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Analysis of organometallic compounds using ion trap mass spectrometry

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Abstract

Ion traps are an increasingly common presence as mass analysers in commercial bench-top mass spectrometers. Such instruments, usually interfaced with electrospray ionisation or nanospray sources, are invariably aimed at organic and biological applications, such as in the analysis of proteins, pharmaceuticals, organics, biomarkers, metabolites, etc. However, the abilities of ion trap mass spectrometers (extraordinary sensitivity, good resolution, MS^n for structural information) can be profitably employed in the analysis of inorganic and organometallic compounds. We highlight these abilities, identify various problems and suggest the areas that will perhaps benefit most from employment of ion trap instruments.

Keywords: Mass spectrometry; Electrospray ionisation; Ion trap; Organometallic compounds; Clusters; Ionic clusters

1. Introduction

The development of powerful new mass spectrometric techniques such as matrix-assisted laser desorption ionisation (MALDI) [1] and electrospray ionisation (ESI) [2] has been driven by the polymer and biological sciences. Workers in other areas, for whom conventional techniques are less useful, such as inorganic and organometallic chemistry, are now embracing these ionisation methods. LDI mass spectrometry is ideally suited to non-volatile substances and has been used to study many inorganic and organometallic compounds. It has been found that gas-phase ion-molecule reactions often occur, resulting in cluster formation, which makes determination of the molecular mass difficult. Metal oxides, phosphides, chalcogenides and carbonyls all result in aggregation products which often have higher relative intensities than the parent ions [3]. LDI mass spectra of anionic clusters [4] or molecular compounds with good chromophores are such as porphyrin complexes [5] contain strong molecular ion peaks, although aggregation products are still sometimes observed.

ESI mass spectrometry is used to study compounds in solution and has become the most effective method for determining the molecular weight of inorganic and organometallic compounds [6]. ESI instruments with Fourier transform ion cyclotron resonance (FT-ICR) cells [7] and quadrupole ion traps [8] have also been used to analyse inorganic and organometallic compounds previously. Despite the increasing use of ESI mass spectrometry for these types of compounds, not all compounds are amenable to the method and in some cases, notably neutral organometallics, derivatisation reagents are required which adds to the complexity of the experiment [9]. Other compounds such as unstable inorganic and organometallic compounds or supramolecular species are less easily studied using ESI mass spectrometry as the temperature of the source (typically set at 100 °C or above) induces fragmentation or decomposition. Coldspray ionisation (CSI), which involves an electrospray ionisation probe with a drying gas cooling device that maintains a temperature below −20 °C, and the source and desolvation chamber are maintained at a low temperature, typically in the range

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−50 to 15 °C, has been developed to overcome such problems. CSI has been effectively applied to the analysis of short-lived intermediates [10] and supramolecular architectures [11]. CSI necessitates modification of commercial instruments, and while very effective, it can be off-putting to the synthetic chemist.

In this paper, we show how inorganic and organometallic compounds are most effectively analysed using ion trap mass spectrometers without the need to modify the instrument. We show how the temperature is critical to the analysis and how other features of these instruments, especially the various collision-induced dissociation (CID) parameters, can be optimised for the study of inorganic and organometallic compounds. In addition, dilution protocols are used to facilitate the analysis of unstable compounds.

2. Results and discussion

With standard ESI mass spectrometers, the in-source parameter that is most critical influencing the extent of fragmentation of the analyte is the voltage applied at the skimmer cone (the point at which the largely desolvated ions enter the mass spectrometer). For ESI-ion trap instruments, the temperature of the capillary used to transport the ions from the skimmer cone into the multipole region may be altered anywhere from around room temperature, typically 30 °C is the lowest accessible (as the capillary is located inside a warm instrument) to 400 °C. Heating the capillary has the effect of desolvating the ions and so the spectra are not complicated by the appearance of adducts, i.e. $[M]^{x+/-}$ is the major peak rather than $[M+n(\text{solvent})]^{x+/-}$. This feature is crucial for highly polar analytes, such as proteins or peptides, which readily associate with solvent molecules. However, electronically saturated organometallic complexes usually interact only weakly with solvent molecules, and in our experiments no evidence was found for solvent adducts, even at the most ambient temperature accessible. Higher temperatures confer no discernible advantages in terms of signal intensity, but do have a profound influence on the spectra recorded. At temperatures above 100 °C, increased fragmentation takes place, invariably through loss of one or more neutral ligands. This phenomenon complicates the spectra as well as spreading the ion intensity across several signals, diminishing the signal-to-noise ratio and the overall sensitivity. As CID can be easily induced inside the ion trap itself (see below), minimisation of in-source fragmentation is highly desirable.

