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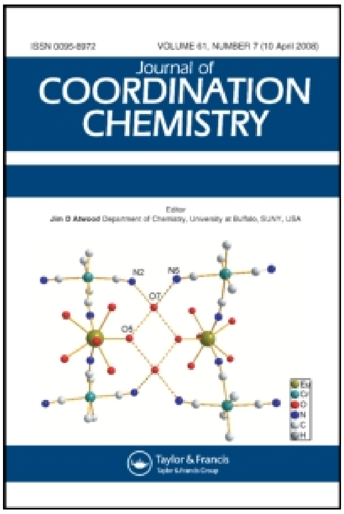

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AMINOALANE DIMERS AND TRIMERS. AN EXAMINATION OF STRUCTURAL AND STERIC TRENDS

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REVIEW

AMINOALANE DIMERS AND TRIMERS. AN EXAMINATION OF STRUCTURAL AND STERIC TRENDS

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Reaction of aluminum alkyls with primary or secondary amines readily affords dimeric or trimeric aminoalanes. Steric constraints of the substituents on aluminum and nitrogen substantially affect the structural nature of the products. Ring size, conformational data, and structural trends are reported for a number of dimeric and trimeric aminoalanes.

KEYWORDS: Aluminum alkyl, amine, aminoalane, condensation reaction, X-ray

INTRODUCTION

Substratal structural aspects of organoaluminum compounds originated with the dimeric trialkylaluminum compounds. Single crystal X-ray diffraction studies of trimethylaluminum unambiguously confirmed the existence of triorganoaluminum dimers and, consequently, the stability of symmetrical 3 center-2 electron ($3c-2e^-$), electron deficient, bridges in organoaluminum chemistry.[1] Thus, technically more rigorous, albeit seldom used, trimethylaluminum is more accurately referred to as Al_2Me_6.

Organoaluminum compounds containing group 15, 16 or 17 elements provide an abundance of compounds which often display similar electron deficient bonding tendencies. Aluminum-nitrogen compounds are particularly interesting. Compounds involving these two elements, often referred to as aminoalanes, have been studied for decades.[2,3,4] Contemporary interest in these compounds is largely due to their role as potential single source molecular precursors to aluminum nitride.[5] In addition, and of more fundamental interest, aminoalanes constitute a novel class of structurally interesting complexes.

The literature reveals a number of excellent reviews regarding the synthesis, reactivity, structure, and solution dynamics of aminoalane systems.[6,7,8,9] The use of X-ray diffraction has become an indispensable tool in the structural study of aminoalane systems. Aminoalane dimers of the form $[R_2Al\text{-}NR'_2]_n$ have been known to undergo various dynamic isomerization processes in solution. In addition,

$$\text{monomer} \rightleftharpoons \text{dimer} \rightleftharpoons \text{trimer}$$

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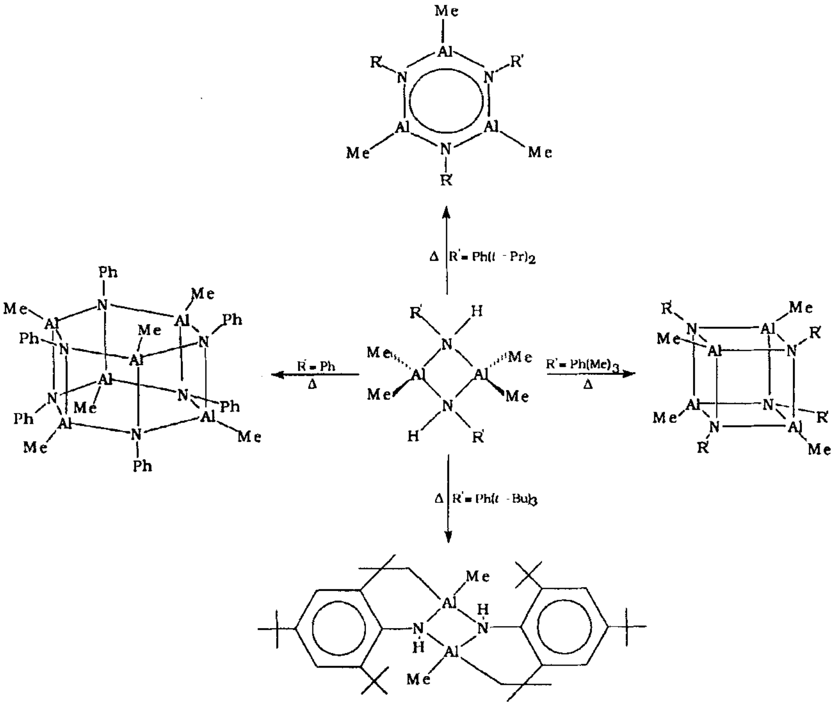
aminoalane dimers such as $[R_2Al\text{-}N(H)R]_2$ and $[RR'Al\text{-}NR''_2]_2$ have also displayed *cis-trans* isomerization.

This brief review is not comprehensive but seeks to bring the effects of ligand steric bulk into sharper focus as ring size, conformational data, and structural trends are reported for a number of dimeric and trimeric aminoalanes, $[R_2Al\text{-}NRR']_n$ (R = alkyl; R′ = H or alkyl; n = 2 or 3). These compounds are readily prepared, often from reaction of R_3Al with primary or secondary amines (equation 1).

$$\begin{array}{c} R_3Al + N(H)RR' \longrightarrow R_3Al\cdot N(H)RR' \\ \textbf{(I)} \\ \Delta \big\downarrow \text{-RH} \\ 1/2\,[R_2Al\text{-}NRR']_2 \\ \textbf{(II)} \end{array} \qquad (1)$$

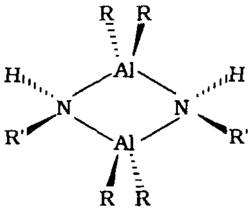
The aluminum alkyl-amine monomer $R_3Al\cdot N(H)RR'$ (**I**) is seldom isolated. Indeed, the recently prepared triphenylaluminum amine monomer, $Ph_3Al\cdot N(H_2)$-*t*-Bu,[10] is a rare example of such a product. Such compounds readily undergo condensation with aluminum alkyls resulting in aminoalane dimers $[R_2Al\text{-}N(H)R']_2$ (**II**). Furthermore, the aminoalane dimer $[Me_2Al\text{-}N(H)R']_2$ is a critical product in that, as shown by Scheme 1, this derivative, when thermolized, yields a host of compounds including trimers (R′ = $C_6H_3(i\text{-}Pr)_2$[11,12]), tetramers (R′ = $C_6H_2Me_3$[12]), metallated products (R′ = $C_6H_2(t\text{-}Bu)_3$[13]), and hexamers (R′ = Ph[14]).



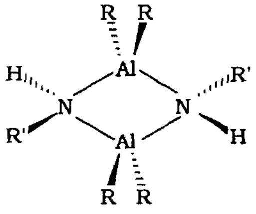
Scheme 1 Reaction scheme for the $[Me_2Al\text{-}N(H)R']$ Dimer.

Table 1 lists aminoalanes which are discussed herein.

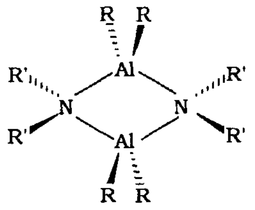
Table 1 Dimeric and trimeric aminoalane compounds grouped according to structure type.



