closely related to the presence of significant quantities of ions containing a metal atom and one to three carbon atoms found in the further degradation of the ion $C_5H_5W^+$ observed in the mass spectra of the compounds $CH_2{=}CHCOW(CO)_3C_5H_5$ and $C_5H_5W(CO)_3H$ (Tables VII and VIII).

A further indication of the increased stability of rhenium–carbon bonds as compared with manganese–carbon bonds is the observation that in the mass spectrum of $C_5H_5Mn(CO)_3$ the abundances of the Mn^+ and $C_5H_5Mn^+$ ions are 30 and 47%, respectively, of all of the manganese-containing ions, whereas in the mass spectrum of $C_5H_5Re(CO)_3$ the abundances of the analogous Re^+ and $C_5H_5Re^+$ ions are only 14 and 2%, respectively, of all of the rhenium-containing ions. High relative abundances of the M^+ and $C_5H_5M^+$ ions indicate weak metal–carbon bond strengths since loss of carbonyl groups is then facile.

Dipositive ions of the type $C_5H_5Re(CO)_n{}^{2+}$ (n = 0–3) are observed in the mass spectrum of the rhenium compound, but analogous ions are not observed in the mass spectrum of the manganese compound. The great tendency for heavy third-row transition metals (*e.g.*, tungsten, ruthenium, osmium) to form compounds exhibiting metal-containing doubly charged ions in their mass spectra has been previously observed.[25] Formation of doubly charged metal-containing ions may be an indication of strong metal–carbon bonds since they have survived two ionization processes.

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(25) R. E. Winters and R. W. Kiser, *Inorg. Chem.*, **4**, 157 (1965).

Mass Spectra of Organometallic Compounds. III. Organosulfur Derivatives of Metal Carbonyls[1]

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Abstract: The mass spectra of the compounds $[CH_3SFe(CO)_3]_2$ (two isomers), $C_7H_8Fe_2(CO)_4(SCH_3)_2$, $C_2H_4S_2Fe_2(CO)_6$, $C_2F_4S_2Fe_2(CO)_6$, $C_7H_6S_2Fe_2(CO)_6$, $CH_3SCH_2Mo(CO)_2C_5H_5$, $CH_3SCH_2Mn(CO)_4$, $CH_3SCH_2CH_2COMn(CO)_4$, $[CH_3SFeCOC_5H_5]_2$, $CH_3SFe(CO)_2C_5H_5$, $C_6H_5COSFe(CO)_2C_5H_5$, and $CH_3SCH_2CH_2SCH_3W(CO)_4$ have been investigated. Generally stepwise loss of carbonyl groups first occurs. Carbonyl-free ions with bridging CH_3S groups then lose the CH_3 group with breaking of the carbon–sulfur bond. The ion $C_2F_4S_2Fe_2(CO)_3{}^+$ in the mass spectrum of $C_2F_4S_2Fe_2(CO)_6$ also undergoes a novel elimination of FeF_2 resulting in the ion $C_2F_2S_2Fe(CO)_3{}^+$.

Within the past few years a variety of organosulfur derivatives of metal carbonyls have been synthesized. However, the mass spectra of such compounds have received relatively little attention to date. Preston and Reed[3] have included a few organometallic compounds with bridging RS groups in a recent mass spectral study. A recent preparative paper[4] includes a brief discussion of the mass spectra of certain bis(trifluoromethyl)ethylene dithiolate complexes.

The present paper describes the mass spectra of a representative selection of organosulfur derivatives of metal carbonyls. Included are π-CH_3SCH_2 complexes,[5] $[RSFe(CO)_3]_2$ complexes and closely related compounds,[6] several different types of organosulfur derivatives of cyclopentadienyliron carbonyls,[7] and a 2,5-dithiahexane derivative of a metal carbonyl.[8]

Experimental Section

The mass spectra were run under the direction of Mr. R. E. Rhodes on a standard MS-9 mass spectrometer located at the Mellon Institute. They are reported in Tables I–XII inclusive. Four typical spectra are illustrated in Figure 1. The operating conditions were 70-ev electron energies, 200–230° inlet temperature, resolution of 1000, and 8-kv accelerating voltage. Samples were introduced into the ion source using a metal probe. The relative peak intensities were estimated by measurement of the heights of the peaks on the galvanometer recorder chart with a millimeter rule. Values are reported relative to an arbitrary value of 100 for the most abundant

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(1) For part II of this series, see R. B. King, *J. Am. Chem. Soc.*, **90**, 1417 (1968).

(2) Department of Chemistry, University of Georgia, Athens, Ga; Fellow of the Alfred P. Sloan Foundation, 1967–1969.

(3) F. J. Preston and R. I. Reed, *Chem. Commun.*, 51 (1966).

(4) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **6**, 469 (1967).

(5) R. B. King and M. B. Bisnette, *ibid.*, **4**, 486 (1965).

(6) R. B. King, *J. Am. Chem. Soc.*, **85**, 1584 (1963); R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 1663 (1965).

(7) R B King, *J. Am. Chem. Soc.*, **85**, 1918 (1963); R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 482 (1965).

(8) H. C. E. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, 4454 (1962).

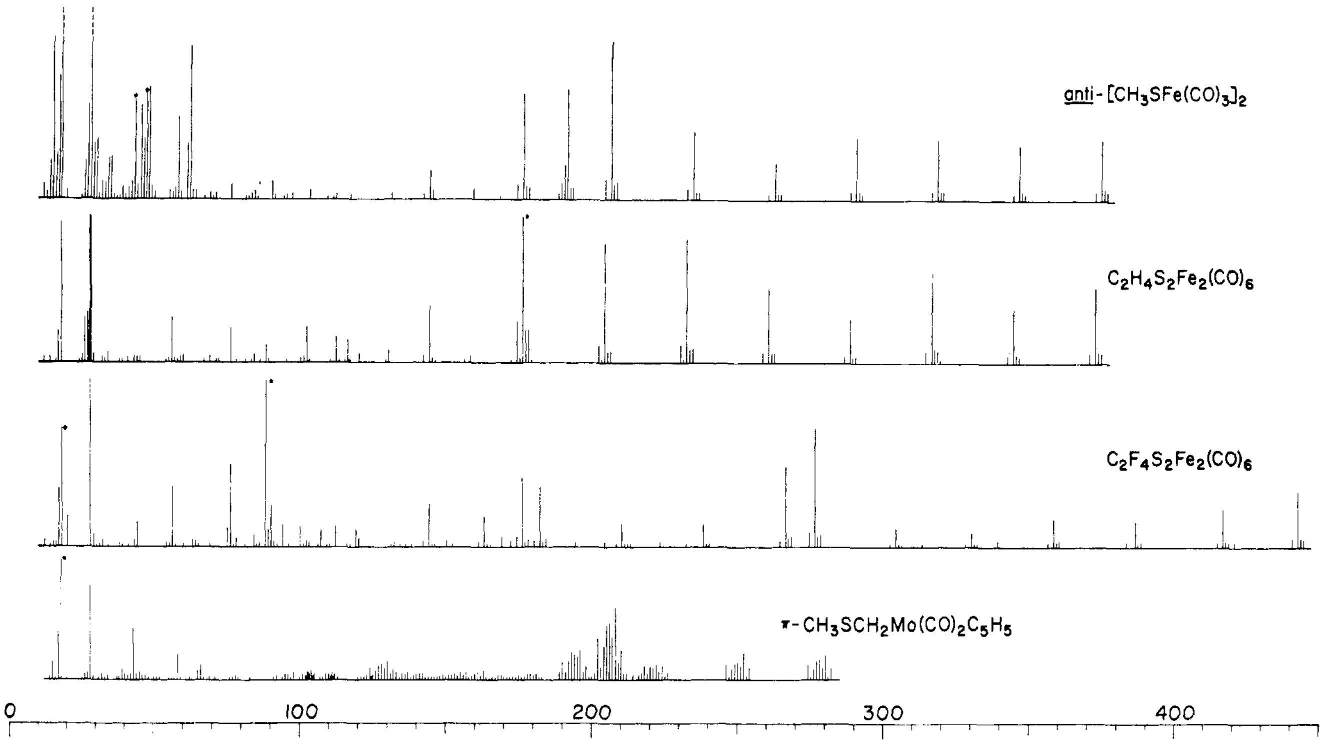

Figure 1. Mass spectra of four of the compounds described in this paper. Peaks designated with an asterisk are drawn half their relative heights in order to fit on the scale. Peaks ending in dotted lines are off-scale.

