1406 *Organometallics* **2010,** *29,* 1406–1412
DOI: 10.1021/om901058a

ORGANOMETALLICS
Article

Hydroalumination and Hydrogallation of 1,2-Bis(trimethylsilylethynyl)benzene: Formation of Molecular Capsules and C−C Bond Activation

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Received December 10, 2009

Treatment of 1,2-bis(trimethylsilylethynyl)benzene with di-*tert*-butylaluminum and di-*tert*-butylgallium hydrides afforded the simple addition products 1,2-[(Me$_3$Si)(R$_2$E)C=C(H)]$_2$C$_6$H$_4$ (R = CMe$_3$; E = Al (**1**), Ga (**2**)), which could not be isolated in a pure crystalline form but have been characterized unambiguously by spectroscopic methods. Addition of the Lewis base ethyldimethylamine initiated condensation reactions which gave cage compounds (**3** and **4**) by the release of the corresponding tri-*tert*-butyl element derivatives. These cages contain two aluminum or gallium atoms which are bridged by three 1,2-bis(trimethylsilylethenyl)benzene spacers to form molecular capsules. The metal atoms are further coordinated by terminal amino groups. The amino ligands could not be removed from the dialuminum compound **4** without decomposition, but the ligand-free gallium compound **5** was obtained upon heating of **3** (E = Ga) to 80 °C under vacuum. Thermolysis of the aluminum compound **1** in boiling *n*-hexane gave a unique reaction by the release of tri-*tert*-butylaluminum and the formal elimination of trimethylsilylethyne (decarbalumination). The product **6** is dimeric in the solid state via Al−C−Al bridges and has a pentacyclic molecular structure.

Introduction

Hydroalumination and hydrogallation reactions[1] with alkynes are facile methods for the generation of a broad variety of unusual oligoaluminum or -gallium compounds.[2] Many reactions proceed by condensation and release of the corresponding trialkylelement derivatives. Alkynylaluminum or -gallium compounds, for instance, gave carbaalane clusters[3] or heteroadamantane cages[4] upon treatment with dialkyl element hydrides, while bis- or tris(*tert*-butylethynyl)benzenes afforded cyclophane-type molecules with two or three bridging metal atoms.[5] ((Trimethylsilyl)ethynyl)benzenes behaved differently.[6–8] Their

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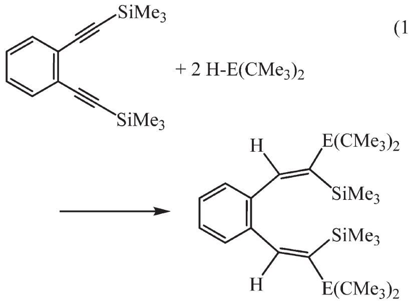
reactions with dialkyl or dichloro element hydrides afforded the relatively persistent simple addition products with intact EX_2 groups attached to one carbon atom of the resulting C=C double bonds. However, cis/trans isomerization occurred, which requires intermolecular activation and is prevented by steric shielding.[7] In these cases the release of trialkylgallium and the formation of divinyl- or trivinylgallium compounds has been observed only by treatment of the monoalkyne $H_5C_6C{\equiv}CSiMe_3$ with dialkylgallium hydrides.[8] We hoped to synthesize novel cage compounds by the application of particularly preorganized bis((trimethylsilyl)ethynes) and treated 1,2-bis((trimethylsilyl)ethynyl)benzene with di-*tert*-butylaluminum and di-*tert*-butylgallium hydrides.

Results and Discussion

Reactions of 1,2-Bis((trimethylsilyl)ethynyl)benzene with H−E(CMe₃)₂ (E = Al, Ga). Reactions of 1,2-bis((trimethylsilyl)ethynyl)benzene with di-*tert*-butylaluminum and di-*tert*-butylgallium hydrides yielded the expected addition products **1** and **2** under different conditions (eq 1). In accordance with our experience from previous experiments[2,5,7] the dialkylaluminum hydride is more reactive and gave the quantitative consumption of the starting compounds by stirring of the mixture at room temperature for 16 h. Probably due to the lower polarity of the Ga−H bond, the corresponding gallium hydride is less reactive, and boiling *n*-hexane was required for completion of the reaction. Any spontaneous secondary reaction such as isomerization or condensation (see the Introduction) was not observed even when the mixtures were stirred at room temperature (**1**) or heated (**2**) for several days. In particular the corresponding tri-*tert*-butyl element compounds could not be detected by NMR spectroscopy as byproducts. This behavior corresponds to results previously obtained with different ((trimethylsilyl)ethynyl)benzene derivatives.[2,6−8] Despite intense efforts we were not able to purify either compound by crystallization from different solvents (cyclopentane, toluene, pentafluorobenzene, etc.). They were isolated as highly viscous liquids which, owing to the NMR spectroscopic characterization, consist of essentially one main component but contain several unknown impurities in concentrations of up to 15%. Nevertheless, NMR spectroscopy allowed an unambiguous identification of these compounds and a clear assignment of their molecular configuration. The integration ratio of the ^1H NMR spectra gave the expected 1:1 ratio of $SiMe_3$ and ER_2 groups. The vinylic hydrogen atoms (δ 7.98 and 7.68, respectively) are bonded to the α-carbon atoms of the ethenyl groups neighboring the central benzene rings. The aluminum and gallium atoms adopted geminal positions with the trimethylsilyl groups. This reaction pattern follows the charge separation in the ethynyl groups, in which the electronegativity difference between the sp-hybridized carbon atoms and silicon causes a partial negative charge at the β-carbon atoms and, hence, favors the attack of the positively charged metal atoms at this position. Hydrogen and metal atoms are in cis positions, as unambiguously derived from the characteristic $^3J_{H-Si}$ coupling constants (20.3 and 19.4 Hz, trans arrangement of Si and H) across the C=C double bonds.[2,6−8]



