

The Aggregation Behavior of Butyllithium in Diethyl Ether in the Presence of LiBr, LiClO₄, and Phenyllithium: A Deuterium-Induced Secondary ⁶Li-NMR Isotope-Effect Study¹⁾

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Dedicated to Professor Dr. Wolfgang Lüttke on the occasion of his 95th birthday

The aggregation of BuLi (LiR) in diethyl ether (Et₂O) in the presence of LiBr was studied by ⁶Li- and ¹³C-NMR spectroscopy. For a 1.0:0.8 mixture of both species, the clusters (LiR)₄, Li₄R₃Br, Li₄R₂Br₂, Li₄RBr₃, and/or Li₂RBr in the ratio 7:81:12 with Li₄RBr₃ and/or Li₂RBr < 1 were detected with the *isotopic fingerprint method* that is based on secondary deuterium (D)-induced isotope shifts for δ(Li). The raising content of bromide ions causes increased shielding for δ(Li). As in the case of a 1:1 MeLi/LiBr mixture in Et₂O, cluster Li₄R₃Br is the most stable one. In the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA), only a mixed dimer was found. For LiClO₄, no inclusion of the ClO₄⁻ ion could be detected. A mixture BuLi/PhLi 1:1 in Et₂O in the presence of TMEDA showed only dimers with the mixed dimer as the most stable cluster. Chemical exchange of Li between the two homodimers was detected by EXSY spectroscopy. This implies an exchange mechanism with a *fluxional* tetramer as intermediate.

Introduction. – One of the most important properties of organolithium compounds – valuable intermediates in organic syntheses – is their aggregation tendency in ethereal and hydrocarbon solvents. NMR Spectroscopy plays since long a major role in the structural investigations of these complexes [2]. While earlier information about the degree of aggregation was obtained from colligative properties such as diffusion constants, vapor pressure or freezing point lowerings [3], NMR studies provide more direct evidence for the size and properties of aggregates like dimers, tetramers, or hexamers. In the beginning, the measurement of scalar ^{6,7}Li,¹³C coupling constants at the lithiated C-atom, pioneered by *Fraenkel* [2f][4] and *Seebach* [5a], yielded important data about aggregate size and aggregate dynamics. The use of the more ‘NMR-friendly’ isotope ⁶Li with its small quadrupolar moment (– 8.08 × 10⁻⁴ barn), which is today the preferred nucleus, led to the empirical *Eqn. 1* [5]:

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

that relates the aggregation state, *n*, (*n* = 1 for a monomer, 2 for a dimer, *etc.*) of a *static* complex, where *inter*- and *intra*-aggregate exchange processes are slow on the NMR timescale, with the magnitude of the scalar ¹³C,⁶Li coupling constant that depends on

¹⁾ NMR Spectroscopy of Organolithium Compounds, Part XXX; for Part XXIX, see [1].

the number of $^{13}\text{C}, ^6\text{Li}$ contacts and decreases for *fluxional* aggregates with *intra*-aggregate exchange processes. Later, chemical-shift *multiplets – isotopic fingerprints* – resulting from deuterium (^2H)-induced isotope effects on $\delta(^6\text{Li})$ were established as a useful analytical tool [6], and more recently the measurement of diffusion coefficients by DOSY spectroscopy led to promising results [7], especially since it also yields through the magnitude of the diffusion coefficients information about the solvent cage of the particular complex that is not available from other spectroscopic techniques.

Apart from homo-aggregation, the aggregation tendency of Li organics leads to the formation of mixed aggregates if Li salts are present, either as by-products of Li/halogen exchange reactions that are used for the synthesis of the Li reagents, or if inorganic salts are added in order to influence the reaction behavior [2g][8][9]. Structural information about these mixed aggregates is thus important for detailed experimental and/or theoretical mechanistic studies of the reactions of organolithium compounds.

We and others have before reported on the aggregation behavior of MeLi in the presence of LiBr and LiI in Et_2O and THF [9–11], where we characterized mixed tetramers by the isotopic fingerprint method [6][10]. In the present communication, we extend these investigations with a study of the aggregation behavior of BuLi – perhaps the most important organolithium compound in the field of organic synthesis – in Et_2O in the presence of LiBr without and with *N,N,N',N'*-tetramethylethylenediamine (TMEDA) as an additional ligand. Also, the formation of mixed aggregates with the ClO_4^- anion, and the aggregation between BuLi and PhLi in the presence of TMEDA were examined. In the latter case, it was of interest if aggregate formation is governed by statistics or if certain aggregates are preferred.

Results. – *The System BuLi/LiBr (1.0:0.8) in Et₂O.* Based on findings for MeLi/LiBr mixtures [9–11] and the earlier literature [12], we can assume dominating tetramer formation with varying substitution of Bu groups by Br^- . This leads to aggregates or clusters drawn in idealized manner in Fig. 1²⁾. As we shall show in the following, this assumption is verified by the ^6Li - as well as the ^{13}C -NMR spectra also for the present investigation. In addition, the LiBr aggregates $(\text{LiBr})_2$ or $(\text{LiBr})_4$, or a dimer \rightleftharpoons tetramer equilibrium between these two clusters is expected [9][14].

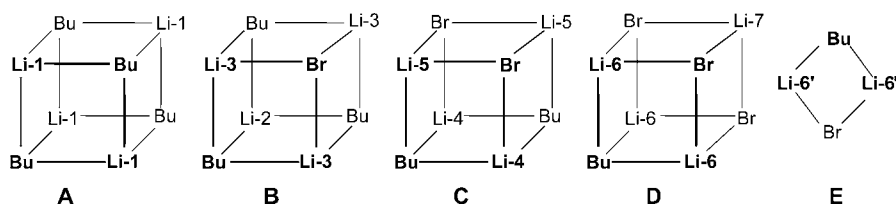


Fig. 1. Possible aggregates of BuLi/LiBr mixtures

²⁾ The cubic structure shown is based on powder diffraction data for solid MeLi [13]. It is clear that the symmetry of cluster **A** is strongly distorted in the remaining clusters by the increasing introduction of Br^- ions (see, e.g., the DFT-calculated mixed tetramers between MeLi and LiBr [11])

In general, at room temperature all aggregates or clusters are in fast chemical exchange. Lowering the temperature, first *inter*-aggregate and later *intra*-aggregate exchange processes can be slowed down until they do not affect the NMR spectrum. In this case, the complex is called *static*. If only *inter*-aggregate exchange is eliminated with respect to the NMR time-scale and *intra*-aggregate exchange still prevails, we speak of *fluxional* aggregates.

Starting with cluster **A** as the pure tetramer (BuLi)₄, different environments for Li⁺ then result by increasing replacement of Bu groups by Br⁻. With next neighbors for static aggregates collected between brackets and remote neighbors outside the brackets, we expect the Li species compiled in *Table 1*. For *fluxional* aggregates, a time-averaged contact between Li and all ligands, next and remote ones, of the particular cluster exists.

Table 1. *Expected Li Environments in BuLi/LiBr Clusters Shown in Fig. 1^a*

Cluster	Li Environment ^b)	Occurrence
Tetramers		
A	Li-1[CH ₂ ,CH ₂ ,CH ₂ ,]CH ₂	4
B	a) Li-2[CH ₂ ,CH ₂ ,CH ₂]Br	1
	b) Li-3[CH ₂ ,CH ₂ ,Br]CH ₂	3
C	a) Li-4[CH ₂ ,CH ₂ ,Br]Br	2
	b) Li-5[CH ₂ ,Br,Br]CH ₂	2
D	a) Li-6[CH ₂ ,Br,Br]Br	3
	b) Li-7[Br,Br,Br]CH ₂	1
Dimer		
E	Li-6'[CH ₂ ,Br]	2

^a) In addition (LiBr)₂ and/or (LiBr)₄. ^b) Next neighbors in brackets.

The proton-decoupled ⁶Li-NMR spectrum obtained for a Bu⁶Li/⁶LiBr mixture (1.0:0.8) at 58.9 MHz and 162 K is shown in *Fig. 2, a*. It was recorded with inverse-gated ¹H decoupling [15] in order to avoid signal-intensity distortions due to nuclear *Overhauser* effects (NOEs) [6] and shows, aside from a few smaller signals as, *e.g.*, 2, six major lines. For the application of the isotopic fingerprint method for signal assignments [6], the principle of which is shortly reviewed in [2c] and in the *Exper. Part*, we prepared a 1.0:0.7:2.0 mixture of Bu⁶Li, [α,α -D₂]Bu⁶Li, and ⁶LiBr. The CD₂ group then leads to geminal isotope shifts, ² Δ (²¹H)⁶Li, in the order of 5 to 10 ppb (!) for directly attached ⁶Li nuclei. Isotope shifts induced by remote neighbors are usually much smaller and can in most cases be neglected. The signals or fingerprints were then observed in the ⁶Li-NMR spectrum recorded under the same conditions as the spectrum shown in *Fig. 2, a* (¹H decoupling, 162 K) and are reproduced in *Fig. 2, b*. The smaller signals between 0 and 0.35 ppm that are not labelled are assigned to unknown impurities. Their intensities varied for different sample preparations, and they showed no isotope effect. Chemical-shift and isotope-effect data are collected in *Table 2*.

