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Hexadentate Poly-Lewis Acids Based on 1,3,5-Trisilacyclohexane

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Dedicated to Professor Hansgeorg Schnöckel on the Occasion of his 80th Birthday.

We report the preparation of hexadentate poly-Lewis acids (PLA) based on 1,3,5-trisilacyclohexane backbones bearing two alkynyl groups attached to each of the silicon atoms. A rigid hexadentate PLA bearing six Lewis-acidic catecholatoboryl-substituents was prepared by a tin-boron exchange reaction. Its structure, determined by X-ray diffraction, is the first of a Lewis-acid-functionalised donor-free trisilacyclohexane. Flexible hexadentate PLA were prepared by hydroboration or hydrosilylation of hexavinyltrisilacyclohexane, resulting in PLA with six 9-BBN, $SiCl_3$, $SiCl_2Me$ or $SiClMe_2$ groups. The Lewis-acidity of the last one was increased by conversion with silver triflate, resulting in a PLA with six highly acidic silyl triflate groups attached to the 1,3,5-trisilacyclohexane unit as $TfOSiMe_2$-C_2H_4- groups. Host-guest experiments of the above PLA demonstrated the suitability of the flexible representatives for complexation of neutral Lewis-based guest molecules under formation of 1:6 adducts (host: guest).

Introduction

The first complexations of cations by crown ethers[1] and cryptants[2] have boosted the interest in the field of host-guest chemistry,[3] a subcategory of supramolecular chemistry. Crown ethers and cryptants represent examples of poly-Lewis bases. Their conceptual counterpart are poly-Lewis acids (PLA). These are molecules with at least two Lewis-acidic atoms linked by a backbone that is usually organic and free of donor functions.[4] PLA find applications in the complexation of small, neutral or anionic Lewis-basic guest molecules.[5] The complexation properties of PLA crucially depends on the organic backbone, because this determines the spatial orientation and distance between the Lewis acidic atoms. PLA with a rigid backbone and a defined distance between the reactive atoms can be obtained by direct multiple metalation of various types of compounds, including aromatic compounds such as benzenes,[6] biphenylenes, naphthalenes[7] or methanes.[8] Examples of poly-Lewis acids based on these four classes of molecules are bis- and tris(dimethylgallyl)benzenes[6a] or a series 9,10-diboraanthracene derviatives, the 1,8-bis(dimesitylboryl)-biphenylene[5a] and the dialuminium compounds that are bridged by a methylene $((Me_3Si)_2HC)_2AlCH_2Al(CH(SiMe_3))_2$[8a] or dicarboxynaphthalene units.[7] Some of these representatives were successfully used in the molecular recognition for chelating complexation of small anions (e.g. halides,[6b] cyanide,[5a] nitrate[8a]) and neutral guest molecules (e.g. dimethyl sulphoxide,[8d] pyridazine[8c]), catalytical[6d; 9] or optical applications.[6e,f]

More complex backbones are derived from anthracenes,[10] trypticenes[11] or tribenzotriquinacenes[12] and were often combined with spacer units like alkyne and vinyl groups. The use of terminal alkyne units also leads to rigid frameworks. Functionalisation of the alkyne groups with Lewis-acidic (semi-)metals can be easily achieved by alkane[13] and salt elimination reactions.[14] In these processes, the rigid properties of the triple bond and the backbone are retained. The results are defined distances between the Lewis acid atoms. In this context, some work in the field of anthracenes has already shown promising results.[10] Boryl- and gallyl-substituted 1,8-anthracenes are capable of complexing amine derivatives, demonstrated by the selective 1:1-adduct formation with tetramethylethylenediamine (TMEDA) and pyrimidine.[10b]

Backbones with higher flexibility can be generated with ethyl- or vinyl spacer units. Hydrometallation reactions, i.e. the formal additions of element hydrides to alkyne or vinyl functions, respectively, offer a straightforward approach under reduction.[15] Hydrometallation reactions also allow regioselective metalations and result in the formation of PLA with (semi-)flexible backbones in high yields.[15a,b;16] Owing to the flexibility of the corresponding PLA, the distances between the Lewis-acid atoms can vary within a certain range.

We have also reported some PLA on the basis of 1,3,5-trisilacyclohexanes.[17] Initially, the preparation of trisilacyclohexanes required harsh conditions and yields were poor.[18] Later, Kriner *et al.* established a synthetic protocol based on the cyclisation of (chloromethyl)silanes affording substituted 1,3,5-trisilacyclohexanes in good yields.[19] The two acyclic substituents at the silicon atoms can occupy either the axial or the

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equatorial position. If they are different, regioisomers of the molecule occur.[17] For the *all-cis*-isomer, the same residues occupy the same position (e.g. *all*-axial).

all-cis-Substituted 1,3,5-trisilacyclohexanes were synthesized by substituting the silicon sites with phenyl residues as well as alkyne units.[17a] Due to their lower steric demand compared to the phenyl substituent, the alkyne units occupy the axial positions of the heterocycle, giving them the same spatial orientation. With this substitution pattern on the backbone, some PLA with *all*-axially directed boryl- and gallyl-functions have already been synthesised by metalations of the alkynes described above.

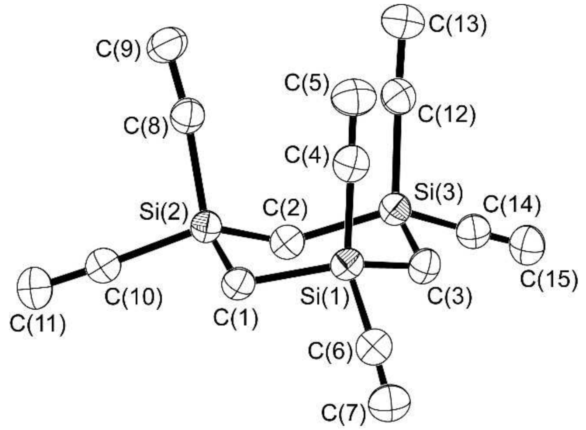


Figure 1. Molecular structure of **3** in the single crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and second molecule are omitted for clarity. Selected distances [Å] and angles [°]: Si(1)–C(1) 1.861(2), Si(1)–C(3) 1.859(2), Si(1)–C(4) 1.822(3), Si(1)–C(6) 1.839(3), Si(2)–C(1)1.858(2), Si(2)–C(2) 1.870(2), Si(2)–C(8) 1.821(3), Si(2)–C(10) 1.834(3), C(1)–Si(1)–C(3) 111.8(1), C(1)–Si(2)–C(2) 109.4(1), C(2)–Si(3)–C(3) 109.1(1), Si(1)–C(1)–Si(2) 116.5(1), Si(1)–C(3)–Si(3) 116.7(1), Si(2)–C(2)–Si(3) 113.5(1), C(4)–Si(1)–C(6) 108.1(1), C(8)–Si(2)–C(10) 103.5(1), C(12)–Si(3)–C(14) 104.4(1), Si(1)–C(4)–C(5) 180.0(3), Si(1)–C(6)–C(7) 177.1(3), Si(2)–C(8)–C(9) 173.4(3).

