The first 1,2-dibora-[2]ferrocenophane and its dynamic behaviour in solution [1]

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Abstract

1,2-Bis(dimethylamino)-1,2-dibora-[2]ferrocenophane (**1**) was prepared by the reaction of 1,1'-dilithioferrocene with 1,2-dichloro-bis(dimethylamino)diborane(4). In addition to hindered rotation about the B–N bond ($\Delta G^{\ddagger} > 80\,kJ\,mol^{-1}$), another dynamic process was revealed by ^{1}H and ^{13}C NMR in solution at low temperature, and interpreted as motion of the cyclopentadienyl rings between staggered and eclipsed conformations ($\Delta G^{\ddagger}_{(233\,K)} = 44 \pm 1\,kJ\,mol^{-1}$).

1. Introduction

The attraction of [n]ferrocenophanes [1] is related to their structural properties (see Ref. [1] and, to compare the molecular structures of [n]ferrocenophanes ($n = 1,2$) containing Group 14 element links: for carbon bridges see Ref. [2]; for silicon bridges see Ref. [3]; for tin bridges see Ref. [4]), to their molecular dynamic properties [5], to the reactivity of element–element bonds in the bridge as a function of the bridge [6], and also to potential ring-opening polymerization to transition-metal-based polymers [6,7]. Although there is renewed interest in borylated ferrocenes [8–10], only a few [5] ferrocenophanes containing boron as heteroatom(s) either in 1,3- [11] or in 2-position [12] of the triatomic bridge are known. We now report on the synthesis of 1,2-bis(dimethylamino)-1,2-dibora-[2]ferrocenophane (**1**) and its dynamic behaviour in solution.
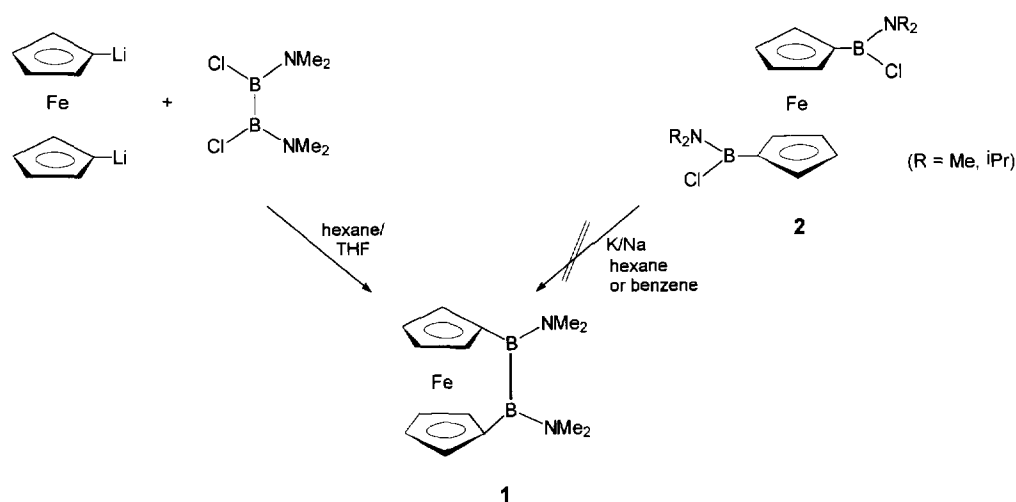
2. Results and discussion

1,2-Dichloro-bis(dimethylamino)diborane(4) was used as starting material, and its reaction with 1,1'-di-

lithioferrocene afforded the 1,2-dibora-[2]ferrocenophane **1** as a moisture-sensitive orange solid in good yield (Scheme 1). So far, it has proved impossible to prepare 1,2-dibora-[2]ferrocenophanes of type **1** by reduction of 1,1'-bis[amino(halogeno)boryl]ferrocenes **2** (Scheme 1), although this type of reaction is well documented [13]. It is conceivable that close contacts between the boryl groups at the cyclopentadienyl rings are unfavourable for steric reasons, whereas the formation of the intramolecular B–B bond in **1** requires the close proximity of the boryl groups. It was shown previously by ^{1}H–^{1}H NOE difference spectra that the boryl groups in **2** or other 1,1'-diborylferrocenes prefer, on average, a trans-arrangement in solution [14]. This is in agreement with solid-state X-ray structural data: the boryl groups occupy trans-positions in the centrosymmetric 1,2-bis(dibromoboryl)ferrocene [15], and a somewhat less symmetric arrangement of the boryl groups was found in 1,2-bis(bis(diisopropyl-amino)boryl)ferrocene [15]; close contacts between the boryl groups in 1,1'-diboryl-ferrocenes have not been observed so far.

