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Synthesis and reactivity of the formally co-ordinatively unsaturated diruthenium hydride $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3\{\mu\text{-}(Pr^iO)_2PNEtP(OPr^i)_2\}_2]^+$ and its co-ordinatively saturated parent $[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PNEtP(OPr^i)_2\}_2]^+$

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Protonation of the co-ordinatively unsaturated species $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-}etipdp)_2]$ [sb = semi-bridging, etipdp = $(Pr^iO)_2PNEtP(OPr^i)_2$] by acids of non-co-ordinating conjugate bases, *e.g.* $HBF_4{\cdot}OEt_2$, produced $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]^+$ which, as established X-ray crystallographically for the PF_6^- salt, contains both a bridging carbonyl and a bridging hydride ligand. This cationic species is very susceptible to attack by both neutral and anionic nucleophiles affording a range of product types. For instance, its reactions with anions X^- which are capable of functioning as monodentate bridging ligands and which preferentially adopt the *closed* bridging co-ordination mode, *e.g.* halide and hydrogensulfide ions, afforded products of the type $[Ru_2(\mu\text{-}X)H(\mu_{sb}\text{-}CO)(CO)_2(\mu\text{-}etipdp)_2]$ (X = Cl, Br, I, SH, *etc.*), resulting from the substitution of a carbonyl group by the nucleophile. On the other hand, anionic nucleophiles such as H^- and CN^- gave addition products of the type $[Ru_2HX(CO)_4(\mu\text{-}etipdp)_2]$ (X = H, CN, *etc.*) in which the hydride and the X^- ligand occupy equatorial sites *trans* disposed with respect to each other, as established in a separate study for $[Ru_2H_2(CO)_4(\mu\text{-}etipdp)_2]$. Carbon monoxide also afforded a simple addition product, *viz.* $[Ru_2H(CO)_5(\mu\text{-}etipdp)_2]^+$, but the majority of the other neutral nucleophiles studied, particularly the unsaturated systems, yielded products resulting from formal insertion of the nucleophile into the Ru–H bond. Thus sulfur produced $[Ru_2(\mu\text{-}SH)(CO)_4(\mu\text{-}etipdp)_2]^+$, while unsaturated nucleophiles of general formula $X'{\equiv}Y'$, *e.g.* $PhC{\equiv}N$ and $RC{\equiv}CH$ (R = H, Ph, *etc.*), gave products of the type $[Ru_2\{\mu\text{-}X'Y'(H)\}(CO)_4(\mu\text{-}etipdp)_2]^+$, *e.g.* $[Ru_2\{\mu\text{-}NC(H)Ph\}(CO)_4(\mu\text{-}etipdp)_2]^+$ or of the type $[Ru_2\{\mu\text{-}\eta^2\text{-}X'Y'(H)\}(CO)_4(\mu\text{-}etipdp)_2]^+$, *e.g.* $[Ru_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CHCHR)(CO)_4(\mu\text{-}etipdp)_2]^+$. Heterocumulenes $X''{=}Y''{=}Z''$ such as CS_2 and PhNCS behaved similarly affording products of general formula $[Ru_2\{\mu\text{-}\eta^2\text{-}X''Y''(H)Z''\}(CO)_4(\mu\text{-}etipdp)_2]^+$ containing five-membered $RuX''Y''Z''Ru$ rings. The co-ordinatively saturated pentacarbonyl $[Ru_2H(CO)_5(\mu\text{-}etipdp)_2]PF_6$ gave products similar to those afforded by $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]PF_6$ on reaction with systems of the type $X'{\equiv}Y'$ and $X''{=}Y''{=}Z''$ except that, for terminal alkynes such as $PhC{\equiv}CH$, alkenylcarbonyl-bridged products, *e.g.* $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(CH{=}CHPh)\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$, are produced. The crystal structures of the following compounds were determined: $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]PF_6$, $[Ru_2(\mu\text{-}I)H(\mu_{sb}\text{-}CO)(CO)_2(\mu\text{-}etipdp)_2]$, $[Ru_2\{\mu\text{-}N(CHPh)\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$, $[Ru_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CHCH_2)(CO)_4(\mu\text{-}etipdp)_2]PF_6$, $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(CHCHPh)\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$ and $[Ru_2\{\mu\text{-}\eta^2\text{-}SC(H)NPh\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$.

The mechanism of activation of small molecule compounds by di- and poly-nuclear transition-metal complexes continues to be a focus of attention in organometallic chemistry. A major aim of studies which form part of this focus is the synthesis of complexes which will function as models for the chemisorption of small molecule compounds on metal surfaces and/or which will themselves function as homogeneous catalysts for, in particular, those reactions which are not catalysed by mononuclear complexes.[1] Homogeneous catalytic processes must involve at least one reaction intermediate which is co-ordinatively unsaturated and thus a prime objective in the design of 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 the substrate molecules with direct access to one or more metal atoms.[2] Also, as well as being potential homogeneous catalysts, these systems are valuable as potential precursors for the synthesis of generally inaccessible products.

In contrast to that for mononuclear systems, the range of known co-ordinatively unsaturated metal complexes of nuclearity two and above is fairly limited. Low-valent unsaturated dinuclear carbonyl, cyclopentadienyl carbonyl and diphosphorus ligand-bridged carbonyl derivatives that have reported and studied 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] $[M_2(cp)_2(\mu_{sb}\text{-}CO)_4]$ (M = Cr, Mo or W; cp = $\eta^5\text{-}C_5H_5$ or $\text{-}C_5Me_5$, sb = semi-bridging),[5–12] $[Re_2(\eta^5\text{-}C_5Me_5)_2(\mu_{sb}\text{-}CO)_2(CO)_2]$,[13] $[Mn_2(\mu\text{-}H)_2(CO)_6\{\mu\text{-}(EtO)_2POP(OEt)_2\}]$,[14,15] $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}dppm)]$ (dppm = $Ph_2PCH_2PPh_2$),[15–18] $[Mn_2(CO)_6(\mu\text{-}dppm)]^{2-}$ (ref. 19) and $[Mn_2(\mu\text{-}H)_2(CO)_4(\mu\text{-}dppm)_2]$.[20]

We have established previously that $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2]$ (R = Me **1a** or Pr^i **1b**), substituted derivatives of diruthenium nonacarbonyl, can be decarbonylated under various reaction conditions to the corresponding tetracarbonyl derivatives $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2]$ (R = Me **2a** or Pr^i **2b**).[21] These unsaturated electron-rich species are highly reactive and react spontaneously with a wide range of nucleophilic as well as electrophilic reagents to afford, in the case of protonation, the dinuclear hydrides $[Ru_2H(\mu\text{-}CO)(CO)_3\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2]^+$.[21] The latter are also co-ordinatively unsaturated and thus, not surprisingly, are equally reactive, again reacting with a range of nucleophilic and electrophilic reagents. The results of the study

Table 1 Selected interatomic distances (Å) and angles (°) for the complex $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]PF_6$ **3**

Ru(1)–Ru(2)	2.816(1)	Ru(1)–P(1)	2.346(1)
Ru(1)–P(2)	2.349(1)	Ru(1)–C(1)	1.935(6)
Ru(1)–C(2)	1.899(5)	Ru(1)–C(3)	2.158(5)
Ru(1)–H(1)	1.81(4)	Ru(2)–P(3)	2.325(1)
Ru(2)–P(4)	2.313(1)	Ru(2)–C(3)	1.954(5)
Ru(2)–C(4)	1.854(6)	Ru(2)–H(1)	1.76(4)
P(1)–Ru(1)–P(2)	177.7(1)	P(1)–Ru(1)–C(1)	92.0(2)
P(1)–Ru(1)–C(2)	89.2(2)	P(1)–Ru(1)–C(3)	90.4(1)
P(1)–Ru(1)–H(1)	92(2)	P(2)–Ru(1)–C(1)	89.2(2)
P(2)–Ru(1)–C(2)	88.8(2)	P(2)–Ru(1)–C(3)	88.9(1)
P(2)–Ru(1)–H(1)	90(2)	C(1)–Ru(1)–C(2)	94.3(2)
C(1)–Ru(1)–C(3)	165.9(2)	C(1)–Ru(1)–H(1)	85(2)
C(2)–Ru(1)–C(3)	99.7(2)	C(2)–Ru(1)–H(1)	179(2)
C(3)–Ru(1)–H(1)	81(2)	P(3)–Ru(2)–P(4)	169.9(1)
P(3)–Ru(2)–C(3)	96.5(1)	P(3)–Ru(2)–C(4)	90.9(2)
P(3)–Ru(2)–H(1)	85(2)	C(3)–Ru(2)–C(4)	102.4(3)
C(3)–Ru(2)–H(1)	89(2)	C(4)–Ru(2)–H(1)	169(2)

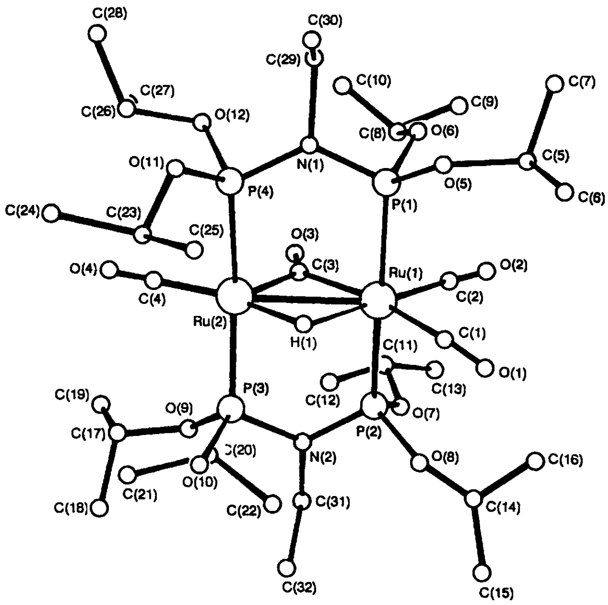
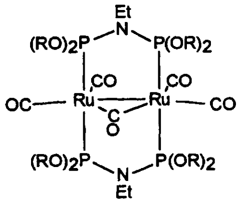
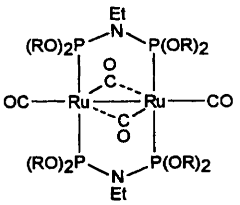


Fig. 1 Structure of the cation in $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]PF_6$ **3** showing the atom labelling scheme



