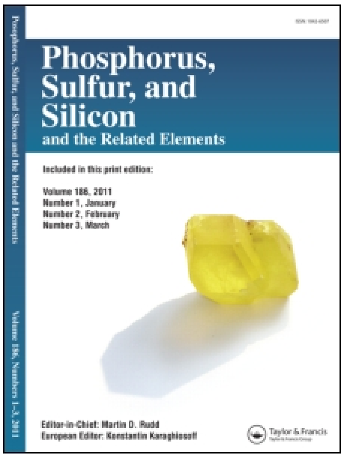

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NEW PRECURSORS TO GROUP 13 NITRIDES

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In searching for ideal unimolecular precursors to group 13 nitrides we have begun examining two new classes of molecules having the formulae, $R_nM(tet)_{3-n}$ (n = 0, 1, 2) and Bn_2MN_3 (where M = Al, Ga; tet = 5-phenyl-1H-tetrazole, and Bn= benzyl). These may be anticipated to undergo low-temperature decompositions according to equations 1 and 2, respectively. The absence of carbon bonds to the nitrogen ultimately incorporated into the material, as well as the presence of excess nitrogen are viewed as particularly advantageous. Preliminary results focused on the formation of aluminum nitride are presented herein.

$$M(tet)_3 \text{ ------> } MN + N_2 + PhCN \qquad (1)$$

$$Bn_2MN_3 \text{ ------> } MN + N_2 + Bn_2 \qquad (2)$$

Keywords: precursor, aluminum nitride

INTRODUCTION

The nitrides of aluminum (AlN) and gallium (GaN) are wide, direct band gap materials (6.2 and 3.45 eV, respectively). Solid solutions of these two materials span the entire UV range.[1] In solid solutions with InN (1.9 eV), a continuum of materials with band gaps in the range of 1.9 eV to 6.2 eV may be obtained (having the thermodynamically preferred wurtzite (hexagonal) form). A more limited range is also theoretically accessible for the zinc-blende polytypes. They have useful physical properties such as high temperature stability, high thermal conductivity and high elastic stiffness. Thus, there is a broad range of potential uses.[2] Some prominent examples include uses as light-emitting diodes[3], high temperature electronics[4], field effect transistors and photodetectors[5]. Due to preferential elimination of nitrogen in these materials low-temperature routes are needed for their formation.

A unimolecular, or single-source, approach may be useful in this regard. By comparison to separate source techniques, the single source precursor approach offers advantages such as reduced toxicity and flammability of reagents, better control of stoichiometry, a simplified reactor design and dramatically reduced deposition temperatures (but still in the range necessary for the formation of crystalline films and particles).[6] Moreover, such a method might become "atom efficient" in both the group 13 and group 15 element. This approach is normally designed to be conducted with inert carrier gases at low pressures. However, use of N_2 or NH_3 as the carrier gas often alleviates problems associated with preferential nitrogen loss during the deposition process.

There are also limitations with regards to the types of molecules that can be used. In a comparison study between precursors containing N-C bonds (eg. $[Me_2Al(NMe_2)]_2$, $[Me_2Al(aziridine)]_3$ and $[Et_2Al\{NH(^tBu)\}]_2$) and those without such bonds (utilizing the azide, N_3^-, group as the nitrogen source), it was clearly established that the first type of precursor led to poor films with a great deal of carbon and oxygen contamination.[7] The use of the azide group (N_3^-) alleviates this problem. In their simplest manifestation they are of the sort, $[R_2MN_3]_3$ (M = Al; R = Me and Et, [12,8]; M = Ga; R = Me[12b,9], Et[10]). They can be decomposed to AlN and GaN at relatively low temperatures through OMCVD.

