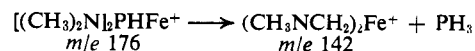


In the case of the tungsten system, an ion, probably  $[(\text{CH}_3)_2\text{N}]_2\text{PWNHCH}_3^+$ , is observed at 14 mass units less than the  $[(\text{CH}_3)_2\text{N}]_3\text{PW}^+$  ion, suggesting that the first step involves loss of a  $\text{CH}_2$  fragment. This may be followed by loss of the methyl group to give the ion  $[(\text{CH}_3)_2\text{N}]_2\text{PWNH}^+$  which is unstable with respect to loss of ammonia by means of the NH group attached to the tungsten atom abstracting two protons from the remaining methyl groups. The net result of these successive losses of methylene, methyl, and ammonia fragments would be loss of 46 mass units and formation of the  $(\text{CH}_3)_2\text{NP}(\text{CH}_2\text{NCH}_2)\text{W}^+$  ion ( $I, M = \text{W}$ ).

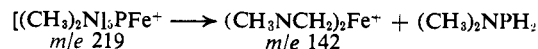
Despite the well-established presence<sup>9</sup> of metal-phosphorus rather than metal-nitrogen bonds in the metal carbonyl complexes of tris(dimethylamino)phosphine, some fragments in the mass spectra of these compounds clearly contain metal-nitrogen bonds. These include the ions  $(\text{CH}_3)_2\text{N}(\text{CrCH}_2\text{NCH}_3)^+$  (Table I),  $(\text{CH}_3)_2\text{N}(\text{Cr})^+$  (Table I),  $(\text{CH}_3\text{NCH}_2)_2\text{Fe}^+$  (Tables III and IV),  $(\text{CH}_3)_2\text{N}(\text{Fe})^+$  (Tables III and IV), and  $\text{C}_5\text{H}_5\text{V}(\text{CH}_2\text{NCH}_3)\text{N}(\text{CH}_3)_2^+$  (Table V). In addition the ions of the type  $[(\text{CH}_3)_2\text{N}]_3\text{PM}^+$  ( $M = \text{Cr, Mo, W, and Fe}$ ) observed in the metal carbonyl complexes containing two tris(dimethylamino)phosphine ligands probably are  $[(\text{CH}_3)_2\text{N}]_3\text{PMN}(\text{CH}_3)_2^+$  with one metal-nitrogen bond, since bonding of four dimethylamino groups and a

metal atom to a single phosphorus atom appears unlikely.

Such ions containing metal-nitrogen bonds appear to be formed by elimination of the phosphorus as phosphine,  $\text{PH}_3$ , since the metastable ion at  $m/e$  114.6 in the mass spectrum of the tris(dimethylamino)phosphine complexes of the iron carbonyls corresponds to the reaction



Substituted phosphines may also be eliminated to form ions with metal-nitrogen bonds as demonstrated by the metastable ion at  $m/e$  92.2 in the mass spectrum of  $[(\text{CH}_3)_2\text{N}]_3\text{PFe}(\text{CO})_4$  corresponding to the reaction



Metastable peaks corresponding to the formation of the other ions believed to contain metal-nitrogen bonds have not been observed.

**Acknowledgment.** I am indebted to the U. S. Air Force Office of Scientific Research for partial support of this work under Grant No. AF-AFOSR-580-66. I am also indebted to Mr. R. E. Rhodes and Mr. J. R. Boal for running the mass spectra.

## Mass Spectra of Organometallic Compounds. II. Some Cyclopentadienylmetal Carbonyl Derivatives<sup>1</sup>

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*Received July 20, 1967*

**Abstract:** Mass spectra of cyclopentadienylmetal carbonyl derivatives exhibit not only stepwise loss of their carbonyl groups but also extrusion of  $\text{C}_2\text{H}_2$  from the  $\text{C}_5\text{H}_5\text{M}^+$  ions to give  $\text{C}_3\text{H}_3\text{M}^+$  ions. Compounds of the type  $\text{RFe}(\text{CO})_2\text{C}_5\text{H}_5$  also exhibit ions in their mass spectra arising from ferrocene and substituted ferrocene pyrolysis products. Sufficient metastable ions have been observed in the mass spectra of the iron compounds  $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$  and  $\text{CH}_3\text{OCOCH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$  to establish degradation pathways from the molecular ion down to the bare metal ion  $\text{Fe}^+$ . The mass spectra of the latter iron compound and of the related molybdenum compound  $\text{C}_5\text{H}_5\text{OCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$  exhibit processes involving fragmentation of ketene ( $\text{CH}_2\text{CO}$ , mass 42). This molybdenum compound as well as the iron compound  $\text{C}_6\text{H}_5\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$  and the tungsten compound  $\text{CH}_2=\text{CHCOW}(\text{CO})_3\text{C}_5\text{H}_5$  do not exhibit the parent ions in their mass spectra. Instead, the highest mass ion in their mass spectra occurs 28 mass units below the expected value for their parent ions, suggesting facile decarbonylation within the mass spectrometer. The mass spectrum of the  $\pi$ -allyl derivative  $\text{C}_3\text{H}_5\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$  exhibits the carbonyl ions  $\text{C}_3\text{H}_5\text{Mo}(\text{CO})_n\text{C}_5\text{H}_5^+$  ( $n = 1$  or  $2$ ) but not the carbonyl-free allyl ion  $\text{C}_3\text{H}_5\text{MoC}_5\text{H}_5^+$ . Instead, the carbonyl-free cyclopropenyl ion  $\text{C}_3\text{H}_3\text{MoC}_5\text{H}_5^+$  is observed in high abundance.

A major portion of the recent synthetic work in transition-metal organometallic chemistry has dealt with cyclopentadienylmetal carbonyl derivatives. However, the mass spectra of relatively few such compounds have been studied. Winters and Kiser<sup>3</sup> report

(1) For part I of this series, see R. B. King, *J. Am. Chem. Soc.*, **90**, 1412 (1968).

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

(3) R. E. Winters and R. W. Kiser, *J. Organometal. Chem.* (Amsterdam), **4**, 190 (1965).

the mass spectra of the simple mononuclear cyclopentadienylmetal carbonyls of the first transition series  $\text{C}_5\text{H}_5\text{M}(\text{CO})_n$  ( $M = \text{V}, n = 4$ ;  $M = \text{Mn}, n = 3$ ;  $M = \text{Co}, n = 2$ ). Schumacher and Taubenest<sup>4</sup> describe the mass spectra of a few other cyclopentadienylmetal carbonyls including the binuclear  $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$  and  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ ; the trinuclear  $(\text{C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ ; and the bromides  $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$  and  $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Br}$ .

(4) E. Schumacher and R. Taubenest, *Helv. Chim. Acta*, **49**, 1447 (1966).

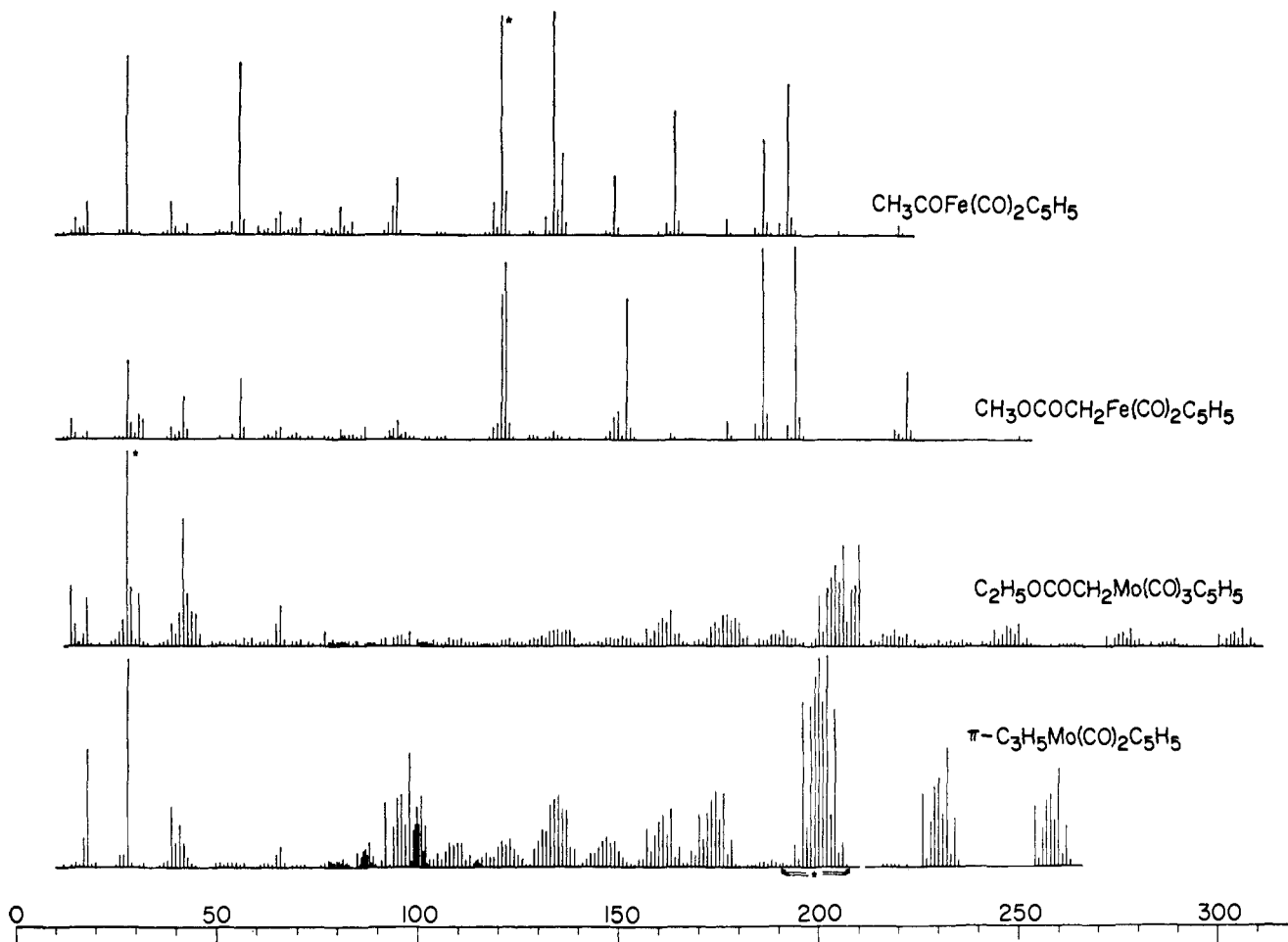


Figure 1. Mass spectra of four of the compounds discussed in this paper. The ions designated by an asterisk are drawn half their relative heights in order to fit on the scale.

Very recently Bruce<sup>5</sup> reported the mass spectra of  $C_6H_5-CH_2Fe(CO)_2C_5H_5$  and  $C_6F_5CH_2Fe(CO)_2C_5H_5$ . This paper discusses mainly the mass spectra of a few representative cyclopentadienylmetal carbonyl derivatives also containing in addition either  $\sigma$ -bonded or  $\pi$ -bonded organic groups.

