Crystal Structure of $[(Ph(Me)C{:}N{:}C(H)Ph)K \cdot (tBuOK)_2 \cdot (thf)_2]_\infty$: A Unimetallic Mixed Anion Model for a "Superbase"?[**]

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In memory of Ron Snaith

Mixed-anion "superbase" complexes of the type $[RM \cdot M'OR]_n$ (M = Li, M′ = Na, K) are of great interest since they can exhibit differing selectivity and greater deprotonating ability in synthetic organic procedures than the alkylmetal complex alone.[1] This behavior has also been described for other alkali metal species such as amides, $[R_2NM \cdot MOR]_n$, and enolates derived from ketones and esters.[2] The reason for the exceptional reactivity of this family of complexes has been attributed to the formation of mixed–anion aggregates in solution; however, in attempts to isolate these aggregates, the heavier alkali metal species and the alkoxide are, more often than not, deposited separately or isolated only as a microcrystalline solid.[3] This explains why there is still limited solid-state structural information on mixed-anion systems, though several examples have now been described in each class.[4] Of most importance and relevance here are the structurally characterized amide/alkoxide complexes; $[\{[iPr_2NLi][(Me_2NCH_2)_2CHOLi]\}_2]$,[5] which is unimetallic, and the mixed-metal complexes, $[\{[PhN(H)]_2(tBuO)LiNaK \cdot (tmen)_2\}_2]$[6] (tmen = *N,N,N′,N′*-tetramethylethylenediamine) and $[\{(MeOPh)N(H)\}_2(tBuO)NaLi_2]$.[7]

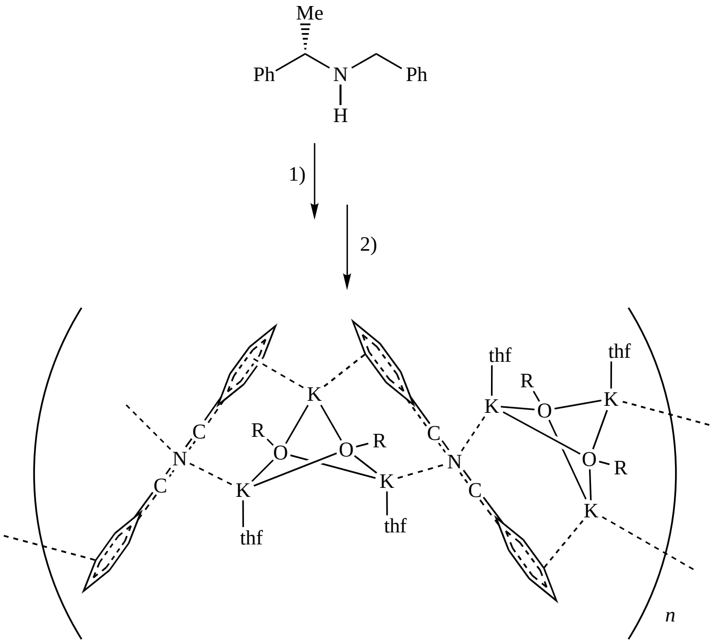
Recently we reported that the chiral secondary amine (S)-α-(methylbenzyl)benzylamine, $[\{Ph(Me)CH\}(PhCH_2)NH]$, readily undergoes transformation to an aza-allylic anion on reaction with *n*BuM (M = Li, Na, K) in the presence of the tridentate N-donor ligand pmdta (*N,N′,N′,N″,N″*-pentamethyldiethylenetriamine) and other ligand systems which reduce the aggregation state of the complexes to a monomer is solution.[8] This is consistent with the detailed structural and theoretical studies that have been described for the formation of the 1,3-diphenyl-2-aza-allyl anion from Group 1 complexes of dibenzylamine.[9] The Na and K complexes of the chiral amine are generally obtained from the reaction with either *n*BuNa or *n*BuK in the presence of various Lewis donors. *n*BuM (M = Na, K) are synthesized by the reaction of *n*BuLi with the appropriate *tert*-butoxide, *t*BuOM, and isolated and stored as solvent-free solids.

Herein we report on the solid-state structure of the potassium mixed-anion complex **1** and its reproducible,

$[(Ph(Me)C{:}N{:}C(H)Ph)K \cdot (tBuOK)_2 \cdot (thf)_2]_\infty$ **1**

moderately high-yielding synthesis. While investigating the conversion of (S)-α-$[(Ph(Me)CH)(PhCH_2)NH]$ to the aza-allylic anion on its reaction with *n*BuK in the presence of tmen and THF, we obtained a small quantity of pale red needlelike crystals from the reaction mixture. Analysis by ^1H NMR spectroscopy showed signals relating to both the aza-allylic and $tBuO^-$ ions in a 1:2 ratio. There were also signals corresponding to THF but, surprisingly, not to tmen. It became clear that a small but significant amount of *t*BuOK remained in the *n*BuK, either from the nonstoichiometric addition of *n*BuLi or from inefficient washing of the solid. Repeated NMR experiments on several samples of the crystals indicated that the anion ratios were consistent and the product homogeneous.

