

# Laser Desorption Ionization *Versus* Electrospray Ionization Mass Spectrometry: Applications in the Analysis of Cluster Anions

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*Received May 5, 2000*

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Mass spectra of transition metal carbonyl cluster anions were recorded using laser desorption ionization time-of-flight (LDI-TOF) and electrospray ionization (ESI) techniques. The LDI spectra generally contain peaks corresponding the intact cluster together with extensive CO loss fragments ions whereas the ESI spectra exhibit peaks corresponding the intact cluster together with few (if any) CO loss fragment ions. The parameters of both techniques can be modified to vary the extent of fragmentation. In all cases no fragmentation of the metal core is observed. Overall, ESI is a more informative method for the analysis of these types of cluster anions.

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**KEY WORDS:** Mass spectrometry laser desorption ionization; electrospray ionization; transition metal clusters.

## INTRODUCTION

The growth of cluster chemistry in the latter part of the 20th century was largely fueled by corresponding developments in analytical and spectroscopic methods, which now allow complicated molecules to be rapidly characterised. While X-ray crystallography is still regarded as the ultimate characterization technique in molecular cluster chemistry, other methods

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are beginning to close the gap. For example, the last few years has witnessed a surge in so-called "soft" ionization mass spectrometry techniques in cluster chemistry [1] that have been used routinely in other areas of chemistry for some time [2]. The two ionization methods now available in most research laboratories are laser desorption ionization (LDI) and electrospray ionization (ESI). LDI [3] and ESI [4] of neutral transition metal clusters is not a routine technique. With the LDI method extensive reactions take place inside the instrument. The first reaction path involves extensive carbonyl stripping which is not in itself unexpected. However, the coordinatively unsaturated species generated go on to react to afford higher nuclearity clusters, which leads to complicated spectra that require extensive analysis. Similar gas phase reactions leading to extensive cluster aggregation products have also been observed using  $^{252}\text{Cf}$  plasma desorption [5] and electron impact Fourier-transform ion cyclotron resonance mass spectrometry [6]. Conversely, the electrospray source does not induce ionization of the substrate and as such, the clusters must be chemically ionised prior immediately prior to analysis. Several successful methods have been employed thus far including use of methoxide and Group 1 metal ions, the specific merits and limitations of these methods being described elsewhere [4a].

In this paper we compare the usefulness of LDI and ESI for the analysis of anionic transition metal carbonyl clusters. The different information that can be obtained by these respective techniques is assessed as is their reliability.

## RESULTS AND DISCUSSION

### Laser Desorption Ionization

The negative ion LDI mass spectra of the cluster anions  $[\text{Ru}_3\text{Co}(\text{CO})_{13}]^-$ ,  $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ ,  $[\text{HRu}_6(\text{CO})_{18}]^-$ ,  $[\text{Ru}_5\text{CoC}(\text{CO})_{16}]^-$ ,  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ ,  $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$  and  $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$  afford spectra that are reasonably straightforward to interpret compared to those obtained using the same technique for neutral compounds [3]. The spectrum of  $[\text{Ru}_5\text{CoC}(\text{CO})_{16}]^-$  is shown in Fig. 1 as an illustrative example and peak assignments are listed in Table I. The peaks correspond to sequential carbonyl ligand loss (spaced approximately  $m/z$  28 apart) commencing with the intact parent ion at  $m/z$  1025 to the ion in which ten carbonyls remain attached to the  $\text{Ru}_5\text{CoC}$  core, *viz.*  $[\text{Ru}_5\text{CoC}(\text{CO})_{10}]^-$ , at  $m/z$  857. The relative intensity of CO loss peaks does not follow an obvious pattern. The highest intensity peak does not correspond to the parent ion but to the species  $[\text{Ru}_5\text{CoC}(\text{CO})_{15}]^-$  at  $m/z$  997 in which a

