

Hydrometallation ($M = \text{Al, Ga}$) of Silicon- and Germanium-centred Oligoalkynes

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

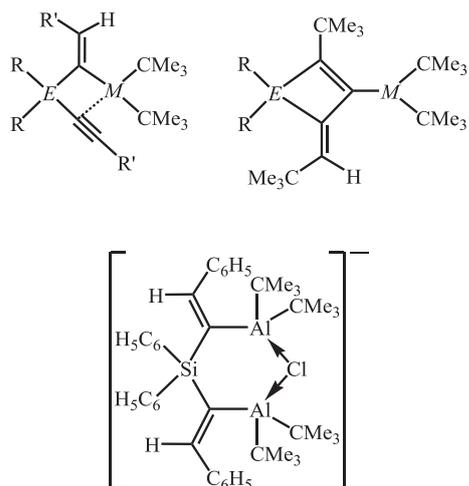
Treatment of a variety of alkyl- and arylsilanes, $\text{R}_{4-n}\text{Si}(\text{C}\equiv\text{C-R}')_n$, and -germanes, $\text{R}_{4-n}\text{Ge}(\text{C}\equiv\text{C-R}')_n$ (**1–7**), with equimolar quantities of the dialkylmetal hydrides HMR''_2 ($M = \text{Al, Ga}$; $\text{R}'' = \text{CMe}_3, \text{CH}_2\text{CHMe}_2$) yielded by reduction of a single alkynyl group a series of mixed alkenyl-alkynyl compounds $\text{R}_{4-n}\text{Si}(\text{C}\equiv\text{C-R}')_{n-1}\{\text{C}(\text{MR}''_2)=\text{CHR}'\}$ ($n = 2, 3$) and $\text{R}_2\text{Ge}(\text{C}\equiv\text{C-R}')\{\text{C}[\text{M}(\text{CMe}_3)_2]=\text{CHR}'\}$ (**8–13**). Reactions with two equivalents of the hydrides afforded the dialkenyl compounds $\text{R}_2\text{E}\{\text{C}[\text{M}(\text{CMe}_3)_2]=\text{CHR}'\}_2$ ($E = \text{Si, Ge}$, **14–17**), $\text{Ge}(\text{C}\equiv\text{C-CMe}_3)_2\{\text{C}[\text{Ga}(\text{CMe}_3)_2]=\text{CH-CMe}_3\}_2$ (**18**) and $\text{MeSi}(\text{C}\equiv\text{C-}i\text{-Tol})\{\text{C}[\text{Ga}(\text{CMe}_3)_2]=\text{CH-}i\text{-Tol}\}_2$ (**19**) [$\text{R} = \text{Ph, Mes, Me, C}_6\text{F}_5$; $\text{R}' = \text{CMe}_3, \text{Ph}$]. 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 $\text{C}_\alpha\equiv\text{C-R}'$.

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

Introduction

Treatment of oligoalkynylsilanes and -germanes, $\text{R}_{4-n}\text{E}(\text{C}\equiv\text{C-R}')_n$ ($E = \text{Si, Ge}$), with equimolar quantities of dialkylaluminium or -gallium hydrides, $\text{H-MR}''_2$ ($M = \text{Al, Ga}$), have been shown to afford mixed alkenyl-alkynylsilicon and -germanium compounds [1–7] by addition of an E -H bond to a $\text{C}\equiv\text{C}$ 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 $\text{C}=\text{C}$ 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 alkenyl-alkynyl derivatives exhibit an intramolecular interac-

tion between the coordinatively unsaturated aluminium and gallium atoms and the α -carbon atoms of the $\text{C}\equiv\text{C}$ 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 $\text{C}\equiv\text{C}$ 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]



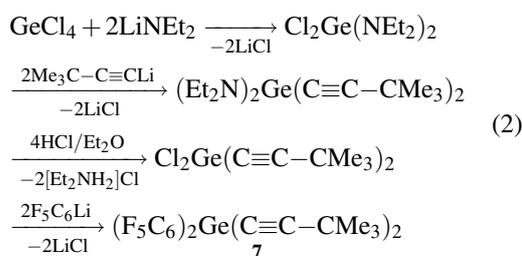
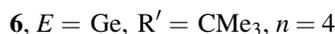
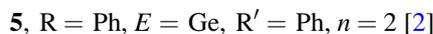
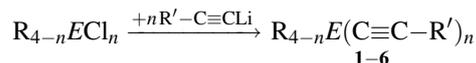
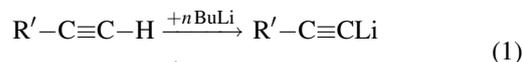
Scheme 1. Hydrometallation of dialkynylsilanes and -germanes: alkenyl-alkynyl compounds, cyclisation and chelating Lewis acid ($E = \text{Si, Ge}; M = \text{Al, Ga}$).

(Scheme 1). Functionalisation of the alkynylsilanes and -germanes by Lewis-basic amino groups or halogen atoms resulted after hydrometallation in strong intramolecular $\text{Al}-\text{X}$ or $\text{Ga}-\text{X}$ interactions which by activation of $\text{Si}-\text{X}$ or $\text{Ge}-\text{X}$ 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 $M \cdots \text{C}$ 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 $\text{R}_2\text{Si}(\text{C}\equiv\text{C}-\text{R}')_2$, $\text{R}-\text{Si}(\text{C}\equiv\text{C}-\text{R}')_3$, $\text{R}_2\text{Ge}(\text{C}\equiv\text{C}-\text{R}')_2$, and $\text{Ge}(\text{C}\equiv\text{C}-\text{R}')_4$ (**1** to **6**; Eq. 1) were synthesised conveniently following standard literature procedures [7, 22–26]. The lithiation of the terminal alkynes $\text{R}'-\text{C}\equiv\text{C}-\text{H}$ ($\text{R}' = \text{CMe}_3$,

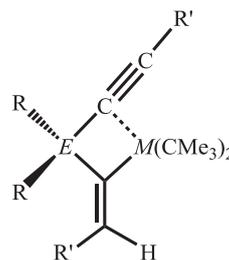
C_6H_5 , $p\text{-C}_6\text{H}_4\text{-Me}$ ($p\text{-Tol}$)) with $n\text{-BuLi}$ at -78°C afforded the corresponding lithium alkynides which *in situ* were reacted with the appropriate element halides $\text{R}_{4-n}\text{ECl}_n$ ($E = \text{Si, Ge}$) to generate the alkynylelement compounds by salt elimination. Only the preparation of the pentafluorophenylgermanium compound **7** required a different strategy to avoid problems associated with the synthesis and purity of the $(\text{F}_5\text{C}_6)_2\text{ECl}_2$ or $\text{Cl}_2\text{E}(\text{C}\equiv\text{C}-\text{R}')_2$ precursors due to non-stoichiometric reactions and the formation of inseparable mixtures of $(\text{F}_5\text{C}_6)_{4-n}\text{ECl}_n$ or $\text{Cl}_{4-n}\text{E}(\text{C}\equiv\text{C}-\text{R}')_n$ ($n = 0-4$). Making use of an amine protecting group was found to minimize these problems [7]. GeCl_4 was therefore treated with two equivalents of LiNEt_2 to give $\text{Cl}_2\text{Ge}(\text{NEt}_2)_2$ which was reacted with $\text{Me}_3\text{C}-\text{C}\equiv\text{C}-\text{Li}$ to yield the dialkynylgermane $(\text{Et}_2\text{N})_2\text{Ge}(\text{C}\equiv\text{C}-\text{CMe}_3)_2$. The latter was deprotected with HCl to afford $\text{Cl}_2\text{Ge}(\text{C}\equiv\text{C}-\text{CMe}_3)_2$ which in the final step was converted with *in situ*-formed $\text{F}_5\text{C}_6\text{Li}$ to $(\text{F}_5\text{C}_6)_2\text{Ge}(\text{C}\equiv\text{C}-\text{CMe}_3)_2$ (**7**) in 54% yield (Eq. 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 $\text{H}-\text{MR}''_2$ ($M = \text{Al, Ga}; \text{R}'' = \text{CMe}_3, \text{CH}_2\text{CHMe}_2$) with the alkynylsilanes or -germanes **1** to **7** at room temperature in toluene or n -hexane (synthesis of **10**) be-

tween 30 min and 12 h yielded the corresponding 1 : 1 addition products **8** to **13** ($E = \text{Si}, \text{Ge}$) 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 $\text{H-M}(\text{CMe}_3)_2$. 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 $\text{Ph}_2\text{Si}(\text{C}\equiv\text{C-CMe}_3)_2$, $\text{Si}(\text{C}\equiv\text{C-CMe}_3)_4$ and $\text{Ph}_2\text{Ge}(\text{C}\equiv\text{C-Ph})_2$ was not successful. In case of $\text{Ph}_2\text{Si}(\text{C}\equiv\text{C-CMe}_3)_2$ 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 regioselective (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.

