

Cleavage of the C≡C bond in the reaction of ferrocenylacetylene with Ru₃(CO)₁₂. Crystal structure of the carbyne cluster Ru₃H(CFc)(CO)₁₀

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Recently, it was demonstrated^{1,2} that the reaction of Ru₃(CO)₁₂ with excess ferrocenylacetylene FcC≡CH (Fc is ferrocenyl) in refluxing hexane affords the Ru₂(C₄H₂Fc₂)(CO)₆, Ru₂(C₄H₂Fc₂CO)(CO)₆, Ru₃H(C₂Fc)(CO)₉ (1), and Ru₄H(C₂Fc)(CO)₁₂ (2) com-

plexes. These complexes contain ligands formed as a result of activation of the C—H bond of alkyne, dimerization of alkyne molecules, or coupling with carbon monoxide. In this work, we report the preparation of the carbyne cluster Ru₃H(CFc)(CO)₁₀ (3) by this reaction;

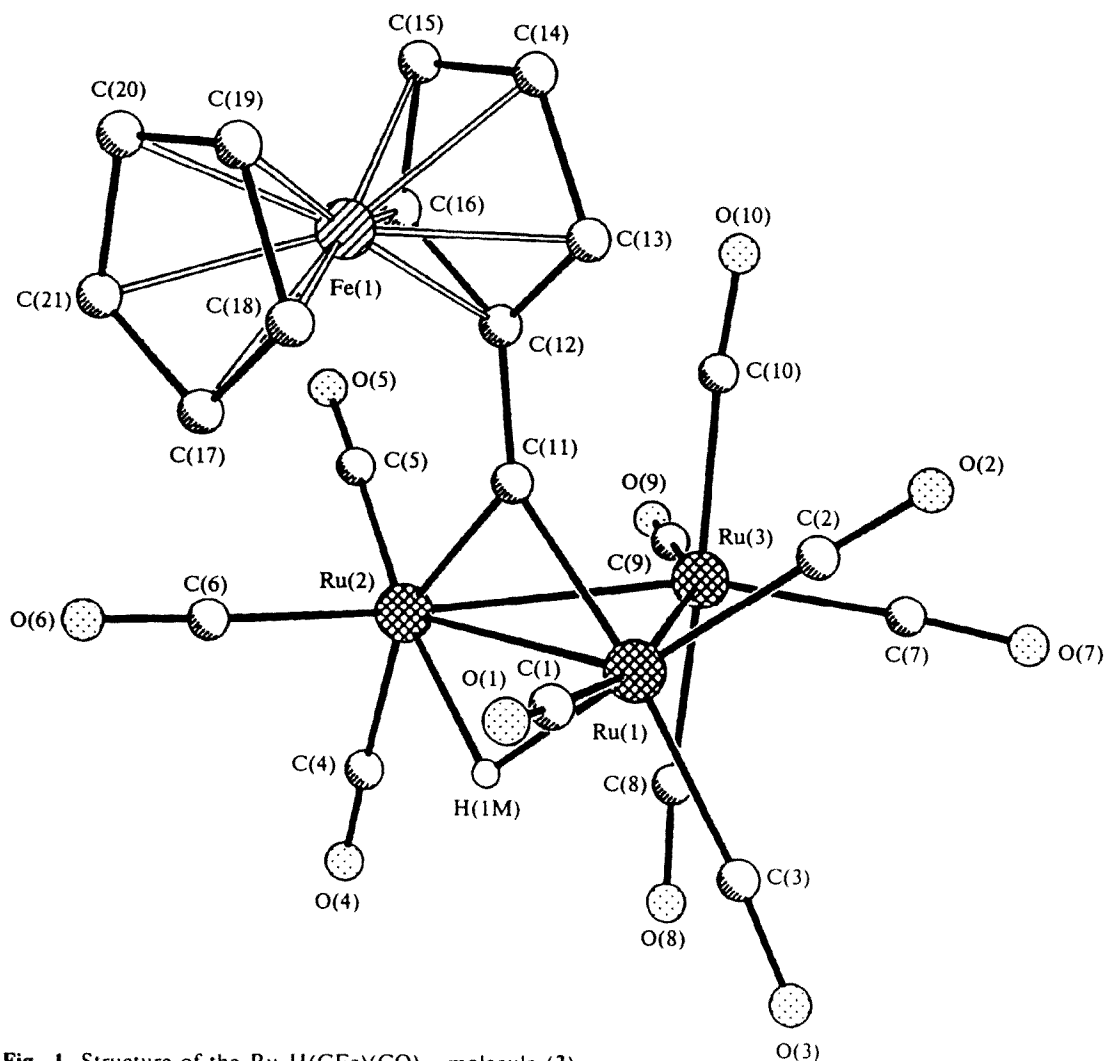


Fig. 1. Structure of the Ru₃H(CFc)(CO)₁₀ molecule (3).

formation of **3** should involve the cleavage of the $\text{C}\equiv\text{C}$ bond in the alkyne molecule.

When the products of the reaction of $\text{Ru}_3(\text{CO})_{12}$ with ferrocenylacetylene were chromatographed on silica gel, compound **3** was separated as a thin crimson-colored band, which was immediately followed by an orange band (complex **1**) and then, by a green band (complex **2**). Evaporation of the eluent (hexane) afforded cluster **3** as dark red crystals.

