REACTIONS OF BIS(DIMETHYLAMINO)BERYLLIUM WITH SEVERAL ALKYLALUMINUM HYDRIDES, ALUMINUM HYDRIDE TRIMETHYLAMINE, AND TRIMETHYLALUMINUM

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INTRODUCTION

The first report of the preparation of a beryllium hydride was made by Burg and Schlesinger[1] in which beryllium borohydride was synthesized from B_2H_6 and Me_2Be. About ten years later Wiberg and Bauer[2] reported the preparation of $Be(AlH_4)_2$ from $BeCl_2$ etherate and $LiAlH_4$. In the same year, Schlesinger *et al.*[3] attempted the preparation of BeH_2 from Me_2Be and $LiAlH_4$, but an ether-free product could not be obtained.

Coates and Glockling[5] reported the preparation of iso-PrBeH from the pyrolysis of iso-Pr_2Be[4] at 200° and a material containing 96.3 mole percent BeH_2 from the pyrolysis of *tert*-Bu_2Be at 200°. Later, Head, Holley, and Rabideau[6] prepared a product containing a maximum of 80 mole percent BeH_2 from the pyrolysis of *tert*-Bu_2Be at 200°.

Recently, Bell and Coates[7] have reported the preparation of $(MeBeH:NMe_3)_2$ by the treatment of a mixture of $NaBeMeH_2$ and $BeCl_2$ with NMe_3. This compound is easily sublimed and has a low melting point (73°). Very recently, the same authors[8] have reported the preparation of a hydride-rich material from the pyrolysis of Me_4BeH_2 at 200°. A maximum hydride to methyl ratio of 10.4:1 was obtained.

The reactions described in this paper were undertaken to see whether the dimethylamino group of $Be(NMe_2)_2$ would exchange with the hydridic hydrogens on $H_3Al:NMe_3$, $MeAlH_2:NMe_3$, $Me_2AlH:NMe_3$ and Me_2AlH, and with the methyl groups on Me_3Al.

EXPERIMENTAL

Apparatus and reagents

Trimethylaluminum was obtained from the Ethyl Corporation and non-volatile residues were removed by vacuum transfer (0.005 mm) from a 25° trap to a —196° trap. Bis(dimethylamino)beryllium was prepared from diethylberyllium and dimethylamine[9] and diethylberyllium was prepared from $BeCl_2$ and ethylmagnesium bromide[10]. Aluminum hydride trimethylamine was prepared from $LiAlH_4$, $AlCl_3$ and NMe_3 by a method previously described[11].

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Most of the experiments were done in a glass high vacuum system equipped with a Toepler pump connected to a calibrated volume. Because the products obtained were moisture- and oxygen-sensitive, operations outside the vacuum system were carried out in a nitrogen atmosphere drybox.

Elemental analyses were submitted to the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Molecular weights were measured with a Bender-Hobein apparatus which could be loaded in a drybox and stirred magnetically. All determinations were made in freezing benzene. Proton resonance spectra were obtained at 60 Mc with a Varian A-60 spectrometer operating at 42°. All samples were dissolved in benzene approximately 10% by weight.

Reaction of trimethylaluminum with bis(dimethylamino)beryllium

Trimethylaluminum (0.480 g, 6.67 mmole) was transferred under vacuum onto 0.603 g (6.22 mmole) of $Be(NMe_2)_2$ at —196°. The mixture was allowed to warm to 25° and was then heated at 50° for 15 h. During this period, approximately 40% by weight of the reaction mixture sublimed onto the wall of the 50 ml reaction vessel. This material was recovered and resublimed under vacuum at 45°. A crystalline sublimate (m.p. 69–72°) was obtained. (Found: C, 49.49; H, 12.50; Al, 15.80; Be, 5.12; N, 16.55. $C_7H_{21}AlBeN_2$ calcd.: C, 49.68; H, 12.50; Al, 15.94; Be, 5.32; N, 16.55%.) Methanolysis of 0.0830 g of the sublimate gave 31.9 ml CH_4 at S.T.P. [1.42 mmole; calcd. for $Me_3Al:Be(NMe_2)_2$: 1.47 mmole]. Although other reaction mixtures with a 1:1 ratio of Me_3Al to $Be(NMe_2)_2$ were heated to 100°, no trace of Me_2Al–NMe_2, the presence of which would have indicated methyl exchange, was found.

