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Communication

Synthesis, Characterization, and X-ray Crystal Structure of a Gallium Monohydroxide and a Hetero-bimetallic Gallium Zirconium Oxide

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A monomeric hydroxide of gallium, LGa(Me)OH, containing terminal hydroxide and methyl groups was prepared by the hydrolysis of LGa(Me)Cl in the presence of N-heterocyclic carbene and water [L = HC{(CMe)(2,6-*i*-$Pr_2C_6H_3N$)}$_2$] in high yield and in a pure form. LGa(Me)OH was used as a synthon to assemble the first hetero-bimetallic compound with a Ga–O–Zr core, [(LGaMe)(Cp_2ZrMe)](μ-O).

The controlled hydrolysis of compounds of group 13 metals has been a topic of wide interest for a long time, particularly of those of aluminum alkyls and aryls.[1] The major interest has been the partial hydrolysis product of trimethylaluminum, viz., methylalumoxane (MAO), an extremely potent cocatalyst in the polymerization of ethylene and propylene.[2] Presently, a wide range of terminal to bridging and monomeric to oligomeric hydroxides of aluminum have been synthesized and structurally characterized.[1,3] However, only a few hydroxides of gallium containing terminal −OH groups have been reported.[3] In 1994, Atwood et al. reported the preparation of the first gallium dihydroxide stabilized by a bulky pincer-type ligand from the corresponding dihydride and water.[4] Monohydroxides of gallium reported previously include hydroxygallium phthalocyanine,[5] (2,6-$Mes_2C_6H_3$)$_2$GaOH;[6] others contain hydroxy-bridged [2,6-$Mes_2C_6H_3$GaMe(μ-OH)]$_2$[6] and [Ga(OH)(SO_4)(terpy)(H_2O)]·H_2O.[7] Our long-standing interest in the synthesis of group 13 hydroxides,[1d,e,8] containing terminal −OH groups, resulted in a series of compounds: LAl(OH)$_2$,[9a,10a] LGa(OH)$_2$,[9b] LAl(Me)OH,[11] and [LAlOH]$_2$(μ-O)[10b] [L = HC{(CMe)(2,6-*i*-$Pr_2C_6H_3N$)}$_2$]. A key factor in this successful assembly has been the choice of an appropriate ligand environment around the metal atom and a synthetic strategy that allows product formation in a rational and predictable manner.[12] Recently, we have shown that the use of N-heterocyclic carbene as a HCl scavenger has proven to be a versatile method in hydrolysis and ammonolysis reactions.[9] The isolation of LAl(Me)OH prompted us to look for a similar gallium derivative. Another driving force was the compound [(LAlMe)(Cp_2ZrMe)](μ-O), which was a very good catalyst for the polymerization of ethylene.[11a] Moreover, LAl(Me)OH has been utilized to prepare a series of aluminum lanthanide hetero-bimetallic complexes.[11c]

A methylgallium hydroxide, MeGa(OH)Pz_2BMe_2 [Pz_2BMe_2 = bis(pyrazolyl)dimethylboron], was isolated by

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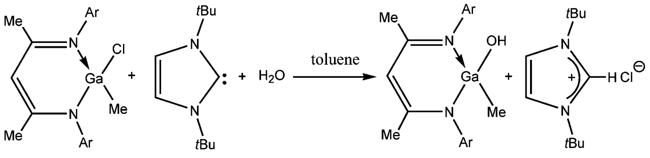
10.1021/ic051769l CCC: $33.50

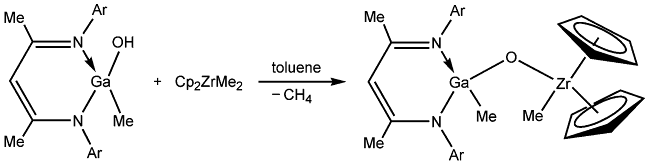
Scheme 1. Preparation of β-Diketiminate Methylgallium Hydroxide **2**



