NMR spectroscopy of organolithium compounds, part XXXIV: Cyclopropyllithium and lithium bromide (1:1) in diethylether/tetrahydrofuran—Identification of a fluxional mixed tetramer

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Abstract
Cyclopropyllithium, \( \text{C}_3\text{H}_5\text{Li} \) (1), was studied in the presence of one equivalent lithium bromide (LiBr) in diethylether (DEE)/tetrahydrofuran (THF) mixtures and in THF as solvents. Increasing the THF concentration in DEE/THF leads in the \( ^{6}\text{Li} \) NMR spectrum to a main signal \( \text{S}_1 \) at \( \delta 0.85 \) (rel. to ext. LiBr/THF) and a second resonance \( \text{S}_2 \) at \( \delta 0.26 \) aside from a minor component at \( \delta 0.07 \). In pure THF, the ratio of these signals was 66:28:6. \( ^{6}\text{Li} \) and \( ^{13}\text{C} \) NMR allowed to identify the main signal as belonging to a mixed dimer, \( 1\cdot\text{LiBr} \), and the signal at 0.26 ppm to a fluxional mixed tetramer, \( 1\cdot2\cdot(\text{LiBr})_2 \). J\((^{13}\text{C},^{6}\text{Li}) \) coupling constants of 11.0 and 9.8 Hz were measured at 168 K for \( \text{S}_1 \) and \( \text{S}_2 \), respectively, and chemical exchange between both signals was detected by 2D \( ^{6}\text{Li},^{6}\text{Li} \) exchange spectroscopy and analyzed by temperature-dependent 1D \( ^{6}\text{Li} \) lineshape calculations. These yielded the equilibrium constants \( K_{\text{eq}} \) for the chemical exchange \( \text{Li}_4(\text{C}_3\text{H}_5)_2\text{Br}_2 \leftrightarrow 2 \text{Li}_2\text{C}_3\text{H}_5\text{Br} \). Their temperature dependence leads to van't Hoff parameters of \( \Delta H^\circ = 4.6 \text{ kJ/mol}, \Delta S^\circ = 41.4 \text{ J/mol K}, \) and \( \Delta G^\circ_{298} = -7.8 \text{ kJ/mol} \). From the rate constants \( k \), Eyring parameters of \( \Delta H^* = 42.0 \text{ kJ/mol}, \Delta S^* = 33.0 \text{ J/mol K}, \) and \( \Delta G^*_{298} = 32.2 \text{ kJ/mol} \) were calculated for the forward reaction \( \text{Li}_4(\text{C}_3\text{H}_5)_2\text{Br}_2 \rightarrow 2 \text{Li}_2\text{C}_3\text{H}_5\text{Br} \) and \( \Delta H^* = 37.5 \text{ kJ/mol}, \) \( \Delta S^* = -8.4 \text{ J/mol K}, \) and \( \Delta G^*_{238} = 40.0 \text{ kJ/mol} \) for the reverse reaction \( 2\text{Li}_2\text{C}_3\text{H}_5\text{Br} \rightarrow \text{Li}_4(\text{C}_3\text{H}_5)_2\text{Br}_2 \).

KEYWORDS
Li exchange dynamic NMR, NMR lithium-6 carbon-13 cyclopropyllithium aggregate

1 | INTRODUCTION
The formation of different aggregates like monomers, dimers, tetramers, and larger species in ethereal and hydrocarbon solvents is a well-known feature of organolithium compounds.\(^{[1]} \) The investigation of their aggregate formation is thus of continued interest and might help to better understand the reactivity of these species.\(^{[1d, 2]} \) The method of choice in this field is in most cases high-resolution NMR spectroscopy using nuclei like \(^1\text{H}, ^{6}\text{Li}, ^7\text{Li}, ^{13}\text{C}, \) and others.\(^{[16, i, j]} \)
We recently presented results for the aggregation behavior of cyclopropyllithium (C₃H₅Li, 1, Scheme 1) and several derivatives of 1 either salt-free or in the presence of lithium bromide (LiBr) in the solvents diethylether (DEE), tetrahydrofuran (THF), and 1:1 mixtures of both.[3, 4a] For salt-free 1, we found dimers in DEE and dimers as well as fluxional tetramers in THF. In the presence of one equivalent LiBr, on the other hand, evidence for a mixed dimer (2, Scheme 1) and a static mixed tetramer (3, Scheme 1) in a ratio of ca. 2:1 was found in the solvent DEE.[4] In the present communication, we discuss the results for 1/LiBr (1:1) in DEE/THF mixtures with increasing THF content up to pure THF, where a continued change in the ⁶Li NMR spectrum was observed.

