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Laser-desorption mass spectrometry of $[Ru_6C(CO)_{17}]$ and its derivatives: cluster aggregation in the gas phase *

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The ultraviolet-laser-desorption mass spectra of $[Ru_6C(CO)_{17}]$, $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ and $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_4Me_2)(\mu\text{-}C_6H_7Me)]$ have been obtained. Positive-ion mass spectra showed abundant singly-charged species: peaks corresponding to the successive loss of carbonyl ligands from an otherwise intact parent cluster and high molecular-weight clusters formed from the aggregation of intact hexaruthenium cores.

There is considerable interest in the synthesis and characterisation of high nuclearity metal clusters.[1] The synthesis of these clusters has been tackled from a number of different perspectives including conventional synthetic (thermolysis, pyrolysis and reductive techniques)[2] and gas-phase methods in which the primary source of characterisation is mass spectrometry.[3] Most of this latter work has focused on experiments involving naked metals rather than on preformed ligated clusters. However, studies of this type have been reported which involve cluster oligomerisation of platinum and gold clusters using ^{252}Cf plasma desorption mass spectrometry.[4]

We recently reported[5] the negative-ion ultraviolet-laser-desorption mass spectra of two ruthenium carbonyl clusters with facially co-ordinated arene ligands, *viz.* $[Ru_6C(CO)_{14}(\mu_3\text{-}C_{16}H_{16})]$ and $[Ru_4(CO)_9\{\mu_3\text{-}C_6H_4(CMeCH_2)_2\}]$, in a preliminary form. Peaks corresponding to the molecular ion together with additional peaks arising from sequential CO loss were obtained. In addition to this a series of peaks extending to much higher molecular weights were observed. This series extended in mass to *ca.* 5000 and *ca.* 10 000 for the hexa- and tetra-ruthenium clusters, respectively.

The present work consists of a more detailed study of the clustering process. Ultraviolet-laser-desorption mass spectrometry has been used to record the positive-ion mass spectra of the hexaruthenium–carbide clusters, $[Ru_6C(CO)_{17}]$ **1**, $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ **2** and $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_4Me_2)(\mu\text{-}C_6H_7Me)]$ **3**. These clusters were prepared according to literature methods.[6–8] They have all been characterised spectroscopically and clusters **1** and **2** have also been characterised in the solid state by single crystal X-ray diffraction.[9,10] The feature which these clusters share is that the central ruthenium core consists of an octahedron of ruthenium atoms encapsulating a carbide atom. Schematic representations of clusters **1**–**3** are shown in Fig. 1.

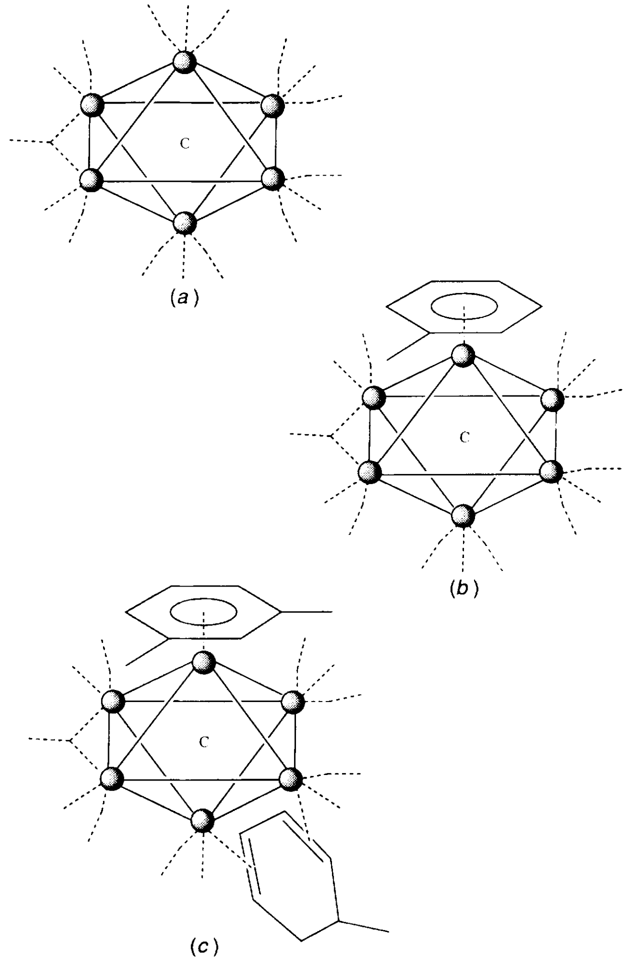

Fig. 1 Schematic representations of (*a*) $[Ru_6C(CO)_{17}]$ **1**, (*b*) $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ **2** and (*c*) $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_4Me_2)(\mu\text{-}C_6H_7Me)]$ **3**

