Construction of Unusual Metal Clusters using Dicarbon (C_2) as a Collar. Examples based on Permetallabicyclo[2.2.0]hexane Frameworks

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The pentanuclear C_2 complex $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ **1** is a source of novel cluster frameworks which incorporate the C_2 ligand as a collar; this is exemplified by the structures of $[FeRu_5(\mu_6\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{14}]$ **2** and $[Co_4Ru_5(\mu_{10}\text{-}C_2)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)_7(CO)_{11}]$ **4**, obtained from reactions between **1** and $[Fe_2(CO)_9]$ or $[Co_2(CO)_8]$, respectively.

We have recently described[1] a high-yield synthesis of the pentanuclear cluster $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ **1** (Scheme 1) which contains a multi-site bound C_2 ligand. Previous examples of clusters containing C_2 include the unreactive $[Ru_4(\mu_4\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{12}]$,[2a] the decanuclear systems $[Ni_{10}(C_2)(CO)_{16}]^{2-}$ [ref 2(*b*)] and $[Co_3Ni_7(C_2)(CO)_{15}]^{3-}$ [ref. 2(*c*)] in which the C_2 ligand is encapsulated by the M_{10} cluster, the long-known $[Co_6(\mu_3,\mu_3\text{-}C_2)(CO)_{18}]$,[2d] and the recently described $[Fe_3Co_3(\mu_3,\mu_3\text{-}C_2)(CO)_{18}]^{2-}$ [ref 2(*e*)]. In the latter two, the C_2 ligand is essentially two μ_3-C atoms linked by a C–C bond, *i.e.* the cluster is a carbon-linked bismethylidyne system. The heterolytic cleavage of CO by early transition metals to give C_2 ligands[3] has been suggested to mimic the early stages of the Fischer–Tropsch process; complex **1** may be a reasonable model for later C–H and C–C insertion reactions involving the C_2 ligand. In considering further how the C_2 ligand may interact with several metal atoms, such as on a surface, we have examined the reactions between **1** and several metal carbonyls.

The reaction between **1** and $[Fe_2(CO)_9]$ was carried out in toluene (Carius tube, 98 °C, 6 h) and afforded black crystalline $[FeRu_5(\mu_6\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{14}]$ **2** and $[Fe_2Ru_5(\mu_6\text{-}C_2)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{15}]$ **3** in 84 and 17% yields, respectively (Scheme 1). Analogous homonuclear complexes have been obtained from reactions with $[Ru(CO)_5]$. A similar reaction with $[Co_2(CO)_8]$ (Carius tube, 100 °C, 3 h) gave black crystalline $[Co_4Ru_5(\mu_{10}\text{-}C_2)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)_7(CO)_{11}]$ **4** in 92% yield.† All three complexes have been fully characterised by single-crystal X-ray studies. The molecular structures of **2** and **4** are shown in Figs. 1 and 2 and significant bond parameters are given in the captions; the structure of **3** is based on that of **2**.‡

The reactions have resulted in a conversion of the ring cluster core of **1** to unprecedented hexametallabicyclo[2.2.0]hexane systems; in **4**, the square faces are capped by cobalt atoms. The six-atom core in **1** is formed by insertion of a metal atom into the Ru_5 ring and formation of metal–metal bonds to generate two square faces sharing one edge, which are held in place by the equally unprecedented $\mu_4,\mu_4\text{-}C_2$ ligand. In **2**, the Fe atom statistically half-occupies each hinge position. The metal core resembles a gabled roof with a dihedral of 83°, the C_2 unit acting as a collar preventing condensation of the two faces. Only the peripheral Ru–Ru bonds are of normal dimensions [av. 2.890(2) Å], the others being somewhat longer [2.90(1)–2.97(1), av. 2.94 Å] with angles within the 'squares' ranging between 89.2–91.0(2)°. Atom C(1) lies 0.38 Å above the plane of metal atoms M(1,2,5,6) while C(2) lies 0.36 Å above the plane of metal atoms M(2,3,4,5). The C(1)–C(2) vector [1.355(9) Å] intersects these planes at angles of *ca.* 41 and *ca.* 42°, respectively.