### Experimental Section

The mass spectra were run on a standard MS-9 mass spectrometer located at the Mellon Institute. They are reported in Tables I-XII, inclusive. In addition Figure 1 depicts the mass spectra of four representative compounds. The standard conditions used were a 70-ev ionizing potential, 200–230° inlet temperature, resolution of 1000, and 8-kv accelerating voltage. Samples were introduced directly 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 relative to an arbitrary value of 100 for the ion  $C_5H_5M^+$  are reported in the tables. The  $m/e$  values reported in the tables are for the ions containing the isotopes  $^{51}V$ ,  $^{56}Fe$ ,  $^{98}Mo$ , and/or  $^{184}W$ .<sup>6</sup> The compounds used in this study were prepared by methods already adequately described in the literature.<sup>7</sup>

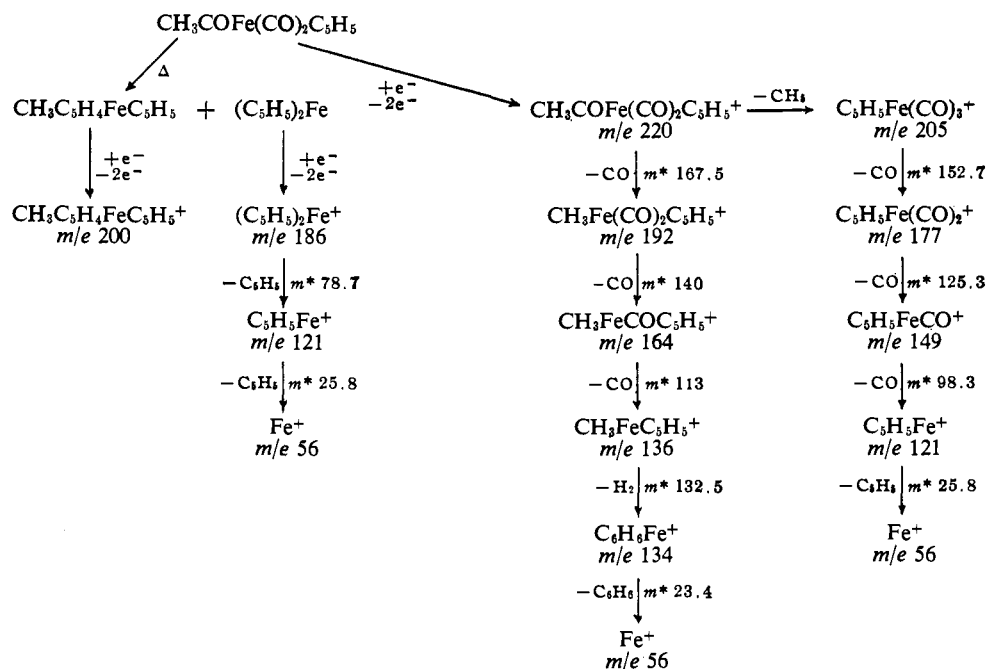
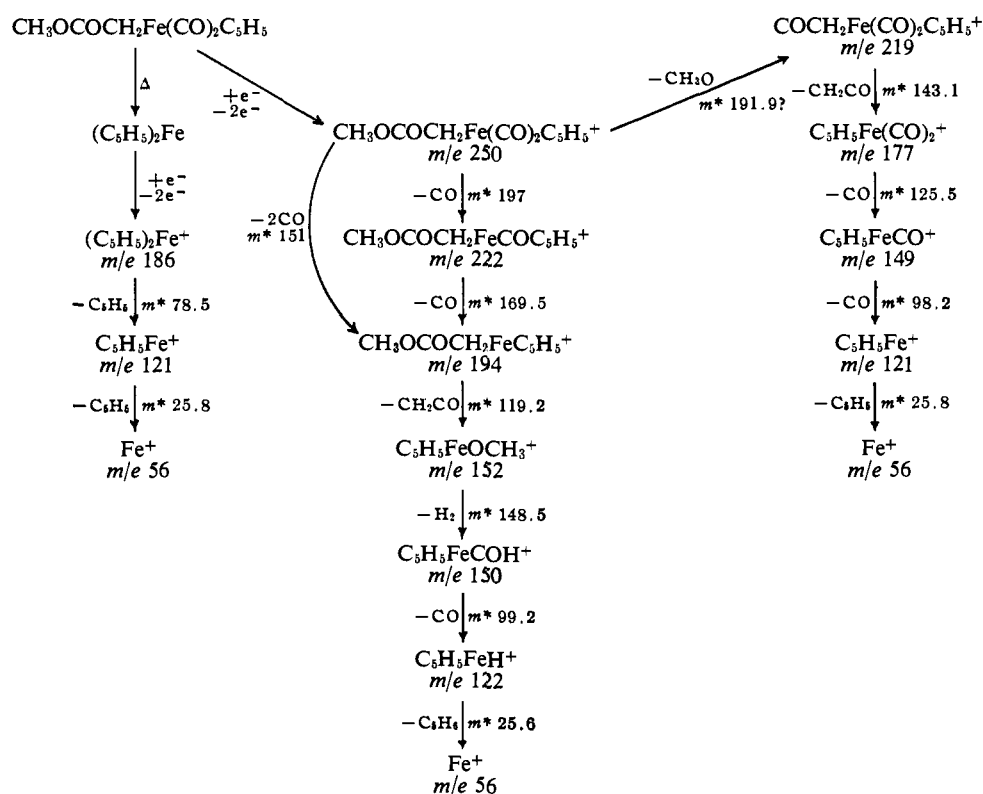
(5) M. I. Bruce, *Inorg. Nucl. Chem. Letters*, **3**, 157 (1967).

(6) In the cases of ions containing molybdenum or tungsten, 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 the tables are for those containing their most abundant isotopes  $^{98}Mo$  and  $^{184}W$ , respectively.

(7) The following references give the preparations of the compounds used in this study: (a)  $CH_3COFe(CO)_2C_5H_5$ , R. B. King, *J. Am. Chem. Soc.*, **85**, 1918 (1963); (b)  $C_6H_5COFe(CO)_2C_5H_5$ ,  $C_6H_5Fe(CO)_2C_5H_5$ ,  $C_6H_5CH=CHCOFe(CO)_2C_5H_5$ , and  $CH_2=CHCOW(CO)_2C_5H_5$ , R. B. King and M. B. Bisnette, *J. Organometal. Chem.* (Amsterdam), **2**, 15 (1964); (c)  $CH_3OCOCH_2Fe(CO)_2C_5H_5$  and  $C_2H_5OCOCH_2Mo(CO)_3C_5H_5$ , R. B. King, M. B. Bisnette, and A. Fronzaglia, *ibid.*, **5**, 341 (1966); (d)  $Br(CH_2)_4Mo(CO)_3C_5H_5$ , R. B. King and M. B. Bisnette, *ibid.*, **7**, 311 (1967); (e)  $C_6H_5W(CO)_3H$ , T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); (f)  $C_6H_5Mo(CO)_2C_7H_7$ , R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964); (g)  $C_6H_5W(CO)_2C_7H_7$ , R. B. King and A. Fronzaglia, *ibid.*, **5**, 1837 (1966); (h)  $C_6H_5Mo(CO)_2CH_2C_5H_5$ , R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966); (i)  $C_6H_5Mo(CO)_2C_5H_5$ , M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963); (j)  $C_6H_5V(CO)_4$ , R. P. M. Werner, A. H. Filbey, and S. A. Manastyrskiy, *Inorg. Chem.*, **3**, 298 (1964); (k)  $C_6H_5Re(CO)_3$ , E. O. Fischer, and W. Fellmann, *J. Organometal. Chem.* (Amsterdam), **1**, 191 (1963).

(8) For a further discussion of metastable ions, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p xiii, and references cited therein.

Figure 2. Fragmentation scheme of  $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ .Figure 3. Fragmentation scheme of  $\text{CH}_3\text{OCOCH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ .

## Discussion

**A. General Comments.** Features observed in previous studies<sup>3,4</sup> of the mass spectra of cyclopentadienylmetal carbonyl derivatives also were observed in this study. These include particularly the stepwise loss of carbonyl groups and the tendency for extrusion of the elements of acetylene ( $\text{C}_2\text{H}_2$ ) from  $\text{C}_5\text{H}_5\text{M}^+$

ions to give the corresponding  $\text{C}_3\text{H}_3\text{M}^+$  ions. The hydrocarbon fragment ions arising from the  $\pi$ -cyclopentadienyl ligand invariably include  $\text{C}_5\text{H}_6^+$ ,  $\text{C}_5\text{H}_5^+$ , and  $\text{C}_3\text{H}_3^+$ .

The mass spectra of all of the cyclopentadienyliron dicarbonyl derivatives exhibited the ion  $(\text{C}_5\text{H}_5)_2\text{Fe}^+$ . A comparison of the mass spectra of  $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$  at inlet temperatures of 70 and 200° (see below)

Table I. Mass Spectrum of  $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ 

<i>m/e</i>	Ion	Relative intensity	
		<i>a</i>	<i>b</i>
220	$\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5^+$	2	9 <sup>c</sup>
205	$\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3^+$	0.8	2
200	$\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_3^+$	0.2	
192	$\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5^+$	36	32 <sup>c</sup>
186	$(\text{C}_5\text{H}_5)_2\text{Fe}$	22	2
177	$\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2^+$	4	5
164	$\text{CH}_3\text{FeCOC}_5\text{H}_5^+$	29	26 <sup>c</sup>
149	$\text{C}_5\text{H}_5\text{FeCO}^+$	14	16 <sup>c</sup>
136	$\text{CH}_3\text{FeC}_5\text{H}_5^+$	18	23
134	$\text{C}_6\text{H}_6\text{Fe}^+$	52	50 <sup>c</sup>
121	$\text{C}_5\text{H}_5\text{Fe}^+$	100	100 <sup>c</sup>
95	$\text{C}_3\text{H}_3\text{Fe}^+$	13	13
94	$\text{C}_3\text{H}_2\text{Fe}^+$	6	7
93	$\text{C}_3\text{HFe}^+$	3	3
84	$\text{FeCO}^+$	3	3
81	$\text{CH}_3\text{C}_5\text{H}_8^+$	6	6
71	$\text{CH}_3\text{Fe}^+$	3	3
66	$\text{C}_5\text{H}_6^+$	5	3
65	$\text{C}_5\text{H}_5$	3	3
56	$\text{Fe}^+$	40	39
39	$\text{C}_3\text{H}_3^+$	5	7

Metastable ions		
<i>m/e</i>	Process	Neutral fragment lost
167.5	220 $\xrightarrow{-28}$ 192	CO
152.7	205 $\xrightarrow{-28}$ 177	CO
140	192 $\xrightarrow{-28}$ 164	CO
132.5	136 $\xrightarrow{-2}$ 134	H <sub>2</sub>
125.3	177 $\xrightarrow{-28}$ 149	CO
113	164 $\xrightarrow{-28}$ 136	CO
98.3	149 $\xrightarrow{-28}$ 121	CO
78.7	186 $\xrightarrow{-65}$ 121	C <sub>5</sub> H <sub>5</sub>
64.5	66 $\xrightarrow{-1}$ 65	H
25.8	121 $\xrightarrow{-65}$ 56	C <sub>5</sub> H <sub>5</sub>
23.4	134 $\xrightarrow{-78}$ 56	C <sub>6</sub> H <sub>6</sub>

<sup>a</sup> AEI MS-9 mass spectrometer, standard conditions, source pressure  $4.7 \times 10^{-6}$  mm, inlet temperature  $\sim 200^\circ$ . <sup>b</sup> Japan Electron Optics Laboratory JMS-01SG mass spectrometer, 75-eV electron energies, inlet temperature  $70^\circ$ . <sup>c</sup> Assignment confirmed by exact mass measurement to three decimal places.

suggests that this ion arises from ferrocene produced by thermal decomposition of the compound during its introduction into the mass spectrometer. The amounts of the  $(\text{C}_5\text{H}_5)_2\text{Fe}^+$  ion produced in the spectra of various  $\text{RFe}(\text{CO})_2\text{C}_5\text{H}_5$  compounds relative to the abundance of the  $\text{C}_5\text{H}_5\text{Fe}^+$  ion taken arbitrarily as 100 are given in Table XIII.<sup>9</sup> In addition certain  $\text{RFe}(\text{CO})_2\text{C}_5\text{H}_5$  compounds exhibited ions  $\text{RC}_5\text{H}_4\text{FeC}_5\text{H}_5^+$  apparently arising from substituted ferrocenes. In a few rare cases (*i.e.*,  $\text{R} = \text{C}_6\text{H}_5$ ) ions of the type  $(\text{RC}_5\text{H}_4)_2\text{Fe}^+$  arising from disubstituted ferrocenes also were noted (Table XIII). Discussion of other more unusual  $\text{R}'\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5$  ions listed in Table XIII will be deferred until the discussion of the individual compound in this paper or a later paper of the series.

The tendency for mass spectra of cyclopentadienylmetal carbonyl derivatives to exhibit  $(\text{C}_5\text{H}_5)_2\text{M}^+$  ions appears to be characteristic of first-row (3d) transition

(9) Details of other aspects of the mass spectra of the compounds in Tables XIII–XV will be presented in future publications of this series.