The effect of temperature on the spectra of $Ru_6C(CO)_{17}$ in MeOH and derivatised with sodium methoxide is illustrated in Fig. 1, in a depiction best described as temperature-dependent electrospray ionisation mass spectrometry (TDESI-MS), by way of analogy with our previously published energy-dependent technique, EDESI [12], which is not only helpful for routine analysis, but can also highlight the presence of compound mixtures [13] and reveal energetically favoured structural rearrangements [14]. The example shown in Fig. 1, a transition metal carbonyl cluster, was chosen due to the high number of neutral ligands that may potentially be lost from the metal core.

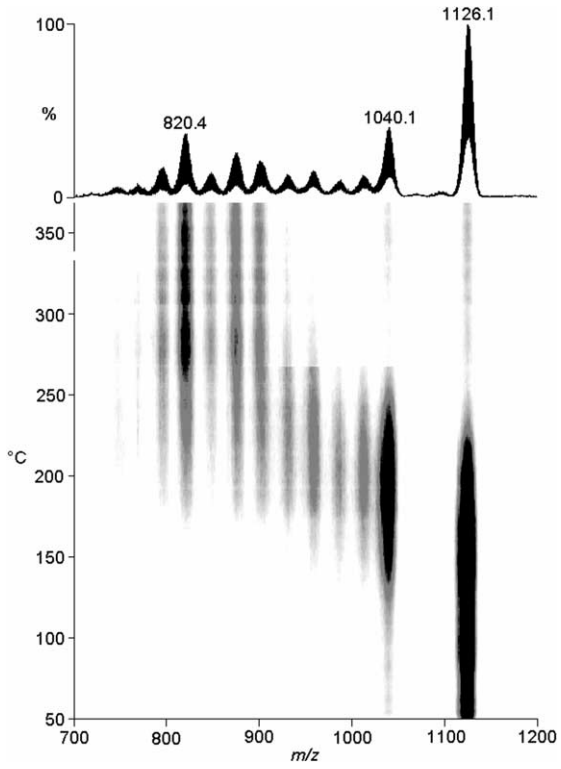

Fig. 1. The negative-ion TDESI mass spectrum of $[Ru_6C(CO)_{16}(COOMe)]^-$ (derived from the reaction of $Ru_6C(CO)_{17}+MeO^-$) in methanol.

The figure is essentially an intensity map, a two-dimensional projection of a 3D surface, with the third dimension, ion intensity, represented by a greyscale, black being the most intense. The x-axis is the m/z ratio, and the spectrum at the top of the map is a summation of all spectra collected. The y-axis is simply the capillary temperature (°C). At the lowest temperature, 50 °C, the parent ion dominates the spectrum and fragmentation is limited to a small loss of a single CO ligand. Increasing the temperature of the capillary from 50 to 100 °C changes the spectra only slightly. However, above 150 °C the intensity of the molecular ion starts to diminish in favour of the fragment ions $[HRu_6C(CO)_n]^-$ ($n=6$–15). Early loss of formaldehyde in the fragmentation pathway of this cluster has been previously observed in the EDESI mass spectrum [15], and the results here for the TDESI spectrum are similar. Both variables (cone voltage in EDESI and capillary

temperature in TDESI) cause CID of ions, and so the similarity between the spectra is not unexpected.

It is worth noting that in order to obtain spectra at the very lowest temperatures, low boiling, volatile solvents must be used, as high boiling solvents may not completely desolvate under such ambient operating conditions.

At higher temperatures, there is no need for NaOMe and methoxylation takes place spontaneously in methanol, further indicating the problem of reactivity under more forcing conditions. In addition, the signal-to-noise decreases significantly and the quality of the spectrum is much better when recorded at lower temperature in the presence of the derivatising agent. Operation of the ESI process under such mild conditions is very rare, and as such, we have termed it ambient temperature ESI, or ATESI, in order to distinguish it from the conditions typical of ESI, and only possible with some instruments.

