The First Solid-State Structure of a Lithiated Diazomethane with C–Li and N–Li Bonds: $\{[Me_3SiC(Li)N_2]_2{\cdot}3\ THF\}_\infty$

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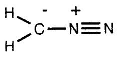
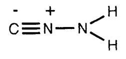
Reaction of *n*-butyllithium with Me_3SiCHN_2 in THF affords the first example of a lithiated diazomethane with C–Li and N–Li bonds.

Diazomethane, H_2CN_2, substituted diazomethanes, $RCHN_2$, and their alkali-metallated derivatives have long had considerable use in synthetic organic chemistry.[1] Many studies, both experimental and calculational, have probed the fundamental structures of, and the bonding within, these species.[2][3][4] Nonetheless, there has been as yet no available solid-state structure of, specifically, a lithiated diazomethane as such. Here we report such a structure, that of a THF complex of lithiated (trimethylsilyl)diazomethane with an empirical formula $[Me_3SiC(Li)N_2]_2 \cdot 3$ THF.

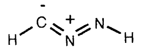
A series of papers stretching over 35 years[2] best epitomises studies on diazomethanes. For H_2CN_2 itself, deprotonation/reprotonation experiments detected species **1a** and **1b**, but not the so-called nitrile isomer **1c**. Recent calculations[4] found that **1a** is the most stable isomer. However, it was further calculated that for *lithiated* diazomethane the N−Li species **2b** (derived formally from **1b**) is more stable than the C−Li one **2a**, with **2c** being of yet lower stability. This already rather complicated chemistry is compounded on considering the results of metallating *monosubstituted* diazomethanes **3**. Experimentally, it was found that here (e.g., when R = Me or Ph) metallation then reprotonation could give cyclised products, the 4,5-disubstituted triazols **4-H**.[2b][2f] On the other hand, calculations on lithiated H_3SiCHN_2 showed that the nitrile isomer **5c** (akin to **2c**; R = H_3Si) is slightly more stable (by 1.4 kcal mol^{-1}) than the C−Li species **5a**.[4] It was thus a neat convergence of experiment and theory that lithiation of Me_3SiCHN_2 in Et_2O afforded a product containing *both* Me_3SiCN_2Li *and* lithiated cyclised units **4**-Li (R = Me_3Si), viz **6**.[4] The solid-state structure of **6** is complicated, but the key feature is that the lithiated diazomethane units show only N−Li attachments and no C−Li ones, thus supporting theory by favouring **5c** over **5a**.



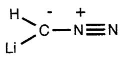
1a



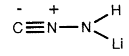
1b



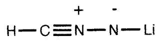
1c



2a

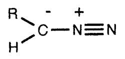


2b

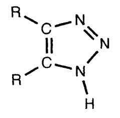


$\mathrm{H{-}C{\equiv}\overset{+}{N}{-}\overset{-}{N}{-}Li}$

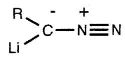
2c



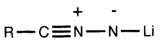
3



4-H



5a



$\mathrm{R{-}C{\equiv}\overset{+}{N}{-}\overset{-}{N}{-}Li}$

5c

$(\mathbf{5c})_6{\cdot}(\mathbf{4}\text{-Li})_2{\cdot}7Et_2O =$ **6** (R = Me_3Si)

$[Me_3SiC(Li)N_2]_2{\cdot}3THF$

$\{[Me_3SiC(Li.THF)N_2]_2{\cdot}[Me_3SiC(Li.2THF)N_2]_2\}_\infty$

7

Our initial interest in lithiated (trimethylsilyl)diazomethane stemmed from its recent use in the syntheses of ynolates, the triple-bond equivalents of enolates.[5] In these syntheses, the first step is lithiation of Me_3SiCHN_2 in THF, followed by CO insertion into the (proposed) C−Li bond and then by elimination of N_2 and rearrangement. Wishing to investigate the mechanism of this unusual synthetic protocol by isolating intermediates along its pathway, we first treated Me_3SiCHN_2 with *n*BuLi in THF at −78°C. The resulting precipitate dissolved on warming, slow cooling then affording pale yellow crystals. These were identified by elemental analyses and by NMR (^{1}H,^{13}C) spectroscopy as being, empirically, $[Me_3SiC(Li)N_2]_2 \cdot 3$ THF (**7**) (see Exper-