Results and Discussion

The trisilacyclohexane backbone was prepared via the cyclisation of chloromethyl(trimethoxy)silane in a Grignard-type reaction. The use of methoxy protecting groups leads to a preferential formation of the cyclic trimer,[19a] instead of disilacyclobutanes or larger partially branched ring systems and oligomers. Deprotection with boron trichloride[20] afforded the hexa-chlorinated trisilacyclohexane **1**. This provides the basis for a hexadentate backbone for PLA synthesis. Alkyne spacer groups were introduced by reacting **1** with ethynylmagnesium bromide. These reactions required nine days under conventional reflux conditions but could be accelerated to only three days by carrying out the reaction in a closed ampoule under overpressure.

The identity of compound **3** was proven by multinuclear NMR spectroscopy as well as by CHN analysis. The proton NMR spectrum shows the signals for the methylene bridge (0.46 ppm) and the alkyne protons (2.03 ppm). The complete functionalisation by ethynyl groups and the resulting C_{3v} symmetry of product **3** follows from the integral ratio (6:6) and the multiplicity (s) of the signal of the methylene bridge. By contrast, asymmetrically substituted trisilacyclohexanes show this signal in the form of two doublets due to geminal coupling.[17]

Single crystals suitable for structure elucidation by X-ray diffraction were obtained by slowly concentrating an *n*-hexane solution of **3**. Its structure is presented in Figure 1. In the crystal there are two molecules per asymmetric unit, both ones adopt an armchair conformation, with clearly distinguishable axial and all equatorial substituents. The Si–C$_{alkyne}$ distances for the substituents in axial positions are shorter by ~1–2% compared to those to the equatorial substituents. Short distances are found between the terminal axial carbon atoms (C(5)/C(9)/C(13), 3.934(4)–4.448(4) Å, C(20)/C(24)/C(28), 3.800(4)–4.525(4) Å), which should carry the Lewis acidic functions in the desired PLA. This is in the same order of magnitude as alkyne distances of an *all*-axial ethynyltrisilacyclohexane (d(C–C): 3.754(3)–4.572(3) Å) bearing phenyl residues in the equatorial position.[17a] As expected, the corresponding carbon atoms in equatorial position (C(7)/C(11)/C(15)) have significantly larger distances of 7.738(4) to 8.139(4) Å to one each other. These are comparable to distances of the trisilacyclohexane derivative *cyclo*-(–Si(CCH)(CH$_3$)–CH$_2$–)$_3$ with all alkyne groups in equatorial positions (d(C–C): 7.648(1) to 7.849(1) Å).[17b] Molecule **3** is deformed (for full structure of the asymmetric unit see S.I.), resulting in large deviations in the distances of the terminal carbon atoms of the alkyne units from each other, especially between the axial substituents (from 3.934(4) to 4.448(4) Å). This deformation affects the angles of the alkynes, albeit to a much lesser extent. These vary in a range from Si(1)–C(4)–C(5) 180.0(3) to Si(2)–C(8)–C(9) 173.4(3)°.

Alternatively, the synthesis of backbone **3** can also be carried out via a TMS-protected alkyne unit following an earlier described procedure for tetraalkynylsilane.[21] In this way, silane **2** was obtained by reaction with lithiated TMS acetylene in 70% yield. Single crystals for a structural analysis grew by slow evaporation of an acetone solution of **2** (see Table 1 and SI). Due to strong disorder, no discussion of the obtained structure is given here. Deprotection of the alkyne using trifluoromethanesulfonic acid afforded product **3** in only 42% yield (total yield over both steps: 29%; compare: the yield using the "Grignard route" was 52%).

Metalations of terminal alkyne groups are usually carried out by deprotonation with lithium organyls followed by reactions with element halides and salt elimination.[14c] However, due to the limited solubilities of multi-lithiated compounds, this approach proved impractical in the present case. Attempts to react the hexaalkyne **3** with gallium organyls under alkane elimination[10a] also resulted in incomplete conversions and product mixtures, probably due to the aggregation of the partially metallated compounds and the resulting limited solubilities.

Tin-boron exchange reactions represent a good alternative for the generation of Lewis-acid functions on alkyne groups.[22]

Using the stannylation reagent dimethylamino-trimethylstannane[23] the sixfold substitution of the alkyne hydrogen atoms by trimethylstannyl groups under dimethylamine elimination afforded compound **4** in very good yields of 90 %.

The reaction of **4** with chlorocatecholatoborane gave the hexadentate poly-Lewis acid **5** in quantitative yield with elimination of trimethylchlorostannane. Compound **5** was characterised by CHN analysis and multinuclear NMR spectroscopy. It is surprisingly well soluble in benzene and halogenated hydrocarbons (e.g. dichloromethane, chloroform). Its ^{1}H NMR spectrum reflects the symmetry of the compound in a simple signal set for the catecholato groups and-analogous to the previously described compounds - a singlet for the methylene bridge at 0.84 ppm. The ^{11}B NMR resonance at 22.0 ppm falls within the characteristic shift range for such substituted boranes.[10b] As a consequence of the coupling to the ^{10}B and ^{11}B quadrupole nuclei, the signal of the boryl-substituted alkyne carbon atom is not observable in the ^{13}C NMR spectrum.

Single crystals for structure analysis by X-ray diffraction were grown by slowly concentrating a chloroform solution of **5**. The solid-state structure in Figure 2 is the first adduct-free molecular structure of a Lewis acid-functionalised trisilacyclohexane. Analogous to the structure of backbone **3**, **5** features an armchair structure of the central ring and axially as well as equatorially aligned alkyne groups. All bond lengths and angles at the silicon atoms of **5** show minor deviations from the values of **3** (Figure 1). The lengths of the C≡C triple bonds (1.195(6) to 1.219(6) Å) of the spacers are also unaffected by the substitution. The distances of the terminal alkyne carbon atoms (C(13)/C(29)/C(45)) show only slight deviations from one another (3.745(5)–3.808(5) Å); they are below all corresponding distances in **3** (smallest distance: C(9)–C(13) 3.934(4) Å, C(24)–C(28) 3.800(4) Å), despite the increased steric requirements of the boryl substituents at the alkyne units. Planar coordination environments are found for the boron atoms, so that the whole catecholatoborylalkyne substituents are approximately planar (angular sum sat all boron atoms is 360(1)°). The axial boron atoms (B(2)/B(4)/B(6)) show only little variance in their respective distances (4.043(6)–4.095(5) Å) from each other, spanning an equilateral triangle with an area of about 7.2 Å^{2}. The distance between the equatorial boron atoms (9.417(6)–10.431(6) Å) is significantly larger, forming a larger triangle (~43.6 Å^{2}). There are no unusual intermolecular interactions between the molecules of **5** in the solid state.

