On the Structure and Mechanism of Formation of the Lansbury Reagent, Lithium Tetrakis(*N*-dihydropyridyl)aluminate[1]

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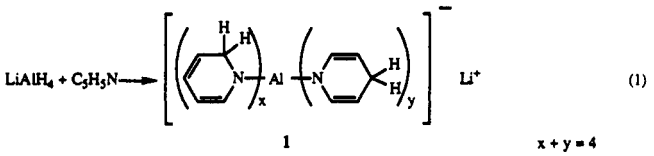
The reaction of lithium aluminum hydride (LAH) and pyridine yields five lithium tetrakis(*N*-dihydropyridyl)aluminate (LDPA) isomers. The LDPA isomers are formed reversibly and contain both 1,2- and 1,4-dihydropyridyl ligands. The 1,2-dihydropyridyl ligands are incorporated as the products of kinetic control while the 1,4-dihydropyridyl ligands are formed as the thermodynamic products. When LDPA is synthesized using lithium aluminum deuteride and the deuterated LDPA is placed in pyridine solvent, the ligands exchange with the pyridine in the solvent pool and form pyridine which is deuterated mainly in the 2- and 4-positions. A small amount of 3-deuterated pyridine is also detected. The formation of 3-deuteriopyridine suggests that the pyridine radical anion is an intermediate present during the reaction of LAH with pyridine. In support of this suggestion, when LAH and pyridine are mixed, the EPR spectrum of the lithium salt of the pyridyl radical anion is observed. The stepwise addition of ligands to form LDPA is observed (NMR). Five aluminate species are detectable (^{27}Al NMR): LAH, mono-, di-, and trisubstituted aluminum hydride, and LDPA. The hydrolysis of LDPA in solvent pyridine-d_5 yields a mixture of 1,4-, 1,2-, and 2,5-dihydropyridines. The dihydropyridines are stable in the absence of oxygen.

Introduction

The reduction reactions of $LiAlH_4$ (LAH) in solvent pyridine were shown by Lansbury and Peterson to proceed selectively when the LAH and pyridine were mixed, "aged" prior to the addition of the hydride to a carbonyl containing substrate.[2,3] The aged mixtures readily reduced certain aldehydes and ketones, but not carboxylic acids and esters. The reagent, which preferentially reduced highly electrophilic carbonyl groups, was subsequently shown to be lithium tetrakis(*N*-dihydropyridyl)aluminate (LDPA), 1.[4] The structure of the newly formed reagent, 1, was analyzed by ^{1}H NMR spectroscopy and found to have both 1,2- and 1,4-dihydropyridyl ligands (3.5 C_5H_5N/LAH).



(1)

1 x + y = 4

The 1,4-dihydropyridyl was proposed to be the thermodynamically more stable ligand since when the reactants were mixed at 0 °C and aged at different temperatures the complex showed a temperature-dependent ratio of 1,4-/1.2-dihydro isomers which favored 1,4-bonding at higher temperatures.

The reagent has been used, since Lansbury's original work, for selective reductions,[5a-g] as a syntheticly useful reagent for the production of 3-substituted pyridines.[5b] The mechanism of its reductions has also been studied.[5i,j]

Since the reduction reactions of derivatives of dihydropyridine (DHP) have been of considerable interest as model compounds for NADH reductions, and for their use as selective reducing agents,[6] a study of the structure and reactivity of LDPA, an inorganically bound derivative of dihydropyridine,[7] was undertaken.

Results and Discussion

Reversible Formation of LDPA. The temperature-dependent isomer distribution of the isomers of LDPA was reinvestigated and shown to be in qualitative agreement with the values reported by Lansbury.[4] When the reactants are mixed an exothermic reaction takes place. In order to determine the thermodynamic distribution of the ligands in the LDPA complex the reactants were mixed and aged at each of the desired temperatures. When a complex formed and aged at a lower temperature was heated to a higher temperature in pyridine solvent the distribution of ligands (1,4-/1,2-) changed to that found in the complex formed at the higher temperature, see Table I.

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Table I. Effect of Temperature on the 1,4-/1,2-Dihydropyridyl Ratio in 1[a]

temp, °C	ratio 1,4-/1,2-	temp, °C	ratio 1,4-/1,2-
−30	0.19	61 (23)[b]	2.45
0	0.47	90	2.53
23	0.62	90 (23)[c]	7.40
61	0.73	90 (0)[d]	>99

[a] The samples were prepared and aged for 5 days. At this time, the thermodynamic equilibrium was not reached. [b] A crystalline sample of LDPA prepared at 23 °C, (1,4-/1,2-) = 0.62, was heated in pyridine at 61 °C for 48 h. [c] The 23 °C complex was heated at 90 °C for 48 h. [d] The sample prepared at 0 °C, (1,4-/1,2-) = 0.47, was heated in pyridine at 90 °C for 100 h.

Table II. Deuterium Distribution in the Tetradeuterated LDPA Complex and the Solvent Pyridine before and after Exchange[a]

$LiAl(C_5H_5DN)_4$		C_5H_4DN			
1,2- (%)	1,4- (%)	2-D- (%)	3-D- (%)	4-D- (%)	
58.3	30.8	9.7	0.4	0.8	(before heating at 90 °C)
22.7	27.7	34.5	2.7	12.4	(4 days of heating at 90 °C)
14.1	23.7	43.0	2.1	17.0	(7 days of heating at 90 °C)

[a] Percentages were calculated from the integrated ^2H NMR spectra.

