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Addition reactions of bis(trimethylsilyl)methyl- and 1-azzallyl-lithium with cyanoamines into triazines or β-diketiminatolithium compounds

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Abstract

Reactions of bis(trimethylsilyl)methyl lithium reagent Li[CHR_2] (R = $SiMe_3$) and 1-azaallyllithium, [$\overline{LiN(R)C(Bu^t)CHR}]_2$ with cyanoamines R′CN (R′ = Me_2N, 1-piperidyl or *o*, *p*-pyridyl) yielded β-diketiminatolithiums (**1**, **2**, **5**, **7**, **8**) or symmetrically and mixed substituted triazines (**3**, **4**, **6**, **9**, **10**), respectively. The mechanistic pathways involve silicotropic rearrangements from C to N or N to N and an unusual elimination of Li[CHR_2]. The complexes **1**, **6**, **7**, and **10** had been characterized by X-Ray diffraction.

Keywords: Diketiminato complexes; Triazines; Crystal structures; Silicotropic rearrangements

1. Introduction

In our former publications, we have shown that the interaction of a trimethylsilylmethyllithium reagent Li[CHR_2] (R = $SiMe_3$) and an α-hydrogen-free nitrile R′CN (R′ = Ph, 2,5-C_6H_3 or Bu^t) can yield an 1-azaallyl-, β-diketiminato- or 1,3-diazaallyl-lithium compound [1–4]. This type of addition reaction firstly causes a C–C coupling to give *N*-lithio-imine, and then following a 1,3- migration of an $SiMe_3$ group from C to N atom to the 1-azaallyl. A further nucleophilic attack via the 1-azaallyl can happen either on C or N atom of the nitrile to give (β-diketiminato-or 1,3-diazaallyl compounds, respectively. A summery is given in Scheme 1 [5,6].

Normally, as a troublesome side reaction, the *N*-lithio-imine (ref. C in Scheme 1) could add further to molecules of nitrile, leading to aggregate or cyclic products such as pyrimidines and triazines [7–10].

However, the triazines, isolated from the addition products which were susceptible to various complications, were often in limited amount; the mechanism by which they were formed was sometimes obscure [11,12]. It was reported that $Ln(OTf)_3$ could catalyze the reaction of nitriles with ammonia or monoamines to yield triazines, at 200 °C, 24 h [13,14]. SmI_2 could catalyze the reaction at 120 °C, 72 h to give 2,4,6-trisubstituted-triazines [15].

In this paper, we report our recent study on addition reactions of bis(trimethylsilyl)methyllithium reagent Li[CHR_2] (R=$SiMe_3$) or l-azaallyllithium [$\overline{LiN(R)C(Bu^t)CHR}]_2$ cyanoamine, which, depended on the polar or non-polar solvent used, lead to β-diketiminatolithium and, interestingly, symmetrically and mixed substituted triazines at mild condition. For the symmetrically substituted triazine the catalytic amount of the lithium reagent can give an almost quantitative yield. This type of reaction may involve a series of silicotropic rearrangements and an unusal elimination of Li[CHR_2], The silicotropic rearrangements alluded to this title show an diversity of Li[CHR_2] addition reaction with nitrile and also their utilization in organic synthesis.

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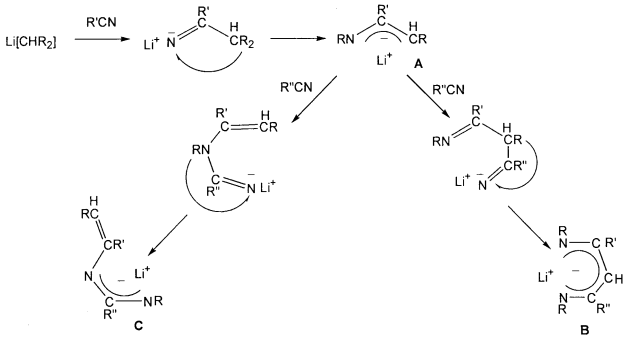


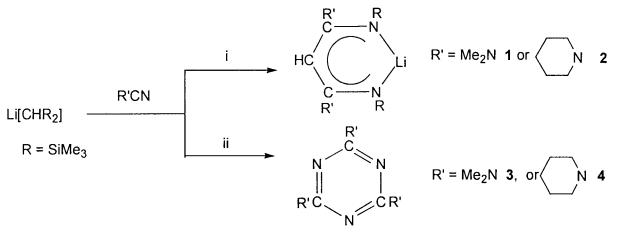
Scheme 1. Reaction routes to 1-azaallyl, β-diketiminato- or 1,3-diazaallyl-lithium compounds.