(1)

1: E = Al
2: E = Ga

Treatment of Compounds 1 and 2 with Ethyldimethylamine. Di-*tert*-butylgallium hydride[9] is accessible by the reaction of tri-*tert*-butylgallium with stoichiometric quantities of the gallane−amine adduct $H_3Ga \leftarrow NMe_2Et$. The amine is removed by distillation under vacuum. Accidentally, one sample of the dialkylgallium hydride contained traces of the amine by incomplete purification, which caused an interesting and unexpected secondary reaction upon treatment with the 1,2-bis(alkyne). Colorless crystals of compound **3** were isolated in trace quantities. Crystal structure determination revealed a unique structural motif with two gallium atoms bridged by three bifunctional dialkenylbenzene spacer ligands. Each gallium atom is further coordinated by a terminal amino ligand (see below for details). An optimized procedure comprises the reaction of the components in a molar ratio of 3:6:2 (1,2-bis(alkyne):gallium hydride:amine; eq 2). Hence, the quantity of the amine is just sufficient to coordinate both gallium atoms of the cage compound **3**. Tri-*tert*-butylgallium was detected in the ^1H NMR spectrum of the raw product (singlet at δ 1.16). Compound **3** is only sparingly soluble in *n*-hexane and precipitated directly from the reaction mixtures. It was isolated in a relatively low yield of 25%. A similar procedure was applied to the synthesis of the corresponding dialuminum compound **4**, which was isolated in 61% yield. The ^1H NMR spectra of **3** and **4** exhibit the resonances of the ethyldimethylamino ligands and the bridging dialkenyl groups in the expected ratios. Resonances of *tert*-butyl groups are missing. The chemical shifts of the spacer ligands are similar to those of the addition products **1** and **2**. The vinylic hydrogen atoms appear at δ 7.83 (**3**) and 8.15 (**4**). The $^3J_{H-Si}$ coupling constants (18.7 and 23.3 Hz, respectively) verify the cis arrangement of hydrogen and metal atoms at the C=C double bonds similar to that in **1** and **2**. Both compounds (**3** and **4**) could not be obtained by the obvious reaction of the trihydrido element compounds $H_3E \leftarrow NMe_2Et$[10] with the bis(alkyne). The gallium trihydride is thermally relatively unstable and decomposed by the precipitation of elemental gallium in boiling *n*-hexane. The trihydridoaluminum compound gave an insoluble precipitate of unknown composition. Ether as a donor instead of the amine did not initiate these condensation reactions.

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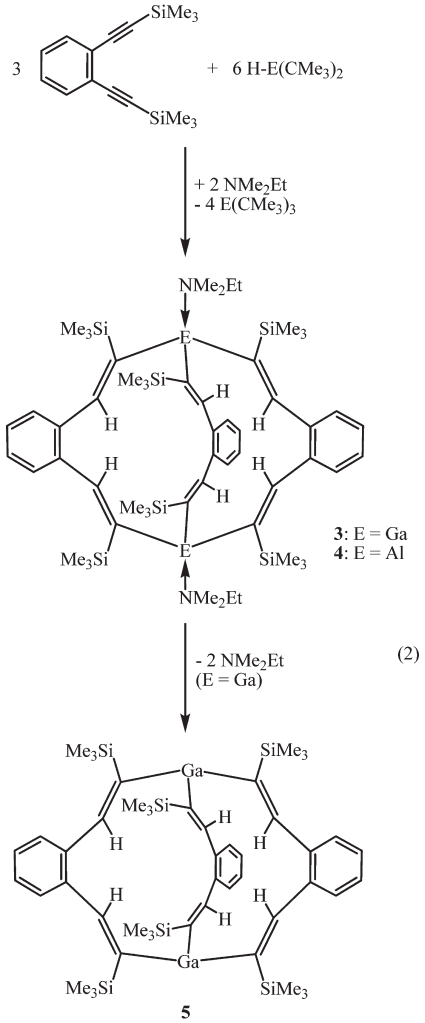

The molecular structures of compounds **3** and **4** (Figures 1 and 2) comprise two metal atoms which are bridged by three 1,2-dialkenylbenzene groups. The phenyl groups of the spacer ligands adopt a paddle-wheel arrangement, and the metal atoms are coordinated by terminal ethyldimethylamino ligands. The overall structural motif is strongly reminiscent of a spinning top. The Ga−N (2.152 Å) and Al−N distances (2.067 Å) resemble standard values of corresponding donor−acceptor interactions.[11] All bond lengths (M−N, C=C, etc.) are in the normal range and do not require a detailed discussion. Only the angles M−C=C (109° on average) and C=C−C (about 130°) deviate from the ideal values expected for sp^2- carbon atoms, which may indicate some steric stress in the cages. The particular and unprecedented arrangement of the bridging ligands forms a cavity in

