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SYNTHESIS AND SOME REACTIONS OF CARBENIUM IONS OF NEW TYPES STABILIZED WITH π-CYCLOPENTADIENYL-π-(3)-1,2-DICARBOLLYL-IRON (II) GROUP. STRUCTURE OF 3-π-$C_5H_5Fe^{II}$-π-1,2-$C_2B_9\bar{H}_{10}$-1-$\overset{+}{C}HC_6H_5$

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Abstract—Stable carbenium zwitterions 3-π-$C_5H_5Fe^{II}$-π-1,2-$C_2B_9\bar{H}_{10}$-1-$^{+}CRR'$ (R=R′=H; R=H, R′=Me; R=H, R′=Ph; R=R′=Me) have been prepared by protonation of the carbinols [3-π-$C_5H_5Fe^{II}$-π-1,2-$C_2B_9H_{10}$-1-CH(OR)R]$^-$(R=H, Me, Ph) and olefins [3-π-$C_5H_5Fe^{II}$-1,2-$C_2B_9H_{10}$-1-C(R)=CH_2]$^-$(R=H, Me). Reactions of the zwitterions with neutral and charged nucleophilic reagents have been studied. Crystal and molecular structure of 3-π-$C_5H_5Fe^{II}$-π-1,2-$C_2B_9\bar{H}_{10}$-1-$\overset{+}{C}HC_6H_5$ have been established. The possibility of direct stabilization of a carbocationic centre by the iron atom was shown. Various derivatives of π-cyclopentadienyl-π-(3)-1,2-dicarbollyliron(III) were obtained.

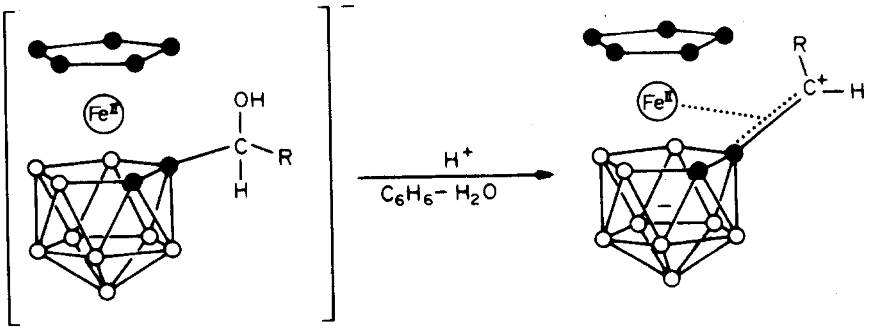
A characteristic feature of the ferrocene derivatives is the ability of the $C_5H_5FeC_5H_4$-group to stabilize carbenium ions at the α-position relative to the ferrocene nucleus.[1] Since the π-cyclopentadienyl-π-(3)-1,2-dicarbollyliron (II) group, π-$C_5H_5Fe^{II}$-π-HCB_9H_9C-,[†] is isoelectronic with the ferrocenyl group, we suggested the possibility of stabilization of the α-carbenium ions with the ferra (II)-carborane nucleus. In fact, it was found that protonation of the carbinols **1**, **2**, and **3** with acids affords, respectively, the primary **4** and secondary (**5** and **6**) carbenium zwitterions,[‡] respectively, in high yields.

Another convenient method for the preparation of secondary **5** and tertiary **7** zwitterions consists of protonation of the corresponding olefins (**8** and **9**) with acids.

The carbenium zwitterions obtained are red crystalline diamagnetic substances. They are stable on storage in air in the solid state but less stable in solution. The relative stability of the carbenium zwitterions on storage in air increases as follows: $\overset{+}{C}H_2 \ll \overset{+}{C}HMe < \overset{+}{C}HPh \approx \overset{+}{C}Me_2$. The secondary carbenium zwitterion **6** was also obtained instead of the expected phenylcarbinol **3** by the unusual reaction of aldehyde **1** with C_6H_5MgBr in ether.

$$\pi\text{-}C_5H_5Fe'''\text{-}\pi\text{-}HCB_9H_9CCHO \xrightarrow[Et_2O]{PhMgBr} 6$$

In this case, as well as in protonation of carbinol **3**, a mixture of two diastereomers of secondary zwitterion **6** was formed which was separated by TLC. The ability of the phenylcarbenium zwitterion **6** to form diastereomers is due to the presence of two asymmetric centres in this molecule: the chiral π-dicarbollyl ligand and carbon cationic atom coordinated by the iron atom (see below). A peculiarity of the carbenium ions obtained resides in compensation of its positive charge with the negative charge of the π-dicarbollyl ligand so that molecule as a whole is electroneutral. We call such types of carbenium



1 R = H

2 R = CH_3

3 R = C_6H_5

● CH

▨ C

○ BH

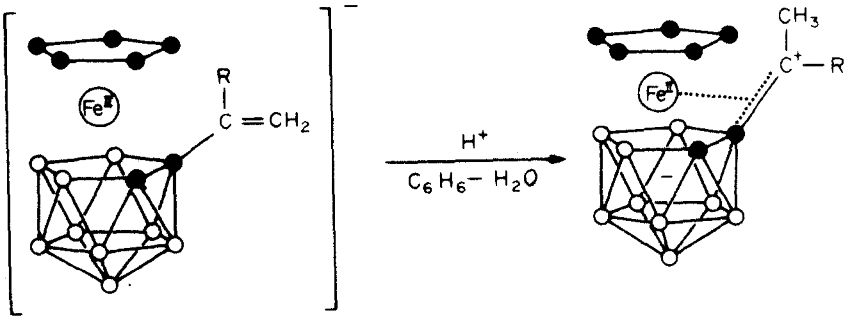
4 R = H

5 R = CH_3

6 R = C_6H_5

[†] The symbol π-$C_5H_5Fe^{II}$-π-HCB_9H_9C- means 3-π-$C_5H_5Fe^{II}$-π-1,2-$C_2B_9H_{10}$-1- group.

[‡] Preliminary report on the preparation of the carbenium zwitterion **4** is given in[2].



8 R = H

9 R = CH_3

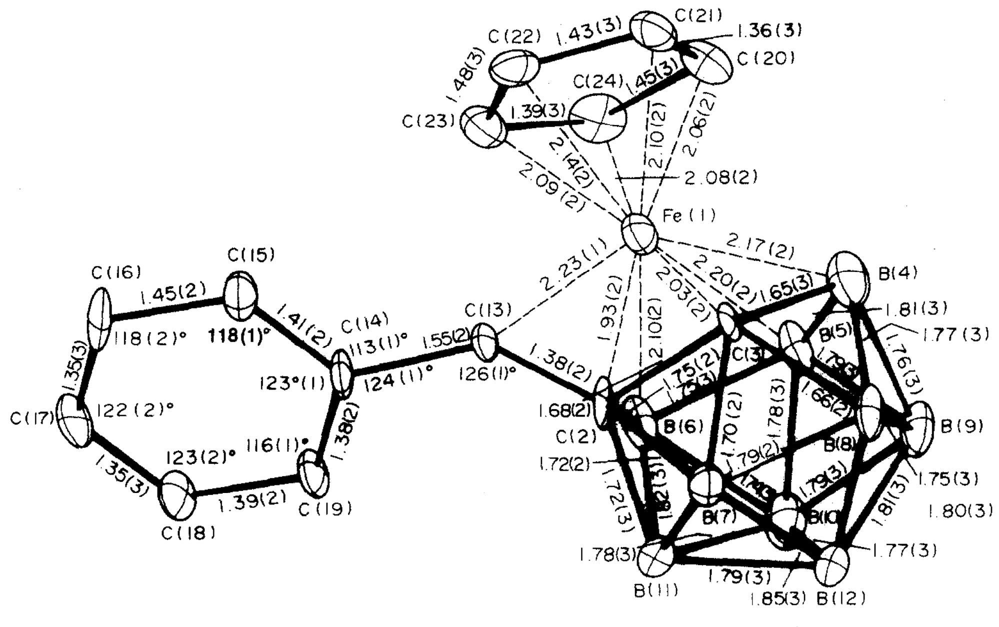
● CH

◍ C

○ BH

5 R = H

7 R = CH_3



Scheme 1. Structure of zwitterion **6** (hydrogen atoms are not shown).

