

Hydroalumination *versus* Deprotonation of Alkynes with Sterically Demanding Substituents

Werner Uhl, Marcus Layh, Ines Rhotert, Agnes Wollschläger, and Alexander Hepp

Institut für Anorganische und Analytische Chemie der Universität Münster, Corrensstraße 30,
48149 Münster, Germany

Reprint requests to Prof. Werner Uhl. E-mail: uhl@uni-muenster.de

Z. Naturforsch. **2013**, 68b, 503–517 / DOI: 10.5560/ZNB.2013-3070

Received February 27, 2013

Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

Treatment of sterically highly shielded terminal alkynes, $\text{H}-\text{C}\equiv\text{C}-\text{aryl}$, with dialkylaluminium and dialkylgallium hydrides, $\text{R}_2\text{E}-\text{H}$, afforded by hydrogen release dimeric dialkylelement alkynides with a four-membered E_2C_2 heterocycle independent of the bulk of the aryl groups. A rare example of a monomeric alkynylaluminium compound was only obtained with very bulky $\text{CH}(\text{SiMe}_3)_2$ groups attached to the metal atoms and by salt elimination reaction. The steric shielding by the bulky aryl groups did not prevent condensation reactions. Hydroalumination of 1-(trimethylsilyl)-2-(2,6-dimethylphenyl)ethyne using $\text{Me}_2\text{Al}-\text{H}$ resulted in a divinyl compound by elimination of trimethylaluminium.

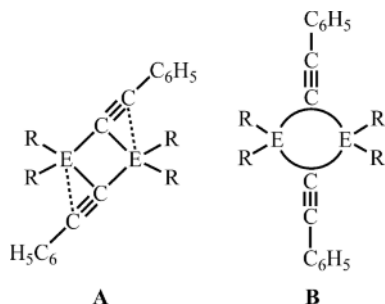
Key words: Aluminium, Gallium, Hydroalumination, Hydrogallation, Alkynes

Introduction

Hydroalumination and to a smaller degree hydrogallation reactions are important tools in organic synthesis and have often been applied for the regioselective reduction of unsaturated compounds with double or more importantly triple bonds by element hydrides $\text{R}_2\text{E}-\text{H}$ ($\text{E} = \text{Al}, \text{Ga}$) [1–9]. The organic products are usually obtained after hydrolytic work-up and typically the organometallic intermediates are not isolated. The intermediate hydrometalation products have recently attracted considerable attention, and it was shown that the underlying chemistry is much more complex and interesting than postulated from the constitution of the isolated products after hydrolysis [10]. It was shown that the reaction of sterically unhindered alkylaluminium alkynides $\text{R}_2\text{Al}-\text{C}\equiv\text{C}-\text{R}'$ with dialkylaluminium hydrides $\text{R}_2\text{Al}-\text{H}$ led *via* dismutation and elimination of R_3Al to carbaalanes which contain clusters of aluminium and carbon atoms with delocalised $\text{Al}-\text{C}$ bonding interactions similar to the closely related carbaboranes [11–14]. The related reactions of the corresponding gallium analogues were found to similarly yield compounds with a Ga_6C_4 heteroadamantane backbone and localised $\text{Ga}-\text{C}$ bonds [15]. The hy-

droalumination and hydrogallation of phenyl-centred *tert*-butylalkynes $\text{C}_6\text{H}_{6-n}(\text{C}\equiv\text{C}-\text{CMe}_3)_n$ ($n \geq 2$) with more than one alkyne group resulted in the case of sterically shielded dialkylelement hydrides in the elimination of ER_3 and the formation of cyclophane-like condensation products while less shielded hydrides gave one-dimensional coordination polymers of the simple addition products [10]. The reactions of $\text{Ph}-\text{C}\equiv\text{C}-\text{CMe}_3$ and phenyl-centred trimethylsilylalkynes $\text{C}_6\text{H}_{6-n}(\text{C}\equiv\text{C}-\text{SiMe}_3)_n$ ($n = 1-4$) did not result in condensation under mild conditions [10]. Hydrometalation of alkynes affords in the first step the kinetically favoured *cis*-addition products which have E and H atoms on the same side of the double bond and rearrange in the absence of steric hindrance to the thermodynamically more stable *trans*-products (E and H *trans* to each other) [16].

Dialkylelement alkynides $\text{R}_2\text{E}-\text{C}\equiv\text{C}-\text{R}'$ are accessible on facile routes by the reaction of $\text{R}'-\text{C}\equiv\text{C}-\text{H}$ with $\text{R}_2\text{E}-\text{H}$ or R_3E by elimination of H_2 or HR [17–19]. This method works well for relatively acidic alkynes such as $\text{Ph}-\text{C}\equiv\text{C}-\text{H}$ at low temperatures, while hydroalumination is observed as a competing reaction with less acidic alkyl- or trimethylsilylalkynes [20]. For these substrates, or for those with the sterically



Scheme 1. Structural motifs of dimeric dialkylaluminium alkynides.

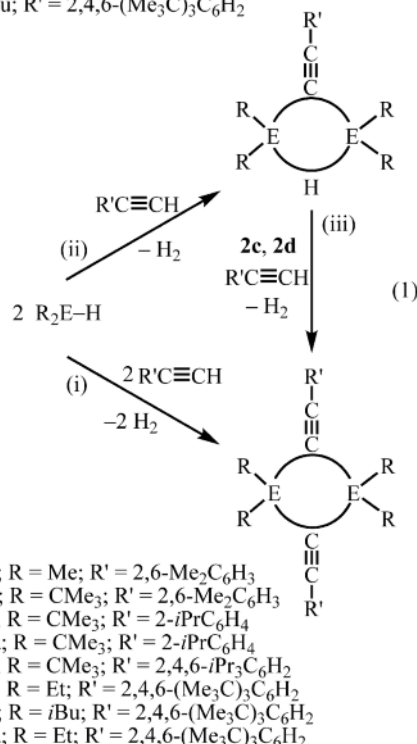
demanding substituent $R = \text{CH}(\text{SiMe}_3)_2$, salt elimination by treatment of $R'-\text{C}\equiv\text{C}-\text{Li}$ with $\text{Cl}-\text{ER}_2$ is the preferred method [17–19]. With very few exceptions these alkynides are dimeric in the solid state with two aluminium or gallium atoms bridged by the terminal carbon atoms of two alkyne groups. Their structures may be classified in two types **A** and **B** (Scheme 1) [17–19]. Type **A** is found in the absence of steric crowding for small substituents R , and type **B** for bulky substituents R . An intermediate type of structure that is somewhere between **A** and **B** was recently described for alkynides with an 1,8-diethynylanthracene backbone [21].

The present paper describes the reaction of sterically encumbered aryl- and aryl(trimethylsilyl)ethynes with element hydrides HER_2 . Within the scope of this study were the synthesis of sterically highly shielded aluminium and gallium alkynides, the influence of the substituents on the structures, in particular with respect to the formation of monomeric species, and the modes of reactivity with the possible generation of new types of carbaalane clusters or unsaturated heterocyclic compounds by hydrometalation and condensation.

Results and Discussion

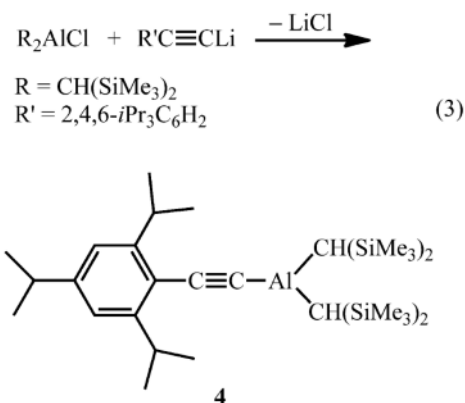
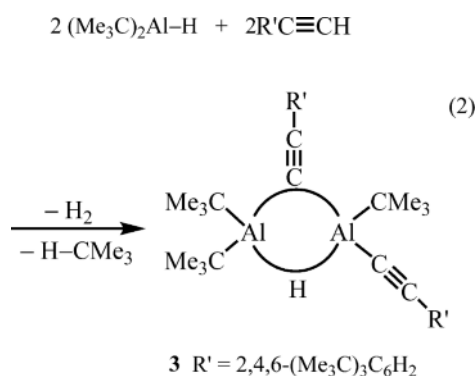
The dialkylelement alkynides $[\text{R}_2\text{E}-\text{C}\equiv\text{C}-\text{R}']_2$ **1a–1f** were easily accessible in moderate to high yields at room temperature from the reaction of the corresponding aryethynes $\text{R}'-\text{C}\equiv\text{C}-\text{H}$ with hydrides $\text{R}_2\text{E}-\text{H}$ in a stoichiometric 1 : 1 ratio [(i), Eq. 1]. As a result of the comparatively high acidity and the steric bulk of the acetylenes, low reaction temperatures were not necessary to prevent competing hydroalumination or -gallation reactions (*c.f.* refs. [17–19]). In case of the extremely shielded supermesitylacetylene 2,4,6-

2a $\text{E} = \text{Al}$; $\text{R} = \text{CH}_2\text{CMe}_3$; $\text{R}' = 2,4,6-(\text{Me}_3\text{C})_3\text{C}_6\text{H}_2$
2b $\text{E} = \text{Ga}$; $\text{R} = \text{CH}_2\text{CMe}_3$; $\text{R}' = 2,4,6-(\text{Me}_3\text{C})_3\text{C}_6\text{H}_2$
2c $\text{E} = \text{Al}$; $\text{R} = \text{Et}$; $\text{R}' = 2,4,6-(\text{Me}_3\text{C})_3\text{C}_6\text{H}_2$
2d $\text{E} = \text{Al}$; $\text{R} = i\text{Bu}$; $\text{R}' = 2,4,6-(\text{Me}_3\text{C})_3\text{C}_6\text{H}_2$



($\text{Me}_3\text{C})_3\text{C}_6\text{H}_2-\text{C}\equiv\text{C}-\text{H}$ independent of the stoichiometric ratio of the reactants only partial H_2 elimination was observed resulting in adducts (**2**) of the initially formed alkynide and excess hydride [(ii), Eq. 1]. Two metal atoms are bridged by one alkyne and one hydride anion. For the relatively bulky dineopentyl derivatives ($\text{E} = \text{Al}$, Ga) **2a** and **2b** no further reaction was observed even when the reaction time was extended or the temperature raised. Prolonged heating of **2b** in the presence of an excess of $(\text{Me}_3\text{CCH}_2)_2\text{Ga}-\text{H}$ to 70°C resulted in the gradual formation of elemental gallium. In contrast, the adducts with the less bulky Et_2Al or $i\text{Bu}_2\text{Al}$ groups reacted further to yield over the course of several days the alkynides **1f** and **1g** [(iii), (i), Eq. 1]. The less reactive Et_2GaH required refluxing in benzene to give the alkynide **1h**. The bulky $(\text{Me}_3\text{C})_2\text{Al}-\text{H}$ behaved again differently, and an intermediate element hydride adduct analogous to **2** was not observed. Instead prolonged stirring at room temperature resulted in the formation of compound **3** that features a bridging and a terminal alkynide group (Eq. 2),

Compound	$EC H_x$ (1H)	EH (1H)	$EC(sp^3)$ (^{13}C)	$EC\equiv C$ (^{13}C)	$EC\equiv C$ (^{13}C)	$C\equiv C$ (IR)
1a	0.06	–	–5.6	102.2	136.1	2062
1b	–	–	18.8	97.1	135.9	2035
1c	–	–	19.3	94.4	136.9	2050
1d	–	–	28.6	95.8	130.0	2048
1e	–	–	19.7	120.2	135.7	2019
1f	0.82	–	3.0	104.5	140.5	2025
1g	0.92	–	25.5	105.3	141.2	2025
1h	1.29	–	8.6	106.0	134.2	2027
2a	0.92	3.79	30.4	104.5	144.9	2029
2b	1.36	4.05	35.0	106.4	138.7	2033
2c	0.52	3.35	–1.0	103.3	142.5	–
2d	0.66/0.69	3.69	22.0	103.7	143.4	2031
3^a	–	3.60	17.9/18.6/19.7	101.8(brdg) 115.6(term)	145.7(brdg) 114.3(term)	2010 2095
4	–0.36	–	12.0	110.6	109.9	2108

Table 1. Selected NMR (ppm) and IR (cm^{-1}) spectroscopic parameters of the alkynyl compounds **1–4**.^a NMR at 230 K.

formed by hydrogen and concomitant isobutane elimination.

