ORGANOMETALLICS

A Unique Chlorine–Methyl Exchange Reaction upon Treatment of Dichloroorganogallium Compounds, RGaCl₂, with the Bulky Alkyllithium Derivative LiC(SiMe₃)₃

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Supporting Information

ABSTRACT: Reaction of the organogallium chlorides $C_6H_{6-n}[C(H)=C(GaCl_2)-SiR_3]_n$ (1 to 4; R = Me, Ph) with the bulky alkyllithium derivative Li(THF)₂C(SiMe₃)₃ did not afford the expected alkylgallium chlorides by salt elimination. Instead, compounds (5 to 7) were isolated that had methyl groups attached to gallium, while chlorine atoms moved to silicon to yield Ga(Me)-C(SiMe₃)₂(SiMe₂Cl) moieties. On the basis of quantum chemical calculations the formation of these



unprecedented structural motifs is caused by kinetic control involving cyclic transition states as initiating steps. The anticipated, but experimentally not observed products having the intact Ga(Cl)- $C(SiMe_3)_3$ subunits (8) were calculated to be thermodynamically favored.

■ INTRODUCTION

Bulky substituents have often been applied in main-group chemistry for the kinetic stabilization of unusual structural motifs such as E-E single or multiple bonds or oligonuclear E_n clusters.¹ Although pentasubstituted cyclopentadienyl or sterically encumbered aryl or silyl groups were employed in most cases, the tris(trimethylsilyl)methyl substituent was alternatively used as a protecting group for, for example, the generation of cluster compounds such as $Ga_4[C(SiMe_3)_3]_4$.² In some recent investigations we found an easy access to various functional dichlorogallium compounds, $C_6H_{6-n}[C(H)=$ $C(GaCl_2)$ -SiMe₃]_n^{3,4} via hydrogallation of oligoalkynes⁵ by dichlorogallane, H-GaCl₂.⁶ These vinylgallium dichlorides are valuable starting compounds for the generation of the corresponding dialkylgallium derivatives by treatment with alkyllithium and salt elimination.^{7,8} We hoped to generate sterically shielded alkylgallium chlorides by the reaction with the bulky alkyllithium compound $Li(THF)_2C(SiMe_3)_3$. The second chlorine atom of each GaCl₂ group should subsequently be used for further functionalization, for instance by reduction with alkali metals. However, an unexpected reaction course was observed.

RESULTS AND DISCUSSION

Synthesis of Dichlorogallium Compounds by Hydrogallation of Alkynes. The reaction of H-GaCl₂ with some trimethylsilylalkynes to yield alkenylgallium compounds has been reported by our group in two previous publications.^{3,4} Two of these compounds, H_5C_6 -C(H)=C(SiMe_3)-GaCl₂ (1) and 1,4- $[Cl_2Ga-C(SiMe_3)=C(H)]_2C_6H_4$ (2), were applied in the studies described in this article. In order to allow more systematic investigations we synthesized two further compounds (3 and 4, eq 1). 3 was obtained by treatment of a suspension of the hydride H-GaCl₂ in *n*-hexane with solid 1,3-(Me₃Si-C=C)₂C₆H₄ and crystallized from the concentrated reaction mixture in 66% yield. Once crystallized, the solubility of 3 in hydrocarbons considerably decreased. Therefore NMR spectra were recorded in THF, which clearly resulted in adduct formation by coordination of the gallium atoms. In contrast to 1 to 3, compound 4 contains a triphenylsilyl instead of a trimethylsilyl substituent attached to its C=C double bond. It is insoluble in *n*-hexane and was isolated as a colorless, amorphous solid by filtration of the reaction mixture. In both cases the ${}^{3}J_{Si-C=C-H}$ coupling constant of about 10.5 Hz indicated the *cis*-arrangement of hydrogen and silicon atoms at the C=C double bonds^{5,8,9} and the formal trans-addition of the H-Ga groups. The mechanism of the cis/ trans-rearrangement with products of hydroalumination and hydrogallation has been discussed previously.⁸ Crystal structure determinations (Figures 1 and 2) verified this particular configuration. They revealed the formation of dimeric compounds via Ga-Cl-Ga bridges similar to the structures of compounds 1 and 2, which have been reported previously.³ A relatively

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interesting tricyclic structure resulted for compound 3 that possesses two Ga_2Cl_2 heterocycles in the bridging positions. The average Ga-Cl bond lengths of 3 and 4 differ according to the different coordination numbers of the chlorine atoms and are 2.14 (terminal) versus 2.34 Å (bridging).^{3,10} Standard values were also observed for the C=C bond lengths (1.34 Å on average).