While capillary temperature had a marked effect on the spectra of transition metal carbonyl clusters, complexes with more strongly complexed ligands (especially multidentate ligands) were not significantly affected by increases in capillary temperature. A classic example of such a compound is the ruthenium complex $[Ru(dppe)(p\text{-cymene})Cl_2]^+$. Ligand loss requires removal of a bidentate (dppe), tridentate (*p*-cymene) or negatively charged ligand (chloride), none of which can be easily removed by CID. As such, increasing the capillary temperature from 40 to 400 °C has little effect on the spectrum (see top two spectra in Fig. 2).

The ineffectiveness of temperature to cause CID contrasts sharply in this case with the effect of CID in the ion trap, using the helium collision gas (see bottom spectrum in Fig. 2). The fragments observed are not due to simple ligand elimination, but rather through disintegration of the periphery of the ligands.

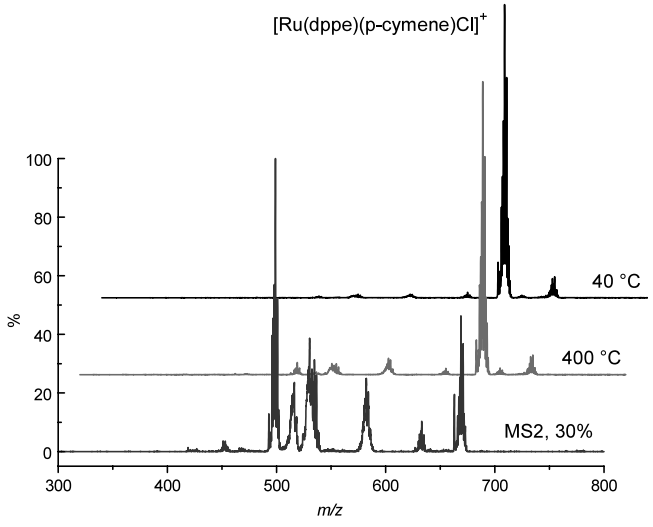

Fig. 2. Positive-ion ESI mass spectra of [Ru(dppe)(*p*-cymene)Cl]Cl at a capillary temperature of 40 °C (top) and 400 °C (middle); daughter ion spectrum after selection of the molecular ion (~ 669 Da) and fragmentation at 30% energy (bottom).

As mentioned above, the cone voltage represents another important in-source parameter which affects the quality of the mass spectrum. Much has already been published on the influence of the cone voltage on inorganic and organometallic analytes [16], but some further comments are worth making here, since these earlier observations were largely based on instruments without ion traps. The effect of in-source fragmentation from 0 to 100 V on the cluster anion $[CoRu_3(CO)_{13}]^-$ is shown in Fig. 3. Compared to other instruments, the in-source CID has limited efficacy and the fragmentation pattern becomes extremely complicated as the energy is increased.

Controlled fragmentation can be achieved using the ion trap to induce CID. The ion trap in this type of instrument differs from that in a Fourier-transform ion cyclotron resonance mass spectrometer in that selected ions are trapped for shorter periods and fragmentation is induced by collisions with helium gas. The velocity at which the trapped ions collide with the helium gas is varied and this gives rise to a relative scale of collision energy. For comparison with in-source CID, the $[CoRu_3(CO)_{13}]^-$ ion was selected in the ion trap and CID induced at several different relative energies. The resulting spectra are shown in Fig. 4, and while at low relative collision energies the spectra are quite clean, at higher energies fragmentation becomes quite indiscriminate.

Indiscriminate fragmentation and loss of signal intensity is apparent when performing MS^n (Fig. 5). Subsequent stages of tandem mass spectrometry in an ion trap are separated by time rather than space [17]. Essentially, the process involves selecting ions of a

