Organometallic Chemistry

Electrophilic substitution reactions of ferracarborane 3-(η^5-Cp)-4-SMe_2-3,1,2-$FeC_2B_9H_{10}$

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Mercuration and bromination reactions of ferracarborane 3-(η^5-Cp)-4-SMe_2-3,1,2-$FeC_2B_9H_{10}$ (**1**) were investigated. Mercuration of **1** under mild conditions (mercury trifluoroacetate in dichloromethane) results in 8-monosubstituted mercury derivative as the only reaction product. Depending on the reaction conditions, bromination of **1** results in 8-mono- or 7,8-disubstituted bromo derivatives. The structures of the monomercury and dibromo derivatives of **1** were established by X-ray analysis.

Key words: ferracarboranes, mercuration, bromination, X-ray analysis.

Previously,[1–3] we studied the reactions of electrophilic substitution of hydrogen atoms in icosahedral carboranes taking mercuration reactions as examples. It was shown that the electron deficiency of carboranes hinders substitution and the reactions proceed only under the action of strong mercurating agents (*e.g.*, mercury trifluoroacetate in trifluoroacetic acid). In this case, substitution in *ortho*- and *meta*-carboranes occurs mainly at the boron atom in position 9, which is the most distant from carbon atoms.

In icosahedral carboranes, one of the boron atoms can be substituted by ML (M = Co, Fe, Ni; L = Cp, $C_2B_9H_{11}$) fragments; in some instances, this allows the use of milder mercurating agents.[4,5]

Depending on the type of metallacarborane and on the reaction conditions, electrophilic substitution can occur either at position 9 and 12, as is the case with *o*-carborane, or at position 8, adjacent to the metal atom.[6–8] For instance, bromination of 3-(η^5-Cp)-3,1,2-$FeC_2B_9H_{11}$ with bromine (1 mole) in the absence or in the presence of catalyst ($AlCl_3$) leads to substitution at position 8. No further bromination occurs in the former case. Treatment of 3-(η^5-Cp)-3,1,2-$FeC_2B_9H_{11}$ with an excess of bromine in the presence of $AlCl_3$ resulted in 8,9-di- and 8,9,12-trisubstituted bromo derivatives.[9]

In a continuation of our studies of electrophilic substitution reactions of icosahedral metallacarboranes, in this work we studied electrophilic bromination and mercuration of ferracarborane 3-(η^5-Cp)-4-SMe_2-3,1,2-$FeC_2B_9H_{10}$ (**1**), a derivative of charge-compensated monoanion [9-SMe_2-7,8-$C_2B_9H_{10}$]$^-$. In this metallacarborane, the SMe_2 substituent is attached to one of the boron atoms bonded to the metal atom.

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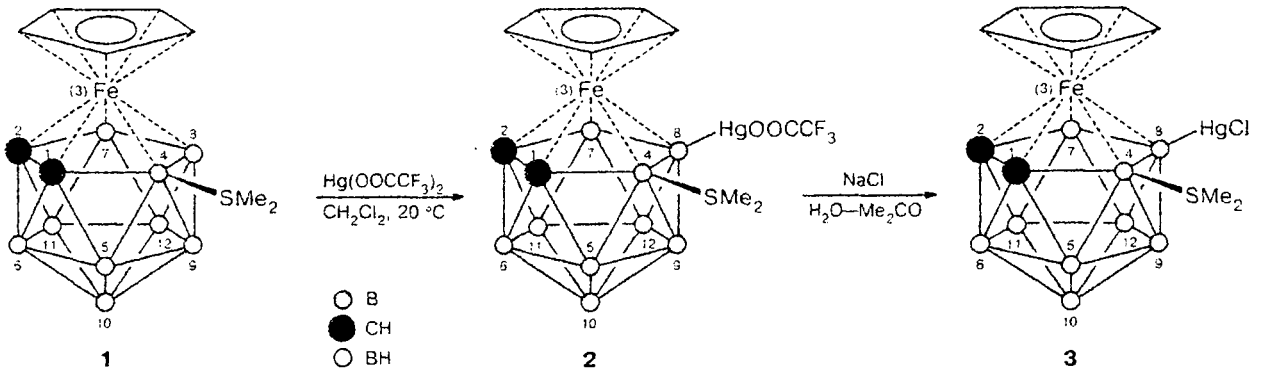
Scheme 1



1 **2** **3**

Results and Discussion

We found that mercuration of the initial ferracarborane **1** with mercury trifluoroacetate at a 1 : 1 ratio in dichloromethane at 20 °C results in the formation of compound **2** (Scheme 1) as the only reaction product.