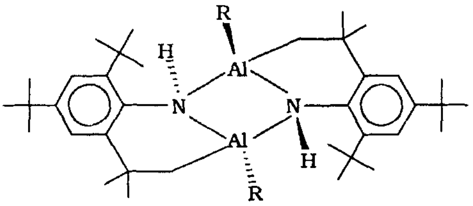
Compound	R	R′
2	Me	*i*-Pr
4	Me	C(H)(Me)Ph
5	Me	C(H)(Me)(1-naphthyl)
17	*i*-Bu	Bp
21	Neo	Ada
22	Neo	Bp
23	Neo	*t*-Bu
24	Neo	C_6H_3-*i*-Pr_2-2,6



Compound	R	R′
3	Me	*i*-Pr
6	Me	Ada
8	Me	Bp
9	Me	C_6H_4 Me-2
10	Me	C_6H_3-*i*-Pr_2
13	Me	$SiPh_3$
14	Me	$SiEt_3$
18	*i*-Bu	$C_6H_2Me_3$-2,4,6
29	Ph	Bp
31	Cl	$SiMe_3$

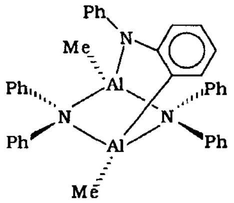


Compound	R	R′
1	Me	Me
7	Me	$[CH_2CH_2)_2$-C-$(OCH_2)_2$
15	Me	$SiMe_2H$
16	Me	$SiMe_2CH_2$
25	Nme_2	Me
26	H, NMe_2	Me
28	$Sime_3$	H
30	Cl	Me
32	Br	Me
33	I	Me



Compound	R
11	Me
19	*i*-Bu

Table 1 *Continued.*



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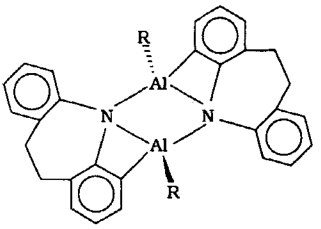

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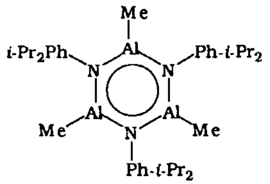

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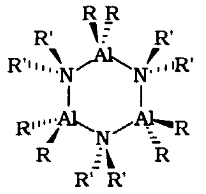
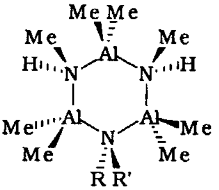


Compound	R	R′
34	H	Me
35	Me	CH_2
36	Me	H
37	*t*-Bu	H



Compound	R	R′
38	H	Me
39	Me	H

DIMERIC AMINOALANES

Methylaluminum derivatives

Partially due to the ready accessibility of trimethylaluminum, Me_3Al, as a starting material, methylaluminum derivatives such as $[Me_2Al\text{-}NR'_2]_2$ are by far the most studied of all aminoalanes. Thus, as the literature reveals a plethora of such compounds, methylaluminum based aminoalanes present a logical introduction.

The first dimeric aminoalane to be structurally characterized, $[Me_2Al\text{-}NMe_2]_2$[15] (**1a**), prepared by reaction of Me_3Al with dimethylamine,[16] was found to possess D_{2h} symmetry. The molecule contained equivalent pairs of Al-N bonds having distances: 1.955 and 1.972 Å. Subsequent to this study, a more accurate determination of the molecular structure of $[Me_2Al\text{-}NMe_2]_2$, **1b**, was reported.[17] **1b** contains Al-N bond lengths of 1.948(7) and 1.967(7) Å and N-Al-N and Al-N-Al internal angles of 88.3 and 91.7°, respectively. **1a** also had similar N-Al-N and Al-N-Al angles of 88.4 and 91.6°, respectively.

The two isomers *cis*-$[Me_2Al\text{-}N(H)i\text{-}Pr]_2$ (**2**) and *trans*-$[Me_2Al\text{-}N(H)i\text{-}Pr]_2$ (**3**) were synthesized from reaction of Me_3Al with isopropylamine.[18] These isomers crystallized in a 2:1 *cis* : *trans* ratio. This same ratio of isomers was also observed in solution by ^1H NMR. The ΔH of conversion from *trans* to *cis* was calculated to be 848 J/mol. The *cis* isomer, **2**, approaches C_{2v} symmetry. However, the central Al_2N_2 ring contains four distinct Al-N bond distances with a mean of 1.949 Å. Two equivalent pairs of Al-N distances with a mean of distance of 1.959 Å were observed for **3**. Other bond distances are comparable between the two isomers. Perhaps the most notable distinction between **2** and **3** is the ring geometry: the Al_2N_2 ring in **3** is planar, whereas **2** is decidedly folded about the Al· · ·Al axis with a dihedral angle of 15.5°.

Two compounds have been prepared with optically active amines. Reaction of (S)-(−)-α-methylbenzylamine ($H_2N\text{-}C(H)(Me)Ph$) with Me_3Al affords *cis*-$[Me_2Al\text{-}N(H)C(H)(Me)Ph]_2$, **4**.[19] The two amine alkyl groups reside in a *cis* configuration relative to the central ring. However, the structure reveals that the alkyl groups are rotated such that the phenyl groups are *trans* to each other. The Al_2N_2 ring is nonplanar, having N-Al-N and Al-N-Al angles of 86.2 and 92.2°, respectively. The average Al-N bond distance is 1.950 Å. The very similar compound, *cis*-$[Me_2Al\text{-}N(H)C(H)(Me)(1\text{-naphthyl})]_2$ (**5**), was synthesized using the chiral amine (R)-(+)-1-(1-naphthyl)ethylamine ($H_2N\text{-}C(H)(Me)(1\text{-naphthyl})$).[20] The geometry of **5** is similar to that of **4** in that the amine alkyls reside is a *cis* configuration while the two naphthyl units are situated *trans* to each other. The Al_2N_2 ring also has a bent geometry, with N-Al-N and Al-N-Al angles of 87.0 and 92.1°, respectively. The molecule contains four distinct Al-N bond lengths with a mean of 1.956 Å.

Utilizing more sterically demanding amines, *trans*-$[Me_2Al\text{-}N(H)H(Ada)]_2$ (**6**), (Ada = 1-adamantyl) was prepared by reaction of Me_3Al with 1-adamantanamine.[12] This compound has a mean Al-N bond distance of 1.963 Å. Reaction of Me_3Al with the secondary amine. 1,4-dioxa-8-azaspiro[4.5]-decane, produced $[Me_2Al\text{-}N(CH_2CH_2)_2\text{-}C\text{-}(OCH_2)_2]_2$ (**7**).[21] It is interesting to note that **7** contains pairs of distinctly different Al-N bond lengths, with values of 1.955(3) and 1.980(3) Å.

