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Hydroalumination of Bis(alkynyl)silanes: Generation of Chelating Lewis Acids, Their Application in the Coordination of Chloride Ions and a 1,1-Carbalumination Reaction

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Treatment of diphenyl–diethynylsilanes, $(H_5C_6)_2Si(C{\equiv}C–R')_2$ ($R' = –C_6H_5$, $–4\text{-Me}–C_6H_4$), with two equivalents of dialkylaluminium hydrides, $R_2Al–H$ ($R = –CMe_3$, $–CH_2CMe_3$), afforded the corresponding dialkenylsilanes (**3**–**5**) by hydroalumination. The mixed alkenyl–alkynyl compounds resulting from the reduction of only one C≡C triple bond occurred as intermediates. Two of these (**1** and **2**) were isolated and characterized by crystal structure determinations. They show close interactions of the α-carbon atoms of the ethynyl groups with the coordinatively unsaturated aluminium atoms and a *cis* arrangement of H and Al atoms across the C=C double bonds. *cis*/*trans* Rearrangement took place upon the formation of the dialkenyl species **3**–**5** with an all-*trans* configuration of the alkenyl groups. These compounds have two tricoordinate aluminium atoms and are ideally preorganized to be applied as chelating Lewis acids, as was shown with the chelating coordination of chloride ions (compound **6**). Rearrangement and 1,1-carbalumination was observed upon heating of a mixed alkenyl–alkynylsilane (**7**). A silacyclobutene derivative (**8**) was isolated, which has a SiC_3 heterocycle and an *endo*- and an exocyclic C=C double bond. Quantum chemical calculations give insight into the reaction mechanism.

Introduction

Molecular oligoacceptors (chelating Lewis acids) have found some interest in recent research because they are potentially applicable in phase-transfer processes, in catalysis or in molecular recognition.[1] Compounds that have two or more coordinatively unsaturated, tricoordinate aluminium or gallium atoms in a single molecule are particularly suitable to act as such inverted chelating ligands. In previous investigations with a sterically, highly shielded methylene-bridged dialuminium compound, $R_2Al–CH_2–AlR_2$ [$R = CH(SiMe_3)_2$],[2] we observed the effective coordination of different anions, such as nitrate, nitrite, hydride, hydroxide, acetate etc., by the formation of ether soluble adducts.[3] Twofold hydroalumination or hydrogallation of alkynes[4] is a facile alternative method for the generation of such Lewis acids possessing a geminal arrangement of two acceptor functions. The resulting compounds were found to coordinate halide, thiolate or benzoate anions.[5] The efficacy of the chelating coordination of hydride ions by two aluminium atoms was impressively shown by the formation of persistent carbocations through C–H bond activation.[6] In many cases, the acceptor atoms occupy geminal positions at a bridging carbon atom, which results in relatively strained four-membered heterocycles upon coordination of single atom donors. Therefore, we were very much interested in synthesizing corresponding compounds that have larger spacers between the acceptor functions in order to gain a higher flexibility in their backbones and their coordinating properties. The twofold hydroalumination of silicon-centred dialkynes seemed to be a suitable method for their preparation.

Results and Discussion

Hydroalumination of Dialkynylsilanes $(H_5C_6)_2Si(C{\equiv}C–R')_2$

Treatment of dialkyl- or diphenyldialkynylsilanes, $R_2Si(C{\equiv}C–C_6H_5)_2$, with equimolar quantities of dineopentyl-, bis(*tert*-butyl)- or bis[bis(trimethylsilyl)methyl]aluminium hydride afforded the mixed alkenyl–alkynylsilanes by hydroalumination of one of their C≡C triple bonds.[7] In most cases, the *cis* addition products were isolated, which have the Al and H atoms on the same side of the resulting C=C double bonds. Only the two sterically less-shielded addition products show spontaneous *cis*/*trans* isomerization, which, in accordance with previous observations and quantum chemical calculations, requires intermolecular activation.[8] With the exception of the bis(trimethylsilyl)methyl compounds, we observed an interesting close intramolecu-

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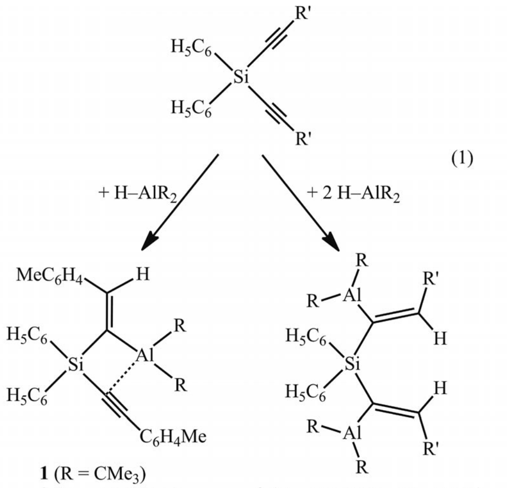
lar interaction between the α-carbon atoms of the alkynyl groups and the aluminium atoms. These interactions may help to stabilize the *cis* addition products and to prevent rearrangement. The *p*-tolyl derivatives **1** and **2** [Equation (1)] have not been reported previously. They were isolated in 41 and 78% yield, respectively, by the reaction of the corresponding diethynylsilane with one equivalent of bis(*tert*-butyl)- or dineopentylaluminium hydride. Their ^{13}C NMR spectra show the resonances characteristic of ethynyl (δ = 92.5 and 117.4 ppm, on average) and ethenyl carbon atoms (δ = 146.5 and 157.9 ppm). The *cis* arrangement of Al and H atoms at the C=C double bond is evident from crystal structure determinations (Figure 1) and from the characteristic $^3J_{H-C=C-Si}$ coupling constant of 25.8 Hz (*trans* positions of H and Si; see below for further discussion). The C=C and C≡C bond lengths (134.9 and 121.1 pm, on average) are in accord with standard values. The relatively short intramolecular Al1–C21 distances [248.2(2) (**1**) and 255.5(1) pm (**2**)], the positions of the Al atoms up to 33.3 pm above the planes of the adjacent atoms (C5, C6, C11) and the small torsion angles Al1–C11–Si1–C21 of 4.37(8)° and –17.58(7)°, respectively, verify the interaction of the Al atoms with the α-carbon atoms of the triple bonds (C21) bearing a relatively high negative charge.[9] Similar structures have been observed for corresponding germanium compounds[10] or were derived from NMR spectroscopic data for some products of hydroboration reactions.[11]



(1)

1 (R = CMe_3)
2 (R = CH_2CMe_3)
3 (R = CH_2CMe_3; R' = C_6H_5)
4 (R = CMe_3; R' = C_6H_5)
5 (R = CMe_3; R' = 4-Me-C_6H_4)

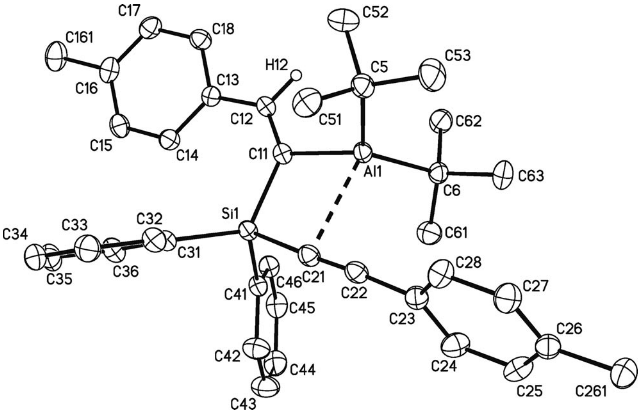


Figure 1. Molecular structure and numbering scheme of **1**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms with the exception of the vinylic hydrogen atom are omitted. Selected bond lengths [pm] and angles [°]: Al1–C11 199.9(2), Al1–C21 248.2(2), C11–C12 134.8(2), C21–C22 121.2(2), Al1–C11–Si1 102.12(7), C11–Si1–C21 96.53(7), Si1–C21–Al1 85.44(6), C11–Al1–C21 75.69(6). Data of the analogous compound **2**: Al1–C11 199.3(1), Al1–C21 255.5(1), C11–C12 135.0(2), C21–C22 120.9(2), Al1–C11–Si1 100.76(6), C11–Si1–C21 98.20(6), Si1–C21–Al1 82.53(5), C11–Al1–C21 75.02(5).

