Substituted triazines and pyrimidines from 1,3,5-triazine and a lithium amidinate, alkyl- or 1-azaallyl

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Treatment of 1,3,5-triazine **1** with an alkyllithium LiR [R = **a** Me, **b** Bu^n, **c** Bu^t, **d** Ph, **e** CH$_2$TMS, **f** CH(TMS)$_2$ or **g** Si(TMS)$_3$(THF)$_3$] yielded the appropriate 1 : 1 addition product **2a**–**2g**, which upon hydrolysis gave the corresponding mono-substituted dihydro-1,3,5-triazine HN̄C(H)NC(H)(R)NCH **3a**–**3g**. ^{1}H NMR spectral data showed that the 1,4-dihydrotriazine **3f** in toluene-d_8 was in equilibrium with its 1,2-dihydro tautomer. Heating **3f** with EtOH or H$_2$O in an acidic medium led to the facile cleavage of a C–Si bond and the formation of EtOTMS or (TMS)$_2$O, respectively. The ^{13}C and ^{15}N NMR spectral data are compared with those obtained by B3LYP/6-31+G* computations on the model compound N̄C(H)NCH$_2$NC̄H. Treatment of **1** with the lithium amidinate [Li{N(TMS)C(Ph)NTMS}]$_2$ or with 1-azaallyllithium [Li{N(TMS)C(Ph)C(H)TMS}(tmen)], [Li{N(TMS)C(Bu^t)C(H)TMS}]$_2$ or [Li{N(TMS)C(Ph)C(TMS)$_2$}(THF)$_2$] yielded 2-phenyltriazine **5**, 4-phenylpyrimidine **6**, 4-*tert*-butylpyrimidine **9** or, in poor yield, the new 4-phenyl-5-trimethylsilylpyrimidine **7**, respectively. In the case of **1** and [Li{N(TMS)C(Bu^t)C(H)TMS}]$_2$ an intermediate was isolated—the thermally unstable [Li{N(TMS)C(H)NC(H)NC(H)C(H)C(Bu^t)NTMS}]$_n$ **8**. A pathway is proposed involving the 1,4-addition of the lithium compound to 1,3,5-triazine **1**, followed by a 1,3-trimethylsilyl shift, ring-opening and the formation of a new C–C or C–N bond to form the appropriate aromatic heterocycle.

Introduction

Triazine derivatives are widespread and have applications in the polymer, pharmaceutical and dye stuffs industry.[1] Although it has been known for more than fifty years that benzonitrile is cyclotrimerised by *n*-butyllithium to yield 2,4,6-triphenyltriazine,[2] the organolithium chemistry of triazine derivatives has only recently received more attention.[3] Wakefield and co-workers have shown that triphenyldihydrotriazines were formed by reacting 2,4,6-triphenyl-1,3,5-triazine with a lithium reagent and they have explored the chemistry of their products.[4]

The parent compound, 1,3,5-triazine **1**, was not structurally identified until 1954, by Grundmann and Kreutzberger.[5] It is used in organic synthesis[6] as a synthon for hydrocyanic acid, for example in Gatterman's aldehyde synthesis.[7] Oakley and co-workers made use of this property to synthesize a silylated formamidine (TMS)$_2$NC(H)N(TMS) from **1** and LiN(TMS)$_2$ [eqn. (1)].[8]

(1)
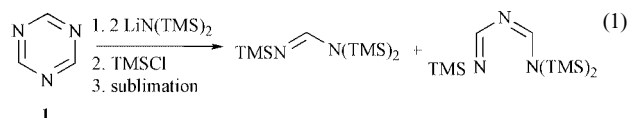
Although the organic chemistry of **1** has been well investigated,[6,9] reactions with metal complexes remain largely unexplored. Recently, we briefly reported the facile synthesis of mono-substituted dihydrotriazines **3**,[10] previously thought to be unstable,[11] from **1** and an alkyllithium reagent and subsequent protonolysis of the presumed lithio(alkyl)triazines **2**. In contrast, treatment of **1** with LiN(TMS)$_2$ afforded a tetraazaheptatrienyllithium compound in good yield [eqn. (2)].[12]

The formation of **2** is best explained by an initial addition reaction, followed by a 1,3-trimethylsilyl shift and ring-opening. Consequently, we reasoned that (i) amidinates, 1-azaallyls and β-diketiminates containing trimethylsilyl groups are potential "ring-openers", (ii) ring-opening was expected to give access to

(2)
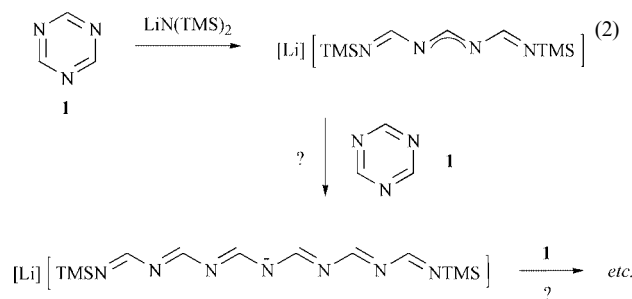
unsaturated poly-aza compounds, and (iii) for the case of the 1-azaallyl, formation of a new C–C or C–N bond was in prospect. In other words, LiN(TMS)$_2$ would have the potential to initiate the anionic oligomerisation of HCN units from triazine **1** as shown in eqn. (2). It has been pointed out that unsaturated poly-aza compounds, being isoelectronic with polyacetylenes, may be of interest because of distinct electrical and optical properties.[13]

An additional point of interest is the extensive study of 1-azaallyls,[14] β-diketiminates[15] and, in particular, the (benz)-amidinates[16] as ligands in coordination chemistry, since they offer the possibility to control the environment of the metal centre, enabling the synthesis of well defined catalysts.[17] The alkali metal benzamidinates, for example, have been widely used as ligand transfer reagents.[18] By contrast, studies into their reactivity towards organic reagents are much more limited.

We now provide full details of the synthesis and characterisation of a series of dihydrotriazines **3a**–**g** and an *N*-trimethylsilyl derivative **4** and report on the surprising formation of substituted triazines and pyrimidines from **1** and lithium amidinates or 1-azaallyllithiums, respectively.