Previous investigations have shown the sterically demanding dialkylaluminum hydride [(Me₃Si)₂-CH]₂Al-H to react even with relatively acidic alkynes such as Ph-C≡C-H exclusively by hydroalumination [22]. The sterically encumbered alkyne **4** was therefore synthesised using the salt elimination route (Eq. 3), which has previously been successful in the preparation of alkyne **1** that carry the Al[CH(SiMe₃)₂]₂ substituent [17–19].

The new dimeric alkyne **1** [R₂E-C≡C-R']₂ have type **B** structures in the solid state with symmetrically bridging alkyne anions connecting two metal atoms *via* E-C-E 3c-2e bonds. In the related compounds **2** and **3** one of the alkyne groups is replaced by a bridging hydride anion. This is evident from a modest lowering of the $\nu(C\equiv C)$ stretching frequency in the IR spectrum (by 50 to 100 cm^{-1}) of the bridging C≡C-R' group as compared to terminal alkynyl groups (Table 1, *c.f.* compound **3**),

type **A** alkyne (Me₂Al-C≡C-Ph 2089 cm^{-1} [11]) or terminal alkynes (Ph-C≡C-H 2119 cm^{-1} , [23]). The different structural motifs may be recognised in the ^{13}C NMR spectrum by a larger (except compound **1e**) difference (≥ 30 ppm) between the chemical shifts of the carbon atoms of the C≡C triple bond as compared to type **A** compounds (≤ 30 ppm) with the signal of the metal bound carbon atom being shifted significantly to higher field in comparison to that of the carbon atom bound to the substituent R'. In terminal fragments, monomeric compounds (*c.f.* compound **4** and ref. [17–19]) or terminal alkynes [24, 25] the difference is usually much smaller. The characteristic shifts $\delta(^1H)$ of the bridging hydride anions in compounds **2** and **3** are found between $\delta = 3$ and 4. Further NMR parameters are summarised in Table 1. Compound **3** is fluxional in solution with the terminal and bridging alkyne fragments and one *t*Bu group on each Al atom rapidly ex-

Table 2. Selected structural parameters (pm, deg) of compounds **1**–**4**.

Compound	E–C≡C	E–C'≡C'	E–C (av.)	E–H	C≡C	E–C–E'	E–H–E	C–E–C'/H	Puckering angle	ER ₂
1a	209.8(2)	203.7(2)	194.7	–	121.4(2)	86.94(6)	–	93.06(6)	0	124.64(8)
1b	209.3(2)	209.6(2)	200.5	–	121.8(2)	88.28(6)	–	91.72(6)	0	118.53(8)
1c	205.9(2)	212.6(2)	200.7	–	121.7(3)	88.94(7)	–	91.06(7)	0	119.68(9)
1d	208.0(2)	219.5(2)	202.0	–	121.6(2)	89.22(6)	–	90.78(6)	0	121.82(7)
1e^a	208.5(2)	208.5(2)	201.4	–	122.2(2)	88.92(7)	–	91.1(av)	0	116.6(av)
	208.4(2)	209.3(2)	200.7	–	122.2(2)	87.89(6)	–	92.09(6)		117.69(9)
1f	206.6(2)	208.7(2)	196.6	–	122.6(3)	85.62(7)	–	94.22(8)	8.78	119.5(1)
	208.8(2)	207.3(2)		–	122.0(3)	85.45(7)	–	93.99(8)		118.0(1)
1g	209.4(2)	207.5(2)	196.6	–	121.9(3)	85.30(7)	–	94.59(7)	4.81	127.8(1)
1h	209.3(2)	213.2(2)	197.5	–	122.5(2)	85.50(6)	–	94.33(7)	7.34	124.0(1)
	212.6(2)	209.6(2)		–	122.4(2)	85.25(6)	–	94.42(7)		121.1(1)
2a	209.4(2)	–	197.2	179(2)	122.4(3)	81.27(7)	101	87.7(8)	(0.41)	128.7(av)
	208.6(2)			173(3)				89.6(8)		
2b	212.6(2)	–	198.0	169(3)	122.1(3)	79.94(6)	104	90(1)	(1.90)	131.7(av)
	213.9(2)			179(3)				86.5(9)		
3^b	208.6(av)	–	199.2	169(3)	122.7(4)	81.4(1)	105	87(1)	(10.53)	122.5(2)
	192.1(3)		198.6	173(3)	121.3(4)			85(1)		117.0(1) ^c
4	191.7(2)	–	194.4	–	121.3(3)	–	–	–	–	120.12(8)

^a Two independent molecules in the asymmetric unit; ^b second row values refer to the terminal alkinide; ^c this value refers to AlR(CCR').

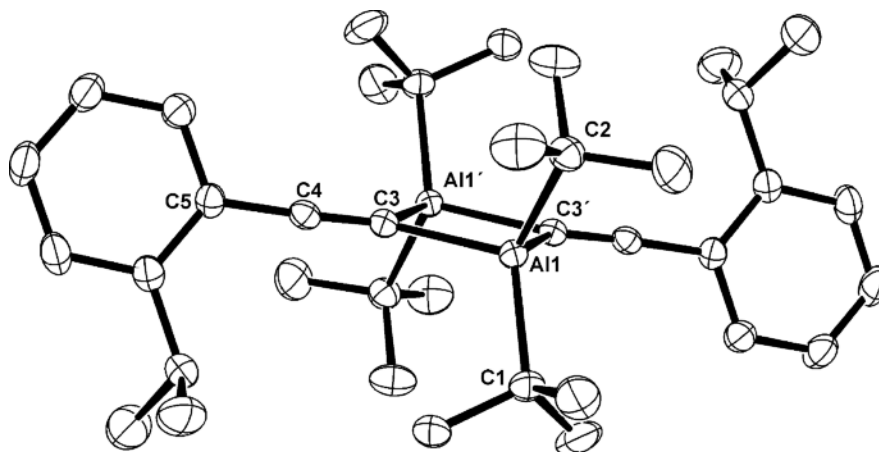


Fig. 1. Molecular structure and atomic numbering scheme of compound **1c**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms have been omitted for clarity.

changing at room temperature. Surprisingly, the second CMe₃ group in the Al(CMe₃)₂ fragment does not participate in the exchange process. To slow down the dynamic exchange and identify individual groups by sharp resonances the NMR spectra were recorded at 230 K.

While compounds **1a**–**1e** are all dimers with a symmetry-imposed planar four-membered Al₂C₂ ring, a small puckering (5–9°) is observed in case of the extremely bulky supermesityl [2,4,6-(Me₃C)₃C₆H₂] derivatives **1f**–**1h** (Table 2) as well

as in the hydride adducts **2** and **3** (see representative Figs. 1, 2 and 3). The alkinide/hydride anions are bridging the metal atoms symmetrically with approximately equal bond lengths between the anions and the metal atoms. The angles in the ring are close to 90° with the CE₂ angles being only slightly smaller than the corresponding endocyclic EC₂ angles at the metal atoms and significantly different from the larger (117–132°) exocyclic ER₂ angles. As expected, the exocyclic E–C bonds are much shorter than the endocyclic 3c–2e E–C bonds. For steric reasons the planes

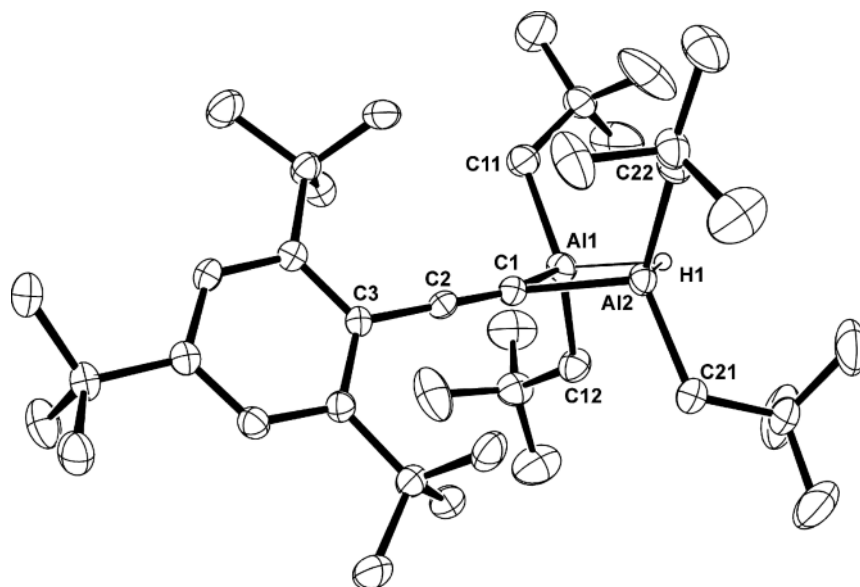


Fig. 2. Molecular structure and atomic numbering scheme of compound **2a**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H1; arbitrary radius) have been omitted for clarity.

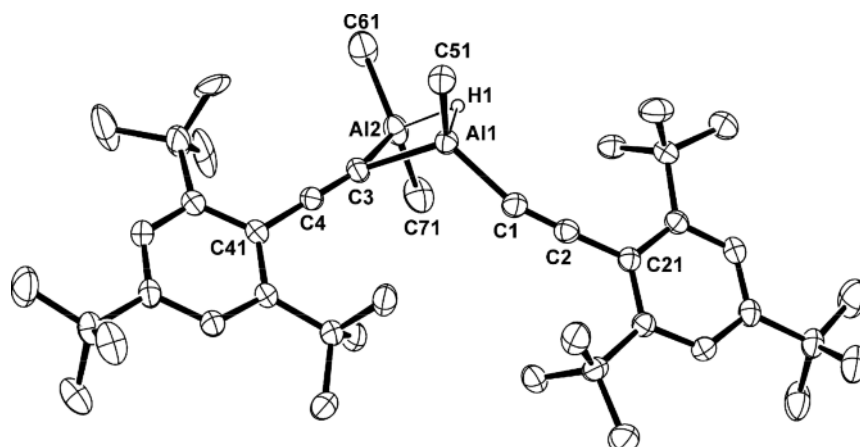


Fig. 3. Molecular structure and atomic numbering scheme of compound **3**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H1; arbitrary radius) and methyl groups of the (*tert*-butyl) substituents on aluminium have been omitted for clarity.

of the aromatic rings are approximately perpendicular ($76\text{--}87^\circ$ for **1**, 65° for **2**, 56° for **3**) to the central Al_2C_2 heterocycle. The $\text{C}\equiv\text{C}$ bond lengths are unexceptional and only slightly longer than those reported for $\text{Me-C}\equiv\text{C-Me}$ (121.1 pm [26]) or $\text{H-C}\equiv\text{C-H}$ (120.3 pm [27, 28]). The overall geometry and the bond lengths are in good agreement with typical type **B** structures published previously [17–20, 29, 30].

Interestingly, the extreme steric shielding of the ethynyl moieties by the bulky aryl groups does not influence the structures of these alkynides, and the usual dimeric formula units were observed in all cases. It was only the very bulky $\text{CH}(\text{SiMe}_3)_2$ substituent attached to the aluminium atom of compound **4** (Fig. 4) which prevented dimerisation resulting in the formation of a rare example of a monomeric alkynide similar

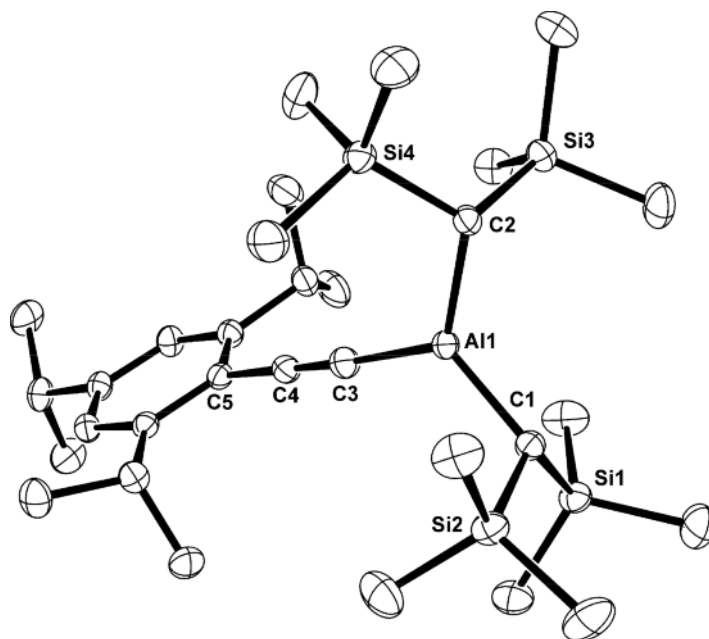


Fig. 4. Molecular structure and atomic numbering scheme of compound **4**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms have been omitted for clarity.

