Structural investigations of aryllithium clusters in solution

II *. A ^{13}C and ^{7}Li NMR study of substituted phenyllithium compounds containing *ortho*-directing NMe$_2$ and CH$_2$NMe$_2$ groups

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Abstract

^{7}Li and ^{13}C NMR spectroscopic studies have been made on the behaviour of several aryllithium compounds containing a *N,N*-dimethylamino substituent suitably positioned for intramolecular coordination to lithium in the presence of accurately known quantities of coordinating solvents (diethyl ether, THF) and ligand (TMEDA). The solvent molecules compete with the internal nitrogen coordination, and if their donor strength is sufficient and the steric situation is favourable they can fully replace intramolecular *N*-coordination. In the presence of more than one equivalent of the solvent, the aryllithium cluster can be broken down to afford solvent coordinated dimeric species. This change is reflected in an upfield shift of ca. 10 ppm for the ^{13}C NMR C-*ipso* signal, with a concomitant change of $^1J(^7Li,^{13}C)$ from ca. 11 to 20 Hz, and by an upfield shift of the ^{7}Li NMR signal by ca. 1 ppm.

Introduction

Though organolithium compounds have long been known as valuable reagents in organic and organometallic synthesis [1], their structural features remained unclear until about 15 years ago. Since then improved crystallographic methods and NMR

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techniques have produced information that provides a clear picture of the structure of these compounds in solution and the solid state [2]. In general they are associated species with electron deficient carbon–lithium bonds. The nature of these organolithium compounds is determined by steric factors and the presence of coordinating molecules that can be either heteroatom-containing substituents in the organic moiety bound to lithium, solvent molecules (e.g. Et_2O, THF), or deliberately added ligands (e.g. TMEDA) [2].

Increased attention has been given in the last decade to organolithium compounds containing heteroatom substituents that are suitably positioned for coordination to lithium, since such substituents are very useful directing groups in *ortho*-lithiation reactions [3]. With these reactions the high selectivity under mild conditions originates from precoordination of the *ortho*-directing group of the organic substrate to the lithiating agent, thus positioning the *ortho* C–H bond in its reaction sphere and hence facilitating the lithiation. Recently, infrared spectroscopic measurements have revealed such precoordination prior to lithiation in the case of N,N-dimethyl-2,4,6-triisopropylbenzamide [4]. With aryllithium compounds having *ortho* substituents there is the interesting possibility of stabilizing the carbon–lithium bond by intramolecular coordination of the heteroatom to the lithium atom. Oxygen-coordination to lithium in the formation of organolithium species has been shown to lower the enthalpy by ca. 41 kJ/mol [3d], and this was assumed to be entirely due to the formation of a Li–O bond.

Numerous studies have been made on the use of *ortho*-directing groups in lithiation reactions [3a–d] and the application of such lithiated species in organic and organometallic synthesis [3e,f]. Despite the interest in the structures of organolithium compounds [2], X-ray crystallographic data for those with heteroatom-containing substituents are still limited. Up to now the X-ray structures of only two heteroatom-containing alkyllithium compounds have been reported, viz. $Li_4\{CH(CH_3)CH_2CH_2OMe\}_4$ [5] and $Li_4(CH_2CH_2CH_2NMe_2)_4$ [6], in which the OMe or NMe_2 group is suitably positioned for heteroatom–lithium coordination. Recently, we reported the structures of aryllithium compounds with CH_2NMe_2 and NMe_2 *ortho*-substituents, viz. $Li_4\{C_6H_4(CH_2NMe_2)-2\}_4$ [7], $Li_2(naphthylNMe_2-8)_2(Et_2O)_2$ [8], and $Li_2\{C_6H(CH_2NMe_2)_4-2,3,5,6\}_2$ [9]. For $Li_4\{C_6H_4(CH_2-NMe_2)-2\}_4$ the tetrameric aggregate structure found shows a striking similarity to that of phenyllithium etherate in the solid state [10] (see Fig. 1). Like the latter it contains four-centre, two-electron bound aryl groups with the coordinating donor atom of the CH_2NMe_2 substituent now taking the place of an ether solvent
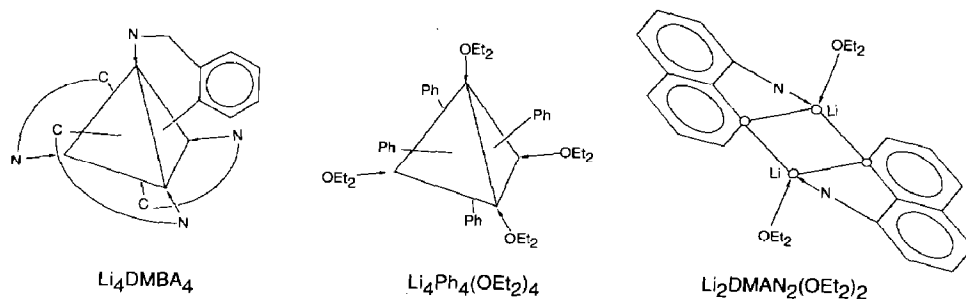

