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New Aspects of Hydrogallation Reactions with Alkynes: Simple Addition versus Formation of Cyclophanes

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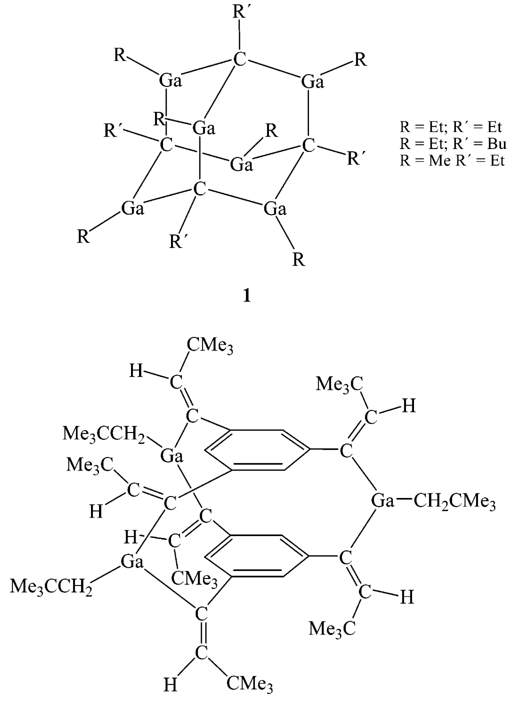
Treatment of 1,4-bis(3,3-dimethyl-1-butynyl)benzene $C_6H_4(C{\equiv}C{-}CMe_3)_2$ with 2 equiv of diethylgallium hydride resulted in addition of one Ga−H bond to each triple bond of the starting compound. Whereas in that case products of secondary reactions could not be isolated, dineopentylgallium hydride afforded a [3,3]-cyclophane derivative with two bridging $Ga{-}CH_2{-}CMe_3$ groups, which may be derived from the simple addition product by condensation and release of trineopentylgallium. A *cis*-arrangement of Ga and H was observed in all cases.

Introduction

The hydrogallation of C=C double or C≡C triple bonds was described in several reports as a facile method for the generation of alkyl- or alkenylgallium compounds.[1] Although clear structural evidence was rarely provided, the structures of the products were often derived from the addition of Ga−H bonds to the unsaturated organic components. Thus, compounds were postulated that have dialkylgallium groups attached to one carbon atom of the respective C_2 couples. Some recent investigations of our group showed, however, that the course of these reactions may be more complicated. For instance, treatment of alkynyldialkylgallium derivatives with the corresponding dialkylgallium hydrides afforded heteroadamantane type compounds (**1**, Scheme 1) possessing cages formed by six gallium and four carbon atoms.[2] Trialkylgallium compounds were isolated as byproducts, which may have been formed in the decomposition of the simple addition products $[(R_2Ga)_2C{=}C(H){-}R']$ that had the potentially unstable geminal dialkylgallium structures. Similar reactions were reported by our group for aluminum compounds, which yielded the first examples of carbaalanes.[3] We observed a similar behavior when we treated 1,3,5-tris(3,3-dimethyl-1-butynyl)benzene, $C_6H_3(C{\equiv}C{-}CMe_3)_3$, with dineopentylgallium hydride.[4] A [3,3,3]-cyclophane type molecule (**2**, Scheme 1) resulted by the release of trineopentylgallium. Compound **2** has two aromatic groups bridged by three C_2Ga spacers and contains three coordinatively unsaturated gallium atoms. To obtain better insight into the course of these hydrogallation reactions, we have systematically changed the alkyne starting compounds and the steric demand of the substituents attached to the gallium atoms of the hydrides. Here we report some reactions with the bisalkyne 1,4-bis(3,3-dimethyl-1-butynyl)benzene, $C_6H_4(C{\equiv}C{-}CMe_3)_2$.

