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Synthesis of Homoleptic Gallium Alkoxide Complexes and the Chemical Vapor Deposition of Gallium Oxide Films

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A general synthetic route to gallium alkoxide complexes involving reactions of gallium tris(dimethylamide) with alcohols was developed and gallium oxide films were prepared by using a gallium alkoxide complex as the precursor in a chemical vapor deposition process. The complex $[Ga(NMe_2)_3]_2$ reacted with *i*-BuOH and *i*-PrOH to yield the tetramers $Ga[(\mu\text{-}OR)_2Ga(OR)_2]_3$ where R = *i*-Bu and *i*-Pr, respectively. Consistent with previous observations, the solution equilibrium $Ga[(\mu\text{-}O\text{-}i\text{-}Pr)_2Ga(O\text{-}i\text{-}Pr)_2]_3 \rightleftarrows 2[Ga(\mu\text{-}O\text{-}i\text{-}Pr)(O\text{-}i\text{-}Pr)_2]_2$ was observed ($\Delta H° = 8.7(0.4)$ kcal/mol, $\Delta S° = 27(1)$ eu, and $\Delta G°_{298} = 0.63(0.04)$ kcal/mol). For the less sterically crowded tetramer $Ga[(\mu\text{-}O\text{-}i\text{-}Bu)_2Ga(O\text{-}i\text{-}Bu)_2]_3$, there was no evidence for a tetramer−dimer equilibrium. In contrast to the results obtained using *i*-BuOH and *i*-PrOH, the bulkier alcohols *t*-BuOH and $EtMe_2COH$ reacted with $[Ga(NMe_2)_3]_2$ at room temperature to yield mixtures of the dimer $[Ga(\mu\text{-}OR)(OR)_2]_2$ and the amine adduct $Ga(OR)_3(HNMe_2)$, while *i*-$PrMe_2COH$ and Et_2MeCOH reacted to produce $Ga(OR)_3(HNMe_2)$ compounds exclusively. Upon heating in an open system, the amine could be removed from the $Ga(OR)_3(HNMe_2)$ compounds to yield the corresponding homoleptic alkoxide dimers. Low-pressure chemical vapor deposition using $[Ga(\mu\text{-}O\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2]_2$ and O_2 precursors gave Ga_2O_3 films at substrate temperatures of 300−700 °C. The as-deposited films were carbon-free, amorphous, and highly transparent in the 350−800-nm region.

Introduction

The first reports on the synthesis of homoleptic gallium alkoxide complexes ($Ga(OR)_3$, R = an alkyl group) appeared in 1964 in separate papers by Mehrotra and Mehrotra and by Funk and Paul.[1,2] In these studies, $GaCl_3$ was reacted with NaOR to form gallium tris(isopropoxide) and tris(ethoxide), respectively. Following these reports, Reinmann and Tanner described the synthesis of gallium ethoxide from $GaCl_3$ and NaOEt and the subsequent synthesis of the isopropoxide derivative by alkoxide/alcohol exchange starting from the ethoxide derivative (eq 1).[3] A process analogous to eq 1 was used by Funk, Paul, and Booch to prepare $Ga(OMe)_3$ and $Ga(OEt)_3$ by using $Ga(OPh)_3$ as the starting material.[4] The first reports on the possible structures of gallium tris(alkoxide) complexes were published in 1969. In that year, Bindal, Mathur, and Mehrotra described the synthesis of an extensive series of normal and branched alkoxides by using $Ga(O\text{-}i\text{-}Pr)_3$/ROH exchange (R = Me, Et, *n*-Pr, *n*-Bu, *s*-Bu, and *t*-Bu) and transesterification (eq 2) reactions.[5] On the basis of ebullioscopic molecular weight determinations, the ethoxide, propoxide, and butoxide derivatives were proposed to be tetramers while the isopropoxide and *t*-butoxide complexes were formulated as dimers having the proposed structure $[Ga(\mu\text{-}OR)(OR)_2]_2$. By using ^1H NMR, Oliver and Worrall confirmed the dimer formulation for $Ga(O\text{-}t\text{-}Bu)_3$ and showed that the isopropoxide derivative existed in solution as an equilibrium mixture of a tetramer and dimer (eq 3).[6,7]

$$Ga(OEt)_3 + 3i\text{-}PrOH \rightarrow Ga(O\text{-}i\text{-}Pr)_3 + 3EtOH \qquad (1)$$

$$Ga(OR)_3 + 3MeCO_2R' \rightarrow Ga(OR')_3 + 3MeCO_2R \qquad (2)$$

$$(R = Et,\ i\text{-}Pr;\ R' = n\text{-}Pr,\ n\text{-}Bu,\ i\text{-}Pr,\ \text{and}\ t\text{-}Bu)$$

$$Ga[(\mu\text{-}O\text{-}i\text{-}Pr)_2Ga(O\text{-}i\text{-}Pr)_2]_3 \rightleftarrows 2[Ga(\mu\text{-}O\text{-}i\text{-}Pr)(O\text{-}i\text{-}Pr)_2] \qquad (3)$$

Our interest in gallium tris(alkoxide) chemistry arose from our recent work in which a series of homoleptic indium alkoxide complexes were synthesized and one of the new compounds, $[In(\mu\text{-}OCMe_2Et)(OCMe_2Et)_2]_2$, was used as a molecular precursor to prepare high-quality indium oxide films by low-pressure chemical vapor deposition (CVD).[8] On the basis of this work, it was reasoned that analogous homoleptic gallium alkox-

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ide complexes should serve as CVD precursors to gallium oxide (Ga_2O_3) films. Gallium oxide films have recently attracted research attention because of their potential for applications. Dielectric films composed of Ga_2O_3 and Gd_2O_3, for example, have been shown to effectively passivate GaAs surfaces in the preparation of metal-oxide-semiconductor field-effect transistors,[9−11] and gallium oxide has been used as a phosphor host material for emissive display applications, such as thin film electroluminescent displays.[12−14] Thin films of gallium oxide have also been tested for use as oxygen and reducing gas sensors.[15−17]

Despite the interest in gallium oxide films for applications, there have been only three reports on their preparation by using the technique of CVD.[18−20] In two of the papers, $Ga(hfac)_3$ (hfac = hexafluoroacetylacetonate) and O_2 were used in low-pressure CVD processes to deposit amorphous Ga_2O_3 films at substrate temperatures of 400−500 °C.[18,19] Similar results were obtained in a study by Mîinea et al., who used $Ga[OCH(CF_3)_2]_3(HNMe_2)$ and moist air in a low-pressure CVD process to deposit Ga_2O_3 films at 250−450 °C.[20]

In this report, the syntheses of new gallium tris(alkoxide) derivatives and a new synthetic route to gallium tris(isopropoxide) and tris(*t*-butoxide) are described. In addition, gallium tris(*t*-butoxide) is demonstrated to be a promising precursor to gallium oxide films in a low-pressure chemical vapor deposition process.

Experimental Section

General Synthetic Considerations. All manipulations were carried out inside an inert atmosphere glovebox unless noted otherwise. Solvents were purified by using standard techniques after which they were stored over 4-Å molecular sieves in the glovebox. Alcohols were purchased from Aldrich. *i*-PrOH was purified by distillation from Mg, and *t*-BuOH and Et_2MeOH were purified by azeotropic distillation. The other alcohols used in this study were degassed and dried over 4-Å molecular sieves before they were used. $LiNMe_2$ was prepared from *n*-BuLi and $HNMe_2$. $GaCl_3$, *n*-BuLi, and $HNMe_2$ were purchased from Strem, Acros, and Matheson, respectively, and used as received. $[Ga(NMe_2)_3]_2$ was prepared by following the literature method.[21] Elemental analyses were performed by Oneida Research Services (Whitesboro, NY) or Midwest Microlab (Indianapolis, IN). NMR spectra were collected on a 300-MHz instrument.

Ga[(*μ*-O-*i*-Bu)$_2$Ga(O-*i*-Bu)$_2$]$_3$ (1). A solution of *i*-BuOH (0.44 g, 5.1 mmol) in hexanes (5 mL) was added dropwise via a pipet to a solution of $[Ga(NMe_2)_3]_2$ (0.39 g, 0.97 mmol) in hexanes (15 mL). After the addition was completed, the reaction mixture was stirred for 1 day. The volatile components were distilled in vacuo and the resulting colorless sticky residue was dissolved in CH_2Cl_2 (5 mL). The flask was transferred to the freezer (−23 °C), and over a 24-h period, colorless crystalline blocks formed (yield 0.32 g, 57%). Anal. Calcd for $C_{48}H_{108}O_{12}Ga_4$: C, 49.88; H, 9.35. Found: C, 49.62; H, 9.27.