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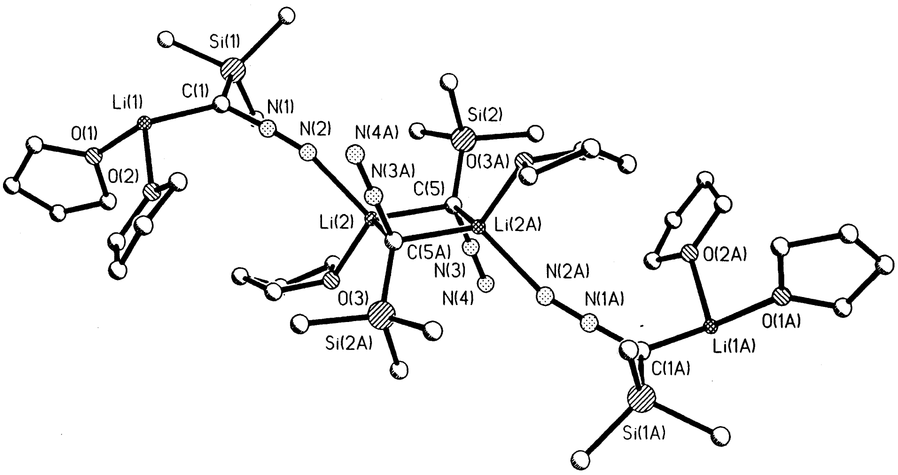
imental Section). The yield of **7** was 74% and no other product could be isolated.

The solid-state structure of **7** (Experimental Section) is polymeric. The repeat unit is tetrameric, consisting of two mono-THF-complexed lithiated diazomethane molecules and two bis-THF-complexed ones, i.e., $[Me_3SiC(Li \cdot THF)N_2]_2 \cdot [Me_3SiC(Li \cdot 2THF)N_2]_2$ (Figure 1). The former associate to give a central C_2Li_2 ring [μ_2-C−Li distances 2.083(10), 2.103(11) Å]. The latter, which are terminally attached to the Li^+ centres of this central ring by N−Li contacts [2.150(12) Å], are also each lithiated at their carbon centre [C−Li distance 1.979(11) Å]. The final nitrogen contact to lithium causes polymerisation of these tetrameric units (Figure 2). Thus, the end-N atoms of the ring diazomethane anions each link to a terminal Li^+ in a neighbouring tetramer [N(4)−Li(1B) 2.183(12) Å].

Figure 1. The repeat tetrameric unit of **7**; the H atoms of Me_3Si groups and THF ligands have been omitted for clarity

