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Treatment of Terminal Alkynes R–C≡C–H with Dialkylaluminum Hydrides: Hydroalumination versus Deprotonation

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Dialkylaluminum hydrides $R_2Al–H$ (R = Me, Et, *i*Bu, CH_2tBu, *t*Bu), reacted with *tert*-butylethyne, $H–C≡C–CMe_3$, by hydroalumination and formation of the corresponding vinylic compounds, $R_2Al–C(H)=C(H)–CMe_3$. The products are dimeric in the solid state with the negatively charged vinylic carbon atoms in the bridging positions and adopt usually a centrosymmetric structure with the C=C double bonds on different sides of the central Al_2C_2 heterocycle. Only with R = Me the C_{2v} structure with the *cis* arrangement of the alkenyl groups was found. Complicated mixtures of isomeric substances were detected in solution. Quantum-chemical calculations revealed a considerable charge separation in the C=C double bonds of the dimeric formula units. The α-carbon atoms coordinated by both aluminum atoms show high negative NBO charges of about –1.0, while the β-carbon atoms are almost uncharged (0.0 to –0.1). The rotational barriers decreased upon dimerization. Hence, the formation of such dimers may be the key step in the well-known *cis*/*trans* isomerization process of hydroalumination and hydrogallation products.

Introduction

Hydroalumination and hydrogallation reactions with alkynes constitute effective methods for the generation of singular organometallic compounds, because in many cases condensation reactions with the release of the corresponding trialkylelement derivatives follow the simple addition processes. Carbaalanes possessing clusters of aluminum and carbon atoms were formed by the treatment of (dialkyl)alkynylaluminum compounds with dialkylaluminum hydrides.[1] Heteroadamantane type molecules resulted from the similar reactions with gallium compounds.[2] Cyclophanes with two or three coordinatively unsaturated aluminum or gallium atoms in the bridging positions were obtained with bis- or tris(*tert*-butylethynyl)benzenes.[3] While from these reactions the simple addition products were isolated only in very rare cases,[3] stable alkenyl-dialkylelement compounds were usually obtained with trimethylsilylethynyl benzenes.[4–6] Depending on steric shielding, these products show spontaneous *cis*/*trans* isomerization, which may be initiated by intermolecular activation.[4–7] The *cis* isomers (Scheme 1) with the aluminum or gallium atoms and the hydrogen atoms on the same side of the C=C double bonds represent the expected initial products by the reasonable assumption of a concerted reaction mechanism. But as shown in Scheme 1, only the *trans* isomers of oligonuclear derivatives may be suitable to act as chelating Lewis acids. Hence, a concise understanding of the rearrangement process is important for a potential application of these compounds. In one case a reversible *trans*/*cis* isomerization was observed, which verifies the small energetic difference between both isomers.[5,6] These reactions are highly regioselective. The metal atoms of the hydrides attack exclusively the alkyne carbon atoms in the α-position on the benzene ring of (*tert*-butylethynyl)benzenes, while the carbon atoms bearing the trimethylsilyl group are attacked by the analogous [2-(trimethylsilyl)ethynyl]benzenes. Butadiynes gave the simple addition products or singular persistent carbocationic species by C–H bond activation.[4b,8]

The reactions of terminal alkynes, H–C≡C–R, proved to be more complicated and resulted in the formation of two fundamentally different types of products. The sterically highly shielded hydride $H–Al[CH(SiMe_3)_2]_2$ gave exclusively hydroalumination (Scheme 2),[7] while hydrogen release with the formation of dimeric alkynylaluminum compounds occurred upon treatment of the relatively acidic phenylethyne with smaller dialkylaluminum hydrides (Scheme 2).[9] These alkynyl derivatives adopted dimeric structures in the solid state with two different structural motifs. One had linear Al–C≡C groups, which showed a side-on interaction with a second aluminum atom via a π-orbital localized at the α-carbon atom. The second type had both C≡C triple

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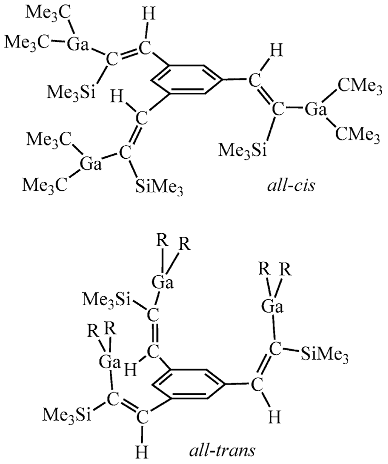
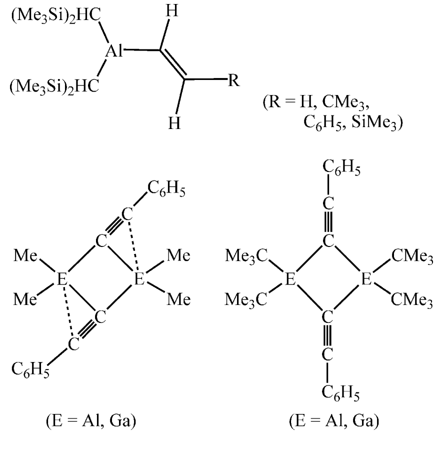


Scheme 1.

bonds perpendicular to the transannular Al···Al axis of the dimers and may be described by two 3c–2e Al–C–Al bonds. Dialkylgallium hydrides gave similar alkynyl compounds also with other, less acidic alkynes.[2,9] In contrast, diisobutylaluminum hydride was reported many years ago to give hydroalumination upon treatment with different aliphatic alkynes.[10] However, the characterization of the products was rather limited. A dimeric formula unit with the terminal vinylic carbon atoms in the bridging positions was verified by a single-crystal X-ray structure determination.[11] We conducted systematic experimental investigations and quantum-chemical calculations with respect to the formation and properties of these dimeric formula units, because they may influence the rotational barrier about the C=C double bonds and may reflect a key step in the above-mentioned, well-known phenomenon of *cis*/*trans* isomerization in the course of hydroalumination and hydrogallation processes. These ideas may help in the development of a concise strategy for the specific generation and a broader application of the *trans* compounds.



Scheme 2.

Results and Discussion

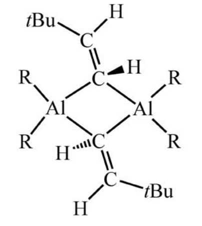
Reactions of Dialkylaluminum Hydrides with *tert*-Butylethyne

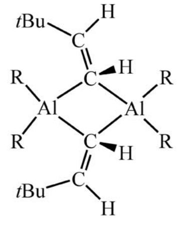
As mentioned before, the dialkylaluminum hydride H–Al[CH(SiMe$_3$)$_2$]$_2$,[7,12] which is highly shielded by two very bulky bis(trimethylsilyl)methyl groups, reacted with various terminal alkynes H–C≡C–R (R = H, C$_6$H$_5$, CMe$_3$, SiMe$_3$) exclusively by hydroalumination and formation of the corresponding vinylic aluminum compounds in high yields.[7] This specific reactivity pattern may depend on monomerization in solution, which is singular amongst the dialkylaluminum hydrides and was established by molar mass determination. In contrast, gas evolution was observed when phenylethyne, H–C≡C–C$_6$H$_5$, was treated with less shielded di(*tert*-butyl)- and dimethylaluminum hydrides.[9] By hydrogen elimination dialkyl-alkynylaluminum compounds were formed in very selective reactions without any detectable by-product. In contrast, gas evolution did not occur when the less acidic *tert*-butylethyne was allowed to react with various dialkylaluminum hydrides [products **1** to **5**, R = Me to *t*Bu; Equation (1)]. A similar reaction of diisobutylaluminum hydride was reported several decades ago.[11] However, experimental details are missing, and the spectroscopic characterization of the product was incomplete. The reactions of hydrides bearing ethyl, isobutyl, and neopentyl groups gave the clearest results. The colorless crystalline compounds **2**–**4** showing the expected simple NMR spectra at room temperature were isolated. Most indicative of a successful hydroalumination was the occurrence of two resonances of vinylic hydrogen atoms, which had chemical shifts of about δ = 6.0 (α-hydrogen atoms, Al$_2$CH) and 7.5 ppm (β-hydrogen atoms) and exhibited coupling constants of 20.8 Hz characteristic of their *trans* arrangement.

