Two Different Structural Motifs Observed for Dimeric Dialkylaluminum and Dialkylgallium Alkynides $[R_2E\text{-}C{\equiv}C\text{-}C_6H_5]_2$

Werner Uhl[a,*], **Frank Breher**[a], **Sima Haddadpour**[a], **Rainer Koch**[b], **and Madhat Matar**[a]

[a] Marburg, Fachbereich Chemie der Philipps-Universität Marburg
[b] Oldenburg, Institut für Reine und Angewandte Chemie der Carl-von-Ossietzky-Universität

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Dedicated to Professor Michael Veith on the Occasion of his 60th Birthday

Abstract. The dialkylaluminum and dialkylgallium alkynides $[R_2E\text{-}C{\equiv}C\text{-}R']_2$ (R = Me, CMe_3; E = Al, Ga; R′ = Ph) containing C≡C triple bonds attached to their central aluminum or gallium atoms are easily obtained by the reactions of dialkylelement chlorides with lithium alkynides or by treatment of the corresponding alkyne R-C≡C-H with dialkylaluminum or dialkylgallium hydrides. The first reaction is favored by the precipitation of LiCl, the second one by the formation of elemental hydrogen. All products form dimers in which the carbanionic carbon atoms of the alkynido groups adopt bridging positions, but, interestingly, different types of molecular structures were observed depending on the steric demand of the substituents terminally attached to the aluminum or gallium atoms. The small methyl substituents gave structures in which the aluminum or gallium atoms seemed to be side-on coordinated by the C≡C triple bonds of almost linear E-C≡C groups. In contrast, the more bulky *tert*-butyl groups forced an arrangement in which the C≡C triple bonds were perpendicular to the E-E axis of the molecules. Different bonding modes result, which were analyzed by quantum-chemical calculations.

Keywords: Alkynes; Aluminum; Gallium; Bridging ligands

Unterschiedliche Struktureinheiten in dimeren Dialkylaluminium- und Dialkylgalliumalkiniden $[R_2E\text{-}C{\equiv}C\text{-}C_6H_5]_2$

Inhaltsübersicht. Die Dialkylaluminium- und Dialkylgalliumalkinide $[R_2E\text{-}C{\equiv}C\text{-}R']_2$ (R = Me, CMe_3; E = Al, Ga; R′ = Ph) enthalten C≡C-Dreifachbindungen koordiniert an ihre inneren Aluminium- oder Galliumatome. Sie sind leicht durch Umsetzung der entsprechenden Dialkylelementchloride mit Lithiumalkiniden oder durch Reaktion von Alkinen H-C≡C-R mit Dialkylaluminium- oder Dialkylgalliumhydriden zugänglich. Die erste Methode wird durch die Ausfällung von LiCl begünstigt, während nach der zweiten Route elementarer Wasserstoff gasförmig entweicht. Alle Produkte enthalten dimere Formeleinheiten, in denen die carbanionischen Kohlenstoffatome der Alkinideinheiten verbrückende Positionen einnehmen. Interessanterweise treten in Abhängigkeit vom Raumanspruch der an Aluminium oder Gallium gebundenen terminalen Substituenten unterschiedliche Molekülstrukturen auf. Die recht kleinen Methylgruppen ergeben Strukturen, in denen die Aluminium- oder Galliumatome scheinbar side-on an die C≡C-Dreifachbindungen nahezu ideal linearer E-C≡C-Einheiten koordinieren. Die voluminöseren *tert*-Butylgruppen erzwingen dagegen eine Anordnung, in der die C≡C-Dreifachbindungen senkrecht zur E-E-Verbindungslinie der inneren viergliedrigen Heterozyklen stehen. Daraus resultieren unterschiedliche Bindungssituationen, die quantenchemisch untersucht wurden.

Introduction

Dialkylaluminum and dialkylgallium alkynides $R_2E\text{-}C{\equiv}C\text{-}R'$ have found considerable interest in recent literature because they are valuable starting compounds for the synthesis of secondary products. The most exciting application was the generation of carbaalanes [1−6] which possess clusters formed by aluminum and carbon atoms such as $[(AlMe)_8(CCH_2Ph)_5H]$ (**1**) or $[(AlMe)_7(CCH_2CH_3)_4H_2]$ (**2**) (Scheme 1). These compounds were obtained by the treatment of dialkylaluminum alkynides with the corresponding dialkylaluminum hydrides. Hydroalumination of the alkynido groups and spontaneous condensation by the release of trialkylaluminum derivatives yielded the cluster compounds, which are thermally quite stable and possess an electronically delocalized bonding system. In contrast, dialkylgalliumalkynides did not yield the analogous cluster compounds upon hydrogallation with dialkylgallium hydrides [7, 8], but gave heteroadamantane structures (**3**, Scheme 1) with six co-ordinatively unsaturated gallium atoms in the bridging positions and a localized bonding system [9]. Whereas many aluminum alkynides have been characterized and published recently [10], only a few derivatives of the particular class of dialkyl or diaryl compounds of aluminum and gallium, $[R_2Al\text{-}C{\equiv}C\text{-}R']_2$ and $[(H_3C)_2Ga\text{-}C{\equiv}C\text{-}Ph]_2$, have been structurally verified so far [11−15]. In the course of our investigations on hydroalumination and hydrogallation, we systematically varied the

