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Hydroalumination and Hydrogallation Reactions with Tri(ethynyl)silanes – Generation of Compounds with up to Three Coordinatively Unsaturated Aluminium Atoms

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Abstract. Hydroalumination or hydrogallation of tri(ethynyl)silanes, $R\mathrm{Si(C{\equiv}C\text{-}Ar)_3}$ (**1a**, R = Ph, Ar = Ph; **1b**, R = Me, Ar = Ph; **1c**, R = Me, Ar = $\mathrm{C_6H_4Me}$), with the element hydrides H-EtBu$_2$ (E = Al, Ga) in stoichiometric ratios of 1:1 to 1:3 at ambient temperature yielded the addition products $\mathrm{(PhC{\equiv}C)_2}(R)\mathrm{Si}[(t\mathrm{Bu}_2E)\mathrm{C{=}C(H)Ph}]$ (**2**, R = Ph, E = Ga; **3a**, R = Me, E = Al; **3b**, R = Me, E = Ga), $\mathrm{(PhC{\equiv}C)(Me)Si}[(t\mathrm{Bu}_2E)\mathrm{C{=}C(H)Ph}]_2$ (**4a**, E = Al, **4b**, E = Ga) and $\mathrm{(Me)Si}[(t\mathrm{Bu_2Al})\mathrm{C{=}C(H)Ar}]_3$ (**5**, Ar = Ph; **6**, Ar = $\mathrm{C_6H_4Me}$). Compounds **2**–**4** show a relatively close interaction between the coordinatively unsaturated aluminium or gallium atoms and one of the $\mathrm{C}_\alpha(\equiv\mathrm{C})$ atoms of unreacted alkyne substituents [245 (E = Al) and 266 pm (E = Ga)] that stabilises the kinetically favoured *cis* addition products with E and hydrogen on the same side of the resulting C=C double bonds. In the absence of these stabilising effects the compounds were found to isomerise to the thermodynamically favoured *trans* isomers.

Introduction

The addition of dialkylaluminium hydrides to the C≡C triple bonds of alkynes (hydroalumination) is a well established method for the synthesis of a wide range of organometallic compounds.[1,2] In contrast, systematic investigations into strongly related hydrogallation reactions[2,3] started only recently with the elaboration of facile methods for the synthesis of the corresponding dialkylgallium hydrides by our group.[4,5] In many cases the simple addition reactions are followed by secondary processes which yield unique compounds with unprecedented molecular structures. The hydroalumination of aluminium alkynides, $R_2\mathrm{Al\text{-}C{\equiv}C}R'$, for instance, was found to result in the elimination of trialkylaluminium species and the formation of stable carbaalanes with clusters of aluminium and carbon atoms[6] that are structurally and electronically related to the well described carbaborane cluster compounds. Heteroadamantane cages with localised Ga–C bonds were isolated instead from the analogous reactions of gallium alkynides with dialkylgallium hydrides.[7] Similar condensation reactions have been observed with oligoalkynes $(t\mathrm{BuC{\equiv}C})_x\mathrm{C_6H}_{6-x}$ (x = 2, 3) which gave compounds with a cyclophane-type molecular structure.[8,9] Steric shielding in the case of the bulky $\mathrm{CH(SiMe_3)_2}$ substituent[10] or coordinative saturation via bridging vinyl groups in the case of small substituents[9] seem to prevent these reactions by stabilisation of the primary addition products. Another important aspect of these hydride addition reactions is *cis*/*trans* isomerisation of the resulting alkenes which has been found in particular with trimethysilyl-substituted alkynes. The *trans* isomer (Al or Ga *trans* to H) was calculated to be thermodynamically favoured. Rearrangement of the primarily formed and kinetically favoured *cis* isomer seems to require intermolecular activation.[11,12] *cis*/*trans* Isomerisation is in most cases fast but may be precluded for steric reasons or as a result of inter- or intramolecular coordination of the three-coordinate metal atom (for examples see below).

The hydride addition products of oligofunctional alkynes are of potential interest as effective chelating Lewis acids.[13] Particularly impressive was the recent synthesis of unusual zwitterionic carbocations,[14] that were stabilised by the chelating coordination of the hydride ion and the formation of Al–H–Al bridges. These reactions show proof of concept for the potential of these compounds for the mobilisation of anions in organic solvents and as phase-transfer catalysts. Only recently we started with investigations into the hydroalumination of bis(alkynyl)silanes or -germanes.[15–17] Novel functional compounds were isolated which beyond their propensity to act as oligoacceptors showed interesting reactions such as dismutation[16] or thermal rearrangement to yield silacyclobutene and spirogermanium derivatives by 1,1-carbalumination.[17] Following these investigations we now present reactions of tri(ethynyl)silanes with $t\mathrm{Bu_2AlH}$ and $t\mathrm{Bu_2GaH}$ that give access to the respective addition products with one, two or three coordinatively unsaturated aluminium or gallium atoms in single molecules.

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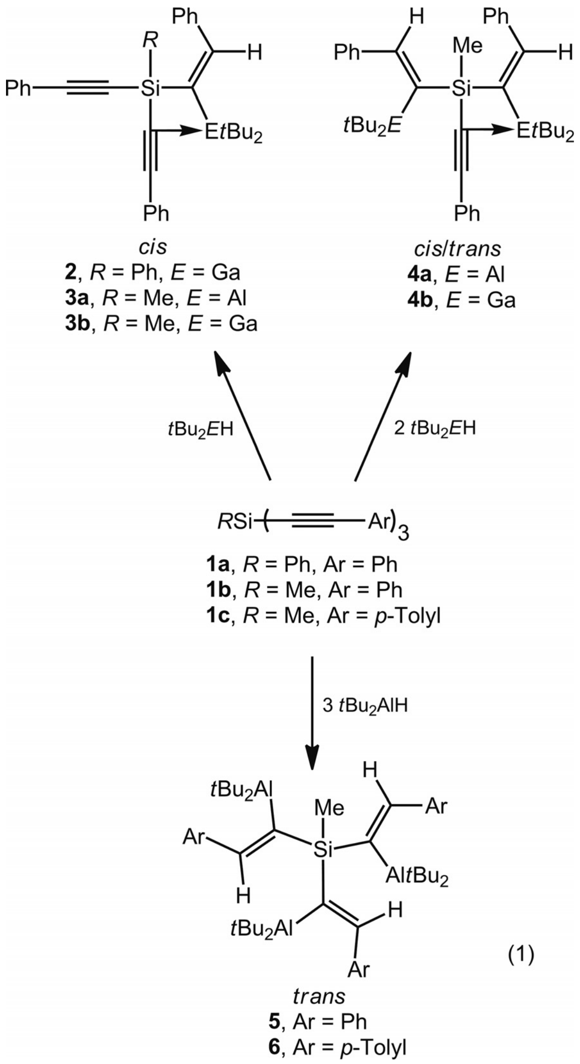
Results and Discussion

Reactions of Tri(ethynyl)silanes with Dialkylaluminium or -gallium Hydrides

The reactions of the triethynyl compounds **1a**–**1c** with $t\mathrm{Bu_2AlH}$ or $t\mathrm{Bu_2GaH}$ in different stoichiometric ratios are summarised in Equation (1). Treatment of **1a** and **1b** with equimolar quantities of $t\mathrm{Bu_2GaH}$ at room temperature yielded the mono-addition products **2** and **3b** as a colourless solid or a yellowish, highly viscous liquid in good yields of 69 and 82 %. Surprisingly, the pure mono-hydroalumination product **3a** was only accessible by using a large excess (two equivalents) of the alkyne **1b**, which then had to be separated by fractional crystallisation, whereas a stoichiometric 1:1 ratio of the starting materials yielded the product of dual hydroalumination (**4a**) in close to quantitative yield together with surplus alkyne. These reactions were complete after relatively short times of less than 4 h. In contrast, the hydroalumination of **1b** or **1c** with two or three equivalents of $t\mathrm{Bu_2}E\mathrm{H}$ gave the corresponding products **4**, **5**, and **6** only in moderate to poor yields and required long reaction times of up to 9 d. The synthesis of compound **6** under optimised reaction conditions was finally carried out by heating a solution in toluene to 75 °C for 4 h. The comparatively poor yields of the latter compounds do not reflect an incomplete or non-uniform reaction but are instead the result of their high solubility in non-polar solvents and the resulting difficulties in purifying the products by crystallisation. Reactions of **1a** with two or three equivalents of $t\mathrm{Bu_2}E\mathrm{H}$ or treatment of the tri(ethynyl)silanes with sterically less shielded element hydrides such as $\mathrm{Me_2AlH}$ gave inseparable mixtures of unknown components.



