

Insights into the elimination of HCHO from the clusters $[\text{M}_n(\text{CO})_m(\text{COOMe})]^-$ ($\text{M}_n = \text{Ru}_6\text{C}$, $m = 16$; $\text{M}_n = \text{Rh}_6$, $m = 15$) provided by electrospray mass spectrometry †

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Loss of formaldehyde in the electrospray ionisation fragmentation process of methoxylated hexanuclear carbonyl clusters can be correlated to their macroscopic chemical properties.

Nucleophilic attack of alkoxide ions, RO^- , at electropositive C-atoms in transition metal carbonyl complexes, $\text{M}_n(\text{CO})_m$, generates anionic species of the type $[\text{M}_n(\text{CO})_{m-1}(\text{COOR})]^-$. The reaction has been widely studied in transition metal carbonyl cluster compounds, and a number of the products crystallographically characterised.¹ Alkoxylation is fast, the product thermodynamically favoured,² and multiple additions of alkoxide ions do not occur, even in the presence of a large excess of the RO^- ion. These properties lend themselves to the *in situ* derivatisation of neutral metal carbonyl complexes for analysis by electrospray mass spectrometry, by simple alkoxylation of the compound prior to injection of the sample as an alcoholic solution.³ Charged organometallic species are readily analysed by electrospray mass spectrometry,⁴ and typically a single envelope of peaks corresponding to $[\text{M}_n(\text{CO})_m + \text{OR}]^-$ is observed in the mass spectrum. We report herein that in the energy-dependent electrospray ionisation (EDES) mass spectra⁵ of hexanuclear ruthenium and rhodium clusters derivatised with H_3CO^- , loss of HCHO takes place during fragmentation processes; differences in fragmentation patterns between the two clusters are correlated to their macroscopic chemical properties. Confirmation of peak assignments was carried out using a Fourier transform ion cyclotron resonance (FTICR) instrument.

The negative-ion EDES mass spectrum of $[\text{Ru}_6\text{C}(\text{CO})_{16}(\text{COOMe})]^-$ (**1a**) (Fig. 1) maps the cone voltage against m/z .⁶ As the cone voltage is increased, collision-induced dissociation (CID) causes progressive fragmentation, resulting in sequential loss of ligands from the cluster core. This process is represented using EDES-MS in two ways: (i) in the mass spectrum generated by summing all the mass spectra obtained at all cone voltages (top); and (ii) in the two-dimensional map where each cross-peak depicts a particular ion, the intensity and height of which is dependent on its relative stability. EDES-MS therefore offers a way to view a vast amount of mass spectrometric data (some 200 spectra) in a convenient, compact format. At the lowest cone voltages, the only peak observed is that of the intact parent ion, $[\text{Ru}_6\text{C}(\text{CO})_{16}(\text{COOMe})]^-$. Upon increasing the fragmentation energy, two CO ligands are lost, and the ions $[\text{Ru}_6\text{C}(\text{CO})_{16}(\text{COOMe}) - x\text{CO}]^-$ ($x = 1, 2$) appear in the

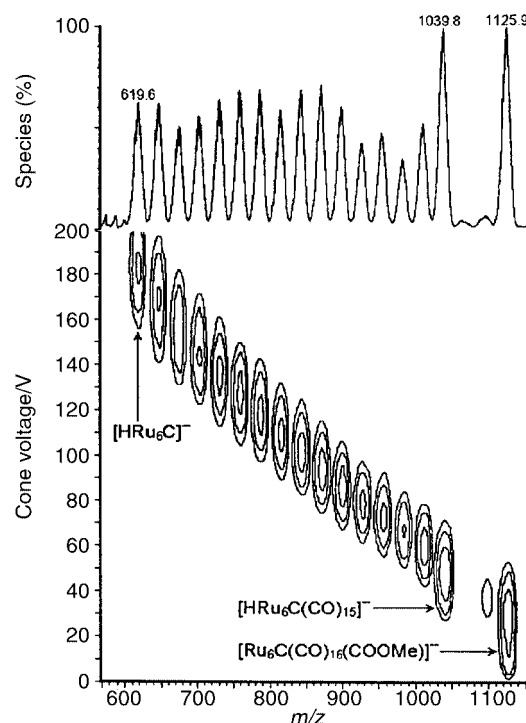


Fig. 1 The negative-ion EDES mass spectrum of $[\text{Ru}_6\text{C}(\text{CO})_{16}(\text{COOMe})]^-$ **1a**.