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[*] Prof. Dr. Werner Uhl
Fachbereich Chemie der Philipps-Universität
D-35032 Marburg, Germany
Fax: +49/(0)6421/2825653
E-mail: uhl@chemie.uni-marburg.de

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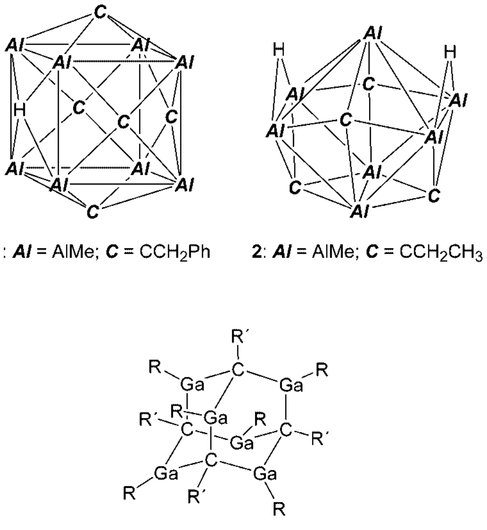


1: *Al* = AlMe; *C* = CCH$_2$Ph **2**: *Al* = AlMe; *C* = CCH$_2$CH$_3$

3: R = Me, Et; R´ = Et, Bu

Scheme 1

steric demand of the substituents attached to the central third main-group atoms. As reported here, we determined some of the crystal structures of these alkynides and, interestingly enough, found two different binding modes of the bridging alkynido groups, which require two different bonding descriptions.

Synthesis of Dialkylaluminum and Dialkylgallium Alkynides

The syntheses of the alkynides succeeded via two different routes. The first involves the treatment of the corresponding element hydrides $(R_2EH)_n$ (E = Al, Ga; n = 2 or 3) with phenylethyne H-C≡C-C$_6$H$_5$, which yielded the alkynides by the release of elemental hydrogen in relatively high yields (eq. 1). The dimethyl compounds **4** and **6** and the di(*tert*-butyl)aluminum ethynide **5** were obtained by such a route. **6** was isolated earlier by the treatment of GaMe$_3$ with H-C≡C-C$_6$H$_5$ at elevated temperature in a sealed ampoule [16]. Di(*tert*-butyl)gallium hydride, which forms trimers in the solid state [7], yielded the corresponding alkynide **7** in low and insufficiently reproducible yield only, which may be caused by its unique solution behavior. As was shown by NMR spectroscopy, a temperature dependent equilibrium exists in solution, which results in the formation of three different compounds: Ga(CMe$_3$)$_3$, H-Ga(CMe$_3$)$_2$, and the novel *sesqui*-hydride [Me$_3$C-GaH$_2$]$_2$[(Me$_3$C)$_2$GaH]$_2$ [7]. Compound **7** was obtained in reasonable yield by the reaction of the corresponding lithium alkynide with di(*tert*-butyl)gallium chloride (eq. 2). The di(*tert*-butyl)aluminum compound **5** was synthesized by a similar route, however, the yield was generally lower compared to that of the reaction of the hydride described before. A similar salt-elimination procedure was employed for the generation of diethylaluminum phenylethynide [2] or the propynido compounds [R$_2$Al-C≡C-Me] (R = Et, *i*Pr, *t*Bu) [4]. These products were usually isolated as highly viscous liquids or as waxy solids, and we did not succeed in growing single crystals in any of these cases. The aluminum compound, [Me$_2$Al-C≡C-C$_6$H$_5$] (**4**), was also isolated before by our group by salt elimination according to equation (2) [1]. As in the case of the di(*tert*-butyl)aluminum compound **5,** the yield was considerably enhanced by starting with the corresponding hydride as reported here (eq. (1)). The complete spectroscopic characterization is given in the former publication [1]. Molar mass determinations with the gallium compounds verified the dimeric formula units in benzene solutions. Dimers were also detected for the solid state, but two different types of molecular structures were determined, which are discussed in more detail below (Scheme 2). The structure type depends on the bulkiness of the substituents, one has almost linear E-C≡C groups side-on coordinated to the second E atom (type A), the other one has the C≡C triple bonds perpendicular to the E-E axis of the cental E$_2$C$_2$ heterocycle (type B).

