Synthesis and X-Ray Structures of Two Complexes Containing Dicarbon (C_2) Attached to Ru_5 Clusters with Unusual Core Geometries

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Addition of Me_2S_2 to $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ **1** resulted in a sequence of Ru–Ru bond cleavage and formation reactions; the structures of two of the products, $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{12}$ **3** and $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ **4**, which contain dicarbon (C_2) attached to open and closed Ru_5 pentagons, respectively, are described.

There is a wide variety of core geometries associated with M_5 clusters, in contrast with the limited range found for M_4 and M_6 clusters. This may reflect their intermediate position between small clusters, in which the electron distribution can be considered localised, *i.e.* each metal atom achieving an 18-electron configuration, and larger clusters, in which valence electrons are delocalised over the whole core.[1] An alternative view is that the M_5 core is flexible and can accommodate itself to the steric demands of the organic ligands present. We have shown earlier that the complex $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ **1** is highly reactive, readily undergoing core rearrangement and P–C(sp) cleavage reactions.[2] There is also much current interest in complexes containing C_n molecules, ranging from simple carbido complexes such as $(Bu^tO)_3W{\equiv}C\text{–}Ru(CO)_2(\eta\text{-}C_5H_5)$[3] through to the intriguing cyclo[18]carbon derivative $(C_{18})\{Co_2\text{-}$