Fig. 1. X-Ray structures of Li_4DMBA_4 (**1a**), $Li_4Ph_4(OEt_2)_4$ and $Li_2DMAN_2(OEt_2)_2$ (**2a**).

molecule. Introduction of a second *ortho*-CH$_2$NMe$_2$ substituent on the aryl ring leads to breakdown of the tetranuclear aggregate, and the X-ray study of a closely related compound Li$_2$\{C$_6$H(CH$_2$NMe$_2$)$_4$-2,3,5,6\}$_2$ revealed a dimeric structure with bridging C(*ipso*) atoms and both nitrogen atoms coordinated to lithium [9]. This latter structure shows a close resemblance to that of [mesityllithium(THF)$_2$]$_2$ [11], in which THF molecules form the same function as the CH$_2$NMe$_2$ units. These comparisons suggest that CH$_2$NMe$_2$ groups can be regarded as suitably positioned intramolecular solvent molecules. For Li$_2$(naphthylNMe$_2$-8)$_2$(Et$_2$O)$_2$ a dimeric structure which contains two lithium atoms bridged by C-(*ipso*) of the naphthyl-amine group was found [8] (see Fig. 1). Here the third and fourth coordination sites of each lithium atom are occupied by a dimethylamino substituent and a diethyl ether molecule. Owing to the bulk of the naphthylamine group, a tetranuclear aggregate has become unfavourable and formation of a dimeric species is more attractive. This clearly illustrates the effect of the change from a flexible CH$_2$NMe$_2$ substituent to a rigid and bulky naphthylNMe$_2$ group on the structure of the resulting compound. From Table 1 it can be seen that neither the introduction of the heteroatom nor the change from an aryl- to an alkyllithium compound has significant influence on the lithium–lithium and the lithium–carbon distances.

In a previous paper [12] we described the structures of phenyllithium and methyl-substituted phenyllithium compounds in solution as indicated by ^{13}C and ^{7}Li NMR spectroscopy. This study revealed that for these 'bare' aryllithium compounds there is a strong tendency for the lithium atom to achieve tetrahedral coordination. In the presence of one equivalent of a monodentate donor molecule, such as diethyl ether, THF, or the potentially bidentate TMEDA, there is formation of discrete solvent-coordinated lithium clusters. Depending on the donor ability and denticity of these solvents, addition of excess solvent results in either (i) coordination of the solvent molecule or (ii) formation of lower order clusters with a change from four-centre, two-electron to three-centre, two-electron carbon–lithium interactions.

The present study concerns the influence of various solvents on the solution structures of organolithium clusters containing aryl ligands bearing potentially intra-molecular-coordinating *ortho* CH$_2$NMe$_2$ and NMe$_2$ groups. Competition between inter- and intra-molecular coordination has been investigated by ^{1}H, ^{13}C and ^{7}Li NMR spectroscopy. The results are discussed in relation to known solid state structures of aryllithium clusters.

Table 1

Li–Li and Li–C distances (Å) in some selected organolithium compounds

Distance	[LiPh(Et$_2$O)]$_4$	[LiDMBA]$_4$	[Li(CH)$_2$)$_3$NMe$_2$]$_2$	[LiCHMe(CH$_2$)$_2$OMe]$_4$
Li–Li	2.684(4)	2.523(8)	2.492(3)	2.495(4)
Li–C	2.318(2)	2.283(5)	2.266(2)	2.313(3)
Li–X [a]	2.049(3)	2.011(9)	2.065(3)	1.923(5)
Ref.	10	7	6	5

[a] X = heteroatom.

Results and discussion

The organolithium compounds **1–3** the subjects of the present investigations can be readily synthesized by direct metallation (**1** or **2**) or halogen exchange (**3**), as depicted in Scheme 1.

The compounds **1–3** have in common the presence of a potentially coordinating dimethylamino group in the position *ortho* relative to the carbon–lithium bond. Coordination of this group to the lithium atom leads to a C–N chelate, which is generally considered to have a stabilizing effect on the carbon–metal bond [3a]. Furthermore, the presence of this substituent can also have an important influence on the structure of the organometallic species as a result of the specific coordinating features of the C–N chelates. (See Ref. 13 for a discussion of the influence of the C–N chelation on the structure of group 11 metal complexes and organocuprates.) It is important to realize that suitable solvent molecules, such as THF or TMEDA, can compete with the intramolecular nitrogen coordination, and give rise to uncoordinated dimethylamino substituents.

