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β-Diketiminate Gallium Amides: Useful Synthons in Gallium Chemistry

Diego Solis-Ibarra,[a] A. Paulina Gómora-Figueroa,[a] Nieves Zavala-Segovia,[a] and Vojtech Jancik*[a]

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The facile preparation of β-diketiminate gallium amides with general formulas of either $LGa(NHR)_2$ {L = $[HC\{C(Me)N(Ar)\}_2]^-$, Ar = 2,6-*i*$Pr_2C_6H_3$; R = Et (**1**), *i*Pr (**2**), *n*Bu (**3**), Ph (**4**)} or LGa(NHR)Cl [R = *t*Bu (**5**); Et (**6**)] was accomplished by the reaction of $LGaCl_2$ with the lithium salt of the corresponding amine in 1:2 (**1**–**4**) or 1:1 (**5**, **6**) molar ratios. Compounds **1**–**6** are useful synthons for further synthesis, as the amide substituents are excellent leaving groups, and the resulting amines can be cleanly and easily removed from the reaction matrix. To demonstrate this, compounds **1** and **5** were treated with ethanol, leading to the alcoholysis products $LGa(OEt)_2$ (**8**) and LGa(OEt)Cl (**9**), respectively. Furthermore, $LGa(OH)_2$ can be obtained in an almost quantitative yield from the hydrolysis of compounds **1**–**4**. Additionally, the aluminum analogue of **1** − $LAl(NHEt)_2$ (**7**) − was obtained to prove that the method is also suitable for other metals. Compounds **1**–**9** were characterized by common spectroscopic methods, and compounds **1**–**8** were also characterized by X-ray single-crystal diffraction.

Introduction

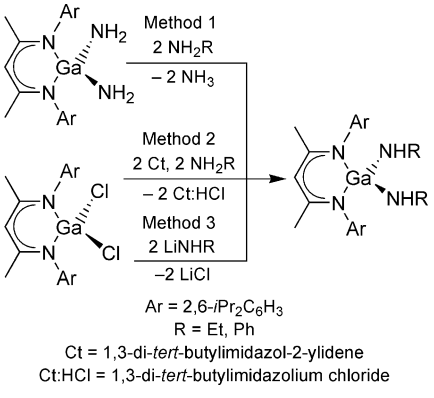
Recently, we reported on the preparation of molecular aluminophosphite $LAl(SH)(\mu\text{-}O)P(OEt)_2$ and aluminosilicates $LAl(EH)(\mu\text{-}O)Si(OH)(O\textit{t}Bu)_2$, (E = O, S; L = $[HC\{C(Me)N(2,6\text{-}\textit{i}Pr_2C_6H_3)\}_2]^-$) and $LAl(Z)(\mu\text{-}O)Si(O\textit{t}Bu)_3$, (Z = H, OH, SH) and their use for the preparation of heterobimetallic systems.[1–3] Thus, we became interested in whether or not it was possible to obtain similar systems based on gallium. However, whereas $LAlH_2$[4] and $LAl(SH)_2$,[5] used as the starting materials for the aluminophosphite and aluminosilicates, are easily accessible precursors, there are very few suitable equivalents available in gallium chemistry. Such suitable gallium compounds should be sufficiently stable but reactive enough to easily undergo, for example, controllable hydrolysis to offer easy access to a functional group such as OH attached to the gallium atom. From this point of view, only Ga–N bonds fulfil these requirements on stability and reactivity, because the hydrolysis of a Ga–Me moiety is rather difficult and LGaMe(OH) has been reported to melt without decomposition at 200 °C.[6] To date, only few such compounds have been reported, and in all cases, their preparation is tedious and/or requires expensive reagents such as Arduengo's imidazoyl carbene[7] [in the case of $LGa(NH_2)_2$][8] or compounds containing the gallium atom in an oxidation state of +I.[9,10] Our aim was to prepare compounds of general formula $LGa(NHR)_2$ starting from the easily accessible $LGaCl_2$[11] and lithium salts of primary amines. Primary amines were chosen because of the large steric demand of the β-diketiminate ligand. The $LGa(NHR)_2$ compounds should have reactivity similar to $LGa(NH_2)_2$, which is known to react cleanly with water to form $LGa(OH)_2$,[8] but their synthesis and purification should be easier, as it was reported that $LGa(NH_2)_2$ always contains inseparable impurities after the synthesis.[8] Therefore, these gallium amides could serve as interesting precursors in gallium chemistry, which are currently missing. Although there are previous reports of gallium diamides, they are mainly oligomeric compounds and the stabilization of monomeric molecules requires the use of bulky arylamides, and thus, their reactivity is limited.[12–17] To the best of our knowledge, only few structurally characterized gallium amides containing at least one terminal alkylamino group have been reported so far. Thus, two terminal *tert*-butylamino groups were observed in $[\{\textit{t}Bu(H)N\}_2Ga\{\mu\text{-}N(H)\textit{t}Bu\}]_2$.[18] and one terminal $N(H)SiMe_3$ group was reported in $Cl_2Ga(THF)N(H)SiMe_3$.[19] Herein we want to report on the preparation of four gallium diamide compounds of general formula $LGa(NHR)_2$ and $LAl(NHEt)_2$, two compounds of general formula LGa(NHR)Cl, and the alcoholysis products $LGa(OEt)_2$ and LGa(OEt)Cl.

[a] Centro de Investigación en Química Sustentable UAEM-UNAM,
Car. Toluca-Atlacomulco km 14.5, Unidad San Cayetano, Personal del Instituto de Química, UNAM
Toluca 50200, Estado de México, México
Fax: +52-55-56-16-22-17
E-mail: vjancik@servidor.unam.mx