The composition of **1** follows from the EI mass spectra which show the peak for the molecular ion with 100% relative intensity. The room temperature ^{1}H, ^{11}B, ^{13}C and ^{14}N NMR data (see Section 3) are fully consistent with the 1,2-dibora-[2]ferrocenophane structure. There is hindered rotation about the B–N bonds with a rotational barrier $\Delta G^{\ddagger} > 80\,kJ\,mol^{-1}$, typical of monoaminoboranes [16]. The N-methyl group (δ^1H =

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[1] Dedicated to Professor W. Siebert on the occasion of his 60th birthday.

Scheme 1.

Fig. 1. Contour plot of the 67.9 MHz 2D ^{13}C–^{1}H HETCOR experiment of **1**, based on $^1J(^{13}$C,^{1}H), carried out at −80 °C in [D$_8$]toluene, showing non-equivalence of the NMe groups and also of the ^{1}H and ^{13}C(2,3,4,5) resonances. The respective 1D ^{1}H and ^{13}C NMR spectra are displayed in the F$_1$ and F$_2$ projections. Note the relatively sharp ^{13}C(1) signal which is extremely broad at room temperature owing to partially relaxed scalar ^{13}C–^{11}B coupling.

2.81) is oriented towards the cyclopentadienyl ring, as shown by ^{1}H–^{1}H NOE difference experiments [17] (saturation of the NMe transitions and observation of the ^{1}H(2,5) resonances), and the C–H connectivity follows from the ^{13}C–^{1}H heteronuclear shift correlation (HETCOR) [18]. The unambiguous assignment of the ^{13}C(2,5) and ^{13}C(3,4) resonances is based on the room temperature ^{13}C INADEQUATE experiment [19] which shows signals according to $^1J(^{13}$C(1),^{13}C(2)) = 39.4 ± 1 Hz and $^1J(^{13}$C(2),^{13}C(3)) = 45.8 ± 0.5 Hz for the ^{13}C(2,5) resonances [14,15,20], whereas in the case of

the ^{13}C(3,4) resonances, there is only one doublet according to $^1J(^{13}$C(2),^{13}C(3)) = 45.8 Hz. The ^{13}C(1) signal for the boron-bonded carbon atoms is readily detected in the low temperature ^{13}C NMR spectra because of quadrupolar decoupling of the ^{11}B nuclei [21] (see the F$_2$(^{13}C) projection in Fig. 1).

Interestingly, another dynamic process ($\Delta G^{\ddagger}_{(233\,K)}$ = 44 ± 1 kJ mol^{-1}) becomes apparent if ^{1}H and ^{13}C NMR spectra are recorded at lower temperatures. Below −40 °C, there are two ^{1}H and ^{13}C resonances each for the 2,5-positions, and also two ^{13}C(3,4) resonances, although the different ^{1}H(3,4) resonances are not resolved. In the 2D ^{13}C–^{1}H HETCOR (Fig. 1), mutual assignment of ^{13}C and ^{1}H resonances is achieved and the plot shows that all ^{1}H resonances are resolved.

The origin of the non-equivalence of the 2,5- and 3,4-positions at low temperature is ascribed to the properties of the B–B bond in **2**. In the case of other amino-diborane(4) derivatives [22], the favoured conformation avoids a parallel orientation of the assumed axes passing through the boron p$_z$-orbitals. It appears that the same phenomenon enforces a staggered conformation of the cyclopentadienyl rings in **1** (see Fig. 2) as a minimum of energy ^{2}. Although an eclipsed conformation of the cyclopentadienyl rings and boron atoms in 1,2′ positions would produce similar NMR data, this is excluded because models indicate considerable strain in the resulting bond angles if the B–B bond length is kept at ca. 170–175 pm. Intramolecular mobility involving rapid fluctuation between eclipsed and staggered conformations has been discussed previously in order to
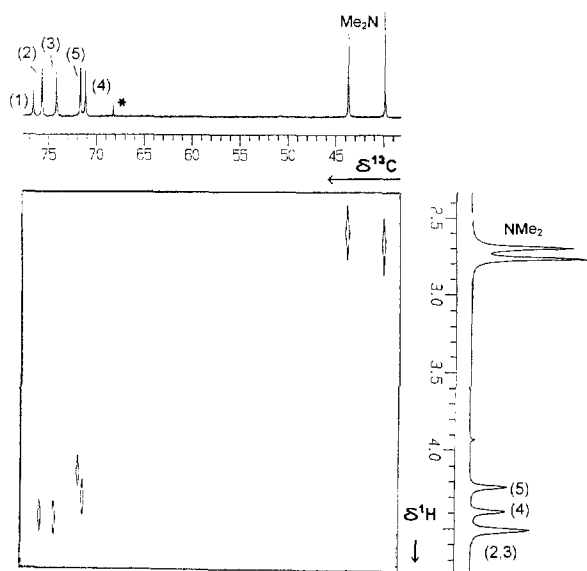
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^{2} Note added in proof: In the meantime this model has been confirmed by an X-ray structural analysis of **1**. (A. Appel and H. Nöth, *Abstracts IMEBORON IX, Heidelberg, 1996*, poster 341.
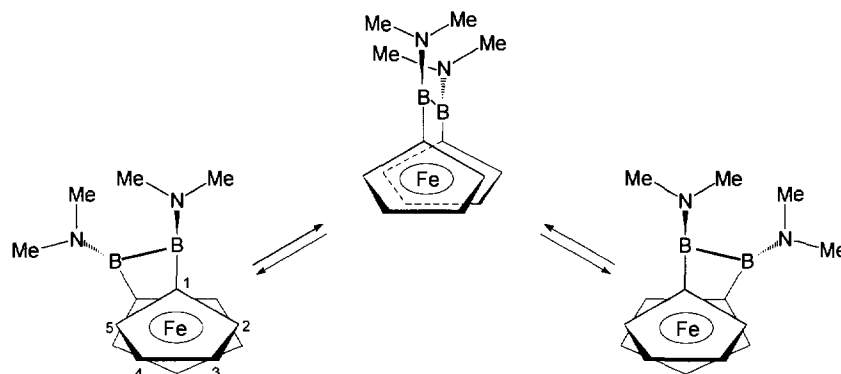
Fig. 2. Conformations of the 1,2-dibora-[2]ferrocenophane **1**; the staggered conformation causes non-equivalence of the 2- and 5-, and 3- and 4-positions at low temperature.

