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Unexpected Formation of $Ga_4C_2H_4$ Heteroadamantane Cages by the Reaction of Carbon-Bridged Bis(dichlorogallium) Compounds with *tert*-Butyllithium

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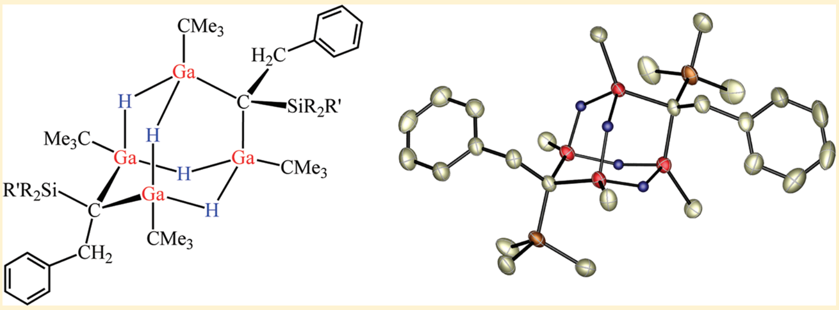
S *Supporting Information*

ABSTRACT:



Reactions of the carbon-bridged bis(dichlorogallium) compounds $(Cl_2Ga)_2C(SiR_2R')$-CH_2-Ph (**1a**, R = R′ = Me; **1b**, R = Ph, R′ = Me; **1c**, R = Me, R′ = CMe_3) with four equivalents of *tert*-butyllithium yielded bis[*tert*-butyl(hydrido)digallium] compounds $\{[(Me_3C)(H)Ga]_2C(SiR_2R')$-$CH_2$-Ph$\}_2$ (**3a** to **3c**), via *β*-elimination and release of isobutene. **3a** to **3c** are dimeric in solution and the solid state and contain unprecedented $Ga_4C_2H_4$ heteroadamantane structures in which four metal atoms are bridged by four hydrogen and two carbon atoms. In contrast, *n*-propyllithium gave the monomeric tetra(*n*-propyl)digallium compound $(^nPr_2Ga)_2C(SiMe_3)$-CH_2-Ph (**2**) under similar conditions, which has two coordinatively unsaturated gallium atoms and may be applicable as a chelating Lewis acid.

INTRODUCTION

The addition of dialkylgallium hydrides to oligoalkynes (hydrogallation)[1] is a facile method for the reduction of unsaturated organic substrates and the generation of oligogallium compounds that are suitable to act as chelating Lewis acids[2] for the effective coordination of donor ions or molecules.[3−5] Vinylic compounds are usually generated by the addition of a single Ga−H bond. Dual hydrogallation was observed in rare cases only and required relatively drastic reaction conditions.[6] Dichlorogallium hydride, $(H$-$GaCl_2)_2$,[7] proved to be more reactive than the corresponding alkyl derivatives and gave the complete reduction of alkynes to aliphatic compounds already at room temperature.[4,8,9] Highly functional carbon-bridged digallium compounds are formed that have a geminal arrangement of two $GaCl_2$ groups and are dimeric in the solid state via Ga−Cl−Ga bridges. Their two Lewis-acidic metal atoms are active for the chelating coordination of halide ions,[4] and their Ga−Cl bonds allow alkylation by treatment with alkyllithium reagents and salt elimination.[5,10] Neopentyllithium was a versatile reagent for these experiments,[5] while *tert*-butyllithium afforded the corresponding di(*tert*-butyl)gallium compounds only upon application of the vinylic dichlorogallium compounds having only a single gallium atom attached to the respective carbon atom.[10] Sterically crowded tris(trimethylsilyl)methyllithium gave strange chlorine−methyl exchange reactions,[7] which have been elucidated in detail only recently. The unexpected reactions of the bis(dichlorogallium) compounds with *tert*-butyllithium are reported in this article.

RESULTS AND DISCUSSION

Synthesis of Bis(dichlorogallium) Compounds by Dual Hydrogallation of Alkynes. The dual hydrogallation of silylalkynes H_5C_6-C≡C-SiR_2R' (R = R′ = Me; R = Ph, R′ = Me; R = Me, R′ = CMe_3) follows a standard procedure.[3] Suspensions of two equivalents of $(H$-$GaCl_2)_2$ in *n*-hexane were treated with the corresponding alkynes. The mixtures were stirred at room temperature for 15 h, and the products $(Cl_2Ga)_2C(SiR_2R')$-CH_2-Ph (**1a** to **1c**, eq 1) precipitated as colorless, amorphous solids in high purity. They are insoluble in noncoordinating solvents. Therefore, the NMR spectra were recorded in THF solutions, which clearly gives rise to the formation of THF adducts with an ether molecule attached to each gallium atom.

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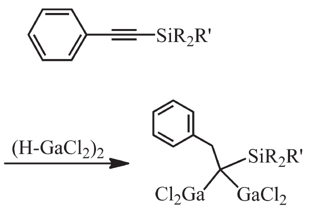
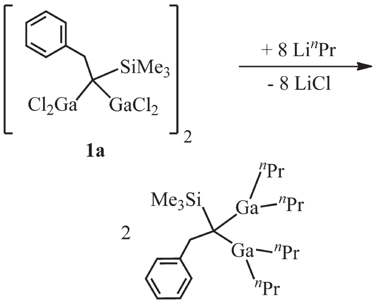
Synthesis and characterization of the trimethylsilyl derivative **1a** have been reported previously.[4] The NMR data of **1b** and **1c** are quite similar and do not require a detailed discussion. Most characteristic is a singlet in the ^{1}H NMR spectra at about $\delta = 3.7$ for the methylene hydrogen atoms. Crystal structure determinations revealed dimeric formula units via Ga−Cl−Ga bridges for similar compounds.[4,8]