We start our analysis with signals 1 and 7. The chemical shift of signal 1 is close to that of the external reference LiBr and can thus be attributed to a LiBr cluster. For

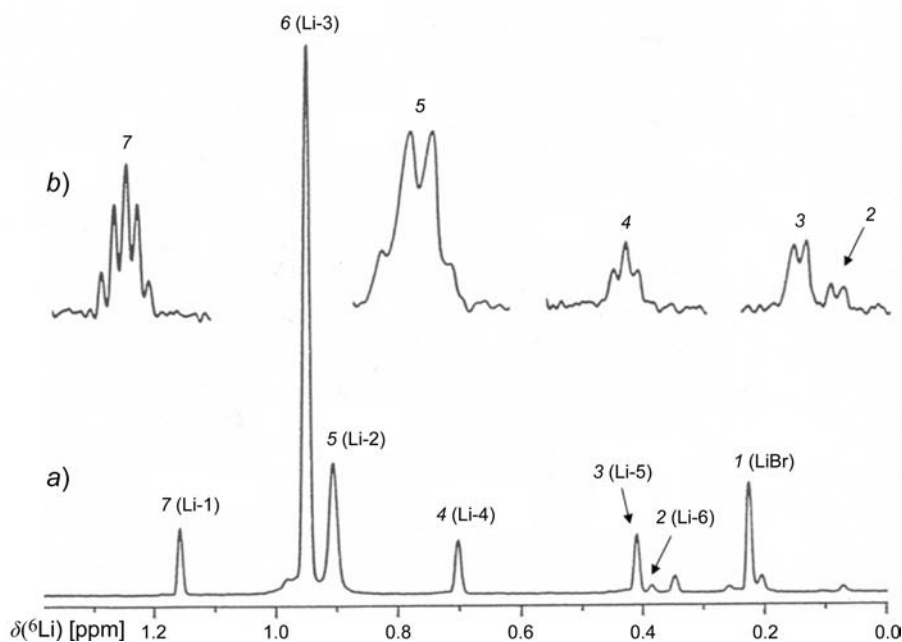


Fig. 2. a) 58.9-MHz Inverse-gated ${}^6\text{Li}\{^1\text{H}\}$ -NMR spectrum of $\text{Bu}^6\text{Li}/\text{LiBr}$ (1.0:0.8) 0.44M in $\text{Et}_2\text{O}/(D_{10})\text{Et}_2\text{O}$ 4:1 at 162 K. δ -Scale relative to external LiBr 0.1M in $[\text{D}_8]\text{THF}$; signal assignments are given above for Li in aggregates **A**–**E**; signals of individual aggregates are 7 (**A**), 5, 6 (**B**), 3, 4 (**C**), and 2 (**D** or **E**). b) Isotopic fingerprints observed in the ${}^6\text{Li}\{^1\text{H}\}$ NMR spectrum of a 1.0:0.7 mixture of Bu^6Li and $[\alpha,\alpha\text{-D}_2]\text{Bu}^6\text{Li}$ 0.35M in the presence of 1 equiv. LiBr in $\text{Et}_2\text{O}/[\text{D}_{10}]\text{Et}_2\text{O}$ (4:1) at 156 K

Table 2. ${}^6\text{Li}$ Chemical Shifts δ [ppm] Relative to External LiBr in THF and ${}^2\text{H}$ -Induced Isotope Effects ${}^2\Delta({}^2\text{H}){}^6\text{Li/ppb}^a$) of Spectra a) and b) of Fig. 1, Respectively

Signal	1	2	3	4	5	6	7
$\delta({}^6\text{Li})$	0.22	0.38	0.41	0.70	0.91	0.95	1.16
Assignment	Li-Br	Li-6	Li-5	Li-4	Li-2	Li-3	Li-1
${}^2\Delta({}^2\text{H}){}^6\text{Li}$	–	–7.5	–7.5	–6.8	–12.7	$> 5.8 $	–8.5
Multiplicity	singlet	doublet	doublet	triplet	quadruplet	$-^b$)	quintuplet

^a) ${}^2\text{H}$ -Induced isotope effects over two bonds on $\delta({}^6\text{Li})$, ${}^2\Delta({}^2\text{H}){}^6\text{Li}$, are high-frequency shifts and have, therefore, a negative sign, if we define ${}^n\Delta$ by $\delta(\text{h}) - \delta(\text{d})$, where $\delta(\text{d})$ is the chemical shift of ${}^6\text{Li}$ in the deuterated compound; for the isotopic fingerprints, only the absolute value is important. ^b) Not resolved.

signal 7 at highest frequency, we observe in Fig. 1, b, a 1:4:6:4:1 quintuplet that characterizes the corresponding complex as a fluxional tetramer where Li has contact with four Bu groups with $\alpha\text{-CH}_2$ and $\alpha\text{-CD}_2$ in the statistical ratio (see *Exper. Part*). Signal 7 is thus due to cluster **A**. In general, for fast *intra*-aggregate exchange the number of NMR signals, n , is correlated with the number c of ligands by $n = c + 1$; for signal 7, we have $n = 4 + 1 = 5$.

The remaining five signals, 2–6, are due to clusters that contain Br^- . According to *Table 1*, however, if these aggregates were also *fluxional* with fast *intra*-aggregate exchange of neighboring and remote ligands, we would expect only four signals for clusters **B–E** of *Fig. 1* instead of five, because in this case the difference between environments labelled *a* and *b* in *Table 1*, *i.e.*, the difference between next and remote neighbors, would vanish. Signals 2 to 6 must, therefore, be attributed to static aggregates where, on the NMR time-scale, all NMR-active dynamic processes are eliminated. In other words, the barrier for *intra*-aggregate exchange in these aggregates is higher than in cluster **A**. They are already in the slow exchange region, while **A** is still in fast exchange. The larger linewidth that we observe for the isotopic fingerprints of signals 2 to 6 as compared to that of signal 7 supports this interpretation: it indicates that the *intra*-aggregate dynamic for signals 2 to 6 is still not fully ‘frozen’ with the consequence of residual line-broadening. Furthermore, we see that the rate for *intra*-aggregate exchange is apparently slowed down by the inclusion of Br^- .

For the static aggregates of signals 2 to 6, the isotopic fingerprints represent next neighbor or local environments [16] which may come from different clusters. For the analysis, we expect ^6Li shielding caused by the introduction of Br^- due to the well-known heavy atom effect [17]. We thus assume an increasing number of Br^- ions in going from signal 7 to 1.

The small shift difference between signals 6 and 5 indicates that they belong to lithium environments with the same number of Br^- ions. We can assign Li-2 of cluster **B** with three neighboring CH_2 groups to signal 5 at 0.91 ppm, because we find a *quadruplet* in *Fig. 2, b*, while Li-3 of cluster **B** with the environment $[\text{CH}_2, \text{CH}_2, \text{Br}]$ should give rise to signal 6 at 0.95 ppm. The relative intensity ratio 5/6 of 1:3 (see also *Fig. 3*) supports this assignment, however, the expected *triplet* for the isotopic fingerprint of signal 6 could not be resolved. From the measured half-width of 0.68 Hz (= 11.5 ppb), we estimate the isotope shift as < 5.8 ppb, *i.e.*, smaller than the shifts observed for the other signals (*cf. Table 2*). In addition, the line-broadening mentioned above masks the expected fine structure. Surprisingly, we note that the shielding effect for the ^6Li resonance due to the introduction of Br^- ion is similar for the directly attached atom Li-3 and for Li-2 at the corner opposite to the halogen. This contrasts with our finding for MeLi/LiBr mixtures [10] where the corresponding Li-2 signal was found close to that of Li-1 (1.80 and 1.72 ppm, resp.). Apparently, the larger size of the Bu group as compared to the Me group leads to different shielding mechanisms.

Signal 4 (δ 0.7) is shifted to lower frequency and shows a fingerprint *triplet*. It can thus be assigned to Li-4 of cluster **C**, if we consider again a shielding effect by Br^- at the opposite corner. Compared to the situation in MeLi/LiBr, Li-4 is now more shielded by 0.34 ppm (1.04 vs. 0.70 ppm). Signal 3 then stems from Li-5 of cluster **C** with the environment $[\text{CH}_2, \text{Br}, \text{Br}]$ and the expected *doublet* as fingerprint. Its shift is similar in both systems, MeLi/LiBr and BuLi/LiBr (0.44 vs. 0.41 ppm). The assignments derived here are supported by the intensity ratio 4/3 of 1:1 (see also *Fig. 3*).

