Inorganic Chemistry

Article

pubs.acs.org/IC

A Synthetic Route to a Molecular Galloxane Dihydroxide and Its Group 4 Heterobimetallic Compounds

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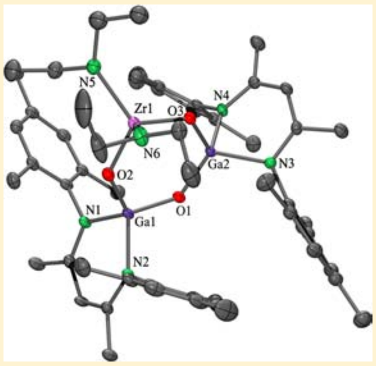
Ⓢ *Supporting Information*

ABSTRACT: Controlled hydrolysis of $^{Me}LGaCl_2$ (^{Me}L = $HC[(CMe)N(2,4,6\text{-}Me_3C_6H_2)]_2^-$) (**1**) in the presence of a *N*-heterocyclic carbene, as a HCl acceptor, led to the unprecedented molecular galloxane dihydroxide $[\{^{Me}LGa(OH)\}_2(\mu\text{-}O)]$ (**2**) in high yield. Compound **2** was used in the assembly of the heterobimetallic galloxanes with group 4 metals $[\{(^{Me}LGa)_2(\mu\text{-}O)\}(\mu\text{-}O)_2\{M(NR_2)_2\}]$ (M = Ti, R = Me (**6**); M = Zr (**7**), Hf (**8**), R = Et).



■ INTRODUCTION

The controlled hydrolysis of compounds with group 13 metals has been a topic of extensive study. The major interest in this issue has focused on the aluminum derivatives due to their potential application as cocatalysts in the polymerization of a wide range of organic monomers.[1] A long-lasting problem of alumoxanes is the difficulty to stabilize them in low aggregation and crystalline forms.[2] In this regard, our research group has been interested in the synthesis of functionalized molecular alumoxanes and their heterobimetallic derivatives.[3,4] In contrast to alumoxanes, structural information concerning soluble molecular galloxanes is limited to a handful of examples,[5−8] none of which contain potentially useful functional groups or can be isolated in suitable yields.[9] Furthermore, the task of assembling compounds with Ga−O−Ga moieties is also hampered by the limited availability of appropriate starting materials for gallium compared to those used for aluminum. Nonetheless, functionalized galloxanes can be used as starting materials for the construction of heterobimetallic species. In fact, heterobimetallic systems containing M−O−M′ frameworks are particularly important because they bring the metals into close proximity with each other allowing pronounced chemical communication between them.[10] However, compounds bearing Ga−O−M moieties[11−13] remain scarce, while heterobimetallic galloxanes are virtually unknown. An interesting strategy used for the preparation of molecular gallium hydroxides was achieved by using a strong nucleophilic reagent, a *N*-heterocyclic carbene, as an HCl acceptor for the controlled hydrolysis of gallium halides.[11,14] Consequently, we focused this strategy on the assembly of functonalized dinuclear gallium species, particularly molecular galloxane dihydroxides, based on the reactivity patterns observed previously for the alumoxane dihydroxide $[\{^{Me}LAl(OH)\}_2(\mu\text{-}O)]$.[3a]

Herein, we report on the preparation of the unprecedented molecular galloxane containing two terminal OH groups $[\{^{Me}LGa(OH)\}_2(\mu\text{-}O)]$ (^{Me}L = $HC[(CMe)N(2,4,6\text{-}Me_3C_6H_2)]_2^-$) (**2**) obtained from the controlled hydrolysis of $[^{Me}LGaCl_2]$ using 1,3-di-*tert*-butylimidazol-2-ilydene as a hydrogen chloride acceptor,[15] along with the synthesis of its group 4 heterobimetallic derivatives $[\{(LGa)_2(\mu\text{-}O)\}(\mu\text{-}O)_2\{M(NR_2)_2\}]$ (M = Ti, R = Me (**6**); M = Zr (**7**), Hf (**8**), R = Et).

■ EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under a dry and oxygen-free atmosphere (N_2) using Schlenk-line and glovebox techniques. The solvents were dried using a MBraun Solvent Purification System. Commercially available chemicals were purchased from Sigma-Aldrich and used without further purification. $Zr(NEt_2)_4$ was prepared according to the literature procedure.[16] C_6D_6 was dried with a Na/K alloy and distilled through vacuum transfer (−196 °C) using a Swagelok system, while a similar procedure was used for $CDCl_3$ using P_2O_5. NMR spectra were recorded on a Bruker Avance III 300 MHz, and ^1H chemical shifts were reported with reference to the residual protons of the deuterated solvent unless otherwise stated. IR spectra were recorded on a Bruker Alpha FT-IR spectrometer with an ATR measurement setup (diamond) under inert atmosphere in a glovebox in the 4000−400 cm^{-1} range. Mass spectra were obtained on a Shimadzu GCMS-QP2010 Plus using the electron impact (EI) ionization technique. Elemental analyses (C, H, N) were performed on an Elementar MicroVARIO Cube analyzer. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus. Crystallographic data for compounds **2**, **3**, **5**, **7**, and **8** were

Received: January 28, 2013
Published: May 31, 2013

dx.doi.org/10.1021/ic4010054 | *Inorg. Chem.* 2013, 52, 6944−6950

Table 1. Crystallographic Data for the Structural Analyses of Compounds 2, 3, 5, 7, and 8

