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Fragmentation of (η^5-cyclopropentadienyl)iron carbonyl derivatives of carboranes(12) under electron impact

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Mass spectra of (η^5-cyclopentadienyl)iron dicarbonyl derivatives of carborane(12), $CpFe(CO)_2C_2H_{11}B_{10}$ and $CpFe(CO)_2COC_2H_{11}B_{10}$, were studied. The effect of the carboranyl radical and the fragmentation of the organometallic moiety (decarbonylation and rearrangement with migration of the Cp ring to the carboranyl radical) and that of the organometallic moiety on the dehydrogenation of carborane were observed.

Key words: mass spectrometry, organometallic derivatives of carborane(12).

Earlier we studied the mass spectral behavior of carboranes(12) (Cb)[1] and their organometallic derivatives, $(1\text{-}Cb)C_6H_5Cr(CO)_3$ [2] and [1(9)-Cb]HgX (X = Cb, Hal)[3] (Cb is the $C_2H_{11}B_{10}$ carboranyl radical), and showed that the nature of the substituent and the type of bonding of the carboranyl moiety strongly affect the fragmentation processes of both carboranyl and organometallic moieties. In this work, for the purpose of investigating the effect of the organometallic substituent on the decomposition of carboranes(12) and the effect of the carboranyl ligand on the fragmentation of iron complexes, we studied the mass spectra of π-cyclopentadienylirondicarbonyl complexes with 9-carboranyl- and 9-carboranylcarbonyl ligands (**1—4**).

$C_5H_5Fe(CO)_2Cb$	$C_5H_5Fe(CO)_2COCb$
1: *o*-Cb	**3**: *o*-Cb
2: *m*-Cb	**4**: *m*-Cb

Molecular ion peaks (M^+) are observed only in the mass spectra of complexes **1** and **2**, whereas in the case of acyl derivatives **3** and **4**, the peaks with the highest *m/z* are M^+-CO ions, which are comparable in intensity to M^+ in **1** and **2** (Table 1). The absence of M^+ is characteristic for most $CpFe(CO)_2COR$ complexes, and the M^+-CO ion arises exclusively due to the loss of the terminal CO group.[4] This conclusion is also supported by the mass spectral analysis of ^{13}C-labeled $CpFe(CO)_2{}^{13}COC_4H_3S$ (C_4H_3S is 2-thienyl), where the M^+-nCO ions (n = 1, 2) contain equal amounts of the isotope label, and the labeled carbonyl group is eliminated at the stage of the formation of the $CpFeC_4H_3S^+$ ion.[5] One can propose that the analogous situation is realized in the decomposition of complexes **3** and **4**. As a whole, the mass spectra of complexes **1—4** are very similar (see Table 1). The derivatives of $CpFe(CO)_2Cb$ and $CpFe(CO)_2COCb$ can be distinguished only by the $CbCO^+$ ions that are formed only in the case of complexes **3** and **4** (see Scheme 1 and Table 1).

Table 1. Relative intensities ($\%\Sigma_{40}$) of major peaks in the mass spectra of $CpFe(CO)_2Cb$ (**1**, **2**) and $CpFe(CO)_2COCb$ (**3**, **4**)