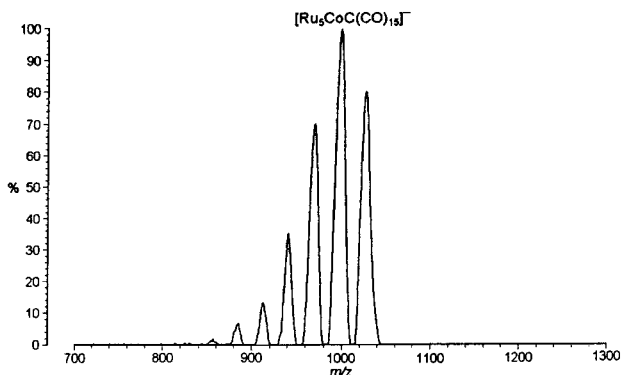


Fig. 1. The negative-ion LDI-TOF mass spectrum from [PPN][Ru<sub>5</sub>CoC(CO)<sub>16</sub>].

carbonyl ligand has been lost. The LDI spectra of the trinuclear clusters [M<sub>3</sub>(CO)<sub>12</sub>] (M = Ru or Os) reported previously [3b] show peaks corresponding to [M<sub>3</sub>(CO)<sub>n</sub>]<sup>-</sup> (n = 0–11). The peak corresponding to [M<sub>3</sub>(CO)<sub>6</sub>]<sup>-</sup> is particularly intense indicating special stability. Density functional calculations have been used to rationalize the electronic structure of this unusually stable highly decarbonylated anion. However, [Ru<sub>5</sub>CoC(CO)<sub>14</sub>]<sup>-</sup> nor any of the other high nuclearity clusters described herein have been, as yet, treated in this way.

The LDI mass spectrum of the tetranuclear cluster [Ru<sub>3</sub>Co(CO)<sub>13</sub>]<sup>-</sup> displays an intact parent ion at *m/z* 728 and a series of CO loss fragment ions [Ru<sub>3</sub>Co(CO)<sub>n</sub>]<sup>-</sup> (n = 6–12). The most intense ion is the fragment [Ru<sub>3</sub>Co(CO)<sub>11</sub>]<sup>-</sup> at *m/z* 672, corresponding to the loss of two CO ligands. A similar pattern is observed for the osmium cluster [H<sub>3</sub>Os<sub>4</sub>(CO)<sub>12</sub>]<sup>-</sup>, though in this case the loss of CO ligands is quite limited. The parent ion is observed at *m/z* 1101 as well as the fragment ions [H<sub>3</sub>Os<sub>4</sub>(CO)<sub>n</sub>]<sup>-</sup> (n = 8–11). However, the most intense peak corresponds to the ion [H<sub>3</sub>Os<sub>4</sub>(CO)<sub>11</sub>]<sup>-</sup> at *m/z* 1073 in which only one CO ligand has been lost.

The LDI mass spectrum of the monoanion [HRu<sub>6</sub>(CO)<sub>18</sub>]<sup>-</sup> is qualitatively similar to that [Ru<sub>5</sub>CoC(CO)<sub>14</sub>]<sup>-</sup>. The most important difference is that the intact parent ion is not observed and the highest mass peak corresponds to the ion [HRu<sub>6</sub>(CO)<sub>17</sub>]<sup>-</sup> at *m/z* 1083. In addition, more extensive carbonyl loss takes place with carbonyl stripping down to *m/z* 775 which corresponds to [HRu<sub>6</sub>(CO)<sub>6</sub>]<sup>-</sup>. The most intense peak at *m/z* 942 corresponds to [HRu<sub>6</sub>(CO)<sub>12</sub>]<sup>-</sup>. The absence of the parent ion [HRu<sub>6</sub>(CO)<sub>18</sub>]<sup>-</sup>, expected at *m/z* 1113 is possibly due to the fact that rearrangement of the cluster to an electron precise bicapped tetrahedral geometry is possible, resulting in facile loss of the first CO ligand. Clearly,

