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New [2]Boraferrocenophane and Diferrocenyldiborane(4) Derivatives

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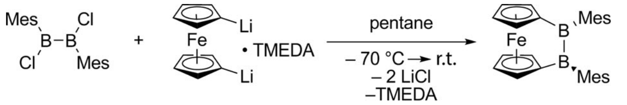
The new [2]boraferrocenophane derivative [Fe(η^5-C_5H_4)–B(Mes)–B(Mes)–(η^5-C_5H_4)] (**2**) was prepared by reaction of 1,1′-dilithioferrocene with $B_2(Mes)_2Cl_2$. In addition, the diborane(4) $B_2(NMe_2)_2Fc_2$ (**3**) was isolated from the reaction of $B_2(NMe_2)_2Cl_2$ and monolithioferrocene. Both species were fully characterized including X-ray diffraction analyses. While $B_2(NMe_2)_2Fc_2$ (**3**) adopts an unstrained geometry, [2]boraferrocenophane **2** features notable molecular ring strain manifested in the tilt-angle $\alpha = 10.5(2)°$.

Introduction

Strained [*n*]metalloarenophanes have sparked tremendous interest during the last decades due to their highly interesting reactivity patterns and promising applications in catalysis and materials science.[1] While the large molecular ring strain present in [1]metalloarenophanes has been extensively exploited in the synthesis of transition metal containing macromolecules, the preeminent example being poly(ferrocenylsilanes),[1,2] strained [2]metalloarenophanes have been shown to possess a copious reactivity at the E–E bond of the *ansa*-bridge.[3] To date, diatomic *ansa*-bridges have been realized with a variety of bridging elements such as B,[3c,3d,4] C,[5] Si,[3f,4e,6] Ge,[7] Sn,[4f,8] and P.[9] With the isolation of [Fe(η^5-C_5H_4)–B(NMe_2)–B(NMe_2)–(η^5-C_5H_4)] (**1**) in 1997 Herberhold and Wrackmeyer successfully accomplished the incorporation of boron into a [2]ferrocenophane for the first time.[4a] During the last five years, additional [2]borametalloarenophanes have appeared in the literature derived from other sandwich systems containing Ti,[4f] V,[3d,4e] Cr,[3c,4b] and Mn[3c] as the transition metal center. In 2005 (and later on) we demonstrated that the B–B bond in [2]borametalloarenophanes is susceptible to oxidative addition to low-valent transition metals such as platinum,[3c,3d,4f] a reactivity that has subsequently been employed in the stoichiometric and catalytic functionalization of organic molecules such as alkynes, isocyanides or diazo compounds.[3e,4e,10] However, the diborane component of the *ansa*-species has been limited to the amino-substituted B(NMe_2)–B(NMe_2) bridge so far. We now report on the isolation of the new [2]ferrocenophane **2**, [Fe(η^5-C_5H_4)–B(Mes)–B(Mes)–(η^5-C_5H_4)], which does not require stabilization of the reactive diboron-bridge via π-donation from nitrogen. Along with these results, we were also able to synthesize and fully characterize a related, symmetric diborane(4) derivative bearing two ferrocenyl substituents, namely $B_2(NMe_2)_2Fc_2$ (**3**; Fc = (η^5-C_5H_4)Fe(η^5-C_5H_5)).

Results and Discussion

[2]Boraferrocenophane **2** was readily prepared by salt-elimination reaction of 1,1′-dilithioferrocene, [Fc]-Li_2·tmeda, with equimolar amounts of *1,2*-dichloro-*1,2*-dimesityldiborane(4), $B_2(Mes)_2Cl_2$, in pentane. After work-up, [Fe(η^5-C_5H_4)–B(Mes)–B(Mes)–(η^5-C_5H_4)] (**2**) was isolated as a red solid in moderate yields of 37% (Scheme 1).



Scheme 1. Preparation of [Fe(η^5-C_5H_4)–B(Mes)–B(Mes)–(η^5-C_5H_4)] (**2**).

