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Hydrogallation of Alkynes: Syntheses of Carbon−Gallium Cages Possessing Heteroadamantane Structures

Werner Uhl,* Lars Cuypers, Bernhard Neumüller, and Frank Weller

Fachbereich Chemie der Philipps Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany

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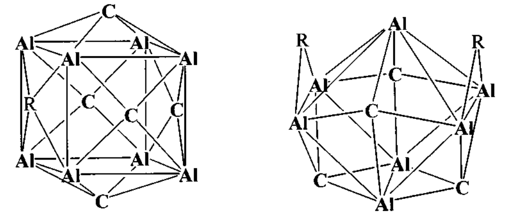
Treatment of the alkynes R′C≡CH (R′ = Me, *n*-Pr) with dialkylgallium hydrides, R_2GaH (R = Me, Et), yielded symmetrical carbon−gallium cage compounds with release of dihydrogen and subsequent addition of Ga−H to the C≡C triple bonds. Heteroadamantane-type compounds $(GaR)_6(CR')_4$ were formed in which the positions of the methylene bridges of the carbon skeleton in adamantane were occupied by coordinatively unsaturated, tricoordinate gallium atoms.

Introduction

In some recent papers we reported the syntheses of carbaalanes, a new class of compounds containing clusters of carbon and aluminum atoms.[1−4] These compounds were obtained in high yield by the reaction of dialkylaluminum hydrides with the corresponding dialkyl(alkynyl)aluminum compounds. Two completely different types of structures were determined. One has the general formula $(AlR')_8(CCH_2R'')_5R$ **1** (R = H, C≡CPh, Scheme 1) and may be derived from a cube of eight aluminum atoms, five faces of which are occupied by carbon atoms. The sixth face is bridged by a hydrogen atom.[2,3] An open cage with one vertex of the aluminum cube unoccupied was observed in one case only $[(AlEt)_7(C{=}CHPh)_2(CCH_2Ph)_3H]$.[4] The second type of carbaalanes $(AlR')_7(CCH_2R'')_4R_2$ (R = H, C≡CMe) comprises cages with four carbon and seven aluminum atoms (**2**, Scheme 1).[3,4] Their structures are quite similar to that of the *closo*-borate $[B_{11}H_{11}]^{2-}$.[5] Corresponding gallium compounds were unknown until now. We report here our first attempts to obtain such compounds by hydrogallation reactions.

Scheme 1



1 (**Al** = AlR′; **C** = CCH_2R''; R = H, CCPh)

2 (**Al** = AlR′; **C** = CCH_2R''; R = H, CCPh)

Results and Discussion

The syntheses of carbaalanes described above required the treatment of dialkyl(alkynyl)aluminum compounds with an excess of the corresponding dialkylaluminum hydride. In some recent papers were published the facile syntheses of some dialkylgallium hydrides, R_2GaH, with R = Me,[6] Et, *i*Pr, *i*Bu, neopentyl,[7] and *t*Bu,[8] which were sufficiently thermally stable to allow a study of their reactivity. In the cases of the gallium compounds, we did not isolate the dialkyl(alkynyl)gallium compounds, but generated them in situ by treatment of the hydrides with the terminal alkynes propyne and 1-pentyne. Hydrogen evolution was observed in each reaction. The postulated intermediates were consumed immediately by the excess of the hydride while the mixtures were stirred at room temperature. Pure, crystalline products were isolated only in the case of the dimethyl- and diethylgallium compounds. The corre-

