Reaction of Amines with [(^{t}Bu)Al(μ_3-O)]$_6$: Determination of the Steric Limitation of a Latent Lewis Acid

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The reaction of primary and secondary amines with the hexameric *tert*-butylalumoxane, [(^{t}Bu)Al(μ_3-O)]$_6$, has been investigated. Reaction of [(^{t}Bu)Al(μ_3-O)]$_6$ with 2 equiv of RNH_2 (R = Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{t}Bu) results in the formation of [(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-O)$_2$(NH_2R)$_2$], R = Et (**1**), ^{n}Pr (**2**), ^{i}Pr (**3**), ^{n}Bu (**4**) and ^{t}Bu (**5**). The molecular structure of compound **4** has been determined by X-ray crystallography, the Al_6O_6 core structure of which consists of two fused boat-conformation Al_3O_3 rings, derived from the opening of two opposing edges of the Al_6O_6 cage of [(^{t}Bu)Al(μ_3-O)]$_6$. The ^{n}BuNH_2 groups are bound to the aluminum atoms of the open cage. Compounds **1**−**3** and **5** are isostructural to compound **4** on the basis of ^{1}H and ^{13}C NMR spectroscopy. No reaction is observed for R_2NH (R = Et, ^{i}Pr, ^{n}Bu, Ph). On the basis of the cone angle (θ) of the amine, we suggest that steric hindrance is the reason for the lack of reactivity of the secondary amines R_2NH. A discussion of the steric constraints imposed on a latent Lewis acid is presented.

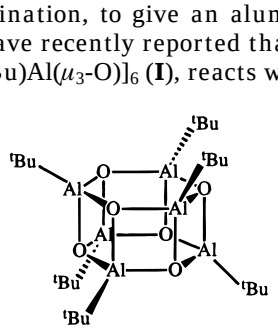
Introduction

The reaction between aluminum alkyls and primary or secondary amines has been extensively investigated since the seminal work by Davidson and Brown,[2] in particular the elimination of alkane and the concomitant formation of an aluminum−amide compound, e.g., eq 1.[3,4] We have demonstrated that in contrast to previously reported organoaluminum−amine reactions, the BHT-substituted compounds, $AlMe_2(BHT)(NH_2R)$,[5] show no propensity for alkane elimination and may be sublimed without decomposition.[6] Heating $AlMe_2(BHT)(NH_2R)$ under an inert atmosphere beyond their melting point results in elimination of BHT-H and not methane. On the basis of spectroscopic data, we have proposed that the presence of a heteroatom donor ligand (e.g., alkoxide, aryloxide, amide, etc.) significantly reduces the basicity of the aluminum alkyl group as a result of high electronegativity at the aluminum atom.[7] Thus, the reaction of a Brönsted acid[8] occurs via protonation of the heteroatom and not the alkyl group. Supporting experimental evidence for this proposal was the formation of an ammonia complex from the reaction of BHT-H with [$Me_2Al(\mu$-$NH_2)]_3$, eq 2.[9]

$$AlR_3 + HNR'_2 \rightarrow {}^1/_2[R_2Al(\mu\text{-}NR'_2)]_2 + RH \quad (1)$$

$$^1/_3[Me_2Al(\mu\text{-}NH_2)]_3 + BHT\text{-}H \rightarrow AlMe_2(BHT)(NH_3) \quad (2)$$

Prior to our work with aryloxide compounds of aluminum[7] it had been reported that reaction of alkylalumoxanes, $[RAlO]_n$ and $[(R_2Al)O]_n$, with primary amines occurred via complexation of the amine followed by alkane elimination, to give an aluminum amide.[10] However, we have recently reported that the *tert*-butyl alumoxane, [(^{t}Bu)Al(μ_3-O)]$_6$ (**I**), reacts with water[11] and



(I)

carboxylic acids[12] via protonation of the alumoxane oxo groups (eqs 3 and 4) and that no alkane elimination

$$[(^t\text{Bu})\text{Al}(\mu_3\text{-O})]_6 + 2H_2O \rightarrow [Al_6(^t\text{Bu})_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4] \quad (3)$$

$$[(^t\text{Bu})\text{Al}(\mu_3\text{-O})]_6 + 2HO_2CR \rightarrow [Al_6(^t\text{Bu})_6(\mu_3\text{-O})_4(\mu\text{-OH})_2(O_2CR)_2] \quad (4)$$

occurs even at elevated temperatures. These results

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(1) (a) Rice University. (b) University of North Texas.

(2) Davidson, N.; Brown, H. C *J. Am. Chem. Soc.* **1942**, *64*, 316.

(3) For a recent review see: Robinson, G. H. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993; Chapter 2.

(4) It has been commonly assumed that the reaction of aluminum alkyls and Brönsted acids proceeds *via* the prior formation of a Lewis acid−base adduct from which the elimination reaction occurs. However, it has been demonstrated that although aluminum alkyls and amines do form adducts, the important step for elimination is the prior dissociation of the adduct. If the recombination of the monomeric aluminum compound and the amine occurs with the appropriate orientation, elimination may occur, possibly via a four-centered S_Ei (substitution, electrophilic, internal) mechanism. See: Beachley, O. T., Jr.; Victoriano, L. *Inorg. Chem.* **1986**, *25*, 1948.