	2	3	5	7·toluene	8·toluene
chemical formula	$C_{46}H_{60}Ga_2N_4O_3$	$C_{46}H_{58}Cl_2Ga_2N_4O$	$C_{25}H_{35}GaN_2$	$C_{57.5}H_{82}Ga_2N_6O_3Zr$	$C_{57.5}H_{82}Ga_2N_6O_3Hf$
formula weight	856.42	893.30	433.27	1135.95	1223.22
space group	*Fdd*2	*Fdd*2	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$
a, Å	20.1713(7)	20.539(3)	13.966(2)	10.4374(4)	10.4382(3)
b, Å	48.0892(16)	47.199(5)	17.174(2)	13.5148(5)	13.4996(4)
c, Å	8.9712(3)	9.343(2)	19.935(3)	21.8467(8)	21.7611(7)
α, deg	90	90	90	95.605(1)	95.8000(10)
β, deg	90	90	90	90.835(1)	90.4520(10)
γ, deg	90	90	90	112.228(2)	112.2750(10)
V, Å^3	8702.3(5)	9057(3)	4781.5(11)	2834.6(2)	2819.48(15)
Z	8	8	8	2	2
temp, K	100(2)	100(2)	100(2)	100(2)	100(2)
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	1.282	1.345	1.163	1.171	2.832
ρ_{calc}/g cm^{-3}	1.307	1.310	1.204	1.331	1.441
R_1 ($I > 2\sigma(I)$)[a]	0.0153, 0.0415	0.0252, 0.0548	0.0548, 0.1055	0.0277, 0.0685	0.0162, 0.0404
wR_2 (all data)[b]	0.0155, 0.0416	0.0268, 0.0553	0.0684, 0.1100	0.0347, 0.0685	0.0174, 0.0410

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

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

	2[a]	3[b]		2[a]	3[b]
Ga(1)−O(1)	1.794(1)	1.783(1)	Ga(1)−O(1)−Ga(1A)	121.6(1)	124.2(1)
Ga(1)−X	1.845(1)	2.197(1)	N(1)−Ga(1)−N(2)	96.7(1)	98.0(1)
Ga(1)−N(1)	1.946(1)	1.933(2)	O(1)−Ga(1)−X	114.1(1)	111.6(1)
Ga(1)−N(2)	1.936(1)	1.925(2)	N(1)−Ga(1)−X	109.1(1)	110.9(1)

[a] X = O(2). [b] X = Cl(1).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compounds 7 and 8

	7·toluene[a]	8·toluene[b]		7·toluene[a]	8·toluene[b]
Ga(1)−O(1)	1.808(2)	1.808(2)	Ga(1)−O(1)−Ga(2)	126.4(1)	112.2(1)
Ga(1)−O(2)	1.825(2)	1.825(2)	N(1)−Ga(1)−N(2)	96.3(1)	96.2(1)
Ga(2)−O(1)	1.788(2)	1.788(2)	N(3)−Ga(1)−N(4)	94.9(1)	94.9(1)
Ga(2)−O(3)	1.833(2)	1.833(2)	O(1)−Ga(1)−O(2)	111.9(1)	111.9(1)
Ga(1)−N(1)	1.942(2)	1.942(2)	O(1)−Ga(2)−O(3)	116.1(1)	116.0(1)
Ga(1)−N(2)	1.937(2)	1.937(2)	O(2)−M(1)−O(3)	103.4(1)	104.1(1)
Ga(2)−N(3)	1.962(2)	1.962(2)	Ga(1)−O(2)−M(1)	133.1(1)	132.5(1)
Ga(2)−N(4)	1.959(2)	1.959(2)	Ga(2)−O(3)−M(1)	128.5(1)	128.3(1)
M(1)−O(2)	1.927(2)	1.920(1)	N(5)−M(1)−N(6)	108.4(1)	108.7(1)
M(1)−O(3)	1.945(2)	1.935(1)			

[a] M = Zr. [b] M = Hf.

collected on a Bruker SMART APEX DUO three-circle diffractometer equipped with an Apex II CCD detector using MoK_α (Microfocus sealed tube with a graphite monochromator). The crystals were coated with a hydrocarbon oil, picked up with a nylon loop, and immediately mounted in the cold nitrogen stream (−173 °C) of the diffractometer. Frames were collected by omega scans, integrated using SAINT program, and semiempirical absorption correction (SADABS) was applied.[17] The structures were solved by direct methods (SHELXS), and refined by the full-matrix least-squares on F^2 with SHELXL-97[18] using the SHELXLE GUI.[19] Weighted R factors, R_w, and all goodness of fit indicators are based on F^2. All non-hydrogen atoms were refined anisotropicaly. Hydrogen atoms were placed in idealized geometrical positions and refined with U_{iso} tied to the parent atom with the riding model, whereas the hydrogen atoms of the OH moieties in **2** were localized from the difference electron-density map and refined isotropically. The crystallographic data and refinement details for compounds **2**, **3**, **5**, **7**, and **8** are given in Table 1. Selected interatomic distances and angles are provided in Tables 2 and 3.