The solution structure, as determined by NMR spectroscopy, confirms the presence of a strained *ansa* complex. The Cp ring protons show the characteristic splitting pattern in the ^{1}H NMR spectrum, and are detected as distinct pseudo triplets at δ = 3.70, 4.18, 4.36 and 4.89. The signals of the mesityl groups appear at lower field with respect to the starting material $B_2(Mes)_2Cl_2$ (δ = 2.16 (*p*-CH_3), 2.67 (*o*-CH_3) and 6.86 (CH)). The ^{11}B NMR spectrum of **2** features one single resonance at δ = 66.0, which is shifted to higher field by 21 ppm upon incorporation into the *ansa* complex [$B_2(Mes)_2Cl_2$ δ = 87.0],[11] but is found down-field shifted by 22 ppm in comparison to the related [2]boraferrocenophane **1** bearing dimethylamino groups at boron.[4a]

Single crystals of **2** suitable for X-ray diffraction analysis were grown from benzene/pentane (1:3) at room temperature (Figure 1). **2** crystallizes in the monoclinic space group

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*C*2/*c*. The B–B bond [1.698(4) Å] is shortened with respect to the unstrained species **3** [1.725(3) Å; see below], which might be ascribed to the reduced π-bonding at the boron center caused by the presence of nitrogen donors in **3**. The B–C1 bond length [1.581(3) Å] is similar to those reported previously for related [2]boraferrocenophanes and -metalloarenophanes.[3,4] The strained character of **2** is readily derived from the deviation of the Cp rings from the coplanar arrangement, which is usually expressed in terms of the tilt-angle α. Thus, **2** [α = 10.5(2)°] features comparable, but less strongly pronounced molecular ring strain than the [2]boraferrocenophane **1** [α = 12.8(2)°],[4d] which is further supported by other geometrical parameters typically used to characterize *ansa* complexes[1d] such as angles β = 25.3°, γ = 63.0(2)° and δ = 173.4° [cf. **1**: α = 12.8(2)°, γ = 42.27(22)°, δ = 170.1°]. The smaller extent of tilting in **2** is also reflected by its UV/Vis absorbance at 453 nm in benzene, which is slightly blue-shifted compared to **3** (465 nm), but appears red-shifted with respect to that of unstrained ferrocene (441 nm).[1d]

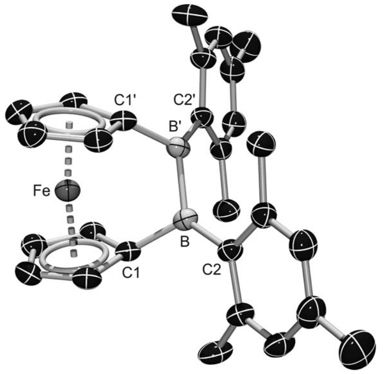
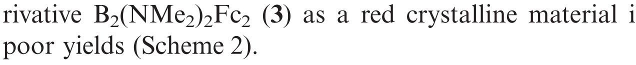


Figure 1. Molecular structure of **2** in the solid state. Hydrogen atoms are omitted for clarity. Symmetry-related positions (–*x* + *y*, –*z* + 3/2) are labelled with ′. Selected bond lengths [Å] and bond angles [°]: B1–B1′ 1.698(4), B1–C1 1.581(3), B1–C2 1.574(3), C1–B1–B1′ 107.20(12), C2–B1–B1′ 129.50(16), C1–B1–B1′–C1′ 63.0(2), C2–B1–B1′–C2′ 99.7(3).

Stoichiometric salt-elimination reaction of *1*,*2*-bis(dimethylamino)-*1*,*2*-dichlorodiborane(4), $B_2(NMe_2)_2Cl_2$, with two equivalents of ferrocenyllithium, FcLi, in toluene at room temperature afforded the unstrained diborane(4) derivative $B_2(NMe_2)_2Fc_2$ (**3**) as a red crystalline material in poor yields (Scheme 2).



Scheme 2. Synthesis of $B_2(NMe_2)_2Fc_2$ (**3**).