Reactions of the Dichlorogallium Compounds with Li(THF)₂C(SiMe₃)₃. In a general procedure suspensions of the gallium chlorides 1 to 4 in *n*-hexane were treated with the solid lithium compound $Li(THF)_2C(SiMe_3)_3$ (one equivalent per $GaCl_2$ group, eq 2). After 16 h at room temperature the mixtures were filtrered. The colorless products (5 to 7) crystallized upon cooling of the concentrated filtrates in 46-76% yield. Only the monoalkenyl compound 1 gave an unclear reaction course with the formation of an oily product, which contained a mixture of several unknown components. We were not able to isolate any compound by crystallization from different noncoordinating solvents. The NMR spectra of the crystalline products 5 to 7 were relatively complicated and did not agree with those expected for the simple substitution products. Crystal structure determinations (Figure 3 to 5) revealed a surprising constitution that did not comprise intact tris-(trimethylsilyl)methyl groups. In all cases both chlorine atoms of the GaCl₂ moieties were replaced by a methyl group and a trisilylmethyl substituent. Only two SiMe3 groups of the latter remained intact; the third one was transformed to an SiMe₂Cl unit with a chlorine atom attached to silicon $[C(SiMe_3)_2SiMe_2Cl]$. The formation of these compounds may be described by rearrangement with an exchange of a chlorine atom attached to gallium and a methyl group of an SiMe₃ substituent. However, the reaction mechanism is complicated, as discussed below. The gallium atoms are coordinatively unsaturated and bonded to three carbon atoms of different ligands. They have an almost ideally planar



Figure 1. Molecular structure of 3. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms and methyl groups of SiMe₃ substituents are omitted. Important bond lengths (Å) and angles (deg): Ga(1)-Cl(1) 2.141(2), Ga(1)-Cl(11) 2.323(2), Ga(1)-Cl(21) 2.346(2), Ga(2)-Cl(2) 2.134(2), Ga(2)-Cl(21) 2.369(2), Ga(3)-Cl(3) 2.144(2), Ga(3)-Cl(31) 2.331(2), Ga(3)-Cl(41) 2.336(2), Ga(4)-Cl(4) 2.140(2), Ga(4)-Cl(41) 2.337(2), C(1)-C(11) 1.358(7), C(2)-C(21) 1.331(7), C(3)-C(31) 1.335(7), C(4)-C(41) 1.323(7), C(1)-C(11)-C(12) 130.5(5), C(2)-C(21)-C(22) 126.4(5), C(3)-C(31)-C(32) 131.2(5), C(4)-C(41)-C(42) 127.6(5).

coordination sphere with a maximum deviation from the plane of the three adjacent carbon atoms of only 0.022 Å. The longest Ga–C distance is observed to the carbon atom of the bulky trisilyl groups. The planes GaC₃ are almost perpendicular to the planes defined by the C=C double bond and the adjacent atoms (angles between the normal of the planes: 77.5° (5) to 81.3° (6)). This preferred conformation is clearly caused by a minimization of steric repulsion. Bond lengths (C=C 134.8 pm; Si-Cl 211.3 pm on average) correspond to standard values and do not require a detailed discussion. The dialkenyl compounds 5 and 6 show different orientations of the Ga-Me groups. In 5 they point toward different directions of the molecules (anti), while they adopt a kind of a synorientation in 6. This observation may help to understand the relatively complicated NMR spectra as discussed below. Due to the molecular geometry, relatively short intramolecular Ga-Cl distances of 292 to 300 pm result for compounds 5 and 6. However, we do not believe in significant Ga-Cl bonding interactions, because we observed ideal planar coordination spheres at the gallium atoms with sums of the angles of 360° and deviations of the metal atoms from the respective C_3 plane of only 0 to 0.02 Å, the torsion angles Ga-C-Si-Cl are relatively large $(25^{\circ} \text{ to } 35^{\circ})$, and much shorter Ga-halogen distances have been reported in the

literature for compounds that clearly had such interactions to organohalogen groups.⁴