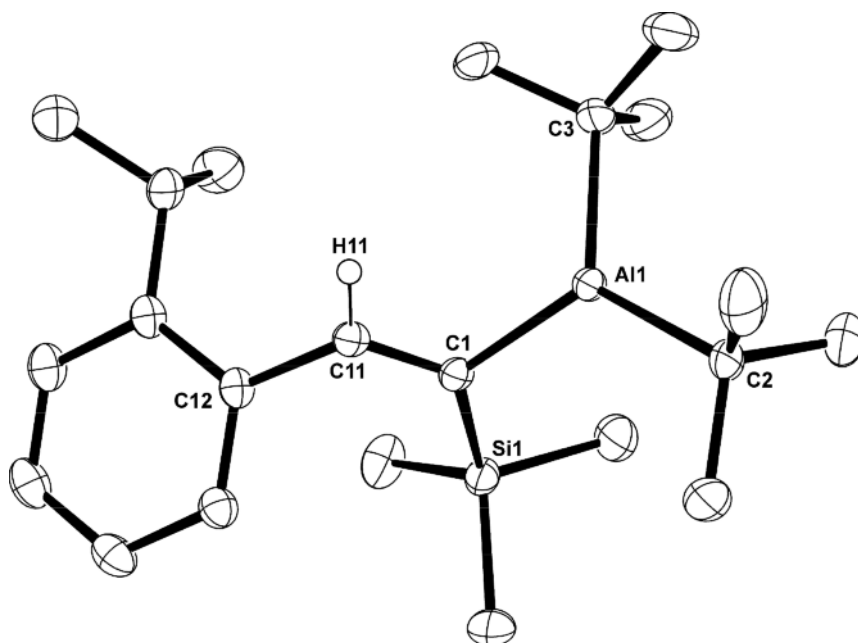


Fig. 5. Molecular structure and atomic numbering scheme of compound **5a**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H11, arbitrary radius) have been omitted for clarity.

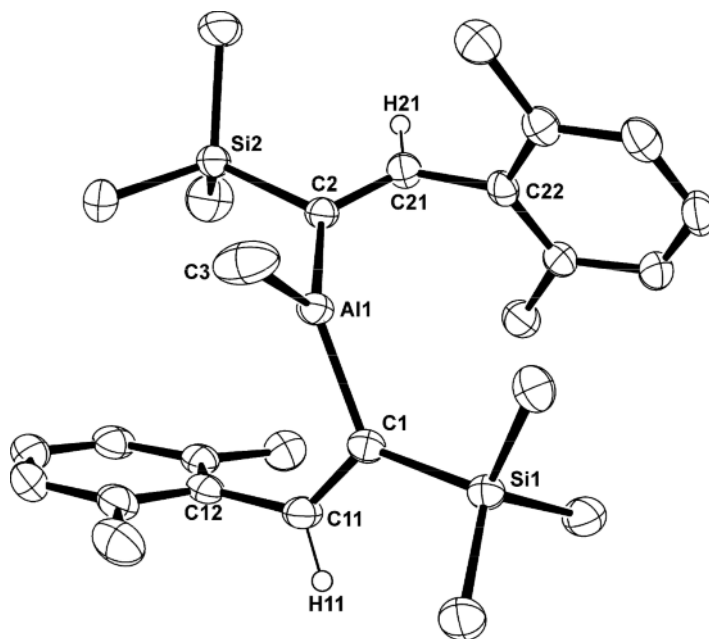


Fig. 6. Molecular structure and atomic numbering scheme of compound **6**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms (except H11, H21, arbitrary radius) have been omitted for clarity.

to related examples with the same substituent [17–19]. The three-coordinate aluminium atom is in a planar configuration (sum of angles 360°) and has much shorter Al–C bonds (Table 2) than those found in the dimeric species with four-coordinate aluminium atoms discussed above. The Al–C distances are different with Al–C(*sp*) bonds (191.7(2) pm) expectedly being shorter than Al–C(*sp*³) bonds (194.4(2) pm).

The reaction of arylsilylalkynes, $R'-C\equiv C-SiMe_3$ ($R' = \text{aryl}$), with R_2E-H has been investigated in some detail and was shown to lead in most cases to the respective simple addition products [16–19, 31, 32]. To investigate the influence of steric bulk on the course of this reaction, 2-*i*PrC₆H₄-C \equiv C-SiMe₃ was treated with (Me₃C)₂E-H ($E = \text{Al, Ga}$). While the reaction proceeded smoothly at room temperature in case of the aluminium hydride to give the corresponding kinetically favoured *cis*-addition product (Eq. 4), the less reactive gallium hydride required a double molar excess of hydride and refluxing in hexane for three days to yield the respective gallium derivative (Eq. 4). Reducing the steric bulk of the aluminium hydride using Me₂AlH and increasing the reaction temperature (three days reflux in hexane) changed the course of the reac-

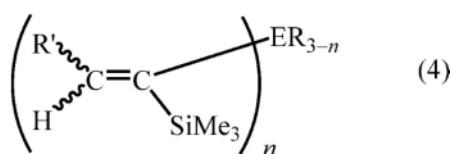
tion considerably and yielded the condensation product **6** that is likely generated from the initial hydroalumination product by elimination of AlMe₃ (Eq. 4). The extended heating at higher temperature also led to an isomerisation of the *cis*-addition products to the thermodynamically more stable *E*-products in which the vinylic H and Al atoms are in *trans* positions to each other. Similar dismutation reactions between Me₂E-H ($E = \text{Al, Ga}$) and alkynes have been observed previously [16].

The configuration at the double bonds in solution is evident from the characteristic $^3J_{Si-H}$ coupling constants [16] which are consistent with the formation of *Z*(**5a**)/*E*(**5b**)- (J_{Si-H} ca. 20 Hz; Si *trans* to H) and *E*-isomers (**6**, J_{Si-H} ca. 12.5 Hz; Si *cis* to H). This was confirmed by the solid-state structures (Figs. 5 and 6). All compounds are monomeric with a planar three-coordinate metal atom (Σ of angles 360° ; Table 3) and nearly planar alkene fragments. Compounds **5** follow the expected trend with E–C(*sp*²) bond lengths being shorter than the corresponding E–C(*sp*³) distances. Surprisingly this trend is reversed in case of compound **6** probably caused by the increased steric bulk in these compound (*c.f.* [31, 32]). Other bond lengths and an-

Table 3. Selected structural parameters (pm, deg) of compounds **5**–**6**.

Compound	E-alkyl	E–C=C	C=C	Σ angles (El)	<i>d</i> (E to C ₃) ^a	E–C=C–C(aryl)
5a	199.2(2) 199.4(2)	196.4(2)	134.5(3)	359.9	3.1	–178.7(2)
5b	200.6(2) 201.0(2)	198.4(2)	134.3(3)	360.0	1.8	179.1(2)
6a	194.6(2)	195.9(2) 196.1(2)	134.1(2) 133.9(2)	360.0	0.2	6.3(2)/4.5(2)
6b ^b	194.7(3) 193.9(3)	197.8(2)/198.7(2) 197.9(3)/198.0(3)	135.0(3)/134.0(3) 134.1(4)/133.4(4)	360.0 359.9	3.4 3.6	–7.8(3)/–7.0(3) –4.6(3)/–3.8(4)

^a Deviation of E from the average plane of the connecting carbon atoms; ^b two independent molecules.



- 5a** E = Al; R = CMe₃; R' = 2-*i*PrC₆H₄; *n* = 1
5b E = Ga; R = CMe₃; R' = 2-*i*PrC₆H₄; *n* = 1
6 E = Al; R = Me; R' = 2,6-Me₂C₆H₃; *n* = 2

gles are unexceptional and may be compared to those of previously described related aluminium and gallium derivatives [31–33].

We have synthesised a large number of different dialkylaluminium and dialkylgallium alkynides with bulky substituents bound to the ethynyl groups. Independent of steric shielding, dimeric compounds were formed in which two metal atoms are bridged by two alkynido groups. A rare example of a monomeric dialkylaluminium alkynide was only obtained with two bulky CH(SiMe₃)₂ groups bound to aluminium. This observation clearly underscores that the bulkiness of the substituents at aluminium is much more important for the resulting structure than the substituents at the ethynyl group which obviously are too far from the coordinatively unsaturated aluminium atoms to prevent dimerisation *via* donor-acceptor interactions. However, the secondary reactions with excess dialkylaluminium hydrides are influenced, and in no case did we observe the addition of an Al–H bond to the C≡C triple bonds of these aluminium alkynides. Also the reactions of trimethylsilylarylethynes with dialkylaluminium hydrides do not de-

pend on steric shielding and result in the products of the expected hydroalumination or the thermally induced condensation.

Experimental Section

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane, cyclopentane and *n*-pentane with LiAlH₄; benzene with Na, 1,2-difluorobenzene and pentafluorobenzene with molecular sieves). NMR spectra were recorded in C₆D₆ or C₇D₈ at ambient probe temperature (except compound **3**) using the 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 as Nujol mulls between CsI plates on a Shimadzu Prestige 21 spectrometer. ClAl[CH(SiMe₃)₂]₂ [34], Me₂AlH [35], (Me₃C)₂AlH [36], (Me₃CCH₂)₂AlH [37], (Me₃C)₂GaH [36], 2-*i*PrC₆H₄–C≡C–H [38], 2,6-Me₂C₆H₃–C≡C–SiMe₃ [39, 40], 2,4,6-*i*Pr₃C₆H₂–C≡C–H [41], 2-*i*PrC₆H₄–C≡C–SiMe₃ [38], 2,6-Me₂C₆H₃–C≡C–H [40] and 2,4,6-*i*Pr₃C₆H₂–C≡C–Li [41] were obtained according to literature procedures. 2,4,6-(Me₃C)₃C₆H₂–C≡C–H [42] was prepared from 2,4,6-(Me₃C)₃C₆H₂Br [42, 43] *via* 2,4,6-(Me₃C)₃C₆H₂–C≡C–CO₂–H [42] which was, in a variation of the procedure described in ref. [42], decarboxylated at 260 °C and sublimed *in vacuo* at 200 °C. Et₂GaH was synthesised from Et₂GaCl and Li[Et₂GaH₂] [44]. The starting material Et₂GaCl [45, 46] previously obtained from GaCl₃ and GaEt₃ [47] (synthesised from EtLi and GaCl₃), was isolated in high yield from the reaction of commercially available ZnEt₂ (Sigma Aldrich) and GaCl₃ (see below). Et₂AlH and *i*Bu₂Al–H were purchased from MOCHEM GmbH, Marburg, Germany, and used without further purification. The assignment of NMR spectra is based on HMBC, HSQC and DEPT135 data.

Improved synthesis of Et₂GaCl

A solution of ZnEt₂ (36 mL, 36 mmol, 1 M in hexane) was added dropwise to a solution of GaCl₃ (6.34 g, 36 mmol) in hexane (20 mL) at room temperature. The reaction mixture was heated and stirred under reflux conditions for 2 h. The precipitated ZnCl₂ was removed by filtration, the filtrate was collected and the solvent removed *in vacuo* to yield Et₂GaCl as a pale-yellow, analytically pure liquid. Yield: 5.88 g (100%). – ¹H NMR: (400 MHz, C₆D₆): δ = 0.80 (q, ³J_{H–H} = 8.0 Hz, CH₂, 4 H), 1.18 (t, ³J_{H–H} = 8.0 Hz, CH₃, 6H) [46].

