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Synthesis and X-ray structure of a [4]ferrocenophane containing a boron–boron bond☆

M.J. Gerry Lesley, Ulricke Mock, Nicholas C. Norman *, A. Guy Orpen, Craig R. Rice, Jonathan Starbuck

University of Bristol, School of Chemistry, Cantock's Close, Bristol, BS8 1TS, UK

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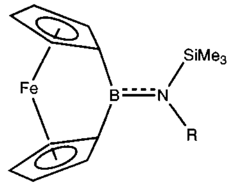
Abstract

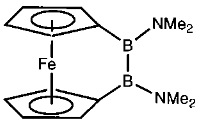
The synthesis and X-ray crystal structure of the [4]ferrocenophane compound [1,2-$B_2(NMe_2)_2\{1,1'-(SC_5H_4)_2Fe\}$] which contains a B–B bond are described. The ferrocene-1,1′-dithiolate group bridges the B–B bond of the diborane(4) unit [B–B 1.709(9) Å] in a 1,2- fashion. Each boron centre is trigonal planar, the angle between these planes being 82.0° such that the conformation about the B–B bond is staggered rather than eclipsed. All other angles fall within expected ranges indicating that there is little strain present in this compound. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ferrocenophane; Diborane(4); Synthesis; Structure

In recent years, [*n*]ferrocenophanes have received renewed attention as precursors to polymeric materials prepared by ring-opening polymerisation (ROP) reactions [1], particularly as a result of work by Manners and coworkers. Numerous compounds are known with silicon [2], carbon [3] and tin containing bridges [4], but only a few boron containing species have been characterised [5]. Two examples are the [1]ferrocenophanes (**1**) reported by Braunschweig and Manners [6] and, of particular interest with respect to this study, the diborane(4) derived [2]ferrocenophane (**2**) prepared by the group of Herberhold [7], this former species being highly strained and undergoing ROP at 190°C. As part of our own interest in diborane(4) compounds [8] and their potential as precusors to boron-containing polymers, we sought to prepare further examples of ferrocenophanes containing B–B bonds, preliminary details of which are reported herein.



1, R = $SiMe_3$ or Bu^t



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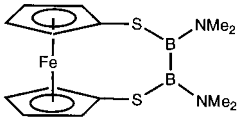
Our target compound was the sulphur derivative [1,2-$B_2(NMe_2)_2\{1,1'-(SC_5H_4)_2Fe\}$] **3** but initial attempts to prepare this species by the reaction of $B_2(NMe_2)_4$ [9] with one equivalent of ferrocene-1,1′-dithiol [10] revealed that a number of products were present as shown by mass spectrometry. Thus although compound **3** was formed, subsequent reactions with ferrocene-1,1′-dithiol resulted in compounds identified as **4** and **5** even under conditions of slow reagent addition and high dilution [11].



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☆ Dedicated to Alan H. Cowley FRS on the occasion of his 65th birthday and in recognition of his many orginal contributions to main group chemistry.

* Corresponding author.

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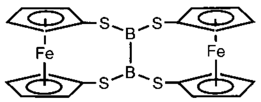

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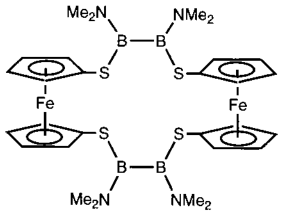

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However, the reaction between the dilithium salt of ferrocene-1,1′-dithiol and 1,2-$B_2Cl_2(NMe_2)_2$ [12] afforded **3** quantitatively as judged by NMR spectroscopy [13]. Compound **3** is very soluble in common solvents and could only be isolated in bulk as a rather oily solid but orange crystals were obtained from hexane solution on prolonged standing; one of these was suitable for X-ray crystallography. The molecular structure is shown in Fig. 1 [14]. Compound **3** crystallises as isolated molecules with no short intermolecular contacts. The ferrocene-1,1′-dithiolate group bridges the B–B bond in a 1,2- fashion consistent with the structure of the precursor, 1,2-$B_2Cl_2(NMe_2)_2$ with each boron also bonded to a NMe_2 group oriented such as to maximise B–N π-bonding (i.e. with NMe_2 and B_2S groups coplanar). The boron centres are both trigonal planar, the angle between these planes being 82.0° such that the conformation about the B–B bond is staggered rather than eclipsed. Although the eclipsed conformation is the one generally observed [8,15] in diborane(4) compounds with good π-donors, the staggered form is found particularly in those compounds containing bulky aryl groups [16] where steric effects are expected to predominate (the barrier to rotation in unhindered diborane(4) compounds is expected to be small [8,15]). As a result of this staggered conformation, the molecule has approximate C_2 symmetry, which results in each of the C_5H_4 hydrogens being inequivalent and since four signals are observed in the ^{1}H-NMR spectrum of **3** [13], even at −80°C, this conformation is presumably retained in solution. All the bond lengths in **3** (Fig. 1) are similar to values in other diborane(4) compounds [8,15] and warrant no special comment. As a final point, the observed (Cp-centroid)–Fe–(Cp-centroid) angle is 179.5° which, together with the unexceptional bond lengths and angles associated with the boron and sulphur centres, indicates that there is little conformational strain in the molecule.

