Characterization of Hexameric and Octameric *sec*-Butyllithium/*sec*-Butoxide Mixed Aggregates

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Solution-state characterization of *sec*-butyllithium in [D₈]toluene was conducted by utilizing a variety of NMR spectroscopic experiments including diffusion-ordered NMR spectroscopy (DOSY) with diffusion-coefficient–formula-weight correlation analyses and other one- and two-dimensional NMR spectroscopic techniques. These results suggest that *sec*-butyllithium exists primarily as a tetramer/hexamer mixture in hydrocarbon solvents. However, the presence of

roughly 2–5 % (by mol ratio) lithium *sec*-butoxide in both commercially available and laboratory-synthesized *sec*-butyllithium solutions due to the reaction with adventitious dioxygen will lead to the formation of a 1:5 *sec*-butoxide/*sec*-butyllithium mixed hexamer. A *sec*-butoxide/*sec*-butyllithium mixed octamer will emerge when the proportion of butoxide to butyllithium increases.

Introduction

Organolithium reagents are among the most widely used in organic synthesis.[1] Alkyllithium reagents, especially butyllithium compounds, are the source of most organolithium reagents, since they can efficiently generate a wide variety of carbanions such as lithium amide, acetylide, and alkoxide.[1] Moreover, the gaseous by-product butane is a saturated hydrocarbon, which can be easily eliminated. As a result, buyllithium reagents have been a focus of research of several groups for more than 40 years.[1,2] Unlike *n*-butyllithium (*n*BuLi) and *tert*-butyllithium (*t*BuLi), the racemic nature of *sec*-butyllithium (*s*BuLi) makes it hard to form single crystals. Until now, only two crystal structures containing *s*BuLi were reported,[3] and thus, solution-state studies play a critical role in revealing the aggregation state of *s*BuLi.[2f,2i,4] By using ⁶Li and ¹³C NMR spectroscopy, Fraenkel and co-workers proposed that *s*BuLi exists as a hexamer/tetramer mixture in hydrocarbons with a tiny amount of dimer at very high concentration.[5] However, the assignment cannot be established unambiguously, because the experimental results are also consistent with other possible complexes. Moreover, McGarrity and co-workers showed that *n*BuLi commonly contains *n*-butoxide because of its reaction with dioxygen[6] and the *n*-butoxide can readily form mixed tetramers with *n*BuLi in tetrahydrofuran (THF). They also showed that there are rate differences between *n*BuLi aggregates and *n*BuLi/lithium butoxide mixed aggregates toward the reaction of *n*BuLi with benzaldehyde.[7] Because it is a similar species, it would not be sur-

prising if a substoichiometric amount of lithium *sec*-butoxide (*s*BuOLi) were present in a *s*BuLi solution. We found that a small amount of *s*BuOLi is present in both brand new commercial and laboratory-synthesized *s*BuLi solutions. The preparation of butoxide-free *s*BuLi solution appears to be very difficult, as there is no known method to crystallize *s*BuLi. We report the formation of mixed aggregate *s*BuLi/*s*BuOLi and our characterization of hexameric and octameric *s*BuLi/*s*BuOLi mixed aggregates. A variety of mixed aggregates have been reported, although the influence of these species remains uncertain.[8]

Results and Discussion

We first examined the ¹H NMR spectrum of *s*BuLi in [D₈]toluene, which is unreactive towards alkyllithium reagents in the absence of coordinating ligands such as THF or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) at room temperature.[9] The proton NMR spectrum shows three peaks in the methine region of *s*BuLi. In an attempt to reveal the nature of the peaks, a variable-temperature NMR spectroscopic study with 1-dodecene (DDE) as internal reference was carried out (Figure 1). Upon a decrease in temperature, the resonance at –1.16 ppm decreases significantly in intensity and the resonance at –0.88 ppm clearly increases, while the middle resonance at –0.97 ppm does not change significantly. The total concentration of *s*BuLi was determined by comparing the integrations of internal standard and the methine signals,[9a] while the ratios between the three peaks were obtained by Lorentzian deconvolution.[10] Thus, the concentration of each species could be determined. According to Fraenkel's report, *s*BuLi exists mainly as a hexamer and a tetramer in hydrocarbon solvents.[5] Accordingly we assigned the peak at –0.88 ppm to

