

Structural studies of the chiral lithium amides [$\{\text{PhC(H)Me}\}_2\text{NLi}\}$ and $[\text{PhCH}_2\{\text{PhC(H)Me}\}\text{NLi}\cdot\text{THF}]$ derived from α -methylbenzylamine †

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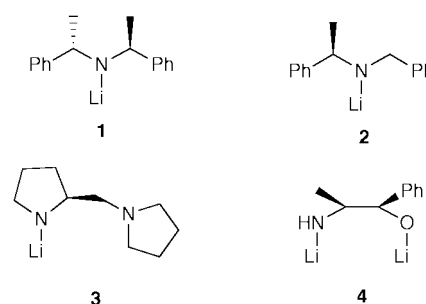
Received 14th June 1999, Accepted 5th October 1999

Reaction of (*R,R'*)- or (*S,S'*)-bis(1-phenylethyl)amine with ⁿBuLi in hexane solution gave the chiral amide [$\{\text{PhC(H)Me}\}_2\text{NLi}\}$ **1**. Complex **1** crystallises with approximate *D*₃ symmetry as a ring trimer (**1**₃) from hexane solution, as determined by X-ray crystallography. In direct contrast to the crystal structure of the related compound dibenzylamidolithium, [$\{\text{PhCH}_2\}_2\text{NLi}\}_3$], no significant agostic Li...C(H) contacts are present in **1**₃. Solution ¹H and ⁷Li NMR spectra of **1** in *d*₈-toluene show the presence of two distinct aggregated species which have been assigned as a trimer and a monomer. The complex $[\text{PhCH}_2\{\text{PhC(H)Me}\}\text{NLi}\cdot\text{THF}]$ **2**·THF, was prepared by reaction of ⁿBuLi with (*R*)-*N*-benzyl- α -methylbenzylamine in a hexane–THF solution and has been determined by X-ray crystallography to adopt a dimeric structure (**2**₂·2THF) in the solid state with *C*₁ symmetry. As in **1**₃, no short Li...C(H) contacts are present in **2**₂·2THF. The lack of Li...C(H) interactions in both **1**₃ and **2**₂·2THF suggests that the rotameric conformations adopted for the benzyl groups in the complexes are governed mainly by steric effects. Using *ab initio* molecular orbital calculations (HF/6-31G*), the minimum energy structure for unsolvated monomeric **1**₁ was determined to be a *C*₂ symmetric molecule, **I**, where the faces of both phenyl groups are directed towards the metal, maximising the Li–aromatic π interactions. The related *C*₂ symmetric molecule with both methyl groups directed towards the metal is 8.68 kcal mol⁻¹ less stable than **I**. Therefore, in the absence of aggregation and external solvation, significant stabilisation is achieved through Li...C(H) benzyl interactions. The energy barrier to rotation for one benzyl sidearm for geometry **I** is 4.76 kcal mol⁻¹, representing a significant lifetime for this conformer.

Introduction

Chiral lithium amides are finding growing use as powerful reagents in asymmetric synthesis. Their utility has been proven in numerous enantioselective reactions including deprotonations of cyclic ketones, rearrangement of epoxides to allylic alcohols and functionalisation of tricarbonyl(η^6 -arene)-chromium complexes.¹ Although a wide variety of chiral amines has been studied for use as bases, those derived from either α -methylbenzylamine or phenylglycine predominate. Some of the more successful amide bases known to date are shown below. This group illustrates some properties known to affect the utility of the bases: (i) the presence of *C*₂ symmetry, in **1**; (ii) the formation of internal chelates, in **3** and (iii) the possibility of dianion formation, in **4**.

Much of the attention surrounding these bases has concentrated on their functionalisation and the effects of steric or electronic changes on their selectivity. In comparison, little is known regarding their solution or solid-state structures.² The *C*₂ symmetric base **1**, in both its *R,R'* and *S,S'* forms, has received most attention as it has proved to be a highly selective asymmetric induction reagent. Additionally, it is easily prepared, and is also commercially available.³ Lithium-6 and ¹⁵N NMR spectroscopic investigations of solutions of **1** in



THF showed the presence of a dimer/monomer equilibrium.⁴ Supporting this assignment, base **1** crystallises as a disolvated dimer, **1**₂·2THF, from THF–hexane solution, as determined by X-ray crystallography.⁵ The growing database of structural information gathered on chiral lithium complexes such as **1** will be useful in determining the mechanism of their enantioselective reactions.² In turn, this should lead to a deeper understanding of the requirements necessary for the rational design of more highly selective reagents. We now report the solution and solid-state structures of **1** in the absence of a polar solvent. *Ab initio* molecular orbital calculations on the possible conformations of unsolvated, monomeric **1** have been performed. In addition, the crystal structure of the THF solvate of **2** has been determined and a discussion of the rotameric forms of the amides **1** and **2** is presented.

† Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/1999/4063/>

Results and discussion

X-Ray crystallography

Base **1** was successfully crystallised from hexane solution and single crystal X-ray analysis revealed a trimeric arrangement, **1₃**, in the solid state (Figs. 1 and 2). Table 1 lists some key bond lengths and angles. Both the *R,R'* and the *S,S'* enantiomers of **1₃** were independently analysed. Discussion of the structural features will be limited to the *S,S'* complex, since the geometrical parameters of the two compounds are effectively identical.

Trimeric aggregates have been found for several bulky secondary lithium amides.⁶ However, other aggregates such as ring tetramers, ladders, dimers and monomers are known for lithium amides and the structure adopted is dependent on the interplay between steric, solvation and electronic factors.^{7,8}

The closest analogue of compound **1₃** is dibenzylamido-lithium, [(PhCH₂)₂NLi] **5**, which also adopts trimeric aggregation, **5₃**, in the absence of a polar solvent (Figs. 3 and 4).^{6,9} A detailed study of the solution and solid-state structures of **5** was carried out as part of the early investigations of lithium amides, and led to the establishment of the ring-stacking, ring-laddering principles.¹⁰ Significant results arising from the study of **5** and its solvates included (i) the observation of a monomer/trimer equilibrium in arene solution, (ii) the evidence for intramolecular Li...C(H) interactions, (iii) the discovery of charge transfer in the unsolvated monomer resulting in pink/red solution colours and (iv) the formation of disolvated dimers in the presence of monodentate Lewis bases.¹¹

Comparison of compound **1₃** with **5₃** reveals some substantial structural differences. Most striking is the disparity in the conformations adopted by the benzyl sidearms. In **5₃** the benzyl groups are twisted towards the central ring to maximise the Li...C(H) interactions. Each lithium has four short methylene carbon contacts (average 2.81, shortest 2.69 Å), two short lithium to *ipso* carbon contacts (average 2.80, shortest 2.60 Å) and two short lithium to *ortho* carbon contacts (average 2.80, shortest 2.70 Å). The structure approximates to *C₂* symmetry and the benzyl groups adopt a propeller arrangement around the central ring, as can be clearly seen from Fig. 4. In contrast, **1₃** has non-crystallographic *D₃* symmetry with all the phenyl groups directed away from the central ring. The side view of **1₃**, shown in Fig. 2, clearly illustrates the approximately parallel phenyl groups above and below the plane of the trimeric ring. Both methyl groups of the ligand are directed towards the central ring. Similarly, the conformation of the sidearms in the dimeric THF solvate **1₂**·2THF also has the methyl groups directed towards the LiNLiN ring core. However, in **1₃** there is no significant bending of the methyl groups towards the coordinatively unsaturated lithium atoms (average for the four shortest distances is 3.19, shortest 2.99 Å). Each lithium has short contact distances to four methylene carbons (average 2.90, shortest 2.84 Å) which are a consequence of steric factors. Finally, relatively long lithium to phenyl contacts are found in **1₃** (the average of the two shortest Li...C(*ipso*) contacts for each lithium is 3.35, shortest 3.10 Å, and for the two shortest Li...C(*ortho*) contacts is 3.08, shortest 2.83 Å).¹² Overall, this implies a reduction in lithium's co-ordination environment compared to **5₃**. However, no significant change in the Li–N distances are found between **1₃** and **5₃** (average 1.977 and 1.953 Å respectively). Going from **1₃** to **5₃** the internal ring angles decrease at lithium (average 148.7 and 143.8° respectively) and increase at nitrogen (average 91.1 and 95.2° respectively). The more acute angles at nitrogen in **1₃** are a consequence of the increase in bulk of the ligand compared to that in **5₃**, and alleviate steric crowding between the amide groups.

Overall, on comparing the frameworks of compounds **1₃** and **5₃** it is found that replacement of a hydrogen for a methyl on each of the benzyl sidearms imparts significant conformational variation between the unsolvated trimers. To investigate the

Table 1 Key bond lengths (Å) and angles (°) for compound **1₃**

Li(1)–N(1)	2.014(7)	Li(3)–N(2)	1.969(8)
Li(2)–N(1)	1.964(7)	Li(1)–N(3)	1.990(7)
Li(2)–N(2)	1.953(7)	Li(3)–N(3)	1.973(8)
N(1)–Li(1)–N(3)	145.9(4)	C(17)–N(2)–C(25)	108.2(3)
N(1)–Li(2)–N(2)	151.5(4)	C(33)–N(3)–C(41)	108.3(8)
N(2)–Li(3)–N(3)	148.7(4)	Li(1)–N(1)–C(1)	111.6(3)
Li(1)–N(1)–Li(2)	90.7(3)	Li(1)–N(1)–C(9)	111.2(3)
Li(2)–N(2)–Li(3)	90.4(3)	Li(2)–N(1)–C(1)	118.4(3)
Li(1)–N(3)–Li(3)	92.2(3)	Li(2)–N(1)–C(9)	115.4(3)
C(1)–N(1)–C(9)	108.4(3)		