The position of substitution for complex **2** was determined by ^{11}B and ^{11}B—^{11}B COSY NMR spectroscopy. Unlike compound **1**, which has a singlet ^{11}B NMR spectrum (δ −5.0), compound **2** exhibits two singlet signals, at δ −5.1 and −2.8. Hence, the virtually unchanged resonance at δ −5.1 in the spectrum of complex **2** can be attributed to the B(4) atom. Analysis of the ^{11}B—^{11}B COSY NMR spectrum of compound **2** (Fig. 1) was based on the fact that there is a cross-peak between the signal from the B(4) atom and the singlet at δ −2.8; in addition, a Hg—B spin-spin coupling constant (J_{Hg-B} = 2192.4 Hz) was observed for the latter signal. Therefore, the structure of complex **2** is described by the formula 3-(η^5-Cp)-4-SMe_2-8-CF_3COOHg-3,1,2-$FeC_2B_9H_9$.

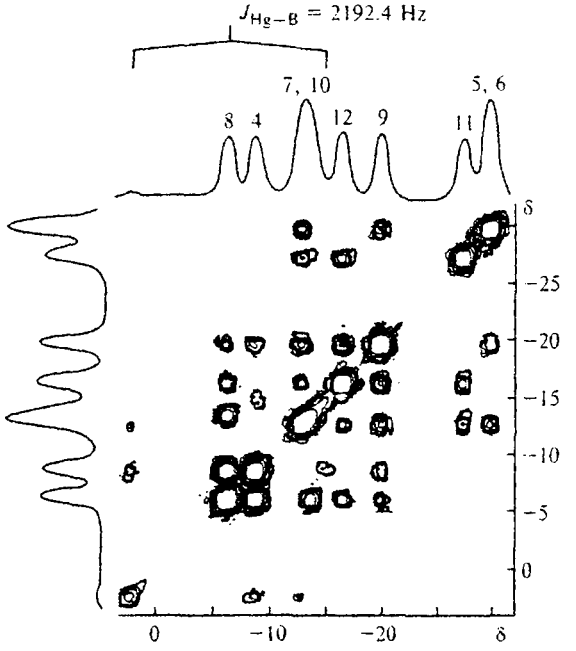


Fig. 1. ^{11}B—^{11}B COSY NMR spectrum of compound **2**.

Treatment of compound **2** with sodium chloride in a water—acetone mixture resulted in a chloromercuro derivative **3**. The structure of **3** was studied by X-ray analysis.

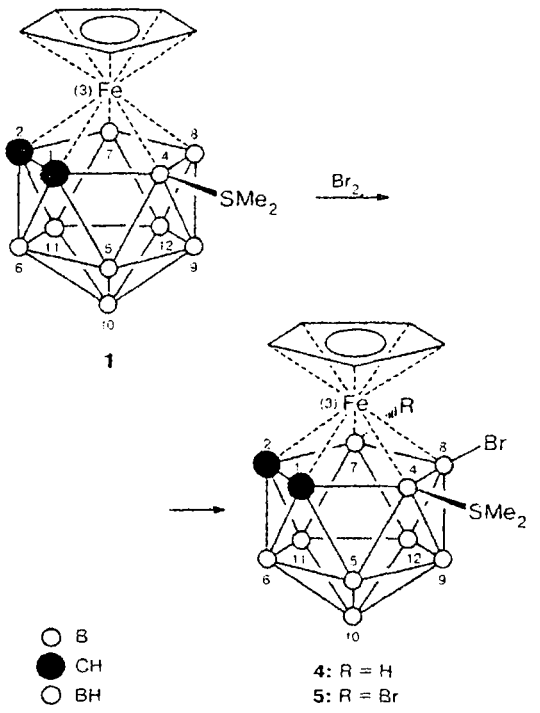
In all reliably established cases, mercuration of previously studied icosahedral metallacarboranes occurs mainly at position 9 and then at positions 12 and 8. Mercuration of 3-(η^5-Cp)-3,1,2-$FeC_2B_9H_{11}$ at position 9 is explained[10] by possible steric hindrances produced by the η^5-C_5H_5Fe fragment at the B(8) atom.

Depending on the reaction conditions, bromination of ferracarborane **1** follows different pathways. Whereas the reaction proceeds with difficulty in CCl_4, bromination of compound **1** with bromine in dichloromethane at a 1 : 1 ratio and high dilution results in the monosubstituted bromo derivative, 3-(η^5-Cp)-4-SMe_2-8-Br-3,1,2-$FeC_2B_9H_9$ (**4**) (Scheme 2), as the only reaction product.

