strain could lead to the much larger rate differences found for the Cr(III) complexes under discussion.

Pink Cr(en)(NH$_3$)(OH$_2$)$_3{}^{3+}$ (unknown configuration), which also has three Cr–N bonds, aquates at 60° at approximately twice the rate of 1,2,3-Cr(dien)(OH$_2$)$_3{}^{3+}$ and $^1/_{140}$th the rate of 1,2,6-Cr(dien)(OH$_2$)$_3{}^{3+}$ (Table VII). The first of these two rate comparisons is about what would be expected if pink Cr(en)(NH$_3$)(OH$_2$)$_3{}^{3+}$ had a 1,2,3-triaquo configuration and if aquation of a Cr–N bond followed the same rate trends as aquation of a Co–Cl (and, by inference, Cr–Cl) bond, as observed in the series *cis*-Co(NH$_3$)$_4$Cl$_2{}^+$, *cis*-Co(en)(NH$_3$)$_2$Cl$_2{}^+$, *cis*-Co(en)$_2$Cl$_2{}^+$,[21] and *cis*-α-Co(trien)Cl$_2$,[18,19] and the series Co(NH$_3$)$_5$Cl^{2+},[22] *cis*-Co(en)$_2$(NH$_3$)Cl^{2+}, *cis*-α-Co(trien)(NH$_3$)Cl^{2+}, and ω-Co(dien)(en)Cl^{2+}.[21] In each series the aquation rates of a chloro ligand decrease with increasing chelation, which has been ascribed[21] to the tendency of the organic ligands to break up the solvation shell, rendering the transition state less stable since it makes greater demands on solvation due to the separating charges. However, Sargeson and Searle[19] question the validity of the solvation explanation since *cis*-β-Co(trien)Cl$_2{}^+$ does not fit the pattern. In the Cr–N (or Co–N) type aquations insufficient data exist to allow examination of the effect of chelation; a solvation effect would perhaps be less important since there would be little separation of charge on forming the transition state, so the above comparison cannot be accepted as strong evidence for a 1,2,3 configuration for pink Cr(en) (NH$_3$) (OH$_2$)$_3{}^{3+}$.

For the complexes with two Cr–N bonds, Cr(dienH)(OH$_2$)$_4{}^{4+}$ aquates at 60° at 7 times the rate of Cr(en)(OH$_2$)$_4{}^{3+}$ (Table VII). The greater rate of the former is expected due to steric crowding from the (CH$_2$)$_2$NH$_3$ group attached to the secondary amino N atom, inasmuch as steric crowding would favor a dissociative mechanism (this type of effect has been demonstrated[23] with N-substituted alkyl groups in chloroaminecobalt(III) substrates, *e.g.*). Comparison with *trans*- and *cis*-Co(NH$_3$)$_2$ (OH$_2$)$_4{}^{3+}$ is ambiguous because of the uncertain configuration assignments and rates of the diammines.

For the complexes with one Cr–N bond, Cr(dienH$_2$)(OH$_2$)$_5{}^{5+}$ aquates at 60° faster than Cr(enH)(OH$_2$)$_5{}^{4+}$, presumably because of steric crowding in the former. The ammine complex, Cr(NH$_3$)(OH$_2$)$_5{}^{3+}$, appears to aquate somewhat slower than either (taking the values in HClO$_4$ medium).

Successive aquations of either 1,2,3- or 1,2,6-Cr(dien) (OH$_2$)$_3{}^{3+}$ to the final product Cr(OH$_2$)$_6{}^{3+}$ are progressively slower, as also observed in aquation of Cr(en)(OH$_2$)$_4{}^{3+}$ and various haloaquoamine complexes of Cr(III). In contrast, successive aquations of Cr(NH$_3$)$_6{}^{3+}$ to Cr(OH$_2$)$_6{}^{3+}$ do not appear to follow any systematic trend of rates. The reasons for this are unknown, and further studies of successive Cr–N bond ruptures in Cr(III) complexes with multidentate amine ligands are needed.

Acknowledgment. The Cary 60 spectropolarimeter used was purchased by the Chemistry Department with funds from National Science Foundation Grant No. GP-1682.

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[21] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

[22] A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955).

[23] See Basolo and Pearson, Table VI, footnote *b*, p 162.

Aluminum–Aluminum Covalent Bonds. II.[1a]
Bis(dimethylamino)trimethyltrialuminum(5)

E. P. Schram,[1b] R. E. Hall, and J. D. Glore

Contribution from the Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210. *Received May 12, 1969*

Abstract: The reduction of [Al(CH$_3$)$_3$]$_2$ by B$_2$[N(CH$_3$)$_2$]$_4$ has been investigated by varying the reactant stoichiometries, Al:B$_2$, according to the mole ratios 1.8, 2.8, 3.9, and large excesses of [Al(CH$_3$)$_3$]$_2$. The reaction products were found to be dependent on the reaction stoichiometry, order of reagent mixing, and reaction temperature. A new catenated aluminum species was prepared and characterized, bis(dimethylamino)trimethyltrialuminum(5), Al$_3$(CH$_3$)$_3$[N(CH$_3$)$_2$]$_2$, as well as a new amino adduct of covalent aluminum, (CH$_3$)$_3$Al·N(CH$_3$)$_2$Al(CH$_3$)$_2$. Hydride formation takes place during *in situ* decomposition of methyldimethylaminodiborane(4) derivatives as well as hydride transfer from boron to aluminum.

The reduction of [Al(CH$_3$)$_3$]$_2$ by B$_2$[N(CH$_3$)$_2$]$_4$ has been reported to afford the catenated aluminum derivative, Al$_4$B[N(CH$_3$)$_2$]$_3$(CH$_3$)$_6$.[1a] The reaction stoichiometry associated with this reduction appears anomalous in that catenated aluminum species are only isolated when the mole ratio of Al(CH$_3$)$_3$:B$_2$[N(CH$_3$)$_2$]$_2$ is greater than *ca.* 3, *i.e.*, employing some minimum quantity of reducing agent. This investigation was undertaken to (a) elucidate the apparent anomaly associated with the reaction stoichiometry, (b) isolate and characterize reaction intermediates, and (c) prepare boron-free catenated organoaluminum species. Item c is of particular importance because interpretation of the experimental data associated with Al$_4$B[N(CH$_3$)$_2$]$_3$(CH$_3$)$_6$ in-

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[1] (a) E. P. Schram, *Inorg. Chem.*, **5**, 1291 (1966); (b) to whom correspondence should be addressed.

