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Formaldehyde elimination from methoxylated transition metal carbonyl clusters.

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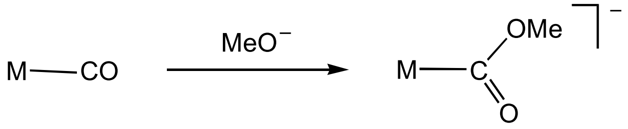
Joseph Chatt’s interests in organometallic chemistry were wide-ranging, from bonding theories to nitrogen fixation. While these areas may not seem of immediate relevance to either carbonyl cluster chemistry or to electrospray mass spectrometry (both of which play a major role in the work described herein), the *chemistry* that is discussed broadly overlaps with Chatt’s contributions in metal hydride, metal phosphine and low oxidation state chemistry.

The following work describes our investigation into some unexpected chemistry resulting from our interest in unsaturated metal clusters.[1] We study such systems primarily by mass spectrometry, and to assist these investigations we developed the new data presentation technique of energy-dependent electrospray mass spectrometry (EDESI-MS). One of the first systems studied was that of alkoxylated transition metal carbonyl clusters, which display loss of formaldehyde in their electrospray ionisation fragmentation process. We have been able to correlate this behaviour with macroscopic chemical properties of these clusters.

Alkoxylation of carbonyl ligands

A well-known reaction in transition metal carbonyl chemistry is nucleophilic attack of alkoxide ions, RO^-, on the electropositive carbon atom of a carbonyl ligand, affording an anionic alkoxycarbonyl species (Equation 1).



(Equation 1)

Alkoxylation occurs very rapidly and the product is thermodynamically favoured.[2] The reaction between alkoxide ions and transition metal carbonyl clusters, $M_n(CO)_m$, generates anionic species of general formula $[M_n(CO)_{m-1}(COOR)]^-$. A number have been isolated and crystallographically characterised, including $[Ir_6(CO)_{15}(COOMe)]^-$,[3] $[HOs_5C(CO)_{14}(COOEt)]^-$ and $[Os_5C(CO)_{14}(COOMe)I]^-$,[4] $[Ir_4(CO)_{11}(COOMe)]^-$ [5] and $[Rh_6(CO)_{15}(COOMe)]^-$.[6]

Chemical derivatisation

The alkoxylation reaction has been exploited in the *in situ* derivatisation of neutral metal carbonyl complexes for analysis by electrospray mass spectrometry (ESIMS).[7] ESI is a relatively new ionisation technique which involves spraying a solution from a charged capillary into a strong electric field. Tiny droplets are formed from which the solvent is evaporated by means of a warm bath gas. Acquisition of charge by the target molecule usually takes place by chemical ionisation, frequently addition of H^+ from a protic solvent (typically acetonitrile/water). However, neutral metal carbonyl compounds do not readily undergo protonation as they are insufficiently basic. Derivatisation by alkoxide ion was subsequently found to be a convenient method for chemically generating $[M + OR]^-$ ions.[8] Charged organometallic species are readily analysed by electrospray mass spectrometry,[9] and typically just a single envelope of peaks corresponding to the parent is observed in the mass spectrum. In ESI-MS, fragmentation is considerably reduced compared to more conventional ionisation techniques, such as electron impact.[10] The alkoxide derivatisation method works equally successfully for clusters, and despite the presence of multiple reaction sites, double alkoxylation to provide $[M + 2(OMe)]^{2-}$ ions has never been observed by ESI-MS. Such a reaction does, however, have precedent, as a double alkoxylation product was recently successfully isolated from the reaction between NaOMe and $[Ir_6(CO)_{16}]$ in methanol and the solid-state structure of the product $[Ir_6(CO)_{14}(COOMe)_2]^{2-}$ was determined.[11] The two methoxycarbonyl fragments are on adjacent metal vertices of the octahedral framework.

Energy-dependent electrospray mass spectrometry

While fragmentation tends to minimal for electrospray ionisation under normal conditions, it can be increased very conveniently by means of the voltage applied at the skimmer cones. Essentially, increasing the cone voltage causes collision-induced dissociation (CID) before the ions are directed into the mass analyser. Analysis of the resulting fragmentation pattern can yield interesting information on the compound in question, and we have been able to correlate the information gained from the mass spectrometric studies with the compounds macroscopic chemical behaviour.

