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Electrospray mass spectrometry of metal carbonyl complexes†

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Methods are described for characterising neutral metal carbonyl complexes using electrospray mass spectrometry, by converting them into ions with suitable reagents. Ionisation techniques included addition of OMe^- generating $[M + OMe]^-$ species, addition of Ag^+ or Na^+ ions giving the appropriate positive ion, abstraction of acidic hydrogen forming $[M - H]^-$ ions, or (in rare cases) oxidation giving radical cations $[M]^{\bullet +}$. The methods can be used on pure compounds or on mixtures. Fragmentation in the mass spectrometer can be minimised so that identification of parent species is unambiguous. Applications are demonstrated with a wide range of compounds including mononuclear and polynuclear binary carbonyls, and with derivatives containing phosphine, cyclopentadienyl, π-arene, σ-aryl and other ligands.

Characterisation of metal carbonyl compounds, particularly the higher-nuclearity cluster compounds, has traditionally relied heavily on single-crystal X-ray crystallography. This is because microanalytical data are usually not particularly informative, ^{13}C NMR data are often limited by low sensitivity and fluxional processes, while structure assignment based on the interpretation of infrared spectra is limited to smaller molecules. The strong reliance on X-ray methods has a corollary; only compounds that form suitable single crystals become fully characterised. There is therefore a need for alternative means of investigating metal cluster compounds.

Mass spectrometry has been applied to organometallic chemistry for many years, but the traditional electron impact method of ionisation is limited to thermally robust, neutral compounds of low molecular mass since appreciable vapour pressure is necessary at temperatures below the decomposition point.[1] The development of FAB (fast-atom bombardment) methods extended the mass spectral technique to non-volatile compounds, but it is a rather violent means of ionisation so extensive fragmentation and recombination processes can make interpretation complicated.[2] An alternative, developing technique based on laser desorption has been applied to organometallic systems,[3] but again aggregation processes complicate interpretation.

In the past decade a new method of sample ionisation has been developed: electrospray mass spectrometry (ESMS).[4] This involves spraying samples in solution from a charged outlet into an atmospheric-pressure source and then rapidly evaporating the solvent, leaving ions in the gas phase which are then transferred to a mass analyser. The process is gentle so that fragile samples can be examined, and fragmentation processes are minimised so that clean parent ions are usually found (although fragmentation can be induced by altering the conditions if further information is needed). It can also be applied directly to ionic species since solubility rather than volatility is the key factor. The new method has been extensively developed by those interested in biological systems since it enables mass spectrometry to be applied to high mass, fragile biomolecules.[5] Only recently has there been corresponding interest from inorganic chemists,[6] as reviewed by Colton *et al.*[6a]

For metal carbonyl compounds in particular, there has been only sporadic use of the method, mainly applied to anionic cluster compounds, with no systematic study so far reported. This is partly because the usual method of forming ions from neutral molecules for biochemical and organic systems (namely protonation or deprotonation) do not work with metal carbonyl compounds because of the low basicity of the oxygen atom in CO complexes.[7]

We now describe methods which allow the routine use of ESMS for the analysis of metal carbonyl compounds. Aspects of this work have been communicated earlier.[8]

Experimental

Electrospray mass spectra were obtained with a VG Platform II mass spectrometer with the mobile phase driven at 0.02 ml min^{-1} using a Thermo Separation products SpectraSystem P1000 LC pump. Samples were injected *via* a Rheodyne valve fitted with a 10 µl sample loop. The nebuliser tip was at 3500 V and 60 °C, with nitrogen used both as a drying and a nebulising gas. The skimmer cone voltage was usually 15 V when clean parent ions were required, and was varied up to 140 V to investigate fragmentation processes.

Samples were prepared by dissolving the metal carbonyl compound (10–100 µg) in the appropriate mobile phase (1 ml). If required, a drop of a solution of $AgClO_4$, $AgNO_3$ or NaOMe in the same solvent (*ca.* 1 mg ml^{-1}) was added immediately before sample injection.

Peaks were assigned from the *m*/*z* values and from the isotope distribution patterns which were simulated using the ISOTOPE program.[9] The *m*/*z* values given are for the most intense peak in the envelope in each case.

The metal carbonyl substrates used for analysis were generally available in our laboratories, were kindly donated, or were prepared using standard methods. Only the more unusual examples are referenced individually.

Pyrolysis of $[Os_3(CO)_{12}]$

The cluster $[Os_3(CO)_{12}]$ (*ca.* 1 mg) was sealed in a small evacuated ampoule and heated at 210 °C for 18 h. The ampoule was opened and the residue extracted with ethyl acetate. A drop of this extract was diluted to *ca.* 1 ml with MeOH. A drop of NaOMe solution was added and the mixture was analysed.

Results and Discussion

(a) Metal carbonyl anions

Compounds which are intrinsically charged are ideal for

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† *Non-SI unit employed*: Da ≈ 1.66×10^{-27} kg.

