Hydrogallation of Trimethylsilylethynylbenzenes: Generation of Potential Di- and Tripodal Chelating Lewis Acids

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Hydrogallation of 1,4-bis(trimethylsilylethynyl)benzene and 1,3,5-tris(trimethylsilylethynyl)benzene with dialkylgallium hydrides R_2GaH (R = Et, *n*Pr, *i*Pr, neopentyl, *t*Bu) afforded the corresponding addition products with intact GaR_2 groups and two or three alkenyl substituents. In all products the gallium atoms attacked those carbon atoms that are attached to the trimethylsilyl groups. The expected *cis* arrangement of gallium and hydrogen atoms at the C≡C double bonds was detected only with di(*tert*-butyl)gallium residues. Smaller alkyl groups gave the spontaneous formation of the *trans*-addition products. *Cis/trans* isomerization is an inevitable step for the formation of effective chelating Lewis acids, and in particular the trisalkene derivatives form interesting chalice-like hollows containing three Lewis-acidic centers at their inner surfaces.

Introduction

The synthesis of chelating Lewis acids based on coordinatively unsaturated group 13 elements found considerable interest in the last decade,[1−5] because they may find important applications in the activation of particular catalysts, in anion recognition, or in phase transfer processes. Recently, we showed that the dialuminum compound $R_2Al-CH_2-AlR_2$[4] [R = CH-$(SiMe_3)_2$] containing two coordinatively unsaturated Al atoms forms a very effective chelating Lewis acid. It coordinated, for example, sodium nitrite (**1**, Chart 1) or lithium nitrate so effectively that dissolution in ethereal solvents succeeded.[5] We hoped to generate further compounds of that type based on three or more coordinatively unsaturated Al or Ga atoms when we treated oligoalkynes with dialkylaluminum or dialkylgallium hydrides (hydroalumination or hydrogallation reactions). However, the courses of these reactions proved to be much more complicated and interesting than might be supposed on the basis of textbook knowledge.

For instance, the treatment of dialkylaluminum alkynides with an excess of the corresponding dialkylaluminum hydrides did not afford the simple addition products; instead a new class of cluster compounds resulted by condensation and release of

Chart 1

(Al = AlMe; *C* = CCH₂Ph)

trialkylaluminum derivatives. These clusters (carbaalanes, **2**, Chart 1) contain aluminum and carbon atoms and have a delocalized bonding situation.[6] Similar condensation reactions occurred upon treatment of dialkylgallium alkynides with dialkylgallium hydrides. Heteroadamantane-type cages resulted that had six coordinatively unsaturated Ga atoms and localized

(1) Some references on Al, Ga, and In compounds that may be suitable to act as chelating Lewis acids. However, in many cases their true applicability as a polyacceptor has not been testet: (a) Saied, O.; Simard, M.; Wuest, J. D. *Organometallics* **1998**, *17*, 1128. (b) Tschinkl, M; Gabbai, F. P.; Bachman, R. E. *Chem. Commun.* **1999**, *15*, 1367. (c) Ooi, T.; Takahshi, M.; Maruoka K. *J. Am. Chem. Soc.* **1996**, *118*, 11307. (d) Cottone, A.; Scott, M. J. *Organometallics* **2002**, *21*, 3610. (e) Tschinkl, M.; Hoefelmeyer, J. D.; Cocker, T. M.; Bachman, R. E.; Gabbai, F. P. *Organometallics* **2000**, *19*, 1826. (f) Hoefelmeyer, J. D.; Brode, D. L.; Gabbai, F. P. *Organometallics* **2001**, *20*, 5653. (g) Hoefelmeyer, J. D.; Schulte, M.; Gabbai, F. P. *Inorg. Chem.* **2001**, *40*, 3833.
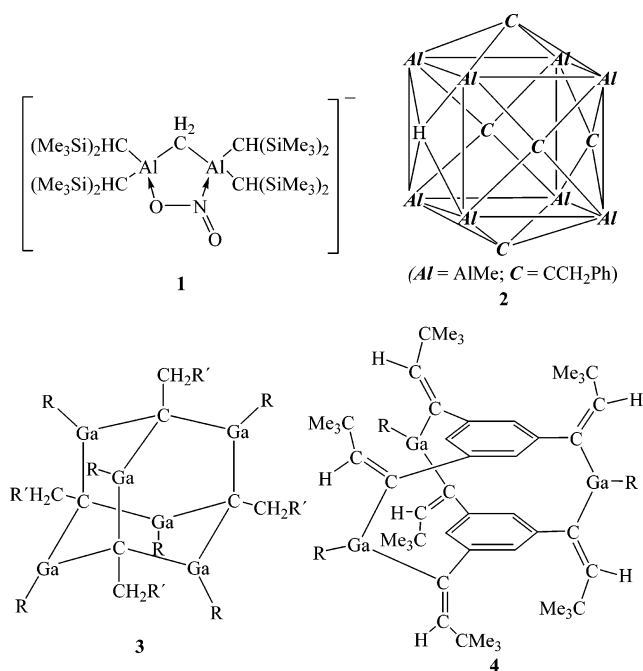
(2) Uhl, W.; Breher, F. *J. Organomet. Chem.* **2000**, *608*, 54.

(3) Uhl, W.; Matar, M. *J. Organomet. Chem.* **2002**, *664*, 110.

(4) (a) Layh, M.; Uhl, W. *Polyhedron* **1990**, *9*, 277. (b) Uhl, W.; Layh, M. *J. Organomet. Chem.* **1991**, *415*, 181.