(5) BHT = 2,6-di-*tert*-butyl-4-methylphenoxide; BHT-H is from the trivial name butylated hydroxyltoluene.

(6) Healy, M. D.; Ziller, J. W.; Barron, A. R. *Organometallics* **1991**, *10*, 597.

(7) Healy, M. D.; Power, M. B.; Barron, A. R. *Coord. Chem. Rev.* **1994**, *130*, 63.

(8) While the reactions of primary and secondary amines are ordinarily that of either a Brönsted or Lewis base, their reactions with Al−C bonds are that of a Brönsted acid.

(9) Healy, M. D.; Leman, J. T.; Barron, A. R. *J. Am. Chem. Soc.* **1991**, *113*, 2776.

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suggest that if the pK_a of primary and secondary amines is sufficiently high, they should react with alkylalumoxanes in a similar manner to that observed for the stronger Brönsted acids, i.e., resulting in protonation of an oxygen in the alumoxane's cage. Alternatively, if proton transfer does not occur, then the Lewis basic amines will react with the latent Lewis acid cites on the alumoxane, to give a Lewis acid−base complex. In either case the steric bulk of the amine (or amide) should allow for the steric limitation of the latent Lewis acid to be determined.

Results and Discussion

The reaction of $[(^tBu)Al(\mu_3\text{-}O)]_6$[13] with an excess of the primary amines RNH_2 (R = Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{t}Bu) allows for the isolation, in near stoichiometric yield, of the hexaaluminum compound, $[(^tBu)_6Al_6(\mu_3\text{-}O)_4(\mu\text{-}O)_2(NH_2R)_2]$, eq 5.

$$[(^tBu)Al(\mu_3\text{-}O)]_6 + 2RNH_2 \xrightarrow{\Delta} [(^tBu)_6Al_6(\mu_3\text{-}O)_4(\mu\text{-}O)_2(NH_2R)_2] \quad (5)$$

R = Et (**1**), ^{n}Pr (**2**), ^{i}Pr (**3**), ^{n}Bu (**4**), ^{t}Bu (**5**)

The structure of compound **4** has been determined by X-ray crystallography and is consistent with the solution ^{1}H and ^{13}C NMR and IR spectroscopy; see below. The molecular structure of compound **4** is shown in Figure 1; selected bond lengths and angles are given in Table 1. The Al_6O_6 core structure consists of two fused boat conformation Al_3O_3 rings and can be described as being derived from the opening of two opposing edges of a hexagonal prism; see Scheme 1. This core structure is analogous to that observed previously in $[(Et_2O)Li]_2[(^tBu)_6Al_6(O)_6Me_2]$[14] and $[(^tBu)_6Al_6(O)_4(OH)_2(O_2CCCl_3)_2]$[11] derived from the reaction of $[(^tBu)Al(\mu_3\text{-}O)]_6$ with MeLi and Cl_3CCO_2H, respectively. The geometries and bond distances around the Al and O atoms, in compound **4**, are similar to those we have previously reported for other *tert*-butylalumoxane compounds.[12,15] The Al−N bond distance [2.029(8) Å] is similar to those expected for aluminum−amine interactions (1.94−2.01 Å) and considerably longer than that expected from the range reported for terminal aluminum amide moieties (1.78−1.81 Å).[16] Similarly, the Al−O bond distances associated with the open edge of the alumoxane cage [Al(1)−O(3) = 1.713(5) Å and Al(2)−O(3a) = 1.703(2) Å] are significantly shorter than those observed remaining Al−O bond distances [1.759(4)−1.890(5) Å] and those of aluminum hydroxide compounds [1.81(1)−1.860(2) Å]. However, they are comparable to those observed for the bridging oxo ligand in $[(^tBu)_2Al]_2(\mu\text{-}O)$ [1.710(1) Å].[12,14] Unfortunately, the hydrogen atoms bonded to N(41) could not be located in the difference map (see Experimental Section) and were fixed in ideal positions. However, the N(41)···O(3) distance (2.96 Å) is within the range associated with N−H···O hydrogen bonding.[17] Furthermore, the N−H···O angle (133°) associated with

