Negative-ion Mass Spectra of Trinuclear Carbonyl Clusters

By **Rosa P. Ferrari, Gian A. Vaglio,*** and **Mario Valle,** Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Torino, Italy

Negative-ion mass spectra at 70 eV of the clusters $[Fe_3(CO)_{12}]$, $[FeRu_2(CO)_{12}]$, $[Ru_3(CO)_{12}]$, $[Ru_2Os(CO)_{12}]$, $[RuOs_2(CO)_{12}]$, and $[Os_3(CO)_{12}]$ are reported. Negative molecular ions are absent, and the trinuclear fragments formed are due to the loss of CO groups mainly by dissociative electron-capture processes. A decreasing intensity of $[M_3(CO)_{11}]^-$, the base peak in the spectrum of $[Os_3(CO)_{12}]$, is observed on passing from Os to Ru and to Fe. The ion $[Ru_3(CO)_{10}]^-$ is the base peak in the spectrum of $[Ru_3(CO)_{12}]$ and $[Fe_3(CO)_9]^-$ in that of $[Fe_3(CO)_{12}]$. The same behaviour is observed in the mixed-metal carbonyls. This trend is explained by the different stability of the ionic species, which it is suggested is mainly related to the strength of the metal–metal bonds. The negative-ion mass spectra of $[Ru_3(CO)_{11}(PEt_2Ph)]$ and $[Os_3(CO)_{11}(PEt_2Ph)]$ indicate that both the M–CO bond strengths and the ionisation potentials of the metals do not play a major role. The negative-ion mass spectra of the compounds $[Fe_3(CO)_9X_2]$ (X = S, Se, or Te) follow a similar behaviour and exhibit $[Fe_3(CO)_7X_2]^-$ as the base peak with a weak $[Fe_3(CO)_8X_2]^-$ when X = Te.

NEGATIVE-ION mass spectra of different classes of metal-containing compounds have been published in the last ten years.[1,2] In particular, metal pentane-2,4-dionates,[3-5] dithiocarbamates,[6] pentane-2,4-dithionates,[1] β-ketoiminates,[1,3] and dimethylglyoximates [1] show negative molecular ions usually accompanied by little fragmentation. Conversely, simple metal carbonyls do not show negative molecular ions,[7-9] except for the electron-deficient $[V(CO)_6]$,[10] and display rather abundant fragment ions.

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We have examined the negative-ion mass spectra of some $[M_3(CO)_{12}]$ carbonyls and of the chalcogen derivatives of $[Fe_3(CO)_{12}]$, and herein describe their fragmentation trends in comparison with the positive-ion mass spectra.

RESULTS AND DISCUSSION

In Table 1 the negative-ion abundances of $[Fe_3(CO)_{12}]$, $[FeRu_2(CO)_{12}]$, $[Ru_3(CO)_{12}]$, $[Ru_2Os(CO)_{12}]$, $[RuOs_2(CO)_{12}]$, and $[Os_3(CO)_{12}]$ at 70 eV are reported.* For each of them the negative molecular ions are absent, as expected and observed for mono-[7,8] and bi-nuclear carbonyls,[11] except $[V(CO)_6]$.[10] It can also be observed that there is a low number of ions, as usual for negative-ion compared with positive-ion spectra, all of them containing the three metal atoms. Only in the case of $[Fe_3(CO)_{12}]$ is the carbonyl-free ion formed and this parallels the presence of Cr^- in the negative-ion mass spectra of Group 6B hexacarbonyls.[7]

