# The effect of polyether ligands on the solution structure of [6Li]-$\alpha$-(phenylthio)benzyllithium in tetrahydrofuran: A $^1$H,$^6$Li-HOESY NMR study [1]

Steffen Schade, Gernot Boche *

*Fachbereich Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany*

## Abstract

[6Li]-$\alpha$-(phenylthio)benzyllithium **1**-$^6$Li was studied in THF/[D$_8$]THF solution (1:1) in the presence of several acyclic and cyclic polyether ligands by $^1$H,$^6$Li-HOESY, $^1$H and $^{13}$C NMR spectroscopy. The question whether these ligands are bonded to lithium or not is important for physical–organic investigations as well as for studies of the ground state of (stereoselective) reactions of organolithium compounds in the presence of such ligands. Dimethoxyethane is not bonded to lithium under these conditions. The acyclic ethers diglyme and triglyme coordinate only weakly to the organolithium compound and form contact ion pairs (CIPs) at 25°C. At −80°C, CIPs are in equilibrium with separated ion pairs (SIPs). Very stable complexes of **1**-$^6$Li are obtained with crown ether ligands. Addition of 12-crown-4 and 15-crown-5, respectively, results in the exclusive formation of SIPs at 25°C and −80°C. With 18-crown-6, a CIP–SIP equilibrium is observed at 25°C which is shifted entirely to the SIP side at −80°C. Graphical analyses of the $^1$H and $^{13}$C NMR spectra of the polyether complexes of **1**-$^6$Li revealed correlations between the chemical shifts of the *para* phenyl carbon C-5, the *para* phenyl proton H-5, the benzylic carbon C-1, and the proton–carbon coupling constant $J$(C-1,H-1) of **1**-Li, which are useful probes for the charge distribution within the carbanionic moiety of **1**-$^6$Li in the respective complexes, and thus for the ion pair character as a function of the polyether complexation of lithium. © 1998 Elsevier Science S.A.

*Keywords:* $^1$H,$^6$Li-HOESY; [6Li]-$\alpha$-(phenylthio)benzyllithium; Polyether ligands; Solution structures in THF/[D$_8$]THF 1:1; Ion pair equilibria

## 1. Introduction

Lewis base ligands can exert significant effects on solution structures and reactivities of organolithium compounds [2–5]. However, although organolithium compounds are among the most commonly used organometallic reagents in contemporary organic synthesis [6], much of the knowledge about the role of coordinating ligands is merely based on empirical observations and 'rules of thumb' [58]. In order to shed some more light on the coordinating abilities of ligands containing N-donor atoms, particularly in competition with the donor solvent tetrahydrofuran (THF), we carried out an NMR spectroscopic study on the THF solution structures of [6Li]-$\alpha$-(phenylthio)benzyllithium

**1**-$^6$Li in the presence of various cyclic and acyclic (poly)amine ligands (for the effect of (poly)amine ligands on the solution structure of [6Li]-$\alpha$-(phenylthio) benzyllithium see [1]):
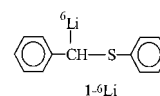


By means of $^1$H,$^6$Li-HOESY [7] (for reviews on NMR spectroscopy of organolithium compounds see refs. in [8]) as well as $^1$H and $^{13}$C NMR spectroscopy, we were able to examine the coordination sphere at lithium and to determine whether a ligand is coordinated to the Li cation, or not. Our results showed that at 25°C in a 1:1 THF/[D$_8$]THF solvent mixture (0.5 M solution; the solution contained approximately 12 THF and 12 [D$_8$]THF solvent molecules per molecule of **1**-$^6$Li) [1,9], **1**-$^6$Li formed monomeric, THF-solvated

---

* Corresponding author. Tel.: 0049 06421 288917.
[1] Dedicated to Professor Ken Wade on the occassion of his 65th birthday.

contact ion pairs **2** [1] which are structurally similar to **1**-$^6$Li $\cdot$ (THF)$_3$, whose solid state structure is known [10]:
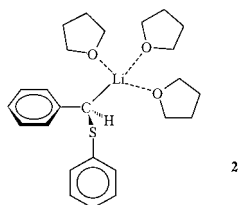


Polyamines as ligands (1 mol. equiv. of $^6$**1**-Li) bonded the stronger to lithium, the more nitrogen atoms they possessed. Coordination of amines with up to three N-donor atoms resulted in the formation of solvated contact ion pairs (CIPs) structurally related to **2**, in which the Li cation is bonded to the anionic benzylic carbon atom in an $\eta^1$-like manner, and with the amine ligands (partially) replacing THF molecules. With tetradentate amines, contact ion pairs (CIPs) are in equilibrium with separated ion pairs (SIPs). If the temperature was lowered to $-80°C$, these equilibria are shifted mainly towards the SIP side [1].

In the present work we have studied the effect of polyether ligands on the THF solution structures of the test compound **1**-$^6$Li. Since it was intended to compare the polyether with the polyamine samples, chelating ether ligands were used which were structurally related to the previously used amine ligands. As in the polyamine case [1], the polyether complexes of **1**-$^6$Li were examined by proton and carbon NMR spectroscopy at 25°C and at $-80°C$, and by $^1$H,$^6$Li-HOESY spectroscopy at 25°C.

## 2. Results and discussion

### 2.1. Complexes of [$^6$Li]-α-(phenylthio)benzyllithium 1-$^6$Li in THF / [D$_8$]THF with acyclic polyether ligands

#### 2.1.1. Measurements at 25°C

First the effects of the ethers 1,2-dimethoxyethane (DME), diethyleneglycol dimethylether (diglyme), and triethyleneglycol dimethylether (triglyme) were studied.
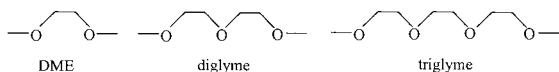


Selected data of the proton and carbon NMR measurements are summarized in Tables 1 and 2 (entries 2–4). The $^6$Li NMR chemical shifts (with respect to an external 1.0 M solution of $^6$LiCl in deuterium oxide) did not follow a specific pattern. Therefore they are not discussed here.

Table 1
Selected $^1$H NMR chemical shifts $\delta$ of the lithiated sulfide **1**-$^6$Li and its complexes with polyether ligands in 1:1 THF/[D$_8$]THF at 25°C

| Entry | Ligand | H-1 | H-3/H-7 | H-4/H-6 | H-5 |
|-------|--------|-----|---------|---------|-----|
| 1[a] | – | 3.03 | 6.70 | 6.59 | 5.94 |
| 2 | DME | 3.03 | 6.71 | 6.59 | 5.94 |
| 3 | diglyme | 3.03 | 6.68 | 6.57 | 5.90 |
| 4 | triglyme | 3.04 | 6.63 | 6.55 | 5.85 |
| 5 | 12-crown-4 | 3.18 | 6.26 | 6.37 | 5.46 |
| 6 | 15-crown-5 | 3.11 | 6.18 | 6.30 | 5.36 |
| 7 | 18-crown-6 | 3.09 | 6.35 | 6.40 | 5.56 |

[a]Data taken from [1].

The 2D NMR spectrum of a DME-containing sample of **1**-$^6$Li (not shown) very strongly resembled the $^1$H,$^6$Li-HOESY spectrum of lithium compound **1**-$^6$Li without any added ligand (for the complete set of NMR data see [1]). It showed four cross-peaks: an intensive one at the resonance of the benzylic proton H-1 ($\delta_H = 3.03$) and a weak peak at the resonance of the aromatic *ortho* protons H-3/H-7 ($\delta_H = 6.71$) (for atomic labels see Fig. 1). Two more cross-peaks appeared at the THF–OCH$_2$ (strong) and THF–CH$_2$ signals (weak), indicating that the Li cation is solvated by THF. Cross-peaks were not observed at either the DME methyl ($\delta_H = 3.23$) or methylene resonances ($\delta_H = 3.39$). Correspondingly, an equimolar amount of DME cannot successfully compete with the solvent THF for coordination sites at lithium, at least in the case of **1**-$^6$Li, even



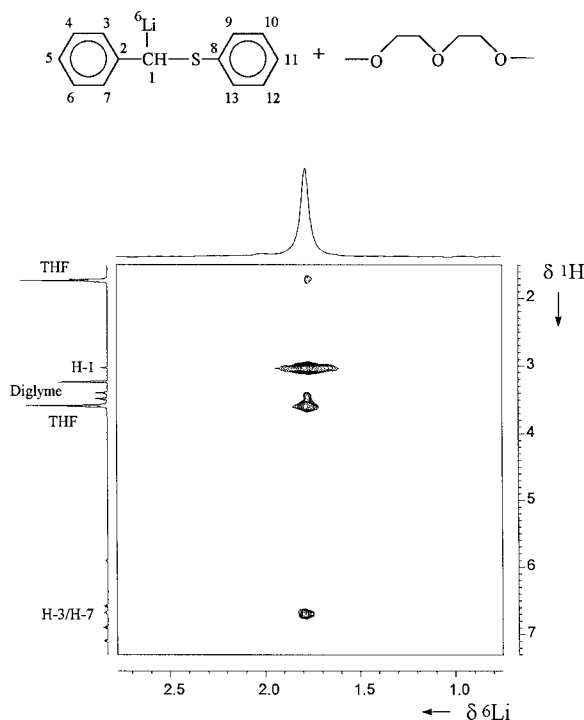Fig. 1. $^1$H,$^6$Li-HOESY spectrum of [$^6$Li]-α-(phenylthio)benzyllithium $^6$Li with 1 mol. equiv. diglyme in 1:1 THF/[D$_8$]THF at 25°C.

Table 2
Selected $^{13}$C NMR chemical shifts $\delta$ and coupling constants $^1J_{CH}$(C-1) of the lithiated sulfide $\mathbf{1}$-$^6$Li and its complexes with polyether ligands in 1:1 THF/[D$_8$]THF at 25°C

| Entry | Ligand | C-1 | $^1J_{CH}$(C-1) (Hz) | C-2 | C-7 | C-3 | C-4 | C-6 | C-5 | C-8 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1[a] | – | 35.8 | 149 | 157.0 | 118.8 | | 128.3 | | 111.8 | 151.8 |
| 2 | DME | 35.8 | 149 | 157.0 | 118.9 | | 128.4 | | 111.9 | 151.8 |
| 3 | diglyme | 36.0 | 150 | 156.9 | 118.6 | | 128.3 | | 111.4 | 151.9 |
| 4 | triglyme | 36.6 | 152 | 156.8 | 118.3 | | 128.4 | | 110.8 | 152.2 |
| 5 | 12-crown-4 | 42.0 | 168 | 155.6 | 113.0 | 118.0 | 128.5 | 128.5 | 105.0 | 153.1 |
| 6 | 15-crown-5 | 42.1 | 168 | 155.7 | 112.4 | 117.1 | 127.8 | 128.7 | 104.1 | 154.1 |
| 7 | 18-crown-6 | 40.1 | 163 | 156.0 | 116.0 | | 128.3 | | 106.5 | 153.2 |

[a] Data taken from [1].

though DME is a bidentate ligand. Only the THF-solvated $\mathbf{2}$ is present ($\geq 97\%$). Thus, compared to the structurally related bidentate amine TMEDA, which is capable of coordinating to $\mathbf{1}$-$^6$Li under the same conditions of a large excess of the solvent THF [1], DME is a far poorer ligand for lithium.

The $^1$H,$^6$Li-HOESY spectrum of $\mathbf{1}$-$^6$Li with diglyme as the ligand is shown in Fig. 1. Cross-peaks are observed at the proton resonances of H-1 ($\delta_H = 3.03$, strong), H-3/H-7 (d$_H$ = 6.68, intermediate), diglyme–CH$_2$ ($\delta_H = 3.39$ and 3.48, weak), THF–OCH$_2$ (intermediate) and THF–CH$_2$ (very weak). A lithium contact to the diglyme methyl groups ($\delta_H = 3.23$) is not observed. The diglyme cross-peaks show that the Li cation is coordinated to the ligand. Besides these signals, the spectrum is very similar to the HOESY spectrum of $\mathbf{1}$-$^6$Li in THF/[D$_8$]THF without added ligand (for the complete set of NMR data see [1]). Apparently, the general structural type of a contact ion pair as in $\mathbf{2}$ with $\eta^1$-coordination of lithium to the anionic benzylic car-

bon C-1 is not changed significantly if diglyme replaces some THF in the solvation sphere around lithium. Diglyme coordination to lithium is not particularly strong, although the tridentate O-donor ligand should be favoured entropically with respect to the monodentate O-donor solvent THF (chelate effect). An average of less than two diglyme oxygen atoms and at least one THF molecule seems to coordinate to Li (Scheme 1, $\mathbf{4}$ and $\mathbf{4'}$). The diglyme chelate $\mathbf{3}$ in which all three ligand O-atoms are bonded to the cation should only be a minor component in the equilibria in THF solution.

