Ferrocenylborane−Amine and Monomeric Diferrocenylborane: Novel Organometallic Hydroborating Reagents

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Summary: The ferrocenylboranes $FcBH_2$·NMe_2Et and Fc_2BH have been synthesized and characterized by X-ray crystallography, which revealed Fc_2BH to be monomeric in the solid state. Both compounds undergo hydroboration reactions upon addition of alkynes.

Boryl- and borate-substituted metallocenes are of great current interest. Applications ranging from homogeneous catalysis to anion sensing and organometallic polymer chemistry have been the topic of two recent reviews.[1] At present, most syntheses of borylated metallocenes simply rely on nucleophilic substitution reactions at the boryl group(s). To get access to ever more sophisticated derivatives, novel reactive building blocks are thus required. Since the hydroboration of alkenes and alkynes offers a convenient route to organoboron compounds,[2] the parent metallocenylboranes $McBH_2$ (Mc = metallocenyl substituent) appear to be attractive starting materials for further reactions. As an example, Chujo et al. pioneered the hydroboration polymerization of diynes[3] for the preparation of π-conjugated macromolecules containing boron in their main chain. The compounds obtained are related to all-carbon systems, from which electrons have been removed by oxidation. Many of these materials possess large third-order nonlinear susceptibilities and show photo- as well as electroluminescent behavior.[3] It is therefore interesting to investigate how the physical properties will change when the polymers' backbones are (partially) reduced. One of our future aims is to create photochemically dopable macromolecules by using metallocenylboranes as the hydroborating reagents. Irradiation of the resulting polymers with laser light can be expected to induce $d\pi-p\pi^*$ transitions and thus inject mobile charge carriers into the polymer chain. Moreover, due to the low steric bulk of the BH_2 substituent, it should be possible to obtain adducts with those Lewis bases that do not form stable acid−base pairs in the case of $McBR_2$ derivatives bearing substituents R larger than H. Novel and interesting reaction pathways may also open up when $McBH_2$ interacts with other boranes (including other $McBH_2$ molecules) via BHB two-electron−three-center bonds.

The purpose of this paper is to present the first two examples of metallocenylborane species $McBH_2$ and Mc_2BH, where Mc equals a ferrocenyl (Fc) substituent. The synthesis of $FcBH_2$, which is isolated as its amine adduct, starts from the well-known derivative FcB(OEt)-Br (**1**)[4] (Scheme 1). **1** and 1 equiv of $Li[AlH_4]$ in ether/pentane give lithium ferrocenylborohydride (**2**) in excellent yield.[5] Subsequent addition of excess NMe_2Et results in the precipitation of ethoxyalane−dimethylethylamine complexes, while **2** remains in solution. After filtration, the filtrate is treated with excess Me_3SiCl, whereupon $FcBH_2$·NMe_2Et (**3**) is formed.[6] Addition of Me_3SiCl to **2** in the absence of amine does not lead to the expected dimeric $[FcBH_2]_2$ but generates diferrocenylborane (**4**) and B_2H_6 (Scheme 1).[7] Jutzi et al. reported 1,1′-$Fe(C_5H_4GaMe_2)_2$ to undergo a similar reaction, yielding the digalla[1.1]ferrocenophane $[\{Fe(C_5H_4)_2\}_2\{GaMe\}_2]$ and $GaMe_3$.[8]

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(5) Synthesis of **2**: a solution of $LiAlH_4$ (0.15 g, 3.95 mmol) in Et_2O (20 mL) was added dropwise at 0 °C to a slurry of **1** (1.12 g, 3.49 mmol) in pentane. The resulting clear solution was stirred at 0 °C for 1 h. The solvent was removed and the solid residue dissolved in 15 mL of Et_2O. After addition of NMe_2Et (2.19 g, 30.0 mmol) in Et_2O (10 mL), a colorless precipitate formed. The suspension was filtered and the precipitate extracted with ether (2 × 10 mL). The ether phases were combined and evaporated to dryness to give **2**·$4NMe_2Et$ as a yellow microcrystalline solid. Yield: 1.45 g (83%). ^1H NMR (250.1 MHz, d_8-THF, 303 K): δ 0.87 (q, $^1J_{BH}$ = 77.1 Hz, 3H, BH_3), 1.15 (tr, $^3J_{HH}$ = 7.4 Hz, 12H, CH_2CH_3), 2.36 (s, 24H, NCH_3), 2.73 (q, $^3J_{HH}$ = 7.4 Hz, 8H, CH_2CH_3), 3.93, 4.01 (2 × virtual tr, 2 × 2H, $^3J_{HH} = {}^4J_{HH}$ = 1.6 Hz, C_5H_4), 3.93 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (62.9 MHz, d_8-THF, 303 K): δ 8.8 (CH_2CH_3), 48.0 (NCH_3), 56.8 (CH_2CH_3), 68.4 (C_5H_5), 69.5, 76.8 (C_5H_4), n.o. (CB). ^{11}B NMR (80.3 MHz, d_8-THF, 303 K): δ −30.7 (q, $^1J_{BH}$ = 77.1 Hz). Anal. Calcd for $C_{26}H_{56}BFeLiN_4$ (498.35): C, 62.66; H, 11.33; N, 11.24. Found: C, 62.69; H, 11.47; N, 11.61.

