Reversible Os–Os Bond Breaking in the High Nuclearity Carbido-dianion $[Os_{10}C(CO)_{24}]^{2-}$ on Reaction with Halogens; *X*-Ray Structure Analysis of $[(Ph_3P)_2N][Os_{10}C(CO)_{24}I]$ and $Os_{10}C(CO)_{24}I_2$

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Summary The carbido-dianion $[Os_{10}C(CO)_{24}]^{2-}$ reacts with halogens (X_2) to give first $[Os_{10}C(CO)_{24}X]^-$ and then $Os_{10}C(CO)_{24}X_2$ ($X = Cl, Br, I$) and these clusters regenerate the dianion on treatment with nucleophilic reagents such as X^-,PR_3 or C_5H_5N; *X*-ray analysis of $[(Ph_3P)_2N]$-$[Os_{10}C(CO)_{24}I]$ and $Os_{10}C(CO)_{24}I_2$ shows that the reactions break Os–Os bonds on the metal surface giving 'butterfly' indentations bridged by I atoms.

ALTHOUGH a large number of high nuclearity transition-metal cluster compounds have recently been synthesised and characterised, comparatively little is known of their chemistry.[1,2] In this communication we report studies of the reactions of halogens (X_2) with the carbido-dianion $[Os_{10}C(CO)_{24}]^{2-}$ which may be viewed as electrophilic attack by X^+ rather than a conventional oxidative-addition reaction of X_2.

The dianionic cluster $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) has a structure in which a central Os_6C core is capped by four $Os(CO)_3$ units.[2] In this way it resembles the neutral osmium carbonyl cluster $[Os_6(CO)_{18}]$ which is also a capped species,[3] but this structural similarity is not reflected in the types of reaction they undergo. Thus, whereas $[Os_6(CO)_{18}]$ undergoes reduction by I^- to yield $[Os_6(CO)_{18}]^{2-}$,[4] an electron-precise non-capped species,[5] the dianion $[Os_{10}C(CO)_{24}]^{2-}$ undergoes an electrophilic attack by I^+ (I_2) according to equation (1).

$$\begin{array}{ccc} [Os_{10}C(CO)_{24}]^{2-} & \xrightarrow{2I_2} & [Os_{10}C(CO)_{24}I]^- + I_3^- \\ (\mathbf{1}) & & (\mathbf{2})\dagger \\ & & \downarrow 2I_2 \\ & & Os_{10}C(CO)_{24}I_2 + I_3^- \\ & & (\mathbf{3})\dagger \end{array} \qquad (1)$$

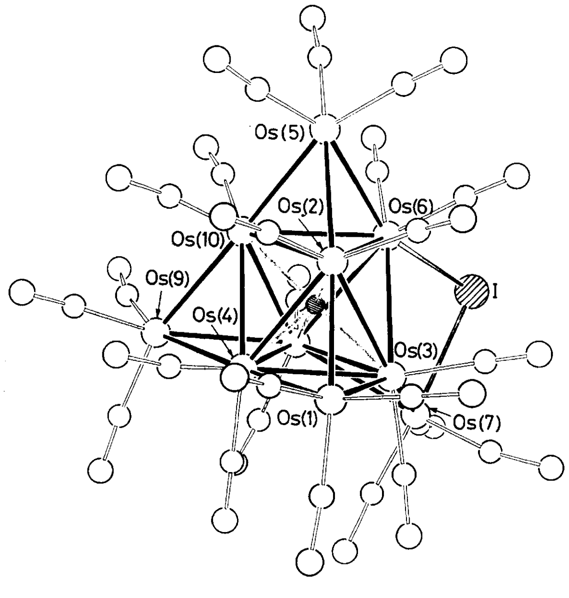

FIGURE 1. The structure of the $[Os_{10}C(CO)_{24}I]^-$ anion. Important bond lengths are Os–Os: (1)–(2) 2·790, (1)–(3) 2·807, (1)–(4) 2·767, (2)–(3) 2·867, (2)–(4) 2·863, (2)–(5) 2·769, (2)–(6) 2·884, (2)–(10) 2·844, (3)–(4) 2·879, (3)–(6) 2·977, (3)–(7) 2·844, (3)–(8) 3·003, (4)–(8) 2·880, (4)–(9) 2·770, (4)–(10) 2·872, (5)–(6) 2·853, (5)–(10) 2·766, (6)–(8) 2·986, (6)–(10) 2·875, (7)–(8) 2·836, (8)–(9) 2·823, (8)–(10) 2·881, and (9)–(10) 2·785 Å; Os(7)–I 2·730, and Os(6)–I 2·717 Å; mean Os–C (carbido) 2·05 Å. Maximum e.s.d's are Os–Os 0·003, Os–I 0·004 Å.