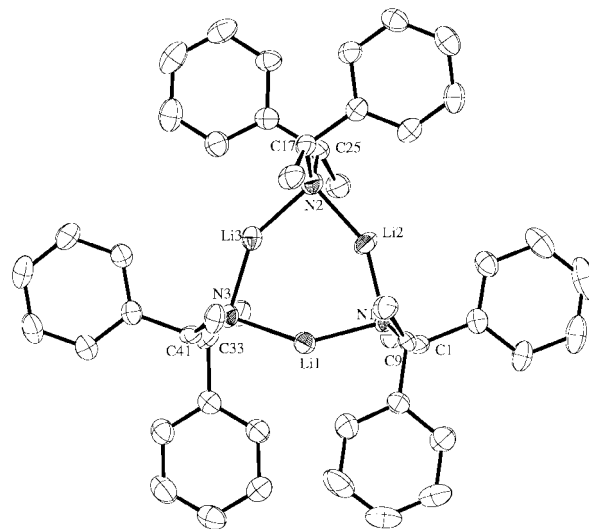


Fig. 1 Crystal structure of [(PhC(H)Me)₂NLi]₃ **1₃**.

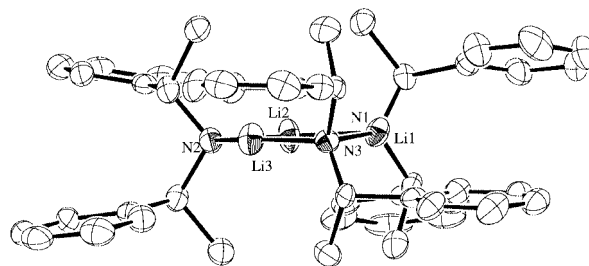


Fig. 2 Alternative view of compound **1₃**.

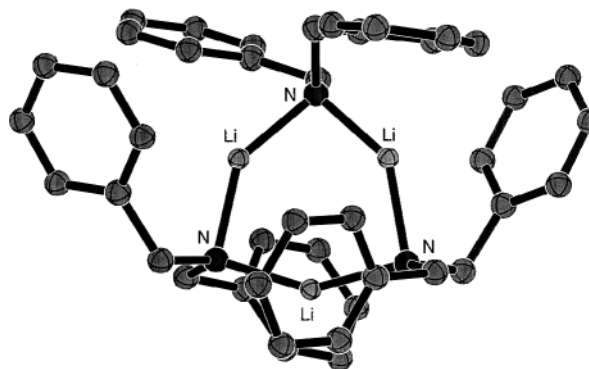
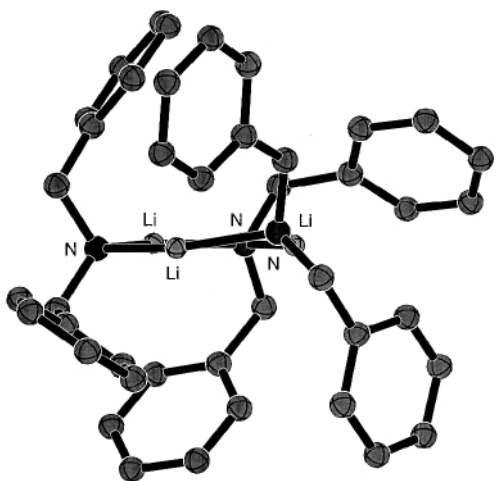
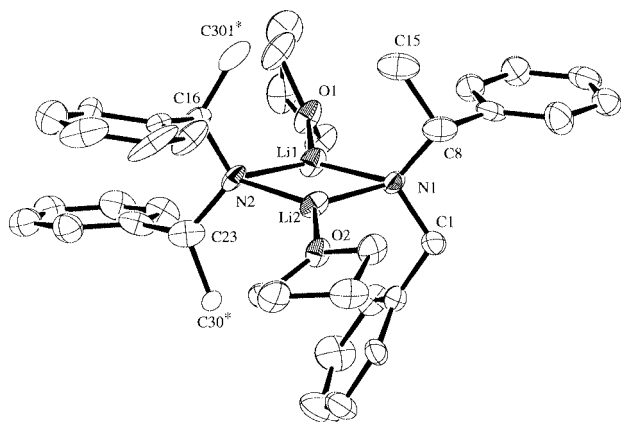


Fig. 3 Crystal structure of [(PhCH₂)₂NLi]₃ **5₃**.

effect of replacing a hydrogen for a methyl on a single benzyl sidearm the characterisation of compound **2** was targeted. Crystallisation of **2** from a hexane–THF solution resulted in the isolation of [(PhCH₂{PhC(H)Me}NLi·THF)₂] **2₂**·2THF, which adopts a disolvated dimer structure in the solid state (Fig. 5). Several interesting features are found in the structure

