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Synthesis and characterization of di-, tri- and tetraboronic acids based on phenyl- and thienylsilane cores

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ABSTRACT

The synthesis of a series of di- tri- and tetraboronic acids based on respective phenyl- and thienylsilane cores is described. The optimal protocols involved lithiation of respective arylsilane precursors using either deprotonative lithiation or halogen/lithium exchange with *n*-BuLi followed by treatment of resultant intermediates with $B(Oi\text{-}Pr)_3$ and subsequent hydrolysis, which afforded final products in good yields. X-ray crystal structures of selected diboronic derivatives were determined showing that hydrogen-bonding interactions of $B(OH)_2$ groups are the main factor governing the supramolecular assembly.

Introduction

Boronic acids are extensively used in current synthetic organic chemistry and a range of other fields. Apart from the use as reagents, compounds possessing more than one boronic acid group were recognized as perspective starting materials for diverse applications, specifically related to molecular recognition and supramolecular chemistry. For example, the presence of two or more boronic groups enables the formation of extended H-bonded assemblies in the solid crystalline state [1,2]. In some cases they may further incorporate additional guest molecules. This was amply demonstrated by Wuest et al. through the synthesis and structural characterization of tetraboronic acids based on tetraphenylmethane and tetraphenylsilane cores [2]. More recently, various oligoboronic acids were employed for the construction of polymeric systems possessing microporous structure and hence classified as Covalent Organic Frameworks (COFs). Their formation is based on the ability of boronic acids to form trimeric anhydrides (boroxines) or cyclic esters with cis-1,2-diols [3]. Due to presence of large voids in their structures they exhibit significant adsorption of gases such as N_2, H_2, CO_2 and CH_4. The density of these materials is very low in some cases which is highly advantageous in view of their potential use as gas nanocontainers.

Oligoboronic acids based on thiophene cores are relatively rare [4]. An exception is commercially available 2,5-thiophenediboronic acid, which was used recently for the synthesis of COF material by the polycondensation with 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) [5]. Some diboronic acids derived from fused thiophene-ring systems were also obtained and employed for the construction of respective COFs [5]. In this paper, we report on the synthesis of a series of novel boronic acids based on various oligophenyl- and oligothienylsilane cores (Chart 1). We believe that compounds described here could be useful alternative for those reported previously. Other applications, for instance, as starting materials in Suzuki-Miyaura coupling reactions leading to various systems bearing silicon atom(s) with attached phenyl or thienyl rings can also be envisioned. This is due to strong interest in such compounds, which is related to their diverse applications in optoelectronics [6].

Results and discussion

Synthesis of arylsilanes

Phenylsilanes **1a**-**1i** were prepared by a standard route involving Br/Li reactions of starting aryl bromides (1,3-$Br_2C_6H_4$, 1,4-$Br_2C_6H_4$

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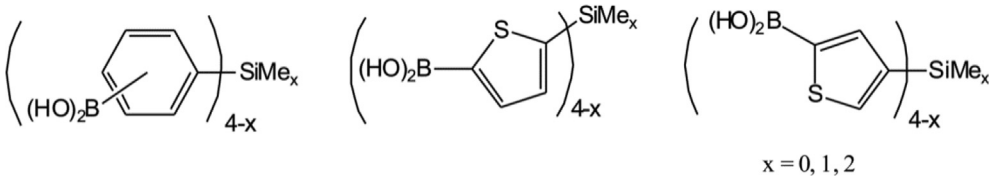


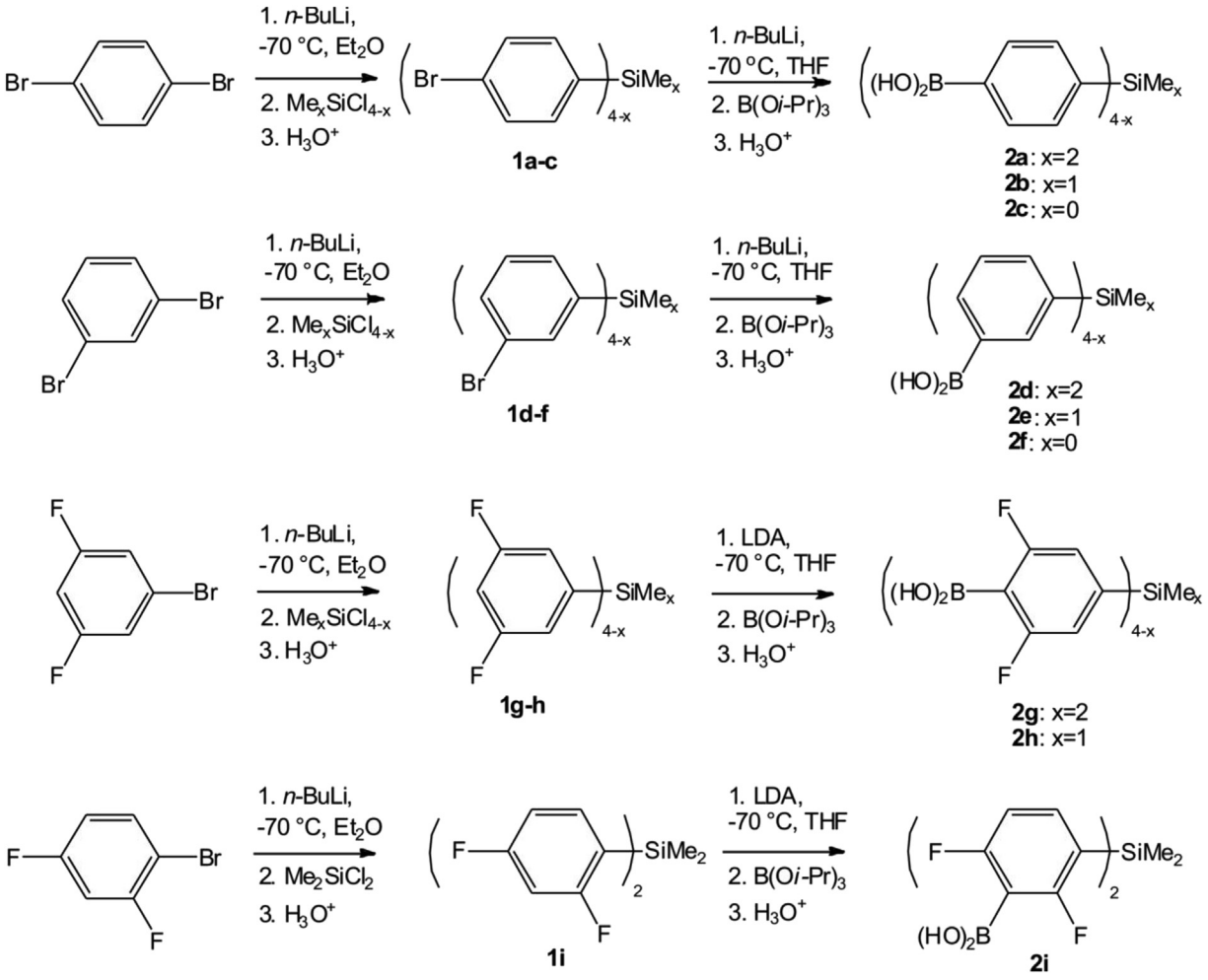
Chart 1. General structures of obtained oligoboronic acids.

or difluoro derivatives 3,5-$F_2C_6H_3Br$ or 2,4-$F_2C_6H_3Br$) followed by the treatment with the appropriate chloromethylsilane Me_xSiCl_{4-x}, x = 0–2 (Scheme 1) [7]. All products were obtained in good yields.

