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Aminodimethylalane (Me_2AlNH_2): Matrix Isolation and *ab Initio* Calculations

Jens Müller

Contribution from the Institut für Anorganische Chemie der Technischen Hochschule Aachen, D-52056 Aachen, Germany

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Abstract: The calculated harmonic frequencies (RMP2(fc)/6-31G*) of the three isomeric alanes $Me_3Al\cdot NH_3$, $Me_3Al\cdot{}^{15}NH_3$, and $Me_3Al\cdot ND_3$ are assigned to the measured IR absorptions of these compounds, matrix isolated in argon at 10 K. The results are compared with the known literature data. The irradiations of the matrix-isolated amine adducts yield aminodimethylalane. The experimental IR data of the three isotopomers Me_2AlNH_2, $Me_2Al^{15}NH_2$, and Me_2AlND_2 agree well with the calculated harmonic frequencies. Elucidated from *ab initio* calculations, Me_2AlNH_2 is a C_{2v}-symmetrical molecule with an AlN bond length of 1.790 Å. This AlN distance is 15% shorter than that of the starting compound $Me_3Al\cdot NH_3$ (2.106 Å). The predicted AlN rotation barrier of 40.7 kJ mol^{-1} is much lower than the known barriers of the isoelectronic silaalkenes and the lighter congeners, aminoboranes and alkenes, respectively.

Introduction

The first aminoalane was prepared by Wiberg over half a century ago.[1] He investigated the pyrolysis of $Me_3Al\cdot NH_3$, which yielded the amino- and iminoalane and, finally, aluminium nitride. Either the alkane elimination or the simple “salt synthesis”, starting from alkali metal amides and aluminium halides, are the common preparation methods for aminoalanes. To date, a large variety of compounds with the general formula $R_2Al(NR'R'')$ are known. They usually exist as dimers or trimers.[2] Power et al. isolated the first monomeric derivatives using sterically demanding substituents.[3] The primary focus of Power’s work had been the study of a π-interaction between aluminium and nitrogen. Based on ^{1}H-NMR experiments, it was possible to estimate an AlN rotation barrier of 38−42 kJ mol^{-1} for a certain derivative.[3] Other examples of unassociated alanes with known structural details are $Al[N(SiMe_3)_2]_3$, $Al(N\mathit{i}Pr_2)_3$, and $MesAl[N(SiMe_3)_2]_2$.[4] These substances exhibit trigonal-planar coordinated Al and N atoms. However, the two respective planes are twisted in the AlN direction and there is no striking correlation between the torsion angles and the AlN bond lengths. Indeed, the bulky ligands provide monomeric species, necessary to examine a possible π-interaction, but the steric effects may be of the same order of magnitude as the electronic effects one is interested in and both effects might be indistinguishable.

$$\mathrm{Me_3Al\cdot NH_3 \longrightarrow (Me_2AlNH_2)_x \longrightarrow (MeAlNH)_y \longrightarrow AlN} \qquad (1)$$

This report describes the synthesis and characterization of aminodimethylalane (Me_2AlNH_2) in an argon matrix, the first monomeric aminoalane without sterically demanding substituents.

Results and Discussion

Starting Compounds. The three isomeric alanes $Me_3Al\cdot NH_3$, $Me_3Al\cdot{}^{15}NH_3$, and $Me_3Al\cdot ND_3$ are readily accessible by the reaction of trimethylalane with ammonia at low temperature. Subsequent sublimation (30 °C, 10^{-3} mbar) gives the pure compounds in high yields (≥95%). Though ammonia trimethylalane has been known for more than five decades[1] and has been reinvestigated several times, the purification and characterization by standard methods has not been described in the literature.[5] We checked the purity of the alanes by NMR (^{1}H, ^{13}C, ^{27}Al), MS, and CHN elemental analysis. As expected, there is a broad resonance in the ^{13}C-NMR spectra and a singlet in the ^{27}Al-NMR spectra for each isotopomer. The ^{27}Al-NMR shift of δ 168 is in the typical range for tetracoordinated aluminium with these kinds of ligands.[6] The isotopic labeling is revealed by the ^{1}H-NMR measurements: two singlets for $Me_3Al\cdot NH_3$, one singlet for the methyl groups with a sharp doublet for the $H_3{}^{15}N$ protons of $Me_3Al\cdot{}^{15}NH_3$, and only one singlet for $Me_3Al\cdot ND_3$. Corresponding results are obtained from the mass spectra where $M^+ - CH_3$ with *m/e* 74, 75, and 77 for $Me_3Al\cdot NH_3$, $Me_3Al\cdot{}^{15}NH_3$, and $Me_3Al\cdot ND_3$, respectively, is the heaviest fragment.

With respect to our *ab initio* calculation at the RMP2(fc)/6-31G* level, ammonia trimethylalane has C_{3v} symmetry (Figure 1).[7] The AlC_3 skeleton of the molecule deviates only slightly from planarity (C−Al−C = 117.3°). The AlN distance of 2.106 Å is relatively long compared to the common range of simple

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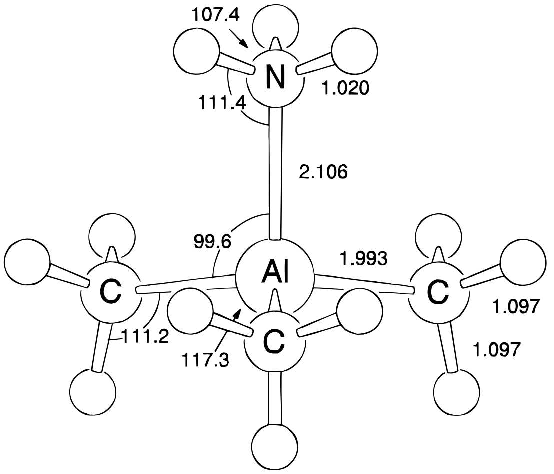

Figure 1. Selected bond distances (Å) and angles (deg) for the equilibrium geometry of $Me_3Al{\cdot}NH_3$ (C_{3v} point group) calculated at the RMP2(fc)/6-31G* level.

amine adducts, which are known to have AlN bond lengths between 1.94 and 2.10 Å.[8] The experimental structure of $Me_3Al{\cdot}NH_3$ is unknown, however, the isomeric molecule $H_3Al{\cdot}NMe_3$ is well-known in the literature.[9] Elucidated from gas-phase electron diffraction, this aluminium hydride exhibits C_{3v} symmetry with a flat AlH_3 pyramid (H−Al−H = 114.1°) and an AlN bond length of 2.063 Å.[9a] These results are in accord with high-level *ab initio* calculations published recently (e.g., AlN = 2.063 Å, H−Al−H = 117.1° at the CISD/DZP level).[9c] The authors searched for other possible equilibrium geometries by using different methyl-group conformations, but only one configuration gave energy minima on the potential surfaces at several levels of theory. As expected, our calculation for $Me_3Al{\cdot}NH_3$ reveals a similar C_{3v}-symmetrical equilibrium geometry, especially concerning the methyl-group conformations (Figure 1).

