Crystal structures of (*R,R*)-{[Ph(Me)CH]$_2$NLi·pmdeta} and {[PhC(=CH$_2$)NH]Na·pmdeta}$_2$: alkali metal amides derived from (*R,R*)-bis(α-methylbenzyl)amine†

Philip C. Andrews,* Peter J. Duggan, Melissa Maguire and Peter J. Nichols

Department of Chemistry, Monash University, Clayton, Melbourne, Victoria 3800, Australia. E-mail: p.andrews@sci.monash.edu.au

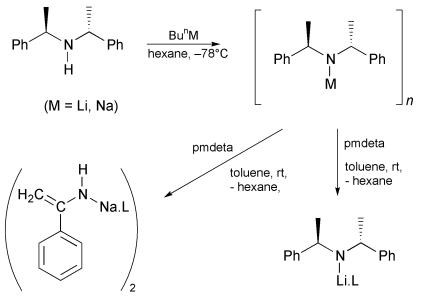
Received (in Cambridge, UK) 14th September 2000, Accepted 31st October 2000
First published as an Advance Article on the web

The reaction of Bu^{n}M (M = Li, Na) with [(*R,R*)]-bis(α-methylbenzyl)amine in the presence of pmdeta results in the formation of the chiral lithium amide complex (*R,R*)-{[Ph(Me)CH]$_2$NLi·pmdeta} and, remarkably, the sodium enamide, {[PhC(=CH$_2$)NH]Na·pmdeta}$_2$; both compounds have been authenticated by single crystal X-ray diffraction.

Our knowledge of the structural chemistry of alkali metal amides is now firmly established and indeed, many of the structural features found in these complexes have become largely predictable. As a result of their widespread applicability in synthesis most of our understanding has come from detailed solution and solid state studies on lithium amides, though there has been a steady increase in the study of the heavier metal (Na, K) complexes.[1,2] Limited hydrocarbon solubility, increased reactivity and possible reductions in selectivity are the reasons often quoted for the limited use of Na and K complexes, though implicit within this is also the belief that while structural differences will occur as a result of increasing cation size, the complex formed and the resulting chemistry will be essentially similar to that of the lithium counterpart. While most structural studies have indicated this is probably the case, there is also the possibility that the change in metal can effect dramatic and unexpected structural outcomes, which is important given that many alkali metal reagents are generated and used *in situ*.[3]

We reported recently that in the presence of pmdeta (*N,N,N′,N′,N″*-pentamethylethylenetriamine), α-(methylbenzyl)benzylamido lithium will produce the expected monomer, (*R*)-[(Ph(Me)CH)(PhCH$_2$)NLi·pmdeta], **1**,[4] while the sodium complex will undergo the facile low-temperature transformation to a 2-azaallylic anion system, {[Ph(Me)C⋯N⋯C(H)Ph-]Na·pmdeta} **2**,[6] as has also been described, in detail, for the analogous alkali metal complexes of dibenzylamine.[7] In comparing the Li complexes, the added methyl group increased the stability of the amide complex to azaallyl formation. We also noted the surprising paucity in solid and solution state structural information which is available on enantiomerically pure chiral alkali metal amides,[4] especially in light of their important role in synthesis.[5] With this in mind, we extended our studies to the complexes of [*R*-(*R**,*R**)]-bis(α-methylbenzyl)amine and herein report the solid state structure of (*R,R*)-{[Ph(Me)CH]$_2$NLi·pmdeta}, **3**, and the remarkable transformation of the amide to an enamide with crystallisation of {[PhC(=CH$_2$)NH]Na·pmdeta}$_2$ **4**. Both structures have been determined by single crystal X-ray diffraction.

The preparative methods towards **3** and **4** are shown in Scheme 1. Complex **3** was prepared by the addition of Bu^{n}Li to a hexane solution of (*R,R*)-bis(α-methylbenzyl)amine at −78 °C. Ligand pmdeta (1 equiv.) was added to the bright orange solution on reaching ambient temperature, resulting in a yellow precipitate which was redissolved on addition of toluene. Cooling the pale brown solution to −20 °C resulted in a large crop of pale yellow prismatic crystals, yield 67%.†



Scheme 1 Synthesis of (*R,R*)-{[Ph(Me)CH]$_2$NLi·pmdeta} **3** and [PhC(=CH$_2$)N(H)Na·pmdeta]$_2$ **4** (L = pmdeta).