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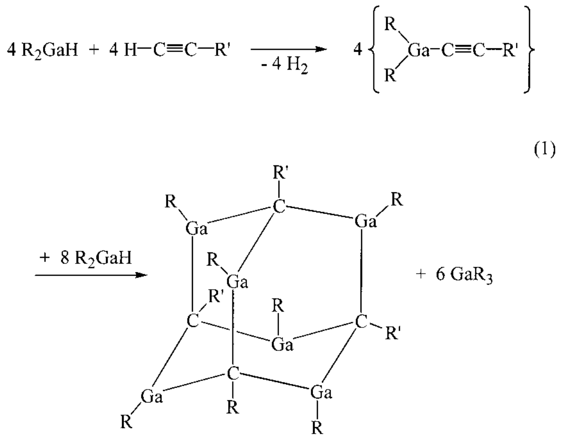
sponding trialkylgallium derivatives were detected as byproducts in all reactions by NMR spectroscopy and were removed in a vacuum at room temperature. As was shown by crystal structure determinations (see below), compounds were formed that differ from the carbaalanes and contain heteroadamantane-like skeletons $(GaR)_6(CR')_4$ with six coordinatively unsaturated gallium atoms bridging four C−R′ groups (eq 1). The different behavior may be caused by the different charge separation in organoaluminum and organogallium compounds. The aluminum atoms bear a considerable positive charge, and they are strong Lewis acids, while the nature of the carbon−gallium bonds is rather covalent with a preference of lower coordination numbers at gallium. The obvious consequence of these differences is the structure of trimethylaluminum, which in contrast to trimethylgallium forms a stable dimer via carbanionic carbon bridges.



3 (R = Et, R' = Et)
4 (R = Et, R' = Bu)
5 (R = Me, R' = Et)

The NMR spectra are in agreement with the observed molecular structures. In the ^{1}H NMR spectra of the ethylgallium compounds **3** and **4** quartets were observed for the different methylene groups in 2:3 intensity ratio. The resonances of the groups attached to gallium are shifted to a higher field ($\delta = 1.0$) compared to those that are bonded to the carbon atoms of the cages ($\delta = 2.8$ on average). An almost identical chemical shift ($\delta = 2.7$) was observed for the methylene protons of the methyl compound **5**, while the methyl groups directly attached to gallium showed a resonance at higher field ($\delta = 0.18$). Similar differences were observed in the ^{13}C NMR spectra with about $\delta = 0-10$ for those carbon atoms of the substituents that are attached to gallium and 26−34 ppm for the methylene groups bonded to the carbon atoms of the cage. The cage atom signals show unusually low-field shifts of $\delta = 93-95$, which may be caused by the coordination of three electropositive, unsaturated gallium atoms and by low-lying excited states. Similar observations were reported for the analogous hexabora adamantanes ($\delta \approx 70$), which are discussed in more detail below. Raman spectra of **3**−**5** revealed very strong emissions at 195 cm^{-1} for both ethyl derivatives and 217 cm^{-1} for the methylgallium compound **5**, which may be assigned to the symmetric breathing mode of the adamantane cage. Further emissions in the range of Ga−C stretching vibrations were detected between 275 and 555 cm^{-1}.

