Journal of Organometallic Chemistry, 249 (1983) 255–272
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

METAL-CARBIDO COMPLEXES OF RUTHENIUM AND OSMIUM *

BRIAN F.G. JOHNSON, JACK LEWIS*, WILLIAM J.H. NELSON, J. NICOLA NICHOLLS and MARIA D. VARGAS
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain)

(Received February 1st, 1983)

Summary

The methods available for the preparation of the carbonylcarbido clusters of ruthenium and osmium are summarised. The various techniques utilised in the determination of the structure of these compounds are reviewed and the reactivity of the deca-, hexa- and pentanuclear carbido cluster compounds are described. The carbido atom in the higher nuclearity systems appears to stabilise the M_nC unit against fragmentation, and allows investigation of an extensive chemistry of the metal cage.

Introduction

One of the most rapidly developing areas of inorganic chemistry is the study of cluster compounds, in particular the polynuclear transition metal carbonyl complexes. One of the more interesting aspects of this work has been the isolation of compounds containing a variety of interstitial atoms, the most extensive group being the carbido clusters in which the carbon is found in a variety of stereochemical environments. Except for the tetranuclear iron carbido-carbonyl derivatives, most studies of carbido compounds have concentrated on their synthesis and structural analysis rather than on their reactivity. Our aim has been to extend these studies to include the reactivity of the ruthenium and osmium carbido derivatives. Whilst our investigations have not revealed direct attack at the coordinated carbon centre, they have illustrated the remarkable stability of these compounds to cluster degradation, and a wide range of metal polyhedral forms have resulted as a consequence of adding electrons to or removing them from the systems.

In this account of the carbido-carbonyls, we first discuss the methods of their preparation. This is followed by a summary of the physical techniques used to

---

* This paper is dedicated to Professor H.J. Emeléus on the occasion of his 80th brithday on 22nd June, 1983. J.L. feels himself fortunate to have been able to work in association with Prof. Emeléus over the past thirteen years.

0022-328X/83/$03.00

TABLE 1

CRYSTALLOGRAPHICALLY CHARACTERISED CARBIDO CLUSTERS OF RUTHENIUM AND OSMIUM

Number of M–C bonds	Framework M_n polyhedron	Carbido cluster	Reference
5	Square pyramid	$[\mathrm{Ru_5C(CO)_{15}}]$	[1]
	Square pyramid	$[\mathrm{Os_5C(CO)_{15}}]$	[2]
	Square pyramid	$[\mathrm{Ru_5C(CO)_{14}PPh_3}]$	[1]
	Square pyramid	$[\mathrm{Ru_5C(CO)_{13}(PPh_3)_2}]$	[3]
	Square pyramid	$[\mathrm{Ru_5C(CO)_{13}(dppb)}]$	[4]
	Square pyramid	$[\mathrm{H_2Ru_5C(CO)_{12}(dppe)}]$	[3]
	Square pyramid	$[\mathrm{HRu_5C(CO)_{12}(PPh_3)(SEt)}]$	[5]
	Square pyramid	$[\mathrm{Os_5C(CO)_{14}}]^{2-}$	[6]
	Square pyramid	$[\mathrm{Os_5C(CO)_{14}(AuPPh_3)_2}]$	[6]
	Square pyramid	$[\mathrm{Os_6C(CO)_{16}(MeC_2Me)}]$	[7]
	Bridged butterfly	$[\mathrm{Ru_5C(CO)_{15}(MeCN)}]$	[8]
	Bridged butterfly	$[\mathrm{HRu_5C(CO)_{14}(SEt)}]$	[8]
	Bridged butterfly	$[\mathrm{Ru_5C(CO)_{15}(AuPPh_3)Cl}]$	[9]
	Bridged butterfly	$[\mathrm{Ru_5C(CO)_{14}(AuPPh_3)Br}]$	[9]
	Bridged butterfly	$[\mathrm{Os_5C(CO)_{16}}]$	[6]
	Bridged butterfly	$[\mathrm{Ru_5C(CO)_{13}(PPh_3)(AuPPh_3)I}]$	[5]
	Bridged butterfly	$[\mathrm{HRu_5C(CO)_{13}(PPh_3)(SEt)}]$	[5]
	Bridged butterfly	$[\mathrm{HRu_6C(CO)_{15}(SEt)_3}]$	[10]
	Bridged butterfly	$[\mathrm{Os_5C(CO)_{15}I}]^-$	[2]
	Bridged butterfly	$[\mathrm{HOs_5C(CO)_{14}\{OP(OMe)_2\}}]$	[11]
	Bridged butterfly	$[\mathrm{HOs_5C(CO)_{13}\{OP(OMe)_2\}\{P(OMe)_3\}}]$	[12]
	Bridged butterfly	$[\mathrm{HOs_5C(CO)_{13}\{OP(OMe)OP(OMe)_2\}}]$	[13]
	Bridged butterfly	$[\mathrm{HOs_5C(CO)_{14}COOEt}]$	[14]
	Bridged butterfly	$[\mathrm{IOs_5C(CO)_{14}COOMe}]$	[14]
	Bridged butterfly	$[\mathrm{HOs_5C(CO)_{14}(NC_5H_4)}]$	[21]
6	Octahedron	$[\mathrm{Ru_6C(CO)_{17}}]$	[15]
	Octahedron	$[\mathrm{Ru_6C(CO)_{16}}]^{2-}$	[16]
	Octahedron	$[\mathrm{Ru_6C(CO)_{14}(NO)_2}]$	[52]
	Octahedron	$[\mathrm{Ru_6C(CO)_{15}(NO)(AuPPh_3)}]$	[52]
	Octahedron	$[\mathrm{HRu_6C(CO)_{15}(NO)}]$	[53]
	Octahedron	$[\mathrm{Ru_6C(CO)_{14}\{1,3,5(Me)_3C_6H_3\}}]$	[17]
	Octahedron	$[\mathrm{Ru_6C(CO)_{16}(PPh_2Et)}]$	[18]
	Octahedron	$[\mathrm{Ru_6C(CO)_{16}(AuPMePh_2)_2}]$	[19]
	Octahedron	$[\mathrm{Ru_6C(CO)_{16}\{Cu(MeCN)\}_2}]$	[29]
	Octahedron	$[\mathrm{Ru_6C(CO)_{15}(C_6H_{10})}]$	[20]
	Octahedron	$[\mathrm{Ru_{10}C_2(CO)_{24}}]^{2-}$	[54]
	Octahedron	$[\mathrm{Os_{10}C(CO)_{24}}]^{2-}$	[21]
	Octahedron	$[\mathrm{Os_{10}C(CO)_{24}I}]^-$	[22]
	Octahedron	$[\mathrm{Os_{10}C(CO)_{24}I_2}]$	[22]
	Octahedron	$[\mathrm{Os_{10}C(CO)_{24}(AuPPh_3)}]^-$	[23]
	Octahedron	$[\mathrm{Os_{10}C(CO)_{24}Cu(MeCN)}]^-$	[23]
	Octahedron	$[\mathrm{Os_{10}C(CO)_{23}(NO)}]^-$	[24]
	Octahedron	$[\mathrm{Os_{10}C(CO)_{24}(NO)}]^-$	[24]
	Octahedron	$[\mathrm{HOs_{10}C(CO)_{24}}]^-$	[25]
	Octahedron	$[\mathrm{Os_{10}C(CO)_{22}(NO)I}]^{2-}$	[26]
	Octahedron	$[\mathrm{Os_{10}C(CO)_{21}\{P(OMe)_3\}_4}]$	[47]
6	Trigonal prism	$[\mathrm{Os_{11}C(CO)_{27}}]^{2-}$	[27]

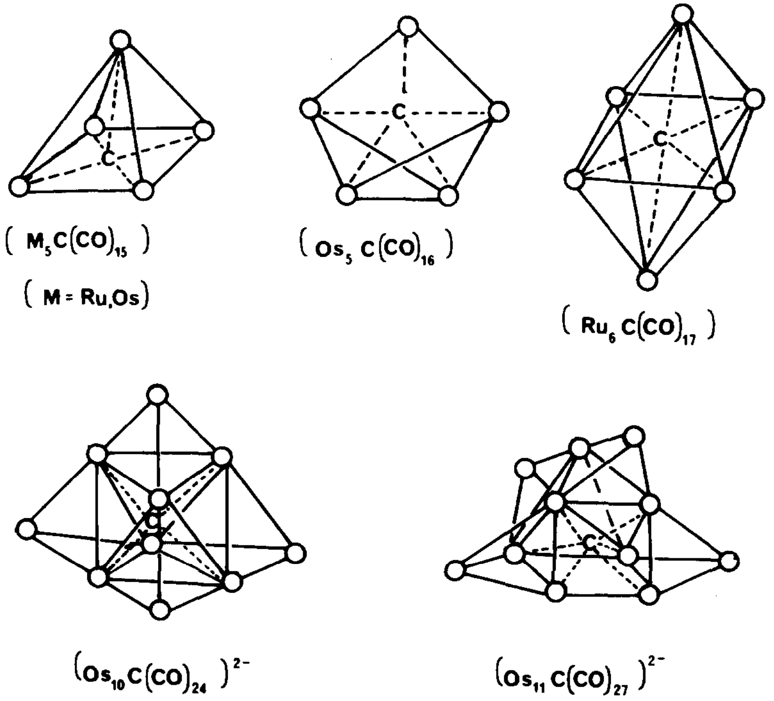


Fig. 1. The four M_nC core geometries exhibited by ruthenium and osmium carbido clusters.

identify and establish their structures. Finally, we discuss the reactions of these compounds with nucleophilic and electrophilic reagents, will special emphasis on the structural rearrangements involved.

