

# The application of electrospray mass spectrometry to ionic inorganic and organometallic systems

Ray Colton and John C. Traeger\*

Department of Chemistry, La Trobe University, Bundoora, Vic. 3083 (Australia)

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## Abstract

Electrospray mass spectra have been observed for a number of ionic inorganic and organometallic compounds in dichloromethane/methanol (1:10) solutions. Intact principal ions were observed directly for  $[\text{PPh}_3\text{Bz}]^+$ ,  $\text{NBu}_4\text{PF}_6$  (positive and negative),  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+$  and *trans*- $[\text{Cr}(\text{CO})_2(\text{dpe})_2]^+$  ( $\text{dpe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ). The non-ionic compound  $\text{Re}(\text{CO})_2\text{Br}(\eta^1\text{-dpm})(\eta^2\text{-dpm})$  ( $\text{dpm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) was reacted with MeI to convert the pendant phosphorus to a phosphonium salt to give  $[\text{Re}(\text{CO})_2\text{Br}(\eta^1\text{-dpmMe})(\eta^2\text{-dpm})]\text{I}$  whose principal ion was observed. The heteropolymolybdate  $(\text{NEt}_4)_4[\text{S}_2\text{Mo}_{18}\text{O}_{62}]$  in acetonitrile solution gave the intact  $[\text{S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$  ion. These systems show that electrospray mass spectrometry has great promise for investigating ionic compounds, particularly those that are not amenable to mass spectrometric studies via other ionization techniques.

## Introduction

Electrospray mass spectrometry (ESMS) is a recently developed technique which has been widely used in the structural analysis of large biomolecules [1, 2]. The compound is dissolved in a suitable solvent, together with a small amount of organic acid to assist protonation, and then passed directly into the ion source. This ionization technique is very soft and causes minimal fragmentation.

Mass spectrometry of inorganic and organometallic compounds has usually involved volatilizing the species prior to forming ions in the gas phase, although assorted desorption techniques have also been used [3]. As a result, most studies have been done on non-ionic compounds, since ionic species are in general relatively involatile. Our approach has been to use ESMS to investigate solutions of inorganic and organometallic compounds which are already ionic and for which the protonation step is unnecessary. An earlier study by Chait and coworkers [4] showed that electrospray ionization could be used to generate intact principal ions for ruthenium(II) dipyrindyl complexes. In this paper we describe the ES mass spectra of a variety of systems in order to demonstrate the wide applicability of this technique which we believe will have a profound impact in inorganic and organometallic chemistry.

## Experimental

All spectra were obtained with a VG Bio-Q triple quadrupole electrospray mass spectrometer (VG BioTech, Altrincham, Cheshire, UK) using 0.2 mM solutions. Unless specified otherwise, the solvent was a 1:10 dichloromethane/methanol mixture which was delivered to the vaporization nozzle at a flow rate of  $2 \mu\text{l min}^{-1}$  by a Phoenix 20 micro LC syringe pump (Carlo Erba, Italy). Sample introduction was via a Rheodyne (Catali, CA) model 7125 injector with typical sample consumptions of 200 pmol.

## Results

### $[\text{PPh}_3\text{Bz}]\text{Cl}$

A solution of this simple phosphonium cation gives the  $\text{PPh}_3\text{Bz}^+$  ion as the base peak at  $m/z$  353 and additional small  $^{13}\text{C}$  isotope peaks of the expected intensities at  $m/z$  354 and 355. This spectrum alone is sufficient to demonstrate that ESMS will directly yield mass spectra of ionic compounds. Although Fenn *et al.* [1] have previously observed intact principal ions in the electrospray spectra for solutions of quaternary ammonium and phosphonium halides, we have obtained additionally MS/MS spectra by selecting parent ions with the first mass filter and optionally allowing them to collide with argon atoms in a collision cell before passing through a second mass analyzer. Without col-

\* Author to whom correspondence should be addressed.