*Preparation of [^{Me}LGaCl$_2$] (**1**).* A solution of ^{n}BuLi (2.5 M in hexanes, 2.39 mL, 5.98 mmol) was added dropwise to a diethylether solution (20 mL) of ^{Me}LH (2.00 g, 5.94 mmol) at −79 °C. After 1 h under stirring at ambient temperature, the reaction mixture was added to a solution of $GaCl_3$ (1.05 g, 5.9 mmol) in diethylether (20 mL) at −79 °C, and the reaction mixture was stirred for 2 h at ambient temperature. The resulting solution was then filtered through Celite, and all of the volatiles were removed under vacuum and the remaining yellow solid was washed with hexane (3 × 3 mL). Yield 84% (2.36 g). Mp 219 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.82 (s, 6H, CH_3), 2.27 (s, 6H, *p*-Ar−CH_3), 2.28 (s, 12H, *o*-Ar−CH_3), 5.21 (s, 1H, γ-*CH*), 6.92 (s, 4H, *m*-Ar−*H*). ^{13}C NMR (75.58 MHz, $CDCl_3$, 25 °C): δ 18.9 (CH_3), 21.0 (*p*-Ar−CH_3), 23.4 (*o*-Ar−CH_3), 96.6 (γ-CH), 129.7 (*o*-Ar−C), 133.6 (*p*-Ar−C), 136.7 (*m*-Ar−C), 138.3 (*i*-Ar−C), 171.4 ppm (C=N). IR: $\tilde{\nu}$ 1538 cm^{-1} (C=N). MS−EI (70 eV) *m*/*z*: 474 [M$^+$]. Anal. Calcd for $C_{23}H_{29}Cl_2Ga_2N_2$ (474.12): C, 58.27; H, 6.17; N, 5.91. Found: C, 58.19; H, 6.12; N, 5.59.

*Preparation of [{^{Me}LGa(OH)}$_2$(μ-O)] (**2**).* **1** (0.5 g, 1.05 mmol), 1,3-di-*tert*-butylimidazol-2-ilydene (0.42 g, 2.37 mmol), and toluene (20 mL) were placed in a Schlenk flask. A solution of H_2O (1.0 M, 1.84 mmol) in THF was slowly added at −79 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 4 h; after this time, the insoluble material was filtered off and the volatiles were removed under vacuum. The white solid obtained was washed with cold hexane (2 × 5 mL) and dried under vacuum. Yield 85% (0.38 g). Mp 279 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): *δ* −1.38 (s, 1H, O*H*), 1.41 (s, 6H, CH_3), 1.97, 2.43 (s, 12H, *o*-Ar−CH_3), 2.24 (s, 6H, *p*-Ar−CH_3), 4.66 (s, 1H, *γ*-C*H*), 6.76, 6.85 ppm (s, 4H, *m*-Ar−*H*). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): *δ* 18.3 (CH_3), 19.0 (*p*-Ar−CH_3), 21.0, 22.4 (*o*-Ar−CH_3), 94.4 (*γ*-CH_3), 129.3, 129.6 (*m*-Ar−*C*), 134.4, 134.6 (*o*-Ar−*C*), 135.2 (*p*-Ar−*C*), 141.6 (*i*-Ar−*C*), 168.5 ppm (C═N). IR (ATR): $\tilde{\nu}$ 3623 cm^{-1} (GaO−H). MS−EI (70 eV) *m*/*z*: 855 [M^+ − H], 838 [M^+ − H_2O]. Anal. Calcd for $C_{46}H_{60}Ga_2N_4O_3$ (856.42): C, 64.51; H, 7.06; N, 6.54. Found: C, 64.53; H, 6.97; N, 6.52.

*Preparation of [{^{Me}LGa(Cl)}$_2$(μ-O)] (**3**).* A modification to the reported procedure for the synthesis of [{LAl(Cl)}$_2$(*μ*-O)] (L = HC[(CMe)N(Me)]$_2^-$) was used.[20] To a solution of **1** (1.0 g 2.1 mmol) in THF (30 mL) was added Ag_2O (0.24 g, 1.05 mmol) at ambient temperature. The reaction mixture was refluxed for 48 h, and the yellow solution was filtered. The volatiles were removed under vacuum, and the resulting white solid was rinsed with hexane (2 × 5 mL). Yield 77% (0.73 g). Mp 345 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): *δ* 1.58 (s, 6H, CH_3), 1.67, 2.31 (s, 12H, *o*-Ar−CH_3), 2.15 (s, 6H, *p*-Ar−CH_3), 4.91 (s, 1H, *γ*-C*H*), 6.64, 6.88 (br s, 4H, *m*-Ar−*H*). ^{13}C (75.58 MHz, $CDCl_3$, 25 °C): *δ* 18.1 (CH_3), 19.0, 22.9 (*o*-Ar−CH_3), 20.9 (*p*-Ar−CH_3), 95.8 (*γ*-CH), 128.7 (*m*-Ar−*C*H), 129.3 (*m*-Ar−*C*H), 133.5, 134.2 (*o*-Ar−*C*), 135.0 (*p*-Ar−*C*), 140.2 (*p*-Ar−*C*), 169.0 ppm (C═N). IR (ATR): $\tilde{\nu}$ 1534 cm^{-1}. MS−EI (70 eV) *m*/*z*: 545 [$C_{22}H_{27}Cl_2Ga_2O$]$^+$. Anal. Calcd for $C_{46}H_{58}Cl_2Ga_2N_4O$ (893.33): C, 61.85; H, 6.54; N, 6.27. Found: C, 61.63; H, 6.38; N, 6.16.