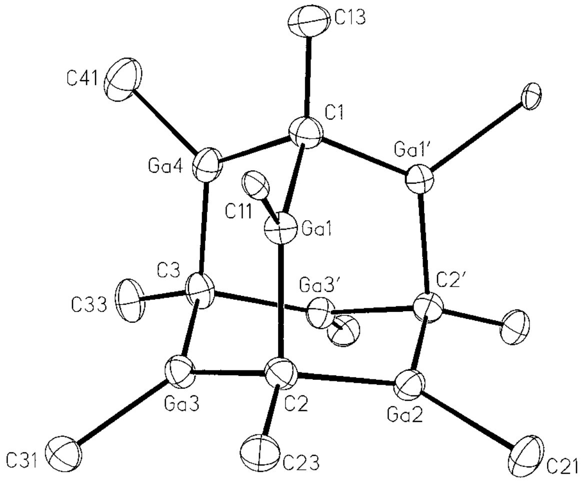


Figure 1. Molecular structure of **3**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups are omitted for clarity. Important bond lengths (Å) and angles (deg): C(1)−Ga(1) 1.965(4), C(1)−Ga(4) 1.992(7), C(2)−Ga(1) 1.980(4), C(2)−Ga(2) 1.968(4), C(2)−Ga(3) 1.981(4), C(3)−Ga(3) 198.1(4), C(3)−Ga(4) 1.989(7), Ga(1)−C(11) 2.067(4), Ga(2)−C(21) 1.981(7), Ga(3)−C(31) 1.984(4), Ga(4)−C(41) 1.976(8), C(1)−Ga(1)−C(2) 120.9(2), C(2)−Ga(2)−C(2′) 118.7(3), C(2)−Ga(3)−C(3) 118.9(2), C(1)−Ga(4)−C(3) 118.2(3), Ga(1)−C(1)−Ga(4) 102.7(2), Ga(1)−C(1)−Ga(1′) 105.0(3), Ga(1)−C(2)−Ga(2) 101.7(2), Ga(2)−C(2)−Ga(3) 109.4(2), Ga(1)−C(2)−Ga(3) 100.7(2), Ga(3)−C(3)−Ga(3′) 106.6(3), Ga(3)−C(3)−Ga(4) 103.5(2); Ga(1′), Ga(3′), and C(2′) generated by x, $-y+0.5$, z.

The molecular structures of compounds **3** and **4** were established by two crystal structure determinations (Figures 1 and 2). They contain heteroadamantane cages comprising four carbon and six gallium atoms with carbon in μ_3-bridging positions. The carbon atoms are in a tetrahedral arrangement, while the gallium atoms span a distorted octahedron. All gallium atoms are coordinatively unsaturated, and this results in highly Lewis acidic molecular centers. In contrast to the carbaalanes,[1−4] which, owing to electronic delocalization, have long Al−C distances in their clusters, the Ga−C distances of the gallium−carbon adamantanes (1.965(4)−1.999(4) Å) do not show a significant dependence on the terminal or inner-cage arrangement. Exceptions are a few terminal Ga−C bonds which are strongly elongated (2.067(4) Å, Ga(1)−C(11) and Ga(1′)−C(11′) in compound **3**; 2.060(7) Å, Ga(3)−C(31) in **4**). They seem to be influenced by some disorder, which, however, could not be resolved satisfactorily in both cases. The intramolecular Ga−Ga contacts are between 3.039 and 3.223 Å, smaller than twice the van der Waals radius (3.8 Å[9]), but much longer than Ga−Ga distances in neutral clusters or than the bond lengths of Ga−Ga single bonds (<2.7 Å[10]).

Carbon−element heteroadamantanes similar to compounds **3**−**5** with elements of the third main group in all μ_2-bridging positions have been completely charac-

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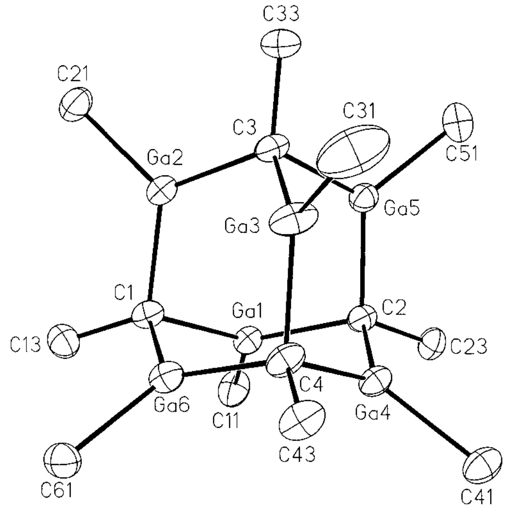

Figure 2. Molecular structure of **4**. The thermal ellipsoids are drawn at the 40% probability level. Methyl and butyl groups are omitted for clarity. Important bond lengths (Å) and angles (deg): Ga(1)−C(1) 1.976(4), Ga(1)−C(2) 1.978(4), Ga(2)−C(1) 1.981(4), Ga(2)−C(3) 1.965(4), Ga(3)−C(3) 1.970(4), Ga(3)−C(4) 1.987(4), Ga(4)−C(2) 1.980(4), Ga(4)−C(4) 1.972(4), Ga(5)−C(2) 1.972(4), Ga(5)−C(3) 1.991(4), Ga(6)−C(1) 199.4(4), Ga(6)−C(4) 1.974(4), Ga(1)−C(11) 1.999(4), Ga(2)−C(21) 1.995(4), Ga(3)−C(31) 2.060(7), Ga(4)−C(41) 1.993(4), Ga(5)−C(51) 1.990(5), Ga(6)−C(61) 1.980(5), C−Ga−C (cage) 119.6 (av), Ga−C−Ga 103.9 (av).

