Synthesis and study of η^5-C_5H_5-3,1,2-$M^{III}C_2B_9H_{11-n}F_n$ (M = Co, Fe; n = 1—4)

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B-Fluorosubstituted cyclopentadienyldicarbollylcobalt and -iron were synthesized. Electrochemical studies of iron η^5-C_5H_5-3,1,2-$FeC_2B_9H_{11-n}F_n$ (n = 2—4) complexes were carried out. ^{19}F NMR, UV, and IR spectra of the cobalt and iron complexes were obtained.

Key words: η^5-cyclopentadienyl-3,1,2-dicarbollylcobalt(III); η^5-cyclopentadienyl-3,1,2-dicarbollyliron(III).

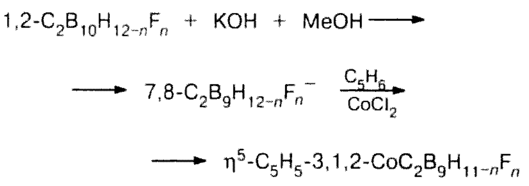
η^5-Cyclopentadienyl-3,1,2-dicarbollylcobalt and -iron, η^5-C_5H_5-3,1,2-$M^{III}C_2B_9H_{11}$ (M = Co, Fe) (**1**, **2**), are the most extensively studied metallacarboranes. Numerous studies have been devoted to the synthesis and transformations of *C*-substituted derivatives of these compounds, but their *B*-substituted derivatives have been studied to a significantly lesser extent.[1] The only *B*-halogenated derivatives of **1** and **2** known are the bromo-derivatives. It has been shown[2,3] that three bromine atoms can be added to the boron atoms through electrophilic bromination of **1** and **2** to form η^5-C_5H_5-8,9,12-Br_3-3,1,2-$CoC_2B_9H_8$ and η^5-C_5H_5-8,9,12-Br_3-3,1,2-$FeC_2B_9H_8$, respectively. The bromine atoms were shown to enter the molecules of **1** and **2**, first, at the B-8 atom and then at the equivalent B-9 and B-12 positions. A number of brominated derivatives of **2** has been obtained from *B*-bromo-derivatives of *nido*-7,8-dicarbaundecaborate salts.[3]

Cobalta- and ferracarboranes of the $CpMC_2B_9H_{11}$ and $(C_2B_9H_{11})_2M^-$ (M = Co, Fe) types containing fluorine atoms at the boron atoms are unknown. Attempts to obtain *B*-fluorosubstituted derivatives of Co-carborane, $(C_2B_9H_{11})_2Co^-$, by fluorination with various reagents have failed.[4]

Previously, we have synthesized *B*-fluorosubstituted *o*-carboranes[5] and 7,8-dicarbaundecaborate salts,[6] from which the fluorine-containing metallacarboranes, η^5-C_5H_5-3,1,2-$CoC_2B_9H_{11-n}F_n$ (n = 1—3) and η^5-C_5H_5-3,1,2-$FeC_2B_9H_{11-n}F_n$ (n = 2—4), were obtained in the present study. These two types of metallacarboranes differ from one another in that ferracarborane is paramagnetic, while cobaltacarborane is a diamagnetic compound. We used the following anions to obtain fluorine-containing ferra- and cobaltacarboranes: 5-F-7,8-$C_2B_9H_{11}^-$; 5,6-F_2-7,8-$C_2B_9H_{10}^-$; a mixture of 5,6,10-F_3-7,8-$C_2B_9H_9^-$ and 1,5,6-F_3-7,8-$C_2B_9H_9^-$ (in a 2 : 1 ratio); and 1,5,6,10-F_4-7,8-$C_2B_9H_8^-$. Attempts to isolate pure isomers from a mixture of anions containing three F atoms were unsuccessful. However, both isomers are easily identifiable with the aid of ^{19}F NMR.[6]

Cobaltacarboranes were synthesized according to Scheme 1, which is analogous to that reported elsewhere.[7]

