Reaction of $(C_2H_5)_4N[(B_{10}H_{12})Ir(CO)(PPh_3)_2]$ with Dideuterium. The literature method[1] was used to prepare $Na[(B_{10}H_{12})Ir(CO)(PPh_3)_2]$. It was converted to the tetraethylammonium salt by metathesis with $(C_2H_5)_4NCl$ and recrystallized from acetone–ethanol. Anal. Calcd for $C_{45}H_{62}B_{10}IrNOP_2$: C, 54.33; H, 6.24. Found: C, 54.62; H, 6.39. A 0.1-g sample of this salt was dissolved in 10 ml of 1,2-dichloroethane. Deuterium, which had previously been passed through a bubbler containing the same solvent, was introduced, after first flushing the apparatus with deuterium, at a rate of approximately 20 bubbles/min. The deuterated product was isolated by evaporation of the solvent.

Under these conditions, no reaction was observed between D_2 and $[(C_2H_5)_4N]_2[(B_{10}H_{12})_2Ni]$, $(Ph_3PCH_3)_2[(B_{10}H_{12})_2Pt]$, or $[(C_2H_5)_4N]_2[(B_{10}H_{12})Rh(CO)(PPh_3)_2]$ although solutions of the latter material appeared to darken and decompose on standing in solution.

$[(C_2H_5)_4N][(6\text{-}PhCH_2B_{10}H_{11})Ir(CO)(Ph_3P)_2]$ was prepared[1] using $6\text{-}PhCH_2B_{10}H_{13}$[35] in place of decaborane. Anal. Calcd for $C_{52}H_{68}B_{10}IrNOP_2$: C, 57.57; H, 6.27. Found: C, 57.31; H, 6.07. ^1H NMR (acetone-d_6): −7.25 (m, 35 H); −3.25 (q, 8 H), −1.22 (t, 12 H); a broad singlet at −1.7 is attributed to the benzylic CH_2 group.

Reaction of $[(C_2H_5)_4N][(B_{10}H_{12})Ir(CO)(PPh_3)_2$ with Carbon Monoxide. Acetonitrile, 4 ml, was condensed onto 0.02 g of the iridaborane which was contained in a small flask attached to the vacuum line. The resulting solution was stirred for 24 h under a 35-mm pressure of 90% enriched ^{13}CO. The exchanged product was isolated by evaporation of the solvent and contained equal amounts of ^{13}C and ^{12}C in the carbonyl group by infrared analysis.

Acknowledgment. The authors thank Dr. A. R. Garber for measuring the ^{11}B NMR spectra. This work was supported in part by the National Science Foundation through Grant GP-42757 (L.J.T.).

Registry No. **1**, 60282-43-1; **2**, 60305-63-7; **3** (tetraphenylarsonium salt), 60282-42-0; **4**, 60282-40-8; **5**, 60282-38-4; **6** (tetraethylammonium salt), 60349-64-6; **6** (tetraphenylarsonium salt), 60349-63-5; **6** (cesium salt), 60305-64-8; **7**, 57373-31-6; **8**, 60282-45-3; **9**, 60282-47-5; $[(C_2H_5)_4N][(6\text{-}Ph\text{-}CH_2B_{10}H_{11})Ir(CO)(Ph_3P)_2]$, 60282-49-7; *N*-bromosuccinimide, 128-08-5; ^{11}B, 14798-13-1.

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Preparation and Characterization of 1,2,3,4,5,6-Hexakis(dimethylamino)-*closo*-hexaborane(6)–Hexakis(dimethylaminodimethylaluminum), a Novel Boron Cluster Compound[1a]

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Received April 26, 1976 AIC602994

Treatment of tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, with aluminum trimethyl, $[Al(CH_3)_3]_2$, under specific reaction conditions, results in the generation of $B_6[N(CH_3)_2]_{12}{\cdot}Al_6(CH_3)_{12}$ (I). Formation of I is a result of the induced disproportionation of $B_2[N(CH_3)_2]_4$ and most likely represents a cluster species with an octahedral boron core. A molecular orbital description of core bonding is presented assuming T_h symmetry. Finally, the reactions of I with H_2O, $N(CH_3)_3$, $P(CH_3)_3$, $HN(CH_3)_2$, NH_3, and acetylacetone are presented.