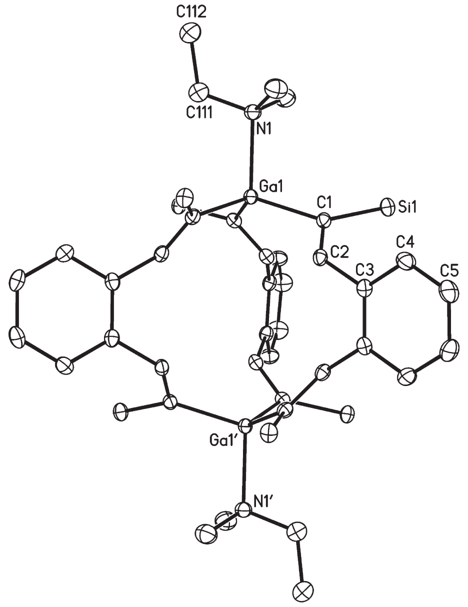

Figure 1. Molecular structure of **3**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms and methyl groups of SiMe$_3$ are omitted. Important bond lengths (Å) and angles (deg): Ga(1)−C(1) = 2.023(3), Ga(1)−N(1) = 2.152(4), C(1)−C(2) = 1.349(4); C(1)−Ga(1)−C(1)′ = 112.35(7), Ga(1)−C(1)−C(2) = 109.1(2), C(1)−C(2)−C(3) = 129.7(3), C(2)−C(3)−C(3)′ = 119.2(2). C(1)′ is generated by $-x + y + 1$, $-x + 1$, z and C(3)′ by $-x + {}^4/_3$, $-x + y + {}^2/_3$, $-z + {}^1/_6$.

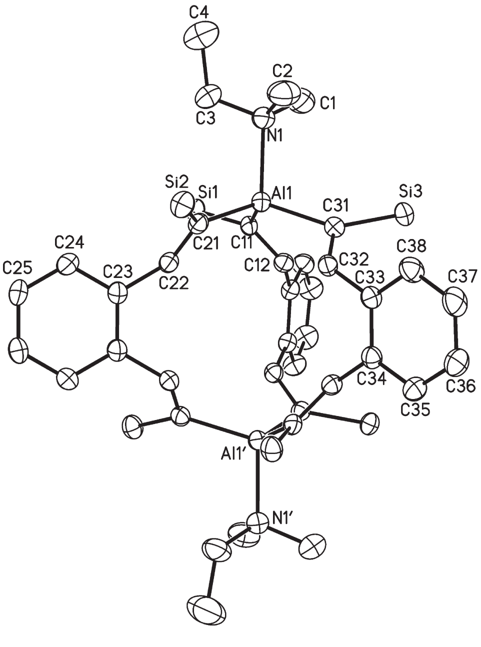

Figure 2. Molecular structure of **4**. The thermal ellipsoids are drawn at the 40% probability level. The hydrogen atoms and methyl groups of SiMe$_3$ are omitted. Important bond lengths (Å) and angles (deg): Al(1)−C(11) = 2.009(4), Al(1)−C(21) = 2.017(4), Al(1)−C(31) = 2.013(4), Al(1)−N(1) = 2.067(3), C(11)−C(12) = 1.348(5), C(21)−C(22) = 1.352(5), C(31)−C(32) = 1.348(5); C(11)−Al(1)−C(21) = 112.5(1), C(11)−Al(1)−C(31) = 111.8(1), C(21)−Al(1)−C(31) = 111.9(1), Al(1)−C(11)−C(12) = 109.1(2), Al(1)−C(21)−C(22) = 108.5(2), Al(1)−C(31)−C(32) = 109.2(2), C(11)−C(12)−C(34)′ = 129.9(3), C(21)−C(22)−C(23) = 130.6(3), C(31)−C(32)−C(33) = 129.7(3). C(34)′ is generated by $-x$, y, $-z + {}^1/_2$.

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the molecular center. The resulting intramolecular metal−metal distances are similar in both compounds (Ga−Ga, 5.86 Å; Al−Al, 5.91 Å). The longest distances between carbon atoms of the cage are slightly shorter (e.g., C12−C12′ or C32−C22′ of compound **3** with 4.82 Å). The resulting relatively small void in the molecular center should in principle be suitable for the encapsulation of atoms or small molecules (see below for further discussion).

Synthesis of the Solvent-Free Compound 5. The addition of the amine initiated the condensation reactions according to eq 2 with the formation of the novel cage compounds **3** and **4**. However, the coordinative saturation of the metal atoms may hinder the application of these compounds in secondary reactions such as adduct formation, formation of coordination polymers, electrochemistry, etc. Hence, it was of particular interest to generate the solvent-free compounds possessing tricoordinated, coordinatively unsaturated metal atoms. The removal of the amino groups succeeded only with the digallium compound **3** by heating of solid samples to 80 °C under vacuum (10^{-3} Torr) (**5**; eq 2). The free amine was collected in a trap cooled with liquid nitrogen and identified by ^{1}H NMR spectroscopy. The stronger Lewis acidity of aluminum compounds prevented a similar reaction of **4**. Heating under vacuum to temperatures above 80 °C gave decomposition by formation of a black solid material. The chemical shifts in the NMR spectra of **5** are almost unchanged compared to those of **3**; only the resonances of the ethyldimethylamino ligands are missing. Despite intense efforts, we were not able to generate single crystals of **5** for a crystal structure determination. However, spectroscopic and analytical characterization, including the detection of the molecular mass in the mass spectrum, gave clear evidence that the cage remained intact. Further evidence came from a DOSY NMR experiment. The ratios between the diffusion coefficients of **3** and **5** and those of the solvent (benzene) or tetramethylsilane are almost identical, which indicates similar Stokes radii and molecular forms.[12]