Dual hydroalumination of dialkynylsilanes to yield the doubly reduced dialuminium species has not been achieved previously. The silane starting compounds $(H_5C_6)_2Si(C{\equiv}C{-}R')_2$ (R′ = C_6H_5, 4-MeC_6H_4) reacted with two equivalents of dineopentyl- or bis(*tert*-butyl)aluminium hydride to give, in the first step, the mixed alkenyl–alkynylsilanes analogous to **1** or **2**. In contrast to the relatively fast hydroalumination of the first triple bond (3–16 h), the addition of the second equivalent of dialkylaluminium hydride to yield the fully reduced dialkenyl derivatives **3**–**5** is very slow and requires reaction times of at least 8 d at room temperature [Equation (1)]. Faster reactions may be prevented by steric shielding and electrostatic repulsion. The reaction rates could not be enhanced by heating of the mixtures under reflux because decomposition took place with the formation of unknown components. Dimethylsilane and silacyclobutane derivatives did not yield the products of twofold hydroalumination at all. Instead, the corresponding dimeric dialkylaluminium ethynides, $(R_2Al{-}C{\equiv}C{-}C_6H_5)_2$,[12] were formed and identified by their characteristic NMR spectroscopic data. Further products could not be isolated or identified. Treatment of compound **2** with an excess of dineopentylaluminium hydride did not result in the formation of the corresponding dialkenyl derivative, and **2** remained unchanged even after a prolonged reaction time. Sterically less-shielded hydrides such as dimethyl- or diethylaluminium hydride gave unclear reaction courses. The corresponding reactions of dialkynylgermanium compounds proved to be even less selective and only a single dialkenyl species could be isolated and applied in secondary reactions.[13]

The central silicon atoms of the dialkenyl compounds **3**–**5** (Figure 2) have a slightly distorted tetrahedral coordination sphere and are bound to two phenyl and two alkenyl groups. As expected by charge separation in the starting bisalkynes, the aluminium atoms selectively attacked the α-carbon atoms of the ethynyl groups. The metal atoms have an almost ideally planar surrounding with a maximum deviation of the aluminium atom from the plane of the three adjacent carbon atoms of only 14.5 pm in compound **5**. The C=C double bond lengths are in a narrow range and deviate only slightly from the average value of 134.8 pm. Minimization of steric repulsion seems to determine the molecular conformation in the solid state, and the bulky dialkylaluminium groups adopt the largest possible distance to one another. Interestingly, *cis*/*trans* isomerization occurs, and the H and Al atoms are on different sides of the C=C double bonds. Hence, the isolation of persistent *cis* isomers with the monoaddition products (e.g. **1**) is not caused by steric shielding. Instead isomerization is prevented in these cases by the intramolecular Al–C interaction and coordinative saturation of the Al atoms, as described above and schematically shown in Equation (1).

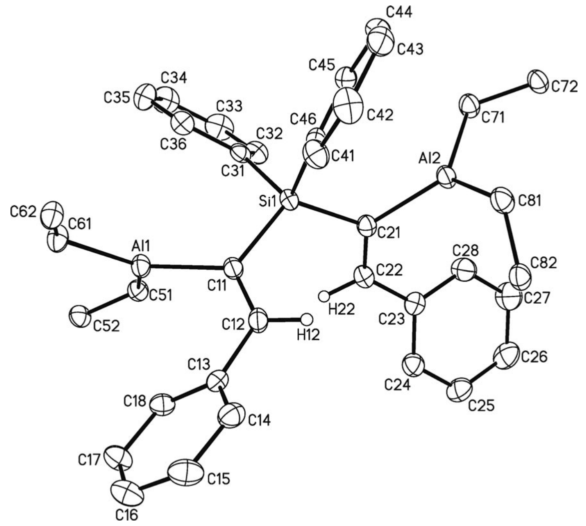
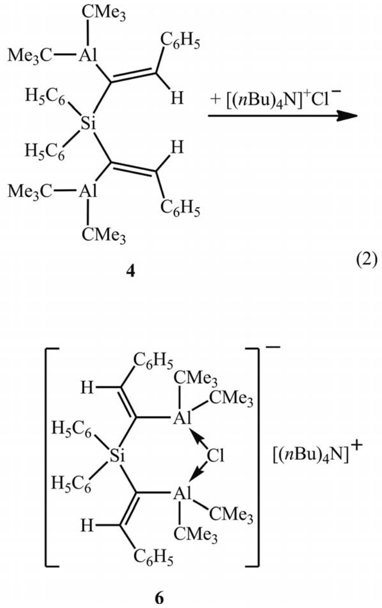


Figure 2. Molecular structure and numbering scheme of **3**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms with the exception of the vinylic hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]: Al1–C11 197.6(2), C11–C12 134.4(2), Al2–C21 198.6(2), C21–C22 134.3(3), C11–Si1–C21 116.10(8), Si1–C11–C12 119.4(1), Si1–C21–C22 117.7(1), Si1–C11–Al1 118.11(9), Si1–C21–Al2 114.61(9), Al1–C11–C12 122.5(1), Al2–C21–C22 127.2(1). Data of compound **4**: Al1–C11 197.8(2), C11–C12 134.7(2), C11–Si1–C11′ 111.7(1), Si1–C11–C12 118.9(1), Si1–C11–Al1 127.09(8), Al1–C11–C12 113.6(1); C11′ generated by $-x + 1.5$, $-y + 0.5$, z. Data for compound **5**: Al1–C11 198.3(3), C11–C12 135.4(3), C11–Si1–C11′ 110.4(2), Si1–C11–C12 117.8(2), Si1–C11–Al1 129.4(1), Al1–C11–C12 112.3(2); C11′ generated by $-x + 1.5$, $-y + 0.5$, z.

NMR spectroscopic data are in accordance with the molecular structures. The resonances for the ethenyl carbon atoms are in a narrow range of the ^{13}C NMR spectrum between $\delta = 157.7$ and 161.8 ppm; signals for ethynyl carbon atoms ($\delta = 90$–120 ppm of **1** and **2** and other mixed alkenyl–alkynyl derivatives[7,10,13]) are missing, which verifies complete hydroalumination. The $^3J_{\text{Si–H}}$ coupling constants across the C=C double bonds (11.4 to 12.4 Hz) are much smaller than those in the monoaddition products (see **1** and **2** above). They clearly indicate the *cis* arrangement of H and Si atoms,[8,14] and hence *cis*/*trans* isomerization.

Dialuminium Compound 4 as a Chelating Lewis Acid

The molecular conformation of the dialkenylsilicon compounds **3**–**5** in which the coordinatively unsaturated aluminium atoms point in opposite directions of the molecules seems to contradict their potential application as chelating Lewis acids. Therefore, it was particularly important to test their acceptor properties in a simple experiment prior to the beginning of systematic investigations. We treated compound **4** with equimolar quantities of tetra(*n*-butyl)ammonium chloride in toluene. A suspension was obtained, which, after evaporation of the solvent and treatment of the residue with *n*-hexane, gave a colourless amorphous solid. It was dissolved in a small volume of 1,2-difluorobenzene. Colourless crystals of adduct **6** were isolated upon cooling of the solution to –15 °C [Equation (2)]. The crystal structure determination verified the complexation of the chloride ion by both aluminium atoms in a chelating manner(Figure 3), which is accompanied by a dramatic change in the



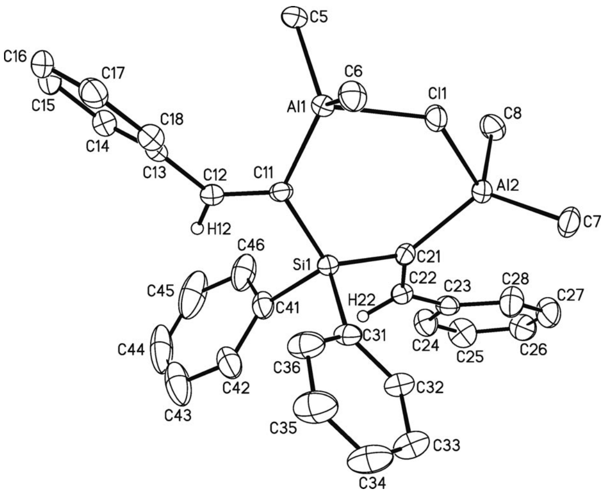
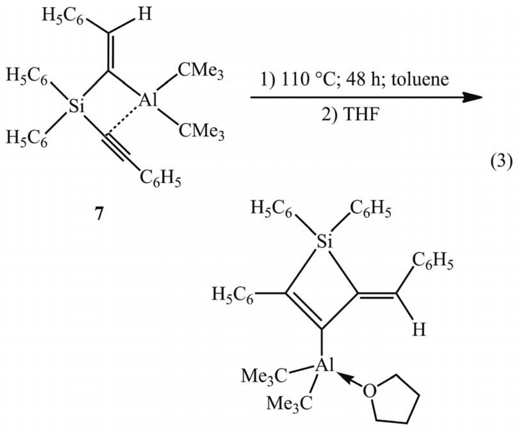