The conventional method of displaying fragmentation data from ESI-MS is to stack a series of spectra gathered at different cone voltages.[12] Such an approach is illustrated in Figure 1, which shows the negative-ion ESI mass spectra of $[Ir_4(CO)_{11}(COOMe)]^-$ (**1**) recorded at cone voltage settings of 25, 75 and 150 V.

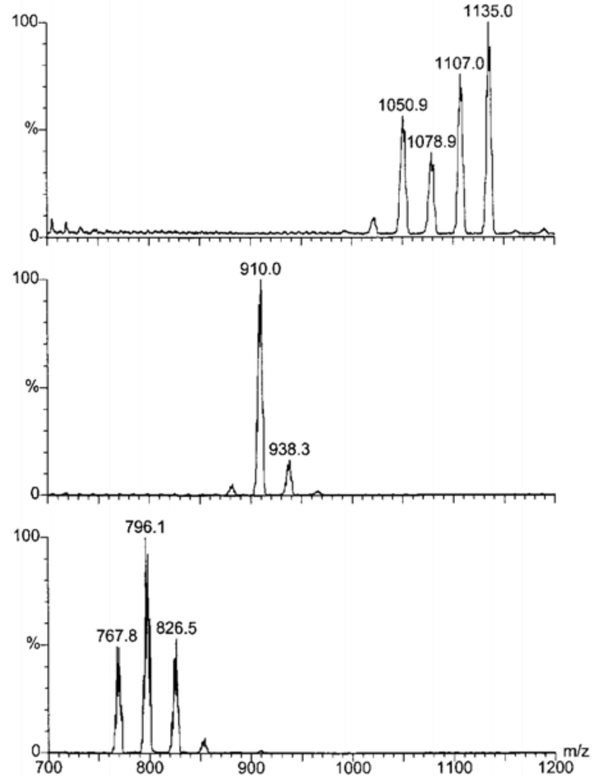


Figure 1 Negative-ion ESI mass spectra of $[Ir_4(CO)_{11}(COOMe)]^-$ (**1**), showing the effect of the cone voltage setting on the fragmentation patterns; (a) 25 V, (b) 75 V; (c) 150 V.

Each spectrum provides a snapshot of the ligand stripping process as a function of increasing cone voltage, and presentation of all the possible data sets in this fashion is clearly not practical. However, the entire fragmentation pattern can be easily visualised using energy-dependent electrospray ionisation mass spectrometry (EDESI-MS). This technique has recently been shown to be useful for the analysis of fragmentation processes of cluster compounds, demonstrated using $[Rh_6(CO)_{15}(COOMe)]^-$ (**2**).[13] A very large amount of data is generated in such studies as a different spectrum is obtained at each increment. EDESI-MS involves plotting this huge amount of data (up to 200 spectra) in a two-dimensional format, generating a map (with mass-to-charge ratio on the horizontal axis and cone voltage on the vertical axis), the contours of which describe the entire fragmentation pattern of the compound in question. An additional feature is a spectrum generated by summing all the spectra used in the map; this spectrum appears at the top of the map. Each cross peak in the EDESI map represents a particular fragment ion, the most intense and/or long-lived of which are generally regarded as having particular stability. For transition metal carbonyl clusters, the primary fragmentation route is via loss of the carbonyl ligands as carbon monoxide

Figure 2 shows the composite 1D/2D EDESI mass spectrum for (**1**). Due to the timespan of the experiment, good signal-to-noise is obtained at the expense of resolution. Each cross peak represents a particular fragment ion, the most intense and/or long-lived of which are generally regarded as having particular stability.