In a more rational approach to the synthesis of **1**, the amine was added to a suspension of three molar equivalents of *t*BuOK in hexane at −78 °C followed by addition of one equivalent of *n*BuLi (1.6 M in hexane; Scheme 1). Replacement of hexane by THF, followed by two equivalents of tmen and cooling, led to a moderate yield of red needlelike crystals; thus, the presence of tmen appears crucial.[10]



Scheme 1. Synthesis of **1**; 1) 3 *t*BuOK, *n*BuLi, hexane, −78 °C; 2) 2 tmen, THF (−hexane). R = *t*Bu.

The red crystals proved to be air- and moisture-sensitive, decomposing to a yellow solid, and have a melting range of between 131–132 °C. Low-temperature single-crystal X-ray diffraction studies revealed the novel polymeric structure of the mixed-anion complex **1** (Figure 1). The addition of tmen, in conjunction with the THF already present, provides the driving force for the elimination of H_2 from the amido unit. This results in an almost planar aza-allylic anion, which in the polymer is interspersed by K_3O_2 clusters comprising three K^+ ions and two $tBuO^-$ ions. The cluster core itself has approximate threefold rotation symmetry with the axis bisecting the two O atoms and structurally is, as far as we are able to ascertain, without precedent. All three K^+ ions are involved in bonding to the aza-allylic units in such a way that

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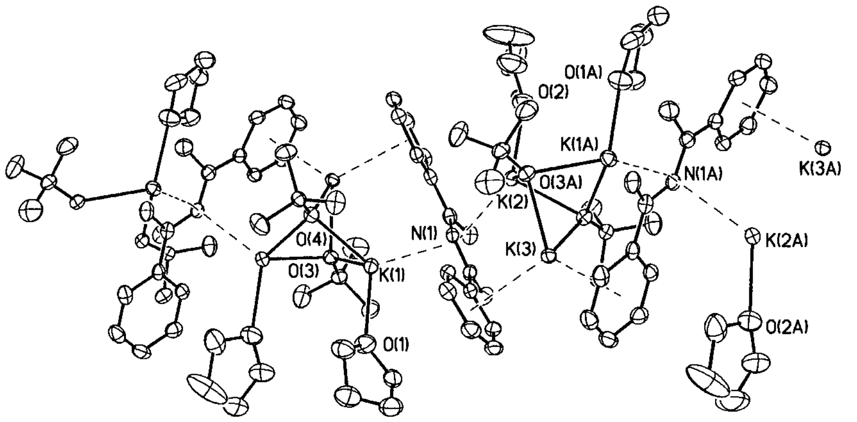

Figure 1. Molecular structure of **1** (30% probability ellipsoids). All hydrogen atoms are removed for clarity. Important bond lengths [Å]; K(1)-O(1, 3, 4) 2.661(3), 2.595(2), 2.572(2), K(1)-N(1) 2.827(3), K(1)-C(1, 8) 3.206(3), 3.294(3), K(2)-O(2, 3, 4) 2.686(3), 2.569(2), 2.600(2), K(2)-N(1) 2.837(3), K(1)-C(1, 8) 3.409(3), 3.256(3), K(3)-O(3, 4), 2.605(2), 2.594(2), K(3)-C(2) 3.263(3), K(3)-C(3) 3.275(3), K(3)-C(4) 3.302(4), K(3)-C(5) 3.333(4), K(3)-C(6) 3.288(3), K(3)-C(7) 3.242(3), K(3)-C(9) 3.273(3), K(3)-C(10) 3.280(4), K(3)-C(11) 3.324(4), K(3)-C(12) 3.359(4), K(3)-C(13) 3.327(3), K(3)-C(14) 3.263(3).