Scheme 1



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Results and Discussion

Reactions of Diethylgallium and Dineopentylgallium Hydride with the Bisalkynylbenzene 1,4-($Me_3C{-}C{\equiv}C{-})_2C_6H_4$. While hydroalumination usually proceeds under relatively mild conditions below room temperature,[5] hydrogallation reactions are slower and require refluxing *n*-hexane as solvent in order to complete the reactions in a reasonable time. Accordingly,

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(1) (a) Nogai, S.; Schmidbaur, H. *Inorg. Chem.* **2002**, *41*, 4770. (b) Schmidbaur, H.; Klein, H. F. *Angew. Chem.* **1966**, *78*, 306. (c) Schmidbaur, H.; Klein, H. F. *Chem. Ber.* **1967**, *100*, 1129. (d) Ohshita, J.; Schmidbaur, H. *J. Organomet. Chem.* **1993**, *453*, 7. (e) Schumann, H.; Hartmann, U.; Wassermann, W. *Polyhedron* **1990**, *9*, 353. (f) Johnsen, E.; Downs, A. J.; Goode, M. J.; Greene, T. M.; Himmel, H.-J.; Müller, M.; Parsons, S.; Pulham, C. R. *Inorg. Chem.* **2001**, *40*, 4755. (g) Pulham, C. R.; Downs, A. J.; Godde, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Am. Chem. Soc.* **1991**, *113*, 5149. (h) Atwood, J. L.; Bott, S. G.; Jones, C.; Raston, C. L. *Inorg. Chem.* **1991**, *30*, 4868. (i) Henderson, M. J.; Kennard, C. H. L.; Raston, C. L.; Smith, G. *J. Chem. Soc., Chem. Commun.* **1990**, 1203. (j) Uhl, W.; Molter, J.; Neumüller, B. *J. Organomet. Chem.* **2001**, *634*, 193. (k) Jennings, J. R.; Wade, K. *J. Chem. Soc. A* **1967**, 1222.

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

(3) (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. *Inorganic Chemistry Highlights*; Meyer, G., Naumann, D., Wesemann, L., Eds.; Wiley-VCH: Weinheim, 2002; p 229.

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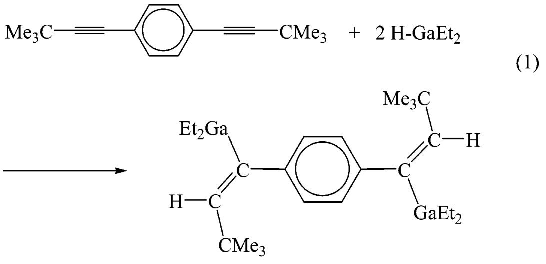
10.1021/om050776e CCC: $33.50

we treated the bisalkyne 1,4-($Me_3C-C\equiv C-)_2C_6H_4$ with 2 equiv of diethylgallium hydride in *n*-hexane at reflux for 24 h until the starting alkyne was completely consumed. The NMR spectrum of the crude product of the reaction showed a complicated pattern of many unassigned resonances. The corresponding trialkylgallium compound could not be detected unambiguously, which is in contrast to the reaction of the trisalkynylbenzene with di(neopentyl)gallium hydride cited above.[4] Despite the confusing NMR spectrum, repeated recrystallization yielded the pure product **3** as a colorless solid in moderate yield. Strong evacuation of solid **3** in order to completely remove the solvent should be avoided, because decomposition seems to occur under these conditions with an alteration of the consistency of the residue and the formation of small drops of a yellow oil. This decomposition reaction proceeds slowly, and its mechanism remains unknown. The characterization of **3** was accomplished using samples that contained different amounts of the solvent *n*-hexane. NMR data, in particular the very characteristic integration ratios, clearly verified that the hydrogallation reaction in this case did not afford a cyclophane type molecule similar to **2** (Scheme 1) by condensation. Instead, the simple addition product with one diethylgallium unit attached to each of the C=C double bonds was isolated (eq 1). Similar addition products were obtained in hydroalumination reactions only in those cases where at least one trimethylsilyl group was attached to the carbon atoms of the C≡C triple bonds.[5] These compounds contain coordinatively unsaturated aluminum and gallium atoms and may be suitable to act as chelating Lewis acids. In view of the relative instability of **3** we did not find the molecular mass of compound **3** in the mass spectrum (EI). Instead, a peak was detected in addition to those of unknown products, which could be assigned to a cyclophane type molecule minus one ethyl group. Triethylgallium-derived peaks were found in only very low intensity. Thus, it seems that decomposition of **3** yielded at least partially a cyclophane type molecule. After isolation of **3** and evaporation of the mother liquor a dark yellow highly viscous liquid remained, which showed a multitude of NMR resonances due to unknown products.



