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Among unsaturated five-membered main group heterocycles, 1H-boroles are very reactive species that add dihydrogen or silane across the Si-H bonds. These systems may engage in various Diels-Alder reactions, which can provide a source of monomeric borole synthons upon thermal treatment. Thus, free boroles undergo Diels-Alder dimerization. These dimers can provide a source of 1,4-dilithiobuta-1,3-diene with metal aryls or the dilithiobutadiene with arylboron dihalides grants access to 1-Ar-2,5-(SiMe3)-3,4-phosphole boroles (Ar = Ph, Mes, Ph*, C6F5). Unlike the generally intensely blue-green 2,3,4,5-tetraaryl boroles, brightly orange/red 2,5-bis(trimethylsilyl) substituted boroles reveal blue-shifted π/π*-transitions due to a lack of n-system interaction between borole and 2,5-bound aryls. Light is shed on the synthetic peculiarities for the synthesis of 2,5-disilylboroles. While direct treatment of the respective 1,1-dimethyl-stannole with ArBCl2 via otherwise well-established B/Sn exchange reactions fails, the selectivity of reactions of 2,3-Ph*,1,4-(SiMe3)-1,4-dilithiobuta-1,3-diene with ArBCl2 is solvent dependent and leads to rearranged 3-boroles in hydrocarbons. Gutmann-Beckett analysis reveals reduced Lewis-acidity of disilylboroles compared to pentaphenyl borole.

Introduction

Among unsaturated five-membered main group heterocycles, 1H-boroles adopt a unique position. Isoelectronic to the elusive cyclopentadienyl cation, with four π-electrons in cyclic conjugation via the empty p-orbital of boron, these systems have been attributed a weakly anti-aromatic character. Free boroles are very reactive species that add dihydrogen or silane Si-H bonds across the n-system, react as potent Lewis-acids also towards weak bases, engage in various Diels-Alder and ring-expansion reactions or readily accept two-electrons to form dianionic 6n-electron systems. Boroles and boronolides are isoelectronic to cyclopentadienyl anions and have thus been used and studied as ligands in transition metal coordination chemistry. Only recently accounts of boroles as π-ligands for p-block elements (Al, Ge) have been reported. Bearing rather small substituents, free boroles undergo Diels-Alder dimerization. These dimers can provide a source of monomeric borole synthons upon thermal treatment.

With free boroles being so reactive, to date, their synthesis and successful isolation is limited to relatively few substituents around the central C6B cycle. Most reports on free borole chemistry discuss pentaaryl boroles and particularly (PhC)2Ar for which reliable synthetic protocols exist. Here, a key reaction involves the commercially available diphenyl acetylene which can be readily reductively coupled with lithium to provide 1,4-dilithiobuta-1,3-diene as valuable precursor for further derivatization. This allowed for the synthesis of tetraphenylboroles with varying boron-bound substituents in the past. The 2,5-bis(trimethylsilyl)-butadiene backbone has recently found application for s- and p-block element metaloles, mainly driven by the groups of Xi (groups 2 and 13), Saito and Müller (group 14). However, only very few examples of 2,5-bis(trimethylsilyl)-substituted boroles are known, all of which have been accessed via synthetically rather unusual routes (Scheme 1). Saito and coworkers obtained free fluoroborole via PhBCl2 exchange reactions starting from donor-stabilized plumbole. Erker and coworkers reported formation of free 2,5-bis(trimethylsilyl) boroles B by 1,1-carboborations after treatment.

This work:

Scheme 1 Examples of 2,5-Disilyl-Boroles.

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Electronic Supplementary Information (ESI) available: Experimental and Synthetic Details, depiction of spectra and crystal structures, computational details See DOI: 10.1039/x0xx00000x
of bis-alkynylboranes with tris(pentafluorophenyl)borane BPh$_3$. Other than these free boroles, the borole motive can be found in Sekiguchi’s and Lee’s dilithio borolediide obtained from reduction of chlorobora pyridazine as well as Müller’s and Alber’s Ge(II) complex of a borolediide. We are eager to extend the library of accessible free boroles with regards to the substituents attached to boron and carbon atoms of the central moiety and to study the electronic impacts of each individual substituent. Here we report on the synthetic access to 2,5-bis-trimethylsilyl substituted boroles.

