Syntheses, Structures, and Coordination of Diborylbipyridines and Bipyridinediborates

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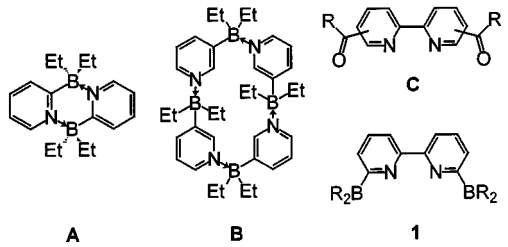
Dedicated to Prof. Dr. Günter Wächtershäuser on the occasion of his 60th birthday

6,6′-Bis(diethylboryl)-2,2′-bipyridine (**1a**) was obtained in low yield by in situ deprotonation of 2,2′-bipyridine in the presence of diethyl(methoxy)borane. 6,6′-Dilithio-2,2′-bipyridine reacts with various alkoxyboranes leading to bipyridinediborates **2** in good yields. The derivatives **2b** and **2c** allow the formation of the free diborylbipyridines **1b** and **1c**. The coordination properties of the diboryl–bipyridines as tetrafunctional donor–acceptor compounds have been used for the formation of the copper complex **4** and of the adduct **5** which is built from diborylbipyridine and a dihydroxydiboroxan derivative. The composition of the products follows from spectroscopic data and from X-ray structure analyses for **2f**, **4**, and **5**.

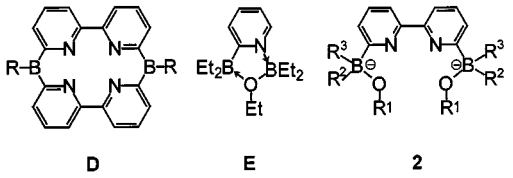
Introduction

The intramolecular presence of Lewis basic (nitrogen) and Lewis acidic centers (boron) results in interesting properties of borylated pyridines and bipyridines. A small number of borylpyridines has been reported,[1] which were synthesized as starting compounds for Suzuki coupling reactions.[2] 2-(Diethylboryl)pyridine[3] and 3-(diethylboryl)-pyridine[4] are known for their stability towards moisture and oxygen. The reason for this is their assembly by intermolecular boron−nitrogen coordination. 2-(Diethylboryl)-pyridine exists as a dimer (**A**) in solution and in the solid state,[5] and 3-(diethylboryl)pyridine as a cyclic tetramer (**B**).



Scheme 1

Bipyridines have been the subject of many studies.[6][7] The π-acceptor properties of this bidentate σ-donor are weak. By introducing electron-withdrawing groups the π*-level is lowered as has been demonstrated with acyl- and carboxybipyridines (**C**).[8] The dπ→π* absorption bands in L_3Ru^{II} complexes (L = bipyridines) are shifted toward the red region of the spectra and this shift increases the quality of these metal complexes as sensitizers in solar energy converting processes.[9] 6,6′-Diboryl-2,2′-bipyridines **1** should also have increased π-acceptor qualities relative to that of non-substituted bipyridines. We are in particular interested in 6,6′-diborylated bipyridines with respect to their donor-acceptor properties and their potential of forming the macrocycle **D**.



Scheme 2

From spectroscopic data the formation of the cyclic adduct **E**, based on the donor−acceptor pattern of 2-(diethylboryl)pyridine was postulated.[3] For the tetrafunctional 6,6′-diboryl-2,2′-bipyridines **1** one may expect a complex donor−acceptor behavior due to their geometric requirements. In the following the coordination properties of the donor−acceptor molecules **1** will be presented. In addition the formation of bipyridinediborates **2** and their behavior as N_2O_2 tetradentate ligands are studied, of which numerous examples have been reported.[10−13]

Results and Discussion

Synthesis

Following a general procedure,[14] we synthesized the diborylbipyridine **1a** by in situ deprotonation of 2,2′-bipyridine with lithium diisopropylamide (LDA) in the presence of an excess of diethyl(methoxy)borane. In this reaction **1a** was obtained in very low yield (1%) besides the monoborylated product **3a** (6%). **1a** is a colorless, high-melting solid of low solubility whereas **3a** is a viscous oil. Both substances are stable toward moisture and air. Their ^{11}B-NMR spectra (δ = 3) indicate tetracoordinate boron atoms in as yet unknown assembly, most likely **1a** and **3a** form donor−acceptor compounds similar to **A**. In the EI mass spectra the fragments of the monomeric species with loss of one

