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Tridentate Lewis acids with phenyl substituted 1,3,5-trisilacyclohexane backbones†

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The 1,3,5-trisilacyclohexane skeleton $[CH_2Si(Ph)(C_2H)]_3$ equipped with three ethynyl groups was synthesised and functionalised to afford tridentate Lewis acids with directed functions. Hydroboration with $HB(C_6F_5)_2$ yielded the ethenylborane $\{CH_2Si(Ph)[C_2H_2B(C_6F_5)_2]\}_3$, while metalation with gallium organyls afforded $\{CH_2Si(Ph)[C_2Ga(R)_2]\}_3$ (R = Me, Et). The new compounds were identified by elemental analyses, multi-nuclear NMR spectroscopy and IR spectroscopy. Crystal structures were obtained for all-*cis*-$[CH_2Si(Ph)(OMe)]_3$, *cis-trans*-$[CH_2Si(Ph)(Cl)]_3$, all-*cis*-$[CH_2Si(Ph)(H)]_3$ and all-*cis*-$[CH_2Si(Ph)(C_2H)]_3$.

Introduction

Supramolecular chemistry, as the name suggests "beyond the molecule", aims at studying the interactions between at least two molecules. It has been established by the synthesis of poly-Lewis bases, such as the crown ethers, and by studying their complexation capabilities for cations.[1] The inverse systems to crown ethers are the poly-Lewis-acids, which consequently are capable of complexing bases. Reported examples of poly-Lewis acids are mostly composed of an organic framework with Lewis acidic functions. The scaffolds used so far are in some cases rings bearing mercury,[2] tin[3] and silicon[4] atoms. In addition to the enumerated cyclic poly-Lewis-acids some scaffolds with directed Lewis acidic functions have also been synthesized using central atoms (carbon),[5] benzene[6] naphthalene[7,8,9] and anthracene[10,11] as rigid skeletons carrying besides silicon, tin and mercury also boron-, aluminium-, gallium- and indium-organyl groups.

In addition to the mentioned scaffolds we have recently reported the synthesis of some new tridentate Lewis acids based on the 1,3,5-trisilacyclohexane skeleton.[12] These backbones offer the placement of three concordantly oriented Lewis acidic functionalities on one side of the molecule. Such molecules are interesting synthetic targets, as they are potentially capable of selectively binding anions or Lewis bases. The affinity to certain multiple Lewis basic substrates is enhanced due the chelating effect, supported by preorientation of the acid sites; the selectivity will be defined by the distance between the acid functions and their positional rigidity. So far we have made use of various multifunctional (semi)rigid backbones including 1,3,5-triethynyl-1,3,5-trimethyl-1,3,5-trisilacyclohexane. This exhibits some unprofitable characteristics such as low solubility in donor-free solvents and an equatorial orientation of ethynyl groups, at least in its energetic ground state. However, moving these to the all-axial state is generally associated with a very small energy barrier of inversion for the 1,3,5-trisilacyclohexane ring.[13] Hence a trifunctional Lewis basic guest can easily influence the orientation of functionalities by a change of its conformation.

This all-equatorial orientation leads to large distances between the three functions, which is defined by the distance between the terminal ethynyl carbon atoms to which these functions are bound (C···C > 7.6 Å).[12] For this reason we decided to modify this 1,3,5-trisilacyclohexane backbone by replacing the methyl groups by units of larger steric bulk. Here we report the formation of new 1,3,5-trisilacyclohexanes and demonstrate all-*cis*-1,3,5-triethynyl-1,3,5-triphenyl-1,3,5-trisilacyclohexane to offer an improved backbone for accessing directed tridentate Lewis acids by hydroboration and metalation in terminal position using gallium trialkyls under alkane elimination.

Results and discussion

An inherent synthetic problem in constructing trifunctional backbones based on 1,3,5-trisilacyclohexane is the variety of possible orientation of substituents at the ring silicon atoms leads to two diastereomers pictured in Scheme 1: the desired

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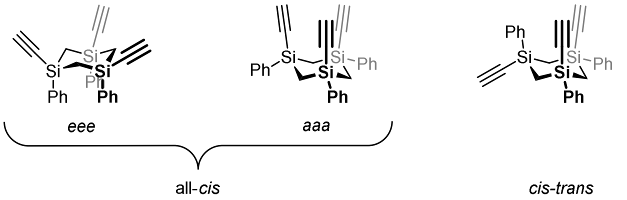
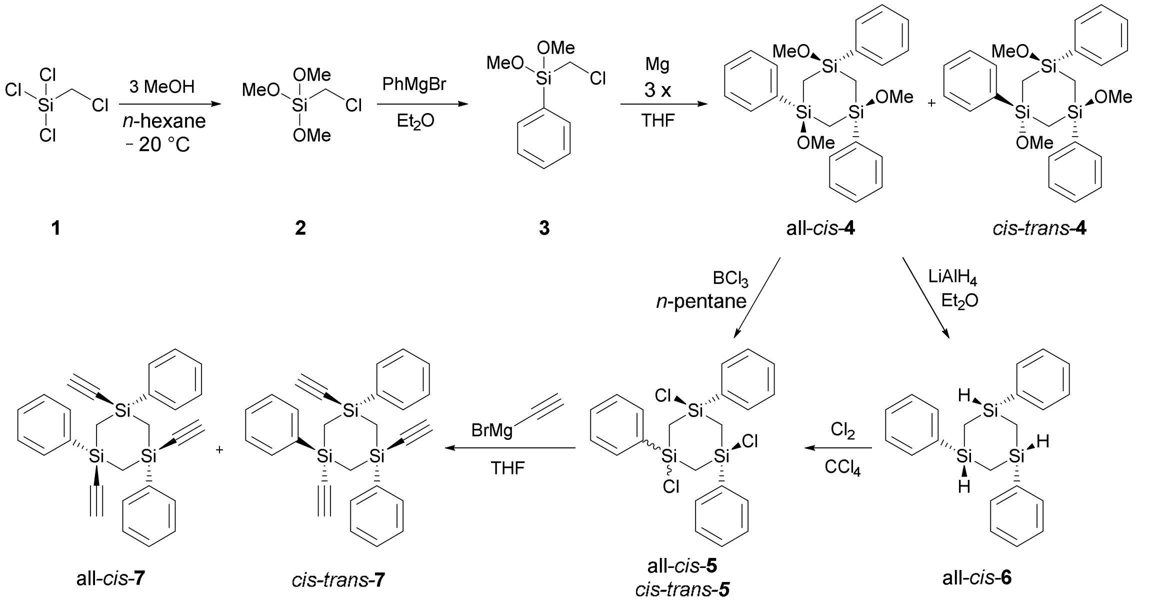
all-*cis* isomer with three functions pointing to the same direction and the *cis-trans* isomer, a by-product of cyclisation. Besides the concordant orientation of substituents the dynamics of ring inversion must be considered. In the case of all-*cis* diastereomer the ethynyl groups can be orientated all-equatorial (denoted *eee*) or all-axial (denoted *aaa*) (Scheme 1). The challenge lies in finding conditions for a preferred formation of the all-*cis*, or, if this cannot be achieved, in finding a suitable way for separation of diastereomers. All subsequent preparative steps after cyclisation have to proceed under retention of configuration.



Scheme 1. Two possible diastereomers resulting from the orientation of substituents at the ring silicon atoms and in the case of all-*cis* the two possible orientation the all-equatorial (*eee*) and all-axial (*aaa*).