Table 1 lists the carbonyl cluster compounds of ruthenium and osmium which have been characterised crystallographically.

The carbido clusters obtained in sufficient yield to allow an investigation of their chemistry are $[M_5C(CO)_{15}]$ M = Ru [1], Os [2], $[Os_5C(CO)_{16}]$ [6], $[Ru_6C(CO)_{17}]$ [29], $[Os_{10}C(CO)_{24}]^{2-}$ [21] and $[Os_{11}C(CO)_{27}]^{2-}$ [27]. As shown in Fig. 1, they exhibit four basic M_nC core geometries. Generally speaking, the main reaction of the neutral clusters is attack by nucleophiles, while for the anions, only electrophilic attack is observed. In both cases, rearrangement of the metal skeleton may occur, leading invariably to one of the four fundamental M_nC core arrangements.

This is in contrast to the behaviour of the binary carbonyls of ruthenium and osmium, for which rearrangements seem to be less restricted. Indeed, although Os_5 clusters may be successfully opened up by addition of nucleophiles (for example the trigonal bipyramidal $[Os_5(CO)_{16}]$ adds CO to give the quasi-planar "bowtie" complex $[Os_5(CO)_{19}]$ [30]), the Os_5C metallic geometry is mainly restricted to two structural forms, (see Fig. 1). This suggests that the carbide exerts a controlling influence on the surrounding metals and hence reactions tend to be restricted to those in which the metal–carbide bonds are maintained throughout. In this respect the carbon atom acts as a "glue" holding the M_nC unit together, but flexibility of the metal cage is still allowed.

Synthesis

So far, the preparation of new carbonyl clusters of ruthenium and osmium containing interstitial carbon atoms has been more the product of chance than of directed synthesis. These carbido clusters are usually produced by the pyrolysis of the trinuclear dodecacarbonyl species $[M_3(CO)_{12}]$ or, in the case of osmium, from some of the substituted carbonyl derivatives (Scheme 1). The substituted compounds often show higher degrees of conversion into carbido species.

The vacuum pyrolysis of $[Os_3(CO)_{12}]$ is the subject of continued investigation, but the yields of carbido clusters from this route are invariably low. We believe that the formation of $[Os_5C(CO)_{15}]$, for example, is sensitive not only to the temperature and duration of the reaction, but also to the presence of trace amounts of air [33].

Previous work has established that the carbido atom can be derived from a CO group or from an external source such as CS_2 [34], $CHCl_3$ [35], or CCl_4; in our studies we only have evidence for the former, either via disproportionation of carbon monoxide to carbon and carbon dioxide, or through loss of the elements of water from hydrido clusters, as shown below:

$$[Ru_3(CO)_{12}] \rightarrow [Ru_6C(CO)_{17}] + CO_2 \text{ [36]}$$

$$[H_2Ru_6(CO)_{18}] \rightarrow [Ru_6C(CO)_{17}] \text{ [37]} + \text{“}H_2O\text{”}$$

Recently, we have developed another route to carbido clusters which may prove of general synthetic value. This involves the controlled degradation of performed carbido species to give compounds containing fewer metal atoms. For example, $[Ru_5C(CO)_{15}]$ is produced in high yield by the reaction of $[Ru_6C(CO)_{17}]$ with CO [1]. The product $[Ru_5C(CO)_{15}]$ is, however, stable to further degradation by CO at standing pressures of up to 400 atm and 100°C for 2 h. In the case of osmium, we have observed selective breakdown of the recently characterized species $[Os_{11}C(CO)_{27}]^{2-}$ [27] to $[Os_{10}C(CO)_{24}]^{2-}$ on treatment with I_2. Furthermore, prolonged reaction of $[Os_{10}C(CO)_{24}]^{2-}$ with halogens does not lead to further degradation at room temperature, but in refluxing $CHBr_3$ breakdown does occur, ultimately producing $[Os_2(CO)_6Br_4]$ [38]. The fate of the encapsulated carbon atom in this reaction has not been established.

Characterisation

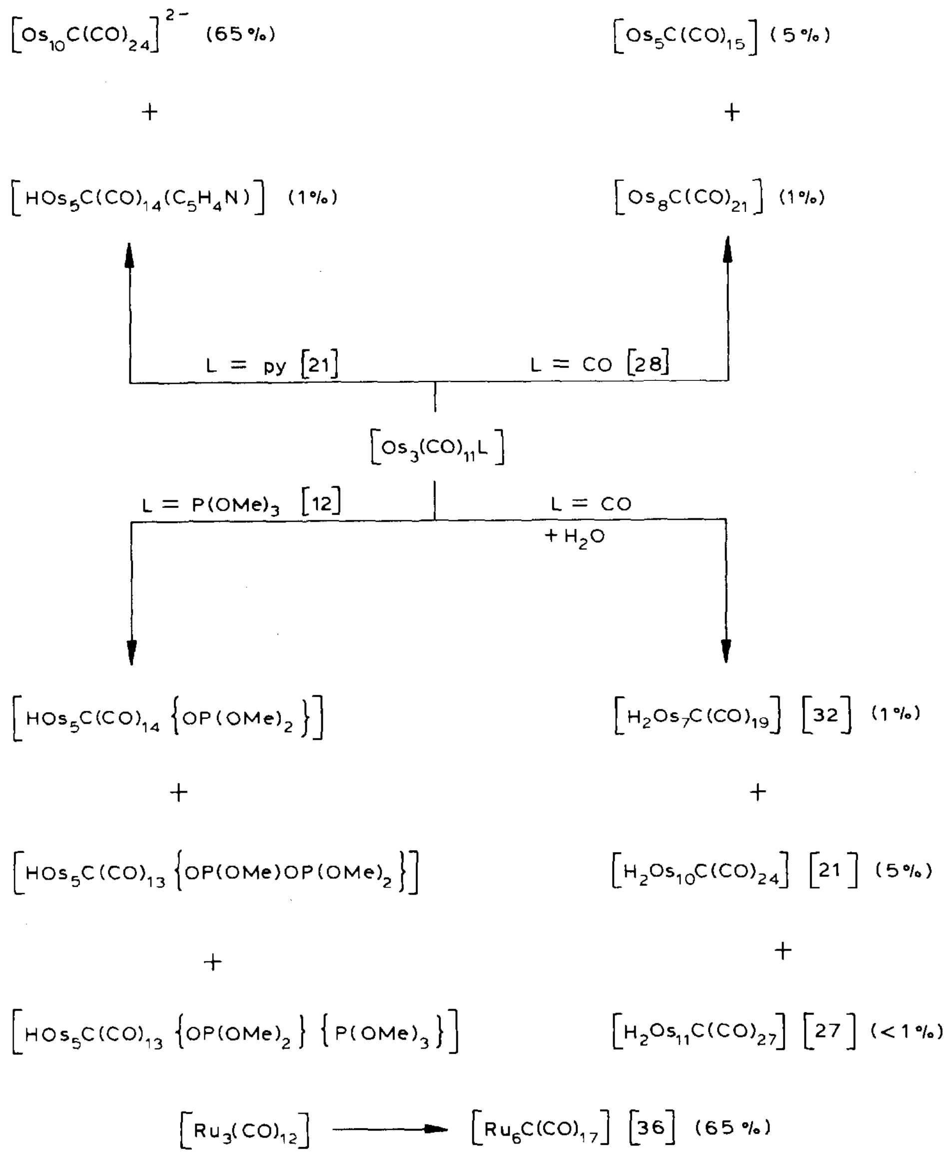
As is usual for most transition metal cluster complexes, elemental analyses alone are insufficient to establish the molecular composition of carbido clusters. Positive determination of their exact nature is usually based on a combination of spectroscopic and crystallographic techniques. Most detailed information is given by X-ray analysis; other useful techniques are IR, NMR and mass spectroscopy.

