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Alkenyl-Alkynylgermanes Functionalised by Lewis Acids: Intramolecular Aluminium– and Gallium–Alkyne Interactions and Potential Ge–C Bond Activation

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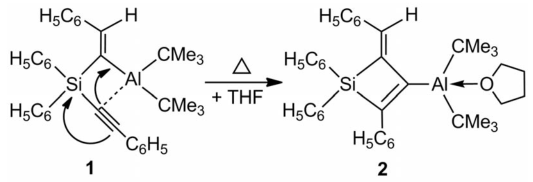
Treatment of various diethynylgermanes, $(R^1)_2Ge(C{\equiv}C–R^2)_2$ ($R^1 = C_6H_5$, CH_3; $R^1–R^1 = C_6H_4–C_6H_4$; $R^2 = CH_3$, CMe_3, *n*Bu, C_6H_5), with equimolar quantities of di(*tert*-butyl)aluminium or -gallium hydride, $R_2E–H$ (E = Al, Ga), afforded mixed alkenyl-alkynylgermanes, $(R^1)_2Ge(C{\equiv}C–R^2)[C\{E(CMe_3)_2\}{=}C(H)–R^2]$, by reduction of one of their C≡C triple bonds. The alkenyl groups have a *cis* arrangement of H and Al or Ga atoms across the C=C double bonds, which reflects the kinetically favoured situation. The *cis*/*trans* isomerisation is probably prevented from yielding thermodynamically favoured *trans* isomers; this is a result of an intramolecular bonding interaction between the α-carbon atoms of the remaining ethynyl groups and the coordinatively unsaturated metal atoms. The higher Lewis acidity of Al compared to Ga results in relatively short Al···C(ethynyl) contacts (>231.2 pm) and a concomitant lengthening of the Ge–C bonds.

Introduction

Silacyclobutenes exhibit pronounced photoluminescent properties[1] that, compared to silicon-free organic unsaturated compounds, resulted in a redshift of the fluorescence maxima, an increase of the Stokes' shifts and a decrease in quantum yields. 1,1-Carbaboration[2,3] and 1,1-carbalumination reactions[4] starting with alkynylsilanes proved to be powerful methods for their facile synthesis. These reactions proceeded by means of the insertion of the α-carbon atom of an alkynyl group into a B–C or Al–C bond and the concomitant formation of a Si–C bond to the β-carbon atom of the alkyne.[4] Although 1,1-carbaboration is a relatively common method for the synthesis of organoboranes,[2,3] 1,1-carbalumination has been reported for the first time only recently. Hydroalumination[5] of $(H_5C_6)_2Si(C{\equiv}C–C_6H_5)_2$ with $H–Al(CMe_3)_2$ afforded a mixed alkenyl-alkynylsilane (**1**) (Scheme 1), which in toluene at reflux slowly rearranged to yield silacyclobutene **2**.[4] Compound **2** was isolated as a THF adduct and had an unsaturated SiC_3 heterocycle with conjugated endocyclic and exocyclic C=C bonds and a dialkylaluminium group bonded to one of its ring carbon atoms (Scheme 1). Similar germacyclobutenes with unsaturated GeC_3 heterocycles are rare. One has been synthesised by treatment of an acetylene-bridged bis(germaethene) with 1,2-dicyanoethene,[6] the other one was obtained by dual hydroalumination of a tetraalkynylgermane with a sterically shielded hydride $R_2Al–H$ [R = $CH(SiMe_3)_2$] and heating of the resulting dialkenyl-dialkynylgermane to 260 °C for 10 min. The latter compound had two GeC_3 heterocycles joint by a germanium atom in a *spiro* position.[7] Inspired by the facile access to such heterocycles through hydrometallation of oligoalkynes followed by the thermally induced rearrangement of alkenyl-alkynyl intermediates we started systematic investigations into the synthesis and the properties of a broad variety of alkenyl-alkynylgermanes. The results, including the synthesis of important dialkynylgermanes, are reported in this article. This data may help to identify promising starting compounds for an application in 1,1-carbometallation or other secondary reactions.



Scheme 1. Generation of a silacyclobutene; the arrows show the movement of the carbon atoms.

Results and Discussion

Dialkynylgermanes $R_2Ge(C{\equiv}C–R')_2$

Dialkyl- and diaryl-dialkynylgermanes were obtained by standard procedures published previously for the synthesis of alkynylsilanes.[8] Treatment of dialkyl- or diarylgerma-

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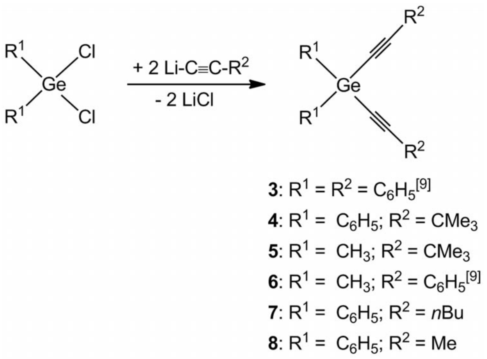
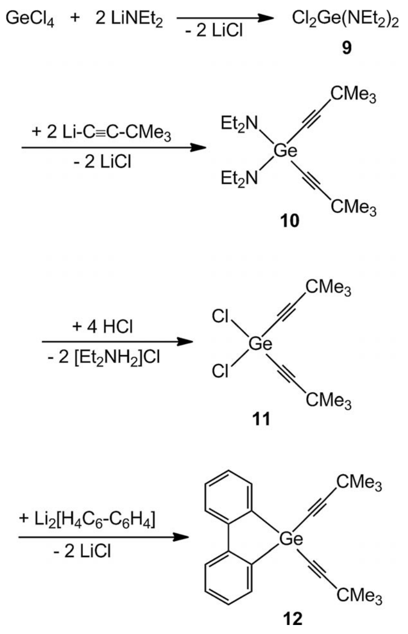
nium dichlorides with in situ generated lithium alkynides (2 equiv.) afforded the dialkynyl derivatives **3** to **8** by salt elimination in high yields (Scheme 2). The syntheses of **3** and **6** have been reported by our group previously.[9]



3: $R^1 = R^2 = C_6H_5$[9]
4: $R^1 = C_6H_5$; $R^2 = CMe_3$
5: $R^1 = CH_3$; $R^2 = CMe_3$
6: $R^1 = CH_3$; $R^2 = C_6H_5$[9]
7: $R^1 = C_6H_5$; $R^2 = n$Bu
8: $R^1 = C_6H_5$; $R^2 = Me$

Scheme 2. Syntheses of dialkynylgermanes.

The synthesis of 9-germafluorene-9,9-dichloride by treatment of $GeCl_4$ with equimolar quantities of biphenyl-2,2′-diyldilithium was reported in the literature,[10] but we were not able to reproduce this procedure and to obtain the pure chloride on this route. Instead we isolated mixtures with the *spiro* compound 9,9′-bis(germafluorene) that could not be separated by repeated recrystallisation. Therefore, we started with the dialkynyl-bis(diethylamine)germane **10** (Scheme 3), which is accessible by treatment of dichloride **9** with LiC≡C–CMe_3.[11] Compound **10** was transformed to dichloride **11** by reaction with HCl (yield 94%). Addition of biphenyl-2,2′-diyldilithium resulted in the formation of dialkynyl-9-germafluorenyl compound **12**, which was isolated as a colourless solid in high purity and 90% yield (55% overall yield based on $GeCl_4$). The dialkynylgermanes showed the expected spectroscopic parameters. The stretching vibrations of the C≡C triple bonds were observed in the IR spectra at about 2185 and 2150 cm^{-1}, and two resonances of ethynyl C atoms were detected in the characteristic range of the ^{13}C NMR spectra ($\delta \approx 115$ and 80 ppm). The molecular structure of **4** (Figure 1) revealed the standard C≡C bond lengths (120.0 pm on average) and almost linear Ge–C≡C–C groups (GeCC: 174.6°; CCC: 179.1°).



Scheme 3. Synthesis of the fluorenyl compound **12**.

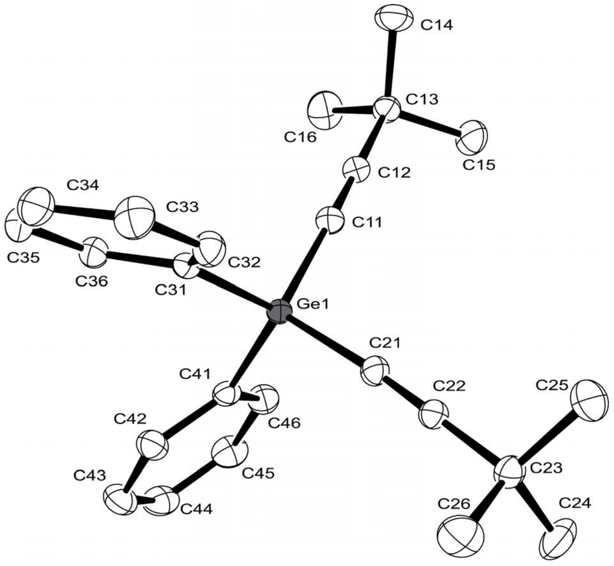
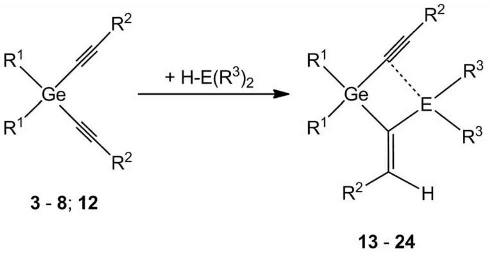


Figure 1. Molecular structure and numbering scheme of **4**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]: Ge1–C11 190.0(1), C11–C12 120.0(2), Ge1–C21 190.0(1), C21–C22 120.0(2); C11–Ge1–C21 109.59(5).