Scheme 2. Synthesis of 1,3,5-trisilacyclohexanes **4** – **6** and the trialkynyl compound **7**. Yields: all-*cis*-**4** (13 %), with BCl$_3$: **5** (100 %), with Cl$_2$: **5** (91 %), all-*cis*-**6** (82 %), **7** (70 %).

Synthesis of 1,3,5-Trisilacyclohexanes

The first elegant synthesis of a 1,3,5-trisilacyclohexane has been established by Kriner.[14] It is the cyclisation of alkoxy(chloromethyl)silanes with magnesium. The advantage of this preparative access is the possibility of introducing substituents before cyclisation. For that reason trichloro(chloromethyl)silane (**1**) was protected with methoxy-substituents[15] (Scheme 2) to favour the formation of 1,3,5-trisilacyclohexane over that of 1,3-disilacyclobutanes.[16] The functionalised monomer **3** was obtained by conversion of (chloromethyl)trimethoxysilane (**2**) with phenyl magnesium bromide, following a literature protocol by Tacke *et al.*[15]

The cyclisation of **3** to **4** was performed by reaction with magnesium shavings in tetrahydrofuran (Scheme 2) yielding a liquid mixture of all-*cis*-**4**, *cis-trans*-**4** (ratio: 60:40) and further oligomers. Crystallization from *n*-pentane allowed obtaining pure all-*cis*-**4** in a yield of 13 %. This is in contrast to the methyl-substituted backbone ([CH$_2$Si(OR)(Me)]$_3$ (R = Me, Et)),[12] for which the mixture of the two methyl-substituted diastereomers could not be separated.

all-*cis*-1,3,5-Triethynyl-1,3,5-triphenyl-1,3,5-trisilacyclohexane

Following the analogous synthetic route to 1,3,5-triethynyl-1,3,5-trimethyl-1,3,5-trisilacylohexane[12] all-*cis*-**4** was first reacted with boron trichloride in *n*-pentane to afford **5**, but this reaction proceeded under loss of stereo information (Scheme 2). Starting with the all-*cis* diastereomer the reaction yielded a mixture of all-*cis*- and *cis-trans*-**5** in a ratio of 1:1. This problem has been reported before.[12] Consequently, we reacted all-*cis*-**4** with LiAlH$_4$ to afford all-*cis*-1,3,5-triphenyl-1,3,5-trisilacyclohexane (all-*cis*-**6**) (this compound has been synthesised earlier in a different way[17]); this reaction proceeded under retention of stereo information. Subsequent conversion of all-*cis*-**6** with elemental chlorine dissolved in carbon tetrachloride was intended to transform the Si-H into Si-Cl functions under retention of configuration, as was described for the cyclic 1-chloro-1-phenyl-1-sila-1,2,3,4-tetrahydronaphthalene.[18] However, this protocol failed when applied to all-*cis*-**6** and led again to a diastereomeric mixture of all-*cis*- and *cis-trans*-**5**. The detour via **6** was thus abandoned and the diastereomeric mixture of **5** was reacted directly with ethynyl magnesium bromide to afford 1,3,5-triethynyl-1,3,5-triphenyl-1,3,5-trisilacyclohexane (**7**) in 70 % yield (Scheme 1). It was a mixture of two diastereomers, and the desired all-*cis*-**7** was obtained by recrystallization from *n*-pentane at −20 °C.

The new compounds described in this section were characterised by single-crystal X-ray diffraction, NMR spectroscopy and mass spectrometry and in most cases by FT-IR spectroscopy. Some discussion of the spectroscopic and structural data follows below.

Crystal Structures

Single-crystalline material suitable for structure determination by X-ray diffraction was obtained of all-*cis*-**4**, *cis-trans*-**5**, all-*cis*-**6** and all-*cis*-**7**. Single crystals were grown by cooling *n*-pentane solutions to −20 °C (all-*cis*-**4** and all-*cis*-**6**) or by gradual evaporation of solutions in *n*-pentane in an H-shaped tube (*cis-trans*-**5** and all-*cis*-**7**). The molecular structures are displayed in Figures 1 – 4. Selected structural parameters are listed in their captions.

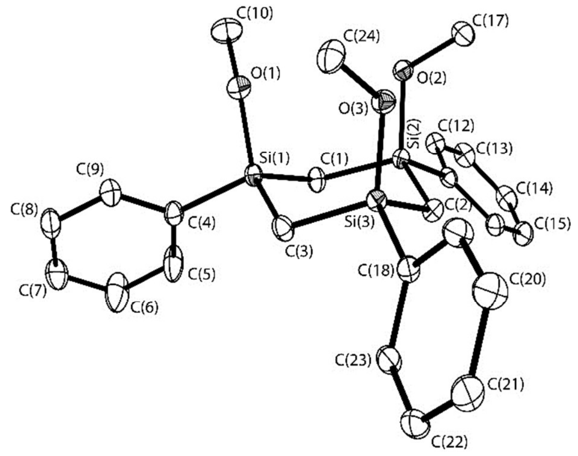


Figure 1. Molecular structure of compound all-*cis*-**4** in the crystalline state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances [Å]: Si(1)–C(1) 1.868(2), C(1)–Si(2) 1.867(2), Si(2)–C(2) 1.869(2), C(2)–Si(3) 1.863(2), Si(3)–C(3) 1.867(2), C(3)–Si(1) 1.858(2), Si(1)–C(4) 1.873(2), Si(2)–C(11) 1.878(2), Si(3)–C(18) 1.872(2), Si(1)–O(1) 1.645(1), Si(2)–O(2) 1.650(1), Si(3)–O(3) 1.646(1). Selected angles [deg]: Si(1)–C(1)–Si(2) 115.6(1), Si(2)–C(2)–Si(3) 113.8(1), Si(3)–C(3)–Si(1) 115.7(1), C(1)–Si(2)–C(2) 111.1(1), C(2)–Si(3)–C(3) 108.5(1), C(3)–Si(1)–C(1) 110.2(1).

All trisilacyclohexane rings of compounds **4** – **7** exhibit chair conformations. The Si–C bond lengths have values comparable with that of $[SiCl_2CH_2]_3$[19] (mean: 1.855 Å), $[SiCl(Me)CH_2]_3$[12] (mean: 1.862 Å), $[SiH(Me)CH_2]_3$[12] (mean: 1.873 Å), $[Si(C_2H)(Me)CH_2]_3$[12] (mean: 1.869 Å) and $[Si(C_2SiMe_3)(Me)CH_2]_3$[12] (mean: 1.870 Å). The shortest Si–C bond in the ring was found in *cis-trans*-**5** (mean: 1.859 Å), while those in all-*cis*-**6** (mean: 1.861 Å) are longer and those in methoxy and ethynyl substituted all-*cis*-**4** (mean: 1.865 Å) and all-*cis*-**7** (mean: 1.864 Å) are the longest.