Table II. Mass Spectra of  $\text{C}_6\text{H}_5\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$  and  $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ 

<i>m/e</i>	Ion	Phenyl deriv <sup>a</sup>	Benzoyl deriv <sup>b</sup>
282	$\text{C}_6\text{H}_5\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$	0	<0.2
262	$\text{C}_6\text{H}_5\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5^+$	22	23
254	$\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5^+$	46	56
226	$\text{C}_6\text{H}_5\text{FeCOC}_5\text{H}_5^+$	148	116
198	$\text{C}_6\text{H}_5\text{FeC}_5\text{H}_5^+$ ( $\text{C}_{11}\text{H}_{10}\text{Fe}^+$ )	275	226
196	$\text{C}_{11}\text{H}_8\text{Fe}^+$	157	48
186	$(\text{C}_5\text{H}_5)_2\text{Fe}^+$	93	52
172	$\text{C}_4\text{H}_3\text{FeC}_5\text{H}_5^+$	82	32
154	$\text{C}_6\text{H}_5\text{-C}_4\text{H}_5^+$ ( $\text{C}_{12}\text{H}_{10}^+$ )	40	16
142	$\text{C}_6\text{H}_5\text{-C}_5\text{H}_5^+$ ( $\text{C}_{11}\text{H}_{10}^+$ )	237	190
141	$\text{C}_{11}\text{H}_9^+$	200	120
133	$\text{C}_6\text{H}_5\text{Fe}^+$	22	21
132	$\text{C}_6\text{H}_4\text{Fe}^+$	18	13
121	$\text{C}_5\text{H}_5\text{Fe}^+$	100	100
115	$\text{C}_5\text{H}_7^+$	82	53
107	$\text{C}_4\text{H}_3\text{Fe}^+$	14	10
106	$\text{C}_4\text{H}_2\text{Fe}^+$	11	6
105	$\text{C}_4\text{HFe}^+$ , $\text{C}_6\text{H}_5\text{CO}^+$	7	23
99	$\text{C}_{11}\text{H}_{10}\text{Fe}^{2+}$	14	3
95	$\text{C}_3\text{H}_3\text{Fe}^+$	19	16
94	$\text{C}_3\text{H}_2\text{Fe}^+$	21	11
89	$\text{C}_3\text{H}_5^+$	14	8
81	$\text{C}_2\text{HFe}^+$	42	15
78	$\text{C}_6\text{H}_6^+$	129	53
77	$\text{C}_6\text{H}_5^+$	37	24
66	$\text{C}_5\text{H}_6^+$	24	8
65	$\text{C}_5\text{H}_5^+$	22	8
63	$\text{C}_5\text{H}_3^+$	24	8
56	$\text{Fe}^+$	197	97
52	$\text{C}_4\text{H}_4^+$	26	11
51	$\text{C}_4\text{H}_3^+$	37	16
50	$\text{C}_4\text{H}_2^+$	25	8
39	$\text{C}_3\text{H}_3^+$	50	16

Metastable ions		
<i>m/e</i>	Ion	Neutral fragment lost
195	198 $\xrightarrow{-2}$ 196	H <sub>2</sub>
173.5	226 $\xrightarrow{-28}$ 198	CO
149.5	198 $\xrightarrow{-26}$ 172	C <sub>2</sub> H <sub>2</sub>
140	142 $\xrightarrow{-1}$ 141	H
102	198 $\xrightarrow{-56}$ 142	Fe
94	141 $\xrightarrow{-26}$ 115	C <sub>2</sub> H <sub>2</sub>
78.6	186 $\xrightarrow{-65}$ 121	C <sub>5</sub> H <sub>5</sub>
76.5	78 $\xrightarrow{-1}$ 77	H
56.6	105 $\xrightarrow{-28}$ 77	CO
25.8	121 $\xrightarrow{-65}$ 56	C <sub>5</sub> H <sub>5</sub>

<sup>a</sup> Source pressure =  $2.3 \times 10^{-6}$  mm. <sup>b</sup> Source pressure =  $1.2 \times 10^{-6}$  mm.

metals. The vanadium compounds  $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$  and  $\text{C}_5\text{H}_5\text{V}(\text{CO})_3\text{P}[\text{N}(\text{CH}_3)_2]_3$  both exhibit appreciable abundances of  $(\text{C}_5\text{H}_5)_2\text{V}^+$  in their mass spectra. However, none of the cyclopentadienylmetal carbonyl derivatives of the second- and third-row transition metals molybdenum, tungsten, or rhenium containing only one cyclopentadienyl ring exhibited detectable concentrations of  $(\text{C}_5\text{H}_5)_2\text{M}^+$  ions in their mass spectra. The presently available data on the presence of  $(\text{C}_5\text{H}_5)_2\text{M}^+$  ions in the mass spectra of cyclopentadienylmetal carbonyl derivatives containing one cyclopentadienyl ring may be rationalized on the basis of the thermal

Table III. Mass Spectrum of  $C_6H_5CH=CHCOFe(CO)_2C_5H_5^a$ 

<i>m/e</i>	Ion	Rel intensity	<i>m/e</i>	Ion	Rel intensity
390	$(C_6H_5CH=CHC_5H_4)_2Fe^+$	0.4	121	$C_5H_5Fe^+$	100
316	$C_5H_5FeC_5H_4COCH=CHC_5H_5^+$	0.2	115	$C_9H_7^+$	15
308	$C_6H_5CH=CHCOFe(CO)_2C_5H_5^+$	0.2	112	$C_6H_5CH=CHFeC_5H_5^{2+}$	2
304	$C_5H_5Fe(CO)_2I^+$	0.3	104	$C_8H_8^+$	46
288	$C_5H_5FeC_5H_4CH=CHC_5H_5^+$	7	103	$C_8H_7^+$	43
280	$C_6H_5CH=CHFe(CO)_2C_5H_5^+$	46	102	$C_8H_6^+$	37
262	$C_5H_5FeC_5H_4C_6H_5^+$	0.2	95	$C_3H_5Fe^+$	16
252	$C_6H_5CH=CHFeCOC_5H_5^+$	82	94	$C_3H_2Fe^+$	9
224	$C_6H_5CH=CHFeC_5H_5^+$	120	93	$C_3HFe^+$	5
223	$C_6H_5C_2HFeC_5H_5^+$	137	91	$C_7H_7^+$	15
206	$C_5H_5Fe(CO)_3H^+$	12	89	$C_7H_5^+$	8
205	$C_5H_5Fe(CO)_3^+$	5	84 (2)	$FeCO^+, C_{13}H_{12}^{2+}$	4
198	$C_5H_5FeC_6H_5^+$	29	83.5	$C_{13}H_{11}^{2+}$	2
186	$(C_5H_5)_2Fe^+$	65	83	$C_{13}H_{10}^{2+}$	10
177	$C_5H_5Fe(CO)_2^+$	4	82.5	$C_{13}H_9^{2+}$	6
172	$C_4H_5FeC_5H_5^+$	5	82	$C_{13}H_8^{2+}$	6
168	$C_{13}H_{12}^+$	79	81.5	$C_{13}H_7^{2+}$	2
167	$C_{13}H_{11}^+$	90	81	$C_2HFe^+$	14
166	$C_{13}H_{10}^+$	54	78	$C_6H_6^+$	19
165	$C_{13}H_9^+$	46	77	$C_6H_5^+$	28
158	$C_8H_6Fe^+$	44	76	$C_6H_4^+$	15
153	$C_{12}H_9^+$	43	66	$C_6H_6^+$	22
152	$C_{12}H_8$	21	65	$C_6H_5^+$	18
142	$C_{11}H_{10}^+$	8	63	$C_5H_5^+$	15
141	$C_{11}H_9^+$	13	56	$Fe^+$	135
139	$C_{11}H_7^+$	6	51	$C_4H_5^+$	28
131	$C_6H_5CH=CHCO^+$	47	50	$C_4H_2^+$	13
128	$C_{10}H_8^+$	12	39	$C_3H_3^+$	28

## Metastable ions

<i>m/e</i>	Process	Neutral fragment lost	<i>m/e</i>	Process	Neutral fragment lost
227	$280 \xrightarrow{-28} 252$	CO	94	$141 \xrightarrow{-26} 115$	$C_2H_2$
199.3	$252 \xrightarrow{-28} 224$	CO	78.7	$186 \xrightarrow{-65} 121$	$C_5H_5$
166	$168 \xrightarrow{-1} 167$	H	64.4	$66 \xrightarrow{-1} 65$	H
152				$66 \xrightarrow{-26} 40$	
149.5	$198 \xrightarrow{-26} 172$	$C_2H_2$	58.5	$104 \xrightarrow{-26} 78$	$C_2H_2$
139.5			33.8	$77 \xrightarrow{-26} 51$	$C_2H_2$
138				$95 \xrightarrow{-39} 56$	$C_3H_3$
124.3	$224 \xrightarrow{-57} 167$	FeH	25.8	$121 \xrightarrow{-65} 56$	$C_5H_5$
102.5	$198 \xrightarrow{-56} 142$	Fe	19.8	$158 \xrightarrow{-102} 56$	$C_6H_6$

<sup>a</sup> Source pressure =  $1.5 \times 10^{-6}$  mm.

stability of the neutral hydride-free  $(C_5H_5)_2M$  compounds. Thus iron and vanadium, but not molybdenum, tungsten, and rhenium, form thermally stable (to at least 200°)  $(C_5H_5)_2M$  derivatives. Molybdenum, tungsten, and rhenium form only the hydrides  $(C_5H_5)_2MoH_2$ ,  $(C_5H_5)_2WH_2$ , and  $(C_5H_5)_2ReH$ , respectively.

The mass spectra of several cyclopentadienylmetal carbonyl derivatives of the types  $RFe(CO)_2C_5H_5$  and  $RMo(CO)_3C_5H_5$  with very diverse R groups  $\sigma$ -bonded to the metal atom exhibit relatively weak ions corresponding to an essentially monoisotopic group of mass 127 being bonded to the  $-Fe(CO)_2C_5H_5$  or  $-Mo(CO)_3C_5H_5$  residue, respectively. Two explanations appear possible for this effect. (1) Iodine atoms remaining in the mass spectrometer from previous studies on iodine compounds ("memory" effect)<sup>10</sup> combine with the  $Fe(CO)_2C_5H_5$  or  $Mo(CO)_3C_5H_5$  residues generated by breakdown of the compound in the mass spectrometer to form  $C_5H_5Fe(CO)_2I$  or  $C_5H_5Mo(CO)_3I$ , respectively. (2) A  $C_{10}H_7$  group is formed by coupling of two  $C_5H_5$

(10) I am indebted to Professor C. E. Melton of the University of Georgia for pointing out this possibility.

rings followed by dehydrogenation. This group then becomes attached to the  $C_5H_5Fe(CO)_2$  or  $C_5H_5Mo(CO)_3$  residue to form  $C_5H_5Fe(CO)_2C_{10}H_7$  or  $C_5H_5Mo(CO)_3C_{10}H_7$ .

A decision between these two explanations is unequivocally possible by investigation of the ratio  $[M + 1]/[M]$  since the effect of the presence of  $^{13}C$  (1.1% natural abundance) in the ten carbon atoms of the  $C_{10}H_7$  group would noticeably affect the intensity of the  $M + 1$  ion relative to the  $M$  ion. Table XIV compares the experimental value for the ratio  $[M + 1]/[M]$  for the ions  $C_5H_5Fe(CO)_nY^+$  ( $Y =$  mass 127 group,  $n = 0-2$ ) with those calculated for the formulas  $C_5H_5Fe(CO)_nI^+$  ( $n = 0-2$ ) and  $C_5H_5Fe(CO)_nC_{10}H_7^+$  ( $n = 0-2$ ).