2. Results and discussion

2.1. Synthesis and discussion of reaction pathways

Treatment of Li[CHR_2] with R′CN (R′ = Me_2N or 1-piperidyl) in diethyl ether at −78 °C led mostly to the addition compounds of β-diketiminates [Li{N(R)C(NMe_2)C(H)C(NMe_2)NR}]$_2$ **1** [Li{N(R)C(piperidinyl)C(H)C(piperidinyl)NR]$_2$ **2**; however, by using hexane instead of ether, to the symmetrical 2,4,6-(tri)dimethylcyano-1,3,5-triazine **3** or 2,4,6-(tri)1-piperidinyl-1,3,5-triazine **4** in good yield (> 90%), Scheme 2. The complex **1** was characterized by X-ray diffraction and shown in Fig. 1.

In our further study it was found that the reaction of catalytic amount of the lithium reagent Li[CHR_2] with cyanoamines in a molecular ratio of 1:10 also gave good yield of triazine (> 90%). However, by treatment of *n*-butyllithium $LiBu^n$ with cyanoamines at same condition there were no phenomena to give the triazine but the complications identified by ^{1}H-NMR. So we deduced that this type of reaction might involve a series of nucleophilic attacks and silicotropic rearrangements, and finally an elimination of Li[CHR_2]. A proposed mechanism are explained in Scheme 3 as steps i–v: (i) C–C coupling and 1–3 silicotropic rearrangement to give β-diketiminato compound, (ii)(iii) C–N coupling reactions and 1–3 silicotropic rearrangements, (iv) nucleophilic attack by N anion at the terminal alkene, and (v) finally an Li[CHR_2] elimination to give triazine.



Scheme 2. Synthesis of β-diketiminatolithium **1** and **2**, and triazines **3** and **4**. Reagents and conditions: (i) Et_2O, −78 °C, 2 h; (ii) hexane, 0 °C to r.t., 12 h.

In order to verify the reaction pathways an azaallyl-lithium compound [LiN(R)C(Bu^t)CHR]$_2$ (prepared in our early work [2]) instead of Li[CHR_2] was used as starting lithium reagent, which was equally to introduce a *tert*-butyl group on the presumed intermediate of azaallyl-lithium in Scheme 4. Practically, treatment of [LiN(R)Bu^t)CHR]$_2$ with R′CN (R′ = Me_2N or *o*, *p*-pyridyl) gave a mixture. The isolated were the addition products of β-diketiminatolithium (Li[N(R)C(Bu^t)C(H)C(NMe_2)NR]$_2$ **5**, [Li{N(R)C(Bu^t)C(H)C(*o*-pyridyl)NR}]$_2$ **7**, [Li{N(R)C(Bu^t)C(H)C(*p*-pyridy)NR}]$_2$ **8**), symmetrically and mixed substituted triazines (2,4,6-(tri)dimethylcyano-l,3,5-triazine **3** and 2,4,-(bis)dimethylcyano-6-tertbutyl-l,3,5-triazine **6**,2,4,-(bis)*o*-pyridyl-6-tertbutyl-l,3,5-triazine **9**,2,4,-(bis)*p*-pyridyl-6-tertbutyl-1,3,5-triazine **10**), respectively.

The molecular structures of **6** and **10** shown in Figs. 4 and 5 were in according to their analysis results and confirmed that the triazines contained a substituted *tert*-butyl group which did come from the reagent [LiN(R)C(Bu^t)CHR]$_2$. The evidences well support the proposed mechanism, and we believe that the reaction routes are similar to that in Scheme 1 as following steps i–iv in Scheme 5: (i) C–C coupling to give β-diketiminato compounds, (ii) (iii) C–N coupling reactions and then an Li[CHR_2] elimination to mixed substituted triazines, (iv) same steps as ii–iv in Scheme 1 to symmetrically substituted triazine since the Li[CHR_2] eliminated is actually the catalyst for triazine as discussed in Scheme 1.