Hydroalumination and Hydrogallation of Dialkynylgermanes

The dialkynylgermanes were treated with H–$E(CMe_3)_2$ (E = Al, Ga) in a stoichiometric 1:1 ratio to yield the mixed alkenyl-alkynyl derivatives by addition of an E–H bond to one of the alkynyl groups (Scheme 4). The reactions proceeded in toluene under mild conditions and were finished within 3 to 21 h at room temperature. Recrystallisation of the crude products yielded the colourless alkenyl-alkynylgermanes in yields higher than 62%. The dimethylgermanium compounds **15** and **16** and the *n*-hexyne derivative **23** were generally isolated as highly viscous liquids. They were directly obtained in high purity, could be characterised unambiguously by spectroscopic methods and are applicable in secondary reactions without further purification. Crystals of **15** were obtained in a low yield of only 15% by crystallisation from 1,2-difluorobenzene. They were extremely air sensitive, pyrophoric and difficult to handle. Compounds **19**, **20** and **22** have been published by our group only recently.[9]



13: E = Al; $R^1 = C_6H_5$; $R^2 = CMe_3$; $R^3 = CMe_3$
14: E = Ga; $R^1 = C_6H_5$; $R^2 = CMe_3$; $R^3 = CMe_3$
15: E = Al; $R^1 = CH_3$; $R^2 = CMe_3$; $R^3 = CMe_3$
16: E = Ga; $R^1 = CH_3$; $R^2 = CMe_3$; $R^3 = CMe_3$
17: E = Al; $R^1,R^1 = H_4C_6\text{-}C_6H_4$; $R^2 = CMe_3$; $R^3 = CMe_3$
18: E = Ga; $R^1,R^1 = H_4C_6\text{-}C_6H_4$; $R^2 = CMe_3$; $R^3 = CMe_3$
19: E = Al; $R^1 = R^2 = C_6H_5$; $R^3 = CMe_3$[9]
20: E = Al; $R^1 = CH_3$; $R^2 = C_6H_5$; $R^3 = CMe_3$[9]
21: E = Ga; $R^1 = CH_3$; $R^2 = C_6H_5$; $R^3 = CMe_3$
22: E = Al; $R^1 = R^2 = C_6H_5$; $R^3 = CH_2CMe_3$[9]
23: E = Ga; $R^1 = C_6H_5$; $R^2 = n\text{Bu}$; $R^3 = CMe_3$
24: E = Ga; $R^1 = C_6H_5$; $R^2 = CH_3$; $R^3 = CMe_3$

Scheme 4. Synthesis of alkenyl-alkynylgermanes.

The NMR spectroscopic characterisation verified the reduction of a single alkynyl group of each bis-alkyne. ^{13}C NMR spectroscopic resonances were observed in the characteristic ranges of ethynyl (Ge–*C*≡C: δ = 79 to 95 ppm; Ge–C≡*C*: δ = 107 to 136 ppm; Table 1) and ethenyl moieties (Ge–*C*=C: δ = 136 to 159 ppm; Ge–C=*C*: δ = 148 to 169 ppm). However, the differences between the resonances of the α- (attached to Ge) and β-carbon atoms ($\Delta\delta$) are more pronounced than in the starting bis-alkynes. A comparison based on all compounds (**13** to **24**) gave two clearly separated areas for the ethynyl and ethenyl groups. The *tert*-butylethyne derivatives **13** to **18** have relatively large differences ($\Delta\delta$) of 38 to 55 ppm between the α- and β-carbon atoms of the ethynyl and 16 to 33 ppm for the ethenyl groups. In pairs of aluminium and gallium compounds the $\Delta\delta$ values of the aluminium compounds are larger. Smaller differences $\Delta\delta$ resulted for the phenyl-, methyl- and *n*-butylethynyl derivatives **19** to **24** ($\Delta\delta$ = 14 to 28 ppm and 2 to 10 ppm, respectively). These data reflect a larger charge separation in the *tert*-butylethynyl compounds,[12] which may essentially be caused by the strong inductive (+*I*) effect of the *tert*-butyl groups. Quantum chemical calculations with *tert*-butyl- and phenylethynyldimesitylphosphines[13] confirmed this hypothesis and gave natural bond orbital (NBO) charges of –0.49/+0.03 and –0.35/–0.004 for the α- and β-carbon atoms of the *tert*-butyl and phenyl compounds, respectively. The knowledge of the different charge distributions in the C=C and C≡C bonds of the alkenyl-alkynylgermanes (and the related silanes) may be highly valuable for their future application in secondary reactions and the prediction and evaluation of specific reactivity patterns. The chemical shifts of the α-carbon atoms of the *tert*-butylethenyl and -ethynyl groups of **13** to **18** are systematically shifted to a higher field, and those of the β-carbon atoms to a lower field relative to the values observed for compounds **19** to **24**. Most of the vinylic H atoms have chemical shifts in a narrow range between δ = 6.6 and 7.3 ppm. Only the phenylethynyl derivatives **19** to **22** deviate significantly and show stronger low-field shifts (δ = 7.7 to 8.3 ppm), which may be influenced by the ring current of the phenyl groups or mesomeric interactions. Usually two absorptions were observed for the stretching vibrations of the C≡C bonds in the IR spectra in narrow ranges at about 2150 and 2100 cm^{-1}. A single absorption was observed only for compounds **14**, **21** and **23** at 2122 to 2151 cm^{-1}. Compared to the starting dialkynylgermanes (2185 and 2150 cm^{-1}) a slight shift to smaller wavenumbers was observed, which may be indicative of the bridging positions of the alkynyl groups and their interaction to aluminium or gallium atoms. Accordingly, absorptions at 2164 and 2151 cm^{-1} were found in an alkenyl-alkynylgermanium compound (see the Introduction) in which bulky bis(trimethylsilyl)methyl groups prevented the interaction between Al atoms and the ethynyl groups.[7,9]

Seven compounds have been characterised by crystal structure determinations (**13–15**, **17**, **18**, **21** and **24**; Figures 2 and 3); the structures of the phenylethyne derivatives **19**, **20** and **22** have been reported in a previous publication.[9] The Ge atoms have a distorted-tetrahedral coordination sphere and are bound to two alkyl or aryl groups, an intact alkynyl substituent (C≡C: ≈120 pm) and a C=C

Table 1. Selected chemical shifts of the alkenyl-alkynylgermanium compounds **13** to **24** (δ in ppm).

	Element	Ge–*C*≡C α-C	Ge–C≡*C* β-C	$\Delta\delta$	Ge–*C*=C α-C	Ge–*C*=C β-C	$\Delta\delta$	Vinylic–H C=C–H	Ref.
13	Al	81.0	135.6	54.6	136.5	166.7	30.2	7.31	
14	Ga	81.4	121.5	40.1	141.2	163.8	22.6	6.85	
15	Al	81.2	134.7	53.5	140.6	164.0	23.4	7.04	
16	Ga	82.7	120.8	38.1	144.6	161.0	16.4	6.63	
17	Al	78.8	133.6	54.8	135.8	169.0	33.2	7.26	
18	Ga	79.4	120.4	41.0	139.2	165.9	26.7	6.83	
19	Al	92.5	117.6	25.1	150.0	154.2	4.2	8.29	[9]
20	Al	93.6	116.4	22.8	155.2	152.1	3.1	8.02	[9]
21	Ga	94.8	108.4	13.6	159.2	149.7	9.5	7.71	
22	Al	95.4	115.7	20.3	153.0	154.9	1.9	8.27	[9]
23	Ga	83.6	111.4	27.8	148.7	154.5	5.8	6.72	
24	Ga	83.1	106.8	23.7	150.0	148.2	1.8	6.70	

double bond (C=C: ≈134 pm, Table 2). The Al or Ga atoms are in geminal positions to Ge. The high regioselectivity of these reactions is caused by the electronegativity difference between Ge and the sp-hybridised C atoms, which induces a relatively high negative partial charge at the α-carbon atoms of the alkynyl groups. Similar results were obtained upon hydroalumination or hydrogallation of trimethylsilylalkynes.[14–16] Al or Ga atoms and the vinylic H atoms are in *cis* positions across the C=C double bonds, which represent the kinetically favoured arrangement and result from a concerted mechanism of the addition reaction.[15] Close intramolecular contacts were observed between the Al or Ga atoms and the α-carbon atoms of the ethynyl groups. They are considered in the schematic drawing of Scheme 4 and in Figures 2 and 3 as dashed lines. In accordance with the higher Lewis acidity of Al and the larger charge separation in the Al–C bonds, the Al···C(ethynyl) distances [231.2(2) to 244.6(1) pm] are expectedly shorter than the Ga···C(ethynyl) distances (269 pm on average, Table 2). The Al–C and Ga–C bond lengths to the terminal *tert*-butyl groups are about 200 pm. Particularly noteworthy is the short Al···C distance of 231.2(2) pm in **13** [238.1(2) pm in **15**], which represents the shortest distance detected so far in alkenyl-alkynylsilicon[17] or -germanium compounds.[9] Although usually these Al···C or Ga···C interactions do not significantly affect the linearity of the Si–C≡C or Ge–C≡C groups [angles >170°; 163.3(1)° for **15**], a relatively small angle of 154.4(1)° resulted for **13** [Al–C≡C 119.4(1)°]. This structural motif resembles that of a particular form of dimeric dialkylaluminium or -gallium alkynides with a short Al–C or Ga–C bond to the first metal atom (Ge–C in **13** to **24**), an almost linear E–C≡C group and a pseudo-side-on coordination of the ethynyl group to the second metal atom with a relatively long E–C distance to the α-carbon atom of the triple bond.[18] The Ge–C distances to the ethynyl group of **13** and **15** are slightly lengthened compared to biphenyl compound **17** [198.4(1) and 198.5(2) vs. 195.8(1) pm], which may indicate an activation of the Ge–C bond and may facilitate interesting secondary processes such as insertion or cyclisation reactions. Sterically demanding substituents attached to germanium may help to further activate these bonds. The relevance of the E···C interactions is underscored by additional structural details: (i) The torsion angles across the Ge–C-(vinyl) bonds are close to 0° (Table 2), which indicates a coplanar arrangement of the four atoms AlGeC$_2$ or GaGeC$_2$ and allows an optimum metal–carbon interaction. (ii) The angles C–Ge–C [94.3 (E = Al) and 97.0° (E = Ga), on average] deviate considerably from the tetrahedral angle and indicate some steric strain in the molecules. (iii) The Al and Ga atoms do not have a planar environment but are situated above the plane of the directly bonded C atoms (34.8 and 24.0 pm, respectively). Similar interactions have been determined by NMR spectroscopy or crystal structure determination for the hydroboration or hydroalumination products of silicon-centred bis-alkynes.[2,17] The intramolecular interactions may help to stabilise the kinetically favoured *cis*-addition products and prevent *cis*/*trans* rearrangement to form the thermodynamically favoured *trans* products.[15]

