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Synthetic and Structural Studies of Donor-Functionalized Alkoxy Derivatives of Gallium

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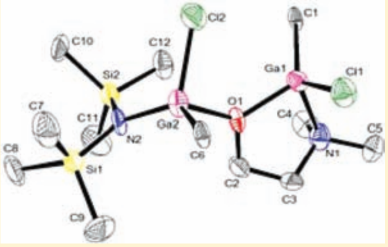
Supporting Information



ABSTRACT: The synthesis of a range of alkyl/chloro-gallium alkoxide and amido/alkoxide compounds was achieved via a series of protonolysis and alcoholysis steps. The initial reaction involved the synthesis of $[Me(Cl)Ga\{N(SiMe_3)_2\}]_2$ (**1**) via methyl group transfer from the reaction of $GaCl_3$ with two equivalents of $LiN(SiMe_3)_2$. Reaction of **1** with varying amounts of ROH resulted in the formation of $[Me(Cl)Ga(OR)]_2$ (**2**, R = CH_2CH_2OMe; **3**, $CH(CH_3)CH_2NMe_2$), $[Me(Cl)Ga\{N(SiMe_3)_2\}(\mu_2\text{-}OR)Ga(Cl)Me]$ (**4**, R = $CH_2CH_2NMe_2$), or $[MeGa(OR)_2]$ (**5**, R = $CH(CH_3)CH_2NMe_2$). Compound **4** represents an intermediate in the formation of dimeric complexes, of the type $[Me(Cl)Ga(OR)]_2$, when formed from compound $[Me(Cl)Ga\{N(SiMe_3)_2\}]_2$. A methylgallium amido/alkoxide complex $[MeGa\{N(SiMe_3)_2\}(OCH_2CH_2OMe)]_2$ (**6**) was isolated when **2** was further reacted with $LiN(SiMe_3)_2$. In addition, reaction of **2** with HO^tBu resulted in a simple alcohol/alkoxide exchange and formation of $[Me(Cl)Ga(O^tBu)]_2$ (**7**). In contrast to the formation of **1**, the *in situ* reaction of $GaCl_3$ with one equivalent of $LiN(SiMe_3)_2$ yielded $[Cl_2Ga\{N(SiMe_3)_2\}]_2$ in low yield, where no methyl group transfer has occurred. Reaction of alcohol with $[Cl_2Ga\{N(SiMe_3)_2\}]_2$ was then found to yield $[Cl_2Ga(OR)]_2$ (**8**, R = $CH_2CH_2NMe_2$), and further reaction of **8** with $LiN(SiMe_3)_2$ yielded the gallium amido alkoxide complex, $[ClGa\{N(SiMe_3)_2\}(OR)]_2$ (**9**, R = $CH_2CH_2NMe_2$), similar to **6**. The structures of compounds **4**, **5**, **7**, and **8** have been determined by single-crystal X-ray diffraction.

INTRODUCTION

Gallium amido[1] and alkoxide[2,3] complexes have been widely studied. Moreover, gallium amides have been extensively investigated as potential precursors to the technologically important material gallium nitride (GaN),[4] which has important electronic applications.[5] However, gallium amides have also been synthesized as useful synthons to a range of novel compounds, such as gallium imides,[6] ketoiminates,[7] and hydrides.[8] Gallium amides can also be used to prepare gallium alkoxides via treatment with alcohol.[2] Both organo- and homoleptic gallium alkoxides, of the types $[R_2GaOR']_2$,[9,10] $[Ga\{(\mu^2\text{-}OR)_2Ga(OR)Me\}_3]$,[11] and $[Ga(OR)_3]_n$[12,13] (R, = alkyl; R′ = donor functionalized alcohol), have been employed as precursors to gallium oxide (Ga_2O_3) films *via* low pressure chemical vapor deposition (CVD). Gallium oxide thin films can act as a gas sensor[14] for reducing gases (e.g., CO, CO_2, EtOH) since they are semiconducting above 500 °C.[15,16] However, above 900 °C, they can detect the concentration of oxygen present, and therefore the function of the gas sensor could be switched from reducing gases to oxidizing gases when using gallium oxide.[17,18] As well as acting as gas sensors, gallium oxide thin films are also used as white-light-emitting luminophores.[19] Thin films of Ga_2O_3 have also been deposited from gallium alkoxides using aerosol-assisted CVD from reactions of $[Ga(NMe_2)_3]_2$[20] or GaR_3 (R = Me,[21] Et[22]) with donor functionalized alcohols, such as $HOCH_2CH_2NMe_2$, $HOCH_2CH_2OMe$, and $HOCH(CH_3)CH_2NMe_2$.[23] In addition, intramolecularly donor-stabilized organogallium alkoxides have been used as alkylating reagents in the cross-coupling of aryl triflates and aryl halides[24,25] and as intermediates to heterometallic complexes.[19]

Gallium alkoxides were first prepared using salt elimination routes,[26,27] followed by alcohol/alkoxide exchange reactions.[2,28] More recently, the synthesis of gallium alkoxides via amide/alcohol exchange starting from $[Ga(NMe_2)_3]_2$ resulted in the formation of a range of gallium alkoxides.[12,13] Indeed, amide/alcohol exchange has been shown to be a facile method for the formation of monomeric chlorogallium bis(alkoxides) of the type $[ClGa(OR)_2]$ (R = donor functionalized group), from the reaction of $[ClGa(NMe_2)_2]$ and two equivalents of alcohol.[29] Gallium bis(alkoxides) are relatively rare species,[30] which are difficult to synthesize,[9] but could be volatile due to their monomeric nature and therefore be excellent CVD precursors.[29] We have been studying the reactivity of gallium amides and alkoxides and their use as precursors to gallium oxide. In order to attempt to introduce selected ligands onto the gallium centers and tune the volatility, we have investigated the reactivity of gallium chloride with a lithiated silylamide followed by the addition of alcohol *via* a range of stepwise reactions. Herein, we report the synthesis and reactivity of a range of alkyl/chloro-gallium alkoxides and amido/alkoxides formed *via* a series of protonolysis and alcoholysis steps and discuss the

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structural changes brought about by the different reaction conditions.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in an MBraun glovebox. All solvents used were stored in alumina columns and dried with anhydrous engineering equipment, such that the water concentration was 5−10 ppm. Chemicals were procured commercially from Aldrich and used without further purification, with the exception of alcohols, which were degassed, distilled, and stored over molecular sieves. All ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on Bruker AMX300 or AMX400 spectrometers, operating at 299.87 and 400.12 MHz, respectively (^{1}H). All spectra were recorded using C_6D_6, which was dried and degassed over molecular sieves prior to use; ^{1}H and ^{13}C{^{1}H} chemical shifts are reported relative to $SiMe_4$ (δ 0.00). Mass spectra were obtained using a Micromass 70-SE spectrometer using chemical ionization (CI) with methane reagent gas. Elemental analyses were carried out at UCL using an elemental analyzer (CE-440; Exeter Analytical Inc.).