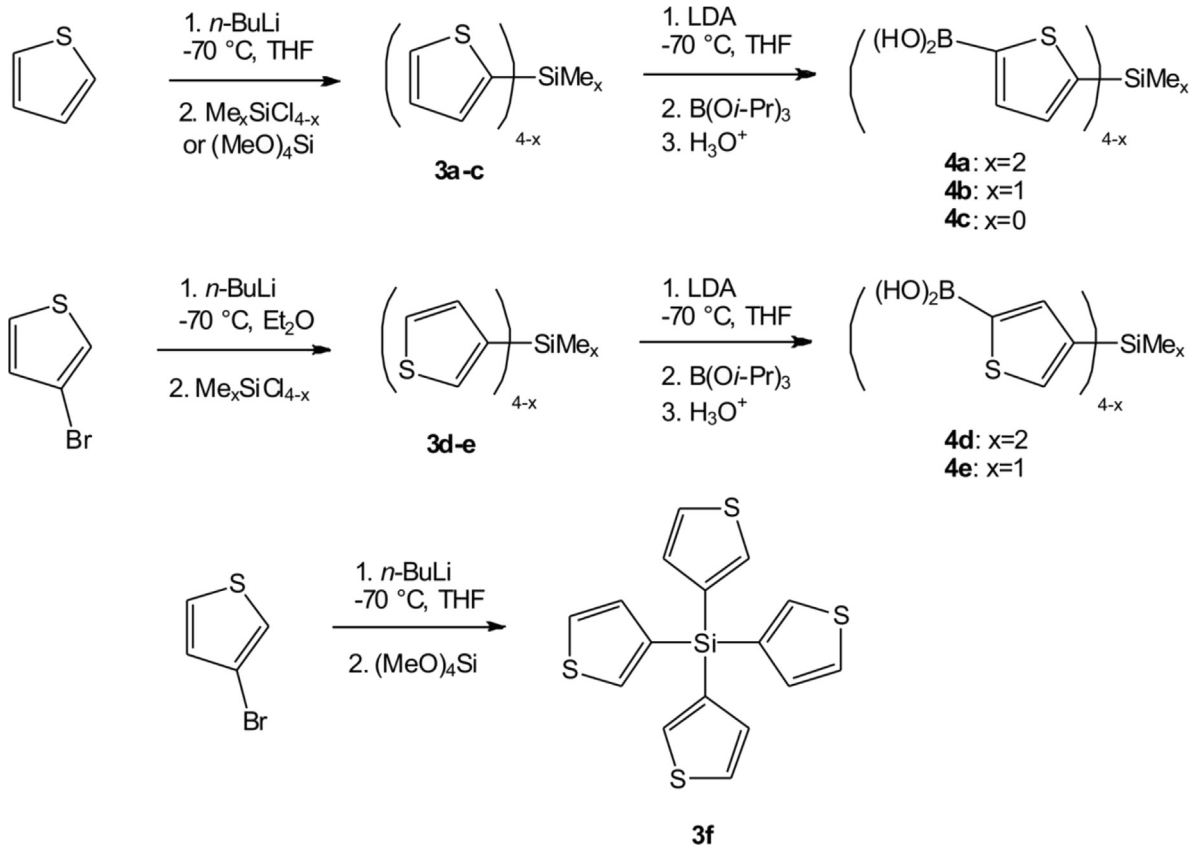
The synthesis of $Me_2Si(2\text{-Th})_2$ (**3a**) and $MeSi(2\text{-Th})_3$ (**3b**) [8] involved deprotonative lithiation of thiophene with *n*-BuLi in THF followed by the metathesis of resultant 2-thienyllithium 2-ThLi with Me_2SiCl_2 and $MeSiCl_3$, respectively (Scheme 2). A slight (ca. 10%) excess of 2-ThLi was used to ensure that all Si–Cl bonds will be substituted with 2-thienyl nucleophiles. Tetrakis(2-thienyl)silane (**3c**) was obtained according to literature method involving tetramethyl orthosilicate $Si(OMe)_4$ as the silicon source [9]. Isomeric (3-thienyl)silanes $Me_2Si(3\text{-Th})_2$ (**3d**) [10], $MeSi(3\text{-Th})_3$ (**3e**), and $Si(3\text{-Th})_4$ (**3f**) were prepared using methods, which were analogous to those used for their respective 2-thienyl counterparts. Since 3-thienyllithium (prepared by bromine–lithium exchange from 3-bromothiophene) is prone to rapid isomerisation in THF to give thermodynamically more stable 2-thienyllithium, the use of Et_2O as the solvent for the preparation of **3d-f** is mandatory [11]. It should be noted that all arylsilanes were obtained on a multigram scale.

Synthesis of oligoboronic acids

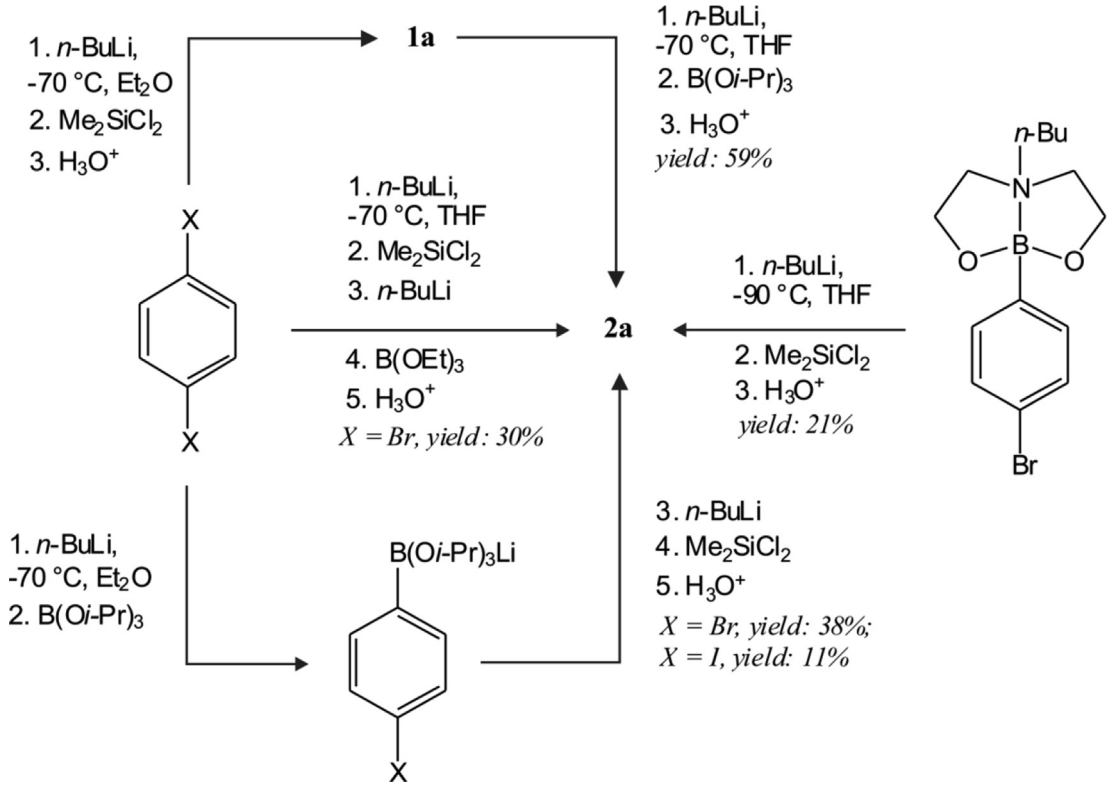
Various synthetic approaches were tested for bis(4-dihydroxyborylphenyl)dimethylsilane (**2a**) as the model target compound (Scheme 3). The first method involved the classical double Br/Li exchange in bis(4-bromophenyl)dimethylsilane (**1a**) and subsequent reaction with $B(Oi\text{-Pr})_3$ followed by hydrolysis. In a simplified version of this protocol, the silane **1a** was not taken as an isolated pure compound but it was generated *in situ* as described above and converted directly into the desired diboronic acid. In this case, however, the purity of the