Increasing the molar ratio of Me_3Al to $Be(NMe_2)_2$ to 2:1 yielded a product of different composition. In one experiment, 1.000 g (13.9 mmole) of Me_3Al was heated at 70° for 16 h with 0.530 g (5.47 mmole) of $Be(NMe_2)_2$. The liquid reaction mixture was vacuum-sublimed (0.01 mm) at 25° onto a —78° cold finger. The resulting sublimate (m.p. 35–37°) represented a yield of 85 mole percent. (Found: C, 48.91; H, 12.92; Al, 23.11; Be, 2.91; N, 12.21. $C_{10}H_{30}Al_2BeN_2$ calcd.: C, 49.75; H, 12.55; Al, 22.37; Be, 3.73; N, 11.60%.)

When the above experiment was repeated at a lower temperature, a material of still different composition was obtained. In this case, while 1.000 g (13.9 mmole) of Me_3Al and 0.610 g (6.30 mmole) of $Be(NMe_2)_2$ heated at 50° for 40 h, a material was vacuum-sublimed (0.01 mm) at 25° onto a —78° cold finger (m.p. 35–37°) and gave the following analysis: Found: C, 48.85; H, 12.18; Al, 27.47; Be, 1.66; N, 9.77. $C_{16}H_{48}Al_4BeN_2$ calcd.: C, 49.85; H, 12.55; Al, 27.99; Be, 2.34; N, 7.27%. The yield of sublimate was approximately 75% by weight based on the starting materials.

The NMR spectra of the products obtained from the first two experiments are given below:

Compound	*Peaks (ppm; $\delta_{benzene} = 0$)*		*Ratios*	*NMe/AlMe*
$C_7H_{21}AlBeN_2$	8.72; 8.78; 8.85; 8.95	(AlMe)	1:2:1:2	
	5.08; 5.12; 5.20	(NMe)	4:1:4	1.35[a]
$C_{10}H_{30}Al_2BeN_2$	7.69; 7.85; 7.96	(AlMe)	15:5:1	
	5.05; 5.11; 5.18	(NMe)	2.5:4:1	0.70[b]

[a] Calcd. 1.33 for $Me_3Al:Be(NMe_2)_2$. [b] Calcd. 0.75 for $(Me_3Al)_2Be(NMe_2)_2$.

eaction of dimethylaluminum hydride with bis(dimethylamino)beryllium

Dimethylaluminum hydride (1.97 g, 34.0 mmole) prepared from LiAlH$_4$ and imethylaluminum[12], was vacuum-transferred into a reaction vessel containing 1.50 g 5.5 mmole) of Be(NMe$_2$)$_2$ and 20 ml of hexane. The mixture was kept for two days t room temperature and then heated at 100° for 11 h. During this period, the hexane istilled and some methane evolved. The mixture was vacuum-sublimed (0.001 mm) nto a —78° cold finger over a temperature range of 25–120°. The sublimate (2.3 g) as identified as Me$_2$Al–NMe$_2$ by comparison of its infrared spectrum with the spec-um of an authentic sample, and the residue (0.9 g), which solidified during the ublimation, gave an elemental analysis in agreement with the formula C$_8$H$_{27}$AlBe$_3$N$_2$. ound: C, 46.08; H, 13.14; Al, 13.26; Be, 13.05; N, 13.70. Calcd.: C, 46.80; H, 13.26; l, 13.14; Be, 13.16; N, 13.64%.)

eaction of dimethylaluminum hydride trimethylamine with bis(dimethylamino)beryllium

Into a 50 ml flask containing 1.00 g (10.3 mmole) of Be(NMe$_2$)$_2$ and 20 ml of -heptane at —196° was vacuum-transferred 1.20 g (10.3 mmole) of Me$_2$AlH:NMe$_3$. he mixture was heated to 50° for 15 h and then heated to 80° until all the heptane ad been transferred to a trap. The mixture was given a final heating at 110° for ve h. During the periods at 80° and 110°, 10.2 mmole of NMe$_3$ evolved. Vacuum ublimation (0.001 mm) of the crude product at 50° yielded 0.6 g of Me$_2$Al–NMe$_2$, hich was identified by its infrared spectrum and melting point (m.p. 146–150°). he sublimation was continued at 160° and 0.11 g of material (m.p. 155–170°) was ollected. Elemental analysis gave results which are in best agreement with the ormula C$_8$H$_{26}$AlBe$_2$N$_3$. (Found: C, 46.72; H, 13.04; Al, 13.29; Be, 5.13; N, 19.99*. alcd.: C, 45.90; H, 12.52; Al, 12.89; Be, 8.61; N, 20.08%.) The sublimation residue pproximately 1 g) was a sticky, viscous material. The NMR spectrum of C$_8$H$_{26}$AlBe$_2$N$_3$ given below:

eaks (ppm; $\delta_{benzene} = 0$)	*NMe/AlMe area ratio*
68 (AlMe)	3:1
85; 4.72(sh) (NMe)	

eaction of methylaluminum dihydride trimethylamine with bis(dimethylamino)beryllium