The reaction with a two-fold excess of bromine results in disubstituted derivative **5**; no complex **4** is formed in this case. This also holds for the reactions of **1** with up to a 30-fold excess of bromine. Only the mass spectrum of the reaction mixture reveals a molecular ion peak with *m/z* 551, corresponding to the trisubstituted product, 3-(η^5-Cp)-4-SMe_2-3,1,2-$FeC_2B_9H_7Br_3$. The positions of substitution for compounds **4** and **5** were determined using the ^{11}B—^{11}B COSY NMR spectra (Figs. 2 and 3). As in the case of complex **2**, interpretation of the spectra was based on consideration of the singlet signal attributed to the B(4) atom.

It was found that in complex **5** the second Br atom is at the B(7) atom and that the structure of the complex is described by the formula 3-(η^5-Cp)-4-SMe_2-7,8-Br_2-3,1,2-$FeC_2B_9H_8$. This was confirmed by X-ray analysis. Thus, unlike unsubstituted 3-(η^5-Cp)-3,1,2-$FeC_2B_9H_{11}$, bromination of compound **1** in the absence of a catalyst proceeds more deeply and virtually ceases at the stage of formation of disubstituted derivative.

Scheme 2



High yields of the mercuration and bromination products of ferracarborane **1** (isomer **2** as the only reaction product and disubstituted complex **5**, respectively) indicate the absence of steric hindrances to substitution at the open face of the dicarbollide ligand even if other substituents are attached to this face. In addition, it is obvious that the electron-acceptor Me_2S group has a strong effect on the electrophilic substitution of compound **1** as compared to the metallacarboranes studied previously. This effect is likely more pronounced at position 9 of the carborane cage and leads to a decrease in the electron density, so that electrophilic substitution occurs at positions 7 and 8.

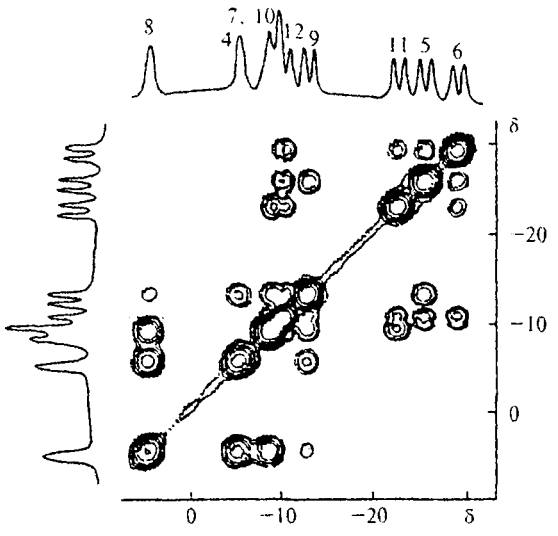


Fig. 2. ^{11}B—^{11}B COSY NMR spectrum of compound **4**.

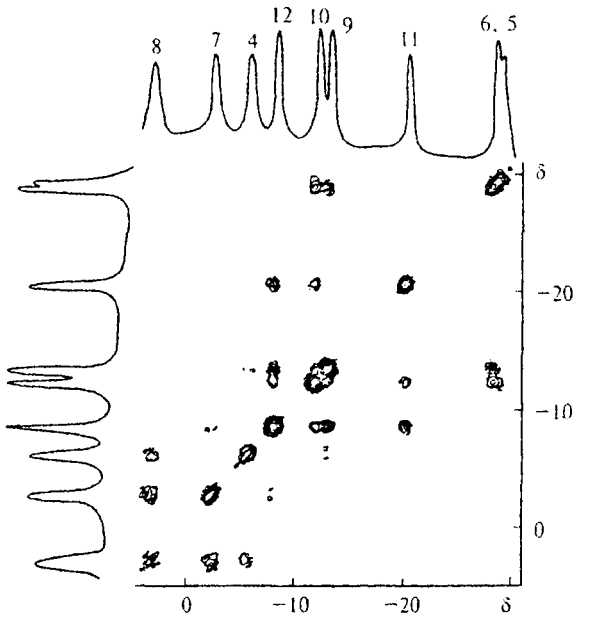


Fig. 3. ^{11}B—^{11}B COSY NMR spectrum of compound **5**.

Compounds **2**—**5** are orange crystalline substances. They are readily soluble in acetone, THF, dichloromethane, and chloroform and insoluble in hexane. The complexes obtained are air-stable in the solid state and decompose slowly in solution.