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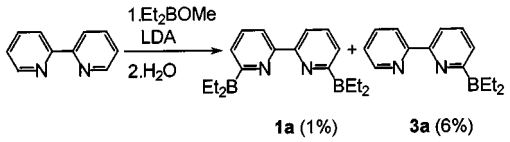
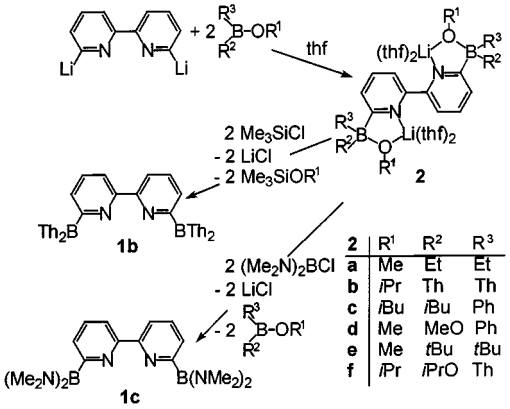
ethyl group appear as highest masses at m/z = 263 [**1a** − Et]$^+$ and 195 [**3a** − Et]$^+$.



Scheme 3

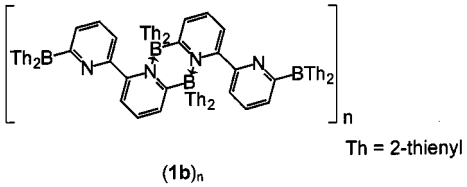
To improve the yields a stepwise synthesis was carried out. 6,6′-Dilithio-2,2′-bipyridine, obtained by a metal/halogen exchange,[15] was treated with various alkoxyboranes to give the borate derivatives **2a−f**.



Scheme 4

Regardless of the steric and electronic properties of the substituents, the products **2a−f** are thermally stable and isolated in 64−89% yields. All are colorless, crystalline substances, which, however, are very sensitive toward hydrolysis to give bipyridine and the corresponding boron compounds. They are characterized by ^{1}H-, ^{13}C-, ^{11}B-NMR spectroscopy and by an X-ray structure analysis of **2f** (see below). In these molecules the expected leaving groups LiOR are bound to the diborylbipyridines. There are interactions between the acceptor function (boron) with the alkoxy group and between the donor function (nitrogen) with the lithium ion. The formation of this five-membered heterocyclic arrangement enhances the stability of the adducts.

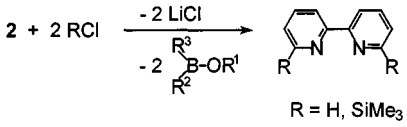
Attempts to synthesize **1a** from **2a** failed. Reaction of **2b** with $ClSiMe_3$ yields the 6,6′-bis-di(2-thienyl)boryl]-2,2′-bipyridine (**1b**) in 36% yield. The combination of steric (*i*Pr) and electronic effects (thienyl) of the substituents destabilizes the coordination in the dianionic borate **2b** and thus allows the formation of the free diborylbipyridine **1b**. Based on the ^{11}B-NMR spectrum in thf (δ = −1), its low solubility and high melting point (> 250°C) we propose an aggregation via N−B donor acceptor interactions to give an oligomer of unknown structure and number of diborylbipyridine units. The appearence of only one ^{11}B-NMR signal may indicate a cyclic arrangement. In a chain-like donor−acceptor compound $(\mathbf{1b})_n$ the two terminal BTh_2 groups could be stabilized by thf molecules forming donor−acceptor adducts.



Scheme 5

The reaction of the diisobutoxy derivative **2c** with chlorobis(dimethylamino)borane results in the formation of 6,6′-bis[bis(dimethylamino)boryl]-2,2′-bipyridine (**1c**). It is obtained in 64% yield as a red oil of limited solubility in thf. In comparison to bis(dimethylamino)organoboranes (δ = 34−36)[16] the ^{11}B-chemical shift of **1c** appears at higher field (δ = 31). Most likely this is caused by π-interaction between the p_z orbital of the boron atom and the π system of the heterocycle. In the ^{1}H NMR there is only one signal for the dimethylamino groups which indicates a free rotation around the B−N and the B−C bonds on the NMR time scale.

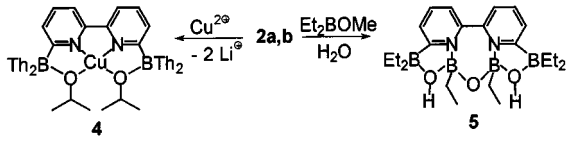
In general the reactivity of **2a−f** is high toward HCl/Et_2O and $ClSiMe_3$ (except **2b**), resulting in the cleavage of the boron−bipyridine bond. Because of their high sensitivity toward moisture, no satisfactory C,H,N analysis could be obtained.