(6) Synthesis of **3**: Me_3SiCl (1.00 g, 9.20 mmol) was condensed on the suspension of **2**·$4NMe_2Et$ (0.25 g, 0.49 mmol) in Et_2O (20 mL) under reduced pressure at liquid nitrogen temperature. The reaction mixture was warmed to room temperature, stirred for 2 h, and filtered and the filtrate evaporated to dryness in vacuo. Single crystals of **3** were obtained from pentane. Yield: 0.12 g (90%). ^1H NMR (250.1 MHz, C_6D_6, 303 K): δ 0.54 (tr, $^3J_{HH}$ = 7.3 Hz, 3H, CH_2CH_3), 1.79 (s, 6H, NCH_3), 2.24 (q, $^3J_{HH}$ = 7.3 Hz, 2H, CH_2CH_3), 2.67 (very broad, 2H, BH_2), 4.26 (virtual tr, 2H, $^3J_{HH} = {}^4J_{HH}$ = 1.8 Hz, C_5H_4), 4.33 (mult, 7H, C_5H_4/C_5H_5). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 303 K): δ 8.2 (CH_2CH_3), 47.1 (NCH_3), 55.7 (CH_2CH_3), 68.6 (C_5H_5), 69.6, 76.6 (C_5H_4), n.o. (CB). ^{11}B NMR (128.4 MHz, C_6D_6, 303 K): δ −3.4 (tr, $^1J_{BH}$ = 92.3 Hz). Anal. Calcd for $C_{14}H_{22}BFeN$ (270.99): C, 62.05; H, 8.18; N, 5.17. Found: C, 62.28; H, 8.38; N, 5.44.

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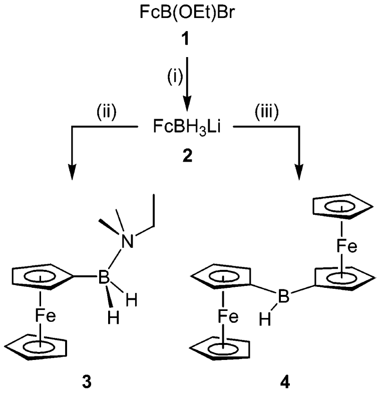
Scheme 1. Synthesis of 2−4[a]



[a] Legend: (i) Li[AlH$_4$] in Et$_2$O/C$_5$H$_{12}$; (ii) excess Me$_3$SiCl/NMe$_2$Et in Et$_2$O; (iii) excess Me$_3$SiCl in Et$_2$O.

The ^{11}B NMR spectrum of **2** shows a quartet at −30.7 ppm ($^1J_{BH}$ = 77.1 Hz)[5] characteristic for a tetracoordinated boron atom[9] bearing three hydrogen substituents. In the ^{1}H NMR spectrum of **2**, a well-resolved quadruplet is visible at δ 0.87 ($^1J_{BH}$ = 77.1 Hz),[5] which has to be assigned to three magnetically equivalent hydrogen atoms coupling with an ^{11}B nucleus. In comparison to **2**, the ^{11}B NMR resonance of **3** is observed at significantly lower field strength (δ −3.4, triplet, $^1J_{BH}$ = 92.3 Hz).[6] Both the chemical shift value and the multiplicity of the signal indicate the presence of a BH$_2$−amine adduct group in the molecule.[9] The B*H*$_2$ protons of **3** appear at δ 2.67. The ^{11}B NMR spectrum of **4**[7] shows a signal at 54.7 ppm, testifying to the presence of three-coordinate boron nuclei.[9] The B*H* hydrogen atom gives rise to a broad hump at δ(^{1}H) 6.23 with an integral value corresponding to one proton. In the infrared spectrum, **4** shows a strong absorption at 2302 cm^{-1} (shoulder at 2400 cm^{-1}), which lies in a region typical of terminal B−H stretching modes.[10]