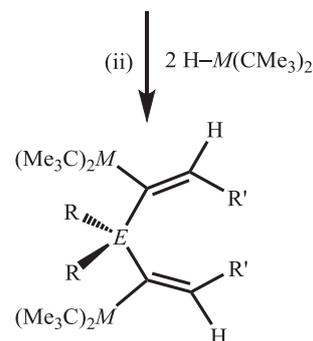


- 8**, $R = \text{Ph}, E = \text{Si}, M = \text{Al}, R' = \text{CMe}_3$
9, $R = \text{Ph}, E = \text{Si}, M = \text{Ga}, R' = \text{CMe}_3$
10, $R = \text{Ph}, E = \text{Ge}, M = \text{Ga}, R' = \text{Ph}$
11, $R = \text{C}_6\text{F}_5, E = \text{Ge}, M = \text{Al}, R' = \text{CMe}_3$



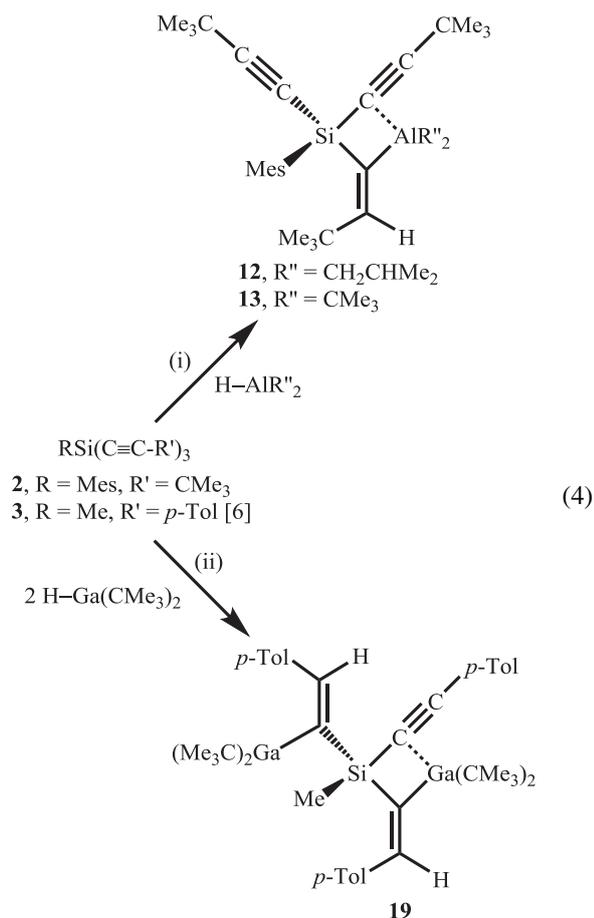
- 1**, $R = \text{Ph}, E = \text{Si}, R' = \text{CMe}_3, n = 2$
4, $R = \text{Ph}, E = \text{Ge}, R' = \text{CMe}_3, n = 2$ [7]
5, $R = \text{Ph}, E = \text{Ge}, R' = \text{Ph}, n = 2$ [2]
6, $E = \text{Ge}, R' = \text{CMe}_3, n = 4$
7, $R = \text{C}_6\text{F}_5, E = \text{Ge}, R' = \text{CMe}_3, n = 2$

(3)



- 14**, $R = \text{Ph}, E = \text{Si}, M = \text{Al}, R' = \text{CMe}_3, n = 2$
15, $R = \text{Ph}, E = \text{Si}, M = \text{Ga}, R' = \text{CMe}_3, n = 2$
16, $R = \text{Ph}, E = \text{Ge}, M = \text{Ga}, R' = \text{CMe}_3, n = 2$
17, $R = \text{Ph}, E = \text{Ge}, M = \text{Ga}, R' = \text{Ph}, n = 2$
18, $R = \text{C}\equiv\text{C-CMe}_3, E = \text{Ge}, M = \text{Ga}, R' = \text{CMe}_3, n = 4$

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 ($\text{C}\equiv\text{C}$ 118.4(3) to 120.1(2) pm; Table 1). Representative examples of



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 $M\cdots\text{C}$ 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 $M\text{-C}_{\text{vinyl}}\text{-E-C}_{\text{ethynyl}}$ 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 ER_2 groups adopt a perpendicular arrangement to this plane. Another consequence of the $M\cdots\text{C}_\alpha\equiv\text{C}$ 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 $\text{C}\equiv\text{C}$ triple bonds which are only

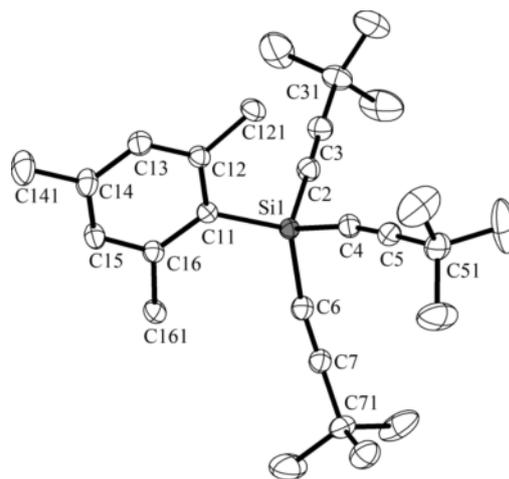


Fig. 1. Molecular structure in the crystal and atomic numbering scheme of compound **2**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms have been omitted for clarity.

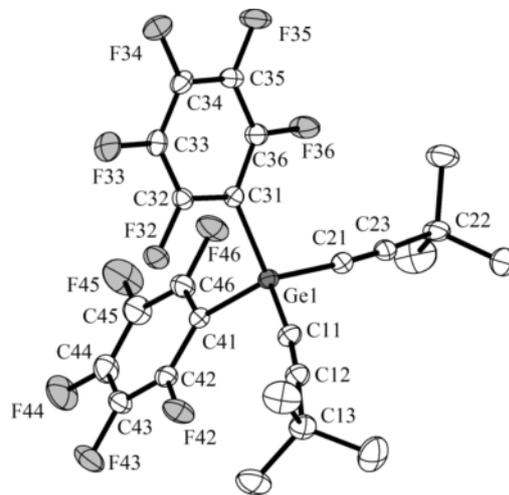


Fig. 2. Molecular structure in the crystal and atomic numbering scheme of compound **7**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms have been omitted for clarity.

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 $M\cdots\text{C}_\alpha\equiv\text{C}$ contact (244.9 pm) and the largest deviation from planarity (37 pm) in the presented series of compounds.

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

Compound	$\text{C}\equiv\text{C}$	$\text{C}=\text{C}$	$M\cdots\text{C}\equiv\text{C}(\text{Ph})^a$	Torsion angle $M-\text{C}(=)-E1-\text{C}_\alpha^b$	$d(M\cdots\text{C}_3)^c$
2	119.6(2)/120.1(2)/119.8(2)	–	–	–	–
7	118.4(3)/118.9(3)	–	–	–	–
8 ($M = \text{Al}$)	120.6(2)	133.9(2)	249.5	7.15(7)	32
9 ($M = \text{Ga}$)	120.6(2)	134.1(2)	271.1	8.47(7)	24
10 ($M = \text{Ga}$)	119.8(3)	134.1(3)	264.5	0.12(2)	25
11 ($M = \text{Al}$)	120.7(2)	133.4(2)	251.2	8.3(1)	36
12 ($M = \text{Al}$)	120.3(2)/120.6(2)	133.7(2)	253.1	4.92(8)	23
13 ($M = \text{Al}$)	120.1(2)/121.7(2)	134.2(2)	244.9	5.22(6)	37
15 ($M = \text{Ga}$)	–	134.9(2)/134.6(1)	278.1/285.0 ^a	18.4(1)/19.0(1)	24/25
16 ($M = \text{Ga}$)	–	133.9(3)/133.7(3)	287.8/290.4 ^a	15.3(2)/13.4(2)	22/22
17 ($M = \text{Ga}$)	–	135.3(2)/135.2(2)	276.8/290.7 ^a	18.7(1)/11.4(1)	21/28
18 ($M = \text{Ga}$)	120.0(4)/120.0(4)	133.2(4)/134.2(4)	281.0/284.5	9.3(2)/10.0(3)	26/26

^a Shortest $\text{Ga}-\text{C}_{ortho}(\text{Ph})$ 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.

