

A study of the gas-phase behaviour of $[\text{Os}_6(\text{CO})_{18}]$ and its high yield synthesis using UV laser desorption/ionisation mass spectrometry

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Abstract

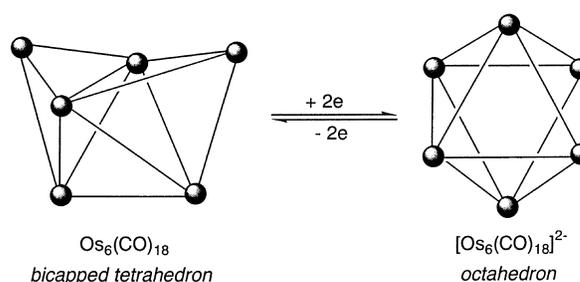
The ultraviolet laser desorption/ionisation time-of-flight mass spectra of $[\text{Os}_6(\text{CO})_{18}]$ recorded in both the positive and negative mode exhibit features that correlate with the macroscopic physicochemical properties of the cluster. In addition, hexanuclear clusters, related to $[\text{Os}_6(\text{CO})_{18}]$, are the major products of the laser desorption/ionisation of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ and $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$, paralleling macroscopic synthetic protocols. ©1999 Elsevier Science S.A. All rights reserved.

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The hexanuclear cluster $[\text{Os}_6(\text{CO})_{18}]$ has been the subject of considerable study [1–13]. It possesses a tritetrahedral (C_{2v} -octahedral) structure [8] and readily undergoes a reversible two-electron addition [4,5,9] to give the *Oh*-octahedral dianion $[\text{Os}_6(\text{CO})_{18}]^{2-}$ (see Scheme 1) [10]. In solution in donor solvents such as MeCN it readily forms adducts of the type $[\text{Os}_6(\text{CO})_{18-n}(\text{NCMe})_n]$ ($n=1-3$) [11], and as a solid reacts with CO to produce the planar raft $[\text{Os}_6(\text{CO})_{21}]$ [13]. It would appear, from these observations, that reaction with ligands such as MeCN and CO follow a course different to simple substitution but involve a polyhedral breathing mechanism, i.e. expansion/contraction of the type shown in Scheme 1.

In this communication we report on the laser desorption/ionisation time-of-flight mass spectrometry of this hexanuclear cluster, that differs from all previous clusters investigated by the technique, due to the unique substitution mechanism of $[\text{Os}_6(\text{CO})_{18}]$. Experiments were performed using a Micromass TofSpec-2E instrument¹.

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Scheme 1. CO ligands omitted for clarity.

The positive ion mass spectrum of $[\text{Os}_6(\text{CO})_{18}]$ (see Fig. 1) exhibits a molecular ion $[\text{Os}_6(\text{CO})_{18}]^+$ centred at mass-

¹ The clusters $[\text{Os}_6(\text{CO})_{18}]$ [26], $[\text{Os}_6(\text{CO})_{21}]$ [27], $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ [28] and $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ [29] were prepared according to the literature methods. The cluster was dissolved in dichloromethane and deposited onto the sample probe and the solvent was allowed to evaporate leaving a thin layer of the pure sample. The sample was then analysed using a Micromass (Wythenshawe, Manchester, UK) TofSpec-2E mass spectrometer, fitted with a time-lag focusing source. Data were generated in the reflectron mode of operation at an accelerating voltage of 20 kV. A mixture of three peptides (Bradykinin, Angiotensin and ACTH) was employed for calibration of the instrument.

