

## Characterisation of Ruthenium Clusters carrying Facial Arene Ligands using Ultraviolet Laser Desorption Mass Spectrometry: Aggregation of Gas-phase Monocharged Anionic Clusters from Neutral Molecular Clusters

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The ultraviolet laser desorption mass spectra of  $[\text{Ru}_4(\text{CO})_9\{\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_4(\eta^2\text{-CMeCH}_2)_2\text{-1,3}\}]$  and  $[\text{Ru}_6\text{C}(\text{CO})_{14}\{\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{16}\text{H}_{16}\}]$  show abundant singly-charged negative ions; peaks corresponding to successive loss of carbonyl ligands from an otherwise intact parent cluster along with a remarkable series of higher mass species formed in the source region of the mass spectrometer are seen.

The potential of mass spectrometry for the characterisation of large metal clusters has previously been demonstrated by McNeal and coworkers<sup>1-4</sup> who used <sup>252</sup>Cf plasma desorption mass spectrometry (PDMS) for the analysis of high-nuclearity platinum and gold clusters. Reported herein is a preliminary account of the application of ultraviolet laser desorption mass spectrometry<sup>5</sup> to the characterisation of ruthenium clusters carrying facial arene ligands. Ion production results from irradiation of the solid target sample, deposited from a suspension in toluene, with the focussed output from a N<sub>2</sub> laser (337 nm).<sup>†</sup> The technique provides abundant singly-charged negative ions. The mass spectra contain a number of peaks which correspond to the loss of successive carbonyls from the parent ruthenium cluster. The arene ligand is retained. In addition, a series of intense peaks at larger *m/z* values are observed. These are the product of gas-phase aggregation in the source region of the mass spectrometer.

The tetraruthenium cluster,  $[\text{Ru}_4(\text{CO})_9\{\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_4(\eta^2\text{-CMeCH}_2)_2\text{-1,3}\}]$  [see Fig. 1(a)], characterised by single crystal X-ray diffraction,<sup>6</sup> represents one of the first examples of a face-capped six-membered ring on a tetranuclear cluster. The laser desorption mass spectrum obtained for this material is shown in Fig. 2. The parent molecular ion region of the mass spectrum is also shown as an insert in this spectrum. Whilst no parent molecular ion was observed, a number of intense peaks at *m/z* 815, 787, 758, 731 and 703 are present which correspond in mass to the successive loss of CO moieties from the core cluster  $[\text{Ru}_4(\text{CO})_n\{\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_4(\eta^2\text{-CMeCH}_2)_2\text{-1,3}\}]$ . A series of much less intense ions are observed below this group which correspond to loss of the arene ligand. This highlights the favourable multi-centre bonding interaction between the 1,3-diisopropylbenzene ligand and the tetraruthenium cluster unit, presumed to be due to a chelating effect. At higher masses the spectrum exhibits a series of less well resolved peaks which extend to *m/z* > 8000. Each of these peaks comprises of a complex envelope which contains ions due to both the differing numbers of carbonyls attached to the ruthenium clusters and the various isotopic contributions for each molecular formula. It may be envisaged that each broad

peak envelope contains decarbonylated species at the low mass limit and increasingly carbonylated species at the high mass limit. As a consequence, the separation between the centroids of these peaks is less at the high mass end of the mass spectrum.

Nevertheless, the regular distribution of peaks in the mass spectrum indicates that aggregation is occurring *via* the addition of units of consistent mass. The separation of the peak centroids, of the order of *m/z* 500, is considerably less than would be expected on aggregation of the parent tetraruthenium complex which has a fully carbonylated *m/z* of 815. As the parent cluster retains the arene ligand it is conceivable that it is also retained by the aggregating species. Although the want of sufficient mass spectral resolution means that it is difficult to predict the exact nature of the clustering unit an attractive hypothesis would be the assembly of  $[\text{Ru}_3(\text{CO})_n\{\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_4(\eta^2\text{-CMeCH}_2)_2\text{-1,3}\}]$  units to the parent cluster, where *n* = integer, yielding a multidecker 'sandwich cluster'.

