atures; however, its solutions in benzene lose SO_2 at 50 °C to regenerate **1**.[14]

The foregoing examples of the behavior of **1** toward various unsaturated compounds demonstrate that metal oxo hydride complexes may react by transfer of oxygen alone or of both oxygen and hydrogen to a substrate. The latter type of reaction appears to be less common than the former, possibly because it requires breaking of an M-H bond, which is generally quite strong.[15] This duality of action of **1** on unsaturated substrates is under further investigation.

Acknowledgment. We are grateful to the National Science Foundation and The Ohio State University for financial support and to Haibin Deng for help with calculations on the structure. Studies on metal complexes of Cyttp were initiated in these laboratories by the late Professor Devon W. Meek; the work reported here has developed from his early investigations.

Supplementary Material Available: Description of reactions, analytical and spectroscopic data for **1**-**7**, and details of structure determination of $\mathbf{1}\cdot{}^3/_4\mathrm{MeOH}$, including an ORTEP plot, crystal data, data collection and refinement, positional parameters, temperature factor expressions, and selected bond distances and angles (15 pages). Ordering information is given on any current masthead page.

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(14) Similar behavior toward SO_2 was recently reported for $(\eta^5\text{-}C_5Me_5)_2Re_2(\mu\text{-}O)_2(O)_2$; see: Herrmann, W. A.; Jung, K. A.; Herdtweck, E. *Chem. Ber.* **1989**, *122*, 2041.

(15) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.

Mixed Aggregates: Crystal Structures of a Lithium Ketone Enolate/Lithium Amide and of a Sodium Ester Enolate/Sodium Amide

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Previously we reported the first structural evidence for a mixed lithium ketone enolate/lithium diisopropyl amide aggregate depicted as **1** in Scheme I.[1] It was suggested that mixed aggregates of general structure **2** are commonly formed when alkali metal amide bases react with enolizable substrates. The salient nature of **1** in enantioselective condensation reactions initiated with chiral amide bases as noncovalently bound auxiliaries was noted.[2] Further support for the existence of these complexes in solution comes from NMR studies.[3] Finally, the correspondence between solid-state and solution structures of enolates is bolstered by recent colligative property and thermochemical measurements.[4] Now we wish to strengthen and generalize our work by presenting the first structural evidence for two, nonchelated enolate/amide base aggregates. These new structures are composed of a simple lithium ketone enolate complexed with lithium hexamethyldisilazide (LHMDS) and of a sodium ester enolate complexed with sodium hexamethyldisilazide (NHMDS). It is important to elucidate the structural details of these mixed aggregates for use as models in stereo- and enantioselectively enhanced enolate and related reactions.[5]

