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Carbide forming and cluster build-up reactions in ruthenium carbonyl cluster chemistry

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Abstract

The reinvestigation of an early synthesis of hexaruthenium carbido clusters has lead to the isolation of a number of new clusters which have been fully characterised by spectroscopic and crystallographic techniques. The thermolysis of $Ru_3(CO)_{12}$ in the presence of mesitylene (1,3,5-trimethylbenzene) at moderate temperatures yields two new clusters, $[Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)]$ (I) and $[HRu_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\mu_2\text{-}\eta^7\text{-}C_6H_3Me_2CH_2)]$ (II), the structures and reactivity of which indicate the origin and mechanism of formation of the carbido-carbon in the hexaruthenium carbido clusters $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)]$ (III) and $[Ru_6C(CO)_{17}]$ (IV). A further product of the reaction is the decaruthenium carbido cluster dianion $[Ru_{10}C(CO)_{24}]^{2-}$ (V) which has the tetracapped octahedral geometry. The monohydrido-cluster anion $[HRu_{10}C(CO)_{24}]^-$ (VI) may be synthesised quantitatively from V by protonation. The nature of the hydrido-ligand in VI has been investigated in the solid state by NMR spectroscopy and it has been found to be fluxional, its location being temperature dependent. The decanuclear dianion V has been found to react with mercury salts to yield the 21 metal atom cluster dianion $[Ru_{18}Hg_3C_2(CO)_{42}]^{2-}$ (VII) which consists of two tricapped octahedral nonaruthenium "subclusters" fused by a bi-facecapping $(Hg_3)^{2+}$ unit.

The reaction of $Ru_3(CO)_{12}$ with mesitylene was first reported in 1967 to yield $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)]$ (III) and $Ru_6C(CO)_{17}$ (IV), and at that time these were the only examples of clusters containing completely encapsulated carbon atoms [1]. Carbido-transition metal carbonyl clusters of many metals have now been characterised [2]. The origin of the carbide atom in these clusters has been the subject of some conjecture. Labelling experiments with ^{13}C have established its origin in some cases however; the carbido atom in $[Rh_6C(CO)_{15}]^{2-}$ has been shown to be derived from solvent $CHCl_3$ for example [3], whilst preparation of some ruthenium or osmium carbido clusters from ^{13}CO enriched precursors has shown that it is the result of the cleavage of coordinated carbon monoxide [4]. In early work the sealed tube pyrolysis of $Ru_3(CO)_{12}$ was shown to give a low yield of IV and CO_2 was detected in the gases evolved during the reaction; thus establishing that in this reaction the carbido atom is the result of the disproportionation of two molecules of carbon monoxide [5] (eq. 1). In contrast, in the pyrolysis of

$$2CO \rightarrow CO_2 + C \qquad (1)$$

$[Ru_5(CO)_{15}(NCBu^t)(\mu_5\text{-}NCBu^t)]$ to give $[Ru_6C(CO)_{16}(NCBu^t)]$, labelling of the $NCBu^t$ ligands with ^{13}C has established that the carbido atom originates from the cyano-carbon. [6]

The mechanism of carbonyl disproportionation has received much attention as the cleavage of the C–O bond of carbon monoxide is of fundamental importance to many homogeneous and heterogeneous catalytic processes. The initial process in Fischer–Tropsch chemistry is thought to involve such a process on the catalyst surface prior to hydrogenation and polymerisation of the resulting hydrocarbyl species. Many studies of the Fischer–Tropsch related chemistry of several transition metals under heterogeneous conditions confirm that disproportionation of CO results in surface carbide species, moreover such pretreated metals produce hydrogenated products more rapidly under pressures of CO/H_2 mixtures than the "clean" metal [7].

The chemistry of larger carbido clusters has developed in recent years to constitute a distinct field of cluster chemistry. For the iron triad the clusters are exclusively based on the octahedral geometry; the tetra- and penta-nuclear clusters being regarded as *arachno* and *nido* derivatives of this basic metal framework, and the higher nuclearity systems being capped octahedra [2]. The tetracapped octahedral geometry is now well established for a number of decanuclear osmium clusters, the metal which has dominated the field of high nuclearity iron triad carbonyl clusters. The reason for the paucity of high nuclearity clusters of ruthenium remains unclear; the isolation of the decaruthenium carbido cluster dianion $[Ru_{10}C(CO)_{24}]^{2-}$ (V) suggests however that this chemistry of ruthenium may develop to parallel that for osmium. Remarkably since our discovery of V, its synthesis by a different route, and structure has been reported by another group [8].

A tetrahedral site for a hydrido ligand was first deduced from the X-ray structure analysis of the tetracapped octahedral decaosmium monohydride anion $[HOs_{10}C(CO)_{24}]^-$ (VIII) where the undistorted close packing of the carbonyl ligands precluded a surface location for the hydrido ligand, and it was proposed that it was located inside one of the Os_4 caps, since the octahedral cavity was occupied by the carbide ligand [9]. This type of site symmetry for a hydrido ligand is still very rare. The hexaruthenium monoanion $[HRu_6(CO)_{18}]^-$ provided the first example of an interstitial hydrido ligand ever reported in a carbonyl cluster, although this was octahedrally sited [10]. There has been no example of a hydrido ligand inside a tetrahedron of ruthenium atoms until now.

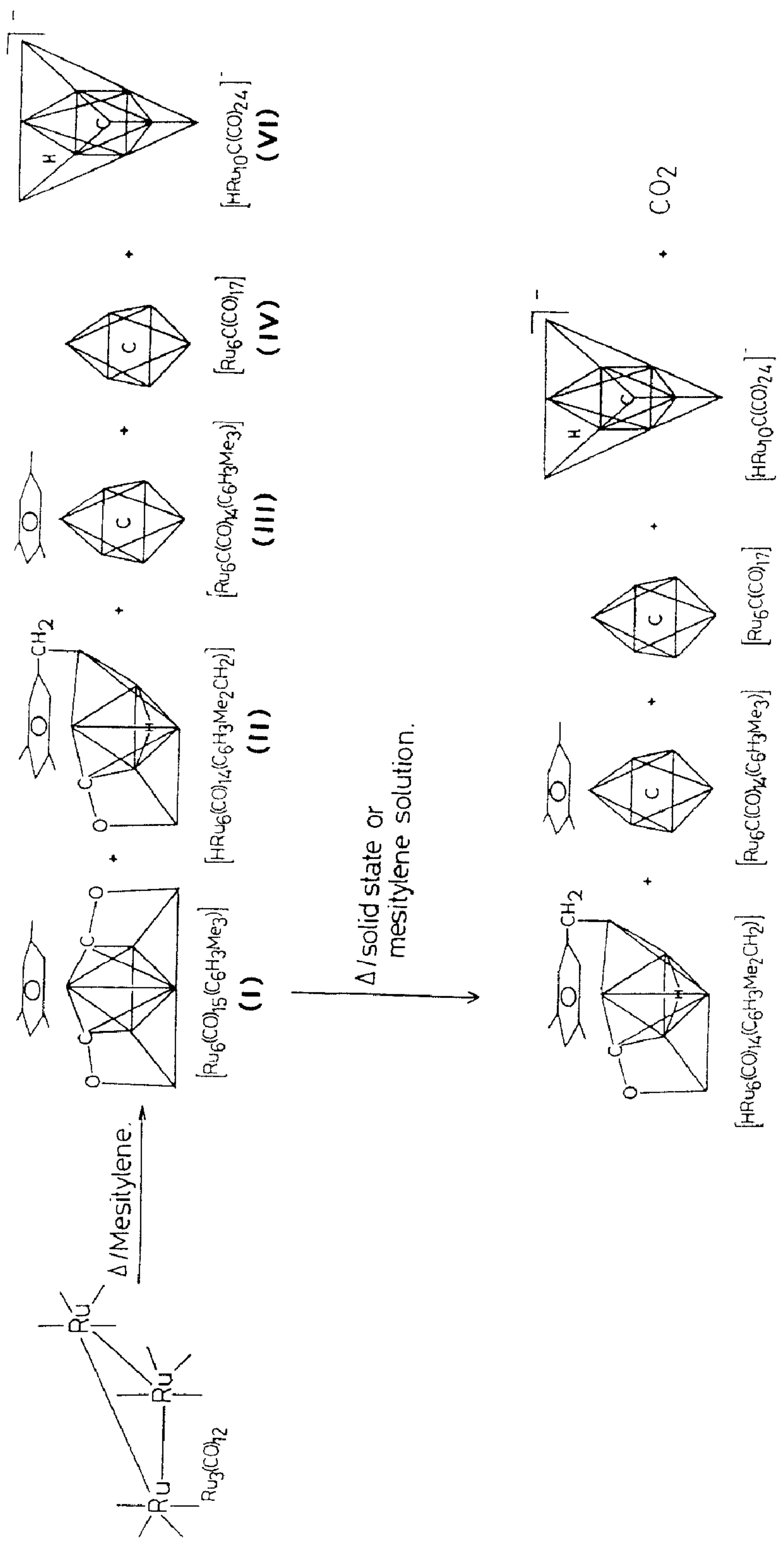
The synthesis and characterisation of the osmium cluster dianion reported as $[Os_{20}HgC_2(CO)_{48}]^{2-}$ (IX) was a significant breakthrough in osmium cluster chemistry since, not only is it the largest ever cluster reported for this metal, its formation and structure suggested a rationale for the synthesis of very large osmium clusters [11].