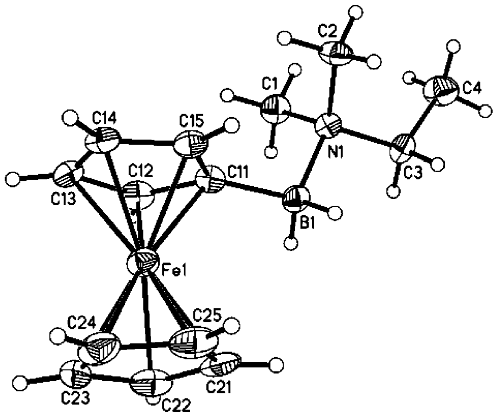


Figure 1. Crystal structure of compound **3**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): B(1)−C(11) = 1.621(9), B(1)−N(1) = 1.655(7); C(11)−B(1)−N(1) = 111.1(4); N(1)−B(1)−C(11)−C(12) = 94.0(6), N(1)−B(1)−C(11)−C(15) = −92.0(6), C(11)−B(1)−N(1)−C(3) = 178.5(5), B(1)−N(1)−C(3)−C(4) = −176.3(5).

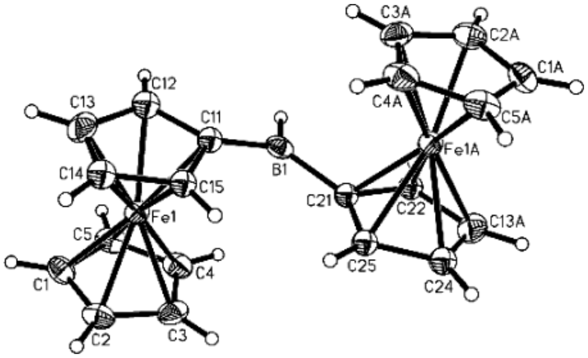


Figure 2. Crystal structure of compound **4**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å), bond angles (deg), torsion angles (deg), and angles between planes (deg): B(1)−C(11) = 1.530(6), B(1)−C(21) = 1.545(6), B(1)−H = 1.12(4); C(11)−B(1)−C(21) = 126.5(3), COG(1)−C(11)−B(1) = 165.6, COG(2)−C(21)−B(1) = 167.4; C(15)−C(11)−B(1)−C(21) = −8.9(6), C(25)−C(21)−B(1)−C(11) = −4.7(6); C(11)C(12)C(13)C(14)C(15)//C(11)B(1)C(21) = 14.4, C(21)C(22)C(13A)C(24)C(25)//C(11)B(1)C(21) = 13.6, C(11)C(12)C(13)C(14)C(15)//C(21)C(22)C(13A)C(24)C(25) = 4.8. COG(1) (COG(2)) is the center of gravity of the plane C(11)C(12)C(13)C(14)C(15) (C(21)C(22)C(13A)C(24)C(25)).

The adduct FcBH$_2$·NMe$_2$Et (**3**) crystallizes from pentane in the triclinic space group $P\bar{1}$ (Figure 1).[11] The B−N bond of **3** is rotated into a position almost perpendicular to the borylated cyclopentadienyl ring (N(1)−B(1)−C(11)−C(12) = 94.0(6)°), with the bulky ethyl group pointing away from the ferrocenyl substituent (C(11)−B(1)−N(1)−C(3) = 178.5(5)°). Single crystals of diferrocenylborane (**4**; monoclinic, $P2_1/c$) were obtained from the reaction mixture (Et$_2$O/pentane) at room temperature (Figure 2).[12] Most interestingly, the molecule is monomeric in the solid state, featuring a planar three-coordinate boron atom and a trans config-

