Macrocyclization of the semiclathrochelate *o*-carboranylboronate and *n*-butylboronate iron(II) oximehydrazonates: synthesis and structure of clathrochelate products and unexpected allosteric effect of the apical substituent*

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The template condensation of diacetylmonooxime hydrazone (HDXO) with *n*-butylboronic acid and dimethyl ester of *o*-carboranyldiboronic acid on the iron(II) ion matrix afforded the $[Fe(DXO)_3(BBu)](BF_4)$ and $[Fe(DXO)_3(Bo\text{-carb})](BF_4)$ semiclathrochelates. The H^+-ion-catalyzed macrocyclization of these precursors with an excess of formaldehyde and triethyl orthoformate (TOF) resulted in the corresponding macrobicyclic complexes. In the case of *o*-carboranylboronate semiclathrochelate, the macrocyclization with TOF gave the clathrochelate with the previously unknown *syn*,*syn*,*anti*-orientation of the ethoxy substituents relative to the 1,3,5-triazacyclohexane capping fragment. The complexes obtained were characterized using elemental analysis, IR, UV-Vis, MALDI-TOF mass, ^1H, ^{11}B, and ^{13}C NMR, and ^{57}Fe Mössbauer spectroscopies and X-ray crystallography.

Key words: clathrochelates, iron(II), organoboranes, carboranes, oximes, hydrazonates, macrocycles, allosteric control, X-ray crystallography.

A number of mono- and binuclear semiclathrochelate iron(II) and cobalt(II,III) tris-oxime-hydrazonates with boron-, tin-, antimony, and- germanium-containing cross-linking apical groups have been obtained up to date; their H^+-catalyzed condensation with triethyl orthoformate (TOF) gave in each case a sole isomer of the clathrochelate complex. In the case of boron-containing clathrochelates, the ethoxy groups and the semiclathrochelate fragment are *syn*,*syn*,*syn*-oriented with respect to the mean plane of the 1,3,5-triazacyclohexane ring,[1] whereas in the tin-, antimony-, and germanium-containing complexes, the ethoxy groups have the *anti*,*anti*,*anti*-orientation.[2—4] This difference was explained[5] by the change in the geometry of the semiclathrochelate precursor from trigonal-prismatic (TP) for boron-containing compounds to trigonal-antiprismatic (TAP) for other types of cross-linking groups.

In this study, we planned to synthesize the binuclear clathrochelate oximehydrazonates using an *o*-carboranyldiboronic acid derivative and to obtain previously unknown *n*-butylboronate iron(II) semiclathrochelate and to perform its macrocyclization with TOF.

Results and Discussion

Only few *o*-carborane-containing organoboron compounds with the C—B bond, obtained by reactions of boron trichloride with appropriate C-lithium derivatives, are described in the literature.[6] We synthesized methyl ester of *o*-carboranyldiboronic acid (**1**) by a similar procedure starting from *o*-carborane with chlorodimethoxyborane as a borylating agent (Scheme 1). According to $^{11}B\{^1H\}$ NMR spectrum of the reaction mixture, the degree of conversion was ~75%. Apart from signals of the boron atoms of the symmetrically substituted carborane polyhedron, this spectrum contained the characteristic

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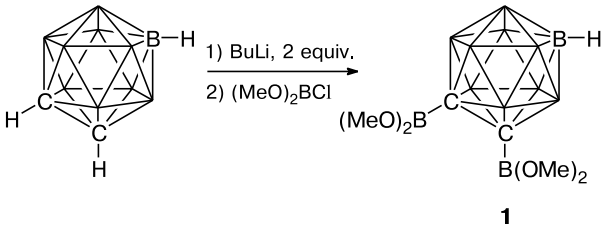
signal of alkyldialkoxyborane at 23.8 ppm. We failed to isolate pure compound **1** because of the side reaction of protolysis of the labile B—C bond caused by the CH-acidic properties of the initial *o*-carborane. After removal of LiCl and the solvent, the reaction product was used without further purification.