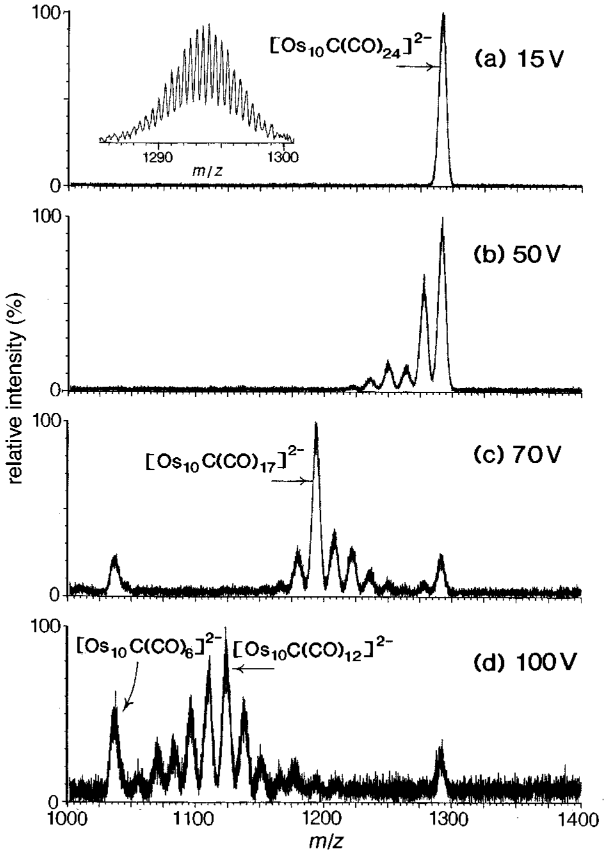


Fig. 1 Negative-ion electrospray spectrum of $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ in MeOH at varying cone voltages (a) 15 V, (b) 50 V, (c) 70 V, (d) 100 V, showing increasing CO loss. Inset: an expansion of the parent ion showing the isotope pattern with 0.5 mass unit separation indicating the doubly-charged ion.

analysis using ESMS, and several examples of the analysis of mononuclear[10] and of cluster metal carbonyl[11] ions have been described in the literature. The ions are transferred from solution to the gas phase directly and give rise to particularly intense parent-ion signals. As examples we discuss here only two anionic clusters, which are well known but which have not been analysed by ESMS before.

The spectrum obtained in the negative-ion mode for $[Os_{10}C(CO)_{24}]^{2-}$ is illustrated in Fig. 1. It gives a clean parent-ion envelope at *m*/*z* 1294, and it is obvious from the half-mass unit separation of the peaks in the isotope pattern (see inset) that it is a dianion, with a mass of 2588 Da as expected. As the cone voltage is increased, fragmentation by loss of CO ligands takes place so that the most intense ion becomes $[Os_{10}C(CO)_{17}]^{2-}$ at 70 V and $[Os_{10}C(CO)_{12}]^{2-}$ at 100 V. However, even at 100 V some parent ion is still detectable, showing the stability of this cluster. This large cluster allows the charge to be well distributed and the resulting low charge density will reduce the tendency to fragment.

Another anion, $[Ru_6C(CO)_{16}]^{2-}$ gave similar results, showing a single envelope at *m*/*z* 534 corresponding to a doubly-charged ion of mass 1068 Da. In this case fragmentation takes place under milder conditions with no parent ion detectable at 50 V, where the $[Ru_6C(CO)_n]^{2-}$ ($n = 10$) ion becomes the dominant one, flanked by ions with $n = 8$–13. Fragmentation will be encouraged by the weaker Ru–CO bond strengths (*cf.* Os–CO) and by the higher charge density on this small cluster; there are other examples of more facile fragmentation occurring where charge density is higher.[12]

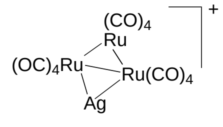
These two illustrative examples demonstrate the ease of analysis of compounds which carry their own charge. A detailed comparison of ES and FAB behaviour of anionic clusters of the type $[Fe_3(CO)_{10}(\mu\text{-HgML}_n)]^-$ [$ML_n = Mo(CO)_3Cp$, $Mn(CO_5)$, *etc.*] has been reported recently and provides extra examples of the technique,[11a] and unpublished results for the $[Pt_{12}(CO)_{24}]^{2-}$ cluster are quoted in ref. 6(*c*).

(b) Neutral metal carbonyls ionised with Ag$^+$

Neutral metal carbonyl compounds generally do not give rise to any ESMS signals under the usual conditions because the low basicity of CO groups towards protons[7] means that they do not undergo protonation reactions to give cationic species. However if small quantities of Ag^+ ions are added to a solution of $[Ru_3(CO)_{12}]$ in MeCN a spectrum consisting of a single envelope at *m*/*z* 789 is readily observed, assignable to the adduct $[Ru_3(CO)_{12} + Ag(MeCN)]^+$. Corresponding $[Ru_3(CO)_{12} + Ag(solvent)]^+$ ions are observed in MeOH, Pr^iOH or thf. Under more forcing conditions, at higher skimmer cone voltages, other peaks arise from loss of the solvent molecule and/or loss of CO ligands [see Table 1 in ref. 8(a) for full details]. Other metal carbonyl compounds undergo a corresponding derivatisation with Ag^+ ions, including $[Os_3(CO)_{12}]$, $[Fe_4(\mu_4\text{-Si})(CO)_{16}]$,[13] $[Re_2(CO)_{10}]$, $[Mo(CO)_3Cp]_2$, $[Ru_4(CO)_{10}(PhCHCHPh)]$ and some substituted derivatives $[Ru_3(CO)_{12-n}L_n]$ ($L = PPh_3$ or $AsPh_3$);[14] details are summarised in Table 1. Identification of adducts is straightforward, helped by the distinctive isotope pattern for silver [^{107}Ag (52%), ^{109}Ag (48%)].

This means of derivatisation with Ag^+ has not proved to be as general as we had initially hoped, since no interpretable ions were found from solutions containing Ag^+ together with mononuclear compounds such as $[W(CO)_6]$ or $[Fe(CO)_4\{P(OPh)_3\}]$, or from dinuclear species $[Mn_2(CO)_{10}]$, $[Fe(CO)_2Cp]_2$ or $[Ru(CO)_2Cp]_2$. The fickle behaviour of Ag^+ is further illustrated by the observation that $[Ru_6C(CO)_{14}(\mu_3\text{-}C_{16}H_{16})]$[19] forms an adduct with Ag^+ but neither the parent complex $[Ru_6(CO)_{17}]$[20] nor the related arene species $[Ru_6C(CO)_{14}(C_6H_5Me)]$[21] do so, although this difference may be attributable to Ag^+ attaching to the free ring of the cyclophane ligand. In some cases, such as with the iron dimer, oxidation reactions appeared to be occurring but with others there was apparently no interaction between the metal carbonyl species and the silver ion. Another significant observation is that similar ion adducts were not found with other metal ions such as Mg^{2+}, Tl^+, Cs^+, Na^+ or Li^+ for most of the compounds for which Ag^+ was an effective derivatisation agent (some exceptions to this are discussed below).

