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Review

Hydroalumination and hydrogallation of alkynes: New insights into the course of well-known reactions

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Contents

Abstract

Hydroalumination reactions are well-known procedures for the reduction of unsaturated organic compounds possessing homonuclear or heteronuclear double or triple bonds and represent textbook knowledge since many years. However, the organoaluminum products of these reactions were isolated in rare cases only. Their structures were deduced from the constitutions of the hydrocarbons which were isolated after the usual hydrolytic work-up. These results are highly misleading. Very interesting secondary reactions remained unrecognized, and unprecedented compounds possessing singular structures were destroyed. That review describes some recent investigations into the characterization and identification of the organoelement products of hydroalumination and hydrogallation reactions with alkynes.

Keywords: Hydroalumination; Hydrogallation; Clusters; Cages; Chelating Lewis-acids

1. Introduction

The addition of Al–H bonds to the double or triple bonds of unsaturated organic compounds (hydroalumination) finds widespread application as a very powerful method for the reduction of specific substrates in organic synthesis [1–9] (Scheme 1). Its importance is underlined by the inclusion and detailed discussion in many textbooks of organic and organometallic chemistry, and a fundamental knowledge of this method is crucial in preparative chemistry. The general application of that procedure is favored by the easy access to a broad variety of different dialkylaluminum hydrides. Owing to the particular reactivity

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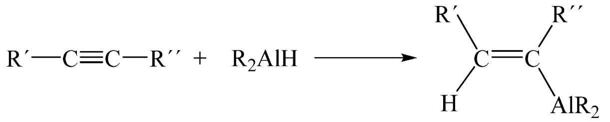


Scheme 1. General equation for the reduction of alkynes by hydroalumination.

of the Al–H bonds, the reactions with alkynes proceed under relatively mild conditions. Their exceptionally high regioselectivity is caused by the specific polarity of the Al–H bond with the negative charge localized at the hydrogen atoms. Hence, the reaction courses are determined by the polarities of the organic substrates with the more negatively charged atoms of the triple bonds exclusively attacked by aluminum. Stereoselectivity depends on the conditions such as the type of solvent or the temperature. However, a *cis* arrangement of the hydrogen and aluminum atoms was postulated to occur in most secondary products containing a C=C double bond. That particular configuration may be representative for the first step of all addition reactions involving dialkylaluminum hydrides by the reasonable assumption that they proceed by a concerted addition process including a heterocyclic transition state. The hydroalumination of alkenes possessing C=C double bonds [4,9,10] was applied to a relatively small extent. These reactions are reported to be slower compared to those of alkynes. Usually they proceed only at elevated temperatures, and catalytic activation seems to be required in some cases. References [11–13] refer to few recently published and completely characterized products of such reactions, which, however, are not in the focus of that review article.

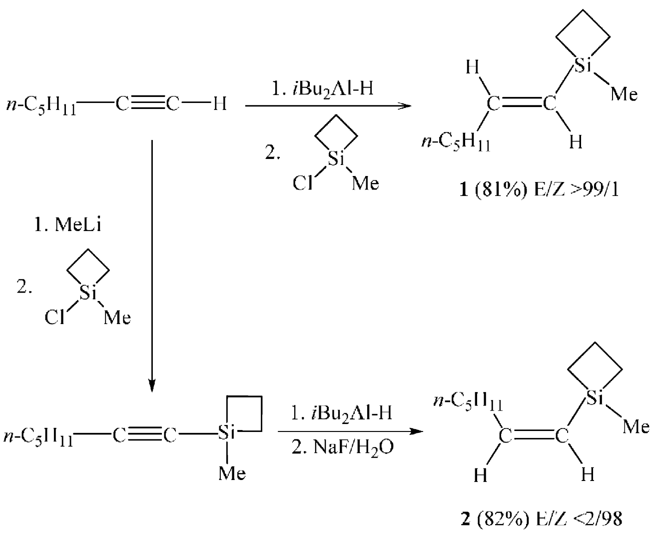
Interestingly the true structures and bonding situations of organoaluminum compounds formed by the addition of Al–H bonds are almost completely unknown. This statement holds in particular for that huge number of products which resulted from the hydroalumination of alkynes. Similar to the typical treatment of products of Grignard reactions these derivatives were usually not isolated, but immediately destroyed by a hydrolytic (or oxidative) work-up. Thus, the suggested structures of the organoaluminum intermediates were essentially based on the constitutions of the finally isolated hydrocarbons and are rather speculative. That procedure is misleading, and it is quite sure now that many singular and unprecedented products were destroyed unrecognized by that way. The interesting point with these organoaluminum compounds is the occurrence of coordinatively unsaturated aluminum atoms, which can easily initiate secondary reactions including exchange processes by bridging groups. Indeed, consideration of such processes is important for the complete understanding of hydroalumination. After a short and more informative survey on typical reactions of C≡C triple bonds reported in the literature, this review article describes our recent investigations into the course of the hydroalumination of alkynes with dialkylaluminum hydrides and gives attention also to the related hydrogallation, which in the past was applied to a far lesser extent. Hydrogallation makes an important addition to the corresponding reactions with aluminum hydrides, its significance goes beyond that of hydroalumination, and with the facile availability of dialkylkgallium hydrides in the last years it merits broader application in preparative chemistry.

While the constitutions of the intermediate organoaluminum derivatives obtained from the reduction of alkynes are mostly rather speculative, many hydroalumination products derived from heteronuclear double or triple bonds were isolated in a pure form and thoroughly characterized by standard methods including crystal structure determinations. Spontaneous secondary reactions, which are important in alkyne chemistry and are reported in detail in the following chapters, are rare because the products tend to form stable dimers by intermolecular Lewis-acid Lewis-base interactions and the coordinative saturation of the aluminum atoms. Completely characterized products of hydroalumination reactions are derived from C≡N triple bonds (nitriles [14–22] and isonitriles [14–16,23]), C=N [24–27] and C=O double bonds [28–30] and further element combinations possessing an unsaturated bonding system such as N=N or B≡N [31–33]. Owing to the lack of suitable dialkylgallium hydrides until recently (see below for further details) the mechanistically comparable hydrogallation did not find a similar broad application. Some examples for the addition of Ga–H bonds to homo- or heteronuclear double or triple bonds are given in Refs. [33–43].

2. Hydroalumination of alkynes—a literature survey

This section does not give a complete survey on the waste number of hydroalumination reactions, which were conducted in organic chemistry and were published in the literature. Instead, the history of that method and some fundamental aspects of the addition of Al–H bonds to C≡C triple bonds are outlined. Although these results in particular with respect to the constitution of the organoaluminum intermediates are essentially based on hydrolysis experiments (see above), they nevertheless are very helpful in understanding the principal reaction courses and give correct insights in many aspects of that chemistry such as regio- and stereoselectivity. Pioneering work with respect to the hydroalumination of alkynes was done by Wilke et al. starting in 1956 [44–46]. Later on important contributions directed towards the reaction mechanisms and the structures of the intermediates came from Eisch and others [47–49]. They investigated reactions of mono- and disubstituted alkynes of the types H–C≡C–R and R–C≡C–R. Beside some alanates, which should not be considered in detail here, they essentially conducted their experiments by employing diisobutylaluminum hydride. The results may be summarized as follows: hydroalumination reactions preferably yielded the products of a *cis* addition of the Al–H bonds as the kinetically favored compounds. The rearrangement to afford the corresponding, but thermodynamically stable *trans* products was facilitated by particular substituents such as trimethylsilyl groups. The addition reactions are highly regioselective, and those carbon atoms are preferably attacked by the aluminum atoms which bear a partial negative charge. Monosubstituted alkynes H–C≡C–R exhibit competitive reaction routes with deprotonation and formation of dialkylaluminum alkynides *versus* hydroalumination and formation of alkenylaluminum compounds. The relatively acidic alkyne H–C≡C–C_6H_5 gave deprotonation by hydrogen release, while the less acidic alkylethynes afforded the addition products. The reaction courses were no doubt correctly recognized in these former investigations. However, owing to the particular work-up procedures there is lack of information concerning the molecular structures and the bonding situations of the organoaluminum intermediates. The formation of dimers important for a fundamental understanding of the molecular properties could not be verified unambiguously. Similarly, secondary reactions could not be detected by hydrolysis experiments. Compounds were postulated having two or more dialkylaluminum groups attached to one carbon atom, which, however, represents a quite unstable situation and causes fast secondary reactions (see next section). These compounds may be isolable in the presence of donor molecules which possibly prevent the release of trialkylaluminum by coordinative saturation [50,51]. But that statement is speculative and requires an experimental confirmation in future investigations.

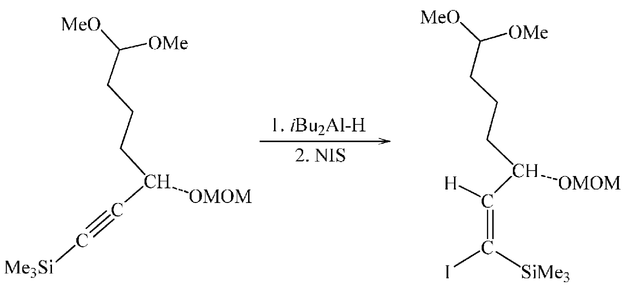
As mentioned before, this article is directed towards the structure and bonding of the organoelement products of hydroalumination and hydrogallation processes. Hence, we shall discuss only two illustrative examples for the application of hydroalumination in current organic synthesis, which actually covers a huge area with an immense diversity of different reaction types. The high stereoselectivity of these processes is demonstrated by two reactions starting with 1-heptyne (Eq. (1)) [52]. Treatment with diisobutylaluminum hydride and subsequently with a cyclic chlorosilane yielded the *E* alkenyl compound **1** in 81% yield with an *E* to *Z* ratio of >99 to 1. In contrast the *Z* alkenyl derivative **2** was isolated in 82% yield with an *E* to *Z* ratio of <2 to 98, when the silylalkyne was generated first by conventional methods and hydroalumination was applied in the second step. An oxidative work-up is illustrated with Eq. (2) [53]. Hydroalumination of the silylalkyne yielded an organoaluminum intermediate which probably had the aluminum and hydrogen atoms on the same side of the C=C double bond and a geminal arrangement of aluminum and silicon at one carbon atom. Oxidative cleavage of the Al–C bond by treatment with *N*-iodosuccinimide (NIS) afforded the iodoalkenyl compound **3**:



1 (81%) E/Z >99/1

2 (82%) E/Z <2/98

(1)



3

(2)

3. Reactions of Group 13-element alkynides $R_2E–C≡C–R'$

3.1. Hydroalumination of aluminum alkynides—synthesis of carbaalanes

Treatment of dialkylaluminum alkynides with the corresponding dialkylaluminum hydrides gave the first evidence that the hydroalumination of alkynes is more complicated and affords much more interesting products than suggested by literature knowledge. Early reports described the products of these reactions by double hydroalumination of the C≡C triple bond with up to three coordinatively unsaturated aluminum atoms geminally attached to one carbon atom [1,54]. However, such a situation is highly unstable, and even in the case of only two dialkylaluminum groups coordinated to one carbon atom fast secondary reactions occurred. Informative examples are the methylene bridged dialuminum compounds $R_2Al–CH_2–AlR_2$ [55], which were shown to yield a complicated equilibrium mixture in hydrocarbon solutions when they bear smaller substituents (R = Me or Et) [56]. Steric shielding by bulky bis(trimethylsilyl)methyl groups was required to isolate and characterize such compounds [57–59], which are of general importance in particular owing to their capability to act as chelating Lewis-acids [60–63]. Wilke and Schneider described the hydroalumination of dialkylaluminum alkynides in a conference report in 1963 [64]. They recognized that the corresponding trialkylaluminum compounds were released. The formation of cage compounds was postulated, the structure of which was derived from a heteroadamantane-like arrangement of aluminum and carbon atoms. Although this prediction proved to be incorrect, this group was the first to approach the true reaction course. As described later on heteroadamantane type compounds were indeed formed by the similar hydrogallation processes.

Unlike alkynes having exclusively organic residues attached to their triple bonds (see below) dialkylaluminum alkynides did not react with the corresponding dialkylaluminum hydrides when equimolar quantities of the starting compounds were mixed in a solvent. Successful transformations required the dissolution of the alkynide in a more or less large excess of the hydride. Exothermic reactions occurred with relatively small substituents as in the case of dimethylaluminum propynide [65], while prolonged heating to 80 °C for 2 days was required with dimethylaluminum phenylethynide [66]. The corresponding tri-

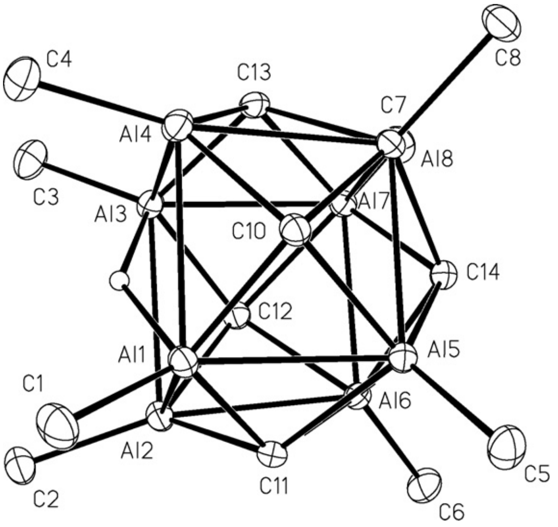
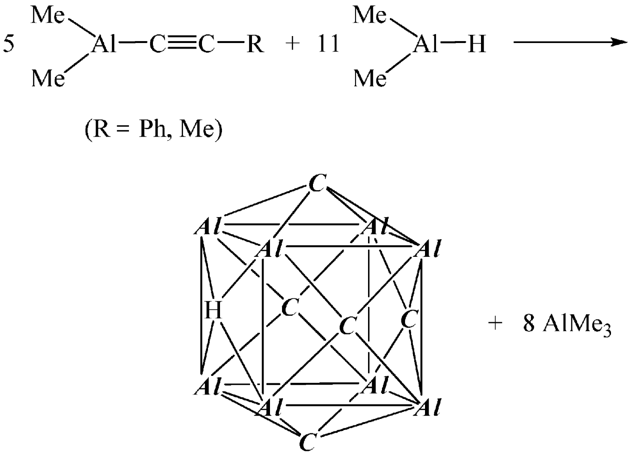


Fig. 1. Molecular structure of compound **4**.

alkylaluminum derivatives were released, and unprecedented clusters of aluminum and carbon atoms resulted by condensation. Owing to some similarities to carbaboranes we claimed the name carbaalanes [66] for this new class of compounds. The courses of these reactions and the structures of the finally isolated products strongly depended on the conditions such as temperature, excess of the hydrides and reaction time.