Synthesis of (Me₂Al-μ-C≡C-2,6-Me₂C₆H₃)₂, 1a

A solution of HC≡C-2,6-Me₂C₆H₃ (0.451 g, 3.47 mmol) in *n*-hexane (10 mL) was added at room temperature to a solution of Me₂AlH (0.201 g, 3.47 mmol) in *n*-hexane (10 mL), and the mixture was stirred for 22 h and then concentrated and cooled to –5 °C to give yellow crystals of compound **1a**. Yield: 0.396 g (61%). – M. p. (under argon; sealed capillary): 215 °C (dec.). – IR (CsI, paraffin): ν = 2062 vs, 2018 m ν(C≡C), 1879 w, 1680 w, 1593 w, 1574 w (phenyl); 1466 vs, 1379 vs (paraffin); 1302 w, 1279 w, 1250 vw δ(CH₃); 1182 s, 1165 s, 1088 w, 1030 m, 843 w, 810 w, 781 w, 770 w ν(CC); 721 vs (paraffin); 694 s (phenyl); 579 w, 557 m, 505 w cm^{–1} ν(AlC). – ¹H NMR (400 MHz, C₆D₆, 300 K): δ = 0.06 (s, 6H, AlCH₃), 2.37 (s, 6H, aryl-CH₃), 6.68 (d, 2H, ³J_{H–H} = 7.6 Hz, *m*-H), 6.86 (t, 1H, ³J_{H–H} = 7.6 Hz, *p*-H). – ¹³C NMR (100 MHz, C₆D₆, 300 K): δ = –5.6 (AlMe), 21.0 (aryl-CH₃), 102.2 (AlC≡C), 120.4 (*ipso*-C), 127.4 (*m*-C), 131.3 (*p*-C), 136.1 (AlC≡C), 144.2(*o*-C). – MS (EI, 20 eV, 298 K): *m/z* (%) = 357 (13) [M–CH₃]⁺, 186 (4) [1/2M]⁺, 130 (100) [alkyne]⁺.

Synthesis of [(Me₃C)₂Al-μ-C≡C-2,6-Me₂C₆H₃]₂, 1b

A solution of (Me₃C)₂AlH (0.685 g, 4.82 mmol) in *n*-hexane (20 mL) was added at room temperature to a solution of HC≡C-2,6-Me₂C₆H₃ (0.628 g, 4.83 mmol) in *n*-hexane (5 mL), and the mixture was stirred for 26 h. A colourless solid precipitated which was isolated and recrystallised from 1,2-difluorobenzene at 5 °C to give pale-yellow crystals of compound **1b**. Yield: 1.11 g (85%). – M. p. (under argon; sealed capillary): 156 °C (dec.). – IR (CsI, paraffin): ν = 2035 m, 2000 sh ν(C≡C); 1744 vw, 1694 vw, 1589 vs, 1580 vs, 1560 vs (phenyl); 1461 vs (paraffin); 1402 s δ(CH₃); 1375 vs (paraffin), 1304 w, 1275 w δ(CH₃); 1194 m, 1167 s, 1117 w, 1090 s, 1045 m, 999 vw, 934 w, 891 vw, 814 s, 772 w ν(CC); 721 vs (paraffin); 654 m (phenyl); 590 m, 563 w, 507 s, 444 s cm^{–1} δ(CC), ν(AlC). – ¹H NMR (400 MHz, C₆D₆, 300 K): δ = 1.41 (s, 18H, CMe₃), 2.60 (s, 6H, aryl-*Me*), 6.69 (d, 2H, ³J_{H–H} = 7.6 Hz, *m*-H), 6.86 (t, 1H, ³J_{H–H} = 7.6 Hz, *p*-H). – ¹³C NMR (100 MHz, C₆D₆,

300 K): δ = 18.8 (br., CMe₃), 22.1 (aryl-*Me*), 32.1 (CMe₃), 97.1 (AlC≡C), 119.8 (*ipso*-C), 127.9 (*m*-C), 132.1 (*p*-C), 135.9 (AlC≡C), 145.5 (*o*-C). – MS (EI, 20 eV, 453 K): *m/z* (%) = 270 (18) [1/2M]⁺, 213 (100) [1/2M–CMe₃]⁺.

*Synthesis of [(Me₃C)₂Al-μ-C≡C-2-*i*PrC₆H₄]₂, 1c*

A solution of (Me₃C)₂AlH (0.467 g, 3.29 mmol) in *n*-hexane (15 mL) was added at room temperature to a solution of HC≡C-2-*i*PrC₆H₄ (0.448 g, 3.11 mmol) in *n*-hexane (10 mL), and the mixture was stirred for 22 h. The solution was concentrated and cooled to –5 °C to yield colourless to pale-yellow crystals of compound **1c**. Yield: 0.667 g (76%). – M. p. (under argon; sealed capillary): 184 °C (dec.). – IR (CsI, paraffin): ν = 2050 vs, 2023 sh ν(C≡C), 1929 vw, 1850 vw, 1817 vw, 1707 vw 1628 vw, 1593, 1580 s, 1566 m (phenyl); 1462 vs, 1375 vs (paraffin); 1362 s, 1306 vw, 1277vw δ(CH₃); 1217 w, 1177 w, 1103 vw, 1080 s, 1030 w, 1003 w, 937 w, 891 m, 812 s, 756 s ν(CC); 720 (paraffin); 667 vw, 644 vw (phenyl); 588 s 536 vs, 478 vw, 442 w cm^{–1} δ(CC), ν(AlC). – ¹H NMR (400 MHz, C₆D₆, 300 K): δ = 1.21 (d, 6H, ³J_{H–H} = 6.9 Hz, CHMe₂), 1.46 (s, 18H, CMe₃), 3.95 (sept, 1H, ³J_{H–H} = 6.9 Hz, CHMe₂), 6.78 (m, 1H, *m*-H(5)), 6.99 (m, 1H, *m*-H(3)), 7.00 (m, 1H, *p*-H), 7.78 (d, 1H, ³J_{H–H} = 7.7 Hz, *o*-H). – ¹³C NMR (100 MHz, C₆D₆, 300 K): δ = 19.3 (br., CMe₃), 23.9 (CHMe₂), 32.0 (CMe₃), 32.1 (CHMe₂), 94.4 (AlC≡C), 118.7 (*ipso*-C), 126.1 (*m*-C(3)), 126.5 (*m*-C(5)), 132.7 (*p*-C), 136.2 (*o*-C(6)), 136.9 (AlC≡C), 154.8 (*o*-C(2)). – MS (EI, 20 eV, 393 K): *m/z* (%) = 511 (5) [M–CMe₃]⁺, 393 (3) [M–butene–C₆H₄*i*Pr]⁺, 284 (3) [1/2M]⁺, 227 (13) [1/2M–CMe₃]⁺, 144 (65) [alkyne]⁺.

*Synthesis of [(Me₃C)₂Ga-μ-C≡C-2-*i*PrC₆H₄]₂, 1d*

A solution of (Me₃C)₂GaH (0.782 g, 4.23 mmol) in *n*-hexane (10 mL) was added at room temperature to a solution of HC≡C-2-*i*PrC₆H₄ (0.589 g, 4.09 mmol) in *n*-hexane (10 mL), and the mixture was stirred for 21 h and then concentrated and cooled to 5 °C to yield colourless crystals of compound **1d**. Yield: 0.773 g (58%). – M. p. (under argon; sealed capillary): 165 °C (dec.). – IR (CsI, paraffin): ν = 2048 vs, 2018 s sh ν(C≡C); 1956 vw, 1925 vw, 1898 vw, 1846 vw, 1815 vw, 1744 w, 1709 w, 1680 w, 1653 w, 1626 w, 1593 s, 1576 m, 1532 vw, 1516 w (phenyl); 1462 vs, 1379 vs (paraffin); 1362 vs, 1310 vw, 1273 w, 1248 vw δ(CH₃); 1215 w, 1184 vs, 1165 vs, 1103 vw, 1080 s, 1011 vs, 941 s, 893 w, 839 w, 810 vs, 756 vs ν(CC); 715 vs (paraffin); 654 vw (phenyl); 615 w, 590 w, 571 w, 532 vs, 509 s cm^{–1} δ(CC), ν(GaC). – ¹H NMR (400 MHz, C₆D₆, 300 K): δ = 1.23 (d, 6H, ³J_{H–H} = 7.0 Hz, CHMe₂), 1.51 (s, 18H, CMe₃), 4.00 (sept, 1H, ³J_{H–H} = 7.0 Hz, CHMe₂), 6.83 (m, 1H, *m*-H(5)), 7.02 (m, 1H, *m*-H(3)), 7.04 (m, 1H, *p*-H), 7.77 (d, 1H, ³J_{H–H} = 7.7 Hz, *o*-H). – ¹³C NMR

(100 MHz, C_6D_6 , 300 K): δ = 24.0 ($CHMe_2$), 28.6 (CMe_3), 32.0 ($CHMe_2$), 32.3 (CMe_3), 95.8 ($GaC\equiv C$), 120.3 (*ipso*-C), 125.9 (*m*-C(3)), 126.4 (*m*-C(5)), 130.0 ($GaC\equiv C$), 131.6 (*p*-C), 135.9 (*o*-C(6)), 154.1 (*o*-C(2)). – MS (EI, 20 eV, 353 K): $m/z(\%)$ = 327 (4) $[1/2M]^+$, 269 (100), 271 (66) $[M_{1/2}-(tBu)]^+$, 183 (3), 185 (2) $[Ga(tBu)_2]^+$.

Synthesis of $[(Me_3C)_2Al-\mu-C\equiv C-2,4,6-iPr_3C_6H_2]_2$, **1e**

A solution of $(Me_3C)_2AlH$ (0.464 g, 3.27 mmol) in *n*-hexane (20 mL) was added at room temperature to a solution of $HC\equiv C-2,4,6-iPr_3C_6H_2$ (0.720 g, 3.16 mmol) in *n*-hexane (15 mL), and the mixture was stirred for 22 h. The solution was concentrated and cooled to $-45^\circ C$ to yield colourless crystals of compound **1e**. Yield: 0.846 g (73%). – M. p. (under argon; sealed capillary): $194^\circ C$ (dec.). – IR (CsI, paraffin): ν = 2019 vs $\nu(C\equiv C)$; 1775 vw, 1653 w, 1605 vs, 1578 vs, 1558 vs (phenyl); 1460 vs (paraffin); 1404 m $\delta(CH_3)$; 1337 vs (paraffin); 1315 m, 1252 w $\delta(CH_3)$; 1173 m, 1152 w, 1113 s, 1070 m, 1057 w, 1001 m, 941 m, 880 s, 847 w, 812 vs, 774 w $\nu(CC)$; 723 vs (paraffin); 656 w (phenyl); 584 m, 561 s, 513 s, 461 m, 434 cm^{-1} $\delta(CC)$, $\nu(AlC)$. – 1H NMR (400 MHz, C_6D_6 , 300 K): δ = 1.09 (d, 6H, $^3J_{H-H}$ = 6.9 Hz, *p*- $CHMe_2$), 1.34 (d, 12H, $^3J_{H-H}$ = 6.8 Hz, *o*- $CHMe_2$), 1.45 (s, 18H, CMe_3), 2.65 (sept, 1H, $^3J_{H-H}$ = 6.9 Hz, *p*- $CHMe_2$), 4.21 (sept, 2 H, $^3J_{H-H}$ = 6.8 Hz, *o*- $CHMe_2$), 7.06 (s, 2 H, *m*-H). – ^{13}C NMR (100 MHz, C_6D_6 , 300 K): δ = 19.7 (br, CMe_3), 23.6 (*p*- $CHMe_2$), 24.8 (*o*- $CHMe_2$), 32.2 (CMe_3), 32.2 (*o*- $CHMe_2$), 35.0 (*p*- $CHMe_2$), 115.2 (*ipso*-C), 120.2 ($AlC\equiv C$), 122.1 (*m*-C), 135.7 ($AlC\equiv C$), 154.2 (*p*-C), 156.6 (*o*-C). – MS (EI, 20 eV, 393 K): $m/z(\%)$ = 368 (8) $[1/2M]^+$, 311 (24) $[1/2M-CMe_3]^+$.