The bonds between silicon and carbon atoms of the phenyl rings are almost of the same length in compounds all-*cis*-**4** (mean: 1.874 Å) and all-*cis*-**7** (1.876 Å), that of all-*cis*-**6** (mean: 1.867 Å) is slightly shorter and that of chlorine derivative *cis-trans*-**5** are the shortest (mean: 1.859 Å). Noteworthy, different Si–C(*i*Ph) bond lengths exist in the chlorine compound: the equatorial ones are 1.867 Å on average and the axial one 1.858(2) Å(Si(2)– C(9)). Similar differences in length between axial and equatorial bonds can be observed for the Si–Cl bonds (ax.: Si(1)–Cl(1) 2.067(1), eq.: Si(2)–Cl(2) 2.101(1) Å). The angles in the rings Si–C–Si and C–Si–C in all-*cis*-**4**, all-*cis*-**6** and all-*cis*-**7** adopt expected values and deserve no discussion. The structure of the chlorine compound *cis-trans*-**5**, however, has a strongly widened angle Si(1)–C(1)–Si(1') of 121.5(2)°.

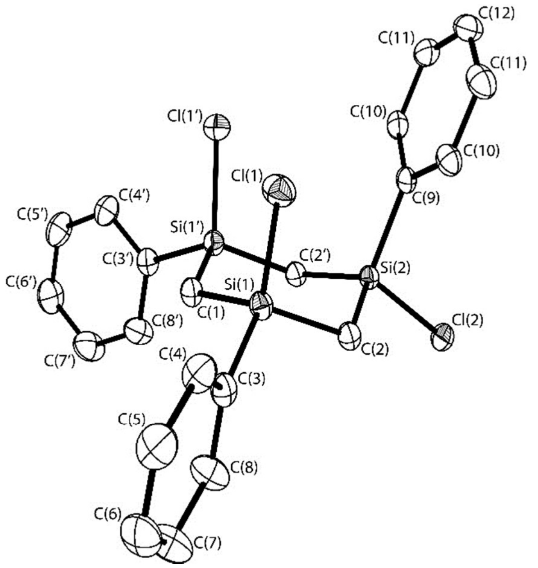


Figure 2. Molecular structure of compound *cis-trans*-**5** in the crystalline state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances [Å]: Si(1)–C(1) 1.848(1), Si(1)–C(2) 1.869(2), C(2)–Si(2) 1.860(2), Si(1)–C(3) 1.865(2), Si(2)–C(9) 1.858(2), Si(1)–Cl(1) 2.067(1), Si(2)–Cl(2) 2.101(1). Selected angles [deg]: C(1)–Si(1)–C(2) 109.4(1), Si(1)–C(2)–Si(2) 115.4(1), C(2)–Si(2)–C(2') 111.3(1), Si(1)–C(1)–Si(1') 121.5(2) (symmetry code: 1−*x*, +*y*, +*z*).

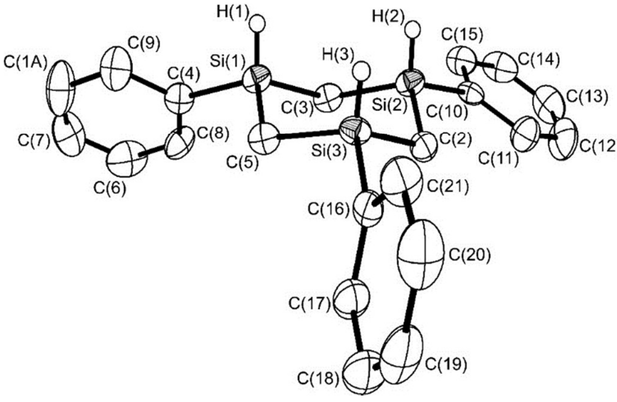


Figure 3. Molecular structure of compound all-*cis*-**6** in the crystalline state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms of methylene and phenyl groups are omitted for clarity. Selected distances [Å]: Si(1)–C(3) 1.863(4), C(3)–Si(2) 1.863(4), Si(2)–C(2) 1.853(4), C(2)–Si(3) 1.855(4), Si(3)–C(5) 1.858(4), C(5)–Si(1) 1.874(4), Si(1)–C(4) 1.864(4), Si(2)–C(10) 1.868(4), Si(3)–C(16) 1.869(4), Selected angles [deg]:Si(1)–C(3)–Si(2) 113.2(2), Si(2)–C(2)–Si(3) 112.4(2), Si(3)–C(5)–Si(1) 115.4(2), C(2)–Si(3)–C(5) 109.6(2), C(5)–Si(1)–C(3) 108.5(2), C(3)–Si(2)–C(2) 108.5(2).

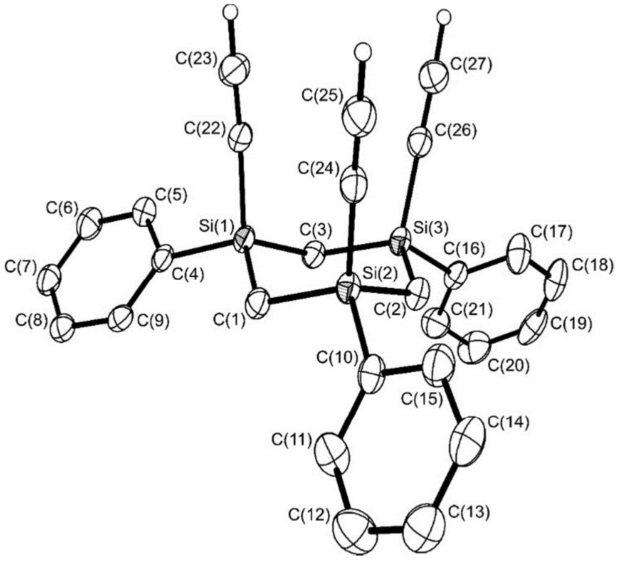


Figure 4. Molecular structure of compound all-*cis*-**7** in the crystalline state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances [Å]: Si(1)–C(1) 1.865(2), C(1)–Si(2) 1.864(2), Si(2)–C(2) 1.867(2), C(2)–Si(3) 1.865(2), Si(3)–C(3) 1.861(2), C(3)–Si(1) 1.863(2), Si(1)–C(4) 1.876(2), Si(2)–C(10) 1.871(2), Si(3)–C(16) 1.880(2), Si(1)–C(22) 1.830(2), Si(2)–C(24) 1.830(2), Si(3)–C(26) 1.825(2), C(22)≡C(23) 1.201(3), C(24)≡C(25) 1.205(3), C(26)≡C(27) 1.203(3), C(23)···C(25) 3.754(3), C(25)···C(27) 4.572(3), C(23)···C(27) 4.096(3). Selected angles [deg]: Si(1)–C(1)–Si(2) 114.3(1), Si(2)–C(2)–Si(3) 119.0(1), Si(3)–C(3)–Si(1) 116.4(1), C(1)–Si(2)–C(2) 108.6(1), C(2)–Si(3)–C(3) 109.1(1), C(3)–Si(1)–C(1) 108.2(1).