*Preparation of [^{Me}LGaH$_2$] (**4**).* A 0.7 M solution of $AlH_3 \cdot NMe_3$ (5.6 mL, 3.9 mmol) in toluene was added to a suspension of **3** (1.0 g, 1.12 mmol) in toluene at −79 °C. The solution was stirred for 12 h and then filtered. The volatile materials were removed under vacuum, and the remaining residue was washed with pentane (2 × 3 mL) giving a white solid. Yield 70% (0.63 g). Mp 149 °C (dec). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): *δ* 1.51 (s, 6H, CH_3), 2.10 (s, 6H, *p*-Ar−CH_3), 2.30 (s, 12H, *o*-Ar−CH_3), 4.69 (s, 1H, *γ*-C*H*), 5.26 (s, 2H, Ga−*H*), 6.74 (br s, 4H, *m*-Ar−*H*). IR (ATR): $\tilde{\nu}$ 1836, 1876 cm^{-1} (GaH_2). MS−EI (70 eV) *m*/*z*: 403 [M^+ − H]. Anal. Calcd for $C_{23}H_{31}Ga_2N_2$ (405.23): C, 68.17; H, 7.71; N, 6.91. Found: C, 68.17; H, 7.74; N, 6.90.

*Preparation of [^{Me}LGaMe$_2$] (**5**).* A solution of $GaMe_3$ (1.0 M in toluene, 6.0 mL, 6 mmol) was added to a solution of ^{Me}LH (2.0 g 6.0 mmol) in toluene (10 mL) at ambient temperature. After the evolution of methane ceased, the solution was stirred for 2 h. The resulting yellow solution was filtered, the volatiles were removed under vacuum, and the residue was washed with pentane (2 × 3 mL) after which a white solid was obtained. Yield 89% (2.31 g). Mp 97.2 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): *δ* −0.67 (s, 6H, GaCH_3), 1.68 (s, 6H, CH_3), 2.20 (s, 6H, *p*-Ar−CH_3), 2.28 (s, 6H, *o*-Ar−CH_3), 4.85 (s, 1H, *γ*-C*H*), 6.89 (s, 4H, *m*-Ar−*H*). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): *δ* −6.90 (GaCH_3), 18.5 (CH_3), 20.8 (*o*-Ar−CH_3), 22.8 (*p*-Ar−CH_3), 94.0 (*γ*-CH_3), 129.4 (*m*-Ar−*C*), 132.9 (*o*-Ar−*C*), 134.4 (*p*-Ar−*C*), 141.9 (*i*-Ar−*C*), 166.9 (C═N). MS−EI (70 eV) *m*/*z* (%): 417 [M^+ − CH_3]. Anal. Calcd for $C_{25}H_{35}Ga_2N_2$ (432.21): C, 69.30; H, 8.14; N, 6.47. Found: C, 69.21; H, 8.12; N, 6.39.

*Hydrolysis Studies for **4** and **5**.* A 0.5 M solution of H_2O in THF (6.0 mL, 3.0 mmol) was added to a solution of **4** (or **8**) (2.0 mmol) in toluene (20 mL) at either −30 °C or ambient temperature. The reactions were stirred at ambient temperature for 48 h or refluxed for the same amount of time. The solvent was removed under vacuum, and the white solid was washed (3 × 3 mL) with hexane. The products from these reactions were identified as the starting materials by ^{1}H NMR analysis.

*Preparation of [{(^{Me}LGa)$_2$(μ-O)}(μ-O)$_2${Ti(NMe$_2$)$_2$}] (**6**).* A solution of $Ti(NMe_2)_4$ (0.08 g, 0.35 mmol) in toluene (10 mL) was added dropwise to a solution of **2** (0.25 g, 0.29 mmol) in toluene (10 mL) at −79 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 2 h after which the solution was filtered. All volatiles were removed under vacuum leaving a white residue, which was treated with cold pentane (2 × 5 mL). After filtration and drying under vacuum, **3** was obtained as a white powder. Yield 64% (0.18 g). Mp 253 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): *δ* 1.29 (s, 6H, CH_3), 1.95, 2.31 (s, 12H, *o*-Ar−CH_3), 2.30 (s, 6H, *p*-Ar−CH_3), 3.13 [s, 6H, N(CH_3)$_2$], 4.77 (s, 1H, *γ*-C*H*), 6.70, 6.83 ppm (s, 4H, *m*-Ar−*H*). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): *δ* = 18.5 (CH_3), 19.1, 22.9 (*o*-Ar−CH_3), 21.1 (*p*-Ar−CH_3), 45.9 [N(CH_3)$_2$], 96.9 (*γ*-CH_3), 129.4, 130.1 (*m*-Ar−*C*), 133.7, 134.3 (*o*-Ar−*C*), 134.4 (*p*-Ar−*C*), 142.51 (*i*-Ar−*C*), 169.5 ppm (C═N). MS−EI (70 eV) *m*/*z*: 990 [M^+ − H], 902 [M^+ − $2NMe_2$]. Anal. Calcd for $C_{50}H_{70}Ga_2N_6O_3Ti$ (990.44): C, 60.63; H, 7.12; N, 8.49. Found: C, 60.61; H, 7.07; N, 8.41.

