Hydroalumination of dialkynylgermanes—synthesis of alkenyl–alkynylgermanes with intramolecular aluminium–carbon interactions†‡

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Reactions of dialkylaluminium hydrides, R_2AlH [R = CH_2CMe_3, CMe_3, $CH(SiMe_3)_2$], with di(phenylethynyl)germanes, $R_2Ge(C{\equiv}C{-}C_6H_5)_2$ [R = CH_3 (**1**), C_6H_5 (**2**)], afforded mixed alkenyl–alkynylgermanes, $R_2Ge(C{\equiv}C{-}C_6H_5)[C(AlR_2){=}C(H){-}C_6H_5]$ (**3** to **7**), by hydroalumination of one of the C≡C triple bonds. In all cases the *cis*-arrangement of the Al and H atoms across the resulting C=C double bond was observed. Crystal structure determinations revealed relatively strong intramolecular bonding interactions between the coordinatively-unsaturated aluminium atoms and the α-carbon atoms of the intact triple bonds bearing a partial negative charge. This interaction is only prevented by application of the very bulky bis(trimethylsilyl)methyl substituent.

Introduction

Hydroalumination is a very effective method for the reduction of unsaturated organic compounds and the generation of a broad variety of mono- or oligonuclear aluminium compounds.[1,2] Recent investigations of our group into the hydroalumination of alkynes showed that in many cases the simple addition products, $R{-}C(H){=}C(AlR'_2){-}R''$, are only transient species which give very fast secondary reactions *via* condensation and release of the corresponding trialkylelement derivatives.[2] Carbaalane clusters[3] or cyclophane-type molecules with up to three aluminium atoms bridging two benzene rings[4,5] are the most prominent products of these reactions. Condensation was prevented with very small alkyl groups attached to aluminium (caused by polymerization),[5] by steric shielding with very bulky substituents[6] or with trimethylsilylethyne derivatives.[7,8] Similar results were obtained upon the addition of Ga–H bonds to alkynes.[8–11] But interestingly hydrogallation proved to be more selective than hydroalumination and more products could be isolated in a pure form. The latter method merits a broader application in preparative chemistry.

Trimethylsilylethynes gave relatively stable addition products[7,8,11] which have up to four coordinatively-unsaturated aluminium or gallium atoms in a single molecule and are applicable as chelating Lewis-acids.[12] So far we were very much focused on the application of benzene centred oligoalkynyl derivatives. In order to systematically change the properties of these oligoacceptors we started with investigations into the hydroalumination of silicon[13] or germanium centred dialkynes possessing a geminal arrangement of two triple bonds. These reactions have importance beyond the generation of simple acceptor molecules. Monoaddition products, for instance, have a coordinatively-unsaturated, highly Lewis-acidic aluminium atom in close proximity to the α-carbon atom of the alkynyl group which bears a relatively high negative charge. This may initiate secondary reactions by rearrangement similar to those observed for organoboron derivatives.[14] We report here on our first results obtained with germanium.

Results and discussion

Synthesis of di(phenylethynyl)germanium compounds

Two different di(phenylethynyl)germanium compounds [$R_2Ge(C{\equiv}C{-}C_6H_5)_2$; R = Me (**1**), C_6H_5 (**2**)] were generated by treatment of the corresponding diorganylgermanium dichlorides with two equivalents of phenylethynyllithium in diethyl ether/*n*-hexane solutions, eqn (1), according to a procedure published for the generation of the corresponding diethynylsilicon compounds.[15] After crystallization from *n*-pentane both products were isolated as colourless solids in 66 to 80% yields and characterized by NMR spectroscopy and mass spectrometry. The carbon atoms of the C≡C triple bonds have the expected chemical shifts in the ^{13}C NMR spectra [δ at about 90 (GeC) and 105]. Absorptions at about 2160 cm^{-1} in the IR spectra are characteristic of the ethynyl moiety. Crystal structure determination of **1** (Fig. 1) revealed an only slightly distorted tetrahedral surrounding of the germanium atom with bond angles between 106.5(1) and 114.3(1)°. The smallest angle is observed between the α-carbon atoms of the ethynyl groups, while the largest one occurs between the methyl substituents. The length of the C≡C triple bonds [119.7(3) pm] corresponds to the standard value.[16] The alkynyl groups are almost ideally linear with bond angles of 177.0(2)° (Ge–C1–C2) and 178.2(2)° (C1≡C2–C3). Only few structurally authenticated diethynylgermanium compounds

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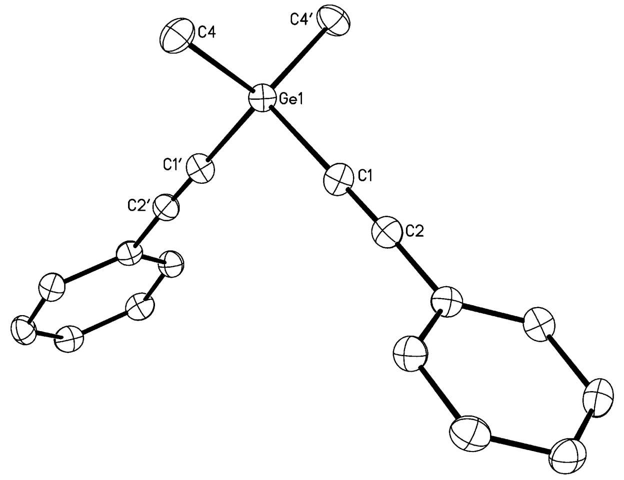
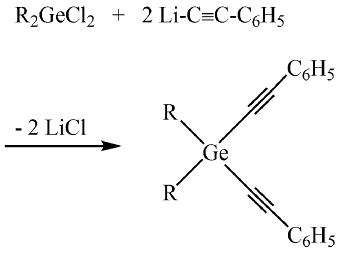