ions "carbenium zwitterions". They are interesting in that they can be chromatographed on silica gel with eluents of moderate polarity. The structures of the carbenium zwitterions were confirmed by the spectral data (see Table 1). In the ^1H NMR spectra, chemical shifts of the carbocationic centre protons in **4** are in the region 3–4.5 ppm. The methylene protons of the primary zwitterion **4** are diastereotopic and correspond to two slightly broadened singlets centered at 3.02 and 3.59 ppm. The singlet form of the signals is apparently due to a small value of the coupling constant for these protons ($J_{HH} <$ 1 Hz). The chemical shift of the carbocationic center proton in the secondary zwitterion **5** is equal to 4.27 ppm, the signal being a quadruplet with $J_{HH} = 7$ Hz. It is noteworthy that, unlike organic carbenium ions having down-field chemical shifts (e.g. 13.5 ppm in $(CH_3)_2\overset{+}{C}HSbF_6^-$), the values of the chemical shifts of the carbenium ion protons in the ferrocene series are close to those obtained by us and are equal to 5.90 ppm for $[C_5H_5FeC_5H_4CH_2]^+HSO_4^-$[3] and 7.03 ppm for $[C_5H_5FeC_5H_4CHMe]^+HSO_4^-$.[4]

Unfortunately, owing to the poor solubility of the zwitterions **6** and **7**, we did not succeed in obtaining satisfactory ^1H NMR spectra of these ions. For the same reason, ^{13}C NMR spectra of all the zwitterions described herein could not be obtained. The conclusion on the structures and probable mechanism of the carbenium zwitterions stabilization was drawn on the basis of the X-ray analysis of one of the diastereomers of phenylcarbenium zwitterion **6**. The crystals of **6** are orthorhombic, a = 11.033(3), b = 11.820(3), c = 13.394(4)Å^3, V = 1745(1)Å^3, Z = 4, $d_{calc.} = 1.314$ g/cm^3, space group $P2_12_12_1$. The structure of the molecule of **6** is shown in Scheme 1.

The atomic co-ordinates and anisotropic thermal parameters of **6** are listed in Table 2.

X-ray study has shown unambiguously that a molecule of **6** contains the iron atom coordinated by the "open" face C_2B_3 of the dicarbollyl ligand and the η^5-C_5H_5

Table 1. ^{1}H NMR spectra

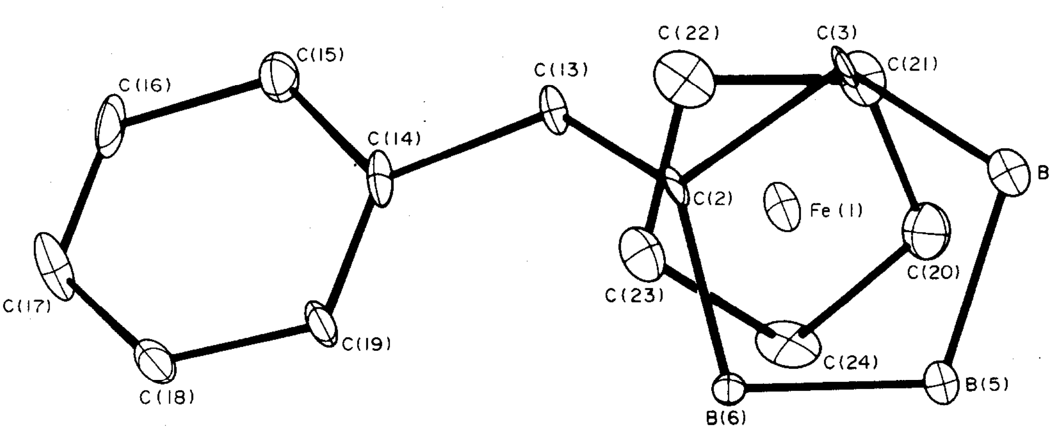
Compound	Chem. shift (δ, ppm, relative to TMS) [J_{HH} Hz]	Assignment
4[a]	0.94 s	Carborane CH
	3.02 s	$\overset{+}{\mathrm{C}}\mathrm{H_2}$
	3.49 s	$\overset{+}{\mathrm{C}}\mathrm{H_2}$
	4.46 s	C_5H_5
5[a]	1.05 d	CH_3
	1.78 s	Carborane CH
	4.27 q	$\overset{+}{\mathrm{C}}\mathrm{H}$
	4.40 s	C_5H_5
8[b]	3.16 s	$(CH_3)_4N$
	3.89 s	Carborane CH
	4.41 s	C_5H_5
	4.49–5.05 m	$CH{=}CH_2$
9[b]	2.09 s	CH_3
	3.25 s	$(CH_3)_4N$
	4.12 s	Carborane CH
	4.41 s	C_5H_5
	4.83 s	$=CH_2$
13[a]	1.34 s	CH_3
	1.65 s	CH_3
	2.03 s	CH_2
	4.35 s	Carborane CH
	4.49 s	C_5H_5
15	2.01 s	CH_2
	2.83 s	OCH_3
	2.99[c] t	$\underline{\mathrm{CH_2}}\mathrm{OCH_3}$
	3.34 s	Carborane CH
	3.47 s	$\overset{+}{\mathrm{O}}\mathrm{CH_3}$
	3.79[c] t	$\underline{\mathrm{CH_2}}\overset{+}{\mathrm{O}}\mathrm{CH_3}$
	4.22 s	C_5H_5
17	2.36 s	CH_2
	3.57 s	Carborane CH
	4.39 s	C_5H_5
	4.81-5.15 m	$CH{=}CH_2$

[a] Solution in benzene.
[b] Solution in pyridine.
[c] Bad resolution of the signal.

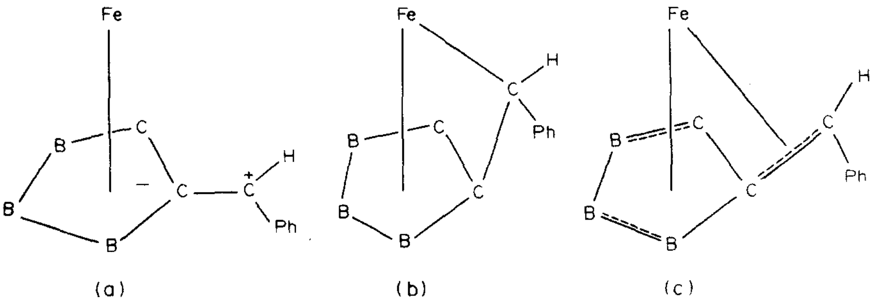
ligand. This atom is displaced by 1.476 and 1.708Å from the C_2B_3 and C_5H_5 planes, respectively. The dihedral angle between the C_2B_3 and C_5H_5 planes is equal to 13.9°. The projection of molecule of **6** on the C_5H_5 plane is shown in Scheme 2.

The carbocationic centre in molecule **6** is connected with the π-dicarbollyl ligand and is stabilized by a strong iron–carbon interaction. One can consider the molecule as an inner salt of the cation, in which the negative charge is delocalized in the ferra (II) carborane fragment. The salts of analogous carbocations, in which the cationic centre is connected with the C_5H_5-ligand coordinating the iron atom,[5–7] as well as the chromium-fulvene complex[8] were previously investigated. Similarly to the π-cyclopentadienyl complexes, for explanation of the interaction of the central atom of the metal with the carbocationic centre in zwitterion **6** one may use one of three models (Scheme 3).

