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Solid state structures of homo- and hetero-bimetallic alkali metal complexes containing the dianion of (*S*)-*N*-(α-methylbenzyl)-allylamine

Philip C. Andrews,* Simone M. Calleja and Melissa Maguire

School of Chemistry, Monash University, PO Box 23, Melbourne, Vic. 3800, Australia.
E-mail: p.andrews@sci.monash.edu.au

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Dilithiation of the chiral amine (*S*)-*N*-(α-methylbenzyl)allylamine in the absence of a coordinating Lewis donor results in formation of crystals of a cyclic hexamer, {[(*S*)-α-(PhC(H)Me)(CH_2CH=CHLi)N]Li}$_6$, **1**, (rhombohedral, *R*3) while the addition of tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) leads to deaggregation and formation of the dimer, {[(*S*)-α-(PhC(H)Me)(CH_2CH=CHLi)N]Li·(tmeda)$_2$}$_2$, **2** (monoclinic, $P2_1$). Reaction with ^{n}BuLi followed by ^{n}BuNa leads to crystals of a cyclic mixed metal tetramer coordinated with thf, {[(*S*)-α-(PhC(H)Me)(CH_2CH=CHNa)N]Li·(thf)}$_4$, **3** (orthorhombic, $P2_12_12_1$). The three bimetallic complexes have been characterised by single crystal X-ray diffraction, NMR and elemental analysis. The allyl moieties in all three complexes retain the bonding pattern expected in an N-allylamine (–N(M)—CH_2–C(H)=C(H)M′, M = Li, M′ = Li or Na) rather than forming a delocalised dianion or an enamide. The anionic amido N and the terminal vinylic C centres form multiple short bonds to all metal centres which in turn form short interactions with all atoms in the allyl groups, and in **1** with the closest Ph carbons.

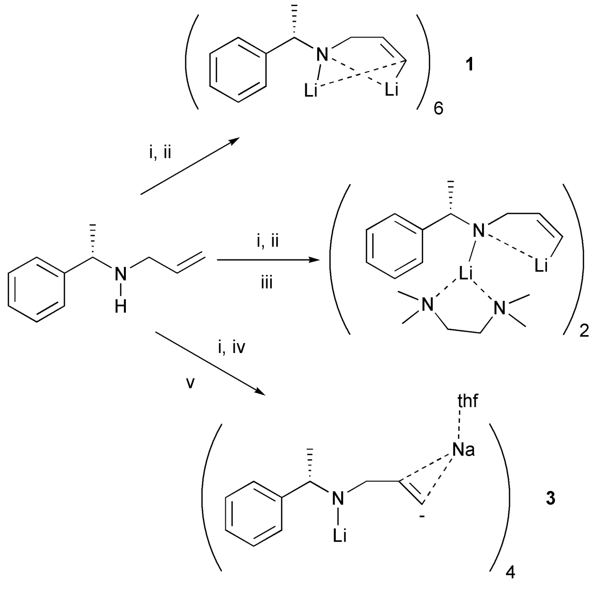
Introduction

Chiral lithium amides have proved to be extremely useful reagents in asymmetric synthesis giving high ee values in enantioselective deprotonation reactions and in Micheal-type addition reactions.[1] Understanding the stereoselectivity in such reactions, and being able to design more effective and efficient reagents, requires a fundamental knowledge of the structural chemistry of the reactive species and the intermediate complexes formed. To this end there have been serious systematic studies into the solid and solution state complexes of both chiral and achiral alkali metal amides[2] and of the enolates and alkoxides formed on their reaction with carbonyl containing compounds and epoxides.[3]

Recently, we have been particularly interested in the study of metal amides formed from reactions with the amines *S*-(α-methylbenzyl)benzylamine and *S*-bis(α-methylbenzyl)amine, which were utilised by Davies and co-workers in the efficient formation of β-amino acids and β-lactams from their highly stereoselective conjugate addition to α,β-unsaturated esters.[4] We have shown that the introduction of heavier alkali metals other than Li can lead to dramatic transformations in the amido moiety.[5] Extending this study led us to examine the analogous amine *S*-(α-methylbenzyl)allylamine, and we noted with interest the report by Yus on the formation of the dilithiated dianion and its subsequent reaction with various electrophiles.[6] The synthetic importance in having two different reactive sites within the molecule was further demonstrated by the use of substituted dimetallated allylamines in the formation of butyrolactams on reaction with $Cr(CO)_6$ and $W(CO)_6$.[7] Williard, in his solid state study on the dilithiation of *N*-silyl allylamines, revealed the fine structural changes which can occur in aggregate formation on introducing small changes within the silyl group itself.[8] We were therefore interested to know what happens when typical Lewis donors and heavier alkali metals are introduced into the system. As such, we now report the synthesis and characterisation of three bimetallic complexes obtained from *S*-α-(methylbenzyl)allylamine, namely, {[(*S*)-α-(PhC(H)Me)(CH_2CH=CHLi)N]Li}$_6$, **1**, {[(*S*)-α-(PhC(H)Me)(CH_2CH=CHLi)N]Li·(tmeda)}$_2$, **2**, and {[(*S*)-α-(PhC(H)Me)(CH_2CH=CHNa)N]Li·(thf)}$_4$, **3**, and their analysis by single crystal X-ray diffraction and solution NMR studies.

Results and discussion

The three complexes were prepared as shown in Scheme 1. Compound **1** was synthesised by two methods, the first based



Scheme 1 Reagents and conditions: i = ^{n}BuLi, hexane, −60 °C; ii = ^{t}BuLi, −10 °C; iii = 1 equiv. tmeda; iv = ^{n}BuNa, hexane, −78 °C; v = 1 equiv. thf.