Using the conventional matrix-isolation technique (Experimental Section) we prepared argon matrices of the three isotopomers $Me_3Al{\cdot}NH_3$, $Me_3Al{\cdot}{}^{15}NH_3$, and $Me_3Al{\cdot}ND_3$. Figure 2b−d depicts the corresponding IR spectra measured at 10 K in the range of 250−4000 cm^{-1}.

Ammonia trimethylalane is expected to have 10 A_1, 5 A_2, and 15 E modes, in which the A_2 modes are IR inactive. For comparison with experiment we calculated the harmonic vibrational frequencies of the adducts at the RMP2(fc)/6-31G* level.[7] Table 1 compiles these data and Figure 2a depicts the scaled theoretical IR spectrum of $Me_3Al{\cdot}NH_3$. Based on these predictions we assigned the detected IR bands and the results are given in Table 2.

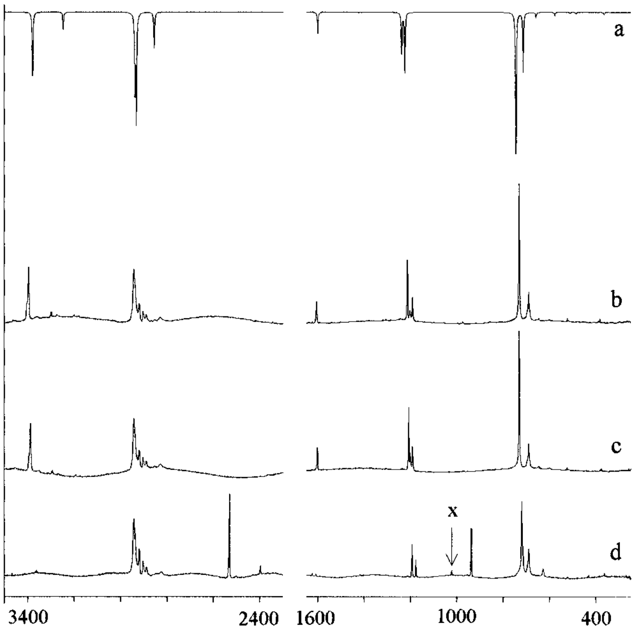

Figure 2. IR spectra of ammonia trimethylalane: *X*-axis, 250−1650 cm^{-1} and 2300−3500 cm^{-1}; *Y*-axis, Absorbance (dimensionless). The absorptions of the 2300−3600-cm^{-1} region are enhanced by a factor of 3 relative to the 250−1650-cm^{-1} range. Spectrum a: $Me_3Al{\cdot}NH_3$ calculated at the RMP2(fc)/6-31G* level (frequencies scaled by 0.93, half band width of 2 cm^{-1}). Spectrum b: $Me_3Al{\cdot}NH_3$ in argon at 10 K. Spectrum c: $Me_3Al{\cdot}{}^{15}NH_3$ in argon at 10 K. Spectrum d: $Me_3Al{\cdot}ND_3$ in argon at 10 K. x (1022.0 cm^{-1}) indicates small amounts of $Me_3Al{\cdot}ND_2H$.[10]

Table 1. Harmonic Frequencies (cm^{-1}) and Intensities (in Parentheses, km mol^{-1}) Calculated at the RMP2(fc)/6-31G* Level

	$Me_3Al{\cdot}NH_3$	$Me_3Al{\cdot}{}^{15}NH_3$	$Me_3Al{\cdot}ND_3$
A_1: ν_1	178.1 (11.8)	177.2 (11.5)	175.3 (11.4)
ν_2	392.8 (6.8)	386.0 (7.2)	371.3 (5.6)
ν_3	521.8 (4.4)	521.8 (4.4)	521.7 (4.2)
ν_4	768.8 (180.2)	768.8 (180.2)	768.8 (181.0)
ν_5	1317.8 (102.3)	1314.3 (160.2)	1322.4 (2.7)
ν_6	1331.9 (129.1)	1328.0 (68.1)	1014.8 (136.9)
ν_7	1531.2 (1.4)	1531.2 (1.4)	1531.2 (1.4)
ν_8	3071.1 (0.2)	3071.1 (0.2)	3071.1 (0.2)
ν_9	3160.0 (74.7)	3160.0 (74.7)	3160.0 (74.7)
ν_{10}	3490.7 (18.3)	3488.3 (17.6)	2496.1 (15.1)
A_2: ν_{11}	82.5 (0.0)	82.5 (0.0)	59.3 (0.0)
ν_{12}	113.8 (0.0)	113.8 (0.0)	112.9 (0.0)
ν_{13}	596.3 (0.0)	596.3 (0.0)	596.3 (0.0)
ν_{14}	1521.8 (0.0)	1521.8 (0.0)	1521.8 (0.0)
ν_{15}	3151.4 (0.0)	3151.4 (0.0)	3151.4 (0.0)
E:[a] ν_{16}	117.3 (1.7)	117.2 (1.8)	115.6 (3.4)
ν_{17}	131.6 (9.8)	130.5 (9.0)	124.8 (4.6)
ν_{18}	171.3 (0.4)	171.2 (0.5)	168.3 (1.3)
ν_{19}	550.8 (3.9)	549.5 (4.4)	454.4 (8.4)
ν_{20}	621.7 (10.5)	621.5 (10.0)	616.9 (5.8)
ν_{21}	708.7 (17.2)	707.2 (19.3)	674.8 (41.3)
ν_{22}	802.0 (432.4)	801.3 (431.4)	788.8 (345.4)
ν_{23}	1317.3 (86.5)	1317.3 (86.5)	1317.3 (83.3)
ν_{24}	1518.4 (1.9)	1518.4 (1.9)	1518.5 (1.5)
ν_{25}	1529.9 (0.9)	1529.9 (0.9)	1530.3 (2.2)
ν_{26}	1721.1 (68.1)	1718.1 (67.4)	1246.2 (39.6)
ν_{27}	3070.1 (36.1)	3070.1 (36.1)	3070.1 (36.1)
ν_{28}	3152.9 (108.7)	3152.9 (108.7)	3152.9 (109.1)
ν_{29}	3158.7 (7.0)	3158.7 (7.0)	3158.7 (7.1)
ν_{30}	3633.2 (65.2)	3623.3 (63.7)	2675.1 (43.9)

[a] Intensities of the E modes are the sum of the two degenerated vibrations.

