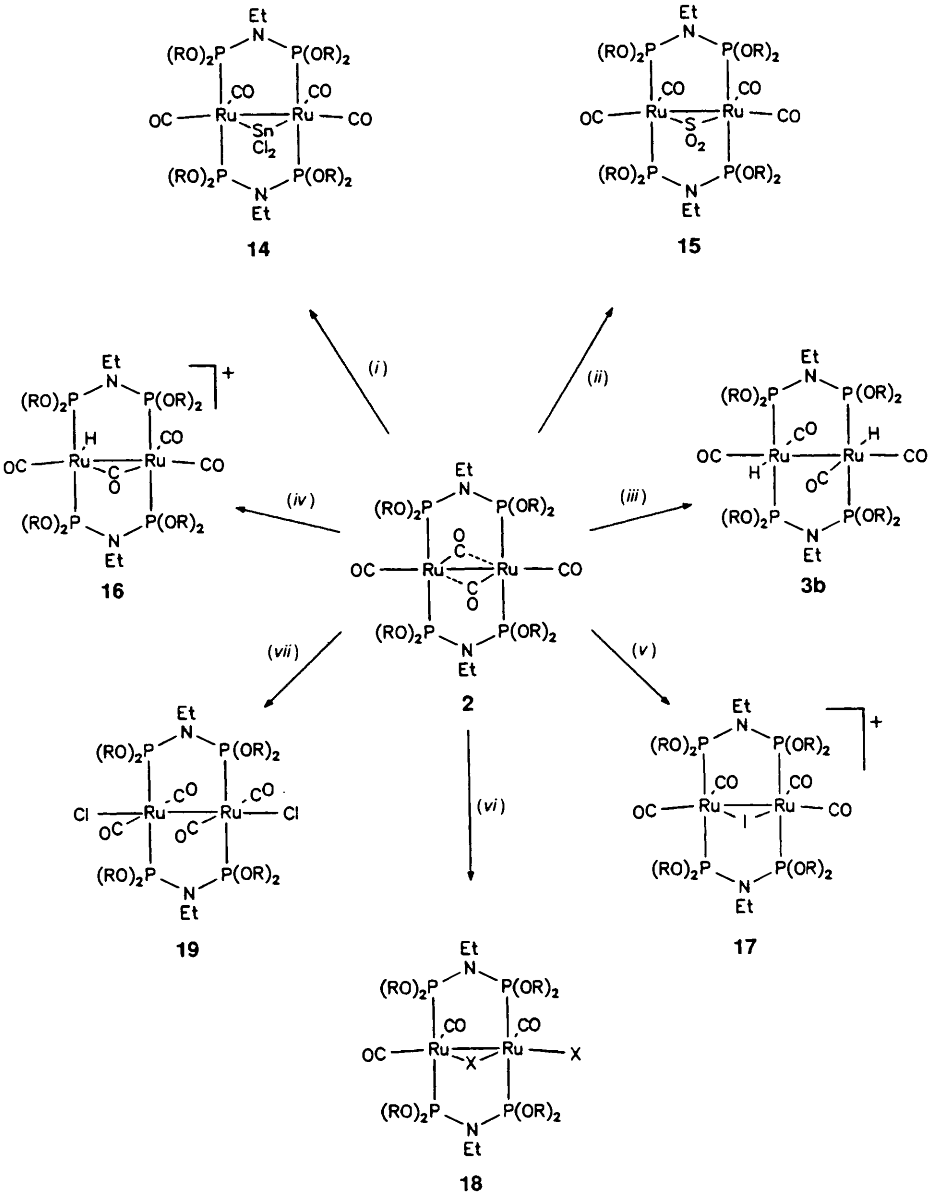
* The reaction is accompanied by some decomposition resulting in the release of carbon monoxide which is rapidly scavenged by $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **2** (R = Pr^i).

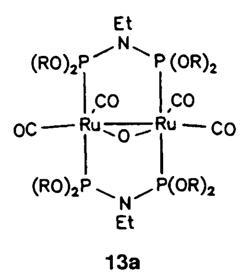


Scheme 3 (*i*) $SnCl_2$ in thf; (*ii*) SO_2 in toluene; (*iii*) H_2 in toluene; (*iv*) $HBF_4{\cdot}OEt_2$ in ether or aqueous HPF_6 in CH_2Cl_2; (*v*) I_2 in toluene; (*vi*) Br_2 in toluene or Cl_2 in CCl_4–toluene; (*vii*) CCl_4. All reactions at r.t.