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on that previously described by Yus[6] involving the sequential addition of ^{n}BuLi and ^{t}BuLi to a hexane solution of the *S*-α-(methylbenzyl)allylamine at −60 and −10 °C respectively. On warming to room temperature the yellow solution was allowed to stir for a further 30 min before storage at 4 °C. Over 24 h a large crop of pale yellow crystals were produced. These were isolated and washed with hexane prior to analysis. We found that dilithiation of the amine could also be achieved simply by the use of 2 equivalents of ^{n}BuLi in toluene though complex formation and crystal growth is slow in comparison with the first method. A moderate yield of crystals of **1** were obtained (*ca.* 28%), again at 4 °C, over a period of 5 days, reflecting the greater insolubility of the dilithiated compound over the monolithiated amide, and relatively close pK_as of all the acidic hydrogens in the hydrocarbons involved in the reaction mixture. Compound **2** was synthesised by the addition of one equivalent of tmeda to the reaction mixture produced following the first procedure and storing the solution at −20 °C over several days. These crystals were also pale yellow and had greater solubility in hexane relative to complex **1**. Complex **3** was synthesised by the addition of a cooled hexane solution of the preformed lithium amide, $\{(PhC(H)Me)(CH_2CH{=}CH_2)N]Li\}_n$, to a hexane suspension of ^{n}BuNa at −78 °C. The reaction mixture was allowed to warm slowly to room temperature before one equivalent of thf was added causing complete dissolution of the pale brown precipitate to a deep red solution. Upon storage of the solution at −20 °C over three days red–orange crystals of **3** were produced. All three complexes proved to be highly sensitive to air and atmospheric moisture. The isolated crystals were investigated by single crystal X-ray diffraction and solution NMR with the chemical composition of the crystalline bulk samples confirmed by elemental analysis.

X-Ray crystallographic studies

A summary of the crystallographic data is given in Table 4. Compound **1** crystallises in the rhombohedral system (space group, *R*3) and forms a cyclic hexamer, as shown in Fig. 1, with the asymmetric unit comprising two dianions and four Li cations, Fig. 2. In fact, the structure approximates to the centrosymmetric $R\bar{3}$ space group though the α-methyl groups destroy the symmetry. The gross structural features are those of a paddlewheel with a prismatic hexagonal core with an outer rim composed of an N–Li chain to which is attached the α-methylbenzyl 'paddles'. The structure is similar to that observed for $\{[(^{t}Bu(Me)_2Si)(CH_2CH{=}CH)N]Li_2\}_6$ though this was found to crystallise in the monoclinic space group $P2_1$.[8]

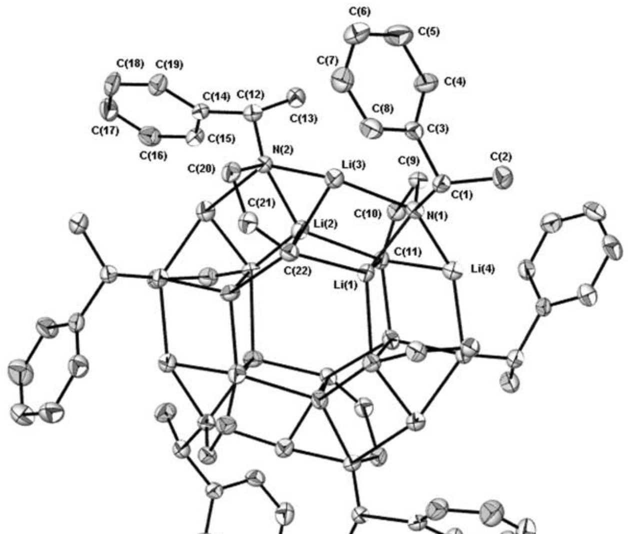

Fig. 1 Molecular structure of $\{[(S)\text{-}\alpha\text{-}(PhC(H)Me)(CH_2CH{=}CHLi)N]Li\}_6$, **1**. Thermal ellipsoids at 50% probability. All H atoms omitted for clarity. Selected bond lengths and angles are given in Table 1.

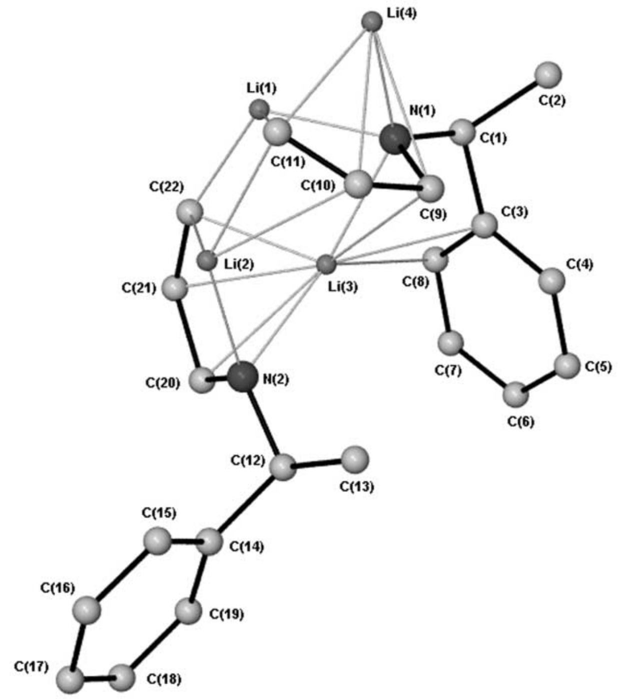

Fig. 2 Close contacts in the bonding environment of the four Li centres in the asymmetric unit of **1**.

The bond lengths within the allyl moieties of both complexes are similar and indicate retention of the vinylic double bond rather than formation of a delocalised anionic system (N(1)–C(9), 1.460(3); C(9)–C(10), 1.508(3); C(10)–C(11), 1.334(3) Å). The bonding pattern of the hexameric inner core of the molecule resembles stacked trimers, as previously established for $[^{n}BuLi]_6$,[9] with each six membered ring comprised of alternating long and short bonds, C(22),C(22)#–Li(1), 2.135(4), 2.325(4) and C(11),C(11)#–Li(2), 2.372(4), 2.147(4) Å (# = symmetry generated atoms, see Table 1). These rings then stack in an eclipsed fashion allowing the long bonds to sit above the short ones. The 'rungs' which join the two rings also have alternating bond lengths of 2.357(5) (C(11)–Li(1)) and 2.381(4) Å (C(22)–Li(2)). By necessity, the allyl and methylbenzyl groups then alternate around the rings allowing the wheel to be constructed from 6 five membered (–N–Li–C=C–C–) rings. Each Li centre is located in a very high coordination environment and forms close contacts with all the Cs within the allyl group, the amido Ns and the *ipso* and *ortho* Cs of the phenyl rings. This is demonstrated for the asymmetric unit, shown in Fig. 2, in which the C–Li bond lengths range from 2.135(4)–2.690(4) Å for C(22)–Li(1) to C(10)–Li(2). Deprotonation at the terminal vinylic C leads to it being connected to four Li centres with the Li which is primarily engaged in the Li–N chain (*e.g.* C(22)–Li(3), 2.211(5) Å) bonding with the π electron density of the vinylic group itself. Despite the significant number of electrostatic interactions, the agostic contacts between the outer Li centres and the closest *ortho* and *ipso* Cs on the phenyl rings of 2.488(5) (C(15)–Li(4)), 2.609(5) (C(14)–Li(4)) and 2.568(5) (C(8)–Li(3)), are all shorter than those observed in the trimer of dibenzylamidolithium[10] where the shortest is 2.7 Å. The outer rim of the wheel is constructed from three sets of four non-equivalent N–Li bonds ranging in length from N(1)–Li(4), 2.109(4), to N(1)–Li(3), 2.203(4) Å. These distances are more comparable with N–Li dative bonding reflecting the coordination of each amido N centre to three Li cations.