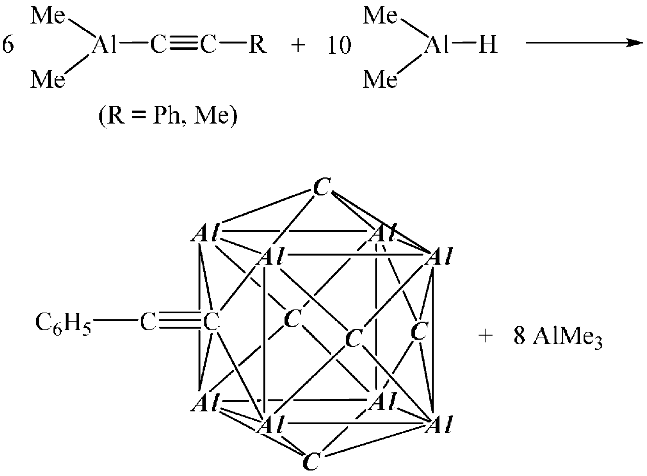
An instructive example is the treatment of Me_2AlH with the corresponding alkynides $Me_2Al–C≡C–R$. For R = phenyl a molar ratio of the starting compounds of 1 to about 5 (alkynide to hydride) afforded the carbaalane **4** in about 60% yield (Eq. (3)) which possesses a cluster of eight aluminum and five carbon atoms (Fig. 1) [66]. The aluminum atoms adopt an almost undistorted cube-like arrangement. Five faces of the cube are bridged by carbon atoms, while the sixth one is occupied by a hydrogen atom. The formation of **4** requires the idealized stoichiometric ratio of 1 to 2.2. A similar compound (**5**) [65,67] was formed as a by-product only (29% yield) by the treatment of $Me_2Al–H$ with the propynide $Me_2Al–C≡C–CH_3$, which has a methyl instead of a phenyl group as the second substituent attached to the triple bond:



4: ***Al*** = AlMe; ***C*** = CCH_2Ph
5: ***Al*** = AlMe; ***C*** = CCH_2Me

(3)

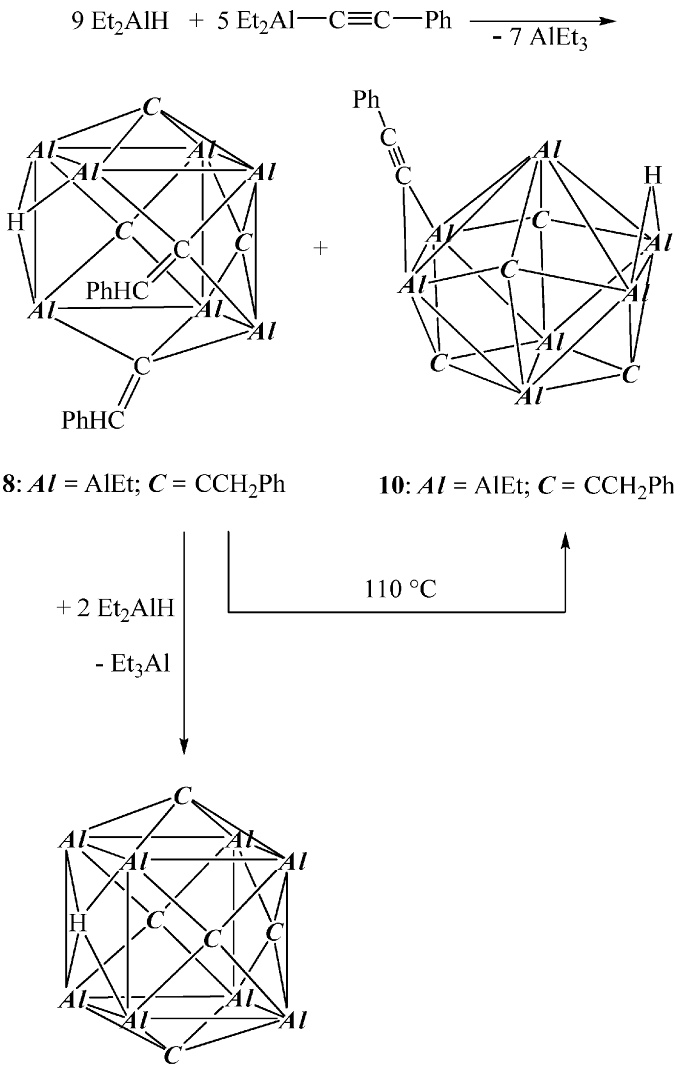
When the molar ratio of the starting compounds ($Me_2Al–H$ and $Me_2Al–C≡C–C_6H_5$) approached the idealized stoichiometry of Eq. (3), another product (**6**) was formed (Eq. (4)) [65]. Compound **6** results from an incomplete hydroalumination. It still has the cube-like arrangement of eight aluminum atoms with five faces bridged by the carbon atoms of alkyl groups, but the sixth face has a bridging alkynido group with short distances of the negatively charged carbon atom to four aluminum atoms. A similar product (**7**) resulted from the reaction of $Me_2Al–H$ with the propynidoaluminum derivative [67]. The phenyl compounds **4** and **6** are moderately air-stable, but the propynido derivatives **5** and **7** are pyrophoric and ignite spontaneously on contact with air. While the hydrido bridged clusters **4** and **5** are colorless, a deep red or yellow color, respectively, was observed for the alkynido compounds **6** and **7**:



6: ***Al*** = AlMe; ***C*** = CCH_2Ph
7: ***Al*** = AlMe; ***C*** = CCH_2Me

(4)

Different types of structures were obtained when the methyl groups attached to aluminum were replaced by the slightly bulkier ethyl groups. Two products resulted from the reaction of diethylaluminum phenylethynide with an excess of diethylaluminum hydride, which could be separated by repeated recrystallization (Eq. (5)) [68]. The orange-red main product (36% yield) was identified as the open cluster **8** which has only seven aluminum atoms in its molecular core. The structure of the cluster may be derived from that one of the preceding octaaluminum compounds **4** to **7** when one of the vertices of the Al_8 cube remains unoccupied. Two C=C double bonds are located at the open site of the cluster, and a hydrogen atom bridges an open triangle of aluminum atoms. Clearly this product results from an incomplete hydroalumination, and just one step including the formal attack of an aluminum dihydride seems to be missing to complete the Al_8 cube. Indeed, we were able to generate the octaaluminum compound (**9**) similar to **4** and **5** by the treatment of **8** with an excess of diethylaluminum hydride in the heat in 70% yield (Eq. (5)) [65]. This reaction gives a very nice insight into the mechanism of the formation of those carbaalane clusters by stepwise hydroalumination and condensation processes. While so far all clusters could be derived from a cube of aluminum atoms, the second product (**10**, Eq. (5)) represents a completely new type of carbaalane clusters [68]. It comprises seven aluminum and four carbon atoms in a kind of a *closo* arrangement and has an alkynido ligand and a hydrogen atom bridging opposite edges of the cluster core. Compounds **8** and **10** are isomers, and prolonged heating of pure samples of **8** to 110 °C gave the quantitative rearrangement to **10**:



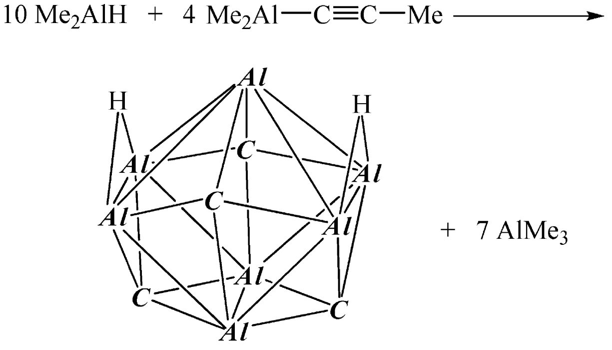
8: ***Al*** = AlEt; ***C*** = CCH$_2$Ph

10: ***Al*** = AlEt; ***C*** = CCH$_2$Ph

9: ***Al*** = AlEt; ***C*** = CCH$_2$Ph

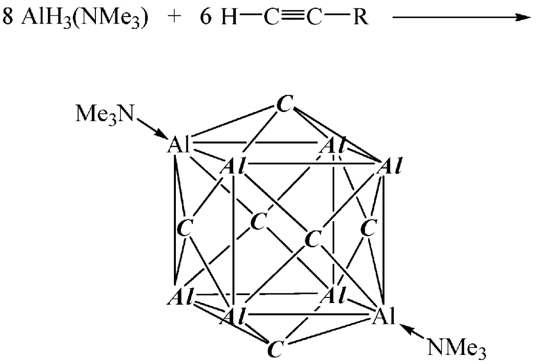
(5)

Treatment of Me$_2$Al–H with Me$_2$Al–C≡C–Me afforded a similar Al$_7$ cluster (**11**) in 63% yield (Eq. (6)) [65]. The bridging situation in this cluster differs from that one of compound **10**, because two hydrogen atoms bridge the opposite Al$_2$ couples. The Al$_8$ cluster compound **5** mentioned before (Eq. (3)) was isolated as a by-product:



11: ***Al*** = AlMe; ***C*** = CCH$_2$CH$_3$ (6)

Later on an alane amine adduct (AlH$_3$·NMe$_3$) was employed instead of dialkylaluminum hydrides by Roesky and co-workers (Eq. (7)) [69,70]. The reactions with alkynes H–C≡C–R yielded carbaalane clusters by hydrogen release and hydroalumination. The structures of the products (**12** and **13**) are similar to those of the compounds **4** and **5** and contain cubes of eight aluminum atoms. Six aluminum atoms bear terminal hydrogen atoms, but two are coordinated by trimethylamino ligands. All six faces of the central cubes are bridged by CCH$_2$R groups:



C = CCH$_2$R; ***Al*** = AlH
12: R = Ph
13: R = CH$_2$SiMe$_3$ (7)

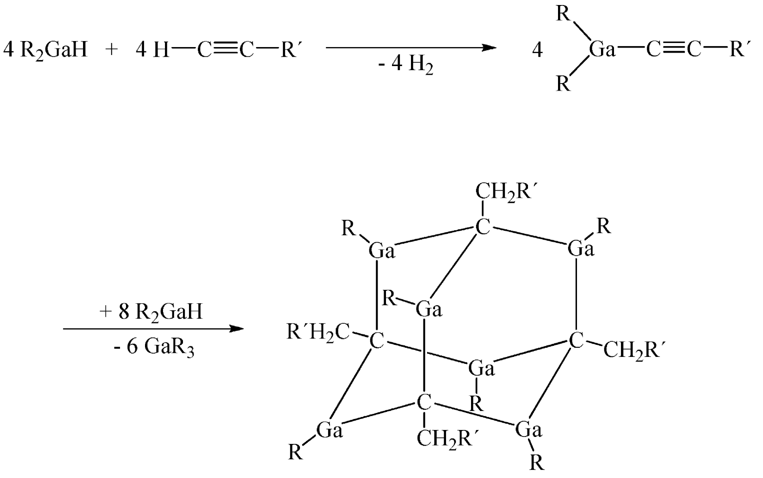
Only the most important aspects of the physical properties of these clusters should be discussed [71–73]. Both Al$_7$C$_4$ clusters are the thermally most stable ones and decompose only above 260 °C. The remaining carbaalanes have decomposition points between 100 and 200 °C. These differences correlate to the electronic configuration of these clusters. As was shown by quantum chemical calculations [65] they possess a delocalized bonding situation. Although we must be very careful with a comparison of these clusters with carbaboranes, some of these fit quite well into the concept of Wade developed for the description of boranes or carbaboranes. Accordingly the Al$_8$ compounds possessing a bridging hydrogen atom have an *arachno* configuration (16 cluster electron pairs and 13 vertices), while the most thermally stable Al$_7$C$_4$ clusters have a *closo* configuration (12 electron pairs for 11 vertices). Interestingly, the core structure of the Al$_7$C$_4$ clusters is almost identical to that one of the *closo*-borate [B$_{11}$H$_{11}$]$^{2-}$ [74,75] and has a four-membered cycle at the bottom, a six-membered cycle in a boat conformation in the middle and an atom of a high connectivity of seven at the top. The Al–C and Al–Al distances are quite similar in all compounds. Owing to the high connectivity of five of the cluster carbon atoms the Al–C distances in the clusters (200–215 pm) are longer than those of the terminal Al–C bonds. The most Al–Al contacts are between 260 and 280 pm. The shorter values confirm strong multicenter bonding interactions in the clusters and are in the range characteristic of 3c–2e Al–X–Al bonds ($X = H, CH_3$) [76–78] or of Al–Al single bonds [79,80]. Resonances at a relatively low field ($\delta = 18$–36) in the ^{13}C NMR spectra are indicative for the cluster carbon atoms. Further unusual low field shifts (up to $\delta = 3.2$) occur for the protons of the CH_2 groups attached to the cluster carbon atoms. The totally symmetric breathing mode of the clusters was determined for the compounds **4** and **11** at about 325 cm^{-1} in the Raman spectra.

These clusters are relatively inert. The formation of an adduct with THF was observed for one compound only (**5**). Two THF ligands in the product are attached to opposite aluminum atoms of the hydrogen bridged face [67]. Surprisingly, the treatment of some clusters with equimolar quantities of the acids $H[BF_4]$ or HCl dissolved in diethyl ether did not result in an attack on the clusters by cleavage of inner Al–C bonds. Instead, the bridging hydrogen atom of the open cluster **8** was replaced selectively by a fluorine atom, and methane was released upon the reaction of compound **4** with HCl yielding a carbaalane possessing a terminal Al–Cl group, which may be suitable for an application in interesting secondary reactions [81].

3.2. Hydrogallation of gallium alkynides—synthesis of heteroadamantane-type molecules

Another type of structures resulted from the similar reactions of dialkylgallium hydrides with dialkylgallium alkynides. These experiments were not trivial at all because with the exception of few sterically very encumbered aryl derivatives [82–84] these hydrides R_2Ga–H were thought to be unstable. Before we started with our investigations only the dimethyl species was known in literature as a thoroughly characterized compound [85,86]. In a series of experiments we recently found two facile routes for the preparation of these important starting compounds with a broad variety of different alkyl substituents [87,88]. Apart from the longest known dimethyl derivative, these hydrides are stable at room temperature in a pure form and can be handled in boiling *n*-hexane without decomposition for many hours. They form dimeric or trimeric formula units by Ga–H–Ga 3c-bonds depending on the bulkiness of the alkyl groups attached to the gallium atoms. Only di(*tert*-butyl)gallium hydride deviates from that scheme and possesses a trimeric formula unit in the solid state despite the bulkiness of its substituents, which may be caused by the packing of the molecules with the *tert*-butyl groups approaching an ideal hexagonal arrangement [87].

