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Solid state structures of the chiral lithium amide complexes (*S*)-[(Ph(Me)CH)(PhCH$_2$)NLi·thf]$_2$ and (*R*)-[(Ph(Me)CH)-(PhCH$_2$)NLi·pmdta]†

Philip C. Andrews,*[a] Peter J. Duggan,[a] Gary D. Fallon,[a] Tom D. McCarthy[b] and Anna C. Peatt[a]

[a] *Department of Chemistry, Monash University, Melbourne, Vic. 3800, Australia*
[b] *Biomolecular Research Institute, Private Bag 10, Melbourne, Vic. 3169, Australia*

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Two chiral lithium amide complexes derived from α-(methylbenzyl)benzylamine have been synthesised and structurally characterised in the solid state by X-ray crystallography. Complexation of (*S*)-{[Ph(Me)CH]-[PhCH$_2$]NLi}$_n$ with thf results in the dimer (*S*)-{[Ph(Me)CH][PhCH$_2$]NLi·thf}$_2$ (space group $P4_32_12$). The dimer is composed of a central four membered (NLi)$_2$ ring with the Ph(Me)C and Ph(CH$_2$) moieties adopting a *cis* orientation relative to the ring rather than the more usual *trans*. The reaction of (*R*)-{[Ph(Me)CH][PhCH$_2$]NLi}$_n$ with the tridentate N donor, pmdta, (*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine) results in the monomer (*R*)-{[Ph(Me)CH][PhCH$_2$]NLi·pmdta} (space group, $P2_1$). In both structures the amido moiety adopts a similar 'butterfly-in-flight' conformation. Heating either the solution or crystals of the monomer results in the loss of H$_2$ at the benzylic carbons and conversion to an aza-allyl structure, as evidenced by NMR.

Introduction

There have been extensive investigations into the solid and solution state structures of Group 1 amides, [RR′NM·(L)$_k$]$_n$, and a rationale for the variety of structures they adopt has been developed.[1]

The underlying principles which inform this rationale, and the implications they have for our understanding of the reactivity and selectivity of lithium complexes in synthetic processes, has come under intense scrutiny in the last few years. In particular, Collum, Williard and co-workers, through detailed studies of several lithium complexes in the presence of a plethora of solvents and Lewis bases, have highlighted the importance of examining the often complicated variety of aggregations states which can co-exist in solution, and of rejecting the traditional assumption that the most reactive species will always be that with the lowest aggregation state, *i.e.* the monomer.[2,3] Indeed, in general the reactive lithium species is most likely to be a dimer, either open or cyclic.

The development of the ring 'laddering' and 'stacking' principles underlines the fact that knowledge and understanding of the solid state structures can be an extremely useful starting point and guide for understanding the reactivity and, perhaps more importantly, the selectivity of lithium complexes.[1]

Most studies on the structures of lithium amides have centered on achiral secondary amines. It is surprising, given their synthetic utility, that still very few enantiomerically pure chiral lithium amides have been examined in the solid state. Such complexes are extremely useful reagents in asymmetric synthesis: in enantioselective deprotonation of prochiral ketones and epoxides, and in Michael addition type reactions.[4] Chiral complexes characterised by single crystal X-ray diffraction include (*R*,*R*)-{[Ph(MeOCH$_2$)CH]$_2$NLi}$_2$,[5] bis-(*R*)-*N*-[neopentyl-1-phenyl-2-piperidinoethylamidolithium]$_2$,[6] (*R*,*R*)-{[Ph(Me)CH]$_2$NLi·thf}$_2$,[7] **1**, and (*R*,*S*)-[{[Ph(Me)CH]-[Ph(MeOCH$_2$)CH]}NLi·(thf)$_{0.5}$]$_2$.[8] Despite the rigorous detailed synthetic investigations[9] one aspect of the chemistry of chiral lithium amide complexes which still remains unclear is the role various Lewis base donor solvents, such as thf and hmpa [(Me$_2$N)$_3$PO], the use of internal donating sites (O, N), and the presence of achiral lithium salts,[10] have on increasing observed ee values.

