COMPARISON OF ELECTRON IMPACT AND CHEMICAL IONIZATION MASS SPECTRA OF SOME ARENETRICARBONYLCHROMIUM COMPLEXES

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(Received September 10th, 1979)

Summary

The mass spectrometric behavior of a) the tricarbonylchromium complexes of a series of aromatic hydrocarbons, b) the dimethyldiphenyl compounds of the Group IV elements (i.e., diphenylpropane, dimethyldiphenylsilane, etc.) and c) the mono- and bis-tricarbonylchromium complexes of these ligands under electron impact and chemical ionization conditions are reported. The MH^+ ion is base peak for all of the simple arenetricarbonylchromium complexes using chemical ionization, whereas $[M - 3\ CO]^+$ or $^{52}Cr^+$ dominate the spectra with electron impact ionization. The chemical ionization spectra of the series of Group IV element ligands do not exhibit signals in the molecular ion region, the base peak being $[M - Ph]^+$. $[M - CH_3]^+$ is the electron impact base peak for each of the ligands except the lead-containing compound, for which the base peak is $^{208}Pb^+$. The mono-tricarbonylchromium complexes yield chemical ionization molecular ion clusters, but their base peaks arise via fragmentation of the Group IV element—aromatic ring bonds. Electron impact ionization spectra of the mono complexes are characterized by losses of CO and the production of Cr^+ ions, neither of which occurs with chemical ionization. For the series of bis-tricarbonylchromium complexes, an MH^+ ion is prominent only in the chemical ionization spectrum of the diphenylpropane complex. The electron impact induced spectra of the bis-tricarbonylchromium complexes are similar to those of the mono-complexes in that loss of CO is a prominent feature.

Introduction

Though mass spectrometry has become a commonly used method for identification of organometallic compounds, systematic studies of the fragmenta-

tion patterns of these complexes have been less frequent [1]. Further, the technique of chemical ionization (CI) which often causes little fragmentation and produces relatively simple mass spectra [2] has been used much less than the more highly energetic electron impact ionization (EI) with organometallic complexes. Hunt et al. [3] have reported the CI mass spectrometry of several organometallic complexes. Also, Anderson and coworkers [4] have discussed the CI mass spectra of a number of benzene and substituted benzene tricarbonylchromium complexes. Müller [5] has discussed the decomposition of organometallic compounds in the mass spectrometer. A field desorption study of benzenetricarbonylchromium produced a mass spectrum very similar to its CI spectrum [6]. Appearance potentials [7] and negative ion mass spectra [8] of arenetricarbonylchromium complexes have also been measured. In 1970, we described the gas chromatography-EI mass spectrometry of a series of arenetricarbonylchromium complexes [9]. We now report the results of an expanded study on the CI and EI mass spectrometric behavior of a number of arenetricarbonylchromium complexes, with particular emphasis on complexes formed from a series of ligands containing group IV elements.

Apparatus and materials

The compounds studied were synthesized by procedures found in the literature [10]. Further details on the synthesis of the complexes of ligands containing the Group IV congeners will be published separately [11]. All compounds used gave satisfactory elemental analyses and NMR and IR spectra. Mass spectra were obtained by direct probe using a Finnigan 3200 quadrupole instrument equipped with 6110 data system. Mass spectrometer operating conditions for CI were as follows: reagent gas, methane; ionizing potential, 150 eV; emission current, 0.8 mA; electron multiplier, 1800 V, source temperature 130°C; EI conditions were: ionizing potential, 70 eV; emission current, 0.8 mA; electron multiplier, 1800 V.