Figure 1. ^{1}H nmr spectrum of $Al_3(CH_3)_3[N(CH_3)_2]_2$.

volved the presence of three Al–Al bonds; an alternate bonding scheme could be one involving B–Al bonds as suggested for $Al_3B_3[N(CH_3)_2]_7H_5$.[2]

Results and Discussion

Investigation of the Active Reducing Agent toward $[Al(CH_3)_3]_2$, $B_2(CH_3)_2[N(CH_3)_2]_2$. Treatment of tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, with increments of aluminum trimethyl dimer, $[Al(CH_3)_3]_2$, results in precipitation of a yellow solid and evolution of boron trimethyl, $B(CH_3)_3$, dimethylaminodimethylborane, $(CH_3)_2NB(CH_3)_2$, 1,2-bisdimethylamino-1,2-dimethyldiborane(4), $B_2(CH_3)_2[N(CH_3)_2]_2$, and dimethylaminodimethylalane dimer, $[(CH_3)_2NAl(CH_3)_2]_2$. The formation of these species is represented by eq 1–4.

$$B_2[N(CH_3)_2]_4 + [Al(CH_3)_3]_2 \longrightarrow B_2CH_3[N(CH_3)_2]_3 + {}^1/_2[(CH_3)_2NAl(CH_3)_2]_2 + {}^1/_2[Al(CH_3)_3]_2 \quad (1)$$

$$B_2CH_3[N(CH_3)_2]_3 + [Al(CH_3)_3]_2 \longrightarrow B_2(CH_3)_2[N(CH_3)_2]_2 + {}^1/_2[(CH_3)_2NAl(CH_3)_2]_2 + {}^1/_2[Al(CH_3)_3]_2 \quad (2)$$

$$B_2(CH_3)_2[N(CH_3)_2]_2 + [Al(CH_3)_3]_2 \longrightarrow Al_2(CH_3)_4 + 2(CH_3)_2NB(CH_3)_2 \quad (3)$$

$$(CH_3)_2NB(CH_3)_2 + [Al(CH_3)_3]_2 \longrightarrow B(CH_3)_3 + {}^1/_2[(CH_3)_2NAl(CH_3)_2]_2 + {}^1/_2[Al(CH_3)_3]_2 \quad (4)$$

Equations 1 and 2 represent the stepwise formation of $B_2(CH_3)_2[N(CH_3)_2]_2$ which in turn reduces $[Al(CH_3)_3]_2$ (eq 3). Tetramethyldialane(4), $Al_2(CH_3)_4$ (eq 3), was not isolated but is discussed in terms of a reaction intermediate in the last section of this report. The oxidation product, $(CH_3)_2NB(CH_3)_2$ (eq 3), was recovered in high yield and its reaction with $[Al(CH_3)_3]_2$ was verified (eq 4).

In order to test the validity of the reaction represented by eq 3, the reaction between $B_2(CH_3)_2[N(CH_3)_2]_2$ and $[Al(CH_3)_3]_2$ was investigated. Treatment of $B_2(CH_3)_2[N(CH_3)_2]_2$ (1 mmol) with $[Al(CH_3)_3]_2$ (0.5 mmol) affords 1 mmol of $B(CH_3)_3$, 0.4 mmol of $(CH_3)_2BN(CH_3)_2$, $[(CH_3)_2AlN(CH_3)_2]_2$, and formation of a dark red solution from which a yellow solid was isolated. The quantity of this latter material was insufficient to permit complete characterization; however, oxidative hydrolysis affords H_2. This material may well be a mixture but was demonstrated to be free from hydride by infrared; therefore, the evolution of H_2 during hydrolysis most likely indicates the presence of aluminum in a reduced oxidation state. It should be noted that when a 1:0.5 molar ratio of $B_2[N(CH_3)_2]_4$ to $[Al(CH_3)_3]_2$ is employed, no reduction of $[Al(CH_3)_3]_2$ takes place. In addition to the cited volatile reaction products, $HB(CH_3)N(CH_3)_2$ was recovered from the reaction mixture as well as an unstable species which contained the BH_2 moiety as established by infrared.

Preparation and Characterization of $Al_3(CH_3)_3[N(CH_3)_2]_2$. Reaction between $[Al(CH_3)_3]_2$ and $B_2[N(CH_3)_2]_4$, in the mole ratio $Al:B_2 = 3.9$, affords $B(CH_3)_3$, $(CH_3)_2BN(CH_3)_2$, $[(CH_3)_2AlN(CH_3)_2]_2$, and a yellow solid which is soluble in hydrocarbons forming red solutions. Within experimental error all the boron originally associated with $B_2[N(CH_3)_2]_4$ is converted to $B(CH_3)_3$ and $(CH_3)_2BN(CH_3)_2$. The yellow solid is formulated as $Al_3(CH_3)_3[N(CH_3)_2]_2$ on the basis of the data summarized in Table I and the interpretation of ^{1}H nmr data. The slightly low Al analysis amounts to only 4 mg of Al (130-mg sample); the total mass recovered (calculated from analyses data) was low by several milligrams, and it should be noted that the acid solution of the hydrolysis residue contained an insoluble white material estimated at several milligrams. The oxidative hydrolysis of bis(dimethylamino)trimethyltrialuminum(5) is represented by eq 5.