Ault previously investigated matrix-isolated ammonia trimethylalane.[10] He used a merged jet of Me_3Al with NH_3 to obtain $Me_3Al{\cdot}NH_3$ in argon matrices. He then assigned seven IR absorptions of both $Me_3Al{\cdot}NH_3$ and $Me_3Al{\cdot}{}^{15}NH_3$ and eight of $Me_3Al{\cdot}ND_3$ (Table 2, numbers in braces). Though we confirmed most of his findings, we disagree on two points. In accord with our calculation, the CH_3-rocking modes ν_{22} are detected at 731.5, 731.0, and 720.0 cm^{-1} for $Me_3Al{\cdot}NH_3$, $Me_3Al{\cdot}{}^{15}NH_3$, and $Me_3Al{\cdot}ND_3$, respectively, whereas Ault assigned the same value (733 cm^{-1}) to each of the three isotopomers. Secondly, we cannot confirm the assignment of the IR band at 627 cm^{-1} of the deuterated compound to the asymmetric AlC_3-stretching mode ν_{20}. This band is more likely the degenerate

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Table 2. Experimental Frequencies (cm^{-1}) and Observed/Calculated Frequency Ratios (in Parentheses)[a]

		$Me_3Al \cdot NH_3$	$Me_3Al \cdot {}^{15}NH_3$	$Me_3Al \cdot ND_3$
A_1: ν_2	ν(AlN)	383.0 (0.9751)	376.5 (0.9754)	364.0 (0.9803)
E: ν_{19}	δ '$(NH_3)_{rock}$	517.5 (0.9395)	516.5 (0.9399)	432.0 (0.9507)
A_1: ν_3	$\nu_s(AlC_3)$	523.0 (1.0023) {523}	523.0 (1.0023) {523}	523.0 (1.0025) {523}
E: ν_{20}	$\nu_{as}(AlC_3)$	601.0 (0.9667)	600.5 (0.9662)	
E: ν_{21}	$\delta'(CH_3)_{rock}$	647.5 (0.9136)	646.5 (0.9142)	627.0 (0.9292)
A_1: ν_4	$\delta'(CH_3)_{rock}$	690.0 (0.8975)	690.0 (0.8975)	689.5 (0.8969)
E: ν_{22}	$\delta'(CH_3)_{rock}$	731.5 (0.9121) {733}	731.0 (0.9123) {733}	720.0 (0.9128) {733}
A_1: ν_5	$\delta_s(CH_3)$	1191.0 (0.9038)	1191.0 (0.9062)	
E: ν_{23}	$\delta_s(CH_3)$	1203.0 (0.9132)	1201.5 (0.9121)	1192.5 (0.9053)
A_1: ν_6	$\delta_s(NH_3)$	1213.0 (0.9107) {1212}	1207.5 (0.9093) {1207}	937.0 (0.9233) {936}
E: ν_{26}	$\delta_{as}(NH_3)$	1605.5 (0.9328) {1606}	1602.0 (0.9324) {1602}	1176.5 (0.9473) {1175}
A_1: $\nu_8 - \nu_9$	$\nu(CH_3)$	2943.0, 2936.0	2942.5, 2936.0	2943.0, 2936.0
E: $\nu_{27} - \nu_{29}$		2920.0, 2904.0	2920.0, 2903.0	2919.5, 2903.5
		2888.0	2888.5	2887.5
		{2942; 2919}	{2942; 2919}	{2942; 2919}
A_1: ν_{10}	$\nu_s(NH_3)$	3296.5 (0.9444) [3300.0 (0.9454)]	3291.5 (0.9436) [3295.5 (0.9447)]	2397.0 (0.9603) [2399.0 (0.9611)]
E: ν_{30}	$\nu_{as}(NH_3)$	3395.5 (0.9346) [3402.5 (0.9365)] {3396}	3387.5 (0.9349) [3402.5 (0.9391)] {3388}	2530.0 (0.9458) [2534.0 (0.9473)] {2530}

[a] Wavenumbers in braces were taken from the literature.[10] Absorptions due to matrix effects are shown in square brackets.

CH_3-rocking mode ν_{21}; the calculated isotopic shifts and the intensities were nicely reproduced by our experiments.[11] Besides, the asymmetric stretch ν_{20} is predicted to be of low intensity; in particular, this vibration should be much weaker for $Me_3Al \cdot ND_3$ compared with the other two isotopomers. We tentatively assign the very weak absorptions at 601.0 and 600.5 cm^{-1} for $Me_3Al \cdot NH_3$ and $Me_3Al \cdot {}^{15}NH_3$, respectively, to ν_{20}; we could not detect a signal for the deuterated molecule.

The most interesting low-energy vibration is the AlN-stretching mode ν_2 at 383.0, 376.5, and 364.0 cm^{-1} (Table 2). An early vibrational study on ammonia trimethylalane assigned the weak IR bands at 461 and 439 cm^{-1}, measured at −196 °C for the solid samples of $Me_3Al \cdot NH_3$ and $Me_3Al \cdot ND_3$, respectively, to the AlN-stretching mode.[5a,12] This assignment had been confirmed by Raman spectroscopy and normal coordinate analysis. The differences between these and our values may be due to different media: the pure solids there and highly diluted matrices here. The isotopic shifts caused by the deuteration are the same in the solid state and in the matrix (solid: $439/461 = 0.9523$; matrix: $364.0/383.0 = 0.9504$), suggesting that we are really looking at the same modes in both cases. A comment should be made on the CH_3 stretches. The calculated values do not reproduce the measured ones exactly (Figure 2). Nevertheless, as predicted by the *ab initio* calculation, no differences between the CH_3 stretches of all three isotopomers should be seen, as confirmed by the experiments.

In summary, we found all expected normal modes between 250 and 4000 cm^{-1} except the three weak vibrations ν_7, ν_{24}, and ν_{25} (Table 1) and the asymmetric AlC_3-stretching mode ν_{20} of $Me_3Al \cdot ND_3$ already discussed.