Scheme 1. The synthesis of arylsilanes and respective oligoboronic acids.



Scheme 2. The synthesis of thienylsilanes and respective oligoboronic acids.



Scheme 3. Testing different approaches for the synthesis of **2a**.

product and the reaction yield was lower. Alternatively, we have checked lithiated aryl boronates [12] in combination with Me_2SiCl_2 as we previously found that these reagents are compatible with the related silicon-based electrophile Me_3SiCl giving rise to a number of silylated arylboronic acids. The anionic lithium 4-lithiophenyl(trialkoxy)borate was generated *in situ* from 1,4-dihalobenzene (Hal = Br, I) using Hal/Li exchange followed by boronation with B(O*i*-Pr)$_3$ and the second Hal/Li exchange with the next equivalent of alkyllithium [13]. The neutral 2-(4'-lithiophenyl)-6-butyl[1,3,6,2]dioxazaborocane was obtained by the Br/Li exchange in its 4-bromophenyl precursor [14]. The quench of obtained lithium–boron intermediates with Me_2SiCl_2 gave **2a** after hydrolysis but again the product was less pure than that obtained from **1a** and the reaction yield was unsatisfactory. Thus, we have decided to prepare other boronic acids using a procedure involving the formation and isolation of appropriate arylsilanes in the first step (Scheme 1). Then, an efficient and selective lithiation/boronation could be performed resulting in the selective high-yield formation of pure oligoboronic acids **2a**-**2i**.

The classical lithiation/boronation approach was also used for the conversion of thienylsilanes into their corresponding boronated derivatives **4a**-**4e** (Scheme 2). Initially, *n*-BuLi was used as the lithiating agent. However, we have found that it is not optimal. In general, it is advisable to use it in excess to ensure the complete deprotonation of all active, *i.e*. sufficiently acidic, positions. Unfortunately, trapping of unreacted *n*-BuLi results in the formation of butylboronic acid byproduct after hydrolysis. This implies that the final product should be purified to remove *n*-BuB(OH)$_2$ impurity. These problems were overcome when a combination of LDA-mediated lithiation/B(O*i*Pr)$_3$ boronation was used. The complete conversion to desired products was achieved. It is known that LDA effectively co-exists with B(O*i*-Pr)$_3$ in solution [15]. Hence, it is plausible that the reaction occurs in a stepwise manner: the initially formed lithiated intermediate is trapped with the added boron reagent. The resultant boronated species is then lithiated with unreacted LDA still remaining in the reaction mixture followed by trapping with the next equivalent of electrophile. The reactions stops when all active positions (α to sulphur atom in thiophene ring) are boronated. The additional advantage of the use of LDA is the fact that its excess can be readily removed during aqueous acidic workup of a reaction mixture. Unfortunately, attempts to a conversion of **3f** into a respective tetraboronic acid eventually proved unsuccessful. Presumably, this is due to the weak solubility of **3f**, which hampers its effective deprotonation. Even the attempted boronation of **3f** with B_2Pin_2 in refluxing THF in the presence of [Ir(cod)(μ-OMe)]$_2$ catalyst [16] did not give the targeted tetraboronated product.

Crystal structures of 2g and 2i

The monocrystals suitable for X-ray diffraction analysis were grown for fluorinated boronic acids **2g** and **2i**. The studied compounds crystallize in triclinic *P*-1 and orthorhombic *Pnna* space groups of symmetry, respectively. The molecular structures are shown in Fig. 1. Central silicon atoms in both compounds exhibit slightly distorted tetrahedral geometry. In the case of **2g** the asymmetric part of the unit cell contains two molecules of diboronic acid (**2g_A** and **2g_B**) accompanied by one molecule of THF, which seems to be disordered. The two aromatic ring planes in **2g_B** creates V-shaped molecule with approximate C_2-symmetry. In turn, in **2g_A** one of the aromatic ring is significantly twisted around Si–C bond (the interplanar angle between mean-squared aromatic ring planes equals to 63.8(1)°). For compound **2i**, the aromatic moieties are related by the C_2 rotation axis passing through the silicon atom and the midpoint between two aromatic ring centroids. The boronic groups in both compounds are rotated around the B–C bonds by torsion angles ranging from 14.0(1)° to 86.6(1)° (Fig. 1). Conformational flexibility of boronic group depends on intramolecular contacts with atoms located at the *ortho*-positions to a boronic group as well as it is influenced by intermolecular interactions with adjacent molecules [1e,17]. According to our latest results, the rotation barrier for a boronic group in 2,6-difluoro-substituted phenylboronic acids is low (*ca.* 5 kJ mol^{-1}) [1e], which allows the occurrence of different conformers in the structure.

Despite the fact, that B2 boronic group in molecule **2g_A** is almost perpendicular to the aromatic ring plane, both boronic groups in this molecule have the same relative orientation as that observed in **2g_B**. Thus, regular hydrogen-bonded chains with alternating sequence of molecules **2g_A** and **2g_B** are formed (Fig. 2a). Such a scheme of hydrogen interactions is commonly observed for crystal structures of diboronic acids [1]. The geometrical parameters of hydrogen bonds are given in Table S1 in the Supporting Information. The adjacent chains associate further by lateral hydrogen bonds formed between two neighboured molecules **2g_A** and between molecules **2g_A** and **2g_B**, which leads to the formation of a molecular layer parallel to (001) crystal plane. In addition, the molecule **2g_B** participates in a lateral H-bond interaction formed between an *anti*-oriented O(5)–H group and THF molecule. It is noticeable that O(8)–H group is only involved in one H-bond within a molecular chain, and does not participate in lateral hydrogen interactions. As a result, the structure **2g** possesses voids (see Fig. 2b) available for guest inclusions. Calculations of the void surface with the Spackman approach [18] show that the pore volume is equal to 403 Å^3 (per unit cell), which constitutes 20% of the total unit-cell volume.