Table I. Analytical Characterization of $Al_3(CH_3)_3[N(CH_3)_2]_2$

	Wt, %			Mg/mmol	Mol	
	N	CH_3	Al	of H_2	wt	CH_3/H_2
Calcd	13.1	21.0	37.8	107	214	1.50
Found	12.9	22.2	34.8	102	255	1.51

$$2Al_3(CH_3)_3[N(CH_3)_2]_2 + 9H_2O + 4H^+ \longrightarrow 3Al_2O_3 + 4H_2 + 6CH_4 + 4H_2N(CH_3)_2^+ \quad (5)$$

^{1}H Nmr. The ^{1}H nmr spectrum of $Al_3(CH_3)_3[N(CH_3)_2]_2$ (Figure 1) consists of two broad absorptions at −2.40 and +0.40 ppm from TMS in the ratio *ca.* 4:3, which are assigned to $N(CH_3)_2$ and CH_3 moieties, respectively, on aluminum. The exact ratio of these two absorptions could not be determined because the extreme breadth of the signals results in an indeterminate baseline position. The multiplet structure, associated with these absorptions, could not be resolved by cooling of the sample from 35 to −90° and is thought to be the result of the presence of isomers.

Infrared Spectrum. The infrared spectrum of $Al_3(CH_3)_3[N(CH_3)_2]_2$ is summarized in Table II. The band at 1200 cm^{-1} is assigned to ρ_{CH_3} on Al with reference to the spectra of $[Al(CH_3)_3]_2$ and $[(CH_3)_2AlN(CH_3)_2]_2$.[2,3] The absence of ν_{asym} and ν_{sym} NC_2 bands at 1165 and 980 cm^{-1} indicates the absence of NC_2 moieties (terminal) by comparison with the spectrum of $[Al\{N(CH_3)_2\}_3]_2$.[2] The absorptions found at 1043 and 905 cm^{-1} are assigned to ν_{asym} and ν_{sym} NC_2 (bridging), respectively, with reference to the spectra of $[Al\{N(CH_3)_2\}_3]_2$ and $[(CH_3)_2AlN(CH_3)_2]_2$. The absorption occurring at 1020 cm^{-1} is unusual for alkylaminoaluminum compounds and the tentative assignment is ν_{asym} NC_2 moieties involved in intermolecular noncyclic bridging; the 877-cm^{-1} band is assigned to the related ν_{sym} NC_2 vibration. The bands at 692 and 588 cm^{-1} are found at approximately the same positions and intensity in $[(CH_3)_2AlCl]_2$, $[(CH_3)_2AlN(CH_3)_2]_2$, $[Al(CH_3)_3]_2$, and $[(CH_3)_2AlH]_3$ but not in $[Al\{N(CH_3)_2\}_3]_2$ or $[CH_3AlCl_2]_2$.[2-5] The bonding in the first four com-

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(2) R. E. Hall and E. P. Schram, *Inorg. Chem.*, **8**, 270 (1969).

(3) E. G. Hoffmann, *Z. Elektrochem.*, **64**, 616 (1960).

(4) A. P. Gray, *Can. J. Chem.*, **41**, 1511 (1963).

(5) E. G. Hoffmann and G. Schomburg, *Z. Elektrochem.*, **61**, 1101 (1957).

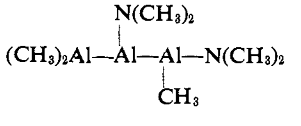
Table II. Infrared Assignments (cm^{-1}) for Boron and Aluminum Aminoalkyls

Assignment	$B_2(CH_3)_2[N(CH_3)_2]_2$	$Al_3(CH_3)_3[N(CH_3)_2]_2$	$(CH_3)_2HAl \cdot N(CH_3)_2AlCH_3(H)$
ν_{CH}	3012 (sh), 2982 (m), 2921 (s), 2890 (m), 2865 (sh), 2793 (m)	2981 (sh), 2922 (s), 2835 (m), 2794 (m)	2930 (s), 2855 (sh), 2810 (sh), 2680 (w)
ν_{AlH}			1869 (sh), 1803 (s), 1769 (sh)
ν_{BN}	1498 (s)		
δ_{CH_3}	1459 (s), 1398 (vs)	1472 (sh), 1452 (s)	1375 (m), 1365 (sh), 1463 (s)
$\delta_{CH_3(B)}$	1295 (s)		
ρ_{CH_3}	1218 (s), 1170 (sh) 1101 (sh)	1237 (m), 1165 (sh), 1122 (m), 1104 (m)	1232 (sh), 1169 (sh), 1122 (m), 1103 (m)
ρ_{CH_3Al} (terminal)		1200 (s)	1204 (s)
ν_{BC}	1139 (s)		
$\nu_{NC_2,asym}$	1062 (m)	1043 (s), 1020 (m)	1048 (m), 1022 (s)
$\nu_{NC_2,sym}$	980 (s)	905 (s)	893 (s)
ν_{AlN}		505 (m)	507 (m)
$\nu_{AlC_2,asym}$		692 (s)	694 (s)
$\nu_{AlC_2,sym}$		588 (m)	588 (m)
Unassigned	1026 (vw), 953 (sh), 840 (w), 697 (w, b), 594 (w, b), 568 (w, b)	877 (sh)	977 (w)

pounds involves terminal $(CH_3)_2Al$ moieties in contrast to the latter two species; therefore, the bands at 692 and 588 cm^{-1} in $Al(CH_3)_3[N(CH_3)_2]_2$ are assigned to ν_{asym} and ν_{sym} AlC_2, respectively.