(1)

The NMR spectra of the products are characterised by a low field signal for the vinylic hydrogen atom (about 8 ppm) in the ^{1}H NMR spectra and a significant low field shift of the ^{29}Si NMR signals in comparison to the free tri(alkynyl)silane. This shift correlates to the increasing number of vinyl groups bonded to the silicon atom and the associated deshielding effect on atoms in the plane of the olefin and ranges from below $\delta = -60$ (**1a**, $\delta = -68.8$; **1b**, $\delta = -63.9$; **1c**, $\delta = -64.2$) in the free alkynylsilanes over about $\delta = -54$ (**2**, **3a**, **3b**), -32 (**4a**, **4b**) to -18 (**5**, **6**). The configuration of the olefinic substituents (hydrogen *cis* or *trans* relative to the silicon atom) was easily determined from the $^3J_{\mathrm{Si-H}}$ coupling constants, that are <15 Hz with hydrogen and silicon atoms on the same side and >20 Hz with hydrogen and silicon atoms on different sides of the C=C double bonds.[10,11] The latter case reflects the kinetically favoured but thermodynamically disfavoured product of *cis* addition of the element hydrides to the alkynes with aluminium and hydrogen on the same side.[11] The coupling constants in compounds **2**–**6** [25.8 Hz (**2**); 27.2 Hz (**3a**); 25.0 Hz (**3b**); 25.2 and 14.4 Hz (**4a**); 24.0 and 13.0 Hz (**4b**); 11.0 Hz (**5**); 10.5 Hz (**6**)] are indicative of the *cis* arrangement of *E* and hydrogen in **2** and **3a/b**. In the case of the doubly reduced compounds **4a** and **4b** only one alkenyl group has the *cis* configuration, whereas the other one is rearranged with aluminium or gallium and hydrogen in *trans* positions. In compounds **5** and **6** all three vinylic substituents adopt a *trans* arrangement of aluminium and hydrogen. The surprising stability of the *cis* configuration in **2**–**4** may be rationalised by an interaction between the coordinatively unsaturated aluminium or gallium atoms with an α-carbon atom of an ethynyl substituent which is schematically shown in Equation (1) and is discussed in detail below. Interestingly, compounds **4a** and **4b** showed three different resonances of *tert*-butyl groups in the ^{1}H and ^{13}C NMR spectra in an intensity ratio of 2:1:1. Temperature dependent ^{1}H NMR experiments with solutions of **4b** (E = Ga) in toluene did not result in a significant change at elevated temperatures, apart from some more or less pronounced changes of the chemical shifts of these three resonances (300 K: $\delta = 1.39$, 1.27 and 1.04; 360 K: $\delta = 1.34$, 1.21 and 1.03). At lower temperatures the resonance at a low field became broad and finally split into two narrow singlet signals (220 K: $\delta = 1.51$ and 1.47; $\delta = 1.31$ and 1.05 for the remaining two resonances). The coalescence temperature was at about 260 K, and the rotational barrier was estimated to be only 13 kcal·mol^{-1}.[18] Interestingly, careful analysis of the spectra gave clear evidence that the alkenyl group with a *trans*-arrangement of gallium and hydrogen showed two signals for the *tert*-butyl resonances over the complete range of temperatures which indicates a relatively high rotational barrier about the Ga–C(vinyl) bond in this case. In this part of the molecule the phenyl and Ga*t*Bu$_2$ substituents are on the same side of the C=C double bond and the resulting close contact between both groups clearly prevents the equilibration of the *tert*-butyl groups. In contrast the almost free rotation of the dialkylgallium moiety in the second alkenyl group (*cis*-arrangement of gallium and hydrogen), which is hindered only at low temperature is in accordance with a relatively weak interaction between the coordinatively unsaturated gallium atom and the α-carbon atom of the remaining C≡C triple bond. However, in spite of its obvious weakness this interaction seems to be strong enough to influence the molecular configuration.

Crystal Structure Determinations

The molecular structures of compounds **2** and **4**–**6** are shown in Figure 1, Figure 2, Figure 3, and Figure 4 (the structure of **4b** is very similar to that of **4a** and is not shown separately) with selected structural parameters being summarised in Table 1. The molecular structures clearly confirm the respective *cis* or *trans* configuration of the vinyl groups as predicted by NMR spectroscopy. Crystal data gives clear evidence that intramolecular interactions influence *cis*/*trans* rearrangement. The partially reduced species with intact C≡C triple bonds (**2** and **4a**/**b**) show a close contact between the coordinatively unsaturated aluminium or gallium atoms and an α-carbon atom of the remaining alkynyl moieties which bear a relatively high negative charge. Relatively short intramolecular *E*···C distances result [267.4 pm (**2**, *E* = Ga); 244.4 and 244.6 pm (**4a**, *E* = Al); 264.2 and 265.0 pm (**4b**, *E* = Ga); compared to about 200 pm for covalent *E*–C bonds], which lead to the formation of almost ideally planar four-membered *E*CSiC heterocycles with torsion angles close to 0°. The significantly shorter contacts in the case of aluminium reflect the higher Lewis acidity of aluminium in comparison to gallium atoms. The E–C$_\alpha$(≡C) interaction causes relatively acute endocyclic C–Si–C angles between the vinylic and alkynyl carbon atoms (97 to 101°). Further, the nominally three-coordinate Group 13 elements deviate from a planar coordination sphere as evident from the distances between the metal atoms and the plane of the three directly bound carbon atoms that range from 32 pm in the aluminium compound **4a** to about 22 pm in the vinylgallium derivatives **2** and **4b**. Similar structures have been observed for the hydroalumination products of silicon or germanium centered dialkynes.[15–17] *cis*/*trans* Rearrangement following the primary *cis* addition of the *E*–H bonds to alkynes requires intermolecular activation by an increased coordination number of the α-carbon atoms in order to reduce the rotational barrier about the C=C double bonds of the alkenyl groups.[11] The interaction between the metal atoms and the alkynyl groups in **2**, **3**, and **4** stabilises the kinetically favoured *cis* addition products (*E* to H) and prevents the generally rapid isomerisation. Interestingly, the remaining vinyl groups in compounds **4a** and **4b** as well as those in **5** and **6** lack the described stabilisation by *E*–C interactions and adopt the thermodynamically more stable *trans* configuration which is stabilised by an approach of the bond angles to ideal values and a weak interaction between the Group 13 element and one of the *ortho*-carbon atoms of the adjacent phenyl rings [approximately 269 pm (Al) and 287 pm (Ga)].[11] The latter causes a relatively small deviation from planarity of the metal coordination sphere in the range of 13 to 18 pm (Al) or 9 pm (Ga) (cf. Table 1). Compounds **4a** and **4b** have both isomeric forms of the alkenyl groups realised in a single molecule. The observed *E*–C, C=C and C≡C bonds are unexceptional. The molecules of compounds **4a** and **4b** are chiral as a consequence of four different substituents attached to the silicon atom, the vinyl substituents become non-equivalent as a result of their different configuration. The presence of racemic mixtures is evident from space group symmetry. Compounds **5** and **6** have three alkenyl groups and three coordinatively unsaturated aluminium atoms. They show approximate *C*3 symmetry along the Me–Si axis that corresponds with the observed chemical equivalence of the three alkenyl fragments in the solution NMR spectra. Compound **6** crystallises as a loosely bonded dimer that is held together in the solid state by van der Waals interactions and four C–H···π contacts between *ortho*-hydrogen and *ortho*-carbon atoms of phenyl groups of the monomeric fragments (C···H 282 pm, Figure 5). The formation of similar weak dimers was observed in the structure of the phenyl derivative **5** (C···H 289 pm). **4a** and **4b** do not show comparably short intermolecular interactions, whereas the alkenyl phenyl group of **2** has short contacts between its *ortho*-carbon atom C18 and two hydrogen atoms of different molecules to give a pseudo-polymer (C···H 290 pm). The CH/π hydrogen bond as a cooperative force and its significance for the structures of organic molecules have been reviewed recently.[19]

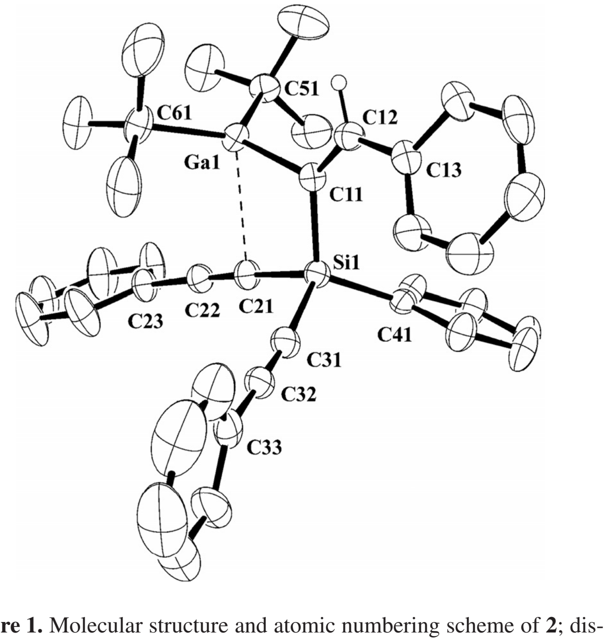


Figure 1. Molecular structure and atomic numbering scheme of **2**; displacement ellipsoids are drawn at the 40 % level. Hydrogen atoms (H12 only) have been drawn with arbitrary radius.