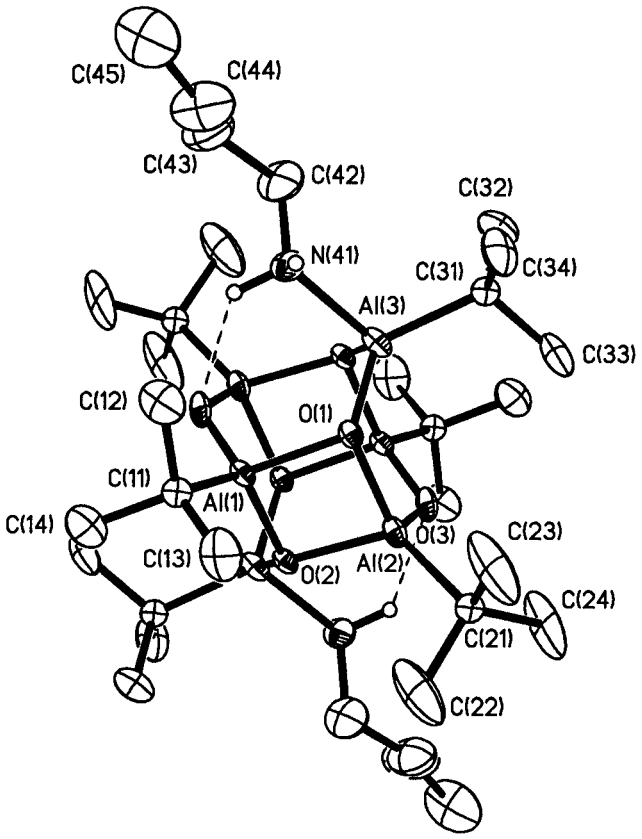
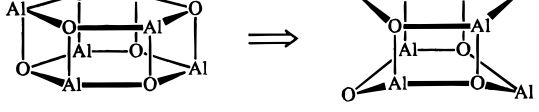


Figure 1. Molecular structure of $[(^tBu)_6Al_6(\mu_3\text{-}O)_4(\mu\text{-}O)_2(NH_2{}^nBu)_2]$ (**4**). Thermal ellipsoids are shown at the 30% level. The organic hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[(^tBu)_6Al_6(\mu_3\text{-}O)_4(\mu\text{-}O)_2(NH_2{}^nBu)_2]$ (4)

Al(1)−O(1)	1.826(3)	Al(1)−O(2)	1.817(5)
Al(1)−O(3)	1.713(5)	Al(1)−C(11)	1.942(7)
Al(2)−O(1)	1.890(5)	Al(2)−O(2)	1.843(3)
Al(2)−O(3a)	1.703(2)	Al(2)−C(21)	1.996(7)
Al(3)−O(1)	1.759(4)	Al(3)−O(2a)	1.785(3)
Al(3)−C(31)	1.935(5)	Al(3)−N(41)	2.030(7)
O(1)−Al(1)−O(2)	88.0(2)	O(1)−Al(1)−O(3)	103.8(2)
O(1)−Al(1)−C(11)	116.3(2)	O(2)−Al(1)−C(3)	108.5(2)
O(2)−Al(1)−C(11)	119.1(3)	O(3)−Al(1)−C(11)	116.8(3)
O(1)−Al(2)−O(2)	85.3(2)	O(1)−Al(2)−C(3a)	106.7(2)
O(1)−Al(2)−C(21)	118.4(3)	O(2)−Al(2)−C(3a)	105.2(1)
O(2)−Al(2)−C(21)	118.1(2)	O(3a)−Al(2)−C(21)	118.0(2)
O(1)−Al(3)−O(2a)	107.8(2)	O(1)−Al(3)−C(31)	119.6(3)
O(1)−Al(3)−N(41)	97.5(2)	O(2a)−Al(3)−N(41)	103.5(2)
O(2a)−Al(3)−C(31)	117.4(2)	C(31)−Al(3)−N(41)	108.1(3)
O(1)−Al(3)−N(41)	97.5(2)	O(2a)−Al(3)−N(41)	103.5(2)
C(31)−Al(3)−N(41)	108.1(3)	Al(1)−O(1)−Al(2)	92.1(2)
Al(1)−O(1)−Al(3)	119.0(2)	Al(2)−O(1)−Al(3)	115.1(2)
Al(1)−O(2)−Al(2)	94.0(2)	Al(1)−O(2)−Al(3a)	115.5(2)
Al(2)−O(2)−Al(3a)	116.4(2)	Al(1)−O(3)−Al(2a)	126.9(3)

Scheme 1. Structural Relationship between the Al_6O_6 Cages in $[(^tBu)_2Al(\mu_3\text{-}O)]_6$ and $[(^tBu)_6Al_6(\mu_3\text{-}O)_4(\mu\text{-}O)_2(NH_2{}^nBu)_2]$ (4)



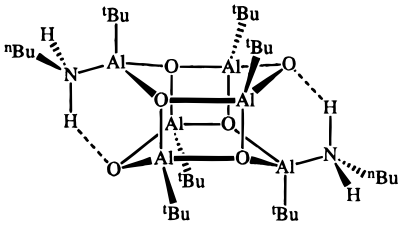
(10) Piotrowski, A.; Kunicki, A.; Pasynkiewicz, S. *J. Organomet. Chem.* **1980**, *186*, 185.
(11) Landry, C. C.; Harlan, C. J.; Bott, S. G.; Barron, A. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1202.
(12) Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 2213.
(13) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971.
(14) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465.
(15) Harlan, C. J.; Mason, M. R.; Barron, A. R. *Organometallics* **1994**, *13*, 2957.
(16) Haaland, A. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993; Chapter 1.
(17) Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320.

