^{7}Li, ^{31}P, and ^{1}H Pulsed Gradient Spin-Echo (PGSE) Diffusion NMR Spectroscopy and Ion Pairing: On the Temperature Dependence of the Ion Pairing in Li(CPh$_3$), Fluorenyllithium, and Li[N(SiMe$_3$)$_2$] amongst Other Salts

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Abstract: ^{7}Li, ^{31}P, and ^{1}H variable-temperature pulsed gradient spin-echo (PGSE) diffusion methods have been used to study ion pairing and aggregation states for a range of lithium salts such as lithium halides, lithium carbanions, and a lithium amide in THF solutions. For trityllithium (**2**) and fluorenyllithium (**9**), it is shown that ion pairing is favored at 299 K but the ions are well separated at 155 K. For 2-lithio-1,3-dithiane (**13**) and lithium hexamethyldisilazane (LiHMDS **16**), low-temperature data show that the ions remain together. For the dithio anion **13**, a mononuclear species has been established, whereas for the lithium amide **16**, the PGSE results allow two different aggregation states to be readily recognized. For the lithium halides LiX (X = Br, Cl, I) in THF, the ^{7}Li PGSE data show that all three salts can be described as well-separated ions at ambient temperature. The solid state structure of trityllithium (**2**) is described and reveals a solvent-separated ion pair formed by a [Li(thf)$_4$]$^+$ ion and a bare triphenylmethide anion.

Keywords: aggregation · diffusion · lithium · NMR spectroscopy · X-ray diffraction

Introduction

Lithium reagents are widely used in both preparative inorganic and organic chemistry.[1] Regrettably, it is often the case that differing degrees of solvation and aggregation of the various lithium salts complicate the structural picture; for example, *tert*-butyllithium can be a monomer, a dimer, or a tetramer.[2] Since the chemistry of many lithium species depends on the details of the interaction between the lithium cation and the solvent,[3] understanding the solution structure of different lithium reagents is important for rationalizing and predicting their reactivity and selectivity.

The measurement of diffusion constants by pulsed gradient spin-echo (PGSE) NMR methods[4,5] has recently attracted increasing interest, as this technique provides data on molecular volumes and thus indirectly on molecular weights.[6] Several groups have used this approach to detect higher aggregation in, for example, a zirconium-based polymerization catalyst,[7] a Cu^{I} cluster catalyst precursor,[8] and an iron-based dendrimer,[9] as well as in the characterization of Pt molecular squares,[10] among others.[11,12] For salts of transition metals, ^{1}H NMR (and ^{19}F NMR) PGSE diffusion measurements on the cation and anion can provide insight into how these charged species interact. The diffusion constants derived for the individual cations and anions directly reflect interactions such as ion pairing between these species.[13–16] Ion pairing can prove both helpful[17] and detrimental[18] to the activity of different homogeneous catalysts. Naturally, the diffusion constants D will be strongly solvent-dependent[19] and, to a lesser extent, concentration-dependent.[20]

The combination of ^{7}Li NMR and PGSE methods is still relatively rare.[21,22] We note only two applications[21a,b] involving lithium diffusion studies in organometallic lithium carbanion chemistry. One of these (on *n*-butyllithium) involved the DOSY[21b] (diffusion-ordered NMR spectroscopy) and not PGSE methodology. We have recently communicated ^{7}Li PGSE results in connection with structural problems in lithium phosphide chemistry.[23] We report here a series of ambient- and low-temperature ^{7}Li, ^{31}P, and ^{1}H PGSE NMR

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. Eight figures showing ^{1}H and ^{7}Li PGSE results (without a correction for the gyromagnetic ratio), and a gHMQC correlation for **13** at 173 K with one figure.

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results on both simple lithium salts and several organolithium species in solution in THF. These new data, when combined with X-ray crystallography, provide novel insight into the question of ion pairing and, in general, on how solvated lithium cations interact with selected inorganic and organometallic anions.

Results and Discussion

Lithium halides: To begin with we consider the lithium halides, LiX. A vapor pressure osmometric study for LiCl suggests a ratio $MW_{apparent}/MW_{real}$ of 1.83.[24] A crystal structure of $[(LiCl)_4(hmpa)_4]$, (hmpa = hexamethylphosphoramide, $P(O)(NMe_2)_3$), has been reported;[25] however, the reaction of lithiated catechol with $[W(O)Cl_4]$ produced LiCl as a side product that crystallizes as the dinuclear species, $[(thf)_2Li(\mu\text{-}Cl)_2Li(thf)_2]$.[26] Furthermore, Reich and co-workers[27] categorize lithium chloride as a sturdy dimer according to HMPA titrations. Consequently, there is some question with respect to the structure of this simple salt.

LiBr is thought to contain about 80% monomeric species and 20% higher aggregates in THF ($MW_{apparent}/MW_{real}$ = 1.23).[24] LiI is considered to be monomeric in THF at room temperature.[24] Moreover, $[LiI(thf)_3]$, obtained from the reaction of LiH and iodine in THF, has a mononuclear structure in the solid state.[28]

To shed further light on the nature of these lithium halide interactions, we measured ^{7}Li PGSE NMR spectra for LiCl, LiBr, and LiI as 60 mM solutions in THF.[29] Table 1 and Figure 1, which show the D values and diffusion data for these, reveal that the cations of all three salts afford identical D values within the experimental error. The observed ^{7}Li chemical shifts are in agreement with ionic Li^+ and the narrow $^7Li^+$ line widths suggest a symmetric environment for this metal cation in all three salts. Clearly, the tetrasolvated cation is the most stable in THF. The hydrodynamic radii r_H, shown in Table 1, were obtained by using the experimental D values together with the Stokes–Einstein equation,[30] and suggest a relatively small solvated cation, such as $[Li(thf)_4]^+$. The viscosity of the (nondeuterated) THF at room temperature was taken from the literature.[31]

Table 1. D [$\times 10^{10}$ m^{2}s^{-1}] and r_H [Å] values[a] for LiX in THF at ambient temperature.

	Nucleus	D[b]	r_H[c]	r[d]	δ (^{7}Li)	$\Delta\nu_{1/2}$
LiCl	^{7}Li	11.1	4.3	4.7	0.48	2.2
LiBr	^{7}Li	11.1	4.3	4.7	0.59	2.4
LiI	^{7}Li	11.2	4.3	4.7	0.48	2.2
HMPA	^{31}P	15.3	3.1	3.0		
	^{1}H	15.3	3.1			
LiCl + HMPA	^{7}Li	9.87	4.8		0.36	3.8
	^{1}H	14.9	3.2	3.0		
	^{31}P	14.9	3.2			
LiCl (20 mM)	^{7}Li	11.4	4.2			
LiCl (60 mM)	^{7}Li	11.1	4.3			
LiCl (100 mM)	^{7}Li	10.8	4.4			

[a] 60 mM solutions, unless otherwise stated. [b] Experimental error is about ±2%; about ±0.06 10^{-10} m^{2}s^{-1}. [c] Standard deviation is about ±0.1 Å. [d] Estimated by using Chem3D, by averaging the distances between the centroid and the outer hydrogen. η (THF, 299 K) = 0.461 Kg s^{-1}m^{-1}.

