## Tridentate Lewis Acids

## Tridentate Lewis Acids Based on 1,3,5-Trisilacyclohexane Backbones and an Example of Their Host–Guest Chemistry

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Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday

**Abstract:** Directed tridentate Lewis acids based on the 1,3,5trisilacyclohexane skeleton with three ethynyl groups  $[CH_2Si(Me)(C_2H)]_3$  were synthesised and functionalised by hydroboration with HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, yielding the ethenylborane  $\{CH_2Si(Me)[C_2H_2B(C_6F_5)_2]\}_3$ , and by metalation with gallium and indium organyls affording  $\{CH_2Si(Me)[C_2M(R)_2]\}_3$  (M = Ga, In, R = Me, Et). In the synthesis of the backbone the influence of substituents (MeO, EtO and *i*PrO groups at Si) on the orientation of the methyl group was studied with the aim to increase the abundance of the all-*cis* isomer. New compounds were identified by elemental analyses, multi-nuclear NMR spectroscopy and in some cases by IR spectroscopy. Crystal structures were obtained for *cis-trans*-[CH<sub>2</sub>Si(Me)(CI)]<sub>3</sub>,

## Introduction

The first attempts to establish poly-Lewis acids were documented in 1968<sup>[1]</sup> and this subject has continued to grow since then. Such functional compounds are able to form complexes with Lewis bases and anions. Issues of molecular recognition have been put into the foreground of such investigations. Parallel to these investigations poly-cations were studied as receptors for certain anions. The first prototypes were synthesised by Park and Simmons.<sup>[1]</sup> These catapinands<sup>[2]</sup> were able to complex halides selectively due to the fitting sizes of cavity and anion. Later on in 1977 Schmidtchen established spherical methylated poly-ammonium systems with high stability constants of their complexes with anions in water.<sup>[3]</sup> Further on some cyclic poly-Lewis acids based on silicon,<sup>[4]</sup> tin<sup>[5]</sup> and mercury<sup>[6,7]</sup> were reported. A prominent example of a mercury-based poly-Lewis acid was synthesised by Sartori and Golloch.<sup>[8]</sup> This tri-

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 Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201501683. all-cis-[CH2Si(Me)(H)]3, all-cis-[CH<sub>2</sub>Si(Me)(C<sub>2</sub>H)]<sub>3</sub>, cis-trans-[CH<sub>2</sub>Si(Me)(C<sub>2</sub>H)]<sub>3</sub> and all-cis-[CH<sub>2</sub>Si(Me)(C<sub>2</sub>SiMe<sub>3</sub>)]<sub>3</sub>. A gasphase electron diffraction experiment for all-cis-[CH<sub>2</sub>Si(Me)(C<sub>2</sub>H)]<sub>3</sub> provides information on the relative stabilities of the all-equatorial and all-axial form; the first is preferred in both solid and gas phase. The gallium-based Lewis acid {CH<sub>2</sub>Si(Me)[C<sub>2</sub>Ga(Et)<sub>2</sub>]}<sub>3</sub> was reacted with a tridentate Lewis base (1,3,5-trimethyl-1,3,5-triazacyclohexane) in an NMR titration experiment. The generated host-guest complexes involved in the equilibria during this reaction were identified by DOSY NMR spectroscopy by comparing measured diffusion coefficients with those of the suitable reference compounds of same size and shape.

dentate Lewis acid shows the complexation of halogens as a polyanionic chain in the crystal.<sup>[9]</sup> Investigations with other substrates like molecules with carbonyl groups<sup>[7, 10]</sup> and acetylenes<sup>[11]</sup> have revealed the potential of this mercury compound in coordination chemistry.

Besides cyclic poly-Lewis acids some representatives with directed Lewis acid functions have also been synthesised. Benzene, naphthalene and anthracene have been used as underlying rigid skeletons. In the case of benzene, functionalities with aluminium, gallium<sup>[12]</sup> and mercury<sup>[13]</sup> have been introduced. In this way bidentate acids have been created that are capable of selectively binding certain Lewis bases. Naphthalene offers also a rigid backbone for selective binding of Lewis bases; examples include compounds with mercury,<sup>[14]</sup> boron,<sup>[15]</sup> indium<sup>[16]</sup> and gallium.<sup>[17]</sup> Based on boron, Katz has synthesised 1,8-anthracenediethynylbis(catecholboronate),<sup>[18]</sup> a bidentate Lewis acid with a fixed distance between the acid functions. Using 1,8-diethynylanthracene we have recently reported a series of bidentate earth metal Lewis acids<sup>[19]</sup> and also a selective complexation of such bidentate Lewis acids with pyridine and pyrimidine as substrates.<sup>[20]</sup> Encouraged by these results with the ethynyl-functionalised scaffolds we have now addressed tridentate backbones based on 1,3,5-trisilacyclohexane to establish directed tridentate Lewis acids.

Herein we present syntheses of several 1,3,5-trisilacyclohexanes and demonstrate their use as versatile backbones for tridentate Lewis acids. We demonstrate that all-*cis*-1,3,5-triethyn-

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yl-1,3,5-trimethyl-1,3,5-trisilacyclohexane offers a possibility to access tridentate Lewis acids by hydroboration and metalation using gallium- and indiumtrialkyls under alkane elimination.

### **Results and Discussion**

In order to place three Lewis acidic functionalities on one side of a molecule that point in the same direction, we chose 1,3,5trisilacyclohexanes as backbones (Scheme 1). The strategy was



**Scheme 1.** Two possible diastereomers resulting from the orientation of substituents at the ring silicon atoms.

to bind three ethynyl groups to the silicon atoms, which will be subsequently carry typical Lewis acidic functions with elements of the boron group.

With one function at each silicon atom there are two possibilities for diastereomers—the desired all-*cis* isomer with three equally oriented substituents and the *cis-trans* isomer, the second product of the cyclisation reaction. The dynamics of ring inversion will change the orientation of these substituents, in the case of all-*cis* isomer from all-equatorial (denoted *eee*) to all-axial (*aaa*). Because the barriers of inversion for 1,3,5-trisilacyclohexanes are known to be very small,<sup>[21,22]</sup> a trifunctional system as a host will be easily adaptable in binding to a guest molecule regarding this change in conformation. The challenges lie in finding conditions for a preferred formation of the all*cis* isomer, the separation of diastereomers and their conversions under retention of configuration.

#### Formation of 1,3,5-trisilacyclohexanes

Kriner has established the first elegant preparative access to 1,3,5-trisilacyclohexanes.<sup>[23,24]</sup>

Based on this and other work<sup>[25,26]</sup> dichloro(chloromethyl)methylsilane (1) was protected with methoxy- and ethoxy-substituents (Scheme 2). In this way the formation of 1,3,5-trisilacyclohexanes is favoured over that of 1,3-disilacyclobutanes.<sup>[27]</sup> Methoxy and ethoxy substituents were tested for an enhanced selectivity in formation of the allcis stereoisomer (compounds 2 and 3); however, with isopropoxy groups, no formation of 1,3,5-trisilacyclohexane was observed. The reaction of chloro-



Scheme 2. Synthesis of 1,3,5-trisilacyclohexanes and the backbone 8. Yields: 2: 83%; 3: 86%; 4: 41%; 5: 32%; 6 with BCl<sub>3</sub>: 89%; 6 with Cl<sub>2</sub>: 100%; all-*cis*-7: 58%; 8: 95%.

methyldimethoxymethylsilane (2) with magnesium led to an overall yield of 41% of a mixture of all-*cis*-4 and *cis*-*trans*-4 in a ratio of 1:1. The diastereomer mixture of 5 was obtained in lower yield (32%), but contains 64% of the desired all-*cis* stereoisomer.

All attempts to separate the diastereomers failed and consequently **5** was employed in subsequent reactions.

#### all-cis-1,3,5-Triethynyl-1,3,5-trimethyl-1,3,5-trisilacyclohexane

A direct route to the desired trisilacyclohexane by reacting ethynyl magnesium bromide with **5** turned out to be not possible. Consequently, we transformed **5** into the trichloro derivative **6** by treatment with boron trichloride. All attempts to separate the diastereomers of **6** failed. Therefore we treacted **5** with LiAlH<sub>4</sub> to afford the corresponding trihydride **7** (Scheme 2), a compound synthesised earlier in a different way.<sup>[28,29]</sup> In contrast to **5** and **6**, the diastereomers of **7** could be separated by fractionated condensation, as was earlier reported.<sup>[28]</sup> The desired all-*cis* stereoisomer of **7** was obtained in a yield of 58% starting from the mixture of **5**.

In order to obtain the all-*cis* isomer of **6**, all-*cis*-**7** was reacted with chlorine gas dissolved in carbon tetrachloride. This procedure has been reported to chlorinate the cyclic 1-chloro-1-phenyl-1-sila-1,2,3,4-tetrahydronaphthalene under retention of configuration.<sup>[30]</sup> However, this protocol failed when applied to **7** and led instead to a diastereomeric mixture of all-*cis*- and *cis-trans*-**6**, that is, a loss of stereo information.

For that reason the detour via all-*cis*-**7** was not further pursued and instead isomer mixture **6** was reacted with ethynyl magnesium bromide to yield an isomer mixture of the desired trisilacyclohexane **8** (Scheme 2). The diastereomeric ratio in several implementations of this reaction was 60:40 in favour of all-*cis*-**8**. At this step the diastereomers could be separated by fractional sublimation at room temperature under high vacuum conditions.

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The compounds described in this section were characterised by multinuclear NMR spectroscopy and elemental analyses, some in addition by FT-IR spectroscopy, mass spectrometry and single-crystal X-ray diffraction. Some discussion of the spectroscopic and structural data follows here.

#### NMR spectroscopy

NMR spectra are provided in the Supporting Information, Figures S6–S69, along with a compilation of NMR shifts in Table S6. The chemical shifts of the geminal hydrogen atoms at the rings cover the range between 0.47 and -0.64 ppm. Variation of the ring substituents has no appreciable effect on the chemical shifts of methyl or methylene hydrogen atoms. In contrast, the <sup>29</sup>Si chemical shifts depend strongly on a change in substituents from chlorine to ethynyl (26.4 to -18.5 ppm), in the case of all-*cis* diastereomers of **6** and **8**.