Table 2. ^{1}H and ^{13}C NMR Chemical Shifts of the Aluminum *tert*-Butyl Groups and IR ν(N−H) Bands in [(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-O)$_2$(NH$_2$R)$_2$] Formed from the Cage Opening of [(^{t}Bu)Al(μ_3-O)]$_6$[a]

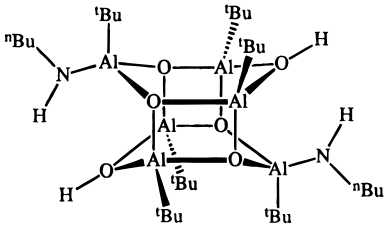
		^{1}H (ppm)[b]		^{13}C (ppm)[b,c]		
compd	amine	^{t}Bu$_a$	^{t}Bu$_b$	^{t}Bu$_a$	^{t}Bu$_b$	IR (cm^{-1})
1	H$_2$NEt	1.19	1.34	30.7	31.6	3295
2	H$_2$N^{n}Pr	1.21	1.35	30.7	31.6	3303
3	H$_2$N^{i}Pr	1.22	1.36	30.8	31.7	3267
4	H$_2$N^{n}Bu	1.24	1.37	30.7	31.6	3300
5	H$_2$N^{t}Bu	1.28	1.37	30.7	31.6	3267

[a] All shifts (δ) in ppm relative to SiMe$_4$ (external). [b] See diagram VI for assignment. [c] Chemical shifts of methyl carbons only; quaternary carbons are not observed.

the idealized hydrogen position is typical for such intramolecular species (mean = 132.5°). The presence of a sharp band in the IR spectrum (3267 cm^{-1}), characteristic of an amine ν(N−H) stretch (3300−3100),[18] and lack of a band associated with an O−H stretch (3700−3300 cm^{-1}), along with the X-ray structure and ^{1}H NMR spectrum (see Experimental Section) are consistent with the formation of an aluminum amine complex and not the formation of an amide/hydroxide compound, i.e., the formation of [(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-O)$_2$(NH$_2$^{n}Bu)$_2$] (**II**) as opposed to [(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-OH)$_2$(NH^{n}Bu)$_2$] (**III**).

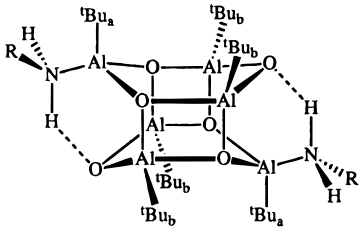


(II)



(III)

The ^{1}H and ^{13}C NMR spectra of compound **4** show the presence of two aluminum *tert*-butyl groups environments in a 2:1 ratio (see Table 2), consistent with the retention of the solid-state structure at room temperature in solution; no evidence is observed for any inter- or intramolecular fluxionality. While none of the other amines provided crystals suitable for X-ray diffraction studies, the similarity in the ^{1}H and ^{13}C NMR chemical shifts of *tert*-butyl groups bound to the aluminum atoms (Table 2, **IV**), and the IR spectra (Table 2), confirmed that compounds **1**−**3** and **5** are structurally analogous to compound **4**. The methyl protons in *tert*-butyl groups bound to the aluminum on the open edge of the alumoxane cage exhibits the greatest shift range (1.13−1.28 ppm). However, the lack of any significant variation of the ^{13}C NMR spectral shifts suggests that any variation in the ^{1}H NMR shifts is due



(IV)

to through-space interactions (rather than as a consequence of significant changes in the Al−C bonding), since the former have been shown to be a better indication of electronic and/or structural environment.[19] It is worth noting that the ^{1}H NMR spectrum for compound **3** shows two N−H resonances, while for **1**, **2**, and **4** the N−H resonances are broad and show evidence for the anisochronous nature of the NH$_2$ group. The amine β-hydrogens (i.e., N-C*H*) in compounds **1**, **2**, and **4** are also anisochronous. While these observations are consistent with hindered rotation about the Al−N and N−C bonds, the sharpness and position of the N−H band in the IR spectrum suggests that any N−H···O hydrogen bonding observed in the crystal structure is weak. In contrast, the presence of a single N−H resonance in the ^{1}H NMR spectrum of compound **5** may be due to either (a) rotation or ligand exchange which is rapid on the NMR experiment time scale or (b) the presence of a mirror plane bisecting the molecule as a consequence of the orientation of the amine's *tert*-butyl group.

No reaction is observed between [(^{t}Bu)Al(μ_3-O)]$_6$ and the secondary amines Et$_2$NH, ^{i}Pr$_2$NH, ^{n}Bu$_2$NH, or Ph$_2$NH. In general secondary amines are slightly stronger Lewis basis than their corresponding primary amines (i.e., Et$_2$NH > EtNH$_2$), and the fact that they do not react with [(^{t}Bu)Al(μ_3-O)]$_6$ suggests that reactivity depends on the steric bulk of the amine.

