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Reaction of Al(^{t}Bu)$_3$ with Ethylene Glycol: Intermediates to Aluminum Alkoxide (Alucone) Preceramic Polymers

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The reaction of Al(^{t}Bu)$_3$ with ethylene glycol ($HOCH_2CH_2OH$) in hexane yields “alucone” polymers, $[Al(^tBu)_{2x}(OCH_2CH_2O)_{1.5-x}]_n$ ($0.3 \leq 2x \leq 0.8$), with the concurrent formation of $[Al_2(^tBu)_3(OCH_2CH_2O)(OCH_2CH_2OH)]$ (**1**). If the reaction is carried out in Et_2O solution, then $[Al_3(^tBu)_5(OCH_2CH_2O)_2]$ (**2**) may be isolated. The molecular structure of compound **1** consists of a dimer formed by the alkoxide termini of two ligands bridging the Al(^{t}Bu) and Al(^{t}Bu)$_2$ units. The Al(^{t}Bu) moiety is chelated by the nonbridging oxygens of the glycolate ligands, one of which remains protonated. Compound **2** consists of two Al(^{t}Bu)$_2$ units and two glycolate ligands forming a cryptand-like 10-membered heterocycle; the Al(^{t}Bu) unit is positioned capping the four oxygen atoms. As with the previously reported ethoxy-substituted alucone polymers, $[Al(OR)_{2x}(OCH_2CH_2O)_{1.5-x}]_n$, thermolysis of $[Al(^tBu)_{2x}(OCH_2CH_2O)_{1.5-x}]_n$, results in the formation of η-alumina (η-Al_2O_3) as determined by XRD. This is in contrast to the formation of γ-Al_2O_3 from the thermolysis of alumoxanes, $[Al(O)(OR)_x(OH)_{1-x}]_n$, and may be rationalized by the structural relationship of compounds **1** and **2**, and hence the alucones, to Bayerite rather than the boehmite core observed for alumoxanes.

Introduction

The sol−gel (solution−gelation) process is a useful chemical synthesis technique for the formation of ceramics at temperatures far lower than conventional ceramic methods.[2] An additional advantages of the sol−gel method is the ability to produce thin films and coatings, rather than simply powders or solid bodies. The sol−gel approach generally involves four stages: dispersion, gelation, drying, and firing. A stable liquid dispersion or *sol* of the colloidal ceramic precursor is initially formed in a solvent with appropriate additives. By changing concentration (aging) or pH, the dispersion is polymerized to form a solid dispersion or *gel*. The excess liquid is removed from this gel by drying and the final ceramic is formed by firing the gel at higher temperatures. Although a large range of materials have been prepared by sol−gel methods, in order for future developments to be made, there must be a better understanding of the pathways, kinetics, mechanisms, and the structures of the species present in sol−gels.[3]

Aluminum oxide (alumina) sol−gels were originally prepared from simple nitrate salts,[4] however, the strong interactions of the freshly precipitated alumina gels with ions from the precursor solutions makes it difficult to prepare these gels in pure form.[5] To avoid this complication alumina gels may be prepared from the hydrolysis of aluminum alkoxides, Al(OR)$_3$. Although this method was originally reported by Adkins in 1922,[6] it was not until the 1970s when Teichmer and coworkers[7] reported the preparation of alumina aerogels and Yoldas[8] showed that transparent ceramic bodies can be obtained by the pyrolysis of suitable alumina gels, that interest increased significantly. As part of a study into the structures of sol−gel materials formed from the hydrolysis of aluminum siloxides,[9] we reported that contrary to contemporaneous proposals, alumina gels or alumoxanes[10] are not polymeric chains, but consist of aluminum oxide−hydroxide nanoparticles with organic substituents on the surface.[11] Furthermore, the core structure is related to that of the mineral boehmite. This discovery has led us to develop simple routes to alumoxanes (alumina gels) directly from boehmite.[12,13]

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(10) Alumoxanes, $[Al(O)(X)]_n$, were traditionally defined as oligomeric or polymeric materials consisting of an Al−O backbone with pendant substituents X. However, a broader definition is that of a molecular species containing at least one oxo group (O^{2-}) bridging (at least) two aluminum atoms, i.e., a compound containing an Al−O−Al subunit.

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Thermolysis of alumoxanes results in the initial formation of γ-Al_2O_3 with subsequent conversion to α-Al_2O_3. The temperature at which this conversion occurs is dependent on the alumoxane particle size.[14] This same transformation series is observed for boehmite itself upon dehydration,[15] thus the phase formed from any alumoxane is expected from their boehmite-like core structure, and this is indeed observed. However, Rees and Hesse,[16−18] have shown that different phases are formed from the thermolysis of alucones. Alucones are polymeric aluminum alkoxide materials with carbon-containing backbones, i.e., ···Al—O—R—O—Al···, rather than the Al−O−Al backbone associated with alumoxanes. Unusually, thermolysis of alucones yields η-alumina (η-Al_2O_3) and not γ-Al_2O_3 as observed for alumoxanes. Rees and Hesse rationalized this interesting result as being due to the lamellar character of their alucone polymers. However, since the phase transformations observed for aluminum sol−gels (alumoxanes) is related to the core structure of the alumoxane, it suggested to us that the core structure of the alucones is responsible for the formation of η-Al_2O_3 and not γ-Al_2O_3 upon thermolysis.

Alucones were originally described by Schlenker[19] in 1958 and subsequently in several technical reports from U.S. Borax in the 1960s.[20] The simplest alucones are formed from the reaction of $Et_2Al(OEt)$ with ethylene glycol (e.g., eq 1).[16−18]

$$Et_2Al(OEt) + HOCH_2CH_2OH \rightarrow [Al(OEt)(OCH_2CH_2O)]_n + 2\ EtH \quad (1)$$

Partially or fully cross-linked alucones may be prepared by subsequent reaction with a larger fraction of ethylene glycol. The structures shown in Figure 1 were proposed by Rees and Hesse for the non-cross-linked and cross-linked alucone polymers based upon solid-state NMR spectroscopy and in comparison with known structures for aluminum alkoxides.[16−18]

Our interest in the relationship between the structures of molecular precursors and the phases formed from these precursors[21] prompted a study of the reaction of ethylene glycol with $Al(^tBu)_3$ to better understand the structure of the alucone polymers. The results of this study are presented herein.