2 | RESULTS

If a solution of 1 in the presence of 1-mol equivalent LiBr in DEE is diluted with THF, the original low temperature ⁶Li NMR spectrum in DEE[4a] changes dramatically (Figure 1 and Table 1): the mixed dimer signal is shifted to a higher frequency, and the signals of the assumed static tetramer have disappeared. Already with 20% THF, a dominating singlet (S1) is observed at 0.85 ppm accompanied by a small additional signal (S2) at 0.26 ppm that indicates the presence of a minor component. Increasing the THF content, the intensity of the small signal S2, IS2, increases until it reaches finally to 28% of IS1 in pure THF. As shown later, S1 and S2 are in dynamic equilibrium. Except for a further small signal at 0.07—6% of IS1—that appears close to the external reference at 0.0 ppm (Figure 1e), no other ⁶Li signals are present. Five samples (I–V in Table 1) that differed in solvent and/or concentration were used to study the observed spectral changes in more detail. The results are summarized in Table 1.

The ¹³C{¹H} NMR spectrum of sample II showed at 163 K, a broadened signal for C-1 at −8.61 ppm, and a sharp singlet at 2.76 ppm (rel. to tetramethylsilane [TMS]) for the C-2 and C-3 resonances (Figure 2a). These data are close to those found for salt-free 1 measured in DEE or THF.[3] The C-1 signal could be resolved in sample I into a quintuplet with a one-bond ¹³C,⁶Li coupling constant, ¹J(¹³C,⁶Li), of 10.94 ± 0.18 Hz, where the line intensities matched the theoretical numbers 1:2:3:2:1 (Figure 2b). For sample V, we found ¹J(¹³C,⁶Li) = 10.87 ± 0.05 Hz.
Similar one-bond $^{13}$C-$^6$Li couplings were measured in DEE/THF (1:1) for the mixed dimers of 2,3-dimethyl-$^1$LiBr (10.1 Hz) and 2,2,3,3-tetramethyl-$^1$LiBr (10.8 Hz).

It is well-known that the aggregate structure of organolithium compounds is reflected in the magnitude of the scalar one-bond $^{13}$C-$^6$Li spin,spin coupling. Measurements for various aggregates lead to the empirical equation (Equation 1):\[1\]

$$^{1}J(13C,6Li)_{\text{obs}} \approx \frac{17 \pm 2}{n}$$

that holds for the $^{13}$C NMR signal of $^{13}$C-$^6$Li spin pairs with $n$ as the aggregation number of the individual cluster. In our case, the main species with a coupling of ca. 11.0 Hz can thus be characterized as a mixed dimer, 1-\text{LiBr}, of 1 and LiBr (2, Scheme 1). The couplings observed for samples I and V are slightly larger than those expected from Equation (1) that yields ca. 8.5 ± 2 Hz for a dimer, but this relation was derived from results for saltfree situations and does not consider a possible influence of the bromide anion on the coupling.\[5c, 7\]

Measurements at lower temperatures were prevented by sample precipitation. In the $^{13}$C{\text{H}} spectrum, on the other hand, two C-1 resonances were now detected: one for the species that gave rise to the $^6$Li signal $S_1$ of the mixed dimer at $\delta(13C) = -8.59$ ppm and a slightly smaller

