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Benzene complex $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Fe(\eta\text{-}C_6H_6)]^+$ as a synthon for the cationic ferracarborane moiety

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The photochemical reaction of $[(\eta^5\text{-}C_6H_7)Fe(\eta\text{-}C_6H_6)]^+$ (**1**) with the $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})]^-$ anion followed by the treatment of the resulting ferracarborane $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Fe(\eta^5\text{-}C_6H_7)$ (**2**) with hydrochloric acid afforded the benzene complex $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Fe(\eta\text{-}C_6H_6)]^+$ (**3**). The reaction of cation **3** with Bu^tNC produced the isonitrile complex $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Fe(^tBuNC)_3]^+$ (**4**). The structure of the complex [**4**]PF_6 was established by X-ray diffraction.

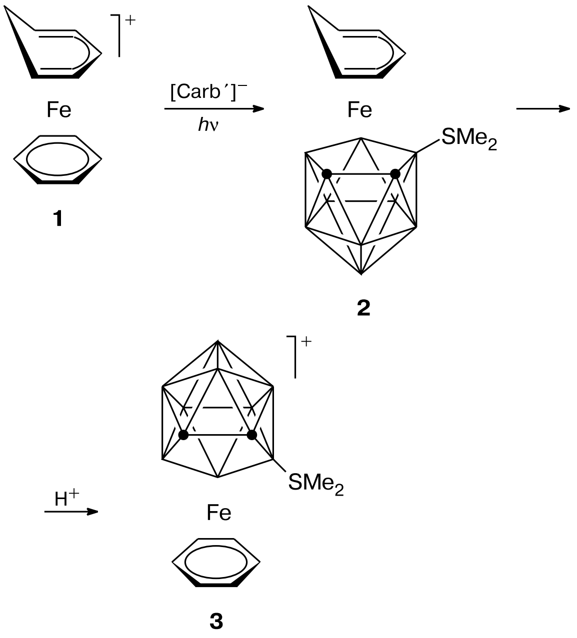
Key words: iron, metallacarboranes, sandwich compounds.

It was found[1] that the visible light irradiation of the iron cyclopentadienyl complex $[CpFe(\eta\text{-}C_6H_6)]^+$ leads to the replacement of benzene by other ligands. More recently, this method has found application in the synthesis of various types of complexes containing the $[CpFe]^+$ fragment.[2—8] In the last 40 years, carborane ligands were widely used in organometallic chemistry.[9] However, the possibility of the generation of cationic metallacarborane moieties was represented by a few examples.[10—12] In particular, we have developed[12] a procedure for the generation of the $[(Carb´)M]^{2+}$ species (Carb´ = $9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}$; M = Rh or Ir) by the elimination of bromide ions from the $[(Carb´)MBr_2]_2$ dimer with $AgBF_4$. In the present study, we report the synthesis of the iron benzene complex $[(Carb´)Fe(\eta\text{-}C_6H_6)]^+$ and give an example of the use of this complex as a synthon for the $[(Carb´)Fe]^+$ cation related to $[CpFe]^+$.

Results and Discussion

Recently, we have demonstrated[13] that the visible light irradiation of the iron cyclohexadienyl complex $[(\eta^5\text{-}C_6H_7)Fe(\eta\text{-}C_6H_6)]^+$ (**1**) leads to the replacement of benzene with MeCN or Bu^tNC to form the corresponding tris(ligand) derivatives $[(\eta^5\text{-}C_6H_7)Fe(L)_3]^+$. In the present study, we performed the photochemical reaction of cation **1** with the charge-compensated carborane anion $[Carb´]^-$ and prepared the ferracarborane complex $(Carb´)Fe(\eta^5\text{-}C_6H_7)$ (**2**) (Scheme 1).* It was found that the cyclohexadienyl ligand in this compound eliminates the hydride ion in the presence of acetic or hydrochloric acid to form the benzene complex $[(Carb´)Fe(\eta\text{-}C_6H_6)]^+$ (**3**). Therefore, the two-step reaction presented in Scheme 1 allows the synthesis of the ferracarborane benzene complex from cation **1**. Apparently, this approach can be used also for the preparation of iron arene complexes with other monoanionic ligands.