A minor signal 2 close to signal 3 to lower frequency shows a *doublet* in *Fig. 2, b*, and could thus arise from Li-6 in cluster **D**. Li-7 of this cluster then coincides with signal 1 of the LiBr cluster or gives rise to one of the small signals around signal 1. However, the shielding effect of Br^- ion at the opposite corner is missing, otherwise the resonance of

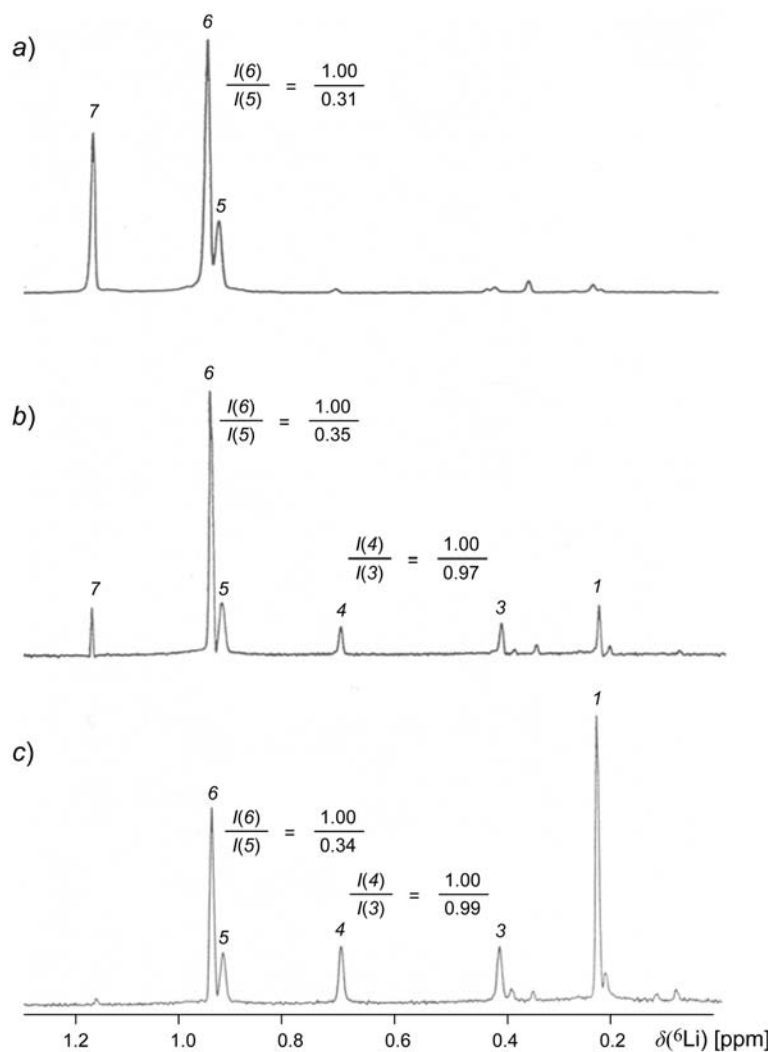


Fig. 3. ${}^6\text{Li}\{^1\text{H}\}$ -NMR Spectra of $\text{Bu}^6\text{Li}/{}^6\text{LiBr}$ mixtures with different mixing ratios at 166 K: a) 1.0:0.2, b) 1.0:0.8, and c) 1.0:2.0

Li-6 should appear at even lower frequency. Its ${}^6\text{Li}$ chemical shift (0.38 ppm), however, is close to that of the corresponding ${}^6\text{Li}$ signal in MeLi/LiBr (0.30 or 0.28 ppm [10]). A simple mixed dimer **E** could also explain the fingerprint of signal 2, then assigned to Li-6', and the missing shielding effect of the Br^- ion from the opposite corner would find an explanation.

From the signal intensities in *Fig. 2, a*, we obtain at 162 K for the concentrations of the dominating aggregates **A/B/C** the distribution 7:81:12, characterizing aggregate **B** as the most stable one, in agreement with the results for MeLi/LiBr . In both cases,

aggregates **D** or **E** are minor species with less than 1% contribution. Spectra recorded for different mixing ratios, shown in *Fig. 3, a–c*, yield, with an excess of BuLi, only signals for **A** and **B**, and with an excess of LiBr, aside from a strong signal for $(\text{LiBr})_n$, only signals for **B** and **C**. The constant intensity ratios found for signals 5/6 and 3/4 give independent support for our signal assignment. Furthermore, spectra recorded at higher temperature reveal coalescences between signals 5 and 6 as well as 3 and 4 (*Fig. 4*). These must be due to an increase of the rate of *intra*-aggregate exchange now also in clusters **B** and **C**. For the exchange system $3 \rightleftharpoons 4$ with equal populations at the two sites, we can calculate the rate constant k at the coalescence temperature T_c (191 K), k_{coal} , from *Eqn. 2* [18] and the chemical shift difference, $\delta\nu$ (in Hz), measured at low temperature:

$$k_{\text{coal}} = \pi \cdot \delta\nu / \sqrt{2} = 2.22 \delta\nu \quad (2)$$

With $\delta\nu = 0.29$ ppm or 17 Hz at 58.9 MHz from *Table 1*, we find $k_{\text{coal}} = 38 \text{ s}^{-1}$; this leads with

$$\Delta G_{T_c}^{\ddagger} = RT_c [22.96 + \ln(T_c / \delta\nu)] \quad (3)$$

and $R = 8.31 \text{ J K}^{-1}$ to a free energy of activation of $\Delta G_{191}^{\ddagger} = 40.4 \text{ kJ mol}^{-1}$. The coalescence temperature for signals 5 and 6 is with 200 K slightly higher, but the chemical shift difference is only 0.7 Hz. This gives a $\Delta G_{206}^{\ddagger}$ value of *ca.* 49 kJ mol⁻¹ as a crude estimate based on *Eqn. 2*³⁾. For cluster **A**, on the other hand, at 162 K still

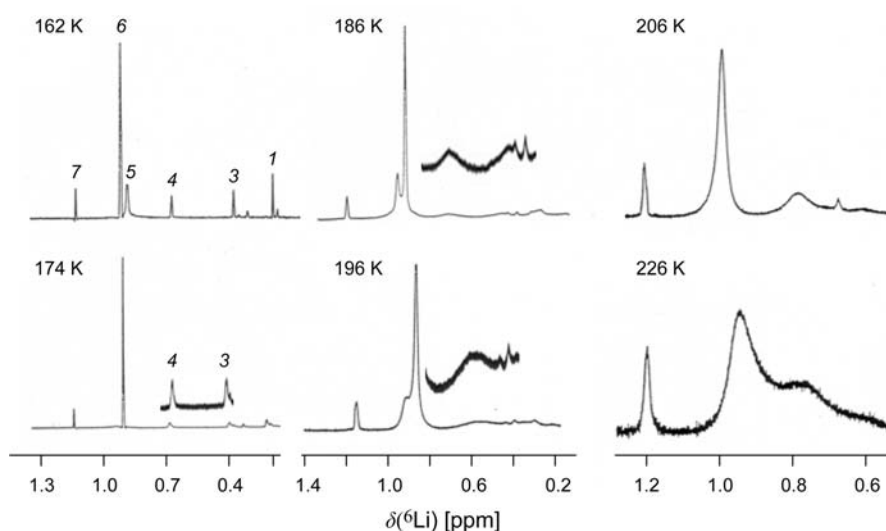


Fig. 4. Temperature dependence of the ${}^6\text{Li}\{^1\text{H}\}$ -NMR spectrum of *Fig. 2, a*. Please note that, for signals 5 and 6, a temperature-dependent change of the relative chemical shift with an isochrony at 174 K exists.

³⁾ *Eqn. 2* is strictly valid only for a two-sites exchange system with equal populations.

characterized as a *fluxional* tetramer, the barrier must be lower. As an upper limit, we estimate on the basis of *Eqn. 2* from the isotope effect of 8.5 ppb, which is only 0.5 Hz for $\delta\nu$ at 58.9 MHz, a k_{coal} value of *ca.* 1 s^{-1} . This gives $\Delta G_{\ddagger}^{\ddagger} < 38.7 \text{ kJ mol}^{-1}$ for the transitions $\text{static} \rightleftharpoons \text{fluxional}$. At temperatures above 206 K, the beginning coalescence between the signals for clusters **B** and **C** indicates the onset of *inter-aggregate* exchange.

Turning now to the ^{13}C -NMR results for the basic mixture $\text{Bu}^6\text{Li}/^6\text{LiBr}$ (1.0:0.8) in Et_2O , we find at 184 K a distorted *multiplet* at $\delta(^{13}\text{C})$ 11.9 ppm that shows a $^6\text{Li},^{13}\text{C}$ coupling constant of 5.5 Hz and a strongly broadened signal around $\delta(^{13}\text{C})$ 11 (Fig. 5, a). That indicates, after *Eqn. 1*, the presence of a static tetramer with three $^6\text{Li}^+$ ions as the next neighbor environment for $^{13}\text{C}(\alpha)\text{H}_2$ of the BuLi groups but leaves the origin of the remaining ^{13}C resonances unclear. The *multiplet* could thus originate from cluster **A** ($3 \times \text{Li-1}$), **B** ($1 \times \text{Li-2}, 2 \times \text{Li-3}$), or **C** ($2 \times \text{Li-4}, 1 \times \text{Li-5}$). This is most clearly documented by the heteronuclear *Overhauser* effects between ^6Li - and the H-atoms of the $\alpha\text{-CH}_2$ group found in the HOESY spectrum [2d][19] of the 1.0:0.2 mixture (Fig. 6, a) where, according to the spectrum shown in Fig. 3, a, the aggregates **A** and **B** dominate. Cross-peaks for **C** could not be observed due to the low intensity of the Li-4 and Li-5 signals.