The composition and structure of complexes **2**—**5** were also confirmed by elemental analysis and by NMR spectroscopy. ^1H NMR spectra of **2**—**5** exhibit singlet signals from the Cp ring protons at δ 5, two singlets from protons at the carborane cage carbon atoms in the region δ 3—4, and singlets from the methyl group protons at the S atom in the region δ 2—3. ^{11}B NMR spectra of compounds **1**—**5** are presented in Table 1. Noteworthy are the low-field shifts of the singlet signals of substituted boron atoms in the ^{11}B NMR spectra of compounds **2**—**5** as compared to the corresponding signals in the ^{11}B NMR spectrum of **1**. The shift magnitude depends on the nature of the substituent and varies from 10 ppm for compounds **4** and **5** to 6 ppm for **3** and 2 ppm for **2**.

Molecular structure description. In the structure of crystal solvate **3** · Me_2CO the molecules of compound **3** (Fig. 4) are united into centrally symmetrical dimers (Fig. 5) by secondary Hg(1)...Cl(1) interaction (the corresponding interatomic distance, 3.175(1) Å, is much shorter than the sum of the van der Waals radii of mercury and chlorine atoms, 2.0 [11] and 1.90 Å,[12] respectively) and by the solvate acetone molecules. The latter are held near the dimers by the Cl(1)...H interaction with the H atoms of the methyl groups of acetone

Table 1. ^{11}B NMR spectral parameters of compounds **1**—**5**

Compound	δ (J_{B-H}/Hz)								
	B(4)	B(5)	B(6)	B(7)	B(8)	B(9)	B(10)	B(11)	B(12)
1	−5.0	−26.2 (177.3)	−27.9 (202.0)	−9.5 (129.3) or −10.4 (93.1)	−5.0	−16.7 (135.2)	−10.4 (93.1) or −9.5 (129.3)	−23.8 (149.7)	−12.3 (143.8)
2	−5.1	−26.4 (157.0)	−26.4 (157.0)	−9.5 (147.2)	−2.8 (2192.4*)	−16.3 (145.1)	−9.5 (147.2)	−23.9 (156.0)	−12.8 (153.4)
3	−4.7	−26.2 (157.9)	−26.2 (157.9)	−8.9 (135.0)	1.1 (2088.6*)	−15.8 (147.3)	−8.9 (135.0)	−23.5 (155.1)	−12.3 (151.8)
4	−5.1	−25.4 (151.9)	−28.9 (168.5)	−8.9 (146.6)	5.0	−12.6 (143.1)	−8.9 (146.6)	−22.6 (154.2)	−10.0 (148.2)
5	−7.7	−30.5 (160.5)	−30.5 (160.5)	−3.9	1.7	−14.8 (122.0)	−13.3 (125.6)	−21.7 (163.9)	−9.4 (153.4)

* The J_{B-Hg} value is given.

molecules and by the O(1)...H interaction with H atoms of the methyl groups of the SMe_2 substituent. The O(1) atom forms two directed contacts, one within the dimer (see Fig. 5) and the other being the similar O(1)...H(4) contact with a methyl group of the SMe_2 substituent of the nearest dimer. Thus dimers are united to form chains extended along the *b* crystallographic axis. All these interactions are rather weak (H...Cl 2.93(1) and 2.94(1) Å, O...H 2.59(1) and 2.70(1) Å) and are close to normal intermolecular contacts (2.97 and 2.45 Å, respectively). However, the fact that these contacts are directed makes it possible to consider them as structure-forming contacts.

The given structure of complex **5** (Fig. 6) includes the molecules bound by the van der Waals interaction only.

Molecules **3** and **5** are structurally similar. However, comparison of the absolute values of their geometric parameters requires taking into account the fact that the X-ray studies were carried out at different temperatures. This means that, since the atomic vibrations in **5** are "frozen" as compared to **3**, the bond lengths in the latter should be somewhat shorter, especially in the most flexible molecular fragments.