Synthesis of $[Et_2Al-\mu-C\equiv C-2,4,6-(Me_3C)_3C_6H_2]_2$, **1f**

Et_2AlH (0.128 g, 1.49 mmol) was added at room temperature to a solution of $HC\equiv C-2,4,6-(Me_3C)_3C_6H_2$ (0.401 g, 1.49 mmol) in *n*-pentane (10 mL), and the reaction mixture was stirred for three days. The solvent was removed *in vacuo*, and the residue was recrystallised from 1,2-difluorobenzene at $2^\circ C$ to yield colourless crystals of compound **1f**. Yield: 0.451 g (86%); the product **1f** may contain the alkyne as an impurity. – M. p. (under argon; sealed capillary): $173^\circ C$ (dec.). – IR (CsI, paraffin): ν = 2025 s $\nu(C\equiv C)$; 1769 w, 1599 s, 1508 s (phenyl); 1462 vs, 1377 vs (paraffin); 1364 s, 1269 m $\delta(CH_3)$; 1219 m, 1101 w, 1053 w, 1024 vw, 974 w, 949 w, 928 w, 881 m, 795 w, 750 m $\nu(CC)$; 725 w (paraffin); 698 w, 658 m (phenyl); 629 m, 611 m, 594 m, 567 m, 532 w, 513 w, 451 m, 434 cm^{-1} $\delta(CC)$, $\nu(AlC)$. – 1H NMR (400 MHz, C_6D_6 , 300 K): δ = 0.82 (q, 4 H, $^3J_{H-H}$ = 8.1 Hz, CH_2), 1.21 (s, 9H, *p*- CMe_3), 1.46 (t, 6H, $^3J_{H-H}$ = 8.1 Hz, CH_2CH_3), 1.70 (s, 18H, *o*- CMe_3), 7.50 (s, 2H, *m*-CH). – ^{13}C NMR (100 MHz, C_6D_6 , 300 K): δ = 3.0

($AlCH_2$), 9.7 (CH_2CH_3), 31.1 (*p*- CMe_3), 31.6 (*o*- CMe_3), 35.6 (*p*- CMe_3), 37.4 (*o*- CMe_3), 104.5 ($AlC\equiv C$), 115.2 (*ipso*-C), 121.7 (*m*-C), 140.5 ($AlC\equiv C$), 154.2 (*p*-C), 158.5 (*o*-C). – MS (EI, 20 eV, 413 K): $m/z(\%)$ = 354 (3) $[1/2M]^+$, 270 (88) [alkyne] $^+$.

Synthesis of $[iBu_2Al-\mu-C\equiv C-2,4,6-(Me_3C)_3C_6H_2]_2$, **1g**

iBu_2AlH (0.158 g, 1.11 mmol) was added at room temperature to a solution of $HC\equiv C-2,4,6-(Me_3C)_3C_6H_2$ (0.300 g, 1.11 mmol) in *n*-pentane (10 mL), and the reaction mixture was stirred for 12 h. The solvent was removed *in vacuo* and recrystallised from pentafluorobenzene at $-20^\circ C$ to yield colourless crystals of **1g**. Yield: 0.092 g (20%); pure samples can only be obtained with difficulties by repeated recrystallisation. – M. p. (under argon; sealed capillary): $176^\circ C$ (dec.). – IR (CsI, paraffin): ν = 2025 w $\nu(C\equiv C)$; 1599 w (phenyl); 1458 vs, 1377 vs (paraffin); 1306 m, 1280 m $\delta(CH_3)$; 1219 w, 1169 m, 1155 m, 1059 w, 1009 w, 964 m, 932 m, 891 w, 845 w $\nu(CC)$; 721 s paraffin; 673 w (phenyl); 629 w, 594 w, 561 w, 515 w, 455 cm^{-1} $\delta(CC)$, $\nu(AlC)$. – 1H NMR (400 MHz, C_6D_6 , 300 K): δ = 0.92 (d, 4H, $^3J_{H-H}$ = 7.1 Hz, $AlCH_2$), 1.16 (s, 9H, *p*- CMe_3), 1.19 (d, 12H, J_{H-H} = 6.5 Hz, $CHMe_2$), 1.76 (s, 18H, *o*- CMe_3), 2.29 (m, 2H, $CHMe_2$), 7.50 (s, 2H, *m*-CH). – ^{13}C NMR (100 MHz, C_6D_6 , 300 K): δ = 25.5 ($AlCH_2$), 26.4 ($CHMe_2$), 28.5 ($CHMe_2$), 31.0 (*p*- CMe_3), 32.0 (*o*- CMe_3), 35.5 (*p*- CMe_3), 37.6 (*o*- CMe_3), 105.3 ($AlC\equiv C$), 115.6 (*ipso*-C), 121.7 (*m*-C), 141.2 ($AlC\equiv C$), 154.0 (*p*-C), 158.5 (*o*-C).

Synthesis of $[Et_2Ga-\mu-C\equiv C-2,4,6-(Me_3C)_3C_6H_2]_2$, **1h**

A solution of $HC\equiv C-2,4,6-(Me_3C)_3C_6H_2$ (0.322 g, 1.19 mmol) in benzene (5 mL) was added to a solution of Et_2GaH (0.307 g, 2.39 mmol), and the mixture was stirred under reflux conditions for 3.5 h. The solvent was removed *in vacuo*, and the residue was recrystallised from 1,2-difluorobenzene at $5^\circ C$ to give colourless crystals of compound **1h**. Yield: 244 mg, (52%); samples of **1h** may contain the terminal alkyne as an impurities. – M. p. (under argon; sealed capillary): $147-150^\circ C$ (dec.). – IR (CsI, paraffin): ν = 2027 s, 2000 sh $\nu(C\equiv C)$; 1769 w, 1599 s, 1535 w (phenyl); 1464 s, 1454 s (paraffin); 1418 w $\delta(CH_3)$; 1375 m (paraffin); 1362 m, 1308 m, 1292 m $\delta(CH_3)$; 1234 vs, br., 1153 vs, 1140 s, 1115 s, 1103 sh, 1026 w, 984 s, 928 w, 880 m, 795 w, 750 w $\nu(CC)$; 721 w (paraffin); 692 vw, 640 m (phenyl); 554 w, 509 s, 440 cm^{-1} $\delta(CC)$, $\nu(GaC)$. – 1H NMR (400 MHz, C_6D_6): δ = 1.25 (s, 9H, *p*- CMe_3), 1.29 (q, 4H, $^3J_{H-H}$ = 7.9 Hz, CH_2), 1.48 (t, 6H, $^3J_{H-H}$ = 7.9 Hz, CH_2Me), 1.72 (s, 18H, *o*- CMe_3), 7.51 (s, 2H, *m*-H). – ^{13}C NMR (100 MHz, C_6D_6): δ = 8.6 (CH_2), 11.1 (CH_2Me), 31.2 (*p*- CMe_3), 31.4 (*o*- CMe_3), 35.5 (*p*- CMe_3), 37.4 (*o*- CMe_3), 106.0 (br., $GaC\equiv C$), 116.7 (*ipso*-C), 121.5 (*m*-C), 134.2 (br., $GaC\equiv C$), 152.8 (*p*-C), 157.2 (*o*-C). – MS (EI,

20 eV, 303 K): m/z (%) = 396 (0.5) $[1/2M]^+$, 367 (9), 369 (6) $[1/2M-CH_3]^+$, 270 (56) $[alkyne]^+$.

Synthesis of

$[(Me_3CCH_2)_2Al]_2(\mu-H)[\mu-C\equiv C-2,4,6-(Me_3C)_3C_6H_2]$, **2a**

A solution of $(Me_3CCH_2)_2AlH$ (0.342 g, 2.01 mmol) in *n*-pentane (20 mL) was added at room temperature to a solution of $HC\equiv C-2,4,6-(Me_3C)_3C_6H_2$ (0.272 g, 1.01 mmol) in *n*-pentane (5 mL), and the mixture was stirred for two days. The solvent was removed *in vacuo*, and the residue was recrystallised from pentafluorobenzene at $-30^\circ C$ to give compound **2a**. Yield: 0.475 g (78%). – M. p. (under argon; sealed capillary): $94^\circ C$ (dec.). – IR (CsI, paraffin): $\nu = 2029$ s, 2000 sh ν ($C\equiv C$); 1771 w ν ($AlHAl$); 1645 w, 1597 s, 1533 m (phenyl); 1460 vs, 1377 vs (paraffin); 1364 vs, 1306 s, 1270 s δ (CH_3); 1221 vs, 1125 m, 1099 m, 1070 w, 999 s, 932 s, 883 s, 781 s, 745 s ν (CC); 723 s (paraffin); 677 s (phenyl); 633 s, 594 m, 554 w, 517 m, 463 m cm^{-1} δ (CC), ν (AlC). – 1H NMR (400 MHz, C_6D_6 , 300 K): $\delta = 0.92$ (s, 8 H, CH_2), 1.17 (s, 9H, *p*- Me_3), 1.27 (s, 36 H, CH_2CMe_3), 1.64 (s, 18 H, *o*- Me_3), 3.79 (s, br., 1H, $AlHAl$), 7.45 (s, 2H, *m*-H). – ^{13}C NMR (100 MHz, C_6D_6 , 300 K): $\delta = 30.4$ (s, br., CH_2), 31.0 (*p*- Me_3), 31.7 (*o*- Me_3), 31.8 (CH_2CMe_3), 35.2 (CH_2CMe_3), 35.6 (*p*- Me_3), 37.4 (*o*- Me_3), 104.5 ($AlC\equiv C$), 115.1 (*ipso*-C), 121.7 (*m*-C), 144.9 ($AlC\equiv C$), 154.3 (*p*-C), 157.8 (*o*-C).

Synthesis of

$[(Me_3CCH_2)_2Ga]_2(\mu-H)[\mu-C\equiv C-2,4,6-(Me_3C)_3C_6H_2]$, **2b**

A solution of $(Me_3CCH_2)_2GaH$ (0.342 g, 1.61 mmol) in *n*-hexane (10 mL) was added at room temperature to a solution of $HC\equiv C-2,4,6-(Me_3C)_3C_6H_2$ (0.163 g, 0.604 mmol) in *n*-hexane (10 mL), and the mixture was stirred under reflux conditions for one day and filtered to remove traces of elemental Ga. The solvent was removed *in vacuo*, and the residue was recrystallised from 1,2-difluorobenzene at $-20^\circ C$ to give colourless crystals of compound **2b**. Yield: 0.371 g (89%); the samples generally contain small quantities of the free alkyne. – M. p. (under argon; sealed capillary): $128^\circ C$ (dec.). – IR (CsI, paraffin): $\nu = 2033$ w ν ($C\equiv C$), 1769 vw, 1700 w, br., 1597 m, 1533 w (phenyl), ν ($GaHGa$); 1466 vs, 1377 vs (paraffin); 1306 s, 1270 s δ (CH_3); 1233 m, 1167 vw, 1136 vw, 1099 w, 1003 w, 930 w, 883 w, 845 w, 770 s ν (CC); 723 vs (paraffin); 625 w, 594 w, 544 vw, 513 w, 455 m cm^{-1} δ (CC), ν (GaC). – 1H NMR (400 MHz, C_6D_6 , 300 K): $\delta = 1.22$ (s, 45 H, *p*- Me_3 and CH_2CMe_3), 1.32 (s, br., 8H, CH_2), 1.72 (s, 18H, *o*- Me_3), 4.06 (s, br., 1H, $GaHGa$), 7.49 (s, 2H, *m*-H). – ^{13}C NMR (100 MHz, C_6D_6 , 300 K): $\delta = 31.2$ (*p*- Me_3), 31.4 (*o*- Me_3), 32.1 (br., CH_2CMe_3), 34.3 (br., CH_2CMe_3), 35.5 (*p*- Me_3), 35.6 (br., CH_2), 37.4 (*o*- Me_3), 117.2 (*ipso*-C), 121.4 (*m*-C), 152.3 (*p*-C), 156.2 (*o*-C). – 1H NMR (400 MHz, C_6D_6 , 275 K): $\delta =$

1.19 (s, 9H, *p*- Me_3), 1.24 (s, 36H, CH_2CMe_3), 1.36 (s, br., 8H, CH_2), 1.70 (s, 18H, *o*- Me_3), 4.05 (s, br., 1H, $GaHGa$), 7.48 (s, 2H, *m*-H). – ^{13}C NMR (100 MHz, C_6D_6 , 275 K): $\delta = 31.1$ (*p*- Me_3), 31.4 (*o*- Me_3), 32.1 (br., CH_2CMe_3), 34.3 (br., CH_2CMe_3), 35.0 (CH_2), 35.4 (*p*- Me_3), 37.4 (*o*- Me_3), 106.4 (br., $GaC\equiv C$), 116.8 (*ipso*-C), 121.5 (*m*-C), 138.7 (br., $GaC\equiv C$), 152.7 (*p*-C), 156.6 (*o*-C). – MS (EI, 20 eV, 333 K): m/z (%) = 480 (1), 482 (1) $[M-HGaNP_2]^+$, 423 (1), 425 (1) $[M-HGaNP_2-CMe_3]^+$, 409 (21), 411 (14) $[M-HGaNP_2-CH_2CMe_3]^+$, 270 (86) $[alkyne]^+$.

