A 1,3-Sigmatropic Rearrangement Revealed in the Solid and Solution State Structures of a Chiral Sodium 1-Azaallyl Complex Derived from (*S*)-*N*-(α-Methylbenzyl)allylamine

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The reaction of *n*BuNa with (*S*)-*N*-(α-methylbenzyl)allylamine, followed by the addition of tmeda, gives a chiral sodium 1-azaallyl complex, $\{[(S)\text{-}\alpha\text{-}[PhC(H)MeN^{\cdot\cdot}C(H)^{\cdot\cdot}CHCH_3)]Na\cdot tmeda\}_2$, as confirmed by single crystal X-ray diffraction and solution NMR spectroscopy, and is most likely the result of a 1,3-sigmatropic rearrangement and subsequent delocalisation within the resulting enamide.

Introduction

There is significant interest in the solution and solid state structures of alkali metal amides and in relating this structural knowledge to explanations of the degree of selectivity that can be achieved when used in enantioselective reactions.[1a−1k] In particular, the successful utilisation of chiral lithium amides in conjugate addition and selective deprotonation reactions with consequent high *ee* values has attracted considerable attention.[2a−2i] In contrast, there have been relatively few investigations into the synthetic utility of Na or K amides in such reactions,[3] not because of unexpected internal structural rearrangements but mainly because these reagents are expected to behave in a similar manner to their Li counterparts, although with greater reactivity and reduced selectivity.

Through recent investigations into the alkali metal complexes derived from commonly used chiral amines, such as α-(methylbenzyl)benzylamine[4a,4b] and α-bis(methylbenzyl)-amine,[5] we have discovered the surprising structural transformations that can occur in the amide moiety on changing the metal from lithium to sodium; α-(methylbenzyl)benzylamine was found to undergo transformation to a 2-azaallyl complex while α-bis(methylbenzyl)amine was cleaved to give a metallated primary enamide. In extending this work we have turned our attention to an analogous amine, (*S*)-*N*-(α-methylbenzyl)allylamine which, because of the ease with which the allyl group is cleaved, has been shown by Davies to be often superior to lithium α-(methylbenzyl)benzylamide in the formation of β-amino acids and β-lactams.[6a−6c] With the allyl group essentially being a less-constrained fragment of a benzyl group we were particularly interested in: (i) whether there would be any close interactions of the metal and the $C(H)=CH_2$ unit, and (ii) the possibility of any β-H elimination processes and the formation of 2-azaallyl species as observed for α-(methylbenzyl)benzylamide and dibenzylamide complexes.[7]

To-date, mono-lithiation reactions of the chiral allylamine in the presence of several typical Lewis donors has produced only a series of deep red and orange coloured oils. However, on moving to studying the heavier metal complexes we found that reaction with *n*BuNa, followed by addition of tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), is one of the few reactions which has, so-far, produced a crystalline product.

The large yellow crystals isolated from the reaction have been identified by single crystal X-ray diffraction to be the dimeric azaallyl complex $\{[(S)\text{-}\alpha\text{-}[PhC(H)MeN^{\cdot\cdot}C(H)^{\cdot\cdot}CHCH_3)]Na\cdot tmeda\}_2$ (**1**), with ^1H and ^{13}C NMR spectroscopy indicating that this configuration is retained in solution.

Results and Discussion

The two methods by which crystals of **1** were obtained are outlined in Scheme 1. The addition of the amine to *n*BuNa produces a pale brown suspension. Subsequent addition of tmeda causes dissolution to a red solution from which crystals are obtained over several days at 4 °C. Since we have not yet been able to obtain a crystalline product using the typical tridentate donor pmdta (*N*,*N*,*N*′,*N*′,*N*′′-pentamethyldiethylenetriamine), one equivalent of THF was added in an attempt to deaggregate the dimer in order to study possible 2-azaallyl formation. However, this again resulted in crystals of **1** as the exclusive product. We did note, though, that if more than one equivalent of THF is

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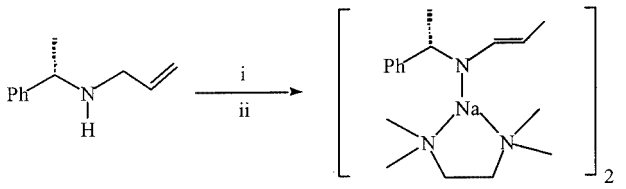
added it can be difficult to obtain a solid product. Over time this solution becomes very dark red and may indicate some further reaction including the base-catalysed ring opening of the THF.