EDES-MS map at very low intensity. The structure of these ions is not clear because the CO ligands may be lost either from the cluster shell or from the COOMe ligand. The third group to be lost is an HCHO molecule rather than a CO ligand, to generate the hydride cluster $[\text{HRu}_6\text{C}(\text{CO})_{15}]^-$. The remaining fifteen cross peaks correspond to the series $[\text{HRu}_6\text{C}(\text{CO})_x]^-$ ($x = 0-14$), and have roughly equal intensity leading ultimately to $[\text{HRu}_6\text{C}]^-$. The closely related anion $[\text{Ru}_6\text{C}(\text{CO})_{16}(\text{COOEt})]^-$ (**1b**) undergoes an analogous fragmentation sequence, except MeCHO is eliminated, instead of HCHO. As expected, $[\text{Ru}_6\text{C}(\text{CO})_{16}(\text{COOPh})]^-$ (**1c**) does not display similar behaviour, as the phenyl ring prevents formation of an exocyclic C=O bond. The CO ligands are progressively stripped in this case, with complex fragmentation occurring at the highest cone voltages (see supporting information).

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

† Electronic supplementary information (ESI) available: the negative-ion EDES mass spectra of compounds **1a**, **1b** and **1c**. See <http://www.rsc.org/suppdata/dt/b0/b002978p/>

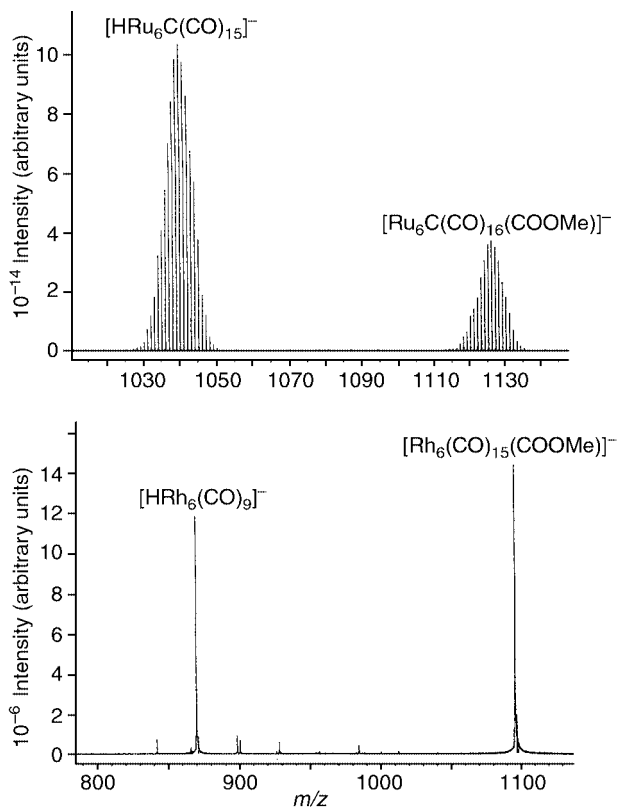
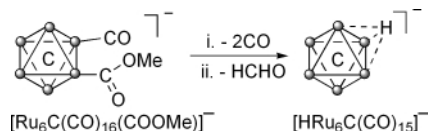


Fig. 2 The negative-ion ESI-FTICR mass spectra of $[\text{Ru}_6\text{C}(\text{CO})_{16}(\text{COOMe})]^-$ **1a** (top) and $[\text{Rh}_6(\text{CO})_{15}(\text{COOMe})]^-$ **2a** (bottom).

