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The effect of (poly)amine ligands on the solution structure of [^{6}Li]-α-(phenylthio)benzyllithium in tetrahydrofuran: A ^{1}H,^{6}Li-HOESY NMR study [1]

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Abstract

Are (poly)amine ligands, added to a tetrahydrofuran solution of an organolithium compound, bonded to lithium, or not? This question is of relevance for physical organic studies as well as for the evaluation of the ground state of (stereoselective) reactions of organolithium species in the presence of such ligands. Therefore, we studied [^{6}Li]-α-(phenylthio)benzyllithium **1**-^{6}Li as a model compound in THF/[D_8]THF solution (1:1) in the presence of several acyclic and cyclic (poly)amine ligands by ^{1}H,^{6}Li-HOESY and ^{1}H and ^{13}C NMR spectroscopy. (Poly)amine complexes of **1**-^{6}Li are obtained in most cases. Ligands with up to three N-atoms afford contact ion pairs (CIPs) while in complexes with tetradentate amines, CIPs are in temperature-dependent equilibrium with separated ion pairs (SIPs). Graphical analyses of the ^{1}H and ^{13}C NMR spectra of the (poly)amine complexes of **1**-^{6}Li revealed that 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) are proportional to each other. These NMR spectroscopic parameters can be used as probes for the charge distribution within the carbanionic moieties of **1**-^{6}Li in the respective complexes, which is especially useful for a classification to CIPs and/or SIPs. © 1998 Elsevier Science S.A.

Keywords: ^{1}H,^{6}Li-HOESY; [^{6}Li]-α-(phenylthio)benzyllithium; (Poly)amine ligands; Solution structures; Ion pair equilibria

1. Introduction

Organolithium compounds are of key importance in contemporary organic synthesis. They have found widespread applications in deprotonation, transmetalation or metal-halogen exchange reactions [1,2]. In many cases Lewis bases as, e.g., chelating polyamines such as N,N,N',N'-tetramethylethylenediamine (TMEDA) are added to increase the reactivity of the organolithium reagent [2,3]. However, in spite of the vast amount of solid state structural data [2], the interactions in solution between metal, added ligands and coordinating solvents are by no means understood. Collum has emphasized that much of the 'knowledge' about the effect of TMEDA is based on empirical observations rather than on systematic studies [7] which led him to perform recently published comprehensive investigations of ligand effects on the structure of lithium amides as, e.g., lithium hexamethyldisilazide (LiHMDS) in hydrocarbon solvents [8–10]. However, there exists still only little information on the coordination of lithium in C-lithiated compounds in the presence of added ligands in coordinating solvents such as tetrahydrofuran (THF). The ether solvent THF is one of the most commonly used solvents in organolithium chemistry. Yet the extent of ligand vs. solvent complexation in THF solution, and the structural and chemical consequences of ligand coordination, are largely unknown. Therefore, we examined in detail the effects of various non-cyclic and cyclic (poly)amine ligands on an organolithium compound in THF solution.

As we intended to study the coordination sphere around lithium, we had to find suitable NMR-spectroscopic tools for that purpose (for reviews on NMR spectroscopy of organolithium compounds, see [11]).

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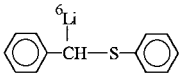
[1] Dedicated to Professor Ken Wade on the occasion of his 65th birthday.

[2] For recent reviews see [4]; for additional reviews on structural studies see [5,6].

Apart from conventional coupled and decoupled ^{13}C NMR spectroscopy, we thus focused on $^{1}H,^{6}Li$-HOESY spectroscopy which was developed by Bauer and Schleyer [12]. This two-dimensional NMR technique correlates via dipolar interactions ^{6}Li atoms and nearby protons. If the distance between a certain ^{6}Li and ^{1}H nucleus is 400 pm or less, a cross-peak can be observed in the 2D NMR spectrum. The intensity of the cross-peak correlates with the distance between ^{6}Li and ^{1}H. Close distances lead to intense signals. It is thus possible to get semi-quantitative informations of lithium–carbanion, lithium–ligand and lithium–solvent interactions. By means of a (partly protonated) 1:1 THF/[D_8]THF–solvent mixture [13], we expected to find cross-peaks of all molecules (anion, ligand and solvent molecules) that were bonded to lithium, thus enabling us to determine whether or not a ligand was coordinated to the metal.

Since the $^{1}H,^{6}Li$-HOESY spectroscopy requires ^{6}Li-labelled organolithium compounds, our test compound had to be easily accessible, preferentially by metalation with *n*-Bu^{6}Li. To avoid complications by changes in the aggregation state, the lithium compound also had to be monomeric under the conditions of our experiments. For this reason, we chose [^{6}Li]-α-(phenylthio)benzyllithium **1**-^{6}Li as the compound to be tested [13–15], a benzyllithium compound which is easily obtained by deprotonating benzylphenylsulfide with *n*-Bu^{6}Li in the THF/[D_8]THF (1:1) solvent mixture [13].



1-^{6}Li (1)

We concentrated on a benzyllithium species because benzyllithium compounds appear to be particularly sensitive to ligand and solvent effects and show a broad structural diversity. In the solid state, they are known to form monomers as well as polymers in which the carbanion can be coordinated to lithium in an η^1-, η^2- or η^3-like manner [14,16]. In solution, contact ion pairs (CIPs) have been reported to be in equilibrium with solvent separated ion pairs (SSIPs) [3]. Moreover, **1**-^{6}Li bears a proton at the lithiated carbon which turned out to be a useful probe in these investigations.

The systematic NMR-spectroscopic studies of (poly)amine-complexes of **1**-^{6}Li by means of ^{1}H and ^{13}C NMR spectroscopy were carried out at 25°C and at −80°C; $^{1}H,^{6}Li$-HOESY spectroscopy was performed at 25°C.

2. Results and discussion

*2.1. [^{6}Li]-α-(phenylthio)benzyllithium **1**-^{6}Li in THF/[D_8]THF*

First we recorded the NMR spectrum of a 0.5 M solution of [^{6}Li]-α-(phenylthio)benzyllithium **1**-^{6}Li in THF/[D_8]THF (1:1) (the solution contained approximately 12 THF and 12 [D_8]THF solvent molecules per molecule of **1**-^{6}Li) without any additives. The $^{1}H,^{6}Li$-HOESY spectrum of this sample at 25°C, which served as a 'standard' for further comparisons, is shown in Fig. 1. Selected proton and carbon chemical shifts are listed in Tables 1 and 2 (entries 1).

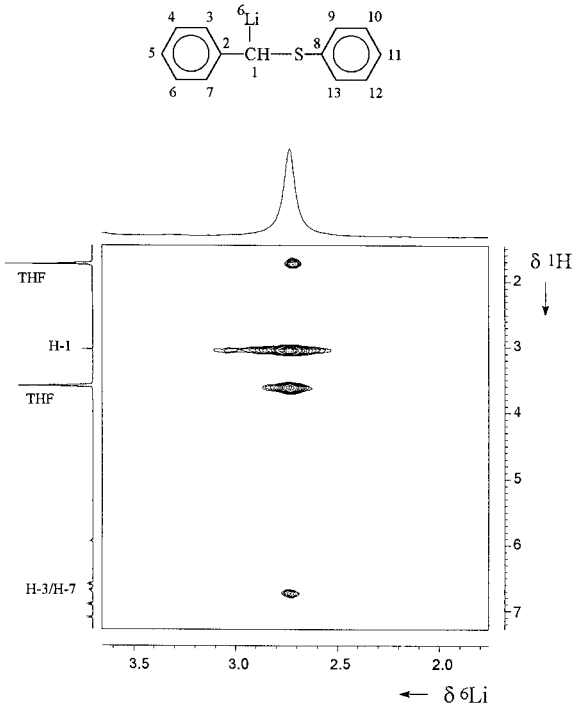


Fig. 1. $^{1}H,^{6}Li$-HOESY spectrum of [^{6}Li]-α-(phenylthio)benzyllithium **1**-^{6}Li in 1:1 THF/[D_8]THF at 25°C.

The 2D NMR spectrum of **1**-^{6}Li in THF/[D_8]THF (1:1) contains four cross-peaks. A very strong one is found at the proton resonance of the benzylic proton H-1 ($\delta_H = 3.03$) and a weaker one at the resonance of the aromatic *ortho* protons H-3/H-7 ($\delta_H = 6.70$). Two more cross-peaks appear at the THF–OCH_2 (strong) and THF–CH_2 (weak) signals. Thus, the spectrum clearly shows that the Li cation is bonded to the benzylic carbon C-1 (strong H-1 cross-peak) and that it is

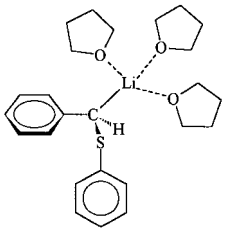
Table 1
Selected ^{1}H-NMR chemical shifts δ of the lithiated sulfide **1**-^{6}Li and its complexes with (poly)amines in 1:1 THF/[D_8]THF at 25°C

Entry	Ligand	H-1	H-3/H-7	H-4/H-6	H-5
1	—	3.03	6.70	6.59	5.94
2	3 NEt_3	3.04	6.72	6.61	5.96
3	TMEDA	3.02	6.72	6.60	5.96
4	(−)-sparteine	3.03	6.71	6.60	5.95
5	PMDTA	3.06	6.71	6.63	5.98
6	HMTTA	3.07	6.48	6.48	5.70
7	Me_3–6N3	3.03	6.70	6.60	5.94
8	Me_3–9N3	3.09	6.71	6.63	5.95
9	Me_4–12N4	3.07	6.38	6.38	5.53

Table 2
Selected ^{13}C-NMR chemical shifts δ and coupling constants $^{1}J_{CH}$(C-1) of the lithiated sulfide **1**-^{6}Li and its complexes with (poly)amines in 1:1 THF/[D_8]THF at 25°C

Entry	Ligand	C-1	$^{1}J_{CH}$(C-1) (Hz)	C-2	C-3/C-7	C-4/C-6	C-5	C-8
1	—	35.8	149	157.0	118.8	128.3	111.8	151.8
2	3 NEt_3	35.7	149	157.0	118.8	128.4	112.0	151.8
3	TMEDA	35.6	148	157.0	118.9	128.3	112.0	151.6
4	(−)-sparteine	35.7	148	157.0	118.9	128.4	112.0	151.7
5	PMDTA	35.5	149	156.6	118.9	128.5	112.2	151.5
6	HMTTA	38.5	158	156.4	117.2	128.4	108.8	152.7
7	Me_3–6N3	35.8	149	157.0	118.7	128.4	111.7	151.8
8	Me_3–9N3	34.8	152	156.0	118.5	128.7	112.0	151.3
9	Me_4–12N4	40.5	162	156.4	116.4	128.3	106.5	153.6

solvated by THF. Compared to the H-1 cross-peak, the H-3/H-7 signal is far less intense, indicating that the metal is not, or only weakly, coordinated to the *ortho* carbons C-3/C-7, or to the *ipso* carbon C-2. Although a dimeric or oligomeric species cannot be fully excluded from these data, we assume that compound **1**-^{6}Li is monomeric due to the largely different cross-peak intensities. In a higher aggregate the steric crowding would give rise to shorter Li–H-3/H-7 bond distances, and the cross-peak intensity of the H-3/H-7 signal would be comparatively larger [3]. Lithium probably is tetracoordinated with η^1-coordination to the carbanion and the three remaining coordination sites being occupied by THF solvent molecules. This leads to the THF-solvated contact ion pair **2**.



(2)

2

The benzyllithium compound **1** had been crystallised before from THF, and its X-ray crystal structure **3** had been determined by our group (Fig. 2) [14].

Similar to the solution structure, **3** forms a monomeric contact ion pair with a tetrahedral geometry at lithium. The metal is coordinated by the benzylic carbon (C1–Li = 221 pm) and three THF molecules (Li–O1/O2/O3 = 194–196 pm). The distance between lithium and the benzylic proton H1 is 263 pm. In solution, such a distance between the two nuclei should give an intense cross-peak in the ^{1}H,^{6}Li-HOESY spectrum, and that is indeed what is found in the NMR experiment (Fig. 1). In the solid state, Li is not coordinated to the *ipso* carbon C2 (Li–C2 = 279 pm) and to the *ortho* carbons C3/C7 (shortest Li–C distance 320 pm) which is in agreement with the interpretation of the 2D NMR spectrum given above.

In the crystal, the anionic benzylic carbon C1 is pyramidalised. In order to find out whether a similar conformation exists in the THF solution we recorded a gated decoupled carbon NMR spectrum. Proton-carbon coupling constants $^{1}J_{CH}$ give informations on the hybridisation of a carbon atom in question. In general, if $^{1}J_{CH}$ of a proton-bearing lithiated carbon atom increases on metalation to values of 165–170 Hz, rehybridisation from sp^3 to sp^2 has taken place [18,19]. In the case of **1**-^{6}Li in THF/[D_8]THF (1:1), a value of $^{1}J_{CH}$(C-1) = 149 Hz was measured, whereas $^{1}J_{CH}$(C-1) of the parent hydrocarbon benzylphenylsulfide amounts to 141 Hz (in $CDCl_3$). This modest increase in $^{1}J_{CH}$ shows that, at 25°C in THF solution, the benzylic carbon C-1 is also largely sp^3-hybridised and thus pyramidalised.

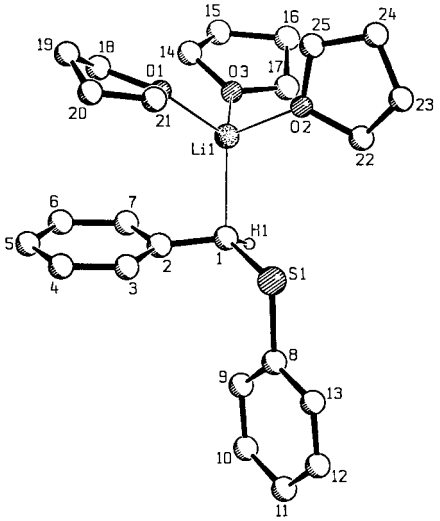


Fig. 2. Solid state structure of [α-(phenylthio)benzyllithium·$(THF)_3$] (**3**).

[3] In the ^{1}H,^{6}Li-HOESY spectra of diethylether-solvated dimers of **1**-^{6}Li in C_6D_6, the intensity of the H-3/H-7 cross-peak is only marginally weaker than the H-1 cross-peak, whereas in the ^{1}H,^{6}Li-HOESY spectrum of THF-solvated monomers of **1**-^{6}Li in C_6D_6, the H-3/H-7 cross-peak is far less intense than the H-1 cross-peak. The latter spectrum is very similar to the spectrum shown in Fig. 1 [17].