The reaction of di(*tert*-butyl)aluminum hydride with *tert*-butylethyne gave colorless crystals of product **5** in 64% yield. Its constitution as a dimeric alkenyl-dialkylaluminum compound analogous to **2**–**4** was clarified by crystal structure determination (see below). But its solutions gave very complicated NMR spectra. We found at least three different species (**5a**–**5c**) for which NMR resonances could be assigned and which had the correct integration ratio of two *tert*-butyl groups attached to aluminum and one alkenyl substituent. The isomers were formed in a ratio of about 0.5:1:0.25 (**5a**/**5b**/**5c**). In accordance with a dynamic behavior, the resonances of the minor component disappeared upon heating of a sample in toluene to 350 K and reappeared upon cooling it to room temperature. The relative intensities of the resonances of **5a** and **5b** remained almost unchanged at elevated temperature. The NMR spectroscopic properties of **5a** deviated considerably from those of the remaining two species. The α-hydrogen atom of the alkenyl group close to aluminum has a chemical shift (δ = 5.93 ppm) similar to that for compounds **2**–**4**, but the hydrogen atom of the β-C–H group attached to *tert*-butyl showed a doublet in the ^{1}H NMR spectrum at δ = 6.20 ppm compared to δ = 8.00 ppm on average for the other isomers

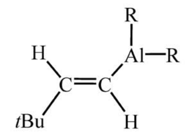
$$x\ \mathrm{H{-}C{\equiv}C{-}}t\mathrm{Bu} + x\ \mathrm{H{-}AlR_2} \xrightarrow[-x\ \mathrm{H_2}]{} [\mathrm{R_2Al{-}C(H){=}C(H){-}}t\mathrm{Bu}]_x \qquad (1)$$

$x = 1, 2$
R = Me: **1**; R = Et: **2**; R = *i*Bu: **3**;
R = CH_2tBu: **4**; R = *t*Bu: **5**

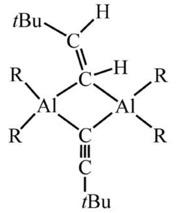




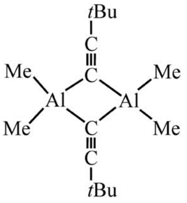
trans: **1a**, **2**, **3a**, **4a**, **5c** (?) *cis*: **1b**, **4b**(?), **5b** (?)



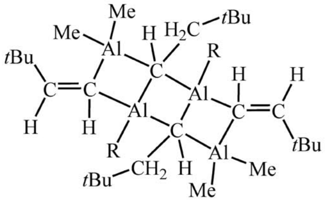
momomeric: **4c** (?), **5a**



1c, **4d**, **5d**



1d



1e

or δ = 7.5 ppm for **2** to **4**. All H–H coupling constants across the C=C double bonds are above 20 Hz, clearly indicating a *trans* configuration. The β-carbon atoms of the C=C double bonds [Al_2–C=*C*] of **5a** give rise to a signal at δ = 161 ppm. This chemical shift is in accordance with values detected for the monomeric vinylic compounds R_2Al–C(H)=C(H)–R [R = $CH(SiMe_3)_2$].[7] The remaining isomers **5b** and **5c** show the resonances of these atoms at about δ = 197 ppm, which is similar to the dimeric compounds **2** to **4**. Interestingly, molar mass determination of compound **5** by cryoscopy in benzene revealed a value between the monomeric and dimeric formula units (calcd. 448 g/mol for the dimer, 224 g/mol for the monomer; found: 333 g/mol) and verifies partial dissociation upon dissolution. We believe that compound **5a** represents the monomeric form possessing a tricoordinate, coordinatively unsaturated aluminum atom [see schematic drawings in Equation (1)], while **5b**, **5c** exist as dimers. Hence, the molecular structures of vinylic aluminum compounds in solution can clearly be assigned on the basis of the characteristic NMR shifts of the β-carbon and hydrogen atoms of the ethenyl moieties. The ^{13}C NMR resonances of main-group vinylic compounds cover a broad range of chemical shifts between δ = 120 and 210 ppm[13] and do not seem to correlate significantly to particular structural motifs. Compound **5b** shows four different *tert*-butyl groups attached to aluminum. But only one resonance was detected for the vinylic *tert*-butyl groups. In accordance with the results of the crystal structure determination, which gave a centrosymmetric dimer (*trans* arrangement of the alkenyl groups), only one resonance of Al–CMe_3 groups was observed for the remaining isomer **5c**. These results may be interpreted in terms of *cis* and *trans* isomers. But there is an inconsistency in the assignment of the NMR spectroscopic data of **5b**, because only two resonances of chemically different *tert*-butyl groups are to be expected for a *cis* arrangement of the alkenyl groups. In the raw product, a further component, $[t\mathrm{Bu_2Al}]_2(\mu\text{-CH=CH-}t\mathrm{Bu})(\mu\text{-C}{\equiv}\text{C-}t\mathrm{Bu})$ (**5d**) [schematic representation in Equation (1)], was identified by its characteristic NMR spectroscopic data (see Exp. Section). It has a bridging alkenyl group beside an alkynyl group and reflects the competitive reaction pathways of terminal alkynes. It is an interesting scope for future investigations to find suitable conditions for its synthesis in a preparative scale. A similar compound, **4d**, was detected in the raw product of the respective reaction with dineopentylaluminum hydride. The occurrence of *cis*/*trans* isomers was observed only upon cooling of solutions of the diisobutyl derivative **3** (see Experimental Section). In contrast, temperature-dependent ^{1}H NMR spectra of **4** (R = neopentyl) did not allow an easy interpretation. The doublet of the α-vinylic hydrogen atoms $Al_2C(H)$=C (δ = 6.18 ppm) remained unchanged upon cooling to 190 K. The second doublet of the alkenyl group, Al_2C=C(*H*) (δ = 7.44 ppm), showed coalescence at about 210 K. However, further cooling to 190 K gave only one doublet at the same position. Hence, the exchange between the *cis* and *trans* isomers (**4a**, **4b**) may be slow at this low temperature, but the chemical shifts of the vinylic hydrogen atoms of the different isomers may be too similar to be clearly resolved. A splitting resulted for the methylene protons of the neopentyl groups at 190 K, which became diastereotopic and gave two doublets at δ = 0.87 and 0.58 ppm ($J_{H,H}$ = 13 Hz). This may be caused by hindered rotation about the Al–C bonds.

