Unexpected structure of 1,3-diphenyl-2-azaallylpotassium–*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine: infinite, zigzag chains of alternating cations and two distinct types of anion, one azaallyl bonded, the other allyl bonded

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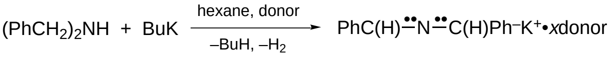
[{[PhC(H)$\overset{\cdots}{-}$N$\overset{\cdots}{-}$C(H)Ph]$^-$K$^+$·pmdeta}$_\infty$] adopts a novel crystal structure exhibiting separate η^3-C$\overset{\cdots}{-}$N$\overset{\cdots}{-}$C and η^3-C$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C ligating modes, surprisingly leaving one electronegative N centre not bonded to K$^+$; reaction of the azaallyl K with its parent imine PhC(H)=NCH$_2$Ph in toluene affords the interesting, metal-free, chiral product PhC(H)=NCH(Ph)CH(Ph)N(H)CH$_2$Ph.

With numerous studies devoted to the structural chemistry of synthetically important lithium organic derivatives having taken place since the early sixties,[1] attention is now turning to their more reactive, and less easily handled, heavier congeners.[2] One recent report[3] focused on the structure of the 1,3-diphenyl-2-azaallyl anion–potassium ion pair [{PhC(H)$\overset{\cdots}{-}$N$\overset{\cdots}{-}$C(H)Ph}$^-$K$^+$] in the presence of 18-crown-6: a simple discrete monomer with the anion η^2-C,N-bonded to the cation. Previously we had described the structure of the pmdeta-ligated sodium analogue [{PhC(H)$\overset{\cdots}{-}$N$\overset{\cdots}{-}$C(H)Ph}$^-$Na$^+$],[4]† which is also monomeric, though its anion is only N-bonded to the smaller Na$^+$ cation. Given this background, the crystal structure of the potassium analogue, [{[PhC(H)$\overset{\cdots}{-}$N$\overset{\cdots}{-}$C(H)Ph]$^-$K$^+$·pmdeta}$_\infty$] **1**, revealed herein, is novel on three counts: first, it is a polymer as opposed to a monomer; second, the anion engages in unique η^3–C$\overset{\cdots}{-}$N$\overset{\cdots}{-}$C interactions with K$^+$; third, and most significantly, a second type of anion–cation coordination is present, remarkable for not involving the central highly electronegative N atom, but the adjacent *o*-C$\overset{\cdots}{-}$*ipso*-C$\overset{\cdots}{-}$α-C units. The existence of the previously reported bis-solvated variant [{PhC(H)$\overset{\cdots}{-}$N$\overset{\cdots}{-}$C(H)Ph}$^-$K$^+$·2pmdeta}] **2**,[5] a suspected monomer,‡ makes these findings all the more intriguing. We also demonstrate the synthetic value of the azaallyl potassium system in reporting an addition reaction which produces the interesting chiral compound PhC(H)=NCH(Ph)CH(Ph)N(H)CH$_2$Ph **3**.

The aforementioned crown complex was prepared by deprotonating the imine PhC(H)=NCH$_2$Ph with KH in a 12 h long reflux procedure.[3] However, our alternative method for generating the azaallyl potassium ion pair starting from dibenzylamine can be accomplished in minutes (Scheme 1). As discussed in depth elsewhere,[5] mechanistically this process appears to involve also the imine and KH, but as short-lived intermediates, of enhanced reactivity. Originally we thought that only bis-adduct **2** was affordable by this method, as 2 equiv. of pmdeta were necessary to achieve complete dissolution of the initially formed dibenzylamidopotassium. But it transpires that hot toluene mixtures containing 1 equiv. of pmdeta, when filtered through Celite to remove fine solids, afford solutions that on cooling deposit some crystalline **1** mixed with **2**.§