(5) (a) Uhl, W.; Layh, M. *Z. Anorg. Allg. Chem.* **1994**, *620*, 856. (b) Uhl, W.; Koch, M.; Heckel, M.; Hiller, W.; Karsch, H. H. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1427. (c) Uhl, W.; Hannemann, F.; Saak, W.; Wartchow, R. *Eur. J. Inorg. Chem.* **1998**, *7*, 921. (d) Uhl, W.; Hannemann, F. *J. Organomet. Chem.* **1999**, *579*, 18.
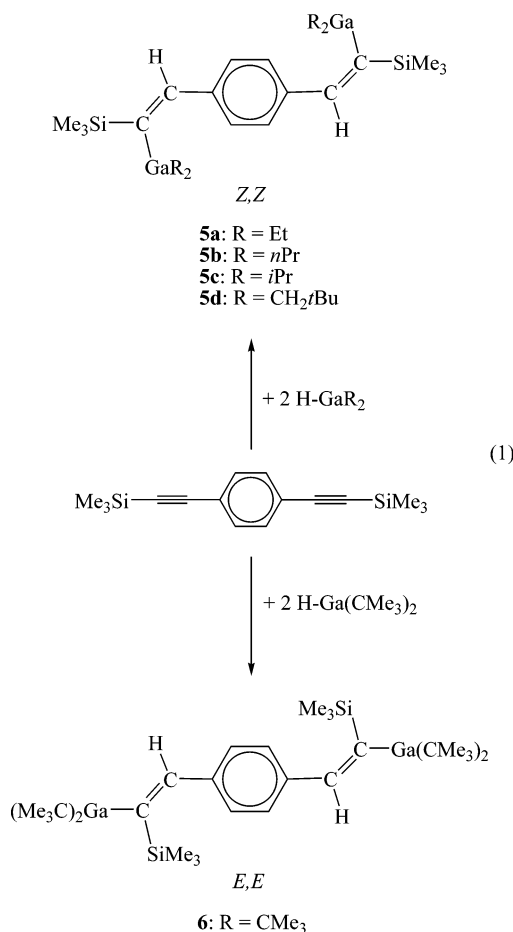
(6) (a) Uhl, W.; Breher, F. *Angew. Chem.* **1999**, *111*, 1578; *Angew. Chem., Int. Ed.* **1999**, *38*, 1477. (b) Uhl, W.; Breher, F.; Lützen, A.; Saak, W. *Angew. Chem.* **2000**, *112*, 414; *Angew. Chem., Int. Ed.* **2000**, *39*, 406. (c) Uhl, W.; Breher, F.; Grunenberg, J.; Lützen, A.; Saak, W. *Organometallics* **2000**, *19*, 4536. (d) Uhl, W.; Breher F.; Mbonimana, A.; Gauss, J.; Haase, D.; Lützen, A.; Saak, W. *Eur. J. Inorg. Chem.* **2001**, *12*, 3059. (e) Stasch, A.; Ferbinteanu, M.; Prust, J.; Zheng, W.; Cimpoesu, F.; Roesky, H. W.; Magull, J.; Schmidt, H.-G.; Noltemeyer, M. *J. Am. Chem. Soc.* **2002**, *124*, 5441.

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Ga−C bonds (**3**, Chart 1).[7] The formation of trialkylgallium derivatives was also observed for the reaction of 1,3,5-tris(*tert*-butylethynyl)benzene with dialkylgallium hydrides R_2GaH (R = Et, *n*Pr, *i*Pr, neopentyl, *t*Bu). [3,3,3]-Cyclophane-type molecules (**4**, Chart 1) were isolated, in which two benzene rings were bridged by three Ga atoms.[8,9] The related dialkyne 1,4-bis(*tert*-butylethynyl)benzene gave, depending on the steric shielding of the hydrides, alternatively a cyclophane-type molecule similar to **4** or addition products R′−(R$_2$Ga)C=C(H)−R″ (R = Et, *n*Pr; R′ = aromatic ring; R″ = CMe$_3$).[9,10] In some reactions of di(*tert*-butyl)aluminum hydride with silyl-substituted alkynes we observed that persistent addition products, Me$_3$Si−(R$_2$Al)C=C(H)−R′ (R′ = phenyl), were formed and that condensation reactions did not occur at all.[2,3] Smaller groups attached to the Al atoms gave complicated reaction mixtures, and up to now we were not able to isolate any pure component of these reactions and to clarify the respective reaction courses. Due to our experience, hydrogallation reactions are slower and more selective than hydroalumination reactions, which may be caused by the lower polarity of the Ga−H bond. Therefore, we started with systematic investigations into hydrogallation reactions with silylalkynes and hoped to find a facile access to chelating Lewis acids based on unsaturated Ga atoms.

Results and Discussion

Reactions of Dialkylgallium Hydrides with 1,4-Bis- and 1,3,5-Tris(*tert*-butylethynyl)benzene. The hydrogallation reactions described here followed a standard procedure. The stoichiometric quantities of the starting compounds (molar ratios 1:2 or 1:3) were dissolved in *n*-hexane, and the solutions were heated under reflux for 15 to 20 h (eq 1). Clear solutions were obtained for most reactions of the bisalkyne 1,4-(Me$_3$Si−C≡C)$_2$C$_6$H$_4$ with the dialkylgallium hydrides R$_2$GaH (R = Et, *n*Pr, *i*Pr, neopentyl, *t*Bu). With one exception the products were isolated as colorless solids after recrystallization from *n*-hexane at low temperature (−80 °C). Although the NMR spectra of the raw products indicated an almost quantitative formation of the addition products in all cases, the exceptionally high solubility in hydrocarbon solvents hindered their quantitative isolation. Only **5a** (R = Et) was obtained as a highly viscous, colorless liquid that could not be purified by recrystallization. As in other cases, purification by distillation in vacuum failed owing to thermal decomposition. The crystals of **5b** (R = *n*Pr) melted upon warming slightly above −80 °C, and those of **5c** (R = *i*Pr) melted above room temperature (32 °C). In contrast to the reactions of R$_2$GaH with *tert*-butylalkynes[8−10] (see Introduction) the formation of the corresponding trialkylgallium derivatives was usually not observed. The only exception was the reaction of dineopentylgallium hydride with the dialkyne, which required an excess of the hydride of 100%. Trineopentylgallium was isolated as a byproduct and identified by its characteristic NMR data. Probably it is formed by partial decomposition of the hydride, and the unusual dark red-brown color of the reaction mixture may indicate the formation of some species containing subvalent gallium atoms. A very slow reaction occurred at room temperature, when we treated the bisalkyne with di(isopropyl)gallium hydride. After about 1.5 months the starting compounds were consumed. The main

product was **5c**, but further resonances in the ^{1}H NMR spectrum may indicate the occurrence of some unknown intermediates, which, however, could not be identified unambiguously.

5a: R = Et
5b: R = *n*Pr
5c: R = *i*Pr
5d: R = CH$_2$*t*Bu

$$+ \ 2 \ \text{H-GaR}_2$$

(1)

$$+ \ 2 \ \text{H-Ga(CMe}_3)_2$$

E,E

6: R = CMe$_3$

The formation of the addition products **5a−d** and **6** containing intact GaR$_2$ groups attached to the C=C double bonds was easily verified by the characteristic integration ratios of their ^{1}H NMR spectra. However, there are some more or less important differences in the NMR data that may be indicative for the different configurations of the products. As was shown by crystal structure determinations (see below), only the *tert*-butyl derivative **6** possesses the expected *cis* arrangement of Ga and H atoms at the C=C double bonds (*E,E* configuration), while spontaneous and quantitative formation of the *trans* products **5a−d** (*Z,Z* configuration) was observed for smaller substituents attached to gallium. The ^{1}H NMR resonances of the benzene protons and the alkenyl hydrogen atoms are in a relatively narrow range for the *E,E* product **6** (δ = 7.31 and 7.46, respectively), while larger differences of about 0.9 ppm are detected for the *Z,Z* products **5** (δ = 6.9 and 7.8 on average). Further NMR data allowing for a systematic differentiation between both configurations are the ^{13}C NMR chemical shifts of the alkenyl carbon atoms attached to gallium [δ = 169 (*Z,Z*) versus 163 (*E,E*)] and the resonances of the silicon atoms of the SiMe$_3$ groups in the ^{29}Si NMR spectra [δ = −7 (*Z,Z*) versus −13 (*E,E*)]. In accordance with the pattern of H−H coupling constants across C=C double bonds, the $^3J_{SiH}$ coupling constants are at about 12 Hz in compounds **5** (H and SiMe$_3$ in *cis* position), while a larger value was detected for compound **6** (20 Hz) with the *trans* arrangement of H atoms and trimethylsilyl groups.