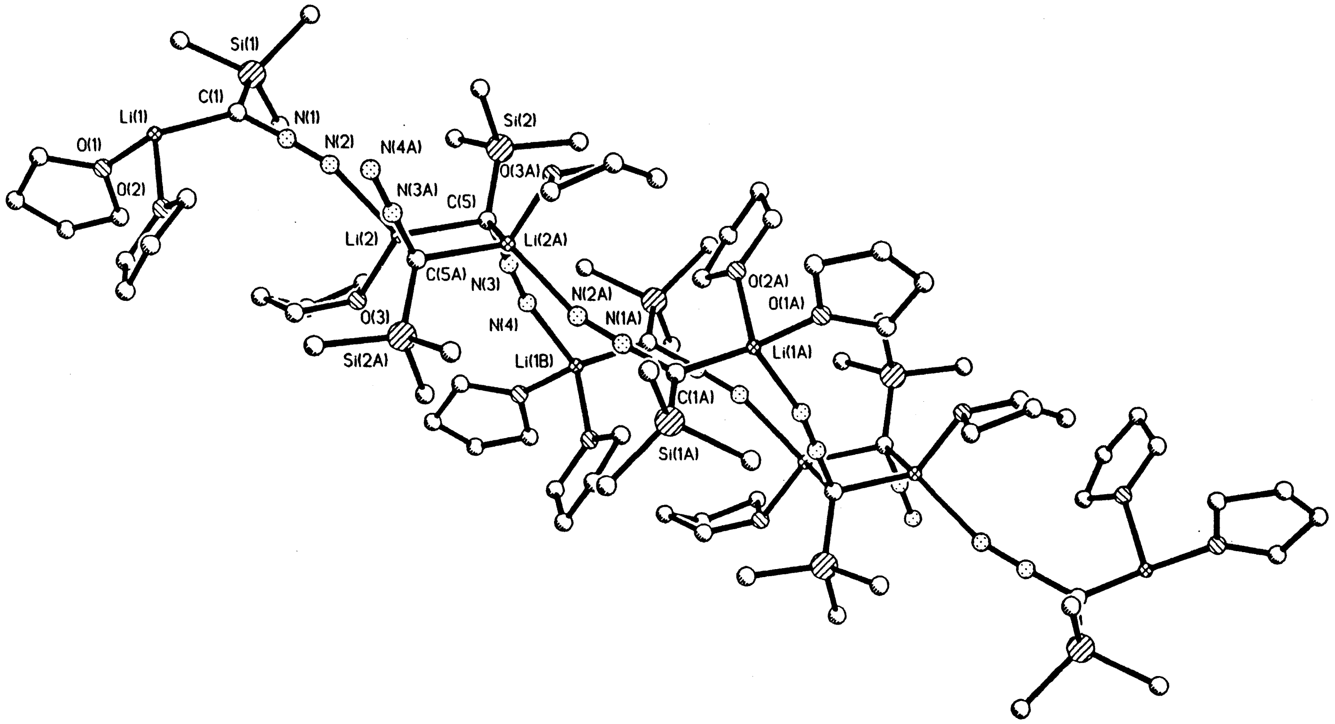


The structure of **7** is in stark contrast to that of **6**, an Et_2O-complexed co-aggregate of **5c** (R = Me_3Si) and a cyclised product **4**-Li (R = Me_3Si). In **6**, the $Me_3SiCN_2^-$ anions display only μ^3-N−Li bonds (mean distance 2.057 Å), supporting the computational finding (R = H_3Si) that **5c** is more stable than **5a**. The THF complex **7** is of $Me_3SiC(Li)N_2$ alone and its individual anions are formally *C*-lithiated (mean distance 2.055 Å), with significantly longer N−Li contacts (mean distance 2.167 Å) being used to effect polymerisation. Thus, the individual units comprising **7** reflect optimised structure **5a** (R = H_3Si) rather than **5c**. Regarding the $(Me_3SiCN_2)^-$ anions in **6** and **7**, in both the C−N−N backbones are near-linear (mean C−N−N 178.9° and 177.7°, respectively). In **6**, the exclusively *N*-bonded anions show mean C−N and N−N distances of 1.20 Å and 1.21 Å, respectively, equating well with those calculated[4] for **5c** (R = H_3Si; 1.221 and 1.218 Å, respectively). In **7**, however, the C−Li- *and* N−Li-bonded anions have a much longer mean C−N bond length of 1.33 Å and a somewhat shorter N−N one of 1.18 Å. These values now tally more closely with those calculated for **5a** (R = H_3Si; 1.287 and 1.172 Å, respectively) and are quite similar to the values found (by microwave spectroscopy)[6] for diazomethane itself (**1a**; 1.32 and 1.12 Å). These different formulations for the diazomethane anions within **6** and **7** do of course reflect the structures adopted. An anion of type $(R{-}C{\equiv}N^+{-}N^-)^-$, incorporating a formally uncharged and saturated C centre, will probably bond to Li^+ cations only through the terminal N atom, as is found in **6**. Similarly, one can see why the $(R{-}C^-{-}N^+{\equiv}N{:})^-$ anions in **7** (R = Me_3Si) will contact Li^+ ions through both C and N.