Results and Discussion

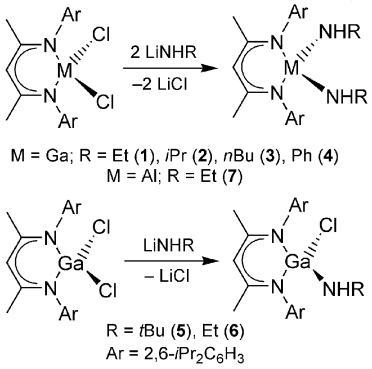
We tried three different methods to prepare these compounds, namely, transamination between $LGa(NH_2)_2$ and a primary amine (Method 1), direct amination of $LGaCl_2$ in

the presence of Arduengo's imidazoyl carbene as HCl scavenger (Method 2), and reaction between $LGaCl_2$ and the lithium salt of the corresponding primary amine (Method 3, Scheme 1). Although all three methods have shown to be feasible for the preparation of the target compounds, we selected Method 3 because of the rather laborious preparation of $LGa(NH_2)_2$ and its difficult purification. Also, the preparation of Arduengo's carbene necessary for Methods 1 and 2 is rather tedious if absolutely anhydrous carbene should be obtained (synthesis of the imidazolium salt, liberation of the corresponding carbene, and its purification either by sublimation or recrystallization).[20] This is necessary, as any trace amounts of water in the reaction lead directly to the formation of $LGa(OH)_2$. As reported elsewhere, lithium salts of primary amines are highly reactive and unstable if not stabilized by a base such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.[18–20] Only the hexameric salt $(t\text{BuNHLi})_6$ has been reported to be stable without any coordinating base.[18] Therefore, the in situ preparation of a known amount of the amine salt was accomplished by slow addition of an excess amount of the corresponding amine to a solution of a known amount of MeLi or *n*BuLi in THF at –78 °C. The resulting suspension was warmed to ambient temperature and after stirring for 30 min added dropwise to a solution of $LGaCl_2$ at –78 °C. The products were isolated as white or slightly yellowish microcrystalline solids in acceptable yields (up to 86%). In the case of ethylamine, isopropylamine, *n*-butylamine, or aniline, the product was the disubstituted derivative $LGa(NHR)_2$ (**1**, R = Et; **2**, R = *i*Pr; **3**, R = *n*Bu; **4**, R = Ph) but in the case of *tert*-butylamine, only the monosubstituted derivative LGa(NH*t*Bu)Cl (**5**) was obtained independently on the ratio of the reactants or the reaction conditions; this is obviously due to the steric effects of the bulky ligand L and the *t*Bu group. However, LGa(NHEt)Cl (**6**) can be obtained if the lithium salt of ethylamine reacts with $LGaCl_2$ in a 1:1 molar ratio. To prove that this method can be also used for different metals, we prepared the aluminum analogue of compound **1**: $LAl(NHEt)_2$ (**7**; Scheme 2).



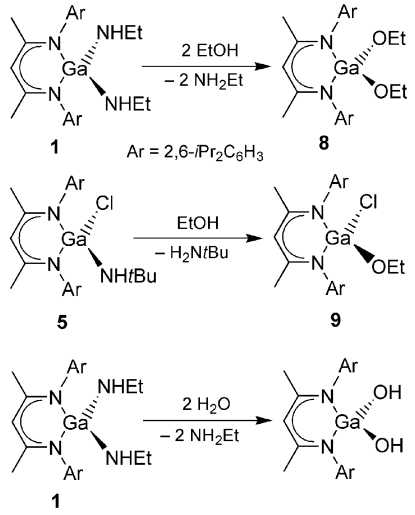
Scheme 1. Methods 1–3 used for the preparation of compounds **1**–**4**.

All compounds are white or slightly yellowish crystalline powders and were characterized by common physical methods, and the molecular and crystal structures of compounds



Scheme 2. Synthesis of compounds **1**–**7**.

1–**8** were confirmed by X-ray single-crystal diffraction. The formation of compounds **1**–**7** was evidenced by ^{1}H NMR spectroscopy in C_6D_6, which revealed the presence of the signals corresponding to the N–*H* protons at δ = –0.27 (for **1**), –0.13 (for **2**), –0.16 (for **3**), 6.16 (for **4**), –0.03 (for **5**), –0.02 (for **6**), and –0.29 ppm (for **7**). The signal appears at low field only in the case of compound **4**, which is probably caused by partial delocalization of the lone electron pair at the nitrogen atom into the π electron system of the aromatic ring. This is supported by the planar environment of the N3 and N4 atoms in **4**. The corresponding signal of the N–*H* proton in compounds **1**–**3** and **7** appears at lower field than the signal for the N–*H* protons in $LAl(NH_2)_2$ (δ = –0.52 ppm)[21] and $LGa(NH_2)_2$ (δ = –0.58 ppm), but at higher field compared to those in **5** and **6**. The latter is caused by the presence of the chlorine atom attached to the same metallic center as the amino group. In case of compounds **1**–**3**, **6**, and **7**, coupling of the N–*H* protons with the α hydrogen atoms of the alkyl chain was observed. The presence of the NH moiety was further confirmed by IR spectroscopy. In compounds **1**–**4** and **7**, the corresponding vibrations were found in a narrow interval $\tilde{\nu}$ = 3371–3381 cm^{-1}, which is in a good agreement with the ν_s vibration of the NH_2 group in $LAl(NH_2)_2$ ($\tilde{\nu}$ = 3396 cm^{-1})[21] and $LGa(NH_2)_2$ ($\tilde{\nu}$ = 3373 cm^{-1}).[8] In cases of compounds **5** and **6**, the matching vibrations were found at lower wavenumbers [$\tilde{\nu}$ = 3338 (for **5**), 3335 cm^{-1} (for **6**)]. These facts suggest that the electronic effects of the alkyl or aryl substituents have only little effect on the wavenumber; however, the presence of only one amino group in the molecule leads to a lower wavenumber when the second substituent is chlorine. The molecular peaks $[M]^+$ for all compounds except **3** were observed by MS (EI), albeit at low intensity [*m*/*z* (%) = 574 (3), **1**; 602 (2), **2**; 670 (6), **4**; 593 (9), **5**; 565 (6), **6**; 532 (2), **7**]. The base peak belongs to $[M – NHR]^+$ in all cases, except **6** [*m*/*z* (%) = 530, **1**; 544, **2**; 558, **3**; 578, **4**; 521, **5**; 488, **7**]. In the case of **6**, the base peak at *m*/*z* = 506 corresponds to $[M – NHEt – Me]^+$. The easy fragmentation of the Ga–N_{exo} bond confirms our expectations of its high reactivity. In the next step, the obtained gallium amides were treated with protic reagents. The reaction of **1** and **5** with ethanol led to $LGa(OEt)_2$ (**8**) and LGa(OEt)Cl (**9**), respectively, in nearly quantitative yields − the products were isolated in 95% yield (Scheme 3).



Scheme 3. Synthesis of compounds **8**, **9**, and $LGa(OH)_2$.

