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# Synthesis, Structure, and Reactivity of a Superbulky low-Valent $\beta$ -diketiminate Ga(I) Complex

Tim Richter,<sup>[a]</sup> Stefan Thum,<sup>[a]</sup> Oliver P. E. Townrow,<sup>[a]</sup> Michael Wiesinger,<sup>[a]</sup> Jens Langer,<sup>[a]</sup> and Sjoerd Harder<sup>\*[a]</sup>

Dedicated to Professor Hubert Schmidbaur on the occasion of his 90<sup>th</sup> birthday

A low-valent Ga<sup>I</sup> complex with the superbulky  $\beta$ -diketiminate ligand <sup>DIPeP</sup>BDI (HC[C(Me)N-DIPeP]<sub>2</sub>, DIPeP = 2,6-C(H)Et<sub>2</sub>-phenyl) was obtained by reduction of (<sup>DIPeP</sup>BDI)Ga<sub>2</sub> (1) with KC<sub>8</sub> in toluene. Considering that (BDI)Ga<sup>I</sup> and analogue (BDI)Al<sup>I</sup> complexes are prone to decomposition and can generally only be obtained in low yields (20–40%), the quantitative formation of (<sup>DIPeP</sup>BDI)Ga<sup>I</sup> (2) is remarkable and no doubt related to its excellent thermal stability even in refluxing toluene. Although the low-valent metal center in 2 is sterically protected by the superbulky <sup>DIPeP</sup>BDI ligand, it is readily oxidized by N<sub>2</sub>O to give intermediate (<sup>DIPeP</sup>BDI)Ga=O which readily decomposed by

abstracting a proton from the backbone Me-substituent. Reaction with trimethylsilyl azide gave an intermediate imido complex (<sup>DIPeP</sup>BDI)Ga=N(SiMe<sub>3</sub>)<sub>2</sub> which reacted with a second equivalent of Me<sub>3</sub>SiN<sub>3</sub> to a mixture of an azide/amido complex (<sup>DIPeP</sup>BDI)GaN<sub>3</sub>[N(SiMe<sub>3</sub>)<sub>2</sub>] (4) and a tetrazagallole complex (<sup>DIPeP</sup>BDI)Ga[N<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>] (5) in a 1:2 ratio. Whereas the azide/amido complex 4 could be structurally characterised, the tetraazagallole complex 5 was identified by NMR spectroscopy. DFT calculations on (<sup>DIPeP</sup>BDI)Ga<sup>I</sup> (2) and its reaction products complement this study.

## Introduction

Owing to the inert-pair effect,<sup>[1]</sup> gallium should be relatively stable in the +I oxidation state. However, first Ga<sup>I</sup> complexes were only obtained at the end of the 20<sup>th</sup> century.<sup>[2,3]</sup> Pioneering studies by Schmidbaur and coworkers led to examples of cationic and anionic Ga<sup>I</sup> complexes (I, II; Scheme 1).<sup>[4,5]</sup> First neutral Ga<sup>I</sup> complexes like III, reported by Uhl,<sup>[6]</sup> show strong tendencies to aggregate and are only monomeric in highly diluted solutions. Similarly, an early complex reported by Schnöckel, Cp\*Ga<sup>I</sup>, crystallized as a large hexameric aggregate.<sup>[7]</sup> Later studies showed that by the use of multidentate or extremely bulky ligands, discrete monomeric Ga<sup>I</sup> complexes could be isolated (IV–VII).<sup>[8–11]</sup> The  $\beta$ -diketiminate (BDI) complex V is isostructural to its earlier reported Al<sup>I</sup> analogue,<sup>[12]</sup> which is arguably the most studied group 13 representative in the +I oxidation state. As the HOMO-LUMO gaps in Ga<sup>I</sup> complexes are generally significantly larger than those in their comparable Al<sup>I</sup> complexes,<sup>[13,14]</sup> the Ga<sup>I</sup> analogues are noticeably less reactive.

This helps to explain why there are less reports on their reactivity.

Herein, we aim to prepare a Ga<sup>I</sup> complex with the very bulky BDI ligand <sup>DIPeP</sup>BDI (HC[C(Me)N-DIPeP]<sub>2</sub>, DIPeP = 2,6-C(H)Et<sub>2</sub>-phenyl). The DIPeP-substituent is considerably bulkier than the ubiquitously used DIPP-substituent (2,6-C(H)Me<sub>2</sub>-phenyl) in V,<sup>[15]</sup> resulting in enhanced steric protection and improved solubility of its complexes in non-polar alkane solvents. The latter is a prerequisite for the isolation of low-oxidation-state complexes of the heavier group 2 metals which have shown high reactivity towards aromatic solvents.<sup>[16]</sup> We recently reported<sup>[16]</sup> on the synthesis, structure and reactivity of (<sup>DIPeP</sup>BDI)Al<sup>I</sup> and now extend this chemistry with investigations on the (<sup>DIPeP</sup>BDI)Ga<sup>I</sup> complex. As Ga<sup>I</sup> complexes are considerably less reactive than their Al<sup>I</sup> counterparts, it is anticipated that increased ligand bulk may allow for isolation of strongly dipolar complexes like (<sup>DIPeP</sup>BDI)Ga=O and (<sup>DIPeP</sup>BDI)Ga=NR.

