Brief Communications

Nonsymmetrical iron bis(carborane) complexes (η-1-Bu^{t}NH-1,7,9-$C_3B_8H_{10}$)Fe(η-9-L-7,8-$C_2B_9H_{10}$) (L = SMe_2, NMe_3)

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Visible light irradiation of the benzene complex [(η-1-Bu^{t}NH-1,7,9-$C_3B_8H_{10}$)Fe(η-C_6H_6)]$^+$ in the presence of the charge-compensated carborane anions [9-L-7,8-$C_2B_9H_{10}$]$^-$ (L = SMe_2, NMe_3) affords ferracarboranes (η-1-Bu^{t}NH-1,7,9-$C_3B_8H_{10}$)Fe(η-9-L-7,8-$C_2B_9H_{10}$). Their structures were established by X-ray diffraction analysis.

Key words: iron, metallacarboranes, sandwich compounds.

The first iron bis(carborane) complex, *viz.*, [Fe(η-7,8-$C_2B_9H_{11})_2]^{2-}$, was prepared[1] by the reaction of $FeCl_2$ with the dicarbollide dianion. Further, the neutral compounds based on the monoanionic carborane ligands, *viz.*, tricarbollide [$C_3B_8H_{11}]^-$ (see Ref. 2) and charge-compensated dicarbollides [$LC_2B_9H_{10}]^-$ were synthesized analogously.[3,4] However, this route is suitable only for the synthesis of symmetrical bis(carborane) complexes. A small group of nonsymmetrical bis(carbollide) compounds, *viz.*, anions [(η-7,8-$C_2B_9H_{11}$)Fe(η-10-SR_2-7,8-$C_2B_9H_{10}$)]$^-$ (R = Me, Et, Pr^n) is described, they were prepared by the reaction of the hydride [HFe(η-7,8-$C_2B_9H_{11})_2]^-$ with dialkyl sulfides.[5] In addition, we synthesized[6,7] the derivative (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Fe(η-9-NMe_3-7,8-$C_2B_9H_{10}$) by the photochemical reaction of [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)-Fe(η-C_6H_6)]$^+$ with [9-NMe_3-7,8-$C_2B_9H_{10}]^-$. In the present work, we report on the synthesis of first nonsymmetrical iron bis(carborane) complexes containing both the tricarbollide and charge-compensated dicarbollide ligands.

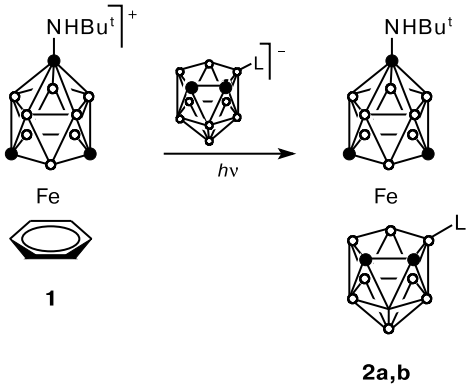
Results and Discussion

Recently,[8] we have shown that the tricarbollide complex [(η-1-Bu^{t}NH-1,7,9-$C_3B_8H_{10}$)Fe(η-C_6H_6)]$^+$ (**1**) exchanges the benzene ligand for the alkyl-substituted ben-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2089—2096, November, 2010.
1066-5285/10/5911-2143

zenes upon visible light irradiation. The lability of benzene in cation **1** can also be used for the synthesis of the complexes of the ferracarborane fragment $[(\eta\text{-}1\text{-}Bu^tNH\text{-}1,7,9\text{-}C_3B_8H_{10})Fe]^+$ with other ligands. For example, we have found that the photochemical reactions of this cation with sodium salts of the charge-compensated dicarbollides $Na[9\text{-}L\text{-}7,8\text{-}C_2B_9H_{10}]$ (L = SMe_2, NMe_3) at 0—5 °C afford the nonsymmetrical ferracarbones $(\eta\text{-}1\text{-}Bu^tNH\text{-}1,7,9\text{-}C_3B_8H_{10})Fe(\eta\text{-}9\text{-}L\text{-}7,8\text{-}C_2B_9H_{10})$ (**2a**,**b**) in yields 50—60% (Scheme 1). In the reaction considered, the bis(tricarbollide) complex $Fe(\eta\text{-}1\text{-}Bu^tNH\text{-}1,7,9\text{-}C_3B_8H_{10})_2$ forms as a side product due to symmetrization of the cationic fragment $[(\eta\text{-}1\text{-}Bu^tNH\text{-}1,7,9\text{-}C_3B_8H_{10})Fe]^+$.* The admixture of this complex can easily be removed due to its high solubility in low-polar solvents. However, the bis(tricarbollide) complex becomes the main product at room temperature, which explains the necessity for performing the reaction at reduced temperature.

