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Silicon-Bridged Bi- and Tridentate Lewis Acidic Host Systems

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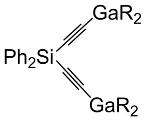
Connecting multiple organic spacer functions via silicon core units leads to various organosilanes that are excellently suited as backbones for poly-Lewis acids (PLAs). Using ethynyl spacer groups, rigid bis- and tris-dioxabenzoborole (BCat)-substituted PLAs were prepared. The fixed orientation of the Lewis acidic functions of the PLAs is reflected in their solid-state structures. Further flexible PLAs were obtained by hydroboration of vinylsilanes using 9-borabicyclo[3.3.1]nonane (9-BBN), which shows the flexibility of the backbone motif. Host-guest experiments of the bidentate representatives with pyridine demonstrate the ability of both PLA-types (BCat or 9-BBN) for complexing neutral guest molecules. The rigid host system shows additionally a 1:1 adduct formation using a bridged diamine as guest compound.

Introduction

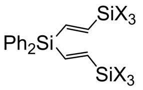
Molecules bearing at least two Lewis acid functions are commonly referred to as poly-Lewis acids (PLAs). They are used in supramolecular chemistry for the complexation of Lewis bases.[1] In this sense they are the counterpart of the well-established poly-Lewis bases (e.g. crown ethers,[2] cryptants[3] etc). For the construction of PLAs, an organic, donor-free molecular framework is required that carries the reactive sites. Simple representatives for such backbones are benzenes[4] e.g. 1,3-bis(dimethylgallyl)benzene reported by Jutzi and co-workers[4b] and alkane derivatives[5] such as 1,2-bis(difluoroboryl) ethane.[5a] Due to the short distance between the two Lewis acid functions, these representatives were only used for chelating complexation of small Lewis bases.[4,5]

By making use of more complex organic molecules such as tribenzotriquinacenes,[6] anthracenes[7] or 1,3,5-trisilacyclohexanes,[8] with further ethynyl, ethenyl or ethyl spacer units, we were able to create a big variety of different frameworks in the recent past. These offer a wide range of sizes concerning the resulting Lewis acidic cavities. The rigid spacer groups (e.g. ethynyl functions), lead to relatively inflexible systems.[7a–c,e,8b,9] The typically fixed distance between the Lewis acidic functions results in higher selectivity in the complexation of Lewis basic guests.[7c;9] In contrast, using the more pliable ethyl and vinyl spacer groups lead to PLAs with (restricted) flexibility in terms of the distance between their reactive sites.[10] Recently, we reported various "pincer-like" PLAs based on diethynyl- or divinyl-diphenylsilanes.[9,10] This simple "backbone" proved to be extremely multifaceted. For example, in complexation experiments with bis-pyridine bases, the rigid gallyl-substituted **A1** (Scheme 1) showed a pronounced selectivity with respect to the distance between the Lewis basic sites of the guest compound.[9] Due to the versatility of the silicon core, semiflexible representatives (**A2**) with comparatively weak Lewis-acidic silyl groups were also described.[10] The fluorinated systems were suitable for complexation of fluoride ions, but owing to the relatively weak Lewis-acidity they showed no complexation ability for neutral guest molecules.

In contrast to silyl acid functions, boryl residues offer a typically more acidic alternative. PLAs functionalized with easily accessible, organically substituted (e.g. aryl, alkyl, alkoxy) boranes have been used for a long time to complex neutral Lewis-basic guests (e.g. for molecular recognition[7c;11] and/or formation of crystalline polymeric systems[12]). The introduction of boryl groups under maintenance of rigid ethynyl backbones can either be accomplished by salt elimination[11a,d] or exchange reactions.[7c,11b] Flexible systems can, alternatively, be achieved via hydroboration reactions using various hydroboranes e.g. 9-BBN[13] (in analogy to hydrosilylation).



A1
R = Me, Et



A2
X = F, Cl

Scheme 1. Examples of rigid (**A1**) and semiflexible (**A2**) poly-Lewis acids based on diphenylsilanes.

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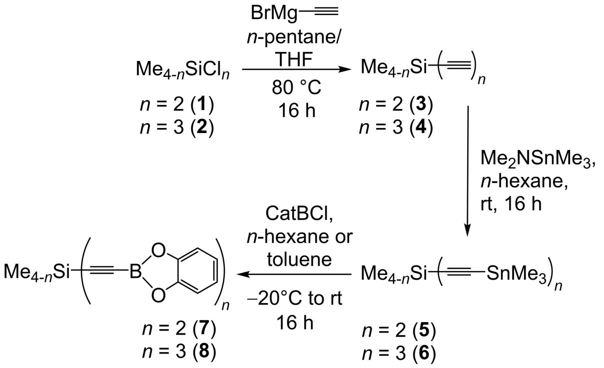
Results and Discussion

Synthesis, characterization and structure

Herein, we report the synthesis of bis- and tris-boryl-substituted PLAs based on a dimethylsilane core. Rigid alkyne spacer groups were introduced following established literature protocols[10] by reaction of the chlorosilanes **1** and **2** with ethynylmagnesium bromide. Owing to similar boiling points of THF, **3** and **4** solvent removal by fractional distillation remained incomplete, so that both ethynyl silanes **3**[14] and **4** could only be obtained as mixtures with THF and identified by NMR spectroscopy.



Scheme 2. Synthetic route via tin-boron exchange to give benzo[*d*][1,3,2]dioxaborole-substituted ethynylsilanes (**7**, **8**).