ion containing the metal atom.[9] The *m/e* values reported in the tables are for the ions containing the isotopes ^{55}Mn, ^{56}Fe, ^{96}Mo, and ^{184}W. Among the compounds discussed in this paper, relatively few metastable ions were observed apparently because the available spectra were too weak. The compounds used in this study were samples which had been prepared by methods adequately described in the literature.[5-8]

Table I. Mass Spectra of $[CH_3SFe(CO)_3]_2$ Isomers

m/e	Ion	Rel abundance Isomer A (*anti*)[b]	Rel abundance Isomer B (*syn*)[c]	Reported rel abundance[a]
374	$(CH_3S)_2Fe_2(CO)_6^+$	34	22	30
346	$(CH_3S)_2Fe_2(CO)_5^+$	31	25	27
318	$(CH_3S)_2Fe_2(CO)_4^+$	35	27	32
290	$(CH_3S)_2Fe_2(CO)_3^+$	35	32	30
262	$(CH_3S)_2Fe_2(CO)_2^+$	21	19	22
234	$(CH_3S)_2Fe_2CO^+$	39	40	44
206	$(CH_3S)_2Fe_2^+$	100	100	100
191	$CH_3SFe_2S^+$	63	51	51
176	$Fe_2S_2^+$	60	53	42
159	$Fe_2SCH_3^+$	6	5	5
144	Fe_2S^+	17	26	23
131	$(CH_3S)_2Fe_2(CO)_2^{2+}$	3	6	6
119	$CH_3SCH_3FeH^+$	<2	4	
117	$(CH_3S)_2Fe_2CO^{2+}$	3	7	6
111		2	6	
109		2	7	
103	$(CH_3S)_2Fe^{2+}$	5	17	15
69	$CHFe^+$	4	5	
62	$CH_3SCH_3^+$	88	13	
61	$CH_3SCH_2^+$	31	6	
56	Fe^+	3	14	8
48	CH_3SH^+	63	4	
47	CH_3S^+	140	5	

[a] Data of K. Edgar, B. F. G. Johnson, J. Lewis, I. G. Williams, and J. M. Wilson, *J. Chem. Soc.*, 379 (1967). [b] Source pressure = ~5.2 × 10^{-6} mm. [c] Source pressure = 2.3 × 10^{-6} mm.

Natural iron contains 5.90% ^{54}Fe in addition to 91.6% of the major isotope (^{56}Fe) and 2.20 and 0.33%, respectively, of the minor isotopes ^{57}Fe and ^{58}Fe. Natural sulfur contains 4.2% ^{34}S in addition to 95.0% of the major isotope (^{32}S) and 0.75 and 0.017%, respectively, of the minor isotopes ^{33}S and ^{36}S. Natural carbon, hydrogen, oxygen, and fluorine contain 98.9% ^{12}C, >99.8% ^{1}H, >99.7% ^{16}O, and 100% ^{19}F, respectively, making other isotopes of these elements of minor significance in these mass spectra. As a result of the relative abundances of the isotopes of these elements, the ion 2 *m/e* units less than the most abundant ion of a given elemental composition arises mainly from substitution of ^{54}Fe for ^{56}Fe. Therefore the ratio (M − 2)/M is often an indication of the number of iron atoms in a given ion according to the relationship $(^{54}Fe/^{56}Fe)w$, *where w is the number of iron atoms in the ion under* consideration. Thus in ions with one or two iron atoms, the value of (M − 2)/M should be 0.0645 or 0.129, respectively, on the basis of this treatment. Naturally, the presence of another ion of mass M − 2 makes the ratio (M − 2)/M no longer meaningful. For this reason analysis of the ratio (M − 2)/M, in order to determine the number of iron atoms present, is most useful in the higher *m/e* region where other ions are least likely to interfere. In certain ions containing two or more atoms of hydrogen, the ratio (M − 2)/M may also no longer be a valid indicator of the number of iron atoms since some of the M − 2 ion may arise by loss of H_2 from the M ion rather than by substitution of ^{54}Fe for ^{56}Fe.

For similar reasons the ratio (M + 2)/M may be an approximate indicator of the number of sulfur atoms in a given ion.[10] For

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(9) In the cases of ions containing molybdenum and tungsten (Tables VI and XII), the characteristic multiline patterns containing the ions of the several isotopes of these metals were observed. In the mass spectra of the molybdenum and tungsten compounds, the relative abundances of the ions containing the metals and of the ions not containing the metals are not directly comparable because the total abundance of the ions of a given type containing the multiisotopic metals will be divided over several ions of relative intensities corresponding to the isotopic abundances, whereas the total abundance of ions of a given type containing no multiisotopic metals such as molybdenum or tungsten will be essentially concentrated in one ion. The relative abundances of the ions containing molybdenum and tungsten cited in Tables VI and XII are for those containing their most abundant isotopes ^{98}Mo and ^{184}W, respectively.

(10) (a) For a further discussion of the application of isotope peaks as an indication of the elemental composition of a given ion, see R. I. Reed, "Application of Mass Spectrometry to Organic Chemistry,"

Table II. Mass Spectrum of $C_7H_8Fe_2(CO)_4(SCH_3)_2$[a]

m/e	Ion	Rel abundance
410	$C_7H_8Fe_2(CO)_4(SCH_3)_2^+$	15
382	$C_7H_8Fe_2(CO)_3(SCH_3)_2^+$	29
354	$C_7H_8Fe_2(CO)_2(SCH_3)_2^+$	26
326	$C_7H_8Fe_2CO(SCH_3)_2^+$	44
298	$C_7H_8Fe_2(SCH_3)_2^+$	63
283	$C_7H_8Fe_2S(SCH_3)^+$	34
268	$C_7H_8Fe_2S_2^+$	100
248		12
242	$C_5H_6Fe_2S_2^+$	26
241	$C_5H_5Fe_2S_2^+$	15
209	$C_5H_5Fe_2S^+$	12
206	$Fe_2(SCH_3)_2^+$	14
191	$Fe_2S(SCH_3)^+$	73
176	$Fe_2S_2^+$	64
149	$C_7H_8Fe_2(SCH_3)_2^{2+}$	18
144	Fe_2S^+	24
141.5	$C_7H_8Fe_2S(SCH_3)^{2+}$	29
92	$C_7H_8^+$	2500
91	$C_7H_7^+$	5400
66	$C_6H_6^+$	2000
65	$C_5H_5^+$	1000
51	$C_4H_3^+$	400
50	$C_4H_2^+$	250
48	CH_3SH^+	400
47	CH_3S^+	590
39	$C_3H_3^+$	1000

[a] Source pressure = ~7.0 × 10^{-7} mm.

Table III. Mass Spectrum of $C_2H_4S_2Fe_2(CO)_6$[a]

m/e	Ion	Rel abundance	(M − 2)/M	(M + 2)/M
372	$C_2H_4S_2Fe_2(CO)_6^+$	24	0.13	0.13
344	$C_2H_4S_2Fe_2(CO)_5^+$	17	0.13	0.11
316	$C_2H_4S_2Fe_2(CO)_4^+$	29	0.13	0.13
288	$C_2H_4S_2Fe_2(CO)_3^+$	14	0.13	0.12
260	$C_2H_4S_2Fe_2(CO)_2^+$	24	0.13	0.11
232	$C_2H_4S_2Fe_2CO^+$	40	0.14	0.10
204	$C_2H_4S_2Fe_2^+$	37	0.13	0.10
176	$Fe_2S_2^+$	100	0.15	0.11
158	$C_2H_4S_2Fe_2(CO)_4^{2+}$	2		
144	Fe_2S^+, $C_2H_4S_2Fe(CO)_3^{2+}$	18	0.13	0.06
130	$C_2H_4S_2Fe_2(CO)_2^{2+}$	3		
120	FeS_2^+	3	0.08	0.12
116	$C_2H_4S_2Fe_2CO^{2+}$	7		
112	Fe_2^+	8	0.14	0.03
102	$C_2H_4S_2Fe_2^{2+}$	11		
88	$Fe_2S_2^{2+}$	5		
76	CS_2^+	10		
56	Fe^+	14	0.07	0.04

[a] Source pressure = 1.8 × 10^{-6} mm.

ions with one or two sulfur atoms, respectively, the value of (M + 2)/M is expected to be 0.0442 or 0.0884 on the basis of this treatment. However, oxygen (^{18}O natural abundance = 0.2%) and iron (^{58}Fe natural abundance = 0.33%) make appreciable contributions to the intensity of the M + 2 ion, making the ratio (M + 2)/M a less exact indicator of the number of sulfur atoms than the ratio (M − 2)/M is of the number of iron atoms.

