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Differing Reactivities of Cp*Ga toward Diazabutadienes: Synthesis of Novel 1-Galla-2,5-diazoles and of the Known Radical Ga[Bu^t-DAB]$_2$

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The heterocycles $[(\eta^1\text{-Cp*})\overline{\text{GaN(Dipp)CH}{=}\text{CHN}}(\text{Dipp})]$ (**1**) and $[(\eta^1\text{-Cp*})\overline{\text{GaN(Dep)CH}{=}\text{CHN}}(\text{Dep})]$ (**2**) were obtained by oxidative addition of (η^5-pentamethylcyclopentadienyl)-gallium(I) (Cp*Ga) to Dipp-DAB (1,4-bis(2,6-diisopropylphenyl)-1,4-diazabuta-1,3-diene) and Dep-DAB (1,4-bis(2,6-diethylphenyl)-1,4-diazabuta-1,3-diene), respectively. Compounds **1** and **2** are the first examples of monomeric gallium-containing heterocycles of the diazabutadiene (DAB) type. **1** was structurally characterized by X-ray crystallography. In contrast, the reaction of Cp*Ga with Bu^t-DAB (1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene) led to the formation of the known radical (Ga[Bu^t-DAB]$_2$) (**3**) in high yield, thus providing an alternative synthesis to the cocondensation technique used previously. Radical **3** was further characterized by ^{1}H NMR spectroscopy and cyclic voltammetric studies, which revealed two reversible oxidation steps and one reversible reduction step.

Introduction

During the last years there has been great interest in heterocycles of the diazabutadiene (DAB) type containing group 13 elements due to the isoelectronic relationship between these heterocycles (type I, Figure 1) and the corresponding cyclic carbenes, silylenes, and germylenes (type II).[1,2] Research in this area has been highlighted by the synthesis of the first carbene analogue with low-valent gallium as the heteroatom by Schmidbaur et al. (III, Figure 1).[3]

Attempts to prepare the desired heterocycles of type I were based for a long time on the reaction of the dilithio derivatives of the DABs with group 13 trihalides or organodihalides.[4,5] Whereas the resulting compounds are monomeric in the solid state in the case of boron, the aluminum and gallium derivatives were found to be dimeric, containing an M_2N_2 ring skeleton. Dimerization can be avoided by providing an additional donor function to the organoaluminum or organogallium unit.[6] The availability of stable organometallic compounds with a group 13 element in the formal oxidation state +I led to a new synthetic approach: the oxidative addition of Cp*Al to Mes-DAB (1,4-bis(2,4,6-trimethylphenyl)-1,4-diazabuta-1,3-diene) resulted in the formation of the first monomeric aluminum-containing heterocycle of the DAB type.[7] Here we report the reaction of Cp*Ga[8] with different *N*-substituted diazabutadienes.

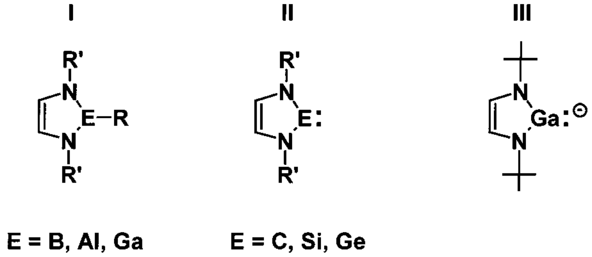

Figure 1. Isoelectronic relationship between heterocycles of the DAB type incorporating group 13 and group 14 elements.

Results and Discussion

The reaction of Cp*Ga with 1 equiv of Dipp-DAB or Dep-DAB in THF at room temperature led to the formation of compounds **1** and **2**, respectively, as indicated by a color change from yellow to red (Scheme 1). Compound **1** was isolated in high yield as an air-sensitive, orange, waxy solid, whereas **2** was obtained as a red oil. Both compounds readily dissolve in *n*-hexane, toluene, and THF. They were shown to be monomeric in *n*-hexane solution by molecular weight determination and in the gas phase by mass spectrometry.

