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# Hydroalumination of bis(alkynyl)germanes and -silanes: Generation of a chelating Lewis-acid and observation of a dismutation reaction

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Dedicated to Prof. W. Kaim on the occasion of his 60th birthday.

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### ABSTRACT

Treatment of diphenyl-di(phenylethynyl)germane with two equivalents of di(*tert*-butyl)aluminum hydride afforded the corresponding dialkenyl derivative,  $Ph_2Ge[C(AltBu_2)=C(H)-Ph]_2$  (1) by dual hydroalumination. The aluminum atoms of **1** are attached to the carbon atoms in  $\alpha$ -position to germanium. They are coordinatively unsaturated and are able to act as chelating Lewis-acids and to coordinate donors such as chloride or bromide anions in a chelating manner (**2**, **3**). The analogous reaction of the corresponding silicon-centered dialkyne with two equivalents of dimethylaluminum hydride gave a mixture of unknown compounds. Interestingly, equimolar quantities of the hydride and the dialkyne resulted in dismutation and the formation of the unprecedented compound MeAl[C(=CH-Ph)-SiPh\_2-C=C-Ph]\_2 (**4**). Compound **4** has two alkenyl groups bonded to the central aluminum atom and a terminal alkynyl group attached to each silicon atom. An attempt to reduce the remaining triple bonds by reaction with di(*tert*-butyl)aluminum hydride resulted in cleavage and isolation of the monoalkenyl compound *t*Bu<sub>2</sub>Al-C[=C(H)-Ph]-SiPh<sub>2</sub>-C=C-Ph (**5**). The molecular structure of **5** showed a close interaction between the  $\alpha$ -carbon atom of the triple bond and the coordinatively unsaturated aluminum atom.

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### 1. Introduction

Oligoacceptors based on coordinatively unsaturated atoms of main-group elements (chelating Lewis-acids) are of interest in phase transfer processes, in catalysis or in molecular recognition. The synthesis of such compounds and their application for the coordination of suitable donors has found considerable interest in recent research [1]. Previously our group has synthesized a methylene bridged dialuminum compound, R<sub>2</sub>Al-CH<sub>2</sub>-AlR<sub>2</sub>  $[R = CH(SiMe_3)_2]$  [2], which features two coordinatively unsaturated aluminum atoms as particularly effective Lewis-acids and was able to coordinate various donors such as hydride, nitrate, azide or acetate anions in a chelating manner [3]. Although this compound proved to be an excellent chelating acceptor, its application is relatively limited due to the low variability of the distance between the coordinating aluminum atoms and the presence of only two coordinatively unsaturated atoms in a molecule. In order to overcome these problems and to achieve a higher flexibility we have used the hydroalumination and hydrogallation of oligoalkynes for the generation of organoelement compounds with up to four tricoordinated metal atoms [4]. Preliminary experiments have confirmed their applicability for the coordination of halide, benzoate or thiophenolate anions [5]. The efficacy of these chelating

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Lewis-acids was impressively shown by the generation of carbocationic species which were formed via C–H bond activation and the chelating coordination of the released hydride anion by two aluminum atoms [6]. The dual hydroalumination or hydrogallation of dialkynylsilanes or -germanes may allow an alternative access to chelating Lewis-acids that have longer chains between the aluminum or gallium acceptor atoms.

### 2. Results and discussion

### 2.1. Reactions of dialkynylgermanes

Only recently we have published the reactions of dimethyl- and diphenyl-(diphenylethynyl)germanes with equimolar quantities of various dialkylaluminum hydrides [7]. One C=C triple bond of each starting compound was reduced, and mixed alkenyl-alkynyl-germanium compounds have been isolated in 55–90% yield. The hydrogen and aluminum atoms of the resulting alkenyl groups were in all cases *cis* to each other. The thermodynamically favored *cis/trans*-isomerisation [8] is prevented by an interaction of the coordinatively unsaturated aluminum atoms with the  $\alpha$ -carbon atoms of the ethynyl groups which carry a relative high negative partial charge. Only the sterically shielded bis(trimethylsilyl)methylaluminum derivatives did not show this interaction [7]. Hydroalumination of both alkynyl groups of the dialkynylgermanium starting compounds was successful only in a single case



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(Scheme 1). Treatment of  $(H_5C_6)_2$ Ge(C=C-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> with two equivalents of di(tert-butyl)aluminum hydride in n-hexane afforded the colorless dialkenylgermanium compound 1 in 53% yield after a relatively long reaction time of 7 d at room temperature. Heating of the reaction mixture in order to increase the reaction rate did not result in a faster reaction, but decomposition occurred with the formation of several unknown products. Other dialkylaluminum hydrides such as Me<sub>2</sub>AlH, (Me<sub>3</sub>CCH<sub>2</sub>)<sub>2</sub>AlH or (Me<sub>2</sub>CHCH<sub>2</sub>)<sub>2</sub>AlH led to the elimination of the corresponding dialkylaluminum alkynides,  $R_2Al-C \equiv C-C_6H_5$  [9], which were identified by NMR spectroscopy and in two cases by determination of unit cell parameters. We were not able to isolate any secondary product containing the germanium atoms. Several resonances in the NMR spectra of the highly viscous residues may indicate an unselective decomposition. Hence, it is not possible to discuss a rational reaction course for these interesting elimination processes. Similar degradation reactions were observed in the case of dimethyldi(phenylethynyl)germanium. In contrast, a broader variety of dialkenyl species could be isolated with analogous silicon-centered dialkynes [10].