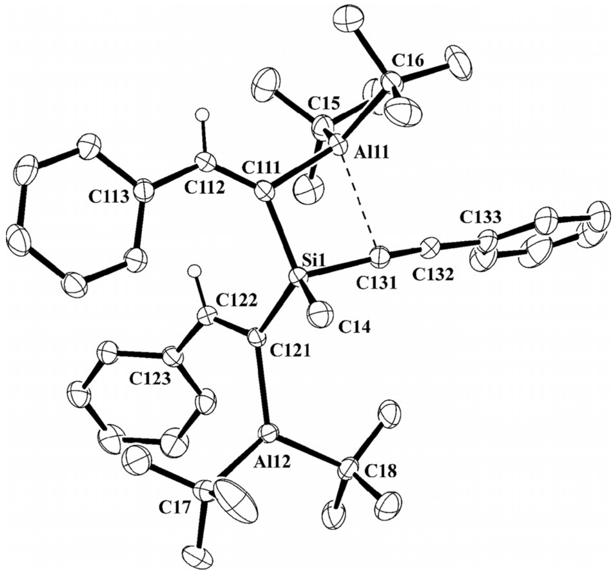


Figure 2. Molecular structure and atomic numbering scheme of **4a** (there are two independent molecules in the unit cell, only the S-enantiomer is shown); displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (H112, H122 only) have been drawn with arbitrary radius. An analogous structure was observed for compound **4b** (E = Ga).

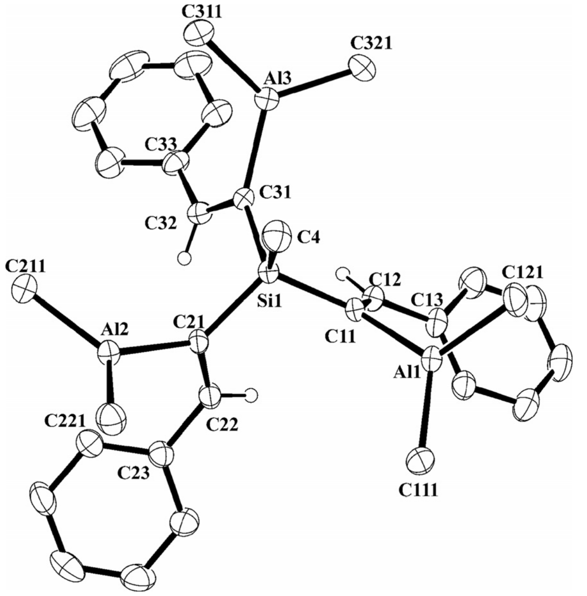


Figure 3. Molecular structure and atomic numbering scheme of **5**; displacement ellipsoids are drawn at the 40% level. Methyl groups (CMe_3) have been omitted for clarity. Hydrogen atoms (H12, H22, H32 only) have been drawn with arbitrary radius.

Experimental Section

General: All procedures were carried out under an atmosphere of purified argon in dried solvents (toluene over Na/benzophenone, *n*-pentane and cyclopentane over $LiAlH_4$, pentafluorobenzene over molecular sieves). NMR spectra were recorded in [D$_6$]benzene at ambient probe temperature using the following Bruker instruments: Avance I (^{1}H, 400.13; ^{13}C, 100.6; ^{29}Si, 79.49 MHz) or Avance III (^{1}H, 400.03; ^{13}C, 100.59; ^{29}Si 79.47 MHz) and referenced internally to residual solvent

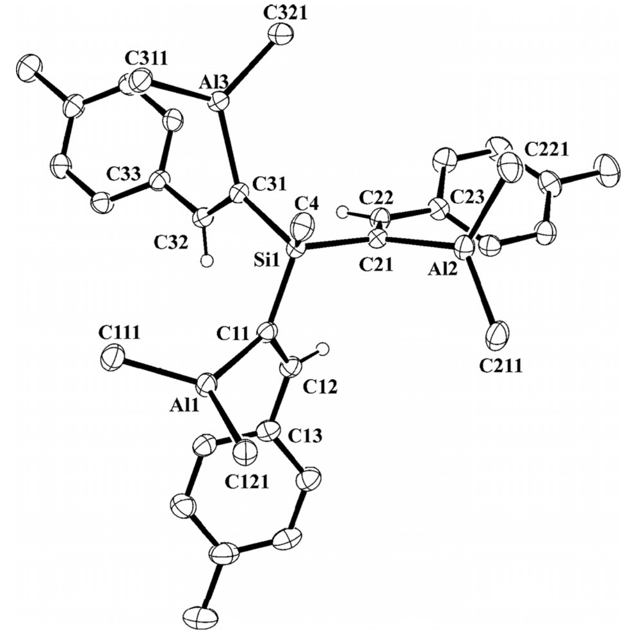


Figure 4. Molecular structure and atomic numbering scheme of **6**; displacement ellipsoids are drawn at the 40% level. Methyl groups (CMe_3) have been omitted for clarity. Hydrogen atoms (H12, H22, H32 only) have been drawn with arbitrary radius.

resonances (chemical shift data in δ). ^{13}C NMR spectra were all proton-decoupled. The assignment of the NMR spectra is based on HSQC, HMBC, H/Si-HMBC, ROESY and DEPT135 data. Elemental analyses were determined by the microanalytic laboratory of the Westfälische Wilhelms Universität Münster. IR spectra were recorded as Nujol mull between KBr or CsI plates with a Shimadzu Prestige 21 spectrometer, electron impact mass spectra with a Varian mass spectrometer. Only the most intensive masses of a particular molecular fragment are given in the description of the mass spectra; the isotopic patterns were in agreement with the calculated ones. $t\mathrm{Bu}_2\mathrm{AlH}$,[4,20] $t\mathrm{Bu}_2\mathrm{GaH}$[3] and the trialkynes **1a** and **1b**[21] were synthesised according to literature procedures. **1c** was synthesised in analogy to **1a** and **1b**.

Synthesis

$\mathbf{MeSi(C{\equiv}CC_6H_4Me)_3}$ (1c): *n*BuLi (12.7 mmol, 7.9 mL, 1.6 M in hexane) was added dropwise to a solution of *p*-tolylethyne (1.47 g, 12.7 mmol) in diethyl ether (50 mL) at –78 °C. The reaction mixture was stirred for 2 h at this temperature and afterwards treated with methyltrichlorosilane (0.63 g, 4.22 mmol). After stirring for 2 h at –78 °C the mixture was allowed to warm to room temperature and stirred for another 16 h. The suspension was treated with HCl (10%) and twice extracted with toluene (20 mL). The organic phase was dried with $MgSO_4$ and filtered. The solvent was removed in vacuo and the residue was dissolved in a small quantity of toluene. The product crystallised when pentane was slowly added to the cooled solution (–30 °C) and was isolated by removal of the solvent and drying in vacuo. Yield: 1.44 g (88%). M.p. (argon, sealed capillary): 148 °C. **^{1}H NMR** (400 MHz, C_6D_6, 300 K): δ = 7.36 (d, $^3J_{\mathrm{H,H}}$ = 8.0 Hz, 6 H, *ortho*-H), 6.69 (d, $^3J_{\mathrm{H,H}}$ = 8.0 Hz, 6 H, *meta*-H), 1.90 (s, 9 H, CH_3 *p*-Tol), 0.86 (s, 3 H, SiCH_3). **^{13}C NMR** (100 MHz, C_6D_6, 300 K): δ = 139.4 (*para*-C), 132.6 (*ortho*-C), 129.3 (*meta*-C), 120.0 (*ipso*-C), 107.5 (Si-C≡*C*), 88.4 (Si-*C*≡C), 21.3 (Me *p*-Tol), 2.1 (SiMe). **^{29}Si NMR** (79.5 MHz, C_6D_6, 300 K): δ = 64.2. **IR** (KBr, paraffin): $\tilde{\nu}$ = 2214

Table 1. Selected bond lengths (pm) and angles (°) of compounds **2** and **4–6**.