It is thus apparent that these ions containing the monoisotopic group of mass 127 arise from iodine present in the mass spectrometer. Table XIV also shows that the ions  $C_5H_5Cr(NO)_nI^+$  ( $n = 0-2$ ) arise in the mass spectrum of  $[C_5H_5Cr(NO)_2]_2$ . Table XV illustrates the variety of compounds which can capture spurious iodine from the mass spectrometer to form  $C_5H_5M(CO)_nI^+$  ions.<sup>9</sup> The presence of these ions

Table IV. Mass Spectrum of  $\text{CH}_3\text{OCOCH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5^a$ 

<i>m/e</i>	Ion	Rel intensity
250	$\text{CH}_3\text{CO}_2\text{CH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5^+$	2
222	$\text{CH}_3\text{CO}_2\text{CH}_2\text{FeCOC}_5\text{H}_5^+$	47
219	$\text{COCH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5^+$	7
194	$\text{CH}_3\text{CO}_2\text{CH}_2\text{FeC}_5\text{H}_5^+$	132
186	$(\text{C}_5\text{H}_5)_2\text{Fe}^+$	131
177	$\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2^+$	12
163	$\text{C}_5\text{H}_5\text{FeCOCH}_2^+$	3
152	$\text{C}_5\text{H}_5\text{FeOCH}_3^+$	98
150	$\text{C}_5\text{H}_5\text{FeCOH}^+$	9
149	$\text{C}_5\text{H}_5\text{FeCO}^+$	14
135	$\text{C}_5\text{H}_5\text{FeCH}_2^+$	3
134	$\text{C}_5\text{H}_5\text{FeCH}^+$	4
129	$\text{CH}_3\text{CO}_2\text{CH}_2\text{Fe}^+$	2
128	$\text{CH}_3\text{CO}_2\text{CHFe}^+$	2
122	$\text{C}_5\text{H}_6\text{Fe}^+$	122
121	$\text{C}_5\text{H}_5\text{Fe}^+$	100
95	$\text{C}_3\text{H}_3\text{Fe}^+$	12
94	$\text{C}_3\text{H}_2\text{Fe}^+$	6
93	$\text{C}_3\text{HFe}^+$	4
87	$\text{FeOCH}_3^+$	8
81.5	$\text{C}_5\text{H}_5\text{FeCOCH}_2^{2+}$	2
81	$\text{C}_6\text{H}_9^+, \text{C}_5\text{H}_5\text{O}^+$	7
70	$\text{FeCH}_2^+$	3
66	$\text{C}_5\text{H}_6^+$	7
65	$\text{C}_5\text{H}_5^+$	5
63	$\text{C}_3\text{H}_3^+$	2
56	$\text{Fe}^+$	41
43	$\text{COCH}_3^+$	7
42	$\text{COCH}_2^+$	30
41	$\text{COCH}^+$	6
39	$\text{C}_3\text{H}_3^+$	8

## Metastable ions

<i>m/e</i>	Process	Neutral fragment lost
197	250 $\xrightarrow{-28}$ 222	CO
169.5	222 $\xrightarrow{-28}$ 194	CO
151	250 $\xrightarrow{-56}$ 194	2CO
148.5	152 $\xrightarrow{-2}$ 150	H <sub>2</sub>
143.1	219 $\xrightarrow{-42}$ 177	CH <sub>2</sub> CO
125.5	177 $\xrightarrow{-28}$ 149	CO
119.2	194 $\xrightarrow{-42}$ 152	CH <sub>2</sub> CO
99.2	150 $\xrightarrow{-28}$ 122	CO
98.2	149 $\xrightarrow{-28}$ 121	CO
78.5	186 $\xrightarrow{-65}$ 121	C <sub>5</sub> H <sub>5</sub>
64.5	66 $\xrightarrow{-1}$ 65	H
25.8	121 $\xrightarrow{-65}$ 56	C <sub>5</sub> H <sub>5</sub>
25.6	122 $\xrightarrow{-65}$ 56	C <sub>5</sub> H <sub>5</sub>

<sup>a</sup> Source pressure =  $1.2 \times 10^{-5}$  mm.

demonstrates the relatively great tendency for formation of the metal carbonyl iodides. In view of the unknown amount of iodine present in the mass spectrometer at any given time, the relative intensities in Table XV have no real significance beyond summarizing actual experimental observations.

**B. Cyclopentadienyliron Carbonyl Derivatives. 1.**  $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$  (Table I). The mass spectrum of this acetyl derivative exhibited enough metastable ions to permit elucidation of its fragmentation scheme as depicted in Figure 2. The parent ion  $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5^+$  (*m/e* 220) appears to break down *via* two

Table V. Mass Spectrum of  $\text{C}_2\text{H}_5\text{OCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5^a$ 

<i>m/e</i>	Ion	Rel intensity
332	$\text{C}_2\text{H}_5\text{OCOCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5^+$	<0.1
304	$\text{C}_2\text{H}_5\text{OCOCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5^+$	55
287	$(\text{C}_2\text{H}_5\text{OC}_2\text{H})\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5^+$	19
276	$\text{C}_2\text{H}_5\text{OCOCH}_2\text{MoCOC}_5\text{H}_5^+$	50
262	$\text{C}_2\text{H}_5\text{OMo}(\text{CO})_2\text{C}_5\text{H}_5^+$	7
248	$\text{C}_2\text{H}_5\text{OCOCH}_2\text{MoC}_5\text{H}_5^+$	61
234	$\text{C}_2\text{H}_5\text{OMoCOC}_5\text{H}_5^+$	15
220	$\text{HOCOCH}_2\text{MoC}_5\text{H}_5^+$	33
217	$\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2^+$	46
204	$\text{C}_5\text{H}_5\text{MoOC}_2\text{H}_3^+$	315
189	$\text{C}_5\text{H}_5\text{MoCO}^+$	50
178	$\text{C}_5\text{H}_5\text{MoOH}^+$	9
177	$\text{C}_5\text{H}_5\text{MoO}^+$	7
161	$\text{C}_5\text{H}_5\text{Mo}^+$	100
149	$\text{C}_4\text{H}_3\text{Mo}^+$	27
135	$\text{C}_3\text{H}_3\text{Mo}^+$	48
102	$\text{C}_5\text{H}_5\text{MoOC}_2\text{H}_3^{2+}$	10
96	$\text{Mo}^+$	39
92	$\text{C}_7\text{H}_8^+$	26
91	$\text{C}_7\text{H}_7^+$	15
80.5	$\text{C}_5\text{H}_5\text{Mo}^{2+}$	9
77	$\text{C}_6\text{H}_6^+$	41
66	$\text{C}_5\text{H}_5^+$	120
65	$\text{C}_5\text{H}_4^+$	70
59	$\text{CH}_3\text{OCO}^+$	22
57	$\text{C}_2\text{H}_5\text{CO}^+$	24
55	$\text{C}_2\text{H}_3\text{CO}^+$	14
42	$\text{COCH}_2^+$	390
39	$\text{C}_3\text{H}_3^+$	63

<sup>a</sup> Source pressure =  $\sim 7.0 \times 10^{-6}$  mm.Table VI. Mass Spectrum of  $\text{Br}(\text{CH}_2)_4\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5^a$ 

<i>m/e</i>	Ion	Rel intensity
380	$\text{Br}(\text{CH}_2)_4\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5^+$	4
352	$\text{Br}(\text{CH}_2)_4\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5^+$	5
324	$\text{Br}(\text{CH}_2)_4\text{MoCOC}_5\text{H}_5^+, \text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Br}^+$	2
296	$\text{Br}(\text{CH}_2)_4\text{MoC}_5\text{H}_5^+, \text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{Br}^+$	28
268	$\text{C}_5\text{H}_5\text{MoCOBr}^+$	43
240	$\text{C}_5\text{H}_5\text{MoBr}^+$	133
214	$\text{C}_3\text{H}_3\text{MoBr}^+$	102
190		39
186		52
161	$\text{C}_5\text{H}_5\text{Mo}^+$	100
135	$\text{C}_3\text{H}_3\text{Mo}^+$	50
107	$\text{C}_5\text{H}_5\text{MoBr}^{2+}$	11
96	$\text{Mo}^+$	26
93	$\text{C}_7\text{H}_8^+$	21
92	$\text{C}_7\text{H}_7^+$	17
91	$\text{C}_7\text{H}_7^+$	17
79 (2)	$\text{C}_6\text{H}_7^+, \text{Br}^+$	38, 9
66	$\text{C}_5\text{H}_5^+$	65
65	$\text{C}_5\text{H}_4^+$	50
56	$\text{C}_4\text{H}_4^+$	152
55	$\text{C}_4\text{H}_7^+$	270
43	$\text{C}_3\text{H}_7^+$	152
41	$\text{C}_3\text{H}_5^+$	378
39	$\text{C}_3\text{H}_3^+$	218

<sup>a</sup> Source pressure =  $\sim 6.5 \times 10^{-7}$  mm.

major pathways. In the first pathway successive losses of carbonyl groups occur to give the carbonyl-free ion  $\text{CH}_3\text{FeC}_5\text{H}_5^+$  (*m/e* 136). This ion then loses hydrogen to give the ion  $\text{C}_6\text{H}_6\text{Fe}^+$  (*m/e* 134). Apparently during this dehydrogenation the carbon atom of the methyl group is inserted into the cyclopentadienyl ring to form a benzene ring. The ion  $\text{C}_6\text{H}_6\text{Fe}^+$  then loses a  $\text{C}_6\text{H}_6$  fragment (presumably benzene) to give the "bare" iron ion  $\text{Fe}^+$  (*m/e* 56). In the second pathway for

Table VII. Mass Spectrum of  $\text{CH}_2=\text{CHCOW}(\text{CO})_3\text{C}_5\text{H}_5^a$ 

$m/e$	Ion	Rel intensity
388	$\text{CH}_2=\text{CHCOW}(\text{CO})_3\text{C}_5\text{H}_5^+$	<0.4
360	$\text{CH}_2=\text{CHW}(\text{CO})_3\text{C}_5\text{H}_5^+$	65
333	$\text{C}_5\text{H}_5\text{W}(\text{CO})_3^+$	31
332	$\text{CH}_2=\text{CHW}(\text{CO})_2\text{C}_5\text{H}_5^+$	46
305	$\text{C}_5\text{H}_5\text{W}(\text{CO})_2^+$	58
304	$\text{CH}_2=\text{CHWCOC}_5\text{H}_5^+$	112
276	$\text{CH}_2=\text{CHWC}_5\text{H}_5^+$	216
249	$\text{C}_5\text{H}_5\text{W}^+$	100
222	$\text{C}_3\text{H}_2\text{W}^+$	62
221	$\text{C}_3\text{HW}^+$	42
210	$\text{C}_2\text{H}_2\text{W}^+$	12
209	$\text{C}_2\text{HW}^+$	12
197	$\text{CHW}^+$	8
184	$\text{W}^+$	12
166	$\text{CH}_2=\text{CHW}(\text{CO})_2\text{C}_5\text{H}_5^{2+}$	4
152	$\text{CH}_2=\text{CHWCOC}_5\text{H}_5^{2+}$	12
138	$\text{CH}_2=\text{CHWC}_5\text{H}_5^{2+}$	54
124.5	$\text{C}_5\text{H}_5\text{W}^+$	31
66	$\text{C}_5\text{H}_6^+$	112
55	$\text{CH}_2=\text{CHCO}^+$	62
41	$\text{C}_3\text{H}_5^+$	38
39	$\text{C}_3\text{H}_3^+$	38

<sup>a</sup> Source pressure =  $\sim 8.0 \times 10^{-7}$  mm.

Table VIII. Mass Spectrum of  $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}^a$ 

$m/e$	Ion	Rel intensity
334	$\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}^+$	43
306	$\text{C}_5\text{H}_5\text{W}(\text{CO})_2\text{H}^+$	46
305	$\text{C}_5\text{H}_5\text{W}(\text{CO})_2^+$	$\sim 19$
278	$\text{C}_5\text{H}_5\text{WCOH}^+$	26
277	$\text{C}_5\text{H}_5\text{WCO}^+$	14
250	$\text{C}_5\text{H}_5\text{WH}^+$	100
249	$\text{C}_5\text{H}_5\text{W}^+$	$\sim 28$
222	$\text{C}_3\text{H}_2\text{W}^+$	28
221	$\text{C}_3\text{HW}^+$	$\sim 23$
209	$\text{C}_2\text{HW}^+$	3
197	$\text{CHW}^+$	2
186		7
184	$\text{W}^+$	2
167	$\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}^{2+}$	1.5
153	$\text{C}_5\text{H}_5\text{W}(\text{CO})_2\text{H}^{2+}$	4.0
152.5	$\text{C}_5\text{H}_5\text{W}(\text{CO})_2^{2+}$	2.1
139	$\text{C}_5\text{H}_5\text{WCOH}^{2+}$	$\sim 4$
138.5	$\text{C}_5\text{H}_5\text{WCO}^{2+}$	$\sim 4$
125	$\text{C}_5\text{H}_5\text{WH}^{2+}$	30
124.5	$\text{C}_5\text{H}_5\text{W}^{2+}$	19
111.5	$\text{C}_3\text{H}_3\text{W}^{2+}$	1.5
101.67	$\text{C}_5\text{H}_5\text{W}(\text{CO})_2^{3+}$	0.05
66	$\text{C}_5\text{H}_6^+$	7
65	$\text{C}_5\text{H}_5^+$	4
40	$\text{C}_3\text{H}_4^+$	2
39	$\text{C}_3\text{H}_3^+$	3

<sup>a</sup> Source pressure =  $2.0 \times 10^{-6}$  mm.

degradation of  $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5^+$  loss of a methyl group from the parent ion first occurs giving the ion  $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3^+$  ( $m/e$  205). This ion loses carbonyl groups stepwise giving the ion  $\text{C}_5\text{H}_5\text{Fe}^+$  ( $m/e$  121) which finally loses the cyclopentadienyl ring to give again the "bare" iron ion  $\text{Fe}^+$  ( $m/e$  56).