Scheme 1



$$1,2\text{-}C_2B_{10}H_{12-n}F_n + KOH + MeOH \longrightarrow$$
$$\longrightarrow 7,8\text{-}C_2B_9H_{12-n}F_n^- \xrightarrow[CoCl_2]{C_5H_6}$$
$$\longrightarrow \eta^5\text{-}C_5H_5\text{-}3,1,2\text{-}CoC_2B_9H_{11-n}F_n$$

3, **4**, **5a,b**

3: n = 1, η^5-C_5H_5-9-F-3,1,2-$CoC_2B_9H_{10}$
4: n = 2, η^5-C_5H_5-9,12-F_2-3,1,2-$CoC_2B_9H_9$
5a,b: n = 3, η^5-C_5H_5-8,9,12-F_3-3,1,2-$CoC_2B_9H_8$ (**a**),
η^5-C_5H_5-9,10,12-F_3-3,1,2-$CoC_2B_9H_8$ (**b**)

Based on the ^{19}F NMR spectra, the ratio of **5a** to **5b** was established to be 2 : 1. An attempt to obtain η^5-C_5H_5-3,1,2-$CoC_2B_9H_7F_4$ from tetrafluoro-*o*-carborane under analogous conditions resulted, apparently, in the formation of a tetrafluoro-derivative of bis(η^5-cyclopentadienyl)dicobalt-(3,6)-1,2-dicarbocanastide, $(C_5H_5)_2$-3,6,1,2-$Co_2C_2B_8H_6F_4$, whose structure and properties will be the subject of subsequent study.

Ferracarboranes were obtained by a known procedure[8] (Scheme 2). The structure of complex **8** is given in Fig. 1.

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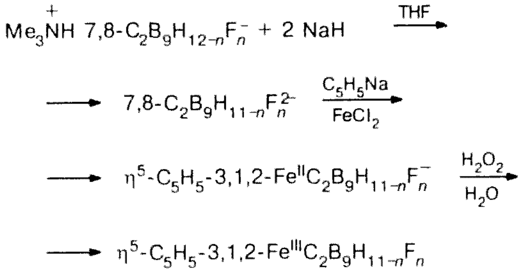
Scheme 2



6—8

6: n = 2, η^5-C_5H_5-9,12-F_2-3,1,2-$FeC_2B_9H_9$
7a,b: n = 3, η^5-C_5H_5-8,9,12-F_3-3,1,2-$FeC_2B_9H_8$ (**a**),
η^5-C_5H_5-9,10,12-F_3-3,1,2-$FeC_2B_9H_8$ (**b**)
8: n = 4, η^5-C_5H_5-8,9,10,12-F_4-3,1,2-$FeC_2B_9H_7$

The **7a** : **7b** ratio is 2 : 1 (based on the ^{19}F NMR data).

It has been observed that, at the stage of oxidation of ferracarboranes in which the iron atom is in a formally bivalent state into iron(III)-carboranes with H_2O_2, as the number of F atoms in the dicarbollyl ligand increases the oxidation becomes slower. To estimate the rate of redox processes, we studied complexes **2**, **6—8** using cyclic voltammetry (CVA) in an aprotic medium on a glassy-carbon electrode. The results of these measurements are listed in Table 1.

