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Preparation of Monomeric $LGa(NH_2)_2$ and of $LGa(OH)_2$ in the Presence of a N-Heterocyclic Carbene as HCl Acceptor

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The reactions of $LGaCl_2$ ($L = HC[C(Me)N(Ar)]_2$, Ar = 2,6-$i$$Pr_2C_6H_3$) with NH_3 and H_2O, respectively, in the presence of a 1,3-bis-*tert*-butylimidazol-2-ylidene (N-heterocyclic carbene) as acceptor for the HCl lead to unique species of composition $LGa(NH_2)_2$ and $LGa(OH)_2$ in high yields under mild conditions. $LGa(NH_2)_2$ is the first known monomeric diamide of gallium.

Introduction

Recently we have shown the possibility of preparing unique species such as $LAl(OH)_2$, $LAl(NH_2)_2$,[1] and LGe(OH)[2] ($L = HC[C(Me)N(Ar)]_2$, Ar = 2,6-$i$$Pr_2C_6H_3$) from the corresponding metal chlorides[3,4] and H_2O and NH_3, respectively, by means of different N-heterocyclic carbenes as HCl acceptors. We became interested in using this method for other metal halides to generate similar species. Compounds containing two NH_2 groups on one gallium are not known. Up to date there are known only five gallium amides containing one NH_2 group on each gallium atom, dimeric $[(Me_3CCH_2)_2GaNH_2]_2$[5] and trimers $(R_2GaNH_2)_3$ (R = H,[6,7] Me,[8,9] Et,[10] and tBu[11]), but only the $(Me_2GaNH_2)_3$ and $(tBu_2GaNH_2)_3$ have been structurally characterized. Compared to the amides, the chemistry of gallium hydroxides is much more explored; numerous examples of species containing bridging OH groups are known, and also several examples with terminal ones have been described.[11−18] In 1994 Atwood et al. reported the preparation of the first gallium dihydroxide containing two terminal OH groups stabilized by a bulky pincer type ligand from the corresponding dihydride and water.[14] Its surprising stability is demonstrated by the presence of 10 equiv of water in the crystal lattice.

Results and Disscussion

A cold toluene solution (−25 °C) of 1,3-bis-*tert*-butylimidazol-2-ylidene[19] saturated by gaseous NH_3 was slowly added to a toluene solution of $LGaCl_2$[3] at −35 °C. Warming the solution to ambient temperature resulted in the formation of a slurry of 1,3-bis-*tert*-butylimidazoyl chloride. After filtration, removal of all the volatiles in vacuo, and recrystallization from pentane, colorless microcrystalline $LGa(NH_2)_2$ (**1**) was isolated in 70% yield. Furthermore, $LGa(OH)_2$ (**2**) is the only product isolated in 80% yield from the reaction between a toluene solution of $LGaCl_2$ and 1,3-bis-*tert*-butylimidazol-2-ylidene in a 1:2 molar ratio with 2 equiv of H_2O at −5 °C. These results confirmed our expectations that the carbene NH_3/H_2O system offers interesting synthetic possibilities also for gallium. As we mentioned earlier,[1] preparation of such species is problematic and very often leads to condensed products, if protic byproducts are not properly trapped (e.g., HCl, $NR_3H^+X^-$).[20] Thus, most of these products were prepared by elimination of small nonprotic molecules such as H_2, alkanes, or weak acids (dialkylamines, etc.).[20] The almost irreversible bonding of the free protons to the

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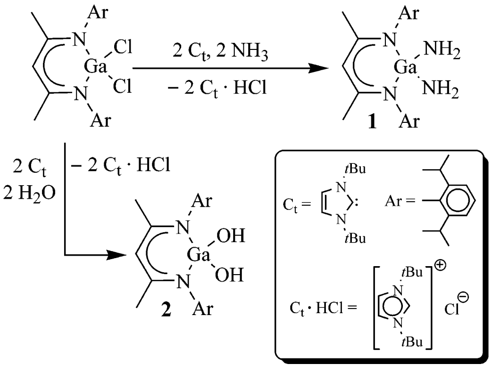
Scheme 1. Synthesis of Compounds 1 and 2



carbene results in high yields of the unique species **1** and **2**. Scheme 1 summarizes the reaction for preparing **1** and **2**.