Table 3
Selected ^{1}H-NMR chemical shifts δ of the lithiated sulfide **1**-^{6}Li and its complexes with (poly)amines 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	—	2.99	6.52	6.68	6.55	6.59	5.87
2	3 NEt_3	2.98	6.54	6.73	6.56	6.60	5.91
3	TMEDA	2.99	6.54	6.71	6.56	6.60	5.89
4	(−)-sparteine	2.98	6.54	6.73	6.56	6.60	5.91
5	PMDTA	3.04	6.57	6.64	6.57	6.62	5.91
6	HMTTA	3.04	6.23	6.70	6.36	6.36	5.49
7	Me_3–6N3	2.99	6.51	6.68	6.54	6.57	5.86
8	Me_3–9N3	3.03	6.61	6.73	6.60	6.65	5.94
9	Me_4–12N4	3.03	6.15	6.15	6.30	6.30	5.39

In summary, NMR-spectroscopic and X-ray crystal structure investigations indicate that **1**-^{6}Li forms a THF-solvated monomeric contact ion pair both in THF solution (**2**) and in the solid state (**3**).

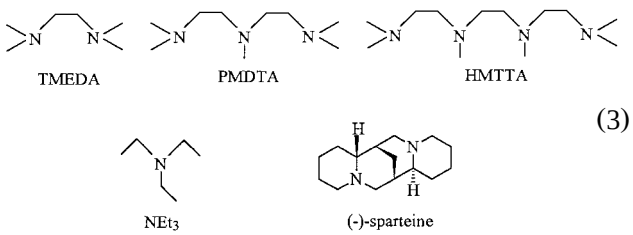
Proton and carbon NMR spectra were also recorded at −80°C (Tables 3 and 4, entries 1).

At this temperature, the phenyl rotation around the C-1–C-2 bond is frozen out (rotational barrier $\Delta G^{\neq}_{298°C}$ = 49.9 kJ/mol [14]), which leads to five different proton and six different carbon signals for the phenyl ring. The rotation around the S–Ph bond is not affected by the lower temperature. Assignment of the aromatic ring protons H-3 to H-7 to the carbons C-3 to C-7 was achieved by means of a C,H-shift-correlated NMR spectrum. ^{13}C,^{6}Li coupling between C-1 and Li was not observed at −80°C [4]. Apart from a shift of the *ortho* proton H-3 of $\Delta\delta = -0.18$ ppm (the negative sign denotes a shift towards lower δ-values), no significant changes were found in the proton (Tables 1 and 3, entries 1) and carbon spectra (Tables 2 and 4, entries 1) on lowering the temperature from 25 to −80°C. One can therefore conclude that C-1 is likewise sp^3-hybridised at low temperatures and that the same solution structure **2** is found at both temperatures.

*2.2. Complexes of **1**-^{6}Li with non-cyclic polyamine ligands*

2.2.1. Measurements at 25°C

Using the same conditions and NMR-spectroscopic parameters as above, ^{1}H,^{6}Li-HOESY as well as proton and carbon NMR spectra of **1**-^{6}Li were recorded at 25°C in the presence of equimolar amounts of the amines N,N,N′,N′-tetramethylethylenediamine (TMEDA), (−)-sparteine, N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDTA), N,N,N′,N′,N″,N‴-hexamethyltriethylenetetramine (HMTTA), and of an excess (3 equivalents) of triethyl amine (NEt_3).



(3)

Selected proton and carbon NMR data are summarized in Tables 1 and 2. Since the ^{6}Li chemical shifts (with respect to an external 1.0 M solution of ^{6}LiCl in deuterium oxide) did not appear to follow a characteristic pattern, they are not discussed here.

The ^{1}H,^{6}Li-HOESY spectrum of **1**-^{6}Li with 1 molar equivalent of TMEDA as ligand is shown in Fig. 3.

Cross-peaks are observed at the proton resonances of H-1 (δ_H = 3.02, strong), H-3/H-7 (δ_H = 6.72, weak), TMEDA–CH_3 (δ_H = 2.13, strong), TMEDA–CH_2 (δ_H = 2.28, weak), THF–OCH_2 (intermediate intensity) and THF–CH_2 (weak). The TMEDA cross-peaks clearly prove that lithium is coordinated to this amine. It is interesting to note that except for the TMEDA signals, the spectrum in Fig. 3 resembles strongly the HOESY spectrum of **1**-^{6}Li without added ligands (Fig. 1). This indicates that the structural type of a solvated contact ion pair as in complex **2** with η^1-coordination of lithium to the anionic benzylic carbon C-1 seems not to be changed significantly by TMEDA. Only in the solvation sphere of the metal changes have occurred, in agreement with the chelating ligand TMEDA having replaced two THF molecules. Monohapto-coordination of lithium by only one of the TMEDA nitrogens is entropically unfavourable and rather unlikely. Thus, the coordination at lithium can be described as an equilibrium between a TMEDA (**4**)- and a THF-solvated (**2**) species (see Scheme 1) with the equilibrium being far on the side of TMEDA-solvated **4**. TMEDA-complexation has to be very favourable, because the molar ratio of THF/[D_8]THF to TMEDA is roughly 24:1.

It is worth noting that there are no differences in the proton and carbon NMR chemical shifts of TMEDA-chelated and THF-solvated **1**-^{6}Li (Tables 1 and 2, entries 1 and 2). Obviously the carbanionic moiety is, at least in that case, not strongly affected by the changes in the coordination sphere around lithium. This result clearly tells that at least in the case of the benzyllithium species **1**-^{6}Li, it is impossible to detect a lithium–TMEDA contact by simply recording the proton and carbon NMR data and not measuring a ^{1}H,^{6}Li-HOESY spectrum of the sample.

With (−)-sparteine, the lithiated sulfide **1**-^{6}Li also forms a complex. Apart from cross-peaks at the proton

[4] In 'normal' benzyllithium compounds, a ^{13}C,^{6}Li-coupling was never observed even at temperatures as low as −150°C [20]. However, if certain (structural) requirements are met, such couplings become observable [13,21].

Table 4
Selected ^{13}C NMR chemical shifts δ and coupling constants $^{1}J_{CH}$(C-1) of the lithiated sulfide **1**-^{6}Li and its complexes with (poly)amines in 1:1 THF/[D_8]THF at −80°C

Entry	Ligand	C-1	$^{1}J_{CH}$(C-1) (Hz)	C-2	C-7	C-3	C-4	C-6	C-5	C-8
1	—	35.1	152	156.1	115.9	119.7	127.8	128.8	110.7	151.2
2	3 NEt_3	34.7	151	156.2	116.2	119.9	127.8	128.8	111.3	151.0
3	TMEDA	35.2	152	156.2	116.2	119.8	127.8	128.8	110.9	151.2
4	(−)-sparteine	35.6	152	156.2	116.2	119.9	127.8	128.8	111.2	151.0
5	PMDTA	35.0	152	155.8	116.6	119.5	127.9	128.9	111.1	150.9
6	HMTTA	40.0	[a]	155.1	113.1	117.6	127.7	128.8	105.6	152.5
7	Me_3–6N3	35.3	152	156.1	115.8	119.6	127.8	128.8	110.6	151.3
8	Me_3–9N3	33.8	153	155.4	116.5	119.6	128.2	129.1	111.7	150.6
9	Me_4–12N4	41.0	168	154.9	112.3	117.1	127.8	128.8	104.7	152.6

[a] Too broad.

resonances of H-1 ($\delta_H = 3.03$), H-3/H-7 ($\delta_H = 6.71$), THF–OCH_2 and THF–CH_2 (as similarly found in the spectra of Figs. 1 and 3), the ^{1}H,^{6}Li-HOESY spectrum reveals another, however, weak cross-peak in the region $\delta_H = 1.33–1.52$ (not shown). This suggests an equilibrium between a (−)-sparteine-coordinated and a THF-solvated complex of **1**-^{6}Li comparable to the equilibrium with TMEDA depicted in Scheme 1. Since the (−)-sparteine proton resonances give broad and complex multiplets between $\delta_H = 0.90–2.70$, the cross-peak could not be assigned in detail to the 26 (−)-sparteine hydrogen atoms.

A ^{1}H,^{6}Li-HOESY spectrum of **1**-^{6}Li in the presence of 3 molar equivalents of triethylamine NEt_3 was also recorded (not shown). In this spectrum, amine-lithium contacts were not observed, and the 2D NMR spectrum looked exactly like the one in Fig. 1 (**1**-^{6}Li in THF/[D_8]THF). Thus, even if 3 molar equiv. of NEt_3 are added, the monodentate amine cannot successfully compete with an excess of THF/[D_8]THF for the coordination sites at Li. This result strongly suggests that the bidentate amines TMEDA and (−)-sparteine bind as chelate ligands with both N-atoms coordinated to the organolithium compound **1**-^{6}Li.

If the tridentate amine PMDTA is employed as the ligand, a strong PMDTA complex **5** results (Fig. 4).

The ^{1}H,^{6}Li-HOESY spectrum shows a close lithium-amine (intense cross-peak with the PMDTA signals at $\delta_H = 2.14–2.37$) and a very weak lithium–THF contact (cross-peak of low intensity at the THF–OCH_2 resonance). PMDTA apparently has displaced THF almost completely from the solvation sphere around the Li cation. However, the strong H-1 ($\delta_H = 3.06$) and the weak H-3/H-7 cross-peaks ($\delta_H = 6.71$) indicate that the position of lithium with regard to the carbanion has not changed essentially. Thus, even in the PMDTA complex, lithium is still coordinated to the benzylic carbon C-1 in an η^1-like manner. Consequently, as in the TMEDA case, the PMDTA complex shows the same proton and carbon NMR chemical shifts as 'amine-ligand-free' **1**-^{6}Li (Tables 1 and 2, entries 5). In THF solution, therefore, an equilibrium exists between a PMDTA-coordinated (**5**) and a partly THF-solvated (**6**) contact ion pair (Scheme 2). Probably, for entropic

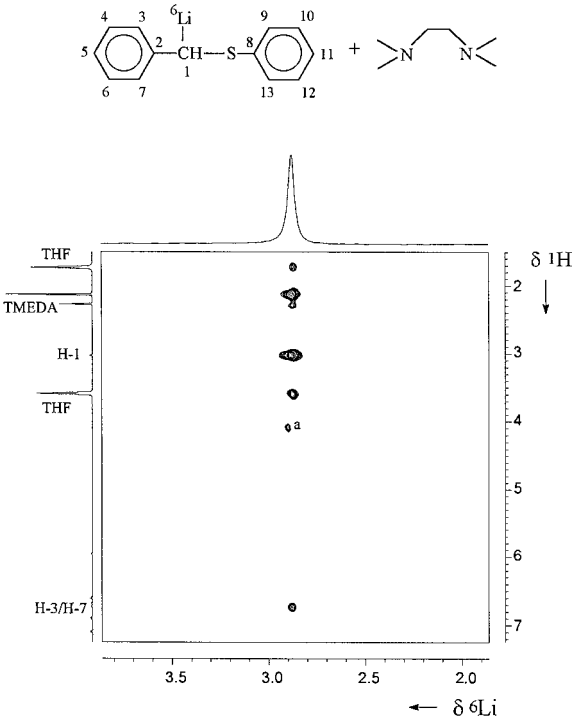
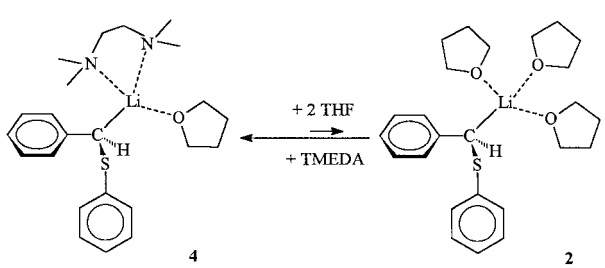


Fig. 3. ^{1}H,^{6}Li-HOESY spectrum of [^{6}Li]-α-(phenylthio)benzyllithium **1**-^{6}Li with 1 mol. equiv. TMEDA in 1:1 THF/[D_8]THF at 25°C (a = axial cross-peak, artefact).



Scheme 1.

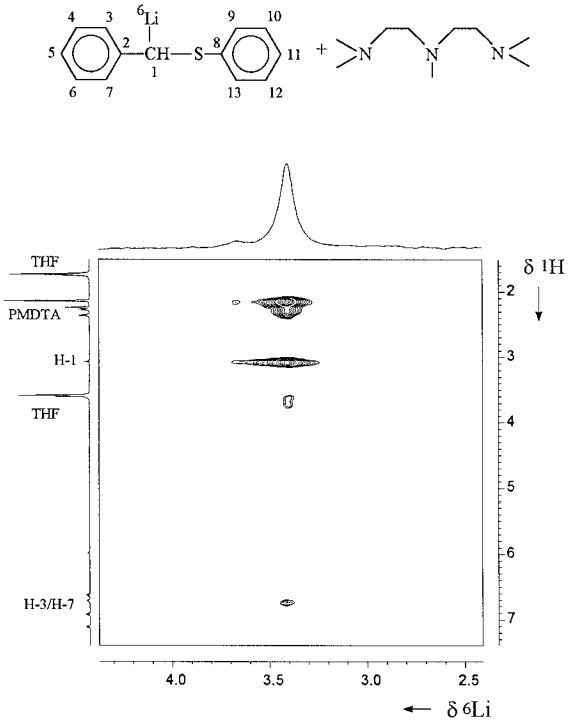


Fig. 4. $^{1}H,^{6}Li$-HOESY spectrum of [^{6}Li]-α-(phenylthio)benzyllithium **1**-^{6}Li with 1 mol. equiv. PMDTA in 1:1 THF/[D_8]THF at 25°C.