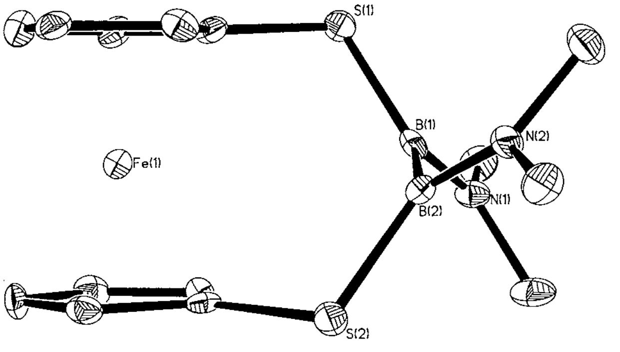

Fig. 1. A view of the molecular structure of **3** showing the atom numbering scheme. Hydrogen atoms are omitted and ellipsoids are drawn at the 30% level. Selected bond lengths (Å) and angles (°) include B(1)–B(2) 1.709(9), B(1)–S(1) 1.862(7), B(2)–S(2) 1.863(6), B(1)–N(1) 1.391(7), B(2)–N(2) 1.396(7); B(2)–B(1)–S(1) 124.0(4), B(2)–B(1)–N(1) 119.4(5), N(1)–B(1)–S(1) 116.3(5), B(1)–B(2)–S(2) 123.8(4), B(1)–B(2)–N(2) 120.2(5), N(2)–B(2)–S(2) 115.7(5).

Further studies are in progress to look at ROP reactions of **3** and to isolate and more fully characterise **4** and **5**.

Acknowledgements

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[13] To a solution of ferrocene-1,1′-dithiol (0.05 g, 0.2 mmol) in Et_2O (20 cm^3), a solution of *n*-butyllithium (0.25 cm^3 of a 1.6 M solution in hexanes) was added and the reaction mixture stirred for 30 min at room temperature affording a red-orange solution. After this time, a solution of 1,2-$B_2Cl_2(NMe_2)_2$ (0.036 g, 0.2 mmol) in Et_2O (10 cm^3) was slowly added over a period of 2 h and the resulting reaction mixture was then stirred for a further 8 h after which time the solution was filtered and all volatiles removed by vacuum affording **3** as an oily yellow solid (> 95%). NMR: ^1H ($CDCl_3$) δ 4.83 (m, 2H, C_5H_4), 4.35 (m, 2H, C_5H_4), 3.97 (m, 2H, C_5H_4), 3.92 (m, 2H, C_5H_4), 2.99 (s, 6H, CH_3), 2.94 (s, 6H, CH_3); ^{13}C-{^1H} ($CDCl_3$) δ 80.1 (C_5H_4), 77.8 (C_5H_4), 73.2 (C_5H_4), 69.8 (C_5H_4), 67.3 (C_5H_4), 43.0 (CH_3), 39.9 (CH_3). ^{11}B-{^1H} ($CDCl_3$) δ 40.4 (br s). Mass spectrum, m/z 358 (M^+, 62%) with correct isotope pattern; hrms, $C_{14}H_{20}B_2FeN_2S_2$ requires 358.060, found 358.061.

[14] Crystal data for **3**. The structure of **3** was determined on a Siemens SMART CCD area detector diffractometer ($\lambda = 0.71073$ Å) at 173 K from a hemisphere of reciprocal space with $2\theta \leq 48°$. The structure was refined by least squares against all F^2 data corrected for absorption, and hydrogen atoms were added in idealised positions. Crystal data: $C_{14}H_{20}B_2FeN_2S_2$, $M = 357.91$, monoclinic, space group $P2_1/c$, $a = 8.770(4)$, $b = 20.278(5)$, $c = 9.351(3)$ Å, $\beta = 92.14(3)°$, $U = 1661.9(10)$ Å^3, $Z = 4$, $\mu = 1.150$ mm^{-1}, 2580 unique data, $R1 = 0.0576$.

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