Scheme 1.

NMR data confirm the molecular structure of 1 which is schematically given in Scheme 1. The <sup>13</sup>C NMR spectrum shows only the characteristic resonances of alkenyl groups ( $\delta = 157.4$  and 163.3), signals of ethynyl moieties are missing. The resonance of the vinylic hydrogen atoms is shifted towards the low field side of the <sup>1</sup>H NMR spectrum ( $\delta$  = 8.35) which is in accordance with previously obtained results [4,10]. A crystal structure determination (Fig. 1) revealed a central germanium atom which is bonded to two phenyl and two alkenyl groups in a slightly distorted tetrahedral arrangement. The bond angles C–Ge–C are in a narrow range between  $106.4(1)^{\circ}$  and  $110.78(9)^{\circ}$  with the largest one between the alkenyl carbon atoms. The tricoordinated aluminum atoms reside 12 pm above the plane formed by the three adjacent carbon atoms. Steric repulsion in this relatively crowded molecule may cause the deviation from planarity; any secondary intramolecular interaction was not observed. The dialkylaluminum groups occupy the  $\alpha$ -positions of the alkenvl groups neighboring the germanium atoms. The reaction of the positively charged aluminum atoms at these positions is favored by the relatively high negative charge of these alkynyl carbon atoms [11]. In contrast to the mixed alkenyl-alkynyl species discussed above trans-configuration results for both alkenyl groups with aluminum and hydrogen atoms on different sides of the C=C double bonds (C=C bond lengths 134.7(2) pm). cis/trans-Rearrangement to yield the thermodynamically favored isomer [8] is not hindered by an intramolecular interaction as described above. Further distances and angles are in the expected ranges and do not require a detailed discussion. The molecular conformation is determined by a minimization of steric repulsion between the bulky di(*tert*-butyl)aluminum groups which arrange themselves as far apart as possible.

Compound **1** has two coordinatively unsaturated aluminum atoms and should behave as a chelating Lewis-acid. In order to check this property in some preliminary experiments we treated solutions of **1** in toluene with equimolar quantities of tetra (n-butyl)ammonium chloride and bromide (Scheme 1). Colorless solids precipitated in both cases and were isolated by filtration. The residues consist of the analytically pure adducts **2** and **3** without further purification. With the exception of the resonances of



**Fig. 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 [°]: Ge1-C11 194.9(2), Ge1-C21 195.6(2), C11-C12 134.7(2), Al1-C11 197.1(2), Al1-C31 198.6(2), Al1-C41 199.2(2), C11-Ge1-C11' 110.78(9), C21-Ge1-C21' 106.4(1), Ge1-C11-Al1 127.05(8), Al1-C11-C12 115.0(1); C11' and C21' generated by -x + 0.5, -y + 0.5, z.

the *n*-butyl groups the NMR parameters are almost identical to those of the starting compound 1. Only the resonances of the vinylic protons are shifted considerably to a higher field in the <sup>1</sup>H NMR spectrum ( $\delta$  = 7.64 on average versus 8.35 of **1**). Crystal structure determinations verified the coordination of the halide anions in a chelating manner by both aluminum atoms of 1 (Figs. 2 and 3). The formation of the complexes caused a dramatic change in the conformation of the germanium compound, because the aluminum atoms must approach to facilitate the twofold donoracceptor interaction. The Al-Cl (234.8 pm) [12] and Al-Br distances (254.6 pm) [13] are in the characteristic range for Al-X bond lengths in Al-X-Al bridges. Due to the larger radius of the bromine atom the Al-X-Al angle (137.81(6)° versus 126.7° on average) is smaller for the complex with the heavier halogen atom. All other angles are almost indistinguishable, e.g. C-Ge-C in the resulting GeC<sub>2</sub>Al<sub>2</sub>X heterocycle 126.9° (on average for **3**) versus 125.8(2)° (2). The shape of the six-membered heterocycles approaches a half-boat (2; Ge1 44 pm, Cl1 11 pm above the plane Al1, Al2, C1, C2) or a twist boat conformation (3). The crystals of compound 3 enclose 1,2-difluorobenzene molecules. The shortest intermolecular H…F distances are in the range of 255–296 pm which is close to the sum of the van der Waals radii (>270 pm) and indicates only weak intermolecular interactions.