Results and discussion

1,3,5-Triazine **1** was reacted with LiR (R = **a** Me, **b** Bu^n, **c** Bu^t, **d** Ph, **e** CH$_2$(TMS), **f** CH(TMS)$_2$ or **g** Si(TMS)$_3$(THF)$_3$;

THF = tetrahydrofuran) in diethyl ether at 0 °C yielding the appropriate adducts **2a**–**2g** [Scheme 1, item (i)]. The resulting
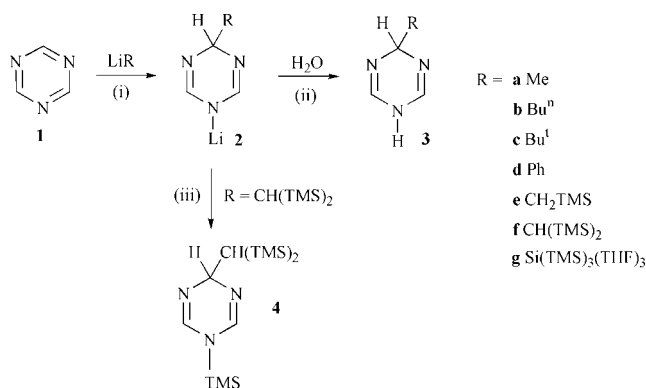
Scheme 1 Reaction of 1,3,5-triazine **1** and LiR [R = **a** Me, **b** Bu^n, **c** Bu^t, **d** Ph, **e** CH$_2$TMS, **f** CH(TMS)$_2$ or **g** Si(TMS)$_3$(THF)$_3$]. *Reagents and conditions*: Et$_2$O and (i) 0 °C, 10 h; (ii) drying (Na$_2$SO$_4$) (**3a** was isolated as its hydrate); (iii) 1.1 equivalent TMSCl.

suspension was treated either with a minimum amount of H$_2$O [Scheme 1, item (ii)] or MeOH to yield the hygroscopic dihydro-triazines **3** in low to moderate yield, or with TMSCl, in the case of **2f** [Scheme 1, item (iii)], to yield the waxy, crystalline solid **4**. Compounds **3** were isolated as a colourless solid **3a**, liquids **3b**–**3d** or colourless crystals **3e**–**g**. In the case of **3d** (R = Ph), the formation of a significant amount of biphenyl was observed, indicative of a radical pathway.

Compounds **3a**–**3d**, **3g** and **3h** were thermally stable, but **3e** decomposed within 48 h and **3f** during *ca.* 1 week at ambient conditions. Satisfactory elemental analyses were obtained for **3a**, **3f**, **3g** and **4**. Compounds **3** and **4** were characterized by their ^{1}H and ^{13}C{^{1}H} NMR and mass spectra.

^{1}H NMR spectroscopic experiments showed that the 1,4-dihydrotriazine **3f** in toluene-d_8 was in equilibrium with its 1,2-dihydro tautomer [eqn. (3)], *ca.* 50 : 1 at 25 °C.
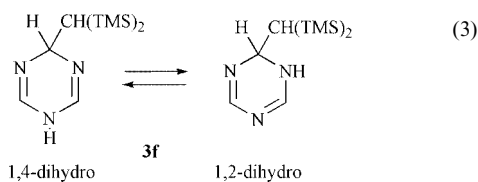
Below −25 °C this equilibrium was frozen out and both isomers were identified by using the NOE pulse sequence. Such tautomerism of the di- and triphenyl-substituted triazines HNC(Ph)NC(R^1)(R^2)NCPh (R^1 and/or R^2 = Bu^n, Bu^t or Ph) had previously been noted.[19]
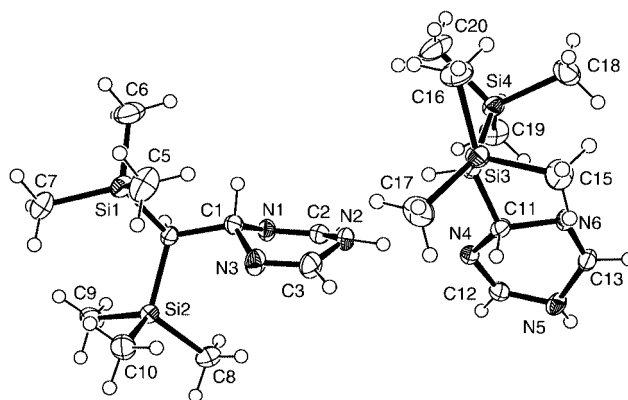
Heating the dihydrotriazine **3f** with EtOH or H$_2$O and [NH$_4$]Br in diethyl ether led to the cleavage of the C–Si bonds and consequent formation of the corresponding trimethylsilyl ethoxide or hexamethyldisiloxane [eqn. (4)].
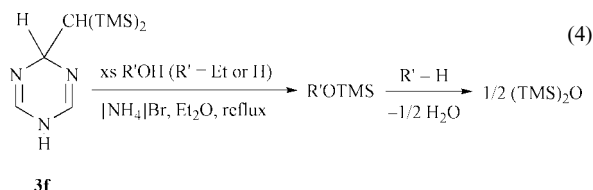
Although the yield of these Si–O compounds was not quantitative and by-products were not isolated, these reactions do illustrate the lability of such a dihydrotriazine, as the C–Si bond in CH$_2$(TMS)$_2$ was not cleaved under identical conditions. Another example of a relatively facile cleavage of a C–Si bond is for (TMS)$_3$CPPh$_2$ with MeOH, explained by initial protona-
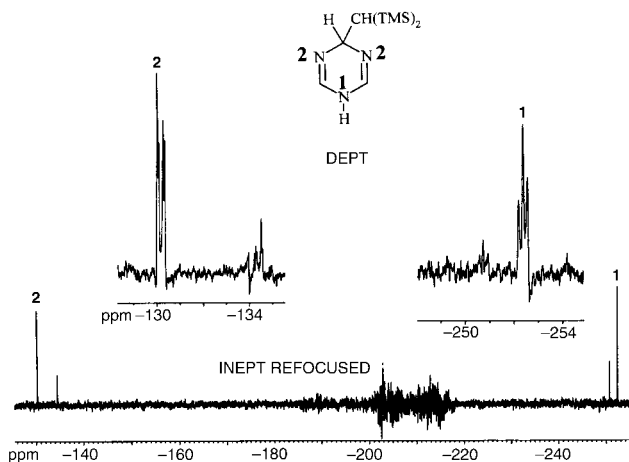
Fig. 1 The ^{15}N NMR (CDCl$_3$, 50.7 MHz, 298 K) spectrum of the dihydrotriazine **3f** was obtained by long-range coupling using an INEPT or DEPT pulse sequence.