Table 1. Selected NMR shifts (in ppm; $CDCl_3$) and wavenumbers (in cm^{-1}) for the alkyne stretching vibration in the IR spectrum of the bidentate compounds **3**, **5** and **7**.

compound	$SiCH_3$	SiCC	SiCC	Si	$\tilde{\nu}$ (C≡C)
7	0.52	109.2	–	−38.0	2174
5	0.33	113.8[15]	114.8[15]	−45.0[15]	2085
3	0.38	86.3	94.6	−38.8	2036

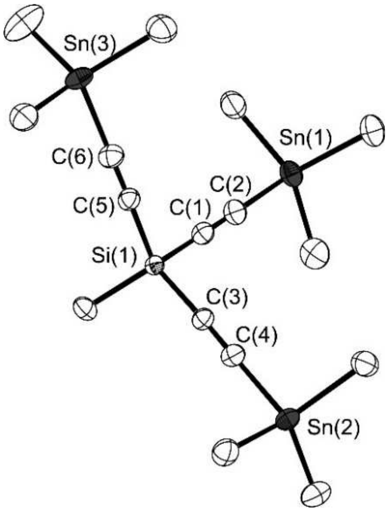


Figure 1. Molecule structure of **6** in the solid state. Ellipsoids are set at 50% of probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)-C(1) 1.823(4), Si(1)-C(3) 1.831(4), Si(1)-C(5) 1.826(4), C(1)-C(2) 1.207(5), C(3)-C(4) 1.198(5), C(5)-C(6) 1.208(5), Sn(1)···Sn(2) 8.457(1), Sn(2)···Sn(3) 8.420(1), Sn(1)···Sn(3) 8.329(1); C(1)-Si(1)-C(3) 109.1(2), C(1)-Si(1)-C(5) 108.5(2), C(3)-Si(1)-C(5) 108.3(2), Si(1)-C(1)-C(2) 179.6(4), Si(1)-C(3)-C(4) 178.0(4), Si(1)-C(5)-C(6) 178.9(4), C(1)-C(2)-Sn(1) 179.4(4), C(3)-C(4)-Sn(2) 179.2(4) C(5)-C(6)-Sn(3) 177.6(4).

Reacting **3** and **4** with dimethylaminotrimethylstannane leads to a terminal stannylation of the alkynes and preserving their triple bonds (Scheme 2). The stannylsilanes **5** and **6** were isolated in good to excellent yields (**5**: 86%; **6**: 98%) and identified (**5**)[15] or characterized (**6**) by NMR spectroscopy. In the IR spectrum of **5**, the characteristic band for the alkyne vibration of Sn–C≡C–Si-fragments[16] ($\tilde{\nu}$ (**5**) = 2085 cm^{-1}) shows a shift to higher wavenumbers and a clear weakening of the intensity compared to the terminal alkyne (cf.: $\tilde{\nu}$(**3**) = 2036 cm^{-1}) (Table 1). By slowly concentrating a solution of **6** in 1,2-difluorobenzene, we obtained crystals for X-ray diffraction allowing to elucidate the solid-state structure (Figure 1).

Figure 1 clearly shows the orientation of the rigid alkyne spacer units. This is due to the almost ideal tetrahedral coordination environment at the central silicon atom. All angles between the alkyne substituents (C(1)-Si(1)-C(3) 109.1(2), C(1)-Si(1)-C(5) 108.5(2), C(3)-Si(1)-C(5) 108.3(2)) deviate only slightly from the ideal tetrahedral angle (109.5°). The alkyne substituents also show no marked deformations, so that the expected rigid arrangement of the backbone finds confirmation. This alignment leads to distances between the tin atoms within the molecule of 8.329(1) to 8.457(1) Å.

For Lewis acid functionalisation, the doubly and triply stannylated silanes **5** and **6** were reacted with 2-chloro-benzo[*d*][1,3,2]dioxaborole in tin-boron exchange reactions. By cooling *n*-hexane solutions of the crude products **7** and **8**, both PLAs were obtained as colourless crystalline solids. Due to the highly selective reaction, excellent and good yields of 94% (**7**) and 82% (**8**) were achieved. The boryl-substituted alkynylsilanes **7** (Table 1) and **8** were characterized by multinuclear NMR spectroscopy and by elemental analyses. Both, the shifts in the ^{11}B NMR spectrum (both at 23.4 ppm) and the absence of signal for the alkyne carbon atom adjacent to the boryl residue in the ^{13}C NMR spectrum (due to the coupling to the ^{10}B and ^{11}B quadrupole nuclei) are characteristic for such boranes.[7c] In the IR spectrum of **7**, the band for the alkyne stretching vibration is observed with only very weak intensity at 2174 cm^{-1} (Table 1), which is comparable to those of other borylethynylsilanes.[17]

By slow evaporation of solutions of **7** in dichloromethane and **8** in 1,2-difluorobenzene, crystals suitable for X-ray diffraction were obtained (Figure 2 and Figure 3). In the molecular structure of **7**, the two Lewis acidic boron sites form a "Lewis-acidic pincer" with a B···B distance of 6.949(3) Å. This is significantly shorter than in the comparable pyridine adduct of PLA **A1** (8.2 Å).[9] The boron atoms exhibit the expected planar coordination environment (angular sum 359.8(4)°), whereas the alkyne substituents show relatively strong deformations and deviations from linearity (e.g. C(2)-C(1)-B(1) 172.6(2)°).