Dimethylaluminum hydride reacted with *tert*-butylethyne to give a complicated reaction mixture. At room temperature the ^{1}H NMR spectrum showed the resonances of one main component, compound **1**, besides at least three further products. They were identified by their characteristic NMR parameters as the mixed alkynyl-alkenyl compound **1c** [Equation (1), similar to **5d**], the dialkyne $[\mathrm{Me_2Al{-}C{\equiv}C{-}CMe_3}]_2$ (**1d**)[9h,14] and the tetranuclear compound **1e**. Furthermore, **1e** is the product of partial double hydroalumination of an alkyne, which so far was only observed for alkynylaluminum and -gallium compounds under relatively drastic reaction conditions[1,2] or with the chlorogallium compound H–$GaCl_2$.[4d] Also these results will stimulate further research activities. At low temperature, the methyl resonances of the main component (**1**) split and indicate the presence of two species. They were identified as *cis*/*trans* isomers of the dimers **1a** and **1b**, in particular on the basis of the resonances of the β-carbon atoms of the C=C double bonds (δ = 195 ppm on average). The *cis* form **1b** exhibits two resonances of the chemically different Al–Me groups, but only one set of resonances of the vinylic hydrogen atoms (see Exp. Section for further details). The centrosymmetric *trans* derivative has chemically equivalent Al–Me groups and shows only a single resonance. The ratio of the two isomers is 2:1 with the *cis* form as the main component. Compound **1** could not be obtained in a pure form by recrystallization from different solvents or sublimation in vacuo. In all cases the concentration of the impurities remained almost unchanged. However, sublimation afforded some colorless crystals embedded in an oil, which were suitable for crystal structure determination.

Molecular Structures

The molecular structures of compounds **1**–**5** are depicted in Figures 1, 2, 3, 4, and 5. They verify the addition of Al–H bonds to the C≡C triple bonds of the alkyne with the formation of alkenyl groups, the selective attack of the aluminum atoms exclusively at the terminal carbon atoms bearing the hydrogen atom,[7] and the *trans* arrangement of the vinylic hydrogen atoms. All compounds possess dimeric formula units in the solid state with central Al_2C_2 heterocycles and the terminal carbon atoms of the alkenyl groups in the bridging positions. However, different configurations resulted with the *trans* arrangement of both C=C double bonds with respect to the central heterocycle in the structures of **2** to **5**, while they are on the same side of the ring in compound **1**. This observation is in accordance with the behavior of **1** in solution, where the *cis* isomer forms the major component at low temperature. The *cis* arrangement of substituents at E_2X_2 heterocycles (E = Al, Ga, In) has been observed before in rare cases, in which bulky substituents forced this unusual configuration by a minimization of the steric stress in the respective molecules.[15] The *cis* configuration usually results in a relatively strong folding of the inner rings, which is 21° on average across the Al1···Al2 axis in **1**. In contrast planar heterocycles were usually observed for the *trans* forms, and the strongest deviation was detected for compound **2** (fold angle 6.4°).

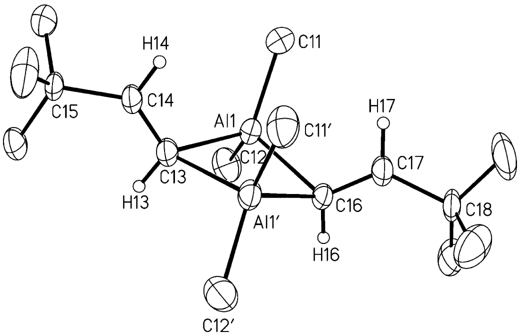


Figure 1. Molecular structure of **1** (R = Me). Hydrogen atoms with the exception of those attached to the C=C double bonds are omitted. Selected bond lengths [pm] and bond angles [°] (data of the second molecule in square brackets): Al1–C11 196.1(3) [194.2(3)], Al1–C12 194.5(3) [195.5(3)], Al1–C13 211.3(3) [211.6(3)], Al1–C16 211.4(3) [211.1(3)], C13–C14 132.2(5) [131.6(5)], C16–C17 131.1(5) [133.4(5)], C13–Al1–C16 99.5(1) [99.5(1)], Al1–C13–Al1′ 78.1(1) [78.1(1)], Al1–C16–Al1′ 78.1(1) [78.3(1)]; Al1′ generated by *x*, *y*, –*z* + 0.5.

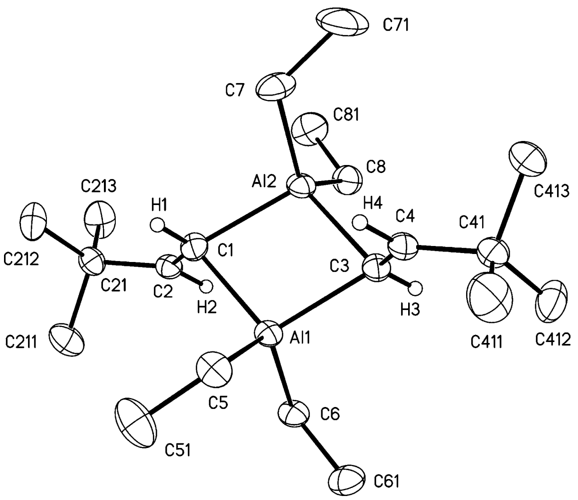


Figure 2. Molecular structure of **2** (R = Et). Hydrogen atoms with the exception of those attached to the C=C double bonds are omitted. Selected bond lengths [pm] and bond angles [°]: Al1–C1 210.5(2), Al1–C3 210.4(2), Al1–C5 196.5(2), Al1–C6 196.3(1), Al2–C1 210.5(2), Al2–C3 211.7(2), Al2–C7 196.4(2), Al2–C8 196.3(2), C1–C2 133.8(2), C3–C4 133.7(2), C1–Al1–C3 101.65(6), C1–Al2–C3 101.17(6), Al1–C1–Al2 78.49(5), Al1–C3–Al2 78.25(5).

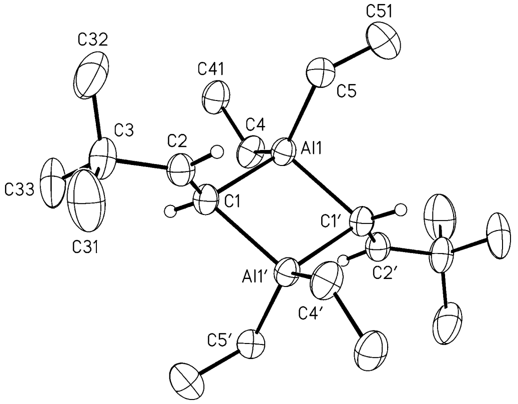


Figure 3. Molecular structure of **3** (R = *i*Bu). Hydrogen atoms with the exception of those attached to the C=C double bonds and methyl groups of the isobutyl substituents are omitted. Selected bond lengths [pm] and bond angles [°]: Al1–C1 210.1(2), Al1–C1′ 212.1(2), Al1–C4 197.2(2), Al1–C5 196.7(2), C1–C2 134.1(3), C1–Al1–C1′ 101.48(8), Al1–C1–Al1′ 78.52(8); Al1′ and C1′ generated by –*x* + 2, –*y*, –*z* – 1.

