Direct Evidence for Alkyne Coupling to the Interstitial Carbon in [$Ru_4H_2(C)(CO)_{12}$]; Crystal and Molecular Structure of [$Ru_4H(CO)_{12}(CCPhCHPh)$]

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The reaction of the 'butterfly' cluster [$Ru_4H_2(C)(CO)_{12}$] with PhCCPh, in hexane, gives [$Ru_4H(CO)_{12}(CCPhCHPh)$] in which direct coupling between the alkyne and the carbide occurs, an *X*-ray analysis of this product indicates that the organic fragment co-ordinates to the metal framework in a manner reminiscent of an allyl group.

Molecular polyhedral clusters containing an exposed carbido-atom are convenient models for examining the properties of surface carbides, and extensive studies have been carried out on tetranuclear iron carbido-clusters.[1] Studies on related tetraruthenium systems had been less extensive until the recent report of a high yield route to [$Ru_4H_2(C)(CO)_{12}$] (**1**).[2] This cluster represents a particularly attractive analogue of surface carbides since the carbido-atom in (**1**) caps a 'butterfly' arrangement of metal atoms in a fashion similar to that of a carbon atom occupying a step site on a metal surface. The work of Bradley[3] and Shriver[4] on the reactivity of the analogous iron systems shows that the reactions of the exposed carbide involve nucleophilic attack with the transfer of carbon monoxide to the carbido-centre. In contrast, in this communication, we describe the reaction of [$Ru_4H_2(C)(CO)_{12}$] (**1**) with the alkyne PhCCPh which interacts directly with the carbido-carbon and leads to carbon–carbon bond formation of a different kind.

The reaction of [$Ru_4H_2(C)(CO)_{12}$] (**1**) with PhCCPh, in hexane, at 60 °C, affords a mixture of products from which [$Ru_4H(CO)_{12}(CCPhCHPh)$] (**2**) was isolated by t.l.c. in 60—70% yield, and was initially characterised from spectroscopic data.† Black crystals, suitable for a single crystal *X*-ray analysis, were obtained by crystallisation from hexane solution at −30 °C. The molecular structure‡ of (**2**) is shown in Figure 1 which includes some selected bond parameters. The

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† *Selected spectroscopic data*: i.r. ν(CO) (hexane): 2093m, 2062vs, 2052vs, 2048sh, 2031s, 2012s, 2000m, 1970w, 1832w, br cm^{-1}. ^{1}H n.m.r. δ (CD_3COCD_3) 5.15 (s, 1H), 7.03 (m, 2H), 7.24 (m, 5H), 7.41 (m, 3H), −21.48 (s, 1H); M^+ *m/z* 936 (^{102}Ru).

‡ *Crystal data*: $C_{27}H_{12}O_{12}Ru_4$, M = 932.65, triclinic, space group $P\bar{1}$ (No. 2), a = 8.943(3), b = 13.008(4), c = 13.807(5) Å, α = 85.81(3), β = 74.07(3), γ = 75.70(3)°, U = 1496.6(9) Å^3, Z = 2, D_c = 2.067 g cm^{-3}, F(000) = 892, λ(Mo-K_α) = 0.71073 Å, μ(Mo-K_α) = 19.9 cm^{-1}, 5690 reflections collected on a Nicolet R3 mV diffractometer in the range $5 \leqslant 2\theta \leqslant 50°$. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by full-matrix least squares (all non-hydrogen atoms anisotropic) to R = 0.029, R_w = 0.032 [$w^{-1} = \sigma^2(F_o) + 0.001\, F_o^2$], for 4753 unique observed reflections [$F > 4\sigma(F)$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

