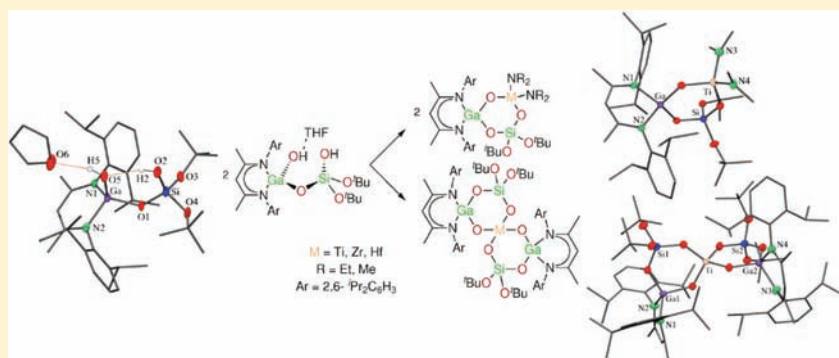


## Molecular Gallosilicates and Their Group 4 Multimetallic Derivatives

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Supporting Information

## ABSTRACT:



Reaction between the silanediol  $(\text{HO})_2\text{Si}(\text{OtBu})_2$  and gallium amides,  $\text{LGaCl}(\text{NH}t\text{Bu})$  and  $\text{LGa}(\text{NHEt})_2$  ( $\text{L} = [\text{HC}\{\text{C}(\text{Me})\text{N}(\text{Ar})\}_2]^-$ ,  $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ), respectively, resulted in the facile isolation of molecular gallosilicates  $\text{LGaCl}(\mu\text{-O})\text{Si}(\text{OH})(\text{OtBu})_2$  (**1**) and  $\text{LGa}(\text{NHEt})(\mu\text{-O})\text{Si}(\text{OH})(\text{OtBu})_2$  (**2**). Compound **2** easily reacts with 1 equiv of water to form the unique gallosilicate-hydroxide  $\text{LGa}(\text{OH}\cdot\text{THF})(\mu\text{-O})\text{Si}(\text{OH})(\text{OtBu})_2$  (**3**). Compounds **1–3** contain the simple Ga–O–Si framework and are the first structurally authenticated molecular gallosilicates. These compounds may be used not only as models for gallosilicate-based materials but also as further reagents because of the presence of reactive functional groups attached to both gallium and silicon atoms. Accordingly, seven molecular heterometallic compounds were obtained from the reactions between compound **3** and group 4 amides  $\text{M}(\text{NMe}_2)_4$  ( $\text{M} = \text{Ti}, \text{Zr}$ ) or  $\text{M}(\text{NEt}_2)_4$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ). Hence, by tuning the reactions conditions and stoichiometries, it was possible to isolate and structurally characterize the complete 1:1 and 2:1 series (**4–10**). Completely inorganic cores of types  $\text{M–O–Ga–O–Si–O}$  and spiro  $\text{M}[\text{O–Ga–O–Si–O}]_2$  were obtained and characterized by common spectroscopic techniques.

## INTRODUCTION

Zeolitic and microporous materials such as aluminosilicates have recently attracted great interest because of their applications as molecular sieves, ion exchangers, and as catalysts in a wide range of technologically and commercially important processes.<sup>1</sup> However, control over the element distribution and the understanding of the catalysis mechanisms in these materials has not yet been accomplished and has been the subject of numerous investigations.<sup>1c,2</sup> Although there have been some molecular approaches for studying aluminosilicate-based materials,<sup>3</sup> up to date, research on molecular gallosilicates have been neglected. Actually, there are no reports of structurally characterized molecular or heterometallic gallosilicates. The closest comparable species are silsesquioxane-based systems;<sup>2e,4</sup> yet, they do not properly resemble silicates or zeolitic materials, and they are not suitable precursors for gallosilicate materials because of the presence of Si–C bonds, which usually lead to carbon and/or silicon carbide contamination in the final products.<sup>2e,4b,5</sup>

Molecular gallosilicates and heterometallic derivatives could serve as model compounds for structural analyses, elucidation of

catalytic mechanisms, as well as precursors in the synthesis of heterogeneous systems. Furthermore, the presence of two different metals arranged in close proximity might lead to a cooperative or simultaneous activation of substrate molecules.<sup>6</sup> Particularly, the incorporation of group 4 metals is of great interest because of their redox and catalytic activities.<sup>7</sup> For example, heterobimetallic complexes with  $\text{M–O–M}^*$  moieties ( $\text{M} = \text{Al}, \text{Ga}$ ;  $\text{M}^* = \text{Ti}, \text{Zr}$ ) have exhibited high catalytic activity in the polymerization of ethylene and have been considered as model systems for the study of olefin polymerization.<sup>6b,c,h,i,8</sup>

Therefore, we became interested in the isolation of gallosilicate precursors similar to those previously reported by our group for aluminum,  $\text{LAl}(\text{EH})(\mu\text{-O})\text{Si}(\text{OH})(\text{OtBu})_2$  ( $\text{E} = \text{O}, \text{S}$ ;  $\text{L} = [\text{HC}\{\text{C}(\text{Me})\text{N}(\text{Ar})\}_2]^-$ ,  $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ).<sup>9</sup> Unfortunately, it is not possible to use the same synthetic methodology as in the case of aluminosilicates, given that there are no equivalent precursors,<sup>10</sup> and thus, it was necessary to design new synthetic

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strategies that would allow easy isolation of analogous gallosilicates. Herein, we report on a facile synthesis of the three molecular gallosilicates LGaCl( $\mu$ -O)Si(OH)(OtBu)<sub>2</sub> (**1**), LGa(NHtEt)( $\mu$ -O)Si(OH)(OtBu)<sub>2</sub> (**2**), and LGa(OH·THF)( $\mu$ -O)Si(OH)(OtBu)<sub>2</sub> (**3**) and their use as synthons for molecular heterobimetallic gallosilicates.

## EXPERIMENTAL SECTION

**General Considerations.** All manipulations described below were performed under a dried nitrogen atmosphere using Schlenk and glovebox techniques. The solvents were purchased from Aldrich and dried prior to use with an MBraun SPS using Grubs' columns. Ti(NMe<sub>2</sub>)<sub>4</sub>, Zr(NMe<sub>2</sub>)<sub>4</sub>, and Hf(NMe<sub>2</sub>)<sub>4</sub> were purchased from Aldrich and used as received, whereas LGaCl(NHtBu),<sup>11</sup> LGa(NHtEt),<sup>21</sup> (HO)<sub>2</sub>Si(OtBu)<sub>2</sub>,<sup>12</sup> Ti(NEt<sub>2</sub>)<sub>4</sub>,<sup>13</sup> and Zr(NEt<sub>2</sub>)<sub>4</sub><sup>13</sup> were prepared according to literature procedures. C<sub>6</sub>D<sub>6</sub> was distilled from Na/K alloy and degassed before use. NMR spectroscopic data were recorded on a Jeol Eclipse 300 MHz or Varian Inova 500 MHz spectrometers and referenced to residual protons of the deuterated solvent. Electronic Impact Mass Spectrometry (EI-MS) for compounds **1–7** was carried on a Shimadzu GCMS-QP2010 Plus using direct injection with the detection range 20 to 1090 *m/z*. The molecular mass of compounds **8–10** is outside of the range of the equipment, and further attempts to obtain their mass spectra on a Bruker microTOFF II were unsuccessful. Therefore, mass spectra for compounds **8–10** are not reported. Elemental analyses were performed by Galbraith Laboratories Inc. at Knoxville, TN. Elemental analyses for compounds **8–10** were realized on samples dried for an hour at 110 °C to remove residual toluene, whereas low nitrogen content (more than 2% difference) was observed in the elemental analyses of single crystals of compounds **4–7**, presumably because of their high reactivity, and are thus not reported. Therefore, the purity of compound **4–7** was confirmed by measuring the cell parameters of several crystals from three different synthesis per compound.

**Synthesis of LGaCl( $\mu$ -O)Si(OH)(OtBu)<sub>2</sub> (**1**).** (HO)<sub>2</sub>Si(OtBu)<sub>2</sub> (0.18 g, 0.85 mmol) and LGaCl(NHtBu) (0.50 g, 0.84 mmol) were dissolved in tetrahydrofuran (THF, 15 mL) at –108 °C and the reaction mixture was allowed to warm to ambient temperature. All volatiles were removed under vacuum after stirring the mixture for 12 h, and finally, the crude product was rinsed with hexane. Compound **1** was obtained as a white solid. Yield: 0.51 g (85%); mp 199–200 °C. Elemental analysis (%): Calcd for C<sub>37</sub>H<sub>60</sub>GaClN<sub>2</sub>O<sub>4</sub>Si (730.33 g·mol<sup>-1</sup>): C 60.86, H 8.28, N 3.84; Found: C 60.6, H 8.0, N 3.7. IR (KBr)  $\tilde{\nu}$  3592 cm<sup>-1</sup> (s, OH). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  1.09 (d, 6H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>COSi), 1.20 (d, 6H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.50 (d, 6H, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.51 (s, 6H, CH<sub>3</sub>), 1.56 (d, 6H, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 2.27 (s, 1H, OH), 3.28 (sept, 2H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.59 (sept, 2H, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.74 (s, 1H,  $\gamma$ -CH), 7.05–7.20 ppm (m, 6H, *m*, *p*-Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  23.5, 24.2, 24.7, 24.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.5, 28.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.2 (CH<sub>3</sub>), 31.4 (C(CH<sub>3</sub>)<sub>3</sub>), 49.9 (C(CH<sub>3</sub>)<sub>3</sub>), 96.7 ( $\gamma$ -CH), 124.4, 125.0, 127.6, 140.3, 144.1, 145.3 (C of Ar), 171.2 ppm (C=N). EI-MS: *m/z* (%) 729(28) [M<sup>+</sup>], 693(30) [M<sup>+</sup>–Cl], 655(92) [M<sup>+</sup>–OtBu], 521(100) [M<sup>+</sup>–Si(O)(OH)(OtBu)<sub>2</sub>].

