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MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

XXI *. ARENE-CHELATE COMPLEXES OF CHROMIUM AND THEIR FORMATION FROM ARENECHROMIUM TRICARBONYL PRECURSORS **

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Summary

The mass spectra of one-, two- or three-bridge arene-chelate complexes of chromium and some of their precursors (arenechromium tricarbonyl complexes with phosphorus-containing groups in the ω-positions of one or more side chains of the arene ligand) have been investigated. It is shown that under electron impact the latter are converted to the corresponding arene-chelate complexes.

In an earlier work [2] we showed that UV-irradiation of arenechromium tricarbonyl complexes with P^{III} atoms in the ω-positions of one or more side chains tends to cleave off the CO ligands, thereby bringing about the intramolecular coordination of the phosphorus-containing groups and formation of the corresponding arene-chelate complexes.

Since, as follows from published data [3—5], it is decarbonylation of the arenechromium tricarbonyl complexes which is the first process to occur upon electron impact, it might be expected that favorable conditions for the formation of the above-mentioned arene-chelate complexes of chromium from their arenechromium tricarbonyl precursors would be realizable in a mass-spectrometer. In this connection we have undertaken a detailed study of the fragmentation of one-bridge arene-chelate complexes I—VI (Ia: R = OPh, n = 1; Ib: R = OPh, n = 2; Ic: R = OPh, n = 3; Id: R = OPh, n = 4; Ie: R = OPh, n = 5; II: R = Ph, n = 2; IIIa: R = OEt, n = 2; IIIb: R = OEt, n = 3; IV: R = F, n = 2; Va: n =

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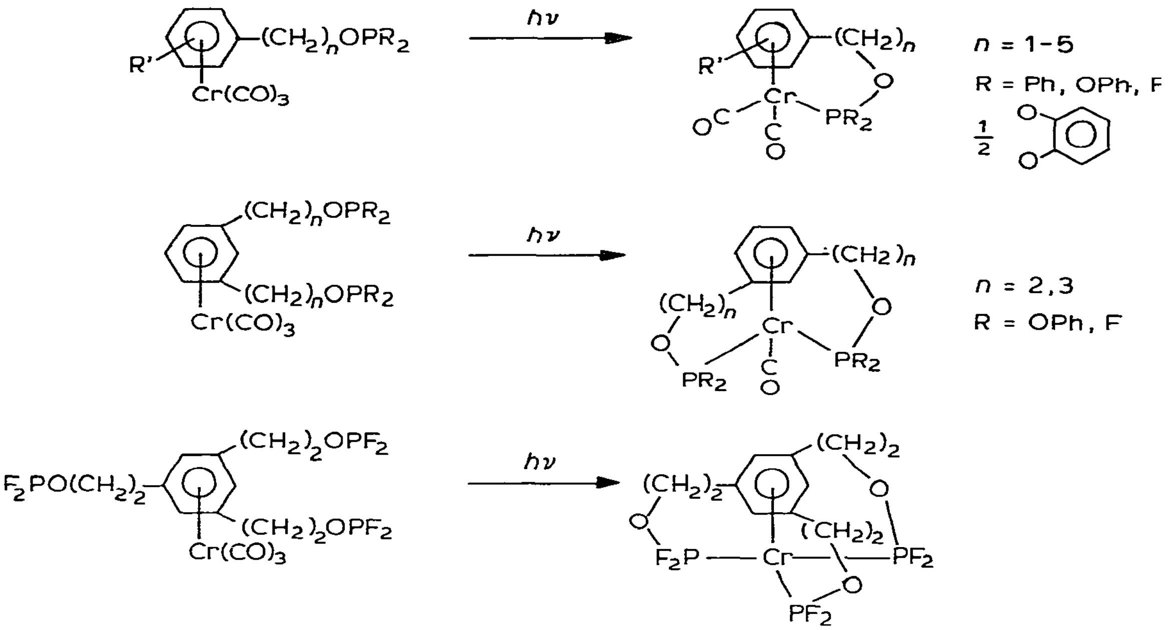
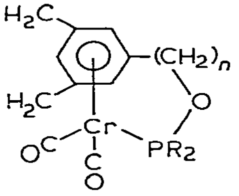
* For Part XX see ref. 1.

