*Journal of Organometallic Chemistry*, 184 (1980) 231—236

# THE EFFECT OF THE STRUCTURE OF ALKYLFERROCENES ON THEIR FRAGMENTATION TYPES UPON ELECTRON IMPACT

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(Received June 5th, 1979)

## Summary

The mass spectra of eight alkylferrocenes: 1,1′-dimethyl-, ethyl-, 1,1′-diethyl-, 1,1′-di-n-propyl-, 1,1′-diisopropyl-, 1,1′-di-n-butyl-, 1,1′-di-t-butylferrocene and tetra-t-butylferrocene, are reported in detail. General and specific fragmentations of these compounds are discussed.

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In the mass-spectra of the alkylferrocenes investigated (see Fig. 1—5 in which mass spectra are shown in monoisotopic form, and also that of ferrocene as the parent compound) the molecular ions show the highest intensity, their relative intensity taken to be 100%. The fragmentation begins with loss of a hydrogen atom and a hydrogen molecule. This pattern is known to be typical for $\pi$-bonded cyclopentadienylmetals [1] with hydrocarbons behaving analogously [2]. Such initial fragmentations are typical since subsequent processes of C—C cleavage, which are traced by metastable peaks, sometimes occur from $[M - \text{H}]^+$ or $[M - \text{H}_2]^+$ (see for example Fig. 3, 4). Fragmentation schemes for $Cp_2Fe$ and its homologues, methyl- and 1,1′-dimethyl-ferrocene, have been considered in detail [3—5]. In the mass spectra of heteroannular polyalkylferrocenes the fragment ion $[C_5H_5Fe]^+$, which is the most characteristic for ferrocene and its derivatives $[C_3H_3Fe]^+$, $[C_3H_2Fe]^+$ and $[C_2H_2Fe]^+$, occurred by rearrangement or fragmentation of ions as a result of processes as shown in eq. 1—3.

$$[\text{Fe}(\text{C}_5\text{H}_4\text{R})_2]^+ \xrightarrow{-(\text{R}-\text{H})} [\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{R})]^+ \xrightarrow{-(\text{R}-\text{H})} [\text{Fe}(\text{C}_5\text{H}_5)_2]^+ \qquad (1)$$

$$[\text{Fe}(\text{C}_5\text{H}_4\text{R})]^+ \xrightarrow{-(\text{R}-\text{H})} [\text{FeC}_5\text{H}_5]^+ \qquad (2)$$

$$[\text{FeC}_5\text{H}_4\text{R}] \xrightarrow{-\text{R}} [\text{FeC}_5\text{H}_4]^+ \qquad (3)$$

It can be seen from Fig. 1—5 that probability of such rearrangements increases

*(Continued on p. 234)*

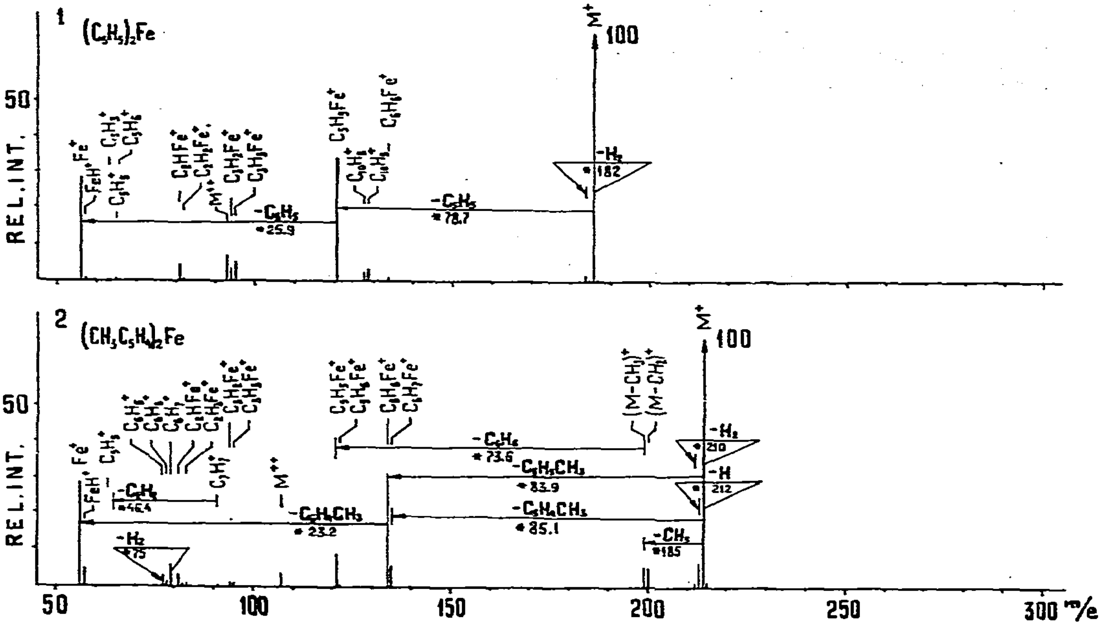


Fig. 1. Mass spectra of ferrocene (1) and 1,1′-dimethylferrocene (2).

