Reactivity of R_2AlH (R = Me, Bu^i) with Selected Aminoarsines and Secondary Amines

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Me_2AlH and $Bu^i{}_2AlH$ were reacted with a series of nine aminoarsines, Me_2AsR (R = NMe_2, $NPr^n{}_2$, $NPr^i{}_2$, $NBu^n{}_2$, $NBu^i{}_2$, NC_4H_8, NC_5H_{10}, NC_6H_{12}, and $N(C_2H_4)_2NMe$), in C_6D_6 at room temperature, and the reactions were monitored by ^1H and ^{13}C NMR spectroscopy. The relative rates for initial As−N bond cleavage and final product formation were dependent on the steric requirements of the alkyl groups attached to aluminum and nitrogen in the starting materials. Overall rates were slower with $Bu^i{}_2AlH$ than with Me_2AlH for a given aminoarsine. For most of the reactions, the predominant Al-containing products were the dimeric aminoalane compounds, $[Me_2AlR]_2$ and $[Bu^i{}_2AlR]_2$. Although Al−N bond formation was the prefered mode of reaction, Al−As bond formation was also observed when the bulky Pr^i and Bu^i aminoarsine derivatives were used. The $[Bu^i{}_2AlR]_2$ compounds were synthesized independently by the reaction of $Bu^i{}_2AlH$ and the respective amine or, in the case of $[Bu^i{}_2AlNBu^i{}_2]_2$, by the reaction of $Bu^i{}_2AlCl$ and $LiNBu^i{}_2$. X-ray crystal structures were determined for the compounds $[Me_2AlNC_6H_{12}]_2$, $[Me_2AlN(C_2H_4)_2NMe]_2$, $[Bu^i{}_2AlNMe_2]_2$, and $[Bu^i{}_2AlN(C_2H_4)_2NMe]_2$. All of the compounds have planar Al_2N_2 rings with the exception of $[Bu^i{}_2AlN(C_2H_4)_2NMe]_2$, which displays a puckered Al_2N_2 ring.

Introduction

Although the reactivity of trialkyl organoalanes toward amines has been extensively studied,[1−5] there are few reported studies involving dialkylaluminum hydrides.[6−9] Reactions of Me_2AlH with primary and secondary amines generally result in Al−N condensed species arising from a 1,2-elimination reaction.

Recently, we reported an NMR study of the reactivity of Me_2AlH[10,11] toward Me_2AsNMe_2 and found that the RT (room temperature) 1:1 mol ratio reaction is very exothermic. The ^1H and ^{13}C NMR spectra indicate that >90% of the reactants are consumed upon mixing with no spectral evidence for an Al−N or Al−As adduct. The major products are $[Me_2AlNMe_2]_2$, $Me_2AsAsMe_2$, and Me_2AsH. Variable-temperature NMR establishes that the reaction is very facile at −90 °C and leads to the observed room-temperature products, which result from As−N bond cleavage and Me_2AsH elimination.

Herein we report an NMR investigation on the reactivity of a series of monoaminodimethylarsines, Me_2AsR [R = NMe_2, $NPr^n{}_2$, $NPr^i{}_2$, $NBu^n{}_2$, $NBu^i{}_2$, NC_4H_8, NC_5H_{10}, NC_6H_{12}, and $N(C_2H_4)_2NMe$], toward Me_2AlH and $Bu^i{}_2AlH$ and note the influence that a variation in the steric bulk of R and the aluminum alkyl moiety has on overall reactivity and aminoalane dimer formation. For the Me_2AlH/Me_2AsR system, the resultant $[Me_2AlR]_2$ products are compared with previously characterized samples from the reactions of Me_3Al with the same aminoarsine series.[12,13] Because only $[Bu^i{}_2AlNMe_2]_2$[14] and $[Bu^i{}_2AlNC_5H_{10}]_2$[15] have been previously reported, we synthesized seven $[Bu^i{}_2AlR]_2$ derivatives [R = NMe_2, $NPr^n{}_2$,$NBu^n{}_2$, NC_4H_8, NC_5H_{10}, NC_6H_{12}, and $N(C_2H_4)_2NMe$] by the reaction of $Bu^i{}_2AlH$ with the corresponding secondary amines and one, $[Bu^i{}_2AlNBu^i{}_2]_2$, by the reaction of $Bu^i{}_2AlCl$ with $LiNBu^i{}_2$. Also reported is the synthesis of the trimeric $[Bu^i{}_2AlAsMe_2]_3$, which is an observed reaction product in the $Me_2AsNPr^i{}_2$ and $Me_2AsNBu^i{}_2$ systems. Synthesized compounds are characterized by ^1H, ^{13}C, and ^{27}Al NMR, IR, MS, and elemental analysis.

X-ray structural data were obtained on four dimers in order to relate the steric bulk of the alkyl moiety on

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(10) In this paper, the designations Me_3Al, Me_2AlH, and $Bu^i{}_2AlH$ are used to simplify the discussions of reaction stoichiometry, although these organoaluminum compounds are known to be oligomeric. See refs 3−5.

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Table 1. Summary of Reactions of Me_2AlH and Bu^i_2AlH with Me_2AsR

R	reaction products	time for >90% parent consumption	time for >80% dimer formation
	Me_2AlH		
NMe_2	$[Me_2AlNMe_2]_2$, $Me_2AsAsMe_2$, Me_2AsH	mixing	1 day
NPr^n_2	$[Me_2AlNPr^n_2]_2$, $Me_2AsAsMe_2$, Me_2AsH	mixing	3 months
NPr^i_2	$[Me_2AlNPr^i_2]_2$, Pr^i_2NH, $Me_2AsAsMe_2$,$[Me_2AlAsMe_2]_3$	1 day	6 months, 40%
NBu^n_2	$[Me_2AlNBu^n_2]_2$, $Me_2AsAsMe_2$, Me_2AsH	mixing	6 months, 70%
NBu^i_2	$[Me_2AlNBu^i_2]_2$, $Me_2AsAsMe_2$, Me_2AsH, $[Me_2AlAsMe_2]_3$	1 day	1 month
NC_4H_8	$[Me_2AlNC_4H_8]_2$, $Me_2AsAsMe_2$, Me_2AsH	mixing	1 week
NC_5H_{10}	$[Me_2AlNC_5H_{10}]_2$, $Me_2AsAsMe_2$, Me_2AsH	mixing	3.5 months
NC_6H_{12}	$[Me_2AlNC_6H_{12}]_2$, $Me_2AsAsMe_2$, Me_2AsH	mixing	2 weeks
$N(C_2H_4)_2NMe$	$[Me_2AlN(C_2H_4)_2NMe]_2$, $Me_2AsAsMe_2$, Me_2AsH	1 day	1 week
	Bu^i_2AlH		
NMe_2	$[Bu^i_2AlNMe_2]_2$, $Me_2AsAsMe_2$, Me_2AsH	1 day	1 day
NPr^n_2	$[Bu^i_2AlNPr^n_2]_2$, $Me_2AsAsMe_2$	2 weeks	6 months, 25%
NPr^i_2	$Me_2AsAsMe_2$, $[Bu^i_2AlAsMe_2]_3$, and uncharacterized Al−N-containing products	6 months, 80%	
NBu^n_2	$[Bu^i_2AlNBu^n_2]_2$, $Me_2AsAsMe_2$	2 weeks	6 months, 28%
NBu^i_2	$[Bu^i_2AlNBu^i_2]_2$, $Me_2AsAsMe_2$, $[Bu^i_2AlAsMe_2]_3$	6 months, 88%	6 months, 18%
NC_4H_8	$[Bu^i_2AlNC_4H_8]_2$, $Me_2AsAsMe_2$	1 week	2 weeks
NC_5H_{10}	$[Bu^i_2AlNC_5H_{10}]_2$, $Me_2AsAsMe_2$	1 month	6 months, 40%
NC_6H_{12}	$[Bu^i_2AlNC_6H_{12}]_2$, $Me_2AsAsMe_2$	5 weeks	6 months, 65%
$N(C_2H_4)_2NMe$	$[Bu^i_2AlN(C_2H_4)_2NMe]_2$, $Me_2AsAsMe_2$, Me_2AsH	1 day	1 day