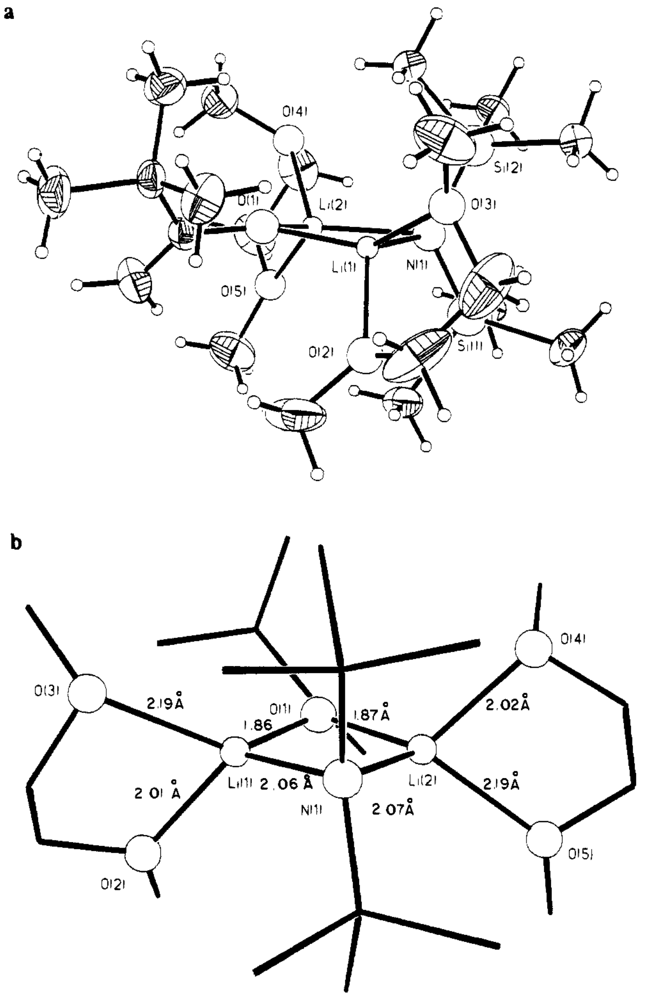

Figure 1. (a) Thermal ellipsoid plot at 50% probability of the mixed pinacolone enolate/LHMDS/DME mixed aggregate **3**. Note that the methyl groups on the DME's point toward the enolate residue. (b) Perspective view of the aggregate **3** emphasizing the main skeletal features. The Li-O-Li-N core is essentially planar; the enolate residue is twisted at an angle of approximately 35.6° around the O(1)-C(2) axis relative to this plane, and the Si-N-Si axis is tilted at an angle of 4.4° relative to the planar core. The enolate oxygen O(1) is slightly pyramidalized by ~0.16 Å out of the plane defined by Li(1), Li(2), and C(2).

Initial attempts to obtain a crystalline sample of a structure analogous to **2** were unsuccessful. When the more symmetrical amide base LHMDS and the bidentate ligand dimethoxyethane (DME) were substituted in place of lithium diisopropylamide (LDA) and THF, respectively, we succeeded in crystallizing the mixed aggregate **3**.[6] Previously, only two lithium ketone enolates with dicoordinate, planar enolate oxygens have been crystallized.[7]

The presence of a bridging enolate oxygen is reflected in the bond lengths of **3**. The Li-(enolate-O) distances are relatively short (av 1.87 Å) and the Li-N distances are slightly longer (av 2.07 Å) than in mixed ketone enolate/LHMDS aggregates with tricoordinate enolate oxygens.[8] Note in Figure 1 that the methyl

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(1) Williard, P. G.; Hintze, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 5539.

(2) (a) Muraoka, J.; Hisashi, K. *Tetrahedron Lett.* **1988**, *29*, 337. (b) Ando, A.; Shioiri, T. *J. Chem. Soc., Chem. Commun.* **1987**, *656*, 1620. (c) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624 (see Table 9). (d) Shirai, R.; Tanaka, M.; Koga, K. *J. Am. Chem. Soc.* **1986**, *108*, 543. (e) See also: Denmark, S. E.; Ares, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 4432.

(3) (a) Heinzer, J.; Oth, J. F. M.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1848. (b) See footnote 141 and p 1632 in ref 2c. (c) Professor D. Collum, Cornell University, private communication.

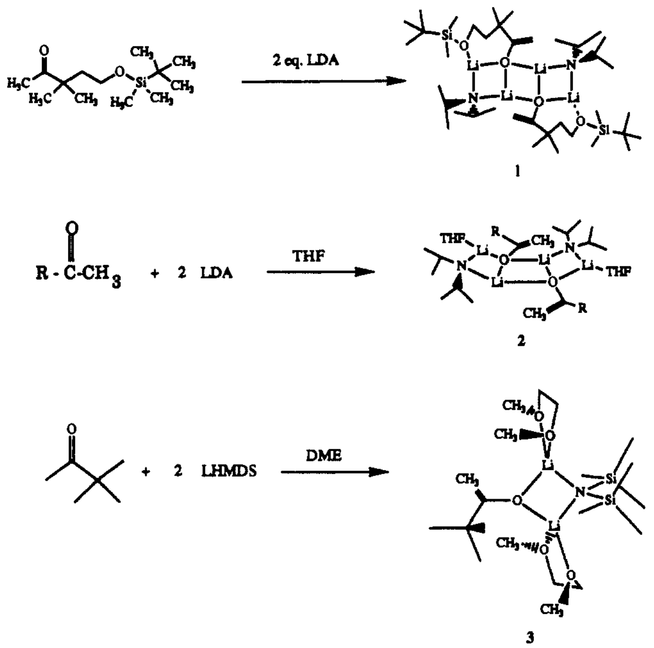
(4) Arnett, E. M.; Fischer, F. J.; Nichols, M. A.; Ribeiro, A. A. *J. Am. Chem. Soc.* **1990**, *112*, 801.