The cyclic voltammogram of complex **2** and its fluorinated derivatives **6—8** has two anodic peaks A and B (Fig. 2), while for tri- and tetrafluorinated complexes **7** and **8** a reduction peak C is observed at high negative potentials (Fig. 3). For the one-electron and reversible peak A, there is an equal in height corresponding cathodic peak A', and the potential difference between them is 60—70 mV. Peaks B and C correspond to an irreversible process. No reverse peaks were observed when the temperature was lowered to −90 °C, which points to high reactivity of the products resulting from the redox processes. Peaks C and B correspond to one-electron and two-electron transfers, respectively. The results obtained are evidence that the consecutive oxidation of iron, $Fe^{II} \leftrightarrow Fe^{III} \leftrightarrow Fe^{IV}$, can occur in all the complexes. Analogous Fe^{II}/Fe^{III} and Fe^{III}/Fe^{IV} redox transitions have been observed for both ferrocene[9] and decamethylferrocene.[10] Only the Fe^{II}/Fe^{III} redox transition has been hitherto reported[8] for complex **2**, while the subsequent Fe^{III}/Fe^{IV} oxidation stage is revealed in the present study for the first time. The similar values of the potential difference of the two oxidation stages, Fe^{II}/Fe^{III} and Fe^{III}/Fe^{IV}, can serve as a proof of the identity of the oxidation processes of complexes **2**, **6—8** (ΔE = 1.52—1.59 V) and ferrocene (1.58 V). Obviously, the one-electron reduction peak observed for complexes **7** and **8** corresponds to the Fe^{II}/Fe^{I} transition.

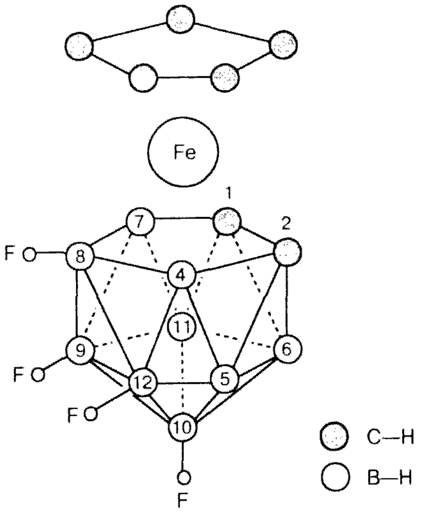


Fig. 1. The structure of the η^5-C_5H_5-8,9,10,12-F_4-3,1,2-$FeC_2B_9H_7$ complex.

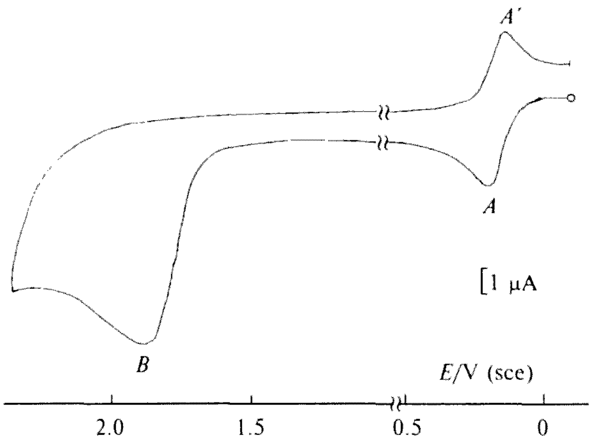


Fig. 2. Cyclic voltammogram of complex **8** (C = $2 \cdot 10^{-3}$ mol·L^{-1}, MeCN, 0.1 M Bu_4NBF_4, glassy-carbon electrode, V = 200 mV·s^{-1}).

Table 1. Oxidation and reduction[a] potentials of η^5-C_5H_5Fe-η^5-L (THF—0.2 M Bu_4NBF_4 or MeCN—0.1 M Bu_4NBF_4, C = $2 \cdot 10^{-3}$ mol·L^{-1}, V = 200 mV·s^{-1}, 20 °C, glassy-carbon electrode, relative to saturated calomel electrode)

L	$E_{1/2}^{ox}$/V		ΔE^b/V	$E_{1/2}^{red}$/V,
	Fe^{II}/Fe^{III}	Fe^{III}/Fe^{IV}		Fe^{II}/Fe^{I}
1,2-$C_2B_9H_{11}$	−0.02	1.50	1.52	
1,2-$C_2B_9H_9$-9,12-F_2	0.06	1.62	1.56	
1,2-$C_2B_9H_8F_3$ [c]	0.10	1.68	1.58	2.69
1,2-$C_2B_9H_7$-8,9,10,12-F_4	0.15	1.74	1.59	2.60

[a] $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ correspond to $E_{3/4}$ of the peak. [b] ΔE = $E_{1/2}^{ox}[Fe^{III}/Fe^{IV}]$ − $E_{1/2}^{ox}[Fe^{II}/Fe^{III}]$. [c] A mixture of 8,9,12-F_3 and 9,10,12-F_3 isomers in a 2 : 1 ratio.