Fig. 1 Molecular structure of **1**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (pm) and angles (°): Ge(1)–C(1) 191.5(2), Ge(1)–C(4) 193.1(2), C(1)–C(2) 119.7(3), C(1)–Ge(1)–C(1)′ 106.5(1), C(1)–Ge(1)–C(4) 107.53(8), C(4)–Ge(1)–C(4)′ 114.3(1), Ge(1)–C(1)–C(2) 177.0(2), C(1)–C(2)–C(3) 178.2(2); C(1)′ and C(4)′ generated by $-x + 1$, y, $-z + 0.5$.

with relatively complicated molecular structures have been published in the literature.[17]

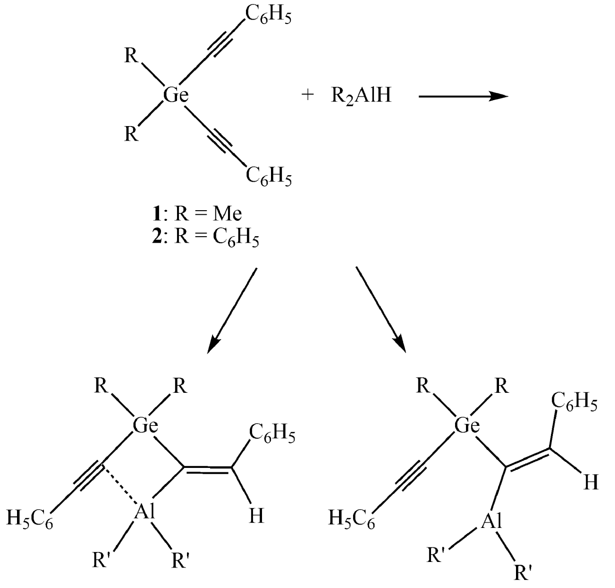


(1)

1: R = Me
2: R = C_6H_5

Reactions of the di(phenylethynyl)germanium compounds with dialkylaluminium hydrides

The di(phenylethynyl)germanium compounds **1** and **2** were treated with equimolar quantities of dialkylaluminium hydrides, R_2AlH [R = CH_2CMe_3, CMe_3, $CH(SiMe_3)_2$], in *n*-hexane as the solvent, eqn (2). Independently of the strongly differing steric shielding by the alkyl groups attached to aluminium the reactions are completed after about 4 h at room temperature. The colourless, solid products **3** to **7** were isolated in 55 to 87% yield. The compounds **3**, **5** and **6** decompose above 95 °C to give yellowish oils. Only the sterically most shielded bis(trimethylsilyl)methyl compounds **4** and **7** melt reproducibly without decomposition at 111 and 119 °C, respectively. This behavior may correlate to the different molecular structures in the solid state as discussed below. NMR spectra show the resonances of two different phenyl substituents as well as resonances characteristic of C=C double and C≡C triple bonds. This is in accordance with the selective hydroalumination of only one alkynyl group. Both signals of the ethenyl carbon atoms are in a narrow range between δ = 150 and 160 of the ^{13}C-NMR spectrum, while the carbon atoms of the ethynyl groups resonate at about δ = 112 (C–Ph) and 95 (C–Ge). The vinylic hydrogen atoms resulting from the addition of the Al–H bond to the triple bond have chemical shifts in the ^{1}H-NMR spectrum at δ = 8.0 to 8.5 which represents the normal range observed also for the hydroalumination products of silylethynyl derivatives.[7,8,11,13] Reactions of the dialkynylgermanes with dimethyl- and diethylaluminium hydrides yielded only mixtures of many unknown products which could not be separated. Diisobutylaluminium hydride gave the addition products in a relatively impure form. They could not be purified by recrystallization of the highly viscous raw products.



1: R = Me
2: R = C_6H_5

3: R = Me, R' = CMe_3
5: R = C_6H_5, R' = CH_2CMe_3
6: R = C_6H_5, R' = CMe_3

4: R = Me, R' = $CH(SiMe_3)_2$
7: R = C_6H_5, R' = $CH(SiMe_3)_2$

(2)

Compounds **3** and **5** to **7** were characterized by crystal structure determinations (Fig. 2–5). The central germanium atoms have a distorted tetrahedral coordination sphere and are bonded to two terminal methyl or phenyl substituents, an alkenyl and an intact alkynyl group. The C=C double (132 to 135 pm) and C≡C triple bond lengths (120 to 121 pm) correspond to standard values.[16] The aluminium atoms are bonded exclusively to the α-carbon atoms of the alkenyl groups even in the case of the very bulky bis[bis(trimethylsilyl)-methyl]aluminium substituent (**7**). The selective attack of the positively charged aluminium atoms at this particular position reflects the charge separation in the starting bisalkynes which results from the electronegativity difference between the sp-hybridized carbon atoms and germanium. The aluminium atom has an almost ideally planar surrounding only in the bis(trimethylsilyl)methyl compound **7** (deviation of the Al atom from the C_3 plane: 1.1 pm). In all other cases (**3**, **5** and **6**) the aluminium atoms deviate considerably from the plane spanned by the three directly bonded carbon atoms by 19.2 (**5**) and about 34 pm (**3** and **6**). The pyramidal configuration of the AlC_3 moieties is caused by an intramolecular interaction of the