These experimental data provide some evidence for the mechanism of adduct formation with Ag^+. No structural details are available directly from the ESMS procedure and in our initial communication we suggested that adduct formation was *via* an isocarbonyl interaction $M{-}CO \cdots Ag^+$ since analogous species involving other cations have been isolated and are well characterised.[7,22] However we now discard this model in favour of one in which the Ag^+ ion interacts with an electron-rich M–M bond to give species of the type **1**, illustrated for $Ru_3(CO)_{12}$.‡ Preference for this mechanism is based on the fact that compounds with Ag^+-bridged M–M bonds are well established,[23] but corresponding species with harder cations such as Cs^+ or Mg^{2+} are not; the isocarbonyl interaction is unlikely to be so selective. This is also consistent with the total lack of spectra with mononuclear metal carbonyls, where an



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‡ We thank Professor M. I. Bruce, University of Adelaide, for this suggestion.

Table 1 Electrospray mass spectral data for metal carbonyl compounds[a]

Compound	Mobile phase	Ionisation aid	Peaks (*m/z*) and assignment
Anions:[b]			
$[Ru_6C(CO)_{16}]^{2-}$	MeOH	None	534 $[M]^{2-}$
$[Os_{10}C(CO)_{24}]^{2-}$	MeOH	None	1294 $[M]^{2-}$
Ag^+ addition:			
$[Re_2(CO)_{10}]$	MeOH	$AgClO_4$	761 $[M + Ag]^+$, 100% 793 $[M + Ag + MeOH]^+$, 40%
$[Ru_3(CO)_{12}]$	thf	$AgClO_4$	820 $[M + Ag + thf]^+$, 100% 748 $[M + Ag]^+$, 55%
$[Ru_3(CO)_{12}]$	Pr^iOH	$AgClO_4$	808 $[M + Ag + Pr^iOH]^+$
$[Ru_3(CO)_{12}]$	MeCN	$AgNO_3$	789 $[M + Ag + MeCN]^+$, 100% 748 $[M + Ag]^+$, 80%
$[Os_3(CO)_{12}]$	MeCN	$AgClO_4$	1056 $[M + Ag + MeCN]^+$
$[Os_3(CO)_{12}]$	MeOH	$AgClO_4$	1047 $[M + Ag + MeOH]^+$, 40% 1015 $[M + Ag]^+$, 100%
$[Mo(CO)_3Cp]_2$	MeCN	$AgClO_4$	638 $[M + Ag + MeCN]^+$, 100% 597 $[M + Ag]^+$, 60%
$[Ru_3(CO)_{11}(PPh_3)]$	MeCN	$AgClO_4$	982 $[M + Ag]^+$
$[Ru_3(CO)_{10}(AsPh_3)_2]$	MeCN	$AgClO_4$	1304 $[M + Ag]^+$
$[Ru_3(CO)_9(PPh_3)_3]$	MeCN	$AgClO_4$	1450 $[M + Ag]^+$
$[Ru_3H(CO)_9(C_{12}H_{17})]$[15]	MeCN	$AgClO_4$	867 $[M + Ag + MeCN]^+$
$[Fe_4Si(CO)_{16}]$	MeOH	$AgClO_4$	839 $[M + Ag + MeOH]^+$ 807 $[M + Ag]^+$
$[Os_4H_2(CO)_{10}(C_6H_6)]$	MeCN	$AgClO_4$	1270 $[M + Ag + MeCN]^+$, 100% 1122 $[M]^{\bullet +}$, 20%
$[Ru_4(CO)_{10}(Ph_2C_2H_2)]$	MeCN	$AgClO_4$	1014 $[M + Ag + MeCN]^+$
$[Ru_6C(CO)_{14}(C_{16}H_{16})]$	MeCN	$AgClO_4$	1369 $[M + Ag + MeCN]^+$
$[NiRu_3H_3(CO)_9Cp]$	MeCN	$AgClO_4$	832 $[M + Ag + MeCN]^+$, 100% 791 $[M + Ag]^+$, 10%
Alkoxide addition:			
$[Fe(CO)_5]$	MeOH	NaOMe	227 $[M + OMe]^-$
$[Cr(CO)_6]$	MeOH	NaOMe	251 $[M + OMe]^-$
$[Mo(CO)_6]$	MeOH	NaOMe	297 $[M + OMe]^-$
$[W(CO)_6]$	MeOH	NaOMe	383 $[M + OMe]^-$
$[Mn_2(CO)_{10}]$	MeOH	NaOMe	421 $[M + OMe]^-$
$[Re_2(CO)_{10}]$	MeOH	NaOMe	683 $[M + OMe]^-$
$[Re_2(CO)_{10}]$	EtOH	NaOEt	697 $[M + OEt]^-$
$[Fe(CO)_2Cp]_2$	MeOH	NaOMe	385 $[M + OMe]^-$
$[Ru(CO)_2Cp]_2$	MeOH	NaOMe	476 $[M + OMe]^-$
$[Mo(CO)_3Cp]_2$	MeOH	NaOMe	521 $[M + OMe]^-$
$[Ru_3(CO)_{12}]$	EtOH	NaOEt	686 $[M + OEt]^-$, 10% 618 $[M + OEt - C_3O_2]^-$, 100%
$[Os_3(CO)_{12}]$	MeOH	NaOMe	939 $[M + OMe]^-$
	EtOH	NaOEt	953 $[M + OEt]^-$
	Pr^iOH	$NaOPr^i$	967 $[M + OPr^i]^-$
$[Fe_3(CO)_{11}(CNBu^t)]$	MeOH	NaOMe	590 $[M + OMe]^-$
$[Ru_3(CO)_{11}(PPh_3)]$	MeOH	NaOMe	906 $[M + OMe]^-$, 100% 878 $[M + OMe - CO]^-$, 15% 850 $[M + OMe - 2CO]^-$, 50%
$[Ru_3H(C_2Bu^t)(CO)_9]$	MeOH	NaOMe	670 $[M + OMe]^-$, 80% 638 $[M - H]^-$, 100%
$[Rh_4(CO)_{12}]$	MeOH	NaOMe	751 $[M + OMe - CO]^-$
$[Ir_4(CO)_{12}]$	MeOH	NaOMe	1137 $[M + OMe]^-$
$[Ru_4H_4(CO)_{12}]$	MeOH	NaOMe	777 $[M + OMe]^-$
$[Os_4H_2(CO)_{10}(C_6H_6)]$	MeOH	NaOMe	1153 $[M + OMe]^-$ 1121 $[M - H]^-$ (see text)
$[Ru_4(CO)_{10}(Ph_2C_2H_2)]$	MeOH	NaOMe	897 $[M + OMe]^-$
$[NiRu_3H_3(CO)_9Cp]$	MeOH	NaOMe	714 $[M + OMe]^-$
$[Ru_5(CO)_9(C_6H_5Me)]$	MeOH	NaOMe	881 $[M + OMe]^-$
$[Ru_6C(CO)_{17}]$	MeOH	NaOMe	1127 $[M + OMe]^-$
$[Ru_6(CO)_{15}(C_6Me_6)]$	MeOH	NaOMe	1221 $[M + OMe]^-$
$[Ru_6C(CO)_{14}(C_6H_5Me)]$	MeOH	NaOMe	1135 $[M + OMe]^-$, 100% 1103 $[M - H]^-$, 20%
$[Ru_6C(CO)_{14}(C_{16}H_{16})]$	MeOH	NaOMe	1251 $[M + OMe]^-$
$[Cp(CO)_3Mo(C{\equiv}C)_2C_6H_5]$[16]	MeOH	NaOMe	403 $[M + OMe]^-$
$[Cp(CO)_3W(C{\equiv}C)_2C_6H_4OMe]$[16]	MeOH	NaOMe	519 $[M + OMe]^-$
$[\{Cp(CO)_3W\}_2(C{\equiv}C)_4{\cdot}Co_2(CO)_4(dppm)]$[16]	MeOH	NaOMe	1407 $[M + OMe]^-$
$[\{Cp(CO)_3W\}_2(C{\equiv}C)_4{\cdot}2Co_2(CO)_4(dppm)]$[16]	MeOH	NaOMe	2021 $[M + OMe]^-$
2a	MeOH	NaOMe	511 $[M + OMe]^-$
2b	MeOH	NaOMe	346 $[M + OMe]^-$
2c	MeOH	NaOMe	347 $[M + OMe]^-$, 30% 319 $[M + OMe - CO]^-$, 30% 315 $[M - H]^-$, 70% 287 $[M - H - CO]^-$, 100%