Results and Discussion

The mass spectrum of cluster **1** is shown in Fig. 2. The peak at *ca.* m/z 1000 corresponds to species associated with the parent molecular ion. At higher mass, the spectrum contains a series of less well resolved peaks which can be attributed to cluster aggregates which extend to masses in excess of m/z 35 000. Each of these peaks comprises an envelope which contains ions due to both the differing numbers of carbonyls attached to the cluster core and the isotopic contributions for each molecular formula. In the case of ruthenium, which has seven isotopes, the latter contribution leads to significant peak broadening; under

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Table 1 Peak maxima measured from the ultraviolet-laser-desorption mass spectrum of $[Ru_6C(CO)_{17}]$ **1** *

	Measured peak maxima (*m*/*z*)	Calculated *m*/*z* of nearest supracluster	Formulae of associated ions
1	1 039	1 039	$[Ru_6C][CO]_{15}^+$
2	1 883	1 881	$[Ru_6C]_2[CO]_{23}^+$
3	2 595	2 584	$[Ru_6C]_3[CO]_{26}^+$
4	3 273	3 286	$[Ru_6C]_4[CO]_{29}^+$
5	3 978	3 988	$[Ru_6C]_5[CO]_{32}^+$
6	4 674	4 663	$[Ru_6C]_6[CO]_{34}^+$
7	5 388	5 393	$[Ru_6C]_7[CO]_{38}^+$
8	6 081	6 067	$[Ru_6C]_8[CO]_{40}^+$
9	6 773	6 770	$[Ru_6C]_9[CO]_{43}^+$
10	7 468	7 473	$[Ru_6C]_{10}[CO]_{46}^+$
11	8 164	8 175	$[Ru_6C]_{11}[CO]_{49}^+$
12	8 864	8 878	$[Ru_6C]_{12}[CO]_{52}^+$
13	9 544	9 552	$[Ru_6C]_{13}[CO]_{54}^+$
14	10 221	10 226	$[Ru_6C]_{14}[CO]_{56}^+$
15	10 882	10 873	$[Ru_6C]_{15}[CO]_{57}^+$
16	11 538	11 547	$[Ru_6C]_{16}[CO]_{59}^+$
17	12 182	12 194	$[Ru_6C]_{17}[CO]_{60}^+$
18	12 855	12 868	$[Ru_6C]_{18}[CO]_{62}^+$
19	13 537	13 543	$[Ru_6C]_{19}[CO]_{64}^+$
20	14 209	14 217	$[Ru_6C]_{20}[CO]_{66}^+$
21	14 849	14 836	$[Ru_6C]_{21}[CO]_{66}^+$
22	15 562	15 566	$[Ru_6C]_{22}[CO]_{70}^+$
23	16 205	16 213	$[Ru_6C]_{23}[CO]_{71}^+$
24	16 909	16 887	$[Ru_6C]_{24}[CO]_{73}^+$
25	17 561	17 562	$[Ru_6C]_{25}[CO]_{75}^+$
26	18 163	18 180	$[Ru_6C]_{26}[CO]_{75}^+$
27	18 904	18 910	$[Ru_6C]_{27}[CO]_{79}^+$
28	19 560	19 557	$[Ru_6C]_{28}[CO]_{80}^+$
29	20 117	20 119	$[Ru_6C]_{29}[CO]_{78}^+$
30	20 880	20 878	$[Ru_6C]_{29}[CO]_{83}^+$

* Measured values are shown alongside those calculated for the supraclusters with generic formula $[Ru_6C]_n[CO]_m$ where *n* and *m* are integers. These calculated supraclusters are those which most nearly correspond to the peak maxima. All *m*/*z* values are rounded to nearest integer.

current experimental conditions the instrument resolution is insufficient to resolve peaks corresponding to successive CO losses at high masses. Inspection of the mass spectrum in Fig. 2, above *m*/*z* 2000, clearly reveals that aggregation of preformed metal clusters can be induced using ultraviolet-laser desorption and that the resultant supraclusters can be determined, with high intensity, as positive ions in the time-of-flight mass spectrometer. In addition, such clustering can be observed in the absence of an arene ligand. Therefore, it can be concluded that whilst the presence of an arene ligand may affect the nature or degree of aggregation it is not essential for supracluster generation.