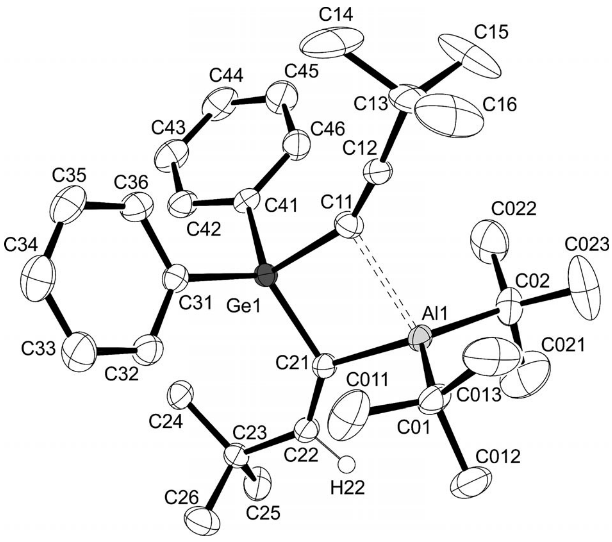


Figure 2. Molecular structure and numbering scheme of **13**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms with the exception of the vinylic hydrogen atom are omitted. Similar structures were observed for compounds **14**, **15**, **21** and **24** (Table 2).

Table 2. Selected structural parameters of the mixed alkenyl-alkynylgermanes **13**, **14**, **15**, **17**, **18**, **21** and **24**.

	Element	C≡C [pm]	C=C [pm]	E···C [pm]	C–Ge–C–E [°]	Ge–C≡C [°]	C–Ge–C [°][a]	EC$_3$ [pm][b]
13	Al	120.5(2)	134.0(2)	231.2(2)	0.80(6)	154.4(1)	93.95(6)	32.9
14	Ga	120.3(2)	133.8(2)	272.7(2)	–7.61(6)	171.1(1)	98.38(5)	23.7
15	Al	120.6(2)	133.4(2)	238.1(2)	3.0(2)	163.3(1)	94.24(6)	35.5
17	Al	121.0(2)	133.7(2)	244.6(1)	–0.81(6)	169.4(1)	94.57(5)	36.0
18	Ga	120.2(3)	133.7(2)	273.3(2)	–0.99(7)	175.0(2)	98.24(8)	25.4
21	Ga	120.6(3)	133.6(3)	261.6(2)	0.2(1)	175.9(2)	95.71(9)	24.1
		120.9(3)	133.5(3)	268.2(2)	–2.4(1)	177.5(2)	96.64(8)	23.2
24	Ga	120.2(2)	133.8(2)	267.6(2)	3.96(8)	175.5(1)	96.73(7)	23.6
		119.4(2)	133.5(2)	272.1(2)	0.83(8)	172.6(1)	96.52(7)	23.8

[a] Angle between the α-carbon atoms of the double and triple bonds. [b] Deviation of E from the plane formed by three directly bonded carbon atoms.

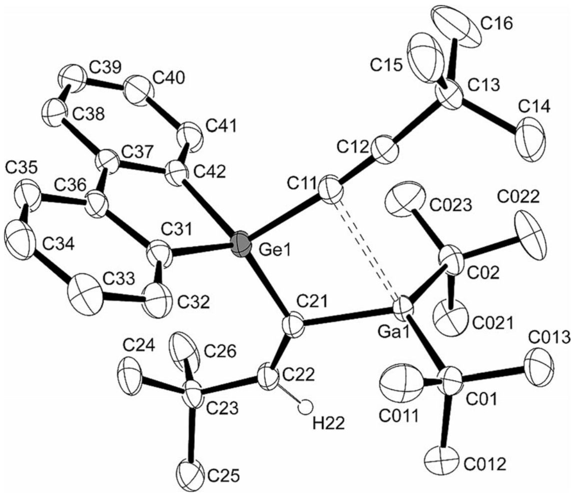


Figure 3. Molecular structure and numbering scheme of the biphenyl derivative **18**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms with the exception of the vinylic hydrogen atom are omitted. A similar structure was observed for compound **17** (Table 2).

Conclusion

Hydroalumination of various dialkynylgermanes with H–E$(CMe_3)_2$ (E = Al, Ga) afforded a broad variety of mixed alkenyl-alkynylgermanes (**13** to **24**). Their structures exhibit an intramolecular interaction of the coordinatively unsaturated Al and Ga atoms with the α-carbon atoms of the remaining alkynyl groups. These interactions are stronger in the Al compounds, reflect the higher Lewis acidity of Al compared to Ga and result in relatively short Al–C distances. A lengthening of the Ge–C(alkynyl) bond was observed in some cases. It may help to activate the Ge–alkynyl bond and to facilitate secondary reactions such as the 1,1-carbometallation, which was discussed above (see the Introduction). Similar compounds with an amine group bonded to Ge and coordinatively unsaturated Ga atoms showed a strong intramolecular Ga–N interaction by means of the lone pair of electrons at N. The significant weakening of the Ge–N bond was derived from quantum chemical calculations and resulted in a facile amine-alkynyl exchange by C–H and Ge–N bond activation.[11] Systematic investigations of the spectroscopic properties of the alkenyl-alkynylgermanes **13** to **24** revealed remarkable tendencies in the ^{13}C NMR spectra. The chemical-shift differences between both carbon atoms of the C=C and C≡C bonds strongly depend on the substituents in the β position. Relatively large differences of 25 and 47 ppm were observed for the *tert*-butylalkynyl derivatives, whereas almost independently of the substituents in the β position (*n*Bu, Me, Ph) all other compounds showed differences of only 4 and 22 ppm. These results indicate a larger charge separation in the *tert*-butylalkynyl derivatives, which may considerably influence the reactivity of these compounds and may allow the prediction of specific reaction courses. Preliminary results verify the applicability of these compounds for the thermally induced formation of germacyclobutenes and show a strong correlation between reactivity and ^{13}C NMR spectroscopic shift differences.

Experimental Section

General: All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane, *n*-pentane and cyclopentane with $LiAlH_4$; 1,2-difluorobenzene with molecular sieves; toluene, diethyl ether and THF with Na/benzophenone). $(Me_3C)_2Al$–H,[19] $(Me_3C)_2Ga$–H,[20] $Cl_2Ge(NEt_2)_2$ (**9**)[11] and $(Et_2N)_2Ge(C{\equiv}C{-}CMe_3)_2$ (**10**)[11] were obtained according to literature procedures. Commercially available $GeCl_4$ (99.9%, ABCR), $Cl_2Ge(C_6H_5)_2$ (95%, ABCR), Cl_2GeMe_2 (99%, ABCR), *tert*-butylethyne, 2,2′-dibromobiphenyl, 1-hexyne, Br–Mg–C≡C–CH_3 and diethylamine were employed as purchased. The assignment of the NMR spectra is based on HMBC, heteronuclear single quantum coherence (HSQC), ROESY and distortionless enhancement by polarization transfer (DEPT135) data.

$(H_5C_6)_2Ge(C{\equiv}C{-}CMe_3)_2$ (4): A solution of *n*-butyllithium in *n*-hexane (1.6 M, 11.0 mL, 17.6 mmol, a small excess amount) was added slowly to a solution of *tert*-butylethyne (2.06 mL, 1.38 g, 16.8 mmol) in diethyl ether (50 mL) at –78 °C. The resulting solution was warmed slowly to room temperature (16 h) and again cooled to –78 °C. A solution of diphenylgermanium dichloride (2.50 g, 8.4 mmol) in diethyl ether (10 mL) was added slowly. The mixture was stirred for 2 h, slowly warmed to room temperature and treated with a solution of HCl in water (10%) to dissolve the precipitate of LiCl. The organic phase was separated, and the aqueous phase was extracted three times with diethyl ether (20 mL). The combined organic phases were dried with $MgSO_4$. The solvent was removed under vacuum, and the remaining yellow oil was recrystallised from cyclopentane (20/–20 °C) to yield **4** as a colourless solid, yield 2.58 g (79%), m.p. (argon; sealed capillary) 78 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.13 [s, 18 H, $C(CH_3)_3$], 7.13 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, *para*-H Ph), 7.19 (t, $^3J_{H,H}$ = 7.2 Hz, 4 H, *meta*-H Ph), 7.96 (dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.4 Hz, 4 H, *ortho*-H Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 28.5 [$\mathit{C}(CH_3)_3$], 30.9 [$C(\mathit{C}H_3)_3$], 76.1 (Ge*C*≡C), 117.7 (GeC≡*C*), 128.7 (*meta*-C Ph), 129.8 (*para*-C Ph), 134.2 (*ortho*-C Ph), 136.3 (*ipso*-C Ph) ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2181 (s), 2147 (s) [ν(C≡C)]; 2113 (m), 1989 (vw), 1964 (m), 1946 (vw), 1909 (w), 1890 (m), 1847 (sh), 1826 (m), 1775 (m), 1711 (vw), 1661 (m), 1618 (w), 1597 (vw), 1570 (vw), 1558 (vw) (phenyl); 1481 (vw), 1466 (sh), 1454 (vs), 1433 (sh), 1377 (vs) (nujol); 1361 (vs), 1308 (m), 1252 (vs) [δ(CH_3)]; 1204 (s), 1186 (m), 1156 (w), 1091 (vs), 1026 (s), 999 (m), 974 (w), 918 (vs), 860 (vw), 779 (w) [ν(CC)]; 750 (s), 735 (s) (phenyl); 721 (m) (nujol); 696 (vs) (phenyl); 673 (m), 617 (w), 549 (w), 486 (s), 463 (s) [ν(GeC)] cm^{-1}. MS (EI, 20 eV, 298 K): *m*/*z* (%) = 390 (8) [M$^+$], 375 (23) [M$^+$ – CH_3], 333 (90) [M$^+$ – $C(CH_3)_3$], 309 (100) [M$^+$ – $CCC(CH_3)_3$], 228 (26) [M$^+$ – 2 $CCC(CH_3)_3$]. $C_{24}H_{28}Ge$ (389.1): calcd. C 74.1, H 7.3; found C 74.5, H 7.4.