The crystal structure of isomeric **2i** presents quite similar picture of supramolecular assembly. Molecules form hydrogen-bonded chains, which propagate further *via* lateral hydrogen bonds to produce a 2-dimensional sheet (Fig. 3). However, in this case, all boronic groups are involved in lateral hydrogen bonds and hence the structure is closely packed. An interesting feature of this structure is the occurrence of auxiliary O–H…F and C–H…F interactions.

Conclusions

In conclusion, a simple and general protocol for the multigram-scale synthesis of a series of oligoboronic acids based on phenyl and thienylsilane cores was developed. Selected products were obtained as crystalline solids which may incorporate solvent molecules in their structure. This is apparently due to the domination of H-bonding interactions which are strongly directional and thus, the possibility for the existence of voids available for guest molecules is opened. This is in line with previous studies on related tetraboronic acids derived from tetraphenylmethane and tetraphenylsilane [2]. Further studies on the application of obtained boronic acids and their derivatives for the preparation of porous materials are currently in progress and the results will be given in due course.

Experimental section

General comments

All reactions involving air- and moisture-sensitive reagents were carried out under an argon atmosphere. Key reagents including *n*-BuLi (10 M solution in hexanes), trialkyl borate, *N*-butyldiethanolamine, diisopropylamine, chloromethylsilanes,

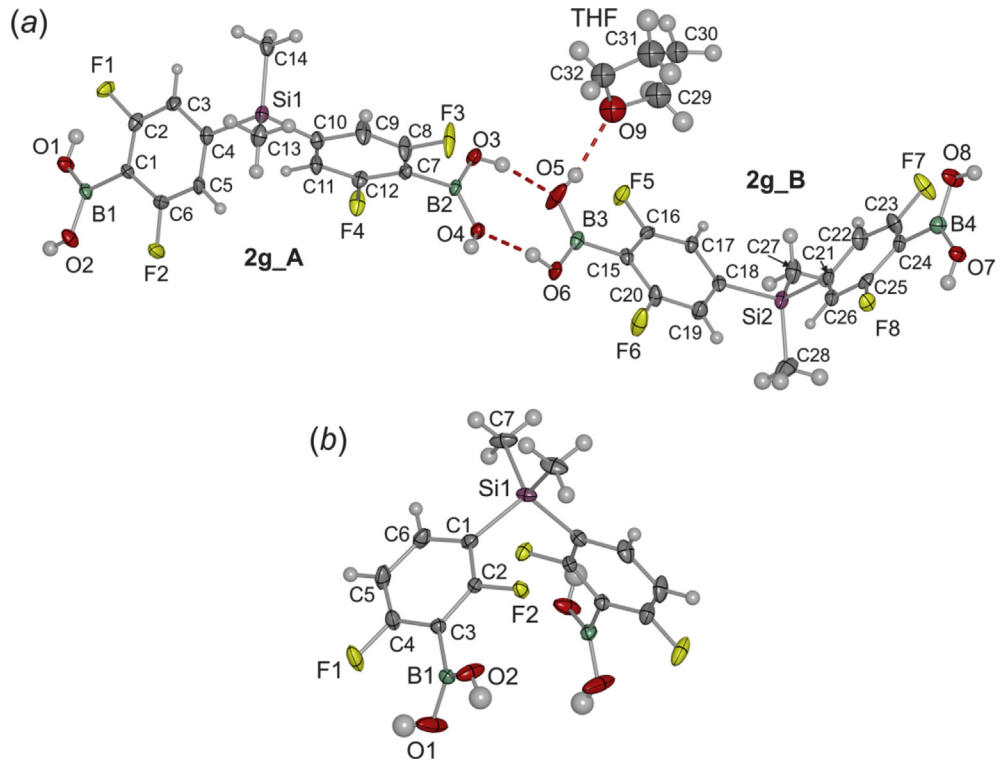


Fig. 1. Labelling of atoms and the atomic thermal motion estimation as ADPs for (*a*) **2g** and (*b*) **2i** (only symmetrically unequivalent atoms). H-bonding interactions are shown as red dashed lines (**2g**). Selected bond lengths (Å) and angles (°) for **2g**: B1–C1 1.587(8), B1–O1 1.349(7), B1–O2 1.36(1), B2–C7 1.600(8), B2–O3 1.356(9), B2–O4 1.352(8), B3–C15 1.586(8), B3–O5 1.367(8), B3–O6 1.35(1), B4–C21 1.578(8), B4–O7 1.35(1), B4–O8 1.354(8), C4–Si1–C10 107.4(3), C18–Si2–C24 107.3(3), C2–C1–B1–O1 22.4(1), C8–C7–B2–O3 86.6(1), C16–C15–B3–O5 28.8(1), C22–C21–B4–O7 14.0(1). Selected bond lengths (Å) and angles (°) for **2i**: B1–C3 1.578(2), B1–O1 1.341(2), B1–O2 1.351(2), C1–Si1–$C1^{(x,1/2-y,1/2-z)}$ 104.0 (1), C2–C3–B1–O2 40.1 (1), C2–C1–$C1^{(x,1/2-y,1/2-z)}$–$C6^{(x,1/2-y,1/2-z)}$ 34.1(1).

$Si(OMe)_4$ were received from Aldrich and used without additional purification. Bis(bromophenyl)dimethyl- (**1a**, **1d**), tris(-bromophenyl)methyl- (**1b**, **1e**) and tetrakis(bromophenyl)lsilanes (**1e**, **1f**), and (2-thienyl)silanes (**3a-c**) were obtained according to the literature procedures [7–10]. Solvents used for reactions were dried by refluxing with sodium/benzophenone and distilled under argon atmosphere. The NMR chemical shifts are given relative to TMS using known chemical shifts of residual proton (^{1}H) or carbon (^{13}C) solvent resonances. For some compounds the ^{1}H NMR resonances of $B(OH)_2$ groups were not observed, presumably due to rapid proton exchange processes involving water molecules introduced with a sample or formed upon a partial dehydration of boronic acids in solution. In the ^{13}C NMR spectra the resonances of boron-bound carbon atoms were not observed in most cases due to their broadening caused by partially relaxed B–C couplings. ^{11}B and ^{19}F NMR chemical shifts are given relative to $Et_2O{\cdot}BF_3$ and $CFCl_3$, respectively.

Description of syntheses and compound characterization

Bis(4-bromophenyl)dimethylsilane (**1a**) [7a]: Yield: 86%, m.p. 74–75 °C (lit. 78 °C).