The chiral lithium amides, derived from the chiral amine α-(methylbenzyl)benzylamine, (*R*)- and (*S*)-{[Ph(Me)CH][Ph-CH$_2$]NLi·(L)$_k$}$_n$, have been shown by Davies and co-workers[11] to be highly selective in the synthesis of β-amino esters *via* conjugate addition reactions to α,β-unsaturated esters. Recently we have become interested in the application of this lithium amide in the synthesis of β-amino acid enzyme inhibitors,[12] and as part of our studies we decided to determine the solid state structures of several of the lithium complexes. As such we have obtained single crystals suitable for X-ray diffraction studies from the reactions of (*S*)- and (*R*)-{[Ph(Me)CH][PhCH$_2$]NLi}$_n$ with the Lewis donors thf and pmdta (pmdta = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine) respectively. Herein we present the solid state structures of two complexes; (*S*)-[(Ph(Me)-CH)(PhCH$_2$)NLi·thf]$_2$, **2**, and (*R*)-[(Ph(Me)CH)(PhCH$_2$)NLi·pmdta], **3**.

Results and discussion

In general, reactions of α,β-unsaturated esters with lithium amides are conducted in ethereal solvents at low temperature, and therefore our first targets were the Et$_2$O and thf solvates. The simple reactions involved the equimolar addition of thf or Et$_2$O to a hexane solution of (*S*)-{[Ph(Me)CH][PhCH$_2$]NLi}$_n$, formed from the reaction of (*S*)-(Ph(Me)CH)(PhCH$_2$)NH with ^{n}BuLi in hexane. Given the facile synthesis and crystallisation of many lithiated secondary amines we were surprised at how difficult it was to obtain a crystalline product of quality suitable for X-ray diffraction studies. In fact, the reaction with Et$_2$O gave no solid product above freezer temperature (*ca.* −25 °C) and we were only able to grow crystals of the thf adduct, **2**, with

† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagrams of complexes **2** and **3** in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b000747l/

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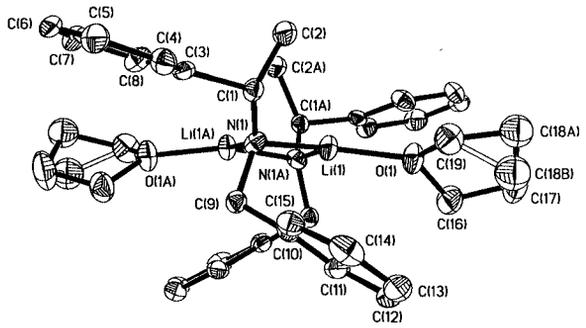

Fig. 1 Molecular structure of complex **2** with all H atoms removed for clarity.

Table 1 Selected bond distances (Å) and angles (°) for **2**

Li1–N1	1.991(4)
Li1–N1A	1.970(4)
Li1–O1	1.905(4)
N1A–Li1–N1	106.11(17)
Li1–N1–LiA	73.68(17)
C1–N1–Li1	116.01(17)
C1–N1–C9	110.47(17)

some difficulty. It is therefore the synthesis and characterisation of **2** which we now describe.

The reaction mixture, which is a bright red coloured solution, would only produce a crystalline product if it was first stored over solid CO_2 overnight, causing precipitation of the amide complex. The pale pink solid thus produced can be redissolved with gentle warming and crystals reformed at 4 °C. However this procedure gave mixed results and a freezer temperature of −25 °C was often used, though with reduced crystal quality as a result. We did not obtain any solid product when the solution was stored at 4 or −25 °C without prior precipitation. Also, excess thf made crystallisation more difficult. Once prepared, the crystals are fairly robust in hexane solution and have a melting point of 83–84 °C.

