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New Insight into Hydrogallation Reactions: Facile Synthesis of a Gallium-Bridged [3,3,3]-Cyclophane

Werner Uhl,* Frank Breher, Sima Haddadpour, and Friedhelm Rogel

Institut für Anorganische und Analytische Chemie der Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany

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Treatment of 1,3,5-tris(3,3-dimethyl-1-butynyl)benzene, $C_6H_3(C\equiv C-CMe_3)_3$, with di(neopentyl)gallium hydride, $HGa(CH_2CMe_3)_2$, resulted in the addition of one Ga−H bond to each $C\equiv C$ triple bond (hydrogallation). Spontaneous condensation by the release of tri(neopentyl)gallium yielded a [3,3,3]-cyclophane derivative (**1**) with three tricoordinated Ga atoms in bridging positions.

Introduction

The addition of Ga−H bonds to C=C double or $C\equiv C$ triple bonds (hydrogallation) is a powerful method for the generation of new alkylgallium compounds. Nevertheless, it has been employed only to a relatively limited extent, in particular because of the limited accessibility of suitable organogallium hydrides. Dichloro- or dibromogallium compounds were obtained by several reactions of $HGaX_2$ (X = Cl, Br) with different alkenes or alkynes.[1] The monochlorogallium derivative $ClGaH_2$ was reported to react with C_2H_4 to yield a mixture of the corresponding mono- and diethyl compounds,[2] while diethylgallium hydride seems to be the main product of the reaction of the trihydride GaH_3 with ethene.[3] The hydrogallation of heteronuclear multiple bonds was investigated by several groups. While 1,4-diazabutadiene yielded ethylenediamine derivatives upon treatment with Lewis base adducts of GaH_3,[4] at least partial cleavage of the inner N−N bonds was observed in the corresponding reaction with tetramethyl-2,3-diazabutadiene.[5] The intermediate formation of diethylgallium hydride was postulated to occur upon reaction of triethylgallium with nitriles,[6] which yielded the characteristic products of the addition of Ga−H bonds to the $C\equiv N$ triple bonds. The hydrogallation of heteronuclear double or triple bonds (C=O, $C\equiv N$) by treatment with $HGaCl_2$ was also reported.[1c,d]

In some recent investigations we found an easy access to various dialkylgallium hydrides R_2GaH (R = Me, Et, *n*-Bu, CH_2*t*Bu, *t*Bu).[7,8] They proved to be sufficiently stable to be isolated in reasonable yield and to be employed in secondary reactions. Their stability increases with the increasing bulkiness of their substituents. First experiments on their chemical reactivity gave some unexpected results. Similar to hydroalumination reactions reported earlier,[9] the treatment of dialkylgallium alkynides with dialkylgallium hydrides resulted in condensation by the release of the corresponding trialkylgallium derivatives. Heteroadamantane type compounds (Scheme 1) were isolated that contain six coordinatively unsaturated gallium atoms bridging four carbon atoms and possess localized Ga−C bonds.[10] Condensation may also occur upon addition of dialkylaluminum or dialkylgallium hydrides to unsaturated organic compounds. Therefore, we started with systematic investigations into the true course of these reactions. The hydroalumination of alkynes of the type $R-C\equiv C-R'$ was often supposed in the literature to yield the corresponding alkenylaluminum compounds $R_2Al-(R)C=C(H)-R'$ bearing a dialkylaluminum group attached to one carbon atom of the C=C double bond.[11] In some preliminary investigations we observed, however, that the corresponding trialkylaluminum or -gallium derivatives were formed as main products of these reactions and that the simple addition products generally do not occur at all.[12] The course of these reactions is not completely clarified now, in particular because insoluble byproducts were obtained. Here, we report the

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[12] We observed exceptions in some hydroalumination reactions of $(Me_3C)_2AlH$ with alkynes bearing $SiMe_3$ groups: (a) Uhl, W.; Matar, M. *J. Organomet. Chem.* **2002**, *664*, 110. (b) Uhl, W.; Breher, F. *J. Organomet. Chem.* **2000**, *608*, 54.