Table 1 (*Contd*)

Compound	Mobile phase	Ionisation aid	Peaks (*m*/*z*) and assignment
Proton abstractions:			
$[Co_2(CO)_6(dppm)]$	MeOH	NaOMe	669 $[M - H]^-$
$[Ru_3H(C_2Bu^t)(CO)_9]$	MeOH	NaOMe	670 $[M + OMe]^-$, 80% 638 $[M - H]^-$, 100%
$[Ru_3H(C_2Ph)(CO)_7(dppm)]$[17]	MeOH	NaOMe	986 $[M - H]^-$
$[Ru_3H(C_2Bu^t)(CO)_7(dppm)]$[17]	MeOH	NaOMe	966 $[M - H]^-$
$[Os_4H_2(CO)_{10}(C_6H_6)]$	MeOH	NaOMe	1153 $[M + OMe]^-$, 100% 1121 $[M - H]^-$, 30%
$[Ru_6C(CO)_{14}(C_6H_5Me)]$	MeOH	NaOMe	1135 $[M + OMe]^-$, 100% 1103 $[M - H]^-$, 20%
2c	MeOH	NaOMe	347 $[M + OMe]^-$, 30% 319 $[M + OMe - CO]^-$, 30% 315 $[M - H]^-$, 70% 287 $[M - H - CO]^-$, 100%
3	MeOH	NaOMe	471 $[M - H]^-$, 100% 347 $[M - H - P(OMe)_3]^-$, 80%
Na^+ addition:			
$[Fe(CO)_3\{P(OPh)_3\}_2]$	MeOH	NaOMe	783 $[M + Na]^+$
$[Co_2(CO)_6(dppm)]$	MeOH	NaOMe	693 $[M + Na]^+$
$[Ru_3(CO)_{10}(AsPh_3)_2]$	MeOH	NaOMe	1220 $[M + Na]^+$
$[Ru_3(CO)_9(PPh_3)_3]$	MeOH	NaOMe	1366 $[M + Na]^+$
$[Ru_3H(C_2Bu^t)(CO)_7(dppm)]$[17]	MeOH	NaOMe	990 $[M + Na]^+$
$[Ru_3H(C_2Ph)(CO)_7(dppm)]$[17]	MeOH	NaOMe	1010 $[M + Na]^+$
$[Ru_4H_4(CO)_9P^aP^bP^c]$[c]	MeOH	NaOMe	1337 $[M + Na]^+$
$[Cp(CO)_3W(C{\equiv}C)_2C_6H_4OMe]$[16]	MeOH	NaOMe	511 $[M + Na]^+$, 100% 543 $[M + Na + MeOH]^+$, 45%
$[\{Cp(CO)_3W\}_2(C{\equiv}C)_4{\cdot}Co_2(CO)_4(dppm)]$[16]	MeOH	NaOMe	1399 $[M + Na]^+$
$[\{Cp(CO)_3W\}_2(C{\equiv}C)_4{\cdot}2Co_2(CO)_4(dppm)]$[16]	MeOH	NaOMe	1990 $[M]^{\bullet +}$, 100% 2013 $[M + Na]^+$, 15%
Oxidation:			
$[Ru_4H_4(CO)_9P^aP^bP^c]$[c]	MeOH	None	1314 $[M]^{\bullet +}$
$[\{Cp(CO)_3W\}_2(C{\equiv}C)_4{\cdot}2Co_2(CO)_4(dppm)]$[16]	MeOH	NaOMe	1990 $[M]^{\bullet +}$, 100% 2013 $[M + Na]^+$, 15%
$[Os_4H_2(CO)_{10}(C_6H_6)]$	MeOH	$AgClO_4$	1270 $[M + Ag + MeCN]^+$, 100% 1122 $[M]^{\bullet +}$, 20%

