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Inorganica Chimica Acta 358 (2005) 1420–1428
Inorganica Chimica Acta
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Novel 1,3,2-diazabora-[3]ferrocenophanes and a 1,4,2,3-diazadibora-[4]ferrocenophane

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Received 18 June 2004; accepted 17 July 2004

Dedicated to Professor F. Gordon A. Stone on the occasion of his 80th birthday

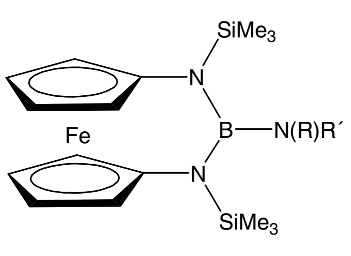
Abstract

N,*N*′-Dilithiated 1,1′-bis(trimethylsilylamino)ferrocene (**2**) reacts with boron halide adducts ($HBBr_2$–SMe_2; BF_3–OEt_2 and BBr_3–SMe_2), boron halides (BCl_3, BBr_3, $BCl_2(OPh)$ and $BCl_2(Ph)$) and 1,1-bis(dimethylamino)dichlorodiborane(4) to give the corresponding 1,3-bis(trimethylsilyl)-1,3,2-diazabora-[3]ferrocenophanes (**3**)–(**8**) and the 2,3-bis(dimethylamino)-1,4-bis(trimethylsilyl)-1,4,2,3-diazadibora-[4]ferrocenophane (**9**). All new complexes were characterised by multinuclear magnetic resonance spectroscopy in solution, and the solid-state molecular structures of the hydride (**3**), fluoride, chloride (**4**, **5**), and of the phenoxy and phenyl derivatives (**7**, **8**) were determined by X-ray analysis.

Keywords: Ferrocenes; Boron; NMR-multinuclear; X-ray

1. Introduction

The 1,1′-bis(trimethylsilylamido)ferrocene ligand possesses attractive chelating ability, which has already been demonstrated for magnesium, titanium [1,2], zirconium [1], tin [3,4] and phosphorus derivatives [5]. The ring closure to the 1,3,2-diazahetero-[3]ferrocenophane system enforces an approximately perpendicular orientation of the lone electron pairs at both nitrogen atoms with respect to the π system of the cyclopentadienyl rings, and if a trigonal-planar coordinated boron atom occupies the position between the two amido nitrogen atoms, efficient BN(pp)π interaction can take place, involving the lone electron pairs at the two nitrogen atoms. Recently, we have reported on the first 1,3,2-diazabora-[3]ferrocenophanes (**1**) [6], in which the boron atom bears an exocyclic amino group, N(R)R′. Depending on the nature of the amino group, either endocyclic (**1b**) or exocyclic BN(pp)π interactions (**1a**) dominate. This became evident by dynamic NMR measurements in solution as well as by significant differences in the solid-state molecular structures [6].



1	a	b
R	Et	Et
R′	Et	Ph

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doi:10.1016/j.ica.2004.07.059

In the present work, we report on our attempts to prepare 1,3,2-diazabora-[3]ferrocenophanes **3**–**8** analogous to **1** with other functional groups at boron (e.g., H, F, Cl, Br, OPh and Ph), and a 1,4,2,3-diazadibora-[4]ferrocenophane (**9**). Except of the hydride, the functionalities at the boron atom in **3**–**8** can be regarded as more or less strong π electron donors, and this property should be reflected by the molecular structure of the respective ferrocenophane. We have therefore determined the molecular structures in the solid state by X-ray analysis, and have also characterised the complexes by ^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR measurements in solution.

