

Preliminary communication

STRUCTURAL ISOMERS OF $\text{H}_2\text{Ru}_4\text{C}(\text{CO})_{12}$; X-RAY CRYSTAL STRUCTURE OF $\text{Ru}_4\text{C}(\text{CO})_{13}$

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(Received February 10th, 1986)

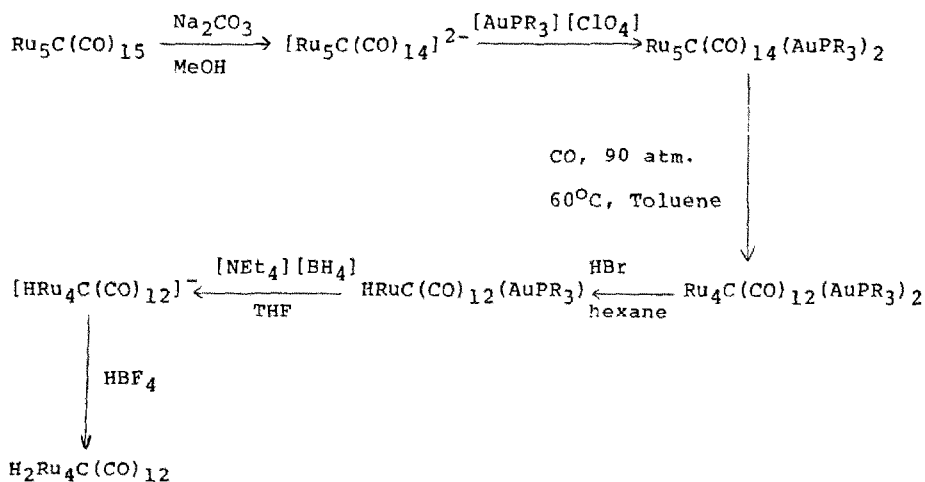
Summary

The anionic hydrido cluster $[\text{HRu}_4\text{C}(\text{CO})_{12}]^-$ and the neutral dihydride $\text{H}_2\text{Ru}_4\text{C}(\text{CO})_{12}$ have been prepared in good yield. Spectroscopic studies of $\text{H}_2\text{Ru}_4\text{C}(\text{CO})_{12}$ indicate that two isomers are formed, one with a structure similar to that of $\text{H}_2\text{Fe}_4\text{C}(\text{CO})_{12}$ the other with metal-bonded hydrido ligands. The parent carbido cluster $\text{Ru}_4\text{C}(\text{CO})_{13}$ has been synthesised from the hydrido anion, and has a structure similar to that of the analogous iron cluster $\text{Fe}_4\text{C}(\text{CO})_{13}$.

Experimental observations [1–5] and simple MO calculations [6–8] have shown that the lower the nuclearity of a carbido cluster the greater the likelihood of the carbon becoming reactive. Thus, carbide reactivity is predominant in the group of clusters containing a “ Fe_4C ” core, and includes the formation of both C–H and C–C bonds [9]. It was of some interest, therefore to examine the chemistry of the related “ Ru_4C ” systems in order to throw light on the effects of variations of the metal on reactivity patterns. We report here the preparation and characterisation of $\text{H}_2\text{Ru}_4\text{C}(\text{CO})_{12}$, which we have obtained in two isomeric forms, and show that the parent carbidocarbonyl, $\text{Ru}_4\text{C}(\text{CO})_{13}$, is isostructural with the iron analogue.

Attempts to synthesize ruthenium analogues of the tetrairon clusters $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$, $\text{Fe}_4\text{C}(\text{CO})_{13}$, and $\text{H}_2\text{Fe}_4\text{C}(\text{CO})_{13}$ by strategies similar to those which have proved successful for the iron systems failed. This is due in part to the different structural and electronic behaviour of $[\text{Ru}_4(\text{CO})_{13}]^{2-}$ on protonation, and in part to the higher stabilities of systems which contain either “ Ru_5C ” or “ Ru_6C ” core frameworks towards degradation. We previously reported the degradation of a “ Ru_5C ” system using the mixed-metal

cluster $\text{Ru}_5\text{C}(\text{CO})_4(\text{AuPR}_3)_2$ to yield $\text{H}_2\text{Ru}_4\text{C}(\text{CO})_{12}$ [10]. The preparation of the hydridocarbido carbonyl is effected by the sequence of reactions shown in Scheme 1.