The dynamics of ring inversion was a subject of earlier studies, but so far there are only theoretically obtained values for the barrier to ring inversion of 1,3,5-trisilacyclohexanes<sup>[21,22]</sup> that estimated this value to be about 5 kcal mol<sup>-1</sup>. We ran lowtemperature NMR spectra for all-*cis*-**8** in toluene at temperatures as low as -90 °C, but, besides some broadening of the lines, no splitting of signals was observable that would allow us to extract a value for an inversion barrier.

#### **Crystal structures**

During these studies we obtained single-crystalline material suitable for structure determination by X-ray diffraction of *cis*-*trans*-**6**, all-*cis*-**7** and both diastereomers of **8**. The structures will be presented in comparison below. Single crystals suitable for X-ray diffraction experiments were obtained of *cis*-*trans*-**6** by sublimation, and of **7** and all-*cis*-**8** (X-ray structure of *cis*-*trans*-**8** is presented in Supporting Information, Figure S3) by gradual evaporation of a solution in *n*-pentane. The molecular structures are displayed in Figures 1–3.

The trisilacyclohexane rings of *cis-trans*-**6**, all-*cis*-**7** and all-*cis*-**8** all exhibit chair conformations. The Si–C bond lengths of the rings have values that are similar to those reported for [SiCl<sub>2</sub>CH<sub>2</sub>]<sub>3</sub>.<sup>[31]</sup> On average, the shortest Si–C bonds are found in the chlorinated species, [SiCl<sub>2</sub>CH<sub>2</sub>]<sub>3</sub> and *cis-trans*-**6** (average 1.862(1) Å), while those in the ethynyl substitute all-*cis*-**8** (average 1.869(1) Å) are longer and those in the hydride species all-*cis*-**7** are the longest (average 1.873(3) Å).

The Si–Cl bond lengths in the chlorine derivative *cis-trans*-**6** vary from 2.086(1) to 2.090(1) Å and are longer than those in  $[SiCl_2CH_2]_3$  (2.043(1)–2.059(1) Å). Increasing substitution by chlorine at silicon leads to a shortening of all bonds to this atom.

Compound all-*cis*-**8** crystallises in the monoclinic space group  $P_{2_1}/n$  with eight molecules per unit cell, that is, two independent ones in the asymmetric unit. In both molecules the ethynyl groups are arranged equatorially. This leads to large distances between the terminal ethynyl carbon atoms: C(5)...C(8) 7.648(1), C(8)...C(11) 7.849(1) and C(5)...C(11) 7.695(1) Å. These values define the distance between the po-



**Figure 1.** Molecular structure of *cis-trans*-**6** in the crystal. Displacements ellipsoids are drawn at the 50% probability level. Methyl hydrogen atoms are omitted for clarity. Selected distances [Å]: Si(1)–C(1) 1.862(1), Si(1)–C(3) 1.858(1), Si(2)–C(1) 1.863(1), Si(2)–C(2) 1.865(1), Si(3)–C(2) 1.862(1), Si(3)–C(3) 1.861(1), Si(1)–C(4) 1.866(1), Si(2)–C(5) 1.863(1), Si(3)–C(6) 1.870(1), Si(1)–C(1(1) 2.090(1), Si(2)–C1(2) 2.086(1), Si(3)–C1(3) 2.089(1). Selected angles [°]: C(1)-Si(1)-C(3) 110.3(1), C(2)-Si(2)-C(1) 110.0(1), C(3)-Si(3)-C(2) 109.2(1), Si(1)–C(1)-Si(2) 118.4(1), Si(2)–C(2)-Si(3) 116.0(1), Si(3)–C(3)-Si(1) 116.9(1).



**Figure 2.** Molecular structure of all-*cis*-**7** in the crystalline state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms of the methyl groups are omitted for clarity. Selected distances [Å]: Si(1)–C(1) 1.875(3), Si(1)–C(3) 1.874(3), Si(2)–C(1) 1.874(3), Si(2)–C(2) 1.870(3), Si(3)–C(2) 1.877(3), Si(3)–C(3) 1.870(3), Si(1)–C(4) 1.863(3), Si(2)–C(5) 1.870(3), Si(3)–C(6) 1.868(3), Si(1)–Cl(1) 1.223(1), Si(2)–Cl(2) 1.214(1), Si(3)–Cl(3) 1.190(1). Selected angles [°]: C(1)-Si(1)-C(3) 109.0(1), C(2)-Si(2)-C(1) 108.7(1), C(3)-Si(3)-C(2) 108.7(1), Si(1)-C(1)-Si(2) 113.7(2), Si(2)-C(2)-Si(3) 114.0(2), Si(3)-C(3)-Si(1) 113.7(2).

tential binding sites for Lewis acidic functions in compounds with all-*cis*-**8** being used as a backbone.

This structure of all-*cis*-**8** in the crystalline state does not necessarily reflect the behaviour of a free molecule in the gas phase or in solution, in which an easy change between the all-axial (*aaa*) or all-equatorial (*eee*) orientation of the ethynyl groups can be expected. More light on this behaviour is shed by the data from a gas-phase structure investigation reported below.

#### Axial verus equatorial orientation of ethynyl groups—quantum-chemical calculations for all-*cis*-8

A series of quantum-chemical calculations of the energies of the conformers of compound all-*cis*-**8** was carried out to esti-



**Figure 3.** Molecular structure of one of the two independent molecules of all-*cis*-**8** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms of methyl groups are omitted for clarity. Selected distances[Å]: Si(1)–C(1) 1.866(1), Si(1)–C(3) 1.870(1), Si(2)–C(1) 1.867(1), Si(2)–C(2) 1.868(1), Si(3)–C(2) 1.870(1), Si(3)–C(3) 1.870(1), Si(1)–C(6) 1.862(1), Si(2)–C(9) 1.865(1), Si(3)–C(2) 1.863(1), Si(1)–C(4) 1.857(1), Si(2)–C(7) 1.844(1), Si(3)–C(10) 1.836(1), C(4)=C(5) 1.195(2), C(7)=C(8) 1.194(2), C(10)=C(11) 1.194(2). Selected angles [°]: C(1)-Si(1)–C(3) 109.6(1), C(2)-Si(2)–C(1) 108.7(1), C(3)-Si(3)–C(2) 107.7(1), Si(1)–C(2)-Si(2) 116.5(1), Si(2)–C(2)-Si(3) 115.4(1), Si(3)–C(3)-Si(1) 116.5(1).

Table 1. Comparison of quantum-chemical results of conformational							
composition concerning the ratio of axial to equatorial orientation of eth-							
ynyl groups for all- <i>cis</i> - <b>8</b> . $\Delta E = E_{aaa} - E_{eee}$ ; $\Delta G = G_{aaa} - G_{eee}$ ; $\chi_{eee}$ calculated for							
$T =$ 379 K from $\Delta G$ .							

Method	$\Delta E$ [kcal mol <sup>-1</sup> ]	$\Delta G$ [kcal mol <sup>-1</sup> ]	χ <sub>eee</sub> [%]
B3LYP/6-31G(d,p)	1.02	0.77	74
PBE0/6-31G(d,p)	1.47	1.52	88
PBE0-D3/6-31G(d,p)	1.51	1.76	91
MP2/cc-pVTZ	-0.27	-0.28	41

mate their relative abundance. The used methods and their results are given in Table 1. The DFT calculations at the B3LYP and PBE0 approximations using the double- $\zeta$  basis set indicate that the dominant component of all-*cis*-**8** is that with equatorially (*eee*) orientated ethynyl groups. Using corrections for dispersion, the *aaa* conformer was not found to be significantly stabilised by dispersive interactions. In contrast to the DFT results, calculations at the MP2 level resulted in a different conformational composition with an *aaa/eee* conformer ratio of 59:41 (Table 1). An attempt to determine a barrier to ring inversion turned out to be complicated due to the flatness of the potential energy surface and in the light of the expected limited reliability was not further pursued.

#### Gas-phase structure of all-cis-8

Experimental studies of the composition and structure of free molecules of all-*cis*-**8** were undertaken by gas-phase electron diffraction (GED). A model for the composition of all-*cis*-**8** consisted of the *eee* (all ethynyl groups equatorial) and *aaa* conformers (all ethynyl groups axially). The experiment showed that conformer *eee* all-*cis*-**8** is the most abundant in the gas



**Figure 4.** Experimental (open circles) and model (line) radial distribution curves of all-*cis*-1,3,5-triethynyl-1,3,5-trimethyl-1,3,5-trisilacyclohexane (*eee* all-*cis*-8) as determined by GED. Vertical bars indicate the contributions of individual interatomic distances, some are labelled. The difference curve for the *eee* conformer model is shown below.

phase. The best fit with the model was achieved for a content of 99% *eee* conformer. The fit of this model is best seen in Figure 4, which displays the radial distribution curve obtained from the GED experiment. However, the accuracy of this composition value is rather limited. The error  $3\sigma$  is 30%, meaning that the amount of *eee* all-*cis*-**8** in the gas phase at the temperature of the experiment (381–388 K) is between 84 and 100%. This is consistent with the DFT calculations, but contradicts the results of the MP2 calculation. The result is also consistent with the data from the solid state, which often represent the conformational ground state in absence of pronounce intermolecular forces.

Experimental structure parameter values of *eee* all-*cis*-**8** are listed in Table 2 together with those from quantum-chemical calculations for comparison. Compound all-*cis*-**8** has similar angles and distances in the crystal and in the gas phase. The angles in the cycle in the gas phase deviate less than one

<b>Table 2.</b> Experimental and calculated structural parameters ( $r_{e'} \gtrless$ ) of
equatorially oriented [CH <sub>2</sub> Si(Me)(C <sub>2</sub> H)] <sub>3</sub> (eee all-cis-8). Levels of theory DFT
(PBE0-D3/6-31G(d,p)), MP2/cc-pVTZ and XRD average values [distances in Å, angles in $^\circ$ ].