The reversible formation of LDPA established that the 1,4-dihydropyridyl complex is the product of thermodynamic control while the complex containing 1,2-dihydropyridyl ligands was the product of kinetic control.

The distribution of ligands in the LDPA complex was determined by integration of the 400-MHz ^1H NMR spectrum of the complex, Figure 1. The isomer distribution obtained from this analysis was presumably an average distribution of five isomeric aluminates, **2–6**, Figure 2. An analysis of the 100.6-MHz ^{13}C NMR of a THF solution of the LDPA complexes formed at different temperatures allowed the assignment of the ^{13}C chemical shifts of the carbon 5 of the 1,2-dihydropyridyl ligands of four of the five isomeric LDPA complexes (**3–6**). Since the 1,4-/1,2- ratio of ligands in LDPA formed at high temperature (90 °C) was >3, then the complex with all 1,4-dihydropyridyl ligands must also have been present. Furthermore, the decoupled ^1H NMR spectrum of LDPA formed with either high or low 1,4-/1,2- ratios of dihydropyridyl ligands showed the same distribution of all five isomers, **2–6**, as was determined using the ^{13}C NMR spectra. The protons at both the 2- and 6-positions of the 1,2-dihydropyridyl ligand, decoupled from their adjacent protons, showed four separate absorbances which corresponded to isomers **3–6**. When the protons at C-2 of the 1,4-dihydropyridyl ligand were decoupled from their adjacent proton, the four separate LDPA isomers **2–5** could be observed.

When $LiAlD_4$ (LAD) was allowed to react with pyridine (23 °C), deuterated LDPA (LDPA-d_4) was formed. The 30.7-MHz ^2H spectrum also showed that the product mixture contained small amounts of three monodeuterated pyridines. When a crystalline sample of the tetradeuterated LDPA which contained occluded pyridine solvent was dissolved in fresh pyridine and heated for 7 days at 90 °C not only did the 1,4-/1,2- ratio of deuterated pyridyl ligands in the LDPA change, but the deuterium was also exchanged from the deuterated LDPA into the solvent pool, see Table II and Figure 3a,b.

The deuterated pyridine was a mixture of three isomers with deuterium substituted at the 2-, 3-, and 4-positions. A mechanism which proceeds via a polar, hydride transfer process is expected to yield only 2- and 4-deuterated pyridines (Scheme I, eqs 2–4). However, small amounts of 3-deuterated pyridine are also formed during the reversible exchange. A homolytic exchange mechanism which may account for these reversible processes is given in Scheme II (eqs 5–8).

Scheme I

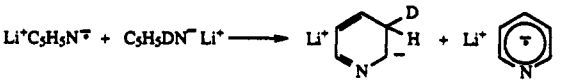
$$Li^+{}^-Al(C_5H_5D)_4 \rightleftharpoons Li^+C_5H_5D^- + Al(C_5H_5DN)_3 \quad (2)$$

$$Li^+C_5H_5DN^- + C_5H_5N \rightleftharpoons C_5H_6{}^-Li^+ + C_5H_4DN \quad (3)$$

$$Al(C_5H_5D)_3 + C_5H_6N{}^-Li^+ \rightleftharpoons Li^+{}^-Al(C_5H_5D)_3(C_5H_6N) \quad (4)$$

Scheme II

$$C_5H_5DN^-Li^+ + C_5H_5N \longrightarrow Li^+C_5H_5N^{\bullet-} + C_5H_5ND^{\bullet} \quad (5)$$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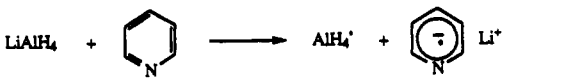
(7)


(8)

Scheme III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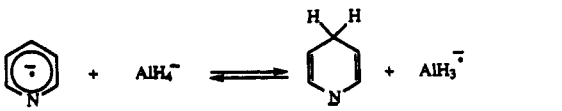
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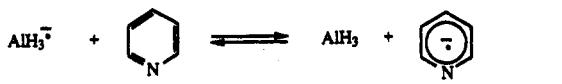
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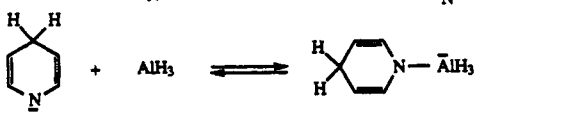
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Although no EPR signals could be detected during the exchange reaction between LDPA and pyridine, the involvement of a radical pathway was considered since it was consistent with substitution at the 2-, 3-, and 4-positions of the pyridyl radical anion. The intermediacy of a radical anion was confirmed when LAH was allowed to react with pyridine. An exothermic reaction took place when a degassed sample of pyridine and a THF solution of LAH were mixed in an EPR tube in the cavity of the EPR spectrometer. A strong signal of the radical anion of pyridine was obtained. The spectrum lasted for several hours, at which time the ^{27}Al NMR showed that all of the LAH had reacted. The spectrum was identical to that of electrochemically generated lithium salt of the radical anion of pyridine. The formation of the radical ion can be rationalized by invoking an electron-transfer reaction between LAH and pyridine with the subsequent formation of the monodihydropyridyl complex, see Scheme III.