In both cases, the ^1H NMR and IR spectra are essentially devoid of the corresponding signals for the N–H protons. However, characteristic peaks of the ethoxy moieties can be observed in the ^1H NMR spectra of compounds **8** and **9**, respectively. It is noteworthy that compound **8** is the first gallium compound containing two terminal ethoxy groups. Up to now, only $[\{(Me_3Si)_3Si\}(EtO)Ga(\mu\text{-}OEt)]_2$,[22] $[(t\text{BuO})HGa(\mu\text{-}Ot\text{Bu})]_2$,[23] $Ga(Ot\text{Bu})_3NHMe_2$,[24] $Ga[(\mu\text{-}Oi\text{Pr})_2Ga(Oi\text{Pr})_2]_3$,[24] $Ga[OCH(CF_3)_2]_3(4\text{-}Me_2Npy)$ (py = pyridine),[25] $Ga[OCMe_2CF_3]_3(4\text{-}Me_2Npy)$,[25] and $[Ga(\mu\text{-}OCMe_2Et)(OCMe_2Et)_2]_2$[24] have been reported to contain at least one terminal alkoxide group. The only other compounds containing nonbridging Ga–O(alkyl) bonds are stabilized against oligomerization by the presence of donor groups that fill vacant coordination sites of the gallium atom and can lead to an increase in the coordination number for gallium to 5 or 6. Some examples of such complexes are $Me_2GaO(CH_2)_nNH_2$ (n = 2 or 3),[26,27] EtGa-

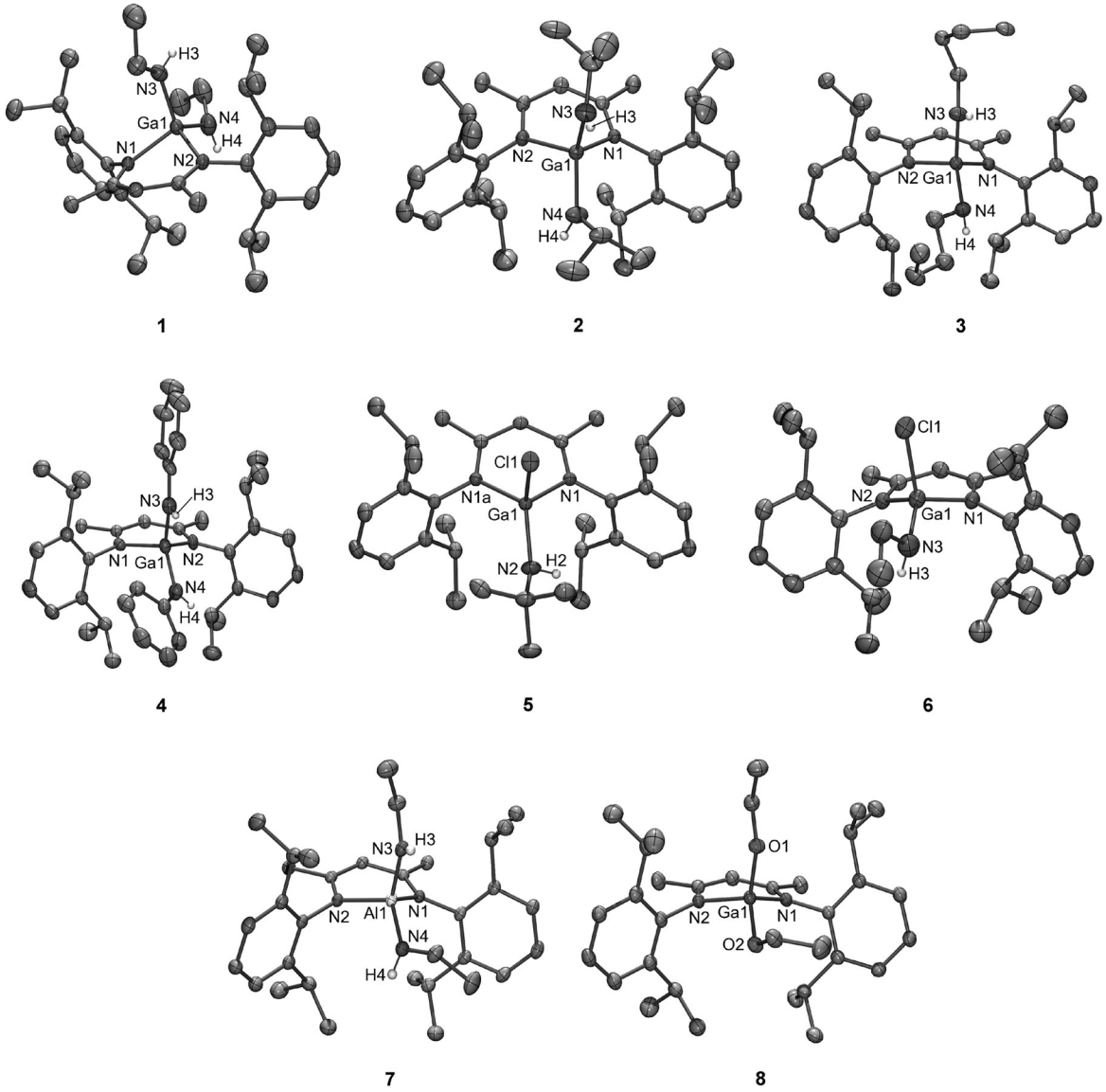


Figure 1. Crystal structures of compounds **1**–**8**. All carbon-bound hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Table 1. Selected bond lengths [Å] and angles [°] for compounds **1**–**8**.

	1[a]	**2**[a]	**3**[a]	**4**[a]	**5**[a,b]	**6**[a]	**8**[a]	**7**[a]
M1–N1	1.997(1)	1.979(2)	1.968(2)	1.945(3)	1.939(2)	1.916(3)	1.949(1)	1.928(2)
M1–N2[b]	1.964(2)	1.978(2)	1.976(2)	1.947(3)	1.939(2)	1.947(3)	1.935(1)	1.908(2)
M1–X1[a]	1.862(2)	1.857(2)	1.846(2)	1.862(3)	1.850(3)	1.825(4)	1.812(1)	1.794(2)
M1–X2[a]	1.843(2)	1.837(2)	1.855(3)	1.851(3)	2.200(1)	2.213(1)	1.802(1)	1.787(2)
N1–M1–N2[a,b]	94.5(1)	94.2(1)	95.2(1)	96.4(1)	97.5(1)	97.5(1)	97.3(1)	95.2(1)
N1–M1–X1[a,b]	106.5(1)	111.9(1	111.9(1)	110.4(1)	116.9(3)	114.5(2)	110.9(1)	108.0(1)
N1–M1–X2[a,b]	116.3(1)	114.3(1)	112.9(1)	115.0(1)	105.6(1)	108.9(1)	114.4(1)	115.3(1)
N2–M1–X1[a,b]	111.7(1	113.3(1)	114.5(1)	116.4(1)	108.9(4)	117.9(2)	114.2(1)	112.0(1)
N2–M1–X2[a,b]	111.5(1)	109.4(1)	106.0(1)	109.0(1)	105.6(1)	103.6(1)	111.1(1)	113.0(1)
X1–M1–X2[a,b]	114.4(1)	112.5(1)	114.7(1)	109.3(1)	119.6(1)	113.0(1)	108.7(1)	112.4(1)

[a] For compounds **1**–**6** and **8**, M = Ga; for compound **7**, M = Al. For compounds **1**–**4** and **7**, X1 = N3; X2 = N4; for compound **5**, X1 = N2; X2 = Cl1; for compound **6**, X1 = N3; X2 = Cl1; for compound **8**, X1 = O1; X2 = O2. [b] In compound **5**, only half of the molecule is in the asymmetric unit; thus, N2 = N1A.