**Synthesis of LGa(NHtEt)( $\mu$ -O)Si(OH)(OtBu)<sub>2</sub> (**2**).** A solution of (HO)<sub>2</sub>Si(OtBu)<sub>2</sub> (0.37 g, 1.74 mmol) in THF was added dropwise to a cold solution (–108 °C) of LGa(NHtEt)<sub>2</sub> (1.00 g, 1.74 mmol) in THF. The reaction mixture was allowed to warm up to ambient temperature and stirred for additional 12 h. All volatiles were removed under vacuum and the crude product was rinsed with cold hexane. Compound **2** was obtained as a white crystalline solid. Yield: 0.63 g (49%); mp 178–180 °C. Elemental analysis (%): Calcd for C<sub>39</sub>H<sub>65</sub>GaN<sub>3</sub>O<sub>4</sub>Si (737.77 g·mol<sup>-1</sup>): C 63.49, H 8.88, N 5.70; Found: C 63.2, H 8.7, N 5.5. IR (Nujol)  $\tilde{\nu}$  3371 cm<sup>-1</sup> (w, NH),  $\tilde{\nu}$  3688 cm<sup>-1</sup> (Si–OH). <sup>1</sup>H NMR (300 MHz,

C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  0.48 (t, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz, NH), 0.95 (t, 3H, <sup>3</sup>J<sub>H-H</sub> = 7.1 Hz, NHCH<sub>2</sub>CH<sub>3</sub>), 1.18 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>COSi), 1.21 (d, 12H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.42 (d, 12H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.56 (s, 6H, CH<sub>3</sub>), 2.90 (dq, 2H, NHCH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>H-H</sub> = 7.1 Hz, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz), 3.55 (sept, 4H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.71 (s, 1H,  $\gamma$ -CH), 7.05–7.15 ppm (m, 6H, *m*, *p*-Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  21.0 (NHCH<sub>2</sub>CH<sub>3</sub>), 23.5 (CH<sub>3</sub>), 24.7, 24.8, 25.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.8, 28.8 ((CH(CH<sub>3</sub>)<sub>2</sub>), 31.5 (OC(CH<sub>3</sub>)<sub>3</sub>), 40.6 (NHCH<sub>2</sub>), 71.2 (OC) 95.9 ( $\gamma$ -CH), 124.3, 124.5, 127.2 (*m*, *p*-C of Ar), 140.8 (*i*-C of Ar), 144.3, 144.8 (*o*-C of Ar), 170.3 ppm (C=N). EI-MS: *m/z* (%) 693(25) [M<sup>+</sup>–NHtEt], 417(100) [M<sup>+</sup>–Ga(NHtEt)(OSi(OH)(OtBu)<sub>2</sub>].

**Synthesis of LGa(OH·THF)( $\mu$ -O)Si(OH)(OtBu)<sub>2</sub> (**3**).** A solution of (OH)<sub>2</sub>Si(OtBu)<sub>2</sub> (0.77 g, 3.64 mmol) in THF was added dropwise to a cold solution (–108 °C) of LGa(NHtEt)<sub>2</sub> (2.00 g, 3.47 mmol) in THF, and the solution temperature allowed to warm to ambient temperature. After 1 h of stirring, the solution was cooled at –108 °C and a solution of water in THF 0.5 M (6.8 mL, 3.40 mmol) slowly was added. The reaction mixture was allowed to warm to ambient temperature and stirred for additional 2 h. All volatiles were removed under vacuum, and the crude product was rinsed with hexane. **3** was obtained as a white crystalline solid. Yield: 2.50 g (92%); mp 197–199 °C. Elemental analysis (%): Calcd for C<sub>41</sub>H<sub>69</sub>GaN<sub>2</sub>O<sub>6</sub>Si (783.80 g·mol<sup>-1</sup>): C 62.83, H 8.87, N 3.57; Found: C 62.6, H 8.7, N 3.6. IR (Nujol)  $\tilde{\nu}$  3362 cm<sup>-1</sup> (Ga–OH),  $\tilde{\nu}$  3682 cm<sup>-1</sup> (Si–OH). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  0.86 (s, 1H, GaOH), 1.10 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 1.14 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>COSi), 1.15 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.1 Hz), 1.40 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.1 Hz), 1.48 (s, 6H, CH<sub>3</sub>), 1.53 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 3.23 (sept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 3.36 (sept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 3.48 (s, 1H, SiOH), 3.56 (m, 4H, OCH<sub>2</sub>-THF), 4.70 (s, 1H,  $\gamma$ -CH), 7.10–7.15 ppm (m, 6H, *m*, *p*-Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  23.1, 24.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.5, 24.6, 25.3, 25.5, (CH(CH<sub>3</sub>)<sub>2</sub>), 27.9 (CH<sub>3</sub>), 31.4 (C(CH<sub>3</sub>)<sub>3</sub>), 49.9 (OC(CH<sub>3</sub>)<sub>3</sub>), 96.7 ( $\gamma$ -CH), 124.4, 125.0, 127.6, 140.3, 144.1, 145.3 (*i*, *o*, *m*, *p*-C of Ar), 171.2 ppm (C=N). EI-MS: *m/z* (%) 710(5) [M<sup>+</sup>–THF], 693(45) [M<sup>+</sup>–OH], 502(100) [M<sup>+</sup>–(HO)<sub>2</sub>Si(OtBu)<sub>2</sub>].

**Synthesis of LGa( $\mu$ -O)<sub>2</sub>[Ti(NMe<sub>2</sub>)<sub>2</sub>]( $\mu$ -O)Si(OtBu)<sub>2</sub> (**4**) and LGa( $\mu$ -O)<sub>2</sub>[Ti(NEt<sub>2</sub>)<sub>2</sub>]( $\mu$ -O)Si(OtBu)<sub>2</sub> (**5**).** A toluene solution of **3** (0.3 g, 0.38 mmol) was added dropwise to a thawing toluene solution of Ti(NMe<sub>2</sub>)<sub>4</sub> (0.09 g, 0.40 mmol) or Ti(NEt<sub>2</sub>)<sub>4</sub> (0.13 g, 0.39 mmol), respectively. The reaction mixture was allowed to warm up to ambient temperature and stirred for additional 2 h. All volatiles were removed under vacuum, and the crude product was rinsed with cold hexane and filtered. Slightly yellowish crystalline solids were obtained.

**Compound 4.** Yield: 0.24 g (75%); mp 233–235 °C. EI-MS: *m/z* (%) 844(41) [M<sup>+</sup>], 839(63) [M<sup>+</sup>–Me], 756(100) [M<sup>+</sup>–Me–O<sup>t</sup>Bu]. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  1.12 (d, 6H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.13 (d, 6H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.25 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>COSi), 1.49 (d, 6H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.52 (s, 6H, CH<sub>3</sub>), 1.72 (d, 6H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 2.97 (s, 12H, N(CH<sub>2</sub>)<sub>2</sub>), 3.35 (sept, 2H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.47 (sept, 2H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.81 (s, 1H,  $\gamma$ -CH), 7.09–7.22 ppm (*m*, 6H, *m*, *p*-Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  24.0, 24.1, 24.2, 24.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.1, 29.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.6 (CH<sub>3</sub>), 44.7 (N(CH<sub>2</sub>)<sub>2</sub>), 71.3 (OC(CH<sub>3</sub>)<sub>3</sub>), 95.9 ( $\gamma$ -CH), 124.6, 127.6, 140.8, 144.5, 144.7 (*i*, *o*, *m*, *p*-C of Ar), 171.1 ppm (C=N).

**Compound 5.** Yield: 0.31 g (91%); mp 248–249 °C. EI-MS: *m/z* (%) 902(10) [M<sup>+</sup>], 887(21) [M<sup>+</sup>–Me], 756(54) [M<sup>+</sup>–2(NEt<sub>2</sub>)]. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  1.11 (d, 6H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.14 (d, 6H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (dd, 12H, <sup>2</sup>J<sub>H-H</sub> = 14.0 Hz, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.26 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>COSi), 1.50 (s, 6H, CH<sub>3</sub>), 1.51 (d, 6H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.71 (d, 6H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.14 (dq, 4H,

$^3J_{\text{H-H}} = 14.0$  Hz,  $^3J_{\text{H-H}} = 7.0$  Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, 3.32 (sept, 1H,  $^3J_{\text{H-H}} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.38 (dq, 4H,  $^2J_{\text{H-H}} = 14.0$  Hz,  $^3J_{\text{H-H}} = 7.0$  Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 3.50 (sept, 1H,  $^3J_{\text{H-H}} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.79 (s, 1H,  $\gamma$ -CH), 7.09–7.21 ppm (*m*, 6H, *m*, *p*-Ar-H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  15.6 (N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>) 24.3, 24.5, 24.7, 25.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.3, 28.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.6 (CH<sub>3</sub>), 47.0 (N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 71.2 (OC(CH<sub>3</sub>)<sub>3</sub>), 96.0 ( $\gamma$ -CH), 124.6, 124.7, 127.5, 128.3, 141.2, 144.4, 144.7 (*i*, *o*, *m*, *p*-C of Ar), 171.3 ppm (C=N).