Synthesis of $(Et_2Al)_2(\mu-H)[\mu-C\equiv C-2,4,6-(Me_3C)_3C_6H_2]$, **2c**

Et_2AlH (0.237 g, 2.76 mmol) was added at room temperature to a solution of $HC\equiv C-2,4,6-(Me_3C)_3C_6H_2$ (0.285 g, 1.06 mmol) in *n*-hexane (10 mL), and the reaction mixture was stirred for 12 h. The solvent was removed *in vacuo* to give a yellow oil which showed only the signals of **2c** and of the excess of Et_2AlH . – 1H NMR (400 MHz, C_6D_6 , 300 K): $\delta = 0.52$ (dq, 8H, $^3J_{H-H} = 3.4$ Hz, $^3J_{H-H} = 8.0$ Hz, CH_2), 1.21 (s, 9H, *p*- Me_3), 1.35 (t, 12H, $^3J_{H-H} = 8.0$ Hz, CH_2CH_3), 1.55 (s, 18H, *o*- Me_3), 3.35 (s, br., 1H, $AlHAl$), 7.43 (s, 2H, *m*-CH). – ^{13}C NMR (100 MHz, C_6D_6 , 300 K): $\delta = 3.0$ ($AlCH_2$), 9.7 (CH_2Me), 31.1 (*p*- Me_3), 31.6 (*o*- Me_3), 35.6 (*p*- Me_3), 37.4 (*o*- Me_3), 104.5 ($AlC\equiv C$), 115.2 (*ipso*-C), 121.7 (*m*-C), 140.5 ($AlC\equiv C$), 154.2 (*p*-C), 158.5 (*o*-C).

Synthesis of $(iBu_2Al)_2(\mu-H)[\mu-C\equiv C-2,4,6-(Me_3C)_3C_6H_2]$, **2d**

iBu_2AlH (0.292 g, 2.06 mmol) was added at room temperature to a solution of $HC\equiv C-2,4,6-(Me_3C)_3C_6H_2$ (0.278 g, 1.03 mmol) in difluorobenzene (2 mL), and the reaction mixture was stirred for 12 h. The solvent was removed *in vacuo* to give **2d** as an analytically pure colourless oil. – IR (CsI, paraffin): $\nu = 2031$ vs ν ($C\equiv C$); 1769 w, 1695 w, br. ν ($AlHAl$); 1599 s, 1537 w, 1508 w (phenyl); 1460 vs (paraffin); 1423 s, 1395 s δ (CH_3); 1375 s (paraffin); 1362 vs, 1319 s, 1267 m, 1248 m δ (CH_3); 1219 s, 1200 m, 1180 s, 1159 m, 1115 w, 1065 s, 1018 vs, 945 m, 910 w, 880 m, 820 s, 806 s, 775 s ν (CC); 731 m (paraffin); 665 s, br. (phenyl); 505 vw, 476 vw, 451 w, 426 w cm^{-1} δ (CC), ν (AlC). – 1H NMR (400 MHz, C_6D_6 , 300 K): $\delta = 0.66$ (dd, 4H, $^2J_{H-H} = 14.0$ Hz, $^3J_{H-H} = 7.2$ Hz, $AlCH_2$), 0.69 (dd, 4H, $^2J_{H-H} = 14.0$ Hz, $^3J_{H-H} = 6.8$ Hz, $AlCH_2$), 1.17 (d, 12H, $J_{H-H} = 6.5$ Hz, $CHMe_2$), 1.19 (d, 12H, $J_{H-H} = 6.5$ Hz, $CHMe_2$), 1.20 (s, 9H, *p*- Me_3), 1.60 (s, 18H, *o*- Me_3), 2.17 (m, 4H, $CHMe_2$), 3.69 (s, br., 1H, $AlHAl$), 7.44 (s, 2H, *m*-CH). – ^{13}C NMR (100 MHz, C_6D_6 , 300 K): $\delta = 22.0$ ($AlCH_2$), 26.8 ($CHMe_2$), 28.2 and 28.3 ($CHMe_2$),

31.1 (*p*-CMe₃), 31.5 (*o*-CMe₃), 35.6 (*p*-CMe₃), 37.3 (*o*-CMe₃), 103.7 AlC≡C, 114.8 (*ipso*-C), 121.7 (*m*-C), 143.4 (AlC≡C), 154.6 (*p*-C), 158.5 (*o*-C).

Synthesis of (Me₃C)₂Al(μ-H)[μ-C≡C-2,4,6-(Me₃C)₃C₆H₂]Al(CMe₃)[C≡C-2,4,6-(Me₃C)₃C₆H₂], **3**

A solution of (Me₃C)₂AlH (0.246 g, 1.73 mmol) in *n*-pentane (10 mL) was added at room temperature to a solution of HC≡C-2,4,6-(Me₃C)₃C₆H₂ (0.460 g, 1.70 mmol) in *n*-pentane (10 mL), and the reaction mixture was stirred for 3 d. The solvent was removed *in vacuo* and the residue recrystallised from 1,2-difluorobenzene at –20 °C to give colourless crystals of compound **3**. Yield: 0.55 g (85 %); impurity of the alkyne. – M. p. (under argon; sealed capillary): 78 °C (dec.). – IR (CsI, paraffin): ν = 2010 m ν (C≡C); 1771 w, 1601 m, 1537 vw ν (AlHAl), (phenyl); 1458 vs, 1375 vs (paraffin); 1302 m, 1269 w, 1248 w δ (CH₃); 1219 m, 1200 vw, 1169 w, 1153 w, 1115 w, 1032 vw, 1003 w, 932 m, 880 m, 847 vw, 810 m, 773 m ν (CC); 723 s (paraffin); 656 w (phenyl); 631 w, 592 m, 554 m, 517 w, 476 vw, 453 w cm^{–1} δ (CC), ν (AlC). – ¹H NMR (400 MHz, C₇D₈, 230 K): δ = 1.20 (s, 9H, *p*-CMe₃, bridge), 1.35 (s, 9H, *p*-CMe₃, terminal), 1.45 (s, 9H, CMe₃ (exchange), Al(CMe₃)₂), 1.47 (s, 9H, CMe₃ (no exchange), Al(CMe₃)₂), 1.50 (s, 9H, Al-CMe₃), 1.74 (s, 18H, *o*-CMe₃, bridge), 1.83 (s, 18H, *o*-CMe₃, terminal), 3.60 (s, br., 1H, ²J_{H–C} = 25.5 Hz, ³J_{H–C} = 7.6 Hz, AlHAl), 7.49 (s, 2H, *m*-H, bridge), 7.56 (s, 2H, *m*-H, terminal). – ¹³C NMR (100 MHz, C₇D₈, 230 K): δ = 17.9 (AlCMe₃), 18.6 (Al(CMe₃)₂, exchange), 19.7 (Al(CMe₃)₂, no exchange), 30.8 (*o*-CMe₃, terminal and *p*-CMe₃, bridge), 31.0 (AlCMe₃), 31.2 (Al(CMe₃)₂, exchange, and *o*-CMe₃, bridge), 31.3 (Al(CMe₃)₂, no exchange, and *p*-CMe₃, terminal), 35.2 (*p*-CMe₃, terminal), 35.5 (*p*-CMe₃, bridge), 37.1 (*o*-CMe₃, bridge), 37.2 (*o*-CMe₃, terminal), 101.8 (AlC≡C, bridge), 113.9 (*ipso*-C, bridge), 114.3 (AlC≡C, terminal), 115.6 (AlC≡C, terminal), 118.8 (*ipso*-C, terminal), 121.0 (*m*-C, terminal), 145.7 (AlC≡C, bridge), 149.5 (*p*-C, terminal), 153.4 (*o*-C, terminal), 154.1 (*p*-C, bridge), 157.5 (*o*-C, bridge).

Synthesis of [(Me₃Si)₂HC]₂Al-C≡C-2,4,6-*i*PrC₆H₂, **4**

A suspension of LiC≡C-2,4,6-*i*PrC₆H₂ (1.13 g, 4.83 mmol) in *n*-hexane (25 mL) was added during a period of one hour to a solution of ClAl[CH(SiMe₃)₂]₂ (1.84 g, 4.84 mmol) in *n*-hexane (50 mL) at –45 °C. The reaction mixture was stirred for another 10 min, the cooling bath was removed, and the mixture was allowed to warm to room temperature and filtered. The LiCl residue was washed with *n*-hexane (3 × 10 mL), the filtrates were collected and the solvent removed *in vacuo*. The residue was then recrystallised from *n*-hexane at –15 °C to yield colourless crystals of compound **4**. Yield: 0.55 g (20 %). – M. p.

(under argon; sealed capillary): 103 °C. – IR (CsI, paraffin): ν = 2108 vs, 2074 sh ν (C≡C); 1927 w, 1883 vw, 1856 w, 1765 w, 1730 vw, 1630 w, 1603 s, 1562 w, 1541 w (phenyl); 1443 vs, 1379 vs (paraffin); 1361 vs, 1316 s, 1248 vs δ (CH₃); 1209 m, 1175 s, 1107 s, 1072 w, 1055 w ν (CC); 1018 vs δ (CHSi₂); 920 s, 843 vs, 774 s, 752 s ρ (CH₃(Si)); 723 s (paraffin); 671 s, 656 m, 637 m, 611 w ν (SiC), phenyl: 569 m, 550 w, 519 m, 503 m, 461 w cm^{–1} δ (CC), ν (AlC). – ¹H NMR (400 MHz, C₆D₆): δ = –0.36 (s, 2H, CH), 0.34 (s, 36H, SiMe₃), 1.21 (d, 6H, ³J_{H–H} = 7.0 Hz, *p*-CHMe₂), 1.36 (d, 12H, ³J_{H–H} = 6.9 Hz, *o*-CHMe₂), 2.77 (sept, 1H, ³J_{H–H} = 7.0 Hz, *p*-CHMe₂, 1H), 3.98 (sept, 2H, ³J_{H–H} = 6.9 Hz, *o*-CHMe₂), 7.09 (s, 2H, *m*-H). – ¹³C NMR (100 MHz, C₆D₆): δ = 4.0 (SiMe₃), 12.0 (AlCH), 23.9 (*o*-CHMe₂), 24.1 (*p*-CHMe₂), 32.2 (*o*-CHMe₂), 35.0 (*p*-CHMe₂), 109.9 (AlC≡C), 110.6 (br., AlC≡C), 119.4 (*ipso*-C), 120.8 (*m*-C), 149.8 (*p*-C), 151.9 (*o*-C). – ²⁹Si NMR (79 MHz, C₆D₆): δ = –3.1 (SiMe₃). – MS (EI, 20 eV, 313 K): m/z (%) = 572 (17) [M]⁺, 557 (82) [M–Me]⁺, 413 (100) [M–CH(SiMe₃)₂]⁺.