Parameters	GED		PBE0-D3	MP2	XRD
	$r_{\rm e}$ or $\gtrless$ $r_{\rm g}$				
r(Si–CH <sub>2</sub> )	1.860(5)	1.871(5)	1.879	1.881	1.869
r(Si–CH₃)	1.885(5)	1.899(5)	1.877	1.880	1.863
r(Si—C≡)	1.843(5)	1.854(5)	1.843	1.843	1.846
r(C≡C)	1.204(3)	1.211(3)	1.225	1.215	1.195
∢(Si–CH₂–Si)	117.2(9)		116.3	116.0	116.1
$\bigstar$ (CH <sub>2</sub> —Si—CH <sub>2</sub> )	106.4(18)		108.9	109.6	108.9
∢(CH₃–Si–C≡)	108.8(28)		106.7	107.0	106.9
∢(CH <sub>2</sub> –Si–C≡)	109.0(10)		108.4	108.2	107.6
∢(CH <sub>3</sub> –Si–CH <sub>2</sub> )	111.8(16)		112.1	111.9	112.1
$\phi$ (Si–CH <sub>2</sub> –Si–CH <sub>2</sub> )	54.0(32)		51.5	50.8	51.8



degree from those in the crystal (Table 2). The distances between the carbon atoms in the ethynyl groups are 0.009 Å shorter in the solid state than in the gas phase.

In summary, the ethynyl groups are arranged equatorially, but it is known from the work of Arnason et al.<sup>[21,22]</sup>—as mentioned above—that the 1,3,5-trisilacyclohexane cycle has an energy barrier for inversion (estimated to 5.5 kcal mol<sup>-1</sup>) of half the height calculated for cyclohexane. Consequently, the three equally oriented functions can easily swing in con-rotatorial fashion for simultaneous binding to a substrate. For that reason compound all-*cis*-**8** was provided with Lewis acid functionalities and converted with a tridentate Lewis base. For details, follow the next chapters.

#### Synthesis of tridentate Lewis acids

Having established a synthesis for all-*cis*-**8**, we now have a backbone available with  $C_3$  symmetry, free of donor units and with ethynyl groups oriented to the same side of the molecule that can be converted into Lewis acid functions, so that the synthesis of directed tridentate Lewis acids becomes feasible.

With the aim of preparing an example for a boron-based tridentate Lewis acid all-*cis*-**8** was reacted with Piers' borane,<sup>[32,33]</sup> HB( $C_6F_5$ )<sub>2</sub>, in *n*-pentane (Scheme 3). The reaction proceeded



Scheme 3. Syntheses of the directed tridentate Lewis acids 9, 10, 11 and 12.

quantitatively and yielded product **9** as beige solid in high purity. Compound **9** was characterised by elemental analysis and multinuclear NMR spectroscopy. All attempts to grow suitable crystals for X-ray diffraction failed. All NMR spectra were recorded in  $C_6D_6$  at ambient temperature. The <sup>1</sup>H NMR spectrum shows a typical signal pattern for the olefin protons of the *trans*-product: two doublets at 7.64 and 7.48 ppm with coupling constants of 21 Hz. Two doublet resonances of the methylene protons in the cycle are observed at 0.10 and -0.06 ppm with a geminal coupling constant of 13.9 Hz (Table 3). The <sup>19</sup>F NMR spectrum shows the three expected resonances: two multiplets at -129.05 and -161.04 ppm (*ortho*-and *meta*-fluorine) and one as a triplet of triplets at -146.71 ppm (*para*-fluorine). The <sup>11</sup>B NMR spectrum shows

Table 3. Selected NMR shifts in [ppm] of solutions of the tridentate Lewis
acids 9 (C <sub>6</sub> D <sub>6</sub> ), 10 (C <sub>6</sub> D <sub>6</sub> /Et <sub>2</sub> O), 11 (C <sub>6</sub> D <sub>6</sub> /Et <sub>2</sub> O), 12 ([D <sub>8</sub> ]THF).

Compound	9	10	11	12
-SiC <b>H</b> <sub>2</sub> Si-	0.10	0.62	0.45	0.11
-SiC <b>H</b> ₂Si-	-0.06	0.17	0.17	-0.06
-SiC <b>H</b> ₃	0.23	0.32	0.23	0.13
-Si <b>C</b> =C-M/-Si <b>C</b> =C-M	173.2	115.6	no resonance	115.9
-SiC= <b>C</b> -M/-SiC= <b>C</b> -M	150.7	no resonance	no resonance	135.6
-CH <sub>2</sub> SiCH <sub>2</sub> -	-4.6	-22.3	-21.2	-24.2

a single broad resonance at 59 ppm corresponding to a tri-coordinate boron atom. The  $^{29}$ Si NMR spectrum contains a single resonance at -4.6 ppm (Table 3).

Tridentate gallium and indium Lewis acids were synthesised using GaMe<sub>3</sub>, GaEt<sub>3</sub> or InMe<sub>3</sub> in alkane elimination reactions in analogy to earlier work of our group, but varying conditions.<sup>[19,34]</sup> Compound **10** was afforded by a solvent-free reaction of **8** with trimethylgallium and heating to 42 °C for 24 h (Scheme 3), while compound **11** formed from **8** and triethylgallium also within 24 h without heating; both reactions proceeded quantitatively. Due to the solid nature of trimethylindium at room temperature, the reaction with this reagent was performed in toluene, affording compound **12** in 80% yield. Products **10–12** are colourless, less soluble (in donor free solvents) solids and were characterised by NMR (Table 3) and FT-IR spectroscopy, as well as elemental analyses. They are likely aggregated in the solid state, but so far all attempts to grow single crystals for structure elucidation failed.

The solubilities of **10–12** are generally very low in hydrocarbon solvents and on the order of about 1 mg mL<sup>-1</sup> for **11**. This is likely due to aggregation. In order to record good quality solution NMR spectra, compounds **10** and **11** were dissolved in  $C_6D_6/Et_2O$  mixtures and **12** in  $[D_8]$ THF. Compounds **10** and **11** are stable in the named solvents, but compound **12** undergoes redistribution as is indicated by the observation of further resonances in all NMR spectra in addition to the expected signals. Only the resonances assigned to the desired compound **12** are listed in Table 3 and in the Experimental Section. The supposed redistribution reaction is shown in Scheme 4.

The metalation of ethynyl groups with gallium organyl groups causes a small downfield shift of the resonances of the methyl and methylene groups. The functionalisation with indium organyl groups (compound 12) has barely an influence on those resonances (compare Table 3 and Table S6 in the Supporting Information). As an example the <sup>1</sup>H NMR spectrum of compound 11 is shown in Figure 5. The corresponding resonances are assigned in the figure. The identity of 11 is confirmed by comparing the NMR shifts of triethylgallium (1.43 ppm [triplet] and 0.93 ppm [quartet], neat, referenced to a C<sub>6</sub>D<sub>6</sub> capillary) with those of the tridentate Lewis acid 11 (1.35 ppm [triplet] and 0.61 ppm [quartet]). The same downfield shift was observed by comparing the proton resonances of 10 (-0.04 ppm) with those of trimethylgallium (0.21 ppm, neat) and 12 (-0.44 ppm) with trimethylindium (-0.24 ppm<sup>[35]</sup>). Resonances of the carbon atoms in the ethynyl groups of the gallium compounds could not be observed,



Scheme 4. Supposed redistribution of compound 12 in THF.



**Figure 5.** <sup>1</sup>H NMR spectrum of 11 in  $C_6D_6$  with 10 equivalents of Et<sub>2</sub>O. # denotes the resonances of Et<sub>2</sub>O. The resonances of 11 are assigned in the figure.

likely due to the strong quadrupole broadening caused by the gallium nucleus. The corresponding chemical shifts of **12** (Table 3) receive a strong downfield shift in comparison to **8** (94.5 and 90.1 ppm). The chemical shifts of the silicon atoms of **8**, **10**, **11** and **12** have almost the same value (compare Table 3 and Table S6 in the Supporting Information), confirming that the silicon atoms all bear ethynyl groups.

Further proof for the identity of these C=C units stems from FT-IR spectra. Bands were observed at 2034 (**10**, **11** and **12**) and 2029 cm<sup>-1</sup> (**12**). Elemental analysis data confirm the above structural assignments.

# Host-guest complex formation observed by DOSY NMR investigations

We have recently reported the complexation of a bidentate gallium Lewis acid based on an anthracene framework with pyridine and pyrimidine under dynamic conditions in solution by a combination of NMR titration and diffusion NMR experiments.<sup>[20]</sup> Here we describe the conversion of **11** (called host, H) with the tridentate Lewis base 1,3,5-trimethyl-1,3,5-triazacy-clohexane (TMTAC, called guest, G) as an example for molecular recognition of a tridentate Lewis acid.

Diffusion NMR spectroscopy is a versatile tool for the analysis of molecular size,<sup>[36]</sup> analysis of compound mixtures and determination of complex formation in solution.[37] The method provides self-transitional diffusion coefficients D that depend on the size and shape of the investigated system. For a reliable interpretation of hydrodynamic radii it is indispensable to compare the diffusion coefficients D of the analyte with values of suitable model systems that are similar in structure (if this is not close to spherical). For these reasons some model compounds (see Scheme 5: 13-16) were synthesised that mimic the structures of likely host-guest adducts in size and shapeas far as achievable with a reasonable synthetic effort. Their syntheses are described in the Supporting Information. Their diffusion coefficients D were determined in [D<sub>8</sub>]toluene. They are shown below the reference compounds and listed in Table 4.