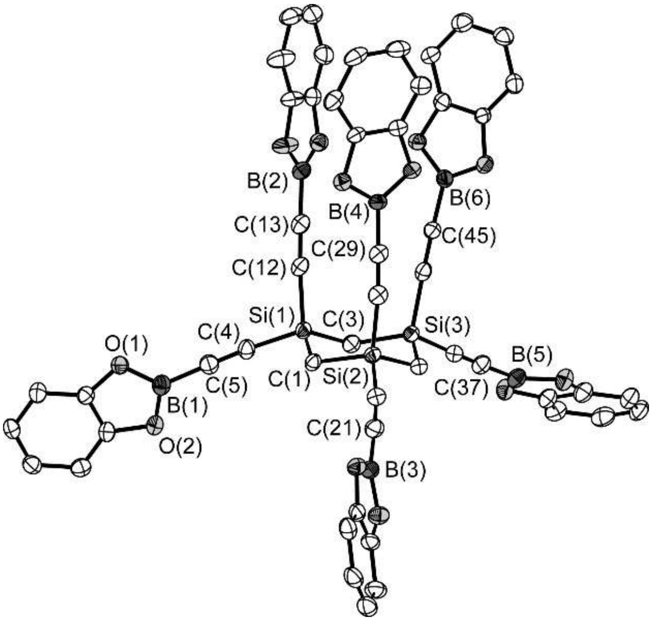
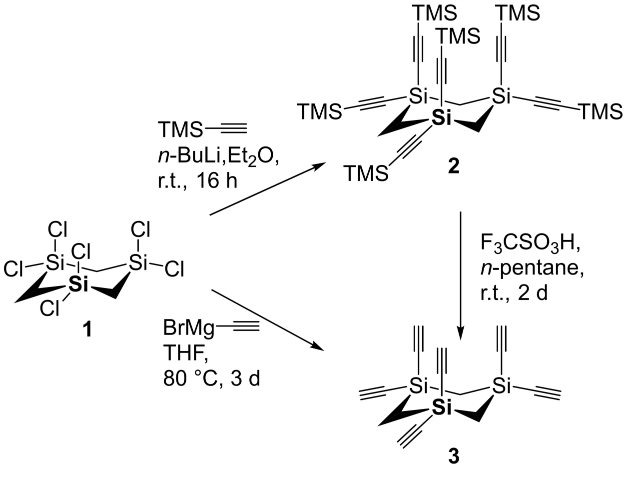


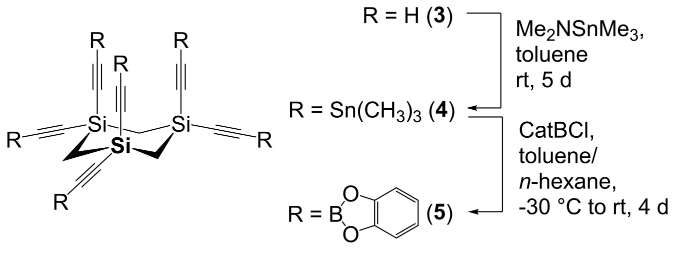
Figure 2. Molecule structure of PLA **5** in the single crystal. Displacement ellipsoids are shown at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Si(1)–C(1) 1.866(4), Si(1)–C(3) 1.859(3), Si(1)–C(4) 1.839(4), Si(1)–C(12) 1.830(4), B(1)–B(3) 9.417(6), B(1)–B(5) 10.407(6), B(3)–B(5) 10.431(6), B(2)–B(4) 4.092(6), B(2)–B(6) 4.095(5), B(4)–B(6) 4.043(6), C(13)–C(29) 3.808(5), C(13)–C(45) 3.785(5), C(29)–C(45) 3.745(5), C(5)–C(21) 7.533(5), C(5)–C(37) 7.932(2), C(21)–C(37) 7.985(6), C(1)–Si(1)–C(3) 109.6(2), Si(1)–C(1)–Si(2) 115.0(2), C(4)–C(5)–B(1) 175.9(4), C(12)–C(13)–B(2) 175.5(4).

Analogous substitution experiments with haloboranes, which are clearly more Lewis acidic than chlorocatecholborane (e.g.: $ClB(C_6F_5)_2$, $ClBPh_2$, $BrBMe_2$), using the model system $Me_3SnC{\equiv}CSiMe_3$ did not lead to the desired exchange reactions, and always resulted in mixtures. Neither experiments under thermodynamic control (starting from −78 °C and slowly warming to r.t.) nor under application of the less acidic triphenylphosphane adducts[24] of the boranes allowed the isolation of the corresponding Si–C≡C–B compounds. Presumably, the increased acidity is at the expense of selectivity of the reaction. Therefore, we refrained from transferring these experiments to sixfold substitution reactions of **4**.

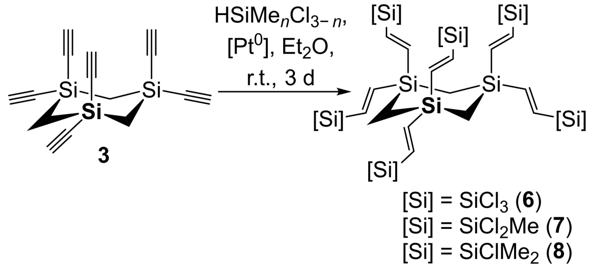
Hydrosilylation reactions can stereoselectively convert alkynes into the slightly more flexible, silylated vinyl groups.[15a,b;16] Reactions of **3** with various chlorosilanes using the Karstedt catalyst system produced the corresponding sixfold hydrosilylated compounds **6**–**8** (Scheme 3). In the ^{1}H NMR spectra, the doublets for the vinylic protons show in all cases a coupling constant of 22 Hz due to the selective formation of the *all-trans*-isomers.



