

Studies of η^6 -Arenetricarbonylmetal Compounds by Negative Ion Mass Spectrometry*

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The negative ion electron impact mass spectra, at 70 eV, of $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_3$ ($R = \text{CH}_3, \text{CH}_2\text{OH}, \text{Cl}$) $[\eta^6\text{-1,3,5-(CH}_3)_3\text{C}_6\text{H}_3]\text{Cr}(\text{CO})_3$, $(\eta^6\text{-C}_6\text{H}_5\text{COR})\text{Cr}(\text{CO})_3$ ($R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}(\text{CH}_3)_3$), $[\eta^6\text{-(o-CH}_3\text{C}_6\text{H}_4\text{COC}_3\text{H}_7)]\text{Cr}(\text{CO})_3$, $(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{COR})\text{Cr}(\text{CO})_3$ ($R = \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$), $(\eta^6\text{-C}_6\text{H}_5\text{COOCH}_3)\text{Cr}(\text{CO})_3$, $[\eta^6\text{-(p-CH}_3\text{C}_6\text{H}_4\text{COOCH}_3)]\text{Cr}(\text{CO})_3$, $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{W}(\text{CO})_3$ ($R = \text{CH}_3, \text{Cl}$) and $(\eta^6\text{-C}_6\text{H}_5\text{-COOCH}_3)\text{W}(\text{CO})_3$ are reported. The negative molecular ion is present in the spectra of the compounds containing the carbonyl function in the ligand, while $[\text{M-CO}]^-$ is the highest mass ion in the spectra of the other compounds. The most abundant fragments are the species $[\text{M}-n\text{CO}]^-$ ($n = 1, 2, 3$). The intensity of the molecular peak is mainly affected by the nature of the moiety bonded to the carbonyl function of the ligand, while the nature of the metal seems to play a minor role. The comparison of the abundances of $[\text{M}]^-$ in the negative ion mass spectra of the metal complexes and of the corresponding free ligands shows that in the gas phase the tricarbonylchromium and tricarbonyltungsten units display a strong electron withdrawing ability, similar to the behaviour shown in solution.

Introduction

Several papers on the negative ion mass spectra of metal-containing compounds have appeared recently [1–12]. The complementary information obtained from the negative and positive ion mass spectra, and the valuable suggestions on the nature of the negative ion species, are in part responsible for this interest [6, 13]. Moreover the study of the negative ion mass spectra of classes of metal-containing compounds permits one to investigate the electron

capture processes and the factors affecting their electrophilic properties in the gas phase. This can be very interesting, because through the comparison with their properties in solution one can understand whether the electron capture ability is a feature related to the molecular structure, or if it is due to factors such as the solvation effect.

In this paper we report the negative ion electron impact mass spectra, at 70 eV, of $(\eta^6\text{-arene})\text{tricarbonylchromium}$ compounds and of analogous tungsten compounds and discuss their electrophilic behaviour. The negative ion mass spectrum of $(\eta^6\text{-C}_6\text{H}_5\text{COOCH}_3)\text{Cr}(\text{CO})_3$ has been published previously [14] and a paper on the negative ion mass spectra of some compounds of this class has also been published [15] while the present work was in progress.

Experimental

All the compounds were prepared as described in the literature [16, 17]. The mass spectra were run on a single focusing Hitachi RMU 6H mass spectrometer with a trap current of 20 μA , when the ionizing energy was 70 eV. All the samples were introduced into the ion source through a direct inlet system. The pressure of the compound in the source was in the range $4\text{--}6 \times 10^{-6}$ torr. Various compounds, such as $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$, were used as mass reference standard.

Results and Discussion

In Fig. 1 the positive and negative ion mass spectra of $(\eta^6\text{-C}_6\text{H}_5\text{COCH}_2\text{CH}_2\text{CH}_3)\text{Cr}(\text{CO})_3$ are compared. A similar alternance of the ion abundances was observed for all compounds analyzed. Note in Fig. 1 the very low abundance of $[\text{M-CO}]^+$ compared with the very high intensity of the peak corresponding to $[\text{M-CO}]^-$.