The tetradentate polyether triglyme, added to a solution of $\mathbf{1}$-$^6$Li, led to a $^1$H,$^6$Li-HOESY spectrum which is shown in Fig. 2. Cross-peaks appear at the H-1 ($\delta_H = 3.04$; strong), H-3/H-7 ($\delta_H = 6.63$; weak) and THF–CH$_2$ (very weak) signals. The THF–OCH$_2$ and
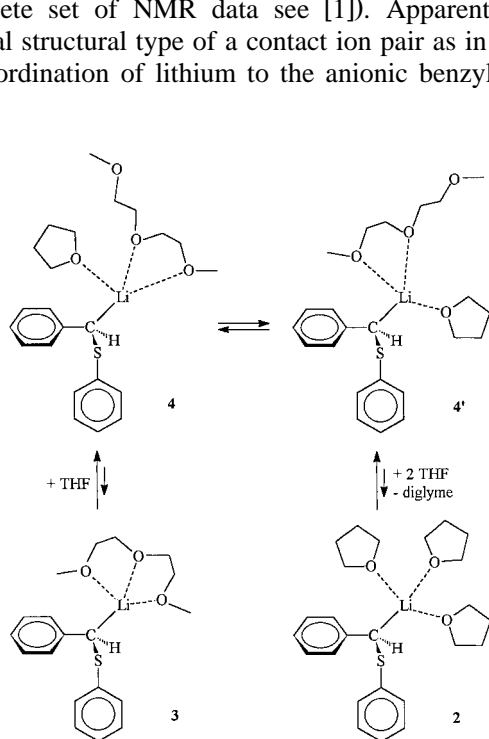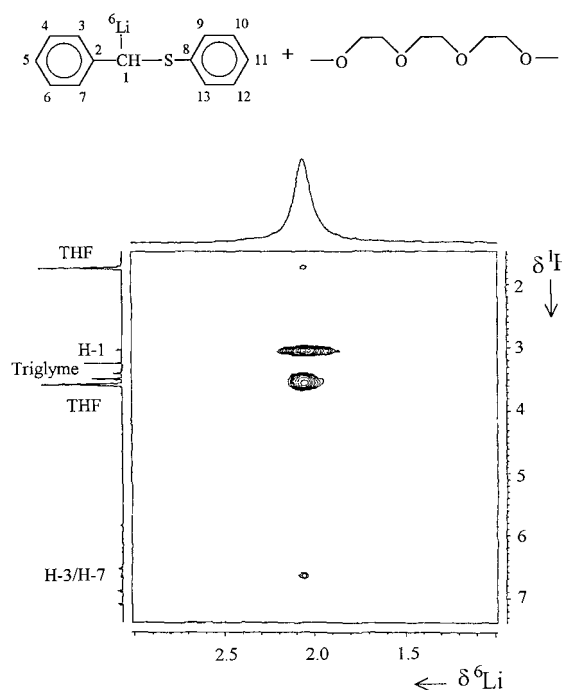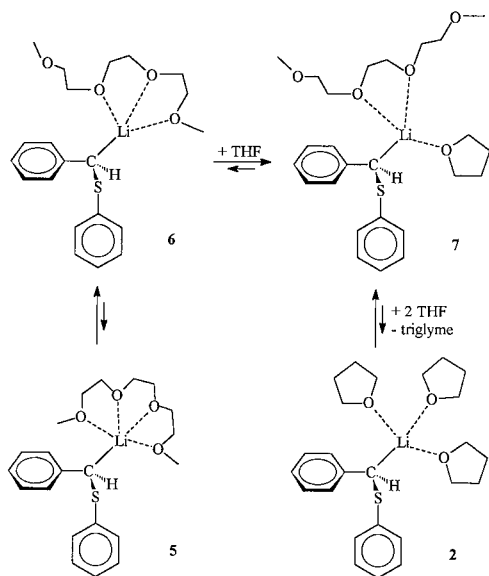




Scheme 1.



Fig. 2. $^1$H,$^6$Li-HOESY spectrum of [$^6$Li]-$\alpha$-(phenylthio)benzyllithium $^6$Li with 1 mol. equiv. triglyme in 1:1 THF/[D$_8$]THF at 25°C.

Scheme 2.

the triglyme–CH$_2$ signals ($\delta_H = 3.41$, 3.49, and 3.50) superimpose each other to one intense cross-peak. As in the diglyme sample (Fig. 1), a cross-peak is not found at the triglyme methyl resonance ($\delta_H = 3.24$). The spectrum indicates that lithium is somewhat stronger coordinated to triglyme than to diglyme. However, a strong lithium–THF contact is still observed in the 2D spectrum. It is therefore reasonable to assume that equilibria between differently solvated contact ion pairs are present in THF solution with the cation being also coordinated to the benzylic carbon atom C-1 (Scheme 2).

A tetracoordination at lithium (**6**, **7**) similar to that in the THF complex **2** and in the diglyme complex of **1**-Li is also dominant in the triglyme complex, but a pentacoordinated complex **5** may also be involved as a minor species (see below). On average, lithium appears to be complexed to 2–3 O-donor atoms of the tetradentate triglyme ligand.

The contact ion pair structures of the samples containing acyclic polyether ligand are nicely supported by the $^1$H and $^{13}$C NMR spectra of the respective samples of **1**-$^6$Li, listed in Tables 1 and 2, entries 2–4; they hardly differ from the spectra of **1**-$^6$Li in neat THF/[D$_8$]THF (Tables 1 and 2, entry 1; for the complete set of NMR data see [1]). The largest differences are observed with triglyme as the ligand (entry 4). A small shift of the benzylic carbon C-1 to higher $\delta$ values ($\Delta\delta = 0.8$ ppm) and slight shifts of the *para* proton H-5 ($\Delta\delta = -0.09$ ppm) and the *para* carbon C-5 ($\Delta\delta = -1.0$ ppm) towards lower $\delta$ values, if compared to THF-solvated **1**-$^6$Li (entry 1), indicate that, in the triglyme complexes, lithium is somewhat weaker bonded to the anionic benzylic carbon C-1, presumably due to the participation of a pentacoordinated complex **5** in the solution equilibria. However,

according to these NMR data, the contact ion pair structures with $\eta^1$-coordination of lithium to C-1 of **1**-Li determine the whole acyclic polyether series at 25°C.

A comparison with the corresponding polyamine ligands reveals remarkable differences to the polydentate ethers at 25°C (Formula 4). While the structurally related tridentate and tetradentate amines PMDTA and HMTTA, respectively, bind strongly to the cation in their complexes with **1**-$^6$Li [1], both diglyme and triglyme coordinate only rather loosely.
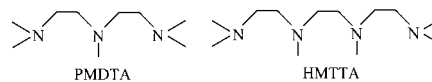


### 2.1.2. Measurements at $-80°C$

The samples of **1**-$^6$Li in the presence of 1 mol. equiv. DME, diglyme, and triglyme were also examined at $-80°C$ by $^1$H and $^{13}$C NMR spectroscopy. Selected chemical shift data are summarized in Tables 3 and 4. At this temperature, the phenyl rotation around the C-1–C-2 bond of **1**-$^6$Li is frozen out, and five different phenyl hydrogen (H-3 to H-7) as well as six different phenyl carbon resonances (C-2 to C-7) are observed [1]. $^{13}$C,$^6$Li coupling between the benzylic carbon C-1 and lithium was not found in any of the low-temperature carbon NMR spectra (in 'normal' benzyllithium compounds, a $^{13}$C,$^6$Li coupling was never observed even at temperatures as low as $-150°C$, see refs. in [12] and [9]). Proton and carbon NMR data of the sample containing DME (Tables 3 and 4, entry 2) are roughly identical with the data of THF-solvated **1**-$^6$Li (entries 1). Although it is not possible to determine reliably whether DME is coordinated to the Li cation at $-80°C$, or not, without recording a $^1$H,$^6$Li-HOESY spectrum at $-80°C$, it seems that not much has changed if compared to the case at 25°C.

In contrast, the spectroscopic data of the samples with diglyme (entry 3) and triglyme (entry 4) as ligands, which are very similar to each other, are notably differ-

Table 3
Selected $^1$H NMR chemical shifts $\delta$ of the lithiated sulfide **1**-$^6$Li and its complexes with polyether ligands in 1:1 THF/[D$_8$]THF at $-80°C$

| Entry | Ligand | H-1 | H-3 | H-7 | H-4 | H-6 | H-5 |
|---|---|---|---|---|---|---|---|
| 1[a] | – | 2.99 | 6.52 | 6.68 | 6.55 | 6.59 | 5.87 |
| 2 | DME | 2.99 | 6.52 | 6.70 | 6.55 | 6.58 | 5.88 |
| 3 | diglyme | 3.00 | 6.37 | 6.46 | 6.46 | 6.46 | 5.67 |
| 4 | triglyme | 3.01 | 6.39 | 6.47 | 6.47 | 6.47 | 5.69 |
| 5 | 15-crown-5 | 3.05 | 6.07 | 6.11 | 6.28 | 6.28 | 5.34 |
| 6 | 18-crown-6 | 3.06 | 6.13 | 6.13 | 6.29 | 6.29 | 5.37 |

[a] Data taken from [1].

ent from the sample of **1**-[6]Li without added ligands (entry 1). A reasonable explanation is that tetradentate triglyme, like tridentate diglyme, binds with three O-donor atoms to the metal and that the fourth triglyme oxygen is not involved in lithium complexation. The shifts of the benzylic carbons C-1 ($\Delta\delta \geq 2.0$ ppm) to higher and of the *para* protons H-5 ($\Delta\delta \approx -0.20$ ppm) and carbons C-5 ($\Delta\delta \geq -2.0$ ppm) to lower $\delta$ values with respect to THF-solvated **1**-[6]Li illustrate the new situation. Such spectral changes are only observed if the negative charge at the anionic C-1 is partly delocalized into the phenyl ring which is bonded to C-1; that is, if the C-1–Li bond is significantly weakened or broken [1,13,14]. The investigations of (poly)amine complexes of **1**-[6]Li [1] have shown that such a breaking of the carbon–lithium bond traces back to solution equilibria between contact ion pairs (CIPs) and separated ion pairs (SIPs). Evidently, comparable CIP–SIP equilibria exist also at $-80°$C in the diglyme and triglyme containing samples of **1**-[6]Li in THF/[D$_8$]THF.

The different behaviour of diglyme and its aza analogue PMDTA in the complexation of **1**-[6]Li is noticeable. As mentioned above, on cooling to $-80°$C, the comparatively loose contact between lithium and diglyme still leads to a situation in which the CIP is partially converted into a SIP, while the rather strong lithium coordination by PMDTA does not lead to a CIP–SIP equilibrium. Instead, a PMDTA–CIP is also found at $-80°$C [1], in which the PMDTA signals are split into seven signals. In the diglyme and triglyme complexes, such a splitting is not observed. Rather, the coordinated ligands remain in fluxion. It is also of interest to consider the consequences of changing the numbers of the donor atoms in the amine and ether series, respectively: increasing the number of N-donor atoms from three (PMDTA; CIP only) to four (HMTTA; CIP–SIP equilibria) causes significant structural changes in the amine series, whereas in the ether series tridentate diglyme and tetradentate triglyme form very similar **1**-[6]Li complexes at ambient temperature and at $-80°$C. At the moment we have no explanation for these differences.

## 2.2. Coordination of glymes to lithium: a comparison with literature data

Our measurements have shown, that 1 mol. equiv. DME in a 24-fold excess of the solvent THF/[D$_8$]THF cannot compete successfully for coordination sites at lithium of **1**-Li. Under the same conditions diglyme and triglyme are bonded to the metal to give contact ions pairs (CIPs). With the latter two acyclic polyethers, solvent-separated ions pairs (SIPs) are also formed at $-80°$C.

However, if DME is used as the solvent it seems to bind to organolithium compounds somewhat better than THF [15,16,59,60]. In general, DME is considered to be a poor ligand for alkali metal cations. Only some specially designed, substituted derivatives of DME are better [17–22]. NMR spectroscopic studies even revealed that DME may be only $\eta^1$-bonded to lithium [23,24]. Similarly in a solid-state structure investigation, diglyme was shown to bind to lithium with only two of its three oxygen atoms [25], as also observed in our solution studies. In the case of fluorenyllithium in dioxan, the tendency of complexation with the metal was found to increase in the order DME < diglyme < triglyme [15,26,59], which corresponds to our observations with **1**-Li in THF. Investigations with lithium–hexamethyldisilazide (LiHMDS) in hydrocarbon solvents fit into the overall picture [11].