 $C_6H_{6-x}[C(H)=C(SiR_3)-GaCl_2]_x$ $\xrightarrow{x Li(THF)_2C(SiMe_3)_3}$

 $C_6H_{6-x}[C(H)=C(SiR_3)-Ga(Me)-C(SiMe_3)_2(SiMe_2Cl)]_x$



Two complete sets of resonances of two different species were detected in the NMR spectra of compounds 5 and 6. Each set reflects the pattern expected from the molecular structures in the solid state. Methyl groups bonded to gallium and the vinylic trimethylsilyl groups gave singlets in the ¹H NMR spectra at about δ = 0.7 and 0.4, respectively. Interestingly, two resonances were observed for both intact trimethylsilyl groups of each CSi₃ substituent and also for the methyl groups of each SiMe₂Cl moiety. This splitting is caused by the particular molecular conformation with the Ga-Me bonds perpendicular to the alkenyl plane and a hindered rotation about the Ga-C(vinyl) bond. Hence, these molecules do not possess mirror planes that would transfer the respective groups in each other. The two different molecular species may result from the different orientation of both Ga-Me groups (syn or anti) in accordance with the different molecular structures observed in the solid state. Hindered rotation is important in these cases, as was shown by a high-temperature NMR experiment with compound 6. Upon warming to 100 °C in toluene, the different sets of resonances in the ¹H NMR spectrum coincided and gave the expected singlets of a single molecule for the GaMe ($\delta = 0.56$), SiMe₂Cl ($\delta = 0.50$, broad), vinylic SiMe₃ ($\delta = 0.30$), and C(SiMe₃)₂ groups $(\delta = 0.16, broad)$. The rotational barrier was estimated from the coalescence temperature of different groups of resonances to be about 19 kcal/mol. The NMR spectra of compound 7 are simpler. Nevertheless hindered rotation about the Ga-C(vinyl)bond resulted in a splitting of the ¹H and ¹³C NMR resonances of the SiMe₂Cl groups into two singlets at room temperature. In the ¹H NMR spectrum these resonances coincided upon warming, and the coalescence temperature was determined to be about



Figure 2. Molecular structure of **4**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): Ga(1)–Cl(1) 2.3350(8), Ga(1)–Cl(1)' 2.339(1), Ga(1)–Cl(2) 2.149(1), C(1)–C(10) 1.337(3), C(1)–C(10)–C(10)–C(101) 128.5(2), Ga(1)–Cl(1)–Ga(1)' 91.86(3), Cl(1)–Ga(1)–Cl(1)' 88.14(3); Ga(1)' and Cl(1)' generated by -x+1, -y+1, -z+1.

80 °C. The intact SiMe₃ groups gave two narrow resonances only upon cooling to 0 °C (¹H NMR, 0 °C: δ 0.65 (GaMe), 0.35 and 0.27 (SiMe₂Cl), 0.055 and 0.050 (SiMe₃)). The activation barrier was estimated to be 17 kcal/mol.

Quantum Chemical Calculations and Reaction Mechanism. In order to gain deeper insight into the mechanism of this series of transformations, high-level gas phase quantum chemical calculations have been carried out. We were particularly interested in elucidating the reaction pathways that starting from 9 and 10 lead to the actually isolated compound 7 or to the originally expected product of the replacement of a chlorine atom by a bulky alkyl group (8). These calculations should help to understand the kinetic and thermodynamic factors governing these competing reactions. Compound 8 (Scheme 1) was calculated to be thermodynamically favored over the experimentally obtained product 7 by 8.6 kcal/mol. For the exploration of the relevant parts of the energy hypersurface, the sum of the energies of (Z)-[2-phenyl-1-(trimethylsilyl)vinyl]gallium dichloride (9) and the adduct of dimethyl ether (as a model for experimentally used tetrahydrofuran) with tris(trimethylsilyl)methyllithium 10 was taken as a reference ($E_{rel} = 0.0$ kcal/mol, Scheme 2). These two species are able to form two different types of complexes (11 and 14). 11 $(E_{\rm rel} = -14.5 \text{ kcal/mol})$ is an essential intermediate for the formation of compound 7 (Scheme 2, left side). Its main structural features are a relatively short distance of the migrating methyl group to the gallium atom of 254.5 pm, a substantial Li-Cl



Figure 3. Molecular structure of **5**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): Ga(1)-C(1) 1.985(2), Ga(1)-C(2) 1.984(2), Ga(1)-C(3) 2.037(2), C(1)-C(10) 1.349(3), Si(31)-Cl(31) 2.123(4), C(1)-Ga(1)-C(2) 112.75(9), C(1)-Ga(1)-C(3) 126.76(9), C(2)-Ga(1)-C(3) 120.5(1); symmetry operation: -x+1, -y+1, -z.

interaction with a Li-Cl distance of 253.3 pm, and a short Li–OMe₂ distance of 194.4 pm. Starting from this complex the transfer of the methyl group from the silicon atom of compound 10 to the gallium atom of compound 9 was calculated. This process is predicted to proceed through a six-membered-ring transition structure, TS-12, of the Zimmerman-Traxler type, which is 10.0 kcal higher in energy than complex 11. The Me-Si distance in TS-12 is calculated to be 212.3 pm, and the Me–Ga distance, 231.7 pm (Li-Cl distances 250.4 and 263.8 pm; Li-OMe₂ 197.6 pm). From IRC calculations starting from TS-12 structure 13 is obtained ($E_{rel} = -22.5 \text{ kcal/mol}$), in which the Me group is attached to the gallium atom and the Li atom is connected to both chlorine atoms. The Li-Cl separations are 238.4 and 239.3 pm (Li–OMe₂ 196.9 pm). The bond between the central carbon atom and the silicon atom, which has lost the Me group, is shortened to 174.1 pm and may have some π -character.