Geometry optimization by quantum-chemical calculations including dispersion correction (B97-D/def2-TZVPP)[13,14] revealed structural parameters of **5** that are closely related to those of **3** and **4**. The gallium atoms deviate from a planar environment and are 0.289 Å above the triangle formed by the three adjacent vinylic carbon atoms. The C−Ga−C angles are 117.9° on average. The Ga···Ga distance in the (calculated) cage of **5** (5.60 Å) is shortened by 0.26 Å compared with the distance detected by X-ray diffraction for the bis(amino) adduct **3**. In order to evaluate the capability of these cages to encapsulate particular guests, DFT calculations on host−guest complexes were performed (Table 1). The inclusion of alkali-metal ions in the center of the host (D_{3h} symmetry) is predicted to be exothermic (−70.9 kcal/mol for Li^+, −17.5 kcal/mol for K^+ in comparison to the sum of energies of the free host and guest). The values decrease systematically with the increasing size of the cation. Silver ions are the most tightly bound (−83.7 kcal/mol). Interestingly, the terminal coordination of Li^+ to a single Ga atom from outside of the cage is also quite exothermic in the gas phase (−59.5 kcal/mol). A size dependence similar to that of the alkali-metal cations was found for the halide anions, for which we calculated exothermic encapsulation energies for fluoride (−90.3 kcal/mol) and chloride (−18.9 kcal/mol) but an endothermic value for bromide (10.4 kcal/mol). The terminal coordination of a Cl^- ion to one of the Ga atoms is calculated to be much more favorable (−65.0 kcal/mol), thus making an encapsulation quite unlikely. Surprisingly, the intramolecular distances between the Ga atoms vary considerably in dependence of the charge and size of the guest ion. The separation is enlarged from 5.6 Å in the empty cage to 5.9−6.0 Å in the case of encapsulated Li^+, Na^+, and K^+ ions but is reduced to 4.1 Å for F^- and 4.8 Å for Cl^-. Larger anions such as CN^- give only a weak exothermic reaction (−25.2 kcal/mol), while the complexation of OCN^- (+54.4 kcal/mol) or molecular nitrogen (+42.2 kcal/mol) is calculated to be strongly endothermic, which is in accordance with the relatively small void in the center of the molecule. NBO-charge calculations show that the negative charge of encapsulated anions is mainly localized at the Ga atoms (ca. 0.4−0.5 e), whereas the positive charge of cations is partially (ca. 0.4 e) delocalized over the carbon atoms of the cage.

Table 1. Calculated Heats of Encapsulation (kcal/mol) Relative to the Sum of the Free Guest and Host and Intramolecular Ga−Ga and Ga−Guest Distances (Å)

guest	E_{rel}	Ga···Ga	Ga···guest
Li^+	−70.93	5.949	2.974
Li^+ on top	−59.51	5.384	2.809
Na^+	−63.16	5.871	2.935
K^+	−17.49	5.989	2.994
Ag^+ (ECP)	−83.67	5.793	2.896
F^-	−90.29	4.077	2.039
Cl^-	−18.90	4.769	2.385
Cl^- (terminal)	−65.04	6.016	2.318
Br^-	10.42	4.975	2.487
CN^-	−25.23	5.114	1.998 (Ga−C); 1.967 (Ga−N)
OCN^-	54.42	6.040	1.855 (Ga−N); 1.861 (O−Ga)
N_2	42.23	5.454	2.180

Currently it is most certainly the aesthetic appeal of these interesting compounds that dominates. Future investigations will show whether the presented method is applicable for the generation of larger cavities and whether the unique bifunctionality of these compounds may be utilized in the preparation of supramolecular structures.

Thermolysis of Compound 1. The amine-free aluminum compound analogous to **5** was not accessible by heating of the amino adduct **4** under vacuum. We hoped to synthesize this compound through another route by the thermally initiated elimination of tri-*tert*-butylaluminum from the addition product **1**. A similar reaction with the diethylgallium compound $Et_2GaC(SiMe_3){=}C(H)C_6H_5$ gave the corresponding trivinylgallium compound $Ga[C(SiMe_3){=}C(H)C_6H_5]_3$ in an almost quantitative yield.[8] We generated the addition product **1** in *n*-hexane as described above and heated the solution under reflux for 5 days (eq 3). As expected, tri-*tert*-butylaluminum was formed in a slow reaction. Concentration of the mixture and cooling to +4 °C gave colorless crystals of the product **6**. NMR spectroscopy clearly revealed that a new compound has been formed which exhibited the resonances of four different aromatic

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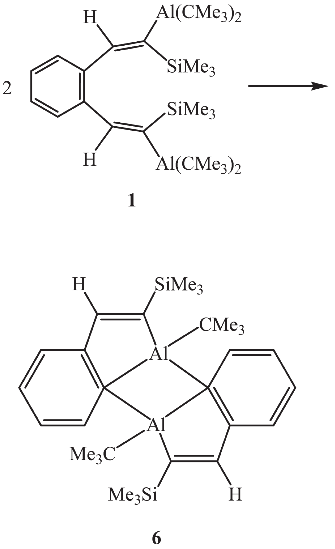
hydrogen atoms and one vinylic hydrogen atom in addition to a *tert*-butyl and trimethylsilyl group in an equimolar ratio.