The mass spectrum also indicates that  $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$  decomposes thermally into ferrocene and methylferrocene. Ionization of the ferrocene to give the  $(\text{C}_5\text{H}_5)_2\text{Fe}^+$  ( $m/e$  186) ion is observed. This ion loses stepwise its two cyclopentadienyl groups, again giving finally the "bare" iron ion  $\text{Fe}^+$  ( $m/e$  56). This mode of degradation of  $(\text{C}_5\text{H}_5)_2\text{Fe}^+$  is observed in all cases where it is present in sufficient quantities to permit

Table IX. Mass Spectra of  $\text{C}_5\text{H}_5\text{M}(\text{CO})_2\text{C}_7\text{H}_7$  Compounds<sup>a,b</sup>

Ion	Relative intensities		
	$\pi$ -Cycloheptatrienyl deriv	$\pi$ -Benzyl deriv	
	M = Mo	M = W <sup>c</sup>	
$\text{C}_5\text{H}_5\text{M}(\text{CO})_2\text{C}_7\text{H}_7^+$	10	56	16
$\text{C}_5\text{H}_5\text{MCOC}_7\text{H}_7^+$	<0.03	$\ll 6$	0.3
$\text{C}_5\text{H}_5\text{MC}_7\text{H}_7^+$	100	100	100
$(\text{C}_5\text{H}_5)_2\text{M}^+$	7	$\sim 50$	<3
$\text{C}_5\text{H}_5\text{MC}_3\text{H}_5^+$			12
$\text{C}_5\text{H}_5\text{MC}_3\text{H}^+$	9		14
$\text{C}_5\text{H}_5\text{MC}_2\text{H}^+$			3
$\text{C}_5\text{H}_6\text{M}^+$	14		8
$\text{C}_5\text{H}_4\text{M}^+$			4
$\text{C}_5\text{H}_5\text{M}^+$	5		8
$\text{C}_5\text{H}_3\text{M}^+$	5		4
$\text{C}_5\text{H}_5\text{M}(\text{CO})\text{C}_7\text{H}_7^{2+}$			4
$\text{C}_5\text{H}_3\text{Mo}^+$	7		8
$\text{C}_5\text{H}_5\text{MC}_7\text{H}_7^{2+}$	10		12
$(\text{C}_5\text{H}_5)_2\text{Mo}^{2+}$	2		2
$\text{C}_5\text{H}_5\text{MoC}_5\text{H}_3^{2+}$			1
$\text{M}^+$	22		14
$\text{C}_7\text{H}_7^+$	28		17
$\text{C}_5\text{H}_6^+$	27		2
$\text{C}_5\text{H}_6^+$	14		4
$\text{C}_5\text{H}_5^+$	15		6
$\text{C}_4\text{H}_4^+$	7		1
$\text{C}_4\text{H}_3^+$	9		2
$\text{C}_4\text{H}_2^+$	10		2
$\text{C}_3\text{H}_3^+$	20		6

<sup>a</sup> The  $\text{C}_5\text{H}_5\text{MC}_7\text{H}_7^+$  ions rather than the more usual  $\text{C}_5\text{H}_5\text{M}^+$  ions were used as the base peaks (*i.e.*, relative intensities assigned to be 100). <sup>b</sup> Source pressures used were  $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{C}_7\text{H}_7$ :  $3.8 \times 10^{-7}$  mm;  $\text{C}_5\text{H}_5\text{W}(\text{CO})_2\text{C}_7\text{H}_7$ :  $5.4 \times 10^{-7}$  mm;  $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{C}_7\text{H}_7$ :  $\sim 1.5 \times 10^{-6}$  mm. <sup>c</sup> This spectrum had an unusually poor signal-to-noise ratio which limited the number of ions unequivocally observed.

Table X. Mass Spectrum of  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5^a$ 

$m/e$	Ion	Rel intensity
258	$\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5^+$	23
230	$\text{C}_5\text{H}_5\text{MoCOC}_5\text{H}_5^+$	28
200	$\text{C}_3\text{H}_3\text{MoC}_5\text{H}_5^+$	100
174	$\text{C}_5\text{H}_6\text{Mo}^+$	18
161	$\text{C}_5\text{H}_5\text{Mo}^+$	14
147	$\text{C}_4\text{H}_3\text{Mo}^+$	7
135	$\text{C}_3\text{H}_3\text{Mo}^+$	18
122	$\text{C}_2\text{H}_2\text{Mo}^+$	7
115	$\text{C}_5\text{H}_5\text{MoCOC}_5\text{H}_5^{2+}$	2
109	$\text{CHMo}^+$	5
100	$\text{C}_3\text{H}_3\text{MoC}_5\text{H}_5^{2+}$	10
96	$\text{Mo}^+$	17
80.5	$\text{C}_5\text{H}_5\text{Mo}^{2+}$	2
66	$\text{C}_5\text{H}_6^+$	5
65	$\text{C}_5\text{H}_5^+$	3
42	$\text{C}_3\text{H}_6^+$	6
41	$\text{C}_3\text{H}_5^+$	10
40	$\text{C}_3\text{H}_4^+$	6
39	$\text{C}_3\text{H}_3^+$	15

<sup>a</sup> Source pressure =  $1.6 \times 10^{-6}$  mm.

observation of the metastable peaks corresponding to the successive losses of cyclopentadienyl rings. By contrast, the ion  $(\text{C}_5\text{H}_5)_2\text{Fe}^+$  has almost no tendency to form a  $\text{C}_3\text{H}_3\text{FeC}_5\text{H}_5^+$  fragment by extrusion of the elements of acetylene.

In an attempt to secure further indications of the significance of pyrolysis processes in the mass spectrum of  $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ , the mass spectrum of this compound was also run on a JEOLCO JMS-O1SG mass

Table XI. Mass Spectrum of  $C_5H_5V(CO)_4$ 

<i>m/e</i>	Ion	Relative intensity	
		This work	Winters and Kiser <sup>a</sup>
228	$C_5H_5V(CO)_4^+$	9	8
200	$C_5H_5V(CO)_3^+$	5	4
181	$(C_5H_5)_2V^+$	30	
172	$C_5H_5V(CO)_2^+$	11	10
155	$C_5H_5VC_3H_3^+$	1	
153	$C_5H_5VC_3H^+$	1	
144	$C_5H_5VCO^+$	9	6
116	$C_5H_5V^+$	100	100
90	$C_5H_5V^+$	28	32
79	$VCO^+$		7
76	$C_2HV^+$	7	
66	$C_3H_6^+$	6	
65	$C_3H_5^+$	3	
58	$C_5H_5V^{2+}$	10	
51	$V^+$	22	59
40	$C_3H_4^+$	2	
39	$C_3H_3^+$	3	18

## Metastable ions

<i>m/e</i>	Process	Neutral fragment lost
175.2	$228 \xrightarrow{-28} 200$	CO
147.9	$200 \xrightarrow{-28} 172$	CO
132.6	$181 \xrightarrow{-26} 155$	$C_2H_2$
120.5	$172 \xrightarrow{-28} 144$	CO
93.3	$144 \xrightarrow{-28} 116$	CO
74.2	$181 \xrightarrow{-65} 116$	$C_3H_3$
69.8	$116 \xrightarrow{-26} 90$	$C_2H_2$
34.7		
32.8		
18.4		

<sup>a</sup> See ref 3.Table XII. Mass Spectra of  $C_5H_5M(CO)_3$  Compounds

Ion	Relative intensities	
	$C_5H_5Mn(CO)_3^a$	$C_5H_5Re(CO)_3^b$
$C_5H_5M(CO)_3^+$	26	111
$C_5H_5M(CO)_2^+$	0.2	40
$C_5H_5MCO^+$	23	200
$C_5H_5M^+$	100	100
$C_3H_3M^+$		37
$C_3H_3M^+$	0.4	29
$C_3H_2M^+$		24
$C_3HM^+$		40
$C_2HM^+$		8
$CHM^+$		24
$CM^+$		8
$M^+$	63	16
$C_5H_5M(CO)_3^{2+}$		8
$C_5H_5M(CO)_2^{2+}$		8
$C_5H_5MCO^{2+}$		18
$C_5H_5M^{2+}$		34

<sup>a</sup> Data of Winters and Kiser.<sup>3</sup> <sup>b</sup> Source pressure =  $2.8 \times 10^{-7}$  mm.

spectrometer operating with an inlet temperature of only 70° in contrast to that of 200–250° used for its mass spectrum on the MS-9 mass spectrometer. Table I presents a comparison of the mass spectra of this compound run at these two different temperatures. The two mass spectra were essentially identical except for the following points. (1) The  $(C_5H_5)_2Fe^+$  (*m/e* 186)

Table XIII. Ferrocene Ions Observed in the Mass Spectra of  $RFe(CO)_2C_5H_5$  Compounds

R group in $RFe(CO)_2C_5H_5$	—Relative abundances ( $C_5H_5Fe^+ = 100$ )—			
	$(C_5H_5)_2Fe^+$	$RC_5H_5^+$	$(RC_5H_5)_2^+$	Other $R'C_5H_5^+$ Rel abund
(1) $NC_5H_4CH_2$	98			
(2) $C_5H_{10}NCH_2CH_2$	99			
(3) $CH_3OCOCH_2$	131			
(4) $C_6H_5$	93	22	2	
(5) $C_6H_5CO$	52	23 <sup>a</sup>	2 <sup>a</sup>	
(6) $C_6F_5$	210	16		
(7) $C_6F_5H_2^b$	260	40		
(8) <i>p</i> - $CF_3C_6F_4$	245	13		
(9) $C_6F_5^c$	34	5		
(10) $CH_3CO$	22			$CH_3$ 0.2
(11) $C_3F_7CO$	74			
(12) $C_6H_5CH=CHCO$	65	0.2		$C_6H_5$ 0.2
		7 <sup>d</sup>	0.2 <sup>d</sup>	
(13) $C_6H_5COS$	330			$C_6H_5$ 1.8 $C_6H_5CO$ 0.6
(14) $CH_3S$	234	0.2		$CH_3$ 1.4

<sup>a</sup> R = phenyl, not benzoyl. <sup>b</sup> 2,3,6-Trifluorophenyl. <sup>c</sup> 1-Perfluorocyclohexyl. <sup>d</sup> R =  $C_6H_5CH=CH$ , not  $C_6H_5CH=CHCO$ .

ion was weaker by a factor of 11 in the mass spectrum run at 70° relative to that run at 200°, supporting the above suggestion that thermal decomposition of  $CH_3COFe(CO)_2C_5H_5$  giving ferrocene is the origin of this *m/e* 186 ion. (2) The  $CH_3COFe(CO)_2C_5H_5^+$  (*m/e* 220) and  $C_5H_5Fe(CO)_3^+$  (*m/e* 205) ions were stronger by factors of 4.5 and 2.5, respectively, in the mass spectrum run at 70° relative to that run at 200°. This indicates that in the mass spectrum taken at 200° some thermal decarbonylation of  $CH_3COFe(CO)_2C_5H_5$  to give  $CH_3Fe(CO)_2C_6H_5$  has occurred prior to ionization. The ions  $CH_3COFe(CO)_2C_5H_5^+$  (*m/e* 220) and  $C_5H_5Fe(CO)_3^+$  (*m/e* 205) are the only ions containing three carbonyl groups and thus the only ions expected to be observed in the mass spectrum of  $CH_3COFe(CO)_2C_5H_5$  but not in the mass spectrum of  $CH_3Fe(CO)_2C_5H_5$ . This thermal decarbonylation of  $CH_3COFe(CO)_2C_5H_5$  to give  $CH_3Fe(CO)_2C_6H_5$  is completely analogous to the thermal decarbonylation of  $C_6H_5COFe(CO)_2C_5H_5$  to give  $C_6H_5Fe(CO)_2C_5H_5$  proposed to occur when the mass spectrum of the benzoyl derivative  $C_6H_5COFe(CO)_2C_5H_5$  is run at 200° (Table II).