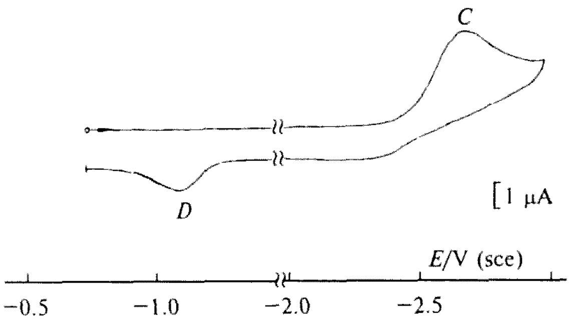


Fig. 3. Cyclic voltammogram of complex **8** (C = $2 \cdot 10^{-3}$ mol $\cdot$ L^{-1}, THF, 0.1 M Bu_4NBF_4, glassy-carbon electrode, V = 200 mV $\cdot$ s^{-1}).

From the data obtained it follows that the Fe^{III} complexes formed by oxidation of Fe^{II} complexes are stable in the CVA time-scale, whereas the Fe^{IV} and Fe^{I} complexes are highly reactive. Apparently, subsequent chemical reactions of Fe^{I} bring about cleavage of the bond between iron and the coordinated dicarbollyl ligand to give $C_2B_9H_{11-n}F_n^{2-}$ anions. This is substantiated by the appearance of anodic peaks D on reverse scanning (see Fig. 3), whose potentials (E_n^{ox} = −1.13 V and −1.07 V for complexes **7** and **8**, respectively) coincide with the oxidation potentials of tetramethylammonium salts of the $C_2B_9H_{12-n}F_n^-$ (n = 3, 4) anions, which we measured under analogous conditions. Possibly, the same anions result from subsequent chemical reactions of the Fe^{IV} complexes. Obviously, the ability of the dicarbollyl anions formed to undergo oxidation is responsible for the fact that peak B in the cyclovoltammograms of complexes **2**, **6—8** corresponds to the transfer of not one, but two electrons. It can be seen from the data of Table 1 that the fluorine atoms in the dicarbollyl ligands have an electron-acceptor effect, shifting the potential of the reversible oxidation peak A to greater positive values by 40 mV per each fluorine atom. The electron-acceptor nature of the fluorine atoms is manifested also in the appearance of the reduction peaks C for complexes **7** and **8**, which are absent in the case of non-substituted (**2**) and disubstituted (**6**) complexes.

All the complexes obtained, **3—5** and **6—8**, were characterized by ^{19}F and ^{11}B NMR, IR, and UV spectra.