**Synthesis of LGa( $\mu$ -O)<sub>2</sub>[Zr(NEt<sub>2</sub>)<sub>2</sub>]( $\mu$ -O)Si(OtBu)<sub>2</sub> (6) and LGa( $\mu$ -O)<sub>2</sub>[Hf(NEt<sub>2</sub>)<sub>2</sub>]( $\mu$ -O)Si(OtBu)<sub>2</sub> (7).** A solution of **3** (0.3 g, 0.38 mmol) in toluene (10 mL) was added dropwise to a thawing solution of the metallic amides (**6**: Zr(NEt<sub>2</sub>)<sub>4</sub>, 0.16 g, 0.42 mmol; **7**: Hf(NEt<sub>2</sub>)<sub>4</sub>, 0.17 g, 0.41 mmol) in toluene (10 mL); the reaction mixture was allowed to warm up to ambient temperature and stirred for an additional 2 h. All volatiles were removed under vacuum, and the crude product was rinsed with cold hexane. Crystalline white solids were obtained in both cases.

**Compound 6.** Yield: 0.28 g (78%); mp 208–211 °C. EI-MS: *m/z* (%) 944(8) [M<sup>+</sup>], 929(4) [M<sup>+</sup> – Me], 872(68) [M<sup>+</sup> – NEt<sub>2</sub>].  $^1\text{H}$  NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  1.12 (d, 6H,  $^3J_{\text{H-H}} = 7.0$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.14 (d, 6H,  $^3J_{\text{H-H}} = 7.0$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.24 (dd, 12H,  $^2J_{\text{H-H}} = 14.0$  Hz,  $^3J_{\text{H-H}} = 7.0$  Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.25 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>COSi), 1.49 (d, 6H,  $^3J_{\text{H-H}} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.50 (s, 6H, CH<sub>3</sub>), 1.70 (d, 6H,  $^3J_{\text{H-H}} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.00 (dq, 4H,  $^2J_{\text{H-H}} = 14.0$  Hz,  $^3J_{\text{H-H}} = 7.0$  Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 3.08 (dq, 4H,  $^2J_{\text{H-H}} = 14.0$  Hz,  $^3J_{\text{H-H}} = 7.0$  Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 3.39 (sept, 1H,  $^3J_{\text{H-H}} = 7.0$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.48 (sept, 1H,  $^3J_{\text{H-H}} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.78 (s, 1H,  $\gamma$ -CH), 7.10–7.20 ppm (*m*, 6H, *m*, *p*-Ar-H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  16.0 (N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>) 23.4, 24.2, 24.6, 24.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.9, 28.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.4 (CH<sub>3</sub>), 44.7 (N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 70.8 (OC(CH<sub>3</sub>)<sub>3</sub>), 95.8 ( $\gamma$ -CH), 124.4, 127.6, 140.9, 144.2, 144.4 (*i*, *o*, *m*, *p*-C of Ar), 170.8 ppm (C=N).

**Compound 7.** Yield: 0.31 g (79%); mp 236–237 °C. EI-MS: *m/z* (%) 1032(12) [M<sup>+</sup>], 1017(15) [M<sup>+</sup> – Me], 960(32) [M<sup>+</sup> – NEt<sub>2</sub>], 888(94) [M<sup>+</sup> – 2(NEt<sub>2</sub>)].  $^1\text{H}$  NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  1.12 (d, 6H,  $^3J_{\text{H-H}} = 7.0$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.14 (d, 6H,  $^3J_{\text{H-H}} = 7.0$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.24 (dd, 12H,  $^2J_{\text{H-H}} = 14.0$  Hz,  $^3J_{\text{H-H}} = 7.0$  Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.24 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>COSi), 1.49 (d, 6H,  $^3J_{\text{H-H}} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.50 (s, 6H, CH<sub>3</sub>), 1.69 (d, 6H,  $^3J_{\text{H-H}} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.03 (dq, 4H,  $^2J_{\text{H-H}} = 14.0$  Hz,  $^3J_{\text{H-H}} = 7.0$  Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 3.15 (dq, 4H,  $^2J_{\text{H-H}} = 14.0$  Hz,  $^3J_{\text{H-H}} = 7.0$  Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 3.39 (sept, 1H,  $^3J_{\text{H-H}} = 7.0$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.48 (sept, 1H,  $^3J_{\text{H-H}} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.78 (s, 1H,  $\gamma$ -CH), 7.10–7.20 ppm (*m*, 6H, *m*, *p*-Ar-H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  16.1 (N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>) 23.4, 24.2, 24.6, 24.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.9, 28.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.4 (CH<sub>3</sub>), 44.7 (N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 70.9 (OC(CH<sub>3</sub>)<sub>3</sub>), 95.8 ( $\gamma$ -CH), 124.4, 127.6, 140.9, 144.2, 144.4 (*i*, *o*, *m*, *p*-C of Ar), 170.9 ppm (C=N).

**Synthesis of [LGa( $\mu$ -O)<sub>2</sub>Si( $\mu$ -O)(OtBu)<sub>2</sub>]<sub>2</sub>Ti (8), [LGa( $\mu$ -O)<sub>2</sub>Si( $\mu$ -O)(OtBu)<sub>2</sub>]<sub>2</sub>Zr (9), and [LGa( $\mu$ -O)<sub>2</sub>Si( $\mu$ -O)(OtBu)<sub>2</sub>]<sub>2</sub>Hf (10).** A THF solution of **3** (0.3 g, 0.38 mmol) was added dropwise to a thawing solution of the metallic amide (**8**: Ti(NMe<sub>2</sub>)<sub>4</sub>, 0.04 g, 0.18 mmol; **9**: Zr(NMe<sub>2</sub>)<sub>4</sub>, 0.05 g, 0.19 mmol; **10**: Hf(NEt<sub>2</sub>)<sub>4</sub>, 0.08 g, 0.19 mmol;) in THF (10 mL); the reaction mixture was allowed to warm up to ambient temperature and stirred for additional 4 h. All volatiles were removed under vacuum, and the crude product was rinsed with cold hexane. White crystalline solids were obtained for all three compounds.

**Compound 8.** Yield: 0.19 g (68%); mp >400 °C.<sup>20</sup> Elemental analysis (%) Calcd for C<sub>74</sub>H<sub>118</sub>Ga<sub>2</sub>N<sub>4</sub>O<sub>10</sub>Si<sub>2</sub>Ti (1467.64 g·mol<sup>-1</sup>): C 60.58, H 8.11, N 3.82; Found: C 59.79, H 7.92, N 3.67.  $^1\text{H}$  NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  1.09 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>COSi), 1.12 (d, 6H,  $^3J_{\text{H-H}} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>COSi), 1.20 (d, 6H,  $^3J_{\text{H-H}} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.34 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz,

CH(CH<sub>3</sub>)<sub>2</sub>), 1.45 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.49 (d, 6H,  $^3J_{\text{H-H}} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.54 (d, 6H,  $^3J_{\text{H-H}} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.57 (s, 6H, CH<sub>3</sub>), 1.66 (s, 3H, CH<sub>3</sub>), 1.69 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.95 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.19 (sept, 2H,  $^3J_{\text{H-H}} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.34 (sept, 2H,  $^3J_{\text{H-H}} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.63 (sept, 2H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.18 (sept, 2H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.88 (s, 2H,  $\gamma$ -CH), 7.25–6.99 ppm (12H, *m*, *p*-Ar-H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  23.5, 24.0, 24.3, 24.6, 27.4, 24.8, 24.9, 25.9, 26.2, 26.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.5, 28.7, 28.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.6, 31.7 (OC(CH<sub>3</sub>)<sub>3</sub>), 70.9, 71.0 (OC(CH<sub>3</sub>)<sub>3</sub>), 97.2 ( $\gamma$ -CH), 124.0, 124.3, 125.1, 125.2, 127.4, 127.6, 128.3, 140.1, 141.2, 143.2, 144.5, 146.0, 146.1 (*o*, *i*, *m*, *p*, C of Ar), 170.9, 171.7 ppm (C=N).

**Compound 9.** Yield: 0.25 g (87%); mp 298 °C. Elemental analysis (%) Calcd for C<sub>74</sub>H<sub>118</sub>Ga<sub>2</sub>N<sub>4</sub>O<sub>10</sub>Si<sub>2</sub>Zr (1510.61 g·mol<sup>-1</sup>): C 58.84, H 7.87, N 3.71; Found: C 57.18, H 7.61, N 3.76.  $^1\text{H}$  NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  1.08 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>COSi), 1.11 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.18 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>COSi), 1.19 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.20 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.33 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.49 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.50 (s, 6H, CH<sub>3</sub>), 1.54 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.61 (s, 6H, CH<sub>3</sub>), 1.62 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.95 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.23 (sept, 2H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.37 (sept, 2H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.61 (sept, 2H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.06 (sept, 2H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.81 (s, 2H,  $\gamma$ -CH), 7.15–7.26 ppm (12H, *m*, *p*-Ar-H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  23.4, 24.0, 24.2, 24.5, 24.6, 24.9, 25.5, 26.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.1, 28.2, 28.7, 28.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.6, 31.7 (OC(CH<sub>3</sub>)<sub>3</sub>), 70.7, 70.8 (OC(CH<sub>3</sub>)<sub>3</sub>), 96.8 ( $\gamma$ -CH), 124.1, 124.4, 124.7, 124.9, 127.3, 127.5, 128.3, 140.3, 141.2, 143.4, 144.5, 145.5 (*o*, *i*, *m*, *p*, C of Ar), 170.8, 171.3 ppm (C=N).