The gallium alkynides were generated in situ by treatment of the alkynes R–C≡C–H with dialkylgallium hydrides. Hydrogen evolution showed the successful formation of the alkynides in the first step. They were directly consumed by the excess of the hydride when the mixtures were slowly warmed to room temperature (Eq. (8)) [89]. The formation of trialkylgallium compounds was verified by their characteristic NMR resonances. Thus, once again condensation occurred. Three products were obtained in a crystalline form (**14–16**), two of these could be characterized by crystal structure determinations. A schematic drawing of the molecular structures is depicted in Eq. (8). Compounds analogous to the carbaalanes were not formed. Instead, heteroadamantane-type molecules $(GaR)_6(C–CH_2R)_4$ (Fig. 2) resulted which had localized Ga–C single bonds and six coordinatively unsaturated tricoordinated gallium atoms in the bridging positions. The four carbon atoms were attached to three gallium atoms and the terminal alkyl groups. The most interesting feature of the NMR spectroscopic characterization was the unusual low field shift observed for the carbon atoms in the cages ($\delta = 95$), which may be caused by the coordination with three relatively electropositive and unsaturated metal atoms and by low-lying excited states. Similar observations were reported for the analogous hexabora heteroadamantanes [90–94]:



14: R = Et; R′ = Me
15: R = Et; R′ = Pr
16: R = Me; R′ = Me (8)

Different structural motifs and bonding situations were realized by hydroalumination and hydrogallation of the corresponding element alkynides. While carbaalanes possessing a delocalized bonding and high connectivities at their constituents were formed with aluminum, heteroadamantane cages with localized Ga–C bonds and coordinatively unsaturated metal atoms resulted for the element gallium. These differences may depend on the quite different polarities of the element–carbon bonds. The relatively low electronegativity of aluminum causes a stronger charge separation in Al–C compared to Ga–C bonds, which favors the higher connectivities in the aluminum case and, hence, the effective delocalization of electron density. This situation may be compared to the formation of relatively stable dimeric formula units of trimethylaluminum [76,77]. In contrast, trimethylgallium is monomeric in solution and in the gas phase, and only in the solid state tetrameric aggregates may be derived from weak intermolecular interactions [95].

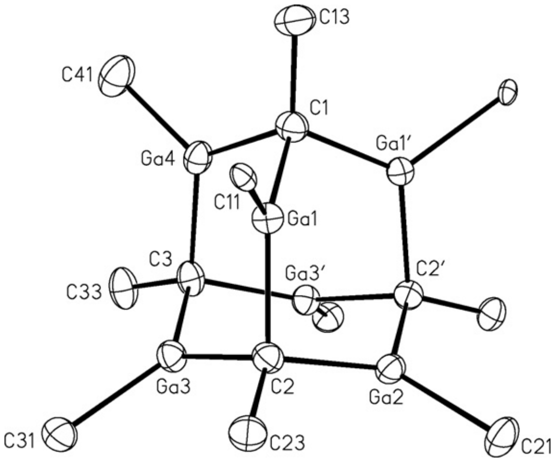


Fig. 2. Molecular structure of compound **14**.

The hydroalumination and hydrogallation reactions discussed so far were highly regioselective. The aluminum and gallium atoms of the hydrides attacked exclusively those carbon atoms of the starting ethynides which were already bonded to a Group 13 element. The preferred attack at this position is clearly a consequence of charge separation, and the positively charged aluminum or gallium atoms of the hydrides approach the most negatively charged carbon atoms of the C≡C triple bonds. Interestingly, the hydroalumination of aluminum alkynides proceeds slower than the corresponding additions of Al–H bonds to the triple bonds of alkyl or aryl alkynes (see below). The reverse is true for hydrogallation reactions. Gallium alkynides react already at room temperature with the corresponding hydrides, while boiling *n*-hexane is required for organic alkynes. The reason for that different behavior is not quite clear yet. However, the relatively low reaction rates of aluminum alkynides may depend on the high stability of their dimeric formula units, which prevent the dissociation required as an initiating step at mild conditions and as a consequence block an easy attack of the hydride. All these reactions were observed for aluminum and gallium compounds bearing small substituents such as methyl or ethyl groups. A complicated mixture of products resulted for isopropyl groups attached to aluminum. The corresponding carbaalane was formed in trace quantities as detected by

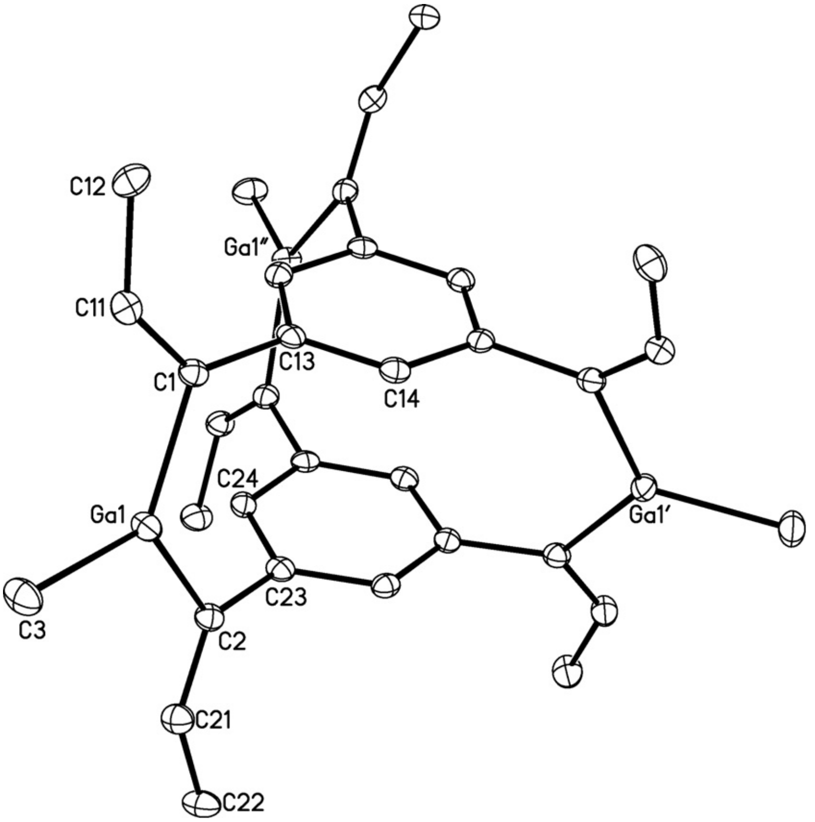


Fig. 3. Molecular structure of compound **18**.

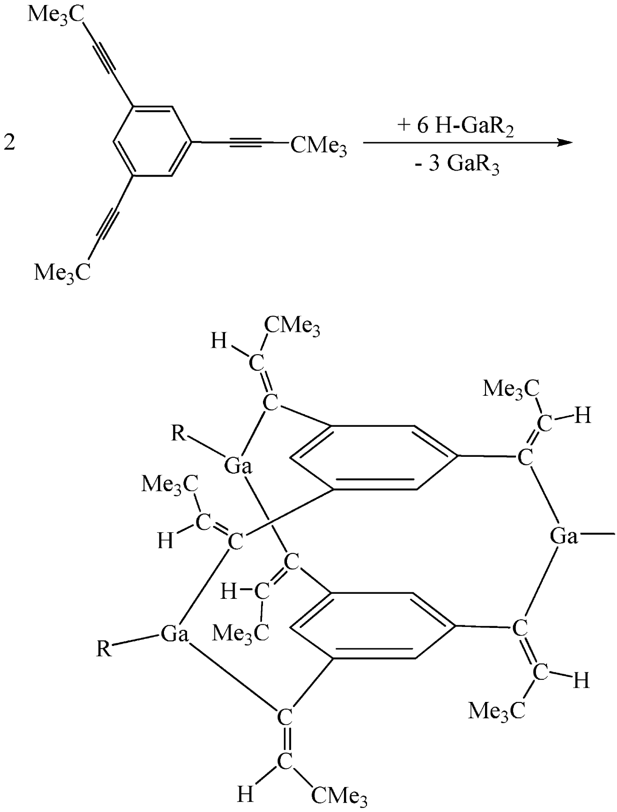
NMR spectroscopy. It could not be isolated in a pure form [67]. Also *tert*-butyl compounds gave a mixture of unknown products, which owing to the NMR spectroscopic characterization did not contain a carbaalane derivative [67]. It is not clear whether hydroalumination occurred at all. Furthermore, only alkyl- or aryl-substituted ethynes gave carbaalanes. Trimethylsilylethyne gave an unclear reaction course which may depend on the competition with respect to the directing properties of aluminum and silicon atoms.

4. Hydroalumination and hydrogallation reactions of phenyl-centered alkynes

4.1. Hydrogallation reactions with tert-butylethynylbenzenes—addition versus condensation

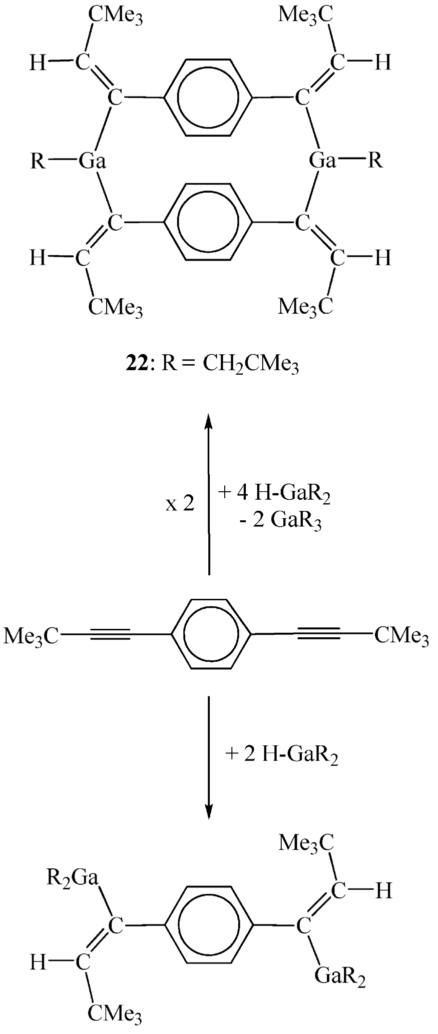
Trimethylsilyl or *tert*-butyl groups as the second substituents attached to the C≡C triple bonds of phenylethynes gave completely different reaction courses upon the addition of Al–H or Ga–H bonds. Therefore, these topics are treated separately. Hydrogallation seems to be more selective compared to hydroalumination. The first one requires elevated temperatures and is usually conducted in boiling *n*-hexane over 16 h, while the second one proceeded quantitatively at room temperature in short times. This behavior may depend on the different polarities of the element–hydrogen groups with the stronger charge separation observed for the Al–H bonds.

The formation of the corresponding trialkylgallium compounds GaR_3 was observed in all reactions of the trialkynylbenzene 1,3,5-$(Me_3C–C≡C–)_3C_6H_3$ with various dialkylgallium hydrides R_2GaH (R = Et, *n*Pr, *i*Pr, CH_2*t*Bu, *t*Bu) [96,97]. Thus, once more condensation occurred as the main process (Eq. (9)). Although the alkenyl compounds were directly formed in a rather selective way, some of them could be isolated in a low yield only. Better results were prevented by the high solubility of the products **17**–**21** in non-polar solvents and by the considerable difficulties to completely remove the trialkylgallium by-products. Only dimethylgallium hydride could not be employed, because it decomposed under the conditions required for successful hydrogallations. Three compounds were characterized by crystal structure determinations (**17**, **18** and **20**). As schematically shown in Eq. (9) [3,3,3]cyclophane-type molecules were formed which had three C–Ga–C groups including three coordinatively unsaturated gallium atoms in the bridging positions (Fig. 3). In a first step, these compounds may originate from the hydrogallation of the three ethyne groups to yield alkenyl derivatives possessing intact dialkylgallium groups. The gallium atoms attacked exclusively those carbon atoms which were bonded to the benzene rings, and the gallium and vinyl hydrogen atoms adopted always a *cis* arrangement across the C=C double bonds. A secondary reaction may involve the intermolecular release of the corresponding trialkylgallanes and the formation of the cages. In view of results discussed later on, which comprise the isolation of persistent addition products, we prefer that particular mechanism over a preceding dismutation equilibrium of the hydride to yield trialkylgallium and alkylgallium dihydride, which subsequently could give double hydrogallation and bridging of the benzene rings. The distances between the aryl groups of the cyclophanes are 340–360 pm, which is in a normal range of van der Waals interactions [98]. The rings are almost ideally coplanar, however, they are slightly rotated with respect to each other by rotation angles of 3–14°. The C=C bond lengths are in the expected range of about 134 pm and do not require any further discussion. Same holds for the other structural parameters. Vinyl protons and hydrogen atoms of the benzene rings have resonances in a narrow range of the ^{1}H NMR spectrum at about $\delta = 6.2$:



17: R = Et
18: R = *n*Pr
19: R = *i*Pr
20: R = CH_2CMe_3
21: R = CMe_3 (9)

As discussed later on, bulky substituents prevent the release of trialkylaluminum in comparable hydroalumination reactions by steric shielding. In these cases, the dialkylaluminum groups cannot approach close enough to allow the exchange of alkyl or alkenyl groups via bridging carbon atoms. Hence, persistent addition products resulted containing dialkylaluminum groups attached to the C=C double bonds. In view of these results we were surprised that similar addition products were isolated from the reaction of the dialkynyl compound 1,4-di(*tert*-butylethynyl) benzene with dialkylgallium hydrides bearing small substituents. Condensation with the release of the corresponding trialkylgallium derivative and formation of a [3,3]cyclophane (**22**) similar to compounds **17**–**21** was only observed upon treatment of this dialkyne with dineopentylgallium hydride (Eq. (10)) [99]. In contrast, trialkylgallium derivatives could not be detected in the reactions of the less sterically shielded dialkylgallium hydrides $Et_2Ga–H$ and $nPr_2Ga–H$ (Eq. (10)) [97,99]. The simple addition products **23** and **24** were isolated, which are stable in solution at room temperature. Even in boiling *n*-hexane or in benzene at 50 °C we did not find any indication of condensation. Di(isopropyl)gallium hydride with an intermediate steric shielding gave at least two different products of unknown constitution, which could not be separated by recrystallization [99]. However, NMR spectroscopic characterization of the raw product clearly excluded the formation of a mixture of the addition and cyclophane-type molecules. Also di(*tert*-butyl)gallium hydride did not yield a pure product. The NMR chemical shifts of the addition products **23** and **24** are almost identical to those of the cyclophane compounds and do not allow a clear differentiation between both types of molecules. Only the integration ratios of the ^1H NMR spectra gave a clear hint on different reaction courses. Hydrogallation reactions with the monoalkyne $Me_3C–C≡C–C_6H_5$ proved to be difficult. Pure compounds were obtained only with di(*n*-propyl)- and diisopropylgallium hydride, but they could not be characterized by crystal structure determinations. NMR spectroscopic data revealed the selective *cis* addition without any secondary reaction:



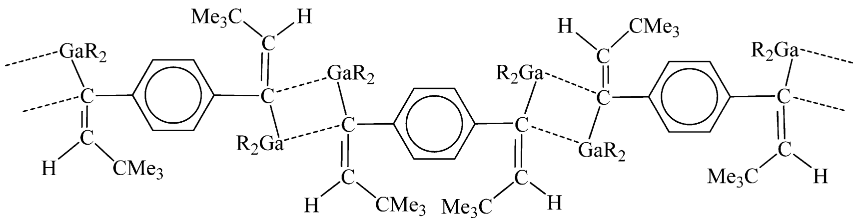
22: R = CH_2CMe_3

23: R = Et
24: R = *n*Pr (10)

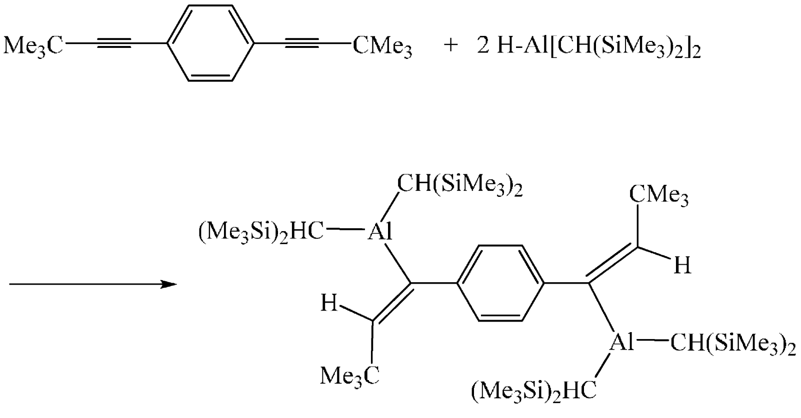
The formation of the persistent addition products (**23** and **24**) with small substituents attached to the gallium atoms showed that steric shielding cannot be the only reason for their surprising stability. Compounds **23** and **24** crystallize isostructural and form one-dimensional coordination polymers by relatively short intermolecular interactions between the gallium atoms and negatively charged alkenyl carbon atoms of neighboring molecules. A schematic drawing of a part of the chain is depicted in Scheme 2. It shows the intermolecular interactions and the different symmetry of the molecules which alternately are localized on crystallographic centers of symmetry and twofold rotation axes. Four-membered Ga_2C_2 heterocycles are formed with Ga–C distances of about 205 and 255 pm. This singular structural motif may provide the key for an understanding of the different behavior of the hydrogallation products. The four-membered Ga_2C_2 heterocycles include exclusively carbon atoms of C=C double bonds, while the alkyl groups are in terminal positions. An exchange process cannot start from such a particular situation. Thus, if the formation of those rings is strongly favored compared to a transition state having an alkyl group in the bridging position, the addition products remain stable as in the case of the dialkenyl compounds **23** and **24**. However, when the approach of the gallium atoms via two alkenyl bridges is prevented or at least hindered by steric shielding as in the case of the 1,3,5-trialkenyls, the exchange may be initiated by the occurrence of transient alkyl bridges.

4.2. Hydroalumination reactions with tert-butylethynylbenzenes

As mentioned before, hydroalumination reactions with *tert*-butylethynylbenzenes proved to be less selective than the corresponding additions of Ga–H bonds. Thus, pure compounds were isolated in few cases only. The quantitative formation of hydroalumination products was observed for the dialkylaluminum hydride $H–Al[CH(SiMe_3)_2]_2$ [16,100] bearing bulky $CH(SiMe_3)_2$ groups. Pure products (**25** and **26**) were isolated in more than 85% yield for the alkynes 1,4-di(*tert*-butylethynyl)benzene and *tert*-butyl(phenyl)ethyne (Eqs. (11) and (12)) [101]. Owing to the NMR spectroscopic characterization also the trialkyne 1,3,5-tri(*tert*-butylethynyl)benzene afforded the corresponding addition product almost quantitatively, however, we were not able to purify it by recrystallization. Caused by the effective steric shielding both compounds **25** and **26** are thermally quite stable, and the corresponding trialkylalane could not be detected in trace quantities after prolonged heating in solution. In accordance with the results obtained on hydrogallation, the aluminum atoms are exclusively bonded to those carbon atoms of the ethenyl moieties which are also attached to the benzene rings, and the Al and H atoms adopt a *cis* arrangement across the C=C double bonds:

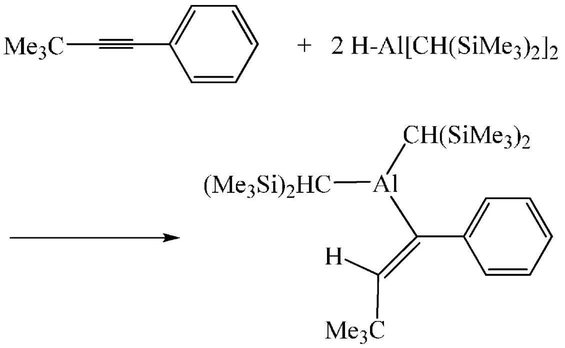


Scheme 2. Schematic drawing of the coordination polymer of **23** and **24**.



25

(11)

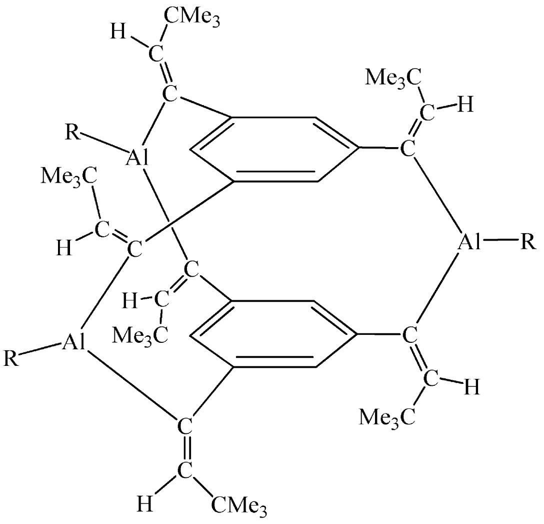


26 (12)

In contrast, the reactions of alkynes with dialkylaluminum hydrides bearing smaller substituents were less successful. Inseparable mixtures of unknown products were obtained with mono- and dialkynes. The trialkyne 1,3,5-tri(*tert*-butylethynyl)benzene gave a cyclophane-type molecule (**27**) by condensation and release of trineopentylaluminum in about 65% yield when it was treated with dineopentylaluminum hydride (Eq. (13)) [102]. Smaller substituents often gave insoluble products probably by the formation of coordination polymers similar to the gallium compounds **23** and **24**. Di(*tert*-butyl)aluminum hydride yielded a cyclophane derivative (**28**). However, despite systematic attempts to improve the conditions the reproducibility was rather poor. Unknown by-products were formed in different concentrations, and the yields of the isolated solid product varied between 10 and 80%. Interestingly, **28** gave an adduct upon treatment with THF, and each of the bridging aluminum atoms of the product is coordinated by a THF molecule [102]. This reaction shows the potential capability of those compounds to act as effective polyacceptors:

$$2\ \ 1,3,5\text{-}(Me_3C\text{-}C{\equiv}C\text{-})_3C_6H_3\ +\ 6\ H\text{-}AlR_2\ \xrightarrow[-\ 3\ AlR_3]{}$$

$$(R = CMe_3,\ CH_2CMe_3)$$

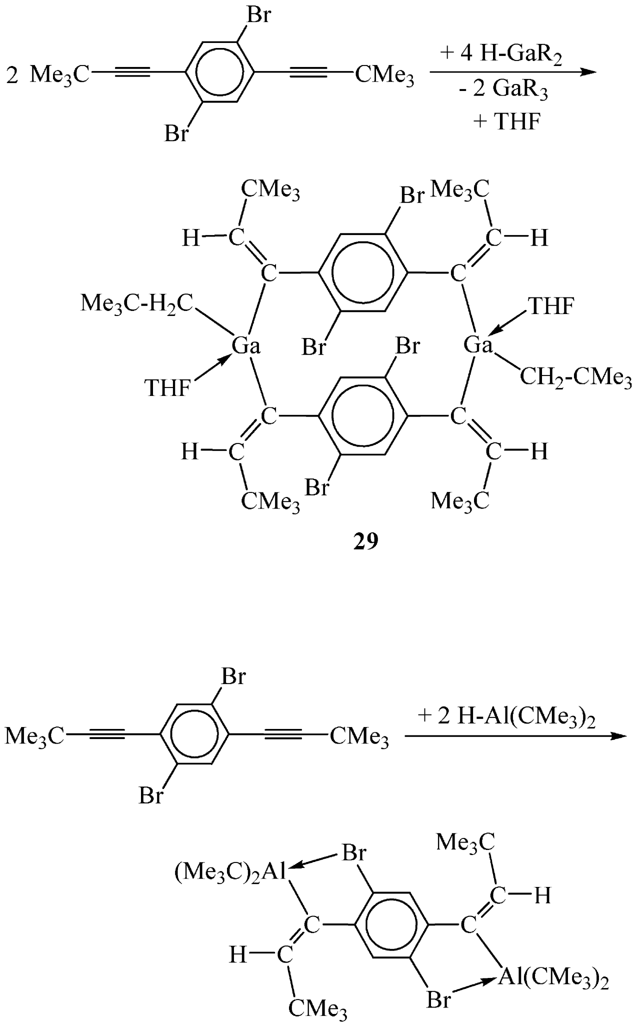


27: R = CH_2CMe_3
28: R = CMe_3

$$\xrightarrow[(R\quad CMe_3)]{+\ 3\ THF}\ [Al(THF)(CMe_3)]_3[C_6H_3(C\quad CH\text{-}CMe_3)_3]_2 \qquad (13)$$

4.3. Reactions with 1,4-dibromo-2,5-di(tert-butylethynyl)benzene—influence of weak intramolecular interactions

Only few experiments were conducted in that direction, which, however, gave an interesting result worth to be mentioned here. Dineopentylgallium hydride and the bromine-substituted alkynylbenzene afforded the expected condensation reaction by the release of trineopentylgallium and the formation of the corresponding cyclophane molecule (**29**, Eq. (14)) [103]. Owing to its extremely high solubility in non-polar solvents the crystalline product was isolated as a THF adduct only. However, the NMR spectroscopic characterization of the raw product clearly indicated the formation of the cyclophane before the donor solvent was added. Interestingly, the expected release of tri(*tert*-butyl)aluminum was not observed when the dibromobenzene starting compound was treated with di(*tert*-butyl)aluminum hydride (Eq. (14)) [103]. Crystal structure determination of **30** revealed an interesting and singular interaction between the coordinatively unsaturated aluminum atoms and the halogen atoms attached to the phenyl ring. The Al–Br distances are expectedly longer than those detected in compounds having polar covalent Al–Br bonds such as in dimeric dialkylaluminum bromides (270.3 pm *versus* about 240 pm). However, they are much shorter than the sum of the van der Waals radii and short enough to indicate a significant bonding interaction. To the best of our knowledge, similar complexes between dialkylaluminum groups and aryl halides have not been observed before. Such complexes were postulated in the mechanisms of aluminum trihalide catalysed substitutions of aromatic systems. Obviously, that interaction is stable enough to prevent any secondary reaction by coordinative saturation of the aluminum atoms. Alkylgallium derivatives are known to be weaker acceptors than the corresponding organoaluminum compounds. Thus, despite a quite similar molecular arrangement the Ga–Br interaction does not seem to be strong enough to effectively saturate the coordination sphere of gallium and to prevent the condensation by the approach of another molecule and the exchange of ligands. These results show that the courses of hydroalumination and hydrogallation reactions are very sensitive towards the respective conditions and depend strongly on influences such as solvent effects or donor–acceptor interactions. These circumstances make it more difficult to provide a generally acceptable reaction scheme:

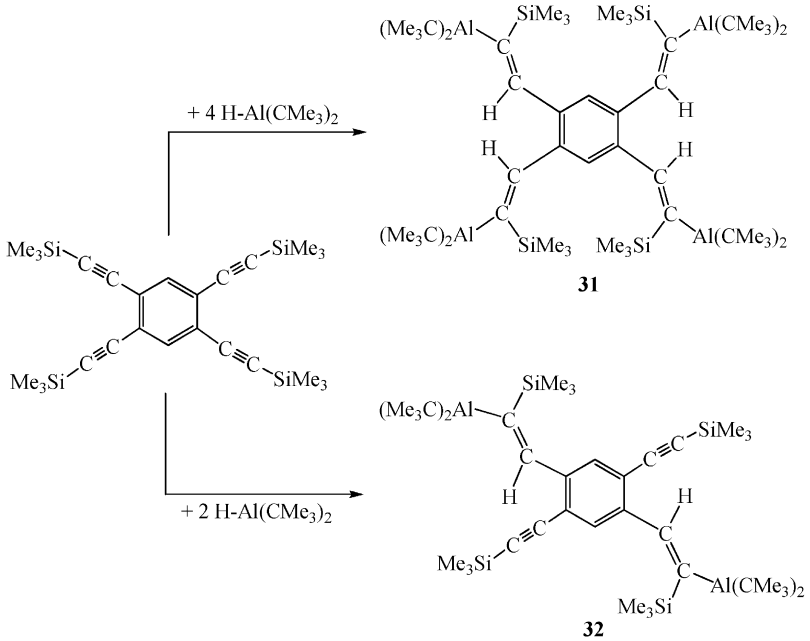


29

30 (14)