The first model (a) does not involve direct interaction between the metal and *exo*-cyclic carbon (C_{exo}). The carbocation may be stabilized only by delocalization of the electron density over the π-$C_2B_9H_{10}$-ligand. The second model (b) corresponds to the σ-bond Fe–C_{exo}. The third model (c) may be treated as intermediate between (a) and (b). According to (c) interaction of the metal with the carbocationic centre is similar to coordination by a fulvene ligand. Geometrical parameters obtained for molecule **6** do not agree with model (a). Indeed, an appreciable shift of the iron atom toward the *exo*-cyclic atom C(13) leads to a significant difference in the distances between the iron atom and the boron and carbon atoms of the C_2B_3 plane (Scheme 2). The iron atom is nearest to the C(2) atom [1.93(2)Å] and rather far removed from the C(3)[2.03(2)Å] and B(6)[2.10(2)Å] atoms. It is most distant from the B(4)[2.17(2)Å] and B(5) [2.20(2)Å] atoms. The distance Fe(1)–C(13)[2.23(2)A] is significantly shorter than that of Fe–C_{exo}: 2.71 and 2.85Å in the case of $(C_5H_5FeC_5H_4)_2\overset{+}{\mathrm{C}}\mathrm{H}$[5] and 2.715Å for $C_5H_5FeC_5H_4\overset{+}{\mathrm{C}}\mathrm{Ph_2}$.[7] On the other hand, the distance Fe–C_{exo} is too long and does not allow one to interpret this interaction as the σ-bond Fe–C_{exo} in accord with model (b) in Scheme 3 (usual value of the Fe–C σ-bond length is equal to 2.04Å[9]). The "pseudofulvene" model (c) is rather unexpected because it suggests an *exo*-cyclic double bond between the *exo*-atom C(13) and the C(2) atom, which occupies one of the vertices of the ferracarborane polyhedron. Nevertheless, this model can explain the very short distance C(2)–C(13) [1.38(2)Å] as well as the sp^2-configuration of the C(13) atom (the bond angle C(2)–C(13)–C(14) is equal to 126(1)°). Because of insufficiently high accuracy in the determination of the geometrical parameters of the zwitterion **6**, it is impossible to draw a sound conclusion on the distribution



Scheme 2. Projection of the molecule of **6** on the C_5H_5 plane (hydrogen atoms are not shown).



Scheme 3. Plausible schemes of interaction between the iron atom and the molecule 6 carbocationic centre.

of bond lengths in the C_2B_3 plane. However, systematic differences in the corresponding distances in molecule 6 also favour the "pseudo-fulvene" structure (c). Like the fulvene–chromium complex studied earlier,[8] the *exo*-atom C(13) in molecule 6 deviates considerably (1.13Å) from the mean plane of the five-membered cycle C_2B_3 which is planar to within 0.03Å. The C(2)–C(13) bond forms an angle of 47° with the C_2B_3 plane. Thus, one may suggest that the structure of molecule 6 is best of all described by model (c) (Scheme 3). However, it is impossible to exclude completely the contribution of model (b). It was shown, by the extended Hückel MO-calculation that bonding in the $C_5H_5FeC_5H_4CH_2$ cation is mainly due to the overlap of the iron atom $3d_{z^2}$ orbital with the π-orbital of the fulvene-type ligand.[10] The authors[10] give some geometrical parameters (Scheme 4) of the theoretical model of the complex obtained by MO-calculation. It is of interest that experimental geometrical parameters of molecule 6 are in better agreement with calculated data than those of previously studied cyclopentadiene complexes (see Table 3). Additional evidence for the contribution of the iron atom to stabilization of the ferrocenylcarbenium ions was obtained by ^{13}C and ^{57}Fe NMR spectra.[11]

Thus complex 6 can be described either as a π-complex with the fulvene-type carborane ligand or as a molecule, containing the carbocationic centre stabilized by the back donation of metal $3d_{z^2}$-electrons to the vacant orbitals of the cationic centre.

As compared with organic carbenium cations or even tropilium cation, the carbenium zwitterions 4–7 are less reactive, probably because of considerable compensation of the positive charge on the carbon atom. However, they are able to enter into addition reactions at the cationic carbon atom with both neutral Lewis bases and charged nucleophilic reagents. Thus, the primary zwitterion 4 reacts with triphenylphosphine, pyridine, and dimethylsulfide to form inner salts 11–13:

$$4 \xrightarrow{L} \pi\text{-}C_5H_5Fe''\text{-}\pi\text{-}HCB_9H_9\bar{C}CH_2\overset{+}{L}$$

11, L = PPh_3
12, L = NC_5H_5
13, L = SMe_2

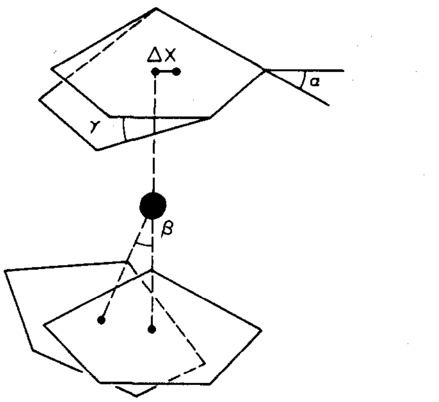
Table 2. Molecule 6. Atomic coordinates (× 10^3, for Fe × 10^4) and anisotropic thermal parameters in the form of $T = \exp[-1/4(B_{11}h^2a^{*2} + \cdots + 2B_{23}klb^*c^*)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	1349(2)	1286(2)	1106(2)	2.03(7)	3.23(8)	4.3(1)	−0.13(9)	0.0(1)	0.0(1)
C(2)	84(1)	−27(1)	111(1)	0.4(5)	6.9(9)	2.9(7)	1.0(6)	0.0(6)	−0.6(9)
C(3)	229(1)	−13(1)	148(1)	0.5(5)	4.4(8)	2.6(7)	−0.5(5)	−0.4(5)	−1.1(6)
B(4)	308(2)	59(2)	65(2)	2.9(8)	7(1)	4(1)	−0.2(9)	−0.2(8)	0.3(9)
B(5)	206(2)	85(2)	−38(1)	2.2(8)	7(1)	3.4(9)	−0.8(8)	−0.1(7)	1.1(9)
B(6)	63(2)	32(2)	−7(1)	2.1(8)	9(1)	1.5(8)	−1.4(9)	−0.1(7)	−0.2(8)
B(7)	178(1)	−143(1)	117(2)	3.2(7)	2.0(7)	5.2(9)	0.3(6)	1.4(8)	0.4(9)
B(8)	323(2)	−89(2)	79(1)	1.3(6)	7(1)	3.5(9)	1.2(7)	−0.1(6)	0.4(8)
B(9)	311(2)	−30(2)	−41(1)	3.1(8)	7(1)	2.9(9)	0.4(9)	1.3(7)	−0.5(9)
B(10)	158(2)	−50(2)	−83(1)	3.3(9)	8(1)	3.0(9)	0.0(9)	0.5(7)	−1.1(9)
B(11)	76(2)	−120(2)	13(1)	3.1(8)	4.1(9)	5(1)	0.1(9)	0.8(7)	−1.4(9)
B(12)	230(2)	−158(2)	−14(2)	3.0(9)	4(1)	8(1)	−0.2(7)	2.0(9)	−2.1(9)
C(13)	14(1)	7(1)	190(1)	1.2(6)	2.8(7)	4.8(9)	0.2(5)	0.4(6)	−0.4(7)
C(14)	−126(1)	18(1)	190(1)	1.0(5)	3.9(7)	5.0(8)	0.2(6)	1.1(7)	0.0(7)
C(15)	−174(1)	55(1)	282(1)	2.5(7)	5.4(9)	4.6(9)	0.2(7)	0.7(6)	−0.6(8)
C(16)	−304(2)	65(2)	291(2)	2.9(8)	8(1)	6(1)	0.8(9)	3.2(9)	0(1)
C(17)	−373(1)	31(2)	212(2)	1.3(6)	7(1)	8(1)	0.0(8)	−0.2(9)	−0.6(9)
C(18)	−322(1)	−7(2)	126(1)	1.8(6)	6.5(9)	4.1(9)	0.3(7)	−0.8(7)	−0.6(9)
C(19)	−198(1)	−12(1)	111(1)	1.2(5)	6.9(9)	3.6(7)	−0.4(6)	−0.2(6)	−1.3(9)
C(20)	210(2)	288(1)	100(2)	4,6(9)	4.3(9)	6(1)	−1.8(7)	−0.3(9)	0.6(9)
C(21)	207(2)	260(1)	198(2)	3,7(9)	2.8(8)	7(1)	−0.7(7)	0.0(9)	−0.3(8)
C(22)	86(2)	238(1)	231(1)	5.2(9)	2.5(7)	6(1)	0.8(7)	−0.8(9)	−0.8(8)
C(23)	11(2)	257(1)	142(2)	3.4(8)	3.9(9)	6(1)	−0.4(7)	−0.5(8)	−0.3(8)
C(24)	86(2)	290(1)	64(1)	6(1)	2.0(7)	6(1)	1.5(7)	−1.5(9)	1.8(7)