Ion	**1**	**2**	**3**	**4**
$CpFe(CO)_2Cb$	0.05	0.2	0.01	0.5
$CpFe(CO)Cb$	5.1	4.9	3.1	3.8
$CpFeCb$	27.1	20.4	24.1	19.6
$CpFe(Cb-nH)$	42.4	49.5	40.3	39.7
	(n = 1—6)	(n = 1—7)	(n = 1—8)	(n = 1—6)
$CpFe(Cb-B_nH_m)$	2.3	1.9	1.6	2.0
$CpCb$	2.8	4.0	0.5	1.5
$CpCb-nH$	1.1	1.7	1.5	1.2
	(n = 1—4)	(n = 1—5)	(n = 1—6)	(n = 1—6)
$CpC_2H_nB_9$	0.8	0.8	0.4	0.1
$FeCb-nH$	1.2	0.7	0.9	1.2
Cb	3.2	3.3	5.5	9.6
$Cb-nH$	5.0	7.6	8.3	5.9
	(n = 1—9)	(n = 1—10)	(n = 1—10)	(n = 1—7)
$C_2H_nB_9$	0.4	0.5	1.0	1.2
CbCO	—	—	2.5	2.3
$CbCO-nH$	—	—	0.6	1.2
	(n = 1—9)	(n = 1—10)	(n = 1—10)	(n = 1—7)
CpFe(CO)	0.1	0.2	0.2	0.3
CpFe	1.3	1.3	3.8	3.1
Fe	4.7	3.4	5.4	4.8
$\frac{[\Sigma(CpFeCb-nH)]}{[CpFeCb]}$	1.6	2.4	1.7	2.0

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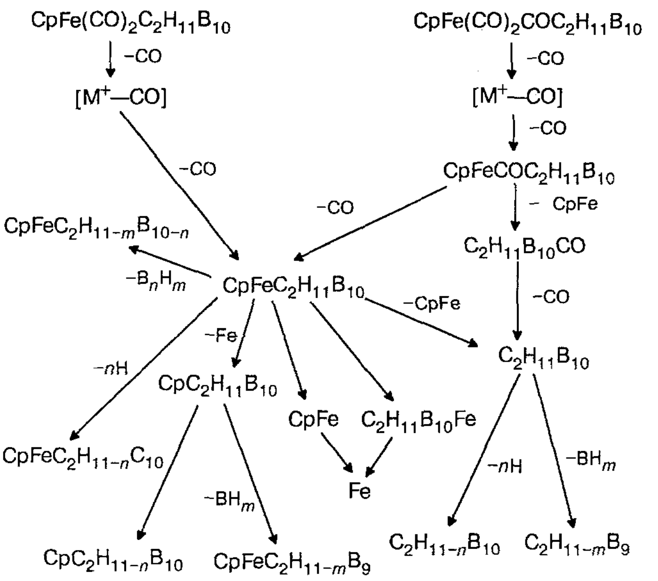
Scheme 1



One can consider compounds **1—4** to be either carboranyl derivatives, $CpFe(CO)_2R$, or carborane derivatives with the $C_2H_{11}B_{10}R$ organometallic substituent. According to this view, it is possible to distinguish two types of fragmentation of these complexes under electron impact.

The first pattern, which is characteristic of all $CpFe(CO)_2R$ derivatives, consists of successive decarbonylation of M^+ to yield intense peaks of $CpFeCb^+$ ions, which further decompose with cleavage of the metal—ligand bonds, resulting in the formation of $CpFe^+$ and $CbFe^+$ ions. Moreover, for the $CpFeCb^+$ ion, migration of the Cp ring to the carboranyl radical with subsequent elimination of the iron atom to lead to the $CpC_2H_{11}B_{10}{}^+$ ion is characteristic (see Table 1 and Scheme 1).

Mass spectral analysis of a large number of $CpFe(CO)_2R$ complexes (R = Hal, Alk, acyl, Ar, Fc) showed that the rearrangement yielding CpR^+ ions is observed only when R is aromatic radical (Ph, thienyl, Fc).[5]

A similar, but more complicated, rearrangement is known for $CpFe(CO)_2EX_3$ complexes (E = Si, Ge, Sn, Pb). In this case, migration of the Cp ligand to the EX_3 group also occurs, yielding intense peaks of CpE^+ ions, which have the structure of *nido*-clusters.[6—8] Therefore, it is not impossible that $CpCb^+$ ions have a semisandwich type structure, where the electron-deficient carboranyl group takes the part of the "central metal atom". As an alternative, we can also consider the classical type structure of cyclopentadienecarborane. Our quantum-chemical calculations (the MNDO method, optimization by the Baker method) showed that the most stable structure is the classical structure of cyclopentadienecarborane with the cyclopentadiene ring bound with the boron atom.

