Direct functionalization at the boron center of antiaromatic chloroborole†

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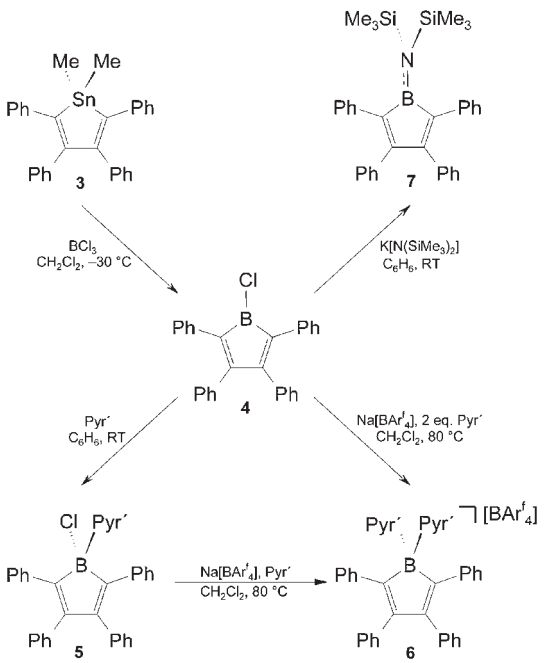
The presence of a reactive B–Cl bond allowed for the direct functionalization of the boron center in antiaromatic chloroborole $ClBC_4Ph_4$, thus allowing for a selective fine tuning of the optical properties of borole derivatives and facilitating a potential new approach toward the introduction of borole moieties into the backbone of organic π-conjugated frameworks.

During the last decades, the functionalization of π-conjugated organic systems with boron-containing substituents has attracted considerable attention because of the remarkable nonlinear optical and electrooptical properties of the resulting polymeric and molecular materials.[1] The success of this methodology is essentially based on the inherent electron deficiency, and hence the strong π-acceptor character of the three-coordinate boron center, which allows for significant delocalization through the vacant p_z orbital.[1,2] These materials are potentially suited for numerous applications such as nonlinear optics,[1a,3] two-photon absorption,[4] luminescence[5] or organic electronic devices.[6] In addition, it has been shown that the incorporation of the boron moiety into cyclic-conjugated borole heterocycles further significantly influences the respective absorption and fluorescence properties with respect to the open-chain analogs.[7] Here, the interaction of the p_z-orbital at boron with the unsaturated carbon backbone also results in a destabilization of the entire 4π-electron system due to antiaromaticity.[8] To date, the number of stable and non-annulated boroles that have been fully characterized is restricted to the pentaphenyl- and ferrocenyl-substituted derivatives RBC_4Ph_4 [R = Ph (**1**), (η^5-C_5H_5)Fe(η^5-C_5H_4) (**2**)].[7a–c,h] Boroles are usually prepared either by salt-elimination[7e,f] or boron–tin exchange reactions[7a–d,h] of appropriate boron reagents with dilithiated ligand precursors and stannole precursors, respectively. Whereas the former approach suffers a lack of selectivity and poor yields, the latter usually proceeds with high selectivity, but requires specific and sufficiently reactive boron halides. For this reason, all attempts to generate amino-substituted borole derivatives according to these two experimental routes have failed so far.[9] Hence, a facile and selective fine tuning of the photophysical properties of boroles remains elusive. In the present work, we report on a new synthetic strategy for the preparation of substituted borole derivatives that might be employed in the incorporation of borole moieties into π-conjugated organic frameworks. We demonstrate the direct functionalization of the reactive boron center in chloroborole $ClBC_4Ph_4$ (**4**) both by halide abstraction and nucleophilic displacement of the chlorine ligand without interfering with the BC_4-backbone.

