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MASS SPECTRA OF ORGANOMETALLIC COMPOUNDS

III*. BENZOCYCLOBUTADIENEIRON CARBONYL DERIVATIVES

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Summary

The mass spectra of the benzocyclobutadieneiron complexes $C_8H_6Fe(CO)_3$ and $C_8H_6Fe(CO)_2E(C_6H_5)_3$ [E = P, As and Sb] have been studied at 80 eV. These complexes undergo fragmentations involving unimolecular carbonyl dissociation and $(C_6H_5)_3E$ elimination which are similar to those of the related manganese complexes, $(\pi\text{-L})Mn(CO)_3$ and $(\pi\text{-L})Mn(CO)_2E(C_6H_5)_3$ [L = cyclopentadienyl, indenyl and fluorenyl; E = P, As and Sb]. Noteworthy are the ions $[C_8H_6]^+$, $[C_8H_6Fe]^+$, $[C_6H_4]^+$ and $[C_6H_4Fe]^+$, which have been assigned the structures of the free and coordinated benzocyclobutadiene and benzyne, respectively. In the case of the more volatile derivative, $C_8H_6Fe(CO)_3$, these ions are formed by processes which are supported by the presence of appropriate metastable ions. The presence of a free benzocyclobutadiene ion, $[C_8H_6]^+$, in the mass spectra of these iron complexes contrasts with the failure to detect related cyclobutadiene (or substituted cyclobutadiene) ions in the mass spectra of the other cyclobutadienemetal complexes. The enhanced stability of $[C_8H_6]^+$ compared with that of $[R_4C_4]^+$ (R = H, CH_3, C_6H_5 etc.) may be explained from its fused ring structure.

Introduction

During the past several years the mass spectra of a variety of cyclobutadienemetal complexes such as $R_4C_4M(CO)_3$ [M = Fe; R = H [2,3], CH_3 [3] and C_6H_5 [1]: M = Ru; R = H [2], CH_3 [2] and C_6H_5 [4], $R_4C_4CoC_5H_5$ [R = H [5], aryl [1,6], $(CH_3)_3Si$ [6], etc.], $(C_6H_5)_4C_4CoC_9H_7$ [1], $C_4H_4RhC_5H_5$ [7], $R_4C_4M(CO)_4$ [M = Cr, Mo and W; R = H and CH_3] [2] and $[(C_6H_5)_4C_4]_2Mo(CO)_2$ [8], have been reported. These spectra have revealed that the loss ot

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* For part II see ref. 1.

cyclobutadiene ring (R_4C_4) from the metallic ions occurs via two successive eliminations of acetylene (R_2C_2) fragments and the absence of the free cyclobutadiene ions $[R_4C_4]^+$ and $[R_4C_4]^{2+}$. Recently, the mass spectrum of the titanium complex $(C_6H_5)_4C_4TiC_8H_8$ has been reported [9] to contain a metastable ion in support of a process involving involving the elimination of neutral $(C_6H_5)_4C_4$ fragment from the molecular ion as well as evidence to the existence of ion $[C_{28}H_{20}]^+$, which could be that of free tetraphenylcyclobutadiene. These features in the spectra of the titanium complex were observed in addition to the two-step sequence of unimolecular $(C_6H_5)_2C_2$ elimination process, originating in the molecular ion, which is supported by the presence of the appropriate metastable ions as well as the metallic fragment ion $[C_8H_8TiC_2(C_6H_5)_2]^+$. The above studies indicate that the dissociation of the cyclobutadiene to metal bond under electron-impact conditions occurs by two possible pathways, 1 and 2, of which the former appears to be much more common. Distinction between these pathways on the basis of metastable ions alone may be misleading, since the summation of the two steps in pathway 1 should give rise to the same metastable ion as that of pathway 2.

$$\underbrace{[M]^+ \xleftarrow{-R_4C_4} [R_4C_4M]^+}_{\text{pathway 2}} \underbrace{\xrightarrow{-R_2C_2} [R_2C_2M]^+ \xrightarrow{-R_2C_2} [M]^+}_{\text{pathway 1}}$$

In order to extend the knowledge on the behavior of cyclobutadienemetal complexes under electron-impact conditions, we have examined the mass spectra of the benzocyclobutadieneiron complexes $C_8H_6Fe(CO)_2X$ [X = CO, Ph_3P, Ph_3As and Ph_3Sb]. The mass spectra of these complexes are of special interest in view of the possible production of novel benzyneiron ions by processes involving acetylene elimination from benzocyclobutadieneiron-containing ions.

Experimental

The mass spectra of several benzocyclobutadieneiron carbonyl derivatives and ethynylbenzene (Tables 1 and 2), were recorded at 80 eV on a Hitachi RMU-7E, mass spectrometer. The solid samples were introduced into the spectrometer under vacuum (~10^{-6} Torr) through a stainless steel inlet. The inlet temperature was kept at 110°C for $C_8H_6Fe(CO)_3$ and ethynylbenzene, and at 120°C for $C_8H_6Fe(CO)_2E(C_6H_5)_3$ [E = P, As and Sb]. The ionization chamber temperature was maintained at 200°C for all samples. Intensities, corrected for background, of molecular ions and fragment ions in the spectra of these complexes are given relative to an arbitrary value of 1000.0 chosen for the base peaks. Intensities in the spectrum of ethynylbenzene are given relative to a value of 80, chosen for the base peak that of $[C_8H_6]^+$, which is also the relative intensity of the same ion in the spectrum of $C_8H_6Fe(CO)_3$. The metastable ions observed in the mass spectra of the benzocyclobutadieneiron carbonyl derivatives and ethynylbenzene are given in Table 3. Ions having high *M/z* value were determined with the aid of an internal PFK (perfluorokerosene) standard. The characteristic isotopic distribution of elements, in particular those of iron (^{54}Fe, 5.84; ^{56}Fe, 91.68; ^{57}Fe, 2.17 and ^{58}Fe, 0.31%) and antimony (^{121}Sb,