Table 3. Some geometrical parameters of the carbocations stabilized by the cyclopentadienyl ligand

Compound	α, degrees	β, degrees	γ, degrees	ΔX, Å	Fe–C_{exo} distance, Å	Reference
$(OC)_3CrC_5H_5CPh_2$	28.9	a	0	a	2.55	8
$C_5H_5FeC_5H_4\underline{CHC_5H_4}FeC_5H_5]^+BF_4^{-\,b}$	19.9	5.1	0	a	2.78	5
$[C_5H_5FeC_5H_4\overline{CHCH(Ph)C}H(Ph)]^+BF_4^-$	14.6	2.7	0	a	a	6
$[C_5H_5FeC_5H_4CPh_2]^+BF_4^-$	20.7	9.3	0	0.08	2.715	7
$C_5H_5FeC_2B_9H_{11}CHPh$	47	13.9	0	0.20[c]	2.23	This work
$[C_5H_5FeC_5H_4CH_2]^{+\,d}$	40	10	0	0.10	a	10

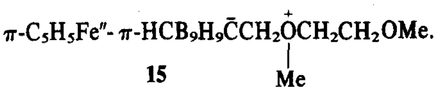
[a] This parameter is not cited in the paper.
[b] The cation contains two ferrocenyl fragments; average parameters are given.
[c] Coordinates of the center of dicarbollyl ligand open face were calculated as the arithmetical mean of the face atom coordinates.
[d] Calculated by the extended Hückel's method.



Scheme 4. Geometrical parameters of the carbocations stabilized by the cyclopentadienyl metal complexes (see Table 3).

It should be noted that, in the ^1H NMR spectrum of the dimethylsulfonium zwitterion **13** (see Table 1), the CH_3 groups are diastereotopic with chemical shifts 1.34 and 1.65 ppm. Because of a low value of the coupling constant (<1 Hz) the CH_2 protons appear as a singlet in the spectrum. The primary zwitterion **4** does not interact with ether even after refluxing for a prolonged time. On the other hand, 1,2-dimethoxyethane slowly reacts with the zwitterion **4** to form the inner salt **15**:

$$4 \xrightarrow[45°C,\ 12\,h]{MeOCH_2CH_2OMe}$$



$$\pi\text{-}C_5H_5Fe''\text{-}\pi\text{-}HCB_9H_9\bar{C}CH_2\underset{\substack{|\\ Me}}{\overset{+}{O}}CH_2CH_2OMe.$$

15

The structure of **4** was proved by spectral data (see Table 1). Nitriles also smoothly react with the primary zwitterion **4** to afford nitrilic inner salts **16** and **17**:

$$4 + N{\equiv}C\text{–}R \rightarrow \pi\text{-}C_5H_5Fe''\text{-}\pi\text{-}HCB_9H_9\bar{C}CH_2\text{–}\overset{+}{N}{\equiv}C\text{–}R$$

16, $R = CH_3$; **17**, $R = CH{=}CH_2$.

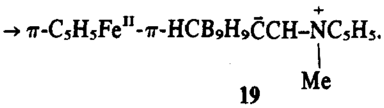
The structure of the vinyl substituted derivative of the zwitterion **17** was confirmed by ^1H NMR spectrum (see Table 1). Hydrolysis of the acetonitrilic zwitterion **16** in acidic medium, with a simultaneous oxidation of the iron atom into Fe^{III} form, leads to the *N*-substituted acetamide **18**:

$$16 \xrightarrow[2.\ H_2O_2]{1.\ H_2O,\ H^+} \pi\text{-}C_5H_5Fe^{III}\text{-}\pi\text{-}HCB_9H_9CCH_2NHCOMe$$

18.

The secondary zwitterion **5**, like the primary zwitterion **4**, adds pyridine to give inner salt **19**:

$$5 + NC_5H_5 \rightarrow$$

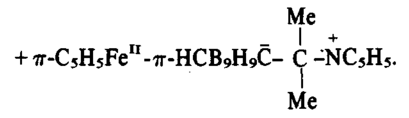


$$\rightarrow \pi\text{-}C_5H_5Fe^{II}\text{-}\pi\text{-}HCB_9H_9\bar{C}\underset{\substack{|\\ Me}}{CH}\text{-}\overset{+}{N}C_5H_5.$$

19

The tertiary zwitterion **7** reacts with pyridine giving mainly the product of addition (**20**). The product of proton elimination—the pyridinium salt of isopropenyl complex **9**—was isolated only in low yield:

$$7 + NC_5H_5 \rightarrow 9 +$$



$$+\,\pi\text{-}C_5H_5Fe^{II}\text{-}\pi\text{-}HCB_9H_9\bar{C}\text{-}\underset{\substack{|\\ Me}}{\overset{\substack{Me\\ |}}{C}}\overset{+}{\text{-}N}C_5H_5.$$

20

It is noteworthy that the rate of Lewis base addition depends upon both the base nature and the spatial environment of the carbocationic centre. Thus, reaction of the primary zwitterion **4** at 20°C is completed in a few minutes. The formation of the acrylonitrilic zwitterion **17** at 50°C proceeds for 1.5 h. The dimethylsulfonium zwitterion **18** was obtained at 20°C for 48 h. Reaction with 1,2-dimethoxyethane at 45°C is completed in 20 h. The addition of pyridine to the secondary zwitterion **5** and tertiary zwitterion **7** at 20°C takes 1 h and 170 h, respectively.

Both the primary **4** and the secondary **5** zwitterions react with organolithium compounds to give products of addition of the organic fragment to the carbocationic center (**A**):

$$4 \xrightarrow[Et_2O]{RLi} [\pi\text{-}C_5H_5Fe^{II}\text{-}\pi\text{-}HCB_9H_9CCH_2R]Li$$

A

$R{=}n\text{-}Bu, Ph, n\text{-}Bu\text{–}C{\equiv}C, o\text{-}C_2B_{10}H_{11}\text{-}1\text{-}.$

The formation of the methyl derivative (**E**), which occurs simultaneously, is the result of abstraction of the hydride-ion from the B–H bond of the intermediate compound (**A**):

$$4+\underset{\mathbf{A}}{\text{B-H}} \rightarrow \underset{\mathbf{E}}{[\pi\text{-}C_5H_5Fe^{II}\text{-}\pi\text{-}HC\text{-}B_9H_9CMe]^-}$$

The products **A** and **E** without isolation, were oxidized by H_2O_2 to afford electroneutral Fe^{III} species:

$$A+E \xrightarrow{H_2O_2,\,H_2O} \pi\text{-}C_5H_5Fe^{III}\text{-}\pi\text{-}HCB_9H_9CMe^{\dagger}$$

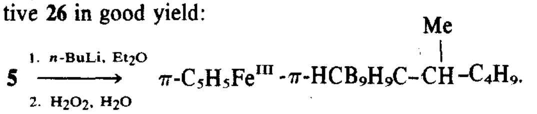
21

$$+\ \pi\text{-}C_5H_5Fe^{III}\text{-}\pi\text{-}HCB_9H_9CCH_2R$$

22, R=*n*-Bu; **23**, R=Ph; **24**, R=*n*-Bu-C≡C;

25, R=o-$C_2B_{10}H_{11}$-1-.