The $\mu\text{-}PPh_2$ groups take up their normal bridging positions along Ru–Ru bonds not involving the hinge atoms, with Ru–P(1,2)–Ru angles of 76.82(5), 78.20(6)°, respectively. The horizontal disposition of one of the phenyl rings from each PPh_2 group may be consequent on the disposition of its *ortho*-hydrogens *vis-à-vis* the pairs of adjacent carbonyl groups to either side. The μ-SMe groups in **1** now tie the two ends of the gable, with Ru–S(1,2)–Ru angles of 104.82(7), 105.98(7)°, respectively.

In **3**, the additional Fe atom now occupies the second hinge position of the bicyclic M_6 core, with an Ru atom bridging one of the Ru–Ru edges, interacting with both SMe groups so that the S_2Ru_3 unit is almost planar. There are also other subtle differences in the locations of the CO and PPh_2 groups. The structure of this and other related complexes will be discussed in the full account.

In the Co_4Ru_5 cluster **4**, the incorporation of the Co atoms has resulted in the formation of a core consisting of two edge-sharing square pyramidal metal atom cores, with Ru(7) bridging the Ru/Co(1)–Ru(6) edge. The 'square' faces of both are held at a dihedral of *ca.* 88° by the $\mu_5,\mu_5\text{-}C_2$ ligand, which also bonds to the apical Co(8,9) atoms, while the SMe groups interact with Ru(3), Ru(4) and Ru(7) to form a nearly planar S_2Ru_3 ring and with Ru/Co(1) and Ru(6) to complete the μ_3-bridging mode. The nucleophilicity of the SMe groups in **1** was highlighted in the earlier theoretical study,[4] the further bonding of each group to a third metal atom being a common feature in the reactions of **1**.

The divergence of the faces defined by metal atoms M(1,2,5,6) and M(2,3,4,5) from rectangular geometry is much greater in **4** than in **2** with angles ranging between 83.3(2) and 97.4(2)°; planarity remains close, however, with $\chi^2(\text{max}) = 2.7$ and the maximum deviation 0.03 Å. Atom C(1) lies *ca.* 0.30 Å out of the M(1,2,5,6) plane and C(2) *ca.* 0.28 Å out of the M(2,3,4,5) plane. The four atoms Co(2,8,9)Co/Ru(5) form a basal rhombus bent about the non-bonded Co(2)···Co/Ru(5) vector (*ca.* 3.25 Å) by *ca.* 163°. Three of the four edges of this rhombus are bridged Ru(3)–Ru(4) and Ru(6)–Ru(7); these two features destroy the plane of symmetry that otherwise relates the two halves of this cluster and are related to the metal atom disorder by which M(1) and M(5) are each statistically half-occupied by Co and Ru.

The spectroscopic properties of **2** and **4** are in accord with their solid-state structures. The ^1H NMR spectra of **2** and **4** each contain two singlet SMe resonances at δ 1.87 and 1.93, and 1.71 and 2.81, respectively, while the ^{13}C NMR spectrum of **2** contains a doublet (J_{CP} 5.4 Hz) at δ 254.93, which is assigned to the nuclei of the C_2 unit; the relative insolubility of **4** precluded the observation of the C_2 resonance(s). The IR ν(CO) spectrum of **4** contains bands for both terminal and bridging CO groups.

There has been considerable discussion about the nature of the C_2 ligand in its complexes [see especially ref. 2(*e*)], a

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† *Selected spectroscopic data.* For **2**: IR: $\nu(CO)/cm^{-1}$ (cyclohexane) 2073s, 2041vs, 2034s, 2020s, 2003w, 1990m, 1977s, 1926 vw. ^1H NMR: δ ($CDCl_3$) 1.87, 1.93 (2 × 3H, s, SMe), 6.90–7.83 (20H, m, Ph). ^{13}C NMR: δ ($CDCl_3$) 18.56, 18.79 (2 × s, SMe), 127.26–132.50 (m, Ph), 139.24 (d, $J_{C,P}$ 20.0 Hz, ipso C), 142.27 (d, $J_{C,P}$ 36.1 Hz, ipso C), 191.03 (d, $J_{C,P}$ 7 Hz), 191.72 (d, $J_{C,P}$ 6.9 Hz), 195.56 (m, br), 196.42 (s), 200.68 (s), 201.36 (s), 212.44 (m, br) (CO), 254.93 (d $J_{C,P}$ 5.4 Hz, C_2). FAB MS (*m/z*): 1442, M^+; 1414–1050, $[M - nCO]^+$ (n = 1–14). For **4**: IR: $\nu(CO)/cm^{-1}$ (cyclohexane) 2065m, 2041vs, 2031s, 2024s, 2010m, 2006(sh), 1995m, 1988(sh), 1976m, 1968w, 1962(sh), 1950vw, 1976m, 1856m, 1843w, 1839(sh), 1832w, 1824w, 1816(sh). ^1H NMR: δ ($CDCl_3$) 1.71, 2.81 (2 × 3H, s, SMe), 6.85–7.68 (20H, m, Ph). FAB MS (*m/z*): 1734, M^+; 1706–1230, $[M - nCO]^+$ (n = 1–18).