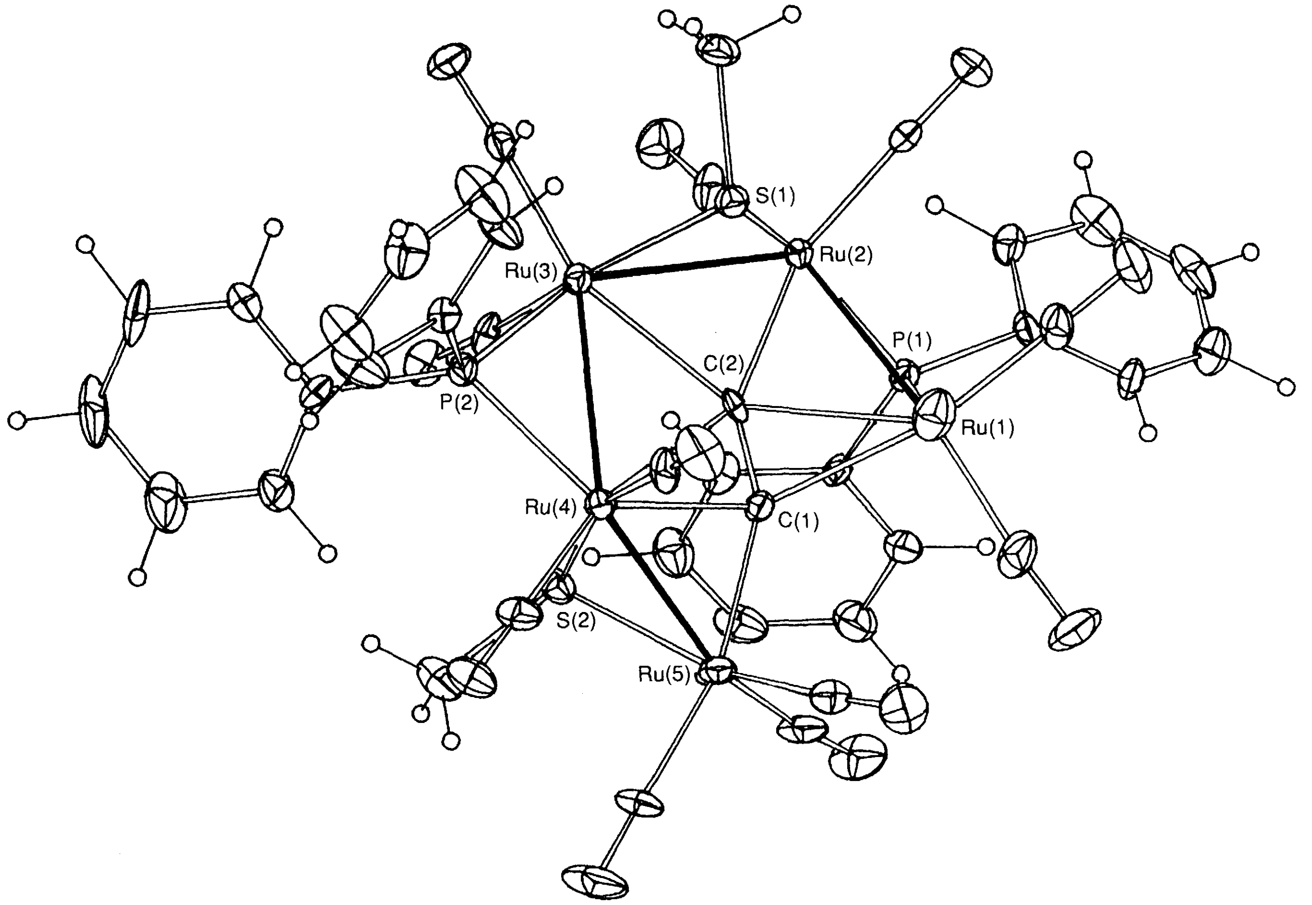

Fig. 1 Molecular structure of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{12}$ **3** (molecule 1). Bond distances (Å) (entries for the two pseudo-symmetrically related molecules): Ru(1)–Ru(2) 2.752(2), 2.770(2); Ru(2)–Ru(3) 2.792(2), 2.794(2); Ru(3)–Ru(4) 2.964(2), 2.947(2); Ru(4)–Ru(5) 2.704(2), 2.716(2); Ru(1)–P(1) 2.350(4), 2.354(5); Ru(2)–P(1) 2.300(5), 2.302(5); Ru(3)–P(2) 2.267(4), 2.249(5); Ru(4)–P(2) 2.309(4), 2.315(4); Ru(2)–S(1) 2.418(5), 2.421(5); Ru(3)–S(1) 2.373(4), 2.370(3); Ru(4)–S(2) 2.458(5), 2.457(4); Ru(5)–S(2) 2.372(4), 2.373(4); Ru(1)–C(1) 2.30(1), 2.29(1); Ru(4)–C(1) 2.27(1), 2.27(2); Ru(5)–C(1) 2.06(1), 2.06(1); Ru(1)–C(2) 2.36(1), 2.41(1); Ru(2)–C(2) 2.10(1), 2.08(1); Ru(3)–C(2) 2.41(1), 2.37(1); Ru(4)–C(2) 2.45(1), 2.44(2); C(1)–C(2) 1.26(2), 1.31(2). Bond angles (°): Ru(1)–Ru(2)–Ru(3) 109.14(6), 109.99(7); Ru(2)–Ru(3)–Ru(4) 99.17(5), 98.20(5); Ru(3)–Ru(4)–Ru(5) 124.14(7), 123.10(7); Ru(2)–C(2)–C(1) 143(1), 142(2); Ru(5)–C(1)–C(2) 153(1), 149(1).

$(\mu\text{-dppm})(CO)_6\}_3$ [dppm = bis(diphenylphosphino)methane] recently reported.[4] This communication describes (*i*) the use of Me_2S_2 to open up an Ru_5 cluster; (*ii*) the sequential formation of three clusters containing a bent Ru_5 chain, and open and closed pentagonal Ru_5 cores; (*iii*) the generation of two clusters containing the dicarbon (C_2) ligand.

The reaction between **1** and Me_2S_2 (C_6H_6, 70 °C, 30 min) afforded the three complexes $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(CO)_{13}$ **2**, $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{12}$ **3** and $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ **4** (Scheme 1)† in a total yield >70%. The three complexes have been fully characterised by single-crystal X-ray studies: full details of the reactions and of the structure of **2** will be given elsewhere. Separate experiments have shown that **3** and **4** are formed on heating **2**, and that **4** can be obtained similarly from **3**. The molecular structures of **3** and **4** are shown in Figs. 1 and 2,‡ important bond distances and angles being given in the captions.