The mechanism which leads to further substitution after the LAH has all reacted may be either heterolytic (eqs 13 and 14) or homolytic (eqs 15–17); however, at this time no further information is available. The stepwise addition of ligands is observed when the ^{27}Al spectra was monitored

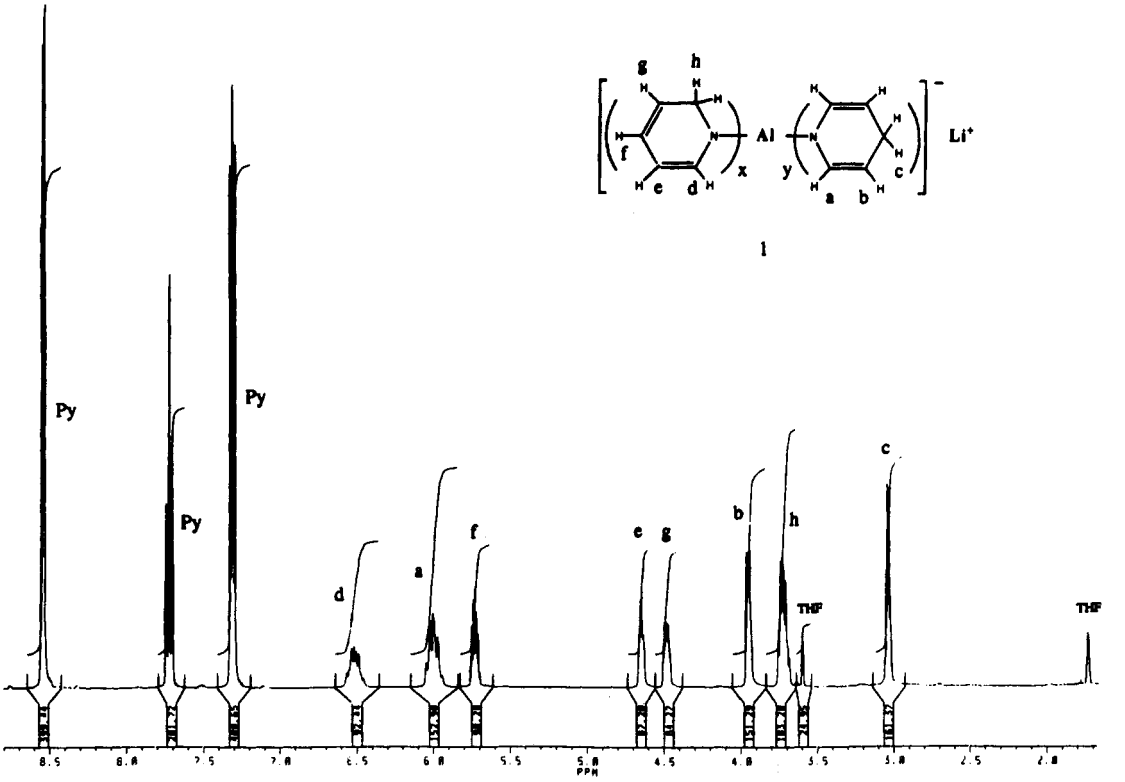
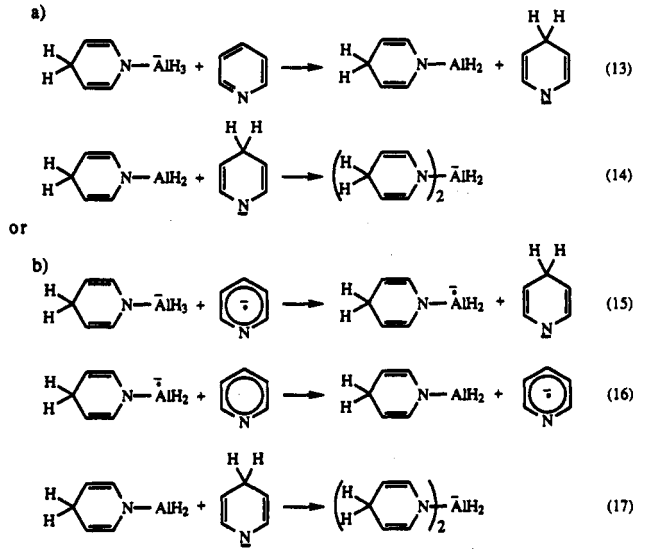
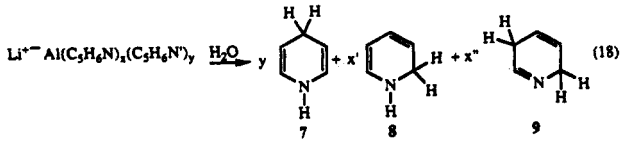


Figure 1. A Typical 400-MHz ^{1}H NMR spectrum of LDPA (THF-d_8).

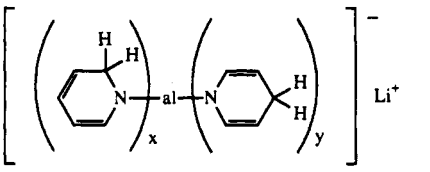
during the formation of LDPA. Five aluminate species are detected: LAH, mono-, di-, and tri-substituted aluminum hydrides, and LDPA. The LDPA was formed at the expense of the hydride species.



Hydrolysis of LDPA. When LDPA is treated with a small amount of water, in the absence of oxygen, the complex is hydrolyzed and a mixture of 1,4-, 1,2-, and 2,5-dihydropyridines is formed, eq 18.



