Lithium enamides, β-diketiminates and 1,3-diazaallyls from the 1 : 1 insertion of an isonitrile into the Li–C bond of LiCH(SiMe$_3$)$_2$†‡

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The diverse behaviour of LiCHR$_2$ A towards an isonitrile R′NC is unravelled; depending on reaction conditions and choice of R′, the product was an enamide Li[N(R′)C(R)=C(H)R](tmen), a β-diketiminate Li[N(R′)C(R)C(H)C(R)N(R′)], a 1,3-diazaallyl (with additionally PhCN) Li[N(Ph)C(R)NC(Ph)=C(H)R](tmen) or a 1 : 1 adduct of A and Li[N(R′)C(R)C(H)C(R)N(R′)](CNR′) (R′ = Bu^t), (R = SiMe$_3$, tmen = Me$_2$NCH$_2$CH$_2$NMe$_2$ and R′ = Bu^t, Ph or C$_6$H$_3$Me$_2$-2,6).

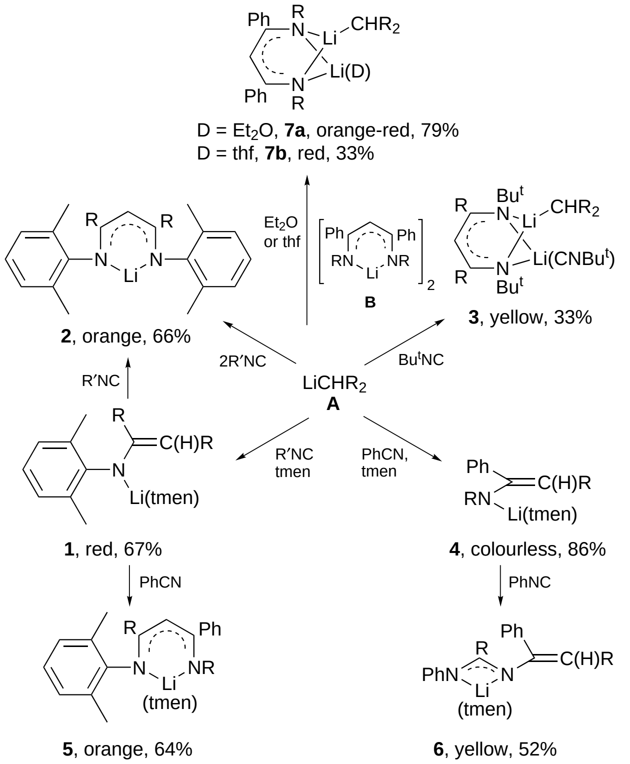
We have previously noted that the reaction between bis(trimethylsilyl)methyllithium LiCHR$_2$ **A** and the α-H-free nitrile PhCN or Bu^{t}CN gave under ambient conditions and irrespective of stoichiometry the 1 : 2 or 1 : 1 adduct, the lithium β-diketiminate [LiN(R)C(Ph)C(H)C(Ph)N(R)]$_2$ **B**[1] or 1-azaallyl [LiN(R)C(Bu^t)C(H)R]$_2$[2] (R = SiMe$_3$). We now report new findings on the LiCHR$_2$–PhCN system and on the variety of reactions between LiCHR$_2$ and the isonitrile R′NC (R′ = Ph, Bu^t or C$_6$H$_3$Me$_2$-2,6).

Treatment of a lithium alkyl LiR^1 and an isonitrile R^{2}NC was shown by Walborsky *et al.* to give the lithioaldimine LiC(R^1)=NR^2, which was not isolated, but used *in situ* as a source of an aldehyde, ketone, α-keto acid, β-hydroxyketone or a heterocycle.[3]

We now report (*i*) the synthesis of three diverse adducts **1**, **2** and **3** formed from LiCHR$_2$ **A** and R′NC (R′ = Bu^t or C$_6$H$_3$Me$_2$-2,6); (*ii*) that the previously examined LiCHR$_2$–PhCN system[1] is modified in the presence of (Me$_2$NCH$_2$)$_2$ (= tmen) to yield the 1 : 1 adduct **4**; (*iii*) that the enamide **1** with PhCN or **4** with PhNC yields the lithium β-diketiminate **5** or 1,3-diazaallyl **6**, respectively; (*iv*) that the β-diketiminate **B**[1] with LiCHR$_2$ and 1 equiv. of Et$_2$O or thf (OC$_4$H$_8$) gives the dilithium [bis(trimethylsilyl)methyl-β-diketiminate] donor (Et$_2$O or thf) adduct **7a** or **7b** (similar in type to the *tert*-butyl isonitrile adduct **3**); and (*v*) the characterisation of each of **1**–**7**,§ including the X-ray structures of **6** (to be published in the full paper) and **7b**.¶ The reactions leading to compounds **1**–**7** are summarised in Scheme 1.