2. Results and discussion

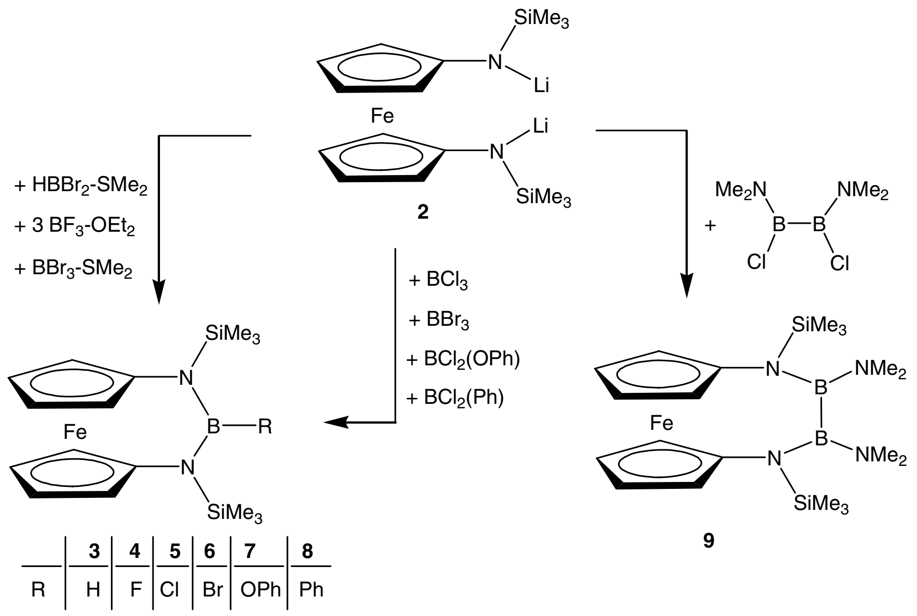
2.1. Syntheses

Both the *N*,*N*′ dilithiated-1,1′-bis(trimethylsilylamino)ferrocene (**2**) and the corresponding *N*,*N*′-magnesium derivative [1,3] are useful starting materials for the reaction with boron halides [6]. In this work, we have always used freshly prepared **2**, which reacted with either boron halides or adducts of boron halides to give the desired aminoboranes **3**–**9** in moderate to good yields (Scheme 1). The compounds **3**–**8** could be isolated as yellow or orange solids or oils, which were purified by crystallisation to give single crystals suitable for X-ray analysis in the cases of **3**, **4**, **5**, **7** and **8**. The diborane(4) derivative **9** was obtained as an orange oil which so far did not crystallise. The aminoboranes **3**–**9**, in particular the boron halides **4**, **5** and **6**, are sensitive towards traces of moisture. They are readily soluble in benzene, toluene, $CDCl_3$ or CD_2Cl_2, and the solutions can be kept for prolonged periods in sealed tubes at −18 °C.

The structure of **9** follows from a consistent set of NMR data (vide infra). Attempts to enforce the potential rearrangement of **9** into **10** (Scheme 2) were not successful. Heating of **9** in toluene for several hours at 80 °C induced decomposition and NMR signals for **10** could not be assigned.

2.2. NMR spectroscopic results

Relevant ^{11}B, ^{13}C and ^{29}Si NMR data for **3**–**9** are listed in Table 1, and ^{1}H NMR data are given in Section 4. The ^{1}H and ^{13}C NMR spectra of **3**–**8** are simple, as expected for a plane of symmetry passing through the atoms B, N, C1, C1′ and Fe. The ferrocene system gives rise to two multiplets in the ^{1}H NMR spectrum for the $H^{2,5}$ and $H^{3,4}$ nuclei and three ^{13}C NMR signals for C^{1}, $C^{2,5}$ and $C^{3,4}$. The $^{1}H(BH)$ NMR signal for **3** is readily detected by a $^{1}H\{^{11}B\}$ double resonance experiment. All ^{11}B NMR signals (Table 1) are found in a narrow range expected [7] for such surroundings where the boron atom is trigonally planar surrounded by two nitrogen atoms and an additional other substituent. Similarly, there is only one ^{29}Si NMR signal for each compound (Table 1) and the ^{29}Si resonance is hardly affected by the substituent at the boron atom. In comparison with **1a**, where the exocyclic NEt_2 group acts as a strong π donor, causing a significant distortion of endocyclic BN(pp) bonding [6], the ^{29}Si NMR signals in **3**–**9** are shifted to higher frequencies by ca. 10 ppm. The ^{19}F NMR signal of **4** is broad, similar to the $^{1}H(BH)$ NMR



Scheme 1. Synthesis of the 1,3,2-diazabora-[3]ferrocenophanes (**3**)–(**8**) and of the 1,4,2,3-diazadibora-[4]ferrocenophane (**9**).