1 **2**

Ar = 2,6-$i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$

Scheme 2. Preparation of the Hetero-bimetallic Gallium Zirconium Oxide Compound **3**



2 **3**

Ar = 2,6-$i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$

Rettig and co-workers as a byproduct of the reaction between $\mathrm{Na[Me_2BPz_2]}$ and $\mathrm{Me_2GaCl{\cdot}OEt_2}$. The formation of $\mathrm{MeGa(OH)Pz_2BMe_2}$ probably resulted from an accidental use of wet solvent.[13] Therefore, it was of interest to prepare a molecule with similar functionalities with a much simpler procedure that rationally allows the assembly of such molecules. Herein we report on the high yield synthesis of a monomeric terminal hydroxide of gallium, LGa(Me)OH (**2**), and its reaction with $\mathrm{Cp_2ZrMe_2}$ to prepare the hetero-bimetallic compound $\mathrm{[(LGaMe)(Cp_2ZrMe)](\mu\text{-}O)}$ (**3**).

The hydrolysis of LGa(Me)Cl (**1**) with a stoichiometric amount of water in the presence of 1,3-di-*tert*-butylimidazol-2-ylidene as a hydrogen chloride acceptor results in the formation of **2** in good yield (Scheme 1). The 1,3-di-*tert*-butylimidazolium chloride formed can easily be separated because of its insolubility in *n*-hexane and affords **2** in pure form. Moreover, upon reduction with *t*-BuOK, 1,3-di-*tert*-butylimidazol-2-ylidene was regenerated and recycled. Compound **2** is a rare example of a monohydroxide of gallium with a methyl group as a substituent on gallium.

The OH groups are one of the most important functional groups for the immobilization of catalytically active metal complexes and also for solid acid catalysts. Because of the stability of the Ga−O bond, the proton of the GaO−H moiety in **2** can be anticipated to be Brönsted acidic. Therefore, the reaction of **2** with $\mathrm{Cp_2ZrMe_2}$ in toluene leads to methane evolution and the formation of **3**. Compound **3** represents the first example of a X-ray-characterized molecule with a Ga−O−Zr core (Scheme 2).

Compounds **2** and **3** have been unambiguously characterized by means of spectroscopic, spectrometric, and crystallographic techniques. Both **2** and **3** are colorless crystalline solids and are thermally quite stable. Compound **2** melts at 200 °C, while **3** melts with decomposition at 318 °C. The electrospray ionization (EI) mass spectrum of **2** revealed that the most intense peak appears at *m*/*z* 503 and corresponds to the loss of one methyl group from the molecular ion.

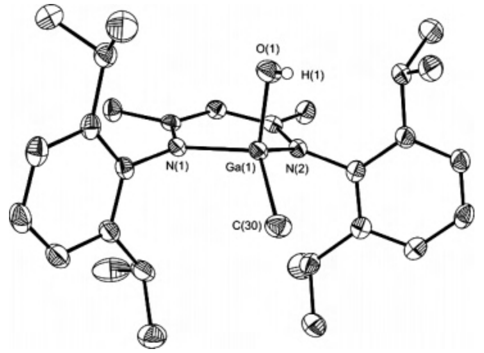


Figure 1. Molecular structure of **2**. The hydrogen atoms of the C−H bonds are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga(1)−O(1) 1.831(1), Ga(1)−N(1) 1.957(1), Ga(1)−N(2) 1.953(1), Ga(1)−C(30) 1.949(2); O(1)−Ga(1)−N(1) 102.8(1), O(1)−Ga(1)−N(2) 105.4(1), N(1)−Ga(1)−N(2) 95.6(1), O(1)−Ga(1)−C(30) 119.5(1), N(1)−Ga(1)−C(30) 116.0(1), N(2)−Ga(1)−C(30) 114.3(1).