Figure 3. Molecular structure and numbering scheme of **6**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms with the exception of the vinylic hydrogen atoms and methyl groups are omitted. Selected bond lengths [pm] and angles [°]: Al1–C11 201.5(3), C11–C12 135.3(5), Al2–C21 202.9(3), C21–C22 136.2(4), Al1–Cl1 234.1(1), Al2–Cl1 232.7(1), Al1–Cl1–Al2 134.60(4), C11–Si1–C21 124.4(1), Si1–C11–C12 113.5(2), Si1–C21–C22 110.4(2), Si1–C11–Al1 127.7(2), Si1–C21–Al2 126.4(2), Al1–C11–C12 118.7(2), Al2–C21–C22 123.1(2).

molecular conformation of the bisacceptor and a reorientation of the alkenylaluminium fragments by rotation about the Si–C bonds. Despite the bulkiness of the bis(*tert*-butyl)aluminium groups, the Al atoms coordinate the halide ion in a chelating manner to give a six-membered $ClAl_2C_2Si$ heterocycle. The C=C double bonds that had an *endo*-type orientation in the starting compound **4** are now in *exo*-positions. The Al–Cl distances (233.4 pm on average) are in the normal range observed for bridging Al–Cl–Al groups in organoaluminium compounds (≈225–240 pm).[13,15] In accordance with the higher coordination numbers of the aluminium atoms, the Al–C bonds of **6** show the usual lengthening relative to those in **4** (203.0 pm vs. 198.7 pm, on average). The C=C double bonds of **6** are only slightly longer [135.8 pm on average, vs. 134.7(2) pm for **4**]. A relatively obtuse angle was observed at the chlorine atom [Al1–Cl1–Al2 134.60(4)°], while the most acute endocyclic angles of the central heterocycle occur at the aluminium atoms (Cl1–Al–C 98.9°). The configuration of the alkenyl groups remains unchanged with a *trans* arrangement of the Al and H atoms. Compound **6** crystallizes isotypically to the corresponding germanium compound.[13] Interestingly, the NMR spectroscopic data of both compounds **4** and **6** are almost identical and obviously do not depend on adduct formation. The only significant alteration involves the chemical shift of the central silicon atom, which in the ^{29}Si NMR spectra changes from δ = –19.0(**4**) ppm to δ = –2.0(**6**) ppm.

Rearrangement and 1,1-Organoalumination Upon Heating of an Alkenyl–Alkynylsilane

The close contact between the coordinatively unsaturated aluminium atoms and the α-carbon atoms of the ethynyl groups in the mixed alkenyl–alkynylsilanes analogous to **1** and **2** should facilitate interesting secondary reactions. However, heating of the solutions in toluene or of the neat materials led to decomposition with the formation of inseparable mixtures of several unknown components in most cases. An exception was the thermal treatment of the compound $(H_5C_6)_2Si(C{\equiv}C{-}C_6H_5)[C(AlR_2){=}C(H){-}C_6H_5]$ (**7**, R = CMe_3), the synthesis of which has been published by our group only recently.[7] A relatively clear reaction course was observed in refluxing toluene with the complete consumption of **7** after 48 h and the formation of an oily product, which shows an intensive resonance of *tert*-butyl groups in the ^1H NMR spectrum in addition to signals of unknown impurities. Despite enormous efforts, we were not able to purify this product by crystallization from different non-coordinating solvents (*n*-pentane to pentafluorobenzene). Addition of THF gave an adduct (**8**), which could be crystallized from diisopropyl ether and was isolated in 73% yield [Equation (3)]. The crystal structure reveals the formation of an unusual heterocyclic silacyclobutene derivative (Figure 4) by insertion of the negatively charged α-carbon atom of the ethynyl group into an Al–C bond (1,1-carbalumination) and formation of a new Si–C bond to the β-carbon atom of the alkyne (see below for details of the reaction mechanism). The central SiC_3 heterocycle contains an endocyclic C=C double bond, which with a length of 138.8(2) pm is relatively long. The third carbon atom of the ring is part of an exocyclic double bond with a normal length of 134.1(3) pm.[16] The relatively long Si–C distances (186.4 pm on average) cause a distortion of the ring with an acute C–Si–C angle of 74.57(8)°. The remaining angles of the ring are 89.2(1) and 93.2(1)° (Si–C–C) and 102.9(1)° (C–C–C). Because of the sp²-hybridization of all carbon atoms, these relatively small angles may indicate considerable strain in the heterocycle. The aluminium atom has a terminal position and is coordinatively saturated by coordination of a THF molecule. The Al–C distance to the ring carbon atom C3 [202.1(2) pm] is in the expected range for tetracoordinate aluminium atoms.



7

8

(3)

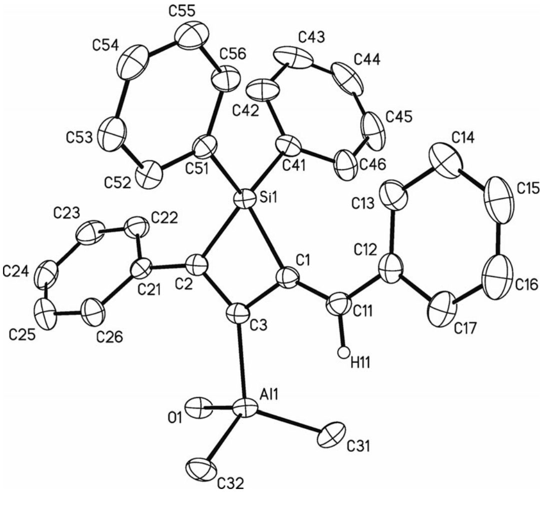
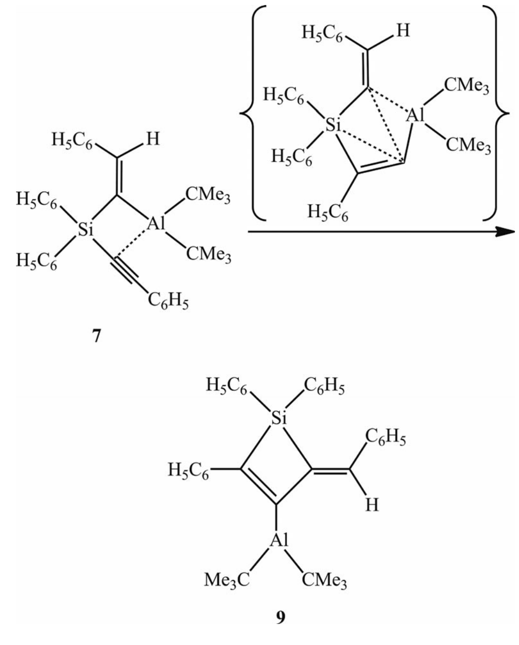


Figure 4. Molecular structure and numbering scheme of **8**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms with the exception of the vinylic hydrogen atom and methyl groups are omitted; only the oxygen atom of the THF ligand attached to aluminium is shown. Selected bond lengths [pm] and angles [°]: Si1–C1 186.7(2), Si1–C2 186.0(2), Al1–C3 202.1(2), C1–C11 134.1(3), C1–C3 150.1(2), C2–C3 138.5(2), C1–Si1–C2 74.57(8), Si1–C1–C3 89.2(1), Si1–C2–C3 93.2(1), C1–C3–C2 102.9(1), Si1–C1–C11 143.1(1), C3–C1–C11 127.5(2).