R	
1a	Me
1b	Pr^i



R	
2a	Me
2b	Pr^i

of the reactivity of the tetraisopropoxy diphosphazane-bridged species $[Ru_2H(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]PF_6$ [etipdp = $(Pr^iO)_2PNEtP(OPr^i)_2$] towards various neutral and anionic nucleophiles as well as that of the saturated pentacarbonyl $[Ru_2H(CO)_5(\mu\text{-}etipdp)_2]PF_6$ towards unsaturated systems of the type X′≡Y′ and X″=Y″=Z″ are reported here; because of the difficulty in synthesising $[Ru_2H(\mu\text{-}CO)(CO)_3(\mu\text{-}etmdp)_2]PF_6$ [etmdp = $(MeO)_2PNEtP(OMe)_2$] in a pure state in high yields its reactivity towards various nucleophiles was not investigated in any detail. Some of the results have been communicated previously.[22,23]

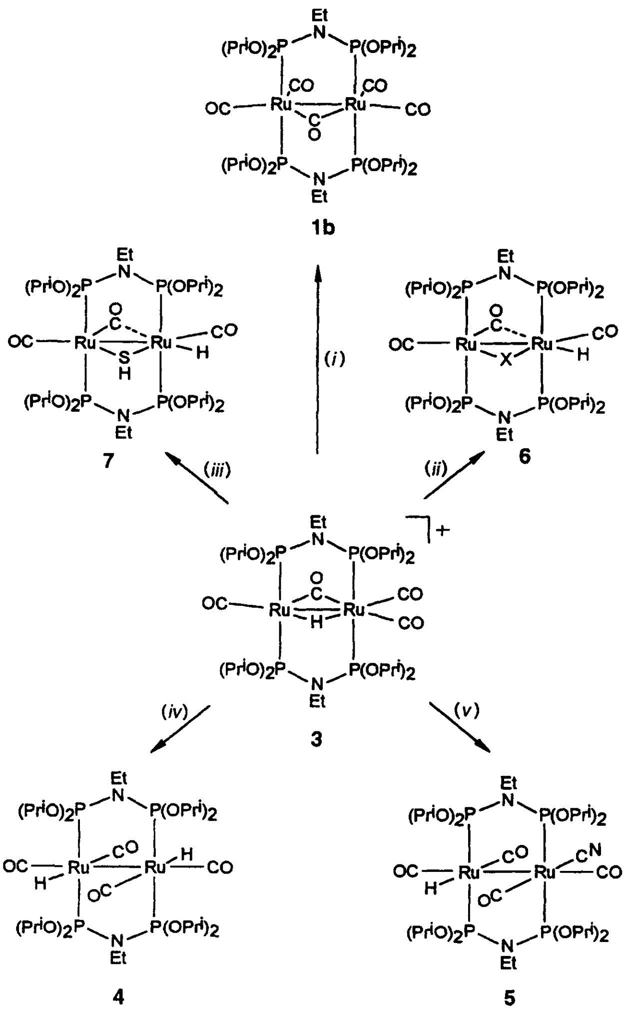
Results and Discussion

Synthesis and structure of $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]PF_6$

As reported previously,[21] treatment of the formally co-ordinatively unsaturated compound $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-}etipdp)_2]$ **2b** with $HBF_4{\cdot}OEt_2$ or aqueous HPF_6 leads to the formation of the dinuclear cationic hydride $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]^+$ **3**, isolated as either the BF_4^- or PF_6^- salt, and which, according to its IR spectral data, contains a bridging as well as terminal carbonyl groups [ν(C–O): 2059s, 2006s, 1956s (br) and 1757ms cm^{-1}, measured in CH_2Cl_2]. The presence of a quintet of chemical shift δ −9.69 in the ^1H NMR spectrum of this species was initially interpreted in terms of the presence of a terminal hydride ligand and the cation adopting a structure analogous to that of the parent pentacarbonyl **1b**.[21] However, this chemical shift may also be interpreted in terms of the hydride adopting a bridging co-ordination mode and, as a consequence, the crystal structure of the PF_6^- salt was determined.

The stereochemistry of compound **3** is illustrated in Fig. 1; selected interatomic distances and angles are listed in Table 1. The two ruthenium atoms, separated by a distance of 2.816(1) Å, are linked, not only by two bridging diphosphazane ligands and a bridging carbonyl group, but by a bridging hydride ligand as well; the hydrogen was reliably located in a difference electron-density map and its position refined. The co-ordination about each ruthenium atom is completed by two terminal carbonyl groups on Ru(1) and a single terminal carbonyl on Ru(2). As shown Ru(1) adopts an approximate octahedral geometry with the angles subtended by the ligands at the metal atom ranging from 81(2) [C(3)–Ru(1)–H] through 90.4(1) [P(1)–Ru(1)–C(3)] to 99.7(2)° [C(2)–Ru(1)–C(3)]. On the other hand Ru(2) adopts an approximate square-pyramidal geometry with C(3) occupying the apical position [C(3)–Ru(2)–H 89(2), C(3)–Ru(2)–P(4) 93(2), C(3)–Ru(2)–C(4) 102.4(3), C(3)–Ru(2)–P(3) 96.5(1)°] and P(4), C(4), P(3) and H occupying the basal positions [P(3)–Ru(2)–P(4) 169.9(1), C(4)–Ru(2)–H 169(2), P(4)–Ru(2)–C(4) 89.9(3), C(4)–Ru(2)–P(3) 90.9(2), P(3)–Ru(2)–H 85(2), P(4)–Ru(2)–H 92(2)°]. This difference in stereochemistry for the two ruthenium atoms can be interpreted in terms of Ru(1) having a formal oxidation state of +2 and of Ru(2) one of zero. In this context it is worth noting that distances associated with Ru(2) are without exception less than the corresponding distances for Ru(1). For instance the distances for Ru(2)–P(3) and Ru(2)–P(4) are 2.325(1) and 2.313(1) Å respectively, whereas those for Ru(1)–P(1) and Ru(1)–P(2) are 2.346(1) and 2.349(1) Å, respectively. Also the carbon of the bridging carbonyl is substantially closer to Ru(2) [Ru(2)–C(3) 1.954(5) Å] than to Ru(1) [Ru(1)–C(3) 2.158(5) Å]. The ruthenium–ruthenium distance of 2.816(1) Å corresponds to a formal bond. However, molecular orbital calculations on the formally co-ordinatively unsaturated species $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and $[M_2(\mu\text{-}H)_2(CO)_8]^{n-}$ (n = 2, M = Cr, Mo or W; n = 0, M = Mn or Re), all of which have been postulated to contain a metal–metal double bond, have indicated small or practically non-existent direct metal–metal bonding with the interaction occurring through the hydrogen bridges.[24,25] It is assumed that a similar situation holds for the cation **3** and that the bonding between the two ruthenium atoms is best explained in terms of *closed* Ru–H–Ru and Ru–C(O)–Ru bridge bonding. The cation is essentially eclipsed as evidenced by the P(1)–Ru(1)–Ru(2)–P(4) and P(2)–Ru(1)–Ru(2)–P(3) torsion angles of 1.9 and 9.4° respectively. A consequence thereof is that the four carbonyl groups and the hydride ligand are basically coplanar, with the projected distances of C(4), Ru(2), H, C(3), Ru(1), C(1) and C(2) from their least-squares plane being 0.015, 0.032, 0.005, 0.017, 0.017, 0.017 and 0.005 Å respectively.

The $^{31}P\text{-}\{^1H\}$ NMR spectra of both the PF_6^- and BF_4^- salts



Scheme 1 Reaction of $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]^+$ with various anionic nucleophiles: (*i*) $Li(C{\equiv}CH)\cdot H_2NC_2H_4NH_2$ or $Li(C{\equiv}CPh)$ in acetone at −15 °C; (*ii*) X^- in acetone at room temperature (r.t.) (X = Cl, Br or I); (*iii*) SH^- in methanol added to **3** in acetone at r.t.; (*iv*) $NaBH_4$ in acetone at r.t.; (*v*) CN^- in acetone at r.t.

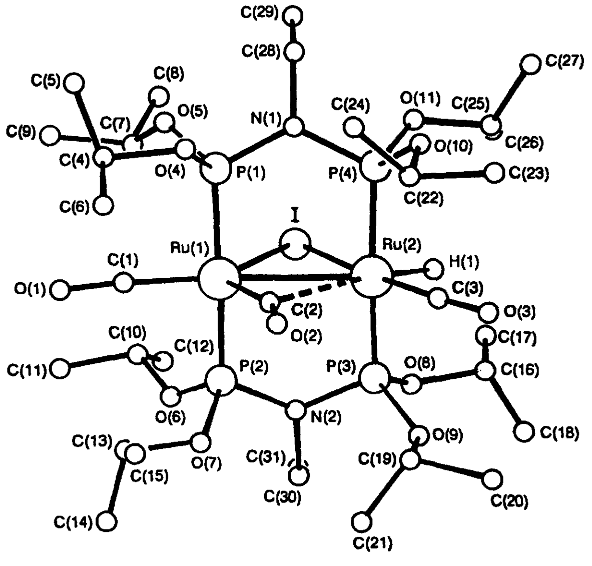


Fig. 2 Molecular structure of $[Ru_2(\mu\text{-}I)H(\mu_{sb}\text{-}CO)(CO)_2(\mu\text{-}etipdp)_2]$ **6** showing the atom labelling scheme

of compound **3**, measured in $(CD_3)_2CO$ at −80 °C, exhibit a symmetrical set of resonances of AA′BB′ pattern, centred at δ 142.0, as predicted for the structure established crystallographically. However, the corresponding room-temperature spectra contain a broad singlet at δ 138.9. This is interpreted in terms of **3** being involved in some fluxional process, as established previously for $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2]^+$ [26]

Reactivity of $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]PF_6$ towards various nucleophiles

Being cationic and formally co-ordinatively unsaturated, compound **3**, is, not unexpectedly, very susceptible to attack by anionic nucleophiles. Thus treatment with $NaBH_4$ in acetone at room temperature was shown to lead to the ready formation of the known dihydride, $[Ru_2H_2(CO)_4(\mu\text{-}etipdp)_2]$ **4**, previously synthesized by reaction of $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-}etipdp)_2]$ with H_2.[21] As established X-ray crystallographically,[21] the two hydride ligands in this complex adopt equatorial positions, essentially *trans* disposed with respect to each other.

A product related to **4** and characterised as the neutral cyanohydride $[Ru_2H(CN)(CO)_4(\mu\text{-}etipdp)_2]$ **5** was obtained by reaction of **3** with NaCN in CH_2Cl_2 at room temperature. Attempts to produce single crystals of this species, suitable for a crystal structure determination, were not successful but the structure of the compound could nevertheless be ascertained from the spectroscopic data. In particular the $^{31}P\text{-}\{^1H\}$ NMR spectrum, measured in C_6D_6 at room temperature, exhibited an AA′BB′ pattern of peaks, indicative of an asymmetric structure, while the ^1H NMR spectrum revealed a quintet at δ −7.58, more readily assigned to a terminal rather than a bridging hydride ligand. The IR spectrum in the C–O stretching region contained peaks corresponding to terminal carbonyls only. These data are consistent with the structure shown in Scheme 1; the sites of co-ordination of the hydride and cyanide ligands could not be established unequivocally but they are presumed to occupy equatorial positions *trans* disposed with respect to each other on the basis that these are the co-ordination sites occupied by the hydride ligands in **4** (see above).