Synthesis of [Me(Cl)GaN(SiMe$_3$)$_2$]$_2$ (1). A suspension of lithium hexamethyldisilylamide (1.86 g, 11.0 mmol) in toluene (15 cm^3) was added dropwise to a suspension of gallium trichloride (0.98 g, 5.6 mmol) in toluene (15 cm^3) at −78 °C and was stirred for 30 min. The reaction mixture was allowed to warm to room temperature with stirring and then heated, under reflux, for 24 h, giving a cloudy solution. After cooling, the solution was filtered and the solvent removed *in vacuo* to give a white viscous liquid. The product was purified by sublimation (10^{-2} Torr/100 °C, 1.04 g, 67% yield). Anal. calcd for $C_{14}H_{42}Cl_2Ga_2N_2Si_4$: C, 29.96; H, 7.54; N, 4.99. Found: C, 30.67; H, 7.22; N, 5.11%. ^{1}H NMR δ/ppm (C_6D_6): 0.28 (s, $N\{Si(CH_3)_3\}_2$), 36H), 0.03 (s, $GaCH_3$, 6H). ^{13}C{^{1}H} NMR δ/ppm (C_6D_6): 23.2 ($GaCH_3$), 4.7 ($N\{Si(CH_3)_3\}_2$). Mass spec. (CI): (m/z) 560 $[M_2]^+$, 279 $[M]^+$, 244 $[M - Cl]^+$, 229 $[GaN(SiMe_3)_2]^+$, 171 $[M - Cl - (SiMe_3)]^+$.

Synthesis of [Me(Cl)Ga(OCH$_2$CH$_2$OMe)]$_2$ (2). 2-Methoxyethanol (0.3 cm^3, 3.6 mmol) was added to a solution of **1** (1.01 g, 1.8 mmol) in toluene (20 cm^3) prepared *in situ*. The reaction was heated under reflux for 24 h, giving a cloudy solution. After cooling, the solution was filtered: the solvent and volatiles were removed *in vacuo* to give a yellow viscous oil. The oil was sublimed in a long Schlenk flask over an oil bath at 50 °C under a dynamic vacuum, affording a free-flowing crystalline solid (0.52 g, 73% yield). Anal. calcd (%) for $C_8H_{20}Cl_2Ga_2O_4$: C, 24.74; H, 5.15. Found (%): C, 25.12; H, 5.21. ^{1}H NMR δ/ppm (C_6D_6): 3.72 (m, OCH_2CH_2, 4H), 3.30 (m, CH_2OMe, 4H), 3.16 (s, OCH_3, 6H), 0.05 (s, $GaCH_3$, 6H). ^{13}C{^{1}H} NMR δ/ppm (C_6D_6): 73.1 (CH_2OMe), 62.1 (OCH_2), 57.9 (OCH_3), 5.7 ($GaCH_3$). Mass spec. (CI): (m/z) 388 $[M_2]^+$, 353 $[M_2 - Cl]^+$, 276 $[M_2 - Cl - (OCH_2CH_2OMe)]^+$, 193 $[MeClGa(OCH_2CH_2OMe)]^+$, 159 $[MeGa(OCH_2CH_2OMe)]^+$.

Synthesis of [Me(Cl)Ga(OCH(CH$_3$)CH$_2$NMe$_2$)]$_2$ (3). Compound **3** was prepared in the same way as **2** but using 1-dimethylamino-2-propanol (0.4 cm^3, 3.6 mmol) and compound **1** (1.01 g, 1.8 mmol). Removal of the solvent *in vacuo* afforded a yellow viscous oil, which after sublimation resulted in the isolation of small colorless crystals (0.56 g, 70% yield). Anal. calcd (%) for $C_{12}H_{30}Cl_2Ga_2N_2O_2$: C, 32.58; H, 6.79; N, 6.33 Found (%): C, 31.98; H, 6.67; N, 6.01. ^{1}H NMR δ/ppm (C_6D_6): 4.05 (m, $OCH(CH_3)$, 2H), 2.31 (br, $OCH(CH_3)CH_2$, 4H), 1.22 (br, $N(CH_3)_2$, 12H), 1.07 (s, $OCH(CH_3)$, 6H), 0.06 ($GaCH_3$, 6H). ^{13}C{^{1}H} NMR δ/ppm (C_6D_6): 67.8 ($OCH(CH_3)$), 66.3 ($CH(CH_3)CH_2$), 64.5 ($N(CH_3)_2$), 48.2 ($OCH(CH_3)$), 5.7 ($GaCH_3$). Mass spec (CI): (m/z) 442 $[M_2]^+$, 412 $[M_2 - 2Me]^+$, 293 $[M_2 - Me - Cl - OCH(CH_3)CH_2OMe]^+$.

Synthesis of [Me(Cl)Ga{N(SiMe$_3$)$_2$}(μ_2-OCH$_2$CH$_2$NMe$_2$)Ga(Cl)Me] (4). Compound **4** was prepared in the same way as **2** but using 2-dimethylaminoethanol (0.2 cm^3, 2.2 mmol) and compound **1** (1.28 g, 2.2 mmol). Removal of the solvent *in vacuo* afforded a yellow viscous oil, which after sublimation resulted in the isolation of small colorless crystals (0.30 g, 21% yield). Anal. calcd (%) for $C_{12}H_{34}Cl_2Ga_2N_2O_1Si_2$: C, 29.63; H, 7.00; N, 5.8. Found (%): C, 30.02; H, 7.51; N 5.5. ^{1}H NMR δ/ppm (C_6D_6): 3.47 (m, OCH_2CH_2, 2H), 2.22 (br, CH_2NMe_2, 2H), 2.12 (s, $N(CH_3)_2$, 6H), 0.34 (s, $N\{Si(CH_3)_3\}_2$, 18H), 0.06 (s, $GaCH_3$, 3H), 0.03 (s, $GaCH_3$, 3H). ^{13}C{^{1}H} NMR δ/ppm (C_6D_6): 60.5 (OCH_2), 58.7 (CH_2NMe_2), 45.1 ($N(CH_3)_2$), 6.0 ($GaCH_3$), 5.7 ($GaCH_3$), 4.9 ($N\{Si(CH_3)_3\}_2$).

Synthesis of [MeGa(OCH(CH$_3$)CH$_2$NMe$_2$)$_2$] (5). Compound **5** was prepared in the same way as **2** but using 1-dimethylamino-2-propanol (0.6 cm^3, 5.5 mmol) and compound **1** (0.97 g, 1.7 mmol). Removal of the solvent *in vacuo* afforded a yellow viscous oil, which after sublimation resulted in the isolation of small colorless crystals (0.82 g, 52% yield). Anal. calcd (%) for $C_{11}H_{27}GaN_2O_2$: C, 45.7; H, 9.42; N, 9.69. Found (%): C, 45.9; H, 9.51; N 9.98 (%). ^{1}H NMR δ/ppm (C_6D_6): 3.60 (m, $OCH(CH_3)CH_2$, 4H), 2.35 (br, CH_2NMe_2, 4H), 2.31 (m, $N(CH_3)_2$, 12H), 1.56 (br, $OCH(CH_3)CH_2$, 6H), 0.05 (s, $GaCH_3$, 3H). ^{13}C{^{1}H} NMR δ/ppm (C_6D_6): 61.2 (CH_2NMe_2), 59.0 ($OCH(CH_3)$), 45.4 ($N(CH_3)_2$), 22.7 ($OCH(CH_3)$), 5.8 ($GaCH_3$). Mass spec. (CI): (m/z) 289 $[M_2]^+$, 186 $[M - OCH_2CH_2NMe_2]^+$.