Despite the different configurations, the structural parameters of these five compounds are quite similar. The Al–C bonds to the terminal alkyl groups steadily increase with their increasing bulkiness from 195 pm in **1** to 202 pm in **5**. The distances between the aluminum and the bridging carbon atoms of the C=C double bonds are expectedly longer and are in a narrow range between 210 and 212 pm. These differences reflect the particular bonding situation with 2c–2e vs. 3c–2e bonds. The C–C distances of the double bonds (131 to 134 pm) correspond to the standard bond length. In all cases, the orientation of the double bonds is almost ideally perpendicular to the transannular Al···Al axes. The

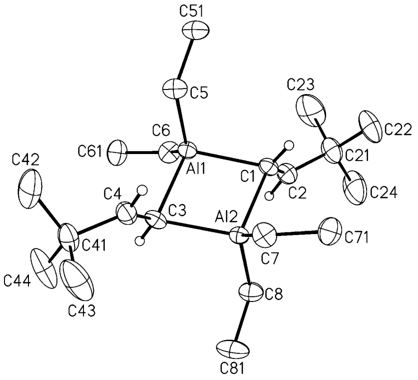


Figure 4. Molecular structure of **4** (R = CH_2tBu). Hydrogen atoms with the exception of those attached to the C=C double bonds and the methyl groups of the neopentyl substituents are omitted. Selected bond lengths [pm] and bond angles [°]: Al1–C5 197.9(2), Al1–C6 198.4(2), Al1–C1 212.2(2), Al1–C3 211.7(2), Al2–C7 198.6(2), Al2–C8 197.9(2), Al2–C1 211.4(2), Al2–C3 211.2(2), C1–C2 133.3(3), C3–C4 134.6(3), C1–Al1–C3 100.70(9), C1–Al2–C3 101.11(8), Al1–C1–Al2 78.97(7), Al1–C3–Al2 79.14(7).

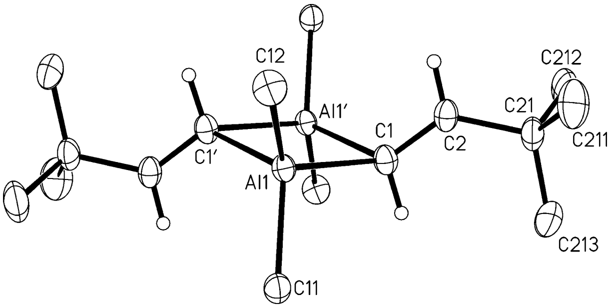
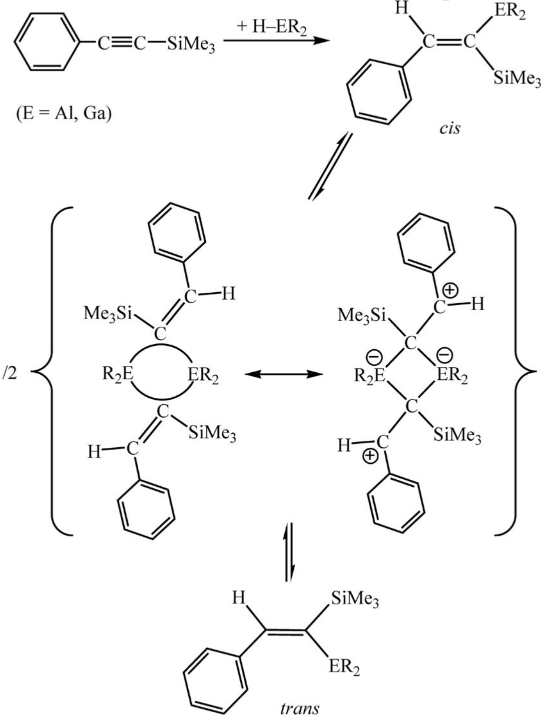


Figure 5. Molecular structure of **5** (R = *t*Bu). Hydrogen atoms with the exception of those attached to the C=C double bonds and methyl groups of the *tert*-butyl substituents attached to aluminum are omitted. Important bond lengths [pm] and angles [°]: Al1–C11 201.4(2), Al1–C12 202.9(2), Al1–C1 212.1(2), Al1–C1′ 212.4(2), C1–C2 131.9(2), C1–Al1–C1′ 98.37(6), Al1–C1–Al1′ 81.63(6); Al1′ and C1′ generated by –*x* + 1, –*y* + 1, –*z*.

angles Al–C=C are in a narrow range between 114 and 119°, larger angles occurred only for the *tert*-butyl compound **5** (118.8 and 124.2°).

cis/*trans* Isomerization and Quantum-Chemical Calculations

As discussed before, *cis*/*trans* isomerization of the products of *cis*-addition to the ones of formal *trans*-addition is a well-known phenomenon in hydroalumination and hydrogallation reactions.[4–6] The *cis*-addition products (*E* isomers of the monomeric alkenyl compounds discussed here) with the hydrogen and metal atoms on the same side of the C=C double bonds may represent the first step in all cases, and they were isolated from many reactions [Equation (2)]. In particular, the products from reactions with trimethylsilylalkynes spontaneously rearrange to give the *trans*-addition products as long as the steric shielding is relatively low. This observation was interpreted in terms of an intermolecular activation required for this rearrangement process.



(2)

In order to get a better insight into the structural and thermodynamic properties of the monomeric and dimeric hydroalumination products obtained from the reaction of *tert*-butylethyne and di(*tert*-butyl)aluminum hydride, quantum-chemical calculations were performed for the compounds in the gas phase. These were carried out by applying the DFT method [B3LYP/6-311+G(d,p)//B3LYP/6-311+G-(d,p)] for geometry optimizations with the GAUSSIAN 03 series of programs.[16] The recently developed SCS-MP2 method [SCS-MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p)] was used for the energy determinations.[17] The reported relative energies are corrected for 0 K by using the DFT zero-point energy (ZPE). The natural charges and the Wiberg bond indices were calculated by the NBO method as implemented into the GAUSSIAN 03 program. For comparison, we used in some cases the functional with dispersion correction B97-D using the TZVP basis (without zero-point correction), which has recently been developed by Grimme.[18]

The *trans*-addition products were calculated to be the thermodynamically favored ones in all cases for the reactions of phenyl-alkyl and phenyl-trimethylsilyl ethynes.[5] In the present study, however, we found only a very modest preference for the monomeric *trans*-addition product of about 1.0 kcal/mol over the *cis*-addition product at the highest computational level employed [SCS-MP2/6-311+G(d,p)]. B97-D also gives a preference of 1.0 kcal/mol for this isomer, whereas B3LYP/6-311+G(d,p) favors the *cis* isomer by 1.9 kcal/mol, indicating the importance of dispersion interactions in these sterically demanding systems. Interestingly, the preferred *trans*-addition product shows a perpendicular arrangement of the $Al(tBu)_2$ moiety with respect to the vinyl group as a result of strong steric interactions (Figure 6). The slightly less stable *cis*-addition product does not show this perpendicular conformation (Figure 7). The bond lengths and Wiberg bond indices for the Al–C_α bond are similar in both isomers (*cis* isomer: 196.2 pm, Wiberg bond index 0.525; *trans* isomer: 197.2 pm, Wiberg bond index 0.473). These values and the relevant molecular orbitals give no hints for a significant vinyl-aluminum π-interaction in both isomers. The C=C bonds of these two isomeric vinylic aluminum compounds exhibit a relatively strong charge separation with a high negative charge localized at the α-carbon atoms (monomers: –0.86 to –0.88 for C_α, –0.10 to –0.15 for C_β of the *cis* and *trans* addition products, respectively). For the monomers, the rotation about the C=C bond probably follows a zwitterionic mechanism as shown in a former investigation.[5] However, the calculated barrier (closed shell) of ca. 62 kcal/mol precludes any isomerization under laboratory conditions. Unrestricted DFT calculations (UB3LYP) for the transition state of the rotation did not converge.