Comparing the ^{19}F NMR spectra of the B-fluorinated derivatives of compounds **1** and **2** (Table 2), one should note that the signals of the F atoms in the cobalt complexes **3—5** are down-field of the NMR signals of the F atoms in the iron complexes **6—8**. This allows one to conclude that the distributions of electron density in the π-carborane ligands of these compounds are different, which is associated with the different nature of the complexes: the F^{III} complexes are paramagnetic, whereas the Co^{III} complexes are diamagnetic. The chemical shift values (δ) of the signals of the F atoms in the ^{19}F NMR spectra of compounds **3** and **4** virtually coincide with the signals in the ^{19}F NMR spectra of 9-F-o-$C_2B_{10}H_{11}$ and 9,12-F_2-o-$C_2B_{10}H_{10}$,[5] respectively, and are considerably down-field compared with those of the original mono- and difluoro-*nido*-7,8-dicarbaundecaborates.[6] The opposite picture is observed for the iron complex **6**. The fluorine signals in the ^{19}F NMR spectra of compound **6** and the original anion coincide, but are markedly up-field compared with 9,12-F_2-o-$C_2B_{10}H_{10}$. It can also be seen from Table 2 that incorporation of a F atom into molecule **3** at position 12 causes the ^{19}F NMR signals to shift (Δδ) by 4.4 ppm; for the 5-F-7,8-$C_2B_9H_{11}^-$ anion[6] the incorporation of a F atom at position 6 gives Δδ = 19.4 ppm. On going from compound **4** to **5a** and from compound **6** to **7a**, in which the third fluorine atom resides at the B(8) atom in the plane of the pentagon of the dicarbollyl ligand, ΔδF(9,12) is 4.2 ppm and −3.9 ppm, respectively; the fluorine atom at the B(10) atom in the 5,6,10-F_3-7,8-$C_2B_9H_9^-$ anion shifts the signals of the F(5,6) atoms by 4.0 ppm. The fluorine atom at the B(10) atom of the dicarbollyl ligand in complexes **5b** and **7b** has Δδ of 6.3 ppm and 1.6 ppm, respectively; incorporation of a fluorine atom at the B(1) atom in the 1,5,6-F_3-7,8-$C_2B_9H_9^-$ anion shifts the signals of F(5,6) by 1.8 ppm. Comparing the chemical shifts (δ) of the F atoms of complex **7a** with those of the F atoms of complex **8**, in which the fourth F atom resides at the B(10) atom, we find ΔδF(9,12) = 54.2 ppm and ΔδF(8) = −4.0 ppm. Incorporation of a fourth F atom into the anion at the B(1) atom shifts the signals of the F(5,6) and F(10) atoms by 16.3 ppm and −9.0 ppm, correspondingly. Correlating the ^{19}F NMR spectra of compounds **7b** and **8**, in which the fourth fluorine atom resides at the B(8) atom of the plane of the pentagon of the dicarbollyl ligand, we find the ΔδF(9,12) shift to be 48.7 ppm, and ΔδF(10) = 57.8 ppm. On going from the 1,5,6-F_3-7,8-$C_2B_9H_9^-$ anion to the 1,5,6,10-F_4-7,8-$C_2B_9H_8^-$ anion, ΔδF(5,6) = 18.5 ppm and ΔδF(1) = 5.0 ppm.

It is known that a large difference in shielding of the boron nuclei in the ^{11}B NMR spectra is characteristic of paramagnetic metallacarborane compounds.[3,11] However, in the case of complexes **6—8**, this statement, as can be seen from Table 2, holds fully for complex **6**, which contains only two F atoms in the η^5-carborane ligand, for which the scatter of signals of the boron nuclei in the ^{11}B NMR spectrum is from 111.9 ppm to −544.31 ppm. Increasing the number of F atoms in the dicarbollyl ligand of complexes **7** and **8** gives rise to narrowing of the region of signals of the boron nuclei in the ^{11}B NMR spectra and shifts them up-field. Furthermore, the larger the number of fluorine atoms in the η^5-dicarbollyl ligand of complexes **7** and **8**, the less the scatter of the signals of the boron nuclei. This shift is not observed in the case of B-bromo-substituted cyclopentadienyldicarbollyl complexes of iron(III)[3] in which an increase in the number of bromine atoms in the dicarbollyl ligand does not significantly change the chemical shifts of the boron nuclei in the ^{11}B NMR spectra. In our case, this strong change in chemical