Binary osmium carbonyl clusters, and indeed all such relatively early group metal clusters, effectively have a maximum nuclearity which is dictated by the electronic requirements of the metal and the steric interactions of the carbonyl ligands on the surface of the cluster. As the nuclearity of a cluster increases the surface area/nuclearity ratio decreases and a critical point is reached at which there is insufficient room on the surface of the cluster to accommodate the number of carbonyl ligands necessary to satisfy the electronic requirements of the metals. This obstacle to the synthesis of very large clusters of these metals may be overcome in two ways. Firstly, the incorporation of interstitial atoms into a cluster decreases the electronic requirement of the metal framework without occupying space on the cluster surface, therefore allowing a higher nuclearity to be achieved before the critical ratio is exceeded. This approach is moderately effective although methods of synthesising clusters containing more than one interstitial atom for these metals have yet to be developed. The second, and potentially far more effective, procedure is to effectively "dilute" the electronic requirements of the cluster relative to its surface area by fusing subcluster units together with late transition, or even *p*-block elements. Such a route to these large clusters is observed in the structure of the new cluster $[Ru_{18}Hg_3C_2(CO)_{42}]^{2-}$ (VII) in which the two nonanuclear subclusters are fused by a Hg_3 triangle.

Results and discussion

We have previously reported that the reaction of $Ru_3(CO)_{12}$ with arenes (hexamethylbenzene, mesitylene, xylenes, toluene) in heptane at 97 °C gave after 3–5 days (depending on the arene) a solid black deposit and deep red/brown solutions from which the clusters analogous to I–IV containing the appropriate arene may be isolated by thin layer chromatography (TLC) [12]. Further investigations were carried out mainly on the mesitylene-derived clusters, however it is apparent that in principle the chemistry applies equally to the clusters derived from other methyl substituted arenes. The yields of the four clusters depend upon the reaction time, I being the first formed product, and the concentrations of II, III and IV increasing as the reaction proceeds, at its expense. However, the reaction conditions may be optimised to give yields of approximately 15% for any one selected product. The rate at which the reaction proceeds is increased by methyl substitution of the arene, and thus by higher electron density in the arene ring. The reaction with hexamethylbenzene is thus complete within 3 days, but for that with toluene at least 5 days is required.

The solution infrared spectrum of I in the carbonyl stretching region shows it to contain one bridging (μ_2-) carbonyl ligand, and the ^1H NMR spectrum contains two singlets at 4.90 and 1.66 ppm in the integration ratio of 1/3, consistent with an η^6-bonded mesitylene ligand. The electron impact (EI) mass spectrum of I shows an identical molecular ion to that given by III at $m/z = 1136$ and successive loss of 14 carbonyl ligands; a peak at 44 daltons attributed to CO_2 was also observed to


$Ru_3(CO)_{12}$
Δ/Mesitylene.
$[Ru_6(CO)_{15}(C_6H_3Me_3)]$
(I)
$[HRu_6(CO)_{14}(C_6H_3Me_2CH_2)]$
(II)
$[Ru_6C(CO)_{14}(C_6H_3Me_3)]$
(III)
$[Ru_6C(CO)_{17}]$
(IV)
$[HRu_{10}C(CO)_{24}]^-$
(VI)
Δ/solid state or mesitylene solution.
CH_2
CO_2

Scheme 1.

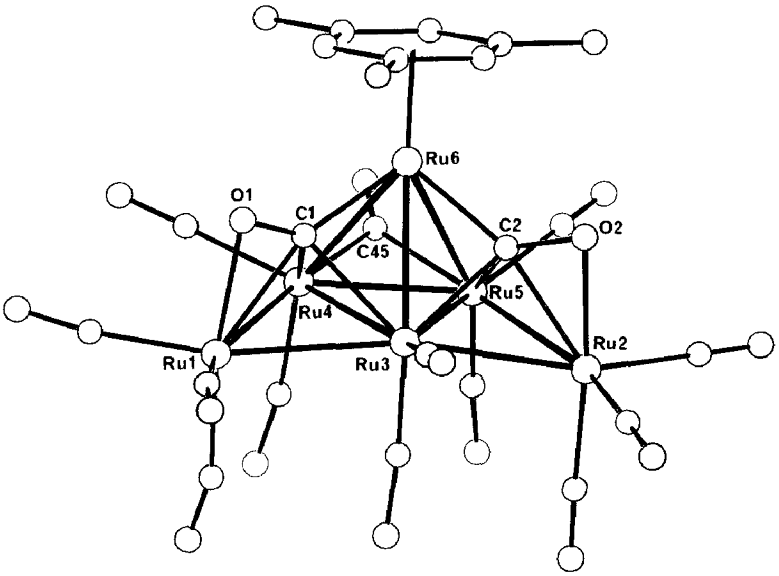


Fig. 1. The molecular structure of $[Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)]$ (I).

increase in intensity relative to that due to O_2 (32 daltons) during the experiment, showing that I is converting into III and CO_2 inside the spectrometer.

In order to elucidate the structure of I a single crystal X-ray structure determination was carried out [12]. The determination confirms the formulation of I as $[Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)]$, and establishes that the metal framework consists of a tetrahedral Ru_4 arrangement with two edge bridging Ru atoms, the first example of this polyhedron for ruthenium (Fig. 1). There are two, 4 electron donating, π-bonded (μ_4-η^2-) carbonyl ligands situated in the two Ru_4 'butterflies' created by the two bridging Ru atoms and the faces of the metal tetrahedron, and there is a symmetrically bridging (μ_2-) carbonyl ligand spanning the unique basal edge of the central Ru tetrahedron. The mesitylene ligand is η^6-bonded to the apical Ru(6) atom, and is planar. The methyl groups of this ligand are staggered with respect to the vectors of the π-bonded carbonyl ligands in the solid state. However, the ^1H NMR spectrum shows all methyl hydrogens to be equivalent in solution at room temperature, as are the methine hydrogens, indicating that the cluster has C_s symmetry on the NMR timescale, with spinning of the mesitylene ring.

Clusters containing η^2-bonded carbonyl ligands are relatively rare [13], and to our knowledge the only other cluster containing two such ligands is $[Ru_5Mo_2(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{14}(\mu_4\text{-}S)(\eta^5\text{-}C_5H_5)]$ [14]. The C–O bond lengths of the η^2-bonded carbonyl ligands in I are equal within experimental error with a mean value of 1.255(10) Å, and are therefore considerably lengthened relative to the terminally coordinated ligands (mean 1.138(18) Å). This may be attributed to electron donation from the C–O π-bond, and increased electron density in the C–O π^* orbital due to the d_π–p_π bonding from three metals. These two carbonyl ligands may therefore be regarded as "activated" (vide infra).

The solution infrared spectrum of II in the carbonyl stretching region indicates that it contains two bridging carbonyl ligands; its EI mass spectrum shows a strong isotopic envelope centred at $m/ = 1122$ and successive loss of 14 carbonyl ligands. The ^1H NMR spectrum can be interpreted if we suppose that it arises from the

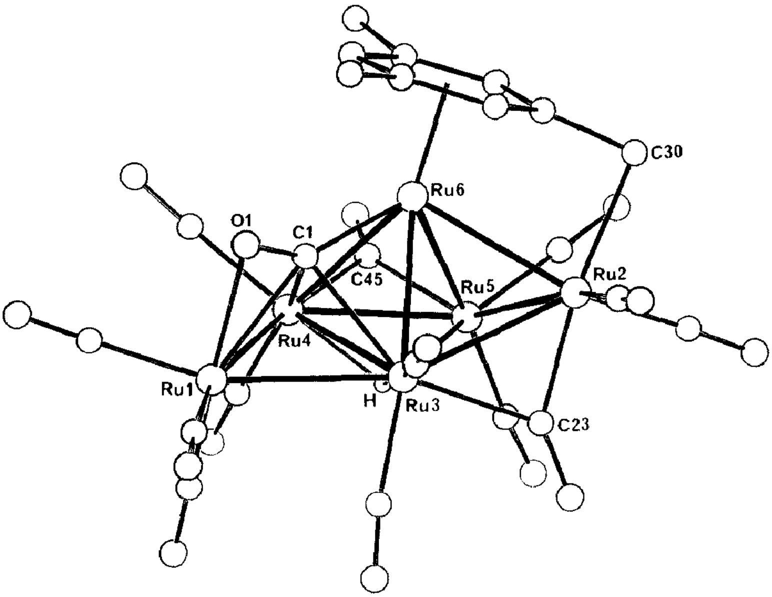


Fig. 2. The molecular structure of $[HRu_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\mu_2\text{-}\eta^7\text{-}C_6H_3Me_3)]$ (II).

mesitylene ligand losing a methyl hydrogen to the metal frame work and the resulting hydride ligand giving a singlet resonance at −19.5 ppm (1H); the remaining methylene group thus created is bonded to the cluster giving rise to two doublets at 3.33 and 2.99 ppm (J 6 Hz). Other resonances in the spectrum are consistent with a $(\mu_2\text{-}\eta^7\text{-})$ coordination mode for the mesityl ligand. This coordination mode anchors the ligand to the asymmetric cluster and prevents it from spinning, and so causes the inequivalence of the methine, methylene and the methyl group hydrogens in the ligand.