Scheme 1. Syntheses of [{(*S*)-α-[PhC(H)MeN⋯CH⋯CHCH$_3$]}Na·tmeda]$_2$ (**1**); i) *n*BuNa, hexane, tmeda, room temp; ii) *n*BuNa, hexane, tmeda/thf, room temp.

The crystal structure of **1**, shown in Figure 1, is a noncentrosymmetric dimer (monoclinic, $P2_1$) in which each of the two "monomers" adopts a different configuration. These are shown in Figure 2 and differ with respect to the positional exchange of the Ph and Me groups within the benzylmethyl moiety. An analysis of the bond lengths in the N1−C9−C10 [1.365(3), 1.345(3) Å] and N2−C20−C21 [1.370(3), 1.331(3) Å] fragments indicates that **1** is best described as an η^1-*N*-azaallyl complex, and most likely results from a 1,3-sigmatropic rearrangement to an enamide and subsequent delocalisation of the negative charge (Figure 3).

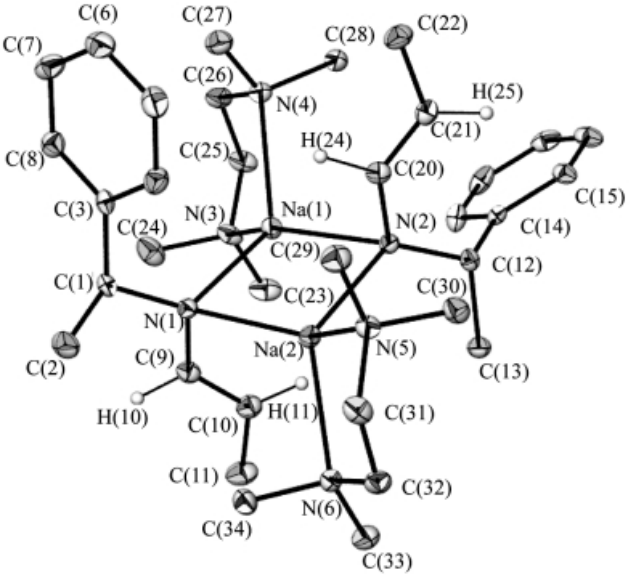


Figure 1. Molecular structure of [{(*S*)-α-[PhC(H)MeN⋯C(H)⋯CHCH$_3$]}Na·tmeda]$_2$ (**1**); thermal ellipsoids at 30% probability; selected bond lengths (Å) and angles (°); Na1−N1 2.410(2), Na1−N2 2.408(2), Na1−N3 2.480(2), Na1−N4 2.516(2), Na2−N1 2.411(2), Na2−N2 2.389(2), Na2−N5 2.500(2), Na2−N6 2.512(2), N1−C1 1.468(3), N1−C9 1.365(3), C9−C10, 1.345(3), C10−C11 1.510(4), N2−C12 1.451(3) N2−C20 1.370(3), C20−C21 1.331(3) C21−C22 1.519(3); N1−Na1−N2 96.78(7), N1−Na2−N2 97.27(7), Na1−N1−Na2 82.43(6), Na1−N2−Na2 82.94(6), C1−N1−C9 112.83(19), N1−C9−C10 128.8(2), C9−C10−C11 123.7(3), N2−C20−C21 134.1(2), C20−C21−C22 123.0(2)