In analogy with the aluminum derivative, **2** forms a dimer, whereas **1** is strictly monomeric in both solid state and solution as proved by X-ray structural analysis and IR spectroscopy. Both compounds are thermally stable and do not decompose even upon heating to 70 °C in a sealed tube as determined by temperature-dependent ^{1}H NMR spectroscopy and MS spectrometry. Compound **1** is very sensitive toward moisture and hydrolyzes rapidly under formation of NH_3 and LGa(NH_2)(OH). The hydrolysis occurs slowly even in a glovebox with water levels below 0.2 ppm and during any manipulation of the sample. Further hydrolysis of LGa(NH_2)(OH) leads to **2** in a quantitative yield as proved by ^{1}H NMR spectroscopy. The LGa(NH_2)(OH) has a solubility similar to that of the diamide; therefore it is necessary to work carefully under strictly moisture-free conditions to obtain pure **1** (more than 95% content of **1**). Compound **1** often contains 3−5% of LGa(NH_2)(OH) as shown by ^{1}H NMR spectroscopy (Figure S1 in the Supporting Information). Nevertheless, pure **1** can be obtained using a closed vacuum line equipped with Teflon Swagelock fittings for the condensation of the solvent and NH_3(l) to the reagents. The reaction flask should be equipped with Teflon Young valves and treated prior to use with Me_3SiCl to eliminate free OH groups on the glass surface. So far, we have not been successful in isolating the LGa(NH_2)(OH).

Single crystals of **1** were obtained by storing its saturated pentane solution at −32 °C. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Table 1) and is isostructural to the Al homologue[1] (Figure 1).

Compound **1** is a discrete monomer in the solid state with no observable hydrogen bonding. The GaN_4 core possesses a distorted tetrahedral geometry with the smallest and largest N−Ga−N angle of 95.4° and 118.5°, respectively. The N(1)−Ga(1)−N(2) angle (95.4°) within the six-membered ring is in the normal range, whereas the N(3)−Ga(1)−N(4) angle (111.8°) is significantly larger than those in the trimeric cyclic species ([(Me_2GaNH_2)$_3$] and [($t$$Bu_2GaNH_2$)$_3$] 93.8−105.6°).[8,9,11] This difference is obviously due to the monomeric nature of **1**, thus, avoiding the characteristic ring strain of the cyclic congeners. As expected, the endocyclic Ga(1)−N(l) and Ga(1)−N(2) bond lengths (1.955, 1.976 Å) are significantly longer than the exocyclic ones (Ga(1)−N(3) and Ga(1)−N(4) 1.852, 1.847 Å). The latter values represent the shortest bond lengths for Ga−NH_2 moieties so far known (compared with 1.928−2.053 Å in [(Me_2GaNH_2)$_3$] and [($t$$Bu_2GaNH_2$)$_3$]).[8,9,11] A similar phenomenon has also been observed for the Al analogue. The hydrogen atoms of the NH_2 groups were localized in the difference electron density map, and the N−H bond lengths (0.81, 0.81, 0.82, and 0.82 Å) are shorter than those in [(Me_2GaNH_2)$_3$] (0.95 Å) and [($t$$Bu_2GaNH_2$)$_3$] (1.05 Å), but comparable to those in LAl(NH_2)$_2$ (0.85−0.88 Å).[1,8,9,11] Selected bond lengths and angles for **1** are listed in Table 2.