Scheme 1



L = SMe_2 (**a**), NMe_3 (**b**)

Ferracarboranes **2a**,**b** are violet solids stable in air. Their structures were confirmed by the data from ^1H and ^{11}B NMR spectroscopy and elemental analysis.

The structures of both compounds were established by X-ray diffraction (Figs 1 and 2). The selected bond lengths and angles are given in Tables 1 and 2. In complex **2a**, the distance from the iron atom to the plane of the tricarbollide ligand $Fe...C_2B_3(C_3B_8)$ (1.469(1) Å) is somewhat shorter than the distance $Fe...C_2B_3(C_2B_9)$ (1.493(1) Å). Both distances are close to the corresponding distances in the symmetric complexes $Fe(\eta\text{-}1\text{-}Bu^tNH\text{-}1,7,9\text{-}C_3B_8H_{10})_2$ (1.448 and 1.485 Å, *av.* 1.467 Å)[4] and $Fe(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})_2$ (1.499 Å).[3,9] The angle between the C_2B_3 planes is 3.2°.

* An analogous symmetrization process has also been observed[7] in the reaction of $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Fe(\eta\text{-}C_6H_6)]^+$ with $[9\text{-}NMe_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$.

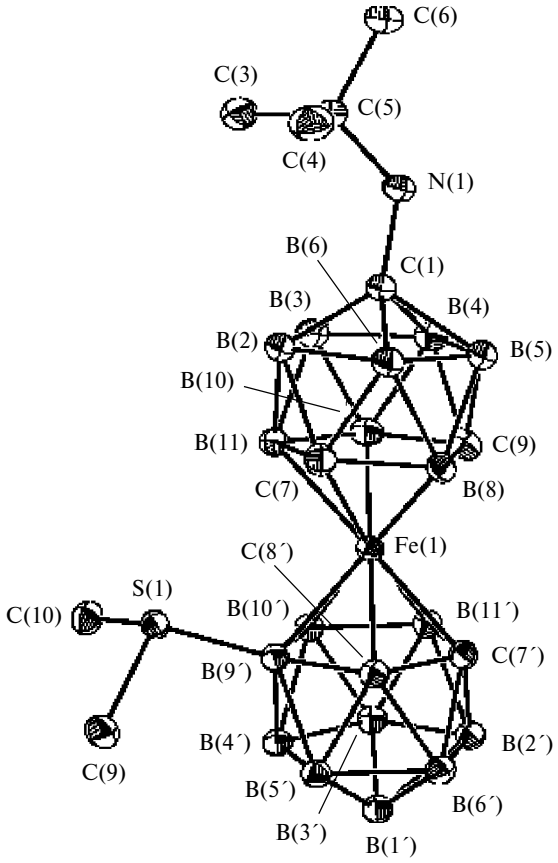


Fig. 1. The structure of complex **2a** (thermal ellipsoids are shown with 50% probability).

In complex **2b**, the distances $Fe...C_2B_3$ (1.499(2) and 1.500(2) Å) are very close. The angle between the planes (8.1°) is significantly larger than that in complex **2a**, which is explained by the greater steric effect of the NMe_3 group compared to SMe_2.

Thus, we synthesized and structurally characterized the first examples of the iron bis(carborane) complexes containing both the tricarbollide and charge-compensated dicarbollide ligands.

Table 1. Selected bond lengths (*d*) and angles (ω) in complex **2a**

Parameter	Value	Parameter	Value
Bond length	*d*/Å	Bond length	*d*/Å
Fe(1)—C(7)	2.0829(11)	Fe(1)—C(8′)	2.0381(10)
Fe(1)—B(11)	2.0754(12)	Fe(1)—B(9′)	2.0951(11)
Fe(1)—B(10)	2.0698(12)	S(1)—B(9′)	1.9199(12)
Fe(1)—C(9)	2.0649(11)	N(1)—C(1)	1.4327(13)
Fe(1)—B(8)	2.0561(11)	C(7′)—C(8′)	1.6253(15)
Fe(1)—B(10′)	2.1559(12)	Angle	ω/deg
Fe(1)—B(11′)	2.1116(12)	C(1)—N(1)—C(5)	126.07(9)
Fe(1)—C(7′)	2.0385(10)	C(8′)—B(9′)—S(1)	122.42(7)