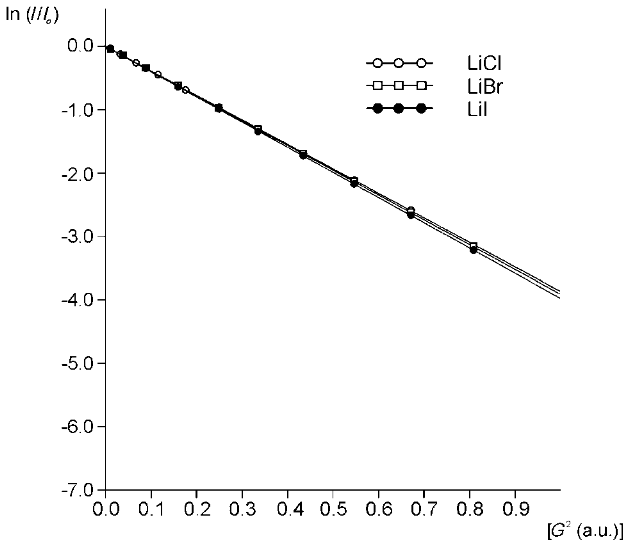


Figure 1. Plot of the $\ln(I/I_o)$ versus arbitrary units proportional to the square of the gradient amplitude for ^{7}Li PGSE NMR diffusion measurements on 60 mM LiX (X = Cl, Br, and I) samples at ambient temperature in THF (^{7}Li: δ = 4 ms; Δ = 70 ms).

Although the local environment about the lithium center is clear, the nature of the solvated halogen remains open. To shed some light on this we have measured the ^{35}Cl NMR spectrum of a LiCl solution in THF (Figure 2), along with

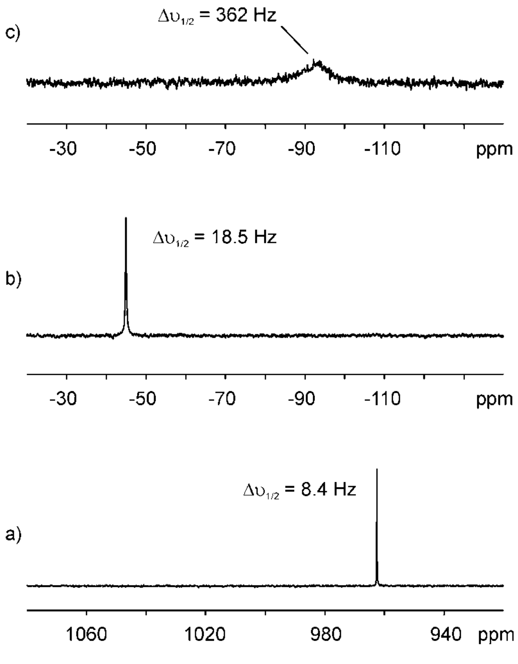


Figure 2. ^{35}Cl NMR spectra (48.99 MHz) at 299 K for 60 mM solutions of a) $LiClO_4$ in D_2O, δ = 962.5 ppm, b) LiCl in D_2O, δ = −45.0, and c) LiCl in [D$_8$]THF δ = −93.2 ppm. General conditions: spectral width = 19596 Hz; repetition delay = 100 ms; 1024 scans; 12 min per spectrum.

two model measurements for 60 mM solutions of $Li(ClO_4)$ and LiCl in water. The marked increase, relative to the aqueous model salts, of the ^{35}Cl line width in THF to 362 Hz suggests that the chloride is no longer in a symmetric environment, perhaps owing to a small percentage of ion pairing.[32]

Table 1 also shows the concentration dependence of the *D* values for samples of LiCl in the 20–100 mM range. The decrease in the diffusion coefficient when the concentration is increased (ca. 7.7%) arises from both aggregation and solvent viscosity effects and is in the range observed by us previously.[20,33]

HMPA is a highly polar, aprotic solvent that has been employed as an additive in lithium chemistry.[34,35] Its usefulness stems from its ability to strongly coordinate the amide oxygen atom to lithium to afford $[Li(hmpa)_n]^+$. The various ^7Li, ^1H, and ^{31}P PGSE data for 60 mM solutions of lithium chloride containing 12 equivalents of HMPA at ambient temperature in THF are also given in Table 1. The agreement between the ^1H and ^{31}P PGSE data provides a check on the reliability of the ^7Li results in that these nuclei reside within the same cation, assuming HMPA complexation.

The coordination of the larger HMPA, in place of THF, to the lithium center slows the translation of the lithium cation and produces a decrease in the ^7Li *D* value ($\Delta D = -1.23\times10^{-10}\,m^2s^{-1}$). Because of equilibrium effects, the movement of the HMPA is slowed as well. As expected, the ^1H, ^7Li, and ^{31}P NMR spectra all show single resonances, owing to facile ligand exchange at ambient temperature.

To suppress the dynamics, a 60 mM solution of LiCl in THF (without HMPA) was cooled to 155 K and studied. Decreasing the temperature had only a small effect on the appearance of the 1D ^7Li NMR spectra for the lithium chloride/THF sample. The observed ^7Li line width at 155 K, $\Delta\nu_{1/2} = 4.1$ Hz, is only slightly larger than that found at 299 K, $\Delta\nu_{1/2} = 2.2$ Hz. The *D* value at 155 K (see Table 2) is much smaller, owing to the increased solution viscosity; however, as this viscosity value has been estimated previously,[23] the radius r_H, calculated from the Stokes–Einstein equation,[30] indicates that the lithium environment is unchanged relative to the ambient-temperature diffusion data.

Table 2. D [$\times10^{10}\,m^2s^{-1}$] and r_H [Å] values[a] in THF at 155 K.

	Nucleus	D[b]	r_H[c]	r[d]	δ (^7Li)	$\Delta\nu_{1/2}$
LiCl	^7Li	0.252	4.3	4.7	0.55	4.1
HMPA	^1H	0.351	3.1	3.0		
	^{31}P	0.350	3.1			
		LiCl + HMPA				
Solvated LiCl	^7Li	[e]			0.14	14.6
	^1H[f]	0.351	3.1			
	^{31}P[f]	0.352	3.1			
$[Li(hmpa)_4]^+$, **1**	^7Li	0.142	7.7	6.7	−0.18	17.6
	^1H	0.142	7.7			
	^{31}P	0.140	7.8			

[a] 60 mM solutions. [b] Experimental error is about ±2%. [c] Standard deviation is about ±0.1 Å. [d] Estimated by using Chem3D, by averaging the distances between the centroid and the outer hydrogen. [e] Not obtained. [f] Free HMPA. η (THF, 155 K) $= 10.431\times10^{-3}\,Kg\,s^{-1}m^{-1}$.

For the LiCl sample with 12 equivalents of HMPA at 155 K, Figure 3 shows two ^7Li signals, $\delta = 0.14$ and -0.18 ppm. The low-frequency resonance appears as a resolved quintet (^2J(P, Li) = 7.6 Hz) owing to the spin-spin coupling of the four ^{31}P atoms of the coordinated HMPA, and thus can be assigned to the $[Li(hmpa)_4]^+$ ion **1**. The remaining signal arises from solvated LiCl. Below 173 K, the ^1H NMR spectrum of this sample reveals two methyl resonances at $\delta = 2.74$ and 2.68 ppm, with the higher frequency signal corresponding to coordinated HMPA. The ^{31}P NMR spectrum shows a new signal at $\delta = 27.36$ ppm ($^2J_{P,Li} = 7.6$ Hz), which is assigned to the $[Li(hmpa)_4]^+$ ion **1**. The corresponding $^{31}P,^{31}P$ 2D exchange spectrum (Figure 4a) clearly shows that, despite the observed multiplicity on the high-frequency signal, the solvent HMPA is *still exchanging* with the complexed HMPA at 155 K. Figure 4b shows an $^1H,^{31}P$ gHMQC spectrum, which permits the assignment of the methyl groups in the complexed HMPA.

