Hydrometallation (M = Al, Ga) of Silicon- and Germanium-centred Oligoalkynes

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Z. Naturforsch. **2014**, *69b*, 1333 – 1347 / DOI: 10.5560/ZNB.2014-4151 Received July 11, 2014

Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

Treatment of a variety of alkyl- and arylsilanes, $R_{4-n}Si(C\equiv C-R')_n$, and -germanes, $R_{4-n}Ge(C\equiv C-R')_n$ (1–7), with equimolar quantities of the dialkylmetal hydrides HMR''_2 (M = Al, Ga; $R'' = CMe_3$, CH_2CHMe_2) yielded by reduction of a single alkynyl group a series of mixed alkenyl-alkynyl compounds $R_{4-n}Si(C\equiv C-R')_{n-1}\{C(MR''_2) = CHR'\}$ (n = 2, 3) and $R_2Ge(C\equiv C-R')\{C[M(CMe_3)_2]=CHR'\}$ (8–13). Reactions with two equivalents of the hydrides afforded the dialkenyl compounds $R_2E\{C[(M(CMe_3)_2]=CHR'\}_2$ (E = Si, Ge, 14–17), Ge(C\equiv C-CMe_3)_2\{C[Ga(CMe_3)_2]=CH-CMe_3\}_2 (18) and $MeSi(C\equiv C-p-Tol)\{C[Ga(CMe_3)_2]=CH-p-Tol\}_2$ (19) [R = Ph, Mes, Me, C_6F_5 ; $R' = CMe_3$, Ph). Most of the products were characterised by X-ray crystallography which for the alkenyl-alkynyl derivatives revealed short intramolecular contacts between the coordinatively unsaturated metal atoms and the α -C atoms of unreacted ethynyl groups $C_{\alpha}\equiv C-R'$.

Key words: Hydroalumination, Hydrogallation, Silicon, Germanium, Alkynes

Introduction

Treatment of oligoalkynylsilanes and -germanes, $R_{4-n}E(C \equiv C - R')_n$ (*E* = Si, Ge), with equimolar quantities of dialkylaluminium or -gallium hydrides, H- MR''_2 (M = Al, Ga), have been shown to afford mixed alkenyl-alkynylsilicon and -germanium compounds [1-7] by addition of an *E*-H bond to a C \equiv C triple bond (hydroalumination, hydrogallation [8]; Scheme 1). These reactions are highly regio- and stereoselective with the aluminium and gallium atoms in the products exclusively localised in a geminal position to silicon or germanium and a cis-arrangement of the metal and vinylic hydrogen atoms across the resulting C=C double bonds as the kinetically favoured orientation [9]. Rearrangement to yield the thermodynamically favoured trans-products has been observed only for very few compounds with relatively small alkyl groups attached to the metal atoms [1]. As a particularly interesting structural motif these alkenylalkynyl derivatives exhibit an intramolecular interac-

tion between the coordinatively unsaturated aluminium and gallium atoms and the α -carbon atoms of the $C \equiv C$ triple bonds bearing a relatively high partial negative charge [1, 2, 4-7]. Only in the case of the very bulky bis(trimethylsilyl)methylaluminium derivatives an approach of the functional groups is prevented by strong steric repulsion [1, 3]. These interactions activate the E-C bonds, and as a consequence a thermally induced rearrangement resulted in the formation of sila- and germacyclobutene derivatives by 1,1-carbametallation [3, 5] (Scheme 1). The obtained heterocycles show an interesting fluorescence behaviour upon irradiation with UV light. Corresponding 1,1-carbaboration reactions have been observed for similar boron compounds by the group of Wrackmeyer [10-18]. Hydroalumination or hydrogallation of two C \equiv C triple bonds of the oligoalkynylsilanes and -germanes has afforded compounds with two unsaturated aluminium or gallium atoms in a single molecule which proved to be effective chelating Lewis acids and coordinated halide atoms in a chelating fashion [4, 5]

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Scheme 1. Hydrometallation of dialkynylsilanes and -germanes: alkenyl-alkynyl compounds, cyclisation and chelating Lewis acid (E = Si, Ge; M = Al, Ga).

(Scheme 1). Functionalisation of the alkynylsilanes and -germanes by Lewis-basic amino groups or halogen atoms resulted after hydrometallation in strong intramolecular Al-X or Ga-X interactions which by activation of Si-X or Ge-X bonds allowed the observation of interesting secondary reactions [19-21]. In this article we report on the continuation of our systematic studies in this field. In particular we were interested in the electronic influence of the substituents attached to silicon or germanium on the strength of the intramolecular $M \cdots C$ interactions and replaced, for instance, phenyl by strong electron-withdrawing pentafluorophenyl groups. We further used a silane with a bulky mesityl group to study the influence of steric interactions on structure, spectroscopic properties and reactivity, since secondary reactions such as cyclisation or the hypothetical release of dialkylelement alkynides strongly depend on the substituents. These studies are crucial for a concise understanding of the unique properties of these highly important new classes of compounds.

Results and Discussion

The alkynylsilanes and -germanes $R_2Si(C\equiv C-R')_2$, R-Si($C\equiv C-R')_3$, $R_2Ge(C\equiv C-R')_2$, and $Ge(C\equiv C-R')_4$ (1 to 6; Eq. 1) were synthesised conveniently following standard literature procedures [7, 22–26]. The lithiation of the terminal alkynes R'-C \equiv C–H (R' = CMe₃, C₆H₅, *p*-C₆H₄-Me (*p*-Tol)) with *n*-BuLi at -78° C afforded the corresponding lithium alkynides which in situ were reacted with the appropriate element halides $R_{4-n}ECl_n$ (E = Si, Ge) to generate the alkynylelement compounds by salt elimination. Only the preparation of the pentafluorophenylgermanium compound 7 required a different strategy to avoid problems associated with the synthesis and purity of the $(F_5C_6)_2ECl_2$ or $Cl_2E(C \equiv C - R')_2$ precursors due to non-stoichiometric reactions and the formation of inseparable mixtures of $(F_5C_6)_{4-n}ECl_n \text{ or } Cl_{4-n}E(C \equiv C - R')_n (n = 0 - 4).$ Making use of an amine protecting group was found to minimize these problems [7]. GeCl₄ was therefore treated with two equivalents of LiNEt₂ to give $Cl_2Ge(NEt_2)_2$ which was reacted with Me₃C-C=C-Li to yield the dialkynylgermane (Et₂N)₂Ge(C=C-CMe₃)₂. The latter was deprotected with HCl to afford $Cl_2Ge(C\equiv C-$ CMe₃)₂ which in the final step was converted with in situ-formed F_5C_6Li to $(F_5C_6)_2Ge(C \equiv C - CMe_3)_2$ (7) in 54% yield (Eq. 2).

$$R'-C \equiv C-H \xrightarrow{+n \operatorname{BuLi}} R'-C \equiv CLi$$
(1)

$$R_{4-n}ECl_n \xrightarrow{+nR'-C \equiv CLi} R_{4-n}E(C \equiv C-R')_n$$
(1)

$$I, R = \operatorname{Ph}, E = \operatorname{Si}, R' = C\operatorname{Me}_3, n = 2$$

$$2, R = \operatorname{Mes}, E = \operatorname{Si}, R' = C\operatorname{Me}_3, n = 3$$

$$3, R = \operatorname{Me}, E = \operatorname{Si}, R' = p\operatorname{Tol}, n = 3$$

$$4, R = \operatorname{Ph}, E = \operatorname{Ge}, R' = C\operatorname{Me}_3, n = 2$$

$$5, R = \operatorname{Ph}, E = \operatorname{Ge}, R' = \operatorname{Ph}, n = 2$$

$$6, E = \operatorname{Ge}, R' = C\operatorname{Me}_3, n = 4$$

$$\begin{array}{c} \operatorname{GeCl}_{4} + 2\operatorname{LiNEt}_{2} \xrightarrow[-2\operatorname{LiCl}]{} \operatorname{Cl}_{2}\operatorname{Ge}(\operatorname{NEt}_{2})_{2} \\ \xrightarrow{2\operatorname{Me}_{3}\operatorname{C}-\operatorname{C}\equiv\operatorname{CLi}}{} (\operatorname{Et}_{2}\operatorname{N})_{2}\operatorname{Ge}(\operatorname{C}\equiv\operatorname{C}-\operatorname{CMe}_{3})_{2} \\ \xrightarrow{4\operatorname{HCl}/\operatorname{Et}_{2}\operatorname{O}}{} \operatorname{Cl}_{2}\operatorname{Ge}(\operatorname{C}\equiv\operatorname{C}-\operatorname{CMe}_{3})_{2} \\ \xrightarrow{2\operatorname{F}_{5}\operatorname{C}_{6}\operatorname{Li}}{} (\operatorname{F}_{5}\operatorname{C}_{6})_{2}\operatorname{Ge}(\operatorname{C}\equiv\operatorname{C}-\operatorname{CMe}_{3})_{2} \end{array}$$
(2)

The hydrometallation of these alkynylsilanes and -germanes proceeded as expected and followed the previously established rules in terms of reactivity and selectivity. Stirring one equivalent of the metal hydride H– MR''_2 (M = Al, Ga; $R'' = CMe_3$, CH_2CHMe_2) with the alkynylsilanes or -germanes 1 to 7 at room temperature in toluene or *n*-hexane (synthesis of 10) between 30 min and 12 h yielded the corresponding 1:1 addition products 8 to 13 (E = Si, Ge) in yields above 63% [(i) in Eqs. 3 and 4]. The addition was in all instances strictly regioselective with the electropositive metal atom binding exclusively to the negatively polarised alkenyl C atom attached to silicon or germanium and stereospecific with a *cis* arrangement of the metal and H atoms in the resulting olefin substituents. No rearrangement of the kinetically favoured cis addition products to the thermodynamically favoured trans products was observed. There is a short contact between the metal atom and the α -C atom of an unreacted alkynyl substituent (see discussion below) which as a consequence becomes unavailable for the bimolecular transition state required for the cis/trans isomerisation [9]. The 1:2 addition products 14 to 19 [(ii) in Eqs. 3 and 4] were obtained in a similar fashion from the corresponding element alkynide and two equivalents of $H-M(CMe_3)_2$. The reactions of a second equivalent of metal hydride required, with the exception of 18, much longer reaction times (3-20 days) to reach completion and in some instances repeated fractional recrystallisation to remove small quantities of the 1:1 addition products. Warming of the solutions to accelerate the transformations resulted in decomposition with the formation of inseparable mixtures of unknown components. The dual hydroalumination of Ph₂Si(C=C-CMe₃)₂, Si(C=C- $CMe_3)_4$ and $Ph_2Ge(C \equiv C-Ph)_2$ was not successful. In case of $Ph_2Si(C \equiv C - CMe_3)_2$ a mixture of the 1 : 1 (8) and 1:2 addition products (14) was obtained that could not be separated into its components. 14 was, however, identified unequivocally in the ¹H NMR spectrum by comparison with the spectra of the analytically pure compounds 8 and 15. The reactions were again regiospecific (geminal arrangement of Si/Ge and Al/Ga) and stereoselective (cis-addition) as discussed for the mono-addition products 8 to 13. Only in case of the dialkenyl-alkynylsilicon compound 19 one of the alkenyl groups showed a spontaneous rearrangement to yield the thermodynamically favoured trans-product with the metal and the H atom on different sides of the C=C bond. The stereoselectivity (cis) is again influenced by an interaction between the Ga and α -C atom of the remaining alkynyl moiety in the cases of compounds 18 and 19 or a similar interaction between the metal atoms and one or more carbon atoms or C-H bonds of phenyl substituents in compounds 14 to 17. Interestingly, the alkenyl group of compound 19 that

adopts the *trans*-configuration is bonded to a coordinatively unsaturated metal atom.