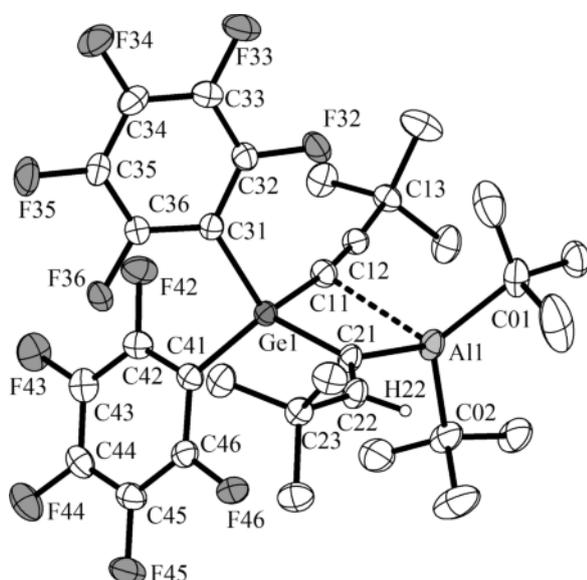


Fig. 3. Molecular structure in the crystal and atomic numbering scheme of compound **11**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H22, arbitrary radius) have been omitted for clarity.

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 $\text{Ga}\cdots\text{C}_\alpha\equiv\text{C}$ distances (281 and 285 pm) resulting in two essentially planar $\text{Ga}-\text{C}_{vinyl}-\text{Ge}-\text{C}_\alpha$ heterocycles that are approximately perpendic-

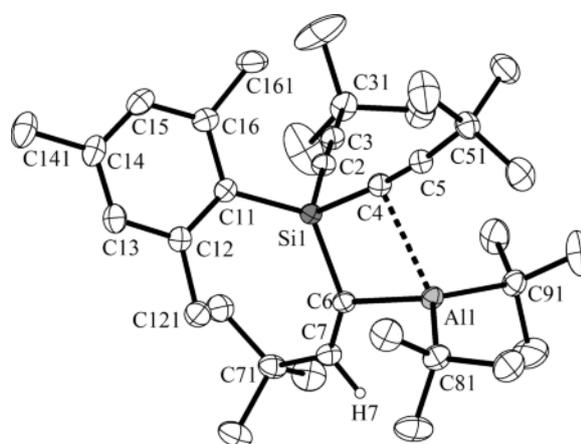


Fig. 4. Molecular structure in the crystal and atomic numbering scheme of compound **13**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H7, arbitrary radius) have been omitted for clarity.

ular to each other. In the absence of uncoordinated “free” alkynyl substituents the short $\text{Ga}\cdots\text{C}_\alpha\equiv\text{C}$ 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 $\text{Ga}-\text{C}_{vinyl}-E-\text{C}_{ipso}$ heterocycles that are perpendicular to each other. The phenyl substituents are rotated towards the Ga atoms to minimise the $\text{Ga}-\text{C}_{ortho}$ 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).

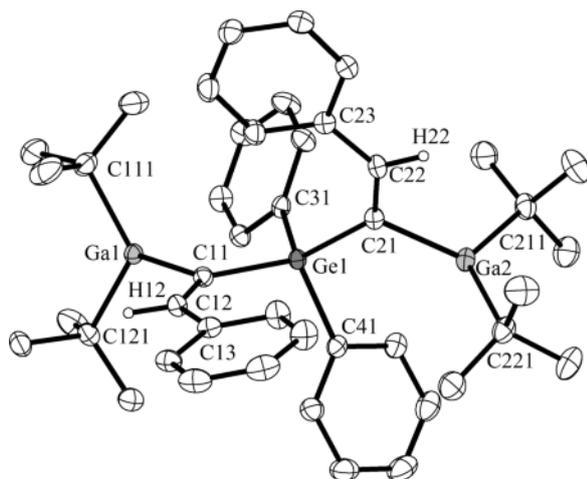


Fig. 5. Molecular structure in the crystal and atomic numbering scheme of compound **17**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H12 and H22, arbitrary radii) have been omitted for clarity.

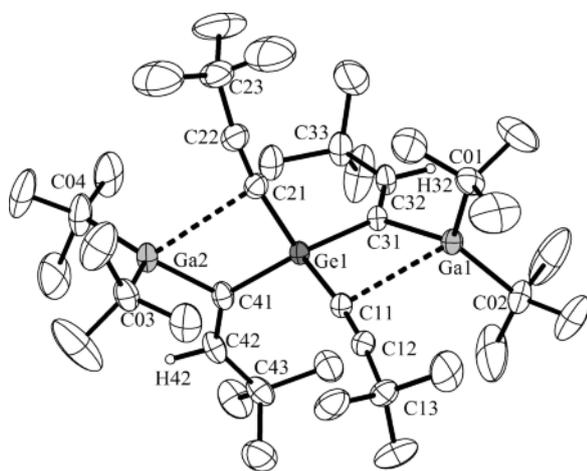


Fig. 6. Molecular structure in the crystal and atomic numbering scheme of compound **18**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H32 and H42, arbitrary radii) have been omitted for clarity.

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 $m\text{-H}\cdots m\text{-C}$ [287 pm (**8**); 285 pm (**9**)], $m\text{-H}\cdots m\text{-C}$ [CHPh, 282 pm (**10**)], $m\text{-H}\cdots o\text{-C}$ [289 pm (**15**)] or $m\text{-H}\cdots$ centroid contacts [277 pm (**16**)] or alternatively the formation of a chain structure with short $m\text{-H}\cdots o\text{-C}$ and $m\text{-H}\cdots ipso\text{-C}$ contacts [266, 285 pm (**17**)]. The dimers of compound **15**

are further connected to an infinite chain by an interaction between the $m\text{-H}$ atom of one dimer with $o\text{-}$, $m\text{-}$ and $p\text{-C}$ 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 $\nu(\text{C}\equiv\text{C})$ stretching frequency in the IR spectrum by 30–50 cm^{-1} (Table 2) relative to the “free” alkynes **1** to **7**. In compounds **12** and **13** we found three $\nu_{\text{C}=\text{C}}$ 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 alkenyl 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 $^3J_{\text{SiH}}$ 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 $\delta(\text{MCMe}_3) > \delta(\text{C}\equiv\text{C}-\text{CMe}_3) \geq \delta(\text{C}=\text{C}-\text{CMe}_3)$ (Table 2). The low-field shift of the MCMe_3 group ($\delta = 1.3\text{--}1.4$ 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 $\delta(\text{MCMe}_3)$ was shifted to higher field ($\delta = 1.03\text{--}1.06$ ppm). For the mixed *cis/trans* compound **19** we observe resonances in two different ranges (δ

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

Compound	C=CH (^1H , δ)	$^3J_{\text{SiH}}$ (Hz)	C \equiv C-R (^{13}C , δ)	C \equiv C-R (^{13}C , δ)	CMe ₃ (^{13}C , δ) ^a	CMe ₃ (^1H , δ) ^a	$\nu(\text{C}\equiv\text{C})$ (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 (<i>trans</i>) 7.98 (<i>cis</i>)	<13 24.3	93.6	111.5	–/–/29.0, 28.8 –/–/29.2	–/–/1.36, 1.13 –/–/1.47	2147, 2133

^a Sequence: C=C–CMe₃/C \equiv 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 ^{13}C NMR spectra, around $\delta = 40$ ppm for C=C–CMe₃ and $\delta = 29$ ppm for C \equiv C–CMe₃ and GaCMe₃. The more electron-rich AlCMe₃ carbon atoms were observed at about $\delta = 18$ ppm.