Scheme 6

Complex Formation

In the borates **2** the bipyridine has an *anti* conformation and acts as a tetradentate ligand toward two lithium cations. Treatment of **2b** with one equivalent of $(Et_4N)_2CuCl_4$ results in the formation of the deep green-blue coordination compound **4**. The copper ion is coordinated by two nitrogen and two oxygen atoms of the alkoxy groups. Because of the paramagnetism of the d^9-Cu^{II} ion the NMR spectra of **4** could not be used for characterization. The cyclovoltammetry of **4** shows a reversible oxidation at $E_{1/2}$ = 0.65 V and an irreversible reduction at −1.1 V.



Scheme 7

An unprecedented coordination mode is observed in the adduct **5**. It is formed by the interaction of **1a** with 1,3-diethyl-1,3-dihydroxydiboroxane. The unknown dihydroxy-

diboroxane molecule is stabilized by the intermolecular aggregation. Treatment of 6,6′-dilithio-2,2′-bipyridine with an excess of diethyl(methoxy)borane and aqueous workup leads to **5** in 42% yield. The Lewis donor−acceptor pattern of **1a** induces the formation of the matching partner with the inverted Lewis functionality. Hydrolysis of the diethyl(methoxy)borane yields 1,3-diethyl-1,3-dihydroxydiboroxane coordinated to the diborylbipyridine **1a**. The free dihydroxydiboroxane is unstable and is expected to give give cyclic 1,3,5-boroxine. **5** is characterized by ^{1}H-, ^{13}C-, ^{11}B-NMR spectroscopy and an X-ray structure analysis (see below). In the ^{11}B-NMR spectrum appears only one broad signal at $\delta = 9$. Therefore all four boron atoms are quaternized. The Lewis acidic diethylboryl groups act as acceptor for the terminal oxygen atoms and the electron pair of the nitrogen atoms donate to the boron atoms of the dihydroxydiboroxane. The chemical shift of the methylene groups of the diethylboroxane at $\delta = -0.2$ corresponds with the high electron density at the boron atoms.

Crystal Structures

Single crystals of **2f** were grown from a tetrahydrofuran solution at room temperature. Figure 1 shows a molecule of **2f**, its lithium centers are tetracoordinated. Besides the bonding to the oxygen atom of the alkoxy group [Li−O: 1.87(1) Å] there is an interaction with the nitrogen atom [Li−N: 2.08(1) Å] of the bipyridine unit. The coordination sphere is completed by two thf molecules [Li−O: 1.97(1) Å]. The five-membered heterocycles are approximately planar with deviations from the best plane being less than 0.02 Å. The bond length B1−C1 is 1.64 Å. The two pyridine units are twisted by 149.6°.

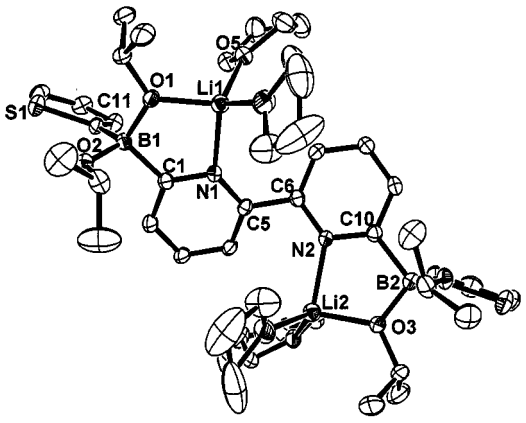


Figure 1. Structure of **2f** in the crystal; selected bond lengths [Å] and angles [°]: B1−C1 1.642(8), B1−O1 1.506(7), B1−O2 1.479(7), Li1−O1 1.87(1), Li1−N1 2.08(1), Li1−O5 1.97(1), C1−B1−O1 106.4(4), C1−B1−O2 112.5(5), C1−B1−C11 107.0(4), N1−C5−C6−N2 30.6

The large variety of possible coordination modes of Cu^{II}[17] are known. Therefore it is of interest to obtain structural information on the copper coordination in **4**. Single crystals suitable for an X-ray diffraction study were grown by slow diffusion of *n*-hexane into the solution of **4** in CH_2Cl_2. Figure 2 shows its structure in the crystal. The copper center has a distorted square-planar coordination by two nitrogen and two oxygen atoms. One of the oxygen atoms (O2) deviates strongly from the plane. The geometry around O2 differs much from that around O1. The distance Cu1−O2 [2.016(3) Å] is larger than Cu1−O1 [1.962(3) Å]. The oxygen atom O1 shows a planar coordination, while O2 is pyramidalized. The five-membered cycle of O1 is planar, that of O2 has an envelope form. The isopropyl group at O1 lies approximately symmetrical to the plane through the ring, while in the case of O2 it is strongly bent to one side, and one of the methyl groups reaches a position above the copper ion. A weak agostic interaction with one of its hydrogen atoms to the copper ion [Cu1−H 2.48(4) Å] is observed. The distances between the boron atoms and the bridging oxygen atoms [1.558(5), 1.575(5) Å] are about 0.1 Å longer than in regular B−O bonds of uncoordinated borates.