X-ray analysis

A carbido atom was first identified by X-ray techniques in 1962 in the pentanuclear iron carbonyl complex $[Fe_5C(CO)_{15}]$ * [39]. Subsequently, X-ray structural determinations have, in the absence of other data, unambiguously shown a number

---

* Structure similar to that of $[M_5C(CO)_{15}]$, M = Ru and Os, see Fig. 1.



SCHEME 1. Pyrolysis reactions of some $[M_3(CO)_{11}L]$ derivatives (M = Os, Ru).

of new cluster compounds, for example $[Os_{10}C(CO)_{24}]^{2-}$, to be carbido species.

The C atom in Ru or Os carbido clusters generally occupies a regular interstitial site. As shown in Fig. 1, it sits in an octahedral site in $[Ru_6C(CO)_{17}]$ [15] or $[Os_{10}C(CO)_{24}]^{2-}$ [21], a *quasi*-octahedral (square pyramidal) site in $[Ru_5C(CO)_{15}]$ [1]. a *quasi*-pentagonal bipyramidal site in $[Ru_5C(CO)_{15}L]$ [3] or $[Os_5C(CO)_{16}]$ [6] and a trigonal prismatic site in the newly discovered species $[Os_{11}C(CO)_{27}]^{2-}$ [27]. In general, the interstitial carbon atom causes a slight expansion (ca. 0.04 Å) of the cavity of these clusters compared with those in their simple binary carbonyl counterparts (see Table 2). It is tempting to associate this expansion with the steric

TABLE 2

EXPANSION OF THE OCTAHEDRAL CAVITY IN Ru AND Os CLUSTERS DUE TO THE PRESENCE OF AN INTERSTITIAL CARBON

Cluster	Mean M–M bond length in M_6 octahedron (Å)	Octahedral hole site radius (Å)	Reference
$[Os_8(CO)_{22}]^{2-}$	2.831	2.002	[55]
$[Os_{10}C(CO)_{24}]^{2-}$	2.883	2.039	[21]
$[Ru_6(CO)_{18}]^{2-}$	2.844	2.011	[56]
$[Ru_6C(CO)_{16}]^{2-}$	2.897	2.048	[16]

demands of a carbon atom or ion of fixed radius. However, it may be dangerous to use the same carbon radius in complexes possessing different metal environments.

Infrared spectroscopy

After X-ray analysis, the technique that we have found most useful in establishing the environment of the carbon, particularly in the pentanuclear osmium and ruthenium carbido species, is infrared spectroscopy. For interstitial metal carbido cluster complexes, ν(MC) bands have been observed in the 820–550 cm^{-1} region [40,41]. The number and position of the bands obtained in each case depends on the geometry of the metal cage which surrounds the carbide atom. For example the two basic M_5C geometries, shown in Fig. 2, may be readily distinguished as shown in Table 3; the square based pyramidal structure gives rise to three closely spaced ν(MC) bands, while the wing-tip bridged butterfly gives rise to two well separated bands, one of which splits into two components at 90 K.

A carbon atom in an octahedral metal cage is also readily identified by this technique [42]. Although the octahedron is the only M_6C geometry which has been studied to date, we would anticipate that changes in the structure would also be discernible in the infrared spectrum.

Clearly, the information obtained in this way can never be as detailed as that provided by an X-ray experiment. Complications in interpreting the infrared spectrum of a carbido compound can arise from the presence in the region of interest of vibrations due to the other groups present in the molecule, such as PR_3, CO or $[PPN]^+$. Nevertheless, particularly when suitable single crystals of the compound are not available, this technique may give the first clues as to the M_nC geometry. In some cases, when this data is combined with information obtained from the other regions of the infrared spectrum, it may provide a good idea of the composition and structure of the molecule.

Mass spectroscopy

Mass spectral data are useful in some cases for establishing whether a novel compound is a carbide derivative. In fact the carbido species $[Ru_6C(CO)_{17}]$ [36] $[Os_5C(CO)_{15}]$ [28] and $[Os_8C(CO)_{21}]$ [28] were first characterized by their mass spectra, which showed strong molecular ions, ions corresponding to the stepwise loss of CO groups and, significantly, a very intense peak due to the fragment $[M_nC]^+$.

This illustrates the high stability of the M_nC unit for M = Ru and Os; in iron clusters, further fragmentation is observed.

^{13}C NMR spectroscopy

The ^{13}C NMR resonance of encapsulated carbon atoms has been detected in several species. However, the observation of a resonance due to encapsulated atoms in clusters is often hindered by relaxation problems or by the limited amount of material available for study. Therefore the absence of a signal does not necessarily mean that an interstitial carbon atom is not present. In all the cases where the signal due to the carbido atom has been observed, it has been found to lie well downfield; for example in the monoanion $[HOs_{10}C(CO)_{24}]^-$ [25] it appears at 409 ppm, in $[Ru_5C(CO)_{15}]$ at 429 ppm, and in $[H_2Ru_5C(CO)_{12}(dppe)]$ at 501 ppm. This is in agreement with data for other carbido species; in $[Fe_4C(CO)_{13}]$ the carbido ^{13}C resonance is observed at 469 ppm [43] and in $[Rh_6C(CO)_{15}]^{2-}$ at 459 ppm [60]. As pointed out by Bradley [44], this is more consistent with their assignment as shielded carbonium ions rather than as carbides.

Reactivity of carbido clusters

Many of the reactions which carbido clusters undergo are similar to those exhibited by their binary carbonyl cluster counterparts. However, it would appear that the interstitial carbido atom has the ability to stabilise the cluster unit towards fragmentation. This is especially true for the compounds $[M_5C(CO)_{15}]$ (M = Ru or Os) and $[Os_{10}C(CO)_{24}]^{2-}$ which have been the most extensively studied.

In addition to the sites of attack available in the binary carbonyls, namely the metal atoms, metal–metal bonds and the peripheral ligands, the carbido cluster may also show reactivity at the carbido atom.

The nature of the carbide atom is not well understood, but recent molecular orbital calculations using extended Hückel methods [31] have given some insight into this question. It has been shown that in the octahedral Fe_6C and square pyramidal Fe_5C species there is a strong interaction between the carbon *p* orbitals and the metal framework. This results in a large separation between the metal-carbido related orbitals and the HOMO and LUMO of the cluster system. Within the simple MO description of these systems, the LUMO and HOMO orbitals may be taken to be primarily metallic in character. Consequently attack by either nucleophilic or electrophilic reagents is expected to bring about a change in their basic metal geometries. However, because the metal-carbide orbitals are relatively low lying, the M–C interactions would be expected to moderate these changes and hence bind the system together. Neither of these clusters displays any reactivity at the carbon atom. For the Fe_6C clusters this may not be surprising as the carbido atom is physically shielded by an octahedron of metal atoms. For the Fe_5C cluster, however, the carbido atom is only semi-interstitial and is therefore theoretically open to attack yet, as predicted, it still shows no reactivity. For the exposed carbon atom of the Fe_4C butterfly species the gap between the highest occupied and lowest unoccupied orbitals is greatly reduced, and, as expected, reaction at the carbon atom is observed.

As yet, no M_4C (M = Ru or Os) clusters are known * but, by analogy with the

---

* However we have synthesised and fully characterised the M_4N clusters $[HRu_4N(CO)_{11}P(OMe)_3]$ [58], $[H_3Ru_4N(CO)_{11}]$ and $[Os_4N(CO)_{12}]^-$ [59].

iron systems, we expect that they too will show reactivity at the carbido atom. In the case of the known ruthenium and osmium carbide clusters no reactivity of the C atom has been observed *, and the principal reactions, discussed in detail below, involve structural rearrangements of the metal cage. This would imply that the LUMO and HOMO are predominantly metallic in character, as predicted again on the basis of the MO calculations performed on the Fe_6C and Fe_5C clusters.