The chemistry of closo polyhedral borane derivatives has been extensively investigated; however, relatively few examples are known in which B–H bonds are totally absent. Several exceptions are B_4Cl_4, B_8Cl_8, B_9Cl_9, $B_{11}Cl_{11}$, $B_{12}Cl_{11}$, $B_{10}Cl_{10}^{2-}$, and $B_{12}Cl_{12}^{2-}$.[2-12] The methods employed for the synthesis of molecular boron chlorides have usually involved electric discharge reactions utilizing BCl_3 or the thermal decomposition of B_2Cl_4. Anionic haloborane species have resulted from halogenation of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ salts taking advantage of the relative inertness of these cage systems

Table I. Characterization of $B_6[N(CH_3)_2]_{12}\cdot Al_6(CH_3)_{12}$

	Wt %				
	B	N	Al	CH_3 (hydrolyzable)	Mol wt
Calcd	6.9	18.0	17.3	19.3	934
Found	6.5	17.7	17.8	18.7	943, 966

toward oxidation of B–B bonds.[12]

One may compare the relative thermal stability of diborane(4) derivatives and relate this order to the relative ability of the ligand associated with boron to "back-bond" to boron. This relative order of thermal stability is usually considered: $B_2[N(CH_3)_2]_4 > B_2(OCH_3)_4 > B_2F_4 > B_2Cl_4 \gg B_2H_4$.[13-15] With regard to the latter species, it is only known in complex derivative form, e.g., $B_2H_4\cdot 2P(C_6H_5)_3$. One can visualize stabilization of the B–B bond, for B_2X_4 species, via electron delocalization from the boron ligand to boron utilizing p_z atomic orbitals to form the π molecular orbital. Theoretical calculations are consistent with this thesis.[16] Consistent with the cited ligand stabilization order of the B–B bond is the apparent Lewis acid strength of the related three-coordinate boron compounds, i.e., $BCl_3 > BF_3 > B(OCH_3)_3 > B[N(CH_3)_3]_3$. That is, the greater the electron density on boron as a consequence of ligand "back-bonding", the weaker the observed Lewis acid property of boron.

This investigation is concerned with the disproportionation product of $B_2[N(CH_3)_2]_4$, $B_6[N(CH_3)_2]_{12}\cdot Al_6(CH_3)_{12}$ (I), which results as a consequence of destabilization of $B_2[N(CH_3)_2]_4$ by way of coordination of the $N(CH_3)_2$ moieties with the Lewis acid $Al(CH_3)_3$.

Results and Discussion

Treatment of $B_2[N(CH_3)_2]_4$ with $[Al(CH_3)_3]_2$ at 25 °C results in the formation of the catenated alane $Al_3(CH_3)_3[N(CH_3)_2]_2$.[17] Initially the reaction mixture is colorless; however, during the reaction a transient yellow color is observed prior to formation of the deep red solution color of catenated aluminum derivatives. When $[Al(CH_3)_3]_2$ is reduced in this manner, all of the boron initially associated with $B_2[N(CH_3)_2]_4$ is converted to a mixture of $B(CH_3)_3$ and $(CH_3)_2NB(CH_3)_2$. In an effort to isolate the species associated with the transient yellow color, the initial reaction conditions were varied extensively. We have succeeded in the isolation and characterization of the reaction intermediate by employing the following reaction condition: (1) reaction temperature is 0 °C for 1.5–2 hr, (2) volatile reaction products must be removed from the reaction environment, and (3) the reaction must be carried out in the absence of light. When these conditions are adhered to this chemical transformation is summarized by eq 1. The known product species $(CH_3)_2NB(CH_3)_2$ and $[(CH_3)_2NAl(CH_3)_2]_2$ were characterized by comparison of their ir spectra, vapor pressure, etc., with those of authentic samples. When a slight excess of $[Al(CH_3)_3]_2$ is present in the reaction mixture, $(CH_3)_2NB(CH_3)_2$ is converted to $B(CH_3)_2$, with accompanying formation of additional $[(CH_3)_2NAl(CH_3)_2]_2$. Fifty percent of the boron originally associated with $B_2[N(CH_3)_2]_4$ is evolved as $B(CH_3)_3$ and $(CH_3)_2NB(CH_3)_2$ while the other half is in the form of I. As synthesized, I is a pale yellow powder which may be recrystallized from cyclopentane in the form of needles with a distorted hexagonal cross section.

$$6B_2[N(CH_3)_2]_4 + 6[Al(CH_3)_3]_2 \rightarrow 6(CH_3)_2NB(CH_3)_2 + 3[(CH_3)_2NAl(CH_3)_2]_2 + B_6[N(CH_3)_2]_{12}\cdot Al_6(CH_3)_{12} \quad (1)$$

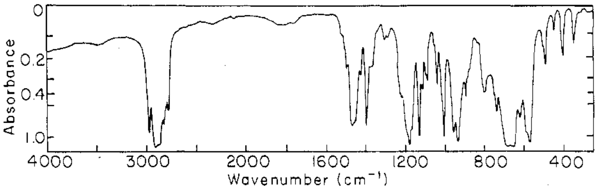

Figure 1. Infrared spectrum of $B_6[N(CH_3)_2]_{12}\cdot Al_6(CH_3)_{12}$.

$$B_6[N(CH_3)_2]_{12}\cdot Al_6(CH_3)_{12} + 24H_2O + 6OH^- \rightarrow 6(5.82)H_2 + 12(11.4)CH_4 + 12(11.81)HN(CH_3)_2 + 6(6.1)Al(OH)_3 + 6(5.6)BO_2^- \quad (2)$$

Characterization of I. Analyses. Treatment of I with water, pH >7, is summarized by eq 2 with the experimental quantities indicated by parentheses. The corresponding analytical data are summarized in Table I. The molecular weight was determined by the isopiestic method utilizing samples of I from two different batch syntheses. In each case a ^1H NMR sample of I, from the same batch synthesis as the molecular weight sample, was thermostated along with the molecular weight sample while the latter system came to equilibrium. After the molecular weight determination was completed, the sample was determined not to have undergone decomposition on the following bases: (1) the related ^1H NMR sample was that of pure I and (2) acid hydrolysis of the molecular weight sample afforded the correct amount of CH_4. The latter data also served as a check on the mass measurement of I used for the molecular weight sample.