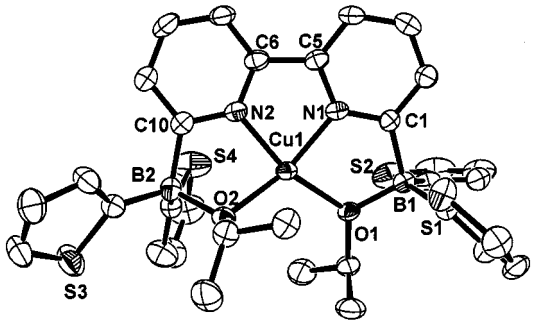


Figure 2. Structure of **4** in the crystal; selected bond lengths [Å] and angles [°]: B1−C1 1.630(6), B1−O1 1.558(5), B2−O2 1.575(5), Cu1−N1 1.938(3), Cu1−N2 1.938(3), Cu1−O1 1.962(3), Cu1−O2 2.016(3), C5−C6 1.483(6), C1−B1−O1 103.7(3), C10−B2−O2 104.8(3), N1−Cu1−N2 80.8(1), N1−Cu1−O1 83.1(1), O1−Cu1−O2 114.8(1), O2−Cu1−N2 83.4(1), B1−O1−C27 116.6(3), C27−O1−Cu1 126.5(3), Cu1−O1−B1 116.9(2), N1−C5−C6−N2 7.4, N1−C1−B1−O1 2.1, N2−C10−B2−O2 23.7

Figure 3 shows the molecule structure of **5** in the crystal. Crystals suitable for X-ray structure analysis were obtained by slow diffusion of *n*-hexane in a CH_2Cl_2 solution of **5**. The molecules of **5** form dimers in the solid state by hydrogen bonds. There are two independent dimers (four molecules) in the cell. They may be described as a donor−acceptor coordination product of **1a** with 1,3-diethyl-1,3-dihydroxydiboroxane, with the nitrogen atoms of the bipyridine and the hydroxy groups of the boroxane acting as donors to the boron atoms. All boron atoms are tetrahedrally coordinated. Three groups of B−O bonds are found, which are clearly distinguished in their distances: One type in the seven-membered ring with the two-coordinated oxygen atoms varying from 1.415−1.445 Å, two types in the five-membered rings with three-coordinated oxygen atoms, where they differ in the coordination of the boron atoms; 1.503−1.536 Å for the boron atoms connected to the nitrogen atoms, and 1.561−1.620 Å for the boron atoms connected to three carbon atoms.

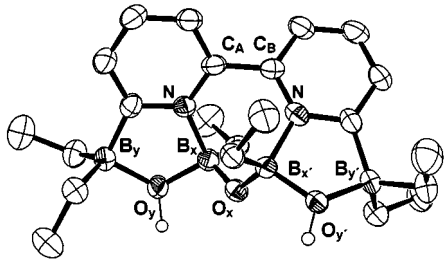


Figure 3. Structure of **5** in the crystal; selected bond lengths [Å] [mean values and range given (esd. 0.006−0.009 Å)]: B_X-O_X 1.440 (1.415−1.445), B_X-O_Y 1.525 (1.503−1.536), B_Y-O_Y 1.595 (1.561−1.620), B_X-N 1.626 (1.611−1.650), C_A-C_B 1.486 (1.479−1.494)

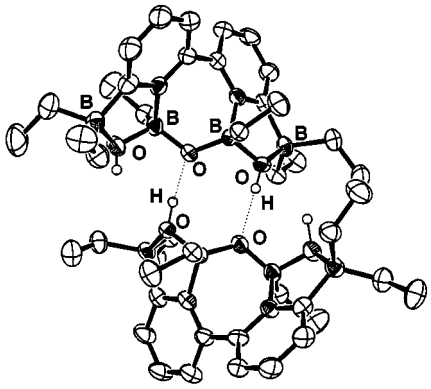


Figure 4. Hydrogen-bridged dimer of **5** in the crystal

Experimental Section

General: Reactions were carried out under dry argon, using standard Schlenk techniques. Solvents were dried, distilled, and saturated with nitrogen. Glassware was dried with a heat-gun in high vaccum. − ^{1}H, ^{13}C, ^{11}B NMR: Bruker AC 200 spectrometer, NMR references are $(CH_3)_4Si$ and $BF_3 \cdot Et_2O$. − Mass spectra were obtained with a Finnigan MAT 8200 plus spectrometer using EI technique. − Melting points (uncorrected) were obtained with a Büchi apparatus, using capillaries which were filled under argon and sealed.