The carbonyl region of the IR spectrum of compound **3** (in hexane) is rather complex, which is indicative of the cluster nature of **3** [$\nu(\text{CO})/\text{cm}^{-1}$: 2099 w, 2078 v.s., 2059 v.s., 2053 s (sh), 2021 v.s., 2011 v.s., 2004 v.s., and 1989 m (br)]. The ^1H NMR spectrum (in CDCl_3) has the signals of the ferrocenyl group at δ 4.96 (t, 2 H), 4.85 (t, 2 H), and 4.20 (s, 5 H) and the signal of the hydride ligand at δ -13.95 (s, 1 H).

Cluster **3** was characterized by complete X-ray structural analysis: $\text{C}_{21}\text{H}_{10}\text{FeO}_{10}\text{Ru}_3$, crystals are triclinic, space group $P\bar{1}$, at 293 K $a = 9.096(4)$ Å, $b = 10.295(4)$ Å, $c = 14.566(4)$ Å, $\alpha = 97.07(3)^\circ$, $\beta = 96.86(3)^\circ$, $\gamma = 115.27(3)^\circ$, $V = 1201.5(7)$ Å³, $Z = 2$, $d_{\text{calc}} = 2.160$ g cm⁻³; $R_1 = 0.0513$ for 2162 reflections with $I > 2\sigma(I)$, $wR_2 = 0.1199$. The structure of complex **3** is shown in Fig. 1; the principal bond lengths are given in Table 1.

Molecule **3** contains an almost equilateral triangle formed by Ru atoms, one side of which is bonded through the bridging hydride and carbyne ligands. Two Ru atoms coordinate three terminal CO ligands each; the third Ru atom coordinates four carbonyl groups. The dihedral angle between the $\text{Ru}(1)\text{Ru}(2)\text{C}(11)$ plane and the plane of the Ru_3 triangle is 91.9° ; the $\text{C}(11)\dots\text{Ru}(3)$ distance between the carbyne C atom and the Ru atom of the $\text{Ru}(\text{CO})_4$ unit is $2.78(1)$ Å. This distance is too large to assume the existence of a normal bond between the $\text{C}(11)$ and $\text{Ru}(3)$ atoms. However, there is a slight twist of the $\text{Ru}(\text{CO})_4$ unit with respect to the $\text{Ru}(3)$ atom, as a result of which the axial $\text{C}(10)-\text{O}(10)$ ligand forms a $\text{Ru}(\text{mdpt})\dots\text{Ru}(3)-\text{C}(10)$ angle of 100.0° , while the other axial ligand forms a $\text{Ru}(\text{mdpt})\dots\text{Ru}(3)-\text{C}(8)$ angle of 76.8° . The analogous distortion of the $\text{Os}(\text{CO})_4$ unit successively decreases in the series of the $\text{Os}_3\text{H}(\text{CH})(\text{CO})_{10}$ (**4**), $\text{Os}_3\text{H}(\text{CPh})(\text{CO})_{10}$, and $\text{Os}_3\text{H}(\text{CCH}_2\text{CHMe}_2)(\text{CO})_{10}$ clusters, in which the μ_3 -carbyne distortion is considered as semitriple-bridging;³⁻⁵ this ligand is absent⁶ in the $\text{Os}_3\text{H}[\text{CC}(\text{Ph})=\text{C}=\text{C}(\text{Ph})\text{Re}(\text{CO})_4\text{PMe}_2\text{Ph}](\text{CO})_{10}$ molecule.

A number of carbyne clusters of ruthenium of composition $\text{Ru}_3\text{H}(\text{CX})(\text{CO})_{10}$ have been described. Based on the spectral data the structure with the μ_3 -carbyne

Table 1. Principal bond lengths (d) in molecule **3**

Bond	$d/\text{\AA}$	Bond	$d/\text{\AA}$
$\text{C}(11)-\text{Ru}(1)$	1.99(1)	$\text{H}(1\text{M})-\text{Ru}(2)$	1.92(9)
$\text{C}(11)-\text{Ru}(2)$	2.01(1)	$\text{Ru}(1)-\text{Ru}(2)$	2.825(2)
$\text{C}(11)-\text{C}(12)$	1.42(1)	$\text{Ru}(1)-\text{Ru}(3)$	2.812(2)
$\text{H}(1\text{M})-\text{Ru}(1)$	1.76(9)	$\text{Ru}(2)-\text{Ru}(3)$	2.822(2)

ligand, which is analogous to that found for compound **4**, was suggested for the rather unstable $\text{Ru}_3\text{H}(\text{CH})(\text{CO})_{10}$ complex.⁷ The amino- and alkoxycarbyne complexes $\text{Ru}_3\text{H}(\text{CNMe}_2)(\text{CO})_{10}$ and $\text{Ru}_3\text{H}(\text{COMe})(\text{CO})_{10}$ contain the μ_2 -carbyne ligand.^{8,9}

Therefore, in the series of tri ruthenium clusters as well as in the series of tri osmium clusters of composition $\text{M}_3\text{H}(\text{CX})(\text{CO})_{10}$, the character of the bonding of the carbyne ligand to the triangle formed by the metal atoms is determined by the electronic properties of the X substituent at the carbyne C atom.

Note that the formation of complex **3** is the first example of the cleavage of the $\text{C}\equiv\text{C}$ bond in an alkyne molecule by a tri ruthenium cluster and the synthesis of a carbyne cluster of ruthenium immediately from alkyne.

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