$(H_3C)_2Ge(C{\equiv}C{-}CMe_3)_2$ (5): A solution of *n*-butyllithium in *n*-hexane (1.6 M, 16.9 mL, 27 mmol, a small excess amount) was added dropwise to a solution of *tert*-butylethyne (3.2 mL, 2.13 g, 26 mmol) in diethyl ether (50 mL) at –80 °C. The mixture was stirred for 1 h and warmed to room temperature. Stirring was continued for 3 h, and the mixture was cooled to –80 °C. A solution of dimethylgermanium dichloride (1.5 mL, 2.26 g, 13 mmol) in diethyl ether (10 mL) was added. After 1 h the mixture was warmed to room temperature and further stirred for 18 h. The suspension was treated with an aqueous solution of HCl (10%) to dissolve LiCl.

The organic phase was separated, and the aqueous phase was extracted four times with diethyl ether (20 mL). The combined organic phases were dried with $MgSO_4$ and filtered. The solvent was removed under vacuum. Compound **5** was obtained as a colourless solid after sublimation under vacuum, yield 2.13 g (62 %), m.p. (argon; sealed capillary) 47 °C. ^1H NMR (400 MHz, C_6D_6): δ = 0.50 [s, 6 H, $(CH_3)_2Ge$], 1.15 [s, 18 H, $C(CH_3)_3$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 1.4 [$(CH_3)_2Ge$], 28.3 [$GeCC\mathit{C}(CH_3)_3$], 31.1 [$GeCCC(\mathit{C}H_3)_3$], 79.2 ($Ge\mathit{C}{\equiv}C$), 114.6 ($GeC{\equiv}\mathit{C}$) ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2183 (s), 2151 (s) [$\nu(C{\equiv}C)$]; 2116 (w), 1861 (vw), 1840 (vw); 1458 (vs), 1375 (s), 1362 (s) (nujol); 1252 (s) [$\delta(CH_3)$]; 1204 (m), 1169 (w), 1096 (w), 1030 (w), 918 (m), 839 (m), 816 (s), 750 (s) [ν(CC)]; 723 (m) (nujol); 617 (m), 594 (m), 550 (w), 480 (m), 401 (m) [ν(GeC)] cm^{-1}. MS (EI, 20 eV, 298 K): m/z (%) = 266 (12) [M^+], 251 (100) [$M^+ - CH_3$], 209 (13) [$M^+ - C(CH_3)_3$]. $C_{14}H_{24}Ge$ (265.0): calcd. C 63.5, H 9.1; found C 63.5, H 9.2.

$(H_5C_6)_2Ge(C{\equiv}C{-}C_4H_9)_2$ (7): Compound **7** was obtained by a procedure similar to that one given above for the synthesis of **5**. It was isolated as a slightly orange oil that was directly applied for further reactions, yield 3.06 g (83 %). ^1H NMR (400 MHz, C_6D_6): δ = 0.72 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, $CH_2CH_2CH_2C\mathit{H}_3$), 1.27 (m, 4 H, $CH_2C\mathit{H}_2C\mathit{H}_2CH_3$), 2.06 (t, $^3J_{H,H}$ = 6.8 Hz, 4 H, $C\mathit{H}_2CH_2CH_2CH_3$), 7.14 (m, 2 H, *para*-H Ph), 7.20 (t, $^3J_{H,H}$ = 7.2 Hz, 4 H, *meta*-H Ph), 7.97 (d, $^3J_{H,H}$ = 6.8 Hz, 4 H, *ortho*-H Ph) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 13.6 ($CH_2CH_2CH_2\mathit{C}H_3$), 19.9 ($\mathit{C}H_2CH_2CH_2CH_3$), 22.2 ($CH_2CH_2\mathit{C}H_2CH_3$), 30.8 ($CH_2\mathit{C}H_2CH_2CH_3$), 78.1 ($GeC{\equiv}\mathit{C}$), 109.6 ($GeC{\equiv}\mathit{C}$), 128.7 (*meta*-C Ph), 129.9 (*para*-C Ph), 134.2 (*ortho*-C Ph), 136.1 (*ipso*-C Ph) ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2178 (s) [$\nu(C{\equiv}C)$]; 1954 (w), 1896 (w), 1881 (w), 1815 (w), 1763 (w), 1647 (w), 1585 (w) (phenyl); 1483 (s), 1458 (vs), 1433 (vs), 1377 (vs) (nujol); 1364 (s), 1354 (sh), 1321 (m), 1302 (m), 1267 (w), 1248 (w) [$\delta(CH_3)$]; 1186 (m), 1157 (w), 1096 (s), 1065 (w), 1026 (m), 999 (m), 974 (w), 947 (m), 925 (w), 914 (w), 897 (w), 853 (m) [ν(CC)]; 735 (s) (nujol); 696 (s), 675 (m) (phenyl); 571 (m), 552 (m), 469 (s), 424 (w) [ν(Ge–C)] cm^{-1}. MS (EI, 20 eV, 333 K): m/z (%) = 390 (36) [M^+], 362 (15) [M^+ – ethene], 348 (75) [M^+ – propene], 334 (100) [M^+ – butene].

$(H_5C_6)_2Ge(C{\equiv}C{-}CMe)_2$ (8): A solution of diphenylgermanium dichloride (2.0 mL, 2.8 g, 9.4 mmol) in diethyl ether (10 mL) was added dropwise to a solution of 1-propynylmagnesium bromide in THF (0.5 M, 38.0 mL, 19.0 mmol) at 0 °C. The solution was warmed to room temperature, stirred for 1 h and heated under reflux conditions for 1 h. After cooling to room temperature the resulting suspension was treated with diethyl ether (40 mL) and a solution of HCl in water (10 %) to dissolve MgX_2. The organic phase was separated, and the aqueous phase was extracted two times with diethyl ether (20 mL). The combined organic phases were dried with $MgSO_4$. The solvent was removed under vacuum, and the remaining brown oil was recrystallised from *n*-pentane/diethyl ether (20/–30 °C) to yield **8** as a colourless solid, yield 2.10 g (73 %), m.p. (argon; sealed capillary) 74 °C. ^1H NMR (400 MHz, C_6D_6): δ = 1.50 (s, 1 H, CH_3), 7.14 (m, 2 H, *para*-H Ph), 7.19 (m, 4 H, *meta*-H Ph), 7.91 (d, $^3J_{H,H}$ = 7.4 Hz, 4 H, *ortho*-H Ph) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 4.6 ($C{\equiv}C\mathit{C}H_3$), 77.5 ($\mathit{C}{\equiv}CCH_3$), 104.9 ($C{\equiv}\mathit{C}CH_3$), 128.8 (*meta*-C Ph), 129.9 (*para*-C Ph), 134.2 (*ortho*-C Ph), 135.8 (*ipso*-C Ph) ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2185 (vs), 2143 (m) [$\nu(C{\equiv}C)$]; 2122 (sh), 2039 (m), 2012 (m), 1985 (w), 1965 (m), 1913 (w), 1892 (m), 1827 (m), 1775 (m), 1726 (m), 1713 (w), 1661 (s), 1645 (m), 1630 (w), 1597 (w), 1566 (s), 1553 (s) (phenyl); 1489 (s) (nujol); 1431 (m), 1406 (w) [$\delta(CH_3)$]; 1381 (w) (nujol); 1337 (vw), 1310 (m), 1267 (m) [$\delta(CH_3)$]; 1186 (m), 1168 (w), 1155 (w), 1092 (s), 1065 (w), 1013 (m), 997 (m), 976 (w), 922 (w), 856 (w), 770 (w) [ν(CC)]; 739 (s) (nujol); 696 (m), 671 (m) (phenyl); 619 (w), 468 (s), 430 (vw), 415 (w) [ν(Ge–C)] cm^{-1}. MS (EI, 20 eV, 313 K): m/z (%) = 306 (100) [M^+], 292 (67) [$M^+ - CH_3 + H$], 268 (14) [$M^+ - CCCH_3 + H$]. $C_{18}H_{16}Ge$ (305.0): calcd. C 70.9, H 5.3; found C 70.7, H 5.3.

$Cl_2Ge(C{\equiv}C{-}CMe_3)_2$ (11): A solution of HCl in diethyl ether (1.0 M, 47 mL, 47 mmol) was added dropwise to a vigorously stirred solution of **10** (4.50 mL, 4.06 g, 10.7 mmol) in *n*-hexane (50 mL) at room temperature. A colourless solid precipitated immediately. Stirring was continued for 16 h. The suspension was filtered, and the solvent was removed under vacuum. Compound **11** was obtained as a colourless solid in a high purity, yield 3.08 g (94 %), m.p. (argon; sealed capillary) 66 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.29 [s, 18 H, $C(CH_3)_3$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 28.5 [$GeCC\mathit{C}(CH_3)_3$], 30.2 [$GeCCC(\mathit{C}H_3)_3$], 75.1 [$Ge\mathit{C}CC(CH_3)_3$], 117.9 [$GeC\mathit{C}C(CH_3)_3$] ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2193 (s), 2158 (s), 2129 (sh) [$\nu(C{\equiv}C)$]; 1458 (vs), 1377 (vs), 1364 (vs) (nujol); 1302 (w), 1252 (s) [$\delta(CH_3)$]; 1202 (m), 1153 (w), 1109 (w), 1030 (w), 964 (vw), 928 (m), 889 (vw), 845 (vw), 758 (s) [ν(CC)]; 721 (m) (nujol); 556 (w), 505 (m), 490 (m), 424 (s), 415 (m) [ν(Ge–C)] cm^{-1}. MS (EI, 20 eV, 300 K): m/z (%) = 289 (4), 291 (6), 293 (4) [$M^+ - CH_3$], 269 (7), 271 (9), 273 (4) [M^+ – Cl], 162 (17) {$[CCC(CH_3)_3]_2^+$}, 81 (100) [$CCC(CH_3)_3$].