A more detailed analysis of the ^{13}C -NMR signals was possible when the ^{13}C spectra of the samples with different ratios $[\text{BuLi}]/[\text{LiBr}]$ were recorded under ^1H as well as ^6Li decoupling that removes line-broadening due to resolved and unresolved coupling constants (Fig. 5, b–d). Accordingly, sharp *singlets* are observed for the resonances of the lithiated C-atoms at 11.9, 11.7, and 10.9 ppm, because the next neighbor environment for the Bu groups, $[\text{Li}, \text{Li}, \text{Li}]$, is identical within the clusters **A**, **B**, and **C**. The assignment can be based on the intensities observed for the same mixtures as those used in the ^6Li -NMR spectrum (Fig. 3). The 1.0:0.2 mixture (Fig. 5, b) with $[\text{B}] > [\text{A}]$ gives resonances at $\delta(^{13}\text{C})$ 11.9 for **B** and $\delta(^{13}\text{C})$ 10.9 for **A**, while, for the 1.0:2.0 mixture

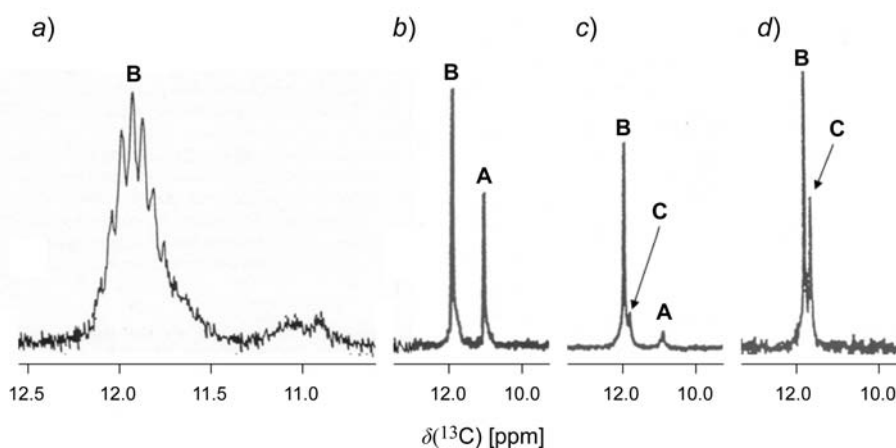


Fig. 5. a) 100-MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR Spectrum of $\text{Bu}^6\text{Li}/^6\text{LiBr}$ (1.0:0.8) 0.44M in $\text{Et}_2\text{O}/[D_{10}]\text{Et}_2\text{O}$ 4:1 at 184 K. δ in ppm relative to TMS. b)–d) Partial $^{13}\text{C}\{^1\text{H}, ^6\text{Li}\}$ NMR spectra of samples with different mixing ratios for Bu^6Li and $^6\text{LiBr}$ at 194 K: b) 1.0:0.2, c) 1.0:0.8, d) 1.0:2.0.

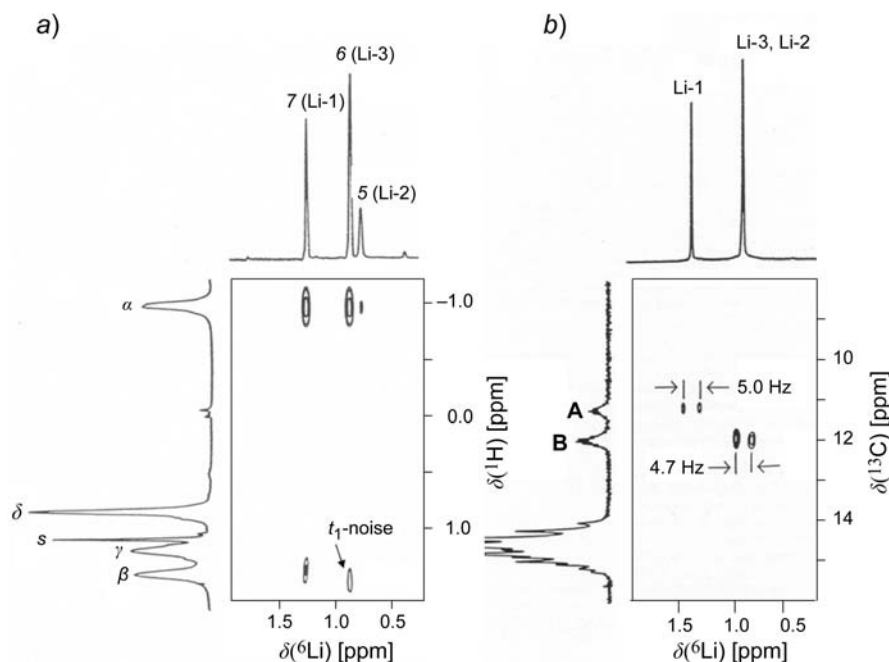


Fig. 6. a) 400/58.9-MHz $^1\text{H},^6\text{Li}$ -HOESY Spectrum of $\text{Bu}^6\text{Li}/^6\text{LiBr}$ (1.0:0.2) 0.7M in $[D_{10}]\text{Et}_2\text{O}$ at 164 K with cross-peaks between $^1\text{H}-\text{C}(\alpha)$ of the Bu groups and Li-1 in cluster **A**, and Li-3 and Li-2 in cluster **B**. The ^1H -NMR signals of the H-atoms of the Bu groups of different clusters are not separated, the known cross-peak between ^6Li and the CH_2 H-atoms at $\text{C}(\beta)$ [19] is seen for cluster **A**; s , residual Et_2O . b) Phase-sensitive $^6\text{Li},^{13}\text{C}$ -HMQC spectrum of the same mixture at 174 K. Please note that, at this temperature, the signals 5 and 6 for Li-2 and Li-3 in cluster **B**, respectively, coincide (see also Fig. 4 for the temperature dependence of these signals).

with ^6Li resonances for **B** and **C**, we observe the ^{13}C signals again at $\delta(^{13}\text{C})$ 11.9 for **B** and now at $\delta(^{13}\text{C})$ 11.7 for **C** (Fig. 5, d). For the 1.0:0.8 mixture, all three ^{13}C signals are recorded (Fig. 5, c). The line splitting of 5.5 Hz observed in the distorted multiplet of Fig. 5, a (cf. above) thus comes from $\text{C}(\alpha)$ -atoms of Bu groups of clusters **B** and **C** and their next neighbor environments [Li-2, Li-3, Li-3] and [L-4, L-4, Li-5], respectively. The small broadened signal around $\delta(^{13}\text{C})$ 11, on the other hand, with unresolved coupling is identified as belonging to cluster **A**. The remaining resonances of BuLi were found between 31 and 34 ppm ($\text{C}(2)$, $\text{C}(3)$) but not assigned; the $\text{C}(4)$ signal was superimposed by solvent signals. As one sees, the influence of Br^- inclusion on $\delta(^{13}\text{C})$ of the lithiated C-atom is small and apparently not systematic.

Further important information for the analysis of the ^{13}C signals was derived from a two-dimensional $^6\text{Li},^{13}\text{C}$ chemical shift-correlation experiment of the HMQC type [20] for the 1.0:0.2 mixture at 194 K, where the signals 5 and 6 of cluster **B** overlap, and the higher intensity of signal 7 allows a closer look on its structure. This experiment yielded $^{13}\text{C},^6\text{Li}$ cross-peaks with splittings of 5.0 Hz for cluster **A** and 4.7 Hz for cluster **B** (Fig. 6, b). According to Eqn. 1, cluster **A** is static on the time-scale of this experiment ($17:5.0 = 3.4$) with three $^6\text{Li},^{13}\text{C}$ contacts. The observed coupling constant agrees with

earlier results for the aggregation state of BuLi in Et₂O [21] that showed at 203 K a ¹³C,⁷Li coupling of 14 Hz again typical for a static tetramer⁴).

For cluster **B**, we find $n = 3.6$ which is a border case between static ($n = 3$) and *fluxional* ($n = 4$). However, considering the approximate nature of Eqn. 1, a static cluster **B** is most likely, because the isotopic fingerprints (Fig. 3, b) characterize **B** as static and the signal overlap 5/6 and low digital resolution (0.18 Hz) in the HMQC spectrum may cause a larger experimental error for the coupling.

An additional point of interest concerns our finding that the isotopic fingerprint for signal 7 and its aggregate at 162 K are typical for a *fluxional* aggregate (Fig. 2, b). This contrasts with the conclusions drawn above from the ¹³C,⁶Li coupling. The different result of the two recordings is a consequence of the different NMR time-scale that governs the coalescence or decoalescence behavior of the appropriate *multiplets*. The couplings of 5.0 or 14 Hz must be compared with the isotope effect of only 0.5 Hz. This leads, according to Eqn. 2, to the decoalescence of the appropriate signals k values of 11 or 31 s⁻¹ and 1 s⁻¹, respectively, for the two experiments with different NMR parameters. A static situation with Li scalar coupled to only three next ¹³CH₂ neighbors in the BuLi tetramer, *i.e.*, the slow exchange region for the *intra*-aggregate exchange, is thus reached in the ¹³C spectrum at higher temperatures. For the chemical shift *multiplet* of the isotopic fingerprint the *intra*-aggregate exchange is still fast enough to average the isotope effect with next and remote neighbors. Only at lower temperatures, that means smaller k values, a static situation can be reached, and the fingerprint *quintuplet* is then transformed into a *quadruplet*. Such a situation was found in our study of the aggregation of BuLi in dimethoxymethane [22]. The labels ‘*static*’ and ‘*fluxional*’ are thus clearly related to the time-scale of the particular NMR experiment.