Table 2 Key bond lengths (Å) and angles (°) for compound **2**₂·2THF

Li(1)–O(1)	1.960(10)	Li(2)–N(1)	1.989(12)
Li(2)–O(2)	1.458(8)	Li(1)–N(2)	1.997(12)
Li(1)–N(1)	2.003(11)	Li(2)–N(2)	1.976(10)
O(1)–Li(1)–N(2)	124.0(5)	C(8)–N(1)–Li(2)	109.6(4)
O(1)–Li(1)–N(1)	128.6(6)	C(8)–N(1)–Li(1)	120.5(5)
N(1)–Li(1)–N(2)	106.0(5)	C(1)–N(1)–Li(1)	121.5(5)
O(2)–Li(2)–N(2)	127.8(6)	C(16)–N(2)–C(23)	110.7(5)
O(2)–Li(2)–N(1)	124.4(5)	C(16)–N(2)–Li(2)	119.1(5)
N(2)–Li(2)–N(1)	107.4(5)	C(23)–N(2)–Li(2)	113.5(5)
Li(1)–N(1)–Li(2)	73.0(4)	C(16)–N(2)–Li(1)	114.0(5)
Li(1)–N(2)–Li(2)	73.4(4)	C(23)–N(1)–Li(1)	122.1(5)
C(1)–N(1)–C(8)	107.7(5)		

**Fig. 4** Alternative view of compound **5**.**Fig. 5** Crystal structure of $[\{\text{PhCH}_2\{\text{PhC}(\text{H})\text{Me}\}\text{NLi}\cdot\text{THF}\}_2]_2\cdot 2\text{THF}$.

of **2**₂·2THF and a list of bond lengths and angles is given in Table 2.

The sidearms of amide N(1) direct the phenyl and methyl groups towards the central ring, whereas amide N(2) has both phenyl groups pointing away from the dimeric ring. The conformation adopted for amide N(1) is similar to that found for both the amido units in the dimeric THF solvate of dibenzylamidolithium $[\{\text{PhCH}_2\}_2\text{NLi}\cdot\text{THF}\}_2]_2\cdot 2\text{THF}$, which approximates to C_2 symmetry.¹¹ In **2**₂·2THF the arrangement of the benzyl groups around N(2) is dictated by *cisoid/transoid* disorder of the methyl group C(30) with respect to the opposite methyl group C(15). A 44:56 mixture of *cisoid* and *transoid* conformers was found on refinement of the structure. No similar movement of the attached phenyl groups to give the expected C_2 symmetric structure is evident.

All $\text{Li}\cdots\text{C}$ distances in compound **2**₂·2THF are >3 Å,

indicating no significant bonding interactions are present. These distances are similar to those found in **5**₂·2THF. However, short $\text{Li}\cdots\text{C}$ methyl contacts of 2.741(14) and 2.782(2) Å are found in **1**₂·2THF. These results suggest the lithium to methyl contact distances are governed by steric factors and not by significant agostic $\text{Li}\cdots\text{C}(\text{H})$ bonding.

Also of note in the structure of compound **2**₂·2THF is the mode of solvation by the two THF molecules. The LiNLiN atoms define a plane with a mean deviation of 0.035 Å and the oxygen atoms of each THF lie in a *transoid* orientation, with O(1) and O(2) lying out of the ring plane (by 5.9 and 9.9° respectively). Unusually, the two THF molecules adopt different rotations with respect to the dimeric ring. The planes defined by the C–O–C atoms of each THF bisect the $(\text{LiN})_2$ ring plane by 64.4 and 28.6° for the molecules associated with O(1) and O(2) respectively, *i.e.* approximating to orthogonal and ‘in-plane’ modes of solvation. In contrast, both **1**₂·2THF and **5**₂·2THF have only one orientation of THF which approaches ‘in-plane’ solvation.