Synthesis of [MeGa{N(SiMe$_3$)$_2$}(OCH$_2$CH$_2$OMe)]$_2$ (6). A suspension of lithium hexamethyldisilylamide (0.43 g, 2.6 mmol) in toluene (15 cm^3) was added to a solution of **2** (0.50 g, 1.3 mmol) in toluene (20 cm^3), which was prepared *in situ*. The reaction was then heated under reflux for 24 h, giving a cloudy solution. After cooling, the solution was filtered and the solvent removed *in vacuo* to give a yellow viscous oil (0.41 g, 49% yield). Anal. calcd (%) for $C_{20}H_{56}Ga_2N_2O_4Si_4$: C, 37.61; H, 8.02; N, 4.38. Found (%): C, 37.33; H, 8.29; N, 4.13. ^{1}H NMR δ/ppm (C_6D_6): 3.79 (m, OCH_2CH_2, 4H), 3.35 (m, CH_2OMe, 4H), 3.15 (s, $O(CH_3)$, 6H), 0.23 (br, $SiCH_3$, 36H), 0.07 (s, $GaCH_3$, 6H). ^{13}C{^{1}H} NMR δ/ppm (C_6D_6): 74.1 (CH_2OMe), 62.0 (OCH_2), 58.5 (OCH_3), 5.7 ($GaCH_3$), 5.1 ($N\{Si(CH_3)_3\}_2$). Mass spec. (CI): (m/z) 638 $[M_2]^+$, 478 $[M_2 - (N\{SiMe_3\}_2)]^+$, 404 $[M_2 - N\{SiMe_3\}_2 - CH_2CH_2OMe_2]^+$, 319 $[M]^+$.

Synthesis of [Cl(Me)Ga(O^{t}Bu)]$_2$ (7). *tert*-Butanol (0.55 cm^3, 5.8 mmol) was added to a solution of **2** (0.19 g, 0.3 mmol) in toluene (20 cm^3) which was prepared *in situ*. The reaction was heated under reflux for 24 h, giving an orange solution. After cooling, solvent and volatiles were removed *in vacuo*, yielding an orange viscous oil. The oil was sublimed in a long Schlenk flask over an oil bath at 100 °C under a dynamic vacuum and afforded small colorless crystals (0.42 g, 37%). Anal. calcd (%) for $C_{10}H_{24}Cl_2Ga_2O_2$: C, 31.05; H, 6.25. Found (%): C, 30.09; H, 6.01. ^{1}H NMR δ/ppm (C_6D_6): 1.2 (m, $C(CH_3)_3$, 18H), 0.22 (s, $GaCH_3$, 6H). ^{13}C{^{1}H} NMR δ/ppm (C_6D_6): 80.2 ($C(CH_3)_3$), 48.3 ($C(CH_3)_3$), 5.12 ($GaCH_3$). Mass spec. (CI): (m/z) 384 $[M_2]^+$, 327 $[M_2 - C(CH_3)_3]^+$, 312 $[M_2 - C(CH_3)_3 - Me]^+$, 277 $[M - Cl - C(CH_3)_3 - Me]^+$, 257 $[Me_2Ga_2(O^tBu)_2]^+$.

Synthesis of [Cl$_2$Ga(OCH$_2$CH$_2$NMe$_2$)]$_2$ (8). 2-Dimethylaminoethanol, (0.3 cm^3, 3.0 mmol) was added dropwise to a solution of $[Cl_2GaN\{SiMe_3\}_2]_2$ (1.00 g, 3.2 mmol) in toluene (20 cm^3) prepared *in situ* from $GaCl_3$ (0.569 g, 3.2 mmol) and $LiN\{SiMe_3\}_2$ (0.541 g, 11.0 mmol) following the procedures for **1**. The reaction was heated under reflux for 24 h, giving a cloudy solution. After cooling, the solution was filtered, and the solvent and other volatiles were removed *in vacuo* to give a yellow viscous oil. The oil was sublimed in a long Schlenk flask over an oil bath at 50 °C under a dynamic vacuum, affording colorless crystals (0.59 g, 42% yield). Anal. calcd (%) for $C_8H_{20}Cl_4Ga_2N_2O_2$: C, 25.06; H, 5.22; N, 7.31. Found (%): C, 25.98; H, 5.37; N, 7.01. ^{1}H NMR δ/ppm (C_6D_6): 3.59 (m, OCH_2CH_2, 2H), 2.57 − 2.15 (m, CH_2NMe_2, 2H), 2.11 (m, $N(CH_3)_2$, 6H). ^{13}C{^{1}H} NMR δ/ppm (C_6D_6): 60.2 (CH_2NMe_2), 57.9 (OCH_2), 44.9 ($N(CH_3)_2$). Mass spec (CI): (m/z) 457 $[M_2]^+$, 386 $[M_2 - Cl]^+$.

Table 1. Crystallographic Data for Compounds 4, 5, 7, and 8

data	4	5	7	8
chemical formula	$C_{12}H_{34}Cl_2Ga_2N_2OSi_2$	$C_{11}H_{27}GaN_2O_2$	$C_{10}H_{24}Cl_2Ga_2O_2$	$C_8H_{20}Cl_4Ga_2N_2O_2$
fw (g mol^{-1})	488.93	289.07	386.63	457.50
cryst size (mm^3)	0.46 × 0.03 × 0.01	0.38 × 0.32 × 0.20	0.10 × 0.10 × 0.10	0.35 × 0.20 × 0.15
cryst syst	trigonal	triclinic	monoclinic	monoclinic
space group	$R3c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	41.8983(16)	7.8482(2)	7.0602(6)	6.9419(6)
b (Å)	41.8983(16)	8.0323(3)	15.1857(13)	10.2530(9)
c (Å)	7.1970(4)	12.0382(3)	9.8564(6)	13.4989(10)
α (deg)	90	99.273(2)	90	90
β (deg)	90	92.909(2)	125.540(4)	118.541(3)
γ (deg)	120	102.636(2)	90	90
V (Å^3)	10941.4(8)	727.90(4)	859.88(12)	844.03(12)
Z	18	2	2	2
ρ_{calcd} (g cm^{-3})	1.336	1.319	1.493	1.800
μ (mm^{-1})	2.535	1.881	3.431	3.820
reflns collected	32747	16783	7072	6904
unique reflns	2833	3344	2019	2008
data completeness	99.6%	99.1%	98.2%	98.7%
R_{int}	0.1385	0.0356	0.0235	0.0199
R_1 and wR_2 [$I > 2\sigma(I)$]	0.0855, 0.1559	0.0280, 0.0723	0.0356, 0.0721	0.0214, 0.0528
R_1 and wR_2 [all data]	0.1065, 0.1645	0.0308, 0.0745	0.0415, 0.0751	0.0234, 0.0535

