

Steric Effects in Aluminum Compounds Containing Monoanionic Potentially Bidentate Ligands: Toward a Quantitative Measure of Steric Bulk

Julie A. Francis,^{1a} C. Niamh McMahon,^{1a} Simon G. Bott,^{*,1b} and Andrew R. Barron^{*,1a}

Department of Chemistry, Rice University, Houston, Texas 77005, and Department of Chemistry, University of Houston, Houston, Texas 77204

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To develop an understanding of the factors that control the strength of the Lewis acid–base interactions in five-coordinate compounds of aluminum, dimeric dialkylaluminum compounds $[\text{R}_2\text{Al}\{\mu\text{-O}(\text{CH}_2)_n\text{ER}'_x\}]_2$ ($n = 2, 3$; $\text{ER}'_x = \text{OR}'$, SR' , NR'_2) have been prepared from AlR_3 and the appropriate substituted alcohol, thiol, or amine: $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$, $\text{R} = \text{}^t\text{Bu}$ (**1**), $\text{}^i\text{Bu}$ (**2**), and Et (**3**); $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{O}^n\text{Bu})]_2$, $\text{R} = \text{}^t\text{Bu}$ (**4**) and Me (**5**); $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{OMe})]_2$, $\text{R} = \text{}^t\text{Bu}$ (**6**) and Me (**7**); $(\text{}^t\text{Bu})_2\text{Al}(\mu\text{-O}^n\text{Bu})(\mu\text{-OCH}_2\text{CH}_2\text{OMe})\text{Al}(\text{}^t\text{Bu})_2$ (**11**); $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{SMe})]_2$, $\text{R} = \text{}^t\text{Bu}$ (**12**), $\text{}^i\text{Bu}$ (**13**), Et (**14**), and Me (**15**); $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{-CH}_2\text{CH}_2\text{SMe})]_2$, $\text{R} = \text{}^t\text{Bu}$ (**16**) and Me (**17**); $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$, $\text{R} = \text{}^t\text{Bu}$ (**18**), $\text{}^i\text{Bu}$ (**19**), Et (**20**), and H (**21**); $(\text{}^t\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NH}_2)]_2$ (**22**); $(\text{}^t\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)]_2$ (**23**). The molecular structures of compounds **1**, **2**, **6**, **7**, **12**, **13**, **16**, **18–22**, and $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{-CH}_2\text{NMe}_2)]_2$ have been determined by X-ray crystallography. The solution structures have been probed by ^{13}C NMR spectroscopy using the alkoxide derivatives, $[\text{R}_2\text{Al}(\mu\text{-O}^n\text{Bu})]_2$, $\text{R} = \text{}^t\text{Bu}$ (**8**), $\text{}^i\text{Bu}$ (**9**), and Et (**10**), as a comparison, which show that compounds **1–7** and **11–23** exist as an equilibrium mixture between the four-coordinate isomer and its five-coordinate isomer, where $K_{\text{eq}} = [4\text{-coord}]/[5\text{-coord}]$. Factors that control the extent of this equilibrium and hence the coordination about aluminum include the steric bulk of the substituents at aluminum (R) and the Lewis base donor (R'), the basicity of the neutral donor group (ER'_x), and the chelate ring size (as determined by n). The intramolecular bond dissociation energies (BDEs) of the Lewis base donor (ER'_x), as determined by variable-temperature NMR spectroscopy, for compounds **1**, **12**, **15**, **16**, $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$, and $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{-CH}_2\text{NMe}_2)]_2$ (2.3–13.2 $\text{kJ}\cdot\text{mol}^{-1}$) are significantly lower than observed for their four-coordinate analogues, $\text{R}_3\text{Al}(\text{ER}'_{x+1})$ (63.8–125.5 $\text{kJ}\cdot\text{mol}^{-1}$). In addition, the relative donor ability (thioether > ether > amine) is the opposite of that expected. The similarity in BDE between compound **1** and **11** suggests that no cooperative effects are present. *Ab initio* calculations on the four- and five-coordinate isomers of the model compound $[\text{H}_2\text{Al}(\mu\text{-OCH}_2\text{-CH}_2\text{OH})]_2$ indicate that the surprisingly weak fifth coordination ligation in $[\text{R}_2\text{Al}\{\mu\text{-O}(\text{CH}_2)_n\text{ER}'_x\}]_2$ is a consequence of significant steric hindrance between the aluminum alkyl groups (R) and the Lewis base donor group. A quantitative measure of the thermodynamic destabilization that occurs upon substitution of H with Me or $\text{}^t\text{Bu}$ is proposed on the basis of the derivation of the Lennard-Jones (12,6) potential from solution thermodynamic and X-ray structural data.

Introduction

Compounds containing various monoanionic potentially bidentate ligands are ubiquitous within the chemistry of aluminum. Although such compounds include β -diketonate ligands (e.g., acetylacetonate), interest in recent years has focused on nondelocalized ligands containing both anionic and neutral Lewis base termini,² an example of which may be given the general formula $[\text{O}(\text{CH}_2)_n\text{ER}'_x]^-$. Equilibria between monomeric chelate (e.g., for $n = 2$, **I** in eq 1) and dimeric compounds

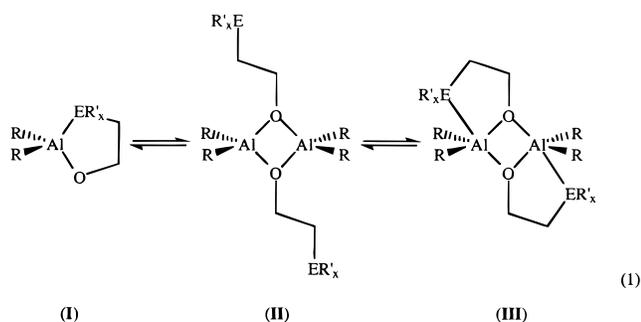
(e.g., for $n = 2$, **II** in eq 1) have been proposed.^{2a} In addition, the nonbridging heteroatoms can interact with

(2) See for example: (a) Beachley, O. T., Jr.; Racette, K. C. *Inorg. Chem.* **1976**, *15*, 2110, and references therein. (b) Atwood, D. A.; Gabbai, F. P.; Lu, J.; Remington, M. P.; Rutherford, D.; Sibi, M. P. *Organometallics* **1996**, *15*, 2308. (c) van Vliet, M. R. P.; van Koten, G.; Rotteveel, M. A.; Schrap, M.; Vrieze, K.; Kojic-Prodic, B.; Spek, A. L.; Duisenberg, A. J. M. *Organometallics* **1986**, *5*, 1389. (d) Jones, C.; Lee, F. C.; Koutsantonis, G. A.; Gardiner, M. G.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* **1996**, 829. (e) Hogerheide, M. P.; Wesseling, M.; Jastrzebski, J. T. B. H.; Boersma, J.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1995**, *14*, 4483. (f) Dzugan S. T.; Goedken, V. L. *Inorg. Chem. Acta* **1988**, *154*, 169. (g) van Vliet, M. R. P.; Buysingh, P.; van Koten, G.; Vrieze, K.; Kojic-Prodic, B.; Spek, A. L. *Organometallics* **1985**, *4*, 1701. (h) McMahon, C. N.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1997**, 3129.

* To whom correspondence should be addressed (<http://python.rice.edu/~arb/Barron.html>).

(1) (a) Rice University. (b) University of Houston.

the aluminum atoms to form compounds that contain five-coordinate aluminum centers (e.g., for $n = 2$, **III** in eq 1).³



Possible factors that control the coordination about aluminum and the degree of association, and hence the position of this proposed three-way equilibrium, include the steric bulk of the substituents at aluminum (R) and the Lewis base donor (R'), the basicity of the neutral donor group (ER'_x) versus the anionic donor atom,⁴ and the chelate ring size as determined by the length of the ligand's backbone (n). In a series of seminal experiments Mole demonstrated that the relative bridging ability of a series of donor groups could be determined for aluminum compounds of the general formula $[R_2Al(\mu-X)]_n$.⁵ However, these results were not aimed at the possible formation of five-coordinate aluminum compounds. Similarly, Beachley et al.² have previously shown that the potential chelate ring size and relative basicity are certainly controlling factors with regard to the degree of association (i.e., the formation of **I** versus either **II** or **III**). However, no indication concerning the relative formation of **II** versus **III** was given at that time. Even with the addition of several structural investigations there has been little attempt to develop a cohesive picture as to the factors controlling the proposed structural equilibria shown in eq 1.

Our initial interest in this area arose from the desire to prepare simple monomeric intramolecularly stabilized compounds as latent Lewis acid catalysts and cocatalysts.⁶ However, while there is an abundance of quantitative thermodynamic data on the strength of Lewis acid–base interactions for four-coordinate aluminum, there is little information for five-coordinate compounds.

Results and Discussion

To investigate the trends and allow for comparisons with previously characterized compounds, the following discussion is divided with respect to the ligand type.

Ether–Alkoxide Ligands. 2-Methoxyethanol and related ether alcohols, $HO(CH_2)_nOR$, represent perhaps the simplest source of chelate-bridging ligands. In fact,

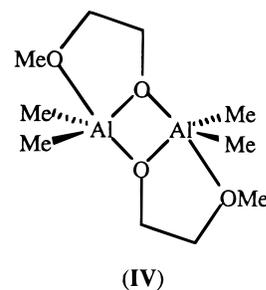
(3) Kumar, R.; Sierra, M. L.; Oliver, J. P. *Organometallics* **1994**, *13*, 4285.

(4) In the present case the anionic donor atom is oxygen; however, other group 16 or group 14 and 15 donor atoms are also possible.

(5) (a) Jeffery, E. A.; Mole, T.; Saunders: J. K. *Aust. J. Chem.* **1968**, *21*, 137. (b) Jeffery, E. A.; Mole, T.; Saunders: J. K. *Aust. J. Chem.* **1968**, *21*, 649.

(6) We have previously proposed the term latent Lewis acidity to describe the cage-opening reactions of alkylaluminum compounds; see: (a) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465. (b) Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 2213. (c) Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 5514.

$[Me_2Al(\mu-OCH_2CH_2OMe)]_2$ (**IV**) was the first aluminum compound of this general class to be crystallographically characterized.⁷



We have previously shown⁸ that for organometallic compounds of aluminum steric effects are more important than electronic effects with regard to substitution of the aluminum alkyl or the steric bulk of the ancillary ligands. To ascertain the effects of the steric bulk of the substituents on aluminum, we have prepared the homologous series $[R_2Al(\mu-OCH_2CH_2OMe)]_2$, R = ^tBu (**1**), ⁱBu (**2**), and Et (**3**). The effects of steric bulk at the Lewis base donor can be observed from the ⁿBu-substituted derivatives $[R_2Al(\mu-OCH_2CH_2O^nBu)]_2$, R = ^tBu (**4**) and Me (**5**), while the effects of variation in the ligand backbone chain length are observed from comparison with $[R_2Al(\mu-OCH_2CH_2CH_2OMe)]_2$, R = ^tBu (**6**) and Me (**7**). Compounds **1–7** were prepared by the reaction of the appropriate ether alcohol with either AlR_3 or (ⁱBu)₂AlH (see Experimental Section).

The molecular structures of [^tBu)₂Al(μ -OCH₂CH₂-OMe)]₂ (**1**) and [ⁱBu)₂Al(μ -OCH₂CH₂-OMe)]₂ (**2**) are shown in Figure 1; selected bond lengths and angles are given in Table 1 along with those previously reported for $[Me_2Al(\mu-OCH_2CH_2OMe)]_2$ (**IV**).⁷ The geometry about aluminum in compounds **1**, **2**, and $[Me_2Al(\mu-OCH_2CH_2OMe)]_2$ is significantly different from the tetrahedral ideal that is observed for simple alkoxide compounds, $[R_2Al(\mu-OR')]_2$,⁹ and is that of a distorted trigonal bipyramid (see Table 1). Despite the larger steric bulk¹⁰ of the *tert*-butyl ($\theta = 126^\circ$) and isobutyl ($\theta = 108^\circ$) groups compared to methyl ($\theta = 90^\circ$), the overall structures of compounds **1** and **2** are remarkably similar to their methyl analogue.⁷ The only significant difference between these three structures is the extent of the axial Al⋯O_(ether) interaction. In compound **2** and $[Me_2Al(\mu-OCH_2CH_2OMe)]_2$ this interaction is longer than ordinary dative Lewis acid–base interactions (1.90–2.02 Å),¹¹ but significantly shorter than in compound **1**, where the Al(1)⋯O(4) distance (2.74 Å) is close to the limits of a van der Waal interaction. As can be seen from Figure 2 the extent of the axial Al⋯O_(ether) interaction is dependent on the steric bulk of the aluminum alkyl,

(7) Benn, R.; Rufinska, A.; Lehmkuhl, H.; Janssen, E.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779.

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

(9) See for example: (a) Haaland, A.; Stokkeland, O. *J. Organomet. Chem.* **1975**, *94*, 345. (b) Cayton, R. H.; Chisholm, M. H.; Davidson, E. R.; DiStasi, V. F.; Du, P.; Huffmann, J. C. *Inorg. Chem.* **1991**, *30*, 1020. (c) Aitken, C. L.; Barron, A. R. *J. Chem. Crystallogr.* **1996**, *26*, 293.

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

(11) See for example: (a) Haaland, A.; Samdal, S.; Stokkeland, O.; Weidlein, J. *J. Organomet. Chem.* **1977**, *134*, 165. (b) Atwood, J. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1967**, *89*, 5362. (c) Srinivas, V.; de Mel, J.; Oliver, J. P. *Organometallics* **1989**, *8*, 827. (d) Rahman, A. F. M. M.; Siddiqui, K. F.; Oliver, J. P. *J. Organomet. Chem.* **1987**, *319*, 161.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$

	$[(^t\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$ (1)	$[(^i\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$ (2)	$\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2^a$
Al(1)–O(1)	1.82(1)	1.840(2)	1.827(3)
Al(1)–O(1a)	1.890(6)	1.909(1)	1.892(3)
Al(1)–C(11)	2.03(2)	1.974(2)	1.940(5)
Al(1)–C(21)	1.98(2)	1.975(3)	1.962(5)
Al(1)–O(4)		2.283(2)	2.269(3)
O(1)–Al(1)–O(1a)	74.8(4)	76.38(7)	76.3
O(1)–Al(1)–O(4)		75.06(9)	75.9
O(1)–Al(1)–C(11)	117.5(7)	122.8(1)	118.2(2)
O(1)–Al(1)–C(21)	119.2(8)	114.7(1)	119.4(2)
O(4)–Al(1)–C(11)		95.2(1)	92.1(2)
O(4)–Al(1)–C(21)		86.9(1)	89.3(2)
C(11)–Al(1)–C(21)	117.8(9)	117.8(9)	120.8(2)
Al(1)–O(1)–Al(1a)	105.2(6)	103.62(9)	103.7

^a Benn, R.; Rufinska, A.; Lehmkuhl, H.; Janssen, E.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779.