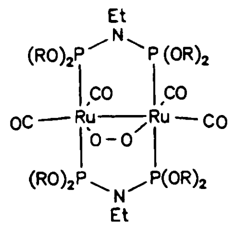
type $[Ru_2(\mu\text{-}L)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (L = bridging ligand) while the frequencies of the peaks are consistent with both compounds being neutral [ν(CO): 2010m, 1986s, 1957ms, 1929m; 1993s, 1958vs, 1925vs, 1904ms cm^{-1}; measured in hexane]. Possible formulations for these products are (R = Pr^i) $[Ru_2(\mu\text{-}O)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **13a**, $[Ru_2(\mu\text{-}\sigma^2\text{-}O_2)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **13b** and $[Ru_2(\mu\text{-}\sigma\text{-}O_2)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **13c**, although **13a** and **13b** appear the most likely, particularly **13a** on the basis of the identity of the product isolated from the reaction involving sulfur.

Tin(II) chloride and sulfur dioxide also reacted very readily with $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **2** (R = Me or Pr^i) at room temperature. In all of the reactions the substrate added across the two ruthenium atoms to afford the symmetrical chlorostannylene- and sulfur dioxide-bridged products $[Ru_2(\mu\text{-}\sigma\text{-}SnCl_2)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **14** and $[Ru_2(\mu\text{-}\sigma\text{-}SO_2)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **15** respectively, see Scheme 3.

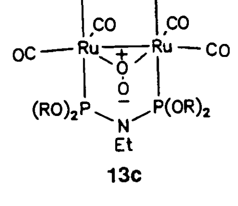
Passage of a stream of dihydrogen through a solution of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **2** (R = Pr^i) in tolu-



13a



13b



13c

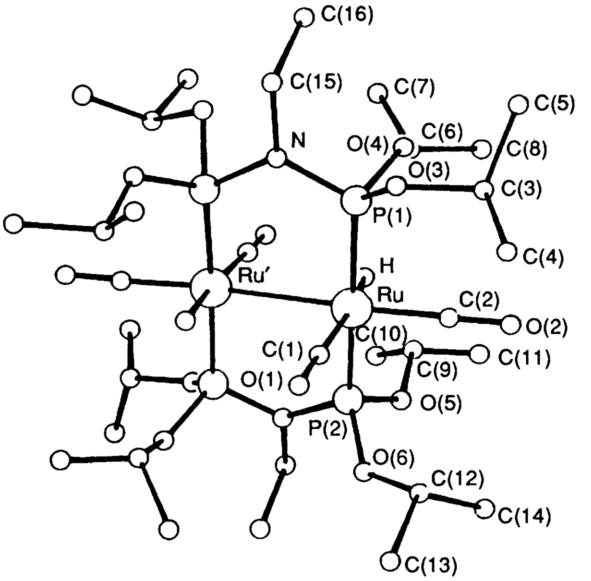


Fig. 3 Molecular structure of $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **3** (R = Pr^i) showing the atom labelling scheme

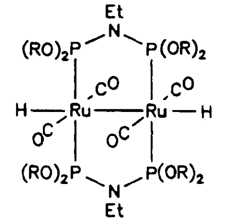
Table 6 Fractional coordinates (× 10^4) for $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru	−394(1)	−1224(1)	5252(1)
P(1)	1611(1)	141(1)	7203(1)
P(2)	−2115(1)	−2584(1)	3200(1)
N	2367(3)	1865(3)	7793(3)
O(1)	−2633(4)	−747(4)	6284(4)
O(2)	−830(4)	−3857(3)	5495(3)
O(3)	1243(3)	−52(3)	8387(2)
O(4)	3050(3)	−69(3)	7459(2)
O(5)	−1905(3)	−3805(2)	2428(2)
O(6)	−3913(3)	−3542(3)	2914(2)
C(1)	−1805(5)	−907(4)	5903(4)
C(2)	−645(5)	−2833(4)	5433(3)
C(3)	1035(6)	−1254(4)	8622(4)
C(4)	−517(7)	−1920(6)	8689(6)
C(5)	2360(8)	−748(7)	9843(5)
C(6)	3656(5)	−453(5)	6549(4)
C(7)	5263(8)	792(7)	6917(6)
C(8)	3711(9)	−1690(7)	6549(10)
C(9)	−449(6)	−3620(5)	2419(4)
C(10)	−264(10)	−3353(9)	1277(8)
C(11)	−545(11)	−4961(9)	2332(9)
C(12)	−4511(5)	−4334(4)	3586(4)
C(13)	−5970(6)	−4304(6)	3551(5)
C(14)	−4802(7)	−5789(5)	2977(5)
C(15)	3404(5)	2785(4)	9161(3)
C(16)	5045(6)	3031(5)	9546(5)
H	823(56)	−1366(48)	4553(43)

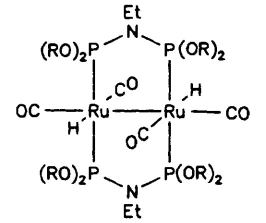
ene at room temperature led to the quantitative formation of the dihydrido species $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **3** (R = Pr^i). The synthesis of this orange compound is best achieved however by passage of a stream of dihydrogen through a solution of the pentacarbonyl species $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **1** (R = Pr^i) in toluene at 80 °C. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of this compound exhibits a single singlet corresponding to the diphosphazane phosphorus atoms, while the ^1H spectrum exhibits a well resolved quintet at δ −8.39 readily assigned to the two hydrido groups. These results are indicative of this compound occurring as a single isomer in solution and furthermore are consistent with the structure established by X-ray crystallography (see below) in which the two hydride ligands are coordinated terminally, have adopted equatorial positions and are *trans* disposed with respect to each other **3b** (R = Pr^i).