Crystal-Structure Determination: Unique sets of intensity data were collected at −70°C with a four-circle diffractometer (Mo-K_α radiation λ = 0.71073 Å, graphite monochromator, ω-scan). Empirical absorption corrections (ψ-scans) for **2f** and **4** were applied. The structures were solved by direct methods [SHELXS86][18] and refined by least-squares methods based on F^2 with all measured reflections [SHELXL97].[19] All non-hydrogen atoms were refined anisotropically.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center: CCDC-102722 (**2f**), -102723 (**4**), and -102724 (**5**). Copies of the data can be obtained free of charge and by application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-001; E-mail: deposit@ccdc.cam.ac.uk].

6,6′-Bis(diethylboryl)-2,2′-bipyridine (1a) and 6-Diethylboryl-2,2′-bipyridine (3a): 3.00 g (30 mmol) of Et_2BOMe and 900 mg (7.5 mmol) of 2,2′-bipyridine were dissolved in 30 ml of Et_2O and cooled to −75°C. 15 mmol of $LiNiPr_2$ in 30 ml of Et_2O was added dropwise within 1 h. The resulting yellow solution was stirred for 6 h at −75°C and was allowed to warm up to room temp. overnight. The red solution was hydrolysed with 100 ml of brine (saturated NaCl solution) and the organic layer was extracted with ethyl acetate (3 × 100 ml). The combined extracts were dried with anhydrous sodium sulfate and the solvent was removed in high vacuo. The residue was column-chromatographed with silica gel (2 × 30 cm) with a mixture of *n*-hexane and ethyl acetate (4:1) to give 27 mg (0.09 mmol, 1%) **1a** and 97 mg (0.4 mmol, 6%) of **3a**. − **1a:** ^{1}H NMR (200.1 MHz, [D$_8$]thf): δ = 0.55 (t, 12 H, CH_2CH_3), 0.82 (q, 8 H, CH_2CH_3), 6.93 (m, 2 H, $C_{10}H_6N_2$), 7.63 (m, 2 H, $C_{10}H_6N_2$), 8.02 (m, 2 H, $C_{10}H_6N_2$). − ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 3.2. − ^{13}C NMR (50.3 MHz, [D$_8$]thf): δ = 8.7 (CH_2CH_3), 10.5 (CH_2CH_3), 16 (br., CH_2CH_3), 123.8, 127.7, 139.0, 147.4 ($C_{10}H_6N_2$). − MS (70 eV, EI); *m*/*z* (%): 263 (26) [M − Et]$^+$, 235 (8) [M − Et − C_2H_4]$^+$, 167 (100) [M − BEt_2 − HCN]$^+$, 78 (16) [C_5H_4N]$^+$. − M. p. > 250°C. − **3a:** ^{1}H NMR (200.1 MHz, [D$_8$]thf: δ = 0.50 (t, 6 H, CH_2CH_3), 0.78 (q, 4 H, CH_2CH_3), 7.24 (m, 1 H, $C_{10}H_7N_2$), 7.50 (m, 1 H, $C_{10}H_7N_2$), 7.96 (m, 1 H, $C_{10}H_7N_2$), 8.06 (m, 1 H, $C_{10}H_7N_2$), 8.40 (m, 2 H, $C_{10}H_7N_2$), 8.52 (m, 1 H, $C_{10}H_7N_2$). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 9.9 (CH_2CH_3), 13.4 (br., CH_2CH_3), 118.9, 123.1, 124.5, 136.9, 138.1, 139.8, 141.9, 146.9, 149.2 ($C_{10}H_7N_2$). − ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 3.4. − MS (70 eV, EI); *m*/*z* (%): 195 (40) [M − Et]$^+$, 180 (3) [M − Et − Me]$^+$, 167 (100) [M − HCN − C_2H_4]$^+$,78 (4) [$C_5H_4N^+$].

