

Electrospray Mass Spectrometry of Neutral Metal Carbonyl Complexes using Silver(I) Ions for Ionisation

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Silver(I) ions are used for chemical ionisation in the electrospray mass spectrometric analysis of neutral metal carbonyls such as $[M_3(CO)_{12}]$ ($M = Ru, Os$), $[Re_2(CO)_{10}]$ or $[SiFe_4(CO)_{16}]$ in a variety of solvents (MeOH, PrⁱOH, THF, or MeCN–H₂O).

Electrospray mass spectrometry (ESMS) is a recent ionisation technique which was originally developed for the analysis of large, polar and involatile biomolecules such as proteins and peptides.¹ The technique can also be used for the analysis of polar, ionic and/or involatile inorganic species; examples include transition-metal oxo² and polyoxo-anions,³ borane anions,⁴ and metal–phosphine complexes.⁵ Organometallic systems have also been studied, including metal alkyls,⁶ cyclopentadienyl⁷ and related π -alkene and -arene complexes.⁸ However, metal carbonyls studied to date have been restricted to charged species,⁹ and no ESMS studies on neutral carbonyls have been reported. The low basicity of the oxygen atom of metal carbonyls apparently precludes the protonation necessary to generate detectable ions in the chemical ionisation step. Mass spectrometric analysis of higher nuclearity metal carbonyl clusters by traditional electron impact (EI) or fast atom bombardment (FAB) methods can be complicated by low volatility, thermal instability, and extensive fragmentation. Triruthenium dodecacarbonyl, $[Ru_3(CO)_{12}]$ is a typical example, which gives relatively complex EI and FAB mass spectra.¹⁰

In this communication we report that silver(I) ions may be used to promote the ionisation, and hence mass spectral analysis, of neutral metal carbonyl compounds. Mass spectral data for the various cluster species investigated in this work are summarised in Table 1.

The positive-ion ES spectrum of $[Ru_3(CO)_{12}]$ in MeCN–H₂O (1 : 1) solution gave no peaks (cone voltage 10–60 V). However, the addition of a small quantity of AgNO₃ solution led to a series of readily assigned peaks. Fig. 1 shows that at a low cone voltage (10 V) a single peak is found in the mass range m/z 600–1000, at m/z 789, assigned to the species $[Ru_3(CO)_{12} + Ag(MeCN)]^+$ **1**, by comparison of the observed and calculated isotope patterns. At a cone voltage of 20 V, the intensity of the MeCN adduct **1** decreases, while that of $[Ru_3(CO)_{12} + Ag]^+$ (m/z 748) increases. Such behaviour is typical of ligated silver

complexes under ESMS conditions, as found previously for various silver(I) complexes of alkenes,⁸ phosphines and phosphine sulfides.¹¹ At higher cone voltages, CO ligand loss gives fragments of the type $[Ru_3(CO)_x + Ag]^+$ ($x = 7–11$), as indicated in Table 1. Multiple loss of CO ligands from metal carbonyls is often unavoidable fragmentation behaviour in EI and FAB mass spectra¹⁰ but can be controlled with ESMS by appropriate choice of cone voltage.

The affinity of $[Ru_3(CO)_{12}]$ for Ag⁺ is obviously high, given that it is formed even in the presence of a large excess of MeCN.‡ Other adducts of the $Ru_3(CO)_{12}$ –Ag⁺ species arise on introduction of a ligand having a greater coordinating ability than acetonitrile. Thus, addition of a small quantity of pyridine (py) to the ESMS solution gave a peak at m/z 827, assigned to $[Ru_3(CO)_{12} + Ag(py)]^+$.

The use of AgClO₄ as the chemical ionisation agent allows ESMS of $[Ru_3(CO)_{12}]$ to be carried out in solvents of low proton-donor ability (MeOH, PrⁱOH) and even non-protic solvents (THF) as shown in Table 1. In the less polar solvents some minor interference from ions of the type $[Ag_n(ClO_4)_{n-1}]^+$ occurs but these are mainly at low masses, are readily identified by the isotope pattern, and can be minimised with choice of cone voltage.