Suggested Structure for $Al_3(CH_3)_3[N(CH_3)_2]_2$. The analytical data, ^1H nmr spectrum, and CH_4/H_2 ratio (from oxidative hydrolysis) all indicate the molecular formulation of the catenated aluminum compound to be $Al_3(CH_3)_3[N(CH_3)_2]_2$. The infrared spectrum is free from absorptions in the range 2500–1500 cm^{-1}, indicating the absence of hydride in this molecule;[6] therefore, H_2 evolution during hydrolysis most likely involves reduction of H_3O^+ by Al, and 1 mol of H_2 is evolved per mol of Al–Al bonds. The CH_4/H_2 ratio of 1.5 indicates the number of $(CH_3)/(Al–Al\ bonds) = 1.5$, or for two Al–Al bonds three CH_3's must be present. From the ^1H nmr spectrum and analytical data the ratio $N(CH_3)_2/CH_3 =$ *ca.* 2/3; therefore, the presence of two Al–Al bonds, three CH_3, and two $N(CH_3)_2$ moieties suggest the molecular formulation $Al_3(CH_3)_3[N(CH_3)_2]_2$. The presence of three Al–Al bonds per molecule would require 4.5 CH_3 moieties and is discarded as would be all odd numbers of Al–Al bonds per molecule. Finally the stoichiometry, $Al_3(CH_3)_3[N(CH_3)_2]_2$, as compared to some multiple thereof, is indicated because the experimental molecular weight is 255 (calcd 214). The slightly high value indicates slight intermolecular association in solution. Indeed, the infrared band at 1020 cm^{-1} already has been suggested to indicate intermolecular bonding by bridging $N(CH_3)_2$ moieties.

The infrared absorptions assigned to $\nu_{AlC_2,\ asym}$ and $\nu_{AlC_2,\ sym}$ indicate the presence of AlC_2 moieties, the inference being formulations of the type



$$(CH_3)_2Al-\underset{\displaystyle CH_3}{\overset{\displaystyle N(CH_3)_2}{Al}}-Al-N(CH_3)_2$$

however, this material may well be a mixture of three possible isomers: 1,1-bisdimethylamino-, 1,2-bisdimethylamino-, and 1,3-bisdimethylaminotrimethyltrialuminum(5). The ^1H nmr absorptions are very broad and the unresolved structure may be associated with several $N(CH_3)_2$ and CH_3 environments.

Reactions of $B_2[N(CH_3)_2]_4$ with Large Excesses of $[Al(CH_3)_3]_2$. The reaction of $B_2[N(CH_3)_2]_4$ with excess $[Al(CH_3)_3]_2$ has been carried out in two ways: (a) dropwise addition of $B_2[N(CH_3)_2]_4$ to large excesses of $[Al(CH_3)_3]_2$ and (b) increment additions of $[Al(CH_3)_3]_2$ to $B_2[N(CH_3)_2]_4$. In the first case the products include $B(CH_3)_3$, $[(CH_3)_2AlN(CH_3)_2]_2$, $Al(CH_3)_3 \cdot N(CH_3)_2Al(CH_3)_2$, Al metal, and a benzene-soluble brown-red solid which was not investigated due to its low yield. The adduct, $Al(CH_3)_3 \cdot N(CH_3)_2Al(CH_3)_2$, is a white crystalline material at −18°, but on warming to room temperature decomposition occurs according to eq 6.

$$Al(CH_3)_3 \cdot N(CH_3)_2Al(CH_3)_2 \longrightarrow \tfrac{1}{2}[Al(CH_3)_3]_2 + \tfrac{1}{2}[AlN(CH_3)_2(CH_3)_2]_2 \quad (6)$$

Adducts of similar stoichiometry have been reported, *e.g.*, $Al_2(CH_3)_5N(C_6H_5)_2$.[7] The preparation of $Al(CH_3)_3 \cdot N(CH_3)_2Al(CH_3)_2$ involves the generation of $(CH_3)_2AlN(CH_3)_2$ in the presence of large excesses of $[Al(CH_3)_3]_2$ such that adduct formation with $[Al(CH_3)_3]_2$ is favored over that of the usual bisamino bridge dimerization affording $[(CH_3)_2AlN(CH_3)_2]_2$. Nitrogen-bridged derivatives of Al are more stable than the corresponding methyl-bridged species; *e.g.*, $[(CH_3)_2AlN(CH_3)_2]_2$ is N bridged rather than CH_3 bridged. Based on this fact the reaction mechanism, associated with formation of $Al(CH_3)_3 \cdot N(CH_3)_2Al(CH_3)_2$, most likely involves nucleophilic attack by generated monomeric $(CH_3)_2AlN(CH_3)_2$ on $[Al(CH_3)_3]_2$ with subsequent cleavage of the bridged system as exemplified by eq 7.

Hydride Formation during the Reaction of $B_2[N(CH_3)_2]_4$ with $[Al(CH_3)_3]_2$. In an effort to prepare additional $B_2(CH_3)_2[N(CH_3)_2]_2$ and study its reactions with $[Al(CH_3)_3]_2$, $[Al(CH_3)_3]_2$ was added in increments to $B_2[N(CH_3)_2]_4$ with stirring with a final mole ratio of $Al:B_2$ of *ca.* 1.8; relatively small amounts of $B(CH_3)_3$ and $(CH_3)_2BN(CH_3)_2$ were evolved. The reaction mix-

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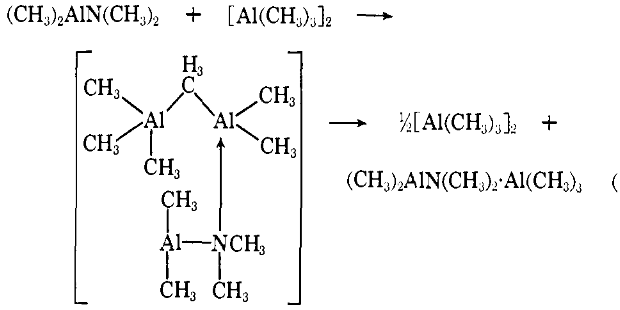
(6) G. Schomburg and E. G. Hoffmann, *Z. Elektrochem.*, **61**, 1110 (1957).

(7) V. R. Magnuson and G. D. Stucky, *J. Amer. Chem. Soc.*, **90**, 3269 (1968).



