Aryl(dimethyl)gallium Compounds and Methyl(diphenyl)gallium: Synthesis, Structure, and Redistribution Reactions

Peter Jutzi,* Joseph Izundu, Beate Neumann, Andreas Mix, and Hans-Georg Stammler

Fakultät für Chemie, Universität Bielefeld, Universitätstrasse 25, 33615 Bielefeld, Germany

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Treatment of diphenylmercury with an excess of trimethylgallium at higher temperatures resulted in the formation of dimethyl(phenyl)gallium (**1**). Similarly, reaction of 1-chloromercurio(4-methylbenzene) and 1-chloromercurio(4-*tert*-butylbenzene) with an excess of trimethylgallium gave dimethyl(4-methylphenyl)gallium (**2**) and dimethyl(4-*tert*-butylphenyl)gallium (**3**), respectively. Treatment of diphenylmercury with an equivalent amount of trimethylgallium resulted in the formation of methyl(diphenyl)gallium (**4**). The X-ray crystallographic studies of compounds **1**, **2**, **3**, and **4** revealed the presence of trigonal planar coordinate gallium atoms in monomeric molecules, which associate to polymeric strands by additional intermolecular gallium π-aryl contacts, thus leading to an overall trigonal bipyramidal coordination geometry at gallium. Compounds **1**−**4** are stable in the solid state and in solution. Substituent redistribution reactions take place at higher temperatures and at room temperature in the presence of THF. Compound **1** could also be prepared by the reaction of triphenylgallium with an excess of trimethylgallium at higher temperatures.

1. Introduction

Organogallium(III) compounds are important tools in organometallic chemistry. Many homoleptic and heteroleptic compounds have already been synthesized and structurally characterized during the last century.[1] The interest in such molecules is based on their Lewis acid properties and on their potential use as precursors in CVD processes.[2−4] The synthesis as well as structural studies of simple homoleptic organogallium(III) compounds such as triphenylgallium [5−9] and trimethylgallium[10−12] have been reported. In the context of our investigations of substituent redistribution reactions in dialkylgallyl-substituted ferrocene derivatives,[13] we became interested in the properties of the corresponding benzene derivatives. Surprisingly, heteroleptic organogallium(III) compounds such as dimethyl(phenyl)gallium and methyl(diphenyl)gallium, which contain simple aryl and alkyl groups in the same molecule, are so far unknown. Redistribution reactions taking place under ordinary conditions might have prevented the isolation of such compounds. The diaryl(methyl)gallium compound (2,6-$MesC_6H_3)_2GaMe$, which contains bulky aryl substituents, is described as a stable species.[14] The comparable diaryl(methyl)gallium compound $\{2,6\text{-}(4\text{-}t\text{BuC}_6H_4)_2C_6H_3\}_2GaMe$ is an unstable species due to redistribution reactions.[15] Comparable observations have been described by Beachley et al. for some dialkylgallyl-substituted cyclopentadienes.[16]

In this report, we describe the preparation of dimethyl(phenyl)gallium (**1**), dimethyl(4-methylphenyl)gallium (**2**), dimethyl(4-*tert*-butylphenyl)gallium (**3**), and methyl(diphenyl)gallium (**4**), following the Hg/Ga metathesis strategy introduced by Oliver et al. for the preparation of some group 13 element organic compounds.[4] The preparation of poly(dimethylgallyl)-substituted benzene derivatives will be presented in a forthcoming paper. The compounds **1**−**4** are characterized by their NMR spectroscopic and X-ray crystallographic data and by their stability with respect to redistribution reactions.

2. Results and Discussion

Synthesis and Characterization. For the synthesis of dimethyl(phenyl)gallium (**1**), diphenylmercury was treated with an excess of trimethylgallium according to eq 1a. The original colorless suspension was heated at 100 °C to afford a clear solution. On cooling to room temperature, a fine precipitate separated from the solution. The volatile components consisting of dimethylmercury and trimethylgallium were removed in vacuo. The residue was washed with *n*-hexane and dried to give compound **1** as an amorphous, colorless solid in 90% yield. **1** was crystallized from trimethylgallium as solvent in 83% yield.

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* Corresponding author. Phone: +49-5211066163. E-mail: peter.jutzi@uni-bielefeld.de.

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A possible alternative strategy for the synthesis of mono-dialkylgallyl-substituted benzene derivatives, but not for poly-dialkylgallyl-substituted ones, is given by the reaction of triphenylgallium with the corresponding trialkylgallium compound. This route has been checked only for the preparation of **1**. Thus, triphenylgallium was treated with an excess of trimethylgallium in *n*-hexane according to eq 1b. The colorless solution was heated at 100 °C for 2 h. After cooling to room temperature, the volatile components consisting of *n*-hexane and trimethylgallium were removed in vacuo. Compound **1** was obtained as an amorphous, colorless solid in 97% yield, which was crystallized from trimethylgallium in 91% yield.

$$Ph_2Hg + 2\ GaMe_3 \xrightarrow[100\ °C]{\text{excess } GaMe_3} 2\ \underset{(\mathbf{1})}{PhGaMe_2} + HgMe_2 \qquad (1a)$$

$$GaPh_3 + 2\ GaMe_3 \xrightarrow[100\ °C]{\text{excess } GaMe_3,\ n\text{-hexane}} 2\ \underset{(\mathbf{1})}{PhGaMe_2} \qquad (1b)$$

Compound **1** is very sensitive to air and moisture, readily soluble in aromatic solvents such as benzene, but only sparingly soluble in aliphatic hydrocarbons.