8, R = Ph, E = Si, M = Al, R' = CMe₃ 9, R = Ph, E = Si, M = Ga, R' = CMe₃ 10, R = Ph, E = Ge, M = Ga, R' = Ph 11, R = C₆F₅, E = Ge, M = Al, R' = CMe₃

(i)
$$H-M(CMe_3)_2$$

$$R_{4-n}E(C\equiv C-R')_n$$

1, R = Ph, E = Si, R' = CMe₃, n = 2 **4**, R = Ph, E = Ge, R' = CMe₃, n = 2 [7] **5**, R = Ph, E = Ge, R' = Ph, n = 2 [2] **6**, E = Ge, R' = CMe₃, n = 4 **7**, R = C₆F₅, E = Ge, R' = CMe₃, n = 2



14, R = Ph, E = Si, M = Al, R' = CMe₃, n = 2 **15**, R = Ph, E = Si, M = Ga, R' = CMe₃, n = 2 **16**, R = Ph, E = Ge, M = Ga, R' = CMe₃, n = 2 **17**, R = Ph, E = Ge, M = Ga, R' = Ph, n = 2 **18**, R = C=C-CMe₃, E = Ge, M = Ga, R' = CMe₃, n = 4

The molecular structures of the bisalkynes 2 and 7 are shown in Figs. 1 and 2. The Group 14 element is coordinated in a distorted tetrahedral fashion, bond lengths and angles are unexceptional ($C \equiv C \ 118.4(3)$ to 120.1(2) pm; Table 1). Representative examples of

(3)



the molecular structures of the 1:1 addition products 8 to 13 are shown in Figs. 3 and 4. The key feature of the structures is a short distance between the coordinatively unsaturated metal atoms and the α -C atoms of one alkynyl substituent with average $M \cdots C$ distances of about 250 pm in the case of Al and 270 pm in the case of Ga. The significance of these interactions becomes evident from the formation of essentially planar four-membered M-Cvinyl-E-Cethynyl heterocycles with the respective torsion angles between 0 and 9° (Table 1). The atoms of the associated alkyne and alkene substituents are in the same plane, and the MR''_2 and ER2 groups adopt a perpendicular arrangement to this plane. Another consequence of the $M \cdots C_{\alpha} \equiv C$ interaction is a pyramidalisation of the coordination sphere of the metal atoms as evident from a 23-37 pm deviation from the planes defined by the directly bonded carbon atoms (Table 1). There is only little influence on the lengths of the C \equiv C triple bonds which are only



Fig. 1. Molecular structure in the crystal and atomic numbering scheme of compound **2**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms have been omitted for clarity.



Fig. 2. Molecular structure in the crystal and atomic numbering scheme of compound 7. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms have been omitted for clarity.

marginally longer than in the alkynylelement starting materials. It is noteworthy that there is no significant difference between the bond lengths of the coordinated and the "free" alkyne in **12**, while in the case of **13** there is a small lengthening [120.1(2) *versus* 121.7(2)] which is associated with the shortest $M \cdots C_{\alpha} \equiv C$ contact (244.9 pm) and the largest deviation from planarity (37 pm) in the presented series of compounds.

Compound	C≡C	C=C	$M \cdots C \equiv C (Ph)^a$	Torsion angle	$d (M \cdots C_3)^c$
				$M-C(=)-El-C_{\alpha}^{b}$	
2	119.6(2)/120.1(2)/119.8(2)	_	_	-	_
7	118.4(3)/118.9(3)	-	-	-	-
8 ($M = Al$)	120.6(2)	133.9(2)	249.5	7.15(7)	32
9 ($M = Ga$)	120.6(2)	134.1(2)	271.1	8.47(7)	24
10 ($M = Ga$)	119.8(3)	134.1(3)	264.5	0.12(2)	25
11 ($M = Al$)	120.7(2)	133.4(2)	251.2	8.3(1)	36
12 (<i>M</i> = Al)	120.3(2)/120.6(2)	133.7(2)	253.1	4.92(8)	23
13 ($M = Al$)	120.1(2)/121.7(2)	134.2(2)	244.9	5.22(6)	37
15 ($M = Ga$)	_	134.9(2)/134.6(1)	278.1/285.0 ^a	18.4(1)/19.0(1)	24/25
16 (<i>M</i> = Ga)	-	133.9(3)/133.7(3)	287.8/290.4 ^a	15.3(2)/13.4(2)	22/22
17 (<i>M</i> = Ga)	_	135.3(2)/135.2(2)	276.8/290.7 ^a	18.7(1)/11.4(1)	21/28
18 $(M = Ga)$	120.0(4)/120.0(4)	133.2(4)/134.2(4)	281.0/284.5	9.3(2)/10.0(3)	26/26

Table 1. Selected structural parameters (pm, deg) of compounds 2, 7–13 and 15–18.

^a Shortest Ga– C_{ortho} (Ph) contacts; ^b absolute values, sign ignored; C_{α} is the α -C atom of an ethynyl group or the *ipso*-C atom of a phenyl group; ^c deviation of *M* from the average plane of the directly connected carbon atoms.



Fig. 3. Molecular structure in the crystal and atomic numbering scheme of compound **11**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H22, arbitrary radius) have been omitted for clarity.

Representative diagrams of the four 1:2 addition products which were crystallographically characterised are shown in Fig. 5 (17) and 6 (18). The molecular structure of the dialkenyldialkynylgermanium compound 18 shows the same features as the already discussed 1:1 addition products. There are two relatively short Ga…C_{α} ≡C distances (281 and 285 pm) resulting in two essentially planar Ga-C_{vinyl}-Ge-C_{α} heterocycles that are approximately perpendic-



Fig. 4. Molecular structure in the crystal and atomic numbering scheme of compound 13. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H7, arbitrary radius) have been omitted for clarity.

ular to each other. In the absence of uncoordinated "free" alkynyl substituents the short Ga…C_{α} \equiv C contacts are replaced in compounds **15**, **16** and **17** by interactions between the metal atom and the *ortho*-C atoms (277–291 pm) and to a lesser degree the *ipso*-C atoms (310–328 pm) of the adjacent phenyl substituents leading to two nearly planar Ga-C_{vinyl}-*E*-C_{ipso} heterocycles that are perpendicular to each other. The phenyl substituents are rotated towards the Ga atoms to minimise the Ga-C_{ortho} distance. This interaction is also associated with a deviation from planarity for the Ga atoms as observed in the above discussed compounds (see Table 1).



Fig. 5. Molecular structure in the crystal and atomic numbering scheme of compound **17**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H12 and H22, arbitrary radii) have been omitted for clarity.



Fig. 6. Molecular structure in the crystal and atomic numbering scheme of compound **18**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H32 and H42, arbitrary radii) have been omitted for clarity.

The crystal structures of all compounds with phenyl substituents feature intermolecular C–H··· π interactions [27–29] that lead to the formation of loosely bonded dimers with short *m*-H···*m*-C [287 pm (8); 285 pm (9)], *m*-H···*m*-C [CHPh, 282 pm (10)], *m*-H···*o*-C [289 pm (15)] or *m*-H···centroid contacts [277 pm (16)] or alternatively the formation of a chain structure with short *m*-H···*o*-C and *m*-H···*ipso*-C contacts [266, 285 pm (17)]. The dimers of compound 15

are further connected to an infinite chain by an interaction between the *m*-H atom of one dimer with *o*-, *m*and *p*-C atoms [GePh, 288, 277, 282 pm].

The spectroscopic characterisation is consistent with the results of the crystal structure determinations. Selected IR- and NMR-spectroscopic parameters are summarised in Table 2. In accordance with a few previously reported observations [19] the crystallographically detected $M \cdots C_{\alpha} \equiv C$ contacts in the hydrometallation products **8** to **13** and **19** correlate to a lowering of the $v(C \equiv C)$ stretching frequency in the IR spectrum by $30-50 \text{ cm}^{-1}$ (Table 2) relative to the "free" alkynes **1** to **7**. In compounds **12** and **13** we found three $v_{C \equiv C}$ stretching vibrations covering the entire range observed for coordinated and free ethynyl groups (2200 to 2120 cm^{-1}) which obviously reflect the structural speciality with the presence of "free" and coordinated alkynyl groups in a single molecule.

In the ¹H NMR spectra all hydrometallation products 8 to 19 showed a characteristic signal in the region of 6.4-8.3 ppm for the olefinic hydrogen atoms, and in case of the silicon compounds ${}^{3}J_{\text{SiH}}$ coupling constants > 24 Hz were observed. Coupling constants > 20 Hz have been shown to be characteristic of cis isomers (Al and H on the same side, Si and H on different sides of the C=C bond), while constants < 15 Hz are indicative of the *trans* isomer [9]. Only in case of the 1 : 2 addition product 19 there is one of the two coupling constants < 15 Hz, and the corresponding alkene substituent was consequently identified as the thermodynamically favoured trans isomer. Although we do not have direct evidence by crystal structure determination in this case these findings verify unambiguously the unique molecular structure of 19. One alkenyl group has the kinetically preferred cis-arrangement of Ga and H atoms while the second one adopted the thermodynamically favoured trans-configuration.