Table I. Peak Relative Intensities in the LDI Mass Spectra

	$[\text{Ru}_3\text{Co}(\text{CO})_{13}]^-$	$[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$	$[\text{HRu}_6(\text{CO})_{18}]^-$	$[\text{Ru}_5\text{CoC}(\text{CO})_{16}]^-$	$[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$	$[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$	$[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$
$[\text{M}]^-$	11	70	—	80	100	100	8
$[\text{M-CO}]^-$	54	100	3	100	80	14	9
$[\text{M-2CO}]^-$	100	35	54	70	31	41	13
$[\text{M-3CO}]^-$	35	5	54	36	10	9	18
$[\text{M-4CO}]^-$	22	6	25	14	9	53	22
$[\text{M-5CO}]^-$	9	—	10	7	8	25	31
$[\text{M-6CO}]^-$	3	—	100	2	7	68	68
$[\text{M-7CO}]^-$	3	—	41	—	6	2	100
$[\text{M-8CO}]^-$	—	—	10	—	5	1	87
$[\text{M-9CO}]^-$	—	—	9	—	4	—	72
$[\text{M-10CO}]^-$	—	—	7	—	3	—	67
$[\text{M-11CO}]^-$	—	—	4	—	2	—	50
$[\text{M-12CO}]^-$	—	—	13	—	2	—	36
$[\text{M-13CO}]^-$	—	—	—	—	2	—	24
$[\text{M-14CO}]^-$	—	—	—	—	—	—	18
$[\text{M-15CO}]^-$	—	—	—	—	—	—	13
$[\text{M-16CO}]^-$	—	—	—	—	—	—	7
$[\text{M-17CO}]^-$	—	—	—	—	—	—	3

a similar rearrangement cannot take place with  $[\text{Ru}_5\text{CoC}(\text{CO})_{16}]^-$  by virtue of the interstitial carbide atom.

The most noteworthy feature in the LDI spectrum of the dianions  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ ,  $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$  and  $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$  is that no peaks with a 2- charge are observed. All the peaks are due to mono-anionic species. This behaviour is not unexpected as electron loss from the cluster is an entirely expected reaction in the ion plume during ablation by the laser, and in our previous LDI studies of clusters [3] we have only observed singly charged ions. For clusters such as these it is possible to ascertain the charge using appropriate electron counting techniques [7], for example, an octahedral cluster requires 86 cve's and  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^-$  has only 85 cve's. Bearing in mind that multiple charges on clusters are *always* oxidised to monoanions by the LDI method it is not unreasonable to assume that the actual structural formula is  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ . However, this simple manipulation becomes less certain as the nuclearity of the clusters increases as the electron counting rules often break down.

The  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^-$  parent ion at  $m/z$  1068 is also the most intense signal in the spectrum. The fragment ions diminish in intensity and the last CO loss peak of significant intensity corresponds to  $[\text{Ru}_6\text{C}(\text{CO})_3]^-$  at  $m/z$  704. In contrast to this pattern, the CO loss peaks for  $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$  vary considerably (Fig. 2). Peak envelopes are observed for the ions  $[\text{Re}_8\text{C}(\text{CO})_n]^-$  ( $n = 16-23$ ), and while the parent ion  $[\text{Re}_8\text{C}(\text{CO})_{24}]^-$  at  $m/z$  2174 has the highest intensity, the fragment ions  $[\text{Re}_8\text{C}(\text{CO})_n]^-$  ( $n = 22, 20, \text{ and } 18$ ) also show strong peak intensity.

The LDI mass spectrum of  $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$  was reported previously [8] and data was acquired using various laser powers. The highest mass peak at  $m/z$  2588 corresponds to  $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^-$ , and the peaks at

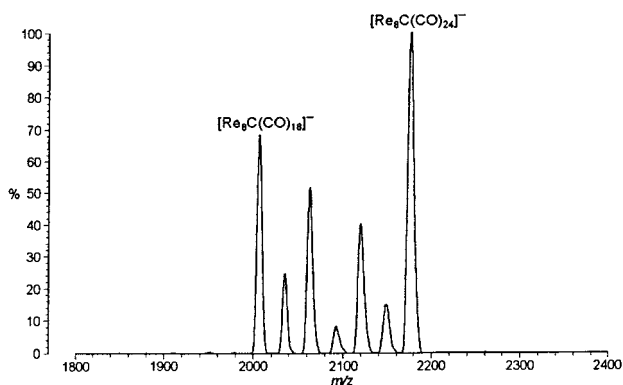


Fig. 2. The negative-ion LDI-TOF mass spectrum of  $[\text{PPN}]_2[\text{Re}_8\text{C}(\text{CO})_{24}]$ .

lower mass to the ions  $[\text{Os}_{10}\text{C}(\text{CO})_n]^-$  ( $n = 5-23$ ). Higher laser power caused further CO stripping to give eventually the naked metal core,  $[\text{Os}_{10}\text{C}]^-$ , whereas lower laser power brought about an increase in the abundance of the molecular ion although CO loss fragments are always observed, even at threshold laser power.

