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FRAGMENTATION OF SYMMETRICALLY SUBSTITUTED METHYLFERROCENES UNDER ELECTRON IMPACT

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Summary

Mass spectra of a series of individual methylferrocenes $(Me_nC_5H_{5-n})_2Fe$ (where $n = 1—5$) are reported. The manner of fragmentation of these compounds is discussed.

Monoisotopic mass spectra of individual compounds of the $(Me_nC_5H_{5-n})_2Fe$ series are given in Tables 1—5 and illustrated in Figs. 1—3 *. The spectra display features characteristic of all alkylferrocenes, i.e., largest intensity for the molecular ion, the presence of $M - H$ and $M - H_2$ ions, a group of doubly charged ions corresponding to the group of ions situated in the vicinity of M, etc. Of interest, the M^{2+} ion has largest intensity after the molecular ion in the spectrum of decamethylferrocene, and the process shown in eq. 1, confirmed by metastable transition, is observed.

$$M^{2+} \xrightarrow[*_{148.5}]{} (M - CH_3)^{2+} + CH_3 \qquad (1)$$

The consecutive accumulation of methyl groups results in an appreciable increase in the summary current of fragment ions in the spectra of moderately substituted members of the series, i.e., 1,1′,3,3′-tetramethylferrocene and 1,1′,2,2′,4,4′-hexamethylferrocene (the maximum, see Fig. 4 and Table 6). The latter also gives extreme values in other physico-chemical investigations of this series. For instance, in its ^{13}C NMR spectra the signal of its C(Cp) atoms exhibits maximum shift towards low field and in it IR absorption spectrum this compound has the highest number of bands [2]. The degree of fragmentation also depends on the symmetry of the molecule. It is expected that the

(Continued on p. 304)

* In Tables 1—5 all peaks of intensity greater than 0.3% are given, the intensity of the molecular ion (M) being regarded as 100%. The data for 1,1′-dimethylferrocene and ferrocene are the same as in ref. 1; ferrocene is included as the parent compound.

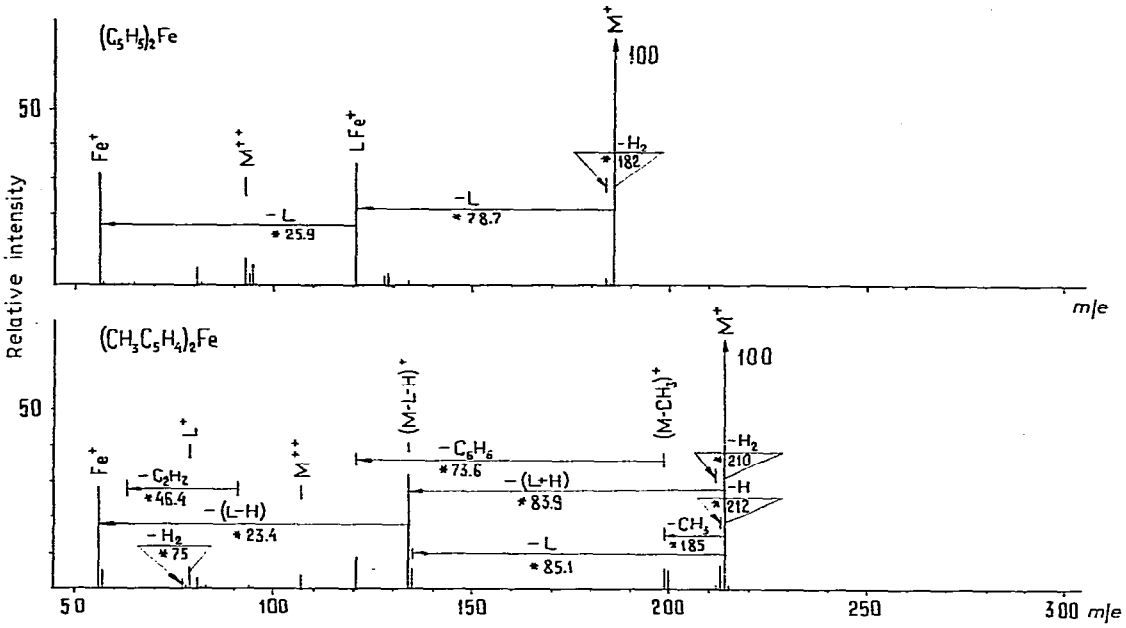

Fig. 1. Mass spectra of ferrocene and 1,1′-dimethylferrocene.