Synthesis of $[ClGa\{N(SiMe_3)_2\}(OCH_2CH_2NMe_2)]_2$ (9). A suspension of lithium hexamethyldisilylamide (0.89 g, 5.3 mmol) in toluene (15 cm^3) was added to a solution of **8** (0.50 g, 1.1 mmol) in toluene (20 cm^3), which was prepared *in situ*. The reaction was then heated under reflux for 24 h, giving a cloudy solution. After cooling, the solution was filtered and the solvent removed *in vacuo* to give a yellow viscous oil, which was purified *via* sublimation to yield a crystalline solid (0.21 g, 23% yield). Anal. calcd (%) for $C_{20}H_{56}Cl_2Ga_2N_4O_2Si_4$: C, 34.09; H, 7.95; N, 7.95. Found (%): C, 34.12; H, 7.89; N, 8.13. ^{1}H NMR (C_6D_6): δ/ppm: 3.90 (m, OCH_2, 2H), 2.31 (m, CH_2CH_2N, 2H), 2.24 (m, NCH_3, 6H), 0.08 (m, $SiCH_3$, 18H). $^{13}C\{^1H\}$ NMR δ/ppm (C_6D_6): 62.9 (CH_2NMe_2), 46.1 (OCH_2), 44.9 ($N(CH_3)_2$), 5.4 ($N\{Si(CH_3)_3\}_2$). Mass spec. (CI): (m/z) 704 $[M_2]^+$, 474 $[M - Cl - 2(N\{SiMe_3\}_2)]^+$, 352 $[M]^+$, 314 $[Ga_2(OCH_2CH_2NMe_2)_2]^+$.

Crystal Structure Determination and Refinement. Crystals of **4**, **5**, **7**, and **8** were obtained from oils via sublimation using an oil bath. A summary of the crystal data, data collection, and refinement for crystallographically characterized compounds is given in Table 1. For compounds **4** and **5**, crystals were mounted on a glass fiber with silicon grease from paraffin oil. Data sets were collected on an Enraf-Nonius Kappa CCD area detector diffractometer with an FR591 rotating anode (Mo Kα radiation) and an Oxford Cryosystems low-temperature device operating at 120(2) K in the ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect,[31] Scalepack, and Denzo.[32] For compounds **7** and **8**, crystals were mounted on a glass fiber with silicon grease from Fomblin vacuum oil. Geometric and intensity data were obtained on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ_1 = 0.71073 Å) at 150(2) K. Data reduction and integration was carried out with SAINT+ and absorption corrections applied using SADABS. For all compounds, solutions and refinements were performed using the WinGX package[33] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model. Compound **4** crystallized as a merohedral twin with a Flack parameter of 0.47(6): 2405 Friedel pairs were merged in the final cycle of refinement. The asymmetric unit of **4** contained a highly disordered CH_2Cl_2 molecule lying on a 3-fold axis, which proved impossible to model satisfactorily; hence, it was removed using the SQUEEZE algorithm. Selected bond distances and angles of these complexes are listed in Tables 2 and 3.

Table 2. Selected Bond Lengths (Å) for Crystallographically Characterized Compounds: a = Bridging Ga−O bond, b = Anionic Ga−N Bond

bond	4	5	7	8
Ga−O	1.904(8)	1.8581(12)	1.909(2)[a]	1.9200(12)
	1.966(9)[a]	1.8598(13)	1.916(2)	1.9491(12)[a]
Ga−N	2.033(12)	2.2446(15)		2.0922(15)
	1.86(1)[b]	2.2245(15)		
Ga−C	1.929(11)	1.9799(17)	1.928(3)	
	2.027(11)			
Ga−Cl	2.165(4)		2.1856(9)	2.2087(5)
	2.236(4)			2.1876(5)

RESULTS AND DISCUSSION

The reaction between $GaCl_3$ and two equivalents of $LiN(SiMe_3)_2$ at −78 °C in toluene resulted, after work up, in a 67% yield of colorless crystalline **1** (Scheme 1). Analytical and spectroscopic data for **1** were consistent with the formulation $[Me(Cl)GaN(SiMe_3)_2]_2$ rather than $[Cl_2GaN(SiMe_3)_2]$.

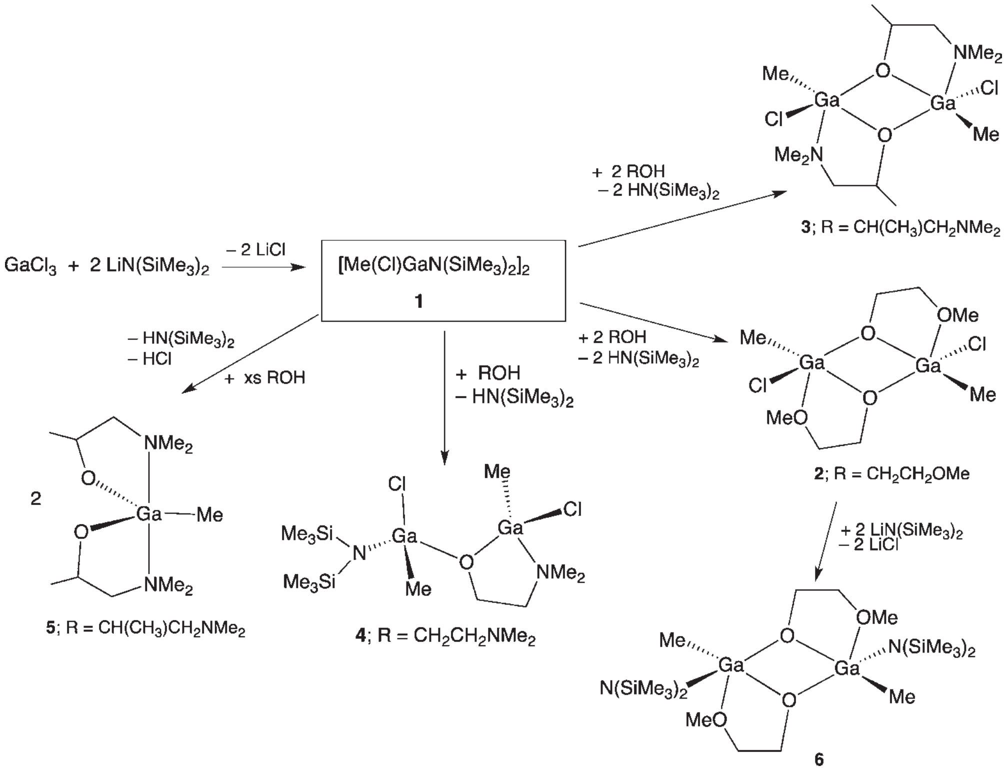
The formation of **1** is the result of a monochloride substitution and transfer of a methyl ligand from the $N(SiMe_3)_2$ group to the Ga center. The mechanism for the formation of **1** is not known; however, related alkyl and aryl group transfers[34] have been previously observed for gallium[35,36] and indium.[37] For example, the reaction of $GaCl_3$ with $LiN(SiMe_2Ph)_2$ afforded $[Ph(Cl)GaN(SiMe_2Ph)_2]_2$, via phenyl group transfer.[35] Similarly, the reaction of

Table 3. Selected Bond Angles (deg) for Crystallographically Characterized Compounds