Photolysis of Ammonia Trimethylalane. The irradiation of matrix-isolated ammonia trimethylalane with UV light at 210 nm[13] yields methane and the hitherto unknown monomeric aminodimethylalalane.

$$Me_3Al \cdot NH_3 \xrightarrow[\text{Ar (10 K)}]{h\nu} Me_2AlNH_2 + CH_4 \qquad (2)$$

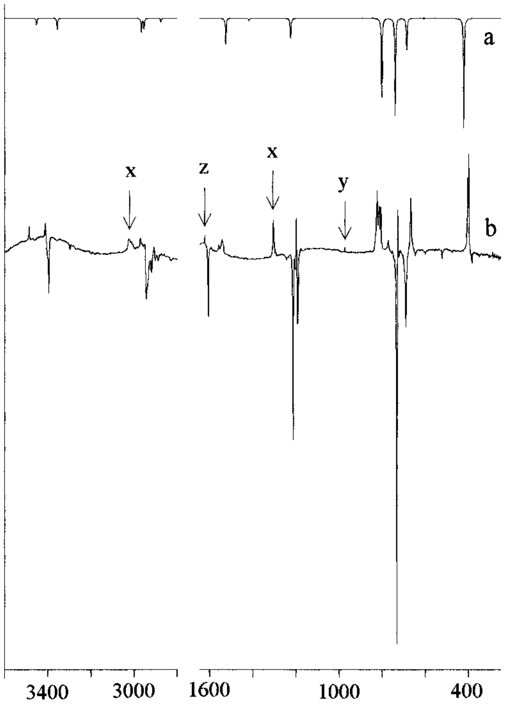

Figure 3. Irradiation of $Me_3Al \cdot NH_3$ in argon at 10 K: *X*-axis, 250−1650 and 2800−3600 cm^{-1}; *Y*-axis, Absorbance (dimensionless). Spectrum a: Me_2AlNH_2 calculated at the RMP2(fc)/6-31G* level (frequencies scaled by 0.93, half band width of 2 cm^{-1}). Spectrum b: Difference IR spectrum after irradiation (210 nm)[13] of $Me_3Al \cdot NH_3$ for 7 h (decreasing absorptions point down, increasing absorptions point up). x indicates CH_4 (1304.0, 1306.5, 3024.0 (br) cm^{-1}), y indicates NH_3 (974.5 cm^{-1}), and z indicates H_2O (1624.0 cm^{-1}).

Figure 3 shows a typical IR spectrum obtained after 7 h of irradiation of $Me_3Al \cdot NH_3$ at 10 K (Figure 3b), with the scaled theoretical spectrum of Me_2AlNH_2 (Figure 3a).[7] Under the

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(11) The weak vibrations between 250 and 650 cm^{-1} cannot be seen easily in Figure 2, but they are readily revealed in a higher magnification.

(12) The AlN-stretching mode was out of Ault's[10] detectable range of 400−4000 cm^{-1}.

(13) UV light with the maximum at 210 nm and a band width of 20 nm was used (see Experimental Section).

(14) DCH_3 has another resonance at 1156.0 cm^{-1} which is hidden by a strong absorption of Me_2AlND_2 (ν_7, Table 4). Herzberg, G. *Molecular Spectra and Molecular Structure*, 1st ed.; D. Van Nostrand Company, Inc.: Princton, NJ, 1945; Vol. II, p 309.

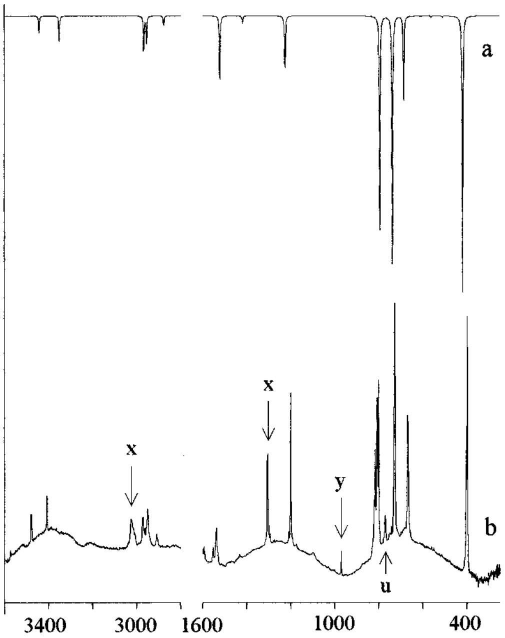

Figure 4. IR spectra of $Me_2Al^{15}NH_2$: *X*-axis, 250−1600 and 2800−3600 cm^{-1}; *Y*-axis, Absorbance (dimensionless). Spectrum a: $Me_2Al^{15}NH_2$ calculated at the RMP2(fc)/6-31G* level (frequencies scaled by 0.93, half band width of 2 cm^{-1}). Spectrum b: $Me_2Al^{15}NH_2$ in argon at 10 K synthesized by the irradiation (20 h, 210 nm[13]) of $Me_3Al{\cdot}^{15}NH_3$ (Figure 2c). x indicates CH_4 (1304.5, 3024.0 (br) cm^{-1}), y indicates $^{15}NH_3$ (970.5 cm^{-1}), and u indicates an unassigned product band (770.0 cm^{-1}).

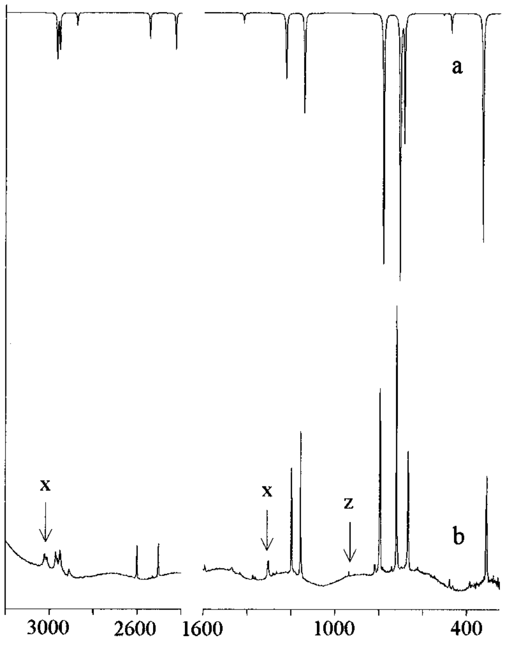

Figure 5. IR spectra of Me_2AlND_2: *X*-axis, 250−1600 and 2400−3200 cm^{-1}; *Y*-axis, Absorbance (dimensionless). Spectrum a: Me_2AlND_2 calculated at the RMP2(fc)/6-31G* level (frequencies scaled by 0.93, half band width of 2 cm^{-1}). Spectrum b: Me_2AlND_2 in argon at 10 K synthesized by the irradiation (20 h, 210 nm[13]) of $Me_3Al{\cdot}^{15}ND_3$ (Figure 2d). x indicates DCH_3 (1303.5, 3010.5, 3020.5 cm^{-1})[14] and z indicates small amounts of $Me_3Al{\cdot}ND_3$ (937.0 cm^{-1}).

conditions employed for our experiments, the methane loss is complete after 20 h; only traces of the starting material are detectable. The corresponding IR spectra of the ^{15}N-labeled sample and of the deuterated compound with their scaled calculated spectra are depicted in Figures 4 and 5, respectively.