Halide ions also react spontaneously with compound **3** in solution at room temperature but significantly the products formed were found to result from carbonyl substitution rather than from simple addition and were characterised as $[Ru_2(\mu\text{-}X)H(\mu_{sb}\text{-}CO)(\mu\text{-}CO)_2(\mu\text{-}etipdp)_2]$ **6** (X = Cl, Br or I). The $^{31}P\text{-}\{^1H\}$ NMR spectra of these compounds were found to contain single AA′BB′ patterns while their ^1H NMR spectra each contained a triplet corresponding to the hydride ligand, of chemical shift more readily assigned to a bridging rather than a terminal hydride. Three peaks of distinctive band pattern were observed in the C–O stretching region of their IR spectra. These results could be interpreted in terms of a structure based on that of the parent cation **3** in which the bridging carbonyl has been replaced by a bridging halide ligand. Alternatively the structure could be based on that of $[Ru_2(\mu\text{-}X)(CO)_4(\mu\text{-}etipdp)_2]^+$ (X = Cl, Br or I)[26] with the hydride occupying a site of one of the terminal carbonyls.

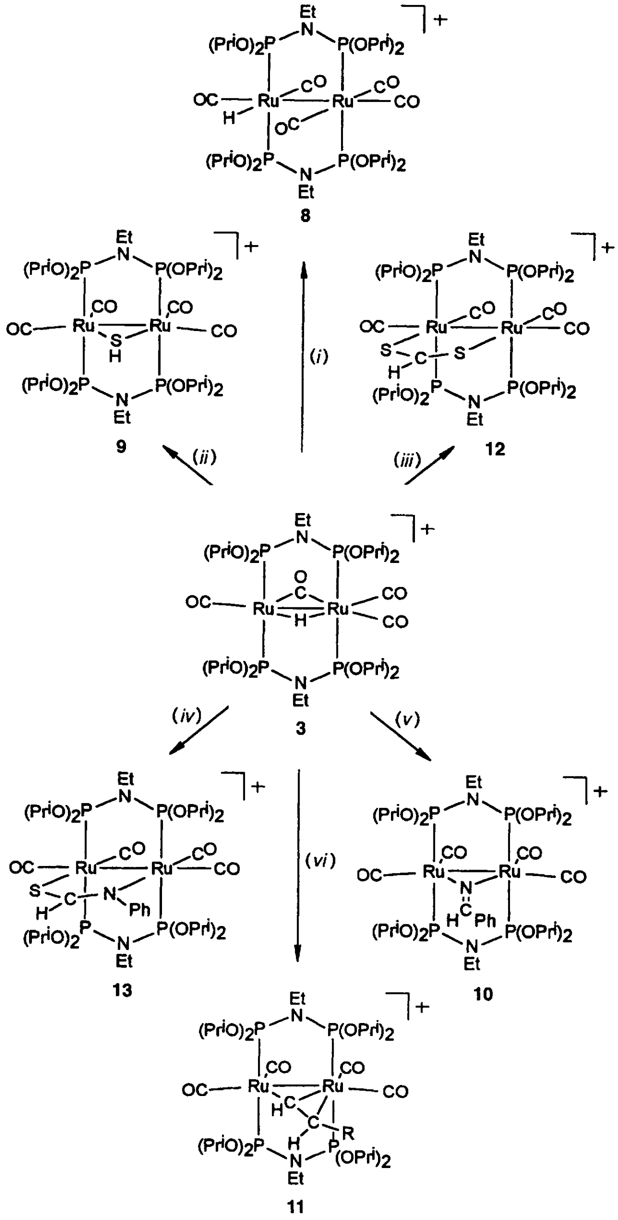
With the object of establishing unequivocally the structure of these species the crystal structure of $[Ru_2(\mu\text{-}I)H(\mu_{sb}\text{-}CO)(CO)_2(\mu\text{-}etipdp)_2]$ **6** (X = I) was determined. The stereochemistry of the complex is illustrated in Fig. 2; selected interatomic distances and angles are given in Table 2. As well as being bridged by two diphosphazane ligands, *trans* disposed with respect to each other, the two ruthenium atoms are linked through an essentially symmetrically disposed bridging iodide [Ru(1)–I 2.795(1), Ru(2)–I 2.754(1) Å]. One of the carbonyl groups bonded to the Ru(1) atom is, to a first approximation, collinear with the ruthenium–ruthenium vector, whereas the other functions as a semi-bridging carbonyl to Ru(2) [Ru(1)–C(2) 1.92(2), Ru(2)–C(2) 2.53(2) Å]. The hydride ligand, the position of which was reliably located, was shown to co-ordinate terminally which contrasts with what is observed for the hydride ligand in the parent cation **3**, as discussed above. Similar to that for the situation in **3**, the two ruthenium atoms in **6** (X = I) adopt different local geometries. Thus, while Ru(1) is

Table 2 Selected interatomic distances (Å) and angles (°) for the complex $[Ru_2(\mu\text{-I})H(CO)_3(\mu\text{-etipdp})_2]$ **6**

Ru(1)–I	2.795(1)	Ru(2)–I	2.754(1)
Ru(1)–Ru(2)	2.821(1)	Ru(1)–P(1)	2.318(3)
Ru(1)–P(2)	2.317(4)	Ru(1)–C(1)	1.84(2)
Ru(1)–C(2)	1.92(2)	Ru(2)–P(3)	2.306(3)
Ru(2)–P(4)	2.308(4)	Ru(2)–C(2)	2.53(2)
Ru(2)–C(3)	1.77(2)	Ru(2)–H(1)	1.40(8)
I–Ru(1)–P(1)	89.1(1)	I–Ru(1)–P(2)	89.7(1)
I–Ru(1)–C(1)	130.2(5)	I–Ru(1)–C(2)	119.9(4)
P(1)–Ru(1)–P(2)	176.6(1)	P(1)–Ru(1)–C(1)	89.0(4)
P(1)–Ru(1)–C(2)	92.0(3)	P(2)–Ru(1)–C(1)	89.4(4)
P(2)–Ru(1)–C(2)	91.4(3)	C(1)–Ru(1)–C(2)	109.9(6)
I–Ru(2)–P(3)	88.0(1)	I–Ru(2)–P(4)	88.9(1)
I–Ru(2)–C(2)	101.7(3)	I–Ru(2)–C(3)	170.8(4)
I–Ru(2)–H(1)	86(3)	P(3)–Ru(2)–P(4)	174.1(1)
P(3)–Ru(2)–C(2)	93.8(3)	P(3)–Ru(2)–C(3)	90.2(4)
P(3)–Ru(2)–H(1)	84(3)	P(4)–Ru(2)–C(2)	91.8(3)
P(4)–Ru(2)–C(3)	92.1(4)	P(4)–Ru(2)–H(1)	91(3)
C(2)–Ru(2)–C(3)	87.4(5)	C(2)–Ru(2)–H(1)	172(3)
C(3)–Ru(2)–H(1)	85(3)		

essentially trigonal bipyramidal with the iodine, the carbon of the semi-bridging carbonyl and the carbon of the terminal carbonyl adopting the equatorial positions [I–Ru(1)–C(1) 130.2(5), I–Ru(1)–C(2) 119.9(4), C(1)–Ru(1)–C(2) 109.9(6)°], Ru(2) is essentially square pyramidal or octahedral if the carbon of the bridging carbonyl is accepted as a sixth site with the hydrogen occupying the apical position for the square-pyramidal geometry. The ruthenium–ruthenium distance of 2.821(1) Å is again consistent with a formal Ru–Ru bond but as for **3** the bonding between the two ruthenium atoms is undoubtedly more appropriately explained in terms of *closed* Ru–I–Ru bridge bonding. As for **3**, the compound adopts an almost eclipsed configuration with the P(1)–Ru(1)–Ru(2)–P(4) and P(2)–Ru(1)–Ru(2)–P(3) torsion angles being 0.1 and 2.6° respectively. The molecular geometry of **6** (X = I) is similar to those reported for $[Ru_2(\mu\text{-I})I(CO)_3(\mu\text{-etipdp})_2]$[27] and $[Ru_2(\mu\text{-I})I(CO)_3(\mu\text{-dppm})_2]$[28] although a close examination of the three structures reveals that that adopted by $[Ru_2(\mu\text{-I})I(CO)_3(\mu\text{-etipdp})_2]$ is in effect a 'frozen' transition state in the transformation of the structure as adopted by $[Ru_2(\mu\text{-I})(CO)_4(\mu\text{-etipdp})_2]^+$ (ref. 27) to that as exhibited by **6**.

Addition of an equimolar amount of NaSH to a solution of compound **3** was found to result in the formation of a product characterised as $[Ru_2(\mu\text{-SH})H(\mu_{sb}\text{-CO})(CO)_2(\mu\text{-etipdp})_2]$ **7** with a structure analogous to that of **6** on the basis of its spectroscopic data and, in particular, the band pattern of the C–O stretching peaks in its IR spectrum being almost identical to that found for **6**. This hydrogensulfido-bridged derivative has been synthesised previously by reaction of $[Ru_2(\mu_{sb}\text{-CO})_2(CO)_2(\mu\text{-etipdp})_2]$ with H_2S.[21] Significantly, while the room-temperature $^{31}P\text{-}\{^1H\}$ NMR spectrum of this species, measured in $[^2H_8]$toluene, exhibits a broad singlet at δ 158.8, the corresponding spectrum measured at −32 °C exhibits two overlapping sets of peaks with one set having a definite AA'BB' pattern. This observation is interpreted in terms of this compound existing in two isomeric forms in solution with the two isomers rapidly interconverting at room temperature by a process which results in the phosphorus atoms being equivalent on the NMR timescale. Treatment of **3** with the acetylide anions $HC{\equiv}C^-$ and $PhC{\equiv}C^-$ led, on the other hand, to the formation of the neutral parent complex $[Ru_2(\mu\text{-CO})(CO)_4(\mu\text{-etipdp})_2]$ **1b**[29] as the only identifiable product, the alkynes $HC{\equiv}CH$ and $PhC{\equiv}CH$ presumably being eliminated and a CO being scavenged during the elimination process.



Scheme 2 Reaction of $[Ru_2(\mu\text{-H})(\mu\text{-CO})(CO)_3(\mu\text{-etipdp})_2]^+$ with various neutral nucleophiles: (*i*) CO in acetone at r.t.; (*ii*) S_8 in toluene added to **3** in acetone at r.t.; (*iii*) CS_2 in acetone at r.t.; (*iv*) PhNCS in acetone at r.t.; (*v*) PhCN in acetone at r.t.; (*vi*) $RC{\equiv}CH$ (R = H or Ph) in CH_2Cl_2 or acetone at r.t.