Scheme 1



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* All cationic complexes were isolated as salts with the PF_6^- anion (anions are omitted in the schemes).

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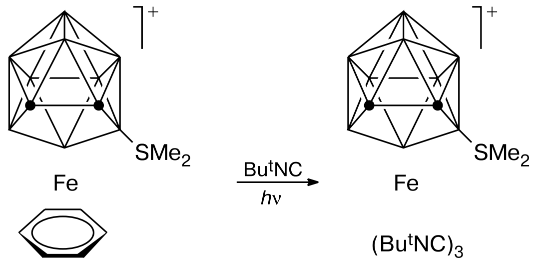
As was observed for the cations $[CpFe(\eta\text{-}C_6H_6)]^+$ and **1**, benzene is eliminated from complex **3** under visible light irradiation. For example, the reaction with Bu^tNC produced the tris(isonitrile) complex $[(Carb')Fe(^tBuNC)_3]^+$ (**4**) (Scheme 2). This example shows that benzene complex **3** can be used as a synthon for the cationic species $[(Carb')Fe]^+$.

Scheme 2



3 **4**

Ferracarborane complexes **2**—**4** were obtained as bright-colored air-stable solids. Their structures were confirmed by ^1H and ^{11}B NMR spectra. The structure of the complex $[\mathbf{4}]PF_6$ was also established by X-ray diffraction (molecular structure of cation **4** is shown in Fig. 1; selected bond lengths are given in Table 1). The lengths of the bonds between the carbon atoms of the isonitrile ligands and the iron atom (aver., 1.847 Å) are similar to the corresponding distances in the related complex $[(\eta^5\text{-}C_6H_7)Fe(^tBuNC)_3]^+$ (aver., 1.854 Å).[13] The distance from the iron atom to the plane of the carborane ligand, $Fe\cdots C_2B_3$ (1.554 Å), is much longer than the corresponding distances in the *meso*- and *DD*/*LL*-$(Carb')_2Fe$ complexes (1.499 Å)[14,15] due to the strong electron-withdrawing properties of the isonitrile ligand and, probably, due to a higher orbital symmetry of the latter compounds.

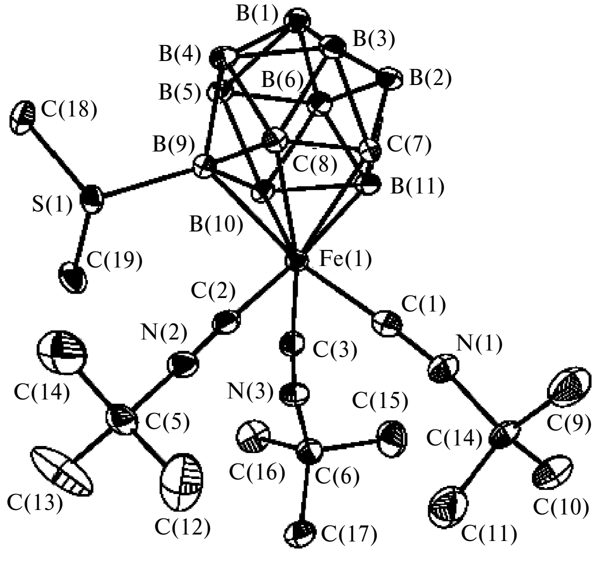


Fig. 1. Structure of cation **4** (displacement ellipsoids are drawn at the 50% probability level).

