

Fragmentation of Transition Metal Carbonyl Cluster Anions: Structural Insights from Mass Spectrometry

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Abstract: The anionic clusters $[\text{HOs}_5(\text{CO})_{15}]^-$, $[\text{PtRu}_5\text{C}(\text{CO})_{15}]^{2-}$, $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$, $[\text{Os}_{17}(\text{CO})_{36}]^{2-}$, $[\text{Os}_{20}(\text{CO})_{40}]^{3-}$, $[\text{Co}_6\text{C}(\text{CO})_{15}]^{2-}$, $[\text{Pt}_3\text{Ru}_{10}\text{C}_2(\text{CO})_{32}]^{2-}$ and $[\text{Pd}_6\text{Ru}_6(\text{CO})_{24}]^{2-}$ have been analysed by energy-dependent electrospray ionisation mass spectrometry (EDESI-MS). Three main features have emerged. Firstly, carbonyl ligands are fragmented from clusters with compact metal cores in an orderly fashion, with each of the ions generated by CO

loss having approximately equal intensity. Secondly, electron autodetachment takes place in multiply charged anionic clusters, but only after elimination of a large proportion of their carbonyl ligands. Thirdly, clusters with open metal

cores do not undergo CO loss in an orderly fashion, but certain peaks are considerably less intense. The appearance of these low-intensity peaks is believed to signify polyhedral core rearrangements, with open clusters folding to form more compact geometries. In some cases, the gas-phase transformations observed by EDESI-MS mirror those that are known to take place in solution.

Keywords: anions • carbonyl ligands • cluster compounds • mass spectrometry • metal–metal interactions

Introduction

Transition metal carbonyl clusters display a vast array of polyhedral core structures.^[1] The adoption of a particular shape is largely determined by the electronic requirements of the metals and ligands, and a variety of electron counting approaches have been developed to rationalise the arrangement of metal atoms in clusters.^[2] Experimental determination of the core structure relies heavily on X-ray and neutron diffraction methods, but these do not give any information on the structure of the cluster in solution. While spectroscopic techniques provide information on the ligands, structural information concerning the metal core is generally limited except in special cases;^[3] for example, EXAFS,^[4] Mössbauer effect spectroscopy on Fe^[5] and Au clusters,^[6] NMR spectroscopy on clusters with NMR active nuclei such as ¹⁰³Rh and ¹⁹⁵Pt^[7] or via indirect methods.^[8]

Mass spectrometry offers some potential for determining the structure of a cluster core, as establishment of the molecular formula allows the application of electron counting rules.^[9] However, this approach is dependent on the effectiveness of the rules, and these can break down even for quite simple systems, especially where Group 10 or 11 elements are concerned. In addition, while other spectroscopic methods give information on the dynamic processes of clusters, this type of information is not provided by standard "one-dimensional" mass spectrometric methods.

In this paper we show that energy-dependent electrospray ionisation mass spectrometry (EDESI-MS)^[10] of transition metal carbonyl clusters, provides information regarding the structural rearrangements of cluster cores. Under pyrolysis or thermolysis conditions, transition metal carbonyl clusters lose carbonyl ligands as free CO. Unsaturated clusters capable of rearranging their polyhedral metal core to form more metal–metal bonds will generally do so, as metal–metal bond formation compensates electronically for the loss of a 2e⁻ donor ligand; the process can even be reversible.^[11] Metal clusters unable to form more compact cores include polytetrahedral (i.e., tetrahedra fused together through triangular faces to generate structures such as the trigonal bipyramid or bicapped tetrahedron; small clusters with polytetrahedral structures have the highest possible packing efficiency) and those with an interstitial atom that completely fills the available cavity (e.g., a carbide inside an octahedron of metal atoms). The ability of EDESI-MS to differentiate between

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structural motifs is because fragmentation in ESI mass spectrometers is performed by means of collision-induced dissociation (CID)—energetic collisions of the ions with an inert gas, such as argon, effectively imparting thermal energy to the ion,^[12] removing ligands and initiating core rearrangement.

Results and Discussion

EDESI-MS is essentially a two-dimensional projection (collision energy vs m/z) of a three-dimensional surface (ion intensity). Each ion is represented on the map as an area of intensity or “crosspeak”. The EDESI-MS maps of low nuclearity anionic transition metal carbonyl clusters are generally quite simple and show that stripping of carbonyl ligands occurs in an orderly progression. It is possible that anomalies from an orderly progression of CO loss peaks, such as, peaks of very high or low intensity, could correlate to certain structural phenomena representing very stable or unstable structures, respectively.