6,6′-Bis-di(2-thienyl)boryl]-2,2′-bipyridine (1b): 630 mg (0.68 mmol) of **2b** was dissolved in 5 ml of CH_2Cl_2. 147 mg (1.36 mmol) of $ClSiMe_3$ in 5 ml of CH_2Cl_2 was added dropwise at 0°C. The yellow solution was stirred at room temp. for 15 h. The mixture was filtered and 20 ml of thf was added to the precipitate. The mixture was again filtered from LiCl. After recrystallisation in thf, 124 mg (0.24 mmol, 36%) of **1b** was obtained as an amorphus solid. − ^{1}H NMR (200.1 MHz, [D$_8$]thf): δ = 7.39 (dd, 2 H, C_4H_3S), 7.65 (dd, 1 H, $C_{10}H_6N_2$), 7.82−7.89 (m, 3 H, $C_{10}H_6N_2/C_4H_3S$), 8.05 (dd, 2 H, C_4H_3S), 8.42 (dd, 1 H, $C_{10}H_6N_2$). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 120.4, 126.1, 131.0, 133.5, 138.5, 140.1, 141.6 ($C_{10}H_6N_2/C_4H_3S$). − ^{11}B NMR (64.2 MHz, [D$_8$]thf): δ = 1.0. − MS (70 eV, EI): *m*/*z* (%): 342 (28) [M − 2 (C_4H_3S)]$^+$, 259 (11) [M − 3 (C_4H_3S)]$^+$, 84 (100) [$C_4H_4S^+$]. − MS (FAB); *m*/*z* (%): 509 [M + 1$^+$]. − M.p. > 250°C.

6,6′-Bis[bis(dimethyamino)boryl]-2,2′-bipyridine (1c): To a solution of 500 mg (0.79 mmol) of **2c** in 5 ml of thf 211 mg (2 mmol) of $ClB(NMe_2)_2$ in 5 ml of Et_2O was added dropwise at room. temp. After some min, a red solid started to precipitate. After stirring at room temp. overnight, the mixture was filtered. The residue was destilled in high vacuo (10^{-2} mbar, 220°C) yielding 179 mg (0.51 mmol, 64%) of **1c** as a red oil. − ^{1}H NMR (200.1 MHz, [D$_8$]thf): δ = 2.52 (s, 12 H, NMe_2), 7.60 (d, 2 H, $C_{10}H_6N_2$), 7.76 (dd, 2 H, $C_{10}H_6N_2$), 8.38 (d, 2 H, $C_{10}H_6N_2$). − ^{13}C NMR (50.3 MHz, [D$_8$]thf): δ = 40.4, [$N(CH_3)_2$], 120.9, 129.8, 140.8, 142.6 ($C_{10}H_6N_2$). − ^{11}B NMR (64.2 MHz, [D$_8$]thf): δ = 31.0. − EI-MS; *m*/*z* (%): 253 (25) [M − $B(NMe_2)_2$]$^+$, 226 (46) [M − $B(NMe_2)_2$ − HCN]$^+$, 79 (100) [$C_5H_5N^+$].

2,2′-Bipyridine-6,6′-diborates 2: 1.57g (5 mmol) of 6,6′-dibromo-2,2′-bipyridine, dissolved in 75 ml of thf, was added dropwise within 20 min to a solution of 10 mmol *n*BuLi in 50 ml of thf at −80°C. After stirring for 45 min, the alkoxyborane, dissolved in 30 ml of Et_2O, was added dropwise within 30 min to the red solution The mixture was allowed to warm up to room temp. overnight. Half of the solvent was removed in vacuo and 30 ml of *n*-hexane was added. After 36 h at 0°C, the mixture was filtered. The borates were obtained as colorless solids.

2a: (2.10 g, 3.2 mmol, 64%). − ^{1}H NMR (200.1 MHz, [D$_8$]thf): δ = 0.19 (q, 4 H, CH_2CH_3), 0.71 (t, 6 H, CH_2CH_3), 3.14 (s, 3 H,