The coupling constants for **1** were determined by simulating the spectra using the commercial program NUTS.[22] ^{1}H NMR (CD_2Cl_2): δ 3.77 and 3.70 (AB part of an $ABMX_3Y_3$ spectrum, 6, $J_{AB} = 10.5$ Hz, $J_{AM} = 6.0$ Hz, $J_{BM} = 7.8$ Hz, $\mathrm{OC}\mathit{H}_2\mathrm{CHMe}_2$), 3.63 and 3.61 (AB part of an $ABMX_3Y_3$ spectrum, 6, $J_{AB} = 9.0$ Hz, $J_{AM} \approx J_{BM} = 5.9$ Hz, $\mathrm{OC}\mathit{H}_2\mathrm{CHMe}_2$), 1.84 (M part of an $ABMX_3Y_3$ spectrum, 6, $J_{AM} = 6.0$ Hz, $J_{BM} = 7.8$ Hz, $J_{MX} = 6.6$ Hz, $J_{MY} = 6.9$ Hz, $\mathrm{OCH_2C}\mathit{H}\mathrm{Me}_2$), 1.67 (M part of an $ABMX_3Y_3$ spectrum, 6, $J_{AM} \approx J_{BM} = 5.9$ Hz, $J_{MX} \approx J_{MY} = 6.6$ Hz, $\mathrm{OCH_2C}\mathit{H}\mathrm{Me}_2$), 0.97 (d, 18, $J = 6.6$ Hz, $\mathrm{OCH_2CH}\mathit{Me}_2$), 0.95 (d, 18, $J = 6.9$ Hz, $\mathrm{OCH_2CH}\mathit{Me}_2$), 0.88 (d, 18, $J = 6.6$ Hz, $\mathrm{OCH_2CH}\mathit{Me}_2$), 0.87 (d, 18, $J = 6.6$ Hz, $\mathrm{OCH_2CH}\mathit{Me}_2$). ^{13}C{^{1}H} NMR ($C_6D_6$): 73.6 and 73.4 ($\mathrm{O}\mathit{C}\mathrm{H_2CHMe_2}$), 32.5 and 32.4 ($\mathrm{OCH_2}\mathit{C}\mathrm{HMe_2}$), 20.2, 19.89, 19.85, and 19.8 ($\mathrm{OCH_2CH}\mathit{Me}_2$).

Ga[(*μ*-O-*i*-Pr)$_2$Ga(O-*i*-Pr)$_2$]$_3$ (2). A solution of *i*-PrOH (0.23 g, 3.8 mmol) in hexanes (5 mL) was added dropwise via a pipet to a solution of $[Ga(NMe_2)_3]_2$ (0.25 g, 0.61 mmol) in hexanes (15 mL). After the addition was completed, the reaction mixture was stirred for 1 day. The volatile components were distilled in vacuo and the resulting white solid residue was dissolved in CH_2Cl_2 (5 mL). The flask was transferred to the freezer (−23 °C), and over a 48-h period, colorless crystalline blocks formed (yield 0.16 g, 53%). Anal. Calcd for $C_{36}H_{84}O_{12}Ga_4$: C, 43.77; H, 8.51. Found: C, 43.69; H, 8.54.

^{1}H NMR ($CDCl_3$): δ 4.62 (septet, 6, $J = 6.0$ Hz, $\mathrm{OC}\mathit{H}\mathrm{Me}_2$), 4.30 (septet, 6, $J = 6.0$ Hz, $\mathrm{OC}\mathit{H}\mathrm{Me}_2$), 1.49 (d, 18, $J = 6.0$ Hz, $\mathrm{OCH}\mathit{Me}_2$), 1.31 (d, 18, $J = 6.0$ Hz, $\mathrm{OCH}\mathit{Me}_2$), 1.19 (d, 18, $J = 6.0$ Hz, $\mathrm{OCH}\mathit{Me}_2$), 1.18 (d, 18, $J = 6.0$ Hz, $\mathrm{OCH}\mathit{Me}_2$). ^{13}C{^{1}H} NMR (−10 °C, toluene-d_8): 68.0 (μ-$\mathrm{O}\mathit{C}\mathrm{HMe}_2$), 66.1 ($\mathrm{O}\mathit{C}\mathrm{HMe}_2$), 28.14 and 28.09 ($\mathrm{OCH}\mathit{Me}_2$), 27.3 and 26.2 ($\mu$-$\mathrm{OCH}\mathit{Me}_2$). IR (Nujol, KBr, cm^{-1}): 1346 m, 1167 m, 1117 s, 1001 s, 943 s, 845 w, 826 m, 640 m, 602 s.

As explained in the Results and Discussion section, the ^{1}H NMR spectrum at high temperature shows only resonances arising from the dimer [Ga(*μ*-O-*i*-Pr)(O-*i*-Pr)$_2$]$_2$ as follows: ^{1}H NMR (90 °C, C_7D_8): δ 4.42 (septet, 2, $J = 6.0$ Hz, μ-$\mathrm{OC}\mathit{H}\mathrm{Me}_2$), 4.33 (septet, 4, $J = 6.0$ Hz, $\mathrm{OC}\mathit{H}\mathrm{Me}_2$), 1.36 (d, 12, $J = 6.0$ Hz, μ-$\mathrm{OCH}\mathit{Me}_2$), 1.29 (d, 24, $J = 6.0$ Hz, $\mathrm{OCH}\mathit{Me}_2$).

[Ga(*μ*-O-*t*-Bu)(O-*t*-Bu)$_2$]$_2$ (3). A solution of *t*-BuOH (2.11 g, 28.4 mmol) in hexanes (20 mL) was added dropwise via a pipet to a solution of $[Ga(NMe_2)_3]_2$ (1.81 g, 4.50 mmol) in hexanes (50 mL). After the addition was completed, the reaction mixture was stirred for 2 days and the volatile components were then distilled in vacuo to yield a white solid residue. A ^{1}H NMR spectrum of the solid (C_6D_6) indicated that it was a 1:4 mixture of [Ga(*μ*-O-*t*-Bu)(O-*t*-Bu)$_2$]$_2$ and the amine adduct Ga(O-*t*-Bu)$_3$($HNMe_2$), respectively. After the solid was heated under dynamic vacuum (50 °C, 2 h), it was dissolved in CH_2Cl_2 (10 mL). The flask was placed in the freezer (−23 °C) where colorless crystalline blocks formed during a 24-h period (yield 1.95 g, 75%). Anal. Calcd for $C_{24}H_{54}O_6Ga_2$: C, 49.88; H, 9.35. Found: C, 49.63; H, 9.10.

^{1}H NMR (C_6D_6): δ 1.56 (s, 18, μ-$\mathrm{OC}\mathit{Me}_3$), 1.48 (s, 36, $\mathrm{OC}\mathit{Me}_3$). ^{13}C{^{1}H} NMR (C_6D_6): 79.0 (μ-$\mathrm{O}\mathit{C}\mathrm{Me}_3$), 72.3 ($\mathrm{O}\mathit{C}\mathrm{Me}_3$), 34.5 ($\mathrm{OC}\mathit{Me}_3$), 32.7 ($\mu$-$\mathrm{OC}\mathit{Me}_3$). IR (Nujol, KBr, cm^{-1}): 1395 m, 1371 s, 1360 s, 1256 m, 1229 m, 1192 s, 1026 m, 982 s, 885 s, 783 m, 764 s, 638 s, 581 m.