EDESI-MS of “closed” clusters: EDESI-MS has previously been used to analyse a number of clusters including $[\text{Ru}_5\text{CoC}(\text{CO})_{16}]^-$, $[\text{Ru}_3\text{Co}(\text{CO})_{13}]^-$, $[\text{RuCo}_3(\text{CO})_{12}]^-$, $[\text{HRu}_4\text{Co}_2\text{C}(\text{CO})_{15}]^-$, $[\text{Ru}_5\text{IrC}(\text{CO})_{16}]^-$, $[\text{Ru}_3\text{Ir}(\text{CO})_{13}]^-$ and $[\text{RuIr}_3(\text{CO})_{12}]^-$.^[13] In each of these spectra the ions generated by CO loss have approximately equal intensity. The heteronuclear clusters listed above were actually analysed as product mixtures without any purification steps, and the two-dimensional maps generated allowed unambiguous resolution of the different clusters formed in the reactions. Since the EDESI-MS technique is not yet in widespread use, a further example is that of $[\text{HOs}_5(\text{CO})_{15}]^-$, which is displayed in Figure 1. At low cone voltages (low fragmentation energy), the only species present is the intact parent ion, $[\text{HOs}_5(\text{CO})_{15}]^-$. At a cone voltage of approximately 30 V the first CO ligand is lost, and as the voltage is further increased, CO stripping continues in a steady and unbroken fashion, producing the series of ions $[\text{HOs}_5(\text{CO})_n]^-$ ($n = 0–14$). No fragmentation of the metal core is observed.

A similarly steady CO loss pattern is seen from the mixed-metal cluster $[\text{PtRu}_5\text{C}(\text{CO})_{15}]^{2-}$, a dianionic octahedral cluster with an interstitial carbide atom. The EDESI map of this cluster is shown in Figure 2, and the most noticeable feature of the map is the major discontinuity present partway through the fragmentation process. This discontinuity is not a result of

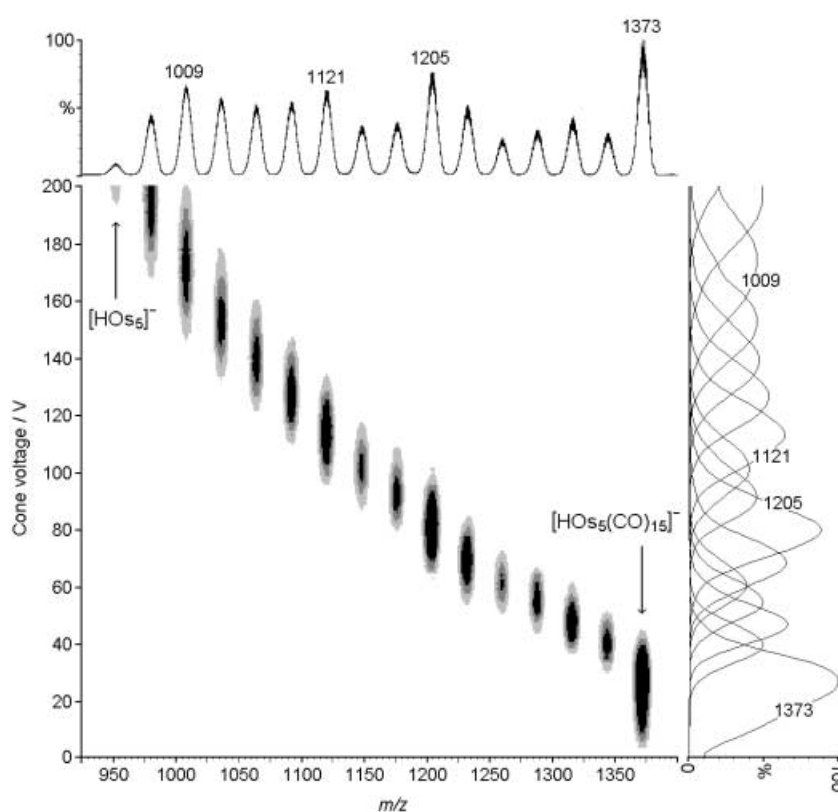


Figure 1. The negative-ion EDESI-MS map of $[\text{HOs}_5(\text{CO})_{15}]^-$ at cone voltage settings of 0–200 V. The top trace is a 1D spectrum generated by combining all 201 spectra together; the side trace is a breakdown graph of all the major ions in the spectrum.

fragmentation of the cluster core, as octahedral carbide-centred clusters are generally very stable;^[14] instead it is caused by loss of an electron and the resultant doubling in mass-to-charge ratio.

Loss of an electron from multiply charged anions (MCAs) in the gas phase is a well-known phenomenon, and is due to the increase in coulomb repulsion between the excess charges upon ligand loss. This makes the MCA unstable towards electron autodetachment.^[15] The process has been studied using photoelectron spectroscopy^[16] and has been applied to the dianionic clusters $[\text{Ru}_6(\text{CO})_{18}]^{2-}$ and $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$.^[17] Both of these clusters exhibit very similar behaviour to $[\text{PtRu}_5\text{C}(\text{CO})_{15}]^{2-}$, with electron autodetachment occurring at around 40 V at $[\text{M}_x(\text{CO})_y]^{2-}$ ($\text{M}_x = \text{Ru}_6$ and Ru_6C , $y = 10, 9$; $\text{M}_x = \text{PtRu}_5\text{C}$, $y = 9, 8$).