Table 1 lists the peak maxima measured from the smoothed mass spectrum shown in Fig. 2. These are shown alongside the masses and molecular formulae of the cluster aggregates which most nearly correspond to the measured values. The ultraviolet-laser desorption readily removes CO ligands from the ruthenium cluster skeleton (see Fig. 3). Therefore, it is unlikely that the molecular formulae listed in Table 1 represent electronically complete supraclusters. Rather, these correspond to supraclusters which have an incomplete shell of CO ligands. It is anticipated that with sufficient mass resolution the high mass peak envelopes would be seen to comprise a series of peaks corresponding to numerous ions differentiated by the number of CO ligands they carry; the highest mass contribution corresponding to a complete shell of CO ligands and, therefore, electronic stability.

At *m*/*z* 1095 a peak is observed with a maxima which corresponds to the molecular weight of cluster **1** (calc. *m*/*z* 1095, see Fig. 3). A number of other peaks, at *m*/*z* 1068, 1039, 1011, 984 and 958, are also present. These may be attributed to the successive loss of five CO ligands, four less intense signals can also be seen which can also be attributed to further CO loss.

The next grouping of peaks is observed with an intensity maximum at *ca.* *m*/*z* 1850 (see Fig. 4) and a high mass of *ca.* *m*/*z* 2020. The condensation of two intact $[Ru_6C(CO)_{17}]$ clusters would result in a species of *m*/*z* 2190. A disparity of *ca.* *m*/*z* 170 can be accounted for by the removal of six CO ligands. It is thought, in the light of this information, that the aggregation occurs *via* a facecapping interaction between two intact $[Ru_6C(CO)_{17}]$ species, with concomitant loss of CO to form an electronically stable supracluster. Condensation of two octahedra through their faces can be achieved in two ways, with the triangular faces eclipsed or staggered resulting in a central trigonal prism and octahedron, respectively. A consideration of the total electron count for the two structures leads the authors to believe that the latter scenario takes place. A cluster of this type has a formal total electron count of 160 which concurs with the formulation of the cluster as $[Ru_{12}C_2(CO)_{28}]$ (calc. *m*/*z* 2020) *i.e.* requiring the removal of six COs from the aggregating species. The formation of the trigonal prism, on the other hand, would only require the removal of four CO ligands. This would result in a species with *m*/*z* 2078 which is clearly of baseline intensity in Fig. 4. Other species to lower mass, which are contained in the broad peak envelope, can be attributed to increasingly decarbonylated species with this cluster core.

Similar reasoning can be applied to the peak with an intensity maximum at *ca.* *m*/*z* 2590. Three of the ruthenium octahedra can undergo simultaneous condensation through a triangular face with the formation of a central tricapped trigonal-prism cavity. However, such a mechanism would be increasingly improbable for larger clusters, requiring the concomitant condensation of more than thirty preformed octahedral clusters for the generation of the largest observable supraclusters. Furthermore, as the high mass clusters contain 200 or more ruthenium atoms it is likely that potential deltahedral structures (in terms of the inner skeleton) would be sterically constrained. Statistically it is more probable that the growth process involves the addition of a single octahedron to the 'dimer' described above and that higher mass clusters are formed from further 'monomer' additions to the existing supraclusters. It is interesting that the intensities of the cluster peaks observed in Fig. 2 diminish monotonically. There appear to be no 'islands of stability', *i.e.* no especially stable supraclusters whose enhanced intensities in the mass spectrum would disrupt the exponential trend to low intensity.