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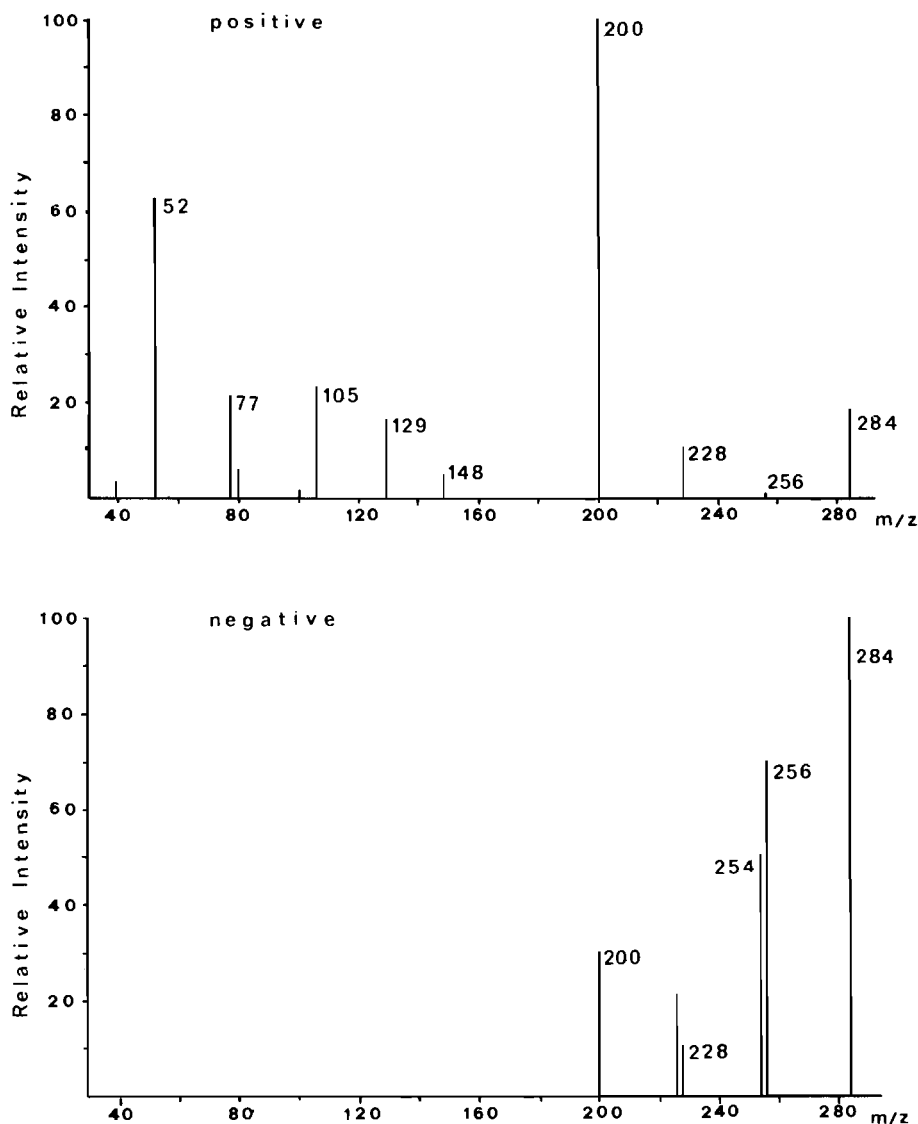


Fig. 1. Positive and negative ion mass spectra of $(\eta^6\text{-C}_6\text{H}_5\text{COCH}_2\text{CH}_2\text{CH}_3)\text{Cr}(\text{CO})_3$ (the ions of the ^{52}Cr isotope are reported).

