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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N00014-91-J-1934

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Alumoxanes: Rationalization of Black Box Materials

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OFFICE OF NAVAL RESEARCH END OF YEAR REPORT

PART II

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c) Cognizant ONR Scientific Officer: Dr. K. Wynne

d) Description of project:

Alumoxanes are defined as oligomeric or polymeric materials consisting of an Al-O backbone with pendant organic substituents. Despite having a diverse range of applications, including components in catalytic systems and preceramic precursors little is understood of their structure or chemical properties and characteristics. The purpose of this study is to; (a) confirm our previous proposal as to the three dimensional structure of the Al-O backbone (or core) of alumoxanes, (b) develop new and improved synthesis of alumoxanes, particular emphasis being placed on the ability to control physical properties, and (c) determine the structural motifs present in alkyl alumoxane catalysts such as methylalumoxane, MAO.

e) Significant Results

Methylalumoxane, $(MeAlO)_n$ or MAO, has been proposed to exist as cyclic or linear structures. We have been the first to show that, by the synthetic analogue approach, alkyl alumoxanes are three dimensional clusters, thus confirming our previous proposal that all alumoxanes are cluster species. X-ray crystallographic evidence for the hexameric, octameric and nonameric forms of *tert*-butyl alumoxane, $[(^tBu)AlO]_n$, have been obtained. In addition, we have isolated the first example of an alkyl alumoxane containing a highly Lewis acidic three coordinate aluminum center.

Initial results indicate that our isolable *tert*-butyl alumoxanes are active cocatalysts in a number of polymerization systems. Thus, they represent very accurate models for the mixture of species present in MAO.

Our most important result has been to demonstrate that the *tert*-butyl alumoxanes show unique activity as co-catalysts with palladium complexes for the synthesis of polyketones, $[CH_2CH(R)C(O)]_n$. The activity observed is comparable to commercial systems but without the instability issues (see below).

Commercial samples of polyketones suffer from severe thermal decomposition during melt processing. The Patent literature describes the use of hydrolyzed $Al(O^iPr)_3$ as a good stabilizing agent. Since we have demonstrated that hydrolyzed alkoxides are alumoxanes with a core structure of boehmite, we reasoned that boehmite itself would be more effective. This is indeed the case. However, based on our previous work with the reaction of boehmite with carboxylic acids we have determined that the most effective stabilization agents are alumoxanes made from boehmite and 1% carboxylic acid.

A detailed study has been undertaken on the equilibria present for $Me_2Al(OR)$ in solution. Importantly it has been shown that both dimeric and trimeric species are present.

f) Summary for Next Year's Work

In the next year we propose to capitalize on our new synthetic routes to alkyl alumoxanes.

With our isolation of well defined alkylalumoxanes we propose to determine the catalytic activity of these materials both as polymerization catalysts themselves and also as Kaminsky co-catalysts with Cp_2ZrMe_2. We propose to synthesis single alumoxane species and determine their relative effectiveness as catalysts. In this way we will be able to determine the effect of the alumoxane structure on the activity of catalysis as well as the structure and molecular weight of the polymer.

We intend to further our work with the catalytic synthesis of polyketones. We will optimize the polymerization conditions as well as investigate the mechanism of initiation.

With all the catalytic systems we will try and isolate transition metal compound-alkylalumoxane complexes.

g) Chris Landry (Graduate)

Allen Apblett (Post-Doctoral)
Mark Mason (Post-Doctoral)
Linda K. Cheatham (Post-Doctoral)

Jason Rogers (undergraduate)

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PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

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Principal Investigator: Andrew R. Barron

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a. Number of papers submitted to refereed journals, but not published: 1
b. * Number of papers published in refereed journals (**for each, provide a complete citation**): 3
c. Number of books or chapters submitted, but not yet published: 0
d. * Number of books or chapters published (**for each, provide a complete citation**): 0
e. * Number of printed technical reports/non-refereed papers (**for each, provide a complete citation**): 0
f. Number of patents filed: 0
g. * Number of patents granted (**for each, provide a complete citation**): 0
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j. * Honors/Awards/Prizes for contract/grant employees (list attached): 1
(This might include Scientific Society Awards/Offices, Selection as Editors,
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k. Total number of **Full-time equivalent** Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:
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Female Post-Doctoral Associates: 1
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Minority* Post-Doctoral Associates: 0
and, the number of
Asian Graduate Students: 0
Asian Post-Doctoral Associates: 0
l. * Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