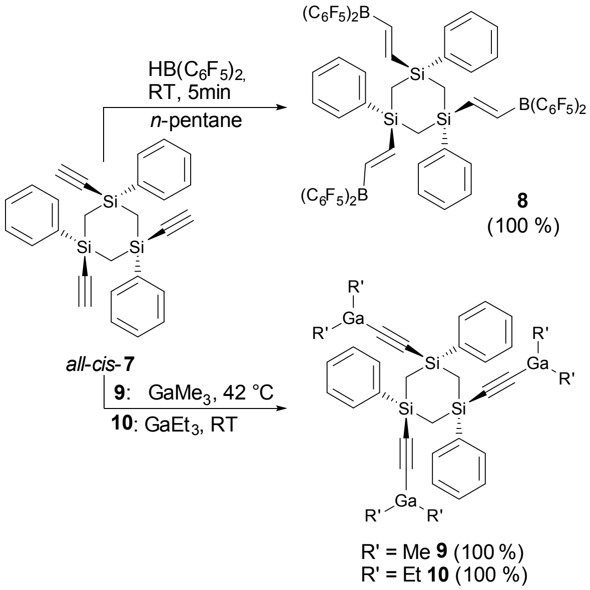
An important structural feature is that the ethynyl groups in compound all-*cis*-**7** are arranged axially. This is in contrast to the structure of the methyl (instead of phenyl) analogue 1,3,5-triethynyl-1,3,5-trimethyl-1,3,5-trisilacyclohexane with ethynyl groups in equatorial position. The change from methyl to phenyl leads to smaller distances between the terminal ethynyl carbon atoms: C(23)···C(25) 3.754(3), C(25)···C(27) 4.572(3), C(23)···C(27) 4.096(3) Å. These values are almost half as large compared to the distances between the terminal ethynyl carbon atoms in the methyl analogue (C···C 7.648(1), 7.849(1), 7.695(1) Å).[12] However, the structure in the solid state does not reflect the behaviour of a molecule in the gas phase or in solution, in which the ring inversion, coupled to the orientation of the ethynyl groups, proceeds very easily.

Synthesis of directed tridentate Lewis acids

With all-*cis*-**7** we have received another Lewis-base-free backbone of C_3 symmetry for the construction of directed tridentate Lewis acids in addition to the already known 1,3,5-triethynyl-1,3,5-trimethyl-1,3,5-trisilacylohexane[12] with its ethynyl groups orientated in the same direction. In order to test the new backbone all-*cis*-**7** for its suitability for Lewis acidic functionalization, it was reacted with Piers' borane[20,21] ($HB(C_6F_5)_2$) and gallium organyls (Scheme 3).

The boron-based tridentate Lewis acid **8** was synthesised by conversion of all-*cis*-**7** with three equivalents of $HB(C_6F_6)_2$ in *n*-pentane. Product **8** was obtained in a quantitative yield and high purity. The tridentate Lewis acids **9** and **10** were synthesised in alkane elimination reactions using excess of $GaMe_3$ or $GaEt_3$ in in the absence of any solvents in analogy to earlier work, but under varied conditions.[11,12,22] To obtain compound **9** the reaction mixture was heated to 42 °C for 48 h, while compound **10** was formed within 48 h without heating. Products **9** and **10** are colourless solids. Compound **9** is only sparingly soluble in donor-free solvents, whereas compound **10** is well soluble in donor free aromatic solvents. All attempts to grow single crystals from solution for structure determination of **8** – **10** failed so far.

The compounds described in this and the previous section (**4** – **10**) were characterised by multinuclear NMR spectroscopy in solution and by elemental analyses, some in addition by FT-IR spectroscopy. A discussion of the obtained data follows in the successive chapters.



Scheme 3. Synthesis of directed tridentate Lewis acids **8**, **9** and **10**.

NMR and IR spectroscopic studies

The NMR spectra of **4** – **10** are provided in Supporting Information, Figures S1 – S26 and the chemical shifts of **4** – **10** are listed in Table 1. Below, the chemical shifts of **4** – **10** are compared among each other and also with the values of 1,3,5-trimethyl-1,3,5-trisilacyclohexane derivatives.[12]

The replacement of substituents at the silicon atoms has neither significant effect on the chemical shifts of the phenyl groups nor on that of the geminal protons at the trisilacyclohexane ring (Table 1). The chemical shifts of geminal protons of all compounds (**4** – **11**) cover a range between 1.09 and −0.06 ppm. On the contrary the carbon atoms at bridging positions are more strongly influenced, since the chemical shifts of the bridging carbon atoms vary due to substitution at the silicon atom within the range between 7.0 and −5.6 ppm. Due to substitution, the silicon atoms show the largest change in chemical shifts of their resonances (Table 1). Comparing all chemical shifts of **4** – **10** with those of methyl derivatives of recently published paper,[12] it is striking that the protons

Table 1. Selected NMR shifts [ppm] of the 1,3,5-trisilacyclohexanes all-*cis*-**4**, all-*cis*-**5**, *cis-trans*-**5** all-*cis*-**6**, all-*cis*-**7**, all-*cis*-**8** (C_6D_6), all-*cis*-**9** and all-*cis*-**10** (C_6D_6 / Et_2O) in solution at 298 K.

Compound	all-*cis*-**4**	all-*cis*-**5**	*cis-trans*-**5**	all-*cis*-**6**	all-*cis*-**7**	all-*cis*-**8**	all-*cis*-**9**	all-*cis*-**10**
-SiC***H***$_2$Si-	0.82	1.05	1.09 / 0.97	0.41	0.85	0.83	1.18	0.91
-SiC***H***$_2$Si-	0.17	0.92	0.85 / 0.59	−0.06	0.24	0.79	0.72	0.55
-Si***C***H$_2$Si-	0.35	7.0	6.6 / 6.5	−3.1	−0.5	−5.6	0.4	0.5
-CH$_2$***Si***CH$_2$-	6.2	15.0	15.8 / 14.3	−15.6	−23.3	−10.0	−26.9	−27.2
o-C***H***	7.52	7.53	7.57 / 7.31	7.49	7.52	7.36	7.61	7.47
m-C***H***	7.32	7.17	7.19 / 7.08	7.25	7.16	7.10	7.10	7.03
p-C***H***	7.32	7.17	7.19 / 7.08	7.25	7.16	7.10	7.10	7.08
i-***C***H	139.1	136.3	136.7 / 135.7	138.1	137.5	135.7	139.6	139.8
o-***C***H	133.9	133.6	133.7 / 133.4	134.3	134.0	134.3	134.4	134.4
m-***C***H	128.1	128.4	128.4 / 128.3	128.4	128.2	128.5	127.8	127.7
p-***C***H	129.7	130.8	131.0 / 130.7	129.7	129.8	130.3	129.0	128.9
-Si***C***≡C-X	--	--	--	--	88.2	--	113.3	114.5
-SiC≡***C***-X	--	--	--	--	97.2	--	131.0	129.3

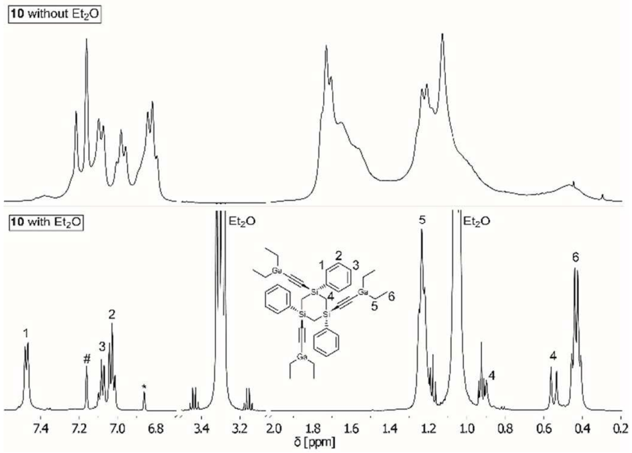


Figure 5. ^{1}H NMR spectra of compound **10** in C_6D_6 (#) (C_6D_6 capillary (*)) at 295 K. Top: compound **10** without Et_2O, formation of agglomerates. Below: compound **10** with Et_2O, formation of adducts with **10** and Et_2O.

receive a downfield chemical shift, while the carbon and silicon nuclei receive an upfield shift.