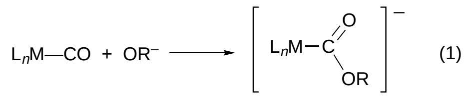
[a] Data presented in this Table were recorded at low cone voltages (15–20 V) to minimise fragmentation; *m*/*z* values are for the most intense peak in the isotopomer envelope. If only one ion is given it implies that no significant (>10%) other ions were observed at low cone voltages. Note that some compounds are entered under more than one heading. [b] As the $[N(PPh_3)_2]^+$ salt. [c] $[P^a = PMe_2Ph, P^b = P(OTol)_3, P^c = P(OCH_2)_3(CEt)]$.[18]

isocarbonyl mechanism could apply, but an Ag^+ bridged one could not.

The conclusion from this part of our studies is therefore that Ag^+ derivatisation has some limited application for electron-rich binary carbonyl clusters with accessible M–M bonds but cannot be regarded as a general technique. It also finds some application[24] where the organometallic species has functional groups such as carbon–carbon double or triple bonds which will co-ordinate to Ag^+; adducts with polyalkyne compounds such as $\{[Cp(CO)_3W]C{\equiv}C{-}C{\equiv}C{-}\}_2$ are readily observed by ESMS.[16]

(c) Derivatisation of neutral metal carbonyls by addition of alkoxide ions

An alternative, more general, method of derivatisation of metal carbonyl compounds for ESMS study makes use of the susceptibility of co-ordinated CO ligands towards nucleophilic attack. Thus when a solution of $[Os_3(CO)_{12}]$ in MeOH was treated with a drop of a solution of NaOMe and injected into the mass spectrometer a single peak corresponding to the $[Os_3(CO)_{12} + OMe]^-$ ion was observed in the negative ion mode, formed as in equation (1). Corresponding $[M + OMe]^-$ peaks were found for a large number of metal carbonyl substrates, ranging from mononuclear to hexanuclear (see Table 1). Quality of spectra was generally excellent, as illustrated in Fig. 2 for the adduct with $[Ru_6C(CO)_{14}(\mu_3\text{-}C_{16}H_{16})]$.[25] Interpretation was straightforward, but if ambiguities arose from overlapping peaks in the fragmentation pattern at higher cone voltages, the corresponding spectra generated from OEt^- in EtOH or OPr^{i-} in Pr^iOH were equally readily obtained, showing the appropriate mass shifts.



$$L_nM{-}CO + OR^- \longrightarrow \left[L_nM{-}C\begin{matrix} {=}O \\ \diagdown OR \end{matrix} \right]^- \qquad (1)$$

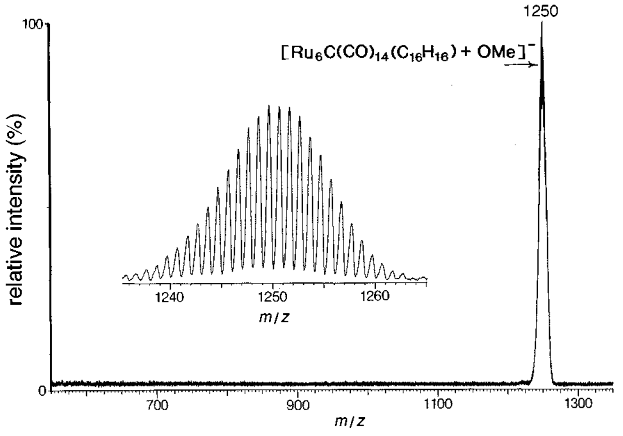


Fig. 2 Negative-ion mass spectrum (cone voltage 18 V) of $[Ru_6C(CO)_{14}(\mu_3\text{-}C_{16}H_{16})]$ in MeOH with added OMe^-. Inset: an expansion of the isotope pattern for the parent ion $[Ru_6C(CO)_{14}(\mu_3\text{-}C_{16}H_{16}) + OMe]^-$.

To assess the effect of varying amounts of added OMe^-, the signal strength was measured for different amounts of OMe^- with a constant amount of $[W(CO)_6]$ in MeOH. The signal increased to a maximum value which corresponded to a ratio of $[OMe^-]$ to $[W(CO)_6]$ of about 2:1, and then slowly diminished with increasing methoxide. For qualitative work the exact ratio can cover a wide range without affecting the quality of the spectra.

This method of ionisation of neutral metal carbonyls has been found to be very general, as the data summarised in Table 1 shows. For binary metal carbonyls nearly all species examined behaved similarly giving strong, clean parent adducts at low cone voltages, though there were differences in the fragmentation behaviour under more vigorous conditions.

