

Supporting Information for *J. Am. Chem. Soc.*, **1992**, 114(19), 7585-7587, DOI: [10.1021/ja00045a054](https://doi.org/10.1021/ja00045a054)

POSPISIL 7585-7587

Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at <http://pubs.acs.org/page/copyright/permissions.html>.



ACS Publications

MOST TRUSTED. MOST CITED. MOST READ.

Copyright © 1992 American Chemical Society

JAG21260M

J-7587-m1

**A Substoichiometric Pyridine-Lithium Enolate Complex:
Solution and X-Ray Data, and Implications to Catalysis in the Aldol Reaction.**

Paul J. Pospisil, Scott R. Wilson, and Eric N. Jacobsen*

**SUPPLEMENTARY MATERIAL PART I
EXPERIMENTAL PROCEDURES**

General. All manipulations of air- and moisture sensitive compounds were carried out in a nitrogen-filled Vacuum Atmospheres Company drybox with attached MO 40-2 Dri-Train or by standard vacuum line techniques. NMR spectra were recorded on a General Electric QE 300 spectrometer (300 MHz ^1H , 75.5 MHz ^{13}C), and delay times of 12-15 seconds were applied between data acquisitions to provide accurate integrations.

Materials. Cyclohexane, pentane, and methylcyclohexane were distilled from CaH_2 . Tetrahydrofuran (THF) was distilled from the sodium benzophenone ketyl solution. Pyridine was distilled over BaO or over KOH. Lithium bis(trimethylsilyl) amide (LiHMDS) (Aldrich 98%) was sublimed at $\sim 70^\circ\text{C}$ (10^{-2} torr). Cyclohexane- d_{12} (Aldrich or Cambridge Isotopes) was distilled over CaH_2 . Pinacolone was distilled over Linde 4 Å molecular sieves. All distillations were performed under a nitrogen atmosphere. The purity of the ligands employed in the binding studies was established to be $\geq 98.5\%$ by GC, elemental analysis, and/or ^1H NMR. All materials employed in the binding studies were stored and handled in the drybox.

Lithium Pinacolate (1). Compound (1) was prepared in the drybox by a modification of the procedure reported by Arnett.¹ A solution of LiHMDS (5.01 g, 30 mmol, 1 equiv.) in pentane (30mL) was cooled to -40°C in the drybox freezer. The solution was then removed from the freezer and stirred vigorously at ambient temperature as freshly distilled pinacolone (3.75 mL, 30 mmol) was added dropwise over 15 min. The solution was then returned to the drybox freezer and kept at -40°C for 3 days. White crystals (1.89 g, 59%) were isolated by decanting the supernatant solution, washing the crystals with cold pentane (2 x 5 mL), and then drying under vacuum for 5 min. ^1H NMR (C_6D_6) δ 4.05 (s, 1 H, vinyl CH_2), 3.92 (s, 1 H, vinyl CH_2), 1.16

JAG21260M-10-19-69

Rec'd: May 4, 1992

Prof. Eric N. Jacobsen, et al.

Box 55, 470 Roser Adams Lab

Dept. of Chemistry, Univ. of Illinois

1209 W. California Street

Urbana, IL 61801-3731

Manuscript type: Communication

J-7587-m2

(s, 9 H, -CH₃); ¹³C NMR (75.5 MHz, C₆D₆) δ 176.7 (C=O), 76.7 (=CH₂), 37.3 (C(CH₃), 29.3 (-CH₃).

¹H NMR Binding Studies. Into oven-dried, 5 mm NMR tubes were charged solutions containing 0.05 mmol of **1** or lithium 5-oxo-2,2,6,6-tetramethyl-3-heptoxide **2**² in cyclohexane-*d*₁₂, benzene-*d*₆ or toluene-*d*₈ (0.4 mL). Sealed capillary tubes containing 1% TMS in CDCl₃ were also placed into the NMR tubes to serve as internal standards. The tubes were septum-sealed and spectra were acquired at room temperature (20 °C). Aliquots of the ligand were injected via microsyringe into the NMR tubes, and the concentration of added ligand was determined by integration.

Job Plots. The stoichiometries of the THF and pyridine-enolate complexes were established by the method of continuous variations.³ Two separate stock solutions containing lithium pinacolate (**1**) and ligand in cyclohexane-*d*₁₂ were prepared in the drybox. A series of individual 400 μL NMR samples of differing enolate to ligand ratios were prepared such that the sum of the concentrations of the two components was equal to 0.2 M. The relative ratios of free and complexed enolate by integration of the *tert*-butyl and/or vinylic resonances.

Molecular Weight Measurements. The molecular weight of the 4:3 enolate•pyridine complex was measured by freezing point depression with an apparatus designed according to the one reported by Seebach.⁴ The cryoscopic cell was equipped with a side arm bearing a vacuum stopcock, and cooling was accomplished by inserting the cell into a fitted, glass jacket through which was circulated an ethylene glycol:water (1:1) mixture at -2 °C. Samples were prepared in the drybox and measurements were performed under an Ar atmosphere. The instrument was calibrated using biphenyl (50-260 mg) in cyclohexane (8.57g). A cryoscopic constant of K_f = 20.78 °C kg/mol and a FP = 6.71 °C were obtained for cyclohexane.⁵ Molecular weights were calculated according to the equation: MW = K_fc/ΔT, where MW is molecular weight, K_f (°C kg/mol) is the cryoscopic constant for the solvent, c is concentration of solute in g per kg solvent, and ΔT is the freezing point depression of the solution relative to pure cyclohexane in °C. Error analysis was performed as reported by Arnett.¹

Into an oven-dried cryoscopic cell was loaded **1** (100 mg, 0.94 mmol, 1 equiv), cyclohexane (8.57g), and pyridine (55.9 μL, 0.69 mmol, 0.74 equiv). The solution was stirred for 10 min at room temperature. The thermistor probe was inserted into the sample through a rubber septum, and plots of temperature vs. time were recorded as the solution was cooled. The temperature of the solution dropped until freezing occurred, as was established by a well defined leveling of the temperature curve. After each measurement, the solution was warmed back to room

J-7587-m3

temperature and cooled again; this process was repeated a total of five times. An average $\Delta T = 0.554\text{ }^{\circ}\text{C}$ was obtained, corresponding to MW = 674 g/mol.

X-Ray Analysis of Complexes (A) and (B). Single clear crystals appropriate for diffraction experiments were obtained as follows: to LiHMDS solutions in methylcyclohexane (2 mL, 1M) and methylcyclohexane/pentane (1.5:2 v/v) (3.5 mL, 0.57 M) pinacolone (250 μL , 2 mmol, 1 equiv) was added dropwise at 0 $^{\circ}\text{C}$. To the solutions were then added respectively pyridine (485 μL , 6 mmol, 3 equiv) for (A) and (105 μL , 1.3 mmol, 0.65 equiv) for (B) followed by cooling of the solutions to -40 $^{\circ}\text{C}$ for several weeks. Prior to X-ray analysis the crystals were handled under an inert atmosphere and kept at -5 $^{\circ}\text{C}$. Selected crystallographic data, data collection, data reduction and refinement specifications, interatomic distances and angles are included in parts II and III.

Notes and References

1. Arnett, E. M.; Fisher, F. J.; Nichols, M. A.; Ribeiro, A. A. *J. Am. Chem. Soc.* **1990**, *112*, 801.
2. Williard, P. G.; Salvino, J. M. *Tetrahedron Lett.* **1985**, *26*, 3931.
3. Zimmerman, S. C.; Wu, W.; Zeng, Z. *J. Am. Chem. Soc.* **1991**, *113*, 196 and references cited in footnotes 18 and 19. (b) Hill, Z. D.; MacCarthy, P. *J. Chem. Ed.* **1986**, *63*, 162.
4. Bauer, W.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 1972.
5. $K_f = 20.0\text{ }^{\circ}\text{C kg/mol}$; $fp = 6.54\text{ }^{\circ}\text{C}$. *Langes Handbook of Chemistry*, 13th Ed.; McGraw Hill: New York, 1985; p. 10-80.