Scheme 1



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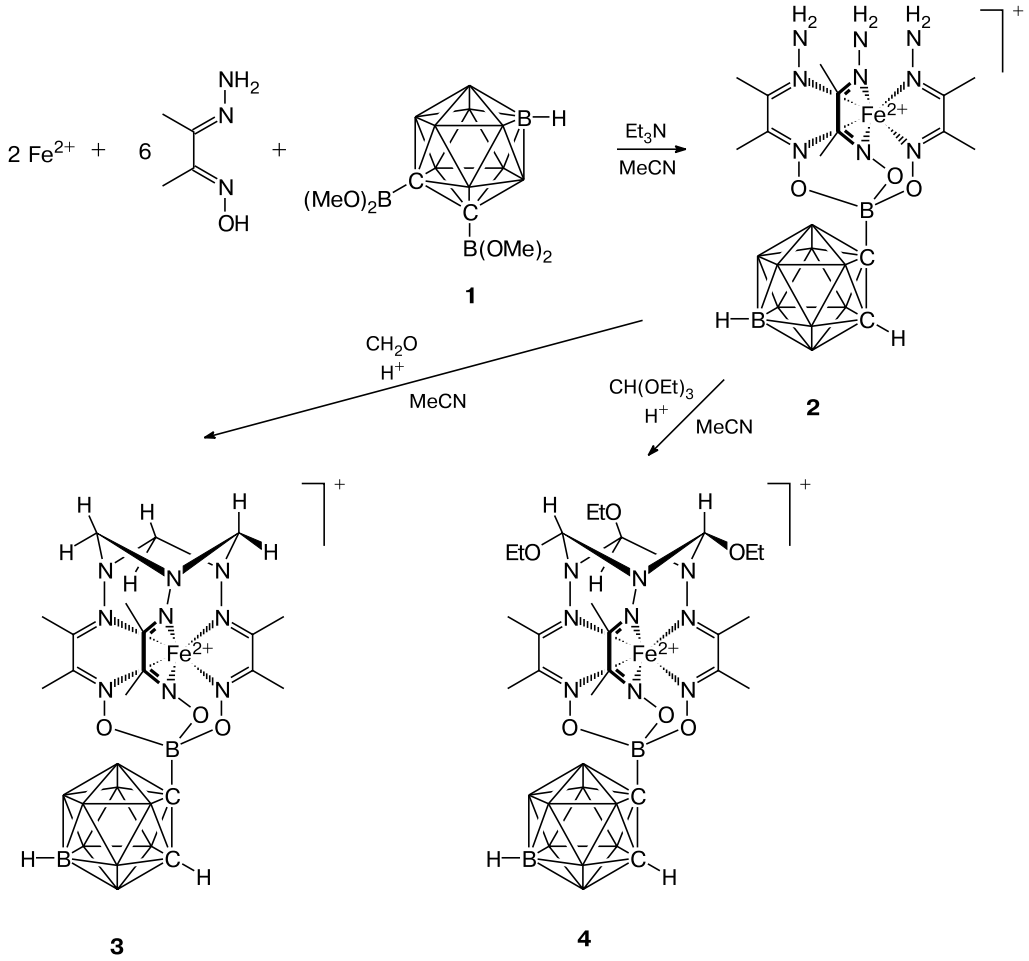
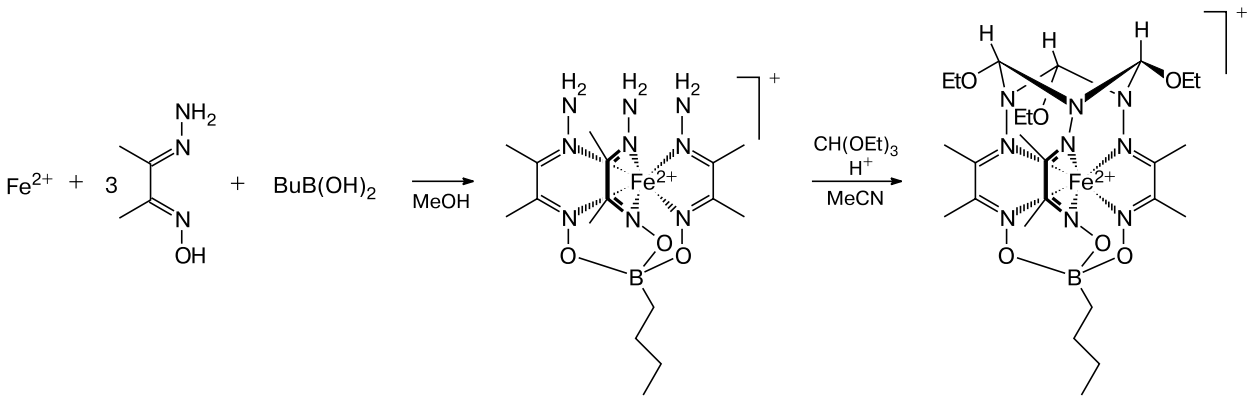
The bifunctionality of compound **1** as a Lewis acid implied the formation of a binuclear semiclathrochelate iron(II) tris-oximehydrazonate with *ortho*-orientation of the apical cross-linking groups of these semiclathrochelate fragments in the carborane polyhedron. The template condensation of HDXO with ester **1** on the Fe^{2+} ion matrix was carried out in acetonitrile in the presence of triethylamine for binding the H^+ ions that formed. This reaction gave the semiclathrochelate iron(II) complex **2** (Scheme 2), which we failed to isolate in a pure state. The $^{11}B^{1}\{H\}$ NMR spectrum of this product contains signals of the RBO_3 cross-linking fragment (3.8 ppm), the BF_4^- counter-ions (−1.4 ppm), and the signals for the boron atoms of unsymmetrically substituted *o*-carborane polyhedron, that proves the elimination of one $B(OMe)_2$ fragment of Lewis acid **1** during condensation with HDXO. The MALDI-TOF mass spectrum of complex **2** contains an intense peak (*m*/*z* 552) of the semiclathrochelate $[Fe(DXO)_3(B(o\text{-carb}))]^+$ cation. Apparently, due to the steric hindrance in the *ortho*-position, in this case the methyl ester of *o*-carboranyldiboronic acid can be a monofunctional Lewis acid only, while the second trigonal dimethoxyboryl group is eliminated in the course of isolation of semiclathrochelate. The H^+-ion-catalyzed con-

Scheme 2



1 **2** **3** **4**

Scheme 3



5 **6**

densation of the semiclathrochelate product **2** with formaldehyde and TOF afforded oximehydrazonate clathrochelates **3** and **4** with the apical 1,3,5-triazacyclohexane fragment (see Scheme 2).

We also performed macrocyclization of the newly isolated iron(II) *n*-butylboronate oxime hydrazonate semiclathrochelate **5** with TOF (Scheme 3), giving rise to clathrochelate **6**.