(3)

+ 2 $Al(CMe_3)_3$

+ 2 "H-C≡C-$SiMe_3$"

The constitution of **6** was clarified by crystal structure determination (Figure 3). In accordance with the NMR spectroscopic characterization it has only one intact vinyl group with a terminal trimethylsilyl substituent in a monomeric formula unit. The aluminum atom is bonded to a terminal *tert*-butyl group. It adopts a bridging position between the β-carbon atom of the C=C double bond and a carbanionic carbon atom of the benzene ring. The latter atom is in an α-position to the carbon atom bearing the intact vinyl group and may represent the position of the missing vinyl substituent. Dimeric formula units are formed via two 3z−2e Al−C−Al bonds in which the negatively charged carbon atoms of the benzene rings are involved. This situation is similar to that in triphenylaluminum or related phenylaluminum compounds.[15] The Al−C distances in the Al_2C_2 ring (2.120(1) and 2.136(1) Å) correspond to the values observed for those derivatives. All other bond lengths are in the expected ranges and do not require a detailed discussion. An overall pentacyclic molecule with an unprecedented molecular structure resulted. A mechanism for the formation of compound **6** may comprise the release of tri-*tert*-butylaluminum to give a heterocyclic compound in which both vinyl substituents are bridged by a single aluminum atom. We observed similar reactions with the formation of cyclophane-type molecules in previous investigations.[7] A heterocycle similar to that postulated here which has two C=C double bonds bridged by a chlorogallium group has been obtained by the reaction of 1,2,4,5-tetrakis(trimethylsilylethynyl)benzene with $HGaCl_2$.[6b,c] The unexpected cleavage of the C−C bond may proceed via β-elimination with the formation of the phenylaluminum group and the release of (trimethylsilyl)ethyne. Such a decarbalumination reaction has been postulated in the literature in conjunction with the β-elimination of alkylaluminum and formation of an alkene.[16] This part of the suggested mechanism seems to be reasonable but relatively speculative, because we were not able to identify the ethyne by spectroscopic methods. We did not observe a similar reaction in our previous experiments. The surprising C−C bond activation will stimulate further investigations.

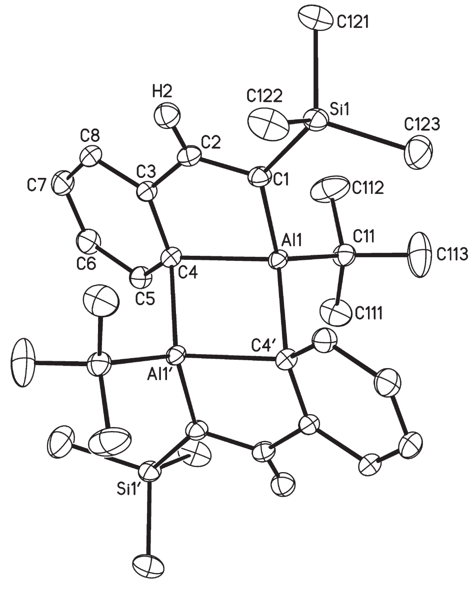


Figure 3. Molecular structure of **6**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms and methyl groups of $SiMe_3$ are omitted. Important bond lengths (Å) and angles (deg): Al(1)−C(1) = 1.976(1), Al(1)−C(4) = 2.120(1), Al(1)−C(4)′ = 2.136(1), C(1)−C(2) = 1.353(2), C(3)−C(4) = 1.429(2); Al(1)−C(4)−Al(1)′ = 76.72(4), C(4)−Al(1)−C(4)′ = 103.28(4), Al(1)−C(1)−C(2) = 106.25(9), C(1)−C(2)−C(3) = 122.2(1), C(2)−C(3)−C(4) = 118.4(1), C(3)−C(4)−Al(1) = 100.84(8), C(3)−C(4)−Al(1)′ = 122.81(9). Al(1)′ and C(4)′ are generated by $-x, -y + 1, -z$.

Experimental Section

All procedures were carried out under purified argon. Cyclopentane and *n*-hexane were dried over $LiAlH_4$ and 1,2-difluorobenzene over molecular sieves. $t\mathrm{Bu}_2\mathrm{AlH}$,[9] $t\mathrm{Bu}_2\mathrm{GaH}$,[9] and 1,2-bis(trimethylsilylethynyl)benzene[17] were obtained according to literature procedures. The assignment of the NMR spectra is based on HMBC, HSQC, ROESY, and DEPT135 data.

Reaction of 1,2-($Me_3SiC{\equiv}C)_2C_6H_4$ with H−Al($CMe_3)_2$; Synthesis of 1. A solution of H−Al($CMe_3)_2$ (0.241 g, 1.70 mmol) in 10 mL of *n*-hexane was treated with a solution of 1,2-($Me_3SiC{\equiv}C)_2C_6H_4$ (0.229 g, 0.85 mmol) in 10 mL of *n*-hexane. The mixture was stirred at room temperature for 16 h. Evaporation of the solvent gave a reddish highly viscous liquid, which could not be purified by crystallization from different noncoordinating solvents. Its purity was sufficient for a spectroscopic characterization. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.98 (2 H, s, $^3J_{\mathrm{H-Si}}$ = 20.3 Hz, vinylic H), 7.33 (2 H, m, 3,6-H of aromatic ring), 7.08 (2 H, m, 4,5-H of aromatic ring), 1.20 (36 H, s, $AlCMe_3$), 0.12 (18 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 159.5 (C=*C*−Al), 153.9 (*C*=C−Al), 141.3 (1,2-C of aromatic ring), 128.7 (3,6-C of aromatic ring), 127.6 (4,5-C of aromatic ring), 29.9 (Al−C*Me*$_3$), 19.2 (Al−C), 1.6 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −13.4.