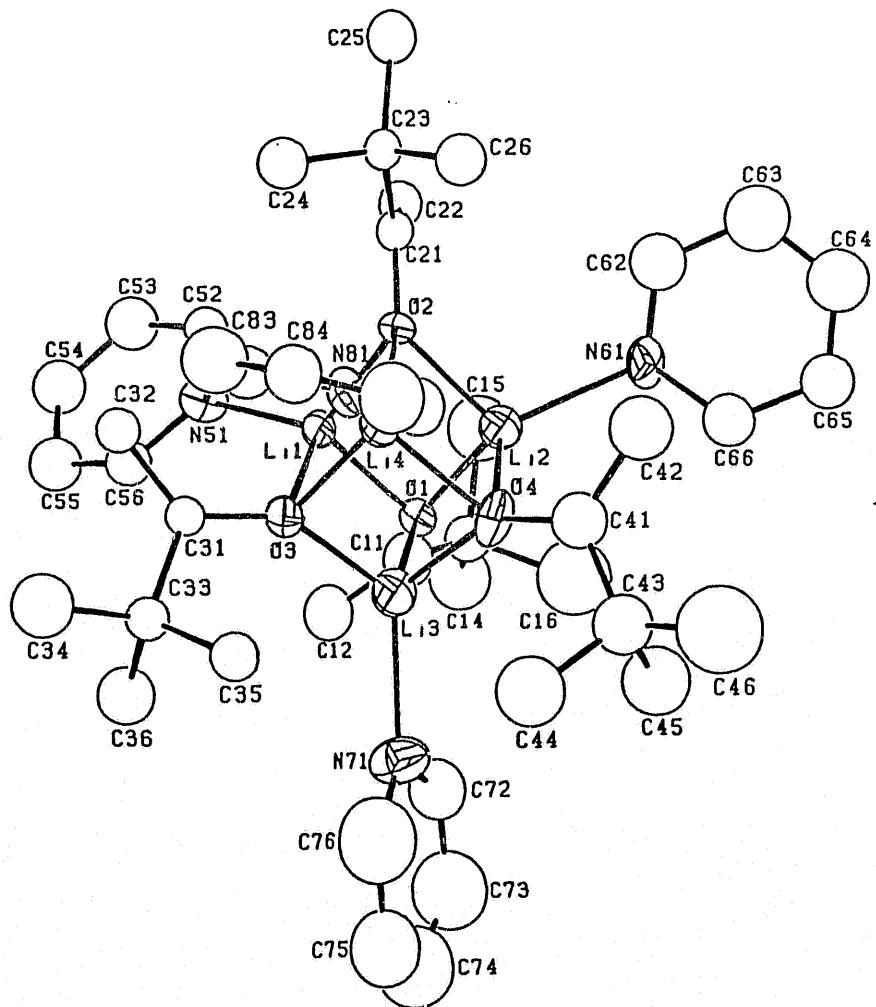
J-7587-m4

A Substoichiometric Pyridine•Lithium Enolate Complex:
Solution and X-Ray Data, and Implications to Catalysis in the Aldol Reaction.

Paul J. Pospisil, Scott R. Wilson, and Eric N. Jacobsen*

SUPPLEMENTARY MATERIAL PART II

X-RAY CRYSTALLOGRAPHIC DATA
FOR A: $[(C_5H_5N)(C_6H_{11}O)Li]_4$



J 7587-m5

Table S1. Crystal and Experimental Data for (A): $[(C_5H_5N)(C_6H_{11}O)Li]_4$

| | |
|--|--|
| crystal system | orthorhombic |
| space group | Pna ₂ ₁ (C_{2v}^9) |
| <u>a</u> , Å | 21.172(7) |
| <u>b</u> , Å | 10.919(4) |
| <u>c</u> , Å | 20.207(6) |
| V, Å ³ | 4671(5) |
| Z | 4 |
| ρ (calcd), g/cm ³ | 1.053 |
| temperature, °C | -100 |
| color, habit | colorless, tear-shaped |
| dimensions (approximate), mm | 0.3 × 0.4 × 0.7 |
| diffractometer | Enraf-Nonius CAD4 (K axis) |
| μ, cm ⁻¹ | 0.61 |
| 2θ limit, deg (octants) | 49.0 (<u>+h+k+l</u>), 16.0 (<u>±h+k+l</u>) |
| ω/θ scan mode width ω, deg | 1.50 (1.00 + 0.35*tan(θ)) |
| variable scan rate range, deg/min | 2 to 16 |
| intensities measd (unique, R _i) | 4600 (4008, 0.029) |
| intensities > 2.58σ(I) | 1879 |
| R | 0.106 |
| R _w (for w=4.43/σ ² (F _o)+pF _o ²) | 0.119 (p=0.02) |
| density range in ΔF map, e/Å ³ | +0.47 to -0.45 |

J-7587-m6

X-ray Crystallographic Analysis of (A): $[(C_5H_5N)(C_6H_{11}O)Li]_4$. The data crystal was mounted using chilled oil (Paratone N, Exxon, 0°C) to a thin glass fiber then cooled to -100°C with the (2 1 6) scattering planes roughly normal to the spindle axis. Preliminary photographs confirmed the Laue class. The three standard intensities monitored every 90 min showed no significant decay. Data were corrected for anomalous dispersion^{1a}, Lorentz and polarization effects. An analytical approximation to the scattering factors^{1b} was used. There was no change in the appearance of the sample during the experiment.

Average values of normalized structure factors supported the acentric space group choice. The structure was solved by direct methods^{2a}; correct positions for all but two non-H atoms were deduced from an E-map. Subsequent cycles of least-squares refinement and difference Fourier syntheses^{2b} revealed positions for the remaining non-H atoms and several H atoms; however, chemically reasonable positions for all eight vinyl H atoms never surfaced. Aromatic and methyl H atoms were included as fixed contributors in "idealized" positions; vinyl H atoms were not included in structure factor calculations. In the final cycle of least-squares refinement, a common isotropic thermal parameter was refined for H atoms, isotropic thermal coefficients were refined for C and Li atoms, and anisotropic thermal coefficients were refined for O and N atoms. Successful convergence was indicated by the maximum shift/error for the last cycle and the successful refinement of the proposed polar model confirmed the space group choice. The final difference Fourier map had a broad range of electron density, but no other significant features. A final analysis of variance between observed and calculated structure factors showed a slight dependence on $\sin(\theta)$.

(1) International Tables for X-ray Crystallography; Ibers, J.A. and Hamilton,

J-7587-m7

-
- W.A., Eds.; Kynoch Press, Birmingham, England, 1976. (a) 149-150. (b) 99-101.
- (2) (a) Sheldrick, G.M. In Crystallographic Computing 3; Sheldrick, G.M., Kruger, C. and Goddard, R., Eds.; Oxford University, 1985, 175-189.
- (b) Sheldrick, G.M.: SHELX-76, a program for crystal structure determination, University Chemical Laboratory, Cambridge, England, 1976.

J7587-m8

Table S2a. Refined Atomic Parameters for (A): $[(C_5H_5N)(C_6H_{11}O)Li]_4$

| | x/a | y/b | z/c | U_{iso} ^a |
|-----|-----------|-----------|-----------|------------------------|
| Li1 | 0.406(1) | 0.635(2) | 0.531(1) | 0.036(6) |
| Li2 | 0.449(1) | 0.521(2) | 0.429(1) | 0.048(7) |
| Li3 | 0.334(1) | 0.614(2) | 0.426(1) | 0.057(8) |
| Li4 | 0.357(1) | 0.416(2) | 0.496(1) | 0.050(7) |
| O1 | 0.4181(4) | 0.6878(8) | 0.4393 | 0.033(5) ^b |
| O2 | 0.4430(4) | 0.4670(8) | 0.5219(7) | 0.038(5) ^b |
| O3 | 0.3172(4) | 0.5791(8) | 0.5166(6) | 0.037(6) ^b |
| O4 | 0.3653(5) | 0.4539(9) | 0.4010(7) | 0.049(7) ^b |
| N51 | 0.4215(6) | 0.768(1) | 0.6052(7) | 0.049(8) ^b |
| N61 | 0.5286(6) | 0.455(1) | 0.3758(8) | 0.056(9) ^b |
| N71 | 0.2747(7) | 0.724(2) | 0.3610(9) | 0.08(1) ^b |
| N81 | 0.3019(5) | 0.260(1) | 0.5257(8) | 0.048(8) ^b |
| C11 | 0.4296(9) | 0.804(2) | 0.427(1) | 0.077(6) |
| C12 | 0.3910(9) | 0.901(2) | 0.454(1) | 0.085(6) |
| C13 | 0.4863(8) | 0.847(1) | 0.3999(9) | 0.058(5) |
| C14 | 0.503(1) | 0.971(2) | 0.387(1) | 0.116(8) |
| C15 | 0.5409(9) | 0.785(2) | 0.436(1) | 0.118(8) |
| C16 | 0.485(1) | 0.780(2) | 0.327(1) | 0.15(1) |
| C21 | 0.4934(7) | 0.444(1) | 0.5595(8) | 0.040(4) |
| C22 | 0.5425(8) | 0.517(2) | 0.5677(9) | 0.056(5) |
| C23 | 0.4883(6) | 0.320(1) | 0.5947(8) | 0.040(4) |
| C24 | 0.4331(7) | 0.323(1) | 0.6443(9) | 0.060(5) |
| C25 | 0.5494(7) | 0.286(2) | 0.6321(9) | 0.069(5) |
| C26 | 0.4757(7) | 0.218(1) | 0.5477(9) | 0.061(5) |

