Lewis Base Mediated Rearrangements of Alkali Metal Imides to η^3-Aza-allyl Complexes: Preparation and N.M.R. Spectroscopic Solution Studies of $[CH_3CH_2CH_2\overline{C(H)\mathrel{\overset{\cdots}{-}}C(Bu^t)\mathrel{\overset{\cdots}{-}}N(H)\cdot M}\cdot(HMPA)_x]_n$ (M = Li, x = 1; M = Na, x = 2) (HMPA = Hexamethylphosphoramide)

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The η^3-aza-allyl complexes $[CH_3CH_2CH_2\overline{C(H)\mathrel{\overset{\cdots}{-}}C(Bu^t)\mathrel{\overset{\cdots}{-}}N(H)\cdot M}\cdot(HMPA)_x]_n$ [M = Li, x = 1, (**1**); M = Na, x = 2, (**2**)] (HMPA = hexamethylphosphoramide) are formed in high yield when HMPA $[O{=}P(NMe_2)_3]$ is added to the metal imides, $[Bu^n(Bu^t)C{=}NM]_n$; complexes (**1**) and (**2**) have been fully characterised by elemental analyses, and by i.r. and n.m.r. (^1H, ^7Li, ^{13}C) spectroscopies.

One classical method of preparing imidolithium compounds $(RR'C{=}NLi)_n$ is by the addition of an organolithium reagent, RLi, across an organic nitrile, $R'C{\equiv}N$.[1] In our present study, we expected such addition reactions on treating $Bu^tC{\equiv}N$ with either Bu^nLi or Bu^nNa in the presence of the donor HMPA $[O{=}P(NMe_2)_3]$ (HMPA = hexamethylphosphoramide). Surprisingly, however, the solid products isolated were not the metal imide complexes $[Bu^n(Bu^t)C{=}NM\cdot(HMPA)_x]_n$ but, rather, the intriguing η^3-aza-allyl species $[CH_3CH_2CH_2\overline{C(H)\mathrel{\overset{\cdots}{-}}C(Bu^t)\mathrel{\overset{\cdots}{-}}N(H)\cdot M}\cdot(HMPA)_x]_n$, (**1**) (M = Li; x = 1) and (**2**) (M = Na; x = 2).† Hitherto, η^3-aza-allyl carbanions have usually been prepared by the direct lithiation of an aldimine, ketimine, or similar unsaturated species;[2] indeed, the only reported crystal structures of such aza-allyl derivatives concern those obtained by lithiation of C–H bonds adjacent to the pyridyl $C\mathrel{\overset{\cdots}{-}}N$ link in $2\text{-}(Me_3Si)_{3-n}CH_nC_5H_4N$ aromatics.[3] In stark contrast, it is by the transfer of a hydrogen atom from the α-CH_2 of the n-butyl chain to the imido nitrogen atom, in a process induced by HMPA addition, which produces the aza-allyl family here reported.

The inherent similarity between (**1**) and (**2**) appears to extend to their solution structures, as their respective ^1H n.m.r. spectra are in concert.‡ Figure 1 shows, with assignments, the spectrum of (**1**) recorded in $[^2H_8]$tetrahydrofuran (THF) at 25 °C. The only significant distinction with the corresponding spectrum of (**2**) is the amount of HMPA present; the larger Na^+ cation bears two molecules compared to lithium's one.

Evidence that HMPA involvement is mandatory for the formation of the aza-allyl ligand in (**1**) [and, by implication, in (**2**)] comes from the isolation of the expected imidolithium $[Bu^n(Bu^t)C{=}NLi]_n$ (**3**), from a control reaction of Bu^nLi with $Bu^tC{\equiv}N$ in the absence of HMPA.§ A key feature in the characterisation of (**3**) is its i.r. spectrum which shows a typical

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† In a typical preparation, Bu^nM (10 mmol) (M = Li or Na) was reacted with $Bu^tC{\equiv}N$ (10 mmol) in hexane solution under a dry argon blanket. The resulting solution was treated with HMPA (10 or 20 mmol), then cooled to −15 °C to afford either the lime green opaque crystals of (**1**) (m.p. 78—79 °C) or the colourless crystalline flakes of (**2**) (m.p. 38—40 °C) (both sets of crystals are air- and moisture-sensitive). Yields based on Bu^nM consumption were 92% and 78%, respectively. Satisfactory analyses (C, H, Li or Na, N, P) were obtained for (**1**) and (**2**).