Table 7 Selected interatomic distances (Å) and angles (°) for $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$

Ru–P(1)	2.297(1)	Ru–P(2)	2.288(1)
Ru–C(1)	1.942(5)	Ru–C(2)	1.873(5)
Ru–H	1.72(6)	Ru–Ru′	2.911(1)
P(1)–Ru–P(2)	171.4(0)	P(1)–Ru–C(1)	91.4(1)
P(2)–Ru–C(1)	97.1(1)	P(1)–Ru–C(2)	90.7(1)
P(2)–Ru–C(2)	88.8(1)	C(1)–Ru–C(2)	102.4(2)
P(1)–Ru–H	91.9(13)	P(2)–Ru–H	79.5(13)
C(1)–Ru–H	172(2)	C(2)–Ru–H	85(2)
Ru′–Ru–P(1)	89.6(1)	Ru′–Ru–P(2)	89.3(1)
Ru′–Ru–H	84(2)	Ru′–Ru–C(2)	168.7(2)
Ru′–Ru–C(1)	88.7(2)		



3a



3b

Treatment of $[Ru_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ **2** (R = Me) with dihydrogen in toluene at room temperature likewise led to the formation of a dihydrido species, *viz*. $[Ru_2H_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$. The product in this case however afforded a $^{31}P\text{-}\{^1H\}$ NMR spectrum containing two singlets and a ^1H NMR spectrum containing two overlapping quintets at δ −8.50 and −8.69 respectively. These results are interpreted in terms of $[Ru_2H_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ occurring as both the equatorial, equatorial isomer **3b** (R = Me) and the axial, axial isomer **3a** (R = Me) in solution, with the concentration of one being approximately three times that of the other. The same isomeric mixture is produced on passage of dihydrogen through a solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ **1** (R = Me) in toluene at 80 °C.

The compound $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ is very susceptible to protic attack and treatment with $HBF_4\cdot OEt_2$ in diethyl ether or aqueous HPF_6 in CH_2Cl_2 led to the ready formation of orange, crystallizable products characterized as the protonated species $[Ru_2H(\mu\text{-}CO)(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]A$ **16** (R = Pr^i, A = BF_4 or PF_6). The solid-state and solution infrared spectra of the hexafluorophosphate salt $[Ru_2H(\mu\text{-}CO)(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$ exhibited similar band patterns in the terminal carbonyl stretching region which in turn were similar to that for $[Ru_2(\mu\text{-}I)I(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ while, furthermore, both exhibited a peak (1757 cm^{-1}, measured in CH_2Cl_2) which can be readily assigned to the stretching vibration of a bridging carbonyl group. The room-temperature ^1H NMR spectrum of this species exhibits a well resolved quintet at δ −9.69, readily assigned to the hydride ligand, while its $^{31}P\text{-}\{^1H\}$ NMR spectrum, measured in $(CD_3)_2CO$ at −80 °C, contains a symmetrical set of resonances of AA′BB′ pattern and centred at δ 142.0. These results are interpreted in terms of this cationic species having a structure based on that established by X-ray crystallography for the parent tetramethoxydiphosphazane-bridged pentacarbonyl derivative, $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ **1** (R = Me),[11] with either an axial or an equatorial carbonyl group having been replaced by an H^+ ion, **16a** or **16b**.

Not surprisingly, $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ is very susceptible to electrophilic attack by halogens to afford, in the presence of a suitable counter ion such as PF_6^-, the cationic iodo-bridged tetracarbonyl derivative $[Ru_2(\mu\text{-}I)(CO)_4\text{-}$

$\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$ **17** (R = Pr^i) in the case of iodine and the neutral dihalogeno-tricarbonyl $[Ru_2(\mu\text{-}X)X(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **18** (R = Pr^i, X = Cl or Br) in the case of chlorine and bromine. These compounds have been synthesised previously by treatment of the pentacarbonyl precursor $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **1** (R = Pr^i) with halogens under appropriate conditions.[14]

Dissolution of $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **2** (R = Me or Pr^i) in redistilled carbon tetrachloride resulted in the immediate formation of yellow solutions from which two products, identified by means of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy as the dichlorotetracarbonyl species $[Ru_2Cl_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **19** and the dichlorotricarbonyl derivatives $[Ru_2(\mu\text{-}Cl)Cl(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **18** (X = Cl) respectively, could be isolated. For R = Pr^i the tetracarbonyl derivative was shown to be the major product, while for R = Me the tricarbonyl species was the major product. These compounds have been synthesised previously with the tetracarbonyl derivatives having been obtained by an analogous process involving the pentacarbonyl derivatives $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ **1** and shown to contain the chloro groups in axial positions.[34]

The reactions of $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) with the substrates described above are summarized in Schemes 2 and 3.