Table 1. Crystallographic Data for Compounds 1 and 2·0.5Toluene

	1	**2**·0.5toluene
formula	$C_{29}H_{45}GaN_4$	$C_{32.50}H_{47}GaN_2O_2$
fw	519.41	567.44
cryst syst	monoclinic	triclinic
temp, K	100	100
λ, Å	1.54178	1.54178
space group	$P2_1/c$	$P\bar{1}$
a, Å	17.016(1)	13.332(1)
b, Å	13.101(1)	14.432(1)
c, Å	13.494(1)	18.190(1)
α, deg		99.08(1)
β, deg	109.14(1)	95.01(1)
γ, deg		114.00(1)
V, Å^3	2842(1)	3112(1)
Z	4	4
ρ_{calcld}, g/cm^3	1.214	1.211
μ, mm^{-1}	1.481	1.426
F(000)	1112	1212
cryst size, mm^3	0.10 × 0.05 × 0.05	0.30 × 0.20 × 0.20
θ range for data collection, deg	2.75 to 58.93	2.50 to 58.98
index ranges	$-17 \le h \le 18$ $-14 \le k \le 13$ $-14 \le l \le 13$	$-14 \le h \le 14$ $-15 \le k \le 15$ $-19 \le l \le 19$
no. of reflns collected	12 292	23 915
no. of indep reflns (R_{int})	4002 (0.0392)	8679 (0.0299)
no. of data/restraints/params	4002/6/336	8679/10/726
GoF on F^2	1.035	1.030
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0282, 0.0722	0.0261, 0.0678
R1,[a] wR2[b] (all data)	0.0320, 0.0745	0.0274, 0.0687
extinction coeff		0.00018(6)
largest diff peak/hole, e·Å^{-3}	0.226/−0.285	0.274/−0.368

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)]^{1/2}$.

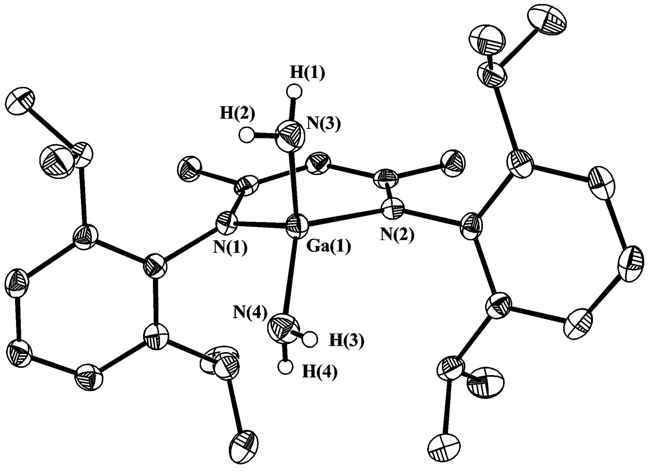


Figure 1. Thermal ellipsoid plot of **1** showing the 50% probability level. H atoms, except N-H, are omitted for clarity.

Although **1** is isostructural with the Al analogue, it reveals one significant difference: the geometry of the

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 1

Ga(1)−N(1)	1.955(2)	Ga(1)−N(3)	1.852(2)
Ga(1)−N(2)	1.976(2)	Ga(1)−N(4)	1.847(2)
N(3)−H(1)	0.81(2)	N(4)−H(3)	0.82(1)
N(3)−H(2)	0.81(2)	N(4)−H(4)	0.82(2)
N(1)−Ga(1)−N(2)	95.4(1)	N(2)−Ga(1)−N(3)	106.4(1)
N(1)−Ga(1)−N(3)	116.5(1)	N(2)−Ga(1)−N(4)	118.5(1)
N(1)−Ga(1)−N(4)	107.8(1)	N(3)−Ga(1)−N(4)	111.8(1)
H(3′)−N(3)−H(3″)	108(3)	H(4′)−N(4)−H(4″)	112(3)
H(3′)−N(3)−Ga(1)	114(2)	H(4′)−N(4)−Ga(1)	115(2)
H(3″)−N(3)−Ga(1)	115(2)	H(4″)−N(4)−Ga(1)	117(2)