‡ *Crystal structure determinations* of **2** and **4**. Both determinations (at *ca.* 295 K) employed unique absorption-corrected diffractometer data sets (monochromatic Mo-Kα radiation), blocked least-squares refinement (statistical weights), anisotropic thermal parameter refinement for non-hydrogen atoms and constrained $(x, y, z, U_{iso})_H$ (estimated) (but see below).

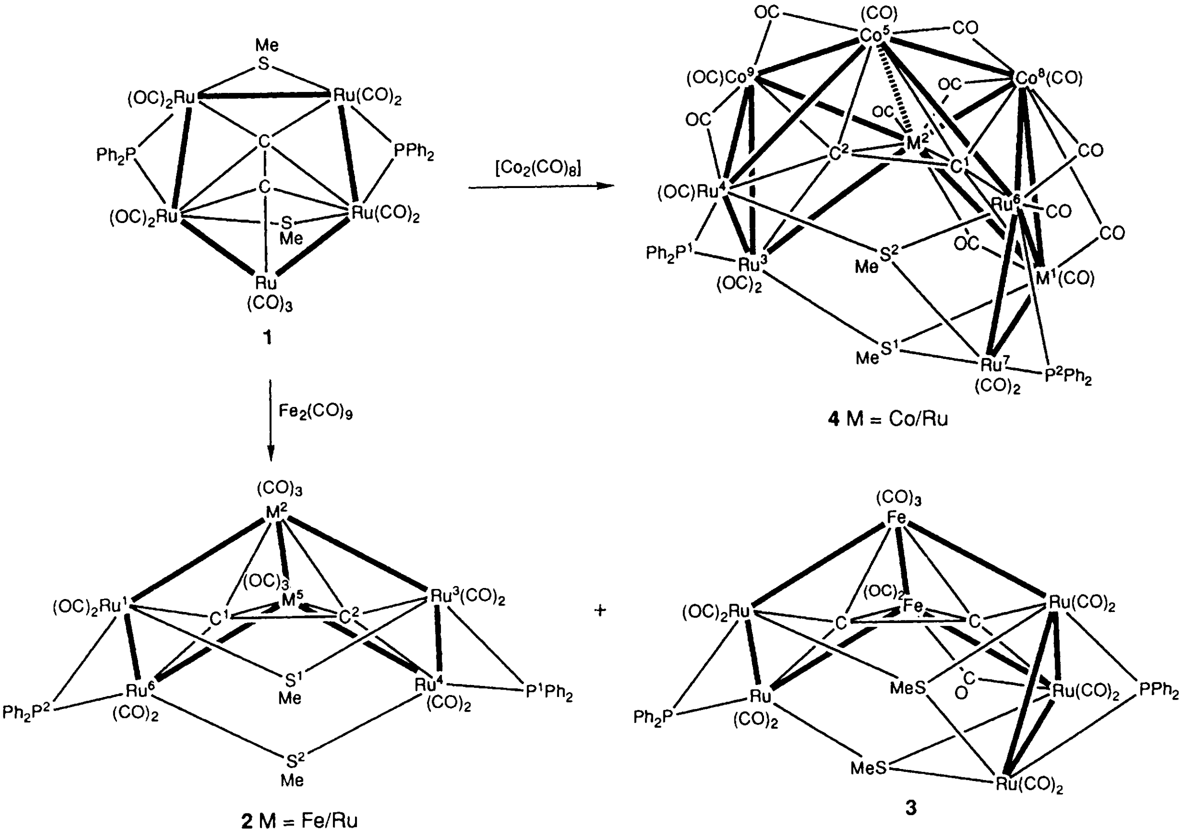
For **2** $[FeRu_5(\mu_6\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{14}]\cdot PhMe \equiv C_{42}H_{26}FeO_{14}P_2Ru_5S_2\cdot C_7H_8$, M = 1534.1. Monoclinic, *C2/c*, a = 44.65(3), b = 11.307(6), c = 21.81(1) Å, β = 102.61(5)°, V = 10745 Å^3, Z = 8, D_c = 1.90 g m^{-3}, μ(Mo-Kα) = 17.0 cm^{-1} (gaussian correction). Crystal dimensions 0.65 × 0.30 × 0.55 nm. N ($2\theta_{max}$ = 50°) = 8881, N_o $[I \geqslant 3\sigma(I)]$ = 5918, R = 0.034, R_w = 0.031.

