Reactions of 1,3,5-triazine with organolithium compounds yielding 1,4-dihydrotriazines or the ring-opened products, a 3-lithio-1,3,5,7-tetraazaheptatriene or -1,3,5-triazaheptatriene†

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1,3,5-Triazine 1 reacts with the lithium alkyl LiR′ (R′ = CHR_2, CH_2R, Me, Bu^n or Ph; R = $SiMe_3$) to give 1,4-adducts which on hydrolysis yield the first simple 1,4-dihydrotriazines; however, 1 with $LiNR_2$ or $LiCR_3(thf)_2$ gives the crystalline ring-opened 3-lithio-1,3,5,7-tetraazaheptatriene 5 or -1,3,5-triazaheptatriene 6 $[Li\{RNC(H)NC(H)NC(H)ER\}]_n(\mu\text{-}L)$ (E = N, *n* = 3 and L is absent 5, or E = CR, *n* = 2 and L = thf = tetrahydrofuran 6).

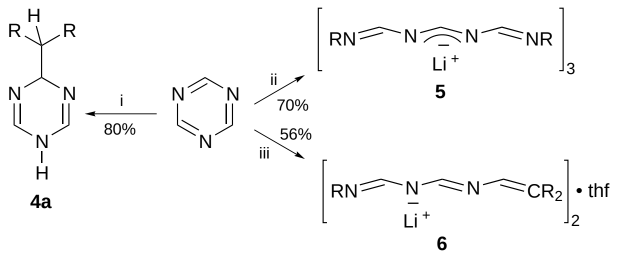
As part of our study of the reactions of nitriles free from α-hydrogen with organometallic reagents such as $LiCH(SiMe_3)_2$,[1] we now describe our initial findings with $(HCN)_3$, the 1,3,5-triazine **1**. The behaviour of **1** towards organometallic reagents is largely unexplored,[2] in contrast to its 2,4,6-triphenyl-derivative $\overline{NC(Ph)NC(Ph)NC}(Ph)$ **2**.[3] In rare cases **1** behaved as an HCN-synthon, but no intermediates were isolated.[4] For example, **1** with 2 $LiNR_2$ and subsequent treatment with RCl gave on sublimation the formamidine $RNC(H)NR_2$ (R = $SiMe_3$).[5]

We now report on the reactions of lithium hydrocarbyls or bis(trimethylsilyl)amide with **1**. Treatment of **1** in benzene with LiR′ (R′ = **a** CHR_2, **b** CH_2R, **c** Me, **d** Bu^n or **e** Ph) at ambient temperature produced 1,4-adducts **1**·LiR′ **3a–e** which, because of their insolubility, were not adequately characterised, but presumably are analogues of 1-lithio-4-alkyltriphenyldihydrotriazines derived from **2**.[6] Hydrolysis of a diethyl ether slurry of each of the compounds **3a–e** with 1.1 equiv. of H_2O and drying of the filtrate (Na_2SO_4) yielded the first 'simple' (*i.e.* monosubstituted) 1,4-dihydrotriazines, the colourless, crystalline **4a** (mp 104–106 °C) (or crystalline **4b** or the liquids **4c–e**), (Scheme 1, i). Such simple dihydrotriazines were hitherto believed merely to be transients[7] unlike the stable 1,4-dihydro adducts of **2** such as 1-*n*-butyl-2,4,6-triphenyl-1,4-dihydrotriazine.[3] Compound **4a**, possibly stabilised by the bulky $CH(SiMe_3)_2$-substituent (**4b** was markedly less robust), gave satisfactory microanalysis, ^1H and $^{13}C\{^1H\}$ NMR spectroscopic‡ and EI MS (parent molecular ion) data; the molecular structure of crystalline (boat-shaped) **4a** was also established by its X-ray structure (to be reported in the full paper). In $C_6D_5CD_3$ **4a** was in equilibrium with its 1,2-dihydro tautomer (*ca.* 50 : 1 at 295 K), a previously observed behaviour of substituted dihydrotriazines.[8]