Table 1. Selected bond lengths (*d*) in cation **4**

Bond	*d*/Å
Fe(1)—C(1)	1.855(3)
Fe(1)—C(2)	1.861(3)
Fe(1)—C(3)	1.825(3)
Fe(1)—C(7)	2.102(3)
Fe(1)—C(8)	2.108(3)
Fe(1)—B(9)	2.125(3)
Fe(1)—B(10)	2.180(3)
Fe(1)—B(11)	2.145(3)
C(1)—N(1)	1.155(4)
C(2)—N(2)	1.151(4)
C(3)—N(3)	1.156(4)
C(7)—C(8)	1.601(4)
C(7)—B(11)	1.704(4)
C(8)—B(9)	1.706(4)
B(9)—B(10)	1.763(4)
B(10)—B(11)	1.809(5)
B(9)—S(1)	1.906(3)

Experimental

The reactions were carried out under argon with the use of anhydrous solvents purified according to standard procedures. The operations associated with the isolation of the reaction products were carried out in air. The starting compounds $[\mathbf{1}]PF_6$ (see Ref. 13) and Na[Carb′] (see Ref. 16) were synthesized according to known procedures. The ^1H and ^{11}B NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 MHz for ^1H and 128.38 MHz for ^{11}B).

(9-Dimethylsulfonio-7,8-dicarbollyl)(η^5-cyclohexadienyl)iron, $(Carb')Fe(\eta^5\text{-}C_6H_7)$ (2). A solution of Na[Carb′] in THF (0.16 mol L^{-1}, 5.5 mL, 0.88 mmol) was added to a solution of the complex $[\mathbf{1}]PF_6$ (300 mg, 0.84 mmol) in acetonitrile (10 mL). The reaction mixture was irradiated using mercury luminescent lamps with a total power of 650 W for 6 h with the use of a running water cooler. Then the reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was washed portionwise with acetone (2×1.5 mL) and reprecipitated from CH_2Cl_2 with petroleum ether. Complex **2** was obtained as a red solid substance in a yield of 85 mg (31%). Found (%): C, 36.54; H, 7.19; B, 29.29. $C_{10}H_{23}B_9FeS$. Calculated (%): C, 36.56; H, 7.06; B, 29.62. ^1H NMR (acetone-d_6), δ: 1.57 (d, 1 H, C_6H_7); 2.49 (m, 1 H, C_6H_7); 2.69 (m, 1 H, C_6H_7); 2.85 (s, 3 H, SMe_2); 3.03 (s, 1 H, CH); 3.09 (s, 3 H, SMe_2); 3.17 (s, 1 H, CH); 4.40 (m, 1 H, C_6H_7); 4.81 (m, 1 H, C_6H_7); 6.25 (m, 1 H, C_6H_7). $^{11}B\{^1H\}$ NMR (acetone-d_6), δ: −28.7, −25.3, −23.7, −15.7, −14.3, −13.0, −11.2 (all s, 1 B each); −3.4 (s, 2 B).

The acetone solution, which was obtained after washing of the crude product, contained a significant amount of complex **2**. To avoid losses, concentrated HCl (0.4 mL) was added to the reaction solution and the mixture was stirred in the dark for 1.5 h. Then an aqueous NH_4PF_6 solution (80 mg, 0.49 mmol) was added. The orange precipitate that formed was filtered off, washed with dichloromethane (4×1 mL), and reprecipitated from acetone with diethyl ether. The complex $[\mathbf{3}]PF_6$ was obtained in a yield of 148 mg (37%).

[(9-Dimethylsulfonio-7,8-dicarbollyl)(η-benzene)iron] hexafluorophosphate, $[(Carb')Fe(\eta\text{-}C_6H_6)]PF_6$ ($[\mathbf{3}]PF_6$). A mixture of **2** (89 mg, 0.27 mmol) and concentrated HCl (0.2 mL) in acetone (3 mL) was stirred in the dark for 1 h. Then an aqueous NH_4PF_6 solution was added. The product was isolated as described above. The yield was 101 mg (79%). Found (%): C, 25.49; H, 4.71; B, 20.62. $C_{10}H_{22}B_9F_6FePS$. Calculated (%): C, 25.42; H, 4.69; B, 20.59. ^{1}H NMR (acetone-d_6), δ: 2.78 (s, 3 H, SMe_2); 2.95 (s, 3 H, SMe_2); 4.58 (s, 1 H, CH); 5.42 (s, 1 H, CH); 6.92 (s, 6 H, C_6H_6). ^{11}B{^{1}H} NMR (acetone-d_6), δ: –24.7, –21.1, –19.1, –11.5, –8.8, –7.1, –4.1, –1.7, –1.2 (all s, 1 B each).