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

	3	4
formula	$C_{24}H_{50}Ga_6$	$C_{32}H_{66}Ga_6$
cryst syst	orthorhombic	tetragonal
space group	*Pnma* (No. 62)[15]	$P4_3$ (No. 78)[15]
Z	4	4
temp, K	193(2)	193(2)
D_{calcd}, g/cm^3	1.706	1.568
a, Å	19.342(2)	16.1617(8)
b, Å	13.2690(10)	16.1617(8)
c, Å	11.4840(10)	14.0998(8)
V, 10^{-30} m^3	2947.4(5)	3682.9(3)
μ, mm^{-1}	5.416	4.345
cryst dimens, mm	0.2 × 0.1 × 0.04	0.2 × 0.2 × 0.1
radiation	Mo Kα; graphite-monochromator	
2θ range, deg	$4.1 \le 2\theta \le 49.7$	$3.5 \le 2\theta \le 49.7$
index ranges	$-21 \le h \le 22$	$-19 \le h \le 19$
	$-15 \le k \le 15$	$-19 \le k \le 19$
	$-13 \le l \le 12$	$-16 \le l \le 16$
no. of unique rflns	2670	6347
	[$R_{int} = 0.0557$]	[$R_{int} = 0.0513$]
no. of params	161	354
R1 (reflns $I > 2\sigma(I)$)	0.0301 (2003)	0.0261 (5771)
wR2 (all data)	0.0579	0.0541
max./min. residual electron density, 10^{30} e/m^3	0.690/−0.413	0.652/−0.502

terized only with the lightest element, boron. They were obtained by different routes: by thermolysis of trimethylborane at 450 °C,[11] by treatment of a 1,5-dicarba-*closo*-pentaborane(5) with potassium and iodine,[12] or by thermolysis of organoboron halides such as $CH(BCl_2)_3$ and Me_2BBr.[13] Remarkably, a rearrangement was observed on heating of one of these compounds, $[(BEt)_6(CMe)_4]$, to 160 °C.[12] A *nido*-carbaborane was formed which, in contrast to the adamantane starting compound, had direct B−B and C−C bonding interactions and which was found to possess a dynamic B_6C_4 molecular center. A similar rearrangement was not observed with the gallium compounds **3** and **4** up to now. Elemental gallium precipitated upon heating of **3** and **4** without a solvent to 200 or 220 °C, respectively, but in all cases the NMR spectra showed the resonances of the starting components almost exclusively. New, unknown compounds were formed in trace amounts, as indicated by their very low NMR intensities; they could not be enriched by recrystallization.

Experimental Section

All procedures were carried out under purified argon. *n*-Pentane was dried over $LiAlH_4$; toluene over Na/benzophenone. Dimethylgallium hydride and diethylgallium hydride were obtained according to literature procedures.[7] Gaseous propyne (Aldrich) was dried by passing it through P_4O_{10}, and 1-pentyne (ACROS Organics) was employed without further purification.