The values of the ratios (M − 2)/M and (M + 2)/M were checked where applicable and possible. They agreed approximately with the proposed assignments except in cases where interference from background or other ions made these ratios unreliable. Tables III–V include the values for (M − 2)/M and (M + 2)/M for many of the ions in the compounds $C_2H_4S_2Fe_2(CO)_6$, $C_2F_4S_2Fe_2(CO)_6$, and $C_7H_6S_2Fe_2(CO)_6$, respectively. Examples of the value of these ratios in indicating assignments of the ions include the assignment of the peaks at *m/e* 266, 238, 210, and 182 in the mass spectrum of $C_2F_4S_2Fe_2(CO)_6$ to the ions $C_2F_2S_2Fe(CO)_n^+$ (n = 3, 2, 1, and 0, respectively) containing only one iron atom and the assignment of the peak at *m/e* 244 in the mass spectrum of $C_7H_6S_2Fe_2(CO)_6$ (Table V) to the iron-free ion $C_{14}H_{12}S_2^+$. The appreciable background level compared with the intensities of some of the weak M − 2 and M + 2 ions make the errors in the (M − 2)/M and (M + 2)/M ratios large (±0.01) and the ratios themselves sometimes somewhat higher than predicted.

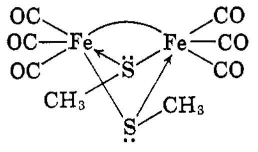
Table IV. Mass Spectrum of $C_2F_4S_2Fe_2(CO)_6$[a]

m/e	Ion	Rel abundance	(M − 2)/M	(M + 2)/M
444	$C_2F_4S_2Fe_2(CO)_6^+$	47	0.13	0.13
416	$C_2F_4S_2Fe_2(CO)_5^+$	32	0.12	0.12
388	$C_2F_4S_2Fe_2(CO)_4^+$	19	0.13	0.16
360	$C_2F_4S_2Fe_2(CO)_3^+$	22	0.13	0.15
341	$C_2F_3S_2Fe_2(CO)_3^+$	5	0.14	0.12
332	$C_2F_4S_2Fe_2(CO)_2^+$	11	0.14	0.13
304	$C_2F_4S_2Fe_2CO^+$	15	0.14	0.10
276	$C_2F_4S_2Fe_2^+$	100	0.12	0.10
266	$C_2F_2S_2Fe(CO)_3^+$	69	0.06	0.11
238	$C_2F_2S_2Fe(CO)_2^+$	18	0.06	0.10
210	$C_2F_2S_2FeCO^+$	19	0.07	0.10
182	$C_2F_2S_2Fe^+$	51	0.07	0.12
176	$Fe_2S_2^+$	57	0.13	0.12
163	Fe_2SF^+	26	0.11	0.06
144	Fe_2S^+	36	0.12	0.05
119	$C_2F_2S_2Fe(CO)_2^{2+}$	15		
112	Fe_2^+	18	0.13	0.02
107	$FeSF^+$	14	0.06	0.07
100	$C_2F_4^+$	17	0.06	
94	FeF_2^+	18	0.07	
90		34		
88	CF_4^+, $Fe_2S_2^{2+}$	262	0.01	
76	CS_2^+	71	0.01	
75	FeF^+	16	0.06	
56	Fe^+	51	0.06	0.02

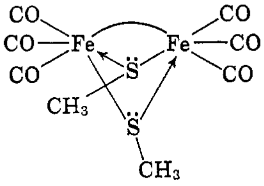
[a] Source pressure = 1.0 × 10^{-6} mm.

Discussion

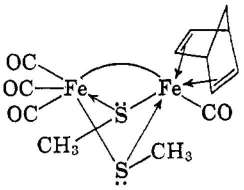
A. $(RS)_2Fe_2(CO)_6$ Derivatives. 1. $[CH_3SFe(CO)_3]_2$ Isomers (Table I). Table I compares the mass spectra of the *anti* and *syn* isomers (I and II, respectively)[11]



I



II



III

of the complex $[CH_3SFe(CO)_3]_2$.[12] In general, the

Academic Press Inc., New York, N. Y., 1966, pp 16–22; and J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, pp 300–302. (b) The presence of ^{13}C in 1.1% natural abundance in natural carbon will also affect the relative abundance of the M + 2 ions. However, this effect is small compared with that of the ^{34}S isotope. Thus ten carbon atoms will contribute only 0.0053 to the relative intensity of the M + 2 ion; (see Beynon, ref 10a p 497).

(11) R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962); L. F. Dahl and C. W. Wei, *Inorg. Chem.*, **2**, 328 (1963).

(12) After this work was completed, a report appeared on the mass spectrum of $[CH_3SFe(CO)_3]_2$ (unspecified isomer): K. Edgar, B. F. G. Johnson, J. Lewis, I. G. Williams, and J. M. Wilson, *J. Chem. Soc., Sect. A*, 379 (1967). Table I gives the data of Edgar, *et al.*, for comparison with the data of the present work.

Table V. Mass Spectrum of $C_7H_6S_2Fe_2(CO)_6$[a]

m/e	Ion	Rel abundance	(M − 2)/M	(M + 2)/M
434	$C_7H_6S_2Fe_2'CO)_6^+$	2	0.14	0.14
406	$C_7H_6S_2Fe_2(CO)_5^+$	26	0.12	0.13
378	$C_7H_6S_2Fe_2(CO)_4^+$	26	0.13	0.11
350	$C_7H_6S_2Fe_2(CO)_3^+$	17	0.14	0.13
322	$C_7H_6S_2Fe_2(CO)_2^+$	22	0.13	0.12
294	$C_7H_6S_2Fe_2CO^+$	39	0.13	0.11
266	$C_7H_6S_2Fe_2^+$	100	0.14	0.11
251	$C_6H_3S_2Fe_2^+$	1		
244	$C_{14}H_{12}S_2^+$	30	0.03	0.12
212	$C_3Fe_2S_2^+$	25	0.13	0.10
211	$C_7H_7S_2Fe^+$	22	0.07	0.23
188	$CFe_2S_2^+$	9	0.16	0.13
176	$Fe_2S_2^+$	23	0.13	0.11
169	$Fe_2SC_2H^+$	5		
161	$C_7H_6S_2Fe_2(CO)_2^{2+}$	5		
147	$C_7H_6S_2Fe_2CO^{2+}$	6		
144	Fe_2S^+	15	0.13	
133	$C_7H_6S_2Fe_2^{2+}$	18		
124	$C_7H_8S^+$	8		
123	$C_7H_7S^+$	3		
122	$C_7H_6S^+$	3		
121	$C_7H_5S^+$	4		
105	$C_7H_6S_2Fe^{2+}$	6		
92	$C_7H_8^+$	5		
91	$C_7H_7^+$	11		
89	$C_7H_5^+$	2		
77	$C_6H_5^+$	3		
71	$C_3H_3S^+$	2		
69	C_3HS^+	2		
66	$C_5H_6^+$	2		
65	$C_5H_5^+$	3		
63	$C_5H_3^+$	3		
60	COS^+, $C_2H_4S^+$	3		
57	C_2HS^+	3		
56	Fe^+	7		
55		3		
51	$C_4H_3^+$	2		
45	CHS^+	3		
43		4		
41	$C_3H_5^+$	3		
39	$C_3H_3^+$	5		

[a] Source pressure = 1.3×10^{-6} mm.

Table VI. Mass Spectra of $CH_3SCH_2Mo(CO)_nC_5H_5$ Compounds[a]

m/e	Ion	Relative abundance n = 2	n = 3
306	$CH_3SCH_2Mo(CO)_3C_5H_5^+$	<0.1	<0.003
278	$CH_3SCH_2Mo(CO)_2C_5H_5^+$	34	38
263	$SCH_2Mo(CO)_2C_5H_5^+$	0.2	0.3
250	$CH_3SCH_2MoCOC_5H_5^+$	36	37
235	$SCH_2MoCOC_5H_5^+$	0.5	0.9
222	$CH_3SCH_2MoC_5H_5^+$	20	20
218	$C_2SHMoC_5H_5^+$	11	10
206	$C_6H_6SMo^+$	100	100
194	$C_5H_5MoSH^+$	41	41
179	$C_3H_3MoSC^+$?	8	8
161	$C_5H_5Mo^+$	11	22
153	$MoSC_2H^+$	10	9
141	$MoSCH^+$	7	7
128	MoS^+	28	29
125	$CH_3SCH_2MoCOC_5H_5^{2+}$	2	2
111	$CH_3SCH_2MoC_5H_5^{2+}$	5	8
103	$C_6H_6SMo^{2+}$	7	11
96	Mo^+	10	12
80.5	$C_5H_5Mo^{2+}$	2	3
66	$C_5H_6^+$	20	23
65	$C_5H_5^+$	11	13
39	$C_3H_3^+$	13	15

[a] Source pressure = $\sim 1.3 \times 10^{-6}$ mm.