Al and of R to the structural parameters of the four-membered dimer rings of the aminoalanes. Of the dimeric $[Me_2AlR]_2$ derivatives discussed in this study, only structural information for $[Me_2AlNMe_2]_2$[16,17] has been reported. No structural data have been reported for $[Bu^i_2AlR]_2$ species. Herein, we report structural data for $[Me_2AlNC_6H_{12}]_2$, $[Me_2AlN(C_2H_4)_2NMe]_2$, $[Bu^i_2AlNMe_2]_2$, and $[Bu^i_2AlN(C_2H_4)_2NMe]_2$. A comparison is given between the Al_2N_2 ring geometries for these aminoalane dimers with those previously reported for species having the general formula $[R'_2AlR_2]_2$ (R = secondary amine, R′ = alkyl).

Experimental Section

General Procedures. Standard inert-atmosphere techniques were used for the synthesis and manipulation of all compounds owing to their extreme air and moisture sensitivity. This included the use of a high-vacuum line in conjunction with an inert-atmosphere drybox (Vacuum Atmospheres HE-43 DriLab). Hexane was distilled under an atmosphere of nitrogen over sodium. All the amines used were purchased from Aldrich and were dried over sodium or KOH and distilled prior to use. Me_2AlH was obtained as a gift from Morton Advanced Materials, Danvers, MA, and Bu^i_2AlH was purchased from Texas Alkyls. Benzene-d_6 and toluene-d_8 were purchased from Aldrich and stored over molecular sieves. Me_2AsNMe_2 was synthesized by the aminolysis of Me_2AsCl.[18] The other aminoarsine derivatives, Me_2AsNR_2, were synthesized by the modified transamination of Me_2AsNMe_2 with the respective amine.[19]

^1H, ^{13}C, and ^{27}Al NMR spectral data were collected on Nicolet NT-300 and Bruker ARX 300 FT NMR spectrometers. The ^1H and ^{13}C chemical shifts were referenced with respect to the solvent, while aqueous $Al(NO_3)_3$ was used as the ^{27}Al external reference. RT spectra for the reported compounds were obtained as 0.4 M solutions in C_6D_6 in 10 mm Pyrex NMR tubes (Wilmad) equipped with screw tops containing a PTFE insert to exclude moisture and air. Toluene-d_8 was used as a solvent for the variable-temperature NMR studies. FT-IR data were collected using a Nicolet IR/42 FT spectrometer. Samples were prepared as Kel-F (halocarbon) and Nujol mulls, for solid samples, or as neat liquids on KBr plates. Low-resolution EI-MS data were obtained using the direct insertion probe on HP 5986A and Finnigan MAT95Q GC/MS spectrometers at 70 eV with a 2400 V electron multiplier. Elemental analyses were performed by E+R Microanalytical laboratory, Inc., Corona, NY. Melting points were taken with a Thomas-Hoover melting point apparatus using sealed capillaries and are uncorrected.

General Reaction of Me_2AlH or Bu^i_2AlH with Aminoarsines, Me_2AsR. In a typical reaction, a solution of Me_2AlH or Bu^i_2AlH (1.0 mmol, 2 mL of C_6D_6) was added to a screw-top NMR tube containing a solution of Me_2AsR (1 mmol) in 1 mL of C_6D_6 at room temperature. ^1H and ^{13}C NMR spectroscopy was used to monitor the reaction mixture as a function of time. Products were identified by comparing the NMR chemical shifts with those of previously synthesized samples. The products observed, time required for parent consumption, and time for dimer formation in these NMR studies are given in Table 1. The ^1H and ^{13}C NMR data for the aminoarsines[19] and the product $[Me_2AlR]_2$ aminoalane dimers[12,13] have been previously reported.

General Synthesis of $[Bu^i_2AlR]_2$. The following procedure was used for the independent synthesis of the $[Bu^i_2AlR]_2$ derivatives, with the exception of $[Bu^i_2AlNBu^i_2]_2$. In a typical synthesis, 21.1 mmol of the secondary amine was added dropwise to Bu^i_2AlH (3.00 g, 21.1 mmol), which was previously cooled to −76 °C using a dry ice/acetone bath. In most cases, an intermediate reaction was observed with gas evolution. Slow warming of the mixture to room temperature resulted in significant gas evolution. The mixtures were then heated to within 20 °C of the boiling point of the corresponding amine and stirred for 12−24 h until no further gas evolution was observed. There was one liquid product, $[Bu^i_2AlNBu^n_2]_2$, which was used without further purification. All other products were obtained in 80−90% yield after recrystallizing from hexane. Melting point, NMR, IR, MS, and elemental analysis data for the previously unreported $[Bu^i_2AlR]_2$ derivatives are as follows:

$[Bu^i_2AlNPr^n_2]_2$. Mp: 108−111 °C. ^1H NMR: δ 0.34 (d, 4 H, $AlCH_2$), 0.76 (t, 6 H, $NCH_2CH_2CH_3$), 1.22 (d, 12 H, $AlCH_2CH(CH_3)_2$), 1.39 (m, 4 H, NCH_2CH_2), 2.12 (non, 2 H, $AlCH_2CH$), 2.80 (m, 4 H, NCH_2). ^{13}C NMR: δ 11.67 ($NCH_2CH_2CH_3$), 20.92 (NCH_2CH_2), 21.56 ($AlCH_2$), 26.65 ($AlCH_2CH$), 29.10 ($AlCH_2CH(CH_3)_2$), 49.70 (NCH_2). ^{27}Al NMR: δ 172. IR (cm^{-1}): 2951 (vs), 2876 (vs), 1461 (s), 1402 (m), 1376 (s), 1360 (m), 1318 (m), 1267 (w), 1209 (w), 1185 (m), 1160 (m), 1137 (w), 1110 (m), 1066 (s), 1020 (m), 953 (s), 899 (m), 880 (w), 850 (m), 818 (m), 750 (w), 722 (w), 668 (vs), 603 (s), 571 (w), 433 (m), 408

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(m). MS (EI): *m/z* 425 ($M^+ - Bu^i$). Anal. Calcd for $C_{28}H_{64}Al_2N_2$: C, 69.64; H, 13.37; N, 5.80. Found: C, 69.15; H, 13.26; N, 5.99.