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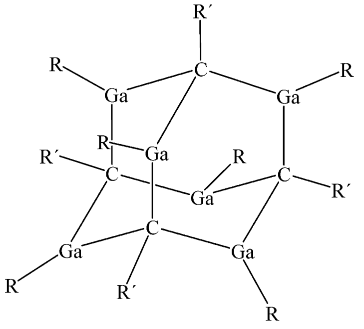
Scheme 1

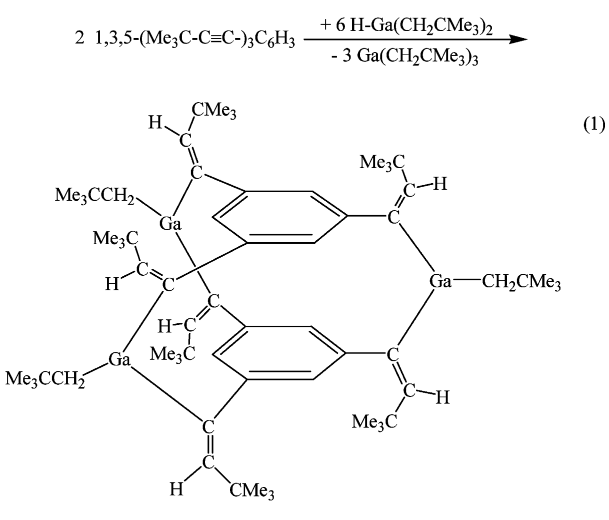


R = Et; R′ = Et
R = Et; R′ = Bu
R = Me R′ = Et

addition of dineopentylgallium hydride to a phenyl-centered trisalkyne, 1,3,5-tris(3,3-dimethyl-1-butynyl)-benzene, which for the first time gave a strictly reproducible result and a clean high-yield reaction.

Results and Discussion

Usually the addition of Al−H bonds to C≡C bonds of organic compounds (hydroalumination reactions) proceeds in reasonable rates even at room temperature.[12] In contrast, the addition of dineopentylgallium hydride to the trisalkyne 1,3,5-($Me_3CC{\equiv}C)_3C_6H_3$ at room temperature did not result in any reaction under similar conditions over several days. Only heating of the mixture in *n*-hexane under reflux for 24 h resulted in the complete consumption of the starting compounds (eq 1). As shown by ^{1}H NMR spectroscopy, trineopentylgallium was formed as one of the major products. It could be removed for the most part by thorough evacuation of the residue that remains after evaporation of the solvent. The product **1**·0.84C_5H_{10} was finally obtained as colorless crystals in 80% yield by recrystallization of the residue from cyclopentane. The NMR spectra are in complete agreement with the molecular structure of **1**, schematically shown in eq 1. All alkynyl groups of the trisalkyne had been hydrogallated. Subsequent condensation by the release of the corresponding trialkylgallium compound gave a cyclophane type molecule with three coordinatively unsaturated gallium atoms in bridging positions between both aromatic rings. Two resonances of equal intensity were observed for the alkenyl and phenyl protons at δ = 6.33 and 6.23, the latter being assigned to the hydrogen atoms attached to the olefinic C=C double bond. Two resonances in the expected integration ratio of 1:2 were detected for different *tert*-butyl groups, which belong to the neopentyl groups attached to gallium and the hydrocarbon backbone of the molecule, respectively. The resonance of the phenyl carbon atoms attached to hydrogen (δ = 121.7) and that of the carbon atoms of the C=C double bonds geminally bonded to gallium and the *ipso*-atoms of the phenyl rings (δ = 145.1) are in the expected ranges. Low-field shifts were detected for those carbon atoms that are in the β-position to the gallium atoms (δ = 155.6 and 156.0).