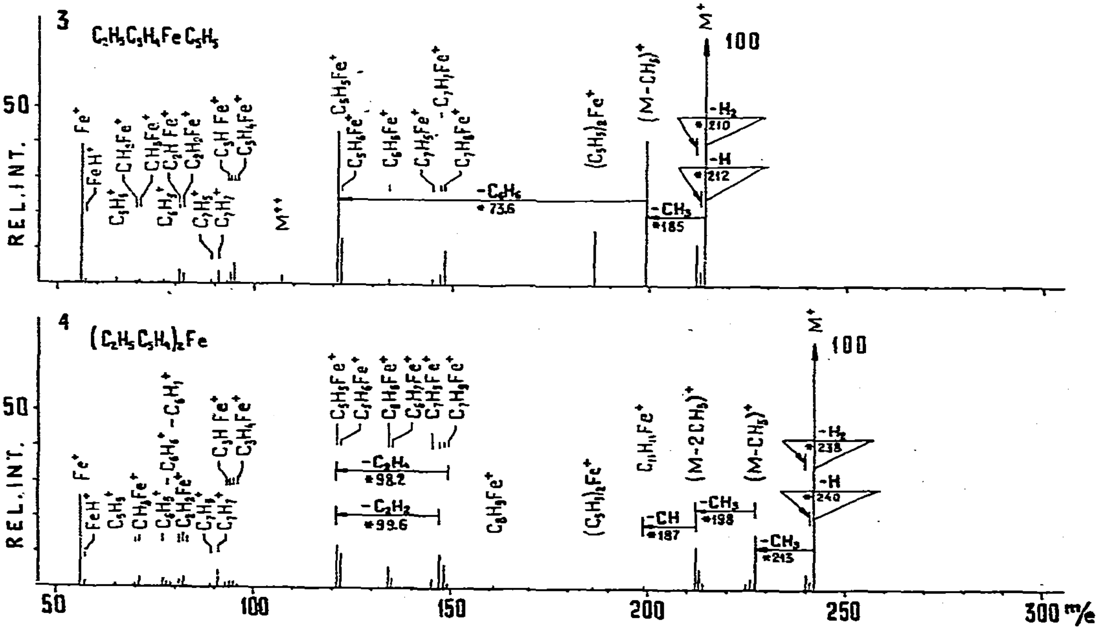


Fig. 2. Mass spectra of ethylferrocene (3) and 1,1′-diethylferrocene (4).

