

## Synthesis and Structural Characterization of (1,4-Dihydropyrid-1-yl)aluminum Complexes

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The reaction between  $\text{LiAlH}_4$  and pyridine, 4-methylpyridine, or 3,5-dimethylpyridine results in hydride transfer to the pyridine ring to give tetrakis(pyridine)lithium tetrakis(1,4-dihydropyrid-1-yl)aluminate(III), **1**, tetrakis(4-methylpyridine)lithium tetrakis(1,4-dihydro-4-methylpyrid-1-yl)aluminate(III), **2**, or tetrakis(3,5-dimethylpyridine)lithium tetrakis(3,5-dimethyl-1,4-dihydropyrid-1-yl)aluminate(III), **3**, respectively. We claim that **1**, instead of lithium tetrakis(1,4-dihydropyrid-1-yl)aluminate(III), is the compound which is known as Lansbury's reagent. Treatment of trimethylamine–alane,  $\text{AlH}_3 \cdot \text{NMe}_3$ , with pyridine yields tris(1,4-dihydropyrid-1-yl)(pyridine)aluminum, **4**. It could be shown that  $\text{AlH}_3 \cdot \text{NMe}_3$  initially reduces pyridine to 1,2-dihydropyridine, which is subsequently converted into its 1,4-isomer. The X-ray crystal structures of **1–4** were determined. While the differences between Al–N distances within each of the compounds **1–3** are not significant, **4** exhibits two distinctly different types of Al–N bonds, the dative bond between Al and N(pyridine),  $d(\text{Al–N}) = 1.959(2)$  Å, and the covalent bonds between Al and N(1,4-dihydropyrid-1-yl),  $d_{\text{av}}(\text{Al–N}) = 1.833$  Å.

### Introduction

The unique ability of nicotinamide adenine dinucleotide (NADH) in biological systems to reduce unsaturated functionalities has prompted considerable interest in the chemistry of dihydropyridines.<sup>1</sup> By contrast, however, there have been very few studies on dihydropyridyl complexes of metals, despite the fact that it is often these metal complexes which are responsible for the reduction of substrates in organic synthetic reactions.<sup>2</sup> Lansbury's reagent is an example of such a complex which has been used to effect selective reduction of ketones, especially in the presence of carboxylic acid and ester groups.<sup>2</sup> The complex is generated in the reaction between  $\text{LiAlH}_4$  and pyridine and is believed to be  $\text{Li}[\text{Al}(1,4\text{-dihydropyrid-1-yl})_4]$ . Extensive NMR studies have shown that the initial reaction between  $\text{LiAlH}_4$  and pyridine produces five isomers of lithium tetrakis(dihydropyridyl)aluminate containing a mixture of both 1,2- and 1,4-dihydropyridyl ligands but that, over time, the dihydropyridyl groups isomerize and the final product contains  $[\text{Al}(1,4\text{-dihydropyridyl})_4]^-$  only.<sup>3</sup> Other metal tetrahydroaluminate

derivatives have been used to generate complexes containing the dihydropyridyl group bound to the metal. For example, treatment of  $\text{Cp}_3\text{U}(\text{AlH}_4)$  produces  $\text{Cp}_3\text{U}(1,4\text{-dihydropyridyl})$ .<sup>4</sup> Metal hydrides themselves have also been used to prepare complexes formulated as  $\text{Cp}_2\text{Y}(1,4\text{-dihydropyridyl})$ ,  $\text{Mg}(1,4\text{-dihydropyridyl})_2$ , and  $\text{Zn}(1,4\text{-dihydropyridyl})_2(\text{py})_2$ .<sup>5–7</sup> The zinc complex has also been structurally characterized by X-ray crystallography.<sup>8</sup> The only other dihydropyridyl complex that has been structurally characterized is  $\text{py}_2\text{Li}(\mu\text{-pyH})_2\text{Li}(\text{py})_2$ , which was recently isolated as an intermediate in the reaction between butyllithium and pyridine.<sup>9</sup> The aim of the present study was to isolate and characterize structurally some dihydropyridyl complexes of aluminum. The reactions between  $\text{LiAlH}_4$  and

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pyridine, 4-methylpyridine, and 3,5-dimethylpyridine were studied as routes to anionic aluminum complexes,  $[\text{Al}(\text{pyH})_4]^-$ , and the reaction between  $\text{AlH}_3 \cdot \text{NMe}_3$  and pyridine was studied as a route to a neutral dihydropyridyl complex.