The crystal structure of **1**¶ consists of infinite chains of contacted ions, the salient feature of which is the two distinct types of bridging-anion (Fig. 1). These lie approximately perpendicular to each other (87.7°). Predictably, type 1 ligates through the central azaallyl C(1)$\overset{\cdots}{-}$N(1)$\overset{\cdots}{-}$C(1A) unit. More surprisingly, type 2 ligates through the off-centre allyl C(8)–C(9)–C(9A) unit, leaving N(2) not bonded to K(1); this N atom lies 3.648 Å from two adjacent K$^+$ ions. Both types use their delocalised π systems to bridge to pairs of K$^+$ cations, disposed on either side of the planar PhC(H)NC(H)Ph frameworks. Chelating tridentate triamine ligands complete the coordination of the cations. Two-fold disorder of each type of anion limits the precision of the structure. Nevertheless, it is still discernible that the metal–anion contacts are decidedly shorter for type 1 than for type 2 (by about 0.35 Å on average), and



$$(\text{PhCH}_2)_2\text{NH} + \text{BuK} \xrightarrow[-\text{BuH},\ -\text{H}_2]{\text{hexane, donor}} \text{PhC(H)}\overset{\cdots}{-}\ddot{\text{N}}\overset{\cdots}{-}\text{C(H)Ph}^-\text{K}^+\bullet x\text{donor}$$

Scheme 1

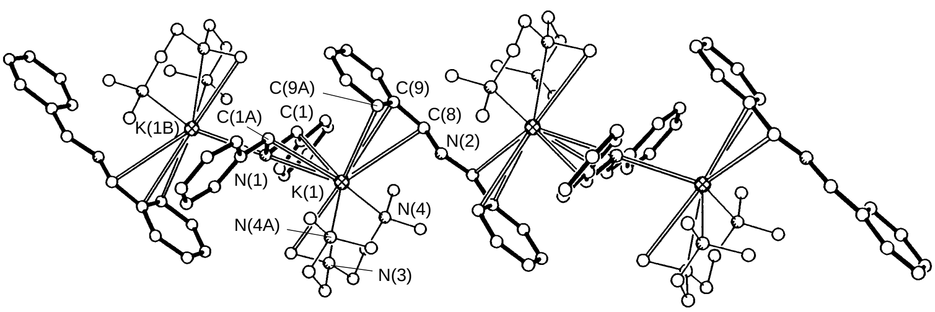


Fig. 1 Section of the infinite chain structure of **1** with labelling of selected atoms. Hydrogen atoms are omitted for clarity and only one disorder component of each anion is shown. Key dimensions (Å): K(1)–N(1) 2.996(2), K(1)–C(1) and K(1)–C(1A) 2.930(6), K(1)–C(8) 3.366(7), K(1)–C(9) and K(1)–C(9A) 3.268(5), K(1)–N(3) 2.868(5), K(1)–N(4) and K(1)–N(4A) 2.889(4), N(1)–C(1) 1.513(6), N(2)–C(8) 1.347(10), K(1)···N(2) 3.648(3). Symmetry operators: A *x*, 1 − *y*, *z*; B 1 − *x*, 1 − *y*, 1 − *z*.

linked to this, that the C$\overset{\cdots}{-}$N bonds in the former have substantially less double bond character than those in the latter. This implies that the structure is primarily dictated by strong metal-to-azaallyl anion (electrostatic) bonding, the steric characteristics of which permit the loose attachment of the allyl fragment of another anion [the ‘loose’ K–C bonds are slightly longer than those producing the polymeric arrangement in the benzyl structure mentioned below, which lie in the range 3.150–3.265 Å; while the strong cation–anion interaction is considerably shorter, and is more representative of that in the monomeric crown analogue described above (3.044 Å)]. The observation that a second pmdeta molecule can readily displace one of the two anions from the coordination sphere of the cation (*i.e.* as in **2**), supports this interpretation. In a search for comparable structures to **1**, $[\{PhCH_2K\cdot pmdeta\cdot 0.5toluene\}_\infty]$[6] stands out in view of its zigzag polymeric set-up and two distinct multihapto anion–K^+ coordinations; however, the similarity is only superficial as it contains a single type of anion, and one devoid of a heteroatom (*i.e.* incapable of offering a seat of high electron density). Pyridyl-substituted $[K(2\text{-}C_5H_4N)CHPPh_2CHPPh_2\cdot 2thf]$[7] is also noteworthy in exhibiting a 1-azaallyl (N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C) unit (**1** displays a 2-azaallyl alternative).