The mononuclear complexes $[M(CO)_6]$ (M = Cr, Mo or W) all show a clean parent adduct at low cone voltages, but only for M = W are all the fragments $[M(CO)_n + OMe]^-$ ($n = 6$–0) clearly observed under more forcing conditions. For M = Mo only the $n = 6$, 4 and 3 ions are observed while for M = Cr just the $n = 6$ and 3 appear. As expected given the relative M–CO bond strengths, fragmentation occurs at lower cone voltages for Cr than for Mo and W. Under the same conditions the mononuclear iron complex $[Fe(CO)_5]$ gave a significantly weaker methoxide adduct in the negative-ion spectrum, though whether this is because of a lower formation tendency, or because of a lower stability of the anionic species is not clear.

The dinuclear complexes $[M_2(CO)_{10}]$ (M = Mn or Re) also differ in their fragmentation processes. Both give a clean $[M_2(CO)_{10} + OMe]^-$ signal, but when the cone voltage is raised the Re example loses successive CO ligands while the Mn example undergoes Mn–Mn bond cleavage to give ions $[Mn(CO)_n]^-$ ($n = 2$–5). No sensible signals were found for either $[Co_2(CO)_8]$ or $[Fe_2(CO)_9]$, presumably because of the reactivity towards MeOH of the former and the insolubility in MeOH of the latter.

The trinuclear cluster $[Os_3(CO)_{12}]$ is the paradigmatic example of the methoxide method. A detailed study showed that all ions $[Os_3(CO)_n + OMe]^-$ could be seen for $n = 12$–0 corresponding to carbonyl loss at appropriate cone voltages, together with some peaks of the type $[Os_3(CO)_m]^-$ ($m = 3$–0) arising from loss of OMe, probably as CO_2Me [see ref. 8(*b*) for details]. Similar behaviour was observed with the adduct from $[Ru_3(CO)_{12}]$ with methoxide ion, although here the spectrum was less clean than for most of the other examples and carbonyl loss was accompanied by a series of peaks arising from an early loss of 'C_3O_2' at relatively low cone voltages. For the substituted complexes $[Ru_3(CO)_{12-n}L_n]$ ($L = PPh_3$, $n = 1$ or 3; $L = AsPh_3$, $n = 2$)[14] a methoxide adduct was observed only for the $[Ru_3(CO)_{11}(PPh_3)]$ example; this is explicable in terms of the proposed adduct-formation mechanism (see below). Similarly for the three complexes $[Ru_3H(C_2R)(CO)_7(L_2)]$ examined, only the unsubstituted one (L = CO) formed an adduct with OMe^- while the substituted ones (L_2 = dppm) did not.

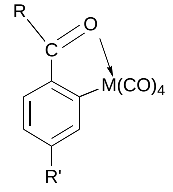
The only isocyanide-substituted example to be examined, $[Fe_3(CO)_{11}(CNBu^t)]$,[26] also gave an excellent spectrum.

For higher nuclearity clusters similar behaviour was found: strong parent ions formed by addition of alkoxide, with CO loss at higher cone voltages for the binary species $[M_4(CO)_{12}]$ (M = Rh or Ir) and for $[Ru_6C(CO)_{17}]$.[20]

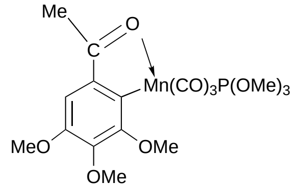
In all the clusters examined, no fragmentation of the metal core was observed, even at the higher cone voltages, which allows confident determination of nuclearity for clusters under all reasonable conditions.

The presence of π-bonded ligands does not interfere with the process as shown by successful alkoxide derivatisation of the dimers $[M(CO)_nCp]_2$ ($n = 2$, M = Fe or Ru; $n = 3$, M = Mo), and for the arene-substituted Ru_4 and Ru_6 clusters listed in Table 1. The complexes $[Ru_6C(CO)_{17}]$ and $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ have recently been examined using laser desorption (LD)[3a] ionisation so a direct comparison of the two methods is possible. There is no evidence of the extensive aggregation processes found for the LD spectra in the ES equivalents.

From other research at Waikato a large range of ortho-manganated and -rhenated aryl ketones of type **2** were available.[27] The rhenium compound **2a** gave a single $[M + OMe]^-$ signal at low cone voltages, and clear losses of up to four CO ligands under more forcing conditions. Similarly, the manganated aldehyde **2b** was well behaved towards OMe^- addition at low cone voltages, though at higher voltages complicated fragmentation occurred after the loss of two CO ligands. In contrast, the acetophenone **2c** showed a relatively weak $[M + OMe]^-$ signal (and an associated CO loss peak), the dominant features being $[M - H]^-$ and $[M - H - CO]^-$ peaks associated with deprotonation reactions [see section (d) below]. The substituted, electron-rich complex **3** did not add OMe^- at all, giving only $[M - H]^-$ and $[M - H - P(OMe)_3]^-$ ions at low cone voltages.



2a M = Re, R = Ph, R' = H
2b M = Mn, R = H, R' = NMe$_2$
2c M = Mn, R = Me, R' = OMe



3

The alkoxide-ionisation method also has use in determining purity, as shown by the spectra obtained with $[Rh_4(CO)_{12}]$. Together with the expected peak at *m*/*z* 779 for $[Rh_4(CO)_{12} + OMe]^-$ there was another observed at *m*/*z* 1097 which corresponds to the adduct of $[Rh_6(CO)_{16}]$, a known decomposition product of the tetramer; this latter signal increased in relative intensity as sample solutions were aged. Similarly for $[Ru_6C(CO)_{14}(C_6H_5Me)]$, additional peaks assigned to $[Ru_5(CO)_9(C_6H_5Me) + OMe]^-$ ions were obvious under conditions where fragmentation was unlikely, suggesting contamination of the sample with a by-product. Of course, in analysing mixtures ESMS can only be regarded as a qualitative method, since ion abundances will reflect relative reactivity towards OMe^- as well as relative concentrations.