each aza-allyl anion actually accommodates four K$^+$ ions in total; two on each side. Thus, two of the K centers in the cluster, K(1) and K(2), which are also coordinated by single THF molecules, bond to the same aza-allyl anion at the delocalized C:N:C unit, while the third K$^+$ center K(3) is sandwiched between phenyl groups from neighboring anions. These phenyl groups tilt towards the K center to allow maximum interaction of the metal with the π-electron density; this leads to a range of bond lengths of between 3.242(3) and 3.359(4) Å for K(3)–C(7) and K(3)–C(12), respectively. These distances are comparable with those observed in [PhCH$_2$K · 0.5 toluene]$_\infty$ which also shows a similar polymeric zigzag arrangement.[11] The aza-allyl anions therefore sit over the two four-membered butterfly-type rings described by K(1A), O(3), O(4), K(3) and K(2), O(3), O(4), K(3) with the two THF molecules occupying the vacant site defined by the third four-membered butterfly ring, K(1), O(4), K(2), O(3) (Figure 2). Closer inspection of the K$_3$O$_2$ core reveals that the O atoms in each butoxo anion bridge the three K centers in a μ_3 manner; all the bonds are approximately equal in length (range between 2.569(2) and 2.605(2) Å for K(2)–O(3) and K(3)–O(3), respectively). The symmetry within the core is highlighted by the angles subtended at the metal cations by O(3) and O(4); K(1) 74.65(7)°, K(2) 74.60(7)°, and K(3) 74.11(7)°.

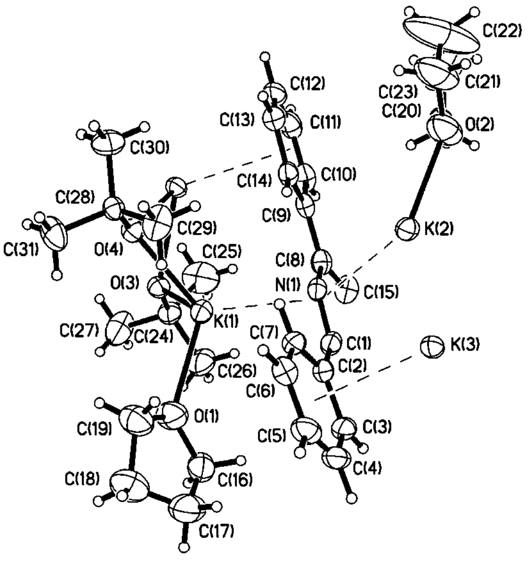

Figure 2. Bonding environment of the aza-allylic anion in **1**.

The dative THF to K bonds are slightly longer (K(2)–O(2) 2.686(3), K(1)–O(1) 2.661(3)). K(1) and K(2) bond with the delocalized π-electron density in the C:N:C units; the K(1)-N-K(2) angle is 146.3(1)°. An interesting comparison can be made here with **2**,[12] which is also polymeric and contains K ions bridging aza-allylic anions,

{[Ph(H)C:N:C(H)Ph]K · (pmdta)]$_\infty$ **2**

although in this case there are two types of cation–anion attachment; one with the aza-allyl unit and the other with an allylic unit with the *ipso*-carbon atom of the phenyl ring at its center and including the benzylic carbon. This type of arrangement is not evident in **1** though there is a degree of asymmetry in the bonding of the K centers to the aza-allylic moieties. The K(1)–N(1) and K(2)–N(1A) distances in **1** of 2.827(3) Å and 2.837(3) Å, respectively, are shorter than those in **2** (2.996(2) Å), though the metal-to-carbon distances are significantly longer; K(1)–C(1, 8) 3.206(3), 3.294(3) Å compared with 2.930(6) Å in **2**, though they are shorter than the K–αC distance of 3.366(7) Å in the allylic group in **2**.

^{1}H and ^{13}C NMR studies were conducted in [D$_8$]THF and showed all the expected chemical shifts and splitting patterns associated with the two anions and the THF molecules. We reported previously that it appears possible that there is a low-energy pathway for the elimination of MeH in these systems which can lead to the formation of the 1,3-diphenyl-2-aza-allyl anion. However, there was no indication in the NMR studies that this was occurring in this case and we are attempting now to reproduce the above results with dibenzylamine.

The stability of **1** can most likely be traced back to several factors; 1) the aza-allyl anion is fully delocalized and thus allows a great deal of flexibility in the way the K$^+$ ions can bond with it, 2) the essentially planar nature of this anion means that as well as offering a large surface area of electron density it has very little three-dimensional bulk, a property which has been described as being important for the stability of mixed-anion systems, and 3) the geometry of the K$_3$O$_2$ cluster core allows exposed K$^+$ vertices, leading to the metal cations being capable of maximizing their bonding interactions and coordination environments.

This provides useful information as to why the addition of tmen may be important in the formation of **1**. Crystal structures of the Group 1 complexes of (S)-[(Ph(Me)CH)(PhCH$_2$)NH] reveal the amido ligand adopts a "butterfly in flight" configuration in which the phenyl groups are almost perpendicular to each other,[8] and as such can be viewed as having significant steric bulk with the charge concentrated on the N$^-$ ion. This is less likely to give stable mixed-anion complexes, and can be contrasted to [{[PhN(H)]$_2$(*t*BuO)LiNaK $\cdot$ (tmen)$_2$}$_2$] and [{(MeOPh)N(H)}$_2$(*t*BuO)NaLi$_2$], both of which are derived from primary amines.