The compound $[Ru_2(\mu\text{-H})(\mu\text{-CO})(CO)_3(\mu\text{-etipdp})_2]PF_6$ is also highly reactive towards neutral nucleophiles. For instance passage of carbon monoxide through a solution of this species leads (Scheme 2) to the immediate formation of $[Ru_2H(CO)_5(\mu\text{-etipdp})_2]PF_6$, also obtained directly by protonation of **1b** with aqueous HPF_6.[26] Significantly sulfur also reacts spontaneously with **3** at room temperature to give the hydrogensulfido-bridged cationic product $[Ru_2(\mu\text{-SH})(CO)_4(\mu\text{-etipdp})_2]PF_6$ **9**, previously synthesised by deprotonation of $[Ru_2(CO)_5(H_2S)(\mu\text{-etipdp})_2][PF_6]_2$ or by protonation of $[Ru_2(\mu\text{-S})(CO)_4(\mu\text{-etipdp})_2]$ with HPF_6.[30] The IR spectrum of this species exhibits a distinctive pattern of peaks in the C–O stretching region typical of cationic species of the type $[Ru_2(\mu\text{-A})(CO)_4(\mu\text{-etipdp})_2]^+$ while its ^1H NMR spectrum contains a quintet at δ 0.63 corresponding to the hydrogen of the hydrogensulfido group. Significantly the $^{31}P\text{-}\{^1H\}$ NMR spectrum revealed an AA'BB' pattern of peaks which is explained in terms of the hydrogen of the hydrogensulfido group being outside of the plane defined by the sulfur and the two ruthenium atoms.

Not surprisingly compound **3** is very susceptible to attack by unsaturated neutral nucleophiles and, in particular, by those of

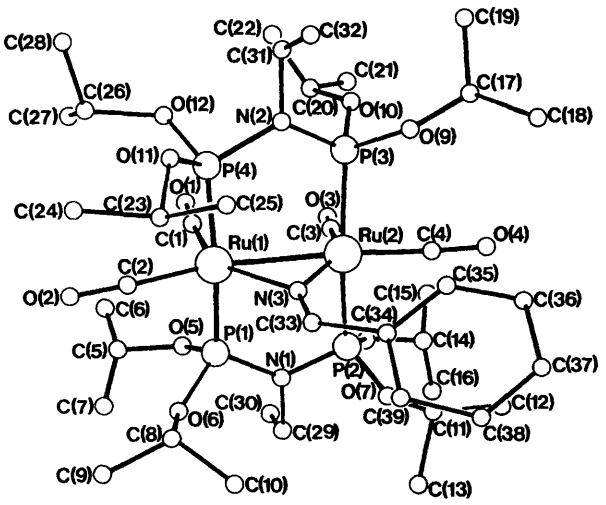


Fig. 3 Structure of the cation in $[Ru_2\{\mu\text{-}N(CHPh)\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$ **10** showing the atom labelling scheme

Table 3 Selected interatomic distances (Å) and angles (°) for the complex $[Ru_2\{\mu\text{-}N(CHPh)\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$ **10**

Ru(1)–Ru(2)	2.716(1)	Ru(1)–P(1)	2.334(1)
Ru(1)–P(4)	2.328(1)	Ru(1)–N(3)	2.097(4)
Ru(1)–C(1)	1.884(6)	Ru(1)–C(2)	1.903(5)
Ru(2)–P(2)	2.344(1)	Ru(2)–P(3)	2.349(1)
Ru(2)–N(3)	2.091(3)	Ru(2)–C(3)	1.903(5)
Ru(2)–C(4)	1.891(6)	N(3)–C(33)	1.272(6)
C(33)–C(34)	1.468(8)		
P(1)–Ru(1)–P(4)	175.7(1)	P(1)–Ru(1)–N(3)	95.3(1)
P(1)–Ru(1)–C(1)	89.1(2)	P(1)–Ru(1)–C(2)	88.6(1)
P(4)–Ru(1)–N(3)	87.7(1)	P(4)–Ru(1)–C(1)	90.2(2)
P(4)–Ru(1)–C(2)	87.3(1)	N(3)–Ru(1)–C(1)	143.7(2)
N(3)–Ru(1)–C(2)	116.1(2)	C(1)–Ru(1)–C(2)	100.0(2)
P(2)–Ru(2)–P(3)	176.3(1)	P(2)–Ru(2)–N(3)	93.0(1)
P(3)–Ru(2)–N(3)	93.0(1)	P(3)–Ru(2)–C(3)	92.1(2)
P(3)–Ru(2)–C(4)	88.7(2)	P(2)–Ru(2)–C(4)	88.7(2)
P(2)–Ru(2)–C(3)	86.2(2)	N(3)–Ru(2)–C(4)	114.8(2)
N(3)–Ru(2)–C(3)	148.4(2)	C(3)–Ru(2)–C(4)	96.5(3)

type X≡Y. Thus addition of an equimolar amount of benzonitrile to a solution of the compound results in an immediate colour change and the formation of a product characterised as $[Ru_2\{\mu\text{-}N(CHPh)\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$ **10**. The structure of this species has been established by X-ray crystallography and is illustrated in Fig. 3; selected interatomic distances and angles are listed in Table 3. The cation adopts a configuration more eclipsed than staggered [P(4)–Ru(1)–Ru(2)–P(3) 9.1, P(1)–Ru(1)–Ru(2)–P(2) 8.3°] with the two ruthenium atoms, separated by a distance of 2.716(1) Å, corresponding to a formal ruthenium–ruthenium bond, being bridged by an azavinylidene group as well as by two diphosphazane ligands; the N(3)–C(33) distance of 1.272(6) Å, corresponding to a nitrogen–carbon double bond, the N(3)–C(33)–C(34) angle of 128.1(7)° and the essential coplanarity of Ru(1), Ru(2), N(3), C(33) and C(34) [projected distances of C(33) and C(34) from the plane defined by Ru(1), Ru(2) and N(3) are 0.001 and 0.017 Å respectively] provided confirmatory evidence of the N(CHPh) group functioning as an azavinylidene ligand. The group co-ordinates solely through the nitrogen atom giving rise to a three-membered dimetallaheterocyclic ring and is produced as a result of the formal insertion of the benzonitrile into the ruthenium–hydrogen bond. A related trinuclear compound $[Ru_3\{\mu\text{-}N(CHPh)\}(CO)_{10}]$ has been synthesized previously by treatment of $[Ru_3(CO)_{12}]$ with benzonitrile in the presence of acetic acid[31] or by reaction of $[Ru_3(CO)_{12}]$ with PhCN in ligroin at 130 °C under an atmosphere of hydrogen.[32]

The alkynes, ethyne and phenylethyne, the latter being isoelectronic with benzonitrile, were also found to react readily with compound **3** in solution at room temperature. In the case of ethyne the product was characterised crystallographically as well as by conventional methods as $[Ru_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CHCH_2)(CO)_4(\mu\text{-}etipdp)_2]PF_6$ **11** (R = H) containing a bridging vinyl group. The stereochemistry of the cation is illustrated in Fig. 4; selected interatomic distances and angles are listed in Table 4. In contrast to **10**, the cation adopts a configuration that is more staggered than eclipsed as reflected by the P(1)–Ru(1)–Ru(2)–P(4) and P(2)–Ru(1)–Ru(2)–P(3) torsion angles of 11.3 and 16.2° respectively. The α-carbon of the vinyl group is nearly symmetrically disposed with respect to the two ruthenium atoms [Ru(1)–C(33) 2.098(8), Ru(2)–C(33) 2.267(8) Å] whereas the β-carbon has only one ruthenium atom within bonding distance [Ru(2)–C(34) 2.32(1), Ru(1)–C(34) 3.16(1) Å]. Furthermore the latter carbon lies well outside of the plane defined by the two ruthenium atoms and C(33), the dihedral angle between this plane and that defined by Ru(2), C(33) and C(34) being 45.4°. Two of the carbonyls are almost collinear with the Ru–Ru vector [Ru(2)–Ru(1)–C(1) 161.6(3), Ru(1)–Ru(2)–C(3) 174.5(3)°] whereas the other two are almost orthogonal to it [C(2)–Ru(1)–Ru(2) 101.0(3), C(4)–Ru(2)–Ru(1) 82.7(3)°]. The ruthenium–ruthenium distance of 2.802(1) Å corresponds to a formal metal–metal bond. The geometry of the bridging vinyl group in this compound is very similar to that adopted by the bridging vinyl groups in $[M_2(cp)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CHCH_2)(\mu\text{-}CO)(CO)_2]BF_4$ (M = Fe or Ru, cp = $\eta^5\text{-}C_5H_5$).[33,34] The $^{31}P\text{-}\{^1H\}$ NMR spectrum of this complex contains an ABCD pattern of peaks which is consistent with the structure established for the solid state while the $^{13}C\text{-}\{^1H\}$ NMR spectrum exhibits a triplet at δ 158.7 corresponding to the methyne carbon and a broad triplet at δ 68.2 corresponding to the methylene carbon, these assignments being based on a distortionless enhancements of polarisation transfer (DEPT) analysis; a multiplet centred at δ 8.10 associated with the hydrogen of the α-carbon and multiplets at δ 5.02 and 4.27 corresponding to the hydrogens of the β-carbon are observed in the ^1H NMR spectrum.

The product isolated from the reaction involving phenylethyne was also found to result from the formal insertion of the alkyne into the ruthenium–hydrogen bond of compound **3**, being characterised as the styryl-bridged product $[Ru_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CHCHPh)(CO)_4(\mu\text{-}etipdp)_2]PF_6$ **11** (R = Ph). The $^{13}C\text{-}\{^1H\}$ NMR spectrum exhibits two quintets at δ 144.0 and 94.7 with a DEPT analysis establishing the presence of a single hydrogen on each of the two carbon atoms associated with these quintets. The ^1H NMR spectrum reveals two doublets of quintets at δ 8.31 and 5.53, the integral of each set corresponding to a single hydrogen and assigned to the hydrogen bonded to the α- and β-carbons respectively. However, the room-temperature $^{31}P\text{-}\{^1H\}$ NMR spectrum exhibits a well resolved AA′BB′ pattern of peaks at δ 135.6. For a structure analogous to that of the vinyl-bridged species discussed above an ABCD pattern of peaks is predicted and on this basis some fluxional process is assumed, possibly involving in a formal sense a windscreen-wiper motion of the CHPh moiety about an axis defined by the α-carbon of the styryl group and the ruthenium atom closest to the β-carbon of the latter.