NH$_2$ groups in LAl(NH$_2$)$_2$ is almost planar with a sum of angles of 357(2)° and 356(2)°[1] compared to those in **1** (sum of angles 337(2)° and 344(2)°). We carried out DFT calculations on both LAl(NH$_2$)$_2$ and LGa(NH$_2$)$_2$ with the program DMOL.[21] The isosurfaces at 0.05 e·Å^{-3} of the HOMO orbitals show that the electron density is mainly localized at the N atom of the NH$_2$ groups of both LAl(NH$_2$)$_2$ and LGa(NH$_2$)$_2$ (Figures S2, S3 in the Supporting Information). The LUMOs are constructed from π-orbitals of the β-diketiminato ligand. To save calculation time, several models can be used. We obtained the best model by replacing the aryl groups at the nitrogen atoms by phenyl groups, because in such a model all the interactions between the π-orbitals of the phenyl rings with the ligand backbone contribute to the proper symmetry of the HOMO orbital of the ligand. However, due to omitting the *i*Pr moieties, the optimized calculation led to planar C$_3$N$_2$M rings. Hence, the coordinates of the metal and the adjacent nitrogen atoms were fixed at the positions given by the experiment, and the optimization was performed for the bonding distances and angles between metal and nitrogen atoms as well as within the NH$_2$ groups (Figures S4, S5 in the Supporting Information). The results show that the most stable conformation for LAl(NH$_2$)$_2$ has the NH$_2$ groups slightly twisted toward each other to allow the overlap of the free orbitals on the nitrogen atoms in the HOMO orbital. Similar stabilization can be found in the Ga derivative, with the difference that the NH$_2$ groups need to "bend" to allow similar overlap, mainly due to the longer endocyclic Ga−N bonds and thus larger distance between the corresponding nitrogen atoms. This results in planar NH$_2$ groups in LAl(NH$_2$)$_2$ (both sums of angles 360(1)°), whereas they are almost tetrahedral in LGa(NH$_2$)$_2$ with the sum of angles of 339(1)° and 335(1)°, respectively. The results are in a good agreement with the experiment (see above). Furthermore, we could observe partial contribution of the d-orbitals of gallium to the HOMO orbital, whereas there is no metal orbital contribution in the aluminum case (Figure S6 in the Supporting Information).

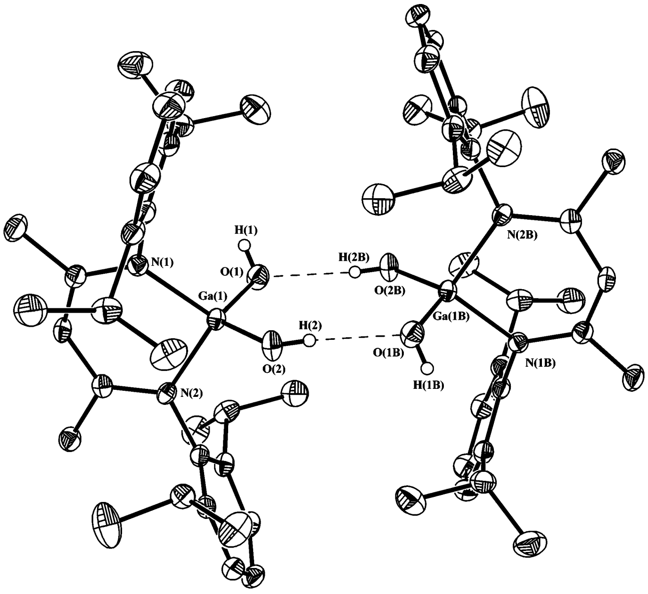


Figure 2. Thermal ellipsoid plot of dimer A of **2** showing the 50% probability level. H atoms, except O-H, are omitted for clarity.

