

Iron and Cobalt Complexes with Thiocarborane Ligands

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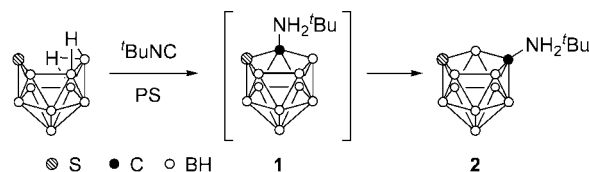
Reaction of ^tBuNC with *nido*-6-SB₉H₁₁ in the presence of Proton Sponge gives the *nido*-thiicarborane 7-^tBuNH₂-7,9-CSB₉H₉ (**2**) apparently via rearrangement of the initially formed *nido*-7-^tBuNH₂-7,8-CSB₉H₉ (**1**) isomer. Deprotonation of **2** gives the anion [*nido*-7-^tBuNH-7,9-CSB₉H₉][−] (**3**), which reacts with [CpFe(C₆H₆)]⁺ and [(C₄Me₄)Co(C₆H₆)]⁺ under visible light irradiation to give *closo*-metallathiacarboranes 1-Cp-4-^tBuNH-1,2,4-FeSCB₉H₉ (**4**) and 1-C₄Me₄-4-^tBuNH-1,2,4-CoSCB₉H₉ (**5**) in 70% yields. At 110 °C, **4** undergoes extrusion of one boron atom, giving the 11-vertex compound *closo*-1-Cp-3-B(OH)₂-1,2,3-FeSCB₈H₈ (**6**, 44%). According to DFT calculations, this process is initiated by nucleophilic attack of amine. The structures of **2**, **4**, **5**, and **6** were confirmed by X-ray diffraction.

Introduction

Metal complexes with polyhedral heteroborane ligands attract considerable attention due to their unusual properties and potential application as precursors for semiconducting materials and catalysts.¹ Particularly, the chemistry of phosphorus-² and sulfur³-containing species has been investigated in detail. The latter, however, are restricted mainly to the derivatives of thiaboranes SB₉H₁₁,⁴ SB₁₀H₁₂,⁵ S₂B₆H₁₀,⁶ S₂B₇H₈,⁷ and S₂B₁₇H₁₇.⁸ To the best of our knowledge, only four thiicarborane metal complexes have been reported.⁹

We are currently exploring the transition metal complexes of monoanionic heteroborane ligands that are similar to Cp[−].¹⁰ In particular, Mn, Fe, Co, Ru, and Rh complexes with

Scheme 1. Synthesis of the Thiicarborane 2



tricarbollide¹¹ [*nido*-R-C₃B₈H₁₀][−] and phosphadycarbollide¹² [*nido*-R-PC₂B₈H₉][−] ligands were synthesized. These compounds are of interest not only due to their close similarity to metallocenes but also because of their tendency to undergo low-temperature polyhedral rearrangements. Herein we describe extension of this chemistry with iron and cobalt complexes of the monoanionic thiicarborane ligand [*nido*-7-^tBuNH-7,9-CSB₉H₉][−].

Results and Discussion

Thiicarborane Ligand. Todd et al. have reported the reaction of ^tBuNC with *nido*-SB₉H₁₁ giving 11-vertex thiicarborane, for which the *nido*-7-^tBuNH₂-7,8-CSB₉H₉ (**1**) structure has been ascribed (Scheme 1).¹³ We have performed the DFT

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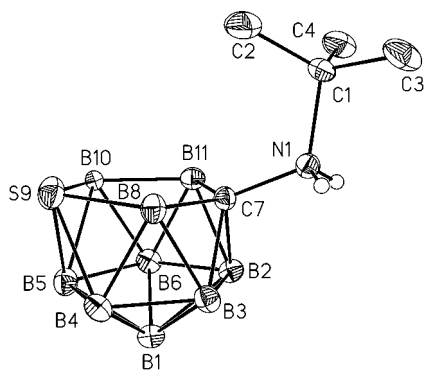


Figure 1. Molecular structure of **2** with ellipsoids at the 50% probability level. All hydrogen atoms except those of the NH₂ group are omitted for clarity. Selected distances (Å): C7–B8 1.610 (2), B8–S9 1.888 (2), S9–B10 1.935 (16), B10–B11 1.698 (14), B11–C7 1.640 (2), N1–C7 1.504 (2), N1–C1 1.557 (2).