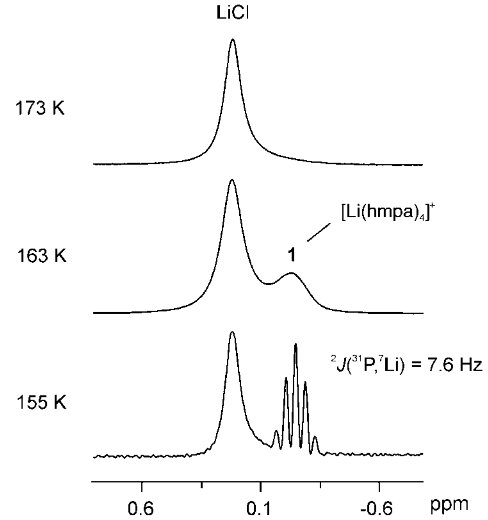


Figure 3. Variable-temperature ^7Li NMR of a 60 mM LiCl solution in THF with 12 equivalents of HMPA added (155.45 MHz).

Table 2 also provides data from the ^1H, ^7Li, and ^{31}P PGSE measurements at 155 K for the HMPA sample, as well as data for the 60 mM reference solution of HMPA. From these low-temperature data we calculate an r_H value of about 7.7 Å in THF for the $[Li(hmpa)_4]^+$ ion. The solid-state structure of $[Li(hmpa)_4]^+$ has been described.[36] From these X-ray data one can estimate the rotational radius[37] to be about 6.7 Å. This discrepancy is to be expected, as the solid-state *r* value does not involve a solvent shell. In any case the PGSE results confirm the simple mononuclear cationic structure in solution.

Lithium triphenylmethane (2): Lithium triphenylmethane, $LiCPh_3$ **2**, has been studied previously by UV spectroscopy,[38] various NMR methods,[39] and X-ray crystallography.[40] These studies demonstrate that the $LiCPh_3$ salt should be considered as a solvent-separated salt in solution, and that

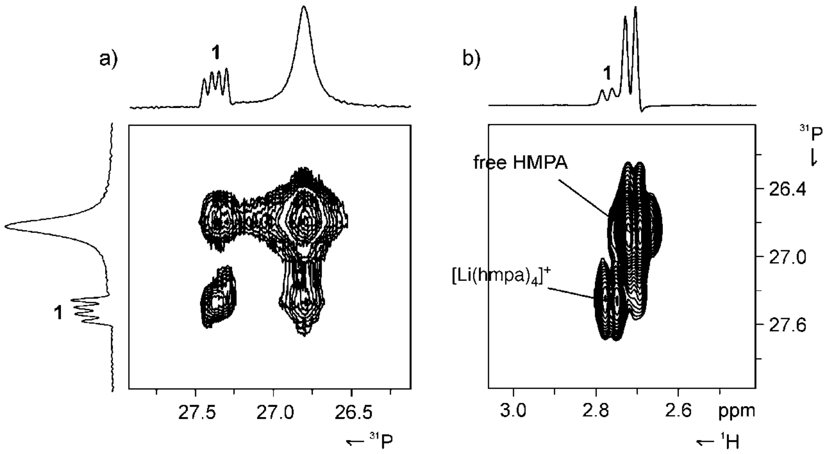


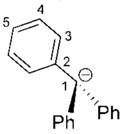
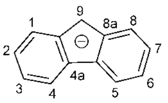
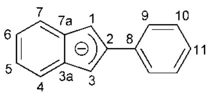
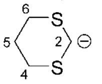
Figure 4. a) 2D ^{31}P,^{31}P EXSY NMR (161.92 MHz) and b) 2D gHMQC (400.13 MHz) of the 60 mM sample LiCl plus HMPA in THF at 155 K. The [Li(hmpa)$_4$]$^+$ ion is indicated as **1**.

decreasing the temperature generally favors the separated ions.[41] However, Bauer and Lochmann[42] report a ^{7}Li,^{1}H HOESY contact for this salt (0.35 M) in THF at room temperature, which implies some (perhaps only brief) contact.

Table 3 shows our ^{1}H and ^{13}C NMR data for LiCPh$_3$ at 299 K in THF. These data are in good agreement with those reported by Sandel and Freedam,[39a] and later by Jackman et al.[39b] The ^{13}C chemical shift of the anionic carbon, δ = 90.1 ppm, is found at higher frequency than that of the sp^3-hybridized precursor, δ = 57.3 ppm, in analogy with the known ^{13}C data for the *ipso*-carbon atom of phenyllithium[43] and other metalated phenyl derivatives.[44] The low-frequency shift of C-4 is consistent with delocalization of some negative charge into the phenyl rings.

Tables 4 and 5 show the PGSE results for 60 mM solutions of LiCPh$_3$ and HCPh$_3$ in THF at both ambient temperature and 155 K. The equivalence of the experimental *D* values for both the cation and anion in LiCPh$_3$ at 299 K indicates strong ion pairing. Moreover, the calculated r_{H} value of 6.4 Å is much larger than that expected for either the isolated [Li(thf)$_4$]$^+$ ion or the triphenylmethide anion. Our PGSE data do not allow us to distinguish between a contact ion pair (CIP) with, perhaps, fewer than four THF solvent molecules, and a solvent-separated ion pair (SSIP). Howev-

Table 3. ^{1}H and ^{13}C NMR data[a] for LiCPh$_3$, LiC$_{13}$H$_9$, Li(2-Ph)C$_9$H$_7$, and LiC$_4$H$_7$S$_2$ in THF at 299 K.

	Site	^{1}H	$J_{\mathrm{H,H}}$	^{13}C
LiCPh$_3$ **2**				
	1	–	–	90.1 (57.3)
	2	–	–	149.7 (144.6)
	3	7.40 (7.20)	8.6, 1.2	123.8 (129.7)
	4	6.60 (7.34)	8.6, 7.0	127.5 (128.4)
	5	6.04 (7.26)	7.0, 1.2	112.5 (126.4)
LiC$_{13}$H$_9$ **9**				
	1, 8	7.37 (7.62)	8.0, 0.9	116.1 (125.2)
	2, 7	6.87 (7.35)	8.0, 6.6, 1.1	119.0 (126.9)
	3, 6	6.50 (7.43)	7.7, 6.6, 0.9	108.1 (126.9)
	4, 5	7.98 (7.90)	7.7, 1.1	118.6 (120.0)
	4a	–	–	123.2 (143.6)
	8a	–	–	137.7 (142.2)
	9	5.98 (3.97)		65.8 (36.9)
Li(2-Ph)C$_9$H$_7$ **10**				
	1, 3	6.38 (3.91, 7.40)		88.2 (39.0, 126.6)
	2	–	–	128.6 (136.5)
	4, 7	7.30 (7.44, 7.55)		117.2 (121.0, 123.7)
	5, 6	6.44 (7.31, 7.23)		111.58 (126.7, 124.9)
	3a, 7a	–	–	129.5 (145.8, 143.6)
	8	–	–	141.2 (146.8)
	9	7.79 (7.80)	8.4, 1.4	128.6 (125.8)
	10	7.22 (7.45)	8.4, 7.2	129.5 (128.8)
	11	6.93 (7.33)	7.2, 1.4	120.5 (127.6)
LiC$_4$H$_7$S$_2$ **13**				
	2	2.75 (3.79)		25.5 (27.1)
	4,6	2.33 (2.81)		33.6 (31.7)
	5	2.07 (2.03)		30.8 (29.9)

[a] The spectral data for the neutral precursor are given in parentheses.