Not surprisingly compound **3** is also very susceptible to attack by the heterocumulenes CS_2 and PhNCS affording $[Ru_2\{\mu\text{-}\eta^2\text{-}SC(H)S\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$ **12** and $[Ru_2\{\mu\text{-}\eta^2\text{-}SC(H)NPh\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$ **13** respectively. As for the products from the corresponding reactions involving benzonitrile, ethyne and phenylethyne a formal insertion of the heterocumulene into the Ru–H bond occurs in the formation of these species. However, in contrast to $[Ru_2\{\mu\text{-}N(CHPh)\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$ and $[Ru_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CH\text{-}$

Table 4 Selected interatomic distances (Å) and angles (°) for the complex [Ru$_2$(μ-η^1:η^2-CHCH$_2$)(CO)$_4$(μ-etipdp)$_2$]PF$_6$ **11**

Ru(1)–Ru(2)	2.802(1)	Ru(1)–P(1)	2.338(2)
Ru(1)–P(2)	2.328(2)	Ru(1)–C(1)	1.89(2)
Ru(1)–C(2)	1.91(1)	Ru(1)–C(33)	2.098(8)
Ru(2)–P(3)	2.348(3)	Ru(2)–P(4)	2.325(4)
Ru(2)–C(3)	1.91(1)	Ru(2)–C(4)	1.91(1)
Ru(2)–C(33)	2.267(8)	Ru(2)–C(34)	2.32(1)
C(33)–C(34)	1.41(1)		
P(1)–Ru(1)–P(2)	176.4(1)	P(1)–Ru(1)–C(1)	88.0(3)
P(1)–Ru(1)–C(2)	93.5(3)	P(1)–Ru(1)–C(33)	85.6(2)
P(2)–Ru(1)–C(1)	89.7(3)	P(2)–Ru(1)–C(2)	89.6(3)
P(2)–Ru(1)–C(33)	92.5(2)	C(1)–Ru(2)–C(2)	97.4(5)
C(1)–Ru(1)–C(33)	108.8(4)	P(3)–Ru(2)–P(4)	177.5(1)
P(3)–Ru(2)–C(3)	88.3(3)	P(3)–Ru(2)–C(4)	90.5(3)
P(3)–Ru(2)–C(33)	103.1(2)	P(3)–Ru(2)–C(34)	83.2(2)
P(4)–Ru(2)–C(3)	89.9(3)	P(4)–Ru(2)–C(4)	88.2(3)
P(4)–Ru(2)–C(33)	79.3(2)	P(4)–Ru(2)–C(34)	157.5(4)
C(3)–Ru(2)–C(4)	102.3(5)	C(3)–Ru(2)–C(33)	128.4(4)
C(3)–Ru(2)–C(34)	99.1(4)	C(4)–Ru(2)–C(33)	127.2(4)
C(4)–Ru(2)–C(34)	157.5(4)		

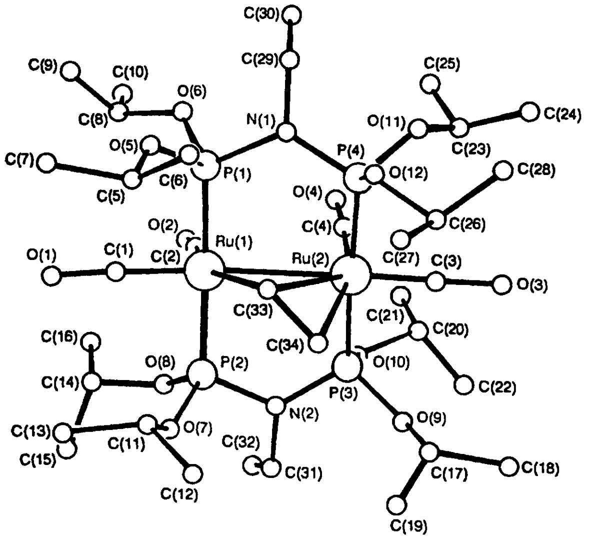


Fig. 4 Structure of the cation in [Ru$_2$(μ-η^1:η^2-CHCH$_2$)(CO)$_4$(μ-etipdp)$_2$]PF$_6$ **11** showing the atom labelling scheme

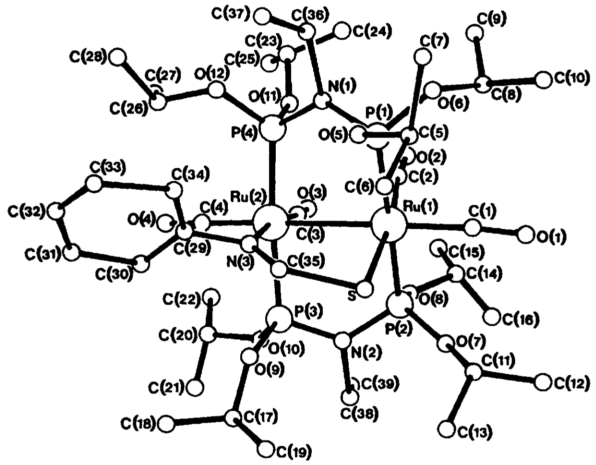
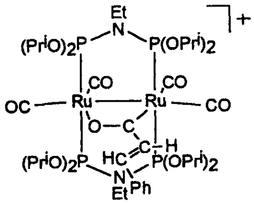


Fig. 5 Structure of the cation in [Ru$_2${μ-η^2-SC(H)NPh}(CO)$_4$(μ-etipdp)$_2$]PF$_6$ **13** showing the atom labelling scheme

Table 5 Selected interatomic distances (Å) and angles (°) for the complex [Ru$_2${μ-η^2-SC(H)NPh}(CO)$_4$(μ-etipdp)$_2$]PF$_6$ **13**

Ru(1)–Ru(2)	2.857(1)	Ru(1)–S	2.427(1)
Ru(1)–P(1)	2.355(1)	Ru(1)–P(2)	2.342(1)
Ru(1)–C(1)	1.909(5)	Ru(1)–C(2)	1.877(3)
Ru(2)–P(3)	2.352(1)	Ru(2)–P(4)	2.358(1)
Ru(2)–N(3)	2.144(3)	Ru(2)–C(3)	1.874(4)
Ru(2)–C(4)	1.909(4)	S–C(35)	1.698(5)
N(3)–C(35)	1.294(6)	N(3)–C(29)	1.454(5)
Ru(2)–Ru(1)–P(1)	89.3(1)	Ru(2)–Ru(1)–P(2)	87.7(1)
Ru(2)–Ru(1)–S	85.3(1)	Ru(2)–Ru(1)–C(1)	176.7(1)
Ru(2)–Ru(1)–C(2)	87.6(1)	P(1)–Ru(1)–P(2)	175.5(1)
P(1)–Ru(1)–S	89.2(1)	P(1)–Ru(1)–C(1)	92.9(1)
P(1)–Ru(1)–C(2)	88.7(1)	P(2)–Ru(1)–C(1)	90.0(1)
P(2)–Ru(1)–C(2)	94.5(1)	S–Ru(1)–C(1)	92.3(1)
S–Ru(1)–C(2)	172.6(1)	C(1)–Ru(1)–C(2)	94.9(2)
Ru(1)–Ru(2)–P(3)	89.4(1)	Ru(1)–Ru(2)–P(4)	86.8(1)
Ru(1)–Ru(2)–N(3)	86.0(1)	Ru(1)–Ru(2)–C(3)	88.1(1)
Ru(1)–Ru(2)–C(4)	179.0(1)	P(3)–Ru(2)–P(4)	176.2(1)
P(3)–Ru(2)–N(3)	89.1(1)	P(3)–Ru(2)–N(3)	89.1(1)
P(3)–Ru(2)–C(3)	89.0(1)	P(3)–Ru(2)–C(4)	91.0(1)
P(4)–Ru(2)–N(3)	91.6(1)	P(4)–Ru(2)–C(3)	89.9(1)
P(4)–Ru(2)–C(4)	92.7(1)	N(3)–Ru(2)–C(3)	173.8(2)
N(3)–Ru(2)–C(4)	94.9(2)	C(3)–Ru(2)–C(4)	91.0(2)



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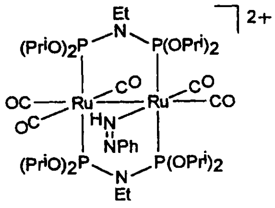

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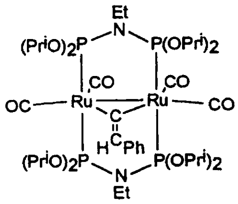

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CH$_2$)(CO)$_4$(μ-etipdp)$_2$]PF$_6$, the cations of these products contain five-membered dimetallaheterocyclic rings, as established crystallographically. The stereochemistry of [Ru$_2${μ-η^2-SC(H)NPh}(CO)$_4$(μ-etipdp)$_2$]$^+$ is illustrated in Fig. 5; selected interatomic distances and angles are listed in Table 5. A surprising feature of the structure of this cation is that unlike [Ru$_2${μ-η^2-OB(F)OH}(CO)$_4$(μ-etmdp)$_2$]$^{+}$[26] and [Ru$_2${μ-η^2-OC(Ph)O}(CO)$_4$(μ-etipdp)$_2$]$^{+}$,[35] this cation adopts a configuration that is substantially staggered [P(1)–Ru(1)–Ru(2)–P(4) 26.5, P(2)–Ru(1)–Ru(2)–P(3) 22.2°]. As a consequence the RuNCSRu ring is puckered. This puckering is interpreted in terms of localised π-orbital overlap involving the carbon and nitrogen ring atoms, as opposed to delocalised π-orbital overlap involving the carbon, nitrogen and sulfur ring atoms. The ring C–N [1.294(6) Å] and C–S [1.698(5) Å] distances are consistent with this interpretation. Related diiron and triosmium compounds have been isolated from the reactions of [Fe$_2${μ-P(C$_6$H$_{11}$)$_2$}(μ-H)(μ-CO)(CO)$_4$(μ-dppm)] and [Os$_3$(μ-H)$_2$(CO)$_{10}$] with CS$_2$ and PhNCS respectively.[36–38]

Reactivity of [Ru$_2$H(CO)$_5$(μ-etipdp)$_2$]PF$_6$ towards various nucleophiles

The pentacarbonyl hydride [Ru$_2$H(CO)$_5$(μ-etipdp)$_2$]PF$_6$ **8** affords, in general, products analogous to those produced by [Ru$_2$(μ-H)(μ-CO)(CO)$_3$(μ-etipdp)$_2$]PF$_6$ in its reaction with various nucleophiles but more forcing reaction conditions are required. Thus reactions of this compound with benzonitrile,