As indicated by eq 2, 6 mol of H_2 is evolved during the hydrolysis of I. Dihydrogen can result as a consequence of B–B, B–Al, or Al–Al bond oxidation as well as from BH or AlH moieties. With regard to the latter, examination of the ir spectra of I, Figure 1, indicates the lack of absorptions characteristic of both bridging and terminal BH and AlH, 2700–1570 cm^{-1}.[18-26] Furthermore, the ^{11}B NMR spectrum exhibits a sharp singlet at −25.8 ppm from $BF_3\cdot O(C_2H_5)_2$ consistent with the lack of terminal BH moieties. With regard to distinguishing between reduced oxidation state B and/or Al, treatment of I with acetylacetone, Hacac, was effected. The details of this reaction are subsequently presented; however, it is sufficient to say that all of the aluminum associated with I is converted to $Al(acac)_3$, no BH bonds are formed, and hydrolysis of the Hacac reaction residue affords all of the H_2 expected from hydrolysis of I. Therefore, the reducing property of I is established to involve oxidation of B–B bonds.

NMR Studies. The ^1H NMR spectrum of I consists of two sharp singlets in benzene at −2.50 and +0.50 ppm from TMS in the area ratio 2.0:1.0, respectively. In cyclopentane these ^1H NMR absorptions are found at −2.65 and +0.82 ppm from TMS and exhibit no change or splittings from +25 to −80 °C. The ^{13}C NMR spectrum exhibits absorptions at −41.4 and +11.6 ppm from TMS. For comparison ^1H, ^{11}B, and ^{13}C data for related compounds are summarized in Table II.

With regard to the assignment of the ^1H NMR absorption at −2.50 ppm in I, the assignment to the $N(CH_3)_2$ moiety is ensured, based on the relative area ratios and the fact that the chemical shift is intermediate in value between the values for $N(CH_3)_2$ associated with B and Al; e.g., for $BN(CH_3)_2$, the shift is −2.78 to −2.51 ppm whereas for $AlN(CH_3)_2$, it is usually found between −1.78 and −2.06 ppm (Table II). The ^1H absorption at +0.50 ppm is assigned to terminal $AlCH_3$. Finally, the ^{13}C absorption at −41.5 ppm is equally assignable to $(CH_3)_2N$ on either B or Al while the absorption at +11.6 ppm is definitely associated with $AlCH_3$.

On the basis of both ^1H and ^{13}C NMR data, I contains equivalent $N(CH_3)_2$ moieties associated with either B or Al or perhaps both, while the equivalent CH_3 moieties are definitely terminally bonded to aluminum.

Infrared Spectrum of I. As previously indicated, the ir spectrum of I lacks absorptions assignable to terminal and bridging H associated with either boron or aluminum.[18-26]

Table II. NMR Chemical Shifts of Pertinent Compounds[a,b]

	^1H[c]	^{11}B[d]	^{13}C[c]
$B(CH_3)_3$	−0.76	−86.3	
$H_3B{\cdot}N(CH_3)_3$	−2.60 (–CH_3)		
$(CH_3)_2NB(CH_3)_2$	−2.68, −0.41	−44.6	−39.2, −3.0
$B_2[N(CH_3)_3]_4$	−2.78	−35.1	
$B_2[N(CH_3)_2]_2(CH_3)_2$	−2.77, −0.25		
$B[N(CH_3)_2]_3$	−2.51		
$[B[N(CH_3)_2]_2{\cdot}Al(CH_3)_2]_6$	−2.50, +0.50	−25.8	−41.4, +11.6 vb
$[(CH_3)_2NAl(CH_3)_2]_2$	−2.06, +0.56	na	−41.5, +11.3 vb
$[H_2NAl(CH_3)_2]_3$	+0.06 +0.71	na	
$[Al(CH_3)_3]_2$	−0.47,[e] +0.67,[f] (−78 °C)	na	+4.6 (25 °C)
$py{\cdot}Al(CH_3)_3$		na	−149.5, −142.9, −128.0, +5.8
$[Al[N(CH_3)_2]_3]_2$	−1.98,[e] −1.78[f]	na	

[a] In order of appearance as formula is written, i.e., in $(CH_3)_2NB(CH_3)_2$, −2.68 ppm for N–CH_3 and −0.41 ppm for B–CH_3. [b] This work. vb = very broad; na = not applicable. [c] Relative to TMS. [d] Relative to $F_3B{\cdot}OEt_2$. [e] Bridge. [f] Terminal.