## Experimental Section

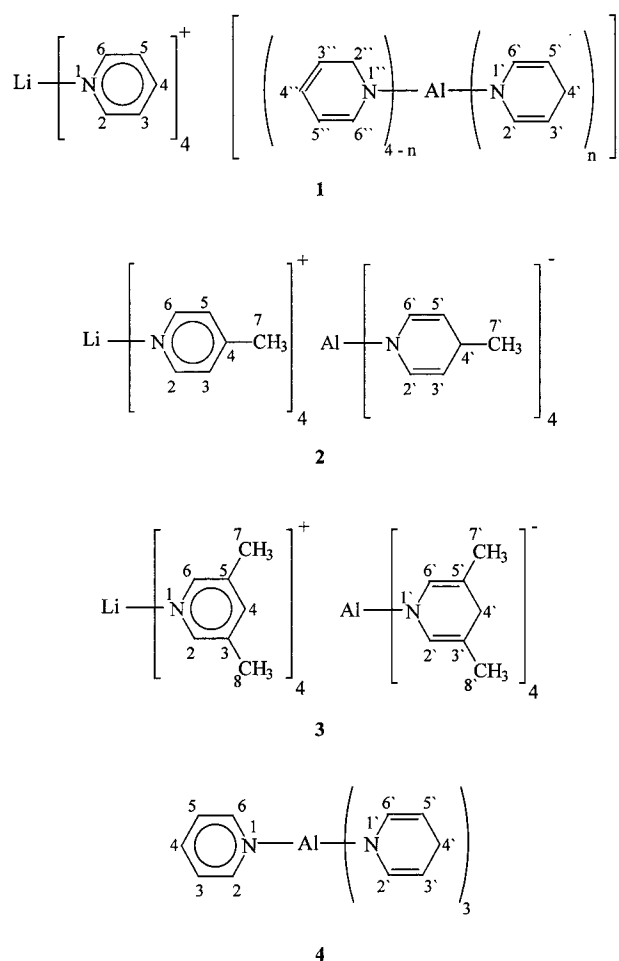
**General Procedures.** The sensitivity of  $\text{LiAlH}_4$ ,  $\text{AlH}_3 \cdot \text{NMe}_3$ , and compounds **1–4** toward moisture and oxygen requires the use of standard Schlenk techniques. Solids were manipulated under dry nitrogen in a drybox. Pyridine, 4-methylpyridine, and 3,5-dimethylpyridine were distilled under  $\text{N}_2$  from  $\text{CaH}_2$  prior to use. NMR chemical shifts are reported in parts per million (ppm) versus TMS.  $\text{LiAlH}_4$  was purchased from Fluka and used as received (**1–3**) or recrystallized from dry diethyl ether (**4**). Elemental analyses were obtained by using a Heraeus CHN-Rapid instrument. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on an AM 250 MHz and a WH 270 MHz NMR spectrometer (Bruker). THF- $d_8$  was purchased from DEUTERO, and benzene- $d_6$  was purchased from Aldrich and stored over activated 4 Å molecular sieves.

**Syntheses. 1.** In a typical preparation of **1**, pyridine (20.0 mL, 250 mM) was condensed via a high-vacuum line onto  $\text{LiAlH}_4$  (500 mg, 13.2 mM), and the system was cooled to  $-196^\circ\text{C}$ . The reaction mixture was allowed to warm to  $-50^\circ\text{C}$  and stirred for 2 h. On further warming to room temperature, the white suspension turned yellow. After 24 h at room temperature, the reaction mixture was heated to  $95^\circ\text{C}$  for 1 h, at which point the pale yellow suspension turned orange. The resulting orange mixture was filtered, most of the pyridine was removed in vacuo from the filtrate, and the residue was stored under argon at  $-5^\circ\text{C}$ . After several days, orange crystals suitable for the X-ray structural determination were obtained.  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta$  8.5 (H-2,6), 7.5 (H-4), 7.15 (H-3,5), 6.4 (H-6''), 5.85 (H-2',6'), 5.05 (H-4''), 4.5 (H-5''), 4.35 (H-3''), 3.7 (H-3',5'), 3.6 (H-2''), 2.9 (H-4').  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta$  150 (C-2), 136 (C-4), 124 (C-3). (For numbering scheme, see Figure 1.) Anal. Calcd for **1** ( $\text{C}_{40}\text{H}_{44}\text{AlLiN}_8$ , fw = 670.79): C, 71.62; H, 6.61; N, 16.71. Found (repeat determination): C, 66.93; H, 6.42; N, 15.91.