A comparison of our investigations of **1**-Li in THF/[D$_8$]THF in the presence of the ether DME and the amine TMEDA, respectively, to give a 5-membered chelate, clearly shows TMEDA to be the better ligand. This was supported by competition experiments, in which DME and TMEDA competed directly for coordination sites at **1**-Li: according to the ^{1}H,[6]Li-HOESY spectrum at 25°C only TMEDA is bonded to **1**-Li. (NMR-spectroscopic competition experiments with the benzyllithium compound **1**-[6]Li in the presence of equimolar quantities of the other glymes and the corresponding polyamines demonstrated also that the organolithium compound was exclusively coordinated to the respective amine [27].)

Table 4
Selected ^{13}C NMR chemical shifts $\delta$ and coupling constants $^1J_{CH}$(C-1) of the lithiated sulfide **1**-[6]Li and its complexes with polyether ligands in 1:1 THF/[D$_8$]THF at $-80°$C

| Entry | Ligand | C-1 | $^1J_{CH}$(C-1) (Hz) | C-2 | C-7 | C-3 | C-4 | C-6 | C-5 | C-8 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1[a] | – | 35.1 | 152 | 156.1 | 115.9 | 119.7 | 127.8 | 128.8 | 110.7 | 151.2 |
| 2 | DME | 35.0 | 152 | 156.2 | 116.1 | 119.8 | 127.8 | 128.8 | 110.9 | 151.2 |
| 3 | diglyme | 37.4 | 159 | 155.7 | 114.5 | 118.6 | 127.7 | 128.7 | 108.2 | 151.8 |
| 4 | triglyme | 37.1 | 158 | 155.7 | 114.6 | 118.8 | 127.7 | 128.7 | 108.4 | 151.7 |
| 5 | 15-crown-5 | 41.3 | 170 | 154.9 | 111.8 | 116.7 | 127.7 | 128.8 | 103.8 | 152.7 |
| 6 | 18-crown-6 | 41.1 | 171 | 155.0 | 112.0 | 116.9 | 127.7 | 128.7 | 104.1 | 152.8 |

[a] Data taken from [1].

There are several reports in the literature on the different quality of polyethers and polyamines, respectively, to coordinate to lithium. Solid-state structure investigations of n-butyllithium with TMEDA and DME, respectively, show that TMEDA coordinates better than DME [28], which agrees with our results. If lithium is chelated intramolecularly by one N-donor atom to give a 5-membered ring, the tendency to form SIPs is much less pronounced, as in the case of an O-donor atom [29,30] (apparently there are exceptions to the rule [31]). We similarly observed that the PMDTA–CIP of **1**-Li in THF is not transformed into a SIP, while this is so if **1**-Li is bonded to diglyme.

Furthermore, the experimental results are corroborated by theoretical studies. Quantumchemical investigations of complexes of methyllithium [32] and Li$^+$ [33], respectively, with N- and O-containing ligands indicate the nitrogen complexes to be the more stable ones. The preference for five-membered ring chelates of the type $R_2N$-$CR_2$-$CR_2$-$NR_2$ with small cations like lithium as compared to those of $RO$-$CR_2$-$CR_2$-$OR$ with lithium originates in the preferred tetrahedral coordination at nitrogen (for coordination at N see [34]) of the former ones as compared to the trigonal planar geometry in the case of the latter ones (for coordination at O see [61]). The chelation with the two oxygen atoms puts more strain on the chelate with the small cation Li$^+$ than the chelation with the two nitrogen atoms, as recently shown in a systematic study of such complexes [35]. (A detailed discussion of the complexation with polyamines is given in the preceding paper [1].) In conclusion, our experimental findings with DME, diglyme and triglyme as compared to TMEDA, PMDTA and HMTTA as ligands to **1**-Li in THF agree nicely with related studies.

### 2.3. Complexes of 1-$^6$Li with cyclic polyether ligands (crown ethers)

#### 2.3.1. Measurements at 25°C

Next, **1**-$^6$Li was examined in the presence of 1 molar equivalent of the crown ethers 12-crown-4, 15-crown-5, and 18-crown-6 under the same conditions and NMR–spectroscopic parameters as before. Selected proton and carbon NMR data of these experiments are summarized in Tables 1 and 2 (entries 5–7).
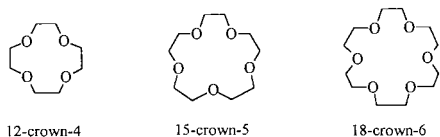


The $^1$H,$^6$Li-HOESY spectrum of **1**-$^6$Li with 12-crown-4 is shown in Fig. 3. In contrast to all previous
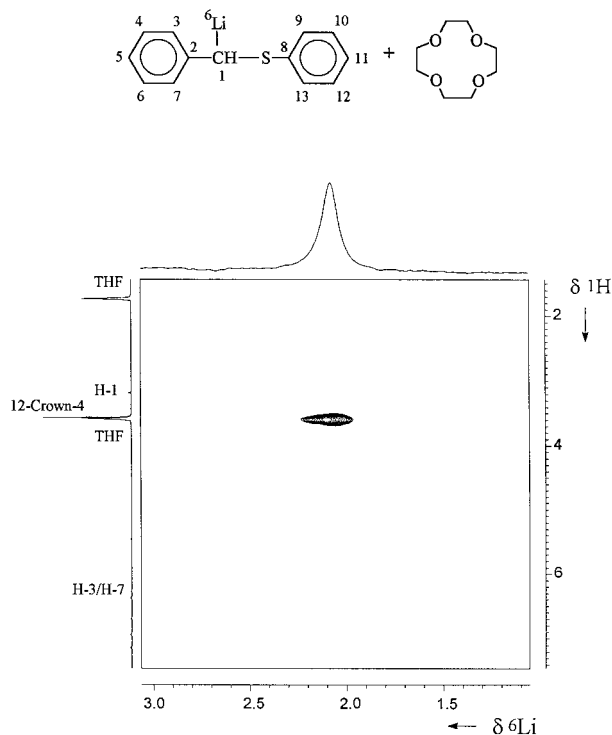


Fig. 3. $^1$H,$^6$Li-HOESY spectrum of [$^6$Li]-$\alpha$-(phenylthio)benzyllithium $^6$Li with 1 mol. equiv. 12-crown-4 in 1:1 THF/[D$_8$]THF at 25°C.

samples, it contains only one cross-peak at the crown ether resonance ($\delta_H = 3.56$). Since this signal is overlapped by the THF–OCH$_2$ signal ($\delta_H = 3.58$), we repeated the experiment in neat [D$_8$]THF to ensure that the signal was indeed caused by the crown ether hydrogens, which is the case. However, we cannot exclude that in THF/[D$_8$]THF part of the cross-peak intensity is caused by the solvent THF. Contacts of lithium to C1 of the benzyl anion **1** are not observed. Thus, complexation of 12-crown-4 to **1**-$^6$Li leads to the formation of a crown ether separated ion pair (12-crown-4-SIP) **8**, in which the carbon C-1–lithium bond is broken:



(12-crown-4 - SIP of 1-Li)
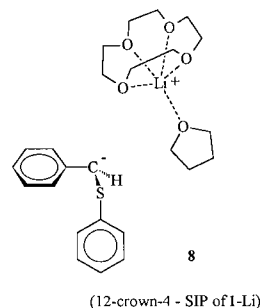
As indicated in structure **8**, the crown ether-complexed lithium cation is presumably located above the plane of the ligand oxygen atoms and, most likely, a pentacoordinated lithium cation **9** with a tetragonal–

pyramidal environment at the metal results. Coordination of the metal within the plane of the 12-crown-4 oxygen atoms (**10**, **11**) is rather unlikely, due to steric effects [36,37]:
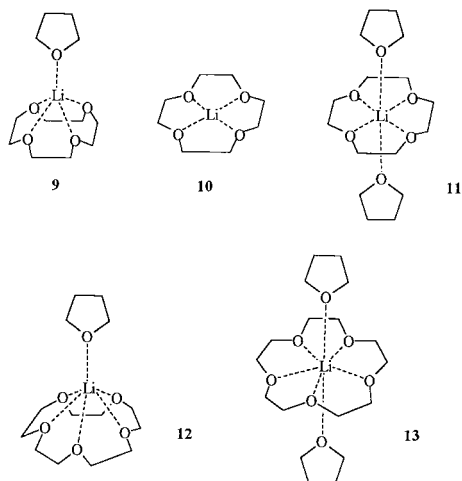


The ion pair separation gives rise to rather drastic changes in the $^1H$ and $^{13}C$ NMR spectra of the benzyl anion **1**$^-$ in this complex (Tables 1 and 2, entry 5). Almost all $\delta$ values are altered in the SIP as compared to a CIP (e.g. the THF-solvated **2**, see Tables 1 and 2, entry 1). In addition the rotation around the benzyl-C-*ipso* phenyl–C bond is hindered. Most notable are the strong shifts in the *para* carbon C-5 ($\Delta\delta = -6.8$ ppm) and the *para* hydrogen H-5 ($\Delta\delta = -0.48$ ppm) to lower as well as the shift of the benzylic carbon C-1 ($\Delta\delta = 6.2$ ppm) to higher $\delta$ values, and the increase in its coupling constant $^1J_{CH}$(C-1) by 19 Hz to 168 Hz, a figure characteristic for $sp^2$-hybridized carbon atoms [38]. These data show that the 'free' benzyl anion **1**$^-$ in this SIP has essentially a planar benzylic carbon atom C-1, and that the negative charge is extensively delocalised into the phenyl ring, which is bonded to this carbon atom. As a consequence, the rotation around the C-1–C-2 bond is slowed down significantly even at 25°C.

Compared to its cyclic tetraaza analogue Me$_4$–12–N4 [1], 12-crown-4 shows a different behaviour in its **1**-$^6$Li complex, which is worthy of note. Coordination with the aza ligand gives rise to a splitting of the methylene proton resonances of the tetramine into two signals of equal intensity although a CIP–SIP equilibrium exists. As a consequence, equilibration between the ion pairs must be slow on the NMR time scale, and/or the conformations are very similar in the two amine complexes. Coordination with the ether ligand, on the other hand, yields only one sharp crown ether signal in the $^1H$ NMR spectrum, although the organolithium compound is 'quantitatively' converted into the SIP. Thus, as shown for acyclic ligands, structurally similar cyclic

ligands containing O- and N-donor atoms, respectively, also behave quite different in their complexation of the lithium compound **1**-$^6$Li.

Increasing the number of donor atoms leads to the crown ether 15-crown-5. The $^1H,^6Li$-HOESY spectrum of its complex with **1**-$^6$Li is shown in Fig. 4. It is very similar to the spectrum shown in Fig. 3. An intensive cross-peak appears at the resonance of the crown ether hydrogens ($\delta_H = 3.50$). Again, a SIP is formed in which the lithium is not coordinated to C-1 of the benzyl anion **1**$^-$. A second weak cross-peak at the THF–CH$_2$ signal proves that lithium is also coordinated to the solvent THF. Again, the lithium cation should be coordinated in a pentagonal–pyramidal environment (**12**) analogous to the 12-crown-4 bonded lithium cation **9**, and not within the plane of the five ether oxygens (**13**).