(1)

1a: R = R' = Me[13]
1b: R = Ph, R' = Me
1c: R = Me, R' = ^{t}Bu

Reactions of the Bis(dichlorogallium) Compounds 1a to 1c with *n*-Propyl- and *tert*-Butyllithium. Treatment of the tetrachlorodigallium compound **1a** with four equivalents of *n*-propyllithium afforded the corresponding tetra(*n*-propyl)-digallium compound (^{n}Pr$_2$Ga)$_2$C(SiMe$_3$)-CH$_2$-Ph (**2**), in a moderate yield of 55% (eq 2). Its methylene protons showed a singlet at $\delta = 3.66$ in the ^{1}H NMR spectrum, and a resonance at a relatively low field of the ^{13}C NMR spectrum ($\delta = 43.3$) was observed for the carbon atom of the CGa$_2$ group. Both shifts are in the characteristic ranges of these carbon-bridged digallium compounds (see above).[5] Crystal structure determination verified the constitution of **2** (Figure 1). The central carbon atom C(1) is bonded to two di(*n*-propyl)gallium groups, a benzyl, and a trimethylsilyl substituent. Ga−C(1) (1.989 Å on average) and Si(1)−C(1) bond lengths (1.862(3) Å) are in the expected ranges. The angle Ga(1)−C(1)−Ga(2) is relatively small (103.8(1)°), and the largest angle at C(1) was observed between Ga(1) and Si(1) (114.8(1)°). The corresponding tetraneopentyl derivative has been obtained previously in a similar route.[5] Ethyl- and isopropyllithium gave the same reactions; however, the products could not be purified by recrystallization and were isolated only as highly viscous substances. NMR data were quite similar to those of **2**, but we abstain from a detailed discussion due to the presence of unknown impurities.

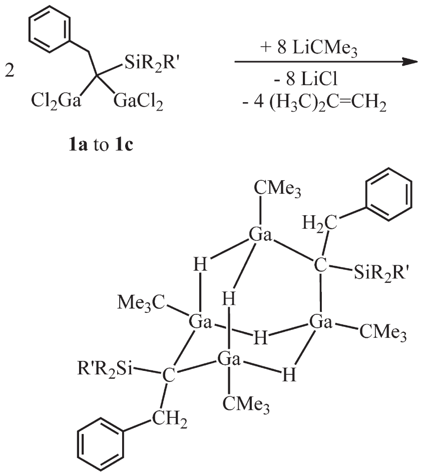


1a

(2)

2

A different result was obtained upon treatment of the starting compounds **1a** to **1c** with four equivalents of *tert*-butyllithium under similar reaction conditions (eq 3). Crystal structure determinations with the colorless products **3a** to **3c** (Figure 2) revealed unexpected constitutions with a Ga$_4$C$_2$H$_4$ heteroadamantane skeleton in the molecular core. Four gallium atoms are terminally bonded to a *tert*-butyl group and bridged by two carbon and four hydrogen atoms. The hydrogen atoms are part of 3c-2e Ga−H−Ga bonds. The carbon atoms of the cages are bonded to terminal benzyl (−CH$_2$C$_6$H$_5$) and trialkylsilyl groups. They are in opposite positions of the cage with a perpendicular arrangement of the (R$_3$)Si−C−C(benzyl) triangles. These molecules are chiral, similar to allenes RR′C=C=CRR′, and possess a noncrystallographic 2-fold rotational axis through the opposite hydrogen atoms H(1) and H(4).[11] These compounds may formally be formed by the replacement of one chlorine atom of each gallium atom by a *tert*-butyl group as originally expected. The second chlorine atom is replaced by a hydride ion that originates from *tert*-butyllithium via β-elimination and release of isobutene. Cages are formed by dimerization of the monomeric formula units [(Me$_3$C)(H)Ga]$_2$C(SiMe$_3$)-CH$_2$-Ph. The gallium atoms are coordinatively saturated with a coordination number of four in a distorted tetrahedral coordination sphere. Ga−C (2.009 Å on average) and Ga−H distances (1.71 Å) in the cages correspond to standard values.[12] The angles in the cage differ considerably. H−Ga−H angles are relatively acute (89°), while the largest angles are observed at the hydrogen atoms (Ga−H−Ga 139°). The Ga−C−Ga angles (102.6°) are almost unaffected compared to those of the tetrachloro- or tetraalkyldigallium compounds (see above).[4,5,8] Steric interactions may cause large C−Ga−C angles between the quaternary carbon atoms of the *tert*-butyl groups attached to gallium and the bridging carbon atoms (136.3° on average).



1a to **1c**

(3)

3a: R = R' = Me
3b: R = Ph, R' = Me
3c: R = Me, R' = ^{t}Bu

The unexpected and unprecedented constitution of compounds **3a** to **3c** is in accordance with their NMR data. Three resonances of relatively low intensity were observed in the ^{1}H NMR spectra at about $\delta = 4$ in an intensity ratio of 1:1:2. They were assigned to the hydrogen atoms attached to gallium. Their splitting pattern results from the particular molecular symmetry and verifies the existence of dimeric formula units also in solution. The molecules of **3a** to **3c** have a 2-fold rotational axis through two opposite bridging hydrogen atoms (H(1) and H(4) in Figure 2) as described above. These two hydrogen atoms are chemically nonequivalent and give the resonances with the lower intensities. H(2) and H(3) are transferred with each other by the C2 axis of the molecules; they show a single resonance with the highest intensity. The molecular symmetry causes also a splitting of the resonances of the Ga-CMe_3 groups, of both phenyl groups in **3b** ($SiPh_2Me$), and of both methyl groups attached to silicon in **3c** ($SiMe_2CMe_3$). The carbon atoms of the CGa_2 moieties have resonances at about $\delta = 40$ in the ^{13}C NMR spectra. We are not able to assign unambiguously a stretching vibration for the Ga−H bonds in the IR spectra. Oligomeric dialkylgallium hydrides usually show strong and broad absorption bands at about 1650 cm^{-1}.[12,13] However, only very weak and broad absorptions were detected in this area for compounds **3a** to **3c**; their assignment to the Ga−H stretching vibrations is questionable. Dimeric Ga_2H_6 exhibits bands for the Ga−H−Ga bridges with lower wave numbers at about 1200 cm^{-1}.[14] Strong absorptions or emissions have been observed in a similar range of the IR and Raman spectra for the heteroadamantane cages **3a** to **3c** (1160 and 1167 cm^{-1}, respectively), but they probably originate from C−C stretching vibrations.