The organoaluminum chemistry of a number of aromatic amines has also been examined. The following compounds were prepared by utilizing 2-aminobiphenyl, 2-methylaniline, and 2,6-diisopropylaniline, respectively: *trans*-$[Me_2Al\text{-}N(H)Bp]_2$ (**8**, Bp = 2-biphenyl),[22] *trans*-$[Me_2Al\text{-}N(H)C_6H_4Me\text{-}2]_2$ (**9**),[23] and *trans*-$[Me_2Al\text{-}N(H)C_6H_3\text{-}i\text{-}Pr\text{-}2,6]_2$ (**10**).[12] Compound **8** and **10** contain nonplanar Al_2N_2 rings, while that of **9** displays a planar ring. Reaction of the sterically demanding 2,4,6-tri-*tert*-butylaniline with Me_3Al also results in a similar dimeric product containing a central Al_2N_2 ring. However, an additional intramolecular condensation reaction occurred between an *ortho* *t*-butyl group and a methyl group on aluminum. The result was the metallated complex *trans*-$\{MeAl\text{-}N(H)C_6H_2\text{-}t\text{-}Bu_2\text{-}4,6\text{-}C(Me)_2CH_2\text{-}2]_2$ (**11**).[13] Another compound with a unique structure was formed using diphenylamine, $HNPh_2$. It is presumed that the intermediate product, $[Me_2Al\text{-}NPh_2]_2$, was formed upon initial reaction with Me_3Al. This compound, in turn, reacted with another equivalent of diphenylamine, producing $[MeAl\text{-}NPh_2]_2\{\mu\text{-}NPh_2\}$ (**12**).[24] Aside from containing the two bridging NPh_2 units producing the Al_2N_2 ring, **12** contains an additional bridge between the two aluminum atoms using the third diphenylamine.

The literature reveals four structurally characterized alkylaluminum derivatives prepared from silazanes, silazalanes. The compounds *trans*-$[Me_2Al\text{-}N(H)SiPh_3]_2$ (**13**) and *trans*-$[Me_2Al\text{-}N(H)SiEt_3]_2$ (**14**) were prepared from (triphenylsilyl)amine and (triethylsilyl)amine, respectively.[25] Both compounds possess comparable internal ring angles and mean Al-N distances (1.971 (**13**) and 1.967 Å (**14**)). In addition, this laboratory reported the syntheses and structures of $[Me_2Al\text{-}N(SiMe_2H)_2]_2$ (**15**) and $[Me_2Al\text{-}N(SiMe_2CH_2)_2]_2$ (**16**) from reaction of Me_3Al with the secondary amines 1,1,3,3-tetramethyldisilazane and 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane, respectively.[26]

Isobutylaluminum derivatives

The literature reveals considerably fewer reports of isobutylaluminum-based aminoalanes. Indeed, only four aminoalanes that have been structurally characterized which fall into the criteria of this review. The reaction of *i*-Bu_2AlH with 2-aminobiphenyl produces a compound similar to **8**, except for the conformation of the groups on the nitrogen atoms. Contrary to **8**, *cis*-$[t\text{-}Bu_2Al\text{-}N(H)Bp]_2$ (**17**)[22] contains biphenyl units *cis* to the Al_2N_2 ring. The average Al-N bond distance is comparable at 1.975 Å. Using 2,4,6-trimethylaniline and 2,4,6-tri-*tert*-butylaniline, the compounds *trans*-$[i\text{-}Bu_2Al\text{-}N(H)C_6HMe_3\text{-}2,4,6]_2$ (**18**) and *trans*-$[i\text{-}BuAl\text{-}N(H)C_6H_2\text{-}t\text{-}Bu_2\text{-}4,6\text{-}C(Me)_2CH_2\text{-}2]_2$ (**19**), respectively, were synthesized from reaction with *i*-Bu_2AlH.[27] The structure of **19** is analogous to compound **11**, in that two of the *tert*-butyl groups are metallated by the aluminum atoms, leaving only one isobutyl ligand bound to each aluminum in a *trans* orientation.

The interesting metallated dimer [*i*-BuAl-(iminodibenzyl)$]_2$ (**20**),[28] results from reaction of the secondary amine iminodibenzyl, 10, 11-dihydro-5*H*-dibenz[*b*,*f*]azepine with diisobutylaluminum hydride. One aromatic group each from opposite sides of the Al_2N_2 ring has undergone an *ortho*-metallation by the aluminum centers, thereby leaving a single isobutyl group on each aluminum atom in a *trans* orientation. As a result of this additional bridging, adjacent Al-N bond distances vary considerably. The Al-N bonds, that are also members of the Al-N-C-C ring, are significantly longer (2.040(7) Å) than the adjacent Al-N bonds (1.949(7) Å).

Neopentylaluminum derivatives

The literature reveals only four neopentylaluminum-based ((2,2-dimethylpropyl)-aluminum) aminoalanes. The four compounds *cis*-$[Neo_2Al\text{-}N(H)Ada]_2$ (**21**), *cis*-$[Neo_2Al\text{-}N(H)Bp]_2$ (**22**), *cis*-$[Neo_2Al\text{-}N(H)\text{-}t\text{-}Bu]_2$ (**23**), and *cis*-$[Neo_2Al\text{-}N(H)C_6H_3\text{-}i\text{-}Pr_2\text{-}2,6]_2$ (**24**) (Neo = neopentyl) were prepared by the reaction of trineopentylaluminum, Neo_3Al, with the appropriate primary amine in toluene.[29] **21** and **24** have analogous methylaluminum derivatives, while **23** is analogous to the two 2-aminobiphenyl derivatives **8** and **17**. The mean Al-N bond distances observed in **21** through **24** vary considerably. The bond distances range from 1.964 Å in **21** to 2.015 Å in **24**. In addition, two of the compounds display planar Al_2N_2 rings (**22** and **24**) and two display bent or puckered rings (**21** and **23**). A notable difference between the neopentylaluminum-based aminoalanes and the methylaluminum derivatives noted above is that the neopentyl compounds all display *cis* conformations exclusively while the others mostly display *trans*.

Miscellaneous derivatives

This section concerns aminoalanes containing non-aliphatic ligands bound to aluminum such as -NMe_2, -$SiMe_3$, -Ph, and halides.

Three compounds with the general formula $H_{3-n}Al(NMe_2)_n$ (n = 1, 2, 3) were reported,[30] of which two are presented here (the third, $[H_2Al\text{-}NMe_2]_3$ will be presented in the section on trimeric species). Tris(dimethylamino)alane was produced by reaction of dimethylamine with AlH_3. In the solid state the compound exists in the dimeric form, $[(Me_2N)_2Al\text{-}NMe_2]_2$ (**25a**). This compound contains pairs of adjacent Al-N bonds that are significantly different with distances of 1.959(2) and 1.980(2) Å. The accuracy of the bond distances from high quality X-ray data, suggests that the two distances are statistically distinct. The structure of $[(Me_2N)_2Al\text{-}NMe_2]_2$ was independently examined.[24] This structure is denoted as **25b**. The Al-N bond distances reported for **25b** confirm the variation in the Al-N bonds with distances of 1.951(2) and 1.979(2) Å. Along with **25a**, the structure of *trans*-$[H(Me_2N)Al\text{-}NMe_2]_2$ (**26**) was reported.[30] As opposed to the two structures of **25**, **26** displays essentially equal adjacent Al-N bond lengths of 1.964(2) and 1.967(2) Å.

The reaction of tris(dimethylamino)alane with H_2N-Ada results in the formation of *trans*-$[(Me_2N)_2Al\text{-}N(H)Ada]_2$.[24] Similar to **25a** and **25b**, this compound also displays adjacent Al-N lengths that appear to be significantly different at 1.938(3) and 1.957(3) Å.