**2.** The synthesis was carried out in a manner analogous to that for **1** using 250 mg (6.6 mM) of  $\text{LiAlH}_4$  and 7.0 mL (72 mM) of 4-methylpyridine and yielding an orange suspension. After standing for 3 weeks at room temperature, the solution turned red and a white solid precipitated. After filtration, the red solution was stored at  $-5^\circ\text{C}$ . Orange crystals suitable for the X-ray structural analysis were obtained after several days. The crystals were handled at this low temperature owing to their high solubility in 4-methylpyridine at room temperature. Neither reproducible CHN analyses nor reproducible  $^1\text{H}$  NMR spectra of **2** could be obtained, a fact that is attributed to the formation of aluminum and lithium carbides and/or nitrides during combustion, giving lower C and N values, and to the high instability toward air and moisture.<sup>2</sup>

**3.** The synthesis was carried out in a manner analogous to the preparation of **1**, with 270 mg (7.1 mM) of  $\text{LiAlH}_4$  and 5.0 mL (44 mM) of 3,5-dimethylpyridine. After warming, further treatment with 3,5-dimethylpyridine (4.0 mL, 35 mM), and stirring at room temperature for 1 h, the resulting yellow mixture was heated to  $80\text{--}90^\circ\text{C}$  for 24 h. After slow removal of the excess of 3,5-dimethylpyridine in vacuo, yellow needles of **3** suitable for X-ray structural analysis were obtained.  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta$  8.05 (H-2,6), 7.2 (H-4), 2.15 (H-7,8), 5.7 (H-2',6'), 2.65 (H-4'), 1.3 (H-7',8').  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta$  148 (C-2,6), 137 (C-4), 134 (C-3,5), 130 (C-2',6'), 100 (C-3',5'), 38 (C-4'), 23 (C-7,8), 18 (C-7',8'). (For numbering scheme, see Figure 1.) Anal. Calcd for **3** ( $\text{C}_{56}\text{H}_{76}\text{AlLiN}_8$ , fw = 895.22): C, 75.13; H, 8.56; N, 12.52. Found (repeat determination): C, 69.03; H, 8.24; N, 11.44.

**4.** Pyridine (10 mL, 38 mmol) was condensed via a high-vacuum line onto a solution of freshly prepared  $\text{AlH}_3 \cdot \text{NMe}_3$  (500 mg, 5.6 mmol) in toluene (15 mL) at  $-196^\circ\text{C}$ .<sup>10</sup> The reaction mixture was stirred and slowly warmed to room temperature, at which point the suspension turned yellow. The solvent was removed in vacuo, the yellow residue was dissolved in 5 mL of toluene, and the solution was stored at  $4^\circ\text{C}$ . From the yellow solution, yellow, air-sensitive crystals of **4** precipitated



**Figure 1.** Structural formulas of tetrakis(pyridine)lithium tetrakis(1,4-dihydropyrid-1-yl)aluminate(III), **1**, tetrakis(4-methylpyridine)lithium tetrakis(4-methyl-1,4-dihydropyrid-1-yl)aluminate(III), **2**, tetrakis(3,5-dimethylpyridine)lithium tetrakis(3,5-dimethyl-1,4-dihydropyrid-1-yl)aluminate(III), **3**, and tris(1,4-dihydropyrid-1-yl)(pyridine)aluminum, **4**.

(yield 70%) after 2 days.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  8.21 (d, H-2,6), 7.16–7.02 (toluene), 6.68 (t, H-4), 6.37 (d, H-6''), 6.32 (dd, H-3,5), 6.25 (m, H-4''), 6.18 (d, H-2',6'), 5.31 (m, H-5''), 4.97 (m, H-3''), 4.56 (dt, H-3',5'), 3.92 (d, H-2''), 3.31 (t, H-4'), 2.14 (toluene). (Locators without primes refer to pyridine, those with one prime to 1,4-, and those with two primes to 1,2-dihydropyrid-1-yl.)  $^{13}\text{C}$  NMR (benzene- $d_6$ ):  $\delta$  147.5, 139.9, 131.8, 128.9, 125.2, 124.8, 98.6, 23.3, 21.0. IR (Nujol, NaCl),  $\text{cm}^{-1}$ : 3067 sh,  $\nu(\text{C}=\text{H})$ ; 3025 sh,  $\nu(\text{C}=\text{H})$ ; 2962.2 vs,  $\nu(\text{C}-\text{H})$ ; 2920 vs,  $\nu(\text{C}-\text{H})$ ; 2854.9 vs,  $\nu(\text{C}-\text{H})$ ; 1653.2 w,  $\nu(\text{C}=\text{C})$ ; 1601.5 w,  $\nu(\text{C}=\text{N})$ . UV/vis (toluene):  $\lambda_{\text{max}} = 421.1$  nm. Anal. Calcd for  $\text{Al}(\text{pyH})_3\text{py} \cdot 0.5\text{tol}$  ( $\text{C}_{23.5}\text{H}_{27}\text{AlN}_4$ , fw = 392.49): C, 71.90; H, 6.93; N, 14.28. Found: C, 70.02; H, 6.79; N, 16.58.