The absence of BCH_3 moieties is also ensured by the absence of a very strong absorption centered at 1300 cm^{-1}.[27] This latter conclusion is consistent with the ^1H NMR assignments.

The broad absorption from 691 to 660 cm^{-1} is assigned to $\nu_{as}(AlC_2)$ by reference to that assignment in $[(CH_3)_2NAl(CH_3)_2]_2$[28] while the strong absorption at 1009 cm^{-1} is assigned to $\nu_{as}(NC_2)$ with reference to $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$[28] and $Al_2B[N(CH_3)_2]_3(CH_3)_4H_2$.[29] Finally, the broad multiple absorptions from 980 to 940 cm^{-1} may be associated with a cage-related vibration with reference to the ir spectrum of boron subchlorides.[10]

Reactions of I with Acetylacetone. Treatment of I with Hacac is summarized by eq 3 with experimentally determined

$$B_6[N(CH_3)_2]_{12}{\cdot}Al_6(CH_3)_{12} + 30(29.8)Hacac \rightarrow 6Al(acac)_3 + 12(11.2)CH_4 + \underset{\text{II}}{\text{red residue}} \qquad (3)$$

quantities indicated by parentheses. The $Al(acac)_3$ was characterized by comparison of ^1H NMR, ir, and melting point data with those of authentic sample. The quantity of $Al(acac)_3$ was not determined; however, it was isolated in high yield and analytical analysis of II proved it to be free of Al. Hydrolysis of the nonvolatile red product, II, results in the evolution of 6 mol of H_2/mol of I initially treated with Hacac. In the absence of BH bond formation, as a consequence of reaction between I and Hacac, H_2 evolution on hydrolysis of II must be a result of B–B bond oxidation. Examination of the ir spectrum of II confirmed the lack of BH moieties based on the lack of absorption in the range 2900–1800 cm^{-1}. Characterization of II as well as the reactions of Hacac with $HN(CH_3)_2$ and $B_2[N(CH_3)_2]_4$ will be reported in the near future.

Suggested Geometry and Nature of Bonding for I. The hydrolysis data for I and II are interpreted to indicate the reducing properties of I are attributable to B–B bond oxidation. Analytical characterization fixes the molecular unit of I as $[B[N(CH_3)_2]_2{\cdot}Al(CH_3)_2]_6$ while the ^{11}B NMR chemical shift, −25.8 ppm from $BF_3{\cdot}OC_2H_5$, is consistent with the absence of four-coordinate boron, i.e., four "electron pairs" associated with each boron. The ^1H NMR data are interpreted to indicate equivalent $N(CH_3)_2$ moieties with a chemical shift value intermediate between those of B–$N(CH_3)_2$ and Al–$N(CH_3)_2$, −2.50 ppm from TMS. The high-field ^1H absorption, +0.50 ppm from TMS, is definitely assigned to terminal CH_3 on aluminum. When one considers all of these data, the most plausible geometry is one involving an octahedron of boron atoms with each boron attached to a $Al(CH_3)_2$ moiety via a double $N(CH_3)_2$ bridge. When one constructs a scale molecular model for I, steric requirements necessitate trans boron atoms having coplanar nitrogen bridges with the resulting geometry of I possessing T_h symmetry, Figure 2.

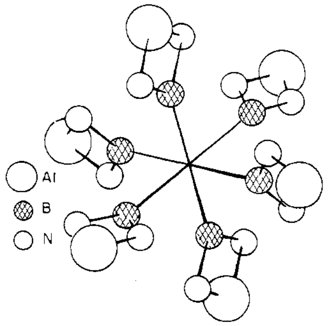

Figure 2. Suggested geometry for $B_6[N(CH_3)_2]_{12}{\cdot}Al_6(CH_3)_{12}$; CH_3 moieties have been omitted for clarity.

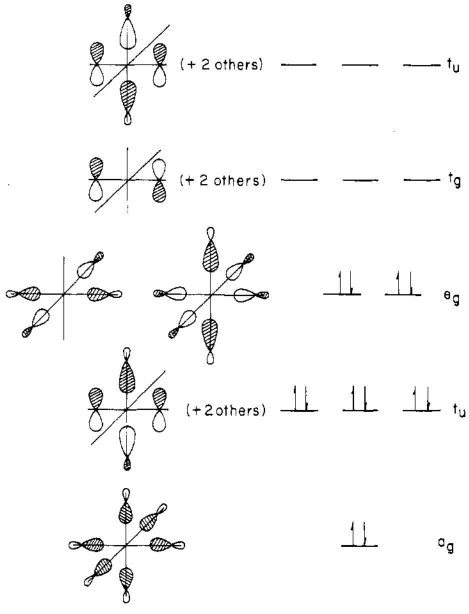

Figure 3. Suggested MO bonding description for $B_6[N(CH_3)_2]_{12}{\cdot}Al_6(CH_3)_{12}$ assuming T_h symmetry.

