Synthesis and Solid-state Structures of 1,3- and 1,4-Bis(diethylgallyl)benzene

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Z. Naturforsch. **2009**, *64b,* 1375 – 1380; received September 16, 2009

Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

The compounds 1,3-bis(diethylgallyl)benzene (**3**) and 1,4- bis(diethylgallyl)benzene (**6**) were prepared by reaction of the corresponding chloromercuriobenzenes with an excess of triethylgallium by applying pressure and higher temperatures. These compounds very easily undergo redistribution reactions in solution and in the solid state. Extremely air-sensitive crystals suitable for an X-ray crystal structure analysis were obtained from triethylgallium as solvent. The structural studies revealed the presence of tetra-coordinated carbon and gallium atoms in symmetric aryl-diethylgallyl bridging units. The coordination behavior of **3** and **6** in the solid state is quite different from that of the corresponding methyl-substituted compounds.

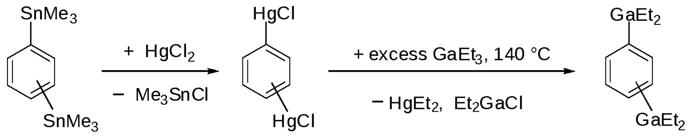
Key words: Bis(diethylgallyl)benzenes, Diethylgallyl Bridging Units, Dialkyl(aryl)gallium Compounds, Organogallium(III) Compounds

Introduction

Homoleptic alkyl- and arylgallium(III) compounds have been thoroughly investigated during the second half of the last century [1]. In this context, the synthesis and the structure in the solid state, in solution and in the gas phase of the simple alkyl and aryl gallium compounds, such as trimethylgallium, triethylgallium [2 – 4] and triphenylgallium [5 – 9], have been documented in great detail. Interestingly, heteroleptic alkyl(aryl)gallium(III) compounds containning the parent substituents (methyl, phenyl) have been described for the first time only very recently [10, 11]. This may be due to redistribution reactions, which take place very easily even at room temperature. In this process, differing amounts of trimethylgallium and of less defined condensation products are formed. The compounds (dimethylgallyl)benzene [10], 1,3- and 1,4-bis(dimethylgallyl)benzene [11], and 1,3,5-tris(dimethylgallyl)benzene [11] could be prepared only in the presence of a large excess of trimethylgallium (trimethylgallium as solvent, shift of the equilibrium). In this paper, we describe the synthesis and the solid-state structure of 1,3- (**3**) and 1,4-bis(diethylgallyl)benzene (**6**). It is shown that their coordination behavior in the solid state is quite different from that observed for the corresponding methyl-substituted compounds.

Results and Discussion

The strategy for the synthesis of the diethylgallyl-functionalized benzene derivatives **3** and **6** is shown in Eq. 1. The reaction sequence starts with the substitution of trimethylstannyl groups in the corresponding (trimethylstannyl)benzenes by chloromercurio groups, which are subsequently replaced by diethylgallyl groups.



1 (1.3)
4 (1.4)

2 (1.3)
5 (1.4)

3 (1.3)
6 (1.4)

(1)

The bis(trimethylstannyl)benzenes **1** [12] and **4** [12–15] and the di(chloromercurio)benzenes **2** [16] and **5** [17] are known from the literature. Rather drastic conditions had to be applied for the last step in the reaction sequence, the introduction of the diethylgallyl groups. The respective (chloromercurio)benzenes have to be treated with an excess of triethylgallium (using the reagent as solvent) at 100–140 °C in a pressure vessel. After cooling of the reaction mixture to room temperature and removal of the liquid components (diethylmercury, chloro(diethyl)gallium and the excess of triethylgallium), the respective diethylgallyl-functionalized benzene derivatives **3** and **6** remained as solid residues which then were recrystallized from triethylgallium as solvent to which, in the case of compound **6**, a small amount of *p*-xylene had been added. The crystalline compounds **3** and **6** are extremely sensitive towards air and moisture.