The ^{1}H NMR spectrum of **1** measured in benzene-d_6 at room temperature revealed a singlet at $\delta = -0.13$ ppm for the two methyl groups, a multiplet at $\delta = 7.27$ ppm for three protons in *para*- and *meta*-positions, and a multiplet at $\delta = 7.62$ ppm for two protons in *ortho*-postion of the phenyl ring. The ^{13}C NMR spectrum in benzene-d_6 showed expected signals at $\delta = -2.9$ (methyl), 128.2 (C-3/5) 129.8 (C-4), 137.2 (C-2/6), and 148.2 (C-1) ppm.[17]

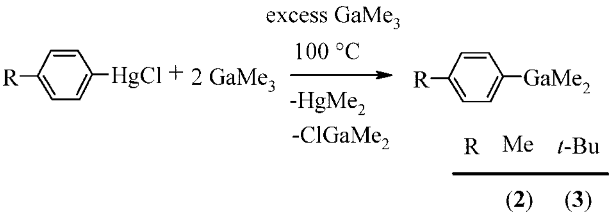
Compound **1** is monomeric in benzene-d_6 solution, as proven by its diffusion coefficient ($D = 1.56 \times 10^{-9}$ m^2 s^{-1}) compared with that of 2-phenylpropane ($D = 1.70 \times 10{-}9$ m^2 s^{-1}). The diffusion coefficients were determined by pulsed field gradient NMR experiments (see Experimental Section).[18] The monomeric structure of **1** in aromatic solvents is in accordance with the low-temperature ^{1}H NMR data. In toluene-d_8, the methyl group signal remained a sharp singlet at 275, 245, and 220 K, respectively, with a nearly unchanged chemical shift. The monomeric molecules presumably are weakly stabilized by π-contacts with the aromatic solvent.

Several experiments were performed with compound **1** to check substituent redistribution reactions. A solution of **1** in benzene remained unchanged after 1 week at room temperature, as checked by ^{1}H NMR spectroscopy, but very slight changes were observed after heating for 2 h at 80 °C. A toluene solution of **1** heated at 120 °C for 4 h decomposed into a mixture of products that could not be individually characterized by ^{1}H NMR spectroscopy. Addition of THF to a benzene-d_6 solution of **1** at room temperature promoted substituent exchange reactions. The formation of the THF adducts of methyl(diphenyl)gallium (compound **4**, vide infra), of trimethylgallium, and of **1** in a ratio of 1:1:4, respectively, was proven by ^{1}H NMR spectroscopy.

Substituent exchange reactions of **1** have been observed not only in solution but also in the solid state. Whereas **1** remained unchanged under reduced pressure (10 mbar) for about 3 h and under normal pressure (1 bar) for over 18 months, the compound decomposed at elevated temperatures under reduced pressure to give the redistribution products trimethylgallium, methyl(diphenyl)gallium (**4**), and triphenylgallium.

A rapid methyl group exchange already at room temperature was observed upon addition of trimethylgallium to a benzene solution of **1**, as indicated by the presence of an averaged methyl group signal at $\delta = -0.15$ ppm in the ^{1}H NMR spectrum and at $\delta = 1.1$ ppm in the ^{13}C NMR spectrum of the reaction mixture.

The compounds dimethyl(4-methylphenyl)gallium (**2**) and dimethyl(4-*tert*-butylphenyl)gallium (**3**) were synthesized by treating 1-chloromercurio(4-methylbenzene) and 1-chloromercurio(4-*tert*-butylbenzene),[19] respectively, with an excess of trimethylgallium (eq 2).



(2)

Contrary to the preparation of compounds **1** and **2**, compound **3** separated already in a crystalline form and nearly quantitatively from the hot reaction mixture on cooling. The remaining solution contained trimethylgallium, chlorodimethylgallium, dimethylmercury, and small amounts of **3**.

The compounds **2** and **3** are more sensitive to air and moisture than **1**. They are readily soluble in aromatic solvents such as benzene, but sparingly soluble in hydrocarbons. In their ^{1}H and ^{13}C NMR spectra, the expected resonance signals were observed (see Experimental Section).

Compounds **2** and **3** showed long-term stability at room temperature in the solid state and in benzene solution. Redistribution reactions were investigated in more detail only with compound **3**. As with **1**, addition of THF to a benzene solution of **3** promoted substituent exchange reactions. The formation of the THF adducts of **3** and of the redistribution products di(4-*tert*-butylphenyl)(methyl)gallium and trimethylgallium in a ratio of 1:3:5, respectively, was detected by NMR spectroscopy. In the solid state, **3** decomposed at elevated temperatures under reduced pressure to give trimethylgallium, di(4-*tert*-butylphenyl)(methyl)gallium, and tri(4-*tert*-butylphenyl)gallium, as concluded from the NMR spectroscopic data.

Methyl(diphenyl)gallium (**4**) was prepared by treating diphenylmercury with a nearly stoichiometric amount of trimethylgallium (eq 3). Crystals of **4** were obtained in 98% yield. The ^{1}H and ^{13}C NMR spectra showed the expected resonance signals (see Experimental Section).

$$Ph_2Hg + GaMe_3 \xrightarrow{100\ °C} \underset{(\mathbf{4})}{Ph_2GaMe} + HgMe_2 \qquad (3)$$

Compound **4** is rather air and moisture sensitive. It showed long-term stability at room temperature in the solid state as well as in solution. It liberated no trimethylgallium when heated at 70 and 120 °C in vacuo (10 mbar) each for a period of 30 min, but when heated at 150 °C in vacuo (10 mbar) for a period of 30 min, it decomposed to give triphenylgallium and trimethylgallium.

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Table 1. X-ray Crystal Structural Data for 1

empirical formula	C$_8$H$_{11}$Ga
fw	176.89
temperature (K)	100(2)
wavelength (Å)	0.71073
cryst syst	monoclinic
space group	*P*2/*c*
unit cell dimensions	
a (Å)	16.8630(4)
b (Å)	7.2520(2)
c (Å)	12.8280(5)
α (deg)	90
β (deg)	95.6040(14)
γ (deg)	90
V (Å^3)	1561.24(8)
Z	8
ρ (Mg/m^3)	1.505
F(000)	720
cryst size (mm^3)	0.30 × 0.30 × 0.20
color	colorless
index range	$-23 \le h \le 23$ $-10 \le k \le 9$ $-17 \le l \le 18$
no. of reflns coll/unique/$>2\sigma(I)$	50 739/4547/3398
completeness	99.4%
transmision:	
$\Delta\rho_{\mathrm{Max}}$	0.5468
$\Delta\rho_{\mathrm{Min}}$	0.4257
no. of data/restraints/params	4547/0/167
goodness-of-fit on F^2	1.055
R factor [$I > 2\sigma(I)$]	
R1	0.0355
wR2	0.0796
R factor (all data)	
R1	0.0559
wR2	0.0862