lision gas,  $m/z$  353 parent ions metastably fragment to produce daughter ions at  $m/z$  262 ( $\text{PPh}_3^+$ ),  $m/z$  185 ( $\text{PPh}_2^+$ ) and  $m/z$  91 ( $\text{Bz}^+$ ) with relative intensities of 1 to 2%. When argon is introduced at a collision energy of 100 eV the spectrum also shows peaks at  $m/z$  183 and 108, with higher collision energies of 250 eV producing daughter ions at  $m/z$  152 and 65. These are due to further fragmentation of  $\text{PPh}_3^+$  and have been previously observed in the electron impact mass spectrum of  $\text{PPh}_3$  itself [5, 6]. Interestingly, we find no evidence for the ion  $\text{PPh}_2\text{Bz}^+$ , showing that the phosphorus benzyl linkage is much weaker than the phosphorus phenyl bond.

#### $\text{NBu}_4\text{PF}_6$

The base peak in the positive ion electrospray mass spectrum of a solution of  $\text{NBu}_4\text{PF}_6$  is the principal ion  $\text{NBu}_4^+$  at  $m/z$  242, with much weaker peaks being observed at  $m/z$  186, 184, 142 and 57; these fragment ions result from metastable decomposition of the parent ions as confirmed by the MS/MS spectrum in the absence of collision gas. Collisional activation at 250 eV produces further daughter ions of  $m/z$  100, 42, 41 and 29. The negative ion mass spectrum of the same solution essentially shows a single peak at  $m/z$  145, due to  $\text{PF}_6^-$ . This system illustrates that ESMS is applicable to both inorganic cations and anions and raises the possibility of studying halo anions of main group elements and the transition metals. This will be particularly useful for compounds for which multinuclear NMR is unavailable, either because of paramagnetism or absence of a suitable nucleus for the method.

#### $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+\text{BF}_4^-$

This example illustrates the ESMS of an organometallic compound. The ferrocenium cation was produced by oxidation of ferrocene with  $\text{NO}^+\text{BF}_4^-$  and its subsequent mass spectrum showed the  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+$  ion at  $m/z$  186 with other isotope peaks of the expected intensities at  $m/z$  187 and 184. The MS/MS spectrum at 200 eV of the  $m/z$  186 parent ion produced only two additional peaks, at  $m/z$  121 and 56, corresponding to the loss of one and both cyclopentadiene ligands, respectively. These two daughter ions are also the major fragmentation products observed in the electron impact mass spectrum of ferrocene.

#### $\text{trans-}[\text{Cr}(\text{CO})_2(\text{dpe})_2]\text{BF}_4$

This example demonstrates the application of the technique to carbonyl compounds of the transition metals. The cation  $\text{trans-}[\text{Cr}(\text{CO})_2(\text{dpe})_2]^+$  ( $\text{dpe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) has been well studied [7, 8] and is conveniently prepared by the oxidation of  $\text{cis-Cr}(\text{CO})_2(\text{dpe})_2$  by  $\text{NO}^+\text{BF}_4^-$  in dichloromethane. The positive ion mass spectrum shows a strong principal