The $M(\text{CMe}_3)_2$ and $E\text{Ar}_2$ 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 ^{13}C 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 \cdots *o*-C interaction that was observed in the solid state. Based on the NMR data the activation barrier for the rotation was estimated to $\Delta G^\ddagger = 53 \text{ kJ mol}^{-1}$ [30] which is very similar to values reported for $M\cdots\text{C}\alpha\equiv\text{C}$ 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 re-

sults 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 ^{13}C 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 alkenyl-alkynylsilanes 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 $\text{C}\equiv\text{C}$ 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 LiAlH_4 ; Et_2O and toluene with Na/benzophenone; 1,2 difluorobenzene and pentafluorobenzene with molecular sieves). NMR spectra were recorded in C_6D_6 at ambient probe temperature or C_7D_8 for variable temperature studies (**15**) using the following Bruker instruments: Avance I (^1H , 400.13; ^{13}C , 100.62; ^{29}Si , 79.49 MHz) or Avance III (^1H , 400.03; ^{13}C , 100.59; ^{29}Si 79.47 MHz) and referenced internally to residual solvent resonances (chemical shift data in δ). ^{13}C NMR spectra were all proton-decoupled. IR spectra were recorded of Nujol mulls between CsI plates on a Shimadzu Prestige 21 spectrometer. $\text{HAl}(\text{CMe}_3)_2$ [31], $\text{HGa}(\text{CMe}_3)_2$ [31], $\text{Me}_3\text{-SiCl}_3$ [32], $\text{Cl}_2\text{Ge}(\text{C}\equiv\text{C-CMe}_3)_2$ [7], $\text{Ph}_2\text{Ge}(\text{C}\equiv\text{C-CMe}_3)_2$ [7], $\text{Ph}_2\text{Ge}(\text{C}\equiv\text{C-Ph})_2$ [2, 22, 23], $\text{Me-Si}(\text{C}\equiv\text{C-C}_7\text{H}_7)_3$ [6], and $\text{Ge}(\text{C}\equiv\text{C-CMe}_3)_4$ [24] were obtained according to literature procedures. Commercially available $\text{HAl}(\text{CH}_2\text{CHMe}_2)_2$, $\text{Me}_3\text{C-C}\equiv\text{C-H}$, $\text{F}_5\text{C}_6\text{Br}$ 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.

$\text{Ph}_2\text{Si}(\text{C}\equiv\text{C-CMe}_3)_2$ (**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 $\text{Me}_3\text{C-C}\equiv\text{C-H}$ (5.24 g, 7.85 mL, 64.0 mmol) in Et_2O (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 Ph_2SiCl_2 (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 mixture was filtered, and the 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 $\text{Ph}_2\text{Si}(\text{C}\equiv\text{C}-\text{CMe}_3)_2$ (**1**) as a colourless, air-stable 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): $\nu = 2201$ s, 2156 vs $\nu(\text{C}\equiv\text{C})$; 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 $\delta(\text{CH}_3)$; 1200 s, 1188 m, 1109 s, 1026 m, 997 s, 945 vs, 933 vs, 853 vw, 775 vs, 765 vs, 738 vs [$\delta(\text{CH})$, $\nu(\text{CC})$]; 712 vs (paraffin); 696 vs $\delta(\text{Ph})$; 621 m, 583 vs, 563 vs, 544 vs, 494 vs, 455 s, 413 s cm^{-1} [$\nu(\text{SiC})$, $\delta(\text{CC})$]. – ^1H NMR (400.13 MHz, C_6D_6): $\delta = 8.07$ (d, $^3J_{\text{HH}} = 7.7$ Hz, 4 H, *o*-H), 7.23 (*pseudo*-t, $^3J_{\text{HH}} = 7.7$ Hz, 4 H, *m*-H), 7.16 (t, $^3J_{\text{HH}} = 7.7$ Hz, 2 H, *p*-H), 1.11 ppm (s, 18 H, CMe_3). – ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 135.2$ (*o*-C), 135.1 (*ipso*-C), 130.2 (*p*-C), 128.3 (*m*-C), 119.8 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 77.6 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 30.6 (CMe_3), 28.6 ppm (CMe_3). – ^{29}Si NMR (79.49 MHz, C_6D_6): $\delta = -48.6$ ppm. – MS ((+)-EI; 20 eV; 298 K): m/z (%) = 344 (33) [$\text{M}]^+$, 329 (6) [$\text{M}-\text{CH}_3$] $^+$, 287 (100) [$\text{M}-\text{CMe}_3$] $^+$. – $\text{C}_{24}\text{H}_{28}\text{Si}$ (344.1): calcd. C 83.8, H 8.2; found C 83.4, H 8.2.

Mes-Si($\text{C}\equiv\text{C}-\text{CMe}_3$)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 $\text{Me}_3\text{C}-\text{C}\equiv\text{C}-\text{H}$ (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 Et_2O (20 mL). The combined organic phases were dried over MgSO_4 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): $\nu = 2201$ m, 2158 s, 2125 sh $\nu(\text{C}\equiv\text{C})$; 1605 m, 1578 m, 1555 w [$\nu(\text{C}=\text{C})$, mesityl]; 1448 vs, 1375 vs (paraffin); 1304 w, 1254 m $\delta(\text{CH}_3)$; 1202 m, 1153 w, 1109 w, 1070 m, 1028 m, 943 s, 889 w, 849 s, 773 s, 762 m [$\delta(\text{CH})$, $\nu(\text{CC})$]; 721 s (paraffin); 687 w, 625 m, 584 m, 507 w, 435 m cm^{-1} [$\nu(\text{SiC})$, $\delta(\text{CC})$]. – ^1H NMR (400.03 MHz, C_6D_6): $\delta = 6.78$ (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, CMe_3). – ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 145.4$ (*o*-C), 139.7 (*p*-C), 129.9 (*m*-C), 127.1 (*ipso*-C), 116.9 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 80.4 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 30.3 (CMe_3), 28.5 (CMe_3), 25.0 (*o*-Me), 21.1 ppm (*p*-Me). – MS ((+)-

EI; 30 eV; 323 K): m/z (%) = 390 (67) [$\text{M}]^+$, 375 (11) [$\text{M}-\text{Me}]^+$, 333 (100) [$\text{M}-\text{CMe}_3$] $^+$.

Ge($\text{C}\equiv\text{C}-\text{CMe}_3$)₄ (**6**) [24]

Preliminary data of $\text{Ge}(\text{C}\equiv\text{C}-\text{CMe}_3)_4$ (**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 $\text{Me}_3\text{C}-\text{C}\equiv\text{CH}$ in 100 mL of Et_2O at -78°C . The reaction mixture was stirred for 2 h at this temperature, and a solution of GeCl_4 (25 mol %) in Et_2O (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 Et_2O (20 mL). The combined organic phases were dried over MgSO_4 . 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): $\nu = 2187$ s, 2153 s, 2126 w $\nu(\text{C}\equiv\text{C})$; 1462 vs, 1375 vs (paraffin); 1302 w, 1252 vs $\delta(\text{CH}_3)$; 1204 m, 1169 vw, 1153 vw, 1101 vw, 1084 vw, 1028 w, 968 vw, 922 s, 889 vw, 847 vw, 752 vs [$\delta(\text{CH})$, $\nu(\text{CC})$]; 723 s (paraffin); 552 vw, 492 s cm^{-1} [$\nu(\text{GeC})$, $\delta(\text{CC})$]. – ^1H NMR (400.03 MHz, C_6D_6): $\delta = 1.04$ ppm (s, 36 H, CMe_3). – ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 114.3$ ($\text{C}\equiv\text{C}-\text{CMe}_3$), 75.8 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 30.5 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 28.3 ppm ($\text{C}\equiv\text{C}-\text{CMe}_3$). – MS ((+)-EI; 30 eV; 323 K): m/z (%) = 397 (8) [$\text{M}-\text{H}]^+$, 383 (100) [$\text{M}-\text{Me}]^+$, 341 (28) [$\text{M}-\text{CMe}_3$] $^+$, 317 (39) [$\text{M}-\text{CCCMe}_3$] $^+$. – $\text{C}_{24}\text{H}_{36}\text{Ge}$ (397.1): calcd. C 72.6, H 9.1; found C 72.0, H 9.2.

