Boryl- and Bridging Boryleneiron Complexes from Aminodichloroboranes

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Depending on the nature of the amino group bound to the boron atom, the reactions of various aminodichloroboranes R_2NBCl_2 with $Na[(\eta^5\text{-}C_5R'_5)Fe(CO)_2]$ yield either boryl or bridging borylene complexes of iron. The compounds $[(C_5R'_5)(CO)_2Fe\{BCl(NR_2)\}]$ (**1a**, $C_5R'_5 = C_5H_5$, R = Me; **1b**, $C_5R'_5 = C_5H_4Me$, R = Me; **1c**, $C_5R'_5 = C_5Me_5$, R = Me) and $[(\eta\text{-}BNR_2)(\mu\text{-}CO)\{(C_5R'_5)Fe(CO)\}_2]$ (**2a**, $C_5R'_5 = C_5H_5$, R = $SiMe_3$; **2b**, $C_5R'_5 = C_5H_4Me$, R = $SiMe_3$) were isolated as orange (**1a−c**) or red (**2a**, **b**) crystalline solids, and characterized by multinuclear NMR methods and IR spectroscopy. The structures of **1c** and **2b** in the crystalline state were determined by single-crystal X-ray studies.

Since 1990, when the first transition-metal complex with a two-center, two-electron bond between the metal and a threefold coordinated boron atom was structurally characterized[1], such boryl complexes have become of increasing interest, as they are known to be important intermediates in transition-metal-catalyzed hydroboration[2][3][4], and, very recently, the selective functionalization of alkanes in terminal position was achieved by photolysis of a boryl-tungsten complex[5]. During the last seven years a large number of structurally authentic boryl complexes have been described and the 1,2-dioxobenzo or "catechol" group, as ligand to boron, has had a pivotal role in obtaining these compounds, since most of them were either obtained by the reaction of an anionic transition-metal complex with CatBCl (Cat = $1,2\text{-}O_2C_6H_4$)[6a][6b][6c][6d], or by oxidative addition of CatBH or CatBBCat to a suitable transition-metal center[7a][7b][7c][7d][7e][7f].

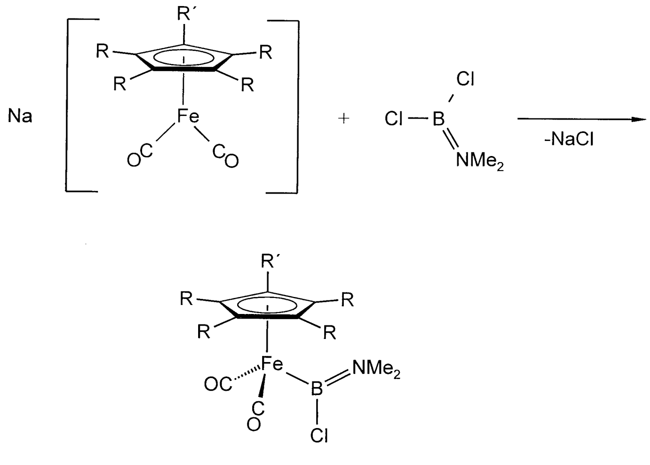
In contrast to the well-developed chemistry of boryl transition metal complexes, knowledge about the corresponding borylene complexes is restricted to only one example (and derivatives of this). Originally, this compound, a bridging dinuclear manganese complex, was obtained by an unprecedented and unexpected reaction of different diboranes(4) with $Na[(C_5H_4Me)Mn(SiMePh_2)(CO)_2]$[8]; more recently, the syntheses of these highly unusual compounds has been significantly improved by employing the corresponding manganese hydride complex $Na[(C_5H_4Me)MnH(CO)_2]$[9]. Interestingly, the borylene complexes of the type $[\eta\text{-}BX\{(C_5H_5)Mn(CO)_2\}_2]$ (X = NMe_2, Cl), undergo substitution reactions at the boron atom with preservation of the central Mn_2B core[10]. Due to their kinetic lability[11], however, boryl complexes generally react with cleavage of the boryl moiety[6a][6d][7e][11], regardless of the strength of the metal−boron bond, which in certain cases was calculated to be stronger than corresponding metal−carbon bonds[12a][12b].

In the course of our investigations on transition-metal complexes of boron with alternative boron-bound ligands[13a][13b], we report on the reactions of different aminodichloroboranes R_2NBCl_2 with $Na[(\eta^5\text{-}C_5R'_5)Fe(CO)_2]$ to yield amino-substituted boryl or bridging borylene complexes of iron.

