Planar tetracoordinate carbon—a novel environment in a pentaruthenium cluster

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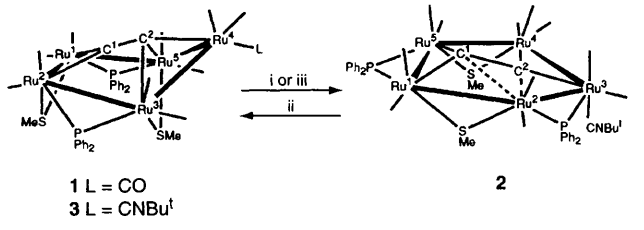
Addition of Bu^{t}NC to $[Ru_5(\mu\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ 1 results in expansion of the Ru_5 polygon and flattening of the C_2Ru_5 cluster so that in the product 2 one carbon atom acquires a planar tetracoordinate configuration; reversible loss of CO from 2 affords a CNBu^t derivative of 1.

There is much current interest in the coordination of all-carbon ligands to metal centres.[1] Since the predictions of theoretical chemists,[2,3] there has also been much activity in the preparation and study of molecules containing planar tetracoordinate carbon atoms. At least three different types of planar tetracoordinate carbon have been found in transition-metal complexes:[4] complexes of Group 4 metals containing alkynes interacting with organometallic main group Lewis acids, such as $M^1(\mu\text{-}\eta^1:\eta^2\text{-}R^1C_2R^2)(\mu\text{-}X)M^2R^3_2$ (M^1 = Zr, Hf; M^2 = B, Al, Ga),[5] binuclear complexes containing the 2,6-dimethoxyphenyl ligand,[6] and in a binuclear Pd–CS_2 complex.[7]

Examples abound of unusual coordination geometries for carbon atoms in metal clusters. Bonds from the carbon atom in $[Fe_4C(CO)_{13}]$ are all directed towards the metal core[8] and in $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ (**1**; Scheme 1),[9] both of the carbon atoms are also exposed to incoming reagents. To date, however, a planar *tetra*coordinate carbon has not been found in a metal cluster. We now describe how one of the carbons of the cluster-bond C_2 ligand in **1** assumes a planar tetracoordinate geometry on addition of CNBu^t to the metal core, reverting to the original conformation upon loss of CO; the latter transformation is reversible.

Addition of Bu^{t}NC to **1** (toluene, room temp., 15 min) afforded two major products which were separated by thin layer chromatography and characterised by spectroscopic methods as $[Ru_5C_2(SMe)_2(PPh_2)(CO)_n(CNBu^t)]$ n = 11 (green, **2**), 10 (purple, **3**) (Scheme 1).‡ Independent experiments showed that **2** and **3** were interconvertible by loss (PhMe, 90 °C, N_2 purge; 82%) or gain (PhMe, 90 °C, CO purge; 58%) of CO. The molecular structures of **2** and **3** have been determined by single-crystal X-ray crystallography:§ that of **3** is closely related to precursor **1** by replacement of a CO ligand by CNBu^t and will be described elsewhere (Scheme 1).

A plot of a molecule of **2** is shown in Fig. 1; a comparison of the C_2Ru_5 cores in **1**, **2** and **3**, with salient structural parameters, is given in Fig. 2. The metal core is an Ru_5 pentagon: compared to that in **1**, the average Ru–Ru separation in **2** is about 0.076 Å



Scheme 1 *Reagents*: i, L = CO: CNBu^t; ii, L = CNBu^t: − CO; iii, L = CNBu^t: + CO

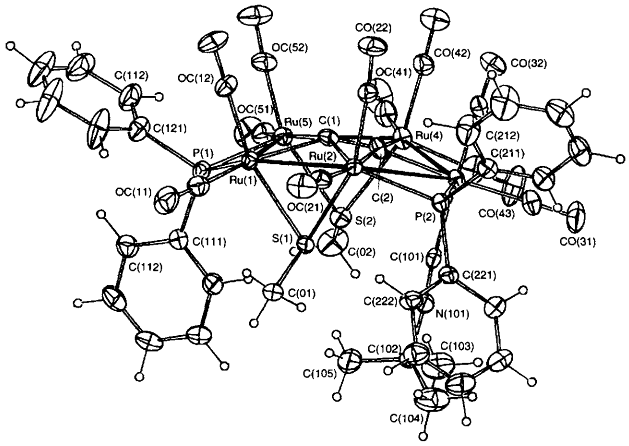


Fig. 1 Plot of a molecule of **2**, oblique to the Ru_5 'plane'