Table 2. ^{19}F and ^{11}B NMR spectra of fluorine-containing metallacarboranes

Compound	^{19}F		^{11}B,
	δ	Assignment	δ (assignment)
3	107.3	F(9)	15.6 (1 B); 6.7 (2 B); −9.8 (2 B); −16.0 (2 B); −24.9 (2 B)
4	111.7	F(9,12)	12.3 (1 B); 1.1 (1 B); −2.4 (2 B); −12.1 (2 B); −21.0 (2 B); −26.0 (1 B)
5a	79.9 115.9	F(8) F(9,12)	24.0 (1 B); 11.0 (2 B); −5.5 (2 B); −7.5 (2 B); −13.5 (1 B); −21.5 (1 B)
5b	87.3 118.0	F(10) F(9,12)	12.1 (2 B); 1.1 (1 B); −6.1 (2 B); −17.1 (2 B); −23.1 (2 B)
6	135.0	F(9,12)	111.9 (1 B, B(6)); 33.62 (2 B, B(5,11)); −46.99 (2 B, B(9,12)); −129.78 (1 B, B(10)); −457.72 (2 B, B(4,7)); −544.31 (1 B, B(8))
7a	115.3 131.1	F(8) F(9,12)	−211.47 (1 B, B(6)); −251.47 (1 B, B(10)); −308.83 (2 B, B(5,11)); −313.88 (2 B, B(9,12)); −474.08 (2 B, B(4,7)); −502.76 (1 B, B(8))
7b	127.5 136.6	F(10) F(9,12)	−229.40 (1 B,B(6)); −310.51 (2 B, B(5,11)); −385.53 (3 B, B(9,10,11)); −389.53 (2 B, B(4,7)); −496.97 (1 B, B(8))
8	111.3 185.3	F(8) F(9,10,12)	−231.858 (1 B, B(6)); −309.733 (2 B, B(5,11)); −381.086 (3 B, B(9,10,12)); −528.586 (2 B, B(4,7)); −530.962 (1 B, B(8))

Table 3. Electronic absorption spectra (in CH_2Cl_2; 1-mm layer)

Compound	λ_{max}/nm (ε)
1	278 (25200); 320 (2200); 426 (450)
3	278 (24600); 309 (11870); 420 (790)
4	276 (29000); 324 (4000); 424 (640)
5	285 (24700); 320 (8010); 405 (880); 566 (98)
2	263 (23100); 289 (17200); 393 (760); 579 (390)
6	263 (26100); 290 (18000); 389 (1000); 573 (500)
7	263 (20600); 290 (14700); 393 (840); 576 (330)
8	266 (19500); 290 (15000); 414 (920); 548 (290); 651 (240)

shifts of boron nuclei is probably associated with the high electronegativity of the F atoms.

It should be noted that the color of metallafluorocarboranes changes depending on the positions of the fluorine atoms in the η^5-dicarbollyl ligand. The colors of cobaltacarboranes **3** and **4** and ferrafluorocarborane **6**, which do not contain fluorine atoms in an open plane of the dicarbollyl ligand, are similar to those of the non-substituted metallacarboranes: purple for ferracarborane and close to yellow for cobaltacarboranes. The presence of a F atom in the open plane of the η^5-dicarbollyl ligand changes the color of the compounds drastically. Thus, ferracarborane **8** is dark green. A change in the color of a compound indicates changes occurring in the electronic structure of a molecule. This is confirmed by the UV spectra of the complexes obtained, which are given in Table 3. It is noteworthy that when the F atoms reside at B atoms relatively remote from the metal atom (positions 9, 10, 12), the UV-VIS spectra of the compounds studied are close to those of non-substituted complexes **1** and **2**, whereas incorporation of a F atom at a B atom in the pentagonal plane directly linked with the metal atom brings about a significant bathochromic shift of almost all the bands of the spectrum (from 20 to 80 nm). An analogous effect was observed previously[3] when Br atoms were introduced into the η^5-dicarbollyl ligand of complex **2**. Consequently, this phenomenon does not depend on the nature of the halogen atom. Notice that a similar bathochromic shift occurs when the oxidation state of the metal atom is changed, for instance, on going from ferrocene to ferrocenium.[12] Hence, incorporation of a halogen atom into the pentagonal plane nearest to the metal atom changes substantially the electronic structure of the π-complex, and, in particular, the electron density at the metal atom.

