Mechanism of Lithium Disopropylamide-Mediated Ester Deprotonation: 
The Role of Disolvated Monomers

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Supporting Information

Experimental Section

Reagents and Solvents. THF and toluene were distilled from blue or purple solutions containing sodium benzoophenone ketyl. The toluene still contained 1% tetrabutylammonium to dissolve the ketyl. The LDA was prepared and purified by recrystallization from hexane as described previously.3b Air and moisture sensitive materials were manipulated under argon or nitrogen using standard glove box, vacuum line, and syringe techniques.

IR Spectroscopic Analyses. Samples were recorded using a ReactIR® 1000 from ASI Applied Systems fitted with a one inch, 30-bounce silicon-tipped (SiComp®) probe optimized for maximum sensitivity. The spectra were acquired in 16 scans per spectrum at a gain of one and a resolution of eight using system ReactIR® 2.0 software. A representative reaction was carried out as follows: The IR probe was inserted through a nylon adapter and FETFE O-ring seal (Ace Glass) into an oven-dried, cylindrical flask fitted with magnetic stir bar and T-joint. The T-joint was fitted with a septum for injections and an N2 line. Following evacuation under full vacuum and flushing with N2, the flask was charged with a solution of LDA (160 mg, 1.5 mmol) in THF or THF/toluene (15 mL) and cooled in a Neslab model ULT80 cooling bath to an internal reaction temperature of -53.0 ± 0.5 °C as determined with a thermocouple. Following the recording of a background spectrum, ester 2 (12 μL, 0.06 mmol, 0.004 M) was added neat with stirring. IR spectra were recorded every 30 seconds over the course of the reaction. To account for mixing and temperature equilibration, spectra recorded in the first 3.0 min were discarded. All reactions were monitored to >5 half-lives. Data manipulation and statistical analyses were carried out using the system 2.0 ReactIR® software in conjunction with the non-linear least squares fitting protocols in the Scientist package provided by Micromath.
**Figure 1.** FT-IR spectroscopic analysis of the metallation of ester 2 (0.004 M) by LDA (0.1 M) in THF (neat) at -53 ± 0.5 °C.
Figure 2. Loss of ester 2 (see Figure 1) vs. time. The non-linear least squares fit derives from the general expression $(\text{abs} - \text{abs}_0) = (\text{abs}_\infty - \text{abs}_0)e^{-kt}$. 