A reasonable pathway for the formation of the experimentally not observed compound 8 comprises the formation of an alternative complex, 14, in which both starting compounds are connected by an interaction between the lithium and a chlorine atom (Li–Cl 260.2 pm; Li–OMe₂ 194.2 pm; Scheme 2 on the right). The resulting transition state **TS-15** ($E_{rel} = -3.8$ kcal/mol), which represents the first step for Ga–C bond formation (Ga–C distance 345.1 pm), is sterically more crowded compared to **TS-12**. Consequently, the Li–OMe₂ distance is relatively long (200.1 pm) despite the lower coordination number of the lithium atom. This transition state gives intermediate **16** ($E_{rel} = -48.2$ kcal/mol), which already contains all features of the not observed product **8**, e.g., a short Ga–carbon bond (206.2 pm). Finally, formal



Figure 4. Molecular structure of 6. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): Ga(1)-C(1) 1.990(2), Ga(1)-C(2) 1.985(2), Ga(1)-C(3) 2.041(2), C(1)-C(10) 1.345(3), Si(31)-Cl(31) 2.124(1), Ga(2)-C(4) 1.994(2), Ga(2)-C(5) 1.985(2), Ga(2)-C(6) 2.039(2), C(4)-C(40) 1.351(3), Si(61)-Cl(61) 2.1341(9), C(1)-Ga(1)-C(2) 114.5(1), C(1)-Ga(1)-C(3) 125.26(9), C(2)-Ga(1)-C(3) 120.2(1), C(4)-Ga(2)-C(5) 114.9(1), C(4)-Ga(2)-C(6) 125.25(9), C(5)-Ga(2)-C(6) 119.8(1).

elimination of LiCl, coordinated by Me₂O, results in the formation of 8. Its relative energy of -21.9 kcal/mol indicates its thermodynamic preference over product 7 (-13.3 kcal/mol).

In conclusion both competitive pathways differ only slightly in their energetic profiles with small thermodynamic and kinetic advantages in the initial steps for the formation of compound 7 (11 versus 14 and TS-12 versus TS-15), but a significant thermodynamic preference for product 8. Since the calculations are carried out for the species in the gas phase, the structures following the transition states TS-12 and TS-15 might be artificial. If formed, one would expect that in solution both transition structures will collapse into the products 7 and 8 by elimination of LiCl. The formation of the crystalline, ionic LiCl certainly will be the main driving force of this transformation. It should be pointed out that consideration of one molecule of dimethyl ether as model solvent was crucial in these calculations. Without the Lewis base, the reaction pathway to the experimentally not observed product 8 is kinetically and thermodynamically favored.

Interestingly, the transfer of a methyl group instead of the replacement of a chlorine atom by the complete $C(SiMe_3)_3$ substituent has been observed previously when particular element chlorides were treated with $LiC(SiMe_3)_3$ (many other reactions, e.g., observed by our group, have not been published at all).¹² Hence, the applicability of this important protecting group proved to be relatively limited. A reasonable mechanism for these unexpected reactions has not been discussed before; however, the heterocyclic compound $[Me_2Si-C(SiMe_3)_2]_2$ has been



Figure 5. Molecular structure of 7. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): Ga(1)-C(1) 2.010(3), Ga(1)-C(2) 1.985(3), Ga(1)-C(3) 1.988(3), C(2)-C(20) 1.345(4), Si(12)-Cl(1) 2.059(1), C(1)-Ga(1)-C(2) 127.2(1), C(1)-Ga(1)-C(3) 121.5(1), C(2)-Ga(1)-C(3) 111.2(1).

identified as a byproduct in several cases. It was probably formed via an intermediate compound containing a Si=C double bond. The unprecedented compounds reported here (5 to 7) and the suggested mechanism may help to understand these reactions. In cases where at least two chlorine atoms are bonded to the central atom a cyclic transition state similar to TS12 may result in formation of methyl-element species and an exchange of a SiMe₃ methyl group by a chlorine atom. The intermediate compound 13 may play a key role in these reactions. Hence, the compounds reported in this article not only are important due to their particular functionality but also help to understand the unique reaction behavior of the important lithium compound LiC- $(SiMe_3)_3$ with the possible formation of three different types of products. The isolation of the expected sterically shielded compounds having intact $C(SiMe_3)_3$ groups may be prevented by alternative reaction pathways that may lead to methyl-element compounds via the elimination of silaethenes or to chlorosilane derivatives similar to 5 to 7 (eq 2). The degradation of a bulky ligand has also been observed in a few reactions of subvalent gallium or germanium compounds with LiSi(SiMe₃)₃, which resulted in the formation of Ga-SiMe3 or Ge-Me groups. The mechanisms were not discussed.¹³