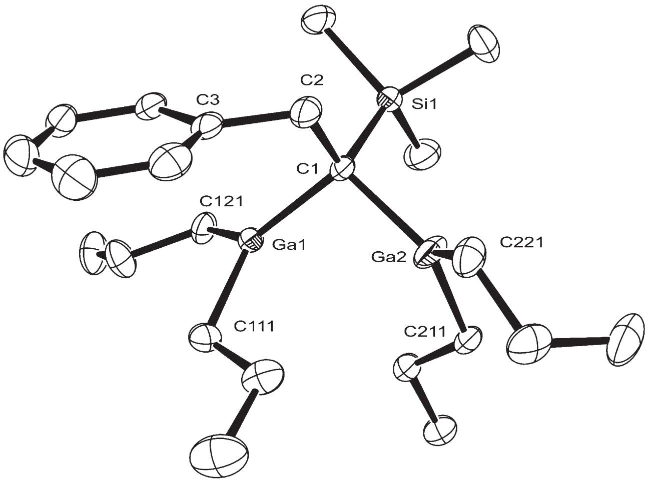


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): Ga(1)−C(1) 2.004(2), Ga(2)−C(1) 1.974(2), Si(1)−C(1) 1.862(3), Ga(1)−C(1)−Ga(2) 103.8(1), Ga(1)−C(1)−C(2) 108.7(2), Ga(1)−C(1)−Si(1) 114.8(1), Ga(2)−C(1)−Si(1) 109.2(1), Si(1)−C(1)−C(2) 109.9(2).

An interesting byproduct (**4**) was isolated in only a few crystals from the reaction of **1c** ($SiMe_2CMe_3$) with *tert*-butyllithium. It was characterized only by crystal structure determination and contains a $Ga_4C_2H_4$ heteroadamantane skeleton analogous to compounds **3a** to **3c** (Figure 3). However, in contrast to these compounds one gallium atom of **4** is bonded to a terminal hydrogen atom (Ga(1)−H(1), 1.48(4) Å) instead of a *tert*-butyl group, which results in the composition $(GaCMe_3)_3(GaH)(\mu\text{-H})_4[\mu\text{-C}(SiMe_2CMe_3)(CH_2C_6H_5)]_2$. Further structural parameters are almost unaffected in comparison to the regular structures of **3a** to **3c** and do not need a detailed discussion.

Reactions of alkyllithium derivatives with the carbon-bridged tetrachlorodigallium compounds $(Cl_2Ga)_2C(SiR_2R')$-CH_2-Ph (**1a** to **1c**) afforded different kinds of products. Neopentyllithium[5] and—despite the presence of *β*-hydrogen atoms—*n*-propyllithium (as well as ethyl- and isopropyllithium) gave the expected tetraalkyldigallium compounds, $(R_2Ga)_2C$-(SiR_2R')-CH_2−Ph (**2**), via simple replacement reactions. In contrast, *tert*-butyllithium gave partial *β*-elimination with the formation of mixed *tert*-butyl-hydrido species, $\{[(Me_3C)(H)\text{-}Ga]_2C(SiR_2R')\text{-}CH_2\text{-}Ph\}_2$ (**3a** to **3c**). These compounds are dimeric in solution and the solid state and form nice $Ga_4C_2H_4$ heteroadamantane structures with all hydrido ligands in bridging positions between two metal atoms. The different reactivity pattern of the alkyllithium derivatives may depend on the steric