CO ligand. Formation of an OMe ligand may be the step prior to elimination of formaldehyde, as the cluster anion $[\text{HRu}_3\text{Ir}(\text{CO})_{12}(\text{OMe})]^-$ is known to eliminate HCHO under carbonyl loss conditions (prolonged heating) to generate the cluster anion $[\text{H}_2\text{Ru}_3\text{Ir}(\text{CO})_{12}]^-$.⁷ This HCHO elimination mechanism is different from one proposed earlier for the reduction of $\text{Ru}_6\text{C}(\text{CO})_{17}$, 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 $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$.⁸

A hydride ligand remains associated with the cluster after the loss of formaldehyde (see Scheme 1), and the ion $[\text{HRu}_6\text{C}(\text{CO})_{15}]^-$



Scheme 1 The elimination of two moles of CO and one of HCHO from **1a** to provide the hydrido cluster $[\text{HRu}_6\text{C}(\text{CO})_{15}]^-$.

$(\text{CO})_{15}]^-$ shows particular stability as represented by its high intensity in the EDESI spectrum. This unsaturated anionic cluster has been claimed to have been isolated and structurally characterised,⁹ from the high-pressure hydrogenation of $[\text{Ru}_6\text{C}(\text{CO})_{16}(\text{Me})]^-$.¹⁰

Fig. 2 shows the ESI-FTICR mass spectra¹¹ of **1a** and $[\text{Rh}_6(\text{CO})_{15}(\text{COOMe})]^-$ (**2a**), derived from the appropriate homoleptic carbonyl cluster by addition of a methanolic solution of sodium methoxide. Two sets of peaks are observed in the spectrum of **1a**; the envelope of peaks centred at 1125.64 m/z (calc. 1125.81) corresponding to the intact species, followed by a clean baseline that leads to a second peak envelope centred at 1039.59 m/z (calc. 1039.77), which corresponds to $[\text{HRu}_6\text{C}(\text{CO})_{15}]^-$. 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 ($\Delta_{\text{obs:calc}} = 0.18 \text{ Da}$). The spectrum of **2a** exhibits an intact parent ion, $[\text{Rh}_6(\text{CO})_{15}(\text{COOMe})]^-$, observed at 1096.45 m/z (calc. 1096.63) followed by another high intensity peak at 870.35 m/z (calc. 870.53), which corresponds to $[\text{HRh}_6(\text{CO})_9]^-$.

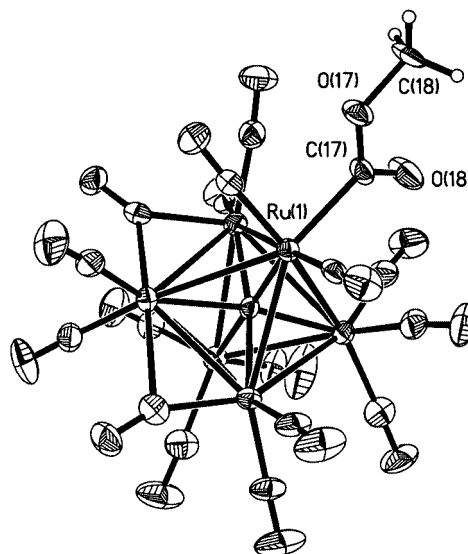


Fig. 3 The molecular structure of the anion $[\text{Ru}_6\text{C}(\text{CO})_{16}(\text{COOMe})]^-$ **1a**. Selected bond lengths (Å) and angles ($^\circ$) include; Ru1–C17 2.079(6), C17–O18 1.209(6), C17–O17 1.356(7), C18–O17 1.461(6); Ru1–C17–O18 125.7(5), Ru1–C17–O17 115.0(4), C17–O17–C18 115.9(5), O17–C17–O18 119.3(5).

This peak arises from loss of seven CO ligands and then HCHO from the parent.

