Electrospray mass spectrometric analysis of neutral metal carbonyl complexes by derivatisation with alkoxide ions

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In situ **derivatisation of metal carbonyl complexes by OR^- in ROH solvents allows for their characterisation by electrospray mass spectrometry; clean $[M + OR]^-$ parent ions are observed from a wide range of mono- and poly-nuclear species.**

We have recently reported that electrospray mass spectrometry (ESMS) can be applied to the analysis of neutral metal carbonyls by ionisation with Ag^+ to allow detection of $[M + Ag]^+$ ions.[1] This extends the use of this technique[2] in organometallic chemistry† to non-polar, poorly basic carbonyl complexes. However the Ag^+ ion method appears to be only applicable to some multinuclear cluster carbonyls and, as an oxidizing species, can react with some low oxidation state complexes. Additionally its use is not completely predictable, *e.g.* $[Ru_6C(CO)_{14}(\mu_3\text{-}C_{16}H_{16})]$ (ref. 3) gives a clean $[M + Ag]^+$ adduct whereas the parent $[Ru_6C(CO)_{17}]$ (ref. 4) does not.[5]

We now report an alternative method for forming cleanly detectable ions from neutral metal carbonyls.

The negative-ion ESMS of $[Os_3(CO)_{12}]$ in MeOH containing NaOMe is shown in Fig. 1.‡ The upper trace, taken at low cone voltages, essentially contains one envelope, readily assignable to the ion $[Os_3(CO)_{12} + OMe]^-$ from a comparison of observed and calculated isotope patterns. The strong parent ion and lack of fragmentation is typical of mass spectra recorded using the gentle electrospray technique and contrasts with traditional electron impact (EI) or fast-atom bombardment (FAB) mass spectra where fragmentation by CO loss is normally extensive for metal carbonyl complexes. CO loss can be induced in ESMS by increasing the voltage between the skimmer cones, as illustrated in the lower traces in Fig. 1 which show that all the ions from $[Os_3(CO)_{12} + OMe]^-$ to $[Os_3 + OMe]^-$ can be detected under the appropriate conditions.

The method appears to be widely applicable. Correspondingly strong, clean $[M + OMe]^-$ parent ions were recorded under the same conditions for mononuclear $[W(CO)_6]$ or $[Mo(CO)_6]$, dinuclear $[Mn_2(CO)_{10}]$ or $[Re_2(CO)_{10}]$, trinuclear $[Ru_3(CO)_{12}]$, tetranuclear $[Ir_4(CO)_{12}]$ or hexanuclear $[Ru_6C(CO)_{17}]$ carbonyl complexes. Substituted species such as $[Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ or $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ (ref. 6) also gave clean OMe^- adducts. The hydride cluster $[Os_4H_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ (ref. 7) also gave a $[M + OMe]^-$ signal, rather than the possible alternative of a $[M - H]^-$ one formed by abstraction of H^+ by OMe^-.

Analogous $[M + OEt]^-$ or $[M + OPr^i]^-$ ions were formed in EtOH or Pr^iOH containing small amounts of the appropriate NaOR. This can be useful for assigning fragmentation peaks, *e.g.* loss of $[n(CO) + OMe]$ differs by only three mass units from loss of $[(n + 1)CO]$ which leads to overlapping isotopomer envelopes. In contrast, the OEt^- system gives separated envelopes.

The ions are undoubtedly formed by nucleophilic attack of the alkoxide ion OR^- at the carbon atom of one of the carbonyl ligands to give a coordinated –C(O)OR group. This type of reaction is one of the most general for metal carbonyl complexes,[8] and has been extensively studied because of its relationship to the water–gas shift reaction, where related attack of OH^- on a coordinated carbonyl group is assumed to be a key step.[8] Addition of OR^- to metal carbonyl clusters is governed by both rapid kinetics and large equilibrium constants[9] so is ideal for *in situ* derivatisation of metal carbonyls. Adducts of this type are often quite stable, and several have been characterised previously by X-ray crystallography[10,11] while others have been characterised spectroscopically.[9,12]

In summary, the use of alkoxide/alcohol as the mobile phase in ESMS allows the technique to be used to characterise neutral metal carbonyl complexes. This should find wide application where traditional mass spectrometry like EI or FAB cannot be used because of problems with volatility or extensive fragmentation. The negative ions generated by this method complement the positive ion adducts with Ag^+ we described previously.[1]

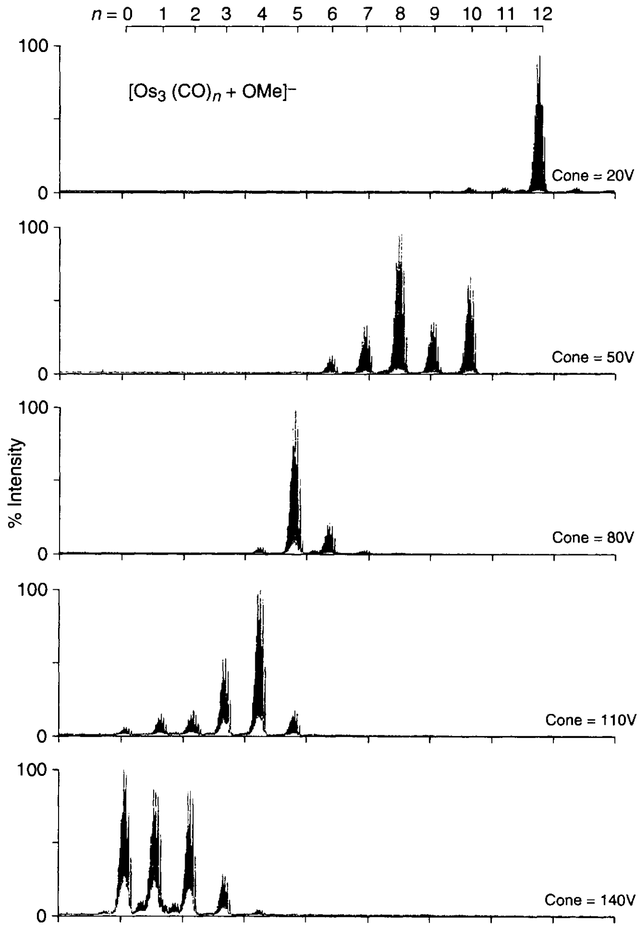

Fig. 1 The electrospray mass spectra of $[Os_3(CO)_{12}]$ run in MeOH with added NaOMe, showing the effect of cone voltage on the fragmentation patterns. For $[Os_3(CO)_n + OMe]^-$ with $n < 9$ the envelopes contain overlapping species arising from loss of OMe (probably as CO_2Me) competing with CO loss.

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Footnotes

† Leading references to other applications in organometallic chemistry are given in ref. 1.

‡ Electrospray mass spectra were obtained in the negative-ion mode with a VG Platform II quadrupole mass spectrometer using the appropriate alcohol as the mobile phase. Typically a dilute solution of the metal carbonyl complex was prepared in the alcohol (*ca.* 1 cm^3) and one drop of a solution of NaOR in the same solvent (*ca.* 1 mg cm^{-3}) was added. The samples were injected *via* a Rheodyne injector fitted with a 10 μl sample loop, and delivered to the spectrometer source (60 °C) at 0.01 cm^3 min^{-1}. Nitrogen was used as the drying and nebulising gas. Cone voltages of under 20 V selectively gave clean parent ions, while increasing cone voltages induced fragmentation (loss of CO and/or CO_2R). Assignment of peaks was by comparison of observed and calculated isotope patterns.[13]

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