Table S2a. (continued)

| | x/a | y/b | z/c | U_{iso}^a |
|-----|------------|----------|------------|-------------|
| C31 | 0.2766(7) | 0.578(1) | 0.5668(9) | 0.037(4) |
| C32 | 0.2958(7) | 0.567(1) | 0.6322(9) | 0.047(4) |
| C33 | 0.2071(7) | 0.593(1) | 0.5479(8) | 0.044(4) |
| C34 | 0.1611(9) | 0.559(2) | 0.604(1) | 0.093(7) |
| C35 | 0.1934(7) | 0.512(1) | 0.4910(8) | 0.054(5) |
| C36 | 0.1974(8) | 0.727(2) | 0.532(1) | 0.079(6) |
| C41 | 0.3669(8) | 0.366(2) | 0.358(1) | 0.073(5) |
| C42 | 0.4055(9) | 0.256(2) | 0.361(1) | 0.092(6) |
| C43 | 0.3249(9) | 0.370(2) | 0.301(1) | 0.082(6) |
| C44 | 0.2575(9) | 0.395(2) | 0.325(1) | 0.109(8) |
| C45 | 0.3492(10) | 0.489(2) | 0.259(1) | 0.111(7) |
| C46 | 0.322(1) | 0.264(2) | 0.254(2) | 0.17(1) |
| C52 | 0.4776(8) | 0.794(1) | 0.6336(9) | 0.050(4) |
| C53 | 0.4829(9) | 0.891(2) | 0.678(1) | 0.077(6) |
| C54 | 0.4337(9) | 0.961(2) | 0.694(1) | 0.079(6) |
| C55 | 0.3764(9) | 0.942(2) | 0.6635(10) | 0.076(6) |
| C56 | 0.3748(8) | 0.839(1) | 0.6217(9) | 0.056(5) |
| C62 | 0.5730(9) | 0.393(2) | 0.407(1) | 0.080(6) |
| C63 | 0.617(1) | 0.322(2) | 0.371(1) | 0.109(7) |
| C64 | 0.6164(10) | 0.327(2) | 0.305(1) | 0.098(7) |
| C65 | 0.5723(9) | 0.389(2) | 0.272(1) | 0.074(6) |
| C66 | 0.5281(8) | 0.452(2) | 0.311(1) | 0.069(5) |
| C72 | 0.301(1) | 0.805(2) | 0.326(1) | 0.093(7) |
| C73 | 0.270(1) | 0.878(3) | 0.281(2) | 0.16(1) |

Table S2a. (continued)

| | x/a | y/b | z/c | U_{iso}^a |
|-----|-----------|----------|-----------|-------------|
| C74 | 0.208(2) | 0.873(3) | 0.274(2) | 0.17(1) |
| C75 | 0.179(1) | 0.786(3) | 0.302(1) | 0.14(1) |
| C76 | 0.215(2) | 0.715(3) | 0.346(2) | 0.18(1) |
| C82 | 0.2712(8) | 0.261(2) | 0.5837(9) | 0.059(5) |
| C83 | 0.2303(9) | 0.164(2) | 0.601(1) | 0.090(6) |
| C84 | 0.2202(8) | 0.075(2) | 0.558(1) | 0.068(5) |
| C85 | 0.248(1) | 0.074(2) | 0.499(1) | 0.102(7) |
| C86 | 0.2925(8) | 0.173(2) | 0.483(1) | 0.070(5) |

^a $U_{iso} = \exp\{-[\sin(\theta)/\lambda]^2/8\pi^2\}$ ^b $U_{eq} = 1/3 \text{ trace } U_{ij}$

J-7587-m11

Table S2b. Calculated Atomic Parameters^a for (A): $[(C_5H_5N)(C_6H_{11}O)Li]_4$

| | x/a | y/b | z/c |
|------|--------|--------|--------|
| H14a | 0.4684 | 1.0108 | 0.3640 |
| H14b | 0.5399 | 0.9742 | 0.3598 |
| H14c | 0.5105 | 1.0130 | 0.4278 |
| H15a | 0.5803 | 0.8128 | 0.4180 |
| H15b | 0.5378 | 0.6977 | 0.4310 |
| H15c | 0.5391 | 0.8053 | 0.4824 |
| H16a | 0.5223 | 0.8021 | 0.3027 |
| H16b | 0.4483 | 0.8062 | 0.3032 |
| H16c | 0.4838 | 0.6928 | 0.3328 |
| H24a | 0.4395 | 0.3882 | 0.6755 |
| H24b | 0.4311 | 0.2464 | 0.6674 |
| H24c | 0.3942 | 0.3364 | 0.6209 |
| H25a | 0.5595 | 0.3497 | 0.6631 |
| H25b | 0.5834 | 0.2774 | 0.6010 |
| H25c | 0.5433 | 0.2104 | 0.6553 |
| H26a | 0.4379 | 0.2350 | 0.5232 |
| H26b | 0.4705 | 0.1432 | 0.5720 |
| H26c | 0.5106 | 0.2101 | 0.5177 |
| H34a | 0.1691 | 0.6102 | 0.6421 |
| H34b | 0.1673 | 0.4747 | 0.6165 |
| H34c | 0.1184 | 0.5705 | 0.5897 |
| H35a | 0.1498 | 0.5204 | 0.4787 |
| H35b | 0.2018 | 0.4285 | 0.5030 |
| H35c | 0.2198 | 0.5346 | 0.4543 |

Table S2b. (continued)

| | x/a | y/b | z/c |
|------|--------|--------|--------|
| H36a | 0.1541 | 0.7399 | 0.5194 |
| H36b | 0.2244 | 0.7490 | 0.4954 |
| H36c | 0.2075 | 0.7756 | 0.5696 |
| H44a | 0.2292 | 0.3983 | 0.2881 |
| H44b | 0.2564 | 0.4720 | 0.3483 |
| H44c | 0.2447 | 0.3307 | 0.3546 |
| H45a | 0.3236 | 0.4983 | 0.2198 |
| H45b | 0.3924 | 0.4773 | 0.2460 |
| H45c | 0.3457 | 0.5611 | 0.2856 |
| H46a | 0.3637 | 0.2460 | 0.2379 |
| H46b | 0.2948 | 0.2833 | 0.2177 |
| H46c | 0.3058 | 0.1936 | 0.2771 |
| H52 | 0.5141 | 0.7461 | 0.6229 |
| H53 | 0.5232 | 0.9074 | 0.6978 |
| H54 | 0.4381 | 1.0245 | 0.7264 |
| H55 | 0.3405 | 0.9938 | 0.6703 |
| H56 | 0.3344 | 0.8199 | 0.6028 |
| H62 | 0.5755 | 0.3958 | 0.4543 |
| H63 | 0.6467 | 0.2708 | 0.3935 |
| H64 | 0.6488 | 0.2860 | 0.2800 |
| H65 | 0.5708 | 0.3899 | 0.2249 |
| H66 | 0.4953 | 0.4957 | 0.2878 |
| H72 | 0.3462 | 0.8168 | 0.3314 |
| H73 | 0.2938 | 0.9333 | 0.2536 |

Table S2b. (continued)

| | x/a | y/b | z/c |
|-----|--------|--------|--------|
| H74 | 0.1859 | 0.9345 | 0.2488 |
| H75 | 0.1352 | 0.7699 | 0.2926 |
| H76 | 0.1922 | 0.6511 | 0.3687 |
| H82 | 0.2772 | 0.3280 | 0.6136 |
| H83 | 0.2099 | 0.1633 | 0.6431 |
| H84 | 0.1920 | 0.0095 | 0.5692 |
| H85 | 0.2402 | 0.0099 | 0.4683 |
| H86 | 0.3138 | 0.1744 | 0.4406 |

^a common isotropic thermal parameter varied for H atoms, $U_{iso} = 0.14(1)$

J-7587-m14

Table S3. Anisotropic Thermal Parameters for (A): $[(C_5H_5N)(C_6H_{11}O)Li]_4$

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|-----|----------|-----------|----------|-----------|-----------|------------|
| 01 | 0.027(5) | 0.030(5) | 0.043(6) | 0.002(5) | 0.001(5) | -0.008(5) |
| 02 | 0.035(5) | 0.043(6) | 0.039(5) | 0.001(5) | -0.008(5) | 0.012(5) |
| 03 | 0.030(5) | 0.044(6) | 0.038(6) | -0.006(5) | 0.000(5) | -0.006(5) |
| 04 | 0.063(7) | 0.048(7) | 0.035(6) | -0.024(6) | -0.001(5) | -0.026(6) |
| N51 | 0.046(8) | 0.040(8) | 0.060(8) | -0.005(7) | -0.008(8) | -0.008(7) |
| N61 | 0.054(8) | 0.066(10) | 0.048(9) | -0.038(8) | -0.010(7) | 0.001(8) |
| N71 | 0.046(9) | 0.12(1) | 0.08(1) | 0.04(1) | -0.007(9) | -0.014(10) |
| N81 | 0.043(7) | 0.043(8) | 0.057(8) | 0.000(8) | 0.007(8) | -0.002(7) |

temperature factor form:

$$\exp\{-2\pi^2(a^* U_{11} \underline{h}^2 + b^* U_{22} \underline{k}^2 + c^* U_{33} \underline{l}^2 + 2b^* c^* U_{23} \underline{kl} + 2a^* c^* U_{13} \underline{hl} + 2a^* b^* U_{12} \underline{hk})\}$$

