Synthesis and Crystal Structure of 1,3-Diphenyl-2-ferrocenyl-1,3,2-diazabora-[3]ferrocenophane

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1,1′-Bis(phenylamino)ferrocene reacts with dibromo(ferrocenyl)borane to yield a [3]ferrocenophane. The experimental details as well as the crystal structure of the product are presented.

Key words: Ferrocenophane, Ferrocene, Boron, Chelating Ligand

Introduction

1,1′-Diaminoferrocene and in particular its benzylated [1, 2], arylated [3 – 5] and silylated [6] derivatives ($[Fe\{(\eta^5\text{-}C_5H_4)NHR\}_2]$; R = CH_2Ph, Ph, $SiMe_3$) have recently been in the focus of attention. Not only have these compounds significant potential as building blocks in polymers, they also have proven their propensity as chelating ligands in combination both with main group elements like phosphorus [7], aluminum [8, 9] and boron [10, 11] and transition metals particularly of group 4 [5]. The latter have attracted attention as suitable non-metallocene (pre-)catalysts for α-olefin polymerization [12]. Especially a large number of 1,3,2-diazabora[3]ferrocenophanes have been synthesized and structurally characterized by Wrackmeyer *et al.* [7 – 11], who investigated the effect of tunable π donors attached to the trigonal planar boron center on the overall structure of these [3]ferrocenophanes. Bearing weak π donors, the lone electron pairs of the two nitrogen atoms in the bridge are delocalized more efficiently into the p_z orbital of the boron atom, resulting in an almost planar arrangement of the bridge (C–N–B–N–C). In contrast, strong π donors lead to a constitution with a considerable out-of-plane bending of the boron center [10].

In continuation of our investigations on [1]- and [2]boraferrocenophanes on the one hand [13 – 15] and ferrocenylboranes of the type $[FcB(\eta^1\text{-}C_5H_5)_2]$, $[FcB(1\text{-}C_9H_7)_2]$ $[FcB(3\text{-}C_9H_7)_2]$, $[FcB(1\text{-}C_9H_7)N(H)\text{-}Ph]$, $[FcB(3\text{-}C_9H_7)N(H)Ph]$, $[FcB(N(H)Ph)_2]$, $[FcB(Br)N(H)t\text{Bu}]$ and $[FcB(Br)N(H)Ph]$ (Fc = Ferrocenyl) as ligands in organometallic compounds on the other [16], we aimed to combine the two structural motifs, thus providing an unusual example of a homodinuclear *ansa* complex of iron.

In the present paper we report on the experimental details of the reaction of 1,1′-bis(phenylamino)ferrocene with dibromo(ferrocenyl)borane and the crystal structure of the resulting dinuclear [3]ferrocenophane.

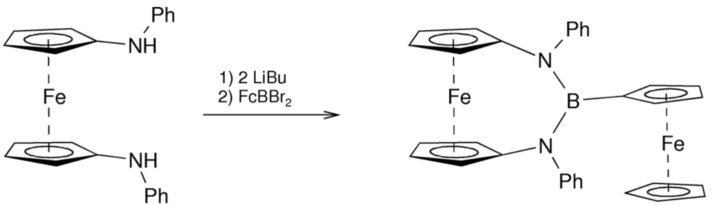
Results and Discussion

Synthesis

The synthesis of 1,3-diphenyl-2-ferrocenyl-1,3,2-diazabora-[3]ferrocenophane (**1**) was carried out by reacting in a first step 1,1′-bis(phenylamino)ferrocene with 2 equivalents of LiBu at −78 °C in hexane. A yellow solid precipitated, when the mixture was allowed to warm up to r. t. The suspension was again cooled to −78 °C, and in a second step a solution of one equivalent of dibromo(ferrocenyl)borane in hexane was added dropwise, according to Eq. 1.

After warming up the reaction mixture to ambient temperature and stirring for further 12 h, **1** was isolated as orange crystals in 85 % yield. The compound is soluble in all common solvents and can be stored under an atmosphere of argon. It shows no sign of decomposition, neither in the solid state nor in solution.

The ^{1}H NMR spectrum of the title compound displays five signals: four pseudotriplets are located at 4.18 (4H), 4.02 (4H), 3.83 (2H) and 3.52 (2H) ppm, and a singlet is found at 4.07 ppm. The former pair of pseudotriplets can be assigned to the protons of the ferrocenophane unit, while the latter pair as well as the singlet arise from the ferrocenyl moiety attached to the boron atom. Additionally, the phenyl substituents are characterized by rather complex signals in the aromatic



1

(1)

Table 1. Selected bond lengths (Å) and angles (deg) for **1** with estimated standard deviations in parentheses.

Distances			
N(1)–C(31)	1.430(4)	B(1)–N(1)	1.443(5)
N(1)–C(51)	1.446(4)	B(1)–N(2)	1.458(5)
N(2)–C(41)	1.437(5)	B(1)–C(21)	1.575(5)
N(2)–C(61)	1.436(4)		
Angles			
N(1)–B(1)–N(2)	121.5(3)	C(61)–N(2)–B(1)	125.1(3)
N(1)–B(1)–C(21)	120.4(3)	C(31)–N(1)–B(1)	126.9(3)
N(2)–B(1)–C(21)	118.1(3)	C(31)–N(1)–C(51)	110.5(3)
C(41)–N(2)–C(61)	110.4(3)	B(1)–N(1)–C(51)	122.6(3)
C(41)–N(2)–B(1)	124.3(3)		