**Crystal Structure Determinations.** Crystal data collection and refinement parameters are given in Table 1. Suitable crystals for single-crystal X-ray diffraction of each compound were selected and mounted in an oil drop on top of a glass fiber on a Siemens CCD three-circle diffractometer (**1–3**) or on a STOE STADI-4 diffractometer (**4**). The unit cell parameters of **1–3** were obtained by the least-squares refinement of the angular settings of the 8192 most intensive reflections ( $2^\circ \leq 2\theta \leq 50^\circ$ ); those of **4**, from the 32 most intensive reflections ( $5.3^\circ \leq 2\theta \leq 55.0^\circ$ ). All structures were solved by direct methods using SHELXS86<sup>11</sup> and refined by full-matrix least-squares procedures using SHELXL97.<sup>12</sup> Absorption corrections for **1–3** were performed

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**Table 1.** Crystallographic Data for the Structural Analyses of **1–4**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
formula	C <sub>40</sub> H <sub>44</sub> AlLiN <sub>8</sub>	C <sub>48</sub> H <sub>60</sub> AlLiN <sub>8</sub>	C <sub>56</sub> H <sub>76</sub> AlLiN <sub>8</sub>	C <sub>23.5</sub> H <sub>27</sub> AlN <sub>4</sub>
fw	670.79	783.01	895.22	392.49
space group	<i>I</i> 4	<i>P</i> 1	<i>P</i> 2/ <i>n</i>	<i>P</i> 1
<i>a</i> /Å	16.3857(2)	9.8484(1)	14.0323(3)	9.202(5)
<i>b</i> /Å	16.3857(2)	10.4148(1)	11.9759(2)	10.888(5)
<i>c</i> /Å	13.7272(2)	11.8007(1)	16.8104(2)	11.756(5)
α/deg	90	89.817(1)	90	109.74(3)
β/deg	90	107.533(1)	107.682(1)	98.28(3)
γ/deg	90	90.358(1)	90	96.43(3)
V/Å <sup>3</sup>	3685.63(8)	1154.13(2)	2691.52(8)	1080.6(9)
Z	4	1	2	2
crystal color	yellow	yellow	yellow	orange
crystal shape	block	block	block	block
<i>D</i> (calcd)/g cm <sup>-3</sup>	1.209	1.127	1.105	1.206
μ(Mo Kα)/cm <sup>-1</sup>	0.95	0.85	0.080	0.110
<i>T</i> /K	173	173	173	220
λ/Å	0.710 73	0.710 73	0.710 73	0.710 73
min transmission	0.9630	0.7800	0.7380	
max transmission	0.9721	1.0000	1.0000	
no. of collected reflns	41 141	20 404	41 198	7090
no. of independent reflns	3786	8894	5493	4950
<i>R</i> (int)	0.0741	0.0357	0.0722	0.1072
no. of obsd reflns, <i>I</i> > 2σ( <i>I</i> )	2233	6121	3520	3656
no. of parameters	226	527	307	383
GOF	1.071	0.955	1.074	1.029
Δρ(min)/e Å <sup>-3</sup>	-0.369	-0.284	-0.180	-0.196
Δρ(max)/e Å <sup>-3</sup>	0.558	0.403	0.209	0.358
H atoms	riding model	riding model	riding model	isotropic
<i>R</i> ( <i>F</i> ), <sup>a</sup> <i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> ) <sup>a</sup>	9.57, 29.26	7.73, 22.80	7.14, 15.53	4.98, 13.54

<sup>a</sup> Quantity minimized  $R_w(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ ;  $R_w(F^2)$  based on all data;  $R(F)$  based on data with  $I > 2\sigma(I)$ .

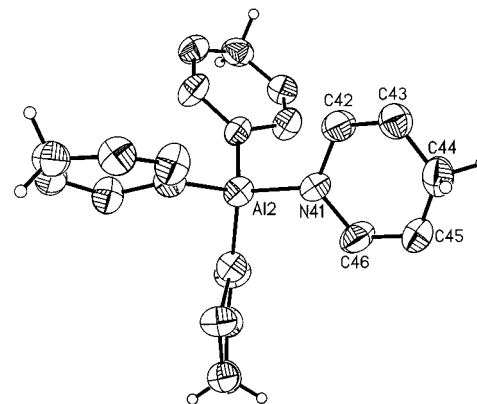
with SADABS.<sup>13</sup> All non-hydrogen atoms were refined anisotropically, hydrogen atoms in **1–3** were refined using a riding model, and hydrogen atoms in **4** were refined isotropically.

## Results and Discussion

The crystal structures of **1–3** reveal that only the thermodynamically favored isomers, in which all dihydropyridines are 1,4-dihydrogenated, crystallized. All three compounds feature an aluminum atom bound to the N atoms of four 1,4-dihydropyridyl systems. (See Figures 2–4 for the structures of the anions.)