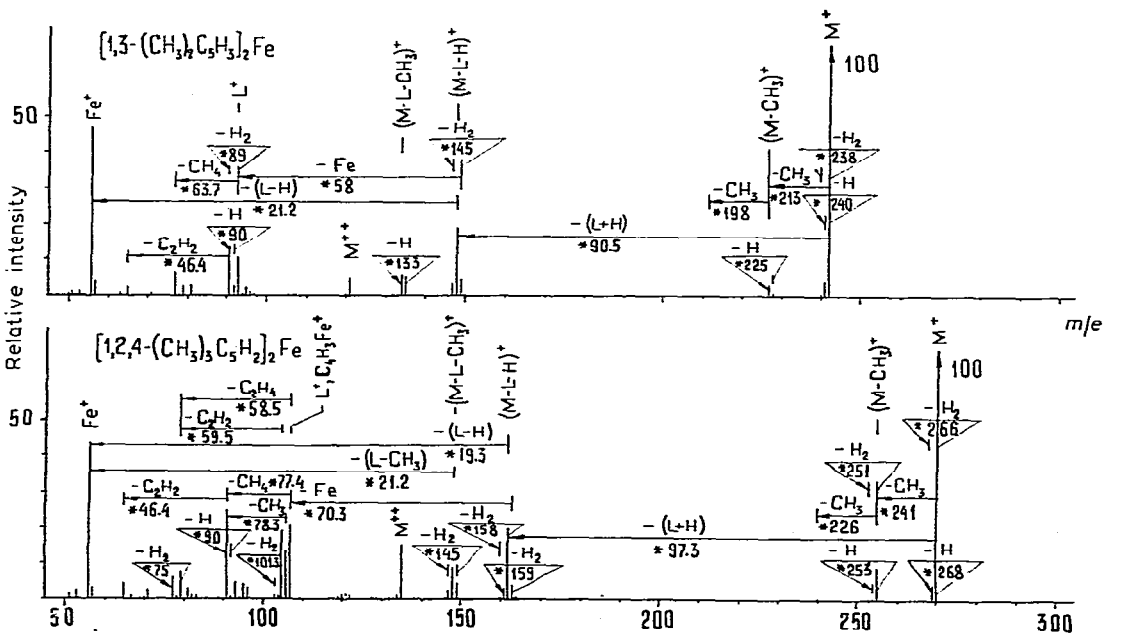

Fig. 2. Mass spectra of 1,1′,3,3′-tetramethylferrocene and 1,1′,2,2′,4,4′-hexamethylferrocene.