(1)

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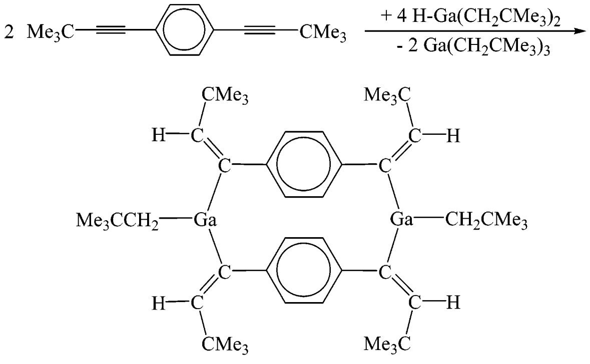

(2)

4

The reactions of dineopentylgallium hydride usually are faster, and the starting compounds were completely consumed on heating at reflux overnight. The slightly different reactivity may depend on the bulkiness of the substituents and the degree of oligomerization (R = Et: trimeric; R = CH_2CMe_3: dimeric).[6,7] Trineopentylgallium was formed in the course of the reaction (eq 2). It was isolated from the crude product by distillation under vacuum in 34% yield. However, it could not be removed completely from the remaining solid. The product (**4**) was isolated in pure form by recrystallization of the residue from toluene. NMR spectroscopic characterization verified a reaction course similar to that described in the Introduction for the trisalkynylbenzene 1,3,5-($Me_3C-C\equiv C)_3C_6H_3$. A [3,3]-cyclophane type compound was formed by condensation and release of trineopentylgallium, which possesses two bridging neopentylgallium groups. Thus, interestingly the simple addition product seems to be unstable in this case and may occur only as an intermediate. From steric shielding we would expect just the reverse behavior, and the bulkier substituents should prevent the facile approach of the molecules to initiate the exchange process. Indeed, stable addition products of the type $R_2Al-(H_5C_6)C=C(H)-CMe_3$ were obtained by employing the very bulky bis(trimethylsilyl)methyl groups attached to aluminum.[8] The most characteristic spectroscopic findings of compounds **3** and **4** are the chemical shifts of the hydrogen atoms attached to the C=C bonds (δ = 6.11 and 6.20), which, however, do not allow a clear distinction between both types of molecules. There is a small difference in the ^{13}C NMR resonances of the *ipso*-carbon atoms of the aromatic groups (δ = 142.5 and 155.2, respectively) and of the α-carbon atoms of the C=C double bond attached to gallium (δ = 153.9 and 142.2). However, it is not yet clear whether these differences are indicative for the respective structures.

An intermediate was detected by NMR spectroscopy in the course of the dineopentylgallium hydride reaction (eq 2). It showed two doublets of equal intensity in the phenyl range (δ = 7.46 and 6.86; J = 8 Hz). These resonances disappeared with the complete consumption of the starting bisalkyne. A *tert*-butyl resonance could not be assigned. The observation of doublets for the phenyl protons is indicative of a nonsymmetric product with, for example, the addition of Ga−H to only one ethynyl group, but it is not clear whether the condensation already occurred at that stage. To isolate this intermediate, we conducted the reaction according to eq 2 with a 1:1 ratio of the starting compounds. The intermediate was formed once again. However, decomposition occurred with the formation of unknown products before the bisalkyne was consumed. A further byproduct was detected, which showed a chemical shift of δ = 6.98. It could be enriched in the mother liquor after isolation of compound **4** together with trineopentylgallium and some unknown impurities, but we could not isolate it in pure form. We are not able to make a reasonable suggestion for its constitution.