A single crystal X-ray study of $[HRu_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\mu_2\text{-}\eta^7\text{-}C_6H_3Me_2CH_2)]$ (II) shows the cluster to be closely related to I, having just one less carbonyl ligand than this cluster [12]. The metal framework of II may be described as a trigonal bipyramidal Ru_5 arrangement with a Ru atom bridging an apical-equatorial edge (Fig. 2). There are two bridging $(\mu_2\text{-})$ carbonyl ligands spanning the edges Ru(2)–Ru(3) and Ru(4)–Ru(5), and a face capping $(\mu_3\text{-})$ hydride ligand is located beneath the basal plane, Ru(3)–Ru(4)–Ru(5), of the central Ru tetrahedron. The position of this hydrido ligand was determined by potential energy minimisation calculations [15]. There is one $(\mu_4\text{-}\eta^2\text{-}CO)$ π-bonded carbonyl ligand coordinated in a similar position to those in $[Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)]$ (I) which shows an equivalent lengthening of the C–O bond relative to the terminal carbonyls. The organic ligand is η^6-bonded to the apical Ru(6) atom and is also bonded via the methylene carbon to Ru(2) (C(30)–Ru(2) 2.25 Å), giving an overall $(\mu_2\text{-}\eta^7\text{-})$ bonding mode for the ligand of the type indicated by the ^1H NMR spectrum. This coordination is similar to that found for the benzyl ligand in $[Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^7\text{-}C_6H_5CH_2)(CO)_{19}]$ [16].

Infrared spectroscopy of I, II and III

Infrared spectra of I, II and III and their ^{13}C enriched analogues in CsI discs were measured at 113 K. The spectra of the unenriched clusters over the frequency

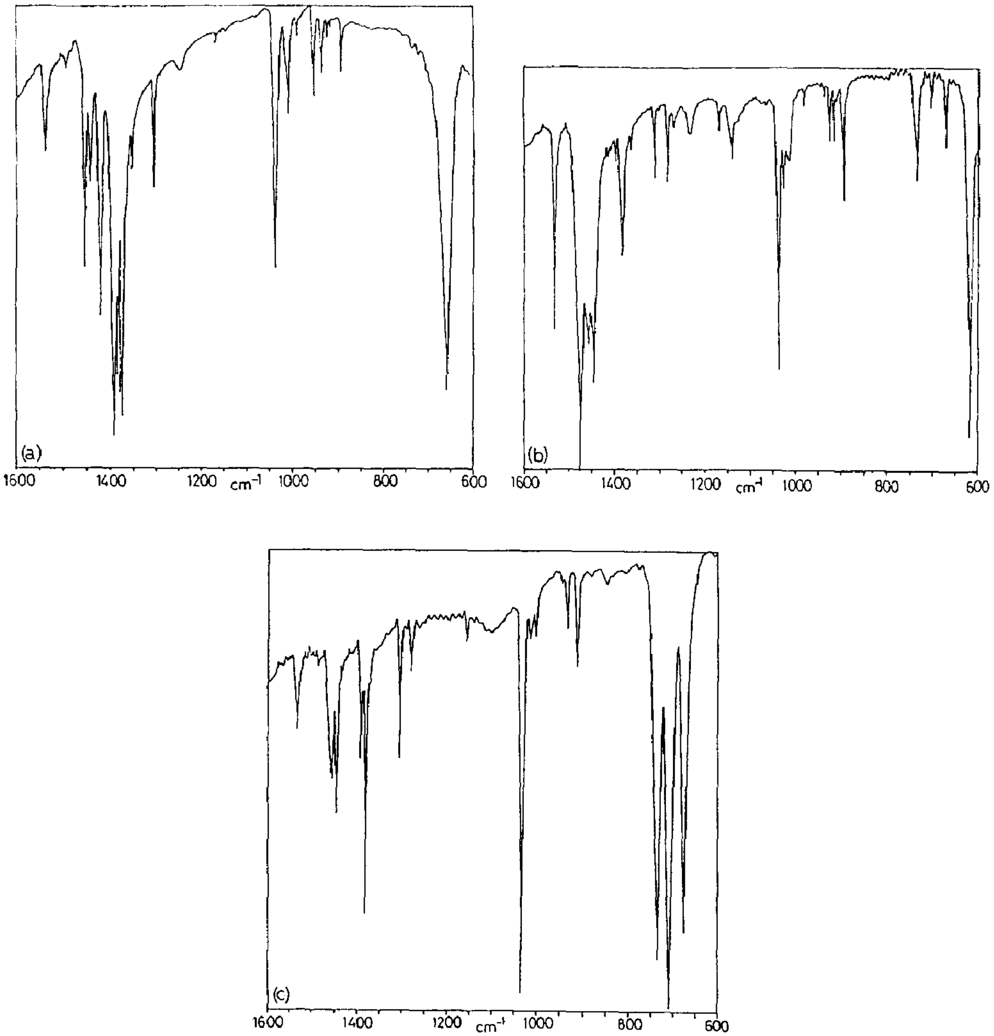


Fig. 3. The infrared spectra of (a) $[Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)]$ (I), (b) $[HRu_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\mu_2\text{-}\eta^7\text{-}C_6H_3Me_3)]$ (II) and (c) $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)]$ (III) in the region 1600–600 cm^{-1}, recorded in CsI discs at 113 K.

range 1600–600 cm^{-1} are shown in Fig. 3. The simplest spectrum is that of III, which is dominated by a triplet of very strong bands at 735, 709 and 674 cm^{-1}, which is characteristic of a carbide ligand inside an octahedral Ru_6 cluster [17]. These bands are reduced in intensity on ^{13}C enrichment, with three new bands appearing in the spectrum at 707, 682 and 651 cm^{-1}. The triplet of bands due to the carbide ligand show shifts very close to the expected $(12/13)^{1/2}$ and are replaced by bands of comparable sharpness, confirming their assignment to a single, vibrationally isolated carbide ligand, and also the derivation of this ligand from a coordinated carbonyl ligand in $[Ru_3(CO)_{12}]$. The remaining bands in this region of the spectrum can be assigned as modes of the mesitylene ligand.

In the spectrum of II, a strong band at 1446 cm^{-1} loses intensity and a new band appears at 1410 cm^{-1} on ^{13}C enrichment, and is assigned to the $\nu(CO)$ mode of the $(\mu_4\text{-}\eta^2\text{-}CO)$ ligand in this cluster. Similar frequencies have been observed for such ligands in other clusters [13]. A weak band at 912 cm^{-1} and a very strong band at 618 cm^{-1} are likewise shifted on enrichment, to 893 and 606 cm^{-1} respectively. The isotope shifts (0.974 and 0.979) are both indicative of modes in which the carbonyl ligand as a whole vibrates against the tetrametal butterfly framework in which it is located. If the carbonyl is formally considered as μ_3-bridging over three of the metal atoms and π-bonded to the fourth, then the most likely assignment of the 917 cm^{-1} band is to a mode which involves deformation of the "Ru_3CO" unit with simultaneous stretching of the Ru–CO π-bond. This mode can most readily be visualised as a "frustrated rotation" of the carbonyl ligand in the plane defined by the two wingtip metal atoms, the ligand itself and and the mid-point of the "hinge". Two bands at 1233 and 694 cm^{-1} which sharpen markedly on cooling, can be assigned to the antisymmetric and symmetric ν(RuH) modes respectively, of the face capping (μ_3-) hydride ligand.