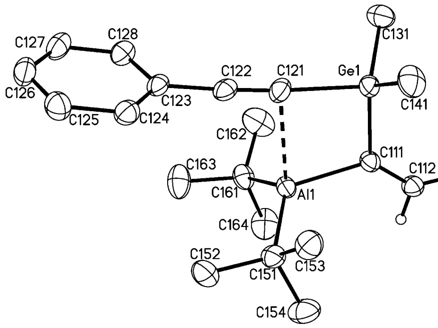


Fig. 2 Molecular structure of **3**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms with the exception of the vinylic hydrogen atom are omitted. Important bond lengths (pm) and angles (°) (values of the second molecule in square brackets): Al(1)–C(111) 198.1(2) [198.9(2)], Al(1)–C(121) 245.1(2) [240.5(2)], Ge(1)–C(111) 193.9(2) [193.8(2)], Ge(1)–C(121) 197.4(2) [198.0(2)], C(111)–C(112) 132.5(3) [132.6(3)], C(121)–C(122) 120.0(3) [120.2(3)], C(111)–Ge(1)–C(121) 94.02(8) [93.45(8)], Ge(1)–C(111)–Al(1) 100.82(8) [100.06(8)], Ge(1)–C(111)–C(112) 130.0(1) [127.7(1)], Ge(1)–C(121)–C(122) 175.3(2) [173.9(2)], C(121)–C(122)–C(123) 176.7(2) [176.9(2)].

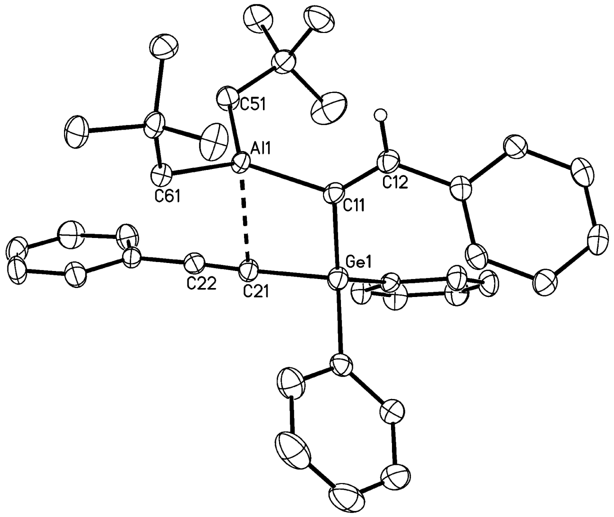


Fig. 3 Molecular structure of **5**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms with the exception of the vinylic hydrogen atom are omitted. Important bond lengths (pm) and angles (°): Al(1)–C(11) 199.4(2), Al(1)–C(21) 248.1(2), Ge(1)–C(11) 194.9(2), Ge(1)–C(21) 195.0(2), C(11)–C(12) 133.4(3), C(21)–C(22) 120.3(3), C(11)–Ge(1)–C(21) 93.21(7), Ge(1)–C(11)–Al(1) 102.26(8), Ge(1)–C(11)–C(12) 124.6(1), Ge(1)–C(21)–C(22) 176.5(2), C(21)–C(22)–C(23) 177.0(2).

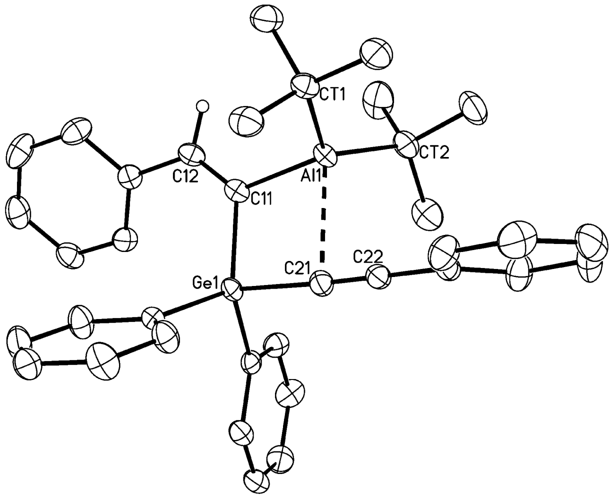


Fig. 4 Molecular structure of **6**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms with the exception of the vinylic hydrogen atom are omitted. Important bond lengths (pm) and angles (°): Al(1)–C(11) 199.6(2), Al(1)–C(21) 244.6(2), Ge(1)–C(11) 193.5(2), Ge(1)–C(21) 196.8(2), C(11)–C(12) 134.1(3), C(21)–C(22) 120.7(3), C(11)–Ge(1)–C(21) 93.46(9), Ge(1)–C(11)–Al(1) 101.2(1), Ge(1)–C(11)–C(12) 128.6(2), Ge(1)–C(21)–C(22) 177.5(2), C(21)–C(22)–C(23) 177.9(2).