Whether compound **3** is a singular case is not clear yet. All attempts to conduct such reactions starting with sterically less

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[5] (a) Uhl, W.; Matar, M. *J. Organomet. Chem.* **2002**, *664*, 110. (b) Uhl, W.; Breher, F. *J. Organomet. Chem.* **2000**, *608*, 54.

[6] Uhl, W.; Cuypers, L.; Geiseler, G.; Harms, K.; Massa, W. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1001.

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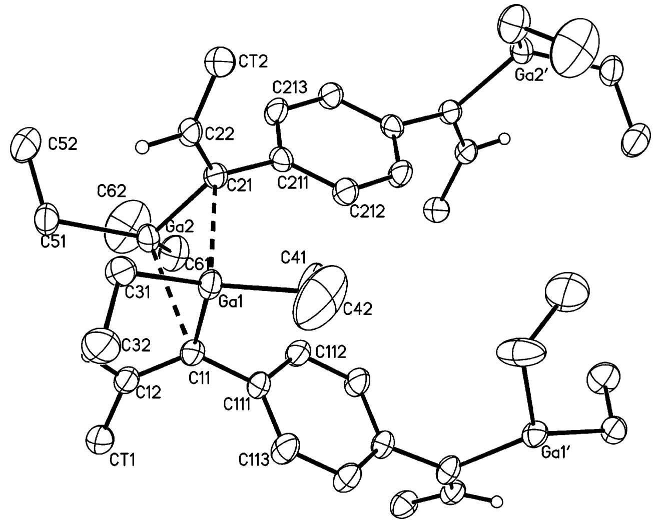

Figure 1. Molecular structure of **3**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups of the *tert*-butyl substituents and hydrogen atoms of the phenyl groups are omitted for clarity. The drawing shows both independent molecules. One resides on a center of symmetry [Ga(2)]; the second one on a 2-fold rotation axis [Ga(1)]. The dashed lines indicate the intermolecular interactions. Important bond lengths (Å) and angles (deg): Ga(1)−C(11) 2.030(3), Ga(1)−C(31) 1.977(3), Ga(1)−C(41) 1.979(4), C(11)−C(12) 1.350(4), C(11)−C(111) 1.500(4), Ga(2)−C(21) 2.045(3), Ga(2)−C(51) 1.982(3), Ga(2)−C(61) 1.976(4), C(21)−C(22) 1.345(4), C(21)−C(211) 1.496(4), Ga(1)−C(21) 2.560(4), Ga(2)−C(11) 2.581(4), C(11)−Ga(1)−C(31) 114.9(1), C(11)−Ga(1)−C(41) 115.0(2), C(31)−Ga(1)−C(41) 116.7(2), C(12)−C(11)−C(111) 123.5(3), C(21)−Ga(2)−C(51) 112.6(1), C(21)−Ga(2)−C(61) 116.4(2), C(51)−Ga(2)−C(61) 117.9(2), C(22)−C(21)−C(211) 122.0(3). The atoms Ga(1)′ and Ga(2)′ were generated by $-x$, y, $-z+0.5$ and $-x$, $-y$, $-z$, respectively.

shielded dimethylgallium hydride failed. That hydride is relatively unstable,[6] and fast decomposition of the hydride was observed for solutions at temperatures > 50 °C without any attack on the alkyne. At room temperature hydrogallation reaction did not occur even after prolonged reaction times of several weeks.