The compounds $Li(C_6H_4CH_2NMe_2-2)$ (**1a**) (LiDMBA) and $Li\{C_6H_3(CH_2-NMe_2)_2-2,6\}$ (**3**) (LiNCN) can be visualized as being derived from the 'bare' aryllithium compounds *ortho*-tolyllithium and 2,6-dimethylphenyllithium, respectively, by replacement of one H atom per Me group by a dimethylamino group. A third compound containing an NMe_2 group, viz. $LinaphthylNMe_2-8$ (**2**) (LiDMAN) has also been studied.

NMR studies

Lithium dimethylaminomethylphenyl derivatives (1)

Compared with LiDMBA (**1a**) the related derivative LiDMBA-5-Me (**1b**) is much more soluble in apolar non-protic solvents, and for this reason was used for our

1a: Li DMBA (R=H)
1b: Li DMBA-5-Me(R=Me)

2: LiDMAN

3: LiNCN
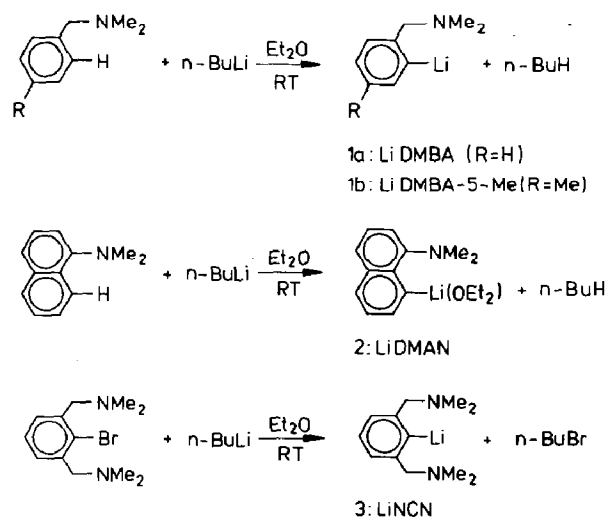
Scheme 1. Methods used for the synthesis of the heteroatom containing aryllithium compounds, showing the numbering used throughout the paper.

solution NMR studies. The molecular weight of **1b**, determined cryoscopically in benzene, indicates that in this solvent it exists as tetrameric Li_4R_4 units. It is likely that many of the primary structural features of this tetramer will be similar to those found for tetrameric **1a**, which in the solid state was found to contain a tetrahedron of lithium atoms. In the LiDMBA-5-Me tetramer, therefore, the aryl groups each bridge a face of the tetrahedron in a four-centre, two-electron bonding mode, with the *ortho*-dimethylamino substituent coordinating to a lithium atom.

The ^{13}C NMR spectrum of **1b** recorded at $-40°C$ in toluene-d_8 showed a broad signal at 176.0 ppm for C(*ipso*). The multiplicity of this signal could not be resolved, though the linewidth of 110 Hz would be consistent with coupling of the ^{13}C nucleus coupled to three ^7Li nuclei, with $^1J(^{13}C,^7Li)$ of about 12 Hz (cf. $^1J(^{13}C,^7Li)$ of 14 and 11 Hz for n-BuLi and t-BuLi tetramers respectively [14]). Owing to the asymmetry of the postulated $Li_4(DMBA-5-Me)_4$ aggregate the methyl groups of the dimethylamino substituent are expected to be diastereotopic. At temperatures up to $90°C$ the spectrum does, in fact, show two signals for the NMe_2 group, which suggests that the tetranuclear aggregate and the Li–N coordination are retained in solution.