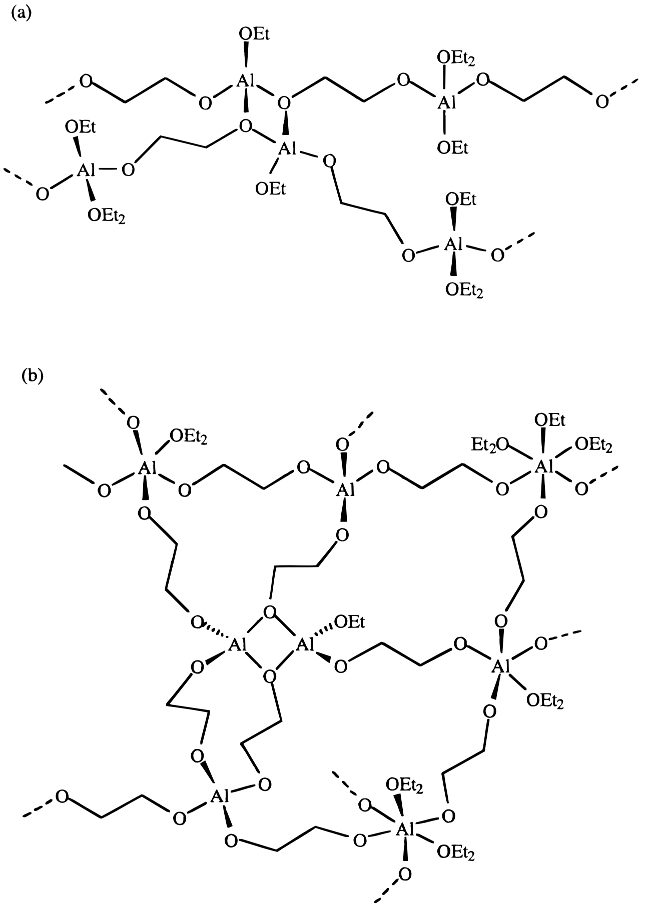

Figure 1. Proposed structures of non-cross-linked (a) and cross-linked (b) ethoxy alucones prepared in Et_2O. (After Rees, W. S., Jr.; Hesse, W. *Inorganic and Organometallic Polymers*; ACS Symposium Series 572; American Chemical Society: Washington, D.C., 1998; Vol. II, p 165.)

Results and Discussion

Reaction of $Al(^tBu)_3$ with Ethylene Glycol. The reaction of ethylene glycol with 2 equiv of $Al(^tBu)_3$ in hexane results in a large quantity of insoluble material being formed, which analyzes as an alucone, $[Al(^tBu)_{2x}(OCH_2CH_2O)_{1.5-x}]_n$, see below. In addition, a low yield of $[Al_2(^tBu)_3(OCH_2CH_2O)(OCH_2CH_2OH)]$ (**1**), is isolated (see the Experimental Section). No alucone is formed if the reaction is carried out in Et_2O solution using a 1:1 molar ratio; however, in this case $[Al_3(^tBu)_5(OCH_2CH_2O)_2]$ (**2**) is isolated as the soluble product. Compounds **1** and **2** were characterized by NMR spectroscopy and their structures determined by X-ray crystallography.

The molecular structure of $[Al_2(^tBu)_3(OCH_2CH_2O)(OCH_2CH_2OH)]$ (**1**) is shown in Figure 2; selected bond lengths and angles are given in Table 1. The molecular structure of compound **1** consists of a dimer formed by the alkoxide termini of two ligands bridging the $Al(^tBu)$ and $Al(^tBu)_2$ units, Al(1) and Al(2), respectively. The resulting Al_2O_2 core is common to dialkylaluminum alkoxides.[22] The 5-fold coordination of the $Al(^tBu)$ moiety is a result of the chelation by the nonbridging oxygens of both glycolate ligands, one of which remains proto-

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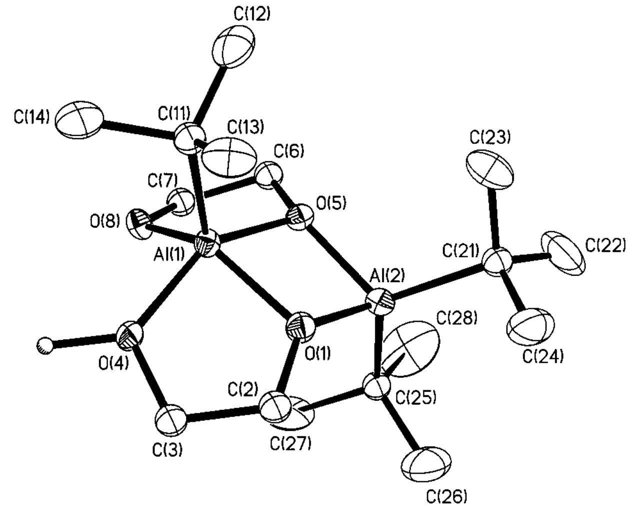

Figure 2. Molecular structure of $[Al_2(^tBu)_3(OCH_2CH_2O)(OCH_2CH_2OH)]$ (**1**). Thermal ellipsoids shown at the 30% level, and hydrogen atoms attached to carbon are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in $[Al_2(^tBu)_3(OCH_2CH_2O)(OCH_2CH_2OH)]$ (1)

Al(1)−O(1)	1.882(7)	Al(1)−O(4)	1.859(6)
Al(1)−O(5)	1.902(6)	Al(1)−O(8)	1.815(6)
Al(1)−C(11)	1.96(1)	Al(2)−O(1)	1.815(7)
Al(2)−O(5)	1.827(6)	Al(2)−C(21)	1.97(1)
Al(2)−C(25)	1.98(1)		
O(1)−Al(1)−O(4)	82.5(3)	O(1)−Al(1)−O(5)	75.9(3)
O(1)−Al(1)−O(8)	134.9(3)	O(1)−Al(1)−C(11)	115.6(3)
O(4)−Al(1)−O(5)	144.7(3)	O(4)−Al(1)−O(8)	92.7(3)
O(4)−Al(1)−C(11)	104.3(4)	O(5)−Al(1)−O(8)	83.6(3)
O(5)−Al(1)−C(11)	110.1(4)	O(8)−Al(1)−C(11)	109.0(4)
O(1)−Al(2)−O(5)	79.4(3)	O(1)−Al(2)−C(21)	110.0(4)
O(1)−Al(2)−C(25)	112.4(4)	O(5)−Al(2)−C(21)	114.7(4)
O(5)−Al(2)−C(25)	112.8(4)	C(21)−Al(2)−C(25)	120.3(5)
Al(1)−O(1)−Al(2)	102.8(3)	Al(1)−O(5)−Al(2)	101.6(3)