$(OCH_2CH_2NMe_2)_2$,[28] $ClGa[OC(CF_3)_2CH_2NMe_2]_2$,[29] and $ClGa[OC(CF_3)_2CH_2CMe{=}NMe]_2$.[29] Moreover, the synthesis of dialkoxygallium derivatives usually requires high temperatures, redistribution, or substitution (synthesis from trialkoxides by replacing one of the alkoxy groups by other substituent, mostly halogen atom) reactions. Therefore, compounds **1**–**6** are interesting precursors for the synthesis of gallium alkoxides, which are important synthons for gallium oxide materials. Furthermore, previously reported $LGa(OH)_2$[8] can be obtained from the controlled hydrolysis of compounds **1**–**4** in an almost quantitative yield (up to 95% isolated product). This is a significant improvement in the synthesis of this compound, as the procedure does not need any expensive reagents and is easily scalable.

The solid-state structures of compounds **1**–**8** were determined by X-ray crystallography (Figure 1). The isomorphous compounds **1** and **7** and compound **8** crystallize in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. Of the remaining compounds, the following also crystallize in the monoclinic system (the corresponding space group and asymmetric unit content are given in the parenthesis): compound **2** ($P2_1$, one molecule), compound **3** ($P2_1/c$, one molecule), compound **5** ($P2_1/m$, half of the molecule), and compound **6** ($P2_1/c$, one molecule). Finally, compound **4** crystallizes in the orthorhombic space group *Pcca* with one molecule of **4** and one half of a toluene molecule in the asymmetric unit. Compounds **1**–**8** are discrete molecules in the solid state with no apparent hydrogen bonding. The general feature of compounds **1**–**4** is the coordination of the central gallium atom to four atoms of nitrogen − two from the β-diketiminate ligand (*endo*) and two from the amine substituents (*exo*). There is a clear difference in the bond lengths for the Ga–N_{exo} [in **1**: 1.862(2), 1.843(2) Å; **2**: 1.857(2), 1.837(2) Å; **3**: 1.846(2), 1.855(2) Å; and **4**: 1.862(2), 1.851(2) Å] and Ga–N_{endo} [**1**: 1.977(1), 1.964(2) Å; **2**: 1.979(2), 1.978(2) Å; **3**: 1.968(2), 1.976(2) Å; and **4**: 1.945(2), 1.947(2) Å] bonds, confirming the partial donor–acceptor character of the latter bonds, which are similar to those observed in $LGa(NH_2)_2$ [1.852(2), 1.847(2), 1.955(2), and 1.976(2) Å]. The values for the Ga–N_{exo} bonds are in general smaller than the sum of the covalent radii for gallium and nitrogen (1.90 Å),[30] which is probably a result of the higher ionic contribution of these bonds.[31,32] This shortening of the Ga–N_{exo} bond is even larger in compound **6** [1.825(1) Å] owing to the presence of the electronegative chlorine atom attached to the gallium center and a small substituent on the nitrogen atom. A similar effect can also be observed in compound **8**, where the Ga–O bonds [1.812(1) and 1.802(1) Å] are nearly 0.1 Å shorter than the sum of the covalent radii of gallium and oxygen (1.90 Å).[30] Nevertheless, they are slightly longer or comparable to the terminal Ga–O(alkyl) bonds in $[\{(Me_3Si)_3Si\}(EtO)Ga(\mu\text{-}OEt)]_2$ [1.785(7) Å],[22] $[(t\text{BuO})HGa(\mu\text{-}O t\text{Bu})]_2$ [1.782(5) Å],[23] $Ga(O t\text{Bu})_3NHMe_2$ [1.799(2)–1.822(2) Å],[24] $Ga[(\mu\text{-}O i\text{Pr})_2Ga(O i\text{Pr})_2]_3$ (av. 1.805 Å, only bonds without disorder),[24] $Ga[OCH(CF_3)_2]_3$-(4-Me_2Npy) (py = pyridine) [1.801(5)–1.811(5) Å],[25] Ga-$[OCMe_2CF_3]_3$(4-Me_2Npy) [1.778(9)–1.802(8) Å],[25] $[Ga(\mu\text{-}OCMe_2Et)(OCMe_2Et)_2]_2$ [1.768(2)–1.782(2) Å],[24] and $LGa(OH)_2$ [1.777(1)–1.820(1) Å],[8] but shorter than those in $(i\text{PrO})Ga(S_2CNEt_2)_2$ [1.932(1) Å][33] and in $LGa(\mu\text{-}O)_2$-GaL [1.848(1) and 1.854(1) Å].[9] Furthermore, the Ga–Cl bond lengths found for **5** [2.200(1) Å] and **6** [2.213(1) Å] are comparable to those in the starting material $LGaCl_2$ [2.218(1), 2.228(1) Å].[11] In all nine compounds, the coordination sphere around the central metal has a distorted tetrahedral geometry, where the N_{endo}–M–N_{endo} (**1**–**6**, **8** M = Ga; **7** M = Al) angle is the most acute one with a relatively narrow range of values [94.2(1)–97.5(1)°]. The other angles around the metal center display significantly higher variations, as the interval is 16° wide with the range 103.6(1)–119.6(1)°. Selected bond lengths and angles for compounds **1**–**8** are reported in Table 1.

Conclusions

Seven group 13 monomeric diamides (**1**–**7**) were synthesized, and their reactivity towards protonolysis was proven through the isolation of $LGa(OEt)_2$, LGa(OEt)Cl, and the previously reported $LGa(OH)_2$ in nearly quantitative yields. The possibilities to use these gallium amido compounds for the preparation of more complex systems are underway.

Experimental Section

General: All manipulations described bellow were performed under a dry nitrogen atmosphere using Schlenk and glove box techniques.