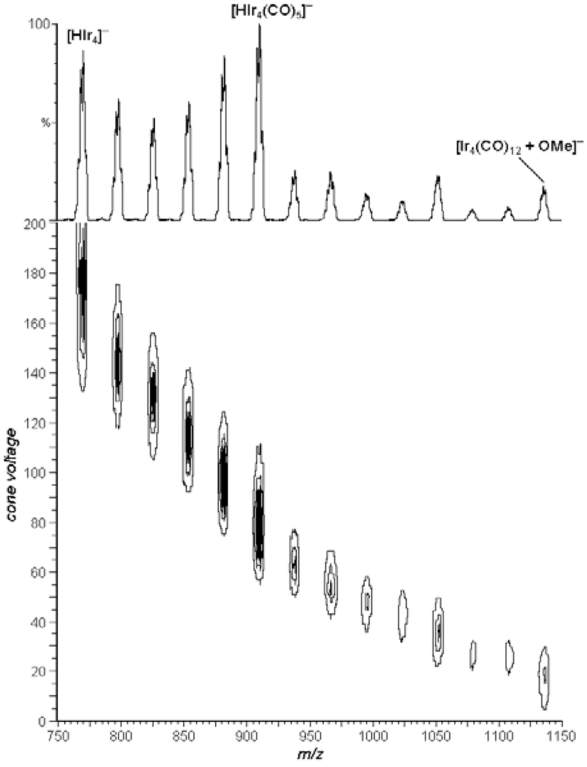


Figure 2 The two-dimensional EDESI-MS map generated from 201 negative-ion ESI-MS spectra of $[Ir_4(CO)_{11}(COOMe)]^-$ (**1**) at cone voltage settings of 0 - 200 V. The top trace is a 1D spectrum generated by combining all 201 spectra together.

The fragment peaks in the spectrum correspond to consecutive loss of CO from the central Ir_4 core. In addition, a formaldehyde molecule, HCHO, is also lost. From the EDESI-MS spectrum shown in Figure 2 it is not immediately clear where the HCHO loss (*m/z* 30) channel occurs relative to the CO loss (*m/z* 28) channel, but careful inspection reveals that the discontinuity probably occurs at *m/z* 969, i.e. $[Ir_4(CO)_6 + OMe]^-$ loses HCHO to form the $[HIr_4(CO)_6]^-$ at *m/z* 939. Unequivocal confirmation of formaldehyde loss is provided by acquiring a conventional high-resolution mass spectrum at the appropriate cone voltage.

Energy-dependent electrospray tandem mass spectrometry

Alternatively, the recent introduction of EDESI-MS/MS provides another useful tool for analysing such systems.[14] Tandem mass spectrometry (MS/MS) allows selection of a single ion using one mass analyser then intruding it to a collision cell. Energetic collisions with an inert gas in this cell causes fragmentation of the ion and a daughter ion spectrum is obtained. MS/MS techniques are especially useful for the analysis of complex mixtures, but their application to molecules with complicated isotopomer envelopes is also useful, as instead of a broad, near-Gaussian distribution of peaks for each ion, a single peak is produced instead. This feature of MS/MS spectra is illustrated in Figure 3, which shows negative-ion daughter ion ESI-MS/MS of $[Ir_4(CO)_{11}(COOMe)]^-$, recorded at collision voltage settings of 25, 75 and 150 V.

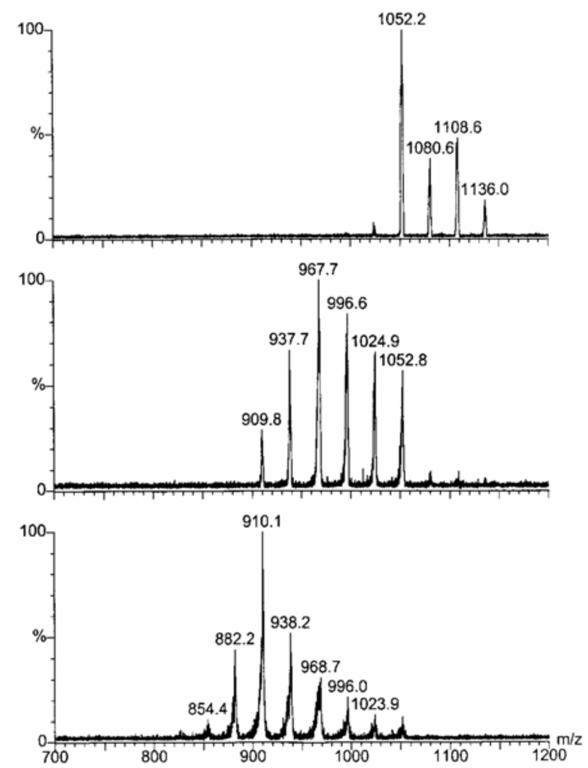


Figure 3 Negative-ion ESI-MS/MS spectra of $[Ir_4(CO)_{11}(COOMe)]^-$ (**1**), showing the effect of the collision voltage setting on the fragmentation patterns; (a) 25 V, (b) 75 V; (c) 150 V.