(5) (a) Corey, E. J.; Kim, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 4976. (b) Tomioka, K.; Shindo, M.; Koga, K. *J. Am. Chem. Soc.* **1989**, *111*, 8266.

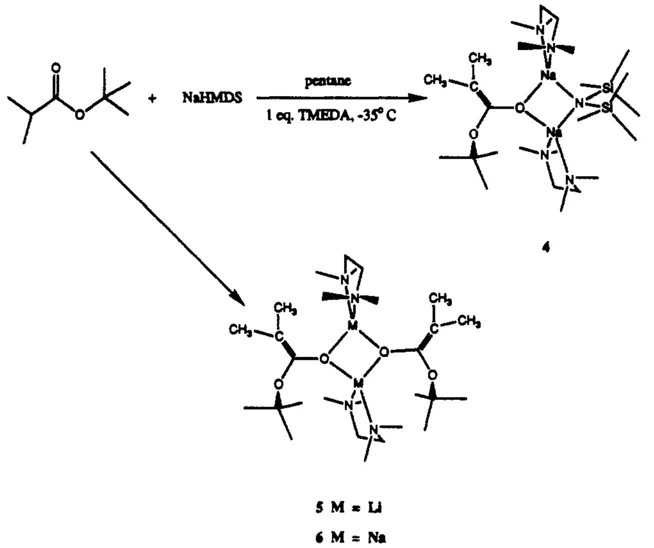
(6) The aggregate **3** of molecular composition $[(C_6H_{11}OLi)\cdot(C_6H_{18}Si_2N\text{-}Li)\cdot(C_4H_{10}O_2)_2]$ crystallized in the centrosymmetric, monoclinic space group $P2_1/c$ with unit cell parameters $a = 8.738$ (9) Å, $b = 12.645$ (7) Å, $c = 27.794$ (8) Å, and $\beta = 90.36$ (2)° after regeneration of the amide base by addition of a second equivalent of *n*-BuLi. Data collection at low temperature, structure solution, and refinement ($R = 0.042$ and $R_w = 0.056$) proceeded normally. Specific details of the diffraction analysis along with tables of atomic coordinates and structural parameters have been submitted as supplementary material and to the Cambridge Crystallographic Database.

(7) (a) Laube, T.; Dunitz, J. D.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1373. (b) Amstutz, R.; Dunitz, J. D.; Laube, T.; Schweizer, W. B.; Seebach, D. *Chem. Ber.* **1986**, *119*, 434.

Scheme I



Scheme II



groups of the DME are directed away from the LHMDS and toward the enolate residue. The four (DME-O)-Li bonds form two sets averaging 2.18 and 2.01 Å, respectively (see Figure 1b). Each DME possesses a short and a long O–Li bond and each set appears on opposite faces of the central four-membered ring. The different bond distances correlate with an observed twist in both the LHMDS and the enolate relative to Li-O-Li-N core (see Figure 1b) and therefore can be attributed to steric interactions. If the difference between the Li-O distances of the DME molecules reflects the relative strength of the Li-O interaction, then these distances represent the ease with which these ligands may undergo substitution by the donor atom of an electrophile. No doubt these subtle structural differences are in dynamic equilibrium in solution.