Table VII. Mass Spectrum of $CH_3SCH_2Mn(CO)_4$

m/e	Ion	Rel abundance
228	$CH_3SCH_2Mn(CO)_4^+$	29
200	$CH_3SCH_2Mn(CO)_3^+$	16
172	$CH_3SCH_2Mn(CO)_2^+$	22
144	$CH_3SCH_2MnCO^+$	20
116	$CH_3SCH_2Mn^+$	100
102	CH_3SMn^+	4
101	CH_2SMn^+	18
100	$CHSMn^+$	7
87	MnS^+	8
83	$MnCO^+$, $MnC_2H_4^+$	7
72	$CH_3SCH_2MnCO^{2+}$	3
70	CH_3Mn^+	33
69	CH_2Mn^+	8
62	$CH_3SCH_3^+$	18
61	$CH_3SCH_2^+$	100
55	Mn^+	93
48	CH_3SH^+	18
47	CH_3S^+	31
46	CH_2S^+	16
45	CHS^+	22
35	CH_3Mn^{2+}	11

Metastable transitions

m/e	Process	Neutral fragment lost
175.2	$228 \xrightarrow{-28} 200$	CO
148.0	$200 \xrightarrow{-28} 172$	CO
120.4	$172 \xrightarrow{-28} 144$	CO
93.5	$144 \xrightarrow{-28} 116$	CO
32.2	$116 \xrightarrow{-55} 61$	Mn

Table VIII. Mass Spectrum of $CH_3SCH_2CH_2COMn(CO)_4$[a]

m/e	Ion	Rel abundance
270	$CH_3SCH_2CH_2COMn(CO)_4^+$	0.3
242	$CH_3SCH_2CH_2Mn(CO)_4^+$ $(CH_3SMn(CO)_5)^+$	31
214	$CH_3SCH_2CH_2Mn(CO)_3^+$ $(CH_3SMn(CO)_4^+)$	8
186	$CH_3SCH_2CH_2Mn(CO)_2^+$ $(CH_3SMn(CO)_3^+)$	12
158	$CH_3SCH_2CH_2MnCO^+$ $(CH_3SMn(CO)_2^+)$	19
142	$CH_3SCH_2CH_2MnC^+$	15
130	$CH_3SCH_2CH_2Mn^+$ (CH_3SMnCO^+)	32
102	CH_3SMn^+	100
87	MnS^+	12
75	$CH_3SCH_2CH_2^+$	13
55	Mn^+	53
48	CH_3SH^+	79
47	CH_3S^+	94
45	CHS^+	41

[a] Source pressure = $\sim 3.8 \times 10^{-6}$ mm.

same ions are observed in the mass spectra of the two isomers. The only significant difference is the greater abundance of the iron-free ions $CH_3SCH_3^+$, $CH_3SCH_2^+$, CH_3SH^+, and CH_3S^+ in the mass spectrum of the *anti* isomer (isomer A) than in that of the *syn* isomer (isomer B).

In both isomers the parent ion $(CH_3S)_2Fe_2(CO)_6^+$ (*m/e* 374) first undergoes stepwise loss of the six carbonyl ligands giving the carbonyl-free ion $(CH_3S)_2Fe_2^+$ (*m/e* 206). The intermediate ions $(CH_3S)_2Fe_2(CO)_n^+$ (n = 5–1, inclusive) are observed in about the same relative abundances in the mass spectra of the two isomers. The carbonyl-free ion $(CH_3S)_2Fe_2^+$ (*m/e* 206) decomposes further by stepwise loss of the two methyl

Table IX. Mass Spectrum of $[CH_3SFe(CO)C_5H_5]_2$[a]

m/e	Ion	Rel abundance
392	$(C_5H_5)_2Fe_2(CO)_2(SCH_3)_2^+$	0.31
364	$(C_5H_5)_2Fe_2(CO)(SCH_3)_2^+$	0.25
336	$(C_5H_5)_2Fe_2(SCH_3)_2^+$	0.62
332	$(C_5H_5)_2Fe_2S_2C_2H_2^+$	0.31
321	$(C_5H_5)_2Fe_2S_2CH_3^+$	0.69
306	$(C_5H_5)_2Fe_2S_2^+$	0.59
286	$(C_5H_5)_2Fe_2CS^+$	1.2
241	$C_5H_5Fe_2S_2^+$	0.41
236		0.31
232	$C_5H_5FeC_5H_4SCH_3^+$	0.28
231	$C_5H_5FeC_5H_4SCH_2^+$	0.28
230	$C_5H_5FeC_5H_4SCH^+$	0.31
217	$C_5H_5FeC_5H_4S^+$	0.25
209		0.28
204	$C_3H_3FeC_5H_4SCH^+$?	0.31
202	$C_3HFeC_5H_4SCH^+$?	1.3
200	$C_5H_5FeC_5H_4CH_3^+$	2.7
192		0.41
186	$(C_5H_5)_2Fe^+$	27
171		1.3
160	$C_5H_5FeC_3H_3^+$	1.2
158	$C_5H_5FeC_3H^+$	1.3
150	$Fe(SCH_3)_2^+$ $(C_5H_5Fe(CO)H^+)$	0.78
149	$CH_2SFeSCH_3^+$ $(C_5H_5FeCO^+)$	1.1
146	$C_5H_5FeC_2H^+$	0.97
134	$C_6H_6Fe^+$	3.6
129	$C_{10}H_9^+$	7.8
128	$C_{10}H_8^+$	7.8
121	$C_5H_5Fe^+$	100
115	$C_9H_7^+$	5.6
112	$C_5H_5SCH_3^+$	6.2
95	$C_3H_3Fe^+$	14
94	$CH_3SSCH_3^+$ $(C_3H_2Fe^+)$	41
93	$CH_3SSCH_2^+$ (C_3HFe^+)	19
81	C_2HFe^+ $(C_6H_9^+)$	11
79	$C_6H_7^+$	18
66	$C_5H_6^+$	21
65	$C_5H_5^+$	16
56	Fe^+	56
48	CH_3SH^+	6.9
47	CH_3S^+	26
46	CH_2S^+	11
45	CHS^+	22
39	$C_3H_3^+$	22

[a] Source pressure = $\sim 8.0 \times 10^{-7}$ mm.

Table X. Mass Spectrum of $CH_3SFe(CO)_2C_5H_5$

m/e	Ion	Rel abundance
304	$C_5H_5Fe(CO)_2I^+$	3.2
276	$C_5H_5FeCOI^+$	3.3
248	$C_5H_5FeI^+$	3.3
232	$C_5H_5FeC_5H_4SCH_3^+$	0.2
224	$CH_3SFe(CO)_2C_5H_5^+$	2.4
200	$C_5H_5FeC_5H_4CH_3^+$	1.4
196	$CH_3SFeCOC_5H_5^+$	3.8
186	$(C_5H_5)_2Fe^+$	234
178	$C_5H_5Fe(CO)_2H^+$	0.8
177	$C_5H_5Fe(CO)_2^+$	1.3
168	$C_5H_5FeSCH_3^+$	3.6
166	$C_6H_6SFe^+$	4.6
160	$C_5H_5FeC_3H_3^+$	1.3
158	$C_5H_5FeC_3H^+$	1.4
150	$C_5H_5FeCOH^+$ $(Fe(SCH_3)_2^+)$	1.0
149	$C_5H_5FeCO^+$ $(CH_2SFeSCH_3^+)$	1.7
142	$C_3H_3FeSCH_3^+$?	5.9
134	$C_6H_6Fe^+$	5.9
130	$C_{10}H_{10}^+$	24
129	$C_{10}H_9^+$	29
128	$C_{10}H_8^+$	19
121	$C_5H_5Fe^+$	100.0
115	$C_2H_3SFe^+$?	15
112	$C_5H_5SCH_3^+$	13
103	CH_3SFe^+	2.9
102	CH_2SFe^+	3.0
97	$C_5H_5S^+$	15
95	$C_3H_3Fe^+$	14
94	$CH_3SSCH_3^+$, $C_3H_2Fe^+$	29
93	$CH_3SSCH_2^+$, C_3HFe^+	15
80	$C_6H_8^+$	27
79	$C_6H_7^+$	44
77	$C_6H_5^+$	19
66	$C_5H_6^+$	38
65	$C_5H_5^+$	51
63	$C_5H_3^+$	17
56	Fe^+	51
48	CH_3SH^+	29
47	CH_3S^+	37
46	CH_2S^+	13
45	CHS^+	25
39	$C_3H_3^+$	60