The most interesting feature of the NMR spectroscopic data of **8** is the unusual chemical shift for the carbon atoms of the endocyclic C=C double bond [δ = 194.5 ppm (C=*C*–Al) and 174.1 ppm (C=*C*–Si)]. In contrast, the resonances of the exocyclic C=C bond are in the normal range (δ = 130.7 and 154.5 ppm). The signals of the vinylic hydrogen atom [$\delta(^1H)$ = 7.11 ppm] and of the silicon atom [$\delta(^{29}Si)$ = –1.4 ppm] are considerably shifted compared to the corresponding resonances of the starting compound **7** (δ = 8.35 and –34.5 ppm[7]). Only compound **1** shows a similar rearrangement upon heating in toluene. However, it was not completely consumed even after prolonged reaction times of 3 d, and several unknown by-products were detected in the NMR spectra. A solid material was isolated in 30% yield by crystallization from *n*-pentane. Its main component had NMR spectroscopic data similar to those of **8**, but it had some impurities of unknown composition. Therefore, we abstain from a detailed discussion.

In order to elucidate the mechanism of the unusual rearrangement of **7** to give **8**, high level quantum chemical calculations at the SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p) level were performed. The structural parameters of the starting material **7** (in comparison to the X-ray data[7]) and of the product **9** as a solvent-free model compound of **8** are well reproduced by the theoretical method. According to the theoretical results, the reaction proceeds through a concerted mechanism via the transition structure TS, as shown in Scheme 1 and Figure 5. The highly ordered structure of the transition state involves essentially five atoms: the silicon and aluminium atoms together with both carbon atoms of the alkynyl group as well as the α-carbon atom of the alkenyl group in a planar tricyclic geometry. The relatively weak intramolecular interaction of the aluminium atom with the α-carbon atom of the alkynyl moiety is indeed the key structural element to initiate the rearrangement. The Si–C bond to the negatively charged carbon atom of the ethynyl group is considerably weakened, and its interaction to the aluminium atom becomes stronger (Al–C 264 pm in **7** to 194 pm in TS; Si–C 188 to 249 pm). At the same time, a new Si–C bond is formed to the original β-carbon atom of the alkyne (Si–C 191 pm). The transannular contact between the sp^2 carbon atoms of the alkenyl groups (indicated by a dashed line) is relatively long at this stage of the reaction (224 pm). It becomes a normal C–C bond (C–C 149 pm) in the next step, while the Al–C bond to the original α-carbon atom of the ethynyl group is almost unchanged upon formation of **9** (Al–C 200 pm). The C–C bond length of the original ethynyl group steadily increases from 122 over 131 to 138 pm [further important calculated parameters of **9**: Si–C 188 and 190 pm; C=C (*exo*) 135 pm]. C–C bond formation yields the four-membered SiC$_3$ heterocycle as the characteristic structural motif of the rearranged product. Overall this mechanism corresponds to the insertion of the negatively charged terminal carbon atom of the alkynyl group in **7** (NBO charge –0.52; Al +1.99) into the Al–C(vinyl) bond and formation of a new Si–C bond. The activation barrier was calculated to be 33.5 kcal/mol, and the reaction is moderately exothermic (–3.7 kcal/mol), which is in accordance with the experimental conditions for thermal rearrangement. A similar activation barrier was calculated for the rearrangement of a germanium-centred alkenyl–alkynyl compound.[9] The calculations also give clear evidence that a mechanism involving the dissociation of the starting compound **7** into diphenyl(2-phenylvinylidene)silane and well-known bis(*tert*-butyl)(phenylethynyl)aluminium[12] followed by 2+2-cycloaddition seems to be rather unlikely because the dissociation products are 62.8 kcal/mol higher in energy than the substrate **7**.



Scheme 1.

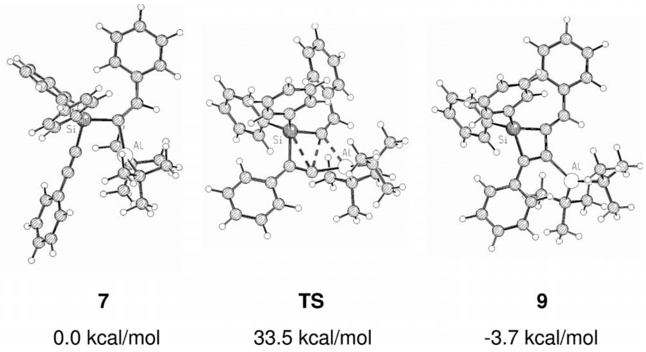


Figure 5. Calculated molecular structures of **7**, **9** (model for **8** without THF) and the relavant transition state TS with their relative energies [kcal/mol] {SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p) incl. ZPE}.

This is only the second time that 1,1-carbalumination has been observed, the first case involved the rearrangement of an alkenyl–alkynylgermanium compound.[9] In principle, this method seems to be a facile procedure for the simple generation of sila- or germacyclobutene derivatives; however, up to now, this route could be applied successfully in only two cases. We hope that optimization of the reaction conditions in future investigations may allow a broader application. In contrast, 1,1-carbaboration is quite common and has been used for the synthesis of several unsaturated heterocyclic compounds.[11,17] Silacyclobutenes similar to compound **8** have also been obtained by other routes.[18] They found some interest in research because they show photoluminescence.[19]

Experimental Section

General: All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane and *n*-pentane with $LiAlH_4$; pentafluoro- and 1,2-difluorobenzene with molecular sieves, diethyl ether, THF and diisopropyl ether with Na/benzophenone). $(Me_3C)_2Al–H$,[20] $(Me_3CCH_2)_2Al–H$,[21] $(H_5C_6)_2Si(C{\equiv}C–C_6H_5)_2$[22] and compound **7**[7] were obtained according to literature procedures. Commercially available tetrabutylammonium chloride was employed as purchased. The assignment of the NMR spectra is based on HMBC, HSQC, ROESY and DEPT135 data. The Si–H coupling constants ($^3J_{Si–H}$) across the C=C double bonds were determined from the ^{29}Si satellite peaks of the vinylic hydrogen atoms in the ^1H NMR spectra.

Synthesis of $(H_5C_6)_2Si(C{\equiv}C\text{-}4\text{-}MeC_6H_4)_2$: A solution of *p*-tolylethyne (8.0 mL, 7.33 g, 63.2 mmol) in diethyl ether (100 mL) was treated with a solution of *n*-butyllithium in *n*-hexane (1.6 M, 39.5 mL, 63.2 mmol) at –78 °C. The mixture was stirred for 2 h at this temperature. Diphenyldichlorosilane (6.0 mL, 7.22 g, 28.5 mmol) was added. After 2 h, the suspension was warmed to room temperature and was further stirred for 16 h. Aqueous HCl (10%; 100 mL) was added to completely dissolve the LiCl precipitate. The organic phase was separated, and the aqueous phase was extracted two times with diethyl ether (25 mL). The combined organic phases were dried with $MgSO_4$ and filtered. All volatiles of the filtrate were removed in vacuo. The residue was dissolved in *n*-pentane. Colourless crystals of the dialkyne were obtained upon cooling to –70 °C. Yield: 8.64 g (74%). M.p. (argon; sealed capillary) 79 °C. ^1H NMR (400 MHz, C_6D_6): δ = 1.91 (s, 6 H, CH_3), 6.71 (d, 4 H, $^3J_{H,H}$ = 8.0 Hz, *meta*-H *p*Tol), 7.21 (m, 2 H, *para*-H Ph), 7.23 (m, 4 H, *meta*-H Ph), 7.35 (d, 4 H, $^3J_{H,H}$ = 8.0 Hz, *ortho*-H *p*Tol), 8.15 (m, 4 H, *ortho*-H Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 21.3 (Me), 88.0 (Si–*C*≡C), 109.8 (Si–C≡*C*), 120.0 (*ipso*-C ethynyl-Ph), 128.5 (*meta*-C $SiPh_2$), 129.3 (*meta*-C ethynyl-Ph), 130.5 (*para*-C Ph_2Si), 132.6 (*ortho*-C ethynyl-Ph), 133.9 (*ipso*-C Ph_2Si), 135.5 (*ortho*-C Ph_2Si), 139.5 (*para*-C ethynyl-Ph) ppm. ^{29}Si NMR (79.5 MHz, C_6D_6): δ = –47.7 ppm. IR (CsI, paraffin): $\tilde{\nu}$ = 2158 [s, ν(C≡C)], 1960 (vw), 1908 (w), 1821 (vw), 1653 (w), 1606 (w), 1580 (w), 1545 (w), 1528 [vw, phenyl], 1466 (vs), 1377 [vs, paraffin], 1321 (m), 1265 (w), 1248 [w, δ(CH_3)], 1218 (w), 1188 (w), 1173 (w), 1153 (w), 1113 (m), 1040 (vw), 1018 (w), 999 (w), 966 (w), 947 (w), 920 (w), 889 (w), 843 (s), 814 (s), 768 (m), 734 [vs, ν(CC), δ(CH)], 721[vs, paraffin], 694 [w, δ(phenyl)], 637 (vw), 619 (w), 588 (s), 565 (s), 536 (s), 491 (m), 472 (m), 426 [m, ν(SiC), ν(AlC), δ(CC)] cm^{-1}. MS (EI, 20 eV, 393 K): *m*/*z* (%) = 412 (100) [M^+], 397 (9) [$M^+ – CH_3$], 335 (17) [M^+ – Ph]. $C_{30}H_{24}Si$ (412.6): calcd. C 87.3, H 5.9; found C 87.6, H 6.0.