Since in the LDPA complex only 1,2- and 1,4-dihydropyridyl ligands are present, the formation of the 2,5-dihydropyridine presumably arises from the 1,2-dihydropyridyl ligand. This assumption was confirmed since the ratio of 1,4-/1,2-ligands in LDPA is the same as the ratio of dihydropyridines, $y/(x' + x'')$. Further confirmation for this assumption is obtained when the LDPA complex formed at 90 °C (>99% 1,4-dihydropyridyl ligands) is hydrolyzed, only 1,4-dihydropyridine is obtained (see Table III).



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2, x = 0, y = 4; 3, x = 1, y = 3

4, x = 2, y = 2; 5, x = 3, y = 1

6, x = 4, y = 0

Figure 2. Five isomeric structures of the LDPA anion.

The assignment of the structure for the three dihydropyridines (DHP's) was made on the basis of the 400-MHz ^{1}H and 100.6-MHz ^{13}C NMR spectra of the hydrolysis mixture, see Figure 4a,b. The assignment of the absorption in the mixture which was due to 1,4-dihydropyridine was confirmed by a comparison of its spectra (^{13}C and ^{1}H NMR) with the value reported in the literature.[6] Although the unsubstituted 1,2- and 2,5-dihydropyridines have not been previously reported, the assignments can be made from analysis of their ^{1}H and decoupled ^{1}H NMR spectra and their APT ^{13}C NMR (Figure 4b), see the Experimental Section. The assignment of the absorption of the 2,5-dihydropyridine was further confirmed by the observation of a NOE enhancement between adjacent protons at the 5- and 6-positions. The spectra of the monodeuterated dihydropyridines, 7–9, were also in agreement with these

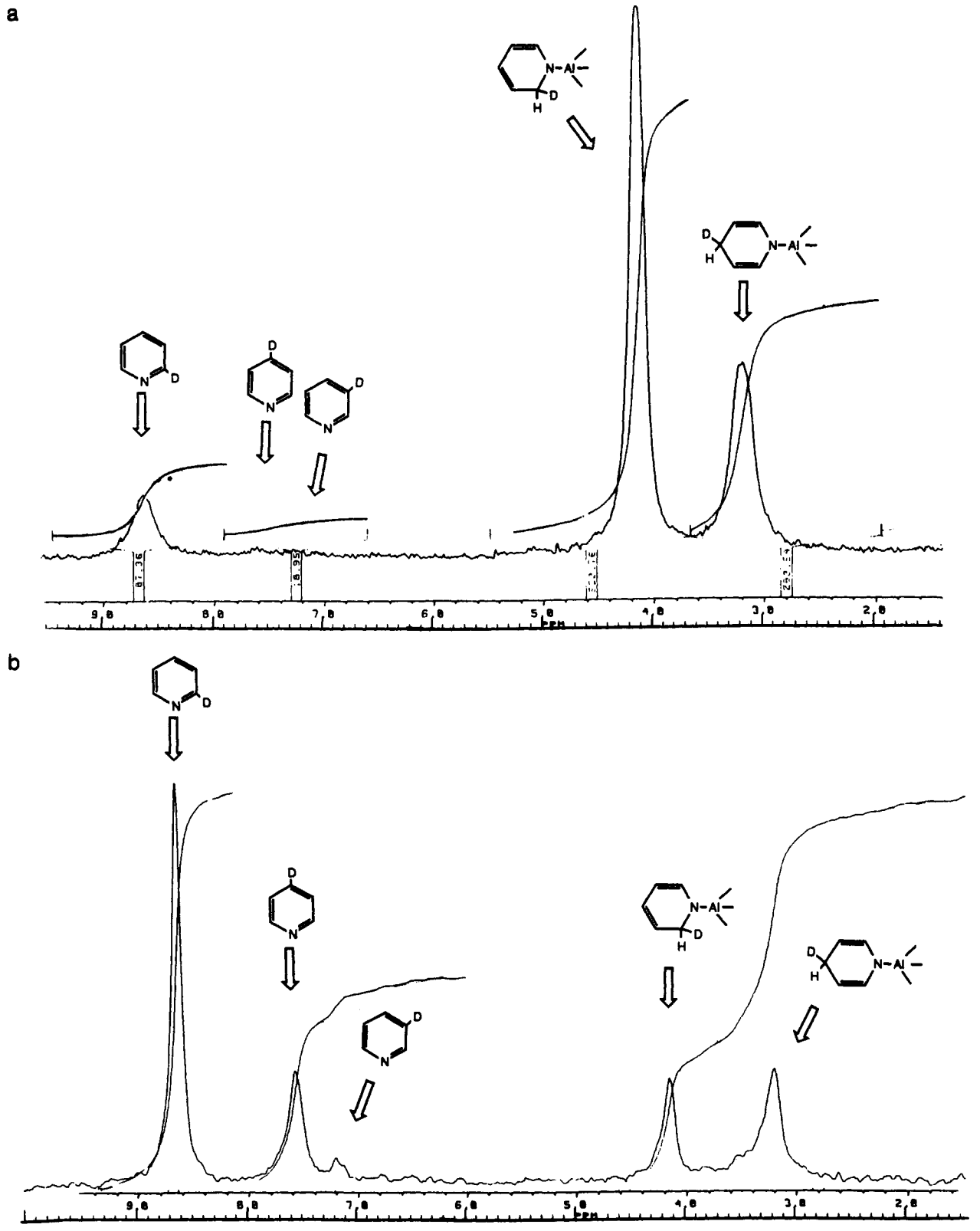


Figure 3. The ^2H distribution in the tetradeuterated LDPA–pyridine solution (a) before (25 °C) and (b) after heating (90 °C, 7 days).

assignements. When LDPA-d_4 which was synthesized with LAD was hydrolyzed, monodeuterated 2-deuterio-8 and 9 were formed as well as 4-deuterated 7 (eqs 21 and 22). When LDPA was hydrolyzed with D_2O (eqs 23 and 24) 5-deuterio-9 and *N*-deuterio-7 and 8 could be detected, see Scheme IV.