Table 1 Selected bond lengths (Å) and angles (°) for **1**. (Symmetry operators #1 = $-y + 1, x - y + 1, z$; #2 = $-x + y, -x + 1, z$)

N(2)–Li(2)	2.061(4)	N(1)–Li(1)	2.013(4)
N(2)–Li(3)	2.138(4)	N(1)–Li(4)	2.109(4)
N(2)–Li(4)#1	2.166(4)	N(1)–Li(3)	2.203(4)
C(20)–Li(3)	2.601(5)	C(9)–Li(4)	2.494(5)
C(20)–Li(4)#1	2.488(5)	C(9)–Li(3)	2.647(5)
C(21)–Li(3)	2.555(5)	C(10)–Li(4)	2.503(5)
C(21)–Li(1)#1	2.586(4)	C(10)–Li(2)	2.690(4)
C(22)–Li(1)	2.135(4)	C(11)–Li(1)	2.357(5)
C(22)–Li(2)	2.381(4)	C(11)–Li(2)	2.372(4)
C(22)–Li(3)	2.211(5)	C(11)–Li(4)	2.239(5)
C(22)–Li(1)#1	2.325(4)	C(11)–Li(2)#2	2.147(4)
N(2)–C(20)	1.469(3)	N(1)–C(9)	1.460(3)
C(21)–C(20)	1.510(3)	C(9)–C(10)	1.508(3)
C(22)–C(21)	1.326(3)	C(10)–C(11)	1.334(3)
C(12)–N(2)–Li(2)	133.6(2)	C(9)–N(1)–Li(1)	117.5(2)
C(20)–N(2)–Li(2)	115.5(2)	C(1)–N(1)–Li(1)	127.7(2)
C(12)–N(2)–Li(3)	121.4(2)	C(9)–N(1)–Li(4)	86.7(2)
C(20)–N(2)–Li(3)	90.3(2)	C(1)–N(1)–Li(4)	119.0(2)
Li(2)–N(2)–Li(3)	71.2(2)	Li(1)–N(1)–Li(4)	72.8(2)
C(12)–N(2)–Li(4)#1	101.2(2)	C(9)–N(1)–Li(3)	90.2(2)
C(20)–N(2)–Li(4)#1	84.0(2)	C(1)–N(1)–Li(3)	97.6(2)
Li(2)–N(2)–Li(4)#1	72.5(2)	Li(1)–N(1)–Li(3)	73.6(2)
Li(3)–N(2)–Li(4)#1	136.3(2)	Li(4)–N(1)–Li(3)	140.1(2)
C(21)–C(22)–Li(1)	160.1(2)	C(10)–C(11)–Li(2)#2	154.0(2)
C(21)–C(22)–Li(3)	88.9(2)	C(10)–C(11)–Li(4)	84.9(2)
Li(1)–C(22)–Li(3)	71.2(2)	Li(2)#2–C(11)–Li(4)	69.6(2)
C(21)–C(22)–Li(1)#1	85.6(2)	C(10)–C(11)–Li(1)	104.3(2)
Li(1)–C(22)–Li(1)#1	106.3(2)	Li(2)#2–C(11)–Li(1)	69.3(2)
Li(3)–C(22)–Li(1)#1	126.0(2)	Li(4)–C(11)–Li(1)	64.3(2)
C(21)–C(22)–Li(2)	103.5(2)	C(10)–C(11)–Li(2)	88.5(2)
Li(1)–C(22)–Li(2)	68.6(2)	Li(2)#2–C(11)–Li(2)	109.8(2)
Li(3)–C(22)–Li(2)	64.3(2)	Li(4)–C(11)–Li(2)	125.5(2)
Li(1)#1–C(22)–Li(2)	66.0(2)	Li(1)–C(11)–Li(2)	65.3(1)

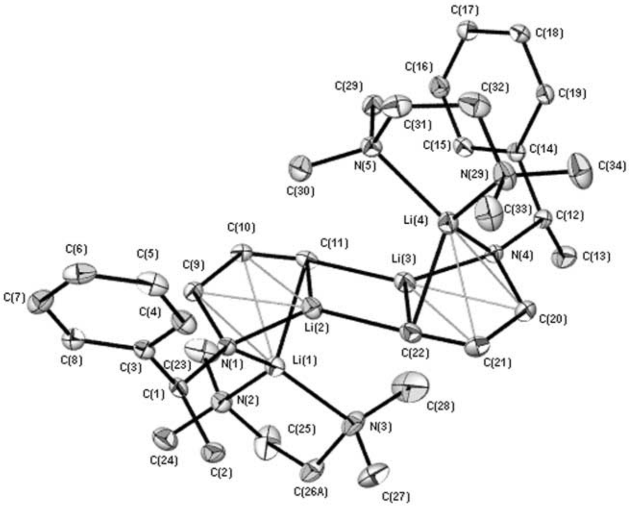

Fig. 3 Molecular structure of {[(*S*)-α-(PhC(H)Me)(CH$_2$CH=CHLi)N]Li·(tmeda)}$_2$, **2**. Thermal ellipsoids are shown at 50% probability. All H atoms omitted for clarity. Selected bond lengths and angles are given in Table 2. C(26) on the tmeda backbone was disordered over two sites modelled at 50% occupancy.