GIAO calculations on the model compound *nido*-7-MeNH₂-7,8-CSB₉H₉ (**1'**).¹⁴ The predicted ¹¹B NMR spectrum displays strong deviations from the experimental one (max and av deviations 14.8 and 4.4 ppm), suggesting that the structure assignment was wrong. At the same time, the experimental spectrum is much closer to that calculated for the isomeric compound *nido*-7-MeNH₂-7,9-CSB₉H₉ (**2'**) (max and av deviations 6.4 and 2.6 ppm). Therefore we suggested that intermediate **1** (formed by direct insertion of the isocyanide carbon atom in the open face of the 10-vertex cage)¹⁵ undergoes room-temperature polyhedral rearrangement to give isomer **2**.

The structure of **2** was unambiguously confirmed by X-ray diffraction (Figure 1). Interestingly, the nitrogen atom forms a shorter bond with the polyhedral carbon atom C7 (1.504 Å) than with the C1 atom of the ^tBu group (1.557 Å). This can be explained by different hybridization modes of the C7 (sp) and C1 (sp³) atoms. Owing to the bulky substituents, the amino group does not form any strong intermolecular interactions (the shortest contacts between two molecules are N1⋯B10 3.503 and N1⋯B11 3.720 Å).

The mechanism of the **1'** → **2'** rearrangement was studied by DFT calculations (Figure 2). Isomer **2'** was found to be 40.1 kcal mol⁻¹ more stable than **1'**, indicating that the process is thermodynamically favorable. The activation barrier for the rearrangement is only 19.0 kcal mol⁻¹, confirming that the conversion **1** → **2** can occur at room temperature.¹⁶ Apparently, the rearrangement is facilitated by repulsion between the electronegative carbon and sulfur atoms, which are adjacent in **1** and become separated in **2**. Similar rearrangement has been suggested earlier for the *nido*-7,8,9-C₂SB₈H₁₀ thiadecaborane.¹⁷

Metal Complexes of Thiadecaborane Ligands. Thiadecaborane **2** is readily deprotonated by strong bases (e.g., NaOH or Proton Sponge), giving the anion [*nido*-7-^tBuNH-7,9-CSB₉H₉]⁻ (**3**), which is expected to form complexes with transition metals. Indeed, the reactions of **3** with benzene complexes [CpFe-

(14) The primed numbers correspond to the compounds with a Me group instead of ^tBu.

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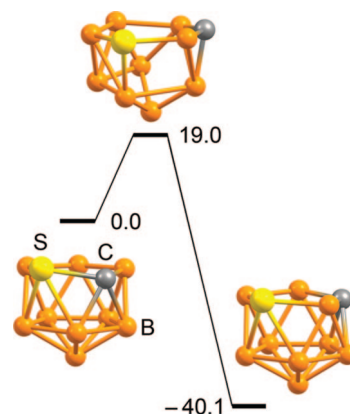
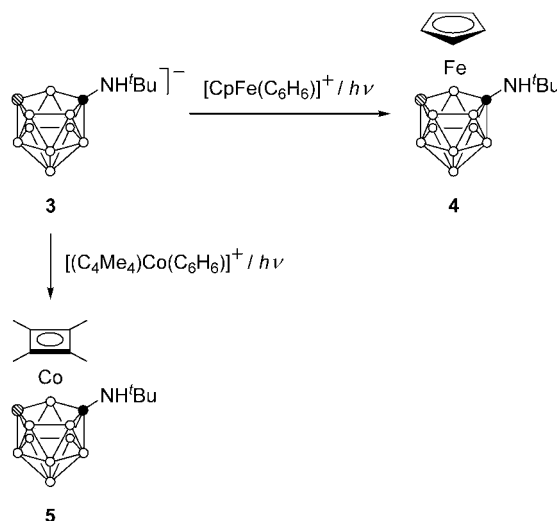


Figure 2. Calculated mechanism for **1'** → **2'** rearrangement. All hydrogen atoms and the MeNH₂ group are omitted for clarity; energies are given in kcal mol⁻¹.