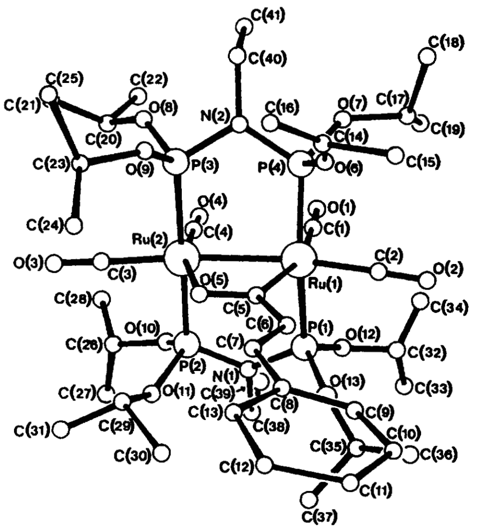

Fig. 6 Structure of the cation in $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(CHCHPh)\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$ **14** showing the atom labelling scheme

Table 6 Selected interatomic distances (Å) and angles (°) for the complex $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(CHCHPh)\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$ **14**

Ru(1)–Ru(2)	2.782(1)	Ru(1)–P(1)	2.311(2)
Ru(1)–P(4)	2.319(2)	Ru(1)–C(1)	1.923(9)
Ru(1)–C(2)	1.884(9)	Ru(1)–C(5)	2.079(5)
Ru(2)–P(2)	2.332(2)	Ru(2)–P(3)	2.335(2)
Ru(2)–O(5)	2.126(5)	Ru(2)–C(3)	1.919(8)
Ru(2)–C(4)	1.857(8)	O(5)–C(5)	1.252(9)
C(5)–C(6)	1.458(11)	C(6)–C(7)	1.38(1)
C(7)–C(8)	1.47(1)		
Ru(2)–Ru(1)–P(1)	91.6(1)	Ru(2)–Ru(1)–P(4)	91.7(1)
Ru(2)–Ru(1)–C(1)	95.0(3)	Ru(2)–Ru(1)–C(2)	163.1(3)
Ru(2)–Ru(1)–C(5)	67.2(2)	P(1)–Ru(1)–P(4)	176.6(1)
P(1)–Ru(1)–C(1)	90.9(3)	P(1)–Ru(1)–C(2)	87.8(3)
P(1)–Ru(1)–C(5)	90.6(2)	P(4)–Ru(2)–C(1)	88.1(3)
P(4)–Ru(1)–C(2)	89.3(3)	P(4)–Ru(1)–C(5)	91.4(2)
C(1)–Ru(1)–C(2)	101.9(4)	C(1)–Ru(1)–C(5)	162.2(3)
C(2)–Ru(1)–C(5)	95.9(3)	Ru(1)–Ru(2)–P(2)	90.8(1)
Ru(1)–Ru(2)–P(3)	90.2(1)	Ru(1)–Ru(2)–O(5)	70.0(1)
Ru(1)–Ru(2)–C(3)	169.0(2)	Ru(1)–Ru(2)–C(4)	91.8(3)
P(2)–Ru(2)–P(3)	178.3(1)	P(2)–Ru(2)–O(5)	91.8(1)
P(2)–Ru(2)–C(3)	88.9(2)	P(2)–Ru(2)–C(4)	87.0(3)
P(3)–Ru(2)–O(5)	89.7(1)	P(3)–Ru(2)–C(3)	90.3(2)
P(3)–Ru(2)–C(4)	91.7(4)	O(5)–Ru(2)–C(3)	99.0(3)
O(5)–Ru(2)–C(4)	161.8(3)	C(3)–Ru(2)–C(4)	99.2(3)

carbon disulfide and phenyl isothiocyanate in 1,2-dichloroethane under reflux give **10**, **12** and **13** respectively. However, the product isolated from the reaction with phenylethyne under the same conditions was shown to be the styrylcarbonyl-bridged product $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(CHCHPh)\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$ **14** and not the styryl-bridged derivative **11** (R = Ph). The characterisation of this complex was achieved X-ray crystallographically as well as by conventional methods. The stereochemistry of the cation is illustrated in Fig. 6; selected interatomic distances and angles are given in Table 6. The cation adopts an almost eclipsed configuration [P(1)–Ru(1)–Ru(2)–P(2) 0.3, P(3)–Ru(2)–Ru(1)–P(4) 0.2°] with the two ruthenium atoms being separated by a distance of 2.782(1) Å, corresponding to a formal ruthenium–ruthenium bond. The salient structural feature is the presence of a four-membered dimetallaheterocyclic ring comprising the two ruthenium atoms and a carbonyl group, with a styryl group bonded to the ring carbon atom. Related diruthenaheterocyclic ring systems and in particular diruthenium compounds containing bridging acyl groups have been reported previously[39] with the reaction of $[Ru_3\{\mu\text{-}\eta^2\text{-}OC(R)\}(\mu\text{-}H)(CO)_{10}]$, synthesized from the triruthenium anionic hydride $[Ru_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$, with ethene affording $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)\}\{\mu\text{-}\eta^2\text{-}OC(Et)\}(CO)_6]$ (R = Et, Pr, *etc*).[40,41] The atoms comprising the 'acyl group' are approximately coplanar, with the projected distances of Ru(2), O(5), C(5), Ru(1), C(6), C(7) and C(8) from the least-squares plane of Ru(2), O(5), C(5), C(6) and Ru(1) being 0.030, 0.034, 0.018, 0.010, 0.032, 0.114 and 0.019 Å respectively.

The benzenediazonium cation PhN_2^+ is isoelectronic with benzonitrile and phenylethyne and thus might be expected to give rise to a product analogous to **10** on reaction with **8**. However, while no reaction was found to occur at room temperature, a monocationic product, which could not be characterised, was formed in the reaction in 1,2-dichloroethane under reflux. On the other hand the dicationic phenyldiazene species, $[Ru_2(N_2HPh)(CO)_5(\mu\text{-}etipdp)_2]^{2+}$ **15**, is readily produced by treatment of $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}etipdp)_2]$ with $[PhN_2]PF_6$ in methanol at room temperature.[42]

Mechanism of formation of various products

The reactions of CS_2 with both $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]^+$ and $[Ru_2H(CO)_5(\mu\text{-}etipdp)_2]^+$ were monitored by means of $^{31}P\text{-}\{^1H\}$ NMR spectroscopy and significantly a common intermediate in the formation of $[Ru_2\{\mu\text{-}\eta^2\text{-}SC(H)S\}(CO)_4(\mu\text{-}etipdp)_2]^+$ **12** and which exhibited an AA′BB′ pattern of peaks was observed for both reactions. On the basis of this evidence it is concluded that the intermediate is a tetracarbonyl species of asymmetric structure and is proposed to be $[Ru_2H(CS_2)(CO)_4(\mu\text{-}etipdp)_2]^+$; migration of the hydride ligand on to the co-ordinated CS_2 would afford a species which would be predicted to rearrange spontaneously to **12**. The formation of **14** in the reaction of **8** with PhC≡CH could be interpreted in terms of this reaction occurring *via* a pentacarbonyl intermediate but the intermediate observed on monitoring the reaction by means of $^{31}P\text{-}\{^1H\}$ NMR spectroscopy exhibited an AA′BB′ pattern of peaks identical in shape and chemical shift to the set of peaks afforded by the product obtained by protonation of $[Ru_2(\mu\text{-}C{=}CHPh)(CO)_4(\mu\text{-}etipdp)_2]$ **16**. Furthermore compound **14** was formed, albeit in low yield, in the reaction of **3** with phenylacetylene.

Experimental

The compounds $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-}etipdp)_2]$ and $[Ru_2H(CO)_5(\mu\text{-}etipdp)_2]X$ (X = BF_4 or PF_6) were synthesised according to literature procedures.[21,26] All reactions and manipulations were carried out under an atmosphere of nitrogen using Schlenk techniques. Solvents were purified and dried using standard literature methods. The IR spectra were measured on a Perkin-Elmer 457 spectrometer, $^{31}P\text{-}\{^1H\}$ NMR spectra on a Varian FT 80A instrument and ^1H NMR spectra on a Varian Gemini 200 spectrometer. Relevant spectroscopic data are summarised in Table 7.

Syntheses

$[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]BF_4$. A solution of an excess of $HBF_4{\cdot}OEt_2$ (0.4 cm^3, 54% in diethyl ether) in ether (3 cm^3) was added dropwise to a stirred solution of $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-}etipdp)_2]$ (0.25 g, 0.24 mmol) in ether (20 cm^3) at room temperature. The solution turned orange and an orange microcrystalline material separated which was isolated, washed with ether and pentane and dried. Recrystallisation from acetone–ether afforded orange crystals. Yield: 70% (Found: C, 35.6; H, 6.5; N, 2.2. Calc. for $C_{32}H_{67}BF_4N_2O_{12}P_4Ru_2$: C, 35.5; H, 6.2; N, 2.6%).

Table 7 Infrared and $^{31}P\text{-}\{^1H\}$ nuclear magnetic resonance spectroscopic data

Compound	$\tilde{\nu}(CO)$[a]/cm^{-1}	$^{31}P\text{-}\{^1H\}$ NMR[b]
$[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]PF_6$[c]	2059s, 2006s, 1956s (br), 1757ms[d]	138.9 (s, br)[e,f]
$[Ru_2H(CO)_5(\mu\text{-}etipdp)_2]PF_6$[g]	2064w, 2031s, 2000vs, 1995 (sh), 1975 (sh)[d]	137.7 (s)[e,h]
$[Ru_2H_2(CO)_4(\mu\text{-}etipdp)_2]$[i]	1997m, 1935s, 1886w[j]	159.3 (s)[k]
$[Ru_2(\mu\text{-}Cl)H(\mu_{sb}\text{-}CO)(CO)_2(\mu\text{-}etipdp)_2]$[l]	1952s, 1888s, 1850w (br)[j]	153.0 (AA'BB')[k]
$[Ru_2(\mu\text{-}Br)H(\mu_{sb}\text{-}CO)(CO)_2(\mu\text{-}etipdp)_2]$[m]	1950s (br), 1890s (br), 1837w[j]	151.8 (AA'BB')[k]
$[Ru_2(\mu\text{-}I)H(\mu_{sb}\text{-}CO)(CO)_2(\mu\text{-}etipdp)_2]$[n]	1951s (br), 1888vs (br), 1812w (br)[o]	149.5 (AA'BB')[k]
$[Ru_2(\mu\text{-}SH)H(\mu_{sb}\text{-}CO)(CO)_2(\mu\text{-}etipdp)_2]$[p]	1946s (br), 1889s (br), 1838 (sh)[j]	158.8 (s)[q]
$[Ru_2H(CN)(CO)_4(\mu\text{-}etipdp)_2]$[r]	2028m, 2001ms, 1994 (sh), 1952s (br)[j]	150.4 (AA'BB')[k]
$[Ru_2(\mu\text{-}SH)(CO)_4(\mu\text{-}etipdp)_2]PF_6$[s]	2030s, 1997vs, 1966s, 1946s[d]	136.2 (AA'BB')[t]
$[Ru_2(\mu\text{-}\eta^1\!:\!\eta^2\text{-}CHCH_2)(CO)_4(\mu\text{-}etipdp)_2]PF_6$[u]	2041s, 2007vs, 1977s, 1958s[d]	143.5 (ABCD)[e,v]
$[Ru_2(\mu\text{-}\eta^1\!:\!\eta^2\text{-}CHCHPh)(CO)_4(\mu\text{-}etipdp)_2]PF_6$[w]	2033s, 2001vs, 1973s, 1951s[d]	135.6 (AA'BB')[t]
$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(CHCHPh)\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$[x]	2033s, 2003vs, 1977s, 1957s[d]	143.4 (ABCD)[y]
$[Ru_2\{\mu\text{-}N(CHPh)\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$[z]	2021vs, 1996vs, 1966s, 1945s*	135.4 (AA'BB')†
$[Ru_2\{\mu\text{-}\eta^2\text{-}SC(H)S\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$‡	2036s, 2006vs, 1986s, 1970s*	133.1 (s)[t]
$[Ru_2\{\mu\text{-}\eta^2\text{-}SC(H)NPh\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$§	2033s, 2004vs, 1979s, 1963s*	139.6 (AA'BB')[e]