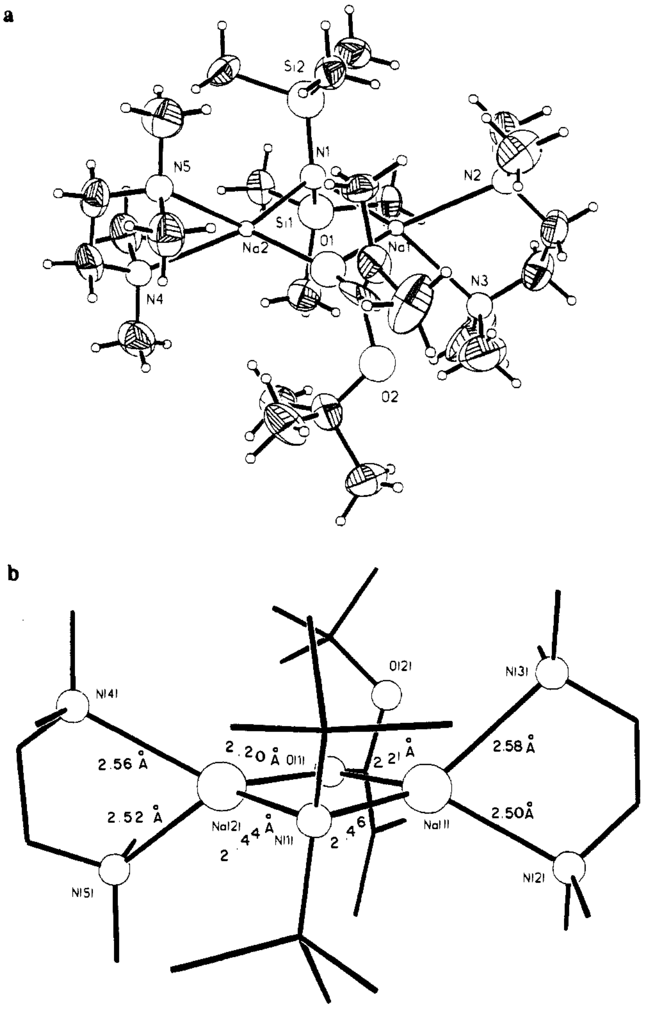


Figure 2. (a) Thermal ellipsoid plot at 50% probability of the Na ester enolate/NHMDS/TMEDA mixed aggregate **4**. Some disorder is observed in the crystal due to an alternative conformation of the *tert*-butyl ester. Only the major conformation is depicted. (b) Perspective view of the aggregate **4** emphasizing the main skeletal features. The Na–O–Na–N core is essentially planar and the Si–N–Si axis is tilted at an angle of ~7.2° relative to this plane. The ester enolate oxygen is ~0.10 Å out of the plane defined by Na(1), Na(2), and C(7).

The three reported ester enolate structures embrace lithium as the cation.[9] We now report the first structural characterization of the sodium ester enolate **4** derived from *tert*-butyl isobutyrate and NHMDS as shown in Scheme II and depicted accurately as a thermal ellipsoid plot in Figure 2.[10] The conformation of the enolate residue in **4** is close to that found in dimer **5**.[9]

Enolate **4** crystallized from a solution made by mixing NHMDS and *tert*-butyl isobutyrate in equivalent stoichiometric quantities in the presence of tetramethylethylenediamine (TMEDA). Consequently, crystallization of mixed aggregate **4** rather than a simple dimer **6** came as a surprise.[11] Few structural comparisons are available for **4** since this is the first structure of a sodium ester enolate. The Na–O distances are slightly shorter (av 2.21 Å) than the corresponding Na–O distances of sodium pinacolone enolate (av 2.25 Å).[11] The Na–N-TMS$_2$ distances (av 2.45 Å) are ~0.1 Å longer than those reported for unsolvated NHMDS.[12] As in

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(8) Aggregates corresponding to structure **1** with 5-, 6-, 7-, and 8-membered chelate rings in the enolate residue have been obtained: Williard, P. G.; Hintze, M. J. Unpublished results.

(9) Seebach, D.; Amstutz, R.; Laube, T.; Schweizer, W. B.; Dunitz, J. *J. Am. Chem. Soc.* **1985**, *107*, 5403.

(10) The aggregate 4 of molecular composition [(C$_8$H$_{15}$O$_2$Na)·(C$_{16}$H$_{18}$Si$_2$NNa)·(C$_6$H$_{16}$N$_2$)$_2$] crystallized in the centrosymmetric, monoclinic space group $P2_1/n$ with unit cell parameters a = 11.047 (6) Å, b = 11.495 (4) Å, c = 29.736 (11) Å, and β = 94.86 (4)°. Data collection at low temperature, structure solution, and refinement (R = 0.065 and R_w = 0.084) proceeded normally. Specific details of the diffraction analysis along with tables of atomic coordinates and structural parameters have been submitted as supplementary material and to the Cambridge Crystallographic Database.

(11) Note that the crystallization of 4 from a solution made up with equivalent quantities of NHMDS and ester suggests that unenolized ester remains in solution. We made a similar but not identical observation upon crystallization of the sodium enolate of 3,3-dimethylbutanone (pinacolone) generated with NHMDS whereupon a mixed aggregate containing enolate and unenolized ketone crystallized from solution, see: Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 462.

(12) Gruning, R.; Atwood, J. L. *J. Organomet. Chem.* **1977**, *137*, 101.