Structural parameters	**2** (Ga)	**4a** (Al)	**4b** (Ga)	**5** (Al)	**6** (Al)
C=C /pm	134.5(3)	134.9(3) [134.8(3)]$^{a)}$ (*cis*) 133.9(3) [134.0(3)] (*trans*)	134.5(4) [134.7(4)]$^{a)}$ (*cis*) 134.1(4) [134.3(4)] (*trans*)	135.2(4) 134.5(4) 134.5(4)	135.3(2) 134.4(2) 135.2(2)
C≡C /pm	120.6(3)	–	–	–	–
C≡C(···*E*) /pm	119.7(3)	120.9(3) [120.6(3)]	120.9(4) [120.5(4)]	–	–
E–C(av.) /pm	200.1	198.6 [198.7]	200.1 [200.3]	199.2	199.5
E···α-C≡C /pm	267.4(3)	244.4(2) [244.6(2)]	264.1(3) [264.9(3)]	–	–
distance ($E^{b)}$···C_3 plane) /pm	21.1	32.1 [32.1]	23.3 [22.9]	–	–
E···*o*-C(Ph) /pm	–	268.2 [285.0]	286.8 [300.7]	268.3 268.8 268.9	266.8 263.7 262.2
distance ($E^{c)}$···C_3 plane) /pm	–	16.8 [13.2]	10.3 [7.9]	13.8 13.6 16.3	18.0 14.7 14.5
∠ (alkenyl)C–Si–C(alkynyl) /°	100.5(1)	96.6(1) [96.6(1)]	99.0(1) [99.2(1)]	107.7(1)$^{d)}$	107.52(8)$^{d)}$
torsion angle C–Si–C(alkenyl)–*E* /°	–0.4(1)	0.7(1) [–80.4(2)]	–0.9(2) [1.4(2)]	–	–

a) Values for the second molecule are given in parenthesis; b) *E* coordinated to C≡C; c) *E* with weak interaction to *o*-C of phenyl; d) smallest C–Si–C angle.

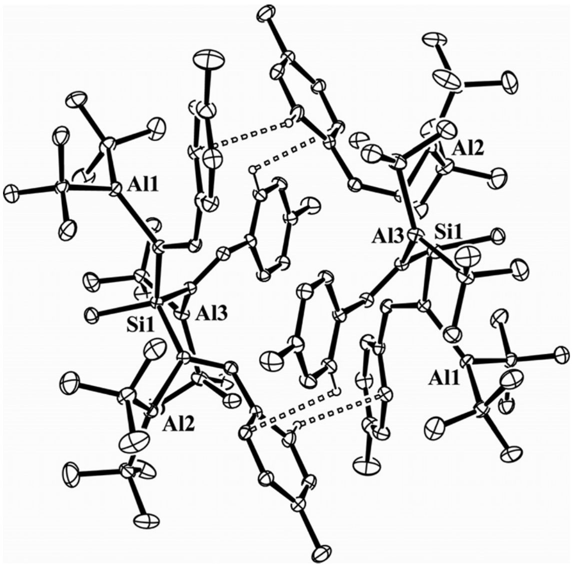


Figure 5. Dimeric formula unit of compound **6** with CH/π hydrogen bonds.

vw, 2160 vs, 2126 sh, 2077 w *ν*C≡C; 1913 w, 1803 vw, 1655 w, 1605 m, 1562 vw, 1506 vs. (phenyl); 1458 vs, 1408 vw, 1377 vs. (paraffin); 1306 vw, 1250 m δCH_3; 1225 s, 1209 w, 1179 w, 1153 vw, 1117 w, 1107 m, 1036 m, 1020 m, 966 vw, 951 w, 918 vw *ν*CC, *δ*CH; 856 vs, 818 vs, 799 vs, 768 vs. $\rho CH_3(Si)$, (phenyl); 719 vs. (paraffin); 694 vw, 627 vw, 579 vs, 538 vs, 465 vw, 440 vw *ν*AlC, *ν*SiC, *δ*CC cm^{-1}. **MS** (EI, 20 eV; 393 K): *m*/*z* (%) = 388 (69) (M^+), 373 (100) ($M^+ - CH_3$). **CHN** ($C_{28}H_{24}Si$) (388.6): calcd. C 86.5, H 6.2; found C 86.2, H 6.2 %.

(PhC≡C)$_2$(Ph)Si[(*t*Bu$_2$Ga)C=C(H)Ph] (2): A solution of (PhC≡C)$_3$-SiPh (0.276 g, 0.68 mmol) in toluene (10 mL) was added at room temperature to a solution of *t*Bu$_2$GaH (0.125 g, 0.68 mmol) in toluene (10 mL). The reaction mixture was stirred for 4 h at room temperature. The solvent was removed in vacuo, the colourless residue was washed with a small amount of *n*-pentane and then dissolved in cyclopentane. Cooling to –15 °C yielded colourless crystals of **2**. Yield: 0.278 g (69 %). M.p. (argon, sealed capillary): 106 °C (dec). **^{1}H NMR** (400 MHz, C_6D_6, 300 K): δ = 8.07 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.5 Hz, 2 H, *ortho*-H PhSi), 7.93 (s, $^3J_{H-Si}$ = 25.8 Hz, 1 H, C=C*H*Ph), 7.70 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, *ortho*-H C=CPh), 7.40 (dd, $^3J_{HH}$ = 8.4, $^4J_{H,H}$ = 1.5 Hz, 4 H, *ortho*-H C≡CPh), 7.13 (m, 2 H, *meta*-H PhSi), 7.08 (m, 1 H, *para*-H PhSi), 7.06 (m, 2 H, *meta*-H C=CPh), 6.93 (tt, $^3J_{H,H}$ = 7.4, $^4J_{H,H}$ = 1.2 Hz, 1 H, *para*-H C=CPh), 6.88 (m, 2 H, *para*-H C≡CPh), 6.86 (m, 4 H, *meta*-H C≡CPh), 1.46 (s, 18 H, *t*Bu). **^{13}C NMR** (100 MHz, C_6D_6, 300 K): δ = 154.8 (C=*C*HPh), 150.8 (*C*=CHPh), 140.9 (*ipso*-C C=CPh), 135.2 (*ortho*-C PhSi), 133.2 (*ipso*-C PhSi), 132.8 (*ortho*-C C≡CPh), 130.5 (*para*-C PhSi), 129.6 (*para*-C C≡CPh), 128.9 (*ortho*-C C=CPh), 128.5 (*meta*-C C≡CPh and PhSi), 128.4 (*meta*-C C=CPh), 128.2 (*para*-C C=CPh), 122.3 (*ipso*-C C≡CPh), 109.9 (Ph*C*≡CSi), 90.3 (PhC≡*C*Si), 30.8 (C*Me*$_3$), 29.6 (*C*Me$_3$). **^{29}Si NMR** (79.5 MHz, C_6D_6, 300 K): δ = –58.5. **IR** (KBr, paraffin): *ν*(bar) = 2160 m, 2141 m *ν*C≡C; 2037 vw, 1973 vw, 1953 vw, 1908 vw, 1888 vw, 1807 vw, 1767 vw, 1682 w, 1595 w, 1555 w *ν*C=C, (phenyl); 1454 vs, 1377 vs. (paraffin); 1305 m, 1269 w δCH_3; 1219 w, 1169 w, 1157 w, 1111 vw, 1070 vw, 1024 w, 968 w, 918 m, 883 m, 843 m, 810 w, 754 s *δ*CH, *ν*CC; 723 vs. (paraffin); 691 m, 654 w, 640 w, 615 vw, 598 w, 538 w, 513 w, 480 vw, 465 vw, 432 vw *ν*GaC, *ν*SiC, *δ*CC, *δ*(phenyl) cm^{-1}. **MS** (EI, 20 eV, 353 K): *m*/*z* (%) = 535 (100), 537 (80) (M^+ *t*Bu); 479 (12), 481 (8) (M^+ *t*Bu – butene). **CHN** ($C_{38}H_{39}GaSi$) (593.5): calcd. C 76.9, H 6.6; found C 75.9, H 6.6 %.

