

Note

Alternative synthesis and crystal structure of a [2]boraferrocenophane

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Abstract

The [2]boraferrocenophane $[(\eta^5\text{-C}_5\text{H}_4)\text{-B}(\text{NMe}_2)\text{-B}(\text{NMe}_2)\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}]$ (**1**) was obtained from the reaction of FeCl_2 and $(\text{Me}_2\text{N})_2\text{B}_2(\eta^1\text{-C}_5\text{H}_5)_2$ as a diborane(4) based ligand precursor in very good yields and fully characterized in the solid by single crystal X-ray diffraction.

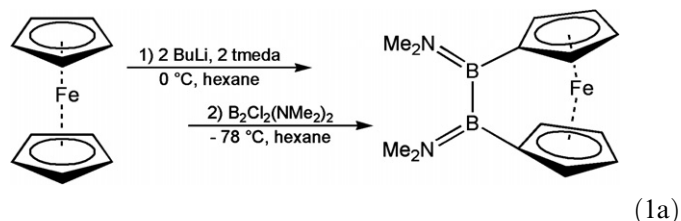
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Keywords: Boron; Iron; Diborane(4); Ansa-complexes

1. Introduction

[1]Borametalloenophanes comprising a three coordinate bridging boron centre have been reported for a variety of transition metals from group 4 [1–5], 5 [6], 6 [7] and 8 [8,9]. These compounds have attracted considerable interest [10,11], since corresponding [1]borazirconocenophanes constitute active catalysts for the polymerization of olefins [1–5,12] and the highly strained [1]boraferrocenophanes proved their propensity to undergo ring-opening polymerization yielding poly(ferrocenyl)boranes [8,9,13]. Two different routes have been applied to the synthesis of these complexes. Strained boron-bridged *ansa*-complexes are obtained from salt elimination reactions between 1,1'-dilithiometalloenes and suitable dihaloboranes, while the non-strained group 4 borametalloenophanes have to rely on the deprotonation of ligand precursors of the type $\text{RB}(\eta^1\text{-C}_x\text{H}_y)_2$ ($\text{C}_x\text{H}_y = \text{C}_5\text{H}_5, \text{C}_9\text{H}_7, \text{C}_{13}\text{H}_9$) [14,15] and their subsequent reaction with a suitable metal halide. An extension of these methods to related reactions of 1,1'-dilithiometalloenes with 1,2-dihalodiboranes(4) [6,7,16–18] and diborane(4) based ligand precursors with metal

halides (Eq. (1b)) [19], respectively, has led to corresponding [2]diborametalloenophanes.



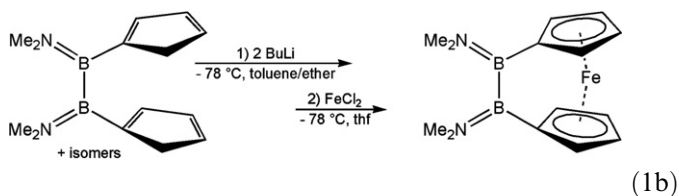
Recent reactivity studies on those compounds showed that [2]borazirconocenophanes, like their monoboron-bridged counterparts, act as active catalysts for olefin polymerization. Related complexes of the later transition metals are characterized by a pronounced reactivity of the bridging B–B-bond [6,17], and thus, served as facile diborane(4) precursors for the metal mediated 1,2-diboration of unsaturated organic substrates under homogeneous and even heterogeneous conditions [18]. $[(\eta^5\text{-C}_5\text{H}_4)\text{-B}(\text{NMe}_2)\text{-B}(\text{NMe}_2)\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}]$ (**1**) was obtained as the first [2]borametalloenophane in 1997 by Herberhold and Wrackmayer from dilithiated ferrocene and $\text{B}_2(\text{NMe}_2)_2\text{Cl}_2$, and thoroughly characterized in solution. Here, we describe an alternative synthesis for this compound, utilizing for the first time in the case of a late transition metal $(\text{Me}_2\text{N})_2\text{B}_2(\eta^1\text{-C}_5\text{H}_5)_2$ as a diborane(4) based ligand precursor. In addition, the structural characterization of **1** by single crystal X-ray diffraction is reported.