The phenomenon of electron autodetachment is also observed in the EDESI maps of the high-nuclearity clusters $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$, $[\text{Os}_{17}(\text{CO})_{36}]^{2-}$ and $[\text{Os}_{20}(\text{CO})_{40}]^{3-}$. Each of these maps were collected in the MS/MS mode, as this provides the considerable advantage that pre-purification of each component is unnecessary; the reaction mixture from the high-temperature pyrolysis of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ was simply diluted and injected straight into the mass spectrometer. The appropriate parent ion was selected and fragmented in the collision cell of a triple quadrupole instrument. In the case of $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$, electron autodetachment occurred at around 100 V, when between two and five CO ligands remained on the cluster core (Figure 3).

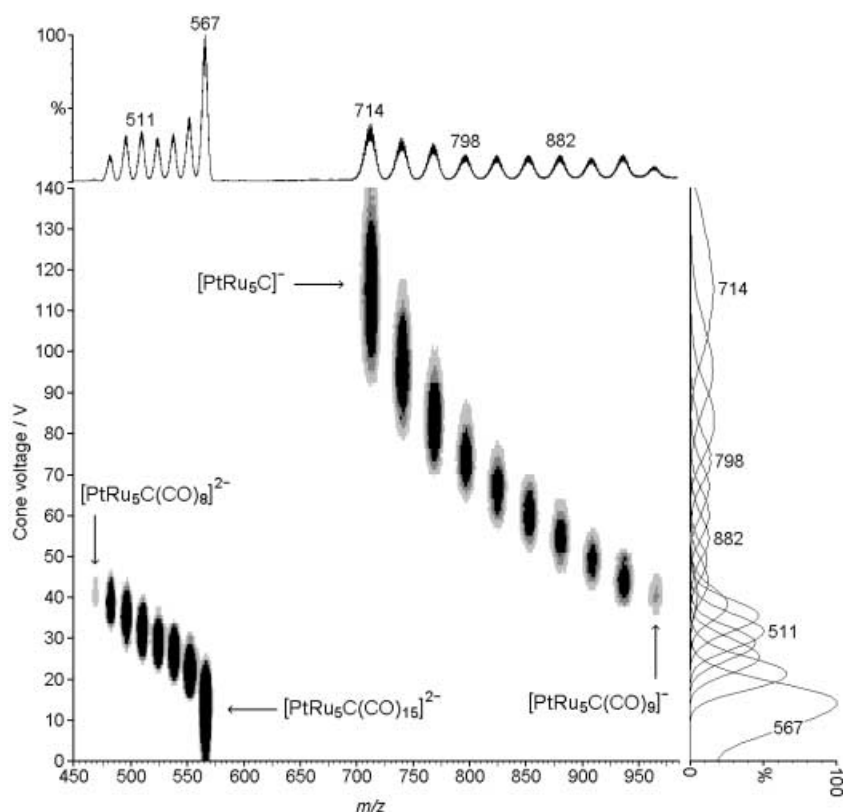


Figure 2. The negative-ion EDESI-MS map of $[\text{PtRu}_5\text{C}(\text{CO})_{13}]^{2-}$ at cone voltages of 0–140 V.

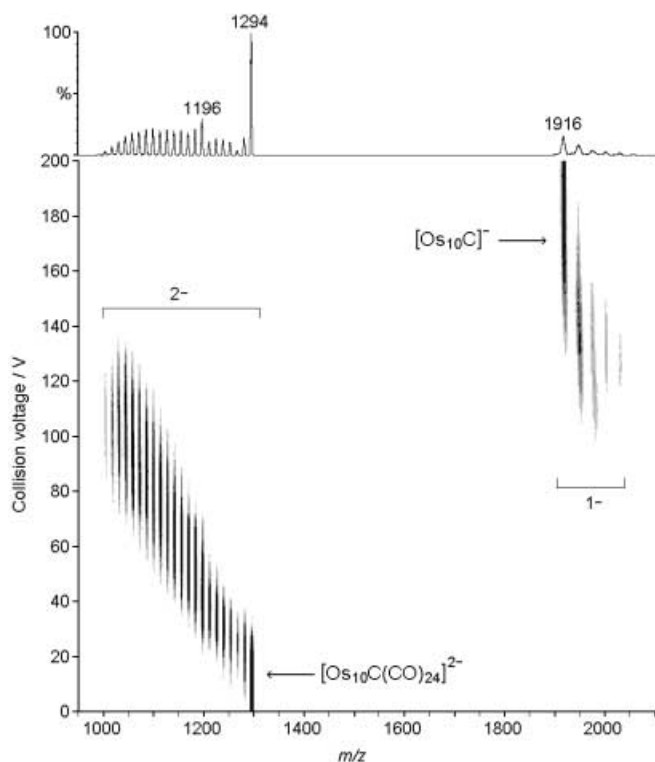


Figure 3. The negative-ion EDESI-MS/MS map of $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ at collision voltages of 0–200 V.

