

π -Complexes of monoanionic carborane ligand $[9-(\text{Me}_2\text{S})-7,8-\text{C}_2\text{B}_9\text{H}_{10}]^-$ with $[\eta-\text{C}_5\text{R}_5\text{Fe}]^+$ ($\text{R} = \text{H}, \text{Me}$) and $[\eta-\text{C}_4\text{Me}_4\text{Co}]^+$ cationic fragments

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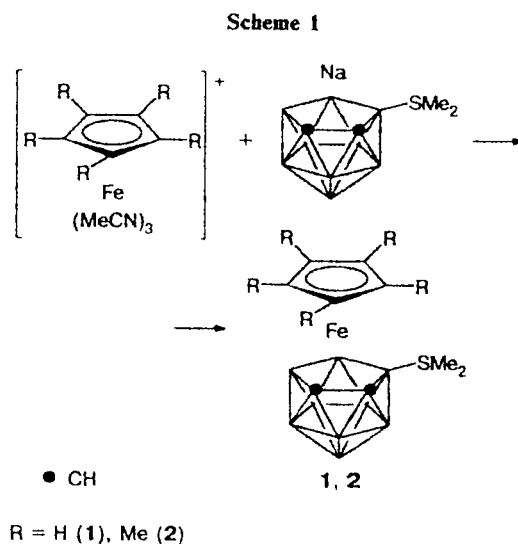
Compounds $(\eta-\text{C}_5\text{R}_5)\text{Fe}[\eta-9-(\text{Me}_2\text{S})-7,8-\text{C}_2\text{B}_9\text{H}_{10}]$ ($\text{R} = \text{H}, \text{Me}$) and $(\eta-\text{C}_4\text{Me}_4)\text{Co}[\eta-9-(\text{Me}_2\text{S})-7,8-\text{C}_2\text{B}_9\text{H}_{10}]$ were synthesized by the reactions of $\text{Na}[9-(\text{Me}_2\text{S})-7,8-\text{C}_2\text{B}_9\text{H}_{10}]$ with complexes $[(\eta-\text{C}_5\text{H}_5)\text{Fe}(\text{MeCN})_3]\text{PF}_6$, $[(\eta-\text{C}_5\text{Me}_5)\text{Fe}(\text{MeCN})_3]\text{BF}_4$, and $[(\eta-\text{C}_4\text{Me}_4)\text{Co}(\text{MeCN})_3]\text{PF}_6$, respectively.

Key words: metallocarboranes, iron complexes, cobalt complexes.

The chemistry of metallocarboranes has been studied sufficiently well.^{1–5} However, the majority of known compounds were synthesized from the $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$ dianion. Derivatives of monoanions, in particular, of the charge-compensated $[9-(\text{Me}_2\text{S})-7,8-\text{C}_2\text{B}_9\text{H}_{10}]^-$ anion, have been less studied. It is known that the $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$ dianion is similar to the cyclopentadienyl $[\text{C}_5\text{H}_5]^-$ anion by the capability of forming π -complexes with transition metals.^{6–8} As for the $[9-(\text{Me}_2\text{S})-7,8-\text{C}_2\text{B}_9\text{H}_{10}]^-$ monoanion, it exhibits a greater resemblance with $[\text{C}_5\text{H}_5]^-$ due to the same charge.^{9–12} Both biscarborane $(\eta-7,8-\text{C}_2\text{B}_9\text{H}_{11})\text{Co}[\eta-9-(\text{Me}_2\text{S})-7,8-\text{C}_2\text{B}_9\text{H}_{10}]$ ⁹ and $\text{Fe}[\eta-9-(\text{Me}_2\text{S})-7,8-\text{C}_2\text{B}_9\text{H}_{10}]_2$ ¹¹ and monocarborane complexes of the $\text{LM}[\eta-9-(\text{Me}_2\text{S})-7,8-\text{C}_2\text{B}_9\text{H}_{10}]$ type, where $\text{LM} = (\text{CO})_3\text{Mn}$,¹² $(\text{CO})_3\text{Rh}$, $[\text{codRh}]^+$ (cod is cycloocta-1,5-diene),¹³ PPh_3Cu ,¹⁴ and PPh_3Au ,¹⁵ were synthesized from this anion. However, complexes of this type with planar cyclic π -ligands are unknown. In this report, we describe the synthesis of the first representatives of these compounds.

