Conjugated Bis(triarylboranes) with Disconnected Conjugation

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Dedicated to Professor Christoph Janiak on the Occasion of his 60th Birthday.

A series of methylene-bridged bis(triarylboranes) has been synthesized via two complementary routes using metal-free catalytic Si/B exchange condensation under mild conditions. The title compounds comprise two borane moieties that show effective internal π-conjugation involving the respective boron centers and the adjacent hetaryl groups. Conjugation between both borane units, however, is disrupted by the aliphatic linker. Cyclic voltammetry revealed minimal electronic communication between the boron centers, as evidenced by two closely spaced reduction processes. The UV-vis spectra showed bathochromic shifted absorption bands compared to related monoboranes, which is attributed to the methylene bridge. A further red-shift results upon introduction of methyl or SiMe$_3$ groups at the terminal thiophene rings.
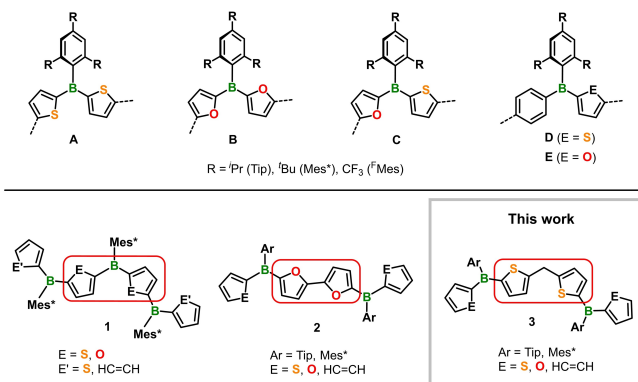
Figure 1. Kinetically stabilized diarylborane building blocks **A**–**E**, tris[(het)arylboranes)] **1** and bifuran-bridged bisboranes **2** previously reported by us, and dithienylmethane-bridged bisboranes **3** presented herein.

π-Conjugated triarylboranes currently attract enormous attention due to intriguing features that result from the interaction of the vacant p orbital on boron with the adjacent π systems (p–π conjugation).[1] This has enabled the application of triarylborane-based materials in various areas such as optoelectronics, sensors, and biological imaging.[1] The combination of trivalent boron with thiophene moieties is of special interest in that respect.[2–5] Jäkle and co-workers extensively explored dithienylboranes, **A** (Figure 1), which feature a bulky aryl group as the third *B*-substituent to ensure resistance towards hydrolysis and oxidation and provide improved thermal stability, as electron-accepting building blocks for π-conjugated polymers and molecular materials, respectively.[4] In the course

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of our studies on conjugated organoborane polymers and oligomers, we accomplished to develop a highly efficient, environmentally benign B–C bond formation method using a novel organocatalytic Si/B exchange condensation procedure.[5] This allowed us to access various molecular and macromolecular materials comprising dithienylborane units (**A**) as well as difurylborane (**B**) or mixed diarylborane building blocks (**C**–**E**). By the combination of boron with furan rings, we particularly broadened the scope of conjugated organoborane materials, as this has been only scarcely studied previously.[6]

Monodisperse oligoboranes such as **1** served as molecular model systems for respective hetarylborane polymers but they are also valuable compounds in their own right. Recently, we reported a series of bifuran-bridged bisboranes **2**. These compounds may be regarded as complementary to **1**, in a sense, as both species feature four conjugated arene and two borane moieties that are in the former case linked by an electron-accepting (i. e., a third borane) unit and in the latter case by an electron-donating (bifuran) bridge.

Bis(triarylboranes) of type **3** comprise a chain of four arene rings as well, but the π conjugation over the chain is disrupted through a methylene-bridge. Herein, we describe the synthesis and characterization of a series of such compounds and compare their photophysical and electrochemical properties with those of **1** and **2** and related monoboranes.