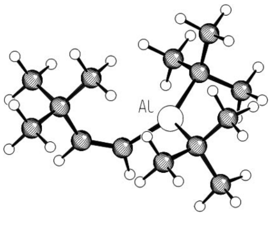


Figure 6. Optimized structure of the monomeric *trans*-addition product of **5**.

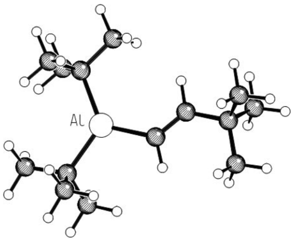


Figure 7. Optimized structure of the monomeric *cis*-addition product of **5**.

With respect to the relatively high charge on C_α, Lewis acids are expected to influence the rotational barrier strongly. Indeed, the addition of lithium cations enhances the polarity of the C=C bond and diminishes considerably the rotational barrier of trimethylsilylethenyl compounds.[5] The formation of dimeric formula units, in which the aluminum atoms act as polarizing Lewis acids similar to the behavior of the lithium cation, may be considered to be the key step for the activation of the *cis*/*trans* isomerization also in the cases discussed here. Therefore, we extended our computational study on the dimeric formula units of the hydroalumination products. Two dimers were considered, a *cis* isomer with respect to the position of the two hydrogen atoms on the four-membered ring (similar to compound **5b**, R = *t*Bu) and a *trans* isomer (compound **5c**, R = *t*Bu). Both compounds are formed from the *cis* addition product in an exothermic reaction (ca. –28.1 kcal/mol at SCS-MP2 and ca. –38 kcal/mol at the B97-D level) and are very similar in energy, the *cis* form being slightly favored (0.2 kcal/mol at SCS-MP2 and 0.8 kcal/mol at B97-D).

A probable mechanism for the *cis*/*trans* isomerization involving dimeric structures is shown in Equation (2). In these dimers, the charge separations in the vinylic part are significantly larger (C_α –1.06 and C_β 0.00) relative to the ones observed in the monomers. We calculated, for a slightly modified model structure (Me at aluminum instead of *t*Bu), a reduced rotational barrier of 48.6 kcal/mol, which is still far beyond realization under normal laboratory conditions. Thus, as experimentally found, for the *tert*-butyl-substituted compounds studied here, *cis*/*trans* isomerization is not to be expected. However, the calculated rotational barrier for the previously studied trimethylsilylethyne-derived hydroalumination products is significantly lower and permits isomerization under laboratory conditions.[5]

The relatively high positive charge at the β-carbon atoms is in accordance with the ^{13}C NMR resonances of these atoms, which show a strong shift to a lower field ($\delta >$ 194 ppm). Calculated chemical shifts for the monomers in the gas phase [C_α: 130.2 (*cis*), 133.2 (*trans*) and C_β: 180.9 (*cis*), 169.7 (*trans*)] and for the dimers [C_α: 118.8 (*trans*), 121.2 (*cis*) and C_β: 212.6 (*trans*), 210.1 (*cis*)] fit with the experimental data. These considerations, based on NMR spectroscopic data, X-ray structure determinations, and quantum-chemical calculations, are in accordance with a mechanism which was postulated amongst others in the literature many years ago.[19]

Experimental Section

General: All procedures were carried out under purified argon in dried solvents (*n*-hexane and *n*-pentane over $LiAlH_4$). Commercially available H–C≡C–CMe_3 was distilled from molecular sieves (4 Å). *i*Bu_2AlH was used as purchased (Aldrich). Me_2AlH,[20] Et_2AlH,[20] $(Me_3CCH_2)_2AlH$[21] and $(Me_3C)_2AlH$[22] were obtained according to literature procedures. The assignment of the NMR spectra is based on HMBC, HSQC, ROESY and DEPT135 data.

Reaction of Me_2AlH with *tert*-Butylethyne. Synthesis of 1: Me_2AlH (0.27 mL, 0.215 g, 3.70 mmol) was added to a solution of H–C≡C–CMe_3 (0.50 mL, 0.337 g, 4.11 mmol, excess) in *n*-hexane (20 mL) at room temperature. The mixture was heated under reflux for 3 h. The solution was concentrated and cooled to –15 °C to yield a colorless solid of **1**, which melted upon warming to room temperature to give a highly viscous liquid. Sublimation in vacuo (10^{-3} Torr) at room temperature afforded colorless crystals embedded in colorless oil. The by-products of the reaction could not be removed by any of these procedures. Thus, yield, melting point, and elemental analysis could not be determined. ^1H NMR (400 MHz, C_6D_6): T = 300 K: fast exchange gave a relatively simple spectrum: δ = –0.34 (s, 12 H, AlMe), 0.86 (s, 18 H, CMe_3), 5.89 (d, $^3J_{H-H}$ = 20.8 Hz, 2 H, Al_2CH=C), 7.51 (d, $^3J_{H-H}$ = 20.8 Hz, 2 H, Al_2C=CH) ppm; T = 185 K ([D_8]toluene): *cis*/*trans* isomers in a molar ratio of about 2:1; ***trans* form 1a:** δ = –0.14 (s, 12 H, AlMe), 0.81 (s, 18 H, CMe_3), 5.89 (d, $^3J_{H-H}$ = 20.8 Hz, 2 H, Al_2CH=C), 7.49 (d, $^3J_{H-H}$

= 20.8 Hz, 2 H, Al$_2$C=C*H*) ppm; ***cis* form 1b:** δ = –0.06 and –0.12 (each s, 6 H, AlMe), 0.81 (s, 18 H, CMe$_3$), 5.61 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 2 H, Al$_2$C*H*=C), 7.57 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 2 H, Al$_2$C=C*H*) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$): *T* = 300 K: δ = –7.4 (AlMe), 27.5 (C*Me*$_3$), 38.4 (*C*Me$_3$), 120.3 (Al$_2$*C*=C), 194.6 (Al$_2$C=*C*) ppm; *T* = 185 K ([D$_8$]toluene), ***trans* form 1a:** δ = –6.7 (AlMe), 26.9 (C*Me*$_3$), 38.6 (*C*Me$_3$), 120.3 (Al$_2$*C*=C), 195.3 (Al$_2$C=*C*) ppm; ***cis* form 1b:** δ = –6.9 and –7.2 (AlMe), 26.9 (C*Me*$_3$), 38.6 (*C*Me$_3$), 119.1 (Al$_2$*C*=C), 195.2 (Al$_2$C=*C*) ppm.

Impurities were detected in the NMR spectra of the raw product of the reaction, which could not be removed completely by sublimation. They were identified by their characteristic resonances and by comparison to the spectra of similar compounds.

(Me$_2$Al)$_2$(μ-C≡C–CMe$_3$)$_2$ (1d):[9h,14] ^{1}H NMR (400 MHz, C$_6$D$_6$, 300 K): δ = –0.06 (s, 12 H, AlMe), 0.96 (s, 18 H, CMe$_3$) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$, 300 K): δ = –5.7 (AlMe), 27.3 (*C*Me$_3$), 29.4 (C*Me*$_3$), 85.6 (Al$_2$*C*≡C), 149.2 (Al$_2$C≡*C*) ppm.