Crystal Structure of $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$.—The molecular structure of the dihydrido species $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **3** (R = Pr^i) has been determined by X-ray crystallography and is illustrated in Fig. 3. This species has again retained the Ru_2P_4 skeletal framework of the parent compound with *trans* disposition of the bridging diphosphazane ligands but each ruthenium atom is now essentially octahedral while the ruthenium–ruthenium distance of 2.911(1) Å is appreciably longer than that for $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ [2.801(2) Å]. The positions of the hydrogen atoms were located and found to be separated from the ruthenium atoms by a distance of 1.72(6) Å which is slightly longer than that for a typical terminal Ru–H bond.[35] The salient feature of the structure is the terminal mode of co-ordination of the hydrogen atoms which contrasts with that observed for most other dinuclear metal hydride compounds where the hydrogen tends to adopt the bridging co-ordination mode as found for instance in $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)]$[6] and $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$.[36] Furthermore, the hydrogen atoms occupy equatorial sites on each ruthenium atom, being *trans* disposed with respect to each other, which contrasts with the chloro groups in $[Ru_2Cl_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ which, as described above, are co-ordinated at the axial positions.[34]

Reactivity of $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$.—As described above, a method of synthesis of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **2** (R = Pr^i) involves the reductive elimination of dihydrogen from $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ by passage of argon through a solution of the dihydride in toluene at 80–90 °C. In fact, the mere application of a vacuum to a solution of $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ in toluene at room temperature is sufficient to enable this elimination to proceed. The dihydride is thus, not surprisingly, highly reactive and behaves overall as a source of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **2** (R = Pr^i). Thus, on treatment with carbon monoxide, it affords $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **1** (R = Pr^i) in quantitative yield while on reaction with the alkynes $R'C{\equiv}CR''$ (R' = H, R'' = H; R' = Ph, R'' = H; R' = $MeCO_2$, R'' = H or $MeCO_2$) it affords the same products *viz.* the vinylidene-bridged species $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CHR')(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **9** (R = Pr^i) and/or the alkenediyl-bridged derivatives $[Ru_2(\mu\text{-}\sigma^2\text{-}R'C{=}CR'')(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **10** (R = Pr^i) in the same relative yields as does the unsaturated tetracarbonyl $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. Likewise, its reaction with protons to produce $[Ru_2H(\mu\text{-}CO)(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ **16** (R = Pr^i) parallels the protonation behaviour of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. No evidence has been obtained thus far for the hydride ligands in $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ to be involved in migratory insertion reactions (no reaction occurred with CS_2 for instance) but minor products in the reaction of the dihydride with iodine arise from hydride-ligand substitution. Thus while the reaction of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ with iodine produces solely the iodo-bridged species $[Ru_2(\mu\text{-}I)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ (see above), the corresponding reaction involving $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ affords, in low yield, the neutral diiodide $[Ru_2I_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ and a neutral species identified as $[Ru_2H(I)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ as well as $[Ru_2(\mu\text{-}I)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ as the major product. The compound $[Ru_2I_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ has been reported previously as the product of the reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ with iodine in the presence of trimethylamine *N*-oxide.[14]

Experimental

The neutral pentacarbonyls $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) were synthesised according to a literature method.[11] All reactions and manipulations were carried out under an atmosphere of argon by Schlenk techniques. Solvents were purified and dried using standard literature procedures and were degassed prior to use. Infrared spectra were measured on a Perkin Elmer 457 spectrometer, $^{31}P\text{-}\{^1H\}$ NMR spectra on a Varian FT 80A instrument, $^{13}C\text{-}\{^1H\}$ and ^1H NMR spectra on a Varian Gemini 200 spectrometer. Spectroscopic data are summarized in Table 1.

Syntheses.—$[Ru_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$. A solution of $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(O)\}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$[13] (0.20 g, 0.26 mmol) in toluene (3 cm^3) was evaporated to dryness at room temperature and the residue warmed at 30 °C under reduced pressure for 1 h. The purple-blue solid was dissolved in toluene (2 cm^3) and the solution kept at −20 °C for 6 h to afford crystals of the required compound. Yield: 60% (Found: C, 24.5; H, 4.2; N, 3.7. $C_{16}H_{34}N_2O_{12}P_4Ru_2$ requires C, 24.9; H, 4.4; N, 3.6%).