J-7587-m15

Table S4. Distances (\AA) and Angles ($^\circ$) for (A): $[(\text{C}_5\text{H}_5\text{N})(\text{C}_6\text{H}_{11}\text{O})\text{Li}]_4$

| | | | |
|----------|---------|----------|---------|
| Li1 -01 | 1.95(3) | Li2 -01 | 1.94(3) |
| Li3 -01 | 1.97(3) | Li1 -02 | 2.00(2) |
| Li2 -02 | 1.97(3) | Li4 -02 | 1.97(3) |
| Li1 -03 | 1.99(2) | Li3 -03 | 1.90(3) |
| Li4 -03 | 2.02(3) | Li2 -04 | 2.00(3) |
| Li3 -04 | 1.94(3) | Li4 -04 | 1.98(3) |
| Li1 -N51 | 2.12(3) | Li2 -N61 | 2.12(3) |
| Li3 -N71 | 2.18(3) | Li4 -N81 | 2.15(3) |
| O1 -C11 | 1.32(2) | C11 -C12 | 1.45(3) |
| C11 -C13 | 1.40(3) | C13 -C14 | 1.43(3) |
| C13 -C15 | 1.53(3) | C13 -C16 | 1.64(3) |
| O2 -C21 | 1.33(2) | C21 -C22 | 1.32(2) |
| C21 -C23 | 1.53(2) | C23 -C24 | 1.54(2) |
| C23 -C25 | 1.54(2) | C23 -C26 | 1.49(2) |
| O3 -C31 | 1.33(2) | C31 -C32 | 1.39(2) |
| C31 -C33 | 1.53(2) | C33 -C34 | 1.55(3) |
| C33 -C35 | 1.48(2) | C33 -C36 | 1.51(2) |
| O4 -C41 | 1.30(2) | C41 -C42 | 1.45(3) |
| C41 -C43 | 1.47(3) | C43 -C44 | 1.54(3) |
| C43 -C45 | 1.63(3) | C43 -C46 | 1.50(4) |
| N51 -C52 | 1.35(2) | C52 -C53 | 1.39(3) |
| C53 -C54 | 1.33(3) | C54 -C55 | 1.38(3) |
| N51 -C56 | 1.31(2) | C55 -C56 | 1.40(2) |
| N61 -C62 | 1.32(2) | C62 -C63 | 1.41(3) |
| C63 -C64 | 1.34(4) | C64 -C65 | 1.32(3) |
| N61 -C66 | 1.32(3) | C65 -C66 | 1.39(3) |

Table S4. (continued)

| | | | |
|--------------|---------|--------------|---------|
| N71 -C72 | 1.26(3) | C72 -C73 | 1.39(4) |
| C73 -C74 | 1.32(5) | C74 -C75 | 1.26(4) |
| N71 -C76 | 1.30(4) | C75 -C76 | 1.42(5) |
| N81 -C82 | 1.34(2) | C82 -C83 | 1.41(3) |
| C83 -C84 | 1.32(3) | C84 -C85 | 1.32(3) |
| N81 -C86 | 1.30(2) | C85 -C86 | 1.47(3) |
| 01 -Li1 -02 | 98(1) | 01 -Li1 -03 | 95(1) |
| 01 -Li1 -N51 | 117(1) | 02 -Li1 -03 | 95(1) |
| 02 -Li1 -N51 | 129(1) | 03 -Li1 -N51 | 117(1) |
| 01 -Li2 -02 | 99(1) | 01 -Li2 -04 | 94(1) |
| 01 -Li2 -N61 | 130(1) | 02 -Li2 -04 | 96(1) |
| 02 -Li2 -N61 | 116(1) | 04 -Li2 -N61 | 116(1) |
| 01 -Li3 -03 | 97(1) | 01 -Li3 -04 | 96(1) |
| 01 -Li3 -N71 | 112(1) | 03 -Li3 -04 | 98(1) |
| 03 -Li3 -N71 | 126(1) | 04 -Li3 -N71 | 122(1) |
| 02 -Li4 -03 | 95(1) | 02 -Li4 -04 | 96(1) |
| 02 -Li4 -N81 | 131(1) | 03 -Li4 -04 | 93(1) |
| 03 -Li4 -N81 | 115(1) | 04 -Li4 -N81 | 119(1) |
| Li1 -01 -Li2 | 82(1) | Li1 -01 -Li3 | 83(1) |
| Li1 -01 -C11 | 119(1) | Li2 -01 -Li3 | 85(1) |
| Li2 -01 -C11 | 145(1) | Li3 -01 -C11 | 122(1) |
| Li1 -02 -Li2 | 81(1) | Li1 -02 -Li4 | 85(1) |
| Li1 -02 -C21 | 116(1) | Li2 -02 -Li4 | 84(1) |
| Li2 -02 -C21 | 123(1) | Li4 -02 -C21 | 146(1) |
| Li1 -03 -Li3 | 84(1) | Li1 -03 -Li4 | 85(1) |

Table S4. (continued)

| | | | |
|---------------|--------|---------------|--------|
| Li1 -03 -C31 | 120(1) | Li3 -03 -Li4 | 84(1) |
| Li3 -03 -C31 | 149(1) | Li4 -03 -C31 | 115(1) |
| Li2 -04 -Li3 | 84(1) | Li2 -04 -Li4 | 83(1) |
| Li2 -04 -C41 | 116(1) | Li3 -04 -Li4 | 85(1) |
| Li3 -04 -C41 | 149(1) | Li4 -04 -C41 | 120(1) |
| Li1 -N51 -C52 | 126(1) | Li1 -N51 -C56 | 118(1) |
| C52 -N51 -C56 | 115(1) | Li2 -N61 -C62 | 120(1) |
| Li2 -N61 -C66 | 121(1) | C62 -N61 -C66 | 118(2) |
| Li3 -N71 -C72 | 118(2) | Li3 -N71 -C76 | 131(2) |
| C72 -N71 -C76 | 111(2) | Li4 -N81 -C82 | 120(1) |
| Li4 -N81 -C86 | 118(1) | C82 -N81 -C86 | 121(1) |
| O1 -C11 -C12 | 122(2) | O1 -C11 -C13 | 123(2) |
| C12 -C11 -C13 | 113(2) | C11 -C13 -C14 | 127(2) |
| C11 -C13 -C15 | 108(2) | C11 -C13 -C16 | 101(2) |
| C14 -C13 -C15 | 109(2) | C14 -C13 -C16 | 105(2) |
| C15 -C13 -C16 | 104(2) | O2 -C21 -C22 | 126(1) |
| O2 -C21 -C23 | 112(1) | C22 -C21 -C23 | 122(1) |
| C21 -C23 -C24 | 110(1) | C21 -C23 -C25 | 112(1) |
| C21 -C23 -C26 | 112(1) | C24 -C23 -C25 | 109(1) |
| C24 -C23 -C26 | 107(1) | C25 -C23 -C26 | 106(1) |
| O3 -C31 -C32 | 123(1) | O3 -C31 -C33 | 116(1) |
| C32 -C31 -C33 | 122(1) | C31 -C33 -C34 | 113(1) |
| C31 -C33 -C35 | 109(1) | C31 -C33 -C36 | 107(1) |
| C34 -C33 -C35 | 108(1) | C34 -C33 -C36 | 108(1) |
| C35 -C33 -C36 | 112(1) | O4 -C41 -C42 | 127(2) |
| O4 -C41 -C43 | 119(2) | C42 -C41 -C43 | 114(2) |