We have been unsuccessful in preparing solutions of the novel compounds in organic solvents such as hexane, toluene, diethyl ether or THF. Concomitant redistribution reactions were observed, which finally led to the formation of triethylgallium and of solid condensation products of so far unidentified composition. The degree of condensation can be judged from the amount of isolated triethylgallium and varies with respect to work-up conditions and from compound to compound. A comparable behavior is described in the literature for several dimethylgallyl-substituted benzene derivatives [10, 11]. With halogenated solvents such as dichloromethane, decomposition reactions were observed. As a result, it was not possible to investigate the physical properties of the novel compounds in solution, for example by determination of the molecular mass or by recording their NMR spectra.

A similar behavior was observed in the solid state of the novel compounds. At reduced pressure (< 10 mbar) or on heating at normal pressure, decomposition and $GaEt_3$ elimination took place. Thus, attempted melting point determinations were unsuccessful. The amount of $GaEt_3$ formed depends on the respective decomposition temperature. As yet, the exact composition of the solid decomposition products could not be elucidated.

As a consequence of the described lability of the novel compounds, it was not possible to obtain reliable elemental analyses. The observed deviations from calculated CH values may be due to partial oxidation of the crystalline material or to the presence of traces of chemisorbed triethylgallium (in case of **6** also due to the inclusion of *p*-xylene). Thus, treatment of the compounds *in vacuo* (< 10 mbar) for the elimination of volatiles, and washing procedures are not indicated. A comparable behavior has already been described for dimethylgallyl-substituted benzene derivatives [10, 11].

Table 1. Crystal structure data for **3** and **6**.

	3	**6**
Formula	$C_{14}H_{24}Ga_2$	$C_{14}H_{24}Ga_2$
M_r	331.77	331.77
Crystal size, mm^3	$0.20\times0.21\times0.24$	$0.05\times0.24\times0.30$
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Cmmm$
a, Å	8.0730(4)	6.3690(4)
b, Å	11.0940(5)	18.033(4)
c, Å	17.0940(13)	9.9060(7)
β, deg	94.966(5)	90
V, Å^3	1525.22(2)	1137.7(3)
Z	4	2
D_{calcd}, g cm^{-3}	1.45	0.97
$\mu(MoK_\alpha)$, cm^{-1}	3.5	2.4
$F(000)$, e	680	340
hkl range	$\pm11, \pm15, \pm24$	$\pm11, -23 \le k \le +21, \pm12$
Θ, deg	2.2–30.0	3.0–27.5
Refl. measured	38334	9913
Refl. unique	4456	771
R_{int}	0.0677	0.0492
Refl. with $I \ge 2\sigma(I)$	2917	741
Param. refined	149	30
$R(F)$ / $wR(F^2)^a$ [$I \ge 2\sigma(I)$]	0.0332 / 0.0623	0.0317 / 0.0809
$R(F)$ / $wR(F^2)^a$ (all refl.)	0.0705 / 0.0702	0.0335 / 0.0820
GoF $(F^2)^b$	1.025	1.135
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.622 / −0.840	0.440 / −1.142

[a] $R(F) = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [b] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

The solid-state structures of compounds **3** and **6** were determined by single crystal X-ray diffraction analysis. Suitable crystals were prepared in a glove box to avoid contact with air or moisture. Crystal structure parameters are listed in Table 1. Parts of the solid-state structures are presented in Figs. 1 (**3**) and 2 (**6**), selected bond lengths and bond angles are incorporated in the Figure captions. Compounds **3** and **6** crystallize in the form of one-dimensional strands as coordination polymers with the benzene carbon atoms C1 and C3 (C4) and the gallium atoms in bridging positions and with a coordination number of 4 of these atoms. A zick-zack arrangement is present in the 1,3-disubstituted species **3**, and a linear arrangement is observed in the 1,4-disubstituted compound **6**.

