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Preliminary communication

AN IMPROVED SYNTHESIS OF THE HEXARUTHENIUM CARBIDO CLUSTER $Ru_6C(CO)_{17}$; X-RAY STRUCTURE OF THE SALT $[Ph_4As]_2[Ru_6C(CO)_{16}]$

BRIAN F.G. JOHNSON, JACK LEWIS*, STEPHEN W. SANKEY, KENNETH WONG,
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)

MARY McPARTLIN and WILLIAM J.H. NELSON
The Chemistry Department, The Polytechnic of North London, London N7 8DB (Great Britain)

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Summary

Reaction of ethylene with $Ru_3(CO)_{12}$ under conditions of moderate pressure and temperature gives $Ru_6C(CO)_{17}$ (I) in ca. 70% yield. Reaction of this carbonyl carbido species with base gives the dianion $[Ru_6C(CO)_{16}]^{2-}$; X-ray analysis of the $[Ph_4As]^+$ salt indicates an octahedral array of metal atoms with the carbon at the centre of the octahedron and twelve terminal and four edge bridging carbonyl ligands giving an approximate overall C_{2v} symmetry.

In contrast to dodecarbonyltriosmium, which undergoes pyrolysis to form a series of cluster carbonyl compounds based on Os_5, Os_6, Os_7 and Os_8 units, dodecacarbonyltriruthenium undergoes thermal decomposition in vacuo to produce low yields of the hexaruthenium carbido cluster $Ru_6C(CO)_{17}$ (I) [1]; the source of the carbido atom is carbon monoxide and CO_2 is produced during pyrolysis. We report an improved synthesis of this cluster from $Ru_3(CO)_{12}$ by reaction with ethylene under conditions of moderate pressure (~ 30 atm) and temperature (150°C); I is the major product of this reaction in yields approaching 70%, a significant improvement on previously reported methods [1]. Mass spectrometry indicates that the products obtained in low yield are mainly Ru_6 species but an Ru_4 cluster has also been isolated; X-ray analyses of these compounds are currently being undertaken.

The hexaruthenium carbide(I) reacts with $OMe^-(Na_2CO_3/MeOH)$ via attack at a coordinated carbonyl group, to yield the anion $[Ru_6C(CO)_{16}(CO_2Me)]^-$ which may be isolated as the $[(Ph_3P)_2N]^+$ salt. Subsequent reaction of this anion with aqueous base yields the dianion $[Ru_6C(CO)_{16}]^{2-}$ which was separated as the

$[(Ph_3P)_2N]^+$ and $[Ph_4As]^+$ salts. The structure of the dianion is of interest in that it has the same number of CO ligands and an electronic equivalence to the clusters $[Fe_6C(CO)_{16}]^{2-}$ [2] and $Rh_6(CO)_{16}$ [3]. Protonation of $[Ru_6C(CO)_{16}]^{2-}$ by H_2SO_4 at −30°C in acetonitrile leads to the formation of a red crystalline material which on the basis of analytical and spectroscopic data (^1H, NMR, τ 25.71) may be formulated as the dihydride $H_2Ru_6C(CO)_{16}$.

X-ray analysis of $[Ph_4As]_2[Ru_6C(CO)_{16}]$ (II) shows the dianion to have the structure illustrated in Figure 1. The carbido atom is situated at the centre of an octahedral array of Ru atoms and of the sixteen carbonyl groups twelve are terminal and four are asymmetrically edge bridging. This arrangement contrasts with that in $Rh_6(CO)_{16}$ where four carbonyl ligands are face rather than edge bridging. Surprisingly this carbonyl distribution is different from that in the tetramethyl ammonium salt of $[Ru_6C(CO)_{16}]^{2-}$ (III) in which the dianion is isostructural with its Fe analogue and has only *three* edge-bridging carbonyl ligands, the remaining thirteen being terminal [4].

The $[Ru_6C(CO)_{16}]^{2-}$ salts of $[Ph_4As]^+$ and $[Me_4N]^+$ therefore appear to be the first example of two different isomeric forms of a metal carbonyl cluster anion, differing only in their carbonyl distribution, to be characterised by X-ray analysis. No details of the Ru—CO bond lengths in III have been published.