We accomplished the synthesis of bisboranes $3a–e^{Tip}$ and $3a–c^{Mes*}$ using our catalytic Si/B exchange approach via either of two alternative routes, *I* and *II* (Scheme 1). Compounds $3a–c^{Tip}$ and $3a–c^{Mes*}$ were accessed by the reaction of bis(trimethylsilyl)dithienylmethane **4** with two equivalents of freshly prepared dibromoboryl arenes **6a–c** in CH_2Cl_2 at ambient temperature in the presence of catalytic amounts of Me_3SiNTf_2 (Tf=CF_3SO_2; 10 mol%; *Route I*). The bulky aryl substituents were subsequently incorporated via reaction of the intermediates **8a–c** with TipLi or Mes*Li in toluene, respectively. The fully air- and moisture-stable compounds $3a–c^{Tip}$ and $3a–c^{Mes*}$ were obtained after purification by column chromatography on silica in moderate yields.

We prepared $3a,b^{Tip}$ additionally via *Route II*, and we also targeted compounds $3d,e^{Tip}$ in the same way. To this end, bis(dibromoboryl)dithienylmethane **5** was obtained in nearly quantitative yield by bisborylation of **4** with BBr_3 and subsequent recrystallization. Our catalytic Si/B exchange procedure using Me_3SiNTf_2 was then applied to **5** in combination with **7a,b,d,e**, respectively. Substitution of the B–Br bonds in the latter using TipLi yielded the desired products $3a,b,d,e^{Tip}$, which were isolated upon column chromatography. Since we have prepared $3a,b^{Tip}$ via both synthesis routes, we were then able to compare both approaches. This revealed that *Route I* is to be preferred in these cases, as it afforded the desired products in slightly better yields. On the other hand, *Route II* offers the opportunity of facile variation of the silylated coupling partner. Note that reactants **7a–e** are fully air-stable and can be easily purified by distillation.

The constitution of $3a–e^{Tip}$ and $3a–c^{Mes*}$ was unambiguously ascertained by multinuclear NMR spectroscopy. High-resolution mass spectrometry and elemental analysis yielded satisfactory results. ^{11}B NMR spectroscopy confirmed the presence of three-coordinate boron. The spectra showed broad signals at about 50–51 ($3b^{Ar}$), 56–57 ($3a^{Ar}$, $3d,e^{Tip}$), 60 ($3c^{Mes*}$) and 64 ppm ($3c^{Tip}$), following the order of decreasing electron-releasing character

of the (het)arenes attached to the boron center (furyl > thienyl > phenyl), which is also consistent with results we reported previously.[5] In the ^1H NMR spectra of the Mes*-featuring derivatives, $3a–c^{Mes*}$, the signals of the aromatic protons adjacent to the boron atom in the terminal thienyl, furyl or phenyl groups appeared significantly broadened. We previously observed this effect for related compounds such as $1^{[5b,c]}$ and $2^{[5e]}$ with Ar=Mes* as well. This can be understood as a result of hindered rotation about the B–C$_{(het)aryl}$ bond caused by the bulky Mes* substituent.