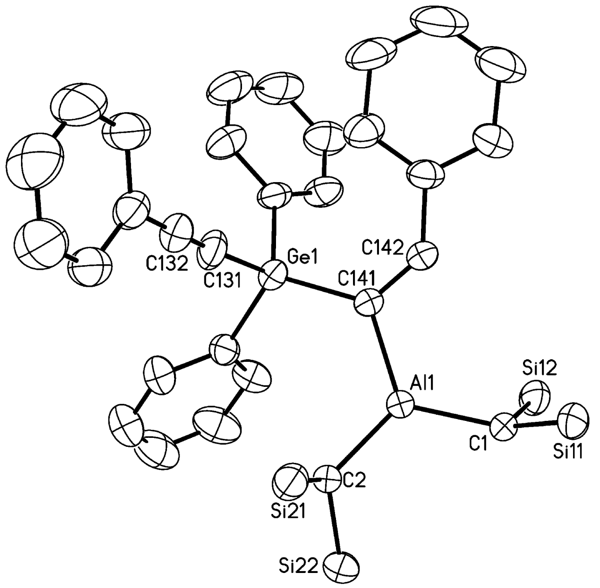


Fig. 5 Molecular structure of **7** (only one of the two independent molecules is shown). The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms with the exception of the vinylic hydrogen atom and methyl groups are omitted. Important bond lengths (pm) and angles (°) (values of the second molecule in square brackets): Al(1)–C(141) 198.1(3) [196.7(4)], Ge(1)–C(131) 189.3(4) [188.9(5)], Ge(1)–C(141) 193.8(3) [195.6(4)], C(131)–C(132) 121.4(6) [121.0(7)], C(141)–C(142) 134.6(5) [133.3(6)], C(131)–Ge(1)–C(141) 110.9(2) [113.0(2)], Ge(1)–C(141)–Al(1) 124.2(2) [122.3(2)], Ge(1)–C(141)–C(142) 124.9(3) [123.5(3)], Ge(1)–C(131)–C(132) 173.8(4) [174.9(6)], C(131)–C(132)–C(133) 179.0(5) [177.7(6)].

coordinatively-unsaturated metal atoms with the α-carbon atoms of the intact ethynyl groups which bear a partial negative charge (the β-carbon atom is too far apart for a significant bonding interaction due to the constraints of the AlCGeCC linkage). The resulting Al–C(α) distances (240.5 to 248.1 pm) are relatively long compared to the values of $<$200 pm for the terminal Al–C bonds, but the relevance of these interactions is underlined by several observations: (i) the aluminium atoms have a pyramidal configuration, (ii) the torsion angles across the Ge–C(vinyl) bonds [C(ethynyl)–Ge–C(ethenyl)–Al] are close to 0° in order to allow an optimum interaction, and (iii) the C–Ge–C angles between the α-carbon atoms of the ethenyl and ethynyl groups are relatively small (94°). Despite this significant interaction the Ge–C≡C groups deviate only slightly from linearity with angles of 173.8 to 179.0°. However, bending is not required because the Lewis-acidic aluminium atom may interact with a π-orbital essentially located at the negatively charged α-carbon atom of the triple bond. Similar interactions have been determined by NMR spectroscopy or crystal structure determinations for products of the hydroboration or hydroalumination of silicon centred bisalkynes.[13,14] The bulky bis(trimethylsilyl)methyl group prevents this interaction. The respective torsion angles across the Ge–C bonds (95.2°) indicate an almost perpendicular arrangement of the relevant groups, and the C–Ge–C bond angle between the ethenyl and ethynyl groups (112.0° on average) resembles the normal tetrahedral angle. IR spectroscopy allows a simple differentiation between both structural motifs. The bis(trimethylsilyl)methyl compounds have only one absorption for the C≡C stretching vibration, while two absorptions result for those compounds which have the intramolecular Al–C interaction. In all cases the H and Al atoms of the ethenyl groups adopt a *cis* arrangement, and *cis*/*trans* isomerisation[8,11] did not take place. Intermolecular activation is required to initiate this rearrangement process which may be prevented here by steric shielding and the intramolecular Al–C interaction.

Conclusion

Hydroalumination of diethynylgermanes with one equivalent of dialkylaluminium hydrides afforded mixed ethynyl–ethenyl germanium derivatives. An interaction between the coordinatively-unsaturated aluminium atoms and the α-carbon atoms of the remaining ethynyl groups was observed for compounds with relatively small R_2Al groups. The different structural motifs may influence the chemical properties of these compounds. An obvious difference is their thermal stability. While bis(trimethylsilyl)methyl derivatives exhibit a well defined melting point, all compounds having the intramolecular Al–C interaction decompose by the formation of a yellow oil. Compounds **3**, **5** and **6** are ideally preorganized to allow elimination of the corresponding dialkylaluminium alkynides which indeed was observed for hydroalumination reactions with diethynylphosphines.[18] Hence, these ethenyl–ethynyl germanes are interesting starting compounds for future investigations.

Experimental section

All procedures were carried out under purified argon. *n*-Hexane, *n*-pentane and cyclopentane were dried over $LiAlH_4$, diethyl ether over Na/benzophenone, and 1,2-difluoro- and pentafluorobenzene over molecular sieves (4 Å). The starting compounds $(tBuCH_2)_2AlH$,[19] tBu_2AlH[20] and $[(Me_3Si)_2CH]_2AlH$[21] were obtained according to literature procedures. Commercially available Cl_2GeMe_2 and $Cl_2Ge(C_6H_5)_2$ (Aldrich) were applied as purchased. Phenylethyne was dried over molecular sieves (4 Å). The assignment of the NMR spectra is based on HSQC, HMBC, ROESY and DEPT135 data.

Syntheses of the diethynylgermanium compounds $R_2Ge(C{\equiv}CPh)_2$ 1 (R = Me) and 2 (R = C_6H_5); general procedure

A solution of *n*-butyllithium (1.6 M) in *n*-hexane was added dropwise to a solution of equimolar quantities of phenylethyne (about 30 mmol) in 50 ml of diethyl ether at −78 °C. The mixture was stirred for 2 h, and half an equivalent of dimethyl- or diphenylgermanium dichloride (about 15 mmol) was added dropwise. After 2 h at −78 °C the mixture was warmed to room temperature and further stirred for 16 h. The suspension was treated with 100 ml of diluted aqueous HCl (10%) and 50 ml of diethyl ether. The organic phase was separated and the aqueous phase was extracted three times with 20 ml of diethyl ether. The combined organic phases were dried over $MgSO_4$ and filtrated. The solvent was removed under reduced pressure. The residue was recrystallized from *n*-pentane (20/−30 °C).