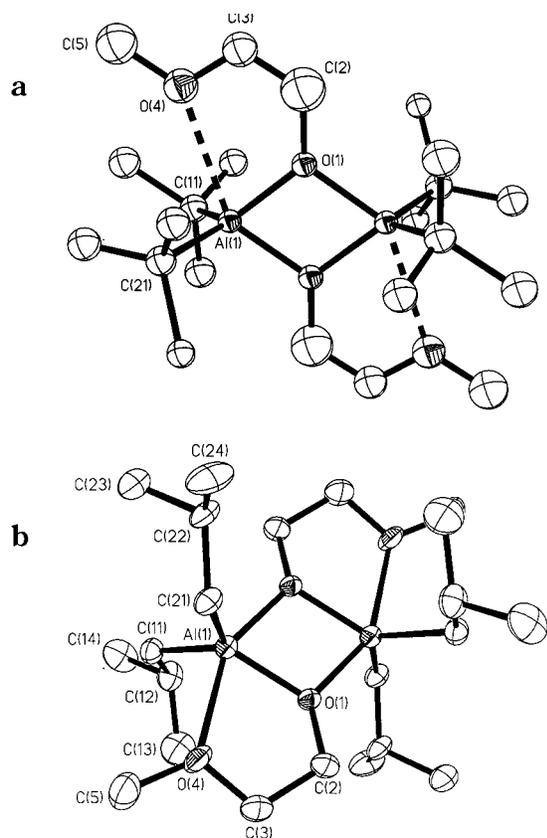


Figure 1. Molecular structures of (a) $[(^t\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$ (1) and $[(^i\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$ (2). Hydrogen atoms are omitted, and only one of the disordered positions of the methyl groups attached to C(11) and C(21) in compound 1 is shown, for clarity.

as measured by the Tolman cone angle (θ).¹⁰ Similar values are observed in the structurally related 2-methoxyphenoxide compounds, $[\text{R}_2\text{Al}(\mu\text{-OC}_6\text{H}_4\text{-2-OMe})]_2$, reported by Oliver¹² and Schumann,¹³ values for which are also included in Figure 2. The extent of the $\text{Al}\cdots\text{O}_{(\text{ether})}$ interactions varies only slightly for compounds with aluminum alkyl substituents sterically less demanding than isobutyl. This suggests that the $\text{Al}\cdots\text{O}$ distance is controlled by the following factors: (a) the ring strain within the AlO_2C_2 cycle, (b) the essentially

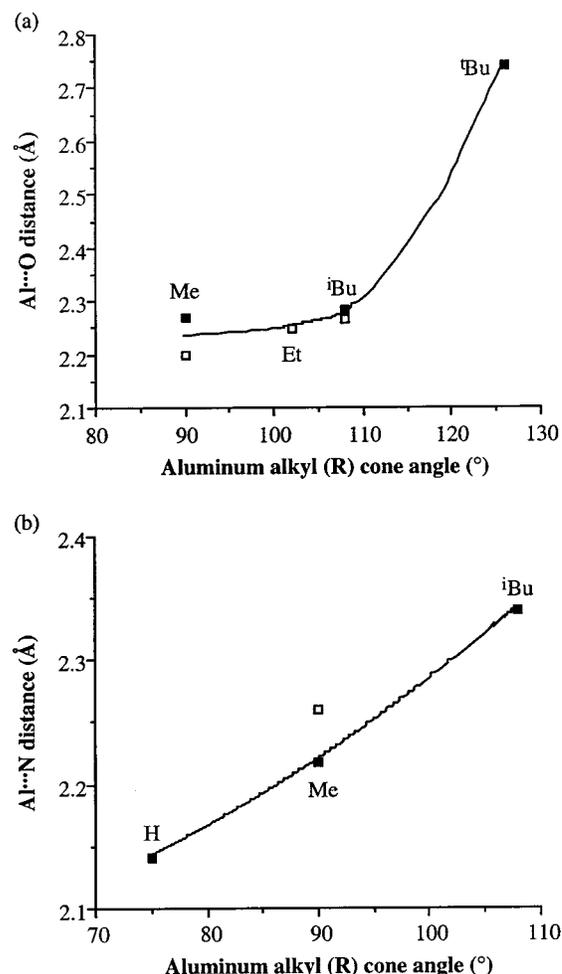


Figure 2. Plot of (a) the $\text{Al}\cdots\text{O}_{(\text{ether})}$ bond distance (Å) in $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$ and (b) the $\text{Al}\cdots\text{N}$ bond distance (Å) in $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ as a function of the aluminum alkyl (R) cone angle (deg). The values for $[\text{R}_2\text{-Al}(\mu\text{-OC}_6\text{H}_4\text{-2-OMe})]_2$ and $[\text{Me}_2\text{Al}\{\mu\text{-OC}(\text{OMe})=\text{C}(\text{H})\text{NMe}_2\}]_2$ are shown (\square) for comparison.

p-character of the axial environment about the aluminum,¹⁴ and (c) the *trans*-influence of the bridging alkoxide ligand.¹⁵ For compounds with aluminum alkyl substituents larger than isobutyl, the ether $\text{Al}\cdots\text{O}$ interaction is clearly determined by the steric repulsion

(12) Hendershot, D. G.; Barber, M.; Kumar, R.; Oliver, J. P. *Organometallics* **1991**, *10*, 3302.

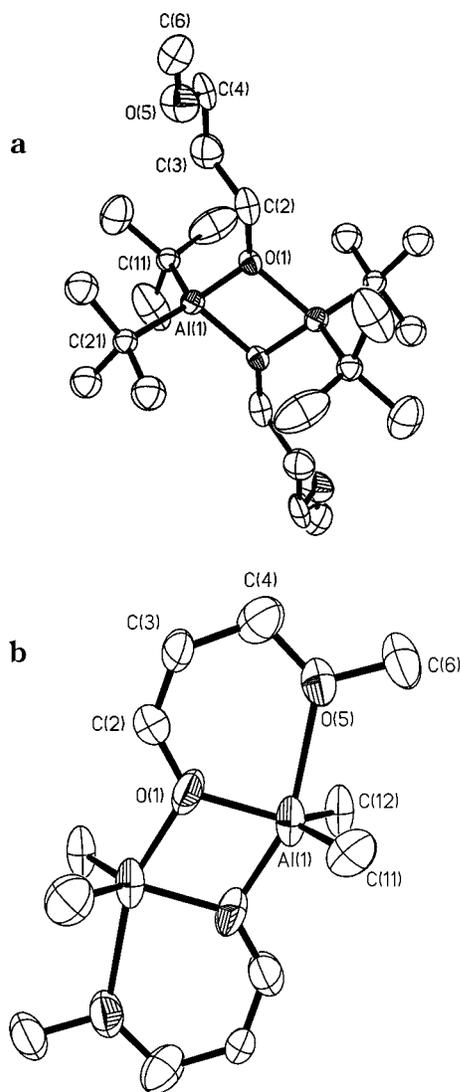
(13) Schumann, H.; Frick, M.; Heymer, B.; Girgsdies, F. *J. Organomet. Chem.* **1996**, *512*, 117.

(14) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*, Wiley: New York, 1985; Chapter 14, p 273.

(15) Appleton, T. C.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

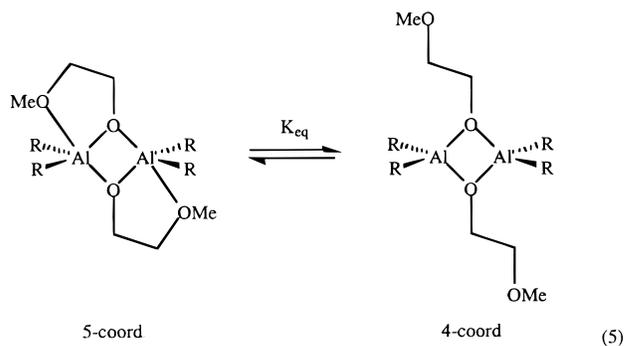
Table 2. Selected Bond Lengths (Å) and Angles (deg) in $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{OMe})_2]_2$, $\text{R} = \text{'Bu}$ (6), Me (7)

	$[(\text{'Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{OMe})_2]_2$ (6)	$[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{OMe})_2]_2$ (7)
Al(1)–O(1)	1.844(5)	1.78(1)
Al(1)–O(1a)	1.852(2)	1.87(2)
Al(1)–C(11)	2.005(7)	1.95(4)
Al(1)–C(21)	1.999(8)	1.96(3)
Al(1)–O(5)	n/a	2.39(2)
O(1)–Al(1)–O(1a)	78.4(2)	74.9(8)
O(1)–Al(1)–C(11)	116.7(3)	118(2)
O(1)–Al(1)–C(21)	114.1(3)	119(1)
C(11)–Al(1)–C(21)	116.2(3)	122.5(9)
O(1)–Al(1)–O(5)	n/a	83.9(7)
Al(1)–O(1)–Al(1a)	101.6(2)	105.1(8)

**Figure 3.** Molecular structures of (a) $[(\text{'Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{OMe})_2]_2$ (6) and (b) $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{OMe})_2]_2$ (7). Hydrogen atoms are omitted, and only one of the disordered positions of the methyl groups attached to C(11) and C(21) in compound 6 is shown, for clarity.

between the MeO group and the two alkyl substituents on aluminum. The molecular structures of $[(\text{'Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{OMe})_2]_2$ (6) and $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{OMe})_2]_2$ (7) are shown in Figure 3; selected bond lengths and angles are given in Table 2. The structure of compound 6 shows no evidence for any intramolecular interaction between the ether oxygen and the aluminum center [$\text{Al}(1)\cdots\text{O}(5) > 5.1 \text{ \AA}$]. In contrast, the structure of compound 7 shows intramolecular interaction be-

tween the ether oxygen and the aluminum center. However, this is significantly larger than observed for $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})_2]_2$; see Tables 1 and 2. The decrease in $\text{Al}\cdots\text{O}$ interaction upon increasing the carbon chain from C_2 in compound $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})_2]_2$ to C_3 in $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{OMe})_2]_2$ may be due to the combination of two effects. First, an increased strain is incurred by the formation of an $\text{Al}\cdots\text{O}$ bond within a six-membered Al-O-C-C-C-O cycle in which the intracyclic angle would be ideally 120° , while that in the five-membered Al-O-C-C-O cycle is 108° . These values may be compared to the ideal of 90° required in a trigonal bipyramidal structure. Second, in the six-membered ring the MeO substituent is pushed closer to the aluminum alkyl groups, resulting in increased steric repulsion and hence a longer $\text{Al}\cdots\text{O}_{(\text{ether})}$ interaction. While molecular weight measurements confirm dimeric structures in solution, it is desirable to have a probe that directly allows for structural information in solution, i.e., the extent of coordination of the ether moiety. For any dimeric 2-methoxyethoxide compound the extent to which the four-coordinate isomer (4-coord) exists relative to the five-coordinate isomer (5-coord) is dictated by the equilibrium shown in eq 5 and can be quantified by its equilibrium constant, K_{eq} (eq 6).



$$K_{\text{eq}} = \frac{[\text{4-coord}]}{[\text{5-coord}]} \quad (6)$$

It is desirable to answer the following questions: Is intramolecular coordination maintained in solution? If not, is there an equilibrium process between coordinated (III) and uncoordinated (II) species? How is that equilibrium, as measured by K_{eq} , affected by the chelate ring size (n), the steric bulk at the aluminum center (R), and the steric bulk of the ether ligand (R')? To answer these questions, the coordination number of the aluminum

Table 3. Selected Room-Temperature Solution ^{27}Al and ^{13}C NMR Spectral Data and Calculated Equilibrium Constants

compound	^{27}Al		^{13}C , Al–OCH ₂ , δ (ppm)	K_{eq}^a
	δ (ppm)	$W_{1/2}$ (Hz)		
[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ OMe)] ₂ (1)	123	4560	64.7	4.00
[(ⁱ Bu) ₂ Al(μ -OCH ₂ CH ₂ OMe)] ₂ (2)	123	7210	60.1	0.236
[Et ₂ Al(μ -OCH ₂ CH ₂ OMe)] ₂ (3)	120	3590	59.5	0.176
[Me ₂ Al(μ -OCH ₂ CH ₂ OMe)] ₂ ^b	121	1830	58.8	0.160
[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ O ⁿ Bu)] ₂ (4)	140	7700	65.5	> 14.0
[Me ₂ Al(μ -OCH ₂ CH ₂ O ⁿ Bu)] ₂ (5)	126	5940	59.6	0.450
[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ CH ₂ OMe)] ₂ (6)	134	2730	64.1	≈ 4.0
[Me ₂ Al(μ -OCH ₂ CH ₂ CH ₂ OMe)] ₂ (7)	144	6560	61.1	≈ 1.7
[(^t Bu) ₂ Al(μ -O ⁿ Bu)] ₂ (8)	137	5880	65.9	n/a
[(ⁱ Bu) ₂ Al(μ -O ⁿ Bu)] ₂ (9)	150	5500	64.6	n/a
[Et ₂ Al(μ -O ⁿ Bu)] ₂ (10)	149	4770	63.9	n/a
[Me ₂ Al(μ -O ⁿ Bu)] ₂ ^c	149	2110	62.8	n/a
(^t Bu) ₂ Al(μ -O ⁿ Bu)(μ -OCH ₂ CH ₂ CH ₂ OMe)- Al(^t Bu) ₂ (11)	<i>d</i>	<i>d</i>	64.6	3.98

^a Equilibrium constant, $K_{\text{eq}} = [4\text{-coord}]/[5\text{-coord}]$. ^b Benn, R.; Rufinska, A.; Lehmkuhl, H.; Janssen, E.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, 22, 779. ^c Rogers, J. H.; Apblett, A. W.; Cleaver, W. M.; Tyler, A. N.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1992**, 3179. ^d Not observed.

and hence the presence or extent of any intramolecular Al...O coordination (i.e., **II** versus **III**) must be determined by spectroscopic methods. In this regard we have investigated the solution NMR of the ether-alkoxide compounds of aluminum, $[\text{R}_2\text{Al}\{\mu\text{-O}(\text{CH}_2)_n\text{OR}'\}]_2$.

Ashe et al.¹⁶ have shown that the temperature-dependent equilibrium constants (K_{eq}) for equilibria between three- and four-coordinate boratabenzene complexes may be determined from ^{11}B NMR spectra. Similarly, the presence of four- or five-coordinate aluminum may be, in principle, determined by the use of ^{27}Al NMR spectroscopy. Unfortunately, as can be seen from Table 3, the ^{27}Al NMR chemical shifts for compounds **1**, **2**, **3**, and **5** are essentially within experimental error (123–120 ppm) and the same as the value previously reported for $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$ (121 ppm),⁷ which would suggest that they are isostructural in solution. In contrast, compounds **4**, **6**, and **7** exhibit chemical shifts within the range (149–137 ppm) observed for the four-coordinate compounds $[\text{R}_2\text{Al}(\mu\text{-O}^n\text{Bu})]_2$ [$\text{R} = \text{}^t\text{Bu}$ (**8**), $\text{}^i\text{Bu}$ (**9**), Et (**10**), Me].¹⁷ Thus, an alternative structural probe must be used, and since neither the alkyl substituent at aluminum (R) nor the Lewis base is constant, we decided to use the chemical shift of the alkoxide α -carbon (i.e., OCH₂) as the diagnostic group. We have previously shown that ^{13}C NMR chemical shifts are good structural probes since they are affected by the bonding environment of the proton, but not by shielding effects and through-space interactions.⁸ Therefore, we have developed the following approach to measure the relative structural trends within a homologous series of compounds. The ^{13}C NMR spectra of all complexes $[\text{R}_2\text{Al}\{\mu\text{-O}(\text{CH}_2)_n\text{OR}'\}]_2$ show a single sharp resonance due to the OCH₂ group over the temperature ranges measured, indicating that equilibrium is rapid on the NMR time scale. Assuming the ^{13}C NMR shift of the OCH₂ group is directly proportional to the mole fraction of the total species present as the four-coordinate isomer (4-coord), $\chi_{4\text{-coord}}$, the ^{13}C NMR chemical shift of the OCH₂, at a given temperature, $\delta_{(\text{obs})}$, may be used to calculate both $\chi_{4\text{-coord}}$ and $\chi_{5\text{-coord}}$.

e.g., eqs 7 and 8, respectively.¹⁸

$$\chi_{(4\text{-coord})} = \frac{\delta_{(\text{obs})} - \delta_{(5\text{-coord})}}{\delta_{(4\text{-coord})} - \delta_{(5\text{-coord})}} \quad (7)$$

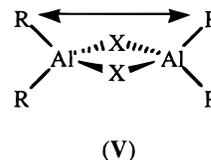
$$\chi_{(5\text{-coord})} = \frac{\delta_{(4\text{-coord})} - \delta_{(\text{obs})}}{\delta_{(4\text{-coord})} - \delta_{(5\text{-coord})}} \quad (8)$$

From this K_{eq} (eq 6) can be defined by eq 9.

$$K_{\text{eq}} = \frac{\chi_{(4\text{-coord})}}{\chi_{(5\text{-coord})}} \quad (9)$$

The same method was used by Ashe et al.;¹⁶ however, in the present case the asymptotic values at high and low temperatures appear to be different for compounds with different alkyl substituents on aluminum (R). In addition, not all the compounds reach an asymptotic value at both temperatures. Thus, a method is needed to determine the chemical shifts for $\delta_{(4\text{-coord})}$ and $\delta_{(5\text{-coord})}$ for compounds with each alkyl group, R.