BuLi/LiBr and TMEDA in Et₂O. The strong coordination tendency of the bidentate diamine ligand TMEDA drastically changes the situation for the aggregation of lithium organics. This is clear from the ⁶Li-NMR spectrum of Bu⁶Li/⁶LiBr (1 : 1) in Et₂O in the presence of an excess of TMEDA (1.5 times the concentration of both lithium compounds) (Fig. 7, a). At 175 K, we observe a strong *singlet* at 1.57 ppm and for the partially deuterated mixture Bu⁶Li/*n*-α,α-[D₂]Bu⁶Li/⁶LiBr(1 : 1 : 2)/TMEDA a *doublet* as isotopic fingerprint (Fig. 7, b). Accordingly, Bu⁶Li and ⁶LiBr form under these conditions a dimer (**E** in Fig. 1). The dimer structure of the BuLi/LiBr/TMEDA cluster is supported by the *quintuplet* at δ(¹³C) 12.1 and a coupling of 9.3 Hz found for the lithiated C-atom in the ¹³C-NMR spectrum of the same sample (Fig. 7, c). Not unexpectedly, the strongly solvating diamine prevents tetramer formation completely, but also stabilizes the mixed dimer to the extent that a BuLi homodimer could not be detected.

BuLi/LiClO₄ in Et₂O. Aside from lithium halogenides, the aggregation of lithium organics was frequently studied in the presence of other Li salts like LiClO₄ that forms in Et₂O a solvent-separated ion pair, Li⁺(Et₂O) _{x} ClO₄⁻ ($x = 1, 2$) [23] [24]. We found that for the aggregation behavior of MeLi in the presence of LiClO₄ different results were reported. While *Ashby et al.* did not find a mixed aggregate [25], a static aggregate

⁴) The magnetogyric ratio, γ , of ⁷Li is larger than that of ⁶Li by a factor of 2.64 that also holds for the ratio of the coupling constants. Eqn. 1 then changes to $^1J(^{13}\text{C}, ^7\text{Li}) \approx 45/n$.

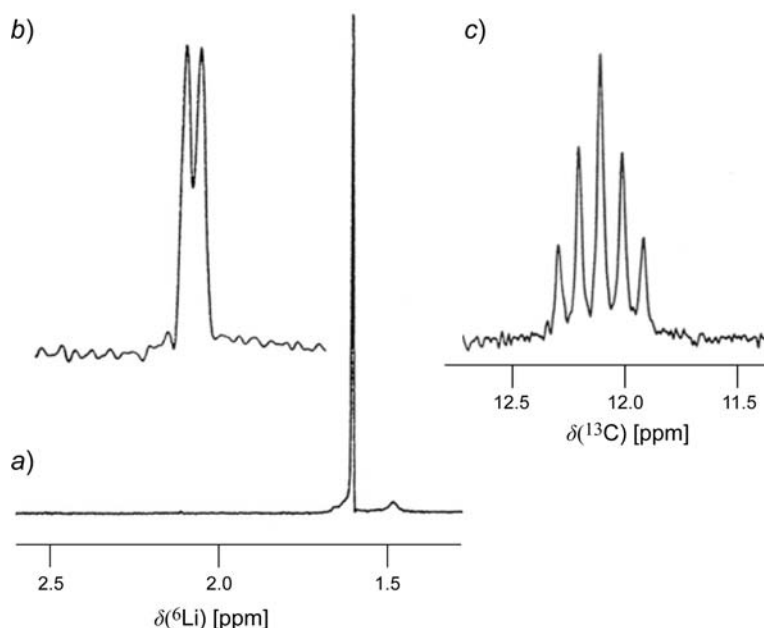


Fig. 7. a) 58.9-MHz ${}^6\text{Li}\{^1\text{H}\}$ -NMR Spectrum of $\text{Bu}^6\text{Li}/^6\text{LiBr}/\text{TMEDA}$ (1:1:1.5) 0.35M in $[\text{D}_{10}]\text{Et}_2\text{O}$ at 175 K. δ -Scale relative to external LiBr 0.1M in $[\text{D}_8]\text{THF}$. b) ${}^6\text{Li}$ Isotopic fingerprint for $\text{Bu}^6\text{Li}/[\alpha,\alpha\text{-D}_2]\text{Bu}^6\text{Li}/\text{LiBr}/\text{TMEDA}$ 1:1:2:1.5. c) ${}^1\text{H}$ -Decoupled ${}^{13}\text{C}$ -NMR signal of the sample used for a at 190 K; δ -scale relative to TMS.

$[\text{Li}_4\text{Me}_3(\text{ClO}_4)]$ in the presence of a MeLi tetramer was proposed by *Jackman et al.* [26] and an experiment with BuLi was, therefore, of interest.

The ${}^6\text{Li}$ -NMR spectrum of a 1:1 mixture $\text{Bu}^6\text{Li}/^6\text{LiClO}_4$ in Et_2O showed, relative to the LiBr standard, two *singlets* at 1.24 and -1.18 ppm. In the isotopic fingerprint spectrum at 173 K, the high-frequency *singlet* changed to a *quintuplet* that characterizes a *fluxional* tetramer of BuLi. The other signal showed no splitting and was assigned to ${}^6\text{LiClO}_4$. Thus, no indication of mixed aggregate formation with BuLi came from these data. This is further supported by the ${}^{13}\text{C}$ -NMR spectrum with only one signal of a lithiated C-atom at 10.7 ppm, typical for $(\text{BuLi})_4$ as seen in *Fig. 5, b*, for cluster **A** and as reported in [21].

BuLi/PhLi (1:1) and *TMEDA* in Et_2O . In addition to the aggregation of organolithium compounds with inorganic salts, aggregation between two lithium organics was repeatedly explored. Again, pioneering work was accomplished by *Seitz* and *Brown*, who reported, among other projects, on mixtures of MeLi and EtLi [16] or MeLi and PhLi in Et_2O [27]. Later, for example, BuLi/PhC \equiv CLi [28a], 1-lithionaphthalene/MeLi [19] or 1-[(dimethylamino)methyl]-2,4,6-trimethylbenzene/BuLi [28b] and, more recently, MeLi/BuLi [28c], $\text{Me}_2\text{NC}_6\text{H}_4\text{Li}/t\text{-BuLi}$ [28d], and lithium amides/PhLi [28e] were investigated. It was also shown that such studies can throw light on the mechanism of lithiation reactions.

Our interest focused on a mixture of BuLi and PhLi, two of the most frequently used lithiation agents in organic synthesis. *Seitz* and *Brown* investigated PhLi mixtures

with MeLi and EtLi in Et₂O, and proposed the presence of two mixed species, a dimer, Li₂(Ph)(Et), and a tetramer, Li₄(Ph)Et₃ [27]. In the presence of TMEDA, we can expect, according to earlier results for BuLi and PhLi solutions in various solvents [2f][5a][12], the exclusive formation of the dimers **F**, **G**, and **H** (Fig. 8).

In the ⁶Li-NMR spectrum of a 1:1 mixture BuLi/PhLi in Et₂O in the presence of a slight excess of TMEDA (Fig. 9, a), we found three signals 8, 9, and 10. Those at highest and lowest frequency with relative intensities of 1:1 are characterized by their chemical

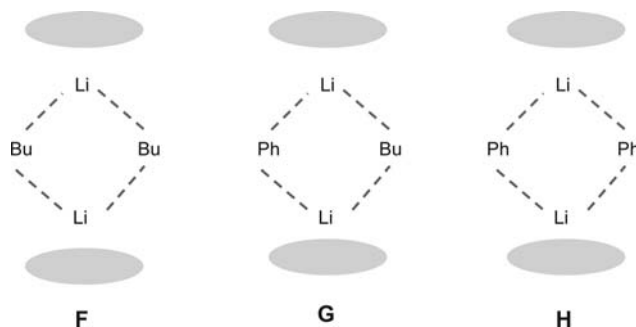


Fig. 8. Expected dimers for a mixture of BuLi and PhLi in the presence of TMEDA

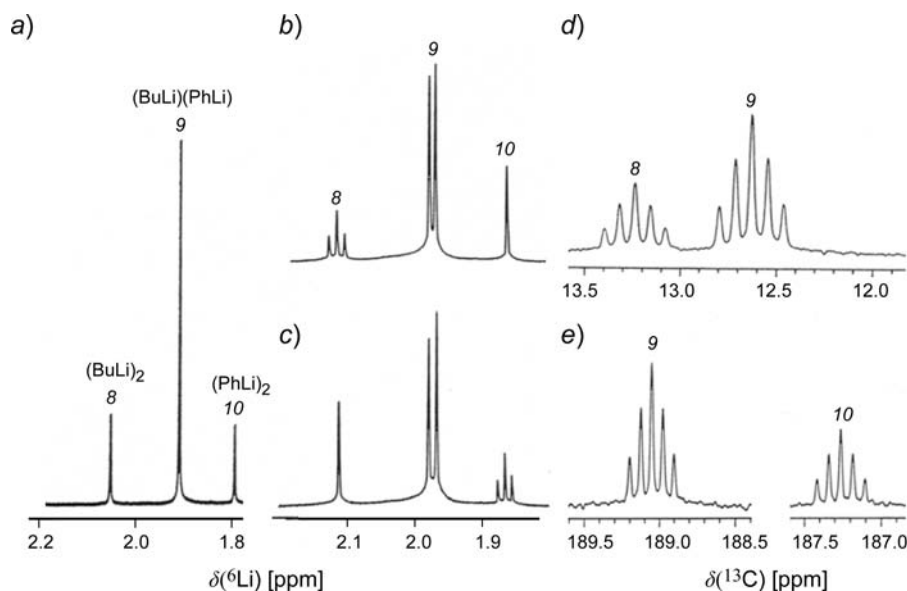


Fig. 9. a) 58.9-MHz ⁶Li-NMR Spectrum of Bu⁶Li/Ph⁶Li (1:1) 0.3M in [D₁₀]Et₂O/TMEDA (c_(TMEDA) 0.7M) at 185 K. External standard 0.1M LiBr/[D₈]THF; 8: (BuLi)₂(TMEDA)₂, 9: (BuLi)(PhLi)(TMEDA)₂, 10: (PhLi)₂(TMEDA)₂. b) Isotopic fingerprints in the ⁶Li-NMR spectrum of Bu⁶Li/[α,α-D₂]Bu⁶Li/Ph⁶Li (1:1:2) 0.3M in [D₁₀]Et₂O/TMEDA at 188 K. c) ⁶Li-NMR Spectrum of Bu⁶Li/Ph⁶Li/[D₃]Ph⁶Li under the same conditions. d) and e) 100-MHz ¹³C{¹H}-NMR Spectra of Bu⁶Li/Ph⁶Li/TMEDA (1:1:2.3) at 200 K in [D₁₀]Et₂O with the signal of C(α) of BuLi and C_{ipso} of PhLi, respectively. Reference, TMS.