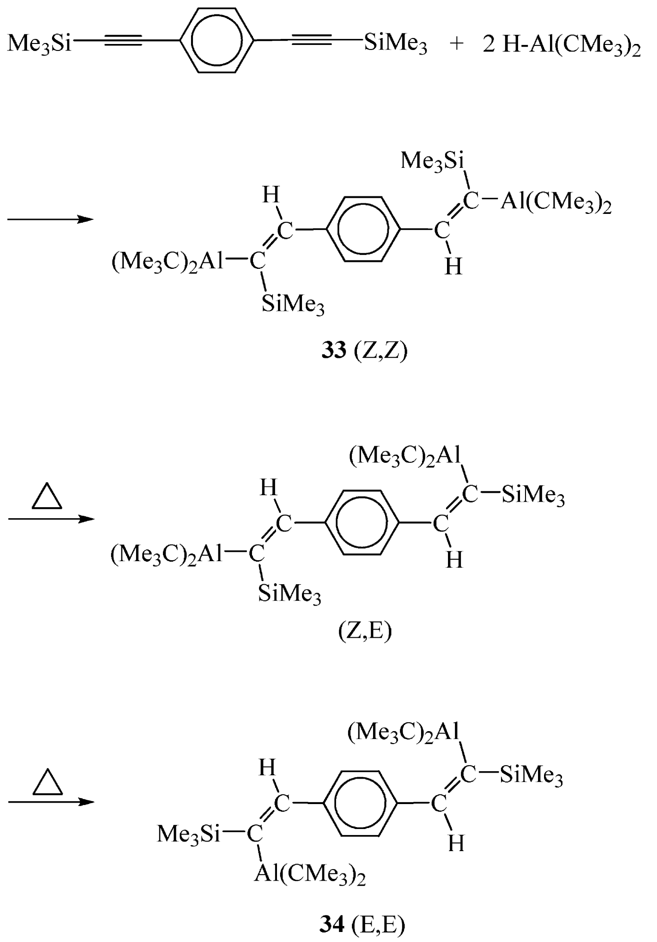
4.4. Hydroalumination reactions with trimethylsilylethynylbenzenes—stable addition products and cis/trans isomerization

Four different alkynylbenzene derivatives having terminal trimethylsilyl groups and up to four C≡C triple bonds were employed in these investigations. Only di(*tert*-butyl)aluminum hydride gave reasonable results, while all experiments involving sterically less shielded hydrides yielded complicated mixtures of products or insoluble compounds of unknown constitution. All reactions occurred already at room temperature. The tetraalkyne 1,2,4,5-tetrakis(trimethylsilylethynyl)benzene gave two crystallographically characterized products depending on the stoichiometric ratio of the starting compounds (Eq. (15)) [104]. Complete hydroalumination afforded the tetraaluminum compound **31** in a high yield which has four coordinatively unsaturated aluminum atoms in one molecule and may be an excellent polyacceptor of donor molecules. A molar ratio of 1 to 2 (alkyne to hydride) afforded product **32**, which has two opposite alkenyl (C=C) and alkynyl groups (C≡C) in one molecule. A second compound was formed which owing to NMR data may be described by the hydroalumination of two neighboring alkynyl groups in 1,2-position at the benzene ring. Regrettably it could not be isolated in a pure form. The aluminum and hydrogen atoms of the alkenyl groups adopted always a *cis* arrangement, and the metal atoms attacked exclusively those carbon atoms which are also attached to the trimethylsilyl groups. This position is favored essentially by two reasons. It has a partial negative charge in the starting alkyne owing to the electronegativity difference between carbon and silicon, and the positively charged aluminum atoms may preferably interact with that particular carbon atom. Furthermore, bonding to the electropositive aluminum atoms in the product causes an additional negative charge at this position, which is best stabilized through hyperconjugation with the trimethylsilyl groups:



(15)

The dialkyne 1,4-bis(trimethylsilylethynyl)benzene yielded a similar product (**33**, Eq. (16)) by complete hydroalumination of both C≡C triple bonds [105]. Pure samples of **33** showed a slow *cis*/*trans* isomerization at elevated temperature which could be monitored by an NMR experiment and which yielded the thermodynamically favored [4] *trans* product. The intermediate compound having one alkenyl group in the original *cis* configuration and the other one in the rearranged *trans* form was identified unambiguously by its characteristic NMR data [105]. The completely rearranged product **34** was isolated in a preparative scale and also characterized by crystal structure determination [105]. The true mechanism of the rearrangement is not yet clear and some speculative suggestions are given in the literature [4]. These compounds having two or even more coordinatively unsaturated aluminum or gallium atoms in one molecule are potentially useful to act as chelating Lewis-acids. However, as easily can be seen from the schematic drawings in Eqs. (15) and (16), only the rearranged all-*trans* products are really suitable to bind donor molecules in a chelating manner. Thus, *cis*/*trans* isomerization is essential for the application of these compounds as effective receptors in secondary processes:



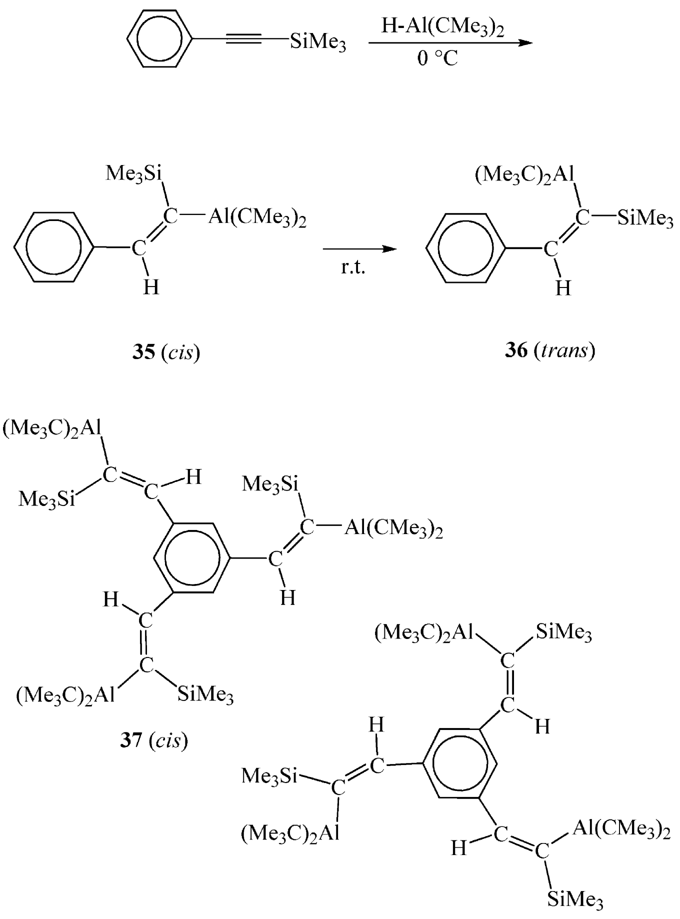
33 (Z,Z)

(Z,E)

34 (E,E)

(16)

The corresponding monoalkyne behaved different and gave the rearranged *trans* product (**36**) already at room temperature and daylight [106]. The *cis* product (**35**), which may represent the first step of all addition reactions, was isolated later on upon thorough work-up of the reaction mixture in the cold and was characterized by its characteristic NMR data (Eq. (17)). The trialkyne yielded the all-*cis* product **37** (Eq. (17)), which after purification was stable in solution and did not show *cis*/*trans* isomerization even upon warming to 60 °C. Instead decomposition occurred. However, when the raw product was stirred in *n*-pentane for several days a 1 to 1 mixture of the all-*cis* (**37**) and all-*trans* products (**38**) was obtained. Compound **38** was isolated from that mixture in a crystalline form and characterized by crystal structure determination. A catalytic influence of specific impurities on the rearrangement processes may be derived from these observations, and intermolecular interactions may favor the formation of the *trans* products. Accordingly, the sterically less shielded monoalkenyl derivative forms the less stable *cis* product. The different spectroscopic findings of the isomers are quite similar for all hydroalumination and hydrogallation products. We will discuss these differences only once in conjunction with the corresponding gallium compounds. Essential results of crystal structure determinations are almost identical and do not show any unusual feature. We therefore abstain from a detailed discussion of any structural parameter here and in the following chapters:



35 (*cis*)

36 (*trans*)

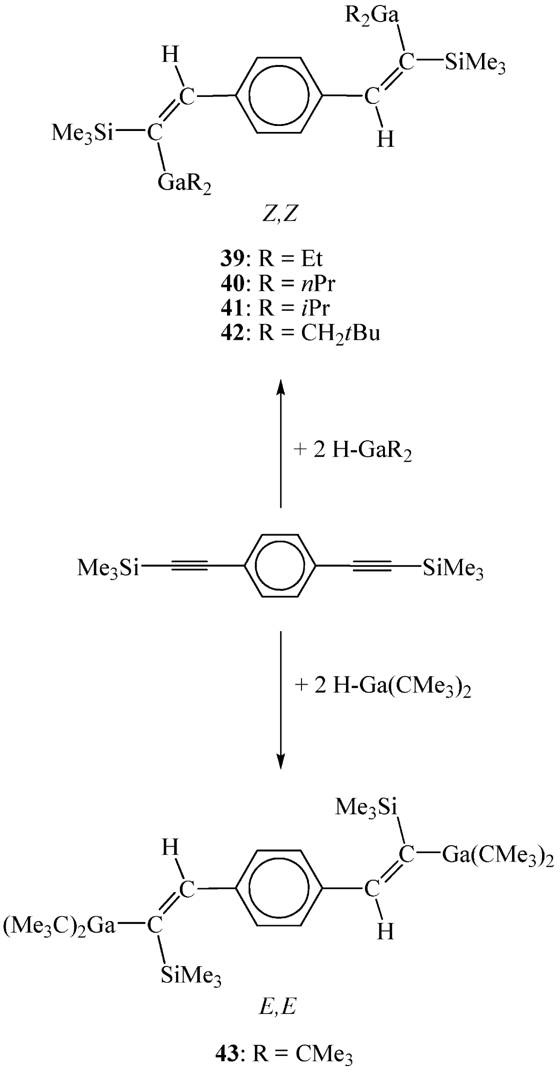
37 (*cis*)

38 (*trans*)

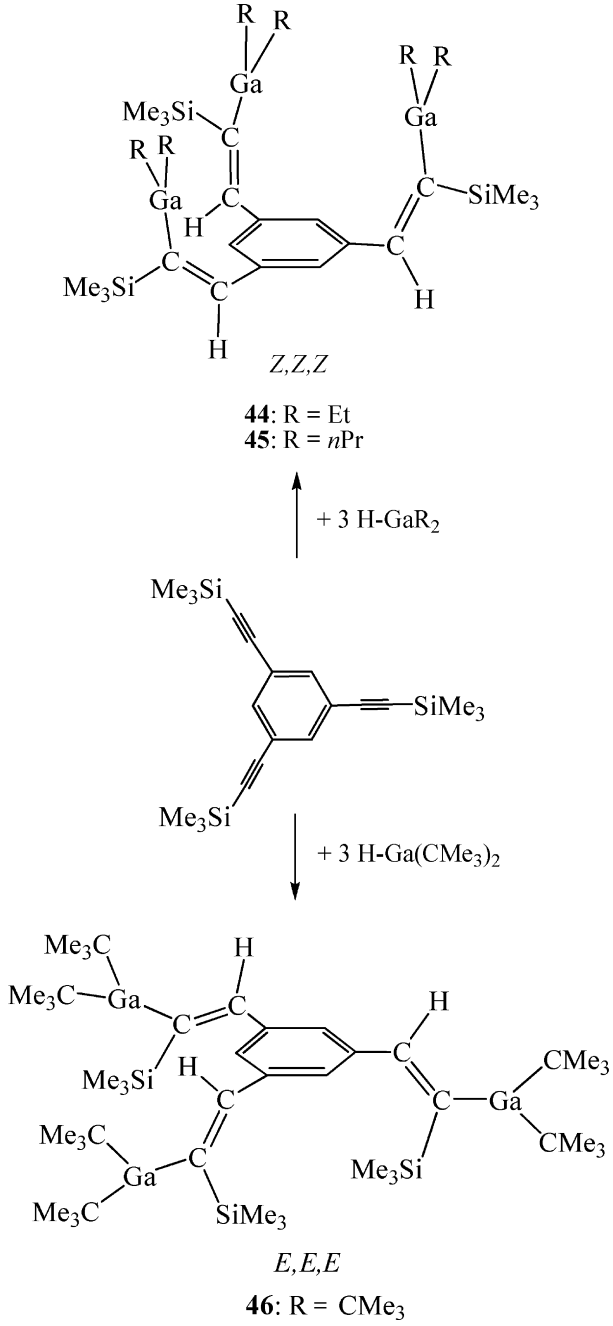
(17)

4.5. Hydrogallation reactions with trimethylsilylethynylbenzenes

Once more hydrogallation was more selective and yielded a broader spectrum of isolated and completely characterized compounds than hydroalumination. Thus, the discussion of particular properties is based on the results of more systematic investigations. The dialkyne, 1,4-bis(trimethylsilylethynyl)benzene, and the trialkyne, 1,3,5-tris(trimethylsilylethynyl)benzene were treated with the stoichiometric quantities of the dialkylgallium hydrides R_2Ga–H (R = Et, *n*Pr, *i*Pr, CH_2*t*Bu, *t*Bu; molar ratios 1 to 2 or 1 to 3, respectively) in refluxing *n*-hexane to obtain the addition products **39**–**46** almost quantitatively (Eqs. (18) and (19)) [107]. However, the high solubility of all compounds in non-coordinating solvents even at low temperatures hindered the purification and quantitative isolation of some of these products by recrystallization. Secondary reactions with the release of trialkylgallium derivatives and the precipitation of solids of unknown constitution were observed only upon treatment of the trialkyne with diisopropyl- and dineopentylgallium hydride. The expected *cis* arrangement of gallium and hydrogen resulted only for both reactions of di(*tert*-butyl)gallium hydride (compounds **43** and **46**). The configuration of these products is very stable, and a rearrangement to give the *trans* forms was not observed even after prolonged heating. In contrast, *trans* configurations at the C=C double bonds were obtained directly with all dialkylgallium hydrides bearing smaller substituents. The *cis* products were not detected in the NMR spectra as intermediates, and even the very slow reaction of diisopropylgallium hydride with the dialkyne at room temperature over several weeks did not give any hint for the formation of that isomer. Surely, *cis* addition is a reasonable assumption to describe the first step of all reactions, however, the rearrangement seems to be rather fast for the sterically less shielded compounds. These observations give further evidence that intermolecular interactions influence the *cis*/*trans* isomerization. The trialkenyl compounds **44** and **45** adopt singular chalice-like molecular structures (Fig. 4). They have three coordinatively unsaturated, tricoordinated gallium atoms at their inner surfaces and are nicely preorganized to act as chelating Lewis-acids:



(18)



(19)