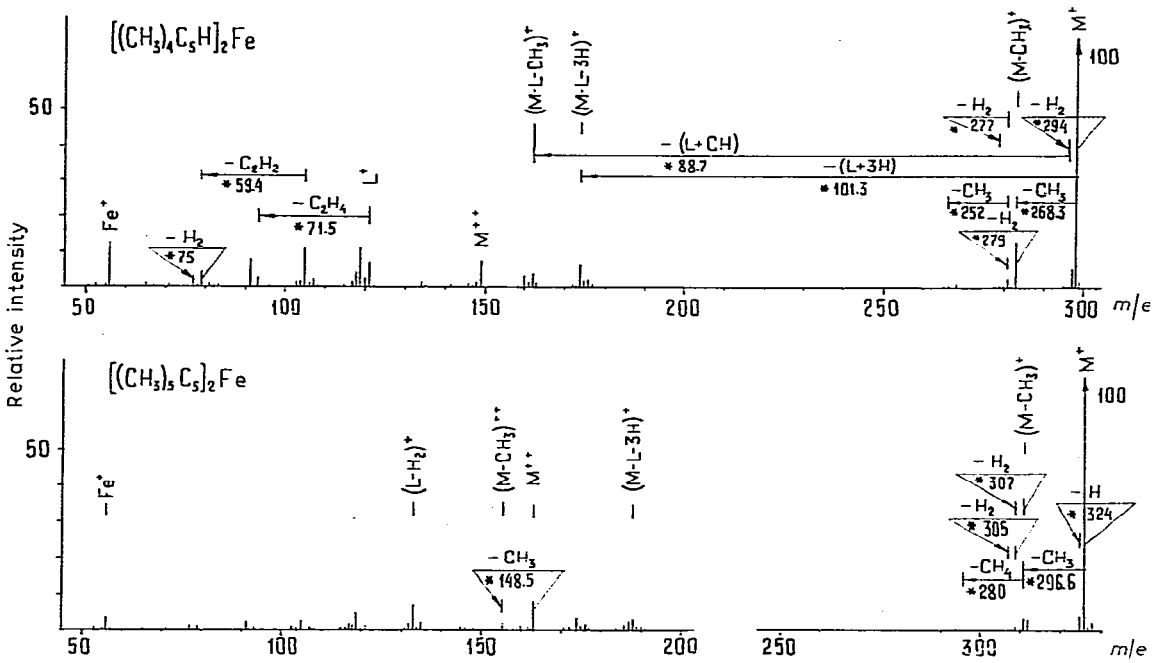

Fig. 3. Mass spectra of octa- and deca-methylferrocene.

TABLE 1. MASS SPECTRA OF FERROCENE AND 1,1′-DIMETHYLFERROCENE

$(C_5H_5)_2Fe$ [a]			$(CH_3C_5H_4)_2Fe$ [b]		
m/e	Ion	*I*	*m/e*	Ion	*I*
89	$C_3H_3^+$	3.9	39	$C_3H_3^+$	1.6
56	Fe^+	31.6	56	Fe^+	28.4
57	FeH^+	0.92	57	FeH^+	5.0
63	$C_5H_3^+$	0.49			
65	$C_5H_5^+$	0.74	77	$C_6H_5^+$	2.8
66	$C_5H_6^+$	0.43	78	$C_6H_6^+$	1.2
81	C_2HFe^+	4.90	79	$C_6H_7^+(L^+)$	6.2
82	$C_2H_2Fe^+$	0.90	81	C_2HFe^+	3.0
93	M^{2+}	7.40	82	$C_2H_2Fe^+$	0.85
94	$C_3H_2Fe^+$	3.90	83	$C_2H_3Fe^+$	1.00
95	$C_3H_3Fe^+$	5.50	91	$C_7H_7^+$	0.36
121	$C_5H_5Fe^+$	34.60	94	$C_3H_2Fe^+$	1.09
122	$C_5H_6Fe^+$	0.30	107	M^{2+}	3.54
128	$C_{10}H_8^+$	2.60	121	$C_5H_5Fe^+$	8.6
129	$C_{10}H_9^+$	3.40	122	$C_5H_5FeH^+$	0.3
134	$C_6H_6Fe^+$	1.19	134	$C_6H_6Fe^+$	31.6
184	$(M-H_2)^+$	1.84	135	$C_6H_7Fe^+(LFe^+)$	5.68
185	$(M-H)^+$	0.58	199	$(M-CH_3)^+$	5.60
186	M^+	100.00	200	$(M-CH_2)^+$	5.40
187	$(M+H)^+$	0.60	212	$(M-H_2)^+$	1.11
			213	$(M-H)^+$	6.47
			214	M^+	100
			215	$(M+H)^+$	1.5