Synthesis of **4** was by essentially the same method, the difference being that the amine was added to a hexane suspension of Bu^{n}Na at −78 °C.† Pale yellow crystals of **4** were obtained at room temperature after *ca*. six days, but only after reduction of solvent to a minimum (*ca*. 5 ml for 5 mmol reaction).†

Complex **3** crystallises in the orthorhombic space group $P2_12_12_1$ and is monomeric, as shown in Fig. 1.‡ In general, the structure is similar to that previously described for **1**;[4] the Li centre is four coordinate, bonding with the three available N atoms of pmdeta and N$_{amido}$, is in a distorted tetrahedral environment and with comparable Li–N bonding distances. The most interesting feature of the structure though is the arrangement of the methyl groups, both in terms of their location in relation to the metal centre and their close proximity to the plane defined by C9, N1 and C1. Close H$_3$C⋯Li interactions of 2.74 and 2.78 Å in the dimer (*R,R*)-{[Ph(Me)CH]$_2$NLi·thf}$_2$ are described as being of possible importance in explaining stereochemical outcomes in deprotonation reactions.[8] Given the similarity in the conformations adopted by the amido moieties

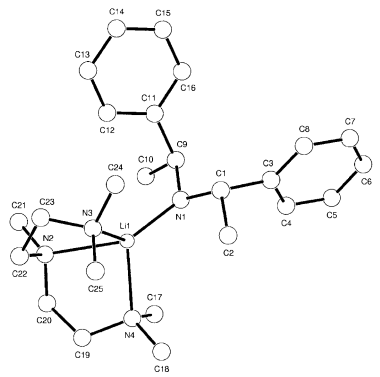


Fig. 1 Molecular structure of (*R,R*)-{[Ph(Me)CH]$_2$NLi·pmdeta}, **3**: all H omitted for clarity. Selected bond distances (Å) and angles (°); Li(1)–N(1) 1.949(6), Li1–N4 2.170(6), Li1–N3 2.222(6), Li1–N2 2.343(6), N1–C1 1.4454, N1–C9 1.446(4); N1–Li1–N4 117.1(3), N1–Li1–N3 119.8(3), N4–Li1–N3 111.2(3), N1–Li1–N2 137.1(3), N4–Li1–N2 81.7(2), N3–Li1–N2 81.9(2), C1–N1–C9 110.4(2), C1–N1–Li1 117.2(3), C9–N1–Li1 125.3(3), N1–C1–C3 115.9(3), N1–C1–C2 109.3(3), C3–C1–C2 106.3(3).

† Electronic supplementary information (ESI) available: analytical data for **3** and **4**. See http://www.rsc.org/suppdata/cc/b0/b007482i/

DOI: 10.1039/b007482i

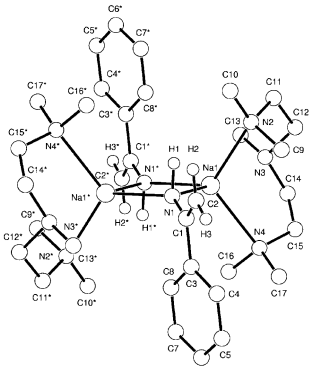


Fig. 2 Molecular structure of $[PhC(=CH_2)N(H)Na{\cdot}pmdeta]_2$ **4**; all H except those on CH_2 and NH omitted for clarity. Selected bond distances (Å) and angles (°); Na1–N1* 2.430(3), Na1–N1 2.406(3), Na1–N2 2.518(4), Na1–N3, 2.577(3), Na1–N4 2.578(4), N1–C1 1.365(4), C1–C2 1.368(5); N1–Na1–N1* 92.9(1), Na1–N1–Na1* 87.1(1), N1–Na1–N2 89.5(1), N1–Na1–N3 160.7(1), N1–Na1–N4 116.7(1), N1–Na1–N2 126.5(1), Na1–N1–C1 128.0(2), Na1–N1–C1 135.4(2), N1–C1–C2 126.5(4), N1–C1–C3 114.3(3).

in the dimeric thf and monomeric pmdeta complexes of $[(Ph(Me)CH)(PhCH_2)NLi]$ it might have been expected that such close interactions and amide conformations would be carried through from (R,R)-$\{[Ph(Me)CH]_2NLi{\cdot}thf\}_2$ into the structure of **3**. As such, in viewing the solid state structure of **3** and the location of the Me groups it would be easy to conclude that the metal centre is dictating the orientation of the Ph(Me)CH moieties. However, while the asymmetry in $Li{\cdots}CH_3$ interactions observed in (R,R)-$\{[Ph(Me)CH]_2NLi{\cdot}thf\}_2$ remains, the analogous distances in **3** are significantly longer at 2.989 Å (C2–Li), and 3.325 Å (C10–Li). The closest distance is therefore only comparable with that observed in **1**, of 3.04 Å. Also, the amido moieties in the thf and pmdeta structures of (R,R)-$[Ph(Me)CH]_2NLi$ do not adopt a similar orientation. In **3** the Me carbons and N_{amido} are almost coplanar, which is evident if we consider a plane defined by N1, C9, C1 above which C10 and C2 lie 4.2 and 15.5°, respectively.