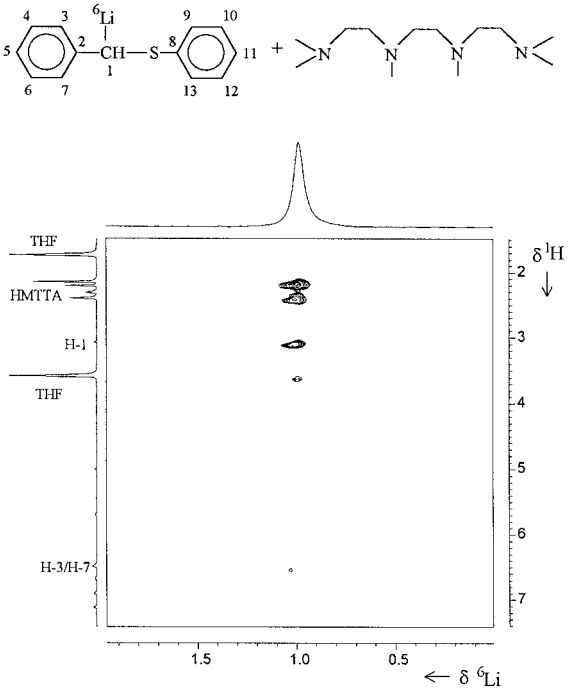
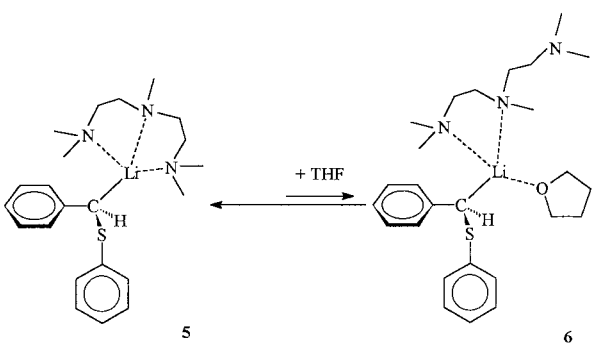


Fig. 5. $^{1}H,^{6}Li$-HOESY spectrum of [^{6}Li]-α-(phenylthio)benzyllithium **1**-^{6}Li with 1 mol. equiv. HMTTA in 1:1 THF/[D_8]THF at 25°C.

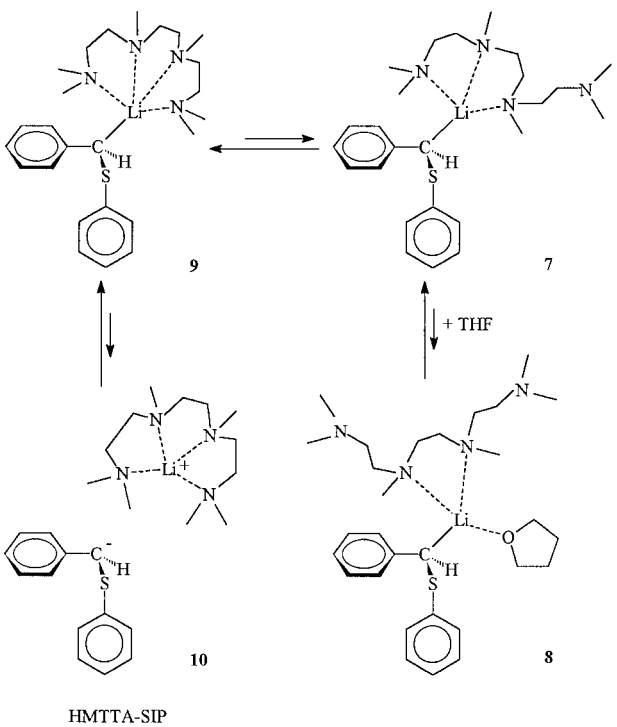
reasons, this equilibrium is strongly shifted to the left.

Increasing the number of N-atoms in the ligand to four leads to the amine HMTTA. The $^{1}H,^{6}Li$-HOESY spectrum of its complex with **1**-^{6}Li is given in Fig. 5.

Cross-peaks appear at the HMTTA ($\delta_H = 2.15–2.40$), H-1 ($\delta_H = 3.07$), THF–OCH_2 and H-3/H-7 ($\delta_H = 6.48$) signals. The spectrum is similar to the 2D NMR spectrum of the PMDTA complex (Fig. 4). Again, a strong lithium–amine and a weak lithium–THF contact is observed, and the Li cation is still coordinated to the benzylic carbon C-1. Nevertheless, since HMTTA is a tetradentate ligand, the equilibria in THF solution are presumably more complex than those in the PMDTA and TMEDA cases. Apart from complexes with tetracoordination at Li (**7**, **8**), species with a pentacoordinated metal (**9**), or a ligand-separated ion pair (HMTTA–SIP **10**), are probably also involved (Scheme 3). Unfortunately the $^{1}H,^{6}Li$-HOESY spectrum only yields the



Scheme 2.



Scheme 3.

time-weighted average of all of these equilibria, and it is difficult to identify the individual species participating in the exchange processes.

At this point, a look at the proton and carbon NMR spectra of the amine complexes discussed so far is helpful. Whereas the same proton and carbon NMR chemical shifts as in THF-coordinated **1**-^{6}Li were found for the NMR samples with the amines outlined in Tables 1 and 2, entries 2–5, one notices some differences in the HMTTA-containing sample (Tables 1 and 2, entries 6). Compared to **1**-^{6}Li without added ligands, the *para* proton H-5 ($\Delta\delta = -0.24$ ppm) as well as the *para* carbon C-5 ($\Delta\delta = -3.0$ ppm) shows a significant shift to lower δ-values ($\Delta\delta$ negative), the benzylic carbon C-1 is shifted to higher δ-values (positive $\Delta\delta$ shift of $\Delta\delta = 2.7$ ppm), and the C,H-coupling constant of this carbon $^{1}J_{CH}$(C-1) is increased by 9 Hz to 158 Hz. These findings indicate that the C-1–Li interaction is weakened, the benzylic carbon atom is less pyramidalized than in the other amine complexes of **1**-^{6}Li, and more negative charge is delocalised into the phenyl ring which is bonded to C-1, which leads to the observed negative $\Delta\delta$ shifts of C-5 and H-5 [22,23]. These observations further support the assumption that a complex with pentacoordinated lithium (**9**), or a HMTTA–SIP **10**, are involved in the equilibria with HMTTA in THF-solution.

2.2.2. Measurements at −80°C

^{1}H and ^{13}C NMR spectra of the amine complexes were also recorded at −80°C. Selected chemical shift data are summarized in Tables 3 and 4. In line with earlier observations with related benzyllithium compounds, a ^{13}C,^{6}Li coupling between C-1 and Li could not be observed in any of the carbon NMR spectra [20,21]. Due to the hindered phenyl rotation around the C-1–C-2 bond, five different proton and six different carbon signals were found in all of the samples. As at 25°C, the ^{1}H and ^{13}C NMR spectra of **1**-^{6}Li in the presence of NEt_3, TMEDA, (−)-sparteine and PMDTA as ligands (entries 2–5) were very similar to the spectrum of **1**-^{6}Li without added amines (entry 1). These results indicate that at −80°C in all these cases the same monomeric contact ion pairs of **1**-^{6}Li are formed as at 25°C. They only differ from THF-solvated **1**-^{6}Li in the coordination sphere around the lithium. With PMDTA as the ligand, seven PMDTA resonances were found in the carbon NMR spectrum at −80°C. Apparently the intramolecular motions of the coordinated amine ligand are hindered at that temperature, and an unsymmetrical PMDTA conformation is frozen out. Thus, the PMDTA complex **5** (Scheme 2) can no longer be in a fast equilibration with a partly THF-solvated species **6**, and the equilibrium is shifted largely to the left. However, the overall structure of the complex **5** remains unchanged.

Remarkable differences are again observed in the ^{1}H and ^{13}C NMR spectra of the HMTTA-containing sample (Tables 3 and 4, entries 6). Both the *para* carbons C-5 and the *para* protons H-5 show negative $\Delta\delta$ shifts (shifts towards lower δ-values) compared to the NMR spectra of the other amine complexes (Tables 3 and 4, entries 2–5) as well as the 25°C spectra (Tables 1 and 2, entries 6). The benzylic carbon C-1 appears at a higher δ-value ($\delta = 40.0$) than at 25°C ($\delta = 38.5$). Thus, the C–Li bond is further weakened at low temperature, and the amount of HMTTA–SIP **10** in the equilibria most likely has increased.

Changes also occur in the spectra of the coordinated HMTTA ligand. Six different HMTTA signals are found in the carbon NMR spectrum which indicate that, as in the PMDTA complex, one distinct HMTTA conformation is now frozen out.

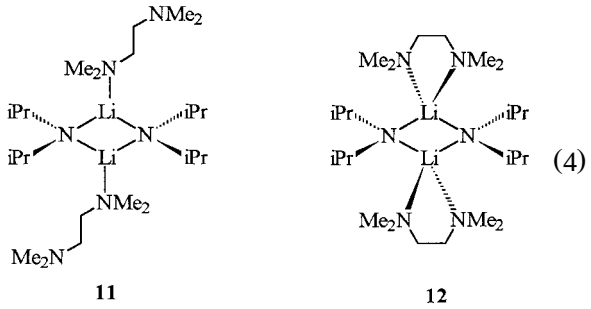
In summary, the spectroscopic data of the acyclic amines discussed here indicate that these ligands bind the better to lithium, the more nitrogen atoms they possess. Ligands with up to three nitrogen atoms cause the formation of contact ion pairs which are structurally similar to THF-solvated **1**-^{6}Li (structure **2**), while coordination with the tetradentate amine HMTTA results in an equilibrium between contact and separated ion pairs.

2.3. The effects of the different amines

Although TMEDA is commonly used in organolithium chemistry [1,2], its role as a ligand is still controversial. For example, Collum has recently stated that ''many applications of TMEDA in the presence of strong donor ligands (THF in particular) may be the result of a placebo effect, with perceived improvements falling within the experimental error'' [7]. How fit our results discussed so far and the data provided by the literature to this statement? Several ^{1}H,^{6}Li-HOESY spectra of TMEDA-containing samples of organolithium compounds have been reported in the literature, and the majority of the spectra shows that the amine is indeed coordinated to lithium, regardless whether THF [12,24] or less polar solvents [25] are used. Similarly, several benzyllithium compounds, as well as α-lithiated methyl phenyl sulfide as studied in this work, led to lithium–TMEDA contacts in THF solution [13,17,26]. Only the two sterically congested phenyllithium compounds (2,4,6-tri-*tert*-butylphenyl)lithium [27] and *ortho*-lithiated *tert*-butyl phenyl thioether [28] failed to show cross-peaks with TMEDA. Thus, the NMR-spectroscopic evidence based on ^{1}H,^{6}Li-HOESY measurements indicates that in THF solution organolithium compounds are, at least in many cases, coordinated to TMEDA. It is also important to note that proton and carbon NMR spectra of the anion often remain unchanged upon addition of the amine although complexation takes place, as shown above. Therefore, if only ^{1}H

and ^{13}C spectra have been measured and used as a criterion, they definitively cannot provide a conclusive answer whether TMEDA complexation takes place, or not.

The role of TMEDA as a ligand for lithium dialkyl amides was extensively examined by Collum, as mentioned in the introduction. Investigations of solution structures revealed solvent- and ligand-dependent aggregates and monomers, respectively [7–10,29,30]. For example, lithium diisopropylamide (LDA) formed a cyclic dimer in neat TMEDA. However, TMEDA was found not to be coordinated as an η^2-ligand (**12**) but as an η^1-ligand (**11**).

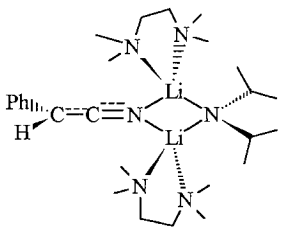


(4)

11 **12**

Dimeric lithium hexamethyldisilazide (LiHMDS) in pentane (**13**) was deaggregated to the 3-coordinated monomer **14** by 5 equivalents of TMEDA (Scheme 4).

In contrast, 5 equivalents of THF only afforded the solvated dimer **15**. Addition of equimolar amounts of TMEDA and THF did not yield the expected monomer **14** but solely dimer **15** [29]. Obviously, in LiHMDS complexes, TMEDA is unable to compete successfully with THF for coordination sites at Li. The main question is, whether this observation allows for a general conclusion concerning the complexation abilities of TMEDA and THF, respectively, to lithium. Since both LDA and LiHMDS contain sterically demanding alkyl groups, and TMEDA, on the other hand, has two vicinal tertiary amino groups, the behaviour of TMEDA towards LDA and LiHMDS is rather the consequence of steric repulsions between these lithium dialkyl amides and the TMEDA ligand in these particular cases [5]. The X-ray crystal structure of the complex [α-lithiophenylacetonitril · lithium diisopropylamide · 2 TMEDA] (**16** · 2 TMEDA) [31] consisting of two TMEDA-chelated lithium cations which bridge the amide and the nitril nitrogen atoms provides an illustration of such a case.



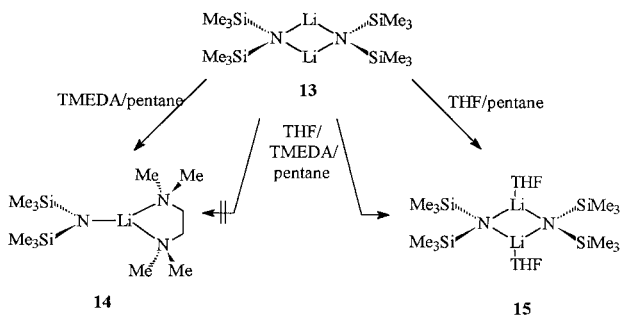
(5)

16 · 2 TMEDA

Due to the steric strain caused by the isopropyl groups, both TMEDA ligands are bent away from the amide, and unusually long Li–N(TMEDA) distances (220–235 pm), i.e. weak Li–N bonds, result. Compared to complex **16** · 2 TMEDA, even stronger steric repulsions should be expected in TMEDA-chelated dimers of LDA and LiHMDS. As a consequence, η^2-coordination by TMEDA is unfavourable, and η^1-complexed LDA dimers **11**, or if the steric demand of the amide is further increased, chelated LiHMDS monomers **14** are obtained instead. This correlates nicely with the earlier mentioned observations that (2,4,6-tri-*tert*-butylphenyl) lithium [27] and *ortho*-lithiated *tert*-butyl phenyl thioether [28] do not show cross peaks with TMEDA.

It thus seems that the lithium amides studied by Collum [7–10] show a coordinational behaviour towards TMEDA (and, perhaps, other chelating amines) which is different from most C-metallated organolithium compounds (except those with strong steric hindrance) for sterical reasons.