With regard to cage bonding one may conveniently consider boron to use two sp^2 orbitals in bonding to two nitrogen atoms associated with the bis-μ bridge while the third hybrid orbital is used in cage bonding along with the fourth p orbital. A consequence of T_h symmetry, unlike $B_6H_6^{2-}$, is that trans p orbitals are components of a MO rather than cis p orbitals. In the latter case a 14-e closed-shell configuration results whereas the MO description represented in Figure 3 results in a 12-e configuration with further reduction of I predicted to reduce its stability.[30] Group theoretical treatment of the six boron sp^2 orbitals used for cage bonding results in MO's of a_g, e_g, and t_u symmetry while the six boron p orbitals have t_g and t_u symmetry. Therefore, the B_6 cage MO's of a_g and e_g symmetry are totally constructed from sp^2 hybrid orbitals whereas the t_u set involves both p and sp^2 hybrid orbitals, Figure 3. Although the lower four MO's (a_g and t_u) are bonding and the upper six MO's (t_u and t_g) antibonding, the nature of the e_g set is not obvious. These latter MO's may be slightly bonding, antibonding, or nonbonding—it is not possible to make this distinction in the absence of further data.

Thermal Stability. I has been found to be stable both in the solid state and in solution for at least 1 year when maintained at or below 0 °C. Although the solid-state ir spectrum of I, after I remains in solution at 25 °C for 3 days, is invariant with respect to pure I, the ^1H NMR spectrum indicates significant rearrangement with absorptions growing in at −2.78 and −2.23 ppm from TMS at the expense of the initial −2.50-ppm signal. Concurrent with these changes in $N(CH_3)_2$ environments is a reduction in intensity of the +0.50-ppm signal and development of absorptions at +0.57 and −0.46 ppm from TMS. After I was in solution for 1 month at 25 °C, the combined signal intensities of the −2.78- and −2.23-ppm absorptions are approximately equal to that of the original −2.50-ppm signals. Apparently decomposition takes place via $BN(CH_3)_2$–$AlCH_3$ exchange with the signal growing in at −0.46 ppm due to BCH_3; see Table II. In a similar fashion the signal at −2.78 ppm can be assigned to terminal $BN(CH_3)_2$ with respect to 1,2-$B_2[N(CH_3)_2]_2(CH_3)_2$ (−2.77 ppm) and $B_2[N(CH_3)_2]_4$ (−2.78 ppm) while the signal at −2.23 is closer to that of a $AlN(CH_3)_2$ moiety than that of the boron analogue. In summary, at this time it is not known if the suggested B_6 cage of I remains intact during solution decomposition; however, most assuredly CH_3–$N(CH_3)_2$ exchange takes place between Al and B, respectively.

Attempts to sublime I, 45 °C (10^{-5} Torr), have not been successful, based on the fact that the yellow sublimate appeared wet and ^{1}H NMR data indicated extensive rearrangement. In addition small quantities of H_2, CH_4, $(CH_3)_2NB(CH_3)_2$, and $(CH_3)_2NH$ were evolved during pyrolysis.

Reaction of I with Nucleophiles. A molecular model of I based on the suggested T_h symmetry indicates considerable steric shielding of boron with respect to Lewis acid–Lewis base reactions. However, aluminum is in the common four-coordination state and may be expected to react with Lewis bases via coordination number expansion providing the steric requirement of the Lewis base is not too large. Treatment of I with both $P(CH_3)_3$ and $N(CH_3)_3$ (separately) results in complete recovery of both nucleophiles. In each case the nucleophiles appeared to function as a nonreactive solvent for I with I following the cited solution decomposition route as evidenced by changes in the ^{1}H NMR spectrum. Both NH_3 and $(CH_3)_2NH$ react with I but in a nonstoichiometric fashion under the employed reaction conditions. Excess NH_3 reacts with I via transmination to produce a 60% yield of $(CH_3)_2NH$ and a high but undetermined yield of $[H_2NAl(CH_3)_2]_3$. The latter can be removed from the nonvolatile reaction residue by sublimation. The nonvolatile product is as yet not characterized but exhibits an ir spectrum almost identical with that of $[H_2NAl(CH_3)_2]_3$. In contrast to the reaction of NH_3 and I, $(CH_3)_2NH$ liberates both H_2 and CH_4 as well as $[(CH_3)_2N]_3B$ indicating cleavage of B–B bonds.