Single crystals suitable for X-ray crystallography were obtained from a concentrated solution of **1** in toluene

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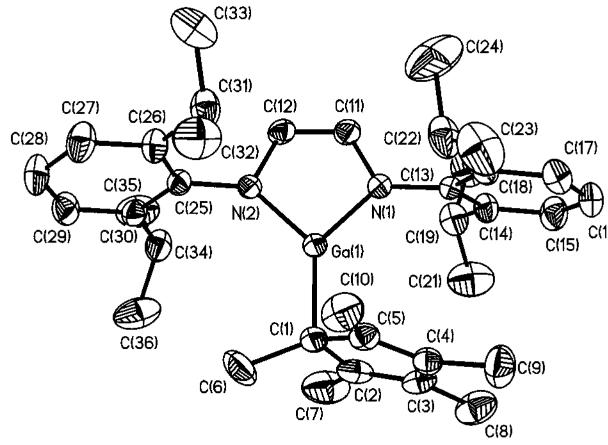
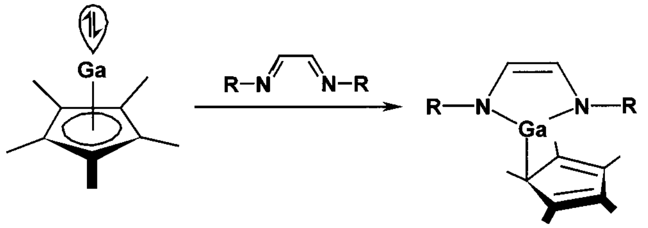


Figure 2. ORTEP plot of **1**.

Scheme 1



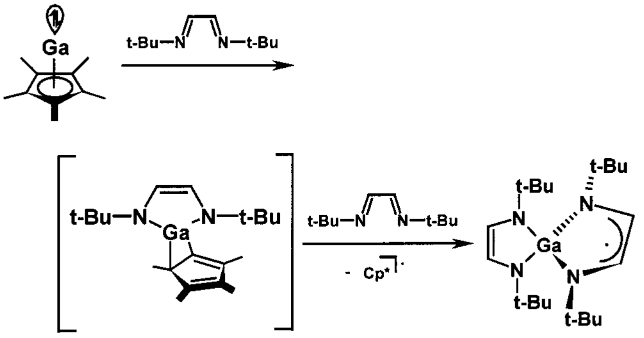
R = 2,6-Diisopropylphenyl 1
2,6-Diethylphenyl 2

at room-temperature. **1** crystallizes in the space group *C*2/*c* (Figure 2).

The Cp* group in **1** is η^1-bonded to gallium. Within the Cp* group the alternating carbon−carbon distances are typical for a σ-bonding mode. The angle Ga−C−Cp*-(ring centroid) is 106°. The expected value for a σ-bonding mode is 127.5°, and a $\eta^1(\pi)$-bonding mode would require an angle smaller than 90°. The experimental value is, therefore, in the borderline region.[9] The sum of the angles at the gallium atom is 360°. The gallium−carbon distance is 1.973(4) Å. The GaN_2C_2 ring is planar within experimental error. The carbon−carbon (1.343(5) Å) and average carbon−nitrogen (1.399(5) Å) distances correspond to bond orders of 2 and 1, respectively, and the average gallium−nitrogen distance (1.850(3) Å) falls within the single-bond range.[10] With regard to the question of heteroaromaticity, the observed data suggest a localized electronic structure. The nitrogen atoms adopt a slightly distorted trigonal planar geometry, with the aromatic substituents being twisted against each other by approximately 10°.

In solution, fast dynamic processes within the Cp* unit on one hand and a hindered rotation of the aromatic substituents on the other can be observed for both **1** and **2**. In the ^{1}H NMR spectrum of **1** in THF-d_8, only one signal at 1.48 ppm is detected for the five methyl groups of the Cp* unit, indicating fast sigmatropic rearrangements. Two doublets detected at 1.19 and 1.27 ppm for the methyl protons of the isopropyl groups are indicative of hindered rotation of the aromatic substituents, leading to diastereotopy within the

Scheme 2



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isopropyl groups. The ^{1}H NMR spectrum of **2** is characterized by a singlet at 1.53 ppm (Cp*) and two quartets at 2.81 and 2.60 ppm (CH_2CH_3) for the same reasons. A triplet for the methyl groups is detected at 1.24 ppm.

The reaction of Cp*Ga with Bu^t-DAB results in the formation of the radical [Ga(Bu^t-DAB)$_2$] (**3**), which can be isolated as dark green crystals in 90% yield. **3** was first isolated in 1989 by Cloke et al. by cocondensation of gallium vapor with Bu^t-DAB in 20% yield.[11] The X-ray crystal structure obtained by our group is identical with the structure reported by Cloke et al. within the limit of experimental error.

The formation of **3** most likely involves the reaction pathway shown in Scheme 2. The first step is a formal [4 + 2] cycloaddition leading to an intermediate similar to **1** and **2** (Scheme 2). The elimination of the Cp* substituent in the second step probably is facilitated by the high nucleophilicity of the nitrogen atoms of Bu^t-DAB due to the strong electron-donating inductive effect of the *tert*-butyl groups.