The cone angle (θ) of an amine may be calculated[20] in a manner similar to that proposed for tertiary phosphines by Tolman.[21] On the basis of this method, the steric bulk of the amides increases in the order shown in eq 6; the values in parentheses are the

$$\begin{aligned} &EtNH_2 \approx {}^nPrNH_2 \approx {}^nBuNH_2\ (90-95°) < \\ &\quad {}^iPrNH_2\ (110°) < {}^tBuNH_2\ (120°) < Et_2NH \approx \\ &\quad {}^nBu_2NH\ (140°) < Ph_2NH\ (145°) < {}^iPr_2NH\ (150°) \end{aligned} \tag{6}$$

calculated amine cone angle, θ_{amine}. Thus, [(^{t}Bu)Al(μ_3-O)]$_6$ appears to react with amines when their steric bulk, as measured by θ, is less than 140°.

Steric Demands of Latent Lewis Acidic Alumoxanes. In spite of the commercial importance of alkylalumoxanes[22] (in particular the methyl derivative methylalumoxane, MAO), as highly active cocatalysts for the polymerization of ethylene and propylene using group 4 metallocene catalysts (e.g., Cp$_2$ZrMe$_2$, Cp = cyclopen-

(18) Kemp, W. *Qualitative Organic Analysis*; McGraw-Hill: New York, 1979.

(19) Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1988**, 3047.

(20) For the purposes of the present study, the cone angle of an amine is defined as the angle subtended by a cone that can exclude the van der Waals surface of all the ligands over all rotational orientations about the Al−N and N−C bonds, with a Al−N bond distance of 2.0 Å.

(21) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(22) See for example: (a) Pasynkiewicz, S. *Polyhedron* **1990**, *9*, 429. (b) Barron, A. R., *Macromol. Symp.* **1995**, *97*, 15.

tadienyl, $C_5H_5^-$).[23] The actual mode of cocatalytic activity for the alumoxanes has been subject to much speculation, due to a lack of understanding of alumoxanes themselves. However, spectroscopic and theoretical data suggest that the role of the MAO is to abstract an alkide, forming a "cationlike" metal center, i.e., eq 7.[24] Since compounds with coordinatively unsaturated

$$Cp_2ZrMe_2 + MAO \rightarrow [Cp_2ZrMe]^+ + [MAO(Me)]^- \quad (7)$$

nonoctet three-coordinate aluminum centers are strong Lewis acids, and compounds with aluminum in a four-coordinate, tetrahedral environment are usually thought not to be Lewis acidic, it was assumed that a three-coordinate aluminum center must be present in the catalytically active species of MAO. The lack of well-characterized alumoxanes precluded further study, and alternative cocatalysts to MAO were pursued.[25,26] It was on the basis of the assumption that three-coordinate aluminum was involved in the activity of the catalyst system that researchers concentrated their investigations on highly Lewis acidic species.[25] However, the analogy between MAO and simple Lewis acidic moieties does not appear to hold. For example, highly Lewis acidic perfluorinated boranes [e.g., $B(C_6F_5)_3$] show enhanced cocatalytic activity when compared to MAO; however, the stability of the resulting "catalyst" is distinctly lower than that formed with MAO. Why? This question prompted our investigation into the structure of alumoxanes and to determine if they were really just Lewis acids.

Our isolation and structural characterization of the nonfluxional alumoxane compounds, $[(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2$ and $[(^tBu)Al(\mu_3\text{-}O)]_n$ ($n = 6, 7, 8, 9$)[13,15] allowed for an investigation of the mode of activity observed for alumoxanes as cocatalysts for the zirconocene polymerization of olefins. The Lewis acidic compound $[(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2$, which contains two three-coordinate aluminum centers, shows no reaction with Cp_2ZrMe_2 and no catalytic activity toward ethylene polymerization. In contrast, the closed-cage electron precise compound $[(^tBu)Al(\mu_3\text{-}O)]_6$ reacts reversibly to give the ion pair complex, $[Cp_2ZrMe][(^tBu)_6Al_6O_6Me]$, which is active as a catalyst for the polymerization of ethylene. Given the prevalent thinking concerning the activity of alumoxane cocatalysts, these results were surprising and begged the following question: Why are the coordinately saturated cage compounds active catalysts? We have proposed that while the cage alumoxanes are not themselves Lewis acidic, *per se*, they possess a "latent Lewis acidity".[14]

We have defined latent Lewis acidity as the ability of a electron precise molecule, e.g., a cage alumoxane, to undergo cage opening, *via* heteroleptic bond cleavage, to generate a Lewis acidic site.[14] For a given bond type (i.e., an Al−O dative bond in alumoxanes) the relative magnitude of the latent Lewis acidity is related to the relative strain present in the cage. Thus, in general four-membered Al_2O_2 rings are more strained than there six-membered Al_3O_3 homologues and, hence, exhibit higher latent Lewis acidity. On the basis of the angular distortions of the cage atoms from an ideal geometry, a qualitative value for the latent Lewis acidity may be obtained, allowing a prediction of the relative reactivity of a series of alumoxane cage structures:

$$[(^tBu)Al(\mu_3\text{-}O)]_7 > [(^tBu)Al(\mu_3\text{-}O)]_9 > [(^tBu)Al(\mu_3\text{-}O)]_6 \approx [(^tBu)Al(\mu_3\text{-}O)]_8 \quad (8)$$