Synthesis of 1: A solution of bis(*tert*-butyl)aluminium hydride (0.296 g, 2.08 mmol) in *n*-hexane (25 mL) was treated with a solution of diphenylbis(*p*-tolylethynyl)silane (0.859 g, 2.08 mmol) in *n*-hexane (25 mL). The mixture was stirred for 16 h at room temperature. The colour changed to yellow. All volatiles were removed in vacuo, and the remaining yellowish solid was recrystallized from 1,2-difluorobenzene or pentafluorobenzene (20/–30 °C) to yield colourless crystals of **1**. Yield: 0.474 g (41%; after thorough evacuation). M.p. (argon; sealed capillary) 135 °C (dec.). ^1H NMR (400 MHz, C_6D_6): δ = 1.36 (s, 18 H, CMe_3), 1.83 (s, 3 H, CH_3 ethynyl-*p*Tol), 1.94 (s, 3 H,CH_3 ethenyl-*p*Tol), 6.66 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, *meta*-H ethynyl-*p*Tol), 6.75 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, *meta*-H ethenyl-*p*Tol), 7.15 (m, 8 H, *meta*-H and *para*-H Ph_2Si), 7.41 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, *ortho-H* ethynyl-*p*Tol), 7.43 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, *ortho*-H ethenyl-*p*Tol), 8.00 (m, 4 H, *ortho*-H Ph_2Si), 8.38 (s, $^3J_{H–Si}$ = 25.8 Hz, 1 H, C=C*H*) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 19.6 (*C*Me_3), 21.0 (CH_3 ethenyl-*p*Tol), 21.4 (CH_3 ethynyl-*p*Tol), 31.1 (C*Me*$_3$), 91.4 (Si–*C*≡C), 117.0 (*ipso*-C ethynyl-*p*Tol), 117.9 (Si–C≡*C*), 128:5 (*meta*-C Ph_2Si), 128.8 (*ortho*-C ethenyl-*p*Tol), 129.3 (*meta*-C ethenyl-*p*Tol), 129.6 (*meta*-C ethynyl-*p*Tol), 130.4 (*para*-C Ph_2Si), 133.9 (*ortho*-C ethynyl-*p*Tol), 134.4 (*ipso*-C Ph_2Si), 136.0 (*ortho*-C Ph_2Si), 138.2 (*para*-C ethenyl-*p*Tol), 138.9 (*ipso*-C ethenyl-*p*Tol), 142.0 (*para*-C ethynyl-*p*Tol), 145.1 (*C*=CH-*p*Tol), 157.4 (C=*C*H-*p*Tol) ppm. ^{29}Si NMR (79.5 MHz, C_6D_6): δ = –37.1 ppm. IR (CsI, paraffin): $\tilde{\nu}$ = 2158 (s), 2126 [vs, ν(C≡C)], 2056 (vw), 1977 (w), 1962 (w), 1911 (m), 1890 (w), 1822 (w), 1795 (vw), 1773 (vw), 1707 (vw), 1655 (w), 1645 (w), 1605 (s), 1584 (s), 1552 (s), 1506 (s), 1483 [s, ν(C=C), phenyl], 1460 (vs), 1379 [vs, paraffin], 1355 (m), 1342 (w), 1304 (m), 1273 (w), 1263 [m, δ(CH_3)], 1219 (w), 1190 (m), 1179 (m), 1157 (vw), 1107 (vs), 1040 (m), 1020 (w), 997 (m), 970 (w), 951 (w), 930 (w), 897 (s), 854 (s), 840 (m), 814 (vs), 789 [s, ν(CC), δ(CH)], 740 [s, δ(C=C)], 698 [vs, phenyl], 653 (s), 627 (s), 588 (s), 561 (m), 536 (m), 520 (w), 491 (m), 471 (s), 446 [m, ν(SiC), ν(AlC), δ(CC)] cm^{-1}. MS (EI, 20 eV, 373 K): *m*/*z* (%) = 497 (13) [$M^+ – CMe_3$], 413 (83) [$M^+ – Al(CMe_3)_2$]. $C_{38}H_{43}AlSi$ (554.8): calcd. C 82.3, H 7.8; found C 81.8, H 7.8.

Synthesis of 2: A solution of dineopentylaluminium hydride (0.151 g, 0.89 mmol) in *n*-hexane (25 mL) was treated with a solution of diphenylbis(*p*-tolylethynyl)silane (0.366 g, 0.89 mmol) in *n*-hexane (25 mL). The solution was stirred at room temperature for 4 h. All volatiles were removed in vacuo. The residue was dissolved in pentafluorobenzene and cooled to +2 °C to obtain colourless crystals of **2**. Yield: 0.403 g (78%). M.p. (argon, sealed capillary) 141 °C (dec.). ^1H NMR (400 MHz, C_6D_6): δ = 0.87 (s, 4 H, CH_2), 1.31 (s, 18 H, CMe_3), 1.84 (s, 3 H, CH_3 ethynyl-*p*Tol), 1.93 (s, 3 H, CH_3 ethenyl-*p*Tol), 6.67 (d, $^3J_{H–H}$ = 7.9 Hz, 2 H, *meta*-H ethynyl-*p*Tol), 6.74 (d, $^3J_{H–H}$ = 7.9 Hz, 2 H, *meta*-H ethenyl-*p*Tol), 7.14 (m, 2 H, *para*-H Ph_2Si), 7.19 (m, 4 H, *meta*-H Ph_2Si), 7.37 (d, $^3J_{H–H}$ = 7.9 Hz, 2 H, *ortho*-H ethynyl-*p*Tol), 7.42 (d, $^3J_{H–H}$ = 7.9 Hz, 2 H, *ortho*-H alkenyl-*p*Tol), 8.02 (pseudo-d, 4 H, *ortho*-H Ph_2Si), 8.34 (s, $^3J_{H–Si}$ = 25.7 Hz, 1 H, C=CH) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 21.0 (CH_3 ethenyl-*p*Tol), 21.3 (CH_3 ethynyl-*p*Tol), 31.9 (*C*Me_3), 33.7 (*C*H_2), 35.3 (C*Me*$_3$), 93.6 (Si–*C*≡C), 116.9 (Si–C≡*C*), 117.7 (*ipso*-C ethynyl-*p*Tol), 128.5 (*meta*-C Ph_2Si), 128.6 (*ortho*-C ethenyl-*p*Tol), 129.3 (*meta*-C ethenyl-*p*Tol), 129.5 (*meta*-C ethynyl-*p*Tol), 130.4 (*para*-C Ph_2Si), 133.2 (*ortho*-C ethynyl-*p*Tol), 134.4 (*ipso*-C Ph_2Si), 136.1 (*ortho*-C Ph_2Si), 138.2 (*para*-C ethenyl-*p*Tol), 139.2 (*ipso*-C ethenyl-*p*Tol), 141.3 (*para*-C ethynyl-*p*Tol), 147.9 (Si–*C*=C–H), 158.3 (Si–C=*C*–H) ppm. ^{29}Si NMR (79.5 MHz, C_6D_6): δ = –35.4 ppm. IR (CsI, paraffin): $\tilde{\nu}$ = 2158 (s), 2126 [m, ν(C≡C)], 2052 (w), 1983 (w), 1964 (w), 1952 (w), 1902 (w), 1827 (w), 1813 (w), 1775 (vw), 1701 (vw), 1649 (w), 1591 (m), 1566 (m), 1555 (w), 1506 [s, ν(C=C), phenyl], 1454 (vs), 1377 [vs, paraffin], 1304 (s), 1267 [s, δ(CH_3)], 1220 (m), 1190 (w), 1177 (w), 1153 (w), 1111 (s), 1038 (m), 1016 (s), 997 (m), 962 (w), 943 (m), 921 (vw), 843 (w), 849 (s), 816 (s), 802 (vw), 775 (w), 752 [w, ν(CC), δ(CH)], 737 [s, δ(C=C)], 721 [s, paraffin], 698 [s, phenyl], 660 (w), 615 (m), 597 (w), 565 (m), 536 (m), 519 (m), 484 (m), 465 (m), 440 [m, ν(SiC), ν(AlC), δ(CC)] cm^{-1}. MS (EI, 20 eV, 413 K): *m*/*z* (%) = 511 (100) [M^+ –

CH_2CMe_3], 413 (46) [M^+ – $AlNp_2$], 336 (22) [M^+ – $AlNp_2$ – Ph]. $C_{40}H_{47}AlSi$ (582.9): calcd. C 82.4, H 8.1; found C 82.2, H 7.8.