TABLE 1

THE MASS SPECTRA OF $C_8H_6Fe(CO)_3$ AND $C_6H_5C{\equiv}CH$

M/z[a]	Ion	Relative intensity	
		$C_8H_6Fe(CO)_3$	$C_6H_5C{\equiv}CH$
242	$[C_8H_6Fe(CO)_3]^+$	73	
214	$[C_8H_6Fe(CO)_2]^+$	137	
186	$[C_8H_6Fe(CO)]^+$	119	
158	$[C_8H_6Fe]^+$	1000	
132	$[C_6H_4Fe]^+$	767	
107	$[C_8H_6Fe(CO)_2]^{2+}$	18	
106	$[C_4H_2Fe]^+$	36	
102	$[C_8H_6]^+$	80	80
93	$[C_8H_6Fe(CO)]^{2+}$, $[C_3HFe]^+$	15;5	
79	$[C_8H_6Fe]^{2+}$	6	
77	$[C_6H_5]^+$	5	$> 1(\simeq 0.7)$
76	$[C_6H_4]^+$	23	
65	$[C_5H_5]^+$		6
64	$[C_5H_4]^+$		8
63	$[C_5H_3]^+$	10	5
62	$[C_5H_2]^+$	7	3
61	$[C_5H]^+$	11	2
56	$[Fe]^+$	299	
52	$[C_4H_4]^+$	8	4
51	$[C_8H_6]^{2+}$; $[C_4H_3]^+$	25	6
50	$[C_4H_2]^+$	23	8
49	$[C_4H]^+$	4	1
39	$[C_3H_3]^+$	7	2
38	$[C_3H_2]^+$; $[C_6H_4]^{2+}$	8	1
37	$[C_3H]^+$	5	$> 1(\approx 0.03)$
26	$[C_2H_2]^+$	4	$> 1(\approx 0.6)$
25	$[C_2H]^+$	3	$> 1(\approx 0.2)$

[a] Monoisotopic presentation, using the most abundant isotopes of the elements involved.

TABLE 2

THE MASS SPECTRA OF $C_8H_6Fe(CO)_2E(C_6H_5)_3$, E = P, As AND Sb

M/z[a] values are given in parentheses

Ion	Relative intensity					
	E = P		E = As		E = Sb	
Ions containing iron						
$[C_8H_6Fe(CO)_2E(C_6H_5)_3]^+$	$> 1(\sim 0.3)$	(476)	3	(520)	$> 1(\sim 0.2)$	(566)
$[C_8H_6Fe(CO)E(C_6H_5)_3]^+$	$> 1(\sim 0.3)$	(448)	4	(492)	$> 1(\sim 0.1)$	(538)
$[C_8H_6FeE(C_6H_5)_3]^+$	1	(420)	12	(464)	2	(510)
$[(C_6H_5)_3EFe]^+$			12	(362)	1	(408)
$[(C_6H_5)_2EFe]^+$	5	(241)	5	(285)	$> 1(\sim 0.1)$	(331)
$[C_{12}H_8EFe]^+$	2	(239)	7	(283)		
$[C_8H_6FeE(C_6H_5)_3]^{2+}$	6	(210)				
$[C_8H_6FeE]^+$					10	(279)
$[C_8H_6Fe]^+$	10	(158)	6	(158)	23	(158)
$[C_6H_5Fe]^+$	6	(133)	4	(133)	2	(133)
$[C_6H_4Fe]^+$	33	(132)			18	(132)
$[C_5H_3Fe]^+$	10	(119)				
$[C_5H_2Fe]^+$	7	(118)			9	(118)
$[C_4H_2Fe]^+$	18	(106)			17	(106)

(continued)

TABLE 2 (continued)

Ion	Relative intensity					
	E = P		E = As		E = Sb	
$[C_8H_6Fe]^{2+}$	4	(79)	6	(79)		
$[Fe]^+$	139	(56)	8	(56)	10	(56)
Non-metallic ions containing E (P, As and Sb)						
$[(C_6H_5)_3E]^+$	59	(262)	1000	(306)	150	(352)
$[C_{15}H_{12}E]^+$	15	(223)				
$[(C_6H_5)_2E]^+$	4	(185)	166	(229)	133	(275)
$[C_{12}H_8E]^+$	25	(183)	642	(227)	65	(273)
$[C_8H_6E]^+$	6	(133)	9	(177)		
$[(C_6H_5)_3E]^{2+}$	5	(131)	206	(153)		
$[C_6H_6E]^+$					77	(199)
$[(C_6H_5)_2E]^+$	10	(108)			1000	(198)
$[C_4H_7E]^+$	303	(86)				
$[C_4H_6E]^+$	37	(85)				
$[C_4H_5E]^+$	91	(84)				
$[C_4H_4E]^+$	10	(83)				
$[C_4H_3E]^+$	4	(82)				
$[C_3H_4E]^+$	174	(71)				
$[C_3H_3E]^+$	47	(70)				
$[C_3H_2E]^+$	97	(64)				
$[C_2H_3E]^+$	1000	(58)				
$[C_2H_2E]^+$	740	(57)				
$[E]^+$	6	(31)	14	(75)	27	(121)
Organic ions						
$[C_{12}H_{11}]^+$					80	(155)
$[C_{12}H_{10}]^+$	4	(154)	208	(154)	530	(154)
$[C_{12}H_8]^+$	5	(152)	208	(152)	116	(152)
$[C_{11}H_9]^+$	16	(141)	4	(141)	1	(141)
$[C_{11}H_7]^+$					9	(139)
$[C_{10}H_8]^+$	6	(128)	30	(128)	18	(128)
$[C_9H_7]^+$	6	(115)	31	(115)	16	(115)
$[C_8H_8]^+$	34	(104)			4	(104)
$[C_8H_7]^+$	16	(103)	7	(103)	6	(103)
$[C_8H_6]^+$	5	(102)	18	(102)	13	(102)
$[C_8H_5]^+$			25	(101)	4	(101)
$[C_7H_7]^+$	50	(91)			28	(91)
$[C_6H_6]^+$	10	(78)	31	(78)	33	(78)
$[C_6H_5]^+$	17	(77)	49	(77)	239	(77)
$[C_6H_4]^+$	6	(76)	14	(76)	17	(76)
$[C_5H_5]^+$	12	(65)			4	(65)
$[C_5H_4]^+$			2	(64)	1	(64)
$[C_5H_3]^+$	9	(63)	13	(63)	8	(63)
$[C_4H_5]^+$	10	(53)			2	(53)
$[C_4H_4]^+$	10	(52)	7	(52)	10	(52)
$[C_4H_3]^+$	30	(51)	61	(51)	8	(51)
$[C_4H_2]^+$	12	(50)	12	(50)	22	(50)
$[C_3H_7]^+$	590	(43)	137	(43)	33	(43)
$[C_3H_6]^+$	342	(42)	126	(42)	23	(42)
$[C_3H_5]^+$	549	(41)	60	(41)	13	(41)
$[C_3H_3]^+$	160	(39)	21	(39)	17	(39)