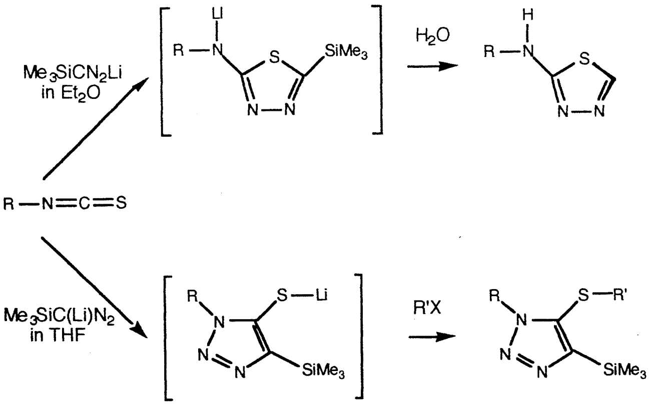
The above findings also explain the well-documented[1][4] lower reactivity of lithiated diazomethane reagents produced in Et_2O compared to those produced in THF. Organic syntheses using such reagents rely usually on loss of N_2 and, obtained from Et_2O solution, **6** contains only diazomethane units of type **5c** with very short, strong C−N bonds and with relatively long N−N bonds. The explanation is completed with the structure of the THF-derived reagent **7** which has diazomethane units of type **5a** with much longer, weaker C−N bonds and with, concomitantly, shorter N−N bonds, making loss of N≡N much more facile. These features also now explain a noted "dramatic solvent effect"[1e][1f] when lithiated (trimethylsilyl)diazomethanes, generated in Et_2O or in THF, are added to thiocyanates RN=C=S (Scheme 1). It is seen that in Et_2O the reagent contains units of type **5c** and so joins its N^- centres to the $C^{\delta+}$ centres of RNCS molecules, whereas in THF the reagent has anions of type **5a** and so C−C bonds result.

One fundamental question remains: why is it that lithiation of Me_3SiCHN_2 gives two such very different products according to whether the solvent is Et_2O or THF? It has been suggested[4] that lithiation in THF is faster, giving "instantaneously" (and presumably quantitatively) the lithiated diazomethane $R{-}C{\equiv}N^+{-}N^-{-}Li$ (**5c**; R = Me_3Si) and so precluding reaction between it and (otherwise unreacted) diazomethane $R{-}^-CH{-}N^+{\equiv}N$ (**3**; R = Me_3Si) to give a cyclised by-product **4**-Li (R = Me_3Si). A slower lithiation in Et_2O would afford **5c** which can react with residual **3** to give the cyclised species. This can then join with **5c** to give the final isolated product **6**: it is noticeable how the exclusively terminal N−Li attachments of **5c** units remove the Me_3Si groups from the space in which such juncture occurs.

Figure 2. A section of the polymeric structure of **7**



Scheme 1



However, more crucially, it is now seen that lithiated diazomethane generated in THF does not in fact contain units of type **5c**, but rather ones of type **5a**, $Me_3Si^{-}C(Li){-}N^{+}{\equiv}N$. Even if the lithiation reaction in THF is slow, these units are unlikely (given the formal charge on their C centres) to react with residual polar diazomethane molecules $Me_3Si^{-}CH{-}N^{+}{\equiv}N$ to form C−C bonds and hence the cyclised co-product **4**-Li.