3, the amide base residue is twisted relative to the central four membered ring. This twist is observed in all mixed aggregates and in the structure of THF-solvated LDA.[13] Since this is consistently observed in different molecular and solid-state environments, it is likely to be intrinsic to the coordination behavior of metalated secondary amides. To our knowledge, this observation has not been predicted by theoretical work on lithium amides[14] nor noted in previous structures of LHMDS[15] or NHMDS.[12]

Structures **1**, **3**, and **4** demonstrate the scope and generality of mixed aggregation. This phenomenon is now observed with three distinct types of enolates, with two different metal amide bases, and with two different metal cations. A complex between LDA and the monoanion of phenyl acetonitrile was also structurally characterized recently.[16] Coupled with this structural information is the chemical evidence suggesting that these mixed aggregates maintain their integrity in solution.[2,3] As these complexes are explored synthetically, they should prove extremely useful in controlling enolate reactivity and selectivity. Experiments designed to probe these points with chiral, ionic, non-covalent auxiliaries are in progress.

Acknowledgment. This work is supported by the National Institutes of Health through Grant GM-35982 and a Research Career Development Award (CA-01330) to P.G.W. The X-ray equipment was purchased with assistance from an instrument grant from the NSF (CHE-8206423).

Supplementary Material Available: Details of the diffraction analysis, plots of atom labels, and tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **3** and **4** (18 pages). Ordering information is given on any current masthead page.

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(13) Williard, P. G.; Salvino, J. M. Unpublished results.

(14) (a) Sapse, A. M.; Raghavachri, K.; Schleyer, P. v. R.; Kaufmann, E. *J. Am. Chem. Soc.* **1985**, *107*, 6483. (b) Sapse, A. M.; Kaufmann, E.; Schleyer, P. v. R.; Gleiter, R. *Inorg. Chem.* **1984**, *23*, 1569. (c) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(15) (a) Lappert, M. F.; Slade, J. J.; Singh, A. *J. Am. Chem. Soc.* **1983**, *105*, 302. (b) Engelhardt, L. M.; May, A. S.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* **1983**, 1671.

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Cross-Bridged Cyclam. Protonation and Li$^+$ Complexation in a Diamond-Lattice Cleft

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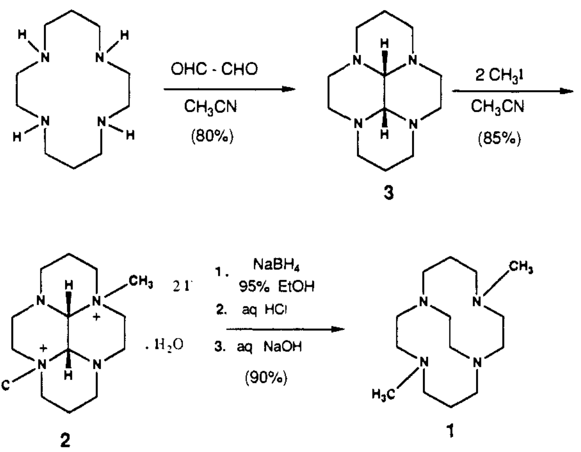
Polycyclic polyamines are of current interest because members of this class of compounds have been shown to exhibit unusual basicity,[3-5] redox behavior,[4] and coordination chemistry.[5,6] Polycyclic tertiary amines also hold promise for the synthesis of alkalides and electrides.[7] Structural modifications of the important macrocyclic ligand cyclam (1,4,8,11-tetraazacyclotetradecane) involving ethylene bridging of adjacent nitrogens have been reported.[8,9] "Cross bridging" of cyclam (i.e., bridging of nonadjacent nitrogens) with CH_2CH_2 would result in a flexible bicyclo[6.6.2] tetraamine that is capable of adopting conformations having all four nitrogen lone pairs convergent on a cleft or cavity for complexation of metal ions. Herein we report a rational and efficient synthesis of the first example of such a cross-bridged cyclam, **1** (4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane), and our preliminary investigations into its basicity and alkali ion complexation.[10]

Scheme I



The synthetic route to **1**[11] (Scheme I) is based upon reductive ring cleavage[12] of dimethylated bisaminal diiodide **2**,[11] prepared in good yield by exhaustive methylation of the readily available bisaminal **3**.[13] The high regioselectivity of the bis quaternization of **2** is a consequence of its conformation.[13] As shown in Figure

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(1) University of New Hampshire.

(2) Keene State College.

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(7) Dye, J. L. *Pure Appl. Chem.* **1989**, *61*, 1555–1562.

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