Reactions with nucleophiles

Reactions with nucleophiles are specific to the neutral carbido clusters. Attack may occur at either the metals or the carbon atom of a carbonyl ligand (see Fig. 2); in the case of alcohols this leads to retention of the CO group with the formation of a carboalkoxy bridge, for example [14]:

$$[Os_5C(CO)_{15}] \xrightarrow{ROH} [HOs_5C(CO)_{14}(\mu_2\text{-COOR})](R = \text{Me, Et, i-Bu})$$

When the nucleophile is OH^- attack at a CO group is followed by the expulsion of CO as CO_2, as in mononuclear species, eventually leading to the formation of the corresponding anionic species, for example [6]:

$$[M_5C(CO)_{15}] \xrightarrow{OH^-} [M_5C(CO)_{14}]^{2-} (M = \text{Ru, Os})$$

The reduction of $[Ru_6C(CO)_{17}]$ by base to an anion of the same nuclearity, $[Ru_6C(CO)_{16}]^{2-}$ [16], is similar to that observed for non-carbido clusters such as $[Rh_6(CO)_{16}]$, but is in contrast to that of other non-carbido carbonyls, for example $[Os_6(CO)_{18}]$. This osmium cluster undergoes nucleophilic addition at the metal atoms, leading ultimately to cluster fragmentation [45]:

$$[Os_6(CO)_{18}] + 3OH^- \rightarrow [Os_5(CO)_{15}]^{2-} + [Os(CO)_3(OH)_3]^-$$

Other common nucleophiles such as CO or PR_3 attack the central M_nC unit. For $[Ru_6C(CO)_{17}]$ and $[Ru_5C(CO)_{15}]$, reaction with phosphines results in the produc-

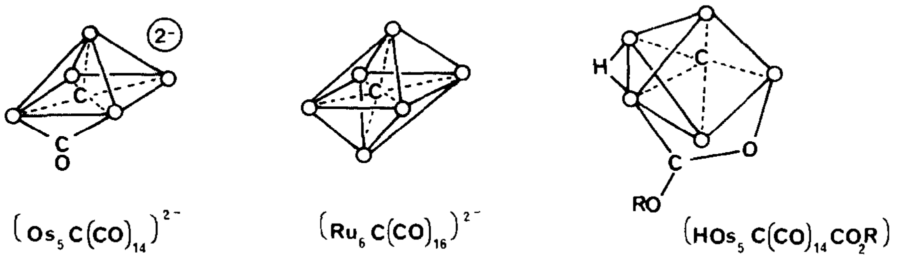


Fig. 2. Products from the reactions potentially involving attack at a carbonyl group of $[Os_5C(CO)_{15}]$ and $[Ru_6C(CO)_{17}]$.

---

* We have some evidence for the extrusion of the carbido atom of $[Ru_5C(CO)_{15}]$ on reaction with hydrogen, but this has not be confirmed.

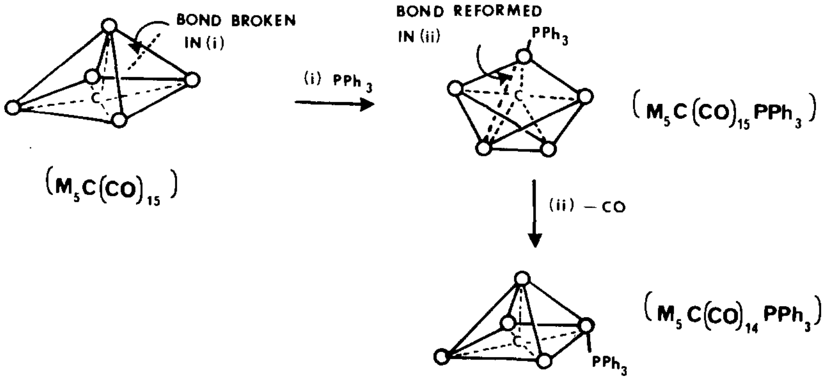
tion of simple substituted derivatives:

$$[\mathrm{Ru_6C(CO)_{17}}] \xrightarrow{n\mathrm{PR_3}} [\mathrm{Ru_6C(CO)_{17\text{-}n}(PR_3)_n}][18]$$

$$[\mathrm{Ru_5C(CO)_{15}}] \xrightarrow{n\mathrm{PR_3}} [\mathrm{Ru_5C(CO)_{15\text{-}n}(PR_3)_n}][3]$$

$(n = 1, 2, 3, 4)$

However, in the corresponding reaction of $[\mathrm{Os_5C(CO)_{15}}]$ the intermediate formation of an adduct, $[\mathrm{Os_5C(CO)_{15}PR_3}]$, is observed. This adduct is unstable, losing CO on warming to yield the substitution product, (see Scheme 2).



SCHEME 2

This observation suggests that the substitution of $[\mathrm{Ru_5C(CO)_{15}}]$ also proceeds via adduct formation. Indeed, adduct formation has been observed for $[\mathrm{Ru_5C(CO)_{15}}]$, in the case of the reversible addition of (MeCN) to give $[\mathrm{Ru_5C(CO)_{15}(MeCN)}]$ [8]. This reaction involves a reversible opening out of the square pyramidal structure to give a wing-tip bridged butterfly, as shown in Fig. 3.

For electron deficient clusters we have previously proposed that nucleophilic addition of a two electron donor will occur at the metal atom with the lowest coordination number, and indeed we see attack of MeCN, CO or PR$_3$, for example, at a metal atom in the square base of $[\mathrm{M_5C(CO)_{15}}]$.

Nucleophilic attack with the formation of an adduct leading to structure rearrangement is not, of course, restricted to carbido clusters. In $[\mathrm{H_2Os_5(CO)_{15}}]$ there is a similar reaction sequence on reaction with CO or PR$_3$ [46]. Attack at the metal

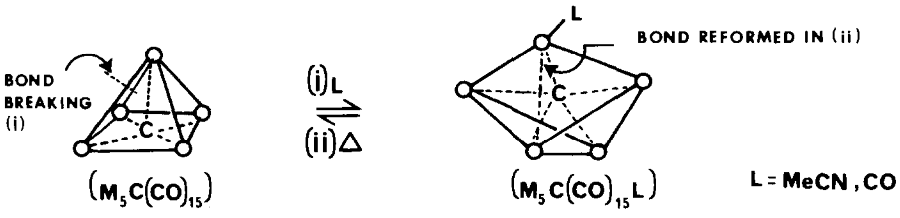
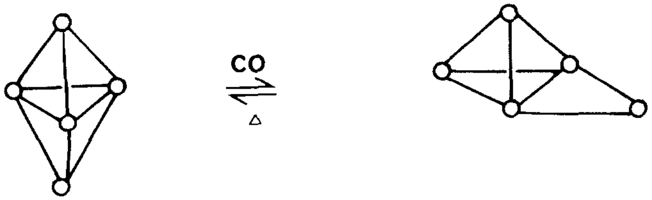


Fig. 3. Reversible addition of L (L = MeCN, CO) to $[\mathrm{M_5C(CO)_{15}}]$ (M = Ru, Os).



($H_2Os_5(CO)_{15}$) ($H_2Os_5(CO)_{16}$)

Fig. 4. Reversible addition of CO to $[H_2Os_5(CO)_{15}]$.

atom with the lowest connectivity, i.e. an apex of the trigonal bipyramid, gives $[H_2Os_5(CO)_{15}L]$ (L = CO, PR_3). Loss of CO occurs on heating to regenerate the trigonal bipyramid (see Fig. 4).

The process of opening out and closing up the M_5C unit mentioned above dominates the chemistry of the $[M_5C(CO)_{15}]$ complexes. The addition of reagents such as BY (B = H or $AuPPh_3$, Y = Cl, Br, I, SH or SEt) to $[M_5C(CO)_{15}]$ further illustrates this point [5]. The compounds produced all possess a wing-tip bridged butterfly metal arrangement (see Fig. 5).

Because of the ability of Y to donate a further electron pair, subsequent nucleophilic addition to an adjacent metal atom may be induced by heating. The formation of the bridging Y group does not, however, lead to major changes in the geometry of the metal polyhedron, and this step may be reversed with CO. Interestingly, when the HCl adduct $[HRu_5C(CO)_{15}Cl]$ is heated, the parent compound $[Ru_5C(CO)_{15}]$ is reformed [5].