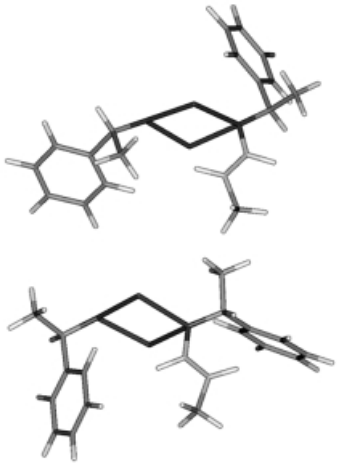


Figure 2. View relative to the $(NaN)_2$ ring of the relationship of the two different "monomers" found in dimeric **1**; tmeda has been omitted for clarity

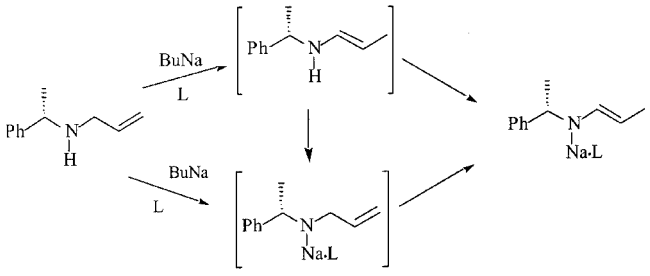


Figure 3. Possible routes of formation for **1**; 1,3 sigmatropic rearrangement and enamide and azaallyl configurations; L = tmeda

The core feature of **1** is the common structural motif of a central four-membered $(NaN)_2$ ring about which the amido moieties are in a *trans* arrangement.[8] However, on this occasion the four-membered ring is not planar but adopts a very shallow butterfly conformation, deviating from the plane by 5.7°. A more general analysis of the structure shows that one phenyl ring adopts an orientation almost co-planar with the $(NaN)_2$ ring and almost perpendicular to the other phenyl ring. This places C13 close to Na2 but, at about 3.4 Å, is beyond what would be considered a reasonable bonding distance (the sum of the van der Waals radii is 3.2 Å). The tetrahedral environment at each N is extremely distorted, most likely for steric reasons, with the azaallyl groups forming acute angles in relation to the $(NaN)_2$ ring. Thus, N2−N1−C9 and N1−N2−C20 are 103.7° and 96.6°, respectively, while the concomitant angles to the benzylic carbon are 142.9° for N2−N1−C1 and 149.0° for N1−N2−C12. So, while the formal coordination number of each Na centre is four, each is able to engage in very short compensatory agostic contacts with nearby C and H atoms of the azaallyl groups. The closest contacts for Na1 are 2.921(3) Å to C9 and 2.818(3) Å to C20, while the comparable distances for Na2 are 3.012(3) Å (C20), 2.923(3) Å (C9) and 3.022(3) Å (C10). Similar close con-

tacts have recently been observed in the uncomplexed sodium amide dimer $[(PhMe_2Si)(Me_3Si)NNa]_2$.[8] The orientation of the azaallyl groups, which deviate from an ideal C20−N2−N1−C1 plane by 14.8°, are nonsymmetrical in relation to the $(NaN)_2$ ring. The hydrogen (H24) on C20 overhangs the $(NaN)_2$ ring, dissecting the two metal centres at distances of 2.75 Å (Na1−H24) and 3.01 Å (Na2−H24), while hydrogen H10 on C9 points away from the ring leaving the hydrogen (H11) on C10 to sit between the two Na cations at distances of 2.74 Å (Na1) and 2.57 Å (Na2). Within the ring the Na−N bond lengths are shorter than those typically observed for dimeric sodium amides {c.f. $[(i\text{Pr})_2\text{NNa·tmeda})]_2$,[9] 2.441(2)-2.453Å; [Cy(*i*Pr)-NNa·tmeda]$_2$ [9] 2.438(2), 2.443(2) Å} but are similar to those observed for $[(PhCH_2)_2\text{NNa·tmeda})]_2$ [10] (2.397, 2.412 Å), which tends to be a reflection of the steric nature of the groups in the amide moiety.