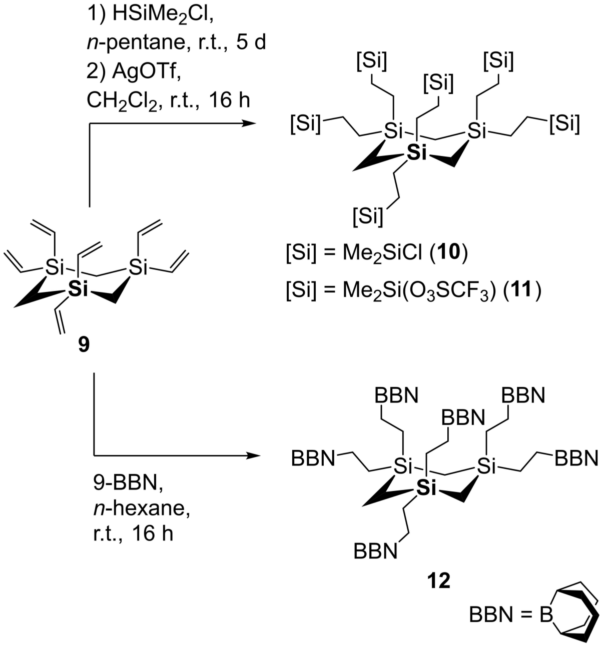
Scheme 1. Preparation of the backbone via reaction of **1** with lithiated TMS-acetylene (→**2**) and subsequent deprotection to **3** or with ethynylmagnesium bromide (→**3**).



Scheme 2. Stannylation of the backbone (**3**→**4**) followed by tin-boron exchange to give the hexadentate dioxaborole-substituted PLA **5**.



Scheme 3. Hydrosilylation of the backbone **3** with various chlorosilanes ($n = 1–3$) to give the *all*-trans products **6**–**8**.



Scheme 4. Lewis-acidic functionalisation of hexa-vinyltrisilycyclohexane **9** by hydrosilylation (→**10**) and subsequent substitution of the chloride by triflate (→**11**) as well as hydroboration with 9-BBN (→**12**).

Under analogous conditions, hydrosilylation was carried out with chlorodimethylsilane on 1,1,3,3,5,5-hexavinyl-1,3,5-trisilacyclohexane (**9**), which was prepared according to a synthetic route (Scheme 4) earlier established in our group.[20]

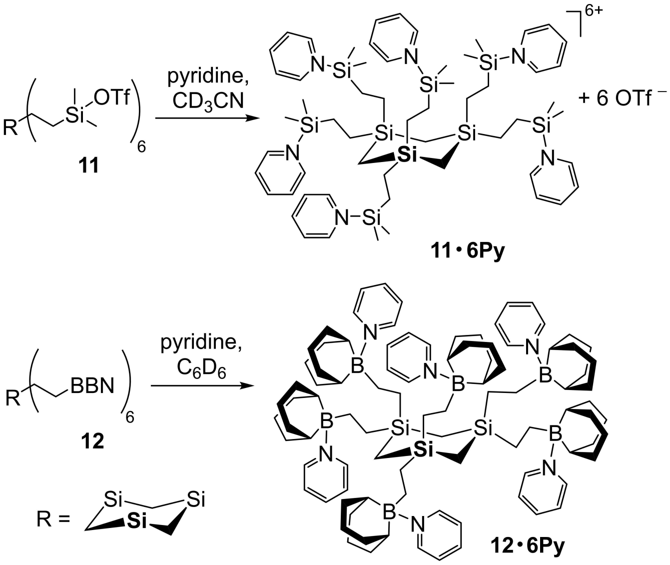
In this way, the terminally silylated, ethyl-bridged PLA **10** was obtained in multimilligram scale. Using the Karstedt catalyst led to regioselective addition in *anti*-Markovnikov position.[15b] Attempts to achieve an increased acidity of the peripheral silicon atoms (for the purpose of complexing neutral Lewis-based guest molecules) by fluorination with antimony trifluoride proved to be of limited success.[15b] Consequently, we looked for an alternative way to increase the reactivity of the corresponding silicon atoms towards neutral donor molecules. For this purpose, PLA **10** was reacted with silver triflate, which leads to a substitution of the chloride by triflate groups. This results in the formation and isolation of PLA **11**, which is an extremely hydrolysis-sensitive compound. The chloride/triflate substitution can be followed by NMR spectroscopy; the resonances of the silicon atoms and all protons in the immediate vicinity receive a clear low-field shift (Table 1). The chemical shifts found for **11** are in excellent agreement with those of trimethylsilyl triflate (Me_3SiOTf).[25] It is therefore to be expected that PLA **11** has an acidity and reactivity towards neutral guest molecules comparable to Me_3SiOTf.

Hydroboration of the vinyl-trisilacyclohexane **9** with 9-borabicyclo[3.3.1]nonane (9-BBN) additionally yielded the hexadentate, flexible, boryl-substituted PLA **12**. By double recrystallization from *n*-hexane at −30 °C, the hydrolysis product of 9-BBN could be removed, providing PLA **12** as a colourless solid. Due to the sterically demanding unit at the boron atom, the hydroboration without catalyst selectively takes place in *anti*-Markovnikov-position.[26] The complete and selective reaction can also be followed by ^1H NMR spectroscopy. The methylene protons of the trisilacyclohexane ring in **12** produce a singlet at 0.04 ppm for symmetry reasons. The ^{13}C NMR spectrum shows the characteristic weak intensity for the signal of the boryl-substituted carbon atom of the ethylene bridge at 20.7 ppm. The ^{11}B NMR resonance at 86 ppm is characteristic for such boranes.[27] Compared to PLA **5** ($\delta(^{11}B) = 22$ ppm), this corresponds to a strong low-field shift, which is expected, because of the donating oxygen atoms present in **5**.

In order to explore the ability to bind various bases in the sense of host-guest chemistry, the hexadentate PLA **5**, **11** and **12** were reacted with monodentate, neutral, Lewis-base guests on the NMR scale. For PLA **11**, the complexations of both pyridine (**Py**; see Scheme 5) and 1,2-dimethylimidazole (**Imi**) with formation of a hexacationic species can be observed in the NMR experiment. Due to the electron-withdrawing character of the silyl group, some significant changes of the ^1H NMR chemical shifts of all signals for the guests as well as for the CH_3 or CH_2 groups at the peripheral silicon atom to lower field were observed. The shifts in the fluorine NMR spectra, the signals for the triflate groups at −79.1 ppm (**11·6Py**) and −79.2 ppm (**11·6Imi**), respectively, indicate the presence of free triflate

Table 1. Selected ^{29}Si and ^1H NMR shifts of the hydrosilylated trisilacyclohexane **10**, the triflate substituted product **11**, and trimethylsilyl triflate[25] for comparison (solvent: dichloromethane-d_2).

Compound	$Si_{term.}$	$CH_2Si_{term.}$	$CH_2CH_2Si_{term.}$	$CH_3Si_{term.}$
10	33.0	0.71	0.57	0.42
11	44.3	0.79	0.57	0.48
Me_3SiOTf	44.1	–	–	0.50



Scheme 5. Host-guest-reactions of flexible PLA **11** and **12** and monodentate guest pyridine with formation of the corresponding.

anions[28] resulting from a substitution by the base molecules. In contrast, large differences in the ^{29}Si NMR shifts were observed for the adducts of these two guests. Owing to the stronger donation capability of imidazole, a significantly stronger high-field shift of the signal for the exocyclic silicon atom is found for **11·6Imi** (24.9 ppm vs. 44.3 ppm in **11**) than for the corresponding pyridine adduct **11·6Py** (41.0 ppm).