We synthesized iron compounds **1** and **2** with cyclopentadienyl ligands on the basis of reactions of iron trisacetonitrile complexes $[(\eta-\text{C}_5\text{R}_5)\text{Fe}(\text{MeCN})_3]^+$ with the sodium derivative of $[9-(\text{Me}_2\text{S})-7,8-\text{C}_2\text{B}_9\text{H}_{10}]^-$ (Scheme 1).

The conditions of the reaction are determined by the stability of the starting compounds. The unsubstituted $[(\eta-\text{C}_5\text{H}_5)\text{Fe}(\text{MeCN})_3]^+$ complex is stable only at temperatures below -40°C ¹⁶ and, hence, it was generated *in situ* from the corresponding benzene complex $[(\eta-\text{C}_5\text{H}_5)\text{Fe}(\eta-\text{C}_6\text{H}_6)]\text{PF}_6$ at -78°C by irradiation with the visible light in a $\text{MeCN}-\text{THF}$ (1 : 4) mixture. The starting $[(\eta-\text{C}_5\text{Me}_5)\text{Fe}(\text{MeCN})_3]^+$ complex used for the synthesis of methylated compound **2** is sufficiently stable,¹⁷ and the reaction was carried out at 0°C in THF or MeCN .

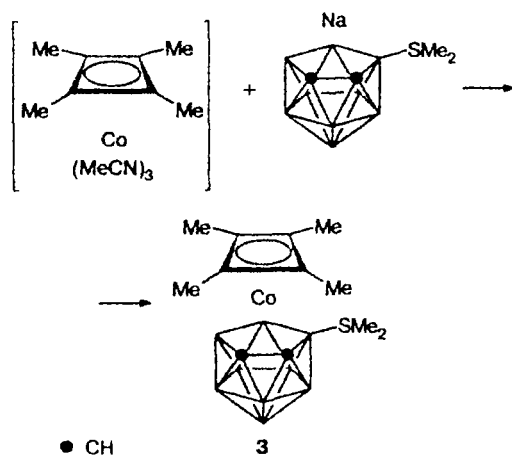


A similar approach was used for the synthesis of cobalt compound **3** with the tetramethylcyclobutadiene ligand (Scheme 2).

The reaction was carried out at 0°C in MeCN . The starting $[(\eta-\text{C}_4\text{Me}_4)\text{Co}(\text{MeCN})_3]^+$ complex was obtained by irradiation of a solution of $[(\eta-\text{C}_4\text{Me}_4)\text{Co}(\eta-\text{C}_6\text{H}_6)]^+$ in MeCN .

It is noteworthy that compounds **1–3** are soluble in CH_2Cl_2 and Me_2CO and poorly soluble in methanol and nonpolar solvents. The low solubility in methanol was used for washing these compounds from admixtures, which facilitated considerably their isolation. The substances obtained are stable in the solid state in air and decompose very slowly in solutions. Their structure was confirmed by elemental analysis and ^1H and ^{11}B spectroscopy (Table 1).

Scheme 2



In addition to the characteristic signals of the hydrocarbon ligand, the ^1H NMR spectra contain two broad signals of protons of CH of the carborane cage and two signals of protons of the Me groups bound to the sulfur atom. The ^1H NMR spectra of other compounds with the $[\text{9}-(\text{Me}_2\text{S})\text{-7,8-C}_2\text{B}_9\text{H}_{10}]^-$ ligand described previously^{11–15} had a similar shape.

The ^{11}B NMR spectra of compounds **1–3** exhibit eight or nine signals. For each of these compounds, all signals, except for one, are doublets ($J_{\text{BH}} = 118\text{--}227\text{ Hz}$), and one of them is a singlet. Evidently, this signal is attributed to the boron atom bound to the Me_2S group.