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the hexamer and that at –1.16 ppm to the tetramer. In order to verify our assignment, we performed a dilution experiment at –30 °C (Table 1).
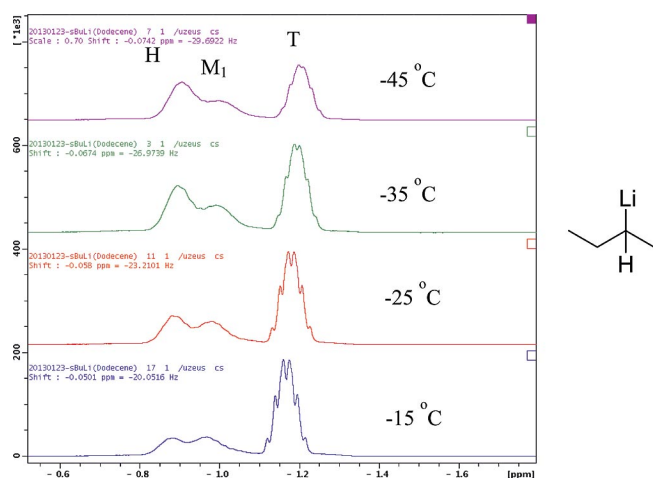

Figure 1. Variable-temperature ^{1}H NMR (400 MHz) spectra of 0.49 M sBuLi in [D$_8$]toluene. H represents the methine signal of sBuLi in hexameric form, T represents the signal in tetrameric form, and M$_1$ represents the signal of sBuLi/sBuOLi mixed hexamer.

Table 1. Concentrations [M] of sBuLi complexes and equilibrium constant (K) at –30 °C in [D$_8$]toluene.

[sBuLi]$_{total}$	[sBuLi]$_a$ at –0.88 ppm	[sBuLi]$_b$ at –1.16 ppm	K[a]
0.487	0.113	0.246	1.54 M^{-1}
0.332	0.068	0.176	1.47 M^{-1}
0.248	0.048	0.135	1.71 M^{-1}

[a] $K = ([s\text{BuLi}]_a/6)^2 / ([s\text{BuLi}]_b/4)^3$.

The result supports our peak assignment, because the equilibrium constants calculated for different dilutions are very similar. The enthalpy (ΔH) and entropy (ΔS) of equilibrium reaction (1) (Scheme 1) were then determined by linear regression (Figure 2). The enthalpy and entropy were calculated to be –64.8 kJ mol^{-1} and –262 J mol^{-1} K^{-1}, respectively. Compared with the cyclopentane solution of sBuLi in which the ΔH and ΔS are –29 kJ mol^{-1} and –117 J mol^{-1} K^{-1}, respectively,[5] the toluene solution of
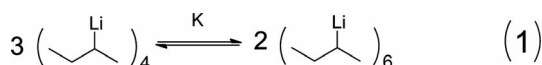
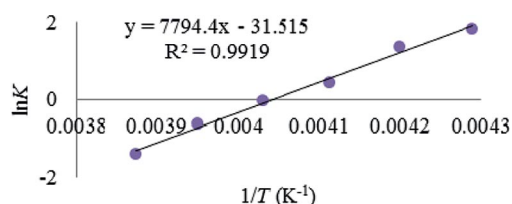Scheme 1. Equilibrium of the hexameric and tetrameric forms of sBuLi.

Figure 2. The van 't Hoff plot of reaction (1).

sBuLi favors the formation of hexamers when the temperature is below –27 °C and it favors the formation of tetramers when the temperature is above –27 °C.

There is evidence that butyllithium can react with adventitious dioxygen to form butoxide, which is known to form mixed aggregates with n-butyllithium.[6] Thus, it is very probable that the unknown peak at –0.97 ppm may belong to a mixed aggregate. To substantiate this prediction, we deliberately added pure dioxygen gas or sec-butyl alcohol into sBuLi samples. Upon the addition of dioxygen or sec-butyl alcohol, the intensity of the unknown peak increased simultaneously with that of the peak at δ = 3.44 ppm, which is the methine proton of sBuOLi (Figure 3).