4		5		7[a]		8[b]	
Ga(1)–O(1)–Ga(2)	124.1(5)	O(1)–Ga(1)–O(2)	112.46(6)	O(1)^i–Ga(1)–O(1)	79.60(9)	O(1)–Ga(1)–Cl(1)	139.42(5)
O(1)–Ga(1)–C(1)	120.0(4)	O(1)–Ga(1)–N(1)	82.28(5)	O(1)^i–Ga(1)–C(1)	119.53(14)	O(1)^i–Ga(1)–Cl(1)	94.66(4)
O(1)–Ga(1)–N(1)	85.9(4)	O(1)–Ga(1)–N(2)	87.68(6)	O(1)–Ga(1)–C(1)	119.98(13)	Cl(2)–Ga(1)–Cl(1)	110.63(2)
C(1)–Ga(1)–N(1)	113.0(5)	O(1)–Ga(1)–C(1)	123.21(7)	C(2)–O(1)–Ga(1)	128.46(18)	O(1)–Ga(1)–N(1)	80.62(6)
O(1)–Ga(1)–Cl(1)	105.5(3)	O(2)–Ga(1)–N(1)	87.26(6)	O(1)^i–Ga(1)–Cl(1)	106.85(7)	O(1)^i–Ga(1)–N(1)	149.54(6)
C(1)–Ga(1)–Cl(1)	121.7(4)	O(2)–Ga(1)–N(2)	82.74(6)	O(1)–Ga(1)–Cl(1)	106.44(7)	O(1)–Ga(1)–O(1)^i	73.75(6)
N(1)–Ga(1)–Cl(1)	104.1(3)	O(2)–Ga(1)–C(1)	124.33(7)	C(1)–Ga(1)–Cl(1)	117.86(12)	O(1)–Ga(1)–Cl(2)	109.77(5)
O(1)–Ga(2)–C(6)	103.0(4)	C(1)–Ga(1)–N(1)	99.12(7)	Ga(1)^i–O(1)–Ga(1)	100.40(9)	O(1)^i–Ga(1)–Cl(2)	101.40(5)
N(2)–Ga(2)–O(1)	108.3(5)	C(1)–Ga(1)–N(2)	98.93(7)			N(1)–Ga(1)–Cl(1)	94.22(4)
N(2)–Ga(2)–C(6)	125.6(4)	N(2)–Ga(1)–N(1)	161.85(7)			N(1)–Ga(1)–Cl(2)	102.57(5)
O(1)–Ga(2)–Cl(2)	95.5(3)						
C(6)–Ga(2)–Cl(2)	105.6(4)						
N(2)–Ga(2)Cl(2)	114.1(4)						

[a] Atoms marked '*i*' are at the equivalent position (1 − *x*, −1 − *y*, 1 − *z*). [b] (−*x*, −1 − *y*, −*z*).

Scheme 1. Synthetic Procedure for the Formation of Compounds 1−6



InCl$_3$ with LiN(SiMe$_3$)$_2$ resulted in the formation of [Me(Cl)InN(SiMe$_3$)$_2$], via methyl group transfer.[37] Unfortunately, X-ray-quality crystals of **1** could not be isolated; however, evidence for the dimeric nature of **1** was obtained from mass spectroscopy where a peak corresponding to the dimer was observed (*m*/*z* 560). The ^{1}H NMR spectrum showed two peaks at 0.03 and 0.28 ppm in a 1:6 ratio, corresponding to Me−Ga and Me−Si, respectively. Compound **1** is similar to previously reported compounds, such as [Me(Cl)GaNR(SiMe$_3$)]$_2$ (R = H, Me).[35,38]

The reaction of **1** (prepared *in situ* from the reaction of GaCl$_3$ and LiN(SiMe$_3$)$_2$) with two equivalents of ROH in toluene resulted, after reflux for 24 h and subsequent workup, in a ∼70% yield of [Me(Cl)GaOR]$_2$ (**2**, R = CH$_2$CH$_2$OMe; **3**, R = CH(CH$_3$)CH$_2$NMe$_2$). The formation of **2** and **3** was confirmed by the analytical and spectroscopic data with the dimeric nature indicated from the presence of a peak corresponding to the dimer (**2**, *m*/*z* 388; **3**, *m*/*z* 442) in the mass spectra of the products. Compounds **2** and **3** are assumed to exist as dimers containing a Ga$_2$O$_2$ four-membered ring, as shown in Scheme 1. The dimeric structures of related complexes, of the type [Me(X)GaOR]$_2$ (X = Cl, Me, Et; R = donor functionalized ligand) have been previously reported.[10,21,22,24,25] A dative ligand−metal interaction in **2** and **3** is confirmed by a comparison of proton resonances of the alkoxide ligand (Experimental Section) in the product to the free

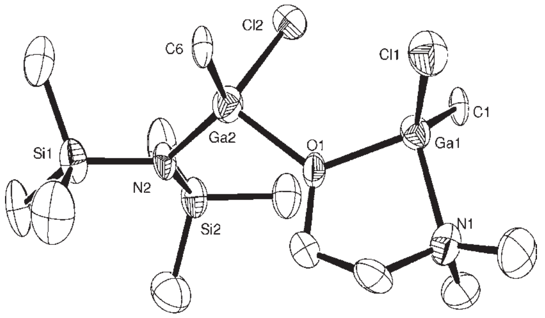


Figure 1. ORTEP representation of compound **4**. Thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity.

ligand. Thus, **2** and **3** are expected to adopt similar structures to those previously reported for $[Me(X)GaOR]_2$, where R = donor functionalized ligand, in which the gallium center is five-coordinate. The Me–Ga peaks in the ^{1}H NMR spectrum were observed at 0.05 and 0.07 ppm for **2** and **3**, respectively.

The formation of **2** and **3** is the result of elimination of two equivalents of amine, $HN(SiMe_3)_2$, from compound **1** upon reaction with two equivalents of alcohol. In contrast, reacting **1** with one equivalent of an alcohol yields an intermediate alkyl(chloro)gallium amido-alkoxide compound (Scheme 1). Thus, the reaction of **1** with 1 equiv of $HOCH_2CH_2NMe_2$ in toluene at −78 °C yielded, after workup, colorless crystals of $[Me(Cl)Ga\{N(SiMe_3)_2\}(\mu_2\text{-}OCH_2CH_2NMe_2)Ga(Cl)Me]$ (**4**). Analytical and spectroscopic data confirmed the formation of **4** with peaks in the ^{1}H NMR spectrum (Experimental Section) corresponding to the alkoxide ligand (3.47, 2.22, and 2.12 ppm), silylamido group (0.34 ppm), and two Me–Ga environments (0.03 and 0.06 ppm) in the expected ratios (10:18:3:3). Compound **4** can be thought of as an intermediate to the formation of $[Me(Cl)Ga(OCH_2CH_2NMe_2)]_2$ from compound **1** and presumably forms *via* the elimination of only one equivalent of $HN(SiMe_3)_2$ from **1**.