Table 4. D [$\times 10^{10}$ m^{2}s^{-1}] and r_H [Å] values[a] in THF at 299 K.

	Nucleus	D[b]	r_H[c]	r[d]	δ (^{7}Li)	$\Delta\nu_{1/2}$
LiCPh$_3$ **2**	^{7}Li	7.40	6.4		−0.45	10.2
	^{1}H	7.38	6.4			
HCPh$_3$	^{1}H	12.5	3.8	4.0		
LiFlu **9**	^{7}Li	8.85	5.4		−1.44	13.8
	^{1}H	8.81	5.4			
HFlu	^{1}H	17.44	2.7	3.2		
LiInd **10**	^{7}Li	8.89	5.3		−3.24	5.0
	^{1}H	9.16	5.2			
HInd	^{1}H	15.96	3.0	3.9		
HDith	^{1}H	20.17	2.4	2.6		
LiHMDS **16**	^{7}Li	11.4	4.2		0.78	11.0
60 mM	^{1}H	11.3	4.2			
LiHMDS[e] **16**	^{7}Li	9.51	5.0		1.10	32.6
600 mM	^{1}H	9.55	5.0			
HMDS		16.7	2.8	3.2		
TMSS		10.9	4.3	4.4		

[a] 60 mM solutions unless otherwise noted. [b] Experimental error is about ±2%. [c] Standard deviation is about ±0.1 Å. [d] Estimated by using Chem3D, by averaging the distances between the centroid and the outer hydrogen. [e] Measurements obtained in a 0.6 M sample using a coaxial NMR tube (ID = 1.96 mm; OD = 2.97 mm) separated by a spacer. η (THF, 299 K) = 0.461×10^{-3} Kg s^{-1}m^{-1}.

Table 5. D [$\times 10^{10}$ m^{2}s^{-1}] and r_H [Å] values[a] in THF at 155 K.

	Nucleus	D[b]	r_H[c]	r[d]	δ (^{7}Li)	$\Delta\nu_{1/2}$
LiCPh$_3$ **2**	^{7}Li	0.224	4.9		−0.41	2.6
	^{1}H	0.258	4.2			
HCPh$_3$	^{1}H	0.282	3.9	4.0		
LiFlu **9**	^{7}Li	0.223	4.9		−1.13	2.8
	^{1}H	0.253	4.3			
HFlu	^{1}H	0.396	2.8			
LiDith[e] **13**	^{7}Li	5.23	4.4		0.11	3.6
252 K	^{1}H	5.22	4.4			
HDith[e]	^{1}H	9.31	2.4	2.6		
252 K						
LiDith **13**	^{7}Li	[f]			0.16	19.5
	^{1}H	0.245	4.5			
HDith	^{1}H	0.447	2.4	2.6		
LiHMDS[e,g] **16**						
mononuclear	^{7}Li	5.14	4.3		0.66	8.5
250 K	^{1}H	5.17	4.3			
dinuclear	^{7}Li	4.32	5.3		1.33	9.8
250 K	^{1}H	4.26	5.3			
HMDS[e,g]	^{1}H	7.83	2.8	3.2		
250 K						
TMSS	^{1}H	0.233	4.3	4.4		

[a] 60 mM solutions unless otherwise noted. [b] Experimental error is about ±2%. [c] Standard deviation is about ±0.1 Å. [d] Estimated by using Chem3D, by averaging the distances between the centroid and the outer hydrogen. [e] A coaxial NMR tube (ID = 1.96 mm; OD = 2.97 mm) separated by a spacer was used. [f] Not obtained. [g] 0.60 M; η (THF, 155 K) = 10.431×10^{-3} Kg s^{-1}m^{-1}; η (THF, 250 K) = 0.825×10^{-3} Kg s^{-1}m^{-1}; η (THF, 252 K) = 0.801×10^{-3} Kg s^{-1}m^{-1}.

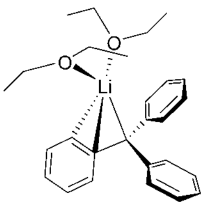
er, we note that the ^{7}Li line width is only slightly broader ($\Delta\nu_{1/2}$ = 10.2 Hz) than that of the [Li(thf)$_4$]$^+$ ion as a Cl$^-$ salt ($\Delta\nu_{1/2}$ = 2.2 Hz), suggesting that the local symmetry at the lithium ion has not changed drastically.

The low-temperature NMR measurements for **2** were both informative and surprising. In contrast to many organolithium compounds, the methanide ^{13}C chemical shift changes by less than 1 ppm between 298 and 155 K. Further, the absence of a detectable ^{13}C,^{7}Li coupling constant over the whole range of temperatures strongly suggests an ionic, as opposed to a covalent, interaction between these two atoms. The ^{7}Li line width, $\Delta\nu_{1/2}$ = 2.6 Hz, is even smaller than that observed at ambient temperature ($\Delta\nu_{1/2}$ = 10.2 Hz), despite the more viscous solvent, which suggests tetrahedral symmetry at the lithium atom.

The ^{1}H and ^{7}Li PGSE data at 155 K show differing rates of translation for the lithium and triphenylmethide moieties and thus smaller and different r_H values of 4.9 and 4.2 Å, respectively. These results imply little or no interaction between these ions at this temperature. The cation and anion are translating independently (thus explaining the smaller line width of the lithium signal) with the 4.9 Å value in good agreement with our expectation for the [Li(thf)$_4$]$^+$ ion. It would appear that, at low temperature in THF solution, mobile ions are favored, whereas at ambient temperature the ions pair strongly. There is no temperature at which covalent bonding between the Li and the anionic carbon is preferred. We shall offer an explanation for this temperature dependence after discussing all of the remaining salts.

We have found three X-ray structures in which a Li(CPh)$_3$ moiety is involved.[40] Compounds **3** and **4** were crystallized from Et$_2$O and n-hexane solution, respectively. Complex **5** was prepared from THF using two moles of crown ether per mole of triphenyl derivative. The solid-state structure of LiCPh$_3$ prepared from THF is not known.