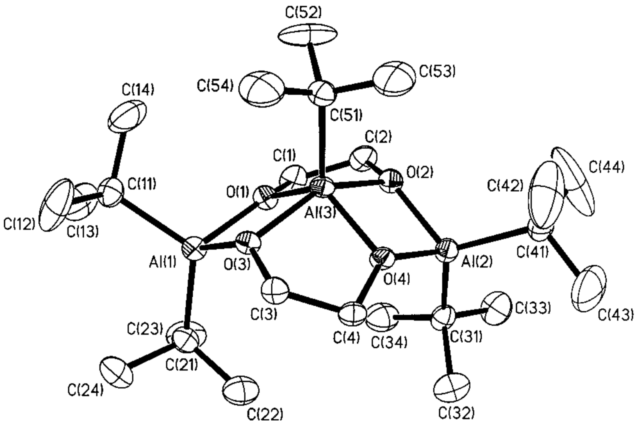

Figure 3. Molecular structure of $[Al_3(^tBu)_5(OCH_2CH_2O)_2]$ (**2**). Thermal ellipsoids shown at the 30% level, and hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in $[Al_3(^tBu)_5(OCH_2CH_2O)_2]$ (2)

Al(1)−O(1)	1.865(3)	Al(1)−O(5)	1.848(3)
Al(1)−C(11)	1.991(5)	Al(1)−C(15)	2.000(5)
Al(2)−O(4)	1.845(3)	Al(2)−O(8)	1.871(3)
Al(2)−C(21)	2.006(6)	Al(2)−C(25)	1.996(6)
Al(3)−O(1)	1.856(3)	Al(3)−O(4)	1.904(3)
Al(3)−O(5)	1.899(3)	Al(3)−O(8)	1.854(3)
Al(3)−C(31)	2.002(5)		
O(1)−Al(1)−O(5)	79.4(1)	O(1)−Al(1)−C(11)	106.9(2)
O(1)−Al(1)−C(15)	119.5(2)	O(5)−Al(1)−C(11)	116.1(2)
O(5)−Al(1)−C(15)	112.5(2)	C(11)−Al(1)−C(15)	116.9(2)
O(4)−Al(2)−O(8)	79.6(1)	O(4)−Al(2)−C(21)	113.0(2)
O(4)−Al(2)−C(25)	115.6(2)	C(21)−Al(2)−C(25)	116.8(2)
O(1)−Al(3)−O(4)	84.5(1)	O(1)−Al(3)−O(5)	78.4(1)
O(1)−Al(3)−O(8)	120.2(3)	O(1)−Al(3)−C(31)	119.7(2)
O(4)−Al(3)−O(5)	146.1(2)	O(4)−Al(3)−O(8)	78.5(1)
O(4)−Al(3)−C(31)	107.2(2)	O(5)−Al(3)−O(8)	85.0(1)
O(5)−Al(3)−C(31)	106.6(2)	O(8)−Al(3)−C(31)	120.1(2)
Al(1)−O(1)−Al(3)	101.5(1)	Al(1)−O(5)−Al(3)	100.5(1)
Al(2)−O(4)−Al(3)	100.4(1)	Al(2)−O(8)−Al(3)	101.3(1)

nated. Unusually, the geometry around Al(1) is closer to a square-based pyramidal structure [i.e., O(1)−Al(1)−O(8) = 134.9(3)°, O(4)−Al(1)−O(5) = 144.7(3)°] than the more common trigonal-bipyramidal geometry. In contrast, the geometry about Al(2) is essentially the same as found for dimeric alkoxides, $[(^tBu)_2Al(\mu\text{-}OR)]_2$.[23] All of the Al−C and Al−O bond lengths are within their respected ranges,[24] and there are no significant intermolecular interactions. The alcohol hydrogen was located in the X-ray difference map as being bonded to O(4) and refined, see Figure 2. There is no evidence for intramolecular hydrogen bonding between O(4) and O(8). The ^{1}H NMR spectrum for compound **1** shows distinct resonances for the OCH_2CH_2O groups, implying that the alkoxide and alcohol groups on Al(1) do not undergo proton exchange, consistent with the location of the alcohol hydrogen in the X-ray crystal structure of compound **1**.

The molecular structure of $[Al_3(^tBu)_5(OCH_2CH_2O)_2]$ (**2**) is shown in Figure 3; selected bond lengths and angles are given in Table 2. The molecular structure of compound **2** consists of a trimer formed by the alkoxide termini of two ligands bridging two $Al(^tBu)_2$ units [Al(1) and Al(2)] and a central $Al(^tBu)$ unit [Al(3)]. The resulting Al_3O_4 core is similar to that observed for $[Al_3(Me)_5\{OCH_2C(H){=}C(H)CH_2O\}_2]$,[25] and similar to the M_3N_4 and $M_3O_2N_2$ cores in a wide range of Group 13 trimetallic compounds.[26−28] Unlike the five-coordinate aluminum in compound **1**, the geometry around Al(3) in compound **2** is closer to a trigonal-bipyramidal geometry [O(4)−Al(3)−O(5) = 146.1(2)°, O(1)−Al(3)−O(8) = 120.2(2)°]. The geometries about Al(1) and Al(2) are essentially the same as found for dimeric alkoxides, $[(^tBu)_2Al(\mu\text{-}OR)]_2$.[23] All the Al−C and Al−O bond lengths are within their respected ranges,[23] and there are no significant intermolecular interactions.