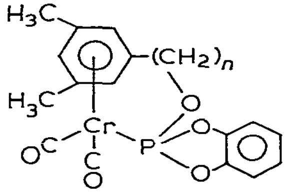
** Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.



2, Vb: $n = 3$; VIa: $n = 2$, VIb: $n = 3$), a two-bridge complex VII and a three-bridge complex VIII, as well as some of their precursors, the arenechromium tricarbonyls IX—XII (IXa: R = OPh, $n = 2$; IXb: R = OPh, $n = 3$; X: R = F, $n = 2$).



(I–IV)



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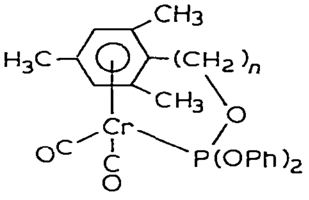

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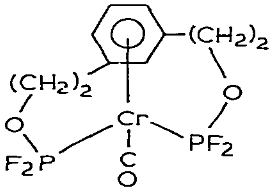

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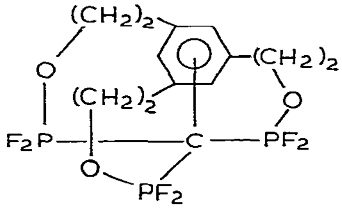

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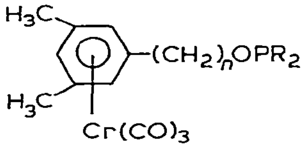
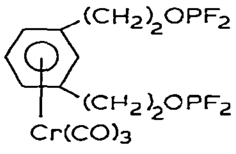
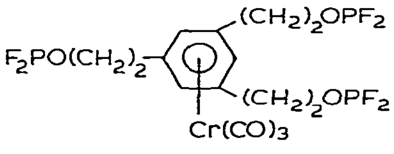


(IX–X)



(XI)



(XII)

The mass spectra of the arene-chelate complexes I—VI show the presence of molecular ions $[M]^+$ which decompose primarily by way of simultaneous ejection of the two carbonyl groups, resulting in the formation of ions $[M - 2\,CO]^+$. Their subsequent fragmentation is controlled chiefly by the nature of the substituent at the phosphorus atom and depends to a smaller degree on the chelate cycle size. Apart from the chromium-containing ions, the mass spectra of these compounds show the presence of intense ligand ions and products of their progressive fragmentation. Such are ions of the type $[Ar(CH_2)_n]^+$ *, phosphorus-containing ions, and some others. The intensities of these ions depend largely on the temperature at which the mass-spectra are recorded. For instance, the relative intensity of the ion $[(CH_3)_2C_6H_4CH_2]^+$ in the mass-spectrum of Ia increases about twofold when the temperatures of the direct insertion system is raised from 100° C to 150° C. This indicates that at least a part of these ions are formed due to the ionization of the thermal decomposition products of the complexes in the sample insertion system. With simultaneous evaporation of the corresponding complexes from the direct inlet system and of heavy water from the all glass inlet heated system, the ions $[C_6H_5OH]^+$ (*m/e* 94) in the mass-spectra of I and VI shift somewhat towards *m/e* 95 $[C_6H_5OD]^+$, implying that these ions are produced in the ionization chamber of the mass spectrometer as a result of the "hydrolysis" of the complexes. For this reason we will consider only metal-containing ions whose intensity does not depend on the temperature conditions during the mass spectrometric measurements.

Common to the mass spectra of all the arene-chelate complexes are the following ions: $[M]^+$, $[M - 2\,CO]^+$, $[Cr]^+$, $[CrPO_2]^+$, $[H_2CArCr]^+$, $[H_2C{=}CH\text{-}(CH_2)_{n-2}ArCr]^+$ (Scheme 1, Tables 1 and 2). All other ions are formed via some specific decomposition routes depending on the nature of the PR_2 group.