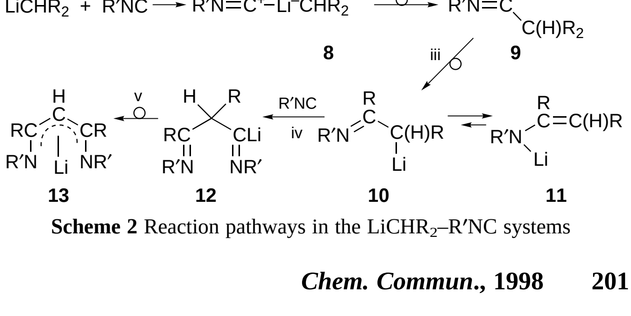
It is noteworthy (Scheme 1) that the nature of the product, a lithium enamide **1** or β-diketiminate **2**, or (irrespective of stoichiometry) an isonitrile adduct of a dilithium [bis(trimethylsilyl)methyl-β-diketiminate] **3**, obtained from LiCHR$_2$ **A** and the isonitrile R′NC, in good yield under ambient conditions in Et$_2$O, was dependent on one or more of the variables: the nature of R′, the stoichiometry and the presence or absence of tmen. A transient lithium β-diketiminate may well have been an intermediate along the pathway to **3**, as evident from the isolation of the related dilithium compounds **7a** and **7b** from **A** and **B**.

The formation of the stable compound **4** (from LiCHR$_2$–PhCN–tmen) lends credence to the suggestion that the previously reported LiCHR$_2$–PhCN reaction (which gave the lithium β-diketiminate **B**)[1] proceeded *via* a transient η^3-1-azaallyl (an isomer of the tmen-free **4**). The function of the tmen may have been to have promoted the η^3 → η^1 isomerisation. This is also consistent with the present observation that **4** + PhNC gave the Li(tmen) 1,3-diazaallyl compound **6** rather than the isomer 0.5 **B** (tmen) (*cf.*, the reaction of the Li enamide **1** + 2,6-Me$_2$C$_6$H$_3$NC → Li β-diketiminate **2**). The possibility (*cf.*, ref. 5) that in this reaction PhNC was initially isomerised into PhCN is discounted because **4** + PhCN gave an isomer of **6**, in which the Ph and Me$_3$Si groups at N(1) and C(2) were exchanged.



Scheme 1 Synthesis of the crystalline compounds **1**–**7** from LiCH(SiMe$_3$)$_2$. Reactions carried out in C$_5$H$_{12}$ or Et$_2$O (**2**–**4**) at −78 °C to *ca.* 25 °C; yields refer to recrystallised complexes; R′ = C$_6$H$_3$Me$_2$-2,6.

The multifarious reaction products observed in the LiCHR$_2$–R′NC system (Scheme 1) may be accommodated by the pathways shown in Scheme 2. Thus, we propose that (i) an initial 1 : 1 complex **8** is (ii) transformed into the lithioaldimine **9**, which (iii) induces a C(1) → C(2) shift of an Me$_3$Si (= R) group yielding the lithium 1-azaallyl **10** ⇌ **11**, this (iv)