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2. Results and discussion

The reaction of 1,2-bis(dimethylamino)-1,2-bis(η^1 -cyclopentadienyl)diborane(4) with 2 equiv of BuLi at -78°C in toluene/ether and subsequent treating of the white residue with FeCl_2 in thf at -78°C gave **1** as a red crystalline material in 61% yield.



All spectroscopic data are identical to those already published [16,19]. Suitable crystals of the compound were grown from a solution of **1** in heptane at -30°C . The structure of **1** in the solid state is shown in Fig. 1.

The molecule is strained, which is reflected by the tilt angle α [$12.82(16)^\circ$] and the $\text{Cp}_{\text{centroid1}}\text{--Fe--Cp}_{\text{centroid2}}$ angle δ (170.1°). The iron atom deviates from the $\text{Cp}_{\text{centroid1}}\text{--Cp}_{\text{centroid2}}$ connection line by $d = 0.141 \text{ \AA}$. Thus, **1** is strained to a lesser extent than the corresponding $\text{C}(\text{H}_2)\text{--C}(\text{H}_2)$ bridged [2]ferrocenophane [$\alpha = 21.6(4)^\circ$, $\delta = 164.1(3)^\circ$, $d = 0.225(7) \text{ \AA}$], but more than the $\text{Si}(\text{Me}_2)\text{--Si}(\text{Me}_2)$ bridged derivative ($\alpha = 4.19^\circ$, $\delta = 176.48^\circ$, $d = 0.027 \text{ \AA}$). This is not only due to the smaller covalence radius of boron compared with silicon but also a result of the trigonal planar arrangement around boron with angles near 120° instead of tetrahedral environments with angles of approx. 109° like in the case of carbon and silicon [20,21]. The extent of tilting in **1** is also reflected by its UV–vis absorbance at 460 nm, which is slightly red-shifted with respect to that of ferrocene (440 nm) but not as distinctive as observed for the highly strained [1]boraferrocenophanes (498–479 nm). As a consequence of distortion,

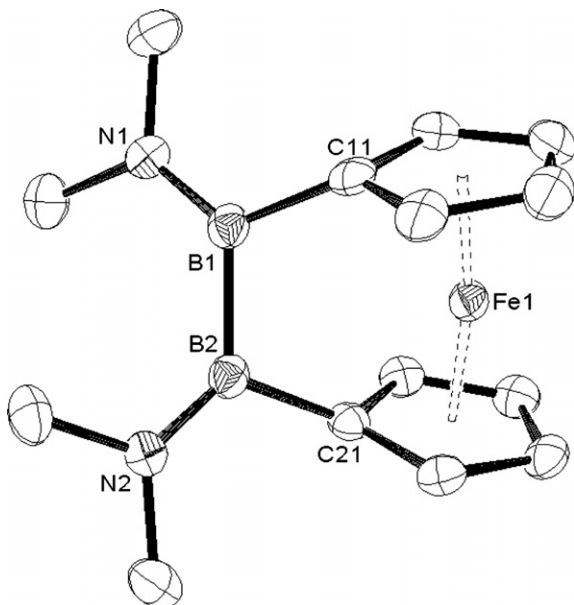


Fig. 1. Structure of **1** in the crystal (ellipsoids at 50% probability).