Table 2. Selected Bond Lengths [Å] and Bond Angles [deg] for Compounds 1A and 1B

1A		1B	
Ga(1)−C(1)	1.972(2)	Ga(2)−C(9)	1.982(2)
Ga(1)−C(8)	1.967(2)	Ga(2)−C(16)	1.965(2)
Ga(1)−C(7)	1.962(2)	Ga(2)−C(15)	1.959(2)
∅Ga−C	1.97	∅Ga−C	1.97
Ga(1)···C(6a)	3.11	Ga(2)···C(14a)	3.16
Ga(1)···C(5b)	3.25	Ga(2)···C(14b)	3.30
C(7)−Ga(1)−C(8)	124.03(10)	C(15)−Ga(2)−C(16)	124.38(10)
C(7)−Ga(1)−C(1)	119.24(9)	C(15)−Ga(2)−C(9)	120.22(10)
C(8)−Ga(1)−C(1)	116.48(10)	C(16)−Ga(2)−C(9)	115.39(10)
∑C−Ga−C	359.8	∑C−Ga−C	360.0
C(2)−C(1)−C(6)	116.8(2)	C(14)−C(9)−C(10)	116.7(2)
C(2)−C(1)−Ga(1)	120.63(17)	C(14)−C(9)−Ga(2)	123.55(17)
C(6)−C(1)−Ga(1)	122.14(17)	C(10)−C(9)−Ga(2)	119.74(17)

X-ray Structural Data. The solid state structures of **1**−**4** were determined by single-crystal X-ray diffraction analysis. Suitable crystals were prepared in a glovebox to avoid contact with air or moisture. The crystals of compounds **1** and **4** were coated with a viscous oil to prevent decomposition before the measurement, whereas the crystals of **2** and **3** were coated with silicon vacuum grease, because they decomposed readily in the viscous oil before the measurement. X-ray structural parameters of **1** are listed in Table 1, and the parameters for **2**−**4** are given as Supporting Information. Selected bond lengths and bond angles of **1** are presented in Table 2, while those of **2**−**4** are collected as Supporting Information. The molecular structure of **1** is presented in Figure 1, whereas those of **2**−**4** are given in the Supporting Information. Typical motifs of the solid state structures of **1**−**4** are given in Figures 2, 3, 4, and 5.

Dimethyl(phenyl)gallium (1). Compound **1** crystallizes in the form of colorless plates in the space group *P*2/*c*. The structural investigation revealed the presence of two independent monomers, **1A** and **1B** (Figure 1), with slightly different bond lengths and bond angles. The gallium aryl−carbon bonds in **1A** and in **1B** are longer than the gallium methyl−carbon bonds.

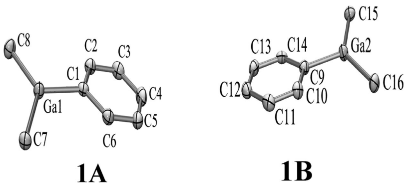

Figure 1. ORTEP representation of the molecular structures of **1A** and **1B** with the thermal ellipsoids given at the 50% probability level. Hydrogen atoms are omitted for clarity.

Both molecules exhibit comparable mean gallium−carbon bond lengths (∅Ga−C). The bond angles within the trigonal plane in **1A** differ slightly from those in **1B** (see Table 2). The sum of the bond angles at the three-coordinate gallium centers in **1A** and **1B** is 360°, in accordance with the presence of sp^2-

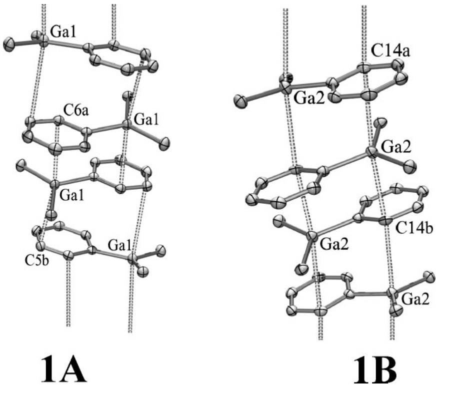

Figure 2. ORTEP representation of gallium−arene intermolecular contacts in **1**. The broken lines represent intermolecular distances: Ga(1)C(6a) 3.11 Å; Ga(1)C(5b) 3.25 Å in **1A** and Ga(2)C(14a) 3.16 Å; Ga(2)C(14b) 3.30 Å in **1B**.

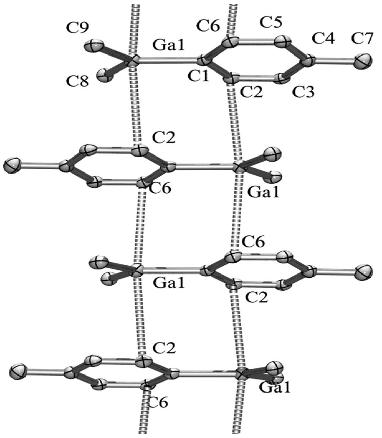

Figure 3. ORTEP representation of the solid state structure of compound **2** with the thermal ellipsoids given at the 50% probability level. Hydrogen atoms are omitted for clarity. The broken lines represent intermolecular distances; Ga(1)C(6) and Ga(1)C(2) 3.12 Å. Intramolecular distances (Å) and angles (deg): Ga(1)−C(9) 1.959(2); Ga(1)−C(8) 1.961(2); Ga(1)−C(1) 1.975(2); C(9)Ga(1)−C(1) 117.06(10); C(8)−Ga(1)−C(1) 117.63(10); C(9)−Ga(1)−C(8) 125.31(11).