The chemical shifts of the *CMe*₃ groups in the ¹H NMR spectra of compounds **8**, **9**, **11**, **12**, **13**, and **18** followed the sequence $\delta(MCMe_3) > \delta(C \equiv C - CMe_3) \geq \delta(C = C - CMe_3)$ (Table 2). The low-field shift of the *MCMe*₃ group ($\delta = 1.3 - 1.4$ ppm) may be a consequence of the higher coordination number of the metal atoms as a result of the discussed $M \cdots C_{\alpha} \equiv C$ interaction. In compounds **15** to **17** that do not have such an interaction the trend was reversed, and $\delta(MCMe_3)$ was shifted to higher field ($\delta = 1.03 - 1.06$ ppm). For the mixed *cis/trans* compound **19** we observe resonances in two different ranges (δ

Compound	C=CH	³ Ic:11	C = C - R	C = C - R	CMe ₂	CMe ₂	$\nu(C=C)$
compound	$(^{1}\text{H}, \delta)$	(Hz)	$(^{13}C, \delta)$	$(^{13}C, \delta)$	$(^{13}C, \delta)^a$	$(^{1}\mathrm{H},\delta)^{a}$	(IR, cm^{-1})
1	_	_	77.6	119.8	-/28.6/-	1.11	2201, 2156
2	_	_	80.4	116.9	-/28.5/-	1.07	2201, 2158, 2125
3 [6]	_	-	88.4	107.5	_	-	2214, 2160, 2126
4 [7]			76.1	117.7	-/28.5/-	1.13	2181, 2147
5 [2]	-	-	87.8	107.9	_	-	2162
6	-	-	75.8	114.3	-/28.3/-	1.04	2187, 2153, 2126
7	-	-	72.8	118.2	-/28.6/-	1.14	2195, 2160
8	7.35	27.8	81.7	131.6	39.9/29.4/19.0	1.01/1.05/1.33	2154, 2114
9	6.84	25.1	81.3	122.4	39.8/28.8/29.4	1.10/1.15/1.29	2156, 2127
10	7.94	-	93.0	110.0	-/-/29.5	-/-/1.38	2154, 2132
11	6.94	-	77.7	n. o.	40.4/29.0/17.8	1.02/1.14/1.21	2193, 2158, 2120
12	6.95	29.8	83.7	122.2	39.6/28.9/27.0 ^b	$1.09/1.13/-^{b}$	2196, 2156, 2116
13	6.99	30.4	82.9	123.9	40.3/29.0/18.7	1.09/1.23/1.43	2197, 2156, 2126
15	6.43	24.2	-	-	39.2/-/30.2	1.33/-/1.03	-
16	6.46	-	-	_	38.8/-/30.1	1.31/-/1.04	-
17	7.63	-	-	_	-/-/30.4	-/-/1.06	-
18	6.49	-	84.7	119.5	38.4/28.8/29.2	1.21/1.17/1.44	2160, 2131
19	8.33 (trans)	<13	93.6	111.5	-/-/29.0, 28.8	-/-/1.36, 1.13	2147, 2133
	7.98 (cis)	24.3			-/-/29.2	-/-/1.47	

Table 2. Selected spectroscopic parameters of compounds 1-13 and 15-19.

^a Sequence: C=C-CMe₃/C=C-CMe₃/MCMe₃; ^b AlCH₂CHMe₂.

= 1.47 and 1.25(av) ppm) which in accordance with the above assignment may be interpreted in terms of the presence of four-coordinated ($\delta = 1.47$; Ga– C_{α} interaction; *cis*-alkenyl) and three-coordinated Ga atoms (*trans*-alken). The quaternary carbon atoms of the CMe₃ substituents were found to have very similar chemical shifts in the ¹³C NMR spectra, around δ = 40 ppm for C=C-CMe₃ and $\delta = 29$ ppm for C≡C-CMe₃ and GaCMe₃. The more electron-rich AlCMe₃ carbon atoms were observed at about $\delta = 18$ ppm.

The $M(CMe_3)_2$ and EAr_2 groups in the 1 : 1 addition products were found to be magnetically equivalent in solution which is in accordance with the molecular symmetry and an almost planar four-membered heterocycle. In case of compound 19 the CMe₃ substituents of the Ga(CMe₃)₂ group trans to H were found to be magnetically inequivalent at room temperature in the ¹H and ¹³C NMR spectra which may be caused by the cis-arrangement of the bulky substituents and a comparatively high barrier of rotation. The Al and Ga analogues of 19 with phenyl instead of tolyl substituents showed similar NMR data [6]. To study the influence of temperature on the solution behaviour of the 1:2 adducts the NMR spectra of compound 17 were recorded at variable temperatures. When a sample of 17 in toluene was slowly cooled to 210 K, the singlet for the magnetically equivalent Ga(CMe₃)₂ groups broadened, then disappeared in the base line at a coalescence temperature of 270 K and on further cooling split into two well-defined singlets at 1.27 and 0.88 ppm. Similarly the doublet for the *o*-H atoms broadened and disappeared in the baseline at 210 K. This behaviour is consistent with a hindered rotation at lower temperature due to the Ga…*o*-C interaction that was observed in the solid state. Based on the NMR data the activation barrier for the rotation was estimated to $\Delta G^{\#} = 53 \text{ kJ mol}^{-1}$ [30] which is very similar to values reported for $M \cdots C_{\alpha} \equiv C$ interactions in the literature (54 kJ mol⁻¹) [6].

Conclusion

Hydroalumination and hydrogallation of oligoalkynylsilanes and -germanes with dialkylmetal hydrides afforded either alkenyl-alkynyl- or dialkenyl compounds depending on the stoichiometric ratio of the starting compounds. It is interesting to note that despite the larger polarity of Al–H compared to Ga– H bonds dual hydroalumination was not successful in most cases, while dual hydrogallation resulted in the formation of dialkenyl compounds after relatively long reaction times. The different behaviour may reflect the relatively strong Al–H–Al three-centre bonds in usually oligomeric dialkylaluminium hydrides which results in a lower reactivity in hydrometallation reactions. The results reported in this article allow a systematic interpretation of some interesting spectroscopic findings. The difference of the chemical shifts between both ethynyl carbon atoms in the ¹³C NMR spectra is a measure for the polarity of the triple bonds. In the case of the alkenyl-alkynyl derivatives it depends essentially on the substituents attached to the β -carbon atoms. For tert-butyl groups there is a large difference between the shifts of both carbon atoms of 39 to 50 ppm, while phenyl or *p*-tolyl groups lead to much smaller differences of only about 18 ppm. A comparison between 8 and 9 suggests that the presence of aluminium atoms result in a higher polarity of the ethynyl group. A second alkynyl group attached to the central Si or Ge atoms does not seem to influence these data significantly. Similar observations were made for the alkenyl groups of these mixed-substituted compounds ($\Delta \delta = 25$ to 35 ppm *versus* about 2 ppm). Interestingly the chemical shift differences of those dialkenyl compounds (14 to 18) which do not have an unreacted alkynyl unit are in a narrow range between 9 and 12 ppm and do not show a correlation to the substituents in β -position. The pentafluorophenyl group of 11 does not affect the NMR spectroscopic data significantly. But in the starting dialkynyl compound 7 we observed the largest difference $\Delta\delta$ between both carbon atoms of an ethynyl group ($\Delta \delta = 45.4$ ppm) which may reflect a slightly increased polarity of these bonds induced by the electron-withdrawing group.

The molecular structures of the alkenylalkynylsilanes and -germanes exhibit a bonding interaction between the coordinatively unsaturated aluminium and gallium atoms and the α -carbon atoms of the unreacted ethynyl groups. Independently of the central atom (Si or Ge) relatively close intramolecular contacts are observed for the aluminium compounds (245 to 253 pm) while longer ones result with gallium (265 to 271 pm). This behaviour reflects the different Lewis acidity of the metal atoms. In the absence of unreacted alkynyl groups aluminium and gallium atoms reach coordinative saturation by interactions with aryl (15 to 17) (see also [19]) or, as reported only recently, tert-butyl groups [19, 20]. Once again the electron-withdrawing pentafluorophenyl group in **11** does not significantly influence the structural properties. Only in the starting compound 7 we observed relatively short $C \equiv C$ bonds which may be caused by a slightly increased charge separation. The

mesityl groups in **12** and **13** seem also not to have a measurable influence. From these results it may be concluded that the substituents at the central silicon or germanium atoms do not influence the properties of these highly functionalised compounds significantly (see for comparison our results with alkyl-substituted silanes or germanes [1, 2]). In contrast the metal atoms (Al *versus* Ga) and the terminal substituents of the alkynyl groups are important for the prediction of specific properties and the course of secondary reactions such as the thermal rearrangement to yield heterocyclic compounds.

Experimental Section

All procedures were carried out under an atmosphere of purified argon in dried solvents (n-hexane, c-pentane and n-pentane with LiAlH₄; Et₂O and toluene with Na/benzophenone; 1,2 difluorobenzene and pentafluorobenzene with molecular sieves). NMR spectra were recorded in C₆D₆ at ambient probe temperature or C₇D₈ for variable temperature studies (15) using the following Bruker instruments: Avance I (¹H, 400.13; ¹³C, 100.62; ²⁹Si, 79.49 MHz) or Avance III (¹H, 400.03; ¹³C, 100.59; ²⁹Si 79.47 MHz) and referenced internally to residual solvent resonances (chemical shift data in δ). ¹³C NMR spectra were all proton-decoupled. IR spectra were recorded of Nujol mulls between CsI plates on a Shimadzu Prestige 21 spectrometer. HAl(CMe₃)₂ [31], HGa(CMe₃)₂ [31], Mes-SiCl₃ [32], $Cl_2Ge(C \equiv C - CMe_3)_2$ [7], $Ph_2Ge(C \equiv C - CMe_3)_2$ CMe_{3}_{2} [7], $Ph_{2}Ge(C \equiv C-Ph)_{2}$ [2, 22, 23], $Me-Si(C \equiv C-Ph)_{2}$ C_7H_7)₃ [6], and $Ge(C \equiv C - CMe_3)_4$ [24] were obtained according to literature procedures. Commercially available HAl(CH₂CHMe₂)₂, Me₃C–C \equiv C–H, F₅C₆Br and *n*-BuLi (1.6 M in n-hexane) were used without further purification. The assignment of NMR spectra is based on HMBC, HSQC and DEPT135 data.