The tendency for  $CH_3COFe(CO)_2C_5H_5$  to exhibit the  $C_5H_5Fe(CO)_3^+$  (*m/e* 205) ion in its mass spectrum appears to be a general characteristic of all  $RCOFe(CO)_2C_5H_5$  derivatives investigated. Salts containing the ion  $[C_5H_5Fe(CO)_3]^+$  have been isolated as stable chemical species.<sup>11</sup>

2.  $C_6H_5COFe(CO)_2C_5H_5$  and  $C_6H_5Fe(CO)_2C_5H_5$  (Table II). The mass spectra of the benzoyl derivative and the phenyl derivative are so similar that they appear to be those of the same compound. This observation coupled with absence of the parent ion  $C_6H_5COFe(CO)_2C_5H_5^+$  (*m/e* 282) in the mass spectrum of the benzoyl derivative indicates that the observed spectrum is actually that of the phenyl derivative  $C_6H_5Fe(CO)_2C_5H_5$ . Further support for the assignment of the observed spectrum of the phenyl derivative is based on the absence of the ion  $C_5H_5Fe(CO)_3^+$  (*m/e* 205) found to be

(11) (a) E. O. Fischer and K. Fichtel, *Ber.*, **94**, 1200 (1961); (b) A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961); (c) R. B. King, *Inorg. Chem.*, **1**, 964 (1962).



Table XIV.  $[M + 1]/[M]$  for  $C_5H_5M(CO)_nY$  Compounds ( $Y = \text{mass } 127 \text{ group}$ )

Compound	Ion	Found	Calcd for $Y = I$	Calcd for $Y = C_{10}H_7$
$CH_3SFe(CO)_2C_5H_5$	$C_5H_5Fe(CO)_2Y^+$	0.12	0.10	0.22
	$C_5H_5FeY^+$	0.11	0.08	0.20
$NC_5H_4CH_2Fe(CO)_2C_5H_5$	$C_5H_5Fe(CO)_2Y^+$	0.11	0.10	0.22
	$C_5H_5FeY^+$	0.09	0.08	0.20
$C_5H_{10}NCH_2CH_2Fe(CO)_2C_5H_5$	$C_5H_5Fe(CO)_2Y^+$	0.10	0.10	0.22
	$C_5H_5FeCOY^+$	0.10	0.09	0.21
	$C_5H_5FeY^+$	0.08	0.08	0.20
	$C_5H_5Cr(NO)_2Y^+$	0.18	0.18	0.29
$[C_5H_5Cr(NO)_2]_2$	$C_5H_5CrNOY^+$	0.16	0.17	0.29
	$C_5H_5CrY^+$	0.17	0.17	0.28

Table XV.  $C_5H_5M(CO)_nI$  Ions Arising from Iodine in the Mass Spectrometer Observed in the Mass Spectra of Cyclopentadienylmetal Carbonyl Derivatives and Related Compounds

A. $C_5H_5Fe(CO)_2I$			
Compound	Relative abundances ( $C_5H_5M^+ = 100$ )		
	$C_5H_5Fe-$ ( $CO)_2I^+$	$C_5H_5-$ $FeCOI^+$	$C_5H_5-$ $FeI^+$
(1) $C_6H_5COSFe(CO)_2C_5H_5$	0.28	0.28	0.32
(2) $CH_3SFe(CO)_2C_5H_5$	3.2	3.3	3.3
(3) $NC_5H_4CH_2Fe(CO)_2C_5H_5$	9.5	10.5	12.0
(4) $C_5H_{10}NCH_2CH_2Fe(CO)_2C_5H_5$	3.6	4.1	4.5
(5) $CH_3OCOCH_2Fe(CO)_2C_5H_5$	0.2	0.1	?
(6) $C_6H_5Fe(CO)_2C_5H_5$	0.9	0.6	?
(7) $C_6H_5CH=CHCOFe(CO)_2C_5H_5$	0.3	0.2	0.3

B. $C_5H_5Cr(NO)_2I$			
Compound	Relative abundances ( $C_5H_5M^+ = 100$ )		
	$C_5H_5Cr-$ ( $NO)_2I^+$	$C_5H_5Cr-$ $NOI^+$	$C_5H_5CrI^+$
$[C_5H_5Cr(NO)_2]_2$	50.0	39.5	48.5

C. $C_5H_5M(CO)_3I$				
Compound	Relative abundances			
	$C_5H_5M-$ ( $CO)_3I^+$	$C_5H_5M-$ ( $CO)_2I^+$	$C_5H_5M-$ $COI^+$	$C_5H_5-$ $MI^+$
(1) $CH_3SCH_2Mo(CO)_3C_5H_5$		1.2	0.6	2.1
(2) $C_5H_5Mo(CO)_3CH_2NCO$	0.1	0.5	0.7	0.8
(3) $(CF_3)_2[Mo(CO)_3C_5H_5]_2$	10.3	11.5	23.0	19.5
(4) $Br(CH_2)_4Mo(CO)_3C_5H_5$	~0.2	2.0	1.5	3.0
(5) $NC_5H_4CH_2W(CO)_3C_5H_5^a$	4.0	8.3	3.1	10.3

<sup>a</sup> Relative to  $NC_5H_4CH_2WC_5H_5^+ = 100$ .

a characteristic constituent of the mass spectra of acyl derivatives of the type  $RCOFe(CO)_2C_5H_5$ .

The benzoyl derivative  $C_6H_5COFe(CO)_2C_5H_5$  thus appears to be decarbonylated to the phenyl derivative  $C_6H_5Fe(CO)_2C_5H_5$  in the mass spectrometer. This observation is somewhat surprising since previous attempts to decarbonylate  $RCOFe(CO)_2C_5H_5$  compounds to  $RFe(CO)_2C_5H_5$  compounds by purely thermal means have been unsuccessful.<sup>12</sup> In prior successful decarbonylations of  $RCOFe(CO)_2C_5H_5$  compounds, ultraviolet irradiation was always used as the source of energy.

Other examples of decarbonylation of metal carbonyl derivatives in the mass spectrometer have been observed and will be discussed in detail elsewhere. The list of compounds exhibiting this behavior includes compounds such as  $CH_3SCH_2Mo(CO)_3C_5H_5$  and  $R_fCOMo(CO)_3C_5H_5$  known to undergo facile thermal decar-

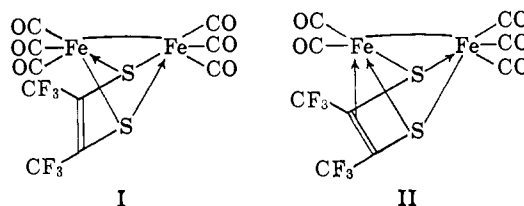
(12) R. B. King and M. B. Bisnette, *J. Organometal. Chem.* (Amsterdam), 2, 15 (1964).

bonylation. A particularly interesting case is the bis-(trifluoromethyl)ethylene dithiolate complex  $(CF_3)_2C_2S_2Fe_2(CO)_6$  (I).<sup>13</sup> The highest  $m/e$  ion in the mass spectrum of this compound is the diiron pentacarbonyl ion  $(CF_3)_2C_2S_2Fe_2(CO)_5^+$ , suggesting that the diiron hexacarbonyl derivative I has been decarbonylated to the diiron pentacarbonyl derivative  $(CF_3)_2C_2S_2Fe_2(CO)_5$  (II) in the mass spectrometer. These observations suggest that caution is indicated when establishing the number of carbonyl groups in a metal carbonyl derivative from its mass spectrum. The minimum, but not always the maximum, number of carbonyl groups can be established by mass spectroscopy.

The parent ion in the mass spectrum of the phenyl derivative  $C_6H_5Fe(CO)_2C_5H_5$  (Table II) undergoes stepwise loss of carbonyl groups, giving finally the carbonyl-free ion  $C_6H_5FeC_5H_5^+$  ( $m/e$  198). This ion then is dehydrogenated to give an ion  $C_{11}H_3Fe^+$  ( $m/e$  196) possibly analogous to the ion  $C_6H_6Fe^+$  observed in the mass spectrum of  $CH_3COFe(CO)_2C_5H_5$ .

Besides undergoing dehydrogenation, the  $C_6H_5FeC_5H_5^+$  ( $m/e$  198) ion can fragment in two other manners. It may expel  $C_2H_2$  to form the ion  $C_9H_3Fe^+$  ( $m/e$  172). It is not yet clear whether the  $C_2H_2$  is expelled from the five-membered ring or from the six-membered ring of  $C_6H_5FeC_5H_5^+$ . Alternatively the  $C_6H_5FeC_5H_5^+$  ion may expel the iron atom to give the metal-free ion  $C_6H_5C_5H_5^+$  ( $m/e$  142). This iron-expulsion process is supported by the observation of a metastable ion at  $m/e$  102 ( $142^2/198 = 101.9$ ). It is related to processes observed in the mass spectra of substituted ferrocenes.<sup>14</sup>

Some pyrolysis products of  $C_6H_5Fe(CO)_2C_2H_5$  are evident in its mass spectrum. Ions from ferrocene ( $m/e$  186), phenylferrocene ( $m/e$  262), and even di-



phenylferrocene ( $m/e$  338) are observed. Furthermore, the  $C_{12}H_{10}^+$  ion at  $m/e$  154 appears to arise from biphenyl, another likely pyrolysis product of  $C_6H_5Fe(CO)_2C_5H_5$ .

(13) R. B. King, *J. Am. Chem. Soc.*, 85, 1584 (1963).

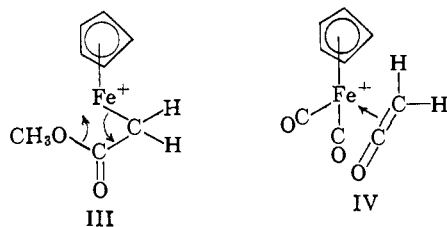
(14) M. Maoz, A. Mandelbaum, and M. Cais, *Tetrahedron Letters*, 2087 (1965).

The smaller fragments in the mass spectrum of  $C_6H_5Fe(CO)_2C_5H_5$  arise from the larger ions already mentioned by the processes of dehydrogenation, acetylene ( $C_2H_2$ ) expulsion, and iron-ligand bond rupture. The  $C_5H_n^+$  and  $C_3H_n^+$  ions probably arise from the cyclopentadienyl ring and the  $C_6H_n^+$  and  $C_4H_n^+$  ions from the phenyl ring.<sup>15</sup>

3.  $C_6H_5CH=CHCOFe(CO)_2C_5H_5$  (Table III). The mass spectrum of this complex corresponds to that expected for the acyl derivative  $C_6H_5CH=CHCOFe(CO)_2C_5H_5$  rather than for the alkenyl derivative  $C_6H_5CH=CHFe(CO)_2C_5H_5$ . Thus a parent molecular ion is observed at  $m/e$  308 corresponding to  $C_6H_5CH=CHCOFe(CO)_2C_5H_5^+$ . Furthermore, an appreciable quantity of the  $C_5H_5Fe(CO)_3^+$  ion ( $m/e$  205) is observed indicative of an  $RCOFe(CO)_2C_5H_5$  compound.

The most distinctive feature of the rather complex mass spectrum of  $C_6H_5CH=CHCOFe(CO)_2C_5H_5$  is the presence of ions with  $C_6H_5$  as well as  $C_3H_7$  substituents. These include not only ions such as  $C_5H_5FeC_6H_5^+$  ( $m/e$  198) but also the substituted ferrocene ion  $C_5H_5FeC_5H_4C_6H_5^+$  ( $m/e$  262). These ions containing  $C_6H_5$  groups appear to arise by expulsion of acetylene from corresponding ions containing  $C_6H_5CH=CH$  groups. A feature of the mass spectrum of  $C_6H_5CH=CHCOFe(CO)_2C_5H_5$  not observed in other compounds studied is the presence of a weak ion at  $m/e$  316 corresponding to the acylferrocene ion  $C_5H_5FeC_5H_4COC_3H_7^+$ . Acylferrocene ions have not yet been observed in the mass spectra of other  $RCOFe(CO)_2C_5H_5$  derivatives. The other important features in the mass spectrum of  $C_6H_5CH=CHCOFe(CO)_2C_5H_5$  have already been encountered in the mass spectra of the other cyclopentadienyliron dicarbonyl derivatives discussed above.

