Synthesis of the Carbido Anion $[Os_5C(CO)_{15}I]^-$ and the *X*-Ray Crystal Structures of $Os_5C(CO)_{15}$ and $[(Ph_3P)_2N][Os_5C(CO)_{15}I]$

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Summary $Os_5C(CO)_{15}$ has been shown to be isostructural (but not isomorphous) with its iron analogue $Fe_5C(CO)_{15}$ which has a square pyramidal metal geometry and its reaction with iodide gives the anion $[Os_5C(CO)_{15}I]^-$ in which the osmium atoms have opened out to a bridged butterfly arrangement; the flexibility of the cluster units in reversibility towards electron donation is illustrated.

MUCH interest has recently been shown in polynuclear carbonyl clusters that contain interstitial atoms. To date H,[1a] C,[1b] N,[1c] P,[1d] and S[1e] have been found embedded in the interstices of metal polyhedra but little is known about their chemistry in these sites since they are usually completely surrounded by the metal atoms and therefore shielded from attack.

We have previously reported the synthesis and characterisation of both $Os_5C(CO)_{15}$[2a,2b] (**1**) and $Ru_5C(CO)_{15}$,[2a] and the similarity of their i.r. spectra to that of their iron analogue $Fe_5C(CO)_{15}$[3] suggested that these three clusters were isostructural [ν(CO)(CH_2Cl_2) 2070s and 2030s cm^{-1} for $Os_5C(CO)_{15}$]. A single crystal *X*-ray analysis has now verified this for the osmium cluster.† Orange air-stable crystals of (**1**),‡ which were characterised by i.r. and mass spectrometry, were fractionally crystallised from an ethyl acetate solution containing several polynuclear species formed by the pyrolysis of $Os_3(CO)_{12}$.[2b] The structure of (**1**) is shown in Figure 1; the osmium atoms define the vertices of a square pyramid, with three terminal carbonyls per metal, and the carbido atom sits slightly below the square face (0·12 Å) as it does in the iron species.[4] Thus $Os_5C(CO)_{15}$ is isostructural with $Fe_5C(CO)_{15}$.

Reaction of $Os_5C(CO)_{15}$ in tetrahydrofuran with iodide, followed by addition of $(Ph_3P)_2NCl$ in methanol, leads to the precipitation of $[(Ph_3P)_2N][Os_5C(CO)_{15}I]$ (**2**) [ν(CO)(CH_2Cl_2) 2091w, 2059s, 2045vs, 2010br s, 1981w, 1959w, and 1938w cm^{-1}]. In order to investigate the solid state geometry, orange air-stable crystals of (**2**) suitable for *X*-ray diffraction were grown from CH_2Cl_2–MeOH.‡ The structure of the anion is shown in Figure 2. As the iodide behaves as a two electron donor group, the anion has two more skeletal electron pairs (*S*) than the six required for the appropriate closed polyhedron[5] (a trigonal bipyramid), so an open structure is expected in which the carbido atom occupies a more exposed position. The metal atoms define five of the seven vertices of a pentagonal bipyramid which has an *arachno*-geometry predicted by Wade theory[5] for a cluster having eight skeletal electron pairs and five skeletal atoms. The carbido atom lies approximately at the centre of this polyhedron but is not equidistant from the five Os atoms (Figure 2).

A similar Os_5C geometry has been observed in $HOs_5C(CO)_{13}[OP(OMe)OP(OMe)_2]$[6a] and $HOs_5C(CO)_{14}[OP(OMe)_2]$[6b] which were isolated in low yield from the pyrolysis of $Os_3(CO)_{11}P(OMe)_3$. Since the central carbon atom in clusters of this geometry is contained in a metal polyhedron that has two vertices missing it is open to attack by incoming molecules. The anion in (**2**) has only simple ligands present so the chemistry of a 'semi-interstitial' carbon atom in such an environment may now be conveniently investigated for the first time. The exciting potential of these clusters as catalysts has recently been demonstrated by Bradley *et al.*[7] who showed that a partially encapsulated carbon atom exhibits a chemistry conducive to C–C bond formation and succeeded in synthesizing methyl acetate from CO and H_2 only.