However, our simplistic approach does not take into account any steric hindrance of the Al−O bond into account (i.e., the steric bulk of the aluminum alkyl group) or the possible strain in the ring opened product.[14] A comparison of the relative catalytic rates for a series of cage alumoxane, eq 9, indicated that a knowledge of the steric effects in the alumoxanes is required to develop a reliable predictive measure of latent Lewis acidity.[12] Thus, the reaction of the amines with the alumoxane cages offers a possible simple experimental method for determining the relative steric limitations of the cage-opening reaction. The reactivity of an alkyl alumoxane would be determined from its reaction with a series of amines with various steric bulks (cone angles). For example, $[(^tBu)Al(\mu_3\text{-}O)]_6$ reacts with $^tBuNH_2$ ($\theta = 120°$) but not Et_2NH ($\theta = 140°$), and therefore we propose the steric limitation of the reactivity of $[(^tBu)Al(\mu_3\text{-}O)]_6$ to be in between these values. Furthermore, a consideration of the structure of compound **4** allows for an estimation of the size limitation of the donor atom in the latent Lewis acid pocket.

$$[(^tBu)Al(\mu_3\text{-}O)]_7 > [(^tBu)Al(\mu_3\text{-}O)]_6 > [(^tBu)Al(\mu_3\text{-}O)]_9 \quad (9)$$

On the basis of closest N···C interligand distances in compound **4**, and with the assumption of the van der Waal radii for the methyl groups of the *tert*-butyl ligand to be 2.0 Å,[27] then the radius of the alumoxanes latent Lewis acid site is approximately 2.0 Å, allowing for binding of CH_3 (2.0 Å), Cl^- (1.80 Å), and oxygen donor (1.40 Å) ligands such as acetate. All of which have previously been shown to react with $[(^tBu)Al(\mu_3\text{-}O)]_6$.

Experimental Section

All synthetic procedures were performed under purified nitrogen using standard Schlenk techniques or in an argon atmospheric VAC glovebox. Solvents were distilled and degassed prior to use. $[(^tBu)Al(\mu_3\text{-}O)]_6$ was prepared as previously reported.[13] A 2 M THF solution of $EtNH_2$ was used as received. $^nPrNH_2$, $^iPrNH_2$, $^nBuNH_2$, $^tBuNH_2$, Et_2NH, and $^nBu_2NH$ were distilled prior to use. Ph_2NH was recrystallized from Et_2O. Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer with an electron beam energy of 70 eV for EI mass spectra. Elemental analysis were performed using a Perkin-Elmer Magna 400 ICP atomic emission spectrometer. All compounds were digested in nitric acid to enable analysis. *Caution! Digestion of organoaluminum compounds in acidic solutions should be undertaken with care.* Analytical results are given as an average of multiple samples. NMR spectra were obtained on Bruker AM-200 spectrometer. ^1H NMR

(23) See for example: (a) Sinn, H.; Kaminsky, W.; Vollmer, H. J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *92*, 390. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.

(24) See for example: (a) Sishta, C.; Hathorn, R. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 1112. (b) Jolly, C. A.; Marynick, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 7968. (c) Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875 and references therein.

(25) See for example: (a) Horton, A. D.; Orpen, A. G. *Organometallics* **1992**, *11*, 8. (b) Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1992**, *434*, C1. (c) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623. (d) Hlatky, G. G.; Eckman, R. R.; Turner, H. W. *Organometallics* **1992**, *11*, 1413 and references therein.

(26) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

(27) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; Chapter 7.

(28) SHELX86: Sheldrick, G. M. In *Crystallographic Computing*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 184−189.

chemical shifts are referenced to the residual ^{1}H signal in C_6D_6 (δ = 7.16), and ^{13}C NMR shifts are referenced to C_6D_6 (δ = 128). IR spectra were obtained on a Perkin-Elmer 1600 Series FT-IR spectrometer using KBr disks.

[(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-O)$_2$(NH$_2$Et)$_2$] (1). [(^{t}Bu)Al(μ_3-O)]$_6$ (164 mg, 0.27 mmol) was dissolved in hexane (5 mL) and then added to a 2 M THF solution of EtNH$_2$ (0.3 mL, 0.60 mmol). The solution mixture immediately developed a white precipitate. After being stirred for 30 min, this suspension was refluxed for 2 h. At the end of this time the white precipitate was dissolved to provide a clear solution. Any insoluble materials were removed by filtration. The solution was cooled (−24 °C) to yield colorless crystals. Isolated yield: 45 mg (24%). MS (EI, %) (*m*/*z*): 600 [M$^+$ − (EtNH$_2$)$_2$, 32%], 543 [M$^+$ − (EtNH$_2$)$_2$ − ^{t}Bu, 100%]. IR (cm^{-1}): 3295 (m), 2915 (s, br), 2833 (s), 1600 (m), 1466 (s), 1388 (m), 1359 (m), 1223 (s), 1067 (m), 1003 (w), 899 (s, br), 815 (w), 702 (m, br). ^{1}H NMR: δ 3.62 (2H, br m, N*H*), 2.47 [4H, m, *J*(H−H) = 7.3 Hz, CH$_3$C*H*$_2$N], 1.34 [36H, s, C(C*H*$_3$)$_3$], 1.19 [18H, s, C(C*H*$_3$)$_3$], 0.59 [6H, t, *J*(H−H) = 7.3 Hz, C*H*$_3$CH$_2$N]. ^{13}C NMR: δ 68.3 (*C*H$_3$CH$_2$N), 31.6 [C(*C*H$_3$)$_3$], 30.7 [C(*C*H$_3$)$_3$], 26.2 (CH$_3$*C*H$_2$N).