[a] The following metastables are observed: 182.0, $M^+ \rightarrow (M-H_2)^+ + H_2$; 78.7, $M^+ \rightarrow C_5H_5Fe^+ + C_5H_5$; 25.9, $C_5H_5Fe^+ \rightarrow Fe^+ + C_5H_5$. [b] The following metastables are observed: 212, $M^+ \rightarrow (M-H)^+ + H$; 210, $M^+ \rightarrow (M-H_2)^+ + H_2$; ~185, $M^+ \rightarrow (M-CH_3)^+ + CH_3$; 85.1, $M^+ \rightarrow (M-L)^+ + L$; 83.8, $M^+ \rightarrow (M-L-H)^+ + (L+H)$; 75, $C_6H_6^+ \rightarrow C_6H_5^+ + H$; 73.5, $(M-CH_3)^+ \rightarrow C_5H_5Fe^+ + C_6H_6$; 46.6, $C_7H_7^+ \rightarrow C_5H_5^+ + C_2H_2$; 23.4, $(M-L-H)^+ \rightarrow Fe^+ + C_6H_6$.

TABLE 2

MASS SPECTRUM OF 1,1',3,3'-TETRAMETHYLFERROCENE [a]

m/e	Ion	I	m/e	Ion	I
39	$C_3H_3^+$	3.07	97	$C_7H_{13}^+(C_5H_7Me_2^+)$	0.87
41	$C_3H_5^+$	1.57	120	$(M - H_2)^{2+}$	0.90
50	$C_4H_2^+$	0.87	121	M^{2+}	4.80
51	$C_4H_3^+$	1.26	122	$C_5H_6Fe^+$	0.49
52	$C_4H_4^+$	0.55	132	$CH_3C_5HFe^+$	0.33
53	$C_4H_5^+$	1.26	133	$CH_3C_5H_2Fe^+$	0.76
56	Fe^+	46.93	134	$CH_3C_5H_3Fe^+$	5.71
57	FeH^+	4.49	135	$CH_3C_5H_4Fe^+$	5.58
63	$C_5H_3^+$	0.47	147	$(CH_3)_2C_5HFe^+$	2.86
65	$C_5H_5^+$	2.68	148	$(CH_3)_2C_5H_2Fe^+$	18.71
71	CH_3Fe^+	1.23		$(M - L - H)$	
77	$C_6H_5^+$	6.38	149	$(CH_3)_2C_5H_3Fe^+$	4.62
78	$C_6H_6^+$	0.87	212	$(CH_3C_5H_3)_2Fe^+$	0.66
79	$C_6H_7^+(C_5H_4CH_3^+)$	2.83		$(M - 2CH_3)^+$	
81	C_2HFe^+	3.31	213	$(M - CH_3 - CH_2)^+$	0.31
82	$C_2H_2Fe^+$	0.74	214	$(M - 2CH_2)^+$	0.32
83	$C_2H_3Fe^+$	0.74	226	$(M - CH_3 - H)^+$	0.81
91	$C_7H_7^+(L - H_2)$	13.34	227	$(M - CH_3)^+$	3.65
92	$C_7H_8^+$	3.11	228	$(M - CH_2)^+$	1.02
93	$C_7H_9^+(L)$	10.46	239	$(M - 3H)^+$	0.35
94	$C_3H_2Fe^+$	1.14	240	$(M - H_2)^+$	0.47
94	$C_7H_{10}^+(LH)$	0.36	241	$(M - H)^+$	3.94
95	$C_3H_3Fe^+$	2.91	242	M^+	100.00
96	$C_3H_4Fe^+$	1.06			
96	$C_7H_{12}^+(LH_3)$	1.59			

[a] The following metastables are observed: 240, $M \rightarrow M - H$; 238, $M \rightarrow M - H_2$; 225, $M - CH_2 \rightarrow M - CH_3$; 213, $M \rightarrow M - CH_3$; 198, $M - CH_3 \rightarrow M - 2CH_3$; 145, $M - L \rightarrow M - L - H_2$; 133, $M - L - CH_2 \rightarrow M - L - CH_3$; 90, $C_7H_8^+ \rightarrow C_7H_7^+$; 89, $C_7H_9^+ \rightarrow C_7H_7^+(L \rightarrow L - H_2)$; 63.7, $L \rightarrow C_6H_5^+ + CH_4$; 58, $M - L \rightarrow L$; 46.4, $C_7H_7^+ \rightarrow C_5H_5^+ + C_2H_2$; 21.2, $M - L - H \rightarrow Fe^+$.

more asymmetric the ring substitution, the higher the influence of vibrations such as ring tilting or perpendicular ring distortion [3] on fragmentation of the molecular ion.