EXPERIMENTAL SECTION

All procedures were carried out under purified argon. *n*-Hexane and cyclopentane were dried over LiAlH₄; 1,2-difluorobenzene was dried over molecular sieves. The starting compounds H-GaCl₂,⁶ (H₅C₆)₃Si-C=C-C₆H₅,¹⁴ 1,3-(Me₃Si-C=C)₂C₆H₄,¹⁵ 1,4-[C(H)=C-(SiMe₃)-GaCl₂]₂C₆H₄ (**2**),³ and Li(THF)₂C(SiMe₃)₃¹⁶ were obtained









according to literature procedures. 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 1,3-[Me₃Si-(Cl₂Ga)C=C(H)]₂C₆H₄ (3). H-GaCl₂ (2.57 g, 18.1 mmol) was suspended in 250 mL of *n*-hexane and treated with solid 1,3-bis(trimethylsilylethinyl)benzene (2.34 g, 8.65 mmol, 0.48 equiv) at room temperature. The mixture was stirred for 16 h. A small quantity of an unknown colorless solid precipitated and was filtered off. The product (3) crystallized from the concentrated filtrate upon cooling to 5 °C. Yield: 3.15 g (66%). Mp (argon, sealed capillary): 150 °C (dec). ¹H NMR (THF-*d*₈, 400 MHz): δ 7.87 (2 H, s, ³J_{H-Si} = 10.3 Hz, C=CH), 7.59 (1 H, s, br, 2-H of phenyl), 7.51 (2 H, m, 4,6-H of

phenyl), 7.32 (1 H, t, br, 5-H of phenyl), 0.26 (18 H, s, SiMe₃). ¹³C NMR (THF- d_{s} , 100 MHz): δ 155.7 (HC=CGa), 148.7 (HC=CGa), 142.6 (1,3-C of phenyl), 129.0 (2-C of phenyl), 128.7 (5-C of phenyl), 127.7 (4,6-C of phenyl), 0.1 (SiMe₃). ²⁹Si NMR (THF- d_{s} , 79 MHz): δ –0.1. IR (CsI plates, paraffin, cm⁻¹): 1597 m, 1584 s, 1553 vs ν (C=C), phenyl; 1470 vs (paraffin); 1435 m, 1408 s, 1402 s δ (CH₃); 1377 s (paraffin); 1337 w, 1315 w, 1300 w, 1250 vs, 1175 w, 1161 w, 1090 s ν (CC), δ (CH); 964 s, 928 vs, 899 vs, 827 vs, 783 vs, 745 vs ρ (CH₃Si); 721 vs (paraffin); 698 vs, 635 vs, 611 vs, 600 vs ν (SiC); 577 vw, 542 vs, 501 s, 476 vw, 455 vs, 417 vs ν (GaCl), ν (GaC). MS (EI, 20 eV, 160 °C): m/z (%) 517 (0.2), 519 (0.2) [M(monomer) – CI]⁺, 443 (10), 445 (10) [M – HCl – SiMe₃] ⁺.

Synthesis of [(H₅C₆)₃Si-(Cl₂Ga)C=C(H)]C₆H₅ (4). H-GaCl₂ (2.02 g, 14.3 mmol, small excess) was suspended in 100 mL of *n*-hexane and treated with solid triphenylsilylethinylbenzene (4.68 g, 13.0 mmol) at room temperature. After a few hours the product started to precipitate. Stirring was continued for 12 h. The colorless product (4) was filtered off, washed with 10 mL of *n*-hexane, and evacuated to 10^{-3} Torr to completely remove all volatiles. Yield: 2.60 g (40%). Mp (argon, sealed capillary): 175 °C. ¹H NMR (THF- d_8 , 400 MHz): δ 7.91 (1 H, s, ³J_{H-Si} = 10.7 Hz, C=CH), 7.71 (6 H, m, ortho-H of Si-phenyl), 7.57 (2 H, m, ortho-H of C=C-phenyl), 7.39 (3 H, m, para-H of Si-phenyl), 7.38 (6 H, m, meta-H of Si-phenyl), 7.32 (2 H, m, meta-H of C= C-phenyl), 7.29 (1 H, m, para-H of C=C-phenyl). ¹³C NMR (THF-d₈, 100 MHz): δ 163.6 (HC=CGa), 142.8 (br, HC=CGa), 142.6 (*ipso*-C of C=C-phenyl), 137.3 (ortho-C of Si-phenyl), 136.1 (ipso-C of Si-phenyl), 130.3 (para-C of Si-phenyl), 129.3 (para-C of C=C-phenyl), 128.9 (meta-C of C=C-phenyl), 128.7 (ortho-C of C=C-phenyl), 128.6 (meta-C of Si-phenyl). ²⁹Si NMR (THF- d_8 , 79 MHz): δ –12.7. IR (KBr plates, paraffin, cm⁻¹): 1962 vw, 1877 w, 1765 w, 1684 w, 1645 m, 1553 s, 1533 w, 1499 w ν (C=C), phenyl; 1466 w, 1427 w, 1375 m (paraffin); 1331 w, 1306 w, 1261 w, 1188 w, 1157 w, 1111 m, 1067 vw, 1026 w, 997 w, 964 vw, 930 m, 885 s, 839 w, 816 m, 799 s, 743 m ν (CC), δ (CH); 698 s, 677 m, 621 m v(SiC); 586 m, 557 s, 507 s, 473 w, 453 m, 428 m ν (GaCl), ν (GaC). MS (EI, 20 eV, 160 °C): m/z (%) 466 (3.4), 464 (3.3) [M(monomer) – HCl]⁺, 395 (100), 396 (30), 397 (37) [M(monomer) – $HGaCl]^+$, 360 (26.0) $[M(monomer) - HGaCl_2]^+$.