$Ph_2Si(C \equiv C - CMe_3)_2$ (1) [25, 26]

A solution of *n*-BuLi (40.0 mL, 64.0 mmol, 1.6 M in *n*-hexane) was added dropwise at -78 °C over a period of 1 h to a solution of Me₃C–C≡C–H (5.24 g, 7.85 mL, 64.0 mmol) in Et₂O (45 mL). The mixture was stirred for 2 h at this temperature and then allowed to warm to room temperature overnight. The yellow solution was then treated with Ph₂SiCl₂ (8.91 g, 7.40 mL, 35.2 mmol) at -78 °C over a period of 90 min. The mixture was stirred for 2 h at the same temperature and then allowed to warm to room temperature overnight. The solvent of residue was washed with *n*-hexane (20 mL). The solvent of the combined filtrates was removed *in vacuo*. The solid residue was dissolved in a small quantity of *n*-pentane. Cooling to

-30 °C gave Ph₂Si(C=C-CMe₃)₂ (1) as a colourless, airstable solid. Spectroscopic data of the previously reported compound [6, 7] are incomplete, and for reasons of comparison we have therefore included a full characterisation. Yield: 8.72 g (79%); m. p. (argon, sealed capillary): 86°C. - IR (CsI, paraffin): v = 2201 s, 2156 vs $v(C \equiv C)$; 1979 w, 1958 w, 1910 w, 1888 m, 1832 w, 1819 m, 1771 w, 1661 w, 1620 vw, 1614 vw, 1589 s, 1566 w , 1557 vw (phenyl); 1454 vs, 1377 vs (paraffin); 1362 vs, 1321 vw, 1304 m, 1254 s δ(CH₃); 1200 s, 1188 m, 1109 s, 1026 m, 997 s, 945 vs, 933 vs, 853 vw, 775 vs, 765 vs, 738 vs [δ(CH), v(CC)]; 712 vs (paraffin); 696 vs δ (Ph); 621 m, 583 vs, 563 vs, 544 vs, 494 vs, 455 s, 413 s cm⁻¹ [v(SiC), δ (CC)]. – ¹H NMR (400.13 MHz, C₆D₆): $\delta = 8.07$ (d, ${}^{3}J_{\text{HH}} = 7.7$ Hz, 4 H, o-H), 7.23 (*pseudo*-t, ${}^{3}J_{\text{HH}} = 7.7$ Hz, 4 H,*m*-H), 7.16 (t, ${}^{3}J_{\text{HH}} = 7.7 \text{ Hz}, 2 \text{ H}, p\text{-H}), 1.11 \text{ ppm} (s, 18 \text{ H}, \text{CMe}_3). - {}^{13}\text{C}$ NMR (100.6 MHz, C₆D₆): $\delta = 135.2$ (o-C), 135.1 (ipso-C), 130.2 (*p*-C), 128.3 (*m*-C), 119.8 (C≡C-CMe₃), 77.6 $(C \equiv C - CMe_3)$, 30.6 (CMe₃), 28.6 ppm (CMe₃). – ²⁹Si NMR $(79.49 \text{ MHz}, \text{C}_6\text{D}_6): \delta = -48.6 \text{ ppm.} - \text{MS} ((+)-\text{EI}; 20 \text{ eV};$ 298 K): m/z (%) = 344 (33) [M]⁺, 329 (6) [M–CH₃]⁺, 287 $(100) [M-CMe_3]^+$. - C₂₄H₂₈Si (344.1): calcd. C 83.8, H 8.2; found C 83.4, H 8.2.

 $Mes-Si(C \equiv C - CMe_3)_3$ (2)

n-BuLi (9.6 mL, 15.4 mmol, 1.6 M in n-hexane) was added dropwise over a period of 15 min to a solution of $Me_3C-C\equiv C-H$ (1.26 g, 15.4 mmol) in Et_2O (50 mL) at -78 °C. The mixture was allowed to warm to room temperature overnight and added dropwise over a period of 20 min to a solution of Mes-SiCl₃ (1.29 g, 5.12 mmol) at -78 °C. The mixture was stirred for 1 h at this temperature, allowed to warm to room temperature and stirred overnight. Inorganic salts were dissolved in aqueous HCl (10%), the organic phase was separated, and the aqueous phase was extracted three times with Et₂O (20 mL). The combined organic phases were dried over MgSO4 and filtered. The solvent was removed in vacuo. Recrystallisation of the residue from c-pentane at -15 °C yielded 2 as a colourless solid (1.94 g, 97 %); m. p. (argon, sealed capillary): 108°C. - IR (CsI, paraffin): v = 2201 m, 2158 s, 2125 sh $v(C \equiv C)$; 1605 m, 1578 m, 1555 w [v(C=C), mesityl]; 1448 vs, 1375 vs (paraffin); 1304 w, 1254 m δ (CH₃); 1202 m, 1153 w, 1109 w, 1070 m, 1028 m, 943 s, 889 w, 849 s, 773 s, 762 m [δ(CH), v(CC)]; 721 s (paraffin); 687 w, 625 m, 584 m, 507 w, 435 m cm⁻¹ [v(SiC), $\delta(CC)$]. – ¹H NMR (400.03 MHz, C₆D₆): δ = 6.78 (s, 2 H, *m*-H), 3.01 (s, 6 H, *o*-Me), 2.09 (s, 3 H, *p*-Me), 1.07 ppm (s, 27 H, CMe₃). – ¹³C NMR (100.6 MHz, C₆D₆): $\delta = 145.4$ (o-C), 139.7 (p-C), 129.9 (m-C), 127.1 (ipso-C), 116.9 (C \equiv C–CMe₃), 80.4 (C \equiv C–CMe₃), 30.3 (CMe₃), 28.5 (CMe₃), 25.0 (o-Me), 21.1 ppm (p-Me). - MS ((+)-

EI; 30 eV; 323 K): m/z (%) = 390 (67) [M]⁺, 375 (11) [M–Me]⁺, 333 (100) [M–CMe₃]⁺.

$Ge(C \equiv C - CMe_3)_4$ (6) [24]

Preliminary data of $Ge(C \equiv C - CMe_3)_4$ (6) have been published previously [5]. We modified the synthetic procedure and conducted a complete characterisation. n-BuLi (1.6 M in *n*-hexane) was added slowly to a solution of equimolar quantities of Me₃C–C \equiv CH in 100 mL of Et₂O at -78 °C. The reaction mixture was stirred for 2 h at this temperature, and a solution of GeCl₄ (25 mol %) in Et₂O (50 mL) was added dropwise. The mixture was stirred for 2 h at this temperature, the cooling bath was removed, and the suspension was stirred at room temperature overnight. Inorganic salts were dissolved in aqueous HCl (10%), the organic phase was separated and the aqueous phase was extracted three times with Et₂O (20 mL). The combined organic phases were dried over MgSO₄. After filtration the solvent was removed in vacuo. Recrystallisation of the residue from *n*-pentane at -30 °C yielded 6 as a colourless solid (83%); m. p. (argon, sealed capillary): 175°C. - IR (CsI, paraffin): v = 2187 s, 2153 s, 2126 w $v(C \equiv C)$; 1462 vs, 1375 vs (paraffin); 1302 w, 1252 vs δ (CH₃); 1204 m, 1169 vw, 1153 vw, 1101 vw, 1084 vw, 1028 w, 968 vw, 922 s, 889 vw, 847 vw, 752 vs [δ (CH), v(CC)]; 723 s (paraffin); 552 vw, 492 s cm⁻¹ [v(GeC), δ (CC)]. – ¹H NMR $(400.03 \text{ MHz}, \text{ C}_6\text{D}_6)$: $\delta = 1.04 \text{ ppm}$ (s, 36 H, CMe₃). – ¹³C NMR (100.6 MHz, C₆D₆): $\delta = 114.3$ (C \equiv C–CMe₃), 75.8 (C≡C-CMe₃), 30.5 (C≡C-CMe₃), 28.3 ppm (C≡C-*C*Me₃). – MS ((+)-EI; 30 eV; 323 K): m/z (%) = 397 (8) [M–H]⁺, 383 (100) [M–Me]⁺, 341 (28) [M–CMe₃]⁺, 317 (39) $[M-CCCMe_3]^+$. – C₂₄H₃₆Ge (397.1): calcd. C 72.6, H 9.1; found C 72.0, H 9.2.

$(F_5C_6)_2Ge(C \equiv C - CMe_3)_2$ (7)

n-BuLi (4.1 mL, 6.56 mmol, 1.6 M in n-hexane) was added dropwise over a period of 5 min to a solution of F_5C_6Br (1.62 g, 6.56 mmol) in Et_2O (50 mL) at -78 °C. The mixture was stirred for 1 h at -78 °C. During this period the temperature must not exceed -50 °C to prevent elimination of LiF and the formation of explosive tetrafluorobenzyne. A solution of $Cl_2Ge(C \equiv C - CMe_3)_2$ [7] (1.00 g, 3.28 mmol) in Et₂O was then added over a period of 20 min at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 5 h. HCl (50 mL, 10%) was added, the aqueous phase was separated and extracted three times with Et₂O (50 mL). The combined organic phases were dried over MgSO₄ and filtered. The solvent of the filtrate was removed *in vacuo*. Recrystallisation from *n*-pentane at -30 °C yielded compound 7 as a colourless oil (1.00 g, 54%). - IR (CsI, paraffin): v = 2195 vs, 2160 vs $v(C \equiv C)$; 1957 vw, 1870 vw, 1724 w, 1699 vw, 1644 vs, 1634 vs, 1603 m, 1586 s, 1549 s, 1516 vs, [v(C=C, aromatic ring]; 1471 vs (paraffin); 1419 m δ(CH₃); 1385 vs (paraffin); 1364 vs, 1344 m; 1288 vs v(CF); 1255 vs δ(CH₃); 1205 s, 1143 s; 1086 vs, 1046 m, 1017 s, 974 vs, 927 s, 818 s, 756 vs [δ (CH), ν (CC), v(CF)]; 724 s (paraffin); 696 vw, 687 vw, 679 vw, 622 s, 583 m, 554 vw, 496 s, 485 s cm⁻¹ [v(SiC), $\delta(CC)$]. – ¹H NMR (400.13 MHz, $C_6 D_6$): $\delta = 1.14$ (s, 18 H, CMe₃). $-^{13}$ C NMR (100.6 MHz, C₆D₆): $\delta = 148.8$ (dm, ¹*J*_{FC} = 246 Hz, o-C), 143.1 (dm, ${}^{1}J_{\text{FC}} = 256 \text{ Hz}$, p-C), 137.7 (dm, ${}^{1}J_{\text{FC}} =$ 253 Hz, m-C), 118.2 (C=C-CMe₃), 106.8 (m, ipso-C), 72.8 $(C \equiv C - CMe_3)$, 30.2 (CMe_3), 28.6 ppm (CMe_3). – ¹⁹F NMR (376.4 MHz, C₆D₆). $\delta = -127.6$ (m, 4 F, *o*-F), -149.3 (tt, ${}^{3}J_{\text{FF}} = 20.7 \text{ Hz}, \, {}^{4}J_{\text{FF}} = 4.1 \text{ Hz}, 2 \text{ F}, \, p\text{-F}), \, -160.1 \text{ ppm} \text{ (m,}$ 4 F, *m*-F). – MS ((+)-EI; 20 eV; 353 K): m/z (%) = 570 (5) [M]⁺, 555 (15) [M–CH₃]⁺, 513 (8) [M–CMe₃]⁺, 489 (7) $[M-CCCMe_3]^+$, 403 (9) $[M-C_6F_5]^+$.