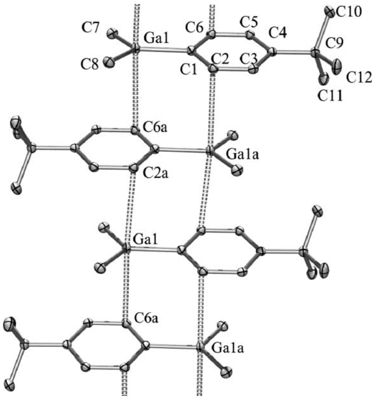

Figure 4. ORTEP representation of the solid state structure of compound **3** with the thermal ellipsoids given at the 50% probability level. Hydrogen atoms are omitted for clarity. The broken lines represent intermolecular distances: Ga(1)C(2a) 3.17 Å and Ga(1)C(6a) 3.11 Å. Intramolecular distances (Å) and angles (deg): Ga(1)−C(1) 1.9808(11); Ga(1)−C(7) 1.9641(12); Ga(1)−C(8) 1.9630 (12); C(8)−Ga(1)−C(7) 126.13(5); C(8)−Ga(1)−C(1) 116.92(5); C(7)−Ga(1)−C(1) 116.95(5).

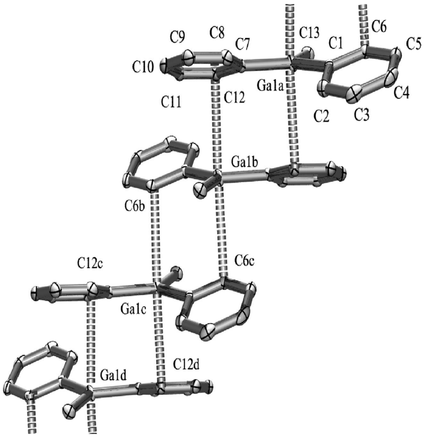

Figure 5. ORTEP representation of the solid state structure of compound **4** with the thermal ellipsoids given at the 50% probability level. Hydrogen atoms are omitted for clarity. The broken lines represent intermolecular distances: Ga(1)C(12a) 2.99(2) Å and Ga(1) C(6a) 3.08(2) Å. Intramolecular distances (Å) and angles (deg): Ga(1)−C(13) 1.949(2); Ga(1)−C(1) 1.976(2); Ga(1)−C(7) 1.976(2); C(13)−Ga(1)−C(1) 118.65(10); C(13)−Ga(1)−C(7) 121.84(10); C(1)−Ga(1)−C(7) 119.46(8).

hybridized atoms. In **1A** as well as **1B**, the gallium-bound methyl groups and the phenyl carbon atoms are not aligned in the same plane. The planes [C(2)C(6)Ga(1)] and [C(1)C(7)C(8)] in **1A** are inclined at an angle of 8.7°, whereas the planes [C(10)C(14)Ga(2)] and [C(9)C(15)C(16)] in **1B** are inclined at 12.1°. Furthermore, the gallium−*ipso*-carbon−*para*-carbon vector deviates from a linear arrangement to give a [C(4)C(1)Ga(1)] dip angle of 6.6° in **1A** and a [C(12)C(9)Ga(2)] dip angle of 2.1° in **1B**.

The coordination sphere of the gallium atoms in **1A** and **1B** is completed by two π-contacts to phenyl systems of neighboring molecules to finally give five coordinate gallium atoms exhibiting a trigonal bipyramidal coordination geometry (Figure 2). In the formed strand structures, the gallium atoms form π-contacts in the range 3.11−3.25 Å with an *ortho*-carbon atom and with a *meta*-carbon atom from adjacent phenyl groups in **1A** and in the range 3.16−3.30 Å with two *ortho*-carbon atoms from adjacent phenyl groups in **1B**. The difference in the coordination behavior of **1A** and **1B** presumably is a result of crystal-packing effects.

Dimethyl(4-methylphenyl)gallium (2). A part of the solid state structure of **2** is presented in Figure 3. As observed for compound **1**, the gallium aryl−carbon distance is slightly longer than each of the gallium methyl−carbon distances. The three-coordinate gallium atom is characterized by the bond angle sum of 360°. The planes [C(2)C(6)Ga(1)] and [C(1)C(8)C(9)] are inclined at an angle of 13.8°. The gallium−*ipso*-carbon−*para*-carbon vector deviates from a linear arrangement to give a [C(4)C(1)Ga(1)] dip angle of 0.7°. As in **1**, the coordination sphere of the gallium atom in **2** is completed by two π-contacts to give an overall five-coordinate gallium atom exhibiting a trigonal-bipyramidal coordination geometry. Comparable gallium−π-arene contacts [Ga(1)C(6) and Ga(1)C(2): 3.12 Å] are observed. In the resulting polymeric strand structure, the gallium atoms are coordinated to *ortho*-carbon atoms of the neighboring phenyl groups.

Dimethyl(4-*tert*-butylphenyl)gallium (3). A part of the solid state structure of **3** is presented in Figure 4. The structural features of **3** are comparable to those of **1** and **2**. The coordination sphere of the trigonal planar gallium atom is completed by two π-contacts to *ortho*-carbon atoms of neighboring phenyl groups [Ga(1)C(2a) 3.17 Å and Ga(1)C(6a) 3.11 Å] to give a trigonal-bipyramidal coordination geometry at gallium in the resulting polymeric strand structure.

Methyl(diphenyl)gallium (4). A part of the solid state structure of **4** is presented in Figure 5. The three-coordinate gallium atom is characterized by the bond angle sum of 360°. Each gallium aryl−carbon distance is slightly longer than the gallium methyl carbon distance. The phenyl groups are arranged in a propeller form, with the plane [C(2)C(6)Ga(1)] inclined at 31.4° to the plane [C(8)C(12)Ga(1)] and the plane [C(1)C(7)C(13)] inclined at 18.8° to the plane [C(2)C(6)Ga(1)] and at 16.6° to the plane [C(8)C(12)Ga(1)]. The gallium−*ipso*-carbon−*para*-carbon vectors deviate from linearity to give a C(4)C(1)Ga(1) dip angle of 5.3° and a C(10)C(7)Ga(1) dip angle of 3.1°. The coordination sphere of the gallium atom is completed by two π-contacts to give an overall five-coordinate gallium atom exhibiting a trigonal-bipyramidal coordination geometry. Gallium−π-arene intermolecular contacts [Ga(1)C(12a) 2.99(2) Å and Ga(1) C(6a) 3.08(2) Å] gave a polymeric strand structure, in which the gallium atoms are coordinated to the *ortho*-carbon atoms of the neighboring phenyl groups.