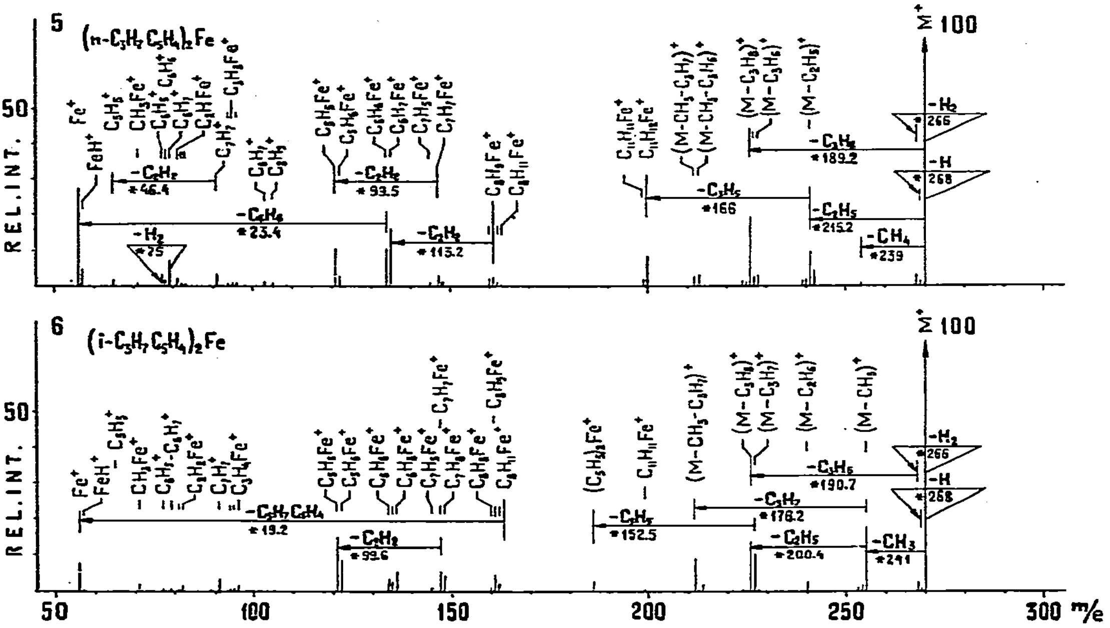


Fig. 3. Mass spectra of 1,1′-di-n-propylferrocene (5) and 1,1′-diisopropylferrocene (6).

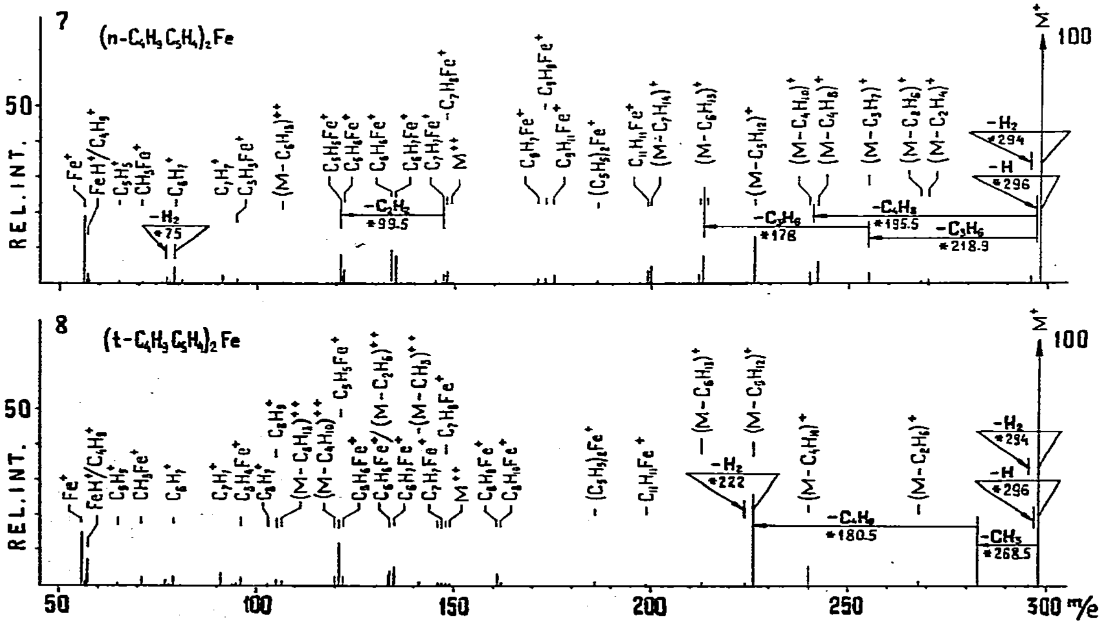


Fig. 4. Mass spectra of 1,1′-di-n-butylferrocene (7) and 1,1′-di-t-butylferrocene (8).

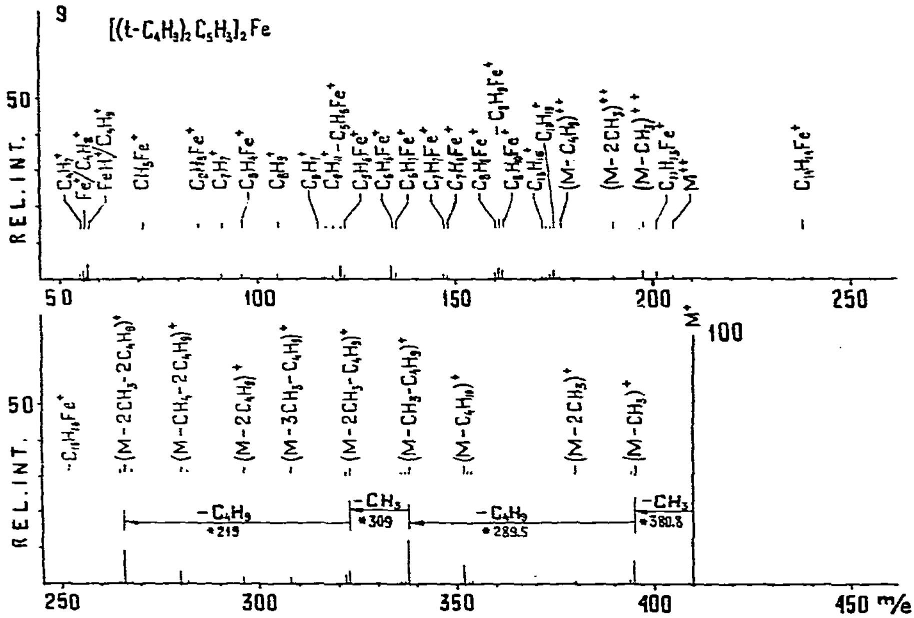


Fig. 5. Mass spectrum of 1,3,1′,3′-tetra-t-butylferrocene (9).