The principal difference between these spectra and those shown in Figure 1 are the disappearance of the isotopomer envelopes; instead, a single peak is observed for each ion. Also, broadening at the base of the peaks can be observed in Figure 3(b) and more obviously in Figure 3(c). An EDESI-MS/MS map for $[Ir_4(CO)_{11}(COOMe)]^-$ can be generated by stacking all the spectra, collected at collision voltages of 0-200 V, in an entirely analogous way to that in EDESI-MS (Figure 4).

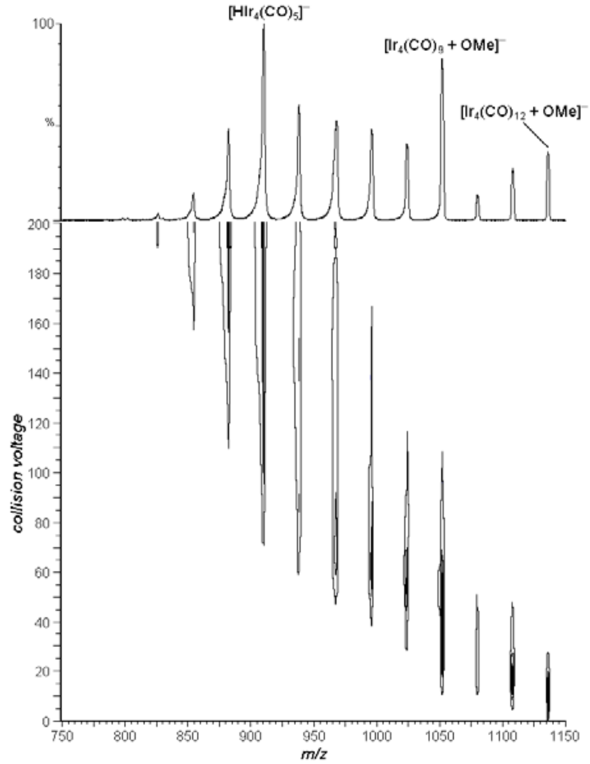


Figure 4 The two-dimensional EDESI-MS/MS map generated from 201 negative-ion daughter ion ESI-MS/MS spectra of $[Ir_4(CO)_{11}(COOMe)]^-$ (**1**) at collision voltage settings of 0 - 200 V. The top trace is a 1D spectrum generated by combining all 201 spectra together.

Comparison between the two EDESI maps reveals the expected similarities, but also some marked differences. In particular, the ability to fragment the parent ion within the collision cell is markedly less than that achieved at the skimmer cone. The EDESI map shows that the ion $[HIr_4]^-$ (in which all CO ligands have been removed) makes its first appearance at a cone voltage of 132 V, and by 175 V is the only ion present. In contrast, the most heavily fragmented ion in the EDESI-MS/MS is $[HIr_4(CO)_2]^-$, which only just appears at a high collision voltage of 190 V. The same ion in the EDESI-MS map appears at 105 V and disappears by 158 V. Despite this behaviour at high voltages, at low voltages fragmentation is induced more readily in the collision cell, as a comparison of the two maps at 20 V makes clear. In the EDESI-MS map, only the intact parent ion $[Ir_4(CO)_{11}(COOMe)]^-$ is present, whereas in the EDESI-MS/MS map, the fragment ions $[Ir_4(CO)_{11}(COOMe) - nCO]^-$ (n = 1-3) are already evident in significant intensity. It should be noted that fragmentation in the collision cell can, however, be increased by the simple expedient of using argon instead of nitrogen as the collision gas.

Apart from the differences in fragmentation power, overall the EDESI-MS and EDESI-MS/MS maps are qualitatively similar. Essentially the same pattern of intensities for each daughter ion is observed, best represented by the summed spectrum at the top of each map. This feature is not surprising given that the mechanism for fragmentation is collision-induced dissociation by N_2 gas in both cases. An advantage of the selection of a single ion is apparent in the EDESI-MS/MS approach in that identification of the point at which HCHO loss *versus* CO loss takes place is more straightforward.