In contrast to the consecutive elimination of C_5H_5 ligands in ferrocene, frag-

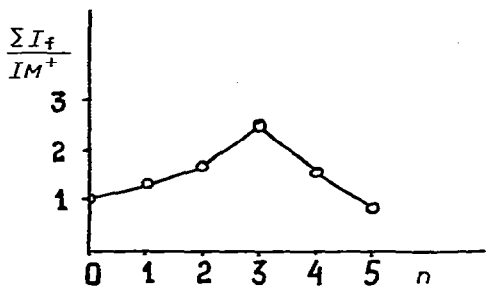

Fig. 4. The ratio of summary fragment ions current to the molecular ion current in the methylferrocene series $(Me_nCp)_2Fe$ (n = 1—5).

TABLE 3

MASS SPECTRUM OF 1,1',2,2',4,4'-HEXAMETHYLFERROCENE [a]

m/e	Ion	I	m/e	Ion	I
39	$C_3H_3^+$	4.61	107	L^+	20.81
41	$C_3H_5^+$	4.37	109	$C_4H_5Fe^+$	0.44
51	$C_4H_3^+$	1.43	119	$C_5H_3Fe^+$	0.40
53	$C_4H_5^+$	2.10	120	$C_5H_4Fe^+$	1.12
56	Fe^+	43.46	121	$C_5H_5Fe^+$	1.64
57	FeH^+	3.12	122	$C_5H_6Fe^+$	1.01
63	$C_5H_3^+$	0.60	127.5	$(M - CH_3)^{2+}$	~0.20
65	$C_5H_5^+$	4.60	132	$(M - L - 2CH_3 - H)^+$	0.45
67	$C_5H_7^+$	1.06	133	$(M - L - 2CH_3)^+$	0.34
69	$CHFe^+$	0.36	134	$(M - L - CH_2 - CH_3)^+$	1.67
70	CH_2Fe^+	0.43	135	M^{2+}	15.17
71	CH_3Fe^+	2.45	146	$(M - L - CH_3 - H_2)^+$	0.53
77	$C_6H_5^+$	5.40	147	$(M - L - CH_3 - H)^+$	2.50
78	$C_6H_6^+$	0.89	148	$(M - L - CH_3)^+$	8.80
79	$C_6H_7^+(C_5H_4CH_3)^+$	7.64	149	$(M - L - CH_2)^+$	4.26
81	C_2HFe^+	2.62	158	$(M - L - 5H)^+$	0.33
82	$C_2H_2Fe^+$	1.43	160	$(M - L - 3H)^+$	0.85
83	$C_2H_3Fe^+$	0.94	161	$(M - L - H_2)^+$	3.36
89	$C_7H_5^+$	0.39	162	$(M - L - H)^+$	20.00
91	$C_7H_7^+$	25.26	163	$(M - L)^+$	3.89
92	$C_7H_8^+(L - CH_3)$	1.43	240	$(M - 2CH_3)^+$	1.32
93	$C_7H_9^+$	4.36	241	$(M - CH_3 - CH_2)^+$	0.47
94	$C_3H_2Fe^+$	0.98	242	$(M - 2CH_2)^+$	0.39
95	$C_3H_3Fe^+$	3.98	253	$(M - CH_3 - H_2)^+$	0.82
96	$C_3H_4Fe^+$	3.11	254	$(M - CH_3 - H)^+$	1.05
103	$(L - 2H_2)^+$	1.57	255	$(M - CH_3)^+$	9.83
104	$(L - 3H)^+$	0.57	267	$(M - 3H)^+$	0.40
105	$(L - H_2)^+$	19.52	268	$(M - H_2)^+$	1.29
106	$(L - H)^+$	13.37	269	$(M - H)^+$	4.34
107	$C_4H_3Fe^+$	15.33	270	M^+	100.00