### Results and Discussion

**Precursor Synthesis**

Free boroles (RC)$_2$BR' are usually accessed via salt metathesis reaction of 1,4-dilithiobuta-1,3-diienes or B/Sn exchange reactions of the respective stannole with boron dihalides RBX. Staniones are again either obtained from 1,4-dilithiobuta-1,3-dienes or Fagan-Nugent-type Sn/Zr transmetallations from the respective zirconacyclopentadiene. 1,4-Dilithiobuta-1,3-diienes are accessed by reductive coupling of acetylenes with hydrocarbon solvents and therefore anticipated 3,5-di-alkynylboranes with tris(pentafluorophenyl)borane. Especially coupling of silylacetylenes over lithium is heavily depending on the substituents.

We are keen to provide systems that are soluble in apolar hydrocarbon solvents and therefore anticipated 3,5-di-t-butylphenyl-trimethylsilyl acetylene C Ph*CCSiMe$_3$ (Ph* = 3,5-t-Bu$_2$C$_6$H$_4$)) to be a suitable building block to start from. Acetylene C however did not reveal any reaction with lithium metal and thus we had to take the detour via established zirconacyclopentadiene protocols using Negishi’s or Rosenthal’s reagents. 2,5-Disilyl-zirconacyclopentadiene 1 forms in excellent yields (>95%) (Scheme 2). However, likely due to steric pressure of the substituents 1 reversibly eliminates alkynole over time (see Supporting information). Our attempts for direct Zr/Sn transmetallation of 1 with Me$_2$SnCl$_2$ to stannole 5 failed (see ESI). Reactions of 1 with boron halides RBCl neither produced boroles 6 or boril-borolenes 7 (vide infra) but led to formation of yet unidentified products.

CuCl-supported iodination of in situ generated zirconacyclopentadiene 1 reliably yields the anticipated (Z,Z)-isomer of 1,4-diido-butadiene 2. In our hands, iodination of previously isolated 1 under identical conditions lead to unfavourable mixtures of (Z,Z) and (E,Z)-isomers of 2 (see SI). 2 is conveniently transformed into the 1,4-dilithiobuta-1,3-diene 3 with tert-butyllithium in essentially quantitative yield (97%). 1,4-Dilithiobuta-1,3-diene 3 is obtained as an intensely orange crystalline solid which revealed a dimeric structure in the solid state (Figure 1). The central distorted [Li$_4$]-tetrahedron reveals its longest Li-Li distances between Li-atoms that are connected to the same butadiene-dianion. All lithium atoms feature a further short contact (Li1-Li2 2.423(3) – 2.472(3)) to one silicon-bound methyl group thus also providing steric protection of the reactive nucleus. A related structure was previously reported by Saito and coworkers.

When Li/I exchange was attempted applying n-butyllithium followed by subsequent quenching of in situ generated 3 with Me$_2$SnCl$_2$ at 0°C, rearrangements were observed to take place and we isolated and identified silole 4 as a major product.

Under these conditions, butyl iodide apparently reacts with...
dilithio-butaadiene 3. Thus, using t-BuLi to produce 3 remained the more reliable approach. In the presence of HMPA (OP(NMe₂)₃), formation of 1,1-dimethylsiloles from rearrangements of 1,4-dilithio-1,4-disilybuta-1,3-dienes, presumably via 2-lithiosilole and MeLi elimination, was described earlier by Xi and coworkers.³³, ⁹⁴, ⁹⁵

