DALTON COMMUNICATION

Amido→azaallyl transformation in sodium amide complexes of (*S*)-α-(methylbenzyl)benzylamine

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Received 15th May 2000, Accepted 22nd June 2000
Published on the Web 12th July 2000

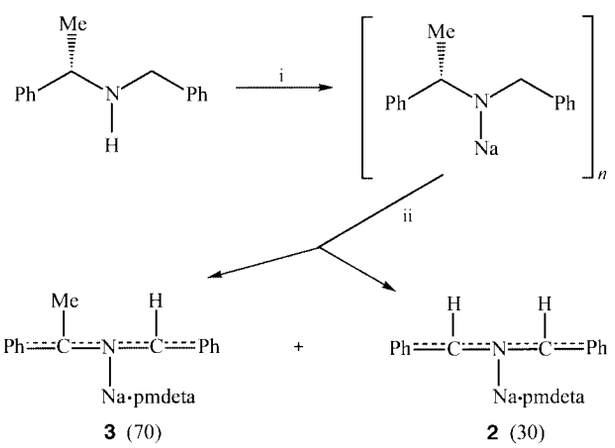
The reaction of (*S*)-{[(Ph(Me)CH)(PhCH$_2$)]NNa}$_n$ with pmdeta (*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine) produces red/green dichroic crystals of the azaallylic complexes {[Ph(Me)CNC(H)Ph]Na·pmdeta}, 3, and {[(PhCH)$_2$N]Na·pmdeta}, 2; by X-ray diffraction 3 is found to be monomeric and structurally similar to the previously characterised 2.

The transformation of the alkali metal (M) complexes of dibenzylamine, [(PhCH$_2$)$_2$NM·(L)$_k$], to give the 1,3-diphenyl-2-azaallyl anion has been studied in detail.[1] It has been shown to occur with Li, Na and K in the presence of the tridentate donor ligand pmdeta (*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine), and with other ligand combinations which allow the complex to adopt a monomeric structure in solution. It has been postulated, and to date all evidence seems to agree, that only when the complex is a monomer in solution is the structural arrangement such that the β-elimination of [MH·(L)$_k$], and its subsequent *in situ* reaction with the imine intermediate thereby formed (PhCH=NCH$_2$Ph), able to occur.[1]

We have been interested in the high degree of selectivity shown by lithium complexes of the closely related chiral amine α-(methylbenzyl)benzylamine, (*R*)- and (*S*)-[(Ph(Me)CH)(PhCH$_2$)NH], in its reactions with α,β-unsaturated esters to give β-amino esters in high ee. As such, we recently reported the solid state structures of two complexes, (*S*)-[(Ph(Me)CH)(PhCH$_2$)NLi·thf]$_2$ and (*R*)-[(Ph(Me)CH)(PhCH$_2$)NLi·pmdeta], **1**; a dimer and monomer respectively.[2] Complex **1** was significant in that no monomer complex of the analogous dibenzylamido anion had been isolated prior to azaallyl formation occuring. However, NMR studies did show that the tranformation could be thermally induced. The synthetic importance of such resonance stabilised anions in heterocycle formation,[3] as well as an interest in the comparative selectivities of Li and Na homochiral amides, has led us to investigate the heavier alkali metal complexes of (*S*)-[(Ph(Me)CH)(PhCH$_2$)NH] and the possibilty of azaallyl complex formation.

Herein, we now report the surprising formation of both {[(PhCH)$_2$N]Na·pmdeta}, **2**, and {[Ph(Me)CNC(H)Ph]Na·pmdeta}, **3**, from the reaction of (*S*)-[(Ph(Me)CH)(PhCH$_2$)NH] with ^{n}BuNa in the presence of pmdeta. We also present the solid state structure of **3**, as authenticated by single crystal X-ray diffraction.

As represented in Scheme 1, the amine, (*S*)-[(Ph(Me)CH)(PhCH$_2$)NH], was added dropwise to a suspension of ^{n}BuNa in hexane producing a red coloured solution and suspension almost instantaneously. The reaction mixture was allowed to stir for 30 minutes before one equivalent of pmdeta was added. After one hour hexane was removed *in vacuo* and toluene added. Gentle warming allowed for complete dissolution of the suspension. On allowing the solution to stand at ambient temperature over 24 h a large crop of dichroic red/green needle crystals was produced (yield 63%, not maximised). Not



Scheme 1 Transformation of the unsolvated sodium amide to the azaallyl complexes, **2** and **3**. Reaction conditions: i, ^{n}BuNa (one equiv.), hexane, 25 °C, 30 min, ii, pmdeta (one equiv.), toluene.