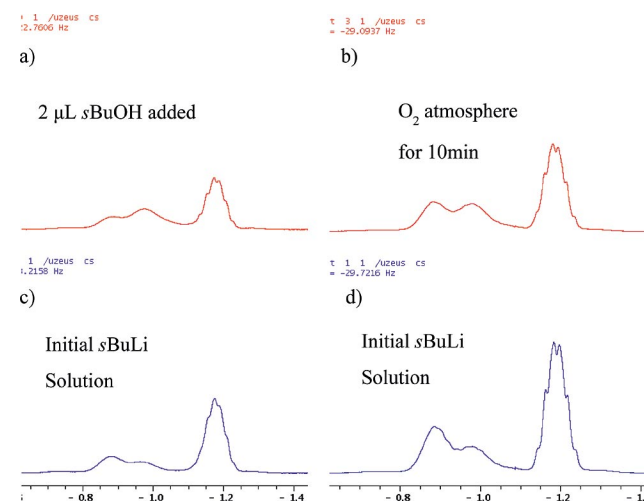Figure 3. The ^{1}H NMR (400 MHz) spectra of a 0.49 M solution of sBuLi in [D$_8$]toluene, showing the methine signals: (a) after the addition of 2 μL sBuOH; (b) after exposure to a dioxygen atmosphere for 10 min; (c,d) the initial sBuLi solution.

This observation confirms that the unknown peak at –0.97 ppm belongs to the methine proton of sBuLi in an sBuLi/sBuOLi mixed aggregate. The fact that the ratio of the integration of the methine peak of sBuOLi to sBuLi is about 1 to 5 leads to the conclusion that it is a 5:1 mixed hexamer. Thomas and co-workers reported that tBuLi can form 1:5 and 2:4 tBuLi/tBuOLi mixed hexamers.[11] Their interpretation was based solely on the assumption of hexameric aggregates. Subsequently, Henderson reported the presence of octamers in hydrocarbon solvents.[12]

In order to unambiguously establish the hexameric structure of the mixed aggregate, diffusion-ordered NMR spectroscopy (DOSY) and diffusion-coefficient–formula-weight (D-FW) correlation analyses were conducted to evaluate the formula weight of the mixed aggregate. Our group previously applied DOSY NMR spectroscopy with internal references for the determination of formula weights of reactive complexes by D-FW correlation analysis. The linear regression plot of the logarithms of diffusion coefficients determined by NMR spectroscopy against the known formula weights of the references is used to deduce the formula weight of the unknown complex from its diffusion characteristics.[13] In this proton DOSY experiment, benzene

(BEN, 78.11 g/mol), cyclooctene (COE, 110.2 g/mol), 1-tetradecene (TDE, 196.4 g/mol), and squalene (SQU, 410.7 g/mol) were added to the sample solution as our internal references.

After the addition of internal references into the [D$_8$]toluene solution of *s*BuLi, the signals of the methyl and methylene protons of *s*BuLi and *s*BuOLi at 1.0 to 2.5 ppm overlapped with the signals of the internal references; thus, distinct peaks of the methine protons were used for our D-FW
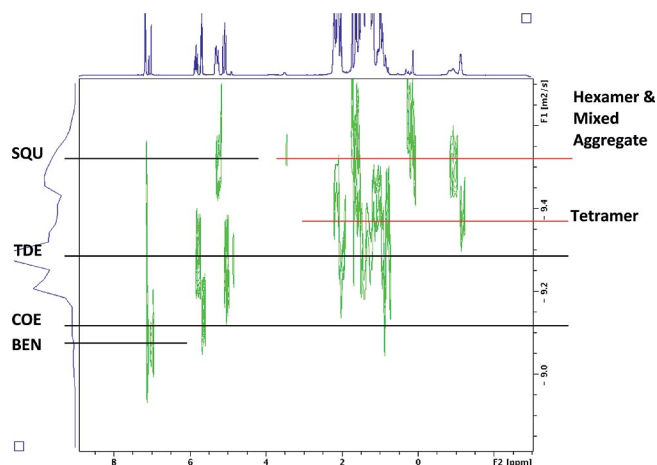
analysis. As shown in the DOSY spectrum (Figure 4), the methine peaks of *s*BuOLi and *s*BuLi have very similar diffusion coefficients.