Studies of $[Ru_6C(CO)_{17}]$ are not as complete as those on $[Ru_5C(CO)_{15}]$. One of the few reactions which does not lead to a simple *closo*-substituted derivative is that with HSEt. This gives, as one of the products, $[HRu_6C(CO)_{15}(SEt)_3]$ [10], which has a structure closely related to that of $[Ru_5C(CO)_{13}(SEt)]$, viz. a wing-tip bridged butterfly arrangement of ruthenium atoms, but in this case with an additional Ru unit bridging along one edge (see Fig. 6). It would appear that in this reaction, as in the reactions of $[Ru_5C(CO)_{15}]$, the reaction pathway involves opening up of the metal polyhedron, and hence the carbido atom becomes more exposed. Such derivatives obviously have more potential for displaying some reactivity at the carbide atom than the more compact parent compounds.

For the higher cluster compounds, relatively few reactions with nucleophiles have

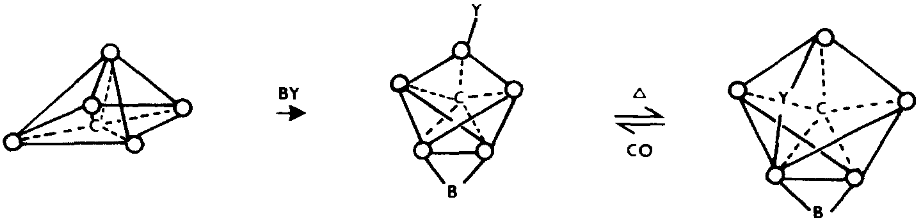


Fig. 5. The reaction of $[Ru_5C(CO)_{15}]$ with BY (B = H, $AuPR_3$; Y = Cl, Br, I, SH, SEt) and subsequent loss of CO.

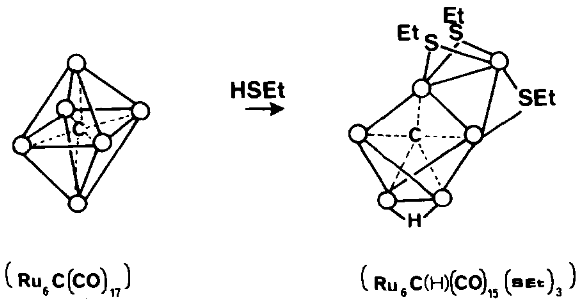


Fig. 6. Reaction of $[Ru_6C(CO)_{17}]$ with HSEt to give $[HRu_6C(CO)_{15}(SEt)_3]$.

been examined. To some extent this is because the most readily available species, $[Os_{10}C(CO)_{24}]^{2-}$, is anionic. Preliminary studies of the reaction of the salt $[PPN]_2[Os_{10}C(CO)_{24}]$ with CO have revealed a surprisingly high stability towards fragmentation the cluster resisting CO at pressures of 1500 atm at 250°C. The closely related neutral compound $[H_2Os_{10}C(CO)_{24}]$, prepared from the dianion by treatment with sulphuric acid, reacts with $P(OMe)_3$ to generate the compound $[Os_{10}C(CO)_{21}\{P(OMe)_3\}_4]$ [47]. Clearly, there are two processes occurring during this reaction: the displacement of H_2 by $P(OMe)_3$, and nucleophilic substitution of three CO groups by $P(OMe)_3$. Again it has not been possible to examine the more detailed mechanistic aspects of this reaction, nevertheless, one might speculate that, just as with the simpler systems, these nucleophilic substitution reactions occur via an associative process leading to opening up of a capping position in the intermediate stage. This would be followed by ligand ejection and reclosure of the metal framework.

The diiodide complex $[Os_{10}C(CO)_{24}I_2]$, another neutral derivative of the carbide dianion $[Os_{10}C(CO)_{24}]^{2-}$, also reacts with nucleophiles such as phosphite, phosphine, pyridine or carbon monoxide [22]. However, this does not lead to the formation of substituted compounds; instead the I^+ groups are removed sequentially as $[IL_2]^+$ and the parent dianion is regenerated via closure of the butterfly identations in the molecule. In contrast, treatment of $[Os_{10}C(CO)_{24}I_2]$ with $[PPN][NO_2]$, which is capable of removing CO ligands as CO_2, gives the species

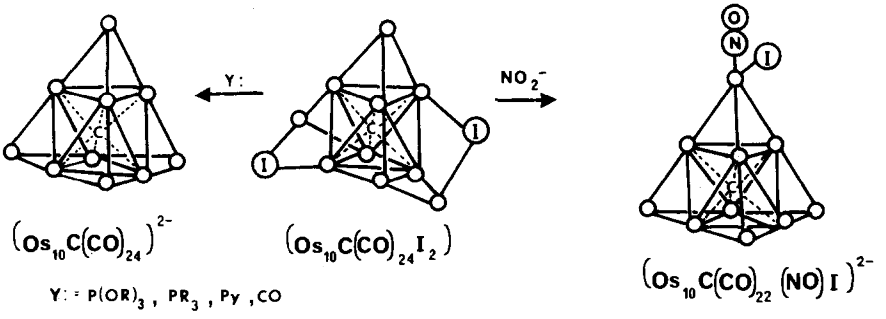


Fig. 7. The reaction of $[Os_{10}C(CO)_{24}I_2]$ with Y ($Y = P(OR)_3$, PR_3, Py and CO) and NO_2^- to give $[Os_{10}C(CO)_{24}]^{2-}$ and $[Os_{10}C(CO)_{22}(NO)I]^{2-}$, respectively.

$[Os_{10}C(CO)_{22}(NO)(I)]^{2-}$ [26] which is *quasi*-isostructural with $[Os_{10}C(CO)_{24}]^{2-}$ itself, (see Fig. 7). This reaction again illustrates the strong tendency for derivatives containing the $Os_{10}C$ unit to revert to a structure having approximate overall T_d symmetry of the metal framework. The substituted dianion $[Os_{10}C(CO)_{22}(NO)(I)]^{2-}$ is expected to show greater reactivity than $[Os_{10}C(CO)_{24}]^{2-}$ for two reasons; firstly polarity has been introduced into the molecule by the iodo atom, and secondly clusters containing the NO ligand are well known to be more reactive than their binary carbonyl analogues.

Reactions with electrophiles

In contrast to nucleophilic addition, electrophilic addition to neutral carbido species has only been observed for one class of compounds; the protonation of $[M_5C(CO)_{15}]$ (M = Ru or Os) yields a cationic species resulting from attack of H^+ at a metal centre, as indicated by the NMR shifts of the hydrogen atoms. Reactions involving electrophilic addition are, however, typical of the anionic carbido clusters. In contrast to the reactions with nucleophiles, for electrophiles it is difficult to predict both the site of attack of the reagent (which may be at a metal centre, a metal–metal bond, or the oxygen atom of a coordinated CO ligand) and its final mode of coordination to the cluster. The latter appears to depend on the donor capacity and bonding ability of the electrophile in question.

It is convenient to consider two groups of electrophilic reagents depending upon the availability of lone pairs for further bonding. The first class is typified by reagents such as $[Cu(MeCN)]^+$, $[AuPR_3]^+$ and H^+ in which no electrons are available for further bonding.

Since the skeletal electron count remains the same no change in geometry of the metal cage is expected. In the case of the Cu and Au reagents low lying empty orbitals may, however, be available for accepting electron density from the cluster. Addition of $[AuPR_3]^+$ fragments to anions has frequently been compared to addition of H^+ [48]; both species are capable of providing one orbital but no electrons for skeletal bonding. Some protonation reactions of carbido complexes will therefore be examined in this section and compared and contrasted with the analogous reactions involving $[AuPR_3]^+$.

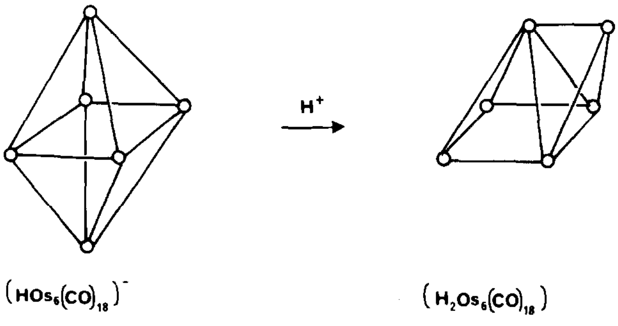
The second class of reagents includes species such as I^+ and NO^+, which have non-bonding electron pairs available for the formation of donor bonds. Thus on addition of these species, a rearrangement of the metal polyhedron involving cleavage of M–M bonds is expected, as the LUMOs of the cluster are predominantly M–M antibonding in character.