Scheme 2. Synthesis of Iron and Cobalt Complexes of the Thiadecaborane Ligand **3**



(C₆H₆)⁺ and [(C₄Me₄)Co(C₆H₆)]⁺ under visible-light irradiation afford the *closo*-metallathiadecaboranes 1-Cp-4-^tBuNH-1,2,4-FeSCB₉H₉ (**4**, 76%) and 1-C₄Me₄-4-^tBuNH-1,2,4-CoSCB₉H₉ (**5**, 71%) (Scheme 2). A similar approach has been used earlier to obtain complexes of other *nido*-heteroborane anions.^{11a,c,d,12c,18,19} Compounds **4** and **5** are air-stable in both solution and the solid state.

The structures of **4** and **5** were determined by X-ray diffraction (Figures 3 and 4). Both structures exhibit a disordered heteroborane cage with mixing of the S2 and B6 positions. Nevertheless, it can be unambiguously stated that upon coordination with a metal atom the CSB₃ pentagonal face becomes significantly larger: the ring perimeter increases from 8.802 Å in **2** to 9.276 Å in **4** and 9.365 Å in **5**. Such expansion can be explained by electron donation from bonding orbitals of the heteroborane ligand to the empty orbitals of the metal fragment. The Fe⋯Cp distance (1.686 Å) in **4** is longer than that in ferrocene (1.660 Å),²⁰ and the Co⋯C₄ distance (1.727 Å) in

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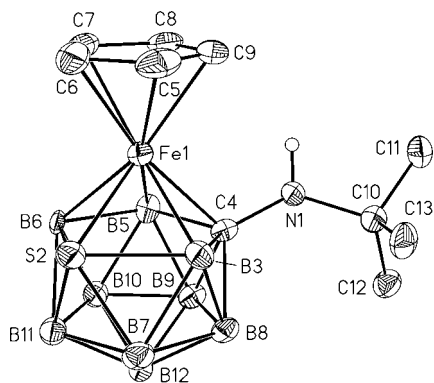


Figure 3. Molecular structure of **4** with ellipsoids at the 50% probability level. All hydrogen atoms except NH are omitted for clarity. Selected distances (Å): Fe1–S2 2.159(2), Fe1–B3 2.053(8), Fe1–C4 2.090(5), Fe1–B5 2.081(7), Fe1–B6 2.140(17), Fe1–C5 2.057(6), Fe1–C6 2.070(6), Fe1–C7 2.071(6), Fe1–C8 2.065(6), Fe1–C9 2.073(6), S2–B3 2.026(7), B3–C4 1.707(9), C4–B5 1.727(9), B5–B6 1.94(2), B6–S2 1.99(3), N1–C4 1.428(7), N1–C10 1.485(8).

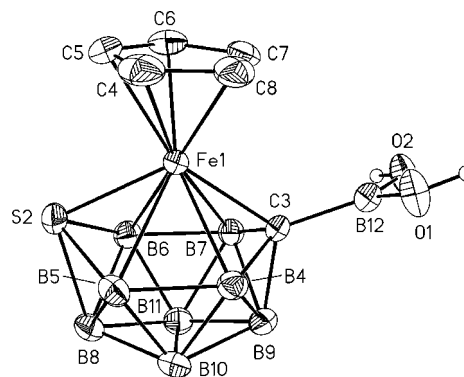


Figure 5. Molecular structure of **6** with ellipsoids at the 50% probability level. All hydrogen atoms except those of the B(OH)₂ group are omitted for clarity. Selected distances (Å): Fe1–C4 2.077(2), Fe1–C5 2.099(2), Fe1–C6 2.093(2), Fe1–C7 2.065(2), Fe1–C8 2.052(2), Fe1–S2 2.1985(6), Fe1–C3 1.9955(19), Fe1–B4 2.266(2), Fe1–B5 2.353(3), Fe1–B6 2.373(3), Fe1–B7 2.280(2), C3–B4 1.596(3), C3–B7 1.597(3), C3–B9 1.657(3), C3–B12 1.555(3).