Comparable results were obtained with other metal carbonyls. With $[Os_3(CO)_{12}]$, the only species observed at low cone voltages (up to 20 V) was $[Os_3(CO)_{12} + Ag(MeCN)]^+$. Loss of MeCN followed by successive CO losses proceeds upon increasing the cone voltage, though the osmium species were more robust, and required higher cone voltages to effect the same degree of fragmentation when compared to the ruthenium system.

Similarly, $[Re_2(CO)_{10}]$ and the spiro cluster $[SiFe_4(CO)_{16}]$ ¹² gave clean $[M + Ag]^+$ ions from MeOH with added AgClO₄ at 25 V, with some loss of CO ligands occurring above 30 V.

The use of a metal ion to provide chemical ionisation of neutral metal carbonyls is so far unique to Ag⁺, since neither a

Table 1 Electrospray mass spectral data for metal carbonyl–silver species†

Compound (solvent)	Cone voltage (V)	Principal ions (m/z) ^a
$Ru_3(CO)_{12} + AgNO_3$ (MeCN)	10	$[Ru_3(CO)_{12} + Ag(MeCN)]^+$ (789)
	20	$[Ru_3(CO)_{12} + Ag(MeCN)]^+$ (789), $[Ru_3(CO)_{12} + Ag]^+$ (748)
	40	$[Ru_3(CO)_{12} + Ag]^+$ (748), $[Ru_3(CO)_{11} + Ag]^+$ (720), $[Ru_3(CO)_{10} + Ag]^+$ (692), $[Ru_3(CO)_9 + Ag]^+$ (664), $[Ru_3(CO)_8 + Ag]^+$ (636)
	60	$[Ru_3(CO)_8 + Ag]^+$ (636), $[Ru_3(CO)_7 + Ag]^+$ (608)
$Ru_3(CO)_{12} + AgClO_4$ (Pr ⁱ OH)	15	$[Ru_3(CO)_{12} + Ag(Pr^iOH)]^+$ (808)
	25	$[Ru_3(CO)_{12} + Ag]^+$ (748)
$Ru_3(CO)_{12} + AgClO_4$ (MeOH)	36	$[Ru_3(CO)_{12} + Ag]^+$ (748), $[Ru_3(CO)_{11} + Ag]^+$ (720), $[Ru_3(CO)_{10} + Ag]^+$ (692)
$Ru_3(CO)_{12} + AgClO_4$ (THF)	23	$[Ru_3(CO)_{12} + Ag(THF)]^+$ (820), $[Ru_3(CO)_{12} + Ag]^+$ (748)
	30	$[Ru_3(CO)_{12} + Ag]^+$ (748)
	38	$[Ru_3(CO)_{12} + Ag]^+$ (748), $[Ru_3(CO)_{11} + Ag]^+$ (720), $[Ru_3(CO)_{10} + Ag]^+$ (692)
	60	$[Os_3(CO)_{12} + Ag(MeCN)]^+$ (1056)
$Os_3(CO)_{12} + AgNO_3$ (MeCN)	20	$[Os_3(CO)_{12} + Ag(MeCN)]^+$ (1056)
	60	$[Os_3(CO)_{12} + Ag]^+$ (1015), $[Os_3(CO)_{11} + Ag]^+$ (987), $[Os_3(CO)_{10} + Ag]^+$ (959), $[Os_3(CO)_9 + Ag]^+$ (931), $[Os_3(CO)_8 + Ag]^+$ (903)
$SiFe_4(CO)_{16} + AgClO_4$ (MeOH)	20	$[SiFe_4(CO)_{16} + Ag(MeOH)]^+$ (839), $[SiFe_4(CO)_{16} + Ag]^+$ (807)
	30	$[SiFe_4(CO)_{16} + Ag]^+$ (807), $[SiFe_4(CO)_{15} + Ag]^+$ (779)
$Re_2(CO)_{10} + AgClO_4$ (MeOH)	25	$[Re_2(CO)_{10} + Ag]^+$ (761)

^a Species are identified by the peak of greatest intensity in the isotope distribution pattern.

hard metal centre (Cs^+) nor an alternative soft metal (Tl^+) produced detectable adducts in the ESMS spectra of $[\text{Ru}_3(\text{CO})_{12}]$.