**TABLE 1** NMR data for 1/lithium bromide (1: 1) at 168 K

| Sample | DEE/THF (%) | Mol/l | $\delta(^6$Li)/ppm, (rel. Intensity) | $\delta(13$C)/ppm, $^{1}J(13$C-1,$^6$Li)/Hz |
|--------|-------------|-------|------------------------------------|-----------------------------------|
| I      | 80: 20      | 0.2   | S1: 0.88 (83) S2: 0.32 (17)        | S1: $^{1}J(13$C-1,$^6$Li) = 10.94 ± 0.18$^b$ |
| II     | 70: 30      | 0.5   | 0.89 (78) S3: 0.33 (22)            | S1: $\delta(C-1) = -8.61$ |
| III    | 60: 40      | 1.0   | S1: 0.82 (74) S2: 0.27 (26)        | S1: $^{1}J(13$C-1,$^6$Li) = 11.0$^c$ |
| IV     | 70: 30      | 3.3   | S1: 0.85 (70) S2: 0.26 (30)        | S1: $^{1}J(13$C-1,$^6$Li) = 11.0$^c$ |
| V      | 0: 100      | 1.6   | S1: $^{1}J(13$C-1,$^6$Li) = 10.87 ± 0.05$^b$ |

Abbreviations: DEE, diethylether; THF, tetrahydrofuran.

$^a$Solvent ratio.

$^b$Splitting of the quintuplet.

$^c$From $^{13}$C satellites in the $^6$Li spectrum.

$^d$Not resolved.

**FIGURE 2** 100 MHz $^{13}$C{\text{H}} spectra of 1 in the presence of one equivalent lithium bromide: (a) sample II (0.5 M) with mixed solvent diethylether (DEE)/tetrahydrofuran (THF) (7:3), (b) enlarged quintuplet of C-1 for sample I with relative signal intensities of 0.7:2.0:3.2:2.3:1.0, and (c) sample IV (3.3 M) with mixed solvent DEE/THF (7:3); x = cyclopropane
one at −10.47 ppm that could now be assigned to the species that gave rise to the $^6$Li signal at δ0.26 (Figure 2c). Furthermore, in the region of the methylene carbons C-2,3, now at 3.37 ppm, smaller signals appeared additionally at 3.14, 2.86, and 2.42 ppm.

For both C-1 signals of sample IV (Figure 2c), fine structure due to $^{13}$C,$^6$Li spin,spin coupling was not resolved (Figure 3a). On the other hand, the half-widths of these $^1$H-decoupled signals differed with 26.8 and 44.7 Hz for S1 and S2, respectively. A spectrum with both $^1$H and $^6$Li decoupled signals (Figure 3b) shows, as expected, further line sharpening (half-widths now 22.4 and 17.9 Hz), but again no line splitting due to coupling. However, the half-widths reduction of 4.4 and 26.8 Hz differs considerably and indicates a higher multiplicity for S2 due to $^{13}$C,$^6$Li coupling than that for S1. Because we found a quintuplet for S1 (Figure 2b), a septuplet (static tetramer with three $^6$Li neighbors) or a nine-fold multiplet (fluxional tetramer with four $^6$Li neighbors) for S2 would explain this difference. The latter experiment revealed also a further small signal at −10.3 ppm—again without line splitting due to coupling—that indicates the presence of an additional minor cluster.

In order to identify the second aggregate by its one-bond $^{13}$C,$^6$Li coupling constant, we tried to measure these data from the $^{13}$C satellites in the $^6$Li spectra. Because of the low natural abundance of $^{13}$C (0.05%), only few clusters with $^{13}$C,$^6$Li coupling exist, and for these, the $^6$Li spectra show $^{13}$C satellites as low intensity doublets close to the baseline (Figure 4). These doublets are the X-part of an A$_n$X spin system, where A stands for $^6$Li and n for the number of lithium cations involved. The coupling in these spin systems is usually measured at the X-part, where the well-known $^{13}$C multiplets caused by the $^6$Li spin-1 nuclei can be observed.[1]:5 If measured at the A-part, because of the low natural abundance of $^{13}$C, only doublets are found.

Two samples, one with a solvent mixture DEE/THF (6:4) and a concentration of 1.0 M (sample III) and another one of 1.6 M in pure THF (sample V), were used with two different spinning rates to avoid mistakes with spinning sidebands (Figure 4). For the $^6$Li signal S1 at δ0.85, we found for both samples satellites with a splitting of 11.0 Hz, which confirmed, within experimental error, the results from the $^1J(^{13}$C,$^6$Li) data of the mixed dimer structure 2 (Scheme 1) derived for S1 from the $^{13}$C spectra of samples I and V (10.94 and 10.87 Hz, respectively).