3 was unambiguously identified by NMR spectroscopy, which is in agreement with the presence of a C_2-symmetric species in solution. The ^{11}B NMR spectrum shows one signal at δ = 47.7, which appears shifted by 10 ppm to lower field with respect to the starting material $B_2(NMe_2)_2Cl_2$ (δ = 37.7).[12] In addition, two distinct resonances are observed for the dimethylamino groups in the ^1H NMR spectrum (δ = 2.91, 2.97). As expected, the aromatic protons of the unsubstituted Cp rings give rise to only one resonance at δ = 4.05, while signals of the other Cp ring protons cannot be detected separately, but feature a single multiplet at δ = 4.25.

The proposed constitution was ascertained in the solid state by crystal structure analysis on single crystals of **3** obtained by crystallization from pentane at –30 °C (Figure 2). **3** crystallizes in the monoclinic space group $P2_1/c$. The molecular structure combines typical features of diboranes(4) as well as unstrained metallocene derivatives. Thus, the B1–B2 bond length [1.719(2) Å] is similar to that observed in $B_2(NMe_2)_2Ph_2$ [1.714(4) Å],[13] and the B–N bond lengths [1.405(2) and 1.401(2) Å] are found in the expected range as well. The torsion angle N1–B1–B2–N2 [–95.61(17)°] is widened by 7° compared to that in $B_2(NMe_2)_2Ph_2$ (88.7°),[13] which is most likely a result of the steric requirements of the bulkier ferrocenyl ligands. The Cp rings are arranged almost parallel to each other, which is demonstrated by tilt-angles α = 2.39 and 3.62°, respectively. These values are significantly smaller than those found for the strained species **1**[4d] and **2** (see above). The unstrained character of **3** is also manifested by small values for the following angles: β_{B1} = –1.64°, β_{B2} = –0.46°, δ_{Fe1} = 178.06°, δ_{Fe2} = 177.29°.

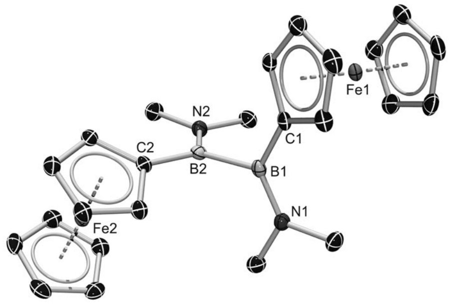


Figure 2. Molecular structure of **3** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: B1–B2 1.719(2), B1–N1 1.405(2), B1–C1 1.575(2), B2–N2 1.401(2), B2–C2 1.578(2), N1–B1–B2 121.44(13), C1–B1–B2 115.33(12), N2–B2–B1 121.62(13), C2–B2–B1 114.76(12), N1–B1–B2–N2 –95.61(17).

Conclusions

In this communication, we report on the successful isolation of a new strained [2]boraferrocenophane, $[Fe(\eta^5\text{-}C_5H_4)\text{–}B(Mes)\text{–}B(Mes)\text{–}(\eta^5\text{-}C_5H_4)]$ (**2**) that lacks any stabilization of the electrophilic boron centers by nitrogen donor substituents. The crystal structure determination confirms the presence of a strained *ansa* complex, supported by a tilt-angle α = 10.5(2)°. A related, albeit unstrained species, was isolated via salt elimination of $B_2(NMe_2)_2Cl_2$ with two equivalents of ferrocenyllithium, namely $B_2(NMe_2)_2Fc_2$ (**3**). The unstrained character was unequivocally validated by X-ray diffraction analysis. The suitability of the two diborane(4) species for further functionalization reactions at the B–B bond is currently tested in our laboratories.

Experimental Section

General: All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques or in a glove box. Solvents were dried according to standard procedures and stored under argon over molecular sieves. $B_2Mes_2Cl_2$,[11] $B_2(NMe_2)_2Cl_2$,[12] [Fc]Li_2·tmeda[14] and [Fc]Li[15] were prepared according to literature procedures. All other chemicals were obtained commercially and used without further purification. The UV/Vis spectra were measured on a Shimadzu UV mini-1240-spectrometer (suprasil-quartz cuvette). NMR experiments were performed on a Bruker Avance 500 (^{1}H, 500.130 MHz; ^{11}B, 160.462 MHz; ^{13}C, 125.758 MHz). ^{1}H NMR and ^{13}C NMR spectra were referenced externally to TMS. ^{11}B NMR spectra were referenced externally to $BF_3·OEt_2$. Elemental analyses were performed on a Vario Micro Cube elemental analyzer.