TABLE 1

Negative-ion mass spectra (percentage abundances) of $[MM'_2(CO)_{12}]$ at 70 eV

Species	M = M′ = Fe	M = Fe, M′ = Ru	M = M′ = Ru	M = Os, M′ = Ru	M = Ru, M′ = Os	M = M′ = Os
$[MM'_2(CO)_{11}]^-$		10	15	15	61	100
$[MM'_2(CO)_{10}]^-$	45	100	100	100	100	95
$[MM'_2(CO)_9]^-$	100	85	33	55	31	90
$[MM'_2(CO)_8]^-$	83	40	25	55	12	78
$[MM'_2(CO)_7]^-$	18	33	16	19	11	64
$[MM'_2(CO)_6]^-$	50	22	24	15	9	90
$[MM'_2(CO)_5]^-$	48	18	12	8	2	45
$[MM'_2(CO)_4]^-$	35	8	8			
$[MM'_2(CO)_3]^-$	28					
$[MM'_2(CO)_2]^-$	1					
$[MM'_2(CO)]^-$	1					
$[MM'_2]^-$	5					

The spectra of $[Fe_3(CO)_{12}]$, $[Ru_3(CO)_{12}]$, and $[Os_3(CO)_{12}]$ in the low-energy region show resonance peaks for the various negative fragments, which is indicative of dissociative electron-capture processes. The capture maxima occur at increasing energy as more carbonyl groups are lost. This indicates the successive loss of CO groups, as is usually found in positive- and negative-ion breakdown patterns of these compounds, and is confirmed by the metastable transitions observed when slow electrons are used.

The data of Table 1 show a characteristic trend in the intensities of the ions, which cannot be casual and seems to be related to the nature of the metal cluster. The $[M - CO]^-$ ion is the base peak of $[Os_3(CO)_{12}]$, is weak in the spectrum of $[Ru_3(CO)_{12}]$, and absent in that of $[Fe_3(CO)_{12}]$. On the other hand, $[Ru_3(CO)_{10}]^-$ is the base peak of $[Ru_3(CO)_{12}]$ and $[Fe_3(CO)_9]^-$ of $[Fe_3(CO)_{12}]$. The spectra of the three mixed-metal dodecacarbonyls confirm the gradual change in the ion intensities on passing from the first to the third transition series. The intensities of the ions of $[M_3(CO)_{12}]$ (M = Fe, Ru, or Os), measured at their electron-capture maxima, follow the same trend found at 70 eV. This suggests that dissociative processes due to secondary electrons are responsible for the major part of the negative-ion current also at 70 eV, and that ion-pair processes make little contribution to the ionic abundances.

The increasing stability of the metal–carbonyl bonds could explain this trend on descending a sub-group, the cleavage of one Os–CO bond being enough to reduce the excitation energy and stabilise $[Os_3(CO)_{11}]^-$, whilst cleavage of two or three M–CO bonds is required to eliminate the excitation energy in the spectra of the other compounds examined. However, an analogous behaviour was not observed in the spectra of all the mononuclear carbonyls, where the $[M - CO]^-$ ion is always the most abundant.

Alternatively one can suggest that this trend arises from the different degrees of back donation from the metals, which is responsible for the partial redistribution of the negative charge to the carbonyl groups. Atomic osmium exhibits the highest ionisation potential (8.5 eV) [12] and hence less back donation, so that the best charge delocalisation should occur in the ionic fragment with the highest number of CO groups, *i.e.* $[Os_3(CO)_{11}]^-$. Similar arguments have been used by Chini [13] to speculate on the different geometries of the polynuclear carbonyls $[M_3(CO)_{12}]$ and $[M_4(CO)_{12}]$, but the ionisation potentials of ruthenium (7.36 eV) [12] and iron (7.87 eV) [12] do not reflect the trend observed here. Thus, the different M–CO bond strengths and the back donations of the metals do not seem to play a major role. In particular, if the back donation were largely involved, substitution of CO with PR_3 in $[Os_3(CO)_{12}]$ should increase the back donation to the carbonyl groups and the negative-ion mass spectrum of $[Os_3(CO)_{11}(PR_3)]$ should exhibit a behaviour similar to $[Fe_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$. We have recorded the spectrum of $[Os_3(CO)_{11}(PEt_2Ph)]$ [14] which displays a behaviour completely analogous to $[Os_3(CO)_{12}]$. At 70 eV $[Os_3(CO)_{10}(PEt_2Ph)]^-$ is the base peak (100%), followed by $[M - 2CO]^-$ (52), $[M - 3CO]^-$ (55), $[M - 4CO]^-$ (35), $[M - 5CO]^-$ (23), $[M - 6CO]^-$ (35), and $[M - 7CO]^-$ (18%). Moreover, the

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 atm = 101 325 Pa.