[a] Monoisotopic presentation, using the most abundant isotopes of the elements involved.

TABLE 3

METASTABLE IONS (M^*) IN THE MASS SPECTRA OF BENZOCYCLOBUTADIENEIRON CARBONYL DERIVATIVES AND ETHYNYLBENZENE

Relative intensities are given in parentheses, s = strong, m = medium, w = weak, vw = very weak

$M^* = M_2^2/M_1$ [a]	M_1	M_2	M_1-M_2
$C_8H_6Fe(CO)_3$			
189.2 (s)	$[C_8H_6Fe(CO)_3]^+$	$[C_8H_6Fe(CO)_2]^+$	CO
161.6 (m)	$[C_8H_6Fe(CO)_2]^+$	$[C_8H_6Fe(CO)]^+$	CO
134.2 (s)	$[C_8H_6Fe(CO)]^+$	$[C_8H_6Fe]^+$	CO
110.3 (s)	$[C_8H_6Fe]^+$	$[C_6H_4Fe]^+$	C_2H_2
85.1 (m)	$[C_6H_4Fe]^+$	$[C_4H_2Fe]^+$	C_2H_2
81.6 (m)	$[C_4H_2Fe]^+$	$[C_3HFe]^+$	CH
56.6 (m)	$[C_8H_6]^+$	$[C_6H_4]^+$	C_2H_2
55.9 (vw)	$[C_8H_6Fe(CO)]^+$	$[C_8H_6]^+$	Fe; CO
$C_8H_6Fe(CO)_2P(C_6H_5)_3$			
181.0 (m)	$[(C_6H_5)_2P]^+$	$[C_{12}H_8P]^+$	H_2
128.2 (w)	$[(C_6H_5)_2P]^+$	$[C_{12}H_{10}]^+$	P
90.5 (vw)	$[(C_6H_5)_3P]^+$	$[C_{12}H_{10}]^+$	C_6H_5, P
39.1 (w)	$[C_3H_7]^+$	$[C_3H_5]^+$	H_2
$C_8H_6Fe(CO)_2As(C_6H_5)_3$			
225.0 (m)	$[(C_6H_5)_2As]^+$	$[C_{12}H_8As]^+$	H_2
224.4 (m)	$[(C_6H_5)_3AsFe]^+$	$[(C_6H_5)_2AsFe]^+$	C_6H_5
150.0 (m)	$[C_{12}H_{10}]^+$	$[C_{12}H_8]^+$	H_2
75.5 (m)	$[(C_6H_5)_3As]^+$	$[C_{12}H_8]^+$	H_2; As; C_6H_5
$C_8H_6Fe(CO)_2Sb(C_6H_5)_3$			
273.0 (m)	$[(C_6H_5)_2{}^{123}Sb]^+$	$[C_{12}H_8{}^{123}Sb]^+$	H_2
271.0 (m)	$[(C_6H_5)_2{}^{121}Sb]^+$	$[C_{12}H_8{}^{121}Sb]^+$	H_2
112.9 (s)	$[(C_6H_5)_3{}^{123}Sb]^+$	$[C_6H_5{}^{123}Sb]^+$	$2C_6H_5$
111.4 (s)	$[(C_6H_5)_3{}^{121}Sb]^+$	$[C_6H_5{}^{121}Sb]^+$	$2C_6H_5$
86.2 (w)	$[(C_6H_5)_2{}^{121}Sb]^+$	$[C_{12}H_{10}]^+$	^{121}Sb
85.6 (w)	$[(C_6H_5)_2{}^{123}Sb]^+$	$[C_{12}H_{10}]^+$	^{123}Sb
$C_6H_5C{\equiv}CH$			
56.6	$[C_8H_6]^+$	$[C_6H_4]^+$	C_2H_2

[a] Monoisotopic presentation using the most abundant isotopes of the elements involved, except for antimony in which case the metastable ions containing both ^{121}Sb and ^{123}Sb isotopes are given.

57.25 and ^{123}Sb, 42.75%), helped in recognizing many of the fragment ions. In the mass spectrum of $C_8H_6Fe(CO)_3$ the peak at M/z 93 due to $[C_8H_6Fe(CO)]^{2+}$ and $[C_3HFe]^+$ was resolved at $M/\Delta M$ ~6500 into a doublet having the ratio of 3/1, respectively.