Compound **4** was prepared *via* boron–tin exchange similar to that previously described for the syntheses of the borole derivatives **1** and **2**.[7h] Hence, 1,1-Me_2-2,3,4,5-tetraphenylstannole [$Me_2SnC_4Ph_4$] (**3**) was treated with a small excess of BCl_3 in CH_2Cl_2 at −30 °C (Scheme 1), whereby the initially yellow color of the solution instantaneously turned deep blue.† The reaction was monitored by multinuclear NMR spectroscopy, and the data confirmed the consumption of the starting materials and the quantitative formation of **4** within 30 minutes. After work-up and recrystallization from toluene, $ClBC_4Ph_4$ (**4**) was isolated analytically pure as a deep blue solid in high yields of 87%.

The identity was confirmed by means of NMR spectroscopy and elemental analysis. The ^{11}B NMR resonance of **4** was



Scheme 1 Synthesis of chloroborole **4** and direct functionalization at the reactive boron center (Pyr′ = 4-Me-C_5H_4N).

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† Electronic supplementary information (ESI) available: Experimental details of all X-ray crystal structure determinations and a figure of the molecular structure of **6**. Experimental section including the syntheses, full characterization, and spectroscopic data of all compounds, as well as figures of the UV-Vis spectra. CCDC reference numbers 685645–685647. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b808483a

observed as a broad signal (δ = 66.4 ppm) in a region comparable to that found for **1** (δ = 65.4 ppm), supportive for the antiaromatic character of **4**.[7h] Compound **4** is very sensitive towards air and moisture and readily decomposes in the solid-state at RT within a few days, but might be stored under an inert atmosphere at −35 °C over a period of several weeks. The stability in solution is even lower, both at RT and at low temperatures. According to ^{1}H NMR spectroscopy, solutions of **4** in C_6D_6 exhibit a half-life of about 12 h at ambient temperature. For this reason, all attempts to obtain single crystals suitable for X-ray diffraction failed.

However, structural characterization of **4** was accomplished as its Lewis-base adduct with 4-Me-C_5H_4N. Treatment of **4** with stoichiometric amounts of 4-Me-C_5H_4N in benzene at RT afforded $Ph_4C_4BCl{\cdot}(NC_5H_4Me)$ (**5**) quantitatively (Scheme 1), as judged by ^{1}H and ^{11}B NMR spectroscopy.† The pure product was isolated after recrystallization from heptane at −60 °C as pale yellow crystals in 93% yield. In agreement with the presence of a four-coordinate boron center, the ^{11}B NMR spectrum of **5** features a single resonance at much higher field (δ = 5.6 ppm) than that of the precursor molecule **4** (δ = 66.4 ppm). Contrary to **4**, compound **5** is much more stable and shows no tendency to decomposition at all. The molecular structure of **5** in the solid-state unambiguously confirms both the coordination of one molecule of 4-Me-C_5H_4N to the boron atom and the constitution of the starting material **4** (Fig. 1).†

The central borole moiety is almost planar (rms deviation: 0.0135 Å). Similar to the molecular structure of pentaphenylborole **1**,[7h] the phenyl ligands are found in a propeller-like arrangement with dihedral angles between 32.7(3)° and 53.2(2)°. The boron center displays a distorted tetrahedral environment, whereas the B–C [B1–C2: 1.6098(24) Å; B1–C5: 1.6099(28) Å], the B–N [1.6022(25) Å] and the B–Cl [1.8757(19) Å] bond distances lie within the expected range for the corresponding single bonds. Upon coordination of 4-Me-C_5H_4N, the former vacant p_z orbital at boron becomes occupied. As a result, a cyclic delocalization of the π-electron system is no longer feasible, which results in the loss of the antiaromatic character of **5** in comparison to **4**. This is further emphasized by the observed bond lengths within the BC_4 ring [B–C: see above; C2–C3: 1.3563(25) Å; C3–C4: 1.5095(24) Å; C4–C5: 1.3600(24) Å], which are comparable to those found for the C–C single and C=C double bonds in a typical diene system such as *cis*,*cis*-1,2,3,4-tetraphenylbuta-1,3-diene [1.356 Å and 1.484 Å].[10]