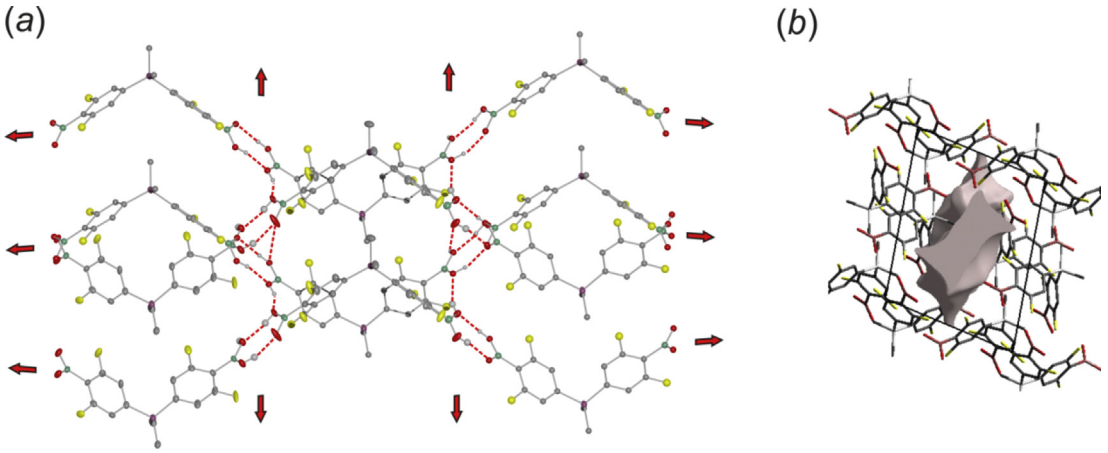


Fig. 2. (a) H-bonded chains and their arrangement into 2D layers in **2g**. (b) Unit cell packing diagram with void surface generated in CrystalExplorer (ρ = 0.0003 au) [18]. Aromatic and aliphatic hydrogen atoms are omitted for clarity.

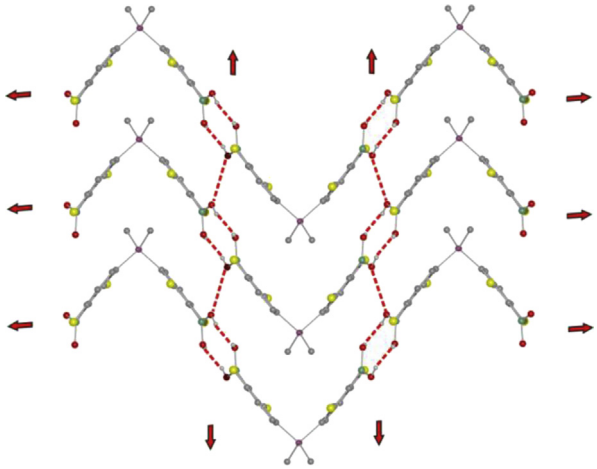


Fig. 3. Molecular layer formed *via* O–H…O bonds (red dashed lines) in **2i**. Aromatic and aliphatic H atoms are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Tris(4-bromophenyl)methylsilane (**1b**) [7a]: Yield: 82%, m.p. 110–112 °C (lit. 106–112 °C).

Tetrakis(4-bromophenyl)silane (**1c**) [7a]: Yield: 69%, m.p. 239–241 °C (lit. 235 °C).

Bis(3-bromophenyl)dimethylsilane (**1d**) [7b]: Yield: 75%, B.p. 90–95 °C (1 Tr).

Tris(3-bromophenyl)methylsilane (**1e**) [7b]: Yield: 60% (oil).

Tetrakis(3-bromophenyl)silane (**1f**) [7e]: Yield: 90%, m.p. 174–175 °C.

Bis(3,5-difluorophenyl)dimethylsilane (**1g**): 1-bromo-3,5-difluorobenzene (11.5 mL, 0.10 mol) was added to a stirred solution of *n*-BuLi (10 M, 10.1 mL, 0.101 mol) in Et_2O (100 mL) at −78 °C. It was stirred for 1 h followed by the addition of Me_2SiCl_2 (5.9 mL, 0.05 mol). The mixture was allowed to warm to −10 °C, then hydrolyzed with aqueous H_2SO_4 (1.5 M) and warmed to the room temperature. The water phase was separated followed by the extraction with Et_2O (2 × 10 mL). The extracts were added to the organic phase, which was concentrated under reduced pressure. Distillation under reduced pressure (b.p. 65–66 °C, 1 Tr) afforded **1g** as a colourless oil. Yield: 60% (8.52 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.98 (m, 4H, Ph), 6.82 (tt, J = 9.0, 2.5 Hz, 2H, Ph), 0.58 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 162.9 (dd, J = 252.0, 10.5 Hz), 141.6 (t, J = 5.0 Hz), 116.1 (dd, J = 16.5, 5.5 Hz), 105.0 (t, J = 25.0 Hz), −3.0 ppm. ^{19}F NMR ($CDCl_3$, 360.6 MHz) δ = −109.7 (ddd, J = 8.5, 6.0, 1.5 Hz) ppm. $C_{14}H_{12}F_4Si$ (284.32) calcd. C 59.14, H 4.25; found C 58.77, H 3.98.

Tri(3,5-difluorophenyl)methylsilane (**1h**): This compound was prepared as described for **1g** using $MeSiCl_3$ (5.9 mL, 0.05 mol), 1-bromo-3,5-difluorobenzene (38.7 g, 0.20 mol) and *n*-BuLi (10 M, 21 mL, 0.21 mol). Yield: 60%, m.p. 127–131 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.00 (m, 9H, Ph), 0.95 (s, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ = 160.3 (dd, J = 245.0, 11 Hz), 140.0 (t, J = 4.5 Hz), 118.9 (dd, J = 17.0, 4.5 Hz), 104.0 (t, J = 24.0 Hz), −2.7 ppm. $C_{19}H_{12}F_6Si$ (382.37) calcd. C 59.68, H 3.16; found C 59.24, H 2.89.

Bis(2,4-difluorophenyl)dimethylsilane (**1i**): This compound was prepared as described for **1g** using Me_2SiCl_2 (5.9 mL, 0.05 mol), 1-bromo-2,4-difluorobenzene (11.3 mL, 0.10 mol) and *n*-BuLi (10 M, 10.5 mL, 0.105 mol). Yield: 81%, b.p. 81–83 °C (1 Tr). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.33 (dd, J = 15.5, 7.0 Hz, 2H, Ph), 6.89 (td, J = 8.5, 2.5 Hz, 2H, Ph), 6.77 (td, J = 9.0, 2.5 Hz, 2H, Ph), 0.64 (s, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ = 167.5 (dd, J = 280.0, 12.0 Hz), 165.0 (dd, J = 287.0, 12.0 Hz), 136.8 (dd, J = 13.0, 9.5 Hz), 118.9 (dd, J = 30.0, 4.0 Hz), 111.4 (dd, J = 20.0, 3.5 Hz), 103.5 (dd, J = 30.0, 24.0 Hz), −2.2 ppm. ^{19}F NMR ($CDCl_3$, 360.6 MHz): δ = −96.06 (dd, J = 16.5, 8.5 Hz), −107.7 (m) ppm. $C_{14}H_{12}F_4Si$ (284.32) calcd. C 59.14, H 4.25; found C 58.98, H 3.86.