Experimental Section

Apparatus. Equipment and techniques employed throughout this study were similar to those previously described.[17]

Reagents. Acetylacetone, $C_5H_8O_2$, Aldrich Chemical Co., Inc., was distilled from Linde 4A Molecular Sieves which were previously dried under dynamic vacuum while heating to slightly greater than 200 °C. The solvent was stored under vacuum over the sieves and distilled at room temperature from the sieves just prior to use. **Ammonia,** NH_3, anhydrous, The Matheson Co., Inc., was distilled onto sodium just prior to use. After being stirred for about 45 min the ammonia was distilled from the sodium for use. **Benzene,** C_6H_6, AR grade, Mallinckrodt Chemical Works, was stored over lithium aluminum hydride and distilled from the hydride just prior to use. **Cyclopentane,** C_5H_{10}, The Matheson Co., Inc., and Chemical Samples Co., was dried over lithium aluminum hydride and then in vacuo over sodium–potassium alloy. Cyclopentane was distilled from this drying agent as needed. **Deuterium oxide,** D_2O, Isotopes, Inc., was used as received. **Dimethylamine,** $(CH_3)_2NH$, anhydrous, The Matheson Co., Inc., was dried over P_2O_5 and distilled prior to use. **Lithium aluminum hydride,** $LiAlH_4$, Alfa Inorganics Inc., was used without further purification. **Phosphorus pentoxide,** P_2O_5, granular, reagent, J. T. Baker Chemical Co., was used as received. **Tetrakis(dimethylamino)diborane(4),** $B_2[N(CH_3)_2]_4$, U.S. Borax Corp., Anaheim, Calif., was distilled under reduced pressure utilizing a Nester-Faust spinning-band column, bp 69 °C (3.5 Torr), lit.[15] bp 69 °C (3.6 Torr). **Toluene,** C_7H_8, ACS Certified, Fisher Scientific Co., was dried over $LiAlH_4$ and distilled from this drying agent just prior to use. **Trimethylaluminum,** $[Al(CH_3)_3]_2$, Ethyl Corp., was used as received. **Trimethylamine,** $N(CH_3)_3$, The Matheson Co., was dried and freed of $(CH_3)_2NH$ by treatment with $LiAlH_4$ while under vacuum and distilled through a −79 °C trap into one maintained at −196 °C. **Trimethylphosphine,** $P(CH_3)_3$, was obtained as the $AgI\cdot P(CH_3)_3$ complex and was released from this complex by heating to ca. 150 °C.

Synthesis of $B_6[N(CH_3)_2]_{12}\cdot Al_6(CH_3)_{12}$ (I). A typical synthesis incorporated $B_2[N(CH_3)_2]_4$ (2.1383 g, 10.805 mmol) which was syringed, in the drybox, into a 50-ml flask equipped with a Kontes valve and O-ring joint. After degassing of $B_2[N(CH_3)_2]_4$, approximately 4.7 ml of $Al(CH_3)_3$ (3.5 g, 49 mmol) was distilled onto the $B_2[N(CH_3)_2]_4$ which was kept at −196 °C. Light was excluded from the reaction flask by wrapping it with aluminum foil, and the two solids were allowed to warm slowly to ca. 0 °C thereby allowing formation of a stirrable homogeneous solution. When homogeneity had been attained, the flask was maintained at 0 °C and all materials with a vapor pressure of greater than ca. 20 Torr at 0 °C were condensed with pumping into a −196 °C trap. Removal of these more volatile materials was accomplished by placing a mercury float valve between the reaction flask and the −196 °C trap and controlling the mercury level in the float valve so that when the pressure on the reaction side of the valve exceeded ca. 20 Torr, the mercury would act as a pressure-release valve. These reaction conditions were maintained for 2 h with occasional stirring by means of a Teflon-coated stirring bar. After 2 h the reaction was terminated by lowering the mercury in the float valve and condensing all volatile materials, with pumping, into the −196 °C trap during a period of 48 h while maintaining the reaction product at 0 °C. The reaction residue consisted of 1.6830 g of a yellow powdery solid, I. Recrystallization of I from cyclopentane results in the isolation of needlelike pale yellow crystals, mp 100–102 °C, which have identical ^{1}H NMR and ir absorptions to that of initial I.

Volatile reaction by-products were separated into pure compounds by fractional distillation through −23, −45, −126, and −196 °C traps. Infrared spectra of the contents of these traps proved the white crystalline solid in the −23 °C trap was $[(CH_3)_2NAl(CH_3)_2]_2$, the clear liquid in the −45 °C trap was unreacted $[Al(CH_3)_3]_2$, the clear liquid in the −126 °C trap was $(CH_3)_2NB(CH_3)_2$, and the colorless gas in the −196 °C trap was $B(CH_3)_3$.

Although the ratio of $B(CH_3)_3$ to $(CH_3)_2NB(CH_3)_2$ varied according to very slight changes made in the reaction conditions, it was found that the total number of millimoles of these species was stoichiometrically constant. In the synthesis under discussion, a total of 10.7 mmol of $(CH_3)_2BN(CH_3)_2$ and $B(CH_3)_3$ was recovered. Although the amounts of $[Al(CH_3)_3]_2$ recovered from various reactions varied with reaction conditions, for this reaction approximately 10 mmol of $[Al(CH_3)_3]_2$ was recovered.