The fact that ligand stripping occurs to a greater extent before electron autodetachment occurs is not surprising; the tetracapped octahedral cluster is significantly larger than the

octahedral clusters, increasing the separation between the two excess charges and reducing the Coulomb repulsion. Perhaps the most unusual feature of the spectrum shown in Figure 3 is the extent to which the parent ion dominates, with an intensity approximately three times that of the next most intense ion, $[\text{Os}_{10}\text{C}(\text{CO})_{17}]^{2-}$. We have not observed such domination by one ion in the EDESI spectra of any other clusters, and the reason for it in the case of $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ may be due to the remarkably stable cubic close packed arrangement of metal atoms, around which the 24 carbonyl ligands bond terminally, six CO ligands to the six metal atoms of each face. Removing the symmetry of the system appears to be difficult, but once it is broken, subsequent CO loss is much easier.

The EDESI-MS/MS map of $[\text{Os}_{17}(\text{CO})_{36}]^{2-}$ is quite similar to that of $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$, with steady stripping of CO ligands until electron autodetachment occurs at around 120 V, when 1–4 ligands remain on the cluster core (see Supporting Information). The map of the trianionic cluster $[\text{Os}_{20}(\text{CO})_{40}]^{3-}$ is somewhat different, as it contains two electron autodetachment events (Figure 4). This species is particularly interesting, as long-lived gas phase trianions are rare.^[18]

The first electron loss occurs at relatively low fragmentation energy (around 40 V), but at this stage between 20–23 carbonyl ligands have already been lost. The rapid loss of CO is mainly due to the high collision gas pressure required to ultimately denude the cluster completely of ligands. The ability to change the gas pressure prior to EDESI-MS/MS collection allows conditions to be set such that complete ligand stripping will occur by maximum fragmentation energy.

The second electron autodetachment event, generating the monoanionic series from the dianionic series, occurs at around 120 V, at which point all but a few of the CO ligands have been stripped from the core. The bare Os_{20} metal core is large enough to support a 2– charge in the gas phase, an observation that is in general agreement with studies on laser ablated metal targets, which showed that for lead and gold, series of dianions were observed starting with Pb_{35}^{2-} and Au_{29}^{2-} .^[19]

EDESI-MS of “open” clusters: EDESI maps in which the ion intensities have been highly variable have been attributed to rearrangement of the ligands, as in the example of $[\text{Ru}_6\text{C}(\text{CO})_{16}(\text{COOMe})]^-$, which undergoes facile elimination of formaldehyde from the methoxycarbonyl ligand.^[20] In most of the clusters studied to date, there has been no possibility of

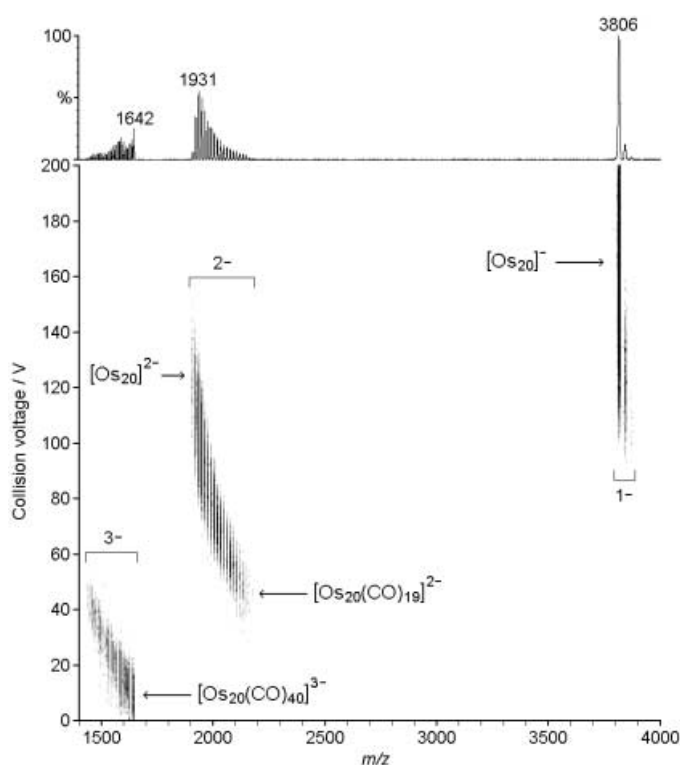


Figure 4. The negative-ion EDESI-MS/MS map of $[\text{Os}_{20}(\text{CO})_{40}]^{3-}$ at collision voltages of 0–200 V.