The chiral ligand (−)-sparteine has been used extensively in recent years by Hoppe [32,33], Beak [34], and others [35] in asymmetric syntheses [36]. As we have noted above, it is weakly coordinated to **1**-^{6}Li in THF solution, but forms strong complexes in diethyl ether [37]. Furthermore, complexation also depends on the nature of the organolithium compound. This is shown in a recent NMR study of 1-methylindenyllithium: in THF, a Li-(−)-sparteine contact is not observed. However, in diethyl ether, a strong coordination of methylindenyllithium to the chiral amine takes place [33,38]. Crystallisation of 1-methylindenyllithium from THF in the presence of 1 molar equivalent of (−)-sparteine correspondingly afforded crystals which did not contain (−)-



Scheme 4.

[5] In Refs. [9] the importance of steric effects on solvation especially of trialkylamines is also discussed. See also the discussion on ground and transition state solvation, respectively, of Klumpp [10].

sparteine, whereas (−)-sparteine-chelated 1-butylindenyllithium was obtained if the organolithium compound was analogously crystallized from ether/hexane. In agreement with these observations, chiral induction is found in diethyl ether, however, not in THF [33]. Therefore, in this particular case, in THF solution (−)-sparteine is a poor ligand for lithium. Furthermore, investigations of the ground state solvation of the organolithium compound allows conclusions concerning the situation in the transition state of its reaction. It is noteworthy that LiHMDS complexes with several chelating diamine ligands in toluene indicated (−)-sparteine to bind even stronger to Li than TMEDA [8].

Because of the chiral induction in reactions with electrophiles, the (−)-sparteine case is more easily to distinguish from a 'placebo-effect' than complex formation with achiral amines, and its effect, e.g. on reaction rates of the lithium compound. A necessary condition for the influence of chiral amines on reactions of organolithium compounds is their bonding to the lithium cation in the transtion state of the reaction. Thus, if addition of the chiral amine (−)-sparteine to an organolithium compound induces enantioselectivity in an otherwise achiral reaction, as shown by many well-documented examples in solvents such as diethyl ether [32–36], it is obvious that the chiral ligand is bonded to the organometallic reagent in the product determining step. The $^{1}H,^{6}Li$-HOESY studies of this work, which reveal the solvation in the ground state of an organolithium compound (**1**-Li), may give a hint on the solvation of the transition state, as shown above.

Comparison of the 'chiral TMEDA' (−)-sparteine with TMEDA itself indicates that due to higher fluxionality, reduced steric hindrance, and smaller chelate ring size (5 vs. 6), chelate formation should be more favourable with the achiral TMEDA than with the chiral (−)-sparteine. Only if the strongly coordinating solvent THF is used, the situation is less clear. Depending on the nature of the individual organolithium compound, either diamine chelation, or THF solvation, can be more favoured. It should be emphasized that even if the $^{1}H,^{6}Li$-HOESY spectrum shows that an amine is coordinated to an organolithium reagent in (THF) solution, the amine-chelate is not necessarily involved in the transition state of a chemical reaction. There still exists the possibility that a minor species which participates in the equilibria in solution but which may not be detected by NMR spectroscopy, is the actual reactive species, or that the transition state is not solvated. The rather complex case of solvation, aggregation and reactivity (i.e. solvation in the ground and transition state, respectively) in the presence of achiral ligands is thoroughly studied by Collum [7–10,29,30].

Added in stochiometric amounts, the η^3-ligand PMDTA converts aggregated organolithium compounds in [D_8]toluene [8], [39,40], in deuterated diethyl ether [41–43] as well as in [D_8]THF [27,41,42] into monomers [44]. Apparently even in strong donor solvents PMDTA binds tightly to lithium, occupying three coordination sites at the metal while the fourth is filled in by the carbanion. Moreover, at low temperatures the tight PMDTA coordination often gives rise to a splitting of the carbon resonances of the coordinated ligand, and up to nine different signals can be observed [8] [41–43], indicating that all carbon atoms of the ligand are different. These findings are in line with our observations, since at −80°C seven ligand signals were found in the carbon NMR spectra of the **1**-^{6}Li–PMDTA complex. Thus, at low temperatures the amine is complexed to lithium in an unsymmetrical manner, and the existence of an unsymmetrically bonded ligand molecule is further supportive for PMDTA coordinating as an η^3-ligand in its complexes with organolithium compounds.

Complexes of the tetradentate amine HMTTA with organolithium compounds have only sparingly been investigated by NMR spectroscopy. In their recent study of LiHMDS in [D_8]toluene, Collum and co-workers found that HMTTA offered no advantage over PMDTA [8]. Instead, the spectroscopic data indicated that the tetradentate amine was only η^3-bonded in its monomeric complex with the amide.

On the other hand, comparison of several TMEDA and HMTTA complexes of compounds lithiated on carbon in benzene solution revealed that the signal of the anionic carbon C_α appeared at higher δ-values if HMTTA was used as a ligand. For example, the benzyllithium–TMEDA complex afforded $\delta_{C\alpha} = 35.3$ compared to $\delta_{C\alpha} = 38.1$ of the HMTTA complex [45]. This chemical shift difference of $\Delta\delta_{C\alpha} = 2.8$ ppm resembles very closely the shift difference of $\Delta\delta_{C\alpha} = 2.9$ ppm observed for the respective amine complexes of **1**-^{6}Li (Table 2, entries 3 and 6). Thus, it seems reasonable to assume that substitution of TMEDA by HMTTA is generally accompanied by a characteristic shift of the NMR signal of the lithiated carbon atom towards higher δ-values. What is the reason of this shift?

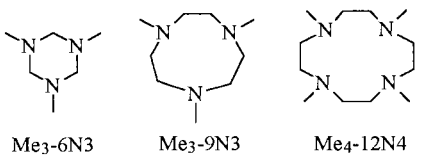
Crystalline benzyllithium complexes with the ligands TMEDA, PMDTA and HMTTA were obtained by Langer [46]. While the first two were stable, the tetramine complex decomposed largely within 24 h. The UV-spectra in benzene of the TMEDA and PMDTA complexes showed only one absorption at 330 nm which could be attributed to the contact ion pair. Apart from the CIP-absorption, the HMTTA complex showed a second small absorption at 367 nm. This band was ascribed to a loose or separated ion pair, indicating that in benzene solution the tetramine complex existed in two forms, a contact ion pair in which only three nitrogens are coordinated to lithium while the fourth remained uncoordinated, and a separated ion pair in which all four N-atoms of the ligand are bonded to Li [46]. Thus, all the available spectroscopic evidence sup-

ports the idea that, independent of the solvent, complexation of a C-lithiated compound with HMTTA causes a weakening of the C–Li bond. This weakening is probably best described as the result of equilibria between several contact ion pairs (CIP) and at least one ligand-separated ion pair (SIP; see Scheme 3). Since the equilibria contain a substantial amount of the HMTTA–SIP even in THF solution at 25°C, it is reasonable that the spectroscopic data of this HMTTA containing sample differ significantly from those of the CIPs of the other amines.

2.4. Complexes of **1**-^{6}Li with cyclic polyamine ligands

2.4.1. Measurements at 25°C

To study the influence of cyclic amines, **1**-^{6}Li was examined in the presence of 1 mol. equiv. of 1,3,5-trimethyl-1,3,5-triazacyclohexane (Me_3–6N3), 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3–9N3), and 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane (Me_4–12N4), using the same conditions and parameters as before [6]. Selected proton and carbon NMR spectroscopic data are summarized in Tables 1 and 2 (entries 7–9).



(6)

First the tridentate ligand Me_3–6N3 was added to a solution of **1**-^{6}Li in THF/[D_8]THF. The ^{1}H,^{6}Li-HOESY spectrum of this sample is shown in Fig. 6.

A weak cross-peak to the ligand methyl resonance at $\delta_H = 2.16$ confirms that the amine is coordinated to the metal. Unfortunately the broad Me_3–6N3 methylene signal at $\delta_H = 3.05$ superimposes the benzyl proton signal H-1 at $\delta_H = 3.03$ [7]. At this chemical shift an intense cross-peak is found. Part of its intensity is probably caused by the amine-CH_2 protons, but it is impossible to separate the contributions of H-1 from those of the ligand CH_2-hydrogens. Besides these peaks, the spectrum resembles that of **1**-^{6}Li without added ligands (see Fig. 1), i.e., the Li atom is still coordinated to THF, as demonstrated by the cross-peak at the THF–CH_2 signal. There are also no significant changes in the carbon and proton NMR spectra of **1**-^{6}Li (Tables 1 and

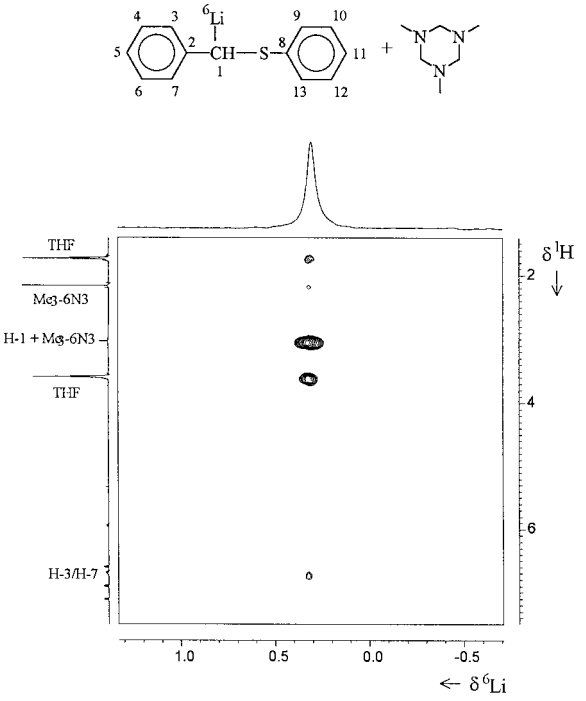
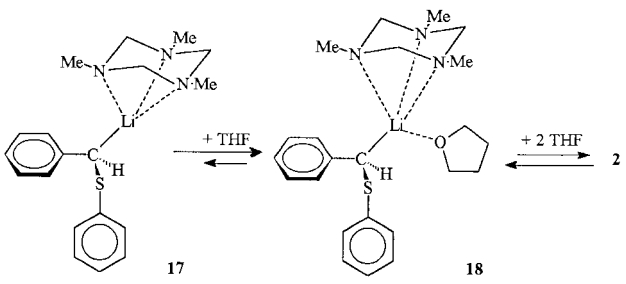


Fig. 6. ^{1}H,^{6}Li-HOESY spectrum of [^{6}Li]-α-(phenylthio)benzyllithium **1**-^{6}Li with 1 mol. equiv. Me_3-6N3 in 1:1 THF/[D_8]THF at 25°C.

2, entries 7). Thus, in the presence of Me_3–6N3, **1**-^{6}Li forms monomeric contact ion pairs, as illustrated in Scheme 5.

Contrary to the non-cyclic, tridentate amine PMDTA, Me_3–6N3 is unable to displace most of the THF from the coordination sphere at Li. This difference can be understood if the geometries of both ligands are compared. The cyclic Me_3–6N3 only forms four-membered ring chelates in its Li complexes which are less favoured than the five-membered ring chelates of the PMDTA and TMEDA complexes [8]. Furthermore, the cyclic ligand is fairly rigid, and presumably its N-donor atoms are too close to each other to coordinate lithium as effectively as the fluxional molecules PMDTA and TMEDA. Therefore, even if Me_3–6N3 is involved with all three nitrogen atoms of the amine as in complex **17**, the Li cation may still be coordinatively unsaturated and require THF molecules to fill in vacant coordination



Scheme 5.

[6] The cyclic amine ligands are abbreviated according to a proposal by Cooper and Rawle [47].

[7] The broadening of the Me_3–6N3 methylene signal is also observed in the spectrum of the uncoordinated ligand and appears to be a result of the reduced conformational fluxionality within the triazacyclohexane ring. It is therefore not caused by tight lithium coordination to the amine.

sites. A coordination at Li by only two of the three amine-N-atoms is unlikely because of the size and the rigidity of the triaza-cyclohexane ring. Consequently, it is reasonable to assume that the formally pentacoordinated lithium complex **18** as shown in Scheme 5 is present to a certain extent in THF solution besides the Me_3–6N3 coordinated ion pair **17** (without Li–THF contact). Furthermore, a THF-solvated ion pair **2** (without Li–Me_3–6N3 contact) may also be involved in the equilibria. The coordination abilities of Me_3–6N3 thus show that in its complexes with **1**-^{6}Li, the formally tridentate ligand Me_3–6N3 behaves more like the bidentate amine TMEDA than the non-cyclic tridentate amine PMDTA.

In contrast to Me_3–6N3, the tribasic cyclic amine Me_3–9N3 is able to form five-membered ring chelates with lithium. This triazacyclononane ligand is interesting because it is the cyclic analogue of PMDTA. The ^{1}H,^{6}Li-HOESY spectrum of its complex with **1**-^{6}Li is shown in Fig. 7.

Unexpectedly, only two cross-peaks to H-1 at δ_H = 3.09 and to the ligand signal at $\delta_H = 2.30$ are observed. Hence, the spectrum shows that lithium is exclusively (within the error limits of the measurement) coordinated to C-1 and to the ligand, but not to the solvent THF. This means that the cyclic amine Me_3–9N3 is a better ligand for Li than the structurally related, non-cyclic ligand PMDTA (see Fig. 4). The complex **19** is essentially not in equilibrium with a THF-solvated contact

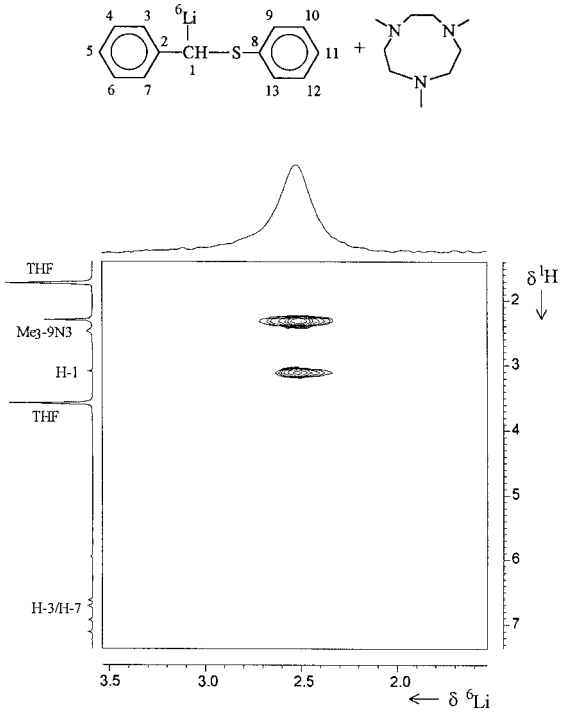
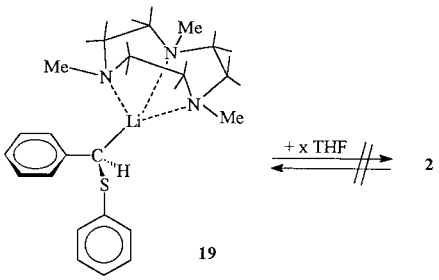


Fig. 7. ^{1}H,^{6}Li-HOESY spectrum of [^{6}Li]-α-(phenylthio)benzyllithium **1**-^{6}Li with 1 mol. equiv. Me_3-9N3 in 1:1 THF/[D_8]THF at 25°C.