* Use the letter and an appropriate title as a heading for your list, e.g.:
b. Published Papers in Refereed Journals, or, d. Books and Chapters published
Also submit the citation lists as ASCII files, preferably on a 3" or 5" PC-compatible floppy disks

* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

b) Papers published in refereed journals

1. The Preparation of $(Al_2O_3)_x(SiO_2)_y$ Thin Films Using $[Al(OSiEt_3)_3]_2$ as a Single-Source Precursor
   C.C. Landry, L.K. Cheatham, A.N. MacInnes, and A.R. Barron, *Adv. Mater. Optics and Electronics*, 1992, **1**, 3-15.

2. Dimethylaluminium Alkoxides: A Physochemical Study.
   J.H. Rogers, A.W. Apblett, W.M. Cleaver, and A.R. Barron, *J. Chem. Soc., Dalton Trans.,* 1992, 3179.

3. Synthesis and Characterization of Triphenylsiloxy-Substituted
   A.W. Apblett, A.C. Warren, and A.R. Barron, *Can. J. Chem.*, 1992, **70**, 771.

4. Hydrolysis of tri-tert-butyl aluminum: the first structural characterization of alkylalumoxanes, $[(R_2Al)_2O]_n$ and $[RAlO]_n$.
   M.R. Mason, J.M. Smith, S.G. Bott, and A.R. Barron, *J. Am. Chem. Soc.*, 1993, (June issue)

j) Honors/Awards/Prizes

1. Alcoa Foundation Fellowship.

l) Other Funding

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Alumoxanes, what are they ?

Al-O macromolecules with a general formula $[Al(O)_x(OH)_y(X)_z]_n$

What are their applications ?

X	Known applications	New applications
alkoxide (OR)	alumina precursor, paints	polymer stabilization
siloxide ($OSiR_3$)	aluminosilicate precursor	adhesives
carboxylate (O_2CR)	alumina precursor	polymer stabilizers
chloride	antiperspirant	?
alkyl (*esp.* CH_3)	Ziegler Natta co-catalyst for olefin polymerization	(The first rational model)

What are their structures ?