We have obtained similar spectra for a range of derivatives of cluster **1** and in this paper we include the spectra of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ **2** and $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_4Me_2)(\mu\text{-}C_6H_7Me)]$ **3** (Figs. 5 and 6, respectively). As seen for cluster **1**, we observed a group of peaks associated with the successive loss of CO from the molecular ion and a series of peaks to higher mass which are associated with the aggregation of the preformed cluster. There is no indication that the arene ligand is readily removed from the hexaruthenium core, as anticipated from other mass spectrometric studies. (We have observed that the electron impact and fast atom bombardment mass spectra of a wide range of arene clusters give a peak corresponding to the molecular parent ion followed by a series of peaks arising from sequential CO loss and not loss of the arene ligand.) The similarity between these spectra and that of **1** is clear despite the fact that they do not extend to such high masses. We propose that the ligands inhibit the condensation process to some extent, thereby preventing build-up to very high masses. Further experiments using a variety of arene ligands are required to clarify this point. We have also found that aggregation of clusters using ultraviolet-laser-desorption mass spectrometry only takes place readily for neutral clusters. We have examined a range of mono- and di-anionic clusters and only obtained peaks in the region of the mass ion.

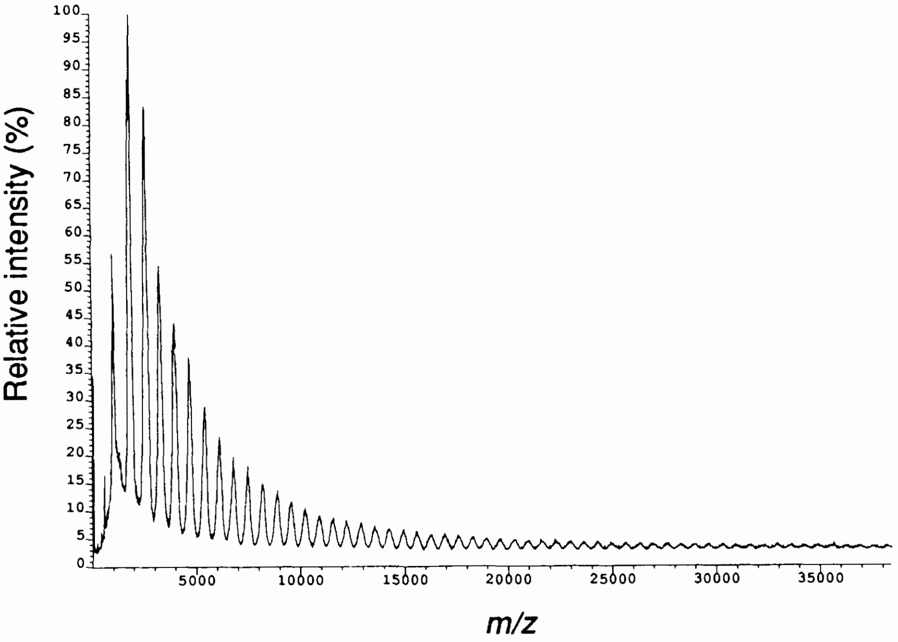

Fig. 2 The ultraviolet-laser-desorption mass spectrum of cluster **1** in the range m/z 600–40 000

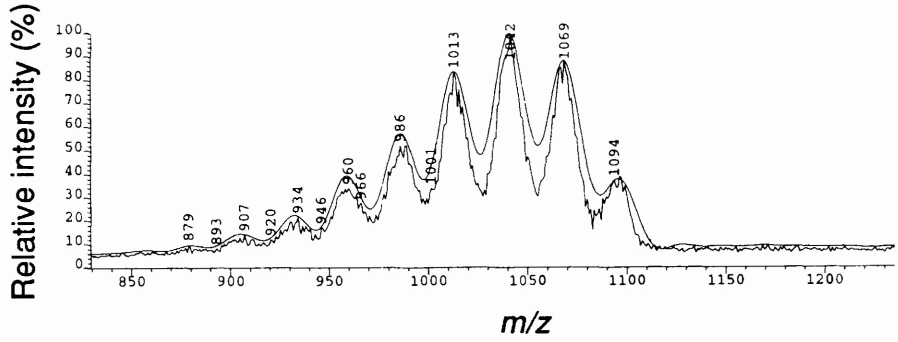

Fig. 3 The ultraviolet-laser-desorption mass spectrum of cluster **1** in the range m/z 800–1200