## Results and Discussion

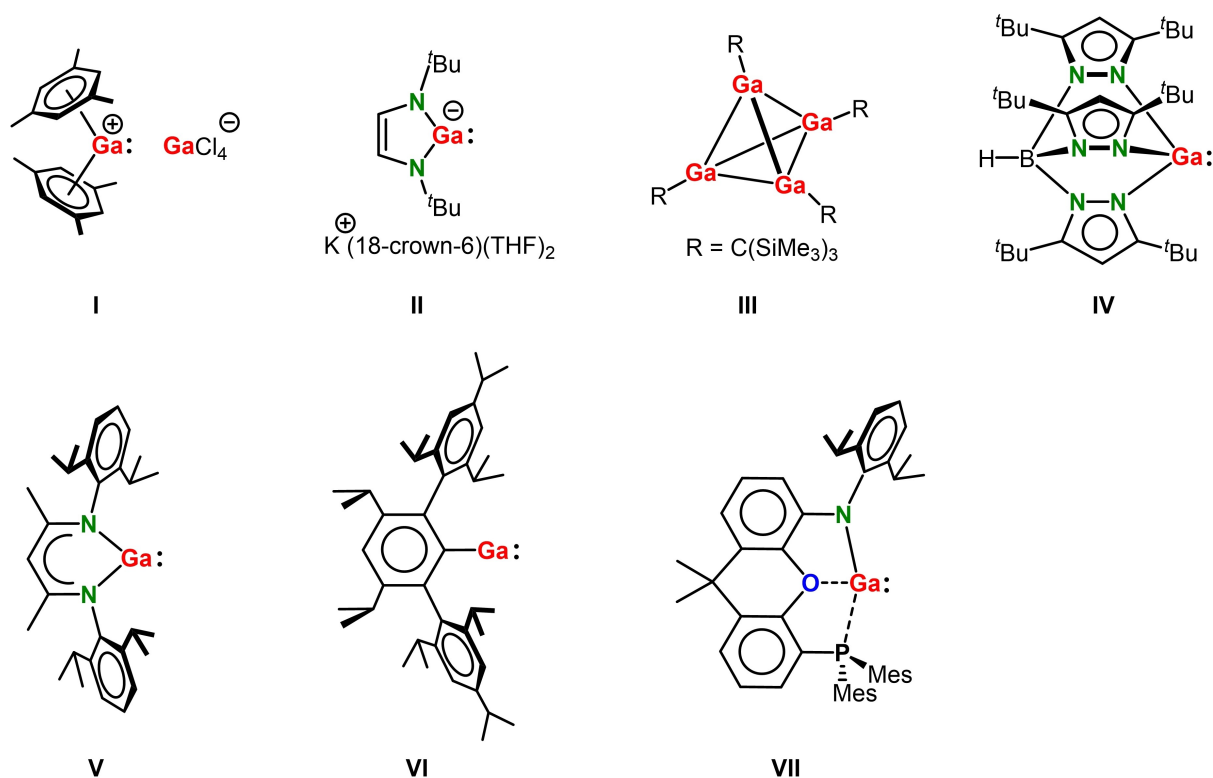
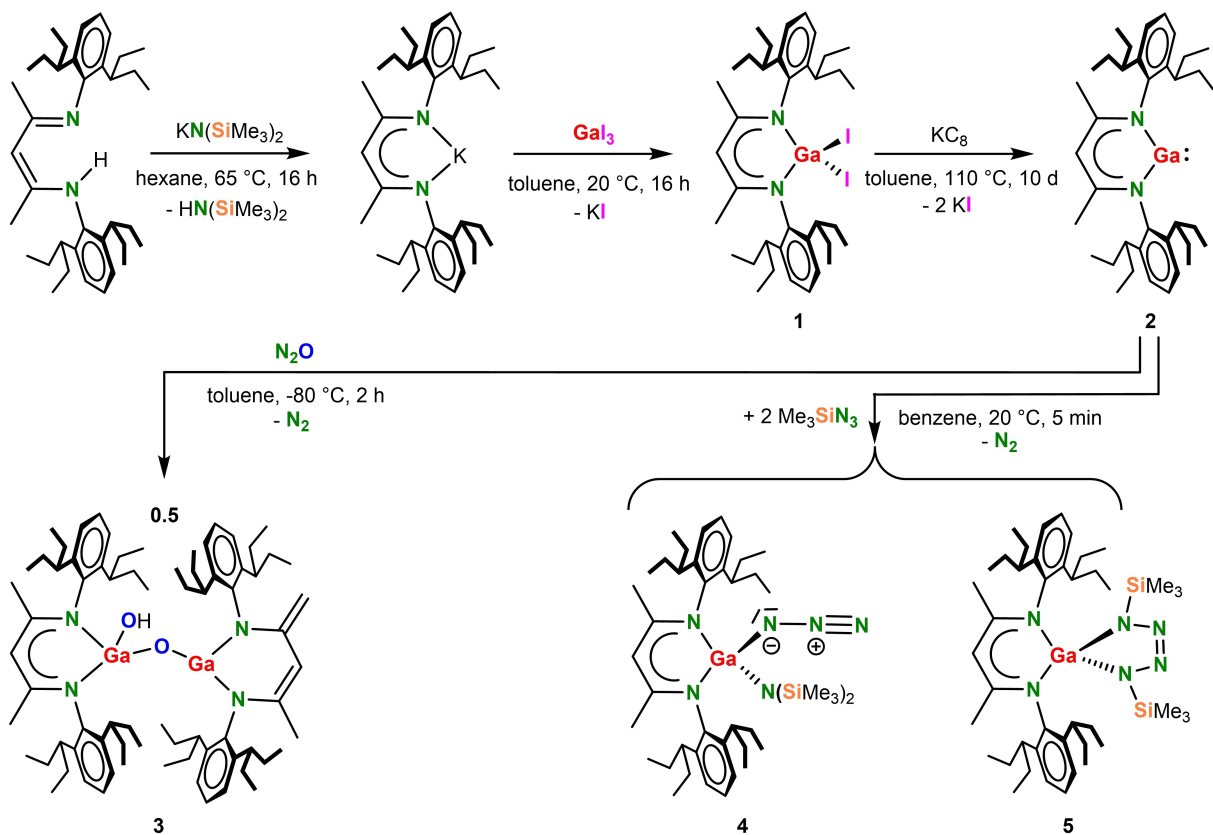
### Syntheses and Structures