As already indicated by elemental analysis and <sup>1</sup>H NMR investigations of **1**, single-crystal X-ray diffraction showed that Lansbury's reagent does not contain just a "naked" Li<sup>+</sup> cation, which hitherto has been anticipated to be the counterion of the dihydropyridyl anion. It is rather a [Li(py)<sub>4</sub>]<sup>+</sup> cation which acts as a counterion to [Al(1,4-dihydropyrid-1-yl)<sub>4</sub>]<sup>-</sup>. The [Li(py)<sub>4</sub>]<sup>+</sup> cation was first reported by Harvey et al.<sup>14</sup> The dimeric four-coordinated [Li(py)<sub>2</sub>(pyH)]<sub>2</sub> with 1,4-dihydropyridyls as bridging molecules was reported by Clegg et al.<sup>15</sup>

Presumably due to the increased steric hindrance of the 3,5-dimethyl-substituted derivative compared with the nonsubstituted and monomethyl-substituted pyridine derivatives, the crystal structure analysis of this isomer is of higher quality than those of **1** and **2** (see Table 1): In the 3,5-dimethyl-1,4-dihydropyrid-1-yl rings distinct differences of C–C bond lengths and angles at C atoms occur which are in accordance with the proposed structures. For instance, the average distance of C(2)–C(3) and C(5)–C(6) is 1.339 Å, which is close to the length of



**Figure 2.** ORTEP diagram of the tetrakis(1,4-dihydropyrid-1-yl)-aluminate(III) anion as determined by single-crystal X-ray diffraction (for clarity only the H atoms in 4-positions are shown). Displacement ellipsoids are at the 50% probability level. Important structural parameters (distances, Å; angles, deg): Al(1)–N(31) 1.863(4), Al(2)–N(41) 1.863(4), N(31)–C(32) 1.381(5), N(41)–C(42) 1.420(6), N(31)–C(36) 1.391(5), N(41)–C(46) 1.370(5), C(32)–C(33) 1.356(6), C(42)–C(43) 1.393(6), C(35)–C(36) 1.366(6), C(45)–C(46) 1.351(6), C(33)–C(34) 1.427(7), C(43)–C(44) 1.397(7), C(34)–C(35) 1.416(7), C(44)–C(45) 1.424(7); C(32)–N(31)–C(36) 113.9(4), C(42)–N(41)–C(46) 114.9(4), C(33)–C(34)–C(35) 115.5(4), C(43)–C(44)–C(45) 117.5(4).

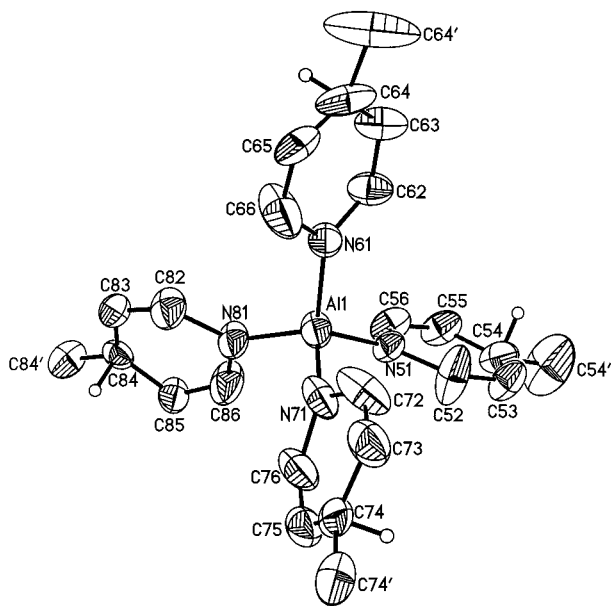
a simple C–C double bond of 1.337 Å.<sup>16</sup> The average C(13)–C(14)–C(15) angle of 112.7(9)° is closer to the tetrahedral angle of 109.47° than to the corresponding angle in 3,5-dimethylpyridine. Furthermore, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of these compounds showed the presence of vinylic hydrogen and carbon atoms, indicating that hydride transfer to the pyridine ring had occurred (see Experimental Section).