Scheme 2 Reaction pathways in the LiCHR$_2$–R′NC systems

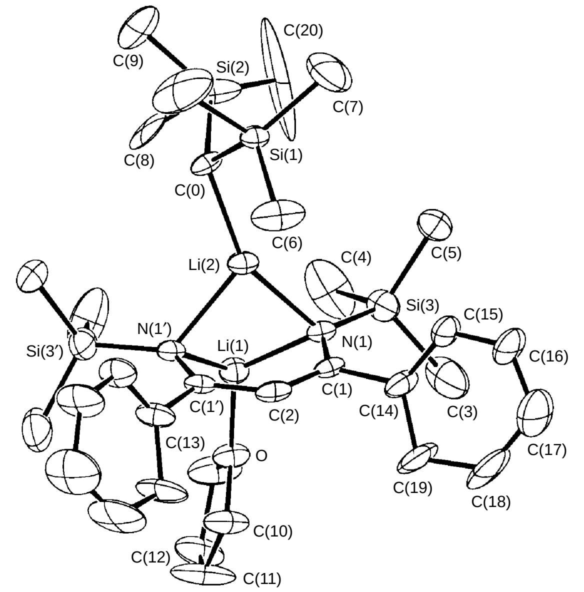


Fig. 1 Molecular structure of **7b** with selected bond distances (Å): N(1)–Li(1) 2.00(2), N(1)–Li(2) 2.13(2), C(0)–Li(2) 2.07(3), N(1)–C(1) 1.32(1), C(1)–C(2) 1.41(1), O–Li(1) 1.86(3).

behaving as a C-centred nucleophile adds to R′NC giving the lithiodiimine **12**, which (v), by a process similar to (*iii*), yields the lithium β-diketiminate **13**.

Although isonitrile complexes of certain transition metals are established, isonitrile adducts of a main group metal are rare {see, *e.g.*, [6a] $Ph_2CNCLi[(-)\text{-sparteine}](thf)_2$ and [6b] $AlPh_3(CNC_6H_{11}\text{-}c)$}, complex **3** may serve as a model for **8**. The propensity for an Me_3Si group to undergo a 1,2- or 1,3-shift in an anionic complex is well documented[4] [*e.g.*,[1,2] 1,3-C → N in the $LiCHR_2$–R′CN systems], and this provides support for propositions (iii) and (v) of Scheme 2. The isolated complexes **1**, **2** and **3** correspond to a tmen adduct of **11**, **13** and a composite of **8** and **13**, respectively.

The nature of the donor adducts **3**, **7a** and **7b**, of a dilithium [bis(trimethylsilyl)methyl-β-diketiminate] requires comment. In principle, each may be regarded as being either a 1:1 cocrystal of $LiCHR_2$(donor) and Li(β-diketiminate) or a discrete compound. We favour the latter for the following reasons. First, repeated recrystallisation of **3** from different solvents led in each case to a product of precise 1:1 composition. Second, their colours (Scheme 1) are distinct from those of their possible factors (**B** is pale yellow). Third, the X-ray structure of **7b** (Fig. 1) shows each lithium atom to be closely bound to the two nitrogen atoms of the β-diketiminate moiety [as, indeed, appears to be the case for **3**, but the quality of the crystals was such that an accurate structure was not established, R_1 $\{I > 2\sigma(I) \approx 0.20\}$]. Finally, the $^7Li\{^1H\}$ NMR spectrum of **7a** in $C_6D_5CD_3$ showed a single signal at δ 2.30 at 293 K, but three separate signals at δ 2.36, 1.44 and 1.37 at 193 K; this is attributed to there being an equilibrium between **7a** and its factors **A** and **B**. Variable temperature NMR spectra of **3** and **7b** are under investigation.

Crystalline **7b** has a mirror plane containing the atoms O and C(13) of the thf molecule, the two lithium, the two silicon atoms and the methyl group C(6), as well as C(2) [corresponding to the C(H) of the β-diketiminate moiety]. The methine carbon, C(0) of the CHR_2 group, and the remaining atoms C(10), C(11) and C(12) of the thf molecule are disordered across the mirror plane. The nitrogen atoms N(1) and N(1′) are bridged by Li(1) (bonded to thf) and Li(2), one above and the other below the nearly planar and completely delocalised diketiminato skeleton, with Li(1)–N(1) 2.00(2) and Li(2)–N(1) 2.13(2) Å. This contrasts with the situation in the dimeric lithium β-diketiminate **B**, which has only one of the two nitrogen atoms of each boat-shaped, incompletely delocalised lithiated ligand in a bridging mode with Li–N 1.952(9) and 2.095(9) Å, for the four- and three-coordinate nitrogens, respectively.[1] The Li(2)–C(0) distance of 2.07(3) Å may be compared with 2.14(3)–2.27(2) Å in crystalline $[LiCHR_2]_\infty$.[7]

The lithium compounds **1**–**7** are available as ligand transfer agents to provide a variety of new s-, p-, d- and f-block metal coordination compounds. We also conclude that isonitriles have an as yet unexplored potential for main group metal chemistry.

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Footnotes and References

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† No reprints available.