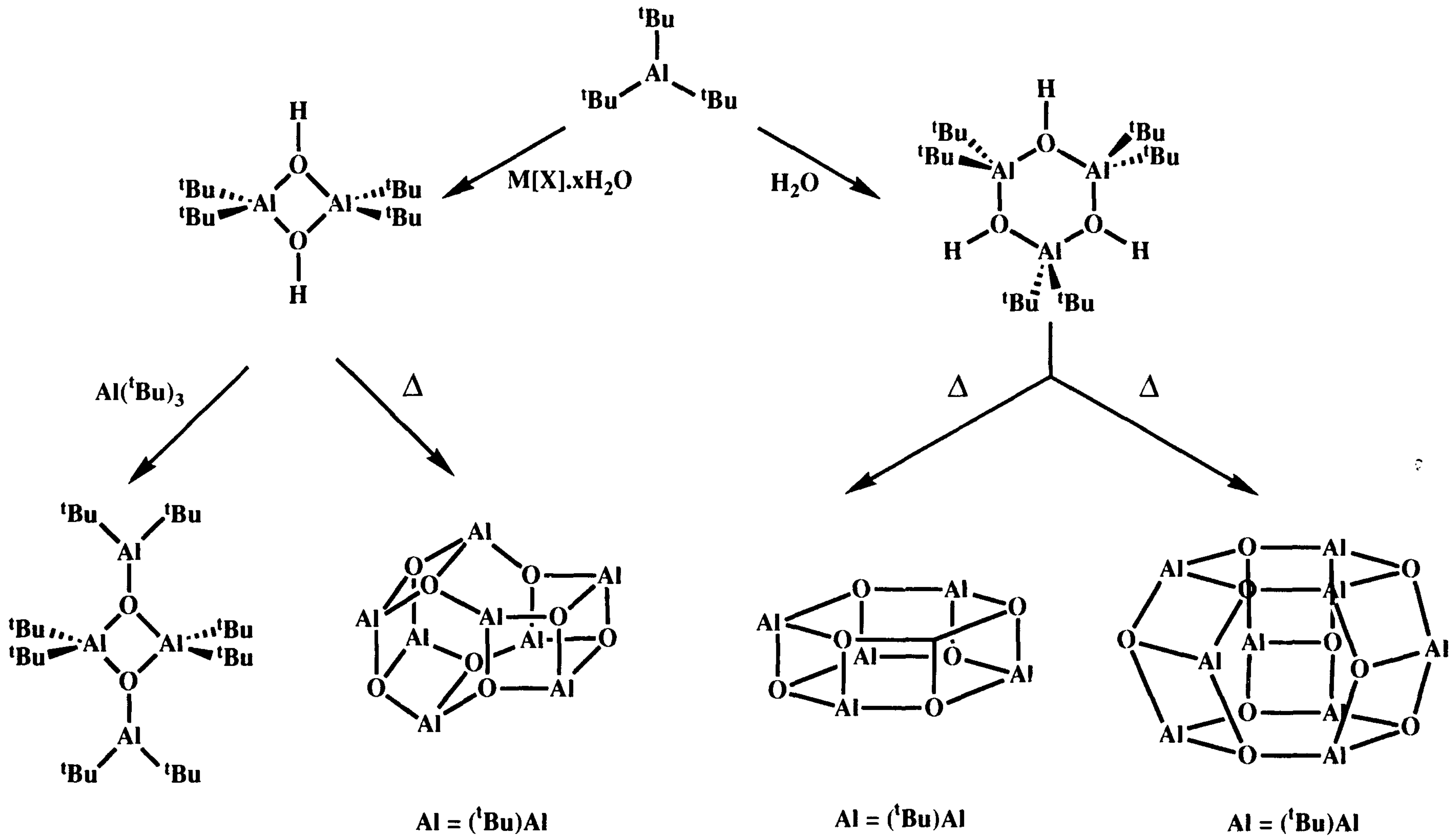
$X \neq$ alkyl

Boehmite Core

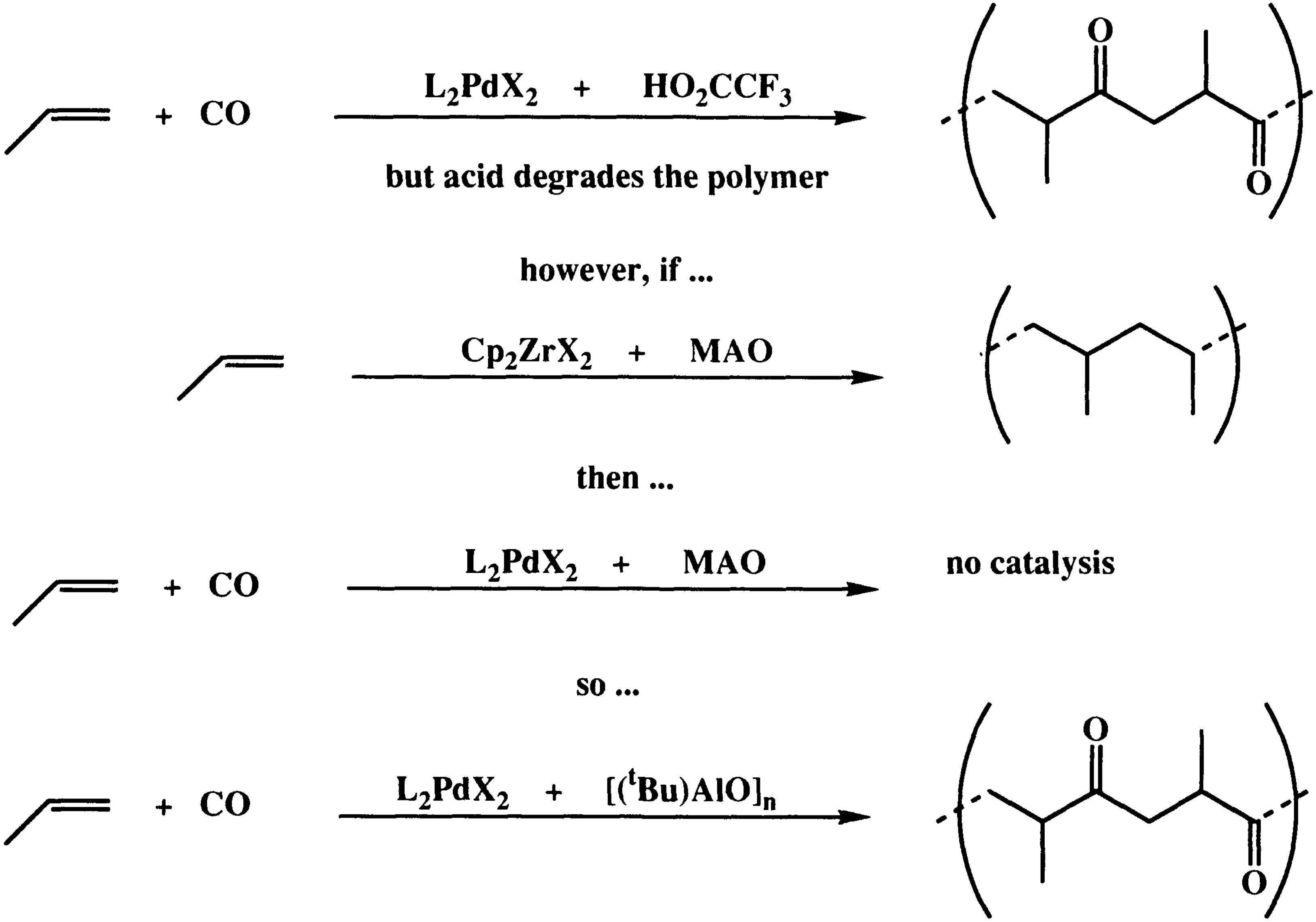
$X =$ alkyl

Always assumed linear or cyclic but actually clusters

Synthesis and Structure of Alkylalumoxanes



New Catalysis with Alkylalumoxanes



+ CO

L_2PdX_2 + HO_2CCF_3

but acid degrades the polymer

however, if ...

Cp_2ZrX_2 + MAO

then ...

+ CO

L_2PdX_2 + MAO

no catalysis

so ...

+ CO

L_2PdX_2 + $[(^tBu)AlO]_n$

Explanatory Paragraph

The term alumoxane is used to describe any macromolecule with an aluminum oxygen backbone. A wide range of applications are known (slide 1) and we are developing new uses. Previous workers have suggested a general formula of $[Al(O)(X)]_n$ where X may be alkyl, alkoxide, siloxide, carboxylate or other organic side chain. We have shown that the stable (non-alkyl) alumoxanes have a general formula $[Al(O)_x(OH)_y(X)_z]_n$ and have a structure based on that of boehmite $[Al(O)(OH)]_n$. In contrast, the alkyl derivatives have until recently eluded characterization despite their application as active polymerization catalysts. We have isolated and crystallographically characterized the first examples of alkyl alumoxanes, and found their structures to be dependent on the synthetic route (slide 2). Polyketone polymers are made commercially by the co-polymerization of CO and olefins using a palladium/tri-fluoroacetic acid catalyst, however, the product is degraded by the acid cocatalyst residues. An alternative non protic acid system should be developed. Using the precedant of zirconacene/MAO olefin catalysis, one may propose a palladium/MAO system, but, this does not give any polymer. However, we have discovered that the new isolable *tert*-butyl alumoxanes must be used (slide 3).