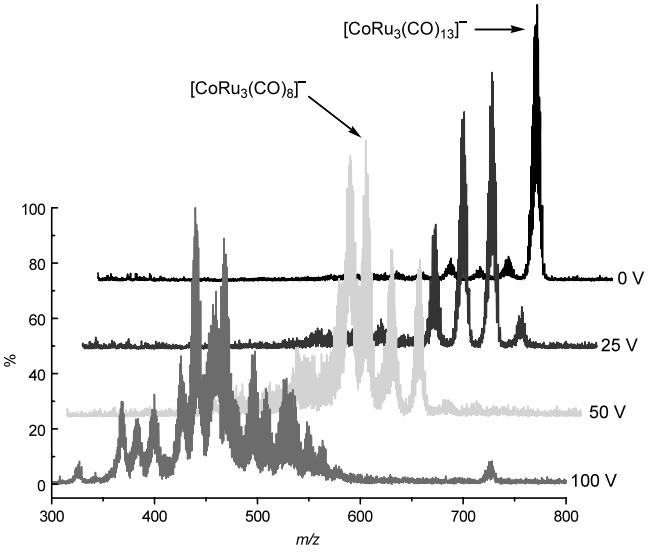

Fig. 3. The effect of cone voltage on CID in the source for the cluster anion $[CoRu_3(CO)_{13}]^-$.

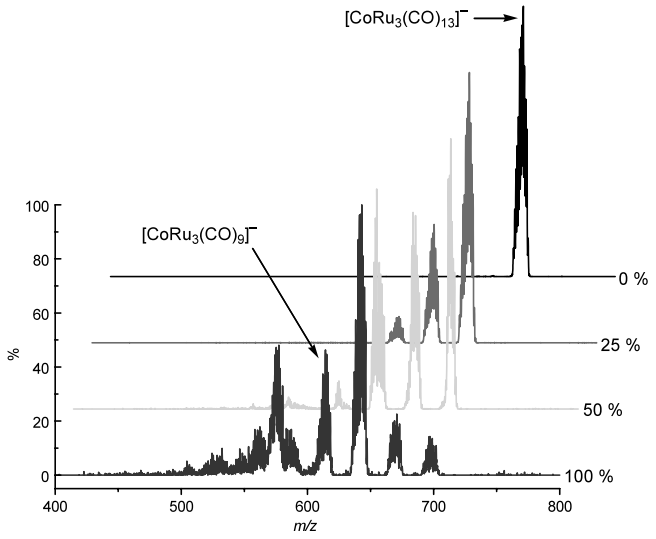

Fig. 4. The effect of collision energy on CID in the ion trap for the cluster anion $[CoRu_3(CO)_{13}]^-$.

certain m/z ratio by ejecting all others from the trap. The selected ions are excited and allowed to collide with the helium gas. At this stage, a spectrum may be collected or a fragment may be selected, allowed to fragment further (a process which may be repeated several times to generate MS^n spectra). While the instrument employed in this study can be used to perform 10 stages of MS (i.e. MS/MS/MS... up to MS^{10}), in practice we found that while first- and second-generation daughter ion spectra (MS^2 and MS^3) were of excellent quality, there was significant degradation of ion intensity by MS^4, and little useful information could be extracted.

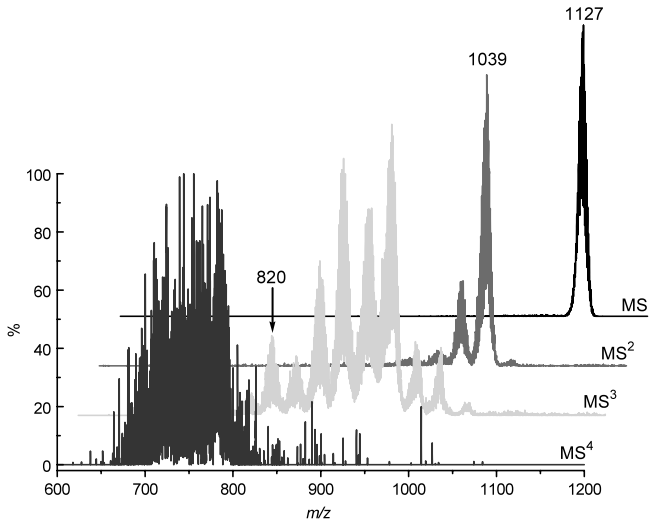

Fig. 5. ESI-MS^n spectra of $[Ru_6C(CO)_{17}]$ in MeOH/NaOMe solution. From the top: the standard MS spectrum carried out at low temperature (50 °C) with no in-source fragmentation; MS/MS spectrum, 50% collision energy on the peak at m/z 1127; MS^3 spectrum, with the m/z 1127 peak selected, fragmented at 50%, followed by selection of the m/z 1039 peak and further fragmentation at 50%; MS^4 spectrum, selection of the m/z 820 after MS^3 and further fragmentation at 50% collision energy.