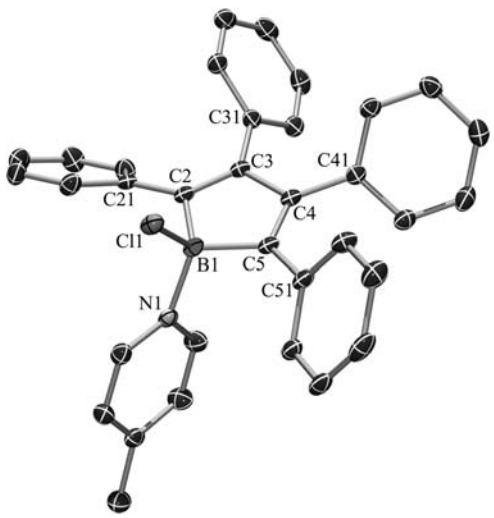

Fig. 1 Molecular structure of $Ph_4C_4BCl{\cdot}(NC_5H_4Me)$ (**5**) in the solid-state.

The following reaction might serve to illustrate the reactivity of the B–Cl bond of **5**. Treatment of a solution of **5** in CH_2Cl_2 with one equivalent of Na[BAr^f_4] (Ar^f = 3,5-CF_3-C_6H_3) and 4-Me-C_5H_4N in a resealable tube at 80 °C afforded the base-stabilized, borole-based boronium cation [$Ph_4C_4B{\cdot}(NC_5H_4$-$Me)_2$][BAr^f_4] (**6**; Scheme 1).† Monitoring the reaction by NMR spectroscopy revealed the quantitative conversion of **5** into **6** within 2 h and the absence of any soluble side and degradation products. Compound **6** can also be prepared directly from **4** by the addition of two equivalents of 4-Me-C_5H_4N to a stirred solution of **4** and Na[BAr^f_4] in CH_2Cl_2 and subsequent heating of the reaction mixture to 80 °C (Scheme 1). Crystallization of the crude product from CH_2Cl_2/hexanes at −35 °C yielded **6** as a golden, crystalline material in 77% yield. As expected, the ^{11}B NMR spectrum of **6** features two distinct resonances for the two non-equivalent boron nuclei (δ = 7.2 and −7.5 ppm). The molecular structure of **6** in the solid-state was determined by X-ray diffraction.† The structural parameters of **6** are very similar to those found for **5**, and hence are not discussed here (a graphical representation can be found in the ESI†).

To further highlight the suitability of **4** to act as a potential borole source, we attempted the functionalization of the boron center with anionic nucleophiles under retention of the trigonal-planar coordination sphere. The reaction of **4** with equimolar quantities of K[$N(SiMe_3)_2$] at RT proceeded smoothly in benzene and was accompanied by a gradual color change from deep blue to red and the formation of a KCl precipitate.† The NMR spectra of the reaction mixture suggested the clean and quantitative conversion of **4** into the amino-substituted borole derivative $Ph_4C_4BN(SiMe_3)_2$ (**7**) over a period of 1 h. Hence, the singlet of the $SiMe_3$ groups in the ^{1}H NMR spectrum shifted somewhat to higher field, *i.e.* from δ = 0.15 ppm in K[$N(SiMe_3)_2$] to δ = 0.11 ppm in **7**, and a new broad resonance at δ = 59.5 ppm was observed in the ^{11}B NMR spectrum (**4**: δ = 66.4 ppm). The relatively low-field shifted ^{11}B NMR signal might indicate a significant antiaromatic character of **7** regardless of the presence of a B=N double bond. Red crystals of **7** were isolated analytically pure after recrystallization from heptane at −35 °C in yields of 84%. The formation of an amino-substituted borole was authenticated by a crystal structure analysis of **7** (Fig. 2).†