Characterization of $Me_2Ge(C{\equiv}CPh)_2$ 1

Yield 80%. Mp (argon, sealed capillary): 93 °C. Found C 70.4, H 5.5%. Calcd for $C_{18}H_{16}Ge$ C 70.9, H 5.3%. Mass spectrum (EI, 20 eV, 30 °C, only the most intense masses are given, the isotopic patterns are in complete agreement with the calculated ones): *m*/*z* (%) = 306 (100) $[M]^+$, 291 (88) $[M - CH_3]^+$, 175 (15) $[Ge(C{\equiv}CPh)]^+$. ^1H NMR (C_6D_6, 400 MHz): δ 0.59 (s, 6H, $GeCH_3$), 6.92 (m, 6H, *meta*-H, *para*-H), 7.47 (m, 4H, *ortho-H*). ^{13}C NMR (C_6D_6): δ 0.8 (CH_3), 91.0 (*C*CPh), 105.5 (C*C*Ph), 123.6 (*ipso*-C), 128.5 (*meta*-C), 128.7 (*para*-C), 132.3 (*ortho*-C). IR (Nujol, cm^{-1}): 2158 m ν(C≡C), 1888 vw, 1597 w (phenyl), 1463 vs, 1377 vs (Nujol), 1300 w, 1242 w δ(CH_3), 1215 m, 1155 w, 1070 w, 1024 m, 968 vw, 914 w, 885 vw, 843 m, 799 s, 754 vs ν(CC), 723 s (Nujol), 689 vs δ(phenyl), 665 w, 608 m, 584 s, 532 s ν(GeC).

Characterization of $Ph_2Ge(C{\equiv}CPh)_2$ 2

Yield 66%. Mp (argon, sealed capillary): 121 °C. Found C 78.2, H 4.7%. Calcd for $C_{28}H_{20}Ge$ C 78.4, H 4.7%. Mass spectrum (EI, 20 eV, 120 °C; only the most intense masses are given, the isotopic patterns are in complete agreement with the calculated ones): *m*/*z* (%) = 429 (100) $[M - H]^+$, 353 (88) $[M - Ph]^+$, 329 (56) $[M - C{\equiv}CPh]^+$, 276 (56) $[Ge(C{\equiv}CPh)_2]^+$. ^1H NMR (C_6D_6, 400 MHz): δ 6.87 (m, 4H, *meta-H* of alkynyl-Ph), 6.89 (m, 2H, *para-H* alkynyl-Ph), 7.16 (m, 2H, *para-H* of $GePh_2$), 7.18 (m, 4H, *meta-H* of $GePh_2$), 7.39 (m, 4H, *ortho-H* of alkynyl-Ph), 7.97 (m, 4H, *ortho-H* of $GePh_2$). ^{13}C NMR (C_6D_6, 100 MHz): δ 87.8 (*C*CPh), 107.9 (C*C*Ph), 123.2 (*ipso-C* of alkynyl-Ph), 128.5 (*meta-C* of alkynyl-Ph), 129.0 (*meta-C* of $GePh_2$, *para-C* of alkynyl-Ph), 130.3 (*para-C* of $GePh_2$), 132.6 (*ortho-C* of alkynyl-Ph), 134.4 (*ortho-C* of $GePh_2$), 134.8 (*ipso-C* of $GePh_2$). IR (Nujol, cm^{-1}): 2162 m ν(C≡C), 1890 vw, 1825 vw, 1595 w, 1574 w (phenyl), 1460 vs, 1377 s (Nujol), 1306 w, 1215 w, 1157 w, 1094 m, 1026 w, 970 vw, 914 w, 814 m, 754 m, 733 s ν(CC), 723 s (Nujol), 694 m δ(phenyl), 581 w, 532 m, 463 m ν(GeC).

Hydroalumination of di(phenylethynyl)germanium compounds; general procedure

A solution of the di(phenylethynyl)germanes **1** and **2** (about 0.6 to 0.8 mmol) in 10 ml of *n*-hexane was added to equimolar quantities of the corresponding dialkylaluminiumhydride dissolved in 10 ml of *n*-hexane. The mixture was stirred at room temperature for 4 h and became yellow in most cases. All volatiles were removed under reduced pressure. The residue was recrystallized from *n*-hexane (20/−30 °C, **3**), cyclopentane (20/+2 °C, **4**), pentafluorobenzene (20/−30 °C, **5**; 20/+2 °C, **7**) or difluorobenzene (20/−30 °C, **6**) to obtain colourless crystals.