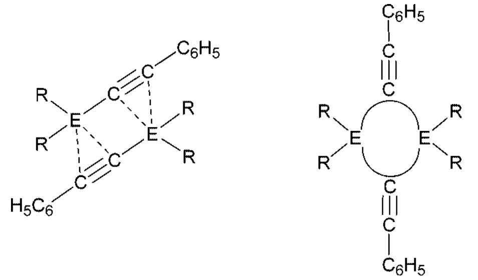
$$2\,R_2E\text{–}H + 2\,H\text{–}C{\equiv}C\text{–}C_6H_5 \longrightarrow [R_2E\text{–}C{\equiv}C\text{–}C_6H_5]_2 + 2\,H_2 \qquad (1)$$

E = Al, Ga

4: R = Me, E = Al
5: R = CMe$_3$, E = Al
6: R = Me, E = Ga
7: R = CMe$_3$, E = Ga

$$2\,R_2E\text{–}Cl + 2(Li)C{\equiv}C\text{–}C_6H_5 \longrightarrow [R_2E\text{–}C{\equiv}C\text{–}C_6H_5]_2 + 2\,LiCl \qquad (2)$$

5: R = CMe$_3$, E = Al
7: R = CMe$_3$, E = Ga



Type A (R = Me; **4** and **6**) Type B (R = CMe$_3$; **5** and **7**)

Scheme 2

The stretching vibrations of the C≡C triple bonds of the compounds **4** to **7** were observed in slightly different regions of the IR spectra. Bands of 2089 and 2100 cm^{-1} were found for the dimethyl derivatives **4** and **6**, respectively, whereas lower wave numbers were detected for the corresponding absorptions of the di(*tert*-butyl) compounds **5** and **7** (2060 and 2052 cm^{-1}). Although these differences may at least partially be influenced by the mass of the alkylelement groups with the heavier di(*tert*-butyl)element groups leading to the lower value of the stretching vibration, they may also reflect the different bonding modes as discussed below. Accordingly and in very good agreement, quantum-chemical calculations of $[Me_2Al\text{-}C\equiv C\text{-}C_6H_5]_2$ with both structure types resulted in two different C≡C stretching vibrations at 2103 and 2066 cm^{-1} depending on the particular bonding mode of the alkynido ligand. The higher value corresponds to the side-on coordination of the C≡C triple bond (typ A, see below). Two ^{13}C resonances were detected for each triple bond according to the different chemical environment. The resonances of the carbon atoms attached to the phenyl substituents have similar shifts in all the compounds independent of the kind of metal atoms and the substituents attached to these atoms (Al compounds **4** and **5**: δ = 119.9; Ga compounds **6** and **7**: δ = 121.5). The remaining resonances of the alkynido groups belong to the carbanionic carbon atoms. They show more pronounced differences depending on the bulkiness of the substituents. The chemical shifts are δ = 96.8 and 98.0 for the dimethyl compounds **4** and **6**, whereas the corresponding resonances of the di(*tert*-butyl) compounds **5** and **7** are at δ = 91.5 and 92.8, respectively. These differences may be caused by the different inductive effects of methyl versus *tert*-butyl groups. Quantum-chemical calculations result in stronger differences in the chemical shifts between the structure types (type A and B). The carbanionic carbon atoms should occur at δ = 88.4 (type B) and 95.6 (type A), which, in particular for the last one, is in quite good agreement with the experimental values. Those carbon atoms, which are attached to the phenyl groups, were predicted to resonate at δ = 141.0 (type B) and 124.7 (type A). While the second one is close to the values obtained by the NMR experiment, the first one deviates significantly. This observation may indicate a fast exchange process in solution with a small contribution of the type B molecules only and is in accordance with the low energy difference calculated between both forms (see below). Packing effects may favor the occurrence of type B in the solid state for the *tert*-butyl derivatives **5** and **7**.

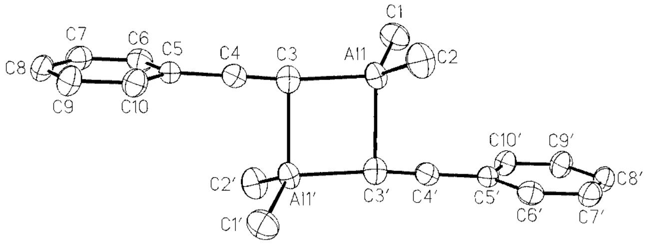


Figure 1 Molecular structure of **4** (E = Al; a similar structure was observed for the gallium compound **6**). The thermal ellipsoids are drawn at the 40 % probability level. Al1′ is generated by −x, −y, −z + 1.