Formaldehyde elimination

We have studied a number of different anionic methoxycarbonyl clusters, and found them all to undergo loss of HCHO at some point during their fragmentation processes. In some cases, we have correlated differences in fragmentation patterns between the various clusters to their macroscopic chemical properties. Confirmation of peak assignments was carried out in some cases using a Fourier transform ion cyclotron resonance (FTICR) instrument.

The elimination of an aldehyde or ketone from a coordinated alkoxide is a well known process in coordination chemistry. For example, treatment of metal halide complexes with alcoholic base is a standard method for the preparation of metal hydride complexes (Equation 2).[15] Labelling experiments have shown that the α hydrogen transforms into the hydride ligand.[16]

$$\text{M-X} + \text{R}_2\text{CHO}^- \longrightarrow \text{M-H} + \text{R}_2\text{CO} + \text{X}^- \qquad \text{(Equation 2)}$$

This process has also been observed in cluster chemistry. For example, the cluster anion $[HRu_3Ir(CO)_{12}(OMe)]^-$ eliminates HCHO under carbonyl loss conditions (prolonged heating) to generate the cluster anion $[H_2Ru_3Ir(CO)_{12}]^-$.[17] Because fragmentation in the mass spectrometer also involves carbonyl loss, it seems plausible that such a process may be simulated under EDESI-MS conditions.

Methoxylation of the hexaruthenium carbide cluster $[Ru_6C(CO)_{17}]$ generates the stable anionic cluster $[Ru_6C(CO)_{16}(COOMe)]^-$ (**3a**), the negative-ion EDESI mass spectrum of which is shown in Figure 5.[18]

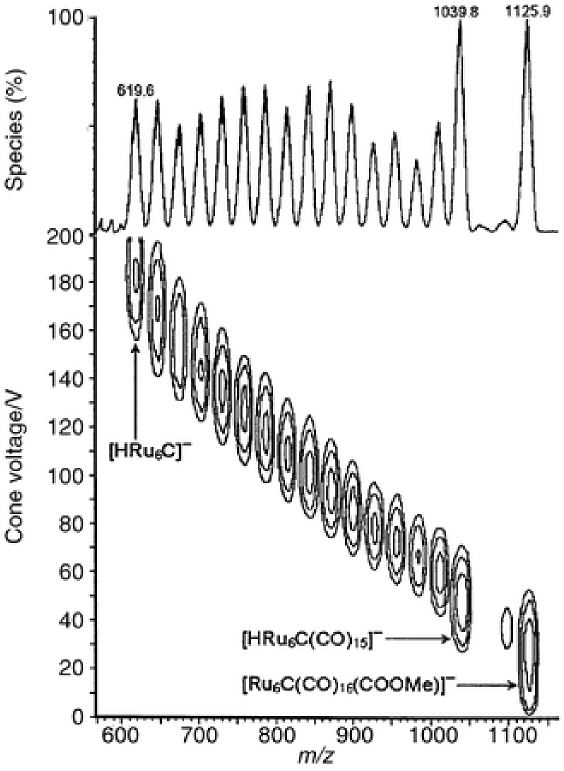


Figure 5 The negative-ion EDESI mass spectrum of $[Ru_6C(CO)_{16}(COOMe)]^-$ **3a**.

Similar to the case for **1** and **2**, at the lowest cone voltages, the only peak observed is that of the intact parent ion. Upon increasing the fragmentation energy, two CO ligands are lost, and the ions $[Ru_6C(CO)_{16}(COOMe) - x\mathrm{CO}]^-$ ($x = 1, 2$) appear in the EDESI-MS map at very low intensity. The structure of these ions is not obvious because the CO ligands may be lost either from the cluster shell or from the methoxycarbonyl ligand. The third neutral molecule to be lost from the cluster is HCHO rather than a CO ligand, to generate the hydride cluster $[HRu_6C(CO)_{15}]^-$. The remaining fifteen cross peaks correspond to the series $[HRu_6C(CO)_x]^-$ ($x = 0 - 14$), and have roughly equal intensity leading ultimately to $[HRu_6C]^-$. The closely related anion $[Ru_6C(CO)_{16}(COOEt)]^-$ (**3b**) undergoes an analogous fragmentation sequence, except CH_3CHO is eliminated instead of HCHO. As expected, $[Ru_6C(CO)_{16}(COOPh)]^-$ (**3c**) does not display similar behaviour, as the phenyl ring prevents formation of an exocyclic C=O bond. The CO ligands are progressively stripped in the case of **3c**, with complex fragmentation occurring at the highest cone voltages.