$[Bu^i_2AlNBu^n_2]_2$. ^1H NMR: δ 0.38 (d, 4 H, $AlCH_2$), 0.89 (t, 6 H, $NCH_2CH_2CH_2CH_3$), 1.24 (m, 4 H, $NCH_2CH_2CH_2$), 1.24 (d, 12 H, $AlCH_2CH(CH_3)_2$), 1.48 (m, 4 H, NCH_2CH_2), 2.16 (non, 2 H, $AlCH_2CH$), 2.91 (m, 4 H, NCH_2). ^{13}C NMR: δ 14.15 ($NCH_2CH_2CH_2CH_3$), 21.09 ($NCH_2CH_2CH_2$), 21.84 ($AlCH_2$), 26.73 ($AlCH_2CH$), 29.11 ($AlCH_2CH(CH_3)_2$), 29.83 (NCH_2CH_2), 47.61 (NCH_2). ^{27}Al NMR: δ 175. IR (cm^{-1}): 2964 (vs), 2863 (vs), 2778 (m), 1464 (vs), 1403 (w), 1376 (s), 1360 (s), 1318 (m), 1178 (s), 1159 (m), 1138 (w), 1118 (s), 1065 (vs), 1017 (s), 876 (s), 815 (m), 714 (s), 673 (vs), 607 (s), 430 (m). MS (EI): *m/z* 481 ($M^+ - Bu^i$). Anal. Calcd for $C_{32}H_{72}Al_2N_2$: C, 71.30; H, 13.47; N, 5.20. Found: C, 70.65; H, 13.38; N 5.60.

$[Bu^i_2AlNC_4H_8]_2$. Mp: 43−45 °C. ^1H NMR: δ 0.20 (d, 4 H, $AlCH_2$), 1.14 (d, 12 H, $AlCH_2CH(CH_3)_2$), 1.41 (m, 4 H, NCH_2CH_2), 2.02 (non, 2 H, $AlCH_2CH$), 2.75 (m, 4 H, NCH_2). ^{13}C NMR: δ 21.41 ($AlCH_2$), 25.50 (NCH_2CH_2), 26.54 ($AlCH_2CH$), 28.97 ($AlCH_2CH(CH_3)_2$), 49.88 (NCH_2). ^{27}Al NMR: δ 164. IR (cm^{-1}): 2947 (vs), 2866 (vs), 2782 (m), 1461 (s), 1401 (w), 1359 (m), 1319 (m), 1206 (w), 1183 (s), 1159 (m), 1065 (vs), 1051 (m), 910 (vs), 816 (m), 676 (vs), 590 (w), 518 (vs), 431 (w). MS (EI): *m/z* 365 ($M^+ - Bu^i$). Anal. Calcd for $C_{24}H_{52}Al_2N_2$: C, 68.19; H, 12.41; N, 6.63. Found: C, 67.53; H, 11.59; N, 6.91.

$[Bu^i_2AlNC_6H_{12}]_2$. Mp: 67−68 °C. ^1H NMR: δ 0.30 (d, 4 H, $AlCH_2$), 1.23 (d, 12 H, $AlCH_2CH(CH_3)_2$), 1.33 (m, 4 H, $NCH_2CH_2CH_2$), 1.46 (m, 4 H, NCH_2CH_2), 2.12 (non, 2 H, $AlCH_2CH$), 2.98 (m, 4 H, NCH_2). ^{13}C NMR: δ 22.24 ($AlCH_2$), 26.61 ($AlCH_2CH$), 27.93 ($NCH_2CH_2CH_2$), 29.14 ($AlCH_2CH(CH_3)_2$), 29.78 (NCH_2CH_2), 50.63 (NCH_2). ^{27}Al NMR: δ 164. IR (cm^{-1}): 2945 (vs), 2857 (vs), 2783 (w), 1476 (m), 1462 (m), 1450 (m), 1374 (w), 1358 (w), 1315 (m), 1184 (m), 1167 (m), 1106 (s), 1068 (s), 1028 (m), 1008 (m), 962 (w), 843 (vs), 818 (m), 742 (vs), 723 (w), 671 (vs), 593 (m), 554 (w), 524 (w). MS (EI): *m/z* 421 ($M^+ - Bu^i$). Anal. Calcd for $C_{28}H_{60}Al_2N_2$: C, 70.23; H, 12.64; N, 5.85. Found: C, 70.26; H, 12.09; N, 5.40.

$[Bu^i_2AlN(C_2H_4)_2NMe]_2$. Mp: 52−53 °C. ^1H NMR: δ 0.27 (d, 4 H, $AlCH_2$), 1.20 (d, 12 H, $AlCH_2CH(CH_3)_2$), 2.02 (s, 3 H, NCH_3), 2.07 (non, 2 H, $AlCH_2CH$), 2.16 (m, 4 H, NCH_2CH_2), 2.86 (m, 4 H, NCH_2). ^{13}C NMR: δ 22.33 ($AlCH_2$), 26.67 ($AlCH_2CH$), 29.18 ($AlCH_2CH(CH_3)_2$), 46.63 (NCH_3), 49.00 (NCH_2), 56.30 (NCH_2CH_2). ^{27}Al NMR: δ 178. IR (cm^{-1}): 2950 (vs), 2864 (vs), 2797 (m), 1569 (w), 1534 (w), 1463 (s), 1453 (s), 1402 (w), 1378 (m), 1371 (m), 1361 (m), 1318 (m), 1294 (s), 1152 (s), 1106 (vs), 1067 (m), 1054 (m), 1003 (s), 913 (m), 893 (w), 870 (vs), 685 (vs), 621 (w), 528 (m), 509 (m), 422 (w), 407 (m). MS (EI): *m/z* 423 ($M^+ - Bu^i$). Anal. Calcd for $C_{26}H_{58}Al_2N_4$: C, 64.96; H, 12.16; N, 11.65. Found: C, 65.20; H, 11.58; N, 11.60.

Synthesis of $[Bu^i_2AlNBu^i_2]_2$. A solution of Bu^i_2AlCl (6.602 g, 37.4 mmol) in hexane (20 mL) was slowly added to a 50 mL hexane solution of $LiNBu^i_2$ (5.068 g, 37.5 mmol, previously prepared from the reaction of $HNBu^i_2$ and $LiBu^n$) at −40 °C. LiCl precipitated from the solution upon warming to room temperature. After the solution was stirred for 1 h at room temperature, the solution was decanted and the solid was washed with hexane. The removal of the hexane *in vacuo* resulted in a slightly yellow oily residue. The residue was dissolved in 20 mL of toluene and cooled to −15 °C, to give 7.65 g (76% yield) of $[Bu^i_2AlNBu^i_2]_2$. Mp: 156−158 °C. ^1H NMR: δ 0.43 (d, 4 H, $AlCH_2$), 0.95 (d, 12 H, $NCH_2CH(CH_3)_2$), 1.23 (d, 12 H, $AlCH_2CH(CH_3)_2$), 2.12 (non, 2 H, NCH_2CH), 2.17 (non, 2 H, $AlCH_2CH$), 2.93 (d, 4 H, NCH_2). ^{13}C NMR: δ 23.11 ($NCH_2CH(CH_3)_2$), 24.00 ($AlCH_2$), 26.68 ($AlCH_2CH$), 27.93 (NCH_2CH), 29.03 ($AlCH_2CH(CH_3)_2$), 56.20 (NCH_2). ^{27}Al NMR: δ 172. IR (cm^{-1}): 2952 (vs), 2871 (s), 1316 (w), 1271 (w), 1207 (w), 1185 (m), 1158 (m), 1128 (w), 1066 (w, sh), 1054 (s), 976 (m), 954 (w), 923 (w), 864 (m), 829 (m), 725 (w), 666 (s), 588 (m), 461 (m). MS (EI): *m/z* 481 ($M^+ - Bu^i$). Anal. Calcd for $C_{32}H_{72}Al_2N_2$: C, 71.32; H, 13.47; N, 5.20. Found: C, 70.98; H, 13.16; N, 5.31.