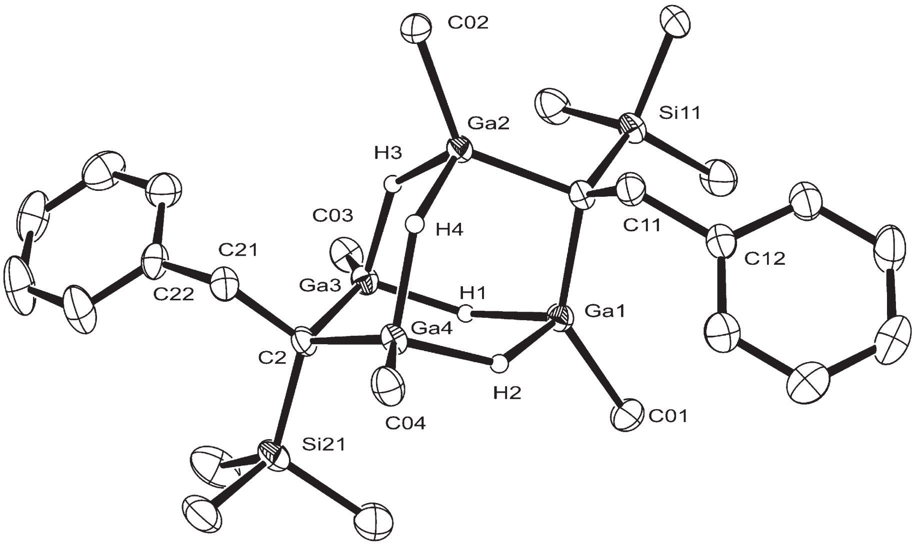


Figure 2. Molecular structure of **3a**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms with the exception of Ga−H and methyl groups of *tert*-butyl substituents are omitted. Important bond lengths (Å) and angles (deg): Ga(1)−C(1) 1.998(2), Ga(2)−C(1) 2.004(2), Ga(3)−C(2) 1.999(2), Ga(4)−C(2) 2.002(2), Ga−H 168(2) − 179(2), C(1)−Ga(1)−C(01) 138.1(1), C(1)−Ga(2)−C(02) 130.72(9), C(2)−Ga(3)−C(03) 138.9(1), C(2)−Ga(4)−C(04) 130.73(9). Data for **3b**: Ga(1)−C(1) 2.011(2), Ga(2)−C(1) 2.017(2), Ga(3)−C(2) 2.020(2), Ga(4)−C(2) 2.012(2), Ga−H 167(2) − 176(2), C(1)−Ga(1)−C(11) 141.93(9), C(1)−Ga(2)−C(21) 129.24(8), C(2)−Ga(3)−C(31) 129.90(8), C(2)−Ga(4)−C(41) 144.09(8). Data for **3c**: Ga(1)−C(1) 2.001(1), Ga(2)−C(1) 1.994(2), Ga(3)−C(2) 2.023(4), Ga(4)−C(2) 2.024(4), Ga−H 161(4)−181(4), C(1)−Ga(1)−C(14) 143.0(5), C(1)−Ga(2)−C(24) 132.0(4), C(2)−Ga(3)−C(31) 143.1(2), C(2)−Ga(4)−C(41) 134.4(2).

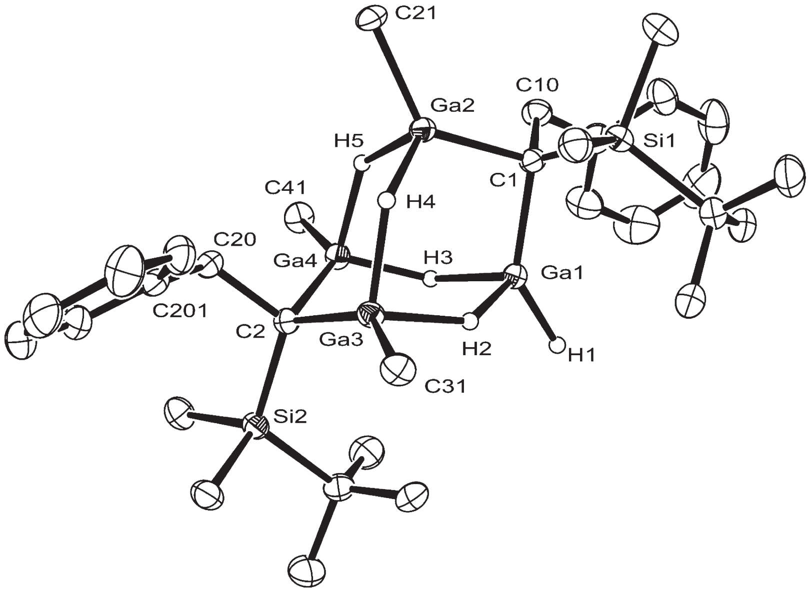


Figure 3. Molecular structure of **4**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms with the exception of Ga−H and methyl groups of *tert*-butyl substituents are omitted. Important bond lengths (Å) and angles (deg): Ga(1)−C(1) 1.979(3), Ga(2)−C(1) 2.015(3), Ga(3)−C(2) 1.997(3), Ga(4)−C(2) 2.016(3), Ga−H(bridge) 166(3) − 183(4), Ga(1)−H(1)(terminal) 148(4), H(1)−Ga(1)−C(1) 140(1), C(1)−Ga(2)−C(21) 131.7(1), C(2)−Ga(3)−C(31) 139.6(1), C(2)−Ga(4)−C(41) 133.7(1).

demand of the alkyl groups, and steric repulsion between the relatively bulky *tert*-butyl groups may favor β-elimination.[15] The heteroadamantane structure influences the reactivity of the Ga−H bonds of compounds **3a** to **3c**. They did not show typical reactions of likewise oligomeric dialkylgallium hydrides such as deprotonation of terminal alkynes or hydrogallation of C≡C triple bonds. Nevertheless, thorough investigations in the reactivity of these interesting tetranuclear compounds are a challenging task for future experiments.

EXPERIMENTAL SECTION

All procedures were carried out under purified argon. Diethyl ether and toluene were dried over Na/benzophenone; *n*-pentane and *n*-hexane, over $LiAlH_4$. The starting compounds $(H\text{-}GaCl_2)_2$,[6] $H_5C_6\text{-}C{\equiv}C\text{-}Si(C_6H_5)_2Me$,[16] $[H_5C_6\text{-}C(H){=}C(SiMe_3)\text{-}GaCl_2]_2$ (**1a**),[17] and $LiCH_2CH_2CH_3$[18] were obtained according to literature procedures. Solutions of *tert*-butyllithium in pentane or hexane were applied as purchased. The assignment of the NMR spectra is based on HMBC, HSQC, ROESY, and DEPT135 data. Only the most intensive masses of the mass spectra are given; the complete isotopic patterns are in accordance with the calculated ones.