**Compound 10.** Yield: 0.21 g (69%); mp 239–241 °C. Elemental analysis (%) Calcd for C<sub>74</sub>H<sub>118</sub>Ga<sub>2</sub>N<sub>4</sub>O<sub>10</sub>Si<sub>2</sub>Hf (1597.87 g·mol<sup>-1</sup>): C 55.63, H 7.44, N 3.51; Found: C 54.83, H 7.67, N 3.53.  $^1\text{H}$  NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  1.08 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>COSi), 1.11 (d, 6H,  $^3J_{\text{H-H}} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.18 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>COSi), 1.19 (d, 6H,  $^3J_{\text{H-H}} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.30 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.47 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.48 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.50 (s, 6H, CH<sub>3</sub>), 1.53 (d, 6H,  $^3J_{\text{H-H}} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.61 (d, 6H,  $^3J_{\text{H-H}} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.62 (s, 6H, CH<sub>3</sub>), 1.95 (d, 6H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.22 (sept, 2H,  $^3J_{\text{H-H}} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.36 (sept, 2H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.64 (sept, 2H,  $^3J_{\text{H-H}} = 6.6$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.06 (sept, 2H,  $^3J_{\text{H-H}} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.85 (s, 2H,  $\gamma$ -CH), 7.15–7.33 ppm (*m*, 12H, *p*-Ar-H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS)  $\delta$  23.4, 24.0, 24.2, 24.5, 24.6, 24.9, 25.5, 26.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.1, 28.2, 28.7, 28.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.6, 31.7 (OC(CH<sub>3</sub>)<sub>3</sub>), 70.7, 70.8 (OC(CH<sub>3</sub>)<sub>3</sub>), 96.8 ( $\gamma$ -CH), 124.1, 124.4, 124.7, 124.9, 127.3, 127.5, 128.3, 140.3, 141.2, 143.4, 144.5, 145.5 (*o*, *i*, *m*, *p*, C of Ar), 170.8, 171.3 ppm (C=N).

**X-ray Structure Determination.** Crystals of compounds **1–10** were mounted on nylon loops and rapidly placed in a stream of cold nitrogen. Diffraction data were collected with a Bruker-APEX II Duo three-circle diffractometer with the use of Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at –100 °C (**1**) or –173 °C (**2–10**). Structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares on  $F^2$ .<sup>14</sup> 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  $U_{\text{iso}}$  tied to the parent atom with distance restraints. The disordered groups were refined using geometry and distance restraints (SAME, SADI) together with the restraints for the  $U_{ij}$  values (SIMU, DELU). For further details see Supporting Information.

## RESULTS AND DISCUSSION

Recently, we have reported on the selective reactivity of gallium amides toward protic reagents.<sup>11</sup> Of particular interest is the reaction of these compounds with OH moieties, that leads to the formation of Ga–O bond with the concomitant loss of a volatile primary amine. The reactivity of these amides, and the fact that similar gallium precursors to those used for related aluminosilicates are either not available or are of difficult access,<sup>10</sup> make the amides ideal candidates for the synthesis of gallosilicates.<sup>16</sup> Thus, the reaction of LGaCl(NH*t*Bu) and LGa(NHEt)<sub>2</sub> with (HO)<sub>2</sub>Si(O*t*Bu)<sub>2</sub> cleanly produces gallosilicates LGaCl(μ-O)Si(OH)(O*t*Bu)<sub>2</sub> (**1**) and LGa(NHEt)(μ-O)Si(OH)(O*t*Bu)<sub>2</sub> (**2**) in high spectroscopic yields (>90%). The remaining amide group in compound **2** can be easily hydrolyzed under controlled conditions to obtain the unique gallosilicate hydroxide LGa(OH·THF)(μ-O)Si(OH)(O*t*Bu)<sub>2</sub> (**3**) in almost quantitative yield. Purification and isolation of compound **2** leads to far lower yields (45–50%), mainly because of its high solubility in common organic solvents. To overcome this problem, one pot synthesis of **3** from LGa(NHEt)<sub>2</sub>, which reacts first with the silanediol (HO)<sub>2</sub>Si(O*t*Bu)<sub>2</sub> followed by the addition of 1 equiv of water, allows the isolation of **3** in multigram quantities and in up to 92% yield (Scheme 1). Compounds **1–3** possess an acidic OH group attached to the silicon center and the gallium atom bonded to a labile group. Hence, a neutralization reaction between the Brønsted base and acid should occur along with the release of hydrogen chloride (**1**), ethylamine (**2**), or water (**3**) and the formation of the Ga(μ-O)<sub>2</sub>Si ring. However, the steric

hindrance of the β-diketiminato ligand and the *tert*-butyl groups, together with the high strain inside the four-membered ring (Ga(μ-O)<sub>2</sub>Si), present an energetic barrier, which is higher than the energy released by the formation of the Ga–O bond and the release of the volatile byproducts, thus, making the isolation of compounds **1–3** feasible.<sup>11</sup>

Compounds **1–3** are white crystalline thermally stable solids (mp >170 °C) and no decomposition was observed even after storing the products under an inert atmosphere for 2 months. As revealed by <sup>1</sup>H NMR spectroscopy, compounds **1** and **2** have been isolated as solvent-free molecules, whereas **3** contains one strongly coordinated THF molecule, which is not possible to remove under vacuum even at elevated temperature. Nevertheless, compound **3** can be obtained as a solvent-free molecule if diethyl ether is used as solvent. However, neither the spectroscopic characterization nor its reactivity are significantly altered by the lack of a solvent molecule coordinated to the Ga–OH group (see Supporting Information for further details regarding the characterization of solvent free **3**).

Initial characterization of compounds **1–3** was carried out through <sup>1</sup>H NMR and IR spectroscopy. Both techniques revealed characteristic pattern of the β-diketiminato ligand (L), signals for (HO)Si(O*t*Bu)<sub>2</sub> groups and the corresponding peaks for the NH moiety in **2** (δ 0.48 ppm, ν̄ 3371 cm<sup>-1</sup>) and the Ga–OH fragment of **3** (δ 0.86 ppm, ν̄ 3363 cm<sup>-1</sup>). The Si–OH signals can be observed at δ 2.27 (**1**), 1.74 (**2**), 3.48 (**3**) ppm and ν̄ 3592 (**1**), 3688 (**2**), and 3681 (**3**) cm<sup>-1</sup>, respectively. The Si–OH signals in <sup>1</sup>H NMR were found at similar shifts, while IR vibrations were found at higher values, than those for the previously reported aluminosilicates: LAl(OH)(μ-O)Si(OH)(O*t*Bu)<sub>2</sub> (δ 2.79 ppm, ν̄ 3357 cm<sup>-1</sup>) and LAl(SH)(μ-O)Si(OH)(O*t*Bu)<sub>2</sub> (δ 1.53 ppm, ν̄ 3462 cm<sup>-1</sup>).<sup>9</sup> Compounds **1–3** were also characterized by EI-MS spectrometry. This technique showed the molecular ion for **1**; however, only [M – NHEt]<sup>+</sup> and [M – THF]<sup>+</sup> ions were found in the spectra of **2** and **3**, respectively.

Crystals suitable for X-ray analysis were obtained from saturated solutions of **1** (toluene/hexane), **2** (hexane), and **3** (THF/hexane) at –30 °C. Compound **1** crystallized in the orthorhombic *Pca*2<sub>1</sub> space group, with two molecules of **1** in the asymmetric unit; however, one of these molecules contains heavy disorder (chlorine atom and whole the OSi(OH)(O*t*Bu)<sub>2</sub> unit are disordered), and thus, only data for the molecule containing Ga(1) will be used in the following discussion (Figure 1).

Scheme 1. Synthesis of Compounds **1–3**

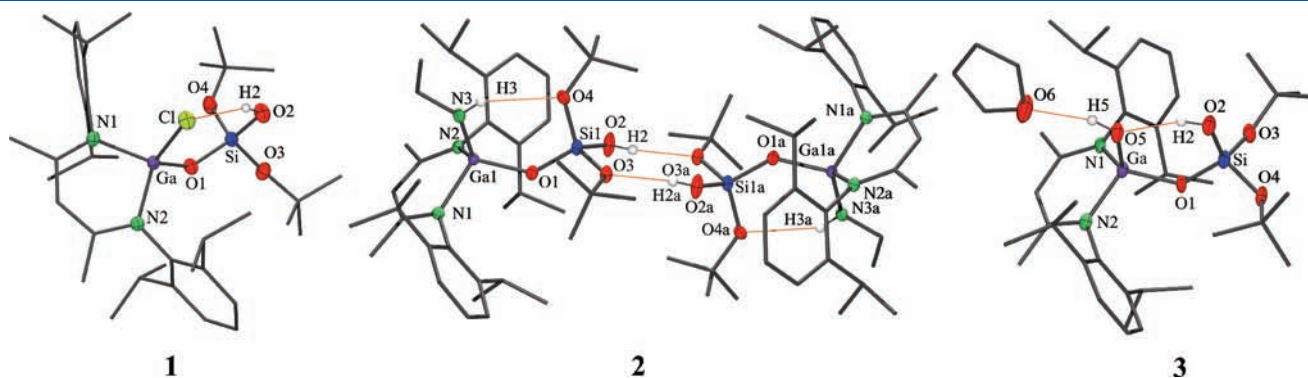
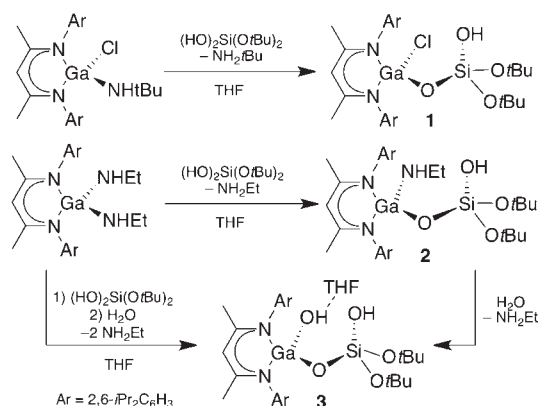


Figure 1. Crystal structures of compounds **1–3**. All carbon-bound hydrogen atoms and carbon ellipsoids have been omitted for the sake of clarity. Thermal ellipsoids for noncarbon atoms are shown at the 50% probability level.