Results and Discussion

The reaction of $Na[(\eta^5\text{-}C_5R'_5)Fe(CO)_2]$ with Me_2NBCl_2 in benzene at room temperature according to Scheme 1 affords the aminoboryl complexes $[(C_5R'_5)(CO)_2Fe\{BCl(NR_2)\}]$ (**1a**, $C_5R'_5 = C_5H_5$, R = Me; **1b**, $C_5R'_5 = C_5H_4Me$, R = Me; **1c**, $C_5R'_5 = C_5Me_5$, R = Me).

Scheme 1



1a, R = R′ = H
1b, R = H; R′ = Me
1c, R = R′ = Me

The products were obtained from hexane at −30°C as air- and moisture-sensitive dark-orange materials in yields

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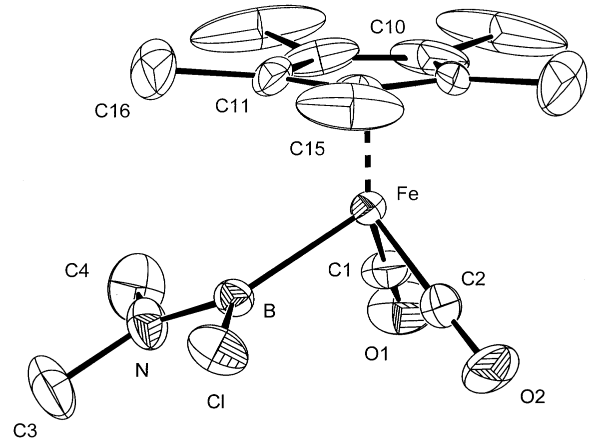
of up to 65%. While **1a**, **c** show melting points of 35°C and 120°C, respectively, **1b** proved to be an oil at room temperature. As might be expected, the spectroscopic data of **1a–c** in solution are to some extent related to those of the corresponding diborane(4)yl complex $[(C_5H_5)Fe(CO)_2\{B_2(NMe_2)_2Cl\}]$[13a]. The ^1H- and ^{13}C-NMR spectra show double sets of signals for the dimethylamino group, due to the restricted rotation with respect to the B–N double bond. In the case of **1b** the variable-temperature ^1H-NMR studies show a coalescence of the two corresponding resonances at 83°C, from which a value for the rotation barrier of $\Delta G^{\neq} = 72.3$ kJ/mol can be calculated. This is in the range expected for aminosubstituted boranes[14a][14b]. The formation of the boron–iron bond results in characteristically deshielded ^{11}B-NMR signals at $\delta = 56.4$ (**1a**), 56.9 (**1b**), and 59.1 (**1c**), which are shifted to low field with respect to the signal of Me_2NBCl_2 at $\delta = 30.5$[15]. For a similar boryliron complex, $[CpFe(CO)_2BCat]$ (Cat = 1,2-$O_2C_6H_4$), a modest Fe–B π bonding in solution was deduced from the high CO stretching frequencies at 2024 cm^{-1} and 1971 cm^{-1}[6c]. In the case of **1a–c** the IR spectra gave no evidence for a metal–boron backbonding, since the CO stretching frequencies (**1a**, 2005 cm^{-1}, 1946 cm^{-1}; **1b**, 2002 cm^{-1}, 1944 cm^{-1}; **1c**, 1988 cm^{-1}, 1928 cm^{-1}) are equal to, or even lower than, those for the corresponding alkyliron complexes at 1999–2005 cm^{-1} and 1938–1944 cm^{-1}[16]. So far this finding is true for all fully characterized nitrogen-substituted boryliron complexes, e.g. $\{(C_5H_5)Fe(CO)_2[B_2(NMe_2)_2Cl]\}$[13a] and $\{[(C_5H_4Me)Fe(CO)_2]_2ClB_3N_3H_3\}$[13b].