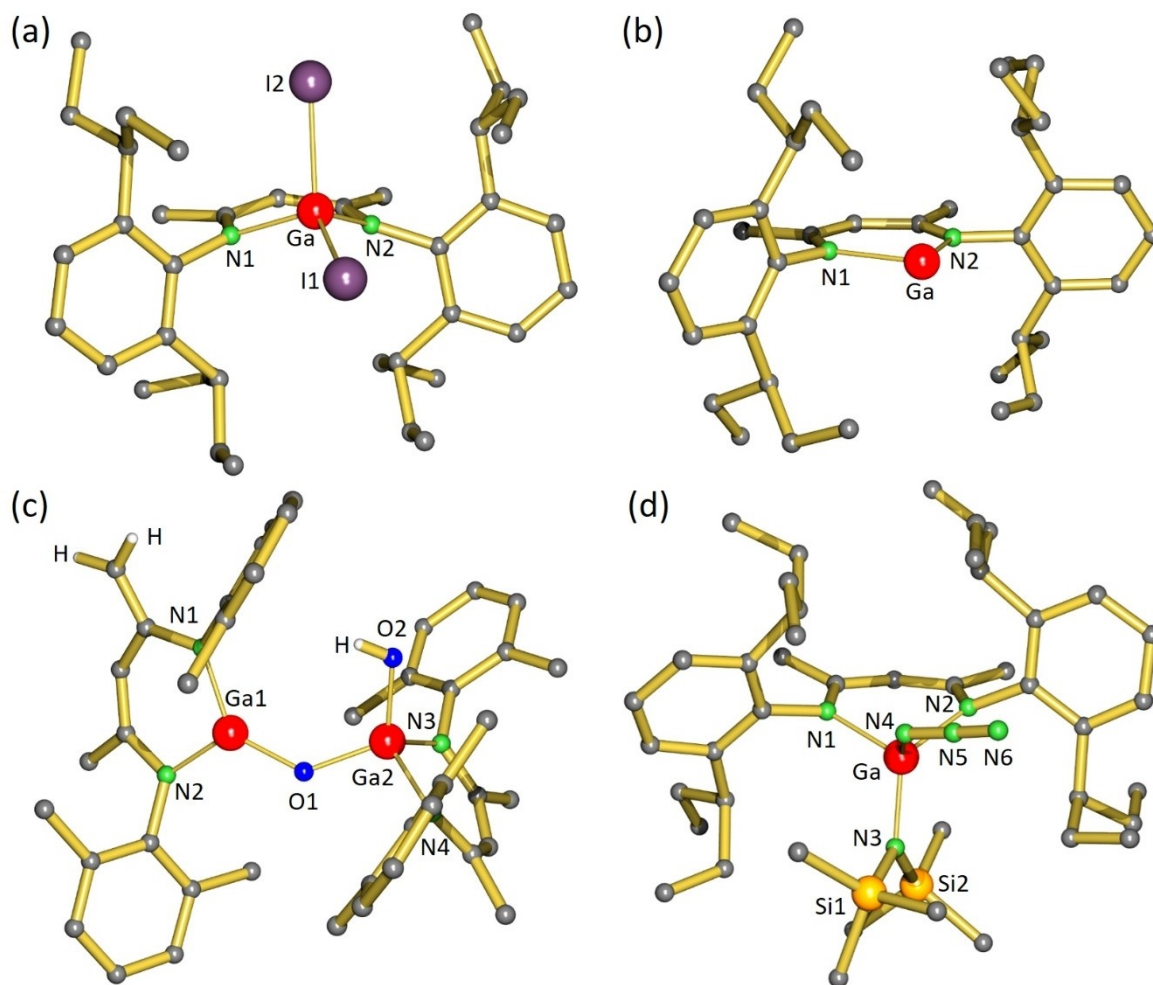
Salt-metathesis between (<sup>DIPeP</sup>BDI)K, obtained according to an earlier reported procedure,<sup>[16a]</sup> and Ga<sub>3</sub> gave (<sup>DIPeP</sup>BDI)Ga<sub>2</sub> (1) in a yield of 47% (Scheme 2). The product crystallized in the form of colorless crystals in the monoclinic space group P2<sub>1</sub>/n. The crystal structure (Figure 1a) is comparable to that of the less bulky (<sup>DIPP</sup>BDI)Ga<sub>2</sub> (Table 1).<sup>[18]</sup> Both structures show a similar out-of-plane bending of the Ga atom which can be quantified by the distance of the metal to the NCCCN least-squares-plane (Table 1: Ga/NCCCN). Increased steric pressure in 1 did not

[a] T. Richter, S. Thum, Dr. O. P. E. Townrow, Dr. M. Wiesinger, Dr. J. Langer, Prof. Dr. S. Harder  
Inorganic and Organometallic Chemistry, Universität Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany  
E-mail: sjoerd.harder@fau.de

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Scheme 1. Selected examples of seminal Ga<sup>I</sup> complexes.Scheme 2. Synthesis and reactivity of (DIPePBDI)Ga<sup>I</sup> (2).



**Figure 1.** (a) Crystal structure of  $(\text{DIPePBDI})\text{Ga}_2$  (1); Selected geometric data in Table 1. (b) Crystal structure of  $(\text{DIPePBDI})\text{Ga}$  (2); Selected geometric data in Table 1. (c) Crystal structure of **3**. Ethyl groups at DIPeP omitted for clarity. Selected bond lengths (Å): Ga1–N1 1.846(2), Ga1–N2 1.847(2), Ga1–O1 1.734(1), Ga2–N3 1.946(2), Ga2–N4 1.955(2), Ga2–O1 1.806(1), Ga2–O2 1.799(2). (d) Crystal structure of **4**. Selected bond distances (Å) and angles ( $^\circ$ ): Ga–N1 1.969(4), Ga–N2 1.941(4), Ga–N3 1.893(3), Ga–N4 1.904(4), N4–N5 1.209(5), N5–N6 1.144(5), N1–Ga–N2 174.9(5), Si1–N3–Si2 120.6(2), N4–N5–N6 174.9(5).

**Table 1.** Comparison of selected geometric parameters for crystal structures of Ga complexes with  $\text{DIPePBDI}$  and  $\text{DIPePBDI}$  ligands; bond lengths in Å and angles in degrees.

Complex	$(\text{DIPePBDI})\text{Ga}_2$	$(\text{DIPePBDI})\text{Ga}_2$ <sup>[17]</sup>	$(\text{DIPePBDI})\text{Ga}$	$(\text{DIPePBDI})\text{Ga}$ <sup>[9]</sup>
Ga–N	1.937(2) 1.938(2)	1.924(1) 1.948(1)	2.039(1) 2.064(1) 2.056(1) 2.058(1)	2.053(1) 2.056(1)
Ga–I	2.4867(3) 2.5678(3)	2.5082(2) 2.5528(2)	–	–
N–Ga–N	99.57(8)	99.25(5)	88.02(4) 88.33(4)	87.53(5)
I–Ga–I	114.62(1)	109.41(1)	–	–
Ga/NCCCN <sup>[a]</sup>	0.762(1)	0.568(1)	0.023(1) 0.030(1)	0.004(1)

<sup>[a]</sup> Defined as the distance between Ga and the NCCCN least-squares plane.

influence the Ga–N and Ga–I distances. The latter are like the N–Ga–N angles quite similar. However, the much wider I–Ga–I angle in **1** is related the considerably larger DIPeP substituents.

Reduction of  $(^{\text{DIPeP}}\text{BDI})\text{GaI}_2$  with  $\text{KC}_8$  in toluene at  $110^\circ\text{C}$  gave the expected low-oxidation-state product  $(^{\text{DIPeP}}\text{BDI})\text{Ga}^{\text{I}}$  (**2**) in quantitative yield as an essentially pure yellow powder suitable for further reactivity studies (Figure S7). Although the reduction is already observed at much lower temperatures, we chose refluxing toluene and long reaction times in order to obtain complete conversion. The flexible DIPeP-substituents in **2** provide extraordinary solubility in non-polar alkane solvents and there is hardly any product decomposition. For additional purification, the product can be recrystallized from *n*-pentane at  $-35^\circ\text{C}$  to give yellow crystals in 80% yield. Since preparative yields for  $(^{\text{DIPP}}\text{BDI})\text{Al}^{\text{I}}$  and  $(^{\text{DIPP}}\text{BDI})\text{Ga}^{\text{I}}$  are low to moderate (20–40%),<sup>[9,19,20]</sup> the extremely high yields in this procedure are remarkable.