Reaction of 3 with a mild electrophile such as Me₂SnCl₂ yielded the 1,1-dimethylstannole 5 in moderate crystalline yields (58%)³³, ⁷¹. Unfortunately however, the well-established boron-stannole exchange reaction with aryloboron dichlorides RBCl₂ (R = Ph, Xyl)⁴ (Xyl = 3,5-(CF₃)₂C₆H₃), that allows convenient and clean access to boroles with 2,3,4,5-tetraaryl-buta-1,3-dienes, ³³, ⁹⁴ does not occur in the case of this 2,5-disil yl system (Scheme 3). No formation of Me₂SnCl₂ is observed in NMR screening reactions. Side reactions leading to intractable product mixtures likely involve methyl abstraction from the tin atom in 5. An abnormal B/Sn exchange reaction behaviour was recently reported by Braunschweig and coworkers.⁹⁷

Being short of one major synthetic pathway to boroles, we thus turned to direct treatment of 1,4-dilithiobutaadiene 3 with organoboronic dihalides. Reactions of 3 and 1 equiv. of ArBCl₂ in THF revealed to cleanly (>90%) by NMR form the aryl boroles and allowed isolation of 6-Ph and 6-Ph⁺ in good yields (Scheme 4). However, quantitative removal of THF from the resulting Lewis-acidic boroles in vacuo (10⁻³ mbar) for several days was found to be tedious. The application of THF is therefore usually avoided when free boroles are targeted. While 6-Ph⁺ was obtained free of donor solvent after drying in vacuo, 6-Ph always contained residual amounts of THF, despite their Lewis-acidities were found to be identical (Gutmann-Beckett method, see below). At mildly elevated temperatures (40°C) THF is liberated from 6-Ph, however substantial decomposition occurs.

With MesBCl₂ the THF route fails completely. In Et₂O, borole formation was much less selective and did not provide satisfyingly pure material. However, when 3 was analogously reacted with phenylboron dichloride in hexane or benzene in order to access free organoboroles, irrespective of the applied stoichiometric ratio of the reagents, a clean consumption of 2 equiv. PhBCl₂ per 3 took place yielding a 2-borylated 3-borole 7-Ph. The structure of racemic mixtures of 7-Ph is confirmed by an X-ray structure (Figure 2) and reveals a double bond between C2 and C3. We reason, that formation of 7-Ph involves the intermediate generation of the anticipated phenyl-borole and rapid subsequent addition of a second equivalent of PhBCl₂ via an electrophilic attack of PhBCl₂ at one C₆ atom in the borole (Scheme 5).

These C₆ positions should be considerably nucleophilic given they bear two electropositive atom substituents (-SiMe₂ and -BR₂) and the Si β-effect should further moderate the α-addition of the B-electrophile in these special cases of vinylsilanes. Within the rearrangement sequence, the B-bound Ph-residue then migrates to the other C₆ when a chloride adds to the borole B-atom. The addition of a second equivalent ArBCl₂ to 6-Ar is facilitated by the removal of anti-aromatic cyclic 4n-electron delocalization and stabilizing lonepair π-donation from Cl into the empty p-orbital of borole. Addition of B-H moieties across a borole to give 2-boryl-3-boroles where reported earlier.¹⁰ Somewhat related chemistry was described for the reaction of azobenzene with (PhC₆)₂BPh.⁹⁸ Similar reaction behavior consuming 2 equiv. of aryl boron dihalides per 3 are also observed for the reactions with ArBCl₂ (Ar = Ph⁺, Xyl⁺). To support the proposed mechanism via formation of the free borole, 1 equiv. of isolated free borole 6-Ph⁺ was treated with the respective Ph⁺BCl₂ to give the same asymmetric compound 2-boryl-3-borole 7-Ph⁺ as the reaction of 3 with 2 equiv. of Ph⁺BCl₂, thus corroborating the proposed mechanism (see ESI). Notably, with Ar = Mes (Mes = 2,4,6-Me₃C₆H₂), no reaction occurred at all, while (PhC₆)₂Mes is reported to be readily formed from (PhC₆)₂Li and MesBCl₂.⁹⁸ Also when the electrophilicity of the boron species is reduced such as in 1-

![Scheme 4](image-url)

Scheme 4 Reaction of 3 towards boron electrophiles in THF (yields after crystallisation).