Complex **2**, Fig. 3, crystallises in the monoclinic space group $P2_1$ and has a unit cell comprised of two independent non-centrosymmetric dimers. As in **1** the allyl groups retain their expected bonding pattern (N(1)–C(9), 1.460(2); C(9)–C(10), 1.521(3); C(10)–C(11), 1.338(3) Å) though on this occasion they are straddled on either side by two Li cations which are slightly unsymmetrical in their bonding to the allyl group. The Li cations which are responsible for dimer formation are located slightly further away (Li(2)–N(1), 1.916(4); Li(2)–C(9), 2.654(4); Li(2)–C(10), 2.703(4), Li(2)–C(11), 2.226(4) Å, see Table 2) than those which bond to tmeda (Li(1)–N(1), 2.021(3); Li(1)–C(9), 2.480(3); Li(1)–C(10), 2.427(4), Li(1)–C(11), 2.287(4) Å).

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

Li(1)–N(2)	2.130(4)	Li(3)–C(11)	2.150(4)
Li(1)–N(3)	2.140(3)	Li(3)–C(21)	2.705(4)
Li(1)–C(11)	2.287(4)	Li(3)–C(22)	2.246(4)
Li(1)–C(10)	2.427(4)	Li(3)–C(20)	2.665(4)
Li(1)–C(9)	2.480(3)	Li(3)–N(4)	1.914(4)
Li(1)–N(1)	2.021(3)	Li(4)–N(29)	2.112(4)
Li(2)–C(22)	2.123(4)	Li(4)–N(5)	2.148(4)
Li(2)–C(11)	2.226(4)	Li(4)–N(4)	2.038(3)
Li(2)–C(9)	2.654(4)	Li(4)–C(21)	2.499(4)
Li(2)–C(10)	2.703(4)	Li(4)–C(22)	2.279(4)
Li(2)–N(1)	1.916(4)	Li(4)–C(20)	2.555(4)
N(1)–C(9)	1.460(2)	N(4)–C(20)	1.458(3)
C(9)–C(10)	1.521(3)	C(20)–C(21)	1.519(3)
C(10)–C(11)	1.338(3)	C(21)–C(22)	1.334(3)
N(1)–Li(1)–N(2)	119.3(2)	N(4)–Li(3)–C(11)	149.3(2)
N(1)–Li(1)–N(3)	139.8(2)	N(4)–Li(3)–C(22)	85.7(2)
N(2)–Li(1)–N(3)	86.3(1)	C(11)–Li(3)–C(22)	113.9(2)
N(1)–Li(2)–C(22)	142.8(2)	N(4)–Li(4)–N(29)	121.4(2)
N(1)–Li(2)–C(11)	85.7(1)	N(4)–Li(4)–N(5)	132.7(2)
C(22)–Li(2)–C(11)	115.8(2)	N(29)–Li(4)–N(5)	85.8(1)
C(10)–C(11)–Li(3)	160.4(2)	C(21)–C(22)–Li(2)	158.5(2)
C(10)–C(11)–Li(2)	95.4(2)	C(21)–C(22)–Li(3)	94.7(2)
Li(3)–C(11)–Li(2)	65.1(1)	Li(2)–C(22)–Li(3)	65.1(1)

In contrast to **1** each terminal vinylic C forms close bonds with only three Li cationic centres (range; 2.123(4)–2.287(4) Å for C(22)–Li(2), Li(1)–C(11)) and surprisingly all the allyl C atoms and the two bridging Li centres are essentially planar with a torsion angle of 5.3° for C(9)–C(11)–C(22)–C(20). The N atoms are then situated above and below this plane due to the sp^3 centres at C(9) and C(20). The tmeda molecules are orientated essentially perpendicular to this plane establishing a distorted tetrahedral environment at the respective Li centres, Li(1) and Li(4). In contrast to **1** there are no close phenyl ··· Li interactions, though, one striking feature in the crystal structure is the relative orientations of the α-methylbenzyl groups. These are such that the phenyl groups, shown in Fig. 4, are located on the same side of the molecule rather than adopting a pseudo-*trans* configuration. It may have been safe to assume that the lowest energy conformation would involve the greatest seperation of the tmeda and methyl moieties on α-methylbenzyl groups, however, as can be seen, in one half of the dimer the methyl group is located over the tmeda molecule while in the other half a 120° rotation situates the Ph group in that position. This would seem to indicate that there is only a small barrier to rotation around the N–C$_{\text{chiral}}$ bond.

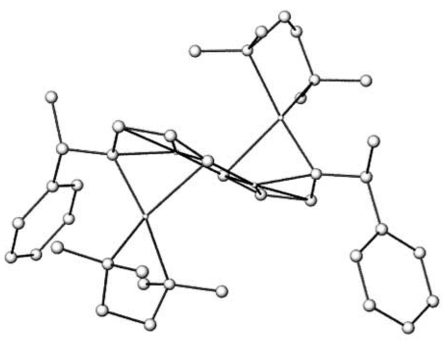

Fig. 4 Orientation of the α-methylbenzyl groups relative to the central plane in **2**.

Complex **3** crystallises in the orthorhombic space group $P2_12_12_1$ with a unit cell comprised of four independent cyclic bimetallic tetramers (see Table 3 for selected bond lengths and angles). The molecular structure is shown in Fig. 5 and resembles a deaggregated form of **1** in that the tetrameric wheel is composed of four allylic groups joined by Na$^+$ cations on the outer rim and Li$^+$ cations in the centre. However, there is a greater degree of asymmetry in **3** as evidenced by an anlaysis of