‡ Dedicated to Professor Dr Manfred Weidenbruch, as a mark of friendship and respect, on the occasion of his 60th birthday.

§ *Selected spectroscopic data* [^1H at 300.1, $^7Li\{^1H\}$ at 116.6 and $^{13}C\{^1H\}$ at 75.5 MHz in C_7D_8 **1**, **2**–**7** in C_6D_6]. **1**: ^1H (values for major rotamer only) δ 0.03 (CHSi*Me*$_3$), δ 0.20 ($SiMe_3$, s), 3.80 (CH, s); $^7Li\{^1H\}$ δ 0.51; $^{13}C\{^1H\}$ δ 84.7 (CH, s), 172.2 (CN, s). **2**: ^1H δ 0.05 ($SiMe_3$, s), 5.48 (CH, 1); $^7Li\{^1H\}$ δ −0.83; $^{13}C\{^1H\}$ δ 104.6 (CH, s), 172.3 (CN, s). **3**: ^1H δ −1.69 ($CHSi_2$, s), 5.40 (CH, s); $^7Li\{^1H\}$ δ 0.83 (s); $^{13}C\{^1H\}$ δ 3.3 ($CHSi_2$, s), 108.5 (CH, s), 179.9 (CN, s). **4**: ^1H δ 0.11 ($SiMe_3$, s), 0.22 ($SiMe_3$, s), 3.67 (CH, s); $^7Li\{^1H\}$ δ 0.88; $^{13}C\{^1H\}$ δ 83.1 (CH, s), 175.9 (CN, s). **5**: ^1H δ 0.07 ($SiMe_3$, s), 0.11 ($SiMe_3$, s), 5.57 (CH, s); $^7Li\{^1H\}$ δ 1.45; $^{13}C\{^1H\}$ δ 105.1 (CH), 169.0, 177.9 (CN, s). **6**: ^1H δ 0.24 ($SiMe_3$, s), 0.45 ($SiMe_3$, s), 4.79 (CH, s); $^7Li\{^1H\}$ δ 1.54; $^{13}C\{^1H\}$ δ 96.7 (CH, s), 154.1 (*C*=CH, s), 165.7 (CN_2, s). **7a**: ^1H δ −1.94 ($CHSi_2$, s), 5.51 (CH, s); $^7Li\{^1H\}$ δ 2.30(s); $^{13}C\{^1H\}$ δ 1.8 ($CHSi_2$, s), 105.4 (CH, s), 177.2 (CN, s). **7b**: ^1H δ −1.90 ($CHSi_2$, s), 5.09 (CH, s); $^7Li\{^1H\}$ δ 2.30 (s); $^{13}C\{^1H\}$ δ 1.4 ($CHSi_2$, s), 105.4 (CH, s), 176.8 (CN, s).

¶ *Crystal data for* **7b**: $C_{32}H_{56}Li_2N_2OSi_4$, M = 611.0, orthorhombic, space group $P2_1nm$ (non-standard no. 31), a = 9.043(4), b = 11.943(5), c = 18.406(10) Å, U = 1980(2) Å^3, Z = 2, D_c = 1.02 Mg m^{-3}, $F(000)$ = 664, λ(Mo-Kα) 0.71073 Å, μ = 0.173 mm^{-1}. Data were collected at 173(2) K on a Enraf Nonius CAD4 diffractometer in the ω–2θ mode for the range $2 < \theta < 25°$. The structure was solved by direct methods (SHELXS86) and refined with full matrix least squares on all F^2 (SHELXL93). The molecule is disordered across the crystallographic mirror plane with ordered sites for the Li, Si, O, C(6), C(7) and C(13) atoms and the [(R)NC(Ph)C(H)C(Ph)N(R)] ligand. Distances from Si(2) to C(8), C(9) and C(20) were fixed at 1.88 Å. Two reflections badly affected by extinction were omitted. All non-hydrogen atoms were anisotropic, and hydrogen atoms were included in the riding mode with $U_{iso}(H)$ = 1.2 $U_{eq}(C)$ or 1.5 U_{eq} for Me groups, except for the disordered thf group for which H atoms were omitted. Final residuals for 1921 independent reflections were R_1 = 0.162, wR_2 = 0.272 and for the 1009 with $I > 2\sigma(I)$, R_1 = 0.092, wR_2 = 0.220. CCDC 182/683.

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