Characterization of $Me_2Ge(C{\equiv}CPh)[C(Al\textit{t}Bu_2){=}C(H)Ph]$ 3

Yield 56%. Mp (argon, sealed capillary): 95 °C (dec). Found C 69.5, H 7.7%. Calcd for $C_{26}H_{35}GeAl$ C 69.8, H 7.9%. Mass spectrum (EI, 20 eV, 20 °C; only the most intense masses are given, the isotopic patterns are in complete agreement with the calculated ones): m/z (%) = 391 (100) $[M - CMe_3]^+$, 307 (10) $[M - Al\textit{t}Bu_2]^+$, 204 (81) $[Me_2GeC{\equiv}C\text{–}Ph - H]^+$. ^{1}H NMR ($C_6D_6$, 400 MHz): δ 0.61 (s, 6H, $GeMe_2$), 1.32 (s, 18H, CMe_3), 6.86 (m, 2H, *meta-H* alkynyl-Ph), 6.90 (m, 1H, *para-H* alkynyl-Ph), 7.05 (m, 1H, *para-H* alkenyl-Ph), 7.12 (m, 2H, *meta-H* alkenyl-Ph), 7.16 (m, 2H, *ortho-H* alkenyl-Ph), 7.52 (m, 2H, *ortho-H* alkynyl-Ph), 8.02 (s, 1H, C*H*Ph). ^{13}C NMR (C_6D_6, 100 MHz): δ 2.1 ($GeMe_2$), 19.2 ($\textit{C}Me_3$), 30.3 ($C\textit{Me}_3$), 93.6 ($\textit{C}{\equiv}CPh$), 116.4 ($C{\equiv}\textit{C}Ph$), 120.7 (*ipso-C* alkynyl-Ph), 127.1 (*ortho-C* alkenyl-Ph), 127.6 (*para-C* alkenyl-Ph), 128.7 (*meta-C* alkenyl-Ph, *meta-C* alkynyl-Ph), 130.8 (*para-C* alkynyl-Ph), 133.8 (*ortho-C* alkynyl-Ph), 142.7 (*ipso-C* alkenyl-Ph), 152.1 ($C{=}\textit{C}HPh$); 155.2 ($\textit{C}{=}CHPh$). IR (Nujol, cm^{-1}): 2158 m, 2114 m ν(C≡C), 1593 m, 1562 m, 1487 s ν(C=C), phenyl, 1462 vs, 1377 s (Nujol), 1238 m $\delta(CH_3)$, 1215 m, 1177 w, 1070 s, 1026 w, 1001 w, 918 m, 878 w, 835 s, 810 s, 756 s ν(CC), δ(CC), 691 s δ(phenyl), 625 w, 590 m, 536 m, 509 w, 436 w, 413 w, 382 w, 361 w ν(AlC), ν(GeC).

Characterization of $Me_2Ge(C{\equiv}CPh)(C[Al\{CH(SiMe_3)_2\}_2]{=}C(H)Ph)$ 4

Colourless, waxy solid, yield 72%. Mp (argon, sealed capillary): 111 °C. Mass spectrum (EI, 20 eV, 30 °C): m/z (%) = 493 (22) $[M - CH(SiMe_3)_2]^+$ (complete isotopic pattern in agreement with a calculated one). ^{1}H NMR (C_6D_6, 400 MHz): δ 0.05 (s, 2H, AlC*H*), 0.33 (s, 36H, $SiMe_3$), 0.54 (s, 6H, $GeMe_2$), 6.95 (m, 1H, *para-H* alkynyl-Ph), 6.99 (m, 2H, *meta-H* alkynyl-Ph), 7.05 (m, 1H, *para-H* alkenyl-Ph), 7.12 (m, 2H, *meta-H* alkenyl-Ph), 7.39 (m, 2H, *ortho-H* alkenyl-Ph), 7.53 (m, 2H, o*rtho-H* alkynyl-Ph), 8.19 (s, 1H, C*H*Ph). ^{13}C NMR (C_6D_6, 100 MHz): δ 3.3 ($GeMe_2$), 4.8 ($SiMe_3$), 10.1 (Al*C*H), 97.9 ($PhC{\equiv}\textit{C}Ge$), 107.8 ($Ph\textit{C}{\equiv}CGe$), 124.1 (*ipso-C* alkynyl-Ph), 127.7 (*ortho-C* alkenyl-Ph), 128.1 (*para-C* alkenyl-Ph), 128.5 (*meta-C* alkynyl-Ph), 128.6 (*para-C* alkynyl-Ph, *meta-C* alkenyl-Ph), 132.4 (*ortho-C* alkynyl-Ph), 142.8 (*ipso-C* alkenyl-Ph), 157.0 ($C{=}\textit{C}HPh$), 159.6 ($\textit{C}{=}CHPh$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −2.8. IR (neat, cm^{-1}): 3080 m, 3059 m, 3022 w, 2949 vs, 2897 vs, 2855 s, 2808 m ν(CH), 2154 vs ν(C≡C), 1946 vw, 1879 vw, 1803 vw, 1751 vw, 1670 vw, 1597 s, 1576 m, 1541 s, 1489 vs ν(C=C), phenyl, 1445 s, 1417 m, 1288 m, 1248 vs $\delta(CH_3)$, 1215 s, 1177 w, 1070 s ν(CC), 1013 m $\delta(CHSi_2)$, 932 m, 843 s, 777 m, 754 s $\rho(CH_3Si)$, 689 s, 677 s δ(phenyl), ν_{as}(SiC), 625 m, 606 m ν_s(SiC), 586 m, 575 m, 532 m, 505 w, 496 w, 476 w, 420 m, 380 w ν(AlC), ν(GeC).