The exact nature of the ions formed between the metal carbonyls and Ag^+ is uncertain, based on the ESMS data alone. The most likely possibility is an isocarbonyl species, in which there is an $\text{M}-\text{C}=\text{O}\cdots\text{Ag}^+$ interaction. Such O-bonded carbonyls have previously been characterised in the solid state in a number of systems.¹³

The Ag^+ method of ionisation is not fully general since we have not yet been able to observe sensible ESMS spectra of $[\text{W}(\text{CO})_6]$ nor $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]_2$, while $[\text{Re}_2(\text{CO})_{10}]$, for example, gives $[\text{Re}_2(\text{CO})_{10} + \text{Ag}]^+$ ions in MeOH but not in MeCN– H_2O (1 : 1). Further studies are in progress with a wider range of substrates and solvents to assess the applicability.

In conclusion, electrospray mass spectrometry of neutral metal carbonyls can be achieved by the use of silver(I) ions for ionisation in a range of solvents. This extends the usefulness of the versatile ESMS technique with non-polar substrates.

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Footnotes

† Electrospray mass spectra were obtained in positive-ion mode with a VG Platform II mass spectrometer using the appropriate mobile phase. A solution of the metal carbonyl was prepared in a few drops of mobile phase, a drop of a solution of either AgNO_3 or AgClO_4 in the mobile phase solvent was added, and samples were injected into the spectrometer via a Rheodyne injector fitted with a 10 μl sample loop. A Thermo Separation products SpectraSystem P1000 LC pump delivered the solution to the mass spectrometer source (60 °C) at a flow rate of 0.01 ml min^{-1} , and nitrogen was employed both as a drying and nebulising gas. Cone voltages were varied from 10 to 60 V, in order to investigate the effect of higher voltages on fragmentation of the parent ions. Excellent agreement between observed and calculated isotope distribution patterns was observed for all major peaks, the latter being calculated using the *Isotope* program.¹⁴

‡ Silver(I) ions have a pronounced tendency to linger in the ESMS spectrometer; subsequent samples may give ions incorporating Ag^+ so other users should be notified.

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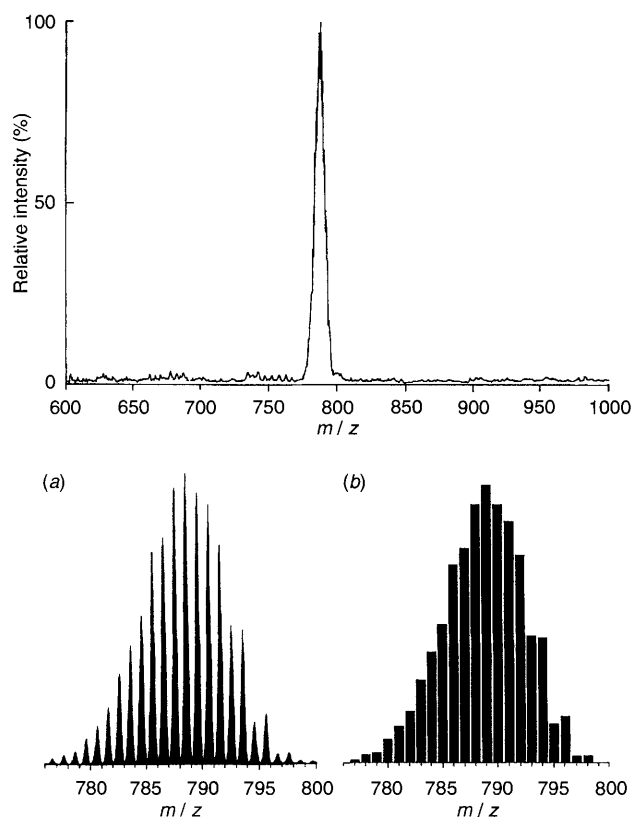


Fig. 1 Positive-ion electrospray mass spectrum (cone voltage 10 V) of an MeCN– H_2O solution of $\text{Ru}_3(\text{CO})_{12}$ containing a small quantity of AgNO_3 , yielding the principal ion $[\text{Ru}_3(\text{CO})_{12} + \text{Ag}(\text{MeCN})]^+$ **1** at m/z 789, with observed (a) and calculated (b) isotope distribution patterns