Novel Ga_2N_2 Ring Systems by Reaction of Pentamethylcyclopentadienylgallium with Organic Azides

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*Summary: Two different types of compounds are observed in the kinetically controlled reaction of pentamethylcyclopentadienylgallium (Cp*Ga) (**1**) with organic azides: the dimeric iminogallane (η^1-Cp*GaNXyl)$_2$ (**2**) and the dimeric azide-bridged gallane [(η^1-Cp*)Ga(μ_2-N_3){N($SiMe_3$)$_2$}]$_2$ (**4**). The solid-state structures of **2** and **4** are discussed.*

Introduction

Compounds that contain the elements gallium and nitrogen and that moreover possess functionalized substituents are currently of special interest because they are regarded as potential single-source precursors for the deposition of GaN. Cyclopentadienyl systems have proven to be substituents with leaving group character in the chemistry of main group elements in general[1] and in particular in the chemistry of gallium.[2] Furthermore, bulky Cp substituents stabilize reactive molecules kinetically.[3] In this context our interest focused on reactions of pentamethylcyclopentadienylgallium (**1**)[4] with organic azides. **1** is now available in large-scale quantities.[5] We show that in these reactions novel Ga_2N_2 ring systems are generated.

Results and Discussion

1 reacts with 2,6-dimethylphenyl azide (Xyl-N_3) in THF at room temperature to yield the dimeric iminogallane **2** (2,4-digalla-1,3-diazetidine) (see Scheme 1). Iminogallanes with coordination number 3 at the Ga and at the N centers are unknown so far, even though there is currently intensive research on this topic.[6] The colorless air and moisture sensitive compound **2** melts at 210−220 °C but decomposes slowly under these conditions.

The solid-state structure of **2** could be determined by X-ray diffraction studies. Crystallographic data are given in Table 1; selected bond length and angles are collected in Table 2. The molecular structure depicted in Figure 1 shows a planar approximately square Ga_2N_2 ring; in fact, the molecule is positioned on a crystallographic center of inversion. Small deviations of the Ga−N−Ga (90.82(8)°) and N−Ga−N angles (89.18(8)°) from 90° and slightly different neighboring Ga−N distances (1.8704(19) and 1.850(2) Å) result in a slightly distorted geometry of the square. As expected, the mean Ga−N distance (1.860(2) Å) is distinctly shorter than in higher associated iminogallanes with coordination number 4 on the Ga and on the N atoms (~1.99 Å).[6] As a result of the strained Ga_2N_2 ring system, the Ga−Ga distance amounts to only 2.6495(6) Å. This value is distinctly shorter than the sum of the van der Waals radii and is found in a region observed for covalent digallanes;[8] nevertheless there is no evidence for a Ga−Ga bond. The four substituents at the Ga_2N_2 ring are bent away from the ring plane by approximately 8−10° (angle Ga(1a)−Ga(1)−C(1) 172.2(1)°; angle N(1a)−N(1)−C(11) 169.8(3)°). The ring planes of the aryl substituents are orientated in a perpendicular fashion to the Ga_2N_2 ring. In contrast to compound **1** the Cp*-substituents are σ-bonded in **2**; within the C_5 perimeter the typical alternating bond lengths are observed. In solution, compound **2** possesses a dynamic structure. Fast sigmatropic rearrangements in the Cp* part of the molecule lead to averaged NMR signals (^{1}H, ^{13}C) for the Cp* methyl groups and for the Cp* ring

Scheme 1

$$\underset{\mathbf{1}}{2\ \eta^5\text{-Cp*Ga}} + 2\ \text{Xyl-N}_3 \longrightarrow 2\ \text{N}_2 + \underset{\mathbf{2}}{(\eta^1\text{-Cp*GaNXyl})_2}$$

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[6] The few so far known oligomeric iminogallanes have with one exception[6a] been synthesized from aminogallanes by elimination of alkanes.[6b−f] The degree of oligomerization depends on the steric size of the substituents. The smallest systems so far known are heterocubanes of the type (RGaNR′)$_4$. In these compounds, the N atoms as well as the Ga atoms exhibit coordination number 4. Owing to the comparatively drastic conditions during synthesis (thermolysis at ~200 °C) C−H activation is observed for systems with sterically demanding substituents at the N atoms.[7] Therefore, alkane elimination does not seem to be an appropriate synthetic pathway for smaller iminogallanes. (a) Kühner, S.; Kuhnle, R.; Hausen, D.-H.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 25−34. (b) Amirkhalili, S.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1206−1212. (c) Belgardt, T.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H. G. *Angew. Chem.* **1993**, *105*, 1101−1102; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1056. (d) Belgardt, T.; Waezsada, S. D.; Roesky, H. W.; Gornitzka, H.; Häming, L.; Stalke, D.; *Inorg. Chem.* **1994**, *33*, 6247−6251. (e) Cordeddu, F.; Hausen, H.-D.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1996**, *622*, 573−578. (f) Schnitter, C.; Waezsada, S. D.; Roesky, H. W.; Teichert, M.; Usón, I.; Parisini, E.; *Organometallics* **1997**, *16*, 1197−1202.