The ^{13}C NMR spectra of **1b** in diethyl ether (-40 to $+30°C$) are similar to those obtained in toluene-d_8 in the same temperature range, and indicate that the tetranuclear aggregate persists in this weakly coordinating solvent. With a more strongly coordinating ether such as THF, which can compete with the intramolecular Li–N coordination, breakdown of the cluster occurs. This was nicely demonstrated by NMR measurements on a toluene solution of **1b** to which known quantities of THF had been added. The ^{13}C NMR spectrum at $-40°C$ obtained after the addition of one equivalent of THF per LiR unit showed two signals for C(*ipso*), at 176.0 and 189.2 ppm, indicating that two species were now present, the signal at 176.0 ppm is from the unchanged organolithium tetramer **1b**, while that at 189.2 ppm can be assigned to the THF-coordinated dimeric species **1c** (see eq. 1). The most likely structure for **1c** is depicted in Fig. 2, and consists of a Li_2 core bridged by two aryl groups with uncoordinated NMe_2 substituents.
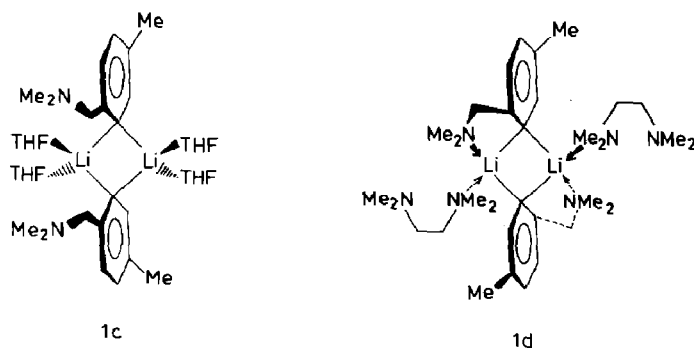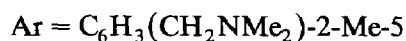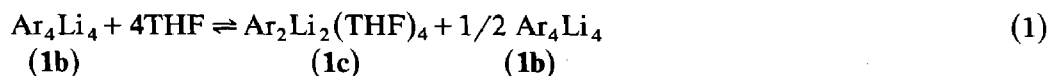
$$Ar_4Li_4 + 4THF \rightleftharpoons Ar_2Li_2(THF)_4 + 1/2\ Ar_4Li_4 \qquad (1)$$
$$\textbf{(1b)} \qquad\qquad\qquad \textbf{(1c)} \qquad\qquad \textbf{(1b)}$$

$$Ar = C_6H_3(CH_2NMe_2)\text{-}2\text{-Me-}5$$

1c   1d

Fig. 2. Proposed structures for $Li_2(DMBA-5-Me)_2L_2$ complexes.

The dimeric nature of **1c** can be deduced from the seven-line pattern observed for C($ipso$) ($-40\,°$C) with an intensity ratio of 1/2/3/4/3/2/1 ($^1J(^{13}C,^7Li)$ 20 Hz). This is consistent with an aryl group bridging two lithium atoms in a three-centre, two-electron bonding mode, as in $Li_2Bu_2THF_4$ [15], for which a value of 20 Hz for $^1J(^{13}C,^7Li)$ was found. Further information on the structure of **1c** comes from the ^{13}C NMR resonance for the NMe_2 group, which is a singlet at δ 46.4 ($-40\,°$C). This shift is similar to that for the Me groups in free H-DMBA-5-Me (δ 46.3), suggesting that in **1c** the CH_2NMe_2 groups are not involved in coordination to lithium.

From variable temperature ^{13}C and ^7Li NMR measurements it was deduced that the dimeric and tetrameric aggregates are in equilibrium with each other. For example, in the ^{13}C NMR spectrum of the mixture of **1b** and **1c**, coalescence of the respective C($ipso$) signals occurs at $0\,°$C. Furthermore, the ^7Li NMR spectrum at $-20\,°$C shows two signals, at 3.58 ppm (**1b**) and 2.78 ppm (**1c**) which coalesce above $0\,°$C to a single line at 3.20 ppm. In separate experiments it was shown that the NMR spectra of pure **1b** and **1c** are temperature-independent in the range -60 to $+80\,°$C.

The ^{13}C NMR spectrum obtained after the addition of four equivalents of TMEDA to a toluene-d_8 solution of $Li_4(DMBA-5-Me)_4$ (**1b**) at $-65\,°$C showed one resonance for the aryl group. The C($ipso$) signal was observed at 189.4 ppm as a seven-line pattern with $^1J(^{13}C,^7Li)$ of 20 Hz. These data are consistent with a structure based on a dimeric unit with two three-centre, two-electron carbon–lithium bonded DMBA-5-Me groups. The NMe_2 substituent on the aryl system is diastereotopic, as evidenced by two resonances at 48.0 and 43.4 ppm, and it can therefore be concluded that the CH_2NMe_2 substituent is coordinated to the lithium atom. For the TMEDA ligand two CH_2 resonances were observed, one at 58.9 ppm and another, much broadened, at 57.0 ppm (see Fig. 3). The NMe_2 groups of TMEDA gave three resonances at 48.0, 46.8, and 45.3 ppm, in a 1/2/1 ratio. Since the positions of the sharp CH_2 and NMe_2 resonances are the same as those found for free TMEDA we conclude that whereas one NMe_2 group of TMEDA is coordinated, resulting in the broadened ^{13}C resonances, the other is uncoordinated. Hence we suggest that at $-65\,°$C this compound, **1d**, is a LiR(TMEDA) dimer in which the TMEDA is monodentate bonded, the CH_2NMe_2 substituent is coordinated, and C($ipso$) bridges two lithium atoms, as shown in Fig. 2. The asymmetry about each chiral lithium atom renders the prochiral NMe_2 group of the aryl substituent as well as the coordinated NMe_2 group of the TMEDA ligand diastereotopic, and so both give two separate signals.