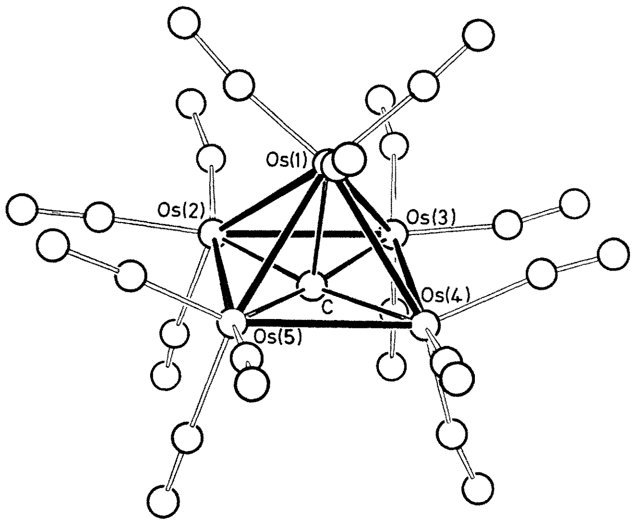

FIGURE 1. The structure of $Os_5C(CO)_{15}$ (**1**). There are 2 independent molecules in the asymmetric unit for (**1**) but the overall geometry is the same for the two molecules. Important mean bond lengths are Os(basal)–Os(basal) 2·88(2), Os(apical)–Os(basal) 2·85(3), and Os–C 2·06(4) Å. The carbido atom lies 0·12 Å below the basal osmium plane.

It is interesting to compare the differing modes of reaction of clusters with iodide. The neutral compound $Os_6(CO)_{18}$ is reduced by I$^-$ to the dianion $[Os_6(CO)_{18}]^{2-}$;[8] this is accompanied by a structural change of the metal skeleton from a bicapped tetrahedron ($S = 6$) to an octahedron ($S = 7$). This reaction is reversible; treatment of $[Os_6(CO)_{18}]^{2-}$ with I_2 regenerates the neutral species and the iodine is reduced to I$^-$. In contrast, the dihydride $H_2Os_5(CO)_{15}$ adds I$^-$ and the metal core changes from a trigonal bipyramid ($S = 6$) to an edge-bridged tetrahedron which is an *arachno* capped-octahedron ($S = 7$).[9] In this case addition of H$^+$ regenerates the neutral species.

Similarly when iodide reacts with $Os_5C(CO)_{15}$ it also functions as a Lewis base and co-ordinates to an osmium atom. Again, an appropriate change in metal polyhedron occurs, but in this system the reaction is irreversible.

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† A new high yield synthesis of $Ru_5C(CO)_{15}$ has given crystals which are isomorphous with those of $OsC(CO)_{15}$ and this therefore confirms that all three carbides are isostructural.

‡ *Crystal data:* (**1**) monoclinic, space group $P2_1/c$, $a = 16{\cdot}404$, $b = 14{\cdot}170$, $c = 20{\cdot}798$ Å, $\beta = 91{\cdot}71°$, $Z = 8$, $I/\sigma(I) \geqslant 3{\cdot}0$, θ-range 3—30°, present *R*-value = 0·0499 for 5946 reflections; (**2**) monoclinic, space group $P2_1/n$, $a = 34{\cdot}337$, $b = 10{\cdot}042$, $c = 16{\cdot}382$ Å, $\beta = 101{\cdot}77°$, $Z = 4$, $I/\sigma(I) \geqslant 3{\cdot}0$, θ-range 3—25°, present *R*-value = 0·0399 for 6134 reflections. Empirical absorption corrections were applied to both data sets [(**1**) $\mu = 252{\cdot}5$ cm^{-1}, (**2**) $\mu = 116{\cdot}3$ cm^{-1}]. The atomic co-ordinates for $[(Ph_3P)_2N][Os_5C(CO)_{15}I]$ are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. The atomic co-ordinates for $OsC(CO)_{15}$, and also for $[(Ph_3P)_2N][Os_5C(CO)_{15}]$, are available on request from Prof. Dr. G. Bergerhoff, Institut für Anogonische Chemie, Universität, Gerhard Domagk-Str. 1, D-5300 Bonn 1, West Germany. Any request should be accompanied by the full literature citation for this communication.