The ion trap can also be used to improve the quality of the spectrum, providing high resolution, while simultaneously delineating the presence of highly unstable ions. Once the full-range spectrum has been used to identify peaks of interest, these peaks can be recollected using slower scans in a narrower range at higher resolution. Essentially, by increasing the time, at which ions of a particular mass spend in the ion trap, the resolution can be considerably improved as the relative energies of ions with the same m/z become closer in value. Fig. 6 shows the effect of collecting data around a window of interest while extending the time of the ions in the trap. The spectrum of the neutral compound $Ru(cymene)(pta)Cl_2$ in methanol in the presence of lithium ions was recorded in normal mode (top) in the m/z range 450–540. The pta ligand in $Ru(cymene)(pta)Cl_2$ contains basic nitrogen centres which readily associate with protons and metal cations allowing its facile ionisation. The dominant peaks comprise the complex with an associated lithium ion, $[M+Li]^+$ at m/z 470 and the complex with an associated lithium ion and methanol solvate, $[M+Li+MeOH]^+$ at m/z 502. In addition, two lower intensity peaks are present at m/z 488 and approximately 522, the former corresponds to the water adduct, $[M+Li+H_2O]^+$, since methanol used in the analysis was not dried, the latter peak cannot be assigned. By selecting a slower scanning mode (termed "zoomscan" on the instrument used) and prolonging the time the ions spend in the ion trap (by a factor of about 10), the spectrum at the bottom of Fig. 6 was obtained.

Only one dominant peak is present, corresponding to the $[M+Li]^+$ ion and the resolution is superior to that of the wide-band spectrum, viz. baseline resolution is obtained. The second lower intensity peak is unresolved and appears at a mass that prevents assignment. This unresolved peak arises because unstable ions formed in the instrument tend to show reduced resolution and also a slight shift in mass to lower values (0.1–0.2 amu). When the ions are scanned out of the trap, unstable species undergo CID by collisions with the helium in the trap. It should be noted that this phenomenon only occurs with very unstable ions, since the ion kinetic energy at this part of the scanning cycle is very low. If an ion undergoes CID while scanning it out, it will be ejected immediately (at slightly lower r.f. potential that the intact ion), and it will appear at slightly lower mass.

In addition, the sensitivity and resolution of the instrument can be enhanced by using the ion trap in the way described above. The sensitivity is perhaps best demonstrated by the ability of the instrument to provide molecular weight (and MS^n) information on complexes dissolved in ionic liquids at catalytic concentrations. Ionic liquids are currently undergoing extensive scrutiny as alternative solvents in which to conduct synthesis and

catalysis [18]. However, compared to catalysed reactions in conventional organic solvents, very few details regarding the active catalytic species that operate in ionic liquids are known as it is not an easy task identifying compounds present in low concentrations in such media. Since ionic liquids have essentially no vapour pressure, they have been used as matrices in MALDI mass spectrometry [19]. However, we have had little success determining the molecular weight of catalysts dissolved in ionic liquids by direct MALDI analysis. The main problem associated with the analysis of compounds in ionic liquids using ESI mass spectrometry is that the concentration of ions in the pure ionic liquids is typically 3–4 mol l^{-1}, vastly in excess of that required for ESI mass spectrometry, which routinely characterises analytes at picomolar levels or less, i.e. 9 orders of magnitude less concentrated. As such, it is crucial that the ionic liquid is diluted by a molecular solvent, but this necessarily lowers the concentration of the catalyst by a corresponding amount, and a balance has to be struck such that the catalyst is present at detectable levels but the ionic liquid is diluted sufficiently so that aggregation of the solvent ions, swamping of the compound of interest and saturation of the detector are not fatal to the experiment. A number of complexes immobilised in ionic liquids were analysed following dilution with methanol to concentrations of 10, 1, 0.1, 0.01 and 0.001 mmol l^{-1} [20]. The corresponding concentration of catalyst was 4 orders of magnitude lower in each case, i.e. 1000, 100, 10, 1 and 0.1 pmol l^{-1}. Despite the overwhelming dominance of ionic liquid species (the cation itself and aggregates of the cation with the anion), the presence of the catalyst can easily be detected and using the slow scan method described above high-resolution spectra of the compound of interest could be obtained following an initial wide-band experiment to pinpoint the analyte. For illustrative purposes, the spectrum of the cluster anion $[HOs_3W(CO)_{14}]^-$ in $[C_4mim][PF_6]$ (C_4mim = 1-butyl-3-methylimidazolium cation) diluted in methanol is shown in Fig. 7.