To complement the diffusion data for LiCPh$_3$, we allowed HCPh$_3$ to react with nBuLi in THF at −30 °C for 60 min. Addition of n-pentane to the red solution, followed by storage overnight at RT, afforded air-sensitive crystals of



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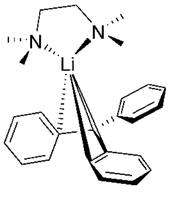

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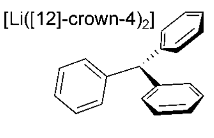

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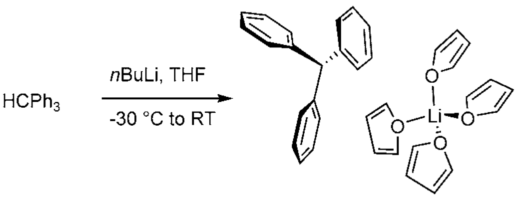
[{Li(THF)$_4$}(CPh$_3$)] **2** suitable for X-ray diffraction (see [Eq. (1)]). Compound **2** is quite stable for several weeks in the absence of air or moisture.



(1)

The X-ray crystal structure determination[45] of **2** (Figure 5) supports the description of the proposed solvent-separated ion pair (SSIP) in which one half of the "free" Ph$_3$C$^-$ carbanion, as well as the cationic [Li(thf)$_4$]$^+$ moiety, are generated by crystallographic twofold symmetry. The main structural feature in the carbanion Ph$_3$C$^-$ is the presence of a central trigonal-planar carbon atom (C1), which allows delocalization of the negative charge into the adjacent rings.[46] This feature is observed in almost all carbanionic moieties attached to heterocycles or phenyl rings reported so far in the literature (e.g., Ph$_3$C$^-$,[40b,47] Ph$_2$pyC$^-$,[48] or py$_2$CH$^-$,[49] with py = pyridyl). The planes of the phenyl rings deviate from the ideal planar alignment (~22.2° for Ph1 and Ph1′ and ~26.4° for Ph2). Consequently, the carbanion reveals a propeller-like structure. The average of the three C1–C$_{ipso}$ bond lengths, about 1.45 Å, is in excellent agreement with those values found in the structure of **5**, 1.45 Å, in which all three separations are identical.

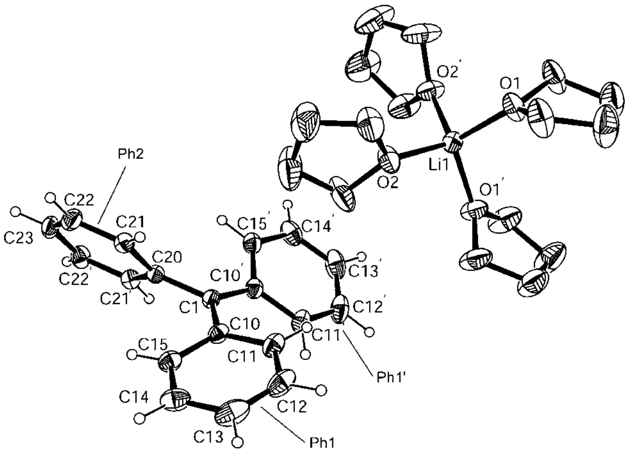
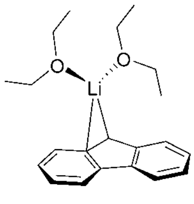


Figure 5. Molecular structure and numbering scheme for [{Li(thf)$_4$}(CPh$_3$)] (**2**). The thermal ellipsoids are drawn at a 30 % probability level. Hydrogen atoms of the THF molecules have been omitted for clarity. Selected bond lengths [pm] and angles [°]: C1–C10 144.2(2), C1–C20 147.2(3), Li1–O1 189.7(3), Li1–O2 190.3(4); C11-C10-C15 113.9(2), C21-C20-C21′ 115.3(2), C10-C1-C10′ 123.7(2), C10-C1-C20 118.1(1); (equivalent atoms generated by $-x+1$, $-y+2$, z and $-x$, $-y+2$, z).

The structure of [(Li([12]crown-4)$_2$](CPh$_3$) (**5**), can also be thought of as a separated ion pair in which the average angle of the propeller ring conformation is 31.2°, similar to that found for **2**. Consequently, the diffusion data at 155 K, together with the X-ray structure for **2**, support separated ions.

Fluorenyllithium (9): Fluorenyllithium has been extensively studied. Ultraviolet-visible[3a,50] and conductivity[3a,51] measurements suggest that this salt forms a solvent-separated ion pair (SSIP) in THF at temperatures below −30 °C, and is predominantly ion paired when the temperature is above 25 °C. These findings were corroborated by Edlund using ^{13}C NMR spectroscopy[52] and later on by Schleyer and Bauer[53] by using a ^{6}Li,^{1}H HOESY NMR approach. Only five X-ray examples of fluorenyllithium (**9**) have been reported.[54] Of these, the most relevant to the present discussion are the diethyl ether complex, [C$_{13}$H$_9$Li(Et$_2$O)$_2$][54c] (**6**), the quinuclidine salt, [C$_{13}$H$_9$Li(NC$_7$H$_{13}$)$_2$][54a] (**7**), and the diglyme complex [Li(C$_{13}$H$_9$)(diglyme)$_2$] (**8**).[54e] Salts **6** and **7** are thought to be CIPs, whereas **8** has been characterized as an SSIP.



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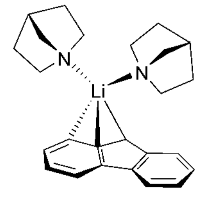

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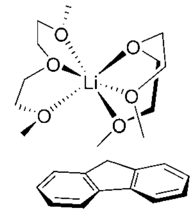

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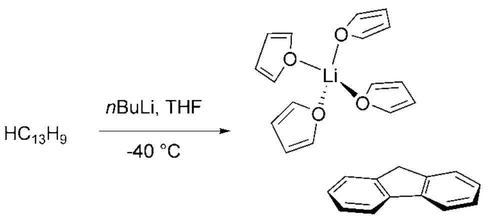
Fluorenyllithium **9** in THF solution could be prepared in an analogous fashion to that used for **2**. ^{13}C and ^{1}H NMR data for **9** are also shown in Table 3. In the ^{13}C NMR spectrum the anionic carbon resonance is found at δ = 65.8 ppm. This represents a high-frequency shift relative to the neutral precursor at δ = 36.9 ppm. These ^{13}C and ^{1}H NMR data are in complete agreement with those described in the literature.[52,55]

The ^{1}H and ^{7}Li PGSE results for a 60 mM solution of **9** in THF at ambient temperature are given in Table 4. The equivalent D values for both the anion and cation point to an ion pair in THF solution. The ^{7}Li line width of 13.8 Hz is, once again, slightly broader, in agreement with our observations for **2**. From the X-ray structure of $[C_{13}H_9Li(Et_2O)_2]$ **6**, one can estimate a rotational radius of 4.9 Å. Therefore, the 5.4 Å r_H value based on the measured D value is satisfactory. Consequently, we suggest that the fluorenyllithium (**9**) exists as a mononuclear ion pair at 299 K in THF. The D and r_H values for a 60 mM sample of the neutral precursor (HFlu) in THF are also shown. Diffusion data from a solution of **9** at 155 K gave r_H values of 4.9 Å and 4.3 Å for the cation and anion respectively. These data point again to well-separated ions ($\Delta\nu_{1/2} = 2.8$ Hz) under these conditions. We assume that the increase in the size of the anion relative to the r_H value for fluorene (HFlu) is related to a solvent shell.