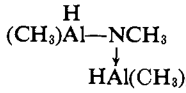
(7)

ture consisted of pale yellow-green viscous liquid. Subsequent heating of this material at 70°, *in vacuo*, affords $B_2(CH_3)_2[N(CH_3)_2]_2$, $(CH_3)_2BN(CH_3)_2$, $HB(CH_3)N(CH_3)_2$, and $[(CH_3)_2AlN(CH_3)_2]_2$. Dimethylaminomethylborane, $HB(CH_3)N(CH_3)_2$, was characterized by comparison of its vapor tension and infrared spectrum with an authentic sample. Furthermore, its reorganization according to eq 8 was observed as previously reported.[8]

$$2HB(CH_3)N(CH_3)_2 \rightleftharpoons {}^1/_2[H_2BN(CH_3)_2]_2 + (CH_3)_2BN(CH_3)_2 \quad (8)$$

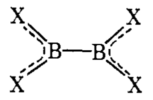
Hydride formation has been observed during the thermal decomposition of 1,2-bisdimethylamino-1,2-bis-*n*-butyldiborane(4) (220°) to afford $HB(n\text{-}C_4H_9)N(CH_3)_2$ and butene;[9] 1,2-bisdimethylamino-1,2-bisdimethyldiborane(4) is stable at least to its boiling point (39° at 12 Torr).[9] Hydride formation takes place when the reaction mixture, $B_2[N(CH_3)_2]_4$–$[Al(CH_3)_3]_2$, is heated to 70° and may arise from *in situ* decomposition of $B_2(CH_3)_2[N(CH_3)_2]_2$. An alternate possibility involves decomposition of $B_2(CH_3)_3N(CH_3)_2$ formed during the pyrolysis of the reaction mixture. One would not expect high yields of this latter species based on the reaction stoichiometry, and indeed only a small quantity of $HB(CH_3)N(CH_3)_2$ was isolated. Treatment of $B_2(CH_3)_2[N(CH_3)_2]_2$ with $[Al(CH_3)_3]_2$ does result in hydride formation (to a small extent), the major reaction being reduction. In this latter case hydride formation takes place at 25° and is thought to arise from decomposition of the unstable species, $B_2(CH_3)_3N(CH_3)_2$.

An additional reaction has been noted, that of hydride transfer from boron to aluminum. This reaction takes place when $[Al(CH_3)_3]_2$ is added in increments to $B_2[N(CH_3)_2]_4$ until excess $[Al(CH_3)_3]_2$ is recovered from the reaction mixture, the reaction condition which results in boron hydride formation. The product is a white crystalline solid which sublimes at 70° *in vacuo*. The infrared spectrum of this material is summarized in Table II. The multiplet structure in the ν_{AlH} range, *ca.* 1800 cm^{-1}, suggests the presence of more than one type of H on Al. Hoffmann has carried out extensive infrared investigations concerning Al hydrides and concluded that the breadth of the ν_{AlH} band is dependent on the coordination number of Al.[6] It is suggested that the multiplet structure is due to overlapping ν_{AlH} vibrations associated with Al of different coordination numbers. The strong absorption at 1204 cm^{-1} is due to ρ_{CH_3} on Al, whereas the bands at 1048 and 893 cm^{-1} are assigned to $\nu_{NC_2,\,asym}$ and $\nu_{NC_2,\,sym}$, respectively.[2] In a similar fashion the bands at 694 and 588 cm^{-1} are assigned to $\nu_{AlC_2,\,asym}$ and $\nu_{AlC_2,\,sym}$, respectively. The ^1H nmr spectrum consists of three absorptions at −2.1, +0.35, and +0.56 ppm from TMS in the ratio 2:2:1, respectively. The absorption at −2.1 ppm is attributed to a $N(CH_3)_2$ moiety on Al whereas the other absorptions are assigned to CH_3 on Al. The infrared spectrum indicates the presence of HAl, $(CH_3)_2Al$, and $(CH_3)_2NAl$ moieties, and the nmr ^1H spectrum indicates two nonequivalent CH_3 moieties on Al (2:1 ratio). The H on Al was not observed by ^1H nmr because of a combination of quadrupole broadening ($I_{Al} = {}^5/_2$) and the relatively low concentration of the nmr sample. Based on these data, this white crystalline material is tentatively formulated as

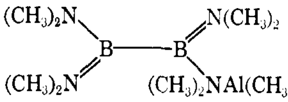


$$\begin{array}{l} \qquad\quad H \\ (CH_3)Al{-}NCH_3 \\ \qquad\quad\downarrow \\ \qquad\; HAl(CH_3)_2 \end{array}$$

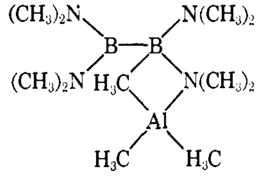
On the Mechanism of Aluminum Alkyl Reduction. Before $B_2[N(CH_3)_2]_4$ can function as a reducing agent toward $[Al(CH_3)_3]_2$, the kinetic stability of $B_2[N(CH_3)_2]_4$ must be decreased. The B–B bond may be envisaged as stabilized by intramolecular p_π–p_π bonding



where X = F, Cl, $N(CH_3)_2$, or OCH_3. The thermal stability of B_2X_4 derivatives is in accord with $N(CH_3)_2 > OCH_3 > F > Cl \gg H$;[10–14] this order represents the generally accepted relative ability for these ligands to backbond to boron. When $B_2[N(CH_3)_2]_4$ (1 mol) is treated with $[Al(CH_3)_3]_2$ (1 mol), the products are $B_2(CH_3)_2[N(CH_3)_2]_2$ and $[(CH_3)_2AlN(CH_3)_2]_2$ which suggests nucleophilic attack by nitrogen on the methyl bridge system of $[Al(CH_3)_3]_2$ with subsequent adduct formation, *e.g.*



The B–B bond in this species would still be stabilized as indicated by this valence-bond representation. Exchange does take place between B and Al, and the mechanism is envisaged to involve the four-center transition state.