The composition and symmetry of the complexes obtained were confirmed by ^{1}H and ^{13}C NMR data, in particular, by the ratio of integral intensities of the proton signals of substituents in the cross-linking apical group (in the case of *n*-butylboronic acid derivatives) and chelate ribbed fragments and by the number and positions of signals in the ^{13}C NMR spectra. The double sets of signals of the methine group of the cross-linking fragment and the ethoxy substituents in the ^{1}H and ^{13}C NMR spectra of clathrochelate **4** showed a decrease in their molecular symmetry. The signals for carbon atoms bound directly to boron cannot be observed because of the high quadrupole moment of the boron nucleus. The ^{1}H NMR signals of the carborane polyhedron are also broadened due to the spin-spin coupling with boron nucleus. The ^{11}B NMR spectra contain signals for the cross-linking tetrahedral boron and the BF_4^- counter-ions, and also the boron atoms of the apical *o*-carboranyl fragment in the case of clathrochelates **3** and **4**.

The parameters of the ^{37}Fe Mössbauer spectra of the synthesized macrobicyclic complexes, *i.e.*, isomer shifts (IS) of 0.33—0.37 mm s^{-1} and quadrupole splittings (QS) of 0.22—0.47 mm s^{-1}, are typical of the low-spin iron(II) complexes with high field ligands and geometry intermediate between the trigonal prism and the trigonal antiprism. In the case of semiclathrochelate **5**, the isomer shift (0.41 mm s^{-1}) is much higher than that in the case of complexes **3**, **4**, and **6**, due to a decrease in the s-electron density on the iron nucleus and, hence, lower field strength of the non-macrocyclic ligand in complex **5** compared to that of the macrobicyclic ligands in complexes **3**, **4**, and **6** (so-called "macrocyclic effect").

The UV-Vis spectra of the obtained boron-containing oximehydrazonate clathrochelates contain two bands with similar intensities in the visible region ($\varepsilon \approx (3—8)\cdot 10^3$ L mol^{-1} cm^{-1}) with maxima from 450 to 500 nm and one weaker band ($\varepsilon \approx (1—2)\cdot 10^3$ L mol^{-1} cm^{-1}) with a maximum from 400 to 450 nm. These bands were assigned to the metal—ligand charge transfer bands (CTB) *Fed* $\rightarrow$ *Lπ**. Meanwhile, the UV-Vis spectra of symmetrical boron-containing iron(II) tris-dioximates contain a single asymmetrical highly intense band ($\varepsilon \approx (1—3)\cdot 10^4$ L mol^{-1} cm^{-1}) of the same nature in the visible region whose deconvolution into Gaussian components gave a more intense band with the maximum from 440 to 490 nm and a less intense band ($\varepsilon \approx (2—3)\cdot 10^3$ L mol^{-1} cm^{-1}) with a maximum at ~400 nm (see Ref. 1).

An increase in the number of CTBs for oximehydrazonate clathrochelates is caused by the presence of two types of donor groups (oxime and hydrazonate ones) in their molecules and the lack of a symmetry plane passing through the midlles of the C—C bonds in the chelate rings and the encapsulated metal ion. Earlier, we could not resolve charge transfer bands corresponding to different donor centers in the UV-Vis spectra of a number of boron-containing clathrochelates of this type.[2] The nonequivalence of the azomethine fragments of the oximehydrazonate macrobicyclic ligands can be clearly seen in the IR spectra of their complexes, which exhibit C=N stretching bands for both the oxime (C=N—O) and hydrazone (C=N—N) groups. The IR spectra of carboranyl-containing clathrochelates contain characteristic bands for the B—H stretching vibrations in apical substituents (ν(B—H) $\approx$ 2500 cm^{-1}).

The molecular and crystal structures of complexes **4**$\cdot$[$FeCl_4^-$] and **6**$\cdot$0.75$CHCl_3$ were established by X-ray

crystallography (Figs 1 and 2). The iron(II) atom has a distorted trigonal-prismatic N_6-environment; the Fe—N distances and distortion angles φ (Table 1) are characteristic of boron-containing clathrochelate tris-oximehydrazonates. All the ethoxy groups and the semiclathrochelate fragment in cation **6** are located on one side of the 1,3,5-triazacyclohexane ring. Hence, the complex is the *syn*,*syn*,*syn*-isomer, like the previously synthesized boron-containing oximehydrazonate clathrochelates, the derivatives of TOF.[1]

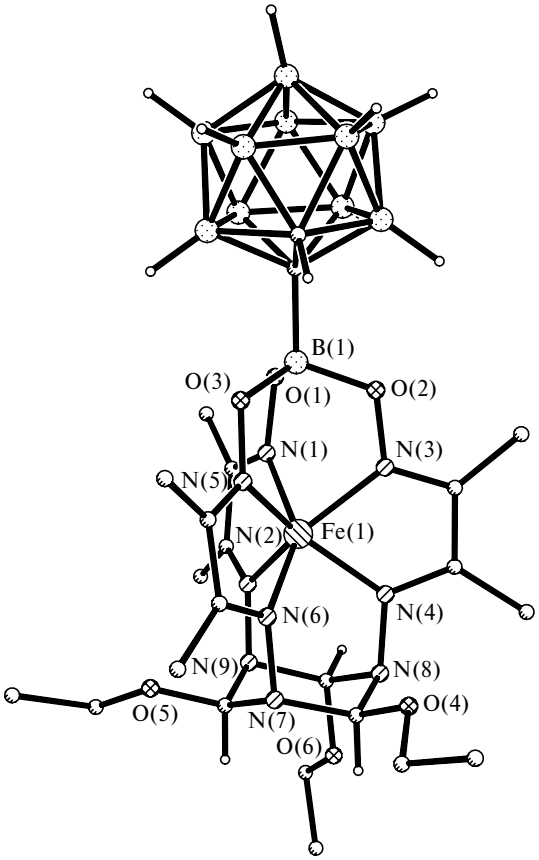


Fig. 1. Molecular structure of cation **4**.