$[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. (*i*) A stream of argon was passed slowly through a solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.25 g, 0.24 mmol) or $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.25 g, 0.25 mmol) or $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(O)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$[13] (0.25 g, 0.24 mmol) in toluene (*ca.* 15 cm^3) at 80 °C for 45 min. The volume of the purple solution was concentrated under reduced pressure to *ca.* 3 cm^3 and crystallization of the product as purple-black rectangular blocks was achieved by keeping this solution at −20 °C for 15 h. Yield: 80–90%.

(*ii*) Solid $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.25 g, 0.25 mmol) or $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(O)\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.25 g, 0.24 mmol) was heated *in vacuo* at 80 °C for 6 h. The purple solid was crystallized from toluene at −20 °C. Yield: 60–70% (Found: C, 38.9; H, 6.8; N, 2.9. $C_{32}H_{66}N_2O_{12}P_4Ru_2$ requires C, 38.6; H, 6.8; N, 2.8%).

$[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. (*i*) A stream of dihydrogen was passed slowly through a solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.25 g, 0.24 mmol) in toluene (5 cm^3) at 80 °C for 1 h. The yellow solution was cooled to room temperature under a flow of dihydrogen and was concentrated under reduced pressure to *ca.* 3 cm^3. Crystallization of the required compound as yellow-orange rectangular blocks was effected by keeping this solution at −20 °C for 15 h. Yield: 90%.

(*ii*) A stream of dihydrogen was passed through a solution of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.20 g, 0.20 mmol) in toluene (2 cm^3) at room temperature for 1 min. Crystallization was effected by keeping this solution at −20 °C for 15 h. Yield: 90% (Found: C, 39.0; H, 6.8; N, 2.6. $C_{32}H_{68}N_2O_{12}P_4Ru_2$ requires C, 38.5; H, 6.9; N, 2.8%).

$[Ru_2(\mu\text{-}CO)(CO)_3(CNC_6H_3Me_2\text{-}2,6)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me *or* Pr^i). (*i*) A slight excess of 2,6-dimethylphenyl isocyanide (0.02 g, 0.15 mmol) was added to a solution of $[Ru_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (0.10 g, 0.13 mmol) or $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.13 g, 0.13 mmol) in toluene (5 cm^3) at room temperature resulting in a change in colour from purple to orange. The solution was concentrated under reduced pressure to *ca.* 1 cm^3 and hexane was added to effect the separation of the required compound in crystalline form. Yield: 80–85%.

(*ii*) A solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (0.32 g, 0.40 mmol) and 2,6-dimethylphenyl isocyanide (0.055 g, 0.42 mmol) in diethyl ether (*ca.* 25 cm^3) was refluxed for 12 h. Hexane (*ca.* 30 cm^3) was added to the resultant yellow-green solution and the volume reduced under vacuum until it was saturated. This solution was kept at −10 °C to effect crystallization of the required compound. Yield: 50% (Found: C, 33.2; H, 4.8; N, 4.7. $C_{25}H_{43}N_3O_{12}P_4Ru_2$ requires C, 33.2; H, 4.8; N, 4.7. Found: C, 42.3; H, 6.8; N, 3.4. $C_{41}H_{75}N_3O_{12}P_4Ru_2$ requires C, 43.6; H, 6.7; N, 3.7%).

$[Ru_2(\mu\text{-}SO_2)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. (*i*) A stream of sulfur dioxide was passed slowly through a solution of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.20 g, 0.20 mmol) in toluene (3 cm^3) at room temperature for 1 min to effect a rapid change in the colour from purple to yellow. Hexane was added to the solution resulting in the separation of the required compound in crystalline form. Yield: 90%.

(*ii*) A solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.31 g, 0.30 mmol) in diethyl ether (60 cm^3) at room temperature was saturated with sulfur dioxide. The colour changed to dark yellow and after 90 min to pale yellow. The volume was reduced to 25 cm^3 and hexane (25 cm^3) added. Continued slow evaporation of this solution led to the separation of the required compound as yellow crystals. Yield: 95% (Found: C, 36.4; H, 6.6; N, 2.7. $C_{32}H_{66}N_2O_{14}P_4Ru_2S$ requires C, 36.2; H, 6.2; N, 2.6%).

$[Ru_2(\mu\text{-}SnCl_2)(CO)_4\{\mu\text{-}MeO)_2PN(Et)P(OMe)_2\}_2]$. A slight excess of tin(II) chloride (0.11 g, 0.60 mmol) was added to a solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (0.40 g, 0.50 mmol) in tetrahydrofuran (thf) (*ca.* 40 cm^3) at room temperature and the solution stirred for 2 h. All volatiles were removed under reduced pressure and the yellow-brown residue was extracted with dichloromethane (30 cm^3). The extract was filtered, the filtrate evaporated to dryness and the residue crystallized from acetone–diethyl ether. Yield: 48% (Found: C, 20.0; H, 3.5; N, 3.6. $C_{16}H_{34}Cl_2N_2O_{12}P_4Ru_2Sn$ requires C, 20.0; H, 3.5; N, 2.9%).