Scheme 6.

ion pair **2**. Instead, coordination of lithium by the amine is so strong that the alkyl group inversion at the ligand N-atoms is inhibited. In the proton NMR spectrum, this gives rise to two broad ligand singlets at $\delta_H = 2.31$ and at $\delta_H = 2.48$, each of them caused by six methylene protons of the triazacyclononane ring. However, in the carbon NMR spectrum only one methylene resonance is found, indicating that the methylene carbons remain equal. Both proton and carbon NMR spectra of the free ligand contain only one methylene signal. The methylene protons at $\delta_H = 2.48$ are not in contact with Li, whereas the signal at $\delta_H = 2.31$ appears at nearly the same resonance frequency as the ligand methyl signal ($\delta_H = 2.30$). It is thus possible that the methylene protons at $\delta_H = 2.31$ contribute to the cross-peak at δ_H = 2.30. These observations, taken together, indicate that the Me_3–9N3 complex does not exchange ligand molecules for THF but rather has the fairly static structure **19** as shown in Scheme 6 (methylene H-atoms are represented by short lines).

In **19**, the Li/Me_3–9N3 unit forms a rigid trigonal pyramid with two different kinds of methylene protons at the base of the pyramid. Six of these protons are in axial positions and point away from lithium, whereas the six equatorial protons are closer to the metal, probably close enough to cause a cross-peak in the HOESY spectrum. Therefore, the axial methylene protons can be assigned to the proton resonance at $\delta_H = 2.48$ and the equatorial methylene protons to the signal at $\delta_H = 2.30$. Three coordination sites at lithium are bonded to the ligand, while the fourth is filled in by the benzylic carbon atom C-1 of the anion.

The third cyclic ligand studied was 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane (Me_4–12N4), the cyclic analogue of HMTTA. As before, 1 mol. equiv. of the ligand was added to a solution of **1**-^{6}Li, and a ^{1}H,^{6}Li-HOESY spectrum was recorded (Fig. 8).

On top of the 2D NMR spectrum in Fig. 8, the ^{6}Li-NMR spectrum of the sample is plotted. Interestingly, it shows two signals at $\delta_{Li} = 0.40$ and $\delta_{Li} = 0.52$ with the relative intensities 1.0 and 0.6. In the proton and carbon NMR spectra of the carbanion, only one set of signals is found. In contrast to all of the previous samples, two different kinds of lithium atoms are found

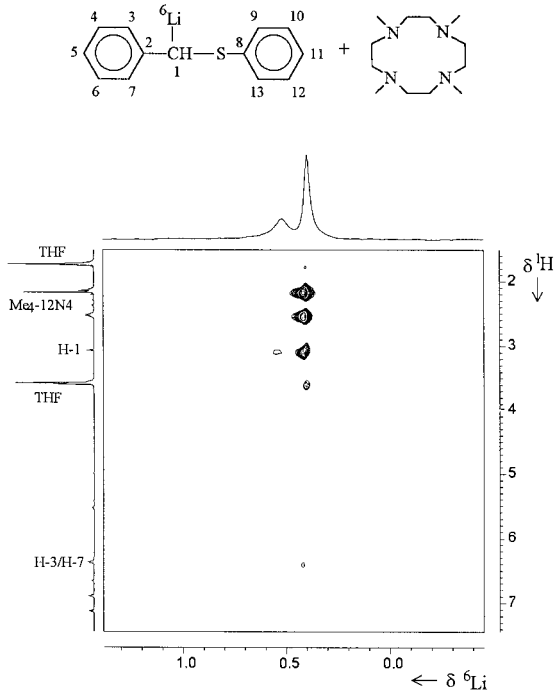


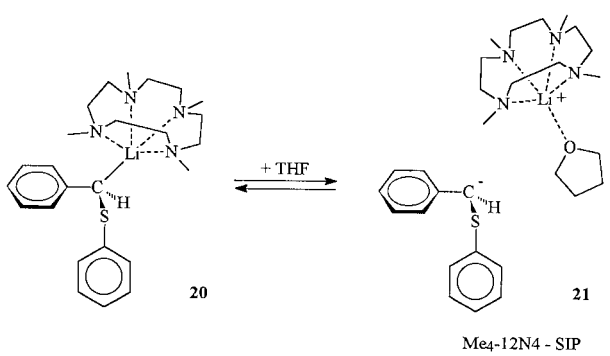
Fig. 8. $^{1}H,^{6}Li$-HOESY spectrum of [^{6}Li]-α-(phenylthio)benzyllithium **1**-^{6}Li with 1 mol. equiv. Me_4-12N4 in 1:1 THF/[D_8]THF at 25°C.

which do not interchange, or only very slowly. The lithium signal at the higher δ-value ($\delta_{Li} = 0.52$) merely shows a single cross-peak of low intensity to the benzylic proton H-1. Unfortunately, the spectroscopic data do not allow to draw conclusions about the nature of this lithium species. The second lithium signal at $\delta_{Li} = 0.40$ has cross peaks to H-1 ($\delta_H = 3.07$, strong), H-3/H-7 ($\delta_H = 6.38$, weak), both THF resonances (weak) and all the ligand signals (strong), clearly indicating that this lithium species is coordinated to the benzyl anion, the solvent THF, and Me_4–12N4. It can be readily assigned to a **1**-^{6}Li–Me_4–12N4 complex. Lithium is bonded to the benzylic carbon C-1 in the same η^1-like manner as, e.g., in **2**. It is also coordinated, but to a lesser extent, to the solvent THF. The most intense cross-peaks are found at the Me_4–12N4 resonances ($\delta_H = 2.14$, 2.17, 2.53). Similar to the Me_3–9N3 complex, two ligand methylene signals of equal intensity are observed at $\delta_H = 2.14$ and $\delta_H = 2.53$, whereas the methyl signal remains a sharp singlet ($\delta_H = 2.17$). In the carbon NMR spectrum as well as in the carbon and proton spectra of the free ligand, only one methylene resonance is observed. Thus, lithium forms also a strong complex with the cyclic tetramine Me_4–12N4. It is coordinated by the four ligand N-atoms, the inversion at these N-atoms is hindered, and a ligand conformation is frozen out in which the axial and equatorial tetraazacyclododecane-CH_2 protons are no longer equal. Apparently the rigid Li/Me_4–12N4 unit forms a tetragonal pyramid similar to the trigonal pyramid found in the Me_3–9N3 complex **19**. However, two important differences are noteworthy. First, in the Me_4–12N4 complex both the CH_2-protons at lower (equatorial methylene hydrogens) and at higher (axial methylene hydrogens) δ-values show strong cross-peaks to lithium. Secondly, in spite of the strong complexation of Li by the ligand, still a contact of the metal to THF is observed.

These results can best be explained by an equilibrium between a contact ion pair (CIP) **20** and a ligand separated ion pair (Me_4–12N4–SIP) **21**, both with pentacoordinated lithium (see Scheme 7).

The structure of the rigid Li/Me_4–12N4 unit should be very similar in the Me_4–12N4–CIP and Me_4–12N4–SIP. The larger diameter of the aza-macrocycle in Me_4–12N4 as compared to the situation in Me_3–9N3 enables lithium to be in a position which is closer to the plane of the N-donor atoms. In other words, the resulting pyramid is flattened. Axial and equatorial methylene protons are different, but since the metal is very close to the ring, both Li–H distances are comparable and afford cross-peaks in the HOESY spectrum. Differences are found with regard to the fifth coordination site at Li. In the CIP, it is filled in by C-1 of the benzyl anion of **1**-^{6}Li; in the Me_4–12N4–SIP, it is occupied by THF. Since the equilibrium is fast on the NMR time scale, only the time-weighted average is observed in the 1D and 2D NMR spectra.

Proton and carbon NMR spectroscopic data at 25°C also reflect the unusual lithium coordination of **1**-^{6}Li to the tetramine Me_4–12N4 (Tables 1 and 2). Spectral differences are not found between THF-solvated **1**-^{6}Li (entries 1) and the Me_3–6N3 containing sample (entries 7). Similarly, apart from a slight shift of δ H-1 ($\Delta\delta$ = 0.06 ppm) to higher and a small shift of d C-1 ($\Delta\delta$ = −1.0 ppm) to lower δ-values, the spectrum of the **1**-^{6}Li–Me_3–9N3 solution also remains largely unchanged (entries 8). Significant differences to THF-solvated **1**-^{6}Li are, however, observed in the spectra of the Me_4–12N4 complex (entries 9). For example, the *para* proton H-5 ($\Delta\delta$ = −0.40 ppm) and the *para* carbon C-5 ($\Delta\delta$ = −4.7 ppm) show shifts to lower, the



Scheme 7.

C-1 resonance ($\Delta\delta = 4.7$ ppm) to higher δ-values, and the coupling constant $^1J_{CH}$(C-1) is increased by 13 Hz.

These spectral changes are similar, but more pronounced than the changes observed in the HMTTA containing sample discussed earlier. Compared to **1**-^{6}Li in THF/[D_8]THF alone, in the Me_4–12N4 sample the C–Li bond is clearly weakened and the negative charge at C-1 is largely delocalised into the phenyl ring. This process is accompanied by a rehybridisation at C-1 from largely sp^3 towards sp^2, as indicated by the value of $^1J_{CH} = 162$ Hz. Since the negative charge is more localised at the anionic carbon in a contact ion pair, but more delocalised in a separated ion pair, these findings support the assumption that, with Me_4–12N4 as the ligand, a SIP is an essential part of the equilibrium in THF solution.

2.4.2. Measurements at −80°C

The samples containing the cyclic amines were also examined at −80°C. Selected proton and carbon NMR data are summarized in Tables 3 and 4 (entries 7–9). The spectra of the sample with Me_3–6N3 as the ligand (entries 7) strongly resemble the spectra of **1**-^{6}Li without added amines (entries 1), indicating that at −80°C monomeric contact ion pairs similar to **17**, **18** or **2** (Scheme 5) are present in THF solution.

Compared to the spectroscopic data obtained at 25°C (Tables 1 and 2, entries 8), the data of the Me_3–9N3 containing sample recorded at −80°C remained also largely unchanged (Tables 3 and 4, entries 8). With regard to 'ligand-free' **1**-^{6}Li at −80°C, the benzylic carbon C-1 showed a slight negative ($\Delta\delta = -1.3$ ppm to $\delta = 33.8$) and the *para* H-5 ($\Delta\delta = 0.07$ ppm) and C-5 ($\Delta\delta = 1.0$ ppm) small positive $\Delta\delta$ shifts in this complex. Apparently the same Me_3–9N3-coordinated contact ion pair **19** without Li–THF contact is present at low temperatures as well as at 25°C. The δ-value of C-1 is unusually low (Table 4, entry 8). In contrast to complexes with other amines, it seems that in this Me_3–9N3–CIP the negative charge remains strongly localized at the benzylic carbon atom, indicating that a strong Li–C-1 bond still exists even at −80°C.

As at 25°C, the sample with Me_4–12N4 behaves differently (Tables 3 and 4, entries 9). Compared to the spectra of the other amine complexes as well as the 25°C spectra, the *para* carbon C-5 and the *para* proton H-5 are observed at lower δ-values, while the benzylic carbon C-1 is found at a higher δ-value. These data show that the C–Li bonds in this sample are weakened at low temperature. They support the assumption that, similar to the HMTTA-containing sample, the amount of Me_4–12N4–SIP in the equilibria has increased. Since the effects are more pronounced in the **1**-^{6}Li–Me_4–12N4 complex, this amine binds stronger to Li than HMTTA.

Proton and carbon NMR data of the coordinated ligand are also interesting. At −80°C, three different methylene hydrogen and two different methylene carbon resonances are observed. Obviously, the ligand is no longer coordinated to Li in a symmetrical manner at that temperature.

2.5. The effects of the different cyclic amines

The tridentate amine ligand Me_3–6N3 has only recently been employed in organolithium chemistry [48–53]. For example, complex formation with LiHMDS was observed in benzene solution [48]. However, computational studies by Schleyer and co-workers indicated that Me_3–6N3 and the non-alkylated compound H_3–6N3 are poorer ligands for lithium than other tridentate amines such as PMDTA [54]. These findings are clearly supported by the results of our NMR experiments: unlike PMDTA, Me_3–6N3 can only displace part of the solvent THF from the coordination sphere at Li in **1**-^{6}Li, and its ability for coordination to Li is more like that of TMEDA than of other tridentate amines. A similar result was obtained in a study of LiHMDS–diamine complexes in toluene in which a distinct preference of 5- versus 6-membered rings and no tendency to form 4- or 7-membered chelates was observed [8].

Several crystal structures of Li–Me_3–6N3 complexes have been determined. In most cases, the metal is coordinated to all three N-atoms of the amine, either in sandwich-type complexes of the general structure $[Li(Me_3\text{–}6N3)_2]^+$ with hexacoordinated lithium [50–52], or by Me_3–6N3 and an amide N-atom in a complex with tetracoordinated Li [50]. One example of an η^2-bonded Me_3–6N3 has also been reported in which lithium is further coordinated by two oxygen atoms [53].