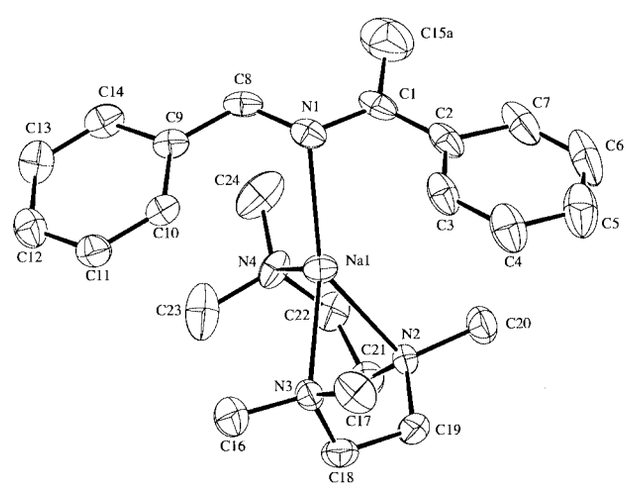


Fig. 1 Molecular structure of **3**. Me is disordered at C1 and C8 sites. Only the Me (65%) on C1 is shown to avoid confusion. All H atoms have been removed for clarity. Selected bond lengths (Å) and angles (°); Na1–N1 2.382(2), Na1–N2 2.451(2), Na1–N3 2.534(2), Na1–N4 2.488(2), N1–C1 1.342(3), N1–C8 1.330(3), C8–C9 1.439(3), C1–C2 1.432(3), C1–N1–Na1 103.2(1), C8–N1–Na1 112.4(1), C1–N1–C8 123.6(2), N1–Na1–N2 140.52(6), N1–Na1–N3 137.23(6), N1–Na1–N3 74.68(6), N1–Na1–N4 99.33(7).

unexpectedly, they closely resemble the crystals produced in the analogous dibenzylamine reaction.†

Prior to any other qualitative analysis, one of the crystals was mounted under oil and placed on the X-ray diffractometer. The result was the crystal structure of the expected complex, **3**, shown in Fig. 1.‡ The complex is monomeric (space group,

DOI: 10.1039/b003826l

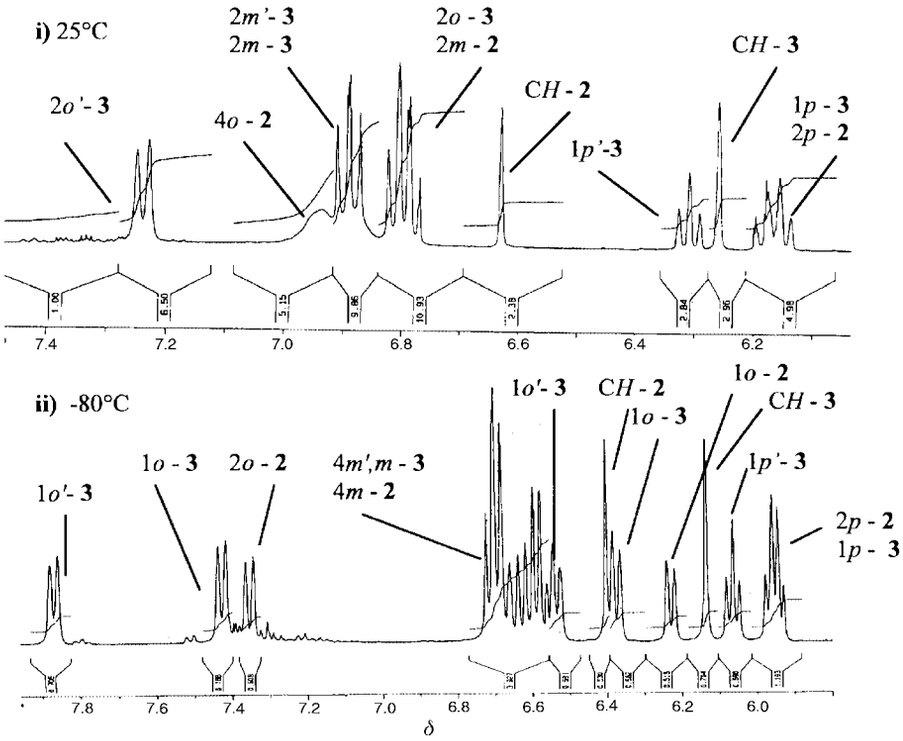


Fig. 2 ^{1}H NMR of **2** and **3** in d_8-thf. (i) 25 °C, (ii) −80 °C. Note; **3** is unsymmetrical and labelled *o*, *m*, *p* and *o*′, *m*′, *p*′.