### 2.2. Reaction of a dialkynylsilane with dimethylaluminum hydride

A broad variety of compounds analogous to **1** has been synthesized via the dual hydroalumination of dialkynylsilanes [10]. In contrast, two equivalents of dimethylaluminum hydride gave an inseparable mixture of many unknown components. Interestingly, we obtained an unexpected, unprecedented compound when we repeated this experiment with equimolar quantities of Me<sub>2</sub>AlH and  $(H_5C_6)_2Si(C=C-C_6H_5)_2$  (Scheme 2). A dismutation reaction took place, and we isolated the dialkenyl compound **4** in 71% yield. Trimethylaluminum was identified by NMR spectroscopy as a byproduct. Compound **4** has a central three-coordinate Al atom which is bonded to a methyl group and two alkenyl groups. The latter result from the reduction of one C=C triple bond of the starting dialkyne. Each alkenyl group carries a silicon atom which is additionally bonded to two phenyl groups and the unaffected, terminal alkynyl substituent. Thus, compound **4** has two alkenyl and



**Fig. 2.** Molecular structure and numbering scheme of **2**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms with the exception of the vinylic hydrogen atoms and methyl groups of the *tert*-butyl substituents (at Al1 and Al2) are omitted. Selected bond lengths [pm] and angles [°]: Ge1–C1 195.8(4), Ge1–C2 194.9(4), C1–C11 136.7(6), C2–C21 135.6(6), Al1–C1 201.1(4), Al2–C2 203.7(4), Al1–Cl1 235.4(2), Al2–Cl1 234.1(2), C1–Ge1–C2 125.8(2), Ge1–C1–Al1 126.4(2), Ge1–C2–Al2 125.0(2), C1–Al1–Cl1 97.7(1), C2–Al2–Cl1 98.4(1), Al1–Cl1–Al2 137.81(6).



**Fig. 3.** Molecular structure and numbering scheme of **3**; hydrogen atoms with the exception of the vinylic hydrogen atoms and methyl groups of the *tert*-butyl substituents (at Al1 and Al2) are omitted. Selected bond lengths [pm] and angles [°] (values of the second molecule in square brackets): Ge1-C11 198.4(3) [197.6(3)], Ge1-C12 198.1(3) [197.2(3)], C11-C111 135.1(5) [134.5(5)], C12-C121 133.9(5) [134.1(5)], Al1-C11 201.4(4) [200.3(4)], Al2-C12 200.5(4) [201.1(4)], Al1-Br1 256.7(1) [253.4(1)], Al2-Br1 254.0(1) [254.3(1)], C11-Ge1-C12 127.7(1) [126.1(1)], Ge1-C11-Al1 123.6(2) [126.0(2)], Ge1-C12-Al2 124.6(3) [125.1(2)], C11-Al1-Br1 97.5(1) [98.1(1)], C12-Al2-Br1 96.6(1) [97.2(1)], Al1-Br1-Al2 126.94(4) [126.54(4)].



two alkynyl groups in a single molecule. A crystal structure determination (Fig. 4) revealed normal C=C double (134.5 pm on average) and C=C triple bond lengths (120.1 pm). The Al-C distances differ slightly with the shortest being observed for the Al-Me



**Fig. 4.** Molecular structure and numbering scheme of **4**; hydrogen atoms are omitted; only the *ipso*-C atoms of the phenyl groups (C113, C123, C131, C141, C213, C223, C231, C241) are shown. Selected bond lengths [pm] and angles [ $^{\circ}$ ]: Al1–C1 194.9(3), Al1–C111 197.3(3), Al1–C211 196.2(3), C111–C112 133.9(4), C211–C212 135.1(4), C121–C122 120.0(4), C221–C222 120.1(4), Al1–C111–Si1 121.2(2), Al1–C211–Si2 123.5(2).

group (194.9(3) versus 196.2(3) and 197.3(3) pm). This may be caused by the different bulk of the substituents. The aluminum atom has a planar coordination sphere and resides only 0.3 pm above the plane of the adjacent carbon atoms. The smallest C-Al-C angle is found between the  $\alpha$ -carbon atoms of the alkenyl groups (C111 and C211, 116.4(1)°), the angles including the methyl carbon atom C1 are 121.0(1) and 122.6(1)°. The crystals of 4 incorporate 1.2-difluorobenzene molecules. Intermolecular H...F distances of >260 pm are in accordance with only weak interactions. The aluminum and hydrogen atoms of the alkenyl moieties are in a *trans*-arrangement on different sides of the C=C double bonds. cis/trans-Rearrangement, for which intermolecular activation is required [8], has to be expected in this case due to the relatively low steric shielding of the aluminum atoms by the methyl group. The *trans*-configuration is also evident from the <sup>1</sup>H NMR spectrum and the  ${}^{3}J_{Si}$  coupling constant (13.5 Hz) which is in the characteristic range of trans-addition products (>20 Hz for cis-configuration). The release of trialkylaluminum or -gallium derivatives and the formation of divinyl- or trivinylelement compounds has been reported previously [4,8]. This method was applied for the selective generation of unprecedented cage compounds and clusters [14].