The triazine has been used as an anticancer reagent. The complexes **9** and **10** were checked in a primary test for anticancer effect. It was found that the mixed substituted triazines **9** exhibited a good pharmaceutical activity for leukemia.

2.2. Crystal structures of complexes *1* and *7*

The molecular structures of β-diketiminates [Li{N(R)C(NMe_2)C(H)C(NMe_2)NR}]$_2$ **1** and [Li{N(R)C(Bu^t)C(H)C(*o*-pyridyl)NR}]$_2$ **7** are illustrated in Figs. 1 and 2; selected bond distances and angles are listed in Tables 1 and 2, respectively.

Both complexes **1** and **7** are dinuclear. The coordinate fragment NCCCN actually is a delocalized system and each molecule is a centrosymmetric dimmer. The complex **1** contains as core of a nearly planar LiNLiN ring, the angle at the lithium atom being wider [102.6(3)°] than that at nitrogen [72.7(4)°]. One of the nitrogen atoms is four co-ordinate and bridging, the other is three co-ordinate. Interestingly, in complex **7** the N atom in *o*-pyridyl group provides an intermolecular bonding to lithium, forming a tridental coordination environment;

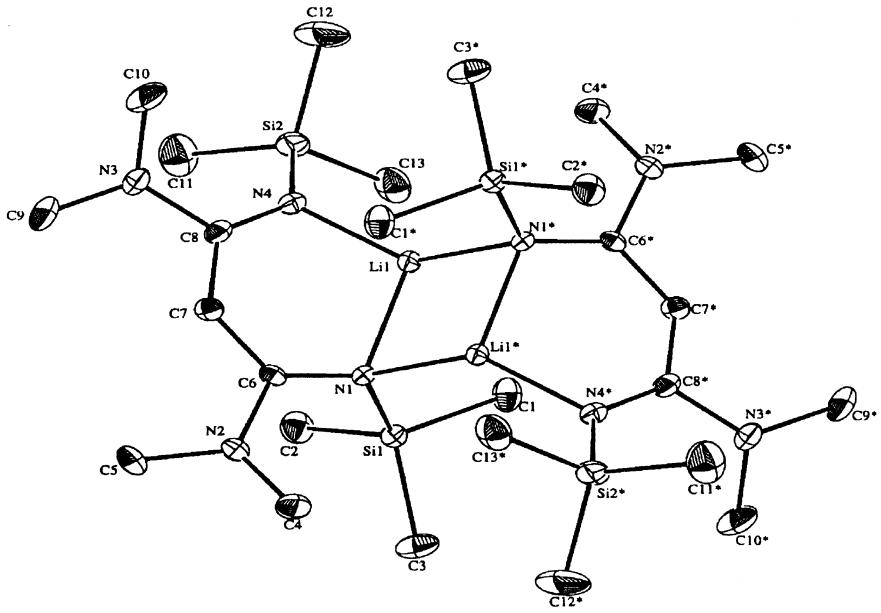
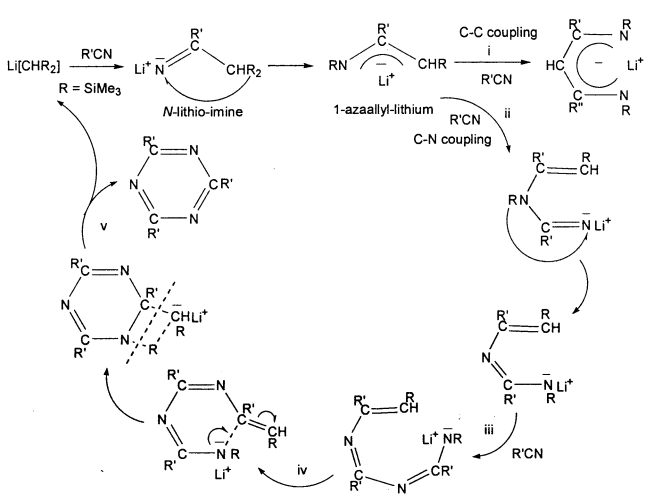
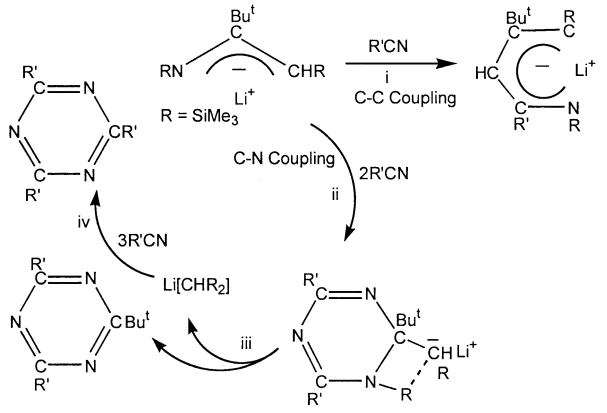