Proton and carbon NMR data of this sample (Tables 1 and 2, entry 6) are also comparable to the data obtained for the complex with the smaller crown ether 12-crown-4. The rotation around the benzyl-C-1–*ipso* phenyl-C bond is restricted, as shown by six different phenyl carbon signals in the 25°C carbon NMR spectrum. Compared to the spectra of **1**-$^6$Li without added ligands, the *para* carbon C-5 ($\Delta\delta = -7.7$ ppm) and the *para* hydrogen H-5 ($\Delta\delta = -0.58$ ppm) are shifted significantly to lower $\delta$ values, whereas the benzylic carbon C-1 is shifted to higher $\delta$ values ($\Delta\delta = 6.3$ ppm), and an increase of its coupling constant $^1J_{CH}$(C-1) by 19 Hz to 168 Hz is found. These data provide further
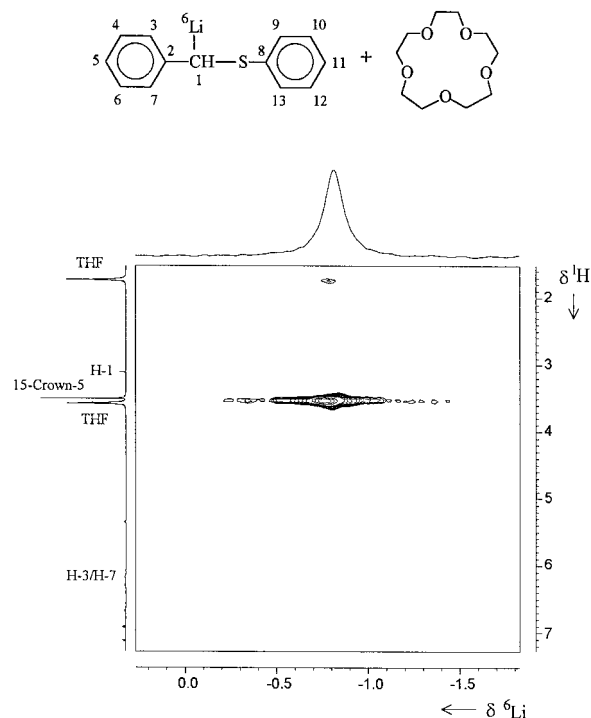


Fig. 4. $^1H,^6Li$-HOESY spectrum of [$^6Li$]-$\alpha$-(phenylthio)benzyllithium **1**-$^6$Li with 1 mol. equiv. 15-crown-5 in 1:1 THF/[D$_8$]THF at 25°C.
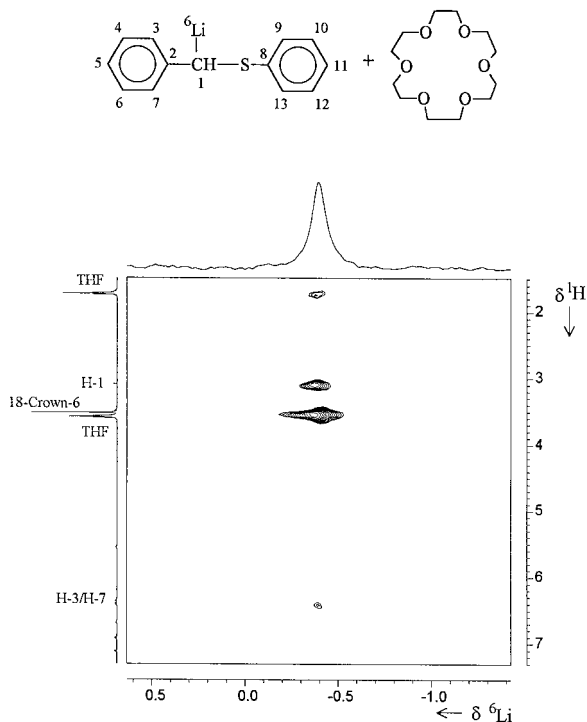
Fig. 5. $^1$H,$^6$Li-HOESY spectrum of [$^6$Li]-$\alpha$-(phenylthio)benzyl-lithium **1**-$^6$Li with 1 mol. equiv. 18-crown-6 in 1:1 THF/[D$_8$]THF at 25°C.

evidence that complexation of **1**-$^6$Li with 15-crown-5 gives rise to the formation of a separated ion pair (15-crown-5–SIP). Thus, apart from the different coordination numbers (five vs. six), the lithium coordination appears to be very similar in both the 12-crown-4 and 15-crown-5 complexes of **1**-Li in THF/[D$_8$]THF.

The $^1$H,$^6$Li-HOESY spectrum of a solution of **1**-$^6$Li with the hexadentate ligand 18-*crown*-6 is shown in Fig. 5. Lithium contacts are found for H-1 ($\delta_H = 3.09$; intermediate), H-3/H-7 ($\delta_H = 6.35$; weak), THF–CH$_2$ (weak), and for THF–OCH$_2$ and 18-crown-6 ($\delta_H = 3.43$; both superimpose each other to one intense cross-peak). Obviously, this 2D spectrum is fairly different from the spectra of the 12-crown-4 and 15-crown-5 complexes. It rather resembles the $^1$H,$^6$Li-HOESY spectra of **1**-Li with acyclic glymes. The lithium cation is coordinated to the anionic benzylic carbon C-1, presumably in the same $\eta^1$-like manner as in the glyme complexes **3**, **4** and **5**–**7**. It is also THF-solvated as well as complexed to the ligand. Apparently, coordination with 18-crown-6 does not lead to the exclusive formation of a solvent separated ion pair. Instead, it seems that a SIP **16** and at least one CIP (**14** or **15**) are in equilibrium with each other (Scheme 3).

This assumption is supported by the proton and carbon NMR data (Tables 1 and 2, entry 7) which lie between the values observed for a **1**-Li CIP (Tables 1 and 2, entry 1) and **1**-Li SIPs (Tables 1 and 2, entries 5 and 6). Moreover, the benzyl–C-*ipso* phenyl–C rotation

is no longer restricted on the NMR time scale at 25°C. Although the spectroscopic data do not allow deduction of detailed structures of the CIP species, complexes such as **15** should be formed in which less than six ligand oxygen atoms are coordinated to the metal, and in which lithium is also solvated by THF. The contact ion pair **14** with hepta-coordinated lithium may only be a minor species. Analogously, in the SIP **16** the cation most likely is not coordinated to all six ligand oxygens, but, rather, is moving around within the fairly large crown ether 'cavity', which is the reason for 18-crown-6 being not capable to convert the organolithium compound **1**-$^6$Li completely into SIPs.

### 2.3.2. Measurements at $-80°C$

The $^1$H and $^{13}$C NMR spectra of the samples containing 15-crown-5 and 18-crown-6, recorded at $-80°C$, are given in Tables 3 and 4, entries 5 and 6. Due to its low solubility, the 12-crown-4 complex could not be examined below 0°C. The low-temperature spectra of the 15-crown-5 and 18-crown-6 complexes hardly differ from each other. A comparison with the spectra of the THF-solvated **1**-$^6$Li (Tables 3 and 4, entry 1) and especially with the $^{13}$C NMR spectra of the 12-crown-4–SIP and the 15-crown-5–SIP at 25°C (Table 2, entries 5 and 6) show that all spectroscopic data indicate that, at $-80°C$, both the 15-crown-5 and the 18-crown-6 complex exist essentially only as crown ether SIPs.

### 2.4. Coordination of crown ethers to lithium: a comparison with literature data

Crown ether complexes with alkali metal cations are well documented [19–21,36,37,39]. They are in general
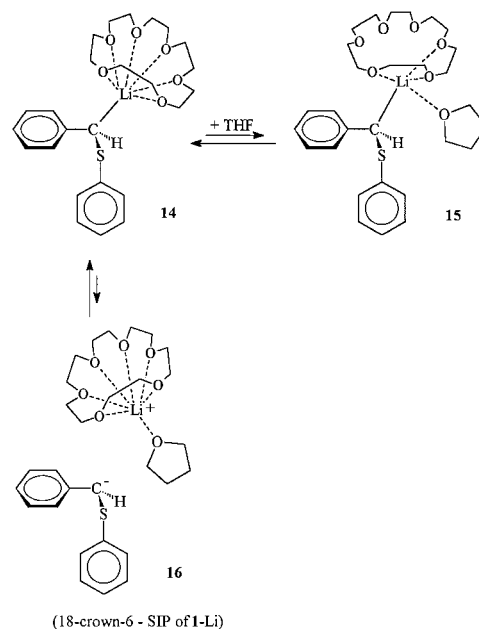


Scheme 3.

much more stable than complexes with acyclic polyethers ('macrocyclic effect') [20,40]. Since the bonds in lithium–crown ether complexes are mainly electrostatic in nature, the lithium cation tries to attain a symmetrical, spherical environment with the coordinating oxygen donor atoms [20,21,41,62]. Apart from temperature, solvent, and gegenion, the stability of a lithium–crown ether complex is particularly dependent on the number and geometrical arrangement of the oxygen atoms in the polyether and on the size and shape of the macrocycle relative to the size of the cation ('size match selectivity'). Comparison of the cavity diameters of crown ethers with ionic diameters of alkali cations suggests that 12-crown-4 (cavity diameter 120–150 pm) selectively binds $Li^+$ (ionic diameter 136 pm), whereas 15-crown-5 (cavity diameter 170–220 pm) is selective for $Na^+$ (ionic diameter 194 pm), and 18-crown-6 (cavity diameter 260–320 pm) for $K^+$ (ionic diameter 266 pm) [42]. However, there is some uncertainty about the correct ionic radius of the lithium cation (60–94 pm) [43–45]. Thus, the most stable lithium complexes should be formed with 15-crown-5 rather than with 12-crown-4. Indeed, several reports on lithium–crown ether complexes show a preference of $Li^+$ for the larger cyclic polyether (e.g. 14-crown-4 > 12-crown-4 [46], or 15-crown-5 > 12-crown-4 [47]). Unfortunately, the NMR spectroscopic data obtained in the present study do not allow us to determine whether 12-crown-4 or 15-crown-5 forms the more stable complex with the benzyllithium compound **1**-$^6$Li. The formation of separated ion pairs in THF solution only demonstrates that the lithium cation is very well coordinated by 12-crown-4 and by 15-crown-5. In contrast, lithium complexation of 18-crown-6 is significantly weaker. Interestingly, recent quantum chemical studies afforded a high gas phase selectivity of 18-crown-6 for lithium ($Li^+ > Na^+ > K^+$). The expected $K^+$ selectivity of this crown ether was only observed if additional solvation was taken into account [48].

X-ray crystal structure determinations of 12-crown-4 complexes with lithium reveal that either 1:1 or 2:1 complexes are formed. In the 2:1 complexes, each cation is sandwiched between two crown ether molecules, and a $Li^+$ coordination number of 8 results (for examples see refs. in [49]). Sandwich complexes are also observed in solution [11,50,63]. In the 1:1 complexes, the cation is usually penta-coordinated to the four O-donor atoms and the anion or a solvent molecule, and resides above the plane of the crown ether oxygens [51–53]. X-ray crystal structures of lithium complexes with 15-crown-5 reveal a hexacoordinated cation in a pentagonal–pyramidal coordination polyhedron [54]. These X-ray crystal structures support the assumption that, in the SIP complexes of the benzyllithium compound **1**-$^6$Li with 12-crown-4 and 15-crown-5 in THF solution, as suggested by our studies,

Table 5
Selected NMR data of the lithiated sulfide **1**-$^6$Li and its complexes with polyether ligands in 1:1 THF/[$D_8$]THF

| Entry | Temp. (°C) | Ligand | δ H-1 | δ C-1 | $1J_{CH}$(C-1) (Hz) | δ H-5 | δ C-5 |
|---|---|---|---|---|---|---|---|
| 1[a] | 25 | – | 3.03 | 35.8 | 149 | 5.94 | 111.8 |
| 2 | 25 | DME | 3.03 | 35.8 | 149 | 5.94 | 111.9 |
| 3 | 25 | diglyme | 3.03 | 36.0 | 150 | 5.90 | 111.4 |
| 4 | 25 | triglyme | 3.04 | 36.6 | 152 | 5.85 | 110.8 |
| 5 | 25 | 12-crown-4 | 3.18 | 42.0 | 168 | 5.46 | 105.0 |
| 6 | 25 | 15-crown-5 | 3.11 | 42.1 | 168 | 5.36 | 104.1 |
| 7 | 25 | 18-crown-6 | 3.09 | 40.1 | 163 | 5.56 | 106.5 |
| 8[a] | −80 | – | 2.99 | 35.1 | 152 | 5.87 | 110.7 |
| 9 | −80 | DME | 2.99 | 35.0 | 152 | 5.88 | 110.9 |
| 10 | −80 | diglyme | 3.00 | 37.4 | 159 | 5.67 | 108.2 |
| 11 | −80 | triglyme | 3.01 | 37.1 | 158 | 5.69 | 108.4 |
| 12 | −80 | 15-crown-5 | 3.05 | 41.3 | 170 | 5.34 | 103.8 |
| 13 | −80 | 18-crown-6 | 3.06 | 41.1 | 171 | 5.37 | 104.1 |

[a]Data taken from [1].

structurally related penta-coordinated cations **9** (12-crown-4) or hexa-coordinated cations **12** (15-crown-5) are formed with additional solvation by one THF molecule. A 15-crown-5 complex **13** seems rather unlikely in the light of the X-ray crystal structure investigations. Coordination of lithium to crown ether oxygens without additional bonding to an axial ligand as in **9** and **12**, however, seems to be rather unfavourable in solution [11,55].