shift values of δ 2.11 and δ 1.86 as belonging to the homodimers of BuLi (**F**) and PhLi (**H**), respectively, each one coordinated with two molecules of TMEDA. This was verified for BuLi by an independent recording in Et₂O in the presence of TMEDA that yielded $\delta(^6\text{Li})$ of 2.16 ppm. The large signal at δ 1.97 of relative intensity 4 is then due to a mixed aggregate **G** of the two organolithium compounds. For an independent proof, isotopic fingerprints were recorded for ⁶Li-enriched 1:1:2 mixtures of BuLi, [$\alpha,\alpha\text{-D}_2$]BuLi and PhLi as well as for PhLi, [D_5]PhLi and BuLi, both with eqimolar amounts of TMEDA, that resulted in ⁶Li spectra shown in *Figs. 9, b* and *c*, respectively⁵). From the signal structure, it is immediately clear that only dimers are formed, as expected: *Fig. 9, b* shows the *triplet* for the BuLi dimer **F**, while *Fig. 9, c* displays the *triplet* for the PhLi dimer **H**. The *doublet* in both spectra is due to the mixed dimer **G** where only one ligand provides the isotope shift. We can assume that in all dimers Li is complexed with two molecules of TMEDA. Relevant spectroscopic data are collected in *Table 3*.

Further support for the above results comes from the ¹H-NMR spectrum recorded at 200 K where the signals of ¹H, ¹³C(α) of the BuLi species and those of the *ortho*-phenyl H-atoms of the PhLi species are doubled in the intensity ratio 1:2. This ratio is the result of the relative intensities of 1:4 of signals 8/9 and 10/9. The mixed dimer, however, contains only one unit of BuLi and PhLi, while the homodimers contain two. The assignment was possible through a 2D-¹H,⁶Li HOESY spectrum that yielded cross-peaks for signal 8 with the CH₂ resonance of the dimer (BuLi)₂ at –1.15 ppm (relative intensity 1) and for signal 9 with that at –0.91 ppm (relative intensity 2) due to BuLi in the mixed dimer [(BuLi)(PhLi)]. The two signals of *o*-¹H of the PhLi species at 7.87 and 8.10 ppm (relative intensity 2:1) correlated with signals 9 and 10, respectively, and are thus assigned to the mixed dimer and the homodimer (PhLi)₂, respectively.

Table 3. ⁶Li-, ¹³C-, and ¹H-NMR Data for the System BuLi/PhLi (1:1) in [D_{10}]Et₂O/TMEDA

⁶ Li Signal	δ [ppm] ^{a)}	Assignment	² $\Delta(^6\text{Li})$ [ppb] ^{b)}	ⁿ $\Delta(^6\text{Li})$ [ppb] ^{c)}	Relative intensity
8	2.11	F	–12.2		0.98
9	1.97	G	–9.3	–11.4	4.00
10	1.86	H		–10.4	1.01
¹³ C Signal	δ [ppm] ^{d)}	¹ J(¹³ C, ⁶ Li) [Hz]	¹³ C Signal	δ [ppm] ^{d)}	¹ J(¹³ C, ⁶ Li) [Hz]
C(α) (F)	13.24	8.0 ± 0.17	C(1) (G)	189.05	7.6 ± 0.17
C(α) (G)	12.63	8.4 ± 0.17	C(1) (H)	187.26	7.9 ± 0.17
¹ H Signal ^{e)}	δ [ppm] ^{d)}	¹ H Signal ^{e)}	δ [ppm] ^{d)}		
¹ H–C(α) (F)	–1.15	<i>o</i> - ¹ H (G)	7.87		
¹ H–C(α) (G)	–0.91	<i>o</i> - ¹ H (H)	8.10		

a) Relative to external 0.1M LiBr in THF at 185 K. b) ¹H/²H isotope shift per CD₂ group. c) ¹H/²H Isotope shift per C₆D₅ group as sum of *o*-, *m*-, and *p*-shifts. d) Relative to TMS at 200 K. e) Additional NMR data are given in the *Exper. Part*.

⁵) In the case of (D₅)PhLi, the dominating deuterium induced isotope effect for ⁶Li is transmitted from the Ph *o*-H-atoms over three bonds as ³ $\Delta(^{21}\text{H})^6\text{Li}$ [29].

It was also of interest to investigate the temperature dependence of the spectra (Fig. 10), where coalescence phenomena yield a ${}^6\text{Li}$ average signal at 1.94 ppm. From the coalescence temperatures of *ca.* 235 and 244 K for the equilibria $8 \rightleftharpoons 9$ and $9 \rightleftharpoons 10$, respectively, we estimate with the $\delta\nu$ values of Fig. 10 and Eqn. 2 *k* values of *ca.* 18 and *ca.* 14 s^{-1} that yield $\Delta G_{\text{coal}}^\ddagger$ values of 51 and 54 kJ mol^{-1} for the *inter-aggregate* exchange systems between the homodimers and the mixed or heterodimer.

The EXSY spectra [30] (Fig. 11) confirm the exchange documented in the line-shape changes, but reveal further information of interest. The spectrum measured at 221 K shows, in addition to the cross-peaks between signals 8/9 and 9/10 that correspond to the signal coalescences in Fig. 10, cross-peaks between signals 8 and 10. If we assume for the exchange processes an association of the dimers to tetramers as intermediates or as transition states, followed by dissociation along different ‘cuts’ of the tetrameric cube, we can analyze the situation with the help of the aggregates outlined in the Scheme. Starting with cluster **I**, formed by homodimer association, $(\text{BuLi})_2/(\text{PhLi})_2$, dissociation along a perpendicular and a horizontal plane leads to an exchange between Li-8 and Li-9, as well as Li-10 and Li-9 (*Path a* and *b*). The same is true if we start with the association of a homo- and a heterodimer ($8+9$) and of two heterodimers ($9+9$) (not shown in the Scheme). A direct Li exchange between the homodimers $(\text{BuLi})_2$ and $(\text{PhLi})_2$, *i.e.*, $8 \rightleftharpoons 10$, is thus not possible, if we consider the tetramers as static. In order to realize such an exchange, indicated by the EXSY cross-peaks, we have to assume that tetramer **I** is *fluxional* and Li-8 and Li-10 interchange their position, *i.e.*, **I** \rightarrow **J**, before dissociation into homodimers (*Path c*). Fluxionality can be expected also for the other tetramers (homodimer + heterodimer and $2 \times$ heterodimer), but only tetramer **I** contains both Li species 8 and 10 and allows chemical

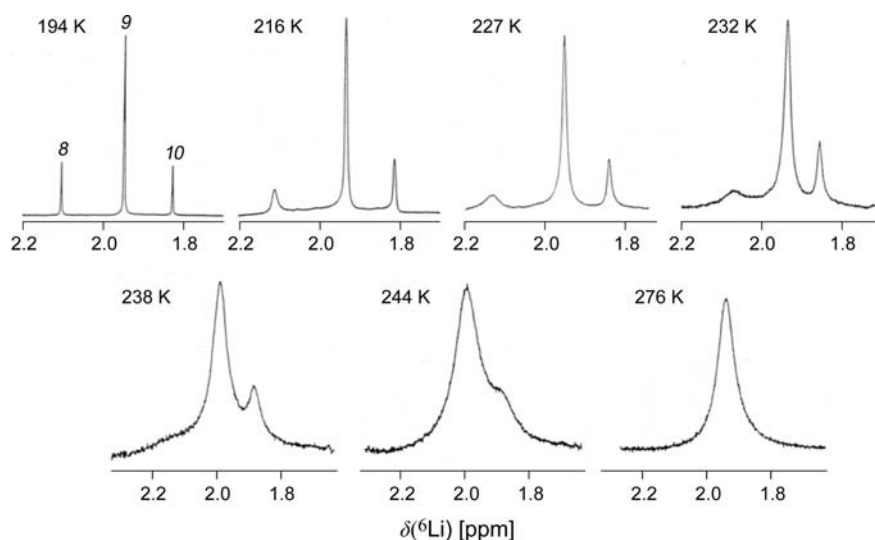
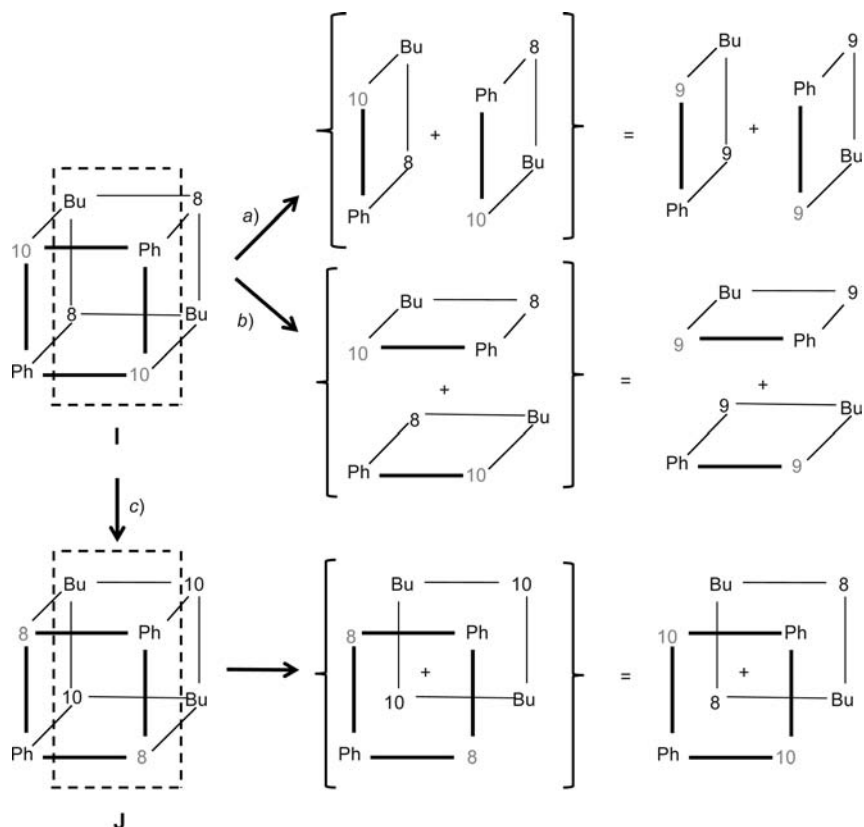