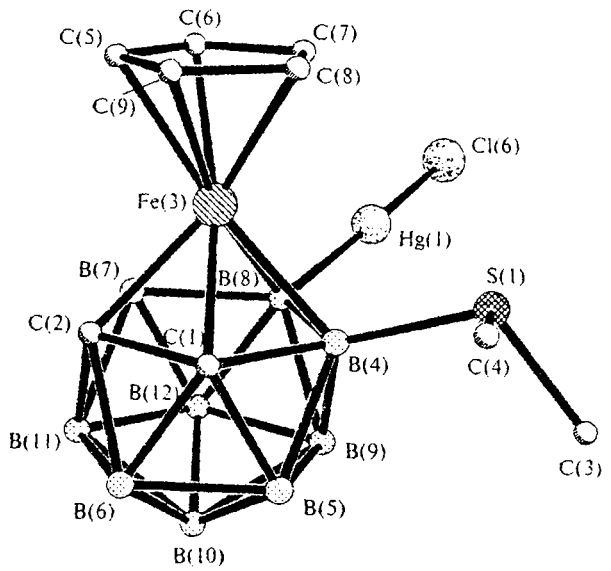


Fig. 4. Molecular structure of compound **3** (hydrogen atoms are not shown).

In both molecules **3** and **5** the cyclopentadienyl ring is nearly parallel to the $\{C_2B_3\}$ open face of the carborane cage (the corresponding dihedral angles are equal to 3.8(6) and 2.8(2)°, respectively). The separation between these planes is 3.125 Å (**3**) and 3.115 Å (**5**). Despite the presence of three substituents attached to the open face of the carborane cage of molecule **5**, here the $\{C_2B_3\}$ face is only slightly (by 0.011 Å) closer to the Fe atom than in molecule **3**, that is, the Fe...$\{C_2B_3\}$ distance is 1.433(1) Å for **5** and 1.444(3) Å for **3**; at the same time, the Fe...Cp ring distances in both molecules are nearly equal (1.681(3) and 1.682(1) Å, respectively). Molecules **3** and **5** have skewed conformations (Fig. 7) in which the angles of twist of the Cp ring with respect to the $\{C_2B_3\}$ face lie between 22.9 and 27.6° for **3** and between 20.9 and 23.7° for **5** (the average values are 25.2° and 22.6°, respectively).

In both molecules, the SMe_2 fragments have the same orientation with respect to the Fe atoms, namely, both Me groups are turned away from the iron atoms. The distance between the S and Fe atoms in **3** and **5** is 3.325(2) and 3.360(1) Å, respectively. On the other hand, the arrangement of Me substituents with respect to the substituents attached to the B(8) atom (the Hg(1) atom in **3** and the Br(2) atom in **5**) is different. As can be seen in Figs. 4, 6, and 7, in molecule **5** the S(1)—C(3) bond is parallel to the C(1)—B(4) edge of the $\{C_2B_3\}$ face (the C(1)—B(4)—S(1)—C(3) torsion angle is 176.0°) and oriented toward the Br atom, while the S(1)—C(4) bond is directed nearly perpendicular to this edge (the C(1)—B(4)—S(1)—C(4) torsion angle is 79.1°). On the contrary, in molecule **3** the S(1)—C(4) bond is oriented in the opposite direction with respect to the mercury atom, being parallel to the C(1)—B(4) edge (the C(1)—B(4)—S(1)—C(4) torsion angle is 9.4°), whereas