Although compound **1** is a minor product from the reaction of Al(^{t}Bu)$_3$ with ethylene glycol, and compound **2** is formed in a coordinating solvent, it is worth considering the pathway by which they are formed as

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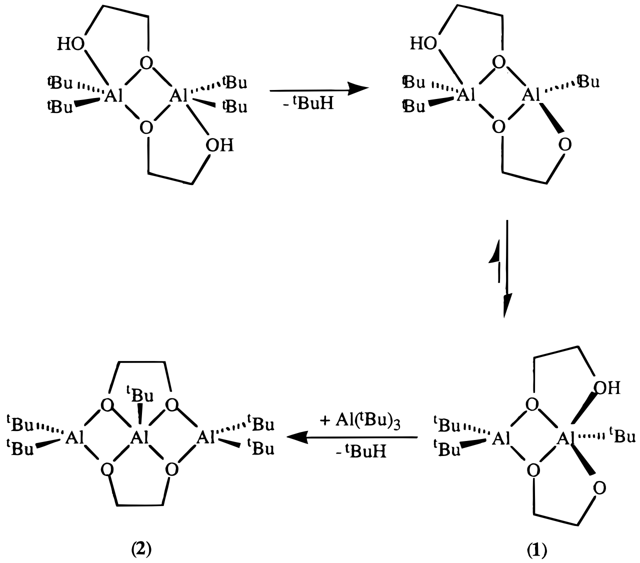
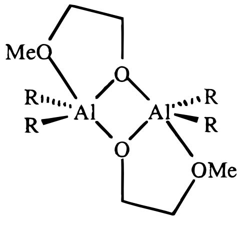
Scheme 1. Proposed Pathway for the Formation of $[Al_2(^tBu)_3(OCH_2CH_2O)(OCH_2CH_2OH)]$ (1) and $[Al_3(^tBu)_5(OCH_2CH_2O)_2]$ (2)



it relates to the structure of the *tert*-butyl alucone polymers. We have previously isolated the products from the reactions of AlR_3 with 2-methoxyethanol (**I**).[29]



(**I**)

Given the related nature of the ligands, and the structure of the related glycolate, $Ba[Al_2(C_2H_4O_2)_4]$,[30] it is reasonable to propose a similar initial product, see Scheme 1. Subsequent intramolecular alkane elimination would result in an isomer of compound **1** in which the remaining alcohol is coordinated to the $Al(^tBu)_2$ moiety. While alkane elimination from this isomer could provide the route to the alucone (see below), the $Al(^tBu)_2$ moiety is more sterically hindered (two *tert*-butyl groups versus one *tert*-butyl group on the aluminum center) and thus a ligand reorganization to compound **1** is likely (Scheme 1). Reaction of compound **1** with an excess of $Al(^tBu)_3$ would yield compound **2**.

Synthesis and Characterization of *tert*-Butyl Alucones. The addition of $Al(^tBu)_3$ to a hexane solution of ethylene glycol results in the immediate formation of a white precipitate, which is isolated by filtration. This material is essentially insoluble in common organic solvents. Further insoluble material is formed from the filtrate upon cooling for a day. Although this material is formed from solution, it is insoluble once formed. As described above, compound **1** is the only soluble product. While both insoluble samples are determined to be *tert*-butyl alucones (see the Experimental Section) their respective formulas are distinct.

In agreement with the results of Rees and Hesse for ethoxy alucones,[16−18] the *tert*-butyl alucones have a general formula of $[Al(^tBu)_{2x}(OCH_2CH_2O)_{1.5-x}]_n$ ($0.3 \leq 2x \leq 0.8$) as determined by microprobe analysis. The product that precipitates upon the initial reaction analyzes as an alucone with a higher *tert*-butyl content (i.e., $x \approx 0.4$). Conversely, the alucone that is formed slowly from solution analyzes as having a lower *tert*-butyl content (i.e., $x \approx 0.15$). It has been suggested that if the reaction of an aluminum compound with ethylene glycol is carried out with an excess of glycol, then the alucone will be “cross-linked”.[16−18] Upon the basis of this prior proposal and the observed *tert*-butyl content of the alucones formed, it appears that the initial reaction of $Al(^tBu)_3$ with ethylene glycol results in the immediate formation of an insoluble lightly cross-linked alucone. Subsequently, a highly cross-linked material is formed at a lower rate. However, the extent of the cross-linking is also dependent on the temperature and time of the reaction.

The morphology of the *tert*-butyl alucones has been determined by scanning electron microscopy (SEM). As was observed previously,[16−18] the more cross-linked the alucone (i.e., the greater the glycol content) the more “open” the morphology. Conversely, low cross-linking (i.e., high *tert*-butyl content) results in a glassy morphology.

The solid-state ^{13}C CPMAS NMR spectra of the *tert*-butyl alucones exhibit a single *tert*-butyl resonance $[C(CH_3)_3]$ at 29.1 ppm irrespective of the extent of ethylene glycol substitution (i.e., the value of x). In both samples of *tert*-butyl alucone, there are two signals which may be assigned to the ethylene glycol ligand (δ = 61.6 and 57.2 ppm). As is expected, the relative intensity of the glycol CH_2 resonances as compared to the *tert*-butyl resonance is dependent on the composition of the alucone; however, the relative intensities of the two CH_2 resonances also varies with glycol content. This is in agreement with the proposal by Rees and Hesse of two types of glycol ligation: backbone and cross-linking.[16−18] Unfortunately, there is insufficient differences in chemical shift as compared to the solution spectra of compounds **1** and **2** to confirm this assignment. ^{27}Al CPMAS NMR spectra of the *tert*-butyl alucones exhibit peaks due to both six- and five-coordinate aluminum. This is in agreement with the published results of Rees and Hesse.[16−18] as well as previous work on aluminoglycolates.[31]

Upon the basis of the foregoing, we propose that the *tert*-butyl alucones are structurally related to compounds **1** and **2**. Thus, the lightly cross-linked alucones may be rationalized as being formed by self-condensation of compound **1** (Scheme 2a). The resulting polymer would consist of asymmetric units where every alternate aluminum is fully chelated by two glycolate ligands. The cross-linking glycols would obviously replace the *tert*-butyl groups shown in Scheme 2. We note that the structure of the $[Al_3(OCH_2CH_2O)_5(OCH_2CH_2OH)_2]^-$ anion reported by Kemmitt and co-workers[32] consist of