Similar reaction courses were observed for the trisalkyne 1,3,5-(Me$_3$Si−C≡C)$_3$C$_6$H$_3$. The sterically most shielded dialkyl-

(7) Uhl, W.; Cuypers, L.; Neumüller, B.; Weller, F. *Organometallics* **2002**, *21*, 2365.

(8) Uhl, W.; Breher, F.; Haddadpour, S. *Organometallics* **2005**, *24*, 2210.

(9) Uhl, W.; Claesener, M.; Haddadpour, S.; Jasper, B.; Hepp, A. *Dalton Trans.*, in press.

(10) Uhl, W.; Haddadpour, S.; Matar, M. *Organometallics* **2006**, *25*, 159.

gallium hydride, $(Me_3C)_2GaH$, gave the product with a *cis* arrangement of hydrogen and gallium at the C=C double bonds (*E,E,E*-**8**), while the corresponding *trans* products **7a** and **7b** (all *Z* configuration) were obtained with smaller alkyl groups (R = Et, *n*Pr; eq 2). Fast secondary reactions with the release of triisopropyl- and trineopentylgallium occurred upon treatment of the trisalkyne with diisopropyl- and dineopentylgallium hydride. Colorless solids precipitated in both cases that proved to be insoluble in nonprotic organic solvents (cyclopentane to acetonitrile). Their constitution is unknown. The spectroscopic findings of the pure compounds **7a,b** and **8** in particular with respect to the differences between the *cis* and *trans* forms are identical to those of the bisalkenyl products **5a**−**d** and **6** and do not require further discussion.

(2)
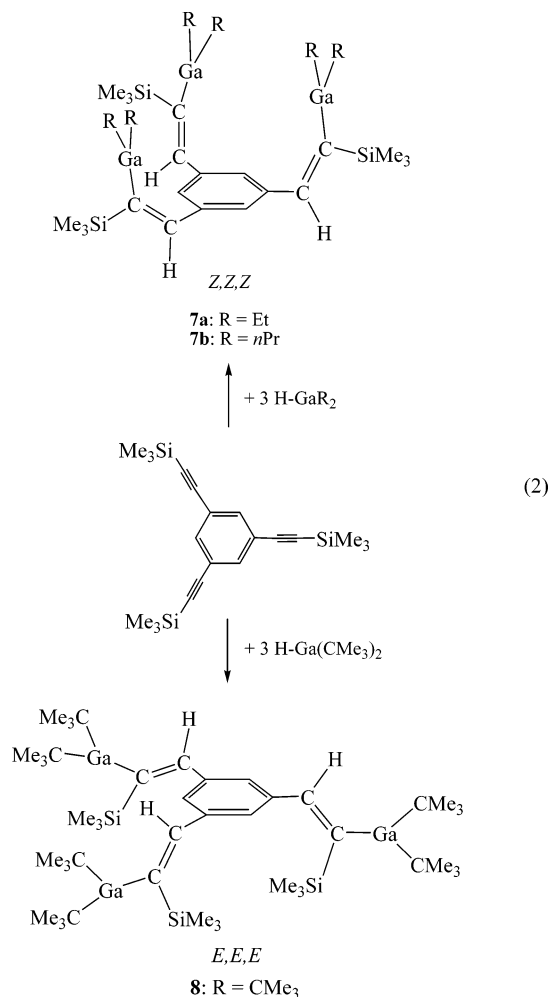
Molecular Structures. The molecular structures of the dialkenyl compounds **5c** and **6** and those of the trialkenyls **7b** and **8** are depicted in Figures 1 to 4. The Ga atoms attacked selectively those C atoms of the C≡C triple bonds that were bonded to trimethylsilyl groups. This high regioselectivity may be caused by the electronegativity difference between C and Si and the preferred attack of the positively charged Ga atoms to those C atoms of the C≡C−SiMe$_3$ groups that bear a partial negative charge. From the product side, that particular position [C=C(Si)Ga] may be favored by the stabilization of the negative charge induced by the electronegativity difference between C and Ga through hyperconjugation with the terminal trimethylsilyl groups.

The alkenyl groups possess different configurations depending on the steric shielding of the dialkylgallium hydrides. Di(*tert*-
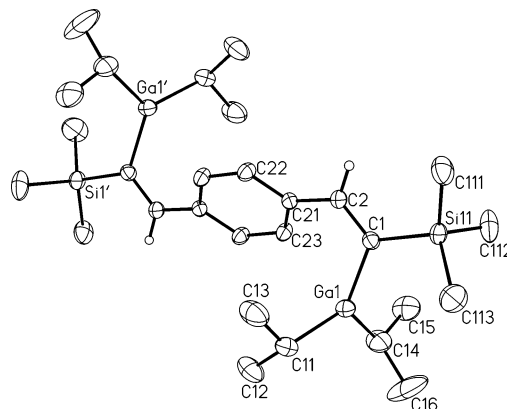

Figure 1. Molecular structure of **5c**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted with the exception of the vinylic hydrogen atoms. Important bond lengths (Å) and angles (deg): Ga(1)−C(1) 1.974(4), Si(11)−C(1) 1.854(4), C(1)−C(2) 1.327(5), Ga(1)−C(1)−C(2) 117.2(3), Si(11)−C(1)−C(2) 120.5(3). Symmetry equivalent atoms were generated by −*x*, −*y*, −*z*+1.
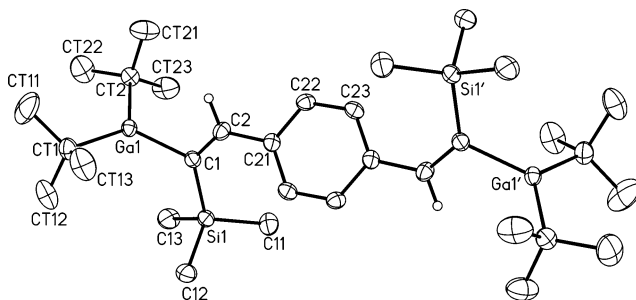