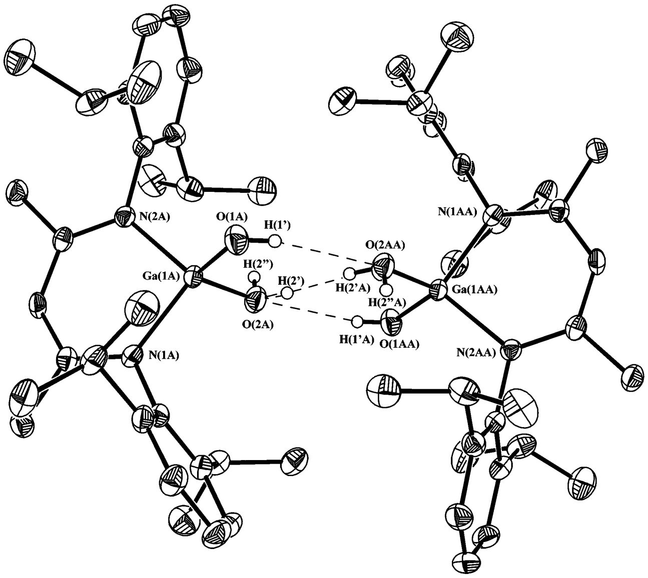


Figure 3. Thermal ellipsoid plot of dimer B of **2** showing the 50% probability level. H atoms, except O-H, are omitted for clarity. The hydrogen atoms bonded to O(2A) and O(2AA) are disordered within two positions with equal occupancy factors.

Triclinic single crystals of **2** suitable for X-ray structural analysis were obtained by keeping its saturated toluene solution at −30 °C. The colorless blocks of **2** crystallize in the space group $P\bar{1}$ and spontaneously fracture when exposed to temperatures above −5 °C. This is due to an irreversible phase change into a monoclinic form under elimination of toluene and crystallizing in the space group $P2_1/n$ with one molecule of **2** in the asymmetric unit. Unfortunately, due to the high disorder of the molecules, we were not able to obtain data of satisfactory quality for the monoclinic form. The triclinic form contains two independent molecules of **2** and one molecule of toluene in the asymmetric unit (Table 1). Different positions of these molecules toward the inversion centers result in the formation of two dimers contrasting in the number and kind of hydrogen bonds between the OH units. Dimer **A** is formed by only two equivalent hydrogen bonds O(1)···H(2)−O(2) (O···H 2.01 Å, O−H−O angle 174°) having still two free terminal hydrogen atoms H(1) (of the OH moieties) (Figure 2), whereas in dimer **B** there are two incompatible O···H interactions (Figure 3).

The first is similar to that in **A**, O(2A)···H(1′)−O(1A) (O···H 2.51 Å, O−H−O angle 159°), and the second is formed by two oxygen atoms equivalent by symmetry.

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 2·0.5Toluene

Molecule 1			
Ga(1)−N(1)	1.931(1)	Ga(1)−O(2)	1.777(1)
Ga(1)−N(2)	1.938(1)	O(1)−H(1)	0.72(2)
Ga(1)−O(1)	1.820(1)	O(2)−H(2)	0.74(2)
N(1)−Ga(1)−N(2)	98.0(1)	N(2)−Ga(1)−O(2)	112.6(1)
N(1)−Ga(1)−O(1)	110.6(1)	O(1)−Ga(1)−O(2)	115.3(1)
N(1)−Ga(1)−O(2)	112.0(1)	H(1)−O(1)−Ga(1)	114(2)
N(2)−Ga(1)−O(1)	107.0(1)	H(2)−O(2)−Ga(1)	113(2)
Molecule 2			
Ga(1A)−N(1A)	1.933(1)	O(1A)−H(1′)	0.72(2)
Ga(1A)−N(2A)	1.933(1)	O(2A)−H(2′)	0.74(2)
Ga(1A)−O(1A)	1.801(1)	O(2A)−H(2″)	0.73(2)
Ga(1A)−O(2A)	1.819(1)		
N(1A)−Ga(1A)−N(2A)	98.3(1)	O(1A)−Ga(1A)−O(2A)	111.5(1)
N(1A)−Ga(1A)−O(1A)	112.3(1)	H(1′)−O(1A)−Ga(1A)	105(2)
N(1A)−Ga(1A)−O(2A)	110.9(1)	H(2′)−O(2A)−Ga(1A)	98(4)
N(2A)−Ga(1A)−O(1A)	114.2(1)	H(2″)−O(2A)−Ga(1A)	113(6)
N(2A)−Ga(1A)−O(2A)	109.0(1)		