All the significant ions observed in the 70 eV electron impact negative ion mass spectra of the compounds $(\eta^6\text{-L})\text{Cr}(\text{CO})_3$ are reported in Table I. The molecular negative ion is always observed in the spectra of the compounds where the ligand L contains the unit $\text{C}_6\text{H}_5\text{CO-}$ or $\text{C}_6\text{H}_5\text{CH}_2\text{CO-}$ and is followed by fragments mainly due to loss of the three carbonyl groups. On the contrary no electron resonance capture process occurs when the substituents on the ligand do not contain the CO function (CH_3 , CH_2OH , Cl). As has been published very recently for some monosubstituted $(\eta^6\text{-benzene})\text{tricarboxylchromium}$ [18] and related compounds [19], in the low-energy region the spectra show resonance peaks for the various negative ions. This is indicative that the fragments are formed by dissociative electron

capture processes. It was not possible to measure accurately the capture maxima, but there is evidence that they occur at increasing energy as more carbonyl groups are lost. This feature indicates the stepwise loss of carbonyl groups, which is usually observed in the positive and negative ion mass spectra of carbonylmetal compounds [13, 20]. This is also confirmed by the metastable transitions, which are better observed when low-energy electrons are used.

In Table II the percentage abundances of the significant ions in the 70 eV negative ion mass spectra of some $(\eta^6\text{-arene})\text{tricarboxyltungsten}$ compounds are reported. The charge transported by $[\text{M}]^{--}$ of $(\eta^6\text{-C}_6\text{H}_5\text{COOCH}_3)\text{W}(\text{CO})_3$ is higher than that of the corresponding chromium compound, but the break-

TABLE I. Percentage Abundances of Significant Ions in the 70 eV Negative Ion Mass Spectra of (η^6 -L)Cr(CO)₃.^a

L	Ions [M] ⁻	[M-CH ₃] ⁻	[M-CO] ⁻	[M-(CO + H ₂)] ⁻	[M-2CO] ⁻	[M-(CO + H ₂)] ⁻	[M-3CO] ⁻	[M-4CO] ⁻
C ₆ H ₅ CH ₃			100		2		3	
1,3,5-(CH ₃) ₃ C ₆ H ₃			100		3		5	
C ₆ H ₅ CH ₂ OH			100		3		25	
C ₆ H ₅ Cl			55		65		100	
C ₆ H ₅ COCH ₃	20		100		11		65	
C ₆ H ₅ COCH ₂ CH ₃	60		100		5		15	
C ₆ H ₅ COCH ₂ CH ₂ CH ₃	100		70		10	22	30	
<i>o</i> -CH ₃ C ₆ H ₄ COCH ₂ CH ₂ CH ₃	100		65	50	15		12	
C ₆ H ₅ COC(CH ₃) ₃	100	12	52	35	21		28	
C ₆ H ₅ CH ₂ COCH ₂ CH ₃	1.5		100		11	12	55	
C ₆ H ₅ CH ₂ COCH ₂ CH ₂ CH ₃	3		62	6	12	14	100	
C ₆ H ₅ CH ₂ COC ₆ H ₅	22		12		10	7	100	
C ₆ H ₅ COOCH ₃	45	1	100		15		28	45
<i>p</i> -CH ₃ C ₆ H ₄ COOCH ₃	50	3	100		18		23	40

^aAll isotopic species were summed up.TABLE II. Percentage Abundances of Significant Ions in the 70 eV Negative Ion Mass Spectra of (η^6 -L)W(CO)₃.^a

L	Ions [M] ⁻	[M-CH ₃] ⁻	[M-CO] ⁻	[M-2CO] ⁻	[M-3CO] ⁻	[M-4CO] ⁻
1,3,5-(CH ₃) ₃ C ₆ H ₃			100	36	22	
C ₆ H ₅ Cl			100	40	15	
C ₆ H ₅ COOCH ₃	100	58	65	20	70	12

^aAll isotopic species were summed up.