The presence of a B—F bond in fluorine-containing metallacarboranes **3—5** and **6—8** results in the appearance of a band at about 1200 cm^{-1} in the IR spectra, and as the number of F atoms in the dicarbollyl ligand increases, the intensity of the IR-band increases. Analogous bands of the IR spectrum are characteristic of 1,2-$C_2B_{10}H_{12-n}F_n$[13] containing a B—F bond. The change in parameters of the bands of C—H stretching vibrations in the dicarbollyl ligand of complexes **3—5** and **6—8** differs substantially from the changes characteristic of 1,2-$C_2B_{10}H_{12-n}F_n$. As the number of F atoms increases, the frequency of the band increases from 3055 to 3075 cm^{-1} for compounds **3—5**, and from 3045 to 3065 cm^{-1} for compounds **6—8**. Moreover, as the number of fluorine atoms in the dicarbollyl ligand increases, the intensity of this band increases.

Experimental

The initial fluorocarboranes used for the synthesis of complexes **3—5** [5] and **6—8** [6] were obtained using known procedures. The reactions were monitored by TLC on Silufol UV-254 plates. Column chromatography was carried out on silica gel L 100/160. ^{19}F NMR spectra were recorded on a Bruker WP-200 SY instrument.

Cyclic voltammograms were registered with the use of a PI-50-1 potentiostat. Glassy carbon (S = 2 mm^2), platinum plate, and saturated calomel electrodes were used as the working, auxiliary, and reference electrodes, respectively. The measurements were performed on solutions in THF or acetonitrile using 0.2 *M* or 0.1 *M* Bu_4NBF_4 as the supporting electrolyte. The concentration of compounds studied was $2 \cdot 10^{-3}$ mol L^{-1}. The rate of potential sweep was 200 mV s^{-1}. The number of electrons involved in the reactions was estimated by comparing the currents of the observed peaks with the current of a one-electron ferrocene/ferrocenium redox process at the same concentrations. THF was refluxed and distilled over sodium benzophenone ketyl, and acetonitrile was purified according to a reported procedure.[14]

UV spectra were obtained on a Specord M-40 instrument in CH_2Cl_2, and IR spectra were recorded on a UR-10 spectrometer (pellets with KBr).

Preparation of η^5-C_5H_5-3,1,2-$CoC_2B_9H_{11-n}F_n$. KOH (0.10 mol) was added to a solution of 0.01 mol of 1,2-$C_2B_{10}H_{12-n}F_n$ (n = 1—3) in 10 mL of MeOH cooled with ice water. The mixture was heated until the starting material disappeared (TLC, benzene). Then a solution of 0.015 mol of $CoCl_2$ in 5 mL of MeOH and 0.02 mol of freshly prepared C_5H_6 were added dropwise to the reaction mixture at ~20 °C. The mixture was refluxed for 1—2.5 h, diluted with 20 mL of water, and filtered. The precipitate was washed with 10% HCl (2×10 mL) and dissolved by washing with acetone (3×5 mL). Water (5 mL) was added to the solution, the acetone was removed under reduced pressure, and the crystals that precipitated were filtered off, washed with $CHCl_3$ (3×3 mL), dried *in vacuo* over P_2O_5, and purified by recrystallization from EtOH and column chromatography (CH_2Cl_2—acetone).

η^5-C_5H_5-9-F-3,1,2-$CoC_2B_9H_{10}$ (3). Dark-yellow crystals, yield 1.1 g (37%), m.p. 197 °C (decomp.). Found (%): C, 31.17; H, 5.58; F, 6.17. $C_7H_{15}B_9CoF$. Calculated (%): C, 30.93; H, 5.47; F, 6.97. IR, ν/cm^{-1}: 1200 (BF); 2570 (BH); 3065 (CH of carborane); 3120 (CH of C_5H_5).