The crystals are colourless, though the bulk sample appears pink, and crystallise in the tetragonal space group $P4_32_12$ with eight molecules in the unit cell. As can be seen in Fig. 1 the structure is dimeric, adopting a common planar four membered Li_2N_2 ring arrangement. All of the complexes listed above, particularly (*R*,*R*)-{[Ph(Me)CH]$_2$NLi·thf}$_2$, as well as the analogous dibenzylamido complexes, [(PhCH$_2$)$_2$NLi·(L′)]$_2$ (L′ = thf,[13] Et$_2$O,[14] hmpa [14]), adopt this dimeric structural motif. Interestingly, rather than adopting the common *trans* configuration for R and R′, the Ph(Me)CH groups in **2** are *cis* to the $(NLi)_2$ ring. A similar unusual *cisoid* geometry has been described for the sodium amide, [(PhCH$_2$)(Me)NNa·tmeda]$_2$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), though in this complex the four membered N_2Na_2 ring buckles into a butterfly configuration.[15]

The bond lengths and angles around the Li centre are not unusual and are within those reported for this class of complex. In **2**, Li–O1, Li–N1 and Li–N1A are 1.905(4), 1.991(4) and 1.970(4) Å respectively (Table 1), which are slightly shorter than those found in **1** (1.984(12), 2.073(13), 1.992(14) Å) and in [(PhCH$_2$)$_2$NLi·thf]$_2$ (1.915(3), 2.028(3), 2.058(3) Å).[12] Close Li–CH_3 bond distances are reported for **1** implicating them in the selective action of the complex, however, these distances are significantly longer in **2**; Li1 · · · C2 3.02, Li1 · · · C2A 3.53 Å as opposed to the two shortest distances in **1** of 2.741(14) and 2.78(2) Å.[7] The N centres in the amido anion in **2** adopt an almost ideal tetrahedral geometry with the C–N–C angles being 110.47(17)°. The Li–N–Li angles in **2**, 73.68(17)°, are midway between the values reported for **1**, av. 72.5(5)°, and for [(PhCH$_2$)$_2$NLi·thf]$_2$, 76.7(1)°, while not unexpectedly the situation is reversed for the N–Li–N angles; 103.0(1)° in [(PhCH$_2$)$_2$NLi·thf]$_2$, 106.11(17)° in **2**, and av. 107.6(6)° in **1**. Therefore, as Me groups are added at the benzylic carbons there is a concomitant increase in the N–Li–N bond angles, presumably as a result of steric effects.

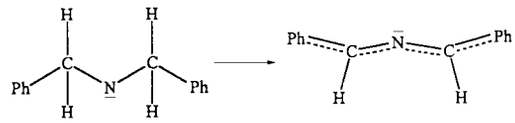

Fig. 2 Aza-allylic anion derived from Group 1 dibenzylamido complexes.[8]

An alternative solid state structure of [(Ph(Me)CH)(PhCH$_2$)NLi·thf]$_2$ was very recently published [16] and makes the solid and solution state investigation of these chiral lithium amides even more intriguing. The structure is again dimeric, however, the complex crystallises in the orthorhombic space group $P2_12_12_1$ and the dimer is not symmetry generated but composed of two different amido moieties. One of the amido moieties adopts the same orientation as that found in **2** while the other adopts the 'butterfly landing conformation' which has close parallel phenyl groups. Clearly the energy difference in the two structures must be small but the fact that the complex can crystallise from solution in the two forms has major mechanistic implications.

The ^{1}H and ^{13}C NMR of **2** in d_6-benzene gave the expected signals, splitting patterns and chemical shifts, and as with the other dimeric solid state structures listed in the introduction there was no evidence that there was any change in the structure in solution.

The reaction of [(Ph(Me)CH)(PhCH$_2$)NLi] with pmdta was of interest to us for several reasons. Firstly, recent models for the transition states for lithium amides in their reaction with organic substrates involve the reactive complex in a dimeric rather than in the monomeric state as previous, more simplistic models had suggested.[17] In fact, within the dimeric model itself there appears to be a structural preference for an open rather than a cyclic configuration, as described for **2** above. We were interested to examine whether there was any variation in the structural arrangement of the Ph(Me)CH and PhCH$_2$ groups in the monomer in comparison with the dimer. Secondly, no monomeric structures have been identified in the analogous work with dibenzylamine, with complexation and deaggregation of [(PhCH$_2$)$_2$NLi]$_n$ with pmdta being implicated in its facile low temperature transition to an aza-allylic structure, Fig. 2.[13]