polyhedral rearrangement of the metal core as they have been either tetrahedral, trigonal bipyramidal, or octahedral with an interstitial carbide atom, none of these geometries can rearrange such that connectivity in the core is increased. However, we have since discovered that fragmentation patterns are more complicated for clusters with open core geometries. Under CO loss conditions (heating), the trigonal prismatic carbido cluster $[\text{Co}_6\text{C}(\text{CO})_{15}]^{2-}$ ($90e^-$, EAN (Effective Atomic Number) rule predicts 9 M–M bonds) forms $[\text{Co}_6\text{C}(\text{CO})_{13}]^{2-}$, which has an octahedral core geometry.^[21] The EDESI-MS map of this cluster (Figure 5) demonstrates an irregular fragmentation pattern consistent with the rearrangement of the metal core.

As with other EDESI-MS maps, the intact parent ion, $[\text{Co}_6\text{C}(\text{CO})_{15}]^{2-}$ loses CO ligands progressively as cone voltage is increased. However, it is immediately evident that unlike other examples, the loss of CO ligands does not occur in a regular fashion. The crosspeak for the $[\text{Co}_6\text{C}(\text{CO})_{14}]^{2-}$ ion has a very low intensity, and it should be noted that the first two CO ligands are being lost by a cone voltage of 6 V, while the loss of the next two ligands takes a further increase of approximately 11 V. We suggest this is due to the fact that the $[\text{Co}_6\text{C}(\text{CO})_{14}]^{2-}$ is an unstable “transition state” of the metal core, as further loss of CO from the species generates $[\text{Co}_6\text{C}(\text{CO})_{13}]^{2-}$, a known cluster with an octahedral core $86e^-$, PSEPT (Polyhedral Skeletal Electron Pair Theory) predicts a *closo* structure. Further rearrangement of the core is impossible, and the remainder of the pattern consists of CO loss crosspeaks of similar intensity.

For certain clusters, a remarkable amount of structural information can be extracted from the EDESI-MS map. A

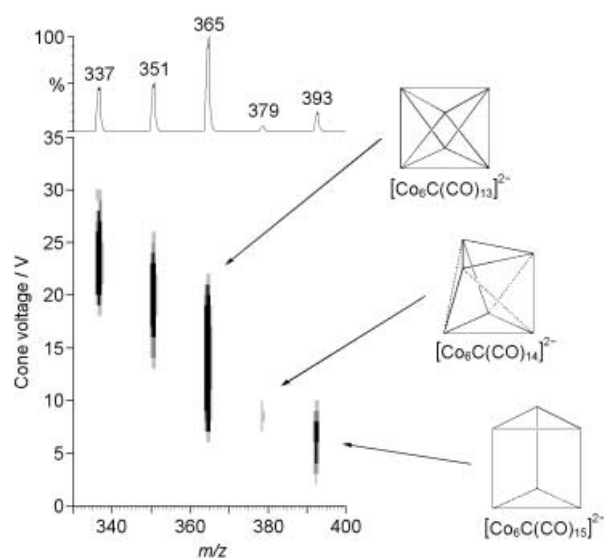


Figure 5. The negative-ion EDESI-MS map of the dianionic cluster $[\text{Co}_6\text{C}(\text{CO})_{15}]^{2-}$ at cone voltage of 0–35 V. Proposed structures for the ions $[\text{Co}_6\text{C}(\text{CO})_{14}]^{2-}$ and $[\text{Co}_6\text{C}(\text{CO})_{13}]^{2-}$ are illustrated on the right.

cluster isolated from the reaction between $[\text{PtRu}_5\text{C}(\text{CO})_{15}]^{2-}$ and $[\text{Pt}(\text{COD})\text{Cl}_2]$ was shown by ESI-MS to be dianionic with the formula $[\text{Pt}_3\text{Ru}_{10}\text{C}_2(\text{CO})_{32}]^{2-}$, 1259 m/z . EDESI-MS of this cluster is dominated by two fragmentation pathways (Figure 6). Both pathways initially involve loss of a single CO to form $[\text{Pt}_3\text{Ru}_{10}\text{C}_2(\text{CO})_{31}]^{2-}$, which we postulate will result in the formation of an extra metal–metal bond.