$(H_4C_6{-}C_6H_4)Ge(C{\equiv}C{-}CMe_3)_2$ (12): 2,2′-Dibrombiphenyl (3.15 g, 10.1 mmol) was dissolved in diethyl ether (50 mL) and treated with a solution of *n*-butyllithium in *n*-hexane (1.6 M, 12.6 mL, 20.2 mmol) at –80 °C. After 1 h the mixture was warmed to room temperature and stirred for 5 h. The solution was added dropwise to a cooled (–100 °C) solution of **11** (3.10 g, 10.1 mmol) in diethyl ether (40 mL). After 1 h the mixture was slowly warmed to room temperature (16 h). LiCl was dissolved by the addition of an aqueous solution of HCl (10 %). The organic phase was separated, and the aqueous phase was extracted four times with diethyl ether (20 mL). The combined organic phases were dried with $MgSO_4$. After filtration the solvent was removed under vacuum. The residue was recrystallised from 1,2-difluorobenzene (20/–30 °C) to yield colourless crystals of compound **12**, yield 3.51 g (90 %), m.p. (argon; sealed capillary) 169 °C. ^1H NMR (400 MHz, C_6D_6): δ = 1.05 [s, 18 H, $C(CH_3)_3$], 7.06 (td, $^3J_{H,H}$ = 7.3 Hz, $^4J_{H,H}$ = 1.2 Hz, 2 H, CH_{ar}), 7.12 (td, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.4 Hz, 2 H, CH_{ar}), 7.52 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, CH_{ar}), 7.85 (d, $^3J_{H,H}$ = 7.0 Hz, 2 H, CH_{ar}) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 28.5 [$GeCC\mathit{C}(CH_3)_3$], 30.7 [$GeCCC(\mathit{C}H_3)_3$], 74.7 [$Ge\mathit{C}CC(CH_3)_3$], 116.6 [$GeC\mathit{C}C(CH_3)_3$], 122.1 (C_{ar}), 128.7 (C_{ar}), 130.8 (C3), 133.4 (C_{ar}), 135.8 (C6), 146.3 (C_{ar}) ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2181 (w), 2147 (w) [$\nu(C{\equiv}C)$]; 1651 (vw), 1589 (vw) (biphenyl); 1462 (s),1377 (m) (nujol); 1248 (w) [$\delta(CH_3)$]; 1200 (w), 1119 (w), 918 (w), 750 (m) [ν(CC)]; 723 (m) (nujol); 673 (w) (biphenyl); 615 (w), 488 (m), 419 (m) [ν(Ge–C)] cm^{-1}. MS (EI, 20 eV, 300 K): m/z (%) = 388 (86) [M^+], 373 (30) [$M^+ - CH_3$], 331 (100) [$M^+ - C(CH_3)_3$], 316 (5) [$M^+ - C(CH_3)_3 - CH_3$]. $C_{24}H_{26}Ge$ (387.1): calcd. C 74.5, H 6.8; found C 74.5, H 6.7.

Synthesis of the Mixed Alkenyl-Alkynylgermanium Compounds 13 to 24

General Procedure: Di(*tert*-butyl)aluminium or -gallium hydride (ca. 1.5 to 2.5 mmol) was dissolved in toluene (50 mL) and cooled to 0 °C (–30 °C for **17**). Equimolar quantities of the neat dialkynylgermanium compound (≈1.5 to 2.5 mmol) were added. The mixture was stirred at 0 °C for 5 min and at room temperature (**13**, **17**, **18**: 2 h; **14**, **15**, **24**: 3 h; **16**: 21 h; **23**: 3.5 h). The solvent was removed under vacuum and the colourless residue was recrystallised from 1,2-difluorobenzene (20/–30 °C) to yield colourless crystals. Compounds **15**, **16** and **23** were isolated as yellowish, highly viscous liquids that could not be purified by recrystallisation. The synthesis of **21** followed a slightly modified procedure: Compound **6** (0.51 g, 1.66 mmol) was dissolved in toluene (10 mL) and added to a cooled solution (0 °C) of $t\mathrm{Bu_2GaH}$ (0.34 g, 1.84 mmol) in toluene (25 mL). After 0.5 h the solution was warmed to room temperature and stirred for 2.5 h. The solvent of the yellowish solution was removed under vacuum. The oily residue was dissolved in cyclopentane. Colourless compound **21** crystallised upon cooling to –30 °C.

Characterisation of 13: Yield 1.11 g (82 %), m.p. (argon; sealed capillary) 133 °C. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ = 1.00 [s, 9 H, $\mathrm{CCHC(C\mathit{H}_3)_3}$], 1.03 [s, 9 H, $\mathrm{CCC(C\mathit{H}_3)_3}$], 1.37 {s, 18 H, $\mathrm{Al[C(CH_3)_3]_2}$}, 7.13 (t, $^3J_{\mathrm{H,H}}$ = 7.4 Hz, 2 H, *para*-H Ph), 7.21 (t, $^3J_{\mathrm{H,H}}$ = 7.4 Hz, 4 H, *meta*-H Ph), 7.31 [s, 1 H, $\mathrm{CC\mathit{H}(CH_3)_3}$], 7.86 (d, $^3J_{\mathrm{H,H}}$ = 7.4 Hz, 4 H, *ortho*-H Ph) ppm. ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{C_6D_6}$): δ = 18.6 {$\mathrm{Al[\mathit{C}(CH_3)_3]_2}$}, 29.5 [$\mathrm{CCC(\mathit{C}H_3)_3}$], 29.6 [$\mathrm{CCHC(\mathit{C}H_3)_3}$], 30.4 [$\mathrm{CCC(\mathit{C}H_3)_3}$], 31.1 {$\mathrm{Al[C(\mathit{C}H_3)_3]_2}$}, 38.8 [$\mathrm{CCH\mathit{C}(CH_3)_3}$], 81.0 [$\mathrm{\mathit{C}CC(CH_3)_3}$], 128.7 (*meta*-C Ph), 129.7 (*para*-C Ph), 135.1 (*ortho*-C Ph), 135.6 [$\mathrm{C\mathit{C}C(CH_3)_3}$], 136.5 [$\mathrm{\mathit{C}CHC(CH_3)_3}$], 139.2 (*ipso*-C Ph), 166.7 [$\mathrm{C\mathit{C}HC(CH_3)_3}$] ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2145 (w), 2093 (m) [ν(C≡C)]; 1969 (vw), 1952 (vw), 1879 (vw), 1813 (vw), 1761 (vw), 1649 (vw), 1599 (w), 1560 (w), 1506 (vw) [ν(C=C), phenyl]; 1458 (vs), 1377 (vs) (nujol); 1303 (m), 1244 (m) [$\delta(\mathrm{CH_3})$]; 1198 (m), 1155 (w), 1084 (m), 1024 (m), 999 (m), 935 (m), 916 (w), 895 (w), 876 (m), 808 (m), 733 (s) [ν(CC)]; 725 (s) (nujol); 696 (m), 669 (w) (phenyl); 577 (s), 501 (m), 457 (m), 419 (m) [ν(GeC), ν(AlC)] cm^{-1}. MS (EI, 20 eV, 300 K): *m*/*z* (%) = 474 (0.4) [$\mathrm{M^+ – C(CH_3)_3 – H}$], 392 (18) [$\mathrm{M^+ – Al\{C(CH_3)_3\}_2 + H}$]. $\mathrm{C_{32}H_{47}AlGe}$ (531.3): calcd. C 72.3, H 8.9; found C 71.8, H 8.7.

Characterisation of 14: Yield 1.07 g (82 %), m.p. (argon; sealed capillary) 107 °C. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ = 1.06 [s, 9 H, $\mathrm{CCHC(C\mathit{H}_3)_3}$], 1.13 [s, 9 H, $\mathrm{CCC(C\mathit{H}_3)_3}$], 1.37 {s, 18 H, $\mathrm{Ga[C(CH_3)_3]_2}$}, 6.85 [s, 1 H, $\mathrm{CC\mathit{H}(CH_3)_3}$], 7.12 (t, $^3J_{\mathrm{H,H}}$ = 7.4 Hz, 2 H, *para*-H Ph), 7.21 (t, $^3J_{\mathrm{H,H}}$ = 7.2 Hz, 4 H, *meta*-H Ph), 7.90 (d, $^3J_{\mathrm{H,H}}$ = 6.8 Hz, 4 H, *ortho*-H Ph) ppm. ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{C_6D_6}$): δ = 28.8 [$\mathrm{CC\mathit{C}(CH_3)_3}$], 29.1 {$\mathrm{Ga[\mathit{C}(CH_3)_3]_2}$}, 29.9 [$\mathrm{CCHC(\mathit{C}H_3)_3}$], 31.0 {$\mathrm{Ga[C(\mathit{C}H_3)_3]_2}$}, 31.1 [$\mathrm{CCC(\mathit{C}H_3)_3}$], 39.1 [$\mathrm{CCH\mathit{C}(CH_3)_3}$], 81.4 [$\mathrm{\mathit{C}CC(\mathit{C}H_3)_3}$], 121.5 [$\mathrm{C\mathit{C}C(\mathit{C}H_3)_3}$], 128.7 (*meta*-C Ph), 129.4 (*para*-C Ph), 134.7 (*ortho*-C Ph), 140.0 (*ipso*-C Ph), 141.2 [$\mathrm{\mathit{C}CHC(CH_3)_3}$], 163.8 [$\mathrm{C\mathit{C}HC(CH_3)_3}$] ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2122 (m) [ν(C≡C)]; 1969 (vw), 1953 (vw), 1894 (vw), 1879 (vw), 1815 (vw), 1759 (vw), 1688 (vw), 1645 (vw), 1599 (m), 1583 (m), 1566 (m) [ν(C=C), phenyl]; 1458 (vs), 1377 (vs) (nujol); 1362 (s), 1301 (w), 1265 (vw), 1249 (s) [$\delta(\mathrm{CH_3})$]; 1197 (m), 1186 (w), 1169 (w), 1155 (w), 1078 (s), 1066 (sh), 1062 (w), 1012 (w), 1001 (w), 970 (vw), 937 (w), 895 (w), 846 (w), 806 (m) [ν(CC)]; 734 (s) (paraffin); 698 (s), 671 (m) (phenyl); 582 (m), 549 (w), 538 (sh), 501 (w), 466 (s), 399 (s) [ν(GeC), ν(GaC)] cm^{-1}. MS (EI, 20 eV, 333 K): *m*/*z* (%) = 517 (100) [$\mathrm{M^+ – C(CH_3)_3}$], 309 (6) [$\mathrm{M^+ – (CH_3)_3CH{=}CGa\{C(CH_3)_3\}_2}$; $\mathrm{Ph_2GeC{\equiv}CCMe_3{}^+}$], 232 (8) [$\mathrm{PhGeC{\equiv}CCMe_3{}^+}$]. $\mathrm{C_{32}H_{47}GaGe}$ (574.1): calcd. C 66.9, H 8.3; found C 66.7, H 8.3.