(Me$_2$Al)$_2$(μ-C≡C–CMe$_3$)(μ-CH=CH–CMe$_3$) (1c): ^{1}H NMR (400 MHz, C$_6$D$_6$, 300 K): δ = –0.21 (s, 12 H, AlMe), 0.81 (s, 9 H, CMe$_3$ of alkenyl), 1.01 (s, 9 H, CMe$_3$ of alkynyl), 5.75 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 1 H, Al$_2$C*H*=C), 7.55 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 1 H, Al$_2$C=C*H*) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$, 300 K): δ = –6.5 (AlMe), 27.3 (C*Me*$_3$ of alkenyl), 27.5 (*C*Me$_3$ of alkynyl), 29.6 (C*Me*$_3$ of alkynyl), 38.6 (*C*Me$_3$ of alkenyl), 85.9 (Al$_2$*C*≡C), 119.3 (Al$_2$*C*=C), 147.0 (Al$_2$C≡*C*), 197.6 (Al$_2$C=*C*) ppm.

[(Me$_2$Al)(μ-CH=CH-CMe$_3$)(μ-CH-CH$_2$-CMe$_3$)(AlMe)]$_2$ (1e): ^{1}H NMR (400 MHz, C$_6$D$_6$, 300 K): δ = –0.26 and –0.22 (each s, 6 H, AlMe$_2$), –0.19 (s, 6 H, AlMe), –0.13 (br., 2 H, Al$_2$C*H*-CH$_2$), 0.91 (s, 36 H, both CMe$_3$ resonances coincide), 1.96 and 2.02 (each d, $^2J_{\text{H-H}}$ = 7 Hz, 2 H, diastereotopic hydrogen atoms of CH$_2$), 5.85 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 2 H, Al$_2$C*H*=C), 7.42 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 2 H, Al$_2$C=C*H*) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$, 300 K): δ = –11.8 (AlMe), –7.1 and –4.7 (AlMe$_2$), –0.1 (Al$_2$*C*H-CH$_2$), 27.5 (C*Me*$_3$ of alkenyl), 29.6 (C*Me*$_3$ of aliphatic group), 32.2 (*C*Me$_3$ of aliphatic group), 38.3 (*C*Me$_3$ of alkenyl), 39.7 (CH$_2$), 120.6 (Al$_2$*C*=C), 192.3 (Al$_2$C=*C*) ppm.

Reaction of Et$_2$AlH with *tert*-Butylethyne. Synthesis of 2: Et$_2$AlH (0.44 mL, 0.353 g, 4.10 mmol) was added to a solution of H–C≡C–CMe$_3$ (0.50 mL, 0.337 g, 4.11 mmol) in *n*-hexane (20 mL) at room temperature. The mixture was heated under reflux for 3 h. The solution was concentrated and cooled to –45 °C to yield colorless crystals of **2**, which melted below 0 °C. Yield 0.352 g (51 %). ^{1}H NMR (400 MHz, C$_6$D$_6$, 300 K): δ = 0.25 (q, $^3J_{\text{H-H}}$ = 8.1 Hz, 8 H, AlCH$_2$), 0.91 (s, 18 H, CMe$_3$), 1.25 (t, $^3J_{\text{H-H}}$ = 8.1 Hz, 12 H, CH$_3$ of Et), 5.81 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 2 H, Al$_2$C*H*=C), 7.50 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 2 H, Al$_2$C=C*H*) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$, 300 K): δ = 2.3 (AlCH$_2$), 9.5 (CH$_3$ of Et), 28.0 (C*Me*$_3$), 38.7 (*C*Me$_3$), 117.2 (Al$_2$*C*=C), 194.9 (Al$_2$C=*C*) ppm. IR (CsI, paraffin): $\tilde{\nu}$ = 1659 (m), 1587 (s), 1557 [vs, *ν*(C=C)] 1471 (sh), 1462 (vs, paraffin) 1408 (m), 1390 [m, *δ* (CH$_3$)] 1364 (s, paraffin) 1331 (w), 1265 [vw, *δ*(CH)] 1227 (s), 1202 (m), 1165 (w), 1099 (s), 1049 (vs), 1028 (m), 1009 (m), 986 (s), 951 (m), 918 (m), 897 (s), 820 (m), 787 (m), 754 [m, *ν*(CC), *δ*(CH), *δ*(CC)] 723 (s, paraffin) 631 (vs), 530 (s), 465 (s), 434 [m, *ν*(AlC)] cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 307 (100) [M$^+$ – Et]. C$_{20}$H$_{42}$Al$_2$ (336.51): calcd. C 71.4, H 12.6; found C 70.9, H 12.4.

Reaction of *i*Bu$_2$AlH with *tert*-Butylethyne. Synthesis of 3:[10] *i*Bu$_2$AlH (0.49 mL, 0.389 g, 2.74 mmol) was added to a solution of H–C≡C–CMe$_3$ (0.33 mL, 0.225 g, 2.74 mmol) in *n*-hexane (20 mL) at room temperature. The mixture was heated under reflux for 2 h. The solution was concentrated and cooled to –30 °C to yield colorless crystals of **3**. Yield 0.356 g (58 %), m.p. (argon, sealed capillary) 127 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 300 K, fast exchange): δ = 0.41 (d, $^3J_{\text{H-H}}$ = 7.2 Hz, 8 H, AlCH$_2$), 0.95 (s, 18 H, CMe$_3$), 1.13 (d, $^3J_{\text{H-H}}$ = 6.6 Hz, 24 H, CH$_3$ of *i*Bu), 2.05 (*pseudo*-sept, $^3J_{\text{H,H}}$ = 7 Hz, 4 H, CH of *i*Bu), 5.89 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 2 H, Al$_2$C*H*=C), 7.51 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 2 H, Al$_2$C=C*H*) ppm; *T* = 190 K ([D$_8$]toluene): *cis*/*trans* isomers in a molar ratio of about 2:3; ***trans* form 3a:** δ = 0.4 and 0.6 (br., each 4 H, diastereotopic protons of AlCH$_2$), 0.9 (br., 18 H, CMe$_3$), 1.2 (br., 24 H, CH$_3$ of *i*Bu), 2.1 (br., 4 H, CH of *i*Bu), 5.90 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 2 H, Al$_2$C*H*=C), 7.39 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 2 H, Al$_2$C=C*H*); ***cis* form 3b:** δ = 0.4 and 0.6 (each br., 4 H, AlCH$_2$), 0.9 (br., 18 H, CMe$_3$), 1.2 (br., 24 H, CH$_3$ of *i*Bu), 2.1 (br., 4 H, CH of *i*Bu), 5.80 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 2 H, Al$_2$C*H*=C), 7.51 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 2 H, Al$_2$C=C*H*) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$, 300 K): δ = 25.2 (AlCH$_2$), 27.0 (CH of *i*Bu), 27.7 (C*Me*$_3$), 28.6 (CH$_3$ of *i*Bu), 38.8 (*C*Me$_3$), 118.9 (Al$_2$*C*=C), 194.4 (Al$_2$C=*C*) ppm; *T* = 190 K ([D$_8$]toluene), ***trans* form 3a:** δ = 24.8 (AlCH$_2$), 38.9 (*C*Me$_3$), 117.4 (Al$_2$*C*=C), 194.4 (Al$_2$C=*C*) ppm; ***cis* form 3b:** δ = 23.6 and 25.2 (AlCH$_2$), 38.9 (*C*Me$_3$), 117.8 (Al$_2$*C*=C), 194.2 (Al$_2$C=*C*); remaining resonances could not be assigned unambiguously. IR (CsI, paraffin): $\tilde{\nu}$ = 1647 (w), 1564 (s), 1555 [s, *ν*(C=C)] 1462 (vs), 1362 (vs, paraffin) 1333 (m), 1296 (w), 1267 [w, *δ*(CH)] 1227 (m), 1192 (s), 1167 (m), 1121 (m), 1045 (vs), 1030 (s), 988 (s), 928 (m), 893 (m), 822 [m, *ν*(CC), *δ*(CH), *δ*(CC)] 719 (s, paraffin) 689 (m), 625 (m), 565 (m), 459 [m, *ν*(AlC)] cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 391 (22) [M$^+$ – Bu], 167 (100) [1/2 M$^+$ – Bu]. C$_{28}$H$_{58}$Al$_2$ (448.73): calcd. C 74.9, H 13.0; found C 74.3, H 13.1.