The second $^6$Li signal S2 at δ0.26 yielded couplings of 9.7 and 9.9 Hz, respectively, for both samples. Using again the Equation (1), which holds for $^{13}$C as well as for $^6$Li measurements, the magnitude of this coupling would fit the expectation of a mixed dimer, but this structure was already proven for the cluster with the larger $^6$Li signal S1. The presence of a static mixed tetramer (3, Scheme 1) can be excluded because this should lead to two $^6$Li signals, one

![Figure 3](image1.png)

**Figure 3** $^{13}$C NMR signals of sample IV (Figure 2c) (a) with $^1$H decoupling and (b) with $^1$H and $^6$Li decoupling

![Figure 4](image2.png)

**Figure 4** Enlarged 58.88 MHz $^6$Li NMR spectra of samples III (a, spinning rate: 12 ± 2 r/s) and V (b, spinning rate: 20 ± 2 r/s) with $^{13}$C satellites (x) and $^1J(^{13}$C,$^6$Li) data (Hz) for S1 and S2; x = signals of rotational side bands and/or unknown impurities
for Li₃ and one for Li₄. Such a situation was found for 1-LiBr in DEE. However, in THF, 1 yielded a dimer and a fluxional tetramer, and it is thus reasonable to assign the structure of a fluxional mixed tetramer to the species of signal S2 despite the relatively large J(13C,²Li) value of 9.8 Hz. This splitting, where a ¹³C nucleus is coupled to four lithium cations, is more than twice the value expected on the basis of Equation (1) and also much larger than the 4.7 Hz observed for the fluxional tetramer of salt-free 1 in THF. The reason for this increase is not clear, but the presence of two Br⁻ ligands might be responsible. The mixed dimer coupling of 10.9 Hz is already 2.4 Hz or 28% larger than that of the 8.5 Hz coupling expected following Equation (1), which is based exclusively on aggregates with carbon–lithium bonds. In addition, the large half-width of S2 and the dramatic half-width reduction upon ⁶Li decoupling discussed above support a larger coupling. Furthermore, it is known that THF favours higher aggregation. For example, the tetramer/dimer ratio recorded by Seebach et al. for n-butyllithium in THF is ca. 2:1, while in DEE, only the dimer was found. Thus, the increase of signal S2 with increasing THF concentration also supports the fluxional mixed tetramer structure.

3 | EXCHANGE STUDIES BY DYNAMIC NMR

Further support for the existence of a fluxional mixed tetramer comes from chemical exchange between the ⁶Li signals S1 and S2. Two-dimensional ⁶Li,⁶Li exchange spectra revealed this dynamic process (Figure 5), and low temperature ¹D ⁶Li NMR spectra showed line broadening and coalescence for S1 and S2 at ca. 192 K (Figure 6). The smaller low-frequency signal at 80.07 shows also broadening, but its behavior at higher temperatures is not clear. From the simulated spectra shown in Figure 6, the temperature-dependent data for the relative intensity of the two signals S1 and S2, the concentration of the two species, and the equilibrium constants Kₑq (Table 3, exp. part) were derived. They yielded the van’t Hoff diagram shown in Figure 7 and the thermodynamic parameters ΔH° = 4.6 kJ/mol, ΔS° = 41.4 J/mol K, and ΔG° = −7.8 kJ/mol. The Kₑq values measured by standard spectral integration in the slow exchange limit are in fair agreement with the data from the spectral simulation (Table 3). The positive entropy change indicates the stronger binding of the species Li⁻, C₅H₅⁻, and Br⁻ in the tetramer, in accord also with its higher free energy. From the line-shape simulation, the rate constants kₐ and kₐ (Table 2) were available for the calculation of the Eyring parameters. For the forward reaction tetramer → dimer (kₐ), we found ΔH° = 42.0 kJ/mol, ΔS° = 33.0 J/mol K, and ΔG° = 32.2 kJ/mol, for the reverse reaction dimer → tetramer (kₐ), ΔH° = 37.5 kJ/mol, ΔS° = −8.43 J/mol K, and ΔG° = 40.0 kJ/mol. All data are collected with their error limits in Table 3.