Synthesis of $H_5C_6\text{-}C{\equiv}C\text{-}SiMe_2CMe_3$. A solution of phenylethyne (4.02 g, 39.4 mmol) in diethyl ether (150 mL) was treated with equimolar quantities of *n*-butyllithium (1.6 M in *n*-pentane, 24.6 mL, 39.4 mmol) at −78 °C. The solution was warmed to room temperature and stirred for 2 h. One equivalent of $Cl\text{-}SiMe_2CMe_3$ was added, and the mixture was heated under reflux for 3 d. After cooling to room temperature the mixture was treated with dilute HCl (6%, 100 mL). The organic phase was separated, washed with a saturated solution of sodium bicarbonate, and dried with anhydrous $MgSO_4$. The solvent was removed *in vacuo*, and the remaining yellow oil was distilled (50 °C, 0.15 mbar) to obtain the silylethyne as a colorless liquid. Yield: 4.43 g (52%). Anal. Calcd for $C_{14}H_{20}Si$ (216.4): C, 77.7; H, 9.3. Found: C, 76.7; H, 9.3. ^1H NMR (C_6D_6, 400 MHz): δ 7.40 (2 H, m, *ortho*-H of C≡C-Ph), 6.91 (1 H, m, *para*-H of C≡C-Ph), 6.90 (2 H, m, *meta*-H of C≡C-Ph), 1.03 (9 H, s, Si-CMe$_3$), 0.17 (6 H, s, Si-CH$_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 132.3 (*ortho*-C of C≡C-Ph), 128.6 (*para*-C of C≡C-Ph), 128.5 (*meta*-C of C≡C-Ph), 123.8 (*ipso*-C of C≡C-Ph), 106.7 (Ph-*C*≡C), 92.6 (C≡*C*-Si), 26.4 (Si−C*Me*$_3$), 16.9 (Si-*C*Me$_3$), −4.4 (Si-CH$_3$). ^{29}Si NMR (C_6D_6, 79 MHz): δ −8.0. IR (KBr plates, paraffin, cm^{-1}): 2158 vs ν(C≡C); 1960 w, 1942 m, 1892 w, 1875 m, 1820 w, 1800 w, 1749 w, 1668 w, 1595 s, 1576 m phenyl; 1487 s, 1462 vs (paraffin); 1408 w δ(CH$_3$); 1377 s (paraffin); 1361 s, 1248 vs δ(CH$_3$); 1219 s, 1175 w, 1155 w, 1096 w, 1069 m, 1028 m, 1007 s ν(CC); 939 m, 912 m, 846 vs, 835 vs, 804 s, 775 s, 756 vs ρ(CH$_3$Si); 721 w (paraffin); 689 vs, 615 s, 565 vw, 536 s ν(SiC). MS (EI, 20 eV, 25 °C): *m*/*z* (%) 217 (3.6), 216 (8.9) $[M]^+$; 160 (16), 159 (100) $[M - {}^tBu]^+$.

Syntheses of $(Cl_2Ga)_2C(SiR_2R')\text{-}CH_2\text{-}Ph$ (1b and 1c): General Procedure. Two equivalents of $H\text{-}GaCl_2$ (based on the monomeric formula unit, ca. 2 g) was suspended in *n*-hexane (100 mL) and treated with one equivalent of the corresponding ethynylsilane ($H_5C_6\text{-}C{\equiv}C\text{-}Si(C_6H_5)_2Me$ or $H_5C_6\text{-}C{\equiv}C\text{-}SiMe_2CMe_3$) at room temperature. The mixture was stirred for 15 h. A colorless solid precipitated, which was filtered off and washed two times with 5 mL of toluene. Both products **1b** and **1c** were directly obtained in high purity.

Characterization of 1b (R = C_6H_5, R′ = Me). Yield: 78%. Mp (argon, sealed capillary): 148 °C. Anal. Calcd for $C_{21}H_{20}Cl_4Ga_2Si$ (581.7; based on the monomeric formula unit): C, 43.4; H, 3.5. Found: C, 43.3; H, 3.5. ^1H NMR (THF-d_8, 400 MHz): δ 7.80 (4 H, m, *ortho*-H of Si-Ph), 7.45 (2 H, m, *ortho*-H of CH$_2$−Ph), 7.27 (2 H, m, *para*-H of Si-Ph), 7.26 (4 H, m, *meta*-H of Si-Ph), 7.09 (2 H, m, *meta*-H of CH$_2$-Ph), 7.08 (1 H, m, *para*-H of CH$_2$-Ph), 3.75 (2 H, s, CH$_2$), 0.93 (3 H, s, Si-CH$_3$). ^{13}C NMR (THF-d_8, 100 MHz): δ 143.7 (*ipso*-C of CH$_2$−Ph), 138.7 (*ipso*-C of Si-Ph), 137.2 (*ortho*-C of Si-Ph), 131.4 (*ortho*-C of CH$_2$−Ph), 129.9 (*para*-C of Si-Ph), 128.7 (*meta*-C of CH$_2$−Ph), 128.0 (*meta*-C of Si-Ph), 127.2 (*para*-C of CH$_2$-Ph), 37.6 (CH$_2$), 31.0 (CGa$_2$Si), 1.3 (Si-CH$_3$). ^{29}Si NMR (THF-d_8, 79 MHz): δ −8.9. IR (KBr plates, paraffin, cm^{-1}): 1946 w, 1881 vw, 1815 w, 1584 m, 1549 m, 1489 m phenyl; 1462 vs (paraffin); 1427 m, 1408 w δ(CH$_3$); 1377 s (paraffin); 1348 w, 1302 w, 1260 s δ(CH$_3$); 1194 w, 1157 m, 1105 vs, 1078 m, 1028 w ν(CC); 999 m, 970 w, 934 m, 908 s, 891 s, 839 s, 787 vs, 754 s, 737 vs ρ(CH$_3$Si); 727 vs (paraffin); 698 vs, 673 m, 654 w, 619 vw ν(Si−C); 588 w, 554 m, 525 m, 488 vs, 471 vs, 434 s ν(GaCl), ν(GaC).

MS (EI, 20 eV, 120 °C): *m/z* (%) 547 (6.1), 545 (8.9), 543 (4.4) [M (monomer) − Cl]$^+$.