Table 1. Crystal data and structure refinement for **2f**, **4**, and **5**

	2f	**4**	**5**
Empirical formula	$C_{46}H_{72}B_2Li_2N_2O_8S_2$	$C_{32}H_{32}B_2Cu_1N_2O_2S_4$	$C_{22}H_{38}B_4N_2O_3$
Formula weight	880.7	690.0	421.8
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1$	$P\bar{1}$	$P\bar{1}$
Unit cell			
a [Å]	10.418(6)	9.950(5)	13.051(7)
b [Å]	14.443(7)	13.434(7)	17.295(9)
c [Å]	17.001(8)	13.389(7)	22.120(11)
α [°]	90	82.29(4)	89.28(3)
β [°]	90.66(4)	68.38(3)	79.56(3)
γ [°]	90	76.47(4)	88.84(3)
V [Å^3]	2558(2)	1615(1)	4909(4)
Z	2	2	8
Calcd. density [g/cm^3]	1.14	1.42	1.14
Absorp.coeff. [mm^{-1}]	0.15	0.97	0.07
F(000)	948	714	1824
Crystal size [mm]	0.2 × 0.9 × 1.0	0.1 × 0.3 × 0.7	0.4 × 0.4 × 0.7
Θ_{max} [°]	25	25	24
Index ranges	−12/+12, 0/+17, 0/+20	−10/+11, −15/+15, 0/+15	−14/+14, −19/+19, 0/+25
No. of reflections			
Unique	4711	5660	15383
Observed [$I > 2\sigma(I)$]	3129	4285	8919
Transmission	0.91−1.00	0.82−1.00	−
Parameters	562	469	1188
Final R indices			
$R1$ [$I > 2\sigma(I)$]	0.052	0.047	0.086
$wR2$	0.140	0.123	0.274
Largest diff.peak/hole [e/Å^3]	0.27/−0.25	0.56/−0.42	0.39/−0.40

OCH_3), 7.26−7.41 (m, 1 H, $C_{10}H_6N_2$), 7.80−7.89 (m, 1 H, $C_{10}H_6N_2$), 8.42−8.46 (m, 1 H, $C_{10}H_6N_2$). − ^{13}C NMR (50.3 MHz, [D$_8$]thf): δ = 9.6 (br., *C*H$_2$CH$_3$), 11.1(CH$_2$*C*H$_3$), 49.5 (OCH_3), 121.0, 124.5, 137.4, 149.9 ($C_{10}H_6N_2$). − ^{11}B NMR (64.2 MHz, [D$_8$]thf): δ = 8.1. − M. p. 212−215°C.

2b: (4.08 g, 4.4 mmol, 87%). − ^{1}H NMR (200.1 MHz, [D$_8$]thf): δ = 0.91 (d, 6 H, CH_3), 3.93 [sept, 1 H, C*H*(CH$_3$)$_2$], 7.04−7.56 (m, 10 H, CH). − ^{13}C NMR (50.3 MHz, [D$_8$]thf): δ = 18.9 (CH_3), 61.3 [*C*H(CH$_3$)$_2$], 111.3 ($C_{10}H_6N_2$), 118.3 (C_4H_3S), 120.6 (C_4H_3S), 122.1 ($C_{10}H_6N_2$), 123.4 (C_4H_3S), 128.0 ($C_{10}H_6N_2$), 148.9 ($C_{10}H_6N_2$). − ^{11}B NMR (64.2 MHz, [D$_8$]thf): δ = 0.7. − M. p. 189−191°C.

2c: (3.49 g, 3.9 mmol, 78%). − ^{1}H NMR (200.1 MHz, [D$_8$]thf): δ = 0.83 (d, 6 H, CH_3), 0.90 [d, 6 H, CH$_2$CH(C*H*$_3$)$_2$], 1.70 [m, 2 H, CH$_2$C*H*(CH$_3$)$_2$], 3.00−3.19 [m, 4 H, C*H*$_2$CH(CH$_3$)$_2$], 6.81−7.02 (m, 3 H, CH), 7.37−7.61 (m, 5 H, CH). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.6 (CH_3), 32.2 [OCH$_2$*C*H(CH$_3$)$_2$], 69.8 [O*C*H$_2$CH(CH$_3$)$_2$], 124.6, 126.7, 133.9, 157.8 ($C_{10}H_6N_2$). − ^{11}B NMR (64.2 MHz, [D$_8$]thf): δ = 6.6. − M. p. 242−244°C.

2d: (2.95 g, 4.1 mmol, 82%). − ^{1}H NMR (200.1 MHz, [D$_8$]thf): δ = 3.06 (s, 6 H, CH_3), 6.79−7.00 (m, 3 H, ar), 7.34−7.52 (m, 5 H, ar). − ^{13}C NMR (50.3 MHz, [D$_8$]thf): δ = 49.7 (OCH_3), 118.8, 124.8, 126.9, 129.3, 133.6, 135.1, 158.3 (ar). − ^{11}B NMR (64.2 MHz, [D$_8$]thf]): δ = 6.7. − M. p. > 250°C (dec.).