Similarly to the primary zwitterion **4**, the secondary ion **5** adds *n*-BuLi at the carbocationic center. Subsequent oxidation with H_2O_2 gives the 2-*n*-hexyl derivative **26** in good yield:



$$5 \xrightarrow[2.\ H_2O_2,\ H_2O]{1.\ n\text{-BuLi},\ Et_2O} \pi\text{-}C_5H_5Fe^{III}\text{-}\pi\text{-}HCB_9H_9C\text{-}\overset{\overset{\displaystyle Me}{|}}{C}H\text{-}C_4H_9.$$

26

The product of the hydride-ion abstraction was not detected in this case. We have studied the interaction between the zwitterions **4**, **5**, **7** and cyanide-, phenolate-, isobutylate-, thiophenolate-, isothiobutylate- and nitronate-ions. Intermediate products of the addition containing a Fe^{II} atom were oxidized with H_2O_2 to form the electroneutral Fe^{III} species. In the case of the primary zwitterion **4**, together with the addition products **27–32**, a product of the hydride-ion abstraction—compound **21**—was obtained:

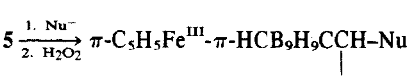
$$4 \xrightarrow[2.\ H_2O_2]{1.\ Nu^-} 21+\pi\text{-}C_5H_5Fe^{III}\text{-}\pi\text{-}HCB_9H_9CCH_2Nu$$

27, Nu=CN; **28**, Nu=*i*-BuO;

29, Nu=PhO; **30**, Nu=*i*-BuS;

31, Nu=PhS; **32**, Nu=CH_2NO_2.

The secondary zwitterion **5** readily adds cyanide- and thiophenolate-ions giving the corresponding products:



$$5 \xrightarrow[2.\ H_2O_2]{1.\ Nu^-} \pi\text{-}C_5H_5Fe^{III}\text{-}\pi\text{-}HCB_9H_9C\underset{\underset{\displaystyle Me}{|}}{C}H\text{-}Nu$$

33, Nu=CN; **34**, Nu=PhS.

The primary zwitterion **4** adds hydride-ion abstracted from $NaBH_4$, $LiAlH_4$ or i-Bu_2AlH to afford, after oxidation with H_2O_2, compound **21** in quantitative yield:

$$4 \xrightarrow{H^-} E \xrightarrow[H_2O]{H_2O_2} 21.$$

Unlike this, interaction between the carbenium zwitterion **4** and H_2AlCl in ether proceeds smoothly and yields the diethyloxonium zwitterion **14** which has been already described by us in:[12]

$$4 \xrightarrow[Et_2O]{H_2AlCl} \pi\text{-}C_5H_5Fe^{II}\text{-}\pi\text{-}HCB_9H_9\overset{-}{C}CH_2\overset{+}{O}(Et)_2.$$

14

Methyl derivative **21** is formed in this process in low yield (5%). Apparently, in the addition reaction only those molecules of ether take part which give the solvate $H_2AlCl\cdot OEt_2$, and thus increase the nucleophility of their oxygen atom. Attempts to add cyanide- and thiophenolate-ions to the tertiary zwitterion **7** failed because of the ready elimination of a proton:

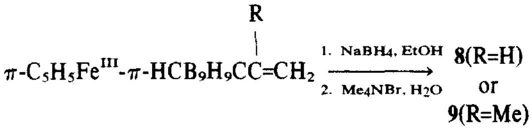
$$7 \xrightarrow{Nu^-} 9+NuH;\ Nu=CN,\ PhS.$$

This reaction proceeds readily in both protic and aprotic solvents. The addition of hydride-ion to the carbocationic centre of the tertiary zwitterion **7** was successfully performed only on treatment with an excess of $NaBH_4$ in MeCN. In this case, the isopropyl derivative **35** was obtained in quantitative yield:

$$7 \xrightarrow[2.\ H_2O_2,\ H_2O]{1.\ NaBH_4,\ MeCN} \pi\text{-}C_5H_5Fe^{III}\text{-}\pi\text{-}HCB_9H_9CCHMe_2.$$

35

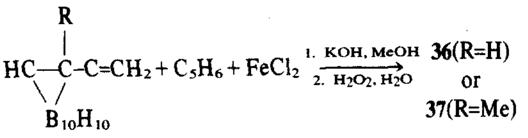
One can consider all the above reactions of the primary **4**, secondary **5**, and tertiary **7** zwitterions with nucleophilic reagents as a convenient tool for preparing various derivatives of π - cyclopentadienyl - π - (3) - 1,2 -dicarbollyliron(III) substituted at carborane carbon atom. Initial compounds **1**, **2**, **10** were prepared according to the technique developed by us.[12] Phenylcarbinol **3** was obtained by reaction of two moles of C_6H_5Li with aldehyde **10** in ether. Olefins **8** and **9** were prepared by reduction of the corresponding Fe^{III} derivatives with $NaBH_4$ in EtOH:



$$\pi\text{-}C_5H_5Fe^{III}\text{-}\pi\text{-}HCB_9H_9C\overset{\overset{\displaystyle R}{|}}{C}{=}CH_2 \xrightarrow[2.\ Me_4NBr,\ H_2O]{1.\ NaBH_4,\ EtOH} 8(R{=}H)\ \text{or}\ 9(R{=}Me)$$

36, R=H; **37**, R=Me

Ferracarboranes **36** and **37** were synthesized from the corresponding o-carboranes,[‡] cyclopentadiene, and $FeCl_2$ in methanolic alkali:



$$\underset{B_{10}H_{10}}{HC{-}\overset{\overset{\displaystyle R}{|}}{C}}\text{-}C{=}CH_2+C_5H_6+FeCl_2 \xrightarrow[2.\ H_2O_2,\ H_2O]{1.\ KOH,\ MeOH} 36(R{=}H)\ \text{or}\ 37(R{=}Me)$$

Complexes **8** and **9** are stable diamagnetic orange crystalline compounds. Their structures were confirmed by spectral data (see Table 1). Ferracarboranes **36** and **37** are stable paramagnetic, dark-green compounds. This colour may be due to conjugation of the double bond

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[†] Compound **25** was earlier described by us.[12]

[‡] o-Carborane = 1,2-dicarba-closo-dodecarborane (12).

π-electrons and the metal-carborane nucleus, which apparently alters the character of the metal-ligand interaction thus shifting the absorption bands into the visible region of the electron spectra. In the electron spectrum of **37**, the bathochromic shift relative to the non-substituted ferracarborane π-$C_5H_5Fe^{III}$-π-HCB_9H_9CH[13] amounts to 40–70 nm.

EXPERIMENTAL

Reagents and materials

Reactions with the use of boron and aluminium hydrides, organolithium and organomagnesium compounds, as well as syntheses of ferracarboranes from carboranes, cyclopentadiene, and $FeCl_2$ were carried out in an atmosphere of dry argon. Freshly distilled cyclopentadiene was used. Ether was purified by distillation over $LiAlH_4$. MeCN was distilled over CaH_2. For column and thin-layer preparative chromatography, silica gel "Chemapol" with grain size 100–160 μm was used. TLC was effected on "Silufol" plates.

Apparatus

IR spectra were recorded with a UR-10 spectrometer (KBr pellets). Electron spectra were measured with a "Hitachi EPS-3T" instrument. ^1H NMR spectra were recorded with a "RYa-2309" spectrometer (90 MHz). Mass-spectra were obtained with an "MS-30" instrument. The cell parameters and intensities of 1002 observed reflections ($F^2 \geq 4\sigma$) were measured at 20°C with an automatic four-circle "Hilger-Watts" diffractometer (CuK_α-radiation, ω-scan, $\theta \leq 57°$). The diffraction experiment was carried out according to the technique described earlier;[14] no absorption correction was applied. The structure was solved by the heavy atom method and refined by the full matrix least squares technique, at first in the isotropic and then in the anisotropic approximation. The hydrogen atoms contribution was taken into account in computation of $F_{calc.}$, although their parameters were not refined. The final R-factor was 0.075. All calculations were performed with an "Eclipse-S/200" computer using modified EXTL programs.