The hydrolysis of the 1,4-dihydropyridyl ligand from LDPA leads only to 1,4-dihydropyridine while the 1,2-dihydropyridyl ligand yields only 1,2- and 2,5-dihydropyridines.

Experimental Section

Materials. Pyridine (reagent grade, ACS) and pyridine-d_5 (99.5% D, Merck Sharp and Dohme Canada Limited) were stored over a mixture of BaO and KOH and were freshly distilled prior to use.

Lithium aluminum hydride (General Intermediates of Canada) was purified by dissolving it in diethyl ether and separating it by filtering from the insoluble LiH. The solid $LiAlH_4$ was isolated from the clear filtrate by distillation.[2] $LiAlD_4$ (Aldrich, 98 atom % D) was used as supplied.

Table III. Percentage of 1,4- and 1,2-Dihydropyridyl Ligands in LDPA before Hydrolysis and the Dihydropyridines Present in the Hydrolysate

sample no.	isomer	% before hydrolysis	% after hydrolysis
1	1,4	47.2	45.4
	1,2	52.8	29.0
	2,5	0.00	25.6
2	1,4	44.0	44.1
	1,2	56.0	27.1
	2,5	0.00	28.9
3	1,4	49.00	52.1
	1,2	51.00	24.0
	2,5	0.00	23.9
4	1,4	>99	100.0

Tetrahydrofuran (Aldrich, HPLC grade) was dried over KOH for >7 days and then distilled from sodium benzophenone ketyl before use. THF-d_8 (GIC, 99% D) was purified by the same method.

Instrumentation. The ^{1}H, ^{27}Al, and ^{13}C NMR spectra were obtained using a 400-MHz (Bruker) NMR spectrometer. All other spectra were obtained using a WH 200-MHz (Bruker) spectrometer.

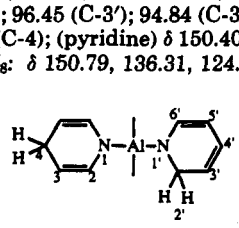
The EPR spectra were obtained using a Bruker ER 200 E/SRC spectrometer fitted with a ER 4102 ST-Universal X-Band Resonator operated at 9.6 GHz. The in situ electrolysis was carried out in a degassed cell fitted with two Pt flag electrodes. The EPR spectrum from the mixture of LAH and pyridine was obtained by mixing the degassed reagents at room temperature in the EPR cell and immediately placing the cell in the cavity of the spectrometer and recording the spectrum.

General Procedure for Preparation of LDPA. Purified LAH (0.200 g, 5.27 mmol) was added in small portions to a stirred aliquot, 20 mL, of freshly distilled pyridine. The pyridine was thermostated at the desired temperature before the addition of LAH. The addition was carried out under an atmosphere of dry nitrogen. After 24 h the reaction mixture was placed in a drybox under a nitrogen atmosphere, any unreacted solid was filtered through sintered glass. The solutions were sealed in NMR tubes and again thermostated at the required temperature and periodically subjected to NMR analysis at that temperature.

When crystalline LDPA was desired a more concentrated pyridine solution of LDPA was prepared (0.5 M LAH). After filtering the unreacted LAH, light-yellow crystals were formed when the solution was allowed to stand at the desired temperature for 3–7 days. The crystals were filtered in a drybox and dried in vacuo over P_2O_5. ^{1}H NMR (400 MHz, THF-d_8): δ 3.03–3.07 (m, 2 H, J_{34} = 3.21 Hz, J_{24} = 1.60 Hz, H-4)·y, 3.70–3.77 (m, 2 H, $J_{2'3'}$ = 4.41 Hz, $J_{2'4'}$ = 1.20 Hz, H-2')·x, 3.94–3.98 (m, 2 H, J_{23} = 8.20 Hz, J_{34} = 3.21 Hz, H-3)·y, 4.46–4.50 (m, 1 H, $J_{3'4'}$ = 9.02 Hz, $J_{2'3'}$ = 4.41 Hz, H-3')·x, 4.62–4.66 (m, 1 H, $J_{4'5'}$ = 5.01 Hz, $J_{5'6'}$ = 6.02 Hz, H-5')·x, 5.70–5.76 (m, 1 H, $J_{3'4'}$ = 9.02 Hz, $J_{4'5'}$ = 5.01 Hz, H-4')·x, 5.95–6.05 (m, 2 H, J_{23} = 8.20 Hz, J_{24} = 1.60 Hz, H-2)·y, 6.47–6.57 (m, 1 H, $J_{5'6'}$= 6.02 Hz, H-6')·x; (pyridine) δ 8.53, 7.76, 7.34 (free pyridine in THF-$d8$: δ 8.64, 7.68, 7.28).

^{1}H NMR (300 MHz, C_5H_5N): δ 6.94–6.89 (m, H-6'), 6.62–6.54 (m, H-2), 6.12–6.04 (m, H-4'), 5.08–5.01 (m, H-5'), 4.84–4.77 (m, H-3'), 4.34–4.25 (m, H-3), 4.24–4.18 (m, H-2'), 3.31–3.26 (m, H-4).