Solution NMR spectroscopy

Using a combination of ^7Li NMR spectroscopy, cryoscopy and molecular orbital calculations it was shown previously that in arene solution compound **5** exists in a trimer/monomer equilibrium.^{9c} Cryoscopy proved to be of limited value in distinguishing between the possible solution equilibria. In large part, the differentiation between a trimer/monomer and a trimer/dimer mixture was made on the basis of molecular orbital bond index (MOBI) calculations.¹³ Computational studies suggested that the solution colour of **5** was associated with a monomer containing enhanced $\text{Li}\cdots\text{C}(\text{H})$ interactions.^{6c} We found that a solution of **1** in d_8 -toluene gives a ^1H NMR spectrum with two quartets in the benzylic region at δ 3.66 and 3.76. These signals represent two distinct aggregation states of **1**. Increasing the concentration of the NMR samples resulted in an increase in intensity of the signal at δ 3.76 and a concomitant decrease in that at δ 3.66. This is consistent with the lower frequency signal arising from the smaller aggregate.¹⁴ The ^7Li NMR spectroscopic studies of d_8 -toluene solutions of **1** also show two signals at δ –1.00 and 1.75. Such a large separation between the ^7Li signals suggests significantly different electronic environments for the metal centres of each aggregate. The presence of distinct ^1H and ^7Li signals at room temperature for **1** illustrates the slow exchange between the solution aggregates on the NMR timescale. Only the two original ^7Li signals were observed on cooling the sample in 20 °C increments to –80 °C. By analogy with the data collected on **5**, the most likely aggregates present for arene solutions of **1** are a trimer and a monomer. Indeed, the 2.75 ppm separation of the ^7Li signals would be expected between a monomer (formally one-co-ordinate Li) and a trimer (formally two-co-ordinate Li) and therefore the solution NMR data support a trimer/monomer equilibrium.

The distinctive pink/red colour observed for solutions of compound **5** is not found for **1**, where colourless solutions are obtained. Since the pink/red colour was attributed to monomeric **5**, the same colour may be expected for **1**, if a similar geometry is adopted for the two monomers. The difference in colour between the solutions of **1** and **5** may be due to a number of factors. More specifically, it is feasible that there is a larger separation between the HOMO (benzyl) and LUMO (Li) in **1**, compared to **5**, resulting in colourless solutions. Nevertheless, the possibility of a trimer/dimer equilibrium for solutions of **1** cannot be fully discounted.

Complex **2**₂·2THF dissolves as a red solution in d_6 -benzene and displays a simple ^1H NMR spectrum at room temperature. The surface of the isolated crystals show a slight red colouration but this is easily removed on successive washing with dry solvent. This suggests the colour is due to surface

contamination of the sample. Indeed, flash-freezing hexane solutions of **2**·2THF in liquid N₂ results in precipitation of the spectroscopically pure compound as a white powder.

Ab initio molecular orbital calculations

Structural information is now available, both in solution and in the solid state, for the unsolvated trimer and disolvated dimer of compound **1**. Molecular mechanics calculations have been shown to be ineffective for determining the relative stability of different conformers of dimer **1**.^{5,15} Accordingly, calculations using the HF/6-31G* level of theory have now been used to assign the minimum energy structures of monomeric **1** (in its *S,S'* enantiomeric form).^{16,17} The energy differences between the conformers are of importance when considering the mechanism of asymmetric reactions.^{1,2} Fig. 6 shows the six geometry-optimised conformations of **1**, **I–VI**, and also details their relative stabilities. All conformers optimised to geometries where either a carbon or a hydrogen β to the nitrogen lies approximately in the C–N–C plane.

The lowest energy geometry was found for conformation **I**, where both phenyl groups are orientated towards the metal. Rotating one phenyl group away from the metal and replacing it with a methyl unit, in **II**, results in a 2.10 kcal mol⁻¹ destabilisation. Further rotation to place a hydrogen beside the metal, in **III**, results in a 7.09 kcal mol⁻¹ destabilisation compared to **I**. Consistent with these observations is the finding that the highest energy structure is obtained when two hydrogen atoms are directed towards the metal, in **VI**. Similarly, a 14.3 kcal mol⁻¹ destabilisation (HF/6-31G*) is involved on rotating the phenyl rings away from the metal in lithium dibenzylamide.^{6c} These results suggest that the unsaturated metal centre is stabilised by both Li···Ph and Li···Me interactions but that the former are relatively much stronger. The face of the phenyl groups tilts towards the metal to maximise the Li–aromatic π interactions. Analysis of the N–Li bond distances shows only small differences between the structures (average distance 1.795, shortest 1.780, longest 1.803 Å). The Li–N–C angles vary depending on which group attached to the α -carbon is directed towards lithium. In the asymmetrical conformers **II**, **III** and **V** the smallest Li–N–C angle is on the side with the stronger interaction with the metal, where the interaction strength increases in the sequence H < Me < Ph. Contact distances between the metal and the adjacent groups are given in Table 3. Clearly, the shortest Li···C distances are associated with the phenyl rings. The shortest contact is 2.376 Å, which is found for the Li···C(*ipso*) bond in isomer **III**, where a phenyl group and a hydrogen are adjacent to the metal (Li···C(*ortho*) 2.493 Å). On bringing the second phenyl group into the proximity of the metal, the bonds lengthen substantially (2.784 *ipso* and 2.737 Å *ortho*). However, the extra Li···C contacts gained on moving from **III** to **I** have a collective stabilising effect.