Synthesis of $[Bu^i_2AlAsMe_2]_3$. Onto a cooled (−76 °C) sample of Bu^i_2AlH (0.71 g, 5.0 mmol) was condensed a 20% excess of Me_2AsH (0.53 mL). The reaction mixture was warmed to 0 °C and stirred until an ^1H NMR spectrum of the resulting clear liquid showed the absence of Bu^i_2AlH (1 week). Occasionally, the sample was cooled (−76 °C) and H_2 was removed under vacuum. Excess Me_2AsH was removed under vacuum at 0 °C. The resulting white crystalline solid, $[Bu^i_2AlAsMe_2]_3$, was obtained in 96% yield. Mp: 47 °C. ^1H NMR: δ 0.44 (d, 4 H, $AlCH_2$), 1.05 (s, 6 H, $AsCH_3$), 1.17 (d, 12 H, $AlCH_2CH(CH_3)_2$), 2.03 (non, 2 H, $AlCH_2CH$). ^{13}C NMR: δ 1.15 ($AsCH_3$), 21.76 ($AlCH_2$), 27.34 ($AlCH_2CH$), 28.60 ($AlCH_2CH(CH_3)_2$). IR (cm^{-1}): 2951 (vs), 2921 (vs), 2889 (vs), 2865 (vs), 2769 (m), 2716 (w), 1463 (vs), 1451 (m), 1437 (w), 1420 (m), 1399 (m), 1377 (s), 1360 (vs), 1316 (vs), 1266 (w), 1244 (w), 1202 (m), 1175 (vs), 1159 (vs), 1062 (vs), 1009 (vs), 1000 (s), 896 (vs), 864 (vs), 800 (s), 653 (vs, br), 588 (s), 485 (w), 419 (s). MS (EI): *m/z* 681 ($M^+ - Bu^i$). Anal. Calcd for $C_{30}H_{72}Al_3As_3$: C, 48.78; H, 9.83; Al, 10.96. Found: C, 48.53; H, 9.79; Al, 10.90.

X-ray Structural Analysis. All measurements were carried out at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Cu Kα or Mo Kα radiation. The crystals of $[Me_2AlNC_6H_{12}]_2$, $[Me_2AlN(C_2H_4)_2NMe]_2$, and $[Bu^i_2AlN(C_2H_4)_2NMe]_2$ were obtained from hexane solutions (−20 °C), while crystals of $[Bu^i_2AlNMe_2]_2$ were obtained by vacuum sublimation. The crystals were sealed in thin-walled glass capillaries under an inert atmosphere of nitrogen. Cell parameters and an orientation matrix were obtained from least-squares refinement of 25 reflections with $25 \le \theta \le 35°$ for $[Me_2AlNC_6H_{12}]_2$, $[Me_2AlN(C_2H_4)_2NMe]_2$, and $[Bu^i_2AlN(C_2H_4)_2NMe]_2$ and $12 \le \theta \le 16°$ for $[Bu^i_2AlNMe_2]_2$. Data were collected by $\omega - 2\theta$ scans, and empirical absorption corrections were applied. Structures were solved by direct methods and refined by full-matrix least-squares procedures that minimized $w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$ using the MolEN package of programs from Enraf-Nonius. Data were weighed using a non-Poisson scheme. All non-hydrogen atoms were refined anisotropically. For $[Me_2AlNC_6H_{12}]_2$ and $[Bu^i_2AlN(C_2H_4)_2NMe]_2$, hydrogen atoms were included in the structure factor calculations but were placed in calculated positions (C−H = 0.95 Å) and were not refined. Hydrogen atom positions for $[Me_2AlN(C_2H_4)_2NMe]_2$ and $[Bu^i_2AlNMe_2]_2$ were located in difference Fourier maps. Their positional parameters, but not their isotropic thermal factors, were refined.

The asymmetric units for $[Me_2AlNC_6H_{12}]_2$, $[Me_2AlNC_4H_8NMe]_2$, and $[Bu^i_2AlNMe_2]_2$ each consisted of one monomer unit situated about a crystallographic inversion center. For $[Bu^i_2AlNC_4H_8NMe]_2$, the entire dimer is unique, occupying a general position in the unit cell. Crystallographic data are given in Table 2, and selected bond distances and angles for $[Me_2AlNC_6H_{12}]_2$, $[Me_2AlNC_4H_8NMe]_2$, $[Bu^i_2AlNMe_2]_2$, and $[Bu^i_2AlNC_4H_8NMe]_2$ are given in Tables 3 and 4. Molecular structures for the compounds are given in Figures 1−4.

In $[Me_2AlNC_6H_{12}]_2$, one methylene group in the amine ring was found to be disordered over two nearly equally occupied sites related by a change in the conformation of the ring about C5. The occupancies of the two related carbon atom positions were refined, with 55.7% assigned to the major component (C5) and 44.3% to the minor (C5a). The hydrogen atoms associated with the disordered carbons atoms were assigned the same occupancy as the atom to which they were bonded. The occupancies were then fixed for use in later least-squares refinements. A small amount of disorder was also observed in one of the isobutyl groups for $[Bu^i_2AlNMe_2]_2$, resulting in an elevated thermal motion reflected in C6. The relatively high *R* values for $[Me_2AlNC_6H_{12}]_2$ and $[Bu^i_2AlNMe_2]_2$ are attributed to the presence of these disorders.