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

Li(1)–C(11)	2.315(6)	N(1)–C(1)	1.451(4)
Li(2)–C(22)	2.323(7)	N(1)–C(9)	1.451(4)
Li(3)–C(33)	2.365(7)	N(1)–Li(1)	1.900(6)
Li(4)–C(44)	2.405(6)	N(1)–Na(2)	3.104(3)
Na(1)–N(1)	2.464(3)	N(2)–C(12)	1.456(4)
Na(1)–N(4)	2.484(3)	N(2)–C(20)	1.448(4)
Na(1)–O(1)	2.296(3)	N(2)–Li(2)	1.937(6)
Na(2)–C(19)	3.069(4)	N(2)–Na(3)	2.510(3)
Na(2)–N(2)	2.855(3)		
Na(2)–O(2)	2.285(3)	N(3)–C(23)	1.445(4)
Na(3)–N(3)	2.530(3)	N(3)–C(31)	1.450(4)
Na(3)–O(3)	2.267(3)	N(3)–Li(3)	1.889(6)
Na(4)–O(4)	2.252(3)	N(3)–Na(4)	2.811(3)
C(9)–C(10)	1.513(5)	N(4)–C(34)	1.448(4)
C(10)–C(11)	1.334(5)	N(4)–C(42)	1.428(4)
C(20)–C(21)	1.508(5)	N(4)–Li(4)	1.896(6)
C(21)–C(22)	1.353(5)	N(4)–Na(4)	2.991(3)
C(31)–C(32)	1.506(5)	C(42)–C(43)	1.525(5)
C(32)–C(33)	1.340(5)	C(43)–C(44)	1.327(5)
C(42)–N(4)–Na(1)	89.9(2)	C(20)–N(2)–Na(2)	72.6(2)
C(34)–N(4)–Na(1)	114.9(2)	C(12)–N(2)–Na(2)	115.5(2)
Li(4)–N(4)–Na(1)	75.5(2)	Li(2)–N(2)–Na(2)	68.8(2)
		Na(3)–N(2)–Na(2)	122.4(1)
O(2)–Na(2)–N(2)	116.0(1)	C(14)–C(19)–Na(2)	96.4(2)
O(2)–Na(2)–C(19)	84.5(1)	C(18)–C(19)–Na(2)	106.3(2)
N(2)–Na(2)–C(19)	61.6(1)		
O(2)–Na(2)–N(1)	117.6(1)	N(1)–Li(1)–C(11)	83.8(2)
N(2)–Na(2)–N(1)	126.1(9)	N(2)–Li(2)–C(22)	82.4(2)
C(19)–Na(2)–N(1)	129.0(1)		
		C(9)–N(1)–Li(1)	115.7(3)
C(20)–N(2)–Li(2)	117.5(3)	C(1)–N(1)–Li(1)	128.9(3)
C(12)–N(2)–Li(2)	128.6(3)	C(10)–C(11)–Li(1)	100.7(3)

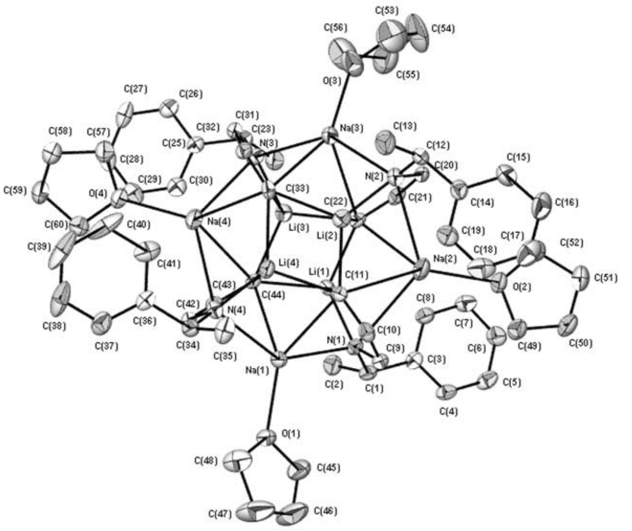

Fig. 5 Molecular structure of {[(*S*)-α-(PhC(H)Me)(CH_2CH=CHNa)N]Li·(thf)}$_4$, **3**. Thermal ellipsoids are shown at 50% probability. All H atoms omitted for clarity. Selected bond lengths and angles given in Table 3.

the M–N and M–C bonds within the molecule's core, and a different configuration with respect to the 'monomeric' units. While in **1** the aryl groups formed a 'paddle–wheel' type structure in **3** the phenyl groups adopt an arrangement where they are essentially co-planar with each other and with the wheel itself, the difference only requiring a 120° rotation around the N–$C_{\mathbf{chiral}}$ bond.

Close analysis of the Li–N bond distances suggest that the molecule is a tetrameric lithium amide, however, it does not aggregate through bridging Li–N interactions but through the formation of a highly distorted central cubane of C–Li bonds. The N–Li bond distances range from 1.896(6) to 1.937(6) Å and are typical of σ-bonded lithium amides[11] and given that the coordination environment of each Li centre can be taken to include one N and three C centres they are remarkably short. The central cubane C–Li bond distances (range 2.223 to 2.405 Å, av. 2.29 Å), which involve terminal vinylic carbons forming bonds to three Li centres and two Na centres, are comparable with those found in tetrameric alkylithium aggregates such as MeLi (av. 2.25 Å)[12] and ^{t}BuLi (av. 2.24 Å).[9]

Each Na cation is coordinated by a single thf molecule two of which are in plane with, and bisect, the phenyl groups on either side of the molecule. The allyl moieties, as in **1** and **2**, retain their expected 'allylic' bonding pattern and are straddled on either side by Na cations which constitute an almost perfect square with internal angles of 90.0 (Na(1)), 88.2 (Na(2)), 92.5 (Na(3)) and 90.3° (Na(4)). The four shortest Na–N distances range from 2.464(3) to 2.530(3) Å and are all found for the bonds formed by Na(1) and Na(3) while the other four bond distances are longer and range from 2.811(3) to 3.104(3) Å for Na(4) and Na(2). These distances are longer than typical Na–N formal bonds and are comparable with Na–N dative bonds.[13] Perhaps then the best representation is to consider the Na cations as being sandwiched between the localised double bonds of the allyl moiety, as represented in Fig. 6, with some significant electrostatic interaction with the negatively charged N centres. These distances range from 2.731(3) (Na(4)–C(33)) to 2.870(3) Å (Na(1)–C(11)) for bonds to the terminal C and from 2.747(3) (Na(4)–C(21)) to 2.960(3) Å (Na(1)–C(10)) for bonds to the accompanying vinylic C. All these distances are typical of compensatory interactions formed by Na cations to localised and aromatic double bonds when the metal is in a low coordination environment though in this case the terminal vinylic carbons are deprotonated and bear significant negative charge.[14] If **3** can be characterised primarily as a lithium amide then it is interesting to consider that no transmetallation occurs when (PhC(H)Me)(CH_2CH=CH_2)NLi is added to ^{n}BuNa, *i.e.* the lithium amide does not convert to a sodium amide which would be expected given the respective bond energies.[15] This process may be offset by the actual stability of the tetramer itself since, as we recently noted, in bimetallic clusters there is a tendency for the heavier alkali metal to adopt outer positions while Li adopts the more central ones, driven by relative cation size and their ability of the larger cation to form stable bonds which are longer. It would not make architectural sense for the cluster to assemble the other way around.[16]

