Shuffling Lithiated Mixed Aggregates: NMR and Car-Parrinello Molecular Dynamics Reveal an Unexpected Associative Pathway

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Supplementary Information

Synthesis section

General Considerations

Argon was dried and deoxygenated by bubbling through a commercial solution of butyllithium in hexane. Commercial tetrahydrofuran- d_8 was distilled over sodium and benzophenone. ⁶Li (95%) was purchased from Aldrich and washed in freshly distilled pentane. Pentane and heptane were distilled over lithium aluminum hydride. *n*-Bromobutane was distilled over CaH₂.

[⁶Li] Methyllithium salt-free solution in diethylether.¹ Finely cut 6-lithium metal ribbon (0.5 g, 83 mmol), 0.5% (weight) of sodium (*ca.* 2,5 mg, 0,11 mmol) and three small pieces of broken glass were introduced in a two necked pear-shaped flask (50 mL) equipped with a glass stopper and a condenser fitted with a balloon of dry argon. The metallic cuttings were covered with octadecane (10 mL) and the solution was heated (reflux of octadecane : 317°C) with a hot air gun while vigorously stirring. When a maximum amount of the lithium was melted, the flask was placed in a cold bath (- 40°C) allowing the lithium to precipitate as a fine shiny shot. The octadecane was extracted with freshly distilled heptane (10 mL) using a syringe. After intensive stirring, the heptane was removed and the metal washed twice with this same solvent. Diethylether was syringed and the condenser was quickly replaced by a CO_2 condenser fitted with a balloon of dry argon. Chloromethane (2,3 mL, 41,5 mmol) was condensed directly from the sealed cylinder to a graduated trap at -40°C and then added very slowly (2,3 mL were added over a period of 45 min) connecting the trap to the top of the CO_2

condenser. The formation of a grey salt corresponding to LiCl was observed and the disappearance of the ⁶Li metal was noticed. After replacing the CO_2 condenser with a septum, the resulting reaction mixture was stirred for 20 h at room temperature under dry argon. The stirring was stopped allowing LiCl to settle. The etheral solution was then pumped off the flask with a syringe and directly inserted into centrifugation tubes placed under dry argon. The residual traces of salt were centrifuged and the clear final solution was collected in a dry flask flushed under dry argon then titrated² (1,4 M, 55% yield) and kept until further use.

[⁶Li] Methyllithium salt-free solution in THF- d_8 . A solution of [⁶Li]-methyllithium in ether prepared above (2,5 mL) was syringed in a tube fitted with a septum and flushed under dry argon. The tube was then placed under vacuum (20 mmHg) for 1 h to evaporate the ether. The resulting white solid was then dissolved in freshly distilled tetrahydrofuran- d_8 and concentrated under vacuum for 1 h to evaporate the last traces of ether. THF- d_8 (3 to 3.5 mL) was finally added and the resulting solution was titrated (0.5 to 0.7 M).

[⁶Li] Lithium chloride solution in THF- d_8 . The salt formed during the synthesis of [⁶Li] methyllithium in diethylether (procedure described above) was dried ender vaccum (20 mmHg) for an 1 h then THF- d_8 until c = 0.3 M. The resulting was left for 15 h at room temperature to completely dissolve.

[⁶Li]-Lithium amides 1Li and 2Li. A solution of amine 1H (0,137 mmol) in freshly distilled THF- d_8 (0,2 mL) was transferred into a dry 5-mm NMR tube fitted with a septum and flushed under argon. A solution of [⁶Li]-methyllithium (1.1 eq) prepared in THF- d_8 was added dropwise at -78°C with a syringe to the above solution. The tube was vigorously shaken and quickly dropped in the pre-cooled (-78°C) NMR probe.

[⁶Li]-1Li/MeLi complexes. A solution of [⁶Li]-methyllithium (1.5 eq) prepared in THF- d_8 was syrringed dropwise at -78°C to the lithium amides prepared above in a dry 5-mm NMR. The tube was vigorously shaken and quickly dropped in the pre-cooled (-78°C) NMR probe.

Addition of the [⁷Li] LiCl. A solution of [⁷Li]-LiCl prepared in freshly distilled THF- d_8 was syrringed dropwise at -78°C in the 5-mm NMR containing the [⁶Li]-1Li/MeLi complexes prepared above.

NMR section

All NMR experiments were performed on a Bruker Avance DMX 500 spectrometer, equipped with z-gradient unit and a 5 mm {¹H, ⁶Li, ¹³C and ¹⁵N} quadruple-resonance probe. Measuring frequencies were 500 MHz (¹H), 125 MHz (¹³C), 73 MHz (⁶Li) and 50 MHz (¹⁵N).

The proton and lithium one dimensional experiments were recorded with standard parameters. ¹H chemical shifts were referenced to the solvent THF- d_8 residual signal at δ 1.73 and lithium spectra were referenced to external 0.3 M ⁶LiCl in MeOH- d_4 (δ 0.0).

Processing of NMR data was performed on SGI O2 computer, using the manufacturer's program Xwinnmr2.1 (Bruker).

Theoretical section

The PINY-MD program was chosen,³ using the BLYP functional,⁴ a plane wave (PW) basis set, and Goedecker (Li)⁵ and Trouiller-Martins (other atoms)⁶ pseudopotentials. We employed the cluster boundary condition method by Martyna and Tuckerman⁷ complemented by a dual box formalism (a 18 Å box centered in a 24 Å one)⁸. The plane wave energy cut-off (E_{cut}) was 80 Rydberg. CP simulations were carried out using optimized BLYP/6-31+G** structures of the interacting fragments as starting points. A fictitious mass of 650 amu was used. The time step was set to 0.125 fs.

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