Addition of one equivalent of pmdta to the pink hexane solution of (*R*)-{[Ph(Me)CH][PhCH$_2$]NLi}$_n$ turns the solution deep red and a precipitate appears after several minutes. This can be redissolved on addition of a small amount of toluene with gentle warming. Slow cooling to room temperature results in a large initial crop (yield 64%) of prismatic pale orange crystals of **3** (space group $P2_1$ (#4)). The crystals melt at 77–78 °C to a red/green dichroic melt, the first indications that a structural change to an aza-allyl structure *via* benzylic H_2 elimination is thermally promoted. The crystal structure is shown in Fig. 3 and reveals that in the solid-state at least the complex is indeed monomeric, as was anticipated. With respect to the N–Li bond the orientation of the Ph(Me)CH and PhCH$_2$ groups is similar to that found in the dimer, **2**, with the exception that in **3** one of the phenyl rings is tilted such that they are set almost perpendicular to one another. Both structures appear to confirm the 'butterfly-in flight' configuration which has been calculated for the amido group on its approach, at 4.5 Å, to the olefin in *tert*-butyl cinnamate.[18]

The short Li1–N1 bond distance of 1.959(7) Å (Table 2) and the three longer bonds to pmdta of 2.143(8), 2.181(8) and 2.231(7) Å are all typical for a four coordinate (distorted) tetrahedral Li cation. (*cf.* [(Me$_3$Si)$_2$NLi·pmdta],[19] 1.988(6), 2.164(6),

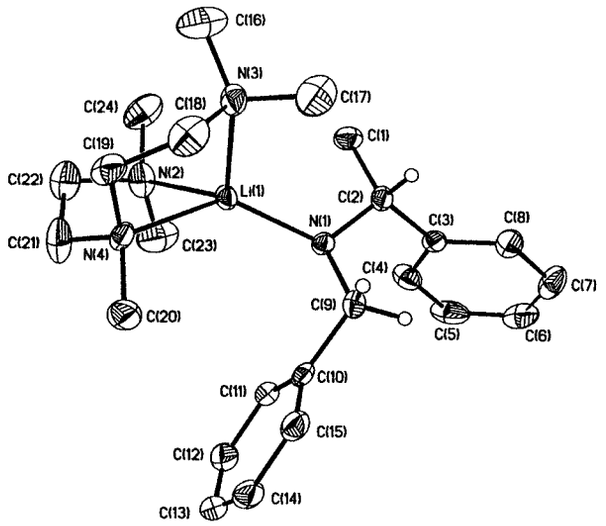

Fig. 3 Molecular structure of complex **3** with all H atoms removed except those on the benzylic carbons.

Table 2 Selected bond distances (Å) and angles (°) for **3**

Li1–N1	1.959(7)
Li1–N2	2.143(8)
Li1–N3	2.181(8)
Li1–N4	2.231(7)
C2–N1–Li1	120.0(3)
C9–N1–Li1	118.3(3)
N1–Li1–N2	123.4(4)
N1–Li1–N3	113.1(3)
N1–Li1–N4	132.5(4)
C2–N1–C9	110.4(3)
C1–C2–N1	109.7(3)

2.229(6) and 2.265(6) Å and [Ph($C_{10}H_7$)NLi·pmdta],[20] 2.00(1), 2.18(1), 2.21(1), 2.22(1) Å). The amido C–N–C angle of 110.4(3)° and the Li–CH_3 distance of 3.09 Å are comparable to that found in **2** indicating that the basic structure adopted by the amido moiety is independent of its aggregation state, whether monomer or dimer.

