

# Energy-dependent electrospray ionisation mass spectrometry: applications in transition metal carbonyl chemistry

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**Maps of electrospray mass spectrometry data, plotted as cone voltage versus mass-to-charge ratio, provide a clear and compact method of visualising the accompanying fragmentation processes, in this case applied to the sequential removal of ligands from transition-metal carbonyl complexes. The technique is described as energy-dependent electrospray ionisation mass spectrometry (EDES-MS). Copyright © 2000 John Wiley & Sons, Ltd.**

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Electrospray ionisation mass spectrometry (ESI-MS) has become an important and powerful tool for the study of high molecular weight compounds.<sup>1</sup> Researchers in the fields of polymer chemistry and the biological sciences have particularly benefited from the development of this technique.<sup>2</sup> Inorganic<sup>3</sup> and organometallic<sup>4</sup> chemists have also, to a lesser extent, taken advantage of the technique, including using ESI-MS to study solution chemistry.<sup>5</sup> Moreover, the technique has become a useful characterisation tool for metal carbonyl compounds in its own right.<sup>6</sup>

ESI is a soft ionisation technique, which means that fragmentation of the target species is minimal and that the molecular weight of the parent ion(s) may be obtained easily. However, there are circumstances in which fragmentation, yielding useful structural information, is desired. Fragmentation may be induced very easily in ESI sources by increasing the voltage between the skimmer cones (referred to as the cone voltage), which increases the energy of ion-neutral collisions (the neutral species being the bath gas, typically nitrogen). This leads to collision-induced decomposition (CID). Such fragmentation can be quite selective, and enables the sequential stripping of ligands from transition-metal complexes.<sup>7</sup> The structure and properties of metal carbonyl clusters with incomplete ligand spheres have attracted some interest,<sup>8</sup> and in the course of related work on the generation of clusters and supraclusters by laser desorption/ionisation mass spectrometry (LDI-MS),<sup>9</sup> we have observed many species of this type. In recent work (as yet unpublished) we have used LDI-MS for the characterisation of high nuclearity osmium carbonyl cluster anions, as well as for studies of the ligand loss processes. ESI-MS provides a complementary means of studying such species, but a considerable amount of fragmentation data is produced that can be difficult to visualise.

## EXPERIMENTAL

ESI mass spectra were collected using a Micromass Quattro LC instrument in negative-ion mode, with methanol as the mobile phase. The nebuliser tip was at 3100 V and 90 °C, and nitrogen was used as the bath gas. Samples were introduced directly into the source at 4  $\mu\text{L min}^{-1}$  via a syringe pump. Data collection was carried out in continuum mode with the cone voltage initially set at 0 V. A scan time of 10 s per spectrum and a low resolution setting (peak width at half-height  $\sim 0.8$  Da) was used to maximise the signal-to-noise ratio. The cone voltage was manually 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 35 min to collect. High resolution (peak-width at half-height  $\sim 0.3$  Da) spectra were also recorded at cone voltages of 25, 75 and 150 V.

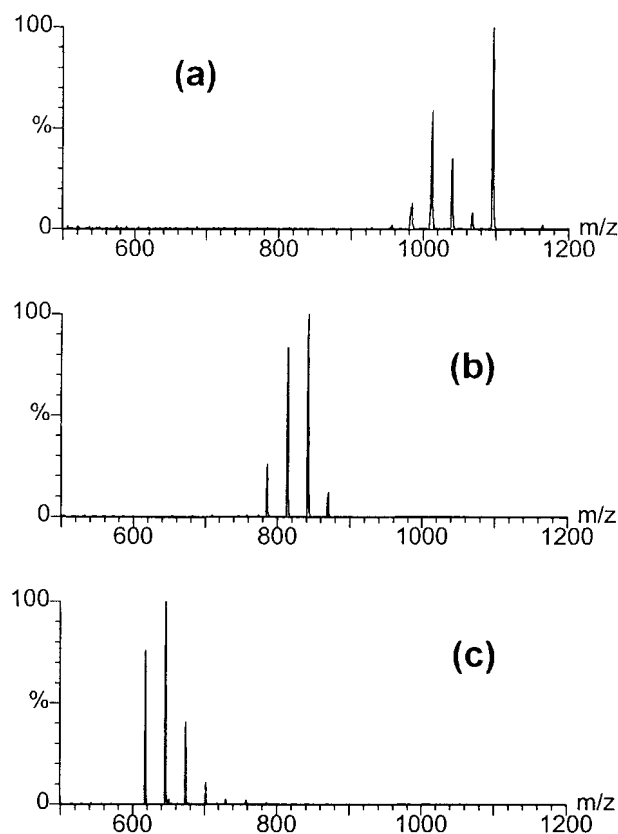
## RESULTS AND DISCUSSION

Figures 1(a)–(c) show negative-ion ESI mass spectra of methoxide-derivatised  $\text{Rh}_6(\text{CO})_{16}$  recorded at cone voltage settings of 25, 75 and 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. In this communication we wish to report a new method for visualising the fragmentation processes that can be observed in ESI mass spectra through use of a ‘two-dimensional’ format. The method involves collecting mass spectra across a range of cone voltages and combining the data into a map, with mass-to-charge ratio on the horizontal axis and cone voltage on the vertical axis. The ‘map’ function on the MassLynx<sup>®</sup> software, designed for use with liquid chromatography/mass spectrometry (LC/MS), was adapted for this purpose. The axis labelling has been changed from retention time to cone voltage. Representation of 201 spectra ( $\sim 15$  MB of data) as a map results in a 300-fold decrease in storage demands. In the map, all the daughter ions generated from successive fragmentation of the parent ion(s) may be observed simultaneously, thereby providing a clear and