Similar to PMDTA, its cyclic analogue Me_3–9N3 converts aggregated organolithium compounds into monomers in etheral ([D_{10}]diethyl ether [41], [D_8]THF [41], [55]) as well as nonpolar solvents ([D_8]toluene [8]) in which lithium is coordinated by the three ligand N-atoms and the anionic carbon C_α [41], [55] or an amide N-atom [8]. In the ^{13}C NMR spectrum of the neopentyllithium complex, the ^{13}C,^{6}Li coupling is observable up to −13°C, implying that the carbon-lithium bond exchange is slow and that the Me_3–9N3–neopentyllithium complex is very stable in the solvent [D_8]THF [41]. Lowering the temperature to −108°C [55] or −113°C [41] causes a splitting of the methylene-C resonances of the complexed ligand, and two signals of equal intensities are observed. Apparently a ring conformation is frozen out in which two types of alternating NCH_2 carbons are differentiated by their distances to lithium. Since we carried out the low-temperature NMR experiments at higher temperatures (−80°C), a comparable splitting could not be detected in the Me_3–9N3-containing sample of **1**-^{6}Li.

Table 5
Selected NMR data of the lithiated sulfide **1**-^{6}Li and its complexes with (poly)amines in 1:1 THF/[D_8]THF

Entry	Temp. (°C)	Ligand	δ H-1	δ C-1	$^{1}J_{CH}$(C-1) (Hz)	δ H-5	δ C-5
1	25	—	3.03	35.8	149	5.94	111.8
2	25	3 NEt_3	3.04	35.7	149	5.96	112.0
3	25	TMEDA	3.02	35.6	148	5.96	112.0
4	25	(−)-sparteine	3.03	35.7	148	5.95	112.0
5	25	PMDTA	3.06	35.5	149	5.98	112.2
6	25	HMTTA	3.07	38.5	158	5.70	108.8
7	25	Me_3–6N3	3.03	35.8	149	5.94	111.7
8	25	Me_3–9N3	3.09	34.8	152	5.95	112.0
9	25	Me_4–12N4	3.07	40.5	162	5.53	106.5
10	−80	—	2.99	35.1	152	5.87	110.7
11	−80	3 NEt_3	2.98	34.7	151	5.91	111.3
12	−80	TMEDA	2.99	35.2	152	5.89	110.9
13	−80	(−)-sparteine	2.98	35.6	152	5.91	111.2
14	−80	PMDTA	3.04	35.0	152	5.91	111.1
15	−80	HMTTA	3.04	40.0	[a]	5.49	105.6
16	−80	Me_3–6N3	2.99	35.3	152	5.86	110.6
17	−80	Me_3–9N3	3.03	33.8	153	5.94	111.7
18	−80	Me_4–12N4	3.03	41.0	168	5.39	104.7

[a] Too broad.

Computational studies indicate that Me_3–9N3 is superior to PMDTA if it is coordinated to Li^+ but inferior if methyllithium is complexed [54]. X-ray crystal structure investigations of lithium complexes of Me_3–9N3 [56,57] [8] showed that the amine indeed coordinates as an η^3-ligand to the metal (Li–N distances 205–215 pm [47a] and 206–214 pm [57]). The fourth coordination site at the tetrahedral lithium belongs to an amide nitrogen. In these complexes, six methylene-H atoms at the base of the Li/Me_3–9N3 unit point away from Li, while the other six H-atoms are positioned roughly in the plane of the three nitrogens. Both types of hydrogens are different; therefore, these structures may serve as a model for the **1**-^{6}Li · Me_3–9N3 complex **19** which also showed two different kinds of ligand methylene hydrogens (see Scheme 6).

Only little information is available on lithium complexes of Me_4–12N4 and related compounds of the type R_4–12N4. The X-ray crystal structure analysis of a lithium chloride complex with a substituted tetraazacyclododecane ligand (R = 2-hydroxyethyl) shows a pentacoordinated Li cation which is coordinated to four nitrogens (Li–N = 208–235 pm) and one oxygen (Li–O = 195 pm) of the ligand. In the resulting tetragonal pyramid, the metal is located above the plane of the four N atoms which form the base of the pyramid. One hydroxyethyl oxygen sits on top of the pyramid, the other three arms of the ligand are not involved in lithium complexation [59]. Hence, the coordination number of the metal exceeds four, and the arrangement of the five donor atoms at lithium resembles the geometries proposed for the Me_4–12N4 complexes in Scheme 7. Molecular mechanics investigations of structures with the non-alkylated ligand H_4–12N4 in the complex point in the same direction: the most stable complexes are obtained if the cation is positioned above the plane spanned by the N-atoms while the ethyl bridges of the macrocycle are located below this plane. The most favourable Li–N distance is 211 pm [60]. In a lithium complex, such a distance would give rise to strong ligand cross-peaks in the ^{1}H,^{6}Li-HOESY spectrum. Therefore, although Me_4–12N4 is sterically more demanding than H_4–12N4, it is reasonable to assume that the methylated ligand also forms similar stable complexes with lithium.

2.6. Correlation of some diagnostic proton and carbon NMR data

Characteristic proton and carbon NMR spectroscopic data of all samples are summarized in Table 5. In Fig. 9, the chemical shifts of the *para* proton δ H-5, in Fig. 10, the chemical shifts of the benzylic carbon δ C-1,

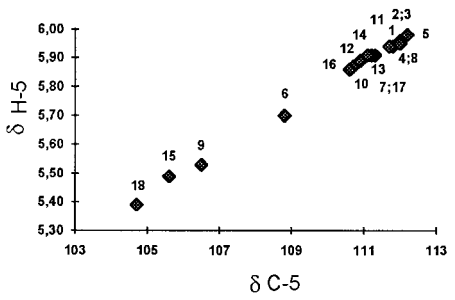


Fig. 9. Correlation of δ H-5 versus δ C-5 of (poly)amine complexes of **1**-^{6}Li. The numbers refer to entries in Table 5.

[8] See also [58].

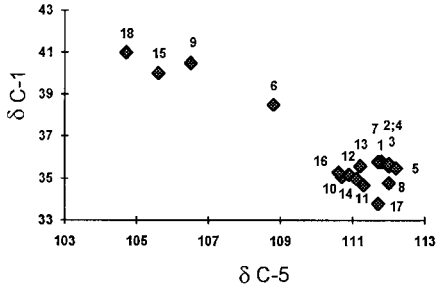


Fig. 10. Correlation of δ C-1 versus δ C-5 of (poly)amine complexes of **1**-^{6}Li. The numbers refer to entries in Table 5.

and in Fig. 11, the coupling constants $^{1}J_{CH}$(C-1) of that carbon atom are plotted against the chemical shifts of the aromatic *para* carbon δ C-5. As mentioned earlier, δ C-5 is a measure of the delocalisation of negative charge from the anionic benzylic carbon C-1 into the phenyl ring which is bonded to that carbon [22,23]. Quite remarkably, linear relationships are found in all three cases. These empirical correlations show that independent from the structure or the lithium coordination of the lithiated sulfide **1**-^{6}Li in THF solution, δ H-5 is always proportional to δ C-5. Apparently, δ H-5 is similar to δ C-5 a probe for the charge delocalisation into the phenyl ring. Fig. 10 and Fig. 11 indicate that the increase of charge density in the phenyl ring (lower values of δ C-5), correlates with a decrease of the negative charge at the benzylic carbon C-1 (higher values of δ C-1), which is accompanied by partial rehybridisation towards sp^2 at C1 (higher values of $^{1}J_{CH}$(C-1)). Thus, the charge distribution within the carbanionic part of the benzyllithium compound **1**-^{6}Li is indicated by several parameters which correlate with each other.

Apart from these general observations, some structural informations concerning the nature of individual ion pairs involved in the solution equilibria can also be deduced from Figs. 9–11. A closer look at the plots reveals that most of the chemical shift data points of C-5 are found at $\delta = 110$–112. Apparently this region can be ascribed to complexes or solvates of **1**-^{6}Li which exist solely as contact ion pairs in THF solution (see Table 5). As shown earlier, changes in the solvation sphere at lithium do not lead to significant changes in the carbon and proton NMR spectra of the monomeric contact ion pairs of **1**-^{6}Li, and this is indeed what is shown in Figs. 9–11. On the other hand, the HMTTA- and Me_4–12N4-containing samples are distinctly different from the others (see entries 6, 15 and 9, 18 in Table 5). Obviously, both tetradentate amines form complexes with **1**-^{6}Li in which part of the negative charge is more delocalized into the phenyl ring which is bonded to C-1 (lower δ C-5 values). Since these amines coordinate to lithium with four N-donor atoms, it was assumed that both ligands are capable of forming separated ion pairs in THF solution (see Scheme 3, HMTTA–SIP **10**, and Scheme 7, Me_4–12N4–SIP **21**), especially at lower temperatures. The plots in Figs. 9–11 clearly support these suggestions: at 25°C (entries 6 and 9, Table 5), the data points of the HMTTA and the Me_4–12N4 sample are found in an intermediate δ C-5 region of the diagrams, whereas at −80°C (entries 15 and 18, Table 5), both data points appear at an exceptionally low δ C-5 value. Therefore, it seems reasonable to ascribe δ C-5 values of approximately 105 to species of **1**-^{6}Li which consist predominantly of separated ion pairs [9]. Thus, at least as far as the benzyllithium compound **1**-^{6}Li is concerned, plots of δ C-5 versus δ H-5, δ C-1 or $^{1}J_{CH}$(C-1) are an appropriate means to determine ion pair structures, and the position of ligand-dependent CIP–SIP equilibria in THF solution, at least qualitatively.

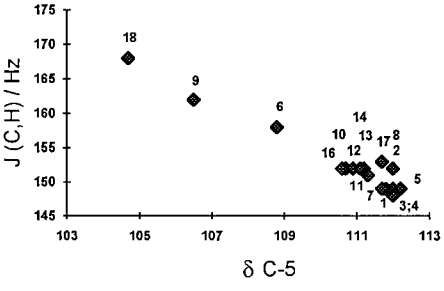


Fig. 11. Correlation of $^{1}J_{CH}$(C-1) versus δ C-5 of (poly)amine complexes of **1**-^{6}Li. The numbers refer to entries in Table 5.

3. Conclusion

The influence of a range of polyamine ligands on the solution structures in THF of the model benzyllithium compound **1**-^{6}Li was investigated by means of ^{1}H,^{6}Li-HOESY as well as proton and carbon NMR spectroscopy. As a general rule, the amines bind the stronger to lithium, the more nitrogen atoms they possess. The monodentate amine NEt_3 does not bind to lithium. Coordination of ligands with two (TMEDA, (−)-sparteine) or three N-donor atoms (PMDTA, Me_3–6N3, Me_3–9N3) resulted in the formation of contact ion pairs (CIPs). These CIPs only differ in the solvation sphere around lithium at which the amine ligands and THF solvent molecules compete for (generally) three coordination sites. The fourth position is occupied by the anionic benzylic carbon atom in an η^1-like manner.

A different situation was observed if amines with four N-atoms (HMTTA and Me_4–12N4) were used as ligands. In these cases, contact ion pairs (CIPs) are in equilibrium with separated ion pairs (SIPs), and the

[9] Separated ion pairs are favoured at lower temperatures [6,61].

coordination number at lithium may exceed four. Compared to the non-cyclic tetramine HMTTA, the amount of the SIP seems to be slightly increased with the cyclic ligand Me_4–12N4. In both cases the equilibria are shifted strongly towards the SIP side if the temperature is lowered from 25 to −80°C.

The formation of contact ion pairs with amine ligands in THF solution is difficult to identify from 1D carbon and proton NMR spectra of **1**-^{6}Li only because the spectra of **1**-Li are essentially identical whether an amine is coordinated to lithium, or not. In these cases ^{1}H,^{6}Li-HOESY spectroscopy provides nicely insights into the solvate shell of coordinated lithium atoms. Significant changes in the carbon and proton NMR spectra of **1**-^{6}Li are only observed if separated ion pairs are involved in the equilibria in solution. In the SIPs the charge distribution within the carbanion $\mathbf{1}^-$ is rather different from the charge distribution within the CIPs. In the case of the benzyllithium compound **1**-^{6}Li, a correlation of the chemical shifts of the *para* phenyl carbons C-5, the *para* phenyl protons H-5, the benzylic carbons C-1 and the proton-carbon coupling constants J(C-1,H-1) is indicative of the position of ligand-dependent CIP ⇌ SIP equilibria in THF solution.

Further studies have to show how organolithium compounds different from **1**-^{6}Li are complexed by amines, and how amine complexation influences the reactivity, i.e. the transition state, of organolithium compounds. This allows for a decision beyond the already observed chiral induction whether the addition of amines to organolithium compounds leads to a 'placebo effect' only [7], or not.

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. [D_8]THF was dried over molecular sieves 4 Å prior to use. Amines were distilled from calcium hydride and stored over molecular sieves in an argon atmosphere. —A *n*-Bu^{6}Li solution in *n*-hexane was prepared according to a literature procedure [20]. —^{1}H, ^{13}C, and ^{6}Li NMR: Bruker ARX 200, Bruker AC 300, Bruker AM 400, and Bruker AMX 500. —^{1}H,^{1}H-COSY, ^{1}H,^{13}C-COSY, and ^{1}H,^{6}Li-HOESY: Bruker AMX 500. –^{6}Li NMR spectra were referenced to an external 1.0 M solution of ^{6}LiCl in deuterium oxide. ^{1}H and ^{13}C NMR spectra were referenced to the THF–CH_2 signal ($\delta_H = 1.73$; $\delta_C = 26.5$). In order to save space, ^{1}H,^{1}H coupling constants J have been omitted. —Phase-sensitive ^{1}H,^{6}Li-HOESY spectra [500 MHz (^{1}H), 73 MHz (^{6}Li), THF/[D_8]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 to 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 $F1$.