Compound **4** possesses two terminal ethynyl groups. Their reduction via a hydroalumination reaction should afford a compound with three coordinatively unsaturated aluminum atoms in a single molecule. We therefore treated **4** with two equivalents of di(*tert*-butyl)aluminum hydride in toluene at room temperature (Scheme 2). Colorless crystals of the product **5** were isolated in 71% yield after recrystallization. Crystal structure determination (Fig. 5) and spectroscopic characterization of **5** revealed the unexpected cleavage of the starting compound **4** resulting in the formation of a mononuclear alkenyl–alkynyl–diphenylsilicon derivative (C=C 133.4(3) pm; C=C 120.3(3) pm). The aluminum atom of **5** is bonded to the  $\alpha$ -carbon atom of the alkenyl group and deviates from a trigonal planar geometry with the aluminum atom. The



**Fig. 5.** Molecular structure and numbering scheme of **5**; 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 200.2(2), Al1…C21 245.8(2), Si1–C11 185.2(2), Si1–C21 187.0(2), C11–C12 133.4(3), C21–C22 120.3(3), C11–Si1–C21 99.61(9), Si1–C21–C22 161.9(2), C21–C22–C23 176.8(2), Si1–C11–C12 120.9(2), Al1–C11–C12 140.6(2).

pyramidal configuration is caused by an intramolecular interaction between the coordinatively unsaturated metal atom and the  $\alpha$ -carbon atom of the ethynyl group with an Al1-C21 distance of 245.8(2) pm. This distance is considerably longer than the normal values for terminal Al-C bonds (<200 pm), nevertheless several other observations support the significance of this interaction: (i) the torsion angle C21-Si1-C11-Al1 is with 8.8° close to the ideal value of 0° which allows an optimum interaction between aluminum and carbon. (ii) The angle C21-Si1-C11 is very small  $(99.61(9)^{\circ})$  and indicates considerable steric strain in the resulting four-membered C<sub>2</sub>SiAl heterocycle. (iii) The group Si1–C21=C22 deviates from linearity (161.9(2)°; C21=C22-C23 176.8(2)°). (iv) The angle Al1–C11=C12 is extraordinarily large (140.6°) which is caused by the close contact between the aluminum atom and the alkyne carbon atom C21. Similar interactions have been verified by NMR spectroscopy or crystal structure determinations for various products of the hydroboration or hydroalumination of dialkynylelement compounds [7,10,15]. Interestingly, 5 is an isomer of a compound recently published by our group. It was obtained by hydroalumination of the corresponding dialkynylsilane with di(tert-butyl)aluminum hydride [10] and had a cis-arrangement of H and Al atoms at the resulting C=C double bond. cis/trans-Isomerisation was prevented in this case by an intramolecular interaction of the aluminum atom with the  $\alpha$ -carbon atom of the alkynyl group and, hence, the coordinative saturation of the metal atom. Rearrangement to the cis-product was not observed even upon warming. In contrast, the trans-arrangement of hydrogen and aluminum atoms was found for compound 5, and the thermodynamically favored isomer was formed via the dialkenyl compound 4. The different configurations can easily be derived from the  ${}^{3}J_{Si\cdots H}$  coupling constants across the C=C double bonds in the <sup>1</sup>H NMR spectra which are 13.7 Hz for **5** (*trans*) and 26.0 Hz (*cis*) for the isomeric compound. We were not able to identify any by-product of the reaction according to Scheme 2. The compound "MeAlH<sub>2</sub>" is postulated to balance the equation. Such dihydrides, RAlH<sub>2</sub>, bearing small alkyl substituents are unknown in the literature, only one derivative is reported which has the bulky tri(*tert*-butyl)phenyl substituent [16].

In conclusion, hydroalumination of oligoalkynes is a powerful method for the generation of efficient oligoacceptors (chelating Lewis-acids) which are suitable for the coordination of halide anions and potentially of other anions or donor molecules. However, in the case of low steric shielding condensation reactions may take place. They prevent the isolation of chelating Lewis-acids, but lead to unprecedented secondary products with interesting functionalities.

### 3. Experimental

### 3.1. General

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane and cyclopentane with LiAlH<sub>4</sub>; 1,2-difluorobenzene with molecular sieves; toluene with Na/benzophenone). (Me<sub>3</sub>C)<sub>2</sub>Al-H [17], Me<sub>2</sub>AlH [18], (H<sub>5</sub>C<sub>6</sub>)<sub>2</sub>Ge(C=C-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> [7] and (H<sub>5</sub>C<sub>6</sub>)<sub>2</sub>Si(C=C-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> [19] were obtained according to literature procedures. Commercially available tetra(*n*-butyl)ammonium chloride and bromide were employed as purchased.