Lithiated diazomethane reagents are of course used in solution and so the above conclusions, based largely on the solid-state structure of **7**, need to be treated with some caution. However, we have made a preliminary examination of the nature of **7** in various solutions. Cryoscopic relative molecular mass (CRMM) measurements on benzene solutions of very varying concentrations $\{2.3 \cdot 10^{-3}$ to $1.6 \cdot 10^{-2}$ mol dm^{-3} with respect to the empirical formula $[Me_3SiC(Li)N_2]_2 \cdot 3$ THF, RMM 456$\}$ gave effectively constant RMM values of 177±10. Clearly, not only does polymeric **7** break up on dissolution but the tetrameric unit (RMM 912) dissociates also. Mere cleavage into the intact central C_2Li_2 ring (including its THF complexants) and two separate bis-THF-complexed monomers (as from Figure 1) would afford an RMM of 304. Obviously, then, further dissociation occurs, involving break up of the dimeric ring and/or loss of Li-coordinated THF. Such complexity is reflected in ^{7}Li-NMR spectra of solutions of **7** in [D$_8$]THF. One sharp resonance ($\delta = -1.47$, relative to Ph^{7}Li in THF) is seen at 298 K, but at 273 K a shoulder develops on this main resonance. At 178 K, two predominant resonances ($\delta = -1.41, -1.57$) are apparent, along with several smaller ones. There are obviously several species present in solutions of **7**, whether in benzene or THF. However, ^{1}H- and ^{13}C-NMR spectra of solutions of **7** in THF (from which solid **7** was isolated) show little change over various concentrations and various temperatures. The implication is that C−Li-bonded units of type **5a** are retained in solution. Such implication is strengthened by points made earlier regarding the general reactivity of THF-generated **7** (viz, ready loss of N_2) and its specific reaction with thiocyanates (Scheme 1).

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Experimental Section

Synthesis of **7**: *n*BuLi (2 mmol, in hexane) was added to a solution of (trimethylsilyl)diazomethane (2 mmol, in hexane) and THF (1.2 ml) at −78°C. An orange precipitate formed on allowing the solution to warm to room temperature. This solid was dissolved by heating to reflux. Slow cooling of the resulting solution over 3 d afforded pale yellow crystals identified as **7**. First batch yield 74%; m.p. >350°C. − $C_{20}H_{42}Li_2N_4O_3Si_2$ (456): calcd. C 52.6, H 9.2, N 12.3; found C 50.1, H 9.2, N 12.2. − ^{1}H NMR {[D$_6$]DMSO, 250 MHz, 25°C}: δ = 3.60 (m, 12 H of 3 THF), 1.76 (m, 12 H of 3 THF), 0.06 (s, 6 H of 2 Me_3Si), −0.18(s, 12 H of 2 Me_3Si). − ^{13}C/APT NMR {[D$_6$]DMSO, 400 MHz, 25°C}: δ = 103.86 [$Me_3SiC(Li)N_2$, no H by APT], 67.13 (C_4H_8O), 25.24 (C_4H_8O), 2.12[$(CH_3)_3Si$], 0.36 [$(CH_3)_3Si$].

X-ray Crystal Data of **7**: $C_{20}H_{42}Li_2N_4O_3Si_2$, M_r = 456.64, triclinic, space group $P\bar{1}$ (No. 2), a = 11.320(3), b = 12.964(3), c = 10.965(2) Å, α = 98.63(2), β = 112.55(2), γ = 102.820(10)°, V = 1398.8(6) Å^3, $F(000)$ = 496, $\mu(\text{Mo-}K_\alpha)$ = 0.151 mm^{-1}, T = 150(2) K, Z = 2, $\rho_{\text{calcd.}}$ = 1.084 Mg/m^3. Data were recorded with a Rigaku R-Axis II imaging plate diffractometer, using 24 frames, each frame covering an 8° oscillation with an exposure time of 8 min per frame. 5120 reflections were recorded in the range 1.67° ≤ θ ≤ 22.26° of which 2891 were independent (R_{int} = 0.048). The structure was solved by direct methods and refinement, based on F^2, was by full-matrix least-squares techniques (G. M. Sheldrick, *SHELXL 93*, Universität Göttingen, **1993**; Si, N, Li, O, and some C atoms were refined anisotropically, and hydrogen atoms were included in calculated positions and allowed to ride on the relevant C atom; the THF groups showed positional disorder and were refined in two different sites with partial occupancies. Final residuals were $R1$ = 0.0887 for 2634 unique data with $I > 2\sigma(I)$ and $wR2$ = 0.2324 (all data). 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-100557. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. [fax: int. code + 44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].

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