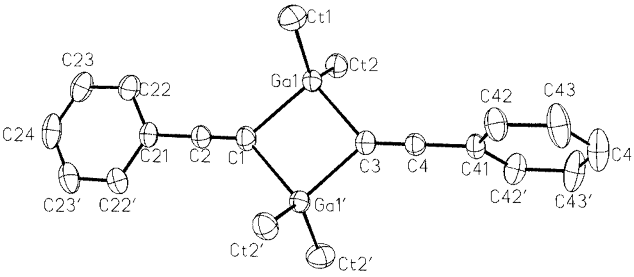


Figure 2 Molecular structure of **7** (E = Ga; similar representations result for the four independent molecules of the corresponding aluminum compound **5**). The thermal ellipsoids are drawn at the 40 % probability level. Methyl groups are omitted for clarity. Ga1′ is generated by −x, y, −z + 0.5.

Molecular Structures

Crystal structure determinations of the compounds **4** to **7** (Figures 1 and 2) revealed two different types of molecular structures depending on the steric demand of the substituents attached to aluminum or gallium. Both forms are schematically depicted in Scheme 2. The molecular structure of **6** was published earlier [11]. We redetermined the structure at low temperature, but did not observe any significant changes in the structural parameters. All compounds are dimeric in the solid state with the carbanionic carbon atoms of the C≡C triple bonds in a bridging position. The compounds differ in the orientation of the C≡C triple bonds with respect to the E···E axes of the central E_2C_2 heterocycles. Lines generated by both groups enclose angles of 53.5° and 54.3° for the methyl compounds **4** and **6**, respectively, indicating a significant tilting of the C-C bond. Almost linear groups, $E\text{-}C\equiv C\text{-}C_6H_5$, result at each aluminum or gallium atom (angles E-C≡C 173.7° and 173.5°, Table 1). The E-C bonds of these E-C≡C groups are relatively short (199.4 and 200.1 pm) and, thus, only 5 pm longer than the terminal E-C bonds to the methyl residues. Bonds actually involving μ_2-bridging carbon atoms with a three-center bonding and two equivalent E-C interactions are usually significantly longer (~210 pm; see for comparison the discussion of the structures of compounds **5** and **7** below). The remaining two E-C distances of the central E_2C_2 heterocycles perpendicular to the E-C≡C groups are strongly elongated to 222.4 and 237.8 pm, respectively. A side-on coordination of the second aluminum or gallium atom seems to occur, however, the distances to the second carbon atom of the triple bond are out of the range of significant bonding interactions (261.6 and 272.4 pm). This interpretation is in accordance with the results of quantum-chemical calculations, which are discussed in more detail below. The same description holds for all dialkyl- or diarylelement alkynides (E = Al, Ga) published in literature so far [11−13], the structure of $[Me_2Al\text{-}C\equiv C\text{-}Me]_2$ in the gas phase may be a borderline case [14].

A second type of molecular structures was observed for the compounds **5** and **7**, bearing the bulky *tert*-butyl groups attached to aluminum or gallium. The C≡C triple bonds are perpendicular to the E···E axes of the central E_2C_2 heterocycles. Owing to crystallographic symmetry, the respect-