For the tridentate host system, the preservation of the rigid backbone as well as the "shell-like" alignment of the three Lewis acidic sites can be seen in the molecular structure in Figure 3. In

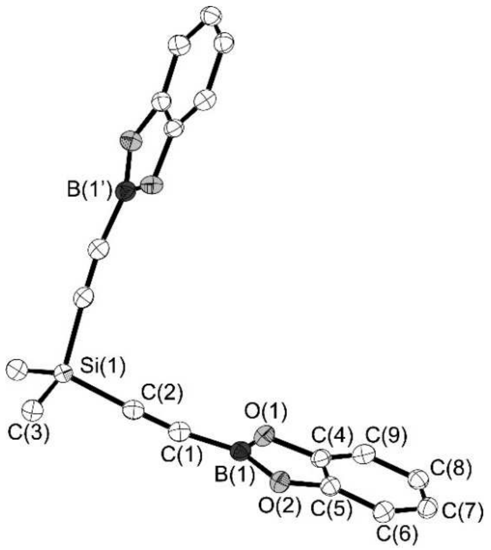


Figure 2. Molecule structure of **7** in the solid state. Ellipsoids are set at 50% of probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)-C(2) 1.853(1), Si(1)-C(3) 1.851(2), C(1)-C(2) 1.203(2), B(1)-C(1) 1.527(2), B(1)-O(1) 1.381(2), B(1)-O(2) 1.385(2) B(1)···B(1^{1}) 6.949(3); C(2)-Si(1)-C(2^{1}) 105.6(2), C(2)-Si(1)-C(3) 107.8(1) Si(1)-C(2)-C(1) 177.3(1), C(2)-C(1)-B(1) 172.6(2), C(1)-B(1)-O(1) 122.9(2), C(1)-B(1)-O(2) 124.6(2), O(1)-B(1)-O(2) 112.4(2).

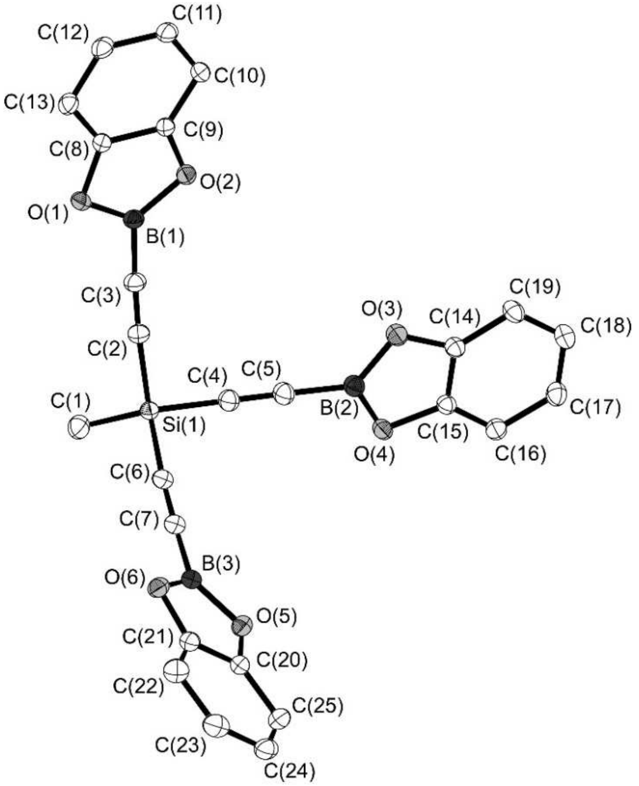
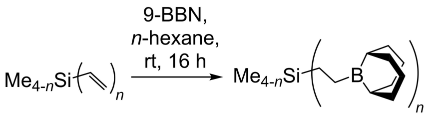


Figure 3. Molecule structure of **8** in the solid state. Ellipsoids are set at 50% of probability; hydrogen atoms and solvent difluorobenzene are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)-C(1) 1.838(1), Si(1)-C(2) 1.831(1), Si(1)-C(4) 1.830(1), Si(1)-C(6) 1.826(1), C(2)-C(3) 1.215(1), C(4)-C(5) 1.214(1), C(6)-C(7) 1.211(1), B(1)···B(2), 7.061(2), B(2)···B(3) 7.013(2), B(1)···B(3) 7.306(2); C(1)-Si(1)-C(2) 112.7(1), C(2)-Si(1)-C(4) 105.4(1), C(2)-Si(1)-C(6) 107.7(1), C(4)-Si(1)-C(6) 105.3(1), Si(1)-C(2)-C(3) 177.0(1), Si(1)-C(4)-C(5) 175.1(1), Si(1)-C(6)-C(7) 176.9(1), C(2)-C(3)-B(1) 177.0(1), C(4)-C(5)-B(2) 177.4(1) C(6)-C(7)-B(3) 177.8(2), C(3)-B(1)-O(1) 124.0(1), C(3)-B(1)-O(2) 123.2(1), O(1)-B(1)-O(2) 112.8(1).



n = 2 (**9**)
n = 3 (**10**)

n = 2 (**11**)
n = 3 (**12**)

Scheme 3. Hydroboration of vinyl silanes **9** and **10** using 9-borabicyclo[3.3.1]nonane to gain flexible, bi- and tridentate PLAs **11** and **12**.

contrast to the precursor compound **6**, a compression of the angles between the alkyne spacer groups (∢≡C–Si–C≡) occurs to **8**; they fall over a range from 105.3(1)° to 107.7(1)° (cf. 6: 108.3(2)° to 109.1(2)°). Consequently, the lower steric demand of the peripheral alkyne-functions and the shorter B–C bonds compared to Sn–C bonds or the electron withdrawing character of the boron residue result in a separation of the terminal boron atoms in **8** with much shorter distances of 7.013(2) to 7.306(2) Å than the tin atoms in **6** (8.329(1) to 8.457(1) Å). These distances are consistent with those found for **7** (d(B(1)···B(1′)) = 6.949(3) Å).

Various attempts to employ Lewis acidic boranes (e.g. chlorodiphenylborane, chloro-bis(pentafluorphenyl)borane) in tin-boron exchange reactions, as described in the syntheses of **7** and **8**, failed due to decomposition of the stannylated substrates. The use of less reactive triphenylphosphane adducts[18] of these boranes did also not improve the situation.