Figure 2. Molecular structure of **6**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted with the exception of the vinylic hydrogen atoms. Important bond lengths (Å) and angles (deg): Ga(1)−C(1) 1.978(3), Si(1)−C(1) 1.866(3), C(1)−C(2) 1.349(4), Ga(1)−C(1)−C(2) 113.0(2), Si(1)−C(1)−C(2) 129.6(3). Symmetry equivalent atoms were generated by −*x*+1, −*y*+1, −*z*+1.

butyl)gallium hydride gave the products of a *cis* addition with both starting alkynes (**6** and **8**); thus, Ga and H are located on the same sides of the C=C double bonds. That particular configuration was claimed as the kinetically favored one in earlier publications.[11] In contrast, the *trans* arrangement of Ga and H was observed for the alkenyl groups of **5c** and **7b**, which have smaller alkyl groups attached to their Ga atoms. As can be easily seen from the schematic drawings in the equations and from Figures 1 to 4, the capability to act as chelating Lewis acids is essentially restricted to the *trans* products, because here the coordinatively unsaturated Ga atoms are able to form cavities that may be suitable to encapsulate a particular donor molecule. While for **5c** a rotation around a C−C single bond to the benzene ring is a necessary initiating step for the formation of such a cavity, interestingly the trialkenyl compound **7b** is highly preorganized with all Ga atoms on the same side of the central aromatic ring. Thus, a chalice-type structure results possessing a Lewis-acidic inner surface with three coordinatively unsatur-

(11) (a) Wilke, G.; Müller, M. *Justus Liebigs Ann. Chem.* **1958**, *618*, 267. (b) Wilke, G.; Müller, H. *Chem. Ber.* **1956**, *89*, 444. (c) Wilke, G; Müller, H. *Justus Liebigs Ann. Chem.* **1960**, *629*, 222. (d) Eisch, J. J.; Foxton, M. W. *J. Org. Chem.* **1971**, *36*, 3520. (e) Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 2213. (f) Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1963**, *85*, 2165. (g) Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, pp 555−682.
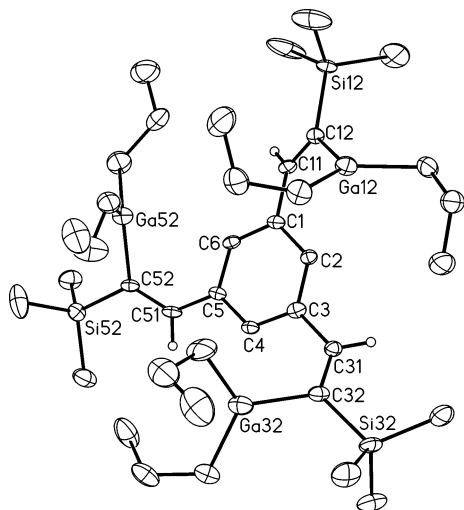
Figure 3. Molecular structure of **7b**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted with the exception of the vinylic hydrogen atoms. Important bond lengths (Å) and angles (deg): Ga(12)−C(12) 1.978(5), Si(12)−C(12) 1.865(5), C(11)−C(12) 1.337(7), Ga(32)−C(32) 1.976(6), Si(32)−C(32) 1.867(5), C(31)−C(32) 1.347(7), Ga(52)−C(52) 1.974(5), Si(52)−C(52) 1.862(5), C(51)−C(52) 1.345(7), Ga(12)−C(12)−C(11) 118.9(4), Si(12)−C(12)−C(11) 120.1(4), Ga(32)−C(32)−C(31) 119.4(4), Si(32)−C(32)−C(31) 122.4(4), Ga(52)−C(52)−C(51) 119.5(4), Si(52)−C(52)−C(51) 123.2(4).
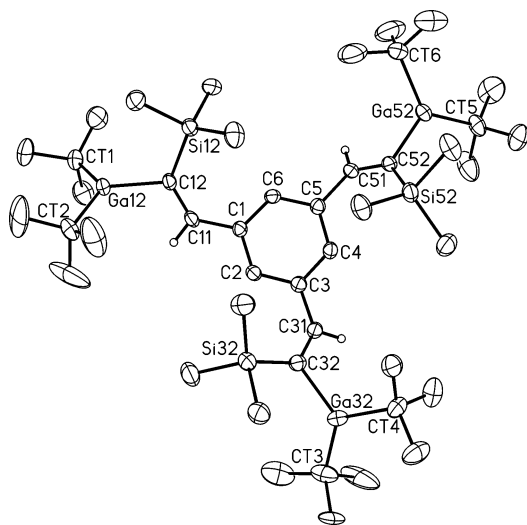

Figure 4. Molecular structure of **8**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted with the exception of the vinylic hydrogen atoms. Important bond lengths (Å) and angles (deg): Ga(12)−C(12) 1.978(3), Si(12)−C(12) 1.868(3), C(11)−C(12) 1.334(4), Ga(32)−C(32) 1.976(3), Si(32)−C(32) 1.864(3), C(31)−C(32) 1.340(4), Ga(52)−C(52) 1.975(3), Si(52)−C(52) 1.872(3), C(51)−C(52) 1.335(4), Ga(12)−C(12)−C(11) 114.3(2), Si(12)−C(12)−C(11) 130.3(2), Ga(32)−C(32)−C(31) 114.9(2), Si(32)−C(32)−C(31) 130.5(2), Ga(52)−C(52)−C(51) 112.3(2), Si(52)−C(52)−C(51) 128.5(2).

ated Ga atoms. To the best of our knowledge, this is an unprecedented structure in group 13 chemistry. The molecular structures of the *cis* compounds **6** and **8** are rather flat, and the Ga atoms deviate from the average planes of the benzene rings by 0.002 (**6**) and 0.542 to 0.823 Å (**8**). Probably caused by the particular steric requirements, the Ga atoms of the *trans* products are 1.836 (**5c**) and 1.468 to 1.845 Å (**7b**) above the benzene planes. In these cases, the coordinatively unsaturated metal atoms are located above C−H bonds of the aromatic rings with

relatively close Ga···H contacts of 2.35 to 2.53 Å. Nevertheless, the environment of the Ga atoms is almost ideally planar in all cases, with sums of the bond angles very close to 360°. The different chemical surroundings cause the characteristic differences in the chemical shifts of the NMR spectra in particular with respect to the data of the phenyl and alkenyl hydrogen atoms, which allow for a clear spectroscopic differentiation between the *cis* and *trans* forms. All bond lengths and angles are in the expected ranges and do not require a more detailed discussion.