$P2_1/n$), and reveals that the amido→azaallyl transformation had indeed occurred. The structure is comparable with that of **2** with the Na cation being 4-coordinate, in an extremely distorted tetrahedral environment, and situated approximately 50° above the almost planar delocalised anion.[4] It does not lie symmetrically between the two phenyl rings but is located slightly towards the N1–C1 bond rather than N1–C8. In comparison with **2**, perhaps as a result of the presence of the methyl group, the azaallylic anion appears to be slightly more concave in nature. The Na–N bonds in **3** are slightly longer than in **2**; Na–N(1–4) 2.382(2), 2.451(2), 2.534(2), 2.488(2) Å for **3** as against 2.348(2), 2.455(3), 2.497(3) and 2.529(3) Å for **2**.

It was with great surprise then that the ^{1}H and ^{13}C NMR spectra, in d_8-thf, revealed that two complexes were present in solution, Fig. 2. Rather than the expected singlet for PhC*H* in the aromatic region the ^{1}H spectrum in fact showed there to be two; at δ 6.25 and 6.66. From a comparison of chemical shifts and integral values, and with the aid of ^{1}H 2D correlation experiments, we have assigned the signals as belonging to **3** and the 1,3-diphenyl-2-azaallyl complex, **2**. From integral values the relative ratio of **2**:**3** is calculated at approximately 30:70, with the overall amine:pmdeta ratio being 1:1. The signals corresponding to complex **2** are located at δ 6.95 (*o*-C*H*), 6.86 (*m*-C*H*), 6.66 (PhC*H*) and 6.18 (*p*-C*H*) which are similar in chemical shift and appearance to those previously described.[1] In contrast to **2**, and highlighting the unsymmetrical nature of the anion in **3**, there are two signals for each set of *ortho* and *para* phenyl protons; δ 7.23, 6.68 (*o*) and 6.32, 6.18 (*p*). The *meta* protons are located at δ 6.91 with PhC*H* at δ 6.25 and Me at 2.11. NMR studies previously undertaken on **2** had shown that close interactions between two of the *o*-CH positions and the Na cation result in the structure being 'locked' at low temperature.[5] A similar locking is evident from variable temperature studies carried out on **3**, 30 to −80 °C, though on this occasion coalescence occurs closer to −45 rather than −15 °C as observed for **2**. NMR studies on the amine itself, which was both synthesised in-house and commercially obtained from Aldrich, showed no contamination by dibenzylamine.

The presence of the two complexes in the solid state, the crystals of which are visually indistinguishable, was further confirmed by a melting point analysis of individual isolated crystals. Some crystals melted between 167 and 169 °C, which corresponds to the literature value for **2**,[1] and others at 156–157 °C, which we assign to complex **3**.

If the proposed mechanism for azaallyl formation in the dibenzylamido to 1,3-dipheny-2-azaallyl transformation is correct, *viz* β-elimination of [NaH·pmdeta] and subsequent H_2 elimination on its reaction with the newly formed imine, then one possibility would be that the formation of **2** and **3** in the above reaction occurs initially *via* the β-elimination of [NaH·pmdeta] and [MeNa·pmdeta] from (*S*)-{[(Ph-(Me)CH)(PhCH$_2$)]NNa·pmdeta}, followed by H_2 and MeH elimination on their reaction with the two imines formed in solution.

The experiment which we describe above, which is the highest ratio of **2**:**3** we have yet obtained, is close to the statistical distribution expected if there was no energy difference between MeNa and NaH elimination. However, elimination of alkyllithiums has been calculated to be energetically, significantly less favourable than for LiH, although the presence of a Lewis donor can influence the process.[6] It has also been noted that alkyllithium elimination is confined to systems in which the anion is highly stabilised,[7] which would be consistent with the formation of the fully delocalised [Ph(H)CNC(H)Ph]$^-$ and [Ph(Me)CNC(H)Ph]$^-$ systems in **2** and **3**. While the elimination of LiH[8] is a well recognised decomposition pathway in many compounds there are very few descriptions of synthetic procedures in which alkyl– or aryl– Group 1 eliminations occur. One recent example of interest is the elimination of benzyllithium, which is implicated in the formation of (Me$_2$CH)C(=NMe)SiMe$_2$Ph from the reaction of PhMe$_2$SiLi with *N*-benzyl-*N*-methylamide.[9]

An alternative, and perhaps more likely mechanism, involves the nucleophilic attack of [NaH·pmdeta] on the Ph(H)C–Me bond in the benzaldimine intermediate. This would result in MeH elimination and the formation of the highly stabilised Na azaallylic anion. Competition with metallation of the imine *via* H abstraction by [NaH·pmdeta] and consequent H_2 elimination would give the observed mixture of **2** and **3**.