Four experiments were conducted employing different reaction conditions and arting ratios of reagents.

In the first experiment, 2.15 g (21.0 mmole) of MeAlH$_2$:NMe$_3$, prepared from e$_3$Al:NMe$_3$ and AlH$_3$:NMe$_3$[11] was transferred under vacuum to a 50 ml vessel ontaining 2.00 g (21.0 mmole) of Be(NMe$_2$)$_2$ at —196°. The mixture was warmed to om temperature and NMe$_3$ evolution commenced as soon as the MeAlH$_2$:NMe$_3$ elted. The mixture was allowed to stand until NMe$_3$ evolution ceased and then

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[*] Although the aluminum values are higher and the beryllium values lower than calculated r the empirical formulas, the total metal content does not equal that calculated for Al and Be. nce the metals are weighed as a mixture of their oxides and the Al is determined by EDTA tration, with Be calculated by difference, the data in this analysis and two others (submitted the same time) indicate difficulties with total oxides and the EDTA titration.

vacuum-sublimed (0.001 mm) at 25° for 6 h onto a —78° cold finger. A mixture of liquid and solid materials deposited on the cold finger and about an equal amount of material did not sublime. Elemental analysis of the residue (m.p. ~ 90°) gave results which gave closest agreement with the formula $C_7H_{24}AlBe_2N_3$. (Found: C, 44.11; H, 12.20; Al, 10.55; Be, 8.76; N, 20.98. Calcd.: C, 43.05; H, 12.39; Al, 13.82; Be, 9.23; N, 21.52%.)

In the second experiment, 1.35 g (13.5 mmole) of $MeAlH_2$:NMe_3 dissolved in 15 ml of *n*-heptane was vacuum-transferred to a 50 ml flask containing 1.0 g (10.3 mmole) of $Be(NMe_2)_2$ at —196°. As the mixture was heated to 80°, the heptane was removed to a trap and trimethylamine evolved. The temperature was kept at 80° until NMe_3 evolution ceased and the melt was allowed to cool to 25° where it partially crystallized. Vacuum sublimation (0.001 mm) of the crude product at 25° onto a —78° cold finger yielded a small quantity of slushy solid. The residue, which still contained some liquid, was dried by placing it on a sintered glass filter and evacuating until no more liquid passed. The residue was then vacuum-sublimed at 130° onto a —15° cold finger. An elemental analysis of the sublimate (m.p. 154–160°) agreed with the values calculated for $C_7H_{24}AlBe_2N_3$. (Found: C, 43.78; H, 12.13; Al, 13.74; Be, 9.33; N, 20.76. Calcd.: C, 43.05; H, 12.39; Al, 13.82; Be, 9.23; N, 21.52%.) When the sublimate was reheated under vacuum at 140°, only a portion sublimed and dimethylamine evolved. The residue would not melt up to 265°, but turned yellow at this temperature. The second sublimate was confirmed by analysis to be $C_7H_{24}AlBe_2N_3$. (Found: C, 43.34; H, 12.07; Al, 13.63; Be, 9.20; N, 21.50%.)