Results and Discussion

NMR Reactivity Studies. Me_2AlH readily reacts with Me_2AsR [R = NMe_2, NPr^n_2, NPr^i_2, NBu^n_2, NBu^i_2,

Table 2. Crystallographic Data for [Me$_2$AlNC$_6$H$_{12}$]$_2$, [Me$_2$AlN(C$_2$H$_4$)$_2$NMe]$_2$, [Bu$^i_2$AlNMe$_2$]$_2$, and [Bu$^i_2$AlN(C$_2$H$_4$)$_2$NMe]$_2$

	[Me$_2$AlNC$_6$H$_{12}$]$_2$	[Me$_2$AlN(C$_2$H$_4$)$_2$NMe]$_2$	[Bu$^i_2$AlNMe$_2$]$_2$	[Bu$^i_2$AlN(C$_2$H$_4$)$_2$NMe]$_2$
mol formula	C$_{16}$H$_{36}$Al$_2$N$_2$	C$_{14}$H$_{34}$Al$_2$N$_4$	C$_{20}$H$_{48}$Al$_2$N$_2$	C$_{26}$H$_{58}$Al$_2$N$_4$
fw	310.44	312.41	370.58	480.74
size, mm	0.25 × 0.25 × 0.46	0.37 × 0.42 × 0.48	0.22 × 0.51 × 0.73	0.20 × 0.20 × 0.35
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
cryst system	triclinic	triclinic	monoclinic	orthorhombic
a, Å	7.571(1)	7.429(1)	8.748(1)	10.120(1)
b, Å	8.397(1)	8.200(1)	9.460(1)	17.439(3)
c, Å	9.141(1)	9.154(1)	15.457(2)	18.066(2)
α, deg	69.65(1)	74.29(1)	90	90
β, deg	68.120(8)	77.79(1)	92.12(1)	90
γ, deg	71.720(9)	63.32(2)	90	90
V, Å^3	494.2(1)	477.0(1)	1278.2(3)	3188.4(7)
Z	2	2	4	4
D_{calcd}, g cm^{-3}	1.043	1.088	0.963	1.001
λ, Å	1.541 84	1.541 84	0.710 73	1.541 84
μ, cm^{-1}	12.545	13.338	2.290	9.286
2$\theta_{\max}$, deg	74	74	55	74
reflns measd	2169	2083	3042	3628
indep reflns obsd, $I \geq 3\sigma(I)$	1140	1554	1005	2514
no. of variables	101	143	182	290
instr uncertainty (p)	0.05	0.03	0.03	0.03
extinction coeff	1.92 × 10^{-6}	3.82 × 10^{-5}	2.29 × 10^{-7}	1.24 × 10^{-6}
R,[a] R_w[b]	0.070, 0.099	0.043, 0.058	0.080, 0.090	0.054, 0.062
max, min $\Delta\rho$, e Å^{-3}	0.384, −0.343	0.269, −0.280	0.451, −0.468	0.293, −0.081
max shift/error	0.00	0.02	0.00	0.00

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$). [b] $R_w = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{0.5}$, $w = (2F_o)^2/|\sigma(I)^2 + (pF_o{}^2)^2|$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Me$_2$AlNC$_6$H$_{12}$]$_2$ and [Me$_2$AlN(C$_2$H$_4$)$_2$NMe]$_2$

[Me$_2$AlNC$_6$H$_{12}$]$_2$			
Al−N	1.959(3)	Al−N′	1.964(4)
Al−C7	1.963(6)	Al−C8	1.980(7)
N−C1	1.498(7)	N−C6	1.465(5)
N−Al−N′	88.7(1)	Al−N−Al′	91.3(1)
N−Al−C7	112.5(2)	N−Al−C8	112.6(2)
C7−Al−C8	115.7(3)	Al−N−C1	114.2(3)
Al−N−C6	110.6(2)	C1−N−C6	114.6(3)
[Me$_2$AlN(C$_2$H$_4$)$_2$NMe]$_2$			
Al−N1	1.968(1)	Al−N1′	1.980(2)
Al−C5	1.957(3)	Al−C6	1.959(3)
N1−C1	1.493(3)	N1−C4	1.494(3)
N1−Al−N1′	88.67(6)	Al−N1−Al′	91.33(6)
N1−Al−C5	112.6(1)	N1−Al−C6	113.16(9)
C5−Al−C6	117.7(1)	Al−N1−C1	117.0(1)
Al−N1−C4	116.7(1)	C1−N1−C4	106.0(2)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [Bu$^i_2$AlNMe$_2$]$_2$ and [Bu$^i_2$AlN(C$_2$H$_4$)$_2$NMe]$_2$

[Bu$^i_2$AlNMe$_2$]$_2$			
Al−N	1.972(6)	Al−N′	1.977(6)
Al−C1	1.956(8)	Al−C5	1.982(8)
N−C9	1.48(1)	N−C10	1.45(1)
Al−N−Al′	91.7(3)	N−Al−N′	88.3(3)
N−Al−C1	109.8(3)	N−Al−C5	113.3(3)
Al−N−C9	113.6(5)	Al−N−C10	114.6(5)
Al−C1−C2	120.4(5)	Al−C5−C6	122.6(7)
C1−Al−C5	119.9(3)	C9−N−C10	108.0(6)
[Bu$^i_2$AlN(C$_2$H$_4$)$_2$NMe]$_2$			
Al1−N1	1.994(4)	Al1−N3	1.966(4)
Al2−N1	1.969(4)	Al2−N3	2.005(4)
Al1−C1	1.981(5)	Al1−C5	1.999(5)
Al2−C9	1.992(5)	Al2−C13	1.963(5)
N1−C17	1.481(6)	N1−C20	1.503(6)
N3−C22	1.493(6)	N3−C25	1.497(6)
N1−Al1−N3	87.7(2)	N1−Al2−N3	87.3(2)
Al1−N1−Al2	90.7(2)	Al1−N3−Al2	90.4(2)
C1−Al1−C5	122.2(2)	N1−Al1−C1	106.0(2)
N1−Al1−C5	109.4(2)	N3−Al1−C1	111.4(2)
N3−Al1−C5	114.1(2)	C9−Al2−C13	122.8(2)
N1−Al2−C9	111.4(2)	N1−Al2−C13	112.8(2)
N3−Al2−C9	106.0(2)	N3−Al2−C13	110.5(2)
C17−N1−C20	106.6(3)	C22−N3−C25	105.8(3)

NC$_4$H$_8$, NC$_5$H$_{10}$, NC$_6$H$_{12}$, and N(C$_2$H$_4$)$_2$NMe] with facile cleavage of the As−N-bond and formation of Al−N bonded species. The time required for >90% parent aminoarsine consumption, as noted from the ^{1}H and ^{13}C NMR spectra of the reaction mixtures, occurs within 1 day for all nine systems. Thus, the nature of the R group in Me$_2$AsR is not significant in determining the time for initial cleavage of the As−N bond. However, the steric nature of the R group may be important in terms of the completion time of the reaction as well as in the possibility of Al−As bond formation. The latter can occur either from the reaction of available Me$_2$AlH with Me$_2$AsH and Me$_2$AsAsMe$_2$[11] or from initial attack of Me$_2$AlH on the respective aminoarsine. In each system, the final AlN-containing product is the dimeric [Me$_2$AlR]$_2$. The final arsenic-containing products are Me$_2$AsAsMe$_2$ and Me$_2$AsH, except for the Me$_2$AsNPr$^i_2$ and Me$_2$AsNBu$^i_2$ systems, where [Me$_2$AlAsMe$_2$]$_3$ is formed.

For the Me$_2$AlH/Me$_2$AsR systems where R = NMe$_2$, NPr$^n_2$, NBu$^n_2$, NC$_4$H$_8$, NC$_5$H$_{10}$, and NC$_6$H$_{12}$, the respective aminoalane dimers are observed immediately after mixing in the ^{1}H and ^{13}C NMR. Several AlN-containing intermediates, analogous to 2Me$_2$AlNMe$_2$·Me$_2$AlH, Me$_2$AlNMe$_2$·Me$_2$AlH, and [Me$_2$AlNMe$_2$·Me$_2$AlH]$_2$, which were previously identified for the Me$_2$AlH/Me$_2$AsNMe$_2$ reaction system,[11] are present in each case. These serve as precursors to the aminoalane dimers. Concurrent with aminoalane dimer formation is the appearance of resonances in the NMR spectra assignable to Me$_2$AsH and Me$_2$AsAsMe$_2$. Reactivity then proceeds toward completion at varying times (Table 1) dependent on the nature of the R group.