The literature-known Al complex  $(^{\text{DIPP}}\text{BDI})\text{Al}^{\text{I}}$  was originally synthesized by reduction of  $(^{\text{DIPP}}\text{BDI})\text{AlI}_2$  with  $\text{K}^0$  over a three-day period,<sup>[12]</sup> but only yields of 21% can be reached (generally lower). This is likely due to overreduction<sup>[19]</sup> or product decomposition.<sup>[20]</sup> A recent report by Kretschmer and co-workers showed that this method could not be improved by the alternative transmetallation between  $(^{\text{DIPP}}\text{BDI})\text{Na}$  and  $\text{Cp}^*\text{Al}^{\text{I}}$  (toluene,  $90^\circ\text{C}$ , 10 h) which gave a similar yield of 21%.<sup>[20]</sup> These authors also showed that this is likely due to the harsh reaction conditions which result in decomposition of  $(^{\text{DIPP}}\text{BDI})\text{Al}^{\text{I}}$  by C–N bond cleavage. The  $\text{Ga}^{\text{I}}$  analogue was originally synthesized in a 39% yield by salt-metathesis between  $(^{\text{DIPP}}\text{BDI})\text{Li}$  and *in situ* generated “Gal” (a mixture of  $\text{Ga}^0$ ,  $\text{Ga}_2\text{I}_3$  and  $\text{Ga}_2\text{I}_2$ )<sup>[21]</sup> and subsequent reduction with excess  $\text{K}^0$ .<sup>[9]</sup> This method also allows for (BDI)Ga complexes with somewhat less bulky BDI ligands but only in moderate yield.<sup>[22]</sup> Kretschmer and co-workers managed to increase the yield to 66% by an alternative route between  $(^{\text{DIPP}}\text{BDI})\text{Na}$  and  $\text{Cp}^*\text{Ga}^{\text{I}}$ .<sup>[20]</sup> We recently showed that increasing the bulk of the BDI ligand and using a recently implemented freeze-drying method<sup>[23]</sup> gave clean conversion to an essentially pure raw product: reduction of  $(^{\text{DIPeP}}\text{BDI})\text{AlI}_2$  with  $\text{KC}_8$  in benzene ultimately gave  $(^{\text{DIPeP}}\text{BDI})\text{Al}$  in an 81% yield.<sup>[17]</sup> The herein reported quantitative yield of  $(^{\text{DIPeP}}\text{BDI})\text{Ga}^{\text{I}}$  therefore likely originates from increased steric protection and diminished decomposition. As a proof of principle, a solution of  $(^{\text{DIPeP}}\text{BDI})\text{Ga}^{\text{I}}$  in toluene was heated to  $110^\circ\text{C}$  for one week with no signs of decomposition.

Although  $\text{Ga}^{\text{I}}$  complexes can crystallize as Ga–Ga bound dimers,<sup>[24]</sup>  $(^{\text{DIPeP}}\text{BDI})\text{Ga}^{\text{I}}$  (**2**) crystallized as a monomeric complex in the space group  $\text{P}\bar{1}$  with two crystallographically inequivalent, but structurally very similar molecules in the asymmetric unit (Figure 1b, Table 1). The complex shows a structure with a close to planar six-membered NCCCN–Ga ring (the Ga atom resides 0.02–0.03 Å out of the least-squares NCCCN plane). As  $\text{Ga}^{\text{I}}$  is larger than  $\text{Ga}^{\text{III}}$ , the Ga–N bond lengths are circa 0.1 Å longer than those in  $(^{\text{DIPeP}}\text{BDI})\text{GaI}_2$  which results also in a more acute N–Ga–N angle of 88.02(4)–88.33(4)°. All distances and angles in the Ga coordination sphere compare very well to those in the less bulky  $(^{\text{DIPP}}\text{BDI})\text{Ga}^{\text{I}}$  complex,<sup>[9]</sup> showing that increased bulk does not affect metal coordination. However,

the larger more flexible DIPeP-substituents do result in increased stability and solubility (the product was crystallized from cold *n*-pentane).

## Reactivity and Structures

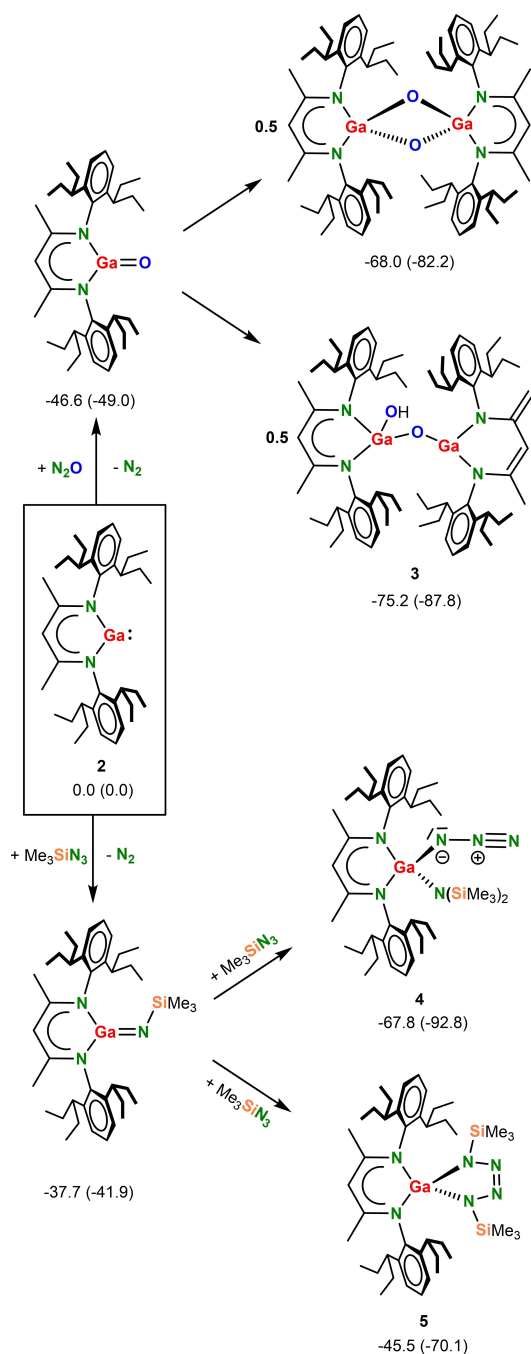
Having access to a well-defined  $\text{Ga}^{\text{I}}$  complex that can be obtained in high yields, we investigated the reactivity of  $(^{\text{DIPeP}}\text{BDI})\text{Ga}^{\text{I}}$  (**2**) aiming to isolate discrete complexes with Ga=O or Ga=NR bonds. Due to more realistic dipolar resonance structures ( $\text{Ga}^+-\text{O}^-$  and  $\text{Ga}^+-\text{NR}^-$ ) such complexes are highly reactive. Like the alumoxanes of type L–Al=O, they can be stabilized by donor bonds to  $\text{Ga}^+$ , acceptor bonds to  $\text{O}^-$  or  $\text{NR}^-$  or by aggregation.<sup>[23]</sup> Monomeric, unstabilised galloxanes of type L–Ga=O have so far never been isolated. The galloxane complex  $(^{\text{DIPP}}\text{BDI})\text{Ga}=\text{O}$ , obtained by oxidation of  $(^{\text{DIPP}}\text{BDI})\text{Ga}^{\text{I}}$  with  $\text{N}_2\text{O}$ , tends to form dimers with  $\mu^2$ -bridging oxides (*cf* Scheme 3, top).<sup>[25]</sup> Such a dimer is an example of a  $\text{Ga}^+-\text{O}^-$  bond that is stabilized by a donor bond to  $\text{Ga}^+$  and an acceptor bond to  $\text{O}^-$ . However, when the monomer is generated *in situ*, it is able to activate a range of aromatic and aliphatic C–H bonds.<sup>[26]</sup>