A feature which characterizes the fragmentation of the phosphite complexes I and VI is the migration of the phenoxy group towards the chromium atom resulting in formation of intense ions, such as $[LCrPhO]^+$ or $[CrPhO]^+$ (L = Ar, $ArCH_2$, $Ar(CH_2)_n$). Similar fragments $[LCrF]^+$ and $[CrF]^+$, corresponding to fluorine migration towards the chromium atom, are found in the mass spectra of complexes IV. It is known [3—5] that the intensities of ions formed by migration of the substituent from the π- or σ-bonded ligand to the central metal atom are increased with increased electronegativity of the migrant group. Considering this, it was to be expected that ions containing the CrR group in the series F > OEt > OPh should have smaller intensity. It is found, however, that these ions do not occur in the mass spectra of III (R = OEt), and their combined intensities in the spectra of I (R = OPh) and IV (R = F) are approximately the same. The abnormally high intensity of ions containing the CrPhO group is perhaps due to the possible coordination (π-type) between the phenoxy group and chromium atom. Apparently, the same is the reason for the presence in the mass spectra of I and VI (R = OPh) of the intense ions $[CrC_6H_5OH]^+$, wherein the chromium—phenol bond may be only of the π-type.

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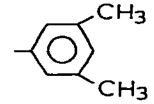
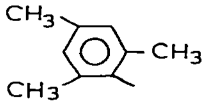
* Ar = 

or 

SCHEME 1

The solid line represents the fragmentation typical of all the complexes.

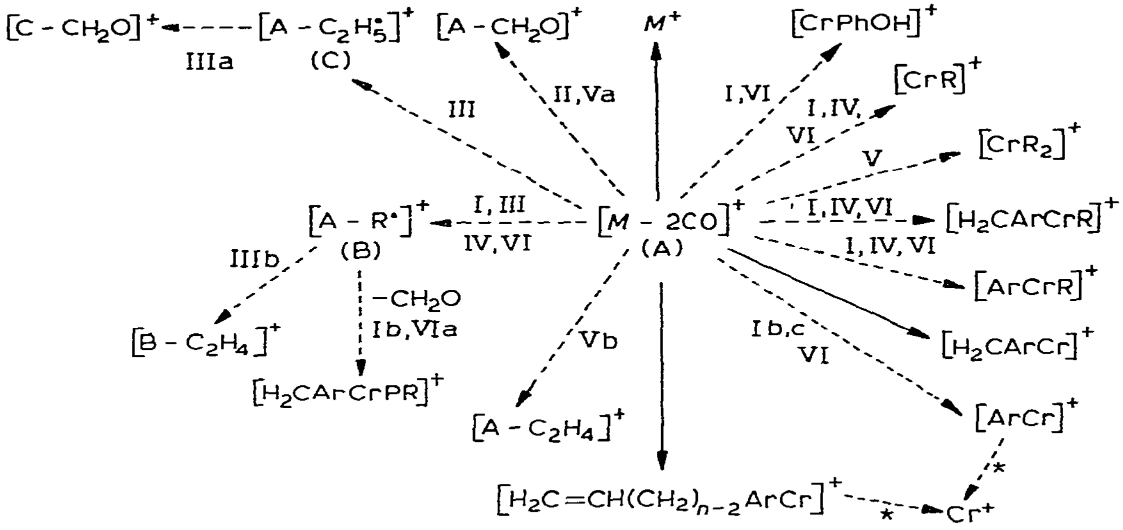


TABLE 1

RELATIVE INTENSITIES OF THE MAJOR IONS IN THE MASS SPECTRA OF THE ARENE-CHELATE COMPLEXES I AND VI (% Σ_{Cr})