[(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-O)$_2$(NH$_2$^{n}Pr)$_2$] (2). To a hexane solution (10 mL) of [(^{t}Bu)Al(μ_3-O)]$_6$ (92 mg, 0.15 mmol) was added ^{n}PrNH$_2$ (38 μL, 0.45 mmol). The solution mixture immediately developed a white precipitate. After being stirred for 30 min, this suspension was refluxed for 2 h to give a clear solution. Insoluble materials were removed by filtration, and the volume was reduced under vacuum to *ca*. 3 mL. The solution was placed in a freezer (−24 °C) overnight to yield colorless crystals. Isolated yield: 30 mg (28%). Anal. Found (calc): Al, 23 ± 1 (22.52). MS (EI, %) (*m*/*z*): 600 [M$^+$ − (^{n}PrNH$_2$)$_2$, 34%], 543 [M$^+$ − (^{n}PrNH$_2$)$_2$ − ^{t}Bu, 100%]. IR (cm^{-1}): 3303 (m), 2930 (s, br), 2830 (s), 1603 (m), 1465 (s), 1388 (m), 1360 (m), 1318 (w), 1286 (w), 1185 (s, br), 1086 (m), 1003 (w), 901 (s, br), 817 (w), 723 (m, br). ^{1}H NMR: δ 3.67 (2H, m, N*H*), 2.52 [4H, m, *J*(H−H) = 7.3 Hz, CH$_3$CH$_2$C*H*$_2$N], 1.36 [36H, s, C(C*H*$_3$)$_3$], 1.22 [18H, s, C(C*H*$_3$)$_3$], 0.95 [4H, q, *J*(H−H) = 7.3 Hz, CH$_3$C*H*$_2$CH$_2$N], 0.50 [6H, t, *J*(H−H) = 7.3 Hz, C*H*$_3$CH$_2$-CH$_2$N]. ^{13}C NMR: δ 43.1 (CH$_3$CH$_2$*C*H$_2$N), 31.6 [C(*C*H$_3$)$_3$], 30.7 [C(*C*H$_3$)$_3$], 25.4 (CH$_3$*C*H$_2$CH$_2$N), 17.0 (*C*H$_3$CH$_2$CH$_2$N).

[(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-O)$_2$(NH$_2$^{i}Pr)$_2$] (3). This compound was prepared in an analogous manner to that for compound **2**. Isolated yield: 45 mg (42%). Anal. Found (calc): Al, 22.8 ± 0.6 (22.52). IR (cm^{-1}): 3267 (m), 2930 (s, br), 2838 (s), 1593 (m), 1465 (s), 1384 (m), 1361 (w), 1341 (w), 1224 (s), 1193 (w), 1164 (w), 1094 (s), 1060 (w), 1005 (w), 895 (s, br), 818 (w), 713 (m, br). ^{1}H NMR: δ 3.49 (1H, s, N*H*), 3.46 (1H, s, N*H*), 2.98 [2H, sept, C*H*(CH$_3$)$_2$, *J*(H−H) = 6.5 Hz], 1.36 [36H, s, C(C*H*$_3$)$_3$], 1.22 [18H, s, C(C*H*$_3$)$_3$], 0.77 [12H, d, CH(C*H*$_3$)$_2$, *J*(H−H) = 6.5 Hz]. ^{13}C NMR: δ 41.6 [*C*H(CH$_3$)$_2$], 31.8 [C(*C*H$_3$)$_3$], 30.9 [C(*C*H$_3$)$_3$], 24.6 [CH(*C*H$_3$)$_2$].