TABLE III. Percentage Abundances of Significant Ions in the 70 eV Negative Ion Mass Spectra of some (η^6 -L)Cr(CO)₃ Complexes and of the Corresponding L Ligands.^a

Compound	Ions [M] ⁻	[M-H] ⁻	[M-CO] ⁻	[M-2CO] ⁻	[M-3CO] ⁻	[C ₆ H ₅ CH ₂] ⁻	[C ₆ H ₅] ⁻	[C ₂ H] ⁻	[O] ⁻
C ₆ H ₅ COCH ₃		10							
(η^6 -C ₆ H ₅ COCH ₃)Cr(CO) ₃	20	100	11	65		12	11	100	
C ₆ H ₅ COC ₂ H ₅		8							
(η^6 -C ₆ H ₅ COC ₂ H ₅)Cr(CO) ₃	60	100	5	15		4	27	100	
C ₆ H ₅ CH ₂ COC ₂ H ₅		5							
(η^6 -C ₆ H ₅ CH ₂ COC ₂ H ₅)Cr(CO) ₃	1.5	100	11	55	29		12	100	

^aThe ion abundances of C₆H₅COCH₃ and C₆H₅COC₂H₅ are taken from reference 21.

down pattern is similar and both (η^6 -C₆H₅COOCH₃)-W(CO)₃ and (η^6 -C₆H₅COOCH₃)Cr(CO)₃ exhibit, in addition to [M]⁻ and [M-nCO]⁻ (n = 1, 2, 3) fragments, the loss of a methyl group from [M]⁻ and the loss of a fourth CO unit with the rearrangement of the methoxy group to give [(C₆H₅OCH₃)-Cr]⁻ and [(C₆H₅OCH₃)W]⁻.

The loss of a methyl group from [M]⁻ and [M-CO]⁻ also occurs in the spectrum of (η^6 -C₆H₅-COC(CH₃)₃)Cr(CO)₃, as well as the loss of two hydrogen atoms from [M-nCO]⁻ (n = 1, 2) ions from some chromium compounds.

In Table III the ionic abundances in the 70 eV negative ion mass spectra of some (η^6 -L)Cr(CO)₃ complexes, and of the corresponding free ligands L, are compared. From these data it appears that the negative ion mass spectra of the organic compounds C₆H₅COR (R = CH₃, C₂H₅) [21] and C₆H₅CH₂-COC₂H₅ display only weak fragments in the high mass region and are devoid of the negative molecular ion. On the contrary the negative ion mass spectra of the metal complexes containing these organic ligands always exhibit a peak corresponding to [M]⁻, whose intensity depends on the nature of the ligand itself. Similar conclusions are drawn from the comparison of the spectra of C₆H₅COOCH₃ [22] and of the complexes (η^6 -C₆H₅COOCH₃)Cr(CO)₃ and (η^6 -C₆H₅COOCH₃)W(CO)₃. Thus it can be deduced that the coordination to the Cr(CO)₃ or W(CO)₃ unit of the organic compounds such as C₆H₅COR (R = alkyl group, OCH₃) and C₆H₅CH₂COR (R = alkyl group) increases their electron capture ability, provided that the abundance of [M]⁻ in a mass spectrum can be taken as indicative of this property in the gas phase. Therefore one can suggest that in the gas phase the Cr(CO)₃ and W(CO)₃ units display the same strong electron withdrawing capacity as exhibited in solution.

However the coordination of an aromatic ligand to the tricarbonylchromium or tricarbonyltungsten moiety is not on its own sufficient to give stable negative molecular ions. A complex, such as (η^6 -C₆H₅Cl)Cr(CO)₃, containing an electron withdrawing substituent, does not give a stable negative molecular ion. [M]⁻ is, in fact, observed only when the ligand contains a function, such as the carbonyl group, on which the electrophilic site for the addition of the incoming electron can be formally generated, and when the delocalization of the negative charge and of the added electron can occur. Even if the captured electron enters a metal-based orbital in some classes of metal containing compounds [9], we assume that the formation of [M]⁻ of the compounds here examined occurs through the electron capture by a ligand-based orbital. In addition to the ester function [15], in these complexes the carbonyl group of ketones, such as C₆H₅COR and C₆H₅CH₂COR (R = alkyl group), is

TABLE IV. Abundances (% Σ) of $[M]^{-}$ in the Negative Ion Mass Spectra of $(\eta^6\text{-L})\text{Cr}(\text{CO})_3$.