Fig. 1. Molecular structure of complex **1**.



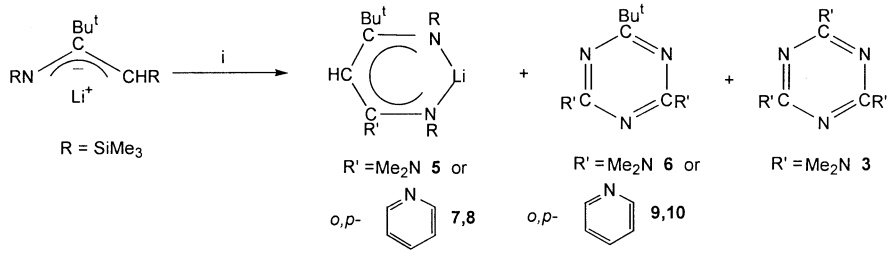
Scheme 3. Proposed mechanism for the formation of complexes **1**–**4**.



Scheme 5. Reaction routes to β-diketiminatolithium and form symmetrically and mixed substituted triazines.

the bond distance of N–Li [2.076(5) Å] was longer than that at terminal N–Li [1.943(5) Å].

The β-diketiminato complexes of the early transition and lanthanide elements have been studied as catalyst for polymerization of olefm. The electrical property of the metal is an important factor for catalyst activity. So it is also our interest to explore what effect could be by introducing an electronegative substituted group on the coordination environment of the five-membered NCCCN moiety. Comparisons of bond distances N–Li for **1** [2.01(1) and 1.94(1) Å] and **7** [1.943(5) and 1.985(6) Å] with phenyl substituted β-diketiminato



Scheme 4. Synthesis of triazines **3**, **6**, **9**, **10** and β-diketiminatolithium **5**, **7**, **8**. Reagents and conditions: (i) Et_2O, −78 °C to ambient temperature, 12 h.

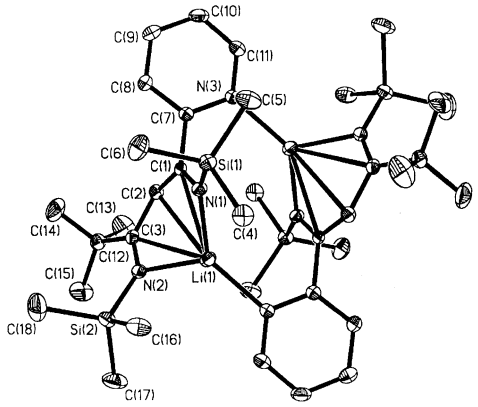


Fig. 2. Molecular structure of complex **7**.