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[Ga(μ-OCMe$_2$Et)(OCMe$_2$Et)$_2$]$_2$ (4). A solution of EtMe$_2$COH (0.40 g, 4.5 mmol) in hexanes (5 mL) was added dropwise via a pipet to a solution of [Ga(NMe$_2$)$_3$]$_2$ (0.30 g, 0.74 mmol) in hexanes (15 mL). After the addition was completed, the reaction mixture was stirred for 24 h. The volatile components were distilled in vacuo to yield a mixture of a colorless thick liquid and colorless crystals. A ^{1}H NMR analysis (C$_6$D$_6$) indicated that the mixture was composed of [Ga(μ-OCMe$_2$Et)(OCMe$_2$Et)$_2$]$_2$ and the amine adduct Ga(OCMe$_2$Et)$_3$(HNMe$_2$) in a 1:4 ratio, respectively. The crude product was heated under dynamic vacuum (50 °C, 3 h), which yielded a white sticky solid. The solid was dissolved in CH$_2$Cl$_2$ (5 mL) and the flask was placed in the freezer (−23 °C). Colorless blocks formed during a 24-h period (yield 0.33 g, 68%). Anal. Calcd for C$_{30}$H$_{66}$O$_6$Ga$_2$: C, 54.42; H, 9.98. Found: C, 54.21; H, 9.92.

^{1}H NMR (C$_6$D$_6$): δ 1.98 (q, 4, J = 7.2 Hz, μ-OC(CH$_3$)$_2$C*H*$_2$CH$_3$), 1.69 (q, 8, J = 7.5 Hz, OC(CH$_3$)$_2$C*H*$_2$CH$_3$), 1.53 (s, 12, μ-OC(C*H*$_3$)$_2$CH$_2$CH$_3$), 1.45 (s, 24, OC(C*H*$_3$)$_2$CH$_2$CH$_3$), 1.07 (t, 12, J = 7.5 Hz, OC(CH$_3$)$_2$CH$_2$C*H*$_3$), 0.83 (t, 6, J = 7.2 Hz, μ-OC(CH$_3$)$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 82.2 (μ-O*C*(CH$_3$)$_2$CH$_2$CH$_3$), 74.4 (O*C*(CH$_3$)$_2$CH$_2$CH$_3$), 39.7 (OC(CH$_3$)$_2$*C*H$_2$CH$_3$), 38.7 (μ-OC(CH$_3$)$_2$*C*H$_2$CH$_3$), 31.6 (OC(*C*H$_3$)$_2$CH$_2$CH$_3$), 29.3 (μ-OC(*C*H$_3$)$_2$CH$_2$CH$_3$), 10.5 (μ-OC(CH$_3$)$_2$CH$_2$*C*H$_3$), 10.1 (OC(CH$_3$)$_2$CH$_2$*C*H$_3$). IR (Nujol, KBr, cm^{-1}): 1360 s, 1339 w, 1323 vw, 1290 m, 1231 m, 1177 s, 1159 s, 1142 s, 1053 s, 1018 m, 988 s, 932 m, 895 m, 858 s, 791 vw, 754 w, 739 m, 633 s.

[Ga(μ-OCMe$_2$-*i*-Pr)(OCMe$_2$-*i*-Pr)$_2$]$_2$ (5). A solution of *i*-PrMe$_2$COH (0.49 g, 4.8 mmol) in toluene (5 mL) was added dropwise via a pipet to a solution of [Ga(NMe$_2$)$_3$]$_2$ (0.32 g, 0.79 mmol) in toluene (15 mL). After the addition was completed, the mixture was refluxed for 7 days. The mixture changed from colorless to yellow after 2 days at reflux. The mixture was cooled to room temperature and the volatile components were removed in vacuo to yield a yellow solid. The solid was dissolved in CH$_2$Cl$_2$ (5 mL) and the flask was transferred to the freezer (−23 °C). During a 48-h period, colorless crystalline blocks formed (yield 0.33 g, 56%). Anal. Calcd for C$_{36}$H$_{78}$O$_6$Ga$_2$: C, 57.95; H, 10.46. Found: C, 57.96; H, 10.27.

^{1}H NMR (C$_6$D$_6$): δ 2.18 (septet, 2, J = 6.3 Hz, μ-OC(CH$_3$)$_2$C*H*(CH$_3$)$_2$), 1.85 (septet, 4, J = 6.9 Hz, OC(CH$_3$)$_2$C*H*(CH$_3$)$_2$), 1.56 (s, 12, μ-OC(C*H*$_3$)$_2$CH(CH$_3$)$_2$), 1.44 (s, 24, OC(C*H*$_3$)$_2$CH(CH$_3$)$_2$), 1.08 (d, 24, J = 6.9 Hz, OC(CH$_3$)$_2$CH(C*H*$_3$)$_2$), 0.99 (d, 12, J = 6.3 Hz, μ-OC(CH$_3$)$_2$CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 84.8 (μ-O*C*(CH$_3$)$_2$CH(CH$_3$)$_2$), 76.7 (O*C*(CH$_3$)$_2$CH(CH$_3$)$_2$), 41.7 (μ-OC(CH$_3$)$_2$*C*H(CH$_3$)$_2$), 40.2 (OC(CH$_3$)$_2$*C*H(CH$_3$)$_2$), 29.3 (OC(*C*H$_3$)$_2$CH(CH$_3$)$_2$), 27.4 (μ-OC(*C*H$_3$)$_2$CH(CH$_3$)$_2$), 19.7 (μ-OC(CH$_3$)$_2$CH(*C*H$_3$)$_2$), 19.2 (OC(CH$_3$)$_2$CH(*C*H$_3$)$_2$). IR (Nujol, KBr, cm^{-1}): 1364 s, 1331 vw, 1310 vw, 1260 w, 1238 w, 1198 m, 1169 s, 1148 s, 1101 s, 1076 w, 1063 w, 991 s, 978 s, 953 s, 912 s, 901 s, 870 m, 841 s, 627 s.

[Ga(μ-OCMeEt$_2$)(OCMeEt$_2$)$_2$]$_2$ (6). A solution of Et$_2$MeCOH (0.31 g, 3.0 mmol) in toluene (5 mL) was added dropwise via a pipet to a solution of [Ga(NMe$_2$)$_3$]$_2$ (0.19 g, 0.46 mmol) in toluene (15 mL). After the addition was completed, the mixture was refluxed for 2 d. During this time, the mixture changed from colorless to yellow. After cooling the reaction mixture to room temperature, the volatile components were distilled in vacuo and the resulting yellow solid residue was dissolved in CH$_2$Cl$_2$ (5 mL). The flask was transferred to the freezer (−23 °C) and over a 48 h period, colorless crystalline blocks formed (yield 0.19 g, 55%). Anal. Calcd for C$_{36}$H$_{78}$O$_6$Ga$_2$: C, 57.95; H, 10.46. Found: C, 57.81; H, 10.27.

The coupling constants for **6** were determined by simulating the spectra using the commercial program NUTS.[22] ^{1}H NMR (C$_6$D$_6$): δ 2.00 and 1.90 (AB part of an ABX$_3$ spectrum, 8, J_{AB} = 14.7 Hz, $J_{AX} \approx J_{BX}$ = 7.3 Hz, μ-OCMe(C*H*$_2$CH$_3$)$_2$), 1.75 and 1.73 (AB part of an ABX$_3$ spectrum, 16, J_{AB} = 14.0 Hz, J_{AX} = 8.1 Hz, J_{BX} = 6.6 Hz, OCMe(C*H*$_2$CH$_3$)$_2$), 1.57 (s, 6, μ-OCMeEt$_2$), 1.45 (s, 12, OC*Me*Et$_2$), 1.02 (X part of an ABX$_3$ spectrum (“triplet”), 24, J = 8.1, J = 6.6 Hz, OCMe(CH$_2$C*H*$_3$)$_2$), 0.94 (X part of an ABX$_3$ spectrum (“triplet”), 12, $J_{AX} \approx J_{BX}$ = 7.3 Hz, μ-OCMe(CH$_2$C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 84.7 (μ-O*C*MeEt$_2$), 76.8 (O*C*MeEt$_2$), 36.1 (OCMe(*C*H$_2$CH$_3$)$_2$), 34.9 (μ-OCMe(*C*H$_2$CH$_3$)$_2$), 29.2 (OC*Me*Et$_2$), 26.9 (2, μ-OC*Me*Et$_2$), 10.1 (OCMe(CH$_2$*C*H$_3$)$_2$), 9.9 (μ-OCMe(CH$_2$*C*H$_3$)$_2$). IR (Nujol, KBr, cm^{-1}): 1335 w, 1325 w, 1308 vw, 1294 w, 1275 w, 1235 w, 1221 w, 1186 m, 1150 s, 1065 s, 1038 s, 1005 s, 991 s, 932 s, 899 m, 876 s, 804 w, 774 w, 743 w, 719 m, 627 s.