X-ray crystal structures of lithium–18-crown-6 complexes show that the cavity within the polyether ring is too large for lithium (some evidence for hexacoordinated $Li^+$ located in the centre of an 18-crown-6 ring has been reported see [56,57]). The cation is only coordinated to two [56,64] or three [65] ligand oxygen atoms. This lithium coordination is nicely corroborated by the $^1H,^6Li$-HOESY spectrum of **1**-$^6$Li with 18-crown-6. In this complex, the cation is probably also bonded simultaneously only to two or three polyether oxygens. Additional contacts to the solvent THF and the anionic benzylic carbon, as observed in the $^1H,^6Li$-HOESY spectrum of **1**-$^6$Li in the presence of 18-crown-6, lead to the reasonable assumption that at ambient temperatures crown ether coordinated CIPs like **14** and **15** are in equilibrium with a crown ether coordinated SIP (**16**).

Finally it should be mentioned that incorporation of a crown ether-like moiety into a benzyllithium compound leads to molecules with interesting properties:



17                              18
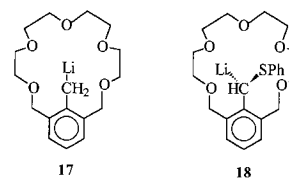
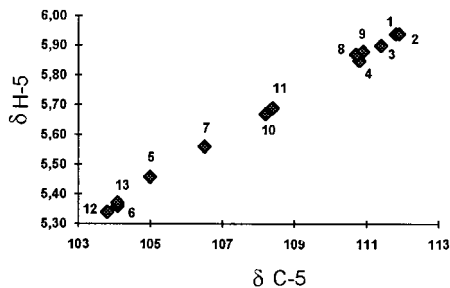In agreement with the above discussion, in **17** and **18**

Fig. 6. Correlation of $\delta$ H-5 versus $\delta$ C-5 of polyether complexes of **1**-[6]Li. The numbers refer to entries in Table 5.

lithium is strongly coordinated to the polyether oxygens. However, since the organolithium compound is part of the crown ether ring, SIPs cannot be formed. Instead, the polyether chain holds the cation in a position very close to the benzylic carbon atoms, and very tight CIPs with strong lithium–benzylic carbon bonds are obtained. As a consequence, carbon–lithium couplings $^1J_{CLi}$ [12] and high racemisation barriers of benzyllithium compounds result [9].

## 2.5. Correlation of the proton and carbon NMR data

Significant proton and carbon NMR data of all samples investigated in this work are summarized in Table 5. In benzyllithium compounds, the chemical shift $\delta$ C-5 of the aromatic *para* carbon is a measure for the delocalisation of negative charge from the anionic benzylic carbon C-1 into the phenyl ring which is bonded to that carbon atom [13,14]. Since we observed in the preceding study of (poly)amine complexes of **1**-[6]Li in THF that the chemical shift of the *para* proton $\delta$ H-5 and the benzylic carbon $\delta$ C-1, as well as the coupling constant $^1J_{CH}$(C-1) of the benzylic carbon atom, correlate linearly with $\delta$ C-5 [1], we expected to find analogous correlations in the polyether series. Therefore, in Fig. 6, $\delta$ H-5, in Fig. 7, $\delta$ C-1, and in Fig. 8, $^1J_{CH}$(C-1) are plotted against $\delta$ C-5.

Again [1], linear correlations are found in all three cases. These empirical correlations show that, in polyether complexes of **1**-[6]Li in THF solution as well, $\delta$ H-5 is proportional to $\delta$ C-5, indicating that $\delta$ H-5 is sensitive to the amount of negative charge which is
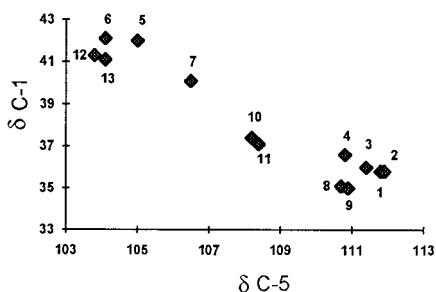


Fig. 7. Correlation of $\delta$ C-1 versus $\delta$ C-5 of polyether complexes of **1**-[6]Li. The numbers refer to entries in Table 5.
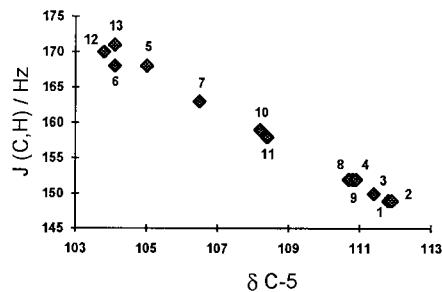


Fig. 8. Correlation of $^1J_{CH}$(C-1) versus $\delta$ C-5 of polyether complexes of **1**-[6]Li. The numbers refer to entries in Table 5.

delocalized into the phenyl ring in the same manner as $\delta$ C-5. Figs. 7 and 8 reveal that an increase in the charge density in the phenyl ring (lower values of $\delta$ C-5) leads to a decrease in the amount of negative charge which is located at the benzylic carbon C-1 (higher values of $\delta$ C-1) and causes a partial rehybridisation at that carbon atom towards sp$^2$ (higher values of $^1J_{CH}$(C-1)). Thus, the four spectroscopic parameters discussed here respond to changes in the charge distribution within the carbanionic part of the benzyllithium compound **1**-[6]Li, irrespective of the nature of the added ligand.

As outlined in the polyamine case [1], the data found at $\delta$ C-5 = 110–112 can be assigned to contact ion pairs (CIPs), while those at $\delta$ C-5 = 103–105 are indicative of separated ion pairs (SIPs). The data in between these extremes reveal CIP–SIP equilibria (see Table 5). Changes exclusively in the solvation sphere or coordination number at lithium of **1**-Li apparently do not lead to significant changes in the carbon and proton NMR spectra of the monomeric contact ion pairs of **1**-[6]Li in THF. Similarly, in the various separated ion pairs of **1**-Li the spectroscopic data of the benzyl anion **1**$^-$ are also very similar to each other.

Thus, at 25°C, glyme-containing samples (entries 2–4) merely form CIPs, while the 12-crown-4 (entry 5) and the 15-crown-5 complexes (entry 6) exist as SIPs. The 18-crown-6 complex (entry 7) is found at an intermediate value. This result supports the $^1$H,$^6$Li-HOESY findings that, in the 18-crown-6-containing sample, CIPs and SIPs are in equilibrium with each other. Furthermore, at −80°C, crown ether complexes exist as SIPs (entries 12 and 13) whereas in the diglyme (entry 10) and triglyme complexes (entry 11) the lithium–ligand interaction leads to both CIPs and SIPs, which is again in agreement with the $^1$H,$^6$Li-HOESY studies.

## 3. Conclusions

The NMR spectroscopic study of polyether complexes of [$^6$Li]-$\alpha$-(phenylthio)benzyllithium **1**-[6]Li in THF solution by means of $^1$H,$^6$Li-HOESY as well as carbon and proton NMR spectroscopy showed that an

equimolar amount of DME does not coordinate to the organolithium compound. Diglyme and triglyme form only weak complexes at 25°C. In these contact ion pairs (CIPs) part of the solvent THF is replaced by the respective polyether ligand and lithium is coordinated in an $\eta^1$-like manner to the anionic carbon C-1 of **1**-Li. Lithium is without contact to the *ipso* or *ortho* carbons of the phenyl ring of **1**-Li. At $-80°C$ contact ion pairs are in equilibrium with separated ion pairs (SIPs). Much better lithium complexation is observed if crown ethers are used as ligands for **1**-Li in THF. With 12-crown-4 and 15-crown-5, only separated ion pairs (SIPs) are obtained in which the coordination number at lithium exceeds four. With 18-crown-6, a CIP-SIP equilibrium is established at 25°C, which is shifted largely to the SIP side at $-80°C$. Apparently, the cavity diameter of 18-crown-6 is too large to coordinate to the lithium cation as effectively as the smaller crown ethers 15-crown-5 and 12-crown-4.

Compared to structurally related polyamines, the acyclic polyethers are weaker ligands for **1**-⁶Li in THF solution. Cyclic polyethers, on the other hand, are better ligands than cyclic polyamines. In all polyether complexes the coordinated ligands are fluxional at ambient and even at low temperatures. In most of the polyamine complexes, distinct ligand conformations are frozen out on coordination with the organolithium compound at $-80°C$, sometimes even at 25°C. These results strongly indicate that the complexation of **1**-Li in THF with polyethers and polyamines, respectively, occurs in a rather different way.

The formation of separated ion pairs (SIPs) from solvent separated ion pairs (CIPs) is accompanied by significant changes in the proton and carbon NMR spectra of **1**-⁶Li, which demonstrates that large changes in the charge distribution within the carbanionic moiety of **1**-⁶Li take place. Plots of the chemical shifts of the *para* phenyl proton H-5, the benzylic carbon C-1, and the proton–carbon coupling constant $^1J_{CH}$ of C-1 versus the chemical shift of the *para* phenyl carbon C-5 reveal that the four parameters correlate nicely with each other. The results of the graphical analyses support the structural conclusions drawn from $^1H,^6Li$-HOESY spectra.

Further studies have to show how glymes and crown ethers coordinate to organolithium compounds which are different from **1**-⁶Li, and how such ground state complexation can be used to influence the reactivity (ground *and* transition state complexation, respectively) of organolithium compounds.

# 4. Experimental

All organolithium compounds were prepared in flame-dried glassware under argon. The sample tubes containing organolithium compounds were thoroughly purged with argon and sealed with septum caps and parafilm. Solvents: THF was freshly distilled from potassium. [D₈]THF was dried over molecular sieves (4 Å) prior to use. Glymes were distilled from calcium hydride and stored over molecular sieves in an argon atmosphere. Crown ethers were used without further purification. A n-Bu⁶Li solution in n-hexane was prepared according to a literature procedure [16]. $^1H$, $^{13}C$, and $^6Li$ NMR: Bruker ARX 200, Bruker AC 300, Bruker AM 400, and Bruker AMX 500. $^1H,^1H$-COSY, $^1H,^{13}C$-COSY, and $^1H,^6Li$-HOESY: Bruker AMX 500. $^6Li$ NMR spectra were referenced to an external 1.0 *M* solution of $^6LiCl$ in deuterium oxide. $^1H$ and $^{13}C$ NMR spectra were referenced to the THF–CH₂ signal ($\delta_H = 1.73$; $\delta_C = 26.5$). In order to save space, $^1H,^1H$ coupling constants, $J$, have been omitted. Phase-sensitive $^1H,^6Li$-HOESY spectra [500 MHz ($^1H$), 73 MHz ($^6Li$), THF/[D₈]THF 1:1, 25°C]: relaxation delay 6.0 s, mixing time 1.6 s; number of experiments: 64 or 128; number of scans: 16–64; data matrix (after zero-filling in $F1$): 128 ($F1$) × 512 ($F2$) points or 256 ($F1$) × 512 ($F2$) points; window function: exponential in $F2$, squared sine bell in $F1$.

## 4.1. [⁶Li]-α-(Phenylthio)benzyllithium (**1**-⁶Li) with 1 mol. equiv. of an ether ligand

General procedure: A solution of 0.55 mmol of n-Bu⁶Li in n-hexane was evaporated to dryness in vacuo. The remaining n-Bu⁶Li was dissolved in 1.0 ml THF/[D₈]THF (1:1) at $-15°C$. To this solution was added 100 mg (0.50 mmol) of benzyl phenyl sulphide, followed after 15 min by 0.55 mmol of the acyclic ether. If a crown ether was used as the ligand, the samples were warmed to 0°C prior to addition of the ether. The samples were kept at the respective temperatures for further 15 min and then transferred into an NMR tube.