Table 1. Crystallographic Data for the Structural Analyses of Compounds 1–3

	1	2	3
chemical formula	C <sub>37</sub> H <sub>60</sub> ClGaN <sub>2</sub> O <sub>4</sub> Si	C <sub>39</sub> H <sub>66</sub> GaN <sub>3</sub> O <sub>4</sub> Si	C <sub>41</sub> H <sub>69</sub> GaN <sub>2</sub> O <sub>6</sub> Si
formula weight	730.13	738.76	783.79
space group	<i>Pca</i> 2 <sub>1</sub> (No. 29) <sup>c</sup>	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14, variant)
<i>a</i> /Å	26.030(3)	11.937(1)	9.441(2)
<i>b</i> /Å	11.536(1)	12.312(2)	22.701(4)
<i>c</i> /Å	26.408(2)	16.403(2)	20.088(3)
$\alpha$ /deg	90	100.16(2)	90
$\beta$ /deg	90	92.80(2)	90.23(3)
$\gamma$ /deg	90	118.28(2)	90
<i>V</i> /Å <sup>3</sup>	7929.8(13)	2065.2(7)	4305.2(13)
<i>Z</i>	8	2	4
<i>T</i> /K	173(2)	100(2)	100(2)
$\lambda$ /Å	0.71073	0.71073	0.71073
$\mu$ /mm <sup>-1</sup>	0.829	0.735	0.712
$\rho_{\text{calc}}$ /g·cm <sup>-3</sup>	1.223	1.188	1.209
<i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>a</sup>	0.0416	0.0328	0.0560
<i>wR</i> <sub>2</sub> (all data) <sup>b</sup>	0.0914	0.0820	0.1161

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ . <sup>c</sup> Flack parameter: -0.007(7).

Compound 2 crystallized in the triclinic *P* $\bar{1}$  space group with one molecule of 2 per asymmetric unit, whereas compound 3 crystallized in the monoclinic *P*2<sub>1</sub>/*n* space group with one molecule of 3 and one THF molecule in the asymmetric unit (Table 1). All hydrogen atoms of the OH and NHR groups in compounds 1–3 are involved in hydrogen bonds. Thus, there is an intramolecular hydrogen bond between the chlorine atom and the HO–Si moiety (SiO–H···Cl 2.53 Å) in compound 1. Compound 2 forms one intramolecular N–H···OtBu (2.03(3) Å) and one intermolecular SiO–H···OtBu (2.49(2) Å) hydrogen bond. Finally, compound 3 exhibits strong intramolecular hydrogen bonds between the SiOH and the GaOH moieties (SiO–H···O(H)Ga; 1.93(2) Å), while the GaOH moiety coordinates to one THF molecule (GaO–H···O; 2.04(3) Å). The X-ray analyses of compounds 1–3 confirmed slightly distorted tetrahedral environments of the silicon atoms in the SiO<sub>4</sub> units, with the O–Si–O bond angles in a relatively narrow interval (105.3(1)–112.4(1)°) and Si–O bond lengths in the range from 1.594(1) to 1.648(1) Å. The above-mentioned values are comparable to those observed for LAl(EH)( $\mu$ -O)Si(OH)-(OtBu)<sub>2</sub> (E = S, O; 106.3(1)–112.9(1)°, 1.591(2)–1.637(2) Å).<sup>9</sup> As expected, the gallium atoms in compounds 1–3 are bonded to two nitrogen atoms of the  $\beta$ -diketiminato ligand, to the silicate's oxygen, and finally, the coordination sphere is completed by a chlorine atom (1), ethylamido (2), or OH (3) group, respectively, resulting in a highly distorted tetrahedral environment. Table 2 shows selected bond angles and distances for compounds 1–3.

The Ga–O–Si angle in 3 is far more acute (128.9(2)) when compared with 1 (138.2(1)°), 2 (136.6(1)°) or other related compounds LGa(Cl)OSiMe<sub>3</sub> (136.2(1)°),<sup>17</sup> {[*c*-C<sub>5</sub>H<sub>9</sub>]<sub>7</sub>Si<sub>7</sub>O<sub>11</sub>(OSiMePh<sub>2</sub>)<sub>2</sub>Ga}<sup>-</sup>{Et<sub>3</sub>NH}<sup>+</sup> (137.5(3)°) or {[*c*-C<sub>5</sub>H<sub>9</sub>]<sub>7</sub>Si<sub>7</sub>O<sub>11</sub>(OH)]GaMe<sub>2</sub>} (134.3(3)°).<sup>2c</sup> The latter can be attributed to the strong hydrogen bonding interaction between the two OH groups oriented in a *cis*-configuration, which together with the proximity of OH groups, make compound 3 a suitable candidate for further reactivity studies. Particularly, organometallic

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1–3

	1 <sup>a</sup>	2	3
Ga–O(1)	1.784(2)	1.809(1)	1.800(1)
Ga–X <sup>b</sup>	2.194(1)	1.836(3)	1.806(1)
Ga–N(1)	1.930(2)	1.947(3)	1.945(3)
Ga–N(2)	1.918(2)	1.959(3)	1.894(3)
Si–O(1)	1.598(2)	1.594(2)	1.604(3)
Si–O(2)	1.632(2)	1.607(2)	1.633(3)
Si–O(3)	1.602(5)	1.648(2)	1.628(3)
Si–O(4)	1.604(4)	1.637(2)	1.632(3)
Ga–O(1)–Si	138.2(1)	136.6(1)	128.9(1)
N(1)–Ga–N(2)	99.2(1)	95.6(1)	97.7(1)
X–Ga–O(1)	109.1(1)	109.2(1)	105.3(1)
O(1)–Si–O(2)	111.9(1)	110.3(1)	111.4(1)
O(1)–Si–O(3)	112.1(5)	112.4(1)	106.5(2)
O(1)–Si–O(4)	106.7(3)	107.7(1)	111.6(2)
O(2)–Si–O(3)	108.4(4)	105.3(1)	113.0(2)
O(2)–Si–O(4)	111.2(4)	110.9(1)	108.6(2)
O(3)–Si–O(4)	106.5(5)	110.2(1)	105.6(2)

<sup>a</sup> Compound 1 crystallized with two molecules of 1 in the asymmetric unit; however, one of these molecules contains heavy disorder, and thus, only data for the molecule containing Ga(1) is used in this table. <sup>b</sup> X = Cl (1), N(3) (2), and O(5) (3).

reagents might be able to react with 3, and upon substitution of one or both of the OH protons, would produce multimetallic compounds.

To explore this possibility, reactions of 3 with 0.5 or 1 equiv of a group 4 metal amide (M(NR<sub>2</sub>)<sub>4</sub>; M = Ti, Zr, Hf, R = Me, Et) were performed. The metallic precursors were selected because of their high reactivity necessary to deprotonate the relatively basic Ga(OH) group and also because the resulting compounds would represent attractive precursor for material science (the incorporation of group 4 metals into porous materials has resulted in

multiple applications because of the redox and photochemical activity of these metals).<sup>18</sup>

In general, two types of species were obtained from these reactions, the 1:1 and 2:1 (3/metal) products (Scheme 2). Reaction of **3** with 1 equiv of  $\text{Ti}(\text{NR}_2)_4$  led to the 1:1 products  $\text{LGa}(\mu\text{-O})_2[\text{Ti}(\text{NMe}_2)_2](\mu\text{-O})\text{Si}(\text{OtBu})_2$  (**4**) and  $\text{LGa}(\mu\text{-O})_2[\text{Ti}(\text{NEt}_2)_2](\mu\text{-O})\text{Si}(\text{OtBu})_2$  (**5**) in good yields. Only trace amounts of the 2:1 product  $[\text{LGa}(\mu\text{-O})_2\text{Si}(\mu\text{-O})(\text{OtBu})_2]_2\text{Ti}$  (**8**) were observed; however, when the stoichiometry is adjusted and only 0.5 equiv of  $\text{Ti}(\text{NR}_2)_4$  is used, **8** can be obtained as the unique product.

Nevertheless, when the zirconium amide  $\text{Zr}(\text{NMe}_2)_4$  reacted with **3**, the main product was the spirocyclic compound  $[\text{LGa}(\mu\text{-O})_2\text{Si}(\mu\text{-O})(\text{OtBu})_2]_2\text{Zr}$  (**9**) independently of the molar ratios and other reaction conditions. The desired 1:1 product  $\text{LGa}(\mu\text{-O})_2[\text{Zr}(\text{NMe}_2)_2]\text{Si}(\mu\text{-O})(\text{OtBu})_2$  could be observed in trace amounts in the reaction mixture by  $^1\text{H}$  NMR, but all our efforts to isolate it were unsuccessful. The difference in the behavior between the titanium and the zirconium amide can be

well explained by the larger size of the zirconium atom, longer M–O bonds, and consequently, the lower steric bulk around the zirconium atom favors the formation of the spirocyclic product **9**. Later, because the covalent radii for both atoms are almost identical (Zr: 1.56 Å, Hf: 1.57 Å),<sup>19</sup> we expected  $[\text{LGa}(\mu\text{-O})_2\text{Si}(\mu\text{-O})(\text{OtBu})_2]_2\text{Hf}$  (**10**) to be the main product of the analogous reaction of **3** with  $\text{Hf}(\text{NEt}_2)_4$ . This assumption was further supported by a general search in CSD, which revealed that the difference between the mean Zr–O (2.129 Å) and Hf–O (2.122 Å) bond lengths could be considered as negligible. However, reaction of **3** with 1 equiv of  $\text{Hf}(\text{NEt}_2)_4$  led to a smooth isolation of  $\text{LGa}(\mu\text{-O})_2[\text{Hf}(\text{NEt}_2)_2]\text{Si}(\text{OtBu})_2$  (**7**) in high yield (79%). This is in striking contrast with our previous observations for zirconium. Therefore, we assumed that the different behavior arose from the slight difference in the steric bulk of the amido groups ( $\text{NMe}_2$  vs  $\text{NEt}_2$ ). To prove our hypothesis, the 1:1 reaction of **3** with the bulkier zirconium amide  $\text{Zr}(\text{NEt}_2)_4$  was performed. Such reaction allowed us to obtain the 1:1 product  $\text{LGa}(\mu\text{-O})_2[\text{Zr}(\text{NEt}_2)_2]\text{Si}(\mu\text{-O})(\text{OtBu})_2$  (**6**) in satisfactory yields, thus corroborating our hypothesis. Finally, the 2:1 reaction ( $3:\text{Hf}(\text{NEt}_2)_4$ ) resulted in the formation of  $[\text{LGa}(\mu\text{-O})_2\text{Si}(\mu\text{-O})(\text{OtBu})_2]_2\text{Hf}$  (**10**), thus completing the series.