In another experiment conducted in a similar manner with equimolar quantities (15 mmole) of $MeAlH_2$:NMe_3 and $Be(NMe_2)_2$, 13 mmole of NMe_3 was obtained and the crude reaction product was purified by two different methods. One portion (0.23 g) was washed with *n*-pentane on a sintered glass vacuum filter until it appeared to be dry. Elemental analysis of this material agreed with the formula $C_7H_{24}AlBe_2N_3$. (Found: C, 43.51; H, 12.36; Al, 15.02; Be, 6.21; N, 20.65%.) The remaining crude product was vacuum-sublimed (0.001 mm) from 110° onto a —15° cold finger. A few drops of liquid appeared at the start of the sublimation, but these were wiped off and the heating continued to 145°. A sublimate (0.45 g) collected between 120 and 145°, leaving 1.0 g of a glass residue. Elemental analysis of the sublimate again showed it to be $C_7H_{24}AlBe_2N_3$. (Found C, 43.19; H, 12.50; Al, 14.61; Be, 6.34; N, 20.93%.) A hydrochloric-acid hydrolysis of 0.1418 g of sublimate, yielded 26 mmole of a mixture of hydrogen and methane. The calculated amounts of gas, assuming the presence of three hydridic hydrogen atoms and one hydrolyzable methyl group on Al or Be in each formula weight (195) of $C_7H_{24}AlBe_2N_3$, is 29 mmole. A mass spectrum of the mixture showed a composition of approximately 70% H_2 and 30% methane. NMR spectra of the sublimate and pentane-washed product are given below:

Sample	*Peaks (ppm; $\delta_{benzene} = 0$)*	*Peak area ratios*	*NMe/AlMe area ratios*
Sublimate	4.73, 4.87 (NMe) 7.66, 7.70 (AlMe)	1:1 3.5:1	 6:1
Washed product	4.26, 4.22; 4.73, 4.88 (NMe) 7.67, 7.72 (AlMe)	1:5:30:40 2:1	 7:1

A fourth experiment was conducted under conditions similar to those of the second experiment described above, but the molar ratio of $MeAlH_2:NMe_3$ to $Be(NMe_2)_2$ was 2:1. The compound $C_7H_{24}AlBe_2N_3$ was again obtained (m.p. 151–154°) (Found: C, 42.78; H, 12.30; Al, 13.62; Be, 9.20; N, 21.40 %.)

Reaction of aluminum hydride trimethylamine with bis(dimethylamino)beryllium

Four experiments were carried out, two with equimolar amounts of starting materials and two with two moles of $H_3Al:NMe_3$ per mole of $Be(NMe_2)_2$.

In the first equimolar experiment, 1.08 g (12.1 mmoles) of $H_3Al:NMe_3$ was mixed with 1.00 g (10.3 mmole) of $Be(NMe_2)_2$. The reaction vessel was placed on a high-vacuum line and 20 ml of *n*-heptane was transferred to the mixture which was at —196°. The solution was heated at 55° for 2 h and the solvent and approximately 0.5 g of $H_3Al(NMe_3)_2$ were removed from the reaction vessel. The crude product was vacuum-sublimed (0.001 mm) at 25° onto a —78° cold finger and approximately 0.2 g of $H_3Al(NMe_3)_2$ sublimed immediately. The sublimation was continued at 75° for three h and 1.0 g of sublimate (m.p. 131–136°) was obtained whose elemental analysis gave closest agreement with the formula $C_5H_{18}AlBeN_2$. (Found: C, 42.16; H, 11.89; Al, 19.69; Be, 6.77; N, 20.48. Calcd.: C, 42.52; H, 12.14; Al, 19.10; Be, 6.38; N, 19,84 %.) Methanolysis of 0.2085 g (1.45 mmole $C_5H_{18}AlBeN_2$) gave 4.43 mmole of hydrogen (calcd. 4.45 mmole if three hydridic hydrogen atoms are present). A continuation of the sublimation to 115° yielded 0.1 g of sublimate melting at approximately 190°.

The second equimolar reaction was carried out by mixing 1.00 g (11.2 mmole) of $H_3Al:NMe_3$ with 0.980 g (10.1 mmole) of $Be(NMe_2)_2$ in a 50 ml flask and heating at 85° under vacuum for 16 h without solvent. During this period 2.52 mmole of hydrogen and 7.16 mmole NMe_3 evolved, also some $H_3Al(NMe_3)_2$ sublimed into the cold neck of the flask. Vacuum sublimation (0.01 mm) at 75° yielded approximately 0.2 g of sublimate (m.p. 100–130°), but by raising the sublimation temperature to 130° for 16 h approximately one gram of sublimate was obtained on the —15° cold finger (m.p. 192–195°). Elemental analysis of this substance gave closest agreement with the formula $C_6H_{22}AlBe_2N_3$. (Found: C, 40.32; H, 11.74; Al, 14.77; Be, 9.96; N, 23.00. Calcd.: C, 39.76; H, 12.23; Al, 14.89; Be, 9.94; N, 23.19 %.) Methanolysis of 0.1455 g (0.803 mmole) of $C_6H_{22}AlBe_2N_3$ gave 3.78 mmole of hydrogen. (Calcd.: 3.22 mmole for four active hydrogen atoms per formula weight.)