Table 1 Selected bond lengths /pm and angles /° of compounds **4** to **7**

$(Me_2Al\text{-}C{\equiv}C\text{-}C_6H_5)_2$ (**4**)			
Al1−C1	194.9(2)	C3−C4	120.8(3)
Al1−C2	194.5(2)	Al1···C4	261.6(3)
Al1−C3	199.4(2)	Al1···Al1′	303.0(1)
Al1−C3′	222.4(2)		
C1−Al1−C2	122.4(1)	C1−Al1−C3′	107.70(9)
C1−Al1−C3	111.5(1)	C2−Al1−C3′	109.5(1)
C2−Al1−C3	111.9(1)	C3−Al1−C3′	88.34(9)
		Al1−C3−Al1′	91.66(9)
		Al1−C3−C4	173.7(2)
C3′ and Al1′ generated by −x, −y, −z+1			
$[(Me_3C)_2Al{-}C{\equiv}C{-}C_6H_5]_2$ (**5**)			
Molecule 1:			
Al1−C1	198.0(4)	Al1−C011−Al1′	87.2(2)
Al1−C2	200.2(4)	C011−Al1−C011′	92.8(2)
Al1−C011	209.5(4)	Al1−C011−C012	129.4(3)
Al1−C011′	207.4(4)	Al1′−C011−C012	143.4(3)
C011−C012	117.7(5)		
Al1···Al1′	287.5(2)		
Molecule 2:			
Al2−C3	198.6(4)	Al2−C021−Al3	87.3(2)
Al2−C4	199.5(4)	Al2−C031−Al3	87.4(2)
Al2−C021	209.5(4)	C021−Al2−C031	92.8(2)
Al2−C031	206.1(4)	C021−Al3−C031	92.6(2)
Al3−C5	197.7(5)	Al2−C021−C022	130.7(3)
Al3−C6	201.5(5)	Al2−C031−C032	142.8(3)
Al3−C021	206.6(4)	Al3−C021−C022	142.0(3)
Al3−C031	209.8(4)	Al3−C031−C032	129.0(3)
C021−C022	116.8(5)		
C031−C032	117.9(5)		
Al2···Al3	287.2(2)		
Molecule 3:			
Al4−C7	199.8(4)	Al4−C041−Al5	87.2(2)
Al4−C8	200.4(5)	Al4−C051−Al5	86.8(2)
Al4−C041	207.0(4)	C041−Al4−C051	92.1(2)
Al4−C042	212.2(4)	C041−Al5−C051	93.9(2)
Al5−C9	199.0(4)	Al4−C041−C042	133.5(4)
Al5−C10	201.7(5)	Al4−C051−C052	122.0(3)
Al5−C041	208.3(4)	Al5−C041−C042	138.9(4)
Al5−C051	204.8(4)	Al5−C051−C052	150.8(4)
C041−C042	117.0(5)		
C051−C052	116.2(5)		
Al4···Al5	286.5(2)		
Molecule 4:			
Al6−C110	200.2(4)	Al6−C061−Al6″	86.4(2)
Al6−C120	202.5(5)	C061−Al6−C061″	93.6(2)
Al6−C061	209.0(4)	Al6−C061−C062	133.3(3)
Al6−C061″	206.1(4)	Al6″−C061−C062	140.0(4)
C061−C062	115.1(5)		
Al6···Al6″	284.2(2)		
Al1′, C011′ generated by −x+1, −y, −z			
Al6″, C061″ generated by −x+1, −y−1, −z			
$[Me_2Ga\text{-}C{\equiv}C\text{-}C_6H_5]_2$ (**6**)			
Ga1-C1	195.8(4)	C1-Ga1-C2	126.6(2)
Ga1-C2	195.0(4)	C1-Ga1-C3	112.0(2)
Ga1-C3	200.1(3)	C2-Ga1-C3	105.6(2)
Ga1-C3′	237.8(4)	C1-Ga1-C3′	103.7(2)
C3-C4	120.9(5)	C2-Ga1-C3′	105.6(2)
Ga1···C4	272.4(3)	C3-Ga1-C3′	86.7(1)
Ga1···Ga1′	319.6(1)	Ga1-C3-Ga1′	93.3(1)
		Ga1-C3-C4	173.5(3)
C3′ and Ga1′ generated by −x+1, −y, −z+1			
$[(Me_3C)_2Ga{-}C{\equiv}C{-}C_6H_5]_2$ (**7**)			
Ga1−CT1	203.8(3)	Ga1−C1−Ga1′	87.1(2)
Ga1−CT2	202.4(3)	Ga1−C3−Ga1′	88.7(2)
Ga1−C1	214.1(3)	C1−Ga1−C3	92.1(1)
Ga1−C3	211.0(3)	Ga1−C1−C2	136.44(8)
C1−C2	120.8(6)	Ga1−C3−C4	135.64(8)
C3−C4	121.2(6)		
Ga1···Ga1′	295.11(6)		
Ga1′ generated by −x, y, −z+0.5			

ive angle is exactly 90° for the gallium compound **7**, whereas an average deviation of 5.9° with respect to the ideal value was observed for the four independent molecules of **5**. In contrast to the structures described before, all four E-C distances of the central rings are in a relatively narrow range. Only small differences were detected with short [206.3 (**5**) and 211.0 pm (**7**), Table 1] and slightly longer E-C distances [209.7 (**5**) and 214.1 pm (**7**)]. The differences are about 3 pm in both compounds compared to 23 or 38 pm in **4** and **6**. The angles E-C≡C are similar in the gallium compound **7** (136.4 and 135.6°). More significant differences are observed for **5**, in which two ranges may clearly be distinguished (129.7 and 143.0°). But even the larger angles are far from the linear arrangement found in **4** and **6**. No systematic difference between both classes of structures was observed with respect to the C≡C triple bond lengths. For the compounds **4** to **6** they are very close to the average value of 121 pm (±0.2 pm), which strongly resembles the standard length of a C≡C triple bond of 120 pm [17]. Only the aluminum compound **5** deviates strongly with a rather short C≡C bond length of 116.8 pm. The transannular E···E distances differ depending on the molecular structure. Short distances [286.4 pm on average (**5**) and 295.1 pm (**7**)] are detected for the *tert*-butyl compounds, whereas longer ones [303.0 (**4**) and 319.6 pm (**6**)] result for the methyl derivatives, which posses the more irregular heterocycles and have almost linear E-C≡C groups.