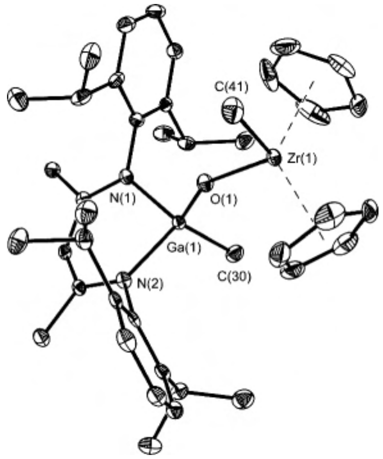


Figure 2. Molecular structure of **3**. The hydrogen atoms of the C−H bonds are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga(1)−O(1) 1.815(1), Ga(1)−N(1) 1.975(2), Ga(1)−N(2) 1.967(2), Ga(1)−C(30) 1.971(2), Zr(1)−O(1) 1.926(1), Zr(1)−C(41) 2.301(3); O(1)−Ga(1)−N(1) 109.0(1), O(1)−Ga(1)−N(2) 109.8(1), N(1)−Ga(1)−N(2) 96.1(1), O(1)−Ga(1)−C(30) 116.2(1), N(1)−Ga(1)−C(30) 112.3(1), N(2)−Ga(1)−C(30) 111.7(1), Ga(1)−O(1)−Zr(1) 146.7(1), O(1)−Zr(1)−C(41) 102.0(1).

Similarly, a peak at *m*/*z* 739 in **3** is due to $[\mathrm{M}^+ - \mathrm{Me}]$. The IR spectrum of **2** shows a sharp band at 3676 cm^{-1}**,** which can be attributed to the GaO−H stretch. The ^{1}H NMR spectrum of **2** shows two resonances (δ +0.08 and −0.57), which can be attributed to the protons of OH and GaMe groups, respectively. In much the same way, resonances (δ −0.12 and −0.32) for **3** correspond to ZrMe and GaMe, respectively. The other resonances for **2** and **3** are characteristic of the β-diketiminate ligand L.

Single crystals of **2** and **3** suitable for X-ray structural analysis were obtained from their *n*-hexane and toluene solutions, respectively. The molecular structures of **2** and **3** are shown in Figures 1 and 2. Compounds **2** and **3** crystallize in the monoclinic space groups $P2_1/c$ and $P2_1/n$, respectively.

The X-ray crystal structure reveals **2** as a monomeric gallium hydroxide (Figure 1). The Ga center exhibits a distorted tetrahedral geometry with two nitrogen atoms of the β-diketiminate ligand, one Me group, and an OH group. The small N−Ga−N angle 95.6(1)° is the result of the formation of the $\mathrm{C_3N_2Ga}$ six-membered ring. The Ga−OH

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bond length [1.831(1) Å] in **2** is considerably shorter than that found in hydroxyl(methyl)gallium bis(pyrazolyl)dimethylboron[13] (2.033(5) Å) and in $[(2,6\text{-Mes}_2C_6H_3Ga(Me)(\mu\text{-OH})]_2$ (average 1.914 Å)[6] but slightly longer than that observed in $(2,6\text{-Mes}_2C_6H_3)_2GaOH$ [1.783(2) Å].[6] The Ga−Me distance 1.949(2) Å in **2** is comparable to 1.957(8) Å observed in hydroxyl(methyl)gallium bis(pyrazolyl)dimethylboron and in $[(2,6\text{-Mes}_2C_6H_3Ga(Me)(\mu\text{-OH})]_2$ (average 1.947 Å).[13]