Synthesis of Compounds 5 to 7: General Procedure. Solid $Li(THF)_2C(SiMe_3)_3$ (about 2.6 mmol, one equivalent per GaCl₂ group) was added in small portions to cooled (0 °C) suspensions of the corresponding dichlorogallium compounds in 50 mL of *n*-hexane. The mixtures were warmed to room temperature and stirred for 16 h. LiCl was filtered off. The pale yellow filtrates were concentrated and cooled to -15 °C to obtain the crystalline products 5 to 7.

Characterization of 5. Yield: 58%. Mp (argon, sealed capillary): 212 °C. Anal. Calcd for C36H78Cl2Ga2Si8 (946.0): C, 45.7; H, 8.3. Found: C, 45.6; H, 8.3. Two conformers A and B were observed in the NMR spectra in a molar ratio of 0.67:0.33 at room temperature. ¹H NMR (C_6D_6) 400 MHz): Isomer A: δ 7.77 (2 H, s, ${}^{3}J_{H-Si}$ = 12.0 Hz, C=CH), 7.17 (4 H, s, aromatic ring), 0.77 (6 H, s, Ga-CH₃), 0.56 and 0.52 (each 6 H, s, ClSiCH₃), 0.37 (18 H, s, C=C-SiMe₃), 0.22 and 0.14 (each 18 H, s, C(SiMe₃)₂); isomer B: δ 7.83 (2 H, s, ${}^{3}J_{H-Si}$ = 12.0 Hz, C=CH), 7.23 (4 H, s, aromatic ring), 0.63 (6 H, s, Ga-CH₃), 0.57 and 0.53 (each 6 H, s, ClSiCH₃), 0.36 (18 H, s, C=C-SiMe₃), 0.21 and 0.17 (each 18 H, s, C(SiMe₃)₂). ¹³C NMR (C₆D₆, 100 MHz): Isomer A: δ 167.1 (HC=CGa), 150.3 (HC=CGa), 144.2 (1,4-C of phenyl), 128.1 (C-H of phenyl), 18.6 (CSi₃), 9.7 (Ga-CH₃), 9.0 and 8.6 (ClSiCH₃), 5.4 and 5.2 (C(SiMe₃)₂), 1.4 (C=C-SiMe₃); isomer B: δ 167.8 (HC=CGa), 150.5 (HC=CGa), 144.6 (1,4-C of phenyl), 128.3 (C-H of of phenyl), 18.9 (CSi₃), 9.8 (Ga-CH₃), 9.2 and 8.6 (ClSiCH₃), 5.4 and 5.3 (C(SiMe₃)₂), 1.4 (C=C-SiMe₃). ²⁹Si NMR (C₆D₆, 79 MHz): Isomer A: δ 27.7 (SiCl), -3.5 (C=C-SiMe₃), -3.6 and -4.4 (C(SiMe₃)₂); isomer B: δ 27.5 (SiCl), −3.6 (C=C-SiMe₃), −3.6 and −4.2 (C(SiMe₃)₂). IR (KBr plates, paraffin, cm⁻¹): 1710 w, 1580 m, 1555 m, 1495 m ν (C=C), phenyl; 1462 vs (paraffin); 1404 w δ(CH₃); 1377 s (paraffin); 1304 w, 1258 s, 1248 s δ (CH₃); 1196 w, 1107 w ν (CC), δ (CH); 984 w, 907 m, 847 vs, 773 w, 750 w ρ (CH₃Si); 721 m (paraffin); 673 s ν_{as} (SiC); 619 m ν_{s} (SiC); 554 m, 540 w, 480 m, 469 m, 434 m ν (SiCl), ν (GaC). MS (EI, 20 eV, 170 °C): m/z (%) 931 (4.5), 929 (4.8) [M – Me]⁺, 693 (1.2) [M – C(SiMe₃)₂SiMe₂Cl]⁺, 594 (28), 592 (21) [M – Ga(Me)C(SiMe₃)₂-SiMe₂Cl – Me]⁺; 337 (100), 335 (92) [GaMeC(SiMe₃)₂SiMe₂Cl]⁺.