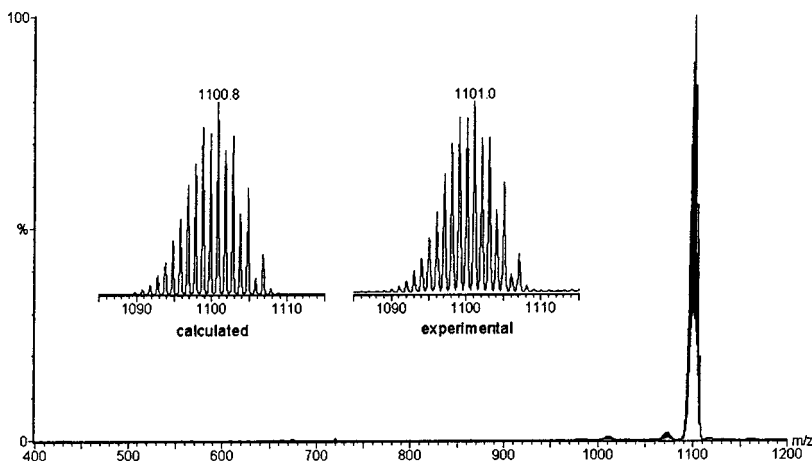
Matrix assisted LDI (*viz.* MALDI) is a far more common method used to analyse other types of compounds, especially biomolecules [2b]. The sample is dissolved (or diluted) in a matrix, and the matrix absorbs most of the energy from the laser, some of which is then transferred to the sample. We have examined the use of several organic matrices and ultrafine cobalt powder [9], but with limited success. Diluting the neutral cluster  $\text{Ru}_3(\text{CO})_{12}$  in a dithranol matrix reduces the amount of gas phase reaction products that are observed in the spectrum. Other matrices simply reduce the signal-to-noise ratio without significantly affecting the product ion distribution.

The absence of higher nuclearity clusters in the LDI mass spectra of anionic clusters contrasts sharply with the situation for similar neutral clusters, the spectra of which are dominated by high-mass cluster aggregates. The reason for this absence is almost certainly the fact that the gas-phase reactivity of like-charged clusters is negligible due to charge repulsion. In the case of the supraclustering of neutral clusters, this observation suggests that all gas-phase reactivity is represented by ion/neutral, positive-ion/negative-ion, or neutral/neutral reactions.

## Electrospray Ionization

Generally, electrospray ionization mass spectra of anionic cluster compounds consist of a single isotope envelope corresponding to the parent ion, and an advantage of ESI over LDI is that the original charge state is preserved. For example, ESI mass spectrometry was used to establish the molecular weight of  $[\text{Os}_{20}(\text{CO})_{40}]^{2-}$ , which affords an intact parent ion for this cluster in which there are no fragments produced [8]. Other compounds formulated as  $[\text{Os}_{20}(\text{CO})_{40}]^{3-}$  and  $[\text{Os}_{19}(\text{CO})_{39}]^{2-}$  that were previously unobserved by other techniques were also identified, illustrating the usefulness of this technique for cluster anions.

The ESI mass spectra of the polynuclear anions  $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ ,  $[\text{Ru}_3\text{Co}(\text{CO})_{13}]^-$ ,  $[\text{Ru}_5\text{CoC}(\text{CO})_{16}]^-$ ,  $[\text{HRu}_6(\text{CO})_{18}]^-$  and  $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$  have been recorded in a methanol or acetone mobile phase;  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$  and  $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$  have been reported previously [4a]. In each case, a single envelope of peaks matching exactly both the  $m/z$  value and predicted isotopic pattern of the cluster in question was observed. An example is shown in Fig. 3 for the cluster  $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ ,



**Fig. 3.** The negative-ion ESI mass spectrum of  $[\text{PPN}][\text{H}_3\text{Os}_4(\text{CO})_{12}]$ , using methanol as the mobile phase. The inset shows the excellent comparison between calculated and experimental isotope patterns.

which displays the near absence of fragmentation and good signal to noise ratio characteristic of the ESI spectra of anionic clusters.