In order to establish the coordination environment of each gallium center in **4**, a single-crystal X-ray diffraction study was carried out, the results of which are shown in Figure 1 and Table 1; selected bond lengths and angles are given in Table 2 and 3. Compound **4** crystallized in the trigonal *R*3*c* space group. Each gallium center adopts a distorted tetrahedral coordination environment with similar Ga–Cl and Ga–Me bond distances [Ga1–C1 1.929(11) Å, Ga2–C6 2.027(11) Å; Ga1–Cl1 2.165(4) Å, Ga2–Cl2 2.236(4) Å] where the bonds to Ga2 are slightly longer due to the sterics of the $N(SiMe_3)_2$ group. The Ga–N bond distances differ considerably for the two gallium centers, indicative of two different bonding modes. The shorter Ga–N distance [Ga2–N2 1.86(1) Å] corresponds to the Ga–N σ bond [$Ga{-}N(SiMe_3)_2$], whereas a long bond distance [Ga1–N1 2.033(12) Å] was observed for the $Ga\leftarrow N$ dative bond from the donor NMe_2 group. The bond angles show distortion from regular tetrahedral coordination with the angles at Ga1 ranging from 104.1(3) to 121.7(4)°, except for O1–Ga1–N1, which has a large deviation from 109.5° [85.9(4)°] due to the steric constraints of the donor functionalized ligand which forms the five-membered (Ga–O–C–C–N) ring. The angles at Ga2 range from 95.5(3)° to 114.1(4)° probably due to the sterics of the $N(SiMe_3)_2$ group. The two gallium centers are linked via an oxygen bridge from the alkoxide ($OCH_2CH_2NMe_2$) group [Ga1–O1, 1.904(8) Å; Ga2–O1, 1.968(8) Å].

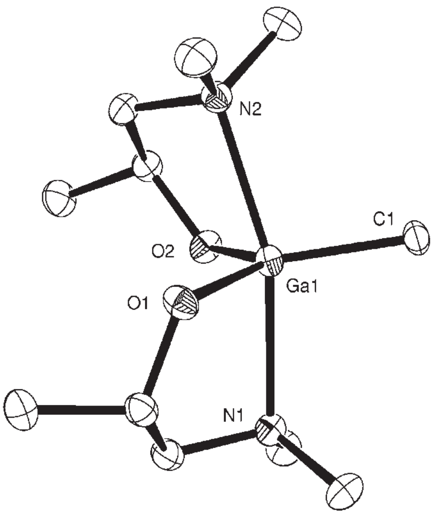


Figure 2. ORTEP representation of compound **5**. Thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity.

In contrast to the formation of the alkyl(chloro)gallium monoalkoxides **2**–**4**, which were formed from the reaction of either one or two equivalents of ROH with compound **1**, the addition of excess ROH yields a monomeric alkylgallium bis(alkoxide), as shown in Scheme 1. Thus, the reaction of **1** with an excess of $HOCH(CH_3)CH_2NMe_2$ in toluene at −78°C, followed by refluxing for 24 h, yielded, after workup, colorless crystals of $[MeGa(OCH(CH_3)CH_2NMe_2)_2]$ (**5**). The formation of compound **5** was confirmed by analytical and spectroscopic data with a molecular ion observed for the monomer at 289 *m*/*z*. The ^{1}H NMR spectrum of **5** had peaks at 0.05, 1.56, 2.31, 2.35, and 3.60 ppm corresponding to Me–Ga, $OCH(CH_3)$, OCH, $OCHCH_2$, and NMe_2, respectively, and in the expected ratio 3:6:2:4:12.

The crystal structure of compound **5** was determined by single-crystal X-ray diffraction, the results of which are shown in Figure 2 and Table 1; selected bond lengths and angles are given in Table 2 and 3. Compound **5** crystallized in the triclinic space group $P\bar{1}$ and is monomeric in the solid state, with the gallium atom adopting a distorted trigonal bipyramidal geometry. The oxygen atoms of each alkoxide ligand and the methyl group occupy the equatorial positions, while the nitrogen atoms of the NMe_2 groups reside in the axial positions. The N1–Ga–N2 bond angle of 161.85(7)° deviates from 180°, but the sum of the bond angles in the equatorial plane of **6** is 360°, which is a measure of the planarity of the equatorial groups. The two equatorial Ga–O bond lengths are identical within experimental error [1.8581(12) and 1.8598(13) Å], indicative of the same Ga–O σ-bond type. The Ga–N distances are 2.2446(15) and 2.2245(15) Å, significantly shorter than the sum of the van der Waals radii, suggesting a strong dative bonding interaction. The Ga–N bond lengths in **5** are longer than the Ga–N donor bond in **4** [2.033(12) Å], which is presumably a result of five- versus four-coordination at the gallium center. The Ga–N bond lengths in **5** are similar to those in related complexes.[21,22] Gallium bis(alkoxides) are still relatively rare complexes, with only a few published previously.[9,29,30] Related trigonal bipyramidal alkoxogallanes incorporating donor functionalized ligands include $[EtGa(OCH_2CH_2NMe_2)_2]$[9] and $[ClGa(OR)_2]$ (R = $CH_2CH_2NMe_2$, $C(CF_3)_2CH_2C(CH_3){=}NMe$, and

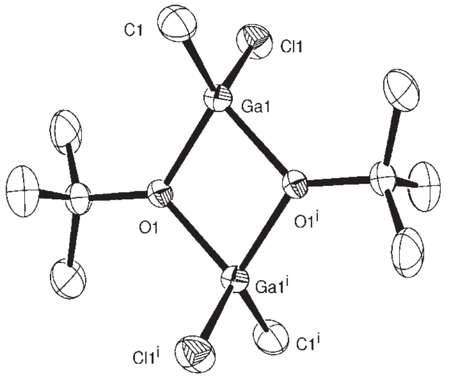


Figure 3. ORTEP representation of compound **7**. Thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity. Atoms marked 'i' are at the equivalent position $(1 - x, -1 - y, 1 - z)$.

$C(CF_3)_2CH_2NMe_2)$,[8,29] and all have Ga−O and Ga−N bond distances similar to those observed in **5**.

In order to investigate whether the chloride ion could be replaced to form a alkylgallium amido/alkoxide, compound **2** was treated with 1 equiv of a lithium silylamide. Reaction of **2** (prepared *in situ* according to the Experimental Section) with 2 equiv of $LiN(SiMe_3)_2$ in toluene, followed by refluxing for 24 h, afforded the dimeric methylgallium amido/alkoxide $[MeGa\{N(SiMe_3)_2\}(OCH_2CH_2OMe)]_2$ (**6**) as a yellow viscous oil (Scheme 1). Analytical and spectroscopic data confirmed the formation of compound **6**, with a peak being observed for the molecular ion at m/z = 638 in the mass spectrum, supporting the proposed dimeric structure. Fragments of the dimeric structure were also observed at m/z = 478 and 404, and an intense peak was seen at m/z = 319, corresponding to the monomeric structure, which may have arisen from the symmetric cleavage of the Ga_2O_2 ring during decomposition. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **6** showed peaks corresponding to the alkoxide, amido, and methyl ligands, which were observed in a 7:18:3 ratio. Peaks at 3.79, 3.35, and 3.25 ppm correspond to the OCH_2, CH_2OMe, and OCH_3 hydrogen environments in the alkoxide ligand, as well as a peak observed at 0.23 ppm assigned to $SiCH_3$ and a sharp single peak at 0.07 ppm for the Ga−Me environment. In the $^{13}C\{^1H\}$ NMR spectrum of compound **6**, peaks are observed for the alkoxide and amido ligand carbon environments, CH_2OMe, OCH_2, OCH_3 and $N(SiMe_3)_2$ (74.1, 62.0, 58.5, 5.1 ppm respectively), as well as a peak at 5.7 ppm for the Ga−Me carbon environment.