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(7) Synthesis of **4**: a solution of LiAlH$_4$ (0.19 g, 5.01 mmol) in Et$_2$O (20 mL) was added dropwise at 0 °C to a slurry of **1** (1.50 g, 4.68 mmol) in pentane. The resulting clear solution was warmed to room temperature and stirred for 1 h. Neat Me$_3$SiCl (1.72 g, 15.83 mmol) was added to the solution via syringe. Stirring was stopped and the clear solution kept at room temperature for 1 h, whereupon X-ray-quality crystals of **4** formed. Yield: 1.38 g (77%). ^{1}H NMR (250.1 MHz, C$_6$D$_6$, 303 K): δ 4.03 (s, 10H, C$_5$H$_5$), 4.48 (mult, 8H, C$_5$H$_4$), 6.23 (very broad, 1H, BH). ^{13}C{^{1}H} NMR (62.9 MHz, C$_6$D$_6$, 303 K): δ 68.8 (C$_5$H$_5$), 75.0, 77.8 (C$_5$H$_4$), n.o. (CB). ^{11}B NMR (128.4 MHz, C$_6$D$_6$, 303 K): δ 54.7 (n.r.). IR: ν (cm^{-1}) 2302 (shoulder at 2400), BH. Anal. Calcd for C$_{20}$H$_{19}$BFe$_2$ (381.86): C, 62.91; H, 5.02. Found: C, 62.51; H, 4.83.

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(11) Crystal data of **3**: C$_{14}$H$_{22}$BFeN, M_r = 270.99, triclinic, $P\bar{1}$, a = 5.9524(18) Å, b = 9.868(3) Å, c = 11.948(3) Å, α = 92.48(2)°, β = 94.08(2)°, γ = 100.60(3)°, V = 686.9(3) Å^3, Z = 2, T = 100 K, μ(Mo Kα) = 1.075 mm^{-1}, 4733 reflections measured, 2425 unique (R_{int} = 0.1140), which were used in all calculations. The final $R_w(F^2)$ value was 0.1415 (all data), and the minimum/maximum residual electron density was −0.73/0.61 e Å^{-3}. The H atom positions were taken from a difference Fourier synthesis and refined using a riding model. The CCDC reference number is 224814.

(12) Crystal data of **4**: C$_{20}$H$_{19}$BFe$_2$, M_r = 381.86, monoclinic, $P2_1/c$, a = 7.5664(9) Å, b = 10.3258(12) Å, c = 10.4377(15) Å, β = 105.299(5)°, V = 786.59(17) Å^3, Z = 2, T = 149 K, μ(Mo Kα) = 1.838 mm^{-1}, 13 317 reflections measured, 2534 unique (R_{int} = 0.0348), which were used in all calculations. The final $R_w(F^2)$ value was 0.0807 (all data), and the minimum/maximum residual electron density was −0.50/0.55 e Å^{-3}. The C$_5$H$_4$−B(H)−C$_5$H$_4$ fragment was disordered about a crystallographic inversion center. Both disordered groups coincide at the positions of atoms C(13) and C(13A) (−x, −y, −z), with an occupancy factor of 0.5. The position of the H atom at B(1) was taken from a difference Fourier synthesis and refined isotropically. The CCDC reference number is 224815.

uration of its ferrocenyl substituents with respect to the C(11)B(1)C(21) plane. There is only one other example of a structurally characterized monomeric organylborane, $HBTrip_2$ (Trip = 2,4,6-*i*-$Pr_3C_6H_2$), known in the literature.[13] The B−C bond lengths of this compound (average value 1.567(6) Å) are significantly longer than those of **4** (average value 1.538(6) Å), whereas the C−B−C angles of both molecules are rather similar ($HBTrip_2$, 128.0(4)°; **4**, C(11)−B(1)−C(21) = 126.5(3)°). In the case of $HBTrip_2$, dimerization is clearly prevented by the extremely bulky Trip substituents. Considering the fact that tetraferrocenylethene exists, which shows a central C═C bond length of only 1.381 Å,[14] while the boron atoms of dimeric $[HBMes_2]_2$ (Mes = 2,4,6-$Me_3C_6H_2$) are as far as 1.851(3) Å apart from each other,[13] steric congestion of the boron atom in **4** is probably not the sole reason for the monomeric nature of this compound. Torsion angles C(15)−C(11)−B(1)−C(21) and C(25)−C(21)−B(1)−C(11) of −8.9(6) and −4.7(6)°, respectively, indicate that the ferrocenyl substituents can act as strong π-donors toward the boron bridge. This conclusion is also supported by the fact that the ^{11}B NMR resonance of **4** (δ 54.7) is shifted by 18.8 ppm to higher field compared to the boron resonance of $HBTrip_2$ (δ 73.5),[13] which reflects a significant accumulation of π-charge density at boron in **4**.[9] Moreover, the boron atom is bent out of the planes of the C_5H_4 rings toward the iron atoms with dip angles α of 14.4 and 12.6°, thereby suggesting[15] some charge transfer from filled d-type orbitals of iron into the vacant p orbital at boron ($\alpha = 180° - \alpha^*$, α^* = COG−C(ipso)−B; COG =center of gravity of the C_5H_4 ring). In addition to steric shielding, electronic factors are thus likely to play an important role in the stabilization of monomeric **4**.