π-$C_5H_5Fe^{II}$-π-$HCB_9H_9\bar{C}\overset{+}{C}H_2$ **(4)**. 20 ml of conc. HCl was added to 1.43 g (3.44 mmol) of the Cs salt of **1**, suspended in 40 ml of benzene, and the mixture was shaken violently for 5 min. The benzene layer was then separated, washed with water (3 × 30 ml), dried over $MgSO_4$, concentrated *in vacuo* at 30°C, and chromatographed on a column 3 × 20 cm with C_6H_6 as an eluent. Recrystallization from benzene–heptane was performed by evaporation of the solvent *in vacuo* at 30°C, 0.67 g (2.52 mmol, 73%) of pink-red crystals of **4** was obtained, t.decomp. 148–150°C. (Found: C 36.14, H 6.21, B 36.51. $C_8H_{17}B_9Fe$. Calc. for: C 36.07, H 6.43, B 36.52, Fe 20.96%). IR (ν, cm^{-1}): 3090, 3115, 3130 (C_5H_5, CH_2), 3060 (carborane CH), 2500–2600 (BH).

π-$C_5H_5Fe^{II}$-π-$HCB_9H_9\bar{C}\overset{+}{C}HMe$ **(5)**. (a) 0.38 g (1.36 mmol, 67%) of complex **5** (light red crystals) was obtained as described above from 0.75 g (2.02 mmol) of tetramethylammonium salt of **2**; t.decomp. 136–138°C (from C_6H_6-heptane). (Found: C 39.21, H 5.92, Fe 20.11. $C_9H_{19}B_9Fe$. Calc. for: C 39.11, H 5.48, Fe 20.20%). IR (ν, cm^{-1}): 3115 (C_5H_5, CH), 3045 (carborane CH), 2985 (CH_3), 2400–2600 (BH).

(b) 0.68 g (2.43 mmol, 72%) of complex **5** was obtained similarly, from 1.2 g (3.39 mmol) of tetramethylammonium salt of **8**.

π-$C_5H_5Fe^{II}$-π-$HCB_9H_9\bar{C}\overset{+}{C}Me_2$ **(7)**. 0.76 g (2.58 mmol, 63%) of red crystals of complex **7** was obtained as described above from 1.5 g (4.08 mmol) of tetramethylammonium salt of **9**. The crystals were suspended in benzene, then filtered and washed with benzene. The filtrates were combined and evaporated *in vacuo* at 30°C. The residue was recrystallized from CH_2Cl_2 to give **7**, m.p. 280–281°C. (Found: C 40.76, H 7.24, Fe 19.32. $C_{10}H_{21}B_9Fe$. Calc. for: C 40.80, H 7.19, Fe 18.96%). IR (ν, cm^{-1}): 3126, 3124 (C_5H_5), 3014 (carborane CH), 2956, 2904 (CH_3), 2400–2600 (BH).

π-$C_5H_5Fe^{II}$-π-$HCB_9H_9\bar{C}\overset{+}{C}HC_6H_5$ **(6)**. (a) 8.95 mmol of C_6H_5Li in 15 ml of ether was added dropwise while stirring to 1.2 g (4.26 mmol) of aldehyde **10** in 150 ml of ether. After stirring for 3 h, ether was removed *in vacuo*. The dry residue was washed with pentane (4 × 25 ml), dried, and suspended in benzene (50 ml). After adding 30 ml of conc. HCl, the mixture was shaken vigorously for 5–7 min. Subsequent operations were performed as described for **4**. 0.7 g (2.04 mmol, 48%) of complex **6** as a mixture of diastereomers was obtained. The mixture was separated by preparative TLC on "Silufol" plates (15 × 15 cm, eluent: C_6H_6-heptane (1:1), 4 runs on a plate). The front diastereomer (red) has m.p. 223–224°C (decomp.) (C_6H_6-heptane). (Found: C 49.35, H 6.28, B 28.30. $C_{14}H_{21}B_9Fe$. Calc. for: C 49.10, H 6.18, B 28.41%). IR (ν, cm^{-1}): 3120 (C_5H_5), 3050, 3030 (carborane CH, C_6H_5), 2000–2600 (BH). The lagging isomer (red-brown) has m.p. 224–225°C (decomp.) ($CHCl_3$–CCl_4). (Found: C 49.17, H 6.23, B 28.80, Fe 15.56. $C_{14}H_{21}B_9Fe$. Calc. for: C 49.10, H 6.18, B 28.41, Fe 16.31%). IR (hexachlorobutadiene, ν, cm^{-1}): 3140, 3130, 3110 (C_5H_5, CH), 3050, 3030 (carborane CH, C_6H_5), 2400–2600 (BH).

(b) 6.38 mmol of C_6H_5MgBr in 15 ml of ether was added dropwise with stirring to 0.88 g (3.12 mmol) of aldehyde **10** in 150 ml of ether. After stirring the mixture for 3 h, ether was removed *in vacuo*, the residue was suspended in 100 ml of water and then filtered. The precipitate was dried and chromatographed on a column (3 × 40 cm, eluent–benzene) to yield 0.45 g (1.31 mmol, 42%) of complex **6** (mixture of diastereomers).

[π-$C_5H_5Fe^{II}$-π-$HCB_9H_9CCH{=}CH_2$]NMe_4 **(8)**. The excess of $NaBH_4$ was added to 1.54 g (5.51 mmol) of complex **36** in 200 ml of abs. ethanol. The mixture was left to stand for 2 h with periodical stirring. The solution was filtered, the filtrate was evaporated to dryness *in vacuo*, the residue was dissolved in water and treated with an excess of an aqueous solution of Me_4NBr. The precipitate thus formed was filtered, washed with iced water, dried *in vacuo* and recrystallized from MeCN–toluene mixture to yield 1.79 g (5.06 mmol, 92%) of orange needles of complex **8**, m.p. 253–254°C. (Found: C 44.48, H 8.30, B 27.55. $C_{13}H_{30}B_9Fe$. Calc. for: C 44.17, H 8.55, B 27.52%). IR (ν, cm^{-1}): 3100 (C_5H_5), 3040 (carborane CH), 2400–2600 (BH), 1620 (C=C).

[π-$C_5H_5Fe^{II}$-π-$HCB_9H_9CC(Me){=}CH_2$]NMe_4 **(9)**. 1.47 g (4.0 mmol, 94%) of complex **9** (orange needles), m.p. 246–247°C (MeCN–toluene) was obtained as described above, from 1.25 g (4.26 mmol) of the complex **37**. (Found: C 46.02, H 8.97, B 26.76. $C_{14}H_{32}B_9Fe$. Calc. for: C 45.75, H 8.76, B 26.48%). IR (ν, cm^{-1}): 3100 (C_5H_5), 3040 (carborane CH), 2980, 2960, 2930 (CH_3), 2400–2600 (BH), 1630 (C=C).

π-$C_5H_5Fe^{III}$-π-$HCB_9H_9CCH{=}CH_2$ **(36)**. 46 g (0.7 mol) of KOH was added in small portions under stirring to a solution of 11.85 g (69.6 mmol) of 1-vinyl-*o*-carborane in 50 ml MeOH. After spontaneous exothermal reaction was completed, the mixture was refluxed under stirring for 3 h. 9.2 g (139.2 mmol) of cyclopentadiene and, 5 min later, a solution of 13.23 g (104.4 mmol) of anhydrous $FeCl_2$ in 50 ml of MeOH were added under stirring at 20°C. The mixture was refluxed under stirring for 4.5 h, diluted with 200 ml of water and filtered. The precipitate was washed with water (4 × 50 ml) and the combined filtrates were concentrated *in vacuo* to the volume of 300 ml. The stream of CO_2 was passed through the reddish-orange suspension up to pH 8-9, and 20 ml of 30% H_2O_2 was added. The green precipitate thus formed was filtered, washed with water and dried. Recrystallization from a benzene–heptane mixture afforded 11.26 g (40.3 mmol, 58%) of dark green crystals of complex **36**, m.p. 138–139°C. (Found: C 39.49, H 6.33, B 34.84, $C_9H_{18}B_9Fe$. Calc. for: C 38.69, H 6.49, B 34.83%). IR (ν, cm^{-1}): 3100 (C_5H_5), 3020 (carborane CH), 2400–2600 (BH), 1620 (C=C).