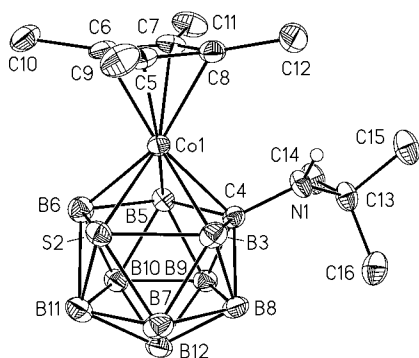
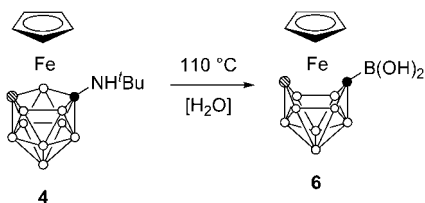


Figure 4. Molecular structure of **5** with ellipsoids at the 50% probability level. All hydrogen atoms except NH are omitted for clarity. Selected distances (Å): Co1–S2 2.155(2), Co1–B3 2.067(3), Co1–C4 2.080(3), Co1–B5 2.070(3), Co1–B6 2.133(13), Co1–C5 2.008(3), Co1–C6 2.006(3), Co1–C7 2.004(3), Co1–C8 2.013(3), S2–B3 2.020(4), B3–C4 1.720(4), C4–B5 1.725(4), B5–B6 1.832(10), B6–S2 2.068(10), N1–C4 1.442(3), N1–C13 1.485(3).

Scheme 3. Polyhedral Contraction of **4**



5 is longer than that in (C₄H₄)CoCp (1.681 Å),²¹ indicating that **3** is a weaker donor (stronger acceptor) than Cp[−].

Metallaheteroboranes are known to undergo polyhedral rearrangements under relatively mild conditions.¹⁰ In an attempt to carry out such rearrangement, ferrathiocarborane **4** was refluxed in toluene for 8 h. Surprisingly, this led to the extrusion of the boron atom from the framework, giving the 11-vertex compound *closo*-1-Cp-3-B(OH)₂-1,2,3-FeSCB₈H₈ (**6**) as the sole metallocarborane product (44% isolated yield; Scheme 3). The same reaction occurs even at room temperature in the solid state within several months. The B(OH)₂ group is probably formed

from oxygen or water during workup in air. Nevertheless, the reaction is well reproducible, always giving the same product, **6**. In sharp contrast, **5** does not exhibit any changes up to 150 °C (refluxing nonane).

The structure of **6** was determined by X-ray diffraction (Figure 5). The Fe⋯Cp distance (1.705 Å) in **6** is notably longer than that in **4** (1.686 Å). Due to the large covalent radii of sulfur, atom Fe1 is significantly shifted from the B5 and B6 (2.353, 2.373 Å) to the B3 and B7 atoms (2.266, 2.280 Å). Interestingly, the distance from the C3 atom to the exopolyhedral boron atom of the B(OH)₂ group (1.555 Å) is shorter than those to the polyhedral boron atoms (av 1.616 Å), in accordance with weakening of multicenter bonds. In the crystal, the molecules of **6** are associated in the dimers via two strong hydrogen bonds between the B(OH)₂ groups (O⋯O 2.857 Å).

Although the formation of **6** was unexpected, some related polyhedral contractions are known.²² A classical example is base degradation of the 12-vertex cobaltacarborane *closo*-1-Cp-1,2,3-CoC₂B₉H₁₁ with KOH followed by peroxide oxidation, giving 11-vertex *closo*-1-Cp-1,2,4-CoC₂B₈H₁₀.^{22a} In the case of the heteroatom-rich ferratricarbollide *closo*-1-Cp-1,2,3,5-FeC₃B₈H₁₁ the analogous process requires only EtOH as a nucleophile and O₂ as an oxidant.^{11c} It can be suggested that the **4** → **6** transformation also proceeds via nucleophilic attack and subsequent oxidation. For example, amine (formed by thermal decomposition of **4**) can act as a nucleophile. Unfortunately, we were unable to detect any intermediates by ¹¹B NMR monitoring.²³ Therefore we tried to clarify the mechanism by DFT calculations for the model reaction of **4'** with MeNH₂. The initial step is the favorable (1.7 kcal mol^{−1}) formation of the hydrogen-bonded associate **7'** (Figure 6). This is followed by nucleophilic attack of the amine at the B3 atom (connected to electronegative S and C vertices) with the formation of intermediate **9'**. The attack is assisted by the hydrogen bond between two MeNH groups and has an activation barrier *E*_a = 16.7 kcal mol^{−1}. Further elimination of the MeNH₂ molecule