Above $-35\,°$C the ^{13}C resonances of the coordinated and uncoordinated NMe_2 groups of the TMEDA coalesce, suggesting the presence of a fast exchange process involving these two forms. That the NMe_2 group of DMBA-5-Me is still coordinated to the lithium atom at this temperature was established by the observation of two signals for this group, i.e. there is a stable intramolecular coordination on the NMR timescale (see Fig. 3). However above $-10\,°$C these resonances also coalesce, with concomitant disappearance of the $^1J(^{13}C,^7Li)$ coupling at C($ipso$). These data suggest an equilibrium between **1d** with another species, in which it is likely that the initially uncoordinated TMEDA function is now involved in coordination to another Li(DMBA-5-Me)TMEDA dimer.

Addition of more TMEDA to this solution did not significantly affect the ^{13}C NMR spectra, indicating that TMEDA can effectively break down the tetranuclear
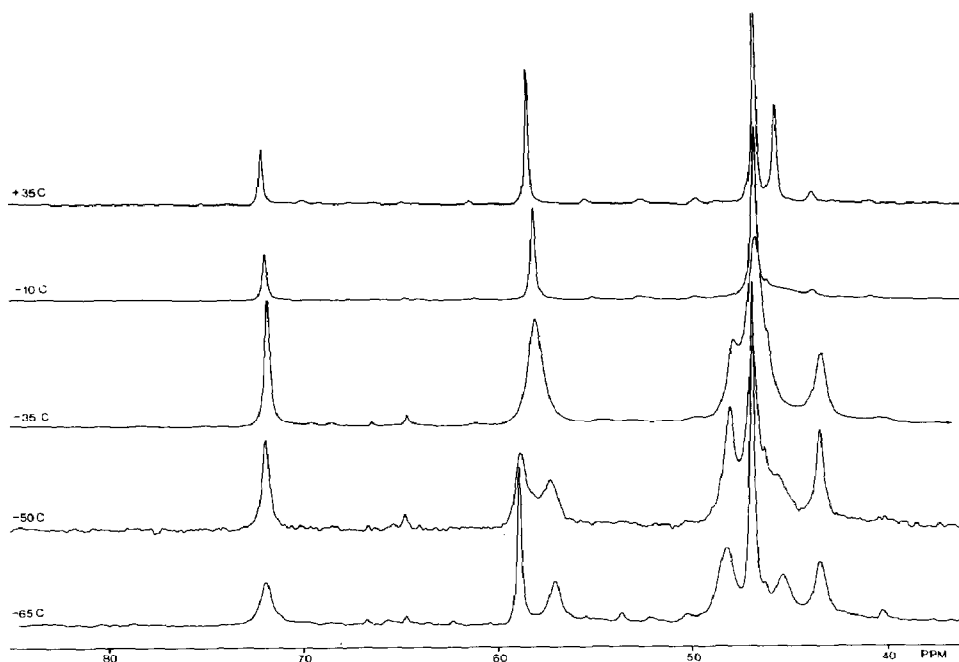
Fig. 3. ^{13}C NMR spectrum of $Li_2(DMBA-5-Me)_2TMEDA_2$ at various temperatures.

cluster **1b** to a dimer, **1d**, but cannot compete as effectively as THF with the intramolecular lithium–nitrogen coordination.

8-(dimethylamino)naphthyllithium derivatives (2)

The ^{1}H NMR spectrum of diethyl ether-free LiDMAN (**2b**) in toluene-d_8 below 0 °C showed two resonances for the NMe_2 groups (δ 1.80 and 2.45 ppm), and these coalesced at 24°C to a resonance at δ 2.10 ppm [8]. The ^{1}H NMR spectrum in toluene-d_8 of the mono-etherate **2a** (or **2b** after addition of diethyl ether in an exact 1/1 molar ratio) showed the resonance pattern observed for pure **2b** along with the resonances for free diethyl ether ($\delta(CH_3)$ 1.05 and $\delta(CH_2O)$ 3.25 ppm). When this solution was cooled, the signals of the second organolithium species appeared, with a concomitant shift of the diethyl ether resonances, which at $-70°C$ have values indicative of complexation ($\delta(CH_3)$ 0.60 and $\delta(CH_2O)$ 2.80 ppm; cf. $Li_2Cu_2(p$-Tol$)_4(OEt_2)_2$ $\delta(CH_3)$ 0.64 and $\delta(CH_2O)$ 2.72) [16].