The crystal decomposed in the X-ray beam; data were collected on the largest possible specimen overnight at maximum speed with periodic reorientation checks. Compensation for about 20% decomposition was by scaling. Following exploratory refinements with variable site populations, the sites of M(2,5) were set at 0.5 : 0.5 Fe : Ru occupancy; although separate components at each site were refinable in a stable manner with meaningful anisotropic thermal parameters, the separation of the two components at each site is small [Ru(2)···Fe(2) 0.03(1); Ru(5)···Fe(5) 0.04(1) Å] and differences in associated geometries are small or effectively of no significance (*e.g.* as above).

For **4** $[Co_4Ru_5(\mu_{10}\text{-}C_2)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)_7(CO)_{11}] \equiv C_{46}H_{26}Co_4O_{18}P_2Ru_5S_2$, M = 1733.9. Monoclinic, space group $P2_1/c$, a = 22.406(12), b = 11.662(4), c = 20.908(13) Å, β = 98.59(5)°, V = 5402 Å^3, Z = 4, D_c = 2.13 g cm^{-3}. CAD4 diffractometer, $2\theta_{max}$ = 50°, μ(Mo-Kα) = 27.7 cm^{-1}. Crystal dimensions 0.08 × 0.16 × 0.25 mm. N ($2\theta_{max}$ = 50°) = 8651, N_o $[I \geqslant 3\sigma(I)]$ = 4095, R = 0.085, R_w = 0.088.

As in the structure of **2**, two of the metal atom sites (1,5) are seemingly occupied at 0.5 : 0.5 Ru : Co population by a mixture of metal atoms. This complex lacks the incipient symmetry of **2**, however, and the disordered sites are not symmetrically disposed in the cluster. In addition, whereas in **2** the locations of Ru and Fe at the mixed sites are effectively identical, here in **4** the separation of the Ru and Co moieties at the two sites is rather greater [0.12(2), 0.08(2) Å, respectively]. Seemingly, this *ca.* 0.1 Å displacement is transmitted through much of the molecule including neighbouring associated light atoms, resulting in a determination of much lower precision. Data presented are for a final refinement in which isotropic thermal parameter refinement was employed for all light atoms.

Atomic coordinates, bond lengths and angles, and thermal parameters for **2** and **4** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