Solution NMR spectra (^{1}H, ^{13}C, COSY and HMQC) were obtained in three solvents; [D$_6$]benzene, [D$_8$]toluene and [D$_8$]THF with variable temperature experiments conducted in [D$_8$]toluene (down to −80 °C) and in [D$_8$]THF (down to −90 °C). At 30 °C the same basic spectra were observed in all three cases, with each confirming that the complex had undergone a 1,3-sigmatropic rearrangement and that the azaallyl configuration, observed in the crystal structure, is retained in solution. In comparing the ^{1}H spectra in [D$_8$]THF of **1**, shown in Figure 4, and the starting allylamine the most telling features are the complete disappearance of the signals of the NCH_2 protons of the amine and the appearance of a doublet at δ = 1.57 ppm (CH_3), which, from 2D experiments, correlates with a doublet of quadruplets at δ = 3.25 ppm (1 H), which in turn correlates with a new doublet at δ = 6.59 ppm ($J_{H,H}$ = 13 Hz, 1 H), which we have assigned to the single H remaining from the transformed NCH_2 group. While this doublet is very sharp in [D$_8$]THF, in spectra obtained in [D$_8$]benzene and [D$_8$]toluene it is slightly broader and is partially obscured by the aromatic signals.

The retention of the azaallyl configuration in solution is supported by an analysis of the change in chemical shift for the central H in the former allyl group (now H25 and H11 in **1**). An upfield shift of 3 ppm is observed relative to its position in the free amine, while the associated C, which now appears at δ = 74.2 ppm, has shifted upfield by almost 60 ppm, both indicating a significant reduction in double bond character and charge distribution. All of the *C*H signals in the ^{13}C spectrum at 30 °C are weak and broad with a large downfield shift observed for the new N*C*H, which ^{1}H/^{13}C correlation and coupling experiments showed to be directly under the signal for the quaternary carbon at δ = 154.1 ppm.

Variable temperature experiments in [D$_8$]THF and [D$_8$]toluene did reveal slightly different solution behaviour for each complex, most likely resulting from deaggregation occurring in THF and retention of the dimer in toluene. As such the [D$_8$]THF spectra are slightly less complex. Looking first at the toluene spectra. At 30 °C the Ph(Me)C*H* protons appear at δ = 4.2 ppm and the C*H* protons (H11 and H25) in the azaallyl group at δ = 3.7 ppm. By −60°C 2D ^{1}H/^{1}H correlation indicates that these split into six distinct signals, four relating to Ph(Me)C*H* protons and two for the azaallyl protons. All the other protons also show substantially differing environments at low temperature. In THF at −60°C the corresponding central azaallylic proton, which is located at δ = 3.25 ppm at 30 °C, splits in two, shifting to δ = 2.86 ppm and δ = 3.57 ppm, with integrals indicating a 2:1 ratio. The Ph(Me)C*H* protons also split in two in a similar ratio, although the signals are not distinct but overlap. The azaallylic protons N⋯C(*H*)⋯C (H10 and H24), initially observed at δ = 6.59 ppm, are also split in two though one is very sharp and the other broad. The Me signals simply broaden.

In attempting to understand the low temperature spectra we undertook some basic molecular modelling experiments.[11] These indicated that the dimer is extremely crowded with very little opportunity for internal reorganisation of the molecule. The *trans* configuration observed within the azaallyl moiety in the crystal structure, and confirmed in solution, is retained due to a significantly restricted rotation around both the azaallyl C⋯N and C⋯C bonds, and the C_{chiral}−N bond, with the latter being a lower energy process. As such, the low temperature spectra in [D$_8$]toluene is consistent with the crystal structure and the two different "monomer" configurations highlighted in Figure 2. The complexity is a consequence of the two different azaallyl environments, with each of the four possible conformations of the benzylmethyl groups resulting from restricted 120° rotations.