(F_5C_6)₂*Ge*($\text{C}\equiv\text{C}-\text{CMe}_3$)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 $\text{F}_5\text{C}_6\text{Br}$ (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 tetrafluorobenzene. A solution of $\text{Cl}_2\text{Ge}(\text{C}\equiv\text{C}-\text{CMe}_3)_2$ [7] (1.00 g, 3.28 mmol) in Et_2O 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 Et_2O (50 mL). The combined organic phases were dried over MgSO_4 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): $\nu = 2195$ vs, 2160 vs $\nu(\text{C}\equiv\text{C})$; 1957 vw, 1870

vw, 1724 w, 1699 vw, 1644 vs, 1634 vs, 1603 m, 1586 s, 1549 s, 1516 vs, [$\nu(\text{C}=\text{C}$, aromatic ring); 1471 vs (paraffin); 1419 m $\delta(\text{CH}_3)$]; 1385 vs (paraffin); 1364 vs, 1344 m; 1288 vs $\nu(\text{CF})$; 1255 vs $\delta(\text{CH}_3)$; 1205 s, 1143 s; 1086 vs, 1046 m, 1017 s, 974 vs, 927 s, 818 s, 756 vs [$\delta(\text{CH})$, $\nu(\text{CC})$, $\nu(\text{CF})$]; 724 s (paraffin); 696 vw, 687 vw, 679 vw, 622 s, 583 m, 554 vw, 496 s, 485 s cm^{-1} [$\nu(\text{SiC})$, $\delta(\text{CC})$]. – ^1H NMR (400.13 MHz, C_6D_6): δ = 1.14 (s, 18 H, CMe_3). – ^{13}C NMR (100.6 MHz, C_6D_6): δ = 148.8 (dm, $^1J_{\text{FC}}$ = 246 Hz, *o*-C), 143.1 (dm, $^1J_{\text{FC}}$ = 256 Hz, *p*-C), 137.7 (dm, $^1J_{\text{FC}}$ = 253 Hz, *m*-C), 118.2 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 106.8 (m, *ipso*-C), 72.8 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 30.2 (CMe_3), 28.6 ppm (CMe_3). – ^{19}F NMR (376.4 MHz, C_6D_6). δ = –127.6 (m, 4 F, *o*-F), –149.3 (tt, $^3J_{\text{FF}}$ = 20.7 Hz, $^4J_{\text{FF}}$ = 4.1 Hz, 2 F, *p*-F), –160.1 ppm (m, 4 F, *m*-F). – MS ((+)-EI; 20 eV; 353 K): m/z (%) = 570 (5) $[\text{M}]^+$, 555 (15) $[\text{M}-\text{CH}_3]^+$, 513 (8) $[\text{M}-\text{CMe}_3]^+$, 489 (7) $[\text{M}-\text{CCMe}_3]^+$, 403 (9) $[\text{M}-\text{C}_6\text{F}_5]^+$.

$\text{Ph}_2\text{Si}(\text{C}\equiv\text{C}-\text{CMe}_3)\{\text{C}[\text{Al}(\text{CMe}_3)_2]=\text{CH}-\text{CMe}_3\}$ (8)

Solid $\text{Ph}_2\text{Si}(\text{C}\equiv\text{C}-\text{CMe}_3)_2$ (**1**) (1.09 g, 3.17 mmol) was added to a solution of $\text{HAl}(\text{CMe}_3)_2$ (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): ν = 2154 m, 2114 s $\nu(\text{C}\equiv\text{C})$; 1971 w, 1956 w, 1900 vw, 1884 w, 1819 w, 1769 vw, 1694 vw, 1657 vw, 1599 s, 1568 s, 1557 m, 1504 w $\nu(\text{C}=\text{C})$, phenyl; 1454 vs (paraffin), 1377 vs (paraffin); 1366 vs, 1302 w, 1254 s $\delta(\text{CH}_3)$; 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 [$\delta(\text{CH})$, $\nu(\text{CC})$]; 719 vs (paraffin); 700 vs, 652 s (phenyl); 619 w, 590 m, 563 m, 529 vs, 490 s, 471 m, 463 m cm^{-1} [$\nu(\text{SiC})$, $\nu(\text{AlC})$, $\delta(\text{CC})$]. – ^1H NMR (400.03 MHz, C_6D_6): δ = 7.93 (d, $^3J_{\text{HH}}$ = 7.2 Hz, 4 H, *o*-H), 7.35 (s, $^3J_{\text{SiH}}$ = 27.8 Hz, 1 H, $\text{C}=\text{CH}$), 7.22 (*pseudo*-t, $^3J_{\text{HH}}$ = 7.2 Hz, 4 H *m*-H), 7.15 (t, $^3J_{\text{HH}}$ = 7.2 Hz, 2 H, *p*-H), 1.33 (s, 18 H, AlCMe_3), 1.05 (s, 9 H, $\text{C}\equiv\text{C}-\text{CMe}_3$), 1.01 ppm (s, 9 H, $\text{C}=\text{C}-\text{CMe}_3$). – ^{13}C NMR (100.59 MHz, C_6D_6): δ = 171.3 ($\text{C}=\text{C}-\text{CMe}_3$), 137.1 (*ipso*-C), 135.9 ($\text{C}=\text{C}-\text{CMe}_3$ and *o*-C), 131.6 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 130.0 (*p*-C), 128.3 (*m*-C), 81.7 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 39.9 ($\text{C}=\text{C}-\text{CMe}_3$), 31.1 (AlCMe_3), 30.4 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 29.6 ($\text{C}=\text{C}-\text{CMe}_3$), 29.4 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 19.0 ppm (AlCMe_3). – ^{29}Si NMR (79.47 MHz, C_6D_6): δ = –32.4 ppm. – MS ((+)-EI; 20 eV; 298 K): m/z (%) = 429 (8) $[\text{M}-\text{CMe}_3]^+$, 346 (9) $[\text{M}-\text{Al}(\text{CMe}_3)_2+\text{H}]^+$, 289 (100) $[\text{M}-\text{Al}(\text{CMe}_3)_2-\text{H}_2\text{C}=\text{CMe}_2]^+$. – $\text{C}_{32}\text{H}_{47}\text{AlSi}$ (486.8): calcd. C 79.0, H 9.7; found C 78.2, H 9.7.

$\text{Ph}_2\text{Si}(\text{C}\equiv\text{C}-\text{CMe}_3)\{\text{C}[\text{Ga}(\text{CMe}_3)_2]=\text{CH}-\text{CMe}_3\}$ (9)

Solid $\text{Ph}_2\text{Si}(\text{C}\equiv\text{C}-\text{CMe}_3)_2$ (**1**) (0.383 g, 1.11 mmol) was added to a solution of $\text{HGa}(\text{CMe}_3)_2$ (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): ν = 2156 m, 2127 m $\nu(\text{C}\equiv\text{C})$; 1969 vw, 1956 vw, 1898 vw, 1883 vw, 1819 w, 1655 vw, 1595 m, 1560 m, 1508 w [$\nu(\text{C}=\text{C})$, phenyl]; 1458 vs, 1375 vs (paraffin); 1300 w, 1252 m $\delta(\text{CH}_3)$; 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 [$\delta(\text{CH})$, $\nu(\text{CC})$]; 708 vs (paraffin); 648 m (phenyl); 619 w, 556 m, 546 s sh, 527 vs, 486 s, 469 m, 449 s cm^{-1} [$\nu(\text{SiC})$, $\nu(\text{GaC})$, $\delta(\text{CC})$]. – ^1H NMR (400.03 MHz, C_6D_6): δ = 7.96 (d, $^3J_{\text{HH}}$ = 7.2 Hz, 4 H, *o*-H), 7.22 (*pseudo*-t, $^3J_{\text{HH}}$ = 7.4 Hz, 4 H, *m*-H), 7.13 (t, $^3J_{\text{HH}}$ = 7.5 Hz, 2 H, *p*-H), 6.84 (s, 1 H, $^3J_{\text{SiH}}$ = 25.1 Hz, $\text{C}=\text{CH}$), 1.29 (s, 18 H, GaCMe_3), 1.15 (s, 9 H, $\text{C}\equiv\text{C}-\text{CMe}_3$), 1.10 ppm (s, 9 H, $\text{C}=\text{C}-\text{CMe}_3$). – ^{13}C NMR (100.59 MHz, C_6D_6): δ = 166.7 ($\text{C}=\text{C}-\text{CMe}_3$), 141.8 ($\text{C}=\text{C}-\text{CMe}_3$), 138.7 (*ipso*-C), 135.2 (*o*-C), 129.8 (*p*-C), 128.6 (*m*-C), 122.4 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 81.3 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 39.8 ($\text{C}=\text{C}-\text{CMe}_3$), 31.2 (GaCMe_3), 30.8 ($\text{C}\equiv\text{C}-\text{CMe}_3$), 30.0 ($\text{C}=\text{C}-\text{CMe}_3$), 29.4 (GaCMe_3), 28.8 ppm ($\text{C}\equiv\text{C}-\text{CMe}_3$). – ^{29}Si NMR (79.47 MHz, C_6D_6): δ = –38.1 ppm. – MS ((+)-EI; 20 eV; 298 K): m/z (%) = 471 (100) $[\text{M}-\text{CMe}_3]^+$, 415 (5) $[\text{M}-\text{CMe}_3-\text{H}_2\text{C}=\text{CMe}_2]^+$, 344 (9) $[\text{M}-\text{HGa}(\text{CMe}_3)_2]^+$. – $\text{C}_{32}\text{H}_{47}\text{GaSi}$ (529.53): calcd. C 72.6, H 8.9; found C 72.0, H 9.0.