We attempted to oxidize the  $\text{Ga}^{\text{I}}$  center in **2** by doing a reaction of solid **2** with various gases that could penetrate the crystal lattice. Whilst crystalline  $(^{\text{DIPeP}}\text{BDI})\text{Ga}^{\text{I}}$  (**2**) did not react with CO or  $\text{CO}_2$ , oxidation with  $\text{N}_2\text{O}$  is fast. Reaction of solid **2** with  $\text{N}_2\text{O}$  led to immediate disappearance of the yellow color of the powder, however, the solid-state conversion is not very selective. Inspection of the  $^1\text{H}$  NMR spectrum revealed that more than five different unidentified products were formed and we have not been able to isolate a pure product.

Reaction of **2** with  $\text{N}_2\text{O}$  in solution is more selective. Although it only gave two major products, we were not able to purify the sample by recrystallization. However, one of them could be identified as **3**. Complex **3** crystallizes in the  $\text{P}\bar{1}$  space group with two crystallographically inequivalent, but structurally very similar molecules in the asymmetric unit (Figure 1c). The complex consists of two  $\text{Ga}^{3+}$  cations bridged by an  $\text{O}^{2-}$  anion, one terminal  $\text{OH}^-$  anion, and two  $^{\text{DIPeP}}\text{BDI}$  ligands. For charge balance, one of the ligands has been deprotonated in the Me backbone which results in a  $(^{\text{DIPeP}}\text{BDI}-\text{H})$  species carrying a 2- charge. An Al compound of very similar composition but with an additional THF ligand has recently been isolated from the analogous reaction between  $(^{\text{DIPP}}\text{BDI})\text{Al}^{\text{I}}$  and  $\text{N}_2\text{O}$ .<sup>[23]</sup> The identity of this decomposition product confirms the very high reactivity of the expected intermediate  $(^{\text{DIPeP}}\text{BDI})\text{Ga}=\text{O}$ . The Ga–OH is unusual in the sense that the OH group is not involved in classical hydrogen bonding. However, there is a short O–H...arene  $\pi$ -interaction to one of the DIPP groups (shortest O–H...C distance: 2.709 Å) which could be considered a non-classical hydrogen bond.<sup>[27]</sup>

The Ga–N bonds to the doubly deprotonated BDI ligand (average: 1.846 Å) are shorter than those to the singly charged BDI ligand (average: 1.951 Å). The 0.1 Å difference in bond lengths is due to increased electrostatic attraction between  $\text{Ga}^{3+}$  and the  $\text{BDI}^{2-}$  anion. Bridging of the  $\text{O}^{2-}$  anion between





**Scheme 3.** Free energy at 298 K and (between brackets) enthalpy differences calculated for reactions of  $(\text{DIPePBDI})\text{Ga}^{\text{I}}$  (**2**) with  $\text{N}_2\text{O}$  and  $\text{Me}_3\text{SiN}_3$  given as  $\Delta G_{298}(\Delta H)$  in  $\text{kcal mol}^{-1}$  (PBE0-D3BJ/def2-SVP//def2-TZVP, benzene (PCM)).

the two Ga cations is slightly asymmetric. The Ga–O distances to the four-coordinate Ga center (average: 1.806 Å) are slightly longer than those to the three-coordinate Ga atom (average: 1.733 Å) and similar in length when compared to the Ga–OH distances (average: 1.800 Å).

We propose that complex **3** is formed by reaction between highly reactive  $(\text{DIPePBDI})\text{Ga}=\text{O}$  intermediates (Scheme 3a). Due to the increased bulk of the DIPeP-substituents, formation of a

stable dimeric aggregate is not possible. The polar  $\text{Ga}^+-\text{O}^-$  bond deprotonates a second galloxane complex in the backbone Me group. Aggregation of the products thus results in **3**.

Power, Roesky and co-workers characterized the first unstabilised Ga-imido complex,  $(\text{DIPePBDI})\text{Ga}=\text{N}(\text{Ar})$ , with an extremely bulky Ar substituent ( $\text{Ar} = 2,6\text{-Trip}_2\text{C}_6\text{H}_3$ ;  $\text{Trip} = 2,4,6\text{-iPr}_3\text{C}_6\text{H}_2$ ).<sup>[28]</sup> We questioned whether a superbuly  $\text{DIPePBDI}$  ligand in combination with a much smaller N-substituent also would allow for the isolation of a Ga-imido complex. As complexes with a  $\text{Ga}=\text{N}(\text{SiR}_3)$  unit were recently shown to be a viable source of  $\text{N}_3^-$ ,<sup>[29]</sup> we chose trimethylsilylazide as a reagent. The reaction between  $(\text{DIPePBDI})\text{Ga}^{\text{I}}$  (**2**) and  $\text{Me}_3\text{SiN}_3$  in benzene at room temperature is complete within minutes.  $^1\text{H}$  NMR shows formation of two products in a *circa* 2:1 ratio. Reaction at lower temperatures in toluene did not markedly change this ratio. Heating did not result in interconversion of the isomers to form the most stable product. The minor component of the reaction mixture could be characterized by X-ray diffraction as the azide-amide complex  $(\text{DIPePBDI})\text{GaN}_3[\text{N}(\text{SiMe}_3)_2]$  (**4**); Figure 1d. Crystals of the major product were not of sufficient quality. Due to the very high solubility of both products in hexane, it was not possible to purify the mixture by crystallization. However, elution of a  $\text{Et}_2\text{O}$  solution of the mixture through a plug of dry silica gel led to full adsorption of the major component and gave pure  $(\text{DIPePBDI})\text{GaN}_3[\text{N}(\text{SiMe}_3)_2]$  (**4**) in 34% yield. NMR data for the major component are consistent with the formation of a tetrazagallole species  $(\text{DIPePBDI})\text{Ga}[\text{N}_4(\text{SiMe}_3)_2]$  (**5**) which is a functional group isomer of **4**. The less bulky  $\text{Ga}^{\text{I}}$  complex  $(\text{DIPePBDI})\text{Ga}^{\text{I}}$  reacted similarly with  $\text{Me}_3\text{SiN}_3$  but gave the azide-amide complex as the major component (ratio  $(\text{DIPePBDI})\text{GaN}_3[\text{N}(\text{SiMe}_3)_2] : (\text{DIPePBDI})\text{Ga}[\text{N}_4(\text{SiMe}_3)_2] = 3:1$ ).<sup>[30]</sup>