Treatment of $B_2[N(CH_3)_2]_4$ with $[Al(CH_3)_3]_2$ affords the 1,2-dimethyl- as opposed to 1,1-dimethyl-2,2-bisdimethylaminodiborane(4). This result suggests $B_2CH_3[N(CH_3)_2]_3$ is again acting as a nucleophile toward $[Al(CH_3)_3]_2$; the valence-bond structure

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[8] A. B. Burg and J. L. Boone, *J. Amer. Chem. Soc.*, **78**, 1521 (1956).

[9] H. Noth and P. Fritz, *Z. Anorg. Allg. Chem.*, **324**, 129 (1963).

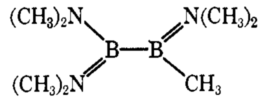
[10] L. Trefonas and W. N. Lipscomb, *J. Chem. Phys.*, **28**, 54 (1958).

[11] H. I. Schlesinger, *et al.*, "Hydrides and Borohydrides of Light Elements," Reports to Office of Naval Research, 1948–1957.

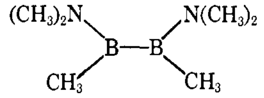
[12] G. Urry, T. Wartik, R. E. Moore, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **76**, 5293 (1954).

[13] A. Finch and H. I. Schlesinger, *ibid.*, **80**, 3573 (1958).

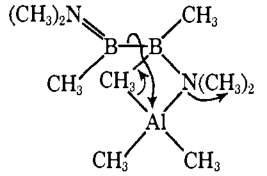
[14] R. J. Brotherton, A. L. McClosky, J. L. Boone, and H. M Manasevit, *ibid.*, **82**, 6245 (1960).



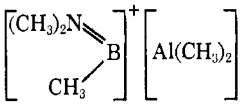
suggests attack by the nonbonding electron pair on additional $[Al(CH_3)_3]_2$ to afford



via another four-center transition-state intermediate. Further treatment of $B_2(CH_3)_2[N(CH_3)_2]_2$ with $[Al(CH_3)_3]_2$ results in reduction of Al; the initial transition state is envisaged to be of the type



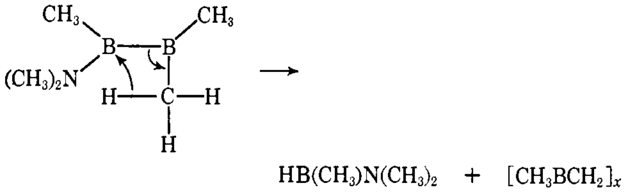
with formation of the ion pair



and $(CH_3)_2BN(CH_3)_2$. A similar reaction mechanism appears likely concerning the very interesting reaction between H_3Ge^- and B_2H_6 affording $[H_3GeBH_3]^-$.[15] $Al(CH_3)_2^-$ is suggested to react with additional $[Al(CH_3)_3]_2$ affording $Al_2(CH_3)_5^-$ which subsequently reacts with the boronium ion to afford $(CH_3)_2NB(CH_3)_2$ and $Al_2(CH_3)_4$. This latter species would be expected to exchange with $(CH_3)_2NB(CH_3)_2$ to afford, *e.g.*, $[(CH_3)_2N]_xAl_2(CH_3)_{4-x}$ and $B(CH_3)_3$. Subsequent attack by additional $Al(CH_3)_2^-$ on dialuminum(4) alkylamino derivatives would afford trialuminum(5) species. The mechanism of chain extension would be expected to continue as long as $Al(CH_3)_2^-$ is a better nucleophile than the amino moieties associated with the catenated aluminum species; *i.e.*, intra- or intermolecular coordination would be expected to inhibit extra nucleophilic attack.

In addition to chain lengthening, the process of degradation has been observed when catenated aminoaluminum species are treated with $[Al(CH_3)_3]_2$. This process most likely involves aminoalkyl exchange affording subalkylaluminum species of the type $-Al(CH_3)-Al(CH_3)_2$ which are believed to disproportionate *via* an alkyl shift affording $-Al(CH_3)_2$ species and aluminum subalkyls, $[AlCH_3]_x$. This type of shift has been postulated in diborane(4) chemistry; B_2Cl_4 affords BCl_3 + boron subchloride, and the nonisolated species, $B_2(CH_3)_4$, has been reported to decompose to afford $B(CH_3)_3$ and black solid residues.[11,16] Thermal stability, associated with aluminum subalkyls, is believed to be dependent on intramolecular coordination which blocks the mechanism of decomposition suggested to be an alkyl shift.

Hydride formation is believed to result from thermal decomposition of *in situ* $B_2(CH_3)_2[N(CH_3)_2]_2$ at 70° and/or from $B_2(CH_3)_3N(CH_3)_2$ at room temperature. In both cases $HB(CH_3)N(CH_3)_2$ is isolated although $B_2(CH_3)_3N(CH_3)_2$ affords additional unstable species which contain the BH_2 moiety (*via* infrared). Hydride formation is envisaged to take place according to



Treatment of $B_2(CH_3)_2[N(CH_3)_2]_2$ with $[Al(CH_3)_3]_2$ affords boron hydride as well as reduced oxidation state aluminum, whereas reactions of $B_2[N(CH_3)_2]_4$ with $[Al(CH_3)_3]_2$ results only in reduction of Al except when $[Al(CH_3)_3]_2$ is added in increments to $B_2[N(CH_3)_2]_4$. In this latter case formation of alkylaminodiborane(4) derivatives is favored with subsequent decomposition taking place as well as reduction of $[Al(CH_3)_3]_2$.

The reduction of aluminum compounds by diborane(4) derivatives is continuing as well as the reactions of postulated species, $Al(CH_3)_2^-$, with Lewis acids. In addition, the reduction of molecular compounds of V, Zr, B, Ga, Si, and Ge is in progress and will be reported in the near future.