Fig. 2 The molecular structure of dihydrotriazine **3f**, with atom labeling.

tion at P, generating [OMe]$^-$ which is then attacked at Si.[20] By analogy, protonation by EtOH or H$_2$O at a N atom of **3f** would produce [OEt]$^-$ or [OH]$^-$ and this may be the initial step of the reaction according to eqn. (4), most likely proceeding in an intramolecular fashion *via* structure **A**.
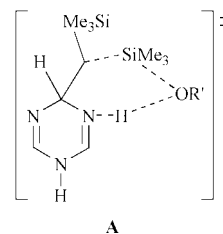
The ^{15}N NMR spectrum of **3f**, obtained using an INEPT sequence, showed chemical shifts at δ −130.4 (dd, ^2J = 12.6 Hz, ^2J = 3.4 Hz, C=*N*–C) and δ −252.6 (t, ^2J = 9.9 Hz, *N*H) for the 1,4-dihydro tautomer (Fig. 1). The absence of a large N–H coupling of *ca.* 80 Hz is consistent with an equilibrium between the 1,2- and 1,4-dihydro tautomers. An additional set of resonances with less intensity at δ −134.4 and δ −250.7 was observed, possibly due to a decomposition product from **3f** in CDCl$_3$.

The molecular structure of **3f** in the solid state was studied by X-ray diffraction. There are two independent molecules of essentially the same geometry. The crystal structure of **3f** together with atom labeling is shown in Fig. 2; selected bond lengths and angles are listed in Table 1. The molecule is boat-shaped; angles between planes N1–C2–C3–N3 and C2–N2–C3 or N1–C1–N3 are 23 or 36°, respectively. Bond lengths are unremarkable: C(sp^2)=N(sp^2) 1.274, C(sp^3)–N(sp^2) 1.479,

Table 1 Selected bond lengths (Å) and angles (°) for one independent molecule of the dihydrotriazine **3f**

N1–C2	1.274(4)	N1–C2–N2	123.4(4)
N3–C3	1.260(5)	C1–N1–C2	113.2(3)
C2–N2	1.371(5)	N1–C1–N3	113.2(3)
C3–N2	1.388(5)	C2–N2–C3	113.7(3)
N1–C1	1.479(5)	N1–C1–C4	110.9(3)
N3–C1	1.471(4)	C4–Si1–C5	111.5(2)
C1–C4	1.550(4)	N2–H2···N4	179.3(52)
C4–Si1	1.890(4)		
C5–Si1	1.867(4)		
N2–H2	0.887(49)		
H2···N4	2.02(5)		

C(sp^2)–N(sp^3) 1.371 and C(sp^3)–C(sp^3) 1.550 Å with the CH(TMS)$_2$-substituent in an equatorial position.

The molecules are linked together in chains along the *c* axis by hydrogen bonds [21] between the nitrogens, N2–H2···N4 and N5–H5···N1 (1.5 − *x*, 1 − *y*, 0.5 + *z*).[22]

We have repeated earlier reported computations by Armstrong *et al.*[3a] on the model 1,4- and 1,2-tautomers HNC(H)NCH$_2$NCH and HNC(H)NC(H)NCH$_2$ and optimised them at the higher B3LYP/6-31+G* level (instead of 6-31G)[3a] using Gaussian 94.[23] However, the inclusion of polarisation and diffuse functions did not yield a significant change in the structural parameters, nor in the energy difference between the two tautomers (ΔΔ*G* = 2.96 kcal mol^{-1} at MP2/6-31+G*), although nitrogen-containing molecules are known to be very sensitive to basis set deficiencies.

The ^{13}C and ^{15}N NMR spectral chemical shifts for HNC(H)NCH$_2$NCH were computed using the GIAO procedure and referenced to Me$_4$Si and MeNO$_2$, respectively;[24] the GIAO magnetic shielding tensor gave ^{13}C chemical shifts of δ 145.5 (N=*C*H) and 74.5 (N*C*H$_2$N), within 5 ppm of the experimental values.[25] The ^{15}N chemical shifts agreed only within 23 ppm (computed value in brackets): δ −252.4 (−229.6) CH$_2$*N*CH and δ −130.2 (−114.1) *N*H, but the difference between the shifts agreed much better: Δδ 122.2 (115.5).

The lithium benzamidinate [Li{N(TMS)C(Ph)NTMS}]$_2$ was treated with **1** in diethyl ether at 0 °C. Surprisingly, the only product isolated [Scheme 2, item (i)] was 2-phenyl-1,3,5-triazine **5**; it was sublimed at 45 °C/10^{-2} mbar from the crude reaction mixture in 81% yield. The reaction of the 1-azaallyllithium [Li{N(TMS)C(Ph)C(H)TMS}(tmen)] (tmen = Me$_2$NCH$_2$CH$_2$-NMe$_2$) under similar conditions [Scheme 2, item (ii)] afforded 4-phenylpyrimidine **6**. The reaction of [Li{N(TMS)C(Ph)-C(TMS)$_2$}(THF)$_2$] with **1** [Scheme 2, item (iii)] afforded the new compound 4-phenyl-5-trimethylsilylpyrimidine **7** in low yield which was characterised by its ^{1}H and ^{13}C{^{1}H} NMR and mass spectra. In contrast with the formation of **5**–**7**, treatment of the 1-azaallyllithium [Li{N(TMS)C(Bu^t)C(H)TMS}]$_2$ with **1** [Scheme 2, item (iv)] yielded the 1,3,5,9-tetraazanonatetra-enyllithium compound **8** (characterised by its ^{1}H, ^{13}C{^{1}H} and ^{7}Li{^{1}H} NMR and mass spectra, and elemental analysis), which only upon prolonged heating (60 °C) in benzene-d_6 [Scheme 2, item (v)] was converted to the 4-*tert*-butylpyrimidine **9**. By-products were formed, but not identified. As a consequence of the transient nature of the tetraazanonatetraenyl systems, the reactions leading to the formation of heterocycles were not very clean, giving difficulties for their complete characterization.