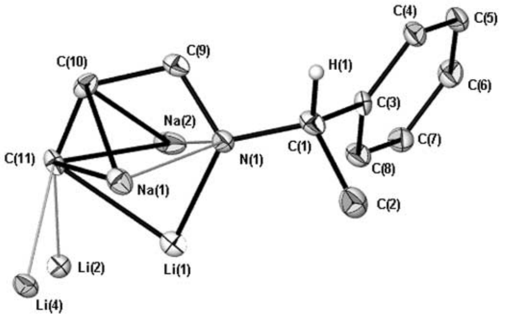

Fig. 6 The high coordinate bonding environment of the terminal vinylic C in **3**.

Solution studies

In allyllithium complexes[17] and in the alkali metal complexes of *N*,*N*-dimethylallylamine[18] the predominant bonding arrangement is that of delocalisation within the allylic anion and an η^3 binding of the metal cation. However, solution NMR studies on **1**, **2** and **3** indicate a retention of the allylic bonding pattern, as observed in the crystal structures, rather than delocalisation. ^{1}H and ^{13}C spectra were obtained on all three complexes in d_6-benzene solution, though **1** proved to be almost completely

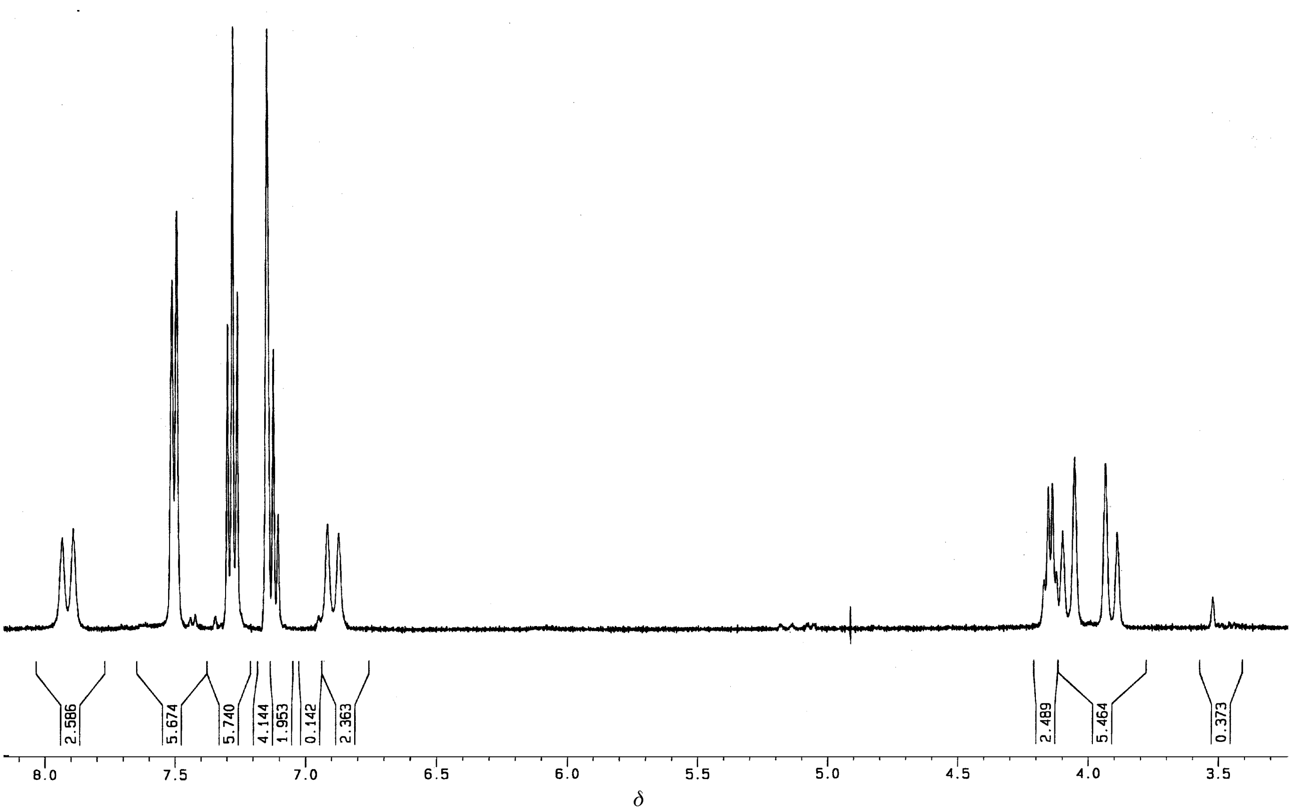

Fig. 7 ^{1}H NMR of **1** in the range $\delta = 3$–8. Me signals are not shown ($\delta = 1.62$).