We have previously reported¹⁹ that in aluminum compounds of the general formula $[\text{R}_2\text{Al}(\mu\text{-X})]_2$ the Al–X–Al angle is directly proportional to the steric bulk of the alkyl ligand, as measured by the Tolman cone angle. This trend is a consequence of steric repulsion between the alkyl groups on adjacent aluminum centers, i.e., **V**.



Thus, for a series of the homologous four-coordinate compounds, $[\text{R}_2\text{Al}(\mu\text{-O}^n\text{Bu})]_2$ for $\text{R} = \text{}^t\text{Bu}$ (**8**), $\text{}^i\text{Bu}$ (**9**), Et (**10**), and Me,¹⁷ the Al–O–Al angle would be proportional to the steric bulk of the alkyl ligand (R). We have previously shown that ^{13}C NMR spectral shifts may be used as a probe of the C–Al–C angle in $\text{Me}_3\text{Al}(\text{PR}_3)$

(16) Ashe, III, A. J.; Kampf, J. W.; Waas, J. R. *Organometallics* **1997**, 16, 163.

(17) Rogers, J. H.; Apblett, A. W.; Cleaver, W. M.; Tyler, A. N.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1992**, 3179.

(18) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.

(19) McMahon, C. N.; Francis, J. A.; Barron, A. R. *J. Chem. Crystallogr.* **1997**, 27, 167.

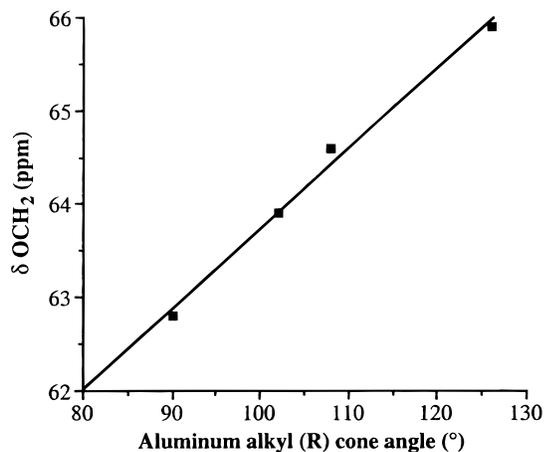


Figure 4. Plot of the ^{13}C NMR shift of the OCH₂ carbon as a function of the Tolman cone angle (θ , deg) for the aluminum substituents (R) in $[\text{R}_2\text{Al}(\mu\text{-O}^n\text{Bu})]_2$ ($R = 0.992$).

complexes.^{8,20} We now propose that, in an analogous manner, the ^{13}C NMR chemical shift of the OCH₂ in $[\text{R}_2\text{-Al}(\mu\text{-O}^n\text{Bu})]_2$ should be dependent on the Al–O–Al bond angle and hence the cone angle of the alkyl ligand. As can be seen in Figure 4, this is indeed observed.

We have observed that the $^{13}\text{C}\{^1\text{H}\}$ NMR shifts observed for the OCH₂ group in $[\text{R}_2\text{Al}(\mu\text{-O}^n\text{Bu})]_2$ ($R = ^n\text{Bu}$ and ^tBu) are identical to those in $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{-CH}_2\text{OR}')]_2$ ($R = ^n\text{Bu}$ and ^tBu) at high temperature. Thus, the $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shift values for OCH₂ in $[\text{R}_2\text{-Al}(\mu\text{-O}^n\text{Bu})]_2$ may be used as a good estimates for the $\delta_{(4\text{-coord})}$ in $[\text{R}_2\text{Al}\{\mu\text{-O}(\text{CH}_2)_n\text{OR}'\}]_2$, $[\text{R}_2\text{Al}\{\mu\text{-O}(\text{CH}_2)_n\text{SR}'\}]_2$, and $[\text{R}_2\text{Al}\{\mu\text{-O}(\text{CH}_2)_n\text{NR}'_2\}]_2$. In contrast, the lack of suitable model compounds for the five-coordinate structures of $[\text{R}_2\text{Al}\{\mu\text{-O}(\text{CH}_2)_n\text{OR}'\}]_2$, $[\text{R}_2\text{Al}\{\mu\text{-O}(\text{CH}_2)_n\text{SR}'\}]_2$, and $[\text{R}_2\text{Al}\{\mu\text{-O}(\text{CH}_2)_n\text{NR}'_2\}]_2$ requires a different estimate of the $\delta_{(5\text{-coord})}$ for each alkyl substituent. At the lowest temperatures for Me, Et, and ^tBu derivatives the ^{13}C NMR chemical shift values reach an asymptote. As per Ashe et al.,¹⁶ we propose that these values can be used directly. However the ^tBu derivative does not reach an asymptote; so assuming the Al–O–Al bond angle and therefore ^{13}C NMR chemical shift for OCH₂ in five-coordinate compounds are linearly dependent on the steric bulk of R, then an estimate of the values for ^tBu and ^iBu derivatives may be made from the extrapolation of the values of Me and Et compounds. Therefore, the ^{13}C NMR chemical shift values for $[\text{R}_2\text{Al}(\mu\text{-O}^n\text{Bu})]_2$ may be used for the four-coordinate chemical shift [i.e., $\delta_{(4\text{-coord})}$], and the extrapolation of the low-temperature data for the Me and Et compounds gives the five-coordinate chemical shift limit [i.e., $\delta_{(5\text{-coord})}$]. On the basis of these data K_{eq} values may be calculated. A further check of the validity of the NMR data involves the synthesis and characterization of the asymmetric dimer (^tBu)₂Al($\mu\text{-O}^n\text{Bu}$)($\mu\text{-OCH}_2\text{CH}_2\text{OME}$)Al(^tBu)₂ (**11**); see the Experimental Section and Table 3.

From the values in Table 3, it is clear that as expected the equilibrium (eq 5) is shifted toward the dissociation of the neutral Lewis base termini (OR') with increased steric bulk at the aluminum center (R). The similarity of K_{eq} values for compounds **1** and **11** suggests that no cooperative effect is present between the two ether-

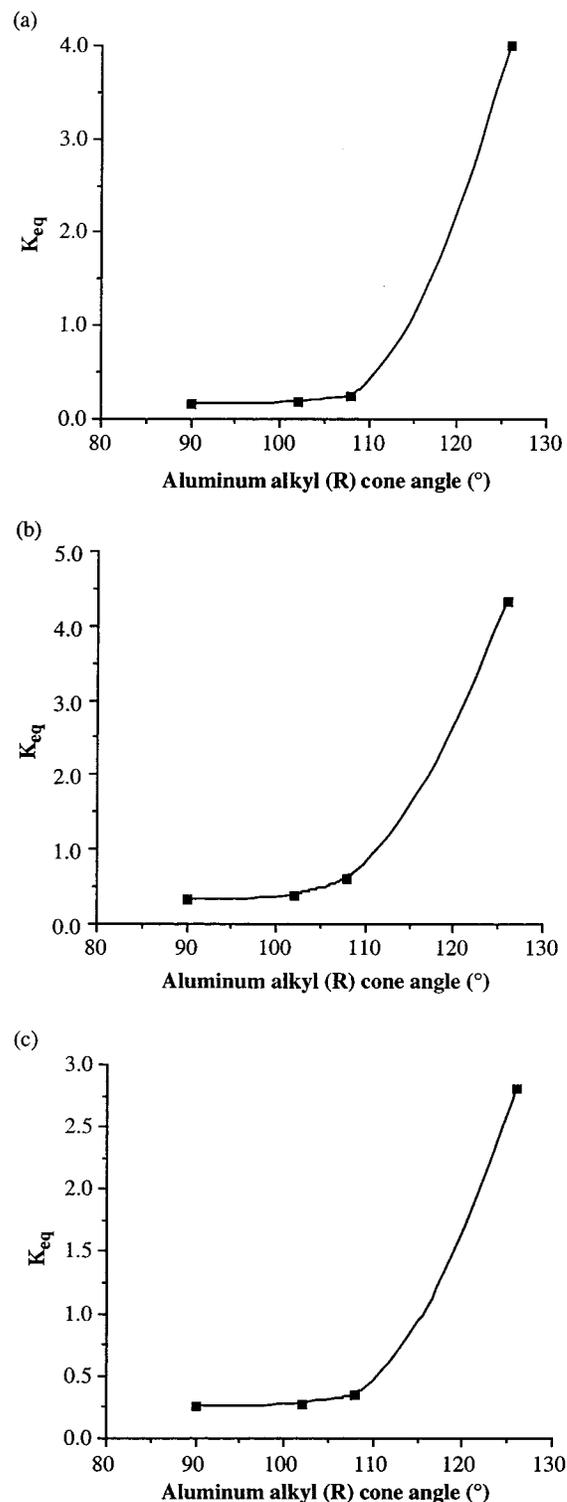
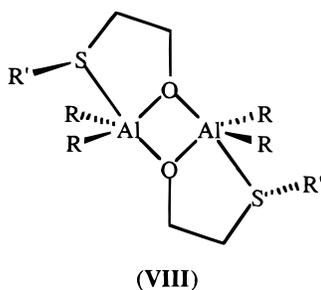
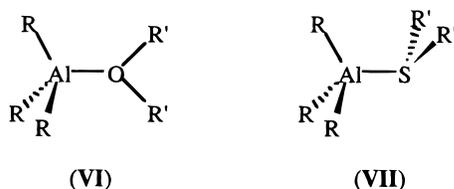


Figure 5. Plot of K_{eq} as a function of the aluminum alkyl (R) cone angle (deg) in (a) $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$, (b) $[\text{R}_2\text{-Al}(\mu\text{-OCH}_2\text{CH}_2\text{SMe})]_2$, and (c) $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$.

alkoxide ligands in compound **1**. The correlation of K_{eq} with the cone angle (θ) for the aluminum alkyl (R) in $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$ is shown in Figure 5a and should be compared to the relationship of the Al \cdots O_(ether) bond distance with the cone angle shown in Figure 2. Similarly, an increased steric bulk of the ether ligand (R') also results in a shift in the equilibrium toward dissociation of the ether ligand. Thus, the K_{eq} observed for $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{O}^n\text{Bu})]_2$ is greater than for their

analogous compounds $[R_2Al(\mu-OCH_2CH_2OMe)]_2$. An increase in the potential chelate ring size results in a general increase in the K_{eq} , consistent with the increased $Al\cdots O_{(ether)}$ distance; see above. Furthermore, the similarity in the values for compounds **6** and **7** suggests that the steric effects of the substituents on aluminum are diminished with increased chelate ring size.

Thioether–Alkoxide Ligands. Thioether complexes of aluminum are ordinarily weaker than their ether analogues²¹ and, as such, represent a suitable comparison to the 2-methoxyethoxide compounds to investigate the effects of a weaker Lewis base donor ligand. The radius of sulfur (1.85 Å) is significantly larger than oxygen (1.40 Å), resulting in a concomitant increase in Al–E bond length, i.e., Al–S = 2.19–2.52 Å versus Al–O = 1.69–2.00 Å.²² In addition, while the hybridization at oxygen in R_2O approximates to sp^2 , resulting in a planar geometry in an aluminum complex (e.g., **VI**), the hybridization about sulfur in R_2S results in a pyramidal geometry in the Lewis acid–base complex (e.g., **VII**). One consequence of this difference is an increased steric interaction between the alkyl substituent on the thioether (R') and the substituents on the aluminum (R), i.e., **VIII** in comparison to **IV**.²³



To ascertain the effects of the Lewis base donor atom, we have prepared and characterized the homologous series $[R_2Al(\mu-OCH_2CH_2SMe)]_2$, R = ^tBu (**12**), ⁱBu (**13**), Et (**14**), and Me (**15**); see the Experimental Section. The effect of variation in the ligand backbone chain length is observed as compared with $[R_2Al(\mu-OCH_2CH_2CH_2SMe)]_2$, R = ^tBu (**16**) and Me (**17**).

The molecular structures of $[(^tBu)_2Al(\mu-OCH_2CH_2SMe)]_2$ (**12**) and $[(^iBu)_2Al(\mu-OCH_2CH_2SMe)]_2$ (**13**) are shown in Figure 6; selected bond lengths and angles are

(21) For example, the dissociation enthalpies, ΔH , of the adduct $AlMe_3(OEt_2)$ is 84.5 kJ·mol⁻¹ compared to 70.2 kJ·mol⁻¹ for $AlMe_3(SEt_2)$; see: (a) Henrickson, C. H.; Eyman, D. P. *Inorg. Chem.* **1967**, *6*, 1461. (b) Henrickson, C. H.; Duffy, D.; Eyman, D. P. *Inorg. Chem.* **1968**, *7*, 1047.

(22) Haaland, A. *Coordination Chemistry of Aluminum*; Robinson G. H., Ed.; VCH: New York, 1993; Chapter 1.

(23) See for example: (a) Stoll, S. L.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1997**, 1315. (b) Banks, M. A.; Beachley, O. T., Jr.; Gysling, H. J.; Luss, H. R. *Organometallics* **1990**, *9*, 1979. (c) Uhl, W.; Layh, M.; Becker, G.; Klinkhammer, K. W.; Hildenbrand, T. *Chem. Ber.* **1992**, *125*, 1547.

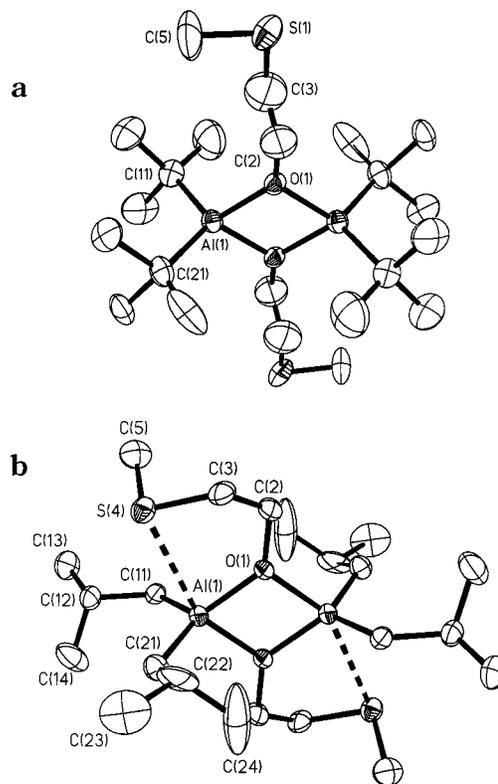


Figure 6. Molecular structures of (a) $[(^tBu)_2Al(\mu-OCH_2CH_2SMe)]_2$ (**12**) and (b) $[(^iBu)_2Al(\mu-OCH_2CH_2SMe)]_2$ (**13**). Hydrogen atoms are omitted, and only one of the disordered positions of the methyl groups attached to C(21) in compound **12** is shown, for clarity.

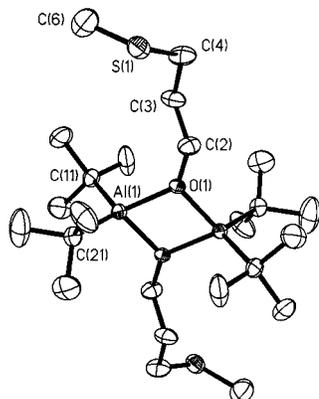
given in Table 4. The large Al(1)···S(4) distance (≈ 5.5 Å) in compound **12** clearly indicates a lack of an interaction between Al(1) and S(4). In contrast, the Al(1)···S(4) distance (2.95 Å) in the isobutyl compound (**13**) is consistent with a weak bonding interaction by comparison with simple Lewis acid–base complexes (2.515–2.718 Å).²⁴ The presence of a fifth coordination site in compound **13** is also indicated by the geometry about Al(1), which is essentially that of a distorted trigonal bipyramid.