Molecular Structures. The molecular structures of the hydrogallation products **3** and **4** are depicted in Figures 1 and 2, respectively. The ethyl compound **3** represents the product of a simple addition of Ga−H to both C≡C triple bonds without a secondary reaction and is thus in complete accordance with the usual formulations of hydroalumination or hydrogallation products found in the literature. The second compound, **4**, bears the bulkier neopentyl groups and may be described as a [3,3]-cyclophane with two bridging GaC$_2$ moieties in *para*-position of the aromatic rings. In both compounds the gallium and hydrogen atoms attached to the C═C double bonds adopt a *cis*-arrangement, and the GaR$_2$ or GaR groups are bonded to those carbon atoms that are in α-position to the phenylene rings. This particular position may be favored by a mesomeric stabilization of the negative charge induced by the bonding of that carbon atom to gallium.

Two independent molecules are found in the crystal structure of compound **3**, which reside on two symmetrically different special positions. One with the atom Ga(1) is located on a crystallographic 2-fold rotation axis, which is perpendicular to the aromatic ring and causes both diethylgallium fragments to be on the same side of the phenylene group. The second molecule possesses a center of symmetry with a *trans*-arrangement of the organometallic substituents. A fast rotation around the C−C bonds to the central phenylene groups may equilibrate both forms in solution so that only one set of NMR resonances was detected. The spectra did not change upon cooling of samples dissolved in toluene to −60 °C. The planes of the phenylene groups are almost perpendicular to the planes defined by each substituent including the C═C double bonds [angles between the normals of the planes 100° with Ga(1) and 91° with Ga(2)]. Thus, a mesomeric stabilization of the molecules by an interaction between the aromatic systems and the C═C double bonds can clearly be excluded at least for the solid state. The C═C double bond lengths (1.348 Å) are almost indistinguishable for both molecules and are in the normal range.[9] Interestingly, the longer Ga−C distances (2.038 versus 1.979 Å on average) are observed for those carbon atoms [C(11) and C(21)] that formally are sp^2-hybridized and are part of the C═C double bonds (see for comparison the structure of **4**). That particular effect is caused by an intermolecular interaction that results in the formation of one-dimensional coordination polymers possessing *zigzag* chains alternating the two types of molecules. Relatively narrow Ga−C contacts to the α-carbon atoms of the C═C double bonds result [Ga(1)⋯C(21) 2.560 Å; Ga(2)⋯C(11) 2.581 Å], which were indicated by dashed lines in Figure 1 and give strongly faulted Ga$_2$C$_2$ heterocycles. These contacts cause a considerable deviation of the gallium atoms from the plane of the three carbon atoms C(11), C(31), C(41) or C(21), C(51), C(61) [0.429 Å and sum of the angles 346.6° for Ga(1); 0.424 Å and sum of the angles 346.9° for Ga(2)].

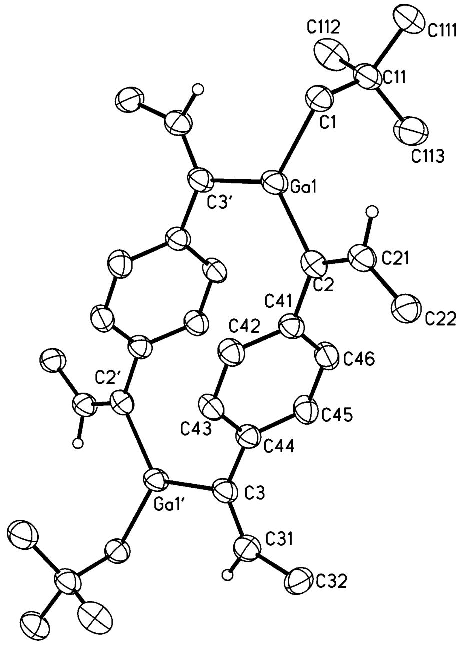

Figure 2. Molecular structure of **4**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups attached to C(22) and C(32) and hydrogen atoms are omitted for clarity. Important bond lengths (Å) and angles (deg): Ga(1)−C(1) 1.994(3), Ga(1)−C(2) 1.975(4), Ga(1)−C(3)′ 1.975(4), C(2)−C(21) 1.345(5), C(2)−C(41) 1.493(5), C(3)−C(31) 1.339(5), C(3)−C(44) 1.492(5), C(1)−Ga(1)−C(2) 117.1(2), C(1)−Ga(1)−C(3)′ 119.1(2), C(2)−Ga(1)−C(3)′ 123.7(2), C(21)−C(2)−C(41) 125.4(3), C(31)−C(3)−C(44) 125.4(4); C(3)′ was generated by $-x+0.5$, $-y+0.5$, $-z+0.5$.