Synthesis of Z-(Me₃C)₂Al-(Me₃Si)C=C(H)-2-*i*PrC₆H₄, **5a**

A suspension of Me₃Si–C≡C-2-*i*PrC₆H₄ (0.431 g, 1.99 mmol) in *n*-hexane (10 mL) was added to a solution of (Me₃C)₂Al–H (0.283 g, 1.99 mmol), and the mixture was stirred under reflux conditions for 3 d. The reaction mixture was concentrated and kept at room temperature to yield colourless crystals of compound **5a**. Yield: 0.299 g (42 %). – M. p. (under argon; sealed capillary): 58 °C (dec.). – IR (CsI, paraffin): ν = 1921 vw, 1695 vw, 1576 vs, 1560 vs, 1547 vs ν (C=C), phenyl; 1462 vs (paraffin); 1402 w δ (CH₃); 1377 s (paraffin); 1337 w, 1302 vw, 1244 w δ (CH₃); 1213 vw, 1184 w, 1078 m, 1036 m, 1007 w ν (CC); 934 w, 814 w, 764 vw ρ (CH₃(Si)); 721 s (paraffin); 592 w, 559 w, 509 vw, 469 w, 438 w cm^{–1} δ (CC), ν (AlC). – ¹H NMR (400 MHz, C₆D₆, 300 K): δ = 0.05 (s, 9H, SiMe₃), 1.19 (s, 18H, CMe₃), 1.21 (d, 6H, ³J_{H–H} = 6.9 Hz, CHMe₂), 3.29 (sept, 1H, ³J_{H–H} = 6.9 Hz, CHMe₂), 7.05 (m, 1H, *m*-H(5)), 7.16 (m, 2H, *m*-H(3) and *p*-H), 7.23 (d, 1H, ³J_{H–H} = 7.4 Hz, *o*-H), 7.93 (s, 1H, ³J_{H–Si} = 20.5 Hz, C=CH). – ¹³C NMR (100 MHz, C₆D₆, 300 K): δ = 1.7 (SiMe₃), 23.3 (CHMe₂), 29.8 (CMe₃), 30.1 (CHMe₂), 30.2 (CMe₃), 124.8 (*m*-C(3)), 125.6 (*m*-C(5)), 128.3 (*p*-C), 129.1 (*o*-C(6)), 142.5 (*ipso*-C), 145.7 (*o*-C(2)), 154.9 (C=CH), 159.0 (br, AlC=CH). ²⁹Si NMR (75 MHz, C₆D₆, 300 K): δ = –12.5 (SiMe₃).

Synthesis of E-(Me₃C)₂Ga-(Me₃Si)C=C(H)-2-*i*PrC₆H₄, **5b**

A suspension of Me₃Si–C≡C-2-*i*PrC₆H₄ (0.750 g, 3.47 mmol) in *n*-hexane (10 mL) was added to a solution of (Me₃C)₂Ga–H (0.320 g, 1.73 mmol), and the mixture was stirred under reflux conditions for 3 d. The reaction mixture was concentrated and stored at –45 °C to yield

Table 4. Crystal data and structure refinement of compounds **1a–1h**.

	1a	1b-(C ₆ H ₄ F ₂) _{2/3} 1c	1d	1e-(hexane) _{0.5}	1f-(C ₆ H ₄ F ₂)	1g	1h-(C ₆ H ₄ F ₂)	
<i>Crystal data</i>								
Empirical formula	C ₂₄ H ₃₀ Al ₂	C ₄₀ H ₅₄ Al ₂ F _{1.33}	C ₃₈ H ₅₈ Al ₂	C ₃₈ H ₅₈ Ga ₂	C ₅₃ H ₈₉ Al ₂	C ₅₄ H ₈₂ Al ₂ F ₂	C ₅₆ H ₉₄ Al ₂	C ₅₄ H ₈₂ F ₂ Ga ₂
<i>M_r</i>	372.44	614.13	568.80	654.28	780.20	823.16	821.27	908.64
Crystal system	monoclinic	hexagonal	triclinic	triclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>R</i> 3̄	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> , pm	1043.8(2)	3282.72(2)	878.26(2)	878.11(6)	1819.57(2)	992.72(2)	2740.92(7)	990.53(2)
<i>b</i> , pm	1285.7(3)	3282.72(2)	1016.98(3)	1017.64(7)	1460.09(2)	1964.46(3)	993.20(3)	1962.87(4)
<i>c</i> , pm	920.2(2)	904.81(1)	1123.42(3)	1123.50(7)	1955.96(3)	2631.86(4)	2122.13(5)	2631.09(5)
α , deg	90	90	77.685(2)	77.892(1)	90	90	90	90
β , deg	111.20(3)	90	73.875(2)	74.149(1)	95.133(1)	90	102.977(2)	90
γ , deg	90	120	71.098(2)	70.727(1)	90	90	90	90
<i>V</i> , × 10 ^{−30} m ³	1.1514(4)	8.4441(1)	0.90352(4)	0.9037(1)	5.1756(1)	5.1326(2)	5.6295(3)	5.1156(2)
$\rho_{\text{calcd.}}$, g cm ^{−3}	1.07	1.09	1.05	1.20	1.00	1.07	0.97	1.18
<i>z</i>	2	9	1	1	4	4	4	4
<i>F</i> (000), e	400	2988	312	348	1732	1800	1824	1944
μ , mm ^{−1}	0.1 (Mo <i>K</i> α)	0.9 (Cu <i>K</i> α)	0.9 (Cu <i>K</i> α)	1.5 (Mo <i>K</i> α)	0.7 (Cu <i>K</i> α)	0.8 (Cu <i>K</i> α)	0.7 (Cu <i>K</i> α)	1.1 (Mo <i>K</i> α)
<i>Data collection</i>								
<i>T</i> , K	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)
Unique reflections	2738	3653	2789	4358	8893	9682	5214	14943
Reflections <i>I</i> > 2 σ (<i>I</i>)	1884	3080	2370	3997	7471	9242	3849	13515
<i>Refinement</i>								
Refined parameters	122	256	220	189	546	596	306	624
Final <i>R</i> 1 ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0337	0.0532	0.0442	0.0255	0.0496	0.0476	0.0589	0.0330
Final <i>wR</i> 2 ^b (all data)	0.0835	0.1607	0.1219	0.0682	0.1475	0.1368	0.1687	0.0847
Flack (<i>x</i>) ^c	—	—	—	—	—	0.00(3)	—	0.006(6)
$\Delta\rho_{\text{fin}}$ (max / min), e Å ^{−3}	0.199 / −0.155	0.787 / −0.355	0.334 / −0.186	0.570 / −0.392	0.546 / −0.364	0.701 / −0.387	0.327 / −0.241	0.413 / −0.509

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

colourless crystals of compound **5b**. Yield: 0.434 g (62%). – M. p. (under argon; sealed capillary): 72 °C (dec.). – IR (CsI, paraffin): $\nu = 1948$ vw, 1921 vw, 1840 vw, 1697 vw, 1578 vs, 1555 vs $\nu(\text{C}=\text{C})$; 1466 vs (paraffin); 1402 vs $\delta(\text{CH}_3)$; 1377 s (paraffin), 1335 w, 1300 w, 1242 m $\delta(\text{CH}_3)$; 1215 w, 1173 m, 1109 w, 1078 s, 1034 m, 1009 w $\nu(\text{CC})$; 972 vw, 949 w, 885 vw, 847 w, 814 m, 766 w $\rho(\text{CH}_3(\text{Si}))$; 723 vs (paraffin); 683 m, 644 m $\nu(\text{SiC})$; 594 m, 556 m, 517 w, 498 w, 467 m, 428 m cm^{−1} $\delta(\text{CC})$, $\nu(\text{GaC})$. – ¹H NMR (400 MHz, C₆D₆, 300 K): $\delta = 0.03$ (s, 9H, SiMe₃), 1.23 (d, 6H, ³*J*_{H–H} = 6.9 Hz, CHMe₂), 1.26 (s, 18H, *t*Bu), 3.32 (sept, 1H, ³*J*_{H–H} = 6.9 Hz, CHMe₂), 7.06 (m, 1H, *m*-H(5)), 7.16 (s, 1H, *p*-H), 7.17 (s, 1H, *m*-H(3)), 7.26 (d, 1H, ³*J*_{H–H} = 7.4 Hz, *o*-H), 7.63 (s, 1H, ³*J*_{H–Si} = 19.5 Hz, C=CH). – ¹³C NMR (100 MHz, C₆D₆, 300 K): $\delta = 1.6$ (SiMe₃), 23.3 (CHMe₂), 29.6 (CMe₃), 30.1 (CMe₃ and CHMe₂), 124.7 (*m*-C(3)), 125.6 (*m*-C(5)), 128.2 (*p*-C), 129.4 (*o*-C(6)), 142.0 (*ipso*-C), 145.9 (*o*-C(2)), 151.1 (AlC=CH), 162.9 (br, AlC=CH). – ²⁹Si NMR (75 MHz, C₆D₆, 300 K): $\delta = -12.2$ (SiMe₃). – MS (EI, 20 eV, 298 K): $m/z(\%) = 344$ (100), 346 (74) [M–butene]⁺.

Synthesis of MeAl[E-(Me₃Si)C≡C(H)-2,6-Me₂C₆H₃]₂, **6**

A solution of Me₃Si–C≡C–2,6-Me₂C₆H₃ (0.870 g, 4.30 mmol) in *n*-hexane (10 mL) was added to a solution of Me₂AlH (0.249 g, 4.29 mmol), and the mixture was stirred

under reflux conditions for 3 d. The reaction mixture was concentrated and recrystallised from cyclopentane at −20 °C to yield colourless crystals of compound **6**. Yield: 0.814 g (42%). – IR (CsI, paraffin): $\nu = 1930$ vw, 1859 vw, 1786 vw, 1699 vw, 1580 s, 1557 s $\nu(\text{C}=\text{C})$; 1462 vs (paraffin); 1402 s $\delta(\text{CH}_3)$; 1377 s (paraffin); 1341 m, 1304 m, 1244 m $\delta(\text{CH}_3)$; 1188 m, 1167 m, 1155 m, 1090 m, 1045 m $\nu(\text{CC})$; 922 vw, 847 w, 827 w, 818 w, 766 w $\rho(\text{CH}_3(\text{Si}))$; 721 s (paraffin); 592 w, 561 w, 511 vw, 473 m, 449 w cm^{−1} $\delta(\text{CC})$, $\nu(\text{AlC})$. – ¹H NMR (400 MHz, C₆D₆, 300 K): $\delta = -0.33$ (s, 3H, AlMe), 0.03 (s, 18H, SiMe₃), 2.17 (s, 12H, ArMe), 6.92 (d, 4H, ³*J*_{H–H} = 7.5 Hz, *m*-H), 6.99 (m, 2H, *p*-H), 7.48 (s, 2H, ³*J*_{H–Si} = 12.5 Hz, C=CH). – ¹³C NMR (100 MHz, C₆D₆, 300 K): $\delta = -3.8$ (br, AlMe), 0.3 (SiMe₃), 20.9 (ArMe), 127.4 (*p*-C), 128.5 (*m*-C), 135.0 (*o*-C), 144.0 (*ipso*-C), 155.6 (AlC=CH), 160.5 (br, AlC=CH). – ²⁹Si NMR (75 MHz, C₆D₆, 300 K): $\delta = -5.8$ (SiMe₃). – MS (EI, 20 eV, 353 K): $m/z(\%) = 448$ (2) [M]⁺, 433 (4) [M–Me]⁺, 245 (100) [MeAlC(SiMe₃)=CHAr]⁺.

X-Ray crystallography

Crystals suitable for X-ray crystallography were obtained by recrystallisation from cyclopentane (**6**), *n*-hexane (**1a**, **1c**, **1d**, **1e**, **2b**, **4**, **5a**, **5b**), 1,2-difluorobenzene (**1b**, **1f**, **1h**, **3**) or pentafluorobenzene (**1g**, **2a**). Intensity data was collected on a Bruker APEX II diffractometer or a Stoe IPDS II (**6**)

Table 5. Crystal data and structure refinement of compounds **2a–6**.