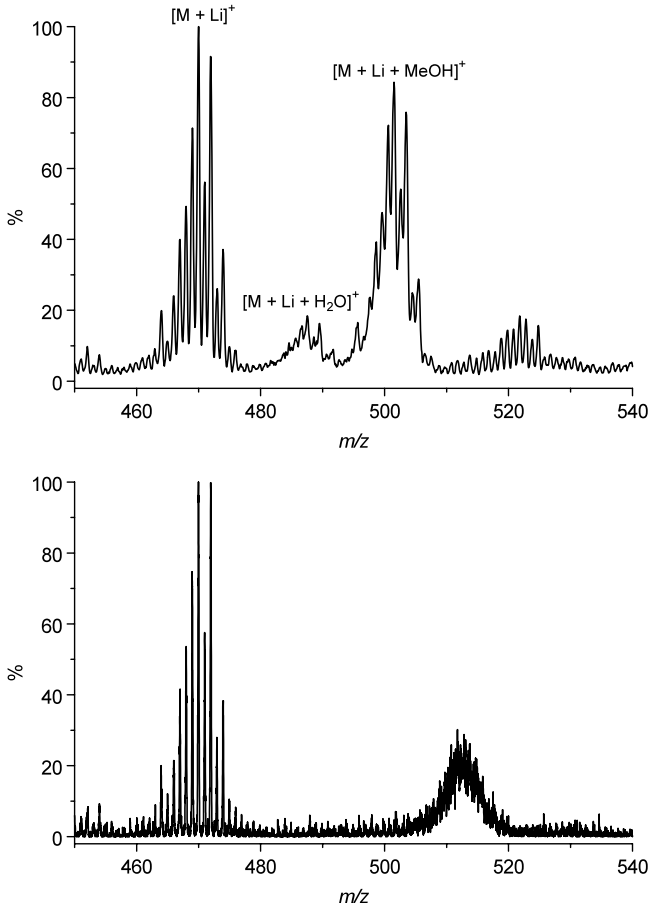

Fig. 6. Ru(cymene)(pta)Cl_2 in methanol in the presence of Li^+: (top) note the broader peaks for the weakly bound solvent adducts; (bottom) the resolution of the $[M+Li]^+$ peak has improved and the weakly bound solvent adducts have disappeared, to be replaced by an unresolved peak.

Even at such low concentrations, the compound is readily detected and any signals suspected as possible species of interest may be checked by using a slow scan across the specific area of interest. The ionic liquids $[C_4mim][BF_4]$, $[C_6mim][BF_4]$ and $[C_8mim][BF_4]$ were examined with essentially analogous results. Overlap of aggregates with signals of interest is extremely unlikely to occur in different ionic liquids, and so changing the counterion is a straightforward solution to suspected interference.

The neutral compound [Ru(cymene)(pta)Cl_2], a pre-catalyst in hydrogenation reactions [21], could also be analysed in the presence of a large excess of ionic liquid. The ion observed was $[M+C_4mim]^+$, the neutral catalyst having associated itself with the ionic liquid