The solvents were purchased from Aldrich and dried prior to use. Aniline, isopropylamine, *n*-butylamine, and *tert*-butylamine (Aldrich, 99%) were dried (CaH_2) and purified by distillation under a protective nitrogen atmosphere. $LGaCl_2$, $LAlCl_2$, and LiNH*t*Bu were prepared according to literature procedures.[11,18] Ethylamine (2.0 M in THF), methyllithium (3.0 M in dimethoxyethane), and *n*-butyllithium (2.0 M in hexane) solutions were purchased from Aldrich and used as received. C_6D_6 was distilled from Na/K alloy and degassed (3×) before use. NMR spectroscopic data were recorded with Jeol Eclipse or Bruker Avance 300 MHz spectrometers and referenced to the residual protons of the deuterated solvent. Elemental analyses were performed with an Exeter Analytical CE-440 analyzer. We were not able to obtain elemental analyses of satisfactory quality for compounds **1** and **7** because of their high reactivity.

$LGa(NHX)_2$ [X = Et (1), *i*Pr (2), *n*Bu (3)]: The corresponding amine (**1**: 2.0 M in THF, 5.00 mL, 10.0 mmol; **2**: 1.00 mL, 11.6 mmol; **3**: 1.00 mL, 10.2 mmol) was added dropwise to a solution of MeLi (3.0 M, 1.25 mL, 3.75 mmol) in THF (15 mL) at –78 °C. The reaction mixture was warmed to ambient temperature, stirred for an additional 30 min, and then slowly added to a solution of $LGaCl_2$ (1.00 g, 1.79 mmol) in THF (15 mL) at –78 °C. The reaction mixture was warmed to ambient temperature and stirred for an additional 2 h. All the volatiles were removed in vacuo, and the products were extracted with hexane. Compounds **1**–**3** were obtained as white crystalline solids.

$LGa(NHEt)_2$ (1): Yield: 0.89 g (86%). M.p. 156–158 °C. IR (KBr): $\tilde{\nu}$ = 3381 (w, νNH) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = –0.27 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, N*H*), 0.95 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, $NHCH_2CH_3$), 1.21 [d, $^3J_{H,H}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$], 1.42 [d, $^3J_{H,H}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$], 1.56 (s, 6 H, CH_3), 2.90 (dq, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,H}$ = 7.3 Hz, 2 H, $NHCH_2CH_3$), 3.55 [sept., $^3J_{H,H}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$], 4.71 (s, 1 H, γ-C*H*), 7.05–7.15 (m, 6 H, *m*-, *p*-Ar-*H*) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): δ = 21.7 ($NHCH_2CH_3$), 23.4 (CH_3), 24.7, 25.4 [$CH(CH_3)_2$], 28.1 [$CH(CH_3)_2$], 40.9 ($NHCH_2$), 95.9 (γ-*C*H), 124.3, 126.9 (*m*-, *p*-*C* of Ar), 141.9 (*i*-*C* of Ar), 144.4 (*o*-*C* of Ar), 169.1 (*C*=N) ppm. MS (EI): *m*/*z* (%) = 574 (3) $[M]^+$, 530 (100) $[M – NHEt]^+$.

$LGa(NHiPr)_2$ (2): Yield: 0.69 g (64%). M.p. 152–154 °C. $C_{35}H_{57}GaN_4$ (603.6): calcd. C 69.65, H 9.52, N 9.28; found C 69.3, H 9.3, N 9.1. IR (KBr): $\tilde{\nu}$ = 3371 (w, νNH) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = –0.13 (d, $^3J_{H,H}$ = 6.6 Hz, 2 H, N*H*), 0.98 [d, $^3J_{H,H}$ = 6.0 Hz, 12 H, $CHN(CH_3)_2$] 1.20 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, $CH(CH_3)_2$], 1.40 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, $CH(CH_3)_2$], 1.52 (s, 6 H, CH_3), 3.22 [dsept., $^3J_{H,H}$ = 6.6 Hz, $^3J_{H,H}$ = 6.0 Hz, 2 H, $NCH(CH_3)_2$], 3.65 [sept., $^3J_{H,H}$ = 6.6 Hz, 4 H, $CH(CH_3)_2$], 4.79 (s, 1 H, γ-C*H*), 7.05–7.15 (m, 6 H, *m*-, *p*-Ar-*H*) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): δ = 23.7 [$CH(CH_3)_2$], 24.5, 25.4 [$CH(CH_3)_2$], 27.8 [$CH(CH_3)_2$], 28.8 (CH_3), 45.6 (N*C*H), 96.8 (γ-*C*H), 123.6, 124.2, 125.0, 126.6, 144.2 (*i*-, *o*-, *m*-, *p*-*C* of Ar), 169.1 (*C*=N) ppm. MS (EI): *m*/*z* (%) = 602 (2) $[M]^+$, 544 (100) $[M – NHiPr]^+$.

$LGa(NHnBu)_2$ (3): Yield: 0.65 g (58%). M.p. 101–102 °C. $C_{37}H_{61}GaN_4$ (631.6): calcd. C 70.36, H 9.73, N 8.87; found C 70.0, H 9.4, N 8.5. IR (KBr): $\tilde{\nu}$ = 3379 (w, νNH) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = –0.16 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, N*H*), 0.84 [t, $^3J_{H,H}$ = 6.9 Hz, 3 H, $NH(CH_2)_3CH_3$], 1.22 [d, $^3J_{H,H}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$], 1.43 [d, $^3J_{H,H}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$], 1.56 (s, 6 H, CH_3), 2.87 (dt, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,H}$ = 6.9 Hz, 2 H, $NHCH_2CH_3$), 3.56 [sept., $^3J_{H,H}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$], 4.72 (s, 1 H, γ-C*H*), 7.05–7.15 (m, 6 H, *m*-, *p*-Ar-*H*) ppm. Remaining signals of the butyl CH_2 groups could not be observed. ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): δ = 14.5 [$HN(CH_2)_3CH_3$], 20.6 [$HN(CH_2)_2CH_2CH_3$], 23.4 (CH_3), 24.7, 25.5 [$CH(CH_3)_2$], 28.1 [$CH(CH_3)_2$], 38.9 ($NHCH_2CH_2CH_2CH_3$), 46.5 ($NHCH_2nPr$), 96.1 (γ-*C*H), 124.3, 126.9 (*m*-, *p*-*C* of Ar), 142.0 (*i*-*C* of Ar), 144.3 (*o*-*C* of Ar), 169.2 (*C*=N) ppm. MS (EI): *m*/*z* (%) = 558 (100) $[M – NHnBu]^+$.