Discussion

The hydrogallation of C≡C triple bonds of phenyl-centered trimethylsilylethynes gave the addition products $Me_3Si−(R_2-Ga)C=C(H)−Ph$ in highly regioselective reactions. Different structures with the Ga atoms attached to the carbon atoms in α-position to the phenyl groups were obtained with the corresponding phenylalkynes bearing terminal *tert*-butyl groups instead of trimethylsilyl substituents. A mesomeric stabilization may influence the regioselectivity in that case. The competitive formation of both forms in a single reaction was not observed. Secondary reactions with the release of trialkylgallium derivatives and the formation of cyclophane-type molecules reflect the usual course of the hydrogallation of *tert*-butylethynylbenzenes. Two exceptions were observed for sterically less shielded dialkylgallium hydrides. In contrast, the trimethylsilyl groups of compounds **5** to **8** stabilize the simple addition products by steric shielding and by delocalization of the negative charge of the alkenyl carbon atom by hyperconjugation. The release of the corresponding trialkylgallium derivatives occurred in two reactions only; however, insoluble products of unknown constitutions were formed.

The stereoselective *trans* arrangement of H and Ga was obtained for the sterically less shielded products **5** and **7**, while under identical reaction conditions in boiling *n*-hexane exclusively the stable *cis* products resulted with di(*tert*-butyl)gallium hydride (**6** and **8**). The occurrence of mixtures of *cis*/*trans* products as an intermediate case was never observed in our experiments. Although the *cis* compounds as intermediates were not verified by any experimental method, their formation in an initiating step of all addition processes seems to be a reasonable assumption. *Cis*/*trans* rearrangements with hydroalumination products were discussed in the literature,[11] but in our opinion a concise mechanism has not been established yet. Recently, we reported on the activation of vinylic C−H bonds by hyperconjugation with Al−C bonds and on the formation of a butadienyl cation by chelating coordination of the respective hydride anion by two aluminum atoms.[12] C−H bond activation may be a key step for an understanding of the isomerization processes. We currently started with more systematic investigations into the C−H bond activation, which may not only result in a better understanding of these reaction courses, but should also result in the formation of interesting novel products.

Experimental Section

All procedures were carried out under purified argon. *n*-Hexane and *n*-pentane were dried over LiAlH$_4$, toluene over Na/benzophenone, and pentafluorobenzene over molecular sieves. Et$_2$GaH,[13]

(12) Uhl, W.; Grunenberg, J.; Hepp, A.; Matar, M.; Vinogradov, A. *Angew. Chem.* **2006**, *118*, 4465; *Angew. Chem., Int. Ed.* **2006**, *45*, 4358.
(13) Uhl, W.; Cuypers, L.; Geiseler, G.; Harms, K.; Massa, W. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1001.

nPr$_2$GaH,[9] iPr$_2$GaH,[13] (Me$_3$CCH$_2$)$_2$GaH,[13] and tBu$_2$GaH[14] were obtained according to literature procedures. Commercially available 1,4-(Me$_3$Si−C≡C)$_2$C$_6$H$_4$ was thoroughly evacuated prior to use. 1,3,5-(Me$_3$Si−C≡C)$_3$C$_6$H$_3$ was obtained according to a standard procedure;[15] experimental details are given below. Only the most intensive peaks of the mass spectra were given; the complete isotopic patterns are in accordance with the calculated ones. The assignment of the NMR spectra is based on HMBC, HSQC, ROESY, and DEPT135 data.

Synthesis of 1,3,5-(Me$_3$Si−C≡C)$_3$C$_6$H$_3$. 1,3,5-Tribromobenzene (9.670 g, 30.7 mmol) was dissolved in 250 mL of diethylamine. Copper(I) iodide (0.050 g, 0.26 mmol) and dichlorobis(triphenylphosphino)palladium(II) (0.40 g, 0.57 mmol) were added at room temperature. Dropwise addition of trimethylsilylethyne (10.85 g, 110.5 mmol) caused a color change from yellow to dark green and brown (the solvent and all reagents were employed as purchased). The mixture was heated to 70 °C for 7 h, which resulted in the precipitation of a brown solid. After cooling to room temperature the solid was filtered off and washed with few milliliters of diethyl ether. All volatiles of the filtrate were removed in vacuum. The residue was dissolved in n-pentane and purified by column chromatography (Al$_2$O$_3$). The solvent was removed in vacuum, and the residue was thoroughly evacuated to 10^{-3} Torr to yield a light yellow powder of the product. Yield: 11.00 g (97%). Mp (argon, sealed capillary): 67−68 °C. Anal. Calcd [C$_{21}$H$_{30}$Si$_3$] (366.7): C, 68.78; H, 8.25. Found: C, 68.6; H, 8.2. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.53 (3 H, s, phenyl), 0.19 (27 H, s, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 135.3 (C−H of phenyl), 124.4 (*ipso*-C of phenyl), 103.8 (C≡*C*-Ph), 95.9 ($^1J_{C-Si}$ = 82.7 Hz, C≡*C*-Si), −0.1 ($^1J_{C-Si}$ = 56.4 Hz, SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −17.6. IR (KBr, neat, cm^{-1}): 2958 vs, 2898 s (νCH$_3$); 2166 vs, 2139 m ν(C≡C); 1580 s phenyl; 1410 vs, 1250 vs δ(CH$_3$); 1162 vs, 981 vs ν(CC); 882 sh, 846 vs, 759 vs, 700 m ρ(CH$_3$(Si)); 680 s ν_{as}-(SiC); 651 s ν_s(SiC). MS (EI, 25 eV) (%): 366 (100) M$^+$; 351 (64) M$^+$ − Me.

Hydrogallation of 1,4-Bis- and 1,3,5-Tris(trimethylsilylethynyl)benzene: General Procedure. A solution of the respective dialkylgallium hydride in n-hexane (1.3 to 3.4 mmol in 20 mL) was treated with a solution of the stoichiometric quantity of the corresponding bis- or trisalkyne (molar ratios 2:1 or 3:1) in n-hexane (0.6 to 1.1 mmol in 20 mL) at room temperature. An excess of the hydride was applied for the synthesis **5a** (50%), **5b** (10%), **5d** (100%), and **7a** (10%). The solutions were heated under reflux for 15 to 20 h and filtered after cooling to room temperature because small quantities of colorless, unknown solids precipitated in some cases. Owing to partial decomposition, elemental gallium precipitated from the reaction of the relatively unstable diethylgallium hydride with the dialkyne (syntheses of **5a**). The filtrates were concentrated in vacuum at room temperature to a few milliliters and cooled to −80 °C to get the colorless, solid products. Only compound **5a** did not give a solid product under these conditions.