Hydroboration reactions are well suited for the synthesis of flexible PLAs starting from poly-alkyne or -vinyl precursors. Both, flexibility and Lewis-acidic functionalisation of the backbone, are achieved within one step. By using 9-borabicyclo[3.3.1]nonane (9-BBN), a regioselective hydroboration of the vinylsilanes **9** and **10**[19] in anti-Markovnikov position afforded products **11** and **12** (Scheme 3). They were isolated as colourless solids by recrystallisation from n-hexane solutions at −80 °C.

The bi- (**11**) and tridentate (**12**) flexible PLAs were characterized by multinuclear NMR spectroscopy and elemental analyses. For both compounds, the ^{13}C NMR spectra show the characteristic attenuation of the signal for the ethyl carbon atom of the spacer adjacent to the boryl residue (SiCH$_2$**C**H$_2$). In both cases, the ^{11}B NMR chemical shift at 86.2 ppm is comparable to those of other 9-BBN-substituted organoboranes.[20] Compared to the catechol-substituted representatives (cf. **7**: 23.4 ppm), the signals of **11** and **12** are low-field shifted due to the lack of donation by the oxygen atoms.

Host-guest chemistry

Initial host-guest experiments with the bidentate systems **7** and **11** and with pyridine as a simple monodentate guest were implemented on the NMR scale.

For the adducts **7**·2Py and **11**·2Py, a clear change in the chemical shifts of the pyridine guest signals can be observed in the ^{1}H NMR spectra compared to free pyridine (Table 2). Due to the addition of the pyridine, the ^{11}B NMR spectra showed high-field shifts of the signal. This shift turned out to be considerably stronger for the BBN-substituted acid **11**. Both chemical shifts are in the range of comparable tetra-coordinate borane-nitrogen compounds.[7c;21] The strong donation of the pyridine to the 9-BBN substituted acid **11** results in high-field shifts ($\Delta\delta\sim$ 0.6 ppm) of the signals of the spacer unit (SiCH_2; $SiCH_2CH_2$) in the ^{1}H NMR spectrum of **11**·2Py. The double addition of the pyridine to the PLA can also be observed in the solid-state structure (Figure 4).

Table 2. Selected NMR shifts (^{1}H and ^{11}B) from for the adducts **7**·2Py and **11**·2Py, as well as the free acids (**7** and **11**) and the non-complexed pyridine[22] (Py) in $CDCl_3$ (*) and C_6D_6 (#), respectively.

		7 / Py*	**7**·2Py*	**11** / Py#	**11**·2Py#
guest	Py-H_{ortho}	8.62[21]	8.85	8.53[21]	8.17
	Py-H_{meta}	7.29[21]	7.65	6.66[21]	6.46
	Py-H_{para}	7.68[21]	8.08	6.98[21]	6.72
host	Si$\mathbf{H}_2$ → SiCH_2	–	–	0.68	0.01
	$SiCH_2CH_2$	–	–	1.22	0.65
	^{11}B	23.4	7.7	86.2	1.5

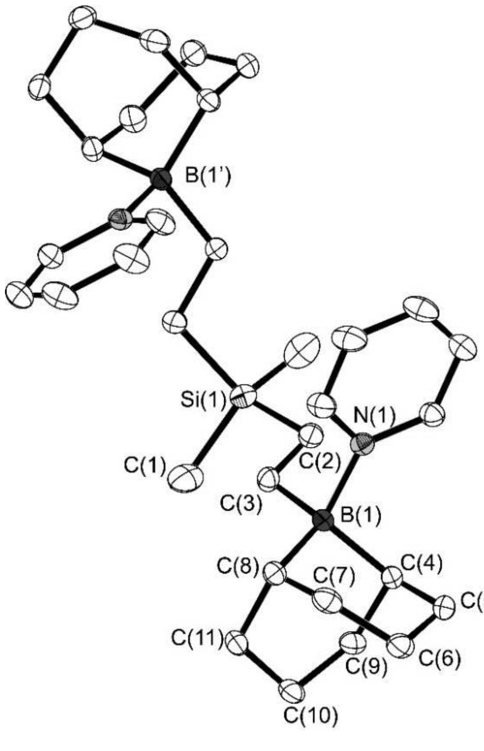
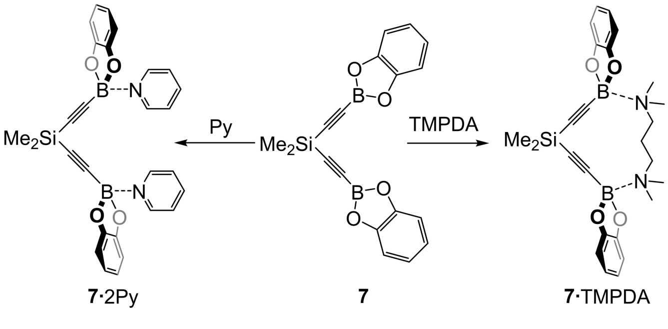


Figure 4. Molecule structure of **11**·2Py in the solid state. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles[°]: Si(1)-C(1) 1.872(2), Si(1)-C(2) 1.870(2), C(2)-C(3) 1.547(2), C(3)-B(1) 1.629(2), C(4)-B(1) 1.627(2), C(8)-B(1) 1.630(2), N(1)-B(1) 1.654(2), B(1)···B(1′) 6.682(4); C(2)-Si(1)-C(1) 109.7(1), C(2)-Si(1)-C(2^1) 111.2(2), Si(1)-C(2)-C(3) 113.4(2), C(2)-C(3)-B(1) 116.7(2), C(3)-B(1)-C(4) 116.0(2), C(3)-B(1)-C(8) 113.8(1), C(3)-B(1)-N(1) 102.7(1), C(4)-B(1)-C(8) 105.0(1).