Crystals of fluorenyllithium were obtained by treatment of fluorene with *n*BuLi in THF at −60 °C for 10 min and then subsequent layering of the orange solution with *n*-pentane at −40 °C for 12 h (see [Eq. (2)]). Diffraction studies on these air-sensitive, low-melting (m.p. ca. −30 °C) crystals support the formulation $[C_{13}H_9Li(thf)_4]$; however, apart from determining the unit cell and recognizing the $[Li(thf)_4]^+$ ion, the data could not be satisfactorily refined owing to disorder.

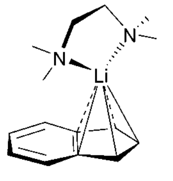


(2)

(2-Phenyl)indenyllithium (10): The indenyl anion represents yet another interesting model system for solvation and ion-pairing studies because of its rigidity and thermal stability. Its lithium salts have been extensively investigated by UV-visible,[56] NMR,[39b,52a,57] and X-ray methods.[58] Table 3 shows our ^{13}C and ^{1}H NMR data for the 2-phenyl derivative **10**. The ^{1}H and the ^{13}C spectra show six and nine individual resonances, respectively, as would be expected from a structure possessing a mirror plane. In the ^{13}C spectrum the observed C-2 ($\delta = 128.6$ ppm) and C-1,3 ($\delta = 88.2$ ppm) resonances (see Table 3) are in accord with what is found for other η^3-C_9H_7 derivatives.[59]

Only two X-ray structures of indenyllithium derivatives have been reported. Both were described as contact ion pairs.[58] For the TMEDA salt $[C_9H_7Li(N_2C_6H_{16})]$ (**11**),[58a] the lithium atom is coordinated to one bidentate TMEDA molecule and to the indenyl group with an equal distance of 2.377 Å. On the other hand, the salt **12**,[58b] crystallized in THF, shows a lithium cation coordinated by three molecules of THF.

Table 4 shows *D* and r_H values for **10** at 299 K. The r_H values for cation and anion, 5.3 Å and 5.2 Å, respectively, are almost identical. The r_H value of 5.3 Å, based on the measured *D* value, is satisfactory when compared to the *r* values estimated from the x-ray structures of **11** and **12** (4.6 and 5.0 Å, respectively). Consequently, we suggest that the (2-phenyl)indenyllithium species **10** exists as a mononuclear ion pair in THF. The *D* and r_H values for a 60 mM sample of the neutral precursor (HInd) in THF are also shown in Table 4.



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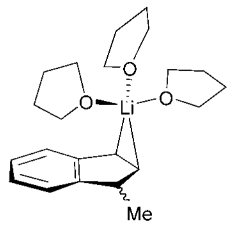
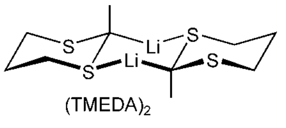


12

2-Lithio-1,3-dithiane (13): There is considerable evidence that the anionic carbon of 2-lithio-1,3-dithiane (**13**) is sp^3-hybridized and very localized. This conclusion is supported by the low-frequency ^{13}C chemical shift of the lithiated carbon ($\delta = 25.8$ ppm) relative to the neutral precursor ($\delta = 31.7$ ppm).[60,61] Low-temperature (173 K) ^{13}C NMR measurements on 2-(^{6}Li)lithio-2-(^{13}C)-dithiane, reported by Seebach and coworkers[61] reveal a triplet, $J(^6Li, ^{13}C) = 10.1$ Hz, for C-2. As this multiplicity implies a single ^{6}Li atom, **13** must be either a mononuclear salt or a dinuclear aggregate with the two components held together by an S−Li−C bridge. Cryoscopic measurements[62] in THF confirm that the 2-methyl derivative of **13** is mononuclear. The HMPA titration technique has been applied to **13** and reveals a contact ion pair (CIP).[63]

X-ray crystal structures for the lithium-bridged dinuclear 2-methyl-2-lithiodithiane TMEDA (**14**)[64] and the mononuclear salt, [(2-phenyl-2-lithiodithiane)(tmeda)(thf)] (**15**)[65] have been described previously.



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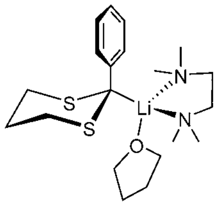


15

To the best of our knowledge the THF solution structure of **13** is as yet unknown. Salt **13** is not stable in THF at 299 K but is stable at 252 K. Our ^{13}C data (δ anionic CH = 25.5 ppm, $^1J(^{13}C, ^1H)$ at 173 K = 132.5 Hz) are in agreement with those reported by Seebach et al..[61] Variable-temperature ^{7}Li spectra reveal a significant temperature dependence of the line width (Figure 6) with $\Delta\nu_{1/2}$ at 173 K = 15.3 Hz relative to 3.6 Hz value at 253 K.[66]

Table 5 gives diffusion data for **13** in THF at 252 K and reveals that ion pairing persists at this temperature (r_H = 4.4 Å for both ions[30]). At 155 K the ^{7}Li resonance is even broader than at 173 K, $\Delta\nu_{1/2} = 19.5$ Hz, and the longitudinal

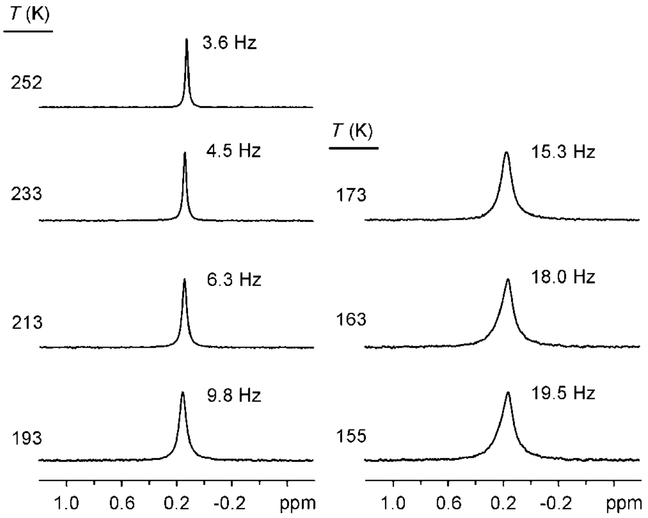
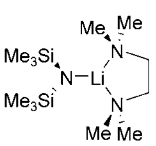


Figure 6. Variable-temperature ^{7}Li NMR spectra of a 60 mM solution of lithium-1,3-dithiane **13** in THF (the ^{7}Li line widths $\Delta\nu_{1/2}$ are indicated).

relaxation time, T_1 = 32 ms, is rather short. Consequently, only the ^{1}H D value was obtained. Nevertheless, the r_H value of 4.5 Å at 155 K, is similar to that found at 252 K and suggests that the two ions remain close. This r_H of 4.5 Å, although smaller[30] than the 5.0 Å estimated for **15**, suggests that, in THF solution, the 2-lithio-1,3-dithiane **13** exists as a mononuclear species. The D and r_H values for a 60 mM sample of the neutral precursor (HDith) in THF are also shown in Tables 4 and 5.