Therefore, the hydrogen atoms of these OH groups are disordered into two positions with equal occupancy factors. The O(2A)···H(2′)−O(2A) hydrogen bond is shorter than the previous one with an O···H distance of 2.09 Å and O−H−O angle of 174°, whereas H(2″) remains terminal. The Ga−O bond lengths vary (1.777−1.820 Å) and are affected by the O···H interactions. However, they are very similar to those in $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Ga(OH)_2]_3\cdot 10H_2O$ (1.81−1.83 Å)[14] and are shorter than those in the bridged hydroxides $[t\mathrm{Bu}_2\mathrm{Ga}(\mu\text{-OH})]_3$ (1.96 Å)[10] and $[\mathrm{Me_2Ga}(\mu\text{-OH})]_4$ (1.94−1.99 Å).[13] Selected bond lengths and angles for **2** are listed in Table 3.

Experimental Section

General Procedures. All reactions and handling of reagents were performed under an atmosphere of dry nitrogen or argon using Schlenk techniques or a glovebox where the O_2 and H_2O levels were usually kept below 1 ppm. All glassware was oven-dried at 140 °C for at least 24 h, assembled hot, and cooled under high vacuum prior to use. Gaseous NH_3 (Messer) was purified by passing through drying tubes filled with KOH and Na wire. $LGaCl_2$[3] and 1,3-bis-*tert*-butylimidazol-2-ylidene[19] were prepared according to literature procedures. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. ^{1}H (200.13 and 500.13 MHz) and ^{13}C (125.77 MHz) NMR spectra were recorded on Bruker Avance 200 and Bruker Avance 500 NMR spectrometers. Chemical shifts are reported in ppm with reference to $SiMe_4$ (external). IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer in the range 4000−350 cm^{-1} as KBr pellets. Only the absorptions of significant groups (NH_2, OH) are listed. Mass spectra were obtained with a Finnigan MAT 8230 or a Varian MAT CH5 instrument (70 eV) by EI-MS methods. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus.

Synthesis of $LGa(NH_2)_2$ (1). 1,3-Bis-*tert*-butylimidazol-2-ylidene (0.814 g, 4.514 mmol) and $LGaCl_2$ (1.500 g, 2.150 mmol) were mixed as solids in a Schlenk flask equipped with a Young valve. Toluene (70 mL) and NH_3 (ca. 10 mL) were subsequently transferred into the flask using a short vacuum line provided with Swagelock fittings at −196 °C and allowed to warm to ambient temperature. As the temperature increased, a heavy precipitate of 1,3-bis-*tert*-butylimidazolium chloride formed. The flask was disconnected from the vacuum line, and the excess of ammonia was released via a mineral oil bubbler attached to the flask. The precipitate was filtered off and washed twice with toluene (10 mL), and all the volatiles were removed in vacuo. The oily residue was treated twice with cold pentane (5 mL), and after filtration and drying in vacuo, **1** was obtained as a white microcrystalline powder: yield 0.78 g (70%); mp 175 °C (dec); ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS) δ −0.58 (brs, J_{N-H} = 65 Hz, 4H, $N\mathit{H}_2$), 1.16 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, $CH(C\mathit{H}_3)_2$), 1.37 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, $CH(C\mathit{H}_3)_2$), 1.60 (s, 6H, $C\mathit{H}_3$), 3.49 (sept, $^3J_{H-H}$ = 6.9 Hz, 4H, $C\mathit{H}(CH_3)_2$), 4.76 (s, 1H, γ-C*H*), 7.05−7.10 ppm (m, 6H, *m*, *p*-Ar-*H*); ^{13}C NMR (125.8 MHz, C_6D_6, 25 °C, TMS) δ 23.5, 24.8 ($CH(\mathit{C}H_3)_2$), 25.3 ($\mathit{C}H(CH_3)_2$), 28.4 ($\mathit{C}H_3$), 95.1 (γ-*C*H), 124.3, 126.9, 141.3, 144.3 (*i*, *o*, *m*, *p*-*C* of Ar), 168.6 ppm (*C*=N); IR (KBr pellet) $\tilde{\nu}$ 3438 vw, 3359 vw (NH) cm^{-1}; EI-MS (70 eV) *m*/*z* (%) 518 (8) [M$^+$], 501 (60) [M$^+$ − NH_3], 486 (100) [M$^+$ − $2NH_2$]. An elemental analysis did not give satisfactory results for nitrogen content due to the very high reactivity of **1** toward moisture and thus partial replacement of the NH_2 groups by OH moieties. This replacement has nearly no influence on the carbon and hydrogen content due to the similar molecular mass of the NH_2 and OH groups.