the bridge (C11--B1--B2--C21) is much more twisted, with a torsion angle of $42.27(22)^\circ$, than in the silicon (8.07°) and carbon (35.15°) analogues. Additionally, the C_5H_4 -rings exhibit a staggered conformation, specified by the $\text{Cp}_{\text{centroid1}}\text{--C11--C21--Cp}_{\text{centroid2}}$ torsion angle (16.0°) which differs conspicuously from the above mentioned compounds with values of 5.5° for the former and 1.2° for the latter, respectively. The values for the ethene-bridged [2]carbaferrocenophane ($\alpha = 23^\circ$, $\delta = 162.5^\circ$, $d = 0.249 \text{ \AA}$) are despite the sp^2 hybridization of the carbon atoms, much more comparable to those of the $\text{C}(\text{H}_2)\text{--C}(\text{H}_2)\text{--}$ and $\text{Si}(\text{Me}_2)\text{--Si}(\text{Me}_2)\text{--}$ bridged [2]ferrocenophanes than to **1** [22]. The boron–boron [$1.725(3) \text{ \AA}$], boron–nitrogen [$1.389(3)$ and $1.390(3) \text{ \AA}$] and boron–carbon distances [$1.598(3)$ and $1.593(3) \text{ \AA}$] are in the range of previously reported [2]boraarenophanes and metallocenophanes [7,17,19].

3. Experimental

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 or by using a MBraun solvent purification system (SPS) and stored under argon over molecular sieves. $\text{B}_2\text{Cp}_2(\text{NMe}_2)_2$ was prepared according to literature procedures [19]. All other chemicals were obtained commercially and used without further purification. The melting point was measured on a Mettler Toledo DSC823 $^\circ$. The UV–vis spectra were measured on a Shimadzu UV mini-1240-spectrometre (suprasil-quartz-cuvette).

4. Synthesis of 1,2-Bis(dimethylamino)-1,2-dibora-[2]ferrocenophane

A solution of 1,2-bis(dimethylamino)-1,2-bis(η^1 -cyclopentadienyl)diborane(4) (0.29 g, 1.21 mmol) in toluene/ether (1:1, 35 mL) was cooled to -78°C and BuLi (2.0 mL, 1.6 mol L^{-1}) was added dropwise. The mixture was allowed to warm up to room temperature, the white precipitate was collected by filtration, dried in vacuo and dissolved in thf (20 mL). The solution was slowly added to a suspension of FeCl_2 (0.15 g, 1.18 mmol) in thf (25 mL) at -78°C . After warming to room temperature, the dark red solution was stirred for 8 h. All volatiles were removed *in vacuo*, the residue was suspended in hexane and the red solid was collected by filtration. Yield: 211 mg, 0.72 mmol, 61%. Single crystals suitable for X-ray diffraction were grown from heptane at -30°C . M.p. 86°C . Spectroscopic properties (^1H , ^{11}B and ^{13}C NMR) are identical to those already published [16].

5. Experimental details on the crystal structure determination

A crystal of appropriate size was mounted on a glass fiber with silicone grease. The crystal was transferred to a

Bruker SMART APEX diffractometer with CCD area detector, centered in the beam, and cooled by a nitrogen flow low-temperature apparatus to an appropriate temperature. Preliminary orientation matrix and cell constants were determined by collection of 100 frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected [23]. The raw data were integrated with SAINT [24]. Cell dimensions were calculated from all reflections. Data analysis was performed with XPREP [25]. The data were corrected for Lorentz and polarization effects and an empirical absorption correction based on comparison of redundant and equivalent reflections was applied with SADABS [26]. The structures were solved via direct methods and refined with the SHELX software package and expanded using Fourier techniques [27]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. Crystal data for **1**: $C_{14}H_{20}B_2FeN_2$ $M_r = 293.79$, orange bricks, $0.30 \times 0.13 \times 0.10$ mm, orthorhombic, space group $P2_12_12_1$, $a = 7.5736(6)$ Å, $b = 13.2775(11)$ Å, $c = 14.2269(11)$ Å, $V = 1430.6(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.364$ g cm⁻³, $\mu = 1.039$ cm⁻¹, $F(000) = 616$, $T = 173(2)$ K, $R_1 = 0.0282$, $wR_2 = 0.0694$, 2937 independent reflections [$2\theta \leq 52.82^\circ$] and 172 parameters.

6. Supplementary material

CCDC 631537 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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