Reactions with $[Cu(MeCN)]^+$, $[AuPR_3]^+$ and H^+

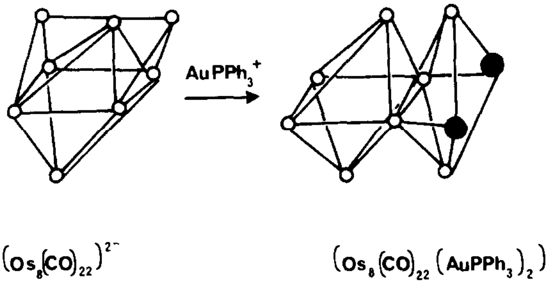
No change in the metal geometry of anionic carbides is observed on addition of species such as $[Cu(MeCN)]^+$, $[AuPR_3]^+$ and H^+. This behaviour is consistent with Wade Theory, since these species donate no electrons to the cluster. It is worth noting however, that addition of these cations to binary carbonyl anions (particularly to the large ones) often leads to drastic changes in the geometries of the metal polyhedra (see Scheme 3). So, again, it may be seen that carbido-centred clusters are more resistant to changes in structure of their metal cores than their non-carbido analogues.

Although the M_nC geometry in these derivatives remains the same, the modes of bonding of $[Cu(MeCN)]^+$ and $[AuPR_3]^+$ to carbide anions varies. This is in part due to the different steric demands of these two species, but is also due to their differing bonding abilities. Mingos has shown [49] that for $[AuPH_3]$ fragments, unlike their Cu analogues, the p_x and p_y orbitals are relatively high lying and cannot accept electron density effectively. Thus prediction of the mode of bonding (or attack) is difficult and unreliable. This point is illustrated by the examples below.

$[HOs_6(CO)_{18}]^- \xrightarrow{H^+} [H_2Os_6(CO)_{18}]$[50]



$[Os_8(CO)_{22}]^{2-} \xrightarrow{[AuPPh_3]^+} [Os_8(CO)_{22}(AuPPh_3)_2]$[51]



SCHEME 3

The dianion $[Os_{10}C(CO)_{24}]^{2-}$ reacts with $[Cu(MeCN)]^+$ to produce $[Os_{10}C(CO)_{24}Cu(MeCN)]^-$ [23]. In the structure of this compound the Cu(MeCN) unit occupies a μ_3-bridging position, which may be taken to indicate that all of the *s* and *p* orbitals of the Cu atom are used for bonding (see Fig. 8). However, when $[Os_{10}C(CO)_{24}]^{2-}$ is treated with $[AuPR_3]^+$ the anion $[Os_{10}C(CO)_{24}AuPR_3]^-$ [23] is formed in which the gold atom this time adopts an edge-bridging position. In this case the Au atom probably utilises an *sp* hybrid orbital for bonding, and attack at the metal cage results in the formation of a three-centre two-electron Os $\cdots$ Au $\cdots$ Os bond. Consistent with this view is the fact that the Os–Os distance bridged by the Au species is significantly longer in comparison to the other Os–Os bonds in this compound. The bonding modes of the Cu and Au moieties also differ completely in the related compounds $[Ru_6C(CO)_{16}\{Cu(MeCN)\}_2]$ [29] and $[Ru_6C(CO)_{16}\{AuPR_3\}_2]$

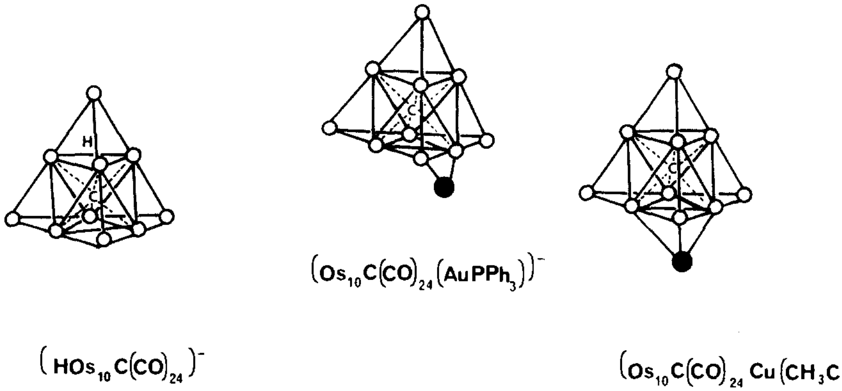


Fig. 8. Metal geometries of $[HOs_{10}C(CO)_{24}]^-$, $[Os_{10}C(CO)_{24}AuPPh_3]^-$ and $[Os_{10}C(CO)_{24}Cu(MeCN)]^-$.

[19] (see Fig. 9); in the former structure a direct Cu–Cu bond is formed, while in the latter the $AuPR_3$ groups adopt edge-bridging positions on opposite sides of the molecule. However, it should be noted that the Au or Cu ligand may adopt different bonding modes even in formally analogous isoelectronic compounds. For example, in the case of the complexes $[M_5C(CO)_{14}\{AuPR_3\}_2]$ (M = Fe, Os), as shown in Fig. 10, for M = Fe [57] a μ_4- and a μ_2-$AuPR_3$ group is present, but for M = Os [6] the $AuPR_3$ groups bridge opposite apical edges of the parent square pyramidal cluster.

The isolobal principle has been widely used to rationalize the addition of $[AuPR_3]^+$ and H^+ ligands to metal carbonyl anions [48]. Thus both are considered to furnish one orbital but no electrons for skeletal bonding, and so derivatives in which H^+ takes the place of $[AuPR_3]^+$ would be expected to be isostructural. This is true for the reaction of $[Ru_6C(CO)_{15}(NO)]^-$ with $[AuPR_3]^+$ and H^+, which gives the complexes $[Ru_6C(CO)_{15}(NO)(AuPR_3)]$ [52] and $[Ru_6C(CO)_{15}(NO)(H)]$ [53], respectively, as shown in Fig. 11. The protonation of $[Os_{10}C(CO)_{24}]^{2-}$ [25] would thus be expected, by comparison with the behaviour of the gold derivative, to yield a species having the hydride ligand bridging an edge of the Os_{10} tetrahedron $[Os_{10}C(CO)_{24}(\mu_2\text{-}AuPR_3)]^-$ [23] (vide supra). However, addition of H^+ to this complex forms a special case; although the initial attack may well follow the same course as the gold compound, and give a species similar in structure, the proton

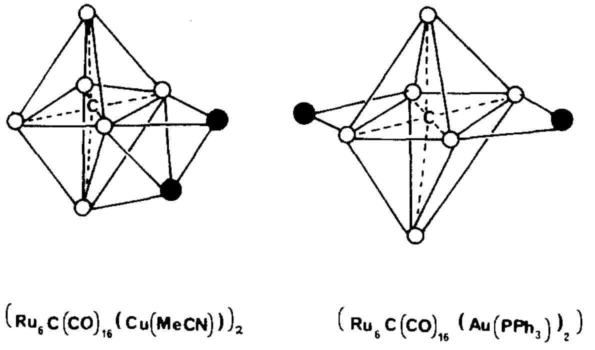


Fig. 9. Metal geometries of $[Ru_6C(CO)_{16}\{Cu(MeCN)\}_2]$ and $[Ru_6C(CO)_{16}(AuPPh_3)_2]$.

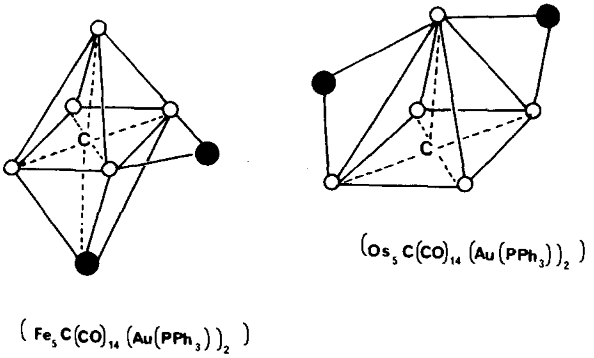


Fig. 10. Metal geometries of $[\mathrm{Fe_5C(CO)_{14}(AuPEt_3)_2}]$ and $[\mathrm{Os_5C(CO)_{14}(AuPPh_3)_2}]$.