Although extensive reaction occurs upon mixing in the Me$_2$AlH/Me$_2$AsN(C$_2$H$_4$)$_2$NMe reaction system, there is no initial dimer formation. The ^{1}H and ^{13}C NMR spectra indicate high intensity peaks for unreacted parent aminoarsine and broad, exchange-averaged reso-

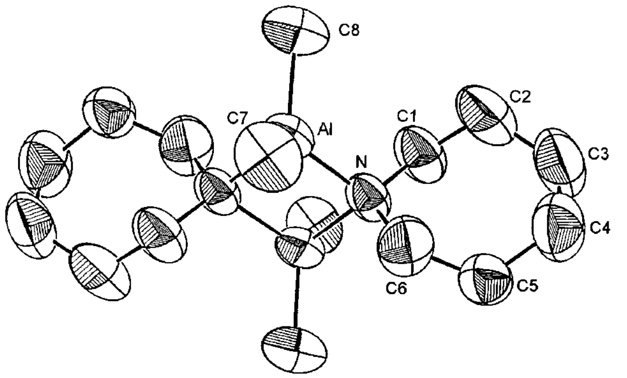

Figure 1. Molecular structure of $[\mathrm{Me_2AlNC_6H_{12}}]_2$, showing one of the two possible orientations of the disordered ring.

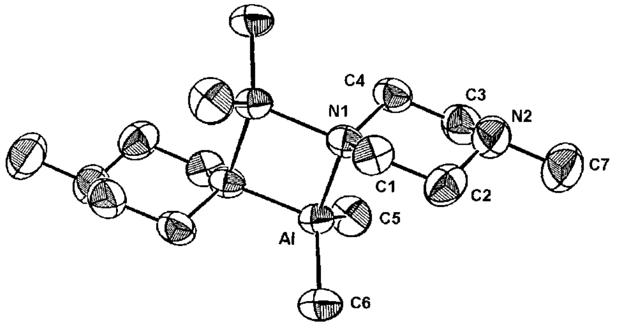

Figure 2. Molecular structure of $[\mathrm{Me_2AlN(C_2H_4)_2NMe}]_2$.

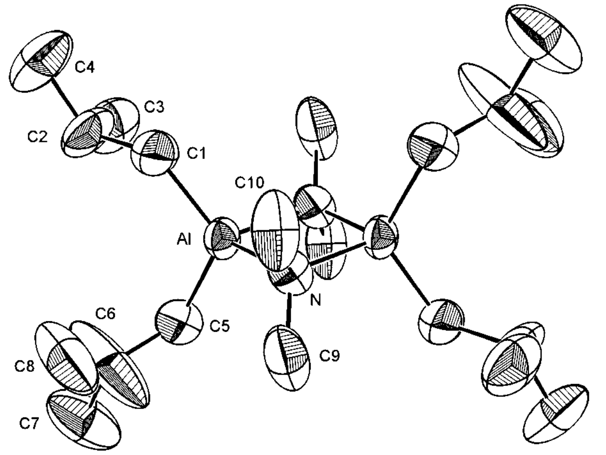

Figure 3. Molecular structure of $[\mathrm{Bu^i{}_2AlNMe_2}]_2$.

nances for AlN-containing species. After 1 day, the parent aminoarsine is consumed. However, 1 week is required for the conversion of the AlN-containing intermediates to $[\mathrm{Me_2AlN(C_2H_4)_2NMe}]_2$, because of the presence of chemical exchange.

In the $\mathrm{Me_2AlH/Me_2AsNBu^i{}_2}$ system, the NMR spectra exibit initially higher intensity peaks for unreacted parent, $\mathrm{Me_2AsH}$, and the Al−N species $\mathrm{Me_2AlNBu^i{}_2{\cdot}2Me_2AlH}$. Lower intensity peaks are observed for $\mathrm{Me_2AsAsMe_2}$, $[\mathrm{Me_2AlAsMe_2}]_3$, and three Al−N species. Within 1e day, the parent is consumed by reaction with the $\mathrm{Me_2AlH}$ bound in $\mathrm{Me_2AlNBu^i{}_2{\cdot}2Me_2AlH}$. Additional amounts of $\mathrm{Me_2AsAsMe_2}$, $\mathrm{Me_2AsH}$, and $[\mathrm{Me_2AlAsMe_2}]_3$ are formed, and all the $\mathrm{Bu^i{}_2N}$ moieties are contained in the three Al−N-containing species, which by analogy with the $\mathrm{Me_2AlH/Me_2AsNMe_2}$ system[11] should be $\mathrm{Me_2AlNBu^i{}_2{\cdot}Me_2AlH}$, $\mathrm{2Me_2AlNBu^i{}_2{\cdot}Me_2AlH}$, and $[\mathrm{Me_2AlNBu^i{}_2{\cdot}Me_2AlH}]_2$. Conversion of these species to $[\mathrm{Me_2AlNBu^i{}_2}]_2$ is complete after 1 month.

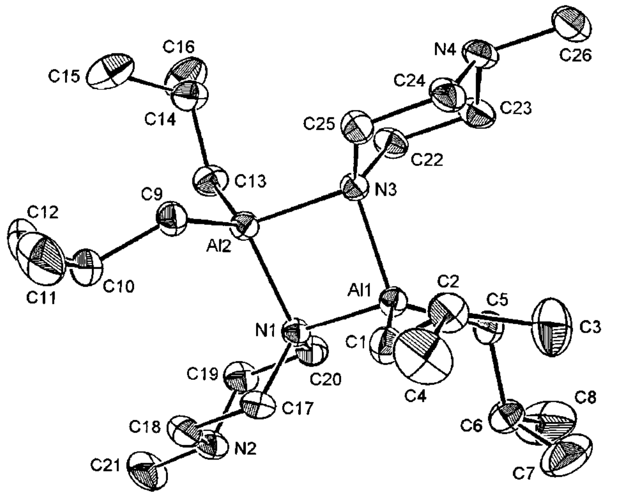

Figure 4. Molecular structure of $[\mathrm{Bu^i{}_2AlN(C_2H_4)_2NMe}]_2$.

These results suggest that with the more bulky $\mathrm{Bu^i{}_2}$-N− group, the As−N cleavage reaction is slower and the $\mathrm{Me_2AlH}$ readily binds to the $\mathrm{Me_2AlNBu^i{}_2}$ moiety. With time the complexed $\mathrm{Me_2AlH}$ reacts with the the parent aminoarsine and with $\mathrm{Me_2AsAsMe_2}$ and $\mathrm{Me_2AsH}$. The latter reactions produce $[\mathrm{Me_2AlAsMe_2}]_3$.