The complexes $C_8H_6Fe(CO)_3$ and $C_8H_6Fe(CO)_2P(C_6H_5)_3$ were prepared by known procedures [10]. The method of preparation of $C_8H_6Fe(CO)_2E(C_6H_5)_3$, E = As (m.p. 142-143°C; found: C, 64.44; H, 4.04; O, 6.30; calcd.: C, 64.64; H, 4.06; O, 6.15%) and E = Sb (m.p. 119-121°C; found: C, 59.57; H, 3.70; O, 5.76; calcd.: C, 59.30; H, 3.73; O, 5.64%), and their chemical and physical properties will be reported elsewhere [11]. Ethynylbenzene was purchased from Matheson, Coleman and Bell (East Rutherford, N.J.).

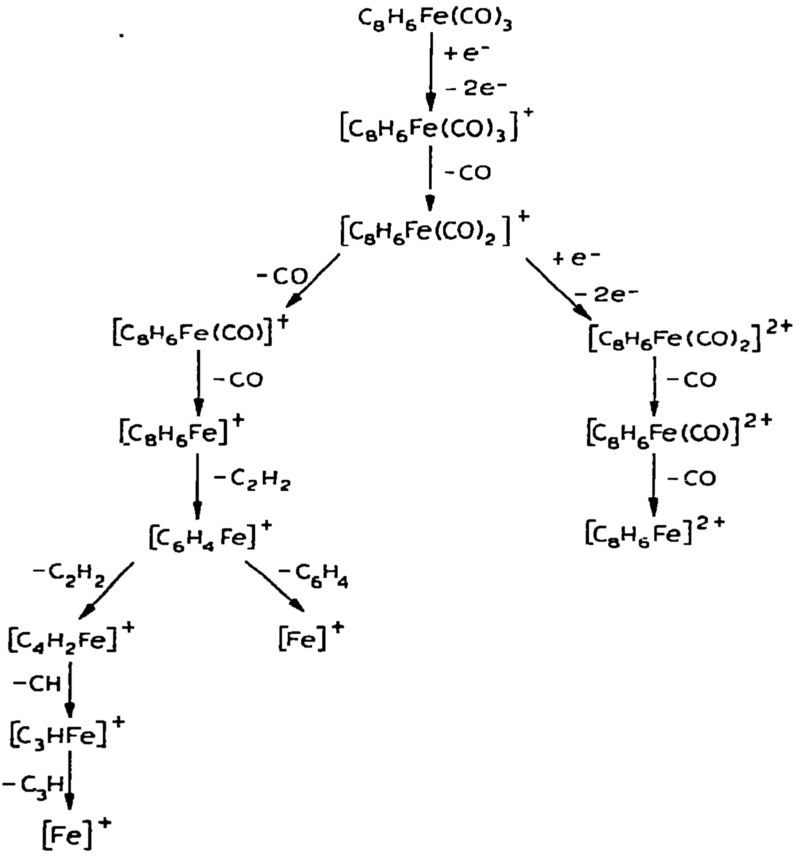
Discussion

$C_8H_6Fe(CO)_3$

The mass spectrum of the benzocyclobutadieneiron tricarbonyl complex (Table 1) is of particular interest since sufficient metastable ions (Table 3) were observed to indicate many of the fragmentation processes depicted in Scheme 1. In the fragmentation processes involving metallic ions (Scheme 1), the monopositive molecular ion (M/z = 186) degrades via two different pathways, by the simultaneous elimination of CO and Fe to give $[C_8H_6]^+$ (M/z = 102) and the further loss of the remaining carbonyl group to afford $[C_8H_6Fe]^{2+}$ (M/z = 158) which is the most abundant ion in the spectrum. A two-step sequence involving successive losses of two C_2H_2 fragments from the carbonyl free ion, $[C_4H_2Fe]^+$, gives rise to the ion $[C_6H_4Fe]^+$ (M/z = 132) and $[C_4H_2Fe]^+$ (M/z = 106), respectively. The latter ion undergoes CH elimination to give $[C_3HFe]^+$ (M/z = 93). Also included in Scheme 1 are the proposed fragmentations involving the dipositive ions, $[C_8H_6Fe(CO)_2]^{2+}$ (M/z = 107) and $[C_8H_6Fe]^{2+}$

SCHEME 1

THE PROPOSED FRAGMENTATION SCHEME OF THE METALLIC IONS IN THE MASS SPECTRUM OF $C_8H_6Fe(CO)_3$

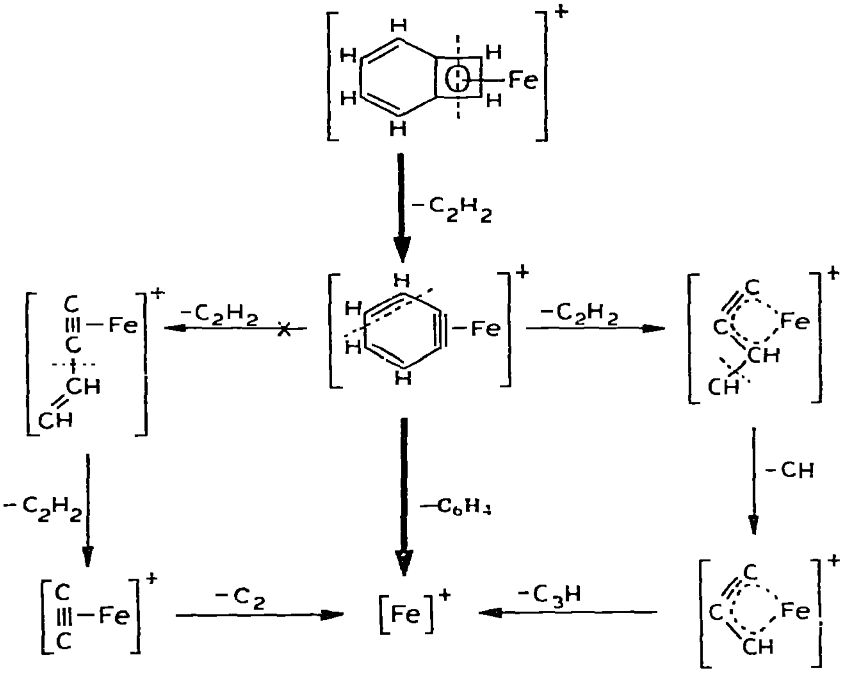


(M/z = 79) as well as that at M/z = 93 which, in part, is due to $[C_8H_6Fe(CO)]^{2+}$.