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Table 2. Crystal Data, Data Collection Parameters, and Structure Refinement Details for Compounds 3, 4, and 6

	$\mathbf{3}\cdot C_6H_{14}$	$\mathbf{4}\cdot 4C_6H_4F_2$	**6**
formula	$C_{62}H_{94}Ga_2N_2Si_6$	$C_{80}H_{110}Al_2F_8N_2Si_6$	$C_{30}H_{46}Al_2Si_2$
cryst syst	rhombohedral	monoclinic	triclinic
space group	$R\bar{3}c$	$C2/c$	$P\bar{1}$
Z	6	4	1
temp, K	153(2)	153(2)	153(2)
D_{calcd}, g/cm^3	1.154	1.154	1.094
a, Å	14.9203(3)	29.474(6)	9.1789(7)
b, Å	14.9203(3)	15.050(3)	9.3838(7)
c, Å	52.633(3)	19.347(4)	10.810(1)
α, deg	90	90	95.770(1)
β, deg	90	98.46(3)	99.954(1)
γ, deg	120	90	118.907(1)
V, 10^{-30} m^3	10 147.1(6)	8489(3)	784.3(1)
μ, mm^{-1}	0.938	0.177	0.185
cryst dimens, mm	0.05 × 0.03 × 0.03	0.40 × 0.23 × 0.03	0.13 × 0.12 × 0.03
radiation	Mo Kα; graphite monochromator		
θ range, deg	1.76−25.04	1.80−29.33	1.96−31.96
index ranges	$-17 \le h \le +17$ $-17 \le k \le +17$ $-62 \le l \le +62$	$-40 \le h \le +40$ $-20 \le k \le +20$ $0 \le l \le +26$	$-13 \le h \le +13$ $-13 \le k \le +13$ $-15 \le l \le +15$
no. of unique rflns	2007 (R_{int} = 0.0778)	11 518 (R_{int} = 0.0604)	4937 (R_{int} = 0.0213)
no. of params	119	412	160
R1 (rflns $I > 2\sigma(I)$)	0.0389 (1606)	0.0789 (5205)	0.0402 (3862)
wR2 (all data)	0.1125	0.2175	0.1110
max/min residual electron density, 10^{30} e/m^3	+1.063/−1.012	+1.084/−0.766	+0.391/−0.222

Reaction of 1,2-($Me_3SiC{\equiv}C)_2C_6H_4$ with H−Ga($CMe_3)_2$: Synthesis of 2. A solution of 1,2-($Me_3SiC{\equiv}C)_2C_6H_4$ (0.290 g, 1.07 mmol) in 10 mL of *n*-hexane was added to a solution of H−Ga($CMe_3)_2$ (0.397 g, 2.15 mmol) in 50 mL of *n*-hexane at room temperature. The mixture was heated under reflux for 16 h. Cooling to room temperature and evaporation of the solvent gave a highly viscous liquid, which could not be purified by crystallization from different noncoordinating solvents. Its purity was sufficient for a spectroscopic characterization. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.68 (2 H, s, $^3J_{H-Si}$ = 19.4 Hz, vinylic H), 7.36 (2 H, m, 3,6-H of aromatic ring), 7.09 (2 H, m, 4,5-H of aromatic ring), 1.27 (36 H, s, GaCMe$_3$), 0.09 (18 H, s, SiMe$_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 163.9 (C=*C*−Ga), 150.1 (*C*=C−Ga), 140.9 (1,2-C of aromatic ring), 129.1 (3,6-C of aromatic ring), 127.3 (4,5-C of aromatic ring), 30.3 (Ga−C*Me*$_3$), 29.4 (Ga−C), 1.7 (SiMe$_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −12.5.

Reaction of 1,2-($Me_3SiC{\equiv}C)_2C_6H_4$ with H−Ga($CMe_3)_2$ and NMe_2Et: Synthesis of 3. A solution of 1,2-($Me_3SiC{\equiv}C)_2C_6H_4$ (0.312 g, 1.16 mmol) and H−Ga($CMe_3)_2$ (0.426 g, 2.31 mmol) in 70 mL of *n*-hexane was treated with 0.083 mL of NMe$_2$Et (0.056 g, 0.77 mmol) at room temperature. The yellow solution was heated under reflux for 16 h. The color of the mixture changed to brown, and a colorless solid precipitated. After the mixture was cooled to room temperature, the solvent was decanted, and the solid was washed several times with small portions of *n*-hexane. Yield of **3**·0.5(*n*-hexane): 0.110 g (25%); **3** can be crystallized from cyclopentane. Mp (argon, sealed capillary): 155 °C dec. Anal. Calcd for $C_{56}H_{94}Ga_2N_2Si_6\cdot 0.5C_6H_{14}$ (1103.3 + 43.1): C, 61.8; H, 8.9; N, 2.4. Found: C, 61.9; H, 8.8; N, 2.4. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.83 (6 H, s, $^3J_{H-Si}$ = 18.7 Hz, vinylic H), 7.34 (6 H, m, 3,6-H of aromatic ring), 7.12 (6 H, m, 4,5-H of aromatic ring), 2.76 (4 H, q, $^3J_{H-H}$ = 7.2 Hz, NCH$_2$), 2.24 (12 H, s, NCH$_3$), 1.23 and 0.89 (*n*-hexane), 0.79 (6 H, t, $^3J_{H-H}$ = 7.2 Hz, NCH$_2$C*H*$_3$), 0.18 (54 H, s, SiMe$_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 159.9 (*C*=C−Ga), 156.6 (C=*C*−Ga), 142.5 (1,2-C of aromatic ring), 128.0 (3,6-C of aromatic ring), 126.9 (4,5-C of aromatic ring), 53.9 (NCH$_2$), 45.0 (NCH$_3$), 32.0, 23.1, and 14.4 (*n*-hexane), 8.3 (NCH$_2$*C*H$_3$), 3.4 (SiMe$_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −10.1. IR (CsI plates, paraffin, cm^{-1}): 1653 w, 1558 w, 1537 s, 1529 s, phenyl, ν(C=C); 1454 vs, 1377 vs (paraffin); 1308 vw, 1254 m, 1242 s, δ(CH$_3$); 1202 vw, 1175 w, 1096 w, 1086 m, 1026 m, 1011 m, ν(CN), ν(CC); 945 vw, 916 s, 899 w, 878 m, 864 m, 824 s, 793 vw, 766 m, 748 s, ρ(CH$_3$Si); 719 w (paraffin); 681 m ν_{as}(SiC); 644 m ν_s(SiC); 602 vw, 557 m, 484 w, 463 vw, 422 m ν(GaN), ν(GaC), δ(CC). MS (EI, 20 eV, 160 °C; *m*/*z* (%)): 954 (1), 956 (2), 957 (1), 958 (1) [M$^+$ − 2NMe$_2$Et], 682 (3), 684 (5), 685 (6), 686 (3) [M$^+$ − 2NMe$_2$Et − $C_6H_4\{C(H){=}C(SiMe_3)\}_2$], 341 (100), 343 (74) [Ga$\{(Me_3Si)C{=}C(H)\}_2C_6H_4$].