groups to give the ion $Fe_2S_2^+$ (*m/e* 176). This ion then loses a sulfur atom to give Fe_2S^+ (*m/e* 144), which loses FeS to give Fe^+ (*m/e* 56). Alternatively, the neutral fragment FeS_2 may be lost from the $Fe_2S_2^+$ ion (*m/e* 176) giving directly the bare Fe^+ ion (*m/e* 56) similar to some fragmentations reported by Preston and Reed.[8]

Doubly charged ions of the type $(CH_3S)_2Fe_2(CO)_n^{2+}$ ($n = 0, 1, 2,$ and 4) are observed. These may be distinguished from singly charged ions with half the formula (and thus the same *m/e* value) by the relative intensity of the ion two mass units below the ion under consideration.

2. $C_7H_8Fe_2(CO)_4(SCH_3)_2$ (Table II). This compound (III) is obtained by the replacement of two carbonyl groups in $[CH_3SFe(CO)_3]_2$ (I) with bicyclo[2.2.1]heptadiene. In the mass spectrum of III, the parent ion $C_7H_8Fe_2(CO)_4(SCH_3)_2^+$ (*m/e* 410) first loses stepwise the four carbonyl groups to give the ion $C_7H_8Fe_2(SCH_3)_2^+$ (*m/e* 298). This latter ion, in turn, loses stepwise the two methyl groups giving the ion $C_7H_8Fe_2S_2^+$ (*m/e* 268), selected as the base ion because of its greatest abundance compared with the other ions containing iron.

Further degradation of the $C_7H_8Fe_2S_2^+$ ion (*m/e* 268) involves the C_7H_8 ligand. Acetylene is lost from this ion to give $C_5H_6Fe_2S_2^+$ (*m/e* 242). This latter ion apparently loses hydrogen to give the ion $C_5H_5Fe_2S_2^+$ (*m/e* 241). This ion may be a cyclopentadienyl derivative. Further decomposition of the $C_5H_5Fe_2S_2^+$ ion appears to involve complete removal of the C_5H_5 group since no ions below $C_5H_5Fe_2S_2^+$ (*m/e* 241) containing both the iron atom and remnants of the C_5H_5 group are observed.

In an alternate fragmentation pathway the ion $C_7H_8Fe_2(SCH_3)_2^+$ (*m/e* 298) first loses the C_7H_8 ligand rather than the methyl groups, giving the ion $Fe_2(SCH_3)_2^+$ (*m/e* 206). This ion then loses stepwise its two methyl groups giving $Fe_2S_2^+$ (*m/e* 176).

The two most intense doubly charged ions are $C_7H_8Fe_2(SCH_3)_2^{2+}$ (*m/e* 149) and $C_7H_8Fe_2S(SCH_3)^{2+}$ (*m/e* 141.5). Only negligible concentrations of doubly charged iron carbonyl ions were observed.

The ions not containing iron atoms are unusually intense in the mass spectrum of $C_7H_8Fe_2(CO)_4(SCH_3)_2$. These possibly arise from pyrolysis reactions in the mass spectrometer. The ions $C_7H_8^+$, $C_7H_7^+$, $C_5H_6^+$, $C_5H_5^+$, $C_4H_3^+$, $C_4H_2^+$, and $C_3H_3^+$ arise from fragmentation of the C_7H_8 ligand and the ions CH_3SH^+ and CH_3S^+ from the CH_3S ligand.

Table XI. Mass Spectrum of $C_6H_5COSFe(CO)_2C_5H_5$[a]

m/e	Ion	Rel abundance
314	$C_6H_5COSFe(CO)_2C_5H_5^+$	0.46
304	$C_5H_5Fe(CO)_2I^+$	0.28
290	$C_6H_5COC_5H_4FeC_5H_5^+$	0.60
286	$C_6H_5COSFeCOC_5H_5^+$	1.6
276	$C_5H_5FeCOI^+$	0.28
262	$C_6H_5C_5H_4FeC_5H_5^+$	1.8
258	$C_6H_5COSFeC_5H_5^+$	13
248	$C_5H_5FeI^+$	0.32
230	$C_6H_5SFeC_5H_5^+$	2.5
214	$C_6H_5OFeC_5H_5^+$	4.4
204	$C_9H_8SFe^+$	3.9
198	$C_6H_5FeC_5H_5^+$	13
186	$(C_5H_5)_2Fe^+$	330
178	$C_7H_6SFe^+$	3.1
177	$C_5H_5Fe(CO)_2^+$ ($C_7H_5SFe^+$)	4.0
171		7.7
164		6.1
154	$C_{12}H_{10}^+$ ($C_5H_5FeSH^+$)	89
153	$C_{12}H_9^+$ ($C_5H_5FeS^+$)	36
152	$C_{12}H_8^+$	35
151	$C_{12}H_7^+$	8.1
150	$C_5H_5FeCOH^+$	6.0
149	$C_5H_5FeCO^+$	4.5
142	$C_{11}H_{10}^+$	56
141	$C_{11}H_9^+$	46
130	$C_{10}H_{10}^+$	16
129	$C_{10}H_9^+$	22
128	$C_{10}H_8^+$	19
127	$C_{10}H_7^+$	8.3
126	$C_{10}H_6^+$	3.7
121	$C_5H_5Fe^+$	100.0
115	$C_9H_7^+$	36
110	$C_6H_6S^+$	64
109	$C_6H_5S^+$	28
105	$C_6H_5CO^+$	206
95	$C_3H_3Fe^+$	14
94	$C_3H_2Fe^+$ ($C_6H_6O^+$)	8.3
93	$C_6H_5O^+$	17
92	$C_6H_4O^+$	15
89	$C_7H_5^+$ ($FeSH^+$)	6.5
84	$FeCO^+$ ($C_4H_4S^+$)	13
81		10
77	$C_6H_5^+$	144
69		
66	$C_5H_6^+$	83
65	$C_5H_5^+$	106
63	$C_5H_3^+$	42
51	$C_4H_3^+$	89
39	$C_3H_3^+$	120

[a] Source pressure = 8.0×10^{-7} mm.

Table XII. Mass Spectrum of $CH_3SCH_2CH_2SCH_3W(CO)_4$[a]

m/e	Ion	Rel abundance
418[b]	$CH_3SCH_2CH_2SCH_3W(CO)_4^+$	84
390[b]	$CH_3SCH_2CH_2SCH_3W(CO)_3^+$	39
362[b]	$CH_3SCH_2CH_2SCH_3W(CO)_2^+$	52
334[b]	$CH_3SCH_2CH_2SCH_3WCO^+$	58
319[b]	$CH_3SCH_2CH_2SWCO^+$	23
306[b]	$CH_3SCH_2CH_2SCH_3W^+$	77
291[b]	$CH_3SCH_2CH_2SW^+$	52
278[b]	$CH_3SWSCH_3^+$	74
276[b]	CH_3SWSCH^+	90
263[b]	CH_3SWS^+	100
248[b]	SWS^+	58
229	$CH_3SCH_2CH_2S(CH_3)SCH_2CH_2SCH_3^+$	184
228	$CH_3SCH_2CH_2SCH_2SCH_2CH_2SCH_3^+$	296
212[b]	WCO^+	48
211	$C_6H_{11}S_4^+$	168
184[b]	W^+	40
153[b]	$CH_3SCH_2CH_2SCH_3W^{2+}$	23
122	$CH_3SCH_2CH_2SCH_3^+$	13,000
107	$CH_3SCH_2CH_2S^+$	181
102	$CH_2SCH_2CH_2CO^+$, $(CH_2)_5S^+$	474
79	CH_3SS^+	726
75	$CH_3SCH_2CH_2^+$	7,200
74	$CH_2SCH_2CH_2^+$	3,700
61	$CH_3SCH_2CH_2SCH_3^{2+}$, $CH_3SCH_2^+$	19,000

[a] Source pressure = 1.7×10^{-6} mm. [b] The characteristic pattern for the tungsten isotopes was observed for this ion. The *m/e* value given here is for the ion containing ^{184}W.