The structure of **4** compares well to that of the analogous complex with the smaller  $\text{DIPePBDI}$  ligand in terms of similar Ga–N distances, similar N–Ga–N and Si–N–Si angles and a similar geometry of the  $\text{N}_3^-$  anion. The significantly unequal N–N bond lengths in the azide anion, (Ga)N–N 1.209(5) Å and N–N (terminal) 1.144(5) Å, are also comparable to those in other Ga azide complexes.<sup>[31]</sup> This inequality indicates that the Ga–N≡N resonance structure, with a formal negative charge on the N atom neighbouring Ga, dominates over the Ga–N=N=N resonance structure, with a formal negative charge on the terminal N atom. Preference for the Ga–N≡N resonance structure is induced by the very high Lewis acidity of the  $\text{Ga}^{3+}$  nucleus. *Cf.* a sodium azide complex with a much less Lewis acidic  $\text{Na}^+$  nucleus shows nearly equal N–N distances: (Na)N–N 1.166(2) Å and N–N (terminal) 1.174(2) Å and are in favor of a Na–N=N=N resonance structure.<sup>[32]</sup>

### DFT Calculations

To gain insight into the formation and electronic structures of the reported complexes, quantum chemical calculations were performed at the PBE0-D3BJ/def2-SVP//def2-TZVP level of theory and energies were corrected for benzene solvation with the PCM method. Analysis of  $(\text{DIPePBDI})\text{Ga}^{\text{I}}$  (**2**) by density functional theory and NBO calculations reveal that it has an

occupied Ga centered lone pair, observable as the major contributor to the Kohn-Sham Highest Occupied Molecular Orbital and by a two-electron NBO with predominantly *s*-character ( $s^{0.93}p^{0.07}$ ). Whilst the LUMO is ligand-centered, the complementary empty *p*-orbital, usually used for electron accepting properties, can be found in the LUMO+1 (Figure S34). Natural Population Analysis (NPA) gave the charges for Ga (+0.71) and the Ns (−0.73/−0.76), which are reasonable for a Ga<sup>I</sup> species.

As postulated above, the formation of **3** from reaction of (DIPePBDI)Ga<sup>I</sup> and N<sub>2</sub>O likely arises from the generation of a highly reactive (DIPePBDI)Ga=O intermediate. Analysis of a DFT optimized model for this intermediate by natural bond orbital (NBO) and atoms in molecules (AIM) calculations indicates that, although the ligated N atoms do not show a change in NPA charges (−0.74/−0.75), the Ga (+1.78) is significantly more positive, owing to the addition of the oxygen atom (−1.28). Inspection of the Ga–O interaction shows that it has a Wiberg-Bond-Index (WBI) of 1.10 which is close to a single bond and indicative of small contribution of the Ga=O resonance structure. Additionally, AIM analysis (Figure S32) and analysis of the electron density ( $\rho = 0.18$ ) and Laplacian ( $\nabla^2\rho = 0.92$ ) for the bond critical point indicate a strong single bond. NBO analysis, however assigns two 2e-electron NBOs to the Ga–O bond (9% Ga, 91% O and 17% Ga, 83% O) and two 2e-electron lone pairs to the terminal oxygen ( $s^{0.79}p^{0.21}$  and  $p^{1.00}$ ). This shows that, although the interaction is heavily polarized towards the oxygen atom, it may have some double bond character. The Ga=O bond in (DIPePBDI)Ga=O is also considerably more covalent than the Al=O bond in (DIPePBDI)Al=O (WBI: 0.96;  $\rho = 0.14$ ,  $\nabla^2\rho = 1.05$ ; NBO charges: Al +2.00, O −1.39).<sup>[17]</sup>

Oxidation of (DIPePBDI)Ga<sup>I</sup> (**2**) to its terminal oxide, (DIPePBDI)Ga=O was calculated to be strongly exergonic ( $\Delta G_{298} = -46.6$  kcal mol<sup>−1</sup>, Scheme 3). Dimerization via oxo-bridging, as observed for the comparable (DIPePBDI)Ga=O complex,<sup>[25]</sup> is shown to be slightly less favorable than deprotonation, as observed in the crystallographically determined structure. This can be justified by the larger steric repulsion of the DIPeP groups in the oxo-bridged dimer.

The reactions of (DIPePBDI)Ga<sup>I</sup> (**2**) with Me<sub>3</sub>SiN<sub>3</sub> to form the complexes **4** and **5**, are linked by a common (DIPePBDI)Ga=N(SiMe<sub>3</sub>) intermediate. The latter is formed by an exergonic Staudinger type reaction between **2** and one equivalent of azide ( $\Delta G_{298} = -37.7$  kcal mol<sup>−1</sup>). A textbook Staudinger reaction involves the use of a tri-substituted phosphine however, owing to the isoelectronic relationship between **2** and a phosphine, it too can take part in complementary reactivity. Reaction of (DIPePBDI)Ga=N(SiMe<sub>3</sub>) with a second equivalent of azide produced two products **4** and **5** in a 1:2 ratio. The substantially different calculated relative free energies ( $\Delta G_{298}$ ) for product formation (**4**: −67.8 kcal mol<sup>−1</sup>, **5**: −45.5 kcal mol<sup>−1</sup>) contradict the experimentally observed preference for complex **5**. This difference may be related to kinetic control. Further in-depth studies will be reported in due course.