The tentative structures of some of the metallic ions, in the spectrum of $C_8H_6Fe(CO)_3$, may be derived by carefully considering their processes of production and decay. There are two main routes to explain the fragmentation of the carbonyl free benzocyclobutadieneiron ion and they are depicted in Schemes 2 and 3. According to Scheme 2, the benzocyclobutadieneiron first undergoes the elimination of C_2H_2 to give benzyneiron ion, $[C_6H_4Fe]^+$, which then degrades further to free benzyne and $[Fe]^+$. Alternatively, the benzyneiron ion eliminates the neutral fragments C_2H_2 and CH in succession to give π-butynyliron and π-propynyliron type ions, respectively. The structure of π-butynyliron for $[C_4H_2Fe]^+$ is preferred over the π-butyneiron type since an ion with the latter structure should favour undergoing the elimination of C_2H_2 to give $[C_2Fe]^+$ instead of the observed elimination of CH which affords $[C_3HFe]^+$. An alternative route of fragmentation envisaged for the benzocyclobutadieneiron ion, Scheme 3, involves two successive eliminations of C_2H_2 fragments from the benzo-ring to give a diradical cyclobutadieneiron which then eliminates neutral CH fragment to afford the π-propynyliron type ion $[C_3HFe]^+$. A clear distinction between the fragmentation modes described in Schemes 2 and 3 may not be possible unless it could be determined first whether the major fragmentation steps in the mass spectrum of $C_8H_6Fe(CO)_3$ are analogous to those characterized in the spectra of the other cyclobutadienemetal complexes. The resemblence between the appearance potentials of related metallic ions in the

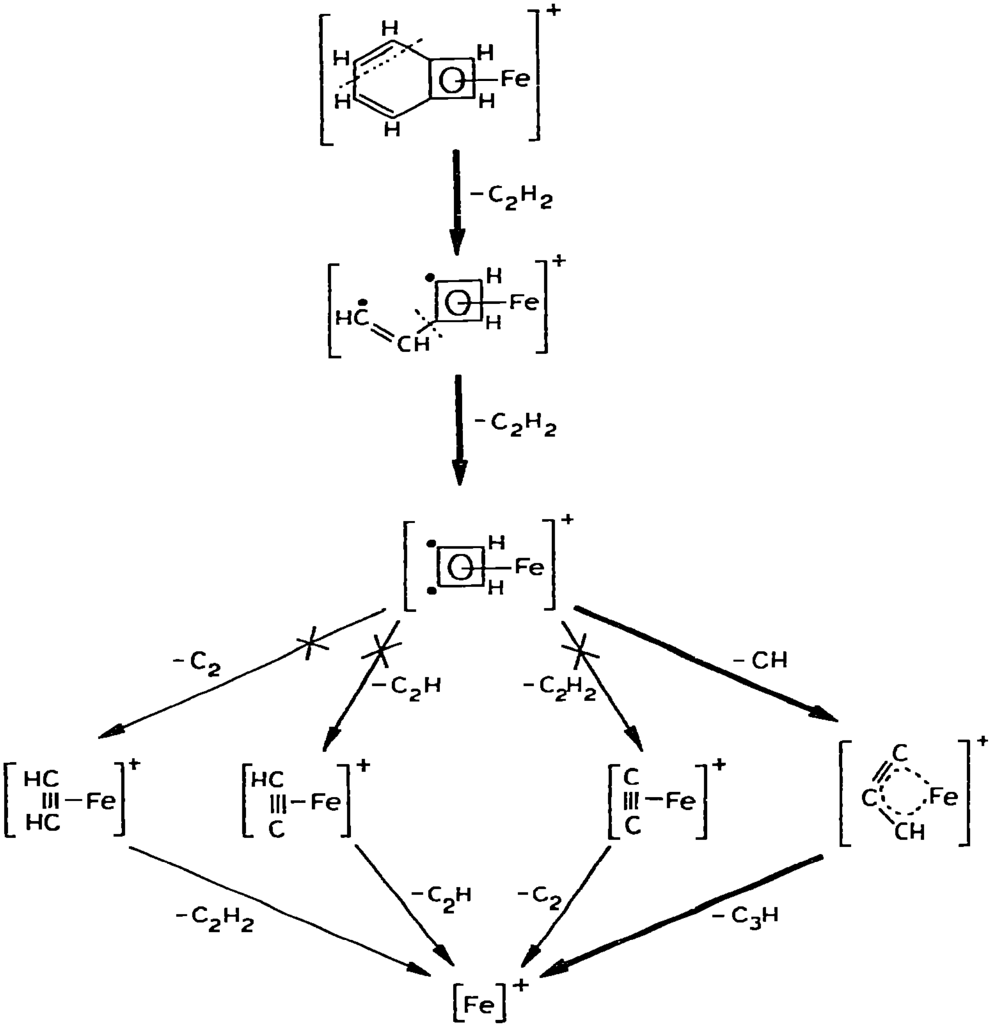
SCHEME 2

STRUCTURES PROPOSED FOR SOME OF THE METALLIC IONS IN THE MASS SPECTRUM OF $C_8H_6Fe(CO)_3$



SCHEME 3

ALTERNATIVE STRUCTURES PROPOSED FOR SOME OF THE METALLIC IONS IN THE MASS SPECTRUM OF $C_8H_6Fe(CO)_3$



mass spectra of $C_8H_6Fe(CO)_3$ [13] and $C_4H_4Fe(CO)_3$ * indicates that these ions are generated by processes of similar energetics. This analogy suggests that