$Ph_2Si(C \equiv C - CMe_3) \{C[Al(CMe_3)_2] = CH - CMe_3\} (8)$

Solid $Ph_2Si(C \equiv C - CMe_3)_2$ (1) (1.09 g, 3.17 mmol) was added to a solution of HAl(CMe₃)₂ (0.474 g, 3.34 mmol) in toluene (50 mL) at room temperature. The mixture was stirred for 30 min, and all volatiles were removed in vacuo. The colourless residue was dissolved in a small quantity of 1,2-difluorobenzene, the solution was concentrated and cooled to -15 °C to yield compound 8 as a colourless solid (1.27 g, 82%); m. p. (argon, sealed capillary): 117°C. - IR (CsI, paraffin): v = 2154 m, 2114 s $v(C \equiv C)$; 1971 w, 1956 w, 1900 vw, 1884 w, 1819 w, 1769 vw, 1694 vw, 1657 vw, 1599 s, 1568 s, 1557 m, 1504 w v(C=C), phenyl; 1454 vs (paraffin), 1377 vs (paraffin); 1366 vs, 1302 w, 1254 s δ (CH₃); 1244 s, 1198 s, 1188 m, 1155 w, 1107 vs, 1065 vw, 1028 w, 1007 m, 997 m, 972 vw, 940 m, 910 m, 899 m, 891 m, 851 vw, 808 vs, 793 s, 750 m, 739 s [δ (CH), v(CC)]; 719 vs (paraffin); 700 vs, 652 s (phenyl); 619 w, 590 m, 563 m, 529 vs, 490 s, 471 m, 463 m cm⁻¹ [v(SiC), $v(AlC), \delta(CC)]. - {}^{1}H NMR (400.03 \text{ MHz}, C_6D_6): \delta = 7.93$ (d, ${}^{3}J_{\text{HH}} = 7.2 \text{ Hz}$, 4 H, o-H), 7.35 (s, ${}^{3}J_{\text{SiH}} = 27.8 \text{ Hz}$, 1 H, C=CH), 7.22 (*pseudo*-t, ${}^{3}J_{\text{HH}} = 7.2 \text{ Hz}$, 4 H *m*-H), 7.15 (t, ${}^{3}J_{\text{HH}} = 7.2 \text{ Hz}, 2 \text{ H}, p-\text{H}), 1.33 \text{ (s, 18 H, AlCMe_3)}, 1.05$ (s, 9 H, C≡C-CMe₃), 1.01 ppm (s, 9 H, C=C-CMe₃). -¹³C NMR (100.59 MHz, C_6D_6): $\delta = 171.3$ (C=C-CMe₃), 137.1 (*ipso*-C), 135.9 ($C = C - CMe_3$ and o - C), 131.6 ($C \equiv C - CMe_3$) CMe₃), 130.0 (*p*-C), 128.3 (*m*-C), 81.7 (C=C-CMe₃), 39.9 (C=C-CMe₃), 31.1 (AlCMe₃), 30.4 (C≡C-CMe₃), 29.6 (C=C-CMe₃), 29.4 (C≡C-CMe₃), 19.0 ppm (AlCMe₃). -²⁹Si NMR (79.47 MHz, C₆D₆): $\delta = -32.4$ ppm. – MS ((+)-EI; 20 eV; 298 K): m/z (%) = 429 (8) [M-CMe₃]⁺, 346 (9) [M-Al(CMe₃)₂+H]⁺, 289 (100) [M-Al(CMe₃)₂-H₂C=CMe₂]⁺. - C₃₂H₄₇AlSi (486.8): calcd. C 79.0, H 9.7; found C 78.2, H 9.7.

$Ph_2Si(C \equiv C - CMe_3) \{C[Ga(CMe_3)_2] = CH - CMe_3\} (9)$

Solid $Ph_2Si(C \equiv C - CMe_3)_2$ (1) (0.383 g, 1.11 mmol) was added to a solution of HGa(CMe₃)₂ (0.216 g, 1.17 mmol) in toluene (25 mL) at room temperature. The mixture was stirred for 30 min, and all volatiles were removed in vacuo. The colourless residue was dissolved in 1,2-difluorobenzene (12 mL). After filtration the filtrate was concentrated and cooled to -15 °C to yield compound 9 as a colourless solid (0.42 g, 71%); m. p. (argon, sealed capillary): 105°C. - IR (CsI, paraffin): v = 2156 m, 2127 m $v(C \equiv C)$; 1969 vw, 1956 vw, 1898 vw, 1883 vw, 1819 w, 1655 vw, 1595 m, 1560 m, 1508 w [v(C=C), phenyl]; 1458 vs, 1375 vs (paraffin); 1300 w, 1252 m δ (CH₃); 1198 m, 1169 w, 1155 w, 1109 s, 1013 w, 999 w, 986 vw, 972 vw, 937 w, 918 m, 901 w, 887 m, 851 vw, 806 m, 793 w, 758 w, 739 s [δ (CH), v(CC)]; 708 vs (paraffin); 648 m (phenyl); 619 w, 556 m, 546 s sh, 527 vs, 486 s, 469 m, 449 s cm⁻¹ [v(SiC), v(GaC), δ (CC)]. – ¹H NMR (400.03 MHz, C₆D₆): δ = 7.96 (d, ³J_{HH} = 7.2 Hz, 4 H, o-H), 7.22 (*pseudo-t*, ${}^{3}J_{\text{HH}}$ = 7.4 Hz, 4 H, *m*-H), 7.13 (t, ${}^{3}J_{\text{HH}} = 7.5 \text{ Hz}$, 2 H, *p*-H), 6.84 (s, 1 H, ${}^{3}J_{\text{SiH}} = 25.1 \text{ Hz}, \text{C}=CH$), 1.29 (s, 18 H, GaCMe₃), 1.15 (s, 9 H, C≡C-CMe₃), 1.10 ppm (s, 9 H, C=C-CMe₃). - ¹³C NMR (100.59 MHz, C_6D_6): $\delta = 166.7$ (C=C-CMe₃), 141.8 (C =C-CMe₃), 138.7 (*ipso*-C), 135.2 (*o*-C), 129.8 (*p*-C), 128.6 (m-C), 122.4 (C=C-CMe₃), 81.3 (C=C-CMe₃), 39.8 $(C=C-CMe_3)$, 31.2 $(GaCMe_3)$, 30.8 $(C\equiv C-CMe_3)$, 30.0 (C=C-CMe₃), 29.4 (GaCMe₃), 28.8 ppm (C≡C-CMe₃). -²⁹Si NMR (79.47 MHz, C_6D_6): $\delta = -38.1$ ppm. – MS ((+)-EI; 20 eV; 298 K): m/z (%) = 471 (100) [M-CMe₃]⁺, 415 (5) $[M-CMe_3-H_2C=CMe_2]^+$, 344 (9) $[M-HGa(CMe_3)_2]^+$. - C₃₂H₄₇GaSi (529.53): calcd. C 72.6, H 8.9; found C 72.0, H 9.0.

$Ph_2Ge(C \equiv C-Ph) \{C[Ga(CMe_3)_2] = CH-Ph\} (10)$

A solution of HGa(CMe₃)₂ (0.127 g, 0.69 mmol) in nhexane (10 mL) was added at room temperature dropwise to a solution of $Ph_2Ge(C \equiv C-Ph)_2$ (5) (0.297 g, 0.69 mmol) in *n*-hexane (10 mL). The mixture was stirred for 3 h, the volatiles were removed in vacuo, and the residue was recrystallised from *n*-pentane at -15 °C to yield compound 10 as a colourless solid (0.267 g, 63%); m. p. (argon, sealed capillary): 134° C. – IR (CsI, paraffin): v = 2154 m, 2132 sh $v(C \equiv C)$; 1661 w, 1597 w, 1551 m [v(C = C), phenyl]; 1460 vs, 1377 vs (paraffin); 1304 vw, 1248 w δ (CH₃); 1169 vw, 1090 m, 1026 m, 930 vw, 914 vw, 812 w, 756 m [δ (CH), v(CC)]; 733 m (paraffin); 694 δ (Ph); 621 vw, 577 w, 532 w, 463 m cm⁻¹ [v(SiC), v(GaC), $\delta(CC)$]. – ¹H NMR (400.13 MHz, C₆D₆): $\delta = 7.94$ (s, 1 H, C=CH), 7.82 (d br, 4 H, ${}^{3}J_{\text{HH}} = 6.8 \text{ Hz}$, o-H, GePh₂), 7.45 (d, 2 H, ${}^{3}J_{\text{HH}} = 7.3 \text{ Hz}$, o-H, C \equiv C-Ph), 7.41 (d, 2 H, ${}^{3}J_{\text{HH}} =$ 6.7 Hz, o-H, C=CHPh), 7.14 (m, 4 H, m-H, GePh₂), 7.09 (m, 2 H, *p*-H, GePh₂), 6.96 (*pseudo*-t, 2 H, ³*J*_{HH} = 6.7 Hz, *m*-H, C=CHPh), 6.92 (t, 1 H, *p*-H, C=CHPh), 6.89 (t, 1 H, *p*-H, C≡C-Ph), 6.88 (*pseudo*-t, 2 H, *m*-H, C≡C-Ph), 1.38 ppm (s, 18 H, GaCMe₃). – ¹³C NMR (100.62 MHz, C₆D₆): δ = 154.2 (*C* =C-Ph), 151.7 (C=*C*-Ph), 141.4 (*ipso*-C, C=CHPh), 137.3 (*ipso*-C, GePh₂), 134.9 (*o*-C, GePh₂), 133.0 (*o*-C, C≡C-Ph), 129.7 (*p*-C, GePh₂), 129.6 (*p*-C, C≡C-Ph), 128.8 (*m*-C, GePh₂), 128.6 (*m*-C, C≡C-Ph and C=CHPh), 128.1 (*o*-C, C=CHPh), 127.9 (*p*-C, C=CHPh), 122.2 (*ipso*-C, C≡C-Ph), 110.0 (C≡*C*-Ph), 93.0 (*C*≡C-Ph), 30.8 (GaC*Me*₃), 29.5 ppm (GaCMe₃). – MS ((+)-EI; 20 eV; 351 K): *m*/*z* (%) = 557 (100) [M–CMe₃]⁺, 501 (6) [M– CMe₃–butene]⁺. – C₃₆H₃₉GaGe (614.0): calcd. C 70.4, H 6.4; found C 70.5, H 6.4.