In compounds **3** and **6**, the planarity of the benzene rings is maintained, but the C–C bond lengths

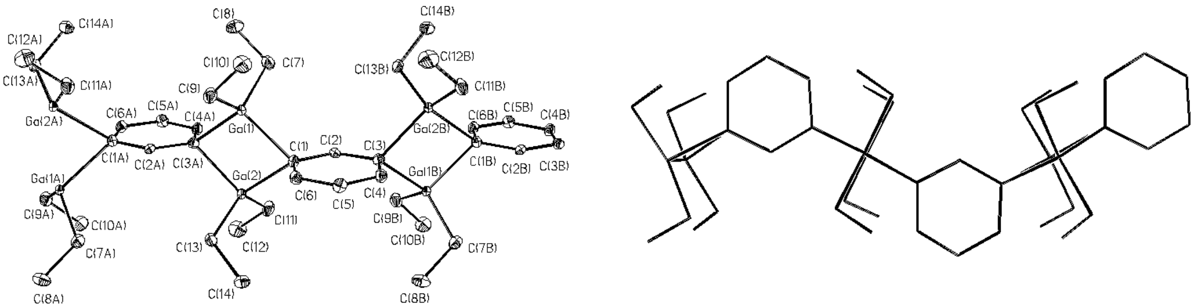


Fig. 1. Solid-state structure of **3**, viewed parallel (left) (ORTEP) and perpendicular (right) to the benzene ring planes. Ga1–C1 2.183(2), Ga1–C3A 2.174(2), Ga1–C7 1.975(2) Å; C3A–Ga1–C1 105.58(9), C7–Ga1–C9 120.20(11), C7–Ga1–C1 108.89(9), Ga1–C1–Ga2 74.45(7)°.

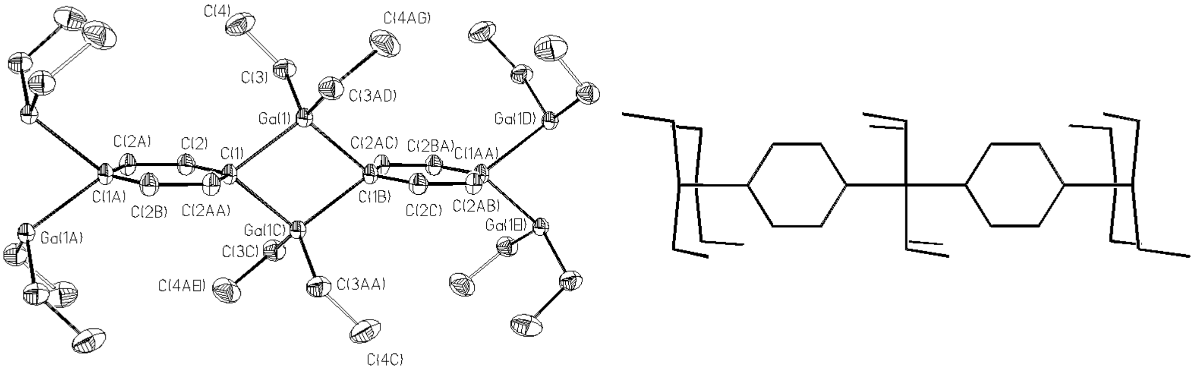


Fig. 2. Solid-state structure of **6**, viewed parallel (left) (ORTEP) and perpendicular (right) to the benzene ring planes. Ga1–C1 2.194(3), Ga1–C2AC 2.194(3), Ga1–C3 1.986(3) Å; C1–Ga1–C1B 104.75(12), C3–Ga1–C3AD 124.45(18), C3–Ga1–C1 106.53(5), Ga1–C1–Ga1C 75.25(12)°.

Table 2. C–C Distances (Å) and C–C–C angles (deg) in the benzene rings of **3** and **6**.

3		**6**	
C1–C2	1.411(3)	C1–C2AA	1.419(3)
C2–C3	1.414(3)	C2AA–C2B	1.402(5)
C3–C4	1.415(3)	C2B–C1A	1.419(3)
C4–C5	1.385(3)	C1A–C2A	1.419(3)
C5–C6	1.389(3)	C2A–C2	1.402(5)
C6–C1	1.414(3)	C2–C1	1.419(3)
C6–C1–C2	116.50(19)	C2–C1–C2AA	116.6(3)
C1–C2–C3	123.31(18)	C1–C2AA–C2B	121.70(16)
C2–C3–C4	116.6(2)	C2AA–C2B–C1A	121.70(16)
C3–C4–C5	122.0(2)	C2B–C1A–C2A	116.6(3)
C4–C5–C6	119.60(19)	C1A–C2A–C2	121.70(16)
C5–C6–C1	122.0(2)	C2A–C2–C1	121.70(16)