(PhC≡C)$_2$(Me)Si[(*t*Bu$_2$Al)C=C(H)Ph] (3a): A solution of an excess of (PhC≡C)$_3$SiMe (0.882 g, 2.55 mmol, 2 equivalents) in toluene (10 mL) was added to a solution of *t*Bu$_2$AlH (0.181 g, 1.27 mmol) in toluene (10 mL) at 50 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was removed in vacuo, and the resulting pale yellow oil was dissolved in a small quantity of cyclopentane. The excess alkyne crystallised upon cooling the mixture to –40 °C and was separated. Removal of the solvent in vacuo yielded compound **3a** as a pale yellow oil. Yield: 0.457 g (74 %). **^{1}H NMR** (400 MHz, C_6D_6, 300 K): δ = 8.10 (s, $^{3}J_{\mathrm{H-Si}}$ = 27.2 Hz, 1 H, C=C*H*Ph), 7.72 (d, $^{3}J_{\mathrm{H,H}}$ = 7.7 Hz, 2 H, *ortho*-H C=CPh), 7.45 (m, 4 H, *ortho*-H, C≡CPh), 7.21 (*pseudo*-t, $^{3}J_{\mathrm{H,H}}$ = 7.7 Hz, 2 H, *meta*-H C=CPh), 7.08 (t, $^{3}J_{\mathrm{H,H}}$ = 7.3 Hz, 1 H, *para-H* C=CPh), 6.91 (m, 2 H, *para*-H, C≡CPh), 6.86 (m, 4 H, *meta*-H C≡CPh), 1.37 (s, 18 H, *t*Bu), 0.68 (s, 3 H, Si*Me*). **^{13}C NMR** (100 MHz, C_6D_6, 300 K): δ = 156.8 (C=*C*HPh), 148.5 (*C*=CHPh), 142.1 (*ipso*-C C=CPh), 133.1 (*ortho*-C C≡CPh), 130.2 (*para*-C C≡CPh), 128.7 (*meta*-C C=CHPh), 128.6 (*meta*-C C≡CPh), 128.5 (*para*-C C=CPh), 128.4 (*ortho*-C C=CPh), 121.5 (*ipso*-C C≡CPh), 111.7 (Ph*C*≡CSi), 90.7 (PhC≡*C*Si), 30.6 ($\mathrm{C}Me_3$), 19.2 ($C\mathrm{Me_3}$), 0.4 ($\mathrm{Si}CH_3$). **^{29}Si NMR** (79.5 MHz, C_6D_6, 300 K): δ = –50.6. **IR** (CsI, paraffin): ν(bar) = 2160 vs, 2129 vs. νC≡C; 2054 vw, 1948 w, 1883 w, 1830 vw, 1803 w, 1755 vw, 1672 vw, 1651 vw, 1585 vs, 1548 vs, 1528 vw, 1487 vs. νC=C, (phenyl); 1462 vs. (paraffin); 1443 vs. $\delta\mathrm{CH_3}$; 1381 m (paraffin); 1358 m, 1329 vw, 1294 vw, 1279 w, 1248 s $\delta\mathrm{CH_3}$; 1219 s; 1177 m, 1157 w, 1098 vw, 1070 m, 1047 vw, 1026 s, 999 m, 966 vw, 926 s, 885 m δCH, νCC; 847 s, 818 w, 787 m, 754 s $\rho\mathrm{CH_3(Si)}$; 721 m (paraffin); 689 vs, 654 m, 625 w, 611 m, 596 m, 569 m, 538 vs, 509 vs, 455 vs, 435 w νAlC, νSiC, δCC $\mathrm{cm^{-1}}$. **MS** (EI, 20 eV, 298 K): m/z (%) = 431 (100) ($\mathrm{M^+}$ – *t*Bu).

$(PhC{\equiv}C)_2(Me)Si[(tBu_2Ga)C{=}C(H)Ph]$ (3b): A solution of $t\mathrm{Bu_2GaH}$ (0.151 g, 0.82 mmol) in toluene (25 mL) was treated at –40 °C with $\mathrm{(PhC{\equiv}C)_3SiMe}$ (0.283 g, 0.82 mmol). The colourless reaction mixture was allowed to warm to room temperature and stirred for another 90 min, which resulted in a gradual colour change to yellow. The solvent was removed in vacuo to yield compound **3b** as an NMR spectroscopically pure yellow oil (0.358 g, 82 %). **^{1}H NMR** (400 MHz, C_6D_6, 300 K): δ = 7.78 (s, $^{3}J_{\mathrm{H-Si}}$ = 25.0 Hz, 1 H, C=C*H*Ph), 7.75 (d, $^{3}J_{\mathrm{H,H}}$ = 7.2 Hz, 2 H, *ortho-H* CH=CPh), 7.45 (m, 4 H, *ortho-H* C≡CPh), 7.22 (*pseudo*-t, $^{3}J_{\mathrm{H,H}}$ = 7.7 Hz, 2 H, *meta*-H CH=CPh), 7.07 (br. s, 1 H, *para*-H CH=CPh), 6.90 (m, 2 H, *para*-H C≡CPh), 6.87 (m, 4 H, *meta*-H C≡CPh), 1.43 (s, 18 H, *t*Bu), 0.65 (s, $^{2}J_{\mathrm{H-Si}}$ = 7.5 Hz, 3 H, Si*Me*). **^{13}C NMR** (100 MHz, C_6D_6, 300 K): δ = 153.5 (*C*=CHPh), 153.4 (C=*C*HPh), 141.6 (*ipso*-C CH=CPh), 132.7 (*ortho*-C C≡CPh), 129.5 (*para*-C C≡CPh), 128.6 (*meta*-C CH=CPh and *meta*-C C≡CPh), 128.5 (*ortho*-C CH=CPh), 128.1 (*para*-C CH=CPh), 122.4 (*ipso*-C C≡CPh), 108.9 (Ph*C*≡CSi), 91.3 (PhC≡*C*Si), 30.7 ($\mathrm{C}Me_3$), 29.2 ($C\mathrm{Me_3}$), 0.4 ($\mathrm{Si}CH_3$). **^{29}Si NMR** (79.5 MHz, C_6D_6, 300 K): δ = 53.2. **IR** (CsI, paraffin): ν(bar) = 2158 vs, 2143 vs. νC≡C; 2054 vw, 1946 w, 1894 vw, 1881 vw, 1802 vw, 1751 vw, 1672 vw, 1582 s, 1557 vs, 1487 vs. νC=C, (phenyl); 1462 vs, 1377 s (paraffin); 1362 s, 1294 vw, 1288 vw, 1248 m $\delta\mathrm{CH_3}$; 1219 m, 1175 w, 1155 vw, 1098 vw, 1070 m, 1026 m, 1013 m, 966 vw, 920 m, 881 m δCH, νCC; 850 vs, 837 vs, 791 v, 754 vs. $\rho\mathrm{CH_3(Si)}$; 716 w (paraffin); 691 vs, 646 m, 625 m, 615 m, 536 vs, 507 s, 451 s, 420 m νSiC, νGaC, δCC $\mathrm{cm^{-1}}$. **MS** (EI, 20 eV, 313 K): m/z (%) = 473 (100), 475 (85) ($\mathrm{M^+}$ *t*Bu), 417 (11), 419 (8) ($\mathrm{M^+}$ butene – *t*Bu).

$[Ph(H)C{=}C(Al\mathit{t}Bu_2)]_2Si(Me)(C{\equiv}CPh)$ (4a): A solution of $\mathrm{(PhC{\equiv}C)_3}$-SiMe (0.357 g, 1.03 mmol) in toluene (10 mL) was added at room temperature to a solution of $t\mathrm{Bu_2AlH}$ (0.293 g, 2.06 mmol) in toluene (10 mL). The reaction mixture was stirred for 16 h at room temperature. The solvent was removed in vacuo to yield a yellow residue that was dissolved in cyclopentane. Cooling to –15 °C afforded colourless crystals of **4a**. Yield: 0.261 g, 40 %). M.p. (argon, sealed capillary): 95 °C (dec). **^{1}H NMR** (400 MHz, C_6D_6, 300 K): δ = 8.30 (s, $^{3}J_{\mathrm{H-Si}}$ = 25.2 Hz, 1 H, *cis*-C=C*H*Ph), 8.23 (s, $^{3}J_{\mathrm{H-Si}}$ = 14.4 Hz, 1 H, *trans*-C=C*H*Ph), 7.64 (m, 2 H, *ortho*-H C≡CPh), 7.53 (d, $^{3}J_{\mathrm{H,H}}$ = 7.5 Hz, 2 H, *ortho*-H *cis*-C=CPh), 7.21 (*pseudo*-t, $^{3}J_{\mathrm{H,H}}$ = 7.7 Hz, 2 H, *meta*-H *cis*-C=CPh), 7.07 (t, $^{3}J_{\mathrm{H,H}}$ = 7.3 Hz, 1 H, *para*-H *cis*-C=CPh), 6.97 (m, 4 H, *ortho*-H and *meta*-H *trans*-C=CPh), 6.90 (m, 3 H, *meta*-H and *para*-H C≡CPh), 6.87 (m, 1 H, *para*-H *trans*-C=CPh), 1.39 (s, br., 18 H, *cis*-C=CAl*tBu*$_2$), 1.19 and 0.93 (each s, 9 H, *trans*-C=CAl*tBu*$_2$), 0.86 (s, 3 H, SiMe). **^{13}C NMR** (100 MHz, C_6D_6, 300 K): δ = 160.2 (*trans*-C=*C*HPh), 158.6 (*trans*-*C*=CHPh), 155.8 (*cis*-C=*C*HPh), 150.7 (*cis*-*C*=CHPh), 149.3 (*ipso*-C *trans*-C=CPh), 141.9 (*ipso*-C *cis*-C=CPh), 133.8 (*ortho*-C C≡CPh), 132.2 (*meta*-C *trans*-C=CPh), 131.2 (*para*-C C≡CPh), 129.0 (*para*-C *trans*-C=CPh), 128.8 (*meta*-C C≡CPh), 128.7 (*meta*-C *cis*-C=CPh), 128.4 (*ortho*-C *cis*-C=CPh), 128.0 (*para*-C *cis*-C=CPh), 122.2 (*ortho*-C *trans*-C=CPh), 120.4 (*ipso*-C C≡CPh), 117.1 (Ph*C*≡CSi), 93.8 (PhC≡*C*Si), 30.9 (br., *cis*-$\mathrm{C}Me_3$), 29.9 and 29.8 (each *trans*-$\mathrm{C}Me_3$), 19.4 (*cis*-$C\mathrm{Me_3}$), 18.9 and 18.8 (each br., *trans*-$C\mathrm{Me_3}$), 1.3 (SiMe). **^{29}Si NMR** (79.5 MHz, C_6D_6, 300 K): δ = 30.3. **IR** (CsI, paraffin): ν(bar) = 2160 vs, 2118 vs. νC≡C; 2072 vw, 2018 vw, 1948 w, 1884 w, 1842 vw, 1823 vw, 1800 vw, 1755 vw, 1676 vw, 1630 vw, 1587 s, 1574 s, 1557 vs, 1526 m, 1491 s νC=C, (phenyl); 1462 vs. (paraffin); 1443 vs, 1402 vw $\delta\mathrm{CH_3}$; 1377 s (paraffin); 1312 w, 1269 vw, 1248 s $\delta\mathrm{CH_3}$; 1217 m, 1179 m, 1155 w, 1099 vw, 1072 s, 1043 sh, 1026 m, 997 m, 964 vw, 932 m, 893 m δCH, νCC; 845 w, 812 w, 783 vw, 754 vw $\rho\mathrm{CH_3(Si)}$; 721 s (paraffin); 689 w, 638 w, 594 m, 559 w, 538 w, 501 s, 488 s, 447 s νAlC, νSiC, δCC $\mathrm{cm^{-1}}$. **MS** (EI, 20 eV, 373 K): m/z (%) = 459 (3) ($\mathrm{M^+}$ – 3*t*Bu), 417 (55) ($\mathrm{M^+}$ – 2butene – C≡CPh), 403 (74) ($\mathrm{M^+}$ – 3*t*Bu – butene), 387 (17) ($\mathrm{M^+}$ – $\mathrm{Al}(t\mathrm{Bu})_2\mathrm{C{=}CHPh}$). **CHN** ($\mathrm{C_{41}H_{56}Al_2Si}$) (631.0): calcd. C 78.0, H 8.9; found 77.1, H 8.7 %.