The literature reveals one aminoalane dimer based upon trimethylsilyl, $SiMe_3$, and one based upon phenyl, Ph, namely $[(Me_3Si)_2Al\text{-}NH_2]_2$[31] (**28**) and $[Ph_2Al\text{-}N(H)(2\text{-}Bp)]_2$[32] (**29**), respectively. **28** results from reaction of tris(trimethylsilyl)aluminum, $(Me_3Si)_3Al$, with ammonia, while **29** is synthesized from reaction of Ph_3Al with 2-aminobiphenyl. **28** contains Al-N bonds with a mean of 1.955(2) Å, while **29** contains two distinct Al-N distances at 1.983(7) and 1.946(6) Å.

The chloride (**30**), bromide (**32**), and iodide (**33**) derivatives of the dimeric $[X_2Al\text{-}NMe_2]_2$ aminoalane may be prepared by reaction of the respective mercury(II) halide with dimethylaminoalane, $H_2Al\text{-}NMe_2$[33,34] The Al-N distance in **30** was determined to be 1.910(4) Å, while values of 1.946(9) and 1.943(12) Å were observed for **32** and **33**, respectively. The related compound *trans*-$[Cl_2Al\text{-}N(H)SiMe_3]_2$ (**31**),35 having an Al-N distance of 1.921(5) Å, has been prepared from reaction of $AlCl_3$ with bis(trimethylsilyl)amine, $HN(SiMe_3)_2$.

TRIMERIC AMINOALANES

A cursory examination reveals that considerably fewer trimeric aminoalanes have been reported. This paucity is qualitatively indicative of a pronounced, yet subtle, influence of ligand size on ring size.

It is interesting that the molecular structure of $[H_2Al\text{-}NMe_2]_3$ (**34**) has been reported in the literature *three* times, each by different authors. The preparation involves one of two routes: (a) reaction of AlH_3 with dimethylamine; or (b) reaction of $LiAlH_4$ with $[H_2NMe_2]Cl$. The first report (**34a**) was in 1972.[36] The Al-N bond distance reported as 1.93(3) Å. The data used for the second determination, **34b** were of higher quality.[30] This trimer contained six independent Al-N distances having an average of 1.946 Å. The third structural determination, **34c**, was reported more recently.[37] This structural determination resulted in an average Al-N bond distance of 1.936 Å, which is slightly shorter than that for **34b**. However, the average N-Al-N and Al-N-Al angles are identical for both **34b** and **34c** at 108.8 and 114.9°, respectively. The N-Al-N (108(2)°) and Al-N-Al (115(2)°) angles for **34a** are also within the same range.

The earliest report of a trimeric organoaluminum derivative, however, concerned $[Me_2Al\text{-}N(CH_2)_2]_3$ (**35**),[38] synthesized from the reaction of Me_3Al with the secondary amine, ethylenimine ($HNCH_2CH_2$). The average Al-N bond distance was reported to be 1.91 Å.

The reaction of ammonia with Me_3Al and $t\text{-}Bu_3Al$ affords the trimeric compounds $[Me_2Al\text{-}NH_2]_3$ (**36**) and $[t\text{-}Bu_2Al\text{-}NH_2]_3$ (**37**), respectively.[39] **36** contains 6 independent Al-N bond lengths having an overall average of 1.934 Å, whereas **37** displays crystallographic three-fold symmetry resulting in a planar six-membered ring having adjacent Al-N distances of 1.985(14) and 1.918(10) Å.

The reaction of Me_3Al with methylamine resulted in the formation of the trimeric compound $[Me_2Al\text{-}N(H)Me]_3$.[17,40] Two distinct stereoisomers of $[Me_2Al\text{-}N(H)Me]_3$ were isolated in the solid state. The *cis* isomer, **38**, taken to be the more thermodynamically stable form, crystallizes with rhombohedral packing. The *trans* isomer, **39**, crystallizes in a monoclinic form, but readily converts to the *cis* isomer at room temperature. **38** and **39** have average Al-N bond lengths of 1.941 and 1.901 Å, respectively.

Thermolysis of *trans*-$[Me_2Al\text{-}N(H)C_6H_3\text{-}i\text{-}Pr_2\text{-}2,6]_2$, **10**, results in the formation of the unique trimeric $[MeAl\text{-}NC_6H_3\text{-}i\text{-}Pr_2,6]_3$, **40**, by condensation of the remaining aza hydrogen with a methyl group on aluminum.[11,12] This compound, although it is trimeric, is in a different class than the trimers **34**–**39**. **40** contains aluminum and nitrogen atoms that are trivalent, making it an iminoalane, while the other trimeric aminoalanes contain tetravalent aluminum and nitrogen atoms. As a result of this lowered valency on aluminum, there exists the possibility for π-bonding between aluminum and nitrogen. Indeed, the Al-N bond distance of 1.782(4) Å is the shortest reported herein. Furthermore, the Al_3N_3 ring is planar, with Al-N-Al and N-Al-N angles of 124.7(5) and 115.3(5)°, respectively.

DISCUSSION

The fact that many aminoalanes display different associations in solution than in the solid state notwithstanding, the degree of association of aminoalanes is, arguably, the most significant singular aspect of these interesting compounds.

In discussions concerning the degree of aminoalane association, the steric bulk of the substituents on aluminum and nitrogen presents a convenient point of entry. Enthalpic and entropic based arguments may be employed to determine potential preferences for the dimer versus the trimer. Generally, ring strain would be expected to be lower in the trimers compared to the dimers. The four-membered rings in the dimers all have internal bond angles well below that required for tetrahedral geometry (109°), usually in the range of 86 to 95°. The bond angles about aluminum and nitrogen atoms in trimers are more obtuse, much closer to 120°. Steric interactions *between* substituents on aluminum and nitrogen may also play an important role. Steric strain between substituents on aluminum and nitrogen would be relieved in dimeric compounds because of the more acute endocyclic angles. Using entropy considerations, one may well expect the dimer to be favored over the trimer as, to a first approximation, there would generally be more molecules present in solution when the compound is dimeric. An interesting discussion along these lines concerning thermodynamic data collected on a series of aminoalanes that undergo

$$\text{dimer} \rightleftharpoons \text{trimer}$$

equilibria in solution has appeared.[41] Also included was some discussion on solvation effects. As solid state structures are not necessarily the same as those observed in solution, it is prudent to consider factors that may influence the crystallization process. Preference for one isomer over another in the solid state may well be a matter, at least in part, of relative solubilities. This would not, however, reflect the relative stabilities of the individual isomers in solution. This argument is also relevant for $[R_2Al\text{-}N(H)R']_2$ derivatives that have the possibility of existing as *cis* or *trans* isomers.