As a representative of the new complexes, an X-ray structure analysis was carried out for $[(C_5Me_5)(CO)_2Fe\{BCl(NMe_2)\}]$ (**1c**) (Figure 1). Suitable crystals of **1c** were obtained, after some days, from solutions in hexane at −30°C. The complex crystallizes in the noncentrosymmetric space group $P2_12_12_1$, and the molecule adopts C_1 symmetry in the crystal. The almost perpendicular orientation (87.4°) of the N–B–Cl plane with respect to the Cp(centroid)–Fe–B plane provides no evidence for an iron–boron π interaction in the crystalline state[6c][17]. This is supported by an Fe–B distance of 202.7(5) pm, which is significantly longer than that in $[CpFe(CO)_2BCat]$ [195.6(6) pm]. For the latter compound a π interaction in the solid state is facilitated by the different orientation of the boryl ligand[6c]. A boron–nitrogen double bond, already established for the aminoboryl complexes **1a–c** in solution, is also found for **1c** in the crystal, as indicated by a B–N distance of 137.7(6) pm.

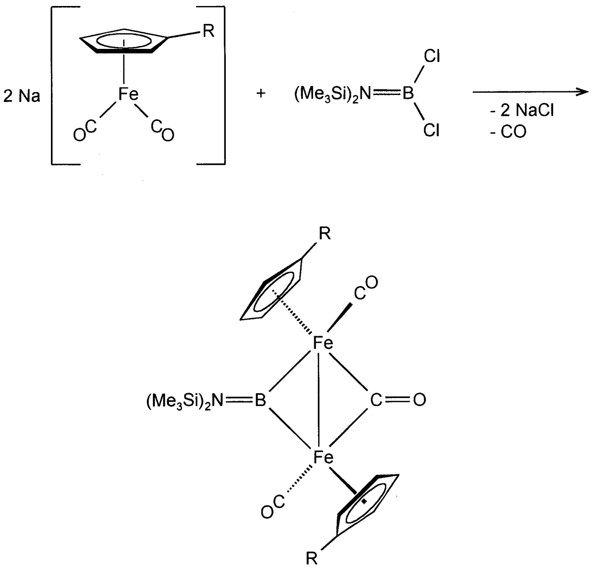
The corresponding bridging borylene complexes $[(\eta\text{-}BNR_2)(\mu\text{-}CO)\{(C_5R'_5)Fe(CO)\}_2]$ (**2a**, $C_5R'_5 = C_5H_5$, R = $SiMe_3$; **2b**, $C_5R'_5 = C_5H_4Me$, R = $SiMe_3$) were obtained by a similar reaction of $[(Me_3Si)_2N]BCl_2$ at room temperature with two equivalents of $Na[(C_5R'_5)Fe(CO)_2]$ in benzene (Scheme 2).

Figure 1. Structure of **1c** in the crystal (ellipsoids at 30% probability[25])[a]



[a] Selected distances [pm] and angles [°]: Fe–B 202.7(5), B–N 137.7(6), B–Cl 183.4(5), Fe–centroid 173.5(1); Fe–B–Cl 116.0(2), Fe–B–N 131.9(4), Cl–B–N 112.0(3).

Scheme 2



2a, R = H
2b, R = Me

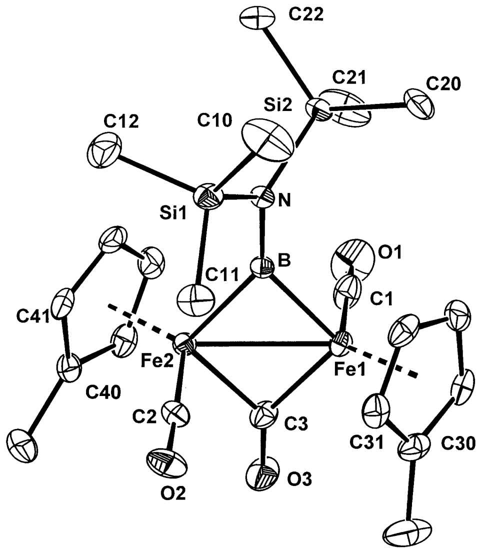
The products, which are formed with loss of one CO group from the initial iron complex, were isolated from hexane at low temperatures as dark-red solids in yields of about 25%, and proved to be extremely sensitive to air and moisture. This is in contrast to the known characteristics of the related borylenemanganese complex $[(\eta\text{-}BNMe_2)\{(C_5H_5)Mn(CO)_2\}_2]$[10]. Interestingly the formation of the borylene complexes **2a**, **b**, as the only boron-containing products, was observed under all conditions, even with an excess of $[(Me_3Si)_2N]BCl_2$, while the reaction of Me_2NBCl_2 with $Na[(C_5R'_5)Fe(CO)_2]$ always led to the formation of the boryl complexes $[(C_5R'_5)(CO)_2Fe\{BCl(NR_2)\}]$ (**1a**, $C_5R'_5 = C_5H_5$, R = Me; **1b**, $C_5R'_5 = C_5H_4Me$, R = Me; **1c**, $C_5R'_5 = C_5Me_5$, R = Me). In the latter cases a further exchange of a boron-bound chloride ligand could not be achieved. We attribute this result to the electronic influence of the silyl groups, which despite their size make the [(Me3-

$Si)_2N]BCl_2$ more reactive by weakening the boron−nitrogen double bond.