Table 2. Selected bond lengths (d) and angles (ω) in complex **2b**

Parameter	Value	Parameter	Value
Bond length	d/Å	Bond length	d/Å
Fe(1)—C(9)	2.106(2)	Fe(1)—C(8′)	2.053(2)
Fe(1)—B(8)	2.081(2)	Fe(1)—B(9′)	2.160(3)
Fe(1)—C(7)	2.093(2)	N(2)—B(9′)	1.632(3)
Fe(1)—B(11)	2.073(2)	N(1)—C(1)	1.432(3)
Fe(1)—B(10)	2.102(2)	C(7′)—C(8′)	1.629(3)
Fe(1)—B(10′)	2.143(2)	Angle	ω/deg
Fe(1)—B(11′)	2.094(2)	C(1)—N(1)—C(4)	126.61(17)
Fe(1)—C(7′)	2.036(2)	N(2)—B(9′)—C(8′)	121.74(18)

Experimental

Reactions were performed in an argon atmosphere using anhydrous solvents prepared conventionally. All procedures associated with isolation of products were carried out in air. The starting compounds **1** · PF_6 and Na[9-L-7,8-$C_2B_9H_{10}$] (see Refs 8 and 10, respectively) were prepared according to known procedures. Irradiation was carried out in a Schlenk tube with a diameter of 15 mm using a 150 W incandescent lamp. The Schlenk tube was cooled with ice. ^{1}H and ^{11}B NMR spectra were recorded on a Bruker Avance-400 (^{1}H, 400.13 MHz; ^{11}B, 128.38 MHz) instrument in acetone-d_6.

(1-*tert*-Butylamino-1,7,9-tricarbollyl)(9-L-7,8-dicarbollyl)-iron, (η-1-Bu^{t}NH-1,7,9-$C_3B_8H_{10}$)Fe(η-9-L-7,8-$C_2B_9H_{10}$) (2a,b). To a solution of complex **1** · PF_6 (30 mg, 0.06 mmol) in CH_2Cl_2 (4 mL), a solution of Na[9-L-7,8-$C_2B_9H_{10}$] (0.56 mL, 0.125 mol L^{-1}, 0.07 mmol) in THF was added. The resulting mixture was irradiated for 3 h. The solvent was removed *in vacuo* and the residue was chromatographed on a column with silica gel (1×15 cm) using a CH_2Cl_2—petroleum ether (1 : 1) mixture as the eluent. The violet band was collected, the solvent was removed *in vacuo*, and the residue was reprecipitated from CH_2Cl_2 with petroleum ether to yield violet solids.

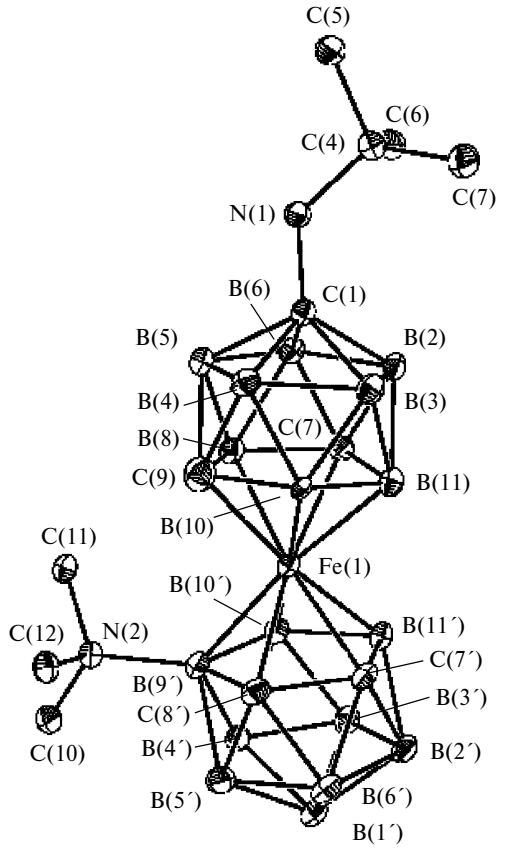


Fig. 2. The structure of complex **2b** (thermal ellipsoids are shown with 50% probability).

Compound 2a, L = SMe_2, yield 18 mg (64%). Found (%): C, 28.87; H, 7.98; B, 40.49; N, 3.04. $C_{11}H_{36}B_{17}FeNS$. Calculated (%): C, 29.09; H, 7.99; B, 40.47; N, 3.09. ^{1}H NMR, δ: 1.22 (s, 9 H, Bu^t); 2.16 (s, 1 H, CH); 2.56 (s, 1 H, CH); 2.66 (s, 3 H, SMe_2); 2.82 (s, 3 H, SMe_2); 3.07 (s, 1 H, NH); 3.80 (s, 2 H,

Table 3. Crystallographic data and refinement parameters for complexes **2a**,**b**