The IR and NMR spectra are quite indicative, the complete lack of the signals for the OH groups in both spectra, confirms the total deprotonation of the OH groups in **4–10** and consequently the formation of M–O bonds. The  $^1\text{H}$  NMR spectra of compounds **4–7** present signals for the protons of the remaining amido groups. Particularly,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^1\text{H}-^1\text{H}$  COSY NMR spectra of compounds **5–7** include characteristic features for diastereotopic  $\text{CH}_2\text{s}$  of the  $\text{NEt}_2$  groups ( $^2J_{\text{H-H}} = 14.0$  Hz,  $^3J_{\text{H-H}} = 7.0$  Hz), indicative of the ring stiffness (Figures 2–4 and in the Supporting Information, Figures S3–S5). The formation of the bicyclic inorganic core in **8–10** is further reflected by the presence of four septuplets and eight

### Scheme 2. Synthesis of Compounds 4–10

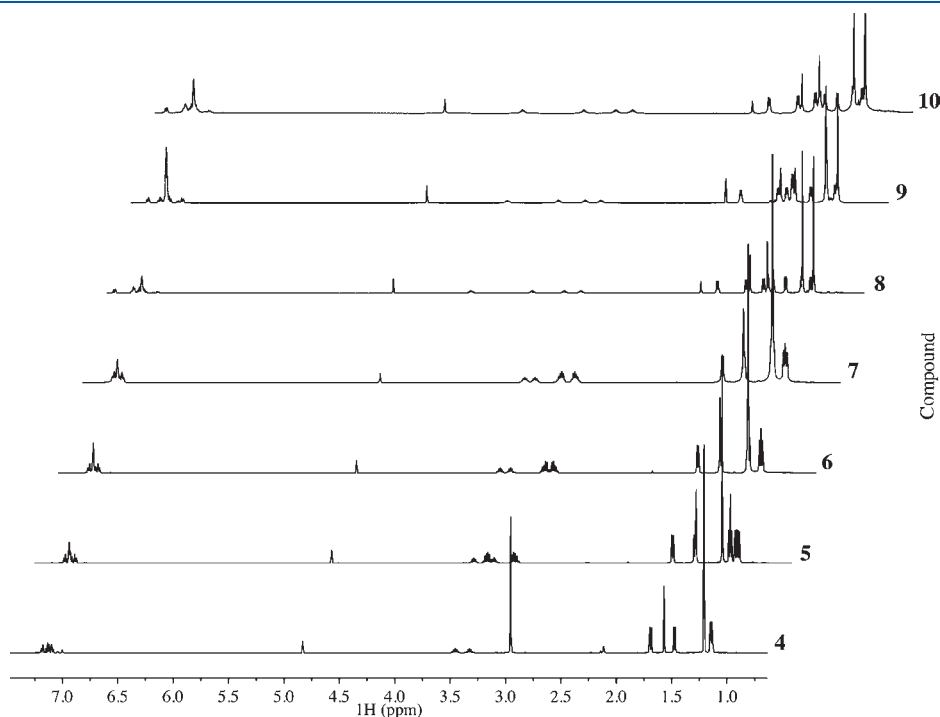
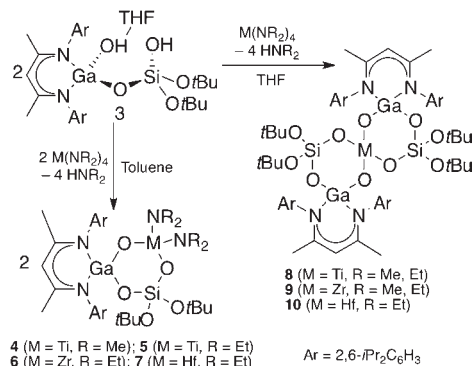


Figure 2. 500 MHz  $^1\text{H}$  NMR spectra of compounds **4–10** ( $\text{C}_6\text{D}_6$ ).

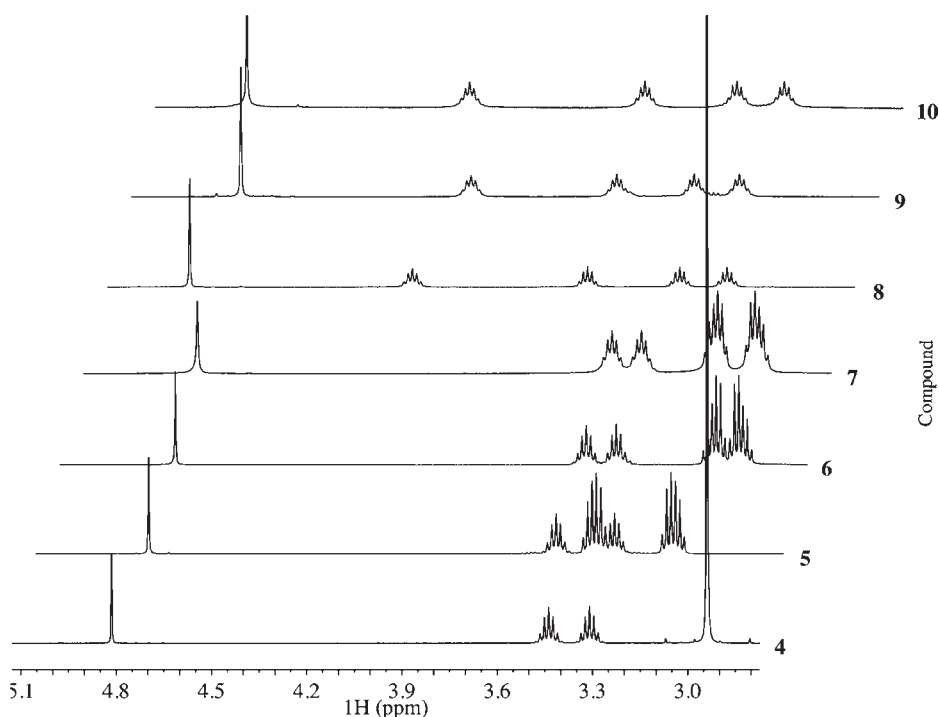


Figure 3. 500 MHz  $^1\text{H}$  NMR spectra of compounds 4–10 ( $\text{C}_6\text{D}_6$ ) showing the  $\delta$  3–5 ppm region.

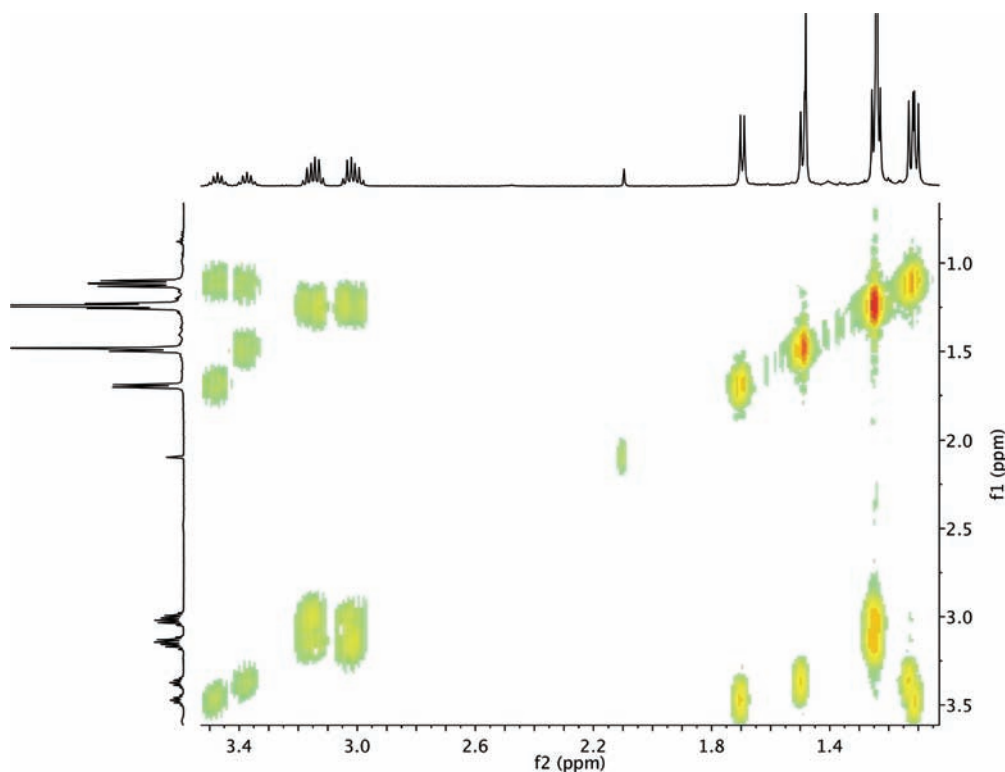


Figure 4. 500 MHz  $^1\text{H}/^1\text{H}$  gCOSY NMR spectra of compound 10 ( $\text{C}_6\text{D}_6$ ).

doublets belonging to the *i*Pr moieties of the ligand. The monocyclic compounds 4–7 still contain a symmetry plane, and thus only two septuplets and four doublets were observed. In general, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compounds 5–7 and