‡ *Spectroscopic data*: for (**1**); ^1H n.m.r. (360.1 MHz), 25 °C, $[^2H_8]$THF solution, δ 1.09 t (3H, Me), 1.25 s (9H, Bu^t), 1.52 m (2H, CH_3CH_2), 1.97 s (1H, NH), 2.13 m (2H, CH_2), 2.74/2.77 d (18H, HMPA), and 3.42 t (1H, CH) relative to tetramethylsilane (TMS); similar spectra were obtained in both $[^2H_6]$benzene and $[^2H_8]$toluene solutions, and assignments were verified by a series of homonuclear decoupling experiments and by the corresponding ^{13}C n.m.r. (90.6 MHz) spectrum; ^7Li n.m.r. (139 MHz) $[^2H_8]$toluene solution, 25 °C, δ −0.25 s. (Ξ value, 38.863 882 MHz). For (**2**); ^1H n.m.r. (360.1 MHz) 25 °C $[^2H_8]$THF solution, δ 1.09 t (3H, Me), 1.26 s (9H, Bu^t), 1.53 m (2H, CH_3CH_2), 2.14 m (3H, CH_2 and NH), 2.74/2.77 d (36H, HMPA × 2), and 3.22 t (1H, CH).

§ The colourless air- and moisture-sensitive crystals of (**3**) (m.p. 237 °C, yield 77%) were prepared in an analogous fashion to (**1**) and (**2**) above. Satisfactory analyses (C, H, Li, N) were obtained for (**3**). *Spectroscopic data*: ^1H n.m.r. (360.1 MHz) 25 °C $[^2H_8]$toluene solution, δ 0.89 t (3H, Me), 0.98 s (9H, Bu^t), 1.30 m (4H, $CH_3CH_2CH_2$), and 2.19 m (2H, $CH_2C{=}N$); ^7Li n.m.r. (139 MHz) $[^2H_8]$toluene solution, 25 °C, δ 0.45 s.