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† ν_{CO}/cm^{-1}: (**2**) 2065s, 2057vs, 2017m, and 2004s; (**3**) 2084vs, 2076m, 2038s, 2027m, and 2011wsh.

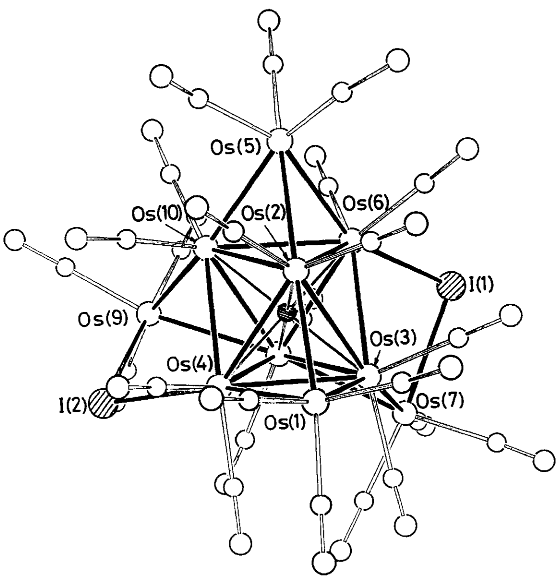

FIGURE 2. The structure of the $Os_{10}C(CO)_{24}I_2$ molecule. Important bond lengths are Os–Os: (1)–(2) 2·753, (1)–(3) 2·752, (1)–(4) 2·878, (2)–(3) 2·832, (2)–(4) 2·893, (2)–(5) 2·740, (2)–(6) 2·883, (2)–(10) 2·837, (3)–(4) 2·897, (3)–(6) 2·950, (3)–(7) 2·823, (3)–(8) 2·957, (4)–(8) 2·941, (4)–(10) 2·949, (5)–(6) 2·851, (5)–(10) 2·767, (6)–(8) 2·915, (6)–(10) 2·896, (7)–(8) 2·833, (8)–(9) 2·826, (8)–(10) 2·980, (9)–(10) 2·835; Os(6)–I(1) 2·730, Os(7)–I(1) 2·746, Os(4)–I(2) 2·737, Os(9)–I(2) 2·732 Å; mean Os–C(carbido) 2·07 Å. Maximum e.s.d's are Os–Os 0·04 and Os–I 0·06 Å.

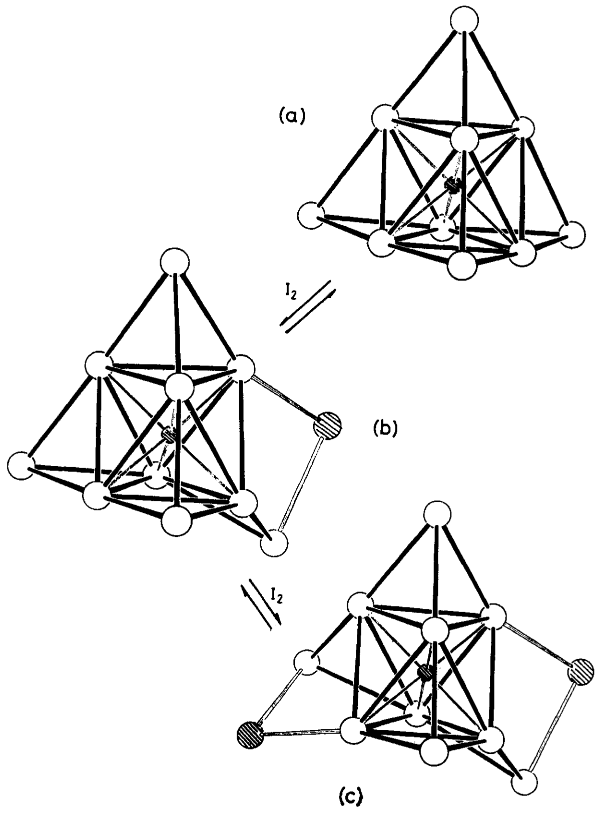

FIGURE 3. The relationship between the cluster cores in (a) $[Os_{10}C(CO)_{24}]^{2-}$, (b) $[Os_{10}C(CO)_{24}I]^-$, and (c) $Os_{10}C(CO)_{24}I_2$.