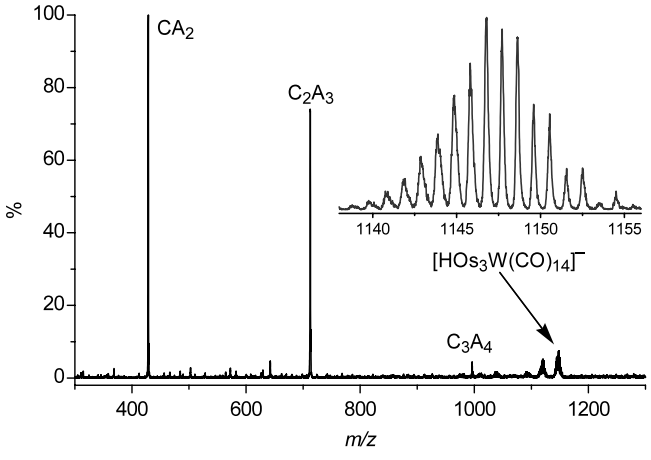

Fig. 7. The negative-ion ESI mass spectrum of $[HOs_3W(CO)_{14}]^-$ in the ionic liquid $[C_4mim][PF_6]$, diluted in methanol to a concentration of 1000 pmol l^{-1} in $[HOs_3W(CO)_{14}]^-$. C corresponds to the cation, A to the anion, and so C_2A_3 is the aggregated ion $\{[C_4mim]_2[PF_6]_3\}^-$. The indicated peak and enlarged isotope pattern correspond to $[HOs_3W(CO)_{14}]^-$.

cation. This phenomenon relies on the high basicity of the pta ligand mentioned above, resulting in an ionisation efficiency sufficiently high enough that the nominally neutral complex can be observed in the mass spectrum.

Another problem encountered in mass spectrometry is the analysis of air-sensitive compounds, due to decomposition in the highly dilute solutions they are general recorded from. A modification to the dilution method described above for ionic liquids can be used for the analysis of air-sensitive compounds. The procedure is ideally suited to studying compounds directly from reaction mixtures in that the sample containing the analyte(s) is injected into the instrument while simultaneously a second solvent is injected as a higher flow rate, which dilutes the analyte solution immediately before analysis. The instrument setup used for this experiment is shown in Fig. 8, although alternative methods, such as using a solvent diluting protocol from an HPLC instrument attached to the mass spectrometer, could also be used. For very air-sensitive materials, a separate syringe pump should be located within an inert atmosphere glovebox and the capillary piped through a wall to the external instrument. In this way, solvents and samples may be kept rigorously dry.

In conclusion, ESI-ion trap mass spectrometers, now widely available in many laboratories, have many features which make them ideally suited to the analysis of inorganic and organometallic compounds, including ones of low volatility, high molecular weight and compounds that are air-and moisture-sensitive. In order to optimise spectra to obtain molecular ion peaks without extensive fragmentation products, the operating temperature is critical, which in turn makes solvent selection very important. The ion trap cannot only be used in a conventional manner to gain structural information from controlled fragmentation studies, but it can also be used to improve signal-to-noise, resolution and to delineate unstable solvent adducts.

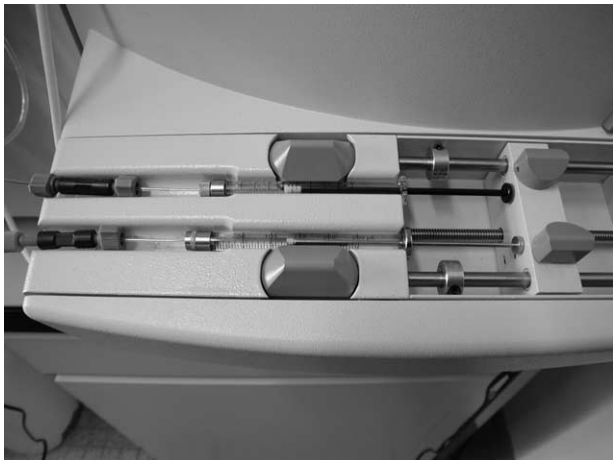

Fig. 8. Photograph showing the double injection system on the ThermoFinnigan LCQ™ DecaXP Plus quadrupole ion trap mass spectrometer which allows co-dilution of samples directly before the sample enters the instrument for analysis.

3. Experimental

The samples of $Ru_6C(CO)_{17}$ [22], [Ru(dppe)(*p*-cymene)Cl]Cl [23], [PPN][$CoRu_3(CO)_{13}$], [PPN][$HOs_3W(CO)_{14}$] [24] and Ru(cymene)(pta)Cl_2 [25] were prepared according to the literature methods. The ionic liquid [C_4mim][PF_6] (C_4mim = 1-butyl-3-methylimidazolium cation) was purchased from Merck.

Mass spectra were collected on a ThermoFinnigan LCQ™ DecaXP Plus quadrupole ion trap instrument. Samples were infused directly into the source at 5 μl min^{-1} using a syringe pump. The spray voltage was set at 5 kV and the capillary temperature at 50 °C, unless indicated otherwise. The MS detector was tuned automatically on the base peak, which optimised the remaining parameters.

Acknowledgements

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