The correlation between $\log FW$ and $\log D$ of the linear regression is very high ($r^2 > 0.99$), and the predicted formula weight for the resonance of tetrameric *s*BuLi (–1.16 ppm) is 255.7 g mol^{-1}, which is very close to the actual value, 256.2 g mol^{-1} (0.2% error) (Figure 5). The predicted formula weight for the resonance of hexameric *s*BuLi (–0.88 ppm) is 401.2 g mol^{-1} (4.4% error), and the predicted formula weight for the resonance of the mixed aggregate at –0.97 ppm is 401.9 g mol^{-1}, which is very close to the formula weight of the 1:5 *s*BuOLi/*s*BuLi (400.3 g mol^{-1}, 1.0% error) aggregate. The predicted formula weight for the resonance of the mixed aggregate at 3.6 ppm is found to be 426.0 g mol^{-1} (6.4% error). Given the estimated 10% error

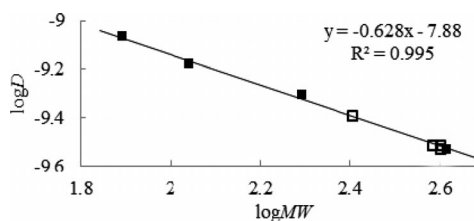Figure 4. ^{1}H DOSY spectrum of a solution of *s*BuLi in [D$_8$]toluene at –20 °C.

Figure 5. D-FW analysis of ^{1}H DOSY data. Internal references are shown as solid squares, and the complexes are shown as empty squares.
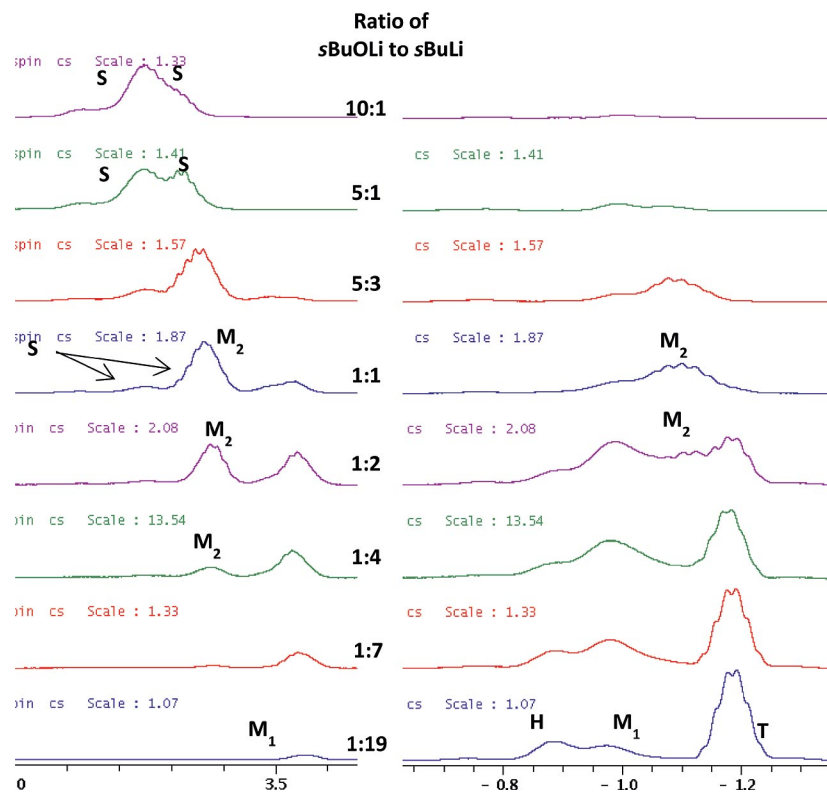
Figure 6. ^{1}H NMR spectra of the titration of a [D$_8$]toluene solution of 0.49 M *s*BuLi with *sec*-butyl alcohol at –20 °C. H represents the resonance of *s*BuLi in hexameric form; T represents the resonance *s*BuLi in tetrameric form; M$_1$ represents the resonances of *s*BuLi/*s*BuOLi mixed hexamer; M$_2$ represents the resonances of *s*BuLi/*s*BuOLi mixed octamer; S represents the resonances of *s*BuOLi in the form of pure aggregates.

in formula weight prediction by the DOSY technique,[13] we were unable to distinguish the 1:5 mixed hexamer (ROLi)(RLi)$_5$ from the 2:4 mixed hexamer (ROLi)$_2$(RLi)$_4$ by the predicted molecular weight solely. However, the integral ratio of the methine peak of sBuOLi to sBuLi is approximately 1 to 5 when there is less than 0.08 equiv. sBuOLi. This indicates that the 1:5 mixed hexamer should be the major species. The integral ratio cannot be determined when there is more than 0.08 equiv. sBuOLi in the solution, because a new mixed aggregate peak overlaps seriously with the sBuLi methine peaks of the other aggregates. We also note that the proportion of butoxide in the sBuOLi/sBuLi mixed hexamer (1:5) is significantly lower than that in the tBuOLi/tBuLi mixed hexamer (5:1 or 4:2) reported by Thomas,[11] because the decrease in steric hindrance of the butyl group allows a higher ratio of butyllithium in the complex.