The complexation of six pyridine molecules can also be observed for PLA **12** in the NMR experiments (Scheme 5). In contrast to **11·6Py**, the ^{1}H NMR signals of the acid **12** are strongly highfield-shifted ($\Delta\delta > 0.8$ ppm) due to the addition of the pyridine and the associated electron donation. Correspondingly, the ^{11}B NMR spectrum shows a strongly broadened signal for the adduct (0.3 ppm vs. 85.8 ppm for **11**), which is within the expected shift range for comparable substituted R_3B–N adducts.[29] Experiments on the complexation of imidazole (**Imi**) with **12** only led to very strong broadening of all NMR signals, so that complexation could not be proven beyond doubt in this case. Additional host-guest experiments with triazacyclononane as a tridentate, "crown-ether-like" guest showed no reactivity of either PLA **11** or **12** towards this tertiary amine.

Although B(cat)-substituted poly-alkynyl compounds are known to serve as suitable receptor systems for various neutral Lewis bases (e.g. pyridine, pyrimidine),[10b;14c] conversion of **5** with pyridine led to a complete decomposition of the hexadentate poly-Lewis acid.

Conclusion

A rigid backbone for hexadentate poly-Lewis acids (PLA) was synthesized by sixfold substitution of trisilacyclohexane with ethynyl-groups. Six Lewis-acidic boryl functions were introduced by stannylation of the alkyne groups followed by a tin-boron exchange. The molecular structure in the single crystal of this hexadentate catecholatoboryl-substituted PLA represents the first structure of a donor free, Lewis-acidic functionalised trisilacyclohexane. Hexadentate flexible backbones based on trisilacyclohexanes were prepared, bearing strongly acidic silyltriflate substituents or 9-BBN groups. The host properties of both the silyltriflate- and 9-BBN functionalised derivatives were evaluated in NMR-scale experiments. Both are capable of complexing neutral, Lewis-based guest molecules (pyridine, 1,2-dimethylimidazole) while affording the corresponding host-guest adducts. In contrast the rigid species **5** was not amenable to host-guest experiments, since decomposition was observed in all attempts. A complexation of a tridentate guest species could not be achieved so far.

Experimental Section

Synthesis

All reactions with oxidation or hydrolysis sensitive substances were carried out using standard Schlenk technique or in gloveboxes under inert nitrogen or argon atmosphere. The solvents used *n*-pentane, *n*-hexane (both via $LiAlH_4$), toluene (sodium), diethyl ether ($LiAlH_4$), THF (potassium), dichloromethane (CaH_2) were dried by common methods and freshly distilled before use. Pyridine and 1,2-dimethylimidazole were also freshly distilled before use. NMR spectra were recorded using the *Bruker Avance III 500HD* spectrometer. The shift is given in ppm (parts per million), using the residual protons and the carbon signal of the solvent (C_6D_6: ^{1}H NMR, $\delta =$ 7.16 ppm, ^{13}C NMR, $\delta = 128.06$ ppm; CD_3CN: ^{1}H NMR, $\delta = 1.94$ ppm, ^{13}C NMR, $\delta = 118.26$ ppm, 1.32 ppm; $CDCl_3$: ^{1}H NMR, $\delta = 7.26$ ppm, ^{13}C NMR, $\delta = 77.16$ ppm) or external standards (^{11}B: $BF_3 \cdot Et_2O$, ^{19}F NMR: $CFCl_3$, ^{29}Si: $SiMe_4$, ^{119}Sn: $SnMe_4$) as references. Elemental analyses were carried out using a *HEKAtech EURO EA* instrument (too low carbon values due to the formation of silicon[30] or boron carbide).

1,1,3,3,5,5-Hexakis(trimethylsilylethynyl)-1,3,5-trisila-cyclohexane (2). Trimethylsilylacetylene (0.35 mg, 3.5 mmol) was dissolved in diethyl ether (30 mL) and *n*-butyllithium (in hexanes, 1.6 M, 1.8 mL, 2.8 mmol) was added at −50 °C. The solution was first kept at 0 °C for 90 min before being stirred at room temperature for 2 h. Then silane **1** (0.12 g, 0.35 mmol) dissolved in diethyl ether (3 mL) was added and the reaction was stirred at room temperature for 16 h. Dist. water (100 mL) was added to the mixture, then extracted with *n*-pentane (3×25 mL) and the combined organic phases were dried over magnesium sulphate. After removal of the solvent, **2** (0.18 g, 0.25 mmol, 70 %) was obtained as a colourless, crystalline solid.–^{1}H NMR (500 MHz, C_6D_6): $\delta = 0.82$ (s, 6H, Si–CH_2), 0.13 (s, 54H, Si($\mathbf{CH_3}$)$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): $\delta = 116.4$ (**C**–$SiCH_3$)$_3$), 110.7 (H_2C–Si–**C**), 2.1 (H_2**C**–Si–C), −0.25 (Si($\mathbf{CH_3}$)$_3$) ppm. ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6): $\delta = -18.5$ (**Si**CH_3)$_3$), −46.5 (**Si**CH_2) ppm. Elemental analysis calcd (%) for $C_{33}H_{60}Si_9$ ($M_r = 708.26$): C 55.86, H 8.52; found: C 54.49, H 8.95.

1,1,3,3,5,5-Hexaethynyl-1,3,5-trisilacyclohexane (3). Method a): 1,1,3,5,5-Hexachloro-1,3,5-trisilacyclohexane (**1**, 0.70 g, 2.1 mmol) was dissolved in THF (10 mL) and ethynylmagnesium bromide solution (in THF, 0.5 M, 36 mL, 18 mmol) was added at 0 °C. The solution was stirred in a PTFE-sealed reaction vessel at 80 °C for 3 d. The solvent was removed under reduced pressure, the residue was dissolved in dichloromethane (200 mL) and quenched with saturated ammonium chloride solution (75 mL) and dist. water (75 mL).