Characterization of the Bisalkenyl Compound 5a (GaEt$_2$). This compound could not be purified by recrystallization. An oily, liquid product resulted at room temperature that had some unknown impurities (about 20%). The NMR, IR, and mass spectroscopic characterization was done with the raw product of the reaction, but we did not carry out elemental analyses. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.82 (2 H, s, C=C−H), 6.86 (4 H, s, phenyl), 1.17 (12 H, t, $^3J_{HH}$ = 8.0 Hz, Me of Et), 0.74 (8 H, t, $^3J_{HH}$ = 8.0 Hz, GaCH$_2$), 0.21 (18 H, s, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 168.3 (C=*C*(Si)Ga), 149.2 (*C*=C(Ga)Si), 145.3 (*ipso*-C of phenyl), 126.2 (C−H of phenyl), 11.3 (GaCH$_2$), 10.1 (Me of Et), −0.17 (SiMe$_3$).

(14) Uhl, W.; Cuypers, L.; Graupner, R.; Molter, J.; Vester, A.; Neumüller, B. *Z. Anorg. Allg. Chem.* **2001**, *627*, 607.

(15) (a) Weber, E.; Hecker, M.; Koepp, E.; Orlia, W; Czugler, M.; Csöregh, I. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1251. (b) Mongin, O.; Papamicael, C.; Hoyler, N.; Grossauer, A. *J. Org. Chem.* **1998**, *63*, 5568.

^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −7.0. IR (CsBr plates, paraffin, cm^{-1}): 1607 w, 1578 m, 1541 m phenyl, ν(C=C); 1458 vs (paraffin); 1420 m δ(CH$_3$); 1375 vs (paraffin); 1340 w, 1301 w, 1257 sh, 1246 vs δ(CH$_3$); 1198 w, 1163 w δ(CH); 1094 w, 1051 w, 1034 w, 999 sh, 986 s, 966 sh ν(CC); 933 vw, 906 sh, 864 vs, 837 vs, 777 vw ρ(CH$_3$(Si)); 748 m, 725 m (phenyl, paraffin); 691 m ν_{as}(SiC); 652 m ν_s(SiC); 563 s, br, 546 sh, 517 sh, 433 w ν-(GaC), δ(CC). MS (EI, 70 eV) (%): 497 (1.2), 499 (1.5), 501 (1.0) M$^+$ − Et; 371 (52.3), 373 (37.1) M$^+$ − GaEt$_2$ − ethene; 127 (87), 129 (68) GaEt$_2$.

Characterization of the Bisalkenyl Compound 5b (GanPr$_2$). Yield: 59%. Mp: slightly above −80 °C; oily liquid at room temperature. Anal. Calcd for **5b** [C$_{28}$H$_{52}$Si$_2$Ga$_2$] (584.3): C, 57.56; H, 8.97; Ga, 23.86. Found: C, 57.6; H, 8.9; Ga, 23.9. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.80 (2 H, s, C=C−H; $^3J_{SiH}$ = 11.7 Hz), 6.93 (4 H, s, phenyl), 1.60 (8 H, pseudosextet, C*H*$_2$CH$_3$), 1.02 (12 H, t, $^3J_{HH}$ = 7.6 Hz, Me of nPr), 0.84 (8 H, br, t, $^3J_{HH}$ = 7.6 Hz, GaCH$_2$), 0.23 (18 H, s, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 168.9 (C=*C*(Si)Ga), 149.0 (*C*=C(Ga)Si), 144.9 (*ipso*-C of phenyl), 126.4 (C−H of phenyl), 23.1 (GaCH$_2$), 20.0 (*C*H$_2$CH$_3$), 19.6 (Me of nPr), 0.0 (SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −7.0. IR (CsBr plates, paraffin, cm^{-1}): 1603 m, 1568 s, 1558 s, 1495 s phenyl, ν(C=C); 1464 vs (paraffin); 1454 vs, 1412 s, 1394 m δ-(CH$_3$); 1373 s (paraffin); 1329 s, 1246 vs δ(CH$_3$); 1209 vw, 1194 w, 1180 w δ(CH); 1103 w, 1057 vs, 1015 m, 986 vs ν(CC); 912 vs, 887 vs, 835 vs, 794 w ρ(CH$_3$(Si)); 748 s, 720 w (phenyl, paraffin); 687 s ν_{as}(SiC); 650 m, 619 s ν_s(SiC); 538 s, br., 490 m, 430 m ν(GaC), δ(CC). MS (EI, 70 eV) (%): 539 (0.6), 541 (0.8), 543 (0.4) M$^+$ − nPr; 427 (3.2), 429 (4.4) M$^+$ − GanPr$_2$; 155 (100), 157 (67) GanPr$_2$.

Characterization of the Bisalkenyl Compound 5c (GaiPr$_2$). Yield: 66%. Mp (argon, sealed capillary): 32 °C. Anal. Calcd for **5c** [C$_{28}$H$_{52}$Si$_2$Ga$_2$] (584.3): C, 57.56; H, 8.97; Ga, 23.86. Anal. Found: C, 57.6; H, 9.0; Ga, 24.1. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.82 (2 H, s, C=C−H; $^3J_{SiH}$ = 11.4 Hz), 6.90 (4 H, s, phenyl), 1.23 (24 H, d, $^3J_{HH}$ = 6.8 Hz, Me of iPr), 1.14 (4 H, m, GaCH), 0.22 (18 H, s, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 168.0 (C=*C*(Si)Ga), 149.4 (*C*=C(Ga)Si), 145.4 (*ipso*-C of phenyl), 126.0 (C−H of phenyl), 20.9 (Me of iPr), 20.8 (GaCH), 0.0 (SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −7.3. IR (CsBr plates, paraffin, cm^{-1}): 1556 s, 1495 m phenyl, ν(C=C); 1463 vs (paraffin); 1402 w δ(CH$_3$); 1378 s (paraffin); 1347 w, 1316 w, 1245 vs δ(CH$_3$); 1214 w, 1153 w δ(CH); 1116 s, 1074 w, 1012 w, 985 s, 950 s ν(CC); 918 s, 887 s, 834 vs ρ(CH$_3$(Si)); 749 m, 734 w (phenyl, paraffin); 688 w ν_{as}(SiC); 619 w, 593 w ν_s(SiC); 523 m, br, 432 m ν(GaC), δ(CC). MS (EI, 70 eV) (%): 539 (42), 541 (64), 543 (24) M$^+$ − iPr; 497 (7), 499 (10), 501 (5) M$^+$ − nPr − propene; 155 (100), 157 (74) GaiPr$_2$.