1. [^{6}Li]-α-(Phenylthio)benzyllithium (**1**-^{6}Li): A solution of 0.55 mmol of *n*-Bu^{6}Li in *n*-hexane was evaporated to dryness in vacuo. The remaining *n*-Bu^{6}Li was dissolved in 1.0 ml of THF/[D_8]THF (1:1) at −15°C. To this solution was added 100 mg (0.50 mmol) of benzyl phenyl sulfide. After 15 min at −15°C, the resulting yellow solution was transferred into an NMR tube. —^{1}H NMR (500 MHz, THF/[D_8]THF 1:1, 25°C): δ = 3.03 (s, 1 H, H-1), 5.94 (t, 1 H, H-5), 6.59 (dd, 2 H, H-4, H-6), 6.67 (t, 1 H, H-11), 6.70 (bd, 2 H, H-3, H-7), 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 = 35.8 (d, $^1J_{CH}$ 149 Hz, C-1), 111.8 (d, $^1J_{CH}$ 157 Hz, C-5), 118.8 (bd, $^1J_{CH}$ 157 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, $^1J_{CH}$ 152 Hz, C-4, C-6), 151.8 (s, C-8), 157.0 (s, C-2). –^{6}Li NMR (73 MHz, THF/[D_8]THF 1:1, 25°C): δ = 2.75. —^{1}H NMR (500 MHz, THF/[D_8]THF 1:1, −80°C): d = 2.99 (s, 1 H, H-1), 5.87 (t, 1 H, H-5), 6.52 (d, 1 H, H-3), 6.55 (dd, 1 H, H-4), 6.59 (dd, 1 H, H-6), 6.68 (d, 1 H, H-7), 6.73 (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 (125 MHz, THF/[D_8]THF 1:1, −80°C): δ = 35.1 (d, $^1J_{CH}$ 152 Hz, C-1), 110.7 (d, $^1J_{CH}$ 157 Hz, C-5), 115.9 (d, $^1J_{CH}$ 155 Hz, C-7), 119.7 (d, $^1J_{CH}$ 154 Hz, C-3), 122.1 (d, $^1J_{CH}$ 158 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, $^1J_{CH}$ 157 Hz, C-10, C-12), 128.8 (d, $^1J_{CH}$ 153 Hz, C-6), 151.2 (s, C-8), 156.1 (s, C-2).

2. [^{6}Li]-α-(Phenylthio)benzyllithium with 3 NEt_3 (**1**-^{6}Li–3 NEt_3): To a solution of 0.50 mmol of **1**-^{6}Li in THF/[D_8]THF (1:1) at −15°C (see above) was added 1.65 mmol of triethyl amine. The solution was kept at −15°C for 15 min and then transferred into an NMR tube. —^{1}H NMR (500 MHz, THF/[D_8]THF 1:1, 25°C): δ = 0.94 (t, 27 H, NCH_2CH_3), 2.42 (q, 18 H, NCH_2CH_3), 3.04 (s, 1 H, H-1), 5.96 (t, 1 H, H-5), 6.61 (dd, 2 H, H-4, H-6), 6.68 (t, 1 H, H-11), 6.72 (bd, 2 H, H-3, H-7), 6.90 (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): δ = 12.9 (q, $^1J_{CH}$ 125 Hz, NCH_2CH_3), 35.7 (d, $^1J_{CH}$ 149 Hz, C-1), 47.5 (t, $^1J_{CH}$ 131 Hz, NCH_2CH_3), 112.0 (d, $^1J_{CH}$ 157 Hz, C-5), 118.8 (bd, $^1J_{CH}$ 155 Hz, C-3, C-7), 122.0 (d, $^1J_{CH}$ 160 Hz, C-11), 125.3 (d, $^1J_{CH}$ 160 Hz, C-9, C-13), $^1J_{CH}$ 128.0 (d, $^1J_{CH}$ 158 Hz, C-10, C-12), 128.4 (d, $^1J_{CH}$ 151 Hz, C-4, C-6), 151.8 (s, C-8), 157.0 (s, C-2). –^{6}Li NMR (73 MHz, THF/[D_8]THF 1:1, 25°C): δ = 1.89. —^{1}H NMR (400 MHz, THF/[D_8]THF 1:1, −80°C): δ = 0.93 (t, 27 H,

NCH_2CH_3), 2.38 (q, 18 H, NCH_2CH_3), 2.98 (s, 1 H, H-1), 5.91 (t, 1 H, H-5), 6.54 (d, 1 H, H-3), 6.56 (dd, 1 H, H-4), 6.60 (dd, 1 H, H-6), 6.71 (t, 1 H, H-11), 6.73 (d, 1 H, H-7), 6.93 (dd, 2 H, H-10, H-12), 7.05 (d, 2 H, H-9, H-13). —^{13}C NMR (100 MHz, THF/[D_8]THF 1:1, −80°C): $\delta = 12.5$ (q, $^1J_{CH}$ 125 Hz, NCH_2CH_3), 34.7 (d, $^1J_{CH}$ 151 Hz, C-1), 46.8 (t, $^1J_{CH}$ 131 Hz, NCH_2CH_3), 111.3 (d, $^1J_{CH}$ 157 Hz, C-5), 116.2 (d, $^1J_{CH}$ 156 Hz, C-7), 119.9 (d, $^1J_{CH}$ 150 Hz, C-3), 122.1 (d, $^1J_{CH}$ 155 Hz, C-11), 124.8 (d, $^1J_{CH}$ 159 Hz, C-9, C-13), 127.8 (d, $^1J_{CH}$ 151 Hz, C-4), 128.1 (d, $^1J_{CH}$ 156 Hz, C-10, C-12), 128.8 (d, $^1J_{CH}$ 153 Hz, C-6), 151.0 (s, C-8), 156.2 (s, C-2).

For comparison: *NEt_3*: ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 0.91$ (t, 9 H, NCH_2CH_3), 2.41 (q, 6 H, NCH_2CH_3). —^{13}C NMR (50 MHz, $CDCl_3$, 25°C): $\delta = 11.5$ (q, $^1J_{CH}$ 125 Hz, NCH_2CH_3), 46.1 (t, $^1J_{CH}$ 132 Hz, NCH_2CH_3).

3. [^{6}Li]-α-(Phenylthio)benzyllithium (**1**-^{6}Li) with 1 mol. equiv. of a polyamine ligand: general procedure: As above, a solution of 0.50 mmol of **1**-^{6}Li in THF/[D_8]THF (1:1) was prepared at −15°C. To this solution was added 0.55 mmol of the polyamine. After 15 min at the same temperature, the solution was transferred into an NMR tube.

4. [^{6}Li]-α-(Phenylthio)benzyllithium with TMEDA (**1**-^{6}Li–TMEDA): —^{1}H NMR (500 MHz, THF/[D_8]THF 1:1, 25°C): $\delta = 2.13$ (s, 12 H, NCH_3), 2.28 (s, 4 H, NCH_2), 3.02 (s, 1 H, H-1), 5.96 (t, 1 H, H-5), 6.60 (dd, 2 H, H-4, H-6), 6.68 (t, 1 H, H-11), 6.72 (bd, 2 H, H-3, H-7), 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): $\delta = 35.6$ (d, $^1J_{CH}$ 148 Hz, C-1), 46.4 (q, $^1J_{CH}$ 132 Hz, NCH_3), 58.8 (t, $^1J_{CH}$ 132 Hz, NCH_2), 112.0 (d, $^1J_{CH}$ 157 Hz, C-5), 118.9 (bd, $^1J_{CH}$ 154 Hz, C-3, C-7), 122.1 (d, $^1J_{CH}$ 160 Hz, C-11), 125.3 (d, $^1J_{CH}$ 160 Hz, C-9, C-13), 128.0 (d, $^1J_{CH}$ 158 Hz, C-10, C-12), 128.3 (d, $^1J_{CH}$ 152 Hz, C-4, C-6), 151.6 (s, C-8), 157.0 (s, C-2). −^{6}Li NMR (73 MHz, THF/[D_8]THF 1:1, 25°C): $\delta = 2.88$. —^{1}H NMR (400 MHz, THF/[D_8]THF 1:1, −80°C): d = 2.14 (s, 12 H, NCH_3), 2.26 (s, 4 H, NCH_2), 2.99 (s, 1 H, H-1), 5.89 (t, 1 H, H-5), 6.54 (bd, 1 H, H-3), 6.56 (dd, 1 H, H-4), 6.60 (dd, 1 H, H-6), 6.71 (bd, 1 H, H-7), 6.72 (t, 1 H, H-11), 6.95 (dd, 2 H, H-10, H-12), 7.07 (d, 2 H, H-9, H-13). —^{13}C NMR (100 MHz, THF/[D_8]THF 1:1, −80°C): $\delta = 35.2$ (d, $^1J_{CH}$ 152 Hz, C-1), 46.6 (q, $^1J_{CH}$ 134 Hz, NCH_3), 58.5 (t, $^1J_{CH}$ 134 Hz, NCH_2), 110.9 (d, $^1J_{CH}$ 158 Hz, C-5), 116.2 (d, $^1J_{CH}$ 153 Hz, C-7), 119.8 (d, $^1J_{CH}$ 148 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: *TMEDA*: ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): $\delta = 2.08$ (s, 12 H, NCH_3), 2.22 (s, 4 H, NCH_2). —^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta = 45.5$ (q, $^1J_{CH}$ 133 Hz, NCH_3), 57.4 (t, $^1J_{CH}$ 132 Hz, NCH_2).

5. [^{6}Li]-α-(Phenylthio)benzyllithium with (−)-sparteine (**1**-^{6}Li–(−)-sparteine): —^{1}H NMR (500 MHz, THF/[D_8]THF 1:1, 25°C): δ = 0.90–2.70 (several weak m, (−)-sparteine), 3.03 (s, 1 H, H-1), 5.95 (t, 1 H, H-5), 6.60 (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), 7.10 (d, 2 H, H-9, H-13). —^{13}C NMR (75 MHz, THF/[D_8]THF 1:1, 25°C): δ = 25.0–68.0 (several weak signals, (−)-sparteine), 35.7 (d, $^1J_{CH}$ 148 Hz, C-1), 112.0 (d, $^1J_{CH}$ 157 Hz, C-5), 118.9 (bd, $^1J_{CH}$ 150 Hz, C-3, C-7), 122.1 (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, $^1J_{CH}$ 152 Hz, C-4, C-6), 151.7 (s, C-8), 157.0 (s, C-2). −^{6}Li NMR (73 MHz, THF/[D_8]THF 1:1, 25°C): $\delta = 0.30$. —^{1}H NMR (400 MHz, THF/[D_8]THF 1:1, −80°C): $\delta = 0.90$–2.70 (several weak m, (−)-sparteine), 2.98 (s, 1 H, H-1), 5.91 (t, 1 H, H-5), 6.54 (d, 1 H, H-3), 6.56 (dd, 1 H, H-4), 6.60 (dd, 1 H, H-6), 6.72 (t, 1 H, H-11), 6.73 (d, 1 H, H-7), 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 = 25.0–67.0 (several weak signals, (−)-sparteine), 35.6 (d, $^1J_{CH}$ 152 Hz, C-1), 111.2 (d, $^1J_{CH}$ 157 Hz, C-5), 116.2 (d, $^1J_{CH}$ 155 Hz, C-7), 119.9 (d, $^1J_{CH}$ 153 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, $^1J_{CH}$ 152 Hz, C-4), 128.1 (d, $^1J_{CH}$ 156 Hz, C-10, C-12), 128.8 (d, $^1J_{CH}$ 152 Hz, C-6), 151.0 (s, C-8), 156.2 (s, C-2).

For comparison: (−)-sparteine: ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 1.00–2.77 (several m, 26 H). —^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 24.7, 24.9, 25.9, 26.0, 27.7, 29.3, 33.1, 34.7, 36.2, 54.0, 55.4, 56.2, 62.0, 64.4, 66.5.

6. [^{6}Li]-α-(Phenylthio)benzyllithium with PMDTA (**1**-^{6}Li–PMDTA): —^{1}H NMR (500 MHz, THF/[D_8]THF 1:1, 25°C): $\delta = 2.14$ (s, 12 H, NCH_3), 2.24 (s, 3 H, NCH_3), 2.27 (m, 4 H, NCH_2), 2.37 (m, 4 H, NCH_2), 3.06 (s, 1 H, H-1), 5.98 (t, 1 H, H-5), 6.63 (dd, 2 H, H-4, H-6), 6.70 (t, 1 H, H-11), 6.71 (d, 2 H, H-3, H-7), 6.92 (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): $\delta = 35.5$ (d, $^1J_{CH}$ 149 Hz, C-1), 44.8 (q, $^1J_{CH}$ 134 Hz, NCH_3), 46.2 (q, $^1J_{CH}$ 133 Hz, NCH_3), 55.9 (t, $^1J_{CH}$ 133 Hz, NCH_2), 58.6 (t, $^1J_{CH}$ 133 Hz, NCH_2), 112.2 (d, $^1J_{CH}$ 157 Hz, C-5), 118.9 (d, $^1J_{CH}$ 151 Hz, C-3, C-7), 122.2 (d, $^1J_{CH}$ 160 Hz, C-11), 125.3 (d, $^1J_{CH}$ 159 Hz, C-9, C-13), 128.1 (d, $^1J_{CH}$ 158 Hz, C-10, C-12), 128.5 (d, $^1J_{CH}$ 152 Hz, C-4, C-6), 151.5 (s, C-8), 156.6 (s, C-2). −^{6}Li NMR (73 MHz, THF/[D_8]THF 1:1, 25°C): δ = 3.41. —^{1}H NMR (500 MHz, THF/[D_8]THF 1:1, −80°C): d = 2.11 (s, 12 H, NCH_3), 2.26 (s, 3 H, NCH_3), 2.42 (bs, 8 H, NCH_2), 3.04 (s, 1 H, H-1), 5.91 (t, 1 H, H-5), 6.57 (bs, 2 H, H-3, H-4), 6.62 (dd, 1 H, H-6), 6.64 (d, 1 H, H-7), 6.75 (t, 1 H,

H-11), 6.97 (dd, 2 H, H-10, H-12), 7.07 (d, 2 H, H-9, H-13). —^{13}C NMR (125 MHz, THF/[D$_8$]THF 1:1, −80°C): δ = 35.0 (d, $^1J_{CH}$ 152 Hz, C-1), 43.7, 45.0, 45.8, 46.6, 53.7, 57.7, 58.7 (7 broad signals, PMDTA), 111.1 (d, $^1J_{CH}$ 157 Hz, C-5), 116.6 (d, $^1J_{CH}$ 152 Hz, C-7), 119.5 (d, $^1J_{CH}$ 154 Hz, C-3), 122.2 (d, $^1J_{CH}$ 158 Hz, C-11), 124.8 (d, $^1J_{CH}$ 158 Hz, C-9, C-13), 127.9 (d, $^1J_{CH}$ 151 Hz, C-4), 128.3 (d, $^1J_{CH}$ 158 Hz, C-10, C-12), 128.9 (d, $^1J_{CH}$ 153 Hz, C-6), 150.9 (s, C-8), 155.8 (s, C-2).

For comparison: PMDTA: ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 2.12 (s, 12 H, NCH_3), 2.15 (s, 3 H, NCH_3), 2.28 (m, 4 H, NCH_2), 2.38 (m, 4 H, NCH_2). —^{13}C NMR (75 MHz, CDCl$_3$, 25°C): δ = 42.7 (q, $^1J_{CH}$ 133 Hz, NCH_3), 45.7 (q, $^1J_{CH}$ 133 Hz, NCH_3), 56.0 (t, $^1J_{CH}$ 132 Hz, NCH_2), 57.3 (t, $^1J_{CH}$ 132 Hz, NCH_2).