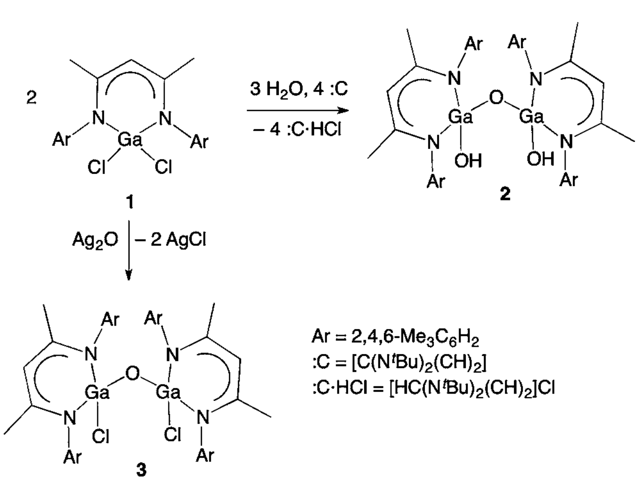
*Preparation of [{(^{Me}LGa)$_2$(μ-O)}(μ-O)$_2${Zr(NEt$_2$)$_2$}] (**7**).* Compound **7** was synthesized using the same procedure outlined above for **6** starting from $Zr(NEt_2)_4$ (0.13 g, 0.35 mmol) and **2** (0.25 g, 0.29 mmol). Yield 55% (0.17 g). Mp 217 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): *δ* 1.30 [t, 6H, N(CH_2CH_3)$_2$], 1.31 (s, 6H, CH_3), 1.97, 2.32 (s, 12H, *o*-Ar−CH_3), 2.31 (s, 6H, *o*-Ar−CH_3), 3.18 [*q*, 4H, N-(CH_2CH_3)$_2$], 4.76 (s, 1H, *γ*-C*H*), 6.73, 6.87 ppm (s, 4H, *m*-Ar−*H*). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): *δ* 16.6 [N(CH_2CH_3)$_2$], 18.6 (CH_3), 19.1, 23.0 (*p*-Ar−CH_3), 21.2 (*p*-Ar−CH_3), 46.1 [N-(CH_2CH_3)$_2$], 97.0 (*γ*-CH_3), 129.4, 130.1 (*m*-Ar−*C*), 133.9, 134.2 (*o*-Ar−*C*), 134.3(*p*-Ar−*C*), 142.6 (*i*-Ar−*C*), 169.4 ppm (*C*═N). MS−EI (70 eV) *m*/*z*: 1017 [M^+ − NEt_2], 944 [M^+ − $2NEt_2$]. Anal. Calcd for $C_{54}H_{78}Ga_2N_6O_3Zr$ (1089.91): C, 59.51; H, 7.21; N, 7.71. Found: C, 60.05; H, 7.19; N, 7.63.

*Preparation of [{(^{Me}LGa)$_2$(μ-O)}(μ-O)$_2${Hf(NEt$_2$)$_2$}] (**8**).* Compound **8** was synthesized using the same procedure outlined above for **6** and **7**, starting from $Hf(NEt_2)_4$ (0.16 g, 0.35 mmol) and **2** (0.25 g, 0.29 mmol). Yield 62% (0.21 g). Mp 261 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): *δ* 1.31 [t, 6H, N(CH_2CH_3)$_2$], 1.32 (s, 6H, CH_3), 1.97, 2.32 (s, 12H, *o*-Ar−CH_3), 2.31 (s, 6H, *p*-Ar−CH_3), 3.20 [q, 4H, N-(CH_2CH_3)$_2$], 4.77 (s, 1H, *γ*-C*H*), 6.73, 6.87 ppm (s, 4H, *m*-Ar−*H*). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): *δ* 16.7 [N(CH_2CH_3)$_2$], 18.6 (CH_3), 19.2, 23.0 (*o*-Ar−CH_3), 21.2 (*p*-Ar−CH_3), 47.0 [N-(CH_2CH_3)$_2$], 97.0 (*γ*-CH_3), 129.4, 130.0 (*m*-Ar−*C*), 133.9, 134.2 (*o*-Ar−*C*), 134.3 (*p*-Ar−*C*), 142.67 (*i*-Ar−*C*), 169.38 ppm (*C*═N). MS−EI (70 eV) *m*/*z*: 1032 [M^+ − $2NEt_2$]. Anal. Calcd for $C_{54}H_{78}Ga_2N_6O_3Hf$ (1177.17): C, 55.10; H, 6.68; N, 7.14. Found: C, 55.26; H, 6.46; N, 6.97.

■ RESULTS AND DISCUSSION

Treatment of [^{Me}LGaCl$_2$] (**1**) (^{Me}L = HC[(CMe)N(2,4,6-$Me_3C_6H_2$)]$_2^-$) with a stoichiometric amount of water in the presence of 1,3-di-*tert*-butylimidazol-2-ilydene results in the formation of **2** in 85% yield (Scheme 1). The 1,3-di-*tert*-

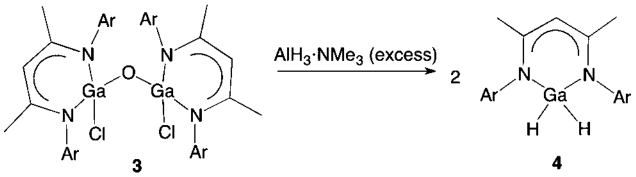
Scheme 1. Synthesis of the Molecular Galloxanes 2 and 3



butylimidazolium chloride formed can be easily separated due to its insolubility in toluene, and thus **2** can be isolated in high purity. Furthermore, attempts to prepare the intermediate galloxane dichloride $[\{^{Me}LGa(Cl)\}_2(\mu\text{-}O)]$ (**3**) starting from 2 equiv of **1**, 1 equiv of H_2O, and 2 equiv of the *N*-heterocyclic carbene failed leading exclusively to **2**. However, an alternative approach for the preparation of **3** was achieved by treating **1** with Ag_2O in THF at ambient temperature (Scheme 1).

Compound **3** was treated with an excess (3 equiv) of $AlH_3{\cdot}NMe_3$ as an endeavor to prepare the galloxane dihydride $[\{^{Me}LGa(H)\}_2(\mu\text{-}O)]$. Instead, the monometallic dihydride gallium complex **4** was obtained in 80% yield (Scheme 2). Similar results, albeit with lower yields, were obtained with a 1:1 molar ratio of **2** and $AlH_3{\cdot}NMe_3$ or with $LiAlH_4$.