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† *Selected spectroscopic data*. For **2**: ν_{max}/cm^{-1} (CO) (cyclohexane) 2074m, 2058vs, 2037s, 2021s, 2014m, 2003m, 1991s, 1975 (sh), 1970m, 1962m. ^1H NMR: $\delta(CDCl_3)$ 1.073, 1.571 (2 × s, 2 × 3H, SMe); 7.03–7.67, 8.28–8.34 (m, 20H, Ph). ^{13}C NMR: $\delta(CDCl_3)$ 19.67, 20.03 (2 × s, SMe), 64.96 (d, J_{CP} 37.9 Hz, C_α), 126.90–134.45, (m, Ph), 138.20–141.58 (m, *ipso* C), 187.11–215.54 (m, CO). For **3**: ν_{max}/cm^{-1} (CO) (cyclohexane) 2081m, 2057m, 2025vs, 2006s, 1994m, 1981m, 1962m, 1949m. ^1H NMR: $\delta(CDCl_3)$ 1.302 (s, 3H, SMe), 2.75 (d, J_{HP} 2.3 Hz, 3H, SMe), 6.91–8.02 (extended m, 20H, Ph). ^{13}C NMR: $\delta(CDCl_3)$ 22.64, 26.00 (2 × s, SMe), 127.26–134.35 (m, Ph), 140.14 (d, J_{CP} 37.5 Hz), 141.99 (d, J_{CP} 32.2 Hz), 142.96 (d, J_{CP} 25.1 Hz) (*ipso* C), 163.01 [dd, J_{CP} 14.4, 3.6 Hz, C(2)], 183.35–205.19 (CO). For **4**: ν_{max}/cm^{-1} (CO) (cyclohexane) 2070m, 2034vs, 2016m, 1996m, 1987w, 1971m, 1966m. ^1H NMR: $\delta(CDCl_3)$ 1.072, 1.933 (2 × s, 2 × 3H, SMe), 7.08–7.78 (m, 20H, Ph). ^{13}C NMR: $\delta(CDCl_3)$ 21.02, 22.65 (2 × s, SMe), 127.53–131.48 (m, Ph), 141.79–142.04 (m, *ipso* C), 143.75–144.16 (m, *ipso* C), 184.89–206.66 (CO).

‡ *Crystal data* for **3**: $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{12} \equiv C_{40}H_{26}O_{12}P_2Ru_5S_2$, M = 1330.1. Triclinic, space group $P\bar{1}$, a = 19.099(7), b = 17.927(5), c = 14.193(6) Å, α = 72.34(2), β = 89.44(3), γ = 76.37(3)°, V = 4490.0 Å^3, Z = 4, D_c = 1.97 g cm^{-3}. CAD4 diffractometer, $2\theta_{max}$ = 50°, μ(Mo-Kα) = 16.9 cm^{-1}. Crystal dimensions 0.17 × 0.18 × 0.09 mm, 7539 observed data [$I \geqslant 3\sigma(I)$] from 15151 data measured were refined to R = 0.054, R_w = 0.052 (statistical weights).

For **4**: $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11} \equiv C_{39}H_{26}O_{11}P_2Ru_5S_2$, M = 1302.1. Monoclinic, space group $P2_1/c$, a = 14.691(9), b = 15.784(9), c = 19.112(8) Å, β = 91.38(4)°, V = 4430.3 Å^3, Z = 4, D_c = 1.95 g cm^{-3}. CAD4 diffractometer, $2\theta_{max}$ = 65°, μ(Mo-Kα) = 17.1 cm^{-1}. Crystal dimensions 0.20 × 0.40 × 0.18 mm, 12756 observed data [$I \geqslant 3\sigma(I)$] from 15981 data measured were refined to R = 0.038, R_w = 0.048 (statistical weights).