We have mainly explored this chemistry using pure metal carbonyl compounds to demonstrate the use of ESMS in characterising compounds. However the technique can also be used routinely to screen reaction mixtures on a small scale, so has use in optimising reaction conditions. In this regard the small quantities needed represent a real advantage. As an illustration of the potential, a 1 mg sample of $[Os_3(CO)_{12}]$ was pyrolysed at 210 °C in an evacuated, sealed ampoule, a reaction that is known to produce a mixture of higher nuclearity clusters.[28] An ethyl acetate extract of the crude reaction mixture was treated with NaOMe in MeOH and the ESMS spectrum shown in Fig. 3 was obtained. This clearly shows the presence of OMe^- adducts of Os_n clusters of nuclearities ranging from $n = 4$ to 7. For comparison, published preparative work[28] under the same conditions found that the $[Os_6(CO)_{18}]$ species is the dominant product, with $[Os_5(CO)_{16}]$, $[Os_7(CO)_{21}]$ and $[Os_8(CO)_{23}]$ also identified after extensive chromatography. In our studies the Os_8 species was not detected (though it was from a higher-temperature pyrolysis run), while we also found small quantities of $[Os_4H_4(CO)_{12}]$ {which gave an $[M + OMe]^-$ adduct and also an $[M - H]^-$ peak arising from deprotonation by the methoxide base, see section (d) for similar processes}. Also observed was a peak at *m*/*z* 1372 which can be assigned to the known species $[Os_5H(CO)_{15}]^-$. This may have been formed directly in the pyrolysis, or may arise from deprotonation of $[Os_5H_2(CO)_{15}]$ (although in this case we would also have expected to

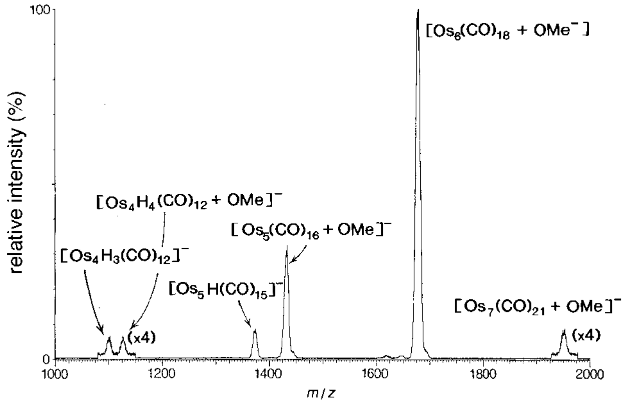


Fig. 3 Negative-ion mass spectrum (cone voltage 18 V) of the mixture of products from the pyrolysis of $[Os_3(CO)_{12}]$ at 210 °C. Spectra obtained in MeOH with added OMe^-. Ions are: *m*/*z* 1951 $[Os_7(CO)_{21} + OMe]^-$, *m*/*z* 1677 $[Os_6(CO)_{18} + OMe]^-$, *m*/*z* 1431 $[Os_5(CO)_{16} + OMe]^-$, *m*/*z* 1373 $[Os_5H(CO)_{15}]^-$, *m*/*z* 1133 $[Os_4H_4(CO)_{12} + OMe]^-$ and *m*/*z* 1101 $[Os_4H_3(CO)_{12}]^-$

see the corresponding OMe^- adduct as well) or possibly by base-induced fragmentation of $[Os_6(CO)_{18}]$ which is a known reaction.[28] Note that it is straightforward to distinguish between deprotonation and alkoxide-addition species by re-running the spectra using OEt^- in EtOH; the peaks arising from the former process remain unchanged while those arising from the latter process move 14 mass units higher compared with the corresponding spectra in MeOH.

Electrospray mass spectrometry screening of this type is far more informative than IR spectroscopy as it does not require separation of components prior to analysis. It is in studies of this type that the ability to minimise fragmentation is important since it can be confidently concluded that each species identified is present in the mixture and is not formed by rearrangement in the mass spectrometer. Although the analysis will be semi-quantitative at best, since the relative ability to attach OR^- and the stability of the different adducts will probably vary with cluster size, ESMS provides a rapid and sensitive means of comparing different reaction conditions.

Ionisation of metal carbonyl compounds by alkoxide ions is readily explained by nucleophilic addition of the OR^- ion to the carbon atom of a CO ligand, as in equation (1). This type of reaction is very general for metal carbonyl compounds[29] and has been extensively studied as a model for the water–gas shift reaction where corresponding attack by OH^- is a key step in the mechanism.[30] There are extensive kinetic and equilibrium constant data for the addition of OR^- to metal carbonyl clusters which show that it is a rapid and favourable process[29] and a number of alkoxide adducts are stable enough for isolation and characterisation by X-ray or spectroscopic means.[31] This ionisation process will be favoured for relatively electron-poor CO ligands, which explains why less-substituted species such as $[Ru_3(CO)_{11}(PPh_3)]$ or $[Ru_3H(C_2R)(CO)_9]$ show adducts with OMe^- whereas the more highly phosphine-substituted analogues do not. All this evidence leaves little doubt as to the mechanism by which ionisation with alkoxide ions in the present ESMS studies occurs.