π-$C_5H_5Fe^{III}$-π-$HCB_9H_9CC(Me){=}CH_2$ **(37)**. 6.91 g (23.55 mmol, 41%) of dark green crystals of complex **37**, m.p. 174–175°C (decomp.) (C_6H_6-heptane) was prepared according to the above procedure, from 10.55 g (57.25 mmol) of 1-isopropenyl-*o*-carborane, 38 g (0.57 mmol) of KOH, 7.57 g (114.49 mmol) of cyclopentadiene and 10.86 (85.87 mmol) of anhydrous $FeCl_2$ in 100 ml of MeOH. (Found: C 41.44, H 6.80, B 33.10. $C_{10}H_{26}B_9Fe$. Calc. for: C 40.94, H 6.87, B 33.16%). IR (ν, cm^{-1}): 3114 (C_5H_5), 3054 (carborane CH), 2994, 2964, 2944 (CH_3), 2400–2600 (BH), 1627

Table 4. Reactions of zwitterions **4**, **5** and **7** with Lewis bases

Zwitterion ion	Lewis base	Ion:base ratio	Solvent	T, °C	Reaction time	Isolation method	Product	Yield %
4	Ph_3P	1.2	$CHCl_3$-hexane	20	1 min	a	**11**	87
4	C_5H_5N	3.9	C_6H_6	20	1 min	a	**12**	95
4	Me_2S	Excess	Me_2S	20	48 h	b	**13**[c]	45
4	$MeOCH_2CH_2OMe$	Excess	$MeOCH_2CH_2OMe$	40–45	20 h	d	**15**	58
4	MeCN	Excess	MeCN	20	30 min	d	**16**[e]	57
4	$H_2C=CHCN$	Excess	$H_2C=CHCN$	50	30 min	d	**17**	61
5	C_5H_5N	1.2	C_6H_6-hexane	20	1 h	a	**19**	72
7	C_5H_5N	Excess	C_5H_5N	20	170 h	f	**20**	30
							37	6

[a] Re-precipitation.
[b] Preparative TLC using C_6H_6-hexane (4:1).
[c] Together with 3% of **25**.
[d] Column chromatography, elution with C_6H_6.
[e] Together with 5% of **25**.
[f] Column chromatography, elution with $CHCl_3$.

Table 5. Melting points and elemental analyses of the inner salts

Compound	M.p., °C (solvent)	Formula	Found/Calcd % C	H	Fe	E
11	156–158[a] (acetone–heptane)	$C_{26}H_{32}B_9FeP$	$\frac{59.16}{59.07}$	$\frac{5.97}{6.10}$		$\frac{5.88}{5.86}$
12	124–125 (C_6H_6)	$C_{13}H_{22}B_9FeN$	$\frac{45.26}{45.20}$	$\frac{6.57}{6.42}$		$\frac{3.66}{4.05}$
13	190–191 (C_6H_6–heptane)	$C_{10}H_{23}B_9FeS$	$\frac{36.97}{36.56}$	$\frac{7.11}{7.06}$	$\frac{16.96}{17.00}$	$\frac{10.12}{9.76}$
15[c]	128–129 (C_6H_6–heptane)	$C_{12}H_{27}B_9FeO_2$	$\frac{40.36}{40.43}$	$\frac{7.72}{7.63}$	$\frac{16.24}{16.67}$	
16	188[b] (C_6H_6)	$C_{10}H_{22}B_9FeN$	$\frac{38.82}{39.07}$	$\frac{6.66}{6.56}$		$\frac{4.54}{4.56}$
17	162–165[b] (C_6H_6–heptane)	$C_{11}H_{20}B_9FeN$	$\frac{41.35}{41.36}$	$\frac{6.08}{6.31}$		$\frac{3.91}{4.38}$
19	>300	$C_{14}H_{24}B_9FeN$	$\frac{46.76}{46.77}$	$\frac{6.44}{6.73}$	$\frac{15.22}{15.50}$	$\frac{3.38}{3.90}$
20[d]	72–74[b] ($CHCl_3$–heptane)	$C_{15}H_{26}B_9FeN$	$\frac{48.00}{48.23}$	$\frac{7.00}{7.02}$		

[a] With decomposition.
[b] Decomposition temperature.
[c] Found: B 27.28%; Calc. for: B 27.19%.
[d] Found: B 25.59%; Calc. for: B 26.05%.

(C=C). Electron spectrum (CH_2Cl_2, λ_{max}, (ϵ)): 265 (21300), 292 (16500), 430 (1090), 625 (620) nm.

Reactions of zwitterions **4**, **5**, *and* **7** *with Lewis bases.* Experimental data are cited in Tables 4 and 5.

π-$C_5H_5Fe^{III}$-π-$HCB_9H_9NHCOMe$ **18**. 100 ml of 0.1 *N* H_2SO_4 and 5 ml of 30% H_2O_2 was added to a solution of 0.24 g (0.78 mmol) of inner salt **16** in 150 ml of benzene. The mixture was shaken for 10 h and was allowed to stand overnight. The benzene layer was separated, washed with water (4 × 50 ml), dried over Na_2SO_4, evaporated *in vacuo*, and chromatographed on a column (3 × 25 cm) using a benzene–acetone mixture (4:1) as eluent. Recrystallization from benzene–heptane furnished 0.18 g (0.57 mmol, 72%) of violet crystals of complex **18**, m.p. 165–166°C (decomp.). (Found: C 37.03, H 6.51, B 29.55. $C_{10}H_{21}B_9FeNO$. Calc. for: C 37.02, H 6.51, B 29.99%). IR (ν, cm^{-1}): 3200–3400 (NH), 3110 (C_5H_5), 3080 (carborane CH), 2990, 2940, 2870, (CH_2, CH_3), 2400–2600 (BH), 1745 (C=O).

Reactions of zwitterions **4**, **5**, *and* **7** *with nucleophilic reagents (standard procedure).* An excess of nucleophilic reagent in ether, THF or ethanol was added to a solution of the zwitterion in the same solvent. The mixture was shaken vigorously for several minutes, its composition being monitored by TLC. After remov-

Table 6. Reactions of the zwitterions **4**, **5**, and **7** with nucleophilic reagents