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Table 1. Crystallographic Data for 2 and 4

empirical formula	$C_{36}H_{48}Ga_2N_2$, **2**	$C_{32}H_{66}Ga_2N_8Si_4$, **4**
fw	648.20	814.73
cryst color, habit	colorless, rhombic	colorless, plates
cryst size	0.50 × 0.50 × 0.30 mm^3	0.05 × 0.20 × 0.30 mm^3
temp	173(2) K	163(2) K
wavelength	Mo Kα 0.710 73 Å (graphite monochromator)	
space group	*P*2(1)/*n*	$P\bar{1}$
unit cell dimens	$a = 12.788(3)$ Å $b = 9.086(2)$ Å $c = 14.702(3)$ Å $\beta = 104.84(2)°$	$a = 9.4749(6)$ Å $b = 9.7282(7)$ Å $c = 13.8581(9)$ Å $\alpha = 88.476(1)°$ $\beta = 70.042(1)°$ $\gamma = 64.883(1)°$
volume	1651.3(6) $Å^3$	1076.56(12) $Å^3$
Z	2	1
density (calcd)	1.304 Mg/m^3	1.257 Mg/m^3
θ range for data collection	2.78−30°	2.33−27°
no of reflns collected	5162	10 351
no. of independent reflns	4805 ($R_{Int} = 0.0153$)	4613 ($R_{Int} = 0.0432$)
abs corr	empirical from Ψ-scans	semiempirical from equivalents
no. of reflns with $I > 2\sigma(I)$	3521	3361
final *R* indices [$I > 2\sigma(I)$]	$R_F = 0.0410$, $wR_{F2} = 0.0823$	$R_F = 0.0420$, $wR_{F2} = 0.0796$
no. of param	188	219
largest diff peak and hole	0.351 and −0.467 e $Å^{-3}$	0.437 and −0.380 e $Å^{-3}$
diffrractometer used	Siemens P2(1) diffractometer	Siemens SMART CCD
programs used	Siemens SHELXTL plus/SHELXL-97	
structure refinement	full-matrix least-squares on F^2	

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 2

Ga(1)−N(1)	1.8704(19)	Ga(1)···Ga(1a)	2.6495(6)
Ga(1)−N(1a)	1.850(2)	Ga(1)−C(1)	1.981(2)
		N(1)−C(11)	1.402(3)
Ga(1)−N(1)−Ga(1a)	90.82(8)	Ga(1a)−Ga(1)−C(1)	172.2(1)
N(1)−Ga(1)−N(1a)	89.18(8)	N(1a)−N(1)−C(11)	169.8(3)
C(1)−Ga(1)−N(1)	131.82(9)	C(11)−N(1)−Ga(1)	133.20(16)
C(1)−Ga(1)−N(1a)	138.15(9)	C(11)−N(1)−Ga(1a)	134.21(16)

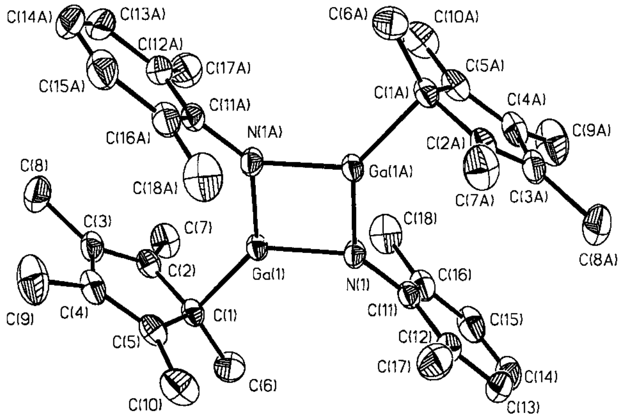


Figure 1. Molecular structure of [η^1-Cp*GaNXyl]$_2$, **2**.