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(23) See ¹¹B NMR spectra in the Supporting Information.

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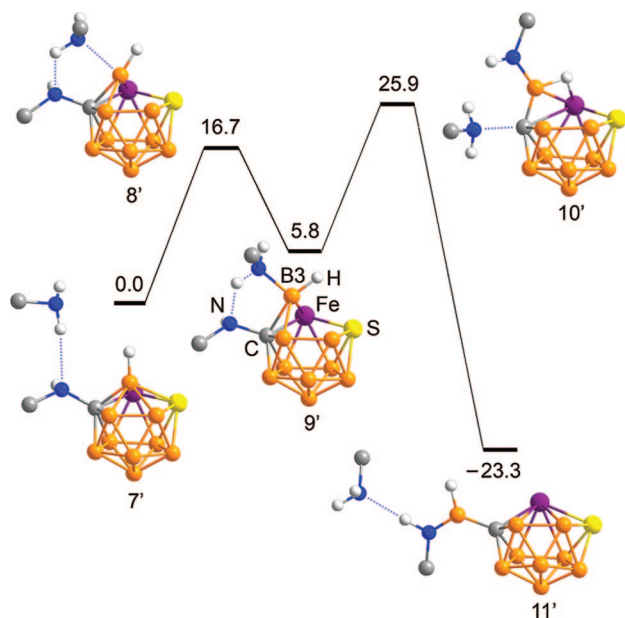


Figure 6. Calculated mechanism for the $7' \rightarrow 11'$ rearrangement. Cp ring and all hydrogen atoms except NH and B3-H are removed for clarity; energies are given in kcal mol⁻¹.

has a barrier $E_a = 25.9$ kcal mol⁻¹. This process transforms the polyhedral B3 atom into the exopolyhedral BHNHMe group (**11'**; -23.3 kcal mol⁻¹).²⁴ Finally, the oxidation of the B-H bond and liberation of amine (which experimentally occurs during reaction workup)²⁵ affords the B(OH)₂ derivative **6'**. It should be emphasized that all the transition states found for the $7' \rightarrow 11'$ rearrangement have E_a less than 30 kcal mol⁻¹, indicating that the process is indeed feasible.

Conclusion

As a result of this study, it was shown that insertion of ^tBuNC into 10-vertex *nido*-thiaborane SB₉H₁₁ is accompanied by a room-temperature polyhedral rearrangement, which separates electronegative sulfur and carbon atoms. The resulting 11-vertex *nido*-thiacarborane anion **3** forms stable complexes with transition metals. Upon heating, iron complex **4** undergoes unusual extrusion of the polyhedral boron atom, giving 11-vertex compound **6**. X-ray structure analysis suggested that the thiacarborane ligand **3** is a stronger acceptor than Cp⁻.

Experimental Section

General Remarks. All reactions were carried out under argon in anhydrous solvents, which were purified and dried using standard procedures. The isolation of products was conducted in air. Starting materials [CpFe(C₆H₆)]PF₆,²⁶ [(C₄Me₄)Co(C₆H₆)]PF₆,²⁷ SB₉H₁₁,²⁸

and ^tBuNC²⁹ were prepared as described in the literature. The salt [Bu₄N][*nido*-7-^tBuNH-7,9-CSB₉H₉] (Bu₄N₃) was prepared by dissolution of **2** in NaOH/MeOH followed by precipitation with Bu₄NBr. Irradiation was conducted in a Schlenk tube using a high-pressure mercury vapor lamp with a phosphorus-coated bulb (Philips HPL Comfort 400W E40 HG CRP). Both the tube and the lamp were placed into a vessel of an appropriate volume covered inside with aluminum foil; cooling was accomplished by running water. The ¹H and ¹¹B NMR spectra were recorded with a Bruker Avance-400 spectrometer operating at 400.13 and 128.38 MHz, respectively. Chemical shifts are given in ppm relative to internal SiMe₄ (¹H) or external BF₃·OEt₂ (¹¹B).