The subsequent discussion of NMR data of compounds **8** – **10** will receive more attention because of the unavailability of single-crystalline material suitable for structure determination. The ^{1}H NMR spectrum of compound **8** contains, besides the resonances of the phenyl groups (Table 1), typical signal patterns for the olefin protons: the *trans*-addition product shows two doublets at 7.77 and 7.62 ppm with a coupling constant of 21 Hz. Two further doublets for the methylene protons of the ring are observed at 0.83 and 0.79 ppm with a geminal coupling constant of 14.4 Hz. The ^{19}F NMR spectrum displays the three expected resonances at −128.9 ppm (multiplet, *ortho*-F), −146.3 ppm (triplet of triplets, *para*-F) and −161.1 ppm (multiplet, *meta*-F). The ^{11}B NMR spectrum contains a single broad resonance at 66.7 ppm assignable to a tri-coordinate boron atom. The ^{29}Si NMR spectrum consists of only a single resonance at −10.0 ppm (Table 1).

The NMR spectra of compounds **9** and **10** were recorded in solutions of mixtures of C_6D_6 and Et_2O because of their low solubility in hydrocarbons (compound **9**) or the formation of aggregates (compound **10**, Figure 5). Thus note, that the addition of ether leads to spectroscopic data of the ether adducts. The terminal metalation of the ethynyl groups with gallium organyl functions has a small influence on the chemical shifts of the methylene and phenyl groups of the skeleton. The identity of **9** and **10** is confirmed by comparison of NMR shifts of trimethylgallium (0.21 ppm, neat, referenced to a C_6D_6 capillary) and of triethylgallium (1.43 ppm triplet and 0.93 ppm quartet, neat, referenced to a C_6D_6 capillary) with those of the tridentate Lewis acids **9** (−0.02 ppm) and **10** (1.23 ppm triplet and 0.43 ppm, quartet). The proton resonances of the methyl and ethyl groups of the tridentate Lewis acids **9** and **10** are shifted to higher field compared to trimethyl- and triethylgallium. The carbon resonances of metal-bound carbon atoms of the ethinyl groups of **9** and **10** are broad and, in comparison to **7**, shifted to lower field (Table 1). The chemical shifts of the silicon atoms of **7** (−23.3 ppm), **9** (−26.9 ppm) and **10** (−27.2 ppm) have almost the same values, confirming that the silicon atoms all bear the same substituents, i.e. intact ethynyl groups (compare: shift of **8** with ethenyl groups –10.0 ppm).

Further proof for the identity of these C≡C units stems from FT-IR spectra with bands observed at 2037 cm^{-1} (**9** and **10**).

Elemental analysis data confirm the above structural assignments.

Conclusion

Tridentate Lewis acids with concordantly orientated functions were synthesised with 1,3,5-trisilacyclohexanes as scaffolds of C_3 symmetry. They bear three ethynyl groups capable of carrying Lewis acidic functions. Two synthetic routes were investigated in order to generate the all-*cis* isomers of these skeletons selectively. The formation of 1,3,5-triethynyl-1,3,5-triphenyl-1,3,5-trisilacyclohexane (**7**) was achieved in three synthetic steps starting with $(MeO)_2PhSiCH_2Cl$. all-*cis*-**7** could be separated from the obtained diastereomeric mixture by fractional crystallisation. Structural analysis by X-ray diffraction proofed the identity and the orientation of the ethynyl groups. In contrast to the recently published 1,3,5-triethynyl-1,3,5-trimethyl-1,3,5-trisilacyclohexane the ethynyl groups of all-*cis*-**7** are all-axially (*aaa*) oriented in the solid state, i.e. the substitution of methyl by phenyl groups is sufficient to dominate the orientation of the substituents.

In conclusion, all-*cis*-1,3,5-triethynyl-1,3,5-triphenyl-1,3,5-trisilacyclohexane (all-*cis*-**7**) offers a scaffold with three concordantly oriented functions and shows in comparison to 1,3,5-triethynyl-1,3,5-trimethyl-1,3,5-trisilacyclohexane a *aaa* orientation of its ethynyl groups. This results in a smaller distance between acidic functions bound to the ethynyl groups. Examples of such tridentate Lewis acids were obtained by conversion of all-*cis*-**7** with Piers' Borane and by reaction of gallium trialkyls in an elimination of alkane.

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 $LiAlH_4$. They were distilled prior to use. (Chloromethyl)trichlorosilane (**1**) (Sigma-Aldrich) was distilled before use. (Chloromethyl)trimethoxysilane (**2**) and (chloromethyl)dimethoxyphenylsilane (**3**) were synthesised according to protocols described by Tacke *et al.*[15] Piers' borane was synthesised according to a reported protocol.[20,21] C_6D_6 was 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 signals of the used protonated solvents (^{1}H, ^{13}C) or external standards (^{11}B: $BF_3{\cdot}OEt_2$, ^{19}F: CCl_3F; ^{29}Si: TMS). GC/EI-MS analyses were performed using a Shimadzu GC-2010/GCMS-QP 2010S instrument (capillary column: Rtx®-200 [Crossbond, trifluoropropylmethylpolysiloxane, 30 m, 25 mm, 0.25 µm). EI 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).

1,3,5-Trimethoxy-1,3,5-triphenyl-1,3,5-trisilacyclohexane (4)

To a dispersion of magnesium turnings (4.6 g, 0.19 mol), surface activated with 1,2-dibromoethane) in THF (250 mL) and a solution of (chloromethyl)-dimethoxyphenylsilane (**3**) (39.1 g, 180 mmol) in 300 mL THF was added dropwise while heating to 70 °C. After the addition of **3** was completed, the grey suspension was refluxed for 2 h. Subsequently the solvent was removed and the remaining grey solid was extracted with pentane. The pentane solution was concentrated and set aside at −30 °C (raw product is a mixture of all-*cis*-**4** and *cis*-*trans*-**4**). The crystallisation from *n*-pentane provided solely the all-*cis*-**4** product as colourless solid. Yield: 3.6 g (8 mmol, 13%). Assignments for all-*cis*-**4**: ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ [ppm] = 7.52 (m, 6H, *o*-C*H*[Ph]), 7.23 (m, 9H, *m*-/ *p*-C*H*[Ph]), 3.49 (s, 9H, -SiOCH_3), 0.82 (d, $^2J_{H,H}$ = 14.1 Hz, 3H, -SiCH_2Si-), 0.17 (d, $^2J_{H,H}$ = 14.1 Hz, 3H, -SiCH_2Si-); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ [ppm] = 139.1 (s, *i*-*C*), 133.9 (s, *o*-*C*), 129.7 (s, *p*-*C*), 128.1 (s, *m*-*C*), 50.8 (s, -SiO*C*H_3), 0.35 (s, -Si*C*H_2Si-); ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 298 K): δ [ppm] = 6.2 (s, -CH_2*Si*CH_2-); GC/EI-MS: retention time 16.9 min (all-*cis*-**4**): *m/z* = 373.1 [100%; M^+− Ph]; MS (ESI, positive): *m/z* = 473.2 [100%; M + Na^+]; accurate mass (MS ESI): calculated ion mass for $C_{24}H_{30}O_3Si_3Na^+$ 473.13950, measured ion mass 473.14020; FT-IR (KBr): ν [cm^{-1}] = 3083, 3064, 3050, 3039, 3014, 3003, 2960, 2922, 2913, 2907, 2868, 2829, 1986, 1965, 1912, 1891, 1846, 1829, 1822, 1779, 1664, 1588, 1567, 1485, 1458, 1429, 1384, 1364, 1350, 1344, 1321, 1309, 1263, 1189, 1160, 1110, 1091, 1042, 1024, 996, 983, 913, 854, 816, 778, 760, 734, 701, 650, 619, 607, 593, 534, 474, 426; elemental analysis calculated (%) for $C_{24}H_{30}O_3Si_3$ (M_r = 450.75): C 63.95, H 6.71; found: C 63.17, H 6.59.