The first 2:1 reaction was conducted by mixing 2.07 g (23.2 mmole) of $H_3Al:NMe_3$, 1.06 g (10.7 mmole) of $Be(NMe_2)_2$, and 15 ml of *n*-octane in a 50 ml flask. The flask was evacuated at —196° and the contents were heated at 50° for three h. During this period, 0.30 mmole of hydrogen and 8.85 mmole of NMe_3 evolved. The solvent and some $H_3Al(NMe_3)_2$ were removed at 25° by vacuum transfer and the solid crude product was vacuum-sublimed (0.01 mm) at 45° for an hour to remove any more $H_3Al(NMe_3)_2$ and then sublimed at 70° for 20 h. A white crystalline sublimate was obtained (m.p. 125–138°) whose elemental analysis agreed with the formula $C_5H_{18}AlBeN_2$. (Found: C, 42.38; H, 11.84; Al, 18.43; Be, 6.62; N, 20.05. Calcd.: C, 42.52; H, 12.14; Al, 19.10; Be, 6.38; N, 19.84%.) Methanolysis of 0.2343 g (1.68 mmole of $C_5H_{18}AlBeN_2$) yielded 5.85 mmole of hydrogen (calcd.: 5.05 mmole assuming three active hydrogen atoms).

The second 2:1 reaction was carried out by mixing 2.19 g (14.8 mmole) of

TABLE 2

SUMMARY OF REACTIONS OF $Be(NMe_2)_2$ WITH ALUMINUM HYDRIDES

Reagents molar ratio (mmole)		*Reaction conditions*	*Products*			*Structural formulas*
			Gases (mmole)	*Sublimates*	*Residues*	
Me_3Al 6.67	+ $Be(NMe_2)_2$ 6.22	−196 to 50° for 15 h	None	$C_7H_{21}AlBeN_2$ m.p. 69–72°	60 wt. % Not analyzed	$C_7H_{21}AlBeN_2$ $Me_3Al:Be(NMe_2)_2$
Me_3Al 13.9	+ $Be(NMe_2)_2$ 5.47	−196 to 70° for 16 h	None	$C_{10}H_{30}Al_2BeN_2$ m.p. 35–37°	15 wt. % Not analyzed	$C_{10}H_{30}Al_2BeN_2$ $(Me_3Al)_2:Be(NMe_2)_2$
Me_3Al 13.9	+ $Be(NMe_2)_2$ 6.30	−196° to 50° for 40 h	None	$C_{16}H_{48}Al_4BeN_2$ m.p. 35–37°	20 wt. % Not analyzed	$C_{16}H_{48}Al_4BeN_2$ $(Me_3Al)_4:Be(NMe_2)_2$[a]
Me_2AlH 34.0	+ $Be(NMe_2)_2$ 15.5	−196° to 100° for 11 h	CH_4[c]	$Me_2Al·NMe_2$ yield 2.3 g	$C_8H_{27}AlBe_3N_2$ yield 0.9 g	None[b]
$Me_2AlH:NMe_3$ 10.3	+ $Be(NMe_2)_2$ 10.3	−196 to 110° for 5 h	NMe_3 10.2	$Me_2Al·NMe_2$ Yield 0.60 g $C_8H_{26}AlBe_2N_3$ Yield 0.11 g m.p. 155–170°	1.0 g Not analyzed	$C_8H_{26}AlBe_2N_3$ $Me_2AlNMe_2:(HBeNMe_2)_2$
$MeAlH_2:NMe_3$ 21.0	+ $Be(NMe_2)_2$ 21.0	−196° to 25° until NMe_3 evolution stopped	NMe_3[c]	solid–liquid mixture not analyzed	$C_7H_{24}AlBe_2N_3$ m.p. 90°	$C_7H_{24}AlBe_2N_3$ $MeHAlNMe_2:(HBeNMe_2)_2$
$MeAlH_2:NMe_3$ 13.5	+ $Be(NMe_2)_2$ 10.3	−196 to 80° until NMe_3 evolution stopped	NMe_3[c]	$C_7H_{24}AlBe_2N_3$ m.p. 154–160°	None	$MeHAlNMe_2:(HBeNMe_2)_2$
$MeAlH_2:NMe_3$ 15.0	+ $Be(NMe_2)_2$ 15.0	−196 to 25°	NMe_3 13.0	$C_7H_{24}AlBe_2N_3$	None	$MeHAlNMe_2:(HBeNMe_2)_2$
$MeAlH_2:NMe_3$ 30.0	+ $Be(NMe_2)_2$ 15.0	−196 to 80°	NMe_3[c]	$C_7H_{24}AlBe_2N_3$	None	$MeHAlNMe_2:(HBeNMe_2)_2$
$H_3Al:NMe_3$ 11.2	+ $Be(NMe_2)_2$ 10.1	25 to 85° for 16 h	H_2 2.52 NMe_3 7.16	$H_3Al:(NMe_3)_2$ (not weighed) $C_6H_{22}AlBe_2N_3$ m.p. 192–195°, yield ~ 1 g	None	$C_6H_{22}N_3AlBe_2$ $H_2AlNMe_2:(HBeNMe_2)_2$
$H_3Al:NMe_3$ 12.1	+ $Be(NMe_2)_2$ 10.3	25 to 55° for 2 h	None	$H_3Al:(NMe_3)_2$ yield 0.70 g $C_6H_{18}AlBeN_2$ m.p. 131–136° yield 1.0 g	0.3 g Not analyzed	
$H_3Al:NMe_3$ 23.2	+ $Be(NMe_2)_2$ 10.7	25 to 50° for 3 h	H_2 0.3 NMe_3 8.85	$H_3Al:(NMe_3)_2$ (not weighed) $C_6H_{18}AlBeN_2$ m.p. 125–138°	Not weighed	
$H_3Al:(NMe_3)_2$ 14.8	+ $Be(NMe_2)_2$ 7.42	25 to 55° for 3 h	H_2 1.43 NMe_3 7.20	$C_6H_{22}AlBe_2N_3$ m.p. 191–194° yield ~ 1 g	None	$H_2AlNMe_2:(HBeNMe_2)_2$