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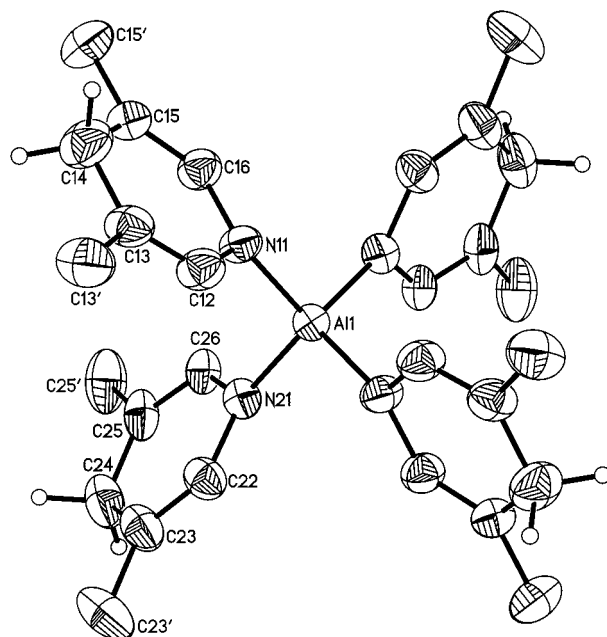
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**Figure 3.** ORTEP diagram of the tetrakis(4-methyl-1,4-dihydropyrid-1-yl)aluminate(III) anion as determined by single-crystal X-ray diffraction (for clarity only the H atoms in 4-positions are shown). Displacement ellipsoids are at the 50% probability level. Important structural parameters (distances, Å; angles, deg): Al(1)–N(51) 1.849(4), Al(1)–N(61) 1.838(4), Al(1)–N(71) 1.853(6), Al(1)–N(81) 1.848(5), N(51)–C(52) 1.400(7), N(61)–C(62) 1.390(8), N(71)–C(72) 1.426(9), N(81)–C(82) 1.419(7), N(51)–C(56) 1.387(7), N(61)–C(66) 1.428(8), N(71)–C(76) 1.378(8), N(81)–C(86) 1.375(8), C(52)–C(53) 1.331(8), C(62)–C(63) 1.307(7), C(72)–C(73) 1.310(10), C(82)–C(83) 1.386(8), C(55)–C(56) 1.314(8), C(65)–C(66) 1.341(8), C(75)–C(76) 1.303(9), C(85)–C(86) 1.322(8), C(53)–C(54) 1.364(9), C(63)–C(64) 1.409(10), C(73)–C(74) 1.423(10), C(83)–C(84) 1.347(7), C(54)–C(55) 1.376(9), C(64)–C(65) 1.315(10), C(74)–C(75) 1.352(10), C(84)–C(85) 1.398(7); C(52)–N(51)–C(56) 111.0(4), C(62)–N(61)–C(66) 112.3(5), C(72)–N(71)–C(76) 109.4(6), C(82)–N(81)–C(86) 111.5(5), C(55)–C(54)–C(53) 120.3(5), C(65)–C(64)–C(63) 119.8(5), C(75)–C(74)–C(73) 119.5(6), C(83)–C(84)–C(85) 120.2(4).

To complement our studies of (1,4-dihydropyrid-1-yl)aluminum complexes, we investigated the reaction of trimethylamine–alane,  $\text{AlH}_3 \cdot \text{NMe}_3$ , with pyridine. Trimethylamine–alane undergoes a wide range of reactions, including ligand displacement, reduction, and metalation.<sup>17,18</sup> For example, treatment of  $\text{AlH}_3 \cdot \text{NMe}_3$  with 2 equiv of 1,3,5-trimethylhexahydro-1,3,5-triazine (TMTZ) yields  $[\text{H}_3\text{Al}(\text{TMTZ})_2]^{19}$  with trigonal bipyramidal coordinated Al, while treatment with  $\text{Me}_4\text{CYCLAM}$  ( $N,N',N'',N'''$ -tetramethylcyclam) gives the ionic aluminum hydride species  $[\text{H}_2\text{Al}(\text{Me}_4\text{CYCLAM})]^+[\text{AlH}_4]^-$ .<sup>20</sup>  $\text{AlH}_3 \cdot \text{NMe}_3$  metalates  $(\text{Bu}^i\text{N}=\text{CH})_2$  to give the radical  $[\text{Al}\{\text{N}(\text{Bu}^i\text{CH})_2\}_2]$ , in which one ligand is reduced to a dianion and the other to a radical.<sup>21</sup> Surprisingly, until now no studies of reactions between  $\text{AlH}_3 \cdot \text{NMe}_3$  and aromatic nitrogen-containing bases have been reported. Although pyridine is a weaker base than  $\text{NMe}_3$ , we were curious to find out whether pyridine could displace  $\text{NMe}_3$  from  $\text{AlH}_3 \cdot \text{NMe}_3$  to form compounds such as  $\text{AlH}_3(\text{py})$  on the basis that facile loss of  $\text{NMe}_3$ , owing to its low boiling point,