Zwitterion	Nucleophilic reagent	Solvent	Nucleophilic reagent: zwitterion ratio (% mol)	Parameters of columns, cm	Eluent	Reaction products	Yield, %
4	*n*-BuLi	Et_2O	1.07	3×25	C_6H_6-hexane (1:1)	**21**	21
5	*n*-BuLi	Et_2O	1.2	2×30	C_6H_6-hexane (1:1)	**26**	35
4	PhLi	Et_2O	1.07	3×25	C_6H_6	**22**[a]	38
4	*n*-BuC≡CLi	Et_2O	1.7	3×25	C_6H_6-hexane (1:1)	**23**	31
						25	12
4	1,2-$C_2B_{10}H_{11}$-1-Li	Et_2O	1.21	3×25	C_6H_6-hexane (2:3)	**24**	5
						25	16
4	$NaBH_4$	MeCN	Excess	3×20	C_6H_6	**25**	97
4	$LiAlH_4$	Et_2O	Excess	3×20	C_6H_6	**25**	95
4	*i*-Bu_2AlH	Et_2O–C_6H_6	Excess	3×20	C_6H_6	**25**	94
4	H_2AlCl	Et_2O	1.05	3×30	C_6H_6	**14**	49
						25	5
7	$NaBH_4$	MeCN	Excess	3×20	C_6H_6	**35**	96
4	NaCN	EtOH	2.34	3×25	C_6H_6	**27**	49
5	NaCN	EtOH	1.7	2×25[b]	C_6H_6	**33**	59
7	NaCN	EtOH	2.15	3×20	C_6H_6	**37**	98
4	*i*-BuONa	*i*-BuOH	1.5	2×25	C_6H_6-hexane (2:3)	**28**	10
						25	8
4	*i*-BuSNa	THF	3.27	2×25	C_6H_6-hexane (2:3)	**30**	20
						25	16
4	PhONa	EtOH	1.51	2×25	C_6H_6-hexane (2:3)	**29**	11
4	PhSNa	THF	2.44	3×40	C_6H_6-hexane (1:1)	**31**	22
						25	15
5	PhSNa	EtOH	2.05	3×40	C_6H_6-hexane (2:3)	**34**	37
7	PhSNa	THF	4.65	3×20	C_6H_6	**37**	95
4	$LiCH_2NO_2$	THF	6.9	3×30	C_6H_6	**32**	36
						25	10

[a] Mass-spectrum (*m*/*e*): 345 (M^+, $^{12}C_{14}{}^{1}H_{22}{}^{11}B_9{}^{56}Fe$).

[b] Silica gel was deactivated by water (10 wt%).

Table 7. Melting points and elemental analyses of the products of reactions of the zwitterions with nucleophilic reagents

Compound	M.p., °C[a]	Formula	$\frac{\text{Found}}{\text{Calc.}}$ % C	H	B	E
21	150–151	$C_{12}H_{26}B_9Fe$	$\frac{44.49}{44.56}$	$\frac{7.88}{8.10}$		
22	156–157	$C_{14}H_{22}B_9Fe$	$\frac{48.99}{48.96}$	$\frac{6.56}{6.46}$	$\frac{28.28}{28.33}$	
23	51–52[c]	$C_{14}H_{26}B_9Fe$	$\frac{48.36}{48.39}$	$\frac{7.53}{7.54}$		
24	171–172[b]	$C_{10}H_{28}B_{19}Fe$	$\frac{29.84}{29.32}$	$\frac{6.62}{6.89}$	$\frac{49.94}{50.15}$	
26	138–139	$C_{13}H_{28}B_9Fe$	$\frac{46.68}{46.26}$	$\frac{8.21}{8.36}$		
27	149–151	$C_9H_{17}B_9FeN$	$\frac{36.99}{36.97}$	$\frac{5.89}{5.86}$		$\frac{4.62}{4.79}$
28	106–108[c]	$C_{12}H_{26}B_9FeO$	$\frac{42.57}{42.45}$	$\frac{7.57}{7.34}$		
29	124–125	$C_{14}H_{22}B_9FeO$	$\frac{46.97}{46.78}$	$\frac{6.16}{6.17}$		
30	69–71[c]	$C_{12}H_{26}B_9FeS$	$\frac{40.51}{40.54}$	$\frac{7.50}{7.37}$		
31	125–126	$C_{14}H_{22}B_9FeS$	$\frac{44.81}{44.78}$	$\frac{6.05}{5.90}$		
32	153–154	$C_9H_{19}B_9FeNO_2$	$\frac{33.18}{33.12}$	$\frac{5.86}{5.87}$		$\frac{4.28}{4.29}$
33	151–152	$C_{10}H_{19}B_9FeN$	$\frac{39.50}{39.15}$	$\frac{6.41}{6.25}$		$\frac{4.51}{4.57}$
34	139–140	$C_{15}H_{24}B_9FeS$	$\frac{46.24}{46.25}$	$\frac{6.29}{6.21}$		
35	169–170[b]	$C_{10}H_{22}B_9Fe$	$\frac{40.92}{40.66}$	$\frac{7.90}{7.51}$	$\frac{33.18}{32.93}$	

[a] From C_6H_6-heptane.
[b] With decomposition.
[c] From pentane.

Table 8. IR spectra of the products of reactions of the zwitterions **4**, **5**, and **7** with electroneutral Lewis bases and nucleophilic reagents

Compound	Frequency, cm^{-1} (assignment)
11	3110 (C_5H_5), 3070 (carborane CH, C_6H_5), 2960, 2910, (CH_2), 2400–2600 (BH)
12	3090, 3670, 3050 (C_5H_5, C_5H_5N, carborane CH), 2400–2600 (BH), 1640 ($C_5H_5N^+$)
13	3120, 3110, 3090 (C_5H_5), 3025 (carborane CH), 2990, 2930 (CH_3), 2400–2600 (BH)
15	3120, 3100 (C_5H_5), 3040 (carborane CH), 2830–3010 (CH_2, CH_3), 2400–2600 (BH)
16	3100 (C_5H_5), 3050 (carborane CH), 2990, 2940, 2930 (CH_2, CH_3), 2400–2600 (BH)
17	3130 (C_5H_5), 3075, 3040 (carborane CH, CH=CH_2), 2400–2600 (BH), 2315 (C≡N), 1600 (C=C)
19	3150, 3120, 3100, 3080 (C_5H_5, C_5H_5N, carborane CH), 2980, 2940, 2880 (CH_3, CH), 2400–2600 (BH), 1630 ($C_5H_5N^+$)
20	3120, 3100, 3064 (C_5H_5, C_5H_5N, carborane CH), 2980, 2960, 2920 (CH_3) 2400–2600 (BH), 1630 ($C_5H_5N^+$)
21	3120 (C_5H_5), 3060 (carborane CH), 2960, 2940, 2880 (CH_3, CH_2), 2400–2600 (BH)
22	3120, 3100, 3080, 3030 (C_5H_5, C_6H_6, carborane CH), 2400–2600 (BH)
23	3120 (C_5H_5), 3040 (carborane CH), 2850–3000 (CH_2, CH_3), 2400–2600 (BH)
24	3110 (C_5H_5), 3035 (carborane CH), 2400–2600 (BH)
26	3115 (C_5H_5), 3060 (carborane CH), 2970, 2930, 2870 (CH_2, CH_3), 2400–2600 (BH)
27	3120 (C_5H_5), 3040, 3030 (carborane CH), 2960, 2930 (CH_2), 2400–2600 (BH), 2260 (C≡N)
28	3115, 3100 (C_5H_5), 3060 (carborane CH), 2870–2975 (CH_2, CH_3), 2400–2600 (BH)
29	3120 (C_5H_5), 3050 (carborane CH, C_6H_5), 2930, 2890 (CH_2), 2400–2600 (BH)
30	3110 (C_5H_5), 3025 (carborane CH), 2875–2965 (CH_2, CH_3), 2400–2600 (BH)
31	3110, 3090 (C_5H_5), 3030 (carborane CH, C_6H_5), 2935 (CH_2), 2400–2600 (BH)
32	3115 (C_5H_5), 3035 (carborane CH), 2960, 2930 (CH_2), 2400–2600 (BH), 1558, 1386, 855 (NO_2)
33	3120 (C_5H_5), 3030 (carborane CH), 3010, 2980, 2940 (CH_3, CH), 2400–2600 (BH)
34	3120 (C_5H_5), 3030, 3020 (carborane CH, C_6H_5), 2990, 2950, 2920 (CH_3, CH)
35	3120 (C_5H_5), 3060 (carborane CH), 2990, 2950, 2890 (CH_3, CH), 2400–2600 (BH)

[a] Not all the absorption bands are given.

ing solvent *in vacuo*, the dry residue was suspended in water, treated with CO_2 up to pH 8–9 and carefully oxidized with 30% H_2O_2. The reaction products were extracted with benzene, the extracts were washed with water, dried over $MgSO_4$, and chromatographed on columns. Experimental data are cited in Tables 6 and 7. IR spectra of inner salts and products of addition of the nucleophilic reagents are given in Table 8.

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