[(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-O)$_2$(NH$_2$^{n}Bu)$_2$] (4). This compound was prepared in an analogous manner to that for compound **2**. Isolated yield: 52 mg (46%). Anal. Found (calc): Al, 21 ± 1 (21.68). IR (cm^{-1}): 3300 (m), 2925 (s, br), 2832 (s), 1597 (m), 1465 (s), 1387 (w), 1359 (w), 1261 (w), 1194 (s), 1099 (m), 1002 (w), 899 (s), 818 (w), 706 (m, br). ^{1}H NMR: δ 3.67 (2H, m, N*H*), 2.60 (4H, m, CH$_3$CH$_2$CH$_2$C*H*$_2$N), 1.37 [36H, s, C(C*H*$_3$)$_3$], 1.24 [18H, s, C(C*H*$_3$)$_3$], 0.98 (8H, br, CH$_3$C*H*$_2$CH$_2$-CH$_2$N, CH$_3$CH$_2$C*H*$_2$CH$_2$N), 0.63 [6H, t, *J*(H−H) = 7.3 Hz, C*H*$_3$-CH$_2$CH$_2$CH$_2$N]. ^{13}C NMR: δ 41.7 (CH$_3$CH$_2$CH$_2$*C*H$_2$N), 34.3 (CH$_3$CH$_2$*C*H$_2$CH$_2$N), 31.6 [C(*C*H$_3$)$_3$], 30.7 [C(*C*H$_3$)$_3$], 19.7 (CH$_3$*C*H$_2$CH$_2$CH$_2$N), 13.8 (*C*H$_3$CH$_2$CH$_2$CH$_2$N).

[(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-O)$_2$(NH$_2$^{t}Bu)$_2$] (5). This compound was prepared in an analogous manner to that for compound **2**. Isolated yield: 65 mg (58%). IR (cm^{-1}): 3267 (m), 2930 (s, br), 2836 (s), 1598 (m), 1460 (s), 1297 (m), 1262 (m), 1182 (s), 1100 (m, br), 890 (s), 818 (w), 713 (m, br). ^{1}H NMR: δ 4.41 (2H, s, N*H*), 1.38 [36H, s, C(C*H*$_3$)$_3$], 1.28 [18H, s, C(C*H*$_3$)$_3$], 0.98 [18H, s, N(H)C(C*H*$_3$)$_3$]. ^{13}C NMR: δ 31.6 [C(*C*H$_3$)$_3$], 31.1 [N(H)C(*C*H$_3$)$_3$], 30.7 [C(*C*H$_3$)$_3$].

Crystallographic Studies. A crystal of [(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-O)$_2$(NH$_2$^{n}Bu)$_2$] (**4**) was sealed in a glass capillary under argon and mounted on the goniometer of the University of North Texas Department of Chemistry's Enraf-Nonius CAD-4 automated diffractometer. Data collection and cell determinations were performed in a manner previously described,[11] using the θ/2θ scan technique. Pertinent details are given in Table 3. The structure was solved by direct methods (SHELX86)[28] and the model refined using full-matrix least-squares techniques. All non-hydrogen atoms except the tertiary carbons were refined anisotropically. Hydrogen atoms were included and constrained to "ride" upon the appropriate atoms [*d*(C−H) = 0.95 Å, *U*(H) = 1.3B_{eq}(C)]. All computations other than those specified were performed using MolEN.[29] The inability to locate the amine hydrogen atoms in the electron difference map precludes the absolute differentiation of the formulation of compound **4** as either [(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-O)$_2$(NH$_2$^{n}Bu)$_2$] (**II**) or [(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-OH)$_2$(NH^{n}Bu)$_2$] (**III**). While refinement of either solution resulted in acceptable R factors, the solution for [(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-O)$_2$(NH$_2$^{n}Bu)$_2$] (*R* = 0.0488, R_w = 0.0638, GoF = 1.67) is slightly better than for [(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-OH)$_2$(NH^{n}Bu)$_2$] (*R* = 0.0464, R_w = 0.0618, GoF = 1.72) consistent with the NMR and IR spectroscopy. A summary of cell parameters and data collection, and structure solution parameters is given in Table 3. Scattering factors were taken from ref 30.

Table 3. Summary of X-ray Diffraction Data for [(^{t}Bu)$_6$Al$_6$(μ_3-O)$_4$(μ-O)$_2$(NH$_2$^{n}Bu)$_2$] (4)

emp form	$C_{32}H_{76}Al_6N_2O_6$
cryst size, mm	0.21 × 0.23 × 0.24
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	10.637(7)
b, Å	10.665(4)
c, Å	11.354(8)
α, deg	65.41(5)
β, deg	87.05(6)
γ, deg	80.55(4)
V, Å^3	1155(1)
Z	1
D(calcd), g/cm^3	1.074
μ, mm^{-1}	1.70
radiation	Mo-Kα (λ = 0.710 73 Å) graphite monochromator
temp, K	298
2θ range, deg	2.0−40.0
no. collcd	2160
no. ind	2160
no. obsd	1217 ($\|F_o\| > 5\sigma\|F_o\|$)
weighting scheme	$\omega^{-1} = \sigma^2\|F_o\| + 0.04(\|F_o\|)^2$
R	0.0464
R_w	0.0618
largest diff peak, e Å^{-3}	0.29

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Supporting Information Available: Full listings of bond lengths and angles, anisotropic thermal parameters, and complete atomic parameters, ^{1}H and ^{13}C NMR spectra for compounds **1**−**5**, and text giving details of the method for the determination of cone angles (θ) for amines (22 pages). Ordering information is given on any current masthead page.

OM960677O

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(30) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.