Table S4. (continued)

| | | | |
|---------------|--------|---------------|--------|
| C41 -C43 -C44 | 108(2) | C41 -C43 -C45 | 104(2) |
| C41 -C43 -C46 | 120(2) | C44 -C43 -C45 | 109(2) |
| C44 -C43 -C46 | 108(2) | C45 -C43 -C46 | 108(2) |
| N51 -C52 -C53 | 121(2) | C52 -C53 -C54 | 122(2) |
| C53 -C54 -C55 | 120(2) | C54 -C55 -C56 | 114(2) |
| N51 -C56 -C55 | 128(2) | N61 -C62 -C63 | 120(2) |
| C62 -C63 -C64 | 119(2) | C63 -C64 -C65 | 121(2) |
| C64 -C65 -C66 | 117(2) | N61 -C66 -C65 | 124(2) |
| N71 -C72 -C73 | 124(2) | C72 -C73 -C74 | 122(3) |
| C73 -C74 -C75 | 118(3) | C74 -C75 -C76 | 116(3) |
| N71 -C76 -C75 | 129(3) | N81 -C82 -C83 | 120(2) |
| C82 -C83 -C84 | 119(2) | C83 -C84 -C85 | 121(2) |
| C84 -C85 -C86 | 119(2) | N81 -C86 -C85 | 118(2) |

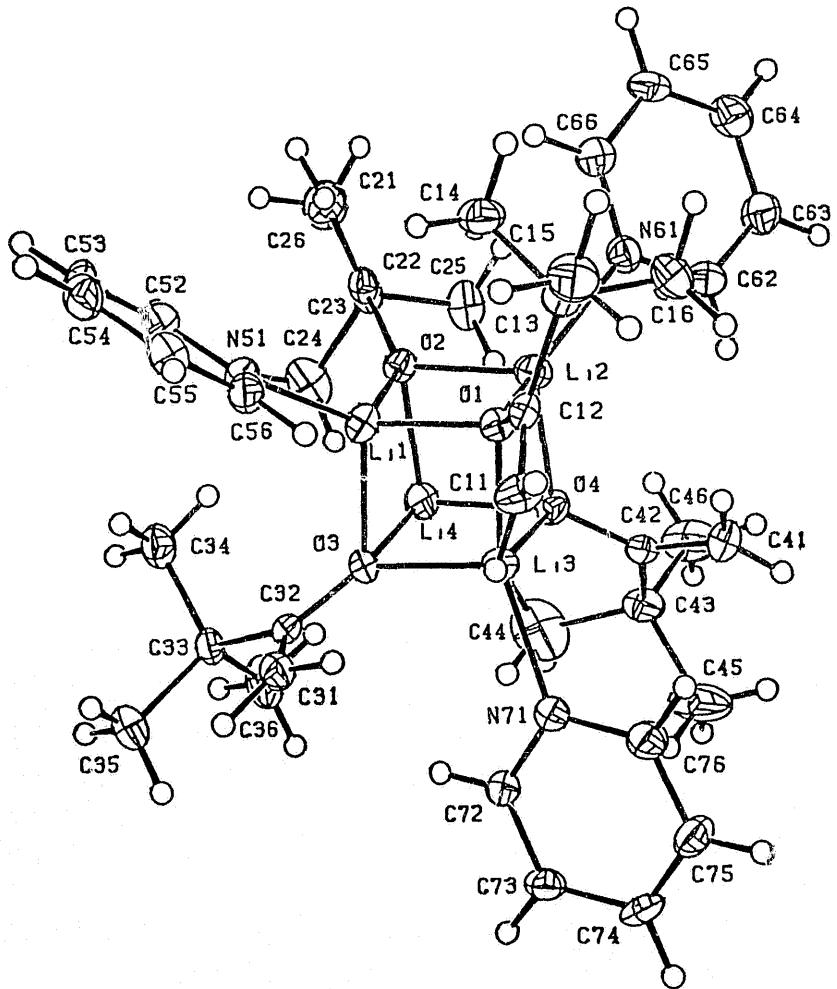
J-7587-m19

**A Substoichiometric Pyridine•Lithium Enolate Complex:
Solution and X-Ray Data, and Implications to Catalysis in the Aldol Reaction.**

Paul J. Pospisil, Scott R. Wilson, and Eric N. Jacobsen*

SUPPLEMENTARY MATERIAL PART III

**X-RAY CRYSTALLOGRAPHIC DATA
FOR B: $(C_6H_{11}O)_4Li_4(C_5H_5N)_3$**



J-7587-m20

Table S1. Crystal and Experimental Data for (B): $(C_6H_{11}O)_4Li_4(C_5H_5N)_3$

| | |
|---|---|
| crystal system | monoclinic |
| space group | I2/a (C_{2h}^6) |
| <u>a</u> , Å | 18.905(9) |
| <u>b</u> , Å | 12.662(4) |
| <u>c</u> , Å | 34.142(16) |
| β , deg | 92.29(4) |
| V, Å ³ | 8166(10) |
| Z | 8 |
| ρ (calcd), g/cm ³ | 1.076 |
| temperature, °C | -100 |
| color, habit | colorless, equidimensional |
| dimensions (faces) or {I forms}, mm | (0 -1 2), 0.18; {0 1 0}, 0.20; {1 -1 -1}, 0.22; (2 0 -3), 0.22; (-1 0 0), 0.25; (0 0 1), 0.27 |
| diffractometer | Enraf-Nonius CAD4 (κ -axis) |
| μ , cm ⁻¹ | 0.63 |
| 2θ limit, deg (octants) | 47.0 ($\pm h+k-1$, $h+k+l=2n$) |
| ω/θ scan mode width ω , deg | 1.50 (1.10 + 0.35*tan(θ)) |
| variable scan rate range, deg/min | 3 to 16 |
| intensities measd (unique, R_i) | 6593 (6034, 0.022) |
| abs corr transmission factor, range | 0.979 to 0.959 (numerical) |
| intensities > $2.58\sigma(I)$ | 2986 |
| R | 0.046 |
| R_w (for $w=1.19/\sigma^2(F_O) + pF_O^{-2}$) | 0.039 (p=0.01) |
| density range in ΔF map, e/Å ³ | +0.18 to -0.19 |

J-7587-m21

X-ray Crystallographic Analysis of (B): $(C_6H_{11})_4Li_4(C_5H_5N)_3$. The data crystal was mounted using chilled oil (Paratone N, Exxon, 0°C) to a thin glass fiber then cooled to -100°C with the (1 1 -3) scattering planes roughly normal to the spindle axis. Preliminary photographs confirmed the Laue class. The three standard intensities monitored every 90 min showed no significant decay. Data were corrected for anomalous dispersion^{1a}, absorption^{1b}, Lorentz and polarization effects. An analytical approximation to the scattering factors^{1c} was used. There was no change in the appearance of the sample during the experiment.

Average values of normalized structure factors supported the centric space group choice. The structure was solved by direct methods^{2a}; correct positions for all non-H atoms were deduced from an E-map. Subsequent cycles of least-squares refinement and difference Fourier syntheses^{2b} revealed positions for most H atoms. Vinyl H atom positions were independently refined; however, owing to the paucity of data, aromatic and methyl H atoms were included as fixed contributors in "idealized" positions. In the final cycle of least-squares refinement, a common isotropic thermal parameter was refined for H atoms, an empirical isotropic extinction parameter³ was refined ($1.8(2) \times 10^{-8}$), and anisotropic thermal coefficients were refined for non-H atoms. Successful convergence was indicated by the maximum shift/error for the last cycle. The final difference Fourier map had no significant features. A final analysis of variance between observed and calculated structure factors showed a slight dependence on $\sin(\theta)$.

-
- (1) International Tables for X-ray Crystallography; Ibers, J.A. and Hamilton, W.A., Eds.; Kynoch Press, Birmingham, England, 1976. (a) 149-150. (b) 61-62.
(c) 99-101.
- (2) (a) Sheldrick, G.M. In Crystallographic Computing 3; Sheldrick, G.M., Kruger, C. and Goddard, R., Eds.; Oxford University, 1985, 175-189.

J 7587-m22

-
- (b) Sheldrick, G.M.: SHELX-76, a program for crystal structure determination,
University Chemical Laboratory, Cambridge, England, 1976.
- (3) Zachariasen, W. H. Acta Crystallogr. 1963, 16, 1139; Acta Crystallogra.,
Sect. A 1968, 24, 212.