Results and discussion

The simplest complex studied was benzenetricarbonylchromium. Its EI mass spectrum contains a molecular ion at m/e 214 (^{52}Cr), with ions assignable to $[M - CO]^+$, $[M - 2\ CO]^+$, $[M - 3\ CO]^+$, $[M - Cr(CO)_3]^+$ and Cr^+ as well as other ions resulting from fragmentation of the benzene portion of the molecule. The base peak is $[M - 3\ CO]^+$. In contrast, the CI mass spectrum of this complex consists essentially of the pseudomolecular ion or $M\text{H}^+$ (base peak) of m/e 215 (protonation of the ^{52}Cr complex), the associated isotope peaks, and the molecular ion (41% relative intensity). Virtually no $[M + C_2H_5]^+$ is observed, nor are more than a trace of ions involving losses of CO. The simplicity of the CI spectrum compared to the EI spectrum is typical of the tricarbonylchromium complexes of other hydrocarbon ligands [4] (and, indeed, of other families of compounds [2]). Mass spectral data for this and several other compounds are presented in Table 1. In all cases, the base peak under CI conditions is the $M\text{H}^+$ ion. We also find relatively intense M^+ ions as did Anderson, et al. [4], who ascribed their large abundance to charge exchange reactions of $C_2H_5^+$.
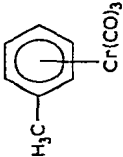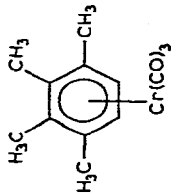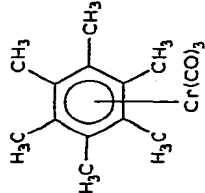
On the other hand, under EI conditions base peaks are $[M - 3\ CO]^+$ or $^{52}Cr^+$ (essentially none of this ion is noted in the CI spectra). The only exceptions among the compounds reported here are the highly strained paracyclophane complex where formation (EI) of the most intense ion involves not only the loss of 3 CO but also the scission of the hydrocarbon into two halves, and the highly aromatic triptycene complex in which this anthracene-derived species undergoes major molecular alteration to produce a base peak of m/e 126. Even with these complexes it is the MH^+ ion which is the CI base peak. The ion of m/e 243 in the CI spectrum of the p-dimethoxybenzene complex is assigned to $[CH_3OC_6H_4Cr(CO)_3]^+$; its appearance results from loss of CH_3OH from MH^+ and may indicate that protonation in this case occurs, in part at least, in one of the oxygen atoms rather than on the metal atom. Non-metal protonation has been invoked by Anderson et al. [4] for the tricarbonylchromium complex of methyl benzoate.
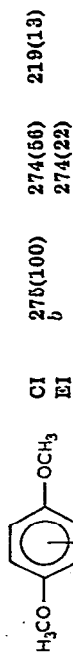
Data for the dimethyldiphenyl compounds of the Group IV elements * and their mono-tricarbonylchromium complexes are given in Table 2. The CI spectra of the free ligands are characterized by very weak or totally absent molecular ion clusters, with no evidence for any MH^+ ions. As these molecules contain sites where protonation can readily occur, the low abundance of MH^+ ions may result from the rapid decomposition of the excited MH^+ ions produced by the exothermic proton transfer reaction. Fish et al. [12] have noted similar behavior in a series of alkyl and aryl organotin compounds. For all five ligands the base peak results from the loss of a phenyl group, indicating the ease of scission of the E—Ph bond (even under the low energy CI conditions) and the stability of the resulting ion, $PhEMe_2^+$ with all of the group IV elements. The only other significant peak observed is that resulting from the loss of a methyl group; this ion is least intense for the carbon compound, increases with silicon (15%) and is essentially constant for germanium, tin and lead (~22%). Under EI conditions the $[M - CH_3]^+$ ion is the base peak of all the ligands except for the lead compound, where Pb^+ and $C_6H_5Pb^+$ are more prominent. Sn^+ also appears in the spectrum of the tin compound. Much less intense than the $M - 15$ ions in these EI spectra are the $M -$ Ph ions, the base peaks of the CI spectra of these five ligands. This suggests that breaking the E—Ph bond requires less energy (CI) than breaking the E—CH$_3$ bond (EI), although factors other than bond breaking may be involved. Moderately intense (~25%) EI molecular ions are observed for the carbon-, silicon- and germanium-containing ligands, in contradistinction to the lack of M^+ (or MH^+) ions produced under CI conditions. This may at first seem to be anomalous, as CI is commonly held to be more likely than EI to yield ions in the molecular ion region. An analogous situation is found with sterol trimethylsilyl ethers, in which only low intensity signals are found in the CI molecular ion region (base peaks of $[MH - 90]^+$), whereas the M^+ is of moderate intensity under EI conditions [13]. The molecular ion regions of the CI and EI spectra are relatively barren of signals for the tin- and lead-containing ligands, again suggesting the influence of the central element upon mass spectrometric behavior.

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* For ions from these compounds, all m/e values refer to those arising from the most abundant isotope-i.e., ^{12}C, ^{28}Si, ^{74}Ge, ^{120}Sn, ^{208}Pb; chromium is always taken as ^{52}Cr.