3. Conclusion

Against our misgivings based on the literature information about the stability of aryl(dialkyl)gallium species, the compounds dimethyl(phenyl)gallium (**1**), dimethyl(4-methylphenyl)gallium (**2**), dimethyl(4-*tert*-butylphenyl)gallium (**3**), and methyl(diphenyl)gallium (**4**) are stable under ordinary conditions of temperature and pressure in the solid state and in solution. In the crystalline solids, the structural motifs found in triphenylgallium[7] are preserved: molecular units with trigonal-planar gallium atoms are connected to strand-like coordination polymers by π-contacts, leading to an overall trigonal-bipyramidal geometry at gallium. The (aryl)C−Ga distances in **1**−**4** are longer than the (methyl)C−Ga distances and thus exclude a pronounced intramolecular aryl gallium back-bonding. Redistribution reactions are observed at higher temperatures and at room temperature after the addition of THF. Several experiments have shown that reaction temperatures of about 100 °C are necessary for the synthesis of **1**−**4**. In most cases, trimethylgallium is required as solvent to shift the equilibrium to the product side. It should be emphasized that easy to perform substituent exchange reactions are a prerequisite for the application of the synthetic concept of dynamic covalent chemistry.[20]

4. Experimental Section

General Comments. All experiments were conducted under a purified argon atmosphere using standard Schlenk techniques. All solvents were commercially available, purified by conventional means, distilled, and stored under argon prior to use. The NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer at 300 K (^{1}H NMR, 500.1 MHz, 600.13 MHz; ^{13}C NMR, 125.8 MHz, 150.9 MHz). The chemical shift values are reported in ppm, and the reference solvent was calibrated benzene-d_6 (^{1}H: $\delta = 7.15$, ^{13}C: $\delta = 128.0$ ppm). The diffusion coefficient NMR experiments were performed on a Bruker Avance DRX 600 FT-NMR spectrometer (600.13 MHz) at 294.7 K using a Bruker 5 mm TBI z-gradient probe and the longitudinal eddy current delay sequence (ledbpgp2s). The diffusion constants were calculated using the SIMFIT program package. The Microanalytical Laboratories of the University of Bielefeld and Beller & Matthies, Goettingen, performed the CH elemental analyses. Mass spectrometric measurements were performed at the University of Bielefeld on a VG Autospec spectrometer (EI; 70 eV; 200 μA emission). X-ray crystal structure data were collected at the University of Bielefeld on a Nonius Kappa CCD X-ray equipment.

Starting Materials. Diphenylmercury was purchased from Aldrich Chemicals. 1-Chloromercurio(4-methylbenzene) and 1-chloromercurio(4-*tert*-butylbenzene)[19] were prepared using a literature procedure.

Caution! Trimethylgallium is a pyrophoric liquid and should be handled with care. Dimethylmercury 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 certainly be avoided.[21−23] It is therefore necessary to use a combination of gloves as suggested by Blayney et al.[24] Dimethylmercury was decomposed by treating with aqua regia. The resulting mercury dichloride was precipitated under basic conditions before it was appropriately disposed.

Dimethyl(phenyl)gallium (1). (a) By Hg/Ga Exchange. In a Schlenk flask, trimethylgallium (3.87 g, 33.70 mmol) was added via septum with a syringe to freshly sublimed diphenylmercury (2.92 g, 8.20 mmol). The septum was replaced with a glass stopper, and the vessel was tightly closed.[25] The colorless suspension was heated at 100 °C for 5 h. A fine precipitate separated from the solution on cooling to room temperature. The volatile components were removed under reduced pressure (10 mbar) and proven by ^{1}H NMR spectroscopy to consist of HgMe$_2$ ($\delta = 0.12$ ppm) and GaMe$_3$ ($\delta = -0.15$ ppm). The residue was washed twice with 5 mL of *n*-hexane at −70 °C to give **1** as a colorless, amorphous solid (2.60 g, 14.70 mmol, 90%). This solid was suspended in trimethylgallium (1.70 g, 15.30 mmol) and heated at 100 °C for 1 h. The formed clear solution was cooled to 40 °C and maintained at this temperature without stirring for 15 h. After this period, colorless crystals separated. Trimethylgallium was removed through a syringe, and the crystals were washed with 3 mL of *n*-hexane and dried in vacuo (10 mbar) for 1 h to give **1** (2.40 g, 13.57 mmol) in 83% yield. Compound **1**: ^{1}H NMR (benzene-d_6): δ −0.13 (s, 6H, methyl), 7.27 (m, 3H, *para*- and *meta*-phenyl), 7.62 (m, 2H, *ortho*-phenyl). ^{13}C NMR (benzene-d_6): δ −2.9 (methyl), 128.2 (C-3/5), 129.8 (C-4), 137.2 (C-2), 148.2 (C-1). The NMR spectrum of the amorphous solid corresponded to that of crystalline **1**. Anal. Found: C: 54.11; H: 5.23. Calcd: C: 54.32; H: 6.27.[14,16,26] MS *m/z* (%): [Ph$_2$Ga$^+$],[27] 223/225 (35/24); [PhGaMe$^+$], 161/163 (86/55); [PhGa$^+$], 146/148 (6/4); [GaMe$_2$$^+$], 99/101 (44/28); [Ga$^+$], 69/71 (44/28).