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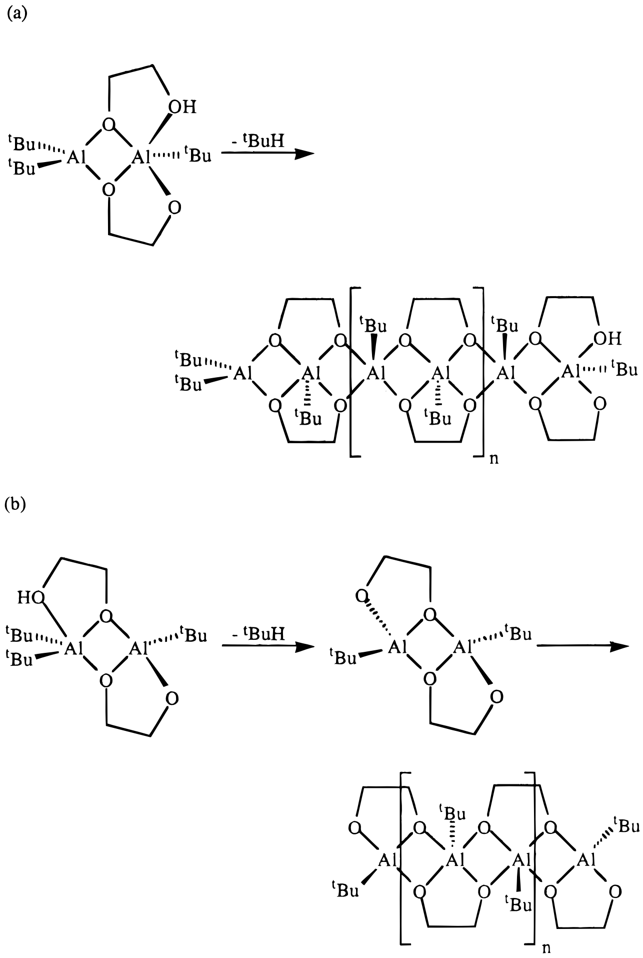
Scheme 2. Proposed Formation and Structure of *tert*-Butyl Alucones



trialuminum unit where two of the aluminum atoms are fully chelated by two glycolate ligands. Alternatively, condensation and oligomerization of the isomer of compound **1** shown as a possible intermediate in Scheme 1, would result in a symmetric polymer where each aluminum is chelated by a single glycolate ligand (Scheme 2b). At this time we cannot differentiate either model, or determine if both are present; however, since compound **1** does not appear to convert to an alucone, the latter is favored. It should be noted that both structural pictures agree with our own spectroscopic data and that previously reported.[16−18]

Thermolysis of *tert*-Butyl Alucones. The thermal decomposition of the *tert*-butyl alucones was studied by thermogravimetric/differential thermal analyses (TG/DTA). The *tert*-butyl alucones decompose at ∼100 °C with no further mass loss observed above 370 °C. The decomposition appears to occur in two steps, with the position and rate being dependent on the *tert*-butyl content. Thus, the differential thermal analysis (DTA) of the alucones with a higher *tert*-butyl content indicates two distinct exotherms (116 and 278 °C), in contrast to the low *tert*-butyl alucones which exhibit a single broad exotherm at 240 °C. The final mass after pyrolysis in air at 900 °C agrees with the aluminum analysis, see the Experimental Section.

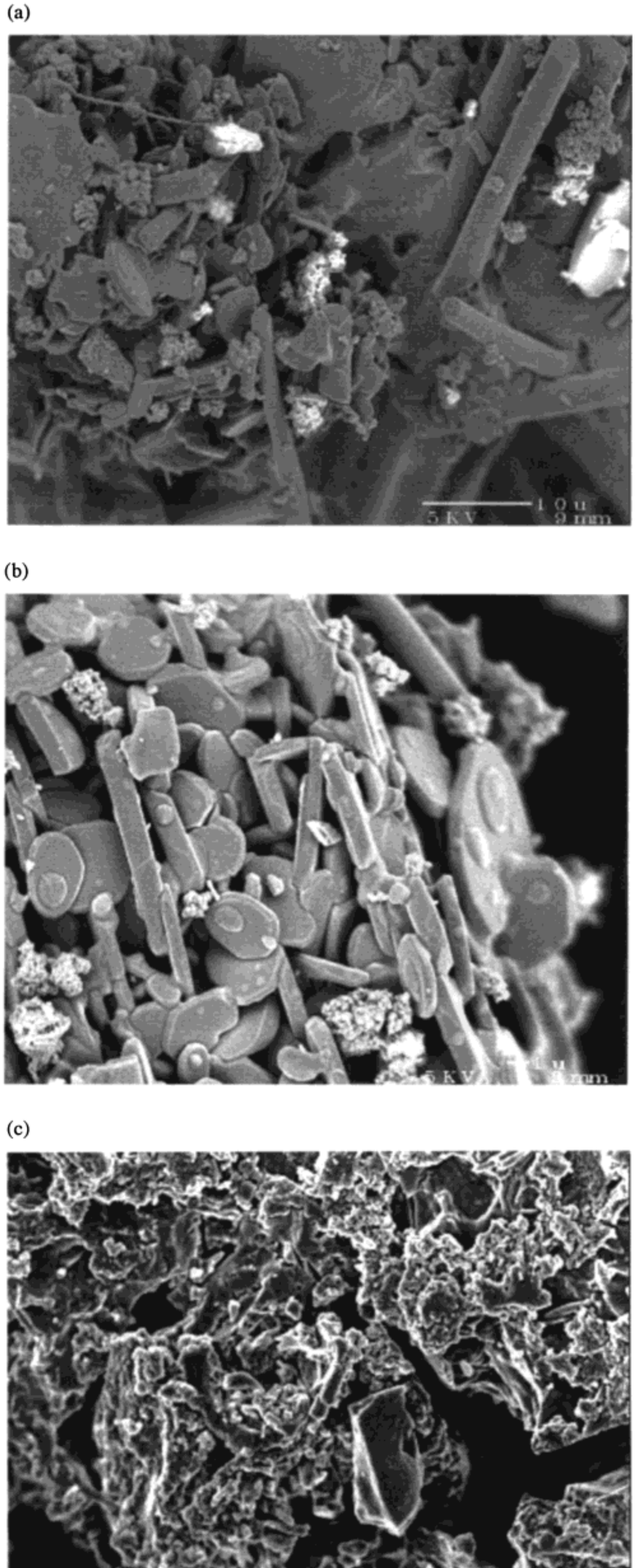


Figure 4. Scanning electron microscopy (SEM) images of the ceramic formed upon thermolysis of (a and b) $[Al(^tBu)_{0.8}(OCH_2CH_2O)_{1.1}]_n$ and (c) $[Al(^tBu)_{0.3}(OCH_2CH_2O)_{1.35}]_n$, at 1100 °C.

The morphologies of the ceramic formed upon thermolysis of the *tert*-butyl alucones, determined by SEM, are shown in Figure 4. The morphology of the final ceramic is generally similar irrespective of the formula

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(32) Gainsford, G. J.; Kemmitt, T.; Milestones, N. B. *Inorg. Chem.* **1995**, *34*, 5244.