The spectrum of I shows two bands at 1423 and 1392 cm^{-1} of medium and strong intensities respectively, which are assigned to the antisymmetric and symmetric stretching modes of the two (μ_4-η^2-CO) carbonyl ligands. On enrichment two new bands at 1394 and 1357 cm^{-1} result from cluster molecules in which two such carbonyls have been replaced by ^{13}CO, and bands at 1413 and 1364 cm^{-1} are assigned to the (^{12}CO)(^{13}CO) isotopomer.

^{13}C NMR spectroscopy of I, II and III

The clusters I, II and III enriched with ^{13}C (approximately 50 atom% ^{13}C) were prepared from ^{13}CO enriched $Ru_3(CO)_{12}$, and their variable temperature ^{13}C-{^{1}H} NMR spectra were recorded. The spectrum of I at 291 K is entirely consistent with its solid state structure assuming C_s symmetry on the NMR timescale (vide supra); it shows seven resonances due to terminal carbonyl ligands between 206 and 187 ppm, a resonance at 224.7 ppm due to the bridging carbonyl and one at 292.1 ppm from the two symmetry related η^2-bonded CO ligands. No changes were observed in this spectrum on cooling to 220 K.

The spectrum of II at 291 K shows only 11 resonances and not the expected 14 for this asymmetric cluster, some form of limited carbonyl fluxionality is therefore proposed at this temperature. The spectrum at 218 K is however, entirely consistent with the solid state structure and contains resonances from one η^2-bonded (279.0 ppm), two bridging (225.0 and 220.6 ppm) and 11 terminal (205–182 ppm) carbonyl ligands. Three of the resonances due to terminal carbonyl ligands are doublets (J(CH) 11 Hz) and this confirms the position of the hydride ligand as (μ_3-) facecapping, vide supra, as in this position it would be expected to couple to three *trans*-carbonyl carbons.

The spectrum of III at 291 K indicates that there is a total carbonyl fluxionality on the NMR timescale since only a single, broad resonance is observed at 203.2 ppm in the terminal carbonyl region of the spectrum. The carbido resonance appears at 442.8 ppm and its intensity shows that it is ^{13}C enriched, and must therefore have originated from a coordinated carbonyl ligand. On cooling to 243 K a second, less intense, resonance develops at 194.2 ppm and the major resonance is further broadened. At the lowest temperature achieved, 170 K in CD_2Cl_2/CCl_2F_2, a number of shoulders develop on the major resonance, and the resonance at 194.2 ppm sharpens considerably, but no further peaks can be resolved. From these data, it is possible to deduce that there are at least two fluxional processes involving the carbonyl ligands occuring in this cluster, and that both involve the bridging carbonyl ligand, since no resonance is observed from this ligand at any temperature.

The formation of the carbido atom in III and IV

The ^{13}C NMR and infrared evidence shows that the carbido atom in III, and by inference that in IV, is derived from a coordinated carbonyl ligand, however the mechanism of the C–O bond cleavage is not apparent from the above arguments. It was found that the thermolysis of I in mesitylene solution or in the solid state gave hexaruthenium carbido clusters. In order to provide evidence indicating the mechanism of the formation of the carbido clusters the thermolyses were carried out in an infrared gas cell and the gaseous products were identified by their infrared spectra in situ.

In the case of solution thermolysis the infrared spectrum of the gaseous products, after freezing out the mesitylene solvent, showed strong absorbtions at 2360 and 2344 cm^{-1} characteristic of CO_2. Separation of the products remaining in solution by TLC showed that clusters II and III had been formed in equal yield. The thermolysis in the solid state also gave CO_2, but in addition the gaseous infrared spectrum showed the characteristic absorptions of CO at 2175 and 2116 cm^{-1} suggesting cluster decomposition. The solid residue consisted mainly of ruthenium metal, however TLC showed that the soluble fraction contained III, IV and unreacted I. The observation of CO_2 in the reaction products confirms that the carbido atoms are the result of the disproportionation of two molecules of CO (eq. 1). Significantly, reaction of I with CO in solution at 20 °C and 1 atm. resulted in complete decomposition to $Ru_3(CO)_{12}$.

Evidence that the coordination of a carbonyl ligand in the (μ_4-η^2-) mode weakens the C–O bond is given by the bond length, infrared stretching frequencies and, to a certain extent, the ^{13}C NMR chemical shift of such a ligand, vide supra, and it is reasonable to conclude that the C–O bond is considerably activated towards cleavage in this situation. The cluster I contains two such activated carbonyl ligands, and it seems probable that the carbido atom contained in III, generated during the thermolysis of I, is derived from one of these ligands. The reaction (eq. 2) is known the generate CO_2, two carbonyl ligands must therefore be involved in the carbido-forming reaction however, an intramolecular process may be ruled out on the grounds of carbon stoichiometry in that the carbido-containing product $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)]$ (III) has an equal number of non-aryl carbon atoms to that of the reactant molecule $[Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)]$ (I). Significantly, the other product of the thermolysis of I, $[HRu_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\mu_2\text{-}\eta^7\text{-}C_6H_3Me_2CH_2)]$ (II), produced in equal molecular amounts to III, has one less carbonyl ligand than III (Scheme 1).

$$2\underset{(\mathrm{I})}{\left[Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)\right]} \xrightarrow{\Delta}$$

$$\underset{(\mathrm{II})}{\left[HRu_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\mu_2\text{-}\eta^7\text{-}C_6H_3Me_2CH_2)\right]}$$

$$+\underset{(\mathrm{III})}{\left[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)\right]} + CO_2 \qquad (2)$$

The following process may therefore be envisaged: two activated carbonyl ligands, one on each of two molecules of cluster I, undergo an intermolecular electronic rearrangement such that a molecule of CO_2 is formed and liberated, leaving a carbido atom coordinated to one of the cluster molecules. This intermediate, therefore has the formula $[Ru_6C(CO)_{14}(C_6H_3Me_3)]$, and rearranges to the most stable structure, which is that observed for cluster III. The other half of the reacting pair, having lost a η^2-bonded carbonyl ligand, is coordinatively unsaturated, and this facilitates formation of a Ru–Ru bond across the cavity where the carbonyl ligand was located, and metallation at one of the methyl groups on the mesitylene ligand, with a hydride ligand migrating to the metal framework. This process results in the formation of the observed structure of cluster II.

The fact that both unreacted cluster I and ruthenium metal along with III and IV are found in the solid residues of the solid state thermolysis of I, and that carbon monoxide is present in the gaseous products, is indicative of non-uniform heating of the reactant, a problem frequently associated with solid state reactions. It may also be associated with the need to disrupt the lattice structure of the crystalline material in order for the reacting molecules to adopt the correct reaction geometry. The reaction therefore proceeds in an atmosphere of carbon monoxide due to this unavoidable decomposition. As a result not only is III formed, by a similar process to that described for the solution reaction, but IV is also formed by ejection of the mesitylene ligand from III, or from an intermediate at some earlier stage in the reaction, in favour of coordination of carbon monoxide.

This is the first observation indicating the mechanism of cleavage of carbon monoxide by its interaction with a metal cluster substrate alone, although the mechanism of cleavage on an Fe_4 cluster by successive protonation has been elucidated by isolation of intermediates [18]. It is possible that if the metal substrate were a metal surface, which would have greater structural stability, instead of a molecular species, the rearrangement of the metal framework surrounding the carbide atom to encapsulate it would be restricted, and it would remain coordinated to a tetrametal site. Such a surface-bound carbide atom has long been postulated as the pivotal intermediate in many heterogeneous catalytic reactions of carbon monoxide.

The isolation and characterisation of $[Ru_{10}C(CO)_{24}]^{2-}$ (V) and $[HRu_{10}C(CO)_{24}]^-$ (VI)

Investigation of the solid residues from the reaction of $Ru_3(CO)_{12}$ with mesitylene has led to the isolation of the decaruthenium carbido-cluster anions $[Ru_{10}C(CO)_{24}]^{2-}$ (V) * and $[HRu_{10}C(CO)_{24}]^-$ (IV) **, in 35% yield (based on

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* Crystal data for $[PPN]_2[Ru_{10}C(CO)_{24}]^{2-}$ (V); $C_{97}H_{60}N_2O_{24}P_4Ru_{10}\cdot C_6H_{14}$, $M = 2858.63$, monoclinic, space group $C2/c$, a 17.349(5), b 27.443(6), c 21.570(6) Å, β 92.74(1)°, U 10257.82 Å^3, $F(000) = 5592$, $\mu(\text{Mo-}K_\alpha)$ 14.09 cm^{-1}, $Z = 4$, D_c 1.85 g cm^{-3}. In the space group $C2$, location of three phenyl rings and the hexane molecule could not be achieved satisfactorily because of pseudo symmetry (a 'c-glide') relating the two independent molecules, each of exact $C2$ symmetry. Consequently the structure was refined in the space group $C2/c$ resulting in an apparent disorder of the counterion and solvent. Present $R = 0.1455$ and $R' = 0.1471$ for 2549 reflections with $I/\sigma(I) > 3$.