As examination of the dimeric and trimeric compounds listed herein suggests that bulkier ligands may well favor dimeric compounds. Compounds listed in Table 4 (with the exception of [*t*-$Bu_2Al\text{-}NH_2]_3$ (**37**) and $[MeAl\text{-}NC_6H_3$-*i*-Pr_2-2,6$]_3$ (**40**)) form trimeric compounds by employing small ligands bound to aluminum or nitrogen. Any combination of larger ligands appears to favor dimer formation. The only aminoalane with hydrogen bound to aluminum, $[H_2Al\text{-}NMe_2]_3$ (**34**), is trimeric with two methyl groups bound to nitrogen. Unfortunately, no other aminoalanes containing H_2Al units have been reported. Based on the observed trends, a dimeric $[H_2Al\text{-}NR_2]_2$ compound should exist, given a sufficiently large R. A similar trend can be observed for the series $[R_2Al\text{-}NH_2]_n$, (R = Me (**36**), *t*-Bu (**37**), and $SiMe_3$ (**28**)). The methyl and *tert*-butyl derivatives are trimeric, while the trimethylsilyl derivative is dimeric. As mentioned above, $[H_2Al\text{-}NMe_2]_3$ (**34**) is trimeric, but should methyl groups be substituted for hydrogen atoms on aluminum, as with $[Me_2Al\text{-}NMe_2]_2$ (**1**), the compound becomes dimeric. However, if the size is slightly reduced utilizing only one methyl on nitrogen (**38** and **39**) or with $N(CH_2)_2$ as in **35**, the compounds return to trimeric species. All of the other $[R_2Al\text{-}NMe_2]_2$ (R = NMe_2, halide) aminoalanes are dimeric. This suggests that there may be a small steric threshold which must be met for a compound to remain trimeric.

Of primary interest in comparing the structures of aminoalane dimers is the nature of the Al_2N_2 four-membered ring. For the most part, however, endocyclic and exocyclic bond distances and angles within the Al_2N_2 ring are the data primarily reported. This generally includes Al-N, Al-R, and to a smaller extent N-R bond distances. The ring geometry is indicated by the endocyclic N-Al-N and Al-N-Al bond angles.

Table 2 contains a list of all the Al-N bond distances along with their averages for the dimeric compounds **1** through **33**. Table 3 lists the average distances according to the substituent on aluminum. From an examination of these data, one observes that there is a wide range of Al-N distances ranging from 1.910(4) Å in $[Cl_2Al\text{-}NMe_2]_2$ (**30**) to 2.040(7) Å in *trans*-[*i*-BuAl-(iminodibenzyl)$]_2$ (**20**). This range of

Table 2 Selected bond distance (Å) for [R$_2$Al-NR$'_2$]$_2$ compounds.

	Compound	Al···Al	Al-N[a]	Al-N$_{avg}$	Al-R$_{avg}$	ref.
1a	[Me$_2$Al-NMe$_2$]$_2$	2.815	1.955 1.972	1.964	1.963	15
1b	[Me$_2$Al-NMe$_2$]$_2$	2.809	1.948(7) 1.967(7)	1.958	1.951	17
2	*cis*-[Me$_2$Al-N(H)-*i*-Pr]$_2$	2.800	1.953(5) 1.936(4) 1.956(4) 1.950(5)	1.949	1.956	18
3	*trans*-[Me$_2$Al-N(H)-*i*-Pr]$_2$	2.789	1.952(4) 1.965(5)	1.959	1.964	18
4	*cis*-[Me$_2$Al-N(H)C(H)(Me)Ph]$_2$	2.809	1.944(5) 1.956(5) 1.952(5) 1.947(5)	1.950	1.930	19
5	*cis*-[Me$_2$Al-N(H)C(H)(Me)(1-naphtyl)]$_2$	2.815	1.947(4) 1.970(3) 1.953(4) 1.955(4)	1.956	1.951	20
6	*trans*-[Me$_2$Al-N(H)Ada]$_2$	2.859	1.968(2) 1.958(2)	1.963	1.958	12
7	[Me$_2$Al-N(CH$_2$CH$_2$)$_2$-C-(OCH$_2$)$_2$]$_2$	2.801	1.955(3) 1.980(3)	1.968	1.949	21
8	*trans*-[Me$_2$Al-N(H)Bp]$_2$	2.854	1.979(3) 1.978(4) 1.980(3) 1.977(4)	1.979	1.946	22
9	*trans*-[Me$_2$Al-N(H)C$_6$H$_4$Me-2]$_2$	—	1.949(7) 1.965(7)	1.957	1.964	23
10	*trans*-[Me$_2$Al-N(H)C$_6$H$_3$-*i*-Pr$_2$-2,6]$_2$	2.894	1.981(12) 1.992(11) 1.971(11) 1.954(11)	1.975	1.949	12
11	*tran*-[MeAl-N(H)C$_6$H$_2$-*t*-Bu$_2$-4,6-C(Me)$_2$CH$_2$-2]$_2$[b]	—	1.957(6) 1.973(6)[d]	1.965	1.966[c] 1.933[e]	13
12	[MeAl-NPh$_2$]$_2$[μ-NPh$_2$]	2.683	1.991(4) 1.990(3) 2.002(3) 1.992(4)	1.994	1.951[c] 1.955[e] 1.842[f]	24
13	*trans*-[Me$_2$Al-N(H)SiPh$_3$]$_2$	2.832	1.971(3) 1.971(3)	1.971	1.952	25
14	*trans*-[Me$_2$Al-N(H)SiEt$_3$]$_2$	2.802	1.965(3) 1.969(3)	1.967	1.958	25
15	[Me$_2$Al-N(SiMe$_2$H)$_2$]$_2$	2.813	1.999(2) 1.990(2) 1.992(2) 1.994(2)	1.994	1.959	26
16	[Me$_2$Al-N(SiMe$_2$CH$_2$)$_2$]$_2$	2.790	2.005(3)	2.005	1.959	26
17	*cis*-[*i*-Bu$_2$Al-N(H)Bp]$_2$	2.891	1.973(9) 1.978(9) 1.980(9) 1.970(8)	1.975	1.944	22

Table 2 *Continued.*

	Compound	Al···Al	Al-N[a]	Al-N$_{avg}$	Al-R$_{avg}$	ref.
18	*trans*-[*i*-Bu$_2$Al-N(H)C$_6$H$_2$Me$_3$-2,4,6]$_2$	2.952	1.982(3) 1.980(3)	1.981	1.977	27
19	*trans*-[*i*-BuAl-N(H)C$_6$H$_2$-*t*-Bu$_2$-4,6-C(Me)$_2$CH$_2$-2]$_2$	2.843	1.956(5)[d] 1.994(5)	1.975	1.978[g] 1.945[e]	27
20	*trans*-[*i*-BuAl-(iminodibenzyl)]$_2$[b]	2.806	2.040(7)[d] 1.949(7)	1.995	1.98[g] 1.954[e]	28
21	*cis*-[Neo$_2$Al-N(H)Ada]$_2$	2.877	1.956(16) 1.971(10)	1.964	2.019	29
22	*cis*-[Neo$_2$Al-N(H)-*t*-Bu]$_2$	2.870	1.970(7) 1.983(7)	1.977	1.986	29
23	*cis*-[Neo$_2$Al—N(H)Bp]$_2$	2.881	1.999(3) 1.979(3) 1.989(3) 1.996(3)	1.989	1.980	29
24	*cis*-[Neo$_2$Al-N(H)C$_6$H$_3$-*i*-Pr$_2$-2,6]$_2$	2.954	2.013(5) 2.007(5) 2.011(5) 2.030(5)	2.015	1.979	29
25a	[(Me$_2$N)$_2$Al-NMe$_2$]$_2$	—	1.959(2) 1.980(2)	1.970	1.814	30
25b	[(Me$_2$N)$_2$Al-NMe$_2$]$_2$	2.822	1.951(2) 1.979(2)	1.965	1.802	24
26	*trans*-[H(Me$_2$N)Al-NMe$_2$]$_2$	—	1.964(2) 1.967(2)	1.966	1.804	30
27	*trans*-[(Me$_2$N)$_2$Al-N(H)Ada]$_2$	2.864	1.957(3) 1.938(3)	1.948	1.793	24
28	[(Me$_3$Si)$_2$Al-NH$_2$]$_2$	2.834	1.953(2) 1.956(2)	1.955	2.473	31
29	*trans*-[Ph$_2$Al-N(H)Bp]$_2$	2.854	1.983(7) 1.946(6)	1.964	1.960	32
30	[Cl$_2$Al-NMe$_2$]$_2$	—	1.910(4)	1.910	2.106	33
31	*trans*-[Cl$_2$Al-N(H)SiMe$_3$]$_2$	—	1.916(4) 1.925(5)	1.921	2.100	35
32	[Br$_2$Al-NMe$_2$]$_2$	—	1.946(9)	1.946	2.260	34
33	[I$_2$Al-NMe$_2$]$_2$	—	1.943(12)	1.943	2.492	34