and the C–C–C bond angles differ to some extent, with longer bonds and smaller angles observed in connection with the carbon atoms C1 and C3/C4, which are involved in the bridging units. The respective bond lengths and angles are collected in Table 2. The differing bond lengths do not allow the postulation of a pronounced carbocation character at the non-bridging carbon atoms of the benzene unit. Thus, the bonding within the bridging units has to be described as mainly electron-deficient, as documented by the enlarged gallium-carbon distances, presumably with some electron delocalization from the benzene systems to the gallium atoms. Changes in benzene ring bond lengths and internal ring angles caused by the electronic effects of other substituents have been discussed in the literature in great detail [18, 19]. The atom arrangement in the bridging units of **3** and **6** is comparable to that found for the bridging unit in dimethyl(phenyl)aluminum [20].

Conclusion

In the class of benzene derivatives with gallyl substituents in 1,3- and in 1,4-position, the dimethylgallyl-substituted compounds have been reported only recently [11], and the diethylgallyl-ubstituted compounds are reported in this paper. Interestingly, quite different structural motifs are observed in the solid-

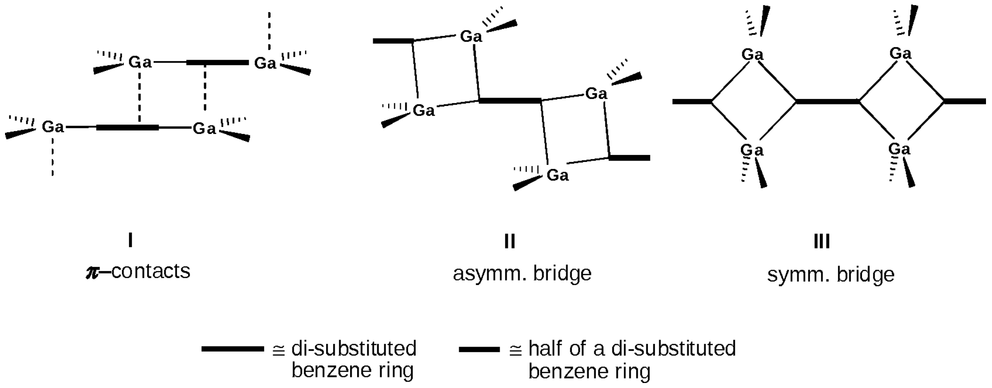


Fig. 3. Coordination modes in bis(dialkylgallyl)benzene derivatives.

state structures of the methyl- and the ethyl-substituted compounds. In the 1,4-disubstituted species, π contacts between the monomeric units are observed for the dimethylgallyl compound, whereas a symmetrical bridging pattern is found for the diethylgallyl compound. In the latter, steric requirements of the ethyl groups prevent the close approach of monomeric units necessary for an effective π contact, so that the bridging mode is the preferred coordination pattern. The observed types of bonding in the 1,4-disubstituted species are represented in Fig. 3 (type I and type III). Comparable effects have been observed already for methyl- and ethyl-substituted 9,10-dialkyl-9,10-dihydro-9,10-digallaanthracenes [21]. In the 1,3-disubstituted species, an asymmetric bridging pattern is observed for the dimethylgallyl compound. This bonding situation may be regarded as a hybrid between a π-interaction and a symmetrical bridging situation. A π-interaction of type I is presumably prohibited by geometric constraints exerted by the 1,3-disubstitution pattern. In contrast, a symmetrical bridging situation is found for the diethylgallyl compound. The observed bonding types for the 1,3-disubstituted species are represented in Fig. 3 (type II and type III).

It is concluded from the above described observations that in dialkylgallyl-substituted benzene derivatives intermolecular π-interactions between benzene rings and the vacant *p* orbitals of tricoordinate gallium atoms are the preferred coordination mode (type I in Fig. 3). If the short distance necessary for such a π-interaction is prohibited by steric or geometric constraints, the next best solution is the formation of symmetric or asymmetric four-membered bridging units between aryl-carbon and gallium atoms (types III and II in Fig. 3). This constellation leads to the rather exceptional effect, that methyl- and ethyl-substituted derivatives in the same class of compounds show different coordination modes in their solid- state structures.