$$2\ 1,3,5\text{-}(Me_3C\text{-}C{\equiv}C\text{-})_3C_6H_3 \xrightarrow[-\ 3\ Ga(CH_2CMe_3)_3]{+\ 6\ H\text{-}Ga(CH_2CMe_3)_2}$$

(1)

1

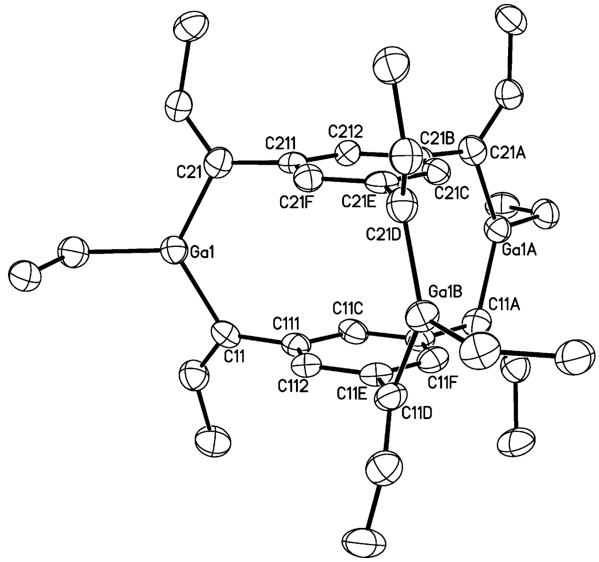


Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at the 40% probability level. Methyl groups and hydrogen atoms are omitted for clarity. Important bond lengths (Å) and angles (deg): Ga(1)−C(11) 1.964(6), Ga(1)−C(21) 1.969(7), Ga(1)−C(31) 1.982(6), C(11)−C(12) 1.342(9), C(11)−C(111) 1.489(9), C(21)−C(22) 1.341(8), C(21)−C(211) 1.502(8), C(11)−Ga(1)−C(21) 123.4(2), C(11)−Ga(1)−C(31) 117.2(3), C(21)−Ga(1)−C(31) 119.5(3), Ga(1)−C(11)−C(111) 119.0(4), Ga(1)−C(21)−C(211) 120.4(4), Ga(1)−C(11)−C(12) 114.7(5), Ga(1)−C(21)−C(22) 113.5(5), C(12)−C(11)−C(111) 126.2(6), C(22)−C(21)−C(211) 126.0(6).

The molecular structure of compound **1** is depicted in Figure 1. Three gallium atoms bridge two 1,3,5-tris(alkenyl)phenyl groups via the α-carbon atoms attached to the phenyl rings. Thus, a cyclophane type structure results ([3,3,3]-cyclophane). The gallium atoms are bonded to three carbon atoms in a trigonal planar coordination sphere (sum of the angles 360°). In all cases the configuration at the C=C double bonds corresponds to a *cis*-addition of the Ga−H bond to the alkyne groups. The Ga−C bond lengths differ slightly; the shorter ones were observed for the inner cage bonds Ga−C11 and Ga−C21 (1.967 compared to 1.982 Å to the terminal neopentyl group). They may reflect the different hybridization of the respective carbon atoms. The C−C distances of C11 and C21 to the *ipso*-carbon atoms of the phenyl groups (1.496 Å), those within the phenyl rings (1.393 Å on average), and those of the C=C double bonds (1.342 Å) are in excellent agreement with standard values observed for organic compounds.[13] Relatively large angles occur at the alkenyl groups ($Me_3C-C=C$ 132.8° and C(*ipso*)−C=C including the *ipso*-C atoms of the phenyl rings 126.1°), which may be caused by steric interactions between the *tert*-butyl groups and the aromatic ring systems. In contrast, the angle C(11)−Ga(1)−C(21) deviates only slightly from the ideal value of 120° (123.4°). Owing to the crystallographic symmetry, both phenyl rings are ideally coplanar. They do not adopt an ideally eclipsed arrangement, but are slightly rotated with respect to each other by 4.2°. The intramolecular separation between the aromatic systems (3.593 Å) corresponds well to standard contact distances (van der Waals contacts).[14] The α-carbon atoms of the C=C double bonds deviate only 0.05−0.08 Å from the average plane of the corresponding phenyl groups. This small bending of the organic backbones of the molecules (angles between the phenyl planes and the corresponding C−C bonds 2.2° and 3.4°) is caused by the specific bonding in the cyclophane cage with a slightly insufficient correspondence of the optimum van der Waals distance between the phenyl groups and the separations determined by the Ga−C covalent bonds. Vinylgallium compounds containing the Ga−C=C group were isolated earlier.[15] However, to the best of our knowledge, hydrogallation has not been employed in these particular cases.