## 4.2. [⁶Li]-α-(Phenylthio)benzyllithium with DME (**1**-⁶Li-DME)

$^1H$ NMR (500 MHz, THF/[D₈]THF 1:1, 25°C): $\delta = 3.03$ (s, 1 H, H-1), 3.23 (s, 6 H, OC$H_3$), 3.39 (s, 4 H, OC$H_2$), 5.94 (t, 1 H, H-5), 6.59 (dd, 2 H, H-4, H-6), 6.67 (t, 1 H, H-11), 6.71 (bd, 2 H, H-3, H-7), 6.89 (dd, 2 H, H-10, H-12), 7.09 (d, 2 H, H-9, H-13). $^{13}C$ NMR (75 MHz, THF/[D₈]THF 1:1, 25°C): $\delta = 35.8$ (d, $^1J_{CH}$ 149 Hz, C-1), 59.1 (q, $^1J_{CH}$ 140 Hz, OCH₃), 72.8 (t, $^1J_{CH}$ 140 Hz, OCH₂), 111.9 (d, $^1J_{CH}$ 157 Hz, C-5), 118.9 (d, $^1J_{CH}$ 157 Hz, C-3, C-7), 122.1 (d, $^1J_{CH}$ 160 Hz, C-11), 125.4 (d, $^1J_{CH}$ 159 Hz, C-9, C-13), 128.1 (d, $^1J_{CH}$ 158 Hz, C-10, C-12), 128.4 (d, $^1J_{CH}$ 152 Hz, C-4, C-6), 151.8 (s, C-8), 157.0 (s, C-2). $^6Li$ NMR (73 MHz, THF/[D₈]THF 1:1, 25°C): $\delta = 0.35$. $^1H$ NMR (400

MHz, THF/[D$_8$]THF 1:1, −80°C): δ = 2.99 (s, 1 H, H-1), 3.21 (s, 6 H, OC$H_3$), 3.36 (s, 4 H, OC$H_2$), 5.88 (t, 1 H, H-5), 6.52 (d, 1 H, H-3), 6.55 (dd, 1 H, H-4), 6.58 (dd, 1 H, H-6), 6.70 (d, 1 H, H-7), 6.71 (t, 1 H, H-11), 6.94 (dd, 2 H, H-10, H-12), 7.06 (d, 2 H, H-9, H-13). $^{13}$C NMR (100 MHz, THF/[D$_8$]THF 1:1, −80°C): δ = 35.0 (d, $^1J_{CH}$ 152 Hz, C-1), 59.7 (q, $^1J_{CH}$ 140 Hz, O$C$H$_3$), 72.7 (t, $^1J_{CH}$ 140 Hz, O$C$H$_2$), 110.9 (d, $^1J_{CH}$ 157 Hz, C-5), 116.1 (d, $^1J_{CH}$ 150 Hz, C-7), 119.8 (d, $^1J_{CH}$ 152 Hz, C-3), 122.1 (d, $^1J_{CH}$ 156 Hz, C-11), 124.8 (d, $^1J_{CH}$ 159 Hz, C-9, C-13), 127.8 (d, $^1J_{CH}$ 151 Hz, C-4), 128.2 (d, $^1J_{CH}$ 156 Hz, C-10, C-12), 128.8 (d, $^1J_{CH}$ 152 Hz, C-6), 151.2 (s, C-8), 156.2 (s, C-2).

For comparison: free DME: $^1$H NMR (200 MHz, CDCl$_3$, 25°C): δ = 3.27 (s, 6 H, OC$H_3$), 3.42 (s, 4 H, OC$H_2$). $^{13}$C NMR (50 MHz, CDCl$_3$, 25°C): δ = 58.7 (q, $^1J_{CH}$ 141 Hz, O$C$H$_3$), 71.5 (t, $^1J_{CH}$ 140 Hz, O$C$H$_2$).

### 4.3. [$^6$Li]-α-(Phenylthio)benzyllithium with diglyme (**1**-$^6$Li-diglyme)

$^1$H NMR (500 MHz, THF/[D$_8$]THF 1:1, 25°C): δ = 3.03 (s, 1 H, H-1), 3.23 (s, 6 H, OC$H_3$), 3.39 (m, 4 H, OC$H_2$), 3.48 (m, 4 H, OC$H_2$), 5.90 (t, 1 H, H-5), 6.57 (dd, 2 H, H-4, H-6), 6.67 (t, 1 H, H-11), 6.68 (d, 2 H, H-3, H-7), 6.89 (dd, 2 H, H-10, H-12), 7.09 (d, 2 H, H-9, H-13). $^{13}$C NMR (75 MHz, THF/[D$_8$]THF 1:1, 25°C): δ = 36.0 (d, $^1J_{CH}$ 150 Hz, C-1), 59.1 (q, $^1J_{CH}$ 140 Hz, O$C$H$_3$), 71.3 (t, $^1J_{CH}$ 141 Hz, O$C$H$_2$), 72.8 (t, $^1J_{CH}$ 141 Hz, O$C$H$_2$), 111.4 (d, $^1J_{CH}$ 157 Hz, C-5), 118.6 (bd, $^1J_{CH}$ 152 Hz, C-3, C-7), 122.0 (d, $^1J_{CH}$ 160 Hz, C-11), 125.3 (d, $^1J_{CH}$ 159 Hz, C-9, C-13), 128.0 (d, $^1J_{CH}$ 158 Hz, C-10, C-12), 128.3 (d, $^1J_{CH}$ 151 Hz, C-4, C-6), 151.9 (s, C-8), 156.9 (s, C-2). $^6$Li NMR (73 MHz, THF/[D$_8$]THF 1:1, 25°C): δ = 1.78. $^1$H NMR (400 MHz, THF/[D$_8$]THF 1:1, −80°C): δ = 3.00 (s, 1 H, H-1), 3.22 (s, 6 H, OC$H_3$), 3.38 (bs, 4 H, OC$H_2$), 3.45 (bs, 4 H, OC$H_2$), 5.67 (t, 1 H, H-5), 6.37 (d, 1 H, H-3), 6.46 (m, 3 H, H-7, H-4, H-6), 6.71 (t, 1 H, H-11), 6.94 (dd, 2 H, H-10, H-12), 7.06 (d, 2 H, H-9, H-13). $^{13}$C NMR (100 MHz, THF/[D$_8$]THF 1:1, −80°C): δ = 37.4 (d, $^1J_{CH}$ 159 Hz, C-1), 59.2 (q, $^1J_{CH}$ 141 Hz, O$C$H$_3$), 70.5 (t, $^1J_{CH}$ 142 Hz, O$C$H$_2$), 72.0 (t, $^1J_{CH}$ 143 Hz, O$C$H$_2$), 108.2 (d, $^1J_{CH}$ 156 Hz, C-5), 114.5 (d, $^1J_{CH}$ 155 Hz, C-7), 118.6 (d, $^1J_{CH}$ 151 Hz, C-3), 121.9 (d, $^1J_{CH}$ 155 Hz, C-11), 124.7 (d, $^1J_{CH}$ 159 Hz, C-9, C-13), 127.7 (d, $^1J_{CH}$ 151 Hz, C-4), 128.1 (d, $^1J_{CH}$ 156 Hz, C-10, C-12), 128.7 (d, $^1J_{CH}$ 150 Hz, C-6), 151.8 (s, C-8), 155.7 (s, C-2).

For comparison: diglyme: $^1$H NMR (200 MHz, CDCl$_3$, 25°C): δ = 3.25 (s, 6 H, OC$H_3$), 3.44 (m, 4 H, OC$H_2$), 3.52 (m, 4 H, OC$H_2$). $^{13}$C NMR (50 MHz, CDCl$_3$, 25°C): δ = 58.7 (q, $^1J_{CH}$ 141 Hz, O$C$H$_3$), 70.3 (t, $^1J_{CH}$ 141 Hz, O$C$H$_2$), 71.7 (t, $^1J_{CH}$ 140 Hz, O$C$H$_2$).

### 4.4. [$^6$Li]-α-(Phenylthio)benzyllithium with triglyme (**1**-$^6$Li-triglyme)

$^1$H NMR (500 MHz, THF/[D$_8$]THF 1:1, 25°C): δ = 3.04 (s, 1 H, H-1), 3.24 (s, 6 H, OC$H_3$), 3.41 (m, 4 H, OC$H_2$), 3.49 (m, 4 H, OC$H_2$), 3.50 (s, 4 H, OC$H_2$), 5.85 (t, 1 H, H-5), 6.55 (dd, 2 H, H-4, H-6), 6.63 (bd, 2 H, H-3, H-7), 6.67 (t, 1 H, H-11), 6.89 (dd, 2 H, H-10, H-12), 7.10 (d, 2 H, H-9, H-13). $^{13}$C NMR (75 MHz, THF/[D$_8$]THF 1:1, 25°C): δ = 36.6 (d, $^1J_{CH}$ 152 Hz, C-1), 59.2 (q, $^1J_{CH}$ 141 Hz, O$C$H$_3$), 71.1 (t, $^1J_{CH}$ 141 Hz, O$C$H$_2$), 72.7 (t, $^1J_{CH}$ 141 Hz, O$C$H$_2$), 110.8 (d, $^1J_{CH}$ 157 Hz, C-5), 118.3 (bd, $^1J_{CH}$ 154 Hz, C-3, C-7), 122.0 (d, $^1J_{CH}$ 160 Hz, C-11), 125.3 (d, $^1J_{CH}$ 159 Hz, C-9, C-13), 128.0 (d, $^1J_{CH}$ 158 Hz, C-10, C-12), 128.4 (d, $^1J_{CH}$ 151 Hz, C-4, C-6), 152.2 (s, C-8), 156.8 (s, C-2). $^6$Li NMR (73 MHz, THF/[D$_8$]THF 1:1, 25°C): δ = 2.07. $^1$H NMR (400 MHz, THF/[D$_8$]THF 1:1, −80°C): δ = 3.01 (s, 1 H, H-1), 3.23 (s, 6 H, OC$H_3$), 3.39 (bs, 4 H, OC$H_2$), 3.47 (bs, 8 H, OC$H_2$), 5.69 (t, 1 H, H-5), 6.39 (d, 1 H, H-3), 6.47 (bs, 3 H, H-7, H-4, H-6), 6.71 (t, 1 H, H-11), 6.94 (dd, 2 H, H-10, H-12), 7.06 (d, 2 H, H-9, H-13). $^{13}$C NMR (100 MHz, THF/[D$_8$]THF 1:1, −80°C): δ = 37.1 (d, $^1J_{CH}$ 158 Hz, C-1), 59.1 (q, $^1J_{CH}$ 141 Hz, O$C$H$_3$), 70.3 (t, $^1J_{CH}$ 142 Hz, O$C$H$_2$), 70.5 (t, $^1J_{CH}$ 142 Hz, O$C$H$_2$), 72.2 (t, $^1J_{CH}$ 141 Hz, O$C$H$_2$), 108.4 (d, $^1J_{CH}$ 156 Hz, C-5), 114.6 (d, $^1J_{CH}$ 153 Hz, C-7), 118.8 (d, $^1J_{CH}$ 153 Hz, C-3), 121.9 (d, $^1J_{CH}$ 157 Hz, C-11), 124.7 (d, $^1J_{CH}$ 159 Hz, C-9, C-13), 127.7 (d, $^1J_{CH}$ 151 Hz, C-4), 128.1 (d, $^1J_{CH}$ 157 Hz, C-10, C-12), 128.7 (d, $^1J_{CH}$ 151 Hz, C-6), 151.7 (s, C-8), 155.7 (s, C-2).

For comparison: triglyme: $^1$H NMR (200 MHz, CDCl$_3$, 25°C): δ = 3.30 (s, 6 H, OC$H_3$), 3.48 (m, 4 H, OC$H_2$), 3.57 (m, 4 H, OC$H_2$), 3.59 (s, 4 H, OC$H_2$). $^{13}$C NMR (50 MHz, CDCl$_3$, 25°C): δ = 58.8 (q, $^1J_{CH}$ 141 Hz, O$C$H$_3$), 70.4 (t, $^1J_{CH}$ 141 Hz, O$C$H$_2$), 71.8 (t, $^1J_{CH}$ 141 Hz, O$C$H$_2$).

### 4.5. [$^6$Li]-α-(Phenylthio)benzyllithium with 12-crown-4 (**1**-$^6$Li-12-crown-4)

Due to the low stability of this sample, NMR spectra were recorded immediately after sample preparation. Low-temperature spectra could not be obtained because part of the sample solution precipitated if the temperature was lowered below 0°C. The broadened *ortho* (C-3, C-7) and *meta* (C-4, C-6) $^{13}$C NMR signals of the phenyl ring which was bonded to the benzylic carbon were only found by means of a C, H shift-correlated spectrum. $^1$H NMR (500 MHz, THF/[D$_8$]THF 1:1, 25°C): δ = 3.18 (s, 1 H, H-1), 3.56 (s, 16 H, OC$H_2$), 5.46 (t, 1 H, H-5), 6.26 (bd, 2 H, H-3, H-7), 6.37 (dd, 2 H, H-4, H-6), 6.69 (t, 1 H, H-11), 6.93 (dd, 2 H, H-10, H-12), 7.14 (d, 2 H, H-9, H-13). $^{13}$C NMR (100 MHz,

THF/[D$_8$]THF 1:1, 25°C): $\delta$ = 42.0 (d, $^1J_{CH}$ 168 Hz, C-1), 69.4 (t, $^1J_{CH}$ 142 Hz, OCH$_2$), 105.0 (d, $^1J_{CH}$ 157 Hz, C-5), ca. 113.0 (bs, too broad, C-7), ca. 118.0 (bs, too broad, C-3), 121.8 (d, $^1J_{CH}$ 157 Hz, C-11), 125.0 (d, $^1J_{CH}$ 160 Hz, C-9, C-13), 128.0 (d, $^1J_{CH}$ 156 Hz, C-10, C-12), ca. 128.5 (bs, too broad, C-4, C-6), 153.1 (s, C-8), 155.6 (s, C-2). $^6$Li NMR (73 MHz, THF/[D$_8$]THF 1:1, 25°C): $\delta$ = 2.08.