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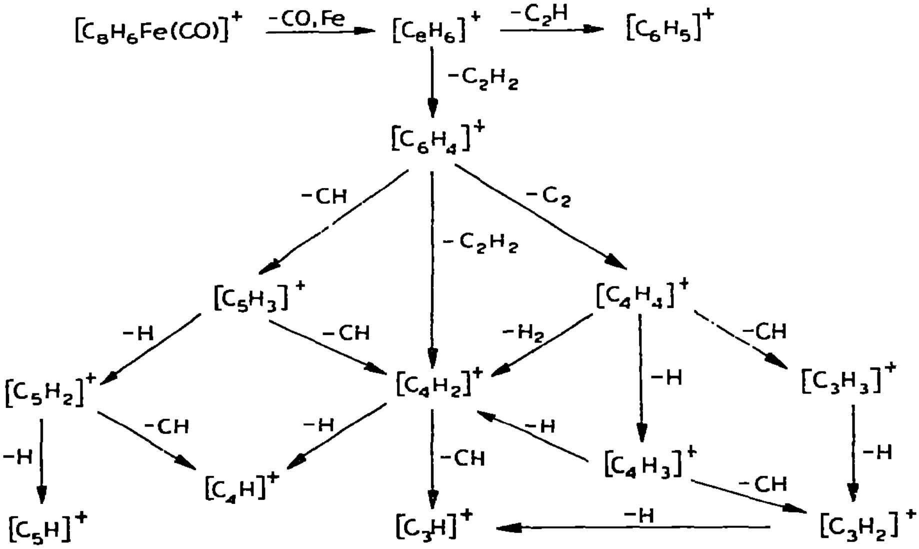
* The appearance potentials of the major metallic ions in the mass spectra of $C_8H_6Fe(CO)_3$ and $C_4H_4Fe(CO)_3$, cited below [13], were determined according to the procedure given in ref. 21 on a modified Hitachi RMU-7E mass spectrometer with a Keithley 427 current amplifier. *$C_8H_6Fe(CO)_3$*: $[C_8H_6Fe(CO)_3]^+$, 7.43 ± 0.02; $[C_8H_6Fe(CO)_2]^+$, 8.08 ± 0.02; $[C_8H_6Fe(CO)]^+$, 9.21 ± 0.02; $[C_8H_6Fe]^+$, 11.33 ± 0.02; $[C_6H_4Fe]^+$, 13.93 ± 0.07 and $[Fe]^+$, 16.00 ± 0.2. *$C_4H_4Fe(CO)_3$* $[C_4H_4Fe(CO)_3]^+$, 8.21 ± 0.02; $[C_4H_4Fe(CO)_2]^+$, 8.92 ± 0.02; $[C_4H_4Fe(CO)]^+$, 10.11 ± 0.03; $[C_4H_4Fe]^+$, 12.18 ± 0.02; $[C_2H_2Fe]^+$, 13.85 ± 0.02 and $[Fe]^+$, 17.88 ± 0.02 eV. These results are part of a comprehensive study of fragmentation energetics of various cyclobutadienemetal complexes which is currently in progress.

the major steps in the fragmentation of the benzocyclobutadieneiron ion are similar to those of the cyclobutadieneiron ion and therefore should follow the two-step sequence earlier described as pathway 1 which is included in Scheme 2. Incidently, the dissociation sequence of the benzyneiron ion starting with the elimination of C_2H_2, Scheme 2, appears to be rather minor since the sum of relative intensities (*RI*) of the ions involved, $\Sigma RI([C_4H_2Fe]^+ + [C_3HFe]^+) \approx 4.3$, is considerably smaller than that of the iron ion, $RI([Fe]^+) \approx 76.7$. Insofar as Scheme 3 is concerned, the fragmentations described are in contrast with pathway 1, since the ion $[C_2Fe]^+$, $[C_2HFe]^+$ and $[C_2H_2Fe]^+$, whose production can be anticipated from the decay of the diradical cyclobutadieneiron ion according to this pathway, are not found at all in the mass spectrum of $C_8H_6Fe(CO)_3$. Moreover, the five-step sequence leading to the formation of $[Fe]^+$ from $[C_8H_6Fe]^+$ according to Scheme 3, suggests that the former ion should have been produced at a considerably higher appearance potential than was actually found.

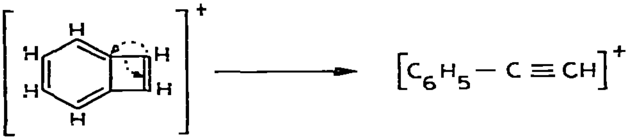
Some of the organic ions observed in the mass spectrum of $C_8H_6Fe(CO)_3$ could be formed directly by the elimination of iron from the carbonyl-free metallic ions described in Scheme 1. The production of other organic ions may be explained in terms of processes involving the elimination of neutral fragments (e.g., C_2H_2, C_2H, C_2 and CH) and dehydrogenation (Scheme 4). In one case, namely the formation of $[C_6H_5]^+$ from $[C_8H_6]^+$, hydrogen migration is presumed to occur in addition to C_2H elimination. Noteworthy are the peaks at *M*/*z* = 51 and 38 which, in part, may correspond to the dipositive ions $[C_8H_6]^{2+}$ and $[C_6H_4]^{2+}$, respectively. Thus, the possibility of having fragmentations via dipositive organic ions, although is not indicated in Scheme 2, could not be ruled out.