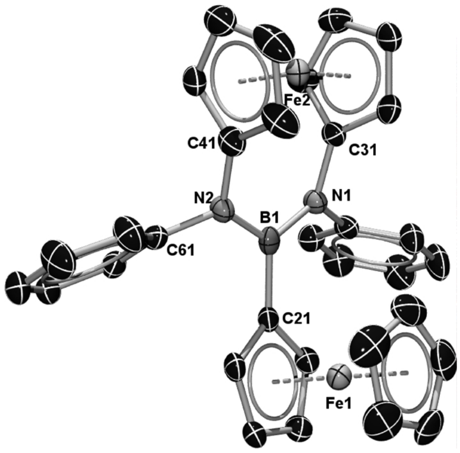


Fig. 1. Molecular structure of **1** in the crystal. Displacement ellipsoids are drawn at the 50 % probability level. Hydrogen atoms and the toluene molecule have been omitted for clarity.

region of the spectrum. In the ^{11}B NMR spectrum, a resonance at 34.7 ppm occurs which is significantly high-field shifted with respect to that of the starting material (at 48.0 ppm), thus accounting for the Br/NR$_2$ substitution.

X-Ray structure determination

Single crystals suitable for X-ray diffraction analysis were grown from toluene at −30 °C. The structure of **1** in the solid state is shown in Fig. 1. Selected bond lengths and angles are given in Table 1.

The boron center as well as both nitrogen atoms are in a trigonal planar configuration. The B–N bond lengths are 1.443(5) and 1.458(5) Å, and the B–C bond length was found to be 1.575(5) Å. The ferrocenyl moiety is known to be a weak π donor, and thus, the lone pairs of both nitrogen atoms are delocalized into the empty p_z orbital of the boron atom. Hence, an overall almost planar arrangement is imposed on the N–B–N-bridge. This result is in full agreement with previously published data of related species [10]. The cyclopentadienyl rings of the [3]ferrocenophane unit are slightly staggered (3.82°) and tilted (13.32°). Furthermore, the boron atom is bent towards the iron atom of the ferrocenyl moiety (10.26°) as observed for many other ferrocenylboranes with Lewis-acidic boron centers [16 – 18].

Experimental Section

All manipulations were performed under an atmosphere of argon using standard Schlenk or glove box techniques. Solvents were dried according to standard procedures or by using a MBraun solvent purification system (SPS) and stored under argon over molecular sieves. Dibromo(ferrocenyl)borane [19] and 1,1′-bis(phenylamino)ferrocene [4] were prepared according to literature procedures. LiBu was purchased from Aldrich as a 2.5 mol L^{-1} solution in hexane. The NMR spectra were recorded on a Bruker AMX 400 spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external TMS *via* the residual proton of the solvent (^{1}H) or the solvent itself (^{13}C). ^{11}B{^{1}H} NMR spectra were referenced to external $BF_3 \cdot OEt_2$. Mass spectra were recorded on a Finnigan MAT 8200 spectrometer.

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0.54 mL of a solution of LiBu (2.5 mol · L^{-1} in hexane, 1.34 mmol) was slowly added to a solution of 246 mg (0.67 mmol) of 1,1′-bis(phenylamino)ferrocene in 30 mL of hexane at −78 °C. The reaction mixture was stirred at −78 °C for 1 h and was then allowed to warm up to r. t. and kept stirring for further 30 min. The formation of a yellow precipitate was observed during the reaction. The suspension was again cooled to −78 °C, and a solution of 238 mg (0.67 mmol) of dibromo(ferrocenyl)borane in 20 mL of hexane was added. The mixture was warmed up to r. t. and was stirred for 12 h. The color changed slightly from yellow to orange. Insoluble material was filtered off, and the solvent was removed *in vacuo*. The residual orange oil was dissolved in a small amount of toluene. The product was obtained at −30 °C as orange crystals (319 mg, 0.57 mmol, 85 %). – ^{1}H NMR (400 MHz; C_6D_6; 25 °C): δ = 3.52 (pt, 2H, CH_{Fc}), 3.83 (pt, 2H, CH_{Fc}), 4.02 (pt, 4H, CH_{Cp-N}), 4.07 (s, 5H, CH_{Fc}), 4.18 (pt, 4H, CH_{Cp-N}), 6.9 – 7.4 (m, 10H, CH_{Ph}). – ^{11}B NMR (64.2 MHz; C_6D_6; 25 °C): δ = 34.7. – ^{13}C NMR (100 MHz; C_6D_6; 25 °C): δ = 69.04 (CH_{Fc}), 71.33, 77.11 (CH_{Cp-N}), 73.62, 74.85 (CH_{Fc}), 102.79 (CN_{Fc}), 124.27, 127.80, 128.87 (CH_{Ph}), 151.97 (CN_{Ph}). – MS (EI): *m/z* (%) = 562 (2) $[M]^+$; 368 (100) $[M-BFc]^+$.

Crystal structure determination

The crystal data of **1** were collected on a Bruker D8 APEX I diffractometer equipped with a CCD area detector with graphite-monochromatized MoK_α radiation. The structure was solved with Direct Methods, expanded using Fourier techniques, and refined with the SHELX [20] software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included as fixed-atom contributions into structure factors calculations.

Crystal data for **1**: $C_{32}H_{27}BFe_2N_2 \cdot 1/2(C_7H_8)$, M_r = 608.13, orange block, 0.11 × 0.07 × 0.05 mm^3, monoclinic space group $P2_1/c$ with a = 17.765(2), b = 9.2601(12), c = 17.215(2) Å, β = 99.328(3)°, V = 2794.5(6) Å^3, Z = 4, ρ_{calcd} = 1.45 g · cm^{-3}, μ = 1.1 mm^{-1}, F(000) = 1260 e, T = 193(2) K, $R1$ = 0.0591, $wR2$ = 0.1073 for $I \geq 4\sigma(I)$, for 5569 independent reflections [$2\theta \leq 52°$] and 398 refined parameters.

CCDC 679421 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.

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