Thus, we synthesized the first complexes of the carborane monoanion $[\text{9}-(\text{Me}_2\text{S})\text{-7,8-C}_2\text{B}_9\text{H}_{10}]^-$ con-

taining planar cyclic π -ligands C_5R_5 ($\text{R} = \text{H}, \text{Me}$) or C_4Me_4 at the metal atom. Compounds **1** and **2** are analogs of ferrocene containing the monoanionic carborane ligand $[\text{9}-(\text{Me}_2\text{S})\text{-7,8-C}_2\text{B}_9\text{H}_{10}]^-$ instead of one similar $[\text{C}_5\text{R}_5]^-$ anion.

Experimental

All reactions were carried out in an argon atmosphere using anhydrous solvents prepared according to standard procedures. The products were isolated in air.

Starting compounds $\text{Na}[\text{9}-(\text{Me}_2\text{S})\text{-7,8-C}_2\text{B}_9\text{H}_{10}]$,¹¹ $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$,¹⁸ $[(\eta\text{-C}_5\text{Me}_5)\text{Fe}(\text{MeCN})_3]\text{BF}_4$,¹⁷ and $[(\eta\text{-C}_4\text{Me}_4)\text{Co}(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ ¹⁹ were prepared according to known procedures.

Irradiation was performed in a tube with a diameter of 15 mm using a DRL-250 luminescence lamp with a power of 250 W.

^1H and ^{11}B NMR spectra were measured on a Bruker AMX-400 instrument.

Complex $(\eta\text{-C}_5\text{H}_5)\text{Fe}[\eta\text{-9}-(\text{Me}_2\text{S})\text{-7,8-C}_2\text{B}_9\text{H}_{10}]$ (1**).** $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ (344 mg, 1 mmol) was dissolved in a mixture of THF (16 mL) and MeCN (4 mL). A 0.25 M solution (4 mL) of $\text{Na}[\text{9}-(\text{Me}_2\text{S})\text{-7,8-C}_2\text{B}_9\text{H}_{10}]$ (1 mmol) in THF was added to the prepared solution of $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ cooled to -78°C . The mixture was irradiated with stirring for 1 h and evaporated *in vacuo*, and the residue was washed 3–4 times with small portions of MeOH (by 2–3 mL). According to the ^1H and ^{11}B spectra, the fine-crystalline red solid substance obtained has 95% purity. To obtain the analytically pure product, the solid substance was dissolved in CH_2Cl_2 , the solution was filtered, and heptane was added. The major portion of CH_2Cl_2 was evaporated in a vacuum of a water aspirator pump. The fine-crystalline precipitate that formed was filtered off and dried *in vacuo*. Complex **1** (255 mg, 80%) was obtained as red microcrystals. Found (%): C, 34.32; H, 6.48; B, 30.8; Fe, 17.44. $\text{C}_9\text{H}_{11}\text{B}_9\text{FeS}$. Calculated (%): C, 34.37; H, 6.73; B, 30.94; Fe, 17.76.

Table 1. Parameters of ^1H and ^{11}B NMR spectra of compounds **1–3** (in CD_2Cl_2)