[Fe(η^5-C_5H_4)-B(Mes)-B(Mes)-(η^5-C_5H_4)] (2): A cooled solution of $B_2Mes_2Cl_2$ (0.48 g, 1.47 mmol) in pentane (30 mL) was added to [Fc]Li_2·tmeda (0.45 g, 1.43 mmol) via syringe at –70 °C. The mixture was allowed to reach ambient temperatures. The color of the solution changed to dark red after stirring for 16 h at room temperature. The solution was filtered and all volatiles were removed under vacuum to afford a red solid, which was recrystallized from pentane at –30 °C overnight. The resulting crystals were isolated and dried in vacuo; yield 37% (0.26 g, 0.58 mmol). ^{1}H NMR (23.7 °C, 500.130 MHz, C_6D_6): δ = 2.16 (s, 6 H, p-CH_3), 2.67 (s, 12 H, o-CH_3), 3.70 (m, 2 H, C_5H_4), 4.18 (m, 2 H, C_5H_4), 4.36 (m, 2 H, C_5H_4), 4.89 (m, 2 H, C_5H_4), 6.86 s, 4 H, *Mes*-C*H*) ppm. ^{11}B{^{1}H} NMR (23.7 °C, 160.462 MHz, C_6D_6): δ = 66.0 (br) ppm. ^{13}C{^{1}H} NMR (23.7 °C, 125.758 MHz, C_6D_6): δ = 21.38 (s, 2 C, p-CH_3), 25.94 (s, 4 C, o-CH_3), 69.76 (s, 2 C, C_5H_4), 77.17 (s, 2 C, C_5H_4), 78.13 (s, 2 C, C_5H_4), 78.59 (s, 2 C, C_5H_4), 141.41 (s, 4 C, *Mes*-CH) ppm. $C_{28}H_{30}B_2Fe$ (444.00): calcd. C 75.74, H 6.81; found C 75.46, H 7.21.

1,2-Bis(dimethylamino)-1,2-diferrocenyldiborane(4) (3): To a stirred suspension of FcLi (0.29 g, 1.55 mmol) in toluene (10 mL) was added $B_2(NMe_2)_2Cl_2$ (0.14 g, 0.77 mmol) via syringe at room temperature. The color of the solution changed from orange-red to dark red after stirring overnight at room temperature. The solution was filtered and all volatiles were removed under vacuum. The red solid was dissolved in hexanes and cooled to –30 °C overnight. The resulting red crystals were isolated and dried under vacuum; yield 10% (0.10 g, 0.35 mmol). ^{1}H NMR (23.7 °C, 500.130 MHz, C_6D_6): δ = 2.91 (s, 6 H, CH_3), 2.97 (s, 6 H, CH_3), 4.05 (s, 10 H, C_5H_5), 4.25 (m, 8 H, C_5H_4) ppm. ^{11}B{^{1}H} NMR (23.7 °C, 160.462 MHz, C_6D_6): δ = 47.7 (br) ppm. ^{13}C{^{1}H} NMR (23.7 °C, 125.758 MHz, C_6D_6): δ = 40.34 (s, 2 C, CH_3), 45.86 (s, 2 C, CH_3), 68.60 (s, 10 C, C_5H_5), 70.51 (s, 2 C, C_5H_4), 70.88 (s, 2 C, C_5H_4), 75.10 (s, 2 C, C_5H_4), 75.38 (s, 2 C, C_5H_4) ppm. ^{14}N{^{1}H} NMR (23.7 °C, 50.697 MHz, C_6D_6): δ = 283.06 [$N(CH_3)_2$] ppm. $C_{24}H_{30}B_2Fe_2N_2$ (479.82): calcd. C 60.08, H 6.30, N 5.84; found C 59.21, H 6.34, N 6.28.

CCDC-782501 (for **2**) and -782502 (for **3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Details on the crystal structure determinations of compounds **2** and **3**.

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