For both structures, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

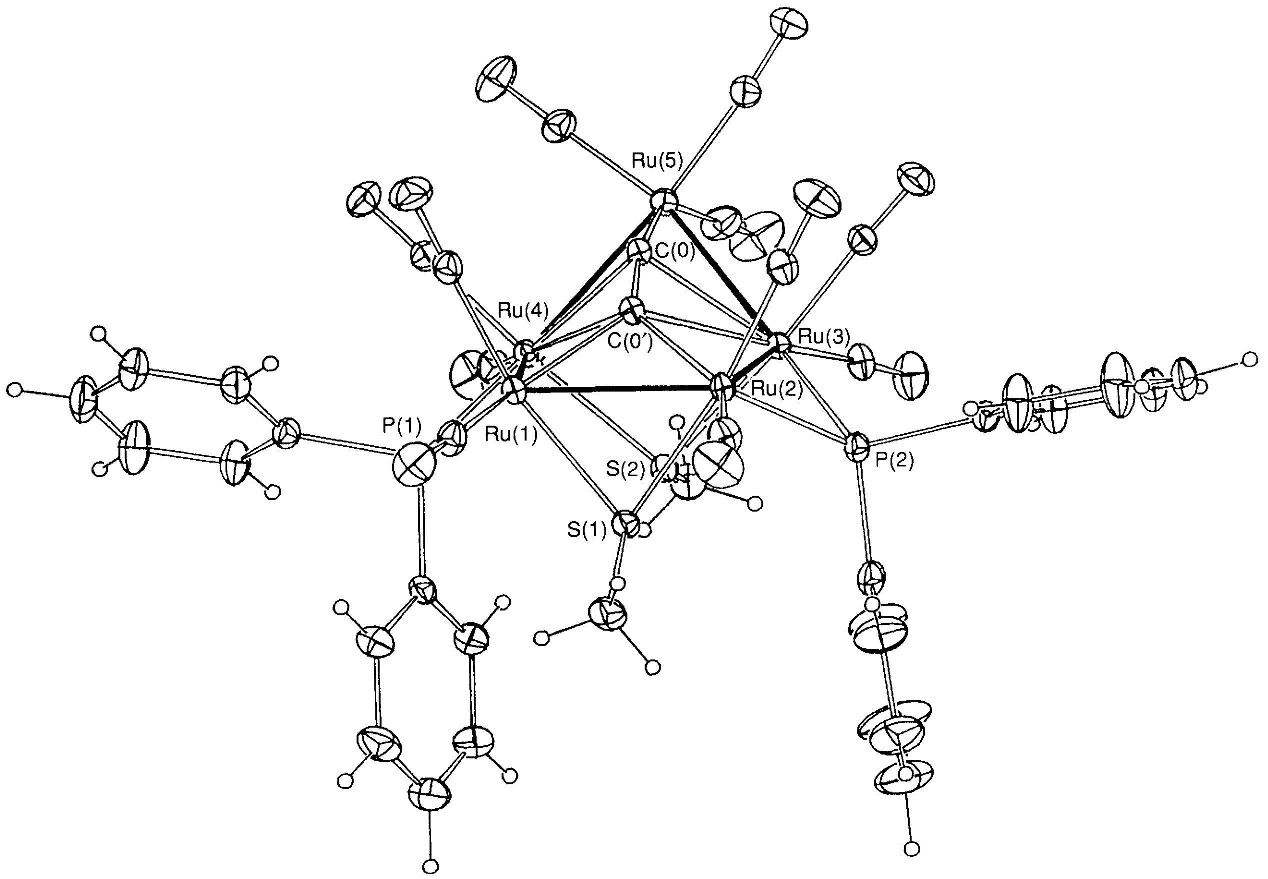
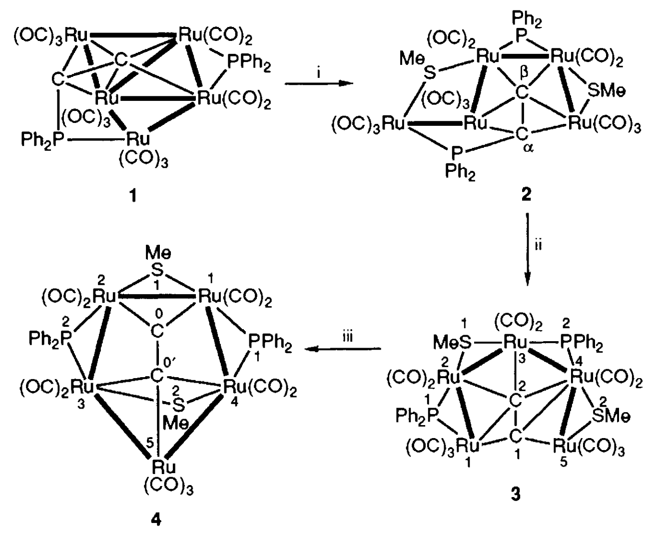