Synthesis of 3: A solution of dineopentylaluminium hydride (0.207 g, 1.22 mmol) in *n*-hexane (10 mL) was treated with a solution of diphenylbis(phenylethynyl)silane (0.234 g, 0.609 mmol) in *n*-hexane (25 mL). The mixture was stirred at room temperature for 8 d. The colour changed to yellow. All volatiles were removed in vacuo. The remaining viscous liquid was dissolved in a few millilitres of pentafluorobenzene. Cooling of the solution to +2 °C afforded colourless crystals of **3**. Yield: 0.157 g (36%). M.p. (argon; sealed capillary) 132 °C (dec.). ^1H NMR (400 MHz, C_6D_6): δ = 0.52 (s, 8 H, CH_2), 0.99 (s, 36 H, CMe_3), 7.02 (m, 2 H, *para-H* alkene-Ph), 7.15 (m, 4 H, *meta-H* alkene-Ph), 7.22 (m, 2 H, *para*-H Ph_2Si), 7.31 (m, 4 H, *meta-H* Ph_2Si), 7.39 (m, 4 H, *ortho-H* alkene-Ph), 7.98 (m, 4 H, *ortho-H* Ph_2Si), 8.32 (s, $^3J_{H-Si}$ = 12.4 Hz, 2 H, C=C*H*Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 31.3 (*C*Me_3), 34.6 (C*Me*$_3$), 34.9 (CH_2), 125.7 (*ortho*-C alkene-Ph), 128.7 (*para*-C alkene-Ph), 129.1 (*meta*-C Ph_2Si), 130.1 (*para*-C Ph_2Si), 130.2 (*meta*-C alkene-Ph), 136.1 (*ortho*-C Ph_2Si), 139.0 (*ipso*-C Ph_2Si), 145.8 (*ipso*-C alkene-Ph), 157.7 (C=*C*HPh), 161.7 (*C*=CHPh) ppm. ^{29}Si NMR (79.5 MHz, C_6D_6): δ = –19.1 ppm. IR (CsI, paraffin): $\tilde{\nu}$ = 1649 (w), 1599 (m), 1574 (m), 1532 [m, ν(C=C), phenyl], 1462 (vs), 1377 [vs, paraffin], 1308 (w), 1250 [vw, δ(CH_3)], 1155 (m), 1109 (w), 1072 (w), 1027 (w), 1013 (w), 991 (m), 931 (m), 920 (m), 833 (m), 797 [w, ν(CC), δ(CH)], 732 [m, δ(C=C)], 723 [m, paraffin], 698 [m, phenyl], 628 (w), 594 (w), 551 (w), 474 [w, ν(SiC), ν(AlC), δ(CC)] cm^{-1}. MS (EI, 20 eV, 333 K): *m*/*z* (%) = 441 (100) [M^+ – 4 CH_2CMe_3 + H], 386 (2) [M^+ – 2 $Al(CH_2CMe_3)_2$]. $C_{48}H_{66}Al_2Si$ (725.1): calcd. C 79.5, H 9.2; found C 79.2, H 8.9.

Synthesis of 4: Bis(*tert*-butyl)aluminium hydride (0.286 g, 2.01 mmol) was dissolved in *n*-hexane (10 mL) and treated with a solution of diphenylbis(phenylethynyl)silane (0.387 g, 1.01 mmol) in *n*-hexane (10 mL). The mixture was stirred at room temperature for 8 d. The colour changed to yellow. All volatiles were removed in vacuo. The residue was dissolved in a few millilitres of pentafluorobenzene and cooled to +2 °C to yield colourless crystals of compound **4**. Yield: 0.316 g (47%). M.p. (argon; sealed capillary) 180 °C (dec.). ^1H NMR (400 MHz, C_6D_6): δ = 0.90 (s, 36 H, CMe_3), 6.99 (m, 2 H, *para*-H alkene-Ph), 7.14 (m, 4 H, *meta*-H alkene-Ph), 7.20 (m, 2 H, *para*-H Ph_2Si), 7.26 (m, 4 H, *ortho*-H alkene-Ph), 7.29 (m, 4 H, *meta*-H Ph_2Si), 7.93 (m, 4 H, *ortho*-H Ph_2Si), 8.47 (s, $^3J_{H-Si}$ = 11.4 Hz, 2 H, C=C*H*Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 19.5 (*C*M_3), 30.4 (C*Me*$_3$), 123.7 (*ortho*-C alkene-Ph), 128.9 (*para*-C alkene-Ph), 129.1 (*meta*-C Ph_2Si), 130.0 (*para*-C Ph_2Si), 131.4 (*meta*-C alkene-Ph), 135.9 (*ortho*-C Ph_2Si), 139.2 (*ipso*-C Ph_2Si), 147.9 (*ipso*-C alkene-Ph), 159.2 (C=*C*HPh), 161.8 (*C*=CHPh) ppm. ^{29}Si NMR (79.5 MHz, C_6D_6): δ = –19.0 ppm. IR (CsI, paraffin): $\tilde{\nu}$ = 1647 (w), 1597 (w), 1533 [w, ν(C=C), phenyl], 1460 (vs), 1377 [vs, paraffin], 1308 (w), 1283 (w), 1269 [w, δ(CH_3)], 1153 (vs), 1078 (vw), 1028 (vw), 999 (vw), 964 (vw) 935 (w), 887 (w), 843 (w), 812 (vw), 798 (vw), 771 [vw, ν(CC), δ(CH)], 732 [m, δ(C=C)], 721 [m, paraffin], 700 (w), 623 [s, phenyl], 594 (w), 524 (vw), 474 [w, ν(SiC), ν(AlC), δ(CC)] cm^{-1}. MS (EI, 20 eV, 310 K): *m*/*z* (%) = 611 (91) [M^+ – CMe_3], 469 (67) [M^+ – Al*t*Bu_3 – H]. $C_{44}H_{58}Al_2Si$ (669.0): calcd. C 79.0, H 8.7; found C 78.5, H 8.8.