Bonding

The different bonding situation of both types of dimeric alkynides was investigated by quantum-chemical calculations of the aluminum compound, $[Me_2Al\text{-}C{\equiv}C\text{-}C_6H_5]_2$. The particular structure of the di(*tert*-butyl) compounds **5** and **7** (type B, Scheme 2), in which the alkynido groups are perpendicular to the E···E axis of the central Al_2C_2 heterocycle, could only be detected upon fixation of the Al-C bond lengths to 210 pm. In all other cases, the optimization of the structural parameters yielded the second structure with an apparently side-on coordination of aluminum or gallium atoms (type A). However, the energy difference between both structures is rather small, and type A is only 3.5 kJ/mol more stable than the second molecule. Molecule B shows a small negative frequency, the corresponding vibration represents the transformation of A into its mirror image. Thus, structure B may be described as a transition state of that interconversion. Replacement of the methyl groups by the more bulky *tert*-butyl substituents yielded structure B as the most stable one, so that, indeed, steric effects seem to determine the type of structure observed experimentally.

The bonding of the type B molecules may simply be described by two 2e-3c bonds with the carbanionic carbon atoms of the alkynido groups in the bridging positions. The carbon atoms use their s-orbitals, which is the most important contribution to the stability of the bond (80 %), thus, the contribution of the aluminum p-orbitals is relatively small. Further stabilization results from interactions of the terminal Al-C bonds with the σ*-orbitals of the C-C bonds of the alkynido groups and from the back-bonding of π-electron density into the σ*-orbitals of the terminal Al-C bonds. Three-center bonds do not occur in the second form (type A). The bonding is essentially determined by localized Al-C σ-bonds formed by sp^3-hybrid orbitals of aluminum and sp-hybrid orbitals at the terminal carbon atoms of the alkynido groups. The particular structural motif of that type with the apparent side-on coordination of aluminum atoms to the triple bonds is the result of interactions involving empty p-orbitals localized at the metal atoms. These metal atom orbitals interact with the molecular orbitals forming the Al-alkynido bonds and with one of the occupied π-orbitals of the C≡C triple bond, both from the other unit.

Experimental Section

All procedures were carried out under dried argon. *n*-Hexane and *n*-pentane were dried over $LiAlH_4$, toluene over Na/benzophenone. The usually oligomeric starting compounds $(Me_3C)_2AlCl$ [18], Me_2AlH [19], $(Me_3C)_2AlH$ [7], Me_2GaH [8, 20], $(Me_3C)_2GaH$ [7], and $(Me_3C)_2GaCl$ [21] were obtained according to literature procedures. Commercially available H-C≡C-C_6H_5 (Aldrich) was employed without further purification.

Synthesis of [Me_2Al-C≡C-C_6H_5]$_2$ (4). A solution of dimethylaluminum hydride (0.6 ml; 0.53 g; 9.14 mmol) in 15 ml of *n*-pentane was slowly added to phenylethyne (0.93 g, 9.12 mmol) dissolved in 15 ml of *n*-pentane at room temperature. Gas evolved and the solution became yellow. The mixture was further stirred for 2 h. The solvent was removed in vacuum. The residue was recrystallized from *n*-pentane (20/−15 °C) to yield colorless crystals of **4**. Yield: 1.24 g (86 %). See reference [1] for characterization.

Synthesis of [$(Me_3C)_2Al$-C≡C-C_6H_5]$_2$ (5). *(i) Starting with di(tert-butyl)aluminum chloride*: *n*-Butyllithium (5.0 ml, 8.05 mmol, 1.6 M solution in *n*-hexane) was added to a cooled (0 °C) solution of phenylethyne (0.82 g, 8.05 mmol) in 20 ml of *n*-pentane. A colorless solid (LiC≡C-C_6H_5) precipitated. After further stirring for 2 h at room temperature and cooling to 0 °C, a solution of di(*tert*-butyl)-aluminum chloride (1.42 g, 8.05 mmol) in 20 ml of *n*-pentane was added. The mixture was warmed to room temperature and further stirred for an additional 2 h. After filtration, all the volatile components were removed in vacuum, and the residue was recrystallized from *n*-pentane. Yield: 1.15 g (59 %). *(ii) Starting with di(tert-butyl)aluminum hydride*: A solution of di(*tert*-butyl)aluminum hydride (1.29 g; 9.08 mmol) in 15 ml of *n*-pentane was slowly added to phenylethyne (0.93 g; 9.08 mmol) dissolved in 15 ml of the same solvent at room temperature. Gas evolution was observed, and the solution turned yellow. The mixture was stirred for another 2 h. All volatile components were removed in vacuum. The solid residue was recrystallized from *n*-pentane. Yield: 1.71 g (78 %); yellowish crystals. Mp (argon, sealed capillary): 185 °C.