The molecular structure of **3** is shown in Figure 2. The Ga atom exhibits a highly distorted tetrahedral geometry with two nitrogen atoms of the β-diketiminate ligand, one Me group, and one μ-O unit. The coordination sphere of Zr is completed by two Cp ligands and one Me group. The Me groups in **3** are bent out of the Ga−O−Zr plane in a trans manner. The Ga−(μ-O) bond length [1.815(1) Å] in **3** is slightly shorter than the Ga−O distance in **2** [1.831(1) Å] and is shorter in other Ga−(μ-O) derivatives, for example, 1.910 Å in $(MesGaO)_9$ [8] and 1.898 Å in $(Mes_2GaOLi)_2\cdot 4THF$.[1e] The Ga−O−Zr angle [146.7(1)°] lies between the Ga−O−Ga angle [91.9(1)° in $(Mes_2GaOLi)_2\cdot 4THF$[1e] and 100.6(2)° in $[(t\text{-BuO})_2GaH]_2$[14]] and the Zr−O−Zr angle [174.1(3)° in $[Cp_2Zr(Me)]_2(\mu\text{-O})$].[15] The Zr−($\mu$-O) bond length [1.926(1) Å] is slightly shorter than those exhibited by compounds $[(Cp_2ZrCl)_2(\mu\text{-O})]$ [1.945(3) Å],[16] $[(Cp_2ZrMe)]_2(\mu\text{-O})$ [1.948(1) Å],[15] and $[\{(Cp_2Zr)(\mu\text{-O})_3]$ [1.959(3) Å][17] but significantly shorter than the Zr−(μ-O) or Zr−(μ-OH) bond lengths observed in the clusters $[(Cp^*Zr)_6(\mu_4\text{-O})(\mu\text{-O})_4(\mu\text{-OH})_8]\cdot 2C_7H_8$ (∼2.106 Å)[18] and $[\{(Cp^*ZrCl)(\mu\text{-OH})\}_3(\mu_3\text{-OH})(\mu_3\text{-O})]\cdot 2THF$ [2.160(2) Å].[19−23] The Zr−Me bond length [2.301(3) Å] in **3** is longer than that found in $(Cp_2ZrMe)_2(\mu\text{-O})$ [2.276(9) Å].[15]

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Supporting Information Available: Full details of the crystal structure determination for **2** (CCDC 280865) and **3** (CCDC 280866) (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) (a) To a solution of 1,3-di-*tert*-butylimidazol-2-ylidene (0.45 g, 2.50 mmol) and LGa(Me)Cl (1.34 g, 2.50 mmol) in toluene (50 mL) was added slowly with vigorous stirring over a period of 30 min degassed and distilled water (45 μL, 2.50 mmol). The mixture was stirred for another 15 min. After removal of all volatiles, the product was extracted with *n*-hexane (60 mL). The final solution was concentrated (15 mL) and stored at −20 °C for 2 days to afford colorless crystals. Yield: 1.00 g (76 %). Mp: 198−200 °C. Anal. Calcd for $C_{30}H_{45}GaN_2O$ (519.41): C, 69.37; H, 8.73, N, 5.39. Found: C, 69.46; H, 8.62; N, 5.42. MS (EI): *m*/*z* (%) 518 (6) [M^+], 503 (100) [$M^+ - Me$], 485 (44) [$M^+ - Me - 3H$]. IR (Nujol): $\tilde{\nu}$ 3676, 1558, 1527, 1442, 1384, 1319, 1262, 1178, 1105, 1056, 1023, 936, 869, 804, 757, 603, 571 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 7.12−7.03 (m, *Ar*), 4.80 (s, 1 H, γ-C*H*), 3.79 (sept, $^3J_{HH} = 6.8$ Hz, 2 H, C*H*Me$_2$), 3.20 (sept, $^3J_{HH} = 6.5$ Hz, 2 H, C*H*Me$_2$), 1.57 (s, 6 H, C*Me*), 1.34 (d, $^3J_{HH} = 6.6$ Hz, 6 H, CH*Me*$_2$), 1.24 (dd, 12 H, CH*Me*$_2$), 1.08 (d, $^3J_{HH} = 6.6$ Hz, 6 H, CH*Me*$_2$), 0.08 (s, 1 H, GaO*H*), −0.57 (s, 3 H, Ga*Me*). (b) Toluene (60 mL) was added at 0 °C to the mixture of **2** (0.52 g, 1.00 mmol) and Cp_2ZrMe_2 (0.25 g, 1.00 mmol). The resulting solution was stirred for 2 h at room temperature and then continuously for 24 h at 100 °C. The colorless solution was kept at room temperature for 48 h to isolate colorless crystals of **3** (0.52 g). An additional crop of **3** (0.18 g) was obtained at 0 °C. Yield: 0.70 g (93%). Mp: 318 °C (dec). Anal. Calcd for $C_{41}H_{57}GaN_2OZr$ (754.85): C, 65.24; H, 7.61; N, 3.71. Found: C, 65.28; H, 7.58; N, 3.73. MS (EI): *m*/*z* (%): 739 (48) [$M^+ - Me$], 501 (100) [$M^+ - 2Me - 2H - ZrCp_2$], 485 (16) [$M^+ - 2Me - 2H - O - ZrCp_2$]. IR (Nujol): $\tilde{\nu}$ 1554, 1526, 1438, 1316, 1384, 1264, 1253, 1179, 1120, 1100, 1023, 934, 791, 769, 703, 637, 620, 552, 449 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.25−7.24 (m, Ar), 5.29 (s, 10 H, C$_5$*H*$_5$), 4.87 (s, 1 H, γ-CH), 3.15 (sept, $^3J_{HH} = 6.8$ Hz, 4 H, C*H*Me$_2$), 1.74 (s, 6 H, C*Me*) 1.38, 1.35 (dd, $^3J_{HH} = 6.8$ Hz, 12 H, CH*Me*$_2$), 1.25 (d, $^3J_{HH} = 6.8$, 6 H, CH*Me*$_2$), 1.08 (d, $^3J_{HH} = 6.8$, 6 H, CH*Me*$_2$), −0.12 (s, 3 H, Zr*Me*), −0.32 (s, 3 H, Ga*Me*).