Scheme 2. Synthesis of Compound 4



Compounds **1**−**4** were unambiguously characterized by means of spectroscopic, spectrometric, and, in the case of **2** and **3**, also by X-ray diffraction techniques. Compounds **2** and **4** are highly soluble in common organic solvents (toluene, THF, CH_2Cl_2) but insoluble in hexane and pentane, whereas **3** is soluble in CH_2Cl_2 and THF. The EI mass spectrum of **2** exhibited a peak at m/z 855 corresponding to the loss of a hydrogen atom from the molecular ion, while the most intense peak appeared at m/z 838 due to the fragment $[M^+ - H_2O]$. Similarly, a peak at m/z 403 in **4** is due to the loss of a hydrogen atom from the molecular ion. On the other hand, a peak at m/z 545 in **3** corresponds to the isotopic pattern of the bimetallic fragment $[C_{22}H_{27}Cl_2Ga_2O]^+$. The IR spectrum of **2** displays a sharp band at $\tilde{\nu}$ 3623 cm^{-1} due to the stretching frequency of the hydroxides groups, while the IR spectrum of **4** shows a set of two sharp bands ($\tilde{\nu}$ 1836 and 1876 cm^{-1}) corresponding to the symmetric and asymmetric stretching of the GaH_2 group.

The ^1H NMR spectra of **2** and **3** exhibit a different pattern for the ligand backbone as compared to that in **1** and **4**, showing two signals for the protons from the methyl group in the ortho position and two signals for the aromatic protons in the meta position. This behavior is consistent with the lower symmetry observed in the bimetallic compounds **2** and **3**, as compared to that in the monometallic complexes **1** and **4**. Furthermore, **2** shows a single signal at δ −1.38 ppm ascribed to the OH groups, which is shifted upfield relative to the OH groups in the alumoxane analogue $[\{^{Me}LAl(OH)\}_2(\mu\text{-}O)]$ (δ −0.64 ppm).[3a] On the other hand, the ^1H NMR spectrum of **4** exhibits a broad signal at δ 5.26 ppm corresponding to the protons from the GaH_2 group.

Suitable X-ray single crystals of **2** and **3** were grown at ambient temperature within several days from a toluene and a toluene/THF solution, respectively. Compounds **2** and **3** crystallize in the orthorhombic space group *Fdd*2 with one-half of the corresponding molecule in the asymmetric unit.

In compounds **2** and **3**, the gallium center exhibits a distorted tetrahedral geometry with coordination to two nitrogen atoms from the β-diketiminate ligand, one oxygen atom, and to the corresponding terminal group (Figures 1 and 2). The Ga−O(H) bond length [1.845(1) Å] in **2** is longer than those in the gallium hydroxides $[(2,6\text{-}Mes_2C_6H_3)_2GaOH]$ (Mes = 2,4,6-$Me_3C_6H_2$) [1.783(2) Å],[21] $[^{iPr}LGa(OH)_2]$ [1.777(1)−1.820(1) Å],[14] and $[^{iPr}LGa(Me)OH]$ [1.831(1) Å].[11] In a similar manner, the Ga−Cl bond in **3** [2.197(1) Å] is more elongated than those in the monometallic species $[\{(2,6\text{-}Mes_2C_6H_3)Ga(Cl)(\mu\text{-}OH)\}_2]$ [2.166(1) and 2.176(1) Å][21] and $[\{(2,6\text{-}Trip_2C_6H_3)Ga(Cl)(\mu\text{-}OH)\}_2]$ (Trip = 2,6-$^iPr_2C_6H_3$) [2.146(2) Å].[22] The Ga−(μ-O) distances in **2** [1.794(1) Å] and **3** [1.783(1) Å] are comparable to those in $[\{[CH(SiMe_3)_2]_2Ga\}(\mu\text{-}O)]$ [1.795(2), 1.787(2) Å],[5] while the Ga−O−Ga angles [121.6(1)° for **2** and 124.6(1)° for **3**] are more acute as compared to those found in $[\{(CH(SiMe_3)_2)_2Ga\}(\mu\text{-}O)]$ [141.4(1)°][5] and $[\{(Mn(CO)_5)ArGa\}(\mu\text{-}O)]$ (Ar = 2,4,6-*t*-$Bu_3C_6H_2$) [150.2(5)°].[6] Furthermore, the terminal groups in these compounds are in a syn conformation with dihedral

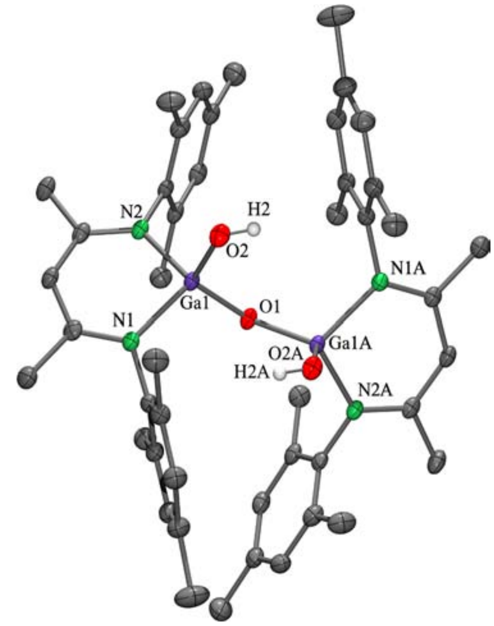


Figure 1. Molecular structure of **2**; hydrogen atoms (except OH) are omitted for clarity. Thermal ellipsoids are set at 50% probability level.