Preliminary studies probing the chemistry of the azaallyl–K ion pair have uncovered the interesting reaction sequence shown in Scheme 2. A second equivalent of imine gives the addition product which appears to metallate toluene. Chiral product **3** with no K present, crystallises from solution, its identity being unambiguously established by a ^1H NMR spectrum.‖ The yield of **3** still needs to be optimised, but it is significant that it is also found in reactions containing a 1 : 1, BuK : imine stoichiometry. Earlier it was reported that the reaction between the azaallyl and $[ZrCl_2(\eta\text{-}C_5H_5)_2]$ yielded $[Zr(\eta^2\text{-}PhCH\text{-}N\text{-}CH(Ph)CH(Ph)\text{-}N{=}CPh\text{-}\eta^1)(\eta\text{-}C_5H_5)_2]$:[3] the coupling of the azaallyl moieties was ascribed to an oxidative addition process in which Zr^{IV} is reduced to Zr^{II} then oxidised back to Zr^{IV}. The implication of our new finding is that similar coupling processes can occur even without the mediation of a transition-metal redox centre.

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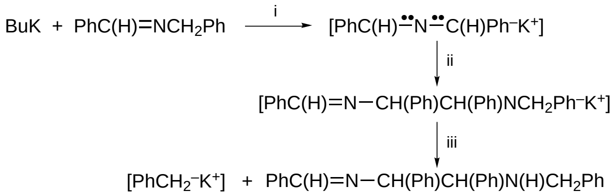

Scheme 2 *Reagents*: i, hexane; ii, $PhC(H){=}NCH_2Ph$; iii, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (3 mol equiv.), toluene

Footnotes

† pmdeta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine.

‡ An attempted crystal structure determination confirmed the monomeric nature and bis-pmdeta solvation; however, the quality of the data was poor and not of a publishable standard.

§ The relative amounts of **1** and **2** appear variable and inconsistent, though **2** generally predominates. As our efforts to separate this mixture have so far failed, we are unable to give an absolute yield of **1**. However, the possibility that **1** is a rogue crystal can be ruled out as the unit-cell parameters of a number of crystals (from repeated syntheses of **1**), have been checked and found to conform to those reported here.

¶ *Crystal data* for **1**: $C_{23}H_{35}KN_4$, M = 406.65, monoclinic, space group $C2/m$, a = 11.1901(8), b = 17.6135(13), c = 12.6609(10) Å, β = 107.272(2)°, U = 2382.9(3) Å^3, Z = 4, D_c = 1.134 g cm^{-3}, μ = 0.24 mm^{-1} (Mo-Kα, λ = 0.710 73 Å), T = 160 K. 6177 Reflections were measured on a Siemens SMART CCD area detector diffractometer, yielding 2165 unique reflections ($2\theta_{max}$ = 50° , R_{int} = 0.0207). The structure was solved by direct methods and refined on F^2 values with anisotropic atomic displacement parameters, constrained hydrogen atoms, and twofold disorder across $2/m$ (C_{2h}) positions for both independent anions. Final $R^1 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{\frac{1}{2}}$ = 0.1938 for all data, conventional R = 0.0861 for F values of 1846 reflections with $F_o^2 > 2\sigma(F_o^2)$, goodness of fit = 1.103 for all F^2 values and 173 refined parameters; extremes of difference map +0.29 and −0.85 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/343.

‖ ^1H NMR (400 MHz, C_7D_8, 298 K): δ 1.91 (m, 1 H, NH), 3.38 (m, 1 H, PhC*H*^{1}H^2), 3.65 m, 1 H, PhCH^1*H*^{2}), 4.16 (m, 1 H, NHC*H*Ph), 4.37 (d, 1 H, C*H*Ph), 7.70 (s, 1 H, PhC*H*=N).

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