$[Ph(H)C{=}C(Ga\mathit{t}Bu_2)]_2Si(Me)C{\equiv}CPh$ (4b): $\mathrm{(PhC{\equiv}C)_3SiMe}$ (0.528 g, 1.53 mmol) was added to a solution of $t\mathrm{Bu_2GaH}$ (0.564 g, 3.05 mmol) in toluene (40 mL). The colourless reaction mixture was stirred for 40 h at room temperature, which resulted in a gradual colour change to yellow. The solvent was removed in vacuo to yield a mixture of a yellow oil and a colourless solid. This residue was dissolved in a small quantity of cyclopentane and cooled to 2 °C to give colourless crystals of compound **4b**. Yield: 0.619 g (57 %). M.p. (argon, sealed capillary): 142 °C. **^{1}H NMR** (400 MHz, C_6D_6, 300 K): δ = 8.27 (s, $^{3}J_{\mathrm{H-Si}}$ = 13.0 Hz, 1 H, *trans*-C=C*H*Ph), 7.95 (s, $^{3}J_{\mathrm{H-Si}}$ = 24.0 Hz, 1 H, *cis*-C=C*H*Ph), 7.60 (m, 2 H, *ortho*-H C≡CPh), 7.58 (m, 2 H, *ortho*-H *cis*-CH=CPh), 7.22 (*pseudo*-t, $^{3}J_{\mathrm{H,H}}$ = 7.6 Hz, 2 H, *meta*-H *cis*-CH=CPh), 7.07 (t, $^{3}J_{\mathrm{H,H}}$ = 7.3 Hz, 1 H, *para*-H *cis*-CH=CPh), 6.99 (m, 2 H, *meta*-H *trans*-CH=CPh), 6.93 (m, 3 H, *para*-H C≡CPh and *meta*-H C≡CPh), 6.92 (m, 1 H, *para*-H *trans*-CH=CPh), 6.90 (m, 2 H, *ortho*-H *trans*-CH=CPh), 1.43 (s, 18 H, *cis*-*t*Bu), 1.30 and 1.07 (each s, 9 H, *trans*-*t*Bu), 0.77 (s, 3 H, Si*Me*). **^{13}C NMR** (100 MHz, C_6D_6, 300 K): δ = 160.2 (*trans*-*C*=CHPh), 156.1 (*trans*-C=*C*HPh), 155.0 (*cis*-*C*=CHPh), 152.5 (*cis*-C=*C*HPh), 147.0 (*ipso*-C *trans*-CH=CPh), 141.3 (*ipso*-C *cis*-CH=CPh), 133.0 (*ortho*-C C≡CPh), 130.5 (*meta*-C *trans*-CH=CPh), 130.0 (*para*-C C≡CPh), 128.7 (*meta*-C *cis*-CH=CPh and *meta*-C C≡CPh), 128.5 (*ortho*-C *cis*-CH=CPh and *para*-C *trans*-CH=CPh), 127.9 (*para*-C *cis*-CH=CPh), 123.9 (*ortho*-C *trans*-CH=CPh), 122.0 (*ipso*-C C≡CPh), 111.1 (Ph*C*≡CSi), 94.3 (PhC≡*C*Si), 31.0 (*cis*-$\mathrm{C}Me_3$), 30.3 and 30.2 (each *trans*-$\mathrm{C}Me_3$), 29.2 (*cis*-$C\mathrm{Me_3}$), 29.0 and 28.8 (*trans*-$C\mathrm{Me_3}$), 1.1 ($\mathrm{Si}CH_3$). **^{29}Si NMR** (79.5 MHz, C_6D_6, 300 K): δ = –34.2. **IR** (CsI, paraffin): ν(bar) = 2153 w, 2129 m νC≡C; 2025 vw, 1946 w, 1883 vw, 1800 vw, 1755 vw, 1690 w, 1580 vs, 1558 vs. νC=C, (phenyl); 1462 vs, 1375 vs. (paraffin; 1306 w, 1246 m $\delta\mathrm{CH_3}$; 1209 w, 1171 s, 1155 m, 1099 w, 1070 s, 1026 w, 1003 w, 928 m, 885 s δCH, νCC; 843 w, 808 s, 775 w, 742 s $\rho\mathrm{CH_3(Si)}$; 721 vs. (paraffin); 698 w, 687 m, 638 m, 611 w, 550 w, 536 m, 503 w, 482 m, 446 s νGaC, νSiC, δCC $\mathrm{cm^{-1}}$. **MS** (EI, 20 eV, 393 K): m/z (%) = 657 (42), 659 (62), 661 (27) ($\mathrm{M^+}$ – *t*Bu); 473 (100), 475 (79) ($\mathrm{M^+}$ – $\mathrm{HGa}t\mathrm{Bu_2}$ – *t*Bu). **CHN** ($\mathrm{C_{41}H_{56}Ga_2Si}$) (716.4): calcd. C 68.7, H 7.9; found 68.7, H 7.7 %.