The molecules of the cyclophane type compound **4** are located on crystallographic centers of symmetry. Its structural parameters are similar to those of the corresponding [3,3,3]-cyclo-

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(9) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 19.

phane, which has three bridging neopentylgallium groups and was published by our group only recently.[4] The Ga−C bond lengths differ slightly. Expectedly, the shorter ones were detected for those Ga−C bonds that include the sp^2-carbon atoms of the C═C double bonds (1.975 compared to 1.994 Å). Probably owing to some strain in the cage, the larger C−Ga−C angles occur in the cyclophane skeleton [C(2)−Ga(1)−C(3′) 123.7° compared to 118.1° on average for the remaining two angles]. An almost ideally planar surrounding of the gallium atoms can be derived from the sum of the C−Ga−C angles of 359.9°. The C═C double bonds have the usual lengths of 1.342 Å on average.[9] As forced by the molecular arrangement, the planes defined by the alkenyl groups are almost perpendicular to the planes of the aromatic rings, and the angles between their normals are 76.4° [Ga(1)] and 80.0° [Ga(1′)]. The phenylene rings are ideally coplanar; however, owing to the particular angles between the molecular planes as discussed before, they are slightly shifted with respect to each other. The distances between the carbon atoms of both aromatic rings are in a normal range of van der Waals interactions (3.41 to 3.52 Å).[10]

Experimental Section

General Procedures. All procedures were carried out under purified argon. *n*-Hexane was dried over $LiAlH_4$; toluene over Na/benzophenone. Dineopentylgallium hydride and diethylgallium hydride were obtained according to literature procedures.[6]

Syntheses of 1,4-Bis(3,3-dimethyl-1-butynyl)benzene. The synthesis of this bisalkyne has been reported before.[11] We employed a simpler coupling reaction, which followed a well-known general procedure.[12] 3,3-Dimethyl-1-butyne (6.99 g, 0.085 mol) was added dropwise to a solution of 1,4-dibromebenzene (10.05 g, 0.043 mol), copper(I) iodide (25 mg, 0.13 mmol), and dichlorobis(triphenylphosphino)palladium(II) (0.200 g, 0.29 mmol) in 300 mL of triethylamine. The mixture was stirred at 70 °C for 7 h. The precipitate was filtered off and washed with *n*-pentane. The solvents were removed in a vacuum. The residue was dissolved in *n*-pentane and filtered through a column of alumina. The purified solution was concentrated and cooled to −30 °C to obtain colorless crystals of the product. Yield: 5.08 g (50%). Mp (argon, sealed capillary): 154 °C. ^1H NMR (C_6D_6, 200 MHz): δ 7.25 (4 H, s, phenyl), 1.23 (18 H, s, CMe_3). ^{13}C NMR (C_6D_6, 200 MHz): δ 131.8 (C−H of phenyl), 123.7 (*ipso*-C of phenyl), 99.9 and 79.8 (C≡C), 31.0 (Me), 28.1 ($\mathit{C}Me_3$). IR (paraffin, CsBr plates, cm^{-1}): 2236 m ν(C≡C). MS (EI, 70 eV): *m*/*z* (%) 238 (M^+, 92), 223 ($M^+ - Me$, 100).