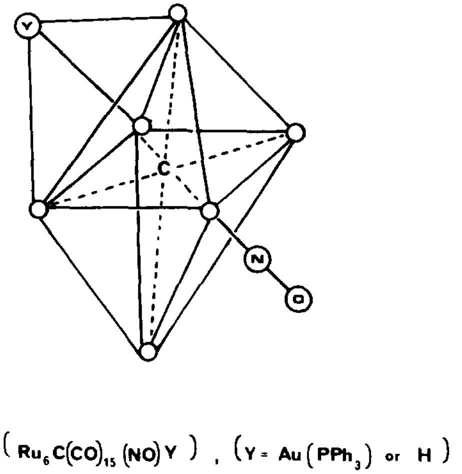


Fig. 11. Metal geometry of $[\mathrm{Ru_6C(CO)_{15}(NO)Y}]$ ($\mathrm{Y = AuPPh_3}$ or H).

eventually occupies a tetrahedral interstitial site, (Fig. 8). Thus, as has been found previously in non-carbido clusters, the isolobal principle breaks down in certain circumstances, and corresponding gold and hydrido derivatives do not necessarily have the same structure.

Reactions with $\mathrm{NO^+}$ and $\mathrm{I^+}$

Electrophilic addition of the species $\mathrm{X^+}$ (generated from $\mathrm{X_2}$, X = Cl, Br, I) and $\mathrm{NO^+}$ ($\mathrm{NOBF_4}$) to anionic carbides leads, in general, to an opening up of the metallic core. The dianion $[\mathrm{Os_{10}C(CO)_{24}}]^{2-}$ provides a good example, since it reacts with $\mathrm{NO^+}$ to produce the monoanion $[\mathrm{Os_{10}C(CO)_{24}(NO)}]^-$ [24] and with $\mathrm{I^+}$ to give $[\mathrm{Os_{10}C(CO)_{24}I}]^-$. The neutral species $[\mathrm{Os_{10}C(CO)_{24}I_2}]$ [22] (see Fig. 12) is formed on further reaction with iodine. In both cases, attack of $\mathrm{I^+}$ or $\mathrm{NO^+}$ occurs at a capping $\mathrm{Os_4}$ group leading to an opening out of this tetrahedral unit. Both I and NO bridge the wing tips of the butterfly $\mathrm{Os_4}$ arrangement in the resulting compounds. In both cases a strong tendency to reform the T_d symmetry $\mathrm{Os_{10}C}$ metal polyhedron has

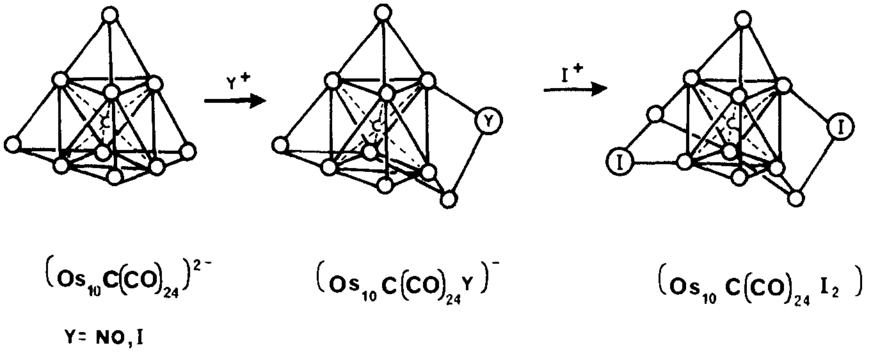


Fig. 12. The reactions of $[Os_{10}C(CO)_{24}]^{2-}$ with I_2 and $NOBF_4$.

been noted. The iodine derivatives react with the iodide ion and other nucleophiles L ($L = P(OMe)_3$, PPh_3, pyridine and MeCN) to give the $[Os_{10}C(CO)_{24}]^{2-}$ dianion through the sequential elimination of the bonded iodine atoms as I_2 and $[IL_2]^+$ respectively (as discussed previously). This reversible opening and closing of capping tetrahedra is a rarely observed process in high nuclearity clusters.

Interestingly, on standing rearrangement of the $[Os_{10}C(CO)_{24}(NO)]^-$ metal polyhedron occurs with loss of CO (see Fig. 12); a change in the coordination mode of the NO from μ_2-bridging to terminal and reformation of an Os–Os bond in the capping unit occurs to give $[Os_{10}C(CO)_{23}(NO)]^-$ [24] (see Fig. 13). Again, the overall molecular geometry is close to that found in the parent dianion $[Os_{10}C(CO)_{24}]^{2-}$.

Thus, the isolation of the species $[Os_{10}C(CO)_{24}(\mu\text{-NO}]^-$, an intermediate in the substitution of a CO for a NO in $[Os_{10}C(CO)_{23}NO]^-$, has brought a new insight into the mechanism of electrophilic addition of I^+ and NO^+ to anionic clusters. Firstly, it has led to the suggestion that the site of these electrophilic additions may be at a M–M bond, and not only at a M atom as previously suggested. Secondly, it suggests the possibility of the formation of an intermediate related to $[Os_{10}C(CO)_{24}(\mu\text{-NO})]^-$ in the reaction of NO^+ with $[Ru_6C(CO)_{15}NO)]^-$ to yield $[Ru_6C(CO)_{14}(NO)_2]$ [52], (see Fig. 14).

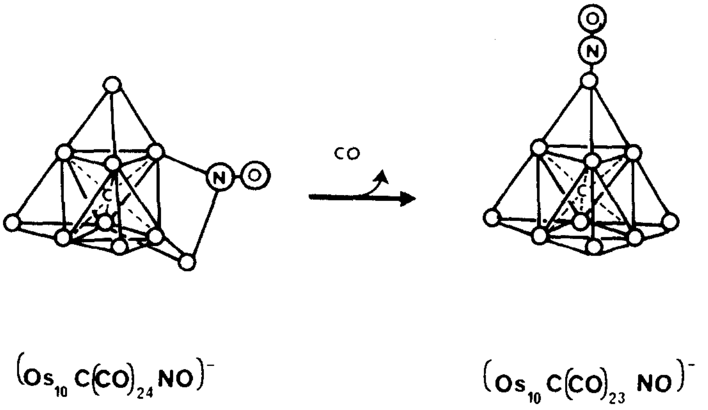


Fig. 13. Loss of CO from $[Os_{10}C(CO)_{24}(NO)]^-$ to give $[Os_{10}C(CO)_{23}(NO)]^-$.

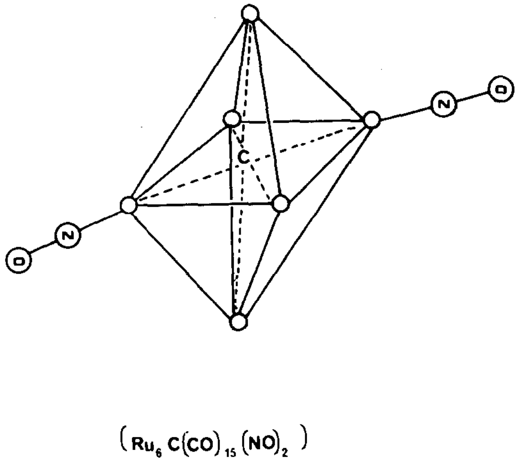


Fig. 14. Structure of $[Ru_6C(CO)_{14}(NO)_2]$.