Characterization of $Ph_2Ge(C{\equiv}CPh)[(AlNp_2){=}C(H)Ph]$ 5

Yield 61%. Mp (argon, sealed capillary): 112 °C (dec). Found C 75.4, H 7.1%. Calcd for $C_{38}H_{43}GeAl$ C 76.2, H 7.2%. Mass spectrum (EI, 20 eV, 60 °C; only the most intense masses are given, the isotopic patterns are in complete agreement with the calculated ones): m/z (%) = 431 (57) $[M - Al(CH_2CMe_3)_2]^+$, 252 (36) $[PhGe(CCPh)]^+$, 228 (100) $[Ph_2Ge]^+$. ^{1}H NMR (C_6D_6, 400 MHz): δ 0.88 (s, 4H, $AlC\textit{H}_2$), 1.31 (s, 18H, CMe_3), 6.87 (m, 2H, *meta-H* alkynyl-Ph), 6.88 (m, 1H, *para-H* alkynyl-Ph), 6.92 (m, 1H, *para-H* alkenyl-Ph), 6.95 (m, 2H, *meta-H* alkenyl-Ph), 7.12 (m, 2H, *para-H* $GePh_2$), 7.15 (m, 4H, *meta-H* $GePh_2$), 7.41 (m, 2H, *ortho-H* alkenyl-Ph), 7.43 (m, 2H, *ortho-H* alkynyl-Ph), 7.82 (m, 4H, *ortho-H* $GePh_2$), 8.27 (s, 1H, C*H*Ph). ^{13}C NMR spectrum (C_6D_6, 100 MHz): δ 31.9 ($\textit{C}Me_3$), 33.6 ($AlCH_2$), 35.2 ($C\textit{Me}_3$), 95.4 ($\textit{C}{\equiv}CPh$), 115.7 ($C{\equiv}\textit{C}Ph$), 121.0 (*ipso-C* alkynyl-Ph), 127.8 (*ortho-C* alkenyl-Ph), 128.0 (*para-C* alkenyl-Ph), 128.7 (*meta-C* alkenyl-Ph, *meta-C* alkynyl-Ph), 128.9 (*meta-C* $GePh_2$), 129.9 (*para-C* $GePh_2$), 130.4 (*para-C* alkynyl-Ph), 133.1 (*ortho-C* alkynyl-Ph), 135.0 (*ortho-C* $GePh_2$), 136.7 (*ipso-C* $GePh_2$), 142.5 (*ipso-C* alkenyl-Ph), 153.0 ($\textit{C}{=}CHPh$), 154.9 ($C{=}\textit{C}HPh$). IR (Nujol, cm^{-1}): 2162 s, 2127 m ν(C≡C), 1952 vw, 1879 vw, 1765 vw, 1697 w, 1647 vw, 1553 m ν(C=C), phenyl, 1458 vs, 1375 vs (Nujol), 1306 vw $\delta(CH_3)$, 1229 m, 1175 vw, 1157 w, 1125 vw, 1094 w, 1028 m, 918 m, 879 vw, 843 w ν(CC), δ(CC), 727 m (Nujol), 692 m δ(phenyl), 534 w, 509 vw, 461 m ν(AlC), ν(GeC).

Characterization of $Ph_2Ge(C{\equiv}CPh)[C(Al\textit{t}Bu_2){=}C(H)Ph]$ 6

Yield 55%. Mp (argon, sealed capillary): 125 °C (dec). Found C 74.8, H 6.9%. Calcd for $C_{36}H_{39}GeAl$ C 75.7, H 6.9%. Mass spectrum (EI, 20 eV, 120 °C; only the most intense masses are given, the isotopic patterns are in complete agreement with the calculated ones): m/z (%) = 515 (23) $[M - CMe_3]^+$, 431 (65) $[M - Al(CMe_3)_2]^+$, 353 (20) $[PhGe(CCPh)_2]^+$, 252 (36) $[PhGe(CCPh)]^+$, 228 (100) $[Ph_2Ge^+]$. ^{1}H NMR (C_6D_6, 400 MHz): δ 1.36 (s, 18H, CMe_3), 6.81 (m, 2H, *meta-H* alkynyl-Ph), 6.89 (m, 1H, *para-H* alkynyl-Ph), 6.93 (m, 1H, *para-H* alkenyl-Ph), 6.95 (m, 2H, *meta-H* alkenyl-Ph), 7.11 (m, 2H, *para-H* $GePh_2$), 7.13 (m, 4H, *meta-H* $GePh_2$), 7.42 (m, 2H, *ortho-H* alkenyl-Ph), 7.47 (m, 2H, *ortho-H* alkynyl-Ph), 7.80 (m, 4H, *ortho-H* $GePh_2$), 8.29 (s, 1H, C*H*Ph). ^{13}C NMR (C_6D_6, 100 MHz): δ 19.6 ($\textit{C}Me_3$), 30.9 ($C\textit{Me}_3$), 92.5 ($\textit{C}{\equiv}CPh$), 117.6 ($C{\equiv}\textit{C}Ph$), 120.6 (*ipso-C* alkynyl-Ph), 127.9 (*ortho-C* alkenyl-Ph), 128.1 (*para-C* alkenyl-Ph), 128.7 (*meta-C* alkenyl-Ph, *meta-C* alkynyl-Ph), 128.9 (*meta-C* $GePh_2$), 130.0 (*para-C* $GePh_2$), 131.0 (*para-C* alkynyl-Ph), 134.0 (*ortho-C* alkynyl-Ph), 135.0 (*ortho-C* $GePh_2$), 136.8 (*ipso-C* $GePh_2$), 142.1 (*ipso-C* alkenyl-Ph), 150.0 ($\textit{C}{=}CHPh$), 154.2 ($C{=}\textit{C}HPh$). IR (Nujol, cm^{-1}): 2160 w, 2141 w ν(C≡C), 1958 w, 1888 w, 1819 w, 1759 w, 1649 w, 1597 w ν(C=C), phenyl, 1458 vs, 1377 vs (Nujol), 1304 m, 1269 m $\delta(CH_3)$, 1157 m, 1086 s, 1026 m, 997 w, 966 w, 918 m, 891 w, 841 m, 812 m, 754 s ν(CC), $\delta(CH_3)$, 723 s (Nujol), 696 s

Table 1 Crystal data, data collection parameters, and structure refinement details for **1**, **3**, **5**, **6** and **7**