Table 1
Selected bond lengths (Å) angles (°) for complex **1**

Bond lengths			
Li(i)–N(l)	2.01(1)	Li(l)–N(4)	1.94(l)
N(1)–C(6)	1.348(6)	C(6)–C(7)	1.408(8)
C(7)–C(8)	1.434(9)	C(8)–N(4)	1.307(8)
Bond angles			
N(4)–C(8)–C(7)	127.9(6)	C(6)–C(7)–C(8)	127.1(5)
N(1)–C(6)–C(7)	127.5(5)	N(l)–Li(l)–N(4)	103.1(4)
Li(l)–N(l)–Li(l)*	71.9(5)	N(l)–Li(l)–N(l)*	108.1(5)

Table 2
Selected bond lengths (Å) angles (°) for complex **7**

Bond lengths			
Li(l)–N(l)	1.943(5)	Li(l)–C(l)	2.567(6)
Li(l)–N(3*)	2.076(5)	N(l)–Si(l)	1.709(2)
N(1)–C(1)	1.301(3)	C(1)–C(2)	1.398(4)
C(2)–C(3)	1.411(4)	C(1)–C(7)	1.498(4)
C(3)–N(2)	1.292(4)	N(2)–Si(2)	1.699(3)
C(7)–C(8)	1.374(4)	C(7)–N(3)	1.324(3)
Bond angles			
N(1)–C(1)–C(2)	128.0(3)	C(1)–C(2)–C(3)	128.2(3)
N(2)–C(3)–C(2)	122.3(3)	N(1)–C(1)–C(7)	118.9(2)
C(1)–C(7)–C(8)	120.8(3)	C(8)–C(7)–N(3)	122.0(3)
C(7)–N(3)–C(11)	116.7(3)	N(l)–Li(l)–N(2)	99.3(2)
N(l)–Li(l)–N(3)*	136.1(3)	C(l)–N(l)–Li(l)	102.8(2)

complex **la** $[Li\{N(SiMe_3)_2C(Ph)\}_2CH]_2$ [1.965(9) and 1.952(10) Å] (prepared in our early work) [6] reveal that they are slightly different. However, the differences of intramolecular bond angles for NLiN [134.6(6)° **1**, 99.3(2)° **7** and 105.0(4)° **la**] are significant as shown in schematically drawing of Fig. 3. The effect of the substituted group on the β-diketiminato complex for polymerization of olefm is being investigated in our recent work and will be discussed in a further report.

2.3. Crystal structures of complexes 6 and 10

The molecular structures of the mixed substituted triazines $[N{=}C(Bu^t)N{=}C(R')N{=}C(R')]$ ($R' = Me_2N$ **6** or *p*-pyridyl **10**) are illustrated in Figs. 4 and 5; selected bond distances and angles are listed in Tables 3 and 4, respectively.

The molecular structures of both complexes show that they are mixed substituted triazines, and clearly the *tert*-butyl is one of substituted groups on the ring. The bond distances of C=N 1.338 and C–N 1.347 are in normal order.

3. Conclusions

Addition reaction of bis(trimethylsilyl)methyllithium reagent $Li[CHR_2]$ ($R = SiMe_3$) or 1-azaallyllithium $[LiN(R)C_3(Bu^t)CHR]_2$ with caynoamines R′CN lead to β-diketiminatolithium (**1**, **2**, **5**, **7**, **8**) and, interestingly, symmetrically and mixed substituted triazines (**3**, **4**, **6**, **9**, **10**). A proposed mechanism, which partly proved by our experimental, involves a series of nucleophilic attacks, silicotropic rearrangements and an unusual $Li[CHR_2]$ elimination. Especially, the reaction discussed is a useful synthetic method for symmetrically substituted triazines.

Six novel β-diketiminatolithium **1**, **2**, **5**, **7**, **8** are synthesized. Recently, the β-diketiminato transition metals as the catalyst for polymerization of olefin have received increasing attention. Practically, a number of the β-diketiminato transition metal have been obtained in our recent work and will be reported later (Table 5).

4. Experimental

All reactions were performed under argon using standard Schlenk techniques. The THF and diethyl ether were dried using sodium-benzophenone, hexane by sodium–potassium alloy. CH_2C1_2 was distilled from CaH_2. The NMR spectra were recorded on Bruker DKX300 instrument, and solvent resonances were used as the internal references for ^1H and ^{13}C spectra.