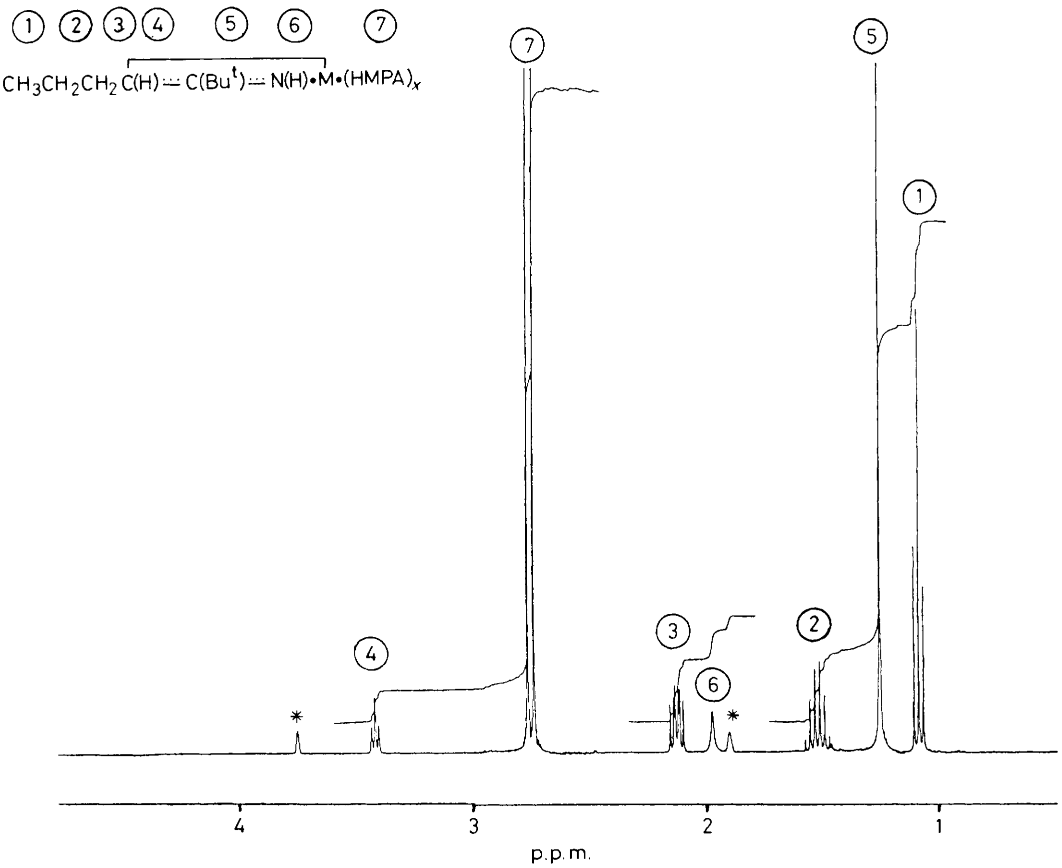

Figure 1. ^1H (360.1 MHz) n.m.r. spectrum of (**1**) (M = Li, x = 1) recorded at 25 °C in [$^2H_8$]THF solution, with assignments. Signals due to the solvent are asterisked.

imidolithium C=N stretching frequency {1630 cm^{-1}; *cf.* 1632 cm^{-1} for [$Bu^t(Ph)C{=}NLi]_6$[1,4]} that is substantially higher than that found for the $C\overset{\cdots}{-}C\overset{\cdots}{-}N$ units in (**1**) and (**2**) (1578—1560 and 1590—1540 cm^{-1}, respectively). Significantly, although (**3**) remains intact in non-donor solvents such as [$^2H_8$]toluene, it rearranges to an aza-allyl species in [$^2H_8$]THF, *e.g.*, its ^1H n.m.r. spectrum is essentially the same (minus the HMPA doublet) as that shown for (**1**) in Figure 1. The implication is that these rearrangements will occur on treatment of imides such as (**3**) with a whole range of donors; interestingly though, *ab initio* MO calculations show that the model aza-allyl structure $CH_2\overset{\cdots}{-}C(CH_3)\overset{\cdots}{-}N(H)Li$ is slightly energetically-preferred (even when uncomplexed) to its imido-isomer $CH_3(CH_3)C{=}NLi$.¶

Hitherto, crystalline imidolithiums ($RR'C{=}NLi)_n$ have proved to be hexamers (n = 6) in the solid, with three-co-ordinate Li atoms.[1] However, these derivatives, having R = R' = Bu^t, Me$_2$N, or R = Ph, R' = Bu^t, Me$_2$N, have, unlike (**3**), all lacked α-CH protons within their R,R' groups; they have in general resisted attempts to reduce their association (hence the co-ordination number of their constituent metal atoms) by treatment with a variety of Lewis bases, including HMPA. It may well be that they so resist since in, for example, monomeric RR'C=NLi·HMPA, there is no obvious way of then increasing the co-ordination number of the Li beyond two. In contrast, (**3**) would provide a monomer $CH_3CH_2CH_2CH_2(Bu^t)C{=}NLi{\cdot}HMPA$ which can, by transfer of an α-CH$_2$ proton to N, generate an η^3-aza-allyl moiety; this, along with the HMPA ligand, allows the Li to reach four-co-ordination, *i.e.*, an actual increase over that found in the uncomplexed hexamer.

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¶ *Ab initio* MO geometry optimisations (at the split-valence level <9s5p/4s2p>) on a model monomeric η^3-aza-allyl structure $CH_2\overset{\cdots}{-}C(CH_3)\overset{\cdots}{-}N(H)Li$ (total energy, −178.9398980 a.u.) show it to be energetically preferred (by 2.1 kcal mol^{-1}) to its imido-isomer $CH_3(CH_3)C{=}NLi$ {−178.9364959 a.u.}. (1 kcal = 4.184 kJ.) A detailed account of these and related calculations will be published in a full paper.