<b>Table 4.</b> Results of the diffusion NMR measurements of host (11), TMTAC (guest) and reference compounds in $[D_8]$ toluene at 294 K.					
Compound	$D [10^{-10} \text{ m}^2 \text{ s}^{-1}]$	Compound	$D [10^{-10} \text{ m}^2 \text{s}^{-1}]$		
11	4.2	14	6.5		
TMTAC	12.4	15	5.9		
13 (monomer)	8.6	16	5.6		

Figure 6 displays the NMR titration of 11 with TMTAC. Ratios of compound 11 (H) and TMTAC (G) are listed on the left side of the figure. Resonances marked with  $\bullet$  represent the signals of TMTAC (in spectra b, c and d the resonances of TMTAC are overlaid by the methyl resonance of the residual protons of toluene). <sup>1</sup>H NMR spectrum Figure 6a shows host 11 without the guest. The resonances of 11 are marked by ① in all spectra. The diffusion coefficients were determined at resonances labelled with a  $\bigstar$ .

The host **11** dissolved in toluene has a diffusion coefficient of  $D = 4.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  (Table 4). Comparison with the diffusion coefficient of compound **13**, as reference for a monomeric host, indicates that compound **11** does not adopt a monomeric structure in solution. In this case, the method of diffusion coefficient formula weight correlation was applied (for more information on this methodology see reference [38]). Therefore, the logarithmic diffusion coefficients *D* were plotted against the logarithmic molecular weights of TMTAC and model com-

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Scheme 5. Model of the monomer 13 and references 14–16 for host molecule 11 and likely structures of host–guest complexes of 11 with TMTAC (1,3,5-trimethyl-1,3,5-triazacyclohexane) 17–19. Experimental diffusion coefficients *D* for 14--16 measured in [D<sub>8</sub>]toluene at 294 K are listed below the compound numbers.



**Figure 6.** <sup>1</sup>H NMR spectra of the host compound **11** (H), the guest TMTAC (G) and the conversion of **11** with TMTAC in different mixtures in  $[D_{g}]$ toluene at 294 K (600 MHz); # denotes the residual proton resonance of toluene; resonances labelled with  $\bullet$  are those of TMTAC.

pounds **14–16**. This yields the equation of a regression line, log D = -0.4597x - 7.9336 ( $x = \log M_w$ ) (Figure S5, Supporting information). Using this equation and the diffusion coefficient derived from the signals of compound **11**, a molecular weight

range between  $4.4 \times 10^{-10}$  and  $4.7 \times 10^{-10}$  m<sup>2</sup>s<sup>-1</sup>. By applying the equation from above and considering the small values of the diffusion coefficient for the ratio 1:0.5 (H:G), we infer the presence of a dimeric host structure in interaction with one

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of  $1378 \text{ gmol}^{-1}$  for this aggregate of **11** was estimated (taking into account the different atomic weight of Si and Ga). This corresponds to trimeric aggregate of **11** in solution.

With further addition of TMTAC the resonances of component 11 (Figure 6b, (1)) become smaller and finally disappear at a ratio of H:G=1:1 (Figure 6 c), while new signals appear (labelled 2), which represent more than one new complex species. This relation can be explained by the fact, that the Lewis base molecules can bind more than one host molecule 11.

The corresponding diffusion coefficients are listed in Table 5 and are a plot of the diffusion coefficients against the equivalents of TMTAC added is displayed in Figure 7. Mixture ratios from 1:0.1 to 1:0.5 (H:G) result in diffusion coefficients in the



<b>Table 5.</b> Results of the diffusion NMR measurements of the conversion ofhost 11 and TMTAC (guest).						
Molar ratio H:G	<i>D</i> (host) [10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> ]	Molar ratio H:G	<i>D</i> (host) [10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> ]			
1:0.1	4.4	1:0.8	6.8			
1:0.2	4.4	1:1	6.8			
1:0.4	4.6	1:1.2	7.0			
1:0.5	4.7	1:1.5	7.0			
1:0.7	6.6					



Figure 7. Diffusion coefficients of the conversion of 11 with TMTAC. Data are listed in Table 5. Horizontal lines shows the reference compound of monomer 13 (dashed line) and a host–guest complex 1:1 14 (dash-and-dot line).

TMTAC molecule (calculated molecular weight: 1079 g mol<sup>-1</sup>; compare  $2M_{W,13} + M_{W,TMTAC} = (2 \times 463.07 + 129.20) \text{ g mol}^{-1} = 1055.34 \text{ g mol}^{-1}$ ).

Spectra of host-guest mixtures of around 1:1 show broad resonances (2) (Figure 6 c), which points to a dynamic arrangement of host and guest molecules. Therefore temperature-dependent <sup>1</sup>H NMR spectra of a 1:1.2 (H:G) mixture were recorded to prove the dynamics.

Figure 8 shows this dynamic behaviour at both the resonance of TMTAC (3.5 ppm, 353 K) and that of component **11** (triplet, 1.5 ppm). At a temperature of 273 K additional resonances appear and upon cooling to 193 K further broad resonances occur. These additional signals represent further coordination species. Diffusion coefficients of 1:0.7 to 1:1.5 mixtures were determined to  $6.6 \times 10^{-10}$  and  $7.0 \times 10^{-10}$  m<sup>2</sup>s<sup>-1</sup> at room temperature (Table 5), which are comparable with that of reference molecule **14** ( $6.5 \times 10^{-10}$  m<sup>2</sup>s<sup>-1</sup>, Table 4).

Despite the dynamic processes at room temperature, compound **11** evidently forms a one-to-one complex with TMTAC at a ratio close to 1:1. The fact that the diffusion coefficient of the host–guest complex is slightly larger than the value of reference **14** indicates a slightly smaller hydrodynamic radius. This suggests that TMTAC coordinates to the three gallium



 $\delta$  /ppm  $\longrightarrow$ 

**Figure 8.** Temperature-dependent <sup>1</sup>H NMR spectra of a 1:1.2 mixture of host 11 and guest TMTAC in  $[D_{e}]$ toluene; # denotes the residual proton resonance of toluene; with  $\bullet$  labelled resonances are those of TMTAC.

Table 6.11 (host)sion coef	Results of the dif and TMTAC (gue ficients <i>D</i> [10 <sup>-10</sup> r	fusion NMR meas st). Listed are the n <sup>2</sup> s <sup>-1</sup> ].	surements of the e molar ratio H:G	conversion of and the diffu-
H:G	D (Host)	D (Host)	D (Host)	D (Guest)
1:1.5	7.0	6.2	11.2	
1:2		6.2	10.5	8.7
1:5	6.6	5.7	8.1	13.1

5.6

atoms of host **11** with all three nitrogen atoms to give the 1:1 aggregate **17** (Scheme 5).

If the ratio is increased to  $\geq$ 1:1.5, other species form (Figure 6, triplets ③, doublets ④, quartets ⑤, singlets ⑥). Their diffusion coefficients (Table 6) are comparable to those of model compounds **15** and **16** (Table 4). This underlines the fact that TMTAC is dynamically bonded to **11**, and —if available—further TMTAC molecules can cleave aggregate **17** and coordinate additional guest molecules at ratios above 1:1.5.

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1

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1:10

5.9

9.5



Scheme 6. Host-guest chemistry of the system 11/TMTAC during the titration with TMTAC. H designates host 11 and guest TMTAC is denoted by G.

In essence, the host–guest chemistry of the system 11/ TMTAC shows a dynamic behaviour, so that at H:G ratios between 1:0 and 1:0.5 host 11 seems to be a dimer with additional TMTAC coordination in solution (Scheme 6, H<sub>2</sub>G) and at ratios of 1:1, a one-to-one complex is present (Scheme 6, HG). At higher concentrations of TMTAC (H:G  $\geq$  1:1.5) a two- and threefold coordination of TMTAC to 11 is observed.

## Conclusion

Tridentate Lewis acids with unidirectional functions were synthesised with 1,3,5-trisilacyclohexanes as basic skeletons that bear three symmetrically bonded ethynyl units carrying the acid functions. Preparative pathways were explored to generate these skeletons in a way with optimised selectivity concerning the formation of the all-cis isomers of the 1,3,5-triethynyl-1,3,5-trisilacyclohexanes. Such a way was found in first cyclising diethoxy(chloromethyl)methylsilane, (EtO)<sub>2</sub>Si(Me)CH<sub>2</sub>Cl, with magnesium to afford 1,3,5-triethoxy-1,3,5-trimethyl-1,3,5-trisilacyclohexane (5), which was then chlorinated with boron trichloride to give 1,3,5-trichloro-1,3,5trimethyl-1,3,5-trisilacyclohexane (6). This was reacted with ethynyl magnesium bromide to give 1,3,5-triethynyl-1,3,5-trimethyl-1,3,5-trisilacyclohexane (8). Only at this step was it possible to separate the diastereomers by fractional sublimation to afford pure all-cis-8. Spectroscopy and structural analysis by Xray diffraction proofed the identity unidirectional functionality. Gas-phase electron diffraction (GED) and quantum chemical investigations showed that the free molecules adopt an all-equatorial arrangement of the ethynyl functions; however, there is a low barrier to ring inversion to the all-axial conformer (too low to be determined in solution by NMR spectroscopy).

Some examples for tridentate Lewis acids were obtained. The reaction of all-*cis*-**8** with three equivalents of Piers' borane yielded 1,3,5-tris[bis(pentafluorophenyl)boranylethenyl]-1,3,5-trimethyl-1,3,5-trisilacyclohexane (**9**) under reduction of the ethynyl units. Metalation with gallium- and indium trialkyls gave the 1,3,5-tris(dialkylmetallynylethynyl)-1,3,5-trimethyl-1,3,5-trisilacyclohexanes,  $[(Me)(R_2M-C=C)SiCH_2]_3$  (M/R = Ga/Me (**10**), Ga/Et (**11**), In/Me (**12**)) under alkane elimination.