Experimental Section

All procedures were carried out under purified argon. Cyclopentane and *n*-hexane were dried over $LiAlH_4$. Dineopentylgallium hydride[8] was obtained by a literature procedure.

Synthesis of 1,3,5-Tris(3,3-dimethyl-1-butynyl)benzene, 1,3,5-($Me_3CC{\equiv}C)_3C_6H_3$. The trisalkyne 1,3,5-($Me_3CC{\equiv}C)_3C_6H_3$ was synthesized by employing standard methods.[16] 1,3,5-Tribromobenzene (4.73 g, 15.0 mmol) was dissolved in 250 mL of diethylamine. Copper(I) iodide (25 mg, 0.13 mmol) and dichlorobis(triphenylphosphine)palladium(II) (0.20 g, 0.29 mmol) were added at room temperature. 3,3-Dimethyl-1-butyne (4.44 g, 54.1 mmol) was added dropwise, which causes a color change from yellow to brown. The mixture was stirred at 70 °C for 7 h. A brown solid precipitated. After cooling to room temperature the solid was filtered, and the solvent was removed in a vacuum. The residue was purified by column chromatography (Al_2O_3) with *n*-pentane as eluting solvent. *n*-Pentane was removed in a vacuum, and the residue was dried at 10^{-3} Torr. Yield: 3.73 g (78%). Mp: 163 °C. Anal. Calcd for $C_{24}H_{30}$ (318.50): C, 90.51; H, 9.49. Anal. Found: C, 90.7; H, 9.3. ^1H NMR (C_6D_6, 300 MHz): δ 7.57 (3 H, s, C_6H_3), 1.19 (27 H, s, CMe_3). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 134.0 (*ipso*-C of phenyl), 125.0 (*ortho*-C of phenyl), 99.2 and 78.7 (C≡C), 30.9 (C*Me*$_3$), 28.0 (*C*Me$_3$). IR (CsBr plates, paraffin, cm^{-1}): 2393 w, 2286 w, 2225 vs ν(C≡C); 1773 w, 1758 m, 1732 w, 1679 w, 1582 vs (phenyl); 1455 vs (paraffin); 1413 vs δ(CH_3); 1365 vs (paraffin); 1266 vs, 1202 vs δ(CH_3); 1154 s, 1080 m, 1031 m, 928 s ν(CC); 873 vs νC_3C; 839 s, 721 s, 681 vs ρ(CH_3).

Table 1. Crystal Data, Data Collection Parameters, and Structure Refinement Details for Compound 1

	1·(cyclopentane)
formula	$C_{63}H_{99}Ga_3$·(cyclopentane)
cryst syst	hexagonal
space group	$R\bar{3}$(No. 148)[19]
Z	6
temp, K	193(2)
D_{calcd}, g/cm^3	1.073
a, Å	16.559(1)
b, Å	16.559(1)
c, Å	41.671(4)
α, deg	90
β, deg	90
γ, deg	120
V, 10^{-30} m^3	9895.4(1)
μ, mm^{-1}	1.248
cryst dimens, mm	0.12 × 0.10 × 0.09
radiation	Mo Kα; graphite-monochromator
θ range, deg	1.72−24.00
index ranges	$-18 \le h \le 18$ $-17 \le k \le 18$ $-43 \le l \le 47$
no. of unique reflns	3452 [$R_{int} = 0.0956$]
no. of params	268
R1 (reflns $I > 2\sigma(I)$)	0.0432 (1705)
wR2 (all data)	0.0853
max./min. residual electron density, 10^{30} e/m^3	0.325/−0.235