SCHEME 1. The Conversion of $\text{Ru}_5\text{C}(\text{CO})_{15}$ to $\text{H}_2\text{Ru}_4\text{C}(\text{CO})_{12}$.

As a synthetic route a six step sequential synthesis is not ideal. However, with optimisation of the yield for each step, an overall yield of $\text{H}_2\text{Ru}_4\text{C}(\text{CO})_{12}$ from $\text{Ru}_5\text{C}(\text{CO})_{15}$ of ~30% was achieved.

Repeated attempts to obtain crystalline samples of $\text{H}_2\text{Ru}_4\text{C}(\text{CO})_{12}$ suitable for X-ray analysis were not successful, and only non-crystalline powders were produced. Consequently, the complex was characterised on the basis of its spectroscopic properties and on a comparison with related "Ru₄C" compounds with established structures [11]. The ¹H NMR spectrum of the product obtained by the protonation of $[\text{HRu}_4\text{C}(\text{CO})_{12}]^-$ exhibits two sets of doublets; the position and relative intensities of these doublets being solvent dependent (the data reported below are for deprotonation at 25°C). We consider that these sets of doublets arise from two different isomers present in solution, and suggest that the structures of these isomers are those shown in Fig. 1 with formulae $\text{HRu}_4\text{C}(\text{H})(\text{CO})_{12}$ and $\text{H}_2\text{Ru}_4\text{C}(\text{CO})_{12}$. Isomer 2 was assigned the structure shown on the basis of the similarity between its spectrum and that of $\text{H}_2\text{Fe}_4\text{C}(\text{CO})_{12}$ (δ -0.78 d, J 0.9 Hz, δ -22.76, J 0.9 Hz). In particular a direct C-M interaction is indicated by both the chemical shift value and the presence of ¹³C satellites either side of H_{2b} (δ -0.78, $J(\text{C-H})$ 100 Hz; cf. $\text{HFe}_4\text{C}(\text{H})(\text{CO})_{12}$ δ -1.31, $J(\text{C-H})$ 103.4 Hz).

For the second isomers 1, the observed chemical shift values are typical of hydrido ligands occupying bridging positions in the cluster (δ -16.44 d, J 2.9 Hz, δ -22.89 d, J 2.9 Hz); the signal at highest field correlating with other hinged-bridging hydrides in clusters with a butterfly geometry. The signal at lower field is similar to that observed for a H-ligand bonded to a Ru₃ triangle. Further, there is no evidence of ¹H-¹³C coupling in the ¹³C spectrum of 1, leading us to conclude that the most probable structure for this species is that shown.

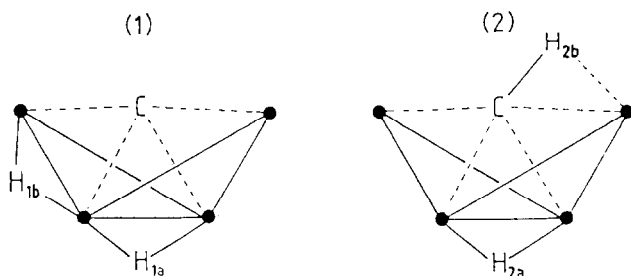


Fig. 1. Proposed structures for the two isomers of $\text{H}_2\text{Ru}_4\text{C}(\text{CO})_{12}$.

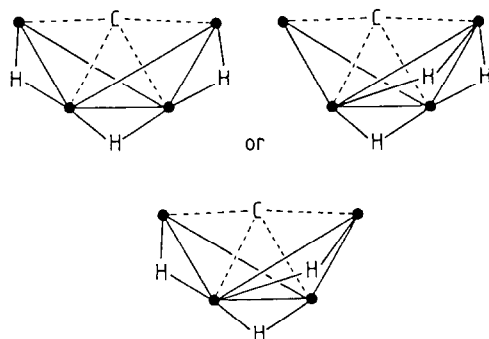


Fig. 2. Possible structures of the cation $[\text{H}_3\text{Ru}_4\text{C}(\text{CO})_{12}]^+$.