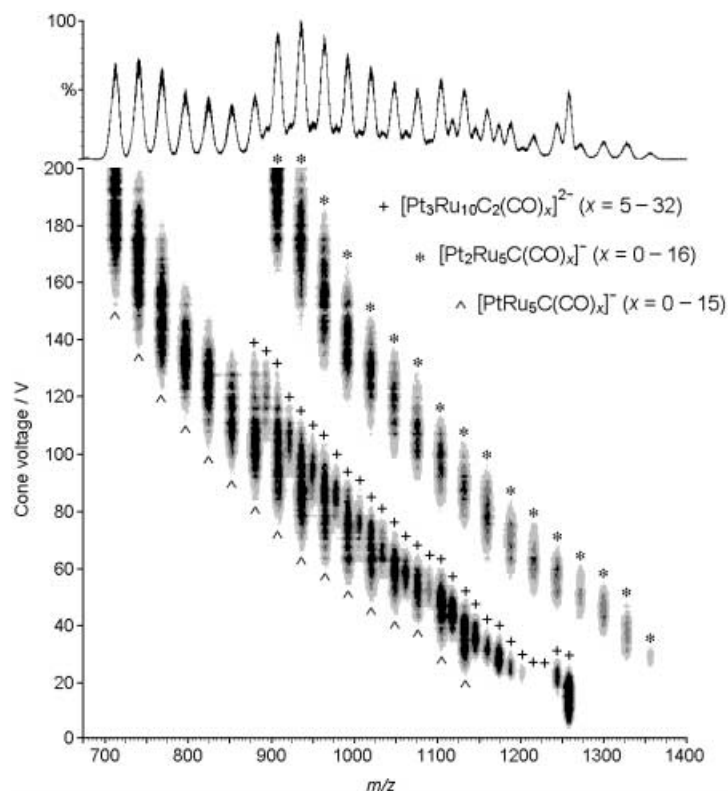
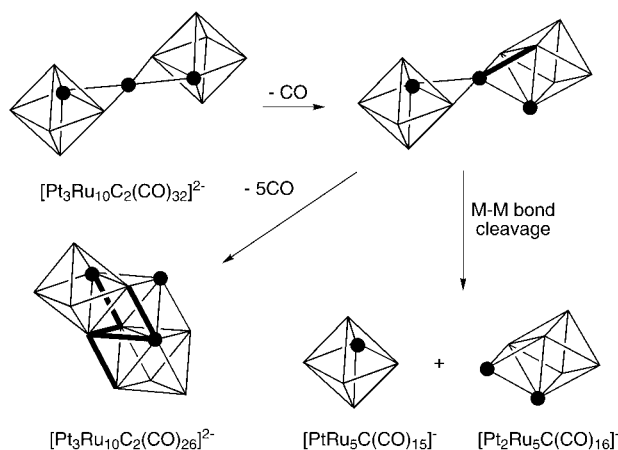


Figure 6. The negative-ion EDESI-MS map of the dianion $[\text{Pt}_3\text{Ru}_{10}\text{C}_2(\text{CO})_{32}]^{2-}$ at cone voltages of 0–200 V.

One of the fragmentation pathways involves the cluster breaking apart to form hexa- and heptanuclear species, $[\text{PtRu}_5\text{C}(\text{CO})_{15}]^-$ (marked “^” on the spectrum) at 1134 m/z and $[\text{Pt}_2\text{Ru}_5\text{C}(\text{CO})_{16}]^-$ (marked “*”) at 1357 m/z . Both of these species appear at similar m/z values to the parent cluster, because although their masses have approximately halved, they are now monoanionic. Note that subsequent CO loss from each of these fragments progresses in a regular fashion, consistent with clusters unable to rearrange to a more condensed form, supporting the formation of uncapped and capped carbide-centered octahedral cores. These observations provided strong evidence that the cluster consisted of two units weakly linked together through a central platinum. The single-crystal X-ray structure of the dianion confirmed this, consisting of two carbide-centered PtRu_5 octahedra linked by a $\text{Pt}(\text{CO})_2$ unit bridging a $\text{Pt}-\text{Ru}$ edge of each octahedron.^[22]

The second fragmentation route apparent in the EDESI-MS map (marked “+”) involves CO loss alone. Note that the initial pattern of CO loss crosspeaks is very irregular until $[\text{Pt}_3\text{Ru}_{10}\text{C}_2(\text{CO})_{26}]^{2-}$, which has an electron count corresponding to a highly compact structure (maximum number of metal–metal bonds) accessible to this cluster by simple “folding up” of the core (i.e., only involving metal–metal bond formation, no breaking of metal–metal or metal–carbon interstitial bonds). As soon as at least two CO ligands are lost, the cluster is no longer susceptible to cleavage (demonstrated by MS/MS studies^[23]), and this fact provides further evidence of polyhedral rearrangement to a more condensed form. The two pathways are summarised in Scheme 1, which also includes a possible structure for $[\text{Pt}_3\text{Ru}_{10}\text{C}_2(\text{CO})_{26}]^{2-}$.



Scheme 1. Two possible fragmentation pathways for $[\text{Pt}_3\text{Ru}_{10}\text{C}_2(\text{CO})_{31}]^{2-}$.