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negative-ion mass spectrum of $[Ru_3(CO)_{11}(PEt_2Ph)]$[15] shows $[Ru_3(CO)_8(PEt_2Ph)]^-$ as the base peak (100%), the other fragments being $[M - CO]^-$ (20), $[M - 2CO]^-$ (75), $[M - 4CO]^-$ (35), $[M - 5CO]^-$ (32), and $[M - 6CO]^-$ (24%), confirming that the influence of different M–CO bond strengths is small.

Since the exact nature of the lowest unoccupied molecular orbitals (l.u.m.o.s) in these species is not known, in an attempt to rationalise the experimental results we have compared their positive- and negative-ion mass spectra. In the positive-ion mass spectrum of $[Fe_3(CO)_{12}]$[16] a large part of the ion current is transported by mono- and bi-nuclear ions, which are present only to a small extent in the spectrum of $[Ru_3(CO)_{12}]$[16] and are absent in that of $[Os_3(CO)_{12}]$.[17] These results have been interpreted in terms of the increase in M–M bond stability on descending a triad of the transition series, in complete agreement with the chemical evidence. On this basis, the trend observed in the negative-ion mass spectra of $[M_3(CO)_{12}]$ can be explained by assuming that the negative ions from $[Os_3(CO)_{12}]$ contain the intact cluster Os_3, which enhances the delocalisation of the single electron and stabilises $[M - CO]^-$. Oppositely, for $[Fe_3(CO)_{12}]$ and partially for $[Ru_3(CO)_{12}]$, we suggest that the redistribution of the added electron is made less favourable by the rupture of one M–M bond, so that stability is reached only after the elimination of one or two more CO groups. This trend is also followed by $[Os_3(CO)_{11}(PEt_2Ph)]$, which exhibits an abundant positive molecular ion and fragments which all contain the Os_3 unit, and by $[Ru_3(CO)_{11}(PEt_2Ph)]$ whose positive-ion mass spectrum contains also bi- and mono-nuclear ions.

In Table 2 the negative-ion mass spectra at 70 eV of the compounds $[Fe_3(CO)_9X_2]$ (X = S, Se, or Te) are reported. The abundances of the positive ions of $[Fe_3(CO)_9Se_2]$ and $[Fe_3(CO)_9Te_2]$, reported while this work was in progress,[18] are also given. The positive-ion mass spectrum of $[Fe_3(CO)_9S_2]$ was reported previously.[19] The ion $[Fe_3(CO)_7X_2]^-$ is the base peak and the highest mass ion for all the three compounds except for the telluro-complex, where a weak $[Fe_3(CO)_8Te_2]^-$ peak is observed. This trend is followed also at the capture maxima, in the low-energy region. The ion intensities do not seem to be obviously related to the nature of X, and this indicates that the added electron occupies an orbital of principally metal character. The behaviour exhibited by the $[Fe_3(CO)_9X_2]$ compounds is similar to that of $[Fe_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$, since in the positive-ion mass spectra of $[Fe_3(CO)_9X_2]$ the current is partially transported by bi- and mono-nuclear ions and the negative base peak originates through the loss of more than one CO group.

An analogous behaviour is shown by $[Mn_2(CO)_{10}]$[11] and $[Re_2(CO)_{10}]$. In the negative-ion mass spectrum of $[Re_2(CO)_{10}]$ the base peak is $[Re_2(CO)_9]^-$ (100%) and the other fragments are $[Re_2(CO)_8]^-$ (14), $[Re_2(CO)_7]^-$ (16), $[Re_2(CO)_6]^-$ (11), and $[Re_2(CO)_5]^-$ (7%).