when R contains two or more C atoms because (R — H) then represents a stable particle viz. an olefin molecule.

The ions $[FeC_5H_4CH_3]^+$ (*m/e* 135) and $[FeC_5H_4CH_2]^+$ (*m/e* 134), together with $[C_5H_5Fe]^+$, are characteristic for methyl homologues and for alkylferrocenes which easily form methyl-containing ligands by rearrangements upon the expulsion of some part of the alkyl radical. This is shown, for example by 1′1-di-n-propyl- and 1′1-di-n-butylferrocenes (Fig. 3, 4). For the ion $[FeC_5H_4CH_2]^+$ an analogy suggests itself with the stable ion $[C_5H_5FeC_5H_4CH_2]^+$ commonly occurring in chemical reactions [6—8]. The latter ions or isomeric ions $[M - CH_3]^+$ are also present in the mass spectrum of 1,1′-dimethylferrocene. It should be mentioned, that alkylferrocenes of the latter type have only iron-free ions corresponding to ligands $[C_5H_4CH_3]^+$ to any pronounced extent in their spectra. In other spectra appear ions $[L - H]^+$, $[L - H_2]^+$ and then related ions $[Fe(L - H)]^+$, $[Fe(L - H_2)]^+$.

Other interesting types of stable ions, $[C_7H_7Fe]^+$ (*m/e* 147) and $[C_7H_7]^+$ (*m/e* 91) are generated by alkylferrocenes with two or more C atoms in the chain [5,9,10]. The presence and fragmentation of these ions are evidenced by appropriate metastable peaks, and are observed in the spectra (Fig. 2—4). The ion $[C_7H_7]^+$ and the metastable peak of process 4 appear even in the spectrum

$$[C_7H_7]^+ \rightarrow [C_5H_5]^+ + C_2H_2 \qquad (4)$$

of 1,1′-dimethylferrocene. Since migration of some groups from the side chain to the iron atom has been traced (e.g. ref. 5 and ref. therein), it may be suggested that formation of the ion $m/e$ 91 is due to the following processes (eq. 5—7).

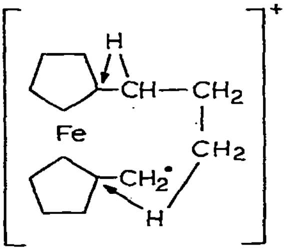
$$\underset{m/e\ 214}{[Fe(C_5H_4CH_3)_2]^+} \rightarrow \underset{m/e\ 148}{(CH_3FeC_5H_4CH)^+} + C_5H_6 \qquad (5)$$

$$[CH_3FeC_5H_4CH]^+ \rightarrow \underset{m/e\ 92}{[C_7H_8]^+} + Fe \qquad (6)$$

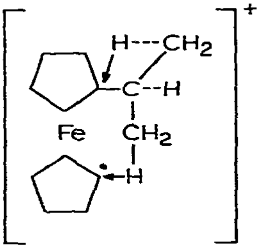
$$[C_7H_8]^+ \rightarrow \underset{m/e\ 91}{[C_7H_7]^+} + H \qquad (7)$$

Because of the high stability of the ferrocene system, the peculiarity of doubly charged ions appeared in practically every spectrum (see Figs. 1, 2, 4 and 5).