Ga(OCMe$_2$-*i*-Pr)$_3$(HNMe$_2$) (7). A solution of HOCMe$_2$-*i*-Pr (0.30 g, 2.9 mmol) in hexanes (5 mL) was added dropwise via a pipet to a solution of [Ga(NMe$_2$)$_3$]$_2$ (0.20 g, 0.49 mmol) in hexanes (15 mL). After the addition was completed, the reaction mixture was stirred for 1 day. The volatile components were distilled in vacuo to yield a colorless thick liquid (yield 0.41 g, 98%). Anal. Calcd for C$_{20}$H$_{46}$O$_3$NGa: C, 57.45; H, 11.01; N 3.35. Found: C, 57.28; H, 10.96; N 3.06.

^{1}H NMR (C$_6$D$_6$): δ 1.90 (d, 6, J = 6.3 Hz, N*Me*$_2$), 1.79 (septet, 3, J = 7.5 Hz, OC(CH$_3$)$_2$C*H*(CH$_3$)$_2$), 1.40 (s, 18, OC(C*H*$_3$)$_2$CH(CH$_3$)$_2$), 1.12 (d, 18, J = 7.5 Hz, OC(CH$_3$)$_2$CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 74.0 (O*C*(CH$_3$)$_2$CH(CH$_3$)$_2$), 41.4 (μ-OC(CH$_3$)$_2$*C*H(CH$_3$)$_2$), 37.7 (N*Me*$_2$), 29.5 (OC(*C*H$_3$)$_2$CH(CH$_3$)$_2$), 19.1 (OC(CH$_3$)$_2$CH(*C*H$_3$)$_2$). IR (neat, KBr, cm^{-1}): 3298 m, 3177 w, 2967 s, 2874 s, 1468 s, 1398 w, 1383 s, 1370 s, 1360 s, 1323 w, 1244 w, 1225 m, 1194 m, 1169 s, 1152 s, 1125 w, 1103 s, 1055 s, 1017 s, 977 s, 953 s, 901 s, 870 m, 858 w, 737 w,736 w, 718 m, 637 s.

Ga(O-*t*-Bu)$_3$(HNMe$_2$) (8). A solution of *t*-BuOH (0.78 g, 10.5 mmol) in hexanes (20 mL) was added dropwise via a pipet to a solution of [Ga(NMe$_2$)$_3$]$_2$ (0.66 g, 1.6 mmol) in hexanes (25 mL). After the solution was stirred for 1 day, the volatile components were distilled in vacuo. A ^{1}H NMR analysis (C$_6$D$_6$) indicated that the resulting white solid residue was composed of a 1:2 mixture of [Ga(μ-O-*t*-Bu)(O-*t*-Bu)$_2$]$_2$ (**1**) and the amine adduct Ga(O-*t*-Bu)$_3$(HNMe$_2$), respectively. The solid was dissolved in methylene chloride (10 mL) and the flask was placed in the freezer (−23 °C). Colorless crystalline blocks formed over a 48-h period (yield 0.76 g). ^{1}H NMR analysis indicated that the crystalline product was composed of a 4:1 mixture of **3** and **7**, respectively.

^{1}H NMR (C$_6$D$_6$): δ 1.86 (d, 6, J = 6.0 Hz, HN*Me*$_2$), 1.53 (s, 27, OC*Me*$_3$).

Determination of Thermodynamic Parameters. The equilibrium Ga[(μ-O-*i*-Pr)$_2$Ga(O-*i*-Pr)$_2$]$_3$ $\rightleftarrows$ 2[Ga(μ-O-*i*-Pr)(O-*i*-Pr)$_2$]$_2$ was studied by using ^{1}H NMR spectroscopy. A solution with a known concentration of **2** in toluene-d_8 was prepared in a sealed NMR tube. The tube was thermally equilibrated in the NMR probe before data collection was begun. The probe temperature was calibrated by using a methanol standard. The equilibrium constants (K_{eq}) 0.271, 0.465, 0.543, 0.693, 0.859, 1.18, and 1.97 mol/L were determined at 20.9, 29.6, 33.9, 40.4, 44.7, 54.4, and 64.1 °C, respectively. The error in the temperature measurement was estimated to be ±1.2 °C from a linear regression analysis[23] applied to the temperature calibration curve. Each equilibrium constant value represents the average of two separate determinations except at 64.1 °C where only one determination was made. The equilibrium constants were calculated by determining the concentrations of **2** and [Ga(μ-O-*i*-Pr)(O-*i*-Pr)$_2$]$_2$ from the intensity ratios of the respective methyl group resonances. A plot of ln K_{eq} vs $1/T$ yielded $\Delta H°$ and $\Delta S°$. The errors in the values of $\Delta H°$ and $\Delta S°$ were estimated from a linear regression analysis.[23]

X-ray Crystallography. X-ray crystallographic studies were carried out on **2**, **4**, and **8**. For the analyses, colorless crystalline blocks of each compound were grown from CH$_2$Cl$_2$ at low temperature. The crystal of **8** was hand-selected from a 4:1 mixture of crystalline **3** and **8** (thick plates vs long rectangular columns, respectively). Data were collected on a Siemens SMART CCD instrument.

Compound **2**: C$_{36}$H$_{84}$O$_{12}$Ga$_4$, fw = 987.91, crystal dimens 0.30 × 0.25 × 0.25 mm, tetragonal, space group $P4_12_12$, a = 12.5566(6), c = 32.0324(17) Å, T = −50(2) °C, Z = 4, V = 5050.5(4) Å^3, D_{calcd} = 1.299 g/cm^3, μ = 2.159 mm^{-1}, R = 0.0280, and R_w = 0.0704. The asymmetric unit consists of one-half molecule situated about a 2-fold axis. Several of the alkoxide ligands are disordered over two different orientations. The

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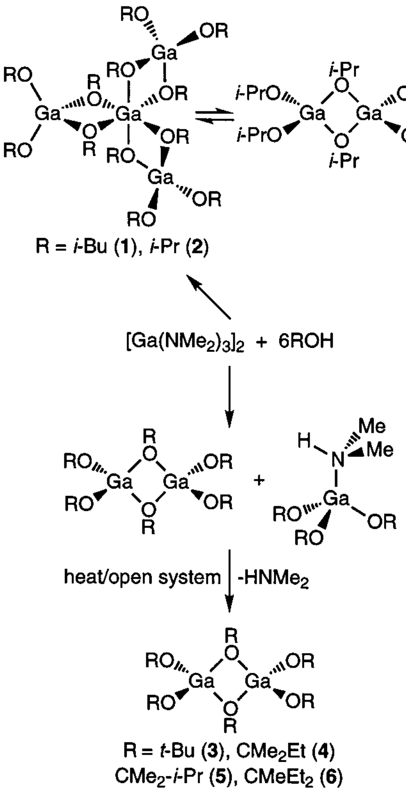
[23] Miller, J. C.; Miller, J. N. *Statistics for Analytical Chemistry*; Wiley: New York, 1988; Chapter V.

Scheme 1



disorder was modeled using distance constraints with occupancies based on the observed isotropic temperature factors.

Compound **4**: $C_{30}H_{66}O_6Ga_2$, fw = 662.27, crystal dimens 0.45 × 0.30 × 0.30 mm, monoclinic, space group $P2_1/c$, $a = 9.1778(5)$, $b = 17.5206(9)$, $c = 33.6060(18)$ Å, $\beta = 93.985(1)$, $T = -50(2)$ °C, $Z = 6$, $V = 5390.8(5)$ Å^3, $D_{calcd} = 1.224$ g/cm^3, $\mu = 1.534$ mm^{-1}, $R = 0.0258$, $R_w = 0.0650$. There are one and a half molecules in the asymmetric unit, one in a general position and one situated about an inversion center. The fold angle across O1/O2 is less than 1° in the molecule in the general position. The molecules differ also in the orientation of some of the terminal ethyl groups. Several of the alkoxide ligands were disordered over two positions that are roughly mirror images. These were modeled using distance constraints with occupancies based on the observed isotropic temperature factors involved.