$[Ru_2(\mu\text{-}SnCl_2)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. A slight excess of $SnCl_2$ (0.03 g, 0.15 mmol) was added to a solution of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.10 g, 0.10 mmol) in thf (10 cm^3) at room temperature and the solution stirred for 10 min. The solvent was removed under reduced pressure and the yellow-orange residue extracted with dichloromethane (10 cm^3). The extract was filtered, the filtrate concentrated under reduced pressure and hexane added to effect crystallization of the product. Yield: 60%. The product was identified as $[Ru_2(\mu\text{-}SnCl_2)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ by means of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.

$[Ru_2(\mu\text{-}S)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. An excess of sulfur (0.10 g) was added to a solution of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.20 g, 0.20 mmol) in toluene (5 cm^3) at room temperature resulting in an immediate change in colour from purple to orange. The solvent was removed under reduced pressure and the residue extracted with hexane (3 × 5 cm^3). The combined extracts were evaporated to dryness and the resultant orange solid crystallized from ethanol. Yield: 80% (Found: C, 38.1; H, 4.4; N, 2.7. $C_{32}H_{66}N_2O_{12}P_4Ru_2S$ requires C, 37.4; H, 4.4; N, 2.7%).

$[Ru_2(\mu\text{-}SH)H(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. A stream of hydrogen sulfide was passed slowly through a solution of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.20 g, 0.20 mmol) in toluene (5 cm^3) at room temperature for 5 s and the solution allowed to stand for up to 3 d. The solvent was removed under reduced pressure to afford a yellow residue which was crystallized from ethanol. Yield 85% (Found: C, 37.3; H, 6.8; N, 2.9. $C_{31}H_{68}N_2O_{11}P_4Ru_2S$ requires C, 37.2; H, 6.8; N, 2.9%).

$[Ru_2H(\mu\text{-}CO)(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]A$ (A = BF_4 *or* PF_6). (*i*) A solution of an excess of $HBF_4{\cdot}OEt_2$ (0.20 cm^3, 54% solution in diethyl ether) in diethyl ether (3 cm^3) was added dropwise to a stirred solution of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.25 g, 0.25 mmol) in ether (20 cm^3) at room temperature. The colour turned orange and an orange microcrystalline solid separated. This was isolated, washed with ether–pentane and crystallized from acetone–ether to afford orange crystals of the required compound (A = BF_4). Yield: 70% (Found: C, 34.6; H, 6.5; N, 2.2. $C_{32}H_{67}BF_4N_2O_{12}P_4Ru_2$ requires C, 35.4; H, 6.2; N, 2.6%).

(*ii*) An excess of HPF_6 (0.3 cm^3, 60%) in water (3 cm^3) was added to a stirred solution of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.25 g, 0.25 mmol) in CH_2Cl_2 (3 cm^3) at room temperature and the resultant two-phase mixture stirred vigorously for 2 h. The organic layer was separated from the aqueous layer, evaporated to dryness and the residue crystallized from acetone–water to afford orange crystals of the required compound (A = PF_6). Yield: 75% (Found: C, 34.1; H, 5.5; N, 2.1. $C_{32}H_{67}F_6N_2O_{12}P_5Ru_2$ requires C, 33.6; H, 5.9; N, 2.5%).

Reactions.—$[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me *or* Pr^i) *with carbon monoxide.* A stream of carbon monoxide was passed slowly through a solution of $[Ru_2(CO)_4\{\mu\text{-}MeO)_2PN(Et)P(OMe)_2\}_2]$ (0.10 g, 0.13 mmol) or $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.10 g, 0.10 mmol) in toluene (5 cm^3) resulting in an immediate colour change from purple to yellow. The solvent was removed under reduced pressure and the residue extracted and crystallized from hexane. The crystalline product was identified as $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ or $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ by means of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.[11] Yield: 90%.

$[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ *with nitrosyl ions.* Solid $[NO][SbF_6]$ (0.035 g, 0.13 mmol) was added to a stirred solution of a slight molar excess of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.137 g, 0.15 mmol) in dichloromethane (20 cm^3) and the solution stirred for 15 min to ensure complete dissolution of the $[NO][SbF_6]$. The solvent was removed under reduced pressure and the residue identified as $[Ru_2(\mu\text{-}NO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2][SbF_6]$ by means of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.[17]

$[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me *or* Pr^i) *with carbon tetrachloride.* Solid $[Ru_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (0.10 g, 0.13 mmol) or $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.13 g, 0.13 mmol) was dissolved in freshly distilled carbon tetrachloride (5 cm^3) resulting in a yellow solution. The solvent was removed under reduced pressure to afford a yellow residue which was identified spectroscopically (IR and $^{31}P\text{-}\{^1H\}$ NMR) as a mixture of the two neutral complexes $[Ru_2Cl_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ and $[Ru_2(\mu\text{-}Cl)Cl(CO)_3\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$.[14,34] For R = Pr^i the tetracarbonyl derivative is the major product while for R = Me the tricarbonyl species is the major product.