The structure of **2a**, **b** in solution is derived from the NMR and IR spectra. Due to the formation of two iron−boron linkages the borylene complexes show ^{11}B-NMR signals at $\delta \approx 119$. These are significantly shifted to low field with respect to the signals found for the boryl complexes **1a**−**c**. The IR and ^{13}C-NMR data resemble those of the isoelectronic vinylidenediiron complexes, where the presence of one bridging and two terminal CO groups has already been established[18].

Suitable single crystals of **2b** were obtained in a similar manner to those of **1c**, and the results of the X-ray structure analysis (Figure 2) showed that the compound crystallizes in the monoclinic space group $P2_1/c$.

Figure 2. Structure of **2b** in the crystal (ellipsoids at 30% probability[25])[a]



[a] Selected distances [pm] and angles [°]: Fe1−Fe2 254.8(1), Fe1−B 200.7(3), Fe2−B 200.2(3), B−N 141.2(4), Fe1−centroid1 175.5, Fe2−centroid2 174.6; Fe1−B−Fe2 78.9(1), Fe1−C3−Fe2 83.6(1).

In the crystal the borylene complex **2c** shows a *trans* orientation of the MeC_5H_4 and CO groups with respect to the Fe_2B unit. These three atoms form an isosceles triangle with Fe−B distances of 200.7(3) and 200.2(3) pm, and an Fe−Fe distance of 254.8(1) pm. Obviously, the Si1−B−Si2 plane is twisted by 53.7(1)° with respect to the Fe1−B−Fe2 plane due to the bulky Me_3Si groups. Hence, in connection with the extended B−N distance of 141.2(4) pm, a less effective backbonding from the nitrogen to the boron atom can be assumed. The overall molecular structure of **2c** resembles that of the structurally characterized vinylidenediiron complexes[18].

Conclusion

This study presents the synthesis and characterization in solution and in the crystal of various amino-substituted boryl and bridging borylene complexes of the type $[(C_5R'_5)(CO)_2Fe\{BCl(NR_2)\}]$ (**1a**, $C_5R'_5 = C_5H_5$, R = Me; **1b**, $C_5R'_5 = C_5H_4Me$, R = Me; **1c**, $C_5R'_5 = C_5Me_5$, R = Me) and $[(\eta\text{-}BNR_2)(\mu\text{-}CO)\{(C_5R'_5)Fe(CO)\}_2]$ (**2a**, $C_5R'_5 = C_5H_5$, R = $SiMe_3$; **2b**, $C_5R'_5 = C_5H_4Me$, R = $SiMe_3$). The formation of the products is obviously dominated by electronic rather than steric criteria, since the more bulky, but also more electrophilic, $[(Me_3Si)_2N]BCl_2$ yields the borylene complexes **2a**, **b** by substitution of both boron-bound chloride ligands by $[(\eta^5\text{-}C_5R'_5)Fe(CO)_2)]$ moieties, whereas the boryl complexes **1a**−**c** are formed from Me_2NBCl_2 by substitution of only one chloride ligand. These results show that aminodichloroboranes may serve as the starting materials for different types of transition-metal complexes of boron, and that the access to bridging borylene complexes is no longer restricted to the use of diborane(4) derivatives.

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Experimental Section

All manipulations were carried out under dry nitrogen in Schlenk glassware. Solvents and reagents were dried by standard procedures, distilled and stored under nitrogen and molecular sieves. $Na[(\eta^5\text{-}C_5R_5)Fe(CO)_2]$[19], Me_2NBCl_2[20], and $[(Me_3Si)_2N]BCl_2$[21] were synthesized according to the literature. − NMR: Varian Unity 500 at 499.843 (^{1}H, standard TMS internal), 150.364 (^{11}B, standard $BF_3\cdot OEt_2$ in C_6D_6 external), 125.639 MHz ($^{13}C\{^1H\}$, APT, standard TMS internal); all NMR spectra were recorded in C_6D_6 as solvent. − Elemental analyses (C, H, N): Carlo-Erba elemental analyzer, model 1106. − IR: Perkin-Elmer FT-IR 1720x.