Compound **8**: $C_{14}H_{34}NO_3Ga$, fw = 334.14, crystal dimens 0.40 × 0.24 × 0.12 mm, monoclinic, space group $P2_1/n$, $a = 10.1444(8)$, $b = 12.8117(10)$, $c = 14.4492(11)$ Å, $\beta = 92.085(1)$, $T = -50(2)$ °C, $Z = 4$, $V = 1876.7(3)$ Å^3, $D_{calcd} = 1.183$ g/cm^3, $\mu = 1.471$ mm^{-1}, $R = 0.0253$, $R_w = 0.0598$. One of the t-butoxide groups (O2) was found to be disordered over two slightly different positions with 50:50 occupancies. These were treated as ideal rigid bodies using the geometry found in the ordered ligands.

Apparatus for Film Depositions. Depositions were performed using a home-built horizontal hot wall low-pressure CVD system equipped with mass flow controllers. The apparatus is described in detail in a dissertation by Mîinea.[24]

Deposition Procedure and Film Characterization. The precursor container was maintained at 60−70 °C. During depositions, the precursor feed line was kept at 75 °C and all other lines were maintained at 100 °C. The argon (UHP grade) carrier gas flow rate through the precursor container was 150 sccm. The oxygen (extra dry grade; 150 sccm) was diluted in argon (500 sccm) before it was mixed with the precursor vapor and argon mixture. The deposition pressure was approximately 2.5 Torr. After each deposition, the precursor feed line was closed while the gas flows and oven temperature were maintained at their deposition values for 45 min. The oven was then shut off and the gas flows were reduced by about 50%. This condition was maintained for 2 h. The sample was then left under a flow of pure argon for 12 h before it was removed from the reactor.

Ion beam data were collected by Dr. Yongqiang Wang at the Ion Beam Analysis Facility, University of Minnesota. The beam was 2-MeV $^4He^+$ ions, and the total charge collected for the spectrum was 10 μC at 10 nA. The detector (fwhm = 18 keV, $\Omega = 4.16$ msr) was located at 165°. The data were analyzed locally using the program RUMP. X-ray diffraction studies were performed using Siemens diffractometers (Cu Kα radiation; 0.01° step size), and X-ray photoelectron spectroscopy studies were carried out using a system (Physical Electronics PHI 5700 ESCA) equipped with a 5-keV Ar$^+$ sputter gun. The electron-energy analyzer was referenced to the Au 4f$_{7/2}$ line at 84 eV. During depth profile analyses, X-ray photoelectron spectra were collected using a standard Al Kα source. The width was set at 11.75 eV throughout. The base pressure was 5×10^{-8} Torr during sputtering. After sputtering into the bulk, spectra were collected using a standard Al source at a pass energy of 11.75 eV. The base pressure was below 10^{-9} Torr. Film morphologies and thicknesses were examined by using scanning electron microscopy (JEOL JSM-6330F).

Silicon, soda lime glass, and quartz substrates were used in this study. To prepare the silicon substrates for depositions, they were first degreased by rinsing them in hexanes and methanol before blow-drying with prepurified nitrogen. Soda lime glass (Corning) and quartz (ChemGlass) substrates were degreased with soap, rinsed with deionized water, and finally rinsed with methanol before being blow-dried by a prepurified nitrogen flow.

Results and Discussion

Synthesis. A summary of the synthetic results is presented in Scheme 1.

The room-temperature reactions of $[Ga(NMe_2)_3]_2$ with i-BuOH or i-PrOH produced the tetramers $Ga[(\mu\text{-}OR)_2Ga(OR)_2]_3$ where R = i-Bu (**1**) and i-Pr (**2**), respectively. The complexes were isolated in moderate yield as colorless crystalline blocks from CH_2Cl_2. In both cases, ^{1}H NMR spectra indicated that the $[Ga(OR)_3]_n$ products were formed exclusively. As explained below, at room temperature in solution the isopropoxide derivative evolved slowly into an equilibrium mixture of the tetramer and the dimer $[Ga(\mu\text{-}O\text{-}i\text{-}Pr)(O\text{-}i\text{-}Pr)_2]_2$.

In contrast to the amine-free products observed from the reactions involving i-BuOH and i-PrOH, the room-temperature reactions of t-BuOH and $EtMe_2COH$ with $[Ga(NMe_2)_3]_2$ yielded mixtures composed of $[Ga(\mu\text{-}OR)(OR)_2]_2$ and an amine adduct $Ga(OR)_3(HNMe_2)$ in approximately 1:2−1:4 ratios (by ^{1}H NMR analyses). Reactions performed at room temperature involving i-$PrMe_2COH$ and Et_2MeCOH produced $Ga(OR)_3(HNMe_2)$ compounds exclusively (i.e., no dimer detected by NMR). In the case of $Ga(OCMe_2\text{-}i\text{-}Pr)_3(HNMe_2)$, the analytically pure compound was isolated as a colorless thick liquid.

To drive off the amine from the amine adducts, it was necessary to heat the mixtures formed by reacting $[Ga(NMe_2)_3]_2$ with ROH. Thus, the homoleptic alkoxide dimers $[Ga(\mu\text{-}OR)(OR)_2]_2$, where R = t-Bu (**3**), CMe_2Et (**4**), $CMe_2\text{-}i\text{-}Pr$ (**5**), or $CMeEt_2$ (**6**), were isolated as crystalline blocks in moderate yields (55−75%) after the isolated solid reaction mixtures were heated under dynamic vacuum (R = t-Bu and CMe_2Et) or toluene solutions of the mixtures open to an oil bubbler were refluxed (R = $CMe_2\text{-}i\text{-}Pr$ and $CMeEt_2$). The conversion of the amine adducts to the dimers under these condi-

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(24) Mîinea, L. Ph.D. Dissertation, University of Houston, Houston, TX, 2000.

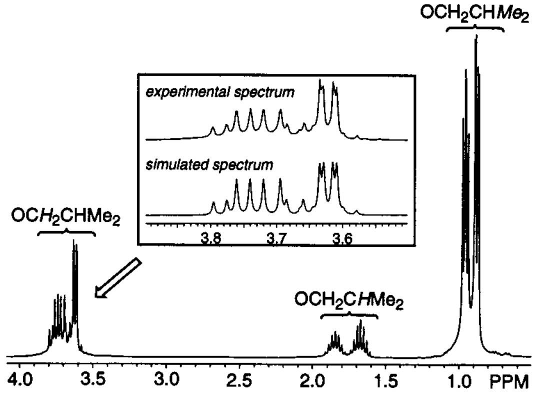

Figure 1. Proton NMR spectrum (CD_2Cl_2) of Ga[(μ-O-*i*-Bu)$_2$Ga(O-*i*-Bu)$_2$]$_3$ (**1**). The inset highlights the methylene proton region and shows the spectrum simulation.

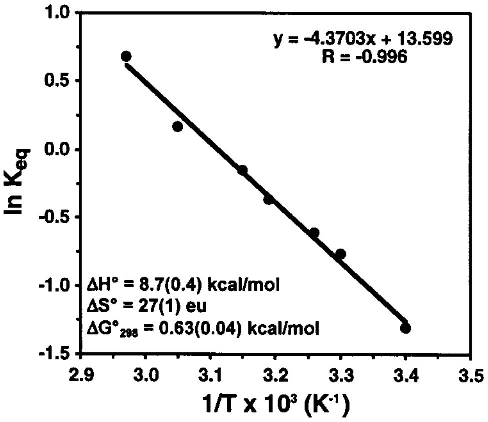

Figure 2. van't Hoff plot for the equilibrium Ga[(μ-O-*i*-Pr)$_2$Ga(O-*i*-Pr)$_2$]$_3$ (**2**) $\rightleftarrows$ 2[Ga(μ-O-*i*-Pr)(O-*i*-Pr)$_2$]$_2$.

tions was essentially quantitative as judged by ^{1}H NMR analyses. In contrast to these results, heating a toluene-d_8 solution of Ga(OCMe$_2$-*i*-Pr)$_3$(HNMe$_2$) (**7**) at 90 °C for 24 h in a sealed NMR tube showed no evidence for dimer formation, indicating that the amine must be removed from the system to allow formation of the dimer. Consistent with this, the addition of a large excess of dimethylamine to hexanes solutions of **3** and **5** (10 h of stirring at 23 °C) followed by removal of the solvent and excess amine under vacuum yielded, respectively, the amine adducts Ga(O-*t*-Bu)$_3$(HNMe$_2$) (**8**) and **7** quantitatively as judged by ^{1}H NMR analysis. These data indicate that the amine adducts are thermodynamically favored over the dimers in the presence of an amine.