Characterization of 1c (R = Me, R′ = CMe$_3$). Yield: 57%. Mp (argon, sealed capillary): 168 °C. Anal. Calcd for $C_{14}H_{22}Cl_4Ga_2Si$ (499.7; based on the monomeric formula unit): C, 33.7; H, 4.4. Found: C, 33.4; H, 4.4. ^{1}H NMR (THF-d_8, 400 MHz): δ 7.63 (2 H, d, $^3J_{H-H}$ = 7.3 Hz, *ortho*-H of Ph), 7.21 (2 H, pseudo-t, *meta*-H of Ph), 7.13 (1H, t, $^3J_{H-H}$ = 7.3 Hz, *para*-H of Ph), 3.67 (2 H, s, CH$_2$), 1.08 (9 H, s, Si-CMe$_3$), 0.11 (6 H, s, Si-CH$_3$). ^{13}C NMR (THF-d_8, 100 MHz): δ 143.8 (*ipso*-C of Ph), 131.6 (*ortho*-C of Ph), 128.7 (*meta*-C of Ph), 127.3 (*para*-C of Ph), 37.5 (CH$_2$), 32.3 (CGa$_2$), 29.7 (SiC*Me*$_3$), 22.4 (SiCMe$_3$), −0.5 (SiCH$_3$). ^{29}Si NMR (THF-d_8, 79 MHz): δ 8.0. IR (KBr plates, paraffin, cm^{-1}): 1956 w, 1938 w, 1819 vw, 1703 w, 1601 m, 1582 m, 1491 m phenyl; 1464 vs (paraffin); 1413 w δ(CH$_3$); 1377 s (paraffin); 1302 w, 1263 m, 1252 m δ(CH$_3$); 1206 w, 1180 vw, 1152 vw, 1078 m, 1007 m ν(CC); 941 w, 912 m, 837 s, 812 s, 770 s, 746 m ρ(SiCH$_3$); 727 s (paraffin); 706 m, 699 m, 656 w ν(SiC); 583 w, 556 w, 428 m ν(GaC), ν(GaCl). MS (EI, 20 eV, 130 °C): *m/z* (%) 485 (1.5), 483 (1.3) [M (monomer) − CH$_3$]$^+$; 463 (11), 461 (5) [M − Cl]$^+$; 443 (100), 441 (91) [M − ^{t}Bu]$^+$; 344 (18), 342 (13) [M − CH$_3$ − GaCl$_2$]$^+$.

Synthesis of (^{n}Pr$_2$Ga)$_2$C(SiMe$_3$)-CH$_2$-Ph (2). A solution of the bis(dichlorogallium) compound **1a** (0.470 g, 1.03 mmol, based on the monomeric formula unit) in 150 mL of toluene was cooled to −78 °C and treated with a solution of *n*-propyllithium in *n*-hexane (2.1 mL, 1.95 M, 4.11 mmol). The mixture was slowly warmed to room temperature, stirred for 24 h, concentrated, and filtered. The residue was washed with *n*-hexane. All volatiles of the filtrate were removed *in vacuo*, and the red-brown residue was dissolved in *n*-pentane. Colorless crystals of compound **2** were obtained upon cooling of the solution to −78 °C. Yield: 0.276 g (55%). Mp (argon, sealed capillary): 99 °C. Anal. Calcd for $C_{23}H_{44}Ga_2Si$ (488.1): C, 56.6; H, 9.1. Found: C, 57.1; H, 9.0. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.08 (2 H, d, $^3J_{H-H}$ = 7.3 Hz, *ortho*-CH), 7.07 (2 H, m, *meta*-CH), 6.92 (1 H, m, $^3J_{HH}$ = 7.3 Hz, *para*-CH), 3.66 (2 H, s, CH$_2$); the hydrogen atoms of the *n*-propyl groups gave an ABC$_2$D$_3$ spin system with A and B as the diastereotopic hydrogen atoms of the CH$_2$ groups attached to gallium: 1.59 (8 H, m, $^3J_{H-H}$ = 7.2 Hz (to CH$_3$), $^3J_{H-H}$ = 7.55 and 8.55 Hz (to the diasterotopic hydrogen atoms of GaCH$_2$), *C*H$_2$CH$_3$), 1.03 (12 H, t, $^3J_{H-H}$ = 7.2 Hz, CH$_2$*C*H$_3$), 0.79 (4 H, m, $^3J_{H-H}$ = 7.55 Hz, $^2J_{H-H}$ = −13.6 Hz, GaCH$_2$), 0.76 (4 H, m, $^3J_{H-H}$ = 8.55 Hz, $^2J_{H-H}$ = −13.6 Hz, GaC*H*$_2$), 0.17 (9 H, s, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 147.9 (*ipso*-C), 130.1 (*meta*-C), 1296.8 (*ortho*-C), 126.7 (*para*-C), 43.3 (CGa$_2$), 37.5 (Ph-CH$_2$), 23.8 (GaCH$_2$), 20.3 (CH$_2$CH$_3$), 20.0 (CH$_2$CH$_3$), 2.4 (SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79 MHz): δ −5.1. IR (CsI plates, paraffin, cm^{-1}): 1960 vw, 1942 w, 1919 vw, 1869 w, 1805 vw, 1599 vs, 1580 m, 1491 vs phenyl; 1452 vs (paraffin); 1406 m δ(CH$_3$); 1371 vs (paraffin); 1323 vs, 1290 w, 1258 vs, 1246 vs δ(CH$_3$); 1207 w, 1173 m, 1155 sh, 1057 vs ν(CC); 982 vs, 949 s, 907 m, 849 vs, 829 vs, 752 vs ρ(CH$_3$Si); 725 s (paraffin); 704 s, 675 s ν_{as}(SiC); 637 vs, 615 vs ν_s(SiC); 548 s, 525 s, 509 s, 457 w ν(GaC), δ(CC). MS (EI, 70 eV, 25 °C): *m/z* (%) 445 (29.6), 443 (22.0) [M − CH$_2$CH$_2$CH$_3$]$^+$; 403 (4.9), 401 (3.6) [M − 2CH$_2$-CH$_2$CH$_3$]$^+$; 333 (7), 331 (11) [M − Ga^{n}Pr$_2$]$^+$; 291 (64), 289 (100) [M − Ga^{n}Pr$_2$ − propene]$^+$.