TABLE 1

CI AND EI MASS SPECTRA OF SOME ARENETRICARBONYLCHROMIUM COMPLEXES

Compound	Type	Ion, m/e (relative intensity, %)							
		MH^+	M^+	$[MH-2\,CO]^+$	$[M-2\,CO]^+$	$[M-3\,CO]^+$	$[MH-Cr(CO)_3]^+$	$[M-Cr(CO)_3]^+$	Other[a]
(benzene)–Cr(CO)₃	CI	215(100) b	214(41)		158(2)				187(2)
	EI		214(5)		158(1)	130(14)		78(9)	52(100)
H₃C–(benzene)–Cr(CO)₃	CI	229(100) b	228(48)		172(3)				
	EI		228(5)		172(2)	144(22)		92(5)	52(100)
(CH₃, H₃C, H₃C–benzene)–Cr(CO)₃	CI	271(100) b	270(44)		214(2)				
	EI		270(3)		214(2)	186(24)		134(4)	52(100)
(CH₃, CH₃, H₃C, H₃C–benzene)–Cr(CO)₃	CI	299(100) b	298(49)		242(2)				
	EI		298(3)		242(3)	214(37)		162(4)	52(100)
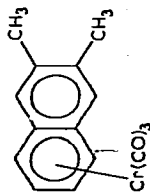
Compound 1 — [H₃CO–C₆H₄–OCH₃ with Cr(CO)₃]

CI	275(100)ᵇ	274(56)	219(13)	218(17)	190(100)	138(12)
EI		274(22)				

Right column — CI: 243(13), 215(6); EI: 52(62), 123(10)

Compound 2 — [dimethyl‑arene (CH₃, CH₃) with Cr(CO)₃]

CI	293(100)ᵇ	292(58)	237(37)	236(19)	208(100)	157(8)	156(21)
EI		292(18)					

Right column — CI/EI: 52(78), 141(29)

Compound 3 — [cyclophane with –Cr(CO)₃]

CI	345(100)ᵇ	344(40)	288(3)	260(77)	209(7)	208(5)
EI		344(7)	288(13)			

Right column — EI: 52(72), 104(48), 156(10⒪)

Compound 4 — [triptycene with –Cr(CO)₃]

CI	391(100)ᵇ	390(43)	335(9)	334(6)	306(5)	254(65)
EI		390(4)			306(65)	

Right column — CI: 307(6); EI: 126(100)

ᵃ 187 = $[MH - CO]^+$; 52 = Cr^+; 243 = $[MH - CH_3OH]^+$; 215 = $[MH - (CH_3OH + CO)]^+$; 123 = $[M - (Cr(CO)_3 + CH_3)]^+$ = 141; 104 = $\left[H_2C{=}\underset{}{\bigcirc}{=}CH_2 \right]^+$

166 = $\left[H_2C{=}\underset{Cr}{\bigcirc}{=}CH_2 \right]^+$; 307 = $[MH - 3\,CO]^+$; 126 = [naphthalene‑type cation]
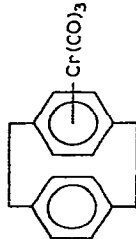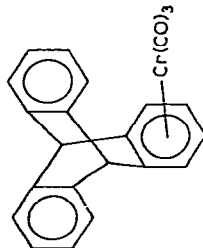
ᵇ The intensities of these ions (actually $M + 1$) are those expected from the corresponding M^+ ions.

sponding M^+ ions.

TABLE 2

CI AND EI MASS SPECTRA OF SOME GROUP IV LIGANDS AND THEIR MONO-TRICARBONYLCHROMIUM COMPLEXES

Structures: Ph$_2$E(CH$_3$)$_2$ (I); and its $Cr(CO)_3$ arene complex (II).

Ion, m/e (relative intensity, %)