insoluble in both benzene and toluene and a small amount of d$_8$-thf (5% v/v) was added to dissolve the sample. Thus, given the tendency of thf to deaggregate lithium oligomers the NMR spectra of **1** are probably of the thf solvate, similar in construction to **3**, and not of the hexamer. Variable temperature studies on **2**, including ^{7}Li, were carried out in d$_8$-toluene. At room temperature the same ^{1}H basic pattern of signals is observed for all three complexes. The signals for the terminal and adjacent vinylic protons are quite distinct and are shifted significantly downfield from their positions in the free amine. Both signals appear as slightly broad doublets and at the operating frequency (400 MHz) we were not able to detect any fine coupling, which may have been expected at least for the central H. Proton signals were therefore assigned on the basis of ^{1}H/^{1}H and ^{1}H/^{13}C correlation experiments. A section of the ^{1}H spectrum of **1** is shown in Fig. 7. The central proton on the allylic moiety (–C*H*=CHM) (M = Li, Na), which is located at δ 5.81 in the free amine, appears at δ 7.91 in **1**, 8.10 in **2** and 8.12 in **3** as broad doublets (half-height line width *ca.* 6 Hz), while the associated C atoms are found at δ 163.9, 160.3 and 165.8 respectively. The terminal proton (–CH=C*H*M) appears at δ 6.89 in **1**, 7.06, in **2** and 7.29 in **3**, though in **2** and **3** the doublet is partially obscured by the *p*-H and *o*-H signals respectively, and represents a shift of *ca.* 2 ppm from the signals observed for the terminal CH$_2$ in the free amine (δ 4.97, 5.07). The large relative shift in **3** is indicative of the strong interaction of the double bond with the sodium cations. The chemical shifts for the associated C atoms are δ 149.2 in **1**, 153.6 in **2** and 152.5 in **3**. The diastereotopic protons of NCH_2 give a well separated doublet of doublets (AB system) in all three complexes though they resonate close to the proton on the chiral carbon (and thf protons in **3**) and so are partially obscured by the MeC*H* quartet. Not surprisingly, given the strong localised interaction of the double bond in the allylic moiety with the sodium cations the protons found furthest upfield are in **3** (δ 4.14 in **1**, 4.10 in **2** and 3.60 in **3**). The J_{AB} coupling constants are 8.0, 18.3 and 21.5 Hz for **1**, **2**, and **3** respectively which may be indicative of a deaggregation and/or complexation of the vinylic Li in **1** by d$_8$-thf leading to a more obtuse N–C–C angle and a concomitant reduction in the geminal H–C–H angle.

At room temperature the ^{1}H spectrum of **2** gave two very broad merged signals for the tmeda protons, indicating a highly fluxional system. We therefore obtained spectra in the temperature range 0 to −80 °C in d$_8$-toluene. The signals for tmeda appear sharpest at −30 °C and highlight the highly non-symmetrical bonding environment in which it is found since there are at least six prominent signals. By −60 °C all the signals begin to broaden again most likely from gradual precipitation of the complex.

The ^{7}Li NMR spectra always indicate the presence of at least two independent Li environments. At 30 °C there is one predominent broad signal at δ 2.5 with a shoulder at δ 1.96. By −30 °C these have separated and appear at δ 2.7 and 0.98. At −60 °C the larger signal broadens dramatically (δ 2.6) and reveals a shoulder at higher frequency (δ 4.0) with the smaller upfield signal (δ 1.55) sharpening. At −80 °C there are again two distinct lithium environments though now the larger signal in a ratio of 2 : 1 is at δ 1.16 and the smaller at δ 4.2. The evidence from both the ^{1}H and ^{7}Li NMR indicates that there is significant deaggregation and reaggregation of the complex occurring in solution and that the tmeda may not always act simply as a bidentate donor on only one Li centre.

Conclusions

We have shown that dimetallation of the chiral secondary allylamine (*S*)-*N*-(α-methylbenzyl)allylamine with BuLi and BuNa leads to the formation of highly aggregated complexes in the solid state with metallation occurring at the amido N and terminal vinylic C. Though both metals are located in high coordination environments, forming many short compensatory interactions with the amido N, the allylic carbons and the phenyl groups, the dianion actually retains an 'allylic' bonding pattern in the solid state and in solution rather than delocalising the charge and invoking a possible mixture of η^3 and η^1 metal binding.

Table 4 Summary of crystallographic data for compounds **1**–**3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{11}H_{13}NLi_2$	$C_{34}H_{58}N_6Li_4$	$C_{60}H_{84}N_4O_4Li_4Na_4$
M_w	173.1	578.62	1045.03
Crystal system	Rhombohedral	Monoclinic	Orthorhombic
Space group	$R3$	$P2_1$	$P2_12_12_1$
a/Å	26.797(4)	9.637(2)	12.814(3)
b/Å	26.797(4)	11.832(2)	18.980(4)
c/Å	7.3661(15)	16.811(3)	25.240(5)
a/°	90	90	90
β/°	90	100.69(3)	90
γ/°	120	90	90
V/Å^3	458.9(13)	1883.7(7)	6139(2)
Z	18	2	4
$2\theta_{max}$/°	56.88	56.58	56.6
D_{calc}/g cm^{-3}	1.129	1.020	1.131
μ/cm^{-1}	0.006	0.006	0.009
T/K	123	123	123
N_{ind}	4967	9111	14999
R_w	0.1136	0.1014	0.1380
R_1 [$I > 2\sigma(I)$]	0.0485	0.0488	0.0724
GooF	0.805	0.929	0.971

Experimental

General remarks

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 4 Å molecular sieves. (*S*)-*N*-(α-Methylbenzyl)allylamine was prepared by a literature procedure.[6] ^{n}BuNa was prepared from the metathesis reaction of ^{n}BuLi and NaO^{t}Bu in hexane and stored as a solid. (Note: this solid is extremely pyrophoric). ^{n}BuLi was purchased from Merck-Schuchardt (1.6 M solution in hexanes) and ^{t}BuLi from Aldrich (1.7 M solution in hexanes). tmeda was refluxed over CaH_2, distilled and stored over 4 Å molecular sieves. NMR spectra were obtained on a Bruker DRX-400 spectrometer with chemical shifts referenced to the appropriate deuterated solvent. Elemental analyses were carried out by CMAS, Australia.

Crystallography

Crystal data and refinement details are summarised in Table 4. Crystals were coated in oil,[19] mounted on a fibre and data collected on an Enraf Nonius KappaCCD at 123 K with Mo-Kα radiation (λ = 0.71073 Å). The structures were solved using direct methods (SHELXS97)[20] and refined by full matrix least-squares on F^2. All H atoms were placed in calculated positions (C–H 0.95 Å) and included in the final least squares refinement. All other atoms were located and refined anisotropically.

CCDC reference numbers 184382–184384.

See http://www.rsc.org/suppdata/dt/b2/b203470k/ for crystallographic data in CIF or other electronic format.