$(F_5C_6)_2Ge(C \equiv C - CMe_3) \{C[Al(CMe_3)_2] = CH - CMe_3\} (11)$

A solution of $(F_5C_6)_2$ Ge(C \equiv C–CMe₃)₂ (7) (0.430 g, 0.76 mmol) in toluene (10 mL) was added to a solution of $HAl(CMe_3)_2$ (0.118 g, 0.83 mmol) at room temperature. The mixture was stirred for 2 h. The solvent was removed in vacuo, and the residue was recrystallised from n-pentane at -30 °C to yield **11** as a colourless solid (0.473 g, 88%); m. p. (argon, sealed capillary): 83°C (dec.). – IR (CsI, paraffin): v = 2193 m, 2158 m, 2120 w $v(C \equiv C)$; 1942 vw, 1869 vw, 1719 vw, 1639 s, 1605 m, 1582 w, 1549 w, 1516 vs [v(C=C), aromatic ring]; 1456 vs, 1377 vs (paraffin); 1341 m, 1304 w; 1285 s v(CF); 1254 s δ (CH₃); 1219 m, 1204 m, 1179 w, 1138 vw, 1084 vs, 1049 w, 1028 w, 1009 m, 972 vs, 934 m, 889 m, 845 w, 812 m, 773 w 752 m [v(CF), $\delta(CH)$, v(CC)]; 723 s (paraffin); 665 w, 635 w, 619 m, 583 m, 571 w, 557 w, 536 w, 494 m cm⁻¹ [v(GeC), v(AlC), δ (CC)]. – ¹H NMR (400.03 MHz, $[D_8]$ toluene): $\delta = 6.94$ (s, 1 H, C=CH), 1.21 (s, 18 H, AlCMe₃), 1.14 (s, 9 H, C≡C–CMe₃), 1.02 ppm (s, 9 H, C=C-CMe₃). - ¹³C NMR (100.59 MHz, [D₈]toluene): $\delta = 169.0 \text{ (C=CH)}, 148.6 \text{ (dm}, {}^{1}J_{\text{FC}} = 240 \text{ Hz}, o\text{-C}), 142.8$ $(dm, {}^{1}J_{FC} = 257 \text{ Hz}, p\text{-C}), 137.9 (dm, {}^{1}J_{FC} = 257 \text{ Hz}, m\text{-C}),$ 134.6 (C =CH), 111.7 (ipso-C), 77.7 (C≡C-CMe₃), C≡C-CMe₃ not observed, 40.4 ($C=C-CMe_3$), 30.4 (AlCMe₃), 30.3 (C≡C-CMe₃), 29.1 (C=C-CMe₃), 29.0 (C≡C-CMe₃), 17.8 ppm (AlCMe₃). – ¹⁹F NMR (376.4 MHz, [D₈]toluene): $\delta = -128.9$ (s br., 4 F, o-F), -148.9 (t, ${}^{3}J_{\text{FF}} = 20.3$ Hz, 2 F, *p*-F), -159.1 ppm (s br., 4 F, *p*-F). - MS ((+)-EI; 20 eV; 343 K): m/z (%) = 655 (100) [M–CMe₃]⁺.

 $Mes-Si(C \equiv C-CMe_3)_2 \{C[Al(CH_2CHMe_2)_2] = CH-CMe_3\}$ (12)

A solution of Mes-Si(C=C-CMe₃)₃ (2) (0.264 g, 0.677 mmol) in toluene (15 mL) was added at room temperature to a solution of HAl(CH₂CHMe₂)₂ (0.096 g, 0.676 mmol) in toluene (15 mL). The mixture was stirred overnight, the volatiles were removed *in vacuo* and the residue was recrystallised from 1,2-difluorobenzene at

-15 °C to yield compound **12** as a colourless solid (0.352 g, 98 %); m. p. (argon, sealed capillary): 87°C. - IR (CsI, paraffin): v = 2196 w, 2156 s, 2116 m $v(C \equiv C)$; 1644 w, 1603 s, 1566 m, 1556 m, 1533 s, 1511 m [v(C=C), aromatic ring]; 1454 vs (paraffin); 1411 w δ (CH₃); 1382 vs (paraffin); 1365 s, 1305 w, 1287 w, 1253 s δ (CH₃); 1202 m, 1179 m, 1138 w, 1112 w, 1071 m, 1044 m, 1030 w, 1006 w, 999 w, 955 m, 940 s, 889 m, 850 m, 835 w, 808 m, 791 m, 767 s, 753 w [δ (CH), v(CC)]; 720 vs (paraffin); 677 m, 660 m (aromatic ring); 639 vw, 615 s, 573 m, 564 m, 520 m, 502 w, 475 w, 448 m cm⁻¹ [v(SiC), v(AlC), δ (CC)]. – ¹H NMR (400.03 MHz, C₆D₆): δ = 6.95 (s, ${}^{3}J_{\text{SiH}} = 29.8 \text{ Hz}, 1 \text{ H}, \text{ C}=CH), 6.76 (s, 2 \text{ H}, m-\text{H}), 2.89$ (s, 6 H, o-Me), 2.37 (m, 2 H, AlCH₂CHMe₂), 2.05 (s, 3 H, *p*-Me), 1.32 (d, ${}^{3}J_{\text{HH}} = 6.5 \text{ Hz}$, 12 H, AlCH₂CHMe₂), 1.13 (s, 9 H, C=C-CMe₃), 1.09 (s, 18 H, (C=C-CMe₃), 0.70 ppm (d, ${}^{3}J_{\text{HH}} = 7.0 \text{ Hz}$, 4 H, AlCH₂CHMe₂). – 13 C NMR (100.59 MHz, C₆D₆): $\delta = 166.8$ (C=C-CMe₃), 144.9 (o-C), 140.9 (br. s, C =C-CMe₃), 139.8 (p-C), 129.9 (m-C and ipso-C), 122.2 (C≡C-CMe₃), 83.7 (C≡C-CMe₃), 39.6 (C=C-CMe₃), 30.1 (C≡C-CMe₃), 29.0 (C=C-CMe₃), 28.9 (C≡C-CMe₃), 28.8 (AlCH₂CHMe₂), 27.0 (AlCH₂CHMe₂), 26.6 (AlCH₂CHMe₂), 25.5 (*o*-Me), 21.1 ppm (*p*-Me). – ²⁹Si NMR (79.5 MHz, C₆D₆): $\delta = -63.1$ ppm. – MS ((+)-EI; 20 eV; 298 K): m/z (%) = 475 (100) [M–CMe₃]⁺.

$Mes-Si(C \equiv C-CMe_3)_2 \{C[Al(CMe_3)_2] = CH-CMe_3\} (13)$

A solution of Mes-Si(C \equiv C–CMe₃)₃ (2) (0.316 g, 0.810 mmol) in toluene (10 mL) was added at room temperature to a solution of HAl(CMe₃)₂ (0.115 g, 0.810 mmol) in toluene (15 mL). The mixture was stirred overnight, the volatiles were removed in vacuo, and the residue was recrystallised from pentafluorobenzene at -20 °C to yield compound 13 as a colourless solid (0.425 g, 98%); m. p. (argon, sealed capillary): 107° C. – IR (CsI, paraffin): v =2197 w, 2156 m, 2126 w v(C=C); 1603 m v(C=C); 1458 vs, 1375 s (paraffin); 1302 w, 1254 m δ(CH₃); 1190 vw, 1169 w, 1153 w, 1067 vw, 1028 vw, 939 w, 891 w, 847 m, 773 m [δ(CH), v(CC)]; 721 s (paraffin); 660 w, 615 w, 567 w, 530 vw, 472 vw cm⁻¹ [v(SiC), v(AlC), δ (CC)]. – ¹H NMR (400.13 MHz, C₆D₆): $\delta = 6.99$ (s, 1 H, ³J_{SiH} = 30.4 Hz, C=CH), 6.76 (s, 2 H, m-H), 2.89 (s, 6 H, o-Me), 2.05 (s, 3 H, p-Me), 1.43 (s, 18 H, AlCMe₃), 1.23 (s, 9 H, C=C-CMe₃), 1.09 ppm (s, 18 H, C≡C-CMe₃). -¹³C NMR (100.62 MHz, C_6D_6): $\delta = 167.8$ (C=C-CMe₃), 145.2 (o-C), 139.7 (p-C), 139.5 (br. s, C = C-CMe₃), 129.9 (*m*-C), 129.8 (*ipso*-C), 123.9 (C≡C–CMe₃), 82.9 (C≡C– CMe₃), 40.3 (C=C-CMe₃), 31.3 (AlCMe₃), 30.3 (C≡C- CMe_3), 29.0 (C=C-CMe_3), 28.6 (C=C-CMe_3), 25.2 (o-Me), 21.0 (p-Me), 18.7 ppm (br. s, AlCMe₃). - ²⁹Si NMR $(79.5 \text{ MHz}, C_6 D_6): \delta = -61.1 \text{ ppm.} - \text{MS} ((+)-\text{EI}; 50 \text{ eV};$ 323 K): m/z (%) = 392 (24) [M-Al(CMe_3)_2+H]^+, 335 (93) [M-Al(CMe_3)_2-butene]^+.

$Ph_2Si\{C[Al(CMe_3)_2]=CH-CMe_3\}_2$ (14)

A solution of HAl(CMe₃)₂ (0.589 g, 4.14 mmol) in toluene (50 mL) was treated with solid Ph₂Si(C≡C–CMe₃)₂ (1) (0.714 g, 2.07 mmol) at room temperature. The colourless solution was stirred for 33 d. All volatiles were removed in a vacuum. Repeated recrystallisation gave a colourless solid which contained the monoaddition product **8** and **14** in a ratio of 0.65 : 0.35. – ¹H NMR data of **14** (400.03 MHz, C₆D₆): δ = 7.74 (d, ³*J*_{HH} = 7.9 Hz, 4 H, *o*-H), 7.35 (*pseudo*-t, ³*J*_{HH} = 7.9 Hz, 4 H, *m*-H), 7.03 (t, ³*J*_{HH} = 7.9 Hz, 2 H, *p*-H), 6.86 (s, ³*J*_{SiH} = 25.6 Hz, 2 H, C=CH), 1.26 (s, 18 H, C=C-CMe₃), 0.97 ppm (s, br, 36 H, AlCMe₃).

$Ph_2Si\{C[Ga(CMe_3)_2]=CH-CMe_3\}_2$ (15)

Solid $Ph_2Si(C \equiv C - CMe_3)_2$ (1) (0.621 g, 1.80 mmol) was added to a solution of HGa(CMe₃)₂ (0.667 g, 3.61 mmol) in toluene (40 mL) at room temperature. The mixture was stirred for 20 d. All volatiles were removed in vacuo. The residue was dissolved in pentafluorobenzene (50 mL), the solution concentrated to about 20 mL and stored at -30 °C to yield compound **15** as a colourless solid (0.96 g, 75%); m. p. (argon, sealed capillary): 157°C. - IR (CsI, paraffin): v = 1558 s v(C=C); 1456 vs, 1377 vs (paraffin); 1306 w,1261 vw, 1250 m δ (CH₃); 1200 m, 1169 w, 1156 w, 1098 s, 1063 w, 1013 w, 1003 w, 972 vw, 939 w, 920 w, 901 w, 876 m, 806 s, 799 s, 743 s, 737 s [δ (CH), ν (CC)]; 714 vs (paraffin); 700 vs, 689 s δ (Ph); 656 m, 619 w, 610 m, 523 s, 480 m, 457 w, 434 w cm⁻¹ [v(SiC), v(GaC), δ (CC)]. – ¹H NMR (400.03 MHz, C₆D₆): δ = 7.69 (d, ³J_{HH} = 7.2 Hz, 4 H, o-H), 7.22 (pseudo-t, ${}^{3}J_{HH} = 7.4$ Hz, 4 H, m-H), 7.07 (t, ${}^{3}J_{\text{HH}} = 7.5 \text{ Hz}$, 2 H, *p*-H), 6.43 (s, ${}^{3}J_{\text{SiH}} = 24.2 \text{ Hz}$, 2 H, C=CH), 1.33 (s, 18 H, C=C-CMe₃), 1.03 ppm (s, br, 36 H, GaCMe₃). – 13 C NMR (100.59 MHz, C₆D₆): δ $= 160.3 (C = C - CMe_3), 148.2 (C = C - CMe_3), 145.6 (ipso-$ C), 133.8 (o-C), 130.5 (m-C), 129.9 (p-C), 39.2 (C=C-CMe₃), 31.3 (GaCMe₃), 30.2 (GaCMe₃), 30.0 ppm (C=C- CMe_3). – ²⁹Si NMR (79.47 MHz, C₆D₆): $\delta = -27.0$ ppm. - MS ((+)-EI; 20 eV; 298 K): m/z (%) = 657 (3) [M-CMe₃]⁺, 471 (100) [M-Ga(CMe₃)₂-HCMe₃]⁺, 415 (12) $[M-Ga(CMe_3)_2-2 CMe_3]^+$. - C₄₀H₆₆Ga₂Si (714.5): calcd. C 67.2, H 9.3; found C 67.1, H 9.4.

