A New Metallic Environment for Carbon in a Carbido Metal Cluster: *X*-Ray Crystal Structure of the Anion $[Re_4C(CO)_{15}I]^-$

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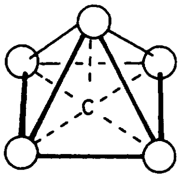
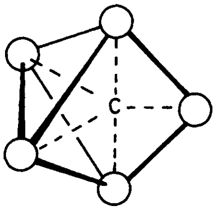
Partial fragmentation of $[Re_7C(CO)_{21}]^{3-}$, by reaction with I_2 in MeCN under CO atmosphere, affords the title compound, which contains a carbide atom at the centre of a tetrahedrally distorted square of rhenium atoms.

Carbide cluster compounds containing the carbon atom in an exposed position have been the object of a great deal of interest in recent years, because of their relevance as models of metal-surface bound carbon atoms.[1] To date only a few examples of compounds with the carbon atom in such a situation have been reported, the metals involved belonging to the iron triad except for the dicarbide $[Co_6C_2(CO)_{14}S]$, which exhibits an exposed C_2 unit.[2] The carbon atom shows either five-fold co-ordination, in square-pyramidal (**1**) and in bridged-butterfly (**2**) clusters, or four-fold co-ordination in butterfly (**3**) clusters. We report here on the isolation and characterization of the $[Re_4C(CO)_{15}I]^-$ anion, which contains an exposed carbide in a novel environment (**4**). This compounds was obtained by oxidative partial fragmentation of a higher nuclearity carbido compound, using a method that exploits the stabilizing effect of the interstitial carbon atom and that has already been used for the synthesis of square-pyramidal or butterfly iron carbido-cluster compounds.[3]

The recently reported[4] monocapped octahedral anion $[Re_7C(CO)_{21}]^{3-}$, was treated with a stoicheiometric amount of I_2 (acetonitrile, room temp., CO atmosphere), resulting in instantaneous cleavage of the $Re(CO)_3$ capping unit, with formation of the new carbido species $[Re_6C(CO)_{19}]^{2-}$.† Further I_2 addition led to a mixture containing mainly the mononuclear compounds $[Re(CO)_3I_n(NCMe)_{3-n}]^{(n-1)-}$ ($n = 0,1,2$). Treatment with (PPN)Br [PPN = bis(triphenylphosphine)iminium], and successive crystallization in acetone–ethanol–n-heptane of the precipitate, allowed the



(1)



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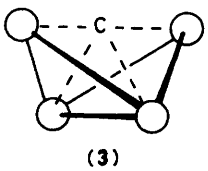

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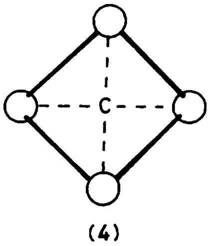

(4)

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† The structure of this compound has been investigated by *X*-ray analysis and the refinements are in progress. It contains an octahedral cluster, centred by the carbide, bearing one doubly-bridging and eighteen terminal CO groups, three for each Re atom.

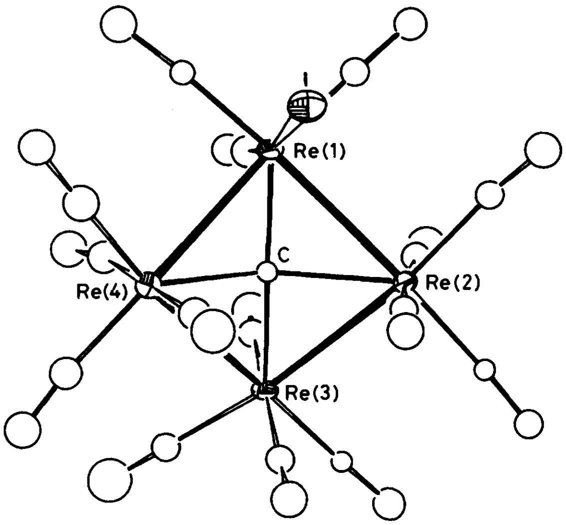

Figure 1. The structure of the anion $[Re_4C(CO)_{15}I]^-$. Relevant bond lengths are: Re(1)–Re(2) 3.007(2), Re(1)–Re(4) 3.012(1), Re(2)–Re(3) 2.992(2), Re(3)–Re(4) 2.986(1), Re(1)–I 2.887(2), Re–C(carbido) 2.08 (mean) Å.