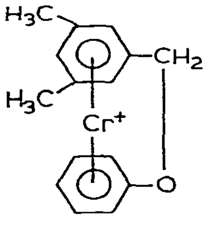
Ion	Ia	Ib	Ic	Id	Ie	VIa	VIb
M^+	0.7	4.0	3.6	3.1	0.5	2.6	2.3
$[M - 2\ CO]^+$	2.8	30.2	24.8	23.9	10.8	23.6	14.2
$[M - OPh]^+$		0.4	0.5			0.3	0.7
$[M - 2\ CO - OPh]^+$		0.8	0.7	0.2		0.6	0.7
$[CrP(O)(OPh)_2]^+$	0.7	1.4	1.0	0.6	1.3	0.8	0.5
$[(CH_2)_nArCrPhO]^+$		2.0	0.5			4.9	
$[CH_2ArCrPhO]^+$	14.1	1.4	33.2	23.3	20.8	1.3	28.7
$[CH_2ArCrPOPh]^+$		0.7				0.9	
$[ArCrPhO]^+$		5.6	0.7	2.4	2.7	15.9	0.5
$[H_2C{=}CH(CH_2)_{n-2}ArCr]^+$		14.1	1.4	4.9	9.4	2.6	0.2
$[(CH_2)_4ArCr]^+$					0.7		
$[(CH_2)_3ArCr]^+$				1.8	1.3		
$[(CH_2)_2ArCr]^+$			1.2				2.5
$[CH_2ArCr]^+$	1.3	1.4	1.9	4.9		2.1	3.4
$[ArCr]^+$		0.8	0.7			0.5	2.0
$[CrPhOH]^+$		7.2	1.9	2.4	4.0	4.7	2.3
$[CrPhO]^+$	8.5	14.1	9.9	11.1	16.2	10.5	8.0
$[CrPO_2]^+$	1.4	1.2	1.6	2.4	4.0	2.1	1.8
$[Cr]^+$	40.6	12.1	11.8	18.4	36.5	17.1	27.5
$[CrPH_3]^+$	10.6						
$[CrPh]^+$	17.3						

TABLE 2

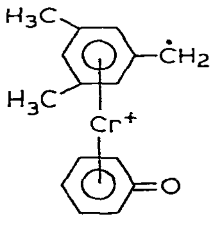
RELATIVE INTENSITIES OF THE MAJOR IONS IN THE MASS SPECTRA OF THE ARENE-CHELATE COMPLEXES OF CHROMIUM II—V (% Σ_{Cr})

Ion	II	IIIa	IIIb	IV	Va	Vb
M^+	4.0	6.7	5.3	9.2	6.3	3.0
$[M - 2\,CO]^+$ (A)	23.0	25.7	17.7	13.9	20.6	12.4
$[M - R^\cdot]^+$		1.2	1.9			
$[A - R^\cdot]^+$ (B)		0.6	0.8	0.1		
$[A - C_2H_4]^+$						4.7
$[A - CH_2O]^+$	20.8				14.8	
$[A - C_2H_5^\cdot]^+$ (C)		2.6	2.9			
$[A - OC_2H_4]^+$ (D)		1.2	0.7			
$[A - C_{13}H_{11}]^+$	2.4					
$[A - PR_2^\cdot]^+$ (E)		1.4	15.8			
$[A - HPR_2]^+$					2.2	16.4
$[B - C_2H_4]^+$			10.1			
$[C - CH_2O]^+$		8.5				
$[D - C_2H_5^\cdot]^+$		8.3				
$[E - CH_3^\cdot]^+$		11.3	13.7			
$[CrP(OH)R_2]^+$	1.8				1.2	1.0
$[CrP(O)R_2]^+$				1.2	0.3	3.2
$[CrP(H)R_2]^+$	1.8					
$[CrPR_2]^+$	1.2				3.8	0.2
$[CrPR_2 - H^\cdot]^+$	2.1					
$[CrPR_2 - H_2]^+$	0.9					
$[CrPO_2]^+$		5.9	5.6		6.6	8.1
$[H_2C{=}CH(CH_2)_{n-2}ArCrR_2]^+$					10.5	4.7
$[H_2C{=}CH(CH_2)_{n-2}ArCr]^+$	0.6	0.6	1.8	17.6	0.3	
$[(CH_2)_2ArCrR]^+$				14.4		
$[CH_2ArCrR]^+$				0.4		
$[ArCrR]^+$				4.9		
$[CrR_2]^+$					11.8	6.8
$[CrR]^+$				6.4		
$[(CH_2)_2ArCr]^+$			6.0			
$[CH_2ArCr]^+$	4.0	6.3	1.0	0.7	3.4	0.6
$[ArCr]^+$	0.1		2.6	0.5	0.1	2.1
$[CrOH]^+$					0.6	0.2
Cr^+	36.8	14.2	14.6	29.8	17.6	25.6

On the basis of these results the ions $[CH_2ArCrPhO]^+$ may be assigned the cyclophane structure XIII or the structure XIV:



(XIII)



(XIV)

The nature of the substituent at the phosphorus atom has a strong effect on the complex fragmentation process. The overall contribution to the fragmentation process from the ions incorporating a chromium—phosphorus bond, an indication of the strength of this bond, decreases more than twofold between the extreme members of the series: Ph > OEt > o-$C_6H_4O_2$ > OPh > F, which parallels the variation of the σ-electron donor capacity of the PR group [6]. The strengthening of the Cr—P bond in complexes located in the left-hand part of this series increases the contribution from the ions formed on breaking of the P—R bonds. Thus the main route of the decomposition of the ethoxy complex IIIa is predominantly via the breaking of the P—OEt and O—Et bonds. This involves successive elimination of acetaldehyde and the ethyl group, ethoxy group, as well as successive abstraction of the ethyl radical and formaldehyde.