Parameter	**2a**	**2b**
Molecular formula	$C_{11}H_{36}B_{17}FeNS$	$C_{12}H_{39}B_{17}FeN_2$
M	454.09	451.07
Crystal system	Triclinic	Orthorhombic
Space group	P-1	*Pbca*
a/Å	6.6511(5)	13.3559(14)
b/Å	8.5081(6)	13.1087(14)
c/Å	22.5241(19)	27.209(3)
α/deg	96.035(2)	—
β/deg	91.750(2)	—
γ/deg	112.7920(10)	—
V/Å^3	1165.03(16)	4763.7(9)
Z	2	8
d_{calc}/g cm^{-3}	1.294	1.258
Crystal sizes/mm	0.45×0.35×0.20	0.50×0.30×0.20
Crystal color, line habitus	Red, lamellar	Red, needle-like

(*to be continued*)

Table 3 (*continued*)

Parameter	**2a**	**2b**
Diffractometer	«Bruker APEX II»	
Radiation (λ/Å)	Mo-Kα (0.71073)	
μ/mm^{-1}	0.739	0.639
Account of absorption	SADABS	
Temperature/K	100(2)	
Scanning mode	ω	
$2\theta_{max}$/deg	60.00	58.00
Total number of reflections	15001	54465
Number of independent reflections (R_{int})	6721 (0.0164)	6284 (0.1037)
R_1 (over F for reflections with $I > 2\sigma(I)$)	0.0269 (6059 reflections)	0.0414 (4304 reflections)
Number of parameters refined	0.0714	0.1160
Number of parameters refined	364	295
Weighing scheme	$w^{-1} = \sigma^2(F_0^2) + (kP)^2 + lP$, where $P = 1/3(F_0^2 + 2F_c^2)$	
k	0.0432	0.0551
l	0.2370	2.2310
GOOF	1.003	1.013
$F(000)$	472	1888
Residual electron density/e $Å^{-3}$, ρ_{max}/ρ_{min}	0.555/−0.214	0.592/−0.391

CH). $^{11}B\{^1H\}$ NMR, δ: −3.8 (s, 1 B); −4.4 (s, 1 B); −8.0 (s, 1 B); −8.7 (s, 1 B); −9.3 (s, 2 B); −10.5 (s, 1 B); −12.6 (s, 1 B); −14.6 (s, 2 B); −15.5 (s, 1 B); −16.8 (s, 1 B); −21.9 (s, 2 B); −22.7 (s, 1 B); −24.6 (s, 1 B); −26.0 (s, 1 B).

Compound 2b, L = NMe_3, yield 12.5 mg (45%). Found (%): C, 31.34; H, 8.23; B, 38.29; N, 5.61. $C_{12}H_{39}B_{17}FeN_2 \cdot 0.25CH_2Cl_2$. Calculated (%): C, 31.15; H, 8.43; B, 38.91; N, 5.93. ^1H NMR, δ: 1.20 (s, 9 H, Bu^t); 2.14 (s, 1 H, CH); 2.59 (s, 1 H, CH); 3.07 (s, 1 H, NH); 3.31 (s, 9 H, NMe_3); 3.67 (s, 1 H, CH); 4.23 (s, 1 H, CH). $^{11}B\{^1H\}$ NMR, δ: 4.3 (s, 1 B); −5.9 (s, 1 B); −7.9 (s, 2 B); −10.0 (s, 1 B); −10.9 (s, 1 B); −12.2 (s, 2 B); −13.1 (s, 1 B); −14.9 (s, 1 B); −15.6 (s, 1 B); −16.8 (s, 1 B); −21.9 (s, 2 B); −22.7 (s, 1 B); −24.6 (s, 1 B); −26.0 (s, 1 B).

X-ray diffraction study of complexes 2a,b. The single crystals of **2a**,**b** were grown by slow diffusion in the two-layer system: a solution of a complex in CH_2Cl_2/petroleum ether. Crystallographic data, experimental details, and interpretations and refinements of structures are given in Table 3. The structures were solved by the direct method and all non-hydrogen atoms were localized in the electron density difference syntheses and refined over F^2_{hkl} in the anisotropic approximation. The hydrogen atoms in the carborane fragment were localized in the electron density difference syntheses and the remaining hydrogen atoms are placed in the geometrically calculated positions. All hydrogen atoms were refined in the isotropic approximation in the riding model with $U(H) = n \cdot U(C)$ where $U(C)$ is the equivalent temperature factor of the carbon atom to which the H atom is bound, and n is equal to 1.2 and 1.5 for the CH and Me groups, respectively. All calculations were performed using the SHELXTL program complex.[11] Atomic coordinates, temperature factors, and comprehensive data on geometric parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC 773211 and 773212 for **2a** and **2b**, respectively).

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Received April 20, 2010;
in revised form October 13, 2010