SCHEME 4

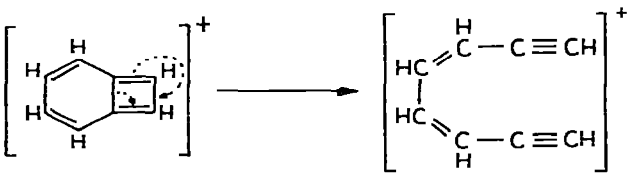
A FRAGMENTATION SCHEME, PROPOSED FOR THE FORMATION OF THE ORGANIC IONS IN THE MASS SPECTRUM OF $C_8H_6Fe(CO)_3$



The ions $[C_8H_6]^+$ and $[C_6H_4]^+$, according to their route of formation (Scheme 4) have been assigned the structures of benzocyclobutadiene and benzyne, respectively. The monopositive benzyne ion has already been characterized previously in the mass spectra of several organic (e.g., diiodobenzene [14]) as well as organometallic (e.g., bis(*o*-iodophenyl)mercury [15]) systems, but the monopositive benzocyclobutadiene ion has not yet been reported. In spite of the notorious instability of the free cyclobutadiene (R_4C_4) ligand and its ions $[R_4C_4]^+$ and $[R_4C_4]^{2+}$, the assignment of the benzocyclobutadiene structure to $[C_8H_6]^+$ is not altogether unreasonable since the generation and trapping of a benzocyclobutadiene intermediate has already been reported [16]. The benzocyclobutadiene ion, due to its fused ring structure, is expected to exhibit considerably higher stability than the hypothetical cyclobutadiene ion. A similar argument may also explain the non-transitory properties of the biphenylene molecule which has been studied extensively in recent years [17]. The possibility of having the benzocyclobutadiene ion rearrange upon formation to ions such as ethynylbenzene (eqn. 1) or octadiyne-3, 5-diene (eqn. 2), although it could not be ruled out completely, appears quite remote for the following reasons. The mass spectrum of ethynylbenzene (Table 1), taken under the same conditions as that of the iron complex, $C_8H_6Fe(CO)_3$, contains relatively intense peaks at M/z = 65 and 64 which are conspicuously absent from the spectrum of the iron complex. Thus, in spite of the observed C_2H_2 elimination from the molecular ion of ethynylbenzene (M^* = 56.6), the differences existing between the spectra of the two compounds suggest strongly against the rearrangement depicted in eqn. 1. The octadiyne-3,5-diene, if formed, should undergo cleavage preferentially at a saturated bond site rather than a process of C_2H_2 elimination which would require the simultaneous cleavage of two unsaturated bonds.



(1)



(2)

The detection of a novel benzynemetal ion in the mass spectrum of $C_8H_6Fe(CO)_3$ is interesting, although not unique. The coordinated benzyne-nickel ion $[C_6H_4NiI_2]^+$ has previously been reported in the mass spectrum of $[C_6H_4Ni(CO)I_2]_2$ [18], a complex thought to be a benzyne derivative. The relative abundance ratios $([C_8H_6Fe]^+)/([C_8H_6]^+) \approx 13.5$ and $([C_6H_4Fe]^+)/([C_6H_4]^+) \approx 33.0$ provide an approximate indication of the stabilization-effect achieved by coordinating the labile ligands benzocyclobutadiene and benzyne on iron(I). According to this approach the stabilization-gain in the case of benzyne is almost three times greater than that of benzocyclobutadiene. The relative abundance ratios ($[C_8H_6Fe]^+$)/($[C_6H_4Fe]^+$) ≈ 1.3 and ($[C_8H_6]^+$)/($[C_6H_4]^+$) ≈ 3.5 tend to indicate that while the complexed ligand ions exhibit comparable stabilities, in the free state the benzyne ion is considerably more reactive and/or thermally unstable than is the benzocyclobutadiene ion. These results suggest that a benzocyclobutadiene intermediate is likely to be more stable than the benzyne intermediate. Although the pure benzocyclobutadiene molecule has not yet been isolated, ample evidence to its existence has already been accumulated. For example, Cava and Mitchell [16] have reported the generation of benzocyclobutadiene, in situ, from the reaction of 1,2-diiodobenzocyclobutadiene and activated zinc dust and its trapping as a stable Diels—Alder adduct with cyclopentadiene.