The oxidation state of the gallium atom in **3** has been the subject of some controversy. Cloke, Raston, and coworkers have referred to **3** as a unique example of a gallium(II) complex.[11−13] They based their assignment on the dominance in its EPR spectrum by a quartet of about 18 G due to the ^{69}Ga and ^{71}Ga isotopes. Kaim et al. believed the assignment of the EPR spectrum to be inadequate and gave reasonable arguments for **3** being an example of a gallium(III) complex with localized, mixed-valent DAB ligands on the EPR time scale in solution.[14] These results were in good agreement with simple extended Hückel calculations carried out later on by Cloke et al. which predict two degenerate HOMOs having only very little gallium contribution.[15] As these HOMOs are filled with three electrons, a Jahn−Teller distortion of the ^{2}E ground state is the consequence, one electron being trapped on one ligand and two on the other.

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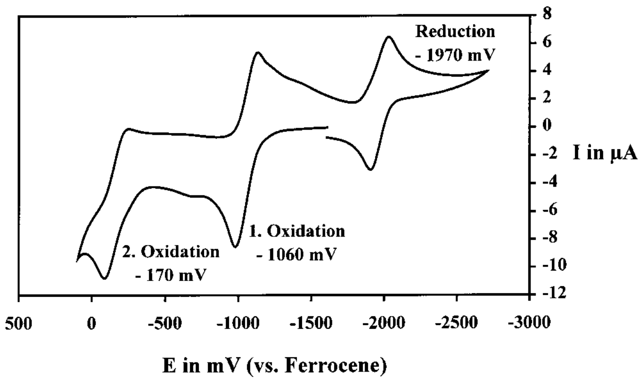

Figure 3. Cyclic voltammogram of **3** in THF/0.1 M $[Bu_4N][BF_4]$ (scan speed 100 mV/s).

In this context it is interesting to note that we have studied **3** by means of ^{1}H NMR spectroscopy. The spectrum in toluene-d_8 is characterized by a very broad signal at −3.73 ppm due to the *tert*-butyl groups. Furthermore, three vinylic proton signals are seen at 1.11, 1.65, and 1.72 ppm, as expected if one assumes localized mixed-valent DAB ligands on the NMR time scale as well.

To determine the redox properties of **3**, we carried out cyclic voltammetric studies. In contrast to the results published by Scott et al., we found that **3** in THF solution undergoes two reversible oxidations at −170 and −1060 mV and one reversible reduction at −1970 mV.[16] The peak separations are 80 mV (**2**/**2**$^+$), 90 mV (**2**$^+$/**2**$^{2+}$), and 70 mV (**2**/**2**$^-$), respectively (Figure 3). The isolation of redox derivatives of **3** is at present the subject of further work by us.

The reactivity of the DABs toward Cp*Ga is strongly dependent on the substituents on the nitrogen atoms. With Xyl-DAB (1,4-bis(2,6-dimethylphenyl)-1,4-diazabuta-1,3-diene) or Dip-DAB (1,4-diisopropyl-1,4-diazabuta-1,3-diene) no definite products could be isolated.

Experimental Section

General Comments. All manipulations were carried out under a purified argon atmosphere using standard vacuum techniques. The solvents were purified by conventional means and distilled immediately prior to use. Cp*Ga,[8] Dipp-DAB,[17] Dep-DAB,[17] and Bu^t-DAB[18] were prepared according to the literature. Mass spectra (CI) were recorded on a Varian 311 A mass spectrometer. Only characteristic fragments and isotopes of the highest abundance are listed. Elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld. NMR spectra were recorded in THF-d_8 or toluene-d_8 using a Bruker Avance DRX 500 spectrometer (^{1}H, 500.1 MHz; ^{13}C{^{1}H}, 125.8 MHz). Chemical shifts are reported in ppm and were referenced to the solvent resonances as internal standard. IR data were collected using a Bruker Vektor 22-FT spectrometer. The samples were measured as KBr pellets. Molecular weight determinations were carried out by the method of Signer.[19]

Electrochemical Measurements. The cyclic voltammogram was recorded on an EG&G potentiostat, Model 273A, controlled by M 250/270 software.The supporting electrolyte was tetrabutylammonium fluoride (TBAPF), which was purchased from Fluka and used without further purification. The electrolyte concentration was 0.1 M. The voltammetric measurements were performed using a platinum-disk electrode (d = 2 mm) which was polished prior to use. Potentials were calibrated by the method of Gagné and are quoted vs the ferrocenium−ferrocene couple as internal standard.[20] A platinum wire was used as a counter electrode.

Preparation of 1. A slight excess of Cp*Ga (0.23 g, 1.10 mmol) was added to a stirred solution of Dipp-DAB (0.38 g, 1.00 mmol) in THF (30 mL) at room temperature. While the reaction mixture was stirred for 1 h, its color changed from initially light yellow to orange. Subsequently, all volatile components were removed in vacuo to yield 0.54 g of **1** (0.93 mmol, 93% based on Dipp-DAB) as an orange crystalline solid. Single crystals suitable for X-ray crystallography were obtained by recrystallization from toluene at room temperature.