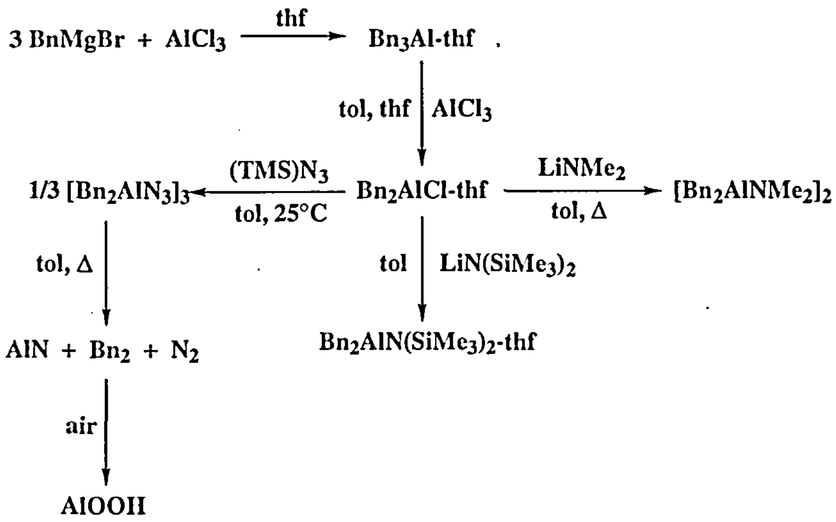
Epitaxial films of GaN can be prepared with $[(Me_2N)_2GaN_3]_2$.[11] Other studies have focused on $[(CH_2)_3NMe_2Ga(N_3)_2]$,[12] $[Ga(N_3)_3]_\infty$[13] and base-stabilized derivatives,[18] $[Cl_2GaN_3]_3$ which contains no carbon or hydrogen, and Cl_2GaN_3-NMe_3.[14]

Taken as a whole, however, past work into unimolecular approaches to nitride materials has demonstrated two principles: 1) N-C bonds should not be present as they lead to carbon incorporation 2) a source of excess nitrogen from some source may be necessary due to elimination of N_2 from the material. Our study will focus on two types of new precursors. The first combines the demonstrated success of the azide group with the ease of elimination of benzyl from aluminum. The second is a precursor using a "new"[15] nitrogen rich group, phenyl-tetrazole.

RESULTS AND DISCUSSION

A. Benzyl Derivatives of Aluminum

Benzyl is an ideal group to be homolytically eliminated from a group 13 element. Its homolysis requires less energy than needed for Me, Et, nPr or tBu. This is important since the loss of the ligands on the group 13 element can represent a severe limitation on the low-temperature decomposition of a precursor molecule. For instance, the Me group of $[Me_2GaAs(^tBu)_2]_2$ eliminates at temperatures above 425°C.[16] The benzyl group may be expected to homolyze at lower temperatures. It has been of demonstrated utility in the formation of metal oxide materials[17] and in the formation of group 14-16 combinations.[18]



SCHEME 1. The formation of $[Bn_2AlN_3]_3$

A good starting point for the preparation of benzyl derivatives of aluminum is the tri-benzyl derivative. It can be used in a redistribution reaction to form Bn_2AlCl which can be isolated or used in situ. Due to the solubility problems inherent to the use of NaN_3, the best route for introducing the $-N_3$ group on Al is with $TMSN_3$. After TMSCl elimination the targeted Bn_2AlN_3 derivative forms. When the reaction is conducted at ambient temperatures the yields are excessively low. However, attempting to improve the yield by heating in toluene leads to immediate decomposition of the molecule with the formation of AlN (potentially nanoparticulate). Further work is being conducted on a better preparation of Bn_2AlN_3; however, it is clear that it must be handled gently to avoid incipient decomposition. Base-stabilization is being explored as a means of stabilizing the molecule. A base stabilized derivative, $Bn_2AlN(SiMe_3)_2$ has been isolated and structurally characterized (Figure 1). Structurally characterized (Figure 2) $[Bn_2AlNMe_2]_2$ is dimeric in the presence of thf. Monomerization is clearly easier to induce in the presence of bulkier amides on aluminum. For Bn_2AlN_3, then, the use of bases stronger than thf will be necessary.