	2a	2b	3·(C ₆ H ₄ F ₂) _{1/2} 4		5a	5b	6	^a
<i>Crystal data</i>								
Empirical formula	C ₄₀ H ₇₄ Al ₂	C ₄₀ H ₇₄ Ga ₂	C ₃₅ H ₈₈ Al ₂ F	C ₃₁ H ₆₁ AlSi ₄	C ₂₂ H ₃₉ AlSi	C ₂₂ H ₃₉ GaSi	C ₂₇ H ₄₁ AlSi ₂	C ₂₉ H ₄₅ AlSi ₂
<i>M_r</i>	608.95	694.43	822.21	573.14	358.60	401.34	448.76	476.81
Crystal system	orthorhombic	orthorhombic	triclinic	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , pm	1063.44(4)	1061.28(1)	1414.66(3)	949.05(5)	908.99(1)	908.72(1)	875.99(4)	1357.7(3)
<i>b</i> , pm	1906.63(7)	1903.28(2)	1487.05(3)	1073.89(5)	960.31(2)	961.08(1)	1020.04(5)	1450.5(3)
<i>c</i> , pm	2103.45(7)	2103.74(3)	1514.87(3)	1838.5(1)	1562.67(2)	1567.74(2)	1705.52(8)	1640.9(3)
α , deg	90	90	61.742(1)	90	75.6000(8)	90.095(1)	86.351(4)	102.06(3)
β , deg	90	90	84.845(1)	92.835(4)	73.2219(8)	106.796(1)	75.213(4)	98.03(3)
γ , deg	90	90	74.557(1)	90	65.0612(9)	115.168(1)	71.753(3)	95.41(3)
<i>V</i> , × 10 ^{−30} m ³	4.2649(3)	4.24937(9)	2.7032(1)	1.8715(2)	1.17150(3)	1.17402(2)	1.3992(1)	3.104(1)
$\rho_{\text{calcd.}}$, g cm ^{−3}	0.95	1.09	1.01	1.02	1.02	1.14	1.07	1.02
<i>z</i>	4	4	2	2	2	2	2	4
<i>F</i> (000), e	1360	1504	906	632	396	432	488	1040
μ , mm ^{−1}	0.8 (Cu <i>K</i> α)	1.7 (Cu <i>K</i> α)	0.7 (Cu <i>K</i> α)	0.2 (Mo <i>K</i> α)	1.2 (Cu <i>K</i> α)	2.1 (Cu <i>K</i> α)	0.2 (Mo <i>K</i> α)	0.2 (Mo <i>K</i> α)
<i>Data collection</i>								
<i>T</i> , K	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)
Unique reflections	7776	7950	8570	8268	3716	3657	6703	14186
Reflections <i>I</i> > 2 σ (<i>I</i>)	6910	7688	6493	7981	3555	3465	4771	8187
<i>Refinement</i>								
Refined parameters	404	404	656	343	254	259	282	594
Final <i>R</i> 1 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0443	0.0258	0.0719	0.0395	0.0517	0.0405	0.0387	0.0559
Final <i>wR</i> 2 ^c (all data)	0.1190	0.0671	0.2134	0.1117	0.1373	0.1061	0.0950	0.1430
Flack (<i>x</i>) ^d	−0.01(3)	−0.02(1)	—	0.01(8)	—	—	—	—
$\Delta\rho_{\text{fin}}$ (max / min), e Å ^{−3}	0.299 / −0.154	0.346 / −0.265	0.980 / −0.348	0.254 / −0.464	0.459 / −0.377	0.877 / −0.398	0.315 / −0.382	0.454 / −0.609

^a Only a few crystals of MeAl[E-(Me₃Si)C=C(H)-2-*i*PrC₆H₄]₂ were isolated from a reaction analogous to that which produced compound **6** after recrystallisation from *n*-hexane; ^b $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^c $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$; ^d absolute structure parameter.

with monochromatised Mo *K* α [**1a**, **1d**, **1h**·(C₆H₄F₂), **4**, **6**] or Cu *K* α [**1b**·(C₆H₄F₂)_{2/3}, **1c**, **1e**, **1f**·(C₆H₄F₂), **1g**, **2a**, **2b**, **3**·(C₆H₄F₂)_{1/2}, **5a**, **5b**] radiation. The collection method involved ω scans. Data reduction was carried out using the program SAINT+ [48]. The crystal structures were solved by Direct Methods using SHELXTL [49, 50]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculations based on *F*² using SHELXTL [49, 51]. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms, except the bridging hydrogen atoms in compounds **2** and **3** which were refined isotropically. The co-crystallised 1,2-difluorobenzene molecules were disordered in all structures and refined in split positions (**1b**, **1f**, **1h**). In the case of **3** the solvent molecule was only refined isotropically. *tert*-Butyl groups were disordered and refined in split positions for compounds **1b** (0.48 : 0.52), **1c** (0.84 : 0.16),

1e (0.55 : 0.45), **1f** (0.275 : 0.525 : 0.200), **1g** (0.63 : 0.37), **1h** (0.48 : 0.15 : 0.37), **3** (0.74 : 0.26, 0.46 : 0.54, 0.60 : 0.40), **5a** (0.62 : 0.38) and **5b** (0.55 : 0.45). Further crystallographic data is summarised in Tables 4 and 5.

CCDC 926663 (**1a**), 926664 (**1b**·(C₆H₄F₂)_{2/3}), 926665 (**1c**), 926666 (**1d**), 926667 (**1e**(hexane)_{1/2}), 926668 (**1f**), 926669 (**1g**), 926670 (**1h**·(C₆H₄F₂)), 926671 (**2a**), 926672 (**2b**), 926673 (**3**·(C₆H₄F₂)_{1/2}), 926674 (**4**), 926675 (**5a**), 926676 (**5b**), 926677 (**6**), and 926678 (MeAl[E-(Me₃Si)C=C(H)-2-*i*PrC₆H₄]₂) 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.

Acknowledgement

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

- [1] G. Zweifel, J. A. Miller, *Org. React.* **1984**, 32, 375.
- [2] E. Winterfeld, *Synthesis* **1975**, 10, 675.
- [3] J. Marek, J.-F. Normani, *Chem. Rev.* **1996**, 96, 3341.
- [4] J. J. Eisch, in *Comprehensive Organic Synthesis*, Vol. 8, (Eds.: B. Frost, I. Fleming), Pergamon, Oxford, **1991**, pp. 733.

- [5] G. Zweifel, in *Aspects of Mechanism and Organometallic Chemistry*, (Ed.: J. H. Brewster), Plenum Press, New York, **1978**, pp. 229.
- [6] G. Zweifel in *Comprehensive Organic Chemistry*, (Eds.: D. H. R. Barton, W. D. Ollis), Pergamon, Oxford, **1999**, pp. 1013.

- [7] E. Negishi, *Organometallics in Organic Synthesis*, Wiley, New York, **1980**.
- [8] S. Saito in *Main Group Metals in Organic Synthesis*, (Eds.: H. Yamamoto, K. Oshima), Wiley-VCH, Weinheim, **2004**, pp. 189.
- [9] J. A. Miller in *Chemistry of Aluminium, Gallium, Indium and Thallium*, (Ed.: A. J. Downs), Blackie Academic, London, **1993**, pp. 372.
- [10] W. Uhl, *Coord. Chem. Rev.* **2008**, *252*, 1540.
- [11] W. Uhl, F. Breher, *Angew. Chem. Int. Ed.* **1999**, *38*, 1477.
- [12] W. Uhl, F. Breher, A. Lützen, W. Saak, *Angew. Chem. Int. Ed.* **2000**, *39*, 406.
- [13] W. Uhl, F. Breher, J. Grunenberg, A. Lützen, W. Saak, *Organometallics* **2000**, *19*, 4536.
- [14] W. Uhl, F. Breher, A. Mbonimana, J. Gauss, D. Haase, A. Lützen, W. Saak, *Eur. J. Inorg. Chem.* **2001**, 3059.
- [15] W. Uhl, L. Cuypers, B. Neumüller, F. Weller, *Organometallics* **2002**, *21*, 2365.
- [16] W. Uhl, H. R. Bock, M. Claesener, M. Layh, I. Tiesmeyer, E.-U. Würthwein, *Chem. Eur. J.* **2008**, *14*, 11557.
- [17] W. Uhl, F. Breher, S. Haddadpour, R. Koch, M. Matar, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1839.
- [18] W. Uhl, E. Er, O. Hübner, H.-J. Himmel, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2133.
- [19] W. Uhl, E. Er, M. Matar, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1011.
- [20] W. Uhl, E. Er, A. Hepp, J. Kösters, M. Layh, M. Rohling, A. Vinogradov, E.-U. Würthwein, N. Ghavtadze, *Eur. J. Inorg. Chem.* **2009**, 3307.
- [21] J. Chmiel, B. Neumann, H.-G. Stammer, N. W. Mitzel, *Chem. Eur. J.* **2010**, *16*, 11906.
- [22] W. Uhl, E. Er, A. Hepp, J. Kösters, J. Grunenberg, *Organometallics* **2008**, *27*, 3346.
- [23] R. A. Nyquist, S. Fiedler, *Vib. Spectrosc.* **1994**, *4*, 149.
- [24] E. Kleinpeter, A. Frank, *Tetrahedron* **2009**, *65*, 4418.
- [25] E. Kleinpeter, A. Frank, *J. Phys. Chem. A* **2009**, *113*, 6774.
- [26] D. Mootz, A. Deeg, *J. Am. Chem. Soc.* **1992**, *114*, 5887.
- [27] E. Pignataro, B. Post, *Acta Crystallogr.* **1955**, *8*, 672.
- [28] R. K. McMullan, Å. Kvik, P. Popelier, *Acta Crystallogr.* **1992**, *B48*, 726.
- [29] B. Teclé, W. H. Ilsley, J. P. Oliver, *Inorg. Chem.* **1981**, *20*, 2335.
- [30] G. Erker, M. Albrecht, C. Krüger, M. Nolte, S. Werner, *Organometallics* **1993**, *12*, 4979.
- [31] W. Uhl, D. Heller, M. Rohling, J. Kösters, *Inorg. Chim. Acta* **2011**, *374*, 359.
- [32] W. Uhl, M. Claesener, S. Haddadpour, B. Jasper, I. Tiesmeyer, S. Zemke, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2889.
- [33] Z. Zhu, X. Wang, M. M. Olmstead, P. P. Power, *Angew. Chem. Int. Ed.* **2009**, *48*, 2027.
- [34] W. Uhl, *Z. Naturforsch.* **1988**, *43b*, 1113.
- [35] H. Lehmkuhl, K. Ziegler, *Methoden der organischen Chemie (Houben Weyl)*, 4th edition, 1952 Vd. XIII/4, p. 58; Thieme Verlag, Stuttgart, **1970**.
- [36] W. Uhl, L. Cuypers, R. Gaupner, J. Molter, A. Vester, B. Neumüller, *Z. Anorg. Allg. Chem.* **2001**, *627*, 607.
- [37] O. T. Beachley Jr., L. Victoriano, *Organometallics* **1988**, *7*, 63.
- [38] M. Tobisu, H. Nakai, N. Chatani, *J. Org. Chem.* **2009**, *74*, 5471.
- [39] T. Saiki, S. Akine, K. Goto, N. Tokitho, T. Kawashima, R. Okazaki, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1893.
- [40] S. Doherty, J. G. Knight, J. P. McGrady, A. M. Ferguson, N. A. B. Ward, R. W. Harrington, W. Clegg, *Adv. Synth. Catal.* **2010**, *352*, 201.
- [41] E. Negishi, A. O. King, W. L. Klima, *J. Org. Chem.* **1980**, *45*, 2526.
- [42] H. E. Zimmermann, J. R. Dodd, *J. Am. Chem. Soc.* **1970**, *92*, 6507.
- [43] D. E. Pearson, M. G. Frazer, V. S. Frazer, L. C. Washburn, *Synthesis* **1976**, 621.
- [44] W. Uhl, L. Cuypers, G. Geiseler, K. Harms, W. Massa, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1001.
- [45] J. J. Eisch, *J. Am. Chem. Soc.* **1962**, *84*, 3830.
- [46] M. Hülsmann, Dissertation, Universität Bielefeld, Bielefeld **2012**.
- [47] R. A. Kovar, H. Derr, D. Brandau, J. O. Callaway, *Inorg. Chem.* **1975**, *14*, 2809.
- [48] SAINT+ (version 6.02; includes XPREP and SADABS), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **1999**; G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **1996**.
- [49] SHELXTL-Plus (release 4.1); Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **1990**.
- [50] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467.
- [51] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.