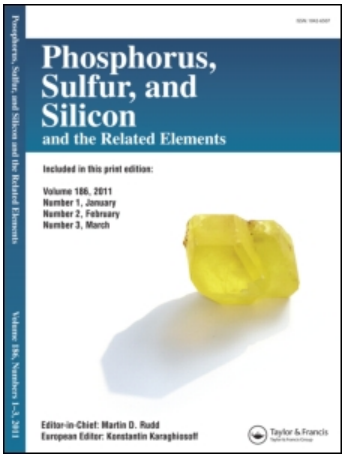

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NOVEL ALUMINUM AND TITANIUM COMPLEXES CHELATED BY TRIS-PHENOXIDE LIGANDS

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NOVEL ALUMINUM AND TITANIUM COMPLEXES CHELATED BY TRIS-PHENOXIDE LIGANDS

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Many elements in the periodic table have been employed as core atoms atranes (traditionally understood to posses three five-membered rings) synthesized from triethanolamine, including main group and transition metal elements.[1] Alumatrane has been described in the literature as dimeric in the gas phase; monomeric, hexameric, and octameric in solution; and tetrameric in the solid state.[1] However, examples of alumatranes having the same structure in the gas, solution, and solid states have not been reported.

Recently, tripodal triphenoxyamine ligands made by deprotonating **1** or derivatives of **1** have been used to make nonmetal and metal complexes resembling the corresponding atranes, except that the three chelating rings are six-instead of five-membered. We were interested in determining whether a six-membered ring alumatrane derived from **1** would be monomeric in the gas, solution, and solid states, and whether the Al atom would be five- or four-coordinate.

The tripodal ligand **3** and some of its derivatives have recently been used to form nonmetal and metal complexes.[2] Although triols, such as 1,1,1-*tris*(hydroxymethyl)ethane and *cis*,*cis*,-1,3,5-cyclohexatriol, are known to form a variety of multinuclear complexes with early transition metals,[2] complexes of transition metal complexes containing **3** have not been reported.

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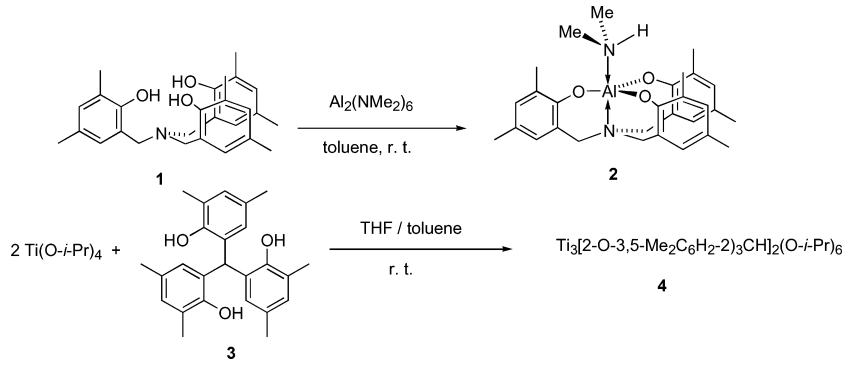


This talk summarizes recent results we have obtained for the synthesis and characterization of complexes **2** and **4**. Also discussed is the use of **4** as a catalyst for the controlled polymerization of *l*-lactide.

DISCUSSION

Surprisingly (in view of the volatility of dimethylamine) reaction 1 gave **2** which was remarkably stable even under vacuum above 200°C. Monomeric behavior of **2** is indicated in the gas phase by its mass spectrum and in the solution phase by its ^{1}H and ^{13}C NMR spectra which display sharp resonances. It is interesting to note the displacement of the aluminum atom from the oxygen plane toward the bridgehead nitrogen by *ca* 0.24 Å in Figure 1a, in contrast to the location of the metal atom above this plane in reported structurally characterized metallatranes. Interestingly, there is only one other known example of a structurally characterized aluminum compound containing a dimethylamine molecule namely, $Me_2NH{\cdot}AlH_3$, which is dimeric.[1] The x-ray structure of complex **4**(**solid**) depicted in Figure 1b represents the first example of a trinuclear titanium complex containing only lower-coordinate metal centers. The initial solution ^{1}H and ^{13}C spectra of **4**(**solid**) in C_6D_6 are consistent with C_3 symmetry (Figure 2a). Although this result is also in accord with **4**(**soln**)/**4**(**solid**) fluxionality, new peaks appear over time in the ^{1}H NMR spectrum of **4**(**soln**) in C_6D_6, at the expense of the resonances in the initial spectrum until only a spectrum in agreement with **4(solid)** is present. Experiments aimed at understanding the origin of this interesting phenomenon are under way.