(21) (a) Crystal data for compound **2** ($C_{30}H_{45}GaN_2O$): $M_w = 519.40$, monoclinic, $P2_1/c$, $a = 8.943(2)$ Å, $b = 9.752(2)$ Å, $c = 33.182(4)$ Å, $\beta = 92.09(2)°$, $V = 2892(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.193$ Mg·m^{-3}, $T = 100(2)$ K, λ(Cu Kα) = 1.541 78 Å, $\mu = 1.462$ mm^{-1}. Out of 19 318 collected reflections, 4120 were independent ($R_{int} = 0.0268$). The final refinements converged at R1 = 0.0268 for [$I > 2\sigma(I)$], wR2 = 0.0671 for all data, CCDC 280865. (b) Crystal data for compound **3** ($C_{41}H_{57}GaN_2OZr$): $M_w = 754.83$, monoclinic, $P2_1/n$, $a = 10.056(2)$ Å, $b = 18.586(3)$ Å, $c = 20.013(3)$ Å, $\beta = 90.20(1)°$, $V = 3740(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.340$ Mg·m^{-3}, $T = 100(2)$ K, λ(Cu Kα) = 1.54178 Å, $\mu = 3.407$ mm^{-1}. Out of 17 776 collected reflections, 4956 were independent ($R_{int} = 0.0195$). The final refinements converged at R1 = 0.0199 for [$I > 2\sigma(I)$], wR2 = 0.0477 for all data, CCDC 280866. (c) The structures were solved by direct methods (*SHELXS-97*)[21] and refined against all data by full-matrix least squares on F^2.[22] All of the C−H hydrogen atoms except H(3A) were included in geometrically idealized positions and refined with the riding model. Localization of the H(3A) hydrogen from the electron density map in both structures proved to be more accurate than its fixing in the idealized position and led to lowering of the R1 and wR2 values. The hydrogen atom from the OH in **2** was localized from the difference electron density map and refined isotropically. (d) Compound **3** crystallizes as a pseudo-merohedral twin emulating orthorhombic crystal system. The twin law was determined as −1 0 0 0 −1 0 0 0 1, and the ratio of the domains was refined as 0.33/0.67.

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