The ^{1}H NMR spectrum of **8** at ambient temperature consisted of very broad signals. This is attributed to the fluxional nature of the compound and to the various possibilities for coordination of the ligand to the lithium cation, resulting in an equilibrium between oligomers. The ^{1}H NMR spectrum at 333 K showed sharp signals: singlets for NC(*H*)N-units at δ 8.28 and 8.17 and two doublets at δ 7.06, 6.51 ($^3J_{HH}$ = 13.1 Hz), the coupling constant being indicative of a *trans* relationship for the C(*H*)=CH unit. The formation of this new C–C bond
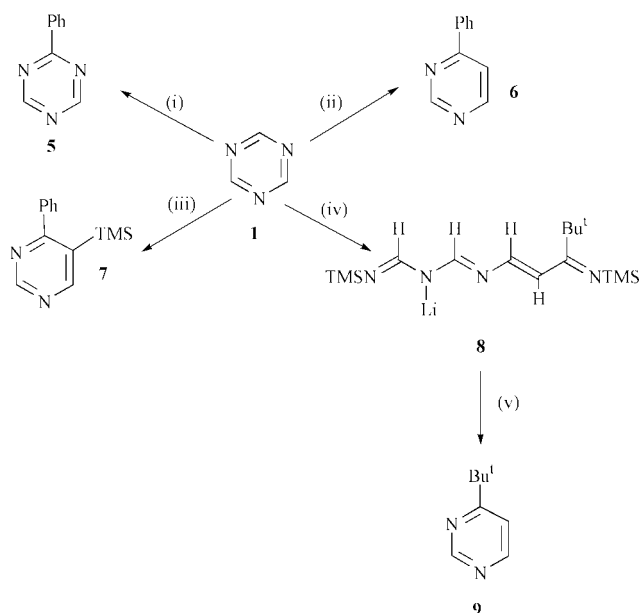

Scheme 2 Synthesis of the heterocycles **5**–**7**, **9** and the tetraaza lithium compound **8** from the triazine **1**. *Reagents and conditions*: Et$_2$O and (i) 1/2 [Li{N(TMS)C(Ph)NTMS}]$_2$, 0 to 20 °C, 12 h; (ii) [Li{N(TMS)C(Ph)C(H)TMS}(tmen)], −50 to 20 °C, 12 h; (iii) [Li{N-(TMS)C(Ph)C(TMS)$_2$}(THF)$_2$], −80 to 20 °C, 12 h; (iv) 1/2 [Li-{N(TMS)C(Bu^t)C(H)TMS}]$_2$, −50 to 20 °C, 12 h, and (v) C$_6$D$_6$, 60 °C, 90 h.

demonstrates that, although the electronegative charge resides mainly at the more negative nitrogen, in particular in the presence of donor solvents,[26] in its chemistry it behaves as a C-centered nucleophile, *i.e.*, a C–C and *not* a C–N bond is formed.

The results show that triazine **1** is reactive towards (new) N- and C-centered nucleophiles. The isolation of compound **8** confirms that an adduct is initially formed, which, after a 1,3-trimethylsilyl shift, underwent C–N bond cleavage, as for **1** and LiN(TMS)$_2$ [eqn. (2)]. However, depending on the stability of this intermediate, a new C–C or C–N bond is formed, presumably under elimination of a lithium bis(trimethylsilyl)form-amidinate [Li{N(TMS)C(H)NTMS}]; the presence of this species was not confirmed, possibly because of its instability. In this connection, it has been noted that silylated formamidines are not easily prepared by literature methods and Oakley and co-workers indeed prepared the trisilylated compound (TMS)$_2$NC(H)NTMS from **1** and LiN(TMS)$_2$, followed by quenching with TMSCl.[8]

The reaction of **1** with an amidine or an amidinium salt has been reported and used for the synthesis of substituted triazines by Schaefer and Peters;[9b] for example, the reaction between **1** and benzamidinium chloride in refluxing methanol yielded 2-phenyltriazine **5** (Scheme 3).

The proposed reaction pathway consisted of initial nucleophilic attack by the amidine HNC(R)NH$_2$ (R = Ph) at one of
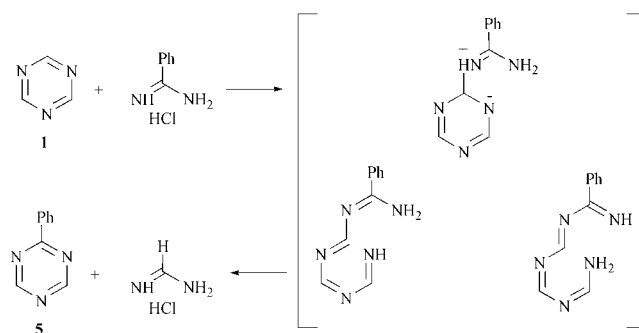
Scheme 3 Reaction between triazine **1** and benzamidinium chloride.[9b]

the electron-deficient carbon atoms of the triazine ring. The resultant transient adduct was believed to be in a tautomeric ring–chain equilibrium, which fragmented to give H$_2$NC(H)-NH and the substituted triazine **5**. This pathway is consistent with our results and we have in fact isolated an analogue of one of the intermediates, *i.e.*, the lithium compound **8**. The success of the reaction was believed to depend on the relative stabilities of the starting materials and products. This is illustrated by the formation of 2-phenyltriazine **5**, for which the additional stability acquired by the aromatic system does not permit the isolation of an intermediate, in contrast to the slow formation of 4-butylpyrimidine **9** in the present study.