In the thermal conversion of Ga(OR)$_3$(HNMe$_2$) to [Ga(μ-OR)(OR)$_2$]$_2$, it was noteworthy that vigorous, prolonged heating (toluene reflux for >2 days) was necessary when R was the large group CMe$_2$-*i*-Pr or CMeEt$_2$, while only moderate heating of the solid (50 °C for 2−3 h) was necessary when R was the less sterically demanding group *t*-Bu or CMe$_2$Et. This observation, coupled with the findings that room-temperature reactions produced no amine adduct when R = *i*-Bu or *i*-Pr, mixtures of a dimer and amine adduct when R = *t*-Bu or CMe$_2$Et, and exclusively an amine adduct when R = CMe$_2$-*i*-Pr or CMeEt$_2$, indicates that sterically demanding R groups favor retention of the amine. The results suggest that amine dissociation is not the rate-limiting step in the formation of the dimer because larger alkoxide ligands would favor dissociation of the coordinated amine more than smaller alkoxide ligands would, which is the opposite of what is observed.

NMR Studies. In all cases, NMR spectra were consistent with the structures shown in Scheme 1 and the solid-state structures of **2**, **4**, and **8** (see below). In the ^{1}H NMR spectrum of **6**, for example, the methyl group protons gave rise to two singlets in a 2:1 ratio and the ethyl group resonances appeared as two ABX$_3$ patterns in a 2:1 ratio. The ABX$_3$ spin systems were confirmed by the successful simulation of the spectra. For the other dimer compounds, the NMR spectra had pairs of resonances in 2:1 integral ratios. It is important to note that in earlier work Oliver and Worrall observed that the ^{1}H NMR spectrum of the *t*-butoxide derivative **3** was consistent with a [Ga(μ-OR)(OR)$_2$]$_2$ structure.[6]

In the ^{1}H NMR spectrum of **1**, the isobutyl groups gave rise to two ABMX$_3$Y$_3$ resonance patterns in a 1:1 ratio, which were simulated successfully (Figure 1). Similarly, the spectrum of **2** showed four doublets of equal intensity arising from the diastereotopic methyl groups of the isopropoxide ligands. Consistent with an earlier study by Oliver and Worrall,[7] the tetramer **2** was observed to evolve slowly into an equilibrium mixture of tetramer and dimer at room temperature (see eq 3). For this reason, it was necessary to obtain the ^{13}C{^{1}H} NMR spectrum of **2** after the sample was cooled to −10 °C to avoid interference from dimer resonances. Conversely, the ^{1}H NMR spectrum of a toluene-d_8 solution of **2** recorded at 90 °C showed only the expected pairs of 2:1 doublet and septet resonances arising from [Ga(μ-O-*i*-Pr)(O-*i*-Pr)$_2$]$_2$.

To better understand the tetramer−dimer equilibrium involving **2**, the thermodynamic parameters for the equilibrium were determined. For the study, equilibrium constants were obtained at seven different temperatures in the range 21−64 °C by using ^{1}H NMR spectroscopy. A van't Hoff plot (Figure 2) yielded $\Delta H°$ = 8.7(0.4) kcal/mol, $\Delta S°$ = 27(1) eu, and $\Delta G°_{298}$ = 0.63(0.04) kcal/mol for the equilibrium as written in eq 3. Thus, the formation of the dimer products is entropy-driven, and at room temperature, the reactant tetramer is favored very slightly over the product dimers.

In contrast to the tetramer−dimer equilibrium observed for **2**, compound **1** showed no evidence for an analogous equilibrium. In an attempt to observe the equilibrium for **1** at elevated temperatures, a toluene-d_8 solution of **1** in a sealed NMR tube was heated for 10 h at 70 °C and a ^{1}H NMR spectrum was recorded at 70 °C. Only resonances arising from the tetramer were observed in the spectrum.

X-ray Crystallographic Studies. To corroborate the structural assignments from the NMR studies and to have data for comparison with analogous aluminum and indium alkoxide complexes, X-ray crystallographic studies of **2**, **4**, and **8** were carried out. Thermal ellipsoid plots are presented in Figures 3−5, respectively, along with selected average bond distances, average bond angles, and bond angle ranges (complete tables, including esd values, can be found in the Supporting Information). In the plots, only the major orientation of each disordered ligand is shown.

Compound **2** has a crystallographically imposed 2-fold axis. The structure consists of a 6-coordinate central Ga atom surrounded by three 4-coordinate Ga atoms.

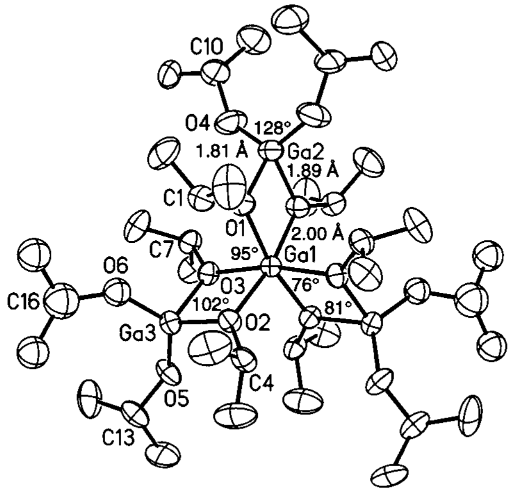

Figure 3. Thermal ellipsoid plot of Ga[(μ-O-*i*-Pr)$_2$Ga(O-*i*-Pr)$_2$]$_3$ (**2**) (40% equiprobability envelopes with hydrogens omitted). Selected bond distance and angle ranges and values: Ga^4-O_{term} = 1.779(4)−1.849(10); Ga^4-O_{bridge} = 1.887(3)−1.894(3); Ga^6-O_{bridge} = 1.996(3)−1.999(3); $O_{term}-Ga^4-O_{term}$ = 124.9(3), 130.9(4); $O_{bridge}-Ga^4-O_{bridge}$ = 80.6(2), 81.1(1); $O_{bridge}-Ga^6-O_{bridge}$ = 75.3(2), 76.0(1) (within the four-membered Ga(μ-O)$_2$Ga rings); Ga−O−Ga = 101.3(1)−102.0(1).

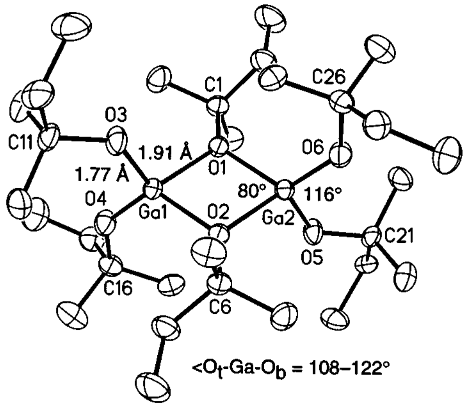

Figure 4. Thermal ellipsoid plot of [Ga(μ-OCMe$_2$Et)(OCMe$_2$-Et)$_2$]$_2$ (**4**) (40% equiprobability envelopes with hydrogens omitted). The range of O_t-Ga-O_b angles and selected average bond distances and angles are shown.

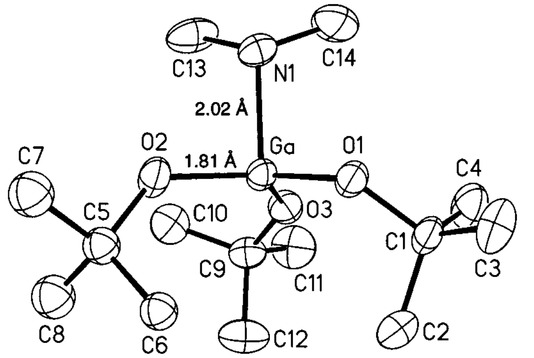

Figure 5. Thermal ellipsoid plot of Ga(O-*t*-Bu)$_3$(HNMe$_2$) (**7**) (40% equiprobability envelopes with hydrogens omitted). The ranges of O−Ga−O and O−Ga−N angles and the Ga−N and average Ga−O bond distances are shown.