The ^1H NMR data correlates well with the data recorded for the closely related butterfly cluster $\text{H}_3\text{Ru}_4\text{N}(\text{CO})_{11}$ ($\delta -15.29$, $\delta -23.11$ ppm) where the hydride ligands are known to bridge the hinge and two wing-tip bonds. At -80°C the limiting $^{13}\text{C}\{-^1\text{H}\}$ spectrum of **1** (recorded in CD_2Cl_2 to minimise the proportion of **2**) exhibits twelve distinct CO resonances in addition to that of the carbido atom consistent with structure **1**. The equilibrium constant $K = [\text{isomer 1}]/[\text{isomer 2}] = 6.7$ (toluene- d_8 , 0°C) has been calculated from ^1H NMR signal intensities. This is dependent on solvent, but indicates that in contrast to iron, the isomer $\text{H}_2\text{Ru}_4\text{C}(\text{CO})_{12}$ is the major isomer ($\sim 85\%$) for ruthenium.

Protonation of **1** and **2** in $\text{CF}_3\text{SO}_3\text{H}$ leads to the formation of two new cationic species, **3** and **4**, of formula $[\text{H}_3\text{Ru}_4\text{C}(\text{CO})_{12}]^+$. The ratio of these isomers is comparable to that found for **1** and **2**, suggesting that **3** and **4** are the direct products of H^+ addition to **1** and **2**, respectively. The ^1H NMR spectra of these cations suggests that each isomer contains an H-hinge bridge (triplet) which is coupled to two Ru(hinge)—Ru(wingtip) bridging hydrides (doublet). Three possible structures consistent with these observations are shown in Fig. 2.

Clearly, there are fundamental differences between the iron and ruthenium " M_4C " systems. These differences may be simply correlated with the change in basicity of the M_4 units, although a more detailed understanding of their fundamental differences must await the result of further more detailed consideration. The hydridoruthenium carbide provides an obvious precursor for the preparation of the parent carbonyl carbido cluster, $\text{Ru}_4\text{C}(\text{CO})_{13}$. This com-