The phases were separated and extracted with dichloromethane (3×50 mL). The combined organic phases were dried over magnesium sulphate and the solvent removed under reduced pressure. The crude product was dissolved in *n*-pentane (100 mL), filtered over silica gel and the solvent removed again under reduced pressure to give 1,1,3,5,5 hexaethynyl-1,3,5-trisilacyclohexane (**3**, 0.30 g, 1.1 mmol, 52%) as a colourless crystalline solid. Method b): 1,1,3,3,5,5-Hexakis(trimethylsilylethynyl)-1,3,5-trisilacyclohexane (**2**, 0.61 g, 0.86 mmol) was dissolved in *n*-pentane (30 mL) and trifluoromethanesulfonic acid (0.77 g, 5.2 mmol) was added dropwise. The reaction was stirred at room temperature for 48 h before dist. water (100 mL) was added. The phases were separated, the organic phase was washed with dist. water (3×100 mL), dried over magnesium sulphate and the solvent was removed under reduced pressure. The crude product was dissolved in *n*-hexane (100 mL) and filtered over silica gel. After removal of the solvent under reduced pressure. 1,1,3,3,5,5-Hexaethynyl-1,3,5-trisilacyclohexane (**3**, 0.10 g, 0.36 mmol, 42%) was obtained as a colourless solid. ^{1}H NMR (500 MHz, C_6D_6): $\delta = 2.05$ (s, 6H, C–**H**), 0.48 (s, 6H, Si–C**H**$_2$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): $\delta = 96.3$ (≡C–H), 85.9 (Si–**C**≡), 1.5 (Si–**C**H$_2$) ppm. ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6): $\delta = -43.0$ ppm. Elemental analysis calcd (%) for $C_{15}H_{12}Si_3$ ($M_r = 276.52$): C 65.16, H 4.37; found: C 65.20, H 4.60.

1,1,3,3,5,5-Hexakis(trimethylstannylethynyl)-1,3,5-trisilacyclohexane (4). 1,1,3,5,5-Hexaethynyl-1,3,5-trisilacyclohexane (**3**, 0.13 g, 0.47 mmol) was placed in toluene (20 mL) and dimethylaminotrimethylstannane (0.68 g, 3.3 mmol) was added. The solution was stirred at room temperature for 5 d, before the solvent was removed under reduced pressure and the crude product was dried in high vacuum, yielding the stannylated product **4** (0.51 g, 0.41 mmol, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.49$ (s, 6H, Si–C**H**$_2$), 0.28 (s, 54H, Sn(C**H**$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): $\delta = 115.8$ (≡**C**–SnCH$_3$)$_3$), 114.6 (H$_2$C–Si–**C**≡), 2.3 (H$_2$**C**–Si), −7.4 (Sn(**C**H$_3$)$_3$) ppm. ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): $\delta = -49.2$ ppm. ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$): −71.1 ppm. Elemental analysis calcd (%) for $C_{33}H_{60}Si_3Sn_6$ ($M_r = 1253.36$): C 31.62, H 4.83; found: C 31.66, H 4.65.

1,1,3,3,5,5-Hexakis(1,3,2-benzodioxaborylethynyl)-1,3,5-trisilacyclohexane (5). 1,1,3,5,5-Hexakis-(trimethylstannylethynyl)-1,3,5-trisilacyclohexane (**4**, 82 mg, 0.07 mmol) was dissolved in toluene (2 mL) and cooled to −30 °C. A solution of 2-chloro-1,3,2-benzodioxaborole (77 mg, 0.43 mmol) in *n*-hexane (2 mL) was added, the solution was warmed to room temperature slowly and stirred for 4 d. The reaction mixture was heated to reflux for 1 h and then all volatiles were removed under reduced pressure. The crude product was washed with *n*-hexane (2×4 mL) and **5** (65 mg, 0.07, quant.) was obtained as a colourless, crystalline solid. Single crystals for X-ray diffraction were obtained by slowly evaporating a chloroform solution of **5**. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.03$ (dd, $^3J_{H,H} = 6$ Hz, $^5J_{H,H} = 3$ Hz, 12H, Cat-**H**), 6.90 (dd, $^3J_{H,H} = 6$ Hz, $^5J_{H,H} = 3$ Hz, 12H, Cat-**H**), 0.84 (s, 6H, Si–C**H**$_2$) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): $\delta = 22.4$ ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): $\delta = 147.6$ (**C**O), 123.3 (Cat-**C**), 112.8 (Cat-**C**), 106.9 (Si–C≡), 1.3 (Si–**C**H$_2$) ppm. No signal for CatB–C was observed. ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): $\delta = -42.5$ ppm. Elemental analysis calcd (%) für $C_{51}H_{30}B_6O_{12}Si_3$ ($M_r = 984.90$): C 62.26, H 3.07; found: C 60.08, H 3.29.

General procedure for hydrosilylation reactions

The trisilacyclohexane was dissolved in diethyl ether (2 mL) and Karstedt's catalyst (1% (wt) Pt in toluene, 2 drops) and an excess of the chlorosilane were added. The solution was stirred at room temperature for 3 d and then the solvent and the excess of chlorosilane were removed under reduced pressure.

1,1,3,3,5,5-Hexakis(trichlorosilylvinyl)-1,3,5-trisilacyclohexane (6). Yield: 0.14 g, 59%. ^{1}H NMR (500 MHz, C_6D_6): $\delta = 6.91$ (d, $^3J_{H,H} = 22$ Hz, 6H, H$_2$C–Si–C**H**), 6.37 (d, $^3J_{H,H} = 22$ Hz, 6H, Cl$_3$Si–C**H**), −0.62 (s, 6H, Si–C**H**$_2$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): $\delta = 155.2$ (H$_2$C–Si–CH), 142.9 (Cl$_3$Si–CH), −6.0 (H$_2$C–Si–CH) ppm. ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6): $\delta = -5.9$ (Cl$_3$**Si**), −12.2 (H$_2$C–**Si**) ppm. Elemental analysis calcd (%) for $C_{15}H_{18}Cl_{18}Si_9$ ($M_r = 1089.17$): C 16.54, H 1.67; found: C 16.76, H 1.87.

1,1,3,3,5,5-Hexakis(dichloromethylsilylvinyl)-1,3,5-trisilacyclohexane (7). Yield: 0.13 g, quant. ^{1}H NMR (500 MHz, C_6D_6): $\delta = 6.96$ (d, $^3J_{H,H} = 22$ Hz, 6H, H$_2$C–Si–C**H**), 6.58 (d, $^3J_{H,H} = 22$ Hz, 6H, (CH$_3$)Cl$_2$Si–C**H**), 0.58 (s, 18H, (C**H**$_3$)Cl$_2$Si–CH) −0.26 (s, 6H, Si–C**H**$_2$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): $\delta = 153.8$ (H$_2$C–Si–CH), 145.4 ((CH$_3$)Cl$_2$Si–CH), 4.7 ((**C**H$_3$)Cl$_2$Si–CH) −5.6 (H$_2$C–Si–CH) ppm. ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6): $\delta = 14.4$ ((CH$_3$)Cl$_2$**Si**), −12.7 (H$_2$C–**Si**) ppm. Elemental analysis calcd (%) for $C_{21}H_{36}Cl_{12}Si_9$ ($M_r = 966.68$): C 26.09, H 3.75; found: C 26.23, H 4.10.