	1	**3**	**5**	**6**	**7**
Formula	$C_{18}H_{16}Ge$	$C_{26}H_{35}AlGe$	$C_{38}H_{43}AlGe$	$C_{36}H_{39}AlGe$	$C_{42}H_{59}AlGeSi_4$
Fw	304.90	447.11	599.29	571.24	775.82
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$ (No. 15)	$P2_12_12_1{}^a$ (No. 19)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z	4	8	4	2	4
a/pm	1625.68(3)	1100.26(2)	1003.03(2)	844.49(3)	1188.18(2)
b/pm	959.68(2)	1377.03(2)	3070.31(5)	991.62(4)	1763.70(3)
c/pm	1102.82(2)	3382.33(5)	1099.98(2)	2011.86(7)	2327.30(3)
α/°	90	90	90	87.777(2)	74.141(1)
β/°	118.958(1)	90	98.733(1)	87.692(2)	81.102(1)
γ/°	90	90	90	66.821(2)	79.039(1)
$V/10^{-30}$ m^3	1505.43(5)	5124.5(1)	3348.2(1)	1547.0(1)	4578.5(1)
T/K	153(2)	153(2)	153(2)	153(2)	153(2)
μ/mm^{-1}	2.609 (CuKα)	1.994 (CuKα)	1.655 (CuKα)	1.768 (CuKα)	2.281 (CuKα)
Unique rflns (R_{int})	1377 (0.0220)	9693 (0.0275)	5984 (0.0266)	5288 (0.0218)	15605 (0.0566)
$R1$ (reflns $I > 2\sigma(I)$)	0.0266 (1304)	0.0261 (9423)	0.0330 (5468)	0.0362 (4697)	0.0760 (12009)
wR_2 (all data)	0.0728	0.0686	0.0884	0.0996	0.2104
CCDC	762758	762760	762762	762761	762759

[a] Flack parameter: −0.007(12).

δ(phenyl), 667 m, 623 m, 577 w, 554 w, 534 w, 496 m, 461 m ν(AlC), ν(GeC).

Characterization of $Ph_2Ge(C{\equiv}CPh)[C(Al\{CH(SiMe_3)_2\}_2){=}C(H)Ph]$ 7

Yield 87%. Mp (argon, sealed capillary): 119 °C. Found C 64.0, H 7.5%. Calcd for $C_{42}H_{59}GeAlSi_4$ C 65.0, H 7.7%. Mass spectrum (EI, 20 eV, 140 °C; only the most intense masses are given, the isotopic patterns are in complete agreement with the calculated ones): m/z (%) = 617 (6) $[M - CH(SiMe_3)_2]^+$, 431 (72) $[M - AlR_2]^+$, 353 (25) $[PhGe(CCPh)_2]^+$, 329 (26) $[Ph_2GeCCPh]^+$, 252 (36) $[PhGe(CCPh)]^+$, 228 (100) $[Ph_2Ge]^+$. ^{1}H NMR (C_6D_6): δ −0.22 (s, 2H, AlC*H*), 0.31 (s, 36H, $SiMe_3$), 6.84 (m, 1H, *para-H* alkenyl-Ph), 6.94 (m, 2H, *meta-H* alkenyl-Ph), 6.99 (m, 3H, *meta-* and *para-H* alkynyl-Ph), 7.05 (m, 2H, *para-H* Ph_2Ge), 7.12 (m, 4H, *meta-H* Ph_2Ge), 7.58 (m, 2H, *ortho-H* alkynyl-Ph), 7.67 (m, 2H, *ortho-H* alkenyl-Ph), 7.84 (m, 4H, *ortho-H* Ph_2Ge), 8.48 (s, 1H, C*H*Ph). ^{13}C NMR (C_6D_6, 100 MHz): δ 4.8 ($SiMe_3$), 9.9 (AlCH), 93.8 (PhC≡*C*Ge), 109.8 (Ph*C*≡CGe), 123.9 (*ipso-C* alkynyl-Ph), 128.3 (*meta-C* alkenyl-Ph), 128.4 (*para-C* alkenyl-Ph), 128.62 (*meta-C* Ph_2Ge), 128.57 (*meta-C* alkynyl-Ph), 128.8 (*ortho-C* alkenyl-Ph), 128.9 (*para-C* alkynyl-Ph), 129.2 (*para-C* Ph_2Ge), 132.4 (*ortho-C* alkynyl-Ph), 134.8 (*ortho-C* Ph_2Ge), 138.9 (*ipso-C* Ph_2Ge), 141.1 (*ipso-C* alkenyl-Ph), 154.1 (*C*=CHPh), 160.6 (*C*HPh). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −3.0 ($SiMe_3$). IR (Nujol, cm^{-1}): 2160 m ν(C≡C), 1948 vw, 1875 vw, 1734 vw, 1690 w, 1647 vw, 1597 w, 1572 w, 1553 w, 1485 s ν(C=C), phenyl, 1454 vs, 1377 vs (Nujol), 1302 w, 1248 s δ(CH_3), 1215 w, 1155 w, 1092 m, 1051 w ν(CC), 1015 m δ($CHSi_2$), 926 m, 845 vs, 779 w, 754 m ρ(CH_3Si), 733 m (Nujol), 696 m, 675 m δ(phenyl), ν(SiC), 581 w, 532 w, 496 w, 467 m, 390 w ν(AlC), ν(GeC).

Crystal structure determinations

Single crystals were obtained by recrystallization from different solvents as described above. The crystallographic data were collected with a Bruker SMART 6000 diffractometer (CuK_α). 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 structures were solved by direct methods and refined with the program SHELXL-97[22] by a full-matrix least-squares method based on F^2. Crystal data, data collection parameters and structure refinement details are given in Table 1. The molecules of **1** are located on crystallographic twofold rotation axes with the germanium atoms on the special positions. Compounds **3** and **7** crystallize with two independent molecules. A phenyl group of **7** was disordered; the atoms were refined on split positions with site occupation factors of 0.54 and 0.46.

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