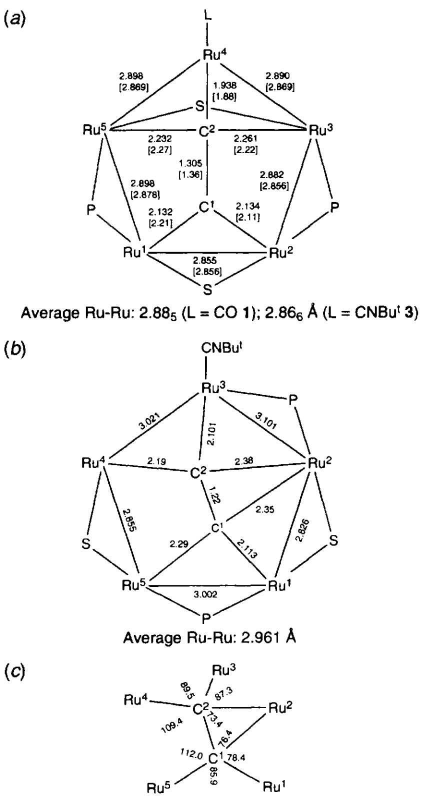


Fig. 2 Plot of the central C_2Ru_5 cores of (*a*) **1** and **3**, and (*b*) **2**, showing distances (Å), and (*c*) angles (°) about C(1) and C(2) in **2**

longer and the ring is considerably flattened [dihedral Ru(2,3,4)C(1,2)/Ru$_4$ planes: 16.17(4)°]. The PPh$_2$ groups bridge the Ru(1)–Ru(5) and Ru(2)–Ru(3) bonds and the SMe ligands are now found bridging the Ru(1)–Ru(2) and Ru(4)–Ru(5) vectors; this contrasts with the transannular interaction of one of the SMe groups with Ru(3) and Ru(5) found in **1** and **3**. Of note is the coordination about Ru(4), which bears three CO ligands: as such it has a formal electron count of 20, although the other four metal atoms have 18 e.

In **2**, the geometry about C(2) is of interest. As can be seen from Fig. 2 (*c*), the Ru(2)–C(2)–Ru(4) vector [174.9(5)°] is almost linear and the Ru(3)–C(2)–C(1) vector [160.2(9)°] also approaches linearity. The angles at C(2) sum to 359.9$_6$°. Atoms C(1), C(2), Ru(2), Ru(3), Ru(4) are nearly coplanar (χ^2 = 84). In contrast, C(1) adopts a more usual configuration, this atom projecting some 0.361(9) Å below the mean plane of the metal core, with C(2)–C(1)–Ru(1,5) being 147.7(9), 112.0(7)°, respectively. Surprisingly, the C(1)–C(2) distance in **2** [1.22(1) Å] is much shorter than in **1** [1.305(5) Å], the usual lengthening on coordination to a metal not being found. A possible explanation for this feature is found in the relatively long Ru(2)–C(1,2) separations, suggesting that this attachment is weak and that there is little back-bonding from the C$_2$ ligand to Ru(2).

Thus, atom C(2) is a further example of a planar tetracoordinate carbon atom. Clearly, the change in coordination of the C$_2$ unit by the five metal atoms is caused by the addition of the Bu^{t}NC ligand to **1** to give an electron-rich cluster, the extra electrons being accommodated in MOs with predominantly Ru–Ru antibonding character. This results in a general expansion of the Ru$_5$ pentagon, sufficient to pull the C$_2$ ligand almost into the plane of the pentagon. The steric interaction between the bulky Bu^t substituent and other ligands present on the cluster, particularly the Me and Ph groups of the bridging ligands, may also play a part in this process. An alternative rationale, involving the C$_2$ ligand acting as a four-electron donor, *i.e.* neglecting the Ru(2)–C(1,2) interaction completely, would result in the cluster being electron-precise and isoelectronic with **1** and **3**. Further discussion of this point will be deferred until theoretical studies are complete.[10]

Formation of **2** seemingly involves displacement of the μ-SMe ligand from Ru(3) by addition of the CNBu^t ligand and recoordination of the SMe group to Ru(4) so that this ligand now bridges the Ru(4)–Ru(5) edge. Meanwhile, the C$_2$ ligand swivels and is pulled down so that it lies almost in the plane of the Ru$_5$ ring; at first sight the attachment resembles that of an alkyne in the familiar 2σ,π coordination mode, if Ru(1) and Ru(3) are considered to be the 'substituents' of the alkyne. However, in contrast to the usual situation, where the alkyne sits above the metal core {*cf.* [M$_3$(μ$_3$-η^2-C$_2$R$_2$)(μ-CO)(CO)$_9$][11]}, the C$_2$ unit is almost coplanar with the five metal atoms.