^{1}H NMR (C_6D_6, 300 MHz): δ = 7.50 − 7.55 and 6.78 − 6.92 (5 H, m, C_6H_5), 1.43 (18 H, s, CMe_3). **^{13}C NMR** (C_6D_6, 125.8 MHz): δ = 137.5, 134.4, 131.8 and 129.0 (C_6H_5), 119.9 and 91.5 (C≡C), 32.0 (Me), 19.1 (AlC of CMe_3). **IR** (CsBr plates, paraffin, cm^{-1}): 2060 m νC≡C; 1595 vw, 1572 vw (phenyl); 1464 vs, 1377 vs (paraffin); 1358 sh, 1310 w, 1283 w δCH_3; 1206 w, 1175 w, 1094 vw, 1067 w, 1024 m, 1003 m, 936 m, 924 w νCC; 810 s (phenyl); 775 sh, 760 vs νC_3C; 721 w, 685 vs, 669 w, 648 w, 629 w, 610 w (phenyl); 584 m, 565 vs, 540 vs, 442 vs, 409 s νAlC; 365 s, 345 vs, 303 w, 278 w δC_3C.

Synthesis of [Me_2Ga-C≡C-C_6H_5]$_2$ (6). Me_2GaH (0.43 g; 4.27 mmol) was dissolved in 25 ml of *n*-hexane and treated with 0.44 g (4.27 mmol) of H-C≡C-C_6H_5 at room temperature. The mixture was stirred at room temperature over night. The colorless mixture became yellow. The solvent was removed in vacuum, and the residue was recrystallized from toluene (20/+8 °C). Yield: 0.42 g (49 %, colorless crystals). Mp. (argon, sealed capillary): 98 °C.

^{1}H NMR (C_6D_6, 300 MHz): δ = 7.30 (2 H, pseudo-d, ortho-H of phenyl), 6.77 (3 H, m, meta- and para-H of phenyl), 0.21 (6 H, s, Me). **^{13}C NMR** (C_6D_6, 75.5 MHz): δ = 133.4, 132.3, 130.4, and 128.7 (phenyl), 121.4 and 98.0 (C≡C), −2.3 (Me). **IR** (CsBr plates, paraffin, cm^{-1}): 2100 m νC≡C; 1572 vw, 1487 m (phenyl); 1461 vs, 1377 s (paraffin); 1307 w, 1283 w δCH_3; 1216 m, 1200 m, 1170 w, 1070 w, 1025 w, 1014 w, 928 w, 912 w νCC; 756 s, 730 s, 690 s, 648 s, 609 w (phenyl); 589 m, 540 m, 463 vw νGaC. **Molar mass** (in benzene, cryoscopy): Found 375; calcd. 401.8.

Synthesis of [$(Me_3C)_2Ga$-C≡C-C_6H_5]$_2$ (7). *(i) Starting with $(Me_3C)_2GaH$:* $(Me_3C)_2GaH$ (0.59 g; 3.19 mmol) was dissolved in 25 ml of *n*-hexane and treated with 0.35 ml (0.33 g, 3.19 mmol) H-C≡C-C_6H_5 at room temperature. The mixture was stirred at room temperature over night. The color of the mixture originally colorless turned yellow-orange. The solvent was removed in vacuum, and the solid residue was recrystallized from *n*-hexane (20/−40 °C). Di(*tert*-butyl)gallium hydride exists as an equilibrium mixture of three compounds in solution. This may be the reason why this procedure does not give sufficiently reproducible yields. *(ii) Starting with $(Me_3C)_2GaCl$:* A solution of $(Me_3C)_2GaCl$ (0.49 g, 2.22 mmol) in 25 ml of *n*-hexane was added dropwise to a suspension of LiC≡C-C_6H_5 (0.24 g, 2.22 mmol) in *n*-hexane (the lithium compound was obtained by the treatment of H-C≡C-C_6H_5 with *n*-butyllithium as described before). The reaction mixture was stirred at room temperature for 24 h and filtered. After concentration of the filtrate, the product was isolated as colorless crystals upon cooling to −30 °C. Yield: 0.36 g (57 %). Dec. p. (argon, sealed capillary): 163 °C.

^{1}H NMR (C_6D_6, 300 MHz): δ = 7.55 (2 H, pseudo-d, ortho-H of phenyl), 6.87 (3 H, m, meta- and para-H of phenyl), 1.51 (6 H, s, Me). **^{13}C NMR** (C_6D_6, 125.8 MHz): δ = 134.2, 130.7, and 128.9 (phenyl, one resonance not detected), 121.5 and 92.8 (C≡C), 32.2 (Me), 28.3 (GaC). **IR** (CsBr plates, paraffin, cm^{-1}): 2052 s νC≡C; 1592 w, 1573 w (phenyl); 1464 vs, 1377 s (paraffin); 1360 m, 1307 vw, 1288 vw, 1280 vw δCH_3; 1198 w, 1163 m, 1094 w, 1068 w, 1024 m, 1010 m, 938 w, 921 vw, 911 vw, 897 vw νCC; 814 m νC_3C; 756 s, 723 w, 689 m, 647 vw, 609 vw (phenyl); 559 m, 532 m, 514 m, 463 w, 391 m νGaC. **Molar mass** (in benzene, cryoscopy): Found 610; calcd. 570.2.