Fig. 2 Molecular structure of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ **4**. Bond distances (Å): Ru(1)–Ru(2) 2.855(2), Ru(1)–Ru(4) 2.898(1), Ru(2)–Ru(3) 2.882(1), Ru(3)···Ru(4) 3.448(2). Ru(3)–Ru(5) 2.890(1), Ru(4)–Ru(5) 2.898(1), Ru(1)–P(1) 2.290(1), Ru(2)–P(2) 2.294(1), Ru(3)–P(2) 2.341(1), Ru(4)–P(1) 2.341(1), Ru(1)–S(1) 2.387(1), Ru(2)–S(1) 2.392(2), Ru(3)–S(2) 2.449(2), Ru(4)–S(2) 2.454(1), Ru(1)–C(0′) 2.132(3), Ru(2)–C(0′) 2.134(4), Ru(3)–C(0) 2.261(4), Ru(3)–C(0′) 2.410(4), Ru(4)–C(0) 2.232(3), Ru(4)–C(0′) 2.471(3), Ru(5)–C(0) 1.938(4), C(0)–C(0′) 1.305(5). Bond angles (°): Ru(1)–Ru(2)–Ru(3) 95.38(2), Ru(2)–Ru(3)–Ru(5) 119.29(2), Ru(3)–Ru(5)–Ru(4) 73.14(4), Ru(5)–Ru(4)–Ru(1) 117.51(2), Ru(4)–Ru(1)–Ru(2) 96.39(2), Ru(5)–C(0)–C(0′) 163.1(3).

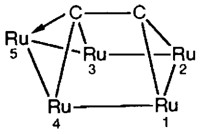
Complex **2** contains a bent Ru_5 sequence formed by opening of three Ru–Ru bonds in **1** as a result of the addition of two SMe groups (6e). The C_2PPh_2 ligand present in **1** is retained in **2**. In complex **3**, however, loss of CO results in cleavage of the P–C(sp) bond to give a second PPh_2 group and a C_2 ligand which spans the five metal atoms. These form a *cis*-bent chain or open pentagon, the Ru–Ru bonds being bridged alternately by μ-PPh_2 and μ-SMe groups. The Ru–Ru separations fall into two groups: three between 2.70 and 2.79 Å, and one longer, at 2.96 Å. The reason for this lengthening is not obvious at this stage. In complex **4** linking of the two ends of the Ru_5 chain has occurred to give an unprecedented closed pentagonal cluster with an envelope conformation [internal dihedral Ru(3)–Ru(4)–Ru(5)/Ru(4)–Ru(1)–Ru(2)–Ru(3) 132.21(1)°] with concomitant loss of a CO group. Of the five Ru–Ru bonds, four are essentially equivalent (av. 2.892 Å) while the fifth is somewhat shorter [Ru(1)–Ru(2) 2.855(1) Å]. Of note is the lengthening of the Ru–S bonds from 2.39 Å [to Ru(1) and Ru(2)] to 2.45 Å {to Ru(3) and Ru(4), which is a non-bonded Ru···Ru vector [3.448(2) Å]}.