[a] Some compounds contain only two Al-N distances due to the symmetry of the structure. [b] Values for one molecule of two in the asymetric unit. [c] Al-Me bonds. [d] These bonds are a part of the ring formed from metallation of the amine alkyl. [c] Al-C$_{bridge}$ bond. [f] Al-N$_{bridge}$ bonds. [g] Al-*i*-Bu bonds.

values may be explained, at least in part, by considering inductive and steric effects due to the large variety of substituents used on aluminum and nitrogen. Although intermolecular crystal packing forces may also influence geometry, it is difficult to determine what, if any, effect this may have on the resultant structure. Since there are a large number of contributing factors that influence the final Al-N bond lengths, it is a perfectly useless exercise to attempt to correlate the Al-N distances to any single variable. However, some general trends begin to emerge as one examines bond lengths and inductive or steric parameters. Haaland has published an informative treatment of dative and covalent bonding characteristics that influence bonding in main group compounds.[42]

By investigating the Al-N bond lengths in the series of compounds. Cl$_3$Al-NMe$_3$,[43] H$_3$Al-NMe$_3$,[44] and Me$_3$Al-NMe$_3$,[45] using X-ray and electron diffraction

Table 3 Average Al-N and Al-R bond distances according to aluminum ligand in $[R_2Al\text{-}NR'_2]_2$ compounds.

Compound class	No. of compounds	Al-N, Å(σ)[a,b]	Al-R, Å(σ)[a,b]
Al-Me	17	1.969(17)	1.954(8)
Al-*i*-Bu	4	1.981(26)	1.970(15)
Al-Neo	4	1.987(21)	1.991(16)
Al-NMe_2	4	1.962(13)	1.803(7)
Al-$SiMe_3$	1	1.955(2)	2.473
Al-Ph	1	1.964(19)	1.960
Al-Cl	2	1.915(6)	2.103(3)
Al-Br	1	1.946	2.260
Al-I	1	1.943	2.492
all Al-alkyl[c]	25	1.974(21)	1.961(17)
all compounds	35	1.966(24)	[d]

[a] The bond distance also includes the standard deviation of the population (σ) in parentheses. [b] Averages derived from Al-N and Al-R_{avg} values in Table 1. [c] Includes all Al-methyl, -isobutyl, and -neopentyl derivatives. [d] This average was not calculated since they do not all represent Al-C bonds.

methods, one obtains distances of 1.96(1), 2.063(8), and 2.099(10) Å, respectively, clearly suggesting that the use of more electronegative substituents on aluminum tends to shorten the Al-N bonds. This can be rationalized by considering that the more electronegative chlorine withdraws electron density from aluminum, thereby requiring the nitrogen with its lone pair to approach closer in order to compensate. The nitrogen does not need to approach as close when electron donating methyls are bound to aluminum. This bond lengthening trend is also observed in the series. $[Cl_2Al\text{-}NMe_2]_2$ (**30**), $[H_2Al\text{-}NMe_2]_3$ (**34b**), and $[Me_2Al\text{-}NMe_2]_2$ (**1b**) with average distances of 1.910, 1.935, and 1.958 Å respectively. The Al-N distances for the other two halide derivatives, $[Br_2Al\text{-}NMe_2]_2$ (**32**) at 1.946 Å and $[I_2Al\text{-}NMe_2]_2$ (**33**) at 1.943 Å, are shorter than distances found in the alkylaluminum derivatives.

There is too much influence by other factors to extensively correlate the Al-N distances with inductive parameters for the different methyl-, isobutyl-, *tert*-butyl-, and neopentyl-, and dimethylaminoaluminum derivatives. For example, a plot of Hammet[46] inductive parameters for these various ligands on aluminum versus the Al-N distances gives only a scatter of points with low correlation. The same type of low correlation plot is obtained when Al-N distances are plotted against steric parameters of either the Al or N substituents. Figure 1 shows a distribution of all the individual Al-N distances[47] as a function of number of compounds for the methyl-, isobutyl-, and neopentyaluminum derivatives.

This shows the general trend that the derivatives containing isobutyl or neopentyl groups on aluminum have slightly longer bond distances. This trend can also be seen in the data from Table 3. It is unclear whether this is due to greater inductive effects by the larger alkyls or simply a manifestation of greater steric demands. The data are somewhat incomplete in that there are no structures reported containing small amines on the isobutyl- and neopentylaluminum derivatives. These data would be necessary to determine the full effect of the larger alkyl groups. Only sterically demanding amines were employed for the neopentylaluminum derivatives **21–24**.

Table 4 contains a list of the trimeric compounds **34–40**, along with some bond distance data. The Al-N distances for compounds **34** through **39** fall generally in the

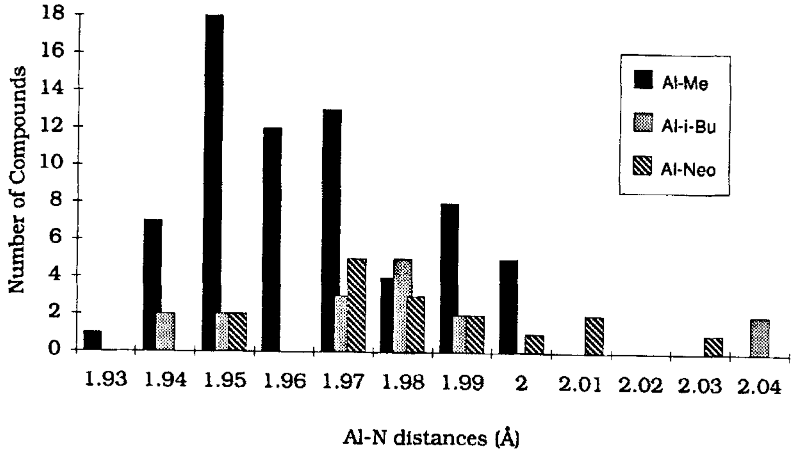


Figure 1 Distribution of Al-N bond distances according to dimeric methyl-, isobutyl-, and neopentylaluminum derivatives.

Table 4 Selected bond distances (Å) for $[R_2Al\text{-}NR'_2]_3$ compounds.