Bis(4-dihydroxyborylphenyl)dimethylsilane (**2a**): *n*-BuLi (10 M in hexane; 1.45 mL, 0.0145 mmol) was added to THF (20 mL) at −78 °C. Then a solution of **1a** (11.5 mL, 0.073 mol) in THF (5 mL) was added while the temperature was kept below −75 °C. The resulting mixture was stirred for 1 h, then B(O*i*-Pr)$_3$ (3.4 mL, 0.0145 mol) was added. The resulting mixture was stirred for 30 min and hydrolyzed with H_2SO_4 (1.5 m aq.; 20 mL) at −15 °C. The organic phase was separated, and the solvents were evaporated under reduced pressure to give the title compound (1.28 g, 59%) as white crystals, m.p. > 300 °C. ^{1}H NMR (acetone-d_6, 400 MHz): δ = 7.88 (d, J = 8.0 Hz, 4H, Ph), 7.88 (d, J = 8.0 Hz, 4H, Ph), 7.21 (broad, 4H, $B(OH)_2$), 0.56 (s, 6H, CH_3) ppm. ^{11}B NMR (acetone-d_6, 64.2 MHz): δ = 31 ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ = 140.4, 133.3, 133.2, −3.3 ppm. $C_{14}H_{18}B_2O_4Si$ (300.12) calcd. C 56.05, H 6.05; found C 56.14, H 6.23.

Tris(4-dihydroxyborylphenyl)methylsilane (**2b**): This compound was prepared as described for **2a** starting with **1b** (5.1 g, 0.01 mol) and using 6 equivalents of *n*-BuLi (10 M, 6.0 mL, 0.06 mol). Yield: 40% (2.06 g), m.p. > 300 °C. ^{1}H NMR (acetone-d_6, 400 MHz): δ = 7.81 (d, J = 8.0 Hz, 6H, Ph), 7.45 (d, J = 8.4 Hz, 6H, Ph), 0.79 (s, 3H, CH_3) ppm. ^{11}B NMR (acetone-d_6, 64.2 MHz): δ = 31 ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ = 140.4, 133.3, 133.2, −3.3 ppm. $C_{19}H_{21}B_3O_6Si$ (406.14) calcd. C 56.22, H 5.21; found 56.52, H 5.41.

Tetrakis(4-dihydroxyborylphenyl)silane (**2c**): This compound was prepared according to the literature procedure [2]. Yield: 60%, m.p. > 300 °C (lit. m.p. > 300 °C).

Bis(3-dihydroxyborylphenyl)dimethylsilane (**2d**): This compound was prepared as described for **2a** using **1d** (3.70 g, 0.01 mol) as starting material. The product (2.64 g, 88%) was isolated as a white powder, m.p. = 258–260 °C. ^{1}H NMR (acetone-d_6, 400 MHz): δ = 8.16 (s, 2H, Ph), 7.90 (d, J = 9.0 Hz, 2H, Ph), 7.59 (d, J = 9.0 Hz, 2H, Ph), 7.35 (t, 2H, Ph), 7.24 (s, 4H, $B(OH)_2$), 0.57 (s, 6H, CH_3) ppm. ^{11}B NMR (acetone-d_6, 64.2 MHz): δ = 29.0 ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ = 139.9, 137.1, 136.1, 134.9, 126.9, −3.0 ppm. $C_{14}H_{18}B_2O_4Si$ (300.12) calcd. C 56.05, H 6.05; found 56.52, H 6.08.

Tris(3-dihydroxyborylphenyl)methylsilane (**2e**): This compound was prepared as described for **2b** using **1e** (5.0 g, 0.01 mol) as starting material. The product (69%) was isolated as a white powder, m.p. > 300 °C. ^{1}H NMR (acetone-d_6, 400 MHz): δ = 8.13 (s, 3H, Ph), 7.84 (d, J = 8.5 Hz, 3H, Ph), 7.63 (d, J = 8.5 Hz, 3H, Ph), 7.30 (t, J = 8.5 Hz, 3H, Ph), 0.57 (s, 3H, CH_3) ppm. ^{11}B NMR (acetone-d_6, 64.2 MHz): δ = 29 ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ = 139.7, 137.3, 135.8, 135.2, 126.8, −1.6 ppm. $C_{19}H_{21}B_3O_6Si \cdot 2H_2O$ (441.92) calcd. C 51.64, H 5.70; found C 52.18, H 5.34.

Tetrakis(3-dihydroxyborylphenyl)silane (**2f**): This compound was prepared as described for **2a** starting with **1b** (6.52 g, 0.01 mol) and using 8 equivalents of *n*-BuLi (10 M, 8.0 mL, 0.08 mol). Resulting product was purified by recrystallization from acetone/hexane (1:1) to give title compound (1.79 g, 35%) as a white powder. M.p. > 300 °C. ^{1}H NMR (acetone-d_6, 400 MHz): δ = 8.24 (s, 4H, Ph), 7.62 (m, 4H, Ph), 7.42 (t, J = 7.5 Hz, 4H, Ph), 7.26 (d, J = 7.5 Hz, 4H, Ph) ppm. ^{11}B NMR (acetone-d_6, 64.2 MHz): δ = 29 ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ = 142.2, 138.3, 136.3, 135.4, 127.1 ppm. $C_{24}H_{24}B_4O_8Si$ (512.16) calcd. C 56.33, H 4.73; found C 56.11, H 4.99.

Bis(4-dihydroxyboryl-3,5-difluorophenyl)dimethylsilane (**2g**): A solution of **1g** (2.81 g, 0.01 mol) in THF (5 mL) was added dropwise to a freshly prepared solution of LDA [diisopropylamine (3.3 mL, 0.022 mol) and *n*-BuLi (10 M; 2.1 mL, 0.021 mol) in THF (20 mL)] at −75 °C. The resulting white slurry was stirred for ca 30 min at −75 °C, and then B(OEt)$_3$ (3.8 mL, 0.022 mol) was added dropwise. The mixture was stirred for 1 h, and then it was hydrolyzed

with H_2SO_4 (1.5 M aq., 20 mL). The aqueous phase was separated and then extracted with Et_2O (2 × 10 mL). The extracts were added to the organic phase, which was concentrated under reduced pressure. The solid residue was filtered and washed consecutively with hexane (5 mL) and toluene (5 mL). Drying *in vacuo* gave the title compound (2.64 g, 72%) as a white powder, m.p. 110–116 °C. ^{1}H NMR (acetone-d_6, 400 MHz): δ = 7.81 (broad, 4H, $B(OH)_2$), 7.06 (dd, J = 6.5, 2.0 Hz, 4H, Ph), 0.64 (s, 6H, CH_3) ppm. ^{11}B NMR (acetone-d_6, 64.2 MHz): δ = 28 ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ = 164.8 (dd, J = 247.5, 13.0 Hz), 128.5 (d, J = 73.0 Hz), 115.53 (d, J = 26.0 Hz), −4.1 ppm. ^{19}F NMR (acetone-d_6, 360.6 MHz): δ = −104.08 (dd, J = 6.0, 2.0 Hz) ppm. $C_{14}H_{14}B_2F_4O_4Si$ (372.08) calcd. C 45.21, H 3.79; found C 45.07, H 3.71.