The phenyl-phosphite complex II and complex Va are characterized by the formation of ions $[CrP(OH)R_2]^+$ and $[CrPR_2]^+$. In the mass spectra of V the characteristic ions $[M - 2\,CO - HPR_2]^+$ and $[H_2C{=}CH(CH_2)_{n-2}ArCrR_2]^+$ are present. Of particular interest is the latter ion which is formed by abstraction of the POH group from the ion $[M - 2\,CO]^+$. This reaction involves breaking of five bonds (Cr—P, two P—O bonds, C—O and C—H bonds) and formation of three new bonds (two Cr—O bonds and C=C). This process is apparently caused by coordination of the chromium atom with the vinyl group of the arene ligand and results in increased coordinate saturation of the central metal atom and stabilization of the ion formed [7].

In all compounds having two methylene links in the chelate cycle, with the exception of complex IV (R = F), we observed ejection of the formaldehyde molecule at various fragmentation process stages (Scheme 1). The extent of this process increases with the strength of the chromium—phosphorus bond. The formaldehyde detachment is most intense in complexes IIa and Va and somewhat less intense in IIIa (20.8%, 14.8% and 8.5%, respectively). Formaldehyde is not eliminated in compounds whose chelate cycle length is other than two. Thus in complexes IIIb and Vb having three methylene groups in the chelate cycle the characteristic process is rather the abstraction of the ethylene molecule (Table 2, Scheme 1).

The stability of the arene-chelate system towards electron attack, which may be assumed to be characterized by the ratio of the sum of intensities of the ions $[M]^+$ and $[M - 2\,CO]^+$ to the net intensity of all the chromium-containing ions, is maximum at $n = 2$. It decreases sharply for smaller cycles ($n = 1$) and slowly decreases with the increase of n. For example, for the phosphite complexes I the arene-chelate system stability varies, as the number of methylene links in the chelate cycle varies from 1 to 5, in the following manner (%): 3.5; 34.2; 28.4; 27; 11.3. Introduction of an additional methyl group into the benzene ring, as well as the nature of the PR_2 group, has only an insignificant effect on this parameter. One may only note a weak tendency for a reduction of arene-chelate system stability in the series: OPh (34.2%) > OEt (32.4%) > Ph (27%) $\geqslant$ o-$C_6H_4O_2$ (26.9%) > F (23.1%).

A study of the possibility of chelate formation under electron attack in the arenechromium tricarbonyl complexes IX—XII has shown that this process does indeed occur under the conditions in question. This is manifested by the coincidence of the mass spectra of IX and X, beginning with the loss of one carbonyl group, with the mass spectra of the corresponding one-bridge chelate complexes (Figs. 1—3). It is interesting to note that the fragmentation of IX and X is a very different process from the decomposition of standard arene-