(d) Ionisation by proton abstraction with OMe^-

The alkoxide ion is strongly basic, as well as being a nucleophile, so it is not surprising that in some cases proton abstraction to give $[M - H]^-$ competed with alkoxide addition to give $[M + OMe]^-$. For hydride clusters this was not completely predictable. For example $[NiRu_3H_3(CO)_9Cp]$,[32] $[Ru_4H_4(CO)_{12}]$ and $[Os_4H_2(CO)_{10}(C_6H_6)]$[33] all gave peaks attributable to OMe^- addition, but only the last of these underwent proton abstraction to give the $[M - H]^-$ ion as well. In section (c) above we noted that $[Os_4H_4(CO)_{12}]$ gave equal intensity peaks for deprotonation and OMe^- addition species. More consistently, when treated with OMe^-, $[M - H]^-$ ions were observed for all three complexes of the type $[Ru_3H(C_2R)(CO)_7(L)_2]$. More surprisingly an $[M - H]^-$ ion was observed for $[Co_2(CO)_6(dppm)]$; the proton must be extracted from the CH_2 group of the dppm ligand which is known to be acidic.[34]

Similarly, as mentioned above, addition of OMe^- to the orthomanganated methyl aryl ketones of type **2c** or **3** consistently gave $[M - H]^-$ ions instead of, or as well as, $[M + OMe]^-$ ones. In this case extraction of the proton from the CH_3 group is probable, since the acidity of this site will be enhanced by co-ordination of the adjacent C=O group to manganese.

Finally, a weak peak corresponding to an $[M - H]^-$ ion was observed for $[Ru_6C(CO)_{14}(C_6H_5Me)]$. Co-ordination of toluene presumably enhances the acidity of the Me group, possibly by stabilising an η^5-$C_6H_5CH_2$ unit related to the η^7-$C_6H_3Me_2CH_2$ ligand derived from mesitylene found in a Ru_6C complex,[33b] although full η^7 bonding is precluded in the absence of CO loss.

(e) Neutral metal carbonyls ionised with Na^+

As discussed above, metal carbonyl compounds with multiple phosphine substitution appear to be too electron rich to encourage attack by OMe^- to give the alkoxide adducts. However during the investigation of these reactions it was noted that the reagent NaOMe sometimes gave clean *positive-ion* mode spectra that could be readily assigned to adducts of the type $[M + Na]^+$. Typical examples include $[Ru_3(CO)_9(PPh_3)_3]$ and $[Fe(CO)_3\{P(OPh)_3\}_2]$. It appears that if the compound is electron rich, sufficient charge resides on the CO ligands for them to attach themselves to the Na^+ cation; for the second example the oxygen atoms of the phosphite provide an alternative site for Na^+ attachment. This process was confirmed by the addition of LiBr, NaBr or KBr to MeOH solutions of $[Ru_3(CO)_9(PPh_3)_3]$ or $[Ru_3(CO)_{10}(AsPh_3)_2]$ which in each case gave ions corresponding to the addition of the different alkali-metal cations to the parent cluster. Alkali-metal adducts are commonly observed with polar organic molecules,[3,4] and have been reported with co-ordination complexes,[35] but the only previous examples of this type of ionisation with metal carbonyl complexes appear to be some rhenium–bipyridyl derivatives.[36] This mode of ionisation also occurs for nitrosyl compounds such as $[Ru(PPh_3)_2(NO)Cl_3]$.[37]

For the examples we have examined so far there appears to be a useful complementarity in behaviour towards the NaOMe reagent. Unsubstituted metal carbonyls add OMe^- but not Na^+, whereas for highly substituted ones it is *vice versa*.

(f) Ionisation of neutral metal carbonyls by oxidation

For some examples we have examined, the ESMS spectrum gave positive ions which appear to have arisen from oxidation to give $[M]^{\bullet +}$ ions. The accuracy and resolution of the spectra are sufficient to distinguish these from $[M + H]^+$ ions, and they were also seen in the presence of OMe^- where protonation would be extremely unlikely. Oxidation at the electrospray source tip is known for other electron-rich substrates,[38] and the metal carbonyl compounds for which it was observed here fall into this category. For $[Ru_4H_4(CO)_9P^aP^bP^c]$[18] [$P^a = PMe_2Ph$, $P^b = P(OTol)_3$ (Tol = tolyl), $P^c = P(OCH_2)_3CEt$] the $[M]^{\bullet +}$ ion was observed in MeOH with nothing added, and gained intensity if Ag^+ was present. For $[Cp(CO)_3W(C{\equiv}C)_4W(CO)_3Cp{\cdot}2Co_2(CO)_4(dppm)]$[16,39] (after treatment with NaOMe), the $[M]^{\bullet +}$ ion was observed along with the $[M + Na]^+$ ion in the positive ion mode and the $[M + OMe]^-$ ion in the negative-ion spectrum.

Another related example was $[Os_4H_2(CO)_{10}(C_6H_6)]$ which, when treated with Ag^+ in MeCN, gave a variable-intensity peak at *m*/*z* 1122 which appeared to be $[M]^{\bullet +}$, in addition to the $[M + Ag]^+$ species. In this case the Ag^+ ion is presumably the oxidising agent since no signal was observed in its absence. It was noted for this example that the relative intensities of the two species varied with time after mixing the cluster solution with Ag^+, for reasons that are not apparent.

Oxidative-ionisation of neutral metal carbonyls appears to be relatively rare, but needs to be considered for larger, electron-rich molecules.

Conclusions

Electrospray mass spectroscopy can be applied as a routine characterisation technique for a wide variety of metal carbonyl compounds. The ionisation reagent of choice is NaOMe (or equivalent alkoxide) in MeOH since this gives clean $[M + OMe]^-$ ions for compounds in which the ligand sphere is predominantly carbonyls, $[M + Na]^+$ ions for higher-substituted electron-rich species, and $[M - H]^-$ ions with compounds containing acidic hydrogen atoms. In some instances Ag^+ ions provide an alternative source of ionisation, but it is a less general method.

We believe routine ESMS will become as useful as solution IR spectra in metal carbonyl chemistry in terms of monitoring reaction mixtures and providing initial identification of products, as we have illustrated in preliminary studies of $[Os_3(CO)_{12}]$ pyrolysis. The only major limitation is where the compounds are very insoluble or are unstable in the appropriate solvents or in the presence of the ionisation reagents.

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