Characterisation of 15: Yield 0.35 g (100 %). Recrystallisation from 1,2-difluorobenzene at –45 °C afforded colourless single crystals of **15** in a low yield of only 15 %. These crystals were extremely air sensitive and ignited spontaneously on contact with air. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ = 0.70 [s, 6 H, $\mathrm{(CH_3)_2Ge}$], 0.98 [s, 9 H, $\mathrm{CCHC(C\mathit{H}_3)_3}$], 1.09 [s, 9 H, $\mathrm{CCC(CH_3)_3}$], 1.34 {s, 18 H, $\mathrm{Al[C(CH_3)_3]_2}$}, 7.04 [s, 1 H, $\mathrm{CC\mathit{H}C(CH_3)_3}$] ppm. ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{C_6D_6}$): δ = 5.6 [$\mathrm{(CH_3)_2Ge}$], 18.1 {$\mathrm{Al[\mathit{C}(CH_3)_3]_2}$}, 29.4 [$\mathrm{CC\mathit{C}(CH_3)_3}$], 29.7 [$\mathrm{CCHC(\mathit{C}H_3)_3}$], 30.6 {$\mathrm{Al[C(\mathit{C}H_3)_3]_2}$}, 30.7 [$\mathrm{CCC(\mathit{C}H_3)_3}$], 38.2 [$\mathrm{CCH\mathit{C}(CH_3)_3}$], 81.2 [$\mathrm{\mathit{C}CC(\mathit{C}H_3)_3}$], 134.7 [$\mathrm{C\mathit{C}C(\mathit{C}H_3)_3}$], 140.6 [$\mathrm{\mathit{C}CHC(CH_3)_3}$], 164.0 [$\mathrm{C\mathit{C}HC(CH_3)_3}$] ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2147 (m), 2097 (m) [ν(C≡C)]; 1605 (m) [ν(C=C)]; 1568 (w), 1539 (w); 1460 (vs), 1377 (vs) (nujol); 1362 (s), 1304 (w), 1248 (s) [$\delta(\mathrm{CH_3})$]; 1200 (m), 1175 (w), 1067 (w), 1028 (w), 1001 (m), 937 (m), 880 (w), 835 (m), 808 (m), 789 (sh), 750 (w) [ν(CC)]; 721 (m) (nujol); 640 (m), 594 (m), 561 (sh), 532 (w), 471 (m), 419 (m) [ν(GeC), ν(AlC)] cm^{-1}. MS (EI, 20 eV, 300 K): *m*/*z* (%) = 351 [$\mathrm{M^+ – CMe_3}$], 268 (39) [$\mathrm{M^+ – Al\{C(CH_3)_3\}_2 + H}$].

Characterisation of 16: Yield 0.65 g (100 %). ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ = 0.66 [s, 6 H, $\mathrm{(CH_3)_2Ge}$], 1.01 [s, 9 H, $\mathrm{CCHC(C\mathit{H}_3)_3}$], 1.16 [s, 9 H, $\mathrm{CCC(CH_3)_3}$], 1.40 {s, 18 H, $\mathrm{Ga[C(CH_3)_3]_2}$}, 6.63 [s, 1 H, $\mathrm{CC\mathit{H}C(CH_3)_3}$] ppm. ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{C_6D_6}$): δ = 4.3 [$\mathrm{(CH_3)_2Ge}$], 28.2 {$\mathrm{Ga[\mathit{C}(CH_3)_3]_2}$}, 28.7 [$\mathrm{CC\mathit{C}(CH_3)_3}$], 30.0 [$\mathrm{CCHC(\mathit{C}H_3)_3}$], 30.7 {$\mathrm{Ga[C(\mathit{C}H_3)_3]_2}$}, 31.4 [$\mathrm{CCC(\mathit{C}H_3)_3}$], 38.1 [$\mathrm{CCH\mathit{C}(CH_3)_3}$], 82.7 [$\mathrm{\mathit{C}CC(\mathit{C}H_3)_3}$], 120.8 [$\mathrm{C\mathit{C}C(\mathit{C}H_3)_3}$], 144.6 [$\mathrm{\mathit{C}CHC(CH_3)_3}$], 161.0 [$\mathrm{C\mathit{C}HC(CH_3)_3}$] ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2156 (m), 2122 (m) [ν(C≡C)]; 1603 (m), 1566 (m), 1501 (w) [ν(C=C)], 1460 (vs), 1360 (vs) (nujol); 1288 (vs) [$\delta(\mathrm{CH_3})$]; 1200 (vs), 1084 (m), 1049 (m), 1009 (s), 972 (w), 937 (vw), 893 (w), 808 (vs) [ν(CC)]; 625 (m), 564 (m), 552 (m), 519 (s), 498 (m), 465 (s) [ν(GeC), ν(GaC)] cm^{-1}. MS (EI, 20 eV, 300 K): *m*/*z* (%) = 393 (100) [$\mathrm{M^+ – C(CH_3)_3}$], 268 (4) [$\mathrm{M^+ – Ga\{C(CH_3)_3\}_2 + H}$].

Characterisation of 17: Yield 1.30 g (90 %), m.p. (argon; sealed capillary) 135 °C. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ = 0.77 [s, 9 H, $\mathrm{CCHC(C\mathit{H}_3)_3}$], 0.83 [s, 9 H, $\mathrm{CCC(CH_3)_3}$], 1.51 {s, 18 H, $\mathrm{Al[C(CH_3)_3]_2}$}, 7.26 [s, 1 H, $\mathrm{CC\mathit{H}C(CH_3)_3}$], 7.13 (t, $^3J_{\mathrm{H,H}}$ = 7.2 Hz, 2 H, $\mathrm{CH_{ar}}$), 7.18 (t, $^3J_{\mathrm{H,H}}$ = 7.4 Hz, 2 H, $\mathrm{CH_{ar}}$), 7.64 (d, $^3J_{\mathrm{H,H}}$ = 7.6 Hz, 2 H, $\mathrm{CH_{ar}}$), 7.95 (d, $^3J_{\mathrm{H,H}}$ = 6.9 Hz, 2 H, $\mathrm{CH_{ar}}$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{C_6D_6}$): δ = 18.9 {$\mathrm{Al[\mathit{C}(CH_3)_3]_2}$}, 29.0 [$\mathrm{CCHC(\mathit{C}H_3)_3}$], 29.3 [$\mathrm{CC\mathit{C}(CH_3)_3}$], 30.2 [$\mathrm{CCC(\mathit{C}H_3)_3}$], 30.7 {$\mathrm{Al[C(\mathit{C}H_3)_3]_2}$}, 39.0 [$\mathrm{CCH\mathit{C}(CH_3)_3}$], 78.8 [$\mathrm{\mathit{C}CC(CH_3)_3}$], 122.2 ($\mathrm{C_{ar}}$), 129.0 ($\mathrm{C_{ar}}$), 130.6 ($\mathrm{C_{ar}}$), 132.9 ($\mathrm{C_{ar}}$), 133.6 [$\mathrm{C\mathit{C}C(CH_3)_3}$], 135.8 [$\mathrm{\mathit{C}CHC(CH_3)_3}$], 140.5 ($\mathrm{C_{ar}}$), 145.0 ($\mathrm{C_{ar}}$), 169.0 [$\mathrm{C\mathit{C}HC(CH_3)_3}$] ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2145 (m), 2100 (m) [ν(C≡C)]; 1911 (w), 1607 (m), 1568 (w), 1506 (m) [ν(C=C), biphenyl]; 1466 (vs), 1448 (vs), 1377 (vs) (nujol); 1302 (w), 1271 (vw), 1246 (m) [$\delta(\mathrm{CH_3})$]; 1200 (m), 1153 (m), 1119 (w), 1049 (w), 1028 (w), 999 (m), 970 (w), 935 (m), 895 (w), 866 (w), 806 (m), 745 (s) [ν(CC)]; 723 (s) (nujol); 671 (w) (phenyl); 615 (w), 586 (m), 557 (w), 534 (vw), 486 (m), 464 (w), 414 (m) [ν(GeC), ν(AlC)] cm^{-1}. MS (EI, 20 eV, 300 K): *m*/*z* (%) = 473 (20) [$\mathrm{M^+ – C(CH_3)_3}$], 390 (100) [$\mathrm{M^+ – Al\{C(CH_3)_3\}_2 + H}$]. $\mathrm{C_{32}H_{45}AlGe}$ (529.3): calcd. C 72.6, H 8.6; found C 72.4, H 8.5.