[a] Includes ν(Ru–H) where appropriate; v = very, s = strong, m = medium, w = weak, br = broad. [b] δ scale in ppm relative to H_3PO_4; s = singlet, d = doublet, t = triplet, qnt = quintet, m = multiplet, br = broad, AA'BB' = centre of an AA'BB' pattern of peaks. [c] ^1H NMR: −9.69 (qnt, $|^2J_{PH} + {}^2J_{P'H}| = 14.8$ Hz, 1 H, Ru–H–Ru); in $(CD_3)_2CO$ at r.t. [d] In CH_2Cl_2. [e] In $(CD_3)_2CO$ at r.t. [f] Low-temperature $^{31}P\text{-}\{^1H\}$ NMR: δ 142.0 (AA'BB'); in $(CD_3)_2CO$ at −80 °C. [g] ^1H NMR: δ −7.57 (qnt, $|^2J_{PH} + {}^3J_{P'H}| = 10.4$ Hz, 1 H, RuH); in $(CD_3)_2CO$ at r.t. [h] $^{31}P\text{-}\{^1H\}$ NMR, in $(CD_3)_2CO$ at −90 °C: δ 144.9 (AA'BB') and 151.0 (AA'BB'). [i] ^1H NMR: δ −8.39 (qnt, $|^2J_{PH} + {}^3J_{P'H}| = 11.1$ Hz, 2 H, RuH); in C_6D_6 at r.t. [j] In hexane. [k] In C_6D_6 at r.t. [l] ^1H NMR: δ −9.39 (t, br, $^2J_{PH} = 18.1$ Hz, 1 H, RuH); in C_6D_6 at r.t. [m] ^1H NMR: δ −9.60 (t, br, $^2J_{PH} = 17.8$ Hz, 1 H, RuH); in C_6D_6 at r.t. [n] ^1H NMR: δ −10.17 (t, br, $^2J_{PH} = 17.2$ Hz, 1 H, RuH); in C_6D_6 at r.t. [o] In $CHCl_3$. [p] ^1H NMR: δ −10.03 (t, br, $^2J = 17.8$, 1 H, RuH) and −1.67 ($^3J_{PH} = 13.8$ Hz, 1 H, SH); in [$^2H_8$]toluene at r.t. [q] In [$^2H_8$]toluene at r.t. Low-temperature $^{31}P\text{-}\{^1H\}$ NMR: two overlapping sets of peaks of apparent AA'BB' pattern; in [$^2H_8$]toluene at −32 °C. [r] ^1H NMR: δ −7.58 (t, br, $^2J_{PH} = 21.6$ Hz, 1 H, Ru–H); in C_6D_6 at r.t. $\tilde{\nu}(CN)$ 2098w cm^{-1}, in hexane. [s] ^1H NMR: 0.63 (qnt, $^3J_{PH} = 13.9$ Hz, 1 H, SH); in $CDCl_3$ at r.t. [t] In $CDCl_3$ at r.t. [u] NMR: ^1H, δ 8.10 (m, 1 H, C*H*CH$_2$), 5.02 (m, 1 H, CHC*H*$_2$) and 4.27 (m, 1 H, CHC*H*$_2$); $^{13}C\text{-}\{^1H\}$, δ 158.7 (t, $J_{PC} = 13.7$, *C*HCH$_2$) and 68.2 (t, br, $J_{PC} = 7.4$ Hz, CH*C*H$_2$); measured in $(CD_3)_2CO$ at r.t. [v] Highest-intensity peak of an ABCD pattern. [w] NMR: ^1H, δ 5.53 (d of qnt, 1 H, CHC*H*Ph) and 8.31 (overlapping d of qnt, 1 H, C*H*CHPh); $^{13}C\text{-}\{^1H\}$, δ 144.0 (qnt, *C*HCHPh) and 94.7 (q, CH*C*HPh); in $CDCl_3$ at r.t. [x] ^1H NMR: δ 5.66 (d of qnt, $^3J_{HH} = 15.2$, $^5J_{PH} = 2.5$, 1 H, CHC*H*Ph) and 8.54 (overlapping d of qnt, $^3J_{HH} = 15.2$, $^4J_{PH} = 7.7$ Hz, 1 H, C*H*CHPh); in $(CD_3)_2CO$ at r.t. [y] Centre of an ABCD pattern; in $(CD_3)_2CO$ at −40 °C. Variable-temperature data: 0 °C, ABCD pattern centred at δ 142.7; 30 °C, two broad peaks; 44 ± 3 °C, coalescence temperature; 80 °C, s, br at 140.5; 130 °C, s at 140.0. [z] ν(CN): 2220w cm^{-1}, in 1,2-dichloroethane. * In 1,2-dichloroethane. † In CD_2Cl_2 at r.t. ‡ ^1H NMR: δ 11.35 (qnt, $^4J_{PH} = 2.2$ Hz, 1 H, SCHS); in $CDCl_3$ at r.t. § ^1H NMR: δ 8.85 (qnt, $^4J_{PH} = 1.8$, 1 H, SC*H*NPh); in $(CD_3)_2CO$ at r.t.

$[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]PF_6$. A solution of an excess of HPF_6 (0.5 cm^3, 60% in water) in water (3 cm^3) was added to a stirred solution of $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-}etipdp)_2]$ (0.25 g, 0.24 mmol) in CH_2Cl_2 (5 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 crystallised from acetone–ether to afford orange crystals. Yield: 75% (Found: C, 34.1; H, 5.5; N, 2.1. Calc. for $C_{32}H_{67}F_6N_2O_{12}P_5Ru_2$: C, 33.7; H, 5.9; N, 2.5%).

$[Ru_2(\mu\text{-}X)H(\mu_{sb}\text{-}CO)(CO)_2(\mu\text{-}etipdp)_2]$ (X = Cl, Br or I). An equimolar amount of $NBu^n{}_4Cl$ (0.02 g, 0.09 mmol), $NBu^n{}_4Br$ (0.03 g, 0.09 mmol) or $NBu^n{}_4I$ (0.03 g, 0.09 mmol) was added to a stirred solution of $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]PF_6$ (0.10 g, 0.09 mmol) in acetone (10 cm^3) and the solution stirred for 30 min. The solvent was removed under reduced pressure to afford a yellow residue which was extracted with toluene. Addition of MeCN to the toluene solution resulted in the separation of the required compound in crystalline form. Yield: 70% (Found: C, 36.9; H, 6.8; N, 2.8. Calc. for $C_{31}H_{67}ClN_2O_{11}P_4Ru_2$: C, 37.1; H, 6.7; N, 2.8. Found: C, 35.7; H, 6.3; N, 2.6. Calc. for $C_{31}H_{67}BrN_2O_{11}P_4Ru_2$: C, 35.5; H, 6.4; N, 2.7. Found: C, 34.6; H, 6.2; N, 2.6. Calc. for $C_{31}H_{67}IN_2O_{11}P_4Ru_2$: C, 34.1; H, 6.2; N, 2.6%).

$[Ru_2H(CN)(CO)_4(\mu\text{-}etipdp)_2]$. An equimolar amount of solid KCN (0.01 g, 0.18 mmol) was added to a stirred solution of $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]PF_6$ (0.20 g, 0.18 mmol) in acetone (15 cm^3) and the solution stirred for 30 min. The solvent was removed under reduced pressure to afford a yellow residue which was extracted with hexane. Removal of the solvent from the hexane extract afforded a residue which was crystallised from toluene–MeCN. Yield: 75% (Found: C, 38.8; H, 6.7; N, 4.0. Calc. for $C_{33}H_{67}N_3O_{12}P_4Ru_2$: C, 38.7; H, 6.6; N, 4.1%).

$[Ru_2\{\mu\text{-}N(CHPh)\}(CO)_4(\mu\text{-}etipdp)_2]PF_6$. (*i*) A solution of an equimolar amount of PhCN (0.01 cm^3, 0.09 mmol) in acetone (3 cm^3) was added dropwise to a stirred solution of $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]PF_6$ (0.10 g, 0.09 mmol) in acetone (10 cm^3) at room temperature resulting in an immediate change from orange to yellow. The solvent was removed under reduced pressure and the residue washed with hexane and crystallised from MeCN–hexane to afford white crystals. Yield: 70%.

(*ii*) A solution of $[Ru_2H(CO)_5(\mu\text{-}etipdp)_2]PF_6$ (0.35 g, 0.30 mmol) and PhCN (0.15 g) in 1,2-dichloroethane (25 cm^3) was heated at reflux for 90 min. The solvent was removed under reduced pressure and the resultant oil washed with hexane to remove the excess of PhCN. The solid residue was crystallised from MeCN–Et$_2$O–hexane (1:8:1) to afford white needles. Yield: 90% (Found: C, 37.9; H, 6.1; N, 3.6. Calc. for $C_{39}H_{72}F_6N_3O_{12}P_5Ru_2$: C, 37.6; H, 5.8; N, 3.4%).

$[Ru_2(\mu\text{-}\eta^1\!:\!\eta^2\text{-}CHCH_2)(CO)_4(\mu\text{-}etipdp)_2]PF_6$. A stream of ethyne was passed slowly through a solution of $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]PF_6$ (0.25 g, 0.22 mmol) in acetone (7 cm^3) at room temperature for 30 min. The resulting yellow solution was concentrated to *ca.* 3 cm^3 and toluene added to afford a pale yellow crystalline material. Yield: 60% (Found: C, 35.2; H, 5.7; N, 2.5. Calc. for $C_{34}H_{69}F_6N_2O_{12}P_5Ru_2$: C, 35.0; H, 6.0; N, 2.4%).