Characterization of 6. Yield: 76%. Mp (argon, sealed capillary): 132 °C. Anal. Calcd for C₃₆H₇₈Cl₂Ga₂Si₈ (946.0): C, 45.7; H, 8.3. Found: C, 46.2; H, 8.2. Two conformers, A and B, were observed in the NMR spectra in a molar ratio of 0.55:0.45 at room temperature. ¹H NMR (C₆D₆, 400 MHz, 300 K): Isomer A: δ 7.78 (2 H, s, ${}^{3}J_{H-Si}$ = 11.6 Hz, C=CH), 7.15 (3 H, m, 2-H and 5-H of phenyl), 7.00 (2 H, d, 4,6-H of phenyl), 0.67 (6 H, s, Ga-CH₃), 0.57 and 0.52 (each 6 H, s, ClSiCH₃), 0.38 (18 H, s, C=C-SiMe₃), 0.18 and 0.16 (each 18 H, s, C(SiMe₃)₂); isomer B: δ 7.83 (2 H, s, ${}^{3}J_{H-Si}$ = 11.7 Hz, C=CH), 7.25 (3 H, m, 2-H and 5-H of phenyl), 7.00 (2 H, d, 4,6-H of phenyl), 0.65 (6 H, s, Ga-CH₃), 0.57 and 0.49 (each 6 H, s, ClSiCH₃), 0.38 (18 H, s, C= C-SiMe₃), 0.22 and 0.15 (each 18 H, s, C(SiMe₃)₂). ¹H NMR (toluene- d_{8} , 400 MHz, 370 K): δ 0.56 (6 H, Ga-CH₃), 0.50 (broad, 12 H, s, SiMe₂Cl), 0.30 (18 H, s, C=C-SiMe₃), 0.16 (broad, 36 H, s, C(SiMe₃)₂). ¹³C NMR (C₆D₆, 100 MHz): Isomer A: δ 167.9 (HC=CGa), 151.2 (HC=CGa), 146.4 (1,3-C of phenyl), 127.1 (2-C and 5-C of phenyl), 125.6 (4,6-C of phenyl), 19.3 (CSi₃), 10.4 (Ga-CH₃), 9.1 and 8.7 (ClSiCH₃), 5.5 and 5.4 $(C(SiMe_3)_2)$, 1.4 (C=C-SiMe_3); isomer B: δ 167.5 (HC=CGa), 151.1 (HC=CGa), 146.0 (1,3-C of phenyl), 127.2 (2-C and 5-C of phenyl), 125.4 (4,6-C of phenyl), 19.0 (CSi₃), 9.8 (Ga-CH₃), 9.0 and 8.6 (ClSiCH₃), 5.6 and 5.3 (C(SiMe₃)₂), 1.5 (C=C-SiMe₃). ²⁹Si NMR (C₆D₆, 79 MHz): Isomer A: δ 27.4 (SiCl), -3.7 and -4.4 $(C(SiMe_3)_2)$, -3.8 (C=C-SiMe_3); isomer B: δ 26.9 (SiCl), -3.4 (C= C-SiMe₃), -3.6 and -4.2 (C(SiMe₃)₂). IR (KBr plates, paraffin, cm⁻¹): 1688 w, 1655 w, 1580 m, 1543 m ν (C=C), phenyl; 1460 s (paraffin); 1402 m δ (CH₃); 1377 s (paraffin); 1304 w, 1250 s δ (CH₃); 1198 m, 1080 w, 1043 w ν (CC), δ (CH); 953 w, 914 w, 864 vs, 847 vs, 783 w, 748 w ρ (CH₃Si); 721 m (paraffin); 673 m ν_{as} (SiC); 619 w ν_{s} (SiC); 592 w, 557 m, 536 w, 471 m, 446 m v(SiCl), v(GaC). MS (EI, 20 eV, 140 °C): m/z (%) 931 (4.9), 929 (4.6) $[M - Me]^+$, 693 (2.7), 695 (1.9) $[M - C(SiMe_3)_2$ - $SiMe_2Cl$ ⁺, 594 (28), 592 (22) [M - Ga(Me)C(SiMe_3)_2SiMe_2Cl -Me]⁺; 337 (100), 335 (90) [GaMeC(SiMe₃)₂SiMe₂Cl]⁺.