Characterisation of 18: Yield 0.52 g (76 %), m.p. (argon; sealed capillary) 146 °C. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ = 0.79 [s, 9 H, $\mathrm{CCHC(C\mathit{H}_3)_3}$], 0.95 [s, 9 H, $\mathrm{CCC(CH_3)_3}$], 1.53 {s, 18 H, $\mathrm{Ga[C(CH_3)_3]_2}$}, 6.83 [s, 1 H, $\mathrm{CC\mathit{H}C(CH_3)_3}$], 7.15 (t, $^3J_{\mathrm{H,H}}$ = 7.1 Hz, 2 H, $\mathrm{CH_{ar}}$), 7.18 (dt, $^3J_{\mathrm{H,H}}$ = 7.3 Hz, $^4J_{\mathrm{H,H}}$ = 1.3 Hz, 2 H, $\mathrm{CH_{ar}}$), 7.64 (d, $^3J_{\mathrm{H,H}}$ = 7.3 Hz, 2 H, $\mathrm{CH_{ar}}$), 7.93 (dd, $^3J_{\mathrm{H,H}}$ = 6.7 Hz, $^4J_{\mathrm{H,H}}$ = 1.3 Hz, 2 H, $\mathrm{CH_{ar}}$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{C_6D_6}$): δ = 28.7 [$\mathrm{CC\mathit{C}(CH_3)_3}$], 29.3 {$\mathrm{Ga[\mathit{C}(CH_3)_3]_2}$}, 29.3 [$\mathrm{CCHC(\mathit{C}H_3)_3}$], 30.8 {$\mathrm{Ga[C(\mathit{C}H_3)_3]_2}$}, 31.0 [$\mathrm{CCC(\mathit{C}H_3)_3}$], 38.9 [$\mathrm{CCH\mathit{C}(CH_3)_3}$], 79.4 [$\mathrm{\mathit{C}CC(CH_3)_3}$], 120.4 [$\mathrm{C\mathit{C}C(CH_3)_3}$], 122.3 ($\mathrm{C_{ar}}$), 128.8 ($\mathrm{C_{ar}}$), 130.3 ($\mathrm{C_{ar}}$), 132.9 ($\mathrm{C_{ar}}$), 139.2 [$\mathrm{\mathit{C}CHC(CH_3)_3}$], 140.9 ($\mathrm{C_{ar}}$), 145.5 ($\mathrm{C_{ar}}$), 165.9 [$\mathrm{C\mathit{C}HC(CH_3)_3}$] ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2154 (m), 2122 (m) [ν(C≡C)]; 1948 (vw), 1911 (vw), 1614 (w), 1564 (w), 1508 (m) [ν(C=C)], biphenyl; 1464 (vs), 1377 (vs) (nujol); 1300 (vw), 1269 (m), 1246 (m) [$\delta(\mathrm{CH_3})$]; 1202 (m), 1157 (w), 1119 (w), 1099 (w), 1009 (w), 970 (vw), 934 (m), 899 (w), 856 (w), 841 (w), 745 (s) [ν(CC)]; 721 (s) (nujol); 671 (w) (biphenyl); 617 (w), 584 (m), 548 (w), 488 (m), 453 (w) [ν(GeC), ν(GeC)] cm^{-1}. MS (EI, 20 eV, 300 K): *m*/*z* (%) = 515 (100) [$\mathrm{M^+ – C(CH_3)_3}$], 459 (3) [$\mathrm{M^+}$ –

$C(CH_3)_3$ – butene], 433 (4) [M^+ – $C(CH_3)_3$ – $CCC(CH_3)_3$ – H]. $C_{32}H_{45}GaGe$ (572.1): calcd. C 67.2, H 7.9; found C 67.7, H 7.5.

Characterisation of 21: Yield 0.50 g (62%), m.p. (argon; sealed capillary) 81 °C. ^1H NMR (400 MHz, C_6D_6): δ = 0.58 (s, 6 H, $GeCH_3$), 1.38 {s, 18 H, $Ga[C(CH_3)_3]_2$}, 6.93 (m, 3 H, *meta*-H Ph-alkyne/*para*-H Ph-alkyne), 7.06 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, *para*-H Ph-alkene), 7.14 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, *meta*-H Ph-alkene), 7.20 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, *ortho*-H Ph-alkene), 7.51 (m, 2 H, *ortho*-H Ph-alkyne), 7.71 (s, 1 H, GeC=CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 1.5 ($GeCH_3$), 28.9 $\{\mathrm{Ga}[\mathit{C}(\mathrm{CH_3})_3]_2\}$, 30.6 $\{\mathrm{Ga}[\mathrm{C}(\mathit{C}\mathrm{H_3})_3]_2\}$, 94.8 (PhC*C*Ge), 108.4 (Ph*C*CGe), 127.3 (*ortho*-C Ph-alkene), 127.5 (*para*-C Ph-alkene), 128.6 (*meta*-C Ph-alkyne/*meta*-C Ph-alkene), 129.5 (*para*-C Ph-alkyne), 132.9 (*ortho*-C Ph-alkyne), 142.2 (*ipso*-C Ph-alkene), 149.7 (Ph*C*HC), 159.2 (PhCH*C*) ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2131 (s) [ν(C≡C)]; 1940 (w), 1892 (vw), 1796 (vw), 1746 (vw), 1595 (w), 1582 (sh) [ν(C=C), phenyl]; 1489 (w), 1468 (s) (nujol); 1445 (s), 1412 (m) [$\delta(CH_3)$]; 1381 (vs) (nujol); 1359 (m), 1308 (vw), 1271 (vw), 1238 (s) [$\delta(CH_3)$]; 1211 (m), 1173 (w), 1101 (vw), 1170 (s), 1028 (m), 1009 (vw), 964 (vw), 939 (w), 914 (w), 872 (m), 841 (m), 808 (vs), 756 (s) [ν(CC)]; 737 (s) (nujol); 691 (s), 665 (vw) (phenyl); 606 (s), 584 (m), 563 (m), 534 (m), 507 (w), 489 (vw), 461 (w), 426 (m) [ν(GeC), ν(GaC)] cm^{-1}. MS (EI, 20 eV, 353 K): *m*/*z* (%) = 433 (100) [M^+ – $C(CH_3)_3$], 307 (6) [M^+ – $Ga\{C(CH_3)_3\}_2$], 204 (70) [$Me_2Ge(H)C{\equiv}CPh^+$]. $C_{26}H_{35}GaGe$ (489.9): calcd. C 63.7, H 7.2; found C 63.2, H 7.2.

Characterisation of 23: Yield 1.280 g (100%). ^1H NMR (400 MHz, C_6D_6): δ = 0.70 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, $\mathrm{CCHCH_2CH_2CH_2C}\mathit{H}_3$), 0.72 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, $\mathrm{CCCH_2CH_2CH_2C}\mathit{H}_3$), 1.10 (m, 2 H, $\mathrm{CCHCH_2CH_2C}\mathit{H}_2\mathrm{CH_3}$), 1.22 (m, 2 H, $\mathrm{CCCH_2CH_2C}\mathit{H}_2\mathrm{CH_3}$), 1.24 (m, 2 H, $\mathrm{CCHCH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$), 1.34 (m, 2 H, $\mathrm{CCCH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$), 1.38 {s, 18 H, $Ga[C(CH_3)_3]_2$}, 2.13 (t, $^3J_{H,H}$ = 7.1 Hz, 2 H, $\mathrm{CCC}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$), 2.21 (dt, $^3J_{H,H}$ = 7.7 Hz, $^3J_{H,H}$ = 7.1 Hz, 2 H, $\mathrm{CCHC}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$), 6.72 (t, $^3J_{H,H}$ = 6.5 Hz, 1 H, $\mathrm{CC}\mathit{H}\mathrm{CH_2CH_2CH_2CH_3}$), 7.13 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, *para*-H Ph), 7.21 (t, $^3J_{H,H}$ = 7.3 Hz, 4 H, *meta*-H Ph), 7.83 (d, $^3J_{H,H}$ = 6.9 Hz, 4 H, *ortho*-H Ph) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 13.6 ($\mathrm{CCCH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$), 14.1 ($\mathrm{CCHCH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$), 20.5 ($\mathrm{CC}\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$), 22.2 ($\mathrm{CCCH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$), 22.6 ($\mathrm{CCHCH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$), 28.6 $\{\mathrm{Ga}[\mathit{C}(\mathrm{CH_3})_3]_2\}$, 31.0 ($\mathrm{CCCH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 31.0 $\{\mathrm{Ga}[\mathrm{C}(\mathit{C}\mathrm{H_3})_3]_2\}$, 31.9 ($\mathrm{CCHCH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 40.8 ($\mathrm{CCH}\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$), 83.6 ($\mathit{C}\mathrm{CCH_2CH_2CH_2CH_3}$), 111.4 ($\mathrm{C}\mathit{C}\mathrm{CH_2CH_2CH_2CH_3}$), 128.7 (*meta*-C Ph), 129.5 (*para*-C Ph), 134.8 (*ortho*-C Ph), 137.7 (*ipso*-C Ph), 148.7 ($\mathit{C}\mathrm{CHCH_2CH_2CH_2CH_3}$), 154.5 ($\mathrm{C}\mathit{C}\mathrm{HCH_2CH_2CH_2CH_3}$) ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2151 (m) [ν(C≡C)]; 1950 (w), 1892 (w), 1879 (w), 1815 (w), 1595 (m), 1568 (w) [ν(C=C), phenyl]; 1481 (m), 1464 (vs) (nujol); 1431 (s) [$\delta(CH_3)$]; 1377 (m) (nujol); 1362 (m), 1301 (w), 1244 (w) [$\delta(CH_3)$]; 1184 (m), 1175 (m), 1090 (s), 1047 (w), 1024 (m), 1013 (m), 1001 (m), 970 (w), 941 (w), 899 (w), 851 (w), 808 (s) [ν(CC)]; 733 (vs) (nujol); 698 (vs), 673 (w) (phenyl); 594 (w), 521 (m), 467 (vs), 430 (m) [ν(GeC), ν(GaC)] cm^{-1}. MS (EI, 20 eV, 298 K): *m*/*z* (%) = 518 (100) [M^+ – butene], 494 (2) [M^+ – $CCCMe_3$ + H], 462 (5) [M^+ – 2 butene], 310 (54) [M^+ – $Ga\{C(CH_3)_3\}_2$ – $CCCH_2CH_2CH_2CH_3$].