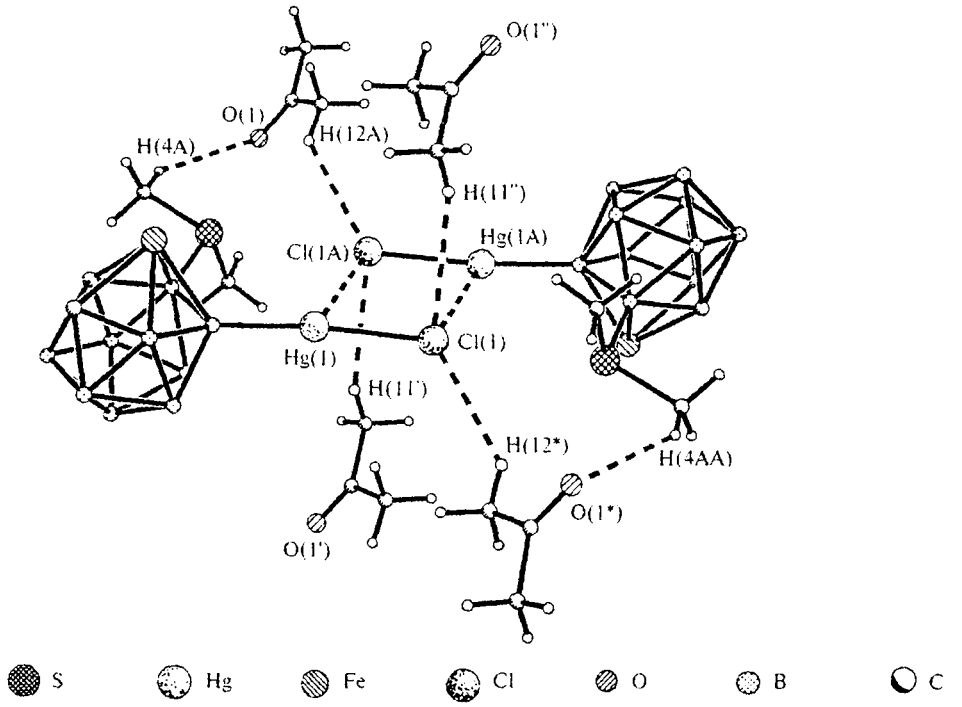


Fig. 5. Geometry of intermolecular dimer in the structure of crystal solvate **3** · Me_2CO (Cp rings and hydrogen atoms are not shown).

the S(1)—C(3) bond makes an angle of 114.4° with this edge. Therefore, in molecule **3** the SMe_2 fragment is rotated about the B(4)—S(1) bond by ~180°. Such an inversion of the Me_2S fragment can be due to steric hindrances produced at the stage of formation of intermolecular dimers in this structure, since the intramolecular contacts between the sulfur atom and substituents (S(1)...Hg(1) 4.212(1) Å in **3** and S(1)...Br(2) 4.206(1) Å in **5**) are longer than the sums of the corresponding van der Waals radii (3.90 and 3.97 Å for **3** and **5**, respectively).

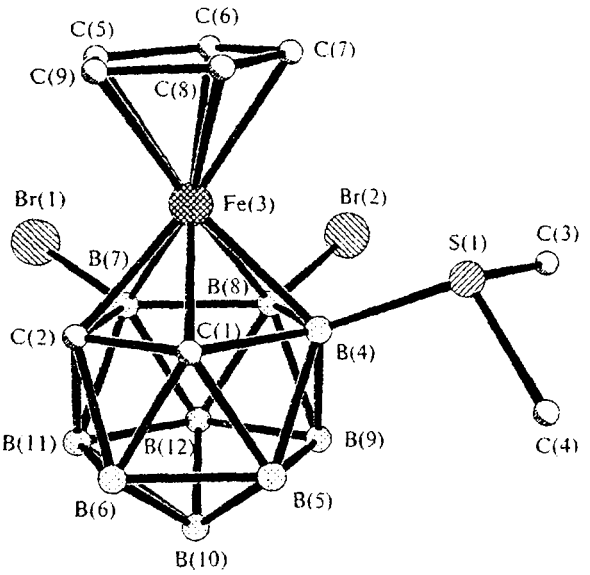
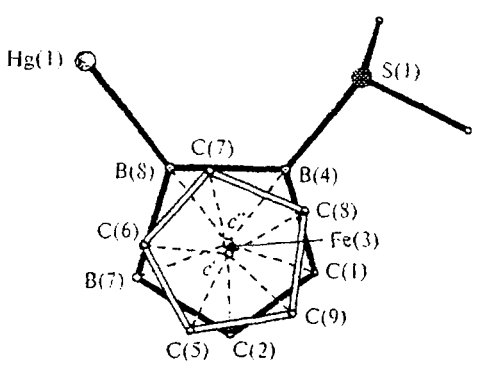


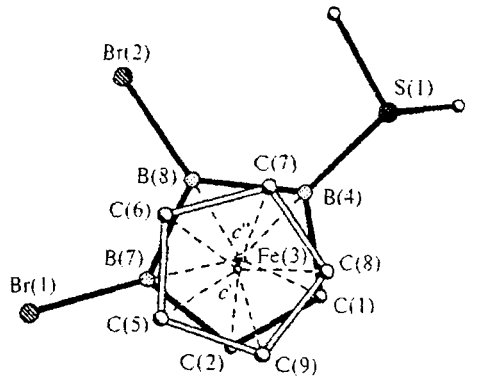
Fig. 6. Molecular structure of compound **5** (hydrogen atoms are not shown).