$Ph_2Ge\{C[Ga(CMe_3)_2]=CH-CMe_3\}_2$ (16)

A solution of $Ph_2Ge(C \equiv C - CMe_3)_2$ (4) (0.337 g, 0.87 mmol) in toluene (5 mL) was added at room temperature to a solution of HGa(CMe_3)_2 (0.353 g, 1.91 mmol) in toluene (50 mL). The resulting colourless mixture was stirred for 6 d at room temperature to yield a pale-brown solution. The volatiles were removed *in vacuo*, and the residue was washed twice at 0° C with *n*-pentane (5 mL) to remove unreacted alkyne and recrystallised from pentafluorobenzene at -30 °C to yield compound 16 (0.47 g, 71%) based on the alkyne); m. p. (argon, sealed capillary): 166°C. - IR (CsI, paraffin): v = 1973 vw, 1958 w, 1902 vw, 1886 w, 1844 vw, 1829 w, 1775 vw, 1738 vw, 1686 vw, 1651 vw, 1593 s, 1555 vs [v(C=C), phenyl]; 1464 vs (paraffin); 1427 m, 1418 vw δ(CH₃); 1377 s (paraffin); 1358 s, 1302 m, 1267 m, 1248 s δ(CH₃); 1200 s, 1169 w, 1153 vw, 1084 vs, 1063 w, 1043 vw, 1022 vw, 1013 w, 1001 m, 974 w, 939 w, 918 m, 895 m, 872 s, 860 m, 806 s, 793 s, 768 vw, 737 vs [δ (CH), v(CC)]; 712 s (paraffin); 696 s, 665 m (phenyl); 619 w, 579 vs, 567 sh, 530 w, 503 s, 473 s, 461 s, 447 s, 408 vs cm⁻¹ [ν (GeC), ν (GaC), δ (CC)]. – ¹H NMR (400.13 MHz, C₆D₆): $\delta = 7.67$ (d, ${}^{3}J_{\text{HH}} = 6.6$ Hz, 4 H, *o*-H), 7.22 (*pseudo*-t, ${}^{3}J_{\text{HH}} = 7.5$ Hz, 4 H, *m*-H), 7.06 (t, ${}^{3}J_{\text{HH}} = 7.4 \text{ Hz}, 2 \text{ H}, p\text{-H}$), 6.46 (s, 1 H, C=CH), 1.31 (s, 18 H, C=C-CMe₃), 1.04 ppm (br, 36 H, GaCMe₃). -¹³C NMR (100.62 MHz, C₆D₆): $\delta = 158.5$ (C=C-CMe₃), 149.5 (C =C-CMe₃), 148.3 (ipso-C), 133.0 (o-C), 130.7 (m-C), 129.5 (p-C), 38.8 (C=C-CMe₃), 31.1 (GaCMe₃), 30.1 (GaCMe₃), 30.0 ppm (C=C-CMe₃). - MS ((+)-EI; 20 eV; 353 K): m/z (%) = 701 (13) [M-CMe₃]⁺, 517 (100) $[M-HGa(CMe_3)_2-CMe_3]^+$. - $C_{40}H_{66}Ga_2Ge$ (759.0): calcd. C 63.3, H 8.8; found C 62.9, H 8.7.

$Ph_2Ge\{C[Ga(CMe_3)_2]=CH-Ph\}_2$ (17)

A solution of Ph₂Ge(C=C-Ph)₂ (5) (0.356 g, 0.83 mmol) in toluene (10 mL) was added at room temperature to a solution of HGa(CMe₃)₂ (0.327 g, 1.77 mmol) in toluene (50 mL). The colourless mixture was stirred for 8 d at room temperature whereupon the colour changed to yellow. The volatiles were removed in vacuo to give a yellow foam, which contained up to 50% of the mono-hydrogallation product $Ph_2Ge(C \equiv CPh)\{C[Ga(CMe_3)_2]=CH-Ph\}$ (10). Repeated recrystallization from pentafluorobenzene (45° C / -30 °C) yielded **17** as a colourless solid (0.127 g, 19%); m. p. (argon, sealed capillary): 184°C (dec). - IR (CsI, paraffin): v = 1996 vw, 1940 vw, 1894 vw, 1883 vw, 1597 sh, 1584 w, 1547 m [v(C=C), phenyl]; 1460 vs, 1375 vs (paraffin); 1304 w, 1265 w, 1249 vw δ (CH₃); 1171 m, 1082 m, 1027 w, 1009 w, 972 vw, 935 w, 916 w, 868 w, 841 w, 804 w [δ (CH), v(CC)]; 728 m (paraffin); 692 m, 669 w δ (Ph); 621 w, 594 vw, 569 w, 532 m, 505 m, 471 m, 457 w, 432 m cm⁻¹ [v(GeC), v(GaC), δ (CC)]. – ¹H NMR (400.03 MHz, C₆D₆): $\delta = 7.66$ [d, ${}^{3}J_{\text{HH}} = 6.6$ Hz, 4 H, o-H (GePh)], 7.63 (s, 2 H, C=CH), 7.53 [d, ${}^{3}J_{HH} = 7.5$ Hz, 4 H, o-H (C=CPh)], 7.12 [m, m-H (C=CPh)], 7.10 [m, 4 H, m-H (GePh)], 7.03 [t, ${}^{3}J_{\text{HH}} = 7.4 \text{ Hz}, 2 \text{ H}, p-\text{H} (\text{GePh})],$ 6.96 [t, ${}^{3}J_{\text{HH}} = 7.4 \text{ Hz}, 2 \text{ H}, p-\text{H} (C=\text{CPh})$], 1.06 ppm (s, 18 H, GaCMe₃). – ¹³C NMR (100.59 MHz, C₆D₆): δ = 160.5 (C = CHPh), 148.9 (C=CHPh), 145.1 [ipso-C (GePh)], 140.0 [*ipso*-C (C=CPh)], 133.3 [*o*-C (GePh)], 130.8 [*m*-C (GePh)], 130.0 [*p*-C (GePh)], 128.4 [*m*-C (C=CPh)], 127.84 [*p*-C (C=CPh)], 127.78 [*o*-C (C=CPh)], 30.7 (GaCMe₃), 30.4 ppm (GaCMe₃). – MS ((+)-EI; 20 eV; 373 K): m/z (%) = 741 (36) [M–CMe₃]⁺, 557 (51) [M–HGa(CMe₃)₂–CMe₃]⁺. – C₄₄H₅₈Ga₂Ge (799.0): calcd. C 66.1, H 7.3; found C 66.1, H 7.3.

$(Me_3C-C\equiv C)_2Ge\{C[Ga(CMe_3)_2]=CH-CMe_3\}_2$ (18)

A solution of Ge(C=C-CMe₃)₄ (6) (0.440 g, 1.11 mmol) in toluene (10 mL) was added at 0°C to a solution of $HGa(CMe_3)_2$ (0.410 g, 2.22 mmol) in toluene (10 mL). The mixture was stirred at this temperature for 30 min and then warmed to room temperature over a period of 16 h. The volatiles were removed in vacuo, and the residue was recrystallised from 1,2-difluorobenzene to yield 18 as a colourless solid (0.451 g, 53 %); m. p. (argon, sealed capillary): 182°C. - IR (CsI, paraffin): v = 2160 sh, 2131 m $v(C \equiv C)$; 1953 vw, 1906 vw, 1886 vw, 1821 vw, 1763 vw, 1676 vw, 1585 w, 1551 vw [v(C=C), phenyl]; 1464 vs, 1377 vs (paraffin); 1306 w, 1279 vw, 1265 w, 1248 w sh δ (CH₃); 1209 vw, 1182 w, 1159 w, 1084 s, 1070 m, 1026 w, 1001 w, 966 w, 937 w, 920 m, 876 w, 841 w, 808 m, 756 s [δ (CH), ν (CC)]; 733 vs (paraffin); 694 s, 671 w δ (Ph); 621 vw, 565 m, 534 m, 501 m, 461 s, 422 m cm⁻¹ [v(GeC), v(GaC), δ (CC)]. – ¹H NMR $(400.03 \text{ MHz}, C_6 D_6)$: $\delta = 6.49$ (s, 2 H, C=CH), 1.44 (s, 36) H, GaCMe₃), 1.21 (s, 18 H, C=C-CMe₃), 1.17 ppm (s, 18 H, C=C-CMe₃). – ¹³C NMR (100.59 MHz, C₆D₆): δ = 160.3 $(C=C-CMe_3)$, 148.5 ($C=C-CMe_3$), 119.5 ($C\equiv C-CMe_3$), 84.7 (C=C-CMe₃), 38.4 (C=C-CMe₃), 31.6 (GaCMe₃), 31.0 (C≡C-CMe₃), 30.2 (C=C-CMe₃), 29.2 (br, GaCMe₃), 28.8 ppm (C=C-CMe₃). – MS ((+)-EI; 20 eV; 353 K): m/z $(\%) = 709 (100) [M-CMe_3]^+, 525 (55) [M-HGa(CMe_3)_2 - 100) [M-HGa(Me_3)_2 - 100) [M-HGa(Me_3$ CMe_3]⁺. – $C_{40}H_{74}Ga_2Ge$ (767.1): calcd. C 62.6, H 9.7; found C 62.5, H 9.7.