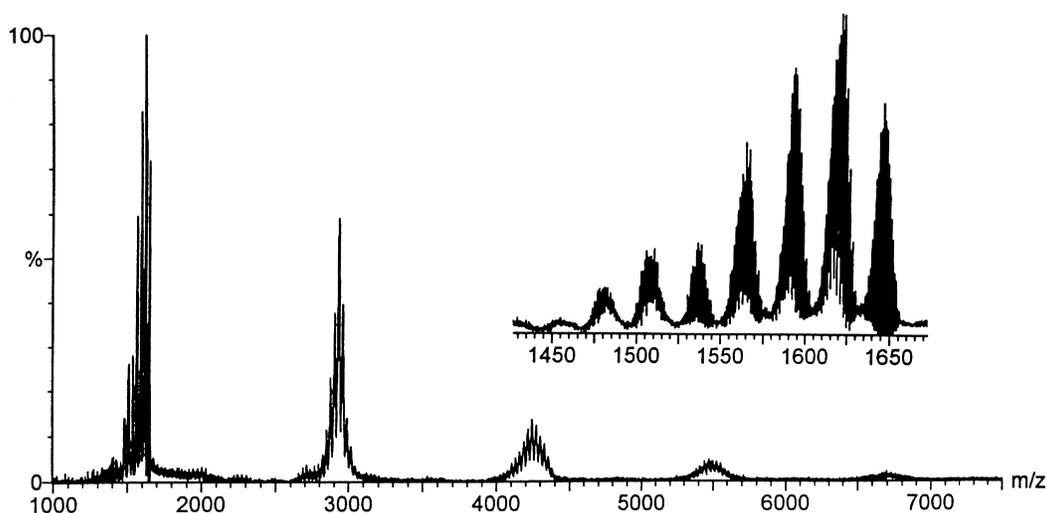


Fig. 1. The positive ion LDI-TOF mass spectrum of $[\text{Os}_6(\text{CO})_{18}]^+$, in the range 1000–7500 Da: insert shows the parent ion region.

to-charge ratio (m/z) 1646 Da (see insert), together with peaks corresponding to $[\text{Os}_6(\text{CO})_{18-n}]^+$ ($n=1-7$), due to sequential loss of the CO ligands. This spectrum is not typical of carbonyl clusters, which usually show a strong parent peak with an additional CO attached $[M+\text{CO}]^+$ when recorded in positive mode [14]. Usually, loss of an electron causes a metal–metal bond to break with concomitant association of a CO ligand. With $[\text{Os}_6(\text{CO})_{18}]$, which has 12 Os–Os bonds and the most compact polyhedron possible for a hexanuclear cluster, one might anticipate that it would rearrange to give an octahedral cluster that would readily take up a CO ligand to provide a more ideal electron count (i.e. $83 \rightarrow 85$ cluster valence electrons, one short of the 86 cve count preferred). While many gas phase reactions involving the cluster skeleton clearly take place even on the very short timescale (ca. 3 ns) of the LDI-TOF experiment, a polyhedral transformation of this nature may be too slow to be observed over this interval.

In the negative ion spectrum (see Fig. 2) the highest molecular ion peak corresponds to $[M-\text{CO}]^-$ at 1618 Da. Again, the failure to observe the parent peak $[\text{Os}_6(\text{CO})_{18}]^-$

is unexpected given the tendency of the cluster to accept two electrons to produce $[\text{Os}_6(\text{CO})_{18}]^{2-}$. However, this result is in line with the observations made on other related cluster systems [14], and can be reconciled with the view that addition of a single electron leads to CO loss (occupancy of an M–CO anti-bonding MO) rather than polyhedral rearrangement.

Clearly, the LDI-TOF-MS of $[\text{Os}_6(\text{CO})_{18}]$ is unusual in that it does not follow the pattern established for other cluster carbonyls and produces $[\text{Os}_6(\text{CO})_{19}]^+$ in the positive mode, and in addition, whereas the ion $[\text{Os}_6(\text{CO})_{18}]^-$ might have been anticipated in the negative mode only $[\text{Os}_6(\text{CO})_{17}]^-$ was observed. These unexpected findings lead us to consider more fully the difficulty in employing LDI-TOF-MS as a reliable analytical technique for establishing molecular formulae. Nevertheless, these data might be taken to indicate that the excited state, $[\text{Os}_6(\text{CO})_{18}]^+$, produced by laser ablation retains the tritetrahedral structure, the most compact form for a six-atom polyhedron. In addition, it would appear that the aggregation of the hexa-osmium cluster into the supra-

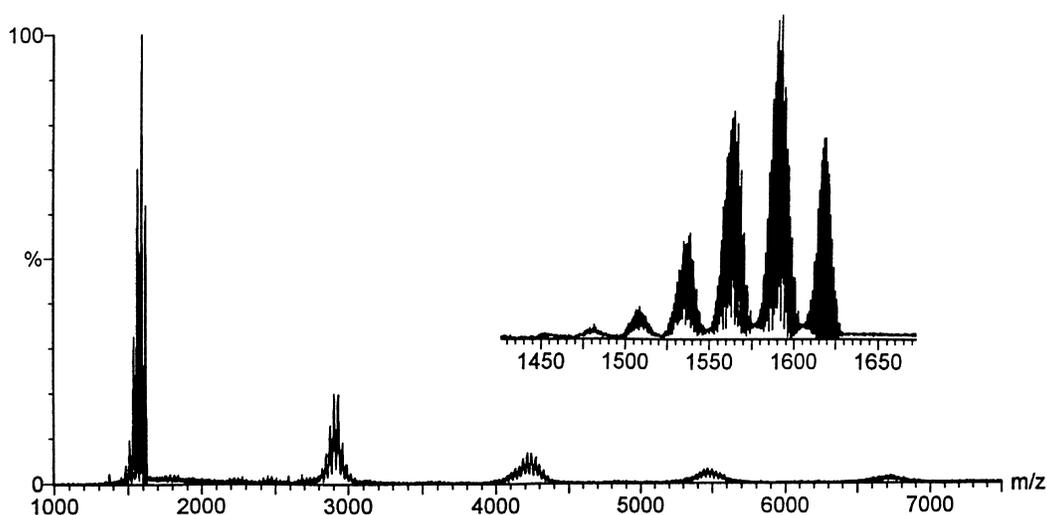


Fig. 2. The negative ion LDI-TOF mass spectrum of $[\text{Os}_6(\text{CO})_{18}]^-$, in the range 1000–7500 Da: insert shows the parent ion region.