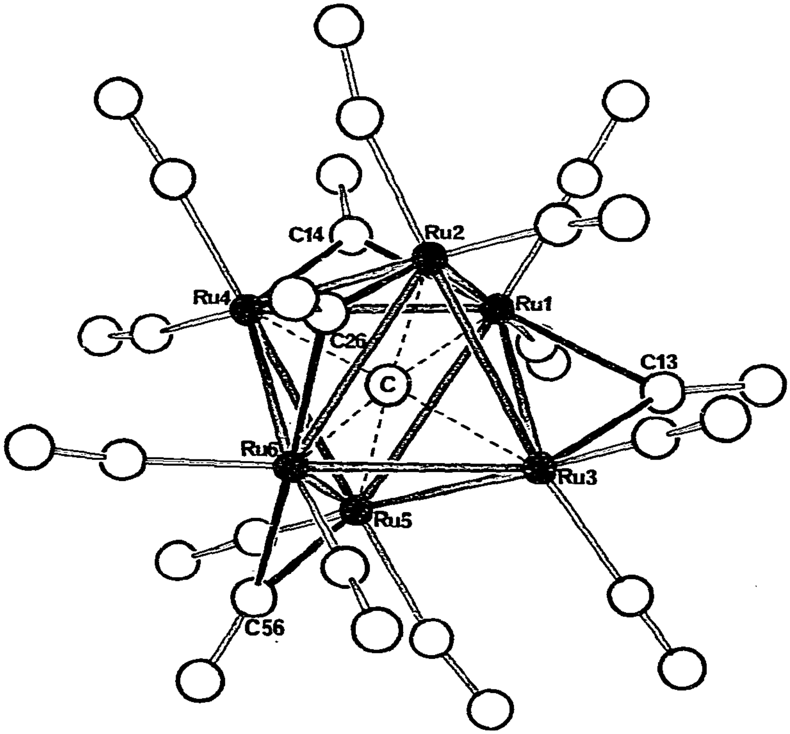

Fig. 1. The structure of the carbido dianion $[Ru_6C(CO)_{16}]^{2-}$ which has approximate C_{2v} symmetry. Important bond lengths are: Ru—Ru (mean) 2.89, Ru—C (mean) 2.05, Ru—CO (terminal, mean) 1.895, Ru(1)—C(13) 2.327, Ru(3)—C(13) 2.015, Ru(1)—C(14) 2.009, Ru(4)—C(14) 2.187, Ru(2)—C(26) 2.104, Ru(6)—C(26) 2.273, Ru(5)—C(56) 1.996 and Ru(6)—C(56) 2.070 Å.

However, comparison of its isostructural $[Fe_6C(CO)_{16}]^{2-}$ analogue (IV), Figure 2, with that of the $[Ru_6C(CO)_{16}]^{2-}$ dianion in II, Figure 1, shows that the only gross difference is the overall arrangement of the carbonyls in these two $[M_6C(CO)_{16}]^{2-}$ clusters is that the bridging carbonyl CO(13) in the Ru dianion in II corresponds to the terminal carbonyl CO(7) in the Fe structure. The mean Fe(4)—C(7) bond length in the two independent Fe clusters is 1.55(7) Å and significantly this "terminal" carbonyl is very close to a second iron atom so that the mean Fe(3) ...C(7) contact {2.65(7) Å} is considerably shorter than any other non-bonded contact within the dianion. The X-ray analysis of the tetramethylammonium salt of IV was very problematic due to poor diffraction and decomposition [2]. A more accurate location of the C in this CO ligand would be expected to show a longer, more normal, Fe(4)—C(7) bond length close to the mean value of 1.72 Å observed for the other terminal Fe—C distances, and this would correspondingly produce an even shorter Fe(3) ... C(7) contact if a normal C—O bond length is retained. As the three bridging carbonyls are very asymmetric in IV with the Fe—C bond lengths ranging from 1.78 to 2.33 Å it is possible that CO(7) should be regarded as a fourth asymmetric edge bridge. The

