Designated Molecular Deconstruction: The Facile Transformation of $Ga(N(SiMe_3)_2)(OSiMe_3)_2py$ (py = pyridine) to GaN

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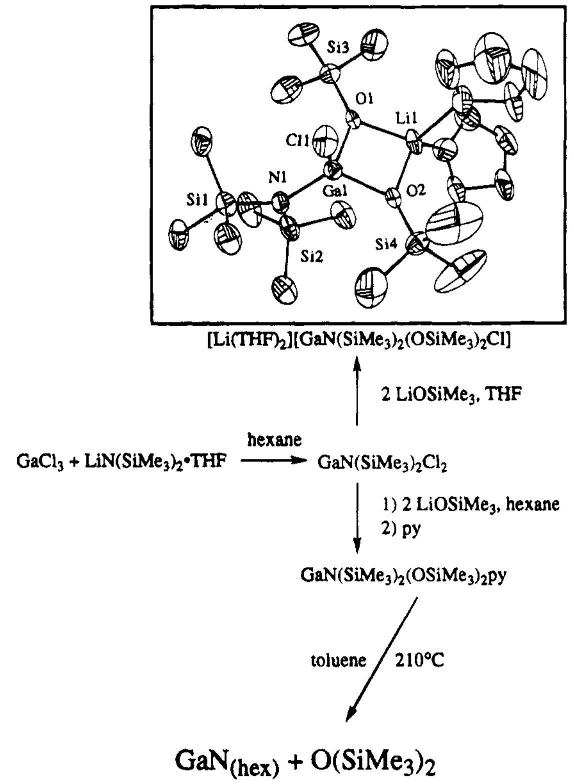
Scheme 1



The recent resurgence of interest in III−V nitrides, and in particular GaN and InN, stems from their potential use in semiconductor device applications.[1,2a] The wide bandgap of GaN (3.39 eV) along with its stability under high temperatures and harsh conditions holds promise for a range of applications that include use in optoelectronic devices operating in the blue region of the visible spectrum. In contrast, the properties of InN remain less understood, and applications for this material may be in heterostructure devices with GaN or as $In_xGa_{1-x}N$ alloys. The synthesis of bulk powders of InN and GaN has been achieved by a variety of methods which employ temperatures from 600 to 900 °C.[3] Cyclotrigallazane, $[H_2GaNH_2]_3$, has been used as a single source molecular precursor for bulk GaN at 200 °C.[4] Thin films of GaN have been grown using molecular precursors by CVD and MBE techniques.[2]

As part of our interest in alternative solid-state synthetic methods, we are exploring low-temperature synthetic routes based on molecular precursors. Our approach to the synthesis of III−V nitrides is to design a molecular precursor with not only a metal−nitrogen core but also an attendant ligand system which has a facile elimination pathway to form volatile side products. One such effort has been the preparation of single-source molecular precursors to group III nitrides (GaN, InN) which take advantage of the formation of strong Si−O and Si−Cl bonds in the elimination reaction as thermodynamic driving forces. To this end, we have prepared a family of complexes with the general formula $Ga[N(SiMe_3)_2]_xCl_{3-x}$.[5] Reaction of these compounds with $Li(OSiMe_3)$ leads to the formation of mixed trimethylsilylamido−siloxo complexes for which the elimination of hexamethyldisiloxane or trimethylsilyl chloride may provide a driving force to formation of the nitride. Similar approaches have been applied to the preparation of materials that have gallium bound to arsenic[6] and phosphorus.[7] Herein we report the preliminaryresults of these efforts including the synthesis of “self-destructing” precursors and thermal transformations which demonstrate their ability to form GaN.