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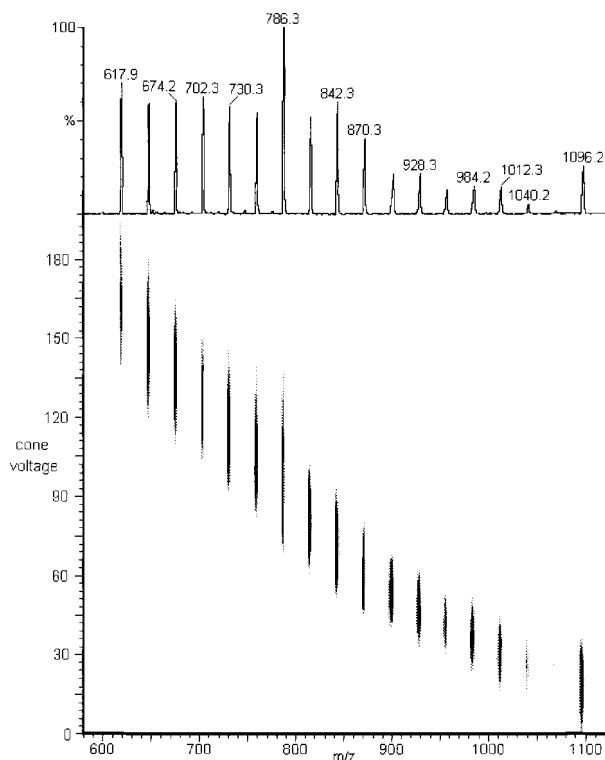
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**Figure 1.** Negative-ion ESI mass spectra of  $[\text{Rh}_6(\text{CO})_{16}]$  run in MeOH with added NaOMe, showing the effect of the cone voltage setting on the fragmentation patterns (a) 25 V, (b) 75 V, (c) 150 V.

compact overall picture of the dominant fragment ions. Combining the spectra that generate the map into a single, 1D spectrum provides an instant comparison between the relative intensities of all the ions across the full cone voltage range. By presenting this 1D spectrum aligned with the 2D spectrum, practically all of the information contained in the contributing spectra can be represented in a single image. The name 'energy-dependent electrospray ionisation mass spectrometry' (EDESI-MS) has been suggested for this method of presenting the data set.

An example of such a composite 1D/2D EDESI-MS diagram is shown for the hexanuclear rhodium complex  $[\text{Rh}_6(\text{CO})_{16} + \text{OMe}]^-$  in Fig. 2.  $\text{Rh}_6(\text{CO})_{16}$  was chemically derivatised with methoxide ion and a 2D fragmentation study carried out immediately. The sequential loss of all 16 CO ligands and the OMe ligand was observed upon increasing the cone voltage setting. It seems probable that the OMe ligand migrates to the metal core soon after the loss of one or two CO ligands, as it is otherwise difficult to rationalise the tenacity of the  $-\text{COOMe}$  ligand, which is likely to be less strongly bound to the metal than a CO ligand (experiments are underway to confirm this hypothesis). In the case of this rhodium complex the OMe ligand is eliminated after the dissociation of seven CO ligands. A loss of 29.9 Da is observed between the peak at  $m/z$  900.2  $[\text{Rh}_6(\text{CO})_9 + \text{OMe}]^-$  and the one at  $m/z$  870.3  $[\text{Rh}_6(\text{CO})_9 + \text{H}]^-$ , representing a loss of  $\text{H}_2\text{CO}$  and leaving the negative charge on the cluster. At very high cone voltages the remaining carbonyl ligands are stripped leaving the metal core naked save for a hydride ligand,  $[\text{Rh}_6 + \text{H}]^-$ . This behaviour is different from that observed for the



**Figure 2.** Two-dimensional EDESI-MS map generated from 201 negative-ion mass spectra of  $[\text{Rh}_6(\text{CO})_{16} + \text{OMe}]^-$  at cone voltage settings of 0–200 V. The top trace is a 1D spectrum generated by combining all 201 spectra together.

trinuclear osmium complex  $[\text{Os}_3(\text{CO})_{12} + \text{OMe}]^-$ , in which the OMe ligand does not dissociate at all, even in the absence of all the CO ligands. In this case the lowest mass ion observed corresponds to  $[\text{Os}_3 + \text{OMe}]^{-6b}$

In conclusion, we have described a means of viewing ESI-MS fragmentation data in an informative and compact fashion. The method is well suited to the analysis of mixtures of compounds, as the fragments from each component are more obviously separated than in conventional 1D ESI mass spectra. We expect this aspect of the technique to be especially useful in the same way that two-dimensional NMR is particularly effective in deconvoluting signals from a mixture of compounds. While collection of the data is not automated, we would expect that inclusion of this capability on future versions of mass spectrometric software is desirable and certainly would not be a difficult programming task. Furthermore, we hope to extend the use of the technique to matrix-assisted laser desorption/ionisation (MALDI) data where the laser power would take the place of the cone voltage in EDESI mass spectrometry.

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