[Ph(H)C=C(Al*t*Bu$_2$)]$_3$Si(Me) (5): A solution of (PhC≡C)$_3$SiMe (0.205 g, 0.59 mmol) in toluene (10 mL) was added at room temperature to a solution of *t*Bu$_2$AlH (0.258 g, 1.82 mmol) in toluene (10 mL). The reaction mixture was stirred for 9 d at room temperature. The solvent was removed in vacuo to yield a yellow, oily residue that was dissolved in a small quantity of pentafluorobenzene and kept at 2 °C to give colourless crystals of **5**. Yield: 0.239 g (52 %). M.p. (argon, sealed capillary): 146 °C (dec). **^{1}H NMR** (400 MHz, C_6D_6, 300 K): δ = 8.27 (s, $^3J_{H-Si}$ = 11.0 Hz, 3 H, C=C*H*Ph), 7.27 (d, $^3J_{H,H}$ = 7.1 Hz, 6 H, *ortho*-H Ph), 7.12 (m, 6 H, *meta*-H Ph), 6.96 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, *para*-H Ph), 1.08 (s, 54 H, *t*Bu), 0.95 (s, 3 H, SiMe). **^{13}C NMR** (100 MHz, C_6D_6, 300 K): δ = 165.9 (*C*=CHPh), 157.3 (C=*C*HPh), 149.4 (*ipso*-C), 132.2 (*meta*-C), 128.8 (*para*-C), 122.7 (*ortho*-C), 30.5 (C*Me*$_3$), 19.3 (*C*Me$_3$), 4.0 (SiMe). **^{29}Si NMR** (79.5 MHz, C_6D_6, 300 K): δ = 17.8. **IR** (CsI, paraffin): *ν*(bar) = 1946 w, 1886 vw, 1807 w, 1715 vw, 1643 m, 1599 s, 1574 s, 1551 m, 1531 m *ν*C=C, (phenyl); 1468 vs, 1375 vs. (paraffin); 1304 m, 1250 m *δ*CH$_3$; 1213 w, 1169 m, 1155 m, 1070 vs, 1043 vs, 1028 vs, 989 m, 978 w, 955 w, 918 m, 889 m *ν*CC, *δ*CH$_3$; 843 m, 812 w, 773 vw *ρ*CH$_3$(Si); 721 vs. (paraffin); 665 vw, 629 m, 592 w, 536 m, 517 m, 472 s, 453 s, 415 m, 365 m, 357 s, 347 m *ν*GaC, *ν*SiC, *δ*CC cm^{-1}. **MS** (EI, 20 eV, 413 K): *m*/*z* (%) = 715 (34), 716 (18) (M$^+$ – *t*Bu); 573 (34), 575 (12) (M$^+$ – HAl*t*Bu$_2$ – *t*Bu); 473 (100), 474 (36) (M$^+$ – CH$_2$=CMe$_2$ – *t*Bu$_2$Al-C=CHPh). **CHN** ($C_{49}H_{75}Al_3Si$) (773.2): calcd. C 76.1, H 9.8; found C 75.5, H 9.8 %.

[(p-MeC$_6$H$_4$)(H)C=C(Al*t*Bu$_2$)]$_3$Si(Me) (6): A solution of (*p*-MeC$_6$H$_4$C≡C)$_3$SiMe (0.206 g, 0.53 mmol) in toluene (10 mL) was added at room temperature to a solution of *t*Bu$_2$AlH (0.226 g, 1.59 mmol) in toluene (10 mL). The reaction mixture was stirred for 4 h at 75 °C. The solvent was removed in vacuo to yield a yellow, oily residue that was dissolved in a small quantity of pentafluorobenzene and kept at 2 °C to give colourless crystals of **6**. Yield: 0.140 g (32 %). M.p. (argon, sealed capillary): 170 °C (dec). **^{1}H NMR** (400 MHz, C_6D_6, 300 K): δ = 8.31 (s, $^3J_{H-Si}$ = 10.5 Hz, 3 H, C=C(*H*)*p*-tol), 7.24 (d, $^3J_{H,H}$ = 7.6 Hz, 6 H, *ortho*-H), 7.01 (d, $^3J_{H,H}$ = 7.6 Hz, 6 H, *meta*-H), 1.98 (s, 9 H, Me *p*-Tol), 1.13 (s, 54 H, *t*Bu), 0.98 (s, 3 H, SiMe). **^{13}C NMR** (100 MHz, C_6D_6, 300 K): δ = 164.7 (*C*=C(H)*p*-tol), 157.0 (C=*C*(H)*p*-tol), 146.8 (*ipso*-C), 138.8 (*para*-C), 132.8 (*meta*-C), 122.7 (*ortho*-C), 30.6 (C*Me*$_3$), 20.8 (*C*H$_3$ *p*-tol), 19.3 (*C*Me$_3$), 4.1 (SiMe). **^{29}Si NMR** (79.5 MHz, C_6D_6, 300 K): δ = –17.7. **IR** (KBr, paraffin): *ν*(bar) = 1931 vw, 1910 vw, 1888 vw, 1805 vw, 1768 vw, 1659 vw, 1605 m, 1566 w, 1510 s, 1497 vs. *ν*C=C, (phenyl); 1462 vs, 1377 vs. (paraffin); 1312 m, 1298 m, 1263 w, 1246 m *δ*CH$_3$; 1219 w, 1175 m, 1155 w, 1112 m, 1069 w, 1043 m, 999 s, 988 m, 966 vw, 943 s, 908 s, 893 m *ν*CC, *δ*CH$_3$; 847 m, 810 vs, 762 w *ρ*CH$_3$(Si); 719 vs. (paraffin); 692 m, 663 vw, 642 m, 590 s, 577 s, 529 w, 505 s, 449 s *ν*GaC, *ν*SiC, *δ*CC cm^{-1}. **MS** (EI, 20 eV, 393 K): *m*/*z* (%) = 758 (33) (M$^+$ – H$_2$C=CMe$_2$); 615 (43), 616 (21) (M$^+$ – *t*Bu – HAl*t*Bu$_2$); 501 (100), 502 (36) (M$^+$ – H$_2$C=CMe$_2$ – *t*Bu$_2$Al-C=CH-C$_6$H$_4$Me). **CHN** ($C_{52}H_{81}Al_3Si$) (815.3): calcd. C 76.6, H 10.0; found C 75.6, H 9.5 %.

Crystal Structure Determinations

Crystals suitable for X-ray crystallography were obtained by recrystallisation from cyclopentane (**2**, **4a**, **4b**) or pentafluorobenzene (**5**, **6**). Intensity data was collected on a Bruker APEX II diffractometer with monochromated Mo-K_α (**2**, **6**) or Cu-K_α (**4a**, **4b**, **5**) radiation. The collection method involved ω-scans. Data reduction was carried out using the program *SAINT+*.[22] The crystal structures were solved by direct methods using *SHELXTL*.[23] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculation based on F^2 using *SHELXTL*. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms with $U = 1.2U_{eq}(C)$. Compound **4a** and **4b** are chiral and there are two independent molecules [R, S (**4a**); R, R (**4b**)] in the asymmetric unit. The respective enantiomers are created by the inversion centre of the space group. Compound **5** incorporates a molecule of pentafluorobenzene in the asymmetric unit which is disordered across the inversion centre. A fluorine atom was refined with an occupancy factor of 0.5; the hydrogen atom was not considered. A *t*Bu group of **5** (C32) was disordered; the respective atoms were refined in split positions (0.5:0.5). A *t*Bu group (C22) was disordered in compound **6** (0.54:0.46). Further crystallographic data is summarised in Table 2.

Table 2. Crystal data and structure refinement for compounds **2**, **4a**, **4b**, **5** and **6**.

Compound	**2**	**4a**	**4b**	**5**·0.5C_6F_5H	**6**
Empirical formula	$C_{38}H_{39}GaSi$	$C_{41}H_{56}Al_2Si$	$C_{41}H_{56}Ga_2Si$	$C_{52}H_{75}Al_3F_{2.50}Si$	$C_{52}H_{81}Al_3Si$
Crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	4	4	4	2	2
T /K	153(2)	153(2)	153(2)	153(2)	153(2)
Density (calc) /g·cm^{-3}	1.173	1.068	1.207	1.090	1.029
a /pm	1759.9(4)	1219.29(2)	1220.51(2)	1371.10(3)	1438.67(6)
b /pm	1080.2(2)	1358.14(2)	1363.41(3)	1371.46(3)	1506.97(6)
c /pm	1768.1(4)	241.49(4)	2461.15(5)	1541.49(4)	1547.1(1)
α /°	90	100.451(1)	100.653(1)	102.094(2)	105.789(1)
β /°	90.54(3)	101.376(1)	101.243(1)	98.415(2)	104.408(1)
γ /°	90	90.682(1)	90.364(1)	108.832(1)	112.404(1)
Volume /nm^3	3.361(1)	3.9250(1)	3.9438(1)	2.6099(1)	2.6315(2)
μ /mm^{-1}	0.877	1.135	1.207	1.195	0.125
Radiation	Mo-K_α	Cu-K_α	Cu-K_α	Cu-K_α	Mo-K_α
Theta range /°	2.21–29.32	1.86–72.37	3.30–72.42	3.01–72.37	1.55–30.04
Independent reflections	9074 (R_{int} = 0.0491)	13352 (R_{int} = 0.0297)	13297 (R_{int} = 0.0268)	8851 (R_{int} = 0.0382)	15233 (R_{int} = 0.0310)
Parameters	367	819	819	582	552
R_1 [$I > 2\sigma(I)$]	0.0421 (4654)	0.0498 (9822)	0.0409 (10652)	0.0582 (6443)	0.0522 (9926)
wR_2(all data)	0.0721	0.1394	0.1082	0.1677	0.1523
Max./ min. residual electron density / e·nm^{-3}	402/–226	428/–289	539/–382	505/–230	481/–387

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma [w(F_o^2-F_c^2)^2]/\Sigma [(F_o^2)^2]\}^{1/2}$

The crystallographic data was deposited as supplementary publication no. CCDC-840609 (for **2**), -840610 (for **4a**), -840611 (for **4b**), -840612 (**5**·0.5C_6F_5 H) and -840613 (for **6**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, Great Britain (Fax: +44-1223-336-033; E-mail: deposit@cccd.cam.ac.uk).