7-^tBuNH₂-7,9-CSB₉H₉ (2**).** A modified procedure of Todd et al. was employed.¹³ A solution of 6-SB₉H₁₁ (3.0 g, 21.1 mmol) in CH₂Cl₂ (50 mL) was treated with Proton Sponge (5.0 g, 23.4 mmol) and ^tBuNC (2.5 mL, 32.5 mmol), and the mixture was stirred under nitrogen at room temperature for 4 h. After adding an excess of CF₃COOH (2 mL) the mixture was evaporated to dryness. Purification by column chromatography on silica gel using benzene as mobile phase gave 3.9 g (82% based on 6-SB₉H₁₁) of 7-^tBuNH₂-7,9-CSB₉H₉ as the main fraction. Colorless crystals suitable for an X-ray diffraction analysis were obtained by diffusion of hexane vapors into the CH₂Cl₂ solution. ¹H NMR (CD₃CN): δ 1.56 (s, 9 H, ^tBu). ¹¹B{¹H} NMR (CD₃CN): δ -6.8 (s, 2 B), -11.8 (s, 1 B), -13.5 (s, 2 B), -17.5 (s, 2 B), -18.7 (s, 1 B), -43.0 (s, 1 B). ¹¹B NMR calcd for **1'**: 11.8, -2.3, -9.4, -10.4, -14.8, -19.8, -21.5, -21.7, -36.8. ¹¹B NMR calcd for **2'**: -8.4, -12.0, -12.1, -13.4, -14.1, -18.0, -19.0, -22.0, -45.2.

1-Cp-4-^tBuNH-1,2,4-FeSCB₉H₉ (4**).** A mixture of Bu₄N₃ (139 mg, 0.3 mmol) and [CpFe(C₆H₆)]PF₆ (103 mg, 0.3 mmol) in 15 mL of CH₂Cl₂ was irradiated at room temperature for 4 h, resulting in a color change from yellow to bright red. The reaction mixture was evaporated under vacuum, and the residue was eluted through a short (5 cm) silica gel column in a CH₂Cl₂/petroleum ether mixture (1:2). The evaporation of the red fraction by passing an argon stream over the solution gives red crystals of **4** suitable for X-ray diffraction (78 mg, 76%). ¹H NMR (toluene-*d*₈): δ 4.31 (s, 5 H, Cp), 0.98 (s, 9 H, ^tBu). ¹¹B{¹H} NMR (toluene-*d*₈): δ 4.1 (s, 1 B), 3.7 (s, 1 B), -4.2 (s, 1 B), -6.2 (s, 2 B), -14.4 (s, 1 B), -15.4 (s, 1 B), -20.4 (s, 1 B), -24.5 (s, 1 B). C₁₀H₂₄B₉FeNS (343.51): calcd C 34.96, H 7.04, B 28.32, N 4.08; found C 35.07, H 7.11, B 28.20, N 4.01.

1-(C₄Me₄)-4-^tBuNH-1,2,4-CoSCB₉H₉ (5**).** A mixture of Bu₄N₃ (139 mg, 0.3 mmol) and [(C₄Me₄)Co(C₆H₆)]PF₆ (117 mg, 0.3 mmol) in 15 mL of CH₂Cl₂ was irradiated at room temperature for 8 h. The mixture was then evaporated under vacuum, and the residue was eluted through a short (5 cm) silica gel column in CH₂Cl₂/petroleum ether mixture (1:2). The evaporation of the yellow fraction gives crystals of **5** suitable for X-ray diffraction (83 mg, 71%). ¹H NMR (toluene-*d*₈): δ 1.37 (s, 12 H, C₄Me₄), 1.05 (s, 9 H, ^tBu). ¹¹B{¹H} NMR (toluene-*d*₈): δ 3.3 (s, 1 B), 2.3 (s, 1 B), -5.1 (s, 1 B), -8.3 (s, 1 B), -11.2 (s, 1 B), -15.2 (s, 1 B), -16.0 (s, 1 B), -18.2 (s, 1 B), -21.7 (s, 1 B). C₁₃H₃₁B₉CoNS (389.69): calcd C 40.07, H 8.02, B 24.97, N 3.59; found C 40.46, H 8.35, B 24.62, N 3.41.