Experimental Section

Crystal structure determinations

Crystallographic data were collected with a Bruker-Nonius Kappa CCD diffractometer with MoK_α (graphite monochromator, λ = 0.71073 Å) at 100 K. Crystallographic programs used for structure solution and refinement were SHELXS/L-97 [22]. The structures were solved by Direct Methods and refined by using full-matrix least squares on F^2 of all unique reflections with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions using a riding model. C(4) of compound **6** is disordered because of the crystallographic mirror plane. The crystal of **6** contains highly disordered solvent molecules, which could not be modelled even with restraints. The SQUEEZE routine of PLATON [23] was used to remove the respective electron density. The molecular formula and the items based on the molecular formula do not include the disordered solvent.

CCDC 744894 and CCDC 744894 contain the supplementary crystallographic information for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

General comments

All experiments were carried out under purified argon atmosphere using standard Schlenk techniques. All solvents were commercially available, purified by conventional means, and distilled and stored under argon prior to use. Elemental analyses were done at the Microanalytical Laboratories of the University of Bielefeld and at Beller & Matthies, Göttingen.

The starting materials 1,3-di(chloromercurio)benzene [16] and 1,4-di(chloromercurio)benzene [17] were prepared using a literature procedure. Triethylgallium was a gift from Professor Lorberth, University of Marburg.

Caution! Triethylgallium is a pyrophoric liquid and should be handled with care. Diethylmercury is poisonous to the central nervous system and has a long latency period before the characteristic symptoms appear. Its characteristic volatility allows transdermal absorption and inhalation of the vapors, which must be avoided [24 – 26]. It is therefore necessary to use a combination of gloves as suggested by Blayney *et al.* [27]. Diethylmercury was decomposed by treatment with *aqua regia*. The resulting mercury dichloride was precipitated under basic conditions and appropriately disposed.

*1,3-Bis(diethylgallyl)benzene (**3**)*

In a Schlenk flask, triethylgallium (15.88 g, 101.2 mmol) was added *via* septum by a syringe to freshly prepared 1,3-di(chloromercurio)benzene (1.61 g, 2.93 mmol). The septum was replaced by a glass stopper, and the vessel was tightly closed [28]. The resulting suspension was heated to 140 °C for 15 h to give a colorless solution. After cooling to r. t., compound **3** separated from the solution within 7 d. After removal of the liquid components, compound **3** remained as a solid residue which was recrystallized in a tightly closed vessel from triethylgallium (12 mL) as solvent. Colorless crystals of **3** (0.84 g, 2.54 mmol, 87 % yield) were separated and quickly dried under reduced pressure (10 mbar). Compound **3** is extremely sensitive towards air and moisture. – CH analysis: calcd. C 50.68, H 7.29; found C 50.01, H 6.70 [29].

*1,4-Bis(diethylgallyl)benzene (**6**)*

Preparation analogous to the synthesis of **3**: Triethylgallium (16.55 g, 105.5 mmol), 1,4-di(chloromercurio)benzene (1.75 g, 3.19 mmol), 2 mL of *p*-xylene (supports crystallization); colorless crystals of **6** (0.91 g, 2.75 mmol, ∼ 87 % yield, containing non-stoichiometric amounts of *p*-xylene) [30]. – CH analysis: calcd. C 50.68, H 7.29; found C 49.83, H 6.34 [29, 30].

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[28] A Schlenk flask and a glass stopper are tightly secured with a screwed-up bracket.

[29] The novel compounds are extremely air-sensitive; deviations from the calculated CH values may be due to partial oxidation of the crystals or to the presence of traces (not detectable by NMR spectroscopy) of chemisorbed triethylgallium. Deviations from calculated CH values in group 13 element-organic compounds have already been reported, for instance in a) L. H. Long, J. F. Sackmann, *Trans. Faraday Soc.* **1958**, *54*, 1797 – 1803; b) O. T. Beachley, Jr., R. B. Hallock, H. M. Zhang, J. L. Atwood, *Organometallics* **1985**, *4*, 1675 – 1680; c) ref. [10]; d) ref. [11].

[30] According to the crystal structure determination, compound **6** contains non-stoichiometric amounts of *p*-xylene.