The host-guest chemistry of  $[(Me)(Et_2Ga-C=C)SiCH_2]_3$  (11) with the tridentate guest 1,3,5-trimethyl-1,3,5-triazacyclohexane (TMTAC) was investigated. NMR titration and DOSY NMR experiments were performed to analyse this dynamic system in solution. The experiments revealed, that 11 forms a one-to-one host guest complex with TMTAC only at ratios around 1:1 (host/guest). At ratios  $\geq$  1:1.5 (host:guest) two and three TMTAC molecules bind to the tridentate Lewis acid 11. At

lower ratios of the experiments (1:0.5 and higher) aggregates of **11** with additional TMTAC ligands are present in solution, while the pure host **11** seems to be trimeric in solution.

In essence, the all-*cis* form of 1,3,5-triethynyl-1,3,5-trisilacyclohexanes offers a well accessible framework for the generation of systems with three concordantly oriented functions. Despite the predefined orientation, the high conformational flexibility of the 1,3,5-trisilacyclohexane rings (inversion) allows for a simultaneous movement of reactive sites to a given substrate. We are currently exploring this ability in our laboratories with a multitude of different reactive sites.

## **Experimental Section**

#### **General methods**

All manipulations were performed under dried argon or nitrogen using Schlenk and glove-box techniques. Tetrahydrofuran was dried with potassium, pentane, hexane and diethyl ether with LiAlH<sub>4</sub>. They were distilled prior to use. Dichloro(chloromethyl)methylsilane (1) (Sigma-Aldrich) was distilled before use. Piers' borane was synthesised according to a reported protocol.<sup>[32,33]</sup> C<sub>6</sub>D<sub>6</sub>, [D<sub>8</sub>]THF and [D<sub>8</sub>]toluene were dried with Na/K alloy and condensed. NMR measurements were performed on Bruker Avance III 500, Bruker Avance III 300 and Bruker DRX 500 instruments. NMR spectra were referenced to the residual signal of used protonated solvents (<sup>1</sup>H, <sup>13</sup>C) or external standards (<sup>11</sup>B: BF<sub>3</sub>·OEt<sub>3</sub>, <sup>19</sup>F: CCl<sub>3</sub>F; <sup>29</sup>Si: TMS). GC/EI-MS analyses were done using a Shimadzu GC-2010/ GCMS-QP 2010S instrument (capillary column: Rtx-200 Crossbond, trifluoropropylmethylpolysiloxane, 30 m, 25 mm, 0.25 µm). El and CI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. FT-IR spectra were recorded on a Bruker ALPHA FT-IR-spectrometer. Elemental analyses were performed with CHNS elemental analyser HEKAtech EURO EA (too low values for carbon are due to the known formation of silicon carbide).

#### Quantum chemical calculations

Quantum-chemical calculations using DFT<sup>[39]</sup> and MP2<sup>[40]</sup> approximations with built-in 6-31G(d,p) and cc-pVTZ basis sets have been carried out by using Gaussian 03 program package.<sup>[41]</sup> In all cases for optimised structures calculations of frequencies have been done to prove the existence of minima on the potential energy surface. Calculations of numeric cubic force fields were performed on the B3LYP/6–31G(d,p) level of theory.

#### Gas-phase electron diffraction experiment

The electron diffraction patterns were recorded using the improved Balzers Eldigraph KD-G2 gas-phase electron diffractometer<sup>[42]</sup> at Bielefeld University. The experimental conditions are presented in Table 7. The electron diffraction patterns were measured on Fuji BAS-IP MP 2025 imaging plates, which were scanned using a calibrated Fuji BAS-1800II scanner. The intensity curves (Figure S1 in Supporting Information) were obtained by applying a method described earlier.<sup>[43]</sup> Sector function and electron wavelengths were refined<sup>[44]</sup> using diffraction patterns of CS<sub>2</sub>, recorded along with the substances under investigation and comparing with standard parameters for CS<sub>2</sub>.<sup>[45]</sup>

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Table 7.	Details	of the	GED	experiments	for	8	for	the	measurements	at
short an	id long o	amera	dista	nces.						

Parameter	Short	Long
d <sub>nozzle-detector</sub> [mm]	250.0	500.0
$U_{\rm acceleration}$ [kV]	60	60
I <sub>fast electrons</sub> [μA]	1.1	0.9
$\lambda_{\text{electron}}^{[a]}$ [Å]	0.048718	0.048736
T <sub>nozzle</sub> [K]	381	388
p <sub>chamber</sub> <sup>[b]</sup> [mbar]	$1.7 \times 10^{-6}$	$1.4 \times 10^{-6}$
p <sub>residual gas</sub> [c] [mbar]	8.3×10 <sup>-8</sup>	$2.3 \times 10^{-7}$
t <sub>exposure</sub> [s]	5	5
s range [Å <sup>-1</sup> ]	7.0-31.2	2.2-16.6
inflection points <sup>[d]</sup>	4	2

[a] Determined from  $CS_2$  diffraction patterns measured in the same experiment. [b] During the measurement. [c] Between measurements. [d] Number of inflection points on the background lines (see Figure S1 of Supporting Information).

#### Gas-phase electron diffraction structural analysis

The structural analysis was performed with the UNEX program.[46] All refinements were done using two intensity curves simultaneously (see Figure S1 of Supporting Information), one from the short and another from the long camera distance. These were obtained by averaging independently measured intensity curves. The total intensities were transformed into molecular intensity curves (Figure S2 of Supporting Information) by background elimination using cubic splines. The structure of **8** was assumed to be of  $C_{3\nu}$ symmetry. For the definition of the geometry in the form of a Zmatrix and grouping of structure parameters in least-squares refinements see Table S1 (Supporting Information). The differences between values of parameters in one group were kept fixed at the values taken from B3LYP/6-31G(d,p) calculations. Scale factors for mean square amplitudes have been refined in groups (see Supporting Information Table S2). Thus, the ratios between different amplitudes in one group were fixed on the theoretical values calculated using the SHRINK program.<sup>[47]</sup> Correlation coefficients are provided in Table S3 (Supporting Information).

#### 1,3,5-Trimethoxy-1,3,5-trimetyl-1,3,5-trisilacyclohexane (4)

A solution of compound 2 (27.85 g, 180 mmol) in THF (250 mL) was added dropwise to a mixture of THF (250 mL) and magnesium turnings (5.0 g, 206 mmol, surface activated with 1,2-dibromoethane) while heating to 70°C. After the addition of 2 was completed, the grey suspension was refluxed for 4 h. Subsequently the solvent was removed and the remaining grey solid was extracted with pentane. The pentane was removed under reduced pressure (50 mbar) and the remaining oil distilled to afford product 4, b.p. 56-59 °C at 2.7 mbar. Yield: 6.49 g (24.5 mmol, 41%). The product was a mixture of two diastereomers: all-cis- and cis-trans-4. Assignments for all-cis-4: <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ , 298 K):  $\delta = 3.31$  (s, 9H; -SiOCH<sub>3</sub>), 0.22 (d,  ${}^{2}J_{H,H} = 13.6$  Hz, 3 H; -SiCH<sub>2</sub>Si-), 0.12 (s, 9 H; -SiCH<sub>3</sub>), -0.12 ppm (d,  ${}^{2}J_{H,H} = 13.6$  Hz, 3 H; -SiCH<sub>2</sub>Si-);  ${}^{13}C{}^{1}H$  NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 49.7$  (s, -SiOCH<sub>3</sub>), 3.5 (s, -SiCH<sub>2</sub>Si-), 1.0 ppm (s, -SiCH<sub>3</sub>);  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta =$ 15.3 ppm (s, -CH<sub>2</sub>SiCH<sub>2</sub>-); assignments for *cis-trans*-4: <sup>1</sup>H NMR (500 MHz,  $C_6 D_{67}$  298 K):  $\delta = 3.30$  (s, 6H; -SiOCH<sub>3</sub>), 3.20 (s, 3H; -SiOCH<sub>3</sub>), 0.23 (s, 6H; -SiCH<sub>3</sub>), 0.19 (s, 3H; -SiCH<sub>3</sub>), 0.16 (d,  ${}^{2}J_{H,H} =$ 13.7 Hz, 1 H; -SiC $H_2$ Si-), 0.01 (d,  ${}^2J_{H,H}$  = 13.8 Hz, 2 H; -SiC $H_2$ Si-), -0.10 (d,  ${}^{2}J_{HH} = 13.7$  Hz, 1H; -SiCH<sub>2</sub>Si-), -0.13 ppm (d,  ${}^{2}J_{HH} = 13.8$  Hz, 2H; -SiCH<sub>2</sub>Si-); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 49.7 (s, -SiOCH<sub>3</sub>),

49.7 (-SiOCH3), 3.8 (s, -SiCH<sub>2</sub>Si-), 3.4 (s, -SiCH<sub>2</sub>Si-), 0.7 (s, -SiCH<sub>3</sub>), 0.6 ppm (s, -SiCH<sub>3</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 16.8 (s, -CH<sub>2</sub>SiCH<sub>2</sub>-), 16.4 ppm (s, -CH<sub>2</sub>SiCH<sub>2</sub>-); GC/EI-MS: retention time 8.13 min (all-*cis*): *m/z* (%): 249.0 (100) [*M*<sup>+</sup>-CH<sub>3</sub>], retention time 7.96 min (*cis*-*trans*): *m/z* (%): 264.0 [*M*<sup>+</sup>], 249.0 (100) [*M*<sup>+</sup>-CH<sub>3</sub>]; FT-IR (KBr):  $\tilde{\nu}$  = 2956, 2913, 2830, 1464, 1409, 1353, 1254, 1190, 1047, 1046, 1044, 1041, 1039, 1038, 1035, 1033, 1029, 940, 847, 842, 840, 837, 834, 832, 830, 828, 826, 824, 820, 815, 814, 809, 807, 803, 791, 789, 785, 782, 762, 741, 623 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>9</sub>H<sub>24</sub>O<sub>3</sub>Si<sub>3</sub> (264.54): C 40.86, H 9.14; found: C 40.41, H 9.11.