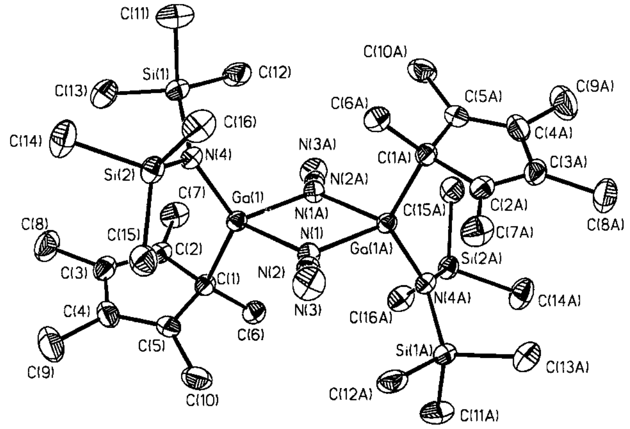
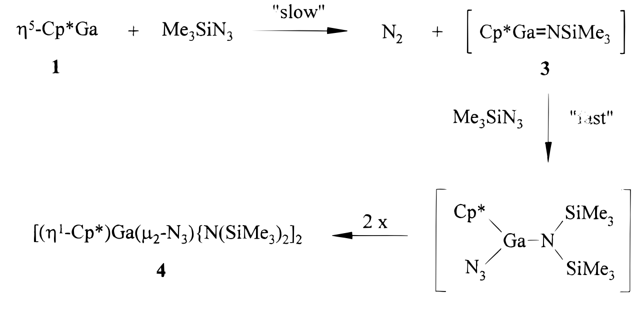


Figure 2. Molecular structure of [(η^1-Cp*)Ga(μ_2-N_3){N($SiMe_3$)$_2$}]$_2$, **4**.

Scheme 2



atoms. The aryl substituents as well show a simple signal pattern in the corresponding NMR spectra. Probably owing to the steric shielding of the Ga_2N_2 ring system by the Cp* and by the aryl substituents, further oligomerization of **2** is prevented.

In comparison to the fast reaction of **1** with Xyl-N_3, the analogous reaction with trimethylsilyl azide (Me_3SiN_3) is much slower. The α,α-azide-bridged dimer [(η^1-Cp*)Ga(μ_2-N_3){N($SiMe_3$)$_2$}]$_2$ (**4**) is formed in almost quantitative yield according to a process described in Scheme 2. The colorless compound melts at 132 °C and shows no tendency to explode by gentle heating or by mechanical treatment despite the presence of covalently bound azide functions. Compound **4** can formally be regarded as the product of an "azidosilylation" of iminogallane **3** generated in the first step of the sequence. Evidence for the presence of **3** could not be found even when only 1 equiv of Me_3SiN_3 was added very slowly to a diluted solution of **1**. Obviously, the second reaction step is much faster than the first one.

Compound **4** exhibits a rhomb-shaped Ga_2N_2 ring system, as could be shown by an X-ray structure analysis (see Figure 2 and Table 3). Within the ring, two small N−Ga−N angles (75.58(19)°) and correspondingly two larger Ga−N−Ga angles (104.42(10)°) are

Table 3. Selected Bond Lengths [Å] and Angles [deg] for 4

Ga(1)−N(1)	2.061(2)	Ga(1)−C(1)	2.020(3)
Ga(1)−N(1a)	2.076(2)	N(1)−N(2)	1.235(3)
Ga(1)−N(4)	1.872(2)	N(2)−N(3)	1.135(3)
N(1)−Ga(1)−N(1a)	75.58(10)	C(1)−Ga(1)−N(4)	128.14(11)
Ga(1)−N(1)−Ga(1a)	104.42(10)	N(1)−N(2)−N(3)	177.8(3)

observed. The Ga_2N_2 ring is planar and positioned on a crystallographic center of inversion. The endocyclic Ga−N bonds are approximately equal in length (mean: 2.069(2) Å); as expected, they are longer than those in **2**. Comparable Ga−N distances are found in the α,α-azide-bridged polymer $\{Me_2Ga(\mu_2\text{-}N_3)\}_n$ (2.039(6) and 2.051(6) Å).[9] A symmetric structure with two Ga atoms α,α-bridged by two azide groups is unprecedented so far, to the best of our knowledge.[10] Compared to the endocyclic bonds, the exocyclic Ga−N distances are significantly shorter (1.872(2) Å). Similar Ga−N distances are found in $\{(Me_3Si)_2N\}_3Ga$ (mean value: 1.865 Å).[11] The N atoms of the bis(trimethylsilyl)amino substituents in **4** are surrounded in a trigonal planar fashion (angle sum: 359.65°). Within the azide groups, a long N(1)−N(2) (1.235(3) Å) and a short N(2)−N(3) distance (1.135(3) Å) are found. The corresponding N(1)−N(2)−N(3) angle amounts to 177.8(3)°. In the room-temperature ^1H NMR spectrum of **4** constrained motion within the $N(SiMe_3)_2$ and within the Cp* moiety is documentated by broad resonances for the respective methyl groups. Sharp signals at 60 °C indicate free rotation of the $N(SiMe_3)_2$ groups and fast sigmatropic rearrangements within the Cp*Ga fragments.