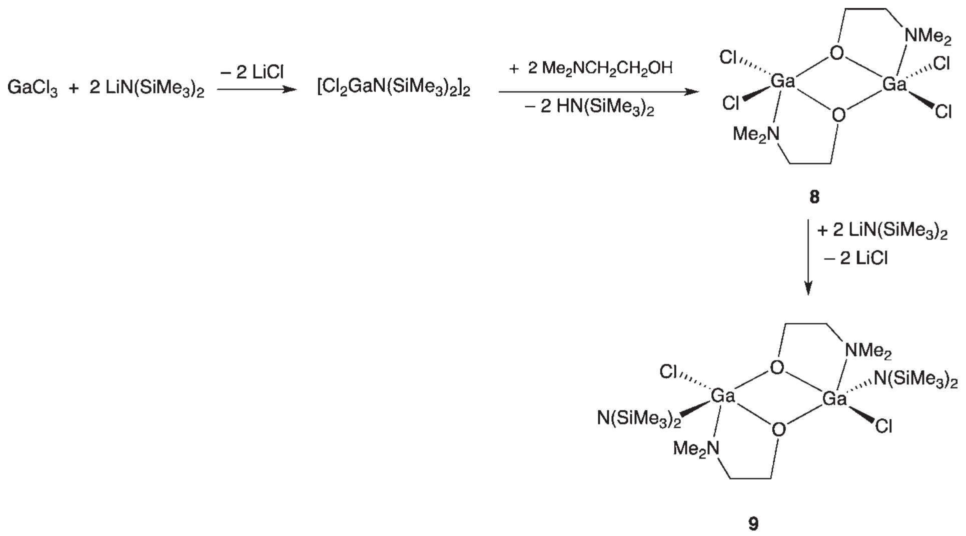
Unfortunately, X-ray-quality crystals could not be isolated from the oil. However, on preparing compound **6** *in situ* from compound **2** (which had been isolated and fully characterized, Scheme 1) and further reacting it with 1 equiv of ^{t}BuOH, a small yield of colorless crystals was obtained from the resulting yellow oil (**7**). This reaction was carried out in an attempt to exchange the amide groups in **6** for O^{t}Bu and form the compound $[MeGa(OCH_2CH_2OMe)(O^tBu)]_n$; however, analytical and spectroscopic data did not support the formation of this complex. Indeed, no peaks corresponding to the donor functionalized alkoxide ligand, OCH_2CH_2OMe, were observed in the ^1H NMR spectrum of **7**, and only peaks corresponding to Me−Ga and ^{t}Bu were seen at 0.22 and 1.20 ppm, respectively, in a 1:3 ratio. Analytical data and the mass spectrum of **7** suggested that the dimeric compound $[Me(Cl)GaO^tBu]_2$ had formed with the presence of the molecular ion at m/z = 384. The crystal structure of compound **7** was determined by X-ray crystallography; the results are shown in Figure 3 and Table 1. Selected bond lengths and angles are given in Table 2 and 3. Compound **7** crystallized into the monoclinic, $P2_1/c$ space group, and as shown in Figure 3, the compound adopts a dimeric molecular arrangement. The centrosymmetric, four-membered Ga_2O_2 ring that is common to this type of complex is planar.[21,22,24,25] The bridging oxygen atoms of the Ga_2O_2 centrosymmetric ring make up two of the corners of the gallium-centered tetrahedra, while methyl and chloro terminal groups make up the remaining two. Comparable bond lengths suggest that both methyl and chloro groups are tightly bound to both gallium centers [C1−Ga1 1.928(3) Å and Cl1−Ga1 2.1856(9) Å]. The difference in bond length between Ga1−O1^i [1.909(2) Å] and Ga1−O1 [1.916(2) Å] is not large enough to be statistically significant. The gallium-centered tetrahedra are slightly distorted, exhibiting bond angles which vary only slightly from the desired 109° seen in typical tetrahedra. The bond angles in the tetrahedra show a range of values from 106.44(7) to 119.98(13)° with the exception of O1−Ga1−O1^i [79.60(9)°]; this large deviation from 109° is due to the steric constraints of the Ga_2O_2 ring. A range of complexes, of the type $[R(Cl)GaOR']_2$, have been previously published, and the bond lengths and angles are comparable to those observed in compound **7** both when R = alkyl[39,40] and in related hydroxyl derivatives (i.e R′ = H).[41]

The formation of **7** is thought to be the result of incomplete formation of compound **6** when formed *in situ*, resulting in the presence of $[Me(Cl)Ga(OCH_2CH_2OMe)]_2$ (compound **2**). Thus, the addition of HO^{t}Bu to **2** simply resulted in exchange of the alkoxide group and formation of **7**, which preferentially crystallizes: test reactions show that **7** can be formed directly from **2** via the reaction shown in eq 1, according to ^1H NMR spectroscopy.

$$\underset{\mathbf{2}}{[Me(Cl)Ga(OCH_2CH_2OMe)]_2} + 2HO^tBu \rightarrow \underset{\mathbf{7}}{[Me(Cl)Ga(O^tBu)]_2} + 2HOCH_2CH_2OMe \qquad (1)$$

In general, the reaction of $GaCl_3$ with two equivalents of $LiN(SiMe_3)_2$ results in methyl group transfer and the formation of compound **1**. However, it is also possible for the methyl transfer not to occur, and the compound $[Cl_2GaN(SiMe_3)_2]_2$ can be formed *in situ* if only one equivalent of $LiN(SiMe_3)_2$ is added, which then further reacts with an alcohol. This is in contrast to indium where related reactions have been found to always result in methyl group transfer from the silyl group to the indium center.[37,42] Evidence for the lack of methyl transfer was obtained from the *in situ* reaction of $GaCl_3$ and $LiN(SiMe_3)_2$ followed by the addition of 2 equiv of $HOCH_2CH_2NMe_2$, as shown in Scheme 2. The reaction initially produced a yellow oil which, after sublimation, formed colorless crystals. Analytical and spectroscopic data suggested the formation of $[Cl_2Ga(OCH_2CH_2NMe_2)]_2$ (**8**) where no methyl transfer has occurred, rather than a product similar to compounds **2** and **3**, namely, $[Me(Cl)Ga(OCH_2CH_2NMe_2)]_2$. Therefore, no peak corresponding to Ga−Me was observed in the ^1H NMR spectrum of **8**; only peaks at 3.59, 2.57, and 2.11 ppm, assigned to OCH_2CH_2, CH_2NMe_2, and $N(CH_3)_2$, in a 1:1:3 ratio were found. In the mass spectrum of **8** taken in toluene, a peak was observed for the molecular ion at m/z = 457, which supports the proposed dimeric structure of **8**. Compound **8** is similar to the previously reported complex $[Cl_2Ga(OCH(CH_3)CH_2OMe)]_2$, which was prepared via the reaction between $[Cl_2GaNMe_2]$ and $HOCH(CH_3)CH_2OMe$.[29]

Scheme 2. Formation of Compounds 8 and 9



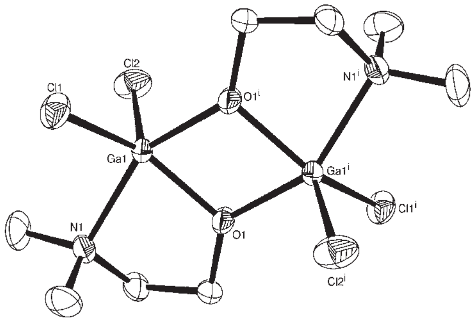


Figure 4. ORTEP representation of compound **8**. Thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity. Atoms marked 'i' are at the equivalent position (−*x*, −1 − *y*, −*z*).