Experimental Section

Apparatus. All chemical reactions were carried out in a standard vacuum line equipped with mercury float valves. ^1H nmr spectra were recorded with a Varian A-60 spectrometer while ^{11}B spectra were recorded with a HA-60 spectrometer at 19.3 Mc. Unless otherwise stated benzene was the solvent employed and ^1H chemical shifts are reported relative to TMS, τ_{benzene} 2.73. **Infrared spectra** were recorded with a Perkin-Elmer 337 spectrophotometer. Volatile compounds were contained in a 10-cm gas cell (KBr windows) whereas nonvolatile species were mulled with dried Nujol and Fluorolube under a nitrogen atmosphere. **Molecular weights** of nonvolatile species were determined isopiestically in cyclopentane employing azobenzene as the standard. **Analyses** for aluminum and nitrogen were by 8-hydroxyquinoline precipitate and the Kjeldahl methods, respectively. Methane and hydrogen were collected and measured by means of a calibrated volume Toepler pump assembly and characterized by combustion over CuO to afford CO_2 and H_2O, respectively.

Reagents. Aluminum trimethyl, obtained from Ethyl Corp., was purified by fractional condensation through a trap maintained at −23°; the contents of this trap exhibited a vapor tension of 8.8 Torr at 20°; lit.[17] 8.8 Torr. **Cyclopentane,** purchased from Matheson Co., Inc., was dried over CaH_2 and fractionated through traps maintained at −45, −78, and −196°. The −78° fraction exhibited a 0° vapor tension of 107 Torr; lit.[17] 107 Torr. **Benzene,** obtained from Mallinckrodt Chemical Works, was dried over CaH_2 and purified by distillation through traps maintained at −23, −45, and −196°. The −45° fraction had a 0° vapor tension of 25 Torr; lit.[17] 25 Torr. **Tetrakisdimethylaminodiborane(4),** $B_2[N(CH_3)_2]_4$, obtained from U.S. Borax Corp., Anaheim, Calif., was distilled, *in vacuo*, utilizing a Nester-Faust spinning-band column. The boiling point of the colorless distillate was 69° (3.5 Torr); lit.[18] 69° (3.6 Torr). **Bis(dimethylamino)borane,** $[(CH_3)_2N]_2BH$, was prepared by treating $[(CH_3)_2N]_2BCl$ with LiH; the observed vapor tension was 30.8 Torr at 23.2°; lit.[8] 30.8 Torr at 23.2°. **Dimethylaminomethylborane,** $HB(CH_3)N(CH_3)_2$, was prepared by treating $HB[N(CH_3)_2]_2$ with $[Al(CH_3)_3]_2$; the vapor tension agreed with the literature values:[19] 34.4 Torr at −30.6°, 13.2 Torr at −45.2°, and 0.8 Torr at

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(16) E. P. Schram and G. Urry, *ibid.*, **2**, 205 (1963).

(17) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley & Sons, Inc., New York, N. Y., 1948.

(18) R. T. Brotherton, A. L. McCloskey, L. Patterson, and H. Steinberg, *J. Amer. Chem. Soc.*, **82**, 6242 (1960).

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−78°. **Dimethylalane,** $[(CH_3)_2AlH]_3$, was prepared by treating $LiAlH_4$ with $B(CH_3)_3$; the vapor tension of the product agreed with the literature value of 1.8 Torr at 24.7°.[20]

Isolation and Characterization of Volatile Species. Common volatile compounds which were isolated during this study included $(CH_3)_2BN(CH_3)_2$, $HB(CN_3)N(CH_3)_2$, $[(CH_3)_2AlN(CH_3)_2]_2$, and $B(CH_3)_3$. Separations were effected by trap-to-trap distillations while characterization consisted of comparison of vapor tension data, ^1H and ^{11}B nmr chemical shifts, and infrared spectra with authentic samples.

Isolation and Characterization of $B_2(CH_3)_2[N(CH_3)_2]_2$. Tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$ (13 mmol), was treated with aluminum trimethyl, $Al(CH_3)_3$ (36 mmol), in *ca.* 4-mmol increments. After each addition of $Al(CH_3)_3$ the reaction mixture was warmed from −196 to 25° with stirring. The initial reaction mixture slowly changed from colorless to pale yellow; after addition of the last portion of $Al(CH_3)_3$ a yellow solid remained in the reaction vessel. This yellow material was insoluble in the generated solvent $(CH_3)_2BN(CH_3)_2$. The volatile reaction products consisted of $B(CH_3)_3$ (2 mmol) and $(CH_3)_2NB(CH_3)_2$ (12 mmol) which were recovered from −196 and −78° traps, respectively. In addition, a fraction was isolated which passed through a −23° trap but stopped at −45°. This material was identified as 1,2-bisdimethylamino-1,2-dimethyldiborane(4), $B_2(CH_3)_2[N(CH_3)_2]_2$. Characterization included interpretation of its infrared spectrum which is summarized in Table II and the ^1H nmr spectrum which consists of signals at −2.77 and −0.25 ppm from TMS in the ratio 2:1. The assignment of these two absorptions to $N(CH_3)_2$ and CH_3 moieties, respectively, was made by comparison to $(CH_3)_2BN(CH_3)_2$: CH_3 −0.54, $N(CH_3)_2$ −2.68; $B_2[N(CH_3)_2]_4$: −2.78; and $B(CH_3)_3$: −0.76 ppm.[1,21] In addition the ^{11}B nmr spectrum consists of one singlet, and its vapor tension at 0° is 1.9 Torr.[9] Lastly, $[(CH_3)_2AlN(CH_3)_2]_2$ was recovered from the reaction mixture; the amount of this material cannot be conveniently determined due to its low volatility, *ca.* 0.2 Torr at 25°.