For comparison: 12-crown-4: $^1$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 3.65 (s, OCH$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 70.5 (t, $^1J_{CH}$ 141 Hz, OCH$_2$).

### 4.6. [$^6$Li]-α-(Phenylthio)benzyllithium with 15-crown-5 (**1**-$^6$Li-15-crown-5)

$^1$H NMR (500 MHz, THF/[D$_8$]THF 1:1, 25°C): $\delta$ = 3.11 (s, 1 H, H-1), 3.50 (s, 20 H, OCH$_2$), 5.36 (t, 1 H, H-5), 6.18 (bs, 2 H, H-3, H-7), 6.30 (dd, 2 H, H-4, H-6), 6.67 (t, 1 H, H-11), 6.91 (dd, 2 H, H-10, H-12), 7.11 (d, 2 H, H-9, H-13). $^{13}$C NMR (75 MHz, THF/[D$_8$]THF 1:1, 25°C): $\delta$ = 42.1 (d, $^1J_{CH}$ 168 Hz, C-1), 69.7 (t, $^1J_{CH}$ 143 Hz, OCH$_2$), 104.1 (d, $^1J_{CH}$ 157 Hz, C-5), 112.4 (bd, $^1J_{CH}$ 152 Hz, C-7), 117.1 (bd, $^1J_{CH}$ 152 Hz, C-3), 121.5 (d, $^1J_{CH}$ 160 Hz, C-11), 125.0 (d, $^1J_{CH}$ 159 Hz, C-9, C-13), 127.8 (bd, $^1J_{CH}$ 146 Hz, C-4), 127.9 (d, $^1J_{CH}$ 158 Hz, C-10, C-12), 128.7 (bd, $^1J_{CH}$ 146 Hz, C-6), 154.1 (s, C-8), 155.7 (s, C-2). $^6$Li NMR (73 MHz, THF/[D$_8$]THF 1:1, 25°C): $\delta$ = −0.81. $^1$H NMR (400 MHz, THF/[D$_8$]THF 1:1, −80°C): $\delta$ = 3.05 (s, 1 H, H-1), 3.46 (s, 20 H, OCH$_2$), 5.34 (t, 1 H, H-5), 6.07 (d, 1 H, H-3), 6.11 (d, 1 H, H-7), 6.28 (dd, 2 H, H-4, H-6), 6.72 (t, 1 H, H-11), 6.95 (dd, 2 H, H-10, H-12), 7.06 (d, 2 H, H-9, H-13). $^{13}$C NMR (100 MHz, THF/[D$_8$]THF 1:1, −80°C): $\delta$ = 41.3 (d, $^1J_{CH}$ 170 Hz, C-1), 69.1 (bt, $^1J_{CH}$ 142 Hz, OCH$_2$), 103.8 (d, $^1J_{CH}$ 157 Hz, C-5), 111.8 (d, $^1J_{CH}$ 152 Hz, C-7), 116.7 (d, $^1J_{CH}$ 149 Hz, C-3), 121.8 (d, $^1J_{CH}$ 157 Hz, C-11), 124.5 (d, $^1J_{CH}$ 160 Hz, C-9, C-13), 127.7 (d, $^1J_{CH}$ 148 Hz, C-4), 128.1 (d, $^1J_{CH}$ 155 Hz, C-10, C-12), 128.8 (d, $^1J_{CH}$ 148 Hz, C-6), 152.7 (s, C-8), 154.9 (s, C-2).

For comparison: 15-crown-5: $^1$H NMR (300 MHz, CDCl$_3$, 25°C): $\delta$ = 3.46 (s, OCH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$, 25°C): $\delta$ = 70.2 (t, $^1J_{CH}$ 141 Hz, OCH$_2$).

### 4.7. [$^6$Li]-α-(Phenylthio)benzyllithium with 18-crown-6 (**1**-$^6$Li-18-crown-6)

$^1$H NMR (500 MHz, THF/[D$_8$]THF 1:1, 25°C): $\delta$ = 3.09 (s, 1 H, H-1), 3.52 (s, 24 H, OCH$_2$), 5.56 (t, 1 H, H-5), 6.35 (bd, 2 H, H-3, H-7), 6.40 (dd, 2 H, H-4, H-6), 6.68 (t, 1 H, H-11), 6.92 (dd, 2 H, H-10, H-12), 7.11 (d, 2 H, H-9, H-13). $^{13}$C NMR (100 MHz, THF/[D$_8$]THF 1:1, 25°C): $\delta$ = 40.1 (d, $^1J_{CH}$ 163 Hz, C-1), 70.6 (t, $^1J_{CH}$ 142 Hz, OCH$_2$), 106.5 (d, $^1J_{CH}$ 157 Hz, C-5), ca. 116.0 (bs, too broad, C-3, C-7), 121.7 (d, $^1J_{CH}$ 156 Hz, C-11), 125.1 (d, $^1J_{CH}$ 161 Hz, C-9, C-13),

128.0 (d, $^1J_{CH}$ 152 Hz, C-10, C-12), 128.3 (d, $^1J_{CH}$ 148 Hz, C-4, C-6), 153.2 (s, C-8), 156.0 (s, C-2). $^6$Li NMR (73 MHz, THF/[D$_8$]THF 1:1, 25°C): $\delta$ = −0.39. $^1$H NMR (400 MHz, THF/[D$_8$]THF 1:1, −80°C): $\delta$ = 3.06 (bs, 1 H, H-1), 3.43 (bs, 24 H, OCH$_2$), 5.37 (bs, 1 H, H-5), 6.13 (bs, 2 H, H-3, H-7), 6.29 (bs, 2 H, H-4, H-6), 6.71 (bs, 1 H, H-11), 6.94 (bs, 2 H, H-10, H-12), 7.07 (bs, 2 H, H-9, H-13). $^{13}$C NMR (100 MHz, THF/[D$_8$]THF 1:1, −80°C): $\delta$ = 41.1 (d, $^1J_{CH}$ 171 Hz, C-1), 70.8 (t, $^1J_{CH}$ 141 Hz, OCH$_2$), 104.1 (d, $^1J_{CH}$ 156 Hz, C-5), 112.0 (d, $^1J_{CH}$ 155 Hz, C-7), 116.9 (d, $^1J_{CH}$ 148 Hz, C-3), 121.7 (d, $^1J_{CH}$ 155 Hz, C-11), 124.6 (d, $^1J_{CH}$ 158 Hz, C-9, C-13), 127.7 (d, $^1J_{CH}$ 145 Hz, C-4), 128.1 (d, $^1J_{CH}$ 156 Hz, C-10, C-12), 128.7 (d, $^1J_{CH}$ 147 Hz, C-6), 152.8 (s, C-8), 155.0 (s, C-2).

For comparison: 18-crown-6: $^1$H NMR (300 MHz, CDCl$_3$, 25°C): $\delta$ = 3.66 (s, OCH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$, 25°C): $\delta$ = 70.7 (t, $^1J_{CH}$ 141 Hz, OCH$_2$).

## Acknowledgements

## References

[1] S. Schade, G. Boche, J. Organomet. Chem. 550 (1998) 359–379.

[2] (a) L. Brandsma, H.D. Vercruijsse, Preparative Polar Organometallic Chemistry, vol. 1, Springer, Berlin, 1987; (b) L. Brandsma, Preparative Polar Organometallic Chemistry, vol. 2, Springer, Berlin, 1990; (c) B.J. Wakefield, Organolithium Methods, Academic Press, London, 1988; (d) T. Durst, in: E. Buncel, T. Durst (Eds.), Comprehensive Carbanion Chemistry, Part B, Elsevier, Amsterdam, 1984, chap. 5; (e) U. Schöllkopf, in: E. Müller (Ed.), Methoden Org. Chem., vol. 13/1, 4th ed., Houben-Weyl, 1970, pp. 87–253.

[3] (a) A.W. Langer (Ed.), Advances in Chemistry Series, vol. 130, American Chemical Society, Washington, DC, 1974; (b) M. Schlosser, Struktur und Reaktivität polarer Organometalle, Springer, Berlin, 1973.

[4] (a) B.L. Lucht, D.B. Collum, J. Am. Chem. Soc., 118 (1996) 2217; (b) B.L. Lucht, D.B. Collum, J. Am. Chem. Soc., 117 (1995) 9863; (c) D.B. Collum, Acc. Chem. Res., 26 (1993) 227.

[5] (a) G. Fraenkel, A. Chow, W.R. Winchester, J. Am. Chem. Soc., 112 (1990) 6190; (b) G. Fraenkel, M.J. Geckle, A. Kaylo, D.W. Estes, J. Organomet. Chem., 197 (1980) 249.

[6] (a) M. Gray, M. Tinkl, V. Snieckus, in: E.W. Abel, F.G.H. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 11, Pergamon, Oxford, 1995, chap. 1. (b) M. Schlosser (Ed.), Organometallics in Synthesis, Wiley, New York, 1994. (c) M. Hanack (Ed.), Methoden Org., vol. E19d, Chem. Houben-Weyl, 1993. (d) B.M. Trost (Ed.), Comprehensive Organic Synthesis, Pergamon, Oxford, 1991. (e) B.J. Wakefield, in: G. Wilkinson, F.G.H. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 7, Pergamon, Oxford, 1982, chap. 44. (f) B.J. Wakefield, The Chemistry of Organolithium Compounds, Pergamon, Oxford, 1974.

[7] (a) W. Bauer, G. Müller, R. Pi, P. v. R. Schleyer, Angew. Chem., 98 (1986) 1130; Angew. Chem. Int. Ed. Engl., 25 (1986) 1103; (b) W. Bauer, T. Clark, P. v. R. Schleyer, J. Am. Chem. Soc., 109 (1987) 970.

[8] (a) H. Günther, D. Moskau, P. Bast, D. Schmalz, Angew. Chem., 99 (1987) 1242; Angew. Chem. Int. Ed. Engl., 26 (1987) 1212. (b) R.D. Thomas, in: E. Buncel, J.R. Jones (Eds.), Isotopes in the Physical and Biomedical Science, vol. 2, Elsevier, Amsterdam, 1991, chap. 7. (c) L.M. Jackman, J. Bortiatynski, Adv. Carbanion Chem. 1 (1992) 45. (d) W. Bauer, P. v. R. Schleyer, Adv. Carbanion Chem. 1 (1992) 89. (e) H. Günther, in: D.M. Grant, R.K. Harris (Eds.), Encyclopedia of Nuclear Magnetic Resonance, vol. 5, Wiley, New York, 1996, p. 2807–2828.

[9] T. Ruhland, R.W. Hoffmann, S. Schade, G. Boche, Chem. Ber. 128 (1995) 551.

[10] W. Zarges, M. Marsch, K. Harms, W. Koch, G. Frenking, G. Boche, Chem. Ber. 124 (1991) 543.

[11] B.L. Lucht, M.P. Bernstein, J.F. Remenar, D.B. Collum, J. Am. Chem. Soc., 118 (1996) 10707; and references cited therein.

[12] (a) D. Seebach, R. Hässig, J. Gabriel, Helv. Chim. Acta 66 (1983) 308. However, if certain (structural) requirements are met, such couplings become observable: (b) D. Hoell, J. Lex, K. Müllen, J. Am. Chem. Soc. 108 (1986) 5983. (c) G. Fraenkel, K.V. Martin, J. Am. Chem. Soc. 117 (1995) 10336.

[13] (a) S.E. Denmark, R.L. Dorow, J. Am. Chem. Soc. 112 (1990) 864. (b) B.A. Keys, E.L. Eliel, E. Juaristi, Isr. J. Chem. 29 (1989) 171. (c) D.H. O'Brien, in: E. Buncel, T. Durst (Eds.), Comprehensive Carbanion Chemistry, Part A, Elsevier, Amsterdam, 1980, chap. 6. (d) P.R. Peoples, J.B. Grutzner, J. Am. Chem. Soc. 102 (1980) 4709. (e) D.H. O'Brien, C.R. Russell, A.J. Hart, J. Am. Chem. Soc. 101 (1979) 633; 98 (1976) 7427. (f) T. Bottin-Strzalko, J. Seyden-Penne, M.-J. Pouet, M.-P. Simonnin, J. Org. Chem. 43, (1978) 4346.