**FIGURE 5** 58.88 MHz ⁶Li,⁶Li exchange spectroscopy spectrum of sample I at 168 K; mixing time 1 s

**FIGURE 6** Experimental (left) and calculated (right) temperature-dependent 58.88 MHz ⁶Li spectra of sample V; lowering the temperature decreases the dimer concentration
Our results support to the best of our knowledge for the first time a fluxional mixed tetramer as an organolithium cluster in chemical exchange with mixed dimers. Homoaggregate formation of 1 must be considered; however, it would require two additional $^6$Li signals, one for 1$_2$ (5) and one for free LiBr. Only the small 6% signal at δ0.07 ppm could be associated with free LiBr while a signal for 5 is missing or covered by signals S1 or S2. In any case, homo-aggregate formation is thus of minor importance, the cleavage of the tetramer [Scheme 2, see diagram b)] proceeds only in a vertical way and a horizontal separation into two LiBr molecules, and a homo-dimer Li$_2$(C$_3$H$_5$)$_2$ is not observed. If this takes place, it could react immediately to form two mixed dimers, and the short lifetime would prevent its detection.

The limited number of $^6$Li NMR signals also excludes a tetramer structure composed of a homodimer and a heterodimer (4, Scheme 1), which is the dominating cluster with two $^6$Li signals in the ratio 1:3 for LiCH$_3$/LiBr$^{[11]}$ (4, R = CH$_3$) and LiC$_3$H$_9$/LiBr (4, R = C$_3$H$_9$) 1:1 mixtures.$^{[12]}$ While the mixed dimer Li$_2$C$_3$H$_5$Br (2) could be proven by $^6$Li and $^{13}$C NMR including $^{13}$C-$^6$Li spin-spin coupling, the proposal of a fluxional mixed tetramer formed by association of two mixed dimers is based on $^{13}$C-$^6$Li coupling measured from the $^{13}$C satellites in the $^6$Li spectrum and the large $^{13}$C line width of S2. The correctness of the $^1$$J$(13C,$^6$Li) value of 9.8 Hz as the average of the two measurements is supported by the 11.0 Hz splitting found in both samples for the mixed dimer signal S1, which was measured independently also in the $^{13}$C-1 multiplet (see Figures 2 and 4).

Of interest, there are also different $^6$Li chemical shifts in the solvent THF (sample V) if compared with those in DEE (Figure 1). In THF, the mixed dimer signal is deshielded by 0.15 ppm, and the fluxional mixed dimer signal is shielded by 0.44 ppm with respect to the average of the two $^6$Li signals of the static tetramer.

We can compare the present equilibrium with that found by Seebach et al.$^{[5c, 7]}$ for salt-free n-butyllithium (LiC$_4$H$_9$) in THF between a static tetramer, coordinated with four THF molecules, and two homodimers, each coordinated again with four THF molecules:

### Table 2

| T/K  | $K_{eq}^a$ | $k_a$ | $k_b$ | $K_{eq}^b$ |
|------|------------|-------|-------|------------|
| 163.7 | 4.65       | 7.1   | 1.5   | 5.3        |
| 166.1 | 5.12       | 12.2  | 2.4   | 5.9        |
| 169.8 | 5.74       | 17.7  | 3.1   | 6.3        |
| 172.4 | 6.16       | 29.2  | 4.7   | 6.3        |
| 175.1 | 6.42       | 59.1  | 9.2   | 6.3        |
| 178.9 | 6.76       | 125.2 | 18.5  | 6.7        |
| 192.5 | 7.25       | 242.6 | 33.5  | 8.3        |
| 190.1 | 8.16       | 1077.4| 132.01| —          |
| 196.5 | 9.03       | 1672.4| 185.1 | —          |
| 202.8 | 9.68       | 4271.8| 441.3 | —          |
| 209.2 | 10.54      | 6787.2| 644.1 | —          |
| 215.5 | 11.36      | 12358.9| 1088.0| —          |
| 226.8 | 12.03      | 52100.6| 4332.6| —          |

Notes: Temperature (K), equilibrium constant $K_{eq}$ (l/mol), and rate constants $k_a$ (s$^{-1}$) for the reaction Li$_4$(C$_3$H$_5$)$_2$Br$_2$ $\rightarrow$ 2 Li$_2$C$_3$H$_5$Br and $k_b$ (s$^{-1}$) for the reverse reaction 2 Li$_2$C$_3$H$_5$Br $\rightarrow$ Li$_4$(C$_3$H$_5$)$_2$Br$_2$; $K_{eq}$ = [dimer]$^2$/[tetramer] = $k_a/k_b$.