4.1. $Li[N(R)C(NMe_2)C(H)C(NMe_2)NR]_2$ (1)

Dimethylcyanamide (0.43 cm^3, 5.30 mmol) was added dropwise to a stirred solution of $LiCHR_2$ (0.44 g, 2.65 mmol) in diethyl ether (ca. 20 cm^3) at −78 °C for 30 min. The resultant mixture was warmed to room temperature (r.t.) and stirred for 1 h and the solvent was removed in vacuo. The residue was dissolved in hexane (ca. 10 cm^3) and filtered. The filtrate was concentrated at −30 °C to give colorless crystal com-

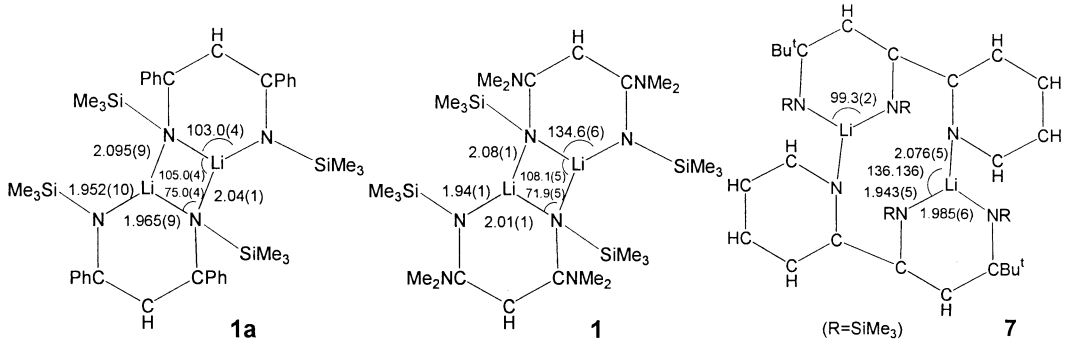


Fig. 3. Comparisons of bond distances N–Li for **1**, **7** and **1a**.

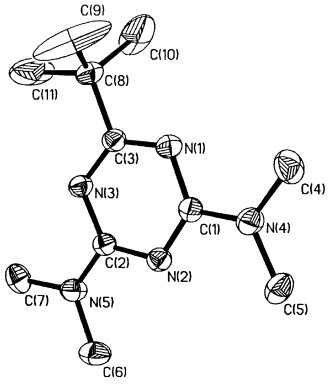


Fig. 4. Molecular structure of complex **6**.

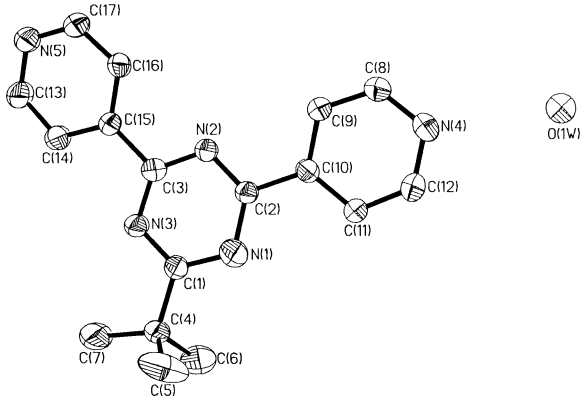


Fig. 5. Molecular structure of complex **10**.

Table 3
Selected bond lengths (Å) angles (°) for complex **6**

Bond lengths			
N(1)–C(3)	1.328(5)	N(1)–C(1)	1.361(5)
C(1)–N(2)	1.339(5)	N(2)–C(2)	1.350(5)
C(2)–N(3)	1.347(5)	N(3)–C(3)	1.331(5)
C(1)–N(4)	1.347(5)	C(2)–N(5)	1.341(5)
C(3)–C(8)	1.505(6)		
Bond angles			
C(3)–N(1)–C(1)	114.5(4)	N(2)–C(1)–N(1)	124.6(4)
C(1)–N(2)–C(2)	115.1(4)	N(2)–C(2)–N(3)	124.7(4)
C(2)–N(3)–C(3)	114.8(4)	N(3)–C(3)–N(1)	126.3(4)
N(1)–C(1)–N(4)	117.3(5)	C(4)–N(4)–C(5)	118.5(4)
C(9)–C(8)–C(10)	104.8		