In the $\mathrm{Me_2AlH/Me_2AsNPr^i{}_2}$ reaction system, the NMR spectra indicate initially high-intensity peaks for $\mathrm{Pr^i{}_2NH{\cdot}Me_2AlH}$ and unreacted $\mathrm{Me_2AsNPr^i{}_2}$ and low-intensity resonances for $\mathrm{Me_2AsAsMe_2}$, $\mathrm{Me_2AsH}$, $[\mathrm{Me_2AlAsMe_2}]_3$, $[\mathrm{Me_2AlNPr^i{}_2}]_2$, and several AlN-containing species. After 1 day, the NMR data indicate consumption of $\mathrm{Me_2AsNPr^i{}_2}$, formation of additional amounts of $\mathrm{Me_2AsAsMe_2}$ and $[\mathrm{Me_2AlAsMe_2}]_3$, and generation of $\mathrm{Pr^i{}_2NH}$, which is in exchange with $\mathrm{Pr^i{}_2NH{\cdot}Me_2AlH}$. With time, the resonances associated with the $\mathrm{Pr^i{}_2NH{\cdot}Me_2AlH/Pr^i{}_2NH}$ exchange shift toward those associated with free amine as the intensities of the $[\mathrm{Me_2AlNPr^i{}_2}]_2$ resonances increase. After 6 months, there is 40 mol % conversion of the $\mathrm{Pr^i{}_2N}$ moiety to $[\mathrm{Me_2AlNPr^i{}_2}]_2$, 27% to AlN-containing species, and 33% to $\mathrm{Pr^i{}_2NH}$. There is 74 mol % conversion of the $\mathrm{Me_2As}$ moiety to $\mathrm{Me_2AsAsMe_2}$ and 26% to $[\mathrm{Me_2AlAsMe_2}]_3$.

These results suggest that the nature of the R group in $\mathrm{Me_2AsR}$ influences the course of the reaction in forming Al−N vs Al−As containing products. With increasing steric bulk of R, there is a greater tendency to form $[\mathrm{Me_2AlAsMe_2}]_3$. The resulting free amine further reacts with $\mathrm{Me_2AlH}$ to form an adduct which ultimately is converted to $[\mathrm{Me_2AlR}]_2$. The nature of R also influences both the extent of and time required for Al−N dimer formation.

The reactions of $\mathrm{Bu^i{}_2AlH}$ with $\mathrm{Me_2AsNMe_2}$ and $\mathrm{Me_2AsN(C_2H_4)_2NMe}$ are relatively straightforward. For the RT 1:1 mol ratio reaction of $\mathrm{Bu^i{}_2AlH}$ with $\mathrm{Me_2AsNMe_2}$, the ^{1}H and ^{13}C NMR spectral data indicate almost complete conversion of reactants to $[\mathrm{Bu^i{}_2AlNMe_2}]_2$, $\mathrm{Me_2AsAsMe_2}$, and $\mathrm{Me_2AsH}$ upon mixing. An independent variable-temperature NMR study of the reaction of $\mathrm{Bu^i{}_2AlH}$ with $\mathrm{Me_2NH}$ in 1:1 mol ratio indicated that $[\mathrm{Bu^i{}_2AlNMe_2}]_2$[14] forms above 10 °C. The reaction of $\mathrm{Bu^i{}_2AlH}$ with $\mathrm{Me_2AsN(C_2H_4)_2NMe}$ goes to completion within 1 day.

The reactions of $\mathrm{Bu^i{}_2AlH}$ with $\mathrm{Me_2AsNPr^n{}_2}$ and $\mathrm{Me_2AsNBu^n{}_2}$ are more complicated than for the $\mathrm{Me_2AsNMe_2}$ system. Upon mixing, about 50% of each aminoarsine is consumed to produce $\mathrm{Me_2AsAsMe_2}$, $\mathrm{Me_2AsH}$, and several AlN-containing intermediates. Over a period of 2 weeks, the parent aminoarsine is consumed. Only after the disappearance of the ^1H and ^{13}C NMR resonances for $Me_2AsNPr^n_2$ and $Me_2AsNBu^n_2$ do peaks appear that are assignable to $[Bu^i_2AlNPr^n_2]_2$ and $[Bu^i_2AlNBu^n_2]_2$. Conversion of the AlN-containing intermediates to the respective aminoalane dimers is very slow with only 25% conversion to $[Bu^i_2AlNPr^n_2]_2$ and 28% conversion to $[Bu^i_2AlNBu^n_2]_2$ after 6 months. Me_2AsH does not appear as a final product due to its reactivity with Me_2AsR.[11,20]

$$Me_2AsH + Me_2AsR \rightarrow Me_2AsAsMe_2 + RH \quad (1)$$

The reactions of Bu^i_2AlH with the sterically demanding $Me_2AsNPr^i_2$ and $Me_2AsNBu^i_2$ are more complex. Initially, the NMR data indicate the formation of Me_2AsH, $Me_2AsAsMe_2$, and AlN-containing species. After 1 day, ^1H and ^{13}C NMR resonances are observed for $[Bu^i_2AlAsMe_2]_3$. [See the Experimental Section for an independent synthesis.] Very slow consumption of the parent aminoarsines occurs. Both Me_2AsH and $Me_2AsAsMe_2$ react with Bu^i_2AlH to produce more $[Bu^i_2AlAsMe_2]_3$:

$$3Bu^i_2AlH + 3Me_2AsH \rightarrow [Bu^i_2AlAsMe_2]_3 + 3H_2 \quad (2)$$

$$6Bu^i_2AlH + 3Me_2AsAsMe_2 \rightarrow 2[Bu^i_2AlAsMe_2]_3 + 3H_2 \quad (3)$$

With time, Me_2AsH is consumed. Independent NMR studies of the Bu^i_2AlH/Me_2AsH and $Bu^i_2AlH/Me_2AsAsMe_2$ systems confirm the formation of $[Bu^i_2AlAsMe_2]_3$ *via* eqs 2 and 3, with (2) occurring at a faster rate than (3). The ^{13}C NMR spectra of the $Bu^i_2AlH/Me_2AsNBu^i_2$ system indicate formation of $[Bu^i_2AlNBu^i_2]_2$ after 2.5 months; however, there is no NMR evidence for the existence of an aminoalane dimer in the $Bu^i_2AlH/Me_2AsNPr^i_2$ system. Instead, as more parent aminoarsine is consumed and $[Bu^i_2AlAsMe_2]_3$ forms, peaks assignable to Pr^i_2NH appear. After 6 months, the ^1H and ^{13}C NMR spectra indicate the presence of unreacted aminoarsine, $Me_2AsAsMe_2$, and $[Bu^i_2AlAsMe_2]_3$ in both reaction systems, in addition to $[Bu^i_2AlNBu^i_2]_2$ and $Bu^i_2AlNMe_2 \cdot HAlBu^i_2$ for the $Bu^i_2AlH/Me_2AsNBu^i_2$ system and Pr^i_2NH and uncharacterized AlN-containing species in the $Bu^i_2AlH/Me_2AsNPr^i_2$ system. The more sterically demanding Pr^i_2N moiety in combination with the sterically bulky Bu^i_2Al- group appears to influence the course of the reaction and prevent AlN dimer formation. In the latter case, the presence of Pr^i_2NH suggests that eq 4 represents another route to $[Bu^i_2AlAsMe_2]_3$.

$$3Bu^i_2AlH + 3Me_2AsNPr^i_2 \rightarrow [Bu^i_2AlAsMe_2]_3 + 3Pr^i_2NH \quad (4)$$

These results suggest there are significant differences in the reactivity of Bu^i_2AlH vs Me_2AlH toward the aminoarsines. As noted in Table 1, the time for >90% parent consumption is much longer for the Bu^i_2AlH than the Me_2AlH reaction systems and is dependent upon R for the Bu^i_2AlH systems. The extent of dimer formation in all systems is dependent upon R.