Interestingly, different products are found in comparable reactions with $(Cp^*Al)_4$. Generally, no "azidosilylations" are observed with silyl azides. With sterically demanding silyl azides, dimeric iminoalanes are formed,[12] whereas the reaction with Me_3SiN_3 leads to an unsymmetric iminoalane after complicated rearrangements.[13] Furthermore, the reaction of $(Cp^*Al)_4$ with an *o*-methylated phenyl azide does not yield the iminoalane counterpart to **2** but the product of a subsequent C−H activation.[13]

In summary, we could build up new Ga_2N_2 ring systems by reaction of **1** with organic azides under kinetic control. A 1,3-dipolar addition can be envisaged as the initial step in these reactions. Future investigations will show whether the variation of organic ligands will allow the stabilization of a monomeric iminogallane. Furthermore, the properties of **2** and **4** as precursors for the deposition of GaN will be examined.

Experimental Section

General Data. All manipulations were carried out under purified argon atmosphere using standard vacuum techniques. The solvents were purified by conventional means and distilled immediately prior to use. Me_3SiN_3 was commercially available; $XylN_3$ was prepared according to literature methods.[14] The melting point determinations were performed using a Büchi 510 melting point apparatus. Elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld. The NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer (^1H 500.1 MHz; $^{13}C\{^1H\}$ 125.8 MHz); $^{29}Si\{^1H\}$ 99.4 MHz). Chemical shifts are reported in ppm and are referenced to the solvent as internal standard.

Preparation of $(\eta^1\text{-}Cp^*GaNXyl)_2$ (2). A solution of 2,6-dimethylphenyl azide (0.38 g, 2.38 mmol) in THF (2 mL) was added dropwise to a solution of **1** (0.47 g, 2.29 mmol) in THF (5 mL) accompanied by rapid gas evolution. After stirring at 25 °C for 1 h, all volatile components were removed in vacuo. Subsequently, the light brown crude product was recrystallized from an *n*-hexane/toluene mixture at −30 °C, to give 0.56 g (0.86 mmol) of $(\eta^1\text{-}Cp^*GaNXyl)_2$, **2** (75% yield based on **1**), as a colorless solid.

Mp: 210−220 °C (slow decomposition). ^1H NMR (C_6D_6): $\delta = 1.56$ (s, 30 H, C_5Me_5), 2.30 (s, 12 H, Ar-Me), 6.38 (t, 2 H, p-Ar−H, $^3J_{H-H} = 7.4$ Hz), 7.11 (d, 4 H, m-Ar−H, $^3J_{H-H} = 7.4$ Hz). ^{13}C NMR (C_6D_6): $\delta = 11.19$ (C_5Me_5), 20.34 (Ar−*Me*), 119.58 (C_5Me_5) 120.22 (p-Ar−C), 127.71 (m-Ar−C), 132.31 (o-Ar−C), 151.80 (ipso-Ar−C). Anal. Calcd for $C_{36}H_{48}Ga_2N_2$ (M = 648.20 g mol^{-1}): C, 66.7; H, 7.46; N, 4.32. Found: C, 66.4; H, 7.74; N, 4.26.

Preparation of $[(\eta^1\text{-}Cp^*)Ga(\mu_2\text{-}N_3)\{N(SiMe_3)_2\}]_2$ (4). A solution of Me_3SiN_3 (1.27 g; 11.0 mmol) and **1** (1.02 g; 4.98 mmol) in 15 mL of THF was stirred for 3 days at 25 °C. The reaction was indicated by a very slow evolution of gas. After all volatile components were removed in vacuo, the light yellow residue was dissolved in pentane (8 mL). Subsequently, the solution was reduced in volume and stored at −30 °C. After 3 days 1.76 g (1.13 mmol; 86% based on **1**) of $[(\eta^1\text{-}Cp^*)Ga(\mu_2\text{-}N_3)\{N(SiMe_3)_2\}]_2$ (**4**) could be isolated as a colorless crystalline solid.

Mp: 132 °C. ^1H NMR (toluene-d_8, 60 °C): $\delta = 0.22$ (s, 36 H, $SiMe_3$); 1.86 (s, 30 H, C_5Me_5). ^{13}C NMR (toluene-d_8, 60 °C): $\delta = 5.26$ ($SiMe_3$), 12.79 (C_5Me_5), 121.22 (C_5Me_5). ^{29}Si NMR (toluene-d_8, 60 °C): $\delta = 1.91$ ($SiMe_3$). Anal. Calcd for $C_{32}H_{66}N_8Ga_2Si_4$ (M = 814.73 g mol^{-1}): C, 47.18; H, 8.17; N, 13.75. Found: C, 47.12; H, 8.13; N, 13.50.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and selected bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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