$LGa(NHPh)_2$ (4): *n*BuLi (2.0 M, 1.9 mL, 3.8 mmol) was added dropwise to a solution of NH_2Ph (0.35 mL, 3.8 mmol) in THF (15 mL) at –78 °C. The reaction mixture was warmed to ambient temperature, stirred for an additional 30 min, and then slowly added to $LGaCl_2$ (1.00 g, 1.79 mmol) in THF (15 mL) at –78 °C. The reaction mixture was warmed to ambient temperature and stirred for an additional 6 h. All the volatiles were removed in vacuo. The product was extracted with toluene and rinsed with hexane. Compound **4** was obtained as a pale-yellow microcrystalline solid. Yield: 0.89 g (74%). M.p. 218–220 °C. $C_{41}H_{53}GaN_4$ (671.6): calcd. C 73.32, H 7.95, N 8.34; found C 72.9, H 7.8, N 8.0. IR (KBr): $\tilde{\nu}$ = 3380 (w, νNH) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = 1.03 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, $CH(CH_3)_2$], 1.19 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, $CH(CH_3)_2$], 1.54 (s, 6 H, CH_3), 3.32 [sept., $^3J_{H,H}$ = 6.9 Hz, 4 H, $CH(CH_3)_2$], 4.98 (s, 1 H, γ-C*H*), 6.16 (br., 2 H, N*H*), 6.57 (br. s, 2 H, *p*-Ph-*H*) 7.05–7.08 (m, 6 H, *m*-, *p*-Ar–*H*), 7.12–7.15 (m, 8 H, *o*-, *m*-Ph-*H*) ppm.^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): δ = 23.2 (CH_3), 24.3, 24.5 [$CH(CH_3)_2$], 28.1 [$CH(CH_3)_2$], 95.9 (γ-*C*H), 114.9 (*p*-*C* of Ph), 116.0 (*i*-*C* of Ph), 124.5, 128.3, 128.8, 129.0, 140.2, 144.4 (*o*-, *m*-, *p*-*C* of Ph and *i*-, *o*-, *m*-*C* of Ar), 169.8 (*C* = N) ppm. MS (EI): *m*/*z* (%) = 670 (6) $[M]^+$, 578 (100) $[M – NHC_6H_5]^+$, 487 (52) $[M – 2\ NHC_6H_5]^+$.

$LGa(NHtBu)Cl$ (5): A solution of LiNH*t*Bu (0.20 g, 2.53 mmol) in THF (10 mL) was added dropwise to a solution of $LGaCl_2$ (1.00 g, 1.79 mmol) in THF (10 mL) at –78 °C. The reaction mixture was warmed to ambient temperature and stirred for an additional 6 h. All the volatiles were removed in vacuo, and the crude product was extracted with toluene and rinsed with hexane to obtained **5** as a pale-yellow solid. Yield: 0.90 g (85%). M.p. 226–230 °C. $C_{33}H_{51}ClGaN_3$ (594.95): calcd. C 66.62, H 8.64, N 7.06; found C 66.5, H 8.5, N 6.8. IR (KBr): $\tilde{\nu}$ = 3338 (w, νNH) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = –0.03 (br. s, 1 H, N*H*), 0.88 [s, 9 H, $(CH_3)_3CNH$], 1.03 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, $CH(CH_3)_2$], 1.19 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, $CH(CH_3)_2$], 1.42 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, $CH(CH_3)_2$], 1.53 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, $CH(CH_3)_2$], 1.55 (s, 6 H, CH_3), 3.31 [sept., $^3J_{H,H}$ = 6.8 Hz, 2 H, $CH(CH_3)_2$], 3.78 [sept., $^3J_{H,H}$ = 6.8 Hz, 2 H, $CH(CH_3)_2$], 4.79 (s, 1 H, γ-C*H*), 7.05–7.15 (m, 6 H, *m*-, *p*-Ar- *H*) ppm. ^{13}C NMR (C_6D_6, 25 °C, TMS): δ = 23.7, 24.2, 24.7, 24.8 [$CH(CH_3)_2$], 26.6, 28.0 [$CH(CH_3)_2$], 29.0 (CH_3), 34.2 [$NC(CH_3)_3$], 49.9 [$NC(CH_3)_3$], 96.7 (γ-*C*H), 123.9, 125.3, 127.6, 140.3, 143.4, 145.9 (*i*-, *o*-, *m*-, *p*-*C* of Ar), 169.6 (*C*=N) ppm. MS (EI): *m*/*z* (%) = 593 (9) $[M]^+$, 521 (100) $[M – NHtBu]^+$.

$LGa(NHEt)Cl$ (6): Compound **6** was prepared in the same manner as compounds **1**–**3** starting from MeLi (3.0 M, 0.60 mL, 1.80 mmol), $EtNH_2$ (2.0 M in THF, 2.50 mL, 5.00 mmol), and $LGaCl_2$ (1.00 g, 1.79 mmol). Yield: 0.83 g (82%). M.p. 80–82 °C. $C_{31}H_{47}ClGaN_3$ (566.90): calcd. C 65.68, H 8.36, N 7.41; found C 65.9, H 8.4, N 7.1. IR (KBr): $\tilde{\nu}$ = 3335 (w, νNH) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = –0.02 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, N*H*) 0.60 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3CH_2NH) 1.07 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, $CH(CH_3)_2$], 1.21 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, $CH(CH_3)_2$], 1.38 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, $CH(CH_3)_2$], 1.54 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, $CH(CH_3)_2$], 1.55 (s, 6 H, CH_3), 2.64 (quint., $^3J_{H,H}$ = 7.2 Hz, 2 H, $NHCH_2CH_3$), 3.28 [sept., $^3J_{H,H}$ = 6.8 Hz, 2 H, $CH(CH_3)_2$], 3.78 [sept., $^3J_{H,H}$ = 6.8 Hz, 2 H, $CH(CH_3)_2$], 4.81 (s, 1 H, γ-C*H*), 7.05–7.17 (m, 6 H, *m*-, *p*-Ar-*H*) ppm. ^{13}C NMR (C_6D_6, 25 °C,

TMS): δ = 23.5, 24.2, 24.5, 24.8 [CH(CH_3)$_2$], 26.8, 28.1 [CH-(CH_3)$_2$], 28.6 (CH_3), 29.0 (NCH$_2$$CH_3$), 39.7 (N$CH_2$), 96.8 ($\gamma$-$CH$), 123.5, 123.9, 127.7, 140.1, 143.5, 145.7 (C of Ar), 170.0 (C=N) ppm. MS (EI): *m*/*z* (%) = 565 (6) [M]$^+$, 550 (14) [M – CH_3]$^+$, 506 (100) [M – NHEt – CH_3]$^+$.