(b) By Substituent Redistribution. To a suspension of triphenylgallium (1.00 g, 3.32 mmol) in 10 mL of *n*-hexane was added through a syringe trimethylgallium (1.00 g, 8.71 mmol). The colorless solution was heated at 100 °C for 2 h. After cooling to room temperature, the volatile components consisting of *n*-hexane and trimethylgallium were removed under reduced pressure (10 mbar). Compound **1** was obtained as an amorphous, colorless solid (1.70 g, 9.61 mmol, 97%). **1** was suspended in 0.5 mL of trimethylgallium and heated at 100 °C for 1 h to give a colorless solution. On cooling, the temperature was maintained at 40 °C without stirring for 15 h. Colorless crystals of **1** separated from the solution, trimethylgallium was removed through a syringe, and the crystals were washed with 2 mL of *n*-hexane and dried in vacuo (10 mbar) for 1 h to give **1** in 91% yield. The cell parameters of the crystals and the NMR spectra in benzene-d_6 were identical to those of **1** prepared by route (a).

Diffusion Coefficient of 1. A NMR tube charged with **1** (3.5 mg, 0.02 mmol) and benzene-d_6 (0.45 mL) was carefully closed, and the diffusion coefficient of the sample was measured as described below. The same parameters were used for **1** and for the reference sample (3.5 mg of 2-phenylpropane in 0.45 mL of C$_6$D$_6$). The diffusion experiments were performed at room temperature ($T = 294.7$ K) without heating the sample. The air flow was switched off and no spinning was applied to the NMR tube. Prior to the measurement the sample was left for 4 h in the magnet in order to assume a constant temperature condition. The diffusion delay (big delta) was set to 50 ms, and the length of the gradient (little delta) was optimized to 3 and 3.2 ms, respectively, and was incremented linearly in 16 steps per experiment. Diffusion coefficients: **1** = 1.56×10^{-9} m^2 s^{-1}; 2-phenylpropane = 1.70×10^{-9} m^2 s^{-1}.

Low-Temperature ^{1}H NMR Data of 1. A NMR tube was charged with **1** (8.00 mg, 0.05 mmol) and toluene-d_8 (0.45 mL). The ^{1}H NMR data were measured at different temperatures. ^{1}H NMR (300 K): δ −0.16 (s, 6H), 7.23 (m, 3H), 7.55 (m, 2H). ^{1}H NMR (275 K): δ −0.20 (s, 6H), 7.27 (m, 3H), 7.57 (m, 2H). ^{1}H NMR (245 K): δ −0.22 (s, 6H), 7.30 (m, 3H), 7.59 (m, 2H). ^{1}H NMR (220 K): δ −0.25 (s, 6H), 7.32 (m, 3H), 7.60 (m, 2H).

Thermal Stability of 1 in Benzene-d_6. A NMR tube was charged with compound **1** (64.0 mg, 0.40 mmol) and 0.6 mL of benzene-d_6 and tightly closed. Identical NMR spectra were obtained before and after heating at 80 °C for 2 h. ^{1}H NMR (benzene-d_6): δ −0.12 (s, 6H, methyl), 7.30 (m, 3H, *meta*/*para*-phenyl), 7.65 (m, 2H, *ortho*-phenyl). ^{13}C NMR (benzene-d_6): δ −2.9 (methyl), 128.2 (C-3/5), 129.7 (C-4), 137.0 (C-2/6), 148.6 (C-1).

Redistribution Reactions in Benzene-d_6 Solution of 1 Promoted by THF. A NMR tube was charged with **1** (64.0 mg, 0.40 mmol), benzene-d_6 (0.4 mL), and THF (0.2 mL, 178 mg, 2.46

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(24) Blayney, M. B.; Winn, J. S.; Nierenberg, D. W. *Chem. Eng. News* **1997**, 7.

(25) A Schlenk flask and a glass stopper are tightly secured with a screwed on bracket.

(26) (a) 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) of chemisorbed trimethylgallium. Deviations from calculated CH values in group 13 element organic compounds have already been reported, for instance in: Long, L. H.; Sackmann, J. F. *Trans. Faraday Soc.* **1958**, *54*, 1797. (b) Beachley, O. T., Jr.; Hallock, R. B.; Zhang, H. M.; Atwood, J. L. *Organometallics* **1985**, *4*, 1675.

(27) Result of substituent redistribution reactions.

mmol). The formation of the THF adducts of methyl(diphenyl)gallium, of trimethylgallium, and of **1** in the ratio of 1:1:4, respectively, was proven by NMR spectroscopy. The ratio was established from the intensity of the ^{1}H NMR signals in relation to the respective Ga-methyl group signals. The THF signals are broadened due to exchange reactions between coordinated and free THF molecules. **1**·THF: ^{1}H NMR (benzene-d_6): δ −0.06 (s, methyl), 1.47 (THF), 3.52 (THF), 7.30 (m, *para*- and *meta*-protons), 7.68 (m, *ortho*-protons). ^{13}C NMR (benzene-d_6): δ −8.9 (methyl), 25.3 (THF), 67.3 (THF), 134.6 (C-3/5), 136.0 (C-4), 137.3 (C-2/6), 150.9 (C-1). Methyl(diphenyl)gallium (**4**·THF): ^{1}H NMR (benzene-d_6): δ 0.08 (s, methyl), 1.47 (THF), 3.52 (THF), 7.30 (m, *para*- and *meta*-protons), 7.77 (m, *ortho*-protons). ^{13}C NMR (benzene-d_6): δ −11.0 (methyl), 25.3 (THF), 67.3 (THF). The aromatic ^{13}C resonances of **1**·THF and of **4**·THF were overlapped with one another. Trimethylgallium·THF: ^{1}H NMR (benzene-d_6): δ −0.23 (s, methyl), 1.47 (THF), 3.52 (THF). ^{13}C NMR (benzene-d_6): δ −5.4 (methyl), 25.3 (THF), 67.3 (THF).[28]