8–10, respectively, are strikingly similar, as only very slight deviations in the chemical shifts were found (Figure 2). In spite of the high thermal stability of these multimetallic compounds (the melting points of compounds 4–10 range from 210 to

Table 3. Crystallographic Data for the Structural Analyses of Compounds 4–10

	4	5	6	7	8 · C <sub>7</sub> H <sub>8</sub> [°]	9 · NHMe <sub>2</sub>	9	10 · C <sub>7</sub> H <sub>8</sub>
chemical formula	C <sub>41</sub> H <sub>71</sub> GaN <sub>4</sub> <sup>+</sup> O <sub>5</sub> SiTi	C <sub>43</sub> H <sub>79</sub> GaN <sub>4</sub> <sup>+</sup> O <sub>5</sub> SiTi	C <sub>48</sub> H <sub>79</sub> GaN <sub>4</sub> <sup>+</sup> O <sub>5</sub> SiZr	C <sub>43</sub> H <sub>79</sub> GaHfF <sub>6</sub> N <sub>4</sub> O <sub>5</sub> Si	C <sub>74</sub> H <sub>118</sub> Ga <sub>2</sub> N <sub>4</sub> <sup>+</sup> O <sub>10</sub> Si <sub>2</sub> Ti · C <sub>7</sub> H <sub>8</sub>	C <sub>76</sub> H <sub>125</sub> Ga <sub>2</sub> N <sub>5</sub> <sup>+</sup> O <sub>10</sub> Si <sub>2</sub> Zr · C <sub>6</sub> H <sub>14</sub>	C <sub>74</sub> H <sub>118</sub> Ga <sub>2</sub> N <sub>4</sub> <sup>+</sup> O <sub>10</sub> Si <sub>2</sub> Zr · C <sub>7</sub> H <sub>8</sub>	C <sub>74</sub> H <sub>118</sub> Ga <sub>2</sub> N <sub>4</sub> <sup>+</sup> O <sub>10</sub> Si <sub>2</sub> Hf · C <sub>7</sub> H <sub>8</sub>
formula weight	845.73	901.82	945.15	1032.42	1559.38	1641.82	1584.68	1689.17
space group	P2 <sub>1</sub> /c (No. 14)	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)	P2 <sub>1</sub> /n (No. 14, variant)	C2/c (No. 15)	P2 <sub>1</sub> /n (No. 14, variant)	P2 <sub>1</sub> /n (No. 14, variant)
a/Å	12.129(2)	11.1360(8)	11.112(2)	11.121(2)	12.320(2)	17.759(2)	12.2083(5)	12.3239(4)
b/Å	36.225(4)	14.162(1)	14.274(2)	14.263(2)	33.568(3)	17.415(2)	34.1395(14)	34.266(1)
c/Å	11.123(2)	17.350(1)	17.383(3)	17.399(3)	20.331(2)	28.487(3)	20.1612(8)	20.2030(6)
$\alpha$ /deg	90	82.718(1)	83.13(2)	82.95(2)	90	91.48(2)	90	90
$\beta$ /deg	111.39(2)	73.453(1)	73.95(3)	73.91(3)	94.22(2)	90	94.12(1)	94.093(1)
$\gamma$ /deg	90	68.203(1)	67.71(2)	67.74(2)	90	90	90	90
V/Å <sup>3</sup>	4550.5(14)	2434.7(3)	2451.4(9)	2453.6(9)	8385.2(18)	8807.3(17)	8390.4(6)	8509.8(5)
Z	4	2	2	2	4	4	4	4
T/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
$\lambda$ /Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
$\mu$ /mm <sup>-1</sup>	0.837	0.787	0.831	0.732	0.815	0.806	0.844	1.929
$\rho_{\text{calc}}/\text{g}\cdot\text{cm}^{-3}$	1.234	1.230	1.280	1.397	1.235	1.238	1.254	1.319
R <sub>1</sub> (I > 2 $\sigma$ (I)) <sup>a</sup>	0.0383	0.0373	0.0310	0.0332	0.0479	0.0431	0.0329	0.0388
wR <sub>2</sub> (all data) <sup>b</sup>	0.0919	0.1049	0.0790	0.0778	0.1158	0.1109	0.0772	0.0898
<sup>a</sup> R <sub>1</sub> = $\sum   F_o  -  F_c   / \sum  F_o $ , <sup>b</sup> wR <sub>2</sub> = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ .								

310 °C),<sup>20</sup> they are still water sensitive and must be kept under dry atmosphere to avoid decomposition.

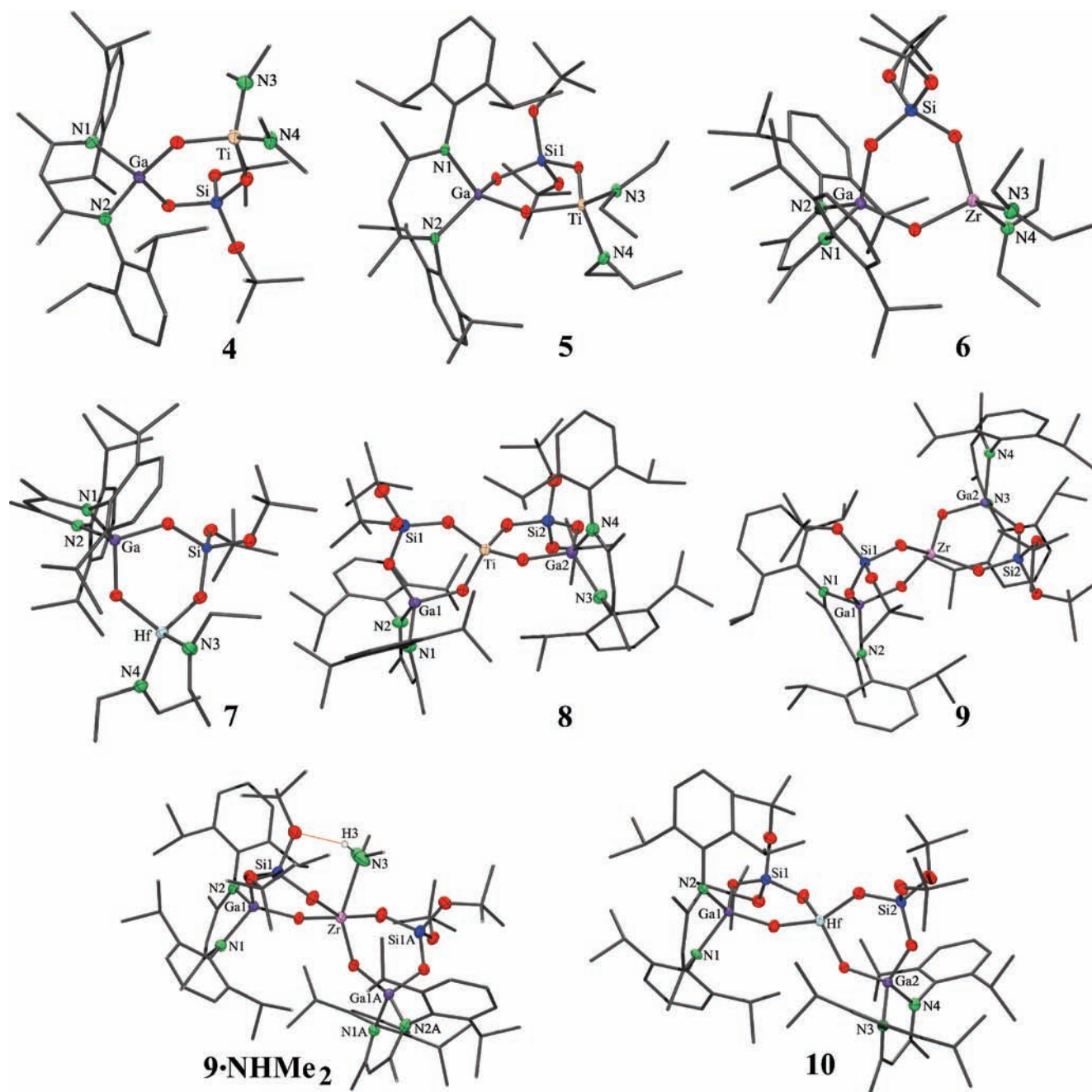
Single crystals suitable for X-ray analysis were obtained from saturated hexane (4–7), toluene/hexane (8, 10), or diethyl-ether (9) solutions. Compound 9 was initially crystallized from a toluene/hexane solution, this yielded an amine adduct of 9 (9 · NHMe<sub>2</sub>); however, the molecule is severely disordered (see Supporting Information for further details) and thus compound 9 was recrystallized from a saturated ether solution to obtain the base free structure. Compound 4 and 9 · NHMe<sub>2</sub> crystallized in the monoclinic P2<sub>1</sub>/c and P2<sub>1</sub>/n space groups, respectively; whereas analyses of 5–7 and 8–10 showed them to be isomorphous and isostructural within each group, with a triclinic P $\bar{1}$  and monoclinic P2<sub>1</sub>/n space groups respectively (Table 3). Compounds 4–10 display six-membered rings, where the corresponding metal atom has substituted both OH protons from 3. Compounds 4–10 have all, one or two almost planar inorganic six-membered rings. Gallosilicates 4–7 hold two amide groups whereas 8–10 form two spirocyclic rings with the group 4 metal atoms in the center. All of the inorganic rings are only slightly deviated from planarity; moreover, the inorganic rings in 8–10 are almost perpendicular to each other with the angle between planes near 90° (Figure 5).