The negative ion mass spectrum obtained for the closely related hexaruthenium carbido cluster  $[\text{Ru}_6\text{C}(\text{CO})_{14}\{\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{16}\text{H}_{16}\}]$

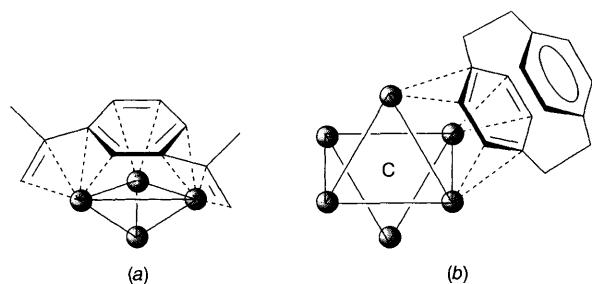


Fig. 1 The solid-state structure of (a)  $[\text{Ru}_4(\text{CO})_9\{\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_4(\eta^2\text{-CMeCH}_2)_2\text{-1,3}\}]$  and (b)  $[\text{Ru}_6\text{C}(\text{CO})_{14}\{\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{16}\text{H}_{16}\}]$

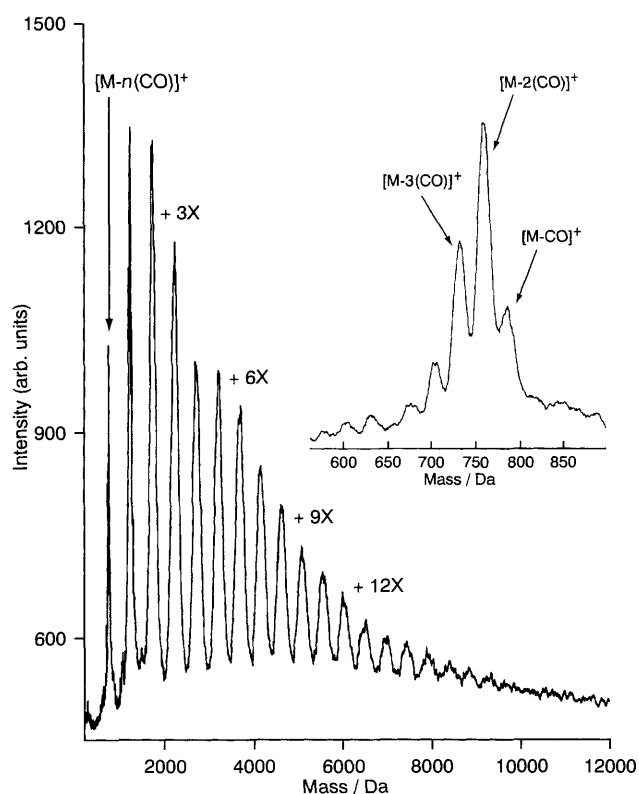
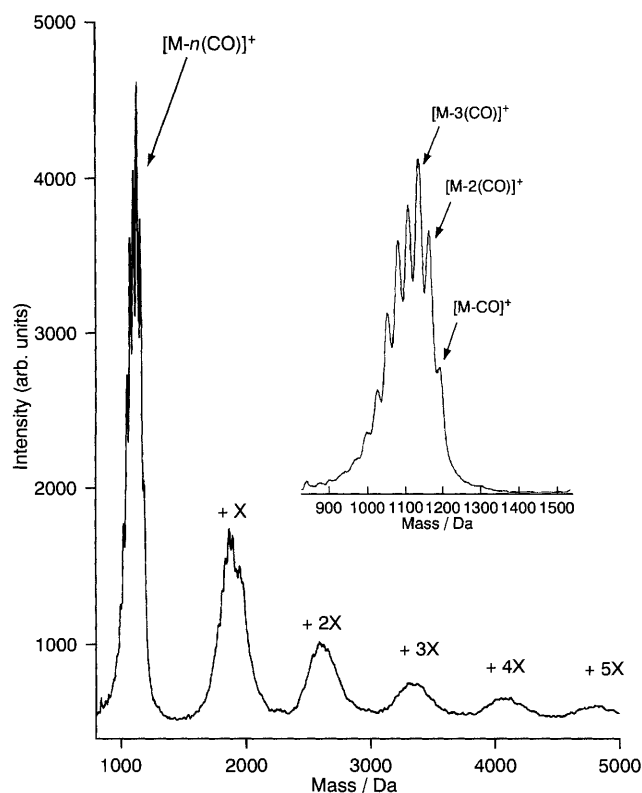