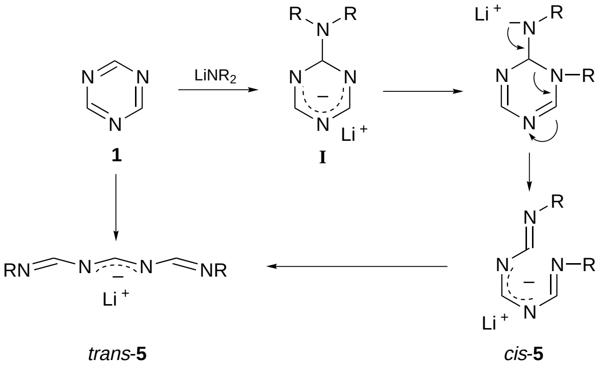
Reaction of **1** with $LiNR_2$ or $LiCR_3(thf)_2$ under similar conditions, however, took a different course: the triazine ring opened and, formally, an $\alpha \rightarrow \omega$ migration of an Me_3Si group occurred; thus the 3-lithio-1,3,5,7-tetraazaheptatriene **5** or -1,3,5-triazaheptatriene **6** was obtained (Scheme 1, ii and iii). Compounds **5** and **6** were air- and moisture-sensitive both in the solid state and in solution and, in marked contrast to **3**, extremely soluble in hydrocarbons. Both have been characterised by microanalysis, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy,‡ EI MS (parent molecular ion) and single-crystal X-ray analysis.

The pathway leading stereospecifically to the *trans*-product **5** or **6** is believed to implicate initially a 1,4-adduct analogous to **3**, followed successively by a 1,3-Me_3Si shift from NR_2 or CR_3 and then its ring scission. This is illustrated for the system **1** + $LiNR_2 \rightarrow$ **5** in Scheme 2. Evidence for the Meisenheimer complex **I** (or its CR_3 analogue for **6**) is supported by NMR-scale experiments, which revealed intermediates having chemical shifts and coupling patterns resembling those of dihydrotriazine **4a**. Relevant precedents exist for anionic 1,3-Me_3Si shifts from N → N[9] or C → N.[1] This migration might be stereoelectronically promoted, since for the case of **1** + $LiCHR_2$ the adduct **3a** was transformed into $Li[RNC(H)NC(H)NC(H)CHR]$ **7** upon heating to 140 °C.

The X-ray molecular structure of crystalline **6** (Fig. 1) shows it to be dinuclear and lying on a crystallographic twofold rotation axis.§ The lithium atoms are bridged by a thf molecule, a rare phenomenon.[10] The atoms C(2), N(1), C(3), N(2), C(4) and N(3) are coplanar, largest deviation from least-squares plane is 0.048, and comparison of the bond lengths with known formamidinates[11,12] suggest that the NC(H)NC(H)N unit has some degree of delocalisation, while the values of 1.406 Å for N(1)–C(2) and 1.351 Å for C(2)–C(1) are unexceptional for a $N(sp^2)–C(sp^2)$ and $C(sp^2)=C(sp^2)$ bond, respectively.[13] The X-ray molecular structure of the crystalline, trinuclear compound **5** will be discussed in more detail in the full paper, but representative fragments of the molecular structures of **5** and **6**



Scheme 1 *Reagents and conditions*: i, $LiCHR_2$, Et_2O, 4 h, −40 to *ca.* 20 °C, then 1.1 H_2O and drying (Na_2SO_4); ii, $LiNR_2$, C_6H_6, 2 h, *ca.* 20 °C; iii, $LiCR_3(thf)_2$, C_6H_6, 2 d, *ca.* 20 °C



Scheme 2 Proposed pathway for formation of **5**

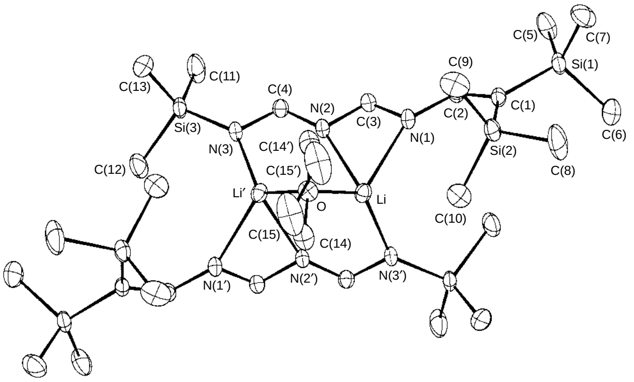
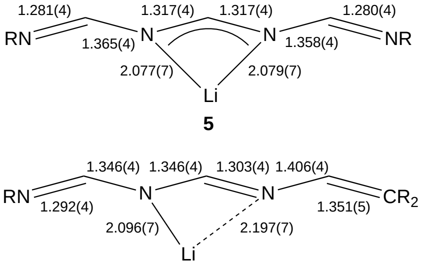


Fig. 1 ORTEP representation of the molecular structure of **6**. Selected bond lengths (Å) and angles (°): Li–O 2.133(7), Li–N(1) 2.197(7), Li–N(2) 2.096(7), Li–N(3′) 2.058(7), C(1)–C(2) 1.351(5), C(2)–N(1) 1.406(4), N(1)–C(3) 1.303(4), C(3)–N(2) 1.346(4), N(2)–C(4) 1.346(4), C(4)–N(3) 1.292(4); N(2)–Li–N(1) 63.9(2), N(2)–Li–O 86.9(2), N(1)–Li–O 114.0(3), N(3′)–Li–O 129.4(3), N(3′)–Li–N(2) 125.4(3), N(3′)–Li–N(1) 115.3(3), Li′–O–Li 77.4(4), C(1)–C(2)–N(1) 124.6(4), N(1)–C(3)–N(2) 118.2(3), N(2)–C(4)–N(3) 120.5(3).