1,1,3,3,5,5-Hexakis(chlorodimethylsilylvinyl)-1,3,5-trisilacyclohexane (8). Yield: 0.15 g, 94%. ^{1}H NMR (500 MHz, C_6D_6): $\delta = 6.93$ (d, $^3J_{H,H} = 22$ Hz, 6H, H$_2$C–Si–C**H**), 6.74 (d, $^3J_{H,H} = 22$ Hz, 6H, (CH$_3$)$_2$ClSi–C**H**), 0.38 (s, 36H, (C**H**$_3$)$_2$ClSi–CH), 0.03 (s, 6H, Si–C**H**$_2$) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): $\delta = 152.3$ (H$_2$C–Si–CH), 148.4 ((CH$_3$)$_2$ClSi–CH), 1.7 ((**C**H$_3$)$_2$ClSi–CH), −5.0 (H$_2$C–Si–CH) ppm. ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6): $\delta = 16.4$ ((CH$_3$)$_2$Cl**Si**–CH), −13.6 (H$_2$C–**Si**) ppm. Elemental analysis calcd (%) for $C_{27}H_{54}Cl_6Si_9$ ($M_r = 844.13$): C 38.41, H 6.45; found: C 37.21, H 6.83.

1,1,3,3,5,5-Hexakis(chlorodimethylsilylethyl)-1,3,5-trisilacyclohexane (10). Yield: 0.83 g, 62%. ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 0.71$ (m, 12H, (CH$_3$)$_2$ClSi–C**H**$_2$), 0.57 (m, 12H, (CH$_3$)$_2$ClSi–CH$_2$–C**H**$_2$), 0.42 (s, 36H, (C**H**$_3$)$_2$ClSi–CH$_2$), −0.29 (s, 6H, Si–C**H**$_2$–Si) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): $\delta = 12.0$((CH$_3$)$_2$ClSi–CH$_2$), 8.3 ((CH$_3$)$_2$ClSi–CH$_2$–CH$_2$), 1.3 ((**C**H$_3$)$_2$ClSi–CH$_2$) −6.1 (Si–H$_2$C–Si) ppm. ^{29}Si{^{1}H} NMR (99 MHz, CD_2Cl_2): $\delta = 33.0$ ((CH$_3$)$_2$Cl**Si**), 7.1 (**Si**–H$_2$C–**Si**) ppm. Elemental analysis calcd (%) for $C_{27}H_{66}Cl_6Si_9$ ($M_r = 856.29$): C 38.43, H 7.96; found: C 37.87, H 7.77.

1,1,3,3,5,5-Hexakis(dimethyl(trifluoromethylsulfonyl)silylethyl)-1,3,5-trisilacyclohexane (11). Silver triflate (0.20 g, 0.76 mmol) was suspended in dichloromethane (1 mL) and a solution of trisilacyclohexane (**10**, 0.10 g, 0.12 mmol) in dichloromethane (1 mL) was added. The suspension was stirred for 4 d in the absence of light at room temperature and then filtered. After removal of the solvent under high vacuum, **11** (0.16 g, 0.10 mmol, 88%) could be isolated as a colourless resin. NMR data were recorded in dichloromethane-d$_2$ as well as acetonitrile-d$_3$ - ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 0.79$ (m, 12H, OTf(CH$_3$)$_2$Si–C**H**$_2$), 0.57 (m, 12H, OTf(CH$_3$)$_2$Si–CH$_2$–C**H**$_2$), 0.48 (s, 36H, OTf(C**H**$_3$)$_2$Si–CH$_2$), −0.25 (s, 6H, Si–C**H**$_2$–Si) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): $\delta = 119.0$ (q, $^1J_{F,C} =$ 318 Hz, CF$_3$), 9.2 (OTf(CH$_3$)$_2$Si–CH$_2$), 7.2 (OTf(CH$_3$)$_2$Si–CH$_2$–CH$_2$), −1.7 (OTf(**C**H$_3$)$_2$Si–CH$_2$) −6.7 (Si–H$_2$C–Si) ppm. ^{19}F NMR (471 MHz, CD_3CN): −77.5 ppm. ^{29}Si{^{1}H} NMR (99 MHz, CD_3CN): $\delta = 44.3$ (OTf(CH$_3$)$_2$**Si**), 7.4 (**Si**-H$_2$C–**Si**) ppm. –^{1}H NMR (500 MHz, CD_3CN): $\delta = 0.81$ (m, 12H, OTf(CH$_3$)$_2$Si–C**H**$_2$), 0.56 (m, 12H, OTf(CH$_3$)$_2$Si–CH$_2$–C**H**$_2$), 0.47 (s, 36H, OTf(C**H**$_3$)$_2$Si–CH$_2$), −0.26 (s, 6 H, Si–C**H**$_2$–Si) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_3CN): $\delta = 119.5$ (q, $^1J_{F,C} =$ 318 Hz, CF$_3$), 9.0 (OTf(CH$_3$)$_2$Si–CH$_2$), 7.2 (OTf(CH$_3$)$_2$Si–CH$_2$–CH$_2$), −1.9 (OTf(**C**H$_3$)$_2$Si–CH$_2$) −6.7 (Si–H$_2$C–Si) ppm. ^{19}F NMR (471 MHz, CD_3CN): −78.2 ppm. ^{29}Si{^{1}H} NMR (99 MHz, CD_3CN): $\delta = 45.8$ (OTf(CH$_3$)$_2$**Si**), 7.5 (**Si**–H$_2$C–**Si**) ppm. Elemental analysis calcd (%) for $C_{33}H_{66}F_{18}O_{18}S_6Si_9$ ($M_r = 1537.97$): C 25.77, H 4.33, S 12.51; found: C 26.62, H 4.64, S 11.70.

1,1,3,3,5,5-Hexakis(2-(9-bora-cyclo[3.3.1]nonan-9-yl)ethyl)-1,3,5-trisilacyclohexane (12). 1,1,3,5,5-Hexavinyl-1,3,5-trisilacyclohexane (**9**, 0.14 g, 0.49 mmol) was placed in *n*-hexane (5 mL), degassed three times by freeze-pump-thaw and 9-BBN solution (0.5 M, 6.2 mL, 0.31 mmol) was added. The reaction solution was stirred at room temperature for 16 h and the solvent was removed under reduced pressure. The crude product was dissolved twice in *n*-hexane (2 mL) and precipitated at −30 °C. After drying the residue, **12** (0.33 g, 0.32 mmol, 65 %) could be isolated as a colourless solid. ^1H NMR (500 MHz, C_6D_6): $\delta = 1.91$ (m, 48H, BBN), 1.81 (m, 24H, BBN), 1.56 (m, 12H, $Si{-}CH_2{-}C\mathbf{H}_2$), 1.28 (m, 12H, BBN), 0.91 (m, 12H, $Si{-}C\mathbf{H}_2{-}CH_2$), 0.04 (s, 6H, $Si{-}C\mathbf{H}_2{-}Si$) ppm. ^{11}B NMR (160 MHz, C_6D_6): $\delta = 85.8$ ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): $\delta = 33.8$ (BBN), 31.7 (BBN), 23.8 (BBN), 20.7 ($Si{-}CH_2{-}CH_2$), 9.2 ($Si{-}CH_2{-}CH_2$) −4.8 ($Si{-}CH_2{-}Si$) ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): $\delta = 7.9$ ppm. Elemental analysis calcd (%) for $C_{63}H_{114}B_6Si_3$ ($M_r = 1020.72$): C 74.13, H 11.26; found: C 72.18, H 11.05.