Reaction of (Me$_3$CCH$_2$)$_2$AlH with *tert*-Butylethyne. Synthesis of 4: A solution of (*t*BuCH$_2$)$_2$AlH (0.226 g, 1.33 mmol) in *n*-pentane (20 mL) was added to a solution of H–C≡C–CMe$_3$ (0.16 mL, 0.109 g, 1.33 mmol) in the same solvent (20 mL) at room temperature. The mixture was stirred at room temperature for 16 h. The solution was concentrated and cooled to –15 °C to yield colorless crystals of **4**. Yield 0.234 g (70 %), the *trans* form (**4a**) was verified by NMR spectroscopy as the main component in solution; m.p. (argon, sealed capillary) 193 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 300 K): δ = 0.65 (s, 8 H, AlCH$_2$), 0.98 (s, 18 H, CMe$_3$ of alkenyl), 1.24 (s, 36 H, CMe$_3$ of neopentyl), 6.14 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 2 H, Al$_2$C*H*=C), 7.54 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 2 H, Al$_2$C=C*H*) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$, 300 K): δ = 27.5 (C*Me*$_3$ of alkenyl), 32.1 (*C*Me$_3$ of neopentyl), 34.0 (AlCH$_2$), 35.6 (C*Me*$_3$ of neopentyl), 39.0 (*C*Me$_3$ of alkenyl), 119.6 (Al$_2$*C*=C), 195.5 (Al$_2$C=*C*) ppm. See the discussion part for a description of low-temperature NMR spectroscopic data. Further resonances of low intensity (<5 %) may be interpreted in terms of a monomeric formula unit (**4c**): ^{1}H NMR (400 MHz, C$_6$D$_6$, 300 K): δ = 5.90 (d, $^3J_{\text{H-H}}$ = 20.5 Hz, 1 H, Al$_2$C*H*=C), 6.40 (d, $^3J_{\text{H-H}}$ = 20.5 Hz, 1 H, Al$_2$C=C*H*) ppm. IR (CsI, paraffin): $\tilde{\nu}$ = 1553 [s, *ν*(C=C)] 1466 (vs), 1379 (vs), 1358 [vs, paraffin, *ν*(C=C)] 1335 (s), 1265 [m, *δ*(CH)] 1227 (s), 1165 (m), 1123 (m), 1101 (s), 1051 (vs), 1015 (vs), 999 (vs), 934 (s), 912 (m), 899 (s), 824 (s), 783 (vw), 762 (s), 748 [s, *ν*(CC), *δ*(CH), *δ*(CC)] 721 (w, paraffin) 664 (s), 629 (vs), 575 (s), 518 (w), 469 (vs), 457 [vs, *ν*(AlC)] cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 446 (58) [M$^+$ – Bu – H], 181 (100) [1/2 M$^+$ – neopentyl]. C$_{32}$H$_{66}$Al$_2$ (504.84): calcd. C 76.1, H 13.2; found C 75.6, H 13.0.

Several impurities were detected in the NMR spectra of the raw product. One set of resonances could clearly be assigned to the mixed alkenyl-alkynyl compound **4d:** ^{1}H NMR (400 MHz, C$_6$D$_6$, 300 K): δ = 6.14 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 1 H, Al$_2$C*H*=C), 7.87 (d, $^3J_{\text{H-H}}$ = 20.8 Hz, 1 H, Al$_2$C=C*H*) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$, 300 K): δ = 75.9 (Al$_2$*C*≡C), 116.0 (Al$_2$*C*=C), 162.3 (Al$_2$C≡*C*), 199.6 (Al$_2$C=*C*) ppm.

Reaction of $(Me_3C)_2Al$–H with Me_3C–C≡C–H. Synthesis of 5: H–C≡C–CMe_3 (0.21 mL, 0.143 g, 1.74 mmol) was dissolved in *n*-hexane (20 mL), cooled to –15 °C and treated with a solution of di(*tert*-butyl)aluminum hydride (0.247 g, 1.74 mmol) in *n*-hexane (20 mL). After warming to room temperature, the mixture was stirred for 1 h. Concentration and cooling to –28 °C yielded colorless crystals of compound **5**. Yield 0.248 g (64%), m.p. (argon sealed capillary) 140 °C. ^{1}H NMR (400 MHz, C_6D_6, 300 K): **monomer 5a:** δ = 1.10 (s, 18 H, Al–CMe_3), 1.11 (s, 9 H, CMe_3 of alkenyl), 5.93 (d, $^3J_{H\text{-}H}$ = 20.5 Hz, 1 H, Al–C*H*=C), 6.20 (d, $^3J_{H\text{-}H}$ = 20.5 Hz, 1 H, AlC=C*H*); **dimer 5b:** δ = 1.01 (s, 18 H, CMe_3 of alkenyl), 1.13, 1.18, 1.19 and 1.28 (each s, 9 H, Al–CMe_3), 5.82 (d, $^3J_{H\text{-}H}$ = 20.5 Hz, 2 H, Al_2C*H*=C), 8.00 (d, $^3J_{H\text{-}H}$ = 20.5 Hz, 2 H, Al_2C=C*H*); dimer **5c**: δ = 0.98 (s, 18 H, CMe_3 of alkenyl), 1.20 (s, 36 H, Al–CMe_3), 5.83 (d, $^3J_{H\text{-}H}$ = 21.0 Hz, 2 H, Al_2C*H*=C), 7.99 (d, $^3J_{H\text{-}H}$ = 21.0 Hz, 2 H, Al_2C=C*H*) ppm. ^{13}C NMR (100 MHz, C_6D_6, 300 K): **monomer 5a:** δ = 20.8 (Al–*C*Me_3), 29.3 (C*Me*$_3$ of alkenyl), 30.6 (Al–C*Me*$_3$), 35.9 (*C*Me_3 of alkenyl), 127.4 (Al_2*C*=C), 161.0 (Al_2C=*C*); **dimer 5b:** δ = 16.6, 17.4, 17.4 and 17.7 (each Al–*C*Me_3), 28.3 (C*Me*$_3$ of alkenyl), 30.2, 31.4, 31.9 and 32.3 (Al–C*Me*$_3$), 39.5 (*C*Me_3 of alkenyl), 114.0 (Al_2*C*=C), 197.3 (Al_2C=*C*); **dimer 5c:** δ = 18.1 (Al–*C*Me_3), 28.5 (C*Me*$_3$ of alkenyl), 32.8 (Al–C*Me*$_3$), 39.8 (*C*Me_3 of alkenyl), 113.5 (Al_2*C*=C), 196.7 (Al_2C=*C*) ppm. IR (CsI, paraffin): $\tilde{\nu}$ = 1581 (m), 1551 [s, *ν*(C=C)] 1452 (vs, paraffin) 1400 [m, $\delta(CH_3)$] 1377 (vs, paraffin) 1340 (sh), 1323 (w), 1306 [m, $\delta(CH_3)$] 1227 (m), 1211 (w), 1169 (m), 1153 (m), 1117 (w), 1076 (m), 1053 (s), 966 (vw), 938 (w), 894 (w), 847 (w), 812 [m, *ν*(CC), *δ*(CH), *δ*(CC)] 721 (vs, paraffin) 595 (w), 561 (w), 516 (vw), 466 (m), 438 [w, *ν*(AlC)] cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 418 (53) [M^+ – 2 Me], 389 (100) [M^+ – BuH – H], 224 (35) [1/2 M^+]. $C_{28}H_{58}Al_2$ (448.73): calcd. Al 12.0, C 74.9, H 13.0; found Al 12.1, C 75.3, H 12.7.