Reaction of 1,2-($Me_3SiC{\equiv}C)_2C_6H_4$ with H−Al($CMe_3)_2$ and NMe_2Et: Synthesis of 4. A solution of 1,2-($Me_3SiC{\equiv}C)_2C_6H_4$ (0.311 g, 1.15 mmol) in 20 mL of *n*-hexane was added to a solution of H−Al($CMe_3)_2$ (0.327 g, 2.30 mmol) in 50 mL of *n*-hexane. The mixture was treated with 0.083 mL of NMe$_2$Et (0.056 g, 0.77 mmol) at room temperature and stirred for 24 h. After about 2 h the product started to precipitate as a colorless solid. The suspension was concentrated. The solvent was removed by decantation, and the solid was washed twice with small portions of *n*-hexane. Yield of **4**·0.5(*n*-hexane): 0.246 g (61%). Mp (argon, sealed capillary): 240 °C dec. Anal. Calcd for $C_{56}H_{94}Al_2N_2Si_6\cdot 0.5C_6H_{14}$ (1017.9 + 43.1): C, 66.8; H, 9.6; N, 2.6. Found: C, 67.1; H, 9.3; N, 2.3. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.15 (6 H, s, $^3J_{H-Si}$ = 23.3 Hz, vinylic H), 7.27 (6 H, m, 3,6-H of aromatic ring), 7.16 (6 H, m, 4,5-H of aromatic ring), 3.20 (4 H, q, $^3J_{H-H}$ = 7.1 Hz, NCH$_2$), 2.35 and 2.36 (each 6 H, s, NCH$_3$), 1.23 and 0.89 (*n*-hexane), 0.65 (6 H, t, $^3J_{H-H}$ = 7.1 Hz, NCH$_2$C*H*$_3$), 0.19 (54 H, s, SiMe$_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 164.2 (*C*=C−Ga), 155.6 (C=*C*−Ga), 144.2 (1,2-C of aromatic ring), 128.1 (3,6-C of aromatic ring), 126.6 (4,5-C of aromatic ring), 52.8 (NCH$_2$), 43.8 (NCH$_3$), 32.0, 23.1, and 14.3 (*n*-hexane), 14.3 (NCH$_2$*C*H$_3$), 4.1 (SiMe$_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −10.4. IR (CsI plates, paraffin, cm^{-1}): 1913 vw, 1692 w, 1643 m, 1551 s, 1524 s, phenyl, ν(C=C); 1449 vs, 1375 s (paraffin); 1305 vw, 1254 m, 1242 s, δ(CH$_3$); 1198 vw, 1171 w, 1084 s, 1022 w, 1003 w, ν(CN), ν(CC); 957 vw, 918 s, 880 m, 864 m, 823 m, 770 m, 748 s, ρ(CH$_3$Si); 721 w (paraffin); 679 m, ν_{as}(SiC); 644 m, 625 w, ν_s(SiC); 573 w, 557 vw, 532 vw, 490 s, 446 vw, 430 s, ν(AlN), ν(AlC), δ(CC). MS (EI, 20 eV, 160 °C; *m*/*z* (%)): 870 (1.5), 871 (1.2), 872 (1) [M$^+$ − 2NMe$_2$Et], 855 (1), 856 (1), 857 (0.7) [M$^+$ − 2NMe$_2$Et − Me], 797 (2), 798 (2), 799 (1) [M$^+$ − 2NMe$_2$Et − SiMe$_3$].