Fig. 10. Temperature-dependent ${}^6\text{Li}$ -NMR spectra of $\text{Bu}^6\text{Li}/\text{Ph}^6\text{Li}$ (1:1, 0.3M) in $[D_{10}]\text{Et}_2\text{O}/\text{TMEDA}$ (0.7M). $\delta\nu(8/9)$ 8.24 Hz, $\delta\nu(9/10)$ 6.48 Hz, coalescence of signals 8 and 9 is followed by that of 9 and 10 (8: $(\text{BuLi})_2(\text{TMEDA})_2$, 9: $(\text{BuLi})(\text{PhLi})(\text{TMEDA})_2$, 10: $(\text{PhLi})_2(\text{TMEDA})_2$).

Scheme. *Proposed Association–Dissociation Mechanism for Li Exchange in the BuLi/PhLi/TMEDA Mixture.* The Li sites are indicated by signal numbers as in Fig. 9.



exchange. Consequently, the tetramers are true intermediates with a certain life time for internal Li exchange and not transition states. The larger cross-peak intensity for the exchange systems 8/9 and 9/10 as compared to that of 8/10 supports this mechanism because of the higher concentration of mixed aggregates (*cf.* signal 9 vs. 8 or 10) the probability for these exchanges is larger. The cross-peaks for 8/10 disappear already at slightly higher temperature (227 K), when the slow exchange region for the Li exchange is over because of the higher reaction rate that results, according to Eqn. 2, from the larger chemical-shift difference (k of *ca.* 36 vs. 18 or 14 s⁻¹).

Discussions. – For the BuLi/LiBr system, we find aggregates like those described earlier for the MeLi/LiBr system [10][11]: (LiR)₄ (**A**), Li₄R₃Br (**B**), Li₄R₂Br₂ (**C**), Li₄RBr₃ (**D**) and/or Li₂RBr (**E**) (Fig. 1). Also the relative abundance of the dominating species is not very different with **A/B/C** 7:81:12 in the present case and 7:66:27 for MeLi/LiBr, and does not follow a statistical distribution. In both systems, cluster **B** is the most stable one, **D** and/or **E** are minor components. A notable difference concerns the ⁶Li chemical shift which changes systematically in the MeLi/

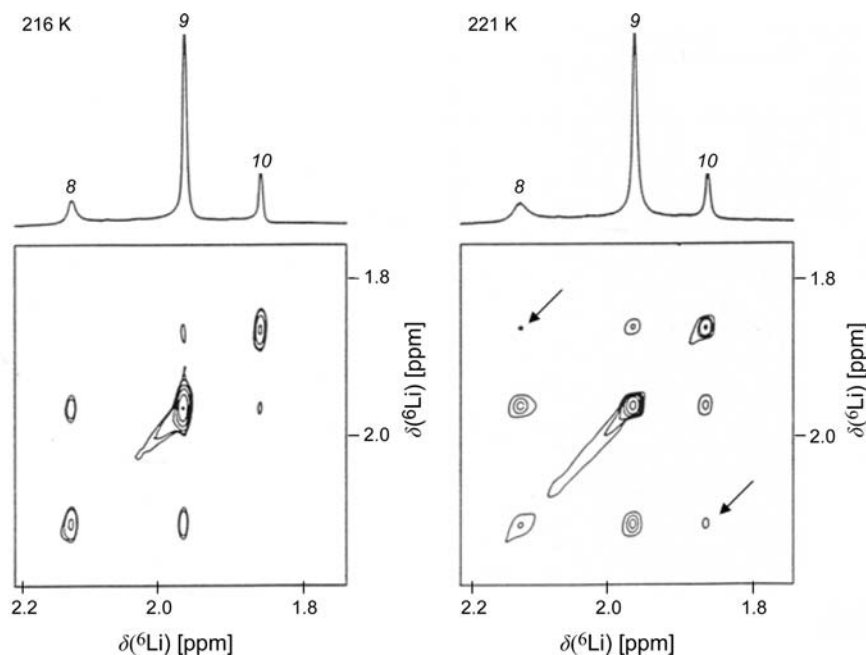


Fig. 11. 2D ${}^6\text{Li}, {}^6\text{Li}$ -EXSY Spectra of $\text{Bu}^6\text{LiPh}^6\text{Li}$ (1:1, 0.3M) in $[\text{D}_{10}]\text{Et}_2\text{O}/\text{TMEDA}$ (0.7M)
 (8: $(\text{BuLi})_2(\text{TMEDA})_2$, 9: $(\text{BuLi})(\text{PhLi})(\text{TMEDA})_2$, 10: $(\text{PhLi})_2(\text{TMEDA})_2$)

LiBr system with increased shielding of *ca.* 0.6 ppm for the successive introduction of bromide in the next neighbor environments: $[(\text{Me})_3] - [(\text{Me})_2\text{Br}] - [\text{MeBr}_2]$. In the case of BuLi/LiBr , $\delta({}^6\text{Li})$ of the environment $[(\text{Bu})_3]$ that exists for Li-1 and Li-2 in clusters **A** and **B**, respectively, differs by 0.25 ppm, and Li-3 of cluster **B** with environment $[(\text{Bu})_2\text{Br}]$ is even deshielded by 0.04 ppm relative to Li-2 with $[(\text{Bu})_3]$. More reasonable is the chemical-shift difference of 0.29 ppm between Li-4 and Li-5 in cluster **C** with environments $[(\text{Bu})_2\text{Br}]$ and $[\text{BuBr}_2]$, respectively. Assuming a shielding effect by Br^- ion across the diagonal of the tetrameric cube, the relation $\delta(\text{Li-2}) < \delta(\text{Li-1})$ can be understood, as well as the relation $\delta(\text{Li-4}) < \delta(\text{Li-3})$. Li-5 is then shielded by a directly attached second Br^- ion. If Li-6 resides in cluster **D**, one would then expect a shielding effect from the Br^- ion across the diagonal and the relation $\delta(\text{Li-6}) < \delta(\text{Li-5})$. The small shift difference of only 0.03 ppm does not support the presence of this shielding mechanism, and the existence of the mixed dimer **E** is more likely. The mechanism of the cross-diagonal shielding is unclear. Certainly, the larger alkyl group in BuLi as compared to MeLi causes severe distortions of the tetramer structure that might involve hitherto unknown shielding effects. That aggregation of organolithium compounds may yield unexpected results was recently shown by studies of MeLi in THF in the presence of LiCl , where *Maddaluno* and co-workers found, aside from the tetramer $(\text{MeLi})_4$ and the dimer $(\text{LiCl})_2$, exclusively a mixed dimer $(\text{MeLi})(\text{LiCl})$ of type **E** [31]. This indicates for the $\text{MeLi}/\text{lithium halogenide}$ 1:1 mixtures in THF as solvent a decrease in the number of mixed aggregates in the order $\text{LiI} > \text{LiBr} > \text{LiCl}$ from 3 (**B**, **C**, and **E**) to 2 (**B** and **E**) to 1 (**E**). In the same order, the proportion

of the homo-aggregate $(\text{LiMe})_4$ decreases, and that of the heterodimer **E** increases. Evidence for the existence of tetramer **D** comes only from samples with an excess of LiX^6 .