Experimental Section

1: (S)-α-(Ph(Me)CH)(PhCH$_2$)NH (5 mmol, 1.05 g) was added dropwise to a chilled (-78 °C) suspension of *t*BuOK (15mmol, 1.55 g) in hexane (20 mL). *n*BuLi (5.5 mmol, 3.2 mL, 1.6 M in hexane) was added dropwise resulting in the formation of a bright red suspension. The reaction mixture was stirred and allowed to warm to room temperature over 2 h during which time the suspension darkened to a deeper red. Hexane was removed in vacuo and THF added (ca. 20 mL) which with gentle warming allowed complete dissolution. The ligand tmen (10 mmol, 1.51 mL) was added, then the solvent was reduced in vacuo by approximately a third and the mixture was placed in the freezer at -20 °C overnight. This resulted in a crop of red needlelike crystals which were isolated and then washed with hexane. Yield 57 % (1.7 g). M.p. 131 – 132 °C; elemental analysis C$_{31}$H$_{48}$NK$_3$O$_4$ (%); calcd: C 60.5, H 7.8, N 2.3; found: C 61.1, H 7.5, N 2.1; ^{1}H NMR ([D$_8$]THF, 25 °C, 300 MHz): $\delta = 7.21$ (d, $J = 7.9$ Hz, 2H; *o*-H), 6.90 (brs, 2H; *o*-H), 6.81 (t, $J = 7.7$ Hz, 2H; *m*-H), 6.72 (t, $J = 7.6$ Hz, 2H; *m*-H), 6.19 (m, 2H, *p*; PhC*H*), 6.06 (t, $J = 7.1$ Hz, 1H; *p*-H), 3.57 (m, 4H; THF), 1.89 (s, 3H; Me), 1.73 (m, 4H; THF), 0.96 (s, 18H; *t*Bu); ^{13}C NMR ([D$_8$]THF, 25 °C, 75.5 MHz): $\delta =$ 146.33 (*q*C), 145.78 (*q*C), 129.14 (*o*C), 129.09 (*o*C), 129.00 (*o*C), 128.70 (*m*C), 127.35 (*m*C), 127.32 (*m*C), 119.16 (PhCH), 115.81 (*p*C), 114.41 (Ph*C*Me), 105.75 (*p*C), 37.5 (*t*Bu), 12.35 (Me).

Crystallographic data for **1**: Data collected on an Enraf Nonius Kappa CCD at 123 K. Crystal mounted under oil. C$_{31}$H$_{48}$NK$_3$O$_4$, $M_r = 615.01$, monoclinic, space group $P2_1/c$ (no. 14), red acicular crystal measuring $0.30 \times 0.24 \times 0.10$ mm, $a = 10.7096(5)$, $b = 16.4210(8)$, $c = 19.8427(9)$ Å, $\beta = 91.875(2)°$, $V = 3487.7(2)$ Å3, $Z = 4$, $\rho_{calcd} = 1.171$ g cm^{-3}, $\lambda(\mathrm{Mo}_{K\alpha}) = 0.71073$ Å, $\mu(\mathrm{Mo}_{K\alpha}) = 4.23$ cm^{-1}, 42594 reflections measured, 8661 unique, 3936 were observed ($I > 3.00\sigma(I)$), $R = 0.043$, $R_w = 0.051$, GoF 1.30. The structure was solved by direct methods with all H atoms placed in idealized positions ($r = 0.95$ Å). The aza-allylic anion is disordered in the crystal, as indicated by the occupancy of Me on C1 and C8 of 50:50. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147738. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Catalytic Asymmetric Aziridination with Arylborate Catalysts Derived from VAPOL and VANOL Ligands[**]

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The ring opening of chiral aziridines is a potent method for the synthesis of optically active amines.[1] The driving force of this process derives from the ring strain of the aziridine and this can be used to extend the ring opening to a variety of nucleophiles to produce difuncational amines with vicinal chiral centers. Since no general method for catalytic asymmetric aziridination exists,[2] chiral aziridines have been largely made from materials in which the chiral centers already exist.[1d] Given the synthetic and strategic advantages of asymmetric catalysis we began a program to find a chiral catalyst for asymmetric aziridination, and recently reported

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[**] This work was supported by the National Institutes of Health and was performed at the University of Chicago. VAPOL = 2,2′-diphenyl-[3,3′-biphenanthrene]-4,4′-diol, VANOL = 3,3′-diphenyl-[2,2′-binaphthalene]-1,1′-diol.

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