Ab initio calculations predict a C_{2v}-symmetry equilibrium geometry for aminodimethylalane (Figure 6).[7] Consequently, one expects 30 normal modes belonging to the irreducible representations A_1 (10), A_2 (5), B_1 (9), and B_2 (6). Table 3 gives a summary of the calculated harmonic frequencies for the three isomers Me_2AlNH_2, $Me_2Al^{15}NH_2$, and Me_2AlND_2. The A_2 modes are IR inactive, and the wavenumbers for ν_1, ν_{16}, ν_{25}, and ν_{26} are too low to be detectable (<250 cm^{-1}). Therefore, 21 fundamentals remain in our accessible range (250−4000 cm^{-1}). Based on the *ab initio* calculation, we assigned 11 resonances in the IR spectra of Me_2AlNH_2 and $Me_2Al^{15}NH_2$, and 12 IR bands for Me_2AlND_2 to 14 and 15 normal modes, respectively (Table 4). The remaining unassigned fundamentals, which were calculated to be very weak (Table 3), have not been measured.

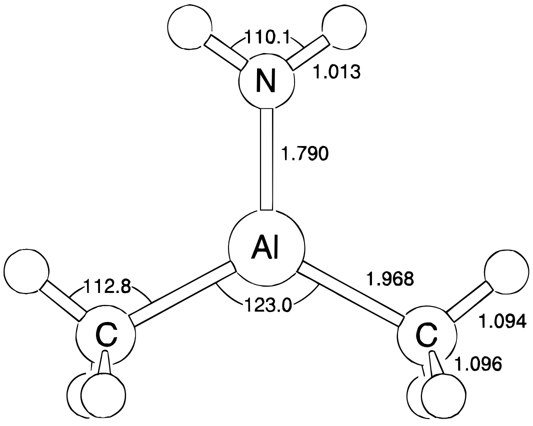

Figure 6. Selected bond distances (Å) and angles (deg) for the equilibrium geometry of Me_2AlNH_2 (C_{2v} point group) calculated at the RMP2(fc)/6-31G* level.

Table 3. Harmonic Frequencies (cm^{-1}) and Intensities (in Parentheses, km mol^{-1}) Calculated at the RMP2(fc)/6-31G* Level

	Me_2AlNH_2	$Me_2Al^{15}NH_2$	Me_2AlND_2
A_1: ν_1	164.0 (2.7)	163.5 (2.6)	163.1 (2.6)
ν_2	551.0 (1.4)	548.6 (1.1)	545.6 (1.0)
ν_3	743.5 (8.1)	738.6 (4.6)	727.8 (1.4)
ν_4	863.0 (181.0)	855.0 (183.8)	839.4 (165.1)
ν_5	1319.1 (17.4)	1319.1 (17.3)	1319.2 (15.0)
ν_6	1523.8 (1.3)	1523.8 (1.3)	1524.1 (2.3)
ν_7	1641.2 (57.4)	1635.7 (54.7)	1226.9 (63.6)
ν_8	3093.1 (1.9)	3093.1 (1.9)	3093.1 (1.9)
ν_9	3189.9 (19.4)	3190.0 (19.4)	3189.9 (19.5)
ν_{10}	3608.8 (24.0)	3603.6 (22.8)	2610.4 (23.9)
A_2: ν_{11}	56.5 (0.0)	56.5 (0.0)	56.4 (0.0)
ν_{12}	402.3 (0.0)	402.3 (0.0)	291.7 (0.0)
ν_{13}	655.7 (0.0)	655.7 (0.0)	644.4 (0.0)
ν_{14}	1515.3 (0.0)	1515.3 (0.0)	1515.3 (0.0)
ν_{15}	3176.3 (0.0)	3176.3 (0.0)	3176.3 (0.0)
B_1: ν_{16}	187.5 (2.5)	185.6 (2.5)	170.3 (1.8)
ν_{17}	604.9 (1.1)	603.7 (1.3)	506.1 (12.9)
ν_{18}	654.0 (0.7)	653.0 (0.5)	641.3 (0.0)
ν_{19}	795.9 (214.0)	793.4 (212.3)	758.7 (175.2)
ν_{20}	1316.5 (37.4)	1316.5 (37.4)	1316.5 (37.1)
ν_{21}	1519.9 (0.0)	1519.9 (0.0)	1519.8 (0.1)
ν_{22}	3092.2 (6.2)	3092.2 (6.2)	3092.2 (6.2)
ν_{23}	3190.0 (10.8)	3190.0 (10.8)	3190.0 (10.8)
ν_{24}	3712.3 (16.0)	3701.8 (15.0)	2736.5 (16.2)
B_2: ν_{25}	68.2 (0.1)	68.1 (0.1)	67.8 (0.1)
ν_{26}	195.3 (6.8)	194.7 (7.0)	192.3 (4.4)
ν_{27}	453.6 (239.5)	450.7 (236.2)	351.8 (146.5)
ν_{28}	738.1 (71.4)	738.1 (70.9)	737.4 (81.9)
ν_{29}	1525.2 (5.1)	1525.2 (5.1)	1525.2 (4.9)
ν_{30}	3176.9 (23.7)	3176.9 (23.7)	3176.9 (23.7)

After the photolysis at 10 K the IR bands of aminodimethylalane show fine structure, which is very sensitive to temperature changes. At 20 K we observed a strong relative intensity change for all product vibrations (Figure 7). A second short warmup to 20 K does not yield this annealing effect again. The change

Table 4. Experimental Frequencies (cm^{-1}) and Observed/Calculated Frequency Ratios (in Parentheses)