3. $C_2H_4S_2Fe_2(CO)_6$ (Table III). The compound $C_2H_4S_2Fe_2(CO)_6$ (IV) is similar to the compounds $[CH_3SFe(CO)_3]_2$ (I and II) discussed above except that the two sulfur atoms in IV are linked by a bridge of two carbon atoms. The mass spectrum of IV is thus somewhat similar to those of the two $[CH_3SFe(CO)_3]_2$ isomers discussed above.

The parent ion $C_2H_4S_2Fe_2(CO)_6^+$ (*m/e* 372) first loses stepwise its six carbonyl groups giving $C_2H_4S_2Fe_2^+$ (*m/e* 204). This latter fragment then loses ethylene to give the ion $Fe_2S_2^+$ (*m/e* 176). This process is supported by a weak metastable ion at *m/e* 151.5 ($176^2/204$ = 151.9). Other features of the mass spectrum of $C_2H_4S_2Fe_2(CO)_6$ are the doubly charged ions $C_2H_4S_2Fe_2(CO)_n^{2+}$ (n = 0–4) and $Fe_2S_2^{2+}$ (*m/e* 88).

4. $C_2F_4S_2Fe_2(CO)_6$ (Table IV). The compound $C_2F_4S_2Fe_2(CO)_6$ (IV, H = F) was studied in order to compare its mass spectrum with that of its hydrogen analog $C_2H_4S_2Fe(CO)_6$ just discussed above. In this mass spectrum, the ratio (M − 2)/M (see Experimental Section) proved to be of value in establishing the number of iron atoms in a given ion.

The parent ion $C_2F_4S_2Fe_2(CO)_6^+$ (*m/e* 444) exhibits the expected stepwise loss of carbonyl groups to give the carbonyl-free ion $C_2F_4S_2Fe_2^+$ (*m/e* 276). However, when the tricarbonyl ion $C_2F_4S_2Fe_2(CO)_3^+$ (*m/e* 360) is reached, two other types of fragmentation compete with further loss of a carbonyl group.

One such fragmentation process of the $C_2F_4S_2Fe_2(CO)_3^+$ ion is loss of fluorine (mass 19) to give the ion $C_2F_3S_2Fe_2(CO)_3^+$ (*m/e* 341). Many fluorocarbon derivatives including certain bis(trifluoromethyl) dithiolate complexes[4] lose fluorine in such a manner in their mass spectra. Typical mass spectra of fluorocarbon derivatives of transition metals will be discussed in a future paper in this series.

The other fragmentation process of $C_2F_4S_2Fe_2(CO)_3^+$ (*m/e* 360) is loss of FeF_2 (mass 94) to give the mononuclear ion $C_2F_2S_2Fe(CO)_3^+$ (*m/e* 266) indicated by a metastable ion at *m/e* 196.5 ($266^2/360$ = 196.5). This process appears to be similar to the loss of CoF_2 from the $C_{12}F_{18}S_6Co_3^+$ ion to give the $C_{12}F_{16}S_6Co_2^+$ ion observed in the recently reported[12] mass spectrum of the trinuclear cobalt complex $[(CF_3)_2C_2S_2Co(CO)]_3$. The $C_2F_2S_2Fe(CO)_3^+$ ion may arise from a dithiooxalyl fluoride complex V related to the hexafluorobutane-2,3-dithione complex of cobalt $C_5H_5CoS_2C_2(CF_3)_2$ (VI)[13,14] by replacement of the CF_3 groups in VI with fluorine atoms and the C_5H_5Co group in VI with the isoelectronic[15] $Fe(CO)_3$ group. Further degradation of the $C_2F_2S_2Fe(CO)_3^+$ (*m/e* 266) ion occurs by stepwise

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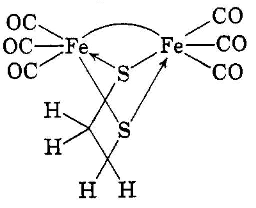
(13) R. B. King and T. F. Korenowski, *Chem. Commun.*, 771 (1966).

(14) R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

(15) For an X-ray crystallographic study supporting formulation of $C_5H_5CoS_2C_2(CF_3)_2$ as a hexafluorobutane-2,3-dithione complex rather than a bis(trifluoromethyl)ethylene dithiolate complex, see H. W. Baird and B. M. White, *J. Am. Chem. Soc.*, **88**, 4744 (1966).

loss of the three carbonyl groups to give $C_2F_2S_2Fe^+$ (*m/e* 182).

The formation of $C_2F_4S_2Fe_2^+$ (*m/e* 276) from $C_2F_4S_2Fe_2(CO)_6^+$ (*m/e* 444) has already been discussed. Loss of tetrafluoroethylene (mass 100) from $C_2F_4S_2Fe_2^+$ (*m/e* 276) appears to occur giving the $Fe_2S_2^+$ ion (*m/e* 176). The tetrafluoroethylene ion, $C_2F_4^+$ (*m/e* 100), is also observed. Other iron-containing fragments appear to be Fe_2SF^+, Fe_2S^+, $FeSF^+$, FeF_2^+, FeF^+, and Fe^+. Doubly charged ions include $C_2F_2S_2Fe(CO)_2^{2+}$ (*m/e* 119) and probably $Fe_2S_2^{2+}$ (*m/e* 88).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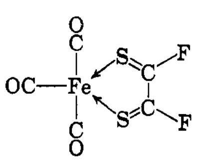
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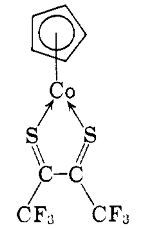
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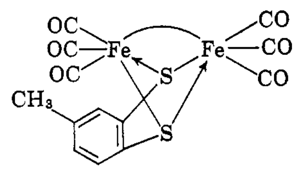
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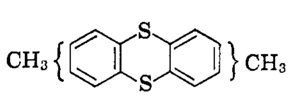
5. **$C_7H_6S_2Fe_2(CO)_6$ (Table V).** The compound $C_7H_6S_2Fe_2(CO)_6$ (VII) is similar to $C_2H_4S_2Fe_2(CO)_6$ (IV) except that the two carbon atoms of the bridge linking the two sulfur atoms are part of a benzene ring derived from 3,4-toluenedithiol. Like the other $[RSFe(CO_3)]_2$ compounds, the parent ion $C_7H_6S_2Fe_2(CO)_6^+$ (*m/e* 434) loses carbonyl groups stepwise giving the ion $C_7H_6S_2Fe_2^+$ (*m/e* 266) used as the base peak. A small portion of this latter ion loses the methyl group giving the ion $C_6H_3S_2Fe_2^+$ (*m/e* 251).

The most surprising feature of the mass spectrum of $C_7H_6S_2Fe_2(CO)_6$ is an ion at *m/e* 244 clearly not containing iron on the basis of its (M − 2)/M ratio of only 0.03. The formula corresponding to this mass is $C_{14}H_{12}S_2^+$. A material of this composition could arise from the condensation of two molecules of 3,4-toluenedithiol, $C_7H_6(SH)_2$, with elimination of two molecules of hydrogen sulfide in a pyrolytic reaction in the mass spectrometer. A possible structure for $C_{14}H_{12}S_2^+$ is a dimethylthianthrenium cation VIII. The exact positions of the methyl substituents are uncertain.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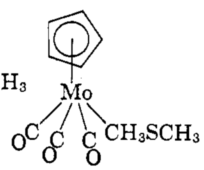
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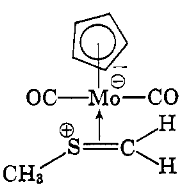
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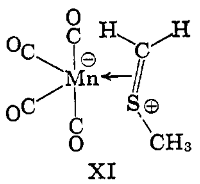
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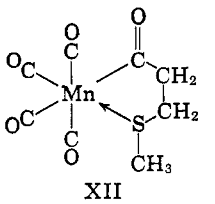
XII

B. CH_3SCH_2 and $CH_3SCH_2CH_2$ Derivatives. 1. $CH_3SCH_2Mo(CO)_nC_5H_5$ Compounds (Table VI). The mass spectra of the tricarbonyl[5] $CH_3SCH_2Mo(CO)_3C_5H_5$ (IX) and the dicarbonyl π-$CH_3SCH_2Mo(CO)_2C_5H_5$ (X) are essentially the same and as expected for the dicarbonyl particularly on the basis of the highest *m/e* ion at 270 corresponding to the dicarbonyl molecular ion. This is consistent with the observed facile decarbonylation[15] of the tricarbonyl to the dicarbonyl upon sublimation.