While the monomeric nature of **3** in the solid state was somewhat predictable the crystalline product and subsequent structure obtained from the Na reaction was not. We were probing whether the additional Me groups on the benzylic carbons would effect the formation of an azaallylic anion, as such the formation of the sodium enamide dimer, **4**, was entirely unexpected.

Complex **4** crystallises in the triclinic space group $P\bar{1}$ and is, as evident in Fig. 2, dimeric.‡ What is initially striking about the complex is that it is an amide, with a formal M–N bond, rather than a 1-azaallyl complex in which the Na cation is located above the N∴C∴C fragment as observed in similar systems,[9] and which may have been anticipated on metalation of a primary enamine. The propensity noted for ketimides to undergo a 1, 3 sigmatropic rearrangement to 1-azallyl complexes may hint at a possible mechanism for the formation of **4** involving the formation of [PhC(Me)=NNa] and $PhC(H)=CH_2$ as intermediates. Whether this involves the formation and subsequent cleavage of a C∴N bond from a 2-azaallyl intermediate complex is under investigation. A proton shift from Me onto N as found in $[\{CH_2{\therefore}C(^tBu){\therefore}N(H)Li{\cdot}hmpa\}_2]$[10] with subsequent stabilisation of the enamide over the 1-azallyl structure *via* dimerisation in the solid state would result in **4**. The ^1H and ^{13}C NMR do not give a conclusive answer as to whether the complex in solution adopts a 1-azaallyl arrangement, though the chemical shift of the CH_2 doublet, centred on δ 2.65, is significantly upfield from the region expected for $PhC{=}CH_2$ and is perhaps indicative of a reduction in the double bond character.

The main features of **4** are the central cyclic $(NNa)_2$ ring core about which the amide moieties adopt a *trans* configuration. This is wholly consistent the two other structurally characterised sodium primary amides with which **4** can be compared, $[PhN(H)Na{\cdot}pmdeta]_2$ **5**,[11] and $[2\text{-}PhOC_4H_6N(H)Na{\cdot}pmdeta]_2$,[12] and is a common feature of many sodium secondary amides.[13] In all three cases the Na cation is five coordinate, however the tripodal connectivity of pmdeta in **5** makes it more closely related to **4**. In **5** the anilino moieties tilt at an angle of 65° relative to the $(NNa)_2$ ring plane, whereas in **4** the amide ligands are directly perpendicular, influenced no doubt by the sp^2 nature of C1.

We thank the Australian Research Council and Monash University for financial support.

Notes and references

‡ *Crystallographic data*: for **3**: $C_{25}H_{41}N_4Li$, M = 404.56, T = 123 K, orthorhombic, space group $P2_12_12_1$, a = 9.987(2), b = 13.692(3), c = 18.553(4) Å, V = 2537.0(9) Å^3, D_c = 1.059 g cm^{-3}, Z = 4; $F(000)$ = 888, μ(Mo-Kα) = 0.64 cm^{-1}, $2\theta_{max}$ = 56.9°, final R, R_w = 0.091, 0.126. N_o = 3246 'observed' [$I > 2\sigma(I)$] reflections out of N = 5769 unique. GOF = 1.10.

For **4**: $C_{13}H_{31}N_4Na$, M = 266.4, T = 123 K, triclinic space group $P\bar{1}$, a = 9.8409(2), b = 9.9864(3), c = 10.7169(2) Å, α = 94.128(1), β = 114.261(2), γ = 98.962(1)°, V = 937.59(4) Å^3, D_c = 0.944 g cm^{-3}, Z = 2; $F(000)$ = 296, μ(Mo-Kα) = 0.77 cm^{-1}, $2\theta_{max}$ = 56.6°, final R, R_w = 0.084, 0.083. N_o = 2457 'observed' [$I > 2\sigma(I)$] reflections out of N = 4391 unique. GOF = 2.04.

Crystallographic data collected on a Nonius Kappa CCD with crystals mounted under oil. All H atoms placed in calculated positions.