Characterization of 7. Yield: 46%. Mp (argon, sealed capillary): 152 °C. Anal. Calcd for C₃₆H₄₈ClGaSi₄ (698.3): C, 61.9; H, 6.9. Found: C, 61.3; H, 6.6. ¹H NMR (C₆D₆, 400 MHz, 300 K): δ 8.14 (1 H, s, ³*J*_{H-Si} = 12 Hz, C=CH), 7.88 (6 H, pseudo-d, *ortho*-H of SiPh₃), 7.21 (9 H, m, meta- and para-H of SiPh₃), 7.10 (2 H, m, ortho-H of C=C-Ph), 7.00 (2 H, m, meta-H of C=C-Ph), 6.99 (1 H, pseudo-t, para-H of C=C-Ph), 0.67 (3 H, s, Ga-CH₃), 0.38 and 0.32 (each 3 H, s, ClSiCH₃), 0.08 (18 H, s, C(SiMe₃)₂). ¹H NMR (toluene- d_{8} , 400 MHz, 270 K): δ 0.65 (3 H, s, GaMe), 0.35 and 0.27 (each 3 H, s, SiMe₂Cl), 0.055 and 0.050 (each 9 H, s, C(SiMe₃)₂). ¹³C NMR (C₆D₆, 100 MHz): δ 159.5 (HC= CGa), 159.0 (HC=CGa), 144.6 (ipso-C of C=C-Ph), 137.3 (ortho-C of SiPh₃), 136.4 (*ipso-C* of SiPh₃), 130.1 (*meta-C* of C=C-Ph), 129.9 (*para-C* of SiPh₃), 128.7 (para-C of C=C-Ph), 128.3 (meta-C of SiPh₃), 127.2 (ortho-C of C=C-Ph), 20.4 (CSi₃), 10.1 (Ga-CH₃), 9.0 and 8.8 (ClSiCH₃), 5.4 (C(SiMe_3)_2). ^{29}Si NMR (C_6D_6, 79 MHz): δ 24.9 (SiCl), -4.1 (SiMe₃), -14.7 (SiPh₃). IR (KBr plates, paraffin, cm⁻¹): 1655 w, 1580 m, 1560 w, 1531 m v(C=C), phenyl; 1460 vs, 1377 s (paraffin); 1306 w, 1252 s δ (CH₃); 1196 w, 1159 w, 1103 s, 1028 w, 997 w ν (CC), δ (CH); 924 w, 881 s, 866 s, 845 s, 793 w, 773 w, 736 s ρ(CH₃Si), phenyl; 723 s (paraffin); 700 s phenyl; 671 m, 650 m v_{as} (SiC); 619 w v_{s} (SiC); 592 m, 547 s, 496 s, 455 m v(SiCl), v(GaC). MS (EI, 20 eV, 120 °C): m/z (%) 683 (4.9), 681 (3.8) $[M - Me]^+$, 447 (6.4), 445 (8.5) [M -C(SiMe₃)₂SiMe₂Cl]⁺, 337 (100), 335 (88) [GaMeC(SiMe₃)₂SiMe₂Cl]⁺.

Crystal Structure Determinations. Single crystals were obtained by crystallization from *n*-hexane $(3, 20/+4 \degree C)$, cyclopentane (4, storing a solution at room temperature), and cyclopentane $(5-7, 20/+5 \degree C)$. The

crystallographic data were collected with a STOE IPDS-II (4) and a Bruker APEX diffractometer. The structures were solved by direct methods and refined with the program SHELXL-9717 by a full-matrix least-squares method based on F^2 . The crystals of compound 3 decomposed rapidly after picking them up from the solvent or upon warming to room temperature. They became amorphous and could be mounted and measured only with difficulties. The only usable crystal was twinned with two domains; the reflections of one domain were used for structure refinement. The molecules of 4 and 5 reside on crystallographic centers of symmetry. The crystals of 5 enclose two molecules of cyclopentane per formula unit; their carbon atoms were refined with isotropic displacement parameters. The C(SiMe₃)₂(SiMe₂Cl) group showed a disorder; the atoms were refined on split positions (0.67:0.33). The crystals of 6 enclose a molecule of cyclopentane per formula unit. The molecular core of 7 showed a disorder; the atoms GaCSi₃Cl were refined on split positions (0.94:0.06). Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-812976 (3), -812977 (4), -812978 $(5 \cdot 2C_5H_{10})$, -812979 $(6 \cdot C_5H_{10})$, and -812980 (7).

Quantum Chemical Calculations. All computations have been performed using the Gaussian 09 suite of programs.¹⁸ The Becke threeparameter exchange functional and the correlation functional of Lee, Yang, and Parr (B3LYP)¹⁹ with the 6-311G(d,p) basis set were used to compute the geometries and the normal mode vibration frequencies of the structures. For single-point energy calculations on DFT-optimized geometries the SCS-MP2 method²⁰ with the def2-TZVP basis set²¹ taken from the EMSL Basis Set Library²² was used. In order to verify the character of the stationary points, they were subjected to frequency analyses. The vibration related to the imaginary frequency corresponds to the nuclear motion along the reaction coordinate under study. Further, intrinsic reaction coordinate calculations were performed in order to unambiguously connect the transition structures with the reactants and the products.

ASSOCIATED CONTENT

Supporting Information. CIF files giving the crystal data for compounds 3 to 7. Table of crystal data and structure refinement. Cartesian coordinates (B3LYP/6-311G(d,p)) and SCS-MP2/def2-TZVP//B3LYP/6-311G(d,p)+ZPE energies of the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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DEDICATION

Dedicated to Hansgeorg Schnöckel on the occasion of his 70th birthday.

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