** Crystal data for $[PPN][HRu_{10}C(CO)_{24}]^-$ (VI); $C_{61}H_{31}NP_2Ru_{10}\cdot CH_2Cl_2$, $M = 2341.39$, monoclinic, space group $P2_1/c$, a 11.777(2), b 17.805(4), c 35.365(5) Å, β 94.03(1)°, U 7397.33 Å^3, $F(000)$ 4476, $\mu(\text{Mo-}K_\alpha)$ 19.45 cm^{-1}, $Z = 4$, $D_c = 2.10$ g cm^{-3}. Final $R = 0.0725$ and $R' = 0.0650$ for 3555 reflections with $I/\sigma(I) > 3$.

$Ru_3(CO)_{12}$) [19]. X-ray structure analysis shows that they are isostructural with their respective osmium analogues $[Os_{10}C(CO)_{24}]^{2-}$ (X) and $[HOs_{10}C(CO)_{24}]^-$ (VIII) [20,9], both having the giant tetrahedral metal framework, well known for a range of decaosmium clusters. For some years, such species have eluded detection in studies of ruthenium clusters by many workers [20].

The ^1H NMR spectrum of V shows no resonances other than those due to the $[N(PPh_3)_2]^+$ counterion, whilst that of VI has an additional singlet at -13.5 ppm corresponding to a hydrido ligand. The negative ion fast atom bombardment (FAB) mass spectrum of VI shows a strong molecular ion at $m/z = 1695$, successive loss of 24 carbonyl ligands and a weak isotopic envelope at $m/z = 1032$ corresponding to the $Ru_{10}C$ metal core. Treatment of VI with base results in complete conversion to V; this reaction can be reversed quantitatively by protonation of VI.

Significantly the structure of the non-hydrido dianion V is indistinguishable from that of the hydrido cluster VI (Fig. 4). In the structure of VI, as in its osmium analogue (VIII), the entire surface of the cluster is covered with close-packed carbonyl ligands (Fig. 5), and there is no space to accommodate an external hydrido ligand; this is consistent with the location of the H-ligand in one of the tetrahedral caps of the cluster.

As the solution infrared spectrum of VI has two absorptions in the carbonyl stretching region and V has three, the structure of V might have been expected to have lower symmetry than VI. Since a cluster $[M_{10}C(CO)_{24}]^{2-}$ of T_d symmetry has four IR, active $\nu(CO)$ modes, it would appear that accidental coincidence of IR absorptions is occurring, and that this, rather than small perturbations in the cluster symmetry, governs the number of bands resolved in the spectra.

The variable temperature (VT) ^{13}C NMR spectra of the clusters V and VI were recorded from ^{13}C enriched samples. The spectra of both anions are temperature dependent, and stacked plots of the spectra obtained are shown in Fig. 6. The spectrum of I at 290 K shows a broad singlet at 204.4 ppm, which on cooling broadens further and separates into two singlets. On further cooling to 200 K two sharp resonances of equal intensity at 213.7 and 192.7 ppm are obtained, the carbido resonance is observed at 362 ppm in this cluster. These spectra are entirely consistent with the solid state structure of V since there are only two carbonyl environments viz. four apical "$Ru(CO)_3$" caps and six "$Ru(CO)_2$" fragments at the apices of the central octahedron. It is clear from the spectra that at 290 K all carbonyl ligands are fluxional, but as the temperature decreases the speed of carbonyl motion is reduced, until at 200 K the structure is static on the NMR timescale.

The VT spectra of the anion VI are somewhat more complex due to the asymmetry introduced into the structure by the hydrido ligand. The spectrum at 290 K shows four broad resonances at 189.9, 206.7, 209.5 and 211.3 ppm, and a shoulder on the high field side of the resonance at 189.9 ppm. As the temperature is decreased the resonances sharpen, but no new resonances are observed, except that the shoulder is resolved into a sharp singlet. The spectrum observed at 210 K thus shows five resonances at 188.1, 189.2, 206.4, 209.1, and 211.2 ppm in the intensity ratio 1/3/2/1/1, the carbido resonance in this anion is observed at 374.5 ppm. This spectrum is consistent with the structural formulation in which the hydrido ligand is located in one of the interstitial tetrahedral sites provided by the "$Ru(CO)_3$" fragments capping the central octahedron, resulting in a structure of $C3_v$ symmetry.

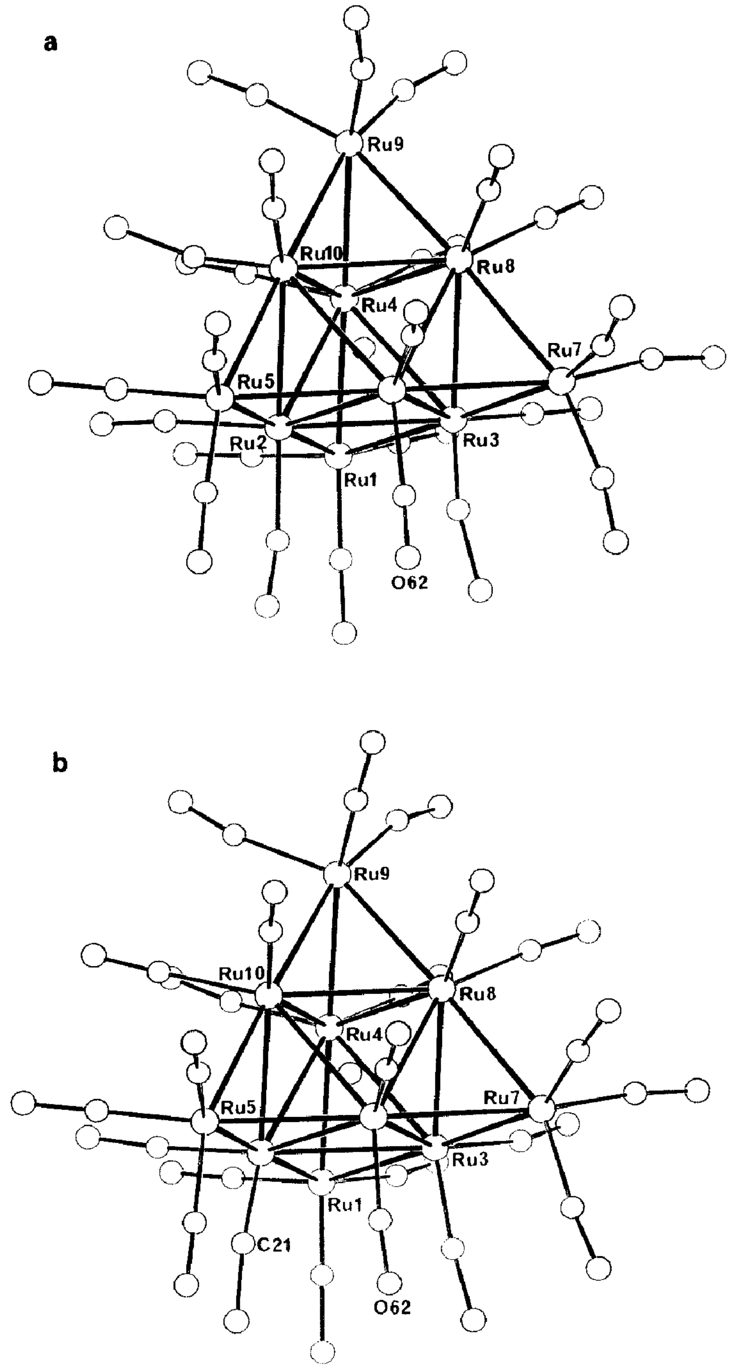

Fig. 4. The molecular structures of the anions (a) $[Ru_{10}C(CO)_{24}]^{2-}$ (V) and (b) $[HRu_{10}C(CO)_{24}]^{-}$ (VI) showing the similarity of the carbonyl ligand distribution between the two clusters.