The structural parameters of the planar BC_4Ph_4 moiety (rms deviation: 0.0193 Å), including associated bond distances and the propeller-like arrangement of the phenyl substituents, are very similar to those described for complexes **2**,[7h] **5** and **6** and will not be discussed here. The most intriguing structural feature relates to the highly twisted arrangement of the $N(SiMe_3)_2$ substituent at boron with respect to the C1–B1–C4 plane [Si1–N1–B1–C1: −55.6(3)°; Si2–N1–B1–C1: 125.4(2)°] due to the steric bulk. Such a disposition should preclude, or at least dramatically reduce the N–B π-donation, which is in agreement with the anticipated antiaromatic character of **7** derived from the ^{11}B NMR shift and its deep red color. It should be kept in mind that the coplanar

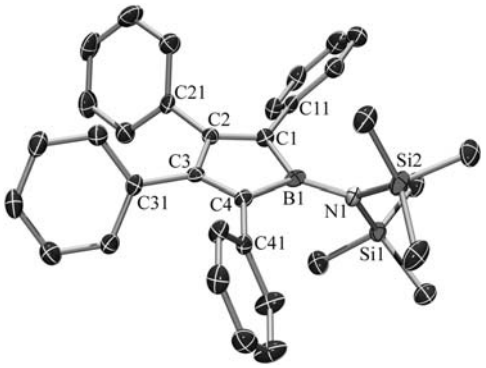

Fig. 2 Molecular structure of $Ph_4C_4BN(SiMe_3)_2$ (**7**) in the solid-state.

arrangement of the substituents typically observed within $R_2B{=}NR_2$ systems usually results in a highly effective N–B π-donation, which would cause the occupation of the vacant p_z orbital at boron in **7**. As a consequence, the antiaromatic delocalization of the π-electrons would be perturbed, accompanied with a color change to yellow (*cf*. formation of **5**). Hence, this structural parameter agrees very well with an antiaromatic character in-between those ascribed to **4** and **5**, respectively. However, both the trigonal-planar geometry [Σ = 359.9°] and the B–N bond length [1.4254(31) Å], which is typical for a B=N double bond (1.41 Å),[11] are in agreement with a boron center featuring a significant degree of a sp^2-hybridization. A similar twist of the $B{=}N(SiMe_3)_2$ moiety has been reported earlier, *e.g*. for the dinuclear borylene-bridged complex $[(\eta^5\text{-}C_5H_4Me)_2(CO)_2Fe(\mu\text{-}CO)(\mu\text{-}BN(SiMe_3)_2)_2]$.[12]

These findings are fully supported by the optical properties of the borole derivatives **4–7**, which were investigated by solution UV-visible spectroscopy in CH_2Cl_2 in the range 200–800 nm. The chlorine-substituted species **4** exhibits the characteristic blue color of a non-annulated borole and an absorption band at λ_{max} = 553 nm, indicative of its antiaromatic character.[7a,b,h] In contrast, this band is missing in the UV-visible spectra of the yellow, tetra-coordinated compounds **5** and **6**, whose lowest energy bands are now observed at λ_{max} = 373 nm and λ_{max} = 425 nm, respectively. Strong visible bands in this region are a common feature of all borole derivatives (**4**: λ = 377 nm) and have already been reported for different ring-annulated and base-stabilized boroles.[7] However, the absence of a low-intensity red-shifted band is a suitable criterion for a reduced or missing antiaromatic character in these species. Compound **7**, on the other hand, seems to lie in-between these two extremes: (i) **7** shows a deep red color both in solution and in the solid-state; (ii) besides the observation of a strong absorption band at λ = 393 nm, a broad shoulder is detected at around λ_{max} = 478 nm that might indicate the population of various rotamers in solution, but strongly suggests the presence of some antiaromatic character in **7**.

In summary, we reported on the syntheses and characterization of several borole derivatives containing unprecedented B–Cl (**4, 5**) and B=N (**7**) linkages, as well as on a cationic borole species (**6**). We presented a new strategy for the preparation of borole derivatives that represents a potential new approach toward the selective introduction of borole moieties into the backbone of organic π-conjugated frameworks, which enables the fine tuning of the optical properties of these highly interesting materials.

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Note added in proof: While this manuscript was being processed, Yamaguchi *et al*. reported on the synthesis of some aryl-substituted borole derivatives *via* boron–tin exchange and their full characterization.[13]

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