1

4 M = Co/Ru

2 M = Fe/Ru

3

Scheme 1

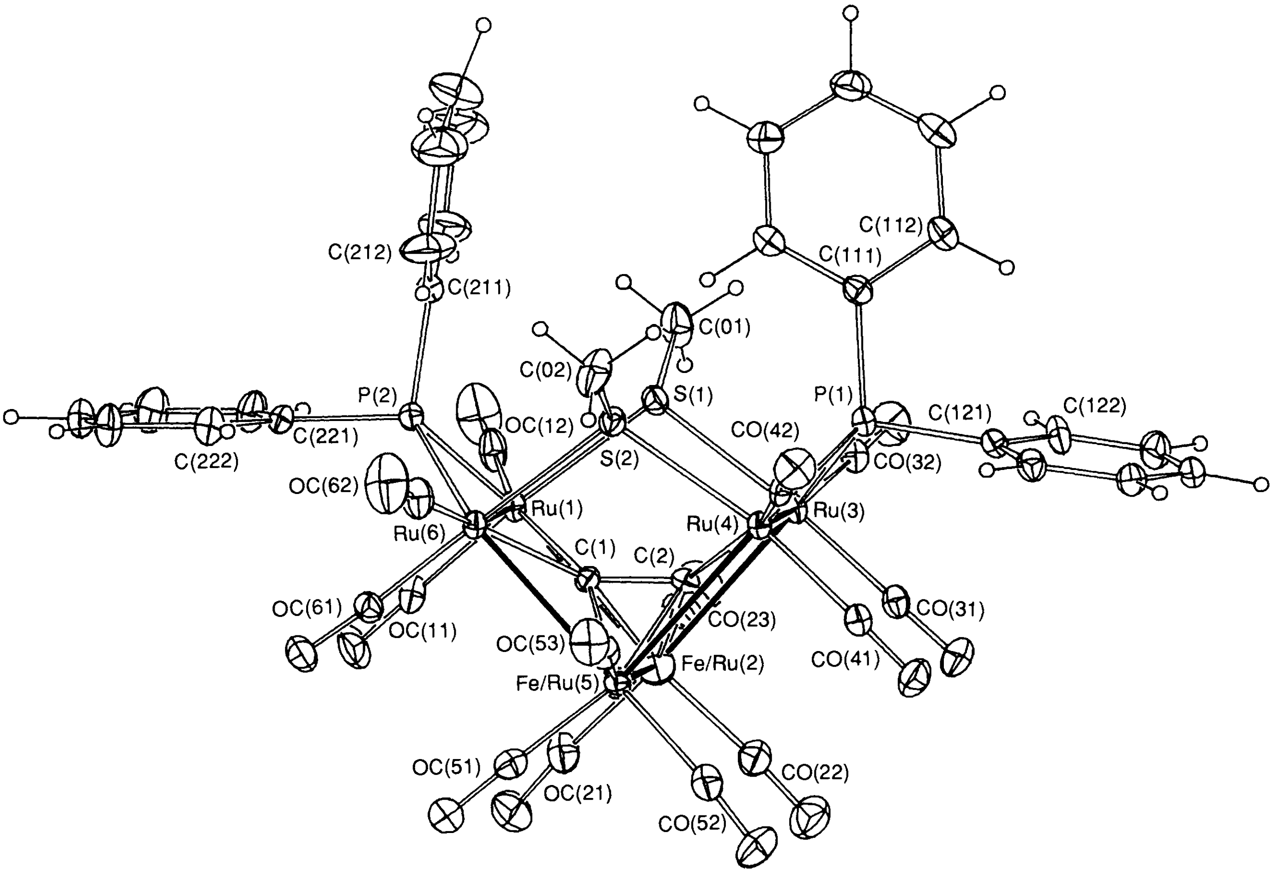


Fig. 1 A molecule of $[FeRu_5(\mu_6\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{14}]$ **2**, showing atom numbering scheme. 20% Thermal envelopes are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. Selected bond distances (Å) (* values for Fe-components of disordered pairs): Ru(1)–M(2) 2.915(9)*, 2.938(2), Ru(1)–Ru(6) 2.899(2), M(2)–Ru(3) 2.932(9)*, 2.944(4), M(2)–M(5) 2.90(1)*, 2.908(7), Ru(3)–Ru(4) 2.880(2), Ru(4)–M(5) 2.97(1)*, 2.967(7), M(5)–Ru(6) 2.92(1)*, 2.924(7); Ru(1)–S(1) 2.442(2), Ru(3)–S(1) 2.451(2), Ru(4)–S(2) 2.454(2), Ru(6)–S(2) 2.459(2); Ru(3)–P(1) 2.309(2), Ru(4)–P(1) 2.326(3), Ru(1)–P(2) 2.294(2), Ru(6)–P(2) 2.302(2); Ru(1)–C(1) 2.111(5), M(2)–C(1) 2.06(1)*, 2.081(7), M(5)–C(1) 2.05(1)*, 2.079(7), Ru(6)–C(1) 2.119(8), M(2)–C(2) 2.06(1)*, 2.081(7), Ru(3)–C(2) 2.120(6), Ru(4)–C(2) 2.117(6), M(5)–C(2) 2.05(1)*, 2.080(7); C(1)–C(2) 1.355(9).