![Scheme 5](image-url)

Scheme 5 Reaction of 3 towards boron electrophiles in hydrocarbons.
Pr₂NBCl₂ or in the Lewis-adduct PhBCl₂(DMAP) (DMAP = 4-(N',N'-dimethylamino)pyridine), disilicon-butyadiene 3 did not reveal any reaction in C₆H₆ or Et₂O.

To our surprise, when a solution of 3 was treated with 1 equiv. of boron trichloride in hexane, chloroborole 8 was isolated in moderate yields of about 60% as an orange-red crystalline solid. Unlike in the previously discussed reactions of aryloboron dihalides, feasibility of the isolation of 8 likely stems from stabilizing np-π-donation interactions reducing both the Lewis-acidity and anti-aromatic character of chloroborole 8. An X-ray crystallographic examination revealed the structure of 8 as only the third example of a crystallographically characterized haloborole (Figure 3).

Bond lengths within the C₈B-ring are essentially identical to A and (PhC)₈B-Cl with the B1-C1 bond of 1.7543(17) Å in 8 being slightly longer than in the latter (1.7433(13) Å). Unlike these haloboroles, the substituents around the central C₈B-ring slightly bend out of the least-square plane through the borole atoms (Figure 3b).

While substituents at C4 and C3 essentially lie within the plane, substituents at B1, C1 and C2 alternatingly bend out above or below the central plane by ca. 11(1)° each. The amount of known 1-haloboroles in total is limited to four stable examples. Eisch’s and Braunschweig’s previously reported 2,3,4,5-tetraphenyl-haloboroles either dimerize at 40°C ((PhC)₈B-Cl)¹⁵ or 55°C ((PhC)₈B-Br)⁵⁷ or even decompose at ambient temperature over time. Marder reported on a transient chloroborole that readily dimerizes.⁹ This 2,5-disilyl chloroborole 8 is remarkably thermally and even forcing conditions in toluene at 130°C (in a teflon-valve sealed NMR-tube) for several hours did not indicate any decomposition of 6. Its thermal stability thus more resembles Pier’s perfluorinated 2,3,4,5-tetraphenyl bromoborole (Ph⁴C)₈B-Br (Ph⁴ = (C₆F₅)₄).⁵⁴ Stable haloboroles are a key synthetic precursor to borolyl-substituted systems. By functionalization of (PhC)₈BCl, Braunschweig and coworkers previously accessed amino-haloboroles or even oxidatively added the B-Cl bond across the zero-valent metal in [Pt(PCy₃)]₂.²,⁵⁶ The ¹¹B-NMR signal of 8 is found as a broad resonance (ω₁/₂ = 1370 Hz) at δ₁₁B = 70.8 ppm. This is more lowfield shifted than in (PhC)₈BBr (δ₁₁B = 66.4 ppm) and (PhF)₈B-Br (δ₁₁B = 67 ppm). Saito’s structurally related example of 1-F-2,5-(SiMe₃)₂-3,4-(Ph₃)₈borole (A), however, features an ¹¹B-NMR resonance at δ₁₁B = 54.9 ppm in line with a pronounced B-F π-interaction.

**Scheme 6** Formation of 6-Ar from 8 (yields after crystallization).

**Figure 3** a) ORTEP plot of the solid-state structure of chloroborole (8). Anisotropic displacement parameters are drawn at 50% probability level. b) Excerpt of the central substituted C₈B-ring. Selected bond length [Å] are given: B1–C1 1.7543(17), B1–C1 1.564(2), C1–C2 1.354(2), C2–C3 1.538(2), C3–C4 1.353(2), B1–C4 1.568(2), C1–Si1 1.8683(15), Si2–C4 1.8725(16).