TABLE 2

Negative- and positive-ion mass spectra (percentage abundances) of $[Fe_3(CO)_9X_2]$

	X	
Species	Se	Te
$[Fe_3(CO)_9X_2]^+$	31	24
$[Fe_3(CO)_8X_2]^+$	54	32
$[Fe_3(CO)_7X_2]^+$	32	29
$[Fe_3(CO)_6X_2]^+$	21	11
$[Fe_3(CO)_5X_2]^+$	16	10
$[Fe_3(CO)_4X_2]^+$	31	31
$[Fe_3(CO)_3X_2]^+$	68	42
$[Fe_3(CO)_2X_2]^+$	40	27
$[Fe_3(CO)X_2]^+$	31	25
$[Fe_3X_2]^+$	100	100
$[Fe_2X_2]^+$	39	30
$[Fe_2X]^+$	24	41
$[Fe_2]^+$	7	9
$[FeX]^+$	6	
Fe^+	44	
$[Fe_3(CO)_8X_2]^{2+}$		4
$[Fe_3(CO)_7X_2]^{2+}$	2	5
$[Fe_3(CO)_6X_2]^{2+}$	1	2
$[Fe_3(CO)_5X_2]^{2+}$	1	2
$[Fe_3(CO)_4X_2]^{2+}$	2	3
$[Fe_3(CO)_3X_2]^{2+}$	4	5
$[Fe_3(CO)_2X_2]^{2+}$	5	5
$[Fe_3(CO)X_2]^{2+}$	5	6
$[Fe_3X_2]^{2+}$	7	8

		X	
Species	S	Se	Te
$[Fe_3(CO)_9X_2]^-$			
$[Fe_3(CO)_8X_2]^-$			2
$[Fe_3(CO)_7X_2]^-$	100	100	100
$[Fe_3(CO)_6X_2]^-$	75	65	68
$[Fe_3(CO)_5X_2]^-$	32	42	27
$[Fe_3(CO)_4X_2]^-$	34	28	19
$[Fe_3(CO)_3X_2]^-$	52	25	11
$[Fe_3(CO)_2X_2]^-$	12	21	6
$[Fe_3(CO)X_2]^-$	25	15	
$[Fe_3X_2]^-$			

It can be concluded that the M–M bond strength is likely to be the main factor controlling the stability of the ionic species in the negative-ion mass spectra of these carbonyl clusters.

EXPERIMENTAL

The mass spectra were recorded on a single-focusing Hitachi RMU 6H mass spectrometer, with a trap current of 20 μA, when the ionising energy was 70 eV. All the compounds were prepared as described in the literature; $[Ru_2Os(CO)_{12}]$ and $[RuOs_2(CO)_{12}]$ were also prepared from $[Ru_2(CO)_6Cl_4]$ and OsO_4 in a high-pressure process. In a typical experiment a methanol solution of $[Ru_2(CO)_6Cl_4]$ (0.303 g) and OsO_4 (0.100 g) in the presence of Zn (1.0 g) was heated at 140 °C for 62 h in an autoclave (0.25 l) under carbon monoxide at 95 atm. The solution was dried under reduced pressure and the residue, dissolved in hot benzene, was separated by t.l.c. [absorbent, Kieselgel $PF_{254 + 336}$; eluant, light petroleum (b.p. 40—60 °C) and 3% benzene] to give four bands: $[Ru_3(CO)_{12}]$, $[Ru_2Os(CO)_{12}]$, $[RuOs_2(CO)_{12}]$, and $[Os_3(CO)_{12}]$. Infrared spectrum in $CHCl_3$: $[Ru_2Os(CO)_{12}]$, 2 062vs, 2 030s, 2 013w, 2 004w(sh); $[RuOs_2(CO)_{12}]$, 2 066vs, 2 032s, 2 014w, and 2 004w cm^{-1}.

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