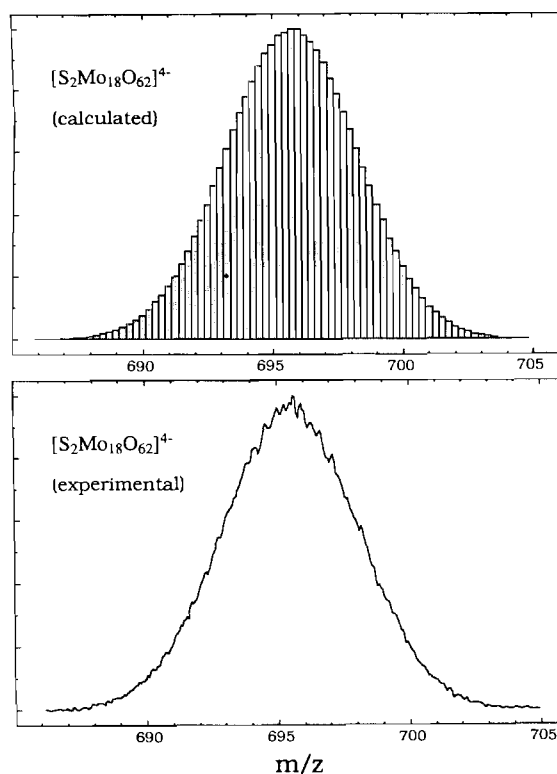


Fig. 1. Comparison of calculated and experimental mass spectral isotope pattern for  $[\text{S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$ .

ion peak at  $m/z$  904 (with accompanying isotope peaks), together with another peak at  $m/z$  848 which corresponds to the loss of both carbon monoxide ligands. The observation of the principal ion of this seventeen electron carbonyl cation, which in solution is labile and reactive, clearly illustrates the power of this technique.

#### $\text{cis/mer-}[\text{Re}(\text{CO})_2\text{Br}(\eta^1\text{-dpmMe})(\eta^2\text{-dpm})]\text{I}$

We have recently been investigating the chemical and electrochemical properties of  $\text{cis/mer-Re}(\text{CO})_2\text{Br}(\eta^1\text{-dpm})(\eta^2\text{-dpm})$  ( $\text{dpm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ). This species (prepared in the same manner as the chloro complex [9]) is of course non-ionic and is therefore not suitable for electrospray mass spectrometry. However, addition of methyl iodide converts the pendant phosphorus into a phosphonium salt to give  $[\text{Re}(\text{CO})_2\text{Br}(\eta^1\text{-dpmMe})(\eta^2\text{-dpm})\text{I}]$  without oxidation of the rhenium. IR spectroscopy and  $^{31}\text{P}$  NMR spectroscopy show that the rest of the molecule is unaffected by this reaction and the NMR spectrum confirms the methylation of the pendant phosphorus. The electrospray mass spectrum of this cation gives a strong peak at  $m/z$  1105 due to the  $[\text{Re}(\text{CO})_2\text{Br}(\eta^1\text{-dpmMe})(\eta^2\text{-dpm})]^+$  principal ion. Collisional activation of the  $m/z$  1105 ion at 200 eV produces only three daughter ions, none of which contains rhenium. The major fragmentation peak at  $m/z$  399 corresponds to  $\text{dpmMe}^+$ ,

as predicted by the NMR results. The process of methylating the pendant phosphorus to produce an ion is analogous to the technique of protonating proteins in order to obtain electrospray mass spectra from neutral compounds.

#### $(\text{NEt}_4)_4[\text{S}_2\text{Mo}_{18}\text{O}_{62}]$

This known [10] heteropolymolybdate was subjected to ESMS in acetonitrile solution. The negative ion mass spectrum shows only intact principal ions with an isotopic mass distribution covering a wide  $m/z$  range centred at 696. Figure 1 compares the experimental and expected mass distribution patterns for  $[\text{S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$ . This spectrum demonstrates that ESMS will provide valuable information on the nature of solutions of polyoxo anions of metals such as molybdenum, tungsten and the Group V metals, to complement that which is being derived from multinuclear magnetic resonance studies [11–13].

### Discussion

The examples cited in this paper serve to illustrate the wide applicability of ESMS in inorganic and organometallic chemistry. In all the cases we have examined so far, the species observed in the gas phase ES mass spectrum are the same as those determined to be present *in solution* by some other technique such as multinuclear magnetic resonance, electrochemistry or ESR spectroscopy. It is our view that ESMS will be applicable to most ionic inorganic and organometallic compounds, provided they are soluble and stable in a suitable solvent, and that it will prove to be an extremely powerful technique, particularly when used in conjunction with other methods such as NMR and electrochemistry. However, it may also be applicable to systems where the use of NMR methods is difficult or

impossible, such as rapidly exchanging systems, paramagnetic systems and those for which suitable NMR nuclei are not available.

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