The five carbonyl environments may be identified as follows: (i) a unique apical $Ru(CO)_3$ fragment of the cap containing the hydride ligand, (ii) three equivalent apical $Ru(CO)_3$ fragments at the corners of the basal Ru_6 plane relative to the cap containing the hydride, (iii) six equivalent carbonyls situated equatorially around

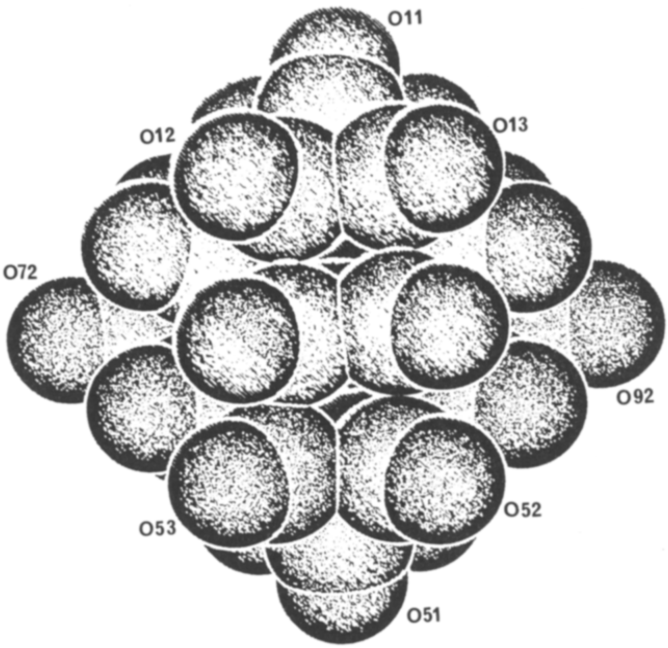

Fig. 5. Computed space filling model for $[HRu_{10}C(CO)_{24}]^-$ (VI) showing the closed packed carbonyl array precluding a surface location for the hydrido ligand.

the base of the tetrahedron containing the hydride ligand, (iv) three equatorial carbonyls on the $Ru(CO)_2$ fragments of the central triangle of the basal Ru_6 plane and (v) three axial carbonyls on the same $Ru(CO)_2$ fragments. It is clear that the broadening of the resonances as the temperature increases indicates some form of fluxional behaviour within the cluster. However, whether this is due solely to motion of the carbonyls, or whether the hydride ligand is also fluxional is unclear from these data. These interpretations of the ^{13}C NMR spectra assume that the carbonyls of the capping $Ru(CO)_3$ fragments are equivalent by virtue of rapid equilibration between the three environments relative to the rest of the cluster, which has proved to be valid for the spectroscopic investigations of other cluster carbonyl systems.

To further characterise the nature of the hydrido ligand in VI variable temperature (VT) ^1H NMR and infrared studies on static powder samples were undertaken [22]. The ^1H NMR spectra obtained are shown in Fig. 7, and are characterised by: (i) at 300 K, a single, relatively sharp, resonance is observed at +0.2 ppm relative to TMS; (ii) as the temperature decreases below 300 K the resonance at +0.2 ppm broadens and features being to appear around −24 ppm with a shoulder at −35 ppm (iii) at 140 K, a spectrum is acquired which has two features centred at approximately −5 and −35 ppm.

Interstitial hydrido ligands in transition metal clusters have previously been observed with low field resonances [10,23]; and the high temperature spectrum is assigned to an a hydrido ligand inside a Ru cap of the tetracapped octahedral structure (δ +0.2 ppm). The sharpness of the resonance is due to very high frequency "hopping" between the four equivalent cap sites. The 140 K spectrum is compatible with the powder spectrum of a hydride with effective axial symmetry. However, the very high field shift of this resonance (the isotropic chemical shift of

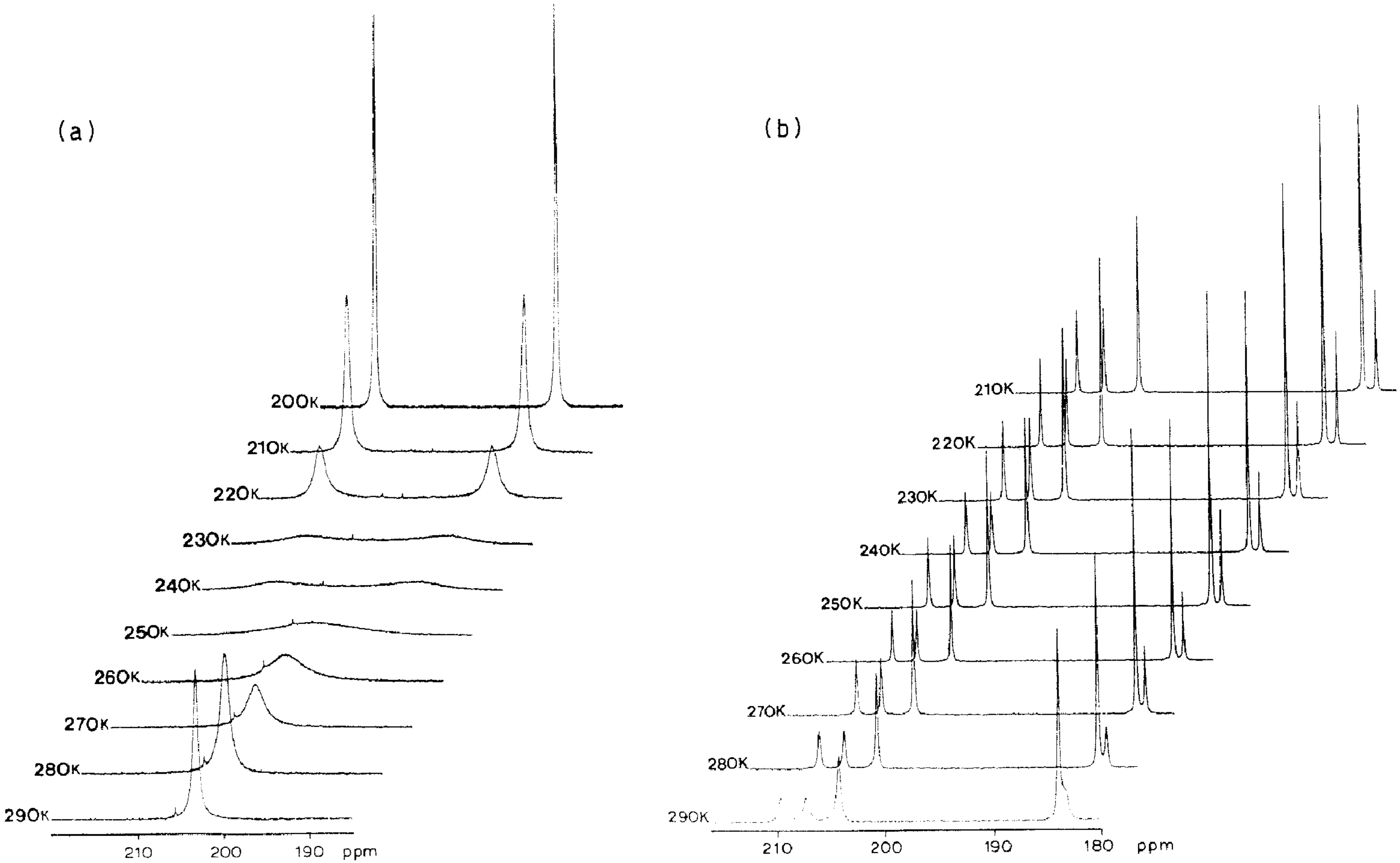

Fig. 6. Variable temperature ^{13}C NMR spectra of the anions (a) $[Ru_{10}C(CO)_{24}]^{2-}$ (V) and (b) $[HRu_{10}C(CO)_{24}]^{-}$ (VI).

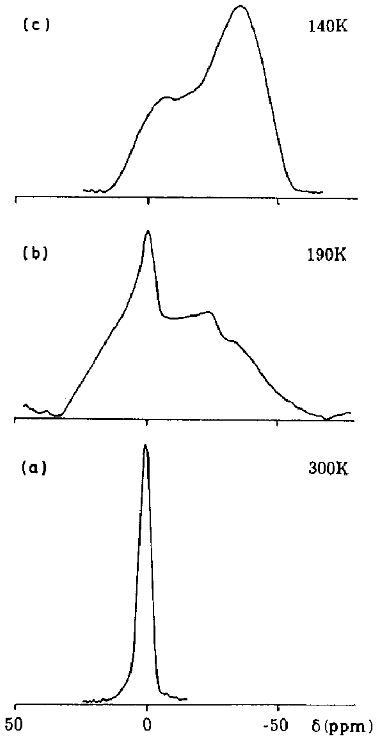

Fig. 7. The VT ^{1}H NMR spectra of a static powder sample of $[\mathrm{HRu_{10}C(CO)_{24}}]^-$ (VI) at (a) 300 K, (b) 190 K and (c) 140 K.

the resonance is -24 ppm) causes us to assign it to an externally bound hydrido ligand. The features in the 190 K spectrum arise from this hydride hopping relatively slowly over equivalent sites on the exterior of the metal framework.

In solution the hydride resonance is observed at -13.5 ppm; this is consistent with the ligand migrating rapidly (on the NMR timescale) between internal and external sites. In the solid state, the isotropic chemical shift for an external site is -24 ppm, while that for an interstitial site is $+0.2$ ppm, giving a mean chemical shift of -12 ppm which is certainly compatible with resonance observed in the solution spectrum. Furthermore we suppose that the external site to which hydride migrates at low temperatures is a face of a tetrahedral $\mathrm{Ru_4}$ cap, then the cluster retains its $C3_v$ symmetry on the NMR timescale, and this is the symmetry demanded by the ^{13}C NMR results.