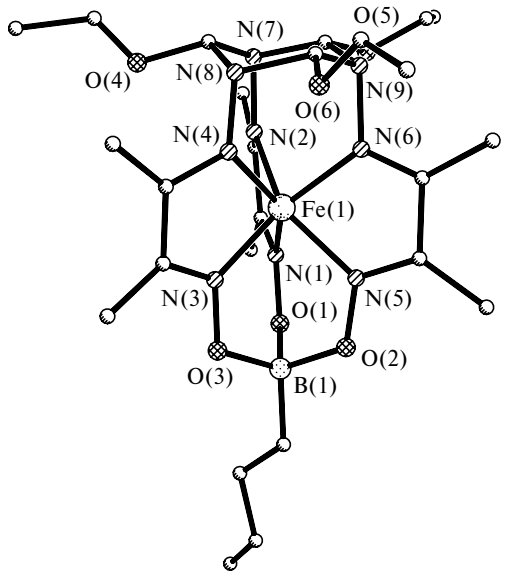


Fig. 2. Molecular structure of one of the two independent cations **6** with identical structures.

Table 1. Some geometrical characteristics of the clathrochelate cations

Parameter	**4**	**6***
Fe—N(1,3,5)/Å	1.92(1), 1.928(9), 1.890(9)	1.911(9), 1.90(1), 1.925(9), 1.91(1), 1.88(1), 1.90(1)
Fe—N(2,4,6)/Å	1.917(9), 1.906(9), 1.885(9)	1.924(9), 1.951(9), 1.91(1), 1.91(1), 1.94(1), 1.90(1)
h/Å	2.31	2.46, 2.34
φ/deg	15.5, 14.9, 16.2	14.5, 14.7, 10.3, 9.0, 14.2, 9.8
C—O—C—C/Å	170, 173, 180	157, 150, 169, 177, 161, 143
N—N/Å	1.41(1), 1.44(1), 1.47(1)	1.45(2), 1.42(2), 1.52(2), 1.41(2), 1.38(2), 1.42(2)

* Data for two independent molecules are presented.

However, the clathrochelate cation **4** has an unusual *syn*,*syn*,*anti*-orientation of the ethoxy groups in the cross-linking 1,3,5-triazacyclohexane fragment.

The wide range of the C—O—C—C torsion angles (143—180°, see Table 1) is caused by the essential thermal lability of the ethyl fragments. The crystal **4**·$[FeCl_4^-]$ is stabilized by a system of Cl...H—C hydrogen bonds between the $FeCl_4^-$ anion and the only ethoxy *anti*-oriented substituent (Fig. 3). The Cl...H contacts shorter than the sum of the van der Waals radii (2.97 Å),[7] are formed between the Cl(1) and Cl(4) atoms and the hydrogen atoms at C(15) and C(8) (the Cl(1)...H(8c), Cl(1)...H(15a), and Cl(4)...H(8b) distances are 2.79, 2.92, and 2.85 Å, respectively). Moreover, similar hydrogen bonds are formed between hydrogen atoms at the C(13) and C(14) atoms of the 1,3,5-triazacyclohexane ring (the Cl(3)...H(13a) and Cl(3)...H(14a) distances are 2.78 and 2.96 Å) and between the H(16a) atom of the ethoxy group O(4)—C(16)—C(17) (2.95 Å). In the **6**·0.75$CHCl_3$ crystal, the solvate chroroform molecule does not form hydrogen bonds of this type with the $[Fe(DXO)_3(HCOEt)_3(BBu)]^+$ cation. The conformations of the 1,3,5-triazacyclohexane ring are the same in both cations.

In our opinion, the formation of the product with *syn*,*syn*,*anti*-orientation of substituent in the case of carboranylboronate clathrochelate may be caused by the structure of the apical substituent: one hydrogen atom, being located between the petals formed by the oximehydrazonate chelate fragments, causes steric hindrance for the ethoxy group in the first stage of macrocyclization with TOF, resulting in its *anti*-orientation.