The molecular weight determination of I was carried out by the isopiestic method. Approximately 10 cm^3 of cyclopentane was allowed to equilibrate between 0.0748 g of I and 0.0100 g (0.0549 mmol) of azobenzene for ca. 4 weeks at −10 °C. At equilibrium, 59.1% of the solvent was associated with I. Acid hydrolysis of this molecular weight sample of I afforded 0.930 mmol of CH_4 and 0.465 mmol of H_2. On a sample of I from a different preparative batch 65.8% of the solvent was associated with 0.1091 g of I; 0.0107 g (0.0587 mmol) of azobenzene constituted the standard sample. Acid hydrolysis of the latter sample of I afforded 1.40 mmol of CH_4 and 0.538 mmol of H_2. Concentrations of the solutions were ca. 0.01 M and measurements were made ca. every week until constant. *Note*: Acid hydrolysis conditions do not result in complete oxidation of I. Ir data for I: 2995 (s), 2987 (s), 2945 (vs, sh), 2935 (vs, sh), 2915 (vs), 2910 (vs, sh), 2882 (vs, sh), 2858 (s, sh), 2850 (s, sh), 2832 (s, sh), 2820 (s, sh), 2795 (s, sh), 2780 (m, sh), 1522 (w, sh), 1508 (w, sh), 1499 (m, sh), 1478 (s, sh), 1470 (s, sh), 1466 (s), 1462 (s, sh), 1454 (s, sh), 1426 (m, sh), 1399 (s), 1369 (m, sh), 1303 (w), 1288 (w), 1230 (s, sh), 1220 (s, sh), 1200 (s, sh), 1188 (vs), 1183 (vs), 1173 (s, sh), 1135 (s), 1118 (m, sh), 1099 (m, sh), 1093 (m), 1060 (w, sh), 1043 (m), 1020 (m, sh), 1009 (s), 980 (m, sh), 960 (s), 940 (vs), 901 (m), 890 (m, sh), 878 (m, sh), 803 (m), 755 (m, sh), 747 (m), 712 (s, sh), 700 (vs, sh), 691 (vs), 685 (vs), 660 (vs), 628 (s), 590 (s, sh), 577 (vs), 510 (w, sh), 498 (m), 453 (w), 410 (m), 350 (m) cm^{-1}.

Reactions of I. Air. When exposed to moist air I, originally a dry powdery yellow solid, immediately took on a wet appearance. With increased exposure time this material lost its color and what remained was a wet white solid. If, prior to complete disappearance of the yellow color, this material came in contact with a combustible material, such as a piece of tissue paper, spontaneous ignition of the latter resulted.

Hydrolysis. Complete oxidative hydrolysis of I was carried out at 50–60 °C for 3 days using 50% NaOH solution. These conditions resulted in a hydrolysis solution which exhibited no reducing capacity toward Ag^+ at pH 6. Under these conditions, I (0.0748 g, 0.0799 mmol) afforded H_2 (0.465 mmol) and CH_4 (0.930 mmol). Boron analyses on aliquots of the hydrolysis solution showed boron to make up 6.3, 6.8, 6.5, and 6.4% the total sample weight. In a separate hydrolysis of a sample of I (0.2286 g, 0.2442 mmol), aluminum and nitrogen analyses exhibited compositions of 17.9, 17.5, 17.6, 18.1, 18.0, and 17.7% aluminum and 17.5, 17.5, 17.8, and 18.0% nitrogen.

Acetylacetone. Excess acetylacetone was condensed onto I (0.1716 g, 0.1833 mmol) at −196 °C. The reaction was allowed to proceed for 18 h at ambient temperature with stirring. Methane (2.17 mmol) was the only volatile material generated and the final weight of the nonvolatile products was 0.6964 g. The latter red solid was treated with aqueous sodium hydroxide for 13 h at 50 °C. Hydrogen (1.07 mmol) was the only noncondensable gas generated. In a separate reaction, aluminum tris(acetylacetonate) was isolated and identified by infrared and ^1H NMR spectroscopy. The red product that remained after removal of tris(acetylacetonato)aluminum exhibited ir absorptions at 2970 (m), 2930 (m), 1710 (w), 1637 (s, sh), 1598 (s), 1567 (vs), 1556–1525 (vs), 1465 (s), 1453 (s), 1445 (s), 1438–1415 (vs), 1395 (vs), 1388 (vs), 1360 (s), 1328 (w), 1292 (s), 1242 (m), 1204 (m), 1174 (s), 1070 (w), 1031 (s), 996 (w), 953 (s), 940 (m, sh), 916 (w), 778 (m), 686 (w), 658 (w), 614 (m), 578 (w), 522 (w), 492 (m), and 418 (w) cm^{-1}.