The common coordination environment of the metal atoms is distorted tetrahedral. The only exception is the zirconium atom in compound 9 · NHMe<sub>2</sub> which presents a five coordinated environment where four coordination sites are occupied by two gallosilicate ligands (3) and the fifth site is occupied by NHMe<sub>2</sub> generated during the synthesis of 9. Because neither trigonal bipyramidal (TBP) or square based pyramid (SBP) geometries describe properly the observed one for the zirconium atom in 9 · NHMe<sub>2</sub>, Addison's analysis<sup>21</sup> was carried out and a value of  $\tau = 0.72$  was obtained suggesting that the geometry of the zirconium atom should be described as distorted TBP with O2 and O2A atoms in the axial positions. The crystallization of both 9 and 9 · NHMe<sub>2</sub> is of great interest; first because four coordinated zirconium compounds are relatively scarce in literature,<sup>8b</sup> but most importantly, this fact exposes the acidity of the metal centers and the capability to expand its coordination environment, both of which are highly desirable features for catalytic applications and are likely to be originated by the electron withdrawing environment imposed by the ligand and the Ga–O–M moiety.

The Ti–( $\mu$ -O) and Ga–( $\mu$ -O) bond lengths of 4, 5, and 8 support the formation of covalent Ti–( $\mu$ -O) and Ga–( $\mu$ -O) bonds ( $R_{\text{Ti}} + R_{\text{O}} = 2.15$  Å,  $R_{\text{Ga}} + R_{\text{O}} = 1.90$  Å). Table 4 shows selected bond lengths and angles for compounds 4–10. Nonetheless, Ti–( $\mu$ -O) bonds are larger than those found in [(tBu)<sub>2</sub>Ga(neol)<sub>2</sub>Ti( $\mu$ -O)Ga(tBu)(HNMe<sub>2</sub>)] (1.725(9) Å) (neol-H<sub>2</sub> = 2,2-dimethylpropane-1,3-diol), and TiGa<sub>6</sub>O<sub>7</sub>(NEt<sub>2</sub>)<sub>2</sub>(Mes)<sub>6</sub> (1.763(3), 1.751(3) Å), whereas the Ga–( $\mu$ -O) bond distances are notably shorter than those found in the latter complexes (1.89(1) and 1.94(1) Å, respectively). It is also noteworthy that the Ti–( $\mu$ -O)–Ga angles in 4, 5, and 8 are larger than those found in [(tBu)<sub>2</sub>Ga(neol)<sub>2</sub>Ti( $\mu$ -O)Ga(tBu)(HNMe<sub>2</sub>)] (106.8(3) °)<sup>8c</sup> and TiGa<sub>6</sub>O<sub>7</sub>(NEt<sub>2</sub>)<sub>2</sub>(Mes)<sub>6</sub> (106.8(1) °);<sup>8b</sup> these differences account for the planarity of the rings in 4, 5, and 8.

The Ga–( $\mu$ -O) and M–( $\mu$ -O) (M = Zr, Hf) bond distances in compounds 6, 7 and 9, 10 are found in a narrow interval of 1.800(2)–1.820(2) Å and 1.914(3)–1.989(2) Å. As expected, the M–O distances have only small variations





**Figure 5.** Crystal structures of compounds 4–10. All carbon-bound hydrogen atoms and carbon ellipsoids have been omitted for the sake of clarity. Thermal ellipsoids for noncarbon atoms are shown at the 50% probability level. Solvent molecules were also omitted.

but are notably larger than Ti–O bonds in 4, 5, and 8. The Ga–( $\mu$ -O) and Zr–( $\mu$ -O) distances in 6 and 9·NHMe<sub>2</sub> are similar to those found in [(LGaMe)( $\mu$ -O)(Cp<sub>2</sub>ZrMe)] (1.815(1), 1.926(1) Å)<sup>6b</sup> but the Ga–( $\mu$ -O)–Zr angle (127.6(1), 132.5(1)°) differs from the above-mentioned compound (146.7(1)°). These variations can be explained in the term of the bulkiness of the cyclopentadienyl ligands and the cyclic nature of 6, 7 and 9, 10.

The Si–O bond distances of compounds 4–10 are comparable to those found in compounds 1–3 as well as to similar bond distances found in related compounds.<sup>3b,9,22</sup> However, the Ga–O–Si angles for the spirocyclic compounds

appreciably differ from the nonspirocyclic ones. All the Ga–O–Si angles in 4–10 are smaller than the ones found for noncyclic moieties in 1 (138.2(1)°, 2 (136.6(1)°), LGa(Cl)OSiMe<sub>3</sub> (136.2(1)°),<sup>17</sup> {[(*c*-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>11</sub>(OSiMePh<sub>2</sub>)]<sub>2</sub>Ga}·{Et<sub>3</sub>NH}<sup>+</sup> (137.5(3)°),<sup>2c</sup> or {[(*c*-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>11</sub>(OH)]<sub>2</sub>GaMe<sub>2</sub>} (134.3(3)°)<sup>2e</sup> but are similar to the angle in 3 (128.9(2)°). Nevertheless, the angles found in compounds 4–10 are larger than the ones in cyclic gallosiloxanes: (OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)[Ga(H)]<sub>2</sub>(OtBu)<sub>2</sub> (112.9(2), 113.2(2)°), [(OSiPh<sub>2</sub>OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)GaH]<sub>2</sub> (110.01(9), 110.46(9), 107.81(9)°) and [(OSiPh<sub>2</sub>OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)GaOtBu]<sub>2</sub> (112.7(1), 111.1(1), 109.5(1)°).<sup>5c</sup>

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compounds 4–10

	4	5	6	7	8·C <sub>6</sub> H <sub>14</sub> <sup>a</sup>	9·NHMe <sub>2</sub> <sup>a</sup>	9·C <sub>4</sub> H <sub>10</sub> O <sup>a</sup>	10·C <sub>6</sub> H <sub>14</sub> <sup>a</sup>
Ga–OM <sup>b</sup>	1.810(2)	1.825(2)	1.812(1)	1.818(3)	1.823(2)	1.812(2)	1.820(2)	1.814(3)
Ga–OSi	1.815(2)	1.813(2)	1.815(2)	1.817(3)	1.819(2)	1.800(2)	1.816(2)	1.818(3)
M–OGa <sup>b</sup>	1.807(2)	1.802(2)	1.936(2)	1.924(3)	1.792(2)	1.934(2)	1.802(2)	1.808(3)
M–OSi <sup>b</sup>	1.834(2)	1.854(2)	1.989(2)	1.960(3)	1.797(2)	2.050(2)	1.803(2)	1.800(2)
Si–OGa	1.611(2)	1.612(2)	1.612(2)	1.612(3)	1.779(2)	1.587(5)	1.928(2)	1.914(3)
Si–OM <sup>b</sup>	1.633(2)	1.635(2)	1.626(3)	1.638(3)	1.776(2)	1.611(5)	1.931(2)	1.924(3)
O–M–O	105.9(1)	104.1(1)	101.1(1)	102.0(1)	1.826(2)		1.974(2)	1.960(3)
O–Ga–O	108.6(1)	107.1(1)	107.4(1)	107.4(1)	1.830(2)		1.973(2)	1.952(3)
O–Si–O	109.9(1)	111.9(1)	112.2(1)	111.9(1)	1.165(2)		1.621(2)	1.620(3)
Ga–O–Si	131.9(1)	129.3(1)	132.3(1)	132.3(2)	1.630(5)		1.600(3)	1.613(8)
M–O–Ga <sup>b</sup>	126.7(1)	127.6(1)	127.6(1)	127.1(1)	1.622(2)		1.618(2)	1.616(3)
M–O–Si <sup>b</sup>	131.4(1)	130.9(1)	130.3(1)	130.3(2)	1.647(5)		1.614(3)	1.645(8)
					103.3(1)		99.5(1)	100.6(1)
					103.1(1)	90.9(1)	100.0(1)	100.5(1)
					109.6(1)		112.5(1)	112.0(1)
					110.8(1)	111.4(1)	110.3(1)	110.5(1)
					110.4(1)		111.2(2)	111.1(1)
					109.2(2)	114.1(1)	110.2(1)	110.3(1)
					129.5(1)		130.3(1)	131.2(3)
					128.2(2)	124.5(2)	131.6(1)	131.6(2)
					128.0(1)		127.9(1)	127.5(1)
					128.1(1)	132.5(1)	127.0(1)	126.7(1)
					136.1(2)		137.0(1)	136.3(3)
					137.4(2)	136.4(2)	136.6(1)	136.6(2)

<sup>a</sup> Only in the case of 9·NHMe<sub>2</sub>, the amine is actually coordinated to the metallic center, all other solvents are present only as guest molecules with no significant interaction. <sup>b</sup> M = Ti (4, 5, 8·C<sub>6</sub>H<sub>14</sub>); Zr (6, 9·NHMe<sub>2</sub>, 9); Hf (7, 10·C<sub>6</sub>H<sub>14</sub>).

## CONCLUSIONS

Gallium amides and diterbutoxysilanediol can be used as reagents in a facile synthetic approach for the isolation of the first structurally characterized gallosilicates. As it was demonstrated in the synthesis of 3, LGa(NH<sub>2</sub>)<sub>2</sub> is a very useful precursor as both the amide groups can be replaced stepwise resulting an asymmetric substitution.

Gallosilicate 3 bears two different labile groups, namely, one Si–OH and one Ga–OH moiety in adequate position to form six-membered rings. Thus, reaction of 3 with group 4 metal amides allowed us to obtain several unprecedented multimetallic species, which confirm that 3 is an excellent precursor for the preparation of multimetallic compounds.

The multicomponent composition and high thermal stability of the inorganic cores in compounds 4–10 (and specially 7–10) suggests that they might enable clean transformations to mixed-metal oxides. Such studies are the subject of ongoing research.

## ASSOCIATED CONTENT

**Supporting Information.** Full crystallographic information, CIF files, as well as additional X-ray details and NMR studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## DEDICATION

Dedicated to Prof. Dr. Raymundo Cea-Olivares on the occasion of his 60th birthday.

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