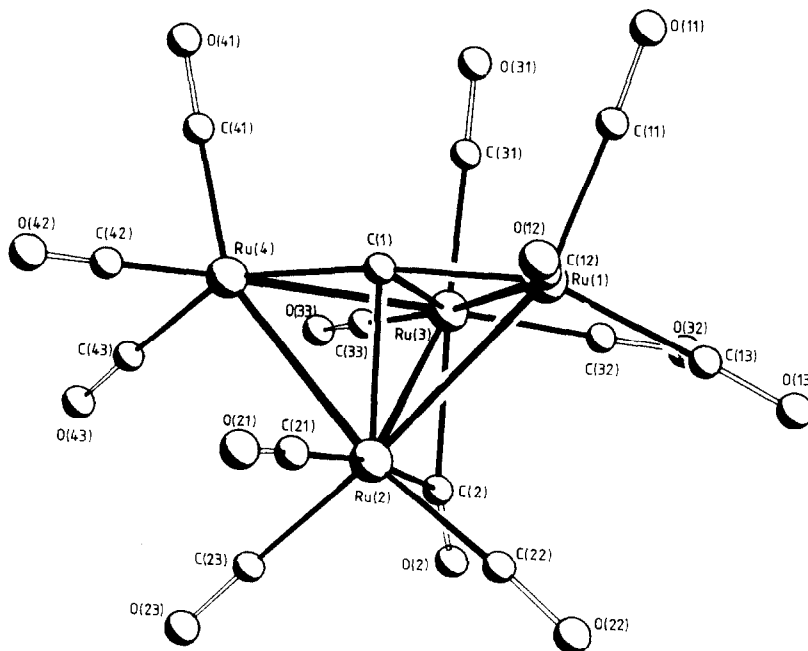


Fig. 3. The molecular structure of $\text{Ru}_4\text{C}(\text{CO})_{13}$. Bond lengths: Ru(1)—Ru(2), 2.814(1); Ru(1)—Ru(3), 2.818(1); Ru(2)—Ru(3), 2.797(1); Ru(2)—Ru(4), 2.807(1); Ru(3)—Ru(4), 2.822(1); Ru(1)—C(1), 1.934(4); Ru(2)—C(1), 2.155(4); Ru(3)—C(1), 2.173(4); Ru(4)—C(1), 1.930(4); Ru(2)—C(2), 2.201(6); Ru(3)—C(2), 2.133(6); C(2)—O(2), 1.130(6) Å. Bond angles: Ru(1)—C(1)—Ru(2), 86.8(2); Ru(1)—C(1)—Ru(3), 86.5(2); Ru(2)—C(1)—Ru(3), 80.5(1); Ru(1)—C(1)—Ru(4), 171.2(3); Ru(2)—C(1)—Ru(4), 86.6(2); Ru(3)—C(1)—Ru(4), 86.7(2); Ru(2)—C(2)—Ru(3), 80.4(2) $^\circ$. Dihedral angle between Ru(1)Ru(2)Ru(3) and Ru(2)Ru(3)Ru(4) planes is 104.1(2) $^\circ$.

pond is obtained in 60% yield by the controlled oxidation of the anion $[\text{HRu}_4\text{C}(\text{CO})_{12}]^-$ with ferricinium tetrafluoroborate in ethylene trichloride in a CO atmosphere. The X-ray structure shows that the complex is isostructural with the iron compound $\text{Fe}_4\text{C}(\text{CO})_{13}$ [12]. The molecular structure* of $\text{Ru}_4\text{C}(\text{CO})_{13}$ is shown in Fig. 3, which includes some important bond parameters. The four Ru atoms define a "butterfly" and the carbide is coordinated to all four metal atoms. The "hinge" vector, Ru(2)—Ru(3), of this framework is bridged by a carbonyl group. The remaining twelve carbonyl groups display essentially linear geometries, and are terminally coordinated to the metals; three to each Ru atom. The trends in metal—metal bond distances are similar to those in the iron analogue [12], with the carbonyl bridged "hinge" bond being ca. 0.02 Å shorter than the average distance (2.815 Å) for the four

*Crystal data. $\text{C}_{14}\text{O}_{13}\text{Ru}_4$, $M = 780.42$, triclinic, space group $P\bar{1}$ (No. 2), a 9.282(1), b 9.400(1), c 13.965(1) Å, α 77.94(1) $^\circ$, β 74.50(1) $^\circ$, γ 64.26(1) $^\circ$, V 1051.6 Å 3 , D_c 1.484 g cm $^{-3}$, $Z = 2$, $F(000) = 728$, $\mu(\text{Mo-K}\alpha)$ 0.71069 Å; $\mu(\text{Mo-K}\alpha)$ 27.98 cm $^{-1}$. Crystal dimensions: 0.28 × 0.29 × 0.30 mm. 5090 data measured on a Stoe—Siemens four-circle diffractometer, corrected for absorption 4053 observed unique reflections with $|F| > 4\sigma(F)$. Structure solved by a combination of centrosymmetric direct methods and Fourier difference techniques, and refined by full-matrix least squares, with all atoms assigned anisotropic thermal parameters, to $R = 0.033$ and $R_w = 0.031$.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

Ru(hinge)—Ru(wingtip) edges. In both the Fe and Ru complexes the M(wingtip)—C(carbide) distances are significantly shorter than the M(hinge)—C(carbide) distances. This trend in M—C distances is also followed in the series of clusters $\text{Ru}_4\text{C}(\text{CO})_{12}(\mu\text{-AuPR}_3(\mu\text{-X}))$ ($\text{X} = \text{H}, \text{AuPR}_3, \text{I}$) [10]. The main difference between the Ru—Ru distances within this series and these in the parent carbide, $\text{Ru}_4\text{C}(\text{CO})_{13}$, is the length of the “hinge” bond. The Ru(2)—Ru(3) distance is shorter than the equivalent distance in any of the three complexes (2.856(1) Å for $\text{X} = \text{H}$; 3.252(3) Å for $\text{X} = \text{AuPR}_3$; 3.427(1) Å for $\text{X} = \text{I}$). This suggests a greater direct Ru—Ru orbital interaction in the carbonyl-bridged system than in the other cases.

We thank the S.E.R.C. for financial support and I.C.I. plc for an award (to A.G.C.)

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