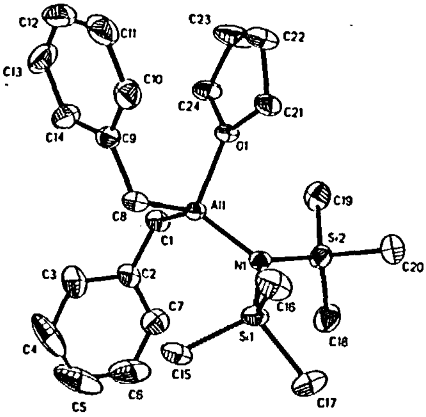


FIGURE 1. Molecular Structure of $Bn_2AlN(SiMe_3)_2$-thf

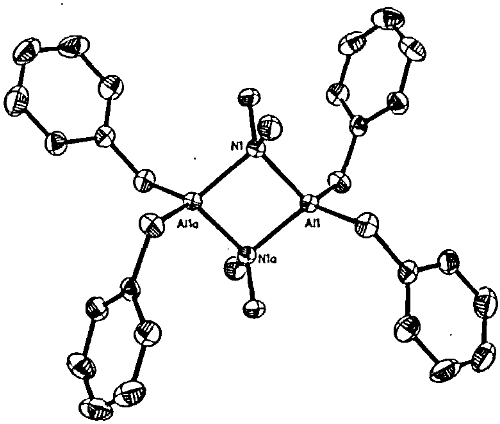
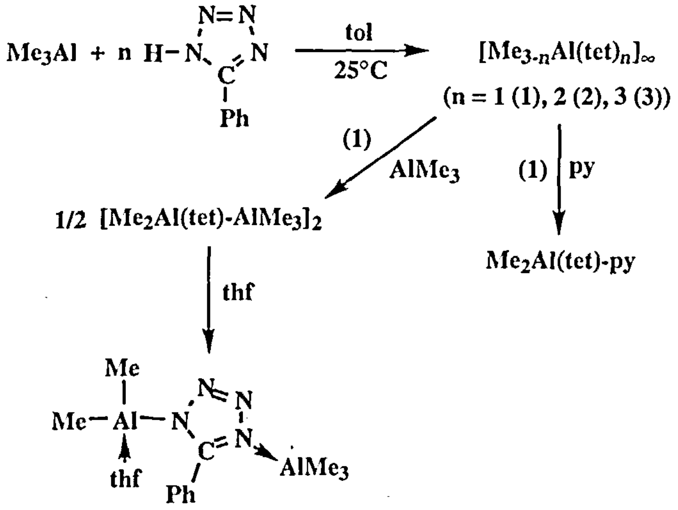


FIGURE 2. Molecular Structure of $[Bn_2AlNMe_2]_2$

B. Tetrazole Derivatives of Aluminum

Three type of aluminum tetrazoles can be obtained by combining the tetrazole with $AlMe_3$ in the appropriate stoichiometry (Scheme 2). These are presumably polymeric in solution and in the solid state. Only the Me_2Al- derivative is soluble in toluene and so most of the



SCHEME 2. Tetrazole derivatives of aluminum.

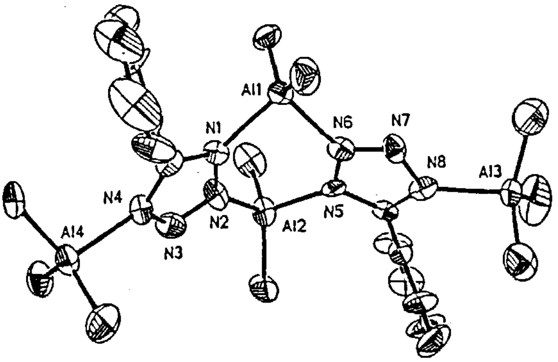
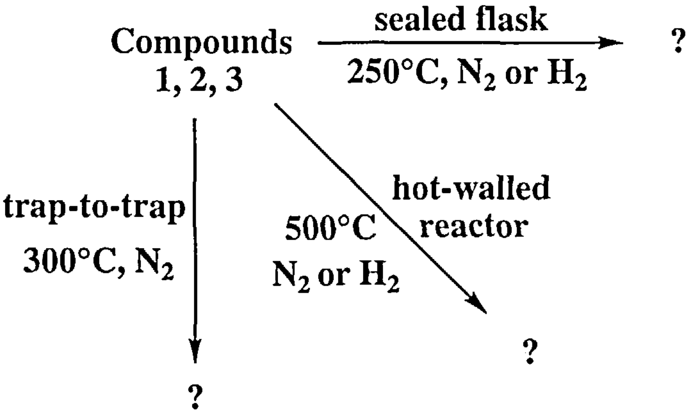