The crystals of **3** are stable at refrigeration temperature, 4 °C, under an argon atmosphere over long periods. However, we noted that when the crystals were stored for several weeks at room temperature (*ca*. 22 °C), they slowly changed to a red oil from which small dichroic crystals would grow. This process is hastened by deliberately heating the crystals in a water bath to 60 °C. ^{1}H and ^{13}C NMR studies in d_6-benzene show clearly that the transformation of **3** to the aza-allyl complex, {[Ph(Me)-CNC(H)Ph]Li·pmdta}, is facile at raised temperatures; the CH_2, δ 4.39, and (Me)CH, δ 4.42, signals disappear with the appearance of a CH singlet at δ 7.00. This is significant since with dibenzylamine the analogous aza-allyl complex is isolated exclusively from the reaction mixture.[13] If, in the initial reaction mixture of the lithium amide and pmdta, the hexane/toluene solution is overheated the yield of crystals of **3** becomes dramatically reduced. Unfortunately, to-date we have been unable to isolate crystals of the aza-allyl complex suitable for X-ray studies. However, the analogous reaction with Na in place of Li produces the aza-allyl complex at low temperature. This complex has been isolated as red/green dichroic needles and the X-ray structure obtained.[21] The NMR spectra obtained on forcing the transformation of **3**, either in solution or from the dichroic oil obtained on heating isolated crystals, are not particularly clear. The phenyl region is largely broad and comprised of overlapping signals, which may be a result of a mixture of products. The analogous reaction with Na showed that MeH as well as H_2 elimination is possible and this may be one explanation for the lack of clarity. In addition, an extensive NMR study of the dibenzylamido complexes showed that while sodium will give exclusively the *trans*,*trans* isomer, for lithium two isomers are formed in solution resulting in a cluster of signals in the phenyl region.

While we have focused the discussion above on the *R* isomer of the amine it should be noted that the analogous reaction of (*S*)-{[Ph(Me)CH][$PhCH_2$]NLi}$_n$ with pmdta, not unexpectedly, produces similar crystals, though we have yet to obtain the solid state structure, and exhibits identical solid and solution state behaviour.

Implicated in the aza-allyl transformation in dibenzylamido complexes is the requirement for a monomeric solution state and the close proximity of the metal to the benzylic protons such that the four membered planar transition state required for β-H elimination can be achieved. However, as can be seen, the available protons in **3** clearly point away from the Li centre, so while undoubtedly there will be rotation around the C–N bonds, this perhaps suggests why the aza-allyl transformation has to be thermally induced.

Experimental

All compound manipulations were carried out under strict inert atmosphere and dry conditions using a vacuum/argon line, Schlenk techniques and a high purity argon gas recirculating dry box. Prior to use, solvents were dried by reflux over Na/K alloy and stored over molecular sieves 4 Å. (*S*)- and (*R*)-α-(methylbenzyl)benzylamine and pmdta were purchased from Aldrich. They were dried over CaH_2 and distilled before use. ^{n}BuLi was purchased from Merck-Schuchardt and was standardised using 1,10-phenanthroline and dried ^{s}BuOH. NMR spectra were obtained on Bruker DRX-400 or AM-300 spectrometers with chemical shifts referenced to the C_6D_6 solvent. Elemental analyses were carried out in the Department of Chemistry, University of Otago, New Zealand. X-Ray crystallography was carried out on an Enraf-Nonius, Kappa CCD, with the crystals mounted under oil and data collected at −150 °C.

Synthesis and characterisation of (*S*)-[(Ph(Me)CH)($PhCH_2$)-NLi·thf]$_2$, 2

The addition of a hexane solution of ^{n}BuLi (10 mmol, 6.5 ml, 1.5 M) to a hexane solution (15 ml) of (*S*)-(Ph(Me)CH)-($PhCH_2$)NH (10 mmol, 2.10 g) at 0 °C resulted in a pale pink solution. One equivalent of thf (10 mmol, 0.80 ml) was added and the pink solution stored over dry ice overnight. The pale pink solid which was formed was redissolved by gentle heating and the solution stored at 4 °C. The solution afforded a moderate yield of large colourless crystals. Yield 1.65 g, 57% (not maximised), mp 83–84 °C. ^{1}H NMR (400 MHz, 25 °C, C_6D_6) δ 7.35 (m, 4H, *o*-CH), 7.21 (m, 4H, *m*-CH), 7.08 (m, 2H, *p*-CH), 3.95 (q, 1H, CH), 3.80 (AB-q, 4H, CH_2), 3.22 (m, 4H, thf), 1.37 (d, 3H, Me), 1.24 (m, 4H, thf). ^{13}C NMR (75.1 MHz, 25 °C, d_6-benzene) δ 152.9 (*ipso*-C), 148.0 (*ipso*-C), 129.1 (CH), 128.5 (CH), 128.2 (CH), 128.0 (CH), 125.5 (CH), 125.3 (CH), 68.5 (thf), 62.3 (CH), 58.3 (CH_2), 26.9 (Me), 25.4 (thf). Elemental analysis; obtained (calc), C 79.4 (78.8), H 8.9 (9.3), N 4.6 (4.8)%.