$[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ *with chlorine and bromine.* A twice molar amount of bromine (0.60 g, 0.40 mmol) in toluene (5 cm^3) or chlorine (10 drops of a CCl_4 saturated solution) in carbon tetrachloride (5 cm^3) was added dropwise to a stirred solution of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$

(0.20 g, 0.20 mmol) in toluene (5 cm^3) and the solution stirred for 1 h. The solvent was removed under reduced pressure and the residue crystallized from hexane. The crystalline products were identified as $[Ru_2(\mu\text{-}Br)Br(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ and $[Ru_2(\mu\text{-}Cl)Cl(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ respectively by means of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.[14] Yield: 60–70%.

$[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ *with iodine.* A twice molar amount of iodine (0.10 g, 0.40 mmol) in toluene (5 cm^3) was added dropwise to a stirred solution of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.20 g, 0.20 mmol) in toluene (5 cm^3) and the solution stirred for 1 h. The product which separated was washed with hexane, dissolved in acetone (10 cm^3) and a solution of NH_4PF_6 (0.08 g, 0.50 mmol) in acetone (5 cm^3) added. Addition of water (15 cm^3) followed by the removal of the acetone under reduced pressure resulted in the separation of a product which was crystallized from acetone–ether and identified spectroscopically (IR and $^{31}P\text{-}\{^1H\}$ NMR) as $[Ru_2(\mu\text{-}I)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$.[14] Yield: 90%.

$[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2]$ (*a*) *with carbon monoxide.* A stream of carbon monoxide was passed slowly through a solution of $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.10 g, 0.10 mmol) in toluene (5 cm^3) for 5 min. The solvent was removed under reduced pressure and the residue identified as $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ by means of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.[11]

(*b*) *With acetylene.* A stream of acetylene was passed slowly through a solution of $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.10 g, 0.10 mmol) in toluene (10 cm^3) for 5 min. The solvent was removed under reduced pressure and the residue identified as being a mixture of the vinylidene derivative $[Ru_2(\mu\text{-}\sigma\text{-}CH{=}CH_2)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (95%) and of the alkenediyl species $[Ru_2(\mu\text{-}\sigma^2\text{-}CH{=}CH)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (5%) by means of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.[32]

(*c*) *With phenylacetylene and methyl acetylenecarboxylate.* A solution of the terminal acetylene (RC≡CH) phenylacetylene (R = Ph) (0.01 g, 0.10 mmol) or methylacetylenecarboxylate (R = $MeCO_2$) (0.01 g, 0.12 mmol) in toluene (1 cm^3) was added dropwise to a stirred solution of $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.10 g, 0.10 mmol) in toluene (5 cm^3) and the solution stirred for 10 min. The solvent was removed under reduced pressure and the residue identified as being a mixture of the vinylidene compound $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CHR)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (R = Ph, 100; R = $MeCO_2$, 25%) and of the alkenediyl isomer $[Ru_2(\mu\text{-}\sigma^2\text{-}CH{=}CR)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (R = Ph, 0; R = $MeCO_2$, 75%) by means of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.[32]

(*d*) *With dimethylacetylenedicarboxylate.* A solution of the internal alkyne (RC≡CR) dimethyl acetylenedicarboxylate (R = CO_2Me) (0.02 g, 0.14 mmol) in toluene (2 cm^3) was added dropwise to a stirred solution of $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.10 g, 0.10 mmol) in toluene (5 cm^3) and the solution stirred for 30 min. The volume was reduced *in vacuo* (to *ca.* 1 cm^3) and methanol was added to effect crystallization of the product, which was identified by means of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.[32]

(*e*) *Protonation.* A solution of an excess of $HBF_4{\cdot}OEt_2$ (0.10 cm^3, 54% solution in ether) in ether (3 cm^3) was added dropwise to a stirred solution of $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.10 g, 0.10 mmol) in ether (10 cm^3) at room temperature. The product which separated from solution was identified as $[Ru_2H(\mu\text{-}CO)(CO)_3\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]BF_4$ by means of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.