The UV-vis absorption spectra for $3a–e^{Tip}$ and $3a–c^{Mes*}$ in THF each display one structured band at $\lambda_{abs,max}=325–350$ nm (Figure 2 and Table 1). This is, as expected, at shorter wavelength compared to the $\pi–\pi*$ absorption bands of oligoboranes **1** ($\lambda_{abs,max}=371–378$ nm)[5b,c] and **2** ($\lambda_{abs,max}=398–417$ nm),[5e] which have conjugatively interconnected boron centers. Comparison of the synthesized derivatives of **3** reveals that substitution of Tip by Mes* leads to a marginal hypsochromic shift. The nature of the conjugated (het)aryl substituents has a stronger impact. Alike in $1^{[5b,c]}$ and 2,$^{[5e]}$ the wavelength of the absorption maximum for **3** increases in the order: phenyl ≪ furyl < thienyl. This proves effective π-conjugation within the isolated B(hetaryl)$_2$ or B(aryl)hetaryl moieties, respectively. Interestingly, the absorption bands of bisboranes **3** are bath-
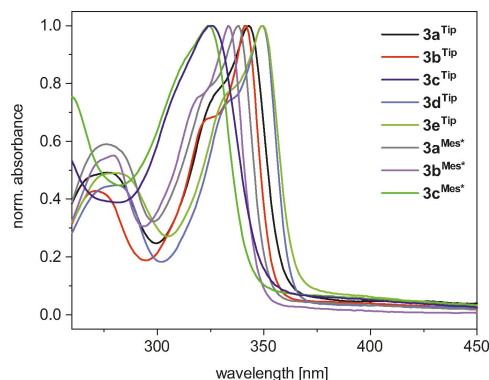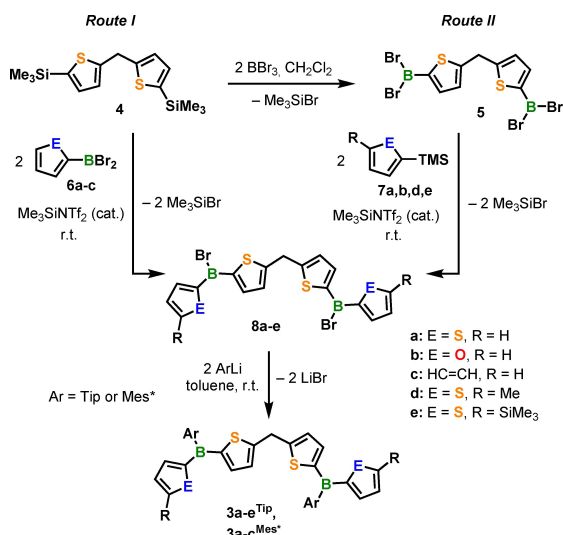

Figure 2. UV-vis absorption spectra for $3a–e^{Tip}$ and $3a–c^{Mes*}$ in THF.

Scheme 1. Synthesis of methylene-bridged bisboranes **3**.

Table 1. Photophysical and electrochemical data for $3a–e^{Tip}$, $3a–c^{Mes*}$, and related monoboranes (all measurements in THF at r.t.).

Compd.	$\lambda_{abs,\,max}$ [nm]	$E_{1/2,1}$ [V]	$E_{1/2,2}$ [V]
TipBThi$_2^{[5a,b]}$	325	–	–
Mes*BThi$_2^{[4]}$	325	–	–
Mes*B(Fur)Thi$^{[5b]}$	320	–	–
$3a^{Tip}$	343	−2.45[a]	[b]
$3b^{Tip}$	341	−2.54[a]	[b]
$3c^{Tip}$	326	−2.49[a]	[b]
$3d^{Tip}$	350	−2.35[a]	[b]
$3e^{Tip}$	350	−2.40[a]	[b]
$3a^{Mes*}$	338	−2.55[c]	−2.62[c]
$3b^{Mes*}$	333	−2.64[c]	−2.75[c]
$3c^{Mes*}$	325	−2.60[c]	−2.69[c]

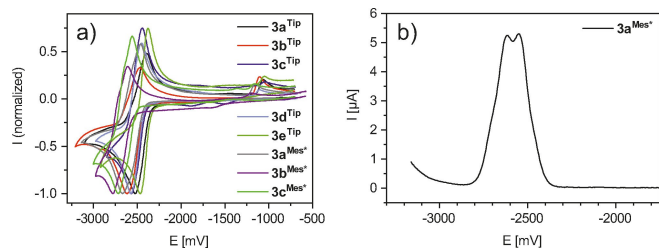[a] From cyclic voltammetry. [b] Not resolved. [c] Determined by differential pulse voltammetry.