2e: (3.49 g, 4.5 mmol, 89%). − ^{1}H NMR (200.1 MHz, [D$_8$]thf): δ = 0.84 (s, 18 H, CH_3), 3.61 (s, 3 H, OCH_3), 7.29−7.45 (m, 2 H, $C_{10}H_6N_2$), 7.65−7.70 (m, 1 H, $C_{10}H_6N_2$). − ^{13}C NMR (50.3 MHz, [D$_8$]thf): δ = 34.2 (CH_3), 32.8 (CH_3), 53.8 [br., B*C*(CH$_3$)$_3$], 53.9 (OCH_3), 117.7 [br., BC($C_{10}H_6N_2$)], 129.2, 130.6, 132.2, 132.7 ($C_{10}H_6N_2$). − ^{11}B NMR (64.2 MHz, [D$_8$]thf): δ = 5.1. − M. p. 212−214°C.

2f: (2.91g, 3.3 mmol, 65%). − ^{1}H NMR (200.1 MHz, [D$_8$]thf): δ = 0.86 (d, 6 H, CH_3), 1.07 (d, 6 H, CH_3), 3.91 [sept, 2 H, C*H*(CH$_3$)$_2$], 6.80 (m, 2 H, ar), 7.09 (d, 1 H, ar), 7.50 (m, 2 H, ar), 7.76 (dd, 1 H, ar). − ^{13}C NMR (50.3 MHz, [D$_8$]thf): δ = 26.3 (CH_3), 26.5 (CH_3), 62.8 [*C*H(CH$_3$)$_2$], 118.9, 124.3, 126.4, 128.6, 130.9, 133.8, 156.9 (ar). − ^{11}B NMR (64.2 MHz, [D$_8$]thf): δ = 5.1. − M. p. 199−201°C.

{2,2′-Bipyridine-6,6′-bisdiisopropoxydi(2-thienyl)borato]}-copper(II) (4): 928 mg (1 mmol) of **2b** and 456 mg (1 mmol) of $(Et_4N)_2CuCl_4$ were dissolved in 10 ml of CH_2Cl_2 at room temp. After stirring for 12 h, the green-blue solution was filtered from Et_4NCl. The solvent was removed in vacuo yielding 650 mg (0.95 mmol, 95%) of **4** as a deep green-blue air-sensitive solid. m. p. > 250°C. Cyclic voltammetry data (EG&G PARC 175 potentiostat): Pt disc (1 mm) working electrode, CH_2Cl_2 solution, 0.1 M Bu_4NPF_6 as supporting electrolyte, Pt wire as auxiliar electrode, SCE as reference electrode. Reversible oxidation at $E_{1/2}$ = 0.65 V, irreversible reduction at −1.1 V.

1,3-Diethyl-1,3-dihydroxydiboroxane Adduct 5 of 1a: 1.57g (5 mmol) of 6,6′-dibromo-2,2′-bipyridine, dissolved in 75 ml of thf, was added dropwise within 20 min to a solution of 10 mmol of *n*BuLi in 50 ml of thf at −80°C. After stirring for 45 min, 2.50 g (25 mmol) of diethyl(methoxy)borane, dissolved in 30 ml of Et_2O, was added dropwise within 30 min to the red solution. The mixture was allowed to warm up to room temp. overnight. The red solution was hydrolysed with 100 ml of brine and the organic layer was extracted with ethyl acetate (3 × 100 ml). The combined extracts were dried with anhydrous sodium sulfate and the solvent was removed in vacuo. The residue was dissolved in 20 ml of thf and 10 ml of *n*-hexane was added. After 40 h at 0°C, the mixture was filtered yielding 884 mg (2.1 mmol, 42%) of **5**. − ^{1}H NMR (200.1 MHz, CD_2Cl_2): δ = −0.21 [q, 2 H, OB(OH)C*H*$_2$CH$_3$], 0.52 [q, 4 H, OB(C*H*$_2$CH$_3$)$_2$], 0.64 [t, 3 H, OB(OH)CH$_2$C*H*$_3$], 0.79 [t, 6 H, OB(CH$_2$C*H*$_3$)$_2$], 3.93 (br., 0.8 H, OH), 7.45−7.67 (m, 2 H, $C_{10}H_6N_2$), 7.93 (t, 1 H, $C_{10}H_6N_2$). − ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 7.8 (CH$_2$*C*H$_3$), 9.6 (CH$_2$*C*H$_3$), 9.8 (CH$_2$*C*H$_3$), 15 (br.,

CH_2CH_3), 123.4, 127.9, 139.6, 146.1 ($C_{10}H_6N_2$). – ^{11}B NMR (64.2 MHz, CD_2Cl_2): δ = 9.2 (br.). – M. p. 156–160°C (dec.).

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