The interaction of $Ga(N(SiMe_3)_2)Cl_2THF$ with $Li(OSiMe_3)THF$ takes one of two routes depending on the presence of coordinating solvents. When the reaction is carried out in THF the compound $[Li(THF)_2][Ga(N(SiMe_3)_2)(OSiMe_3)_2Cl]$ (**1**) was produced.[8,9] Assignment of this formula was based on spectroscopic data and satisfactory elemental analysis. Structural characterization by single-crystal X-ray diffraction confirmed the molecular connectivity of this complex (Scheme 1). The structure consists of a gallium center in a pseudotetrahedral coordination sphere composed of a hexamethyldisilazido ligand (Ga−N1 1.883(10) Å), two siloxo oxygens (Ga−O1 1.865(9) Å, Ga−O2 1.850(9) Å), and a chloride ligand (Ga−Cl1 2.210(4) Å). A bridging interaction of the lithium cation with the lone pair of electrons on each of the siloxide oxygen atoms generates a molecular core which is made up of a planar Ga−O1−Li−O2 distorted square (O1−Ga1−O2 92.8(4)°, Ga1−O2−Li1 91.1(9)°, O1−Li1−O2 87.9(10)°, Ga1−O1−Li1 88.0(8)°). Consistent with the spectroscopic data are the presence of two THF ligands completing the coordination of the Li cation. It is presumably the stabilizing

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[8] The reagents and reaction stoichiometries for the preparation of complexes **1**−**4** are indicated in Scheme 1 and eq 1. Complete synthetic procedures for these compounds are given in the supplementary material.

[9] Satisfactory elemental analyses (C, H, N) were obtained for compounds **1**−**4**. ^1H NMR data (C_6D_6): **1** δ 3.48 (m, 4H, THF), 1.33 (m, 4H, THF), 0.55 (s, 18H, NSi*Me*$_3$), 0.33 (s, 18H, OSi*Me*$_3$)); **2** δ 8.52 (m, 2H, py), 6.87 (m, 1H, py), 6.54 (m, 2H, py), 0.37 (s, 18H, NSi*Me*$_3$), 0.29 (s, 18H, OSi*Me*$_3$); **3** δ 8.54 (m, 2H, py), 6.94 (m, 1H, py), 6.67 (m, 2H, py), 0.53 (s, 18H, NSi*Me*$_3$), 0.23 (s, 18H, OSi*Me*$_3$); **4** δ 8.44 (m, 4H, py), 6.96 (m, 2H, py), 6.64 (m, 4H, py), 0.50 (s, 18H, NSi*Me*$_3$), 0.32 ppm (s, 27H, OSi*Me*$_3$).

effect of excess THF that results in the formation of this bimetallic species. This complex meets the criteria that we set forth as a precursor to GaN.

Compound **1** is thermally stable up to 120 °C, after which point its thermal rearrangements result in a plethora of signals in the methyl region of the NMR. Thus, it appears that $[Li(THF)_2][Ga(N(SiMe_3)_2)(OSiMe_3)_2Cl]$ is a poor GaN precursor. However, among the products of this transformation are $(Me_3Si)_2O$ and $(Me_3Si)_2NH$ which could be identified by ^1H NMR. Based on the idea that the presence of chloride and/or lithium in **1** may be inhibiting the smooth rearrangement of this species, attempts were made to remove LiCl. Abstraction of the chloride by silver tetraphenylborate and removal of LiCl by refluxing **1** in toluene were both ineffective in generating the LiCl-free material. Therefore, synthesis in a noncoordinating solvent was attempted.

A similar synthetic procedure using hexane as the solvent yielded an oily material from which a crystalline solid could be isolated upon addition of pyridine (Scheme 1). The assignment of the formula $Ga(N(SiMe_3)_2)(OSiMe_3)_2py$ (**2**) for this complex was confirmed by elemental analysis and spectroscopic (IR, ^1H NMR) characterization.[8,9] A monomeric, four-coordinate structure, similar to that of the gallium center in **1**, is proposed.

When this material was heated to 155 °C and the thermal rearrangement is monitored by ^1H NMR, loss of the two methyl singlets for the starting material, formation of free pyridine and growth of a new peak at 0.11 ppm, consistent with formation hexamethyldisiloxane, was observed. GC/MS of the mother liquor from this reaction confirmed the presence of $O(SiMe_3)_2$.[10] The gray solid which precipitated from a similar reaction (210 °C, toluene) showed no noticeable change when subjected to strong mineral acids. The powder X-ray diffraction pattern of the native material did not show any features. However, after annealing under a nitrogen atmosphere at only 350 °C (8 h) the onset of crystallinity is evident. A rapid (5 min) anneal at 900 °C substantially increases the crystalline nature of this material. Figure 1 shows the evolution of crystallinity of a sample of the solid upon annealing to the indicated temperatures. Comparison of the diffraction patterns with the graphical representation for the hexagonal (wurtzite) phase for gallium nitride, also in Figure 1, shows there to be an excellent match with our experimental data.[11] We speculate that the features of this spectrum are broad due to the low crystalline order of the material as might be anticipated for a refractory material which is produced in solution and subsequently undergoes little if any of the self–ordering that would occur at high temperatures.