Thermally Induced Redistribution Reactions of 1. Two Schlenk flasks, A and B, were connected by a bent ground-glass joint. Flask A was charged with compound **1** (500.0 mg, 2.80 mmol) and the system was evacuated (10 mbar). Flask B was then cooled with liquid nitrogen. Flask A was heated in three subsequent steps to 70, 120, and 150 °C, respectively, each for a period of 30 min. After each heating period, flask A was reweighed and thereafter the system was reassembled for the next reaction step. After this procedure, colorless crystals had deposited on the cooler region of flask A. The ^{1}H and ^{13}C NMR spectra of the deposited crystals indicated the formation of methyl(diphenyl)gallium (**4**) (~8%) and of triphenylgallium. Compound **1** liberated 135.0 mg (1.20 mmol), 168.70 mg (1.50 mmol), and 194.5 mg (1.70 mmol) of trimethylgallium at 70, 120, and 150 °C, respectively. Methyl(diphenyl)gallium (**4**) (vide infra): ^{1}H NMR, (benzene-d_6): δ −0.09 (s, methyl), 7.29 (m, *para*-and *meta*-protons), 7.70 (m, *ortho*-protons). The ^{13}C NMR signals of **4** overlapped with those of triphenylgallium. Triphenylgallium: ^{1}H NMR (benzene-d_6): δ 7.29 (m, 3H), 7.74 (m, 2H). ^{13}C NMR (benzene-d_6): δ 128.2 (C-3/5), 129.6 (C-4), 138.1 (C-2), 145.1 (C-1).

Redistribution Reaction between 1 and Trimethylgallium. A NMR tube was charged with **1** (64.0 mg, 0.40 mmol) and with a mixture of benzene-d_6 (0.5 mL) and trimethylgallium (0.2 mL, 170.0 mg, 1.50 mmol). The NMR tube was closed and allowed to stand at room temperature for a period of 30 min. Complete equilibration of **1** and trimethylgallium was proven by averaged Ga-Me group signals in the NMR spectra. ^{1}H NMR (benzene-d_6): δ −0.15 (s,), 7.24 (m, 3H), 7.56 (m, 2H). ^{13}C NMR (benzene-d_6): δ 1.1, 128.2 (C-3/5), 129.8 (C-4), 137.2 (C-2), 148.2 (C-1). For comparison: GaMe$_3$: ^{1}H NMR (benzene-d_6): δ 0.15. ^{13}C NMR (benzene-d_6): δ = 1.5.

Dimethyl(4-methylphenyl)gallium (2). Trimethylgallium (4.34 g, 37.80 mmol) was added through a syringe to 1-chloromercurio(4-methylbenzene) (2.06 g, 6.40 mmol). The resulting colorless suspension was heated at 110 °C for 5 h in a closed vessel to give a colorless solution. After the solution was cooled to room temperature, the volatile components were removed under reduced pressure. The residue was washed with *n*-hexane (5 mL) and dried in vacuo (10 mbar) for 3 h to give compound **2** as an amorphous, colorless solid (0.92 g, 4.80 mmol, 75%). Trimethylgallium (1.15 g, 10.0 mmol) was added to the solid (0.92 g), and the resulting colorless suspension was heated at 80 °C for 1 h in a closed vessel to give a colorless solution. After 3 days at room temperature, colorless crystals of **2** (0.80 g, 4.17 mmol, 65%) separated from the solution. Compound **2**: ^{1}H NMR, (benzene-d_6): δ −0.05 (s, 6H, methyl), 2.20 (s, 3H, Ar-Me), 7.17 (d, 2H, *meta*-Ar, $^3J_{\mathrm{HH}} = 8$ Hz), 7.73 (d, 2H, *ortho*-Ar, $^3J_{\mathrm{HH}} = 8$ Hz). ^{13}C NMR (benzene-d_6): δ −5.2 (methyl), 21.7 (Ar-Me), 129.0 (C-3/5), 137.8 (C-2/6), 139.2 (C-4), 143.6 (C-1). Anal. Found: C: 54.97; H: 6.13. Calcd: C: 56.61; H: 6.86.[14,16a,26] MS data: The MS data of compound **2** were not conclusive due to the substituent exchange reactions at elevated temperature.

Dimethyl(4-*tert*-butylphenyl)gallium (3). Trimethylgallium (5.95 g, 51.80 mmol) was added through a syringe to 1-chloromercurio(4-*tert*-butylbenzene) (3.19 g, 8.60 mmol). The resulting colorless suspension was heated at 100 °C for 5 h in a closed vessel to give a colorless solution. The solution was cooled to 30 °C without stirring and kept at this temperature for 15 h. During this period, colorless crystals of **3** separated from the solution (1.9 g, 8.20 mmol, 95%). Compound **3**: ^{1}H NMR (benzene-d_6): δ −0.09 (s, 6H, methyl), 1.30 (s, 9H, *t*-Bu), 7.43 (d, 2H, *meta*-protons, $^3J_{\mathrm{HH}} = 8$ Hz), 7.73 (d, 2H, *ortho*-protons, $^3J_{\mathrm{HH}} = 8$ Hz). ^{13}C NMR (benzene-d_6): δ −2.8 (methyl), 31.4 (Ar-Me), 34.7 (C-Me$_3$), 125.2 (C-3/5), 137.5 (C-2/6), 144.7 (C-1), 152.6 (C-4). Anal. Found: C, 58.96; H, 8.31. Calcd: C, 61.85; H, 8.22.[14,16a,26] MS *m/z* (%): [M$^+$], 233/235 (10/7); [t-BuC$_6$H$_4$GaMe$^+$], 218/220 (11/7); [t-BuC$_6$H$_4$Ga$^+$], 203/205 (13/8); [t-BuC$_6$H$_4$Me$^+$], 150 (7); [t-BuC$_6$H$_5$$^+$], 135 (34); [Me$_2CC_6H_5$$^+$],[27] 119 (100); [GaMe$_2$$^+$], 99/101 (70/48); [C$_6H_4Me^+$], 91 (60); [Ga$^+$], 69/71 (18/12).