References

1 D.H. Farrar, P.F. Jackson, B.F.G. Johnson, J. Lewis, J.N. Nicholls and M. McPartlin, J. Chem. Soc., Chem. Commun., (1981) 415.
2 P.F. Jackson, B.F.G. Johnson, J. Lewis, J.N. Nicholls, M. McPartlin and W.J.H. Nelson, J. Chem. Soc., Chem. Commun., (1980) 564.
3 B.F.G. Johnson, J. Lewis, J.N. Nicholls, J. Puga, P.R. Raithby, M.J. Rosales, M. McPartlin and W. Clegg, J. Chem. Soc., Dalton Trans., (1983) 277.
4 J. Evans, B.P. Gracey, L.R. Gray and M. Webster, J. Organomet. Chem., 240 (1982) C61.
5 A.G. Cowie, B.F.G. Johnson, J. Lewis, J.N. Nicholls, P.R. Raithby and M.J. Rosales, J. Chem. Soc., Dalton Trans., submitted for publication.
6 B.F.G. Johnson, J. Lewis, J.N. Nicholls, W.J.H. Nelson, J. Puga and M.D. Vargas, J. Chem. Soc., Dalton Trans., submitted for publication.
7 C.R. Eady, J.M. Fernandez, B.F.G. Johnson, J. Lewis, P.R. Raithby and G.M. Sheldrick, J. Chem. Soc., Chem. Commun., (1978) 421.
8 J. Lewis, B.F.G. Johnson, J.N. Nicholls, I.A. Oxton, P.R. Raithby and M.J. Rosales, J. Chem. Soc., Chem. Commun., (1982) 289.
9 J.N. Nicholls, B.F.G. Johnson, J. Lewis, J. Puga and K.H. Whitmire, J. Chem. Soc., Dalton Trans., in press.
10 B.F.G. Johnson, J. Lewis, K. Wong and M. McPartlin, J. Organomet. Chem., 185 (1980) C17.
11 J.M. Fernandez, B.F.G. Johnson, J. Lewis, P.R. Raithby and G.M. Sheldrick, Acta Cryst., B34 (1978) 1994.
12 J.M. Fernandez, B.F.G. Johnson, J. Lewis and P.R. Raithby, J. Chem. Soc., Dalton Trans., (1981) 2250.
13 A.G. Orpen and G.M. Sheldrick, Acta Cryst., B34 (1978) 1992.
14 D. Braga, B.F.G. Johnson, J. Lewis, M. McPartlin, W.J.H. Nelson, J.N. Nicholls and M.D. Vargas, J. Chem. Soc., Chem. Commun., (1982) 966.
15 A. Sirigu, M. Bianchi and E. Benedetti, J. Chem. Soc., Chem. Commn., (1969) 596.
16 G.B. Ansell and J.S. Bradley, Acta Cryst., B36 (1980) 726; B.F.G. Johnson, J. Lewis, S.W. Sankey, K. Wong, M. McPartlin, and W.J.H. Nelson, J. Organomet. Chem., 191 (1980) C3.
17 R. Mason and W.R. Robinson, J. Chem. Soc., Chem. Commun., (1968) 468.
18 S.C. Brown, J. Evans and M. Webster, J. Chem. Soc., Dalton Trans., (1981) 2263.
19 H.D. Holden, B.F.G. Johnson, J. Lewis and G.N. Pain, unpublished results.
20 B.F.G. Johnson, P.F. Jackson, J. Lewis, M. McPartlin, W.J.H. Nelson, G. Will and P.R. Raithby, J. Chem. Soc. Chem. Commun., (1981) 1190.

21 P.F. Jackson, B.F.G. Johnson, J. Lewis, W.J.H. Nelson and M. McPartlin, J. Chem. Soc., Dalton Trans., (1982) 2099.
22 D.H. Farrar, P.G. Jackson, B.F.G. Johnson, J. Lewis, W.J.H. Nelson and M.D. Vargas, J. Chem. Soc., Chem. Commun., (1981) 1009.
23 D. Braga, B.F.G. Johnson, J. Lewis, M. McPartlin, W.J.H. Nelson and M.D. Vargas, to be published.
24 D. Braga, K. Henrick, B.F.G. Johnson, J. Lewis, M. McPartlin, W.J.H. Nelson and J. Puga, J. Chem. Soc., Chem. Commun., (1982) 1083.
25 P.F. Jackson, B.F.G. Johnson, J. Lewis, M. McPartlin and W.J.H. Nelson, J. Chem. Soc., Chem. Commun., (1982) 49.
26 D. Braga, B.F.G. Johnson, J. Lewis, M. McPartlin, W.J.H. Nelson and J. Puga, to be published.
27 D. Braga, B.F.G. Johnson, J. Lewis, M. McPartlin, W.J.H. Nelson, A. Sironi and M.D. Vargas, unpublished results.
28 C.R. Eady, B.F.G. Johnson, J. Lewis and T. Matheson, J. Organomet. Chem., 57 (1973) C82.
29 J.S. Bradley, R.L. Pruett, E. Hill, G.B. Ansell, M.E. Leonowicz and M.A. Modrick, Organometallics, 1 (1982) 748.
30 D.H. Farrar, M.J. Rosales, B.F.G. Johnson, J. Lewis and P.R. Raithby, J. Chem. Soc., Dalton Trans., (1982) 2051.
31 J. Kolis, F. Basolo and D.F. Schriver, J. Am. Chem. Soc., 104 (1982) 5626.
32 C.R. Eady, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1977) 838.
33 M.J. Rosales, Ph.D. Thesis, Cambridge University, 1982.
34 G. Bor, G. Gervasio, R. Rossetti and P.L. Stanghellini, J. Chem. Soc., Chem. Commun., (1978) 841.
35 V.G. Albano, P. Chini, S. Martinengo, D.J. McCaffrey, D. Strumolo, B.T. Heaton, J. Am. Chem. Soc., 96 (1974) 8106; V.G. Albano, P. Chini, S. Martinengo, D. Strumolo and M. Sansoni, J. Chem. Soc., Chem. Commun., (1974) 299.
36 C.R. Eady, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1975) 2606.
37 D.H. Farrar, P.F. Jackson, B.F.G. Johnson, J. Lewis and J.N. Nicholls, J. Chem. Soc., Dalton Trans., (1982) 1395.
38 W.J.H. Nelson and M.D. Vargas, unpublished results.
39 E.H. Braye, L.F. Dahl, W. Hübel and L. Wampler, J. Am. Chem. Soc., 84 (1962) 4633.
40 D.H. Farrar, B.F.G. Johnson, J. Lewis, J.N. Nicholls and I.A. Oxton, Inorg. Chem., 20 (1981) 4302.
41 G. Bor and P.L. Stanghellini, J. Chem. Soc., Chem. Commun., (1979) 886.
42 I.A. Oxton, S.F.A. Kettle, P.F. Jackson, B.F.G. Johnson and J. Lewis, J. Mol. Struct., 71 (1981) 117.
43 J.S. Bradley, G.B. Ansell, M.E. Leonowicz and E.W. Hill, J. Am. Chem. Soc., 103 (1981) 4968.
44 J.S. Bradley, G.B. Ansell and E.W. Hill, J. Am. Chem. Soc., 101 (1979) 7417.
45 G.R. John, B.F.G. Johnson and J. Lewis, J. Organomet. Chem., 169 (1979) C9.
46 G.R. John, B.F.G. Johnson, J. Lewis, W.J.H. Nelson and M. McPartlin, J. Organomet. Chem., 171 (1979) C14.
47 D. Braga, R.J. Goudsmit, B.F.G. Johnson, J. Lewis and M. McPartlin, unpublished results.
48 E.g. J.W. Lauher and K. Wald, J. Am. Chem. Soc., 103 (1981) 7648; B.F.G. Johnson, D.A. Kaner, J. Lewis, P.R. Raithby and M.J. Taylor, J. Chem. Soc., Chem. Commun., (1982) 314.
49 D.G. Evans and D.M.P. Mingos, J. Organomet. Chem., 232 (1982) 171.
50 M. McPartlin, C.R. Eady, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Chem. Commun., (1976) 883.
51 B.F.G. Johnson, J. Lewis, W.J.H. Nelson, P.R. Raithby and M.D. Vargas, to be published.
52 D. Braga, W. Clegg, B.F.G. Johnson, J. Lewis, M. McPartlin, W.J.H. Nelson, J. Puga and P.R. Raithby, J. Organomet. Chem., 243 (1983) C13.
53 J. Lewis, B.F.G. Johnson, M. McPartlin, W.J.H. Nelson, J. Puga and A. Sironi, unpublished results.
54 C.M.T. Hayward, J.R. Shapley, M.R. Churchill, C. Bueno and A.L. Rheingold, J. Am. Chem. Soc., 104 (1982) 7347.
55 P.F. Jackson, B.F.G. Johnson, J. Lewis and P.R. Raithby, J. Chem. Soc., Chem. Commun., (1980) 60.
56 P.F. Jackson, B.F.G. Johnson, J. Lewis and W.J.H. Nelson, J. Chem. Soc., Chem. Commun., (1979) 735.
57 B.F.G. Johnson, D.A. Kaner, J. Lewis, P.R. Raithby and M.J. Rosales, J. Organomet. Chem., 238 (1982) C73.
58 D. Braga, B.F.G. Johnson, J. Lewis, J.M. Mace, M. McPartlin, J. Puga, W.J.H. Nelson, P.R. Raithby and K.H. Whitmire, J. Chem. Soc., Chem. Commun., (1982) 1081.
59 M.A. Collins, B.F.G. Johnson, J. Lewis, J.M. Mace, J. Morris, M. McPartlin, W.J.H. Nelson, J. Puga and P.R. Raithby, to be published.
60 V.G. Albano, M. Sansoni, P. Chini and S. Martinengo, J. Chem. Soc., Dalton Trans., (1973) 651.