1,3,5-Trichloro-1,3,5-triphenyl-1,3,5-trisilacyclohexane (5)

a) all-*cis*-1,3,5-Trimethoxy-1,3,5-triphenyl-1,3,5-trisilacyclohexane (all-*cis*-**4**, 3.42 g, 7.6 mmol) was dissolved in *n*-pentane (130 mL). After three freeze-pump-thaw cycles boron trichloride (25.4 mmol measured as gas) was condensed onto the frozen solution of **4** at −196 °C. The reaction mixture was warmed to −20 °C. At this temperature the reaction started under formation of a colourless solid. After warming to room temperature overnight all volatiles were removed under reduced pressure and the product **5** was obtained as a colourless solid in a yield of 100% (3.52 g, 7.6 mmol).

b) all-*cis*-1,3,5-Trimethyl-1,3,5-trisilacyclohexane (all-*cis*-**6**, 82 mg, 0.23 mmol) was dissolved in tetrachloromethane (5 mL). A saturated solution of chlorine in tetrachloromethane (1.5 mL) was added dropwise within 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 colourless, crystalline solid; yield 91% (98 mg, 21 mmol).

In both synthesis protocols, a) and b) a loss of stereo information takes place. A diastereomeric mixture of all-*cis*-**5** and *cis*-*trans*-**5** in a ratio of 1:1 was obtained. Assignments for all-*cis*-**5**: ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ [ppm] = 7.53 (m, 6H, *o*-C*H*[Ph]), 7.17 (m, 9H, *m*- / *p*-C*H*[Ph]), 1.05 (d, $^2J_{H,H}$ = 14.5 Hz, 3H, -SiCH_2Si-), 0.92 (d, $^2J_{H,H}$ = 14.5 Hz, 3H, -SiCH_2Si-); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ [ppm] = 136.3 (s, *i*-*C*), 133.6 (s, *o*-*C*), 130.8 (s, *p*-*C*), 128.4 (s, *m*-*C*), 7.0 (s, -Si*C*H_2Si-); ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 298 K): δ [ppm] = 15.0 (s, -CH_2*Si*CH_2-); Assignments for *cis*-*trans*-**5**: ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ [ppm] = 7.57 (m, 4H, *o*-C*H*[Ph]), 7.31 (m, 2H, *o*-C*H*[Ph]), 7.19 (m, 6H, *m*-/ *p*-C*H*[Ph]), 7.08 (m, 3H, *m*-/ *p*-C*H*[Ph]), 1.09 (d, $^2J_{H,H}$ = 14.4 Hz, 1H, -SiCH_2Si-), 0.97 (d, $^2J_{H,H}$ = 14.5 Hz, 2H, -SiCH_2Si-), 0.85 (d, $^2J_{H,H}$ = 14.5 Hz, 2H, -SiCH_2Si-), 0.59 (d, $^2J_{H,H}$ = 14.4 Hz, 1H, -SiCH_2Si-); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ [ppm] = 136.7 (s, *i*-*C*), 135.7 (s, *i*-*C*), 133.7 (s, *o*-*C*), 133.4 (s, *o*-*C*), 131.0 (s, *p*-*C*), 130.7 (s, *p*-*C*), 128.4 (s, *m*-*C*), 128.3 (s, *m*-*C*), 6.6 (s, -Si*C*H_2Si-), 6.5 (s, -Si*C*H_2Si-); ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 298 K): δ [ppm] = 15.8 (s, -CH_2*Si*CH_2-), 14.3 (s, -CH_2*Si*CH_2-); GC/EI-MS: retention time 18.6 min (mixture of both diastereomers): *m/z* = 385.9 [100%; M^+− Ph], 307.9, 195.0, 105.0, 91.1, 77.0, 63.0; elemental analysis calculated (%) for $C_{21}H_{21}Cl_3Si_3$ (M_r = 464.01): C 54.36, H 4.56; found: C 54.62, H 4.69.

1,3,5-Triphenyl-1,3,5-trisilacyclohexane (6)

To a suspension of $LiAlH_4$ (95% purity, 448 mg, 11.2 mmol) in diethyl ether (20 mL) all-*cis*-1,3,5-trimethoxy-1,3,5-triphenyl-1,3,5-trisilacyclohexane (all-

cis-**4**, 528 mg, 1.1 mmol) was added at 0 °C. The reaction mixture was refluxed for two days. All volatiles were removed under reduced pressure to afford a grey solid, which was extracted with 20 mL *n*-pentane. The pentane solution was concentrated and set aside at −80 °C. The product all-*cis*-**6** crystallises as colourless solid. Yield: 0.33 g (0.9 mmol, 82 %). Reaction results exclusively in all-*cis*-**6** under retention of diastereomeric information. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ [ppm] = 7.49 (m, 6H, *o*-C*H*[Ph]), 7.25 (m, 9H, *m*-/ *p*-C*H*[Ph]), 4.98 (t, $^{3}J_{H,H}$ = 8.8 Hz, 3H, -Si*H*), 0.41 (d, $^{2}J_{H,H}$ = 13.5 Hz, 3H, -SiH_eSi-), −0.06 (dt, $^{2}J_{H,H}$ = 13.5 Hz, $^{3}J_{H,H}$ = 8.8 Hz, 3H, -SiH_aSi-); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ [ppm] = 138.1 (s, *i*-*C*), 134.3 (s, *o*-*C*), 129.7 (s, *p*-*C*), 128.4 (s, *m*-*C*), −3.1 (s, -SiCH_2Si-); ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 298 K): δ [ppm] = −15.6(s, -CH_2*Si*CH_2-); GC/EI-MS: retention time 16.5 min (all-*cis*-**6**): *m/z* = 356.9 [M^+], 282.0 [M^+ − PhH], 204.0 [100%; M^+ − 2PhH], 105; FT-IR (KBr): ν [cm^{-1}] = 3133, 3085, 3065, 3055, 3048, 3041, 3017, 3004, 2998, 2975, 2961, 2925, 2916, 2878, 2852, 2131 (-Si–H), 2119 (-Si–H), 2107 (-Si–H), 2097 (-Si–H), 1587, 1485, 1428, 1363, 1334, 1303, 1263, 1113, 1068, 1038, 1024, 998, 863, 791, 750, 737, 727, 699, 661, 638, 618, 481, 455, 408; elemental analysis calculated (%) for $C_{21}H_{21}Cl_3Si_3$ (M_r = 360.12): C 69.93, H 6.71; found: C 69.18, H 6.66.