4.  $CH_3OCOCH_2Fe(CO)_2C_5H_5$  (Table IV). The mass spectrum of this methyl ester derivative (like that of the acetyl derivative  $CH_3COFe(CO)_2C_5H_5$  discussed above) exhibited enough metastable ions to permit elucidation of its fragmentation scheme as depicted in Figure 3. The parent ion  $CH_3OCOCH_2Fe(CO)_2C_5H_5^+$  ( $m/e$  250) appears to break down *via* two major pathways. In the first pathway losses of carbonyl groups occur to give the ion  $CH_3OCOCH_2FeC_5H_5^+$  ( $m/e$  194). Analysis of the metastable ions shows that the two metal carbonyl groups can be lost from the parent ion either individually or simultaneously.<sup>16</sup> Further degradation of the  $CH_3OCOCH_2FeC_5H_5^+$  ion occurs by a novel elimination of ketene and concurrent shift of a methoxy group from carbon to iron as depicted in III to give the ion  $C_5H_5FeOCH_3^+$  ( $m/e$  152). This ion then loses hydrogen to form the ion  $C_5H_5FeCOH^+$



(15) The tendency for cyclic aromatic  $C_nH_m$  ( $m \leq n$ ) ions to fragment primarily by loss of the two-carbon fragment  $C_2H_2$  and not by loss of one- or three-carbon fragments is the basis for this suggestion.

(16) The simultaneous loss of two carbonyl groups has already been encountered in the mass spectra of the tris(dimethylamino)phosphine complexes  $[(CH_3)_2N]_3PF_6Fe(CO)_3P[(CH_3)_2N]_3$  and  $C_5H_5V(CO)_3P[(CH_3)_2N]_3$  (ref 1).

( $m/e$  150) which then is decarbonylated to give  $C_5H_6Fe^+$  ( $m/e$  122). Loss of cyclopentadiene from the latter ion converts it to the simple "bare" iron ion,  $Fe^+$  ( $m/e$  56).

The second pathway for degradation of the parent  $CH_3OCOCH_2Fe(CO)_2C_5H_5^+$  ion first involves loss of the methoxy group to give the ion  $C_5H_5Fe(CO)_2CH_2CO^+$  ( $m/e$  219). A tentative formulation of this ion as a  $\pi$ -complexed ketene cation IV analogous to the  $\pi$ -complexed ethylene cation  $[C_5H_5Fe(CO)_2C_2H_4]^+$  appears reasonable.<sup>17</sup> This structure IV for  $C_5H_5Fe(CO)_2CH_2CO^+$  ( $m/e$  219) is also reasonable in view of its next degradation step which involves loss of ketene to give the  $C_5H_5Fe(CO)_2^+$  ( $m/e$  177) ion. Further degradation of  $C_5H_5Fe(CO)_2^+$  to the bare iron ion  $Fe^+$  occurs by successive losses of the two carbonyl groups followed by the  $\pi$ -cyclopentadienyl ring as discussed above.

The only ferrocene-type ion observed in the mass spectrum of  $CH_3OCOCH_2Fe(CO)_2C_5H_5$  is that of ferrocene itself,  $(C_5H_5)_2Fe^+$  ( $m/e$  186), presumably formed by pyrolysis. The degradation of this ion to  $Fe^+$  by stepwise loss of the two cyclopentadienyl rings is indicated by the metastable ions at  $m/e$  78.5 and 25.8. The ions of  $C_5H_5Fe(CO)_2I$  arising from reactions with iodine present in the mass spectrometer are observed in low abundance in the mass spectrum of  $CH_3OCOCH_2Fe(CO)_2C_5H_5$  (see Table XV).

C. Cyclopentadienylmolybdenum Tricarbonyl Derivatives. 1.  $C_2H_5OCOCH_2Mo(CO)_3C_5H_5$  (Table V). The parent ion  $C_2H_5OCOCH_2Mo(CO)_3C_5H_5^+$  ( $m/e$  332) was not observed in the mass spectrum of this complex. Instead the highest  $m/e$  ion observed was the dicarbonyl ion  $C_2H_5OCOCH_2Mo(CO)_2C_5H_5^+$  ( $m/e$  304). Analogy to the behavior of species such as  $C_6H_5COFe(CO)_2C_5H_5$  suggests that the tricarbonyl  $C_2H_5OCOCH_2Mo(CO)_3C_5H_5$  is decarbonylated to the dicarbonyl  $C_2H_5OCOCH_2Mo(CO)_2C_5H_5$  in the mass spectrometer. This is somewhat surprising in view of the lack of success in effecting this decarbonylation either thermally or photochemically.<sup>18</sup>

The fragmentation pattern of  $C_2H_5OCOCH_2Mo(CO)_3C_5H_5$  presents several features of interest. Stepwise loss of carbonyl groups from the dicarbonyl ion is observed to give the carbonyl-free ion  $C_2H_5OCOCH_2MoC_5H_5^+$  ( $m/e$  248). The ethyl group of this ion apparently then loses ethylene to give the ion  $HOCOCH_2MoC_5H_5^+$  ( $m/e$  220). Further degradation apparently involves oxygen shifts giving the ions  $C_5H_5MoOH^+$  ( $m/e$  178) and  $C_5H_5MoO^+$  ( $m/e$  177).

Loss of a ketene (mass 42) fragment from the ion  $C_2H_5OCOCH_2Mo(CO)_2C_5H_5^+$  ( $m/e$  304) to give the ethoxymolybdenum ion  $C_2H_5OMo(CO)_2C_5H_5^+$  ( $m/e$  262) by a scheme analogous to that given in III for the iron complex competes effectively with carbonyl loss from this dicarbonyl ion. This latter ion ( $m/e$  262) then loses one carbonyl group to give the corresponding monocarbonyl ion  $C_2H_5OMoCOC_5H_5^+$  ( $m/e$  234). However, loss of the final carbonyl group from this monocarbonyl ion is accompanied by loss of  $H_2$  (dehy-

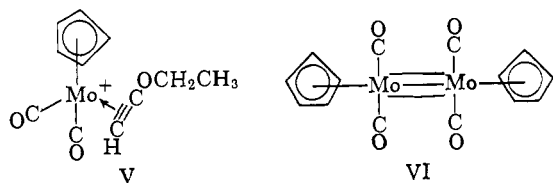
(17) Ketenimine complexes of the type  $C_5H_5Fe(CO)_2(HN=C=CHR)^+$  ( $R = H$  or  $CH_3$ ) closely related to IV have been reported as stable salts by J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, 2976 (1963). An iron tricarbonyl complex of a vinylketene derivative has been reported by R. B. King, *Inorg. Chem.*, 2, 642 (1963).

(18) R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometal. Chem.* (Amsterdam), 5, 341 (1966).

drogenation) leading to the ion  $C_5H_5MoCOCH_3^+$  ( $m/e$  204). This ion can then lose acetylene to give the ion  $C_5H_5MoOH^+$  ( $m/e$  178). Since the ion  $C_5H_5MoCOCH_3^+$  ( $m/e$  204) is formed from an ion with a molybdenum-oxygen bond and fragments to another ion with a molybdenum-oxygen bond, it probably also has a molybdenum-oxygen bond. The vinyloxy structure  $C_5H_5MoOCH=CH_2^+$  with a molybdenum-oxygen bond to the  $C_2H_3O$  group is thus more likely for this  $m/e$  204 ion than the isomeric acetyl structure  $C_5H_5MoCOCH_3^+$  with a molybdenum-carbon bond to the  $C_2H_3O$  group.

A third observed mode of fragmentation of the  $C_2H_5OCOCH_2Mo(CO)_2C_5H_5^+$  ion ( $m/e$  304) is the loss of a hydroxide (OH, mass 17) fragment to give the ion  $(C_2H_5OC_2H)Mo(CO)_2C_5H_5^+$  ( $m/e$  287), possibly an ethoxyacetylene derivative (V). The expected facile loss of ethoxyacetylene from this ion would give the observed  $C_5H_5Mo(CO)_2^+$  ( $m/e$  217) ion which can then go to the  $C_5H_5Mo^+$  ( $m/e$  161) ion by stepwise loss of the two carbonyl groups. Appreciable quantities of  $C_3H_3Mo^+$  ( $m/e$  135) and of  $Mo^+$  ( $m/e$  96) are also observed.

As expected particularly for derivatives of the 4d and 5d transition metals, appreciable concentrations of dipositive ions were observed. The major dipositive ions in the mass spectrum of  $C_2H_5OCOCH_2Mo(CO)_3C_5H_5$  are the presumed vinyloxy derivative  $C_5H_5MoOC_2H_3^{2+}$  ( $m/e$  102) and  $C_5H_5Mo^{2+}$  ( $m/e$  80.5).



A further feature of the mass spectrum of  $C_2H_5OCOCH_2Mo(CO)_3C_5H_5$  not given in Table V is the presence of weak ions at  $m/e$  434, 406, 378, and 322. These correspond to the unknown  $[C_5H_5Mo(CO)_2]_2$  and its possible decarbonylation products except for the monocarbonyl. Such a compound,  $[C_5H_5Mo(CO)_2]_2$ , would be expected to have structure VI with a molybdenum-molybdenum triple bond.<sup>19</sup> Further discussion of the mass spectra of molybdenum carbonyl derivatives which might contain a metal-metal triple bond will be deferred to a future paper.

2.  $Br(CH_2)_4Mo(CO)_3C_5H_5$  (Table VI). The mass spectrum of this compound exhibits no new features. The usual phenomena of stepwise loss of carbonyl groups and expulsion of an acetylene fragment from  $C_5H_5$  groups are observed in this case. Ions containing molybdenum-bromine bonds including  $C_5H_5Mo(CO)_nBr^+$  ( $n = 0-3$ , inclusive) and  $C_3H_3MoBr^+$  are observed. These correspond to the ions observed in the mass spectrum<sup>4</sup> of  $C_5H_5Mo(CO)_3Br$ , a probable product from the thermal decomposition of  $Br(CH_2)_4Mo(CO)_3C_5H_5$ .<sup>20</sup>

D. Cyclopentadienyltungsten Tricarbonyl Derivatives. 1.  $CH_2=CHCOW(CO)_3C_5H_5$  (Table VII). This compound, like the benzoyliron derivative,  $C_6H_5COFe(CO)_2C_5H_5$ , is an example of a compound

exhibiting a mass spectrum where the highest  $m/e$  ion is 28 mass units (one CO group) less than the predicted parent ion. Decarbonylation of the acryloyl derivative  $CH_2=CHCOW(CO)_3C_5H_5$  to the corresponding vinyl derivative  $CH_2=CHW(CO)_3C_5H_5$  thus occurs in the mass spectrometer. The vinyltungsten ion  $CH_2=CHW(CO)_3C_5H_5^+$  ( $m/e$  360) decomposes both by loss of carbon monoxide to give the ion  $CH_2=CHW(CO)_2C_5H_5^+$  ( $m/e$  332) and by loss of the vinyl group to give the ion  $C_5H_5W(CO)_3^+$  ( $m/e$  333). The ions  $CH_2=CHW(CO)_nC_5H_5^+$  ( $n = 0-3$ ) and  $C_5H_5W(CO)_n^+$  ( $n = 0-3$ ) are all observed. The major doubly charged ions are  $CH_2=CHW(CO)_nC_5H_5^{2+}$  ( $n = 0-2$ ).

Intermediates in the fragmentation of the  $C_5H_5W^+$  ion ( $m/e$  249) to  $W^+$  ( $m/e$  184) are of interest. In the mass spectra of both  $CH_2=CHCOW(CO)_3C_5H_5$  (Table VII) and  $C_5H_5W(CO)_3H$  (Table VIII), the intermediate ions  $C_3H_2W^+$ ,  $C_3HW^+$ ,  $C_2H_2W^+$ ,  $C_2HW^+$ , and  $CHW^+$  are all observed in significant abundances.<sup>21</sup> This contrasts with the fragmentation of the  $C_5H_5M^+$  ions in cyclopentadienyl derivatives of iron and molybdenum where only the  $C_3H_3M^+$  ion is generally observed between  $C_5H_5M^+$  and  $M^+$ . The presence of significant quantities of ions containing a tungsten atom and one or two carbon atoms in the fragmentation of  $C_5H_5W^+$  is probably a consequence of the much greater strength of bonds from carbon to the heavy third-row transition metal tungsten as compared with the lighter first- and second-row transition metals which include iron and molybdenum.<sup>22</sup> In the degradation of  $C_5H_5W^+$  or  $C_3H_3W^+$ , the greater stability of the tungsten-carbon bonds means that in some cases the bond between the tungsten atom and the  $C_nH_n$  ligand remains intact during a more extensive fragmentation of the  $C_nH_n$  ligand by carbon-carbon bond cleavage than is the case with the first- and second-row transition metals.