The molecular ion $CH_3SCH_2Mo(CO)_2C_5H_5^+$ (*m/e* 278) can fragment by two routes. The first route is the loss of a carbonyl group to give the monocarbonyl ion $CH_3SCH_2MoCOC_5H_5^+$ (*m/e* 250). The second and much less favored route is the loss of a methyl group to give the ion $SCH_2Mo(CO)_2C_5H_5^+$ (*m/e* 263). This tendency for cleavage of a methyl–sulfur bond was noted above as a degradation pathway for the $(CH_3S)_2Fe_2^+$ ion in the mass spectrum of $[CH_3SFe(CO)_3]_2$.

The fragmentation routes for the monocarbonyl ion $CH_3SCH_2MoCOC_5H_5^+$ (*m/e* 250) appear to be similar to those of the dicarbonyl molecular ion. However, when all carbonyl groups are lost giving $CH_3SCH_2MoC_5H_5^+$ (*m/e* 222), the further mode of fragmentation changes. The most favored process at this stage appears to be loss of methane, CH_4 (mass 16), to give the ion $C_6H_6SMo^+$ (*m/e* 206). This ion is the most abundant ion of the mass spectrum and is used for the base peak (abundance 100). Also some evidence for dehydrogenation of $CH_3SCH_2MoC_5H_5^+$ to give $C_2SHMoC_5H_5^+$ (*m/e* 218) is noted. Another predominant ion at this point is $C_5H_5MoSH^+$ (*m/e* 194) apparently arising by ethylene elimination from $CH_3SCH_2MoC_5H_5^+$. Further fragmentation gives the ion $C_5H_5Mo^+$ (*m/e* 161) typical of nearly all mass spectra of cyclopentadienylmolybdenum carbonyl derivatives. The cyclopentadienyl-free fragments $MoSC_2H^+$ (*m/e* 153), $MoSCH^+$ (*m/e* 141), MoS^+ (*m/e* 128), and Mo^+ (*m/e* 96)[2] are also observed. Appreciable abundances of the dipositive ions $CH_3SCH_2MoCOC_5H_5^{2+}$ (*m/e* 125), $CH_3SCH_2MoC_5H_5^{2+}$ (*m/e* 111), $C_6H_6SMo^{2+}$ (*m/e* 103), and $C_5H_5Mo^{2+}$ (*m/e* 80.5) are found. Molybdenum-free fragments in this mass spectrum include the ions $C_5H_6^+$, $C_5H_5^+$, and $C_3H_3^+$ usually observed in π-cyclopentadienyl complexes.

2. **$CH_3SCH_2Mn(CO)_4$ (Table VII).** The mass spectrum of this manganese complex XI exhibits the stepwise loss of the four carbonyl groups from the molecular ion $CH_3SCH_2Mn(CO)_4^+$ (*m/e* 228) as demonstrated by the metastable ions at *m/e* 175.2, 148.0, 120.4, and 93.5. These processes leave the ion $CH_3SCH_2Mn^+$ (*m/e* 116) which interestingly enough appears to break into $CH_3SCH_2^+$ (*m/e* 61) and a manganese atom as indicated by the metastable ion at *m/e* 32.2. Fragments of the type CH_nSMn^+ (n = 1–3) are also observed as well as MnS^+ (*m/e* 87) and Mn^+ (*m/e* 55). The ions at *m/e* 69 and 70 may be assigned to CH_2Mn^+ and CH_3Mn^+, respectively. In these cases the manganese–carbon bond has been preserved while the sulfur has been expelled from the molecule in some form. The metal-free fragments $CH_3SCH_3^+$ (*m/e* 62), $CH_3SCH_2^+$ (*m/e* 61), CH_3SH^+ (*m/e* 48), CH_3S^+ (*m/e* 47), CH_2S^+ (*m/e* 46), and CHS^+ (*m/e* 45) appear to arise from the CH_3SCH_2 ligand.

3. **$CH_3SCH_2CH_2COMn(CO)_4$ (Table VIII).** The mass spectrum of this compound XII exhibits a weak but equivocally detectable parent ion at *m/e* 270. Much

more abundant are the ions $CH_3SCH_2CH_2Mn(CO)_n^+$ (n = 0–4) arising from the loss of one or more carbonyl groups from the parent ion.[16] The ion $CH_3SCH_2CH_2MnC^+$ (*m/e* 142) is also observed in which the carbon–oxygen bond of the last carbonyl group rather than the metal–carbon bond is broken. Similar ions (*e.g.*, WC^+ and WC_2O^+) were observed by Winters and Kiser[17] in the mass spectrum of $W(CO)_6$ (and other related compounds).

Further fragmentation of the *m/e* 130 ion gives the ion CH_3SMn^+ (*m/e* 102), the most abundant ion in the mass spectrum and the one selected as the base peak. This process (or one of the preceding ones) must involve loss of ethylene. The ion CH_3SMn^+ appears to undergo cleavage of its S-methyl group giving MnS^+ (*m/e* 87). The bare metal ion Mn^+ (*m/e* 55) is also observed.

Metal-free fragments apparently arising from the $CH_3SCH_2CH_2$ ligand are $CH_3SCH_2CH_2^+$ (*m/e* 75), CH_3SH^+ (*m/e* 48), CH_3S^+ (*m/e* 47), and CHS^+ (*m/e* 45). Again the tendency for elimination of ethylene is apparent.

C. Cyclopentadienyliron Derivatives with Organosulfur Ligands. 1. $[CH_3SFe(CO)C_5H_5]_2$ (Table IX). Only a relatively weak mass spectrum of this compound (XIII) was observed. The most intense of the observed peaks were $(C_5H_5)_2Fe^+$ (*m/e* 186) and $C_5H_5Fe^+$ (*m/e* 121) from ferrocene arising as a pyrolysis product in the mass spectrometer.

The parent ion $(C_5H_5)_2Fe_2(CO)_2(SCH_3)_2^+$ (*m/e* 392) first loses stepwise the two carbonyl groups to give the ion $(C_5H_5)_2Fe_2(SCH_3)_2^+$ (*m/e* 336). Stepwise loss of the two methyl groups then gives the ion $(C_5H_5)_2Fe_2S_2^+$ (*m/e* 306). These processes correspond entirely to the degradation of the parent ion of $[CH_3SFe(CO)_3]_2$ discussed above.

Other ions not a part of this degradation scheme are observed. The most intense of these ions has *m/e* 286 and appears to be $(C_5H_5)_2Fe_2CS^+$.

Numerous ions from substituted ferrocenes are also observed in the mass spectrum of $[CH_3SFe(CO)C_5H_5]_2$. The ion of this type with the highest *m/e* value is $C_5H_5FeC_5H_4SCH_3^+$ (*m/e* 232) suggesting that ferrocenylmethyl sulfide, $C_5H_5FeC_5H_4SCH_3$, might be a pyrolysis product of $[CH_3SFe(CO)C_5H_5]_2$.

Numerous iron-free ions were observed in this mass spectrum. These include $C_{10}H_9^+$ (*m/e* 129) and $C_{10}H_8^+$ (*m/e* 128) apparently arising from combination of two cyclopentadienyl rings, $C_5H_5SCH_3^+$ (*m/e* 112) arising probably from the $C_5H_5FeC_5H_4SCH_3$, and the usual ions expected for both the π-C_5H_5 and CH_3S ligands.

2. $CH_3SFe(CO)_2C_5H_5$ (Table X). The mass spectrum of this complex XIV exhibits not only ions from $CH_3SFe(CO)_2C_5H_5$ but also from the pyrolysis products $CH_3SC_5H_4FeC_5H_5$, $CH_3C_5H_4FeC_5H_5$, and ferrocene and the iodination[18] product $C_5H_5Fe(CO)_2I$.