[a] The following metastables are observed: 268, $M \rightarrow M - H$; 266, $M \rightarrow M - H_2$; 253, $M - CH_3 \rightarrow M - CH_3 - H$; 251, $M - CH_3 \rightarrow M - CH_3 - H_2$; 241, $M \rightarrow M - CH_3$; ~226, $M - CH_3 \rightarrow M - 2CH_3$; 159, $M - L \rightarrow M - L - H_2$; 158, $M - L - H \rightarrow M - L - 3H$; 145, $M - L - CH_2 \rightarrow M - L - CH_4$; 101, $L - H_2 \rightarrow L - 2H_2$; ~97, $M \rightarrow (LFe{-}H)^+ + (L + H)$; 90, $C_7H_8^+ \rightarrow C_7H_7^+$; 78.3, $L - H \rightarrow C_7H_7^+ + CH_3$; ~77.5, $L \rightarrow C_7H_7^+ + CH_4$; 75, $C_5H_4CH_3^+ \rightarrow C_5H_4CH^+$; ~70, $LFe \rightarrow L$; 59.5, $L - H_2 \rightarrow C_5H_4CH_3^+ + C_2H_2$; 58.5, $L \rightarrow C_5H_4CH_3^+ + C_2H_4$; 46.4, $C_7H_7^+ \rightarrow C_5H_5^+ + C_2H_2$; 23.4, $C_5H_5^+ \rightarrow C_3H_3^+ + C_2H_2$; 21.2, $(L - CH_3)Fe^+ \rightarrow Fe^+ + (L - CH_3)$; 19.3, $(L - H)Fe^+ \rightarrow Fe^+ + (L - H)$.

mentation of methylferrocene $(Me_nCp)_2Fe$ (n = 1—3) occurs mainly by elimination of neutral fragments, corresponding to the initial methylcyclopentadienes (L + H) and then to methylfulvenes (L — H). The more methylated, symmetrical octa- and decamethyl-ferrocenes eliminate fragments corresponding to methylcyclopentenes and tetramethylbenzene, the product of methine (CH) incorporation into the tetramethylcyclopentadienyl ligand. All these processes may result only from rearrangements involving the transfer of C and H atoms from one ligand to another. The fact that all of them are confirmed by metastable transitions shows that they involve low-lying excited doublet states with long lifetimes [4], another indication of the stabilizing effect of electron-donor methyl groups on molecular ions of polymethylferrocenes.

TABLE 4

MASS SPECTRUM OF *sym*-OCTAMETHYLFERROCENE [a]