As was observed for the ether derivatives, the extent of the axial Al···S_(thioether) interaction is dependent on the steric bulk of the aluminum alkyl; increased steric bulk results in weaker interactions. However, there also appears to be a dependence on the ligand geometry. Thus, whereas the O–C–C–S unit is planar in $[(^tBu)_2Al(\mu-OC_6H_4-2-SMe)]_2$,¹² it is nonplanar in $[(^tBu)_2Al(\mu-OCH_2CH_2SMe)]_2$. While this change did not appear to greatly affect the relative Al···O interactions in the ether derivatives, the pyramidal geometry about the thioether sulfur means that the change in configuration of the O–C–C–S unit results in the methyl group on the sulfur exhibiting a greater steric repulsion from the aluminum alkyl substituents. In comparing the thioether ligands to their ether analogues, $[R_2Al(\mu-OCH_2CH_2EMe)]_2$, it is clear that the Al···E interactions are influenced by both the steric bulk of the aluminum

(24) See for example: (a) Weiss, A.; Plass, R.; Weiss, A. *Z. Anorg. Allg. Chem.* **1956**, *283*, 390. (b) Robinson, G. H.; Zhang, H.; Atwood, J. L. *Organometallics* **1987**, *6*, 887. (c) Burford, N.; Royan, B. W.; Spence, R. E. v. H.; Rogers, R. D. *J. Chem. Soc., Dalton Trans.* **1990**, 2111.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in [(^tBu)₂Al(μ-OCH₂CH₂SMe)]₂ (12**) and [(^tBu)₂Al(μ-OCH₂CH₂SMe)]₂ (**13**)**

	[(^t Bu) ₂ Al(μ-OCH ₂ CH ₂ SMe)] ₂ (12)	[(^t Bu) ₂ Al(μ-OCH ₂ CH ₂ SMe)] ₂ (13)
Al(1)–O(1)	1.852(3)	1.841(2)
Al(1)–O(1a)	1.851(2)	1.888(1)
Al(1)–C(11)	1.994(9)	1.973(4)
Al(1)–C(21)	1.984(9)	1.969(4)
Al(1)⋯S(4)	n/a	2.95(1)
O(1)–Al(1)–O(1a)	78.8(1)	77.31(8)
O(1)–Al(1)–C(11)	113.8(2)	117.2(1)
O(1)–Al(1)–C(21)	114.1(3)	120.2(2)
O(1)–Al(1)–S(4)		
C(11)–Al(1)–C(21)	116.8(3)	118.6(2)
C(11)–Al(1)–S(4)		
Al(1)–O(1)–Al(1a)	101.2(2)	102.7(1)

**Figure 7.** Molecular structure of [(^tBu)₂Al(μ-OCH₂CH₂CH₂SMe)]₂ (**16**). Hydrogen atoms are omitted for clarity.**Table 5. Selected Bond Lengths (Å) and Angles (deg) in [(^tBu)₂Al(μ-OCH₂CH₂CH₂SMe)]₂ (**16**)**

Al(1)–O(1)	1.857(2)	Al(1)–C(11)	1.998(3)
Al(1)–C(21)	2.006(3)		
O(1)–Al(1)–O(1a)	78.6(1)	O(1)–Al(1)–C(11)	115.1(1)
O(1)–Al(1)–C(21)	114.1(1)	C(11)–Al(1)–C(21)	117.8(1)
Al(1)–O(1)–Al(1a)	101.40(8)		

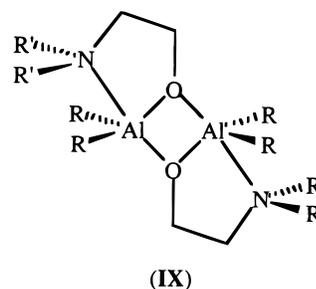
alkyl substituents and the orientation of the substituents on sulfur.

The molecular structure of [(^tBu)₂Al(μ-OCH₂CH₂CH₂SMe)]₂ (**16**) is shown in Figure 7; selected bond lengths and angles are given in Table 5. As with [(^tBu)₂Al(μ-OCH₂CH₂CH₂OMe)]₂ (**7**), the structure of compound **16** shows no evidence for any intramolecular interaction between the thioether and the aluminum center [Al(1)⋯S(5) > 5.5 Å].

The ¹³C NMR spectral shifts and the derived *K*_{eq} values for compounds **12**–**17** are given in Table 6. As with the ether donor ligands, the equilibrium (cf., eq 5) is shifted toward the dissociation of the neutral Lewis base termini (SMe) with increased steric bulk at the aluminum center (R) and increase in the potential chelate ring size (*n*). The variation of *K*_{eq} with the cone angle (*θ*) for the aluminum alkyl (R) in [R₂Al(μ-OCH₂CH₂SMe)]₂ is shown in Figure 5b and should be compared to the relationship observed for [R₂Al(μ-OCH₂CH₂OMe)]₂ (Figure 5a). The shift toward more dissociated complexes (i.e., **II** versus **III**) for the sulfur versus oxygen donor ligands is consistent with the increased covalent radius and hybridization of sulfur.

Amine–Alkoxide Ligands. On the basis of the above results it is clear that the strength of the aluminum–Lewis base interaction has a significant

influence on the extent of coordination, i.e., the position of the equilibrium shown in eq 1. It is also apparent from the comparison of the crystal structures of compounds **2** and **13** that the steric interactions between the substituent on the Lewis base and aluminum are important in determining the extent of coordination of the fifth ligand site. While the radius of nitrogen (1.5 Å) is similar to that of oxygen (1.4 Å) and hence they form similar bonds similar to aluminum, i.e., Al–N = 1.78–2.08 Å versus Al–O = 1.69–2.00 Å, amines form significantly stronger Lewis acid–base complexes to aluminum than ethers.²⁵ However, the sp³ hybridization at nitrogen in an aluminum complex results in an increased steric interaction between the alkyl substituent on the amine (R') and the substituents on the aluminum (R), i.e., **IX** in comparison to **IV**.



To ascertain the combined effects of the substituents on aluminum and the Lewis base donor, we have prepared the homologous series [R₂Al(μ-OCH₂CH₂NMe₂)]₂, R = ^tBu (**18**), ⁱBu (**19**), Et (**20**), Me,^{2a} and H (**21**), as well as [(^tBu)₂Al(μ-OCH₂CH₂NH₂)]₂ (**22**). In addition, [(^tBu)₂Al(μ-OCH₂CH₂CH₂NH₂)]₂ (**23**) was prepared in order to determine the effects of the substituents on nitrogen as compared with [(^tBu)₂Al(μ-OCH₂CH₂CH₂NMe₂)]₂.^{2h} Compounds **18**–**23** were prepared and characterized in a manner similar to that employed for their ether analogues. In addition, the solid-state molecular structures of compounds **18**–**23** and [Me₂Al(μ-OCH₂CH₂NMe₂)]₂ have been determined by X-ray crystallography.

The molecular structures of [(^tBu)₂Al(μ-OCH₂CH₂NMe₂)]₂ (**18**), [(^tBu)₂Al(μ-OCH₂CH₂NMe₂)]₂ (**19**), [Me₂Al(μ-OCH₂CH₂NMe₂)]₂, [H₂Al(μ-OCH₂CH₂NMe₂)]₂ (**21**), and [(^tBu)₂Al(μ-OCH₂CH₂NH₂)]₂ (**22**) are shown in Figure 8; selected bond lengths and angles are given in Table 7. Poor data precluded complete structural char-

(25) The dissociation enthalpy (*ΔH*) of the adduct AlMe₃(NMe₃) is 124 kJ·mol⁻¹; see ref 21.

Table 6. Selected Room-Temperature Solution ^{27}Al and ^{13}C NMR Spectral Data and Calculated Equilibrium Constants

compound	^{27}Al		^{13}C , Al–OCH ₂ , δ (ppm)	K_{eq}^a
	δ (ppm)	$W_{1/2}$ (Hz)		
$[(^t\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{SMe})_2]$ (12)	142	5280	64.5	4.33
$[(^t\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{SMe})_2]$ (13)	146	6950	60.3	0.605
$[\text{Et}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{SMe})_2]$ (14)	134	5410	59.1	0.370
$[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{SMe})_2]$ (15)	142	3440	58.5	0.324
$[(^t\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{SMe})_2]$ (16)	138	5220	65.1	≈ 8.1
$[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{SMe})_2]$ (17)	153	5130	64.4	≈ 5.1

^a Equilibrium constant, $K_{\text{eq}} = [4\text{-coord}]/[5\text{-coord}]$.

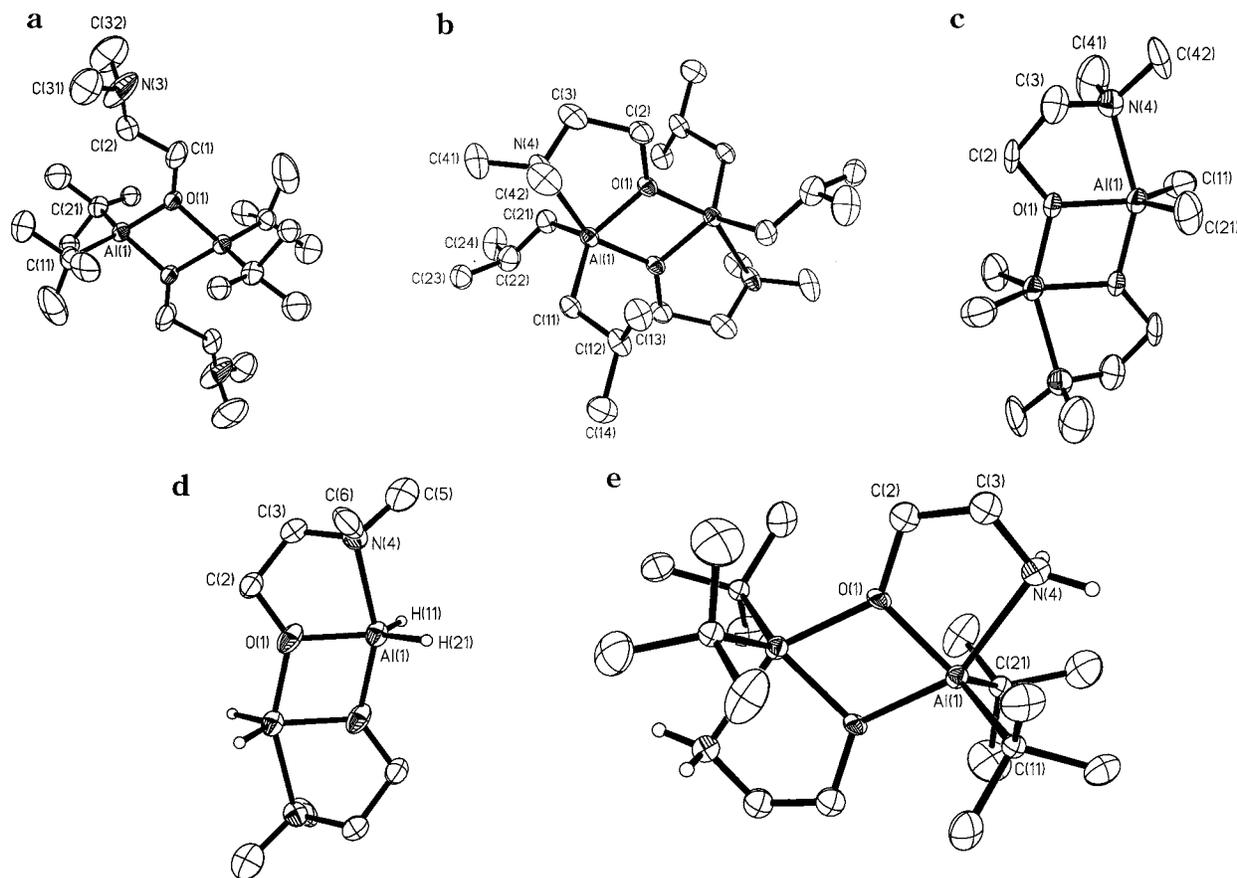


Figure 8. Molecular structures of (a) $[(^t\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ (**18**), $[(^t\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ (**19**), (c) $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$, (d) $[\text{H}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ (**21**), and (e) $[(^t\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NH}_2)]_2$ (**22**). Organic hydrogen atoms are omitted for clarity. Only one of the disordered positions of the methyl groups attached to C(21) in compound **18** and only one of the disordered positions of C(2), C(3), and the methyl groups attached to N(4) are shown for compound **19**.

acterization of $[\text{Et}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ (**20**); however, a partial solution²⁶ showed it to be similar to the methyl analogue.

The structure of $[(^t\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ (**18**) shows neither intra- or intermolecular association with aluminum. In contrast, compounds **19**, **21**, **22**, and $[\text{Me}_2\text{-Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ all exist as dimers with significant intramolecular interaction, although the Al–N bonds are significantly longer than those typical for simple Lewis acid–base adducts (1.94–2.10 Å).²⁷ Unlike

the Al···O(ether) interactions in $[\text{R}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})_2]$ (see above), the axial Al···N interaction is strongly dependent on the steric bulk of the aluminum alkyl substituents. This relationship is shown in Figure 2b with the value for $[\text{Me}_2\text{Al}\{\mu\text{-OC(OMe)=C(H)NMe}_2\}]_2$ shown for comparison.²⁸ We propose that the increased dependency is due to the increased steric bulk of the NMe₂ group versus OMe. The latter is a planar “blade-like” ligand which is positioned between the aluminum alkyl groups. In contrast, the two amine methyl groups potentially eclipse the aluminum alkyl groups.

Unlike $[(^t\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ (Figure 8a), the amine in $[(^t\text{Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NH}_2)]_2$ (Figure 8e) is strongly coordinated to the aluminum, demonstrating that the structure is dependent not only on the steric bulk of the aluminum alkyls but also on the steric

(26) Crystal data for $[\text{Et}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ (**19**): C₁₆H₄₀O₂Al₂N₂, monoclinic, $P2_1/n$, $a = 8.407(1)$ Å, $b = 10.239(1)$ Å, $c = 13.046(9)$ Å, $\beta = 92.229(8)^\circ$, $V = 1122.2(2)$ Å³, $Z = 2$.

(27) See for example: (a) Henrickson, C. H.; Eymann, D. P. *Inorg. Chem.* **1967**, *6*, 1461. (b) Robinson, G. H.; Zhang, H.; Atwood, J. L. *J. Organomet. Chem.* **1987**, *331*, 153. (c) Goebel, D. W.; Hencher, J. L.; Oliver, J. P. *Organometallics* **1983**, *2*, 746. (d) Almennigen, A.; Gundersen, G.; Haugen, T.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 3928. (e) Atwood, J. L.; Seale, S. K.; Roberts, D. H. *J. Organomet. Chem.* **1973**, *51*, 105.

(28) van der Steen, F. H.; van Mier, G. P. M.; Spek, A. L.; Kroon, J.; van Koten, G. *J. Am. Chem. Soc.* **1991**, *113*, 5742.