(*f*) *With iodine.* A solution of an equimolar amount of iodine (0.025 g, 0.10 mmol) in toluene (5 cm^3) was added dropwise to a stirred solution of $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (0.10 g, 0.10 mmol) in toluene (5 cm^3) and the solution stirred for 30 min. The solution was filtered and the orange microcrystalline precipitate washed with several aliquots of toluene (4 × 2 cm^3) and dried. The washings were combined with the filtrate and the toluene removed under reduced pressure to afford an orange residue. The original precipitate (major product) was identified as an iodide salt of the cation $[Ru_2(\mu\text{-}I)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ while the residue from the filtrate was established to be a mixture of $[Ru_2H(I)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ and $[Ru_2I_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ by means of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.[14]

Crystal Structure Determinations.—Crystal data for $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. $C_{32}H_{66}N_2O_{12}P_4Ru_2$, $M = 997.0$, purple-black crystals of dimensions 0.69 × 0.46 × 0.27 mm, grown from toluene, monoclinic, space group $P2_1/n$, $a = 17.535(6)$, $b = 9.926(4)$, $c = 13.257(6)$ Å, $\beta = 95.54(3)°$, $U = 2296.5$ Å^3, $Z = 2$, $D_c = 1.44$ g cm^{-3}, μ(Mo-Kα) = 8.45 cm^{-1}, $F(000) = 1032$.

Intensity data were collected on a Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ 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 $3 \leqslant \theta \leqslant 23°$ 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 a decrease in intensity of 17% on completion of the intensity data collection; the data were corrected accordingly. Empirical absorption corrections were made using the ψ-scan method. Of the 2993 unique reflections measured, 2593 were classed as observed $[I > 3\sigma(I)]$ and used for the solution and refinement of the structure.

The ruthenium and phosphorus atoms were located using the direct methods routine of the program SHELX 76.[37] Subsequent Fourier syntheses gave the positions of the remaining non-hydrogen atoms. The H atoms were not located. All the non-H atoms were assigned anisotropic thermal parameters. A final refinement (SHELX 76) using the weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$ converged at final R and R' values of 0.066 and 0.069 respectively (235 parameters; maximum shift/e.s.d. = 0.085). A final Fourier difference map showed two peaks of electron density of *ca.* 2 e Å^{-3} within 1 Å of the Ru atom but was otherwise featureless. Fractional atomic coordinates are listed in Table 2 and selected interatomic distances and angles in Table 3.

Crystal data for $[Ru_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$. $C_{16}H_{34}N_2O_{12}P_4Ru_2$, $M = 772.5$, red crystal of dimensions 0.38 × 0.18 × 0.15 mm, triclinic, space group $P\bar{1}$, $a = 8.069(2)$, $b = 9.405(3)$, $c = 10.941(2)$ Å, $\alpha = 115.16(2)$, $\beta = 92.75(2)$, $\gamma = 101.61(2)°$, $U = 727.65$ Å^3, $Z = 1$, $D_c = 1.76$ g cm^{-3}, μ(Mo-Kα) = 12.50 cm^{-1}, $F(000) = 516$.

The experimental conditions for the intensity data collection were the same as those described above. Of the 1946 unique reflections measured, 1860 were classed as observed $[I > 3\sigma(I)]$ and these were used for the solution and refinement of the structure.

The ruthenium and phosphorus atoms were located from a Patterson map using the program SHELX 86[38] while the positions of the remaining non-H atoms were obtained from successive Fourier syntheses. The H atoms were not located. The non-H atoms were all assigned anisotropic thermal parameters. A final refinement (SHELX 76) with the same weighting scheme as above gave final R and R' values of 0.031 and 0.038 respectively (163 parameters; maximum shift/e.s.d. = 0.217). A final Fourier difference map was featureless with a maximum electron density of 0.5 e Å^{-3}. Fractional atomic coordinates are listed in Table 4, selected interatomic distances and angles in Table 5.

Crystal data for $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. $C_{32}H_{68}N_2O_{12}P_4Ru_2$, $M = 999.0$, yellow crystal of dimensions 0.38 × 0.23 × 0.13 mm, triclinic, space group $P\bar{1}$, $a = 10.432(1)$, $b = 11.730(2)$, $c = 12.075(2)$ Å, $\alpha = 105.72(1)$,

$\beta = 103.65(1)$, $\gamma = 115.11(1)°$, $U = 1178.7$ Å^3, $Z = 1$, $D_c = 1.46$ g cm^{-3}, μ(Mo-Kα) = 8.30 cm^{-1}, $F(000) = 518$.

The experimental conditions for the intensity data collection were the same as those described above. Of the 3216 unique reflections measured, 3081 were classed as observed $[I > 3\sigma(I)]$ and these were used for the solution and refinement of the structure.

The ruthenium atoms were located from a Patterson map using the program SHELX 86 while the positions of the remaining non-H atoms were obtained from successive Fourier syntheses. The position of the hydrogen atom bonded to the ruthenium atom was located and assigned an isotropic thermal parameter while the ruthenium, phosphorus, oxygen, nitrogen and carbon atoms were all assigned anisotropic thermal parameters. A final refinement (SHELX 76) using the same weighting scheme as above gave final R and R' values of 0.036 and 0.044 respectively (240 parameters; maximum shift/e.s.d. = 0.331). A final Fourier difference map was featureless with a maximum electron density of 0.2 e Å^{-3}. Fractional atomic coordinates are listed in Table 6, selected interatomic distances and angles in Table 7.

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

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