Figure 6 shows the ESI-FTICR mass spectra [11] of **3a** and **2**. These high-resolution spectra were collected to ensure the accuracy of the peak assignments.

Figure 6 The negative-ion ESI-FTICR mass spectra of $[Ru_6C(CO)_{16}(COOMe)]^-$ **3a** (top) and $[Rh_6(CO)_{15}(COOMe)]^-$ **2a** (bottom).

Two sets of peaks are observed in the spectrum of **3a**; the envelope of peaks centred at 1125.64 *m/z* corresponding to the intact parent ion, and a second peak envelope centred at 1039.59 *m/z*, which corresponds to $[HRu_6C(CO)_{15}]^-$. The high-resolution spectrum confirms that the latter peak is produced by loss of two CO ligands and HCHO and *not* the loss of one CO ligand and the -COOMe moiety. The spectrum of **2** exhibits an intact parent ion, $[Rh_6(CO)_{15}(COOMe)]^-$, observed at 1096.45 *m/z*, followed by a second high intensity peak at 870.35 *m/z*, which corresponds to $[HRh_6(CO)_9]^-$. This peak arises from loss of seven CO ligands and then HCHO from the parent ion.

Compound **3a** is quite stable and we have isolated $[PPN][Ru_6C(CO)_{16}(COOMe)]$ and established its solid-state structure (see Figure 7 for the structure of the anion);[15] the structure of **2** is known.[9]

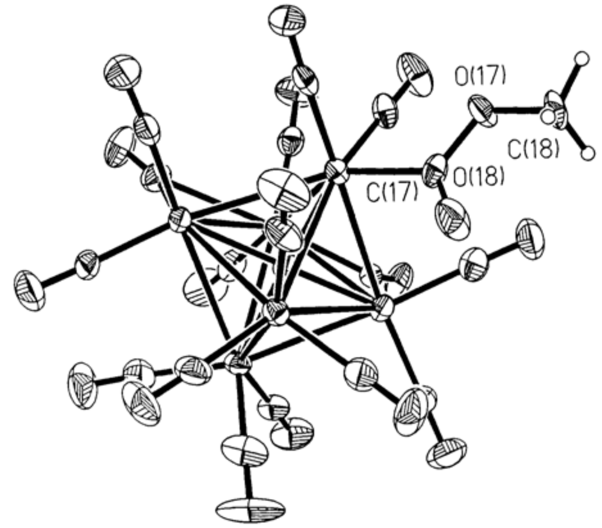


Figure 7 The molecular structure of the anion $[Ru_6C(CO)_{16}(COOMe)]^-$ **3a**.

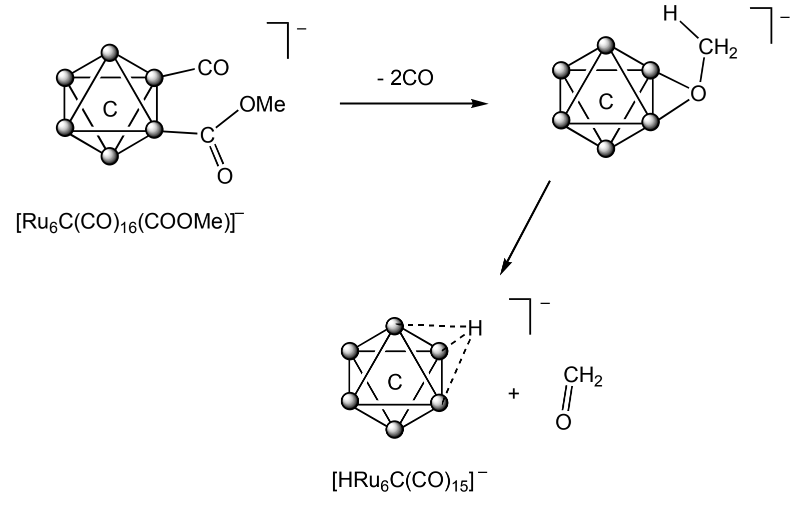
The phosphine-substituted derivative of **3a**, $[Ru_6C(CO)_{15}(PPh_3)(COOMe)]^-$ (**4**) was prepared by treatment of $[Ru_6C(CO)_{16}(PPh_3)]$ with sodium methoxide. The EDESI mass spectra of **4** is shown in Figure 8.