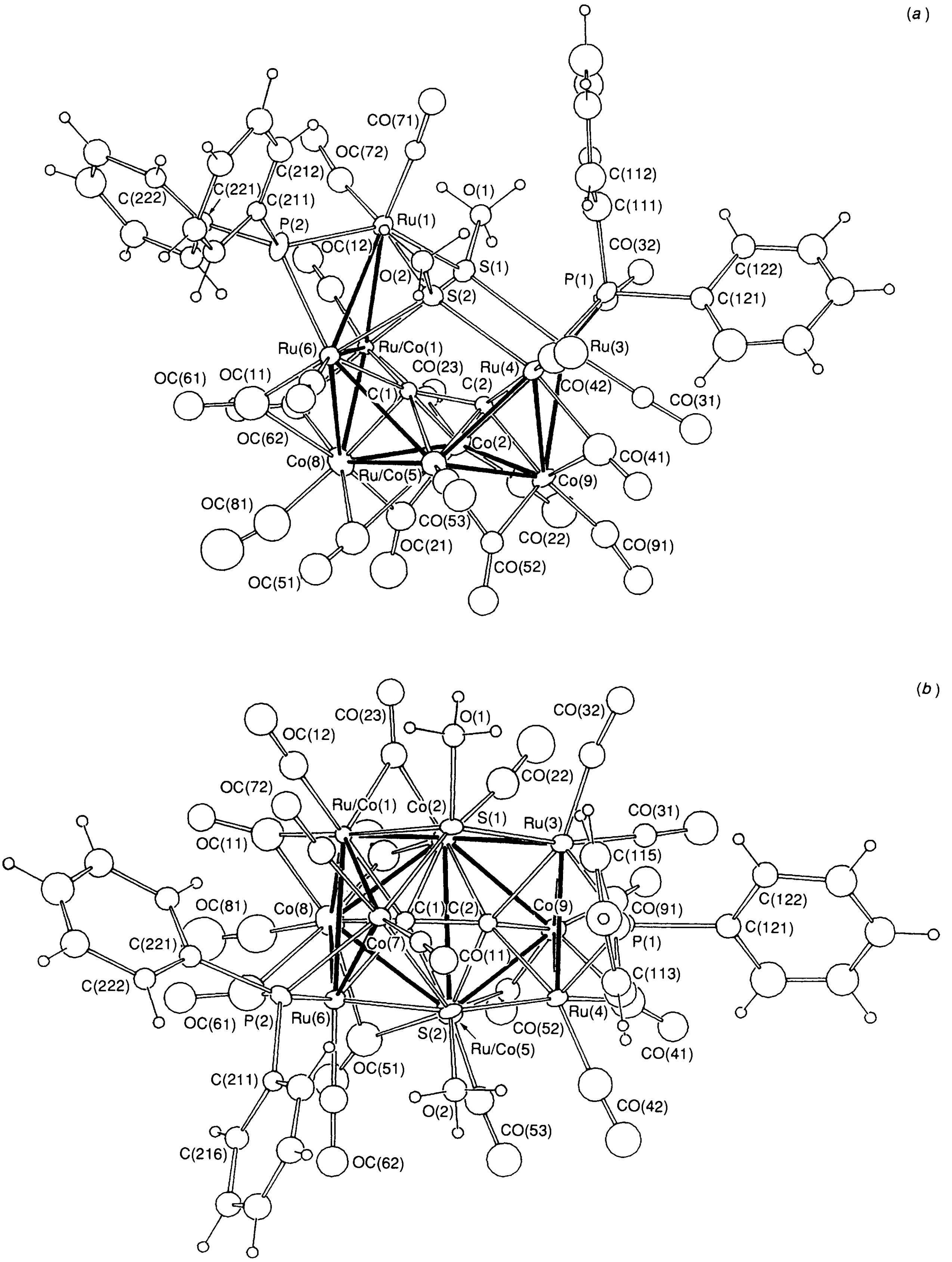


Fig. 2 (*a*) Plan and (*b*) elevation of a molecule of [$Co_4Ru_5(\mu_{10}$-C_2)- (μ_3-SMe$)_2(\mu$-PPh$_2)_2(\mu$-CO$)_7$(CO$)_{11}$] **3**, showing atom-numbering scheme. Selected bond distances (Å) (* values for Co-components of disordered pairs): M(1)–Co(2) 2.67(2)*, 2.63(1), M(1)–Ru(6) 3.12(2)*, 3.06(1), M(1)–Ru(7) 3.04(2)*, 3.09(1), M(1)–Co(8) 2.80(2)*, 2.69(1), Co(2)–Ru(3) 2.926(6), Co(2)···M(5) 3.22(2)*, 3.253(8), Co(2)–Co(8) 2.551(6), Co(2)–Co(9) 2.619(6), Ru(3)–Ru(4) 2.841(3), Ru(3)–Co(9) 2.860(4), Ru(4)–M(5) 2.84(3)*, 2.908(9), Ru(4)–Co(9) 2.689(5), M(5)–Ru(6) 2.88(2)*, 2.920(9), M(5)–Co(8) 2.61(3)*, 2.61(1), M(5)–Co(9) 2.59(2)*, 2.609(9), Ru(6)–Ru(7) 2.920(3), Ru(6)–Co(8) 2.811(5), M(1)–S(1) 2.30(3)*, 2.39(1), Ru(3)–S(1) 2.471(8), Ru(7)–S(1) 2.398(7), Ru(4)–S(2) 2.451(7), Ru(6)–S(2) 2.430(8), Ru(7)–S(2) 2.416(7), Ru(3)–P(1) 2.300(9), Ru(4)–P(1) 2.250(8), Ru(6)–P(2) 2.369(8), Ru(7)–P(2) 2.283(8), M(1)–C(1) 2.11(3)*, 2.05(3), Co(2)–C(1) 2.05(2), M(5)–C(1) 2.13(3)*, 2.19(2), Ru(6)–C(1) 2.20(2), Co(8)–C(1) 1.94(3), Co(2)–C(2) 2.06(3), Ru(3)–C(2) 2.21(2), Ru(4)–C(2) 2.10(3), M(5)–C(2) 2.09(4)*, 2.16(2), Co(9)–C(2) 1.94(2); C(1)–C(2) 1.41(4).

common view being that it is the acetylide dianion, C_2^{2-}. In the present case, an alternative (formal) view of **2**, for example, is of a tetrametallated ethyne [Ru(1,6) and Ru(3,4) as 'substituents' on C(1) and C(2), respectively, with the C≡C triple bond between the carbons bridging the M(2)–M(5) vector]. In accord with this interpretation is the C(1)–C(2) separation of 1.355(9) Å, considerably lengthened over the value of 1.305(5) Å found for **1**.[1] Similar comments can be made about **4**, with the 'substituents' being M(1)Co(8)Ru(6) and Co(9)Ru(3,4) and the Co(2)M(5) vector being that bridged by the C≡C triple bond. The imprecision of the C(1)–C(2) bond length [1.41(4) Å] precludes any meaningful discussion.