$\text{Ph}_2\text{Ge}(\text{C}\equiv\text{C}-\text{Ph})\{\text{C}[\text{Ga}(\text{CMe}_3)_2]=\text{CH}-\text{Ph}\}$ (10)

A solution of $\text{HGa}(\text{CMe}_3)_2$ (0.127 g, 0.69 mmol) in *n*-hexane (10 mL) was added at room temperature dropwise to a solution of $\text{Ph}_2\text{Ge}(\text{C}\equiv\text{C}-\text{Ph})_2$ (**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): ν = 2154 m, 2132 sh $\nu(\text{C}\equiv\text{C})$; 1661 w, 1597 w, 1551 m [$\nu(\text{C}=\text{C})$, phenyl]; 1460 vs, 1377 vs (paraffin); 1304 vw, 1248 w $\delta(\text{CH}_3)$; 1169 vw, 1090 m, 1026 m, 930 vw, 914 vw, 812 w, 756 m [$\delta(\text{CH})$, $\nu(\text{CC})$]; 733 m (paraffin); 694 $\delta(\text{Ph})$; 621 vw, 577 w, 532 w, 463 m cm^{-1} [$\nu(\text{SiC})$, $\nu(\text{GaC})$, $\delta(\text{CC})$]. – ^1H NMR (400.13 MHz, C_6D_6): δ = 7.94 (s, 1 H, $\text{C}=\text{CH}$), 7.82 (d br, 4 H, $^3J_{\text{HH}}$ = 6.8 Hz, *o*-H, GePh_2), 7.45 (d, 2 H, $^3J_{\text{HH}}$ = 7.3 Hz, *o*-H, $\text{C}\equiv\text{C}-\text{Ph}$), 7.41 (d, 2 H, $^3J_{\text{HH}}$ = 6.7 Hz, *o*-H, $\text{C}=\text{CHPh}$), 7.14 (m, 4 H, *m*-H, GePh_2), 7.09

(m, 2 H, *p*-H, GePh_2), 6.96 (*pseudo-t*, 2 H, $^3J_{\text{HH}} = 6.7$ Hz, *m*-H, $\text{C}=\text{CHPh}$), 6.92 (t, 1 H, *p*-H, $\text{C}=\text{CHPh}$), 6.89 (t, 1 H, *p*-H, $\text{C}\equiv\text{C-Ph}$), 6.88 (*pseudo-t*, 2 H, *m*-H, $\text{C}\equiv\text{C-Ph}$), 1.38 ppm (s, 18 H, GaCMe_3). – ^{13}C NMR (100.62 MHz, C_6D_6): $\delta = 154.2$ ($\text{C}=\text{C-Ph}$), 151.7 ($\text{C}=\text{C-Ph}$), 141.4 (*ipso*-C, $\text{C}=\text{CHPh}$), 137.3 (*ipso*-C, GePh_2), 134.9 (*o*-C, GePh_2), 133.0 (*o*-C, $\text{C}\equiv\text{C-Ph}$), 129.7 (*p*-C, GePh_2), 129.6 (*p*-C, $\text{C}\equiv\text{C-Ph}$), 128.8 (*m*-C, GePh_2), 128.6 (*m*-C, $\text{C}\equiv\text{C-Ph}$ and $\text{C}=\text{CHPh}$), 128.1 (*o*-C, $\text{C}=\text{CHPh}$), 127.9 (*p*-C, $\text{C}=\text{CHPh}$), 122.2 (*ipso*-C, $\text{C}\equiv\text{C-Ph}$), 110.0 ($\text{C}\equiv\text{C-Ph}$), 93.0 ($\text{C}\equiv\text{C-Ph}$), 30.8 (GaCMe_3), 29.5 ppm (GaCMe_3). – MS ((+)-EI; 20 eV; 351 K): m/z (%) = 557 (100) $[\text{M-CMe}_3]^+$, 501 (6) $[\text{M-CMe}_3\text{-butene}]^+$. – $\text{C}_{36}\text{H}_{39}\text{GaGe}$ (614.0): calcd. C 70.4, H 6.4; found C 70.5, H 6.4.

$(\text{F}_5\text{C}_6)_2\text{Ge}(\text{C}\equiv\text{C-CMe}_3)\{\text{C}[\text{Al}(\text{CMe}_3)_2]=\text{CH-CMe}_3\}$ (**11**)

A solution of $(\text{F}_5\text{C}_6)_2\text{Ge}(\text{C}\equiv\text{C-CMe}_3)_2$ (**7**) (0.430 g, 0.76 mmol) in toluene (10 mL) was added to a solution of $\text{HAl}(\text{CMe}_3)_2$ (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): $\nu = 2193$ m, 2158 m, 2120 w $\nu(\text{C}\equiv\text{C})$; 1942 vw, 1869 vw, 1719 vw, 1639 s, 1605 m, 1582 w, 1549 w, 1516 vs $[\nu(\text{C}=\text{C})$, aromatic ring]; 1456 vs, 1377 vs (paraffin); 1341 m, 1304 w; 1285 s $\nu(\text{CF})$; 1254 s $\delta(\text{CH}_3)$; 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 $[\nu(\text{CF})$, $\delta(\text{CH})$, $\nu(\text{CC})$]; 723 s (paraffin); 665 w, 635 w, 619 m, 583 m, 571 w, 557 w, 536 w, 494 m cm^{-1} $[\nu(\text{GeC})$, $\nu(\text{AlC})$, $\delta(\text{CC})$]. – ^1H NMR (400.03 MHz, $[\text{D}_8]\text{toluene}$): $\delta = 6.94$ (s, 1 H, $\text{C}=\text{CH}$), 1.21 (s, 18 H, AlCMe_3), 1.14 (s, 9 H, $\text{C}\equiv\text{C-CMe}_3$), 1.02 ppm (s, 9 H, $\text{C}=\text{C-CMe}_3$). – ^{13}C NMR (100.59 MHz, $[\text{D}_8]\text{toluene}$): $\delta = 169.0$ ($\text{C}=\text{CH}$), 148.6 (dm, $^1J_{\text{FC}} = 240$ Hz, *o*-C), 142.8 (dm, $^1J_{\text{FC}} = 257$ Hz, *p*-C), 137.9 (dm, $^1J_{\text{FC}} = 257$ Hz, *m*-C), 134.6 ($\text{C}=\text{CH}$), 111.7 (*ipso*-C), 77.7 ($\text{C}\equiv\text{C-CMe}_3$), $\text{C}\equiv\text{C-CMe}_3$ not observed, 40.4 ($\text{C}=\text{C-CMe}_3$), 30.4 (AlCMe_3), 30.3 ($\text{C}\equiv\text{C-CMe}_3$), 29.1 ($\text{C}=\text{C-CMe}_3$), 29.0 ($\text{C}\equiv\text{C-CMe}_3$), 17.8 ppm (AlCMe_3). – ^{19}F NMR (376.4 MHz, $[\text{D}_8]\text{toluene}$): $\delta = -128.9$ (s br., 4 F, *o*-F), -148.9 (t, $^3J_{\text{FF}} = 20.3$ Hz, 2 F, *p*-F), -159.1 ppm (s br., 4 F, *p*-F). – MS ((+)-EI; 20 eV; 343 K): m/z (%) = 655 (100) $[\text{M-CMe}_3]^+$.