### 3.2. Synthesis of $Ph_2Ge[C(AltBu_2)=CHPh]_2(1)$

A solution of di(phenyl)di(phenylethynyl)germane (0.160 g, 0.373 mmol) in 10 mL of *n*-hexane was added dropwise to a solution of di(tert-butyl)aluminum hydride (0.106 g, 0.746 mmol) in 10 mL of *n*-hexane at room temperature. The mixture was stirred for 7 d and adopted a pale yellow color. All volatiles were removed in vacuum. The solid residue was recrystallized from *n*-hexane (20/ -15 °C). Yield: 0.142 g (53%). M.p. (sealed capillary, argon): 188 °C (dec.). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 8.35 (s, 2H, CHPh), 7.89 (pseudo-d, 4H, ortho-H GePh<sub>2</sub>); 7.28 (pseudo-t, 4H, meta-H GePh<sub>2</sub>), 7.23 (m, 4H, ortho-H CHPh), 7.19 (m, 2H, para-H GePh<sub>2</sub>), 7.12 (pseudo-t, 4H, meta-H CHPh), 6.98 (pseudo-t, 2H, para-H CHPh), 0.92 (s, 36H, CMe<sub>3</sub>).  $^{13}\text{C}$  NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta$  163.3 (CCHPh), 157.4 (CCHPh), 147.9 (ipso-C CHPh), 140.8 (ipso-C GePh<sub>2</sub>), 135.2 (ortho-C GePh<sub>2</sub>), 131.4 (meta-C CHPh), 129.6 (para-C GePh<sub>2</sub>), 129.2 (meta-C GePh<sub>2</sub>), 128.7 (para-C CHPh), 123.5 (ortho-C CHPh), 30.3 (CMe<sub>3</sub>), 19.4 (CMe<sub>3</sub>). IR (cm<sup>-1</sup>, nujol, CsI plates): 1649 vw, 1578 m v(C=C), phenyl; 1464 vs, 1377 vs (nujol); 1304 w, 1267 w  $\delta$  (CH<sub>3</sub>); 1155 m, 1088 w, 1026 w, 935 w, 918 m, 845 w, 808 w, 773 m v(CC),  $\delta$  (CC); 723 s (nujol); 621 vw, 588 w, 548 w, 463 m v(AlC), v(GeC). MS (EI, 20 eV, 100 °C, m/z; only the most intensive peaks are given, the complete isotopic patterns are in agreement with the calculated ones): 657 (73%)  $[M-CMe_3]^+$ , 415 (100%)  $[M-C(AltBu_2)=CH-Ph-butene]^+$ . Anal. Calc. for C44H58Al2Ge (713.5): C, 74.1; H, 8.2. Found: C, 73.2; H, 8.0%.

## 3.3. Synthesis of $[Ph_2Ge{C(AltBu_2)=CHPh}_2X][N(n-Bu)_4]$ (2 and 3); general procedure

The tetra(*n*-butyl)ammonium halides (about 0.3 mmol) were dissolved in 10 mL of toluene and slowly added at room temperature to a solution of an equimolar quantity of the diphenyl-dialkenylgermanium compound 1 in 10 mL of the same solvent. After about 10 min the products started to precipitate from the clear solutions. Stirring was continued for 1.5 h. The suspensions

were filtered. The residues were evacuated to completely remove all volatiles.

### 3.3.1. $[Ph_2Ge\{C(AltBu_2)=CHPh\}_2Cl][N(n-Bu)_4]$ (2)

Yield: 86%. M.p. (sealed capillary, argon): 201 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 7.65 (s, 2H, CHPh), 7.58 (pseudo-d, 4H, ortho-H GePh<sub>2</sub>), 7.27 (pseudo-d, 4H, ortho-H CHPh), 7.15 (m, 4H, meta-H GePh<sub>2</sub>), 7.13 (m, 4H, meta-H CHPh), 7.09 (pseudo-t, 2H, para-H GePh<sub>2</sub>), 7.03 (pseudo-t, 2H, para-H CHPh), 3.19 (m, 8H, NCH<sub>2</sub>), 1.64 (m, 8H, NCH<sub>2</sub>CH<sub>2</sub>), 1.38 (m, 8H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.99 (t, 12H,  ${}^{3}J_{H-H}$  = 7.3 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.74 (s, 36H, CMe<sub>3</sub>).  ${}^{13}C$ NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta$  161.5 (CCHPh), 157.6 (CCHPh), 147.3 (ipso-C CHPh), 146.6 (ipso-C GePh<sub>2</sub>), 137.2 (ortho-C GePh<sub>2</sub>), 128.4 (ortho- and meta-C CHPh), 127.4 (meta-C GePh<sub>2</sub>), 127.1 (para-C GePh<sub>2</sub>), 126.6 (para-C CHPh), 59.3 (NC), 32.8 (CMe<sub>3</sub>), 24.5 (NCC), 20.6 (NCCC), 17.7 (CMe<sub>3</sub>), 13.9 (Me of *n*-Bu). IR (cm<sup>-1</sup>, nujol, CsI plates): 1829 vw. 1734 vw. 1699 w. 1657 vw. 1585 m. 1528 m v(C=C), phenyl; 1458 vs, 1377 vs (nujol); 1306 m, 1261 w  $\delta$  (CH<sub>3</sub>); 1171 m, 1153 m, 1107 w, 1078 m, 1026 m, 1005 m, 928 s, 885 m, 860 s, 812 s, 737 s v(CC), v(CN), δ (CC); 723 s (nujol); 700 m, 664 w, 623 m, 584 s, 523 m, 482 w, 465 m, 442 m v(AlC), v(GeC). Anal. Calc. for C<sub>60</sub>H<sub>94</sub>Al<sub>2</sub>ClGeN (991.4): C, 72.7; H, 9.6; N, 1.4. Found: C, 72.3; H, 9.5, N, 1.2%.