In [D$_8$]THF the NMR spectra are consistent with deaggregation to a monomer containing coordinated THF. A model monomer with a single tmeda and a THF was only marginally less restricted than the dimer. However the lower energy barriers to rotation at each of the N−C bonds means that the various more simple possible configurations caused by rotation of the benzylmethyl group are not evident until lower temperatures. And, in fact, they do begin to appear in the spectrum obtained at −90 °C.

1-Azaallyl complexes of the alkali metals are almost exclusively formed by deprotonation of ketimines or aldimines, or by the 1,2-addition to nitriles. The variety of complexes and their bonding modes formed have been reviewed recently.[12] However, it is only in the last few years that an η^1 structural arrangement has been observed with characterisation of the complexes $[\{CH_3CH_2CH_2C(H)C⋯(t\text{Bu})⋯N(H)Li·(hmpa)\}]_n$ and $[\{CH_3CH_2CH_2C(H)C⋯(t\text{Bu})⋯N(H)Na·(hmpa)_2\}]_n$, formed in the reaction of either *n*BuLi or *n*BuNa with *t*BuCN followed by a 1,3-sigmatropic H shift.[13] The azaallyl arrangement in these complexes is calculated as the most stable configuration and is retained in solution, as we observed for **1**. In contrast, though, **1** is formed by deprotonation and metallation of a secondary allylamine leading to the formation of a metal enamide. Several studies have indicated that the base-catalysed isomerisation of *N*,*N*-allylamines in the presence of *t*BuOK, LDA or KH to give the corresponding enamine is energetically favourable.[14a−14e] Whether this isomerisation can oc-

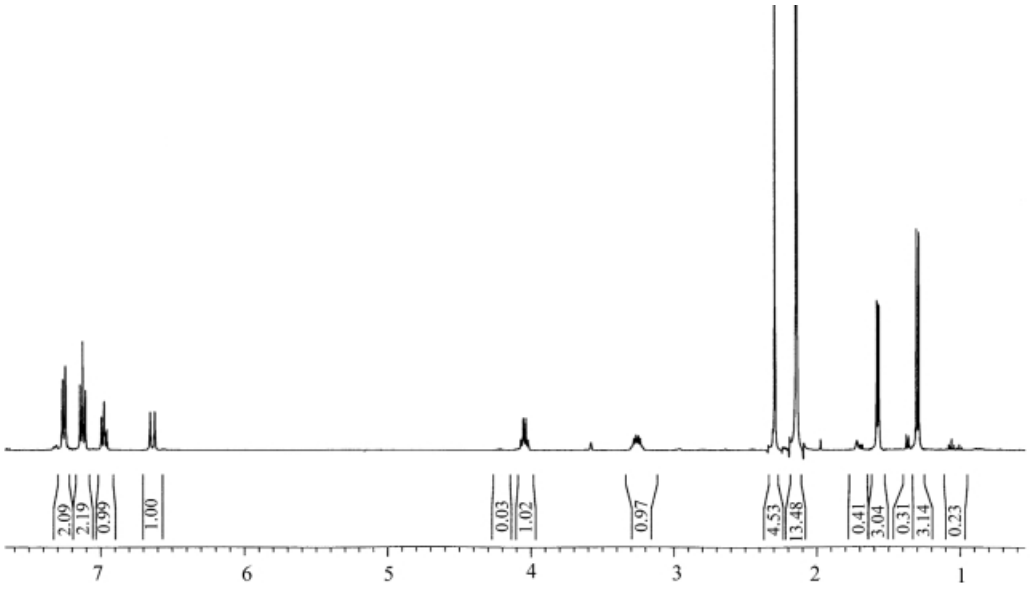


Figure 4. ^{1}H NMR of **1** in [D_8]THF showing the new CH_3 (δ = 1.57 ppm) and CH (δ = 6.59 ppm) signals from the rearrangement of the allyl group

cur with secondary allylamines prior to deprotonation taking place or occurs after metallation requires further study. We did not observe any isomerisation of the (*S*)-*N*-(α-methylbenzyl)allylamine prior to addition of the metallating reagent.