Complex **4** was used as a catalyst in the ring opening polymerization of *l*-lactide (LA) in toluene solution at 130°C using an [LA]/[**4**] ratio of 200 with [LA] = 2.8 M. Greater than 90% conversion to polylactide

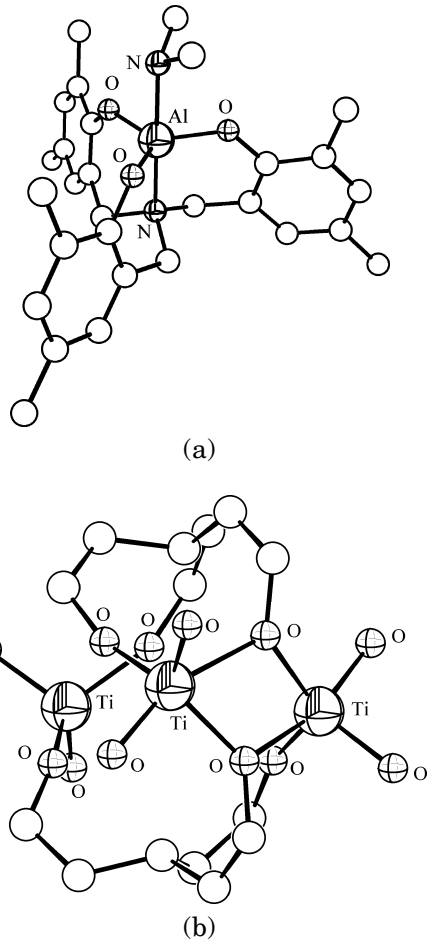
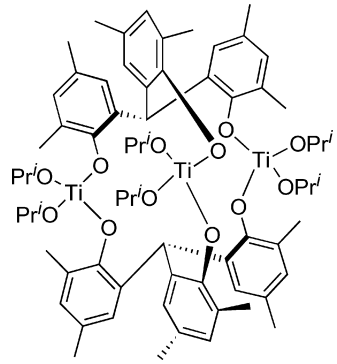


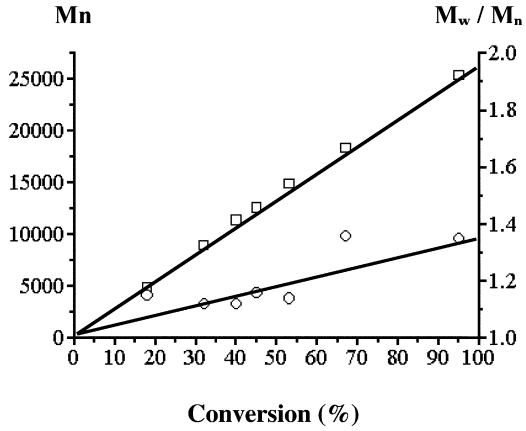
FIGURE 1 (a) Computer drawings of **2** and (b) **4**(**ss**) showing 50% probability thermal ellipsoids, but with H atoms omitted for clarity. The aryl rings in **44**(**ss**) also are omitted for clarity.

occurred within 12 h (M_W = 10,100–34,300, PDI = 1.12–1.36). Polymerization control was high, as shown by the linear increase in M_n with conversion and the low polydispersity index (PDI) of the polymer produced (Figure 2b). However, the PDI values increased with conversion.

The ^{1}H NMR spectrum of the PLA shows an hydroxy as well as an *i*-Pr ester chain terminus, suggesting that initiation occurs through insertion of the O-*i*-Pr group from compound **4** into LA via a coordination insertion mechanism. This is supported by a homonuclear decoupled ^{1}H NMR spectrum which reveals only one resonance in the methane



(a)



(b)

FIGURE 2 (a) Proposed structure of **4**(**soln**)] in a fresh C_6D_6 solution. (b) Plot of Mn (open squares, GPC) vs. monomer conversion (determined by ^{1}H NMR spectroscopy), with polydispersity indices indicated by open circles (GPC).

region for poly(*l*-LA), a result which also indicates lack of epimerization of the chiral centers in poly(*l*-LA) during polymerization.

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