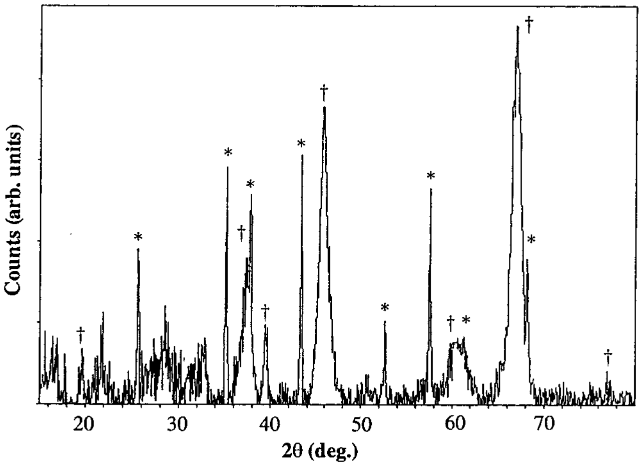

Figure 5. XRD of the ceramics formed from the *tert*-butyl alucones sintered at 1000 °C for 24 h. Peaks due to η-Al_2O_3 (JCPDS 04-0875) and α-Al_2O_3 (corundum, JCPDS 42-1468) are marked with daggers (†) and asterisks (*), respectively.

of the alucone, having a low pore density and high porosity. However, it is interesting to note that the ceramic formed from alucones with high *tert*-butyl content have additional features including: rods and disks, see Figure 4, parts a and b, respectively. However, the differences in morphology are not apparent in the X-ray diffraction (XRD) of the powdered ceramics. XRD of the ceramics formed from the *tert*-butyl alucones sintered at 1000 °C for 24 h (Figure 5) exhibit the peaks for η-Al_2O_3 (JCPDS 04-0875) along with a smaller amount of α-Al_2O_3 (corundum, JCPDS 42-1468).[33] It should be noted that thermolysis of the alucones is in contrast to the thermolysis of glycolate−alumoxanes prepared from boehmite. The latter resulting in the formation of γ-Al_2O_3 with subsequent conversion to α-Al_2O_3.[34]

It is interesting to note that the samples formed from alucones with a higher *tert*-butyl content have a greater proportion of η-Al_2O_3 to α-Al_2O_3. This also suggests that the rods and disks shown in parts a and b of Figures 4 may be related to the presence of η-Al_2O_3. Since the η-Al_2O_3 to θ-Al_2O_3 transformation ordinarily occurs below 900 °C, it appears that the stabilization of η-Al_2O_3 is a common property of the alucone polymers as proposed previously.[16−18]

Structural Relationship of *tert*-Butyl Alucones to Gibbsite and Bayerite. η-Alumina (η-Al_2O_3) is ordinarily formed from the thermolysis of $Al(OH)_3$, either gibbsite or bayerite.[35] The structures of gibbsite and bayerite are similar, both consisting of the same basic layers of Al−OH octahedra,[36] with the difference between the two minerals being the relative positions of the hydroxides in successive layers. Clearly in the case of the alucones where no hydrolysis reaction occurs, neither gibbsite or bayerite is present, and the formation of η-Al_2O_3 is most unexpected. Rees and Hesse rationalizatized that the lamellae morphology of the alucone polymers was responsible. However, upon the basis of a comparison of the structures of compounds **1** and **2**, our proposed structures of the alucones, and those of gibbsite and bayerite, we suggest the following alternative possibility.

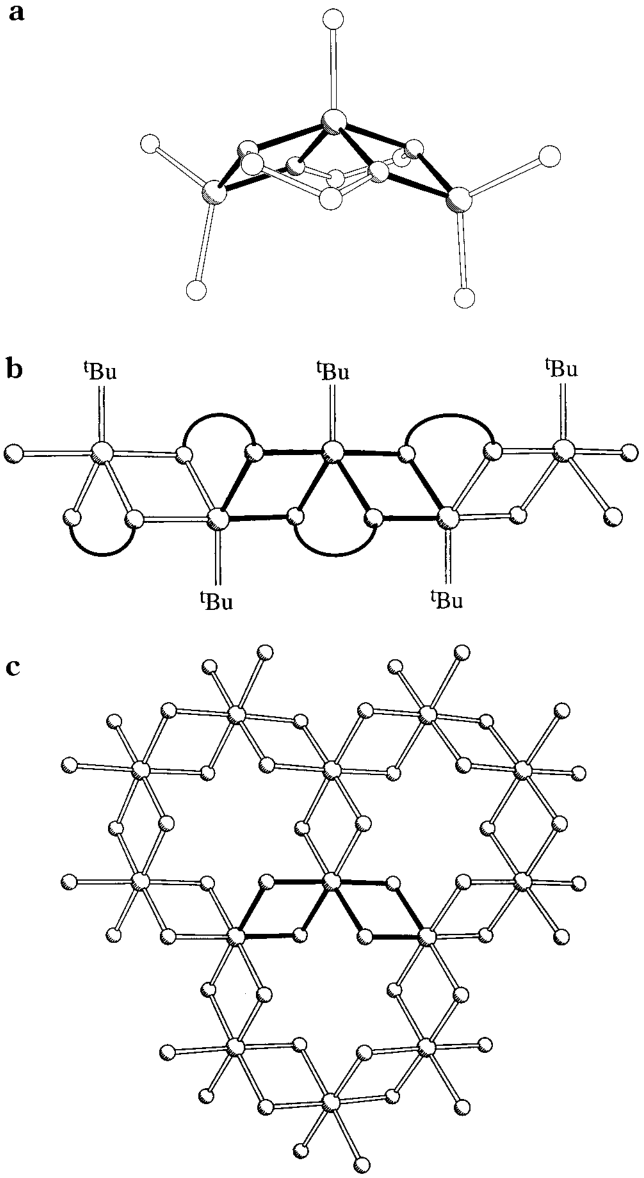

Figure 6. Core structures of (a) $[Al_3(^tBu)_5(OCH_2CH_2O)_2]$ (**2**) and (b) the proposed structure of the *tert*-butyl alucone (the glycol "CH_2CH_2" fragments are represented as a curve for simplicity). The solid bonds represents the structural fragment present in the mineral gibbsite and/or bayerite (c).