1-Cp-3-B(OH)₂-1,2,3-FeSCB₈H₈ (6**).** A solution of compound **4** (68 mg, 0.2 mmol) in 5 mL of toluene was refluxed for 8 h, resulting in a color change from red to violet and precipitation of gray solids. The reaction mixture was evaporated under vacuum, and the residue was dissolved in CH₂Cl₂ and eluted through a short (5 cm) silica gel column. The violet fraction was evaporated to small volume (ca. 3 mL), and 20 mL of petroleum ether was added on the top to give, after slow interdiffusion of solutions, crystals of **6** suitable for X-ray diffraction (27 mg, 44%). ¹H NMR (acetone-*d*₆): δ 5.03 (s, 5 H, Cp). ¹¹B{¹H} NMR (acetone-*d*₆): δ 32.0 (s, 1 B), 22.8 (s, 1 B), -1.6 (s, 1 B), -8.2 (s, 2 B), -14.7 (s, 2 B),

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Table 1. Crystal Data and Structure Refinement for Compounds 2, 4, 5, and 6

	2	4	5	6
formula	C ₅ H ₂₀ B ₉ NS	C ₁₀ H ₂₄ B ₉ FeNS	C ₁₃ H ₃₁ B ₉ CoNS	C ₆ H ₁₅ B ₉ FeO ₂ S
<i>M</i>	223.57	343.50	389.67	304.38
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	<i>Pca</i> 2 ₁	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	18.4915 (2)	9.441(2)	9.3712(11)	6.7953(3)
<i>b</i> (Å)	6.7105 (3)	15.717(4)	16.954(2)	13.2340(7)
<i>c</i> (Å)	10.2849 (5)	22.341(5)	12.8825(16)	15.1439(8)
β (deg)			97.711(2)	94.4360(10)
<i>V</i> (Å ³)	10.2849 (5)	3315.1(14)	2028.3(4)	1357.80(12)
<i>Z</i>	4	8	4	4
<i>D</i> _{calc} (g·cm ⁻³)	1.164	1.376	1.276	1.489
θ _{max} (deg)	27.5	26	26	29
abs coeff, μ (Mo K α) (mm) ⁻¹	0.21	1.021	0.945	1.245
no. reflns collected; <i>R</i> _{int}	15 608; 0.044	19 674	5575	14 698
completeness	0.997	0.999	0.941	0.996
no. indep reflns	2761	3253	3757	3594
no. obsd reflns (<i>I</i> > 2 σ (<i>I</i>))	2663	1787	2744	2297
no. params	195	243	269	204
<i>R</i> ₁ (on <i>F</i> for obsd reflns)	0.032	0.0537	0.0400	0.0343
<i>wR</i> ₂ (on <i>F</i> ² for all reflns)	0.080	0.1347	0.0582	0.0653
weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, $P = 1/3(F_o^2 + 2F_c^2)$			
<i>a</i>	0.0307	0.010	0.050	0.025
<i>b</i>	0.4642	20.0		
<i>F</i> (000)	472	1424	816	616
GOOF	1.14	1.039	0.980	1.011
largest diff peak/hole, e·Å ⁻³	0.31/−0.16	0.594/−0.545	0.743/−0.446	0.472/−0.284

−19.2 (s, 2 B). C₆H₁₅B₉FeO₂S (304.39): calcd C 23.67, H 4.97, B 31.97; found C 23.82, H 5.14, B 31.88.