Compound	Type	MH^+	M^+	$[M - Me]^+$	$[M - Ph]^+$	$[M - 3\,CO]^+$	$[M - (Cr(CO)_3 + Me)]^+$	$PhEMe_2^+$	PhE^+	E^+	Other[a]
Ia, E = C	CI	b	196(1)	181(3)	119(100)			119(100)	89(5)		77(27), 165(20)
	EI	c	196(22)	181(100)	119(5)			119(5)			
IIa, E = C	CI	333(20)	332(16)		255(<0.5)			119(100)	89(1)		52(83)
	EI	333(4)	332(12)		256(<0.5)	248(100)	118(16)				
Ib, E = Si	CI	b	212(0.5)	197(15)	135(100)			135(100)	105(46)		77(12), 181(7)
	EI	c	212(26)	197(100)	136(17)			135(17)			
IIb, E = Si	CI	349(22)	348(18)		271(40)			135(100)	105(6)		52(49)
	EI	349(4)	348(12)			264(100)	197(6)	135(14)			
Ic, E = Ge	CI	b	258(<0.5)	243(21)	181(100)			181(100)	151(65)		77(11), 227(31)
	EI	c	258(26)	243(100)	181(16)			181(16)			
IIc, E = Ge	CI	395(19)	394(37)		317(100)			181(66)	151(20)		52(61), 280(4)
	EI	395(2)	394(7)			310(100)	243(22)	181(10)			
Id, E = Sn	CI	b	304(<0.5)	289(23)	227(100)			227(100)	197(23)	120(29)	77(8), 273(2)
	EI	c	304(1)	289(100)	227(4)			227(4)			
IId, E = Sn	CI	441(9)	440(28)		363(100)			227(48)	197(27)	120(19)	52(100), 326(23)
	EI	441(3)	440(10)			356(90)	289(9)	227(3)			
Ie, E = Pb	CI	b	392(<0.5)	377(22)	315(100)			315(100)	285(40)	208(100)	77(11), 361(0,5)
	EI	c	392(<0.5)	377(27)	315(4)			315(4)			
IIe, E = Pb	CI	529(8)	528(30)		451(100)			315(52)	285(10)	208(28)	52(100), 414(13)
	EI	529(2)	528(5)			444(25)	377(2)	315(1)			

[a] $77 = C_6H_5^+$, $165 = 181 = 227 = 273 = 361 = [M - 31]^+$; $52 = Cr^+$; $280 = 326 = 414 = [M - (3\,CO + 2\,Me)]^+$. [b] No evidence for an MH^+ ion. [c] The intensities of these ions (actually $M + 1$) are those expected from the corresponding M^+ ions.

As is frequently the case with many types of compounds, the CI spectra of the complexes are considerably simpler than the corresponding EI spectra, with only a few fragment ions being observed. The mono complexes, in contrast to the free ligands, do yield CI molecular ion clusters (Table 2). However, for none of the complexes is either M^+ or MH^+ the base peak, which is $[M - PhCr(CO)_3]^+$ (or $[PhEMe_2]^+$) for carbon and silicon, and $[M - Ph]^+$ for germanium, tin and lead (the same as for all the uncomplexed ligands). When the intensity of the $[M - PhCr(CO)_3]^+$ ion is high, that of the $[M - Ph]^+$ ion is low, and vice versa in the series IIa—IIe; with the higher members of the series, scission of the E—Ph bond is predominant, and breaking of the E—PhCr(CO)$_3$ bond is more readily accomplished when E is C or Si. A true MH^+ ion is noted only for the carbon and silicon complexes, the CI $[M + 1]^+$ peak being more intense than the M^+ peak; the opposite is true for the germanium, tin and lead complexes. The ratio of $M^+/[M + 1]^+$ for the latter two complexes under CI conditions is not greatly different from that observed in the EI spectra. The CI $M^+/[M + 1]^+$ ratio for the germanium complex is significantly less than the analogous EI ratio, indicating a modest production of MH^+ ions with IIc. Formation or stability of MH^+ ions in these complexes is thus related to the nature of the Group IV element. It is also interesting to note that the sum of the intensities of the M^+ and $[M + 1]^+$ peaks is practically identical for all complexes except germanium, where it is considerably higher than for the others. Further, protonation apparently occurs more readily in the complexes than in the free ligands (or the more abundant MH^+ ions in the spectra of the complexes result from a lower decomposition rate). This suggests that the Cr(CO)$_3$ moiety plays a role in the protonation process and confirms the previous observation [4] that the Cr atom can act as a protonation site. The contrast in mass spectrometric behavior between these complexes and those of "simple hydrocarbon" ligands listed in Table 1 is also apparent, the latter displaying "classical CI spectra" (i.e., MH^+ as base peak).

EI mass spectrometry of the mono complexes is characterized by losses of CO and the production of Cr$^+$ ions, neither of which occur with CI. These are thus processes requiring the higher energy ionization procedure. $[M - 3\ CO]^+$ is base peak for complexes of carbon-, silicon- and germanium-containing ligands and is an intense ion in the tin and lead complexes (for which the base peak is Cr$^+$). The $[M - Ph]^+$ peak so prominent under CI conditions is absent in all cases, and $[M - PhCr(CO)_3]^+$ is of minor to moderate intensity. Other ions of interest include $[M - (Cr(CO)_3 + CH_3)]^+$ and $[M - (3\ CO + 2\ CH_3)]^+$.