Tris(4-dihydroxyboryl-3,5-difluorophenyl)methylsilane (**2h**): This compound was prepared as described for **2g** starting with **1h** (7.64 g, 0.02 mol) and using 20% excess of LDA (0.072 mol). Yield: 72% (7.4 g), m.p. 133–137 °C. ^{1}H NMR (acetone-d_6, 400 MHz): δ = 7.03 (d, J = 8.0 Hz, 6H, Ph), 0.97 (s, 3H, CH_3) ppm. ^{11}B NMR (acetone-d_6, 64.2 MHz): δ = 29 ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ = 163.0 (dd, J = 251.5, 11.0 Hz), 117.3 (dd, J = 17.0, 6.0 Hz), 105.5 (t, J = 25.5 Hz), −5.2 ppm. ^{19}F NMR (acetone-d_6, 360.6 MHz): δ = −110.36 (ddd, J = 9.0, 6.0, 2.0 Hz) ppm. $C_{19}H_{15}B_3F_6O_6Si$ (514.08) calcd. C 45.41, H 2.94; found C 45.55, H 2.78.

Bis(3-dihydroxyboryl-2,4-difluorophenyl)dimethylsilane (**2i**): This compound was prepared as described for **2g** starting with **1i**. Yield: 63% (11.7 g), m.p. 127–129 °C. ^{1}H NMR (acetone-d_6, 400 MHz): δ = 7.81 (broad, 4H, $B(OH)_2$), 7.41 (dd, J = 15.5, 8.0 Hz, 2H, Ph), 6.92 (t, J = 8.0 Hz, 2H, Ph), 0.58 (s, 6H, CH_3) ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz) δ = 167.5 (dd, J = 280, 12.0 Hz), 165.0 (dd, J = 287, 12.0 Hz), 136.8 (dd, J = 13.0, 9.5 Hz), 118.9 (dd, J = 30.0, 4.0 Hz), 111.4 (dd, J = 20.0, 3.5 Hz), 103.5 (dd, J = 30.0, 24.0 Hz), −2.2 ppm. ^{19}F NMR (acetone-d_6, 360.6 MHz): δ = −89.5 (t, J = 8.0 Hz), −102.0 (dd, J = 16.5, 8.5 Hz) ppm. $C_4H_{14}B_2F_4O_4Si$ (372.08) calcd. C 45.21, H 3.79; found C 45.30, H 3.64.

Bis(2-thienyl)dimethylsilane (**3a**) [8a]: Yield: 78%, b.p. 131–134 °C (2 Torr).

Tris(2-thienyl)methylsilane (**3b**) [8b]: Yield: 75%, b.p. 203–206 °C (2 Torr).

Tetrakis(2-thienyl)silane (**3c**) [9]: Yield: 70%, m.p. 128–131 °C (lit. 135 °C).

Bis(3-thienyl)dimethylsilane (**3d**) [10]: Yield: 83%, b.p. 153–155 °C (2 Torr).

Tris(3-thienyl)methylsilane (**3e**): A solution of 3-bromothiophene (48.9 g, 0.30 mol) in Et_2O (50 mL) was added dropwise at −65 °C to a solution of *n*-BuLi (10 M, 31 mL, 0.31 mol) in Et_2O (300 mL). The resulting white suspension was stirred at −78 °C for 30 min followed by dropwise addition of $MeSiCl_3$ (15.0 g, 11.8 mL, 0.10 mol) in Et_2O (40 mL) while maintaining the temperature below −50 °C, then it was allowed to warm to room temperature. The resultant white suspension was quenched with aq. H_2SO_4 (1.5 M aq., 100 mL). Et_2O (100 mL) was added to the mixture and the organic phase was separated. The aqueous phase was extracted with Et_2O (2 × 50 mL). Collected organic phases were dried over anhydrous $MgSO_4$ and concentrated. The crude product was crystallized from cold (ca. −20 °C) hexane (70 mL) to give a pale yellow crystalline solid, m.p. 70–73 °C, yield 17.3 g (59%). ^{1}H NMR (acetone-d_6, 300 MHz): δ = 7.63 (dd, J = 2.5, 1.0 Hz, 3H, Th), 7.55 (dd, J = 5.0, 2.5 Hz, 3H, Th), 7.26 (dd, J = 5.0, 1.0 Hz, 3H, Th), 0.82 (s, 3H, CH_3) ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ = 138.0, 134.7, 132.8, 126.9, −1.7 ppm. $C_{13}H_{12}S_3Si$ (359.96): calcd. C 53.38, H 4.13, S 32.82; found C 53.01, H 4.12, S 32.32.

Tetrakis(3-thienyl)silane (**3f**): The title compound was obtained from 3-thienylithium (generated as described for **3e**, 0.4 mol) and $Si(OMe)_4$ (15.2 g, 0.1 mol). It was obtained as a white solid by recrystallization of a crude product from hot toluene, m.p. 217–219 °C, yield 22.2 g (61%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 7.70 (dd, J = 5.0, 3.0 Hz, 4H, Th), 7.66 (dd, J = 3.0, 1.0 Hz, 4H, Th), 7.21 (dd, J = 5.0, 1.0 Hz, 4H, Th) ppm. ^{13}C NMR (DMSO-d_6, 100.6 MHz): δ = 135.5, 135.1, 132.4, 127.2 ppm. $C_{16}H_{12}S_4Si$ (359.96): calcd. C 53.29, H 3.35, S 35.57; found: C 53.58, H 3.87, S 35.39.

Bis(5-dihydroxyborylthiophen-2-yl)dimethylsilane (**4a**): Diisopropylamine (8.4 mL, 0.06 mol) was added to a solution of *n*-BuLi (10 M, 6.3 mL, 0.063 mol) in THF (150 mL) at −70 °C. The mixture was stirred for 30 min at −78 °C followed by dropwise addition of **3a** (6.72 g, 0.03 mol) in THF (40 mL). After 30 min the reaction mixture was allowed to warm to −10 °C and then cooled again to −78 °C. Then triisopropyl borate (13.9 mL, 0.06 mol) was added dropwise. The mixture was stirred for 30 min and allowed to warm to the room temperature. The resulting pale yellow solution was hydrolyzed with aq. 1.5 M H_2SO_4 (70 mL) followed by the addition of Et_2O (100 mL). The water phase was extracted with Et_2O (50 mL). The collected organic solutions were dried with anhydrous $MgSO_4$ and concentrated to give a pale yellow solid. It was stirred with toluene-hexane mixture (1:1, 50 mL) and filtered to give the title compound as a white solid, m.p. 104–105 °C, yield 6.41 g (69%). ^{1}H NMR (acetone-d_6, 400 MHz): δ = 7.75 (d, J = 3.0 Hz, 2H, Th), 7.42 (d, J = 3.0 Hz, 2H, Th), 7.35 (s, 4H, $(B(OH)_2)$), 0.64 (s, 6H, CH_3) ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ = 143.7, 136.6, 136.1, −0.9 ppm. ^{11}B NMR (acetone-d_6, 96 MHz): δ = 26.2 ppm. $C_{10}H_{14}B_2O_4S_2Si$ (312.03): calcd. C 38.49, H 4.52, S 20.55; found C 38.13, H 4.92, S 20.83.