Scheme 1 *Reagents and conditions*: i, Me_2S_2, C_6H_6, 35–40 °C, 2 h; ii, C_6H_6, 50 °C, 1 h; iii, C_6H_6, 70 °C, 2 h

The C_2 ligand acts as a six-electron donor in both complexes **3** and **4**. In the former, it is not symmetrically disposed with respect to the Ru chain. A formal description of the bonding involves η^2-interactions with Ru(1) and Ru(4), and σ interactions with Ru(2) and Ru(5). The C_2 unit may be described as a *trans*-bent ethynyl dianion and, neglecting the weak interaction with Ru(3), is similar to that found in $Ru_4(\mu_4\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{12}$.[5] The internal dihedral Ru(1)–C(1)–C(2)/C(1)–C(2)–Ru(4) is 139.0(4), 137.8(4)° (for the two independent molecules), which may be compared with values of 169° in $Ru_4(\mu_4\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{12}$[5] and of *ca.* 90° in $Co_2(\mu\text{-}C_2R_2)(CO)_6$.[6]

In **4**, the C–Ru separations fall into four types: the unique Ru(5)–C(0) bond of 1.938 Å and three pairs of 2.13, 2.25 and



A

2.44 Å. This arrangement corresponds to a dipolar C_2 ligand with a formal electron distribution of two to Ru(5) and one each to the other four Ru atoms (as in **A**); there is probably little bonding interaction between C(0′) and Ru(3) or Ru(4). In this case, the Ru(3)–C(0)–C(0′)/C(0)–C(0′)–Ru(4) dihedral is 78.5(1)°.

It has not been possible to assign unequivocally the resonances of the C_2 moieties in the three complexes. In **2**, a doublet (J_{CP} 37.9 Hz) at δ 64.96 is assigned to C_α; in **3**, a signal at δ 163.01, showing coupling to two ^{31}P nuclei, is assigned to C(2). In each case, the other carbon resonance is probably in the aromatic region. In **4**, there are no signals clearly separate from the plethora of Ph or CO resonances, although the aromatic *ipso* C region is more complex than found in **3** and may contain one or both of the C_2 resonances. A detailed commentary on these spectra will be given in the full account.

The metal cores in the three complexes are of interest. The three edge-fused triangles in **1** (seven Ru–Ru bonds) have been opened out by the addition of the two SMe groups to form five-atom chains (four Ru–Ru bonds) in **2** and **3**, the two ends of which have become linked in **4** (which contains five Ru–Ru bonds). The electron counts of all three complexes are in accord with the effective atomic number (EAN) rule. In **2** and **3** the EAN rule predicts 82 cve (cluster valence electrons). In **2** this is satisfied by 5 Ru (40e), 13 CO (26e), PPh_2 (3e), 2SMe (6e) and C_2PPh_2 (7e). In **3**, 5 Ru (40e), 12 CO (24e), 2 PPh_2 (6e), 2 SMe (6e) and C_2 (6e) provide the required 82 cve. In **4**, where there is an extra Ru–Ru bond, the EAN rule requires 80e. This is satisfied by 5 Ru atoms (40e), 11 CO (22e), 2 PPh_2 (6e), 2 SMe (6e) and C_2 (6e). Although a large number of main group homo- and hetero-nuclear ring compounds are known, transition metal ring compounds have up until now been limited to three and four metal atoms. Transition metal ring compounds contain 16*n* cve.[7] In **4** this corresponds to 16 × 5 = 80 cve.

These reactions point to a novel method of opening polyatomic clusters without fragmentation; a related example of the use of a sulfur-donor to open up a cluster is the reaction of $Ru_6C(CO)_{17}$ with HSEt, in which four Ru–Ru bonds were cleaved to give $Ru_6(\mu_5\text{-}C)(\mu\text{-}H)(\mu\text{-}SEt)_3(CO)_{15}$.[8] Apart from the interesting geometrical changes which are apparent during this reaction, the isolation of **3** and **4** afford further examples of C_2 cluster complexes. While $Ru_4(\mu_4\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{12}$[5] proved to be disappointingly unreactive, preliminary experiments have shown that these complexes are the source of much interesting chemistry which may be related to that of surface-adsorbed carbon.

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