Structural information can be obtained from ESI by fragmenting the ions before mass analysis by the use of collision-activated dissociation (CAD). Such fragmentation is most conveniently induced by means of increasing the voltage at the skimmer cone (the cone voltage) [10]. Generally, in the study of transition-metal cluster compounds, CAD causes progressive stripping of the CO ligands down to the metal core without the metal core itself breaking up [4b]. Such compounds have also been studied using the recently developed technique of energy-dependent ESI mass spectrometry (EDES), which presents the complete fragmentation pattern as a two-dimensional map [11]. In addition to the structural information provided, mechanistic information can also be extracted from these maps. An example of this is the EDES study of the cluster  $[\text{Ru}_6\text{C}(\text{CO})_{17}(\text{COOMe})]^-$ , which in addition to CO loss also loses formaldehyde early in the fragmentation process, a feature which provided insight into the reduction of  $\text{Ru}_6\text{C}(\text{CO})_{17}$  by  $\text{KOH}/\text{MeOH}$  [12].

An example of the EDES-MS technique is shown in Fig. 4 for the anionic hydrido cluster  $[\text{HRu}_6(\text{CO})_{18}]^-$ . Each cross-peak on the map corresponds to an individual ion. The parent ion  $[\text{HRu}_6(\text{CO})_{18}]^-$ , 1111.4  $m/z$ , appears in the bottom right-hand corner of the map, and as the cone voltage is increased (moving up the  $y$  axis), the greater fragmentation energy causes stripping of the CO ligands. The protonated metal core

$[\text{HRu}_6]^-$  at 607.7  $m/z$  is the only ion present at the highest cone voltage, and no sign of core fragmentation is observed. The ions  $[\text{HRu}_6(\text{CO})_n]^-$  ( $n=0-18$ ) appear with varying intensity. Especially notable is the low intensity of the  $[\text{HRu}_6(\text{CO})_{13}]^-$  ion, which displays a weak and short-lived crosspeak, in contrast to the strong signal for the  $[\text{HRu}_6(\text{CO})_{12}]^-$  ion. This pattern duplicates that seen in the LDI spectrum of the same compound, so given the very different fragmentation processes of the two ionization techniques, it seems likely that the  $[\text{HRu}_6(\text{CO})_{12}]^-$  ion is fundamentally more stable than the  $[\text{HRu}_6(\text{CO})_{13}]^-$  ion. It is tempting to attribute the extra stability to the fact that the  $[\text{HRu}_6(\text{CO})_{12}]^-$  possesses an even two CO ligands per ruthenium atom and this high symmetry explains the high intensity of the peak in the mass spectra. In any event, detailed interpretation of the EDESI fragmentation pattern is not a trivial

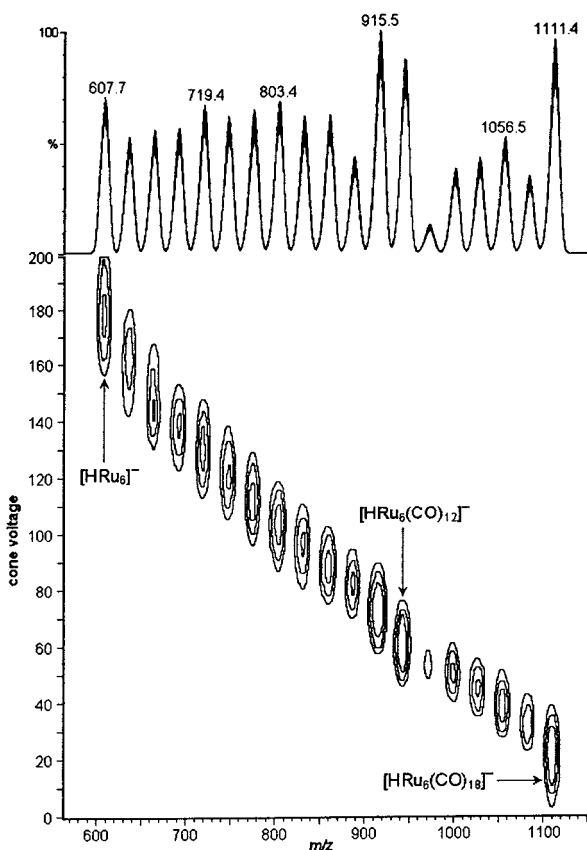


Fig. 4. The negative-ion EDESI map from  $[\text{PPN}][\text{HRu}_6(\text{CO})_{18}]$ .



exercise and provides more information than required for a simple structural characterization.