	Compound	Al-N[a]	Al-N_{avg}	Al-R_{avg}	ref.
34a	$[H_2Al\text{-}NMe_2]_3$	1.93(3)	1.93	[b]	36
34b	$[H_2Al\text{-}NMe_2]_3$	1.955(2)	1.946	[b]	30
		1.938(3)			
		1.946(2)			
		1.951(2)			
		1.951(2)			
		1.937(3)			
34c	$[H_2Al\text{-}NMe_2]_3$	1.927(3)	1.936	1.55	37
		1.934(3)			
		1.941(3)			
		1.936(3)			
		1.930(3)			
		1.945(3)			
35	$[Me_2Al\text{-}N(CH_2)_2]_3$	1.91(2)	1.91	1.96	38
		1.94(1)			
		1.88(2)			
36	$[Me_2Al\text{-}NH_2]_3$	1.927(6)	1.934	1.958	39
		1.940(5)			
		1.938(5)			
		1.921(5)			
		1.933(5)			
		1.942(5)			
37	$[t\text{-}Bu_2Al\text{-}NH_2]_3$	1.985(14)	1.952	1.999	39
		1.918(10)			
38	*cis*-$[Me_2Al\text{-}N(H)Me]_3$	1.951(12)	1.941	1.973	17, 40
		1.931(12)			
39	*trans*-$[Me_2Al\text{-}N(H)Me]_3$	1.943(13)	1.901	1.987	17, 40
		1.926(12)			
		1.833(8)			
40	$[MeAl\text{-}NC_6H_3\text{-}i\text{-}Pr_2\text{-}2,6]_3$	1.782(4)	1.782	1.978	11, 12

[a] Some compounds have less than six Al-N bond lengths due to symmetry in the molecule. [b] Al-H bond length was not reported.

range 1.91 to 1.95 Å. These values are slightly lower than those for the dimeric compounds.

The observed shortening of the Al-N bond lengths in **40** is also observed in another compound containing trivalent aluminum and nitrogen, $Al[N(SiMe_3)_2]_3$,[48] with a distance of 1.78(2) Å. A method of approximating bond lengths has been suggested for aluminum-nitrogen compounds which relies on the extent of covalent versus dative bonding character associated with each Al-N bond.[42] Al-N bonds that contain more covalent character are generally observed to be shorter than those with more dative character.

In addition to Al-N bond distances, one can examine the internal N-Al-N and Al-N-Al angles to ascertain the manner in which the shape of the Al-N ring varies. Table 5 and 6 contain endocyclic ring angle data along with information about the

Table 5 Selected average bond angles (°) for $[R_2Al\text{-}NR'_2]_2$ compounds.

	Compound	N-Al-N	Al-N-Al	R-Al-R	Ring geometry
1a	$[Me_2Al\text{-}NMe_2]_2$	88.4	91.6	115.9	planar
1b	$[Me_2Al\text{-}NMe_2]_2$	88.3	91.7	115.7	planar
2	*cis*-$[Me_2Al\text{-}N(H)\text{-}i\text{-}Pr]_2$	87.2	91.9	121.5	bent
3	*trans*-$[Me_2Al\text{-}N(H)\text{-}i\text{-}Pr]_2$	89.2	90.8	120.6	planar
4	*cis*-$[Me_2Al\text{-}N(H)C(H)(Me)Ph]_2$	86.2	92.2	119.7	bent
5	*cis*-$[Me_2Al\text{-}N(H)C(H)(Me)(1\text{-naphthyl})]_2$	87.0	92.1	121.5	bent
6	*trans*-$[Me_2Al\text{-}N(H)Ada]_2$	86.5	93.5	116.2	planar
7	$[Me_2Al\text{-}N(CH_2CH_2)_2\text{-}C\text{-}(OCH_2)_2]_2$	89.2	90.8	118.7	planar
8	*trans*-$[Me_2Al\text{-}N(H)Bp]_2$	86.3	92.8	119.6	bent
9	*trans*-$[Me_2Al\text{-}N(H)C_6H_4Me\text{-}2]_2$	86.8	93.2	118.8	planar
10	*trans*-$[Me_2Al\text{-}N(H)C_6H_3\text{-}i\text{-}Pr_2]_2$	83.3	94.3	115.6	bent
11	*trans*-$[MeAl\text{-}N(H)C_6H_2\text{-}t\text{-}Bu_2\text{-}4,6\text{-}C(Me)_2CH_2\text{-}2]_2$	87.9	92.1	116.3	planar
12	$[MeAl\text{-}NPh_2]_2\{\mu\text{-}NPh_2\}$	85.6	84.6	111.7[a]	bent
13	*trans*-$[Me_2Al\text{-}N(H)SiPh_3]_2$	88.2	91.8	118.3	planar
14	*trans*-$[Me_2Al\text{-}N(H)SiEt_3]_2$	89.2	90.8	118.8	planar
15	$[Me_2Al\text{-}N(SiMe_2H)_2]_2$	90.3	89.7	109.9	planar
16	$[Me_2Al\text{-}N(SiMe_2CH_2)_2]_2$	90.5	89.5	109.6 117.3[b]	planar
17	*cis*-$[i\text{-}Bu_2Al\text{-}N(H)Bp]_2$	85.8	94.1	116.9	planar
18	*trans*-$[i\text{-}Bu_2Al\text{-}N(H)C_6H_2Me_3\text{-}2,4,6]_2$	83.7	96.3	118.3	planar
19	*trans*-$[i\text{-}BuAl\text{-}N(H)C_6H_2\text{-}t\text{-}Bu_2\text{-}4,6\text{-}C(Me)_2CH_2\text{-}2]_2$	88.1	91.9	115.5	planar
20	*trans*-$[i\text{-}BuAl\text{-}(iminodibenzyl)]_2$	90.6	89.4	130.7	planar
21	*cis*-$[Neo_2Al\text{-}N(H)Ada]_2$	81.6	94.2	118.5	bent
22	*cis*-$[Neo_2Al\text{-}N(H)t\text{-}Bu]_2$	83.5	93.1	114.7	bent
23	*cis*-$[Neo_2Al\text{-}N(H)Bp]_2$	87.1	92.9	123.2	planar
24	*cis*-$[Neo_2Al\text{-}N(H)C_6H_3\text{-}i\text{-}Pr_2\text{-}2,6]_2$	85.7	94.3	123.0	planar
25a	$[(Me_2N)_2Al\text{-}NMe_2]_2$	88.1	91.9	114.4	planar
25b	$[(Me_2N)_2Al\text{-}NMe_2]_2$	88.2	91.8	114.9	planar
26	*trans*-$[H(Me_2N)Al\text{-}NMe_2]_2$	87.7	92.3	[c]	planar
27	*trans*-$[(Me_2N)_2Al\text{-}N(H)Ada]_2$	85.3	94.7	112.2	planar
28	$[(Me_3Si)_2Al\text{-}NH_2]_2$	86.9	93.1	123.6	planar
29	*trans*-$[Ph_2Al\text{-}N(H)Bp]_2$	86.9	93.1	116.4	planar
30	$[Cl_2Al\text{-}NMe_2]_2$	88.6	91.4	112.6	planar
31	*trans*-$[Cl_2Al\text{-}N(H)SiMe_3]_2$	90.1	89.9	112.4	planar
32	$[Br_2Al\text{-}NMe_2]_2$	90.9	89.1	111.2	planar
33	$[I_2Al\text{-}NMe_2]_2$	89.1	90.9	110.7	planar

[a] C-Al-N angle. [b] C-Al-C angle. [c] The H-Al-NMe_2 angle was not reported.