Synthesis of 5: Bis(*tert*-butyl)aluminium hydride (0.234 g, 1.65 mmol) was dissolved in *n*-hexane (10 mL) and treated with diphenylbis(*p*-tolylethynyl)silane (0.339 g, 0.822 mmol) dissolved in the same solvent (25 mL). The mixture was stirred at room temperature for 8 d. Toluene (5 mL) was added after 1 d in order to dissolve the colourless precipitate. All volatiles were removed in vacuo. The remaining solid was dissolved in pentafluorobenzene. Cooling of the solution to +2 °C afforded colourless crystals of compound **5**. Yield: 0.362 g (63%). M.p. (argon; sealed capillary) 185 °C (dec.). ^1H NMR (400 MHz, C_6D_6): δ = 0.94 (s, 36 H, CMe_3), 2.00 (s, 6 H, CH_3 *p*Tol), 7.02 (d, $^3J_{H-H}$ = 8.2 Hz, 4 H, *meta*-H *p*Tol), 7.21 (m, 2 H, *para*-H Ph_2Si), 7.23 (dd, $^3J_{H-H}$ = 8.2, $^4J_{H-H}$ = 1.4 Hz, 4 H, *ortho*-H *p*Tol), 7.30 (m, 4 H, *meta*-H Ph_2Si), 7.95 (m, 4 H, *ortho*-H Ph_2Si), 8.49 (s, $^3J_{H-Si}$ = 11.8 Hz, 2 H, C*H*Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 19.4 (*C*Me_3), 21.0 (CH_3 *p*Tol), 30.5 (C*Me*$_3$), 123.7 (*ortho*-C *p*Tol), 129.0 (*meta*-C Ph_2Si), 129.9 (*para*-C Ph_2Si), 132.1 (*meta*-C *p*Tol), 136.0 (*ortho*-C Ph_2Si), 138.9 (*para*-C *p*Tol), 139.4 (*ipso*-C Ph_2Si), 145.3 (*ipso*-C *p*Tol), 159.1 (C=*C*HPh), 160.2 (*C*=CHPh) ppm. ^{29}Si NMR (79.5 MHz, C_6D_6): δ = –18.8 ppm. IR (CsI, paraffin): $\tilde{\nu}$ = 1904 (w), 1829 (vw), 1798 (vw), 1777 (vw), 1699 (vw), 1649 (vw), 1605 (m), 1564 [vw, ν(C=C), phenyl], 1466 (vs), 1377 [vs, paraffin], 1312 (m), 1265 [m, δ(CH_3)], 1219 (vw), 1204 (vw), 1177 (m), 1153 (vw), 1109 (vs), 1063 (vw), 1040 (m), 1028 (m), 1001 (s), 962 (vw), 939 (m), 908 (m), 885 (s), 841 (m), 804 [m, ν(CC), δ(CH)], 735 [s, δ(C=C)], 721 [s, paraffin], 702 (w), 660 (vw), 642 (m), 623 [w, phenyl], 596 (s), 542 (m), 521 (m), 502 (w), 480 (vw), 463 (m), 440 [m, ν(SiC), ν(AlC), δ(CC)] cm^{-1}. MS (EI, 20 eV, 310 K): *m*/*z* (%) = 640 (100) [M^+ – butene], 498 (60) [M^+ – Al*t*Bu_3]. $C_{46}H_{62}Al_2Si$ (697.1): calcd. C 79.3, H 9.0; found C 78.5, H 9.0.

Synthesis of 6: The dialuminium compound **4** (0.342 g. 0.511 mmol) was dissolved in toluene (25 mL) and added to a suspension of tetra(*n*-butyl)ammonium chloride (0.142 g, 0.512 mmol) in toluene (25 mL). The mixture was stirred at room temperature for 16 h. All volatiles were removed in vacuo. The oily residue was washed with a few millilitres of *n*-hexane to obtain a colourless solid material. It was recrystallized from 1,2-difluorobenzene (20/–15 °C) to yield colourless crystals of **6**. Yield: 0.128 g (26%). M.p. (argon; sealed capillary) 84 °C (dec.). ^1H NMR (400 MHz, [D_8]THF): δ = 0.71 (s, 36 H, CMe_3), 0.98 [t, $^3J_{H-H}$ = 7.3 Hz, 12 H, $N(CH_2CH_2CH_2CH_3)_4$], 1.38 [m, 8 H, $N(CH_2CH_2CH_2CH_3)_4$], 1.64 [m, 8 H, $N(CH_2CH_2CH_2CH_3)_4$], 3.20 [m, 8 H, $N(CH_2CH_2CH_2CH_3)_4$], 7.03 (m, 2 H, *para*-H alkene-Ph), 7.10 (m, 2 H, *para*-H Ph_2Si), 7.13 (m, 4 H, *meta*-H alkene-Ph), 7.13 (m, 4 H, *meta*-H Ph_2Si), 7.26 (m, 4 H, *ortho*-H alkene-Ph), 7.62 (m, 4 H, *ortho*-H Ph_2Si), 7.71 (s, $^3J_{H-Si}$ = 14.2 Hz, 2 H, C*H*Ph) ppm. ^{13}C NMR (100 MHz, [D_8]THF): δ = 14.0 [$N(CH_2CH_2CH_2CH_3)_4$], 17.8 (*C*Me_3), 20.6 [$N(CH_2CH_2CH_2CH_3)_4$], 24.6 [$N(CH_2CH_2CH_2CH_3)_4$], 32.9 (C*Me*$_3$), 59.3 [$N(CH_2CH_2CH_2CH_3)_4$], 126.6 (*para*-C alkene-Ph), 127.1 (*meta*-C Ph_2Si), 127.4 (*para*-C Ph_2Si), 128.4 (*ortho*-C alkene-Ph), 128.5 (*meta*-C alkene-Ph), 138.1 (*ortho*-C Ph_2Si), 144.4 (*ipso*-C Ph_2Si), 148.1 (*ipso*-C alkene-Ph), 159.6 (C=*C*HPh), 160.9 (*C*=CHPh) ppm. ^{29}Si NMR (79.5 MHz, [D_8]THF): δ = –2.0 ppm. IR (KBr, paraffin): $\tilde{\nu}$ = 1701 (vw), 1597 (w), 1580 (m), 1560 [vw, ν(C=C), phenyl], 1463 (vs), 1377 [vs, paraffin], 1304 (w), 1261 (vw), 1213 (vw), 1169 (w), 1153 (w), 1111 (m), 1099 (m), 1076 (w), 1026 (s), 1005 (s), 926 (m), 887 (m), 845 (vw), 812 (vw), 772 [m, ν(CC), δ(CH)], 721 [s, paraffin], 627 [m, phenyl], 592 (vw), 522 (s), 463 [m, ν(AlC), δ(CC)], 422 [m, ν(SiC), ν(AlC), ν(AlCl), δ(CC)] cm^{-1}. $C_{60}H_{94}Al_2ClNSi$ (946.9): calcd. C 76.1, H 10.0, N 1.5; found C 75.4, H 10.0, N 1.5.

Synthesis of 8: The mixed alkenyl–alkynylsilane $(H_5C_6)_2Si(C\equiv C-C_6H_5)[C(AlR_2)=C(H)-C_6H_5]$ (**7**, R = CMe_3[7]) (0.826 g, 1.57 mmol) was dissolved in toluene (25 mL). The solution was heated under reflux for 48 h. All volatiles were removed in vacuo at room temperature. The residue was dissolved in a few millilitres of THF, the solvent was removed in vacuo, and the residue was dissolved in diisopropyl ether. Crystals of compound **8** were obtained upon slow concentration of the solution at room temperature under slightly reduced pressure. Yield: 0.683 g (73 %). M.p. (argon; sealed capillary) 196 °C (dec.). ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 1.08 (s, 18 H, CMe$_3$), 1.77 and 3.61 (each m, 4 H, THF), 6.98 (pseudo-t, 1 H, *para*-H vinylic phenyl), 7.07 (pseudo-t, 2 H, *meta*-H vinylic phenyl), 7.11 (m, 2 H, vinylic H and *para*-H phenyl attached to heterocycle), 7.22 (pseudo-t, 2 H, *meta*-H phenyl attached to heterocycle), 7.28 (m, 2 H, *ortho*-H vinylic phenyl), 7.30 (m, 4 H, *meta*-H Ph$_2$Si), 7.32 (m, 2 H, *para*-H Ph$_2$Si), 7.37 (m, 2 H, *ortho*-H phenyl attached to heterocycle), 7.67 (m, 4 H, *ortho*-H Ph$_2$Si) ppm. ^{13}C NMR (100 MHz, [D$_8$]THF): δ = 16.6 (*C*Me$_3$), 32.2 (C*Me*$_3$), 121.7 (*ortho*-C phenyl attached to heterocycle), 126.9 (*para*-C vinylic phenyl), 127.2 (*para*-C phenyl attached to heterocycle), 127.3 (*ortho*-C vinylic phenyl), 128.9 (*meta*-C vinylic phenyl, *meta*-C phenyl attached to heterocycle and *meta*-C Ph$_2$Si), 130.5 (*para*-C Ph$_2$Si), 130.7 [H–*C*=C(Si)], 136.3 (*ortho*-C Ph$_2$Si), 136.1 (*ipso*-C Ph$_2$Si), 141.0 (*ipso*-C vinylic phenyl), 143.6 (*ipso*-C phenyl attached to heterocycle), 154.5 [H–C=*C*(Si) heterocycle], 174.1 (Al–C=*C*–Si heterocycle), 194.5 (Al–*C*=C–Si heterocycle) ppm. ^{29}Si NMR (79.5 MHz, [D$_8$]THF): δ = –1.4 ppm. IR (CsI, paraffin): $\tilde{\nu}$ = 1593 [m, ν(C=C), phenyl], 1464 (vs), 1375 [vs, paraffin], 1306 (s), 1265 (m), 1250 [w, δ(CH$_3$)], 1184 (vw), 1169 (m), 1157 (m), 1109 (s), 1055 (vw), 1026 (w), 1003 (m), 960 (w), 951 (w), 918 (w), 903 (w), 845 (s), 806 (s), 764 [s, ν(CC), δ(CH)], 741 [s, δ(C=C)], 719 [vs, paraffin], 696 (m), 682 (w), 646 (m), 621 [w, phenyl], 596 (s), 567 (m), 542 (s), 515 (vs), 469 (m), 441 [m, ν(SiC), ν(AlC), δ(CC)] cm^{-1}. MS (EI, 20 eV, 373 K): *m*/*z* (%) = 526 (0.4) [M$^+$ – THF]; 469 (17) [M$^+$ – THF – *t*Bu]; 386 (100) [*cyclo*-Ph$_2$Si–C{=C(H)–C$_6$H$_5$}–CH=C–C$_6$H$_5$]$^+$. C$_{40}$H$_{47}$AlOSi (598.9): calcd. C 80.2, H 7.9; found C 79.3, H 7.8.