CCDC 182/1835. See http://www.rsc.org/suppdata/cc/b0/b007482i/ for crystallographic files in .cif format.

1 R. E. Mulvey, *Chem. Soc. Rev.*, 1998, **27**, 339; R. E. Mulvey, 1991, **20**, 167.

2 J. D. Smith, *Adv. Organomet. Chem.*, 1999, **43**, 267; M. A. Beswick and D. S. Wright, *Comprehensive Organometallic Chemistry II*, ed. E. W. Abels, F. G. A. Stone and G. Wilkinson, Pergamon Press, New York, 1995, ch. 1; E. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1501; F. S. Mair and R. Snaith, *Dictionary of Organometallic Compounds*, Chapman & Hall, London–New York, 1995, ch. 1; K. Gregory, P. v. R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47.

3 C. Lambert and P. v. R. Scheleyer, *Methods in Organic Chemistry*, Thieme, Stuttgart, 1993, vol. 19d; L. Brandsma, *Preparative Polar Organometallic Chemistry*, Springer-Verlag, Berlin–New York, 1987; B. J. Wakefield, *The Chemistry of Organolithium Compounds*, Pergamon Press, Oxford, 1974, p. 204.

4 P. C. Andrews, P. J. Duggan, G. D. Fallon, T. D. McCarthy and A. C. Peatt, *J. Chem. Soc., Dalton Trans.*, 2000, 1937.

5 J. Busch-Peterson and E. J. Corey, *Tetrahedron Lett.*, 2000, **41**, 6941; K. Koga, *Pure Appl. Chem.*, 1994, **66**, 1487; P. J. Cox, A. Persad and N. S. Simpkins, *Synlett*, 1992, **57**, 5438; T. Honda, N. Kimura and M. Tsubuki, *Tetrahedron: Asymmetry*, 1993, **4**, 21; T. Honda, N. Kimura and M. Tsubuki, *Tetrahedron: Asymmetry*, 1993, **4**, 1475; K. Aoki, H. Naguchi, K. Koga and K. Tomioka, *Tetrahedron Let.*, 1993; **34**, 5105; B. J. Bunn and N. S. Simpkins, *J. Org. Chem.*, 1993, **58**, 533; P. J. Cox and N. S. Simpkins, *Tetrahedron: Asymmetry*, 1992, **2**, 1.

6 P. C. Andrews, P. J. Duggan, G. D. Fallon, T. D. McCarthy and A. C. Peatt, *J. Chem. Soc., Dalton Trans.*, 2000, 2505

7 P. C. Andrews, D. R. Armstrong, D. R. Baker, R. E. Mulvey, W. Clegg, L. Horsburgh, P. A. O'Neill and D. Reed, *Organometallics*, 1995, **14**, 427; P. C. Andrews, D. R. Armstrong, R. E. Mulvey and D. R. Reed, *J. Organomet. Chem.*, 1990, **386**, 287.

8 E. J. Edwards, S. Hockey, F. S. Mair, P. R. Raithby, R. Snaith and N. S. Simpkins, *J. Org. Chem.*, 1993, **58**, 6942.

9 M. F. Lappert, *J. Organomet. Chem.*, 2000, **600**, 144; A. Antiñolo, C. Huertas, I. del Hierro, M. F. Lappert, A. Otero, S. Prashar, A. M. Rodriguez and E. Villaseñor, *Organometallics*, 1998, **17**, 5874; B.-J. Deelman, M. F. Lappert, H.-K. Lee, T. C. W. Mak, W.-P. Leung and P.-R. Wei, *Organometallics*, 1997, **16**, 1247; M. F. Lappert and D.-S. Sui, *J. Organomet. Chem.*, 1995, **500**, 203.

10 D. R. Armstrong, W. Clegg, L. Dunbar, S. T. Liddle, M. MacGregor, R. E. Mulvey, D. Reed and S. Quinn, *J. Chem. Soc., Dalton Trans.*, 1998, 3431.

11 D. Barr, W. Clegg, L. Cowton, L. Horsburgh, F. M. MacKenzie and R. E. Mulvey, *J. Chem. Soc., Chem. Commun.*, 1995, 891.

12 I. Cragg-Hine, M. G. Davidson, A. J. Edwards, P. R. Raithby and R. Snaith, *J. Chem. Soc., Dalton Trans.*, 1994, 2901.

13 P. C. Andrews, N. D. R. Barnett, R. E. Mulvey, W. Clegg, P. A. O'Neil, D. Barr, L. Cowton, A. J. Dawson and B. J. Wakefield, *J. Organomet. Chem.*, 1996, **518**, 85.