m/e	Ion	*I*	*m/e*	Ion	*I*
39	$C_3H_3^+$	1.26	121	C_5H_5Fe	0.54
41	C_3H_5	4.33	121	*L*, $C_5H(CH_3)_4$	6.85
43	C_3H_7	0.86	122	C_5H_6Fe	0.34
51	C_4H_3	0.45	134	$CH_2C_5H_4Fe$	1.63
53	C_4H_5	1.11	135	$CH_3C_5H_4Fe$	0.37
55	C_4H_7	0.87	141.5	$(M - CH_3)^{2+}$	0.56
56	Fe	12.41	146	$(CH_3)_2C_5H_3Fe—3H$	0.80
57	FeH	0.95	147	$(CH_3)_2C_5H_3Fe - 2H$	0.34
65	C_5H_5	1.21	148	$(M - H_2)^{2+}$	1.66
67	C_5H_7	0.49	149	M^{2+}	7.20
71	CH_3Fe	1.17	158	$(M - L - CH_3 - 2H_2)^+$	0.52
77	C_6H_5	3.75	160	$(M - L - CH_3 - H_2)^+$	3.47
78	C_6H_6	0.68	161	$(M - L - CH_3 - H)^+$	1.54
79	$C_5H_4CH_3$	4.21	162	$(M - L - CH_3)$	3.73
81	C_2HFe	0.71	163	$(M - L - CH_2)$	1.07
82	C_2H_2Fe	0.55	172	$(M - L - 5H)$	0.74
83	C_2H_3Fe	0.61	174	$(M - L - 3H)$	6.21
91	C_7H_7	7.66	175	$(M - L - H_2)$	1.92
93	$C_7H_9(L - 2CH_2)$	2.61	176	$(M - L - H)$	2.79
96	C_3H_4Fe	0.88	177	$(M - L)$	1.31
103	$L - CH_2 - 2H_2$	1.56	266	$(M - 2CH_3 - H_2)$	0.82
104	$L - CH_2 - 3H$	1.36	268	$(M - 2CH_3)$	0.77
105	$L - CH_2 - H_2$	10.79	279	$(M - CH_3 - 2H_2)$	0.65
106	$L - CH_3$	1.39	280	$(M - CH_3 - 3H)$	0.60
107	$L - CH_2$	2.38	281	$(M - CH_3 - H_2)$	2.76
108	C_4H_4Fe	0.62	282	$(M - CH_3 - H)$	0.60
109	C_4H_5Fe	0.31	283	$(M - CH_3)$	13.15
115	$L - 3H_2$	0.82	285	$(M - CH)$	0.35
116	$L - 5H$	0.36	293	$(M - 5H)$	0.34
117	$L - 2H_2$	1.48	295	$(M - 3H)$	0.47
118	$L - 3H$	4.25	296	$(M - H_2)$	0.76
119	$L - H_2$	11.00	297	$(M - H)$	5.83
120	C_5H_4Fe	0.34	298	M	100.00
120	$L - H$	2.29	299	$(M + H)$	1.77

[a] The following metastables are observed: 294, $M \rightarrow M - H_2$; 279, $M - CH_3 \rightarrow M - CH_3 - H_2$; 277, $M - CH_3 - H_2 \rightarrow M - CH_3 - 2H_2$; ~268.5, $M \rightarrow M - CH_3$; ~252.5, $M - CH_3 - H_2 \rightarrow M - 2CH_3 - H_2$; ~101, $M \rightarrow (M - L - 3H)^+ + (L + 3H)$; ~89, $M - H_2 \rightarrow (M - L - CH_3)^+ + (L + CH)$; 75, $(C_5H_4CH_3)^+ \rightarrow C_6H_5^+$; 71.5, $L \rightarrow (CH_3)_2C_5H_3^+ + C_2H_4$; 59.5, $(L - CH_3 - H)^+ \rightarrow (C_5H_4CH_3)^+ + C_2H_2$.

Among the ions corresponding to the ligand *L*, the spectra contain L^+, $(L - H)^+$, $(L - 2H)^+$, etc.; the following series results from elimination of *n* CH_2 groups from these ions ($n = 1—4$). In the mass spectra of tetramethyl- and more methylated ferrocenes the $C_7H_7^+$ ion, *m/e* 91, is one of the most intensive hydrocarbon ions. In the spectra of hexa-, octa- and deca-methylferrocene its intensity is proportional to that of $(M - LH_m)^+$ ions ($m = 1, 3$) and Fe^+ (see Table 7).

The mass spectra were recorded on a Varian-MAT CH-8 spectrometer with the ionization potential 70 eV and the ion source temperature 150°C. The purity of the compounds was confirmed by GLC and by elemental analysis. The compounds were obtained as usual.

TABLE 5

MASS-SPECTRUM OF DECAMETHYLFERROCENE [a]