**Figure 4** ORTEP plots of the solid-state structure of boroles (6-Ar). Anisotropic displacement parameters are drawn at 50% probability level. Lattice solvent molecules and disordered t-Bu groups are omitted for the sake of clarity. Top: 6-Ph*, Middle: 6-Mes, Bottom: 6-PhF. Key structural features are summarized in Table 1.
To explore the synthetic potential of chloroborole 8, we probed the accessibility of boroles by salt-metathesis approaches starting from 8. When (Ph*Li)$_2$, (MesLi) or Zn(Ph)$_2$ were added to toluene solutions of 8, NMR monitoring indicates the crude to primarily contain the respective aryl boroles 6-Ar (>80%), however for 6-Ph* and 6-Ph* isolated crystalline yields were lower. Notably, attempts to obtain 6-Ph from this approach with PhLi or Ph$_2$Zn in toluene failed and gave intractable product mixtures, that contained intensely colored side products. An intensely green side product (<1% NMR) of unknown constitution was also observed in case of 6-Ph* when prepared via the Ph*Li route. Only reactions of 8 with 0.5 equiv MgPh$_2$ in THF led to clean formation of 6-Ph which was again contamminated by THF. X-ray structures were obtained for 6-Ph$_2$ (Ar = Ph*, Mes, Ph$^+$) (Figure 4). Crystals of 6-Ph were repeatedly found to be thin needles that diffracted poorly. Comparable bond length within the central C$_2$B ring of all boroles 6-Ar are virtually identical and are well in the range of Erker’s related 1-Ph-2,5-Disilylborole (B-Ph, Scheme 1) and pentaaryl boroles 34, 54, 84 (except for (PhC$_6$)$_2$BPh). 6-Ar are found at comparatively low field (Ar = Ph: 76.6 ppm; = Ph$^+$: 77.1 ppm; = Mes: 79.9 ppm; = Ph$: 77.4$ ppm). Pentaaryl boroles 13B resonances are usually found between 65 and 75 ppm 1, 30, 54, 84 and Erker’s B-Ph (Scheme 1) at 74.7 ppm. 82 Previously, only sterically congested mesityl substituted (ArC)$_2$BMes boroles revealed 13B resonances that low-field shifted (Ar = Ph: 79 ppm; Ar = thienyl: 77 ppm) indicating, that increasing perpendicularity of the B-bound aryl correlates with low-field shifts.

Properties of 2,5-Disilylboroles

NICS$^{101-103}$ values for 6-Ar and 8 were calculated and NICS(0) and NICS(1) are tabulated in Table 1. The impact of the 2,5-disilyl substitution pattern on the (anti)aromaticity of boroles causes the NICS(0) values to be lower than the parent E (20.6), but higher (with a maximum of 16.7 for 6-Ph$^+$) than D (PhC$_6$)$_2$BPh (13.6). However the NICS-profiles of 6-Ar drop steeper and NICS(1) values do not differ significantly from D (see SI). The Lewis acidity of 2,5-disilylboroles was probed by means of the Gutmann-Becket approach that correlates the 31P chemical shift of Et$_3$PO interacting with Lewis acids with their acidity. 104-106 For steric reasons the Lewis-acidity of 6-Mes is poorly accounted for by this method but 8 (70.7), 6-Ph$^+$ (72.1), 6-Ph (72.1) and even 6-Ph$^+$ (73.8) all reveal similar acceptor numbers (AN) well below those previously determined under identical conditions for D (78.7). 100 The bulky and electropositive silyl groups seem to lower the Lewis-acidity, however the method cannot provide insight which influence is dominating.