### 3.3.2. $[Ph_2Ge\{C(AltBu_2)=CHPh\}_2Br][N(n-Bu)_4]$ (3)

Yield: 83%. M.p. (sealed capillary, argon): 138 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 7.63 (s, 2H, CHPh), 7.62 (pseudo-d, 4H, ortho-H GePh<sub>2</sub>), 7.24 (pseudo-d, 4H, ortho-H CHPh), 7.14 (m, 4H, meta-H GePh<sub>2</sub>), 7.12 (m, 4H, meta-H CHPh), 7.07 (m, 2H, para-H GePh<sub>2</sub>), 7.02 (m, 2H, para-H CHPh), 3.23 (m, 8H, NCH<sub>2</sub>), 1.66 (m, 8H, NCH<sub>2</sub>CH<sub>2</sub>), 1.39 (m, 8H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.00 (t, 12H, <sup>3</sup>J<sub>H-</sub>  $_{\rm H}$  = 7.4 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.73 (s, 36H, CMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta$  161.7 (CCHPh), 157.7 (CCHPh), 147.7 (ipso-C CHPh), 146.9 (ipso-C GePh2), 137.3 (ortho-C GePh2), 128.5 (ortho- and meta-C CHPh), 127.5 (meta-C GePh<sub>2</sub>), 127.1 (para-C GePh<sub>2</sub>), 126.6 (para-C CHPh), 59.4 (NC), 32.9 (CMe<sub>3</sub>), 24.6 (NCC), 20.6 (NCCC), 17.9 (CMe<sub>3</sub>), 13.9 (Me of *n*-Bu). IR (cm<sup>-1</sup>, nuiol, CsI plates): 1655 m, 1599 m, 1574 m v(C=C), phenyl: 1466 vs, 1377 vs (nujol); 1304 m, 1265 w  $\delta$  (CH<sub>3</sub>); 1169 s, 1153 s, 1082 m, 1068 m, 1028 m, 1001 w, 922 m, 889 w, 854 w, 812 m v(CC), v(CN), δ (CC); 723 vs (nujol); 703 sh, 629 w, 584 m, 521 m, 465 s, 436 w v(AlC), v(GeC). Anal. Calc. for C<sub>60</sub>H<sub>94</sub>Al<sub>2</sub>BrGeN (1035.9): C, 69.6; H, 9.1; N, 1.4. Found: C, 69.9; H, 9.0, N, 1.4%.

### 3.4. Synthesis of MeAl[C(=CH-Ph)-SiPh<sub>2</sub>-C=C-Ph]<sub>2</sub> (**4**)

A solution of dimethylaluminum hydride (0.045 g, 0.776 mmol) in 10 mL of *n*-hexane was treated with a solution of diphenylbis(phenylethinyl)silane (0.298 g, 0.776 mmol) in 10 mL of n-hexane. The solution was heated under reflux for 4 h. All volatiles were removed in vacuum at room temperature. The residue was dissolved in a few mL of cyclopentane. Colorless crystals were obtained on cooling to -15 °C. Yield: 0.224 g (71%). M.p. (sealed capillary, argon): 75 °C (dec.). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 8.14 (s, 2H,  ${}^{3}J_{H-Si}$  = 13.5 Hz, CHPh), 8.00 (m, 8H, ortho-H Ph<sub>2</sub>Si), 7.50 (pseudo-d, 4H, ortho-H alkynyl-Ph), 7.31 (pseudo-d, 4H, ortho-H alkenyl-Ph), 7.25 (m, 8H, meta-H Ph<sub>2</sub>Si), 7.24 (m, 4H, para-H Ph<sub>2</sub>Si), 6.94 (m, 2H, para-H alkynyl-Ph), 6.92 (m, 4H, meta-H alkynyl-Ph), 6.85 (pseudo-t, 2H, para-H alkenvl-Ph), 6.65 (pseudo-t, 4H, meta-H alkenyl-Ph), -0.92 (s, 3H, AlCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta$  160.9 (CHPh), 155.9 (C=CHPh), 145.6 (ipso-C alkenyl-Ph), 136.4 (ortho-C Ph<sub>2</sub>Si), 135.6 (ipso-C Ph<sub>2</sub>Si), 132.6 (ortho-C alkynyl-Ph), 130.1 (meta-C alkenyl-Ph), 130.0 (para-C Ph<sub>2</sub>Si), 128.9 (para-C alkynyl-Ph), 128.6 (para-C alkenyl-Ph), 128.5 (meta-C alkynyl-Ph), 128.4 (meta-C Ph<sub>2</sub>Si), 125.7 (ortho-C alkenyl-Ph), 123.6 (*ipso-C* alkynyl-Ph), 110.3 (PhC=CSi), 91.9 (PhC=CSi), -7.2