The reversible conversion of **2** to **3** involves loss of CO and shrinking of the Ru$_5$ pentagon so that the C$_2$ ligand is once again standing proud of the ring: one of the SMe groups bridges non-adjacent Ru atoms. However, it is not so easy to describe a mechanism for this change. Assuming least motion of bridging ligands, an attractive possibility is loss of CO from Ru(4), followed by a 1,2-shift of the CNBu^t ligand from Ru(3) to Ru(4), perhaps *via* an intermediate containing bridging isocyanide; the SMe group bridging Ru(4)–Ru(5) reverts to its previous position spanning the pentagon. Further discussion of other possible routes will be given elsewhere. We note that the C$_2$ ligand in **2** is still relatively unobstructed towards attack by reagents approaching from the 'bottom' of the cluster (as presented in Scheme 1) and further aspects of the reactivity of these complexes will be reported later.

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Footnotes

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‡ *Preparation and Characterisation*: Bu^{t}NC (20 μl, 0.18 mmol) was added to a solution of **1** (50 mg, 0.038 mmol) in toluene (15 cm^3). Preparative TLC (light petroleum–acetone 10:3) gave a purple band (R_f 0.5) which was recrystallised (CH$_2$Cl$_2$–MeOH) to yield [Ru$_5$(μ$_5$-C$_2$)(μ-PPh$_2$)$_2$(μ-SMe)$_2$-(Bu^{t}NC)(CO)$_{10}$] **3** (16 mg, 31%). IR: ν(CO) (cyclohexane) 2043s, 2028s, 2023vs, 2015s, 2012vs, 2004m, 1998m, 1977m, 1964(sh), 1961s, 1956(sh), 1950(sh) cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 1.02 (3 H, s, SMe), 1.59 (9 H, s, Bu^t), 1.91 (3 H, s, SMe), 7.07–7.81 (20 H, m, Ph). FAB MS: *m/z* 1358 (M$^+$), 1329–1077, (M − *n*CO)$^+$ (*n* = 1–10). A green band (R_f 0.45) was recrystallised (CH$_2$Cl$_2$–MeOH) to yield [Ru$_5$(μ$_5$-C$_2$)(μ-PPh$_2$)$_2$(μ-SMe)$_2$-(Bu^{t}NC)(CO)$_{11}$] **2** (34 mg, 65%). IR: ν(CO) (cyclohexane) 2064(sh), 2060vs, 2035s, 2024vs, 2012m, 2002w, 1987m, 1975m, 1965w, 1950w, 1944w cm^{-1}. ^{1}H NMR: δ (CDCl$_3$) 0.57 (9 H, s, Bu^t), 1.39 (3 H, s, SMe), 1.68 (3 H, s, SMe). 7.05–8.39 (20 H, m, Ph). ^{13}C NMR: δ (CDCl$_3$) 19.33, 21.65 (2 × s, SMe), 28.78 (s, *C*Me$_3$), 56.43 (s, C*Me*$_3$), 110.28 (s, C ≡ N), 146.02 (d, J_{CP} 15.7 Hz, CC), 146.96 (d, J_{CP} 14.6 Hz, CC). FAB MS: *m/z* 1386 (M$^+$), 1358–1078, [M − *n*CO]$^+$ (*n* = 1–11).

‡ *Crystal data* for **2**: dark green shard (0.32 × 0.29 × 0.07 mm), triclinic, space group $P\bar{1}$, a = 18.269(10), b = 13.406(5), c = 11.573(2) Å, α = 68.75(3), β = 86.09(3), γ = 72.39(3)°, U = 2515(3) Å^3, Z = 2, μ = 16.3 cm^{-1}, D_c = 1.83 g cm^{-3}. A unique diffractometer data set was measured at *ca.* 295 K to $2\theta_{max}$ = 50° (2θ–θ scan mode; monochromatic Mo-Kα radiation, λ 0.7107$_3$ Å); 8589 independent reflections were obtained, 5917 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R = 0.046, R_w = 0.048 based on $|F|$, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computations used the XTAL 2.6 program system[12] implemented by S. R. Hall; neutral atom complex scattering factors were employed. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/28.

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