Compound	^1H , δ^a			^{11}B , δ (J/Hz) ^b
	CH of carborane	SMe_2	C_nR_n	
1	4.08 (1 H); 3.52 (1 H)	2.73 (3 H); 2.46 (3 H)	4.54 (5 H, C_5H_5)	–6.04 (1 B, BH, $J_{\text{BH}} = 136$); –6.04 (1 B, BSMe ₂); –10.20 (1 B, BH, $J_{\text{BH}} = 142$); –11.30 (1 B, BH, $J_{\text{BH}} = 142$); –13.24 (1 B, BH, $J_{\text{BH}} = 139$); –17.87 (1 B, BH, $J_{\text{BH}} = 138$); –24.55 (1 B, BH, $J_{\text{BH}} = 152$); –27.11 (1 B, BH, $J_{\text{BH}} = 165$); –28.71 (1 B, BH, $J_{\text{BH}} = 202$)
2	5.32 (1 H); 2.35 (1 H)	2.59 (3 H); 2.39 (3 H)	1.79 (15 H, C_5Me_5)	–4.90 (1 B, BH, $J_{\text{BH}} = 195$); –6.02 (1 B, BSMe ₂); –9.19 (1 B, BH, $J_{\text{BH}} = 144$); –12.90 (1 B, BH, $J_{\text{BH}} = 130$); –13.80 (1 B, BH, $J_{\text{BH}} = 130$); –18.18 (1 B, BH, $J_{\text{BH}} = 138$); –25.28 (1 B, BH, $J_{\text{BH}} = 159$); –27.27 (1 B, BH, $J_{\text{BH}} = 176$); –29.13 (1 B, BH, $J_{\text{BH}} = 227$)
3	2.80 (1 H); 2.30 (1 H)	2.56 (3 H); 2.40 (3 H)	1.56 (12 H, C_4Me_4)	–6.35 (1 B, BH, $J_{\text{BH}} = 140$); –9.21 (1 B, BSMe ₂); –11.02 (1 B, BH, $J_{\text{BH}} = 158$); –13.96 (1 B, BH, $J_{\text{BH}} = 144$); –17.61 (1 B, BH, $J_{\text{BH}} = 150$); –17.61 (1 B, BH, $J_{\text{BH}} = 136$); –24.82 (1 B, BH, $J_{\text{BH}} = 126$); –26.56 (1 B, BH, $J_{\text{BH}} = 128$); –28.13 (1 B, BH, $J_{\text{BH}} = 118$)

^a All signals are singlet.

^b Signals in the ^{11}B NMR spectrum were measured relative to the external standard $\text{BF}_3 \cdot \text{Et}_2\text{O}$.

Complex $(\eta\text{-C}_5\text{Me}_5)\text{Fe}[\eta\text{-9-(Me}_2\text{S)-7,8-C}_2\text{B}_9\text{H}_{10}]$ (2). A 0.25 M solution (2 mL) of $\text{Na}[\eta\text{-9-(SMe}_2\text{)-7,8-C}_2\text{B}_9\text{H}_{10}]$ (0.5 mmol) in THF was added to a solution of $[(\eta\text{-C}_5\text{Me}_5)\text{Fe}(\text{MeCN})_3]\text{BF}_4$ (200 mg, 0.5 mmol) in THF (10 mL) at 0 °C, and the reaction mixture was stirred at this temperature for 1 h. Complex 2 was isolated similarly to compound 1. The substance was obtained (155 mg, 80%) in the form of orange-red microcrystals. Found (%): C, 41.44; H, 8.18; B, 29.18; Fe, 14.17; S, 7.03. $\text{C}_{14}\text{H}_{11}\text{B}_9\text{FeS}$. Calculated (%): C, 43.72; H, 8.13; B, 25.30; Fe, 14.52; S, 8.34.

Complex $(\eta\text{-C}_4\text{Me}_4)\text{Co}[\eta\text{-9-(Me}_2\text{S)-7,8-C}_2\text{B}_9\text{H}_{10}]$ (3). MeCN (10 mL) was added to $[(\eta\text{-C}_4\text{Me}_4)\text{Co}(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ (195 mg, 0.5 mmol), and the mixture was irradiated with stirring and cooling with running water at room temperature for 3 h. Then a 0.25 M solution (2 mL) of $\text{Na}[\eta\text{-9-(SMe}_2\text{)-7,8-C}_2\text{B}_9\text{H}_{10}]$ (0.5 mmol) in THF was added at 0 °C to the orange-red solution of $[(\eta\text{-C}_4\text{Me}_4)\text{Co}(\text{MeCN})_3]\text{PF}_6$ that formed, and the reaction mixture was stirred for 1 h. Complex 3 was isolated similarly to compounds 1 and 2. The substance was obtained (100 mg, 39.5%) as orange fine crystals. Found (%): C, 38.69; H, 8.99; B, 26.57; Co, 15.30; S, 8.50. $\text{C}_{12}\text{H}_{28}\text{B}_9\text{CoS}$. Calculated (%): C, 39.96; H, 7.83; B, 26.98; Co, 16.34; S, 8.89.

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