Although **2** is the first structurally characterized example of a gallium complex with this structure type, the structure closely resembles those of Al[(μ-O-*i*-Pr)$_2$Al(O-*i*-Pr)$_2$]$_3$ and In[(μ-OCHEt$_2$)$_2$In(OCHEt$_2$)$_2$]$_3$.[8,25] Compound **4** has the edge-shared tetrahedron structure common to dimeric group 13 alkoxide complexes. Structurally characterized homoleptic group 13 alkoxide complexes of this type are [M(μ-OR)(OR)$_2$]$_2$ where M = Al or In, R = *t*-Bu and M = In, R = CMe$_2$(CF$_3$).[8,26,27] Structures analogous to **8** include the gallium examples Ga(OR)$_3$(py-4-NMe$_2$) where R = CH(CF$_3$)$_2$ or CMe$_2$(CF$_3$) (py-4-NMe = 4-(dimethylamino)pyridine)[20] and several aluminum and indium derivatives.[8,20,27,28] In the crystals of **8**, the molecules form dimers through mutual hydrogen bonding involving the amine hydrogen and one of the alkoxide ligand oxygen atoms (N1−O1 = 3.195(3) Å). Consequently, the Ga−O1 distance (1.8217(17) Å) is slightly longer than the other two Ga−O distances (1.7993(19) and 1.807(11) Å) and the Ga−O1−C1 angle (123.58(16)°) is smaller than the other two Ga−O−C angles (132.9(6) and 133.44(17)°).

For Al, Ga, and In compounds of the type M[(μ-OR)$_2$M(OR)$_2$]$_3$,[8,25] [M(μ-OR)(OR)$_2$]$_2$,[8,26,27] and M(OR)$_3$(amine)[8,20,27,28] (tables of selected structural parameters can be found in the Supporting Information), the $M-O_{terminal}$ and $M-O_{bridge}$ distances in the aluminum complexes are around 0.08 Å shorter than those in the corresponding gallium complexes, which are in turn about 0.2 Å shorter than those in the corresponding indium derivatives. The trends in the M−O distances follow the M^{3+} radii: Al^{3+}, 0.57 Å; Ga^{3+}, 0.62 Å; and In^{3+}, 0.92 Å.[29] A comparison of the M−N distances in the M(OR)$_3$(amine) complexes is more problematic because of the differing donor abilities of the amines (4-(dimethylamino)pyridine vs secondary alkylamines) and the presence of fluorinated substituents on some of the alkoxide ligands, which would affect the donor ability of the alkoxide ligand. Differences between the various angles in the M[(μ-OR)$_2$M(OR)$_2$]$_3$ and [M(μ-OR)(OR)$_2$]$_2$ complexes are not striking, but a comparison of the O−M−O and N−M−O angles in the M(OR)$_3$(amine) complexes reveals that Ga(O-*t*-Bu)$_3$(HNMe$_2$) is distorted slightly more toward a trigonal pyramidal geometry than the Al, In, and other Ga derivatives.

Chemical Vapor Deposition. The primary goal of this research was to identify a suitable precursor for the chemical vapor deposition of gallium oxide films. Thermally stable, volatile liquid precursors, or solid precursors with low melting points, are most desirable because they can be transported reliably to the CVD reactor for deposition using inexpensive precursor evaporator assemblies and conventional mass flow controllers. Among the homoleptic alkoxide complexes examined in this study, the *t*-butoxide derivative **3** was the most viable precursor candidate. Although **3** was not a liquid nor did it have a low melting point, it was selected as the precursor over the other dimers because it sublimed most rapidly without decomposition at the lowest temperature (85 °C/17 mTorr).

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(26) Cayton, R. H.; Chisholm, M. H.; Davidson, E. R.; DiStasi, V. F.; Du, P.; Huffman, J. C. *Inorg. Chem.* **1991**, *30*, 1020.

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(28) Chisholm, M. H.; DiStasi, V.; Streib, W. E. *Polyhedron* **1990**, *9*, 253.

(29) Emsley, J. *The Elements*; Clarendon Press: Oxford, 1989.

Table 1. Compositions and Growth Rates for Films Deposited from $[Ga(\mu\text{-}O\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2]_2$

deposition T^a (°C)	O/Ga^b	growth rate^c (Å/min)
300	1.55	14
400	1.53	10
400^d	1.52	7
500	1.62	24
700	1.49	14

[a] For the film deposited at 300 °C, the precursor container was maintained at 70 °C while at all other deposition temperatures the container was maintained at 65 °C. [b] From simulation of RBS spectra. The error is estimated to be ±5%. [c] Film thicknesses were obtained by SEM. [d] Oxygen was not used in this deposition.

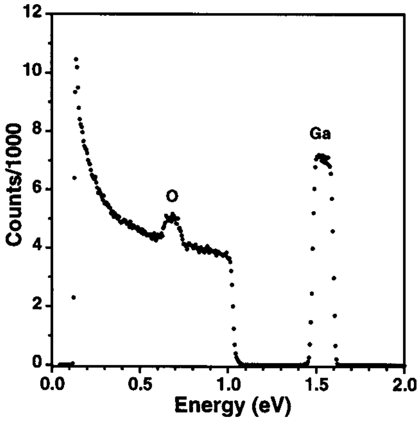

Figure 6. Rutherford backscattering spectrum of a film deposited at 700 °C on silicon.

Compound **3** and oxygen were used as precursors in a low-pressure CVD process to produce films on silicon, quartz, and glass substrates at substrate temperatures of 300−700 °C. A film was also produced at 400 °C without added oxygen. This film was of similar quality to the films prepared using oxygen as a co-precursor. Despite this, it was decided that the depositions would be carried out with the oxygen co-precursor based on earlier studies on the deposition of indium oxide films from $[In(\mu\text{-}OCMe_2Et)(OCMe_2Et)_2]_2$ where it was found that oxygen was necessary for good film adhesion.[8]

In Table 1 are presented composition data for films grown on silicon. The range of O/Ga ratios (1.49−1.62), which were determined from Rutherford backscattering spectra (e.g., Figure 6), is consistent with the expected Ga_2O_3 composition. A carbon peak was not observed in any of the spectra, indicating a low level of carbon contamination in the films (<2−3 atom %).

X-ray photoelectron survey spectra were collected for films deposited on silicon at 300, 400, 500, and 700 °C after removing surface contaminants by sputtering (5−10 min, 1-keV Ar^+). The spectra before sputtering showed surface contamination by carbon, but after the shallow sputtering process, the carbon peak was not observed (e.g., Figure 7). After the sputtering, the Ga $2p_{3/2}$, Ga 3d, and O 1s peaks were observed in the four spectra at the averaged positions 1119.1(0.5), 21.1(0.5), and 531.8(0.6) eV, respectively. These Ga $2p_{3/2}$ and 3d values are close to those reported for sputtered Ga_2O_3 grown thermally on gallium nitride (1119.5 eV for Ga $2p_{3/2}$ and 20.8 eV for Ga 3d).[11] Other reported values include those for bulk Ga_2O_3 (1117.0−1117.9 eV for Ga $2p_{3/2}$, 20.2−21.0 eV for Ga 3d, and 530.9−531.1 eV for O 1s),[30−34] native Ga_2O_3 grown on GaAs (19.6−20.9 eV for Ga 3d and 531.6−531.8 eV for O 1s),[35] and Ga_2O_3 deposited on GaAs using a gallium oxide beam (21.2 eV for Ga 3d).[36]

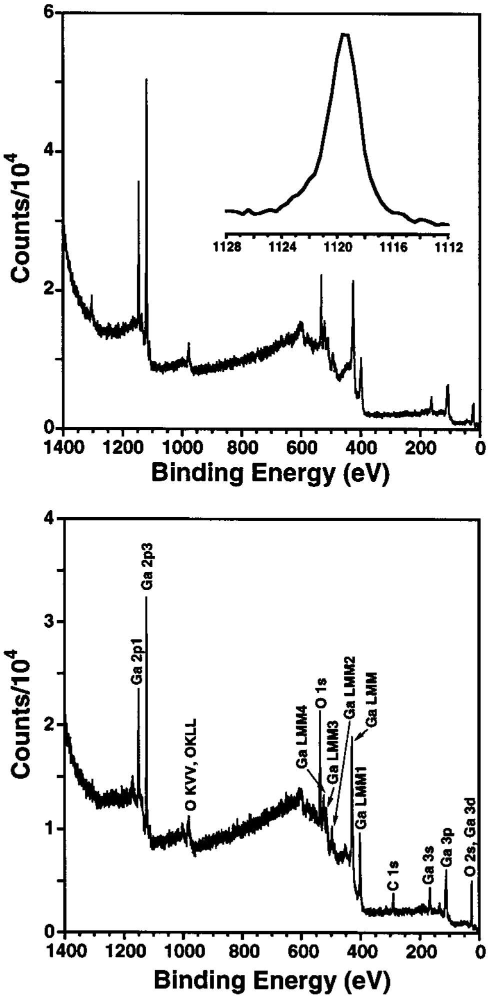

Figure 7. X-ray photoelectron survey scan before (bottom) and after (top) sputtering for 10 min (1-keV Ar^+) a film deposited at 500 °C on silicon. The inset in the spectrum taken after sputtering highlights the Ga $2p_{3/2}$ peak.