$[Ru_2(\mu\text{-}\eta^1\!:\!\eta^2\text{-}CHCHPh)(CO)_4(\mu\text{-}etipdp)_2]BF_4$. A solution of an excess of PhC≡CH (0.10 g, 1.0 mmol) in CH_2Cl_2 (2 cm^3) was added dropwise to a stirred solution of $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3(\mu\text{-}etipdp)_2]BF_4$ (0.20 g, 0.18 mmol) in CH_2Cl_2 (15 cm^3) and the resulting mixture stirred for 15 min. The solvent was removed under reduced pressure and the pale yellow residue crystallised from $CHCl_3$–pentane to afford crystals of the required compound. Yield: 80% (Found: C, 40.6; H, 6.3; N, 2.3. Calc. for $C_{40}H_{73}BF_4N_2O_{12}P_4Ru_2$: C, 40.5; H, 6.2; N, 2.4%).

Table 8 Crystallographic data

	3	6	10	11	13	14
Formula	$C_{32}H_{67}F_6N_2O_{12}P_5Ru_2$	$C_{31}H_{67}IN_2O_{11}P_4Ru_2$	$C_{39}H_{72}F_6N_3O_{12}P_5Ru_2$	$C_{34}H_{69}F_6N_2O_{12}P_5Ru_2$	$C_{39}H_{72}F_6N_3O_{12}P_5Ru_2S$	$C_{41}H_{73}F_6N_2O_{13}P_5Ru_2$
M	1142.89	1096.82	1246.01	1168.93	1278.07	1273.04
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/c$	*Pbca*	$P2_1/c$	$Pna2_1$	$P\bar{1}$	$P2_1/c$
a/Å	11.361(2)	17.366(2)	11.512(2)	16.377(2)	11.823(1)	17.394(1)
b/Å	32.020(2)	22.633(2)	24.955(3)	22.287(3)	14.242(1)	12.552(2)
c/Å	14.459(1)	25.234(2)	20.479(2)	14.433(4)	17.852(1)	27.044(3)
α/°					97.520(5)	
β/°	98.97(2)		108.444(9)		98.815(4)	95.119(8)
γ/°					101.323(5)	
U/Å^3	5195(1)	9918(2)	5581(1)	5268(2)	2872.1(3)	5881(1)
Z	4	8	4	4	2	4
D_c/g cm^{-3}	1.460	1.469	1.483	1.474	1.478	1.438
F(000)	2344	4448	2560	2400	1312	2616
μ/cm^{-1}	7.96	14.01	7.50	7.88	7.65	7.15
Crystal size/mm	0.61 × 0.19 × 0.12	0.15 × 0.15 × 0.08	0.52 × 0.31 × 0.12	0.49 × 0.29 × 0.20	0.84 × 0.69 × 0.42	0.77 × 0.32 × 0.25
Measured reflections	7709	7542	10 048	4098	7321	8822
Independent reflections	6351	5267	8865	3531	5539	6775
Observed reflections [$I > 3\sigma(I)$]	5216	2818	7122	2970	5113	4988
No. variables	595	465	607	552	616	625
g in weighting scheme	0.0006	0.0002	0.0004	0.0004	0.0165	0.0003
R	0.037	0.036	0.041	0.034	0.033	0.047
R'	0.042	0.034	0.045	0.034	0.042	0.050
Δ/σ (maximum)	0.93	0.05	0.19	0.11	0.48	0.78
Δρ/e Å^{-3}	0.40	0.47	0.73	0.34	0.41	0.85

Weighting scheme: $w = 1/[\sigma^2(F) + gF^2]$, $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}F_o$.

$[Ru_2\{\mu\text{-}\eta^2\text{-OC(CHCHPh)}\}(CO)_4(\mu\text{-etipdp})_2]PF_6$. An excess of PhC≡CH (0.09 g, 1.0 mmol) was added to a solution of $[Ru_2H(CO)_5(\mu\text{-etipdp})_2]PF_6$ (0.35 g, 0.30 mmol) in tetrahydrofuran (thf) (25 cm^3) and the mixture heated at reflux for 4 h. The solvent and unreacted PhC≡CH were removed *in vacuo* and the yellow oil which remained was washed with warm hexane (2 × 20 cm^3, 50 °C). The residue was crystallised from acetone–Et_2O-hexane (1:2:3) to afford yellow crystals. Yield: 85% (Found: C, 38.4; H, 5.8; N, 2.2. Calc. for $C_{41}H_{73}F_6N_2O_{13}P_5Ru_2$: C, 38.7; H, 5.8; N, 2.2%).

$[Ru_2\{\mu\text{-}\eta^2\text{-XC(H)S}\}(CO)_4(\mu\text{-etipdp})_2]PF_6$ (X = S or NPh). (*i*) A solution of an excess of CS_2 (0.08 g, 1.0 mmol) or PhNCS (0.02 cm^3, 0.2 mmol) in acetone (2 cm^3) was added dropwise to a stirred solution of $[Ru_2(\mu\text{-H})(\mu\text{-CO})(CO)_3(\mu\text{-etipdp})_2]PF_6$ (0.1 g, 0.1 mmol) in acetone (10 cm^3) and the solution stirred for 30 min to 2 h. The solvent was removed under reduced pressure to afford a yellow-orange residue which was crystallised from acetone–hexane (1 : 1) (for the CS_2 reaction) or from acetone–Et_2O–hexane (1 : 1 : 1) (for the PhNCS reaction). Yield: 85–95%.

(*ii*) A solution of $[Ru_2H(CO)_5(\mu\text{-etipdp})_2]PF_6$ (0.35 g, 0.3 mmol) and CS_2 (0.5 cm^3) or PhNCS (0.05 g, 0.4 mmol) in 1,2-dichloroethane (30 cm^3) was refluxed for 1.5–2 h. The solvent was removed under reduced pressure to afford a yellow-orange residue which was crystallised as above. Yield: 80–90% (Found: C, 32.7; H, 5.7; N, 2.5. Calc. for $C_{33}H_{67}F_6N_2O_{12}P_5Ru_2S_2$: C, 32.5; H, 5.5; N, 2.3. Found: C, 36.8; H, 5.7; N, 3.2. Calc. for $C_{39}H_{72}F_6N_3O_{12}P_5Ru_2S$; C, 36.6; H, 5.6; N, 3.3%).

Reactions of $[Ru_2(\mu\text{-H})(\mu\text{-CO})(CO)_3(\mu\text{-etipdp})_2]PF_6$

With sodium tetrahydroborate. An equimolar amount of solid $NaBH_4$ (0.01 g, 0.18 mmol) was added to a stirred solution of $[Ru_2(\mu\text{-H})(\mu\text{-CO})(CO)_3(\mu\text{-etipdp})_2]PF_6$ (0.20 g, 0.18 mmol) in acetone (15 cm^3) and the solution stirred for 30 min. The solvent was removed under reduced pressure and the yellow residue extracted with hexane. The hexane extract was evaporated to afford a yellow microcrystalline material which was identified as the neutral dihydride $[Ru_2H_2(CO)_4(\mu\text{-etipdp})_2]$[21] by means of IR and NMR spectroscopy. Yield: 75%.

With sodium hydrogensulfide. A solution of an equimolar amount of NaSH (0.01 g, 0.18 mmol) in methanol (2 cm^3) was added dropwise to a stirred solution of $[Ru_2(\mu\text{-H})(\mu\text{-CO})(CO)_3(\mu\text{-etipdp})_2]PF_6$ (0.20 g, 0.18 mmol) in acetone (15 cm^3) and the solution stirred for 30 min. The solvent was removed under reduced pressure and the yellow residue extracted with toluene. The toluene extract was evaporated to afford a yellow microcrystalline solid identified as the neutral hydrogensulfide-bridged species $[Ru_2(\mu\text{-SH})H(\mu_{sb}\text{-CO})(CO)_2(\mu\text{-etipdp})_2]$[21] by IR and NMR spectroscopic means. Yield: 65%.

With lithium acetylide–ethane-1,2-diamine and lithium phenylacetylide. A slight excess of $Li(C{\equiv}CH){\cdot}NH_2C_2H_4NH_2$ (0.02 g, 0.19 mmol) or Li(C≡CPh) (0.02 g, 0.19 mmol) was added to a stirred solution of $[Ru_2(\mu\text{-H})(\mu\text{-CO})(CO)_3(\mu\text{-etipdp})_2]PF_6$ (0.20 g, 0.18 mmol) in acetone (15 cm^3) at −15 °C. The solution turned brown and a yellow crystalline material separated. This was isolated, washed with cold hexane, dried under reduced pressure and identified as the parent neutral pentacarbonyl $[Ru_2(\mu\text{-CO})(CO)_4(\mu\text{-etipdp})_2]$[29] by IR and NMR spectroscopic means. Yield: 50%.

With carbon monoxide. A stream of carbon monoxide was passed slowly through a solution of $[Ru_2(\mu\text{-H})(\mu\text{-CO})(CO)_3(\mu\text{-etipdp})_2]PF_6$ (0.10 g, 0.09 mmol) in acetone (5 cm^3) at room temperature resulting in an immediate change from orange to clear white. The solvent was removed under reduced pressure to afford a white crystalline material identified spectroscopically, IR and NMR, as the pentacarbonylhydride $[Ru_2H(CO)_5(\mu\text{-etipdp})_2]PF_6$.[26] Yield: 90%.

With sulfur. An excess of sulfur (0.01 g, 0.19 mmol) in toluene (3 cm^3) was added to a solution of $[Ru_2(\mu\text{-H})(\mu\text{-CO})(CO)_3(\mu\text{-etipdp})_2]PF_6$ (0.10 g, 0.09 mmol) in acetone (10 cm^3) resulting in an immediate change from orange to yellow. The solution was stirred for 30 min and the solvent removed under reduced pressure to produce a beige residue which was extracted with CH_2Cl_2. The CH_2Cl_2 extract was evaporated to give an orange crystalline solid which was identified as $[Ru_2(\mu\text{-SH})(CO)_4(\mu\text{-etipdp})_2]PF_6$[30] by means of IR and NMR spectroscopy. Yield: 75%.

Crystallography

Crystal data for the complexes **3**, **6**, **10**, **11**, **13** and **14** are given in Table 8, together with information on the data collections and structure determinations. Data were collected at 295 K on a Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) and ω–2θ scans. Lorentz-polarisation corrections were applied and as well as absorption corrections from empirical φ scans.[43] The structures were solved from Patterson and heavy-atom electron-density syntheses and refined by full-matrix least squares on *F* using the program SHELX 76.[44] The non-hydrogen atoms were assigned anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and allowed to ride on the atom to which they were attached with a common thermal parameter. The only exceptions were the hydride ligands in **3** and **6** both of which were located in Fourier-difference maps and their positions refined with individual isotropic thermal parameters.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/197.

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