Synthesis of $LGa(OH)_2$ (2). H_2O (97 μL, 5.374 mmol) was added quickly to a solution of $LGaCl_2$ (1.500 g, 2.687 mmol) and 1,3-bis-*tert*-butylimidazol-2-ylidene (1.017 g, 5.642 mmol) in toluene (45 mL) cooled to −5 °C. Immediately after the addition of water, a slurry of the 1,3-bis-*tert*-butylimidazolium chloride was formed. The suspension was vigorously stirred for an additional 10 min and filtered. The precipitate was washed twice with toluene (5 mL), and all the volatiles were removed in vacuo. The solid residue was treated twice with cold pentane (5 mL), and after filtration and drying in vacuo, **2** was obtained as a white powder: yield 1.12 g (80%); mp 200 °C (dec); ^{1}H NMR (200 MHz, C_6D_6, 25 °C, TMS) δ −0.27 (s, 2H, O*H*), 1.14 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, $CH(C\mathit{H}_3)_2$), 1.43 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, $CH(C\mathit{H}_3)_2$), 1.57 (s, 6H, $C\mathit{H}_3$), 3.45 (sept, $^3J_{H-H}$ = 6.8 Hz, 4H, $C\mathit{H}(CH_3)_2$), 4.79 (s, 1H, γ-C*H*), 7.04−7.10 ppm (m, 6H, *m*, *p*-Ar-*H*); ^{13}C NMR (125.77 MHz, C_6D_6, 25 °C, TMS) δ 23.3, 24.8 ($CH(\mathit{C}H_3)_2$), 25.0 ($\mathit{C}H(CH_3)_2$), 28.4 ($\mathit{C}H_3$), 95.1 (γ-*C*H), 124.5, 127.5, 139.9, 144.6 (*i*, *o*, *m*, *p*-*C* of Ar), 170.1 ppm (*C*=N); IR (KBr pellet) $\tilde{\nu}$ 3465 wbr (OH) cm^{-1}; EI-MS (70 eV) *m*/*z* (%) 520 (5) [M$^+$], 502 (22) [M$^+$ − H_2O], 487 (100) [M$^+$ − H_2O − CH_3]. Anal. Calcd (%) for $C_{29}H_{43}GaN_2O_2$ (521.39): C, 66.7; H, 8.2; N, 5.4. Found: C, 66.8; H, 8.3; N, 5.4.

Crystal Structure Determination. Data for the structures **1** and **2** were collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector. The structure was solved by direct methods (SHELXS-97)[22] and refined with all data by full-matrix least-squares on F^2.[23] The hydrogen atoms of C−H bonds were placed in idealized positions, whereas the hydrogen atoms of the NH_2 and OH groups were localized from the difference electron density map and refined isotropically with distance restraints. Further details are listed in Table 2.

Computational Details. Density functional methods were applied by the use of the program DMOL,[21] as implemented in the Cerius program suite.[24] To take into account the density distribution within the extended ligand systems of the investigated compounds in a suitable way, the nonlocal density functionals for exchange and correlation interactions according to Becke[25] and Lee, Yang, and Parr[26] (BLYP) were chosen. Double numerical basis sets were used for all elements and extended by polarization functions for Al, Ga, and N.

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Supporting Information Available: CIF files for compounds **1** and **2**·0.5toluene and Figures S1−S6 (pdf) are available free of charge via the Internet at http://pubs.acs.org.

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