#### 1,3,5-Triethoxy-1,3,5-trimetyl-1,3,5-trisilacyclohexane (5)

Compound 5 was synthesized by using a protocol analogous to that for 4, but with compound 3 as the starting material. B.p. 83  $^\circ$ C at 1 mmHg (1.3 mbar) (Literature values:  $^{[23,2\bar{4}]}$  68–69  $^{\circ}\text{C}$  at 0.2– 0.25 mmHg/97 °C at 1.7 mmHg). Yield: 32% (Literature values: 30.4-33.2%). The product was a mixture of two diastereomers, allcis and cis-trans. Assignments for all-cis-5: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 3.58$  (q,  ${}^{3}J_{\rm H,H} = 7.0$  Hz, 6H; -SiOCH<sub>2</sub>CH<sub>3</sub>), 1.16 (t,  ${}^{3}J_{\rm H,H} =$ 7.0 Hz, 9H; -SiOCH<sub>2</sub>CH<sub>3</sub>), 0.25 (d, <sup>2</sup>J<sub>H,H</sub> = 13.6 Hz, 3H; -SiCH<sub>2</sub>Si-), 0.15 (s, 9H; -SiCH<sub>3</sub>), -0.06 ppm (d,  ${}^{2}J_{H,H} = 13.6$  Hz, 3H; -SiCH<sub>2</sub>Si-);  ${}^{13}C{}^{1}H$ NMR (126 MHz,  $C_6D_6$ , 298 K):  $\delta = 57.9$  (s,  $-SiOCH_2CH_3$ ), 18.9 (s, -SiOCH $_2$ CH $_3$ ), 4.6 (s, -SiCH $_2$ Si-), 1.6 ppm (s, -SiCH $_3$ ); <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz,  $C_6D_6$ , 298 K):  $\delta = 12.7$  ppm (s, -CH<sub>2</sub>SiCH<sub>2</sub>-); assignments for *cis-trans-***5**: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 3.57$  (d, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 4H; -SiOCH<sub>2</sub>CH<sub>3</sub>), 3.47 (q,  ${}^{3}J_{H,H}$  = 7.0 Hz, 2H; -SiOCH<sub>2</sub>CH<sub>3</sub>), 1.16 (t,  ${}^{3}J_{H,H} = 7.0 \text{ Hz}$ , 6H; -SiOCH<sub>2</sub>CH<sub>3</sub>), 1.10 (t,  ${}^{3}J_{H,H} = 7.0 \text{ Hz}$ , 3H; -SiOCH<sub>2</sub>CH<sub>3</sub>), 0.26 (s, 6H; -SiCH<sub>3</sub>), 0.23 (s, 3H; -SiCH<sub>3</sub>), 0.19 (d, <sup>2</sup>J<sub>H,H</sub>= 13.9 Hz, 1 H; -SiCH<sub>2</sub>Si-), 0.04 (d,  ${}^{2}J_{H,H}$  = 13.6 Hz, 2 H; -SiCH<sub>2</sub>Si-), -0.06 (d,  ${}^{2}J_{H,H} = 13.9$  Hz, 1 H; -SiCH<sub>2</sub>Si-), -0.08 ppm (d,  ${}^{2}J_{H,H} = 13.6$  Hz, 2 H; -SiCH<sub>2</sub>Si-); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 58.0 (s, -SiOCH<sub>2</sub>CH<sub>3</sub>), 57.9 (s, -SiOCH<sub>2</sub>CH<sub>3</sub>), 18.9 (s, -SiOCH<sub>2</sub>CH<sub>3</sub>), 18.7 (s, -SiOCH<sub>2</sub>CH<sub>3</sub>), 4.8 (s, -SiCH<sub>2</sub>Si-), 4.5 (s, -SiCH<sub>2</sub>Si-), 1.4 (s, -SiCH<sub>3</sub>), 1.4 ppm (s, -SiCH<sub>3</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 14.1$  (s, -CH<sub>2</sub>SiCH<sub>2</sub>-), 13.8 ppm (s, -CH<sub>2</sub>SiCH<sub>2</sub>-); GC/EI-MS: retention time 8.5 min (all-cis and cis-trans): m/z (%): 291 (100) [M<sup>+</sup>-CH<sub>3</sub>], 261 [*M*<sup>+</sup>-OEt], 247 [*M*<sup>+</sup>-CH<sub>3</sub>-OEt], 217, 203, 189, 175, 145, 117, 103, 85, 73, 59, 45; MS (ESI, positive): *m*/*z* = 329.2 (100) [*M*<sup>+</sup>+Na], 307.2  $[M^++H]$ ; accurate mass (MS ESI): m/z calcd for  $C_{12}H_{30}O_3Si_3Na^+$ : 329.13950; found: 329.13980; FT-IR (KBr):  $\tilde{\nu} = 2973$ , 2925, 2896, 2873, 1481, 1443, 1391, 1354, 1293, 1255, 1166, 1109, 1084, 1037, 947, 824, 783, 761, 739, 625 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>12</sub>H<sub>30</sub>O<sub>3</sub>Si<sub>3</sub> (*M*<sub>r</sub> = 306.62): C 47.01, H 9.86; found: C 46.64, H 9.89.

#### 1,3,5-Trichloro-1,3,5-trimethyl-1,3,5-trisilacyclohexane (6)

a) Compound **5** (7.54 g, 24.6 mmol) was dissolved in *n*-pentane (80 mL). After three freeze-pump-thaw cycles boron trichloride (81.2 mmol measured as gas) was condensed onto the frozen solution of **5** at -198 °C. The reaction mixture was warmed to -20 °C. At this temperature the reaction started under formation of a waxy solid. After warming to room temperature overnight all volatiles were removed under reduced pressure and the residual colourless solid was sublimed at 50 °C and 0.03 mbar. Product **6** was obtained as a colourless solid in a yield of 89% (6.08 g, 21.9 mmol).

b) Compound **7** (39 mg, 0.22 mmol) was dissolved in tetrachloromethane (2 mL). A saturated solution of chlorine in tetrachloromethane (2 mL) was added dropwise over a period of 1 min. The formed hydrogen chloride and excess of chlorine were removed by purging nitrogen through the solution. Tetrachloromethane was removed under reduced pressure to afford the product as a waxy solid; yield 100% (60.5 mg, 22 mmol).

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Assignments for all-cis-6: <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ , 298 K):  $\delta = 0.34$ (s, 9H; -SiCH<sub>3</sub>), 0.18 (d, <sup>2</sup>J<sub>H,H</sub> = 14.0 Hz, 3H; -SiCH<sub>2</sub>Si-), 0.13 ppm (d,  $^2J_{\rm H,H}\!=\!$  14.0 Hz, -SiCH\_2Si-);  $^{13}{
m C}\{^1{
m H}\}$  NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta\!=$ 10.1 (s, -SiCH<sub>2</sub>Si-), 5.2 ppm (s, -SiCH<sub>3</sub>);  ${}^{29}$ Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 26.4$  ppm (s, -CH<sub>2</sub>SiCH<sub>2</sub>-); assignments for *cis-trans*-**6**: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 0.47$  (d, <sup>2</sup>J<sub>H,H</sub> = 14.2 Hz, 1 H; -SiCH<sub>2</sub>Si-), 0.39 (d, <sup>2</sup>J<sub>H,H</sub> = 14.2 Hz, 2 H; -SiCH<sub>2</sub>Si-), 0.32 (s, 6 H; -SiCH<sub>3</sub>), 0.16 (d, <sup>2</sup>J<sub>H,H</sub>=14.2 Hz, 1 H; -SiCH<sub>2</sub>Si-), 0.12 (d, <sup>2</sup>J<sub>H,H</sub>=14.2 Hz, 2 H; -SiCH<sub>2</sub>Si-), 0.08 ppm (s, 3H; -SiCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 10.9$  (s, -SiCH<sub>2</sub>Si-), 10.5 (s, -SiCH<sub>2</sub>Si-), 5.4 (s, -SiCH<sub>3</sub>), 4.8 ppm (s, -SiCH\_3);  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz, C\_6D\_6, 298 K):  $\delta\!=\!26.1$  (s, -CH<sub>2</sub>SiCH<sub>2</sub>-), 25.4 ppm (s, -CH<sub>2</sub>SiCH<sub>2</sub>-); GC/EI-MS: m/z (%): 261 (100), [*M*<sup>+</sup>-Me], 241 [*M*<sup>+</sup>-Cl], 225 [*M*<sup>+</sup>-HCl-Me], 169, 147, 133, 113, 93, 79, 63, 43; MS (ESI, negative): m/z (%): 257.0 (100) [M-CI+O]-; FT-IR (KBr):  $\tilde{\nu} = 2963$ , 2926, 2901, 2872, 2858, 1406, 1349, 1259, 1160, 1050, 951, 831, 772, 748, 719, 633, 621, 610, 530, 508, 486, 466 cm<sup>-1</sup>; elemental analysis calcd (%) for  $C_6H_{15}Si_3Cl_3$  ( $M_r = 277.80$ ): C 25.94, H 5.44; found: C 25.77, H 5.42.