[Dicarbonyl{chloro(dimethylamino)boryl}(η^5-cyclopentadienyl)iron] (**1a**): 1.92 g (9.60 mmol) of $Na[(C_5H_5)Fe(CO)_2]$ was suspended in 50 ml of benzene and 1.21 g (9.60 mmol) of Me_2NBCl_2 was added dropwise by a syringe at ambient temp. After stirring for 20 min, all volatiles were removed in vacuo and the solid residue was treated with 40 ml of hexane, filtered, and the remaining solid washed with 20 ml of hexane, 1.65 g (65%) of **1a** was recovered from the filtrate at −30°C as orange crystals, m.p. 35°C. − ^{1}H NMR: δ = 2.70 (s, 3 H, NMe), 2.91 (s, 3 H, NMe), 4.11 (s, 5 H, C_5H_5). − ^{11}B NMR: δ = 56.4. − ^{13}C NMR: δ = 41.14 (NMe), 43.60 (NMe), 83.80 (C_5H_5), 215.76 (CO). − IR (toluene): $\tilde{\nu}$ = 2006 cm^{-1}, 1946 (CO). − $C_9H_{11}BClFeNO_2$ (267.29): calcd. C 40.44, H 4.15, N 5.24; found C 39.88, H 4.32, N 5.30.

[Dicarbonyl{chloro(dimethylamino)boryl}(η^5-methylcyclopentadienyl)iron] (**1b**): As described for **1a**, 0.93 g (4.35 mmol) of $Na[(C_5H_4Me)Fe(CO)_2]$ was treated with 0.55 g (4.35 mmol) of Me_2NBCl_2, and 0.78 g (64%) of **1b** was obtained as a dark orange oil by evaporating the filtrate in vacuo. − ^{1}H NMR: δ = 1.57 (s, 3 H, C_5H_4Me), 2.77 (s, 3 H, NMe), 2.93 (s, 3 H, NMe), 4.09 (m, 4 H, C_5H_4Me). − ^{11}B NMR: δ = 56.9. − ^{13}C NMR: δ = 12.90 (C_5H_4Me), 41.17 (NMe), 43.66 (NMe), 82.55, 84.62, 101.28 (C_5H_4Me), 216.19 (CO). − IR (toluene): $\tilde{\nu}$ = 2002 cm^{-1}, 1944 (CO). − $C_{10}H_{13}BClFeNO_2$ (281.33): calcd. C 42.69, H 4.66, N 4.98; found C 42.06, H 4.85, N 4.72.

[Dicarbonyl{chloro(dimethylamino)boryl}(η^5-pentamethylcyclopentadienyl)iron] (**1c**): As described for **1a**, 0.24 g (0.90 mmol) of $Na[(C_5Me_5)Fe(CO)_2]$ was treated with 0.11 g (0.90 mmol) of Me_2NBCl_2, and 0.17 g (55%) of **1c** was obtained as orange crystals, m.p. 120°C. − ^{1}H NMR: δ = 1.53 (s, 15 H, C_5Me_5), 2.87 (s, 3 H, NMe), 2.96 (s, 3 H, NMe). − ^{11}B NMR: δ = 59.1. − ^{13}C NMR: δ = 9.76 (C_5Me_5), 41.37 (NMe), 43.82 (NMe), 95.23 (C_5Me_5), 217.60 (CO). − IR (toluene): $\tilde{\nu}$ = 1988 cm^{-1}, 1928 (CO). −

$C_{14}H_{21}BClFeNO_2$ (337.42): calcd. C 49.83, H 6.27, N 4.15; found C 49.68, H 6.52, N 4.13.

[μ-{Bis(trimethylsilyl)aminoboranediyl}-bis{(η^5-cyclopentadienyl)dicarbonyliron}Fe-Fe] (**2a**): As described for **1a**, 2.69 g (13.45 mmol) of Na[$(C_5H_5)Fe(CO)_2$] were reacted with 1.30 g (5.38 mmol) of [$(Me_3Si)_2N$]BCl_2 and 0.70 g (26%) of **2a** isolated as dark red crystals. − ^{1}H NMR: δ = 0.32 (s, 18 H, $SiMe_3$), 4.41 (s, 10 H, C_5H_5). − ^{11}B NMR: δ = 118.4 . − ^{13}C NMR: δ = 4.75 ($SiMe_3$), 87.75 (C_5H_5), 215.52 (CO), 276.63 (μ-CO). − IR (hexane): $\tilde{\nu}$ = 1924 cm^{-1}, 1770 (CO). − $C_{19}H_{28}BFe_2NO_3Si_2$ (497.11): calcd. C 45.90, H 5.68, N 2.82; found C 45.84, H 5.80, N 2.67.