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[a] Sublimate may also be a mixture of $Me_3Al + C_{10}H_{30}Al_2BeN_2$. [b] Presence of Me_2AlNMe_2 shows hydride exchange with $Be(NMe_2)_2$. [c] Not measured.

$H_3Al(NMe_3)_2$ with 0.720 g (7.42 mmole) of $Be(NMe_2)_2$ and 15 ml of *n*-octane in a 50 ml flask, evacuating at −196°, followed by heating at 55° for three h. During the heating, 1.43 mmole of hydrogen and 7.20 mmole of NMe_3 evolved and after this period, the solvent and any unreacted $H_3Al(NMe_3)_2$ were removed at 25° by vacuum transfer to a −196° trap. The crude product was vacuum-sublimed (0.01 mm) at 115° onto a −15° cold finger. Elemental analysis of the sublimate (yield: approximately 1 g; m.p. 191–194°) gave results which are in fair agreement with the formula $C_6H_{22}AlBe_2N_3$. (Found: C, 42.88; H, 11.92; Al, 14.01; Be, 9.95; N, 21.15. Calcd.: C, 39.76; H, 12.23; Al, 14.89; Be, 9.94; N, 23.19%.)

The NMR spectra of $C_6H_{22}AlBe_2N_3$ and $C_5H_{18}AlBeN_2$ are given below:

Sample	*NMe peaks (ppm; $\delta_{benzene} = 0$)*	*Peak ratios*
$C_5H_{18}AlBeN_2$	4.77, 4.90	1:2
$C_6H_{22}AlBe_2N_3$	4.75, 4.90	2:1

Molecular weight data, obtained from those compounds which were soluble in benzene, are shown in Table 1 below:

TABLE 1

MOLECULAR WEIGHTS OF MIXED BERYLLIUM ALUMINUM COMPOUNDS

Compound	*Molecular weight*		*x*	*Sample conc. (molal)*
	Found	*Calcd.*		
$C_{10}H_{30}Al_2BeN_2$	246	240	1.02	0.0233
	252	240	1.05	0.0273
$C_7H_{24}AlBe_2N_3$	456	195	2.34	0.0755
	460	195	2.36	0.0403
$C_5H_{18}AlBeN_2$	266	142	1.87	0.0572
	273	142	1.92	0.0410
$C_6H_{22}AlBe_2N_3$	629	181	3.47	0.0224
	639	181	3.53	0.0467