Syntheses of the Heteroadamantane Compounds {[(Me$_3$C)(H)Ga]$_2$C(SiR$_2$R′)-CH$_2$-Ph}$_2$ 3a to 3c: General Procedure. A suspension of the corresponding bis(dichlorogallium) compound (about 1.2 g) in toluene (100 mL) was treated with four equivalents (based on monomeric **1a** to **1c**) of *tert*-butyllithium (1.6 M in *n*-pentane) at −78 °C. The mixture was warmed to room temperature and stirred for 16 h (2 h for **3c**). The solvent was removed *in vacuo*, and the dark residue was suspended in 20 mL of *n*-pentane. LiCl was filtered off and washed two times with 5 mL of *n*-pentane. The red filtrate was concentrated and cooled to −45 °C to yield the corresponding product as colorless crystals.

Characterization of 3a (R = R′ = Me). Yield: 30%. Mp (argon, sealed capillary): 174 °C (dec). Anal. Calcd for $C_{38}H_{72}Ga_4Si_2$ (864.0): C, 52.8; H, 8.4. Found: C, 52.8; H, 8.5. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.41 (4 H, d, $^3J_{H-H}$ = 7.3 Hz, *ortho*-CH), 7.16 (4 H, m, *meta*-CH), 7.03 (2 H, t, $^3J_{HH}$ = 7.3 Hz, *para*-CH), 4.28 (1 H, br, t, $^2J_{H-H}$ = 4.9 Hz, Ga-H), 4.17 (2 H, br, pseudo-t, $^2J_{H-H}$ = 4.7 Hz, Ga-H), 3.98 (1 H, br, t, $^2J_{H-H}$ = 4.6 Hz, Ga-H), 3.62 (4 H, s, CH$_2$), 1.33 and 1.22 (each 18 H, s, CMe$_3$), 0.32 (18 H, s, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 146.2 (*ipso*-C), 129.3 (*ortho*-C), 129.2 (*meta*-C), 126.7 (*para*-C), 42.4 (CGa$_2$), 38.8 (Ph-CH$_2$), 32.2 and 32.1 (C*Me*$_3$), 29.9 and 29.0 (CMe$_3$), 4.9 (SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79 MHz): δ −0.4. IR (CsI plates, paraffin, cm^{-1}): 1678 w, 1580 w ν(GaH, ?), phenyl; 1454 vs, 1377 vs (paraffin); 1304 w, 1244 m δ(CH$_3$); 1167 m, 1030 w, 1009 w ν(CC); 962 w, 935 m, 907 w, 841 s, 831 s, 808 m, 754 m, 743 m ρ(CH$_3$Si); 721 w (paraffin); 700 m ν_{as}(SiC); 656 w, 644 vw ν_s(SiC); 554 w, 461 w, 417 w ν(GaC), δ(CC). MS (EI, 70 eV, 150 °C): *m/z* (%) 807 (100), 805 (92) [M − CMe$_3$]$^+$; 431 (30), 429 (23) [1/2 M − H]$^+$; 375 (3.8), 373 (4.0) [1/2 M − CMe$_3$]$^+$.

Characterization of 3b (R = C$_6$H$_5$; R′ = Me). Yield: 62%. Mp (argon, sealed capillary): 187 °C. Anal. Calcd for $C_{58}H_{80}Ga_4Si_2$ (1112.3): C, 62.6; H, 7.2. Found: C, 62.7, H, 7.3. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.73 (8 H, m, *ortho*-H of Si-Ph; both resonances coincide), 7.53 (4 H, d, $^3J_{H-H}$ = 7.2 Hz, *ortho*-H of CH$_2$-Ph), 7.18 (8 H, m, *meta*-H of Si-Ph; both resonances coincide), 7.14 (4 H, m, *meta*-H of CH$_2$-Ph), 7.13 (4 H, m, *para*-H of Si-Ph; both resonances coincide), 7.03 (2 H, t, $^3J_{H-H}$ = 7.5 Hz, *para*-H of CH$_2$-Ph), 4.95 (1 H, br, t, $^2J_{H-H}$ = 5.0 Hz, Ga-H), 4.45 (2 H, br, pseudo-t, $^2J_{H-H}$ = 4.5 Hz, Ga-H), 4.11 and 4.03 (each 2 H, d, $^2J_{H-H}$ = 15.3 Hz, CH$_2$), 3.96 (1 H, br, t, $^2J_{H-H}$ = 4.2 Hz, Ga-H), 1.18 and 1.02 (each 18 H, s, Ga-CMe$_3$), 0.96 (6 H, s, Si-CH$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 145.4 (*ipso*-C of CH$_2$Ph), 141.6 and 140.7 (*ipso*-C of Si-Ph), 136.0 and 135.9 (*ortho*-C of Si-Ph), 129.5 (*ortho*-C of CH$_2$-Ph), 129.31 and 129.28 (*para*-C of Si-Ph), 129.0 (*meta*-C of CH$_2$-Ph), 128.23 and 128.20 (*meta*-C of Si-Ph), 126.8 (*para*-C of CH$_2$-Ph), 39.1 (CGa$_2$), 38.6 (CH$_2$), 32.3 and 32.0 (C*Me*$_3$), 31.1 and 30.2 (CMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79 MHz): δ −9.7. IR (KBr plates, paraffin, cm^{-1}): 1954 w, 1883 w, 1813 vw, 1663 vw, 1601 w, 1578 w, 1558 vw ν(GaH, ?), phenyl; 1460 vs, 1377 vs (paraffin); 1302 w, 1248 w δ(CH$_3$); 1159 m, 1099 s, 1074 w, 1009 w ν(CC); 961 w, 935 m, 893 m, 849 w, 806 m, 779 m ρ(Si−C); 723 s (paraffin); 696 m, 664 w, 627 m ν(SiC); 552 m, 517 w, 482 s, 455 w ν(GaC), δ(CC). Raman (neat, 1064 nm, cm^{-1}): 3052 s, 2959 m, br, 2843 s, 2769 w, 2705 w ν(CH$_3$); 1605 w, 1587 m, 1567 w phenyl; 1462 w, 1439 w δ(CH$_3$); 1167 s, 1101 vw, 1031 m, 1001 s ν(CC); 809 m ρ(SiMe$_3$); 661 vw, 621 w, 518 s ν(SiC), ν(GaC). MS (EI, 20 eV, 160 °C): *m/z* (%) 555 (2.7), 553 (5.0), 551 (3.1) [1/2 M − 3H]$^+$; 499 (98), 497 (100), 495 (38) [1/2 M − ^{t}Bu − 2H]$^+$.