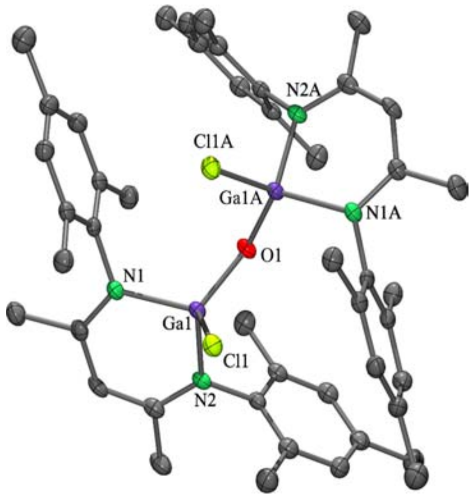


Figure 2. Molecular structure of **3**; hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability level.

angles defined by the planes X−Ga(1)−O(1) and O(1)−Ga(1A)−Y corresponding to 50.6° for **2** [X = O(2), Y = O(2A)] and 56.3° for **3** [X = Cl(1), Y = Cl(1A)].

It is noteworthy that several other reactions were studied as alternative synthetic routes for **2**. In this regard, our primary interest in the synthesis of $[^{Me}LGaMe_2]$ (**5**) (Figure 3) was the development of readily available precursors for the formation of **2**. Experiments were performed on both **4** and **5** in NMR tubes using 0.06 mmol of the corresponding gallium compound, and the progress of the reactions was monitored by ^{1}H NMR spectroscopy. It should be pointed out that controlled hydrolysis reactions of **4** and **5** were also performed in boiling toluene at a larger scale. However, in all of these cases, the only identifiable products were the corresponding starting materials. Furthermore, attempts to obtain **2** from the controlled hydrolysis of **1** using amines as HCl scavengers (triethylamine, pyridine, and 1,8-bis(dimethylamino)naphthalene) were unsuccessful leading exclusively to the starting material.

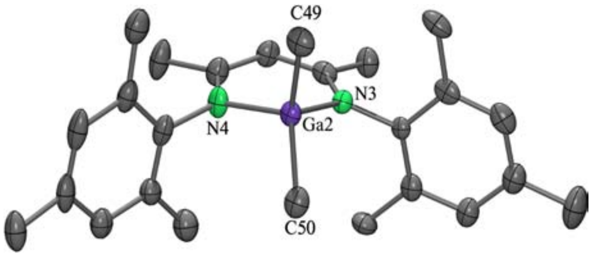
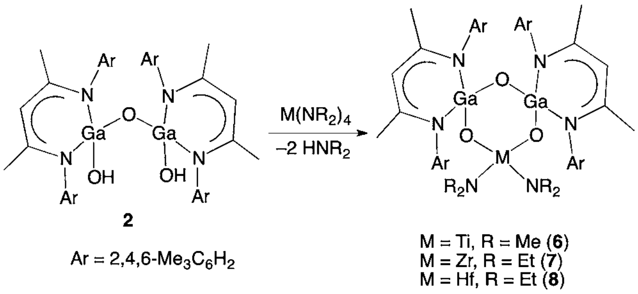


Figure 3. Molecular structure of **5** showing one of the two crystallographically independent molecules; hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability level.

The thermal stability of **2** and the apparent Brönsted acidity of the GaO−H protons make it an advantageous starting material for the synthesis of heterometallic systems. Nonetheless, attempts to react **2** with the organometallic reagents RLi (R = ^{n}Bu, ^{t}Bu, Me), MMe$_3$ (M = Al, Ga, In), and $Me_2M'Cp_2$ (M′ = Ti, Zr, Hf) were unsuccessful leading to the isolation of the starting materials. The limited reactivity of the former compounds may be due to the inherent strength of their M−C bonds and thus results in their resistance to facile substitution.[23] However, compound **2** reacts smoothly with the group 4 amides $M(NR_2)_4$ (M = Ti, R = Me; M = Zr, H, R = Et) in toluene leading to the formation of the heterobimetallic compounds **6**−**8** (Scheme 3).

Compounds **6**−**8** are extremely air and moisture-sensitive and are highly soluble in common organic solvents including aliphatic hydrocarbons. The IR spectra of these compounds are devoid of GaO−H stretching vibration, thus confirming the deprotonation of the hydroxyl groups. The ^{1}H NMR spectra of **6**−**8** show the same pattern for the galloxane backbone as that in **2** along with the corresponding signals for the NR$_2$ moieties (δ 3.13 ppm for **6**, δ 1.31 and 3.18 ppm for **7**, and δ 1.32 and 3.21 for **8**). The EI−MS spectra of **6**−**8** show peaks with the characteristic isotopic patterns at m/z 990 $[M - H]^+$, 1017 $[M - NEt_2]^+$, and 1032 $[M - 2NEt_2]^+$, respectively.

Scheme 3. Preparation of the Heterobimetallic Galloxanes 6−8



Suitable X-ray single crystals of **7** and **8** were obtained from their saturated toluene solutions at room temperature within several days. Compounds **7** and **8** are isomorphous and crystallize in the triclinic space group $P\overline{1}$ with one molecule of the heterobimetallic compound and one molecule of toluene in the asymmetric unit (Figures 4 and 5).