Mp: 56 °C. ^{1}H NMR (THF-d_8): δ 1.19 (d, 12H, isopropyl), 1.27 (d, 12 H, isopropyl), 1.48 (s, 15 H, Cp* methyl), 3.58 (sep, 4 H, isopropyl), 5.70 (s, 2 H, vinyl-H), 7.11 (m, 6 H, aryl H). ^{13}C NMR (THF-d_8): δ 12.78 (Cp* methyl), 23.67 (isopropyl), 26.55 (isopropyl), 28.67 (isopropyl), 120.39 (aryl), 121.00 (Cp* ring), 123.58 (aryl), 125.56 (aryl), 146.53 (aryl), 147.09 (C=C). IR (cm^{-1}, KBr): 3061 (w), 2960 (s), 2865 (m), 1661 (w), 1623 (w), 1440 (m), 800 (w). MS (CI+, relative intensity): m/z 581 (M$^+$, 2), 447 (M − Cp*, 5), 379 (Dipp-DAB, 100), 333 (Dipp-DAB − isopropyl, 44), 205 (Cp*Ga, 56), 137 (Cp*H, 34), 69 (Ga, 12). Anal. Calcd for $C_{36}H_{51}N_2Ga$ (M_r = 581.53): C, 74.36; H, 8.84; N, 4.82. Found: C, 74.06; H, 8.88; N, 4.80.

Preparation of 2. The same procedure was used in the reaction of Cp*Ga (0.23 g, 1.10 mmol) with Dep-DAB (0.32 g, 1.00 mmol) in THF (30 mL). A color change from orange to red was observed. Compound **2** (0.48 g, 0.91 mmol; 91% yield based on Dep-DAB) was obtained as a red oil.

^{1}H NMR (THF-d_8): δ 1.21 (t, 12H, ethyl), 1.47 (s, 15 H, Cp* methyl), 2.54 (q, 4 H, ethyl), 2.76 (q, 4 H, ethyl), 5.69 (s, 2 H, vinyl-H), 7.06 (m, 6 H, aryl H). ^{13}C NMR (THF-d_8): δ 12.12 (Cp* methyl), 12.12 (ethyl), 15.80 (ethyl), 25.59 (ethyl), 119.25 (aryl), 120.72 (Cp* ring), 125.07 (aryl), 125.55 (aryl), 141.44 (aryl), 148.10 (C=C). IR (cm^{-1}, KBr): 3062 (w), 2963 (s), 2871 (m), 1665 (w), 1622 (w), 1454 (m), 802 (w). MS (CI+, reative intensity): m/z 320 (Dep-DAB, 100), 291 (Dep-DAB − ethyl, 18), 137 (Cp*H, 75). Anal. Calcd for $C_{32}H_{43}N_2Ga$ (M_r = 525.55): C, 73.13; H, 8.25; N, 5.35. Found: C, 72.76; H, 8.29; N, 5.33.

Preparation of 3. Cp*Ga (0.20 g, 1.00 mmol) was added to a stirred solution of Bu^t-DAB (0.34 g, 2.00 mmol) in toluene (30 mL). While the reaction mixture was stirred for 12 h, it slowly became dark green. Subsequently, all volatile components were removed in vacuo to crystallize the crude product. Recrystallization from toluene at −30 °C yielded 0.37 g of **3** (0.91 mmol, 91%) as dark green crystals.

Mp: 192 °C. ^{1}H NMR (298 K, toluene-d_8): δ −3.73 (s, 36H, *tert*-butyl), 1.11 (s, 1 H, vinyl H), 1.65 (s, 1 H, vinyl H), 1.72 (s, 1 H, vinyl H). IR (cm^{-1}, KBr): 3041 (w), 2967 (s), 1631 (w), 1553 (w), 1476 (m), 1456 (m), 1382 (w), 1369 (m), 1354 (m), 1263 (m), 1224 (s), 1108 (s), 775 (w), 620 (w), 572 (w), 478 (w). MS (EI, relative intensity): m/z 406 (M$^+$, 22), 169 (DAB$^+$, 7), 69 (Ga$^+$, 6), 57 ($C_4H_9^+$, 100). Anal. Calcd for $C_{20}H_{40}N_4Ga$ (M_r = 406.28): C, 59.13; H, 9.92; N, 13.79. Found: C, 59.42; H, 9.93; N, 13.58.

Supporting Information Available: Tables of crystal data, positional and thermal parameters, and selected bond lengths and angles of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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