Crystallographic data. $C_{19}H_{24}NOLi$, $M = 289.35$, $T = 123$ K, tetragonal $P4_32_12$ (no. 96) $a = b = 11.5270(2)$, $c = 25.4810(5)$ Å, $V = 3385.70(9)$ Å^3, $D_c = 1.135$ g cm^{-3}, $Z = 8$; $F(000) = 1248$, $\mu_{MoK\alpha} = 0.68$ cm^{-1}, $2\theta_{max} = 55.8°$, final R, $R_w = 0.068$, 0.118. $N_o = 3102$ 'observed' ($I > 2\sigma(I)$) reflections out of $N = 4039$ unique. GOF 1.08. C18 on thf disordered with site occupancy of 0.7 : 0.3.

Synthesis and characterisation of (*R*)- [(Ph(Me)CH)($PhCH_2$)-NLi·pmdta], 3

The addition of a hexane solution of ^{n}BuLi (10 mmol, 6.5 ml, 1.5 M) to a hexane solution (15 ml) of (*R*)-(Ph(Me)CH)-

($PhCH_2$)NH (10 mmol, 2.10 g) at 0 °C resulted in a pale pink solution. Addition of one equivalent of pmdta (10 mmol, 2.08 ml) caused the solution to become dark red with the formation of a yellow precipitate after several minutes. The hexane was removed *in vacuo* and toluene (10 ml) added. The solution was allowed to stand at ambient temperature overnight producing a large crop of pale orange prismatic crystals. Yield 2.49 g, 64% (not maximised), mp 77–78 °C. ^{1}H NMR (300 MHz, 25 °C, d_6-benzene) δ 7.76 (m, 4H, *o*-CH), 7.39 (m, 4H, *m*-CH), 7.19 (m, 2H, *p*-CH), 4.42 (q, 1H, CH), 4.39 (m, 2H, CH_2), 1.89 (s, 12H, NMe_2), 1.70 (d of m, 8H, NCH_2), 1.58 (s, 3H, NMe). ^{13}C NMR (75.1 MHz, 25 °C, d_6-benzene) δ 157.3 (q-C), 156.2 (q-C), 129.1, 128.6, 128.3, 127.9, 125.1, 65.7 (CH), 62.3 (CH_2), 61.6 (NCH_2), 57.8 (NCH_2), 46.3 (NMe), 43.3 (NMe), 28.6 (CH_3). Satisfactory elemental analysis was not obtained, most likely as a result of compound decomposition.

Crystallographic data. $C_{24}H_{39}N_4Li$, $M = 390.54$, $T = 123$ K, monoclinic $P2_1$ (no. 4), $a = 9.0295(2)$, $b = 12.6622(4)$, $c = 10.5340(3)$ Å, $\beta = 96.161(2)°$, $V = 1197.43(5)$ Å^3, $D_c = 1.083$ g cm^{-3}, $Z = 2$; $F(000) = 428$, $\mu_{MoK\alpha} = 0.64$ cm^{-1}, $2\theta_{max} = 55.8°$, final R, $R_w = 0.078$, 0.173. $N_o = 2470$ 'observed' ($I > 2\sigma(I)$) reflections out of $N = 2943$ unique. GOF 1.09.

CCDC reference number 186/1925.

See http://www.rsc.org/suppdata/dt/b0/b000747l/ for crystallographic files in .cif format.

Acknowledgements

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