As noted in the Introduction, we have previously demonstrated that alumina sol−gels (alumoxanes) have a boehmite-like core[11] and that thermolysis of alumoxanes results in the initial formation of γ-Al_2O_3 with subsequent conversion to α-Al_2O_3. Given that the thermolysis of the mineral boehmite [Al(O)(OH)] results in the formation of γ-Al_2O_3 and then α-Al_2O_3, it is therefore reasonable that alumoxanes, having a boehmite-like (condensed) core, should also form these phases. It can be clearly seen from the highlighted sections in Figure

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(33) It should be noted that no intermediate phases were observed and γ-Al_2O_3 was not observed at any time during the thermolysis and/or sintering.

(34) (a) Inoue, M.; Kondo, Y.; Inui, T. *Chem. Lett.* **1986**, 1421. (b) Inoue, M.; Kondo, Y.; Inui, T. *Inorg. Chem.* **1988**, *27*, 215. (c) Inoue, M.; Kominami, H.; Inui, T. *J. Chem. Soc., Dalton Trans.* **1991**, 3331. (d) Inoue, M.; Kominami, H.; Inui, T. *J. Mater. Sci.* **1994**, *29*, 2459.

(35) (a) Tertian, R.; Papée, D. *J. Chim. Phys.* **1958**, *55*, 341. (b) Torkar, K.; Egghart, H.; Krischner, H.; Worel, H. *Montash. Chem.* **1961**, *92*, 512. (c) Sato, T. *J. Appl. Chem.* **1962**, *12*, 9.

(36) (a) Pauling, L. *Proc. Natl. Acad. Sci.* **1930**, *16*, 123. (b) Megaw, H. D. *Z. Kristallogr.* **1934**, *A87*, 185. (c) Montoro, V. *Ricerca Sci. Prog. Tecnol. Roma* **1942**, *13*, 565.

6 that there exists a definite structural similarity between the core of compound **2** (Figure 6a), the proposed structure of the alucones (Figure 6b) and the structure of gibbsite and/or bayerite (Figure 6c). Thus, the formation of η-Al_2O_3 from the alucones may be rationalized. The "open" structure of the alcones (as compared to that of the alumoxanes) results, upon thermolysis, in a structure similar to that formed upon the dehydration of "open" gibbsite and/or bayerite, and hence leads to the formation of η-Al_2O_3.

Conclusion

We have determined that the reaction of Al(^{t}Bu)$_3$ with ethylene glycol leads to the formation of insoluble alucones, $[Al(^tBu)_{2x}(OCH_2CH_2O)_{1.5-x}]_n$ ($0.3 \leq 2x \leq 0.8$). In addition, small molecular models of the alucones $[Al_2(^tBu)_3(OCH_2CH_2O)(OCH_2CH_2OH)]$ (**1**) and $[Al_3(^tBu)_5(OCH_2CH_2O)_2]$ (**2**), have been isolated and structurally characterized. Upon the basis of the structures of compounds **1** and **2**, we propose that the differences observed between the ceramic phases formed from the thermolysis of the alucones and the more common alumoxanes, $[Al(O)_x(OH)_y(X)_z]_n$, is inherently due to their structural relationships to the minerals gibbsite (bayerite) and boehmite, respectively. If such a relationship is indeed the controlling factor, then this provides a rational approach to phase specific synthesis of aluminum oxide ceramics.

Experimental Section

Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra. IR spectra (4000−400 cm^{-1}) were obtained using an Nicolet 760 FT-IR infrared spectrometer. IR samples were prepared as Nujol mulls between KBr plates. NMR spectra were obtained on Bruker AM-250 and Avance 200 spectrometers using C_6D_6 solutions. Chemical shifts are reported relative to internal solvent resonances (^{1}H and ^{13}C) and external $[Al(H_2O)_6]^{3+}$ (^{27}Al). ^{13}C CPMAS NMR spectra were obtained on a Bruker Avance 200 spectrometer. Elemental analysis was determined by WDS microprobe analysis on a Cameca SX-50 electron microprobe, relative to calibration standards. Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. XRD data was collected on a Siemens D5000 diffractometer. FESEM studies were performed on JEOL JSM-6320F field emission scanning microscope. The synthesis of Al(^{t}Bu)$_3$ was performed according to the literature methods.[37] Ethylene glycol was obtained from Aldrich and was used without further purification.

Reaction of Al(^{t}Bu)$_3$ with $HOCH_2CH_2OH$ in Hexane. A solution of ethylene glycol (0.13 g, 2.0 mmol) in hexane (50 mL) was cooled to −78 °C. To this was added Al(^{t}Bu)$_3$ (0.8 g, 4.0 mmol), and the reaction allowed to warm to room temperature and stirred overnight. The insoluble precipitate (*alucone* polymer) was removed by filtration. The mother liquor was placed in the freezer (−20 °C), and a second batch of alucone was formed after 1 day. Refiltration and cooling for 1 week resulted in the formation of a small quantity of colorless crystals.

$[Al(^tBu)_{0.8}(OCH_2CH_2O)_{1.1}]_n$. Yield: ~50%. Analysis (calcd, %): Al, 19.39 (19.45). TGA (calcd, %): 35.5 (36.7). ^{13}C CPMAS: δ 61.6 (major, OCH_2), 57.2 (minor, OCH_2), 29.1 [C(CH_3)$_3$].

$[Al(^tBu)_{0.3}(OCH_2CH_2O)_{1.35}]_n$. Yield: ~20%. Analysis (calcd, %): Al, 21.40 (21.55). TGA (calcd, %): 41.6 (43.0). IR (cm^{-1}): 3696 (w), 3585 (w), 2697 (m), 1357 (s), 1259 (s), 1185 (m), 1059 (vs), 934 (m), 897 (s). ^{13}C CPMAS: δ 61.6 (minor, OCH_2), 57.2 (major, OCH_2), 29.1 [C(CH_3)$_3$].