As observed for chloroborole 8, in all cases the silyl-groups, and in some cases but much less pronounced Ph$_2$B*, bend out of the central C$_2$B-plane by 9-15°. Even for aryls (such as Ph or Ph$^+$) that do not feature substituents in ortho-position that would directly govern this torsion angle, the boron-bound aryls reveal rather large torsion angles between the respective C$_2$B- and aryl-planes of >50°. This is likely owing to the bulky silyl groups. With pentaaryl boroles, this torsion angle usually lies between 15-30°. The torsion of the C$_2$B-bound aryl is much less affected. For 6-Ar these torsions are found between 52-58° not much different from the torsions in (PhC$_6$)$_2$BAr (45-55°) 1,34 or (Ph$^*$C)$_2$B-Ar (52-58°). 84

To the synthetic potential of chloroborole 8, we probed the accessibility of boroles by salt-metathesis approaches starting from 8. When (Ph$^*$Li)$_2$, (MesLi) or Zn(Ph$^*$) were added to toluene solutions of 8, NMR monitoring indicates the crude to primarily contain the respective aryl boroles 6-Ar (>80%), however for 6-Ph* and 6-Phf isolated crystalline yields were lower. Notably, attempts to obtain 6-Ph from this approach with PhLi or Ph$_2$Zn in toluene failed and gave intractable product mixtures, that contained intensely colored side products. An intensely green side product (<1% NMR) of unknown constitution was also observed in case of 6-Ph* when prepared via the Ph$^*$Li route. Only reactions of 8 with 0.5 equiv MgPh$_2$ in THF led to clean formation of 6-Ph which was again contaminated by THF. X-ray structures were obtained for 6-Ph$_2$ (Ar = Ph*, Mes, Ph$^+$) (Figure 4). Crystals of 6-Ph were repeatedly found to be thin needles that diffracted poorly. Comparable bond length within the central C$_2$B ring of all boroles 6-Ar are virtually identical and are well in the range of Erker’s related 1-Ph-2,5-Disilylborole (B-Ph, Scheme 1) 82 and pentaaryl boroles 34, 54, 84 (except for (PhC$_6$)$_2$BPh D) 1.
Pentaphenylborole (PhC)BPh however reveals major contributions both from the boron-bound (accepting) and Cα-bound (donating) phenyl π-systems. From comparison with our 2,5-disilylboroles we reason that particularly co-planarily arranged Cα- and (to a reduced extent due to eventual collapsing overlap) Cβ-bound aryls to coplanarity allows a qualitative insight into the individual effects. While co-planarily bound B-Ph groups lead to only mild blue-shifted absorptions likely due to a LUMO raise on account of more effective π-interaction, particularly co-planarily arranged Cα-bound phenyls reveal a strong red-shifting effect. This further corroborates the essential impact of Cα-bound aryls on the color and HOMO/LUMO gap of boroles that we identified from their substitution by silyl groups. The vast influence of the Cα aryl torsion may also be a reason for the broad bands (ω1/2 ≈ 200 nm) commonly observed for these transitions in pentaphenyl boroles. Some previous studies on heteroaryl substituted boroles already suggested the importance of torsion-angle dependent π-interaction affecting the spectroscopic features.53, 60

Conclusion
In summary we presented various synthetic approaches to 2,5-disilyl boroles and shed light on their limitations. While traditional routes via boron-tin exchange reactions from stannoles fail, the reaction of the 1,4-dilithiobutadiene with aryl borondichlorides provides access to substituted boroles when the reaction is conducted in THF. In hydrocarbons two equivalents of arylboron dihalides react with 1,4-dilithiobutadiene to afford 2-boryl-3-borolenes, putatively via the free borole. Treatment of 1,4-dilithiobutadiene with BCl3 grants access to a thermally robust chloroborole. The reactions of the chloroborole with common available aryl-carbon nucleophiles such as aryllithium, Grignard reagents and arylzinc.
generous and supportive mentorship. We are grateful to the theses of T.H. and L.N. There are no conflicts to declare.

Experimental

Extensive synthetic and analytical details are given in the Electronic Supplementary Information.

Conflicts of interest

Content of this manuscript is or will be included in the PhD/BSc theses of T.H. and L.N. There are no conflicts to declare.

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