Crystal Structure Determinations of Compounds 4 to 7

Single crystals of compounds **4**, **5**, and **7** were obtained on cooling of solutions in *n*-hexane to +8 or −15 °C. Crystals of **6** grew from a solution in toluene at +8 °C. The crystallographic data were collected with a STOE IPDS diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97 [22] by a full-matrix least-squares method based on F^2. Crystal data, data collection parameters, and structure refinement details are given in Table 2. Four dimers, which were located on crystallographic centers of symmetry, were observed in the unit cell of **4**. Compound **5** crystallizes in the triclinic space group $P\bar{1}$ with six dimeric molecules in the unit cell, two of which are on crystallographic inversion centers. Some *tert*-butyl groups are disordered, their methyl groups were refined on optimized split positions. The gallium compounds **6** and **7** crystallize in the orthorhombic space groups Pbca and Pbcn, respectively. Four dimeric formula units

Table 2 Crystal data and structure refinement for **4**, **5**, **6**, and **7**

	4	**5**	**6**	**7**
Chem. formula	$C_{20}H_{22}Al_2$	$C_{32}H_{46}Al_2$	$C_{20}H_{22}Ga_2$	$C_{32}H_{46}Ga_2$
Crystal system	orthorhombic	triclinic	orthorhombic	orthorhombic
Space group [23]	Pbca, no. 61	$P\bar{1}$, no. 2	Pbca, no. 61	Pbcn, no. 60
Z	4	6	4	4
T/K	193	193	193	193
Calcd. density/g·cm^{-3}	1.093	1.020	1.399	1.232
a/pm	1089.58(8)	909.67(6)	1087.62(9)	941.24(7)
b/pm	773.70(4)	1895.3(2)	767.32(6)	2121.0(2)
c/pm	2280.7(1)	2772.9(2)	2286.5(2)	1539.1(1)
α/°		94.99(1)		
β/°		95.800(8)		
γ/°		92.187(9)		
V/Å^3	1922.7(2)	4732.9(7)	1908.2(3)	3072.6(4)
μ/mm^{-1}	0.146	0.108	2.818	1.770
Crystal size/mm	0.39 × 0.15 × 0.06	0.48 × 0.36 × 0.15	0.27 × 0.21 × 0.21	0.42 × 0.30 × 0.24
Diffractometer		STOE IPDS		
Radiation		Mo-K$_\alpha$; graphite monochromator		
Theta range for data collection	2.59−25.92	1.91−25.86	1.78−26.00	1.92−26.03
Index ranges	$-13 \le h \le 13$	$-11 \le h \le 11$	$-13 \le h \le 12$	$-11 \le h \le 11$
	$-9 \le k \le 8$	$-23 \le k \le 23$	$-9 \le k \le 8$	$-25 \le k \le 26$
	$-25 \le l \le 25$	$-33 \le l \le 33$	$-28 \le l \le 28$	$-18 \le l \le 17$
Unique reflections	1790 [R(int) = 0.0576]	17088 [R(int) = 0.1019]	1869 [R(int) = 0.0812]	3011 [R(int) = 0.0680]
Reflections with I > 2σ	1211	5770	1336	1914
Parameters	102	1172	102	164
R [I > 2σ(I)]$^{a)}$	0.0379	0.0589	0.0399	0.0363
wR$_2$ (all Data)$^{b)}$	0.1169	0.1781	0.0957	0.1095
Largest diff. peak/hole/Å^3	0.192/−0.144	0.254/−0.288	1.044/−0.630	0.529/−0.321

a) $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$
b) $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$
Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-236998 (**4**), -236999 (**5**), -237000 (**6**), and -237001 (**7**).

were found in each unit cell, these are located on either crystallographic inversion centers (**6**) or twofold rotation axes (**7**).

Quantum Chemical Calculations

Both structure types A and B were optimized at the HF/6-31G(d) level of theory which has previously proven to be reliable for related systems [24]. All calculations were performed with Gaussian 98 [25]. After optimization, the nature of the stationary points was characterized by calculating the harmonic frequencies. These frequencies are scaled by 0.8929 in order to account for anharmonicity [26]. ^{13}C NMR chemical shifts were determined with the GIAO (gauge-including atomic orbital) method [27] as implemented in Gaussian 98. The obtained shielding tensors are referenced against tetramethylsilane (TMS) to yield relative chemical shifts.

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