Table 3. Summary of X-ray Diffraction Data

compound	$[Al_2(^tBu)_3(OCH_2CH_2O)$-$(OCH_2CH_2OH)]$ (**1**)	$[Al_3(^tBu)_5$-$(OCH_2CH_2O)_2]$ (**2**)
empirical formula	$C_{16}H_{36}Al_2O_4$	$C_{24}H_{53}Al_3O_4$
crystal size, mm	0.12 × 0.13 × 0.21	0.11 × 0.21 × 0.25
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$
a, Å	11.210(1)	25.340(5)
b, Å	14.314(2)	13.567(3)
c, Å	13.782(1)	18.623(4)
β, deg	97.489(6)	102.68(3)
V, Å^3	2192.6(3)	6246(2)
Z	4	8
D(calcd), g/cm^3	1.049	1.035
μ, cm^{-1}	1.40	1.44
temp, K	298	298
2θ range, deg	3.0−44.0	4.3−45.0
no. collected	2966	6179
no. ind	2810	3035
no. obsd	954 ($\|F_o\| > 6.0\sigma \|F_o\|$)	2121 ($\|F_o\| > 2.0\sigma \|F_o\|$)
weighting scheme	$w^{-1} = 0.04(\|F_o\|)^2 + \sigma(\|F_o\|)^2$	$w^{-1} = 0.04(\|F_o\|)^2 + \sigma(\|F_o\|)^2$
R	0.055	0.053
R_w	0.059	0.149
largest diff peak, eÅ^{-3}	0.29	0.42

$[Al_2(^tBu)_3(OCH_2CH_2O)(OCH_2CH_2OH)]$ (1). Yield: ~15%. Analysis (calcd, %): C, 56.6 (55.5); H, 10.1 (10.4). Mp > 230 °C. MS (EI, %): m/z 635 (2M$^+$ − ^{t}Bu, 18), 578 (2M$^+$ − 2^{t}Bu, 25), 519 (2M$^+$ − 2^{t}BuH − ^{t}Bu, 45), 375 $[Al_3(^tBu)_2(OCH_2CH_2O)_3$, 40]. ^{1}H NMR ($C_6D_6$): δ 3.50 (2H, m, CH_2), 3.48 [4H, d, J(H−H) = 3.9 Hz, CH_2], 3.14 (2H, m, CH_2), 1.32 [9H, s, C(CH_3)$_3$], 1.15 [9H, s, C(CH_3)$_3$], 1.12 [9H, s, C(CH_3)$_3$]. ^{13}C NMR (C_6D_6): δ 60.7 (OCH_2), 60.3 (OCH_2), 32.3 [C(CH_3)$_3$], 31.3 [C(CH_3)$_3$], 30.9 [C(CH_3)$_3$].

$[Al_3(^tBu)_5(OCH_2CH_2O)_2]$ (2). A solution of ethylene glycol (0.26 g, 4.0 mmol) in Et_2O (350 mL) was cooled to −78 °C. To this was added Al(^{t}Bu$_3$) (0.8 g, 4.0 mmol), and the reaction was allowed to warm to room temperature. After stirring overnight, the solution was placed in the freezer and crystals suitable for X-ray diffraction studies were formed. Subsequent reduction in the volume of the solution and cooling resulted in further quantities of colorless crystals. Yield: >70%. Mp: 166−168 °C. Analysis (calcd, %): Al, 16.71 (16.65). MS (EI, %): m/z 429 (M$^+$ − ^{t}Bu, 35), 57 (^{t}Bu, 43). IR (cm^{-1}): 1358 (m), 1259 (s), 1186 (m), 1059 (s, br), 898 (s). ^{1}H NMR (C_6D_6): δ 3.49 (8H, m, OCH_2), 1.28 [18H, s, C(CH_3)$_3$], 1.23 [9H, s, C(CH_3)$_3$], 1.03 [18H, s, C(CH_3)$_3$]. ^{13}C NMR (C_6D_6): δ 61.8 (OCH_2), 32.6 [C(CH_3)$_3$], 32.2 [C(CH_3)$_3$], 31.8 [C(CH_3)$_3$].

Thermolysis of *tert*-Butyl Alucones. The *tert*-butyl alucones were converted to alumina by heating in an alumina crucible in a tube furnace from 25 °C to 1000 °C at the rate of 10 °C min^{-1}, which was then maintained for 24 h. Samples were heated to lower temperatures for shorter soak times to confirm the presence/abscence of specific phases.

X-ray Crystallography. Crystals of $[Al_2(^tBu)_3(OCH_2CH_2O)(OCH_2CH_2OH)]$ (**1**) and $[Al_3(^tBu)_5(OCH_2CH_2O)_2]$ (**2**) were sealed in a glass capillaries under argon. Crystal and data collection and solution details are given in Table 3. Standard procedures in our laboratory have been described previously.[38] Data were collected on either an Enraf-Nonius CAD-4 (**1**) or Rigaku four-circle diffractometer (**2**) equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz and polarization effects. The structures were solved by using direct methods SHELXS-86[39] (**1**) or SHELXTL[40] (**2**),

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[39] Sheldrick, G. M. *Acta Crystallogr*. **1990**, *A46*, 467.

[40] Sheldrick, G. M. SHELXTL, Release 5.03; Siemens Analytical X-ray Instruments Inc.: Madison WI, 1994.

and difference Fourier synthesis and refined using full-matrix least squares.[41] Disorder was noted as follows: in compound **2** one of the *tert*-butyl groups attached to Al(2) [C(26)−C(28)] suffered from resolvable disorder about the Al−C bond. Two possible positions were resolved for each methyl carbon which refined to have relative site occupancies of 1:1. The extent of inclusion of anisotropic thermal parameters depended on the number of data collected. In compound **2**, all non-hydrogen atoms were treated in this way; all but the ethylene glycol carbon atoms and the tertiary carbon of the *tert*-butyl groups in compound **1** were refined anisotropically. Hydrogen atoms were generally located from difference maps and included in the model in idealized positions [$d_{C-H} = 0.95$ Å, $U(H) = 1.3\ U_{eq}$ (attached atom)] and not refined. The exceptions to this were compounds **1** where the hydrogen bonded to O(4) was refined isotropically. Scattering factors were taken from the usual source.[42] No variation of $w(|F_o| - |F_c|)$ versus $|F_o|$ or $(\sin \theta/\lambda)$ was observed.

Acknowledgment. Financial support for this work is provided by the National Science Foundation and the Robert A. Welch Foundation. M. Pierson (Rice) is acknowledged for his assistance with microprobe analysis. The Bruker Avance 200 NMR spectrometer was purchased with funds from ONR Grant N00014-96-1-1146. A.R.B. acknowledges the support of the Alexander von Humboldt Foundation for a Senior Scientist Fellowship and Prof. H. W. Roesky for his support, hospitality, and useful scientific discussion.

Supporting Information Available: Full listings of atomic coordinates, bond length and angles, anisotropic thermal parameters, and hydrogen atom parameters and tables of calculated and observed structure factors. This material is available free of charge via the Internet at http://pubs.acs.org.

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(41) MolEN − Enraf-Nonius. MolEN, An interactive Structure Solution Procedure; Enraf-Nonius: Delft, Netherlands, 1990.

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