The second pattern of fragmentation involves dehydrogenation and destruction of the carborane frame. In this case the dehydrogenation process predominates in the mass spectra of unsubstituted carboranes.[1] In the case of complexes **1—4**, this reaction proceeds intensely in $CpFeCb^+$ ions, *i.e.*, after the loss of all carbonyl groups. The total intensity of dehydrogenated ions ($CpFeCb^+—nH$) (n = 1 to 8) is 40 to 50 % (see Table 1). The degree of dehydrogenation of the $CpFeCb^+$ ions, which is indicated by the ratio of the total intensities of the dehydrogenated ions to the intensity of the decarbonylated ion ($CpFeCb^+$-nH)/($CpFeCb^+$), depends slightly on the structure of the carboranyl ligand; only a small increase in this value is observed on the transition from the *o*- to the *m*-isomer (see Table 1). The most intense ions in the mass spectra of **1—4** are the [$CpFeCb^+$—2H] ions, which constitute 50 to 70 % of the total intensity of the dehydrogenated ions ($CpFeCb^+—nH$). The elimination of an even number of hydrogen atoms is characteristic of the dehydrogenation of unsubstituted carboranes (12).[1]

Thus, the predominant type of fragmentation of the molecular ions of complexes **1—4** is the "metallocarbonyl" pattern, which involves successive elimination of carbonyl groups and the carboranyl radical. The "carboranyl" fragmentation pattern, which involves further dehydrogenation of the carborane moiety, is realized only after complete decarbonylation of the molecular ion. The same pattern is characteristic of carboranyl derivatives of benzenetricarbonylchromium[2], which are dehydrogenated only after the loss of three carbonyl groups, *i.e.*, the introduction of an organometallic radical into the carborane moiety suppresses dehydrogenation of the molecular ions.

Experimental

Mass spectra were recorded using a Kratos MS-30 instrument with a DS-50 data processing system at an ionizing voltage of 70 V. The emission current was 100 μA, the temperature in the ionization chamber was 250 °C, the temperature of direct sample feeding was from 50 to 70 °C. The mass spectra were reduced to the monoisotope form using the AELITA program.[9]

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References

1. N. I. Vasyukova, Yu. S. Nekrasov, Yu. N. Sukharev, V. A. Mazunov, and Yu. L. Sergeev, *Izv. Akad. Nauk SSSR, Ser.*

Khim., 1985, 1337 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 1223 (Engl. Transl.)].

2. N. I. Vasyukova, Yu. S. Nekrasov, Yu. N. Sukharev, G.-K. I. Magomedov, and A. D. Frenkel', *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1548 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 1417 (Engl. Transl.)].
3. N. I. Vasyukova, Yu. S. Nekrasov, V. Ts. Kampel', and V. I. Bregadze, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 567 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 517 (Engl. Transl.)].
4. J. J. Akexander, *J. Am. Chem. Soc.*, 1975, **95**, 1729.
5. Yu. S. Nekrasov, D. Sci. (Chem.) Thesis, *Proceedings of the Institute of Organoelement Compounds, Russian Academy of Sciences*, 1985.
6. Yu. S. Nekrasov, D. V. Zagorevskii, V. F. Sizoii, and F. S. Denisov, *J. Organometal. Chem.* 1975, **97**, 253.
7. G. Inorta, A. Foffani, and S. Torroni, *Inorg. Chem. Acta*, 1976, **19**, 263.
8. Yu. S. Nekrasov, V. F. Sizoii, D. V. Zagorevskii, and Yu. A. Borisov, *J. Organometal. Chem.* 1981, **205**, 157.
9. Yu. N. Sukharev and Yu. S. Nekrasov, *Org. Mass Spectrometr.*, 1976, **11**, 1232.

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