Reactions of alkynes with cluster-bound dicarbon (C_2); X-ray structures of $[Ru_5(\mu_5\text{-}CCCPhCR)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ (R = H, Ph)

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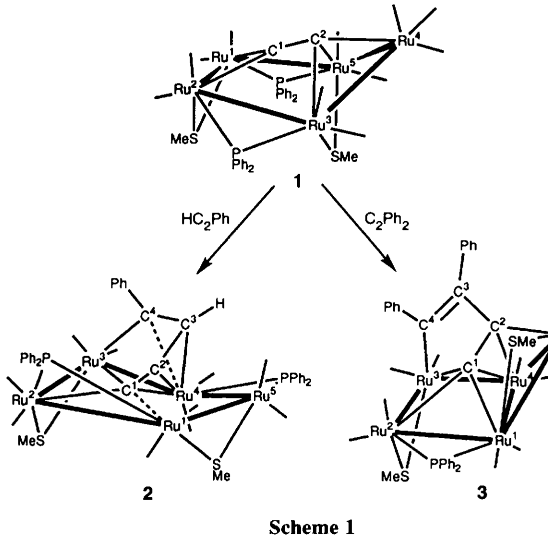
Addition of PhC≡CR (R = H, Ph) to $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2\text{-}(CO)_{11}]$ 1 results in the formation of $[Ru_5(\mu_5\text{-}CCCPhCR)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2\text{-}(CO)_{10}]$ (R = H 2, Ph 3), the μ_5-CCCPhCR ligand being formed by coupling of the alkyne with the C_2 ligand of 1; in 2 the pentagonal Ru_5 cluster of 1 is retained while 3 an extra Ru–Ru bond is formed, yielding an envelope-type structure; corresponding differences in the attachment of the organic ligand to the Ru_5 cluster are found.

Whereas the encapsulated carbon atom in carbido clusters such as $[Ru_5C(CO)_{15}]$ or $[Ru_6C(CO)_{17}]$ is relatively unreactive, incoming ligands tending to add to apices or faces,[1,2] exposed atoms, such as that in $[Fe_4C(CO)_{13}]$, for example, are more reactive.[3] Similar observations have been made for the C_2 ligand on Fe_3 clusters, which readily couple to give a C_4 complex.[4] These results are generally in accord with Muetterties's idea of modelling metal surfaces with metal cluster complexes.[5] We have described the synthesis of the pentagonal Ru_5 cluster 1 which contains a C_2 ligand relatively unhindered by other groups present.[6] In examining the reactivity of the C_2 fragment, we have described its insertion into the H–H bond of H_2,[7] the ≡C–H bonds of terminal alkenes[7,8] and (formally) a C=C bond of cyclopentadiene.[9] We report here reactions between 1 and alkynes, which proceed to give different types of products, in which the organic ligand is formed by coupling rather than by insertion.

Thus, the reaction between 1 and phenylacetylene (toluene, 110 °C, 5 h) afforded black $[Ru_5(\mu_5\text{-}CCCPhCH)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **2** (Scheme 1)‡ in 41% yield. A better yield (68%) could be obtained by reacting the acetonitrile derivative of **1**, $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}(NCMe)]$, with phenylacetylene (toluene, 100 °C, 5 min). The reaction between **1** and diphenylacetylene (toluene, 110 °C, 7 h) afforded black $[Ru_5(\mu_5\text{-}CCCPhCPh)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **3**‡ in 50% yield. Complexes **2** and **3** have been fully characterised by single-crystal X-ray studies. The molecular structures§ of **2** and **3** are shown in Figs. 1 and 2, important bond distances and angles being given in the captions. Spectroscopic properties appear to be consistent with the solid-state structures.



Scheme 1

Complex **2** retains the Ru_5 cluster found in **1**, the pentagon being decidedly non-planar but flattened compared with **1**. Around the Ru_5 ring, edges Ru(1)–Ru(5) and Ru(2)–R(3) are bridged by SMe groups, and Ru(1)–Ru(2) and Ru(3)–Ru(4) by PPh_2 groups. This contrasts with **1**, in which one of the SMe groups spans a non-bonded Ru···Ru vector.

Attack of the alkyne on C(2) in **1** has resulted in formation of the C(2)–C(3) bond; cyclisation occurs by formation of the Ru(3)–C(4) σ bond to give a five-membered ruthenacycle. In **2**, the strong interaction found between the original C_2 unit and the Ru_5 cluster in **1** is considerably weakened, as evidenced by the short C(1)–Ru(2,3) distances of 2.064(5) and 2.067(7) Å and long C(1)–Ru(1,4) separations [2.432(7), 2.301(5) Å]; the former is essentially non-bonding. Only atoms C(1,2,3) interact with Ru(4), C(4) being too far away [2.415(5) Å] for there to be any significant bonding interaction with Ru(4). The separation Ru(5)–C(2) [2.340(5) Å] is consistent with there being a weak bonding interaction. The C(3)–C(4) bond is 1.42(1) Å.