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References

[1] G. Zweifel, J. A. Miller, *Org. React.* **1984**, *32*, 375; E. Winterfeldt, *Synthesis* **1975**, *10*, 617; J. Marek, J.-F. Normant, *Chem. Rev.* **1996**, *96*, 3241; J. J. Eisch, in: *Comprehensive Organic Synthesis* (Eds.: B. Frost, I. Flemming), Pergamon, Oxford, **1991**, vol. 8, p. 733; G. Zweifel, in: *Aspects Mech. Organomet. Chem.* (Ed.: J. H. Brewster), Plenum Press, New York, **1978**, p. 229; G. Zweifel, in: *Comprehensive Organic Chemistry* (Eds.: D. H. R. Barton, W. D. Ollis), Pergamon, Oxford, **1979**, p. 1013; E. Negishi, *Organometallics in Organic Synthesis* Wiley, New York, **1980**; S. Saito, in: *Main Group Metals in Organic Synthesis* (Eds.: H. Yamamoto, K. Oshima), Wiley-VCH, Weinheim, **2004**, p. 189; J. A. Miller, in: *Chemistry of Aluminum, Gallium, Indium and Thallium* (Ed.:A. J. Downs), Blackie Academic, London, **1993**, p. 372.

[2] W. Uhl, *Coord. Chem. Rev.* **2008**, *252*, 1540.

[3] Further contributions to hydrogallation reactions: J. Ohshita, H. Schmidbaur, *J. Organomet. Chem.* **1993**, *453*, 7; H. Schmidbaur, H. F. Klein, *Angew. Chem.* **1966**, *78*, 306; H. Schmidbaur, H. F. Klein, *Chem. Ber.* **1967**, *100*, 1129; W. Uhl, M. Claesener, *Inorg. Chem.* **2008**, *47*, 4463; W. Uhl, M. Claesener, D. Kovert, A. Hepp, E.-U. Würthwein, N. Ghavtadze, *Organometallics* **2011**, *30*, 3075; H. Schumann, U. Hartmann, W. Wassermann, *Polyhedron* **1990**, *9*, 353; E. Johnsen, A. J. Downs, M. J. Goode, T. M. Greene, H. J. Himmel, M. Müller, S. Parsons, C. R. Pulham, *Inorg. Chem.* **2001**, *40*, 4755; C. R. Pulham, A. J. Downs, M. J. Goode, D. W. H. Rankin, H. E. Robertson, *J. Am. Chem. Soc.* **1991**, *113*, 5419; J. L. Atwood, S. G. Bott, C. Jones, C. L. Raston, *Inorg. Chem.* **1991**, *30*, 4868; M. J. Henderson, C. H. L. Kennard, C. L. Raston, G. Smith, *J. Chem. Soc., Chem. Commun.* **1990**, 1203; W. Uhl, J. Molter, B. Neumüller, *J. Organomet. Chem.* **2001**, *634*, 193; J. R. Jennings, K. Wade, *J. Chem. Soc. A* **1967**, 1222.

[4] W. Uhl, L. Cuypers, R. Graupner, J. Molter, A. Vester, B. Neumüller, *Z. Anorg. Allg. Chem.* **2001**, *627*, 607.

[5] W. Uhl, L. Cuypers, G. Geiseler, K. Harms, W. Massa, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1001; W. Uhl, M. Claesener, S. Haddadpour, B. Jasper, A. Hepp, *Dalton Trans.* **2007**, *4*, 417; see also: P. L. Baxter, A. J. Downs, M. J. Goode, D. W. H. Rankin, H. E. J. Robertson, *J. Chem. Soc., Dalton Trans.* **1990**, 2873.

[6] W. Uhl, F. Breher, *Angew. Chem.* **1999**, *111*, 1578; *Angew. Chem. Int. Ed.* **1999**, *38*, 1477; W. Uhl, F. Breher, A. Lützen, W. Saak, *Angew. Chem.* **2000**, *112*, 414; *Angew. Chem. Int. Ed.* **2000**, *39*, 406; W. Uhl, F. Breher, J. Grunenberg, A. Lützen, W. Saak, *Organometallics* **2000**, *19*, 4536; W. Uhl, F. Breher, A. Mbonimana, J. Gauss, D. Haase, A. Lützen, W. Saak, *Eur. J. Inorg. Chem.* **2001**, 3059; A. Stasch, M. Ferbinteanu, J. Prust, W. Zheng, F. Cimpoesu, H. W. Roesky, J. Magull, H.-G. Schmidt, M. Noltemeyer, *J. Am. Chem. Soc.* **2002**, *124*, 5441; S. S. Kumar, J. Rong, S. Singh, H. W. Roesky, D. Vidovic, J. Magull, D. Neculai, V. Chandrasekhar, M. Baldus, *Organometallics* **2004**, *23*, 3496; W. Uhl, H. W. Roesky, in: *Molecular Clusters of the Main Group Elements* (Eds.: M. Driess, H. Nöth), Wiley-VCH Verlag, Weinheim, **2004**, p. 357.

[7] W. Uhl, L. Cuypers, B. Neumüller, F. Weller, *Organometallics* **2002**, *21*, 2365.

[8] W. Uhl, A. Hepp, M. Matar, A. Vinogradov, *Eur. J. Inorg. Chem.* **2007**, 4133; W. Uhl, F. Breher, S. Haddadpour, *Organometallics* **2005**, *24*, 2210.

[9] W. Uhl, M. Claesener, S. Haddadpour, B. Jasper, A. Hepp, *Dalton Trans.* **2007**, 417; W. Uhl, S. Haddadpour, M. Matar, *Organometallics* **2006**, *25*, 159; W. Uhl, M. Claesener, A. Hepp, B. Jasper, A. Vinogradov, L. van Wüllen, T. K.-J. Köster, *Dalton Trans.* **2009**, 10550.

[10] W. Uhl, M. Matar, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1177.

[11] W. Uhl, H. R. Bock, M. Claesener, M. Layh, I. Tiesmeyer, E.-U. Würthwein, *Chem. Eur. J.* **2008**, *14*, 11557.

[12] W. Uhl, M. Claesener, S. Haddadpour, B. Jasper, I. Tiesmeyer, S. Zemke, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2889.

[13] W. Uhl, M. Claesener, A. Hepp, *Organometallics* **2008**, *27*, 2118; W. Uhl, M. Claesener, *Inorg. Chem.* **2008**, *47*, 729.

[14] W. Uhl, J. Grunenberg, A. Hepp, M. Matar, A. Vinogradov, *Angew. Chem.* **2006**, *118*, 4465; *Angew. Chem. Int. Ed.* **2006**, *45*, 4358; W. Uhl, A. Vinogradov, S. Grimme, *J. Am. Chem. Soc.* **2007**, *129*, 11259.

[15] W. Uhl, M. Rohling, J. Kösters, *New J. Chem.* **2010**, *34*, 1630; W. Uhl, D. Heller, *Z. Anorg. Allg. Chem.* **2010**, *636*, 581.

[16] W. Uhl, D. Heller, M. Rohling, J. Kösters, *Inorg. Chim. Acta* **2011**, *374*, 359.

[17] W. Uhl, M. Rohling, E.-U. Würthwein, N. Ghavtadze, K. Bergander, *Organometallics* **2010**, *29*, 5236; W. Uhl, D. Heller, J. Kösters, E.-U. Würthwein, N. Ghavtadze, *Eur. J. Inorg. Chem.* **2011**, accepted, DOI: 10.1002/ejic.201100890.

[18] H. Günther, *NMR-Spektroskopie*, Thieme, Stuttgart, **1973**, p. 248.

[19] M. Nishio, *CrystEngComm* **2004**, *6*, 130; M. Nishio, *Phys. Chem. Chem. Phys.* **2011**, *13*, 13883; O. Takahashi, Y. Kohno, M. Nishio, *Chem. Rev.* **2010**, *110*, 6049.

[20] W. Uhl, L. Cuypers, G. Geiseler, K. Harms, W. Massa, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1001.

[21] M. E. Freeburger, L. Spialter, *J. Org. Chem.* **1970**, *35*, 652; A. Boudin, G. Cerveau, C. Chuit, R. J. P. Corriu, C. Reye, *Angew. Chem.* **1986**, *98*, 472; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 473.

[22] *SAINT+*, Version 6.02 (includes XPREP and SADABS), Bruker AXS INC., Madison, Wisconsin, USA, **1999**; G. M. Sheldrick, *SADABS*, Universität Göttingen, Germany, **1996**.

[23] *SHELXTL-Plus*, REL. 4.1; Siemens Analytical X-RAY Instruments Inc.: Madison, WI, **1990**; G. M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structures; Universität Göttingen, Germany, **1997**.

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