Synthesis of Decaethyl-2,4,6,8,9,10-hexagallaadamantane $(GaEt)_6(CEt)_4$, 3. Diethylgallium hydride (3.01 g, 0.023 mol) was frozen with liquid nitrogen. Propyne (0.234 g, 0.0058 mol) was distilled onto the solid in a vacuum. The mixture was warmed to −30 °C and stirred for 1 h. Stirring was continued for 2.5 h after warming to room temperature. Gas evolution was observed. All volatile components were removed in a vacuum (10^{-3} Torr). The yellow residue was recrystallized from *n*-pentane (20/−30 °C). Yield: 0.931 g (85%), yellow crystals. Mp (argon, sealed capillary): 95 °C. Anal. Calcd for $C_{24}H_{50}Ga_6$ (757.0): C, 38.1; H, 6.7. Anal. Found: C, 37.8; H, 6.7. ^{1}H NMR (C_6D_6, 200 MHz): δ 2.78 (8 H, q, $^3J_{H\cdots H} = 7.3$ Hz, $Ga_3C{-}CH_2$), 1.25 (12 H, t, $^3J_{H\cdots H} = 7.3$ Hz, $Ga_3C{-}C{-}CH_3$), 1.22 (18 H, t, $^3J_{H\cdots H} = 7.8$ Hz, $Ga{-}C{-}CH_3$), 0.97 (12 H, q, $^3J_{H\cdots H} = 7.8$ Hz, $Ga{-}CH_2$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 94.8 ($Ga_3\mathit{C}$), 26.6 ($Ga_3C{-}\mathit{C}$), 24.1 ($Ga_3C{-}C{-}\mathit{C}H_3$), 10.5 ($Ga\mathit{C}H_2$), 9.2 ($GaC{-}\mathit{C}H_3$). IR (CsBr plates, paraffin, cm^{-1}): 1302 m δ(CH); 1084 w, 1067 w, 1043 m, 1000 w, 981 w, 966 w, 931 w, 891 m ν(CC), δ,ρ(CH); 722 m, 664 vs, 650 vs, 633 vs δ(CC); 519 s, 431 s ν(GaC). Raman (powder, 633 nm, cm^{-1}): 1449 w, 1419 vw, 1372 vw, 1308 vw, 1268 vw δ(CH); 1188 m, 1170 w, 1074 vw, 1047 w, 958 vw, 906 vw, 891 vw ν(CC), δ,ρ(CH); 534 m, 518 m, 440 m, 427 w, 275 m, 195 vs ν,δ(GaC). UV/vis (*n*-hexane; λ_{max}, nm (log ϵ)): 260 (3.8), 280 (3.9).

Synthesis of 2,4,6,8,9,10-Hexaethyl-1,3,5,7-tetrabutyl-2,4,6,8,9,10-hexagallaadamantane $(GaEt)_6(CBu)_4$, 4. Diethylgallium hydride (1.82 g, 0.014 mol) was treated with 0.24 g (0.0035 mol) of 1-pentyne without a solvent at room temperature. The mixture was stirred at that temperature for 4 h. Gas evolution was observed, and a solid precipitated. All volatile components were removed in a vacuum (10^{-3} Torr). The yellowish residue was recrystallized from *n*-pentane (20/−30 °C). Yield: 0.603 g (79%), colorless crystals. Mp (argon, sealed capillary): 114 °C. Anal. Calcd for $C_{32}H_{66}Ga_6$ (869.2): C, 44.2; H, 7.7. Anal. Found: C, 43.8; H, 7.6. Molar mass (in benzene by cryoscopy). Found: 842 g/mol. ^{1}H NMR (C_6D_6, 300 MHz): δ 2.82 (8 H, pseudo-t, $Ga_3C{-}CH_2$), 1.54 (16 H, m, br, $Ga_3C{-}C{-}CH_2CH_2$), 1.26 (18 H, t, $^3J_{H\cdots H} = 7.9$ Hz, $Ga{-}C{-}CH_3$), 1.04 (12 H, t, $^3J_{H\cdots H} = 7.4$ Hz, $Ga_3C{-}C_3{-}CH_3$), 1.00 (12 H, q, $^3J_{H\cdots H} = 7.9$ Hz, $Ga{-}CH_2$, partially covered by the preceding resonance). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 93.0 ($Ga_3\mathit{C}$), 43.8 ($Ga_3C{-}CH_2{-}\mathit{C}_2H_4{-}Me$), 34.3 ($Ga_3C{-}\mathit{C}H_2{-}C_2H_4{-}$