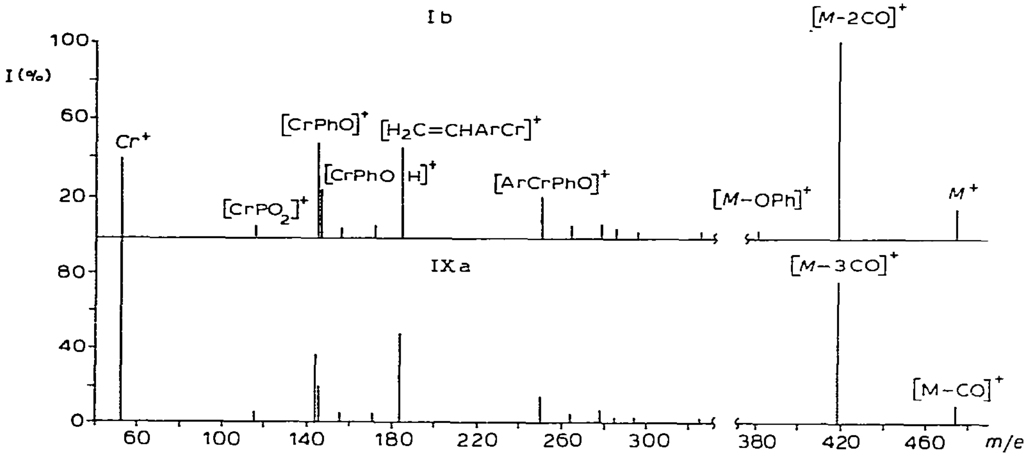


Fig. 1. Mass spectra of the arene-chelate complex of chromium Ib and its arenechromium tricarbonyl precursor IXa.

chromium tricarbonyl complexes [2]. In the mass spectra of the latter there is always a molecular ion and the ion $[M - 2\ CO]^+$ whose intensities are, as a rule, a whole order of magnitude greater than that of the ion resulting from the elimination of one carbonyl group $[M - CO]^+$. Vice versa, in the mass spectra of the precursors IX and X of arene-chelate complexes molecular ions are either absent completely, as they are in IX, or their intensity is very low, as in X whereas ions $[M - CO]^+$ are observed to have a high enough intensity (about 10—15%), and ions $[M - 2\ CO]^+$ are totally lacking.

The processes involving formation of two or three chelate cycles in arenechromium tricarbonyls XI and XII are somewhat more complex. The absence of molecular ions and the high intensity of $[M - CO]^+$ in the mass spectra of XI, XII indicate unambiguously that the first chelate cycle is formed at the

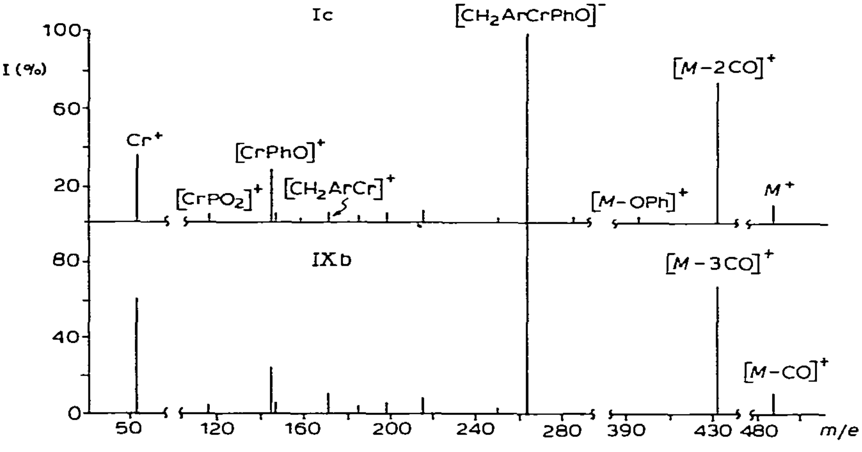


Fig. 2. Mass spectra of the arene-chelate complex of chromium Ic and its arenechromium tricarbonyl precursor IXb.

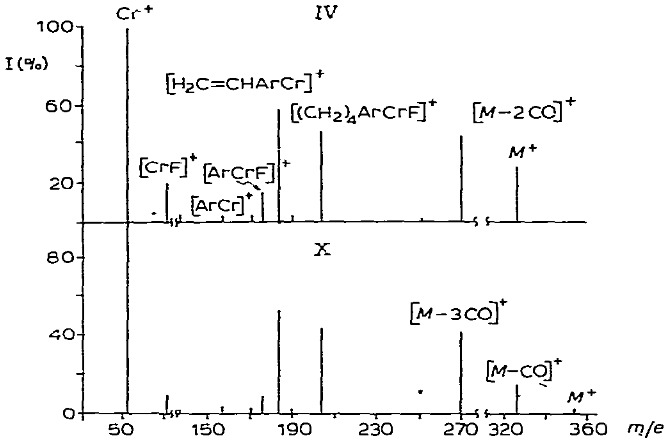


Fig. 3. Mass spectra of the arene-chelate complex of chromium IV and its arenechromium tricarbonyl precursor X.