One more feature of the structure of molecule **3** should be pointed out. The Fe(3)—B(7) and Fe(3)—B(8) bonds are appreciably (by about 0.1 Å) longer than the corresponding bonds in molecule **5** (2.090(6) *vs.* 2.069(3) Å and 2.103(6) *vs.* 2.097(3) Å, respectively), whereas the Fe(3)—B(4) bond lengths are virtually the same (2.042(5) Å for **3** and 2.052(3) Å for **5**). This is likely due to the electronic effect of the HgCl substituent attached to the B(8) atom. The position of the iron atom with respect to the centers of the Cp ring and the $\{C_2B_3\}$ carborane face (*c'* and *c"*, respectively) is also different. The *c'*—Fe(3)—*c"* angle is 169.5° for **3** and 178.1° for **5**. In Fig. 7, the projections of the molecules on the Cp ring plane are shown. As can be seen, in molecule **3** the arrangement of the *c'* and *c"* centers differs appreciably and the Fe(3) atom is some distance away from the line connecting the two centers. On the contrary, in molecule **5** the iron atom is exactly above the centers of the rings.

Thus, we showed that attachment of the Me_2S substituent to the carborane cage has a pronounced effect on the pathways of electrophilic substitution. Compound **1** is mercurated at position 8 rather than 9, as in the case of 3-(η^5-Cp)-3,1,2-$FeC_2B_9H_{11}$, while bromination of 3-(η^5-Cp)-3,1,2-$FeC_2B_9H_{11}$ without a catalyst proceeds more deeply and the second Br atom is attached to position 7 rather than 9(12). The results obtained show



3



5

Fig. 7. Mutual orientation of the cyclopentadienyl ring and the (C_2B_3) open face of the carborane ligand in molecules **3** and **5** (*c'* and *c''* are the centers of the corresponding rings).

that the substituent attached to the boron atom of the open face of the dicarbollide ligand produces no great steric hindrances to substitution reactions.

Experimental

All reactions were performed in inert atmosphere using dry solvents prepared following standard procedures. Reaction products were isolated in air. The initial 3-(η^5-Cp)-4-SMe_2-3,1,2-$FeC_2B_9H_{10}$ complex was synthesized following the known procedure.[13]

NMR spectra were recorded on a Bruker WP-200 SY spectrometer. The operating frequencies were 200, 188.31, and 64.2 MHz for ^1H, ^{19}F, and ^{11}B, respectively. ^{11}B—^{11}B Correlation NMR spectra were recorded on a Bruker AMX-400 spectrometer operated at a frequency of 128.3 MHz. Mass spectra were recorded on a Kratos MS-890 mass spectrometer (energy of ionizing electrons 70 eV, temperature of the ion chamber of 230 °C).

3-Cyclopentadienyl-4-dimethylsulfido-8-trifluoroacetomercuro-3-ferra-1,2-dicarba-*closo*-dodecaborane (2). To a solution of compound **1** (0.5 g, 1.59 mmol) in 50 mL of CH_2Cl_2, $Hg(OCOCF_3)_2$ (0.8 g, 1.88 mmol) was added with stirring at 20 °C and the reaction mixture was stirred for an additional 30 min at the same temperature, filtered, concentrated, and recrystallized from a CH_2Cl_2—hexane mixture to give compound **2** (0.54 g, 56%), m.p. 178—179 °C. ^{19}F NMR (acetone-d_6, δ): 4.11 (s). ^1H NMR (acetone-d_6, δ): 4.85 (s, 5 H, Cp); 4.47, 3.70 (both s, 1 H each, C—H_{carb}); 2.88, 2.85 (both s, 3 H each, Me). Found (%): C, 21.38; H, 3.36; B, 15.55. $C_{11}H_{10}B_9F_3FeHgO_2S$. Calculated (%): C, 21.07; H, 3.21; B, 15.52.

8-Chloromercuro-3-cyclopentadienyl-4-dimethylsulfido-3-ferra-1,2-dicarba-*closo*-dodecaborane (3). To a solution of compound **2** (0.1 g) in acetone, a saturated aqueous NaCl solution was added slowly with stirring at 20 °C. The residue that precipitated was filtered off, washed with water, and dried *in vacuo* to give product **3** (0.09 g, 100%).

8-Bromo-3-cyclopentadienyl-4-dimethylsulfido-3-ferra-1,2-dicarba-*closo*-dodecaborane (4). To a solution of compound **1** (0.2 g, 0.6 mmol) in 30 mL of CH_2Cl_2, Br_2 (0.1 g, 0.6 mmol) in 30 mL of CH_2Cl_2 was added dropwise with stirring at 20 °C, and the reaction mixture was stirred for an additional 6 h. The solvent was removed *in vacuo*, the residue was chromatographed

Table 2. Selected crystallographic data and the refinement parameters for compounds **3** and **5**