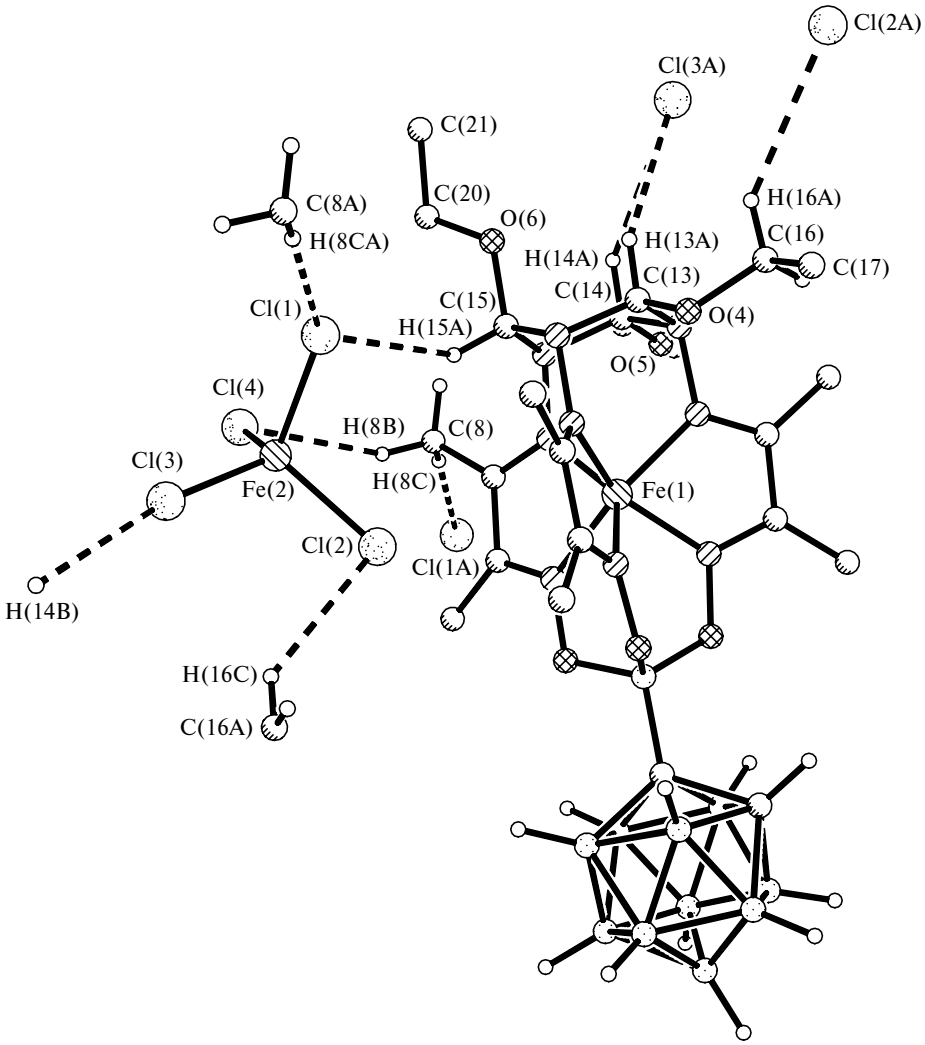


Fig. 3. Hydrogen bonds Cl...H—C in the crystal of **4**·[$FeCl_4^-$], which stabilize the *anti*-configuration of the C(15)—O(6)—C(20)—C(21) fragments.

Thus, *n*-butylboronate and *o*-carboranylboronate semiclathrochelate iron(II) oximehydrazonates were obtained for the first time by template synthesis on the iron(II) matrix. Macrocyclization of these ions with active carbonyl agents afforded oximehydrazonate clathrochelates. In the case of *o*-carborane and TOF derivative, the clathrochelate molecule contains ethoxy substituents with an unusual *syn*,*syn*,*anti*-orientation with respect to the 1,3,5-triazacyclohexane ring due to the allosteric effect of the apical *o*-carboranyl substituent.

Experimental

Commercial $FeCl_2 \cdot 4H_2O$, triethyl orthoformate, $N_2H_4 \cdot H_2O$, and *n*-butylboronic acid (Fluka); boron trichloride (Aviabor); BuLi (Aldrich); and trimethyl borate (Merck) were used. Diacetylmonooxime hydrazone (HDXO) and chlorodimethoxyborane were synthesized as described previously.[8,9]

Analytical data (C, H, and N contents) were obtained on a Carlo Erba 1106 microanalyzer; iron was determined spectrophotometrically.

^1H, ^{11}B, and ^{13}C NMR spectra were recorded on a Bruker AC-200P spectrometer (working frequencies 200.13 (^1H), 50.32 (^{13}C), and 64.21 MHz (^{11}B)) in CD_2Cl_2 and CD_3CN. The chemical shifts are given in the δ scale and referred to residual proton signals of the solvent (δ_H CD_2Cl_2 5.20, δ_H CD_3CN 1.94) and the carbon signals of the solvent (δ_C 53.7 and 0.3, respectively). The ^{11}B NMR chemical shifts are referred to external boron trifluoride etherate $BF_3 \cdot Et_2O$.

MALDI-TOF mass spectra were recorded with a MALDI-TOF-MS Autoflex Bruker time-of-flight mass spectrometer in the reflecto-mol operation mode. Ionization was induced by a UV laser at a wavelength of 336 nm. A nickel plate served as the target and 2,5-dihydroxybenzoic acid was used as a matrix. The measurement accuracy was 0.1%.

The ^{57}Fe Mössbauer spectra were obtained with a YaGRS-4M spectrometer with constant acceleration mode and

collected with a 256-channel analyzer. The isomer shifts were measured relative to sodium nitroprusside, and α-Fe foil was used for velocity scale calibration. The radiation source was ^{57}Co in a chromium matrix, which was always kept at room temperature. The minimum absorption linewidth in the spectrum of a standard sodium nitroprusside sample was 0.24 mm s^{-1}.

UV-Vis spectra of solutions of the complexes in CH_2Cl_2 in the 230—800 nm range were obtained with a Perkin—Elmer Lambda 9 spectrophotometer. The spectra were deconvoluted into the Gaussian components using the SPECTRA program.

1,2-Bis(dimethoxyboryl)-1,2-dicarba-*closo*-dodecaborane (1). A solution of *ortho*-carboranyldilithium (30 mmol), prepared by the reaction of *ortho*-carborane (4.3 g) with a 2.5 *M* solution of BuLi in hexane (24 mL) by a known procedure,[6] was added under argon to a solution of chlorodimethoxyborane (5.9 mL, 60 mmol) in THF (50 mL) at such a rate as to maintain the temperature below −78 °C. The reaction mixture was heated to room temperature and stirred for 1 h. The LiCl precipitate was filtered off, and the filtrate was concentrated to oily residue. According to ^{11}B NMR spectrum, the mixture contained 75% of product **1**. ^{11}B{^{1}H} NMR (THF—hexane), δ: −13.1 (B(3), B(6)); −10.1 (B(4), B(5), B(7), B(11)); −8.7 (B(8), B(10)); −2.9 (B(9), B(12)); 23.8 ($B(OMe)_2$).