		Me_2AlNH_2	$Me_2Al^{15}NH_2$	Me_2AlND_2
B_2: ν_{27}	$\kappa(NH_2)_{wagg}$	399.0 (0.8796)	396.5 (0.8797)	307.5 (0.8741)
		[407.0 (0.8973)]	[404.5 (0.8975)]	[313.5 (08911)]
B_1: ν_{17}	$\delta'(NH_2)_{rock}$			478.0 (0.9448)
B_2: ν_{28}	$\delta_{as}(CH_3)$	668.0 (0.9050)	668.0 (0.9050)	666.5 (0.9039)
B_1: ν_{19}	$\delta'(CH_3)_{rock}$	728.0 (0.9147)	726.5 (0.9157)	720.0 (0.9490)
		[732.0 (0.9197)]	[730.5(0.9207)]	
A_1: ν_4	$\nu(AlN)^b$	807.5	800.5	794.0 (0.9459)
		817.0	809.0	[796.0 (0.9483)]
		823.5	816.5	
B_1: ν_{20}	$\delta_s(CH_3)$	1199.5 (0.9111)	1199.5 (0.9111)	1197.5 (0.9096)
A_1: ν_5	$\delta_s(CH_3)$	1199.5 (0.9093)	1199.5 (0.9093)	1197.5 (0.9077)
A_1: ν_7	$\delta_s(NH_2)$	1544.0 (0.9408)	1536.0 (0.9390)	1156.0 (0.9422)
B_1: ν_{22}	$\nu_s(CH_3)$	2909.0 (0.9408)	2909.0 (0.9408)	2910.0 (0.9411)
A_1: ν_8	$\nu_s(CH_3)$	2909.0 (0.9405)	2909.0 (0.9405)	2910.0 (0.9408)
B_2: ν_{30}	$\nu_{as}(CH_3)$	2951.5 (0.9291)	2951.0 (0.9289)	2951.5 (0.9291)
A_1: ν_9	$\nu_{as}(CH_3)$	2971.0 (0.9314)	2971.5 (0.9315)	2970.5 (0.9312)
B_1: ν_{23}	$\nu_{as}(CH_3)$	2971.0 (0.9313)	2971.5 (0.9315)	2970.5 (0.9312)
A_1: ν_{10}	$\nu_s(NH_2)$	3411.0 (0.9452)	3406.5 (0.9453)	2503.0 (0.9589)
B_1: ν_{24}	$\nu_{as}(NH_2)$	3486.5 (0.9392)	3478.5 (0.9397)	2600.5 (0.9503)

[a] Absorptions due to matrix effects are shown in square brackets. [b] See discussion on the ν(AlN) of Me_2AlNH_2 and $Me_2Al^{15}NH_2$.

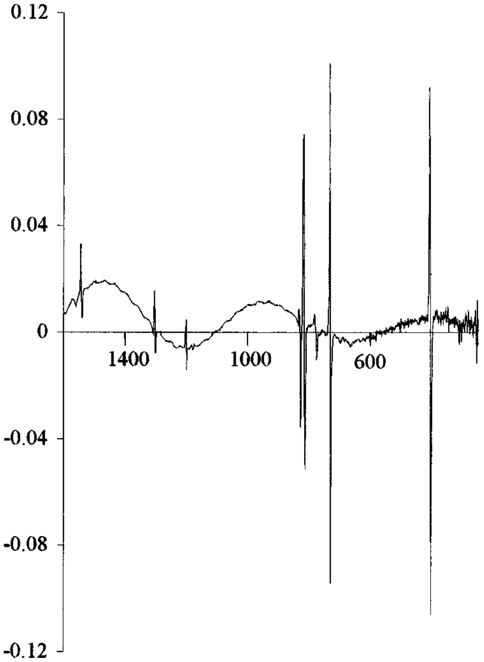

Figure 7. Difference IR spectrum (250−1600 cm^{-1}) of matrix-isolated Me_2AlNH_2 synthesized by the irradiation (20 h, 210 nm[13]) of $Me_3Al{\cdot}NH_3$ (Figure 2a), before (down) and after (up) a warmup from 10 to 20 K.

in intensity initially observed may arise from a release of the hydrostatic pressure built up in the matrix by the reaction (eq 2). Consistent with this conclusion, the methane vibrations are also affected by the warmup, the pressure being exerted on both molecules generated in the argon matrix. Similar hydrostatic pressure effects are known in the literature.[15] Due to matrix effects some bands remain split (Table 4: ν_{27}, ν_{19}, and ν_4, numbers in brackets), with the largest splitting for the NH_2-wagging mode ν_{27} (6.0−8.0 cm^{-1}).

A comment should be made on the assignment of the AlN-stretching vibration ν_4. In the case of the deuterated compound (Figure 5) the intense absorption at 794.0 cm^{-1} unequivocally corresponds to this stretching mode. Considering the calculated isotopic shifts, the AlN stretches of Me_2AlNH_2 and $Me_2Al^{15}NH_2$ are expected at 816.3 and 808.8 cm^{-1}, respectively. Instead of one band, three bands were measured in the range of 800−825 cm^{-1} (Table 4, Figures 3 and 4). This is probably the result of Fermi resonance between ν_4 and the overtone of the intense mode ν_{27}. The situation is complex, because the ν_{27} fundamental, as mentioned earlier, consists of two bands. Simple doubling of the wavenumber of ν_{27} would cause the two overtone couples 798.0/814.0 cm^{-1} (Me_2AlNH_2) and 793.0/809.0 cm^{-1} ($Me_2Al^{15}NH_2$) as a zero approximation. The value of the higher frequency in each couple is very close to calculated value of the AlN-stretching mode ν_4 (816.3 and 808.8 cm^{-1}). In the deuterated molecule the estimated frequencies of the ν_{27} overtones (615.0/627.0 cm^{-1}) are too far away from the ν_4 vibrational level (794.0 cm^{-1}) to allow Fermi resonance.

Besides the frequencies, Table 4 exhibits the observed/calculated frequency ratios (numbers in parentheses). The worst fit has been found for the low-energy NH_2-wagging mode ν_{27} (0.8741−0.8797) and the best fit for the asymmetric NH_2 stretch (0.9452−0.9589). Within a certain margin of error, one would expect the same ratio for all three isotopomers for a certain mode, if the isotopic shifts had been correctly calculated. Actually, only the fundamental ν_{19} deviates from that expectation for unknown reasons (Table 4).

In summary, we found all normal modes with predicted intensities larger than 10 km mol^{-1}. Nevertheless, two medium strong IR bands at 770.0 and 772.0 cm^{-1} for Me_2AlNH_2 and $Me_2Al^{15}NH_2$, respectively, have not yet been assigned (Figure 4, u). These two absorptions are sensitive to the warmup procedure (Figure 7) discussed earlier. Therefore, we assume them to be absorptions of aminodimethylalane, probably combination vibrations. No comparable vibration was found for the deuterated species.