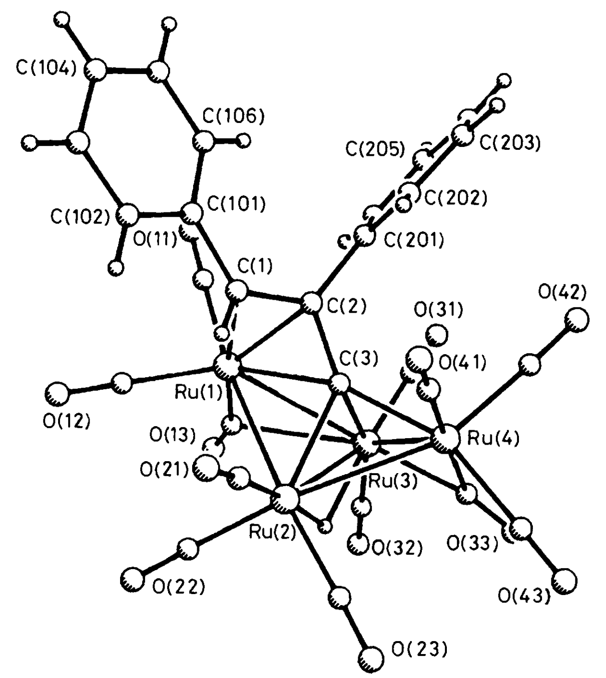

Figure 1. The molecular structure of $[Ru_4H(CO)_{12}(CCPhCHPh)]$ (**2**) showing the atom numbering scheme. Bond distances: Ru(1)–Ru(2), 2.875(3); Ru(1)–Ru(3), 2.907(3); Ru(2)–Ru(3), 2.846(3); Ru(2)–Ru(4), 2.845(3); Ru(3)–Ru(4), 2.812(3); Ru(1)–C(1), 2.363(4); Ru(1)–C(2), 2.235(4); Ru(1)–C(3), 2.223(5); Ru(2)–C(3), 2.168(5); Ru(3)–C(3), 2.202(4); Ru(4)–C(3), 2.077(4); C(1)–C(2), 1.402(5); C(2)–C(3), 1.445(6); Ru(2)–H(23), 1.72(4); Ru(3)–H(23), 1.79(5); Ru(1)....Ru(4), 4.236(3) Å. Bond angles: Ru(2)–Ru(1)–Ru(3), 59.0(1); Ru(1)–Ru(2)–Ru(3), 61.1(1); Ru(1)–Ru(2)–Ru(4), 95.6(1); Ru(3)–Ru(2)–Ru(4), 59.2(1); Ru(1)–Ru(3)–Ru(2), 59.9(1); Ru(1)–Ru(3)–Ru(4), 95.6(1); Ru(2)–Ru(3)–Ru(4), 60.4(1); Ru(2)–Ru(4)–Ru(3), 60.4(1); Ru(1)–C(1)–C(2), 67.4(2); Ru(1)–C(2)–C(1), 77.3(2); Ru(1)–C(2)–C(3), 70.6(2); C(1)–C(2)–C(3), 119.2(4); Ru(1)–C(3)–Ru(2), 81.8(1); Ru(1)–C(3)–Ru(3), 82.2(1); Ru(2)–C(3)–Ru(3), 81.3(1); Ru(1)–C(3)–Ru(4), 160.3(2); Ru(2)–C(3)–Ru(4), 84.2(2); Ru(3)–C(3)–Ru(4), 82.1(1); Ru(2)–H(23)–Ru(3), 108(2)°. Dihedral angle between Ru(1)Ru(2)Ru(3) and Ru(2)Ru(3)Ru(4) planes is 117.2°.

four Ru atoms adopt a 'butterfly' arrangement with the hydride, which was located directly in the analysis, bridging the 'hinge' Ru(2)–Ru(3) edge. A carbon atom, C(3), presumed to be the original carbido-carbon in (**1**), caps the 'butterfly' framework, and is also bound to a carbon atom, C(2), of the diphenylacetylene ligand, which interacts in a π-bonding mode with a 'wingtip' metal atom, Ru(1). This C(1)C(2)C(3) unit may also be viewed as a π-allylidene ligand bound η^3 to Ru(1), one terminal carbon, C(3), of which is also co-ordinated to the Ru(2)Ru(3)Ru(4) triangular unit. The cluster-bound hydride is the source of the H on C(1). The bond parameters within this C_3 unit are similar to those found in other allyl-substituted clusters,[5] although this type of bonding mode including the carbido-like interaction of C(3) has not been observed previously in clusters of the iron triad. Within the metal framework of (**2**), the Ru(1)–Ru(2) and Ru(1)–Ru(3) edges are *ca.* 0.04 Å longer than the two other 'hinge–wingtip' edges, the latter being similar in length to those found in $[Ru_4C(CO)_{13}]^2$ and a number of derivatives.[6] The dihedral angle between the two 'butterfly wings' is *ca.* 15° greater than in related tetrairon carbido-clusters,[1] presumably reflecting the bonding requirements of the allylic ligand.

The mechanism by which the reaction occurs is not well understood but appears to involve an electrophilic attack at the alkyne by the carbido-cluster. Further investigations are in progress with a range of unsaturated organic molecules to establish the detailed mechanism.

We thank the S.E.R.C. for financial support.

Received, 23rd May 1988; Com. 8/02022A

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