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6. AUTHOR(S)

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Andrew R. Barron

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13. ABSTRACT (*Maximum 200 words*)

Tert-butyl substituted alumoxanes have been prepared and characterized by multinuclear magnetic resonance spectroscopy, mass spectrometry and X-ray crystallography. The low temperature (-78 °C) hydrolysis of $Al(^tBu)_3$ in pentane results in the formation of the trimeric hydroxide $[(^tBu)_2Al(\mu\text{-}OH)]_3$ (**1**) as the major product. Hydrated salt hydrolysis of $Al(^tBu)_3$ in toluene followed by thermolysis of the reaction mixture yields the tetrameric alumoxane $[(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2$ (**2**), and the octameric alumoxane $[(^tBu)Al(\mu_3\text{-}O)]_8$ (**3**). In contrast the thermolysis of **1** yields the hexameric and nonameric alumoxanes, $[(^tLu)Al(\mu_3\text{-}O)]_6$ (**4**) and $[(^tBu)Al(\mu_3\text{-}O)]_9$ (**5**). Dissolution of compound **1** in THF or MeCN yields the hydrogen-bound complexes $[(^tBu)_2Al(\mu\text{-}OH)]_3.2(THF)$ (**6**) and $[(^tBu)_2Al(\mu\text{-}OH)]_3.2(MeCN)$ (**7**) respectively, while no adduct is observed in Et_2O solution. The reaction of **1** with pyridine results in a disproportionation reaction to yield the dimeric compound $[(^tBu)_2Al(py)]_2(\mu\text{-}O)$ (**8**). Compound **8** may be prepared directly from the partial hydrolysis of $Al(^tBu)_3$ in pyridine, in which it exists as the Lewis acid base complex $Al(^tBu)_3(py)$ (**9**), or from the addition of pyridine to **2**. The molecular structures of compounds **1**, **2**, **4**, and **6** - **8** have been determined by X-ray crystallography. The relationship between the *tert*-butylalumoxanes and the Kaminsky co-catalyst methylalumoxane, MAO, is discussed.

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13. ABSTRACT *(Maximum 200 words)*

Compounds of the type $[Me_2Al(\mu\text{-}OR)]_x$ (R = Me **1**, Et **2**, Pr^n **3**, Pr^i **4**, Bu^n **5**, Bu^i **6**, Bu^s **7**, Bu^t **8**, $Pent^n$ **9**, $Pent^i$ **10**, $Pent^{neo}$ **11**, Hex^n **12**, Oct^n **13**, Dec^n **14**, $Dodec^n$ **15**) have been synthesised and studied by ^1H, ^{13}C, ^{17}O and ^{27}Al NMR and IR spectroscopy and mass spectrometry. With the exception of **10**, all the compounds with branched chain alkoxide substituents are purely dimeric (x = 2), while **10** and the n-alkyl derivatives exist in solution as an equilibrium between dimeric (x = 2) and trimeric (x = 3) forms. Equilibrium constants, ΔH and ΔS for the trimer-dimer equilibria in solution were obtained for **3**. These results, and those for the NMR spectroscopic data, are interpreted on the basis of steric interactions and ring strain. The kinetics of the conversion of $[Me_2Al(OPr^n)]_3$ to $[Me_2Al(OPr^n)]_2$ have been investigated, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ determined, and the identity of the reaction intermediates has been probed by NMR spectroscopy and mass spectrometry. *Ab initio* molecular orbital calculations have been carried out on the model compounds $[H_2Al(\mu\text{-}OH)]_2$ **16** and $[H_2Al(\mu\text{-}OH)]_3$ **17**. The relative energies and calculated structures for **16** and **17** are considered in relation to experimental data.

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13. ABSTRACT (Maximum 200 words)

Amorphous $(Al_2O_3)_x(SiO_2)_y$ thin films have been grown by atmospheric pressure metal-organic chemical vapor deposition using the single source precursor $[Al(OSiEt_3)_3]_2$. Characterization by X-ray photoelectron spectroscopy indicated that the films consisted of a mixture of Al_2O_3, SiO_2 and an aluminosilicate. The relative amount of each species was dependent on the deposition temperature and the carrier gas composition. Use of NH_3 as the carrier gas resulted in the increased volatility of the precursor by the *in situ* formation of the low melting Lewis acid-base adduct $Al(OSiEt_3)_3(NH_3)$, however, no nitrogen incorporation was observed in these deposited films.

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