Crystal Structure Determinations: Single crystals were obtained directly from the reaction mixtures as described above. The crystallographic data were collected with a Bruker APEX diffractometer with graphite-monochromated Cu-K_α or Mo-K_α radiation. The crystals were coated with perfluoropolyether, picked up with a glass fiber and immediately mounted in the cooled nitrogen stream of the diffractometer. The crystallographic data and details of the final *R* values are provided in Tables 1 and 2.[25] All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were calculated on ideal positions and allowed to ride on the bonded atom with U = 1.2U_{eq}(C). The crystals of compound **1** enclose one molecule of pentafluorobenzene per formula unit. The molecules of **4** and **5** reside on crystallographic twofold rotation axes. One *tert*-butyl group of **4** (C31) showed a disorder, the atoms were refined on split positions (0.66:0.34).

Quantum Chemical Calculations: All computations were performed by using the Gaussian 09 suite of programs.[26] The Becke three-parameter exchange functional and the correlation functional of Lee, Yang, and Parr (B3LYP) with the 6-311G(d,p) basis set were used to compute the geometries and the normal mode vibration frequencies of the starting structure **7**, the corresponding transition structure TS, and the model compound **9**. For single-point energy calculations on DFT-optimized geometries, the SCS-MP2 method was used.[27] The transition structure was localized by the option: opt = qst3, by using approximate geometries of the corresponding starting compound, transition state and product. In order to verify the character of the stationary points, they were subjected to frequency analyses. In the text, total energies (0 K, kcal/mol) are discussed, which contain zero-point corrections. The vibration related to the imaginary frequency corresponds to the nuclear motion along the reaction coordinate under study. An intrinsic reaction coordinate (IRC) calculation was performed in order to unambiguously interconnect the transition structure with the reactant and the product.

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Table 1. Crystal data and structure refinement for compounds **1**–**4**.[a,b]

	1·C$_6$F$_5$H	**2**	**3**	**4**
Empirical formula	C$_{44}$H$_{44}$AlF$_5$Si	C$_{40}$H$_{47}$AlSi	C$_{48}$H$_{66}$Al$_2$Si	C$_{44}$H$_{58}$Al$_2$Si
Temperature [K]	153(2)	153(2)	153(2)	153(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group[23]	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	*Pccn* (no. 56)
a [pm]	1450.97(2)	960.40(6)	1290.95(3)	1290.38(5)
b [pm]	1105.09(2)	1093.04(7)	1877.33(4)	1624.45(6)
c [pm]	2483.31(4)	1874.0(2)	1866.25(4)	1970.80(8)
α [°]	90	96.476(1)	90	90
β [°]	103.352(1)	103.069(1)	97.078(1)	90
γ [°]	90	112.222(1)	90	90
V [nm^3]	3.8742(1)	1.7306(2)	4.4885(2)	4.1311(3)
Z	4	2	4	4
$D_{calcd.}$ [g cm^{-3}]	1.239	1.119	1.073	1.076
μ [mm^{-1}]	1.204 (Cu-K_α)	0.119 (Mo-K_α)	1.049 (Cu-K_α)	1.104 (Cu-K_α)
Crystal size [mm]	0.17 × 0.15 × 0.09	0.21 × 0.16 × 0.04	0.15 × 0.13 × 0.04	0.26 × 0.12 × 0.07
θ range [°]	3.13 ≤ 72.68	1.14 ≤ 28.69	3.35 ≤ 72.33	4.38 ≤ 72.43
Index ranges	$-17 \leq h \leq 17$	$-12 \leq h \leq 12$	$-14 \leq h \leq 15$	$-15 \leq h \leq 15$
	$-13 \leq k \leq 13$	$-14 \leq k \leq 14$	$-21 \leq k \leq 21$	$-20 \leq k \leq 20$
	$-29 \leq l \leq 30$	$-25 \leq l \leq 25$	$-22 \leq l \leq 22$	$-23 \leq l \leq 24$
Independent reflections	7402 (R_{int} = 0.0304)	8885 (R_{int} = 0.0249)	8482 (R_{int} = 0.0409)	4008 (R_{int} = 0.0452)
Parameters	468	387	472	250
$R1$ [$I > 2\sigma(I)$][c]	0.0426 (6481)	0.0425 (7166)	0.0438 (6657)	0.0447 (3333)
$wR2$ (all data)[c]	0.1241	0.1193	0.1210	0.1299
Max./min. residual electron density [10^{30} e m^{-3}]	+0.457/–0.354	+0.388/–0.307	+0.402/–0.202	+0.372/–0.190

[a] Programme SHELXL-97;[24] solutions by direct methods, full-matrix refinement with all independent structure factors. [b] See ref.[25] for CCDC reference numbers. [c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. Crystal data and structure refinement for compounds **5** to **6** and **8**.[a,b]

	5	**6**	**8**
Empirical formula	$C_{46}H_{62}Al_2Si$	$C_{60}H_{94}Al_2ClNSi$	$C_{40}H_{47}AlOSi$
Temperature [K]	153(2)	153(2)	153(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group[23]	*Pccn* (no. 56)	$P2_1$ (no. 4)[c]	$P2_1/c$ (no. 14)
a [pm]	1263.69(2)	1202.42(6)	2043.49(3)
b [pm]	1716.16(3)	1984.98(7)	1029.78(2)
c [pm]	1996.22(3)	1239.51(5)	1763.94(3)
α [°]	90	90	90
β [°]	90	99.084(3)	106.631(1)
γ [°]	90	90	90
V [nm^3]	4.3292(1)	2.9213(2)	3.5567(1)
Z	4	2	4
$D_{calcd.}$ [g cm^{-3}]	1.069	1.076	1.118
μ [mm^{-1}]	1.071 (Cu-K_α)	1.320 (Cu-K_α)	1.026 (Cu-K_α)
Crystal size [mm]	0.16 × 0.04 × 0.04	0.14 × 0.12 × 0.11	0.49 × 0.48 × 0.09
θ range [°]	$4.34 \leq 72.81$	$3.61 \leq 72.26$	$2.26 \leq 72.52$
Index ranges	$-14 \leq h \leq 15$	$-12 \leq h \leq 14$	$-23 \leq h \leq 24$
	$-21 \leq k \leq 19$	$-24 \leq k \leq 20$	$-12 \leq k \leq 10$
	$-22 \leq l \leq 19$	$-15 \leq l \leq 15$	$-18 \leq l \leq 21$
Independent reflections	4188 (R_{int} = 0.0591)	8600 (R_{int} = 0.0502)	6248(R_{int} = 0.0392)
Parameters	229	602	394
$R1$ [$I > 2\sigma(I)$][d]	0.0656 (3174)	0.0519 (7766)	0.0495 (5353)
$wR2$ (all data)[d]	0.1950	0.1358	0.1457
Max./min. residual electron density [10^{30} e m^{-3}]	+0.753/–0.539	+0.658/–0.261	+0.452/–0.247

[a] Programme SHELXL-97;[24] solutions by direct methods, full-matrix refinement with all independent structure factors. [b] See ref.[25] for CCDC reference numbers. [c] Flack parameter: 0.003(17). [d] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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