Synthesis

Synthesis of {[(*S*)-α-(PhC(H)Me)(CH_2CH=CHLi)N]Li}$_6$, 1. (*S*)-*N*-(α-Methylbenzyl)allylamine (5 mmol, 0.81 g) in hexane (8 ml) was cooled to −60 °C and ^{n}BuLi (5 mmol, 3.13 ml, 1.6 M) added dropwise. This caused immediate precipitation of a yellow solid which gave way to a pale yellow solution on stirring and warming slowly to −10 °C. At this temperature ^{t}BuLi (5 mmol, 2.9 ml, 1.7 M) was added and the reaction mixture allowed to warm to ambient temperature. It was stirred for a further 30 min and stored at 4 °C. After several days the large crop of highly air and moisture sensitive pale yellow crystals which had formed were isolated and washed with hexane. They were later identified as {[(*S*)-α-(PhC(H)Me)-(CH_2CH=CHLi)N]Li}$_6$. Yield 0.63 g (72%, not maximised). Mp 141–143 °C. ^{1}H NMR (400 MHz, d_6-benzene, d_8-thf (5% v/v), 30 °C): δ 1.62 (d, J = 5.0 Hz, 3H), 3.99 (dd, J = 8.0 Hz, 2H), 4.14 (q, J = 6.4 Hz, 1H), 6.89 (d, J = 17.2 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 7.28 (t, J = 7.5 Hz, 2H), 7.50 (d, J = 7.4 Hz, 2H), 7.91 (d, J = 17.0 Hz, 1H). ^{13}C NMR (100.5 MHz, d_6-benzene, d_8-thf (5% v/v), 30 °C): δ 22.7 (CH_3), 61.8 (NCH_2), 64.5 (MeC(H)), 126.4 (*p*-C), 127.4 (*m*-C), 128.7 (*o*-C), 149.2 (CH), 150.5 (*i*-C), 163.9 (CH). ^{7}Li NMR (155.5 MHz, d_6-benzene, d_8-thf (5% v/v), 30 °C): δ 1.73. Elemental analysis ($(C_{22}H_{26}Li_4N_2)_3$): found (calc.), C 75.8 (75.9); H 8.1 (8.1); N 8.0 (8.1)%.

Synthesis of {[(*S*)-α-(PhC(H)Me)(CH_2CH=CHLi)N]Li·(tmeda)}$_2$, 2. {[(*S*)-α-(PhC(H)Me)(CH_2CH=CHLi)N]Li} was synthesised as described above. tmeda (5 mmol, 0.75 ml) was added to the pale yellow solution at room temperature. The solvent was reduced *in vacuo* to approx. 60% of original volume and the solution stored at −20 °C. Over several days a modest crop of pale yellow crystals were obtained. These were isolated, washed with cold hexane, and identified as {[(*S*)-α-(PhC(H)Me)(CH_2CH=CHLi)N]Li·(tmeda)}$_2$. Yield 0.88 g (61%, not maximised). Mp 115–117 °C. ^{1}H NMR (400 MHz, d_6-benzene, 30 °C): δ 1.74 (m, b, 7H), 1.93 (s, b, 12H), 4.1 (m (= dd (J = 18.3 Hz) + q), 3H), 7.06 (d, J = 16 Hz, 1H), 7.11 (t, J = 7.4 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.61 (d, J = 7.4 Hz, 2H), 8.10 (d, J = 16.6 Hz, 1H). ^{13}C NMR (100.5 MHz, d_6-benzene, 30 °C): δ 27.6 (CH_3), 46.1 (NCH_3), 57.3 (NCH_2 (tmeda)); δ 63.6 (NCH_2), 66.4 (MeC(H)), 125.6 (*p*-C), 127.6 (*m*-C), 128.4 (*o*-C), 153.6 (CH), 154.7 (C), 160.3 (CH). ^{7}Li NMR (155.5 MHz, d_6-benzene, 30 °C): δ 1.95, 2.5; (−30 °C) 0.98, 2.7; (−60 °C): δ 1.15, 2.6 (b); (−80 °C): δ 1.1, 4.16. Elemental analysis ($C_{34}H_{58}N_6Li_4$): found (calc.), C 69.4 (70.6); H 10.2 (10.0); N 13.8 (14.5)%.

Synthesis of {[(*S*)-α-(PhC(H)Me)(CH_2CH=CHNa)N]Li·(thf)}$_4$, 3. ^{n}BuLi (5 mmol, 3.13 ml,) was added dropwise to a clear solution of (*S*)-*N*-(α-methylbenzyl)allylamine (5 mmol, 0.81 g) in hexane (8 ml) at −78 °C. On warming to −20 °C the pale yellow solution was transferred *via* cannula into a light brown suspension of ^{n}BuNa (0.4 g, 5 mmol) in hexane (10 ml) at −78 °C. The reaction mixture was allowed to warm slowly to ambient temperature. Subsequent addition of an equimolar amount of thf (0.41 ml, 5 mmol) facilitated the dissolution of the precipitate to a deep brown solution. The solvent was reduced by approx. 40% and stored at −20 °C for 72 hours. The solution yielded a crop of red–orange crystals which were identified as $\{[(S)\text{-}\alpha\text{-}(PhC(H)Me)(CH_2CH{=}CHNa)N]Li\cdot(thf)\}_4$. Yield 0.83 g (68%, not maximised). Mp 107–109 °C. ^{1}H NMR (400 MHz, d_6-benzene, 30 °C): δ 1.36 (m, 4H, thf), 1.66 (d, $J = 6.6$ Hz, 3H), 3.43 (m, 4H, thf), 3.60 (dd, $J = 21.5$ Hz, 2H), 3.65 (q, $J = 6.1$ Hz, 1H), 6.87 (t, $J = 7.2$ Hz, 1H), 7.07 (t, $J = 7.5$ Hz, 2H), 7.29 (d, $J = 7.2$ Hz, 2H), 8.12 (d, $J = 16.5$ Hz, 1H). ^{13}C NMR (100.5 MHz, d_6-benzene, 30 °C): δ 26.0 (thf), 26.6 (CH_3), 65.0 (NCH_2), 65.6 (MeC(H)), 68.3 (thf), 126.2 (*p*-C), 152.5 (CH), 157.8 (*i*-C), 165.8 (CH). Elemental analysis ($C_{60}H_{84}Li_4N_4Na_4O_4$): found (calc.): C 69.5 (69.5); H 7.5 (7.4); N 7.6 (7.4)%.

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