$C_8H_6Fe(CO)_2E(C_6H_5)_3$, $E = P$, As and Sb

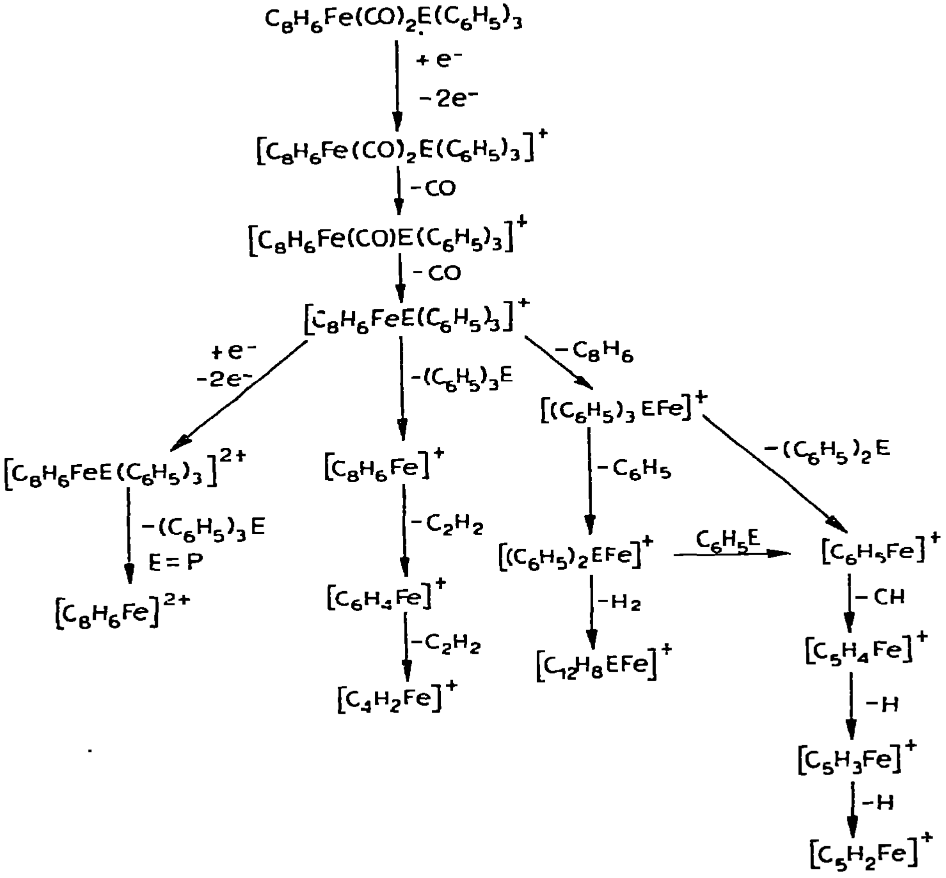
The complexes $C_8H_6Fe(CO)_2E(C_6H_5)_3$ [E = P, As and Sb] studied in this work possess sufficient volatility and thermal stability for their mass spectra to be obtained (Table 2). These spectra show a relatively large number of fragment ions of which rather few are metastable ions (Table 3). The proposed fragmentation processes of the metallic ions in the mass spectra of the iron complexes $C_8H_6Fe(CO)_2E(C_6H_5)_3$, are depicted in Scheme 5. In all three cases the molecular ion was observed to undergo stepwise losses of its two carbonyl groups. The resulting carbonyl-free ion, $[C_8H_6FeE(C_6H_5)_3]^+$, degrades further through two main pathways, by losing either the σ-ligand $(C_6H_5)_3E$ to give ion $[C_8H_6Fe]^+$ or the C_8H_6 ring to give ion $[(C_6H_5)_3EFe]^+$. The fragmentation of the benzocyclobutadiene iron ion via a two-step sequence involving successive losses of two C_2H_2 units may explain the formation of $[C_6H_4Fe]^+$ and $[C_4H_2Fe]^+$. Noteworthy are the identical C_2H_2 elimination processes in the mass spectrum of $C_8H_6Fe(CO)_3$ which were supported by the presence of appropriate metastable ions. Missing from the spectra of $C_8H_6Fe(CO)_2E(C_6H_5)_3$ complexes is the ion $[C_3HFe]^+$, whose formation by CH elimination from $[C_4H_2Fe]^+$ in the spectrum of $C_8H_6Fe(CO)_3$ was supported by the presence of an appropriate metastable ion at $M/z = 81.6$.

The fragmentation of the ion $[(C_6H_5)_3EFe]^+$ is suggested to occur by two main pathways. The first pathway involving consecutive eliminations of C_6H_5, 2H and $C_{12}H_8E$ fragments may explain the formation of ions $[(C_6H_5)_2EFe]^+$, $[C_{12}H_8EFe]^+$ and the bare iron ion, $[Fe]^+$, respectively. The second pathway is suggested to include the following steps; phenyl migration with simultaneous elimination of $[(C_6H_5)_2E]^+$, elimination (possible step) and dehydrogenations to give ions $[C_6H_5Fe]^+$, $[C_5H_4Fe]^+$ (ion not observed), $[C_5H_3Fe]^+$ and $[C_5H_2Fe]^+$, respectively (Scheme 5). The possibility of having the ions $[C_5H_3Fe]^+$ and $[C_5H_2Fe]^+$ originate from $[C_6H_4Fe]^+$ by processes of CH elimination and dehydrogenation, respectively, was excluded since these ions are not present in the spectrum of $C_8H_6Fe(CO)_3$. An alternative route to ion $[C_6H_5Fe]^+$ may involve phenyl migration with simultaneous elimination of the C_6H_5E fragment from $[(C_6H_5)_2EFe]^+$.

The presence of the ions $[C_8H_6FeP(C_6H_5)_3]^{2+}$ ($M/z = 210$) and $[C_8H_6Fe]^{2+}$ ($M/z = 79$) in the mass spectra of the iron derivatives, $C_8H_6Fe(CO)_2E(C_6H_5)_3$, suggests the possibility of having fragmentation processes involving dipositive

SCHEME 5

A FRAGMENTATION SCHEME PROPOSED FOR THE FORMATION OF SOME OF THE METALLIC IONS IN THE MASS SPECTRA OF THE IRON DERIVATIVES, $C_8H_6Fe(CO)_2E(C_6H_5)_3$ [E = P, As AND Sb]



ions. Several phenyl elimination processes from metal-free ions, supported by metastable ions (Table 3), were observed in the mass spectra of these iron derivatives. Some phenyl elimination processes also occur with metallic ions as indicated for example by the presence of the antimony-containing ion $[C_8H_6FeSb]^+$ (M/z = 279). Many of the metal-free ions in the mass spectra of $C_8H_6Fe(CO)_2E(C_6H_5)_3$ (Table 2), may be derived by omitting metallic iron from the fragment ions described in Scheme 5. Other non-metallic ions in these spectra probably originate in secondary fragmentation processes especially those to do with the free ligands $(C_6H_5)_3E$ (E = P, As and Sb). For instance, the 9-phosphorenefluorenyl ($[C_{12}H_8P]^+$) is a major component in the reported mass spectrum of triphenylphosphine [19]. Likewise, the 9-heterofluorenyl ions, $[C_{12}H_8E]^+$ (E = P, As and Sb), are all major components in the mass spectra of the structurally related cyclopentadienyl-, indenyl-, fluorenyl- and pyrolyl-manganese dicarbonyl derivatives, $QMn(CO)_2E(C_6H_5)_3$ [Q = C_5H_5, C_9H_7, $C_{13}H_9$ and C_4H_4N; E = P, As and Sb] [20].

Acknowledgements

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