Conclusion

We have shown that treatment of 1,3,5-triazine **1** with an alkyllithium and subsequent protonolysis afford stable mono-substituted 1,4-dihydrotriazines **3**. The crystalline 4-bis(trimethylsilyl)methyl-1,4-dihydro-1,3,5-triazine **3f** showed a supramolecular motif in its solid state structure.

In contrast, we have demonstrated that the reaction of **1** with a lithium amidinate or 1-azaallyl [Li{N(TMS)C(R^1)ZTMS}L]$_n$ [R^1 = Bu^t or Ph; Z = N, CH or C(TMS); L = absent, tmen or THF] gives a thermally unstable, poly-aza unsaturated lithium compound, which cyclizes to form a substituted triazine or pyrimidine **5**–**7** and **9**, providing a new regiospecific synthesis of these heterocycles. These results also demonstrate that although a 1-azaallyllithium may have been expected to behave as an N-centered nucleophile, a new C–C, and *not* a C–N, bond is formed.

Experimental

General

All manipulations of organometallic compounds were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled over potassium–sodium alloy under nitrogen gas prior to use. LiCH-(TMS)$_2$,[27] LiSi(TMS)$_3$(THF)$_3$,[28] [Li{N(TMS)C(Ph)NTMS}]$_2$,[29] [Li{N(TMS)C(Ph)C(H)TMS}(tmen)],[30] [Li{N(TMS)C(Ph)-C(TMS)$_2$}(THF)$_2$][31] and [Li{N(TMS)C(Bu^t)C(H)TMS}]$_2$ [32] were prepared by known procedures. 1,3,5-Triazine **1** and solutions of LiMe, LiBu^n, LiBu^t, LiPh and LiCH$_2$TMS in hexanes and/or diethyl ether were obtained from Aldrich and used as such. Microanalyses were carried out by Medac Ltd., Uxbridge, Middlesex or the Canadian Micro-analytical Service Ltd., Delta, Canada. The NMR spectra were recorded using a Bruker WM-300 at 300.13 (^{1}H), 75.42 (^{13}C{^{1}H}), 116.64 (^{7}Li{^{1}H}), or AMX-500 spectrometer at 500.13 (^{1}H), 50.69 (^{15}N) MHz at *ca.* 295 K in C$_6$D$_6$ and referenced internally to residual solvent resonances unless stated otherwise.

Syntheses

4-Methyl-1,4-dihydro-1,3,5-triazine hydrate 3a· OH$_2$. Methyllithium (4.6 cm^3 of a 1.5 M solution in diethyl ether, 6.9 mmol) was added by syringe to a stirred solution of 1,3,5-triazine **1** (0.56 g, 6.9 mmol) in diethyl ether (25 cm^3) at 0 °C; a white suspension was formed. Stirring was continued overnight, followed by quenching with two equivalents of water. Drying (Na$_2$SO$_4$) and filtering of the mixture, followed by concentration of the filtrate yielded the colourless solid **3a** (0.25 g, 37%), mp 77–80 °C (Found: C, 41.7; H, 7.89; N, 36.4. C$_4$H$_9$N$_3$O requires C, 41.7; H, 7.88; N, 36.5%). ^{1}H NMR (C$_5$D$_5$N, 333 K): δ 8.57 (br s, 1H, N*H*), 7.47 (d, ^4J = 0.9 Hz, 2H, N=C*H*), 5.16 [qd, ^3J = 6.4 Hz, 1H, C(*H*)Me], 4.62 (br s, 2H, H$_2$O), 1.64 [d, 3H, C(H)*Me*]. ^{13}C NMR: δ 143.7 (d, ^1J = 200.5 Hz, N=CH), 66.4 [br d, ^1J = 155.5 Hz, *C*(H)Me], 24.0 [q, ^1J = 124.5 Hz, C(H)*Me*]. MS (EI): *m/z* 97 ([*M*]$^+$, 33%), 82 ([*M* − Me]$^+$, 86), 69 ([*M* − H$_2$CN]$^+$, 11), 55 (28), 42 (64), 28 ([H$_2$CN]$^+$, 100).

4-*n*-Butyl-1,4-dihydro-1,3,5-triazine 3b. *n*-Butyllithium (3.0 cm^3 of a 1.6 M solution in hexane, 4.8 mmol) and **1** (0.40 g, 4.9 mmol) were mixed in diethyl ether (40 cm^3). The white suspension was stirred for 12 h and then quenched with water (6 cm^3). After extraction of the aqueous layer with diethyl ether (2 × 10 cm^3), the combined organic layers were washed with water, dried (Na$_2$SO$_4$) and concentrated yielding the colourless oil **3b** (0.41 g, 60%). ^{1}H NMR (C$_6$D$_6$/C$_5$D$_5$N): δ 9.52 (br s, 1H, N*H*), 7.29 (s, 2H, 2 N=CH), 5.24 [t, ^3J = 5.9 Hz, 1H, NC(*H*)(Bu^n)N], 2.27 (dt, ^3J = 7.7 Hz, 2H, C*H$_2$*CH$_2$CH$_2$CH$_3$), 1.96 (tt, ^3J = 7.5 Hz, 2H, CH$_2$C*H$_2$*CH$_2$CH$_3$), 1.56 (qt, ^3J = 7.3 Hz, 2H, CH$_2$-CH$_2$C*H$_2$*CH$_3$), 1.06 (t, 3H, CH$_2$CH$_2$CH$_2$C*H$_3$*). ^{13}C NMR: δ 145.6 (br d, ^1J = 183.4 Hz), 69.3 (br d, ^1J = 145.4 Hz), 37.7 (t, ^1J = 125.0 Hz, CH$_2$), 26.9 (t, ^1J = 121.8 Hz, CH$_2$), 22.9 (t, ^1J = 122.2 Hz, CH$_2$), 14.2 (q, ^1J = 124.7 Hz, CH$_3$). MS (EI): *m/z* 139 ([*M*]$^+$, 47%), 96 ([*M* − C$_3$H$_7$]$^+$, 29), 82 ([*M* − C$_4$H$_9$]$^+$, 100), 69 ([*M* − C$_5$H$_{11}$]$^+$, 25), 55 ([*M* − C$_4$H$_9$ − HCN]$^+$, 48).