^{13}C NMR (100 MHz, THF-d_8): δ 145.00 (C-6'); 135.53, 135.45 (C-2); 127.05, 127.02, 126.99, 126.96 (C-4'); 102.42, 102.32, 102.21, 102.11 (C-5' in **3**–**6**); 96.45 (C-3'); 94.84 (C-3); 45.23 (C-2'); 24.91, 24.88, 24.85, 24.81 (C-4); (pyridine) δ 150.40, 137.17, 124.85 (free pyridine in THF-d_8: δ 150.79, 136.31, 124.38).



When deuterated LDPA was formed from LAD and pyridine, the product showed deuterium in both the 2-position of 1,2-dihydropyridyl ligand and the 4-position of the 1,4-dihydropyridyl ligands.

^{2}H NMR (C_5H_5N, 61.4 MHz), LiAl(C_5H_5D)$_4$: δ 4.09, 3.10 and δ 8.53, 7.29 (^{2}H on pyridine-d_x).

APT ^{13}C NMR (100.6 MHz, THF-d_8) of LiAl(C_5H_5D)$_4$ shows CHD (δ 44.85) and CHD (δ 24.44).

The crystalline material was transferred to an NMR tube in the absences of air and moisture (drybox, N_2 atmosphere). The proton absorption resonances were assigned from the decoupled spectra.

The above assignments would be confirmed by preparing a LDPA complex using LAH and pyridine-d_5. The ^{1}H NMR of a pyridine-d_5 soulution of the LiAl (C_5H_5NH)$_4$ complexes showed ^{1}H absorption at δ 4.07 and 3.19.

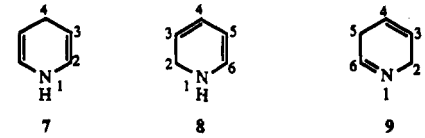
^{27}Al NMR: Reaction of LiAlH$_4$ with Pyridine. Stepwise Formation of LDPA. A THF solution of pyridine (0.64 M) and LAH (0.13 M) was prepared under a nitrogen atmosphere at −30 °C. The ^{27}Al NMR spectrum was taken, and only the absorbance of LAH (δ 101.05, J_{Al-H} = 172.6 Hz, quintet, [Al(H_2O)$_6^{3+}$] as external standard) was observed (15 min). The temperature was gradually increased (20 min) to room temperature (30 °C), and the formation of a product assigned to LiAl(C_5H_6N)H_3 appeared (δ 125.07, broad mult). A new absorbance at δ 124.97 (broad mult) became apparent after approximately 30 s. The new absorbance was assigned to LiAl(C_5H_6N)$_2H_2$. After a subsequent 3 min the absorbance attributed to LiAl(C_5H_6N)$_3$H began to appear (δ 112.58, J_{Al-H} = 208.0 Hz, doublet), as the absorption of LDPA (δ 98.84, singlet) appeared. The absorbance of LAH disappears after 2.5 h. After 20 h only the absorbance of LDPA could be detected.

In an independent experiment carried out in an EPR tube in the cavity of an EPR spectrometer after the LAH has all reacted (~2.5 h), no EPR signal could be detected.

Exchange between Solvent Pyridine and the 4- and 2-Monodeuterated Dihydropyridyl Ligands in the LDPA Complex. A solution of LiAl(C_5H_5DN)$_4$ was prepared from crystalline LiAl(C_5H_5DN)$_4$ and dry pyridine at 23 °C. An aliquot of the solution was placed in a NMR tube which was then degassed and sealed. The ^{2}H NMR spectrum was recorded. A small amount of deuterated pyridine occluded in the crystalline material was initially observed. The tube was thermostated at 90 °C for 4 or 7 days, and its ^{2}H NMR spectra were periodically recorded. The distribution of ^{2}H in the mixture is given in Table II.

The deuterated LDPA was prepared in the same manner as the protiated material but from LAD. The ^{2}H and ^{13}C NMR absorption resonances were assigned by analogy to the ^{1}H and ^{13}C NMR spectra of LDPA.

Hydrolysis of LDPA. Crystalline LDPA (0.050 g, 1.49 × 10^{-4} mol) dissolved in dry pyridine-d_5 (0.50 mL) was placed in a NMR tube, and H_2O (0.013 mL, 6.9 × 10^{-4} mol) was added. The hydrolysis was carried out under a nitrogen atmosphere. The tube was degassed and sealed, and NMR (^{1}H and ^{13}C) spectra were taken (see Figure 4). The identities of the DHP's, **7**–**9**, were assigned to the individual compounds on the basis of their ^{1}H NMR integrated intensities, and the structure for each compound was assigned by a consideration of the decoupled ^{1}H NMR and the APT ^{13}C spectra.



7 **8** **9**

The APT ^{13}C spectra of the mixture showed four methylene carbons, one each for **7** and **8** and two belonging to **9**.

1,4-Dihydropyridine (7, 1,4-DHP). ^{1}H NMR (400 MHz, C_5D_5N): δ 7.01–6.95 (b, NH), 6.16–6.10 (m, 1 H, J_{23} = 8.02 Hz, J_{24} = 1.50 Hz, J_{12} = 4.45 Hz, H-2), 4.37–4.34 (m, 1 H, J_{23} = 8.02 Hz, J_{34} = 3.27 Hz, H-3), 3.12–3.08 (m, 1 H, J_{34} = 3.27 Hz, J_{24} = 1.50 Hz, H-4). ^{13}C NMR (100.6 MHz, C_5D_5N): δ 128.62 (C-2), 96.11 (C-3), 22.3 (C-4). The chemical shifts obtained for **7** were consistent with the 100-MHz values previously reported for 1,4-dihydropyridine[8a] (lit.[8a] ^{1}H NMR (C_5D_5N) δ 5.87, 4.24, 2.98; ^{1}H NMR (C_6D_6) δ 5.73, 4.42, 3.15; ^{13}C NMR (C_5D_5N) δ 127.3, 95.3, 22.3).