stage of elimination of one carbonyl group (Figs. 4 and 5). The low intensity of the ions $[M - 2\ CO]^+$ in the mass-spectra of XI and XII (about 2%) suggests that the process of formation of two-bridge monocarbonyl chelates only occurs to a small extent. This assumption is further supported by the ratio $[M - 3\ CO]^+/[M - 2\ CO]^+$ which for XI, XII is 30 whereas in the corresponding two-bridge chelate complex VII the ratio of the similarly composed ions $[M - CO]^+/[M]^+$ is 1.4. At the same time, the fragmentation processes of fully decarbonylated ions are similar to those taking place in the ions $[M - CO]^+$ of the chelate VII and $[M]^+$ of the chelate VIII (Figs. 4 and 5). What this shows is that two- and three-chelate cycles are formed during the elimination of three CO groups in compounds XI and XII.

Thus, the arenechromium tricarbonyl complexes, such as $Ar(CH_2)_nOPR_2Cr(CO)_3$, $Ar[(CH_2)_2OPF_2]_n$ ($n = 2, 3$) are converted under electron impact into

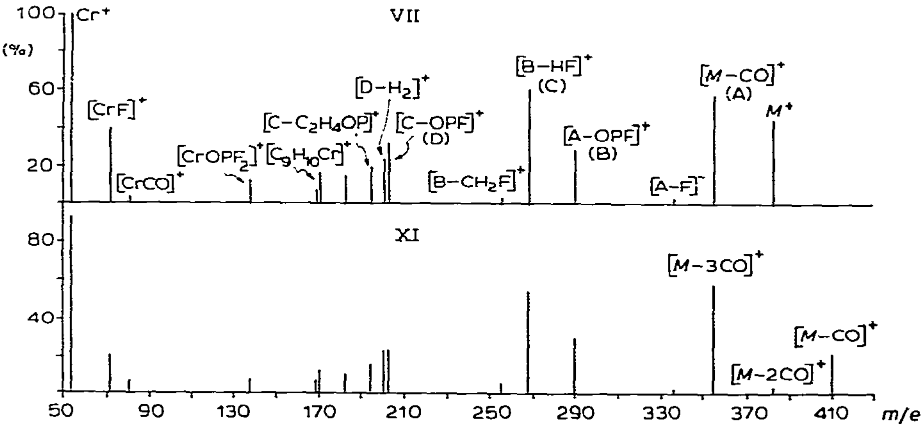


Fig. 4. Mass spectra of the arene-chelate complex of chromium VII and its arenechromium tricarbonyl precursor XI.

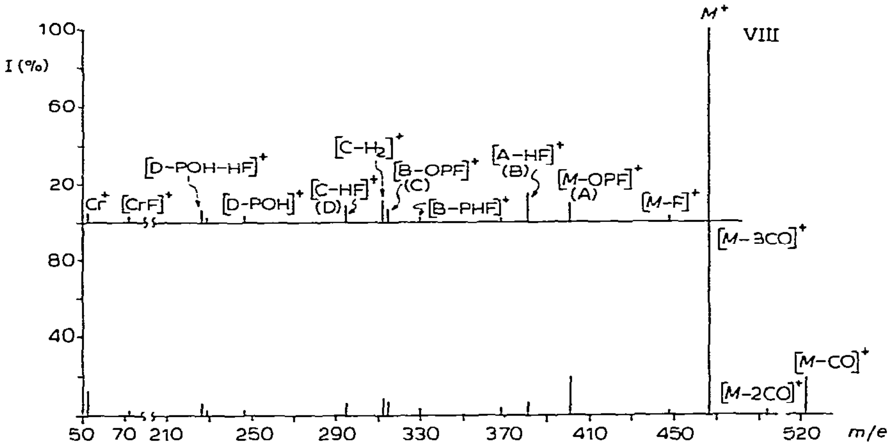


Fig. 5. Mass spectra of the arene-chelate complex of chromium VIII and its arenechromium tricarbonyl precursor XII.

the corresponding arene-chelate analogs at various stages of the decarbonylation.

Experimental

The mass spectra were recorded in an AEI MS-30 instrument coupled to a DS-50 data acquisition system; direct inlet system temperature between 50 and 200° C, ionization chamber temperature 250° C, emission current 100 μA, and ionizing electron energy 70 eV.

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