1,3,5-Triethynyl-1,3,5-triphenyl-1,3,5-trisilacyclohexane (7)

To a solution of 1,3,5-trichloro-1,3,5-triphenyl-1,3,5-trisilacyclohexane (**6**, 4.0 g, 8.6 mmol) in tetrahydrofuran (25 mL) a solution of ethynyl magnesium bromide (84 mL, 0.5 M, 42 mmol) was added dropwise. The mixture was refluxed for 48 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 × 50 mL). The combined organic phases were washed twice with water (2 × 25 mL) and dried over $MgSO_4$. The solvent was removed and the remaining solid was recrystallised from *n*-pentane at −20 °C. The product 1,3,5-triethynyl-1,3,5-triphenyl-1,3,5-trisilacyclohexane (**7**) was obtained as colourless solid. Yield: 2.6 g (6.0 mmol, 70% diastereomeric mixture, ratio all-*cis*:*cis-trans* 50:50). The separation of the diastereomers was performed by fractional crystallization from *n*-pentane. Assignments for all-*cis*-**7**: ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ [ppm] = 7.52 (m, 6H, *o*-C*H*[Ph]), 7.16 (m, 9H, *m*-/ *p*-C*H*[Ph]), 2.34 (s, 3H, -SiC≡C*H*), 0.85 (d, $^{2}J_{H,H}$ = 14.0 Hz, 3H, -SiCH_2Si-), 0.24 (d, $^{2}J_{H,H}$ = 14.0 Hz, 3H, -SiCH_2Si-); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ [ppm] = 137.5 (s, *i*-*C*), 134.0 (*o*-*C*), 129.8 (*p*-*C*), 128.2 (*m*-*C*), 97.2 (s, -SiC≡*C*H), 88.2 (s, -Si*C*≡CH), −0.5 (s, -SiCH_2Si-); ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 298 K): δ [ppm] = −23.3 (s, -CH_2*Si*CH_2-); FT-IR (KBr, all-*cis*-**7**): ν [cm^{-1}] = 3281 (C≡*C*–*H*), 3273 (C≡*C*–*H*), 3067, 3053, 3043, 3022, 3010, 2997, 2976, 2937, 2861, 2037 (C≡C), 1487, 1427, 1391, 1362, 1346, 1326, 1308, 1263, 1191, 1109, 1087, 1068, 1055, 1047, 1028, 1020, 997, 974, 853, 774, 764, 747, 739, 698, 687, 677, 672, 667, 638, 550, 528, 476, 460, 430; GC/EI-MS: retention time 16.9 min (all-*cis*-**7**): *m/z* = 431.6 [M^+ − H], 128.8, 105.1 [100%; SiPh], 53.0; elemental analysis calculated (%) for $C_{27}H_{24}Si_3$ (M_r = 432.12): C 74.94, H 5.59; found: C 74.82, H 5.79.

1,3,5-Tris(bis(pentafluorophenyl)boranylethenyl)-1,3,5-triphenyl-1,3,5-trisilacyclohexane (8)

Piers' borane ($HB(C_6F_5)_2$, 60.2 mg, 0.17 mmol) and all-*cis*-**7** (25 mg, 0.06 mmol) were placed in a flask equipped with a Young's greaseless tap. The mixture was frozen in liquid nitrogen; *n*-pentane (5 mL) was condensed onto it and warmed after that to r.t. 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 **8** remained. Yield: 88.0 mg (0.17 mmol, 100 %). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ [ppm] = 7.77 (d, $^{3}J_{H,H}$ = 21 Hz, 3H, -B*H*C=CHSi-), 7.62 (d, $^{3}J_{H,H}$ = 21 Hz, 3H, -BHC=C*H*Si-), 7.36 (m, 6H, *o*-C*H*[Ph]), 7.10 (m, 9H, *m*-/ *p*-C*H*[Ph]), 0.83 (d, $^{2}J_{H,H}$ = 14.4 Hz, 3H, -SiCH_2Si-), 0.79 (d, $^{2}J_{H,H}$ = 14.4 Hz, 3H, -SiCH_2Si-); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ [ppm] = 170.0 (s, -BHC=*C*HSi-), 152.7 (s, br, -BH*C*=CHSi-), 148.2 (dm, $^{1}J_{F,C}$ = 247 Hz, *m*-*C*[Ph^F]), 143.9 (dm, $^{1}J_{F,C}$ = 259 Hz, *p*-*C*[Ph^F]), 137.7 (dm, $^{1}J_{F,C}$ = 253 Hz, *o*-*C*[Ph^F]), 135.7 (s, *i*-*C*[Ph]), 134.3 (s, *o*-*C*[Ph]), 130.3 (s, *p*-*C*[Ph]), 128.5 (s, *m*-*C*[Ph]), 113.4 (m, *i*-*C*[Ph^F]), −5.6 (s, -SiCH_2Si-); ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 298 K): δ [ppm] = 66.7 (s, br); ^{19}F NMR (470 MHz, C_6D_6, 298 K): δ [ppm] = −128.89 (m, *o*-*F*[Ph^F]), −146.3 (tt, $^{3}J_{F,F}$ = 20.7 Hz, $^{4}J_{F,F}$ = 4.9 Hz, *p*-*F*[Ph^F]), −161.11 (m, *m*-*F*[Ph^F]); ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 298 K): δ [ppm] = −10.0 (s, -CH_2*Si*CH_2-); elemental analysis calculated (%) for $C_{63}H_{27}B_3F_{30}Si_3$ (M_r = 1470.53): C 51.46, H 1.85; found: C 49.59, H --.

1,3,5-Tris(dimethylgallanylethynyl)-1,3,5-triphenyl-1,3,5-trisilacyclohexane (9)

All-*cis*-1,3,5-triethynyl-1,3,5-triphenyl-1,3,5-trisilacyclohexane (all-*cis*-**7**) (55 mg, 0.13 mmol) was dissolved in trimethylgallium (1.00 mL, 1.13 g, 9.8 mmol) and this mixture was stirred at room temperature for 48 h at 42 °C. During the reaction a colourless solid was formed. After the reaction was finished, the excess of trimethylgallium was condensed off and the residual colourless solid was dried in vacuum. Yield: 94.5 mg (0.13 mmol, 100 %). ^{1}H NMR (500 MHz, C_6D_6, Et_2O, 298 K): δ [ppm] = 7.61 (m, 6H, *o*-C*H*[Ph]), 7.10 (m, 9H, *m*-/ *p*-C*H*[Ph]), 1.18 (d, $^{2}J_{H,H}$ = 14.2 Hz, 3H, -SiCH_2Si-), 0.72 (d, $^{2}J_{H,H}$ = 14.2 Hz, 3H, -SiCH_2Si-), −0.02 (s, 18H, -Ga(CH_3)$_2$); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, Et_2O, 298 K): δ [ppm] = 139.6 (s, *i*-*C*), 134.4 (s, *o*-*C*), 131.0 (s, br, -C≡*C*–Ga), 129.0 (s, *p*-*C*), 127.8 (s, *m*-*C*), 113.3 (s, -Si*C*≡C–Ga), 0.4 (s, -SiCH_2Si-), −3.8 (s, -Ga(CH_3)$_2$); ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, Et_2O, 298 K): δ [ppm] = −26.9 (s, -CH_2*Si*CH_2-); FT-IR (KBr): ν [cm^{-1}] = 3088, 3070, 3050, 3012, 3000, 2957, 2924, 2865, 2697, 2037 (C≡C), 1996, 1955, 1881, 1827, 1814, 1798, 1589, 1568, 1487, 1454, 1428, 1357, 1304, 1263, 1201, 1158, 1111, 1042, 1026, 998, 968, 772, 733, 695, 640, 618, 590, 538, 506, 476, 430; elemental analysis calculated (%) for $C_{33}H_{39}Ga_3Si_3$ (M_r = 729.09): C 54.36, H 5.39; found: C 54.98, H 5.64.