X-ray Crystallography. A single crystal of **2** on a Lindemann capillary was measured on a Nonius KappaCCD diffractometer by monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) at 150(2) K (Cryostream Cooler; Oxford Cryosystem). Absorption was neglected. Cell parameters from 1709 reflections ($\theta = 1$ –27.5°). The structure was solved by direct methods (SIR92)³⁰ and refined by full-matrix least-squares based on *F*² (SHELXL97). The hydrogen atoms were localized on a difference Fourier map and refined isotropically except those of the *t*Bu group, which were recalculated and fixed into idealized positions (riding model) during refinement with assigned temperature factors $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{pivot atom})$. The precision of structure determination is hampered due to disorder of the carborane cage, which appears to consist of two overlapping positions, the second one generated by a mirror through atoms C(1), B(5), and B(1). The ratio of these two orientations of the carborane moiety is 9:1 within the crystal; therefore the main disturbances caused by disorder is localized on the B(10) atom, which is overlapping with electron density of 10% of the S(9) atom. The disorder was included in the refinement by splitting the position of S(9) and B(10) into two atoms, refined with restricted displacement parameters. The refinement converged ($\Delta/\sigma_{\text{max}} = 0.001$). The only orientation forming 90% of the crystal is used for further discussion.

Single-crystal X-ray diffraction experiments for **4**, **5**, and **6** were carried out with a Bruker SMART 1000 CCD area detector, using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å), ω -scans with a 0.3° step in ω , and 10 s per frame exposure at 120 K. The low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow N₂ gas cryostat. Reflection intensities were integrated using SAINT software^{31,32} and the semiempirical method of SADABS.³³ The structures were solved by the direct method and refined by full-matrix least-squares against *F*² in anisotropic (for non-hydrogen atoms except the

disordered B6 atom in **5**) approximation. All hydrogen atoms of the carborane moiety and OH and NH groups were located from the difference Fourier syntheses, and the H(C) atoms were placed in geometrically calculated positions. The positions of the hydrogen atoms were refined in isotropic approximation in a riding model with the $U_{\text{iso}}(\text{H})$ parameters equal to $1.5U_{\text{eq}}(\text{C}_i)$, where $U(\text{C}_i)$ are the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded. All calculations were performed on an IBM PC/AT using the SHELXTL software.³⁴ Crystallographic data and refinement parameters for compounds are presented in Table 1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 692902 for **2**, CCDC 692903 for **4**, CCDC 692904 for **5**, and CCDC 692905 for **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi).

Computational Details. All DFT calculations were carried out using PRIRODA 6 software kindly provided by Dr. D. N. Laikov.³⁵ The generalized gradient approximation (GGA) for the exchange–correlation functional by Perdew, Burke, and Ernzerhof (PBE) was employed.³⁶ The 3z basis set (similar to TZVP) of contracted Gaussian-type functions of the size (4s1p)/[2s1p] for H, (8s4p1d)/[4s2p1d] for B–N, (15s11p2d)/[10s6p2d] for S, and (17s13p8d)/[12s9p4d] for Fe was used. Geometry optimization was performed in *C*₁ symmetry using analytical gradients. Preliminary search for transition states was performed at the B3LYP/6-31G* level QST3 procedure available in the Gaussian 98 program.³⁷ This was followed by transition state optimization carried out by PRIRODA 6 software. Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. The path of the reaction was traced from the transition state to the product and back to the reactant using the intrinsic reaction coordinate method (IRC).³⁸ For GIAO calculation of ¹¹B NMR shifts *ortho*-carborane was used as a standard instead of the more commonly used B₂H₆.³⁹

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as this provides a notable improvement for prediction of NMR spectra of the polyhedral compounds. Particularly, the isotropic shielding tensors were first calculated for *ortho*-carborane and summed with corresponding experimental chemical shifts, giving an average-weighted conversion value of 98.2 (vs 93.8 calculated from data for B₂H₆ at the PBE/3z level). From this the isotropic shielding tensors of **1'** and **2'** were subtracted to give chemical shift

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values. The visualization of calculation results was performed by ChemCraft (version 1.5) software (www.chemcraftprog.com).

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Supporting Information Available: Crystallographic information (cif files) for compounds **2**, **4**, **5**, and **6**; details of DFT calculations for structures **1'**, **2'**, **4'**, and **7'–11'** (atomic coordinates, energy and frequency data). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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