Evidence from the use of adducts of lithium *N*-(α-methylbenzyl)allylamide in conjugate addition reactions suggests that the amide moiety is in the allylic form prior to final deallylation, although cleavage of the allyl group requires ketimine formation prior to hydrolysis.[6,15] In light of this we are continuing our attempts to structurally characterise a lithium complex in the hope of discovering whether this rearrangement is general for the alkali metals and whether there are any important synthetic implications.

Experimetal Section

General Remarks: All compound manipulations were carried out under 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.[16] *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). 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.

Synthesis of 1: (*S*)-*N*-(α-Methylbenzyl)allylamine (0.81 g, 5.0 mmol) was added dropwise to a suspension of *n*BuNa (0.43 g 5 mmol) in hexane (20 mL) at room temperature resulting in a light brown coloured suspension. After 30 min tmeda (0.76 mL, 5.0 mmol) was added causing dissolution of the suspension and formation of a deep red solution. On filtration and cooling to 4 °C over several days pale yellow crystals of X-ray quality were produced. Yield 0.91 g, 61% (not maximised), m.p. 85−87 °C. ^{1}H NMR (400 MHz, 30 °C, [D_8]THF): δ = 7.25 (d, ^1J = 7.06 Hz, 2 H, *o*-H), 7.13 (t, ^1J = 7.45, 2 H, *m*-H), 6.97 (t, ^1J = 7.27, 1 H, *p*-H), 6.65 [d, ^1J = 12.54 Hz, 2 H, N-C(*H*)=C], 4.06 (q, ^1J = 6.56, 1 H, PhC(*H*)CH_3], 3.25 (dq, ^1J = 5.78, ^2J = 11.76, 2 H, C-C(*H*)=CH_3), 2.29 (s, 4 H, NCH_2), 2.14 (s, 12 H, NCH_3), 1.57 (d, ^1J = 5.86 Hz, 3 H, C=CH_3), 1.29 [d, ^1J = 6.62 Hz, 3 H, PhC(H)CH_3] ppm. ^{13}C NMR (100.6 MHz, 30 °C, [D_8]THF): δ = 17.2 (CH_3), 27.3 [PhC(H)CH_3], 46.1 (CH_3N), 58.8 (NCH_2), 62.7 [PhC(H)CH_3], 74.2 [C=C(H)-CH_3], 125.3 (*p*-*C*), 127.4 (*m*-*C*), 128.1 (*o*-*C*), 154.1 [*q*-*C*, N-*C*(H)=C] ppm. $C_{34}H_{60}N_6Na_2$ (598.9): calcd. C 68.2, H 10.1, N 14.0; found C 68.4, H 9.8, N 13.8.

Crystallographic Data for 1: $C_{34}H_{60}N_6Na_2$, M = 598.86, T = 123 K, monoclinic $P2_1$, a = 11.006(2), b = 12.009(2), c = 14.255(3) Å, β = 96.51(3)°, V = 1871.9(7) Å^3, D_c = 1.062 g·cm^{-3}, Z = 2; F(000) = 656, $\mu_{Mo\text{-}K_\alpha}$ = 0.83 cm^{-1}, $2\theta_{max}$ = 56.6°, final R, R_w = 0.052, 0.094. N_o = 5318 observed reflections [$I > 2\sigma$ (I)] out of N = 9213, R_{int} = 0.057. GooF = 0.955. The Flack parameter was indeterminate and the final stereochemistry was based on that of the starting amine. The crystal was coated in oil,[17] mounted on a fibre and data collected at 123 K on an Enraf Nonius Kappa CCD diffractometer equipped with Mo-K_α radiation (λ = 0.71073Å). The structure was solved by direct methods (SHELXS-97)[18] and refined by full-matrix least-squares on F^2. All H atoms were located in the difference map and refined isotropically. All other atoms were refined anisotropically.

CCDC-172280 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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