When more than 0.1 equiv. of sBuOH was added to the sBuLi solution, a small peak emerged at δ = 3.63 ppm, and its intensity continued to increase when more sBuOH was added (Figure 6). Moreover, a methine peak of sBuLi at –1.06 ppm was observed to increase with the ascending sBuOLi peak. The result indicated that another type of sBuOLi/sBuLi mixed aggregate was formed. The fact that the new peak at δ = 3.63 ppm, which can only belong to the methine proton of sBuOLi, increases at the expense of the methine peak of sBuOLi of the mixed hexamer when the temperature decreases from –20 °C to –40 °C indicates that the new mixed aggregate should be larger than a hexamer (Figure 7).
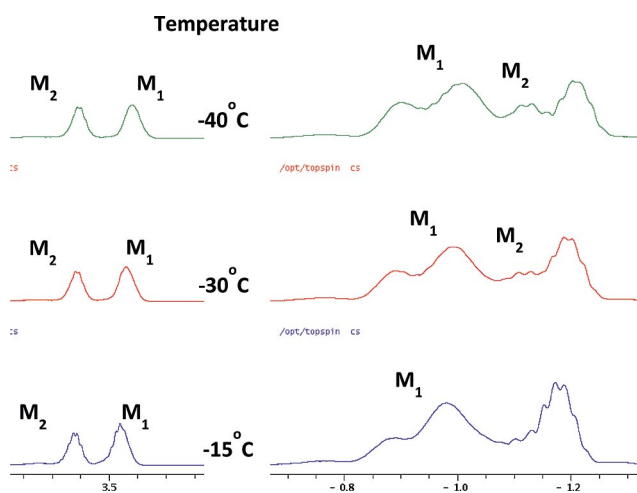

Figure 7. Variable-temperature ^{1}H NMR (400 MHz) spectra of 2:7 sBuOLi/sBuLi in [D$_8$]toluene solution. M$_1$ represents the resonances of sBuLi/sBuOLi mixed hexamer; M$_2$ represents the resonances of sBuLi/sBuOLi mixed octamer.

To establish the aggregation state of the new mixed aggregate in solution, we applied the same ^{1}H DOSY and D-FW analysis to the sBuOLi/sBuLi [D$_8$]toluene solution. Two DOSY experiments were conducted with different sBuOLi to sBuLi ratios, because the methine peak of sBuLi of the new aggregate overlapped with the methine peaks of other sBuLi aggregates when the methine peak of sBuOLi

of the new aggregate was distinct. However, the latter overlapped seriously with the methine peak of sBuOLi of a pure sBuOLi aggregate when the methine peak of sBuLi of the new aggregate was distinct (Figure 6). The resulting DOSY spectra are shown in Figure 8.
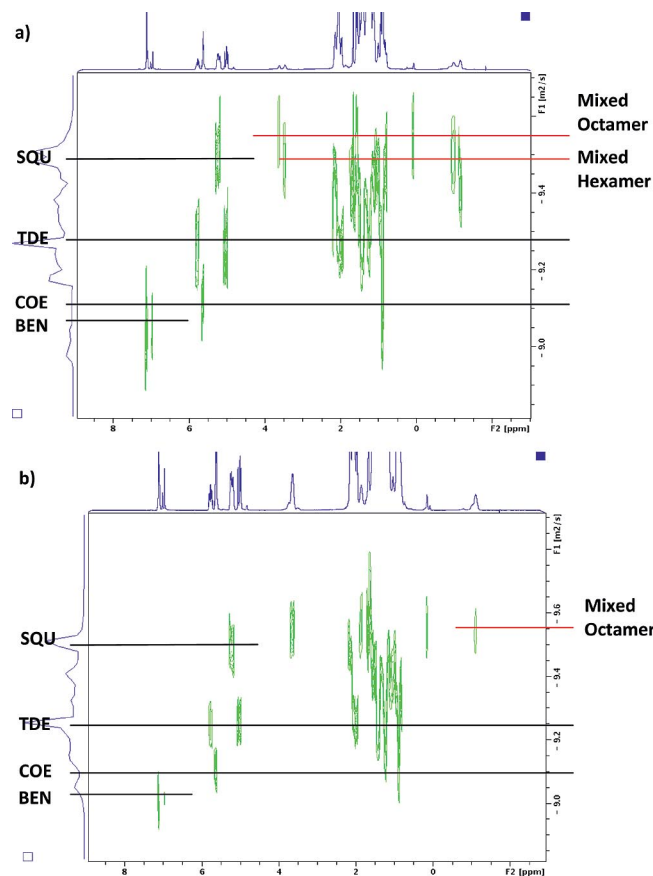