#### 1,3,5-Trimethyl-1,3,5-trisilacyclohexane (7)

Compound 3 (3.29 g, 12.5 mmol) was added dropwise to a suspension of LiAlH<sub>4</sub> (95%, 576 mg, 14.4 mmol) in diethyl ether (80 mL) at 0°C. During this addition the suspension became white. The reaction mixture was refluxed for 24 h. All volatiles were passed through a series of cold traps (-45 and  $-198\,^\circ\text{C}$ ) under vacuum and the product was collected in the  $-45^{\circ}C$  trap, while diethyl ether passed to the -198 °C trap. Yielded was 1.55 g of a product mixture of all-cis and cis-trans (8.9 mmol, 71%). The diastereomers were separated according to a protocol reported by I. Arnason<sup>[28]</sup> in a fractional condensation with the help of an U-tube (yield of all-cis: 58%); Assignments for all-cis-7: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 4.36$  (ttq,  ${}^{3}J_{\text{H,H}} = 1.3$  Hz (H<sub>e</sub>),  ${}^{3}J_{\text{H,H}} = 3.7$  Hz (H<sub>Me</sub>),  ${}^{3}J_{\text{H,H}} =$ 7.6 Hz (H<sub>a</sub>), 3 H; -Si*H*), 0.14 (d,  ${}^{3}J_{H,H} = 3.7$  Hz, 9 H; -SiCH<sub>3</sub>), -0.13 (d,  $^{2}J_{\text{H,H}} = 13.6 \text{ Hz}, 3 \text{ H}; -\text{SiCH}_{e}\text{Si-}), -0.64 \text{ ppm} (dd, ^{2}J_{\text{H,H}} = 13.6 \text{ Hz}, 3 \text{ H};$ -SiCH<sub>a</sub>Si-);  ${}^{13}C{}^{1}H$  NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 0.4 (s, -SiCH<sub>3</sub>), -1.4 ppm (s, -SiCH<sub>2</sub>Si-); <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta =$ -14.4 ppm; GC/EI-MS (all-cis): m/z (%): 173 [M<sup>+</sup>-H], 159 (100) [M<sup>+</sup> -Me], 129, 113, 99, 85, 73, 59, 43, retention time: 4.1 min; FT-IR (KBr):  $\tilde{\nu} = 2958$ , 2916, 2871, 2102 (Si-H), 1358, 1261, 1253, 1243, 1056, 1044, 1002, 868, 788, 738, 694, 681, 668, 614, 574 cm<sup>-1</sup>; elemental analysis calculated (%) for  $C_6H_{18}Si_3$  ( $M_r = 174.43$ ): C 41.31, H 10.41; found: C 38.55, H 10.33.

#### 1,3,5-Triethynyl-1,3,5-trimethyl-1,3,5-trisilacyclohexane (8)

A solution of ethynyl magnesium bromide (70 mL, 0.5 M, 35 mmol) was added dropwise to a solution of compound 8 (2.14 g, 7.7 mmol) in THF (100 mL). The mixture was refluxed for 37 h. After hydrolysis with a saturated aqueous solution of ammonia chloride, the organic phase was separated and the aqueous phase was extracted three times with *n*-pentane  $(3 \times 100 \text{ mL})$ . The combined organic phases were washed twice with water (2×100 mL) and dried over MgSO<sub>4</sub>. The solvent was removed and the remaining solid was sublimed at room temperature and 0.003 mbar. Compound 8 was obtained as colourless solid. Yield: 1.79 g (7.3 mmol, 95% diastereomeric mixture, ratio all-cis:cis-trans 60:40). The separation of the diastereomers was performed by fractional sublimation at room temperature and 0.003 mbar. Assignments for all-cis-8: <sup>1</sup>H NMR (500 MHz,  $C_6 D_{67}$  298 K):  $\delta = 2.15$  (s, 3 H; -SiC=CH), 0.38 (d, <sup>2</sup>J<sub>HH</sub> = 14.1 Hz, 3 H; -SiCH<sub>2</sub>Si-), 0.11 (s, 9 H; -SiCH<sub>3</sub>), -0.20 ppm (d, <sup>2</sup>J<sub>H,H</sub> = 14.1 Hz, 3 H; -SiCH<sub>2</sub>Si-); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 94.5$  (s, -SiC=CH), 90.1 (s, -SiC=CH), 2.2 (s, -SiCH<sub>2</sub>Si-), 1.8 ppm (s, -SiCH<sub>3</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = -18.5$  (s, -CH<sub>2</sub>SiCH2); assignments for *cis-trans-***8**: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta =$ 2.13 (s, 2H; -SiC=CH), 2.01 (s, 1H; -SiC=CH), 0.35 (s, 6H; -SiCH<sub>3</sub>), 0.34 (s, 3H; -SiCH<sub>3</sub>), 0.25 (d,  ${}^{2}J_{H,H} = 14.1$  Hz, 2H; -SiCH<sub>2</sub>Si-), 0.01 (d,  ${}^{2}J_{H,H} = 14.0$  Hz, 1H; SiCH<sub>2</sub>Si), -0.03 (d,  ${}^{2}J_{H,H} = 14.0$  Hz, 1H; SiCH<sub>2</sub>Si), -0.16 ppm (d, <sup>2</sup>J<sub>HH</sub>=14.1 Hz, 2H; SiCH<sub>2</sub>Si); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 94.8 (s, -SiC≡CH), 94.4 (s, -SiC≡CH), 90.7 (s, -SiC≡ CH), 90.5 (s, SiC=CH), 2.3 (s, -SiCH2Si-), 2.1 (s, -SiCH2Si-), 1.9 (s, SiCH<sub>3</sub>), 1.4 ppm (s, SiCH<sub>3</sub>);  $^{29}$ Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta =$ -18.7 (s, -SiCH<sub>3</sub>), -18.5 ppm (s, -SiCH<sub>3</sub>); GC/EI-MS (all-cis): m/z (%): 231 (100) [*M*<sup>+</sup>-Me], retention time: 7.3 min; GC/EI-MS (*cis-trans*): m/z (%): 231 (100)  $[M^+ - Me]$ , retention time: 7.0 min; EI-MS: m/z(%): 245.0 [*M*<sup>+</sup>-H], 231.0 (100) [*M*<sup>+</sup>-Me], 93.0, 67.0; FT-IR (KBr) (all-*cis*):  $\tilde{\nu}$  = 3282 (C≡C−H), 3265 (C≡C−H), 2962, 2925, 2905, 2877, 2035 (C=C), 2030 (C=C), 1411, 1361, 1349, 1261, 1047, 820, 783, 716, 693, 680, 592, 578 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>12</sub>H<sub>18</sub>Si<sub>3</sub> (*M*<sub>r</sub> = 246.53): C 58.46, H 7.36; found: C 57.92, H 7.48.

#### 1,3,5-Tris[bis(pentafluorophenyl)boranylethenyl]-1,3,5-trimethyl-1,3,5-trisilacyclohexane (9)

Piers' borane (HB( $C_6F_5$ )<sub>2</sub>, 212 mg, 0.6 mmol) and **8** (50 mg, 0.2 mmol) were placed in a flask equipped with a Young greaseless tap. The mixture was frozen in liquid nitrogen, *n*-pentane (10 mL) was condensed onto it and warmed after that to RT. After a few minutes both solids were dissolved and the reaction was over. All volatiles were removed under reduced pressure and a solid residue of **9** remained. Yield: 259.1 mg (0.2 mmol, 100%). <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ , 298 K):  $\delta = 7.64$  (d,  ${}^{3}J_{H,H} = 21.0$  Hz, 3 H; -SiHC=CHB-), 7.48 (d, <sup>3</sup>J<sub>HH</sub>=21 Hz, 3H; -SiHC=CHB-) 0.23 (s, 9H; -SiCH<sub>3</sub>), 0.10 (d,  $^{2}J_{H,H} = 13.9$  Hz, 3 H; -SiCH<sub>2</sub>Si-), -0.06 ppm (d,  $^{2}J_{H,H} = 13.9$  Hz, 3 H; -SiCH<sub>2</sub>Si-); <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 58.5$  ppm (brs); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 173.2$  (s, (<sup>F</sup>Ph)<sub>2</sub>BCH=CH-), 150.7 (brs, (<sup>F</sup>Ph)<sub>2</sub>BCH=CH-), 148.1 (dm, <sup>1</sup>J<sub>F,C</sub>=250.6 Hz, *m*-C), 143.8 (dm,  ${}^{1}J_{F,C} = 266.2$  Hz, p-C), 137.8 (dm,  ${}^{1}J_{F,C} = 250.2$  Hz), 113.6 (brs, *i*-C), -0.2 (s, -SiCH\_3), -1.6 ppm (s, -SiCH\_2Si-);  $^{19}\text{F}$  NMR (282 MHz,  $C_6\text{D}_6\text{,}$ 298 K):  $\delta = -129.05$  (m, 2F; o-F), -146.71 (tt,  ${}^{3}J_{F,F} = 20.7$  Hz,  ${}^{4}J_{F,F} =$ 4.8 Hz, 1F; *p*-F), -161.04 ppm (m, 2F; *m*-F); <sup>29</sup>Si{<sup>1</sup>H} NMR (60 MHz,  $C_6D_{6r}$  298 K):  $\delta = -4.6$  ppm; elemental analysis calcd (%) for  $C_{48}H_{21}B_3F_{30}Si_3$  ( $M_r$ =1284.32): C 44.89, H 1.65; found: C 45.05, H 1.81.

#### 1,3,5-Tris(dimethylgallanylethynyl)-1,3,5-trimethyl-1,3,5-trisilacyclohexane (10)

Compound 8 (70 mg, 0.28 mmol) was dissolved in trimethylgallium (1.00 mL, 1.13 g, 9.8 mmol) and the reaction solution was stirred at room temperature for 72 h (or 24 h at 42 °C). During the reaction a colourless solid was formed. After the reaction was finished, residual trimethylgallium was removed by condensation and the remaining colourless solid was dried in vacuum. Yield: 152.0 mg (0.26 mmol, 100%); m.p. 97  $^{\circ}$ C (decomp); <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, Et\_2O, 298 K):  $\delta = 0.62$  (d,  ${}^2J_{\rm H,H} = 13.9$  Hz, 3 H; -SiCH2Si-), 0.32 (s, 9H; -SiCH<sub>3</sub>), 0.17 (d,  ${}^{2}J_{H,H} = 13.9$  Hz, 3 H; -SiCH<sub>2</sub>Si-), -0.04 ppm (s, -Ga(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, Et<sub>2</sub>O, 298 K):  $\delta$  = 115.6 (brs, -SiC=C-Ga), 3.8 (s, -SiCH<sub>2</sub>Si-), 3.1 (s, SiCH<sub>3</sub>), -4.2 ppm (s, -Ga(CH<sub>3</sub>)<sub>2</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, Et<sub>2</sub>O, 298 K):  $\delta = -22.3$  ppm (-CH<sub>2</sub>SiCH<sub>2</sub>-); FT-IR (KBr):  $\tilde{\nu}$  = 3436, 3288, 2961, 2920, 2034 (C=C), 1359, 1260, 1043, 826, 782, 756, 712, 669, 666, 614, 585, 538 cm<sup>-1</sup>; elemental analysis calcd (%) for  $C_{18}H_{33}Ga_{3}Si_{3}$  ( $M_{r} = 542.88$ ): C 39.82, H 6.13; found: C 39.19, H 6.32.