The bimetallic hexacapped octahedral cluster $[\text{Pd}_6\text{Ru}_6(\text{CO})_{24}]^{2-}$ ^[24] provides further evidence for the idea of gas-phase polyhedral rearrangement. The EDESI-MS map for this compound (Figure 7) shows profound irregularities in the ion intensities at low cone voltages.

$[\text{Pd}_6\text{Ru}_6(\text{CO})_{24}]^{2-}$ has high potential for rearrangement of the metal core, not just because of the possible alternative structures that have more metal–metal contacts, but also because of the bimetallic nature of the cluster, allowing the

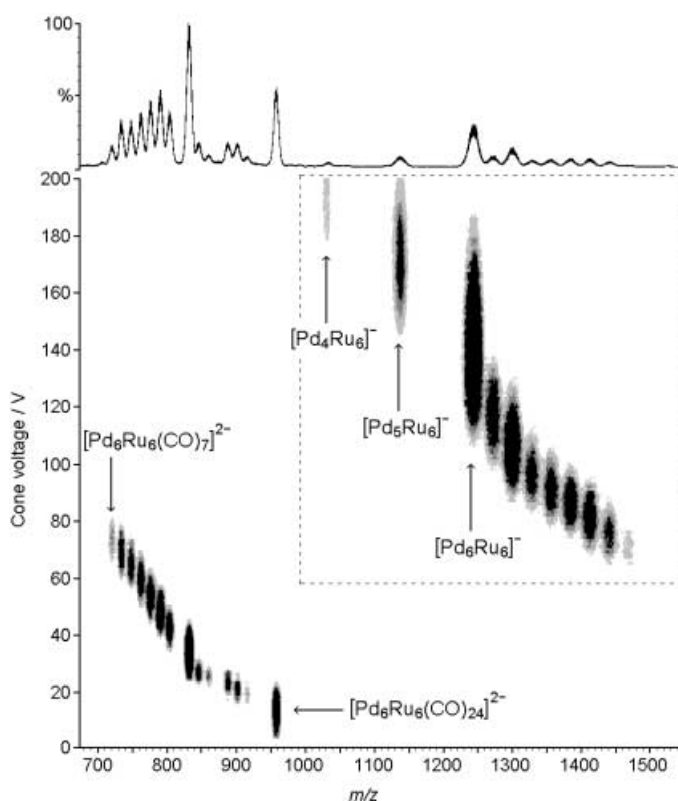


Figure 7. The negative-ion EDESI-MS map of the dianion $[\text{Pd}_6\text{Ru}_6(\text{CO})_{24}]^{2-}$ at cone voltages of 0–200 V. The intensity of the crosspeaks in the outlined region has been enhanced ($\times 10$).

two metals to take up different sites in clusters with the same polyhedral arrangement. Figure 8a shows the hexacapped octahedral core of the parent cluster which possesses 30 M–M contacts, and two possible dodecanuclear core geometries with 33 and 36 M–M contacts are shown in Figure 8b and c, respectively. The *nido*-icosahedral structure shown in Figure 8c is essentially polytetrahedral.

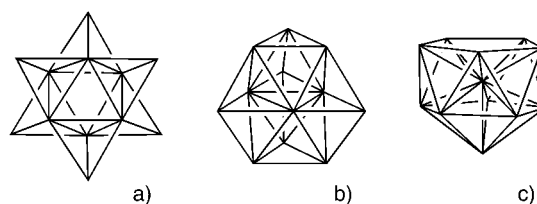


Figure 8. Possible cluster geometries for an M_{12} cluster.

Irregularities in crosspeak intensity extend out as far as $[\text{Pd}_6\text{Ru}_6(\text{CO})_{14}]^{2-}$, and it is clear from electron-counting considerations^[25] that at this extent of CO stripping these ions do not represent saturated species. However, unlike the previous two examples, all conceivable polyhedral rearrangements must necessarily involve a profound reorganisation of the metal atoms, rather than a simple “folding-up” of the core. This clearly complicates the picture considerably, and straightforward assignment of structure to the various ions is no longer possible. Additional evidence of polyhedral rearrangement comes from the EDESI-MS map at very high

cone voltages. At these high fragmentation energies the core itself starts to break up and the sequential expulsion of two palladium atoms is observed. Because the initial core structure consists of an octahedron of palladium atoms surrounded by ruthenium caps, it seems unlikely that the Pd atoms would be lost first unless some rearrangement of the core had occurred. Note that in both Figure 8b and c, at least some of the Pd atoms occupy surface sites on the cluster. Non predictable rearrangements have been observed for heteronuclear clusters on loss of CO in work conducted on a laboratory scale.^[26]