$Me-Si(C \equiv C-p-Tol) \{C[Ga(CMe_3)_2] = CH-p-Tol\}_2 (19)$

Solid Me-Si(C=C-*p*-Tol)₃ (**3**) (0.283 g, 0.73 mmol) was added at room temperature to a solution of HGa(CMe₃)₂ (0.270 g, 1.46 mmol) in toluene (25 mL). The colourless mixture was stirred for 3 d to give an orange solution. All volatiles were removed *in vacuo*. The residue was recrystallised from *c*-pentane at -15 °C to yield **19** as an amorphous solid (0.451 g, 81%). [Assignment of NMR spectra: signals in the alkenyl group are labelled *cis* (H *cis* to Ga) or *trans* (H *trans* to Ga)]. – IR (CsI, paraffin): v = 2147 s sh, 2133 vs v(C=C); 2058 m, 1904 w, 1790 w, 1650 w, 1643 w, 1607 m, 1580 m, 1573 m, 1556 m, 1542 w, 1504 vs [v(C=C, phenyl]; 1462 vs, 1454 vs, 1377 vs (paraffin); 1366 vs, 1302 w, 1269 vw, 1246 m $\delta(CH_3)$; 1219 w, 1177 m, 1109 w, 1070 w, 1038 w, 1020 m, 1015 m, 943 w, 897 m,

837 w, 816 s, 806 s, 785 w [δ(CH), v(CC)]; 721 vs (paraffin); 694 w δ (Ph); 652 w, 615 m, 552 m, 536 s, 517 m, 505 m, 455 w, 436 w cm⁻¹[v(SiC), v(GaC), δ (CC)]. – ¹H NMR (400.13 MHz, C₆D₆): $\delta = 8.33$ [s, ³*J*_{SiH} <13 Hz, 1 H, C=CH (trans)], 7.98 [s, ${}^{3}J_{SiH} = 24.3$ Hz, 1 H, C=CH (cis)], 7.57 [d, ${}^{3}J_{\text{HH}} = 8.0 \text{ Hz}$, 4 H,o-H (*cis*) and o-H (ethyne)], 7.08 [d, ${}^{3}J_{\text{HH}} = 8.0 \text{ Hz}, 2 \text{ H}, \text{ m-H} \text{ (cis)}$], 6.87 [d, ${}^{3}J_{\text{HH}} =$ 2.6 Hz, 4 H, o- and m-H (trans)], 6.77 [d, ${}^{3}J_{\text{HH}} = 7.8$ Hz, 2 H, m-H (ethyne)], 2.11 [s, 3 H, p-Me (cis)], 1.96 [s, 3 H, p-Me (trans)], 1.89 [s, 3 H, p-Me (ethyne)], 1.47 [s, 18 H, GaCMe₃ (cis)], 1.36 and 1.13 [each s, 9 H, GaCMe₃ (trans)], 0.83 ppm (s, 3 H, SiMe). $-{}^{13}$ C NMR (100.62 MHz, C₆D₆): $\delta = 158.6 [C = C - p - Tol (trans)], 156.1 [C = C - p - Tol (trans)],$ 153.3 [C =C-p-Tol (cis)], 152.4 [C=C-p-Tol (cis)], 144.4 [ipso-C (trans)], 140.4 [p-C (ethyne)], 138.9 [ipso-C (cis)], 138.4 [p-C (trans)], 137.4[p-C (cis)], 133.1 [o-C (ethyne)], 131.2 [m-C (trans)], 129.6 [m-C (ethyne)], 129.4[m-C (cis)], 128.6 [o-C (cis)], 124.0 [o-C (trans)], 119.0 [ipso-C (ethyne)], 111.5 (C≡C-p-Tol), 93.6 (C≡C-p-Tol), 31.1 [GaCMe₃ (cis)], 30.4 and 30.3 [GaCMe₃ (trans)], 29.2 [GaCMe₃ (cis)], 29.0 and 28.8 [GaCMe₃(2) (trans)], 21.3 $(C \equiv C - C_6 H_4 Me)$, 21.2 $[C = C - C_6 H_4 Me (cis)]$, 20.9 $[C = C - C_6 H_4 Me (cis)]$ C₆H₄Me (trans)], 1.1 ppm (SiMe). – ²⁹Si NMR (79.5 MHz, C₆D₆): $\delta = -34.1$ ppm. – MS ((+)-EI; 30 eV; 353 K): m/z $(\%) = 701 (20) [M-CMe_3]^+, 517 (100) [M-2Tol-CMe_3-2H]$ or M-Ga(CMe₃)₂-butene]⁺. - C₄₄H₆₂Ga₂Si (758.5): calcd. C 69.7, H 8.2; found C 68.9, H 8.2.

X-Ray crystallography

Crystals suitable for X-ray crystallography were obtained by recrystallisation from *n*-pentane (7, 10, 11), 1,2difluorobenzene (2, 8, 9, 12, 18) or pentafluorobenzene (13, 15, 16, 17). Intensity data were collected on a Bruker APEX II diffractometer with monochromated MoK_{α} or CuK_{α} (10) radiation. The collection method involved ω scans. Data reduction was carried out using the program SAINT+ [33]. The crystal structures were solved by Direct Methods using SHELXTL [34, 35]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using SHELXTL. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. Compound 7 crystallised with one *n*-pentane molecule per unit cell, which was disordered across the inversion centre, compound 2 crystallised with one 1,2-difluorobenzene molecule per formula unit, which showed rotational disorder over two positions (0.61 : 0.39). Similarly, 15 and 18 crystallised with half a molecule of pentafluorobenzene each which were disordered across the inversion centre. Compounds 12, 16 and 18 had peripheral alkyl substituents that were disordered and refined in split positions (12, CMe₃: C31 0.60 : 0.24 : 0.16, C71 0.51 : 0.49; CMe₂: C91 0.83 : 0.17; 16, CMe₃: C04

	2	$7 \cdot 0.5$ pentane	8	9	10	11
Crystal data						
Empirical formula	C33H42F2Si	C26.5H24F10Ge	C32H47AlSi	C32H47GaSi	C ₃₆ H ₃₉ GaGe	C32H37AlF10Ge
M _r	504.75	605.05	486.76	529.50	613.98	711.18
Crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic	monoclinic
Space group	$P2_{1}/c$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	C2/c
<i>a</i> , pm	1228.56(5)	963.84(7)	910.46(2)	911.49(1)	851.95(1)	3690.9(1)
<i>b</i> , pm	1037.99(4)	1088.69(8)	1115.99(2)	1113.17(1)	986.46(1)	1049.48(4)
<i>c</i> , pm	2457.4(1)	1473.9(1)	1722.41(3)	1731.42(2)	2015.27(3)	1822.45(8)
α , deg	90	77.440(2)	71.458(1)	71.3133(6)	87.9904(8)	90
β , deg	96.705(1)	89.546(2)	78.985(1)	79.6900(7)	87.5809(8)	108.510(1)
γ, deg	90	64.099(2)	78.820(1)	73.0344(7)	66.9190(8)	90
$V, \times 10^{-30} \text{ m}^3$	3111.6(2)	1351.3(2)	1576.06(5)	1584.64(3)	1556.38(3)	6694.2(4)
$ ho_{ m calcd.}$, g cm ⁻³	1.08	1.49	1.03	1.11	1.31	1.41
Z	4	2	2	2	2	8
F(000), e	1088	610	532	568	636	2912
μ , mm ⁻¹	0.1	1.2	0.1	0.9	2.4	1.0
Data collection						
Т, К	153	153	153	153	153	153
Unique reflections/ R_{int}	7885/0.027	7750/0.067	9177/0.042	9200/0.026	5046/0.020	9758/0.023
Reflections $I > 2 \sigma(I)$	6758	6695	6419	8102	4471	7922
Refinement						
Refined parameters	435	344	319	319	349	409
Final <i>R</i> 1 $[I > 2 \sigma(I)]^a$	0.0564	0.0412	0.0484	0.0294	0.0309	0.0374
Final wR2 ^b (all data)	0.1653	0.1108	0.1309	0.0766	0.0837	0.1004
$\Delta ho_{ m fin}$ (max/min), $e \ { m \AA}^{-3}$	0.44/-0.36	0.56/-0.64	0.30/-0.26	0.61, /-0.22	0.46/-0.39	0.56/-0.39

Table 3a. Crystal data and structure refinement for compounds 1, 7–11.

^a $R1 = \Sigma \parallel F_{o} \mid -|F_{c} \parallel /\Sigma|F_{o}|;$ ^b $wR2 = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}, w = [\sigma^{2}(F_{o}^{2}) + (AP)^{2} + BP]^{-1}, where P = (Max(F_{o}^{2}, 0) + 2F_{c}^{2})/3.$

Table 3b. Crystal data and structure refinement for compounds 12 , 13 , 15–18 .	
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	12	13	$15\cdot0.5C_6F_5H$	16	17	$18\cdot0.5C_6F_2H_4$	
Crystal data							
Empirical formula	C35H57AlSi	C35H57AlSi	C44H66.5F2.5Ga2Si	C40H66Ga2Ge	C44H58Ga2Ge	C43H76FGa2Ge	
M _r	532.87	532.87	798.49	758.95	798.93	824.06	
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	C2/c	$P\overline{1}$	C2/c	
a, pm	1114.73(3)	1237.82(7)	1563.74(2)	3216.45(8)	993.94(6)	4928.4(3)	
b, pm	1941.94(4)	1638.7(1)	1298.79(2)	1774.27(3)	1452.48(9)	1067.88(6)	
<i>c</i> , pm	1710.49(4)	1751.3(1)	2129.10(3)	1478.34(4)	1494.24(9)	1870.2(1)	
α , deg	90	90	90	90	97.5976(9)	90	
β , deg	100.875(1)	90.520(2)	92.0049(8)	103.501(2)	103.2638(9)	105.976(1)	
γ, deg	90	90	90	90	100.0523(9)	90	
$V, \times 10^{-30} \text{ m}^3$	3636.3(2)	3552.2(4)	4321.5(1)	8203.5(2)	2033.8(2)	9462.7(9)	
$ ho_{ m calcd.}$, g cm ⁻³	0.97	1.00	1.23	1.23	1.31	1.16	
Ζ	4	4	4	8	2	8	
F(000), e	1176	1176	1692	3200	832	3496	
μ , mm ⁻¹	0.1	0.1	1.3	2.1	2.1	1.8	
Data collection							
<i>T</i> , K	233	153	153	153	153	153	
Unique reflections/ R_{int}	8671/0.033	10436/0.025	12587/0.027	9831/0.071	9824/0.016	13809/0.050	
Reflections $I > 2 \sigma(I)$	6525	8890	11 146	7566	8431	9024	
Refinement							
Refined parameters	450	352	505	437	436	559	
Final <i>R</i> $[I > 2 \sigma(I)]^a$	0.0509	0.0459	0.0245	0.0397	0.0240	0.0439	
Final wR2 ^b (all data)	0.1619	0.1402	0.0689	0.0969	0.0641	0.1221	
$\Delta ho_{ m fin}$ (max/min), $e \ { m \AA}^{-3}$	0.36/-0.20	0.55/-0.42	0.53/-0.28	0.79/-0.74	0.51/-0.54	1.23/-0.70	

^a $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|;$ ^b $wR2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}, w = [\sigma^2 (F_o^2) + (AP)^2 + BP]^{-1},$ where $P = (Max (F_o^2, 0) + 2F_c^2) / 3.$

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0.84 : 0.16; **18**, CMe₃: C13 0.69 : 0.31, C01 0.46 : 0.54, C04 0.57 : 0.43). Further crystallographic data is summarised in Table 3.

CCDC 1002760 (7), 1002761 (2), 1002762 (8), 1002763 (9), 1002764 (11), 1002765 (12), 1002766 (13), 1002767 (15), 1002768 (16), 1002769 (17), 1002770 (18), and 1013176 (10) contain the supplementary crystallographic

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data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www. ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

We are grateful to the Deutsche Forschungsgemeinschaft for generous financial support.

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