explain the temperature dependence of the ^{1}H NMR spectra of 1,2,3-trichalcogena-[3]ferrocenophanes [5].

3. Experimental details

All handling of compounds and synthetic work was carried out in an inert atmosphere of either N_2 or Ar, using dry glassware and carefully dried solvents. The ferrocene derivatives **2** [8,14,15], 1,1'-dilithioferrocene [23], and 1,2-dichloro-bis(dimethylamino)diborane(4) [24] were prepared as described. Mass spectra: Finnigan MAT CH 5. NMR spectra: Bruker ARX 250 and AC 300 (multinuclear probe heads), and Jeol EX 270 (^{1}H, ^{13}C), all equipped with variable temperature-control units. Chemical shifts are given with respect to Me_4Si ($\delta^1H(C_6D_5H)$ = 7.15; $\delta^1H(C_6D_5CD_2H)$ = 2.03; $\delta^{13}C(C_6D_6)$ = 128.0; $\delta^{13}C(C_6D_5CD_3)$ = 20.4), Et_2O–BF_3 ($\delta^{11}B$ = 0 for $\Xi(^{11}B)$ = 32.083971 MHz), and neat $MeNO_2$ ($\delta^{14}N$ = 0 for $\Xi(^{14}N)$ = 7.226455 MHz).

3.1. 1,2-Bis(dimethylamino)-1,2-dibora-[2]ferrocenophane (1)

A suspension of freshly prepared 1,1'-dilithioferrocene/4 tmeda (2.9 mmol) in 40 ml of hexane–THF (1:1) was cooled to −78 °C, and 1,2-bis(dimethylamino)-1,2-dichlorodiborane(4) (0.50 g, 2.9 mmol), dissolved in 10 ml of hexane, was added dropwise. The reaction mixture was stirred for 1 h at room temperature before the solvents were removed in vacuo. The residue was taken up in 40 ml of hexane, and insoluble material was filtered off. After removing most of the hexane in vacuo, the filtrate was kept at −78 °C, and 0.49 g (58%) of compound **1** were obtained as an orange precipitate (m.p. 60–61 °C). EI-MS (70 eV): m/z (%) 294 M^+ (100), 279 M^+ − Me (33), 250 M^+ − NMe_2 (16). ^{1}H NMR (270 MHz, C_6D_6, 25 °C): δ^1H = 2.77 s, 6H, 2.81 s, 6H (NMe_2); 4.26 m, 4H (H(2,5)); 4.38 m, 4H (H(3,4)). ^{11}B NMR (96.3 MHz, C_6D_6, 25 °C): $\delta^{11}B$ = 44.4 ($h_{1/2}$ = 400 Hz). ^{13}C NMR (67.9 MHz,

[D_8]toluene, 25 °C): $\delta^{13}C$ = 40.1 (NMe, correlation with δ^1H = 2.81); 43.1 (NMe, correlation with δ^1H = 2.77); 76.2 (C(1) measured at −60 °C), 73.8 (C(2,5)), 72.6 (C(3,4)). ^{14}N NMR (18.1 MHz, [D_8]toluene, 25 °C): $\delta^{14}N$ = −290 ± 5.

Acknowledgements

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