$\text{Mes-Si}(\text{C}\equiv\text{C-CMe}_3)_2\{\text{C}[\text{Al}(\text{CH}_2\text{CHMe}_2)_2]=\text{CH-CMe}_3\}$ (**12**)

A solution of $\text{Mes-Si}(\text{C}\equiv\text{C-CMe}_3)_3$ (**2**) (0.264 g, 0.677 mmol) in toluene (15 mL) was added at room temperature to a solution of $\text{HAl}(\text{CH}_2\text{CHMe}_2)_2$ (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): $\nu = 2196$ w, 2156 s, 2116 m $\nu(\text{C}\equiv\text{C})$; 1644 w, 1603 s, 1566 m, 1556 m, 1533 s, 1511 m $[\nu(\text{C}=\text{C})$, aromatic ring]; 1454 vs (paraffin); 1411 w $\delta(\text{CH}_3)$; 1382 vs (paraffin); 1365 s, 1305 w, 1287 w, 1253 s $\delta(\text{CH}_3)$; 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 $[\delta(\text{CH})$, $\nu(\text{CC})$]; 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} $[\nu(\text{SiC})$, $\nu(\text{AlC})$, $\delta(\text{CC})$]. – ^1H NMR (400.03 MHz, C_6D_6): $\delta = 6.95$ (s, $^3J_{\text{SiH}} = 29.8$ Hz, 1 H, $\text{C}=\text{CH}$), 6.76 (s, 2 H, *m*-H), 2.89 (s, 6 H, *o*-Me), 2.37 (m, 2 H, $\text{AlCH}_2\text{CHMe}_2$), 2.05 (s, 3 H, *p*-Me), 1.32 (d, $^3J_{\text{HH}} = 6.5$ Hz, 12 H, $\text{AlCH}_2\text{CHMe}_2$), 1.13 (s, 9 H, $\text{C}=\text{C-CMe}_3$), 1.09 (s, 18 H, ($\text{C}\equiv\text{C-CMe}_3$), 0.70 ppm (d, $^3J_{\text{HH}} = 7.0$ Hz, 4 H, $\text{AlCH}_2\text{CHMe}_2$). – ^{13}C NMR (100.59 MHz, C_6D_6): $\delta = 166.8$ ($\text{C}=\text{C-CMe}_3$), 144.9 (*o*-C), 140.9 (br. s, $\text{C}=\text{C-CMe}_3$), 139.8 (*p*-C), 129.9 (*m*-C and *ipso*-C), 122.2 ($\text{C}\equiv\text{C-CMe}_3$), 83.7 ($\text{C}\equiv\text{C-CMe}_3$), 39.6 ($\text{C}=\text{C-CMe}_3$), 30.1 ($\text{C}\equiv\text{C-CMe}_3$), 29.0 ($\text{C}=\text{C-CMe}_3$), 28.9 ($\text{C}\equiv\text{C-CMe}_3$), 28.8 ($\text{AlCH}_2\text{CHMe}_2$), 27.0 ($\text{AlCH}_2\text{CHMe}_2$), 26.6 ($\text{AlCH}_2\text{CHMe}_2$), 25.5 (*o*-Me), 21.1 ppm (*p*-Me). – ^{29}Si NMR (79.5 MHz, C_6D_6): $\delta = -63.1$ ppm. – MS ((+)-EI; 20 eV; 298 K): m/z (%) = 475 (100) $[\text{M-CMe}_3]^+$.

$\text{Mes-Si}(\text{C}\equiv\text{C-CMe}_3)_2\{\text{C}[\text{Al}(\text{CMe}_3)_2]=\text{CH-CMe}_3\}$ (**13**)

A solution of $\text{Mes-Si}(\text{C}\equiv\text{C-CMe}_3)_3$ (**2**) (0.316 g, 0.810 mmol) in toluene (10 mL) was added at room temperature to a solution of $\text{HAl}(\text{CMe}_3)_2$ (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): $\nu = 2197$ w, 2156 m, 2126 w $\nu(\text{C}\equiv\text{C})$; 1603 m $\nu(\text{C}=\text{C})$; 1458 vs, 1375 s (paraffin); 1302 w, 1254 m $\delta(\text{CH}_3)$; 1190 vw, 1169 w, 1153 w, 1067 vw, 1028 vw, 939 w, 891 w, 847 m, 773 m $[\delta(\text{CH})$, $\nu(\text{CC})$]; 721 s (paraffin); 660 w, 615 w, 567 w, 530 vw, 472 vw cm^{-1} $[\nu(\text{SiC})$, $\nu(\text{AlC})$, $\delta(\text{CC})$]. – ^1H NMR (400.13 MHz, C_6D_6): $\delta = 6.99$ (s, 1 H, $^3J_{\text{SiH}} = 30.4$ Hz, $\text{C}=\text{CH}$), 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, AlCMe_3), 1.23 (s, 9 H, $\text{C}=\text{C-CMe}_3$), 1.09 ppm (s, 18 H, $\text{C}\equiv\text{C-CMe}_3$). – ^{13}C NMR (100.62 MHz, C_6D_6): $\delta = 167.8$ ($\text{C}=\text{C-CMe}_3$), 145.2 (*o*-C), 139.7 (*p*-C), 139.5 (br. s, $\text{C}=\text{C-CMe}_3$), 129.9 (*m*-C), 129.8 (*ipso*-C), 123.9 ($\text{C}\equiv\text{C-CMe}_3$), 82.9 ($\text{C}\equiv\text{C-CMe}_3$), 40.3 ($\text{C}=\text{C-CMe}_3$), 31.3 (AlCMe_3), 30.3 ($\text{C}\equiv\text{C-CMe}_3$), 29.0 ($\text{C}\equiv\text{C-CMe}_3$), 28.6 ($\text{C}=\text{C-CMe}_3$), 25.2 (*o*-Me), 21.0 (*p*-Me), 18.7 ppm (br. s, AlCMe_3). – ^{29}Si NMR (79.5 MHz, C_6D_6): $\delta = -61.1$ ppm. – MS ((+)-EI; 50 eV;

323 K): m/z (%) = 392 (24) [M–Al(CMe₃)₂+H]⁺, 335 (93) [M–Al(CMe₃)₂–butene]⁺.

*Ph*₂Si{C[Al(CMe₃)₂]=CH–CMe₃}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, ³J_{HH} = 7.9 Hz, 4 H, *o*-H), 7.35 (*pseudo*-t, ³J_{HH} = 7.9 Hz, 4 H, *m*-H), 7.03 (t, ³J_{HH} = 7.9 Hz, 2 H, *p*-H), 6.86 (s, ³J_{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(CMe₃)₂]=CH–CMe₃}₂ (**15**)

Solid Ph₂Si(C≡C–CMe₃)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): ν = 1558 s ν(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} [ν(SiC), ν(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, ³J_{HH} = 7.4 Hz, 4 H, *m*-H), 7.07 (t, ³J_{HH} = 7.5 Hz, 2 H, *p*-H), 6.43 (s, ³J_{SiH} = 24.2 Hz, 2 H, C=CH), 1.33 (s, 18 H, C=C–CMe₃), 1.03 ppm (s, br, 36 H, GaCMe₃). – ¹³C NMR (100.59 MHz, C₆D₆): δ = 160.3 (C=C–CMe₃), 148.2 (C=C–CMe₃), 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–CMe₃). – ²⁹Si NMR (79.47 MHz, C₆D₆): δ = –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(CMe₃)₂–2 CMe₃]⁺. – C₄₀H₆₆Ga₂Si (714.5): calcd. C 67.2, H 9.3; found C 67.1, H 9.4.