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#### 1,3,5-Tris(diethylgallanylethynyl)-1,3,5-trimethyl-1,3,5-trisilacyclohexane (11)

Compound 8 (63 mg, 0.26 mmol) was dissolved in triethylgallium (1.00 mL, 1.07 g, 6.8 mmol) and the reaction solution was stirred at room temperature for 24 h. During the reaction colourless solid was formed. After the reaction was finished, triethylgallium was condensed off and the residual colourless solid was dried in vacuum. Yield: 163.0 mg (0.26 mmol, 100%); m.p. 78°C (decomp); <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, Et<sub>2</sub>O, 298 K):  $\delta = 1.35$  (t, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 18H;  $CH_{3}CH_{2}Ga$ -), 0.61 (q,  ${}^{3}J_{H,H}$ =8.1 Hz, 12 H;  $CH_{3}CH_{2}Ga$ -), 0.45 (d,  ${}^{2}J_{H,H}$ = 14.1 Hz, 3 H; -SiCH<sub>2</sub>Si-), 0.23 (s, 9 H; SiCH<sub>3</sub>), 0.17 ppm (d,  ${}^{2}J_{H,H}$ = 14.1 Hz, 3H; -SiCH<sub>2</sub>Si-); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, Et<sub>2</sub>O, 298 K):  $\delta = 10.7$  (s, CH<sub>3</sub>CH<sub>2</sub>Ga-), 6.3 (s, CH<sub>3</sub>CH<sub>2</sub>Ga-), 4.1 (s, -SiCH<sub>2</sub>Si-), 2.5 ppm (s, -SiCH<sub>3</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, Et<sub>2</sub>O, 298 K):  $\delta =$ -21.2 ppm (-CH<sub>2</sub>S*i*CH<sub>2</sub>-); FT-IR (KBr):  $\tilde{\nu} = 3290$ , 3223, 2950, 2901, 2865, 2814, 2034 (C=C), 1460, 1418, 1375, 1359, 1261, 1192, 1043, 1003, 961, 940, 827, 780, 758, 713, 655, 609, 565, 515 cm<sup>-1</sup>; elemental analysis calcd (%) for  $C_{24}H_{45}Ga_3Si_3$  ( $M_r$ =627.05): C 45.97, H 7.23; found: C 44.53, H 7.34.

#### 1,3,5-Tris(dimethylindanylethynyl)-1,3,5-trimethyl-1,3,5-trisilacyclohexane (12)

Compound 8 (50 mg, 0.20 mmol) and trimethylindium (97.4 mg, 0.61 mmol) were placed in toluene (4 mL). The solution received was heated for four days to 60 °C. During the reaction a colourless solid was formed. All volatiles were removed in vacuum and the colourless solid was washed with toluene (1 mL). The residual colourless solid was dried in vacuum. Yield: 109.0 mg (0.16 mmol, 80%); m.p. 181 °C (decomp). <sup>1</sup>H NMR (500 MHz,  $[D_8]$ THF, 298 K):  $\delta =$ 0.13 (s, 9H; SiCH<sub>3</sub>), 0.11 (d,  ${}^{2}J_{H,H} = 13.9$  Hz, 3H; -SiCH<sub>2</sub>Si-), -0.06 (d,  ${}^{2}J_{H,H} = 13.9 \text{ Hz}, 3 \text{ H}; -\text{SiCH}_{2}\text{Si-}), -0.44 \text{ ppm} (s, 18 \text{ H}; -\ln(CH_{3})_{2}); {}^{13}\text{C}{}^{1}\text{H}$ NMR (126 MHz, [D<sub>8</sub>]THF, 298 K):  $\delta = 135.6$  (s, -SiC=Cln-), 115.9 (s, -SiC≡Cln-), 5.7 (s, -SiCH<sub>2</sub>Si-), 3.3 (s, -SiCH<sub>3</sub>), -7.7 ppm (s, -In(CH<sub>3</sub>)<sub>2</sub>); <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, [D<sub>8</sub>]THF, 298 K):  $\delta = -24.2$  ppm (s, -CH<sub>2</sub>S*i*CH<sub>2</sub>-); FT-IR (KBr):  $\tilde{\nu}$  = 3287, 3282, 3272, 3265, 2966, 2922, 2034 (C=C), 2029 (C=C), 1407, 1359, 1261, 1160, 1041, 1000, 824, 780, 756, 709, 681, 650, 604, 582, 522 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>18</sub>H<sub>33</sub>In<sub>3</sub>Si<sub>3</sub> (*M*<sub>r</sub>=678.17): C 31.88, H 4.90; found: C 32.39, H 5.06.

#### **Diffusion NMR and titration experiments**

General remarks: Diffusion <sup>1</sup>H NMR measurements were performed on a Bruker Avance 600 NMR spectrometer in  $[D_a]$ toluene (294 K,  $\delta$ =7.09, 7.00, 6.98, 2.09 ppm) using the LED sequence with bipolar gradients (ledbpgp2s). The NMR tube with the sample was allowed to equilibrate for at 3 h within the probe/magnet prior to data recording. The duration of the gradients was incremented linearly in 16 steps. The maximum length of the gradient pulse  $\delta$  and the diffusion time were set to  $\delta$ =3.80 ms and  $\Delta$ =79.95 ms, respectively, for all experiments. The diffusion coefficients have been calculated by using the relaxation module of the Bruker software TOPSPIN.

Diffusion coefficients of host 11, TMTAC and reference compounds: Small amounts of the reference compounds 13, 14, 15, 16, host 11 and TMTAC (1,3,5-trimethyl-1,3,5-triazacyclohexane, guest) were dissolved in  $[D_g]$ toluene. Their diffusion coefficients were determined according to the procedure described in the general remarks. Results are listed in Table 4.

Conversion of **11** with TMTAC: Compound **11** (2 mg, 3.2 µmol) was dissolved in [D<sub>8</sub>]toluene (0.6 mL); small amounts solution of the TMTAC (TMTAC: 35 mg, 270.9 µmol in 3.669 g [D<sub>8</sub>]toluene; 0.064 µmol µL<sup>-1</sup>) were added using a 50 µL syringe (ITO CORPORA-

TION, Fuji, Japan). Their diffusion coefficients were determined according to the procedure described in general remarks. Results are listed in Table 5.

#### Crystallographic structure determination

Single crystals suitable for X-ray diffraction measurement were picked, suspended in a Paratone-N/paraffin oil mixture, mounted on a glass fibre and transferred onto the goniometer of the diffractometer. The measurements were carried out with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods and refined by full-matrix least-squares cycles (programs: SHELX-97).<sup>[48]</sup> Crystallographic details of compounds *cis-trans*-6, all-*cis*-7, all-*cis*-8

Table 8. Crystallographic data for compounds cis-trans-6, all-cis-7 and all-cis-8.				
	cis-trans- <b>6</b>	all-cis- <b>7</b>	all-cis- <b>8</b>	
formula	$C_6H_{15}CI_3Si_3$	$C_6H_{18}Si_3$	$C_{12}H_{18}Si_3$	
<i>M</i> <sub>r</sub>	277.80	174.47	246.53	
T [K]	100(2)	100.0(2)	100.0(2)	
crystal size [mm]	0.30×0.29×0.20	0.38×0.09×0.09	$0.27 \times 0.25 \times 0.13$	
crystal system	monoclinic	orthorhombic	monoclinic	
space group	P2 <sub>1</sub> /n	Pna2 <sub>1</sub>	P2 <sub>1</sub> /n	
a [Å]	6.3145(2)	16.8261(2)	13.7663(2)	
b [Å]	13.3052(2)	12.7130(2)	12.4516(2)	
c [Å]	15.9629(2)	5.0042(2)	17.3185(2)	
β [°]	98.3904(8)	90	96.615(2)	
V [ų]	1326.78(3)	1070.45(3)	2948.83(6)	
Ζ	4	4	8	
$ ho_{ m calcd}~[ m gcm^{-1}]$	1.391	1.083	1.111	
$\mu$ [mm <sup>-1</sup> ]	0.917	0.377	0.293	
F(000)	576	384.0	1056.0	
2 <i>θ r</i> ange [°]	3.00 to 30.00	4.02 to 52.73	5.76 to 60.07	
index range	$-8 \le h \le 8$	$-21 \le h \le 21$	$-19 \le h \le 19$	
	$-18 \le k \le 18$	$-16 \le k \le 16$	$-17 \le k \le 17$	
	$-22 \le l \le 22$	$-6 \le l \le 6$	$-24 \le l \le 24$	
reflns collected	51627	37 800	11 0551	
unique reflns	3860	3736	8627	
observed reflns (2 $\sigma$ )	3483	3359	7872	
R <sub>int</sub>	0.041	0.059	0.030	
data/restraints/pa-	3860/0/112	3736/1/155	8627/0/277	
rameters				
GoF (F <sup>2</sup> )	1.048	1.006	1.096	
$R_1, WR_2 [l > 2\sigma(l)]$	0.0238, 0.0597	0.0319, 0.0809	0.0258, 0.0749	
$R_1$ , w $R_2$ (all data)	0.0277, 0.0613	0.0363, 0.0831	0.0287, 0.0767	
$\Delta  ho_{(max/min)}$ [e Å <sup>-3</sup> ]	0.32/-0.29	0.34/-0.23	0.39/-0.26	

reported in Table 8. CCDC 1059729 (*cis-trans-***6**), 1059730 (all-*cis-***7**) and 1059731 (all-*cis-***8**) contain the supplementary crystallographic data. These data can be obtained free of charge by The Cambridge Crystallographic Data Centre

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