Synthesis of 3. A solution of freshly sublimed 1,4-bis(3,3-dimethyl-1-butynyl)benzene (0.800 g, 3.36 mmol) in 30 mL of *n*-hexane was treated with diethylgallium hydride (0.898 g, 6.98 mmol) at room temperature. The mixture was heated at reflux for 24 h. After cooling to room temperature the yellow solution was concentrated and cooled to +8 °C to obtain a relatively impure precipitate of compound **3**. Repeated recrystallization from *n*-hexane afforded colorless crystals of **3**. Owing to the instability of **3** in a vacuum, the solid material was evacuated to a minimum pressure of 5×10^{-2} Torr for a short period only. Thus, solid **3** includes *n*-hexane in different concentrations. The characterization was done with this substance containing 0.5 to 2 solvent molecules per formula unit of **3**. Yield: 0.912 g (47% based on one hexane molecule per formula unit). Mp (argon, sealed capillary): 52 °C; owing to the easily changing concentration of *n*-hexane, elemental analysis was not conducted. ^1H NMR (C_6D_6, 400 MHz): δ 6.78 (4 H, s, phenyl), 6.11 (2 H, s, C═C−H), 1.16 (12 H, t, $^3J_{H\cdots H}$ = 8 Hz, CH_3 of ethyl), 1.08 (18 H, s, CMe_3), 0.54 (8 H, q, $^3J_{H\cdots H}$ = 8 Hz, CH_2 of ethyl); resonances of *n*-hexane are ignored. ^{13}C NMR (C_6D_6, 200 MHz): δ 153.9 (both resonances of the C═C double bond coincide), 142.5 (*ipso*-C of phenyl), 126.5 (C−H of phenyl), 37.1 ($\mathit{C}Me_3$), 31.7 ($C\mathit{Me}_3$), 10.0 (CH_3 of ethyl), 8.6 ($GaCH_2$); resonances of *n*-hexane are ignored. IR (CsBr plates, paraffin, cm^{-1}): 1678 w, 1652 w, 1602 m, 1558 w phenyl, ν(C═C); 1463 vs, 1377 s (paraffin); 1363 s δ(CH); 1299 w, 1276 w δ(CH_3); 1231 w, 1202 w, 1164 w, 1100 m, 1058 m, 1034 sh, 963 w, 939 w, 895 w, 863 w ν(CC); 722 m (paraffin); 653 m phenyl; 562 m, 506 w, 462 w ν(GaC), δ(C_3C). MS (EI, 70 eV): *m*/*z* (%) 649 (cyclophane type molecule minus ethyl, 1.6), 551 (cyclophane type molecule minus $GaEt_2$, 3.3), 339 and 341 ($M^+ - GaEt_2 -$ ethene, 72 and 46), 127 and 129 ($GaEt_2$, 100 and 68).

Table 1. Crystal Data, Data Collection Parameters, and Structure Refinement Details for Compounds 3 and 4

	3	4·toluene
formula	$C_{26}H_{44}Ga_2$	$C_{52}H_{70}Ga_2$
cryst syst	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)[14]	*I*2/*a* (No. 15)[14]
Z	8	4
temp, K	193(2)	193(2)
D_{calcd}, g/cm^3	1.226	1.102
a, Å	27.869(3)	16.753(1)
b, Å	11.2663(7)	14.144(1)
c, Å	18.501(2)	21.247(2)
α, deg	90	90
β, deg	112.30(1)	92.495(6)
γ, deg	90	90
V, 10^{-30} m^3	5374.8(8)	5029.8(7)
μ, mm^{-1}	2.013	1.101
cryst dimens, mm	0.21 × 0.21 × 0.09	0.24 × 0.18 × 0.06
radiation	Mo Kα; graphite monochromator	
θ range, deg	1.97−26.03	1.73−26.11
index ranges	$-34 \leq h \leq 34$ $-13 \leq k \leq 13$ $-22 \leq l \leq 22$	$-20 \leq h \leq 20$ $-17 \leq k \leq 17$ $-23 \leq l \leq 26$
no. of obsd reflns	3499	3108
no. of unique reflns	5240 [R_{int} = 0.0505]	4982 [R_{int} = 0.0658]
no. of params	263	238
R1 (reflns $I > 2\sigma(I)$)	0.0356	0.0512
wR2 (all data)	0.0829	0.1253
max./min. residual electron density, 10^{30} e/m^3	0.715/−0.638	0.724/−0.331