Table 7. Selected Bond Lengths (Å) and Angles (deg) in [R₂Al(μ-OCH₂CH₂NR')₂]

	R, R'				
	^t Bu, Me (18)	ⁱ Bu, Me (19)	Me, Me	H, Me (21)	^t Bu, H (22)
Al(1)–O(1)	1.860(3)	1.837(2)	1.833(6)	1.845(2)	1.868(6)
Al(1)–O(1a)	1.863(1)	1.958(5)	1.931(6)	1.897(2)	1.923(6)
Al(1)–N(4)		2.340(3)	2.128(8)	2.141(2)	2.126(9)
Al(1)–C(11)	1.995(7)	1.987(4)	1.96(1)	1.56(2), H(11)	2.058(9)
Al(1)–C(21)	1.983(7)	1.985(5)	1.99(1)	1.60(2), H(21)	2.04(1)
O(1)–Al(1)–N(4)		77.14(9)	77.6(3)	79.51(8)	78.9(3)
O(1)–Al(1)–C(11)	115.4(2)	124.1(1)	124.9(4)	124.1(9), H(11)	122.4(3)
O(1)–Al(1)–C(21)	116.4(2)	116.4(1)	116.7(4)	115.5(9), H(21)	119.2(4)
O(1)–Al(1)–O(1a)	78.9(1)	75.00(7)	74.4(2)	75.66(6)	72.7(2)
N(4)–Al(1)–C(11)		97.6(1)	92.9(4)	95.9(9), H(11)	90.8(4)
N(4)–Al(1)–C(21)		95.4(2)	98.4(4)	92.1(9), H(21)	92.6(4)
N(4)–Al(1)–O(1a)		152.13(7)	151.7(2)	154.34(7)	151.6(3)
C(11)–Al(1)–C(21)	116.8(2)	119.5(1)	118.4(5)	120(1), H(11)/H(21)	117.8(4)
C(11)–Al(1)–O(1a)	111.2(2)	97.2(1)	99.2(3)	100.5(9), H(11)	104.7(3)
C(21)–Al(1)–O(1a)	111.9(2)	97.7(1)	98.1(4)	96.4(9), H(21)	100.6(3)
Al(1)–O(1)–Al(1a)	101.1(1)	105.0(1)	105.6(3)	104.34(8)	107.3(3)

Table 8. Selected Room-Temperature Solution ²⁷Al and ¹³C NMR Spectral Data and Calculated Equilibrium Constants

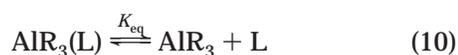
compound	²⁷ Al		¹³ C, Al–OCH ₂ , δ (ppm)	K _{eq} ^a
	δ (ppm)	W _{1/2} (Hz)		
[(^t Bu) ₂ Al(μ-OCH ₂ CH ₂ NMe ₂) ₂ (18)]	149	3980	63.9	2.76
[(ⁱ Bu) ₂ Al(μ-OCH ₂ CH ₂ NMe ₂) ₂ (19)]	113	5450	59.9	0.340
[Et ₂ Al(μ-OCH ₂ CH ₂ NMe ₂) ₂ (20)]	107	2230	59.5	0.2727
[Me ₂ Al(μ-OCH ₂ CH ₂ NMe ₂) ₂] ^b	108	1810	59.2	0.250
[H ₂ Al(μ-OCH ₂ CH ₂ NMe ₂) ₂ (21)]	91	1250	58.7	<0.1
[(^t Bu) ₂ Al(μ-OCH ₂ CH ₂ NH ₂) ₂ (22)]	92	4580	62.7	≈1.37 ^d
[(^t Bu) ₂ Al(μ-OCH ₂ CH ₂ CH ₂ NMe ₂) ₂] ^c	143	4400	64.9	≈6.60 ^d
[(^t Bu) ₂ Al(μ-OCH ₂ CH ₂ CH ₂ NH ₂) ₂ (23)]	118	2240	64.0	≈3.00 ^d

^a Equilibrium constant, K_{eq} = [4-coord]/[5-coord]. ^b Beachley, O. T., Jr.; Racette, K. C. *Inorg. Chem.* **1976**, *15*, 2110. ^c McMahon, C. N.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1997**, 3129. ^d Estimated, see text.

hindrance at the Lewis base. It is interesting to note that the Al–N distance in compound **22** is close to that in [Me₂Al(μ-OCH₂CH₂NMe₂)₂], suggesting that the combined steric bulk of the Al–R and N–R' groups determines the magnitude of the Lewis base interaction.

The ¹³C NMR spectral shifts and derived K_{eq} values are given for compounds **18–23** and [Me₂Al(μ-OCH₂CH₂NMe₂)₂] in Table 8. The amine moiety does not cleave the Al(μ-OR)₂Al unit, and the equilibrium (cf., eq 5) is shifted toward the dissociation of the neutral Lewis base (NMe₂) with increased steric bulk at the aluminum center (R) and increase in the potential chelate ring size (*n*). The correlation of K_{eq} with the cone angle (θ) for the aluminum alkyl (R) in [R₂Al(μ-OCH₂CH₂NMe₂)₂] is shown in Figure 5c. The shift toward more association (i.e., **III** versus **II**) for the amine versus oxygen donor ligands is consistent with the general increase in the basicity (donor ability) of the former. Furthermore, the increase in K_{eq} for [(^tBu)₂Al(μ-OCH₂CH₂NMe₂)₂] (6.60) versus [(^tBu)₂Al(μ-OCH₂CH₂OMe)₂] (4.00) is consistent with the greater steric bulk of NMe₂ versus OMe, and the steric interaction between the alkyl substituents on the amine and those on the aluminum (i.e., **IX**).

Determination of Intramolecular Bond Dissociation Energies. The bond dissociation energies (BDEs) for Lewis acid–base complexes of aluminum have previously been determined from the temperature dependence of the equilibrium constant, K_{eq} (i.e., eq 10).



Given the temperature dependence of the equilibrium constants for the intramolecular coordination complexes described above, it is reasonable to propose that the enthalpy (Δ*H*) and entropy (Δ*S*) for the reaction shown in eq 5 should be associated with the bond dissociation energy of the intramolecular Lewis acid–base coordination.²⁹

The temperature dependence of the equilibrium constants for compounds **1**, **11**, **12**, **15**, **18**, [Me₂Al(μ-OCH₂CH₂OMe)₂], and [Me₂Al(μ-OCH₂CH₂NMe₂)₂] was measured, and the Δ*H* and Δ*S* values were determined from the appropriate van't Hoff plots (e.g., Figure 9).³⁰ All calculated Δ*H* and Δ*S* values (with esd's) are given in Table 9, along with the calculated values for Δ*G* at 298 K. It should be noted that the values calculated directly from the van't Hoff plots are for a single intramolecular interaction, i.e., half the value for the reaction shown in eq 5. However, since a comparison with monomeric Lewis acid–base complexes is required, the value per intramolecular bond is used in all tables and the following discussion. This is clearly justified from the similarity of the values for compounds **1** and **11**.

As would be expected for a dissociative process, Δ*S* is positive (14–38 J·K⁻¹·mol⁻¹) for all the compounds measured. Furthermore, consistent with the intramolecular nature of the reaction, these values are significantly smaller than those reported for the dissociation

(29) It should be noted that this assumes that solvation of the 4-coord and 5-coord isomers of [R₂Al(μ-OCH₂CH₂ER')₂] are not significantly different.

(30) Unfortunately reequilibration of the solution results is too rapid to allow the enthalpy (Δ*H*[‡]) and entropy (Δ*S*[‡]) of activation to be determined from an appropriate Eyring plot.

Table 9. Selected Equilibrium and Thermodynamic Data

compound	K_{eq}^a at 298 K	ΔH (kJ·mol ⁻¹) ^b	ΔS (J·K ⁻¹ ·mol ⁻¹) ^b	ΔG at 298 K (kJ·mol ⁻¹)
[Me ₂ Al(μ -OCH ₂ CH ₂ OMe)] ₂ ^c	0.179	9.1(6)	16(2)	4.3
[Me ₂ Al(μ -OCH ₂ CH ₂ SMe)] ₂ (15)	0.456	13.2(2)	37.7(5)	1.9
[Me ₂ Al(μ -OCH ₂ CH ₂ NMe ₂)] ₂ ^d	0.275	7.4(5)	14(2)	3.2
[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ OMe)] ₂ (1)	4.236	5.2(4)	29(1)	-3.4
(^t Bu) ₂ Al(μ -O ⁿ Bu)(μ -OCH ₂ CH ₂ -CH ₂ OMe)Al(^t Bu) ₂ (11)	4.229	5.0(5)	35(2)	-3.3
[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ SMe)] ₂ (12)	4.972	4.94(2)	29.9(1)	-3.9
[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ NMe ₂)] ₂ (18)	2.766	2.3(1)	16.2(5)	-2.5

^a Equilibrium constant, $K_{\text{eq}} = [4\text{-coord}]/[5\text{-coord}]$. ^b Error given in parentheses. ^c For synthesis and characterization, see: Benn, R.; Rufinska, A.; Lehmkuhl, H.; Janssen, E.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779. ^d For synthesis and characterization, see: Beachley, O. T., Jr.; Racette, K. C. *Inorg. Chem.* **1976**, *15*, 2110.

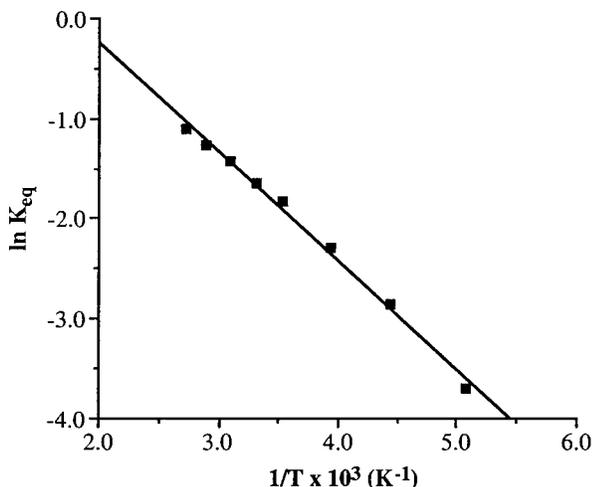


Figure 9. Temperature dependence of the equilibrium constant (K_{eq}) for the conversion of the 5-coord to 4-coord forms of [Me₂Al(μ -OCH₂CH₂OMe)]₂ ($R = 0.995$).

of a Lewis base from a four-coordinate aluminum complex, e.g., for the reaction shown in eq 10 ($\Delta S = 160\text{--}240 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$).³¹ The ΔH values for the *tert*-butyl derivatives are approximately half those of the methyl compounds, i.e., [(^tBu)₂Al(μ -OCH₂CH₂OMe)]₂ (**1**) versus [Me₂Al(μ -OCH₂CH₂OMe)]₂. This is in agreement with the expected steric interaction between the alkyl substituents on aluminum (R) and those on the Lewis base (R').

On the basis of a comparison of the appropriate Al–O, Al–S, and Al–N bond lengths for Lewis base donors with those of typical aluminum complexes, it is obviously expected that the intramolecular dative bonds should be weaker. However, what is unexpected is that the ΔH values are almost an order of magnitude smaller than those of complexes of four-coordinate aluminum with comparable Lewis bases (Table 10).^{21,32,33} In addition, the relative bond strength (Al–S > Al–O > Al–N) is in the opposite order of that expected on purely electronic grounds, i.e., Al–N (125.5 kJ·mol⁻¹ for Me₃Al–NMe₃) > Al–O (84.9 kJ·mol⁻¹ for Me₃Al–OMe₂) > Al–S (75.7 kJ·mol⁻¹ for Me₃Al–SMe₂).²¹

(31) (a) Power, M. B.; Nash, J. R.; Healy, M. D.; Barron, A. R. *Organometallics* **1992**, *11*, 1830. (b) Power, M. B.; Ziller, J. W.; Barron, A. R. *Organometallics* **1993**, *12*, 4908.

(32) It is worth noting that the sign of the calculated value for ΔG at 298 K correlates well with the position of the equilibrium (K_{eq}) at 298 K.

(33) The observed values are toward the low end of typical O–H···N hydrogen bonds (4–40 kJ·mol⁻¹), see: (a) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, 1960. (b) Joesten, M. D.; Schaad, L. J. *Hydrogen Bonding*; Dekker: New York, 1974.

Table 10. Selected Enthalpies, ΔH , of Lewis Acid–Base Complexes of Aluminum

donor atom	compound	ΔH (kJ·mol ⁻¹)	ref
oxygen	AlMe ₃ (OMe ₂)	84.9	<i>a</i>
	AlMe ₃ (OEt ₂)	84.5	<i>a</i>
	AlBr ₃ (OEt ₂)	152.7	<i>b</i>
	AlMe ₂ (BHT)(OEt ₂)	63.8	<i>c</i>
	[Me ₂ Al(μ -OCH ₂ CH ₂ OMe)] ₂	9.1	<i>d</i>
	[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ OMe)] ₂ (1)	5.2	<i>d</i>
sulfur	AlMe ₃ (SMe ₂)	75.7	<i>e</i>
	AlMe ₃ (SEt ₂)	70.3	<i>e</i>
	AlCl ₃ (SMe ₂)	126.7	<i>b</i>
	AlCl ₃ (SEt ₂)	125.1	<i>b</i>
	AlBr ₃ (SEt ₂)	128.0	<i>b</i>
	[Me ₂ Al(μ -OCH ₂ CH ₂ SMe)] ₂ (15)	13.2	<i>d</i>
[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ SMe)] ₂ (12)	4.9	<i>d</i>	
nitrogen	AlMe ₃ (NMe ₃)	125.5	<i>a</i>
	AlMe ₃ (NEt ₃)	110.8	<i>a</i>
	AlCl ₃ (NMe ₃)	200.8	<i>f</i>
	AlBr ₃ (NEt ₃)	187.4	<i>b</i>
	[Me ₂ Al(μ -OCH ₂ CH ₂ NMe ₂)] ₂	7.4	<i>d</i>
	[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ NMe ₂)] ₂ (18)	2.3	<i>d</i>

^a Henrickson, C. H.; Duffy, D.; Eymann, D. P. *Inorg. Chem.* **1968**, *7*, 1047. ^b Guryonova, E. N.; Goldstein, I. P.; Romm, I. P. *Donor–Acceptor Bond*; Wiley: New York, 1975. ^c Power, M. B.; Nash, J. R.; Healy, M. D.; Barron, A. R. *Organometallics* **1992**, *11*, 1830. ^d This work. ^e Henrickson, C. H.; Eymann, D. P. *Inorg. Chem.* **1967**, *6*, 1461. ^f Anderson, G. A.; Forgaard, F. R.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 1947.

These results prompt the following questions: *why are these intramolecular coordinate bonds so weak, and why is the relative order of the intramolecular bond strengths Al–S > Al–O > Al–N?*

Toward a Quantitative Measure of Steric Bulk. The concept of steric bulk was first developed by Hofmann in 1872³⁴ to explain differences in reactivity in organic chemistry. However, it was the work of Meyer in 1894 that provided the first quantifiable steric effect.³⁵ Subsequently researchers were able to provide a rationalization of reactivity in organic systems by the recognition of steric effects.³⁶ In inorganic and particularly organometallic systems the quantification of steric effects has been standardized by the work of Tolman.^{10,37} Subsequently, there have been several developments toward providing quantification of steric bulk,³⁸ in particular thermodynamic values for the destabilization of a molecule due to steric interactions.³⁹ Clearly the

(34) Hofmann, A. W. *Chem. Ber.* **1872**, *5*, 704.

(35) Meyer, V. *Chem. Ber.* **1894**, *27*, 510.

(36) For a review of the early developments of steric effects in organic chemistry see: Mosher, H. S.; Tidwell, T. T. *J. Chem. Educ.* **1990**, *67*, 9.

(37) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953.

(38) For a recent review see: White, D.; Coville, N. J. *Adv. Organomet. Chem.* **1994**, *36*, 95.