*Ph*₂Ge{C[Ga(CMe₃)₂]=CH–CMe₃}₂ (**16**)

A solution of Ph₂Ge(C≡C–CMe₃)₂ (**4**) (0.337 g, 0.87 mmol) in toluene (5 mL) was added at room temperature to a solution of HGa(CMe₃)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): ν = 1973 vw, 1958 w, 1902 vw, 1886 w, 1844 vw, 1829 w, 1775 vw, 1738 vw, 1686 vw, 1651 vw, 1593 s, 1555 vs [ν(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), ν(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): δ = 7.67 (d, ³J_{HH} = 6.6 Hz, 4 H, *o*-H), 7.22 (*pseudo*-t, ³J_{HH} = 7.5 Hz, 4 H, *m*-H), 7.06 (t, ³J_{HH} = 7.4 Hz, 2 H, *p*-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): δ = 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(CMe₃)₂–CMe₃]⁺. – C₄₀H₆₆Ga₂Ge (759.0): calcd. C 63.3, H 8.8; found C 62.9, H 8.7.

*Ph*₂Ge{C[Ga(CMe₃)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 Ph₂Ge(C≡CPh){C[Ga(CMe₃)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): ν = 1996 vw, 1940 vw, 1894 vw, 1883 vw, 1597 sh, 1584 w, 1547 m [ν(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), ν(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} [ν(GeC), ν(GaC), δ(CC)]. – ¹H NMR (400.03 MHz, C₆D₆): δ = 7.66 [d, ³J_{HH} = 6.6 Hz, 4 H, *o*-H (GePh)], 7.63 (s, 2 H, C=CH), 7.53 [d, ³J_{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, ³J_{HH} = 7.4 Hz, 2 H, *p*-H (GePh)], 6.96 [t, ³J_{HH} = 7.4 Hz, 2 H, *p*-H (C=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.

(Me₃C–C≡C)₂Ge{C[Ga(CMe₃)₂]=CH–CMe₃]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(CMe₃)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): *ν* = 2160 sh, 2131 m *ν*(C≡C); 1953 vw, 1906 vw, 1886 vw, 1821 vw, 1763 vw, 1676 vw, 1585 w, 1551 vw [*ν*(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} [*ν*(GeC), *ν*(GaC), *δ*(CC)]. – ¹H NMR (400.03 MHz, C₆D₆): *δ* = 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–CMe₃), 148.5 (C=C–CMe₃), 119.5 (C≡C–CMe₃), 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–CMe₃]⁺, 525 (55) [M–HGa(CMe₃)₂–CMe₃]⁺. – C₄₀H₇₄Ga₂Ge (767.1): calcd. C 62.6, H 9.7; found C 62.5, H 9.7.

Me–Si(C≡C–*p*-Tol)₃{C[Ga(CMe₃)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): *ν* = 2147 s sh, 2133 vs *ν*(C≡C); 2058 m, 1904 w, 1790 w, 1650 w, 1643 w, 1607 m, 1580 m, 1573 m, 1556 m, 1542 w, 1504 vs [*ν*(C=C), phenyl]; 1462 vs, 1454 vs, 1377 vs (paraffin); 1366 vs, 1302 w, 1269 vw, 1246 m *δ*(CH₃); 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), *ν*(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} [*ν*(SiC), *ν*(GaC), *δ*(CC)]. – ¹H NMR (400.13 MHz, C₆D₆): *δ* = 8.33 [s, ³J_{SiH} < 13 Hz, 1 H, C=CH (*trans*)], 7.98 [s, ³J_{SiH} = 24.3 Hz, 1 H, C=CH (*cis*)], 7.57 [d, ³J_{HH} = 8.0 Hz, 4 H, *o*-H (*cis*) and *o*-H (ethyne)], 7.08 [d, ³J_{HH} = 8.0 Hz, 2 H, *m*-H (*cis*)], 6.87 [d, ³J_{HH} = 2.6 Hz, 4 H, *o*- and *m*-H (*trans*)], 6.77 [d, ³J_{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). – ¹³C NMR (100.62 MHz, C₆D₆): *δ* = 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≡C–C₆H₄Me), 21.2 [C=C–C₆H₄Me (*cis*)], 20.9 [C=C–C₆H₄Me (*trans*)], 1.1 ppm (SiMe). – ²⁹Si NMR (79.5 MHz, C₆D₆): *δ* = –34.1 ppm. – MS ((+)-EI; 30 eV; 353 K): *m/z* (%) = 701 (20) [M–CMe₃]⁺, 517 (100) [M–2Tol–CMe₃–2H 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**), 1,2-difluorobenzene (**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

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

	2	7 · 0.5 pentane	8	9	10	11
<i>Crystal data</i>						
Empirical formula	C ₃₃ H ₄₂ F ₂ Si	C _{26.5} H ₂₄ F ₁₀ Ge	C ₃₂ H ₄₇ AlSi	C ₃₂ H ₄₇ GaSi	C ₃₆ H ₃₉ GaGe	C ₃₂ H ₃₇ AlF ₁₀ Ge
<i>M_r</i>	504.75	605.05	486.76	529.50	613.98	711.18
Crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<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
<i>V</i> , × 10 ^{−30} m ³	3111.6(2)	1351.3(2)	1576.06(5)	1584.64(3)	1556.38(3)	6694.2(4)
$\rho_{\text{calcd.}}$, g cm ^{−3}	1.08	1.49	1.03	1.11	1.31	1.41
<i>Z</i>	4	2	2	2	2	8
<i>F</i> (000), <i>e</i>	1088	610	532	568	636	2912
μ , mm ^{−1}	0.1	1.2	0.1	0.9	2.4	1.0
<i>Data collection</i>						
<i>T</i> , K	153	153	153	153	153	153
Unique reflections/ <i>R</i> _{int}	7885/0.027	7750/0.067	9177/0.042	9200/0.026	5046/0.020	9758/0.023
Reflections <i>I</i> > 2 σ (<i>I</i>)	6758	6695	6419	8102	4471	7922
<i>Refinement</i>						
Refined parameters	435	344	319	319	349	409
Final <i>R</i> [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0564	0.0412	0.0484	0.0294	0.0309	0.0374
Final <i>wR</i> ^b (all data)	0.1653	0.1108	0.1309	0.0766	0.0837	0.1004
$\Delta\rho_{\text{fin}}$ (max/min), e Å ^{−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

^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 $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$.

Table 3b. Crystal data and structure refinement for compounds **12**, **13**, **15–18**.

	12	13	15 · 0.5C₆F₅H	16	17	18 · 0.5C₆F₂H₄
<i>Crystal data</i>						
Empirical formula	C ₃₅ H ₅₇ AlSi	C ₃₅ H ₅₇ AlSi	C ₄₄ H _{66.5} F _{2.5} Ga ₂ Si	C ₄₀ H ₆₆ Ga ₂ Ge	C ₄₄ H ₅₈ Ga ₂ Ge	C ₄₃ H ₇₆ FGa ₂ Ge
<i>M_r</i>	532.87	532.87	798.49	758.95	798.93	824.06
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> , pm	1114.73(3)	1237.82(7)	1563.74(2)	3216.45(8)	993.94(6)	4928.4(3)
<i>b</i> , 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
<i>V</i> , × 10 ^{−30} m ³	3636.3(2)	3552.2(4)	4321.5(1)	8203.5(2)	2033.8(2)	9462.7(9)
$\rho_{\text{calcd.}}$, g cm ^{−3}	0.97	1.00	1.23	1.23	1.31	1.16
<i>Z</i>	4	4	4	8	2	8
<i>F</i> (000), <i>e</i>	1176	1176	1692	3200	832	3496
μ , mm ^{−1}	0.1	0.1	1.3	2.1	2.1	1.8
<i>Data collection</i>						
<i>T</i> , K	233	153	153	153	153	153
Unique reflections/ <i>R</i> _{int}	8671/0.033	10436/0.025	12587/0.027	9831/0.071	9824/0.016	13809/0.050
Reflections <i>I</i> > 2 σ (<i>I</i>)	6525	8890	11 146	7566	8431	9024
<i>Refinement</i>						
Refined parameters	450	352	505	437	436	559
Final <i>R</i> [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0509	0.0459	0.0245	0.0397	0.0240	0.0439
Final <i>wR</i> ^b (all data)	0.1619	0.1402	0.0689	0.0969	0.0641	0.1221
$\Delta\rho_{\text{fin}}$ (max/min), e Å ^{−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 $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$.

0.84 : 0.16; **18**, CMe_3 : 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

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.

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