$^a$From spectral simulation.

$^b$From spectral integration.

### Table 3

| van’t Hoff | Eyering, forward reaction | Eyering, reverse reaction |
|------------|----------------------------|--------------------------|
| $\Delta H^\circ$ [kJ/Mol] = 4.6 ± 2.5 | $\Delta H^\circ$ [kJ/Mol] = 42.0 ± 2.3 | $\Delta H^\circ$ [kJ/Mol] = 37.5 ± 2.3 |
| $\Delta S^\circ$ [J/Mol K] = 41.4 ± 8.2 | $\Delta S^\circ$ [J/Mol K] = 33.0 ± 6.3 | $\Delta S^\circ$ [J/Mol K] = −8.4 ± 6.3 |
| $\Delta G^\circ_{298}$ [kJ/Mol] = −7.8 ± 0.9 | $\Delta G^\circ_{298}$ [kJ/Mol] = 32.2 ± 1.1 | $\Delta G^\circ_{298}$ [kJ/Mol] = 40.0 ± 1.1 |

$^r = 0.996$

4 | DISCUSSION

Our results support to the best of our knowledge for the first time a fluxional mixed tetramer as an organolithium cluster in chemical exchange with mixed dimers. Homoaggregate formation of 1 must be considered; however, it would require two additional $^6$Li signals, one for 1$_2$ (5) and one for free LiBr. Only the small 6% signal at δ0.07 ppm could be associated with free LiBr while a signal for 5 is missing or covered by signals S1 or S2. In any case, homo-aggregate formation is thus of minor importance, the cleavage of the tetramer [Scheme 2, see
Li₄(C₄H₉)₄(THF)₄ + 4 THF ⇌ 2 [Li₂(C₄H₉)₂(THF)]₂ (2). Here, the negative reaction entropy (−78.66 J/mol K) required the assumption of four THF molecules in order to satisfy the tetra-coordination of THF in the two homodimers.

The positive reaction entropy found for the equilibrium (1-LiBr)₂ ⇌ 2(1-LiBr) (3) is in accord with a tetramer structure that yields two mixed dimers, where each Li⁺ cation is coordinated to only one THF molecule. This may be seen as a consequence of the large bromine anion that prevents a second coordination with a solvent molecule. The different sign of ΔS for equilibria (2) and (3) is also apparent from the temperature gradient of dimer formation, where lower temperature yields an increase of LiC₄H₉ homodimers, (n-C₄H₉)₂Li₂, while in our case, the formation of heterodimers 1-LiBr decreases.

We believe that the Eyring parameters support a transition state for (1-LiBr)₂ ⇌ 2(1-LiBr), where two heterodimer fragments of the tetramer before the complete separation are still weakly coordinated in the solvent cage because the entropy of activation, ΔS*, is smaller than the reaction entropy, ΔS (33.00 vs 41.43 J/mol K) (Table 3 and Scheme 2). As a consequence, the entropy of activation for the reverse reaction 2(1-LiBr) ⇌ (1-LiBr)₂ is negative because degrees of freedom are lost as two dimers coordinate for tetramer formation. The Eyring free activation barriers of ΔG* = 32.2 and 40.0 kJ/mol for the forward and reverse reactions, respectively, are in the order of barriers found for homodimer-heterodimer exchange via a mixed tetramer in mixtures of n-BuLi and phenyllithium (ΔG* ≈ 50 kJ/mol) and exchange barriers between homo-tetramers and homodimers like (MeLi)₄ ⇌ 2(MeLi)₂ in DEE (ΔG* = 48 kJ/mol) and (n-BuLi)₄ ⇌ 2(n-BuLi)₂ in THF (ΔG* = 48 and 46.9 kJ/mol, calculated from the reported activation parameters) and the dimer-tetramer exchange system of vinylithium (ΔG* = 50.4 kJ/mol). Our data of the dynamic process thus support the conclusion given above that was derived from the NMR parameters at 168 K: the hitherto unexplained signal S2 found for 1/LiBr (1:1) in DEE/THF and in THF is due to a fluxional mixed tetramer (1-LiBr)₂ in equilibrium with two mixed dimers 1-LiBr. The static mixed tetramer (1-LiBr)₂ found in the solid by X-ray crystallography and at 163 K in DEE is thus fluxional in the presence of THF.