isolation, in very low yield, of a red-brown species identified by X-ray analysis as the salt $(PPN)[Re_4C(CO)_{15}I]$.‡

The structure of the anion is shown in Figure 1. The carbon atom is located inside a tetrametal core, of idealized D_{2d} symmetry, exhibiting an unusual 'cyclobutane' type geometry, *i.e.* a tetrahedrally distorted square. The folding of the metal core (see Figure 2 for a side view) around the two 'square' diagonals (42°) is comparable with that found in cyclobutane (35°). The distortion of the square is large, but not toward the butterfly geometry, because of the presence of two non-bonding 'square' diagonals (mean 4.09 Å). To our knowledge the only other species exhibiting a similar tetrametal geometry is the complex $[Fe_4(CO)_{11}(HC_2Et)_2]$, with a smaller tetrahedral distortion.[5]

Each rhenium atom, neglecting the central carbide, exhibits an almost octahedral co-ordination, being bound to two (*cis*) metal atoms and to four ligands, all carbonyl groups except for one iodine bound to Re(1).

The actual geometry of the metal cluster derives from the necessity of minimizing the ligand–ligand repulsions, since an exactly planar square array should give an eclipsed situation for the ligands on adjacent metals.

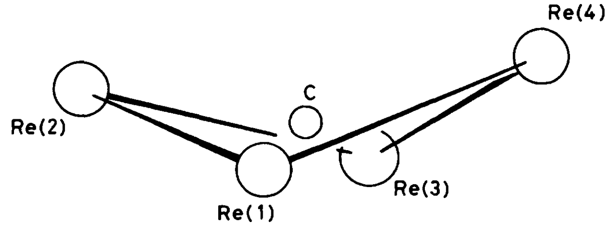

Figure 2. A side view of the metal core. The folding angles have a mean value of 42° while the Re–Re–Re angles have a mean of 86°. The two 'square' diagonals have a mean value of 4.09 Å.

The carbide is slightly shifted away from the centre [Re–C bond lengths in the range 1.95(2)—2.17(2) Å], being closer to the iodine bearing Re(1) atom, probably for the necessity of delocalizing the anionic charge, formally assigned to that metal. In line with this fact, shorter Re(1)–C(carbonyl) interactions are also observed. The angles at the carbide atom have a mean value of 92.1° for the *cis* interactions and 157.4° for the *trans* ones, indicating that the environment of the carbon atom is closer to square-planar than to tetrahedral geometry.

The anion possesses 64 cluster valence electrons, in agreement with the effective atomic number (E. A. N.) rule and with the number found in other square cluster compounds, *e.g.* $[Co_4(CO)_{10}(\mu_4\text{-}PPh)_2]$,[6] $[Fe_2Co_2(CO)_{11}(\mu_4\text{-}S)_2]$,[7] and $[Fe_4(CO)_{11}(\mu_4\text{-}NEt)(\mu_4\text{-}\eta^2\text{-}ONEt)]$.[8] While all the other species with this cluster geometry contain bridging ligands above and below the plane of the square or on the square edges, this is a unique example stabilized by a central atom.

A comparison of this M_4C moiety (**4**) with that of the butterfly-like (**3**) [both formally derived from an M_6C octahedral unit upon removal of two metals, in *trans* position for (**4**) and in *cis* for (**3**) respectively] clearly shows that the carbide has a more exposed location in the second case, lying at a vertex of a heteroatomic distorted trigonal-bipyramidal polyhedron. In the present anion, the carbon atom is hindered by the axial ligands and reagents may have some difficulty in reaching it. Nevertheless, attempts are in progress to improve the synthetic procedure, in order to test the reactivity of the carbide.

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‡ *Crystal data* for $C_{52}H_{30}INO_{15}P_2Re_4$; M = 1842.5, orthorhombic, space group $Cc2a$ (non-standard setting of $Aba2$ n. 41), a = 18.825(4), b = 31.291(6), c = 18.651(4) Å, U = 10986.4 Å^3, $F(000)$ = 6816, Z = 8, D_c = 2.23 g cm^{-3}, Mo-K_α radiation, λ = 0.71073 Å, μ(Mo-K_α) = 95.8 cm^{-1}. Current R value 0.052 for 2904 reflections with $I > 3\sigma(I)$ corrected for absorption. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.