#### Table 1

Crystal data and structure refinement for compounds 1-5.<sup>a,b</sup>

|   | 1   | 2  | <b>3</b> 1,2-F <sub>2</sub> C <sub>6</sub> H <sub>4</sub>  | <b>4</b> 1,2-F <sub>2</sub> C <sub>6</sub> H <sub>4</sub>   | 5   |
|---|---|--|--|---|---|
| Empirical formula<br>Temperature (K)<br>Crystal system<br>Space group [18]<br>a (pm)<br>b (pm)<br>c (pm)<br>$\alpha$ (°)<br>$\beta$ (°)<br>$\gamma$ (°)<br>V (nm <sup>3</sup> )<br>Z<br>$D_{calc}$ (g cm <sup>-3</sup> )<br>$\mu$ (mm <sup>-1</sup> )<br>Crystal size (mm)<br>$\Phi$ range for data collection (°)<br>Independent reflections ( $R_{int}$ ) | $\begin{array}{c} 1 \\ C_{44}H_{58}Al_2Ge \\ 153(2) \\ orthorhombic \\ Pccn (no. 54) \\ 1292.18(2) \\ 1631.96(3) \\ 1973.66(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 4.1620(1) \\ 4 \\ 1.139 \\ 1.598 (Cu K\alpha) \\ 0.45 \times 0.42 \times 0.21 \\ 4.36 \leqslant 72.57 \\ 4037 (0.0297) \end{array}$ | $\begin{array}{c} \textbf{2} \\ \hline \\ C_{60}H_{94}Al_2CIGeN \\ 153(2) \\ monoclinic \\ P2_1 (no. 4)^c \\ 1208.91(2) \\ 1986.45(2) \\ 1239.31(1) \\ 90 \\ 98.985(1) \\ 90 \\ 2.93961(6) \\ 2 \\ 1.120 \\ 1.667 (Cu K\alpha) \\ 0.41 \times 0.32 \times 0.28 \\ 3.61 \leqslant 72.62 \\ 9145 (0.0470) \end{array}$ | $\begin{array}{c} {\bf 3} \ 1,2\mbox{-}F_2C_6H_4 \\ \hline C_{66}H_{98}Al_2BrF_2GeN \\ 153(2) \\ triclinic \\ P\bar{1} \ (no.\ 2) \\ 1365.2(1) \\ 2284.47(7) \\ 2394.11(8) \\ 115.778(1) \\ 99.703(1) \\ 94.500(1) \\ 6.5297(7) \\ 4 \\ 1.170 \\ 1.150 \ (Mo \ K\alpha) \\ 0.16 \times 0.13 \times 0.05 \\ 1.54 \leqslant 27.79 \\ 30 \ 683 \ (0.0444) \\ \end{array}$ | $\begin{array}{c} {\bf 4} 1,2\text{-}F_2\text{C}_6\text{H}_4 \\ \hline C_{63}\text{H}_{48}\text{AlF}_2\text{Si}_2 \\ 153(2) \\ \text{triclinic} \\ P\bar{1} (no. 2) \\ 1206.16(5) \\ 1260.78(6) \\ 1903.96(9) \\ 105.883(3) \\ 96.349(3) \\ 109.903(3) \\ 2.5512(2) \\ 2 \\ 1.206 \\ 1.164 (\text{Cu K}\alpha) \\ 0.16 \times 0.08 \times 0.05 \\ 3.91 \leqslant 72.97 \\ 8632 (0.0376) \\ \end{array}$ | $\begin{array}{c} \textbf{5} \\ \hline \\ C_{36}H_{39}AlSi \\ 153(2) \\ monoclinic \\ Cc (no. 9)^c \\ 1683.15(2) \\ 1641.22(2) \\ 1128.80(1) \\ 90 \\ 94.988(1) \\ 90 \\ 3.10641(6) \\ 4 \\ 1.126 \\ 1.088 (Cu K\alpha) \\ 0.15 \times 0.13 \times 0.07 \\ 3.77 \leqslant 72.34 \\ 4951 (0.0245) \end{array}$ |
| Parameters  | 219   | 602  | 1297   | 624   | 350   |
| $R_1 [I > 2\sigma(I)]$  | 0.0327 (3798)   | 0.0699 (9005)  | 0.0592 (19 817)  | 0.0545 (5761)   | 0.0330 (47 60)  |
| $\Phi$ range for data collection (°)  | 4.36 ≤ 72.57  | 3.61 ≤ 72.62   | 1.54 ≤ 27.79   | $3.91 \leqslant 72.97$  | 3.77 ≤ 72.34  |
| Independent reflections ( $R_{int}$ )   | 4037 (0.0297)   | 9145 (0.0470)  | 30 683 (0.0444)  | 8632 (0.0376)   | 4951 (0.0245)   |
| Parameters  | 219   | 602  | 1297   | 624   | 350   |
| $W_{R_2}$ (All data)  | 0.0936  | 0.1788   | 0.1693   | 0.1549  | 0.0854  |
| Maximum/minimum residual electron density (10 <sup>30</sup> em <sup>-3</sup> )  | +0.606/-0.403   | +0.924/-0.775  | +1.631/-0.877  | +0.452/-0.259   | +0.253/-0.175   |
|   |   |  |  |   |   |

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

<sup>a</sup> Programme sheLxL-97 [20]; solutions by direct methods, full matrix refinement with all independent structure factors.

<sup>b</sup> See Supplementary material for CCDC reference numbers.

<sup>c</sup> Flack parameter: 0.00(2).

(CH<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta$  –28.4. IR (cm<sup>-1</sup>, nujol, Csl plates): 2156 m v(C=C); 2054 vw, 1954 w, 1892 w, 1825 vw, 1813 vw, 1771 vw, 1668 w, 1616 m, 1591 m, 1578 w, 1530 m, 1506 m v(C=C), phenyl; 1456 vs, 1377 s (nujol); 1334 sh, 1302 w, 1267 s  $\delta$  (CH<sub>3</sub>); 1206 m, 1179 m, 1155 m, 1105 s, 1076 m, 1024 m, 997 w, 966 w, 928 m, 893 s, 831 m, 800 m, 752 vs, 737 vs v(CC),  $\delta$  (CC); 700 s  $\delta$  (phenyl); 631 m, 615 w, 590 m, 565 m, 534 s, 494 s, 478 s, 467 s, 438 m, 411 s, 363 m, 334 w v(AlC), v(SiC),  $\delta$  (CC). MS (EI, 20 eV, 90 °C, m/z): 384 (100%) [Ph<sub>2</sub>Si(C=CH-Ph)(C=C-Ph)-H]<sup>+</sup>, 307 (42%) [PhSi(C=CH-Ph)(C=C-Ph)-H]<sup>+</sup>.