Ammonia. Treatment of I, 0.4275 g (0.4567 mmol), with NH_3 was effected first as a vapor–solid reaction and then as a liquid–solid reaction. The first aliquot of NH_3 (2.71 mmol) was allowed to react for 1 h yielding $(CH_3)_2NH$ (1.71 mmol) as the major volatile product and $(CH_3)_2NB(CH_3)_2$ as a very minor volatile product. Both substances were identified by a comparison of their infrared spectra with authentic samples. The vapor–solid reaction was not very vigorous and proceeded for ca. 10 min before complete disappearance of the yellow color of I and disappearance of a clear liquid. The second aliquot of ammonia (2.41 mmol) was condensed at −196 °C into the reaction vessel and allowed to react for ca. 1 h at ambient temperature. Formation of a white solid replaced the clear liquid that was previously present. The recovered volatiles were NH_3 (ca. 1.11 mmol) and $(CH_3)_2NH$ (ca. 1.61 mmol). A third aliquot of NH_3 (2.71 mmol) was added and allowed to react as described above for ca. 2 h. Because the volatile material isolated after this third aliquot addition was almost all NH_3 (2.63 mmol), further additions of ammonia were not performed. After the residue was pumped on for several hours, the reaction flask was found to have lost 0.1717 g. Overall, 7.83 mmol of NH_3 was added to I with a recovery of 3.74 mmol of unreacted NH_3 and 3.32 mmol of generated $(CH_3)_2NH$.

The white solid residue was transferred to a sublimator and heated to ca. 75 °C with the evolution of trace amounts of H_2, CH_4, NH_3, $(CH_3)_2NH$, and benzene (benzene was used previous to sublimation as a solvent for transference of the white solid residue into the sublimator). Ammonia, $(CH_3)_2NH$, and benzene were identified by their infrared spectra. The white solid sublimate was identified as $[H_2NAl(CH_3)_2]_3$ by comparison of its ir and ^1H NMR spectra with those of an authentic sample.[33] The white solid residue left after sublimation exhibited an ir spectrum very similar to that of $[H_2NAl(CH_3)_2]_3$.

Dimethylamine. Treatment of I, 0.4712 g (0.5034 mmol), with 58.5 mmol of $(CH_3)_2NH(l)$ was effected for 1 hr at 25 °C. No H_2 or CH_4 was evolved; however, increase in the reaction temperature to 70 °C for 5 h resulted in the liberation of H_2, 0.189 mmol, CH_4, 0.068 mmol, and a trace amount of $B[N(CH_3)_2]_3$, while 56.9 mmol of $(CH_3)_2NH$ was recovered. Continued reaction between I and the recovered $(CH_3)_2NH$ for an additional 24 h at 70 °C afforded H_2, 0.289 mmol, and CH_4, 0.108 mmol. The reaction residue consisted of a nonvolatile clear liquid and a nonvolatile white solid.

Trimethylphosphine. Trimethylphosphine, $P(CH_3)_3$ (6.7 mmol), was condensed on a sample of I (ca. 0.2 g, 0.2 mmol). The reaction was allowed to proceed for ca. 18 h at ambient temperature. In addition to the production of a viscous liquid residue, a trace amount of $(CH_3)_2NH$, identified by ir spectroscopy, was recovered along with 6.7 mmol of $P(CH_3)_3$. The ^1H NMR spectrum of the viscous liquid residue was very similar to that resulting from the solution decomposition of I at 25 °C.

Trimethylamine. Trimethylamine, $N(CH_3)_3$ (33 mmol), was allowed to come into vapor–solid contact with I (ca. 0.2 g, 0.2 mmol). After about 1 h at 25 °C, 33 mmol of $N(CH_3)$ was recovered. The $N(CH_3)_3$ was next condensed on I and allowed to react at 25 °C for 1 h more. Removal of the $N(CH_3)_3$ (33 mmol) left a liquid residue that again exhibited a ^1H NMR spectrum similar to that of I undergoing solution decomposition.

Acknowledgment. Support of this investigation by National Science Foundation Grant No. GP 40832X is most appreciated.

Registry No. I, 60372-83-0; $B_2[N(CH_3)_2]_4$, 1630-79-1; $Al(CH_3)_3$, 75-24-1; acetylacetone, 123-54-6; ammonia, 7664-41-7; dimethylamine, 124-40-3; trimethylphosphine, 594-09-2; trimethylamine, 75-50-3; $B(CH_3)_3$, 593-90-8; $H_3B{\cdot}N(CH_3)_3$, 75-22-9; $(CH_3)_2NB(CH_3)_2$, 1113-30-0; $B_2[N(CH_3)_2]_2(CH_3)_2$, 19162-07-3; $B[N(CH_3)_2]_3$, 4375-83-1; $[(CH_3)_2NAl(CH_3)_2]_2$, 22450-81-3; $[H_2NAl(CH_3)_2]_3$, 60363-54-4; $[Al(CH_3)_3]_2$, 15632-54-9; py·$Al(CH_3)_3$, 15628-87-2; $[Al[N(CH_3)_2]_3]_2$, 32093-39-3; ^{11}B, 14798-13-1; ^{13}C, 14762-74-4.

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