Characterization of the Bisalkenyl Compound 5d [Ga-(CH$_2$$t$Bu)$_2$]. Yield: 36%; recrystallization from n-hexane after removal of trineopentylgallium at 55 °C and 10^{-3} Torr (yield: 0.34 g of trineopentylgallium related on a starting quantity of 0.87 g of dineopentylgallium hydride). Mp (argon, sealed capillary): 92−94 °C. Anal. Calcd for **5d** [C$_{36}$H$_{68}$Si$_2$Ga$_2$] (696.6): C, 62.07; H, 9.84; Ga, 20.02. Anal. Found: C, 62.3; H, 9.8; Ga, 19.8. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.76 (2 H, s, C=C−H; $^3J_{SiH}$ = 11.7 Hz), 7.00 (4 H, s, phenyl), 1.13 (8 H, s, Ga−CH$_2$), 1.07 (36 H, s, CMe$_3$), 0.28 (18 H, s, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 169.7 (C=*C*(Si)Ga), 149.2 (*C*=C(Ga)Si), 143.9 (*ipso*-C of phenyl), 127.1 (C−H of phenyl), 41.9 (Ga−CH$_2$), 34.2 (*C*Me$_3$), 31.9 (Ga*C*Me$_3$), 0.7 (SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −6.8. IR (CsBr plates, paraffin, cm^{-1}): 1556 m, 1495 m phenyl, ν(C=C); 1462 vs (paraffin); 1400 w δ(CH$_3$); 1377 s (paraffin); 1362 s, 1346 w, 1261 m, 1244 s δ(CH$_3$); 1169 vw, 1136 w, 1101 w, 1061 w, 1015 w, 1003 m, 988 w ν(CC); 918 s, 891 s, 835 vs ρ(CH$_3$(Si)); 748 s, 721 m (phenyl, paraffin); 685 m ν_{as}(SiC); 619 m ν_s(SiC); 590 vw, 559

Table 1. Crystal Data, Data Collection Parameters, and Structure Refinement Details for Compounds 5c, 6, 7b, and 8

	5c	6	7b	8
formula	$C_{28}H_{52}Ga_2Si_2$	$C_{32}H_{60}Ga_2Si_2$	$C_{39}H_{75}Ga_3Si_3$	$C_{45}H_{87}Ga_3Si_3$
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Z	1	2	4	2
temp, K	153(2)	153(2)	120(2)	153(2)
D_{calcd}, g/cm^3	1.196	1.151	1.199	1.117
a, Å	8.679(1)	17.144(7)	13.8729(4)	10.369(2)
b, Å	8.860(2)	9.001(4)	22.0394(7)	15.673(2)
c, Å	11.516(2)	12.230(5)	15.4207(4)	18.682(3)
α, deg	90	90	90	104.741(3)
β, deg	73.845(17)	101.642(7)	100.265(2)	100.162(4)
γ, deg	90	90	90	104.962(3)
V, 10^{-30} m^3	811.4(2)	1849(1)	4639.4(2)	2739.7(7)
μ, mm^{-1}	1.747	1.539	1.830	1.555
cryst dimens, mm	$0.50 \times 0.50 \times 0.20$	$0.23 \times 0.15 \times 0.02$	$0.35 \times 0.20 \times 0.13$	$0.27 \times 0.23 \times 0.14$
radiation	Mo Kα; graphite-monochromator			
θ range, deg	4.67−26.00	1.21−31.16	1.63−26.04	1.42−31.38
index ranges	$-10 \leq h \leq 10$	$-24 \leq h \leq 23$	$-16 \leq h \leq 16$	$-14 \leq h \leq 14$
	$-10 \leq k \leq 10$	$-13 \leq k \leq 12$	$-25 \leq k \leq 26$	$-22 \leq k \leq 22$
	$-14 \leq l \leq 14$	$-17 \leq l \leq 17$	$-18 \leq l \leq 18$	$-27 \leq l \leq 27$
no. of unique reflns	2925 [$R_{int} = 0.1188$]	5633 [$R_{int} = 0.0773$]	8669 [$R_{int} = 0.0941$]	16285 [$R_{int} = 0.0473$]
no. of params	152	172	467	577
R1 (reflns $I > 2\sigma(I)$)	0.0580 (2581)	0.0497 (3522)	0.0568 (5253)	0.0568 (9740)
wR2 (all data)	0.1562	0.1190	0.1640	0.1351
max./min. residual electron density, 10^{30} e/m^3	0.677/−0.682	0.521/−0.503	0.621/−0.548	0.835/−0.412

w, 523 w, br., 453 m ν(GaC), δ(CC). MS (EI, 20 eV) (%): 623 (68), 625 (100), 627 (47) M$^+$ − CH$_2t$Bu; 211 (76), 213 (62) GaCH$_2t$Bu$_2$.

Characterization of the Bisalkenyl Compound 6 (GatBu$_2$). Yield: 28%. Mp (argon, sealed capillary): 111 °C. Anal. Calcd for **6** [C$_{32}$H$_{60}$Si$_2$Ga$_2$] (640.4): C, 60.02; H, 9.44; Ga, 21.77. Anal. Found: C, 60.1; H, 9.4; Ga, 21.8. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.46 (2 H, s, C=C−H; $^3J_{SiH}$ = 19.6 Hz), 7.31 (4 H, s, phenyl), 1.25 (36 H, s, CMe$_3$), 0.18 (18 H, s, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 163.1 (C=C(Si)Ga), 150.5 (C=C(Ga)Si), 141.4 (*ipso*-C of phenyl), 128.0 (C−H of phenyl), 30.2 (CMe_3), 29.5 (GaCMe$_3$), 1.5 (SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −13.0. IR (CsBr plates, paraffin, cm^{-1}): 1913 w, 1767 vw, 1553 s, 1497 s phenyl, ν(C=C); 1458 vs (paraffin); 1408 m δ(CH$_3$); 1375 s (paraffin); 1362 s, 1269 s, 1246 vs δ(CH$_3$); 1201 w, 1173 m, 1107 m, 1092 vw, 1007 m, 987 w, 954 vw ν(CC); 937 m, 899 vs, 879 sh, 839 vs, 806 vs ρ(CH$_3$(Si)); 750 s, 732 m (phenyl, paraffin); 692 s ν_{as}(SiC); 642 s ν_s(SiC); 577 w, 519 s, br., 438 s, 390 w, 353 w, 324 s ν-(GaC), δ(CC). MS (EI, 70 eV) (%): 581 (2.0), 583 (5.0), 585 (1.1) M$^+$ − tBu; 399 (100), 401 (89) M$^+$ − GatBu$_2$ − butane; 183 (5), 185 (4) GatBu$_2$.