FIGURE 3. Molecular structure of $[Me_2Al(tet)\text{-}AlMe_3]_2$

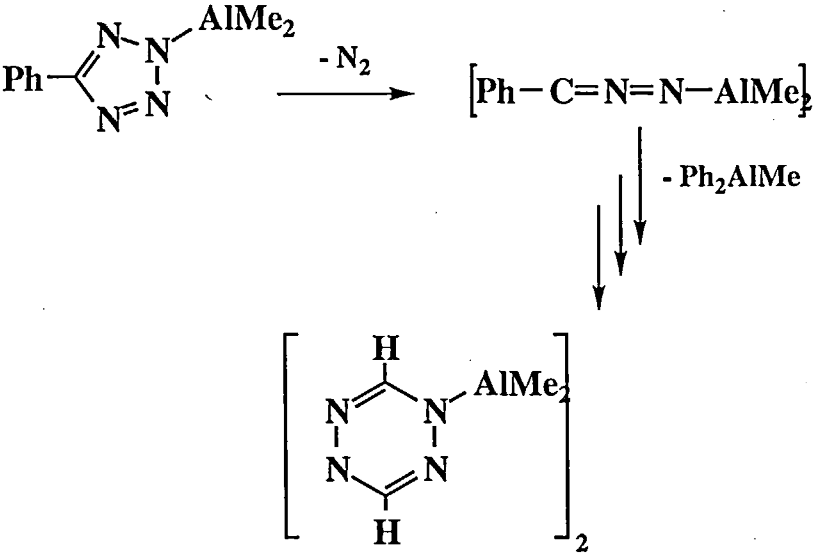
work has involved this species. It can be de-polymerized by adding either a Lewis base such as pyridine or a Lewis acid, such as $AlMe_3$. This compound is a dimer in the solid state (Figure 3). The Al_2N_4 six-membered ring is in a boat conformation with the Al atoms from 0.5 - 0.6 Å above the plane of the four nitrogen atoms. It can be further reduced in oligomerization by addition of thf. This leads to a four-coordinate monomeric species.



SCHEME 3. General decomposition conditions.

Each of the three polymeric derivatives, $R_nM(tet)_{3-n}$ ($n = 0, 1, 2$), was examined with regards to AlN formation. Under a variety of conditions (Scheme 3) clearly-defined products were not obtained. In most cases an insoluble solid resulted from the heating with the concomitant formation of an oily solid. In a test decomposition the $Me_2Al(tet)$ material was heated for several days with a cold-water sublimation unit (Equation 3). When the heating was terminated there was a white solid on the sublimation unit and a yellow solid remaining in the flask. Spectroscopic characterization of the yellow solid indicated that it was the starting material. The white material did not demonstrate a Ph-group in either the ^{1}H NMR or IR spectra. The Me_2Al group was, however, confirmed. Based upon elemental analyses and mass-spectral data a de-phenylated tetrazole derivative is tentatively assigned (Scheme 4). Such a coupled product has some precedent in the literature of tetrazoles although not in combination with a bound metal.[15] Further work is being conducted to fully characterize this product and to determine the utility of the transformation leading to a dephenylated tetrazole.

$$[Me_2Al(tet)]_\infty \xrightarrow[N_2,\ days]{250°C} \text{sublimate} + \text{starting material} \qquad (3)$$



SCHEME 4. Tentative $Me_2Al(tet)$ decomposition products

ACKNOWLEDGMENTS.

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