A further compound was detected in the raw product of the reaction: **$[(Me_3C)_2Al]_2$(μ-C≡C–CMe_3)(μ-CH=CH–CMe_3) (5d):** ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ = 0.95 (s, 9 H, CMe_3 of alkenyl), 1.09 (s, 9 H, CMe_3 of alkynyl), 1.27 (s, 36 H, Al–CMe_3), 5.68 (d, $^3J_{H\text{-}H}$ = 21.1 Hz, 1 H, Al_2C*H*=C), 8.01 (d, $^3J_{H\text{-}H}$ = 21.1 Hz, 1 H, Al_2C=C*H*) ppm. ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ = 17.8 (Al–*C*Me_3), 28.4 (C*Me*$_3$ of alkenyl), 29.6 (*C*Me_3 of alkynyl), 30.6 (C*Me*$_3$ of alkynyl), 40.1 (*C*Me_3 of alkenyl), 79.8 (Al_2*C*≡C), 113.3 (Al_2*C*=C), 149.8 (Al_2C≡*C*), 199.3 (Al_2C=*C*) ppm.

Crystal Structure Determinations: Single crystals of **1** were obtained by sublimation in vacuo (5×10^{-3} Torr) at room temperature. All other crystals were obtained upon cooling of the concentrated reaction mixtures (–15 to –45 °C). The crystallographic data were collected with a Bruker APEX diffractometer with Cu-K_α (for **1**–**4**) and Mo-K_α (for **5**) radiation. The crystals were coated with a perfluoro polyether, picked up with a glass fiber and immediately mounted in the cooled nitrogen stream of the diffractometer. Crystallographic data and details of the final *R* values are provided in Table 1.[25] All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms attached to carbon were calculated on ideal positions and allowed to ride on the bonded atom with $U = 1.2U_{eq}$(C). The molecules of **1** reside on crystallographic mirror planes; two independent molecular halves were found in the asymmetric unit. Three *tert*-butyl groups of **1** are disordered over the mirror plane (C15, C18, C28, occupation factors 0.5). The atoms C41, C42, and C43 of an isobutyl group of **3** and the methyl group C53 were refined on split positions (0.57 to 0.43 and 0.75 to 0.25). The molecules of **3** and **5** reside on crystallographic centers of symmetry. Compound **4** showed complete disorder of the central Al_2C_2 ring over two positions (0.93 to 0.07). In addition, *tert*-butyl groups of neopentyl groups (C022, C032, C042)

Table 1. Crystal data and structure refinement for the compounds **1** to **5**.[a,b]

	1	**2**	**3**	**4**	**5**
Formula	$C_{16}H_{34}Al_2$	$C_{20}H_{42}Al_2$	$C_{28}H_{58}Al_2$	$C_{32}H_{66}Al_2$	$C_{28}H_{58}Al_2$
Temperature [K]	153	153	153	153	173
Crystal system	orthorhombic	orthorhombic	triclinic	monoclinic	triclinic
Space group[23]	*Pbcm* (no. 57)	*Pccn* (no. 56)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a [pm]	1321.99(4)	2004.81(4)	946.4(3)	1043.29(1)	880.1(3)
b [pm]	2479.78(8)	1219.29(3)	963.7(3)	2101.18(3)	974.9(3)
c [pm]	1203.33(5)	1932.29(5)	1015.8(4)	1693.35(2)	1038.1(3)
α [°]	90	90	74.979(2)	90	66.903(6)
β [°]	90	90	65.899(2)	103.385(1)	75.776(6)
γ [°]	90	90	74.261(2)	90	71.953(6)
V [10^{-30} m^3]	3944.8(2)	4723.4(2)	802.4(5)	3611.23(8)	771.2(4)
Z	8	8	1	4	1
$D_{calcd.}$ [g cm^{-3}]	0.944	0.946	0.929	0.928	0.966
μ [mm^{-1}]	1.197	1.061	0.872	0.815	0.106
Crystal size [mm]	$0.42 \times 0.15 \times 0.04$	$0.30 \times 0.15 \times 0.10$	$0.10 \times 0.08 \times 0.06$	$0.28 \times 0.24 \times 0.15$	$0.43 \times 0.26 \times 0.18$
Theta range [°]	$3.34 \le \theta \le 71.64$	$4.24 \le \theta \le 72.86$	$4.84 \le \theta \le 72.45$	$3.41 \le \theta \le 72.40$	$2.15 \le \theta \le 30.11$
Index ranges	$-14 \le h \le 15$ $-29 \le k \le 30$ $-13 \le l \le 14$	$-24 \le h \le 23$ $-13 \le k \le 14$ $-21 \le l \le 23$	$-11 \le h \le 10$ $-11 \le k \le 11$ $-12 \le l \le 12$	$-12 \le h \le 12$ $-24 \le k \le 25$ $-20 \le l \le 20$	$-12 \le h \le 12$ $-13 \le k \le 13$ $-14 \le l \le 14$
Independent reflections	3986 [R_{int} = 0.054]	4561 [R_{int} = 0.070]	2741 [R_{int} = 0.105]	6858 [R_{int} = 0.035]	4461 [R_{int} = 0.036]
Parameters	221	217	188	451	180
R[c]	0.0727 (2487)	0.0402 (3878)	0.0594 (2169)	0.0603 (5595)	0.0583 (3379)
wR_2[d] (all data)	0.2032	0.1157	0.1698	0.1811	0.1609
Max./min. residual e$^-$ density [10^{30} e m^{-3}]	0.914/–0.327	0.369/–0.290	0.432/–0.380	0.651/–0.248	0.383/–0.229

[a] Program SHELXL-97;[24] solutions by direct methods, full-matrix refinement with all independent structure factors. [b] See ref.[25] for CCDC reference number. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ [$I > 2\sigma(I)$]. [d] $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma|F_o|^2]^{1/2}$.

were disordered (occupancy factors: 0.51:0.49; 0.61:0.39; 0.61:0.39). One *tert*-butyl group of **5** was refined on split positions (0.73:0.27).

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