Parameter	**3**·Me_2CO	**5**
Empirical formula	$C_{12}H_{26}B_9ClFeHgOS$	$C_9H_{19}B_9Br_2FeS$
M	607.57	472.26
Crystal habit	Plate	Needle
Crystal color	Red	Red
Crystal dimensions /mm	0.4×0.2×0.1	0.45×0.25×0.20
Space group	$P2_1/c$	$P2_1/n$
T/K	293(2)	110(2)
a/Å	12.091(2)	7.3634(3)
b/Å	8.876(2)	14.5543(6)
c/Å	19.905(4)	15.7959(7)
α/deg	—	—
β/deg	91.80(3)	97.390(1)
γ/deg	—	—
V/Å^3	2135.1(7)	1678.77(12)
Z	4	4
d_{calc}/g cm^{-3}	1.890	1.869
Diffractometer	CAD-4	Bruker SMART
Radiation	λ-Mo-Kα	λ-Mo-Kα
μ/cm^{-1}	80.83	57.65
Absorption correction	ψ-curves	SADABS software
T_{min}/T_{max}	0.400/0.982	0.361/1.000
Scan type	θ-5/3θ	ω-ω
$2\theta_{max}$/deg	56	60.1
Number of independent reflections	5134 (R_{int} = 0.0271)	4867 (R_{int} = 0.0806)
R_1 (*F*-refinement for reflections with $I > 2s(I)$)	0.0425 (4162 reflections)	0.0396 (3900 reflections)
wR_2 (F^2-refinement for all reflections)	0.1236	0.1014
Number of refined parameters	271	275
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (\alpha P)^2 + \beta P$, where $P = 1/3(F_o^2 + 2F_c^2)$	
α	0.0812	0.0576
β	0	0
GOOF	1.021	0.945
F(000)	1160	920

on a column with SiO_2 (with a CH_2Cl_2—hexane (1 : 1) mixture as eluent), concentrated, and recrystallized from a benzene—hexane mixture to give compound **4** (0.13 g, 52%), decomp.p. 216 °C. Found (%): C, 27.57; H, 5.10; Br, 19.86. $C_9H_{20}B_9FeBrS$. Calculated (%): C, 27.48; H, 5.12; Br, 20.31.

7,8-Dibromo-3-cyclopentadienyl-4-dimethylsulfido-3-ferra-1,2-dicarba-*closo*-dodecaborane (5). ***A.*** To a solution of compound **1** (0.4 g, 1.2 mmol) in 30 mL of CH_2Cl_2, a solution of Br_2 (0.12 mL, 0.4 g, 2.4 mmol) in 15 mL of CH_2Cl_2 was added with stirring at 20 °C. The solution was stirred at 20 °C until the brown solution turned pale-yellow and a yellow residue precipitated (~4 h). The substance was chromatographed on a column with SiO_2 (with a CH_2Cl_2—hexane (2 : 1) mixture as eluent) to give product **5** (0.17 g, 28%).

B. To a solution of compound **1** (0.2 g, 0.6 mmol) in 30 mL of CH_2Cl_2, a solution of Br_2 (1 mL, 3 g, 18.6 mmol) in 20 mL of CH_2Cl_2 was added with stirring at 20 °C. The solution was stirred at 20 °C until the brown solution turned pale-yellow and a yellow residue precipitated. The residue was chromatographed on a column with SiO_2 (with a benzene—hexane (1 : 1) mixture as eluent) and recrystallized from a benzene—hexane mixture to give product **5** (0.2 g, 67%), decomp.p. 242 °C. ^1H NMR (acetone-d_6, δ): 4.74 (s, 5 H, Cp); 4.43, 4.24 (both s, 1 H each, $C-H_{carb}$); 2.89, 2.85 (both s, 3 H each, Me). Found (%): C, 22.89; H, 4.06; Br, 33.84. $C_9H_{19}B_9FeBr_2S$. Calculated (%): C, 22.68; H, 3.90; Br, 33.78.

X-ray study of compounds 3 and 5. Red single crystals of solvate **3** · Me_2CO and **5** were recrystallized from acetone and a dichloromethane—hexane system, respectively. Experimental sets of intensities were collected on Enraf—Nonius CAD-4 and Bruker SMART automatic diffractometers. Selected crystallographic parameters and details of the refinement of the structures are listed in Table 2.

The structures were solved by direct methods and then the least-squares F^2_{hkl}-refinement in anisotropic approximation was performed for non-hydrogen atoms. Hydrogen atoms were located from difference Fourier syntheses and refined anisotropically (except for hydrogen atoms in the Cp ring and Me groups in structure **3**, which were found geometrically and refined using the "riding" model).

All calculations were performed using the SHELXTL PLUS 5 program package.[14]

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