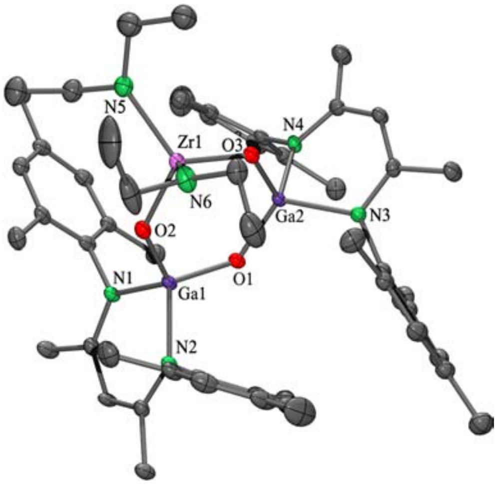


Figure 4. Molecular structure of **7**; hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability.

In both compounds, the group 4 metal displays a distorted tetrahedral geometry with coordination to two oxygen atoms and two nitrogen atoms from the amide groups. The six-membered inorganic MOGaOGaO rings display planar arrangements with a mean deviation from the plane of 0.04 and 0.05 Å for **7** and **8**, respectively. The M−O bond lengths in

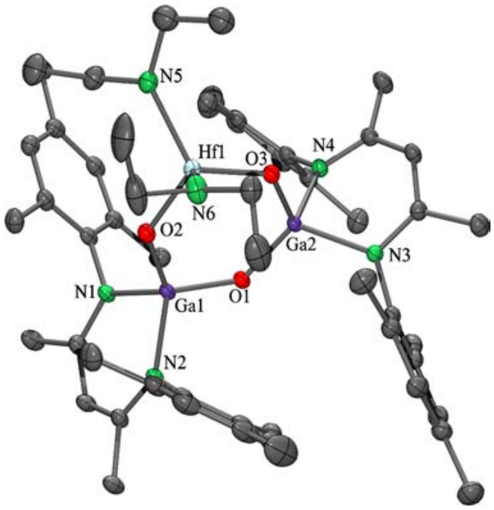


Figure 5. Molecular structure of **8**; hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability.

7 [1.927(2) and 1.945(2) Å] and **8** [1.920(2) and 1.935(1) Å] are comparable to those in [{(^{iPr}LGaMe)(Cp_2ZrMe)}(μ-O)] [1.926(1) Å],[11] but significantly longer than those in the six-membered gallosilicate systems [{^{iPr}LGa(μ-O)Si(O*t*Bu)$_2$}(μ-O)$_2${M(NEt_2)$_2$}] [M = Zr (1.812(1) Å); M = Hf (1.818(3) Å].[12] The Ga−O−M angles [133.1(1)° and 128.5(1)° for **7** and 132.5(1) and 128.3(1)° for **8**] are more acute than those reported for [{(^{iPr}LGaMe)(Cp_2ZrMe)}(μ-O)] [146.7(1)°] but more obtuse than those in [{^{iPr}LGa(μ-O)Si(O*t*Bu)$_2$}(μ-O)$_2${M(NEt_2)$_2$}] [M = Zr (127.6(1)°; M = Hf (127.1(1)°)] and in the spirocyclic compounds [{(^{iPr}LGa(μ-O)Si(O*t*Bu)$_2$)-(μ-O)$_2$}$_2$M] [M = Zr (127.9(1)°, 127.0(1)°); Hf (127.5(1)°, 126.7(1)°)].[12] The O−M−O angles [103.4(1)° for **7** and 104.1(1)° for **8**] are more obtuse as compared to the corresponding endocyclic angles in [{^{iPr}LGa(μ-O)Si(O*t*Bu)$_2$}-(μ-O)$_2${M(NEt_2)$_2$}][M = Zr (101.1(1)°); Hf (102.0(1)°)] and [{^{iPr}LGa(μ-O)Si(O*t*Bu)$_2$}(μ-O)$_2$]$_2$M [M = Zr (99.5(1)°, 100.0(1)°); Hf (100.6(1)°, 100.5(1)°)].

The Ga−O−M framework present in these compounds makes them potential candidates for catalytic studies, particularly for olefin polymerization. Consequently, preliminary screening of compounds **6** and **8** for their ability to catalyze ethylene polymerization was undertaken using MAO as a cocatalyst.[24] These compounds were active in the polymerization of ethylene under mild conditions, albeit with low yields.

In summary, a facile method for the preparation of a molecular galloxane bearing terminal OH groups was achieved. The structural arrangement exhibited in this molecule allowed the preparation of multimetallic systems with group 4 metal amides (**6**−**8**). Compounds **6**−**8** are, to the best of our knowledge, the first examples of fully characterized heterobimetallic galloxanes. Furthermore, preliminary studies on the reactivity of these compounds show promising chemical features. Overall, the synthetic approach developed in this work provides access to a new class of annular systems with main group, transition, or lanthanide metals, through oxygen bridging. The preparation of such multimetallic systems is the subject of ongoing research.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information in cif format for **2**, **3**, **5**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Dirección General de Asuntos del Personal Académico from the UNAM (PAPIIT Grant IN210710). E.B.-P. thanks the CONACyT for the Ph.D. fellowship (227105). M. Granados, A. Núñez, L. Triana, and N. Zavala are acknowledged for their technical assistance.

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was added into the system, and stirring was kept for 20 min for activation. After this step, the system was closed and set under vacuum. The polymerization was initiated by starting the flux of ethylene into the reactor, the system was set at 0.2 mbar, and the polymerization was carried for 1 h. The ethylene consumption was continuous but low. The reaction was quenched using 15% acidified methanol, and the white polyethylene formed was collected by filtration and dried. 0.1 and 0.2 g of polyethylene were collected for **6** and **8**, respectively.