Synthesis of $[Bu^i_2AlR]_2$ from the Reaction of Bu^i_2AlH and Secondary Amines. The $[Bu^i_2AlR]_2$ compounds were synthesized independently by reacting Bu^i_2AlH with the respective secondary amines to confirm the formation of the aminoalane dimers produced in the Bu^i_2AlH/aminoarsine systems. $[Bu^i_2AlNMe_2]_2$[14] and $[Bu^i_2AlNC_5H_{10}]_2$[15] have been prepared to obtain characterization data required in this study.

The ^{13}C and ^1H NMR data, listed in the Experimental Section, are comparable to those reported for the corresponding methylaluminum derivatives, $[Me_2AlR]_2$.[12,13] The EI-MS data for the compounds confirmed their dimeric nature by giving masses for the appropriate dimer minus an isobutyl group ($M^+ - Bu^i$). Al−N compounds of this type typically give mass peaks that result from cleavage of an alkyl ligand off the aluminum atom.[6,13−15,21] The IR data show no peaks in the range 3200−3300 cm^{-1} (indicative of N−H stretches derived from adducted secondary amines)[13] nor in the range 1700−1850 cm^{-1} (derived from Al−H stretches).[22]

Although NMR evidence showed that $[Bu^i_2AlNBu^i_2]_2$ was synthesized by the reaction of Bu^i_2AlH with $HNBu^i_2$, $[Bu^i_2AlNBu^i_2]_2$ could not be isolated from the reaction mixture. Instead, it was synthesized in 76% yield by the reaction of Bu^i_2AlCl with $LiNBu^i_2$. $[Bu^i_2AlNPr^i_2]_2$ could not be synthesized and isolated by either method.

X-ray Crystallographic Studies. The X-ray structures of four aminoalanes were determined in order to identify any structural differences in the compounds arising from the steric requirements of the various amine fragments and of the methyl or isobutyl groups bound to aluminum. ORTEP drawings of $[Me_2AlNC_6H_{12}]_2$, $[Me_2AlN(C_2H_4)_2NMe]_2$, $[Bu^i_2AlNMe_2]_2$, and $[Bu^i_2AlN(C_2H_4)_2NMe]_2$ are given in Figures 1−4, respectively, with selected structural data given in Tables 2−5. The structures of $[Me_2AlNC_6H_{12}]_2$, $[Me_2AlN(C_2H_4)_2NMe]_2$, $[Bu^i_2AlNMe_2]_2$, and $[Bu^i_2AlN(C_2H_4)_2NMe]_2$ each consist of a dimeric four-membered ring Al_2N_2 core. Although there have been several structurally characterized aminoalanes,[23] few have the general formula $[R_2AlNR'_2]_2$ (R, R′ = alkyl) and none have isobutyl groups bound to aluminum. For comparison, Table 5 contains a compilation of selected X-ray structural data for these aminoalanes along with the others derived from secondary amines.[16,17,24−28]

For each of these structures, the Al−N and Al−C bond distances are within the expected range of values for dimeric aminoalanes.[23] The angles about the aluminum and nitrogen atoms in all the compounds are highly distorted from tetrahedral, typical for four-membered

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Table 5. Selected Average X-ray Structural Data (Å, deg) for Al−N Complexes Derived from Secondary Amines

compd	Al−N	Al−C	N−Al−N	Al−N−Al	C−Al−C	ring geometry	ref
$[Me_2AlNMe_2]_2$	1.964	1.963	88.4(3)	91.6(3)	115.9(4)	planar	16
$[Me_2AlNMe_2]_2$	1.958(7)	1.951(12)	88.3(3)	91.7(2)	115.7(5)	planar	17
$[Me_2AlN(C_2H_4)_2C(OCH_2)_2]_2$	1.968(3)	1.949(5)	89.2(1)	90.8(1)	118.7(2)	planar	24
$[Me_2AlN(c\text{-}C_6H_{11})_2]_2$	2.001(2)	1.971(3)	89.3(1)	87.5(1)	109.8(2)	bent	25
$[Me_2AlNC_6H_{12}]_2$	1.962(4)	1.972(7)	88.7(1)	91.3(1)	115.7(3)	planar	this work
$[Me_2AlN(C_2H_4)_2NMe]_2$	1.974(2)	1.958(3)	88.7(1)	91.3(1)	117.7(1)	planar	this work
$[Me_2AlN(SiMe_2H)_2]_2$	1.992(2)	1.959(4)	90.3(1)	89.7(1)	109.9(2)	planar	26
$[Me_2AlN(SiMe_2CH_2)_2]_2$	2.005(3)	1.959(4)	90.5(2)	89.5(3)	104.9(2)	planar	26
$[Et_2AlNPr^{i}_2]_2$	2.007(3)	1.980(5)	88.0(1)	87.8(1)	109.7(2)	bent	27
$[Et_2AlN(C_2H_4)_2S]_2$	1.976(5)	1.977(7)	87.8(2)	89.3(2)	113.0(3)	bent	28
$[Bu^{i}_2AlNMe_2]_2$	1.975(6)	1.969(8)	88.3(3)	91.7(3)	119.9(3)	planar	this work
$[Bu^{i}_2AlN(C_2H_4)_2NMe]_2$	1.984(4)	1.984(5)	87.5(2)	90.6(2)	122.5(2)	bent	this work

rings.[23] The internal Al−N−Al and N−Al−N angles are significantly smaller than the external C−Al−C and C−N−C angles but consistent with previously reported values for this class of compounds.[23] The Al−N−Al and N−Al−N angles are similar in all the compounds with the Al−N−Al angles usually having slightly larger values than the N−Al−N angles. C−Al−C bond angles show the greatest deviation in values, and there appears to be little correlation between the C−Al−C angles and other geometrical parameters, but the compounds listed in Table 5 follow the order of increasing C−Al−C angle according to the aluminum alkyl group: Et < Me < Bu^{i}.

The nature of the ligands on aluminum and nitrogen influences the geometry of the central Al_2N_2 ring. All the Me−Al derivatives contained in Table 5, as well as $[Bu^{i}_2AlNMe_2]_2$, have planar Al_2N_2 rings, except the very sterically demanding cyclohexylamine derivative.[25] However, $[Et_2AlNPr^{i}_2]_2$,[27] $[Et_2AlN(C_2H_4)_2S]_2$,[28] and $[Bu^{i}_2AlN(C_2H_4)_2NMe]_2$, each of which have more sterically demanding ligands on both nitrogen and aluminum, have puckered Al_2N_2 rings. For $[Bu^{i}_2AlN(C_2H_4)_2NMe]_2$, the torsion angle N1−Al1−N3−Al3 is 14.8(2)°.

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Supporting Information Available: Tables listing positional and thermal parameters, complete bond distances and angles, and torsional angles (25 pages). Ordering information is given on any current masthead page.

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