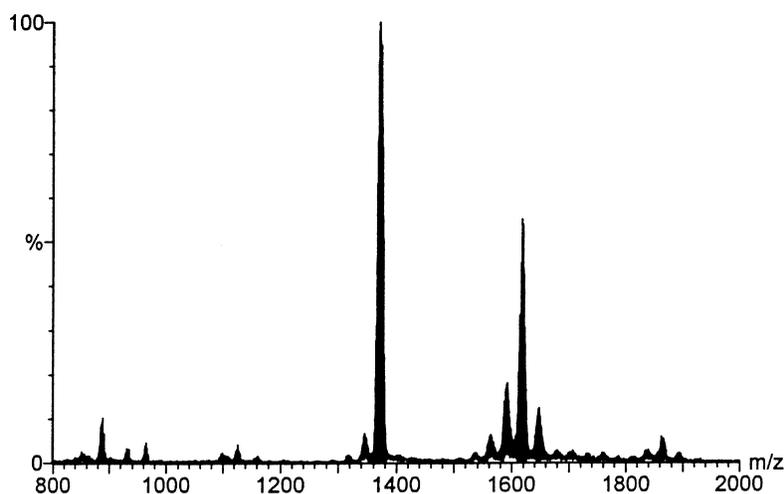


Fig. 3. The negative ion spectrum of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ in the range 800–2000 Da.

clusters, observed at masses above the parent region, occurs in multiples of six. While we do not intend to describe these higher mass clusters in detail in this communication, it is possible that the tritrahedral geometry of the parent remains intact. Similar aggregation phenomena have been reported before using laser desorption/ionisation [14–16] and other ionisation techniques [17–25].

We have also found that $[\text{Os}_6(\text{CO})_{18}]$ and related species may be prepared from lower nuclearity clusters in the mass spectrometer. In the laboratory $[\text{Os}_6(\text{CO})_{18}]$ is prepared in ca. 80% yield from the high temperature vacuum pyrolysis of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ [26]. The negative ion spectrum of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ is shown in Fig. 3 in the range 800–2000 Da. The peak centred at 1649 Da clearly indicates the presence of $[\text{Os}_6(\text{CO})_{18}]^-$. Although this cluster-anion is presumably derived from the hypothetical neutral species $[\text{Os}_6(\text{CO})_{19}]$ (see above description of negative spectrum of $[\text{Os}_6(\text{CO})_{18}]$) it is not unreasonable to assume that it has a tritrahedral structure. The most intense peak centred at 1371 Da corresponds to the cluster $[\text{Os}_5(\text{CO})_{15}]^-$. Laser ablation of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ affords a similar series of hexa-osmium clusters, which differ in that their masses are centred slightly higher because of the presence of hydride ligands. The gas-phase reactivity of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ has been studied using electron impact ionisation in conjunction with Fourier-transform ion cyclotron resonance mass spectrometry [21]. The LDI-TOF and FT-ICR mass spectra are qualitatively similar although in the LDI-TOF experiment the number of highly decarbonylated species is appreciably greater. Finally, laser desorption/ionisation of the open raft cluster $[\text{Os}_6(\text{CO})_{21}]$ [27] affords similar anionic products to those described above. The highest mass peak in this case is at 1618 Da and corresponds to $[\text{Os}_6(\text{CO})_{17}]^-$. This would suggest partial decarbonylation results in the closure of open metal core to give a tritrahedron since this cluster is formally derived from neutral $[\text{Os}_6(\text{CO})_{18}]$. Rearrangement to this structure is more favourable than rearrangement to an octa-

hedron since bonds only need to form without others needing to be cleaved.

To conclude, the reactivity patterns observed in these gas phase studies parallel those found using more conventional chemical methods. The laser ablation process is clearly closely related to the corresponding thermal process, in fact, much heat is imparted to the system during laser desorption/ionisation. A dense gas plume containing highly energetic molecules and ions forms and presumably it is here where the reactions take place. The similarity with pyrolysis leads us to speculate that photolysis with lasers may become a useful synthetic tool in organometallic/cluster synthesis.

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