It is interesting to compare the free activation barriers that we calculated from the temperature-dependent ^6Li spectra for the *intra*-aggregate or *fluxional* exchange in aggregates **A**, **B**, and **C** with data published by *Thomas* and coworkers for *fluxional* exchange in *t*-BuLi and *t*-pentyllithium [32]. For *t*-BuLi one derives from the given ΔH^\ddagger and ΔS^\ddagger values of 25 kcal mol⁻¹ and 44 cal K⁻¹ mol⁻¹, respectively, $\Delta G_{191}^\ddagger = 69$ kJ mol⁻¹. This compares reasonably well with ΔG_{191}^\ddagger and ΔG_{206}^\ddagger values 40.4 and 49 kJ mol⁻¹ we found for cluster **C** and **B**, respectively. At 162 K, cluster **A**, the tetramer of BuLi, is still *fluxional*, and our estimated barrier of < 38.7 kJ mol⁻¹ at coalescence to the static structure at lower temperature comes close to the value of 33 kJ mol⁻¹ estimated for *t*-pentyllithium at 188 K [32].

Our finding for the BuLi/PhLi mixture supports the proposal of the formation of a mixed dimer $\text{Li}_2(\text{Ph,R})$ in the mixtures of PhLi with MeLi and EtLi, respectively [27]. The presence of TMEDA prevented in our case the formation of a mixed tetramer. Of general interest is the *experimental proof* that the Li exchange between different heterodimers proceeds *via* tetramers formed by dimer association as *intermediates* with a lifetime that allows *intra*-aggregate Li exchange before dissociation.

Again, a mixture of PhLi with alkyllithium compounds does not lead to a statistical distribution of the products as was found for mixtures of alkyllithium compounds [16][28c], but shows stabilization of the mixed aggregates. The intensity ratio 1:4:1 for signals 8–10 deviates appreciably from the ratio 1:2:1 expected for a statistic distribution [9] of the two Li compounds. According to *Eqn. 4*, neglecting the coordination of each species with two molecules of TMEDA, we have for the equilibrium constant K (*Eqn. 5*) [33], and the mixed dimer is thus more stable than the homodimers by $\Delta G_{185}^\circ = -RT \ln K = -4.3$ kJ mol⁻¹:



$$K = [(\text{BuLi,PhLi})]^2 / [(\text{BuLi})_2][(\text{PhLi})_2] = 16 \quad (5)$$

The interconversion barriers ΔG_{240}^\ddagger of *ca.* 50 kJ mol⁻¹ derived above for the *inter*-aggregate homodimer/heterodimer exchange $8 \rightleftharpoons 9$ and $9 \rightleftharpoons 10$ can be compared with exchange barriers between homotetramers and homodimers. For the dissociation of $(\text{MeLi})_4 \rightarrow 2(\text{MeLi})_2$ in Et_2O $\Delta G_{238}^\ddagger = 48$ kJ mol⁻¹ was reported [34] and for the reaction $(\text{BuLi})_4 \rightarrow 2(\text{BuLi})_2$ in THF barrier values of 48 [35] and 46.9 [36] kJ mol⁻¹ at 238 K can be calculated from the reported activation parameters. $\Delta G_{238}^\ddagger = 50.4$ resulted for the dimer/tetramer exchange system of vinylithium [2f]. A much higher barrier of $\Delta G_{302}^\ddagger = 102 \pm 25$ kJ mol⁻¹ was, however, measured for the dissociation of $(t\text{-BuLi})_4$ in cyclopentane [34b][37]. It seems surprising that these values – except the last one – are comparable to the barriers discussed before for *intra*-aggregate or *fluxional* exchange. This suggests that the free-energy difference between the homodimers and the tetramer

⁶⁾ Preliminary investigations for the system BuLi/LiI (1:1) in Et_2O show that, aside from cluster **A**, cluster **B** ($X = \text{I}$) is the dominant species (B. Böhrer, H. Günther, unpublished).

intermediates of the (BuLi)/(PhLi)/TMEDA system is small, otherwise ΔG_{240}^\ddagger should be much higher. Alternatively, the barrier to *fluxional* exchange of Li in these tetramer intermediates could be much lower than that in the stable aggregates in order to fit the overall barrier of *ca.* 50 kJ mol⁻¹ that also includes the *formation* of the intermediates.

In all cases cited above, the tetramer is a stable, detectable species in contrast to the BuLi/PhLi/TMEDA system where the tetramers are short-lived intermediates that could only indirectly be detected by the EXSY experiment. We can assume that their instability is a consequence of the aggregation with the strong donor TMEDA, as it is known that, for example, BuLi tetramers are destabilized by this ligand [35]. An alternative interpretation follows a proposal made by *T. L. Brown* for the intermediate assumed in the dissociation of *t*-BuLi [34b]: instead of tetramers in the strict sense, the intermediates could be solvent-caged species of the type {(BuLi)₂(PhLi)₂}, {(BuLi)₂, BuLi, PhLi}, or {BuLi, PhLi, (PhLi)₂}. As a consequence, the barriers of formation and internal Li exchange could be much lower.

For the characterization of minor components of mixtures between organolithium compounds, and metal salts or other additives, the isotopic fingerprint method with deuterated and non-deuterated species, and ⁶Li enrichment is superior to the use of ¹³C spectroscopy and ¹³C,⁶Li coupling constants, because the nucleus of high natural abundance is measured, and ⁶Li labelling clearly does not suffer from the difficulties of ¹³C labelling. Deuteration of the ligands is generally easy to achieve. The EXSY results for the BuLi/PhLi mixture demonstrate again the advantage of the 2D over the 1D method, because in 1D spectra small exchange systems like $8 \rightleftharpoons 10$ may be completely masked by the exchange broadening of the larger lines.

We are indebted to Prof. Dr. *A. Maercker* for helpful comments, and to the *Fonds der Chemischen Industrie*, Frankfurt, for financial support.

Experimental Part

General. Butyl(Li⁶)lithium was prepared as hexane soln. from 1-chlorobutane by a standard procedure [5a] with commercially available ⁶Li. (α,α -D₂)[⁶Li]butyllithium was synthesized by the same procedure from 1,1-(D₂)butan-ol *via* 1-chloro[1,1-D₂]butane, available as described [38]. For the isotopic fingerprint measurements the mixtures of deuterated and non-deuterated BuLi were directly prepared from the appropriate mixtures of deuterated and non-deuterated chlorobutane. *Gilman* titrations [39] were used to determine the concentrations. The synthesis of ⁶Li enriched LiBr and LiClO₄ from LiOH and Li₂CO₃, resp., was accomplished as described in [40]. Salt-free PhLi was prepared according to [41], and for the partially deuterated samples we used bromobenzene/bromo[D₅]benzene (1:1) as starting materials as described in [2f].

The NMR tubes (5 mm) were carefully dried on the vacuum line and filled under Ar with the hexane solns. of the Li compounds and the appropriate amount of Li salts or TMEDA dissolved under Ar in O₂-free Et₂O, dried over Li[AlH₄]. The solvents were evaporated on the vacuum line from the frozen samples (acetone/liquid N₂) and then replaced at r.t. by the necessary amount of Et₂O/[D₁₀]Et₂O (4:1). After freezing again at liquid N₂ temp., the NMR tubes were sealed under vacuum.

Spectra. The NMR spectra were recorded with a *Bruker* 400 MHz NMR spectrometer with frequencies of 400.13, 100.62, and 58.88 MHz for ¹H, ¹³C, and ⁶Li, resp. The MLEV-16 sequence [42] was used for ¹H broadband decoupling. For the 2D and triple-resonance experiments a ¹H,¹³C, BB triple resonance probehead with appropriate frequency filters was employed. The *Bruker* low-temp. unit was used for variable-temp. spectra, and the temps. were measured with the MeOH thermometer. The ¹H- and ¹³C spectra were referenced to Me₄Si, ⁶Li spectra to 0.1M LiBr in [D₈]THF as external reference.

Additional ^1H -NMR data determined for the BuLi/PhLi mixture by a 2D-COSY-45 [43] experiment and not given in Table 3 are for the BuLi homodimer H_β 1.51, H_γ 1.20, H_δ 0.85 ppm and for the mixed dimer H_β 1.67, H_γ 1.30, H_δ 0.91 ppm; for the PhLi homodimer *m*-H 6.96, *p*-H 6.85 ppm and for the mixed dimer *m*-H 6.87, *p*-H 6.78 ppm. Spectral parameters: $^6\text{Li}, ^1\text{H}$ 2D-HOESY: SW 2551 Hz (F_1), 166 Hz (F_2), 22×64 scans, mixing time 1.5 s, exp. time 2.3 h; $^6\text{Li}, ^{13}\text{C}$ 2D-HMQC: SW 1008 Hz (F_1), 177 Hz (F_2), 32×128 scans, preparation delay 85 ms, exp. time 7.8 h; $^6\text{Li}, ^6\text{Li}$ 2D-EXSY: sweep width, 58.9 Hz (F_1 and F_2), 64 t_1 increments with 32 scans; mixing time, 1 s, time of experiment, 4.9 h. The isotopic fingerprint method [6] rests on the secondary D-induced isotope shift that yields for 1:1 mixtures of non-deuterated (h) and deuterated (d) ligands ^6Li -NMR signals in the environment LiR as 1:1 *doublet* (R = h or d), in the environment LiR₂ as 1:2:1 *triplet* (R₂ = hh, (hd, dh), dd), in the environment LiR₃ as 1:3:3:1 *quadruplet* (R₃ = hhh, (hhd, hdh, dhh), (hdd, dhd, ddh), ddd), and in the environment LiR₄ as *quintuplet* 1:4:6:4:1 (R₄ = hhhh, (hhhd, hhdh, hdhh, dhhh), (hhdd, hdhd, hddh, dhhd, dhhd, ddhh), (hddd, dhdd, ddhd, dddd).

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Received November 20, 2014