Reaction 2 represents a photochemical elimination of methane. As expected, this is a 1,2-elimination, which is proven for $Me_3Al{\cdot}ND_3$ by the formation of DCH_3 (Figure 5). So far, the nature of the electron transitions involved is not known. The corresponding thermolytic version of eq 2 had been investigated first by Wiberg in 1939.[1] Heating of $Me_3Al{\cdot}NH_3$ in benzene under reflux yielded the trimer of aminodimethylalane, $(Me_2AlNH_2)_3$.[16] Sauls et al. examined the kinetics of this process revealing a complex mechanism.[5b] They proposed that monomeric Me_2AlNH_2 acts as a catalyst. The same authors elucidated the equilibrium constant for the dimer−trimer interconversion from ^1H-NMR experiments (30−100 °C) with-

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out detecting the monomer.[17] Recently, Power et al. isolated the first monomeric aminodialkylalanes using bulky ligands.[3] With one exception, these compounds show trigonal-planar coordinated Al and N atoms, but the two corresponding planes are twisted along the AlN bond axis. The torsion angles vary between 5.5 and 84.9°, without exhibiting a strong correlation with the AlN bond lengths (1.784−1.880 Å). The *ab initio* calculation for Me_2AlNH_2 reveals a C_{2v} symmetry (Figure 6) with an AlN distance of 1.790 Å. A similar molecular structure, based on valence bond theory, was predicted by Messmer et al. (AlN = 1.797 Å).[18] In a simple MO description, this equilibrium geometry allows a maximum of $p\pi-p\pi$ interaction between aluminium and nitrogen; hence, it fulfills the expectations for a classical double bond.

It is common to judge single- or double-bond character either by bond lengths or rotation barriers. With a calculated AlN distance of 2.106 Å ($Me_3Al{\cdot}NH_3$, Figure 1), the AlN bond shortening in Me_2AlNH_2 becomes 15.0%. This is a large value, if compared with the 9.4% found for the isoelectronic silaalkene Me_2SiCH_2, whose corresponding SiC bond length of 1.692 Å[19] contrasts with the SiC single bond length of 1.868 Å (both values from microwave spectra).[20] For the lighter congeners, aminoboranes and alkenes, the corresponding values are 10.8 and 13.6%, respectively.[21] One has to be careful not to overestimate the 15% shortening in the present case. First, we are comparing calculated bond lengths that may be slightly different from the real ones. Second, the AlN distances of simple amine adducts are known to vary in quite a broad range of 1.94−2.10 Å,[8,9] making a well-defined distance for a single bond unavailable. Third, it is unknown how much of the shortening goes back to the π-bond interaction, on the one hand, or to the decrease in coordination number from four to three, which usually causes a decrease in the covalent radii, on the other hand.

The optimized transition-state geometry for the AlN rotation (Figure 8) corresponds to a barrier of 40.7 kJ mol^{-1}.[22] This is a small value in comparison with silaalkenes (148−149 kJ mol^{-1} in H_2SiCH_2),[23] aminoboranes (123−139 kJ mol^{-1} in H_2BNH_2),[24] and ethylenes (272 kJ mol^{-1}). The transition state reveals a weak pyramidalization of the NH_2 group and a slight increase of the AlN distance (Figure 8). If the nitrogen lone pair is not involved in any π-bond, the value of 1.823 Å corresponds to a "pure" AlN single bond. This would mean that the π-overlap alone causes a decrease of the AlN distance by 0.033 Å (1.8%). Two recently published *ab initio* calculations of the parent aminoalane H_2AlNH_2 led to similar findings: The AlN bond differences between the ground and the transition states were 0.023 (1.3%)[25] and 0.019 Å (1.1%)[26] with barriers of 46.8 and 44.8 kJ mol^{-1}, respectively. To our knowledge, the only experimental AlN rotation barrier of a monoaminoalane was measured for tBu$_2$AlNH(Diip) (Diip = 2,6-diisopropylphenyl). Based on ^{1}H-NMR experiments it was estimated to be 38−42 kJ mol^{-1},[3] in good agreement with our calculation. Certainly, every method for separating a π-bond from a σ-bond includes approximations. In the case of a rotation barrier the $p\pi-p\pi$ interaction is minimized for the transition state, whereas the same geometry meets the optimum conditions for other π-type overlaps like "negative hyperconjugation",[25] which is —although present—quite probably of minor importance for Me_2AlNH_2. Despite these uncertainties, aminodimethylalane contains a weak AlN double bond, concluded from the rotation barrier.

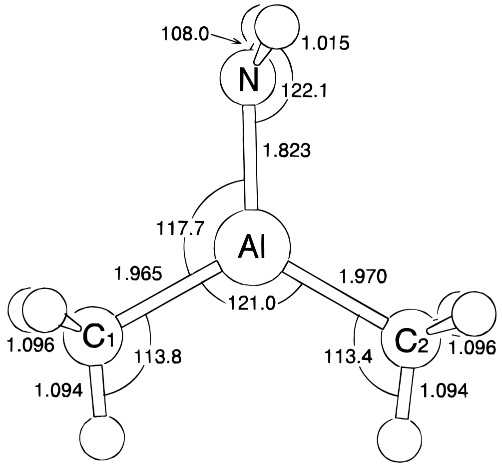

Figure 8. Selected bond distances (Å) and angles (deg) of the transition state (C_s point group) for the AlN rotation of Me_2AlNH_2 calculated at the RMP2(fc)/6-31G* level.

Table 5. Calculated Total Energies *E* (au) and Zero-Point Energies ZPE (Scaled by 0.93 in kJ mol^{-1}) with the Number of Imaginary Frequencies Shown in Parentheses

		E	ZPE
$Me_3Al{\cdot}NH_3$	C_{3v}	−417.60357	365.1 (0)
Me_2AlNH_2	C_{2v}	−377.27170	243.3 (0)
Me_2AlNH_2	C_s	−377.25459	239.1 (1)
Me_3Al	C_{3h}	−361.20348	267.1 (0)
CH_4	T_d	−40.33255	113.2 (0)
NH_3	C_{3v}	−56.35421	86.2 (0)

The *ab initio* calculation for Me_2AlNH_2 yields a heat of reaction (eq 2) of −10.4 kJ mol^{-1} (Table 5). The experimental value for this methane loss is not known, but the overall decompositon reaction (eq 3) of the neat liquid amine adduct was found to proceed with ΔH = −82.2 kJ mol^{-1}.[5b] The heat of the cyclotrimerization of Me_2AlNH_2 is then approximately −71.8 kJ mol^{-1}.

$$Me_3Al{\cdot}NH_3\,(l) \longrightarrow \tfrac{1}{3}\,(Me_2AlNH_2)_3\,(l) + CH_4\,(g) \qquad (3)$$

To check the reliability of the predicted thermodynamic data, we calculated the dissociation enthalpy of the amine adduct. A value of ΔH = 93 ± 5 kJ mol^{-1} was measured for this process

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(22) Calculated with the inclusion of zero-point energies scaled by 0.93 (Table 5).