In the ^{13}C NMR spectra of pure **2b** at 20°C, C($ipso$) gives a broad signal at 175.9 ppm. This is characteristic of the presence of a four-centre, two-electron carbon–lithium bond, suggesting a tetrameric aggregate related to that established for Li_4DMBA_4. Below $-20°C$ a new resonance pattern appears, with $\delta(C$-$ipso)$ at 185.9 ppm (having a seven-line pattern with $^1J(^7Li,^{13}C)$ of 20.5 Hz) consistent with the formation of the dimeric species **2a**. These changes in the ^{1}H and ^{13}C NMR spectra, which are fully reversible with temperature, can be accounted for in terms of the equilibrium shown in eq. 2.

$$R_4Li_4 + 4\ Et_2O \rightleftharpoons 2\ \left[R_2Li_2(OEt_2)_2\right] \qquad (2)$$
$$\quad \textbf{(2b)} \qquad\qquad\qquad \textbf{(2a)}$$
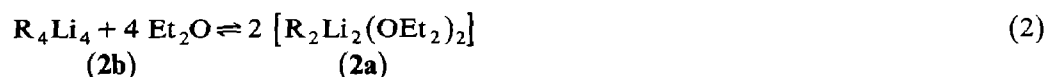
$(R = naphthylNMe_2-8)$

More direct evidence for the existence of equilibrium of eq. 2 was obtained from ^{7}Li NMR spectra at various temperatures (see Fig. 4). At probe temperature, only a somewhat broad resonance attributed to the uncomplexed organolithium species **2b**, was observed at δ 3.72 ppm. Lowering of the temperature gave rise to an additional signal at δ 2.45 ppm, assigned to the etherate complex **2a**. At $-90\,^\circ$C the signal of **2b** had almost disappeared, i.e. **2a** was now the major species in solution. These data indicate that **2a** and **2b** are both stable on the NMR timescale but are in equilibrium with each other on the laboratory time scale.

2,6-bis{(dimethylamino)methyl}phenyllithium (3)

The ^{1}H and ^{13}C NMR solution spectra of **3** in toluene-d_8 are temperature dependent. At $20\,^\circ$C ^{1}H NMR signals of both the NMe_2 and the CH_2 groups are observed as singlets whereas at $-20\,^\circ$C both groups afford anisochronous signals [7]. The anisochronism of the NMe_2 signals was also observed in the ^{13}C NMR spectra at $-20\,^\circ$C. These data indicate a fluxional process between uncoordinated and coordinated NMe_2 sites, in which the coordinated situation corresponds to the slow exchange limit. At $-20\,^\circ$C the ^{13}C NMR spectrum showed a seven-line pattern for C(*ipso*) at 189.3 ppm with an intensity ratio of 1/2/3/4/3/2/1, characteristic of a three-centre, two-electron carbon–lithium bond, which points to an aryl group bridging two lithium atoms. Cryoscopic molecular weight determinations in benzene revealed that the compound is dimeric, and in view of this result and the conclusion from the ^{13}C NMR data we propose the structure shown in Fig. 5 for **3**. This dimeric structure contains a dilithium core with two bridging C(*ipso*) atoms and coordinated CH_2NMe_2 substituents.

Addition of strong donor molecules such as THF or TMEDA to a solution of **3** in toluene-d_8 or dissolution of **3** in pure THF-d_8 gave solutions with ^{13}C NMR
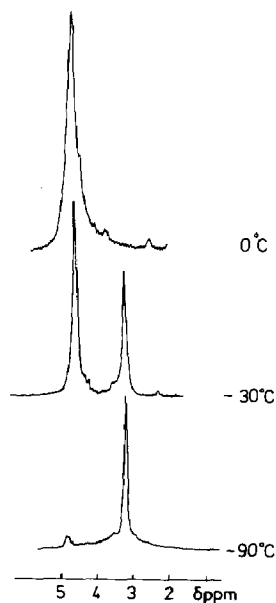

Fig. 4. ^{7}Li NMR spectra of the LiDMAN (**2b**)/Et$_2$O system in toluene-d_8 at 0, -30 and $-90\,^\circ$C, respectively.
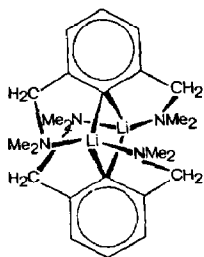
Fig. 5. Proposed structure for $Li_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}_2$.