DISCUSSION

From the data obtained on the reactions of $Be(NMe_2)_2$ with $AlH_3{:}NMe_3$, $MeAlH_2{:}NMe_3$, Me_2AlH, $Me_2AlH{:}NMe_3$, and Me_3Al, summarized in Table 2, it is apparent that, under similar conditions, hydride exchange occurs, but methyl exchange does not. In the reaction between Me_3Al and $Be(NMe_2)_2$, the NMR data indicate the compound whose formula was $C_7H_{21}AlBeN_2$ is $Me_3Al{:}Be(NMe_2)_2$ and the compound $C_{10}H_{30}Al_2BeN_2$ is $(Me_3Al)_2{:}Be(NMe_2)_2$. Although some reaction mixtures were heated to 100°, there was no sign of $Me_2Al{-}NMe_2$, which would have resulted from exchange, in the sublimate. In fact, there is some indication that $(Me_3Al)_2{:}Be(NMe_2)_2$ is a labile material to which more Me_3Al molecules may be bonded. The material, $C_{16}H_{48}Al_4BeN_2$, obtained from a 2:1 reaction of Me_3Al with $Be(NMe_2)_2$, may be a 4:1 complex, $(Me_3Al)_4{:}Be\ (NMe_2)_2$, or a mixture of $(Me_3Al)_2{:}Be(NMe_2)_2$ and uncomplexed Me_3Al.

The reactions of $Be(NMe_2)_2$ with Me_2AlH and $Me_2AlH:NMe_3$ demonstrate that exchange has occurred, because substantial amounts of $Me_2Al{-}NMe_2$ were obtained. Although no proof has been found for the structure of the sublimate with the empirical formula $C_8H_{26}AlBe_2N_3$, the atomic ratios of Al:Be:N of 1:2:3 suggest the formula $(Me_2AlNMe_2)(HBeNMe_2)_2$.

The reaction of $MeAlH_2:NMe_3$ with $Be(NMe_2)_2$ provides no positive evidence that exchange has occurred by the isolation of $MeAlH{-}NMe_2$ or $MeAl(NMe_2)_2$, but the empirical formula of the sublimate $C_7H_{24}AlBe_2N_3$ has the same Al:Be:N ratio as $C_8H_{26}AlBe_2N_3$ and, by analogy, the formula for this material is $(MeAlHNMe_2)(HBeNMe_2)_2$.

The reaction of $H_3Al:NMe_3$ and $H_3Al(NMe_3)_2$ with $Be(NMe_2)_2$ yields two products, one of which appears to be similar to those obtained from the reactions with Me_2AlH and $MeAlH_2:NMe_3$. The sublimate, $C_6H_{22}AlBe_2N_3$, would have the formula $(H_2AlNMe_2)(HBeNMe_2)_2$.

With the data available, it has not been possible to assign a reasonable structural formula for the compound $C_5H_{15}AlBeN_2$.

To summarize, there appear to be two reaction paths, one leading to 1:1 adducts such as $Me_3Al:Be(NMe_2)_2$, and the other, where hydride exchange is possible, to compounds having an Al:Be ratio of 1:2. This general reaction, which is independent of the ratio of starting materials and generally requires temperatures near 100°, may be summarized by the equation:

$$Be(NMe_2)_2 + Me_{3-n}AlH_n(NMe_3) \rightarrow Me_{3-n}AlH_{n-1}NMe_2:(HBeNMe_2)_2 + \text{Al-rich residue}(+ NMe_3).$$

The general complexity of the NMR proton spectra has not enabled us to make any clear choices among the many structural formulas that are possible. Part of the difficulty in making interpretations of the spectra is the fact that Al-H and Be-H protons are not resolved. The NMR spectra have been of some use in establishing empirical formulas for those compounds containing AlMe and NMe protons.

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SUMMARY

The reactions of $Be(NMe_2)_2$ with $H_3Al:NMe_3$, $MeAlH_2:NMe_3$, $Me_2AlH:NMe_3$, Me_2AlH, and Me_3Al have led to the following compounds and complexes which have been assigned the formulas: $H_2AlNMe_2:(HBeNMe_2)_2$, $MeHAlNMe_2:(HBeNMe_2)_2$, $Me_2AlNMe_2:(HBeNMe_2)_2$, $(Me_3Al)_2:Be(NMe_2)_2$, and $Me_3Al:Be(NMe_2)_2$. These studies indicate incomplete hydride exchange between aluminum hydrides and $Be(NMe_2)_2$, but no exchange with Me_3Al under similar conditions.

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