Synthesis of 3c (R = Me, R′ = CMe$_3$). Yield: 52%. Mp (argon, sealed capillary): 156 °C. Anal. Calcd for $C_{44}H_{84}Ga_4Si_2$ (948.2): C, 55.7; H, 8.9; C, 56.7; H, 9.0. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.38 (4 H, d, $^3J_{H-H}$ = 8.0 Hz, *ortho*-H of Ph), 7.18 (4 H, pseudo-t, *meta*-H of Ph), 7.04 (2 H, t, $^3J_{H-H}$ = 7.4 Hz, *para*-H of Ph), 4.65 (1 H, br, t, $^2J_{H-H}$ = 4.3 Hz, GaH), 4.40 (2 H, br, pseudo-t, $^2J_{H-H}$ = 4.5 Hz, GaH), 4.10 (1 H, br, t, $^2J_{H-H}$ = 4.3 Hz, GaH), 3.77 (4 H, s, CH$_2$), 1.40 and 1.38 (each 18 H, s, Ga-CMe$_3$), 1.02 (18 H, s, Si-CMe$_3$), 0.12 and 0.06 (each 6 H, s, Si-CH$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 145.3 (*ipso*-C of Ph), 129.5 (*ortho*-C of Ph), 128.9 (*meta*-C of Ph), 126.8 (*para*-C of Ph), 40.4 (CH$_2$), 36.9 (CGa$_2$), 33.2 and 33.1 (Ga-C*Me*$_3$), 30.8 and 29.9 (Ga-CMe$_3$), 28.8 (Si-C*Me*$_3$), 18.8 (Si-CMe$_3$), 0.2 and −0.1 (SiCH$_3$). ^{29}Si NMR (C$_6$D$_6$, 79 MHz): δ 12.1. IR (KBr plates, paraffin, cm^{-1}): 1938 vw, 1719 w, 1649 w, 1578 m, 1558 m ν(GaH, ?), phenyl; 1458 vs, 1377 vs (paraffin); 1364 sh, 1302 w, 1244 s δ(CH$_3$); 1161 m, 1076 w, 1030 w, 1007 m ν(CC); 961 w, 939 s, 899 s, 826 s, 810 s, 762 m, 744 s ρ(Si−C); 723 w (paraffin); 700 m, 635 m ν(SiC); 573 w, 550 m, 507 w, 424 m ν(GaC), δ(CC). Raman (neat, 1064 nm, cm^{-1}): 3070 w, 3051 m, 3034 w, 2924 m, br, 2844 s, 2770 w, 2708 w ν(CH$_3$); 1602 w, 1585 vw phenyl; 1464 m, 1442 m

$\delta(CH_3)$; 1200 w, 1167 s, 1031 w, 1004 m $\nu(CC)$; 942 vw, 916 vw, 812 m $\rho(SiMe_3)$; 655 vw, 634 vw, 623 vw, 577 w, 524 m, 510 m, 430 vw, 394 vw $\nu(SiC)$, $\nu(GaC)$, $\delta(CC)$. MS (EI, 20 eV, 130 °C): m/z (%) 419 (32), 417 (100), 415 (75) $[1/2\ M - CMe_3]^+$; 289 (23), 287 (36) $[Ga\text{-}C(Si^tBuMe_2)CH_2Ph]^+$.

Crystal Structure Determinations. Single crystals were obtained by crystallization from n-pentane (**2**, −80 °C; **3a** to **3c**, −45 °C). The crystallographic data were collected with a Bruker APEX diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97[19] by a full-matrix least-squares method based on F^2. Hydrogen atoms (except Ga-H of compounds **3** and **4**, which were refined isotropically) were positioned geometrically and allowed to ride on their respective parent atoms. Two n-propyl groups of **2** were disordered; the atoms were refined on split positions (C122, 0.55 to 0.45; C221, 0.61 to 0.39). Compound **3c** showed a disorder of a complete $C(SiMe_2CMe_3)CH_2Ph$ group; site-occupancy factors were 0.77 and 0.23. A *tert*-butyl group of **4** was disordered (split positions 0.55 to 0.45). Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-830856 (**2**), -830857 (**3a**), -830858 (**3b**), -830859 (**3c**), and -830860 (**4**).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. CIF files giving the crystal data for compounds **2**, **3a** to **3c**, and **4**. Table of crystal data and structure refinement. This material is available free of charge via the Internet at http://pubs.acs.org.

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