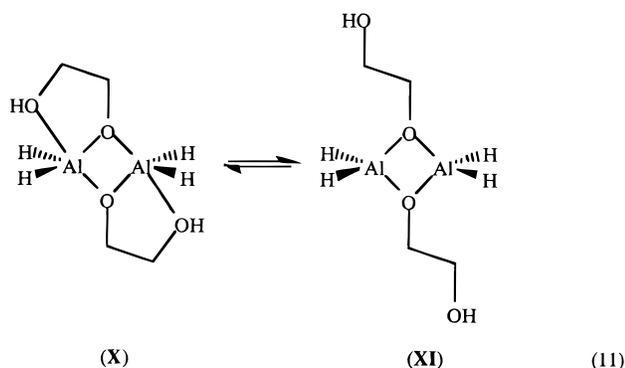
Table 11. Structural Parameters for Five- and Four-Coordinate Dimeric Isomers of $[\text{H}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OH})]_n$ in Comparison with Experimental Values^a

	five-coordinate dimer		four-coordinate dimer	
	calculated	experimental ^b	calculated	experimental ^c
Al–O	1.839, 1.894	1.827(3), 1.892(3)	1.833	1.844(5)–1.860(3)
Al \cdots O _(ether)	2.019	2.269(3)		
Al–H	1.622	1.56(2), 1.60(2) ^d	1.597	n/a
O–Al–O'	76.2	76.3	81.8	78.4(2)–78.9(1)
O–Al–O _(ether)	77.1	75.9		
O–Al–H	121.0	118.2(2), 119.4(2)	112.6	113.8(2)–116.7(3)
O _(ether) –Al–H	93.3	92.1(2), 89.3(2)		
H–Al–H	117.6	120.8(2)	118.8	116.2(3)–117.8(1)
Al–O–Al'	103.8	103.7	98.2	101.1(1)–101.6(2)
Al–O–C	127.3	124.6	135.0, 126.0	131.0(4)–132.1(4)

^a Distances in Å, angles in deg. ^b $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$ from: Benn, R.; Rufinska, A.; Lehmkuhl, H.; Janssen, E.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779. ^c Compounds **6**, **12**, **16**, and **18**. ^d Compound **21**.

presence or absence of weak Lewis acid–base interactions in the dimeric dialkylaluminum compounds $[\text{R}_2\text{-Al}\{\mu\text{-O}(\text{CH}_2)_n\text{ER}'_x\}]_2$ ($n = 2, 3$; $\text{ER}'_x = \text{OR}'$, SR' , NR'_2) is related to steric hindrance. It is of interest to examine whether it is possible to use the BDE data to provide a quantitative measure of steric repulsion.⁴⁰

To understand the relative stability of five- and four-coordinate isomers of $[\text{R}_2\text{Al}\{\mu\text{-O}(\text{CH}_2)_n\text{ER}'_x\}]_2$, we have performed ab initio calculations at the HF/3-21G(*) level (see Experimental Section) on the model compound $[\text{H}_2\text{-Al}(\mu\text{-OCH}_2\text{CH}_2\text{OH})]_2$ in the five- and four-coordinate isomers: designated as $[\text{H}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OH})]_2$ (**X**) and $[\text{H}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OH})]_2$ (**XI**). The optimized calculated structural parameters for each model are given in Table 11. For both dimeric isomers the calculated Al–H distances are comparable to those determined experimentally.⁴¹ As can be seen from Table 11, the Al–O distance and O–Al–O and Al–O–Al angles in the dimers are within experimental error of the ranges reported from X-ray diffraction studies. This is in line with our previous suggestion that the Al_2O_2 core is relatively insensitive to steric effects from the bridging alkoxide²¹ and indicates that the 3-21G(*) level faithfully models the overall geometry.⁴² However, it should be noted that the calculated Al–O_(ether) bond (2.019 Å) is significantly shorter than that in $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{-OMe})]_2$ [2.269(3) Å].⁷



The total energies of the model compounds were determined at the MP2/3-21G(*) level for the optimized structures. The five-coordinate compound $[\text{H}_2\text{Al}(\mu\text{-OCH}_2\text{-$

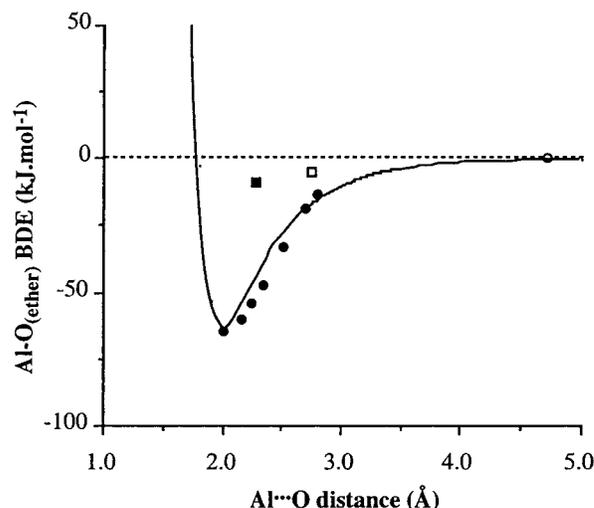


Figure 10. Dependence of the intramolecular Al \cdots O_(ether) bond strength in $[\text{H}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OH})]_2$ (●) as a function of the Al \cdots O_(ether) distance. Data are fitted to a Lennard-Jones (12,6) potential ($\epsilon = -64.9 \text{ kJ}\cdot\text{mol}^{-1}$ and $\sigma = 1.796 \text{ Å}$). Values for the four-coordinate isomer of $[\text{H}_2\text{Al}(\mu\text{-OCH}_2\text{-CH}_2\text{OH})]_2$ (○), $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$ (■), and $[(\text{tBu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$ (□) are included for comparison.

$\text{CH}_2\text{OH})]_2$ is stabilized by $-129.8 \text{ kJ}\cdot\text{mol}^{-1}$ with respect to the four-coordinate compound $[\text{H}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{-OH})]_2$, i.e., eq 11. This stabilization is equivalent to $64.9 \text{ kJ}\cdot\text{mol}^{-1}$ per Al–O bond-breaking reaction, i.e., the bond dissociation energy (BDE) of the intramolecular Al–O_(ether) interaction, cf., eq 5. This calculated bond energy is in the expected range for a Lewis acid–base interaction with aluminum. The stabilization energy follows the expected series $\text{H} \gg \text{Me} > \text{tBu}$, while the bond lengths follow the reverse (but also expected) trend. It is unclear, however, as to why the calculated value is considerably greater than the experimental values for compound **1** and $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$. It is to this

(40) We note that any experimental observation must be accounted for by a combination of steric and electronic factors. However, we have previously shown that for a homologous series of Lewis acid–base complexes of the group 13 elements the percentage of steric character of any structural change is approximately 90% (see ref 8). Thus, we feel justified in approximating the use of experimentally determined BDEs as a measure of steric bulk if, and only if, a homologous series is compared.

(41) Barron, A. R.; Wilkinson, G. *Polyhedron* **1986**, *5*, 1897.

(42) Barron, A. R.; Dobbs, K. D.; Francl, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 39, and references therein.

(39) See for example: (a) Brown, T. L. *Inorg. Chem.* **1992**, *31*, 1286. (b) Staskun, B. J. *Org. Chem.* **1981**, *46*, 1643. (c) Schlenkluhn, H.; Rahman, M. M.; Belmonte, J.; Giering, W. P. *Organometallics* **1985**, *4*, 1981.

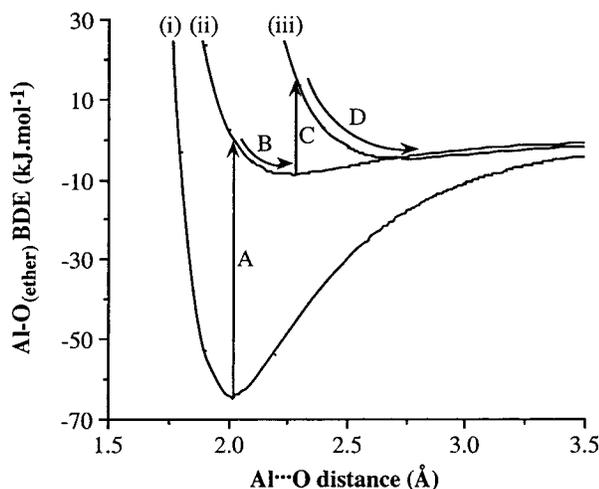


Figure 11. Lennard-Jones (12,6) potentials for the Al...O_(ether) interactions in [H₂Al(μ-OCH₂CH₂OH)]₂ (i), [Me₂Al(μ-OCH₂CH₂OMe)]₂ (ii), and [(^tBu)₂Al(μ-OCH₂CH₂OMe)]₂ (iii). For an explanation of labels see text.

variation that we must look for an explanation of the surprisingly weak intramolecular Al–O_(ether) interactions.

As was noted above, the calculated Al–O_(ether) distance for [H₂Al(μ-OCH₂CH₂OH)]₂ is significantly shorter than that in compounds **1**, **2**, and [Me₂Al(μ-OCH₂CH₂OMe)]₂ (see Table 11). It is possible that the Al–O_(ether) bond strength is simply a function of Al–O_(ether) bond length. In this regard the optimized geometries and total energies were calculated by ab initio methods MP2/3-21G(*) as a function of Al...O_(ether) distance for [H₂Al(μ-OCH₂CH₂OH)]₂. A comparison relative to the four-coordinate dimer [H₂Al(μ-OCH₂CH₂OH)]₂ allows for the determination of the bond dissociation energy of the intramolecular Al–O_(ether) interaction as a function of Al...O_(ether) distance in [H₂Al(μ-OCH₂CH₂OH)]₂; see Figure 11.

The data in Figure 11 has the appearance of an intermolecular energy curve and can be fitted to a Lennard-Jones (12,6) potential in the form shown in eq 12, where ϵ is the depth of the minimum (–64.9 kJ·mol^{–1}) of the curve and σ (1.796 Å) is derived from the equilibrium bond distance (R_e), eq 13.

$$\text{BDE}_R - 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right] \quad (12)$$

$$R_e = 2^{1/6}\sigma \quad (13)$$

On the basis of a simplistic view of the relationship between bond strength and bond length, it may be expected that the decreased Al–O_(ether) bond strengths in compound **1** and [Me₂Al(μ-OCH₂CH₂OMe)]₂ are a consequence of the steric interactions and thus increased Al–O_(ether) distance. However, it should be noted that the experimental values for compound **1** and [Me₂Al(μ-OCH₂CH₂OMe)]₂ (shown in Figure 10) do not fit the calculated Lennard-Jones (12,6) potential for [H₂Al(μ-OCH₂CH₂OH)]₂. On the basis of the bond energies ($\Delta H_{\text{Al-O}}$) and Al–O_(ether) distances determined for compound **1** and [Me₂Al(μ-OCH₂CH₂OMe)]₂, the appropriate Lennard-Jones (12,6) potentials may be determined for each compound; see Figure 11 and Table 12. Using these Lennard-Jones (12,6) potentials, a semiquantitative

Table 12. Lennard-Jones (12,6) Potential Parameters for [R₂Al(μ-OCH₂CH₂OR')₂]₂

compound	ϵ (kJ·mol ^{–1})	σ (Å)
[H ₂ Al(μ-OCH ₂ CH ₂ OH)] ₂	–64.9	1.796
[Me ₂ Al(μ-OCH ₂ CH ₂ OMe)] ₂	–9.08	2.021
[(^t Bu) ₂ Al(μ-OCH ₂ CH ₂ OMe)] ₂ (1)	–5.15	2.447

measure of the steric bulk of methyl and *tert*-butyl groups may be obtained.

If one considers the structure of the model compound [H₂Al(μ-OCH₂CH₂OH)]₂ to be absent of steric interactions between the substituents on either the aluminum or the ether oxygen, then the substitution of the hydrogens on aluminum and oxygen for methyl groups will result in an increase in repulsive force between the aluminum and ether oxygen.⁴³ This is estimated to be ca. 65 kJ·mol^{–1} (see Figure 11, A). To relieve the repulsive forces between the Al–CH₃ and O–CH₃ groups, the Al–O_(ether) bond lengthens to a new equilibrium value (Figure 11, B). The result of the substitution of hydrogen with methyl is therefore to lengthen and weaken the Lewis acid–base interaction. In a similar manner, substitution of the aluminum methyl groups for *tert*-butyl groups results in the destabilization of the structure found for [Me₂Al(μ-OCH₂CH₂OMe)]₂ by ca. 28 kJ·mol^{–1} (see Figure 11, C), with a subsequent bond lengthening to the equilibrium value observed for compound **1** (Figure 11, D). Thus, in total, the substitution of the aluminum hydrogen groups for *tert*-butyl groups, and “ether” hydrogen for a methyl group, results in the destabilization of the “ideal” structure calculated for [H₂Al(μ-OCH₂CH₂OH)]₂ by ca. 200 kJ·mol^{–1}. The *tert*-butyl may be considered to destabilize the Al–O_(ether) interaction by a factor of 3 as compared to methyl.

As would be expected, the repulsive interaction is significantly increased for the substitution of methyl for *tert*-butyl; however, it is surprising that the substitution of hydrogen for methyl (i.e., [H₂Al(μ-OCH₂CH₂OH)]₂ versus [Me₂Al(μ-OCH₂CH₂OMe)]₂) is also a significant effect. This result suggests that the steric effects of alkyl groups such as methyl should not be ignored in considering both structural and thermodynamic data as compared to the idealized model compounds commonly used in higher level computations.

On the basis of the above discussion it is possible to rationalize the experimental results for the thioether and amine ligands and answer the questions posed above. The apparent weakness of the intramolecular coordinate bonds in [R₂Al(μ-OCH₂CH₂ER')₂]₂ is clearly due to the steric repulsion between the alkyl groups on aluminum and the substituents on the Lewis base. Therefore the bond strengths of the fifth coordination ligand are actually very low.

The relative order of the intramolecular bond strengths Al–S > Al–O > Al–N may be explained by a consideration of the effects of increased steric bulk at the aluminum and heteroatom.⁴⁴ Thus, the steric destabilization that occurs from the substitution of hydrogens

(43) For an alternative approach to quantification of repulsion forces see: (a) Choi, M.-G.; Brown, T. L. *Inorg. Chim. Acta* **1992**, *198*, 823. (b) Choi, M.-G.; Brown, T. L. *Inorg. Chem.* **1993**, *32*, 1548.

(44) A comparison of the Al–O versus Al–S versus Al–N BDEs may only be made with the proviso that the electronic donor ability of each ligand is clearly different. However, since we are trying to explain reversal of the expected trend based on electronic factors, we believe the comparison is justified.

for methyl groups is dependent on the initial ligand... ligand distance. Since the radius for sulfur (1.84 Å) is significantly larger than for oxygen (1.40 Å), the ligands will be at a greater distance apart. Consequently in order to overcome the interligand repulsion, the Al–S bond does not have to relax as far as the equivalent Al–O_(ether) bond, resulting in a smaller weakening of the Al–S bond relative to the analogous oxygen system. In contrast, the radii of oxygen and nitrogen (1.5 Å) are similar and therefore would expect similar effects for specific alkyl substitution. However, as was discussed above, the sp³ hybridization about nitrogen results in increased steric interaction between the alkyl substituents on the amine and the alkyl groups on aluminum. Thus for any given substitution (i.e., H for Me) the amine complex must relax further than the ether complex, resulting in a greater decrease in the Al–E bond strength.

Conclusions

We have prepared a range of dialkylaluminum compounds with bifunctional ligands of the general formula [R₂Al{μ-O(CH₂)_nER'_x}]₂, where *n* is 2 or 3, ER'_x is OR', SR', or NR'₂, and R is ^tBu, ⁱBu, Et, or Me. All these compounds are dimeric species where the interaction of the nonbridged heteroatoms (E) to form a five-coordinate aluminum center is an equilibrium in solution. Equilibrium constants (where *K*_{eq} = [4-coord]/[5-coord]) have been determined from ¹³C NMR measurements and are found to be controlled by the following factors: Increase in the ligand backbone (*n*), the steric bulk of the alkyl substituents on aluminum (R), and/or on the heteroatom donor (R') all result in greater dissociation of the neutral Lewis base donor. The extent of coordination of the fifth ligand is also dependent on the identity of the heteroatom donor (E).

Determination of the enthalpy associated with the equilibrium shows that the fifth ligand is only weakly bound. In fact, the bond dissociation energies (5.2–13.2 kJ·mol⁻¹) are in the range expected for solvation rather than formation of stable Lewis acid–base interactions. However, ab initio calculations on the model system [H₂-Al(μ-OCH₂CH₂OH)]₂ indicate that, in the absence of steric interactions, the strength of the fifth ligand should be comparable to Lewis acid–base complexes in four-coordinate compounds. We have found that this discrepancy is predominantly due to interligand steric repulsion and may be used as a thermodynamic measure of steric bulk. Although an increased effect of steric bulk in five-coordinate compounds as compared to four-coordinate compounds is not unexpected due to the smaller interligand (X–Al–X) bond angles in the former, the dramatic difference between hydrogen and methyl is unexpected. Consequently, this indicates that the commonly held assumption that hydrogen atoms may simulate larger alkyl groups in calculations is invalid.

We are at present continuing our investigations of the quantitative measure of steric bulk, through the structural and thermodynamic characterization of a homologous series of trialkyl aluminum Lewis acid–base complexes. We hope that such an effort will provide a quantitative measure of steric bulk to be used in conjunction with the readily applied concept of cone angle.