LAl(NHEt)$_2$ (7): Compound **7** was prepared in the same manner as compounds **1**–**3**, starting from MeLi (3.0 M, 1.36 mL, 4.08 mmol), $EtNH_2$ (2.0 M in THF, 2.42 mL, 4.84 mmol), and $LAlCl_2$ (1.00 g, 1.94 mmol). Yield: 0.64 g (62%). M.p. 126–128 °C. IR (KBr): $\tilde{\nu}$ = 3381 (w, νNH) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = –0.29 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, NH), 0.98 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, NHCH$_2$CH_3), 1.25 [d, $^3J_{H,H}$ = 7.0 Hz, 12 H, CH(CH_3)$_2$], 1.46 [d, $^3J_{H,H}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.61 (s, 6 H, CH_3), 2.90 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,H}$ = 7.3 Hz, 2 H, NHCH_2CH$_3$), 3.59 [sept.,

Table 2. Crystallographic and data collection details for compounds **1**–**8**.

	1	**2**	**3**	**4·0.5C$_7$H$_8$**
Formula	$C_{33}H_{53}GaN_4$	$C_{35}H_{57}GaN_4$	$C_{37}H_{61}GaN_4$	$C_{44.50}H_{57}GaN_4$
Fw	575.51	603.57	631.62	717.66
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1$	$P2_1/c$	$Pcca$
T [K]	173(2)	173(2)	100(2)	173(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
a [Å]	12.818(1)	9.875(1)	12.947(2)	38.964(5)
b [Å]	16.470(2)	16.478(2)	13.065(2)	11.938(2)
c [Å]	16.050(2)	11.561(2)	20.945(3)	17.126(3)
β [°]	105.70(1)	111.31(2)	91.89(2)	90
V [Å^3]	3261.9(6)	1752.6(4)	3541.0(9)	7966(2)
Z	4	2	4	8
$D_{calcd.}$ [g cm^{-3}]	1.172	1.144	1.185	1.197
μ [mm^{-1}]	0.870	0.812	0.807	0.726
F(000)	1240	652	1368	3064
Crystal size [mm^3]	0.39 × 0.21 × 0.15	0.56 × 0.40 × 0.38	0.44 × 0.25 × 0.25	0.26 × 0.18 × 0.04
θ range [°]	1.81–25.37	1.89–25.36	1.84–25.04	1.05–25.11
Index ranges	$-15 \le h \le 15$	$-11 \le h \le 11$	$-15 \le h \le 15$	$-46 \le h \le 46$
	$-19 \le k \le 19$	$-19 \le k \le 19$	$-15 \le k \le 15$	$-14 \le k \le 14$
	$-19 \le l \le 19$	$-9 \le l \le 13$	$-24 \le l \le 24$	$-20 \le l \le 20$
No. reflns collected	44002	10965	24409	61506
No. indep. reflns (R_{int})	5955 (0.0436)	6151 (0.0291)	6187 (0.0518)	7058 (0.1084)
No. data/restr./parameters	5955/160/404	6151/302/465	6187/429/476	7058/625/596
GoF on F^2	0.935	0.900	1.015	1.042
R_1,[a] wR_2[b] [$I > 2\sigma(I)$]	0.0315, 0.0757	0.0305, 0.0570	0.0461, 0.1168	0.0546, 0.1060
R_1,[a] wR_2[b] (all data)	0.0405, 0.0783	0.0351, 0.0579	0.0568, 0.1225	0.0850, 0.1173
Abs. struct. par.	–	–0.009(7)	–	–
Largest diff. peak/hole [e Å^{-3}]	0.399/–0.239	0.346/–0.214	1.846/–0.496	0.392/–0.342
	5	**6**	**7**	**8**
Formula	$C_{33}H_{51}ClGaN_3$	$C_{31}H_{47}ClGaN_3$	$C_{33}H_{53}AlN_4$	$C_{33}H_{51}GaN_2O_2$
Fw	594.94	566.89	532.77	577.48
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/m$	$P2_1/c$	$P2_1/n$	$P2_1/n$
T [K]	173(2)	173(2)	100(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
a [Å]	9.079(2)	12.746(2)	12.603(2)	11.854(2)
b [Å]	20.265(3)	13.538(2)	16.464(3)	16.604(2)
c [Å]	9.842(2)	18.782(3)	15.966(3)	16.518(3)
β [°]	113.05(2)	107.00(2)	105.17(3)	104.21(2)
V [Å^3]	1666.2(6)	3099.3(9)	3197.4(10)	3151.7(9)
Z	2	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.186	1.215	1.107	1.217
μ [mm^{-1}]	0.930	0.997	0.090	0.903
F(000)	636	1208	1168	1240
Crystal size [mm^3]	0.34 × 0.31 × 0.24	0.36 × 0.16 × 0.15	0.39 × 0.34 × 0.32	0.33 × 0.23 × 0.23
θ range [°]	2.01–25.36	1.67–25.03	1.81–25.03	1.77–25.36
Index ranges	$-10 \le h \le 10$	$-14 \le h \le 15$	$-15 \le h \le 15$	$-14 \le h \le 14$
	$-23 \le k \le 24$	$-16 \le k \le 15$	$-19 \le k \le 19$	$-20 \le k \le 19$
	$-11 \le l \le 11$	$-22 \le l \le 22$	$-18 \le l \le 19$	$-19 \le l \le 19$
No. reflns collected	11327	20111	20740	25238
No. indep. reflns (R_{int})	3114 (0.0388)	5458 (0.0724)	5613 (0.0501)	5732 (0.0330)
No. data/restr./parameters	3114/253/272	5458/67/365	5613/2/364	5732/87/388
GoF on F^2	1.048	1.001	1.046	1.033
R_1,[a] wR_2[b] [$I > 2\sigma(I)$]	0.0348, 0.0806	0.0543, 0.1187	0.0475, 0.1127	0.0299, 0.0739
R_1,[a] wR_2[b] (all data)	0.0405, 0.0833	0.0823, 0.1329	0.0614, 0.1210	0.0344, 0.0765
Largest diff. peak/hole [e Å^{-3}]	0.592/–0.222	0.823/–0.272	0.425/–0.208	0.417/–0.170

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$.