Preliminary investigations into the reactions of (*S*)-[(Ph(Me)-CH)(PhCH$_2$)NH] with ^{n}BuK and two equivalents of pmdeta, and ^{n}BuNa with the pseudo-tridentate system tmen/thf,

have also shown the formation of the 1,3-diphenyl-2-azallyl complex, though in reduced quantity (*ca*. 10%). The yield of the MeH eliminated product is not consistent and we are currently optimising the reaction conditions and investigating which Lewis donors, or combination of Lewis donors, best promote the elimination and what the extent of variation is when using Li, Na, or K. We are also undertaking MO calculations in order to compare the relative energetics of elimination of MeM and MH from model complexes and ascertaining whether other elimination pathways are possible.

Acknowledgements

We thank the Australian Research Council and Monash University for financial support. We would also like to thank the referees for very useful observations.

Notes and references

† Analytical data for **3**. Overall yield 63% (**2** + **3**), mp 156–157 °C, ^{1}H NMR (400 MHz, d_8-thf, 25 °C): signals relating to **3**; δ 7.23 (d, 2H, J^2 8 Hz, *o*-C*H*), 6.91 (m, 4H, *m*-C*H*), 6.68 (m, 2H, *o*-C*H*), 6.32 (t, 1H, J^3 12 Hz, *p*-C*H*), 6.25 (s, 1H, PhC*H*), 6.18 (m, 1H, *p*-C*H*), 2.11 (s, 3H, Me). Signals relating to **2**; δ 6.95 (s (br), 4H, *o*-C*H*), 6.86 (m, 4H, *m*-C*H*), 6.66 (s, 2H, PhC*H*), 6.18 (m, 2H, *p*-C*H*). pmdeta; δ 2.34 (d of m, 8H, J^2 28 Hz, NCH_2), 2.19 (s, 12H, NMe_2), 2.05 (s, 3H, NMe).

Note: overall ratio of amido (**2** + **3**):pmdeta is 1:1 and of **2**:**3** approximately 30:70. Integral values given are only consistent within each moiety and not with each other. ^{13}C NMR (100.6, 25 °C, d_8-thf): δ 146.2 (*ipso*-*C*, **2**), 145.8 (*ipso*-*C*, **3**), 145.4 (*ipso*-*C*, **3**), 129.3 (*o*-*C*H), 129.1 (*m*-*C*H), 128.9 (o, *m*-*C*H), 119.1 (Ph*C*H), 116.4 (*o*-*C*H), 115.5 (Ph*C*H), 114.9 (*p*-*C*H), 111.3 (*p*-*C*H), 111.2 (Ph*C*(Me)), 106.1 (*p*-*C*H), 58.6 (NCH_2), 56.7 (NCH_2), 46.0 (NMe_2), 43.1 (NMe), 12.8 (Me).

‡ Crystallographic data for **3** (Enraf Nonius, Kappa CCD, crystals mounted in oil). $C_{24}H_{37}N_4Na$, $M = 404.57$, $T = 123$ K, monoclinic, $P2_1/n$ (no. 14), $a = 10.7674(4)$, $b = 15.6032(3)$, $c = 14.1064(4)$ Å, $\beta = 94.866(1)°$, $V = 2361.4(1)$ Å^3, $D_c = 1.138$ g cm^{-3}, $Z = 4$; $F(000) = 880$, $\mu_{MoK\alpha} = 0.84$ cm^{-1}, $2\theta_{max} = 55.8°$, final R, $R_w = 0.061$, 0.043. $N_o = 3156$ 'observed' ($I > 2\sigma(I)$) reflections out of $N = 7094$ unique. GoF 2.82. The methyl group on [Ph(Me)CNC(H)Ph]$^-$ is disordered over the C8 and C1 sites 35:65. CCDC reference number 186/2051. See http://www.rsc.org/suppdata/dt/b0/b003826l/ for crystallographic files in .cif format.

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