Figure 8. ^{1}H DOSY of sBuLi/sBuOLi [D$_8$]toluene solution at –20 °C. The ratio of sBuOLi to sBuLi is 2:7 in (a) and 5:3 in (b).

The predicted formula weight based on the resonance of the methine proton of sBuOLi of the new mixed aggregate was deduced to be 561.4 g mol^{-1} by D-FW analysis, while the predicted formula weight based on the resonance of the methine proton of sBuLi of the new mixed aggregate was 536.3 g mol^{-1}. The result indicates an aggregate larger than hexamer because the (sBuOLi)$_5$(sBuLi) mixed hexamer has a formula weight of 464.3 g mol^{-1}, which is significantly smaller than the experimental results. Consequently, an octameric structure is proposed for the structure of the new mixed aggregate. However, it is not obvious whether the mixed aggregate is a 2:6 sBuOLi/sBuLi mixed octamer, which has a formula weight of 544.5 g mol^{-1}, or a 4:4 mixed octamer (576.4 g mol^{-1}) because our D-FW DOSY technique has an intrinsic 10% error. The integrations of the methine peaks in the ^{1}H NMR spectrum cannot be compared quantitatively as noted above. We believe that this new aggregate is more likely to be a 4:4 mixed complex because a 2:6 mixed aggregate should have a higher-intensity methine peak for sBuLi and the mixed octamer may possibly adopt the same pattern as the crystal structure of

the (nBuLi)$_4$(tBuOLi)$_4$ octamer obtained by Boche;[8b] however, no definitive evidence is present. Nevertheless, it is evident that an sBuOLi/sBuLi mixed octamer is present when the amount of sBuOLi in the toluene solution of sBuLi is between 0.08 and 2 equiv. The characterization of an octamer in solution by conventional ^{6}Li–^{13}C coupling is exceptionally difficult, because the outermost peaks of the multiplets can hardly be distinguished[11] and the racemic nature of sBuLi may further complicate the spectra.

Conclusions

In summary, sBuLi exists mainly as a mixture of tetramers and hexamers in hydrocarbon solvents. However, the presence of a small amount of sBuOLi in both commercially available and laboratory-synthesized sBuLi solution due to the reaction of sBuLi with adventitious dioxygen definitely leads to the formation of a 1:5 sBuOLi/sBuLi mixed hexamer that is difficult to avoid. A sBuOLi/sBuLi mixed octamer will emerge when the proportion of sBuOLi to sBuLi increases. The effectiveness of DOSY NMR spectroscopy with D-FW correlation analyses over the conventional ^{6}Li–^{13}C coupling experiments in revealing the aggregation states of the sBuOLi/sBuLi complexes is clearly useful in this analysis.

Experimental Section

General: The values of the concentrations were expressed in monomer units unless otherwise specified. The sec-butyl alcohol used in the NMR spectroscopy experiments was distilled from calcium hydride under nitrogen gas and stored over 4 Å molecular sieves prior to usage. The 2-chlorobutane used in the synthesis of sec-butyllithium was dried with anhydrous calcium chloride under nitrogen gas and stored over 4 Å molecular sieves prior to usage.