7. [^{6}Li]-α-(Phenylthio)benzyllithium with HMTTA [62] (**1**-^{6}Li–HMTTA): —^{1}H NMR (500 MHz, THF/[D$_8$]THF 1:1, 25°C): δ = 2.15 (s, 12 H, NCH_3), 2.20 (s, 6 H, NCH_3), 2.30 (m, 4 H, NCH_2), 2.39 (s, 4 H, NCH_2), 2.40 (m, 4 H, NCH_2), 3.07 (s, 1 H, H-1), 5.70 (bs, 1 H, H-5), 6.48 (bs, 4 H, H-3, H-7, H-4, H-6), 6.67 (t, 1 H, H-11), 6.90 (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): δ = 38.5 (d, $^1J_{CH}$ 158 Hz, C-1), 43.7 (q, $^1J_{CH}$ 134 Hz, NCH_3), 46.1 (q, $^1J_{CH}$ 133 Hz, NCH_3), 56.2 (t, $^1J_{CH}$ 133 Hz, NCH_2), 56.3 (t, $^1J_{CH}$ 133 Hz, NCH_2), 58.3 (t, $^1J_{CH}$ 133 Hz, NCH_2), 108.8 (d, $^1J_{CH}$ 157 Hz, C-5), 117.2 (bd, too broad, C-3, C-7), 121.8 (d, $^1J_{CH}$ 161 Hz, C-11), 125.2 (d, $^1J_{CH}$ 160 Hz, C-9, C-13), 128.0 (d, $^1J_{CH}$ 159 Hz, C-10, C-12), 128.4 (d, $^1J_{CH}$ 147 Hz, C-4, C-6), 152.7 (s, C-8), 156.4 (s, C-2). −^{6}Li NMR (73 MHz, THF/[D$_8$]THF 1:1, 25°C): δ = 0.99. —^{1}H NMR (400 MHz, THF/[D$_8$]THF 1:1, −80°C): δ = 2.14 (s, 12 H, NCH_3), 2.19 (bs, 6 H, NCH_3), 2.34 (bs, 12 H, NCH_2), 3.04 (s, 1 H, H-1), 5.49 (bs, 1 H, H-5), 6.23 (bs, 1 H, H-3), 6.36 (bs, 2 H, H-4, H-6), 6.70 (m, 2 H, H-7, H-11), 6.94 (dd, 2 H, H-10, H-12), 7.07 (d, 2 H, H-9, H-13). —^{13}C NMR (100 MHz, THF/[D$_8$]THF 1:1, −80°C): δ = 40.0 (bd, too broad, C-1), 43.6, 46.2, 46.6, 54.6, 57.4, 58.6 (6 broad signals, HMTTA), 105.6 (bd, $^1J_{CH}$ 159 Hz, C-5), 113.1 (bd, $^1J_{CH}$ 153 Hz, C-7), 117.6 (bd, $^1J_{CH}$ 156 Hz, C-3), 121.8 (d, $^1J_{CH}$ 157 Hz, C-11), 124.7 (d, $^1J_{CH}$ 159 Hz, C-9, C-13), 127.7 (d, $^1J_{CH}$ 146 Hz, C-4), 128.1 (d, $^1J_{CH}$ 158 Hz, C-10, C-12), 128.8 (d, $^1J_{CH}$ 150 Hz, C-6), 152.5 (s, C-8), 155.1 (s, C-2).

For comparison: *HMTTA*: ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 2.11 (s, 12 H, NCH_3), 2.14 (s, 6 H, NCH_3), 2.27 (m, 4 H, NCH_2), 2.36 (m, 4 H, NCH_2), 2.39 (m, 4 H, NCH_2). —^{13}C NMR (75 MHz, CDCl$_3$, 25°C): δ = 42.8 (q, $^1J_{CH}$ 133 Hz, NCH_3), 45.7 (q, $^1J_{CH}$ 133 Hz, NCH_3), 55.0 (t, $^1J_{CH}$ 132 Hz, NCH_2), 55.9 (t, $^1J_{CH}$ 132 Hz, NCH_2), 57.3 (t, $^1J_{CH}$ 132 Hz, NCH_2).

8. [^{6}Li]-α-(Phenylthio)benzyllithium with Me$_3$–6N3 (**1**-^{6}Li–Me$_3$–6N3): —^{1}H NMR (500 MHz, THF/[D$_8$]THF 1:1, 25°C): δ = 2.16 (s, 9 H, NCH_3), 3.03 (s, 1 H, H-1), 3.05 (bs, 6 H, NCH_2), 5.94 (t, 1 H, H-5), 6.60 (dd, 2 H, H-4, H-6), 6.68 (t, 1 H, H-11), 6.70 (bd, 2 H, H-3, H-7), 6.90 (dd, 2 H, H-10, H-12), 7.10 (d, 2 H, H-9, H-13). —^{13}C NMR (50 MHz, THF/[D$_8$]THF 1:1, 25°C): δ = 35.8 (d, $^1J_{CH}$ 149 Hz, C-1), 40.7 (q, $^1J_{CH}$ 133 Hz, NCH_3), 78.4 (t, $^1J_{CH}$ 142 Hz, NCH_2), 111.7 (d, $^1J_{CH}$ 157 Hz, C-5), 118.7 (bd, $^1J_{CH}$ 154 Hz, C-3, C-7), 122.0 (d, $^1J_{CH}$ 156 Hz, C-11), 125.3 (d, $^1J_{CH}$ 159 Hz, C-9, C-13), 128.0 (d, $^1J_{CH}$ 157 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). −^{6}Li NMR (73 MHz, THF/[D$_8$]THF 1:1, 25°C): δ = 0.31. —^{1}H NMR (400 MHz, THF/[D$_8$]THF 1:1, −80°C): d = 2.13 (s, 9 H, NCH_3), 2.53 (s, 6 H, NCH_2), 2.99 (s, 1 H, H-1), 5.86 (t, 1 H, H-5), 6.51 (d, 1 H, H-3), 6.54 (dd, 1 H, H-4), 6.57 (dd, 1 H, H-6), 6.68 (d, 1 H, H-7), 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): δ = 35.3 (d, $^1J_{CH}$ 152 Hz, C-1), 40.6 (q, $^1J_{CH}$ 133 Hz, NCH_3), 78.2 (t, $^1J_{CH}$ 142 Hz, NCH_2), 110.6 (d, $^1J_{CH}$ 157 Hz, C-5), 115.8 (d, $^1J_{CH}$ 154 Hz, C-7), 119.6 (d, $^1J_{CH}$ 151 Hz, C-3), 122.0 (d, $^1J_{CH}$ 157 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, $^1J_{CH}$ 157 Hz, C-10, C-12), 128.8 (d, $^1J_{CH}$ 151 Hz, C-6), 151.3 (s, C-8), 156.1 (s, C-2).

For comparison: *Me$_3$–6N3*: ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 2.13 (s, 9 H, NCH_3), 3.04 (bs, 6 H, NCH_2). —^{13}C NMR (75 MHz, CDCl$_3$, 25°C): d = 39.9 (q, $^1J_{CH}$ 134 Hz, NCH_3), 77.0 (t, $^1J_{CH}$ 142 Hz, NCH_2).

9. [^{6}Li]-α-(Phenylthio)benzyllithium with Me$_3$–9N3 [63] (**1**-^{6}Li–Me$_3$–9N3): —^{1}H NMR (500 MHz, THF/[D$_8$]THF 1:1, 25°C): δ = 2.30 (s, 9 H, NCH_3), 2.31 (bs, 6 H, NCH_2), 2.48 (bs, 6 H, NCH_2), 3.09 (s, 1 H, H-1), 5.95 (t, 1 H, H-5), 6.63 (dd, 2 H, H-4, H-6), 6.71 (t, 1 H, H-11), 6.71 (d, 2 H, H-3, H-7), 6.92 (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): δ = 34.8 (d, $^1J_{CH}$ 152 Hz, C-1), 46.2 (q, $^1J_{CH}$ 135 Hz, NCH_3), 54.4 (t, $^1J_{CH}$ 133 Hz, NCH_2), 112.0 (d, $^1J_{CH}$ 158 Hz, C-5), 118.5 (d, $^1J_{CH}$ 153 Hz, C-3, C-7), 122.3 (d, $^1J_{CH}$ 160 Hz, C-11), 125.3 (d, $^1J_{CH}$ 159 Hz, C-9, C-13), 128.2 (d, $^1J_{CH}$ 158 Hz, C-10, C-12), 128.7 (d, $^1J_{CH}$ 152 Hz, C-4, C-6), 151.3 (s, C-8), 156.0 (s, C-2). −^{6}Li NMR (73 MHz, THF/[D$_8$]THF 1:1, 25°C): δ = 2.52. —^{1}H NMR (400 MHz, THF/[D$_8$]THF 1:1, −80°C): δ = 2.26 (s, 9 H, NCH_3), 2.27 (bs, 6 H, NCH_2), 2.49 (bs, 6 H, NCH_2), 3.03 (s, 1 H, H-1), 5.94 (t, 1 H, H-5), 6.60 (dd, 1 H, H-4), 6.61 (d, 1 H, H-3), 6.65 (dd, 1 H, H-6), 6.73 (d, 1 H, H-7), 6.74 (t, 1 H, H-11), 6.97 (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 = 33.8 (d, $^1J_{CH}$ 153 Hz, C-1), 46.0 (q, $^1J_{CH}$ 134 Hz, NCH_3), 53.9 (bt, $^1J_{CH}$ 130 Hz, NCH_2), 111.7 (d, $^1J_{CH}$ 157 Hz, C-5), 116.5 (d, $^1J_{CH}$ 157 Hz, C-7), 119.6 (d, $^1J_{CH}$ 152 Hz,

C-3), 122.3 (d, $^1J_{CH}$ 156 Hz, C-11), 124.8 (d, $^1J_{CH}$ 159 Hz, C-9, C-13), 128.2 (d, $^1J_{CH}$ 150 Hz, C-4), 128.4 (d, $^1J_{CH}$ 156 Hz, C-10, C-12), 129.1 (d, $^1J_{CH}$ 150 Hz, C-6), 150.6 (s, C-8), 155.4 (s, C-2).

For comparison: Me_3–9N3: ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): $\delta = 2.32$ (s, 9 H, NCH_3), 2.60 (s, 12 H, NCH_2). —^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta = 46.7$ (q, $^1J_{CH}$ 133 Hz, NCH_3), 57.1 (t, $^1J_{CH}$ 131 Hz, NCH_2).

10. [^{6}Li]-α-(Phenylthio)benzyllithium with Me_4–12N4 [64] (**1**-^{6}Li–Me_4–12N4): —^{1}H NMR (500 MHz, THF/[D_8]THF 1:1, 25°C): $\delta = 2.14$ (m, 8 H, NCH_2), 2.17 (s, 12 H, NCH_3), 2.53 (m, 8 H, NCH_2), 3.07 (s, 1 H, H-1), 5.53 (bs, 1 H, H-5), 6.38 (bs, 4 H, H-3, H-7, H-4, H-6), 6.66 (t, 1 H, H-11), 6.89 (dd, 2 H, H-10, H-12), 7.12 (d, 2 H, H-9, H-13). —^{13}C NMR (75 MHz, THF/[D_8]THF 1:1, 25°C): $\delta = 40.5$ (d, $^1J_{CH}$ 162 Hz, C-1), 44.6 (q, $^1J_{CH}$ 134 Hz, NCH_3), 54.8 (t, $^1J_{CH}$ 133 Hz, NCH_2), 106.5 (d, $^1J_{CH}$ 157 Hz, C-5), 116.4 (bs, C-3, C-7), 121.6 (d, $^1J_{CH}$ 160 Hz, C-11), 125.2 (d, $^1J_{CH}$ 160 Hz, C-9, C-13), 127.9 (d, $^1J_{CH}$ 159 Hz, C-10, C-12), 128.3 (d, $^1J_{CH}$ 152 Hz, C-4, C-6), 153.6 (s, C-8), 156.4 (s, C-2). –^{6}Li NMR (73 MHz, THF/[D_8]THF 1:1, 25°C): $\delta = 0.40$ (A), 0.52 (B) (rel. intensities A: B = 1.0: 0.6). —^{1}H NMR (400 MHz, THF/[D_8]THF 1:1, −80°C): $\delta = 2.10$ (bs, ca. 8 H, NCH_2), 2.15 (s, ca. 12 H, NCH_3), 2.61 (bs, ca. 4 H, NCH_2), 3.00 (bs, ca. 4 H, NCH_2), 3.03 (bs, ca. 1 H, H-1), 5.39 (t, 1 H, H-5), 6.15 (m, 2 H, H-3, H-7), 6.30 (dd, 2 H, H-4, H-6), 6.70 (t, 1 H, H-11), 6.93 (dd, 2 H, H-10, H-12), 7.07 (d, 2 H, H-9, H-13). —^{13}C NMR (100 MHz, THF/[D_8]THF 1:1, −80°C): $\delta = 41.0$ (d, $^1J_{CH}$ 168 Hz, C-1), 44.1 (q, $^1J_{CH}$ 134 Hz, NCH_3), 52.8 (t, $^1J_{CH}$ 135 Hz, NCH_2), 55.6 (t, $^1J_{CH}$ 134 Hz, NCH_2), 104.7 (d, $^1J_{CH}$ 154 Hz, C-5), 112.3 (d, $^1J_{CH}$ 151 Hz, C-7), 117.1 (d, $^1J_{CH}$ 153 Hz, C-3), 121.7 (d, $^1J_{CH}$ 154 Hz, C-11), 124.7 (d, $^1J_{CH}$ 158 Hz, C-9, C-13), 127.8 (d, $^1J_{CH}$ 149 Hz, C-4), 128.1 (d, $^1J_{CH}$ 153 Hz, C-10, C-12), 128.8 (d, $^1J_{CH}$ 148 Hz, C-6), 152.6 (s, C-8), 154.9 (s, C-2).

For comparison: *Me_4–12N4*: ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): $\delta = 2.09$ (s, 12 H, NCH_3), 2.39 (s, 16 H, NCH_2). —^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta = 44.5$ (q, $^1J_{CH}$ 132 Hz, NCH_3), 55.8 (t, $^1J_{CH}$ 131 Hz, NCH_2).

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