X-Ray analysis‡ of species (**2**) and (**3**) (Figures 1 and 2) reveals that attack by I^+ occurs at a capping Os_4 group leading to breaking of an Os–Os bond and bending back of an $Os(CO)_3$ 'hinged' unit and producing a sequential opening of the basic $Os_{10}C$ core (Figure 3). In these structures the I atom functions as a bridge across a 'butterfly' Os_4 arrangement and as such may be regarded as a three-electron donor. Thus, in proceeding from (**1**) to (**2**) to (**3**) there is a net gain of two and four electrons, respectively. In this way, these cluster opening reactions at the capping tetrahedra are similar to that observed for $[H_3Os_4(CO)_{12}]^-$ when the basic tetrahedral core of four osmium atoms opens to a similar 'butterfly' arrangement on treatment with I^+ (I_2).[6] The dianion (**1**) also reacts with Cl_2 and Br_2 to produce the corresponding chloro- and bromo-species. On prolonged treatment with halogen the $Os_{10}C(CO)_{24}X_2$ cluster undergoes further reaction and cluster cleavage to produce smaller halogeno-clusters [*e.g.* $Os_2(CO)_6X_4$].

Reaction of the iodo-compounds (**2**) and (**3**) with iodide ion eliminates the bonded iodine atoms sequentially as I_2 reforming the capping Os–Os bonds and giving eventually the dianion (**1**). Reversible opening and closing of capping tetrahedra on large clusters has not been observed before but resemble the known reactions of discrete tetrahedral clusters.[6] Similarly, reaction with a range of substrates including $P(OMe)_3$, $P(OEt)_3$, PPh_3, C_5H_5N, and MeCN, brings about the formation of the dianion. It would appear that the iodine atoms are removed as I^+ which is stabilised by two donor ligands as $[IL_2]^+$. The di-iodo-compound (**3**) is also more reactive towards CO than the dianion, (**1**). Thus although no reaction is observed between the dianion and CO under extreme conditions, (**3**) reacts to give a mixture of compounds under moderate conditions (65 atm at 175 °C). These compounds are, however, unstable and efforts to separate them have failed; the reaction mixture readily loses CO to reform mainly the dianion.

‡ *Crystal data:* $[C_{36}H_{30}NP_2][C_{25}IO_{24}Os_{10}]$, triclinic, space group $P\bar{1}$, $a = 19{\cdot}161(3)$, $b = 19{\cdot}086(3)$, $c = 10{\cdot}446(2)$ Å, $\alpha = 91{\cdot}12$, $\beta = 84{\cdot}07$, $\gamma = 109{\cdot}60°$, $Z = 2$, $I/\sigma(I) \geqslant 3{\cdot}0$, present *R*-value = 0·094 for 7934 reflections before absorption correction; $C_{25}I_2O_{24}Os_{10}$, orthorhombic, space group $P2_12_12_1$, $a = 30{\cdot}676(4)$, $b = 12{\cdot}323(2)$, $c = 11{\cdot}700(2)$ Å, $Z = 4$, $I/\sigma(I) \geqslant 3{\cdot}0$, present *R*-value 0·0586 for 2405 absorption-corrected reflections. Data were collected on a Philips PW1100 diffractometer in the θ-range 3—25° using Mo-K_α radiation.

The atomic co-ordinates for $[(Ph_3P)_2N][Os_{10}C(CO)_{24}I]$ are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW and those for $Os_{10}C(CO)_{24}I_2$ from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-3500 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

This work emphasises the ability of cluster systems to undergo either reduction or electrophilic addition reactions at capping Os tetrahedra.

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