The length of the bond B(1)-N(1) is 1.654(2) Å, which is in the medium range of dative B-N bonds[23] and for instance longer than the dative bond of $Me_3B–NMe_3$ in the solid state.[24] Consequently and confirming the partial B–N bond character, the coordination geometry at the boron atom in **11**·2Py is strongly distorted tetrahedral. All C–B–C angles are wider (C(3)–B(1)–C(4) 116.0(2)°, C(3)–B(1)–C(8) 113.8(1)°) and all C–B–N angles are less than for an ideal tetrahedral coordination (e.g. C(3)–B(1)–N(1) 102.7(1)°). Again, the two boron atoms form a "pincer" with d(B(1)··· B(1′)) = 6.682(4) Å, which is slightly shorter than the value found for the rigid bidentate Lewis acid **7** (Figure 2, d(B(1)···B(1′)) = 6.949(3) Å) due to the greater flexibility of the spacer units in **11**.

The bidentate Lewis acids **7** and **11** were also combined with the alkyl-bridged diamine *N*,*N*,*N*′,*N*′-tetramethylpropanediamine (TMPDA) in an NMR scale experiment. Compound **11** showed no signs of adduct formation in the NMR spectra with the diamine. For **7**, an adduct formation with TMPDA was detected by NMR spectroscopy. Integration of the signals in the ^{1}H NMR spectra of **7**·TMPDA indicates an equimolar host:guest ratio of 1:1. Furthermore, the ^{11}B NMR shift at 6.6 ppm prove the coordination of all boron atoms by nitrogen donor functions of the guest (cf. δ(**7**·2Py) = 7.7 ppm). Keeping this in mind, a bridging coordination of two boron atoms of one molecule **7** by one TMPDA in the form of an 1:1 ring adduct formation (cf. **7**·TMPDA in Scheme 4) or, alternatively, ring formation of several **7**·TMPDA units (e.g. 2:2) can be assumed. A more precise distinction cannot be made at this point, as multiple attempts to crystallise this adduct failed so far.

We want to note that host guest experiments of **7** with guest compounds that feature smaller distances between the nitrogen atoms (e.g. pyrimidine, TMEDA) always led to complexation of half of the boryl residues and a dynamic exchange with free Lewis-acidic functions (δ(^{11}B) ~ 15 ppm).



7·2Py **7** **7**·TMPDA

Scheme 4. Host-guest experiments with the bis-batecholatoboryl substituted derivative **7** and pyridine (Py) as monodentate and *N*,*N*,*N*′,*N*′-tetramethylpropanediamine (TMPDA) as a bidentate guest compound.

Conclusion

New synthetic routes for the synthesis of polydentate Lewis-acids based on various organosilane core units were presented. Doubly and triply boryl-substituted PLAs were prepared, whose reactive sites were connected via one central silicon atom. By using ethynyl spacer units and terminal stannylation, rigid ethynyl-bridged PLAs were finally obtained by tin-boron exchange reactions with 2-chloro-benzo[*d*][1,3,2]dioxaborole. The spatial orientation of the Lewis acidic boryl residues of both, **7** and **8**, was proven by X-ray diffraction structural analysis. Furthermore, the easy access to the different silyl core units was exploited using flexible ethyl spacer units as part of the framework for flexible PLA derivatives. Hydroboration of vinylsilanes with 9-BBN led to flexible representatives via the selective formation of anti-Markovnikov products. In host-guest experiments, the suitability of both bidentate PLAs **7** and **11** as receptor systems for neutral guest compounds was proven. So, the pyridine adducts of both Lewis-acids as well as a bridging complex of **7** with the bidentate amine TMPDA was observed.

Experimental Section

Experimental Details: All reactions with oxidation- or hydrolysis-sensitive substances were carried out using standard Schlenk techniques or in gloveboxes under inert nitrogen or argon atmosphere. The solvents used, *n*-pentane and *n*-hexane (both over $LiAlH_4$), were dried by standard methods and freshly distilled before use.

Pyridine (Py) and tetramethylpropylenediamine (TMPDA) were also freshly distilled before use. Dimethyldivinylsilane was purchased from *TCI* chemicals. NMR spectra were recorded using a *Bruker Avance III 500HD* and a *Bruker Avance III 300* spectrometer. The chemical shifts are given in parts per million (ppm), using the residual protons or the carbon signal of the solvent (C_6D_6: ^1H NMR, $\delta = 7.16$ ppm, ^{13}C NMR, $\delta = 128.06$ ppm; $CDCl_3$: ^1H NMR, $\delta = 7.26$ ppm, ^{13}C NMR, $\delta = 77.16$ ppm) as references. For the NMR measurements of heteronuclei external standards were used (^{11}B: $BF_3 \cdot Et_2O$, ^{19}F NMR: $CFCl_3$, ^{29}Si: $SiMe_4$, ^{119}Sn: $SnMe_4$). Elemental analyses were performed using an *HEKAtech EURO EA* instrument.

General procedure for the preparation of ethynyl- and vinylsilanes. Chloromethylsilane was dissolved in *n*-pentane, cooled to 0 °C and ethynyl- or vinylmagnesium bromide solution (both in THF) was added dropwise. The solution was heated to reflux for 16 h, then *n*-pentane (100-200 mL) was added and the mixture was quenched with saturated ammonium chloride solution (50 mL) and water (50 mL). Extraction was carried out with *n*-pentane (2 × 75 mL), the combined organic phases were dried over magnesium sulphate and the solvent was removed by distillation. Fractional distillation gave the corresponding ethynyl- or vinylmethylsilanes. The THF could not be completely removed, so the compounds were obtained as mixtures with THF and were used as such for further experiments.