Tris(5-dihydroxyborylthiophen-2-yl)methylsilane (**4b**): This compound was obtained using a procedure described for **4a** using **3b** (2.92 g, 0.01 mol) as the starting material. White solid, m.p. > 400 °C; yield 2.67 g (63%). ^{1}H NMR (acetone-d_6, 300 MHz): δ = 7.76 (d, J = 3.5 Hz, 3H, Th), 7.45 (d, J = 3.5 Hz, 3H, Th), 0.93 (s, 3H, CH_3) ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ = 142.3, 138.4, 137.6, 0.2 ppm. ^{11}B NMR (acetone-d_6, 96 MHz): δ = 26.7 ppm. $C_{13}H_{15}B_3O_6S_3Si$ (424.01): calcd. C 36.83, H 3.57, S 22.69; found C 37.01, H 3.78, S 22.57.

Tetrakis(5-dihydroxyborylthiophen-2-yl)silane (**4c**): This compound was obtained using a procedure described for **4a** using **3c** (3.60 g, 0.01 mol) as the starting material. White solid, m.p. 157–160 °C; yield 3.8 g (67%). ^{1}H NMR (acetone-d_6, 300 MHz): δ = 7.82 (d, J = 3.5 Hz, 4H, Th), 7.54 (d, J = 3.5 Hz, 4H, Th), 7.49 (s, 8H, $B(OH)_2$) ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ = 140.4, 139.7, 137.5 ppm. ^{11}B NMR (acetone-d_6, 96 MHz): δ = 27.3 ppm. $C_{16}H_{16}B_4O_8S_4Si \cdot 2H_2O$ (571.91): calcd. C 33.60, H 3.52, S 22.43; found C 33.73, H 3.91, S 22.63.

Bis(4-dihydroxyborylthiophen-2-yl)dimethylsilane (**4d**): This compound was obtained using a procedure described for **4a** using **3d** (2.24 g, 0.01 mol) as the starting material. White solid, m.p. 119–122 °C, yield 2.88 g (68%). ^{1}H NMR (acetone-d_6, 300 MHz): δ = 7.84 (d, J = 1.0 Hz, 2H, Th), 7.78 (d, J = 1.0 Hz, 2H, Th), 0.52 (s, 6H, CH_3) ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ = 141.7, 141.1, 139.6, −1.0 ppm. ^{11}B NMR (acetone-d_6, 96 MHz): δ = 26.93 ppm. $C_{10}H_{14}B_2O_4S_2Si$ (312.03): calcd. C 38.49, H 4.52, S 20.55; found C 38.76, H 4.60, S 20.93.

Tris(4-dihydroxyborylthiophen-2-yl)methylsilane (**4e**): Diisopropylamine (4.62 mL, 0.033 mol) was added to a solution of *n*-BuLi (10 M, 3.3 mL, 0.033 mol) in THF (50 mL) at −70 °C. The mixture was stirred for 30 min at −78 °C followed by dropwise addition of a solution of **3e** (2.92 g, 0.01 mol) in THF (20 mL). After 30 min the reaction mixture was warmed slowly to −10 °C and then cooled again to −78 °C. Then triisopropyl borate (6.92 mL, 0.03 mol) was added to a colourless solution. After 30 min the mixture was left to warm to the room temperature and hydrolyzed with water (25 mL) and 1.5 M H_2SO_4 (15 mL) (pH ca.7–8) followed by the addition of Et_2O (50 mL). The resultant white slurry was filtered. The obtained white solid was stirred with 1.5 M H_2SO_4 (10 mL), water (25 mL) and diethyl ether (50 mL). The product was precipitated from

organic phase with hexane (150 mL) followed by filtration and drying *in vacuo* to give a white solid, m.p. 166–169 °C, yield 1.70 g (40%). ^{1}H NMR (acetone-d_6, 400 MHz): δ = 7.86 (d, J = 0.5 Hz, 3H, Th), 7.81 (d, J = 0.5 Hz, 3H, Th), 7.36 (s, 6H, CH_3), 0.80 (s, 3H) ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ = 142.1, 140.8, 139.6, −1.3 ppm. ^{11}B NMR (acetone-d_6, 96 MHz): δ = 27.2 ppm. $C_{13}H_{15}B_3O_6S_3Si$ (424.01): calcd. C 36.83, H 3.57, S 22.69; found C 37.17, H 3.72, S 23.07.

Crystal structure determination

Single crystals of **2g** and **2i** were measured on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo-Kα radiation and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. Data reduction and analysis were carried out with the *CrysAlisPro* program [19]. All structures were solved by direct methods using *SHELXS-97* and refined using *SHELXL-2013* [20]. All non-hydrogen atoms were refined anisotropically and all of the CH (phenyl, methylene) hydrogen atoms were placed in calculated positions with C–H distances of 0.95 Å (phenyl) and 0.99 Å (methylene). The positions of all OH hydrogen atoms were refined freely constraining their U_{iso} parameters. Hydrogen atoms were included in the refinement in riding-motion approximation with U_{iso}(phenyl H) = 1.2·U_{eq}(C), and U_{iso}(methyl H) = 1.5·U_{eq}(C). The positions of OH hydrogen atoms were refined with U_{iso}(hydroxyl H) = 1.5·U_{eq}(O). In all cases except of the disordered THF molecule in the compound **2g**, hydrogen atoms were clearly visible on the residual density maps. A large peaks of residual electron densities (1.0–2.5·e·Å^{-3}) found near THF molecule in **2g** indicate presence of disorder. It is also possible that other guest molecules (for example acetone) partially incorporated during the crystal growth. However, we were unable to propose any reasonable model for this case. The unrefined density results in relatively high R and wR parameter values and also, in consequence, many *CHECKCIF's* B and C alerts appeared. Crystal data for **2g**: $2(C_{14}H_{14}B_2F_4O_4Si)\cdot C_4H_8O$, M_r = 816.03 a.u.; T = 100 K; triclinic; space group: P-1, a = 11.372 (1) Å, b = 14.212 (1) Å, c = 14.377 (1) Å, α = 67.67 (1)°, β = 70.99 (1)°, γ = 67.21 (1)°, V = 1937.5 (3) Å^3; d_{calc} = 1.399 g cm^{-3}; μ = 0.18 mm^{-1}; Z = 2; F(000) = 840; number of collected/unique reflections (R_{int} = 8.9%) = 28,547/8925, $R[F]/wR[F]$ ($I \geq 3\sigma(I)$) = 9.3%/31.7%, GoF = 1.052, $\Delta\varrho_{res}^{max/min}$ = +2.28/−0.93·e·Å^{-3}. Crystal data for **2i**: $C_{14}H_{14}B_2F_4O_4Si$, M_r = 371.96 a.u.; T = 100 K; orthorhombic; space group: *Pnna*, a = 12.286 (1) Å, b = 18.087 (1) Å, c = 7.335 (1) Å, V = 1629.9 (1) Å^3; d_{calc} = 1.516 g cm^{-3}; μ = 0.02 mm^{-1}; Z = 4; F(000) = 760; number of collected/unique reflections (R_{int} = 3.8%) = 25,930/2811, $R[F]/wR[F]$ ($I \geq 3\sigma(I)$) = 4.5%/12.8%, GoF = 1.042, $\Delta\varrho_{res}^{max/min}$ = +0.63/−0.73·e·Å^{-3}.

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Appendix A. Supplementary data

CCDC 1034407 (**2g**) and 1034408 (**2i**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.01.024.

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