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Me), 24.4 ($Ga_3C-CH_2-C_2H_4-Me$), 15.0 ($Ga-CH_2-CH_3$), 10.9 ($Ga-CH_2-CH_3$), 9.8 ($Ga_3C-CH_2-C_2H_4-Me$). IR (CsBr plates, paraffin, cm^{-1}): 1337 w, 1297 w, 1247 w, 1231 w δ(CH); 1187 vw, 1106 w, 1064 w, 1020 m, 972 m, 950 s, 897 vw, 874 vw ν(CC), δ,ρ(CH); 793 vw, 721 w, 649 vs δ(CC); 521 s, 498 s, 393 w ν(GaC). Raman (powder, 633 nm, cm^{-1}): 2960 w, 2932 m, 2899 m, 2870 m, 2858 m, 2824 m ν(CH); 1457 w, 1440 w, 1417 w, 1300 vw δ(CH); 1191 s, 1108 vw, 1069 w, 1032 w, 985 w, 964 vw, 939 vw, 899 vw, 876 w ν(CC), δ,ρ(CH); 534 sh, 512 vs, 398 vw, 196 vs ν,δ(GaC).

Synthesis of 2,4,6,8,9,10-Hexamethyl-1,3,5,7-tetraethyl-2,4,6,8,9,10-hexagallaadamantane $(GaMe)_6(CEt)_4$, 5. Dimethylgallium hydride (0.836 g, 0.0083 mol) was frozen with liquid nitrogen. Propyne (0.083 g, 0.0021 mol) was distilled onto the solid in a vacuum. The mixture was allowed to warm to −30 °C and stirred for 1 h. After warming to room temperature, stirring was continued for 2.5 h. Gas evolution occurred. All volatile components were removed in a vacuum, and the colorless residue was recrystallized from toluene (20/−30 °C). Yield: 0.262 g (74%), colorless crystals. Dec pt (argon, sealed capillary): >250 °C. Anal. Calcd for $C_{18}H_{38}Ga_6$ (672.8): C, 32.1; H, 5.7. Anal. Found: C, 31.6; H, 5.5. ^{1}H NMR (C_6D_6, 300 MHz): δ 2.72 (8 H, q, $^3J_{H\cdots H} = 7.4$ Hz, Ga_3C-CH_2), 1.24 (12 H, t, $^3J_{H\cdots H} = 7.4$ Hz, $Ga_3C-C-CH_3$), 0.18 (18 H, s, $Ga-CH_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 94.4 (Ga_3C), 26.6 (Ga_3C-CH_2), 22.8 ($Ga_3C-C-CH_3$), 0.0 ($Ga-CH_3$). IR (CsBr plates, paraffin, cm^{-1}): 1307 s δ(CH); 1187 m, 1152 s, 1083 m, 1068 m, 1044 s, 892 vs ν(CC), δ,ρ(CH); 793 w, 733 s, 683 vs δ(CC); 608 vs, 538 vs, 432 vs ν(GaC). Raman (powder, 633 nm, cm^{-1}): 2958 w, 2926 w, 2896 w, 2865 m, 2833 w ν(CH); 1448 w δ(CH); 1190 m, 1167 m, 1057 w, 1049 w, 905 w, 895 w ν(CC), δ,ρ(CH); 690 vw, 654 vw, 612 vw δ(CC); 555 s, 538 s, 442 m, 430 sh, 310 vw, 286 m, 217 vs, 148 w ν,δ(GaC).

Crystal Structure Determinations of 3 and 4. Single crystals of **3** and **4** were obtained by cooling saturated solutions in toluene (**3**) or *n*-pentane (**4**) to −30 °C. The crystallographic data of both compounds were collected with a STOE image plate diffractometer. The structure was solved by direct methods and refined with the program SHELXL-97[14] by a full-matrix least-squares method based on F^2. The molecules of **4** are located on a crystallographic mirror plane with the atoms Ga2, Ga4, C1, and C3 on special positions. Crystal data, data collection parameters, and structure refinement details are given in Table 1. Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-177349 (**3**) and -177350 (**4**).

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.

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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