spectra similar to that of **3** in toluene-d_8. This indicates that these donor molecules do not interact with this organolithium compound. The ^7Li NMR spectrum of **3** (δ 2.41 ppm; see Table 2) showed a single peak, whose chemical shift was independent of added solvent. These results are very similar to those obtained with 2,6-dimethylphenyllithium, which is unreactive towards donor molecules and for which a dimeric structure has been proposed [3].
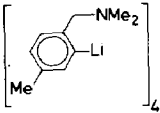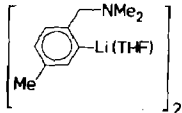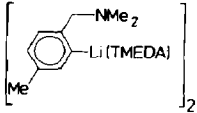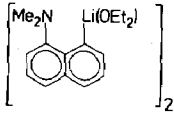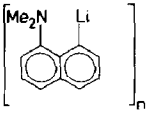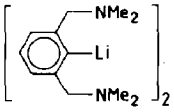
Concluding remarks

These studies have shown that the heteroatom-substituted phenyllithium derivatives show a close structural resemblance to the unsubstituted analogues in both the solid state and in solution. Both types of complex have electron deficient carbon–lithium bonds and aggregate structures in which the tendency of lithium to attain a tetrahedral coordination geometry seems to be the dominant factor. In these clusters the Li–Li and Li–C distances are rather insensitive not only to the presence of the built-in ligands but also to the change from an aryl group to an alkyl group. Whereas in the absence of heteroatom-containing substituents solvent molecules complete the tetrahedral coordination geometry about each lithium atom, in the heteroatom containing compounds the role of the solvent molecules is taken over by the built-in ligand. There are two main effects arising from the presence of the built-in ligand. First the coordination ability of the heteroatom facilitates an easy lithiation reaction; the heteroatom enables precoordination of the reacting aryl ligand with the lithiating reagent, thus positioning the *ortho* carbon–hydrogen bond in the reaction sphere of the lithium atom. Second, the internal coordination of the substituent has a stabilizing effect on the formed C–Li bond.

In the presence of solvents which can compete with Li–N coordination, the bulk of the *ortho* heteroatom-substituents is important in determining whether dimeric or tetrameric aggregates are formed. For tetrameric aggregates containing bulky substituents, ready formation of dimeric species is observed. However, for the dimeric aggregates the situation which would arise after replacement of *ortho*-substituent coordination by a solvent determines whether such solvation can take place.

It is evident that ^{13}C as well as ^7Li NMR are powerful tools in structural investigations of aryllithium compounds in solution. When in the ^{13}C NMR spectra the C(*ipso*) signal can be observed as a multiplet resulting from the coupling $^1J(^{13}C,^7Li)$ it is immediately clear whether this carbon atom is four-centre, two-electron bonded (10-line pattern with $^1J(^{13}C,^7Li)$ 12 Hz). This differentiation is further evidenced by a downfield shift of about 10 ppm for C(*ipso*) on going from a four-centre, two-electron bonded aryl group to a three-centre, two-electron bonded aryl group.

Table 2

Relevant ^{13}C [a] and ^7Li [b] NMR data

Compound		Temp.	C_1 [c]	C_2	C_6	$\delta(^7Li)$	Other groups
	1b	−40	176.0(12)	150.2	141.0	3.58	NCH$_2$ 70.4; NMe$_2$ 46.7, 44.0 [d]
	1c	−40	189.2(20) [h]	149.8	145.3	2.74	NCH$_2$ 72.4; NMe$_2$ 45.4
	1d	−65	189.4(20) [h]	149.6	145.2		NCH$_2$ 72.0; NMe$_2$ 48.0, 43.4 [f]; TMEDA CH$_2$ 58.9, 57.0 [e]; NMe$_2$ 48.0, 46.8, 45.3 [e]
	2a	−60	185.9(20) [h]	156.3		2.45	NMe$_2$ 48.0
	2b	−20	175.9(12)	156.9		3.72	NMe$_2$ 51.7, 45.2
	3	−20	189.3(20.5) [h]	152.5	152.5	2.41	NCH$_2$ 73.0; NMe$_2$ 47.9, 43.9 [g]

[a] In toluene-d_8 relative to TMS internal. [b] Relative to 70% LiCl in D_2O. [c] $^1J(^7Li,^{13}C)$ in parentheses. [d] Coalescense at about 20°C. [e] Coalescence at about −35°C. [f] Coalescence at about −10°C. [g] Coalescence at about 0°C. [h] $^1J(^7Li,^{13}C)$ was not observed above 0°C.