[Tris(*tert*-butylisocyanide)(9-dimethylsulfonio-7,8-dicarbollyl)iron] hexafluorophosphate, [(Carb´)Fe(^{t}BuNC)$_3$]PF$_6$ ([4]PF$_6$). A solution of the complex [3]PF_6 (30 mg, 0.06 mmol) and Bu^{t}NC (0.1 mL, 0.89 mmol) in acetonitrile (1.5 mL) was irradiated with the use of a 100 W incandescent lamp at 0 °C for 1.5 h. The solvent was removed *in vacuo*. The residue was reprecipitated from dichloromethane with diethyl ether. The complex [**4**]PF_6 was obtained as a yellow solid substance in a yield of 39 mg (95%). Found (%): C, 35.31; H, 6.74; N, 6.37; B, 14.94. $C_{19}H_{43}B_9F_6FeN_3PS$. Calculated (%): C, 35.45; H, 6.73; N, 6.53; B, 15.11. ^{1}H NMR (acetone-d_6), δ: 1.63 (s, 27 H, Bu^{t}NC); 2.73 (s, 3 H, SMe_2); 2.89 (s, 3 H, SMe_2); 3.26 (s, 1 H, CH); 4.18 (s, 1 H, CH). ^{11}B{^{1}H} NMR (acetone-d_6), δ: –26.0, –20.1, –17.5, –12.7, –11.3, –8.7, –8.0, –2.6, –0.3 (all s, 1 B each).

X-ray diffraction study of the complex [4]PF$_6$. Yellow prismatic crystals with the composition $C_{19}H_{43}B_9F_6FeN_3PS$, which were grown by slow diffusion in a two-layer system consisting of Et_2O and a solution of the complex in CH_2Cl_2, are triclinic. The unit cell parameters are a = 12.1774(6) Å, b = 15.2921(8) Å, c = 19.3818(11) Å, α = 109.0340(10)°, β = 97.0680(10)°, γ = 100.9430(10)°, V = 3282.7(3) Å^3, space group $P\bar{1}$, Z = 4, d_{calc} = 1.303 g cm^{-3}. A total of 31863 reflections were collected on a Bruker SMART APEX2 CCD diffractometer at 100 K (Mo-Kα radiation, $2\theta_{\max}$ = 53.00°) from a single crystal of dimensions 0.32×0.12×0.08 mm. After merging of equivalent reflections, the data set consisted of 13587 independent reflections (R_{int} = 0.0547), which were used for the structure solution and refinement. An absorption correction (μ = 0.622 mm^{-1}) was applied with the use of the APEX2 program ($T_{\max}$ and $T_{\min}$ are 0.948 and 0.864, respectively).[17] The structure was solved by direct methods. All nonhydrogen atoms were located in difference electron density maps and refined based on F^2_{hkl} with anisotropic displacement parameters. The hydrogen atoms of the carborane fragment were located in difference electron density maps, and the other hydrogen atoms were positioned geometrically. All hydrogen atoms were refined isotropically using a riding model with U(H) = nU(C), where U(C) are the equivalent thermal parameters of the corresponding pivot carbon atoms; n = 1.2 and 1.5 for the CH and Me groups, respectively. The final R factors were as follows: R_1 = 0.0485 (calculated based on F_{hkl} for 9166 reflections with $I > 2\sigma(I)$), wR_2 = 0.0975 (calculated based on F^2_{hkl} for all 13587 reflections), 773 parameters were refined, GOOF = 0.997. All calculations were carried out with the use of the SHELXTL PLUS 5 program package.[18] The atomic coordinates, displacement parameters, and complete data on the geometric parameters were deposited with the Cambridge Structural Database.

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