Metal-free fragments in the mass spectrum of  $CH_2=CHCOW(CO)_3C_5H_5$  include  $C_5H_6^+$  ( $m/e$  66) and  $C_3H_3^+$  ( $m/e$  39) from the  $\pi$ -cyclopentadienyl ligand and  $CH_2=CHCO^+$  ( $m/e$  55) from the vinyl group.

2.  $C_5H_5W(CO)_3H$  (Table VIII). The presence of the complete series of ions  $C_5H_5W(CO)_nH^+$  ( $n = 0-3$ ) indicates that the usual stepwise loss of carbonyl groups is also important in the mass spectrum of  $C_5H_5W(CO)_3H$ . However, the concurrent presence of the ions  $C_5H_5W(CO)_n^+$  ( $n = 0-2$ ) indicates that, once one carbonyl group is lost from the parent ion  $C_5H_5W(CO)_3H^+$ , loss of the single hydrogen ligand competes noticeably with the further loss of carbonyl groups. Similar observations were made by Smith, Mehner, and Kaesz<sup>23</sup> and by Edgell and Risen<sup>24</sup> in the mass spectra of other transition-metal hydride derivatives, which, like  $C_5H_5W(CO)_3H$ , contain terminal hydride ligands. Doubly charged ions are observed of the two types  $C_5H_5W(CO)_nH^{2+}$  ( $n = 0-3$ ) and  $C_5H_5W(CO)_n^{2+}$

(21) The observation of these same ions in the mass spectrum of  $C_5H_5W(CO)_3H$  indicates that none of their carbon atoms come from the vinyl group but all from the  $\pi$ -cyclopentadienyl group.

(22) For further indications by other physical techniques of the greater stability of tungsten-carbon bonds as compared with analogous molybdenum-carbon and chromium-carbon bonds, see R. B. King, *J. Organometal. Chem.* (Amsterdam), **8**, 129 (1967) (nmr studies on  $C_5H_5M(CO)_3$  compounds), and R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **87**, 5586 (1965) (kinetic studies on  $C_{10}H_8N_2M(CO)_4$  compounds).

(23) J. M. Smith, K. Mehner, and H. D. Kaesz, *ibid.*, **89**, 1759 (1967).

(24) W. F. Edgell and W. M. Risen, *ibid.*, **88**, 5451 (1966).

(19) For a report of a completely methyl-substituted analog  $[(CH_3)_5C_5Mo(CO)_2]_2$  with an apparent molybdenum-molybdenum triple bond, see R. B. King, *J. Organometal. Chem.* (Amsterdam), **8**, 287 (1967).

(20) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964).

analogous to the ions just cited. In addition, a very weak peak (relative intensity only 0.05) at about  $m/e$  101.67 may arise from the triply charged ion  $C_5H_5W(CO)_2^{3+}$ . The extreme weakness of this peak apparently arising from a triply charged ion relates to the extreme infrequency of observation of triply charged ions in mass spectra.

**E. Cyclopentadienylmetal Dicarbonyl Derivatives of Molybdenum and Tungsten.** 1.  $C_5H_5M(CO)_2C_7H_7$  Compounds ( $M = Mo$  and  $W$ ) (Table IX). By far the most intense ions in the mass spectra of these compounds were the ions  $C_5H_5MC_7H_7^+$ , which were selected as the base peaks. The normally strong  $C_5H_5M^+$  ions were relatively weak in the mass spectra of these compounds.

A surprising feature of the mass spectra of the  $C_5H_5M(CO)_2C_7H_7$  compounds was the complete absence of the monocarbonyl ions  $C_5H_5MCOC_7H_7^+$ . Apparently the two carbonyl groups of the  $C_5H_5M(CO)_2C_7H_7^+$  ions are lost in a single step.<sup>16</sup>

A characteristic feature of the mass spectra of the  $\pi$ -cycloheptatrienyl  $C_5H_5M(CO)_2C_7H_7$  compounds is the ion  $(C_5H_5)_2M^+$  not observed in other cyclopentadienylmetal carbonyl derivatives of molybdenum and tungsten containing only one  $\pi$ -cyclopentadienyl ring. The second cyclopentadienyl group in the  $(C_5H_5)_2M^+$  ion appears to arise by expulsion of acetylene from the  $\pi$ - $C_7H_7$  ring. Interestingly enough, the mass spectrum of the isomeric  $\pi$ -benzyl derivative  $C_5H_5Mo(CO)_2CH_2C_6H_5$  does not exhibit significant concentrations of the  $(C_5H_5)_2Mo^+$  ion, indicating the more difficult loss of acetylene from the  $\pi$ -benzyl ligand. However, the  $\pi$ -benzyl ligand unlike the  $\pi$ -cycloheptatrienyl ligand appears to lose ethylene ( $C_2H_4$ , mass 28) readily as indicated by the appreciable abundance of the  $C_5H_5MoC_5H_5^+$  ion in the mass spectrum of the  $\pi$ -benzyl derivative.

2.  $\pi$ - $C_3H_5Mo(CO)_2C_5H_5$  (Table X). The parent ion ( $m/e$  258) in the mass spectrum of  $C_3H_5Mo(CO)_2C_5H_5$  first loses one of its two carbonyl groups to form the monocarbonyl ion  $C_3H_5MoCOC_5H_5^+$  ( $m/e$  230) which still appears to contain the  $\pi$ -allyl ligand. This monocarbonyl ion has an appreciable abundance in the mass spectrum of this  $\pi$ -allyl derivative in contrast to the negligible abundance of the similar monocarbonyl ion in the mass spectrum of the  $\pi$ -cycloheptatrienyl derivative  $C_5H_5Mo(CO)_2C_7H_7$ . However, the next fragmentation step of this monocarbonyl ion involves a loss of 30 mass units rather than the usual 28 mass units corresponding to loss of a carbonyl group. This mass loss of 30 indicates that the monocarbonyl ion loses both CO and  $H_2$  (possibly as formaldehyde HCHO) to give the  $\pi$ -cyclopropenyl ion  $C_3H_3MoC_5H_5^+$  ( $m/e$  200). Ions containing  $\pi$ -cyclopropenyl ligands thus appear to be especially favored in mass spectra since they not only arise by expulsion of acetylene from carbonyl-free  $\pi$ -cyclopentadienylmetal ions but also by expulsion of hydrogen from carbonyl-free  $\pi$ -allylmetal ions. In the case of the mass spectrum of  $C_3H_5Mo(CO)_2C_5H_5$ , this  $C_3H_3MoC_5H_5^+$  ( $m/e$  200) ion is by far the most abundant and has been selected as the base peak.

Further fragmentation of the ion  $C_3H_3MoC_5H_5^+$  appears to involve losses of acetylene or similar two-carbon fragments, giving the ions  $C_6H_6Mo^+$  ( $m/e$  174),

$C_4H_3Mo^+$  ( $m/e$  147), and  $C_2H_2Mo^+$  ( $m/e$  122). The ion  $C_5H_5Mo^+$  ( $m/e$  161) is also observed and appears to lose successively acetylene fragments, first giving  $C_3H_3Mo^+$  ( $m/e$  135) and then  $CHMo^+$  ( $m/e$  109). Also present in the mass spectrum of  $C_3H_5Mo(CO)_2C_5H_5$  are the dipositive ions  $C_3H_5MoCOC_5H_5^{2+}$  ( $m/e$  115),  $C_3H_3MoC_5H_5^{2+}$  ( $m/e$  100), and  $C_5H_5Mo^{2+}$  ( $m/e$  80.5). Metal-free hydrocarbon ion fragments are observed containing five, four, and three carbon atoms.

**F. Miscellaneous Cyclopentadienylmetal Carbonyl Derivatives.** 1.  $C_5H_5V(CO)_4$  (Table XI). The mass spectrum of  $C_5H_5V(CO)_4$  has already been reported by Winters and Kiser.<sup>3</sup> Table XI compares the mass spectrum of  $C_5H_5V(CO)_4$  observed in this work with the A.E.I. MS-9 mass spectrometer with that observed by Winters and Kiser<sup>3</sup> on their Bendix Model 12-100 linear time-of-flight mass spectrometer. This provides a good test of the general comparability of our mass spectra with those reported by Winters and Kiser.

The relative intensities of the ions  $C_5H_5V(CO)_n^+$  ( $n = 0-4$ ) observed in the present work and in the work of Winters and Kiser<sup>3</sup> are quite similar. The presently reported mass spectrum of  $C_5H_5V(CO)_4$ , unlike that of Winters and Kiser,<sup>3</sup> exhibits a strong ion at  $m/e$  181 corresponding to  $(C_5H_5)_2V^+$  and a weak ion at  $m/e$  155 corresponding to  $C_5H_5VC_3H_3^+$  formed by loss of acetylene from  $(C_5H_5)_2V^+$ . These ions probably arise from formation of some  $(C_5H_5)_2V$  (vanadocene) by pyrolysis of some of the  $C_5H_5V(CO)_4$  on the probe of the mass spectrometer. The doubly charged ion  $C_5H_5V^{2+}$  ( $m/e$  58) was also noted in the present work.

The metastable peaks in the mass spectrum of  $C_5H_5V(CO)_4$  are now reported for the first time. The metastable ions at  $m/e$  175.2, 147.9, 120.5, and 93.3 correspond to the stepwise loss of the four carbonyl groups from the  $C_5H_5V(CO)_4^+$  ion giving ultimately  $C_5H_5V^+$ . The metastable ions at  $m/e$  132.6 and 69.8 correspond to the loss of acetylene fragments from the ions  $(C_5H_5)_2V^+$  and  $C_5H_5V^+$ , respectively. The metastable ion at  $m/e$  74.2 corresponds to loss of one cyclopentadienyl ring from the ion  $(C_5H_5)_2V^+$ .

The mass spectrum of  $C_5H_5V(CO)_4$  described here appears to possess features similar to those involving the  $\pi$ -cyclopentadienyl and carbonyl ligands in the tris(dimethylamino)phosphine complex  $C_5H_5V(CO)_3P-[N(CH_3)_2]_3$  discussed in the first paper of this series.<sup>1</sup>

2.  $C_5H_5Re(CO)_3$  (Table XII). This table compares the mass spectrum of  $C_5H_5Re(CO)_3$  with that of its manganese analog reported by Winters and Kiser.<sup>3</sup> Both compounds exhibit the expected stepwise loss of carbonyl groups in their mass spectra. However, in the case of the manganese compound, the only ion between  $C_5H_5Mn^+$  and  $Mn^+$  in the mass spectrum is the  $C_3H_3Mn^+$  ion, and even this ion is very weak. By contrast, ions intermediate between  $C_5H_5Re^+$  and  $Re^+$  in the mass spectrum of  $C_5H_5Re(CO)_3$  are varied and reasonably intense including  $C_5H_3Re^+$ ,  $C_3H_3Re^+$ ,  $C_3HRe^+$ ,  $C_2HRe^+$ , and  $CR^+$ .

The presence of significant quantities of ions containing a metal atom and one to three carbon atoms in the fragmentation of  $C_5H_5Re^+$  is probably a consequence of the much greater strength of bonds from carbon to the heavy third-row (5d) transition metal rhenium as compared with the lighter first-row (3d) transition metal manganese. This phenomenon is

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.<sup>25</sup> 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<sup>1</sup>

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**Abstract:** The mass spectra of the compounds  $[CH_3SFe(CO)_3]_2$  (two isomers),  $C_7H_8Fe_2(CO)_4(SCH_3)_2$ ,  $C_2H_4S_2Fe_2(CO)_6$ ,  $C_2F_4S_2Fe_2(CO)_6$ ,  $C_7H_8S_2Fe_2(CO)_6$ ,  $CH_3SCH_2Mo(CO)_2C_5H_5$ ,  $CH_3SCH_2Mn(CO)_4$ ,  $CH_3SCH_2CH_2COMn(CO)_4$ ,  $[CH_3SFeCOC_5H_5]_2$ ,  $CH_3SFe(CO)_2C_5H_5$ ,  $C_6H_5COSFe(CO)_2C_5H_5$ , 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<sup>3</sup> have included a few organometallic compounds with bridging RS groups in a recent mass spectral study. A recent preparative paper<sup>4</sup> 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  $\pi-CH_3SCH_2$  complexes,<sup>5</sup>  $[RSFe(CO)_3]_2$  complexes and closely related compounds,<sup>6</sup> several different types of organosulfur de-

derivatives of cyclopentadienyliron carbonyls,<sup>7</sup> and a 2,5-dithiahexane derivative of a metal carbonyl.<sup>8</sup>

### 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

(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).