General procedure for host-guest-experiments

The acid was placed in a Young-NMR tube in acetonitrile-d_3 (**11**) or benzene-d_6 (**12**) and six equivalents of the monodentate guest were added. The solution was thoroughly mixed.

1,1,3,3,5,5-Hexakis(dimethyl(trifluoromethylsulfonyl)silylethyl)-1,3,5-trisilacyclohexane·pyridine (11·6Py). ^1H NMR (500 MHz, CD_3CN): $\delta = 8.72$ (m, 12H, $\mathbf{H}_{ortho}$), 8.30 (t, $^3J_{H,H} = 8$ Hz, 6H, $\mathbf{H}_{para}$), 7.82 (t, $^3J_{H,H} = 7$ Hz, 12H, $\mathbf{H}_{meta}$) 1.02 (m, 12H, $Py(CH_3)_2Si{-}C\mathbf{H}_2$), 0.67 (s, 36H, $Py(C\mathbf{H}_3)_2Si{-}CH_2$), 0.44 (m, 12H, $Py(CH_3)_2Si{-}CH_2{-}C\mathbf{H}_2$), −0.25 (s, 6H, $Si{-}C\mathbf{H}_2{-}Si$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN): $\delta = 148.1$ ($\mathbf{C}_{ortho}$), 144.5 ($\mathbf{C}_{para}$), 127.6 ($\mathbf{C}_{meta}$), 122.1 (q, $^1J_{F,C}$ = 321 Hz, $\mathbf{C}F_3$), 7.7 ($Py(CH_3)_2Si{-}CH_2$), 7.4 ($Py(CH_3)_2Si{-}CH_2{-}CH_2$), −3.0 ($Py(\mathbf{C}H_3)_2Si{-}CH_2$) −6.8 ($Si{-}H_2C{-}Si$) ppm. ^{19}F NMR (471 MHz, CD_3CN): − 79.1 ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, CD_3CN): $\delta = 41.0$ ($Py(CH_3)_2\mathbf{Si}$), 8.1 ($\mathbf{Si}{-}H_2C{-}\mathbf{Si}$) ppm.

1,1,3,3,5,5-Hexakis(dimethyl(trifluoromethylsulfonyl)silylethyl)-1,3,5-trisilacyclohexane·1,2-dimethylimidazole (11·6Imi). ^1H NMR (500 MHz, CD_3CN): $\delta = 7.30$ (s, 6H, $H_{Ar,Imi}$), 7.16 (s, 6H, $H_{Ar,Imi}$), 3.71 (s, 18H, $\mathbf{H}_{Me,Imi}$), 2.54 (s, 18H, $\mathbf{H}_{Me,Imi}$), 0.91 (m, 12H, $Imi(CH_3)_2Si{-}C\mathbf{H}_2$), 0.55 (s, 36H, $Imi(C\mathbf{H}_3)_2Si{-}CH_2$), 0.45 (m, 12H, $Imi(CH_3)_2Si{-}CH_2{-}C\mathbf{H}_2$), −0.22 (s, 6H, $Si{-}C\mathbf{H}_2{-}Si$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN): $\delta =$ 126.0 (N–C–N), 124.5 ($\mathbf{C}_{Ar,Imi}$), 123.5 ($\mathbf{C}_{Ar,Imi}$), 122.1 (q, $^1J_{F,C}$ = 321 Hz, $\mathbf{C}F_3$), 35.4 ($N\mathbf{C}_{Me,Imi}$), 12.8 ($C\mathbf{C}_{Me,Imi}$), 8.1 ($Imi(CH_3)_2Si{-}CH_2$), 7.7 ($Imi(CH_3)_2Si{-}CH_2{-}CH_2$), −2.5 ($Imi(\mathbf{C}H_3)_2Si{-}CH_2$) −6.6 ($Si{-}H_2C{-}Si$) ppm. ^{19}F NMR (471 MHz, CD_3CN): −79.2 ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, CD_3CN): $\delta = 24.9$ ($Imi(CH_3)_2\mathbf{Si}$), 7.9 ($\mathbf{Si}{-}H_2C{-}\mathbf{Si}$) ppm.

1,1,3,3,5,5-Hexakis(2-(9-boracyclo[3.3.1]nonan-9-yl)ethyl-1,3,5-trisilacyclohexane·pyridine (12·Py). ^1H NMR (500 MHz, C_6D_6): $\delta =$ 8.26 (s, 12H, H_{ortho}), 7.00 (t, $^3J_{H,H} = 8$ Hz, 6H, H_{para}), 6.72 (t, $^3J_{H,H} = 7$ Hz, 12H, H_{meta}), 2.33 (m, 24H, BBN), 2.10 (m, 24H, BBN), 1.93-1.58 (m (br), 24H, BBN), 1.24 (s, 12H, BBN), 0.32 (m, 12H, $Si{-}CH_2{-}CH_2$), −0.24 (m, 12H, $Si{-}CH_2{-}CH_2$), −0.77 (s, 6H, $Si{-}CH_2{-}Si$) ppm. ^{11}B NMR (160 MHz, C_6D_6): $\delta = 0.30$ (br) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): $\delta = 145.6$ (C_{ortho}), 138.0 (C_{para}), 124.4 (C_{meta}), 33.1 (BBN), 31.2 (BBN), 25.8 (BBN), 19.9 ($Si{-}CH_2{-}CH_2$), 10.2 ($Si{-}CH_2{-}CH_2$) −5.3 ($Si{-}CH_2{-}Si$) ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): $\delta = 5.0$ ppm.

Crystal structure determinations

Data collection were performed on Rigaku Supernova instruments at 100.1(1) K. Using the program Olex2,[31] the structure was solved with the ShelXT[32] structure solution program using Intrinsic Phasing and refined with the ShelXL[33] refinement package using Least Squares minimisation. Details of the X-ray diffraction experiments are given in Table S1

Deposition Numbers 2081153 (for **2**), 2081154 (for **3**), and 2081155 (for **5**) 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: trisilacyclohexanes · poly-Lewis acids · host systems · silyl-triflate · boron

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