## Conclusions

The synthesis of a new Ga<sup>I</sup> complex stabilized by a superbulky  $\beta$ -diketiminato ligand was achieved by reducing the corresponding Ga<sup>III</sup> diiodide complex with two equivalents of KC<sub>8</sub>. As a consequence of the low stability of low-valent Ga<sup>I</sup> and related Al<sup>I</sup> species, they are generally only isolated in rather low yields. In contrast, (DIPePBDI)Ga<sup>I</sup> (**2**) could be obtained in quantitative yield. This is due to its very high thermal stability. A toluene solution of **2** could be heated for one week to 110 °C with no signs of decomposition. Although the high stability is related to protection of the metal center by the superbulky DIPePBDI ligand, the complex is still highly reactive showing facile conversion in contact with N<sub>2</sub>O or Me<sub>3</sub>SiN<sub>3</sub>. Reaction of (DIPePBDI)Ga<sup>I</sup> (**2**) with N<sub>2</sub>O gave (DIPePBDI)Ga=O. This highly reactive intermediate decomposed by deprotonation of one of the backbone methyl groups. This means that also the superbulky DIPePBDI ligand is not able to stabilize the monomeric galloxo species (DIPePBDI)Ga=O. We were also not able to stabilize the Ga imido species (DIPePBDI)Ga=N(SiMe<sub>3</sub>)<sub>2</sub>. Reaction of (DIPePBDI)Ga<sup>I</sup> (**2**) with Me<sub>3</sub>SiN<sub>3</sub> led to a mixture of the azide/amido complex (DIPePBDI)GaN<sub>3</sub>[N(SiMe<sub>3</sub>)<sub>2</sub>] (**4**) and a tetrazagallole species (DIPePBDI)Ga[N<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>] (**5**) in a 1:2 ratio. Both products are formed by fast reaction of (DIPePBDI)Ga=N(SiMe<sub>3</sub>) with a second equivalent of Me<sub>3</sub>SiN<sub>3</sub>.

## Experimental Section

### General Experimental Procedures

All experiments were conducted under an inert atmosphere by applying standard Schlenk techniques or using nitrogen-filled gloveboxes (MBraun, Labmaster SP). Benzene, hexanes, *n*-pentane, and toluene were degassed with nitrogen, dried over activated aluminum oxide (Innovative Technology, Pure Solv 400–4-MD, Solvent Purification System), and stored under inert atmosphere over molecular sieves (3 Å). C<sub>6</sub>D<sub>6</sub> (Sigma Aldrich) was dried over 3 Å molecular sieves. Gallium(III) triiodide (99%, abcr), graphite (99.9%, abcr), potassium (chunks, washed with hexanes, 98% trace metal basis, Sigma-Aldrich), potassium *bis*(trimethylsilyl)amide (95%, Sigma-Aldrich), and trimethylsilyl azide (95%, abcr) were purchased as indicated and used without further purification. N<sub>2</sub>O was purchased from Messer N25. (DIPePBDI)K was synthesized by a literature procedure.<sup>[15]</sup>

NMR spectra were recorded with a Bruker Avance III HD 400 MHz or 600 MHz NMR spectrometer. Chemical shifts ( $\delta$ ) were reported in parts per million (ppm) and the spectra were referenced to solvent residual signal. Coupling constants (*J*) were given in Hertz (Hz).

Elemental analysis was performed with a Hekatech Eurovector EA 3000 analyzer. All crystal structures were measured on a SuperNova diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector. Details for crystal structure determinations can be found in the Supporting Information. The crystal structure data have been deposited with the Cambridge Crystallographic Data Centre. CCDC-numbers 2334628 (**1**), 2334629 (**2**), 2334630 (**3**), 2334631 (**4**) contain the supplementary crystallographic data for this compound. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**(<sup>DIPeP</sup>BDI)Ga<sub>2</sub> (1)**

(<sup>DIPeP</sup>BDI)K (320 mg, 562 μmol, 1.00 eq.) was dissolved in toluene (5 mL) in a Schlenk tube. Ga<sub>3</sub> (253 mg, 562 μmol, 1.00 eq.) was added to the colorless solution. The reaction mixture was left stirring at room temperature overnight. After filtering the suspension, the solvent was removed under reduced pressure and the residue was dried *in vacuo* yielding the raw product in the form of a colorless powder. Recrystallization from a saturated toluene solution by vapor diffusion with hexanes at −35 °C gave (<sup>DIPeP</sup>BDI)Ga<sub>2</sub> in the form of colorless crystals suitable for X-ray diffraction analysis (227 mg, 266 μmol, 47%).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 298 K): δ = 7.16–7.12 (m, 2H, aryl-H), 7.03 (s, 2H, aryl-H), 7.01 (s, 2H, aryl-H), 4.99 (s, 1H, CH-backbone), 3.63–3.57 (m, 4H, CH), 1.93–1.76 (m, 8H, CH<sub>2</sub>), 1.62–1.52 (m, 8H, CH<sub>2</sub>), 1.50 (s, 6H, CH<sub>3</sub>-backbone), 1.07 (t, *J* = 7.4 Hz, 12H, CH<sub>3</sub>), 0.90 (t, *J* = 7.5 Hz, 12H, CH<sub>3</sub>) ppm.

<sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 101 MHz, 298 K): δ = 172.42 (CN-backbone), 143.28 (aryl-C), 141.61 (aryl-C), 126.78 (aryl-CH), 126.70 (aryl-CH), 99.54 (CH-backbone), 40.39 (CH), 28.87 (CH<sub>2</sub>), 28.19 (CH<sub>2</sub>), 24.64 (CH<sub>3</sub>), 11.89 (CH<sub>3</sub>), 10.99 (CH<sub>3</sub>) ppm.

**Elemental Analysis:** Calculated values (%) for C<sub>37</sub>H<sub>57</sub>N<sub>2</sub>Ga<sub>2</sub> (853.41 g/mol): C 52.07, H 6.73, N 3.28; Found (%): C 52.89, H 6.88, N 3.79. Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.

**(<sup>DIPeP</sup>BDI)Ga (2)**

(<sup>DIPeP</sup>BDI)Ga<sub>2</sub> (205 mg, 240 μmol, 1.00 eq.) was dissolved in toluene (5 mL) in a Schlenk tube. K<sub>2</sub>C<sub>8</sub> (66.5 mg, 50.4 μmol, 2.10 eq.) was added to the solution. The reaction mixture was stirred at 110 °C for 10 days. The mixture was filtered through celite, the solvent was removed under reduced pressure, and the residue was dried *in vacuo* to obtain (<sup>DIPeP</sup>BDI)Ga as an essentially pure yellow powder in quantitative yield. Yellow crystals suitable for X-ray diffraction analysis were grown from a saturated *n*-pentane solution of an aliquote of the obtained product at −35 °C in 80% yield.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 600 MHz, 298 K): δ = 7.22–7.18 (m, 2H, aryl-H), 7.12 (s, 2H, aryl-H), 7.11 (s, 2H, aryl-H), 5.15 (s, 1H, CH-backbone), 2.86 (quint, *J* = 6.7 Hz, 4H, CH), 1.88–1.81 (m, 4H, CH<sub>2</sub>), 1.79 (s, 6H, CH<sub>3</sub>-backbone), 1.75–1.68 (m, 4H, CH<sub>2</sub>), 1.64–1.57 (m, 8H, CH<sub>2</sub>), 0.96 (t, *J* = 7.4 Hz, 12H, CH<sub>3</sub>), 0.89 (t, *J* = 7.4 Hz, 12H, CH<sub>3</sub>) ppm.

<sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 151 MHz, 298 K): δ = 163.28 (CN-backbone), 146.40 (aryl-C), 140.51 (aryl-C), 125.53 (aryl-CH), 124.91 (aryl-CH), 98.82 (CH-backbone), 42.47 (CH), 29.14 (CH<sub>2</sub>), 27.51 (CH<sub>2</sub>), 24.01 (CH<sub>3</sub>), 12.64 (CH<sub>3</sub>), 12.50 (CH<sub>3</sub>) ppm.

**Elemental Analysis:** Calculated values (%) for C<sub>37</sub>H<sub>57</sub>N<sub>2</sub>Ga (599.60 g/mol): C 74.12, H 9.58, N 4.67; Found (%): C 71.99, H 9.53, N 4.29. Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.

**Reaction of (<sup>DIPeP</sup>BDI)Ga (2) with N<sub>2</sub>O**

(<sup>DIPeP</sup>BDI)Ga (49.1 mg, 81.9 μmol) was dissolved in deuterated toluene-d<sub>8</sub> (600 μL) in a J. Young NMR tube. The solvent was degassed via three freeze-pump-thaw cycles and saturated with dry N<sub>2</sub>O gas (1 atm). The reaction mixture was left at −80 °C for two hours until full conversion was indicated by <sup>1</sup>H NMR spectroscopy. The solvent was removed under reduced pressure, and the residue was dried *in vacuo* to obtain a yellow powder which is a mixture of

at least two different species. Crystallization from a saturated *n*-pentane solution at −35 °C allowed for X-ray diffraction analysis of **3** but a sufficiently pure sample for NMR characterization or elemental analysis could not be obtained.

**(<sup>DIPeP</sup>BDI)GaN<sub>3</sub>[N(SiMe<sub>3</sub>)<sub>2</sub>] (4)**

(<sup>DIPeP</sup>BDI)Ga (142 mg, 237 μmol, 1.00 eq.) was dissolved in toluene (10 mL) in a Schlenk tube. Trimethylsilyl azide (54.6 mg, 474 μmol, 2.00 eq.) was added at room temperature. The reaction was finished immediately as indicated by <sup>1</sup>H NMR spectroscopy. The solvent was removed under reduced pressure, and the residue was dried *in vacuo* to obtain a mixture of (<sup>DIPeP</sup>BDI)Ga(N<sub>3</sub>)(NTMS<sub>2</sub>) and (<sup>DIPeP</sup>BDI)Ga(N<sub>4</sub>TMS<sub>2</sub>) in a ratio of 38:62 (determined by integration of the corresponding signals in the <sup>1</sup>H NMR spectrum) as a colorless powder. The mixture was eluted through a plug of dry silica gel using Et<sub>2</sub>O as eluent. NMR analysis showed that only the amide/azide gallium species was present in the eluent. Drying the sample *in vacuo* and recrystallizing the solid from a saturated hexanes solution at −35 °C afforded colorless crystals of (<sup>DIPeP</sup>BDI)Ga(N<sub>3</sub>)(NTMS<sub>2</sub>) (26.2 mg, 32.0 μmol, 34%) suitable for X-ray diffraction analysis. All attempts to isolate the other isomer, (<sup>DIPeP</sup>BDI)Ga[N<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>] (**5**), in pure form failed but it could be characterized by NMR analysis (Figure S25), showing great similarity to NMR data for (<sup>DIPeP</sup>BDI)Ga[N<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>].<sup>[30]</sup>

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 600 MHz, 298 K): δ = 7.29 (m, 3H, aryl-H), 6.95 (dd, *J* = 7.2, 2.1 Hz, 3H, aryl-H), 4.92 (s, 1H, CH-backbone), 3.14–3.09 (m, 2H, CH), 3.01–2.97 (m, 2H, CH), 1.57 (s, 6H, CH<sub>3</sub>-backbone), 1.12 (t, *J* = 7.0 Hz, 5H, CH<sub>2</sub>/CH<sub>3</sub>), 1.03 (t, *J* = 7.4 Hz, 8H, CH<sub>2</sub>/CH<sub>3</sub>), 0.87 (t, *J* = 7.2 Hz, 11H, CH<sub>2</sub>/CH<sub>3</sub>), 0.82 (t, *J* = 7.5 Hz, 8H, CH<sub>2</sub>/CH<sub>3</sub>), 0.74 (t, *J* = 7.4 Hz, 8H, CH<sub>2</sub>/CH<sub>3</sub>), 0.58 (s, 9H, TMS-CH<sub>3</sub>), −0.04 (s, 9H, TMS-CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 151 MHz, 298 K): δ = 173.71 (CN-backbone), 143.85 (aryl-C), 142.39 (aryl-C), 139.12 (aryl-C), 137.90 (aryl-C), 129.33 (aryl-CH), 127.34 (aryl-CH), 127.00 (aryl-CH), 125.70 (aryl-CH), 125.65 (aryl-CH), 99.88 (CH-backbone), 39.71 (CH), 29.12 (CH<sub>2</sub>), 27.30 (CH<sub>2</sub>), 26.59 (CH<sub>2</sub>), 26.16 (CH<sub>2</sub>), 24.94 (CH<sub>3</sub>), 21.43 (CH<sub>3</sub>), 11.62 (CH<sub>3</sub>), 10.80 (CH<sub>3</sub>), 10.76 (CH<sub>3</sub>), 10.39 (CH<sub>3</sub>), 2.50 (TMS-CH<sub>3</sub>), 1.60 (TMS-CH<sub>3</sub>) ppm.

<sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 119 MHz, 298 K): δ = 8.20 (TMS), 5.03 (TMS) ppm.

**Elemental Analysis of the Mixture of Isomers**

Calculated values (%) for C<sub>43</sub>H<sub>75</sub>N<sub>6</sub>GaSi<sub>2</sub> (802.01 g/mol): C 64.40, H 9.43, N 10.48; Found (%): C 63.80, H 8.95, N 9.88. Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.

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**Conflict of Interest**

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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