Four compounds were characterized by crystal structure determinations. But the constitution with intact GaR_2 groups attached to the C=C double bonds can easily be derived for all products from the very indicative integration ratios of the ^1H NMR spectra. In accordance with the hydroalumination of trimethylsilylethynes reported before, the gallium atoms of compounds **39**–**46** are exclusively attached to those carbon atoms of the ethenyl units which also bear the trimethylsilyl groups. As mentioned before, the sterically most shielded di(*tert*-butyl)gallium compounds **43** and **46** adopt a *cis* arrangement (*E* configuration), while all other products have a *trans* configuration (*Z* form). There are some important NMR spectroscopic observations which allow an unambiguous differentiation between both forms. The ^1H NMR resonances of the benzene

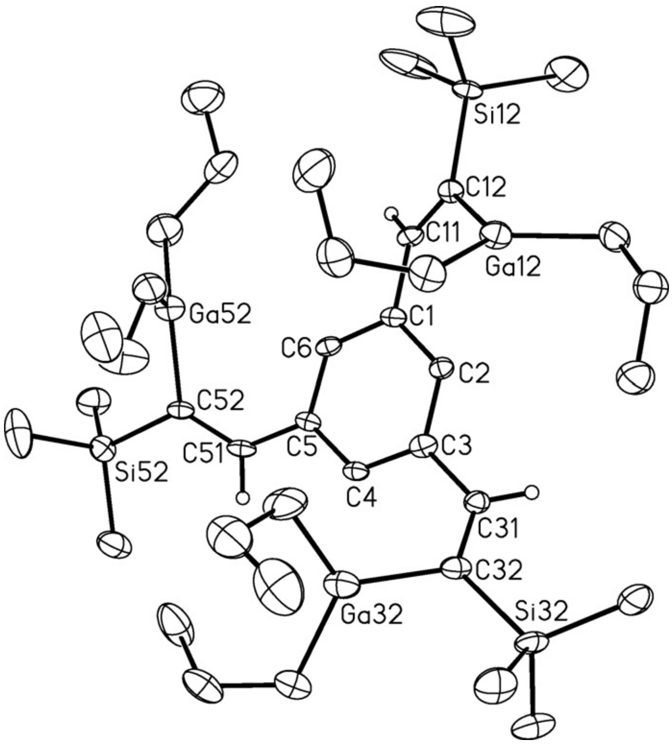
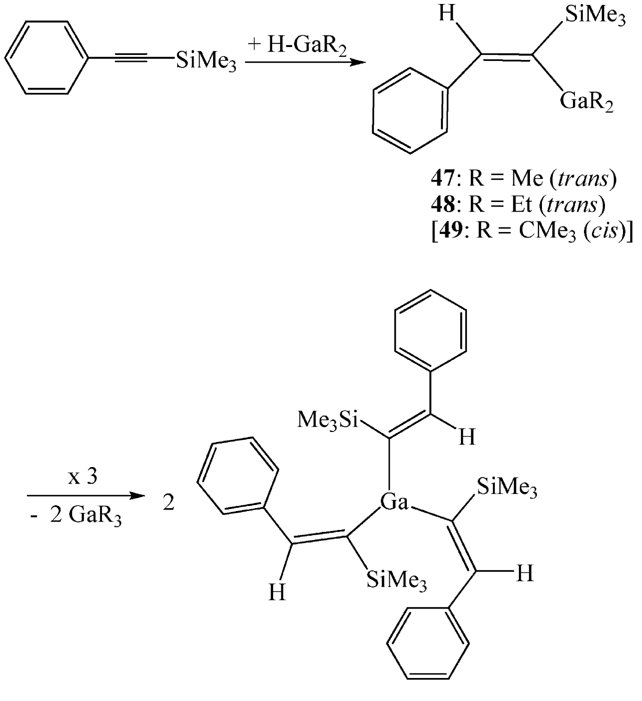


Fig. 4. Molecular structure of compound **45**.

and vinyl protons are in a very narrow range for the *cis* compounds **43** and **46** (δ = 7.4 and 7.5 on average), while larger differences of about 0.9 ppm were observed for the *trans* products (δ = 6.9 *versus* 7.8). Further important NMR data are the ^{13}C NMR shifts of the alkenyl carbon atoms attached to gallium [δ = 169–172 (*trans*) *versus* 163 (*cis*)] or the chemical shifts of the trimethylsilyl groups in the ^{29}Si NMR experiments [δ = −7 (*trans*) *versus* −13 (*cis*)]. However, the most indicative data came from coupling constants between silicon and hydrogen atoms. In accordance with the pattern of the H–H coupling across C=C double bonds, the $^3J_{Si-H}$ coupling constants were at about 12 Hz in the *trans* addition products (Si and H *cis*), while considerably larger values were detected in the *cis* addition products (Si and H *trans*, >20 Hz).

The reactions of the monoalkyne $Me_3Si–C\equiv C–C_6H_5$ with dialkylgallium hydrides $R_2Ga–H$ (R = Et, *n*-Pr, *t*Bu) proved to be more complicated [108]. In the first step the expected monoaddition products (**47**–**49**) resulted in an almost quantitative yield (Eq. (20)). They remain as highly viscous liquids after usual work-up and decomposed on attempts of distillation by the formation of GaR_3. Single crystals of **48** (R = *n*Pr) were obtained at a very low temperature. Crystal structure determination and NMR spectroscopic data verified a *trans* configuration for **47** and **48**, while a *cis* arrangement of Ga and H atoms was detected for the *tert*-butyl compound **49**. Decomposition with the precipitation of colorless crystals occurred upon storage of the products in *n*-hexane at −15 °C over several weeks. By the release of trialkylgallium a singular trivinyl compound (**50**) resulted which had three alkenyl groups attached to one gallium atom. That dismutation is accompanied by a partial rearrangement of the alkenyl groups. Two ethenyl groups retained their *trans* configuration, while the remaining alkenyl moiety adopted the *cis* configuration. This observation verifies the reversibility of the *cis*/*trans* isomerization under particular circumstances. The corresponding divinyl compounds may occur as intermediates. In one case (R = Et) we were able to identify it by NMR spectroscopy. Up to now we did not succeed in developing a reproducible method for the generation of compound **50** in a high yield and in short reaction times. A reasonable idea seemed to be the heating of the monoaddition products under vacuum in order to remove the trialkylgallium compounds from equilibrium. However, that procedure clearly failed and resulted in the formation of mixtures of unknown compounds with only small quantities of the trivinyl derivative **50**. There is a note in literature that similar decomposition pathways may occur with hydroalumination products. However, only the respective trialkylaluminum derivative was identified [48]:



47: R = Me (*trans*)
48: R = Et (*trans*)
[**49**: R = CMe$_3$ (*cis*)]

50 (2 x Z, 1 x E)

(20)

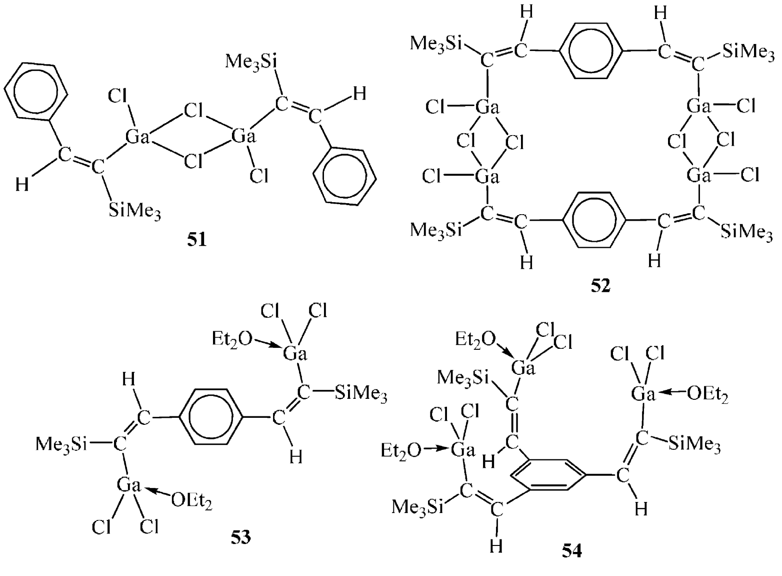
5. Hydrogallation reactions of trimethylsilylethynylbenzenes with H–GaCl$_2$—generation of chelating Lewis-acids

H–GaCl$_2$ constitutes an interesting alternative to the application of dialkylgallium hydrides reported so far. Investigations into the reactivity of that compound towards trimethylsilylethynes seemed to be promising because of several reasons. (i) The products are expected to possess several GaCl$_2$ groups in one molecule which owing to the enhanced Lewis-acidity of halogenated species compared to dialkylgallium groups should be able to act as effective chelating Lewis-acids. (ii) Interesting macrocycles or cage compounds should result via the formation of Ga–Cl–Ga bridges as long as donor solvents are not involved. (iii) The hydrogallation products containing GaCl$_2$ groups are highly functionalized and, hence, important organogallium starting compounds for the generation of secondary products by salt elimination, for instance. H–$GaCl_2$ is available on a facile route by a procedure optimized by Schmidbaur et al. some years ago [109]. They also conducted the first hydrogallation reaction with an alkene derivative [34]. Hydroalumination reactions employing the corresponding aluminum hydride H–$AlCl_2$ were also reported [110,111]. However, as usual the organoaluminum intermediates were not isolated and characterized.

Because of the low solubility of dichlorogallium hydride in hydrocarbons very dilute hexane solutions were employed (Eq. (21)) [112]. In contrast to hydrogallations with dialkylgallium hydrides these reactions succeeded already at room temperature, and only for completion boiling *n*-hexane was applied for 14 h. A clear solution was obtained only with phenyl(trimethylsilyl) ethyne, from which the colorless addition product **51** was isolated in 82% yield. 1,4-Bis(trimethylsilylethynyl)benzene gave a sparingly soluble compound (**52**), while a completely insoluble product was obtained with the trialkyne 1,3,5-tris(trimethylsilylethynyl)benzene. The last two products were both treated with diethyl ether to give the soluble etherates **53** and **54**. All compounds were characterized by crystal structure determinations. Schematic drawings of the molecular structures are depicted in Eq. (21). Compounds **51** and **52** gave dimers via Ga–Cl bridges. A singular cyclophane-type structure resulted for compound **52** which has two bridging Ga_2Cl_2 heterocycles. The Ga–Cl bridges were cleaved upon treatment with diethyl ether to yield monomeric formula units (**53** and **54**). Each gallium atom of these etherates is coordinatively saturated by the coordination of one ether oxygen atom. A spontaneous *cis/trans* isomerization occurred in all reactions, and we isolated only those products which had the gallium and hydrogen atoms on different sides of the C=C double bonds. Similar to compounds **44** and **45** the trialkenyl derivative **54** adopts a chalice-like structure and may be able to act as a chelating Lewis-acid, if the ether molecules could be replaced by suitable multiple donors:

$$C_6H_{6-x}(C\equiv C\text{-}SiMe_3)_x \;+\; x\;H\text{-}GaCl_2 \longrightarrow C_6H_{6-x}[C(H){=}C(SiMe_3)\text{-}GaCl_2]_x$$

51: x = 1; **52**: x = 2



51

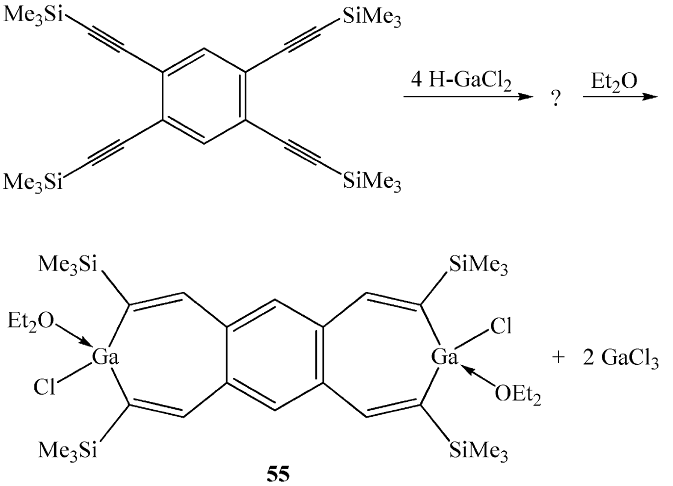
52

53

54

(21)

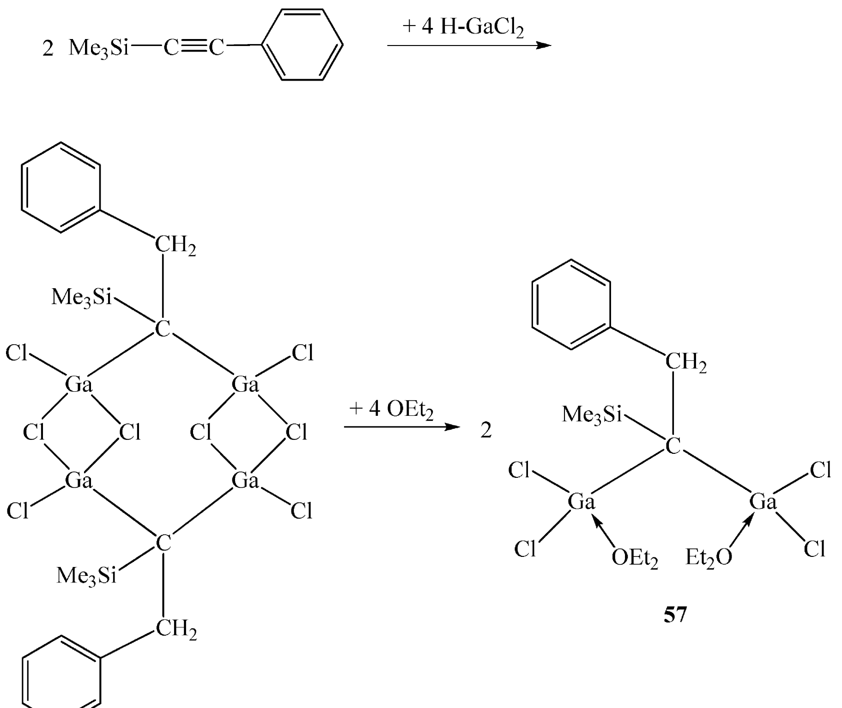
The tetraalkyne 1,2,4,5-tetrakis(trimethylsilylethynyl)benzene gave a different and completely unexpected reaction course upon treatment with H–$GaCl_2$ (Eq. (22)) [112]. The raw product was completely insoluble in hydrocarbons such as pentane or toluene, and dissolution succeeded in diethyl ether only. Colorless crystals of the tricyclic etherate **55** were isolated from these solutions in a moderate yield of 46%. Compound **55** contains 2 seven-membered GaC_6 heterocycles connected to the inner benzene ring by common C–C bonds. The tricyclic ring system deviates considerably from planarity. Its formation may be described by intramolecular condensation and involves the unexpected release of $GaCl_3$. However, we were not able to isolate this by-product by recrystallization or sublimation, and it is absolutely not clear whether the tricyclic product was formed directly or only after treatment with diethyl ether:



55

(22)

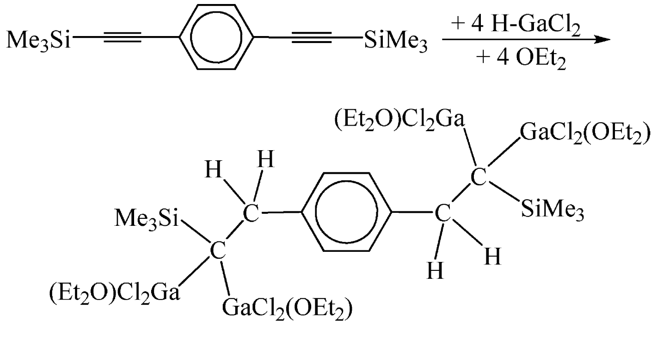
Double hydrogallation of alkynes should yield alkane derivatives. However, such reactions could not be realized with dialkylgallium hydrides even when an excess of the hydrides was applied. Exceptions were observed for dialkylgallium alkynides only (Eq. (8)). In contrast, H–$GaCl_2$ gave the double hydrogallation already at room temperature. Phenyl(trimethylsilyl)ethyne yielded the digallium compound **56** (Eq. (23)) which is dimeric in the solid state by the formation of two Ga_2Cl_2 heterocycles (Fig. 5) [113]. A monomeric etherate (**57**) was formed upon addition of diethyl ether (Eq. (23)). The dialkyne 1,4-bis(trimethylsilylethynyl)benzene afforded a product which was insoluble in hydrocarbons. It dissolved readily upon treatment with diethyl ether to yield the corresponding tetragallium compound **58** (Eq. (24)) [113]:



57

56

(23)



58

(24)

These completely hydrogallated products are important starting compounds for secondary reactions. The addition of at least the second equivalent of H–$GaCl_2$ is reversible. This important point was verified by the treatment of the digallium compound **56** with an equimolar quantity of phenyl(trimethylsilyl)ethyne (Eq. (25)) [113]. Owing to the NMR spectroscopic characterization the alkenylgallium derivative **51** formed quantitatively by commutation in hot *n*-hexane without any detectable by-product. As was shown in some preliminary experiments **56** is an effective chelating Lewis-acid and formed stable complexes with halide anions (**59**, Scheme 3). All chlorine atoms of **56** were replaced by alkyl groups upon treatment with neopentyllithium (**60**, Scheme 3). Also this tetraalkyl compound is an effective chelating Lewis-acid and coordinated thiophenolate, for instance, by both gallium atoms (**61**) [113]:

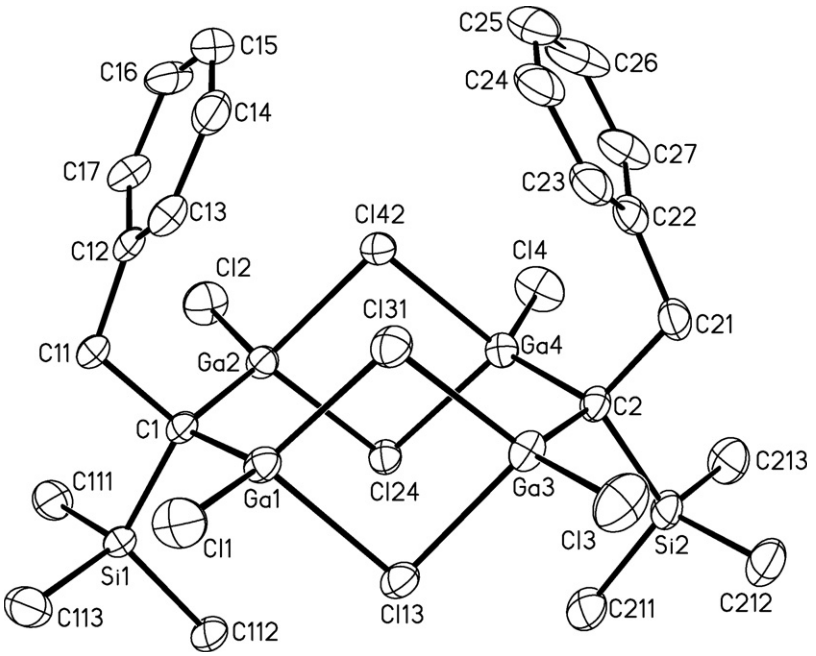
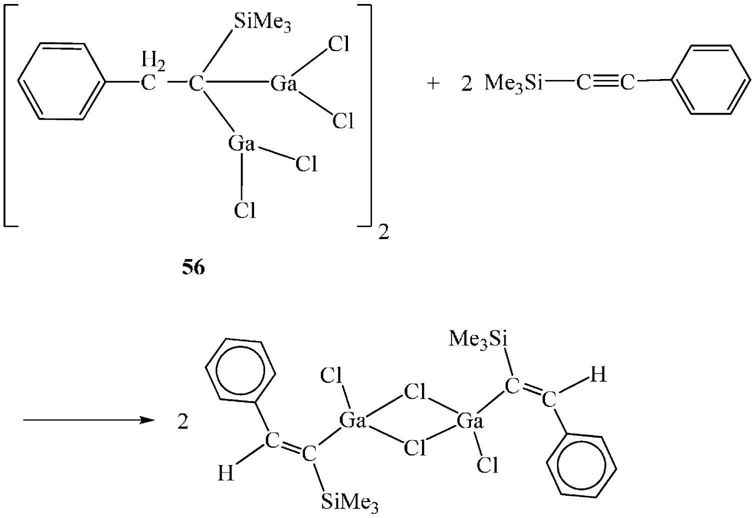


Fig. 5. Molecular structure of compound **56**.



56

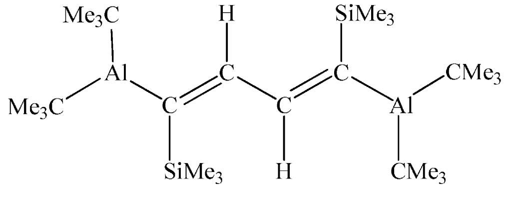
51

(25)

6. Hydroalumination reactions with butadiynes—facile synthesis of persistent carbocations

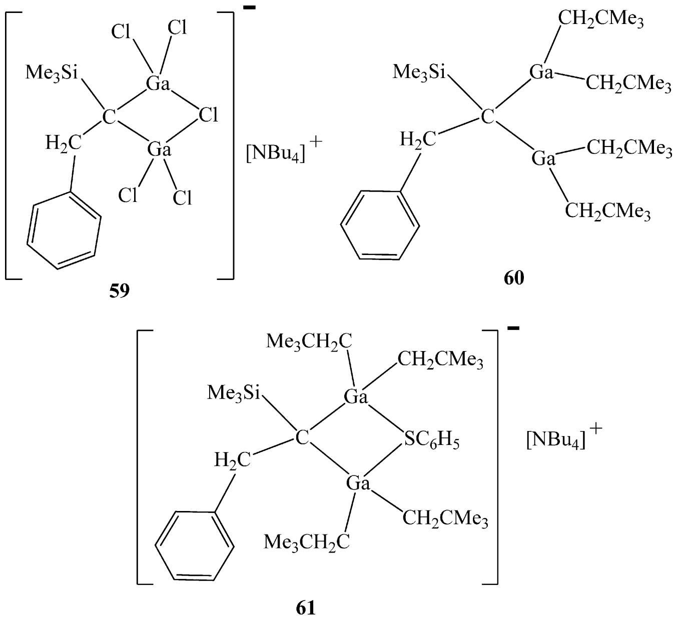
Bis(trimethylsilyl)butadiyne afforded the expected product of hydroalumination (**62**) when it was treated with two equivalents of di(*tert*-butyl)aluminum hydride (Eq. (26)) [105]. In accordance with results described before, the aluminum atoms attacked exclusively those carbon atoms of both C≡C triple bonds which were bonded to trimethylsilyl groups. The aluminum atoms and the hydrogen atoms were on the same side of the C=C double bonds indicating the selective *cis* addition. Rearrangement to yield the *trans* isomer was not observed in hot benzene, instead decomposition occurred with the formation of many unknown secondary products:

$$Me_3Si—C{\equiv}C—C{\equiv}C—SiMe_3 + 2\,(Me_3C)_2AlH \longrightarrow$$



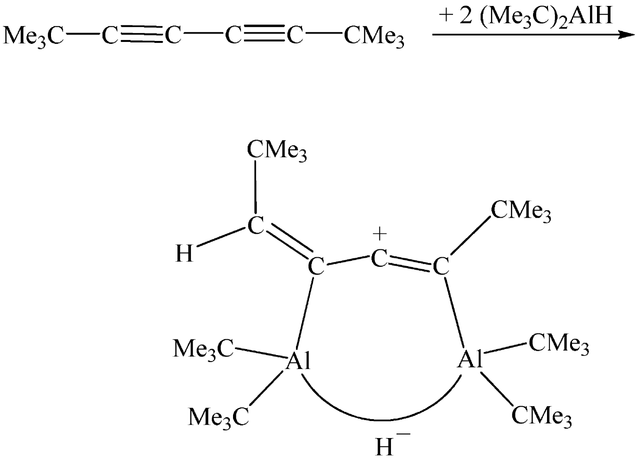
62

(26)



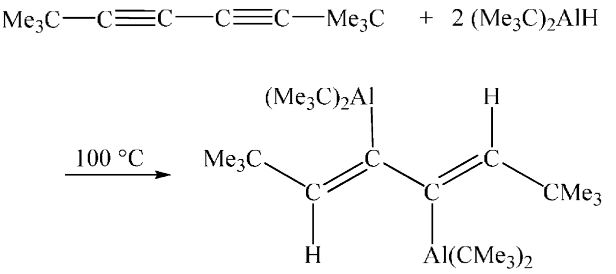
Scheme 3. Schematic representations of secondary products of compound **56**.

In contrast, di(*tert*-butyl)butadiyne gave a quite unexpected and singular product (**63**, Eq. (27)). Owing to the results of crystal structure determination and quantum chemical calculations a butadienyl cation was formed, which slowly decomposed in solution at room temperature [114]. Similar compounds were obtained before only in superacidic media and were not isolated in a pure form [115]. Structural parameters calculated for these cations [116–120] agree well with the experimental data of **63**. The dialuminum compound contains a six-membered heterocycle in the molecular core which comprises an Al–H–Al 3c–2e bond and three carbon atoms of the organic backbone including the central cationic carbon center. The length of the exocyclic C=C double bond corresponds to the standard value of 134 pm. The remaining C–C distances of the tetracarbon skeleton reflect an unusual bonding situation. The inner bond is shorter than that one of a single bond between two sp-hybridized carbon atoms (136.7 pm), and the third one is in between the standard bond lengths of C–C double and triple bonds (125.6 pm). Compound **63** may result from the hydroalumination of both triple bonds of the starting diyne. One half of the molecule corresponds to the expected product in which the aluminum atom did not attack a carbon atom attached to a *tert*-butyl group. The second aluminum atom is bonded to a terminal carbon atom of the C_4 backbone. However, the second hydrogen atom is not coordinated to the butadienyl moiety. C–H bond activation occurred by hyperconjugation with Al–C bonds and to a smaller extent by an interaction to the exocyclic C=C double bond. A hydride ion is removed and is effectively coordinated by both aluminum atoms in a chelating manner to yield a zwitterionic compound. In particular, the dramatic lengthening of the Al–C bond to the terminal carbon atom (216.3 pm) and the short C–C distance of 125.6 pm indicate the stabilization of the cation by hyperconjugation. The occurrence of a cationic carbon atom is further verified by its unusual chemical shift to a low field ($\delta = 160$) [121,122]. The formation of a persistent carbocation shows impressively the effectiveness of chelating Lewis-acids based on coordinatively unsaturated aluminum atoms. Owing to quantum chemical calculations the situation observed for compound **63** with a butadienyl cation stabilized by hyperconjugation and the hydride anion coordinated in a chelating manner is energetically clearly favored compared to that one having an additional C–H bond and coordinatively unsaturated tricoordinated aluminum atoms [123]:



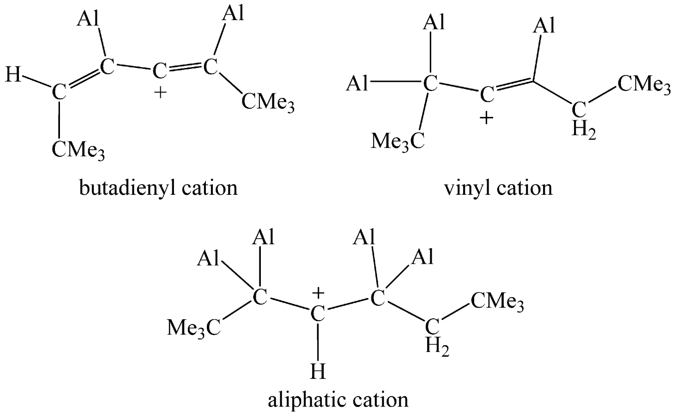
63 (27)

Another product (**64**) resulted in a relatively low yield of about 30% when the di(*tert*-butyl)aluminum hydride was treated with di(*tert*-butyl)butadiyne under more drastic conditions in tri(*tert*-butyl)alane as a solvent and at a temperature of 100 °C (Eq. (28)) [124]. Double hydroalumination occurred, and the aluminum atoms are bonded to both neighboring inner carbon atoms of the resulting butadienyl moiety. Both hydrogen atoms adopt positions at the terminal carbon atoms, and *trans* configurations resulted for the C=C double bonds. The constitution of **64** is inverse to that one of the trimethylsilyl substituted butadiene derivative **62**, where a *cis* configuration occurred and the aluminum atoms were attached to the terminal carbon atoms of the butadiene backbone. Thus, these reactions represent further interesting examples for the influence of the alkyne substituents on the regioselectivity of these reactions. Compound **64** possesses a quite interesting molecular structure and may be suitable for an application as a chelating Lewis-acid:

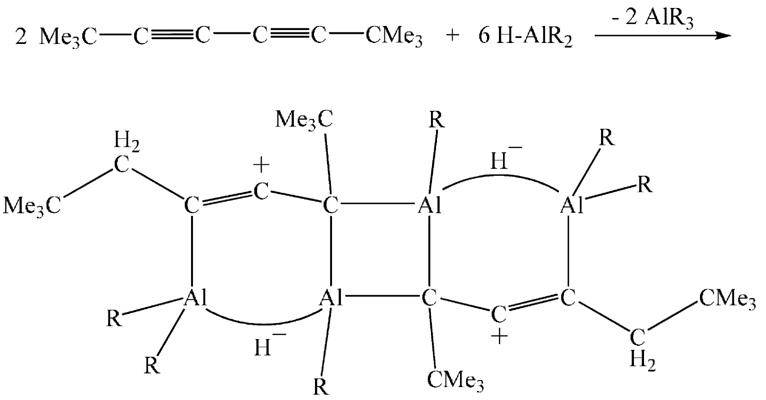


64 (28)

Treatment of di(*tert*-butyl)butadiyne with sterically less shielded dialkylaluminum hydrides afforded two other types of carbocationic species. The dimethyl compound, $Me_2Al–H$, yielded **65** in 27% yield (Eq. (29)) when only a small excess of the hydride was applied [123]. The formation of **65** resulted from threefold hydroalumination. It may be described as a vinyl cation. Condensation and release of trimethylaluminum gave a dimeric formula unit with a central Al_2C_2 heterocycle. C–H bond activation was once more achieved by hyperconjugation with Al–C bonds, and the hydride anion formally resulting from the heterolytic cleavage of the C–H bond was stabilized by chelating coordination through coordinatively unsaturated aluminum atoms. Similar compounds (**66** and **67**) were obtained in about 55% yield upon treatment of the diyne with diethyl- or di(isobutyl)aluminum hydride [124]. Vinyl cations stabilized by hyperconjugation with C–Si bonds were published only recently [125–127]. An excess of dimethylaluminum hydride afforded compound **68** in 70% yield which has four aluminum atoms attached to the tetracarbon backbone and was formed by the twofold hydroalumination of both C≡C triple bonds (Eq. (30)) [123]. As schematically shown, **68** possesses a relatively complicated cage consisting of four chemically different aluminum atoms bridged by three hydrogen atoms. Complete saturation of all C–C bonds, C–H activation and chelating coordination of the hydride anion as before gave an aliphatic carbocation. Two aluminum atoms of **68** have two terminal methyl groups and the remaining ones are attached to only one terminal ligand. Trimethylaluminum was detected as a by-product by NMR spectroscopy. All cations can easily be identified by low field resonances at about $\delta = 200–220$ for the cationic carbon atoms. Hydroalumination of di(*tert*-butyl)butadiyne with dialkylaluminum hydrides is an effective method for the generation of persistent carbocationic species. Three different motifs were realized yet: a butadienyl cation, a vinyl cation and an aliphatic carbocation (Scheme 4) by twofold to fourfold hydroalumination of the starting dialkyne. All compounds are zwitterionic with an intramolecular compensation of the respective charges. They have the immense advantage that they are soluble in nonpolar solvents such as pentane or benzene. Most of them are stable in solution at room temperature over several days and may be applicable in secondary reactions:

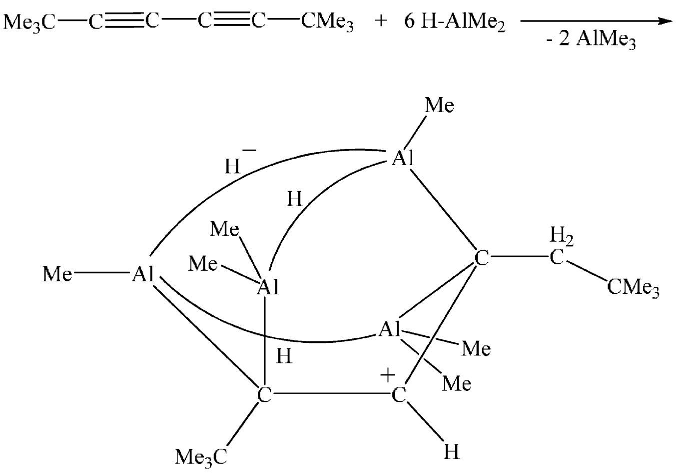


Scheme 4. Schematic representation of the different cationic systems obtained by hydroalumination.



65: R = Me
66: R = Et
67: R = *i*Bu

(29)



68

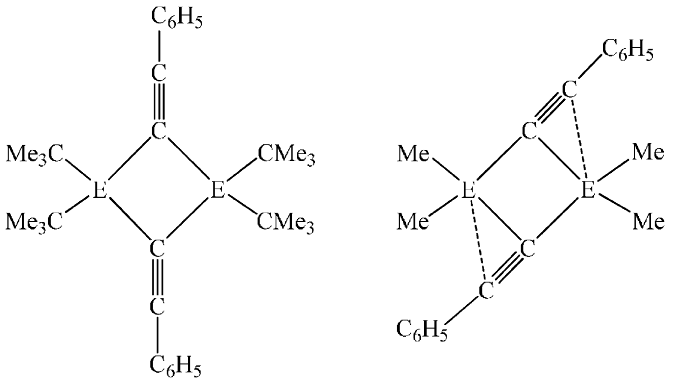
(30)

7. Reactions of dialkylaluminum and dialkylgallium hydrides with alkynes R–C≡C–H—hydrogen release *versus* addition of E-H bonds

Treatment of phenylethyne $H–C≡C–C_6H_5$ with dialkylelement hydrides $R_2E–H$ (E = Al, Ga; R = Me, *t*Bu) is a very effective method for the generation of the corresponding dialkylelement alkynides (**69**) by hydrogen elimination (Eq. (31)) [128]. With gallium hydrides similar reactions were also observed for alkyl substituted ethynes [89]. These alkynides adopted two different structural motifs, which are depicted in Eq. (31). They have 3c–2e Al–C–Al bonds or alternatively a side-on coordination of the alkynes to one metal atom. Reports were published in the literature about 30–40 years ago [1,4] which described the addition of Al–H bonds to the unsaturated organic compounds as a competitive pathway. Phenylethyne possessing a relatively high acidity favors the hydrogen release, while the less acidic alkylethynes give hydroalumination. Owing to the usual hydrolytic work-up, the true structures and bonding situations of these intermediates remained unknown:

$$2\,R_2E\text{-}H + 2\,H\text{-}C{\equiv}C\text{-}R' \longrightarrow \underset{\mathbf{69}}{(R_2E\text{-}C{\equiv}C\text{-}R')_2} + H_2$$

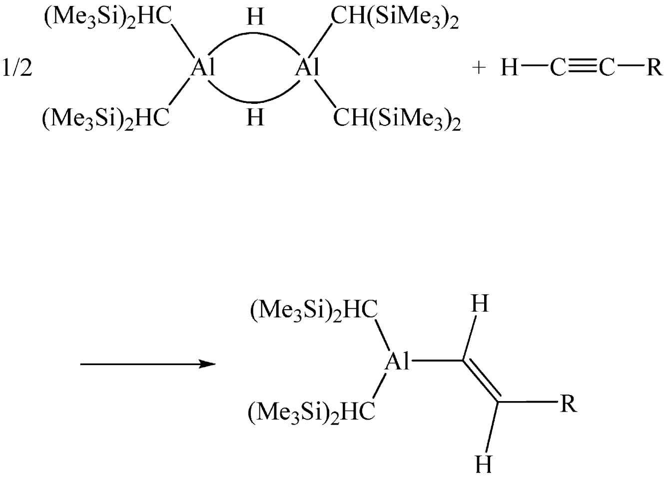
R = Me, CMe_3; E = Al, Ga; R′ = C_6H_5
R = Me, Et; E = Ga; R′ = Me, *n*Pr



(E= Al, Ga) (E = Al, Ga)

(31)

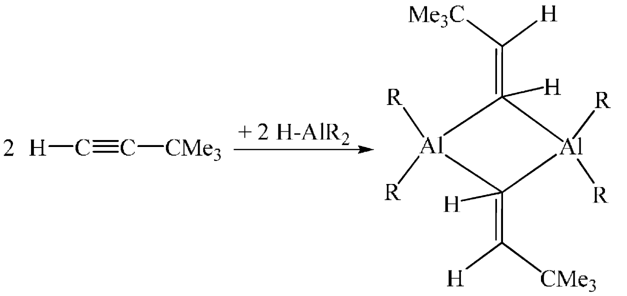
We observed the addition of Al–H bonds to the C≡C triple bonds of ethynes H–C≡C–R as the only reaction when we treated the sterically highly shielded hydride $R_2Al–H$ [$R = CH(SiMe_3)_2$] with different ethynes having *tert*-butyl, phenyl or trimethylsilyl substituents (**70**–**72**, Eq. (32)) [129]. The aluminum atoms attacked those carbon atoms of the triple bonds which bear the hydrogen atoms. As was shown by crystal structure determinations and the H–H coupling constant across the C=C double bond (>20 Hz) both hydrogen atoms of the alkenyl groups adopted a *trans* arrangement, which corresponds to a selective *cis* addition of the Al–H bonds. While the syntheses of compounds **70** and **71** proceed quantitatively, a by-product was formed with $H–C≡C–SiMe_3$. Although it was not isolated in a pure form, the occurrence of two doublets in the range of vinyl hydrogen atoms with a relatively small coupling constant of 5 Hz indicated the formation of the compound $H_2C=C(SiMe_3)AlR_2$ [$R = CH(SiMe_3)_2$] (**73**). It was formed by the attack of the aluminum atom to that carbon atom of the alkyne, which was attached to the trimethylsilyl group. The ratio of the products was 1 to 0.1 (**72** to **73**). This particular reaction gives a good insight into the similar directing capabilities of hydrogen atoms and trimethylsilyl groups with a small advantage for the hydrogen atoms. It was the first time that we isolated a mixture of products, which had the aluminum or gallium atoms attached to different carbon atoms of the alkenyl groups:



70: R = CMe_3
71: R = C_6H_5
72: R = $SiMe_3$

(32)

The sterically less shielded hydride $H–Al(CMe_3)_2$ gave a similar addition reaction with *tert*-butylethyne (Eq. (33)) [129]. The product **74** is dimeric in the solid state via bridging carbon atoms of the alkenyl groups. In solution a complicated mixture of at least four compounds exists. One of these represents the monomeric formula unit formed by dissociation. Accordingly, the molar mass determination in benzene solution by cryoscopy gave the average value between those of the monomeric and dimeric compounds. A similar di(isobutyl)aluminum derivative was reported before [130,131]. In contrast to the sterically more crowded di(*tert*-butyl) compound it did not seem to dissociate in solution. Trimethylsilylethyne gave a complicated mixture of unknown products under similar conditions. We were not able to isolate any pure component:



74 (R = CMe_3, Me) (33)

8. Conclusion

The course of hydroalumination and hydrogallation reactions of alkynes depends strongly on the respective conditions such as temperature, solvents, substituents, impurities, etc. Hence, it is difficult to suggest a generally applicable simple scheme for predicting unambiguously the formation of a particular product. But some patterns may be recognized from the results described here and are shortly summarized in this chapter. All experiments described here were conducted in non-coordinating solvents. A different behavior has to be expected for ethereal solutions.

Both reaction types are highly regioselective, and the constitution of the products is determined by the substituents attached to the starting alkynes. The directing properties with respect to the preferred attack of the aluminum or gallium atoms vary in the following order: $H \geq SiMe_3$, ER_2 (E = Al, Ga) > phenyl > alkyl, with hydrogen possessing the strongest directing influence. Up to now, we are not able to differentiate between $SiMe_3$ and ER_2 owing to the lack of suitable starting alkynes. Interestingly, a mixture of products with aluminum or gallium attached to different carbon atoms of the alkenyl groups resulted only by the hydroalumination of H–C≡C–$SiMe_3$ (Section 7) which verifies the competitive behavior of both substituents.

Treatment of dialkylaluminum or dialkylgallium alkynides with the corresponding aluminum or gallium hydrides afforded condensation with the release of trialkylelement derivatives. Carbaalanes possessing clusters of carbon and aluminum atoms and a delocalized bonding situation were formed with aluminum, while gallium gave heteroadamantane-type cages with localized Ga–C bonds and coordinatively unsaturated metal atoms. Successful reactions are restricted to relatively small substituents attached to the metal atoms.

Trimethylsilyl groups attached to the C≡C triple bonds of the starting alkynes favor the formation of persistent addition products containing intact AlR_2 or GaR_2 units without any indication of condensation. Sterically less shielded dialkylelement groups give spontaneous *cis*/*trans* isomerization of the alkenyl residues, while bulky substituents [R = CMe_3, $CH(SiMe_3)_2$] prevent or at least hinder the isomerization process and stable products of a *cis* addition can be isolated. This may be taken as a hint for an intermolecular activation process.

The behavior of *tert*-butyl(phenyl)ethynes depends strongly on steric shielding. Very bulky substitutents attached to aluminum [R = $CH(SiMe_3)_2$, the corresponding gallium hydride is unknown] gave persistent monoaddition products without a secondary reaction. The trialkyne 1,3,5-tri(*tert*-butylethynyl) benzene afforded cyclophane-type molecules by condensation for all hydrides H–ER_2 with R = Me to *t*Bu. In contrast, the dialkyne 1,4-di(*tert*-butylethynyl)benzene gave condensation only with dineopentylelement hydrides, while stable addition products containing intact ER_2 groups were isolated for R = Et und *n*Pr. For the smaller substituents, a particular intermolecular interaction was verified by crystal structure determination which may prevent substituent exchange. Rearrangement to give the *trans* products was not observed yet.

Double hydroalumination or hydrogallation occurred with aluminum and gallium alkynides, and the products of a monoaddition were not detected at all. Further experiments with respect to the twofold addition of Al–H or Ga–H bonds employing dialkylelement hydrides failed. The dichloro compound H–$GaCl_2$ showed a different behavior and the selective addition of one or two Ga–H bonds to each C≡C triple bond succeeded under mild conditions.

The products of hydroalumination exhibit a strong C–H bond activation by hyperconjugation with Al–C bonds in β-position. This particular property may open a facile access to novel organoaluminum compounds suitable for an application in interesting secondary processes and may possibly help to understand the mechanism of some rearrangement reactions.

Hydroalumination and hydrogallation reactions are facile methods for the generation of unprecedented and highly functionalized organoelement compounds. The importance of these methods goes far beyond the simple reduction of organic substrates, and it is rather valuable to have a closer look on the organometallic intermediates and to clarify their constitutions. It is quite sure that further unprecedented and highly interesting compounds will be isolated in future work.

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