Hydroboration of *tert*-butylacetylene using **3** (stoichiometric ratio 2:1, CD_2Cl_2, 50 °C, sealed NMR tube) is complete after a few hours and selectively stops at the olefin stage.[16] Two doublets for the olefinic protons are observed (δ 6.25, 6.59) with a coupling constant $^3J_{HH}$ of 17.9 Hz, which points toward a vicinal rather than to a geminal position of the two H atoms.[17] The ^{13}C DEPT-135 NMR spectrum of the product shows one resonance for an olefinic *C*H group (δ 162.1). The signal of the second *C*H group (δ 127.6) is extremely broadened, which has to be attributed to the quadrupolar relaxation of the adjacent boron nucleus. No resonances assignable to olefinic CH_2 groups could be detected. It has to be concluded, therefore, that borylation has occurred at the terminal position of *tert*-butylacetylene. Hydroboration of *tert*-butylacetylene with **4** (stoichiometric ratio 1:1, C_6D_6, room temperature, 30 min) gives a similar result and leads to the corresponding 1,2-disubstituted olefin in quantitative yield.[18]

Work is in progress to synthesize organic−inorganic hybrid materials by using the ferrocenylborane adduct $FcBH_2{\cdot}NMe_2Et$ in the hydroboration polymerization of aromatic diynes. Moreover, the B−C coupling reaction underlying the formation of **4** may provide facile access to oligomers $[-(H_4C_5)Fe(C_5H_4)B(H)-]_n$, starting from $[1,1'\text{-}Fe(C_5H_4BH_3)_2]Li_2$ and 2 equiv of Me_3SiCl.

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Supporting Information Available: Tables giving crystallographic data for **3** and **4**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] Hydroboration product of *tert*-butylacetylene with **3**: ^1H NMR (400.1 MHz, CD_2Cl_2, 303 K) δ 1.12 (s, 18H, CH_3), 4.02 (s, 5H, C_5H_5) 4.45, 4.62 (2 × virtual tr, 2 × 2H, $^3J_{HH} = {}^4J_{HH}$ = 1.8 Hz, C_5H_4), 6.25 (d, 2H, $^3J_{HH}$ = 17.9 Hz, B−CH), 6.59 (d, 2H, $^3J_{HH}$ = 17.9 Hz, *t*Bu−C*H*); $^{13}C\{^1H\}$ NMR (62.9 MHz, CD_2Cl_2, 303 K) δ 29.5 (CH_3), 35.4 (CCH_3), 69.5 (C_5H_5), 74.7, 76.0 (C_5H_4), 127.6 (B−*C*H), 162.1 (*t*Bu−*C*H); ^{11}B NMR (128.4 MHz, CD_2Cl_2, 303 K) δ 54.2.

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[18] Hydroboration product of *tert*-butylacetylene with **4**: ^1H NMR (250.1 MHz, C_6D_6, 303 K) δ 1.11 (s, 9H, CH_3), 4.00 (s, 10H, C_5H_5) 4.47, 4.65 (2 × virtual tr, 2 × 4H, $^3J_{HH} = {}^4J_{HH}$ = 1.7 Hz, C_5H_4), 6.52 (d, 1H, $^3J_{HH}$ = 18.1 Hz, B−CH), 6.84 (d, 1H, $^3J_{HH}$ = 18.1 Hz, *t*Bu−C*H*); $^{13}C\{^1H\}$ NMR (62.9 MHz, C_6D_6, 303 K) δ 29.6 (CH_3), 35.1 (CCH_3), 69.4 (C_5H_5), 73.9, 76.7 (C_5H_4), 128.8 (B−CH), 159.7 (*t*Bu−*C*H); ^{11}B NMR (128.4 MHz, C_6D_6, 303 K) δ 56.9.