Addition of C_2Ph_2 follows a similar course to give **3**, in which C(2) of **1** is bonded to C(3) from the alkyne, with the second alkyne carbon σ-bonded to Ru(3). In this complex, however, C(1) interacts strongly with the four metal atoms [Ru(1,2,3,4)–C(1) 2.123(9)–2.218(8) Å]. In **3**, the C(3)–C(4) bond [1.36(1)

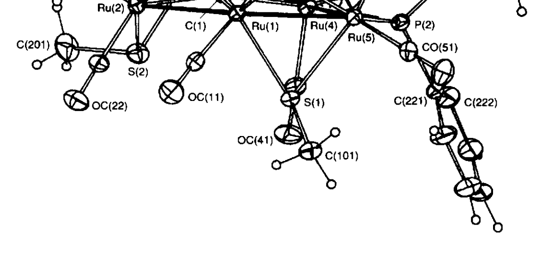


Fig. 1 Molecular structure of $[Ru_5(\mu_5\text{-}CCCPhCH)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **2**. Selected bond distances (Å) not mentioned in the text: Ru(1)–Ru(2) 2.981(1), Ru(1)–Ru(5) 2.8206(8), Ru(2)–Ru(3) 2.821(1), Ru(3)–Ru(4) 2.781(1), Ru(4)–Ru(5) 3.008(1), Ru(1)–C(2) 2.173(6), Ru(3)–C(4) 2.071(7), Ru(4)–C(2) 2.232(6), Ru(4)–C(3) 2.294(6), C(1)–C(2) 1.394(9), C(2)–C(3) 1.462(8).

Å] of the original alkyne is not bonded to Ru(4) and the separation is consistent with there being a double bond. Atom C(4) is attached to Ru(3) [2.117 (8)Å], but in this case the metallacycle is attached to Ru(4) only by an η^2 interaction from C(1)–C(2), the latter bond [1.42(1) Å] is some 0.02_5 Å longer than that found in **2** [1.394(9) Å].

The nature of the Ru_5 clusters in **2** and **3** is subtly different. The pentagon found in **2** is bent across the Ru(1)···Ru(4) vector [dihedral 171.16(3)°], but these atoms are too far apart [4.001(1) Å] for there to be any significant bonding interaction. For **3**, the Ru(1)–Ru(4) separation has closed to 2.944(2) Å, so that the cluster now has the open envelope conformation [dihedral angle 118.91(4)°]. There is also a reversal of the asymmetry of bonding of the two PPh_2 groups, and differences in the relative positions of the bridging groups around the edges of the pentagons. The average Ru–Ru separation is 2.882 Å in **2** and 2.844 Å in **3**.

In **3**, the organic ligand can be considered as an alkylidenecarbide, by analogy with the alkylidynecarbide formulation originally proposed by Carty and coworkers for μ_4-alkynyl clusters.[10] In this case, the diphenylethenyl substituent interacts further with the cluster, and Ru(5) is now found attached to C(2) [2.108(7) Å]. The situation is not so clear in the case of **2**, C(1) interacting with only three of the five Ru atoms and the organic ligand an η^3 attachment to Ru(4). The interaction of C(1)–C(2) with the cluster in **3** is stronger than in **2**. The ^{13}C NMR parameters for C(1) and C(2) in **2** and **3** are consistent with these structural differences [C(1) δ 243.8 and 325.8, C(2) δ 147.6 and 265.1, for **2** and **3**, respectively].

Although the two organic ligands in **2** and **3** are similar (both contribute six electrons to the clusters), complex **2** has 78 cluster valence electrons (c.v.e), while **3** has 76 c.v.e. The two structures represent two different ways of accommodating the ligand formed by coupling of the alkyne and C_2 groups on the Ru_5 cluster, probably as a result of the differing steric requirements of the substituent R on C(3) in **2** (R = H) *vs.* that in **3** (R = Ph). At present, we do not have any evidence for the interconversion of these two structural types.