4-*tert*-Butyl-1,4-dihydro-1,3,5-triazine 3c. *tert*-Butyllithium (3.3 cm^3 of a 1.7 *M* solution in hexane–diethyl ether, 5.1 mmol) and **1** (0.41 g, 5.1 mmol) in diethyl ether (40 cm^3) were stirred at −20 °C for 3 h, then quenched with water (5 cm^3). After extraction of the aqueous layer with diethyl ether (2 × 10 cm^3), the combined organic layers were washed with water, dried (Na$_2$SO$_4$) and concentrated affording the colourless oil **3c** (0.40 g, 57%), mp *ca.* 0 °C. ^{1}H NMR: δ 7.13 (d, ^4J = 0.8 Hz, 2H, 2 N=CH), 4.24 [s, 1H, NC(*H*)(Bu^t)N], 0.92 (s, 9H, CMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 145 (br, 2 N=CH), 77.2 [N*C*(H)-(Bu^t)N], 32 (*C*Me$_3$), 25.4 (C*Me$_3$*). MS (EI): *m/z* 139 ([*M*]$^+$, 5%), 82 ([*M* − C$_4$H$_9$]$^+$, 100), 55 ([*M* − C$_4$H$_9$ − HCN]$^+$, 9).

4-Phenyl-1,4-dihydro-1,3,5-triazine 3d. Phenyllithium (4.0 cm^3 of a 2.0 *M* solution in cyclohexane–diethyl ether, 8.0 mmol) and **1** (0.65 g, 8.0 mmol) in diethyl ether (25 cm^3) were mixed at 0 °C. The suspension was stirred during 1 d, then quenched with water (1.5 cm^3). Extraction of the reaction mixture with CH$_2$Cl$_2$ (2 × 10 cm^3), drying of the combined organic layers (Na$_2$SO$_4$) and evaporation of volatiles *in vacuo* yielded the low melting, colourless solid **3d** (0.30 g, 24%). ^{1}H NMR (C$_5$D$_5$N): δ 10.69 (br s, 1H, N*H*), 7.94 (d, ^3J = 7.4 Hz, 2H, *o*-H), 7.65 (s, 2H, N=CH), 7.44 (dd, ^3J = 7.4 Hz, 2H, *m*-H), 7.32 (t, 1H, *p*-H), 6.19 [s, 1H, NC(*H*)(Ph)N]. ^{13}C{^{1}H} NMR (C$_5$D$_5$N): δ 145.5 (*ipso*), 144.1 (N=CH), 128.6, 127.7, 126.4, 72.3 [N*C*(H)(Ph)N].

4-Trimethylsilylmethyl-1,4-dihydro-1,3,5-triazine 3e. Trimethylsilylmethyllithium (3.5 cm^3 of a 1.0 M solution in hexane, 3.5 mmol) and **1** (0.29 g, 3.6 mmol) were mixed in diethyl ether (*ca.* 40 cm^3) at 0 °C. Stirring was continued for 5 h; the mixture was quenched with excess water (1 cm^3). Drying (Na$_2$SO$_4$) of the organic layer and concentration of the filtrate afforded colourless crystals of **3e** (0.45 g, 76%) which decomposed within 24 h at ambient temperature, mp 51 °C. ^{1}H NMR: δ 7.36 (br s, 1H, N*H*), 6.75 (br s, 2H, 2 N=CH), 5.12 [t, ^3J = 7.1 Hz, 1H, NC(*H*)(CH$_2$TMS)N], 1.28 (d, 2H, C*H$_2$*TMS), 0.21 (s, 9H, TMS). ^{13}C{^{1}H} NMR: δ not observed (too br, N=CH), 67.9 [N*C*(H)(CH$_2$TMS)N], 27.0 (CH$_2$), 1.4 (SiMe$_3$). MS (EI): *m/z* 169 ([*M*]$^+$, 14%), 154 ([*M* − Me]$^+$, 17), 127 ([*M* − Me − HCN]$^+$, 80), 100 ([*M* − Me − 2HCN]$^+$, 39), 82 ([*M* − CH$_2$TMS]$^+$, 100), 73 ([TMS]$^+$, 84).

4-Bis(trimethylsilyl)methyl-1,4-dihydro-1,3,5-triazine 3f. Bis(trimethylsilyl)methyllithium (5.83 g, 35.1 mmol) and **1** (2.84 g, 35.1 mmol) were mixed in diethyl ether (50 cm^3). Stirring was continued for 12 h. The green suspension was quenched with water (1 cm^3, 55.6 mmol). Drying (Na$_2$SO$_4$) and concentration of the filtrate gave colourless crystals of **3f** (5.73 g). A second crop of **3f** (0.80 g) from the mother liquor brought the total yield to 80%. Compound **3f** was recrystallised from pentane, yielding orthorhombic crystals suitable for X-ray analysis, mp 105 °C (Found: C, 49.1; H, 9.59; N, 17.55. C$_{10}$H$_{23}$N$_3$Si$_2$ requires

C, 49.7; H, 9.60; N, 17.4%). ^{1}H NMR (C_6D_6, 500.13 MHz): δ 6.22 (dd, ^3J = 2.5 Hz, ^4J = 2.3 Hz, 2H, N=CH), 5.01 [dt, ^3J = 3.9 Hz, 1H, NC(*H*)(CHR$_2$)N], 4.74 (br s, 1H, N*H*), 1.04 [d, 1H, C*H*(TMS)$_2$], 0.38 (s, 18H, 2 TMS). ^{13}C{^{1}H} NMR: δ 141 (H*C*N), 71 [N*C*(H)(CHR$_2$)N], 25 [*C*H(TMS$_3$)$_2$], 2 (2 TMS). ^{15}N NMR (CDCl$_3$): δ −130.2 (dd, $^2J_{NH}$ = 12.6 Hz, $^2J_{NH}$ = 3.4 Hz, =*N*), −252.4 (t, $^2J_{NH}$ = 9.9 Hz, N*H*). MS (EI): m/z 241 ([M]$^+$, 5), 226 ([M − Me]$^+$, 41), 199 ([M − Me − HCN]$^+$, 71), 168 ([M − TMS]$^+$, 20), 146 (60), 127 (64), 82 {[M − (TMS)$_2$CH]$^+$, 90}, 73 ([TMS]$^+$, 100). IR (Nujol): v/cm^{-1} 3132br (N–H), 1689s (C=N).