To examine the uniformity of the films, complete XP depth profiles (5-keV Ar^+ sputtering) were determined for films deposited at 500 (Figure 8) and 700 °C. Except near the surface and at the substrate−film interface, the films were uniform in composition. In the bulk of the films, the O/Ga ratios averaged 1.1 and little or no carbon was observed. The O/Ga atom ratios obtained by RBS, which suggest that the films are stoichiometric Ga_2O_3, are probably better indicators of the true compositions because possible preferential sputtering makes

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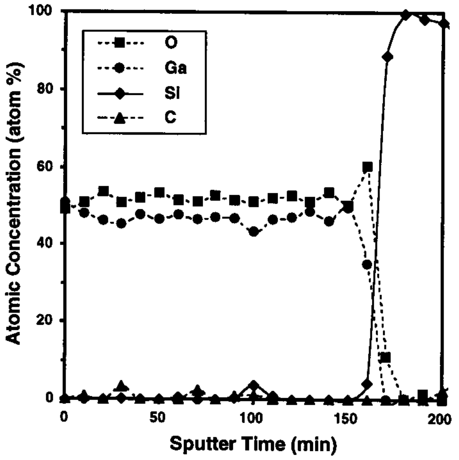

Figure 8. X-ray photoelectron depth profile for a film deposited at 500 °C on silicon (5-keV Ar^+). Before collection of the data shown in the plot, surface contaminents were removed by sputtering for 10 min with 1-keV Ar^+.

the O/Ga ratios obtained by XPS suspect. In addition, the average difference (four different spectra) in energy between the Ga $2p_{3/2}$ and Ga $L_3M_{45}M_{45}$ peaks in the survey spectra was 694.0(0.1) eV, which is consistent with gallium(III) in Ga_2O_3.[11]

Scanning electron micrographs for films deposited at 300, 350, 400, 450, 500, and 700 °C (400−2220-Å thick) showed that they have a fine-grained surface structure. The film grown at 700 °C had the most well-defined grains. Films that had been deposited at 400 and 500 °C on silicon were annealed for 4 h at 700 °C under an argon flow and 1000 °C under an argon−oxygen mixture (18% O_2), respectively. There was no significant change in the surface morphology after annealing under these conditions. Film growth rates, which were calculated from the film thicknesses obtained by cross-sectional SEM, were <24 Å/min. The effect of changing the temperature of the precursor container while keeping the deposition temperature (400 °C) and gas flow rates constant was examined. When the temperature of the precursor container was decreased from 65 °C, the temperature used primarily in this study, to 60 °C, the growth rate decreased about 2-fold (from 10 to 5.0 Å/min) and when the temperature was increased to 70 °C, the growth rate increased 5.4 times (from 10 Å/min to 51 Å/min). These growth rates are lower than those for CVD gallium oxide films prepared by Battiston et al. (117 Å/min),[18] who used gallium tris(hexafluoroacetylacetonate) and oxygen at substrate temperatures of 450−500 °C and by Mîinea et al. (2700−3800 Å/min), who used $Ga(OCH(CF_3)_2)_3(HNEt_2)$ and air at 350−450 °C.[20]

X-ray diffraction data indicated that the films deposited at 400, 500, and 700 °C on quartz substrates were amorphous. In an attempt to form crystalline material, the films deposited at 400 and 500 °C on quartz were annealed for 4 h under argon at 700 and 1000 °C, respectively. X-ray diffraction data indicated that the film annealed at 700 °C remained amorphous while the film annealed at 1000 °C produced an X-ray pattern most consistent with polycrystalline β-Ga_2O_3.[37] Amorphous as-deposited gallium oxide films were also obtained by Battiston et al. using gallium tris(hexafluoroacetylacetonate) and oxygen precursors at a substrate temperature of 470 °C in a CVD process,[18] and by Passlack et al.,[11] using electron-beam evaporation from a $Gd_3Ga_5O_{12}$ source at <350 °C. In both of these reports, β-Ga_2O_3 polycrystalline films were obtained after annealing the amorphous films above 700 °C. Our results are consistent with these findings.

UV−vis spectra were collected for films deposited at 300, 500, and 700 °C on quartz. The films showed >80% transmittance in the 350−800-nm region. This value is comparable to the 80% average transmittance reported by Wu et al. for Ga_2O_3 thin films deposited on silica by an ultrasonic nebulization and pyrolysis method using gallium acetylacetonate as the precursor.[38] Direct band gaps were calculated from the data by plotting $(OD\cdot h\nu)^2$ vs $h\nu$ and extrapolating the linear portion of the curve to $(OD\cdot h\nu)^2 = 0$, where OD is the optical density.[39] For films deposited at 300, 500, and 700 °C, the band gaps were 5.05, 4.95, and 5.12 eV, respectively. These values are higher than the typical band gaps (4.2−4.8 eV) reported previously in the literature.[11,38−40]

Conclusion

A general synthetic route to homoleptic gallium alkoxide complexes involving the reactions of gallium tris(dimethylamide) with alcohols has been developed. By using this method, $Ga(OR)_3$ compounds, where R = *i*-Bu, *i*-Pr, *t*-Bu, CMe_2Et, CMe_2-*i*-Pr, and $CMeEt_2$, were prepared. The reactions with alcohols less sterically demanding than *tert*-butyl alcohol (i.e., *i*-BuOH and *i*-PrOH) produced $Ga(OR)_3$ complexes having a tetrameric $Ga[(\mu\text{-}OR)_2Ga(OR)_2]_3$ structure in the solid state. In solution, $Ga[(\mu\text{-}O\text{-}i\text{-}Pr)_2Ga(O\text{-}i\text{-}Pr)_2]_3$ was found to be in equilibrium with the dimer $[Ga(\mu\text{-}O\text{-}i\text{-}Pr)(O\text{-}i\text{-}Pr)_2]_2$, but no equilibrium was observed for the less sterically crowded *i*-butoxide derivative. In contrast to the reactions involving *i*-BuOH and *i*-PrOH, the reactions of gallium tris(dimethylamide) with *t*-BuOH and other more sterically demanding tertiary alcohols yielded mixtures of the amine adducts $Ga(OR)_3(HNMe_2)$ and the dimers $[Ga(\mu\text{-}OR)(OR)_2]_2$. Upon heating of the amine adducts in an open system, they converted to the dimers.

Among the complexes synthesized in this study, $[Ga(\mu\text{-}O\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2]_2$ was found to be the best candidate for use as a CVD precursor because of its volatility and thermal stability. Low-pressure chemical vapor deposition using $[Ga(\mu\text{-}O\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2]_2$ and O_2 precursors gave Ga_2O_3 films at substrate temperatures of 300−700 °C. The films were carbon-free and amorphous as-deposited. Upon annealing, an amorphous film was converted to one containing polycrystalline β-Ga_2O_3.

In general, liquid CVD precursors are more desirable than solid precursors because the latter tend to sinter when they are sublimed, which produces variable precursor delivery rates to the film substrate. For this reason, future studies will focus on the preparation of liquid $Ga(OR)_3$ complexes. Alkoxide ligands that may favor the formation of liquids include those having

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unsymmetrical substituents.[41] Mixed alkoxide complexes, Ga(OR)$_{3-n}$(OR′)$_n$, are also likely to be liquids.[42]

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Supporting Information Available: Three complete X-ray crystallographic files (CIF) and three tables (PDF) of structural parameters for group 13 M[(μ-OR)$_2$M(OR)$_2$]$_3$, [M(μ-OR)(OR)$_2$]$_2$, and M(OR)$_3$(amine) complexes are available free of charge via the Internet at http://pubs.acs.org.

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