1-(1,2-Dicarba-*closo*-dodecaboran-1-yl)-4,5,13,14,19,20-hexamethyl-2,16,17-trioxa-3,6,7,9,11,12,15,18,21-nonaaza-1-boratricyclo[7.7.5.1^{7,11}]docosa-3,5,12,14,17,19-hexaene(−1)iron(II) tetrafluoroborate, [Fe(DXO)$_3$(CH$_2$)$_3$(B(*o*-carb))](BF$_4$) (3). A solution of the methyl ester of *o*-carboranyldiboronic acid (0.95 g, 3.5 mmol) and triethylamine (2 mL, 14 mmol) in acetonitrile (2 mL) was added dropwise with stirring under argon to a solution/suspension of $FeCl_2 \cdot 4H_2O$ (1.31 g, 7 mmol) and HDXO (2.43 g, 20 mmol) in acetonitrile (5 mL). The dark-orange reaction mixture was stirred for 15 min, an excess of $NaBF_4$ (0.75 g) was added, and the mixture was stirred for 2 h and allowed to stand for 12 h at 4 °C. Then the precipitate was filtered off, washed with acetonitrile (3 mL), Et_2O (2×15 mL), and hexane (2×15 mL), and dried *in vacuo*. The yield of the precursor **2** was 1.9 g (~75%). ^{11}B{^{1}H} NMR (CD_2Cl_2), δ: −13.1 (B(3), B(6)); −10.1 (B(4), B(5), B(7), B(11)); −8.7 (B(8), B(10)); −2.9 (B(9), B(12)); 23.8 ($B(OMe)_2$). MS, *m/z*: 552 [M − BF_4^-]$^+$.

Gaseous formaldehyde obtained by distillation of an excess of paraformaldehyde (2 g) was passed for 5 min through a solution of semiclathrochelate **2** (0.65 g) in acetonitrile (10 mL) and then trifluoroacetic anhydride (5 μL) was added. The reaction mixture was kept for 72 h and filtered, the filtrate was concentrated to a small volume, and Et_2O was added. The precipitate formed was reprecipitated from CH_2Cl_2 with an excess of Et_2O and dried *in vacuo*. The solid was reprecipitated from DMSO with water. The precipitate thus formed was dissolved in a minimum amount of acetonitrile and a reprecipitated with an aqueous $NaBF_4$ solution. The red-orange precipitate was dried *in vacuo* and reprecipitated from a $CHCl_3$—acetonitrile mixture (5 : 1) with hexane. The yield of compound **3** was 0.15 g (24%). Found (%): C, 30.01; H, 5.14; Fe, 8.40; N, 18.30. $C_{17}H_{35}B_{12}F_4FeN_9O_3$. Calculated (%): C, 30.24; H, 5.24; Fe, 8.27; N, 18.68. MS, *m/z*: 588 [M − BF_4^-]$^+$. ^{1}H NMR (CD_3CN), δ: 2.52 (br.s, 6 H, CH_2); 3.48, 5.22 (both s, 9 H each, DXO). ^{13}C{^{1}H} NMR (CD_3CN), δ: 15.0 (CH_3(DXO)); 18.7 (CH_3(DXO)); 76.3 (CH_2N); 155.1 (C=N—O); 169.0 (C=N—N). ^{11}B{^{1}H} NMR (CD_3CN), δ: −12.0 (B(3), B(6)); −9.9 (B(4), B(5), B(7), B(8), B(10), B(11)); −4.7 (B(9), B(12)); −0.7 (BF_4^-); 4.5 (RBO_3). IR (KBr), ν/cm^{-1}: 940, 976, 1000, 1036 (ν(N—O)), 1104 m (ν(B—O)), 1578 (ν(C=N—O)), 1627 (ν(C=N—N)); 2592 (ν(B—H)). UV-Vis ($CHCl_3$), λ_{max}/nm (ε·10^{-3}/L mol^{-1} cm^{-1}): 212 (3.4), 262 (5.8), 276 (7.4), 311 (4.5), 350 (2.1), 433 (1.7), 483 (7.7), 496 (5.3). ^{57}Fe Mössbauer spectrum (mm s^{-1}): IS 0.33, QS 0.22.