Synthesis of the Amine-Free Compound 5. The solid amino adduct **3** (0.303 g, 0.28 mmol) was heated under vacuum (10^{-3} Torr) to 80 °C for 16 h. The amine was removed quantitatively. It was collected in a trap cooled by liquid nitrogen. The amine-free compound **5** remained as a colorless solid in a quantitative yield and in very high purity. Yield: 0.250 g (95%). Mp (argon, sealed capillary): 181 °C dec. Anal. Calcd for $C_{48}H_{72}Ga_2Si_6$ (957.1): C, 60.2; H, 7.6. Anal. Found: C, 59.5; H, 7.5. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.83 (6 H, s, $^3J_{H-Si}$ = 17.7 Hz, vinylic H), 7.37 (6 H, m, 3,6-H of aromatic ring), 7.05 (6 H, m, 4,5-H of aromatic ring), 0.20 (54 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 160.3 (C=*C*−Ga), 155.7 (*C*=C−Ga), 140.1 (1,2-C of aromatic ring), 127.4 (4,5-C of aromatic ring), 127.3 (3,6-C of aromatic ring), 2.4 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −10.0. IR (CsI plates, paraffin, cm^{-1}): 1921 vw, 1595 vw, 1568 vw, 1537 s, phenyl, ν(C=C); 1458 vs, 1375 vs (paraffin); 1304 vw, 1273 w, 1259 s, 1244 vs, $\delta(CH_3)$; 1177 m, 1153 w, 1088 m, 1038 w, 1024 w, 1008 w, ν(CC); 974 vw, 948 vw, 916 s, 897 s, 872 vs, 839 vs, 795 sh, 741 vs, $\rho(CH_3Si)$; 721 s (paraffin); 683 m, ν_{as}(SiC); 644 m, ν_s(SiC); 604 vw, 561 w, 529 w, 476 w, 413 s, ν(GaC), δ(CC). MS (EI, 20 eV, 160 °C; *m*/*z* (%)): 956 (3), 957 (5), 958 (4), 959 (3) [M^+ + H], 681 (3), 683 (8), 684 (5), 685 (8) [$M^+ - C_6H_4\{C(H){=}C(SiMe_3)\}_2 - H$], 341 (100), 343 (82) [$GaC_6H_4\{C(H){=}C(SiMe_3)\}_2{}^+$].

Thermolysis of Compound 1: Synthesis of 6. A solution of 1,2-bis((trimethylsilyl)ethynyl)benzene (0.194 g, 0.72 mmol) in 10 mL of *n*-hexane was added to a solution of di-*tert*-butylaluminum hydride (0.204 g, 1.44 mmol) in 10 mL of *n*-hexane. As shown by ^{1}H NMR spectroscopy, compound **1** was formed as an intermediate. The mixture was heated under reflux for 5 days. Its color changed to red. The solution was concentrated at room temperature and cooled to +4 °C to isolate a colorless solid of **6**. Yield: 0.105 g (56%). Mp (argon, sealed capillary): 134 °C dec. Anal. Calcd for $C_{30}H_{46}Al_2Si_2$ (516.8): C, 69.7; H, 9.0; Al, 10.4. Found: C, 69.7; H, 9.0; Al, 10.4. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.31 (2 H, d, $^3J_{H-H}$ = 7.0 Hz, H−C6 of the aromatic ring, Al−C−CH), 8.11 (2 H, s, $^3J_{H-Si}$ = 9.6 Hz, vinylic H), 7.17 (2 H, m, H−C4 of the aromatic ring), 7.11 (2 H, m, H−C3 of the aromatic ring), 7.10 (2 H, m, H−C5 of the aromatic ring), 0.69 (18 H, s, CMe_3), 0.40 (18 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 167.3 (C=*C*−Al), 164.2 (C2 of the aromatic ring attached to the vinylic carbon atom), 160.0 (*C*=C−Al), 148.5 (C6 of the aromatic ring), 136.4 (C4 of the aromatic ring), 127.5 (C3 of the aromatic ring), 127.2 (C5 of the aromatic ring), 124.5 (C1 of the aromatic ring attached to Al), 29.2 (C*Me*$_3$), 17.7 (Al-*C*Me$_3$),1.0 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −6.6. IR (CsI plates, paraffin, cm^{-1}): 1923 w, 1869 w, 1593 w, 1537 m, 1514 w, phenyl, ν(C=C); 1456 vs, 1375 vs (paraffin); 1307 w, 1246 vs, $\delta(CH_3)$; 1171 m, 1159 m, 1107 w, 1088 w, 1038 m, 1001 m, ν(CC); 934 m, 918 m, 839 s, 810 sh, 752 s, $\rho(CH_3Si)$; 721 s (paraffin); 687 w, ν_{as}(SiC); 645 w, 629 w, ν_s(SiC); 592 m, 529 w, 455 m, 428 m, ν(AlC), δ(CC). MS (EI, 20 eV, 100 °C; *m*/*z* (%)): 459 (37) [$M^+ - CMe_3$], 258 (38) [$^1/_2M^+$], 201 (100) [$^1/_2M^+ - CMe_3$].

Crystal Structure Determinations of Compounds 3, 4, and 6. Single crystals were obtained by crystallization from a dilute solution in *n*-hexane (**3**, +20/−45 °C; **6**, +20/+4 °C) or from 1,2-difluorobenzene (+20/−25 °C; **4**). The crystallographic data were collected with Bruker APEX (**3** and **6**) and Stoe IPDS diffractometers (**4**). The structures were solved by direct methods and refined with the program SHELXL-97[18] 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. The Ga and N atoms of compound **3** are located on crystallographic 3-fold rotation axes. Hence, the ethyldimethylamino ligands are statistically disordered; the methyl and ethyl groups were refined on split positions. The crystals enclose one disordered *n*-hexane molecule per formula unit of **3**. Compound **4** crystallized as very thin platelets. The molecules are located on crystallographic 2-fold rotation axes. The crystals enclose four molecules of 1,2-difluorobenzene per formula unit of **4**. The dimeric molecules of **6** are located on crystallographic centers of symmetry. Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository number CCDC-756900 (**3**·C_6H_{14}), CCDC-756901 (**4**·4$C_6H_4F_2$), and CCDC-756902 (**6**).

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

Supporting Information Available: CIF files giving the crystal data for compounds **3**·C_6H_{14}, **4**·4$C_6H_4F_2$, and **6** and tables giving optimized geometries of compound **5** and the complexes given in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] *SHELXTL-Plus, REL. 4.1*; Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1990. Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Structures*; Universität Göttingen, Göttingen, Germany, 1997.