The crystal structure of compound **8** was determined by X-ray crystallography, and the results are shown in Figure 4 and Table 1. Selected bond lengths and angles are given in Table 2 and 3. Compound **8** crystallized in the monoclinic, $P2_1/c$ space group and adopts a dimeric molecular arrangement. The centrosymmetric, four-membered Ga_2O_2 ring, which is common to this type of complex, is planar, and the bidentate ligand forms a five-membered ring. Each gallium atom in **8** adopts a distorted square-based pyramidal geometry with Cl2 in the axial position. The "degree of trigonality", τ, is a measure of how distorted a five-coordinate complex is away from the two ideals of square-based pyramidal ($\tau = 0$) and trigonal bipyramidal ($\tau = 1$).[43] The τ value of 0.17 indicates that the distortion away from ideal square-based pyramidal is obvious but not severe. The bridging alkoxide groups are located in equatorial positions, while the nitrogen atom of the alkoxide group is also in an equatorial position with the trans $O1^i-Ga-N1$ bond angle being 149.54(6)°. The other trans bond angle of 139.42(12) Å corresponds to the O1−Ga−Cl1 angle and demonstrates the slightly distorted square-based pyramidal nature of compound **8**. The Ga−O1 bond length [1.9200(12) Å] is slightly shorter than the bridging $Ga-O1^i$ bond distance [1.9491(12) Å], which is indicative of two active bonding Ga−O bond types. The longer Ga−N1 distance [2.0922(15) Å] in **8** can be attributed to N1→Ga dative bonding. The structure of compound **8** is similar to the related compound $[Cl_2Ga(OCH(CH_3)CH_2OMe)]_2$ with comparable bond lengths and angles. Similar distorted square-based pyramidal and also trigonal bipyramidal geometries at the metal center have also been observed in closely related intramolecularly stabilized diorganoalkoxometallanes of the type $[Me_2MOR]_2$ (M = Ga, In; R = $CH_2CH_2NMe_2$, CH_2CH_2OMe, $CH(CH_3)CH_2NMe_2$, and $CH(CH_3)CH_2OMe$).[21,22,24,25] These structures are also dimeric in the solid state and consist of planar, or nearly planar, M_2O_2 rings with comparable bond lengths and angles.

In order to investigate the reactivity of **8** and form a chlorogallium amido/alkoxide complex similar to **6**, the reaction of **8** with two equivalents of $LiN(SiMe_3)_2$ was carried out in toluene with stirring for 30 min, then under reflux conditions for 24 h (Scheme 2). A yellow viscous oil was isolated after workup, the analytical and spectroscopic data for which indicated that the dimeric chlorogallium amido/alkoxide $[ClGa\{N(SiMe_3)_2\}(OCH_2CH_2NMe_2)]_2$ (**9**) had been formed. The ^1H NMR spectrum of **9** had peaks corresponding to the alkoxide and $N(SiMe_3)_2$ ligands in a 1:1 ratio. Peaks at 3.90, 2.31, and 2.24 ppm correspond to the OCH_2, CH_2CH_2N, and NCH_3 hydrogen environments in the alkoxide ligand, respectively, and were in a 1:1:3 ratio. An additional peak observed at 0.08 ppm can be assigned to the amide ligand, $N\{Si(CH_3)_3\}_2$. In the mass spectrum of **9**, a peak was observed for the molecular ion at *m*/*z* = 704, which supports the proposed dimeric structure. An intense peak observed at *m*/*z* = 352 corresponding to the monomeric structure may have arisen from the symmetric cleavage of the Ga_2O_2 ring during decomposition.

■ CONCLUSIONS

The synthesis and characterization of a range of chloro- and alkylgallium alkoxide and mixed amido/alkoxide complexes have been described. The reaction of $GaCl_3$ with excess lithium silylamide $LiN(SiMe_3)_2$ results in methyl group transfer to afford $[Me(Cl)GaN(SiMe_3)_2]_2$ (**1**) in good yield. The reaction of $[Me(Cl)GaN(SiMe_3)_2]_2$ with 2 equiv of an alcohol results in amine elimination and the formation of dimeric $[Me(Cl)GaOR]_2$ (**2**, R = CH_2CH_2OMe; **3**, R = $CH(CH_3)CH_2NMe_2$). In contrast, the reaction of $[Me(Cl)GaN(SiMe_3)_2]_2$ with 1 equiv of alcohol

($HOCH_2CH_2NMe_2$) yields the intermediate complex [$MeGa(Cl)\{N(SiMe_3)_2\}(\mu_2\text{-}OCH_2CH_2NMe_2)Ga(Cl)Me$] (**4**), whereas an alternative monomeric complex, [$MeGa(OCH_2CH_2NMe_2)_2$] (**5**), can be isolated from the reaction of [$Me(Cl)GaN(SiMe_3)_2$]$_2$ with excess alcohol ($HOCH_2CH_2NMe_2$). Further reaction of [$Me(Cl)GaOR$]$_2$ with $LiN(SiMe_3)_2$ yields the expected methylgallium amido alkoxide complex, [$MeGa\{N(SiMe_3)_2\}OR$]$_2$ (**6**, R = CH_2CH_2OMe). The reaction of [$Me(Cl)Ga(OCH_2CH_2OMe)$]$_2$ (**2**) with ^{t}BuOH resulted in simple alkoxide exchange to yield [$Me(Cl)Ga(O^tBu)$]$_2$ (**7**). The reaction of $GaCl_3$ with one equivalent of lithium silylamide $LiN(SiMe_3)_2$ resulted in the formation of [$Cl_2Ga\{N(SiMe_3)_2\}$]$_2$ rather than [$Me(Cl)GaN(SiMe_3)_2$]$_2$, suggesting that two equivalents of $LiN(SiMe_3)_2$ are required for the methyl group transfer to occur. Treatment of [$Cl_2Ga\{N(SiMe_3)_2\}$]$_2$ with alcohol resulted in the formation of dimeric [$Cl_2Ga(OR)$]$_2$ (**8**, R = $CH_2CH_2NMe_2$), which was further reacted with $LiN(SiMe_3)_2$ to form [$MeGa\{N(SiMe_3)_2\}OR$]$_2$ (**9**). This is in contrast to indium where reaction with $LiN(SiMe_3)_2$ was observed to always result in methyl group transfer, suggesting that the reactions are more facile for indium.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic data in CIF format for the structures of compounds **4**, **5**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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