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in benzene (eq 4).[5b] The heat of complexation of $AlMe_3(g)$ to

$$Me_3Al\cdot NH_3 \longrightarrow Me_3Al + NH_3 \qquad (4)$$

benzene and the heat of solution of $NH_3(g)$ in benzene are -8 and -12 kJ mol^{-1}, respectively.[5b] The heat of solution of $Me_3Al\cdot NH_3$ is not known, but it is probably slightly exothermic. Considering these figures, we obtain $\Delta H \leq 113 \pm 5$ kJ mol^{-1} for reaction 4 in the gas phase, which agrees very well with our calculation of 108.6 kJ mol^{-1} (Table 5).[22]

Experimental Section

The matrix apparatus consists of a vacuum line (Leybold Turbovac 151; Leybold Trivac D4B) and a Displex CSW 202 cryogenic closed-cycle system (APD Cryogenics Inc.) fitted with CsI windows. In a typical experiment, argon (Linde 5.6) was deposited for 1$-$2 h at 15 K (CsI window) with an argon flow of ca. 4 mmol h^{-1}. The samples were mixed with the rare gas by sublimation between -10 and -15 °C in *high vacuo* (10^{-6} to 10^{-7} mbar). The concentrations of the samples in the matrices are unknown. Therefore, several experiments under various conditions for each isotopomer were conducted, to make sure that the molecules were indeed matrix isolated. A higher argon flow (8 mmol h^{-1}) and lower sublimation temperature (-20 °C) reduces the amount of the starting material significantly, but no differences in the IR spectra of the adducts and products were observed. Of course, at higher concentrations the IR spectra of the starting material change; i.e., the half band widths of the IR bands increase and new broad IR bands appear. That indicates that significant parts of the molecules are no longer matrix isolated under these conditions (e.g., sublimation temperatures of 0 °C).

The IR spectra of the matrices were recorded at 10 K on a Perkin-Elmer FTIR 1720x from 250 to 4000 cm^{-1} with a resolution of 1 cm^{-1}. A 450-W xenon arc lamp (Osram XBO 450W/4, PTI Inc. lamp housing A 5001) and a grating monochromator (PTI Inc. Model 001-01) were used for the irradiations. To obtain a high-energy output at 210 nm, the slit width of the monochromator was kept at 5 mm resulting in a band width of 20 nm.

The GAUSSIAN 92 package run on the Siemens-Nixdorf Vektorrechner S600/20 (Rechenzentrum der RWTH Aachen) was applied for *ab initio* calculations.[7]

All synthetic procedures were carried out under dry nitrogen in Schlenk glassware. Me_3Al (2.0 M in hexane) and $^{15}NH_3$ (98 atom % ^{15}N) were purchased from Aldrich and ND_3 (99.4 atom % D) from MSD Isotopes. NMR: Varian Unity 500 in C_6D_6 (24 °C) at 499.657 (^1H, standard: TMS intern), 130.195 (^{27}Al, standard: $[Al(acac)_3]$ in C_6D_6 extern), and 125.639 MHz ($^{13}C\{^1H\}$, standard: TMS intern). MS: Varian Mat-CH-5 (70 eV). Elemental analyses (C, H, N): Heraeus Elementaranalysator CHN-O-RAPID.

$Me_3Al\cdot NH_3$. Gaseous NH_3 (250 mL at room temperature) was solidified with liquid nitrogen and 5.0 mL of $AlMe_3$ (2 M in hexane) was added. The cooling bath was removed, and the reaction mixture was stirred for 30 min at room temperature. After removal of the solvent in *vacuo*, sublimation (30 °C, 10^{-3} mbar) gave the pure product (0.86 g, 96%) as a colorless solid. ^1H NMR: δ -0.62 (s, 9H, CH_3), 0.26 (br s, 3H, NH_3). ^{13}C NMR: δ -8.06 (br). ^{27}Al NMR: δ 169 ($h_{1/2}$ = 1400 Hz). MS: *m/e* 74 ($M^+ - 15$, 100). Anal. Calcd for $C_3H_{12}AlN$: C, 40.43; H, 13.57; N, 15.72. Found: C, 40.64; H, 13.93; N, 14.93.

$Me_3Al\cdot{}^{15}NH_3$. Following the procedure described for $Me_3Al\cdot NH_3$, $^{15}NH_3$ (500 mL) and 10.0 mL of $AlMe_3$ (2 M in hexane) yield 1.72 g of $Me_3Al\cdot{}^{15}NH_3$ (95%) after sublimation. ^1H NMR: δ -0.62 (s, 9H, CH_3), 0.26 (d, $J(^1H^{15}N)$ = 65.6 Hz, 3H, NH_3). ^{13}C NMR: δ -8.06 (br). ^{27}Al NMR: δ 169 ($h_{1/2}$ = 1400 Hz). MS: *m/e* 75 ($M^+ - 15$, 100). Anal. Calcd for $C_3H_{12}Al^{15}N$: C, 39.99; H, 13.42; N, 16.65. Found: C, 40.14; H, 13.43; N, 16.20.

$Me_3Al\cdot ND_3$. Following the procedure described for $Me_3Al\cdot NH_3$, ND_3 (250 mL) and 5.0 mL of $AlMe_3$ (2 M in hexane) yield 0.89 g of $Me_3Al\cdot ND_3$ (97%) after sublimation. ^1H NMR: δ -0.62 (s, CH_3). ^{13}C NMR: δ -8.15 (br). ^{27}Al NMR: δ 169 ($h_{1/2}$ = 1400 Hz). MS: *m/e* 77 ($M^+ - 15$, 100). Anal. Calcd for $C_3H_9D_3AlN$: C, 39.11; N, 15.20. Found: C, 39.22; N, 14.56.

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