η^5-C_5H_5-9,12-F_2-3,1,2-$CoC_2B_9H_9$ (4). Dark-yellow crystals, yield 1.3 g (45%), m.p. 230 °C (decomp.). Found (%): C, 28.89; H, 4.69; F, 11.71. $C_7H_{14}B_9CoF_2$. Calculated (%): C, 28.77; H, 4.79; F, 12.74. IR, ν/cm^{-1}: 1200 (BF); 2570 (BH); 3065 (CH of carborane); 3120 (CH of C_5H_5).

η^5-C_5H_5-3,1,2-$CoC_2B_9H_8F_3$ (5a + 5b). Dark-brown crystals, yield 1.3 g (43%), m.p. 257 °C (decomp.). Found (%): C, 28.95; H, 4.38; F, 17.97; Co, 19.46. $C_7H_{13}B_9CoF_3$. Calculated (%): C, 28.10; H, 4.19; F, 18.33; Co, 19.03. IR, ν/cm^{-1}: 1200 (BF); 2570 (BH); 3075 (CH of carborane); 3120 (CH of C_5H_5).

Preparation of η^5-C_5H_5-3,1,2-$FeC_2B_9H_{11-n}F_n$. A solution of 0.01 mol of Me_3N^+H-7,8-$C_2B_9H_{12-n}F_n^-$ (n = 2—4) in 10 mL of dry THF was added dropwise to a suspension of 0.05 mol of NaH in 20 mL of dry THF. The mixture was refluxed until the evolution of Me_3N ceased. Then, 0.02 mol of freshly prepared C_5H_6 were added dropwise, and the mixture was stirred for 1 h at 23 °C. The upper layer was decanted under Ar, and 0.015 mol of anhydrous $FeCl_2$ was added to the solution. The reaction mixture was refluxed for 1.5—2 h and filtered. The THF was evaporated, the residue was dissolved in distilled water, and the insoluble part was filtered off. H_2O_2 (5.5 mL) was added dropwise to the aqueous solution. The precipitate that formed was filtered off, dried *in vacuo* over P_2O_5, and purified by column chromatography (CH_2Cl_2—light petroleum).

η^5-C_5H_5-9,12-F_2-3,1,2-$FeC_2B_9H_9$ (6). Purple crystals, yield 0.25 g (10%), m.p. 190 °C. Found (%): C, 28.92; H, 5.13; F, 12.93; Fe, 19.27. $C_7H_{14}B_9F_2Fe$. Calculated (%): C, 29.06; H, 4.84; F, 13.15; Fe, 19.38. IR, ν/cm^{-1}: 1200 (BF); 2570 (BH); 3045 (CH of carborane); 3120 (CH of C_5H_5).

η^5-C_5H_5-3,1,2-$FeC_2B_9H_8F_3$ (7a + 7b). Dark crystals, yield 0.3 g (10%), m.p. 198 °C. Found (%): C, 26.93; H, 4.83; F, 17.84. $C_7H_{13}B_9F_3Fe$. Calculated (%): C, 27.13; H, 4.23; F, 18.07. IR, ν/cm^{-1}: 1200 (BF); 2570 (BH); 3055 (CH of carborane); 3120 (CH of C_5H_5).

η^5-C_5H_5-8,9,10,12-F_4-3,1,2-$FeC_2B_9H_7$ (8). Dark-green crystals, yield 0.6 g (18%), m.p. 212 °C. Found (%): C, 26.06; H, 3.98; F, 22.76. $C_7H_{12}B_9F_4Fe$. Calculated (%): C, 25.84; H, 3.68; F, 23.00. IR, ν/cm^{-1}: 1200 (BF); 2570 (BH); 3065 (CH of carborane); 3120 (CH of C_5H_5).

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