Lithium hexamethyldisilazide Li[N(SiMe$_3$)$_2$]: It was reported early on that Li[N(SiMe$_3$)$_2$] (**16**) demonstrates a mononuclear/dinuclear equilibrium in THF.[67] Subsequent studies using ^{6}Li and ^{15}N-labeled Li[N(SiMe$_3$)$_2$],[68] confirmed the earlier conclusions. Solid-state structures of Li[N(SiMe$_3$)$_2$] aggregates containing oxygen or nitrogen polydentate ligands reveal the existence of both mononuclear and dinuclear solvated species. The most relevant for our discussion are the mononuclear structures **17** and **18**, containing TMEDA and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine, respectively,[69] and the bridged mono-solvated dinuclear salt **19**.[70]



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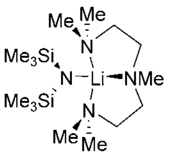

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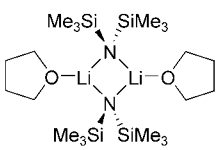

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The position of the equilibrium for [Li{N(SiMe$_3$)}$_2$] in THF is recognized to be a function of concentration.[67] The observed mononuclear/dinuclear ratio for a 0.69 M sample is 51:49; for a 0.069 M solution, this ratio changes to 88:12.[67] For this reason, two samples of different concentration, 0.060 M and 0.60 M were prepared. At room temperature the ^{1}H NMR of a 0.060 M solution of Li[N(SiMe$_3$)$_2$] in THF consists of a sharp singlet at δ = −0.09 ppm, whereas in the ^{7}Li NMR spectrum a single resonance with a line width of $\Delta\nu_{1/2}$ = 11.0 Hz at δ = 1.10 ppm is found. For the 0.6 M sample, the observed lithium resonance was considerably broader, $\Delta\nu_{1/2}$ = 32.6 Hz (see Table 4). ^{1}H and ^{7}Li PGSE diffusion data for the two concentrations, 0.060 M and 0.60 M, at 299 K are given in Table 4.

When the temperature for the 0.6 M sample is decreased (see Figure 7), two distinct species are observed in both ^{1}H and ^{7}Li NMR spectra. Integration of the ^{1}H NMR spectrum afforded a mononuclear/dinuclear ratio of 44:56. ^{1}H and ^{7}Li PGSE measurements at 250 K,[71] a temperature at which the two lithium resonances are relatively sharp, gave the diffusion data shown in Table 5. Representative ^{7}Li diffusion data for the 0.6 M sample are shown in Figure 8. From the X-ray structure of model **19**, we can estimate a radius of about 5.6 Å. We find a D value for the mononuclear salt that corresponds to a fairly small r_H value of 4.3 Å.[31] The D value for the presumed dinuclear species affords an r_H value of 5.3 Å, which is much closer to the 5.6 Å suggested from the solid-state study on **19**. To the best of our knowledge this represents the first application of ^{7}Li PGSE measurements to the recognition of different lithium aggregates in solution, in this case mononuclear and dinuclear lithium amides.

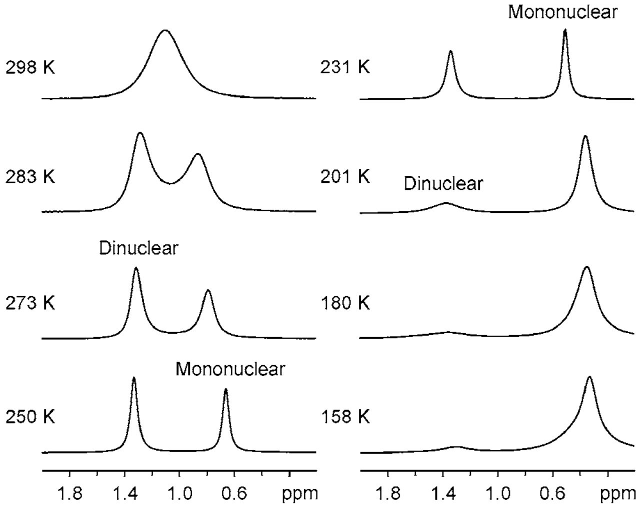

Figure 7. Variable-temperature ^{7}Li NMR spectra of a 0.6 M solution of LiHMDS **16** in THF (155.45 MHz).

Conclusion

These various lithium salts nicely show that PGSE methods are quite useful for recognizing ion pairing (or the lack thereof) and aggregation in THF solution. For several of the organolithium species it is now clear that ion pairing is fa-

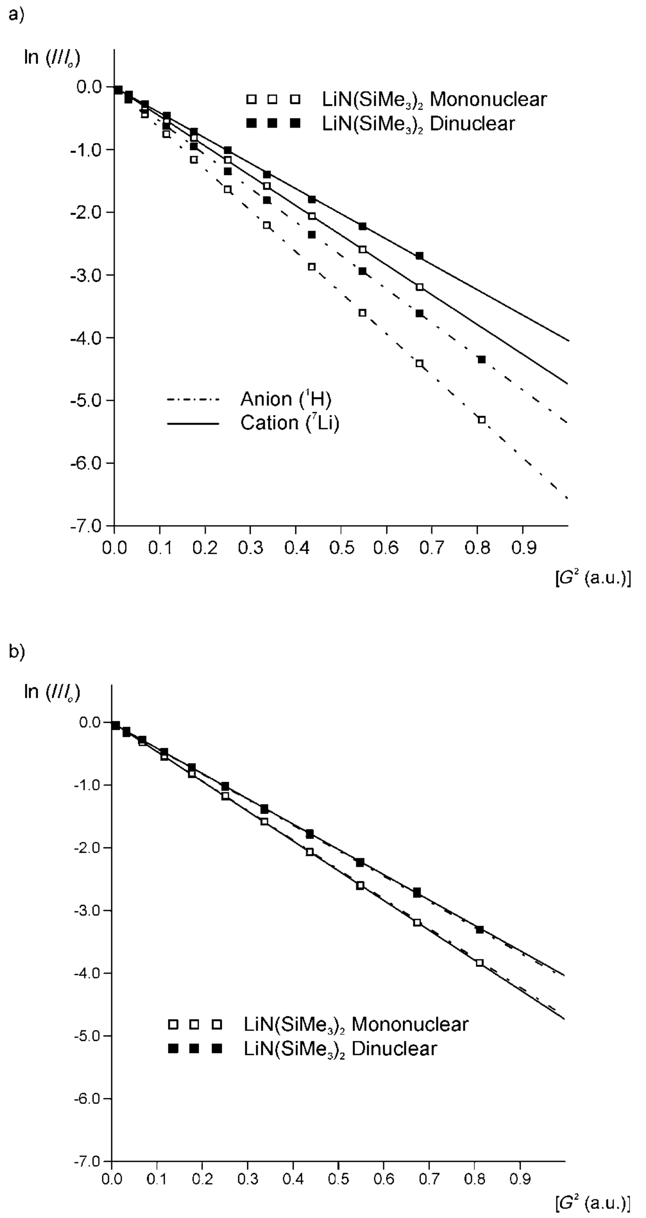

Figure 8. a) Plot of the $\ln(I/I_o)$ versus arbitrary units proportional to the square of the gradient amplitude for ^{1}H (anion) and ^{7}Li (cation) PGSE diffusion measurements on a 0.6 M sample of LiHMDS (HMDS = $N(SiMe_3)_2$) in THF solution at 250 K. ^{1}H (δ = 3 ms; Δ = 69 ms); ^{7}Li (δ = 11 ms; Δ = 28 ms); b) After correcting for the gyromagnetic ratio of ^{7}Li, Δ and δ, the slopes observed for the ^{1}H and ^{7}Li measurements are identical within the experimental error.

vored at 299 K but the ions are well separated at 155 K; however for the dithianyl salt **13**, the low-temperature data show that the ions remain together. The explanation for the observed temperature dependence of the ion pairing is not completely clear; however, it is known[72] that the dielectric constant of THF increases markedly (more than doubles!) on cooling from ambient temperature to 155 K. Consequently, we assign the increased stability of the separated ions at 155 K to a marked increase in the stability of the separated ions due to increased solvation. For the lithium amide, the PGSE results allow the two different aggregation states to be readily recognized and, where available, the solid-state structures support the PGSE data. The D values for the simple LiX salts reflect the relative stability of the $[Li(thf)_4]^+$ ion. Clearly, THF represents a "special" solvent in that, in contrast to dichloromethane,[6,20] where partial ion pairing is normal, THF shows a tendency to separate the ions at low temperature.