$^3J_{H,H}$ = 6.8 Hz, 4 H, C*H*(CH_3)$_2$], 4.92 (s, 1 H, γ-C*H*), 7.15–7.20 (m, 6 H, *m*-, *p*-Ar-*H*) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): δ = 21.5 (NHCH$_2$*C*H$_3$), 23.4 (*C*H$_3$), 24.5, 25.1 [CH(*C*H$_3$)$_2$], 27.8 [*C*H(CH$_3$)$_2$], 38.5 (NH*C*H$_2$), 96.9 (γ-*C*H), 123.9, 126.3 (*m*-, *p*-*C* of Ar), 141.3 (*i*-*C* of Ar), 144.3 (*o*-*C* of Ar), 169.2 (*C*=N) ppm. MS (EI): *m*/*z* (%) = 532 (2) [M]$^+$, 488 (100) [M – NHEt]$^+$.

LGa(OEt)$_2$ (8): A solution of ethanol (0.30 mL, 5.14 mmol) in THF (15 mL) was added dropwise to a solution of **1** (1.00 g, 1.74 mmol) in THF. The reaction mixture was stirred for 2 h, and **7** was obtained as a white crystalline solid after removing all volatiles. Yield: 0.95 g (95%). M.p. 156–158 °C. $C_{33}H_{51}GaN_2O_2$ (577.5): calcd. C 68.63, H 8.90, N 4.85; found C 68.4, H 8.8, N 4.7. ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = 1.09 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 1.16 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.48 [d, $^3J_{H,H}$ = 6.6 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.52 (s, 6 H, C*H*$_3$), 3.52 [sept., $^3J_{H,H}$ = 6.9 Hz, 4 H, C*H*(CH$_3$)$_2$], 3.84 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.73 (s, 1 H, γ-C*H*), 7.10–7.20 (m, 6 H, *m*-, *p*-Ar-*H*) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): δ = 20.7 (OCH$_2$*C*H$_3$), 23.4 (*C*H$_3$), 24.7, 25.0 [CH(*C*H$_3$)$_2$], 28.6 [*C*H(CH$_3$)$_2$], 60.9 (O*C*H$_2$), 96.0 (γ-*C*H), 124.3, 128.3, 140.7 (*C* of Ar), 144.5 (*o*-*C* of Ar), 170.5 (*C*=N) ppm. MS (EI): *m*/*z* (%) = 576 (2) [M]$^+$, 531 (33) [M – OEt]$^+$, 515 (50) [M – OEt – Me – H]$^+$, 486 (78) [M – 2OEt]$^+$, 471 (100) [M – 2OEt – Me]$^+$.

LGa(OEt)Cl (9): Ethanol (0.5 M in THF, 2.0 mL, 1.00 mmol) was dissolved in THF (10 mL) and added dropwise to a solution of **5** (0.29 g, 0.49 mmol) in THF (15 mL) at –78 °C. The reaction mixture was warmed to ambient temperature and stirred for overnight. All volatiles were removed in vacuo, and **9** was obtained as a white solid after washing the crude product with hexane. Yield: 0.27 g (93%). M.p. 173–175 °C. $C_{31}H_{46}ClGaN_2O$ (567.9): calcd. C 65.57, H 8.16, N 4.93; found C 65.3, H 8.1, N 4.8. ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = 0.77 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, OCH$_2$C*H*$_3$), 1.14 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.19 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.53 [d, $^3J_{H,H}$ = 6.6 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.56 (s, 6 H, C*H*$_3$), 3.38 [sept., $^3J_{H,H}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$], 3.61 [sept., $^3J_{H,H}$ = 6.6 Hz, 2 H, C*H*(CH$_3$)$_2$], 3.64 (q, $^3J_{H,H}$ = 6.9 Hz, 2 H, OC*H*$_2$CH$_3$), 4.78 (s, 1 H, γ-C*H*), 7.10–7.20 (m, 6 H, *m*-, *p*-Ar-*H*) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): δ = 19.6 (OCH$_2$*C*H$_3$), 23.8 (*C*H$_3$), 24.3, 24.8, 24.9, 25.6 [CH(*C*H$_3$)$_2$], 28.1, 28.5 [*C*H(CH$_3$)$_2$], 60.4 (O*C*H$_2$), 96.5 (γ-*C*H), 124.2, 124.5, 127.5, 138.9 (*C* of Ar), 144.5, 144.7 (*o*-*C* of Ar), 170.9 (*C*=N) ppm. MS (EI): *m*/*z* (%) = 566 (3) [M]$^+$, 531 (10) [M – Cl]$^+$, 521 (88) [M – OC_2H_4]$^+$, 506 (100) [M – OC_2H_4 – CH_3]$^+$, 471 (39) [M – OC_2H_5 – Cl – Me]$^+$.

LGa(OH)$_2$: Water (0.5 M in THF, 6.60 mL, 3.30 mmol) was added dropwise to a solution of **1** (1.00 g, 1.74 mmol) in THF (15 mL) at –78 °C. The reaction mixture was warmed to ambient temperature and stirred for 2 h. All volatiles were removed in vacuo, and LGa(OH)$_2$ was obtained as a white microcrystalline solid after washing the crude product with hexanes. Yield: 0.86 g (95%). The spectroscopic data were identical to those reported previously.[7]

X-ray Structure Determination: Crystals of compounds **1**–**8** were mounted on nylon loops and rapidly placed in a stream of cold nitrogen. Diffraction data were collected with a Bruker-APEX three-circle diffractometer with the use of Mo-K_α radiation (λ = 0.71073 Å) at –100 °C (**1**, **2**, and **4**–**6**) or at –173 °C (**3**, **7**, and **8**). Structures were solved by direct methods (SHELXS-97)[34] and refined against all data by full-matrix least-squares on F_2.[34] The hydrogen atoms of the C–H bonds were placed in idealized positions, whereas the hydrogen atoms from the NH and OH moieties were localized from the difference electron density map, and their position was refined with U_{iso} tight to the parent atom with distance restraints (SADI) when applicable. The Flack parameter[35] [–0.009(7)] was used to determine the correct enantiomorph of compound **2**. The disordered groups (2NHEt in **1**, 2NH*i*P and Ph*i*Pr in **2**, 2*n*Bu and Ph*i*Pr in **3**, 2,6-*i*Pr$_2$C$_6$H$_3$ and toluene in **4**, NH*t*Bu and Ph*i*Pr in **5**, NHEt in **6**, Ph*i*Pr in **8**) were refined using geometry and distance restraints (SAME, SADI) together with the restraints for the U_{ij} values (SIMU, DELU). Table 2 contains relevant crystallographic and data collection details for compounds **1**–**8**. CCDC-735439 (for **1**), -735440 (for **2**), -735441 (for **3**), -735442 (for **4**), -735443 (for **5**), -735444 (for **6**), -735445 (for **7**), and -735446 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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