1,2-Dihydro tautomer: [1]H ($C_6D_5CD_3$, 500.13 MHz): δ 8.55 (br s, 1H, NH), 7.49 (m, 1H), 6.49 (d, J = 4.5 Hz, 1H), 5.11 (dd, 1H), 1.11 (dd, J = 6.2 Hz, 1H), 0.33 (s, 18H).

4-Tris(trimethylsilyl)silyl-1,4-dihydro-1,3,5-triazine 3g.
The compound [LiSi(TMS)$_3$(THF)$_3$] (3.00 g, 7.5 mmol) was added to a stirred suspension of **1** (0.61 g, 7.5 mmol) in diethyl ether (50 cm^3) at −25 °C. Stirring was continued for 12 h; the reaction mixture was quenched with H$_2$O (0.24 g, 13.3 mmol). The mixture was quickly extracted with diethyl ether (2 × 10 cm^3). The combined organic layers were washed with water, dried (Na$_2$SO$_4$) and concentrated *in vacuo* yielding **3g**. Colourless, feather-like crystals of **3g** (1.63 g, 66%) were obtained from diethyl ether at −20 °C. Elemental analysis was consistent with **3g**·OH$_2$ (Found: C, 42.3; H, 9.61; N, 11.8. $C_{12}H_{33}N_3OSi_4$ requires C, 41.4; H, 9.56; N, 12.1%). ^{1}H NMR (CDCl$_3$): δ 6.07 (d, ^4J = 2.6 Hz, 2H, N=CH), 5.57 [t, 1H, NC(*H*)(Si(TMS)$_3$)N], 4.24 (br s, 1H, N*H*), 0.38 (s, 27H, Si(TMS)$_3$). ^{13}C{^{1}H} NMR: δ 140.4, 67.0, 1.7 (TMS). MS (EI): m/z 329 ([M]$^+$, 34), 287 ([M − CN$_2$H$_2$]$^+$, 14), 256 ([M − TMS]$^+$, 12), 229 ([M − TMS − HCN]$^+$, 48), 202 ([M − TMS − H$_2$C$_2$N$_2$]$^+$, 25), 173 ([M − TMS − C$_3$N$_3$H$_5$]$^+$, 87), 73 ([TMS]$^+$, 100).

4-Bis(trimethylsilyl)methyl-1-trimethylsilyl-1,4-dihydro-1,3,5-triazine 4.
Bis(trimethylsilyl)methyllithium (0.70 g, 4.2 mmol) was added in portions at 0 °C to a stirred solution of **1** (0.31 g, 3.8 mmol) in diethyl ether (25 cm^3). The white suspension was allowed to warm to ambient temperature; stirring was continued for 5 h; the mixture was quenched with RCl (0.40 g, 3.8 mmol). After stirring for 0.5 h, the volatiles were removed *in vacuo* and vacuum distillation of the residue at 120 °C/10^{-2} mbar yielded the pale yellow waxy, crystalline solid **4** (0.90 g, 76%) (Found: C, 48.7; H, 9.92; N, 13.8. $C_{13}H_{31}N_3Si_3$ requires C, 49.8; H, 9.96; N, 13.4%). ^{1}H NMR (CDCl$_3$): δ 7.04 (d, ^4J = 1.9 Hz, 2H, N=CH), 5.21 (dt, ^3J = 3.3 Hz, 1H, NC(*H*)-{CH(TMS)$_2$}N], 0.65 [d, 1H, C*H*(TMS)$_2$], 0.31 (s, 9H, NTMS), 0.11 [s, 18H, CH(TMS)$_2$]. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 142.1 (2 N=CH), 70.5 [N*C*(H){CH(TMS)$_2$}N], 27.1 [*C*H(TMS)$_2$], 1.3 (TMS), −1.0 (TMS). MS (EI): m/z 313 ([M]$^+$, 9), 298 ([M − Me]$^+$, 25), 240 ([M − TMS]$^+$, 40), 154 (88), 73 ([TMS]$^+$, 100).

Treatment of dihydrotriazine 3f with H$_2$O or EtOH.
The dihydrotriazine **3f** (1.91 g, 7.9 mmol) and [NH$_4$]Br (2.39 g, 25.6 mmol) were mixed in diethyl ether (30 cm^3) with an excess of water or ethanol (*ca.* 5 cm^3) and stirred for 2 d at 40 °C. The organic layer was decanted off and carefully distilled yielding (TMS)$_2$O (74%) or EtOTMS (65%, GC), respectively; no attempt was made to separate the latter from ethanol.

2-Phenyl-1,3,5-triazine 5.
1,3,5-Triazine **1** (0.14 g, 1.7 mmol) was added in one portion to a solution of [Li{N(TMS)C(Ph)-NTMS}]$_2$ (0.47 g, 0.9 mmol) in diethyl ether (15 cm^3) at 0 °C. The suspension was stirred for 12 h at ambient temperature. The volatiles were removed *in vacuo*. The crude product was sublimed (*ca.* 45 °C/10^{-2} mbar) from the residue to give 2-phenyltriazine **5** (0.21 g, 81%), mp 65 °C (lit.,[9b] 63–65 °C).