The EDESI mass spectrum of **2a** confirms that loss of HCHO occurs after that of seven carbonyl groups.⁵ 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 **1a** compared to **2a** during the fragmentation process equates to the differences in chemical reduction of the two clusters. Treatment of $\text{Ru}_6\text{C}(\text{CO})_{17}$ with methanolic KOH provides $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ cleanly¹² whereas reduction of $\text{Rh}_6(\text{CO})_{16}$ requires stronger reducing agents such as Na/Hg to produce the corresponding dianion. The hexaruthenium dianion $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ is a widely used precursor in cluster chemistry¹³ and the mechanism of its formation presumably commences similarly to the reaction with NaOMe. Treatment of **1a** with OH^- quantitatively yields $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$.^{12c}

Compound **1a** is quite stable and we have isolated $[\text{N}(\text{PPh}_3)_2][\text{Ru}_6\text{C}(\text{CO})_{16}(\text{COOMe})]^{14}$ and established its solid-state structure (see Fig. 3 for the structure of the anion);¹⁵ the structure of **2a** is known.¹⁴ The structure of **1a** is based on a carbide atom centred octahedral core of ruthenium atoms decorated with fourteen terminal and two bridging carbonyl ligands and one COOMe group. Ru–Ru bond lengths lie in the range $2.8068\text{--}3.1354 \text{ \AA}$ (mean 2.9098 \AA).

Experiments are in progress to confirm the mechanism of formaldehyde elimination and to see whether related systems display the same behaviour.

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- 10 Given the reaction conditions, it is possible that the compound is actually the electron-precise cluster $[\text{H}_3\text{Ru}_6\text{C}(\text{CO})_{15}]^-$. The fact that the metal hydride signal in the ^1H NMR spectrum splits into two singlets in a 2:1 ratio at low temperature indicates that $[\text{H}_3\text{Ru}_6\text{C}(\text{CO})_{15}]^-$ is a more likely candidate than the unprecedented unsaturated cluster $[\text{HRu}_6\text{C}(\text{CO})_{15}]^-$.
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- 14 To a dichloromethane (5 mL) solution of $\text{Ru}_6\text{C}(\text{CO})_{17}$ (30 mg, 0.027 mmol) was added a methanolic solution of sodium methoxide (0.037 M, 0.75 mL, 0.028 mmol), followed by a solution of bis-(triphenylphosphino)imidium chloride in dichloromethane (20 mg, 0.034 mmol, in 2 mL CH_2Cl_2). The solution was left overnight. The deep-red product $[\text{N}(\text{PPh}_3)_2][\text{Ru}_6\text{C}(\text{CO})_{16}(\text{COOMe})]$ was crystallised by layering hexane on the CH_2Cl_2 solution at 4 °C (35 mg, 0.021 mmol, 76%). IR (CH_2Cl_2): $\nu(\text{CO}) = 2070\text{w}, 2025(\text{sh}), 2019\text{vs}, 1965\text{w}, 1812\text{vw cm}^{-1}$.
- 15 Crystal data for $\text{C}_{55}\text{H}_{33}\text{NO}_{18}\text{P}_2\text{Ru}_6$ **1a**: $M = 1664.18$, monoclinic, $a = 37.43090(10)$, $b = 9.2751(2)$, $c = 33.8359(11)$ Å, $\beta = 103.9600(10)^\circ$, $U = 11400.0(4)$ Å³, $T = 180(2)$ K, space group $C2/c$, $Z = 8$, $\lambda(\text{Mo-K}) = 0.71070$ Å, $\mu = 1.678$ mm⁻¹, 21175 reflections collected, 9566 unique ($R_{\text{int}} = 0.0523$) which were used in all calculations. The final $wR(F^2)$ was 0.0898 (all data). Single crystals of $[\text{N}(\text{PPh}_3)_2][\text{Ru}_6\text{C}(\text{CO})_{16}(\text{COOMe})]$ were crystallised from hexane/dichloromethane, mounted in inert oil and transferred to the cold gas stream of the diffractometer. The structure was solved using direct methods and refined by full-matrix least-squares on F^2 . CCDC reference number 186/1986. See <http://www.rsc.org/suppdata/dt/b0/b002978p/> for crystallographic files in .cif format.