[μ-{Bis(trimethylsilyl)aminoboranediyl}bis{dicarbonyl(η^5-methylcyclopentadienyl)iron}Fe−Fe] (**2b**): As described for **1a**, 1.76 g (8.23 mmol) of Na[$(C_5H_4Me)Fe(CO)_2$] was treated with 0.99 g (4.11 mmol) of [$(Me_3Si)_2N$]BCl_2 and 0.86 g (25%) of **2b** isolated as dark-red crystals. − ^{1}H NMR: δ = 0.36 (s, 18 H, $SiMe_3$), 1.96 (s, 6 H, Me), 4.01−4.61 (br., 8 H, C_5H_4). − ^{11}B NMR: δ = 119.1. − ^{13}C NMR: δ = 4.82 ($SiMe_3$), 12.29 (C_5H_4Me), 84.39, 85.09, 88.30, 90.35, 103.73 (C_5H_4Me), 215.83 (CO), 279.26 (μ-CO). − IR (hexane): $\tilde{\nu}$ = 1925 cm^{-1}, 1770 (CO). − $C_{21}H_{32}BFe_2NO_3Si_2$ (525.14): calcd. C 48.03, H 6.14, N 2.67; found C 48.30, H 6.28, N 2.61.

X-ray Structure Determination for **1c**: $C_{14}H_{21}BClFeNO_2$, M = 337.44 g mol^{-1}, crystal data a = 8.2617(6), b = 9.915(1), c = 20.100(3) Å, V = 1646.5(3) Å^3, orthorhombic, $P2_12_12_1$ (No. 19), Z = 4, $\rho_{calcd.}$ = 1.361 g cm^{-3}, μ(Mo-K_α) = 10.77 cm^{-1}, F(000) = 704. Orange platelet, crystal size [mm] 0.6 × 0.6 × 0.4. ENRAF-Nonius CAD4; Mo-K_α radiation (λ = 0.7107 Å, graphite monochromator); intensity data from ω-2-Θ scans at 203 K. 7812 reflections in the range 3° < Θ < 27°, structure solution[23] with 3592 independent reflections, refinement[24] with 2819 observations with $I > \sigma(I)$ for 181 variables; H atoms were included as riding in idealized geometry [C−H = 98 pm, $U_{iso}(H) = 1.3 \cdot U_{eq}(C)$]. Pronounced anisotropic displacement parameters were encountered for the carbon atoms in the pentamethylcyclopentadienyl ring and these indicate librational or static disorder of this moiety. Convergence at R = 0.051, R_w = 0.056, $w^{-1} = \sigma^2(F_o)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100790. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (int. code) + 44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk, World Wide Web: http://www.ccdc.cam.ac.uk].

X-ray Structure Determination for **2b**: $C_{21}H_{32}BFe_2NO_3Si_2$, M = 525.17 g mol^{-1}, unit cell dimensions a = 10.684(2), b = 28.917(5), c = 8.337(5) Å, β = 108.26(3)°, V = 2446(2) Å^3, monoclinic, $P2_1/c$ (No. 14), Z = 4, $D_{calcd.}$ = 1.426 g cm^{-3}, μ(Mo-K_α) = 13.03 cm^{-1}, F(000) = 1096; dark-red transparent platelet, crystal size [mm] 0.65 × 0.54 × 0.15. ENRAF-Nonius CAD4; Mo-K_α radiation (λ = 0.7107 Å, graphite monochromator); intensity data from ω-2-Θ scans at 203 K., 6443 reflections in the range 3° < Θ < 26°, numerical absorption correction (transmission min. 0.528, max. 0.830) by Gaussian integration[22], 3680 independent observations with $I > \sigma(I)$ in structure solution[23] and refinement[24] for 271 variables; H atoms were included as riding in idealized geometry [C−H = 98 pm, $U_{iso}(H) = 1.3 \cdot U_{eq}(C)$]. Convergence at R = 0.039, R_w = 0.047, $w^{-1} = \sigma^2(F_o)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100790. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (int. code) + 44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk, World Wide Web: http://www.ccdc.cam.ac.uk].

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