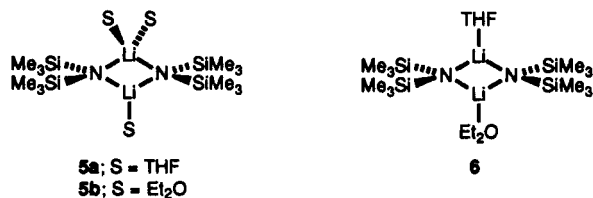


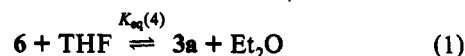
corresponding ^{13}C NMR spectra contain the resonances of the disolvated dimers to the exclusion of those for the monosolvated dimers or free ligand. As the added ligand concentration exceeds 1.0 equiv/Li, ^{13}C resonances corresponding to uncoordinated ligand appear without any other detectable spectral changes. The distinct discontinuity at 1.0 equiv/Li demonstrates a marked preference for disolvated (rather than more highly solvated) dimers. Upon incrementally progressing to neat ethereal solvent, we observe the appearance of ^6Li doublets and ^{15}N triplets characteristic of monomers (4). The monomer 4a becomes the major species in neat THF, while 4b remains minor in neat Et_2O .⁷ We suspect from semiempirical computational studies and other indirect evidence that the monomers and dimers are disolvated,¹⁴ but we are unable to obtain experimental verification.

Having attained the slow solvent exchange limit, we were poised to address some basic questions pertaining to solvation. For example, we were interested in ascertaining whether ligand substitution proceeds by a dissociative mechanism *via* monosolvated dimers (2) or an associative mechanism *via* trisolvated dimers (5).¹⁵ Variable temperature ^{13}C NMR spectroscopy of LiHMDS (0.1 M) in toluene- d_8 containing 2.0 equiv of ligand/Li revealed coalescences of free and coordinated ligands ($-47 \pm 3^\circ\text{C}$ for THF; $-76 \pm 3^\circ\text{C}$ for Et_2O) corresponding to the following activation free energies for ligand exchange: $\Delta G^\ddagger_{226\text{K}}(\text{THF}) = 10.8 \pm 0.2$ kcal/mol; $\Delta G^\ddagger_{197\text{K}}(\text{Et}_2\text{O}) = 8.6 \pm 0.2$ kcal/mol.^{16,17} The observed coalescence temperatures and calculated free energies were found to be invariant over a 20-fold range in free ligand concentration (0.02–0.4 M), indicating that *ligand exchange in the disolvated dimers proceeds by a dissociative process via monosolvated dimers.*



The activation energies for ligand dissociation *appear* to correlate with metal–ligand bond strengths. More to the point, however, we were in a position to directly measure the relative metal–ligand bond strengths. Solutions of 0.1 M [$^6\text{Li}, ^{15}\text{N}$]-

LiHMDS in toluene- d_8 containing 2.0 equiv/Li each of THF and Et_2O contain exclusively THF-solvated dimer 3a. ^6Li and ^{15}N NMR spectra recorded on LiHMDS solutions containing 0.5 equiv/Li of THF and 5.0 equiv/Li of Et_2O display resonances corresponding to dimers 3a and 3b along with new ^6Li , ^{15}N , and ^{13}C resonances consistent with mixed solvate 6. The approximate 1:2:1 mixture of 3a/6/3b indicates that, despite the differential solvation energies of THF and Et_2O , there is no anomalous cooperativity in the solvation energies of mixed solvate 6.¹⁸ The ^{13}C resonances of coordinated ligands on 3a and 6 as well as free THF and free Et_2O could be integrated (173 K) and the four concentrations fitted to eq 2 to obtain $K_{\text{eq}} = 9.7 \pm 0.5 \times 10^2$ corresponding to $\Delta G^\circ_{173\text{K}} = -2.3 \pm 0.2$ kcal/mol.



$$K_{\text{eq}}(4) = \frac{[3a][\text{Et}_2\text{O}]}{[6][\text{THF}]} \quad (2)$$

To the best of our knowledge this represents the first instance in which exchange of simple ethereal solvents has been frozen out on NMR time scales. The consequent demonstration of dissociative ligand substitution and the direct measurement of relative solvation energies provide fundamental insight into the coordination chemistry of lithium underlying macroscopically observable structure–reactivity relationships. Demonstration that solvation of the two lithium sites on the LiHMDS dimer are nearly independent processes sheds light on issues of cooperative solvation relevant to mixed solvent systems as well as substrate precomplexation. Moreover, the activation barriers for ligand exchange could be sufficiently large to render solvent dissociation rate limiting in fast substrate metalations.

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Supplementary Material Available: ^6Li , ^{13}C , and ^{15}N NMR spectra of LiHMDS with added THF or Et_2O (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(16) Application of DNMR (Stempfle, W.; Klein, J.; Hoffmann, E. G. QCPE Program No. 450) afforded activation energies scaled to -100°C that varied only slightly. Unfortunately, we have reason to question their validity and must defer reporting additional details to a later time.

(17) Enthalpies of alkyl lithium solvation by THF have been shown through calorimetric measurements to be approximately 7–10 kcal/mol per Li. Quirk, R. P.; McFay, D. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1445. Quirk, R. P.; Kester, D. E.; Delaney, R. D. *J. Organomet. Chem.* **1973**, *59*, 45. See also: Arnett, E. M.; Fisher, F. J.; Nichols, M. A.; Ribeiro, A. A. *J. Am. Chem. Soc.* **1990**, *112*, 801.

(18) Similarly, solutions of LiHMDS containing 0.5 equiv of Et_2O and 0.5 equiv of THF show an approximate 1:2:1 mixture of 3a/6/3b.