Diethynyldimethylsilane (3). Yield: 2.33 g, 0.02 mmol (1 eq THF), 53 %. ^1H NMR (500 MHz, $CDCl_3$): 3.74 (m, 4H, THF), 2.48 (s, 2H, CC**H**), 1.85 (m, 4H, THF), 0.38 (s, 6H, C**H**$_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): 94.6 (C**C**H), 86.3 (**C**CH), 68.1 (THF), 25.8 (THF), −0.07 (**C**H$_3$). $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$): −38.8.

Triethynylmethylsilane (4). Yield: 1.83 g, 0.02 mol (5 eq THF), 62 %. ^1H NMR (500 MHz, $CDCl_3$): 3.74 (m, 20H, THF), 2.57 (s, 3H, CC**H**), 1.85 (m, 20H, THF), 0.54 (s, 3H, C**H**$_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): 95.6 (C**C**H), 83.0 (**C**CH), 68.1 (THF), 25.8 (THF), 0.4 (**C**H$_3$). $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$): −64.7.

Methyltrivinylsilane (10). Yield: 0.18 g, 1.4 mol (0.25 eq THF), 38 %. ^1H NMR (500 MHz, C_6D_6): 6.17 (dd, $^3J_{H,H} = 20$ Hz, $^3J_{H,H} = 15$ Hz, 3H, C**H**CH$_2$), 5.98 (dd, $^3J_{H,H} = 15$ Hz, $^3J_{H,H} = 4$ Hz, 3H, CHC**H**$_{cis}$), 5.76 (dd, $^3J_{H,H} = 20$ Hz, $^3J_{H,H} = 4$ Hz, 3H, CHC**H**$_{trans}$), 3.57 (m, 1H, THF), 1.42 (m, 1H, THF), 0.20 (s, 3H, C**H**$_3$). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): 136.2 (**C**HCH$_2$), 133.9 (CH**C**H$_2$), 67.8 (THF), 25.8 (THF), −4.8 (**C**H$_3$). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): −20.5.

Tris(trimethylstannylethynyl)methylsilane (6). Triethynylmethylsilane (**4**, 0.24 g, 2.0 mmol; 5 eq THF) was dissolved in *n*-hexane (30 mL) and dimethylaminotrimethylstannane (1.40 g, 6.72 mmol) was added at room temperature. The solution was stirred at room temperature for 16 h and then all volatiles were removed under reduced pressure to give the stannylated silane **6** (1.21 g, 1.99 mmol, 98 %). ^1H NMR (500 MHz, $CDCl_3$): 0.47 (s, 3H, SiC**H**$_3$), 0.30 (s, 27H, SnC**H**$_3$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): 116.6 (SiC≡**C**), 110.9 (Si**C**≡C), 2.3 (Si**C**H$_3$), −7.5 (Sn**C**H$_3$) ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$): −74.0 ppm. $^{119}Sn\{^1H\}$ NMR (186 MHz, $CDCl_3$): −68.4 ppm.

General procedure for reactions with 2-chloro-benzo[*d*][1,3,2]-dioxaborole. 2-Chloro-benzo[*d*][1,3,2]-dioxaborole (1.1 eq per $SnMe_3$ function) was dissolved in *n*-hexane (1 mL per 0.15 g) and a solution of the stannylated silane (**5**, **6**) in *n*-hexane (**5**: 5 mL) or toluene (**6**: 5 mL) was added at −20 °C. Within 16 h the solution was slowly warmed to room temperature. All volatile substances were removed under reduced pressure. The crude products were dissolved in *n*-hexane (5 mL) and precipitated at −30 °C. The supernatant solution was removed, and the residue was dried in vacuo to give compounds **7** and **8** as colourless solids.

Bis(benzo[*d*][1,3,2]dioxaborol-2-yl)ethynyl)dimethyl-silane (7). Yield: 0.26 g, 0.74 mmol, 94 %. ^1H NMR (500 MHz, $CDCl_3$): 7.26 (dd, $^3J_{H,H} = 7$ Hz, $^4J_{H,H} = 3$ Hz, 4H, Cat**H**), 7.14 (dd, $^3J_{H,H} = 7$ Hz, $^4J_{H,H} = 3$ Hz, 4H, Cat**H**), 0.52 (s, 6H, C**H**$_3$) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): 23.4 ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): 147.7 (Cat**C**O), 123.5 (Cat**C**H), 113.0 (Cat**C**H), 109.2 (Si**C**≡) −0.6 (**C**H$_3$) ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$): −38.0 ppm. Elemental analysis calcd (%) for $C_{18}H_{14}B_2O_4Si_1$ ($M_r = 344.01$): C 62.85, H 4.10; found: C 60.75 H 4.20.

Tris(benzo[*d*][1,3,2]dioxaborol-2-yl)ethynyl)methylsilane (8). Yield: 0.54 g, 1.1 mmol, 82 %. ^1H NMR (500 MHz, $CDCl_3$): 7.27 (dd, $^3J_{H,H} = 7$ Hz, $^4J_{H,H} = 4$ Hz, 6H, Cat**H**), 7.16 (dd, $^3J_{H,H} = 6$ Hz, $^4J_{H,H} = 3$ Hz, 6H, Cat**H**), 0.75 (s, 3H, C**H**$_3$) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): 23.4 ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): 147.6 (Cat**C**O), 123.7 (Cat**C**H), 113.0 (Cat**C**H), 104.2 (Si**C**≡), −0.2 (**C**H$_3$) ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$): −64.9 ppm. Elemental analysis calcd (%) for $C_{25}H_{15}B_3O_6Si_1$ ($M_r = 471.90$): C 63.63, H 3.26; found: C 62.02, H 3.26.