Conclusion

Energy-dependent mass spectrometric techniques have been applied to a range of anionic transition metal carbonyl clusters. The dominant fragmentation pattern seen for all the clusters under collision-induced dissociation conditions is the steady, progressive loss of carbonyl ligands as CO. Major discontinuities in the fragmentation pattern occur for multiply charged anions, due to electron autodetachment. However, features most diagnostic of core structure occur in the early part of the fragmentation pattern. Clusters with an “open” metal core framework will electronically compensate for loss of a CO ligand by forming metal–metal bonds, and this process is represented in the EDESI map by a greatly decreased intensity for appropriate ions. Ions with lowest intensity appear to be those intermediate between the parent ion and the ion which represents the electronically saturated structure with the maximum number of metal–metal bonds possible, as exemplified by the fragmentation of $[\text{Co}_6\text{C}(\text{CO})_{15}]^{2-}$. The parent ion corresponds in this case to a trigonal prism, whereas the electronically saturated structure with the maximum number of metal–metal bonds (an octahedron) is $[\text{Co}_6\text{C}(\text{CO})_{13}]^{2-}$. The intermediate ion has very low intensity, presumably because the cluster can easily compensate for loss of an additional CO ligand. A similar explanation can be applied to $[\text{Pt}_3\text{Ru}_{10}\text{C}_2(\text{CO})_{32}]^{2-}$, and the spectra of this compound provides even more structural information beyond suggesting an open core. In this case, facile cleavage of the cluster into two singly charged fragments reveals the unusual geometry of this cluster, in which two octahedral units are linked by a single platinum atom. Caution does need to be applied when interpreting variable ion intensities near the start of a fragmentation pattern, and this is illustrated starkly by the example of $[\text{Pd}_6\text{Ru}_6(\text{CO})_{24}]^{2-}$, in which irregularities in ion intensities extend well beyond that expected for simple condensation to a polytetrahedral (decapped icosahedral) configuration. However, the EDESI experiment does show that new, potentially stable compounds could be made by CO loss, and eventually they may be made in the laboratory.

We expect that the utility of the EDESI approach will become more apparent as additional examples are investigated. At present, the technique can certainly provide evidence for diversity in the core structure of metal clusters, and as such is best applied to the rapid screening of product mixtures, where its potential for identifying interesting

candidates for further study is evident. The technique is not restricted to anionic clusters, but, in principle, could be applied to positively charged^[27] and neutral clusters derivatised with a suitable reagent to induce charge^[28] or by substitution of one or more CO ligands for an “electrospray-friendly” phosphine.^[29]

Experimental Section

The anionic clusters $[\text{HOs}_5(\text{CO})_{15}]^{-}$,^[30] $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$,^[31] $[\text{Os}_{17}(\text{CO})_{36}]^{2-}$ ^[32] and $[\text{Co}_6\text{C}(\text{CO})_{15}]^{2-}$ ^[33] were all prepared as the $[\text{PPN}]^+$ salts by using literature methods. $[\text{Os}_{20}(\text{CO})_{40}]^{3-}$ is a known^[34] component of the product mixture from which $[\text{Os}_{20}(\text{CO})_{40}]^{2-}$ can be isolated,^[35] and was selected by using MS/MS techniques. $[\text{Pd}_6\text{Ru}_6(\text{CO})_{24}]^{2-}$ ^[22] was prepared as the $[\text{NET}_4]^+$ salt, $[\text{PtRu}_5\text{C}(\text{CO})_{15}]^{2-}$ ^[36] and $[\text{Pt}_3\text{Ru}_{10}\text{C}_2(\text{CO})_{32}]^{2-}$ ^[21] as the $[\text{PPh}_4]^+$ salts. Mass spectra were collected using a Micromass Quattro LC with the following settings. The nebuliser tip was set at 3100 V and 100 °C, and nitrogen was used as the bath gas. Samples were introduced directly to the source at 8 $\mu\text{L min}^{-1}$ by using a syringe pump. Data collection was carried out in continuum mode. For the EDESI mass spectrum, the cone voltage was initially set at 0 V. A scan time of eight seconds per spectrum and a relatively low resolution setting (peak width at half-height ~ 0.8 Da) was used to maximise the signal-to-noise ratio. The cone voltage was increased by increments of 1 V after every scan up to a maximum of 200 V. A full scan from 0–200 V therefore took approximately 25 minutes to collect. The EDESI-MS/MS spectra were collected in a similar fashion, but by adjusting the collision voltage in the argon-filled collision cell rather than by altering the cone voltage. The gas pressure in the collision cell was generally set at 10^{-4} mbar, but increased for the EDESI-MS/MS of the osmium clusters $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$, $[\text{Os}_{17}(\text{CO})_{36}]^{2-}$, $[\text{Os}_{20}(\text{CO})_{40}]^{3-}$ such that at maximum collision voltage, all of the CO ligands were removed. This required a gas pressure of 5×10^{-3} mbar.

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