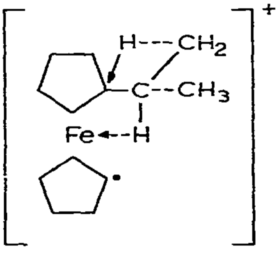
The effect of branching in alkyl radicals on the C—C band cleavage position, on subsequent fragmentation and rearrangements of the iron-containing part of the original molecule has been observed clearly in the substituted homologues with three or more C atoms. In the spectrum of 1,1′-di-n-propylferrocene there are substantial signals in the regions $[M - C_2H_4]^+$, $[M - C_2H_5]^+$ which are not typical for the isopropyl homologue (Fig. 3). The latter, however, has an intensive peak $[M - CH_3]^+$ which is practically absent in the spectrum of the n-propyle isomer. These facts, and also some difference in intensity of the ions $[M - C_3H_7]^+$, and $[M - C_3H_8]^+$, are explained by the difference in structure of the alkyl radicals. Undoubtedly easy loss of propene from $[M - H_2]^+$ from the isopropyl homologue and of propyl from the normal compound have similar explanations. It is noticeable that although the stable allyl radical is extracted from both isomers, their original fragmentation ions are different, being $[C_3H_7C_5H_4FeC_5H_4]^+$ for the iso compound and $[C_3H_7C_5H_4FeC_5H_4CH_2]^+$ for the n-isomer. The rest of the molecule may be stabilized in different ways for both normal and iso compounds as suggested in structures I—III.



(I)



(II)



(III)

As a result the intensity ratio of ions with composition $[FeC_5H_4CH_3]^+$ is 6/1 in favour of the normal homologue. On the contrary, while the intensity of the ion $m/e$ 186 is negligibly small for the normal homologue, it is twenty times more intense in the case of 1′1-diisopropylferrocene. Variations in intensities of $[C_5H_5Fe]^+$, $[C_5H_5FeH]^+$ or $[C_5H_6Fe]^+$ ($m/e$ 122) and $[CH_3C_5H_4FeH]^+$ ($m/e$ 136) are also in accordance with above reasoning.

Similar relations are observed for spectra of 1,1′-di-n-butyl- and 1,1′-di-t-butyl-ferrocenes. Scission of long alkyl chains ($C_3$, $C_4$) is typical for the normal isomer and, once again, loss of the methyl radical begins the skeletal fragmentation of the iso homologue. The absence of hydrogen at the central C-atom of the t-butyl radical eliminates the intensity difference of the ion *m/e* 186, between the two isomers, reduces the intensity ratio of ions *m/e* 122 and *m/e* 121, and diminishes the intensity of ions $[C_7H_7Fe]^+$ and $[C_7H_8Fe]^+$ for the t-butyl isomer. Some enhancement of the ion *m/e* 91 in the t-butyl isomer may be due to fragmentation of ions *m/e* 105—107 with composition $[C_5H_4C_3H_7]^+$, $[C_5H_4C_3H_6]^+$ and $[C_5H_4C_3H_5]^+$. In general the spectrum of the t-butyl compound is poorer than that of the normal isomer.

The trend of losing methyl followed by scission of butyl, which manifested itself in 1,1′-di-t-butylferrocene, is developed in tetra-t-butylferrocene. Two subsequent stages of alkyl radical scission are clearly documented: at the beginning loss of methyl and butyl occurs, then this process is repeated. It is interesting that this compound and the previous one exhibit scission processes for only one half of their t-butyl and methyl groups. For tetra-t-butylferrocene it maybe suggested that the processes proceed in both rings similarly since peak intensities in the region of ions $[Fe(L - C_nH_m)]^+$ are very small. The fragmentation has virtually finished at the stage $[M - 2\ CH_3 - 2\ C_4H_9]^+$.

The fragmentation of alkylferrocenes upon electron impact bears a strong resemblance to the behaviour of alkylaromatic hydrocarbons in the mass spectrometer [2,5] and characterizes once again the stability of these organoiron sandwich complexes.

The mass spectra were recorded on "CH-8 Varian-MAT" apparatus with ionisation voltage of 70 eV and ion source temperature 150°C. Purity of the compounds was ascertained by GLC and NMR methods. The alkylferrocenes were synthesized by known techniques [11].

## References

1 J. Müller, Angew. Chem., 84 (1972) 725.
2 J. Beynon, Mass-spectroscopy and its application in Organic Chemistry, Mir publishers, Moscow, 1964, p. 333.
3 J. Müller and L.D'Or, J. Organometal. Chem., 10 (1967) 313.
4 N.V. Zakurin, S.P. Gubin and V.P. Bochin, J. Organometal. Chem., 23 (1970) 535.
5 I.J. Spilners and J.G. Larson, Org. Mass. Spectr., 3 (1970) 915.
6 M. Cais, Organometal. Chem., Rev., 1 (1966) 435.
7 D.W. Slocum and C.R. Ernst, Organometal. Chem. Rev. A, 6 (1970) 337.
8 M.I. Bruce, Organometal. Chem. Rev. B, 6 (1970) 666.
10 D.T. Roberts, E.F. Little, M.M. Bursey, J. Amer. Chem. Soc., 90 (1968) 973.
11 A.N. Nesmeyanov, Chemistry of Ferrocene, Nauka publishers, Moscow, 1969.