5 | EXPERIMENTAL

5.1 | Synthesis and sample preparation

As described, 1 was prepared under argon from cyclopropylbromide and an excess of lithium-6 chips in DEE. After crystallisation, DEE was replaced by DEE/THF mixtures or by pure THF. After filtration from the metal, the solution was transferred into an NMR tube that was degassed at −90°C and sealed. Deuterated solvents [D₁₀]DEE and [D₈]THF, carefully dried, were used throughout. The ¹H NMR data of 1/LiBr in the fast-exchange region at 231 K (δ₁: −2.5, δsyn: −0.1, δanti: 0.4, 3J₁,.syn: 8.4 Hz, 3J₁,anti: 11.2 Hz) agree with those from the literature.

5.2 | NMR spectra

A Bruker Analytische Meßtechnik NMR spectrometer AMX 400 together with the standard Bruker software was used to record one- and two-dimensional NMR spectra at 400.13 MHz (¹H), 100.61 MHz (¹³C), and 58.88 MHz (⁶Li). All ¹³C spectra were measured with proton decoupling. Low temperature spectra were controlled with the Bruker low-temperature unit, which was calibrated with the methanol thermometer. Solvent signals, which were referenced to TMS, served as internal standards for ¹H and ¹³C, while an external reference of LiBr (0.1 or 0.2 M in THF) was
used for $^6{\text{Li}}$. The 90° pulse widths were 27 μs ($^1{\text{H}}$) and 67 μs ($^6{\text{Li}}$). Line-shape calculations were performed with the program LINESH using a known algorithm.\(^{[18]}\) A four-channel probehead with two coils of two frequencies each, $^{13}{\text{C}}/^2{\text{H}}$ and $^{19}{\text{F}}/^1{\text{H}}$, were used for simultaneous $^{13}{\text{C}}$, $^2{\text{H}}$, $^{19}{\text{F}}$, and $^1{\text{H}}$ decoupling at 100.61 and 58.6 MHz, respectively. In this case, the $^{19}{\text{F}}$ resonance of dibromotetrafluoroethan was used as lock signal. Because of the small difference of only 2.52 MHz at the AMX 400 spectrometer, the $^2{\text{H}}$ coil could be adjusted for $^6{\text{Li}}$ irradiation.

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[6] It is worthwhile to remember that $^{13}{\text{C}},^6{\text{Li}}$ spin, spin coupling in organolithium aggregates is best described as being transmitted through multicenter coordinate bonds (T. L. Brown, *Acc. Chem. Res.*, 1968, 1, 23) and thus varies with the aggregate structure. This forms the basis of Equation (1). The magnitude of $^1{\text{J}}(^{13}{\text{C}},^6{\text{Li}})$ coupling constants reflects the electron density of the particular coordinate C–Li bonds. For example, in a static tetramer like 3 (Scheme 1), each carbon has three Li+ as next neighbors, and the electron density of the negative charge is distributed between three lithium sites. The coupling is thus smaller than that in the dimer 2 (Scheme 1), where only two lithium cations participate (~6 vs ~9 Hz). In a fluxional tetramer, the fourth lithium is also involved, and the coupling is again smaller (~4 Hz). In contrast, the $^{13}{\text{C}}–^1{\text{H}}$ couplings over classic bonds as, for instance, in sp3 groups like C–$^1{\text{CH}}_3$, C–$^{13}{\text{CH}}_3$, and C–$^{13}{\text{CH}}_3$ are all close to 125 Hz.

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