The fragmentation pattern of $CH_3SFe(CO)_2C_5H_5^+$ (*m/e* 224) is fairly straightforward. Stepwise loss of carbonyl ligands occurs to form $C_5H_5FeSCH_3^+$ (*m/e* 168). This carbonyl-free ion appears to undergo dehydrogenation, since an ion at *m/e* 166 is observed corresponding to $C_6H_6SFe^+$. The ion $C_6H_6Fe^+$ (*m/e* 134) may arise by loss of H_2S from $C_5H_5FeSCH_3^+$ (*m/e* 168). The iron-free ions are similar to those observed in the mass spectrum of $[CH_3SFe(CO)C_5H_5]_2$ discussed above.

A predominant process in the mass spectra of the compounds $[CH_3SFe(CO)_3]_2$, $C_7H_8Fe_2(CO)_4(SCH_3)_2$, and $[CH_3SFe(CO)C_5H_5]_2$ with *bridging* CH_3S groups is loss of a methyl group from a CH_3S group of the carbonyl-free ions. An analogous process does not occur in the mass spectrum of $CH_3SFe(CO)_2C_5H_5$ with a *terminal* CH_3S group as indicated by the negligible concentration of the ion $C_5H_5FeS^+$ (*m/e* 153). This indicates the expected tighter bonding of metal atoms with bridging sulfur groups with two or more metal–sulfur bonds than with terminal sulfur groups with only one metal–sulfur bond.

3. $C_6H_5COSFe(CO)_2C_5H_5$ (Table XI). The mass spectrum of this complex XV exhibits not only ions from $C_6H_5COSFe(CO)_2C_5H_5$ but also ions from the pyrolysis products $C_6H_5COC_5H_4FeC_5H_5$, ferrocene, and biphenyl and from the iodination[18] product $C_5H_5Fe(CO)_2I$. The behavior of $C_6H_5COSFe(CO)_2C_5H_5$ on pyrolysis thus resembles that of $CH_3SFe(CO)_2C_5H_5$ discussed above, except for the additional production of biphenyl arising from pyrolytic cleavage of phenyl groups.

The parent molecular ion $C_6H_5COSFe(CO)_2C_5H_5^+$ (*m/e* 314) first appears to lose stepwise its two carbonyl ligands giving $C_6H_5COSFeC_5H_5^+$ (*m/e* 258). This ion appears to fragment both by loss of CO to give $C_6H_5SFeC_5H_5^+$ (*m/e* 230) and by loss of CS to give $C_6H_5OFeC_5H_5^+$ (*m/e* 214). The ions $C_9H_8SFe^+$ (*m/e* 204) and $C_7H_6SFe^+$ (*m/e* 178) then arise by two successive losses of C_2H_2 from $C_6H_5SFeC_5H_5^+$. It is presently unclear whether the acetylene fragments are lost from the five-membered ring or the six-membered ring of $C_6H_5SFeC_5H_5^+$. However, relatively few cyclopentadienyliron ions with other ligands have been observed to lose acetylene, suggesting that the acetylene fragments are lost from the six-membered ring of $C_6H_5SFeC_5H_5^+$.

The most abundant metal-free ion is the benzoyl ion $C_6H_5CO^+$ (*m/e* 105) arising by cleavage of the benzoyl–sulfur bond, a relatively favored process. Other very abundant metal-free ions are $C_6H_5^+$ and $C_4H_3^+$ arising from the phenyl group and $C_5H_6^+$, $C_5H_5^+$, and $C_3H_3^+$ arising from the π-cyclopentadienyl group. The ions of medium abundance $C_6H_5S^+$ (*m/e* 109) and $C_6H_5O^+$ (*m/e* 93) may arise from $C_6H_5SFeC_5H_5^+$ (*m/e* 230) and $C_6H_5OFeC_5H_5^+$ (*m/e* 214), respectively.

D. The 2,5-Dithiahexane Derivative $CH_3SCH_2CH_2SCH_3W(CO)_4$ (Table XII). The complex $CH_3SCH_2CH_2SCH_3W(CO)_4$ (XVI) was examined as an available representative metal carbonyl derivative where an organic sulfide has replaced carbonyl groups. The multiisotopic nature of natural tungsten was particularly helpful in analyzing this mass spectrum, since it permitted a rapid and unequivocal indication of the presence or absence of tungsten in the observed ions. The absence of tungsten in the ions at *m/e* 228 and 229 was clearly demonstrated, indicating assignment of these

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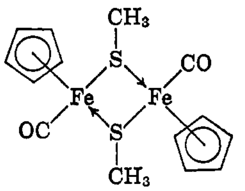
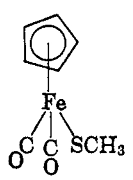
(16) For a more detailed discussion of the electronic equivalence of a π-cyclopentadienyl ring and three carbonyl groups, see R. B. King, *Inorg. Chem.*, 5, 2227 (1966).

(17) This assignment of the ions at *m/e* 242, 214, 186, 158, and 130 is somewhat uncertain owing to the identical *m/e* values for the ions $CH_3SCH_2CH_2Mn(CO)_n^+$ and $CH_3SMn(CO)_{n+1}^+$.

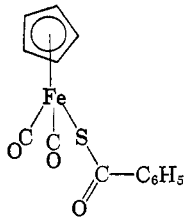
(18) For a discussion of the formation of iodine derivatives from a "memory" effect in the mass spectrometer, see ref 1.



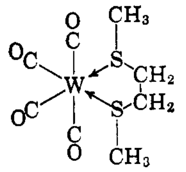
XIII



XIV



XV



XVI

ions to be $CH_3SCH_2CH_2S(CH_3)SCH_2CH_2SCH_3^+$ and $CH_3SCH_2CH_2SCH_2SCH_2CH_2SCH_3^+$ apparently arising from a compound such as $CH_3SCH_2CH_2SCH_2SCH_2CH_2SCH_3$, a possible condensation product from two 2,5-dithiahexane molecules.

The parent molecular ion $CH_3SCH_2CH_2SCH_3W(CO)_4^+$ (*m/e* 418) undergoes the stepwise loss of its four carbonyl groups giving $CH_3SCH_2CH_2SCH_3W^+$ (*m/e* 306). However, once the monocarbonyl $CH_3SCH_2CH_2SCH_3WCO^+$ (*m/e* 334) is reached, loss of a methyl group by cleavage of a methyl–sulfur bond also begins to occur. Loss of the ethylene bridge between the two sulfur atoms can also occur from the ion $CH_3SCH_2CH_2SCH_3W^+$ (*m/e* 306) to give $CH_3SWSCH_3^+$ (*m/e* 278). A prior example of a similar loss of an ethylene bridge between two sulfur atoms was noted above for the ion $C_2H_4S_2Fe_2^+$ (*m/e* 204) in the mass spectrum of $C_2H_4S_2Fe_2(CO)_6$ (Table III). By the three processes of carbonyl loss, methyl cleavage, and ethylene cleavage, the molecular ion $CH_3SCH_2CH_2SCH_3W(CO)_4^+$ (*m/e* 418) is converted to WS_2^+ (*m/e* 248).

The ion WCO^+ (*m/e* 212) is also observed in the mass spectrum of $CH_3SCH_2CH_2SCH_3W(CO)_4$ suggesting that some of the monocarbonyl ion $CH_3SCH_2CH_2SCH_3WCO^+$ (*m/e* 334) loses completely its 2,5-dithiahexane ligand before losing its carbonyl group in contrast to the more usual tendency for metal carbonyl ions to lose all of their carbonyl groups before losing other ligands. The abnormal behavior in this case apparently relates to the relatively high stability of tungsten–carbon bonds.[19]

Tungsten-free ions clearly arising from the 2,5-dithiahexane ligand are very abundant, suggesting some pyrolysis of the complex in the mass spectrometer to give the free ligand. The ligand parent molecular ion $CH_3SCH_2CH_2SCH_3^+$ (*m/e* 122) appears either to lose one methyl group giving $CH_3SCH_2CH_2S^+$ (*m/e* 107) or one CH_3S group giving $CH_3SCH_2CH_2^+$ (*m/e* 75). Further fragmentation of $CH_3SCH_2CH_2S^+$ (*m/e* 107) appears to involve loss of the ethylene bridge giving CH_3SS^+ (*m/e* 79). The origins and, in some cases, the assignments of the tungsten-free ions at *m/e* 211, 102, and 61 are still unclear.

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(19) For a further discussion of the relative strengths of bonds between carbon and the three metals chromium, molybdenum, and tungsten, see R. B. King, *J. Organometal. Chem.* (Amsterdam), **8**, 129 1967), and references cited therein.