[14] S. Bradamante, G.A. Pagani, J. Chem. Soc. Perkin Trans. II (1986) 1035, 1047.

[15] (a) L.L. Chan, K.H. Wong, J. Smid, J. Am. Chem. Soc. 92 (1970) 1955. (b) J. Smid, in: M. Szwarc (Ed.), Ions and Ion Pairs in Organic Reactions, vol. 1, Wiley, New York, 1972, chap. 3. (c) T.E. Hogen-Esch, Adv. Phys. Org. Chem. 15 (1977) 153.

[16] (a) E. Buncel, B.C. Menon, J.P. Colpa, Can. J. Chem. 57 (1979) 999. (b) L.M. Jackman, N.M. Szeverenyi, J. Am. Chem. Soc. 99 (1977) 4954.

[17] (a) H. Sieger, F. Vögtle, Angew. Chem. 90 (1978) 212; Angew. Chem. Int. Ed. Engl. 17 (1978) 198. (b) F. Vögtle, F. Weber, Angew. Chem. 91 (1979) 813; Angew. Chem. Int. Ed. Engl. 18 (1979) 753.

[18] F. Vögtle, E. Weber, Kontakte (Merck) 1 (1977) 11.

[19] N.S. Poonia, A.V. Bajaj, Chem. Rev. 79 (1979) 389.

[20] D.E. Fenton, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, vol. 3, Pergamon, Oxford, 1987, chap. 23.

[21] E. Weber, F. Vögtle, Top. Curr. Chem. 98 (1981) 1.

[22] R. Hilgenfeld, W. Saenger, Top. Curr. Chem. 101 (1982) 1.

[23] G. Hilmersson, Ö. Davidsson, J. Org. Chem. 60 (1995) 7660.

[24] H. Günther, O. Eppers, H. Hausmann, D. Hüls, H.-E. Mons, K.-D. Klein, A. Maercker, Helv. Chim. Acta 78 (1995) 1913.

[25] G. Becker, B. Eschbach, O. Mundt, N. Seidler, Z. Anorg. Allg. Chem. 620 (1994) 1381.

[26] D. Hoffmann, W. Bauer, P. v. R. Schleyer, J. Chem. Soc. Chem. Commun. (1990) 208.

[27] S. Schade, Dissertation, Univ. Marburg, 1995.

[28] (a) M.A. Nichols, P.G. Williard, J. Am. Chem. Soc. 115 (1993) 1568. (b) N.D.R. Barnett, R.E. Mulvey, W. Clegg, P.A. O'Neil, J. Am. Chem. Soc. 115 (1993) 1573.

[29] H.J. Reich, K.J. Kulicke, J. Am. Chem. Soc. 117 (1995) 6621.

[30] T.R. Elworthy, A.I. Meyers, Tetrahedron, 50 (1994) 6089.

[31] (a) R.E. Gawley, Q. Zhang, Tetrahedron, 50 (1994) 6077. (b) R.E. Gawley, Q. Zhang, J. Am. Chem. Soc. 115 (1993) 7515.

[32] A.V. Yakimansky, L.V. Vinogradova, B.L. Erussalimsky, Macromol. Theory Simul. 3 (1994) 633.

[33] E. Kaufmann, J. Gose, P.v.R. Schleyer, Organometallics 8 (1989) 2577.

[34] E.J. Corey, J.C. Bailar, J. Am. Chem. Soc. 81 (1959) 2620.

[35] B.P. Hay, J.R. Rustad, J. Am. Chem. Soc. 116 (1994) 6316, and references cited therein.

[36] K. Bowman-Jones, in: R.B. King (Ed.), Encyclopedia of Inorganic Chemistry, Wiley, New York, 1994, pp. 1999–2016.

[37] (a) G.W. Gokel, H.D. Durst, Synthesis (1976) 168; (b) G.A. Melson (Ed.), Coordination Chemistry of Macrocyclic Compounds, Plenum Press, New York, 1979; (c) F. de Jong, D.N. Reinhoud, Adv. Phys. Org. Chem. 17 (1980) 279; (d) A.D. Hamilton, in: A.R. Katritzky (Ed.), Comprehensive Heterocyclic Chemistry, vol. 7, Pergamon, Oxford, 1984, chap. 5.21; (e) G.W. Gokel (Ed.), Cation Binding by Macrocycles, Dekker, New York, 1990.

[38] (a) H.O. Kalinowski, S. Berger, S. Braun, $^{13}$C-NMR-Spektroskopie, Thieme, Stuttgart, 1984; (b) M.D. Newton, J.M. Schulman, M.M. Manus, J. Am. Chem. Soc. 96 (1974) 17.

[39] (a) C.J. Pedersen, J. Am. Chem. Soc. 89 (1967) 2495, 7017; (b) C.J. Pedersen, H.K. Frensdorf, Angew. Chem. 84 (1972) 16; Angew. Chem. Int. Ed. Engl. 11 (1972) 16; (c) C.J. Pedersen, Angew. Chem. 100 (1988) 1053; Angew. Chem. Int. Ed. Engl. 27 (1988) 1021; (d) C.J. Pedersen, Science 241 (1988) 536.

[40] (a) R. Hilgenfeld, W. Saenger, Top. Curr. Chem. 101, 1982, 1–82, (b) R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, Chem. Rev. 85 (1985) 271.

[41] W.N. Setzer, P.v.R. Schleyer, Adv. Organomet. Chem. 24 (1985) 353.

[42] C.L. Liotta, J. Berkner, in: L.A. Paquette (Ed.), Encyclopedia of Reagents for Organic Synthesis, vol. 2, Wiley, New York, 1995, pp. 1401–1402, 1402–1403, 1403–1407.

[43] B. Lindman, S. Forsen, in: R.K. Harris, B.E. Mann (Eds.), NMR and the Periodic Table, Academic Press, New York, 1978, chap. 6.

[44] M. Szwarc, in: M. Szwarc (Ed.), Ions and Ion Pairs in Organic Reactions, vol. 1, Wiley, New York, 1972, chap. 1.

[45] J. Burgess, Ions in Solution, Ellis Horwood, Chichester, 1988.

[46] (a) Y. Inoue, T. Hakushi, Y. Liu, L.H. Tong, J. Org. Chem. 58 (1993) 5411; (b) R.D. Hancock, P.W. Wade, M.P. Ngwenya, A.S. de Sousa, K.V. Damu, Inorg. Chem. 29 (1990) 1968; (c) R.D. Hancock, J. Chem. Educ. 69 (1992) 615.

[47] (a) E. Karkhaneei, A. Afkhami, M. Shamsipur, J. Coord. Chem. 39 (1996) 33; (b) A.F. Danil de Namor, M.A.L. Tanco, J.C.Y. Ng, M. Salomon, Pure Appl. Chem. 67 (1995) 1095; (c) A. Gerhard, D.P. Cobranchi, B.A. Garland, A.M. Highley, Y.-H. Huang, G. Konya, A. Zahl, R. von Eldik, S. Petrucci, E.M. Eyring, J. Phys. Chem. 98 (1994) 7923; (d) E.M. Eyring, D.P. Cobranchi, B.A. Garland, A. Gerhardt, A.M. Highley, Y.-H. Huang, G. Konya, S. Petrucci, R. von Eldik, Pure Appl. Chem. 65 (1993) 451.

[48] (a) E.D. Glending, D. Feller, M.A. Thompson, J. Am. Chem. Soc. 116 (1994) 10657; (b) S. Lee, T. Wyttenbach, G. van Helden, M. Bowers, J. Am. Chem. Soc. 117 (1995) 10159; (c) L. von Szentpaly, I.L. Shamovsky, V.V. Nefedova, V.E. Zubkus, J. Mol. Structure (Theochem), 308 (1994) 125; (d) H.P. Hopkins Jr., A.B. Norman, J. Phys. Chem. 84 (1980) 309.

[49] (a) P. Jutzi, W. Wieland, B. Neumann, H.-G. Stammler, J. Organomet. Chem. 501 (1995) 369; (b) M.J. Duer, N.A. Page, M.A. Paver, P.R. Raithby, M.-A. Rennie, C.A. Russell, C. Stourton, A. Steiner, D.S. Wright, J. Chem. Soc. Chem. Commun. (1995) 1141; (c) D.R. Armstrong, A.J. Edwards, D. Moncrieff, M.A. Paver, P.R. Raithby, M.-A. Rennie, C.A. Russell, D.S. Wright, J. Chem. Soc. Chem. Commun. (1995)

927; (d) H. Gornitzka, D. Stalke, Organometallics, 13 (1994) 4398; (e) H. Gornitzka, D. Stalke, Angew. Chem. 106 (1994) 695; Angew. Chem. Int. Ed. Engl. 33 (1994) 693; (f) F. Zaegel, J.C. Gallucci, P. Meunier, B. Gautheron, M.R. Sivik, L.A. Paquette, J. Am. Chem. Soc. 116 (1994) 6466; (g) H. Chen, P. Jutzi, W. Leffers, M.M. Olmstead, P.P. Power, Organometallics, 10 (1991) 1282; (h) F. Pauer, J. Rocha, D. Stalke, J. Chem. Soc. Chem. Commun. (1991) 1477; (i) P. Jutzi, J. Organomet. Chem. 400 (1990) 1; (j) P.P. Power, Acc. Chem. Res. 21 (1988) 147; (k) S. Kamitori, K. Hirotsu, T. Higuchi, J. Am. Chem. Soc. 109 (1987) 2409; (l) M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 107 (1985) 2174; (m) H. Hope, M.M. Olmstead, P.P. Power, X. Xu, J. Am. Chem. Soc. 106 (1984) 819.

[50] (a) R. Colton, S. Mitchell, J.C. Traeger, Inorg. Chim. Acta, 231 (1995) 87; (b) H.-J. Buschmann, J. Solution Chem. 16 (1987) 181.

[51] (a) W. Hiller, S. Frey, J. Strähle, G. Boche, W. Zarges, K. Harms, M. Marsch, R. Wollert, K. Dehnicke, Chem. Ber. 125 (1992) 87; (b) G.A. Underiner, R.P. Tan, D.R. Powell, R. West, J. Am. Chem. Soc. 113 (1991) 8437; (c) R.A. Bartlett, H.V.R. Dias, H. Hope, B.D. Murray, M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 108 (1986) 6921; (d) P.P. Power, X. Xiaojie, J. Chem. Soc. Chem. Commun. (1984) 358; (e) P. Groth, Acta Chem. Scand. A, 35 (1981) 463; (f) P. Groth, Acta Chem. Scand. A 35 (1981) 460.

[52] Hexacoordinated Li$^+$ in a 12-crown-4 complex: A. Blaschette, K.-H. Nagel, P.G. Jones, Z. Naturforsch. 49b (1994) 36.

[53] For a solid state NMR study see: C.I. Ratcliffe, G.W. Buchanan, J.K. Denike, J. Am. Chem. Soc. 117 (1995) 2900.

[54] (a) M.P. Murchie, J.W. Bovenkamp, A. Rodrigue, K.A. Watson, S. Fortier, Can. J. Chem. 66 (1988) 2515; (b) P.C. Stark, M. Huff, E.A. Babaian, L.M. Barden, D.C. Hrncir, S.G. Bott, J.L. Atwood, J. Inclusion Phenom. 5 (1987) 683.

[55] (a) F. Wehrli, Annu. Rep. NMR Spectrosc. 9 (1979) 125.

[56] L.J. Dye, R.H. Huang, Pure Appl. Chem. 65, (1993) 435.

[57] M. Tahiri, P. Doppelt, J. Fischer, R. Weiss, Inorg. Chim. Acta, 127 (1987) L1.

[58] D.B. Collum, Acc. Chem. Res. 25 (1992) 448.

[59] J.L. Wardell, in: G. Wilkinson, F.G.H. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 1, Pergamon, Oxford, 1982, chap. 2.

[60] G. Fraenkel, M.P. Hallden-Abberton, J. Am. Chem. Soc. 103 (1981) 5657.

[61] P. Chakrabarti, J.D. Dunitz, Helv. Chim. Acta 65 (1982) 1482.

[62] F.S. Mair, R. Snaith, in: R.B. King (Ed.), Encyclopedia of Inorganic Chemistry, Wiley, New York, 1994, pp. 35–54.

[63] A.J. Smetana, A.I. Popov, J. Solution Chem. 9 (1980) 183.

[64] P. Groth, Acta Chem. Scand. A 36 (1982) 109.

[65] K.A. Watson, S. Fortier, M.P. Murchie, J.W. Bovenkamp, A. Rodrigue, G.W. Buchanan, C.I. Ratcliffe, Can. J. Chem. 68 (1990) 1201.