J-7587-m23

Table S2a. Refined Atomic Parameters for (B): $(C_6H_{11}O)_4Li_4(C_5H_5N)_3$

| | x/a | y/b | z/c | U_{eq} ^a |
|-----|------------|------------|------------|-----------------------|
| Li1 | 0.0039(3) | 0.1246(5) | 0.1339(2) | 0.033(4) |
| Li2 | -0.0760(3) | 0.2225(5) | 0.0824(2) | 0.035(4) |
| Li3 | -0.0975(3) | 0.2418(5) | 0.1596(2) | 0.034(4) |
| Li4 | 0.0097(3) | 0.3251(5) | 0.1289(2) | 0.035(4) |
| O1 | -0.0991(1) | 0.1228(2) | 0.12282(6) | 0.028(2) |
| O2 | 0.0273(1) | 0.2210(2) | 0.09172(6) | 0.029(1) |
| O3 | 0.0055(1) | 0.2402(2) | 0.17317(6) | 0.026(2) |
| O4 | -0.0853(1) | 0.3465(2) | 0.11618(6) | 0.031(2) |
| N51 | 0.0520(2) | -0.0161(2) | 0.14770(8) | 0.030(2) |
| N61 | -0.1039(2) | 0.2383(3) | 0.02349(9) | 0.034(2) |
| N71 | -0.1512(2) | 0.3069(2) | 0.20409(8) | 0.031(2) |
| C11 | -0.1666(2) | 0.0212(3) | 0.1639(1) | 0.040(3) |
| C12 | -0.1422(2) | 0.0413(3) | 0.1288(1) | 0.026(2) |
| C13 | -0.1610(2) | -0.0246(3) | 0.0928(1) | 0.034(3) |
| C14 | -0.0933(2) | -0.0526(3) | 0.0718(1) | 0.049(3) |
| C15 | -0.1984(2) | -0.1272(3) | 0.1027(1) | 0.051(3) |
| C16 | -0.2098(2) | 0.0386(3) | 0.0650(1) | 0.044(3) |
| C21 | 0.0893(2) | 0.1116(3) | 0.0498(1) | 0.038(3) |
| C22 | 0.0743(2) | 0.2070(3) | 0.0636(1) | 0.029(2) |
| C23 | 0.1072(2) | 0.3079(3) | 0.0494(1) | 0.034(2) |
| C24 | 0.1465(2) | 0.3636(3) | 0.0834(1) | 0.053(3) |
| C25 | 0.0498(2) | 0.3822(3) | 0.0326(1) | 0.047(3) |
| C26 | 0.1602(2) | 0.2892(3) | 0.0177(1) | 0.056(3) |
| C31 | 0.0084(2) | 0.1554(3) | 0.2340(1) | 0.036(3) |

Table S2a. (continued)

| | x/a | y/b | z/c | U_{eq}^a |
|-----|------------|------------|------------|------------|
| C32 | 0.0368(2) | 0.2193(3) | 0.2080(1) | 0.027(2) |
| C33 | 0.1092(2) | 0.2721(3) | 0.2149(1) | 0.031(2) |
| C34 | 0.1604(2) | 0.2257(3) | 0.1861(1) | 0.043(3) |
| C35 | 0.1400(2) | 0.2567(3) | 0.2565(1) | 0.050(3) |
| C36 | 0.1019(2) | 0.3912(3) | 0.2079(1) | 0.054(3) |
| C41 | -0.2055(2) | 0.3839(4) | 0.1089(1) | 0.049(3) |
| C42 | -0.1385(2) | 0.4146(3) | 0.1151(1) | 0.031(3) |
| C43 | -0.1188(2) | 0.5299(3) | 0.1208(1) | 0.042(3) |
| C44 | -0.0455(3) | 0.5409(3) | 0.1390(1) | 0.085(4) |
| C45 | -0.1694(3) | 0.5862(3) | 0.1474(1) | 0.077(4) |
| C46 | -0.1205(2) | 0.5842(3) | 0.0810(1) | 0.066(3) |
| C52 | 0.1173(2) | -0.0420(3) | 0.1375(1) | 0.032(3) |
| C53 | 0.1465(2) | -0.1402(3) | 0.1446(1) | 0.037(3) |
| C54 | 0.1073(2) | -0.2147(3) | 0.1628(1) | 0.042(3) |
| C55 | 0.0406(2) | -0.1889(3) | 0.1742(1) | 0.039(3) |
| C56 | 0.0154(2) | -0.0891(3) | 0.1660(1) | 0.035(3) |
| C62 | -0.1449(2) | 0.3191(3) | 0.0129(1) | 0.037(3) |
| C63 | -0.1597(2) | 0.3483(3) | -0.0252(1) | 0.045(3) |
| C64 | -0.1288(2) | 0.2924(3) | -0.0543(1) | 0.053(3) |
| C65 | -0.0869(2) | 0.2083(3) | -0.0443(1) | 0.051(3) |
| C66 | -0.0754(2) | 0.1843(3) | -0.0055(1) | 0.045(3) |
| C72 | -0.1156(2) | 0.3720(3) | 0.2286(1) | 0.033(2) |
| C73 | -0.1471(2) | 0.4428(3) | 0.2528(1) | 0.035(3) |
| C74 | -0.2194(2) | 0.4473(3) | 0.2526(1) | 0.038(3) |

Table S2a. (continued)

| | x/a | y/b | z/c | U_{eq} ^a |
|------|------------|-----------|------------|-----------------------|
| C75 | -0.2573(2) | 0.3801(3) | 0.2283(1) | 0.044(3) |
| C76 | -0.2213(2) | 0.3129(3) | 0.2047(1) | 0.041(3) |
| H11a | -0.156(2) | 0.064(3) | 0.188(1) | 0.058(2) ^b |
| H11b | -0.195(2) | -0.039(3) | 0.168(1) | |
| H21a | 0.068(2) | 0.047(3) | 0.059(1) | |
| H21b | 0.125(2) | 0.101(3) | 0.030(1) | |
| H31a | -0.040(2) | 0.125(3) | 0.2296(10) | |
| H31b | 0.029(2) | 0.144(3) | 0.261(1) | |
| H41a | -0.217(2) | 0.306(3) | 0.105(1) | |
| H41b | -0.241(2) | 0.433(3) | 0.109(1) | |

^a $U_{eq} = 1/3 \text{ trace } U_{ij}$ ^b common isotropic thermal parameter for hydrogen atoms

J7587-m26

Table S2b. Calculated Atomic Parameters for (B): $(C_6H_{11}O)_4Li_4(C_5H_5N)_3$

| | x/a | y/b | z/c |
|------|---------|---------|---------|
| H14a | -0.0688 | 0.0111 | 0.0653 |
| H14b | -0.1054 | -0.0910 | 0.0483 |
| H14c | -0.0632 | -0.0952 | 0.0887 |
| H15a | -0.1685 | -0.1684 | 0.1202 |
| H15b | -0.2084 | -0.1665 | 0.0791 |
| H15c | -0.2419 | -0.1115 | 0.1151 |
| H16a | -0.1873 | 0.1038 | 0.0584 |
| H16b | -0.2533 | 0.0535 | 0.0776 |
| H16c | -0.2198 | -0.0016 | 0.0416 |
| H24a | 0.1145 | 0.3766 | 0.1040 |
| H24b | 0.1651 | 0.4296 | 0.0745 |
| H24c | 0.1847 | 0.3198 | 0.0932 |
| H25a | 0.0156 | 0.3953 | 0.0521 |
| H25b | 0.0268 | 0.3502 | 0.0100 |
| H25c | 0.0709 | 0.4478 | 0.0252 |
| H26a | 0.1371 | 0.2542 | -0.0042 |
| H26b | 0.1983 | 0.2460 | 0.0280 |
| H26c | 0.1787 | 0.3558 | 0.0093 |
| H34a | 0.1415 | 0.2350 | 0.1598 |
| H34b | 0.1668 | 0.1518 | 0.1914 |
| H34c | 0.2051 | 0.2612 | 0.1890 |
| H35a | 0.1453 | 0.1827 | 0.2618 |
| H35b | 0.1087 | 0.2873 | 0.2748 |
| H35c | 0.1854 | 0.2905 | 0.2590 |

Table S2b. (continued)

| | x/a | y/b | z/c |
|------|---------|---------|---------|
| H36a | 0.0826 | 0.4037 | 0.1819 |
| H36b | 0.1476 | 0.4239 | 0.2108 |
| H36c | 0.0709 | 0.4207 | 0.2266 |
| H44a | -0.0122 | 0.5061 | 0.1229 |
| H44b | -0.0439 | 0.5093 | 0.1646 |
| H44c | -0.0335 | 0.6144 | 0.1413 |
| H45a | -0.2169 | 0.5805 | 0.1365 |
| H45b | -0.1565 | 0.6593 | 0.1495 |
| H45c | -0.1669 | 0.5542 | 0.1729 |
| H46a | -0.1670 | 0.5779 | 0.0689 |
| H46b | -0.0867 | 0.5515 | 0.0646 |
| H46c | -0.1089 | 0.6576 | 0.0844 |
| H52 | 0.1450 | 0.0102 | 0.1246 |
| H53 | 0.1937 | -0.1558 | 0.1369 |
| H54 | 0.1260 | -0.2843 | 0.1675 |
| H55 | 0.0123 | -0.2393 | 0.1875 |
| H56 | -0.0313 | -0.0713 | 0.1740 |
| H62 | -0.1656 | 0.3598 | 0.0332 |
| H63 | -0.1909 | 0.4063 | -0.0314 |
| H64 | -0.1365 | 0.3120 | -0.0813 |
| H65 | -0.0657 | 0.1664 | -0.0641 |
| H66 | -0.0453 | 0.1255 | 0.0013 |
| H72 | -0.0648 | 0.3691 | 0.2293 |
| H73 | -0.1189 | 0.4883 | 0.2696 |