Synthesis of 1. A solution of dineopentylgallium hydride (0.89 g, 4.18 mmol) in 25 mL of *n*-hexane was added to a solution of the trisalkyne 1,3,5-($Me_3CC{\equiv}C)_3C_6H_3$ (0.44 g, 1.38 mmol) in 25 mL of the same solvent. The mixture was heated at reflux for 24 h. After cooling to room temperature the solvent was removed in a vacuum. The residue was evacuated (<10^{-2} Torr) for 16 h to remove most of the trineopentylgallium byproduct and was subsequently recrystallized from cyclopentane (20/−15 °C) to yield colorless crystals of **1**, which according to the integration of the ^1H NMR spectrum contained up to one molecule of the solvent per formula unit of **1**. Yield: 0.63 g (80%). Mp (argon, sealed capillary): 210 °C. Anal. Calcd for **1**·(cyclopentane)$_{0.84}$ [$C_{63}H_{99}Ga_3$·$0.84C_5H_{10}$] (1065.64 + 58.91): C, 71.77; H, 9.62; Ga, 18.60. Anal. Found: C, 71.12; H, 10.06; Ga, 18.3. ^1H NMR (C_6D_6, 500 MHz): δ 6.33 (6 H, s, phenyl), 6.23 (6 H, s, C=C-H), 1.45 (0.84 equiv of cyclopentane), 1.26 (27 H, s, CMe_3 of neopentyl), 1.18 (6 H, s, Ga-CH_2), 1.13 (54 H, s, CMe_3 attached to the C=C double bond). ^{13}C NMR (C_6D_6, 125.8 MHz): δ 156.0 (Ga-C=*C*-H), 155.6 (*ipso*-C of phenyl), 145.1 (Ga-*C*=C-H), 121.7 (C-H of phenyl), 36.8 (*C*Me$_3$ attached to C=C double bond), 35.3 (C*Me*$_3$ of neopentyl), 32.3 (*C*Me$_3$ of neopentyl), 31.9 (C*Me*$_3$ attached to C=C double bond), 28.5 ($GaCH_2$), 26.1 (cyclopentane). IR (CsBr plates, paraffin, cm^{-1}): 1587 m, 1562 m phenyl, ν(C=C); 1463 vs, 1377 s (paraffin); 1363 s δ(CH); 1307 vw, 1227 m, 1202 m δ(CH_3); 1136 vw, 1095 vw, 1039 w, 1015 w, 992 w, 939 vw, 914 w, 897 w, 882 w ν(CC); 798 vw, 723 m, 704 m (phenyl), 644 vw, 611 w, 598 w, 456 w ν(GaC).

Crystal Structure Determination of 1. Single crystals of **1** were obtained by recrystallization from cyclopentane (20/−15 °C). They contain solvent molecules strongly disordered over crystallographic $\bar{3}$ axes. We did not succeed in resolving that disorder to a reasonable model. Therefore, refinement was completed by employing the SQUEEZE program.[17] The crystallographic data were collected with a STOE image plate diffractometer. The structure was solved by direct

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methods and refined with the program SHELXL-97[18] 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 reside on crystallographic 3-fold rotation axes. Two *tert*-butyl groups (C13 and C23) were disordered. Their methyl groups were refined on split positions with site occupancy factors of 0.5.

Further details of the crystal structure determination are available from the Cambridge Crystallographic Data Center on quoting the depository number CCDC-254172 (**1**).

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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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