Because in ^7Li NMR spectroscopy chemical shift differences are small and are greatly influenced by substituent effects [17] it is difficult to make structural conclusions based on the absolute chemical shift value. However when related clusters having the same substituents are studied (e.g. tetramer-dimer equilibria) conclusive results can be drawn from the relative chemical shift differences. For example on going from clusters in which the aryl group is four-centre, two-electron bonded to those in which the aryl group is three-centre, two-electron bonded, there is an upfield ^7Li shift of 0.5 to 1 ppm.

Experimental

The preparation of NMR solutions and details of NMR measurements are as described in a previous paper [12]. The organolithium compounds were prepared by published methods: 8-(dimethylamino)naphthyllithium etherate (2) [8], 2-[(dimethyl-

amino)methyl]phenyllithium **(1a)** [18] and 2,6-bis[(dimethylamino)methyl]phenyl-lithium **(3)** [7]. The 2-[(dimethylamino)methyl]-5-methylphenyllithium **(1b)** was prepared in the same way as **1a**.

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References

1 B.J. Wakefield, The Chemistry of Organolithium Compounds, Pergamon Press, Oxford, 1974.
2 (a) J.L. Wardell, in G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Vol. 1, p. 43; (b) W.N. Setzer and P.v.R. Schleyer, Adv. Organometallic Chemistry, 24 (1985) 39.
3 (a) H.W. Gschwend and H.R. Rodriguez, Org. React., 26 (1979) 1; (b) P. Beak and V. Snieckus, Acc. Chem. Res., 15 (1982) 306; (c) V. Snieckus, Heterocycles, 14 (1980) 1649; (d) G.W. Klumpp, Recl. Trav. Chim. Pay-Bas, 105 (1986) 1; (e) I. Omae, Chem. Rev., 79 (1979) 287; (f) N.S. Narasimkan and R.S. Mali, in Topics in Current Chemistry, Springer-Verlag, Berlin, 1987, Vol. 138, p. 63.
4 M. Al-Aseer, P. Beak, D. Hay, D.J. Kempf, S. Mills and S.G. Smith, J. Am. Chem. Soc., 105 (1983) 2080.
5 A.L. Spek, A.J.M. Duisenberg, G.W. Klumpp and P.J.A. Geurink, Acta Cryst., C40 (1984) 372.
6 K.S. Lee, P.G. Williard and J.W. Suggs, J. Organomet. Chem., 299 (1986) 311.
7 J.T.B.H. Jastrzebski, G. van Koten, M. Konijn and C.H. Stam, J. Am. Chem. Soc., 104 (1982) 5490.
8 J.T.B.H. Jastrzebski, G. van Koten, K. Goubitz, C. Arlen and M. Pfeffer, J. Organomet. Chem., 246 (1983) C75.
9 W.J.J. Smeets, A.L. Spek, A.A.H. van der Zeijden and G. van Koten, Acta Cryst., C43 (1987) 1429; Recl. Trav. Chim. Pays Bas, 107 (1988) 431.
10 H. Hope and P.P. Power, J. Am. Chem. Soc., 105 (1983) 5320.
11 M.A. Beno, H. Hope, M.M. Olmstead and P.P. Power, Organometallics, 4 (1985) 2117.
12 E. Wehman, J.T.B.H. Jastrzebski, J.M. Ernsting, D.M. Grove and G. van Koten, J. Organomet. Chem., 353 (1988) 133.
13 G. van Koten, J.T.B.H. Jastrzebski, C.H. Stam and C. Brevard, in K.D. Karlin, J. Zubieta (Eds.), Biological and Inorganic Copper Chemistry, Adenine Press, New York, 1985.
14 L.D. McKeever and R. Waack, J. Chem. Soc., Chem. Commun., (1969) 750.
15 D. Seebach, R. Hässig and J. Gabriel, Helv. Chim. Acta, 66 (1983) 308.
16 G. van Koten, J.T.B.H. Jastrzebski and J.G. Noltes, J. Organomet. Chem., 140 (1972) C23.
17 (a) J.A. Ladd and J. Parker, J. Organomet. Chem., 28 (1971) 1; (b) J.A. Ladd and J. Parker, J. Chem. Soc., Dalton Trans., (1972) 930; (c) P.A. Scherr, R.J. Hogan and J.P. Oliver, J. Am. Chem. Soc., 96 (1974) 6055.
18 F.N. Jones, M.F. Zinn and C.R. Hauser, J. Org. Chem., 28 (1963) 663.