General prodcedure for hydroboration of vinylsilanes. Vinylsilane 9 or 10 (0.72 g, 6.4 mmol; for 10 0.25 eq THF) was dissolved in *n*-hexane, degassed three times by freeze-pump-thaw and mixed with 9-BBN solution (0.5 M in THF, 1.0 eq per vinyl residue). The solution was stirred at room temperature for 16 h before the solvent was removed under reduced pressure. The residue was dissolved in *n*-hexane and product 10 or 12 recrystallized at −80 °C. The supernatant solution was removed, and the residue dried under vacuo, yielding the hydroborated silanes 10 or 12, respectively.

Bis(2-(9-borabicyclo[3.3.1]non-9-yl)ethyl)-dimethylsilane (11). Yield: 0.10 g, 0.28 mmol, 12 %. ^1H NMR (300 MHz, C_6D_6): 1.93-1.65 (m, 24H, **H**-BBN), 1.40 (m, 4H, SiCH$_2$C**H**$_2$), 1.22 (m, 4H, **H**-BBN), 0.68 (m, 4H, SiC**H**$_2$CH$_2$), 0.13 (s, 6H, C**H**$_3$) ppm. ^{11}B NMR (96 MHz,

Table 3. Crystal data for compounds **6**, **7**, **8** and **11**·2Py.

compound	**6**	**7**	**8**	**11**·2Py
Empirical formula	$C_{16}H_{30}SiSn_3$	$C_{18}H_{14}B_2O_4Si$	$C_{28}H_{17}B_3O_6Si$	$C_{32}H_{52}B_2N_2Si$
M_r	606.56	344.00	528.93	514.46
Temperature/K	140.0(1)	100.0(1)	100.0(1)	100.0(1)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$C2/c$	$I2/a$	$P\bar{1}$	$C2/c$
a/Å	15.9607(4)	11.7052(3)	6.9580(1)	8.8947(3)
b/Å	11.5014(3)	5.1794(1)	12.9622(2)	17.0941(7)
c/Å	27.4482(7)	27.3493(6)	15.2109(2)	20.6242(8)
α/°	90	90	71.054(2)	90
β/°	106.368(3)	93.983(2)	82.520(2)	99.879(4)
γ/°	90	90	81.761(2)	90
Volume/Å^3	4834.5	1654.07(6)	1279.04(4)	3089.3(2)
Z	8	4	2	4
ρ_{calc}/g cm^{-3}	1.667	1.381	1.373	1.106
μ/mm^{-1}	3.118	1.426	0.142	0.099
F(000)	2320.0	712.0	542.0	1128.0
Crystal size/mm^3	0.29×0.11×0.08	0.40×0.22×0.02	0.30×0.24×0.12	0.40×0.32×0.06
λ/Å	0.71073	1.54184	0.71073	0.71073
2Θ range/deg	4.9 to 70.0	6.5 to 152.3	5.0 to 90.4	4.0 to 64.4
Index ranges h	−25 to 25	−12 to 14	−13 to 13	−13 to 13
Index ranges k	−18 to 28	−6 to 6	−25 to 25	−25 to 25
Index ranges l	−44 to 44	−34 to 34	−30 to 30	−29 to 30
Reflections collected	70424	17197	141731	16381
Indep. reflections	10638	1741	21162	5645
R_{int}	0.0496	0.0541	0.0416	0.0359
Refl. [$I > 2\sigma(I)$]	8933	1603	16812	4708
Data/param	10638/191	1741/142	21162/448	5645/170
GooF on F^2	1.260	1.057	1.086	1.069
R_1/wR_2 [$I > 2\sigma(I)$]	0.0519/ 0.0969	0.0358/ 0.0983	0.0447/0.1295	0.0500/ 0.1411
R_1/wR_2 [all data]	0.0645/ 0.1008	0.0383/ 0.1015	0.0594/ 0.1384	0.0605/ 0.1455
$\rho_{fin\ min/max}$/e Å^{-3}	2.16/−2.09	0.38/−0.30	0.66/−0.26	0.38/−0.22
CCDC–No.	2085640	2085641	2085642	2085643

C_6D_6): 86.2 ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): 33.7 (**C**-BBN), 31.5 (B**C**-BBN), 23.7 (**C**-BBN), 20.5 ($SiCH_2$**C**H_2), 7.2 (Si**C**H_2CH_2), −3.6 (**C**H_3) ppm. $^{29}Si\{^1H\}$ NMR (60 MHz, C_6D_6): 6.4 ppm. Elemental analysis calcd (%) for $C_{22}H_{42}B_2Si$ (M_r = 356.28): C 74.14, H 11.88; found: C 74.98, H 12.59.

Tris(2-(9-borabicyclo[3.3.1]non-9-yl)ethyl)-dimethylsilane (12). Yield: 0.46 g, 0.95 mmol, 66 %. ^1H NMR (500 MHz, C_6D_6): 1.94-1.80 (m, 24H, **H**-BBN), 1.75 (m, 12H, **H**-BBN); 1.49 (m, 6H, $SiCH_2C$**H**$_2$), 1.24 (m, 6H, **H**-BBN), 0.82 (m, 6H, SiC**H**$_2CH_2$), 0.21 (s, 3H, C**H**$_3$) ppm. ^{11}B NMR (96 MHz, C_6D_6): 86.3 ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): 33.7 (**C**-BBN), 31.5 (B**C**-BBN), 23.7 (**C**-BBN), 20.6 ($SiCH_2$**C**H_2), 5.5 (Si**C**H_2CH_2), −5.5 (**C**H_3) ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): 9.2 ppm. Elemental analysis calcd (%) for $C_{31}H_{57}B_3Si$ (M_r = 490.31): C 75.94, H 11.72; found: C 74.65, H 11.74.