Characterization of the Trisalkenyl Compound 7a (GaEt$_2$). Yield: 55%. Mp: below −20 °C; oily product. Slow decomposition occurred at room temperature; therefore, we did not conduct an elemental analysis. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.87 (3 H, s, C=C−H; $^3J_{SiH}$ = 10.8 Hz), 6.73 (3 H, s, phenyl), 1.20 (18 H, t, $^3J_{HH}$ = 7.8 Hz, Me of Et), 0.76 (12 H, br, GaCH$_2$), 0.20 (27 H, s, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 172.2 (C=C(Si)Ga), 149.0 (*ipso*-C of phenyl), 148.1 (C=C(Ga)Si), 120.2 (C−H of phenyl), 11.2 (GaCH$_2$), 10.2 (Me of Et), −0.2 (SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −6.6. IR (CsBr plates, paraffin, cm^{-1}): 1609 w, 1578 m, 1541 m phenyl, ν(C=C); 1458 vs (paraffin); 1420 m δ-(CH$_3$); 1375 s (paraffin); 1361 sh, 1340 vw, 1302 w, 1258 sh, 1246 vs δ(CH$_3$); 1198 w, 1163 w, 1098 w, 1051 w, 1034 w, 999 m, 986 s, 966 sh ν(CC); 864 vs, 837 vs ρ(CH$_3$(Si)); 748 m, 725 m (phenyl, paraffin); 691 m ν_{as}(SiC); 652 m ν_s(SiC); 563 s,br., 546 sh, 516 sh, 432 m ν(GaC), δ(CC).

Characterization of the Trisalkenyl Compound 7b (GanPr$_2$). Yield: 73%. Mp (argon, sealed capillary): 12 − 14 °C; oily product at room temperature. Anal. Calcd for **7b** [C$_{39}$H$_{75}$Si$_3$Ga$_3$] (837.4): C, 55.94; H, 9.03; Ga, 24.98. Found: C, 56.0; H, 8.9; Ga, 25.0. ^{1}H

NMR (C$_6$D$_6$, 400 MHz): δ 7.85 (3 H, s, C=C−H; $^3J_{SiH}$ = 10.0 Hz), 6.73 (3 H, s, phenyl), 1.64 (12 H, pseudosextet, CH$_2$CH$_3$), 1.05 (18 H, t, $^3J_{HH}$ = 7.2 Hz, Me of nPr), 0.85 (12 H, br., pseudo-t, GaCH$_2$), 0.23 (27 H, s, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 171.9 (C=C(Si)Ga), 147.9 (*ipso*-C of phenyl), 147.8 (C=C(Ga)-Si), 120.6 (C−H of phenyl), 23.0 (GaCH$_2$), 19.7 (CH$_2$CH$_3$), 19.5 (Me of nPr), −0.5 (SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −6.6. IR (CsBr plates, paraffin, cm^{-1}): 1931 w, 1578 vs, 1543 vs phenyl, ν(C=C); 1457 vs (paraffin); 1447 vs, 1404 s δ(CH$_3$); 1373 s (paraffin); 1327 s, 1302 w, 1246 vs δ(CH$_3$); 1200 w, 1175 w δ-(CH); 1059 vs, 1014 m, 984 s ν(CC); 874 vs, 837 vs ρ(CH$_3$(Si)); 748 s, 718 m (phenyl, paraffin); 689 s ν_{as}(SiC); 650 m, 629 m, 613 m, 606 m ν_s(SiC); 533 m, br, 432 s, 393 w ν(GaC), δ(CC). MS (EI, 70 eV) (%): 791 (0.1), 793 (0.3), 795 (0.2), 795 (0.05) M$^+$ − nPr; 427 (3.2), 429 (4.4) M$^+$ − GanPr$_2$; 155 (100), 157 (77) GanPr$_2$.

Characterization of the Trisalkenyl Compound 8 (GatBu$_2$). Yield: 35%. Mp (argon, sealed capillary): 113 °C. Anal. Calcd for **8** [C$_{45}$H$_{87}$Si$_3$Ga$_3$] (921.6): C, 58.65; H, 9.51; Ga, 22.70. Found: C, 59.1; H, 9.39; Ga, 22.3. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.55 (3 H, s, C=C−H; $^3J_{SiH}$ = 19.5 Hz), 7.41 (3 H, s, phenyl), 1.26 (54 H, s, CMe$_3$), 0.21 (27 H, s, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 164.0 (C=C(Si)Ga), 150.4 (C=C(Ga)Si), 142.2 (*ipso*-C of phenyl), 126.4 (C−H of phenyl), 30.2 (CMe_3), 29.5 (GaCMe$_3$), 1.8 (SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −13.0. IR (CsBr plates, paraffin, cm^{-1}): 1929 w, 1815 w, 1580 s, 1564 s, 1514 m ν(C=C); 1464 vs (paraffin); 1447 vs δ(CH$_3$); 1374 s (paraffin); 1360 s, 1337 m, 1315 m, 1246 s δ(CH$_3$); 1206 w, 1171 m, 1152 w δ(CH); 1101 w, 1076 vw, 1011 s, 982 m ν(CC); 937 s, 912 s, 856 vs, 837 vs, 814 sh ρ(CH$_3$(Si)); 752 m, 725 m (phenyl, paraffin); 687 m ν_{as}(SiC); 656 m, 617 m ν_s(SiC); 600 m, 534 s, 436 m, 411 m, 370 m ν(GaC), δ(CC). MS (EI, 70 eV) (%): 679 (0.9), 681 (1.3), 683 (0.9) M$^+$ − GatBu$_2$ − butene; 183 (61), 185 (39) GatBu$_2$.

Crystal Structure Determinations of Compounds 5c, 6, 7b, and 8. Single crystals of **5c** and **7b** were obtained from the reaction mixtures upon cooling to −80 °C. Single crystals of **6** and **8** were grown from saturated solutions in toluene (4 °C) and pentafluoro-

benzene (−45 °C), respectively. The crystallographic data were collected with a Bruker APEX (**6** and **8**), a STOE IPDS (**5c**), and a Bruker Smart 6000 diffractometer (**7b**). The structures were solved by direct methods and refined with the program SHELXL-97[16][17] by a full-matrix least-squares method based on F^2. Crystal data, data collection parameters, and structure refinement details are given in Table 1. The molecules of **5c** and **6** reside on crystallographic centers of symmetry. Further details of the crystal structure determinations are available from the Cambridge Crystallographic

Data Center on quoting the depository numbers CCDC-630125 (**5c**), -630126 (**6**), -630127 (**7b**), and -630128 (**8**).

Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) *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: Germany, 1997.

(17) Hahn, T., Ed. *International Tables for Crystallography, Space-Group Symmetry*; Kluwer Academic Publishers: Dordrecht, 1989; Vol. A.