Table 6 Selected average bond angles (°) for $[R_2Al\text{-}NR'_2]_3$ compounds.

Compound	N-Al-N	Al-N-Al	R-Al-R	R-Al-R	Ring orient.
34a	$[H_2Al\text{-}NMe_2]_3$	108	115	[a]	chair
34b	$[H_2Al\text{-}NMe_2]_3$	108.8	114.9	[a]	chair
34c	$[H_2Al\text{-}NMe_2]_3$	108.8	114.9	[a]	chair
35	$[Me_2Al\text{-}N(CH_2)_2]_3$	102.3	120.0	115.7	skew-boat
36	$[Me_2Al\text{-}NH_2]_3$	101.4	122.1	118.3	skew-boat
37	$[t\text{-}Bu_2Al\text{-}NH_2]_3$	106.1	133.9	117.8	planar
38	*cis*-$[Me_2Al\text{-}N(H)Me]_3$	102.1	122.3	117.6	chair
39	*trans*-$[Me_2Al\text{-}N(H)Me]_3$	100.6	123.2	117.5	skew-boat
40	$[MeAl\text{-}NC_6H_3\text{-}i\text{-}Pr_22,6]_3$	115.3	124.7	—	planar

[a] H-Al-H bond angles were not reported.

geometry of the four- or six-membered ring. For the dimeric compounds, there are two general structural features that may be observed: the planarity of the ring and the observance of *cis* or *trans* isomers in $[R_2Al\text{-}N(H)R']_2$ type compounds.

Of the 33 dimeric compounds examined, eight demonstrate a puckering or bending of the ring resulting in a non-planar four-membered ring. Table 5 contains the geometry for all the dimeric compounds. For a planar four-membered ring containing four bond lengths of approximately the same values, the sum of the four endocyclic angles should, in theory, approach 360°. For the puckered rings, this sum would then be slightly less, as the angles are more acute. Figure 2 shows a plot of N-Al-N versus Al-N-Al angles for compounds **1**–**33**. The aminoalanes possessing planar cores fall along the general line, $x + y = 180$. However, the eight compounds that contain bent rings fall below this line; the distance from the line is a qualitative

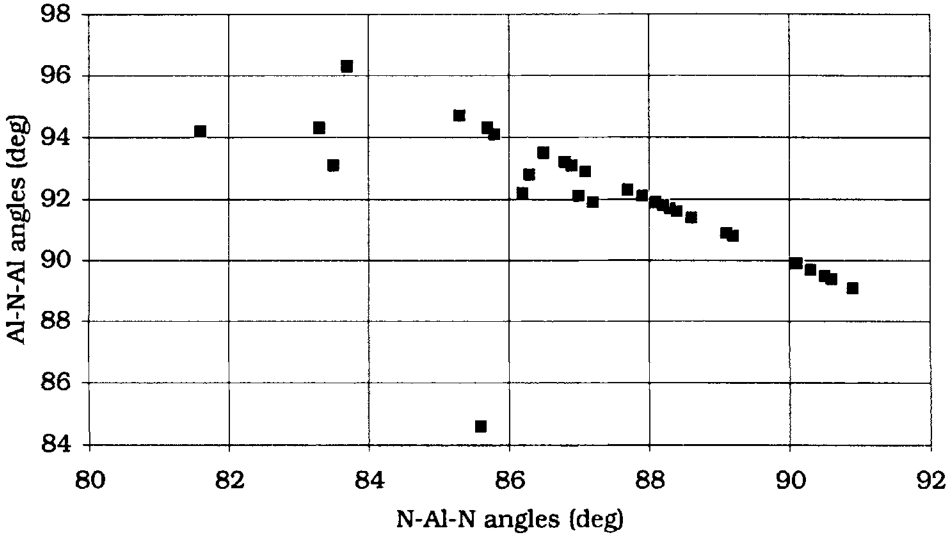


Figure 2 Plot of average N-Al-N versus Al-N-Al angles in aminoalane dimers.

estimate of the extent of ring puckering. By examining those compounds that do have bent rings, all of them except one, **16**, are compounds that have only one alkyl bound to nitrogen from using primary amines. Five of the compounds have *cis* conformations and two are *trans*. It is not surprising that the eighth one, $[MeAl\text{-}NPh_2]_2\{\mu\text{-}NPh_2\}$ (**16**), has a bent geometry considering the NPh_2 unit that bridges between the two aluminum atoms.

A majority of the planar compounds contain N-Al-N angles that are less than 90°, while the Al-N-Al angles are greater than 90°, meaning that the Al_2N_2 rings are slightly elongated along the Al· · ·Al line. However, compounds **13**, **14**, **20**, **31**, and **32** are slightly elongated the N· · ·N line, having N-Al-N angles slightly greater than 90° and Al-N-Al angles slightly less. Planar compounds with the general form $[R_2Al\text{-}NR'_2]_2$, having two equivalent alkyl groups bound to nitrogen have N-Al-N angles with an average of 89.1(13)°. On the other hand, those with the general formula $[R_2Al\text{-}N(H)R']_2$, with only one alkyl group and a hydrogen atom bound to nitrogen, have N-Al-N angles with an average of 87.2(17)°. This can be rationalized by realizing that nitrogen atoms that contain one hydrogen are more likely to have slightly larger Al-N-Al and Al-N-R angles because of the smaller steric requirements of the hydrogen.

For the trimeric compounds, there is a greater variety in the goemetry of the ring owing to its greater flexibility. It has been suggested that the greater degree of ionic character in the Al-N bridging bonds relaxes the geometric requirements for sp^3 hybridization, increasing the flexibility.[39] Table 6 lists the ring conformations for compounds **34** through **39**. The average N-Al-N angles range from 100.6° in *trans*-$[Me_2Al\text{-}N(H)Me]_3$ (**38**) to 108.8° in $[H_2Al\text{-}NMe_2]_3$ (**34**). The large angles for **34** are probably due to the small spatial requirements of the two hydrogens on aluminum. Likewise, **34** conains the smallest angles about nitrogen with an average of 114.9°. $[t\text{-}Bu_2Al\text{-}NH_2]_3$ (**37**) contains the largest Al-N-Al angles with a value of 133.9 (5)°. **36** and **37** present an interesting comparison. While both are trimeric, there are significant differences between the two compounds in the Al_3N_3 six-membered ring. **36** resides about a skewed boat core while **37** resides about an Al_3N_3 planar core which has D_{3h} symmetry. An examination of all the individual Al-N bond distances in Table 4 reveals that the bond lengths vary within a molecule to a greater extent than in the dimers. The endocyclic Al-N-Al and N-Al-N bonds in **40** are 124.7(5) and 115.3(5)°, respectively, giving this compound an almost hexagonal shape to the Al_3N_3 planar ring.

CONCLUSIONS

The chemistry of aminoalanes has become a major segment of organoaluminum chemistry. As increasing numbers of workers have joined the fray, the field has correspondingly expanded. Tetrameric and hexameric aminoalanes are becoming increasingly common. The extent to which aminoalanes associate in the solid state is a deceptively complex synergic phenomenon dependent upon a number of variables. This brief review has sought to bring observed structural and steric trends for dimeric and trimeric aminoalanes into shaper focus.

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