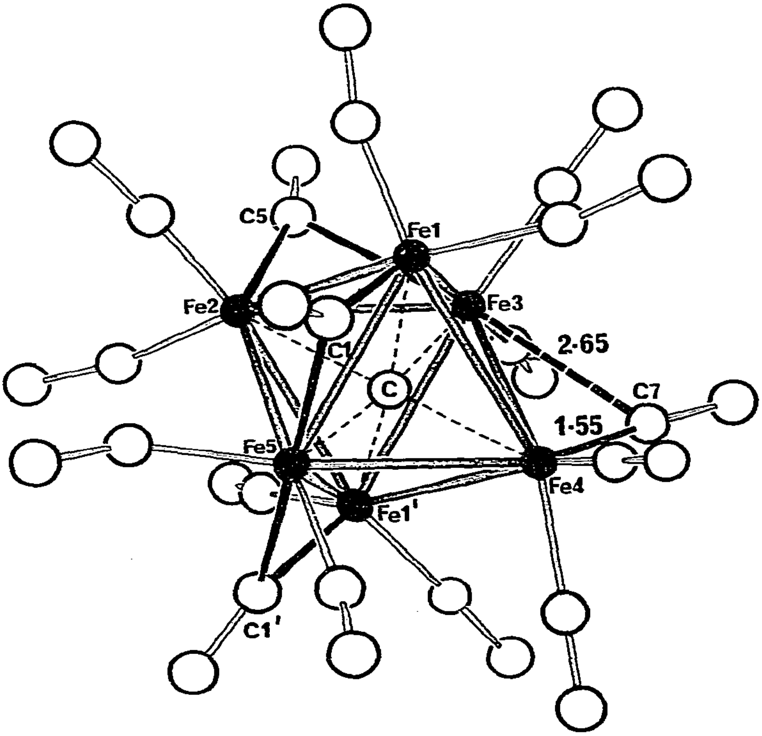

Fig. 2. The reported structure [2] of the carbido dianion $[Fe_6C(CO)_{16}]^{2-}$ drawn in a comparable manner to Figure 1 to emphasize the similarity between the two structures. The Fe—C bond lengths (mean value from two independent clusters) in the bridging carbonyls are Fe(5)—C(1) 2.188, Fe(1)—C(1) 1.785, Fe(5)—C(1') 2.188, Fe(1')—C(1') 1.785, Fe(4)—C(7) 1.554, Fe(3)—C(7) 2.650, Fe(2)—C(5) 1.937 and Fe(3)—C(5) 2.165. For ease of comparison with II symmetry related bond lengths have been quoted separately.

marked similarity in distribution of the rest of the CO ligands in IV to those in II supports this conclusion.

Further details of the $[Me_4N]_2[Ru_6C(CO)_{16}]$ structure should confirm whether the dianion in this salt is a different isomer from that in $[Ph_4As]_2[Ru_6C(CO)_{16}]$ or whether the two differ only in the degree of asymmetry of the bridging carbonyls.

The metal atoms surrounding the carbon in carbido carbonyl clusters are usually observed in one of two alternative arrangements. For the species $[Co_6C(CO)_{15}]^{2-}$ [5], $[Rh_6C(CO)_{15}]^{2-}$ [6], $Co_6C(CO)_{12}S_2$ [7] and $Rh_8C(CO)_{19}$ [8], a prismatic arrangement of metal atoms occurs whilst for $Ru_6C(CO)_{17}$ [9], $Ru_6C(CO)_{14}$(arene) [10], $[Ru_6C(CO)_{16}]^{2-}$, $[Fe_6C(CO)_{16}]^{2-}$ [2], $[Co_6C(CO)_{14}]^{4-}$ [11] and $[Co_8C(CO)_{18}]^{2-}$ [12] an antiprismatic geometry is found. In $[Rh_{15}C_2(CO)_{28}]^-$ [13] the two carbon atoms also reside in antiprismatic cavities. For the second row elements, as may be anticipated, the M—C distance varies between these two alternative environments having a value of 2.13 Å in the prismatic cavity of $[Rh_6C(CO)_{15}]^{2-}$ and $Rh_8C(CO)_{19}$ whilst in the octahedral cavities of $[Rh_{15}C_2(CO)_{28}]^-$ a value of 2.04 Å is observed. In the ruthenium carbido species the octahedral hole has a radius of 2.05 Å, similar to that observed in the Rh_{15} cluster. Interestingly, the Ru—C distance of 2.05 Å in $[Ru_6C(CO)_{16}]^{2-}$ is close to the Ru—H distance (2.04 Å) observed [14] in the interstitial hydride $[Ru_6H(CO)_{18}]^-$. Thus since there is plenty of room within an Ru_6 octahedron to accommodate a neutral H atom without distortion the expansion of the polyhedron in these species appears to be caused by electronic rather than steric factors.

Crystal data

II, monoclinic space group Pn, $a = 19.329$, $b = 14.958$, $c = 11.498$ Å, $\beta = 101.33°$, $Z = 2$, $I/\sigma(I) \geq 3.0$, θ range 3—25°, present R-value 0.0805 for 4520 reflections. The positions of the Ru, As, and half the phenyl carbon atoms and eight CO ligands are nearly centrosymmetrically related. This posed some difficulty in refinement in the non-centric spacegroup Pn. However, refinement in the centric spacegroup $P2_1/n$ would require that most of the atoms in both the anion and cation be treated as disordered. The two atoms of each of the pairs related by the approximate centre of symmetry were refined in separate cycles with equivalent bond lengths constrained to be equal. Refinement converged satisfactorily giving an R-value of 0.0805 and a final difference Fourier revealed no electron density $> 1\ e\ Å^{-3}$ except in the region of the metal atoms.

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