Compound	Abundance (% Σ)
$(\eta^6\text{-C}_6\text{H}_5\text{COCH}_3)\text{Cr}(\text{CO})_3$	10.2
$(\eta^6\text{-C}_6\text{H}_5\text{COC}_2\text{H}_5)\text{Cr}(\text{CO})_3$	33.3
$(\eta^6\text{-C}_6\text{H}_5\text{COC}_3\text{H}_7)\text{Cr}(\text{CO})_3$	35.4
$(\eta^6\text{-o-CH}_3\text{C}_6\text{H}_4\text{COC}_3\text{H}_7)\text{Cr}(\text{CO})_3$	44.0
$(\eta^6\text{-C}_6\text{H}_5\text{COC}(\text{CH}_3)_3)\text{Cr}(\text{CO})_3$	46.9
$(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{COC}_2\text{H}_5)\text{Cr}(\text{CO})_3$	0.8
$(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{COC}_3\text{H}_7)\text{Cr}(\text{CO})_3$	1.5
$(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{COC}_6\text{H}_5)\text{Cr}(\text{CO})_3$	14.5

therefore a good electron capture stabilization unit and behaves similarly to the nitro group bonded to aromatic skeletons [23].

If one reports the intensity of the molecular peak as the percentage of the total ion current intensity (% Σ), as in Table IV, the abundance of $[M]^{-}$ of the $(\eta^6\text{-C}_6\text{H}_5\text{COR})\text{Cr}(\text{CO})_3$ compounds appears to increase with the increased electron donor capacity of R. The presence of an *o*-CH₃ group on the aromatic ring gives the same effect. The variation of the electron density on the electrophilic site does not explain this trend, because the charge transported by $[M]^{-}$ of the $(\eta^6\text{-C}_6\text{H}_5\text{COR})\text{Cr}(\text{CO})_3$ and $(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{COR})\text{Cr}(\text{CO})_3$ complexes should change in the opposite direction. A reasonable explanation, which helps understanding of the experimental observations, can be found by considering the effect of the substituent on the Cr–CO bond strength, since an increase of this strength should reduce the fragmentation and give higher abundances of $[M]^{-}$ and *vice-versa*. If one considers that the change of the Cr–CO bond strength in $[M]^{-}$ is parallel to that observed in the neutral molecule, one can deduce, from a study on the transmission of effect of substituents in $(\eta^6\text{-arene})\text{tricarboxylchromium}$ complexes [24], that the increase of electron donor capacity of R in $(\eta^6\text{-C}_6\text{H}_5\text{COR})\text{Cr}(\text{CO})_3$ increases the Cr–CO bond strength. Therefore this is in agreement with the fact that the stability of $[M]^{-}$ in $(\eta^6\text{-C}_6\text{H}_5\text{COR})\text{Cr}(\text{CO})_3$ compounds increases with increasing electron donor ability of R. The stability of $[M]^{-}$ in $(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{COR})\text{Cr}(\text{CO})_3$ changes in the same way, even if the abundance of $[M]^{-}$ of these compounds is much weaker than that of the corresponding $(\eta^6\text{-C}_6\text{H}_5\text{COR})\text{Cr}(\text{CO})_3$, because the delocalization is much less pronounced.

Therefore the overall features of these spectra, which are affected mainly by the nature of the ligands while the influence of the metal plays a minor role, provide information on the inherent electrophilic properties of this class of carbonyl metal compounds and on the factors which affect such properties.

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