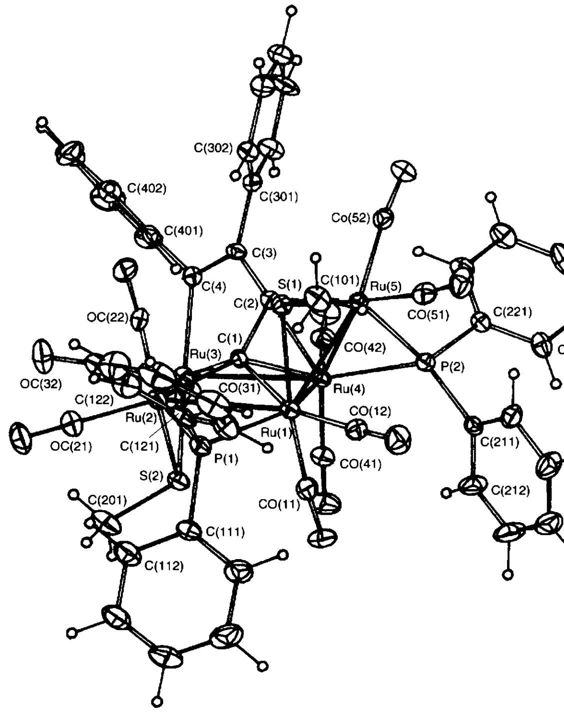


Fig. 2 Molecular structure of $[Ru_5(\mu_5\text{-CCCPh})(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_{10}]$ **3**. Selected distances (Å) not mentioned in the text: Ru(1)–Ru(2) 2.883(1), Ru(1)–Ru(5) 2.834(1), Ru(2)–Ru(3) 2.780(2), Ru(3)–Ru(4) 2.928(1), Ru(4)–Ru(5) 2.696(2), Ru(4)–C(1) 2.129(8), Ru(4)–C(2) 2.203(9), C(3)–C(4) 1.36(1).

In conclusion, we have shown that a new type of coupling between a cluster-bound C_2 ligand and alkynes leads to further examples of alkylated carbides which contain additional interactions with the cluster framework. Further examples of these novel clusters will be described elsewhere.

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Footnotes

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‡ Satisfactory analytical data were obtained for both complexes. *Selected spectroscopic data*: for **2**: ν(CO) (cyclohexane) 2046m, 2034s, 2018vs, 2001s, 1984m, 1970s, 1960m, 1942m cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.83 (3 H, d, J_{HP} 1.9 Hz, SMe), 2.86 (3 H, d, J_{HP} 3.5 Hz, SMe), 4.66 (1 H, d, J_{HP} 3.3 Hz, CCH), 6.78 (2 H, dd, J_{HP} 7.9 2.1 Hz, Ph), 6.99–7.76 (23 H, m, Ph). ^{13}C NMR ($CDCl_3$): δ 26.88 (s, 2 × SMe), 88.86 [s, C(3)], 113.09 [s, C(4)], 147.58 [s, C(2)], 243.84 [t, J_{CP} 10.8 Hz, C(1)]. FAB MS: *m/z* 1377, (M^+), 1349–1069, $(M - nCO)^+$ (n = 1–10). For **3**: ν(CO) (cyclohexane) 2046w, 2030vs, 2019s, 2008s, 1997m, 1990w, 1983w, 1966m, 1953w cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.68 (3 H, d, J_{HP} 0.4 Hz, SMe), 2.16 (3 H, s, SMe), 6.81–7.97 (30 H, m, Ph). ^{13}C NMR ($CDCl_3$): δ 23.62, 23.72 (s, 2 × SMe), 159.97 [s, C(3)], 179.52 [s, C(4)], 265.13 [s, C(2)], 325.81 [dd, J_{CP} 9.5, 4.6 Hz, C(1)]. FAB MS: *m/z* 1453, (M^+), 1425–1173, $(M - nCO)^+$ (n = 1–10).

§ *Crystal data*: **2** $[Ru_5(\mu_5\text{-CCCPhCH})(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_{10}$, $C_{46}H_{32}O_{10}P_2Ru_5S_2$, M = 1376.2; triclinic, space group $P\bar{1}$, a = 16.954(7), b = 12.806(4), c = 12.375(4) Å, α = 115.77(3), β = 92.57(3), γ = 95.87(3)°, U = 2395 $Å^3$, Z = 2, D_c = 1.91 g cm^{-3}. $2\theta_{max}$ = 50°, μ(Mo-Kα) = 15.9 cm^{-1}. Crystal dimensions 0.30 × 0.22 × 0.08 mm. 6428 observed diffractometer data [$I > 3\sigma(I)$] from 8417 data measured (absorption corrected) were refined to R = 0.035, R_w = 0.038 (statistical weights). H(3) was located in a difference map.

3 $[Ru_5(\mu_5\text{-CCCPhCPh})(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_{10}]\cdot PhMe$, $C_{52}H_{36}O_{10}P_2Ru_5S_2\cdot C_7H_8$, M = 1544.4; monoclinic, space group $P2_1/c$, a = 12.705(7), b = 24.03(1), c = 20.159(9) Å, β = 108.50(4), U = 5836 $Å^3$, Z = 4, D_c = 1.76 g cm^{-3}. $2\theta_{max}$ = 50°, μ(Mo-Kα) = 12.8 cm^{-1}. Crystal dimensions 0.08 × 0.19 × 0.27 mm. 5634 observed data [$I > 3\sigma(I)$] from 10326 data measured were refined to R = 0.042, R_w = 0.039 (statistical weights). Solvent toluene thermal motion was high and it was refined as a rigid group. 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 182/27.

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