The possibility of a similar pathway to InN directed us to explore the synthesis of the indium analogs to compounds **1** and **2**. Unlike $GaCl_3$, $InCl_3$ is not soluble in hydrocarbon solvents and only moderately soluble in weakly coordinating solvents such as diethyl ether. Consequently, an analogous set of reactions was carried out using hexane-soluble $InCl_3(THF)_3$ as a starting material. The reaction of $InCl_3(THF)_3$ with $Li(N(SiMe_3)_2)$-THF and 2 equiv of $LiOSiMe_3$ led to the formation of a complex which could be crystallized only after the addition of pyridine. The formulation of this compound as $[Li(py)_2][In(N(SiMe_3)_2)(OSiMe_3)_2Cl]$ (**3**) was suggested by spectroscopic (NMR, IR) evidence and elemental analysis (eq 1).[8,9] The material is assumed to have a similar structure to **1** (Scheme 1). Reaction of $InCl_3$-THF_3 with $Li(N(SiMe_3)_2)THF$ followed by addition of 3 equiv of $LiOSiMe_3$ and subsequent addition of excess pyridine resulted in the isolation of $[Li(py)_2][In(N(SiMe_3)_2)(OSiMe_3)_3]$ (**4**) as suggested by spectroscopic characterization and confirmed by elemental analysis and a single-crystal X-ray diffraction study (eq 2).[5,9] Complex **4** exhibits a structure analogous to that of **1** (Scheme 1).

$$InCl_3(THF)_3 \xrightarrow[2LiO(TMS)THF]{LiN(TMS)_2THF} \underset{\mathbf{3}}{[Li(py)_2][In(N(TMS)_2)(OTMS)_2Cl]} \quad (1)$$

$$InCl_3(THF)_3 \xrightarrow[3LiO(TMS)THF]{LiN(TMS)_2THF} \underset{\mathbf{4}}{[(py)_2Li][InN(TMS)_2(TMSO)_3]} \quad (2)$$

Subsequent thermal studies (heating to 220−260 °C) of both **3** and **4** demonstrate that these compounds are more robust to rearrangement than their gallium counterparts and refuse to rearrange to InN at these temperatures. Further investigations of these and related precursors are ongoing.

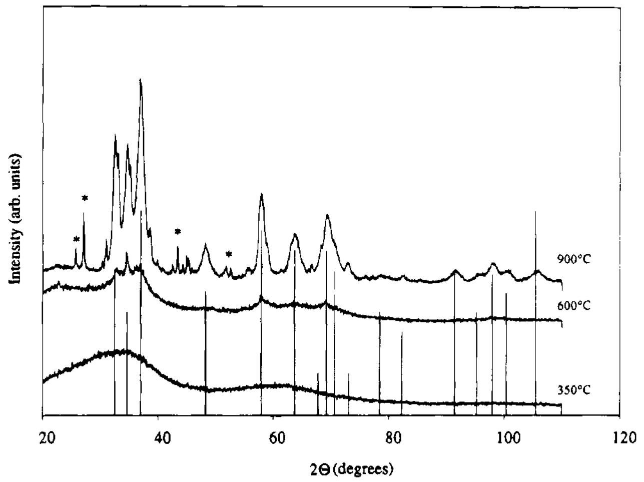

Figure 1. X-ray powder diffraction results for GaN obtained from $Ga(N(SiMe_3)_2)(OSiMe_3)_2py$. The patterns were obtained from a sample heated under an N_2 atmosphere to the specified temperatures. The calculated diffraction pattern for hexagonal GaN is shown as a series of vertical lines in the figure. Asterisks indicate as yet unidentified material.

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Supplementary Material Available: Experimental procedure for the synthesis of **1**−**4** and description of the structural solution, tables of atomic positions, thermal parameters, crystallographic data, bond distances and angles, and an ORTEP drawing for compound **1** (11 pages); structure factor table (31 pages). Ordering information is given on any current masthead page.

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(12) X-ray fluorescence spectroscopy indicated %Si less than the detection limit of the instrument. Elemental analysis consistently found %C < 4% and %H < 0.7%.