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 a Nicolet 760 FT-IR infrared spectrometer. NMR spectra were obtained on Bruker AM-250, AM-300, and Avance 200 spectrometers using (unless otherwise stated) benzene-*d*₆ solutions. Chemical shifts are reported relative to internal solvent resonances (¹H and ¹³C) and external [Al(H₂O)₆]³⁺ (²⁷Al). Elemental analysis were performed using a Perkin-Elmer Magna 400 ICP atomic emission spectrometer. All compounds were digested in concentrated nitric acid to enable analysis. *Caution: Digestion of organoaluminum compounds in acidic solutions should be undertaken with care.* Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Molecular weight measurements were made in CH₂Cl₂ with the use of an instrument similar to that described by Clark.⁴⁵ The synthesis of Al(^tBu)₃ was performed according to a modification of the literature method.⁴⁶ AlMe₃, AlEt₃, Al(^tBu)₃, and (^tBu)₂AlH were generously donated by Akzo Nobel. [Me₂Al(μ-OCH₂CH₂NMe₂)]₂^{2a} and [(^tBu)₂Al(μ-OCH₂CH₂CH₂NMe₂)]₂^{2b} were prepared as previously reported. HOCH₂CH₂NMe₂, HOCH₂CH₂CH₂NMe₂, HOCH₂CH₂OMe, HOCH₂CH₂CH₂OMe, and Me₂NCH₂CH₂SH·HCl were obtained from Aldrich and (except for HOCH₂CH₂NMe₂ and HOCH₂CH₂OMe, which were distilled prior to use) were used without further purification.

[(^tBu)₂Al(μ-OCH₂CH₂OMe)]₂ (1). To a cooled (–78 °C) hexane (50 mL) solution of Al(^tBu)₃ (1.50 g, 7.58 mmol) was added HOCH₂CH₂OCH₃ (1.9 mL, 7.58 mmol) with stirring. The reaction was allowed to warm to room temperature and stirred overnight. After filtering the supernatant was concentrated and cooled to –22 °C. The resulting white crystals were collected by filtration. Several crops were obtained by successive recoling of the filtrate. Yield: ca. 76%. Mp: 123–125 °C. Anal. (calcd, %): C, 61.3 (61.1); H, 11.6 (11.7); Al, 12.3 (12.5). MS (EI, %): *m/z* 375 (2M⁺ – ^tBu, 100), 216 (M⁺, 60), 159 (M⁺ – ^tBu, 60), 57 (^tBu, 100).

[(^tBu)₂Al(μ-OCH₂CH₂OMe)]₂ (2). **2** was prepared in a manner similar to compound **1**, but using (^tBu)₂AlH (1.81 g, 12.7 mmol) and HOCH₂CH₂OCH₃ (0.97 g, 12.7 mmol). Yield: ca. 40%. Mp: 76–78 °C. Anal. (calcd, %): C, 60.6 (61.1); H, 11.2 (11.6). MS (EI, %): *m/z* 375 (2M⁺ – ⁱBu, 100), 159 (M⁺ – ⁱBu, 7), 57 (ⁱBu, 20), 43 (ⁱBu – Me, 75). Molecular weight determination: 431 (432).

[Et₂Al(μ-OCH₂CH₂OMe)]₂ (3). **3** was prepared in a manner similar to compound **1**, but using AlEt₃ (1.45 g, 12.7 mmol) and HOCH₂CH₂OCH₃ (0.97 g, 12.7 mmol). Yield: ca. 60%. Mp: 38–40 °C. MS (EI, %): *m/z* 291 (2M⁺ – Et, 100), 261 (2M⁺ – 2Et, 18), 247 (2M⁺ – 2Et – Me, 10), 131 (M⁺ – Et, 10), 103 (M⁺ – 2Et, 5), 45 (CH₂OMe, 20).

[(^tBu)₂Al(μ-OCH₂CH₂OⁿBu)]₂ (4). **4** was prepared in a manner similar to compound **1**, but using Al(^tBu)₃ (1.58 g, 7.9 mmol) and HOCH₂CH₂OⁿBu (1.04 mL, 7.9 mmol). Yield: 71%. Mp: < 25 °C. Anal. (calcd, %): C, 65.7.0 (65.1); H, 12.5 (12.1). MS (EI, %): *m/z* 459 (2M⁺ – ^tBu, 60), 399 (2M⁺ – OCH₂CH₂OⁿBu, 10), 201 (M⁺ – ^tBu, 50), 117 (OCH₂CH₂OⁿBu, 25), 57 (^tBu, 80).

[Me₂Al(μ-OCH₂CH₂OⁿBu)]₂ (5). **5** was prepared in a manner similar to compound **1**, but using AlMe₃ (2.23 g, 31.0 mmol) and HOCH₂CH₂OⁿBu (3.66 g, 31.0 mmol). Yield: ca. 60%. Mp: < 25 °C. Anal. (calcd, %): C, 55.8 (55.2); H, 10.7 (11.0). MS (EI, %): *m/z* 333 (2M⁺ – Me, 35), 261 (2M⁺ – 2Me – ⁿBu, 25), 117 [OCH₂CH₂OⁿBu, 25].

[(^tBu)₂Al(μ-OCH₂CH₂CH₂OMe)]₂ (6). **6** was prepared in a manner similar to compound **1**, but using Al(^tBu)₃ (2.1 g,

(45) Clark, E. P. *Ind. Eng. Chem. Anal. Ed.* **1941**, *13*, 820.

(46) (a) Uhl, W. Z. *Anorg. Allg. Chem.* **1989**, *570*, 37. (b) Lehmkuhl, H.; Olbrysch, O.; Nehl, H. *Liebigs Ann. Chem.* **1973**, *708*. (c) Lehmkuhl, H.; Olbrysch, O. *Liebigs Ann. Chem.* **1973**, *715*.

10.7 mmol) and HOCH₂CH₂CH₂OCH₃ (0.97 g, 10.7 mmol). Mp: 146–148 °C. Anal. (calcd, %): C, 62.9 (62.6); H, 12.0 (11.8); Al, 11.3 (11.7). MS (EI, %): *m/z* 403 (2M⁺ - ^tBu, 100), 173 (M⁺ - ^tBu, 20), 73 [OCH₂CH₂CH₂OCH₃, 75], 57 (^tBu, 16).

[Me₂Al(μ-OCH₂CH₂CH₂OMe)]₂ (7). 7 was prepared in a manner similar to compound 1, but using AlMe₃ (0.84 g, 11.8 mmol) and HOCH₂CH₂CH₂OCH₃ (1.06 g, 11.8 mmol). Yield: ca. 40%. Mp: 85–87 °C. Anal. (calcd, %): C, 50.0 (49.3); H, 10.1 (10.3); Al, 18.9 (18.5). MS (EI, %): *m/z* 277 (2M⁺ - Me, 80), 131 (M⁺ - Me, 75).

[^t(Bu)₂Al(μ-OⁿBu)]₂ (8). 8 was prepared in a manner similar to compound 1, but using Al(^tBu)₃ (2.37 g, 0.012 mol) and ⁿBuOH (1.1 mL, 0.012 mol). Yield: ca. 70%. Mp: 90–92 °C. Anal. (calcd, %): C, 67.0 (67.2); H, 12.1 (12.7). MS (EI, %): *m/z* 371 (2M⁺ - ^tBu, 55), 315 (2M⁺ - 2^tBu, 10), 257 (2M⁺ - 3^tBu, 7), 59 [(CH₂)₂OCH₃, 100].

[^t(Bu)₂Al(μ-OⁿBu)]₂ (9). 9 was prepared in a manner similar to compound 1, but using (^tBu)₂AlH (4.69 g, 32 mmol) and ⁿBuOH (1.5 mL, 16 mmol). Yield: ca. 80%. Mp: 134–135 °C. Anal. (calcd, %): C, 67.7 (67.2); H, 12.8 (12.7). MS (EI, %): *m/z* 387 (2M⁺ - ⁱBu, 12), 315 (2M⁺ - 2ⁱBu, 8), 85 (AlⁱBu, 5).

[Et₂Al(μ-OⁿBu)]₂ (10). 10 was prepared in a manner similar to compound 1, but using AlEt₃ (2.505 g, 22 mmol) and ⁿBuOH (2.0 mL, 22 mmol). After removal of all volatiles under vacuum, the remaining liquid was distilled under vacuum. Yield: ca. 70%. Anal. (calcd, %): C 59.7 (60.7), H 11.8 (12.1). MS (EI, %): *m/z* 287 (2M⁺ - Et, 100), 259 (2M⁺ - ⁿBu, 80), 201 (2M⁺ - ⁿBu - 2Et, 40), 56 (AlEt, 80).

(^tBu)₂Al(μ-OⁿBu)(μ-OCH₂CH₂CH₂OMe)Al(^tBu)₂ (11). To a mixture of ⁿBuOH (0.37 g, 4.99 mmol) and HOCH₂CH₂OCH₃ (0.38 g, 4.99 mmol) dissolved in hexane (50 mL) and cooled to -78 °C was added Al(^tBu)₃ (1.98 g, 9.98 mmol). The reaction mixture was allowed to stir overnight, as it warmed to room temperature. A mixture of compounds 1, 8, and (^tBu)₂Al(μ-Oⁿ-Bu)(μ-OCH₂CH₂OMe)Al(^tBu)₂ (11) was isolated by removal of the volatiles and characterized by NMR spectroscopy.

[^t(Bu)₂Al(μ-OCH₂CH₂SMe)]₂ (12). To a solution of HOCH₂-CH₂SMe (1.47 g, 15.9 mmol) in hexane (50 mL) was added Al(^tBu)₃ (3.16 g, 15.9 mmol) at -78 °C. The mixture was allowed to warm to room temperature and stirred overnight. Filtration, reduction of the solvent under vacuum, and cooling to -20 °C resulted in the formation of colorless crystals. Yield: ca. 80%. Mp: 150–152 °C. Anal. (calcd, %): C, 56.7 (56.8); H, 10.1 (10.8). MS (EI, %): *m/z* 407 (2M⁺ - ^tBu, 60), 133 (M⁺ - 2^tBu, 80), 75 (^tBu, 100). Molecular weight determination: 459 (464).

[^t(Bu)₂Al(μ-OCH₂CH₂SMe)]₂ (13). Prepared in a manner similar to compound 11, but using (^tBu)₂AlH (1.64 g, 11.5 mmol) and HOCH₂CH₂SMe (1.06 g, 11.5 mmol). Yield: ca. 30%. Mp: 33–35 °C. MS (EI, %): *m/z* 407 (2M⁺ - ^tBu, 100), 177 (M⁺ - ^tBu, 7), 389 (M⁺ - ^tBu - Me, 25), 75 (OCH₂CH₂S, 55).

[Et₂Al(μ-OCH₂CH₂SMe)]₂ (14). 14 was prepared in a manner similar to compound 11, but using AlEt₃ (2.62 g, 23.0 mmol) and HOCH₂CH₂SCMe (2.12 g, 23.0 mmol). Removal of solvent yielded a viscous oil. Yield: ca. 60%. Mp: <25 °C. Anal. (calcd, %): C, 48.0 (47.7); H, 9.9 (9.7); Al, 15.0 (15.3). MS (EI, %): *m/z* 351 (2M⁺, 15), 323 (2M⁺ - Et, 100), 147 (M⁺ - Et, 10).

[(Me)₂Al(μ-OCH₂CH₂SMe)]₂ (15). 15 was prepared in a manner similar to compound 11, but using AlMe₃ (1.24 g, 17.2 mmol) and HOCH₂CH₂SMe (1.59 g, 17.2 mmol). Yield: ca. 70%. Mp: 85–87 °C. Anal. (calcd, %): C, 41.0 (40.5); H, 9.0 (8.8). MS (EI, %): *m/z* 281 (2M⁺ - Me, 60), 221 (2M⁺ - CH₂CH₂-SMe, 30), 131 (M⁺ - Me, 20), 75 (CH₂CH₂SMe, 100). Molecular weight determination: 306 (296).

[^t(Bu)₂Al(μ-OCH₂CH₂CH₂SMe)]₂ (16). Prepared in the same manner as compound 11, but using Al(^tBu)₃ (3.16 g, 15.96 mmol) and HOCH₂CH₂CH₂SMe (1.695 g, 15.96 mmol). Yield: ca. 80%. Mp: 110–112 °C. Anal. (calcd, %): C, 59.2 (58.5); H, 11.3 (11.1). MS (EI, %): *m/z* 435 (2M⁺ - ^tBu, 100), 189 (M⁺ -

^tBu, 10), 147 (M⁺ - 2^tBu, 20), 106 (OCH₂CH₂SMe, 20). Molecular weight determination: 496 (492).

[Me₂Al(μ-OCH₂CH₂CH₂SMe)]₂ (17). 17 was prepared in the same manner as compound 11, but using AlMe₃ (0.698 g, 9.7 mmol) and HOCH₂CH₂CH₂SMe (1.03 g, 9.7 mmol). Yield: ca. 40%. Mp: <25 °C. Anal. (calcd, %): C, 43.1 (44.4); H, 9.0 (9.3). MS (EI, %): *m/z* 309 (2M⁺ - Me, 100), 235 (2M⁺ - CH₂CH₂-CH₂SMe, 70), 147 (M⁺ - Me, 55), 105 (OCH₂CH₂CH₂SMe, 30), 89 (CH₂CH₂CH₂SMe, 60).

[^t(Bu)₂Al(μ-OCH₂CH₂NMe₂)]₂ (18). Al(^tBu)₃ (2.00 g, 10.1 mmol) was dissolved in hexane (40 mL) and the solution cooled to -78 °C, to which was added a hexane (20 mL) solution of HOCH₂CH₂NMe₂ (0.90 g, 10.1 mmol). The reaction was warmed to room temperature and stirred overnight. The solution was filtered, concentrated in vacuo, and cooled (-22 °C). Several crops of colorless crystals were collected by filtration and subsequent recooling of the filtrate. Yield: ca. 61%. Mp: 97–100 °C. Anal. (calcd, %): C, 63.0 (62.9); H, 12.6 (12.3); N, 6.2 (6.1); Al, 11.6 (11.8). MS (EI, %): *m/z* 401 (2M⁺ - ^tBu, 5), 172 (M⁺ - ^tBu, 25), 128 (M⁺ - 2^tBu, 97), 72 (CH₂-CH₂NMe₂, 46), 57 (^tBu, 53). Molecular weight determination: 430 (458).

[^t(Bu)₂Al(μ-OCH₂CH₂NMe₂)]₂ (19). ⁱBu₂AlH (6.94 g of a 2.75% Al solution in heptane, 7.00 mmol) was dissolved in degassed hexane (ca. 50 mL). HOCH₂CH₂NMe₂ (0.63 g, 7.10 mmol) was syringed into the solution at -78 °C. The solution was allowed to warm to room temperature and then stirred overnight. The solution was filtered, reduced in volume, and cooled to -23 °C to give colorless crystals. Yield: 20%. Mp: 98–102 °C. Al, 11.4 (11.7). MS (EI, %): *m/z* 401 (2M⁺ - ^tBu, 6), 172 (M⁺ - ^tBu, 38), 116 (M⁺ - 2^tBu, 25), 57 (^tBu, 87). Molecular weight determination: 420 (459).

[Et₂Al(μ-OCH₂CH₂NMe₂)]₂ (20). 20 was prepared in the same manner as compound 17, but using AlEt₃ (1.00 g, 8.80 mmol) and HOCH₂CH₂NMe₂ (0.78 g, 8.80 mmol). Yield: 23%. Mp: 82–84 °C. Anal. (calcd, %): C, 55.0 (55.5); H, 11.9 (11.6); N, 8.0 (8.1); Al, 16.0 (15.6). MS (EI, %): *m/z* 317 (2M⁺ - Et, 100), 144 (M⁺ - Et, 22), 72 (CH₂CH₂NMe₂, 30).

[H₂Al(μ-OCH₂CH₂NMe₂)]₂ (21). AlH₃(NMe₃) (1.00 g, 11.2 mmol) was suspended in degassed hexane (ca. 60 mL) and the solution cooled to -78 °C. HOCH₂CH₂NMe₂ (1.00 g, 11.2 mmol) was syringed into the cooled solution. The solution was warmed, refluxed for 1 h, and then stirred overnight at room temperature. The resultant precipitate was recrystallized from hot toluene. Yield: 33%. Mp: 173–176 °C. Anal. (calcd, %): C, 40.0 (41.0); H 10.1 (10.3); N, 11.3 (11.9). MS (EI, %): *m/z* 89 (OCH₂CH₂NMe₂, 10), 58 (AlOCH₂, 100). Molecular weight determination: 250 (234).