Characterisation of 24: Yield 0.57 g (70%), m.p. (argon; sealed capillary) 139 °C. ^1H NMR (400 MHz, C_6D_6): δ = 1.33 {s, 18 H, $Ga[C(CH_3)_2]$}, 1.52 (s, 3 H, $CCCH_3$), 1.81 (d, $^3J_{H,H}$ = 6.1 Hz, 3 H, $\mathrm{CCHC}\mathit{H}_3$), 6.70 (q, $^3J_{H,H}$ = 6.1 Hz, 1 H, $\mathrm{CC}\mathit{H}\mathrm{CH_3}$), 7.14 (m, 2 H, *para*-H Ph), 7.19 (m, 4 H, *meta*-H Ph), 7.80 (m, 4 H, *ortho*-H Ph) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 5.1 ($\mathrm{CC}\mathit{C}\mathrm{H_3}$), 25.9 ($\mathrm{CCH}\mathit{C}\mathrm{H_3}$), 28.6 $\{\mathrm{Ga}[\mathit{C}(\mathrm{CH_3})_3]_2\}$, 30.7 $\{\mathrm{Ga}[\mathrm{C}(\mathit{C}\mathrm{H_3})_3]_2\}$, 83.1 ($\mathit{C}\mathrm{CCH_3}$), 106.8 ($\mathrm{C}\mathit{C}\mathrm{CH_3}$), 128.7 (*meta*-C Ph), 129.6 (*para*-C Ph), 134.9 (*ortho*-C Ph), 137.2 (*ipso*-C Ph), 148.2 ($\mathrm{C}\mathit{C}\mathrm{HCH_3}$), 150.0 ($\mathit{C}\mathrm{CHCH_3}$) ppm. IR (CsI, nujol): $\tilde{\nu}$ = 2178 (w), 2151 (w) [ν(C≡C)]; 1599 (w) [ν(C=C)]; 1454 (vs), 1375 (vs) (nujol); 1304 (w), 1269 (w) [$\delta(CH_3)$]; 1169 (w), 1155 (w), 1090 (m), 1026 (w), 1009 (w), 991 (w), 935 (w), 918 (w), 889 (w), 847 (w), 821 (sh), 808 (w), 754 (w) [ν(CC)]; 696 (m), 673 (w) (phenyl); 627 (w), 527 (w), 490 (w), 463

Table 3. Crystal data and structure refinement for compounds **4**, **13**, **14** and **15**.[a]

	4	**13**	**14**	**15**
Empirical formula	$C_{24}H_{28}Ge$	$C_{32}H_{47}AlGe$	$C_{32}H_{47}GaGe$	$C_{22}H_{43}AlGe$
Temperature [K]	153(2)	153(2)	153(2)	153(2)
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a [pm]	1758.30(6)	911.35(1)	913.06(4)	932.18(5)
b [pm]	1022.55(4)	1297.79(2)	1121.05(4)	1445.81(8)
c [pm]	1163.99(4)	1334.88(2)	1741.56(7)	1908.2(1)
α [°]	90	81.8557(7)	71.3369(5)	90
β [°]	91.242(2)	85.7151(7)	79.2417(6)	95.829(2)
γ [°]	90	84.3400(7)	72.9041(5)	90
V [nm^3]	2.0923(1)	1.55231(4)	1.6058(1)	2.5585(2)
Z	4	2	2	4
$D_{calcd.}$ [$g\,cm^{-3}$]	1.235	1.137	1.187	1.057
μ [mm^{-1}]	1.467 (Mo-K_α)	1.032 (Mo-K_α)	1.791 (Mo-K_α)	1.233 (Mo-K_α)
Crystal size [mm]	0.47 × 0.35 × 0.18	0.39 × 0.28 × 0.18	0.30 × 0.28 × 0.15	0.34 × 0.12 × 0.05
Θ range [°]	2.30 ≤ 30.01	2.06 ≤ 30.01	1.24 ≤ 30.14	2.20 ≤ 30.09
Index ranges	$-24 \le h \le 24$	$-12 \le h \le 12$	$-12 \le h \le 12$	$-13 \le h \le 13$
	$-14 \le k \le 14$	$-18 \le k \le 18$	$-15 \le k \le 15$	$-20 \le k \le 20$
	$-16 \le l \le 16$	$-18 \le l \le 18$	$-24 \le l \le 24$	$-26 \le l \le 26$
Independent reflections	6101 (R_{int} = 0.0225)	8992 (R_{int} = 0.0240)	9363 (R_{int} = 0.0135)	7472 (R_{int} = 0.0290)
Parameters	232	350	319	231
$R1$ [$I > 2\sigma(I)$]	0.0213 (5543)	0.0310 (8007)	0.0238 (7913)	0.0307 (6187)
$wR2$ (all data)	0.0582	0.0820	0.0633	0.0798
Max./min. residual electron density [$10^{30}\,e\,m^{-3}$]	+0.436/–0.183	+0.935/–0.360	+0.350/–0.349	+0.373/–0.251

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. Programme SHELXL-97.[20]

Table 4. Crystal data and structure refinement for compounds **17**, **18**, **21** and **24**.[a]

	17	**18**	**21**	**24**
Empirical formula	$C_{32}H_{45}AlGe$	$C_{35}H_{47}FGaGe$	$C_{26}H_{35}GaGe$	$C_{26}H_{35}GaGe$
Temperature [K]	153(2)	153(2)	153(2)	153(2)
Crystal system	triclinic	triclinic	orthorhombic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)[b]	$P\bar{1}$ (no. 2)
a [pm]	884.13(2)	917.54(7)	1100.91(9)	820.0(2)
b [pm]	1248.17(2)	1121.49(8)	1389.9(1)	1435.4(3)
c [pm]	1421.49(3)	1676.8(1)	3370.3(3)	2147.8(4)
α [°]	79.4098(8)	90.225(6)	90	88.37(3)
β [°]	87.3022(9)	94.100(6)	90	81.13(3)
γ [°]	87.6891(9)	104.283(6)	90	87.08(3)
V [nm^3]	1.53945(5)	1.6674(2)	5.1571(7)	2.4940(9)
Z	2	2	8	4
$D_{calcd.}$ [g cm^{-3}]	1.142	1.253	1.262	1.305
μ [mm^{-1}]	1.040 (Mo-K_α)	1.735 (Mo-K_α)	2.218 (Mo-K_α)	2.294 (Mo-K_α)
Crystal size [mm]	0.51 × 0.15 × 0.06	0.30 × 0.25 × 0.05	0.46 × 0.27 × 0.24	0.25 × 0.08 × 0.08
Θ range [°]	1.46 ≤ 30.10	1.87 ≤ 27.94	1.58 ≤ 30.23	1.70 ≤ 28.29
Index ranges	$-12 \le h \le 12$	$-12 \le h \le 12$	$-15 \le h \le 15$	$-10 \le h \le 10$
	$-17 \le k \le 17$	$-14 \le k \le 14$	$-19 \le k \le 19$	$-19 \le k \le 19$
	$-20 \le l \le 20$	$-22 \le l \le 21$	$-47 \le l \le 47$	$-28 \le l \le 28$
Independent reflections	8960 (R_{int} = 0.0244)	7939 (R_{int} = 0.0447)	15237 (R_{int} = 0.0362)	80565[c]
Parameters	319	364	521	522
$R1$ [$I > 2\sigma(I)$]	0.0276 (7934)	0.0280 (6157)	0.0297 (13026)	0.0487
$wR2$ (all data)	0.0812	0.0685	0.0634	0.1183
Max./min. residual electron density [10^{30} e m^{-3}]	+0.375/–0.246	+0.584/–0.492	+0.434/–0.326	+1.731/–0.982

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. Programme SHELXL-97;[20] solutions by direct methods, full-matrix refinement with all independent structure factors. [b] Flack parameter: 0.051(6). [c] Twinned crystal; HKLF-5 refinement without averaging of reflections.

(m), 432 (w) [ν(GeC), ν(GaC)] cm^{-1}. MS (EI, 20 eV, 300 K): m/z (%) = 432 (91) [M$^+$ – C(CH$_3$)$_3$ – H], 376 (4) [M$^+$ – 2 C(CH$_3$)$_3$], 308 (11) [M$^+$ – Ga{C(CH$_3$)$_3$}$_2$ + H]. $C_{26}H_{35}GaGe$ (489.9): calcd. C 63.7, H 7.2; found C 63.5, H 7.1.

Crystal Structure Determinations: Single crystals were obtained directly from the reaction mixtures as described above. Crystals of compound **15** were obtained by recrystallisation from 1,2-difluorobenzene at –45 °C. They are extremely air sensitive and could be mounted on the diffractometer only with great difficulty. The crystallographic data were collected with a Bruker QUAZAR and a STOE STADIVARI (**24**) diffractometer with microsource multilayer optics (Montel mirror) (Mo-K_α radiation). The crystals were coated with a perfluoropolyether, picked up with a glass fibre and immediately mounted in the cooled nitrogen stream of the diffractometer. The crystallographic data and details of the final R values are provided in Tables 3 and 4.[21] 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). A *tert*-butyl group is disordered in the structure of **13** (C13); the methyl groups were refined on split positions (0.65:0.35). The crystals of compound **18** enclose one molecule of 1,2-difluorobenzene per unit cell. The solvent molecule is disordered over a centre of symmetry. Two independent molecules were found in the asymmetric units of compounds **21** and **24**. Compound **24** crystallised as a non-merohedric twin with two independent domains.

CCDC-989299 (for **4**), -989300 (for **13**), -989301 (for **14**), -989302 (for **15**), -989303 (for **17**), -989304 (for **18**), -989305 (for **21**), and -989306 (for **24**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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