Figure 3. (a) Cyclic voltammograms for $3a$–e^{Tip} and $3a$–c^{Mes} and (b) differential pulse voltammogram for $3a^{Mes*}$ (in THF at r.t; vs. Fc^+/Fc).

ochromic shifted compared to those of their respective monoborane congeners ($3a^{Tip}$ vs. TipBThi$_2$:[5a,b] $\Delta\lambda = 18$ nm; $3a^{Mes*}$ vs. Mes*BThi$_2$:[4a] $\Delta\lambda = 13$ nm; $3b^{Mes*}$ vs. Mes*B(Fur)Thi:[5b] $\Delta\lambda = 13$ nm). This appears to be an effect of the aliphatic methylene bridge. An additional methyl or a silyl group at the terminal thiophene ring causes a further red-shift by $\Delta\lambda = 7$ nm ($3d^{Tip}$ and $3e^{Tip}$ vs. $3a^{Tip}$). Both effects can be explained by an increase in the HOMO energy caused by electron-rich substituents such as alkyl or $SiMe_3$ groups, which thereby reduces the HOMO-LUMO gap. All compounds **3** are virtually non-fluorescent.

The redox behavior of compounds $3a$–e^{Tip} and $3a$–c^{Mes*} was characterized by cyclic and pulse voltammetry in THF (Figure 3) using tetrabutylammonium hexafluorophosphate as the supporting electrolyte. For each compound, the voltammograms indicate only partially reversible reduction processes as they feature a return oxidation peak at around −1.1 V. In the case of the Mes*-substituted bisboranes, the overlapping first and second reduction waves in the cyclic voltammogram could be resolved by square wave or differential pulse voltammetry, revealing relatively small separations of 70–100 mV (see Figures S59–S67 in the SI). The corresponding pulse voltammograms for the Tip-substituted bisboranes displayed a more complicated behavior, precluding a clear determination of their peak potential separations. However, they can be estimated to be smaller than ca. 150 mV. Therefore, the electrochemical data indicates only a small degree of negative charge distribution or "electronic communication" between the two boron atoms in these bisboranes.

In conclusion, we have successfully synthesized a series of new bis(triarylboranes) comprised of four hetarenes and two boron centers connected by a methylene-bridge. While both borane entities are internally effectively conjugated, π-conjugation along the hetarylborane chain and, thus, communication between the boron centers is disrupted by the aliphatic linker unit. Currently, we are exploring the use of these methylene-linked bisboranes as novel building blocks for the construction of extended π-conjugated scaffolds.

Experimental Section

General procedure for the synthesis of bisboranes $3a$–c^{Tip} and $3a$–c^{Mes*} via Route I. To a solution of **4** (0.325 g, 1 mmol) in

dichloromethane (4 mL), freshly prepared **6a–c** (2 mmol) and TMS-NTf$_2$ (0.071 g, 0.2 mmol) were added and the reaction mixture was stirred at room temperature for 2 d. Subsequently, the solvent was removed in vacuo to afford crude **8a–c**. The obtained oily solid was suspended in toluene (3.0 mL) and a solution of TipLi (0.462 g, 2.2 mmol) or a suspension of Mes*Li (0.555 g, 2.2 mmol) in toluene (3.0 mL) was added at room temperature, respectively. The reaction mixture was stirred for 2 d at room temperature followed by quenching with water. After aqueous work-up, all volatiles were removed in vacuo to afford crude **3**. Purification by column chromatography (silica, PE - > PE/DCM, 96:4) afforded compound **3** in high purity.

General procedure for the synthesis of bisboranes $3a,b,d,e^{Tip}$ via Route II. To a solution of **5** (0.2598 g, 0.5 mmol) in dichloromethane (2 mL), **7a,b,d,e** (1 mmol) and TMS-NTf$_2$ (0.035 g, 0.1 mmol) were added and the reaction mixture was stirred at room temperature for 2 d. Subsequently, the solvent was removed in vacuo to afford crude **8a,b,d,e**. The obtained oily solid was suspended in toluene (1.5 mL) and a solution of TipLi (0.231 g, 1.1 mmol) or a suspension of Mes*Li (0.278 g, 1.1 mmol) in toluene (1.5 mL) was added at room temperature, respectively. The reaction mixture was stirred for 2 d at room temperature, then the reaction mixture was quenched with water. After aqueous work-up, all volatiles were removed in vacuo to afford crude **3**. Purification by column chromatography (silica, PE− > PE/DCM, 96:4) yielded compound **3** in high purity.

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