Preparation and *in situ* Decomposition of $B_2(CH_3)_3N(CH_3)_2$. $B_2[N(CH_3)_2]_4$ (30 mmol) was treated with $Al(CH_3)_3$ (55 mmol) in *ca.* 5-mmol increments. After addition of the last aliquot of $Al(CH_3)_3$ the reaction mixture consisted of a viscous pale yellow-green material. The initial volatile products included $B(CH_3)_3$ (3.9 mmol), $(CH_3)_2BN(CH_3)_2$ (6.9 mmol), and $[(CH_3)_2AlN(CH_3)_2]_2$. The nonvolatile viscous liquid was heated to *ca.* 70° affording $[(CH_3)_2AlN(CH_3)_2]_2$, $(CH_3)_2BN(CH_3)_2$, $B_2(CH_3)_2[N(CH_3)_2]_2$, and $HB(CH_3)N(CH_3)_2$. Dimethylaminomethylborane, $(CH_3)_2N(CH_3)BH$, was characterized by its vapor pressure, 30 Torr at 23°, and its infrared spectrum. In addition, a small amount of material, trapped at −78°, was isolated which did not contain $(CH_3)_2N(CH_3)_2BH$ but had infrared bands at 2620 and 2450 cm^{-1} indicating a BH_2 moiety. Nonvolatile liquid(s) and solid(s) remained in the reaction vessel.

Reaction of $B_2(CH_3)_2[N(CH_3)_2]_2$ with $Al(CH_3)_3$. 1,2-Bis(dimethylamino)-1,2-dimethyldiborane(4), $B_2(CH_3)_2[N(CH_3)_2]_2$ (0.92 mmol), was condensed on to $Al(CH_3)_3$ (1.04 mmol) maintained at −196°, and the reaction mixture slowly warmed to room temperature with stirring. At *ca.* 15° the reaction solution turned dark red and a brown solid precipitated from solution. Boron trimethyl (0.92 mmol), $(CH_3)_2BN(CH_3)_2$ (0.36 mmol), traces of $HB(CH_3)N(CH_3)_2$, and $[(CH_3)_2AlN(CH_3)_2]_2$ were recovered from the volatile reaction mixture. In addition a volatile fraction was isolated which originally passed through a 0° trap but stopped at −45°. After this fraction remained at 25° for 0.5 hr it passed through a −45° trap but stopped at −78°. The infrared spectrum of this fraction contains absorptions at 2413 (m) and 2478 (m) cm^{-1}, clearly indicating a BH_2 moiety. A nonvolatile residue was present but in insufficient quantity to permit characterization.

Preparation and Characterization of $Al_3(CH_3)_3[N(CH_3)_2]_2$. Treatment of $B_2[N(CH_3)_2]_4$ (14 mmol) with $Al(CH_3)_3$ (54 mmol) at −196°, and subsequently allowing the reaction mixture to slowly warm to 25° with stirring, results in the formation of $B(CH_3)_3$ (11.9 mmol), $(CH_3)_2BN(CH_3)_2$ (*ca.* 15 mmol), and $[(CH_3)_2AlN(CH_3)_2]_2$. The nonvolatile reaction products consist of a brown solid insoluble in benzene, and a benzene-soluble yellow solid. The yellow solid was freed of all volatile aluminum compounds by alternately heating at 80°, *in vacuo*, and subsequent solution formation in cyclopentane. This procedure was repeated ten times and the sample finally filtered, *in vacuo*. A 130-mg sample of this yellow solid was hydrolyzed with H_2O–HCl affording H_2 (1.28 mmol) and CH_4 (1.93 mmol). The hydrostat afforded N (16.8 mg, 52.7 mg $-N(CH_3)_2$) and Al (45.2 mg). No boron was present based on (a) the absence of a boron green flame test on both the hydrostat and the original yellow solid, (b) no change in the pH of a neutral solution of the hydrostat upon addition of *d*-mannitol, and (c) the absence of a ^{11}B nmr signal. The molecular weight of the yellow solid, 0.02 *M* in cyclopentane, is 255. The ^1H nmr spectrum consists of two broad signals (*ca.* 0.4 ppm at half-height) at −2.40 and +0.40 ppm from TMS in the ratio *ca.* 4:3, respectively (Figure 1). The infrared spectrum of this yellow solid is summarized in Table II.

Reaction of $B_2[N(CH_3)_2]_4$ with Excess $Al(CH_3)_3$. Dropwise addition of $B_2[N(CH_3)_2]_4$ (*ca.* 1 ml) to $Al(CH_3)_3$ (*ca.* 10 ml maintained at 25°) affords $B(CH_3)_3$, $[(CH_3)_2AlN(CH_3)_2]_2$, and $Al(CH_3)_3 \cdot (CH_3)_2AlN(CH_3)_2$. This latter material stops in a −18° trap (white crystalline solid) and has a vapor tension of *ca.* 2.8 Torr at 28°. Its infrared spectrum is almost identical with that of $[(CH_3)_2AlN(CH_3)_2]_2$. Repeated fractionation after allowing this materal to remain at 25° for several hours affords only $[Al(CH_3)_3]_2$ and $[(CH_3)_2AlN(CH_3)_2]_2$ in an approximate mole ratio of 1:1. The nonvolatile reaction mixture consists of a brown-red benzene-soluble phase and a black solid which is insoluble in benzene, CH_2Cl_2, H_2O, and dilute HCl, but soluble in dilute NaOH. Analysis of this black solid for B and Al indicates only the presence of Al; this material contains no absorptions in the infrared between 4000 and 500 cm^{-1}.

Another sample of $B_2[N(CH_3)_2]_4$ (22.8 mmol) was treated with excess $Al(CH_3)_3$, but in 2.5-mmol increments; $Al(CH_3)_3$ was recovered from the final reaction mixture. Under these reaction conditions an additional product was isolated, a white solid which can be sublimed at 70° *in vacuo*. The infrared spectrum for this species is summarized in Table II. The ^1H nmr spectrum of this white solid consists of absorptions at −2.10, +0.35, and +0.56 ppm from TMS in the ratios 2:2:1, respectively. Qualitative analysis indicates the absence of boron in this material.

Acknowledgment. Support of this work by the National Science Foundation under Grant GP-9308 is most appreciated.

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(20) T. Wartik and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **75**, 835 (1953).

(21) In this referenced paper an old τ value of 3.10 for benzene was employed; hence −0.36 ppm should be added to the previously referenced ^1H nmr chemical shifts except for $[Al(CH_3)_3]_2$ for which τ is correct, and $B(CH_3)_3$ for which τ should be changed to −0.76 ppm.