4-Phenylpyrimidine 6.
1,3,5-Triazine **1** (0.27 g, 3.3 mmol) was added in one portion to a solution of [Li{N(TMS)C(Ph)-

C(H)TMS}(tmen)] (1.17 g, 3.0 mmol) in diethyl ether (50 cm^3) at −50 °C. The resulting yellow suspension was allowed to warm to ambient temperature and stirred for 12 h. Evaporation of volatiles *in vacuo* yielded a yellow powder (0.81 g). After 2 d at ambient temperature colourless crystals of compound **6** (< 0.25 g, 42%), mp 65 °C (lit.,[33] 66 °C), separated from the solid. ^{1}H and ^{13}C{^{1}H} NMR and mass spectra were consistent with the literature.[33] An unidentified, air-sensitive by-product gave the following NMR spectral data. ^{1}H NMR (CDCl$_3$): δ 4.27 (s, 1H, *H*CN), 3.24 (br s, 1H, N*H*), 0.13 (s, 9H, TMS), −0.27 (s, 9H, TMS). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 96.8, 0.75, −0.1. ^{1}H NMR (C_6D_6): δ 4.53 (s, 1H, *H*CNTMS), 3.20 (br s, 1H, N*H*), 0.11 (s, 9H, TMS), −0.01 (s, 9H, TMS).

4-Phenyl-5-trimethylsilylpyrimidine 7.
A solution of [Li{N(TMS)C(Ph)C(TMS)$_2$}(THF)$_2$] (2.00 g, 4.1 mmol) in diethyl ether (*ca.* 10 cm^3) was added to a stirred suspension of **1** (0.32 g, 4.0 mmol) at −80 °C. The reaction mixture was allowed to warm to ambient temperature, stirred for 12 h and finally refluxed for 2 h. The volatiles were removed *in vacuo* and the residue was extracted with hot toluene. The precipitate obtained from the toluene solution consisted of a mixture. This precipitate was sublimed at 65 °C (10^{-2} mbar) to afford a few colourless drops of an oil **7** (0.05 g), which, over the course of 3 d, crystallised. ^{1}H NMR: δ 9.40 [s, 1H, NC(*H*)N], 8.81 [s, 1H, NC(*H*)CTMS], 7.41–7.37 (m, 2H, *o*), 7.09 (m, 3H, *m* and *p*), −0.14 (s, 9H, TMS). ^{13}C{^{1}H} NMR: δ 172.6 (*ipso*, *C*TMS), 163.2 (N*C*H), 159.1 (N*C*H), 142.0 (*ipso*), 129.7 (*ipso*), 129.1, 128.3, 126.1 (*p*), −0.2 (TMS). MS (EI): m/z 228 ([M + H]$^+$, 4.5%), 227 ([M]$^+$, 7.5), 213 ([M − Me]$^+$, 100), 197 (8), 160 (13), 73 ([TMS]$^+$, 26).

8-*tert*-Butyl-1,9-bis(trimethylsilyl)-1,3,5,9-tetraazanona-1,4,6,8-tetraen-3-yllithium 8.
1,3,5-Triazine **1** (0.47 g, 5.8 mmol) was added in one portion to a solution of [Li{N(TMS)-C(Bu^t)C(H)TMS}]$_2$ (1.45 g, 2.9 mmol) in diethyl ether (40 cm^3) at −50 °C. The yellow suspension was allowed to warm to ambient temperature and stirred for 12 h. The suspension was filtered and the filtrate concentrated *in vacuo*. Crystallisation of the residue from hexane afforded the yellow powder **5** (0.85 g, 44%), mp 139 °C (Found: C, 53.4; H, 9.12; N, 17.65. $C_{15}H_{31}$-LiN$_4$Si$_2$ requires C, 54.5; H, 9.45; N, 16.95%). ^{1}H NMR (C_6D_6, 333 K): δ 8.28 [s, 1H, NC(*H*)N], 8.17 [s, 1H, NC(*H*)N], 7.06 [d, ^3J = 13.1 Hz, 1H, C(*H*)=C(H)], 6.51 [d, 1H, C(H)=C(*H*)TMS], 1.38 (s, 9H, C*Me$_3$*), 0.35 (s, 9H, TMS), 0.21 (s, 9H, TMS). ^{7}Li{^{1}H} NMR (C_6D_6, 333 K): δ 0.71. ^{13}C{^{1}H} NMR (C_6D_6, 333 K): δ 181.3 [N*C*(H)N], 172.8 (*ipso*), 172.8 [N*C*(H)N], 147.7, 117.65, 42.5 (*C*Me$_3$), 29.1 (C*Me$_3$*), 2.1 (TMS), 0.6 (TMS). MS (EI): m/z 337 ([M + Li]$^+$, 16), 273 ([M − Bu^t]$^+$, 29), 188 (47), 168 (71.5), 147 (92), 146 (89.5), 121 (100).

4-*tert*-Butylpyrimidine 9.
A solution of the lithium compound **8** in benzene-d_6, in an NMR sample tube, was heated to 60 °C for 90 h. ^{1}H NMR: δ 9.26 [d, ^4J = 0.7 Hz, 1H, NC(*H*)N], 8.30 [d, ^3J = 5.3 Hz, 1H, C(Bu^t)C(*H*)], 6.63 (dd, 1H, NC*H*), 1.16 (s, 9H, C*Me$_3$*). ^{13}C{^{1}H} NMR: δ 177.5 (*ipso*), 158.7, 157.0, 156.8, 116.6, 37.4 (*C*Me$_3$), 29.2 (C*Me$_3$*). Evaporation of the solvent and redissolving the residue in CDCl$_3$ yielded NMR spectral data consistent with the literature.[34]

Crystal data and refinement details for 3f†

Crystal data for **3f**: $C_{10}H_{23}NSi_2$, M = 241.49, orthorhombic, space group $P2_12_12_1$ (No.19), a = 13.449(9), b = 13.597(3), c = 16.399(9) Å, V = 2999(3) Å^3, Z = 8, μ(Mo-Kα) = 2.2 cm^{-1}, 4027 independent reflections were collected for 2 < θ < 28° on an Enraf-Nonius CAD4 diffractometer with Mo-Kα radiation

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