Synthesis of 4. A solution of dineopentylgallium hydride (0.659 g, 3.10 mmol) in 20 mL of *n*-hexane was added to a solution of the bisalkyne 1,4-$(Me_3CC{\equiv}C)_2C_6H_4$ (0.378 g, 1.59 mmol) in 20 mL of the same solvent. The mixture was heated at reflux for 14 h. After cooling to room temperature the solvent was removed in a vacuum. The residue was evacuated (<10^{-2} Torr) at 50 °C for 3 h to remove the trineopentylgallium byproduct (0.15 g, 0.531 mmol, 34%) and was subsequently recrystallized from toluene (20/−15 °C) to yield colorless crystals of **4**. The mother liquor remaining after isolation of **4** still contained considerable quantities of trineopentylgallium, which thus could not be completely removed from the crude product by distillation. Yield: 0.38 g (**4**; 63%). Mp (argon, sealed capillary): 146 °C. Anal. Calcd for **4** [$C_{46}H_{70}Ga_2$] (762.5): C, 72.46; H, 9.25; Ga, 18.29. Found: C, 72.6; H, 9.35; Ga, 18.05. ^1H NMR (C_6D_6, 600 MHz): δ 6.55 (8 H, s, phenyl), 6.20 (4 H, s, C═C−H), 1.27 (18 H, s, CMe_3 of neopentyl), 1.15 (4 H, s, Ga−CH_2), 1.05 (36 H, s, CMe_3 attached to the C═C double bond). ^{13}C NMR (C_6D_6, 125.8 MHz): δ 156.1 (Ga−C═*C*−H), 155.2 (*ipso*-C of phenyl), 142.2 (Ga−*C*═C−H), 126.6 (C−H of phenyl), 37.1 ($\mathit{C}Me_3$ attached to C═C double bond), 35.3 ($C\mathit{Me}_3$ of neopentyl), 32.3 ($\mathit{C}Me_3$ of neopentyl), 31.5 ($C\mathit{Me}_3$ attached to C═C double bond), 28.1 ($GaCH_2$). IR (CsBr plates, paraffin, cm^{-1}): 1646 w, 1605 m, 1572 m, 1497 m phenyl, ν(C═C); 1464 vs (paraffin); 1396 m δ(CH_3); 1377 s (paraffin); 1359 s, 1251 w δ(CH_3); 1229 m, 1201 s, 1185 m, 1163 m δ(CH); 1120 w, 1098 m, 1040 w, 1018 m, 1013 w, 947 w, 917 m, 890 w, 818 m ν(CC);

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759 w, 740 w, 721 s (phenyl, paraffin); 607 w, 580 w, 532 s, 453 m ν(GaC), δ(C_3C). MS (EI, 70 ev) (%): 760 (1.3), 762 (2) M^+; 689 (7), 691 (10) $M^+ - CH_2CMe_3$; 381 (100), 383 (84) $^1/_2M^+$; two most intensive mass peaks of each group.

Crystal Structure Determination of 3 and 4. Single crystals of **3** and **4** were obtained by recrystallization from *n*-hexane (20/+8 °C) and toluene (20/−15 °C), respectively. The crystals of **4** enclose toluene molecules, which are highly disordered over a crystallographic 2-fold rotation axis. Only the carbon atoms of the phenyl rings could be detected. They were refined with isotropic displacement factors, with occupancy factors of 0.5 and with restrictions of bond lengths and angles. Hydrogen atoms were not considered. The crystallographic data were collected with a STOE IPDS diffractometer. The structure was solved by direct methods and refined with the program SHELXL-97[13] 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 **4** 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-286806 (**3**) and -286807 (**4**).

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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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