1-(1,2-Dicarba-*closo*-dodecaboran-1-yl)-4,5,13,14,19,20-hexamethyl-8-*syn*,10-*syn*,22-*anti*-triethoxy-2,16,17-trioxa-3,6,7,9,11,12,15,18,21-nonaaza-1-boratricyclo[7.7.5.1^{7,11}]-docosa-3,5,12,14,17,19-hexaene(−1)iron(II) tetrafluoroborate, [Fe(DXO)$_3$(HCOEt)$_3$(*o*-carb)](BF$_4$) (4·BF$_4^-$). An excess of TOF (2 mL) and trifluoroacetic anhydride (5 μL) were added to a solution of precursor **2** (0.5 g) in acetonitrile (5 mL). The reaction mixture was kept for 72 h, the dark-orange solution was filtered off. The filtrate was concentrated to a small volume (3 mL), and Et_2O was added. The oily precipitate formed was dissolved in dichloromethane (2 mL) and precipitated with hexane. The precipitate was washed with hexane and dried *in vacuo*. The solid residue was precipitated from a minimum volume of acetonitrile (2 mL) with a saturated aqueous $NaBF_4$ solution. The precipitate was washed with water and Et_2O, dried *in vacuo*, and reprecipitated from CH_2Cl_2 with hexane. The resulting dark-orange precipitate was washed with hexane and dried *in vacuo* to give 0.27 g (48%) of **4**·BF_4^-. Found (%): C, 34.11; H, 5.69; Fe, 7.05; N, 15.81. $C_{23}H_{47}B_{12}F_4FeN_9O_6$. Calculated (%): C, 34.22; H, 5.88; Fe, 6.92; N, 15.62. MS, *m/z*: 720 [M − BF_4^-]$^+$. ^{1}H (CD_2Cl_2), δ: 0.98 (t, 6 H, CH_3(*syn*-OEt)); 1.27 (t, 3 H, CH_3(*anti*-OEt)); 2.35, 2.41 (both s, 9 H each, CH_3(DXO)); 3.59 (q, 4 H, CH_2(*syn*-OEt)); 3.90 (q, 2 H, CH_2(*anti*-OEt)); 5.73 (s, 1 H, *syn*-HC); 5.88 (s, 2 H, *anti*-HC). ^{13}C{^{1}H} NMR (CD_2Cl_2), δ: 14.1, 14.8 (CH_3(DXO)); 18.3 (CH_3(*anti*-OEt)); 18.6 (CH_3(*syn*-OEt)); 66.0 (CH_2(*syn*-OEt)); 66.7 (CH_2(*anti*-OEt)); 95.4 (*anti*-HC); 97.4 (*syn*-HC); 153.3 (*syn*-C=N—O); 154.2 (*anti*-C=N—O); 170.9 (C=N—N). ^{11}B{^{1}H} NMR (CD_2Cl_2), δ: −11.5 (B(3), B(6), B(7), B(11)); −10.3 (B(4), B(5), B(8), B(10)); −5.0 (B(9), B(12)); −1.3 (BF_4^-), 4.0 (RBO_3). IR, (KBr), ν/cm^{-1}: 927, 997, 1070 (ν(N—O)), 1100 m (ν(B—O)), 1583 (ν(C=N—O)); 1620 m (ν(C=N—N)); 2592 (ν(B—H)). UV-Vis ($CHCl_3$), λ_{max}/nm (ε·10^{-3}/L mol^{-1}·cm^{-1}): 259 (8.9), 280 (5.6), 304 (3.6), 343 (2.3), 421 (1.8), 463 (5.7), 504 (6.4). ^{57}Fe Mössbauer spectrum (mm s^{-1}): IS 0.35, QS 0.46.

Butyltris(4-amino-2,3-dimethyl-1,4-diazabuta-1,3-dien-1-yloxy)borate(−1)iron(II) terpafluoroborate [Fe(DXO)$_3$(BBu)](BF$_4$) (5). The salt $FeCl_2 \cdot 4H_2O$ (1.98 g, 9.97 mmol), $BuB(OH)_2$ (1.02 g, 9.97 mmol), and excess $NaBF_4$ (2 g) were added with stirring under argon to a solution of HDXO (3.44 g, 30 mmol) in dry MeOH (15 mL). The dark-red reaction mixture was stirred for 3 h at 30 °C and filtered. The precipitate was washed with Et_2O and dissolved in a minimum volume of acetonitrile. The acetonitrile solution was filtered off and precipitated with Et_2O. The precipitate was washed with hexane and dried *in vacuo*. Yield 2.96 g (59%). Found (%): C, 34.52; H, 5.96; Fe, 10.07; N, 22.64. $C_{16}H_{33}B_2F_4FeN_9O_3$. Calculated (%): C, 34.75; H, 6.03; Fe, 10.10; N, 22.80. MS, *m/z*: 466 [M − BF_4^-]$^+$. ^{1}H (CD_3CN), δ: 0.47 (br.s, 3 H, CH_3(Bu)); 0.89 (m, 4 H, CH_2(Bu)); 1.35 (m, 2 H, CH_2(Bu)); 2.30 (s, 18 H, CH_3(DXO)); 6.33 (br.s, 6 H, NH_2). ^{13}C{^{1}H} NMR (CD_3CN), δ: 13.2 (CH_3(Bu)); 13.5, 13.8 (CH_3(DXO)); 26.6, 25.7 (CH_2(Bu)); 153.3 (C=N—O); 159.36 (C=N—N).

$^{11}B\{^1H\}$ NMR (CD_3CN), δ: −0.5 (BF_4^-); 8.8 (RBO_3). IR (KBr), ν/cm^{-1}: 911, 1050 sh (ν(N—O)), 1081 m (ν(B—O)), 1580 (ν(C=N—O)), 1595 (ν(C=N—N)), 1641 (δ(N—H)). UV-Vis ($CHCl_3$), λ_{max}/nm: (ε · 10^{-3}/L mol^{-1} cm^{-1}): 278 (8.8), 287 (3.7), 308 (2.2), 350 (1.3), 408 (1.5), 450 (4.6), 483 (8.0). ^{57}Fe Mössbauer spectrum (mm s^{-1}): IS 0.41, QS 0.18.