Bis(2-(9-borabicyclo[3.3.1]non-9-yl)ethyl)-dimethylsilan·pyridine (11·2Py). Bis-Lewis-acid **11** (0.06 g, 0.2 mmol) was dissolved in chloroform (2 mL) and pyridine (0.03 g, 0.4 mmol, 28 μL) was added. The solution was stirred for 10 min and the solvent removed in vacuo. The crude product was washed with *n*-hexane (1 mL) and dried in vacuo to give **11**·Py (0.05 g, 0.1 mmol, 59 %) as a colourless solid. ^1H NMR (300 MHz, C_6D_6): 8.17 (s, 4H, Py**H**$_{ortho}$), 6.74 (s, 2H, Py**H**$_{para}$), 6.46 (s, 4H, Py**H**$_{meta}$), 2.50-1.90 (m(br), 18H, **H**-BBN), 1.61 (s(br), 6H, **H**-BBN), 1.31 (s(br), 4H, **H**-BBN), 0.65 (m, 4H, $SiCH_2C$**H**$_2$) 0.06 (s, 6H, C**H**$_3$), 0.01 (m, 4H, SiC**H**$_2CH_2$) ppm. ^{11}B NMR (96 MHz, C_6D_6): 1.78 ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): 145.5 (Py**C**$_{ortho}$), 137.7 (Py**C**$_{para}$), 124.7 (Py**C**$_{meta}$), 35.8 (**C**-BBN), 32.2, 29.7, 26.2, 25.7, 8.2 (Si**C**H_2CH_2), −3.1 (**C**H_3) ppm. ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): 4.3 ppm. Elemental analysis calcd (%) for $C_{32}H_{52}B_2Si$ (M_r = 514.49): C 74.71, H 10.19, N 5.45; found: C 75.11, H 10.46, N 5.45.

Host guest NMR-scale experiments of 7

Bis-Lewis-acid **7** was dissolved in $CDCl_3$ (0.5 mL) in an NMR tube and pyridine (2 eq) or TMPDA (1 eq) was added.

Bis(benzo[*d*][1,3,2]dioxaborol-2-yl)ethynyl)dimethyl-silane·pyridine (7·2Py). ^1H NMR (500 MHz, $CDCl_3$): 8.85 (dt, $^3J_{H,H}$ = 5 Hz, $^4J_{H,H}$ = 2 Hz, 4H, Py**H**$_{ortho}$), 8.08 (tt, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 2 Hz, 2H, Py**H**$_{para}$), 7.65 (m, 4H, Py$_{meta}$), 6.83 (dd, $^3J_{H,H}$ = 6 Hz, $^4J_{H,H}$ = 3 Hz, 4H, Cat**H**), 6.75 (dd, $^3J_{H,H}$ = 6 Hz, $^4J_{H,H}$ = 3 Hz, 4H, Cat**H**), 0.31 (s, 6H, C**H**$_3$) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): 7.7 ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): 150.5 (**C**O), 143.6 (PyC$_{ortho}$), 142.6 (PyC$_{para}$), 126.1 (PyC$_{meta}$), 120.1 (CatCH), 110.6 (CatCH), 102.2 (Si**C**≡), 0.6 (**C**H_3) ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$): −41.7 ppm.

Bis(benzo[*d*][1,3,2]dioxaborol-2-yl)ethynyl)dimethyl-silane·*N*,*N*,*N'*,*N'*-tetramethyl-1,3-propanediamine (7·TMPDA). ^1H NMR (500 MHz, $CDCl_3$): 6.68 (dd, $^3J_{H,H}$ = 6 Hz, $^4J_{H,H}$ = 3 Hz, 4H, Cat**H**), 6.74 (dd, $^3J_{H,H}$ = 6 Hz, $^4J_{H,H}$ = 3 Hz, 4H, Cat**H**), 2.83 (s, 4H, NC**H**$_2$), 2.47 (s, 12H, NC**H**$_3$), 2.15 (s, 2H, NCH_2C**H**$_2$), 0.29 (s, 6H, SiC**H**$_3$) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): 6.6 ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): 151.4 (**C**O), 119.7 (Cat**C**H), 109.9 (Cat**C**H), 101.9 (Si**C**≡), 56.4 (br, TMPDA), 43.8 (br, TMPDA), 0.6 (**C**H_3) ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$): −42.2 ppm.

Crystal structure determinations. Suitable crystals were obtained by slow evaporation of saturated solutions of 1,2-difluorobenzene (**6**, **8**) or dichloromethane (**7**, **11**·2Py). They were coated with paratone-N oil, mounted on glass fibre and transferred onto the goniometer and into the nitrogen stream of the diffractometer. Data collection were performed on Supernova using monochromated Cu–Kα or Mo–Kα radiation. Using Olex2,[25] the structures were solved with the *ShelXT*[26] structure solution program using Intrinsic Phasing and refined with the *ShelXL*[27] refinement package using Least Squares minimisation without restraints. Table 3 contains crystallographic details for the individual compounds **6**, **7**, **8** and **11**·2Py.

Deposition Numbers 2085640 (for **6**), 2085641 (for **7**), 2085642 (for **8**), and 2085643 (for **11**·2Py) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Boron · Complexation · Host systems · Poly-Lewis acids · Tin-boron exchange

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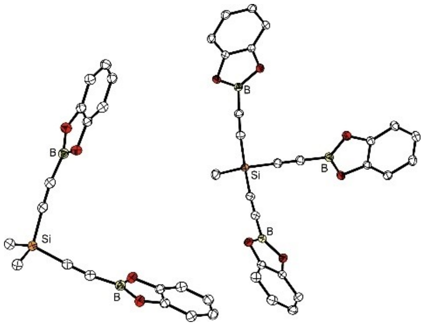
Bis- and tris-Lewis acids, based on alkynylsilanes with terminal boron functions, were prepared and tested for their ability to accept neutral Lewis base molecules.



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Silicon-Bridged Bi- and Tridentate Lewis Acidic Host Systems