**Figure 4.** ORTEP diagram of the tetrakis(3,5-dimethyl-1,4-dihydropyrid-1-yl)aluminate(III) anion as determined by single-crystal X-ray diffraction (for clarity only the H atoms in 4-positions are shown). Displacement ellipsoids are at the 50% probability level. Important structural parameters (distances, Å; angles, deg): Al(1)–N(11) 1.856(2), Al(1)–N(21) 1.855(2), N(11)–C(12) 1.401(3), N(21)–C(22) 1.400(3), N(11)–C(16) 1.394(3), N(21)–C(26) 1.402(3), C(12)–C(13) 1.339(3), C(22)–C(23) 1.338(3), C(15)–C(16) 1.344(3), C(25)–C(26) 1.336(3), C(13)–C(14) 1.478(4), C(23)–C(24) 1.497(4), C(14)–C(15) 1.491(4), C(24)–C(25) 1.497(4); C(12)–N(11)–C(16) 113.7(2), C(22)–N(21)–C(26) 113.3(2), C(13)–C(14)–C(15) 112.7(2), C(23)–C(24)–C(25) 111.8(2).

would drive the reaction in favor of formation of the pyridine adduct. The reaction at ambient temperature between  $\text{AlH}_3 \cdot \text{NMe}_3$  and an excess of pyridine in toluene gave a yellow solution from which yellow, air-sensitive crystals of **4** were obtained.

The infrared spectrum of this compound showed no absorption attributable to Al–H stretching modes, and the  $^1\text{H}$  NMR spectrum showed the presence of vinylic protons. Confirmation that again hydride transfer to the pyridine ring has occurred comes from the X-ray crystal structure determination (illustrated in Figure 5). The average Al–N distances for the Al bound to dihydropyridyl groups in compounds **1–4** are slightly longer than the average Al–N<sub>terminal</sub> bonds of 1.802(2) Å in  $(\text{Me}_2\text{N})_2\text{Al}(\mu\text{-NMe}_2)_2\text{Al}(\text{NMe}_2)_2$ <sup>21</sup> and 1.793(4) Å in  $[(\text{Me}_2\text{N})_2\text{Al}\{\mu\text{-NCH}(1\text{-ad})\}_2]$  (where ad = adamantyl).<sup>22</sup>

Crystal structure analyses of **1–4** reveal that, within all four complexes, the N–Al–N angles are close to the tetrahedral angle of 109.47°. It is noteworthy that, in **4**, a slight deviation from the tetrahedral angle could be found because this complex contains two different types of Al–N bonds, one longer bond between Al and N(pyridine),  $d(\text{Al}–\text{N}) = 1.959(2)$  Å, and three shorter bonds between Al and N(1,4-dihydropyrid-1-yl),  $d_{\text{av}}(\text{Al}–\text{N}) = 1.833$  Å. Furthermore the calculated sums of all valences<sup>23</sup> of **1–4** are 3.50, 3.65, 3.57, and 3.52, respectively. It is remarkable that all complexes exhibit similar calculated valence numbers which are significantly greater than 3.

The conversion of initially formed 1,2- into 1,4-dihydropyrid-1-yl ligands mentioned by Tanner et al.<sup>3</sup> is mirrored by our studies. We find that a toluene solution of  $\text{AlH}_3 \cdot \text{NMe}_3$  and

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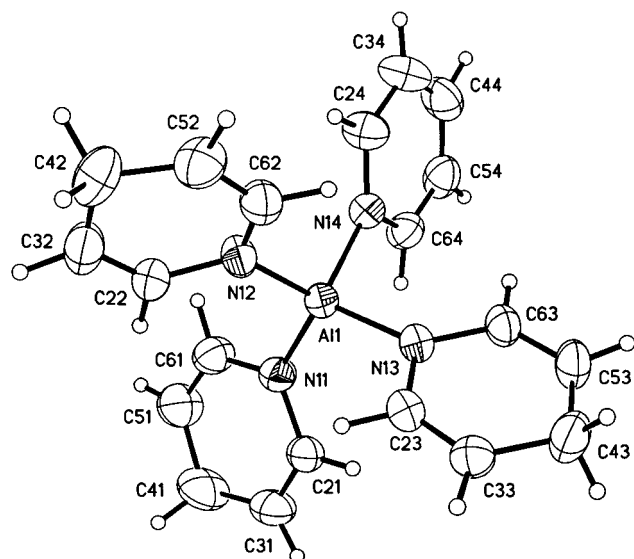
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**Figure 5.** ORTEP diagram of **4** (for clarity only the H atoms in 4 positions are shown). Displacement ellipsoids are at the 50% probability level. Important structural parameters (distances, Å; angles, deg): Al(1)–N(11) 1.826(2), Al(1)–N(12) 1.842(2), Al(1)–N(13) 1.831(2), Al(1)–N(14) 1.959(2), N(11)–C(21) 1.397(3), N(12)–C(22) 1.392(3), N(13)–C(23) 1.402(3), N(14)–C(24) 1.344(3), N(11)–C(61) 1.402(3), N(12)–C(62) 1.2385(3), N(13)–C(63) 1.400(2), N(14)–C(64) 1.353(3), C(21)–C(31) 1.323(3), C(22)–C(32) 1.331(3), C(23)–C(33) 1.326(3), C(24)–C(34) 1.383(3), C(51)–C(61) 1.328(3), C(52)–C(62) 1.333(3), C(53)–C(63) 1.326(3), C(54)–C(64) 1.367(3), C(31)–C(41) 1.493(4), C(32)–C(42) 1.494(4), C(33)–C(43) 1.493(4), C(34)–C(44) 1.373(4), C(41)–C(51) 1.489(4), C(42)–C(52) 1.494(4), C(53)–C(43) 1.495(4), C(54)–C(44) 1.372(4); N(11)–Al(1)–N(12) 112.05(9), N(11)–Al(1)–N(13) 112.58(9), N(12)–Al(1)–N(13) 111.96(9), N(11)–Al(1)–N(14) 107.05(9), N(12)–Al(1)–N(14) 109.13(8), N(13)–Al(1)–N(14) 103.54(8), C(21)–N(11)–C(61) 113.6(2), C(22)–N(12)–C(62) 114.7(2), C(23)–N(13)–C(63) 113.4(2), C(24)–N(14)–C(64) 118.2(2), C(31)–C(41)–C(51) 109.5(2), C(32)–C(42)–C(52) 109.2(2), C(33)–C(43)–C(53) 109.4(2), C(34)–C(44)–C(54) 119.3(2).