J-7587-m28

page 3

Table S2b. (continued)

| | x/a | y/b | z/c |
|-----|---------|--------|--------|
| H74 | -0.2431 | 0.4964 | 0.2690 |
| H75 | -0.3081 | 0.3800 | 0.2278 |
| H76 | -0.2485 | 0.2672 | 0.1875 |

J-7587-m29

Table S3. Anisotropic Thermal Parameters for (B): $(C_6H_{11}O)_4Li_4(C_5H_5N)_3$

| | U ₁₁ | U ₂₂ | U ₃₃ | U ₂₃ | U ₁₃ | U ₁₂ |
|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Li1 | 0.029(4) | 0.029(4) | 0.042(4) | 0.001(3) | 0.005(3) | 0.002(3) |
| Li2 | 0.035(4) | 0.038(4) | 0.032(4) | -0.004(3) | 0.001(3) | -0.003(3) |
| Li3 | 0.035(4) | 0.036(4) | 0.030(4) | -0.004(3) | 0.002(3) | 0.002(3) |
| Li4 | 0.030(4) | 0.035(4) | 0.039(4) | -0.004(3) | 0.000(3) | -0.006(3) |
| O1 | 0.028(2) | 0.026(2) | 0.030(2) | -0.001(1) | 0.003(1) | -0.003(1) |
| O2 | 0.028(1) | 0.031(2) | 0.028(1) | 0.003(1) | 0.007(1) | -0.001(1) |
| O3 | 0.025(1) | 0.029(2) | 0.025(2) | 0.001(1) | -0.004(1) | 0.000(1) |
| O4 | 0.031(2) | 0.023(2) | 0.038(2) | -0.002(1) | 0.000(1) | 0.006(1) |
| N51 | 0.030(2) | 0.030(2) | 0.030(2) | 0.003(2) | 0.003(2) | 0.002(2) |
| N61 | 0.034(2) | 0.035(2) | 0.033(2) | 0.001(2) | -0.003(2) | 0.002(2) |
| N71 | 0.029(2) | 0.034(2) | 0.031(2) | -0.004(2) | 0.000(2) | 0.001(2) |
| C11 | 0.039(3) | 0.037(3) | 0.044(3) | -0.003(2) | 0.017(2) | -0.009(2) |
| C12 | 0.021(2) | 0.023(2) | 0.035(3) | -0.000(2) | 0.001(2) | 0.002(2) |
| C13 | 0.032(3) | 0.028(2) | 0.041(3) | -0.003(2) | 0.000(2) | -0.004(2) |
| C14 | 0.052(3) | 0.050(3) | 0.046(3) | -0.020(2) | 0.004(2) | -0.001(2) |
| C15 | 0.055(3) | 0.038(3) | 0.061(3) | -0.010(2) | -0.004(2) | -0.007(2) |
| C16 | 0.041(3) | 0.046(3) | 0.046(3) | -0.004(2) | -0.008(2) | -0.012(2) |
| C21 | 0.041(3) | 0.037(3) | 0.037(3) | 0.003(2) | 0.010(2) | 0.012(2) |
| C22 | 0.025(2) | 0.037(3) | 0.026(2) | 0.008(2) | 0.001(2) | 0.000(2) |
| C23 | 0.028(2) | 0.043(3) | 0.030(2) | 0.010(2) | 0.001(2) | -0.002(2) |
| C24 | 0.053(3) | 0.057(3) | 0.050(3) | 0.015(3) | -0.004(2) | -0.020(3) |
| C25 | 0.041(3) | 0.045(3) | 0.055(3) | 0.017(2) | -0.000(2) | -0.008(2) |
| C26 | 0.046(3) | 0.075(3) | 0.048(3) | 0.017(3) | 0.016(2) | -0.004(3) |
| C31 | 0.034(3) | 0.043(3) | 0.031(3) | 0.003(2) | 0.000(2) | 0.003(2) |

Table S3. (continued)

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|-----|----------|----------|----------|-----------|-----------|-----------|
| C32 | 0.027(2) | 0.027(2) | 0.028(2) | -0.005(2) | -0.001(2) | 0.008(2) |
| C33 | 0.027(2) | 0.033(3) | 0.033(2) | -0.000(2) | -0.007(2) | 0.003(2) |
| C34 | 0.031(2) | 0.057(3) | 0.041(3) | 0.007(2) | -0.001(2) | -0.000(2) |
| C35 | 0.042(3) | 0.064(3) | 0.043(3) | -0.004(2) | -0.013(2) | 0.002(2) |
| C36 | 0.043(3) | 0.046(3) | 0.072(3) | -0.002(3) | -0.021(2) | -0.010(2) |
| C41 | 0.039(3) | 0.056(3) | 0.051(3) | -0.007(3) | -0.004(2) | 0.018(3) |
| C42 | 0.037(3) | 0.034(3) | 0.023(2) | -0.005(2) | -0.003(2) | 0.008(2) |
| C43 | 0.068(3) | 0.026(3) | 0.033(3) | -0.001(2) | -0.005(2) | 0.016(2) |
| C44 | 0.115(5) | 0.026(3) | 0.113(4) | -0.010(3) | -0.037(4) | -0.011(3) |
| C45 | 0.148(5) | 0.043(3) | 0.039(3) | -0.002(2) | 0.005(3) | 0.033(3) |
| C46 | 0.105(4) | 0.040(3) | 0.053(3) | 0.002(3) | 0.009(3) | 0.007(3) |
| C52 | 0.030(3) | 0.035(3) | 0.031(2) | 0.002(2) | 0.003(2) | -0.003(2) |
| C53 | 0.032(3) | 0.039(3) | 0.040(3) | 0.007(2) | 0.001(2) | 0.012(2) |
| C54 | 0.051(3) | 0.031(3) | 0.044(3) | 0.004(2) | -0.008(2) | 0.007(3) |
| C55 | 0.038(3) | 0.038(3) | 0.040(3) | 0.007(2) | -0.005(2) | -0.010(2) |
| C56 | 0.030(3) | 0.041(3) | 0.034(3) | 0.003(2) | 0.000(2) | 0.002(2) |
| C62 | 0.043(3) | 0.041(3) | 0.032(3) | -0.001(2) | 0.006(2) | -0.001(2) |
| C63 | 0.051(3) | 0.043(3) | 0.041(3) | 0.006(2) | -0.000(2) | 0.010(2) |
| C64 | 0.069(3) | 0.058(3) | 0.031(3) | 0.010(3) | -0.005(2) | 0.011(3) |
| C65 | 0.065(3) | 0.061(3) | 0.026(3) | -0.013(2) | -0.003(2) | 0.017(3) |
| C66 | 0.048(3) | 0.049(3) | 0.038(3) | -0.003(2) | -0.003(2) | 0.012(2) |
| C72 | 0.028(2) | 0.039(3) | 0.031(2) | -0.000(2) | 0.001(2) | 0.004(2) |
| C73 | 0.046(3) | 0.032(3) | 0.027(2) | -0.006(2) | 0.000(2) | 0.003(2) |
| C74 | 0.046(3) | 0.034(3) | 0.035(3) | -0.003(2) | 0.018(2) | 0.011(2) |

Table S3. (continued)

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|-----|----------|----------|----------|-----------|-----------|-----------|
| C75 | 0.028(3) | 0.049(3) | 0.056(3) | -0.013(3) | 0.009(2) | 0.002(2) |
| C76 | 0.037(3) | 0.043(3) | 0.044(3) | -0.015(2) | -0.001(2) | -0.003(2) |

temperature factor form:

$$\exp\{-2\pi^2(\underline{a}^*{}^2 U_{11} \underline{h}^2 + \underline{b}^*{}^2 U_{22} \underline{k}^2 + \underline{c}^*{}^2 U_{33} \underline{l}^2 + 2\underline{b}^* \underline{c}^* U_{23} \underline{kl} + 2\underline{a}^* \underline{c}^* U_{13} \underline{hl} + 2\underline{a}^* \underline{b}^* U_{12} \underline{hk})\}$$