The infrared spectrum of the $[\mathrm{Bu^tN}]^+$ salt of $[\mathrm{HRu_{10}C(CO)_{24}}]^-$ (VI) was recorded in a CsI disc, and the spectra in the region 600–800 cm^{-1} at 293 and 113 K are shown in Fig. 8. The strong bands in this region of the spectrum may be assigned to the vibrational modes of the carbide atom. The carbide ligand in these decanuclear clusters is well isolated from adjacent molecules within the unit cell by virtue of its location within the central octahedral cavity. As a result the vibrational modes of the carbide ligand may be regarded, to a good approximation, as reflecting the symmetry of its local environment. It is well established that the width of infrared absorption bands decreases as the the temperature of the sample is lowered due mainly to the dampening of the librational modes of the crystal lattice. It is thus often the case that additional bands to those observed at ambient temperature may be resolved by cooling the sample.

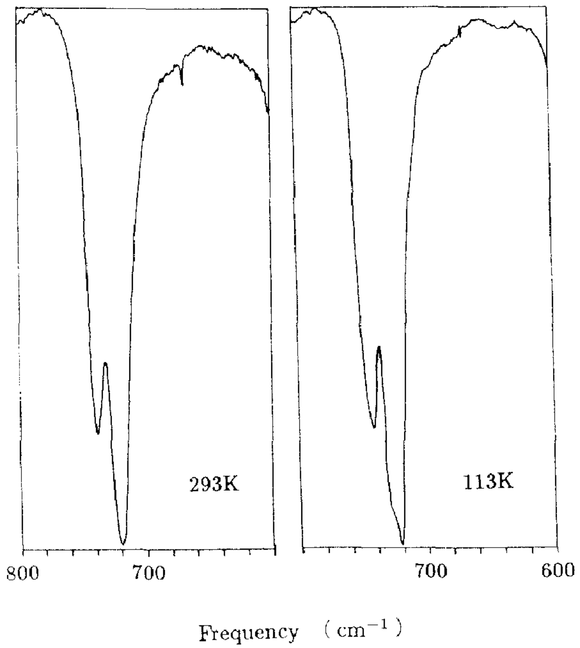

Fig. 8. The infrared spectrum of $[HRu_{10}C(CO)_{24}]^-$ (VI) at (a) 300 K and (b) 113 K in a CsI disc.

If the hydrido ligand in VI is located in one of the tetrahedral caps the cluster would have $C3_v$ symmetry and the carbide ligand would have an A and a degenerate E vibrational mode. The observed spectrum at 293 K is entirely consistent with this structural formulation; and shows a band at 738 cm^{-1} and a more intense band at 720 cm^{-1} which may be assigned to the A and E modes respectively. The spectrum at 113 K however, shows the lower frequency band to have split to give a distinct shoulder at 728 cm^{-1}. This band can be unequivocally assigned as a new band, and not simply a result of the higher resolution achieved at low temperatures, since the new band has resulted in an increase of the width of the absorption assigned to the degenerate E mode at ambient temperature, and not a narrowing which would be expected if the shoulder was a result of enhanced resolution. This low temperature spectrum is consistent with a cluster of $C2_v$ symmetry or lower, since for point groups lower than $C3_v$ the degeneracy of the E modes is lifted whilst the A mode remains unchanged.

This is therefore further evidence that the hydride ligand is being expelled from the interior of the cluster at low temperature, as its location on one of the triangular faces of one of the caping tetrahedra would result in a structure of $C2_v$ symmetry. Such a process would therefore fully explain the observed infrared spectra.

The synthesis and characterisation of $Ru_{18}C_2Hg_3(CO)_{42}]^{2-}$ (VII)

The dianion V has been found to react with mercury(II) trifluoroacetate to give a larger cluster dianion together with a small quantity of an uncharacterised precipitate. An X-ray structure determination of this new compound shows it to be the fused cluster dianion $[Ru_{18}C_2Hg_3(CO)_{42}]^{2-}$ (VII) (Fig. 9) [24], in which two decaruthenium clusters have each lost a capping $Ru(CO)_3$ fragment, and the

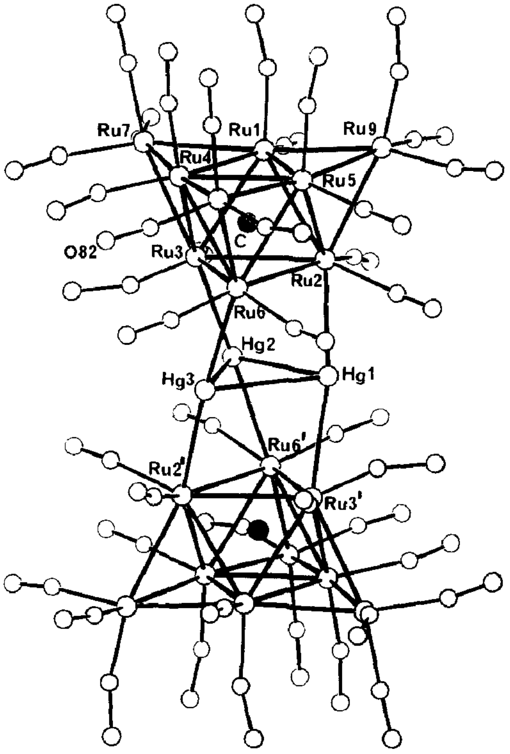

Fig. 9. The molecular structure of the dianion $[Ru_{18}Hg_3C_2(CO)_{42}]^{2-}$ (VII).

resulting nonaruthenium species are fused by a bi-facecapping $(\eta^3\text{-}\mu_6\text{-}Hg_3)^{2+}$ unit *: The ruthenium atom 'sub-clusters' have a tricapped octahedral framework, an expected geometry for a 120 electron species; however this has not been reported previously for any cluster of the iron triad metals. Mercury has been noted previously for its ability to bridge between small metal aggregates to form larger clusters; as in $[Ru_7Hg_2(CO)_{22}(\mu_3\text{-}C_2Bu^t)_2]$ [25] and $[Os_3(CO)_{11}Hg]_3$ [26] for example.

In the solid state the cluster VII has virtual $C3$ symmetry, the mean twist angle of 30° between the central Hg_3 triangle and the two adjacent Ru_3 triangles (which together from a central 'spiral' linking unit) results in the two faces Ru2–Ru3–Ru6 and Ru2′–Ru3′–Ru6′ of the Ru_9 units being exactly staggered with respect to each other, with a total twist angle of 60°. The simple infrared spectrum in the CO stretching region in solution is consistent with the $C3$ symmetry of the dianion. The ^{13}C NMR spectrum shows only four sharp resonances in the region 211–190 ppm in the intensity ratio 1/1/2/3 which is consistent with the solid state structure, the resonance due to the carbide ligands in this cluster is observed at 371.4 ppm (Fig. 10). The resonance at 203.7 ppm, of relative intensity two, is considerably broad-

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* Crystal data for $[PPN]_2[Ru_{18}Hg_3(C)_2(CO)_{42}]$ (VII): $C_{116}H_{60}N_2O_{42}P_4Ru_{18}Hg_3 \cdot CH_2Cl_2$, $M =$ 4697.12 (4782.05), space group $P\bar{1}$ (No. 2), a 19.042(4), b 15.729(3), c 15.197(3) Å, α 115.59(2), β 68.51(2), γ 115.46(2)°, U 2983.18 Å^3, D_c 2.66 g cm^{-3}, $F(000) = 2240$, μ(Mo-K_α) 48.48 cm^{-1}, a black crystal of size 0.19×0.14×0.16 mm was used in the data collection on a Phillips PW1100 diffractometer in the θ range 3–25°, with a scan width of 0.8°, final $R = 0.0720$ and $R_w = 0.0720$ for 2761 reflections with $I/\sigma(I) > 3$.