The electron count of **2** is in accord with the effective atomic number (EAN) rule if the C_2 ligand contributes six electrons; complex **2** has 94 cluster valence electrons (c.v.e.). The electron counts of **3** and **4** (110 and 132, respectively) do not agree with those predicted by the PSEP (polyhedral skeletal electron pair) rules[5] if the μ_3-SMe groups contribute five electrons each.

In conclusion, we have shown that complex **1** shows a novel reactivity towards $[Fe_2(CO)_9]$ and $[Co_2(CO)_8]$ to produce medium-sized mixed-metal clusters with unusual geometries, in which a C_2 ligand acts as a spacer (collar) between 'square' faces of edge-fused polyhedra. The reaction is not limited to these species, however: similar clusters have been obtained with other ligand–metal combinations, such as $[Ni(\eta\text{-}C_5H_5)]$, and will be described elsewhere. Comparison with the Ni_{10} and Co_3Ni_7 species mentioned above shows that the C_2 unit is gradually being encapsulated, although the additional presence of the SMe groups is a hindrance to completion of the metal cage. In contrast with the reactions of $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$, the precursor of **1**, which with $[Fe(CO)_5]$ afforded mono- and bis-carbido clusters derived from the cleavage of both the C–C and P–C bonds,[6] the C_2 unit in **1** is robust and thus a useful building block for medium-sized clusters.

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