To confirm that lithium has a critical role to play in determining the structures and relative stabilities of the conformers, calculations on the non-metallated anions **VII–IX** were performed using the geometries of **I–III** as starting points. Fig. 7 shows the structures obtained on minimisation. Clearly, the structures vary significantly from the metallated derivatives,

Table 3 Calculated short contact distances (Å) for lithium in monomeric compound **1**

Isomer	Li–C(<i>ipso</i>)	Li–C(<i>ortho</i>)	Li–C(Me)	Li–H
I	2.784 (×2)	2.737 (×2)	—	—
II	2.401	2.504	3.255	—
III	2.376	2.493	—	3.023
IV	—	—	2.921 (×2)	—
V	—	—	2.817	2.796
VI	—	—	—	2.654 (×2)

especially the orientation of the phenyl groups. Moreover, the lowest energy structure is **VIII**, which is related to **II**, and not **VII**, which is related to **I** (although the energy difference is less than 1 kcal mol⁻¹). This further verifies the strong polarising influence of lithium on the stability of monomeric **1**.

The energy barriers to rotation of a single benzyl sidearm about the C–N bond was determined by locating the transition-state structures **X–XII**, where the groups β to the nitrogen are

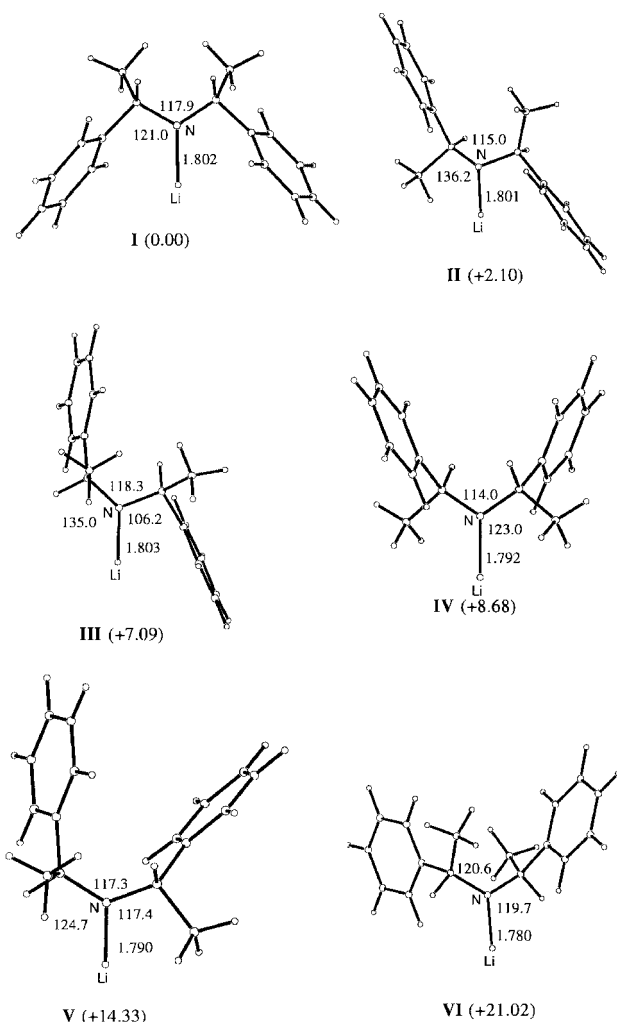


Fig. 6 Geometry-optimised structures of monomers of compound **1** with relative energies (kcal mol⁻¹) in parentheses.

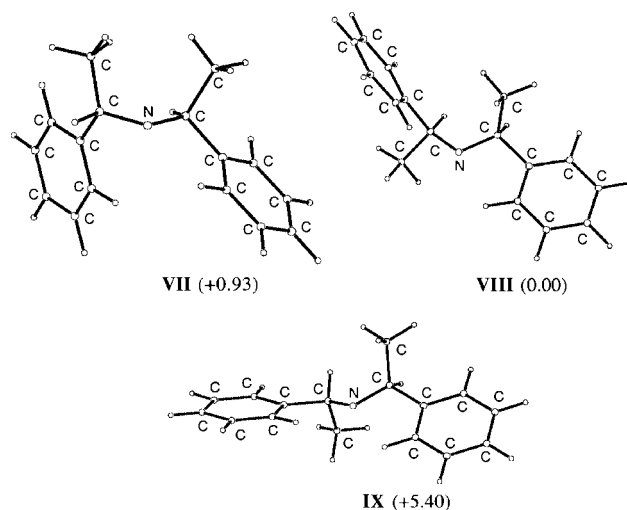


Fig. 7 Geometry-optimised structures of the anions **VII–IX** with relative energies (kcal mol⁻¹) in parentheses.