Fig. 2 The laser desorption mass spectrum of  $[\text{Ru}_4(\text{CO})_9\{\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_4(\eta^2\text{-CMeCH}_2)_2\text{-1,3}\}]$ , X = cluster aggregate unit. *Insert*: an expansion of the molecular ion region. (Da = Dalton  $\approx 1.66 \times 10^{-27}$  kg).

$\eta^2 : \eta^2 : \eta^2\text{-C}_{16}\text{H}_{16}$ ], is shown in Fig. 3.<sup>7</sup> The spectrum is similar to that shown in Fig. 2. Again, the mass spectrum provides much desirable information. The parent cluster region, shown as an insert in Fig. 3, exhibits peaks at  $m/z$  1191, 1163, 1135, 1107, 1079, 1051 and 1023, corresponding to the successive loss of CO from the parent cluster. In this case, this group of peaks are the most intense observed in the mass spectrum. Again, there is little evidence that the face-capping paracyclophane is lost in the desorption process. The higher mass ion peaks, corresponding to the products of gas-phase aggregation, are observed with diminishing intensity up to  $m/z$  values of 5000. The additive unit is not easily assigned, but could feasibly comprise of  $[\text{Ru}_3\text{-}(\text{CO})_n(\mu_3\text{-}\eta^2 : \eta^2 : \eta^2\text{-C}_{16}\text{H}_{16})]$ . However, it cannot be ruled out



**Fig. 3** The laser desorption mass spectrum of  $[\text{Ru}_6\text{C}(\text{CO})_{14}(\mu_3\text{-}\eta^2 : \eta^2 : \eta^2\text{-C}_{16}\text{H}_{16})]$ , X = cluster aggregate unit. *Insert:* shows an expansion of the molecular ion region.

that a complete polyhedral rearrangement takes place for both compounds yielding a larger ruthenium polyhedron.

This work illustrates the utility of laser desorption mass spectrometry for the analysis of metal cluster complexes. It also suggests that the technique has intriguing potential for the investigation of novel aggregation mechanisms and the study of self-assembling gas-phase cluster species. We are currently broadening our investigations in order to compare the gas-phase aggregation behaviour of ruthenium clusters which have arene ligands in face-capping or apical bonding modes and ruthenium clusters which are solely ligated by carbonyl groups. Examination of the latter compounds will clarify the role of the arene ligand in the aggregation process. We also intend to carry out microsyntheses of these cluster aggregates in the mass spectrometer in tandem with an investigation into their potential preparative scale synthesis in the laboratory.

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### Footnote

† UVLDMS was performed using a home-built laser desorption time-of-flight mass spectrometer modelled on the Linear 1700 (Hewlett Packard, formerly Linear Scientific). This consists of a two-stage Wiley-McLaren ion source and a 1.8 m linear flight tube with a two-stage chevron microchannel plate detector. Ions were extracted with an acceleration voltage of 20 kV. The maximum instrumental resolution was in the region 600–700. A description of the instrument and the data acquisition system may be found in the literature.<sup>5</sup>

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