J 7587-m32

Table S4. Distances (\AA) and Angles ($^\circ$) for (B): $(\text{C}_6\text{H}_{11}\text{O})_4\text{Li}_4(\text{C}_5\text{H}_5\text{N})_3$

| | | | |
|-----------|----------|-----------|----------|
| Li1 -01 | 1.968(6) | Li2 -01 | 1.933(6) |
| Li3 -01 | 1.961(6) | Li1 -02 | 1.953(6) |
| Li2 -02 | 1.967(6) | Li4 -02 | 1.869(7) |
| Li1 -03 | 1.983(6) | Li3 -03 | 1.983(6) |
| Li4 -03 | 1.860(7) | Li2 -04 | 1.961(7) |
| Li3 -04 | 2.008(6) | Li4 -04 | 1.850(6) |
| Li1 -N51 | 2.046(7) | Li2 -N61 | 2.068(7) |
| Li3 -N71 | 2.036(7) | C11 -H11a | 1.01(3) |
| C11 -H11b | 0.95(3) | O1 -C12 | 1.336(4) |
| C11 -C12 | 1.327(6) | C12 -C13 | 1.515(5) |
| C13 -C14 | 1.533(5) | C13 -C15 | 1.524(5) |
| C13 -C16 | 1.525(5) | C21 -H21a | 0.97(4) |
| C21 -H21b | 0.97(3) | O2 -C22 | 1.347(4) |
| C21 -C22 | 1.330(6) | C22 -C23 | 1.510(5) |
| C23 -C24 | 1.527(5) | C23 -C25 | 1.531(5) |
| C23 -C26 | 1.522(5) | C31 -H31a | 0.99(4) |
| C31 -H31b | 0.98(4) | O3 -C32 | 1.335(4) |
| C31 -C32 | 1.329(5) | C32 -C33 | 1.532(5) |
| C33 -C34 | 1.523(5) | C33 -C35 | 1.528(5) |
| C33 -C36 | 1.533(5) | C41 -H41a | 1.01(4) |
| C41 -H41b | 0.91(4) | O4 -C42 | 1.324(5) |
| C41 -C42 | 1.334(6) | C42 -C43 | 1.517(5) |
| C43 -C44 | 1.502(6) | C43 -C45 | 1.523(6) |
| C43 -C46 | 1.522(5) | N51 -C52 | 1.337(5) |
| C52 -C53 | 1.379(5) | C53 -C54 | 1.365(6) |
| C54 -C55 | 1.374(6) | N51 -C56 | 1.326(5) |

Table S4. (continued)

| | | | |
|--------------|----------|--------------|----------|
| C55 -C56 | 1.375(6) | N61 -C62 | 1.327(5) |
| C62 -C63 | 1.370(6) | C63 -C64 | 1.370(6) |
| C64 -C65 | 1.363(6) | N61 -C66 | 1.333(5) |
| C65 -C66 | 1.367(6) | N71 -C72 | 1.337(5) |
| C72 -C73 | 1.371(5) | C73 -C74 | 1.368(6) |
| C74 -C75 | 1.371(6) | N71 -C76 | 1.328(5) |
| C75 -C76 | 1.371(6) | | |
| 01 -Li1 -02 | 96.7(3) | 01 -Li1 -03 | 97.3(3) |
| 01 -Li1 -N51 | 117.4(3) | 02 -Li1 -03 | 92.3(3) |
| 02 -Li1 -N51 | 127.0(3) | 03 -Li1 -N51 | 119.5(3) |
| 01 -Li2 -02 | 97.4(3) | 01 -Li2 -04 | 94.3(3) |
| 01 -Li2 -N61 | 134.6(3) | 02 -Li2 -04 | 91.4(3) |
| 02 -Li2 -N61 | 111.8(3) | 04 -Li2 -N61 | 118.0(3) |
| 01 -Li3 -03 | 97.6(3) | 01 -Li3 -04 | 92.0(3) |
| 01 -Li3 -N71 | 142.5(3) | 03 -Li3 -04 | 92.3(3) |
| 03 -Li3 -N71 | 110.1(3) | 04 -Li3 -N71 | 111.0(3) |
| 02 -Li4 -03 | 99.1(3) | 02 -Li4 -04 | 98.2(3) |
| 03 -Li4 -04 | 101.7(3) | Li1 -01 -Li2 | 83.2(3) |
| Li1 -01 -Li3 | 83.0(3) | Li1 -01 -C12 | 125.8(3) |
| Li2 -01 -Li3 | 87.5(3) | Li2 -01 -C12 | 140.3(3) |
| Li3 -01 -C12 | 119.3(3) | Li1 -02 -Li2 | 82.7(3) |
| Li1 -02 -Li4 | 83.6(3) | Li1 -02 -C22 | 128.3(3) |
| Li2 -02 -Li4 | 84.3(3) | Li2 -02 -C22 | 124.4(3) |
| Li4 -02 -C22 | 135.9(3) | Li1 -03 -Li3 | 82.0(3) |
| Li1 -03 -Li4 | 83.0(3) | Li1 -03 -C32 | 116.8(3) |
| Li3 -03 -Li4 | 82.9(3) | Li3 -03 -C32 | 127.4(3) |

Table S4. (continued)

| | | | |
|----------------|----------|---------------|----------|
| Li4 -03 -C32 | 143.9(3) | Li2 -04 -Li3 | 85.5(3) |
| Li2 -04 -Li4 | 84.9(3) | Li2 -04 -C42 | 126.2(3) |
| Li3 -04 -Li4 | 82.5(3) | Li3 -04 -C42 | 110.0(3) |
| Li4 -04 -C42 | 146.2(3) | Li1 -N51 -C52 | 124.0(3) |
| Li1 -N51 -C56 | 118.7(3) | C52 -N51 -C56 | 117.2(3) |
| Li2 -N61 -C62 | 117.6(3) | Li2 -N61 -C66 | 125.3(3) |
| C62 -N61 -C66 | 116.2(3) | Li3 -N71 -C72 | 117.5(3) |
| Li3 -N71 -C76 | 124.3(3) | C72 -N71 -C76 | 115.6(3) |
| H11a-C11 -H11b | 113(3) | H11a-C11 -C12 | 125(2) |
| H11b-C11 -C12 | 121(2) | O1 -C12 -C11 | 121.5(3) |
| O1 -C12 -C13 | 115.2(3) | C11 -C12 -C13 | 123.3(3) |
| C12 -C13 -C14 | 109.6(3) | C12 -C13 -C15 | 112.7(3) |
| C12 -C13 -C16 | 109.4(3) | C14 -C13 -C15 | 108.1(3) |
| C14 -C13 -C16 | 109.1(3) | C15 -C13 -C16 | 108.1(3) |
| H21a-C21 -H21b | 114(3) | H21a-C21 -C22 | 124(2) |
| H21b-C21 -C22 | 122(2) | O2 -C22 -C21 | 121.9(3) |
| O2 -C22 -C23 | 114.2(3) | C21 -C22 -C23 | 124.0(3) |
| C22 -C23 -C24 | 110.0(3) | C22 -C23 -C25 | 110.2(3) |
| C22 -C23 -C26 | 112.8(3) | C24 -C23 -C25 | 108.5(3) |
| C24 -C23 -C26 | 107.4(3) | C25 -C23 -C26 | 107.8(3) |
| H31a-C31 -H31b | 114(3) | H31a-C31 -C32 | 122(2) |
| H31b-C31 -C32 | 124(2) | O3 -C32 -C31 | 122.6(3) |
| O3 -C32 -C33 | 114.2(3) | C31 -C32 -C33 | 123.1(3) |
| C32 -C33 -C34 | 108.7(3) | C32 -C33 -C35 | 113.0(3) |
| C32 -C33 -C36 | 109.4(3) | C34 -C33 -C35 | 108.8(3) |
| C34 -C33 -C36 | 109.6(3) | C35 -C33 -C36 | 107.3(3) |

Table S4. (continued)

| | | | |
|----------------|----------|---------------|----------|
| H41a-C41 -H41b | 121(3) | H41a-C41 -C42 | 120(2) |
| H41b-C41 -C42 | 119(2) | O4 -C42 -C41 | 122.0(4) |
| O4 -C42 -C43 | 116.1(3) | C41 -C42 -C43 | 121.9(4) |
| C42 -C43 -C44 | 111.1(3) | C42 -C43 -C45 | 111.7(3) |
| C42 -C43 -C46 | 108.9(3) | C44 -C43 -C45 | 107.5(3) |
| C44 -C43 -C46 | 108.4(4) | C45 -C43 -C46 | 109.2(3) |
| N51 -C52 -C53 | 122.9(3) | C52 -C53 -C54 | 118.8(4) |
| C53 -C54 -C55 | 119.1(4) | C54 -C55 -C56 | 118.3(4) |
| N51 -C56 -C55 | 123.6(4) | N61 -C62 -C63 | 124.2(4) |
| C62 -C63 -C64 | 118.2(4) | C63 -C64 -C65 | 118.8(4) |
| C64 -C65 -C66 | 119.1(4) | N61 -C66 -C65 | 123.5(4) |
| N71 -C72 -C73 | 124.1(3) | C72 -C73 -C74 | 118.8(3) |
| C73 -C74 -C75 | 118.4(4) | C74 -C75 -C76 | 118.7(4) |
| N71 -C76 -C75 | 124.4(4) | | |