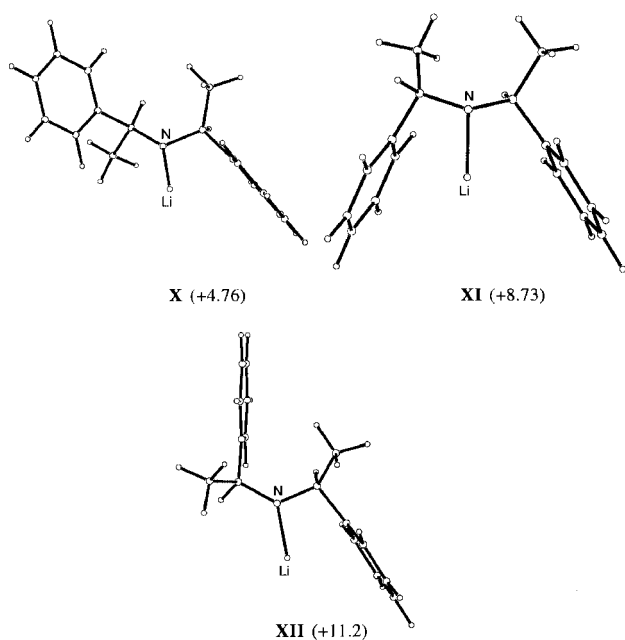


Fig. 8 Geometry-optimised structures of the transition states X–XII with relative energies to **I** given (kcal mol⁻¹) in parentheses.

no longer in the C–N–C plane (Fig. 8). The energy barriers are calculated to be as follows: **I** to **II** is 4.76, **I** to **III** is 8.73, and **II** to **III** is 4.17 kcal mol⁻¹. These figures represent a significant energy barrier to rotation between the possible conformers.

Conclusion

Compound **1** crystallises as an unsolvated trimer from hydrocarbon solution and, in contrast to the previously characterised related compound **5**, no significant Li⋯C(H) interactions are present within the molecule. Hence, the substitution of a hydrogen for a methyl on each benzyl arm is responsible for the significant change in conformation between **1**₃ and **5**₃. The structure adopted for **1**₃, with the methyl groups directed towards the central ring, minimises the intra- and inter-ligand contacts. Any stabilisation gained by possible Li⋯C(H) contacts in the trimer must therefore be less than the destabilisation caused by ligand–ligand repulsions.

The crystal structure of compound **2**₂·2THF demonstrates the shallow energy surface separating the different rotameric forms of the disolvated dimer for the amide **2**. Additionally, the two different solvation modes of the THF molecules represent alternative possible pre-enolisation geometries for the initial co-ordination by a reactive molecule.¹⁸ Either factor or a combination of both may explain the generally poorer enantioselectivity displayed by **2** compared to **1**.

In arene solution compound **1** exists in at least two distinct aggregation states. By analogy with studies on **5** a trimer/monomer mixture is predicted.⁹ The NMR spectroscopic data collected are consistent with this hypothesis. Indeed, monomer is known to be present as the minor component in THF solution. However, the solvation environment surrounding the metal in THF solution has not yet been determined. *Ab initio* molecular orbital calculations on unsolvated monomeric **1** indicate that the C₂ symmetric molecule **I**, with both phenyl groups directed towards the metal, is the global energy minimum geometry. Hence, in the absence of steric influences caused by aggregation or solvation, significant stabilisation is achieved through Li⋯C(H) contacts in monomeric **1**. This assessment is supported by calculations on the non-metallated anions of **1**, **VII–IX**, which illustrate the conformational control exerted by the lithium in conformers **I–III**. The 4.76 kcal mol⁻¹ rotation barrier between **I** and **II** also confirms that the

C₂ symmetric geometry **I** is likely involved as a reactive species during enantioselective reactions of base **1**.

Experimental

General preparative techniques

All experimental manipulations were performed under an argon atmosphere using standard Schlenk techniques or in an argon filled glove-box.¹⁹ All solvents were distilled from sodium–benzophenone and used directly from the still. The amines (*R,R'*)- and (*S,S'*)-bis(1-phenylethyl)amine were purchased from Oxford Asymmetry as the hydrochloride salt, and (*R*)-*N*-benzyl- α -methylbenzylamine was purchased from Aldrich Chemical Co. The free amines were dried by distillation from calcium hydride, followed by storage over 4A molecular sieves. *n*-Butyllithium was used as received from Aldrich as a 1.6 M solution in hexane. The NMR spectroscopic data were obtained on a Bruker AMX 400 spectrometer, at 298 K unless otherwise stated. Elemental analyses were carried out on a Perkin-Elmer 240 elemental analyser.