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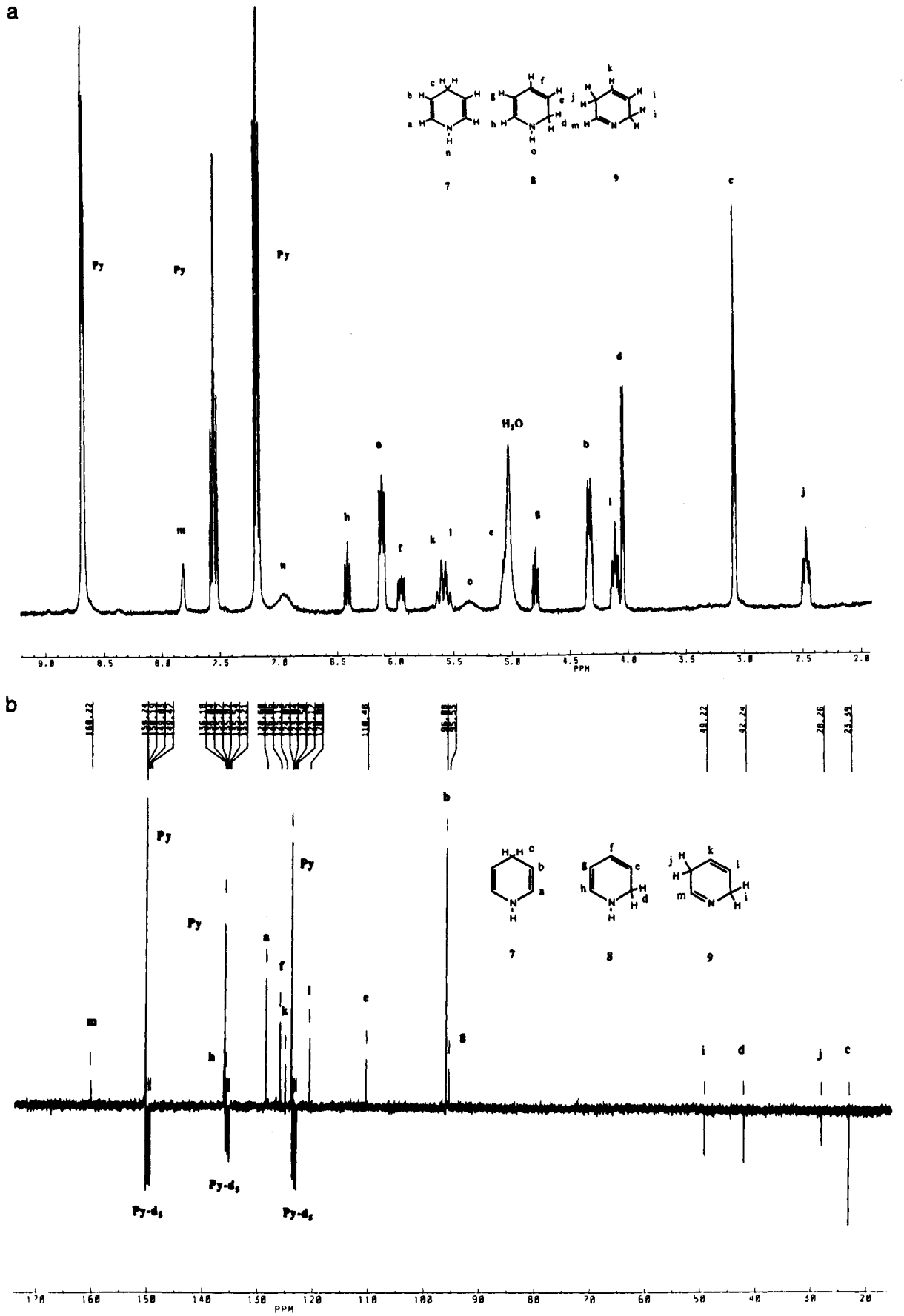
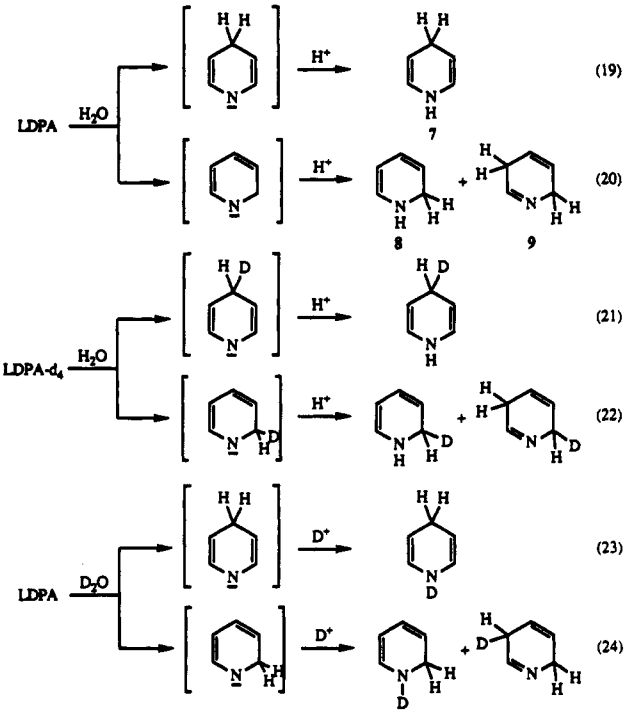


Figure 4. (a) ^{1}H NMR spectrum of the LDPA hydrolysate in pyridine-d_5. (b) APT ^{13}C NMR spectrum of the LDPA hydrolysate.