m/e	Ion	*I*	*m/e*	Ion	*I*
41	C_3H_5	2.16	135	*L*	1.14
43	C_3H_7	0.44	145	$(CH_3)CH_2C_5Fe$	0.51
53	C_4H_5	0.86	146	$(CH_3)_2C_5HFe$	0.53
55	C_4H_7	0.17	148	$(CH_3)_2C_5H_2Fe$	0.55
56	Fe	3.58	155.5	$(M - CH_3)^{2+}$	1.40
57	FeH	0.32	160	$(M - L - 2CH_3 - H)$	1.10
65	C_5H_5	0.45	162	$(M - H_2)^{2+}$	0.71
71	CH_3Fe	0.42	162.5	$(M - H)^{2+}$	0.31
77	C_6H_5	1.17	163	M^{2+}	7.99
79	$C_5H_4CH_3$	1.02	172	$(M - L - CH_3 - 2H_2)$	0.35
81	C_2HFe	0.31	174	$(M - L - CH_3 - H_2)$	3.24
91	C_7H_7	2.58	175	$(M - L - CH_3 - H)$	0.66
93	$(L - 3CH_2)$	0.77	176	$(M - L - CH_3)$	1.28
95	C_3H_3Fe	0.35	177	$(M - L - CH_2)$	0.37
95	$(L - 3CH_2 + H_2)$	0.43	184	$(M - L - 7H)$	0.30
103	$(L - 2CH_3 - H_2)$	0.52	186	$(M - L - 5H)$	1.17
104	$(L - 2CH_3 - H)$	0.31	188	$(M - L - 3H)$	2.73
105	$(L - 2CH_3)$	2.52	189	$(M - L - H_2)$	0.85
107	$(L - 2CH_2)$	0.59	190	$(M - L - H)$	0.90
108	C_4H_4Fe	0.32	191	$(M - L)$	0.46
115	$(L - CH_2 - 3H_2)$	0.63	294	$(M - 2CH_3 - H_2)$	0.46
116	$(L - CH_2 - 5H)$	0.46	296	$(M - 2CH_3)$	0.60
117	$(L - CH_2 - 2H_2)$	1.43	307	$(M - CH_3 - 2H_2)$	0.85
118	$(L - CH_2 - 3H)$	1.30	308	$(M - CH_3 - 3H)$	0.41
119	$(L - CH_2 - H_2)$	4.94	309	$(M - CH_3 - H_2)$	0.84
120	$(L - CH_3)$	0.54	310	$(M - CH_3 - H)$	0.48
121	$(L - CH_2)$	1.08	311	$(M - CH_3)$	3.44
131	$(L - 2H_2)$	0.38	312	$(M - CH_2)$	3.01
132	$(L - 3H)$	1.79	321	$(M - 5H)$	0.59
133	$(L - H_2)$	7.12	325	$(M - H)$	4.33
134	$CH_2C_5H_4Fe$	0.56	326	*M*	100.00
134	$(L - H)$	0.57	327	$(M + H)$	1.29
135	$CH_3C_5H_4Fe$	2.04	328	$(M + H_2)$	2.73

[a] The following metastables are observed: 324, $M \rightarrow M - H$; 307, $M - CH_3 \rightarrow M - CH_3 - H_2$; 305, $M - CH_3 - H_2 \rightarrow M - CH_3 - 2H_2$; 296.6, $M \rightarrow M - CH_3$; ~280, $M - CH_3 \approx (M - 2CH_3 - H)^+ + CH_4$; 148, 5, $M^{2+} \rightarrow (M - CH_3)^{2+}$.

TABLE 6

THE RATIO OF SUMMARY FRAGMENT IONS CURRENT TO THE MOLECULAR ION CURRENT IN THE $(Me_nCp)_2Fe$ SERIES

n	0	1	2	3	4	5
$\Sigma I_f/I_M$	1.05	1.30	1.65	2.60	1.55	0.9

TABLE 7

THE RATIO BETWEEN INTENSITIES OF Fe^+(A), $C_7H_7^+$(B) AND $(M - LH_m)^+$ (C) IONS IN MASS SPECTRA OF $(1,2,4\text{-}Me_3Cp)_2Fe$, $(Me_4Cp)_2Fe$ AND $(Me_5Cp)_2Fe$

Compound	A	B	C	B/A	B/C	B'(A + C)
$(1,2,4\text{-}Me_3Cp)_2Fe$	43.5	25.5	20.0	0.58	1.37	0.40
$(Me_4Cp)_2Fe$	12.0	7.0	6.5	0.58	1.07	0.38
$(Me_5Cp)_2Fe$	4.0	2.5	3.0	0.62	0.83	0.37

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