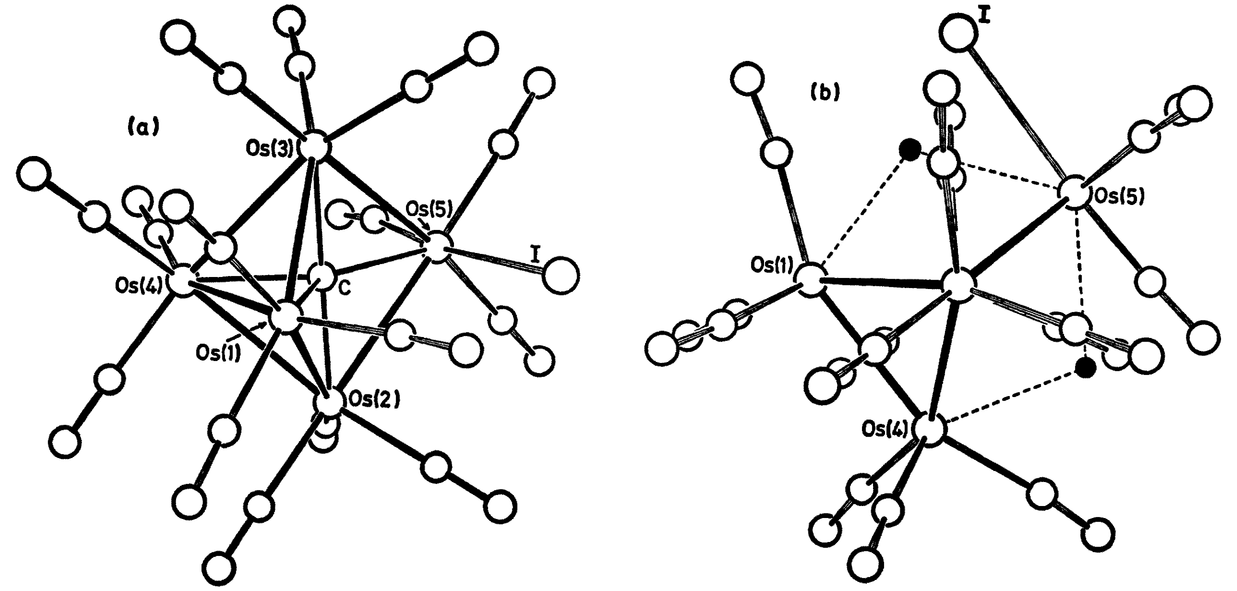

Figure 2 The structure of the $[Os_5C(CO)_{15}I]^-$ anion (**1**) (a) a view showing the partially encapsulated carbido atom, (b) the cluster viewed down Os_2 and Os_3 to illustrate the *arachno*-pentagonal bipyramidal metal geometry Important bond lengths are Os(1)–Os(2) 2 903, Os(1)–Os(3) 2 921, Os(1)–Os(4) 2 748, Os(2)–Os(4) 2 899, Os(2)–Os(5) 2 933 Os(3)–Os(4) 2 896, Os(3)–Os(5) 2 934, Os(1)–C 2 108, Os(2)–C 1·978, Os(3)–C 1 995, Os(4)–C 2 108, and Os(5)–C 2 174 Å Max e s d's are Os–Os 0 001, Os–C 0 012 Å

However, protonation of $[Os_5C(CO)_{15}I]^-$ in acetonitrile yields the neutral complex $HOs_5C(CO)_{15}I$ Reaction of this with silver nitrate and subsequent protonation produces a nitrate complex which dissociates in decane at 150 °C to yield the parent carbonyl carbide $Os_5(CO)_{15}C$ Thus, in these series of complexes, owing to the flexibility in the metal framework, it is possible to generate a new co-ordination site within the metal polyhedra *via* the breaking of metal–metal bonds The reversibility of this process also adds to the potential use of complexes of this type as catalytic intermediates

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