1-Butyl-4,5,13,14,19,20-hexamethyl-8-*syn*,10-*syn*,22-*syn*-triethoxy-2,16,17-trioxa-3,6,7,9,11,12,15,18,21-nonaaza-1-boratricyclo[7.7.5.1^{7,11}]docosa-3,5,12,14,17,19-hexaene(−1)iron(II) tetrafluoroborate [Fe(DXO)$_3$(HCOEt)$_3$(BBu)](BF$_4$) (6). Triethyl ortoformate (2 mL) and trifluoroacetic anhydride (5 μL) were added to a solution of complex **4** (0.3 g, 0.5 mmol) in acetonitrile (5 mL), and the reaction mixture was kept for 72 h. The resulting dark-orange crystals were filtered off and dried in air to give the first portion of the clathrochelate. The filtrate was concentrated to a small volume and the residue was precipitated with Et_2O to give the second portion of clathrochelate. The combined product was washed with Et_2O and hexane and dried *in vacuo*. The total yield was 0.15 g (39%). Found: C, 41.43; H, 6.30; Fe, 7.92; N, 17.52. $C_{25}H_{45}B_2F_4FeN_9O_6$. Calculated (%): C, 41.63; H, 6.30; Fe, 7.74; N, 17.48. MS, *m/z*: 634 [M − BF_4^-]$^+$. ^1H NMR (CD_2Cl_2), δ 0.65 (br.s, 3 H, CH_3(Bu)); 0.82 (t, 9 H, CH_3(OEt), J = 6.6 Hz); 0.99 (m, 4 H, CH_2(Bu)); 1.34 (br.s, 2 H, BCH_2); 2.30, 2.41 (both s, 9 H each, CH_3(DXO)); 3.64 (q, 6 H, CH_2(OEt), J = 6.6 Hz); 5.78 (s, 3 H, HC). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ: 13.8 (CH_3(Bu)); 14.2, 14.7 (CH_3(DXO)); 18.5 (CH_3(Et)); 26.1, 26.7 (CH_2(Bu)); 65.8 (OCH_2); 97.3 (HC); 151.8 (C=N—O); 170.4 (C=N—N). $^{11}B\{^1H\}$ NMR (CD_2Cl_2), δ: −1.1 (BF_4^-); 8.6 (RBO_3). IR, KBr), ν/cm^{-1}: 924, 992, 1056 (ν(N—O)), 1106 m (ν(B—O)), 1573 (ν(C=N—O)), 1621 (ν(C=N—N)). UV-Vis spectra ($CHCl_3$), λ_{max}/nm: (ε · 10^{-3}/L mol^{-1} cm^{-1}): 258 (3.0), 271 (3.9), 307 (2.9), 346 (1.4), 447 (0.8), 484 (2.7), 493 (5.5). ^{57}Fe Mössbauer spectrum (mm s^{-1}): IS 0.37, QS 0.47.

X-ray diffraction study. The single crystals of [Fe(DXO)$_3$(HCOEt)$_3$(*o*-carb)][$FeCl_4$] (**4** · [$FeCl_4^-$]) were obtained by slow evaporation of a mother liquor after hexane precipitation of the product formed without $NaBF_4$. The single crystals of clathrochelate **6** · 0.75$CHCl_3$ were obtained by slow evaporation of a saturated solution in a $CHCl_3$—heptane mixture.

The single crystals of **4** · [$FeCl_4^-$] are thin brittle plates, while the crystals of compound **6** · 0.75$CHCl_3$ proved to be systematic twins. These specific features of the crystals considerably complicated the X-ray diffraction studies and made impossible obtaining the results with smaller errors in the geometric parameters of molecules.

The reflection intensities were measured with a Bruker APEX II CCD diffractometer equipped with a graphite monochromator (Mo-Kα radiation, λ = 0.71073 Å) at 100 K. The intensities of reflections were integrated using the SAINT Plus and SADABS program packages.[10,11] The structures were solved by the direct method and refined by full-matrix least squares on F^2 in the anisotropic approximation for nonhydrogen atoms.

Table 2. Crystallographic data, X-ray diffraction experiment details, and structure refinement parameters for **4** · [$FeCl_4^-$] and **6** · 0.75$CHCl_3$

Compound	**4** · [$FeCl_4^-$]	**6** · 0.75 $CHCl_3$
Formula	$C_{23}H_{47}B_{11}Cl_4Fe_2N_9O_6$	$C_{25.75}H_{45.75}B_2Cl_{2.25}F_4FeN_9O_6$
Molecular weight	918.11	809.70
Space group	$P2_1/c$	$P2_1$
a/Å	21.726(8)	12.026(1)
b/Å	9.015(3)	31.695(3)
c/Å	21.112(7)	12.029(1)
β/deg	92.757(6)	119.998(2)
V/Å^3	4130(3)	3970.8(7)
Z	4	4
d_{calc}/g cm^{-3}	1.477	1.356
Color and habit	Dark-orange plates	
Crystal dimensions/mm	0.35×0.28×0.10	0.60×0.52×0.20
μ/mm^{-1}	1.01	0.597
$2\theta_{max}$/deg	50	48
All reflections	35469	24127
The number of independent reflections (R_{int})	7234 (0.1852)	12338 (0.0366)
R_1 (on F for reflections with $I > 2\sigma(I)$)	0.1033 (2315 refl.)	0.0991 (9527 refl.)
wR_2 (on F^2 for all reflections)	0.2118	0.2217
The number of parameters	496	956
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, где $P = 1/3(F_o^2 + 2F_c^2)$	
a	0.0316	0.0166
b	0	35.178
GOOF	1.078	1.071
F(000)	1884	1686

The positions of hydrogen atoms were located from the difference Fourier synthesis and included in the refinement using the riding model with $U_{iso}(H) = nU_{eq}(C)$, where $n = 1.5$ for methyl groups and 1.2 for other groups and $U_{eq}(C)$ is the equivalent isotropic factor of the carbon atom. All calculations were carried out using SHELXTL PLUS5 software,[12] atom coordinates were deposited with the Cambridge Crystallographic Data Center. The details of experimental data collection and structure refinement parameters are presented in Table 2.

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