Figure 8

The spectrum of **4** is very similar to that of **3a**. The PPh_3 ligand is clearly lost first, as shown by the large space between cross peaks in the EDESI map, followed by a single CO ligand then prompt loss of HCHO. The remainder of the pattern involves straightforward CO stripping, from $[HRu_6C(CO)_{15}]^-$ down to the $[HRu_6C]^-$ core, as for **3a**.

While caution must be applied to any direct comparisons between fragmentation patterns observed in the gas phase and chemical properties observed in solution, in this case there is an obvious correlation. The early loss of formaldehyde from **3a** (and **4**) compared to **2** during the fragmentation process equates to the differences in chemical reduction of the two clusters. Treatment of $Ru_6C(CO)_{17}$ with methanolic KOH provides $[Ru_6C(CO)_{16}]^{2-}$ cleanly [19] whereas reduction of $Rh_6(CO)_{16}$ requires stronger reducing agents such as Na/Hg to produce the dianion. The hexaruthenium dianion $[Ru_6C(CO)_{16}]^{2-}$ is a widely used precursor in cluster chemistry [20] and the mechanism of its formation presumably commences similarly to the reaction with NaOMe. Treatment of $[Ru_6C(CO)_{17}]$ with OH^- quantitatively yields $[Ru_6C(CO)_{16}]^{2-}$.[12c] Based on the EDESI data, we would also expect that treating $[Ru_6C(CO)_{16}(PPh_3)]$ with OH^- should yield $[Ru_6C(CO)_{15}(PPh_3)]^{2-}$, and preliminary synthetic results show that this seems to be the case (though some $[Ru_6C(CO)_{16}]^{2-}$ is also formed).

It is reasonable to assume that the -COOMe group rearranges to form a relatively strong multicentre bonding interaction, probably driven, in the first instance, by the loss of a CO ligand (Scheme 1). Formation of an -OMe ligand is likely to be the step prior to elimination of formaldehyde, and as already mentioned, the cluster anion $[HRu_3Ir(CO)_{12}(OMe)]^-$ is known to eliminate HCHO under carbonyl loss conditions (prolonged heating) to generate the cluster anion $[H_2Ru_3Ir(CO)_{12}]^-$. The hydride ligand is likely to be abstracted from the cluster by OH^- (this step, of course, is not observed in the mass spectrometer). The resulting cluster will be short of one CO ligand, but as two have been lost, there will be plenty of CO present in solution for the unsaturated cluster to pick up.



Scheme 1

This HCHO elimination mechanism is different from one proposed earlier for the reduction of $Ru_6C(CO)_{17}$, involving nucleophilic addition of OH^- to a CO ligand to form a –COOH intermediate, followed by expulsion of CO_2 and then removal of H^+ by OH^- to form $[Ru_6C(CO)_{16}]^{2-}$.[21] Further experiments are in progress to confirm the mechanism.

Acknowledgements

We would like to thank the Royal Society for a University Research Fellowship (P.J.D.). Thanks also to Paul Skelton for collecting the FTICR data.

Figure Captions

1. Negative-ion ESI mass spectra of $[Ir_4(CO)_{11}(COOMe)]^-$ (**1**), showing the effect of the cone voltage setting on the fragmentation patterns; (a) 25 V, (b) 75 V; (c) 150 V.
2. The two-dimensional EDESI-MS map generated from 201 negative-ion ESI-MS spectra of $[Ir_4(CO)_{11}(COOMe)]^-$ (**1**) at cone voltage settings of 0 - 200 V. The top trace is a 1D spectrum generated by combining all 201 spectra together.
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7. The molecular structure of the anion $[Ru_6C(CO)_{16}(COOMe)]^-$ **3a**.
8. The negative-ion EDESI mass spectrum of $[Ru_6C(CO)_{15}(PPh_3)(COOMe)]^-$ **4**.

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