Redistribution Reactions in Benzene-d_6 Solution of 3 Promoted by THF. An NMR tube was charged with compound **3** (32.40 mg, 0.10 mmol), benzene-d_6 (0.4 mL), and THF (0.2 mL, 0.18 g, 2.46 mmol). The formation of the THF adducts of di(*tert*-butylphenyl)(methyl)gallium, trimethylgallium, and **3** in a ratio of 1:3:5, respectively, was proven by NMR spectroscopy. The ratio was concluded from the intensity of the respective methyl group signal at gallium. The THF signals were broadened due to exchange reactions between coordinated and free THF molecules. **3**·THF: ^{1}H NMR (benzene-d_6): δ −0.02 (s, methyl), 1.29 (s, *t*Bu), 1.45 (THF), 3.52 (THF), 7.40 (m, *meta*-protons), 7.69 (d, *ortho*-protons). ^{13}C NMR (benzene-d_6): δ −8.1 (methyl), 25.8 (THF), 31.4 (Me), 34.6 (C-Me$_3$) 67.8 (THF), 124.4 (C-3/5), 137.2 (C-2/6), 145.7 (C-1), 149.9 (C-4). Di(*tert*-butylphenyl)(methyl)gallium·THF: ^{1}H NMR (benzene-d_6): δ 0.13 (s, methyl), 1.28 (s, *t*Bu), 1.45 (THF), 3.52 (THF), 7.41 (m, *meta*-protons), 7.79 (d, *ortho*-protons). ^{13}C NMR (benzene-d_6): δ −10.2 (methyl), 25.8 (THF), 31.5 (Me), 34.6 (C-Me$_3$), 67.8 (THF). The aryl-group ^{13}C resonances of **3**·THF and of di(*tert*-butylphenyl)(methyl)gallium·THF were overlapped with one another. Trimethylgallium·THF: ^{1}H NMR (benzene-d_6): δ −0.20 (s, methyl) 1.47 (THF), 3.52 (THF). ^{13}C NMR (benzene-d_6): δ −4.8 (methyl), 25.8 (THF), 67.8 (THF). For comparison GaMe$_3$·THF: ^{1}H NMR (benzene-d_6); δ −0.17 (s, methyl) 1.39 (THF), 3.46 (THF). ^{13}C NMR (benzene-d_6): δ −4.7 (methyl), 25.6 (THF), 68.2 (THF).

Thermal Decomposition of 3. Analogously to the procedure used in the thermal decomposition of **1**, 256.0 mg (1.10 mmol) of **3** was heated in three subsequent steps to 70, 120, and 150 °C in vacuo (10 mbar), for a period of 30 min each. Upon heating, **3** liberated 20.60 mg (0.20 mmol), 67.0 mg (0.60 mmol), and 84.0 mg (0.70 mmol) of trimethylgallium at 70, 120, and 150 °C, respectively. The ^{1}H and ^{13}C NMR data of the remaining colorless, amorphous solid material indicated the formation of tri(4-*tert*-butylphenyl)gallium and di(4-*tert*-butylphenyl)(methyl)gallium (~3%). These compounds were not isolated in the pure form. Tri(*tert*-butylphenyl)gallium: ^{1}H NMR (benzene-d_6): δ 1.29 (s, *t*Bu) 7.43 (d, *meta*-protons), 7.84 (d, *ortho*-protons). ^{13}C NMR (benzene-d_6): δ 31.4 (Me), 34.7 (*C*Me$_3$), 125.4 (C-3/5), 138.0 (C-2/6), 142.9 (C-1), 152.3 (C-4). Di(4-*tert*-butylphenyl)(methyl)gallium: ^{1}H NMR (benzene-d_6): δ −0.04 (Me), 1.25 (s, *t*Bu), 7.41 (d, *meta*-protons), 7.83 (d, *ortho*-protons). The aryl-group ^{13}C resonances of di(4-*tert*-butylphenyl)(methyl)gallium overlapped with those of tri(*tert*-butylphenyl)gallium.

Methyl(diphenyl)gallium (4). Trimethylgallium (0.28 g, 2.40 mmol) was added to freshly sublimed diphenylmercury (0.75 g,

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[28] Jones, A. C.; Cole-Hamilton, D. J.; Holliday, A. K.; Ahmad, M. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1047.

2.10 mmol). The resulting colorless suspension was heated at 100 °C in a closed vessel for 3 h to give a colorless solution. Upon cooling to room temperature without stirring, compound **4** separated from the solution as colorless crystals. All volatiles were removed in vacuo (10^{-2} mbar), and the remaining crystals (0.49 g, 2.0 mmol, 98%) were washed with *n*-hexane (0.5 mL) and dried in vacuo (10^{-2} mbar) for 2 h. Compound **4**: ^{1}H NMR (benzene-d_6): δ −0.09 (s, 3H, methyl), 7.29 (m, 2H *para*- and 4H *meta*-protons), 7.69 (m, 4H *ortho*-protons). ^{13}C NMR (benzene-d_6): δ −4.6 (methyl), 128.5 (C-3/5), 129.6 (C-4), 137.4 (C-2), 147.4 (C-1). Anal. Found: C: 63.44; H: 5.21. Calcd: C: 65.34; H: 5.48.[14,16a,26] The MS data of compound **4** were not conclusive due to substituent exchange reactions at elevated temperature.

Thermal Decomposition of 4. The experimental setup was the same as that already described for the thermal decomposition of **1** and **3**. Compound **4** (92.40 mg, 0.40 mmol) was heated at 70, 120, and 150 °C in three subsequent steps in vacuo (10 mbar) for a period of 30 min each. Compound **4** liberated on heating at 70 and 120 °C no trimethylgallium, but on heating at 150 °C it liberated trimethylgallium (9.0 mg, 0.08 mmol). On the cooler region of the flask, a crystalline material deposited, consisting of triphenylgallium and **4** (∼5%) as proven by NMR spectroscopy. Triphenylgallium: ^{1}H NMR (benzene-d_6): δ 7.30 (m, *meta*-protons), 7.74 (m, *ortho*-protons).[17] ^{13}C NMR (benzene-d_6): δ 128.5 (C-3/5), 129.6 (C-4), 137.9 (C-2), 145.4 (C-1). Methyl(diphenyl)gallium (**4**): ^{1}H NMR (benzene-d_6): δ −0.09 (s, methyl), 7.29 (m), 7.73 (m).

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Supporting Information Available: The crystallographic data for compounds **1**−**4** are deposited, including the intramolecular distances, bond angles, and the calculated positions of hydrogen atoms. This information is available free of charge via the Internet at http://pubs.acs.org.

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