[^t(Bu)₂Al(μ-OCH₂CH₂NH₂)]₂ (22). HOCH₂CH₂NH₂ (0.19 g, 3.10 mmol) was dissolved in degassed hexane (ca. 50 mL). Al(^tBu)₃ (0.64 g, 3.20 mmol) was syringed into the solution at -78 °C. The solution was warmed to room temperature and then stirred overnight. The resultant precipitate was filtered, and the supernatant produced crystals suitable for X-ray diffraction studies after 24 h at -23 °C. Yield: 71%. Mp: 178–181 °C. Anal. (calcd, %): C, 60.0 (59.7); H, 12.2 (12.0); N, 7.0 (6.9); Al, 14.0 (13.4). MS (EI, %): *m/z* 144 (M⁺ - ^tBu, 40). Molecular weight determination: 428 (430).

[^t(Bu)₂Al(μ-OCH₂CH₂CH₂NH₂)]₂ (23). 23 was prepared in the same manner as compound 21, but using HOCH₂CH₂CH₂-NH₂ (0.25 g, 3.30 mmol) and Al(^tBu)₃ (0.64 g, 3.20 mmol). Yield: 55%. Mp: 188–191 °C. Anal. (calcd, %): C, 61.0 (61.4); H, 12.1 (12.2); N, 6.2 (6.5); Al, 13.0 (12.5). MS (EI, %): *m/z* 158 (M⁺ - ^tBu, 85).

Equilibrium Studies. Since a variation in ¹³C NMR shifts for the α-carbon (OCH₂) is observed between different solvents, the same solvent (toluene-*d*₈) was used for all the variable-temperature NMR measurements. Although the equilibrium constant is concentration independent, care was taken to ensure similar concentrations were used for all samples (0.1–1.0 mM). All the samples were heated to the appropriate

Table 13. Summary of X-ray Diffraction Data for 1 and 2

	[(^t Bu) ₂ Al(μ-OCH ₂ CH ₂ OMe)] ₂ (1)	[(^t Bu) ₂ Al(μ-OCH ₂ CH ₂ OMe)] ₂ (2)
empir formula	C ₂₂ H ₅₀ Al ₂ O ₄	C ₂₂ H ₅₀ Al ₂ O ₄
cryst size, mm	0.22 × 0.25 × 0.28	0.12 × 0.31 × 0.34
cryst system	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1
<i>a</i> , Å	8.9670(8)	8.6257(9)
<i>b</i> , Å	8.9127(7)	9.597(1)
<i>c</i> , Å	17.703(1)	10.0584(9)
α, deg		69.894(8)
β, deg	99.460(7)	88.889(8)
γ, deg		65.659(8)
<i>V</i> , Å ³	1395.6(2)	705.1(1)
<i>Z</i>	2	1
<i>D</i> (calcd), g/cm ³	1.029	1.019
μ, cm ⁻¹	1.20	1.19
temp, K	298	298
2θ range, deg	2.0–44.0	3.0–50.0
no. collected	1970	2477
no. ind	1844	2477
no. obsd	668 (<i>F</i> _o > 5.0σ <i>F</i> _o)	1738 (<i>F</i> _o > 6.0σ <i>F</i> _o)
weighting scheme	<i>w</i> ⁻¹ = 0.04(<i>F</i> _o) ² + σ(<i>F</i> _o) ²	<i>w</i> ⁻¹ = 0.04(<i>F</i> _o) ² + σ(<i>F</i> _o) ²
<i>R</i>	0.1345	0.0475
<i>R</i> _w	0.1480	0.0475
largest diff peak, e Å ⁻³	0.55	0.24

Table 14. Summary of X-ray Diffraction Data for 6 and 7

	[(^t Bu) ₂ Al(μ-OCH ₂ CH ₂ CH ₂ OMe)] ₂ (6)	[Me ₂ Al(μ-OCH ₂ CH ₂ CH ₂ OMe)] ₂ (7)
empir formula	C ₂₄ H ₅₄ Al ₂ O ₄	C ₁₂ H ₃₀ Al ₂ O ₄
cryst size, mm	0.12 × 0.14 × 0.61	0.21 × 0.24 × 0.32
cryst system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2
<i>a</i> , Å	9.372(1)	12.425(3)
<i>b</i> , Å	18.745(3)	9.6446(2)
<i>c</i> , Å	8.459(2)	7.754(2)
β, deg	100.37(2)	104.15(2)
<i>V</i> , Å ³	1461.8(5)	901.1(3)
<i>Z</i>	2	2
<i>D</i> (calcd), g/cm ³	1.046	1.077
μ, cm ⁻¹	1.18	1.65
temp, K	298	298
2θ range, deg	3.0–44.0	4.0–40.0
no. collected	1968	682
no. ind	1848	319
no. obsd	857 (<i>F</i> _o > 6.0σ <i>F</i> _o)	251 (<i>F</i> _o > 6.0σ <i>F</i> _o)
weighting scheme	<i>w</i> ⁻¹ = 0.04(<i>F</i> _o) ² + σ(<i>F</i> _o) ²	<i>w</i> ⁻¹ = 0.04(<i>F</i> _o) ² + σ(<i>F</i> _o) ²
<i>R</i>	0.0664	0.103
<i>R</i> _w	0.0668	0.228
largest diff peak, e Å ⁻³	0.25	0.37

temperature within the NMR spectrometer, and the ¹³C NMR spectra were collected. Constancy of the spectrum was taken as evidence for the attainment of equilibrium. The temperature of the NMR spectrometer probe was calibrated using the chemical shifts of ethylene glycol.⁴⁷ This process was repeated for a minimum of six temperatures over a minimum temperature range of 80 K. Alternate points on the ln *K*_{eq} versus 1/*T* plot were obtained during upward and downward passages over the temperature range spanned. Because both sets of points fell on the same line, we consider that equilibration was achieved. The temperature dependence of the equilibrium constant, *K*_{eq}, allows for the determination of the Δ*H* and Δ*S* for the conversion of five-coordinate to four-coordinate. A summary of calculated values is given in Table 9.

Crystallographic Studies. Crystals of compounds **1**, **2**, **6**, **11**, **12**, **15**, **17–21**, and [Me₂Al(μ-OCH₂CH₂NMe₂)]₂ were sealed in a glass capillaries under argon. Crystal and data collection and solution details are given in Tables 13–18. Standard procedures in our laboratory have been described previously.^{6a} Data were collected on either an Enraf-Nonius CAD-4 or a Rigaku four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and corrected

for Lorentz and polarization effects. The structures were solved by using direct methods (**18** using SIR,⁴⁸ remainder using SHELXS-86⁴⁹) and difference Fourier synthesis and refined using full-matrix least squares.⁵⁰ Disorder and/or high thermal motion was noted as follows: in compounds **1**, **6**, **11**, and **17**, at least one *tert*-butyl group suffered from resolvable disorder about the Al–C bond; in each case, two possible positions were resolved for each methyl carbon, which refined to have relative site occupancies of 1:1 and 2:1 for **1**, 11:9 for **6**, and 2:1 for **11** and **17**. In compounds **12** and **21**, the thermal parameters and electron density maps indicated possible disorder; this could not be resolved, however. The side chains in compound **18** exhibited static disorder resulting from two different chain conformations (the so-called “slinky effect”⁵¹) and the disorder of the carbons attached to nitrogen.

The extent of inclusion of anisotropic thermal parameters depended on the number of data collected. In compounds **2**, **12**, **15**, **20**, and [Me₂Al(μ-OCH₂CH₂NMe₂)]₂, all non-hydrogen

(48) Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spangna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389.

(49) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(50) *MolEV*, An Interactive Structure Solution Procedure; Enraf-Nonius: Delft, Netherlands, 1990.

(51) Aitken, C. L.; Barron, A. R. *J. Chem. Crystallogr.* **1996**, *26*, 297.

(47) (a) van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227. (b) Gordon H. J.; Ford, R. A. *The Chemists Companion*; Wiley: New York, 1972.

Table 15. Summary of X-ray Diffraction Data for 12 and 13

	[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ SMe)] ₂ (12)	[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ SMe)] ₂ (13)
empir formula	C ₂₂ H ₅₀ Al ₂ O ₂ S ₂	C ₂₂ H ₅₀ Al ₂ O ₂ S ₂
cryst size, mm	0.18 × 0.24 × 0.29	0.09 × 0.21 × 0.32
cryst system	triclinic	monoclinic
space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	8.529(1)	8.4518(6)
<i>b</i> , Å	9.1211(9)	17.913(2)
<i>c</i> , Å	10.689(1)	9.8953(6)
α , deg	67.168(8)	
β , deg	80.302(9)	100.755(5)
γ , deg	73.495(9)	
<i>V</i> , Å ³	733.2(1)	1471.8(2)
<i>Z</i>	1	2
<i>D</i> (calcd), g/cm ³	1.052	1.003
μ , cm ⁻¹	2.46	2.43
temp, K	298	298
2 θ range, deg	3.0–50.0	3.0–50.0
no. collected	2566	2844
no. ind	2566	2667
no. obsd	1637 ($ F_o > 6.0\sigma F_o $)	1647 ($ F_o > 6.0\sigma F_o $)
weighting scheme	$w^{-1} = 0.04(F_o)^2 + \sigma(F_o)^2$	$w^{-1} = 0.04(F_o)^2 + \sigma(F_o)^2$
<i>R</i>	0.0999	0.0487
<i>R</i> _w	0.1354	0.0489
largest diff peak, e Å ⁻³	0.87	0.28

Table 16. Summary of X-ray Diffraction Data for 16 and 18

	[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ CH ₂ SMe)] ₂ (16)	[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ NMe ₂)] ₂ (18)
empir formula	C ₂₄ H ₅₄ Al ₂ O ₂ S ₂	C ₂₄ H ₅₆ Al ₂ N ₂ O ₂
cryst size, mm	0.15 × 0.21 × 0.42	0.48 × 0.51 × 1.22
cryst system	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1
<i>a</i> , Å	8.787(2)	8.845(1)
<i>b</i> , Å	15.990(2)	9.428(1)
<i>c</i> , Å	10.964(1)	10.826(3)
α , deg		65.59(2)
β , deg	95.17(1)	74.69(2)
γ , deg		69.13(1)
<i>V</i> , Å ³	1534.2(4)	760.9(3)
<i>Z</i>	2	1
<i>D</i> (calcd), g/cm ³	1.067	1.001
μ , cm ⁻¹	2.38	1.10
temp, K	298	298
2 θ range, deg	3.0–50.0	2.0–50.0
no. collected	2976	2672
no. ind	2800	2672
no. obsd	1667 ($ F_o > 6.0\sigma F_o $)	1752 ($ F_o > 6.0\sigma F_o $)
weighting scheme	$w^{-1} = 0.04(F_o)^2 + \sigma(F_o)^2$	$w^{-1} = 0.04(F_o)^2 + \sigma(F_o)^2$
<i>R</i>	0.0417	0.0915
<i>R</i> _w	0.0548	0.0950
largest diff peak, e Å ⁻³	0.25	0.32

atoms were treated in this way; all but the minor occupancy carbon atoms in compounds **6**, **11**, **17**, and **19** were refined anisotropically; in compound **21**, the non-methyl carbons were refined isotropically; finally, the very weak scattering observed from the crystal of compound **1** resulted in insufficient data to treat any atoms with other than isotropic parameters. Hydrogen atoms were generally located from difference maps and included in the model in idealized positions [$d_{C-H} = 0.95$ Å, $U(H) = 1.3U_{eq}$ (attached atom)] and not refined. The exceptions to this were compounds **1** and **6**, where most hydrogens could not be found from the maps; compound **20**, where all hydrogen atoms were refined isotropically; and compound **21**, for which the amine protons were left in their observed positions. Scattering factors were taken from the usual source.⁵² No variation of $w(|F_o| - |F_c|)$ versus $|F_o|$ or $(\sin \theta/\lambda)$ was observed.

Computational Methods. Ab initio all-electron molecular orbital (MO) calculations were performed using the GAUSS-

IAN 92⁵³ suite of programs. Optimization of all structures was carried out at the Hartree–Fock level with the 3-21G(*) basis set.⁵⁴ To determine the relative energy of each species with electron correlation included, second-order Møller–Plesset (MP2) calculations were performed.⁵⁵ The calculated structural and geometrical data for [H₂Al(μ -OCH₂CH₂OH)]₂ and [H₂Al(μ -OCH₂CH₂OH)]₂ at the HF/3-21G(*) level are given in Table 11 along with the appropriate values found from the X-ray structures of [R₂Al(μ -OCH₂CH₂OMe)]₂. To determine the relative energy of [H₂Al(μ -OCH₂CH₂OH)]₂ as a function of the Al···O_(ether) distance, the geometries of a series of models was

(53) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92/DFT, Revision G.2*; Gaussian, Inc.: Pittsburgh, PA, 1993.

(54) (a) First-row elements: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Second-row elements: Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(55) (a) Møller C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

(52) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4.

Table 17. Summary of X-ray Diffraction Data for 19 and [Me₂Al(μ -OCH₂CH₂NMe₂)₂]

	[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ NMe ₂) ₂] (19)	[Me ₂ Al(μ -OCH ₂ CH ₂ NMe ₂) ₂]
empir formula	C ₂₄ H ₅₆ Al ₂ N ₂ O ₂	C ₁₂ H ₃₂ Al ₂ N ₂ O ₂
cryst size, mm	0.21 × 0.25 × 0.29	0.09 × 0.10 × 0.21
cryst system	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	9.2094(8)	7.464(4)
<i>b</i> , Å	9.989(1)	10.340(4)
<i>c</i> , Å	10.2321(8)	11.982(2)
α , deg	118.219(8)	
β , deg	101.880(7)	91.37(3)
γ , deg	104.787(8)	
<i>V</i> , Å ³	740.6(2)	924.5(6)
<i>Z</i>	1	2
<i>D</i> (calcd), g/cm ³	1.028	1.043
μ , cm ⁻¹	1.14	1.51
temp, K	298	298
2 θ range, deg	3.0–50.0	3.0–50.0
no. collected	2595	1844
no. ind	2595	1719
no. obsd	1829 ($ F_o > 6.0\sigma F_o $)	655 ($ F_o > 6.0\sigma F_o $)
weighting scheme	$w^{-1} = \sigma(F_o)^2$	$w^{-1} = 0.04(F_o)^2 + \sigma(F_o)^2$
<i>R</i>	0.0576	0.0762
<i>R</i> _w	0.0576	0.0814
largest diff peak, e Å ⁻³	0.38	0.31

Table 18. Summary of X-ray Diffraction Data for 21 and 22

	[H ₂ Al(μ -OCH ₂ CH ₂ NMe ₂) ₂] (21)	[(^t Bu) ₂ Al(μ -OCH ₂ CH ₂ NH ₂) ₂] (22)
empir formula	C ₈ H ₂₄ Al ₂ N ₂ O ₂	C ₂₀ H ₄₈ Al ₂ N ₂ O ₂
cryst size, mm	0.14 × 0.19 × 0.25	0.07 × 0.09 × 0.10
cryst system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	6.1306(5)	9.5626(7)
<i>b</i> , Å	10.6772(9)	11.495(1)
<i>c</i> , Å	10.7957(6)	11.2648(8)
α , deg		
β , deg	94.836(6)	95.436(6)
γ , deg		
<i>V</i> , Å ³	704.1(1)	1232.7(2)
<i>Z</i>	2	2
<i>D</i> (calcd), g/cm ³	1.105	1.085
μ , cm ⁻¹	1.85	1.29
temp, K	298	298
2 θ range, deg	3.0–50.0	3.0–45.0
no. collected	1428	1814
no. ind	1313	1708
no. obsd	892 ($ F_o > 6.0\sigma F_o $)	814 ($ F_o > 6.0\sigma F_o $)
weighting scheme	$w^{-1} = 0.04(F_o)^2 + \sigma(F_o)^2$	$w^{-1} = 0.04(F_o)^2 + \sigma(F_o)^2$
<i>R</i>	0.0321	0.0541
<i>R</i> _w	0.0331	0.0568
largest diff peak, e Å ⁻³	0.14	0.32

determined at the HF/3-21G(*) level with a fixed Al–O distance, and MP2 calculations were performed on these optimized structures.

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Supporting Information Available: Full listings of IR and ¹H, ¹³C, and ²⁷Al NMR spectral data; bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters; equilibrium data; and optimized structural parameters and energies for ab initio calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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