1,3,5-Tris(diethylgallanylethynyl)-1,3,5-triphenyl-1,3,5-trisilacyclohexane (10)

All-*cis*-1,3,5-triethynyl-1,3,5-triphenyl-1,3,5-trisilacyclohexane (all-*cis*-**7**) (50 mg, 0.12 mmol) was dissolved in triethylgallium (1.00 mL, 1.07 g, 6.8 mmol) and this mixture was stirred at r.t. for 48 h. A colourless solid formed during the reaction. After the reaction was finished, and the excess of triethylgallium was condensed off and the residual colourless solid was dried in vacuum. Yield: 97.4 mg (0.26 mmol, 100 %). ^{1}H NMR (500 MHz, C_6D_6, Et_2O, 298 K): δ [ppm] = 7.47 (d, $^{3}J_{H,H}$ = 7.2 Hz, 6H, *o*-C*H*[Ph]), 7.08 (m, 3H, *p*-C*H*[Ph]), 7.03 (m, 6H, *m*-C*H*[Ph]), 1.23 (t, $^{3}J_{H,H}$ = 8.1 Hz, 18H, -Ga(CH_2CH_3)$_2$), 0.91 (d, $^{2}J_{H,H}$ = 14.2 Hz, 3H, -SiCH_2Si-), 0.55 (d, $^{2}J_{H,H}$ = 14.2 Hz, 3H, -SiCH_2Si-), 0.43 (q, $^{3}J_{H,H}$ = 8.1 Hz, 12H, -Ga(C$H_2$$CH_3$)$_2$); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, Et_2O, 298 K): δ [ppm] = 139.8 (s, *i*-*C*), 134.4 (s, *o*-*C*), 129.3 (s, br, -C≡*C*–Ga), 128.9 (s, *p*-*C*), 127.7 (s, *m*-*C*), 114.5 (s, -Si*C*≡C–Ga), 10.6 (s, -Ga(CH_2CH_3)$_2$), 5.3 (s, br, -Ga(CH_2CH_3)$_2$), 0.5 (s, -SiCH_2Si-); ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, Et_2O, 298 K): δ [ppm] = −27.2 (s, -CH_2*Si*CH_2-); FT-IR (KBr): ν [cm^{-1}] = 3088, 3070, 3051, 3011, 3000, 2941, 2900, 2864, 2813, 2727, 2696, 2037 (C≡C), 1953, 1881, 1814, 1589, 1487, 1461, 1454, 1428, 1374, 1357, 1336, 1303, 1263, 1233, 1191, 1158, 1111, 1047, 1027, 999, 960, 940, 895, 876, 773, 748, 735, 696, 677, 662, 631, 564, 513, 474; elemental analysis calculated (%) for $C_{39}H_{51}Ga_3Si_3$ (M_r = 813.25): C 57.60, H 6.32; found: C 55.37, H 6.67.

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-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.5418 Å). Using Olex2[23] the structures were solved by direct methods and refined by full-matrix least-squares cycles SHELX-97.[24] Crystallographic data (excluding structure factors) for the structures reported in this publication have been deposited with The Cambridge Crystallographic Data Centre as supplementary publications. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. The deposition numbers and crystallographic details of compounds all-*cis*-**4**, *cis-trans*-**5**, all-*cis*-**6** and all-*cis*-**7** reported in Table 2.

Table 2. Crystallographic data for compounds all-*cis*-**4**, *cis-trans*-**5**, all-*cis*-**6** and all-*cis*-**7**.

	all-*cis*-**4**	*cis-trans*-**5**	all-*cis*-**6**	all-*cis*-**7**
Formula	$C_{24}H_{30}O_3Si_3$	$C_{21}H_{21}Cl_3Si_3 \times 0.5\ C_5H_{12}$	$C_{21}H_{24}Si_3$	$C_{27}H_{24}Si_3$
M_r	450.75	500.07	360.67	432.73
T [K]	100.0(2)	100.0(2)	150.0(1)	100.0(1)
Crystal size [mm]	0.37×0.34×0.07	0.37×0.34×0.07	0.26×0.05×0.02	0.30×0.15×0.07
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic
Radiation used	Mo-Kα	Cu-Kα	Mo-Kα	Mo-Kα
Space group	$P2_1/n$	*Cmca*	$P\bar{1}$	$P2_1/c$
a [Å]	9.6472(2)	21.5592(2)	10.5469(3)	19.9247(5)
b [Å]	21.6495(2)	7.9734(1)	13.7178(7)	10.2169(3)
c [Å]	11.6623(2)	28.7174(3)	14.6783(6)	12.3529(4)
α [°]	90	90	94.574(4)	90
β [°]	91.649(1)	90	100.085(3)	107.103(3)
γ [°]	90	90	100.821(4)	90
V [Å^3]	2434.74(5)	4936.49(8)	2039.1(2)	2403.5(2)
Z	4	8	4	4
ρ_{calcd} [g cm^{-1}]	1.230	1.346	1.175	1.196
μ [mm^{-1}]	0.217	4.823	0.233	1.889
F(000)	960	2088	768	912
2Θ range [°]	5.14 to 60.2	6.2 to 152.6	3.9 to 50.5	9.3 to 144.2
Index range	$-13 \leq h \leq 13$	$-26 \leq h \leq 26$	$-12 \leq h \leq 12$	$-24 \leq h \leq 24$
	$-30 \leq k \leq 30$	$-10 \leq k \leq 9$	$-16 \leq k \leq 16$	$-12 \leq k \leq 12$
	$-16 \leq l \leq 16$	$-35 \leq l \leq 36$	$-17 \leq l \leq 17$	$-15 \leq l \leq 15$
Reflns collected	112581	45373	26795	81599
Unique reflns	7153	2495	7390	4735
Observed reflns [$I > 2\sigma(I)$]	6714	05	3899	4521
R_{int}	0.032	0.042	0.0630	0.0793
Data/restr./param	7153 / 0 / 274	2495 / 0 / 130	7390 / 0 / 434	4735 / 0 / 367
GoF (F^2)	1.122	1.080	0.894	1.110
R_1, wR_2 [$I > 2\sigma(I)$]	0.0324, 0.0861	0.0294, 0.0826	0.0516, 0.1225	0.0422, 0.1141
R_1, wR_2 (all data)	0.0347, 0.0874	0.0315, 0.0842	0.1046, 0.1338	0.0434, 0.1160
$\Delta\rho_{(max/min)}$ [e Å^{-3}]	0.40 / −0.21	0.45 / −0.24	0.49 / −0.30	0.34 / −0.29
remarks		a)	b)	
CCDC-no.	1419877	1419878	1419879	1419880

a) A pentane molecule is heavily disordered about a two-fold axis, so data were treated with the SQUEEZE procedure implemented in Olex2.[24]; b) Crystal was non-merohedrically twinned by a rotation around 100, ratio 78:22.

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A new 1,3,5-trisilacyclohexane scaffold with axially orientated ethynyl groups provides opportunities to create new tridentate Lewis acids. Some examples of these Lewis acids have been synthesized.