pyridine (as well as a solution of  $\text{LiAlH}_4$  in pyridine) initially contains a mixture of 1,2- and 1,4-dihydropyridyl groups bound to aluminum but dissolution of the crystals formed after aging gives a solution in which only the 1,4-dihydropyridyl isomers are present. No initial formation of 1,2-dihydro-3,5-dimethylpyrid-1-yl was observed for the reaction of  $\text{LiAlH}_4$  with 3,5-dimethylpyridine. For the reaction of  $\text{LiAlH}_4$  and 4-methylpyridine, good-quality NMR spectra are generally lacking.

The reaction between  $\text{AlH}_3\cdot\text{NMe}_3$  and pyridine to produce **4** suggests that other nitrogen-containing aromatic compounds might undergo similar reactions, thereby providing a route to aluminum compounds with elusive nitrogen-containing ligands.

It is interesting to note that the reaction between  $\text{GaH}_3\cdot\text{NMe}_3$  and pyridine under similar conditions did not proceed in an analogous fashion. This suggests that the hydride character of the M–H bond is important in these reactions; i.e., the Al–H bond is more polar than the Ga–H bond. This explanation has also been invoked to explain the much greater ease with which secondary amine adducts of  $\text{AlH}_3$  eliminate dihydrogen compared with adducts of  $\text{GaH}_3$ .<sup>24</sup>

A further avenue for investigation is the potential of compound **4** as a selective reducing agent, particularly in view of its solubility in nonpolar solvents such as benzene and toluene, unlike compound **1**.

**Solid State Structures.** (For data see Table 1.) **1** crystallizes with two-fourths of a formula unit in the asymmetric unit. Li and Al are located on a site of symmetry  $\bar{4}$ , and only one of the four rings attached to a metal atom is symmetry independent.

The anisotropic displacement parameters of the methyl groups in the dihydropyridyl rings of **2** indicate that the dihydropyridyl rings are disordered about a 2-fold rotation axis through the N atom and the C atom in the 4-position. On the other hand, the methyl groups of the pyridine rings attached to the Li atom are well ordered. A thorough inspection of bond lengths and angles in all rings reveals unambiguously the different kinds of substituents, i.e., pyridine versus dihydropyridyl.

**3** crystallizes with two half formula units in the asymmetric unit. Li and Al are located on a 2-fold rotation axis.

**4** crystallizes with one  $\text{Al}(\text{pyH})_3\text{py}$  and half a toluene in the asymmetric unit. The toluene is situated on an inversion center and is therefore disordered. The Al atom is bonded to one pyridine and three 1,4-dihydropyridyls. The Al–N bond lengths are significantly different: for Al–N(1,4-dihydropyridyl) a mean value of 1.85(2) Å was found, whereas the Al–N(pyridine) bond is longer at 1.959(2) Å. The C2–C3 and C5–C6 bonds of the three dihydropyridyl moieties are unambiguously double bonds, which is proven by the values of 1.323(3)–1.325(3) Å, typical for a C=C double bond. The pyridine ring, on the other hand, displays typical aromatic bond lengths and angles.

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, for all structures presented. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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