### 3.5. Synthesis of $tBu_2Al-C[=C(H)-Ph]-SiPh_2-C\equiv C-Ph$ (5)

A solution of compound 4 (0.278 g, 0.342 mmol) in 25 mL of toluene was treated with a solution of di(tert-butyl)aluminum hydride (0.097 g, 0.685 mmol) in 10 mL of toluene at room temperature. The solution was stirred for 4 h. All volatiles were removed in vacuum. The residue was dissolved in 1,2-difluorobenzene. Pale yellow crystals of 5 were obtained upon cooling of the solution to -15 °C. Yield: 0.254 g (71%). M.p. (sealed capillary, argon): 109 °C (dec.). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 300 K):  $\delta$  8.17 (s, 1H,  ${}^{3}J_{H-Si}$  = 13.7 Hz, CHPh), 8.00 (m, 4H, ortho-H Ph<sub>2</sub>Si), 7.51 (pseudo-d, 2H, ortho-H alkynyl-Ph), 7.27 (m, 4H, meta-H Ph<sub>2</sub>Si), 7.22 (m, 2H, para-H Ph<sub>2</sub>Si), 7.14 (pseudo-d, 2H, ortho-H alkenyl-Ph), 7.07 (pseudo-t, 2H, meta-H alkenyl-Ph), 6.97 (pseudo-t, 1H, para-H alkenyl-Ph), 6.92 (m, 2H, meta-H alkynyl-Ph), 6.91 (m, 1H, para-H alkynyl-Ph), 1.12 (s, 18H, CMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta$  158.8 (CHPh), 157.1 (C=CHPh), 146.8 (ipso-C alkenyl-Ph), 135.9 (ortho-C Ph<sub>2</sub>Si), 135.0 (ipso-C Ph<sub>2</sub>Si), 132.8 (ortho-C alkynyl-Ph), 130.8 (meta-C alkenyl-Ph), 130.1 (para-C Ph<sub>2</sub>Si), 129.6 (para-C alkynyl-Ph), 129.0 (para-C alkenyl-Ph), 128.6 (meta-C alkynyl-Ph), 128.5 (meta-C Ph<sub>2</sub>Si), 124.3 (ortho-C alkenyl-Ph), 122.7 (*ipso-C* alkynyl-Ph), 111.8 (PhC≡CSi), 92.1 (PhC≡CSi), 30.5 (CMe<sub>3</sub>), 19.4 (CMe<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ −34.5. IR (cm<sup>-1</sup>, nujol, CsI plates): 2156 m v(C≡C); 2122 m, 2033 vw, 1965 w, 1948 vw, 1890 vw, 1817 vw, 1769 vw, 1694 vw, 1653 vw, 1597 m, 1539 vw, 1506 m v(C=C), phenyl; 1460 vs, 1377 s (nujol); 1304 m, 1269 m δ (CH<sub>3</sub>); 1217 w, 1169 m, 1155 m, 1101 vs,

1072 vs, 1043 vs, 1024 vs, 928 m, 885 m, 847 m, 797 m, 752 vs, 737 s v(CC),  $\delta$  (CC); 721 s (nujol); 698 m  $\delta$  (phenyl); 627 m, 586 w, 523 s, 465 s, 420 w v(AlC), v(SiC),  $\delta$  (CC). MS (EI, 20 eV, 100 °C, m/z): 469 (17%) [M–Bu]<sup>+</sup>, 385 (91%) [M–AltBu<sub>2</sub>]<sup>+</sup>, 308 (100%) [PhSi(C=CH–Ph)(C=C–Ph)]<sup>+</sup>.

### 3.6. Crystal structure determinations

Single crystals were obtained by crystallization from *n*-hexane (20/-15 °C, 1), 1,2-difluorobenzene (20/-15 °C, 2 and 5) and cyclopentane with a small quantity of 1,2-difluorobenzene (20/+2 °C, **3**·1,2-C<sub>6</sub>F<sub>2</sub>H<sub>4</sub>; 20/-15 °C, **4**·1,2-C<sub>6</sub>F<sub>2</sub>H<sub>4</sub>). The crystallographic data were collected with a Bruker APEX diffractometer. The crystals were coated with a 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 Table 1. 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 molecules of compound **1** reside on a crystallographic twofold rotation axis with the germanium atom on a special position. Compound 3 has two independent molecules in the asymmetric unit. One of the 1,2-difluorobenzene molecules and a butyl group are disordered; their atoms were refined on split positions. The crystals of 4 enclose one molecule of 1,2-difluorobenzene per formula unit. A fluorine atom is disordered and occupies two positions. Only three hydrogen atoms were considered in this case.

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### Appendix A. Supplementary material

CCDC 808916–808920 contain the supplementary crystallographic data for **1–5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.02.070.

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