Procedures for NMR Spectroscopy Experiments

Samples for NMR spectroscopic analysis were prepared in tubes sealed with rubber septa, caps, and Parafilm. NMR tubes were evacuated, flame-dried and filled with argon before use. ^{1}H NMR chemical shifts are referenced to [D$_8$]toluene at δ = 7.09 ppm and ^{13}C NMR chemical shifts are referenced to [D$_8$]toluene at δ = 137.86 ppm. All NMR spectra were acquired with a Bruker DRX400 spectrometer equipped with an Accustar z-axis gradient amplifier and an ATMA BBO probe with a z-axis gradient coil. The maximum gradient strength was 0.214 T/m. ^{1}H DOSY experiments were performed by using the standard Bruker dstebpgp3s program, employing a double stimulated echo sequence, bipolar gradient pulses for diffusion, and 3 spoil gradients. The diffusion time was 200 ms, and the rectangular gradient pulse duration was 800 µs. Gradient recovery delays were 200 µs. Individual rows of the quasi-2-D diffusion databases were phased and baseline-corrected. Actual diffusion coefficients used for D-FW analysis were obtained in the Bruker Topspin software using the $T$1/$T$2 analysis module. Lorentzian deconvolution was performed on the overlapping methine protons by using Bruker's Topspin 3.2 software.

The solution of sec-butyllithium (sBuLi) in [D$_8$]toluene was prepared either from commercially available sec-butyllithium cyclohexane solution (Aldrich, 1.4 M) or from laboratory-synthesized sec-

butyllithium cyclohexane solution (1.06 M). The samples were prepared by two methods:

Method 1: sBuLi cyclohexane solution (about 200 µL) was added by syringe to an NMR tube (A PTFE filter purchased from VWR International was required for preparing the sample from commercial sBuLi solution because the solution was milky with some solid material in it even though it was brand new.) [D$_8$]Toluene was added by syringe to bring the total volume up to 600 µL.

Method 2: After the addition of sBuLi cyclohexane solution (200 µL) to an NMR tube, the NMR tube was evacuated for 30 min at 0 °C in order to remove the cyclohexane. After filling the tube with argon, [D$_8$]toluene was added by syringe to bring the total volume up to 600 or 650 µL.

Method 2 was implemented most of the time, because the spectrum obtained was cleaner after the elimination of cyclohexane.

For the variable-temperature experiments for determining the equilibrium constants and thermodynamic data, 1-dodecene (about 20 mg) was added by syringe to the solution in order to accurately measure the concentration of sBuLi in [D$_8$]toluene solution. The exact mass of 1-dodecene added was accurately measured.

The concentration of sBuLi was about 0.4 M. The internal references (in a ratio of 1:3:3:1 for BEN, COE, TDE, and SQU, respectively) were titrated into the NMR tube and monitored by ^{1}H NMR spectroscopy. The titration was stopped when the peak intensity of benzene was about half that of sBuLi.

Synthesis of sBuLi: Finely cut Li metal (about 1.00 g, 144 mmol) was placed into a flame-dried flask with a condenser attached that was flushed with argon. The condenser was fitted with a serum septum and sealed with Parafilm. The metal was washed with dry pentane by adding pentane (10 mL) to the flask by syringe. The flask was then placed in an ultrasound bath for 15 min. Pentane was then removed by syringe. This was repeated until the washings were clear, and no white solid was suspended in the wash (3 times). Dry cyclohexane (10 mL) was added to the flask, and the flask was placed in an oil bath at 50 °C with stirring. A drop of methyl $tert$-butyl ether was added to 2-chlorobutane (5.60 g , 60.5 mmol), and the resulting solution was added by syringe to the hot mixture of lithium metal and cyclohexane over 2.5 h by using a syringe pump. After the addition of 2-chlorobutane, the mixture was stirred overnight at room temperature, after which a purple slurry was obtained. The suspension was transferred by syringe to a clean, flame-dried vial flushed with argon and fitted with a serum septum. The vial was centrifuged until the solid was separated. The supernatant was transferred to a second identical vial and centrifuged again. The supernatant was transferred to a third identical vial. This sBuLi solution in cyclohexane was titrated using 2,2-diphenylacetic acid in tetrahydrofuran and found to be 1.06 M. It is worth noting that the light yellow transparent sBuLi solution turned milky after being kept in a –20 °C freezer for about 7 to 14 days. Samples to be analyzed by NMR spectroscopy were prepared from the transparent sBuLi solution.

Supporting Information (see footnote on the first page of this article): NMR spectra, D-FW analyses.

Acknowledgments

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