Experimental Section

General: Glassware was dried overnight in a 110°C oven to remove moisture. THF was freshly distilled from potassium before use. All chemicals used for sample preparation were obtained from Merck, Sigma–Aldrich, or Fluka and were of reagent grade. HMPA was distilled from CaH_2, and stored under N_2 over molecular sieves. HMPA is a carcinogenic agent, so adequate precautions were taken to avoid all forms of exposure. All reactions and sample manipulations were carried out using standard Schlenk techniques under nitrogen. The NMR samples were prepared in standard 5-mm NMR tubes, which were flushed with nitrogen, oven dried, and fitted with a plastic cap. The outside top portion of the tube was held securely by paraffin film and grease.

Lithium halides: [D$_8$]THF (0.5 mL) was added to oven-dried 5-mm NMR tubes containing the corresponding salt. The addition of HMPA (31.5 μL, 360 mmol) was performed on a 60 mM sample of LiCl (0.64 mg, 60 mmol) placed in an N_2 flushed Schlenk tube. To get the HMPA to dissolve, the tube had to be repeatedly warmed slightly and shaken.

Organolithiums: $LiCPh_3$, $LiC_{13}H_9$, Li(2-Ph)C_9H_7, $LiC_4H_7S_2$, and Li[N(SiMe$_3$)$_2$] were obtained as air-sensitive species by adding 1.1 equivalent of *n*BuLi (1.6 M in *n*-hexane) to a cooled solution (N_2 liquid/acetone) of the neutral precursors $HCPh_3$, $HC_{13}H_9$, H(2-Ph)C_9H_7, $HC_4H_7S_2$, and $HN(SiMe_3)_2$ in [D$_8$]THF solution. Lithium triphenylmethane ($LiCPh_3$) was generated by the addition of *n*BuLi (21 μL, 1.6 M in *n*-hexane) to oven-dried NMR tubes containing triphenylmethane (60 mmol, 7.33 mg) and freshly distilled [D$_8$]THF (0.5 mL) cooled to −78°C. The addition generated a dark red solution upon mixing.

The same protocol was applied for the remaining lithium species, which became dark orange, green, colorless, and light yellow upon shaking, for fluorenyllithium ($LiC_{13}H_9$), (2-phenyl)indenyl lithium (Li(2-Ph)C_9H_7), 2-lithio-1,3-dithiane (LiC_4H_7S), and lithium bis(trimethylsilane) amide (LiHMDS), respectively.

NMR spectroscopy: All multinuclear room- and low-temperature experiments were performed on a 400 MHz Bruker AVANCE spectrometer equipped with a microprocessor-controlled gradient unit and an inverse multinuclear probe with an actively shielded *z* axis gradient coil. ^{1}H NMR spectra were referenced to the residual signal of [D$_7$]THF at δ = 1.76 ppm as an internal standard. ^{31}P and ^{7}Li NMR chemical shifts are referred to external 85% H_3PO_4 for ^{31}P (161.923 MHz) and LiCl 9.7 M in D_2O for ^{7}Li (155.454 MHz).

The PGSE NMR diffusion measurements were carried out using the stimulated echo pulse sequence.[5,6] The shape of the gradient pulse was rectangular, and its strength varied automatically in the course of the experiments. The *D* values were determined from the slope of the regression line $\ln(I/I_o)$ versus G^2, according to Equation (a). I/I_o = observed spin echo intensity/intensity without gradients, G = gradient strength, Δ = delay between the midpoints of the gradients, D = diffusion coefficient, δ = gradient length.

$$\ln\left(\frac{I}{I_0}\right) = -(\gamma\delta)^2 G^2 \left(\Delta - \frac{\delta}{3}\right) D \tag{a}$$

The measurements were carried out without spinning. The sample temperature was calibrated before the PGSE measurements by introducing a thermocouple inside the bore of the magnet. The calibration of the gradients was carried out by means of a diffusion measurement of HDO in D_2O ($D_{HDO} = 1.9\times10^{-9}\,m^2s^{-1}$)[73], which afforded a slope of 2.022 10^{-4}). We believe that our previously reported experimental error in D values, ±2%, can be extended to the measurements performed here. All of the data leading to the reported D values afforded lines whose correlation coefficients were above 0.999. To check the reproducibility, three different measurements with different diffusion parameters (Δ and/or δ) were carried out. The gradient strength was incremented in 8% steps from 10% to 90%, so that 8–10 points could be used for regression analysis. A measurement of ^1H, ^7Li, and ^{31}P T_1 was carried out before each diffusion experiment, and the recovery delay set to (3–5)T_1. Table 6 below gives the ^7Li T_1 (ms) values for all the lithiated species of interest.

Table 6. ^7Li longitudinal relaxation times T_1 [ms] of lithiated species.

	1	**2**	**9**	**10**	**13**	**16**	**16**	
							(60 mM)	(600 mM)
T_1 (299 K)	–	710	621	1200	–	112	118	
T_1 (250 K)	–	–	–	–	150	–	79	49
T_1 (155 K)	498	1680	1590	1630	32	–	30	16

Details for the PGSE measurements:

^1H PGSE diffusion measurements: Room-temperature diffusion parameters: $\Delta = 19$–68 ms, $\delta = 2$–3 ms; at low temperature: $\Delta = 27$–68 ms, $\delta = 3$–12 ms. The number of scans varied between 8 and 16 per increment. Typical experimental times were 0.5–1 h.

^7Li and ^{31}P PGSE diffusion measurements: To obtain a suitable attenuation for these nuclei, the diffusion delay Δ and/or the gradient strength δ were increased. With Δ values higher than 200 ms no signal could be acquired. The most suitable option available was then a considerable increment of the gradient lengths (δ):

^{31}P PGSE: At room temperature: $\Delta = 16$–33 ms, $\delta = 3$–8 ms; at low temperature: $\Delta = 38$–60 ms, $\delta = 19$–24 ms. The number of scans varied between 64 and 512 scans per increment. Typical experimental times were 1–4 h.

^7Li PGSE: At room temperature: $\Delta = 18$–95 ms, $\delta = 4$–6 ms; at low temperature: $\delta = 28$–77 ms, $\delta = 10$–26 ms. The number of scans varied between 64 and 200 scans per increment. Typical experimental times were 1–4 h.

To avoid convection, the PGSE diffusion measurements at 250 K were carried out using a commercial coaxial insert (ID = 1.96 mm, OD = 2.97 mm) inserted into a standard 5 mm NMR tube and held in a concentric manner with a spacer.[74]

Acknowledgement

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