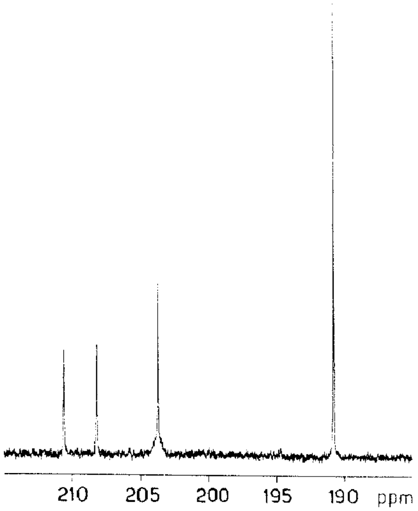

Fig. 10. The ^{13}C NMR spectrum of $[Ru_{18}C_2Hg_3(CO)_{42}]^{2-}$ (VII) in CD_2Cl_2 solution showing the significant broadening at the base of the resonance at 203.7 ppm, assigned to the carbonyl ligands of the ruthenium atoms adjacent to the mercury atoms, due to ^2J(Hg–C) coupling to ^{199}Hg.

ened at its base; this broadening may be attributed to the presence of weak satellite resonances due to ^2J coupling to ^{199}Hg (16.8% natural abundance), since this resonance may be assigned to the 12 carbonyl ligands equatorially disposed above and below the Hg_3 plane. There is evidence from the crystal structure analysis that there is an interaction between the mercury atoms and these carbonyl carbon atoms (mean Hg $\cdots$ C (carbonyl) 2.64(9) Å), and the molecule VII is consequently extremely congested about the central Hg_3 triangle; the carbonyl ligands on each nonaruthenium unit are displaced toward the other sub-cluster.

Conclusions

It is clear that, contrary to expectations, ruthenium exhibits a wide and diverse higher nuclearity chemistry. So far, this chemistry has been based on species containing interstitial carbido atoms which may be essential in the stabilisation of aggregates of more than six ruthenium atoms. This, of course remains to be seen and our efforts are also directed towards an investigation of higher clusters which do not contain interstitial carbon. In this work we have also established that for the lower nuclearity species, containing six or less metal atoms, the chemistry differs from that of osmium in that, as mentioned above, it tends to be dominated by carbido derivatives. This is presumably due to mechanistic requirements, and here we have presented data which clearly provide a probable source and route for carbide formation. Nevertheless, it is interesting to note that a clear relationship between the chemistry of Ru_6 and Os_6 exists and further steps are underway to more fully appreciate the factors which govern the mechanistic pathway adopted.

Experimental

(i) General

All reactions were performed using freshly distilled solvents and under an atmosphere of dry nitrogen. Thin layer chromatography (TLC) was performed using Merck silica gel 60 F-254 plates. Infrared spectra were recorded on a Perkin–Elmer 1710 Fourier transform spectrometer, the low temperature spectra were obtained using a liquid nitrogen cooled, evacuable apparatus supplied by Specac Ltd. ^{1}H NMR spectra were obtained on a Bruker WH 250 spectrometer, whilst ^{13}C NMR spectra were recorded on a Bruker AM 400 instrument. For the ^{13}C spectra chromium(III) trisacetylacetonate was routinely added to the sample as a relaxation agent.

(ii) Thermolyses of $Ru_3(CO)_{12}$ in arene-containing hydrocarbon solutions

In a typical experiment 1 g (1.565 mmol) of $Ru_3(CO)_{12}$ was dissolved in 250 cm^3 of a 10% v/v solution of the arene (hexamethylbenzene, mesitylene, xylenes or toluene) in the hydrocarbon. The solution was heated under reflux until TLC (hexane/dichloromethane, 4/1) showed that a reasonable balance between consumption of $Ru_3(CO)_{12}$ and deposition as a black material had been achieved. A delicate balance between reaction time, temperature, arene and product yields and distribution was observed, however reflux for approximately 3 d at 97 °C in heptane/mesitylene gave a reasonable yield of clusters (I–IV). Reflux in hexane/arene solutions (68 °C) favoured I in a very slow reaction, whilst refluxing octane or nonane solutions (125, 150 °C) favoured the carbido-clusters III and IV. The resulting solution was filtered and the solvent removed from the dark red/brown filtrate in vacuo. The residue was dissolved in the minimum of dichloromethane and separated by TLC (hexane/dichloromethane, 4/1) to give orange IV (R_F 0.9), green II (R_F 0.55), brown III (R_F 0.45) and purple I (R_F 0.35); the maximum yield for each product, achieved after optimisation of the reaction conditions, was 15%.

(iii) Thermolysis of I in mesitylene

10 mg (0.008 mmol) of I was placed in the bulb in the floor of an infrared gas cell with NaCl windows and path length 10 cm, along with 1 cm^3 of mesitylene. The cell was evacuated whilst the mesitylene was frozen down with liquid nitrogen. The cell was then placed in the IR spectrometer and a background spectrum recorded. The bulb of the cell containing the reactants was then heated to approximately 100 °C for 5 min, taking care not to completely evaporate the mesitylene, the mesitylene was again frozen out and the spectrum of the gaseous products obtained. Although strong bands due to the hydrocarbon modes were present in the spectrum, the characteristic P and R bands of the ν(CO) mode of gaseous CO_2 could clearly be seen centred at 2352 cm^{-1}, and further thermolysis resulted in an increase in intensity of these bands. The thermolysis products remaining in solution were identified by TLC separation (hexane/dichloromethane, 4/1), followed by solution IR spectroscopy, as a small amount of unreacted I, and approximately equal yields of II and III.

(iv) Solid state pyrolysis of I

A similar procedure to that in (iii) above was adopted, without the necessity of freezing out the mesitylene. After 2 min of pyrolysis at approximately 150 °C a ruthenium mirror had been deposited on the inside of the bulb containing the reactant. The IR spectrum of the gaseous products showed clearly that CO_2 had been evolved as above, but additionally the characteristic *P* and *R* bands of the $\nu(CO)$ mode of gaseous CO were present in the spectrum centred at 2143 cm^{-1}. Dissolution of the solid residues in dichloromethane followed by tlc. showed that the products of the pyrolysis were Ru metal, II, III, and a small amount of unreacted I.

(v) Synthesis of $[PPN][HRu_{10}C(CO)_{24}]$ (VI) and $[PPN]_2[Ru_{10}(CO)_{24}]$ (V)

In a typical experiment 1 g (1.565 mmol) of $Ru_3(CO)_{12}$ was heated to reflux in 50 cm^3 of a 10% solution of mesitylene in n-heptane. The thermolysis was continued for 4–5 days and resulted in a solution containing mostly III and IV along with a finely divided black deposit. The black material was filtered off and dissolved in 50 cm^3 of an acetone/methanol mixture containing an excess (0.50 g, 0.87 mmol) of [PPN]Cl resulting in a dark green solution of $[PPN][HRu_{10}C(CO)_{24}]$ (VI). Slow evaporation of the solution at this stage resulted in the deposition of black microcrystals of the salt (377 mg, 0.168 mmol, 36% from $Ru_3(CO)_{12}$) which was washed with cold methanol followed by ether and dried in vacuo. If the acetone/methanol solution of the crude product was heated to reflux for 1 h, quantitative deprotonation of VI resulted yielding $[PPN]_2[Ru_{10}C(CO)_{24}]$ (VI) (450 mg, 0.162 mmol, 35% from $Ru_3(CO)_{12}$) which may be isolated in a similar manner. Crystals of V and VI suitable for X-ray examination were obtained from CH_2Cl_2/hexane solution. Spectroscopic data for $[PPN]_2[Ru_{10}C(CO)_{24}]$(V): IR ($CH_2Cl_2$): $\nu(CO)$ 2027vs, 2000m, 1983s cm^{-1}; ^1H NMR (CD_2Cl_2): δ 7.70 ppm (multiplet). Spectroscopic data for $[PPN][HRu_{10}C(CO)_{24}]$ (VI): IR (CH_2Cl_2): $\nu(CO)$ 2053vs, 2009s cm^{-1}; ^1H NMR (CD_2Cl_2): δ 7.70 ppm (multiplet, 30H), −13.5 ppm (s, 1H).

(vi) Synthesis of $[PPN]_2[Ru_{18}Hg_3(C)_2(CO)_{42}]$ (VII)

40 mg (0.0144 mmol) of $[PPN]_2[Ru_{10}C(CO)_{24}]$ (V) was dissolved in 40 cm^3 of CH_2Cl_2 and 6.2 mg (0.0146 mmol) of freshly sublimed $Hg(CF_3CO_2)_2$ was added in 5 cm^3 of CH_2Cl_2. The solution immediately changed colour from green to brown. After a period of 4 d the product was precipitated from solution as brown microcrystals by addition of ether (11 mg, 0.0023 mmol, 18%). Crystals for X-ray examination were obtained from CH_2Cl_2/hexane solution. Spectroscopic data for $[PPN]_2[Ru_{18}Hg_3(C)_2(CO)_{42}]$ (VII): IR (CH_2Cl_2): $\nu(CO)$ 2065s, 2055vs, 2002s, cm^{-1}; ^1H NMR (CD_2Cl_2): δ 7.70 ppm (multiplet); ^{13}C NMR (CD_2Cl_2): δ 210.6, 208.2, 203.7, 190.6 ppm; Negative ion fast atom bombardment mass spectrum $M^+ = 3623$.

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