6

Fig. 2 Bond lengths of selected fragments of the molecular structures of **5** and **6**

(Fig. 2) show that for **5**, unlike **6**, there is complete delocalisation of the central NC(H)N moiety with a bond length of *ca*. 1.32 Å.

On the basis of further exploratory experiments we consider that the results here reported have significant implications in that (*i*) compounds such as **4** upon hydrolysis in acidic or basic media are sources of aldehydes, (*ii*) compounds **5–7** are of interest as both sources of unusual tetra- or tri-azaheptatrienyl ligands and of nitrogen macrocycles.

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Footnotes and References

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† No reprints available.

‡ *Selected NMR spectroscopic data* (^{1}H 300.13, ^{13}C{^{1}H} 75.48, ^{7}Li{^{1}H} 116.64 MHz, *ca*. 293 K, C_6D_6). **4a**: ^{1}H: δ 6.23 (dd, ^3J 2.5, ^4J 2.3 Hz, 2 H, HCN), 5.01 [dt, ^3J 3.9 Hz, 1 H, NC(H)N], 4.74 (br s, 1 H, NH), 1.04 (d, 1 H, C*H*R_2), 0.38 (s, 18 H, 2 R). ^{13}C{^{1}H}: δ 141 (HCN), 71 [NC(H)N], 25 (*C*R_2), 2 (2 R). **5**: ^{1}H: δ 8.24 (s, 6 H), 7.85 (s, 3 H), 0.37 (s, 54 H, 6 NR). ^{13}C{^{1}H}: δ 177.83, 170.48, 0.84. ^{7}Li{^{1}H}: δ 5.18 (1 Li), 4.39 (2 Li) **6**: ^{1}H: δ 8.20 (s, 2 H), 7.89 (br s, 2 H), 7.47 (s, 2 H), 3.59 (ddd, 4 H, thf), 1.41 (m, 4 H, thf), 0.36, (s, 18 H, *C*R), 0.34 (s, 18 H, *C*R), 0.17 (s, 18 H, NR). ^{13}C{^{1}H}: δ 171.48, 169.95, 159.84, 121.7 (*C*R_2), 68.07, 25.65, 2.67, 1.18, 0.31. ^{7}Li{^{1}H}: δ 3.85.

§ *Crystal data* for **5** and **6** [*T* 173 K: Enraf-Nonius CAD-4 diffractometer, λ(Mo-Kα) 0.710 73 Å, no crystal decay, direct methods, full-matrix least-squares refinement on F^2 (SHELXL-93) with non-hydrogen atoms anisotropic]. Hydrogens were included in riding mode with $U_{iso} = 1.2\ U_{eq}$ or 1.5 U_{eq} for methyl groups. **5**: $C_{27}H_{63}Li_3N_{12}Si_6(C_5H_{12})_{\frac{1}{2}}$, $M = 781.3$, monoclinic, space group $P2_1/n$ (non-standard no. 14), $a = 18.869(7)$, $b = 14.603(4)$, $c = 19.523(4)$ Å, $\beta = 112.10(2)°$, $U = 4984(3)$ Å^3, $Z = 4$, $D_c = 1.04$ g cm^{-3}, $F(000) = 1692$, μ(Mo-Kα) = 2.0 cm^{-1}, specimen 0.4 × 0.4 × 0.4 mm^3. 8753 unique reflections for $2 < \theta < 25°$, $R_1 = 0.061$ [for 5240 reflections with $I > 2\sigma(I)$], $wR_2 = 0.132$ (all data). **6**: $C_{30}H_{68}Li_2N_6OSi_6$, $M = 711.3$, monoclinic, space group $P2/n$ (non-standard no. 13), $a = 13.022(3)$, $b = 8.134(4)$, $c = 22.607(6)$ Å, $\beta = 106.43(2)°$, $U = 2296.8(14)$ Å^3, $Z = 2$, $D_c = 1.03$ g cm^{-3}, $F(000) = 776$, μ(Mo-Kα) = 2.1 cm^{-1}, specimen 0.3 × 0.3 × 0.2 mm^3. 4041 unique reflections for $2 < \theta < 25°$, $R_1 = 0.062$ [for 2570 reflections with $I > 2\sigma(I)$], $wR_2 = 0.162$ (all data). CCDC 182/592.

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