1,2-Dihydropyridine (8, 1,2-DHP). ^{1}H NMR (400 MHz, C_5D_5N): δ 6.44–6.40 (m, 1 H, J_{16} = 5.65 Hz, J_{56} = 7.05 Hz, J_{36} = 1.00 Hz, J_{46} = 1.25 Hz, H-6), 6.00–5.95 (m, 1 H, J_{34} = 9.35 Hz, J_{45} = 5.51 Hz, J_{24} = 1.50 Hz, J_{46} = 1.25 Hz, H-4), 5.38 (b, 1 H, J_{16} = 5.65 Hz, J_{13} = 1.00 Hz, J_{12} = 1.70 Hz, J_{15} = 1.35 Hz, NH), 5.10–5.05 (m, 1 H, J_{23} = 3.95 Hz, J_{34} = 9.35 Hz, J_{13} = 1.00 Hz, J_{35} = 1.50 Hz, J_{36} = 1.00 Hz, H-3), 4.84–4.78 (m, 1 H J_{45} = 5.51 Hz, J_{56} = 7.05 Hz, J_{35} = 1.50 Hz, J_{51} = 1.35 Hz, H-5), 4.07-4.04

Scheme IV



(m, 1 H, J_{23} = 3.95 Hz, J_{24} = 1.50 Hz, J_{21} = 1.70 Hz, H-2). ^{13}C NMR (100 MHz, C_5D_5N) δ 136.20 (C-6), 125.19 (C-4), 110.48 (C-3), 95.54 (C-5), 42.25 (C-2). The high field H-2 proton (δ 4.07) of 8 couples to the NH and H-3 protons. The chemical shift of H-2 was similar that of *N*-phenyl-1,2-dihydropyridine (δ 4.26, H-2)[8b] and H-2 of the LDPA (1,2-dihydropyridyl ligand, δ 4.24 in pyridine). The chemical shifts of the remaining protons in 8 were assigned from the decoupled ^{1}H NMR spectra. The APT ^{13}C absorption of C-2 in the 1,2-DHP (8) (δ 42.25) was similar to the chemical shift for the 1,2-dihydropyridyl ligand C-2 absorption of 1 (δ 45.21).

2,5-Dihydropyridine (9, 2,5-DHP). ^{1}H NMR (400 MHz, C_5D_5N): δ 7.85 (m, 1 H, J_{56} = 0.5 Hz, J_{26} = 0.8 Hz, H-6), 5.66–5.55 (AB quartet, 2 H, J_{34} = 10.8 Hz, J_{45} = 3.1 Hz, J_{35} = 2.0 Hz, J_{24} = 1.5 Hz, both lines of the downfield doublet appear as broad multiplets, and both lines of the upfield doublet appear as multiplets, H-3,4), 4.13 (tm, 2 H, J_{23} = 2.5 Hz, J_{25} = 8.0 Hz, J_{24} = 1.5 Hz, H-2), 2.49 (tm, 2 H, J_{35} = 2.0 Hz, J_{45} = 3.1 Hz, J_{56} = 0.5 Hz, H-5). ^{13}C NMR (100 MHz, C_6D_5N): δ 160.13 (C-6), 126.08 (C-4), 120.82 (C-3), 49.27 (C-2), 28.26 (C-5).

When D_2O is used to hydrolyze 1, the ^{1}H NMR spectrum assigned to 9 changed. The H-3 doublet of multiplets at δ 5.55 became simpler since the coupling with one of the H-5 protons was removed. The H-2 absorption at δ 4.12 changed from a (1:2:1) triplet of multiplet to a (1:1) doublet of multiplets. The signal at δ 2.50 was diminished by one proton.

When LDPA was synthesized with LAD, after hydrolysis with H_2O, the spectrum assigned to 9 changed. The intensity of the signal at δ 4.12 assigned to H-2 was diminished by one proton and the H-5 signal at δ 2.50 was reduced to a doublet. Irradiation at δ 2.50 (H-5) changed the signal at δ 4.12 to a complex singlet.

EPR Spectroscopy of a Mixture of LAH and Pyridine. Two separate THF solutions, one of pyridine (4 mL, 0.55 M) and one of LAH (0.5 mL, 1.60 M), were placed in the divided arms of a H tube containing an EPR sidearm. The solutions were degassed, sealed, and mixed, and the EPR tube was immediately placed in the cavity of the EPR spectrometer and an EPR spectrum was taken. A strong EPR signal was observed (54 lines, g = 2.0026). The same EPR spectrum was obtained when pyridine was allowed to react with LAD.

Electrolytic Reduction of Pyridine. A THF solution of pyridine (0.5 M) and dry $LiClO_4$ (0.5 M) was electrolyzed in a degassed EPR cell. The EPR spectrum of the radical anion of pyridine ($Li^+C_5H_5N^\cdot$) was recorded.[9] The spectrum was identical to that recorded for the radical anion formed during the reaction of LAH with pyridine.

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