## Concluding Remarks

LDI of cluster ions affords spectra that contain the parent ion (in most cases) together with extensive CO loss fragments. The extent of CO loss fragments depends somewhat upon the laser power but even at threshold power some fragmentation occurs. Neither fragmentation of the metal core nor clustering of the core is observed (whereas neutral clusters undergo extensive cluster aggregation reactions). Furthermore, only monoanionic species are observed even when multiply charged clusters are examined.

ESI mass spectrometry of cluster anions affords strong, clean spectra dominated almost exclusively by  $[M]^-$ . Structural information can be obtained by inducing fragmentation by collision-activated dissociation, and in the case of energy-dependent ESI, this information can be extremely detailed.

Overall, ESI is a more reliable method for the analysis of these types of cluster anions than LDI, providing molecular weight information and preserving the charge. The structural information provided by the fragmentation induced by the laser desorption process in LDI can be reproduced using ESI by means of collision-activated dissociation, and a more detailed information on the fragmentation process can be obtained by means of energy-dependent ESI.

## EXPERIMENTAL

### Sample Preparation

The clusters  $[PPN][HRu_6(CO)_{18}]$  [13],  $[PPN][Ru_6C(CO)_{16}]$  [14],  $[PPN]_2[Os_{10}C(CO)_{24}]$  [15],  $[PPN][H_3Os_4(CO)_{12}]$  [16],  $[PPN][Ru_3Co(CO)_{13}]$  [17] and the complex  $[PPN][Co(CO)_4]$  [18] were prepared according to literature procedures. The heteronuclear cluster  $[PPN][Ru_5CoC(CO)_{16}]$  is new and was prepared as follows. A thf (10 ml) solution of  $[PPN][Co(CO)_4]$  (38 mg, 0.053 mmol) was added to a thf (20 ml) solution of  $Ru_5C(CO)_{15}$  (50 mg, 0.053 mmol) and then refluxed for 3 h. The solution was cooled to room temperature, filtered and solvent removed in vacuo to leave a wine-red product  $[PPN][Ru_5CoC(CO)_{16}]$  (80 mg, 97%). IR ( $CH_2Cl_2$ ):  $\nu(CO)$  2053w, 2019vs, 1995sh, 1827vw  $cm^{-1}$ . The cluster  $[PPN]_2[Re_8C(CO)_{24}]$  is a known compound [19] but was made by a new route. The cluster  $[H_3Re_3(CO)_9(MeCN)_3]$  [20] (100 mg, 0.11 mmol) was vacuum pyrolysed for 24 h at 200°C. The

ampoule was opened and the contents extracted with acetone (3–10 ml). The solution was filtered and [PPN]Cl added (63 mg, 0.11 mmol). The product was precipitated with hexane and recrystallised from acetone/ethanol to provide red crystals of [PPN]<sub>2</sub>[Re<sub>8</sub>C(CO)<sub>24</sub>] (96 mg, 40%). IR (thf):  $\nu(\text{CO})$  2010sh, 2004s, 1950w, 1930m, 1890w  $\text{cm}^{-1}$ .

### Mass Spectrometric Analysis

LDI-TOF mass spectra were obtained using a Kratos Kompact MALDI-4 instrument in linear mode or a TOFSpec2E instrument in reflectron mode. Dilute dichloromethane solutions of the clusters were evaporated directly on to the sample slide (no matrix was used). The laser power was typically modulated to maximise the signal to noise ratio. In all cases the instruments were run in negative-ion mode.

ESI and EDESI mass spectra were collected using a Micromass Quattro LC instrument in negative-ion mode, with acetone or 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 to the source at 4  $\mu\text{l min}^{-1}$  via a syringe pump. The cone voltage was set at 15 V to minimise fragmentation for the ESI spectra, and ramped from 0 to 200 V for the EDESI spectrum.

### ACKNOWLEDGMENTS

We would like to thank the Royal Society for a University Research Fellowship (P.J.D.), the EPSRC and ICI for financial support (A.K.H.) and the New Zealand Foundation for Research, Science and Technology for a Postdoctoral Fellowship (J.S.M., contract CAM801).

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