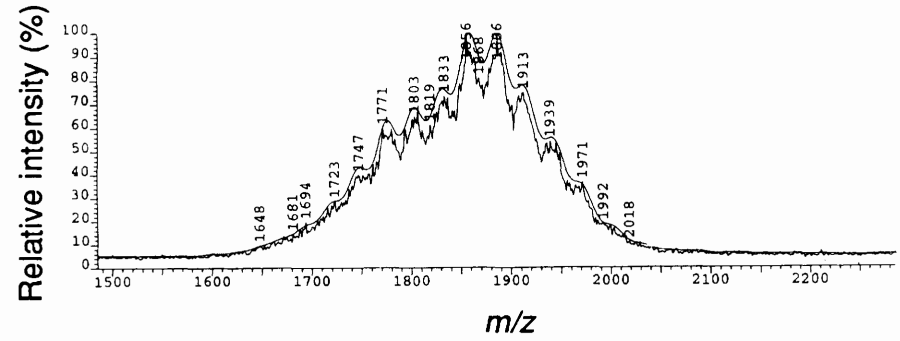

Fig. 4 The ultraviolet-laser-desorption mass spectrum of cluster **1** in the range m/z 1500–2300

Conclusion

It would appear that clusters which are made up of fused octahedral ruthenium components are produced in the laser-desorption mass spectrometer. For arene-containing clusters derived from **1** similar mass spectra were obtained. We have examined a range of other neutral carbonyl clusters of Co, Rh, Ir, Fe and Os with nuclearities between three and six and found that cluster build-up takes place, to varying extents, in many cases. However, many of the spectra are very different from those shown in this paper and we believe different mechanisms of cluster aggregation are in operation. For example, with trinuclear clusters the complexity of the spectra suggests that instead of clustering intact triangulated metal units, complete fragmentation takes place followed by recombination. We intend to study these other clusters in more detail in due course.

Experimental

Compounds **1**–**3** were prepared according to the literature methods and characterised by spectroscopy.[6–8] Samples were dissolved in dichloromethane and deposited onto the sample probe. The solvent was allowed to evaporate leaving a thin layer of the pure sample. These were then analysed without further treatment using a VG TOFSPEC time-of-flight mass spectrometer. Experiments were performed with UV intensities slightly above threshold for cluster formation and were maintained at a similar level for all three samples investigated in

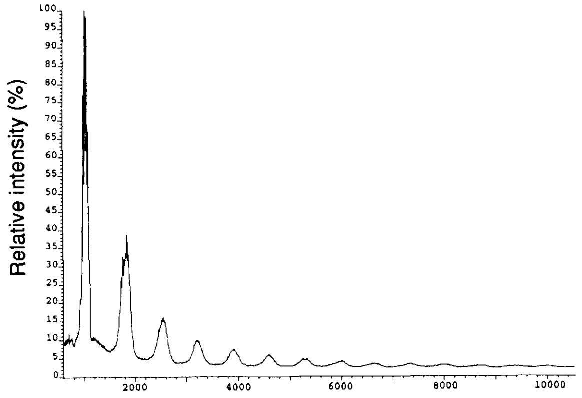

Fig. 5 The ultraviolet-laser-desorption mass spectrum of cluster **2** in the range *m*/*z* 0–10 000

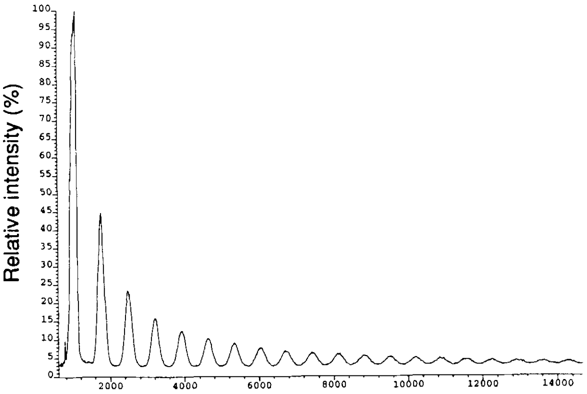

Fig. 6 The ultraviolet-laser-desorption mass spectrum of cluster **3** in the range *m*/*z* 0–14 000

this paper. The instrument was operated in linear mode with a typical resolution of *ca*. 200. Ions were extracted with an acceleration voltage of 25 kV and detected using a two-stage chevron microchannel plate detector. Typically, the data from between 50 and 100 successive laser shots were averaged to improve the signal-to-noise ratio.

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