An MH^+ ion is prominent only in the case where E is carbon in the CI spectra of the series of bis-tricarbonylchromium complexes (see Table 3). Some indication of a modestly enhanced $[M + 1]^+$ ion (CI compared to EI) is found for complex IIIb, in which E is silicon. The most characteristic signal for all bis-complexes is the $[M - PhCr(CO)_3]^+$ ion; this is the base peak for all members of the series except lead, for which it shows a relative intensity of 75%. The base peak (m/e 215) for the lead complex is probably protonated benzenetricarbonylchromium (produced by pyrolysis of the lead complex); the problem of pyrolysis and/or hydrolysis of organometallic compounds in the mass spectrometer has been recently discussed [14]. The same ion is found with the tin, germanium, silicon and carbon compounds, but at much lower intensities. It is

TABLE 3

CI AND EI MASS SPECTRA OF bis-TRICARBONYLCHROMIUM COMPLEXES OF SOME GROUP IV LIGANDS

(III)
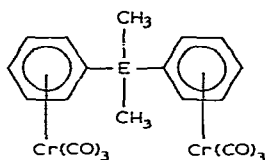
Compound	Type	Ion, m/e (relative intensity, %)					
		$M\text{H}^+$	M^+	$[M-3\ CO]^+$	$[M-4\ CO]^+$	$[M-6\ CO]^+$	$[M - \text{PhCr(CO)}_3]^+$
IIIa, E = C	CI	469(33)	468(24)				255(100)
	EI	469(3)	468(7)	384(7)	356(19)	300(29)	
IIIb, E = Si	CI	485(12)	484(20)				271(100)
	EI	485(3)	484(7)	400(10)	372(17)	316(32)	
IIIc, E = Ge	CI	531(5)	530(12)				317(100)
	EI	531(3)	530(7)	446(10)	418(18)	362(38)	
IIId, E = Sn	CI	577(4)	576(10)				363(100)
	EI	577(4)	576(9)	492(15)	464(20)	408(35)	
IIIe, E = Pb	CI	665(2)	664(5)				451(80)
	EI	665(2)	664(5)	580(3)			

^{a} 215 = $[C_6H_6Cr(CO)_3H]^+$; 328 = 344 = 390 = 436 = $[M - 5\ CO]^+$; 52 = Cr^+; 105 = 151 = 197 = PhE^+; 258 = $[M - (E + 2\ CH_3 + 6\ CO)]^+$ 120 = 208 = E^+; 280 = 326 = $[M - (Cr(CO)_3 + 3\ CO + 2\ CH_3)]^+$.

noteworthy that the relative intensities of the molecular ion clusters and the m/e 215 ions are inversely proportional to each other within this series of compounds. This suggests that the higher members of the series (especially the lead complex) are less stable in the mass spectrometer inlet system, and thus such an inverse relationship is not surprising.

The EI spectra of the bis-tricarbonylchromium complexes are similar to those of the mono-complexes in that loss of CO is a prominent feature, the bis-complexes losing chromium along with CO to a greater extent than do the mono-complexes. The base peak is $[M - (Cr(CO)_3 + 3\ CO)]^+$ for the carbon, silicon and germanium members of the series. This ion is very intense (84%) in the tin compound but absent in the case of lead. These ions may be compared with the base peaks observed in the CI spectra of the bis-complexes, $[M - PhCr(CO)_3]^+$, three additional CO groups being lost in the EI case. $[M - 3\ CO]^+$, $[M - 4\ CO]^+$ and $[M - 6\ CO]^+$ are ions of moderate intensity. The ions $[M - (6\ CO + PbMe_2)]^+$ and $[M - (6\ CO + SnMe_2)]^+$ are quite prominent in the spectra of the tin- and lead-containing complexes; the corresponding ion is of low to moderate intensity in IIIc (germanium) and absent in IIIa (carbon) and IIIb (silicon). These fragments of m/e 258 are assignable to a $[PhCr]_2^+$ ion, its ease of formation being related to the nature of the element E.

$[M - (Cr(CO)_3 + 3\ CO)]^+$	$[M - (2\ Cr(CO)_3 + CH_3)]^+$	$[PhE(CH_3)_2]^+$	Other [a]
		119(30)	215(1)
248(100)	181(10)		52(45), 328(5)
			215(2)
264(100)	197(13)		52(28), 105(5), 344(3)
		181(12)	215(7)
310(100)	243(21)		52(100), 151(14), 258(9), 280(5), 390(2)
		227(2)	215(13)
356(84)	289(10)		52(12), 197(33), 258(100) 120(10), 326(21), 436(1)
		315(1)	215(100)
			52(100), 208(12), 258(45)

Acknowledgement

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