Preparations and characterisations

Compound 1₃. Either *R,R'*- or *S,S'*-bis(1-phenylethyl)amine (0.45 g, 2 mmol) was dissolved in 5 mL of dry hexane and the solution cooled to 0 °C. *n*-Butyllithium (1.25 mL of a 1.6 M solution in hexane, 2 mmol) was added dropwise over two minutes. A white solid was precipitated on allowing the reaction mixture to warm to room temperature over one hour with continuous stirring. The solid was dissolved on mild heating and single crystals of **1**₃ were grown at room temperature over twelve hours; yield 82%, mp 162–164 °C (Found: C, 83.1; H, 8.3; N, 5.7. Requires C, 83.1; H, 7.8; N, 6.1%). ¹H NMR (+25 °C, 400 MHz, internally referenced to C₇D₈): δ 1.04, d, ³J 6.2, CH₃; 1.28, d, ³J 6.8, CH₃; 3.66, q, ³J 6.2, CH; 3.76, q, ³J 6.8 Hz, CH; 7.05–7.28, overlapping multiplet, *o*-, *m*-, *p*-H of Ph: ⁷Li NMR (155.37 MHz, externally referenced to ⁷LiCl in D₂O, C₇D₈): δ -1.00 and 1.75. A ⁷Li NMR spectroscopic variable-temperature study (between +27 and -80 °C) on a C₇D₈ solution of **1** showed no further splitting of the two signals observed at room temperature.

Complex 2₂·THF. (*R*)-*N*-Benzyl- α -methylbenzylamine (0.84 mL, 4 mmol) and THF (0.32 mL, 4 mmol) were dissolved in dry hexane (5 mL) and the solution cooled to 0 °C. *n*-Butyllithium (2.5 mL of a 1.6 M solution in hexane, 4 mmol) was added dropwise over five minutes. The solution was left to react for one hour at 0 °C and then allowed to warm to room temperature. Crystals of **2**₂·2THF were deposited on cooling overnight at -20 °C; yield 43%, mp 83–86 °C (Found: C, 77.6; H, 8.1; N, 4.8. Requires C, 78.9; H, 8.3; N, 4.8%). ¹H NMR (+25 °C, 400 MHz, internally referenced to C₆D₆): δ 1.23, m, CH₂CH₂O; 1.34, d, ³J 6.6, CH₃; 3.26, m, OCH₂; 3.73, d, ²J 12.5, NCH₂; 3.82, d, ²J 12.5, NCH₂; 3.92, q, ³J 6.6 Hz, NCH; 7.02–7.35, overlapping multiplet, *o*-, *m*-, *p*-H of Ph.

X-Ray crystallography

Crystals of compounds **1**₃ and **2**₂·2THF were taken directly from the crystallisation vessel and mounted using a protective oil blanket.²⁰

Crystal data for compound 1₃. C₄₈H₅₄Li₃N₃, *M* = 693.80, -150 °C, orthorhombic, space group *P*2₁2₁2₁, *V* = 4087(2) Å³, *Z* = 4, *D*_c = 1.127 Mg m⁻³, 2 θ _{max} = 50°, 8102 reflections collected, 7209 unique reflections, *R*_{int} = 0.025, full-matrix least-squares refinement on *F* using 487 parameters and 5570 observed reflections with *I* > 2 σ (*I*) converged to *R* = 0.070, *R'* = 0.075 and *S* = 1.91.

Crystal data for compound 2₂·2THF. C₃₈H₄₈Li₂N₂O₂, *M* = 578.66, −150 °C, orthorhombic, space group *P*2₁2₁2₁, *V* = 3413.7(14) Å³, *Z* = 4, *D*_c = 1.126 Mg m^{−3}, 2θ_{max} = 46°, 5598 reflections collected, 4745 unique reflections, *R*_{int} = 0.0519, full-matrix least-squares refinement on *F*² using 411 parameters and all 4745 reflections converged to *R* = 0.065, *R*' = 0.214 and *S* = 1.045.

Neither structure could be assigned its absolute configuration from the X-ray data alone, so those given are based on the starting materials.

CCDC reference number 186/1674.

See <http://www.rsc.org/suppdata/dt/1999/4063/> for crystallographic files in .cif format.

Computational details

The GAUSSIAN 94 program (revision E.2) run on a Silicon Graphics Origin 200 workstation, was used for the calculations.¹⁶ No symmetry constraints were imposed and all molecules were allowed freely to optimise. All calculations used the general basis set 6-31G*, which is known to be accurate for modelling lithium-based organometallics.^{17,21,22} Frequency analysis was used to confirm that the three lowest energy monomers **I–III** and the transition states **X–XII** were true minima and transition states respectively. Absolute energy values for the calculated molecules are as follows (hartrees): **I** −678.27392, **II** −678.27058, **III** −678.26267, **IV** −678.26008, **V** −678.25108, **VI** −678.24042, **VII** −670.75692, **VIII** −670.75840, **IX** −670.74980, **X** −678.26639, **XI** −678.26006 and **XII** −678.25603.

Acknowledgements

We gratefully acknowledge the EPSRC for a grant (GR/M12711), The Carnegie Trust for the Universities of Scotland for a postgraduate studentship (to J. H. M.) and The Royal Society for a University Research Fellowship (to K. W. H.).

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Paper 9/04725E