Table 4
Selected bond lengths (Å) angles (°) for complex **10**

Bond lengths			
C(1)–N(1)	1.397(4)	C(1)–N(3)	1.340(4)
C(1)–C(4)	1.527(5)	N(1)–C(2)	1.392(4)
C(2)–N(2)	1.337(4)	C(2)–C(10)	1.486(5)
N(2)–C(3)	1.330(4)	C(3)–N(3)	1.334(4)
C(3)–C(15)	1.499(4)		
Bond angles			
N(3)–C(1)–N(1)	121.5(3)	N(3)–C(1)–C(4)	117.9(3)
C(2)–N(1)–C(1)	117.0(3)	C(9)–C(10)–C(I1)	116.7(3)

pound of **1** (0.46 g, 72%). ^{1}H-NMR (300 Hz, C_6D_6): δ 0.45 (s, 18H, $SiMe_3$), 2.79 (s, 12H, NMe_2), 4.35 (s, 1H, CH). ^{13}C-NMR (75 MHz, C_6D_6): $\delta = 3.48$ (s, $SiMe_3$), 41.32 (s, NMe_2), 83.4 (s, CH), 173.32 (s, CM).

4.2. $[\overline{Li\{N(R)C(piperidinyl)C(H)C(piperidmyl)NR\}_2}$ (**2**)

1-Piperidinecarbonnitrile (0.56 cm^3, 4.83 mmol) was added dropwise to a stirred solution of $LiCHR_2$ (0.404 g, 2.43 mmol) in diethyl ether (ca. 20 cm^3) at −78 °C for 30 min, and stirred for a further 3 h. The solvent was removed in vacuo. The remaining solid was dissolved in hexane (ca. 10 cm^3) and filtered. The filtrate was concentrated at −30 °C to give colorless crystal of **2** (0.77 g, 83%). ^{1}H-NMR (300 Hz, C_6D_6): δ 0.32 (s, 18H, $SiMe_3$), 1.42–1.57 (d, 6H, CH_2), 3.12 (d, 4H, NCH_2), 4.62 (s, 1H, CH).

4.3. 2,4,6-(tri)Dimethyicyano-1,3,5-triazine (**3**)

Dimethylcyanamide (0.498 cm^3, 6.00 mmol) was added by syringe to a stirred solution of $LiCHR_2$ (0.40 g, 3.00 mmol) in hexane (ca. 20 cm^3) at 0 °C. The mixture was warmed to r.t., stirred for 12 h, and concentrated to give crystalline complex of **3** (0.38 g, 91%). (Found: C, 53.25; H, 8.75; N, 38.04, $C_9H_{18}N_6$ requires C, 51.43; H, 8.75; N, 40.00%.) ^{1}H-NMR (300 MHz, C_6D_6): $\delta = 3.09$ (s, 18H, NMe_2); ^{13}C-NMR (75

Table 5
Crystallographic data for compounds **1**, **7**, **6**, and **10**

	1	**7**	**6**	**10**
Formula	$C_{13}H_{31}LiN_4Si_2$	$C_{36}H_{64}Li_2N_2Si_4$	$C_{11}H_{21}N_5$	$C_{17}H_{18}N_5$
Formula weight	306.53	707.17	223.32	300.36
Color	Colorless	Yellow	colorless	Yellow
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$C2/c$	$P2(1)/c$	$Pccn$
a (Å)	10.69(1)	190 852(2)	9.970(3)	13.309(3)
b (Å)	10.989(3)	9.5885(12)	10.093(3)	22.607(5)
c (Å)	8.900(3)	23.397(3)	14.051(4)	10.871(2)
α (°)	100.50(2)	90	90	90
β (°)	103.54(4)	99.677(2)	104.966(6)	90
γ (°)	96.30(4)	90	90	90
V (Å^{-3})	986.5700	4390.3(9)	1366.5(7)	3270.7
Z	2	4	3	8
D_c (g cm^{-3})	1.032	1.070	1.086	1.220
μ (mm^{-1})	0.176	0.165	0.070	0.079
F(000)	336	1536	488	1272
Crystal size (mm)	0.40 × 0.30 × 0.30	0.08 × 0.25 × 0.30	0.20 × 0.25 × 0.30	0.50 × 0.30 × 0.30
2θ Range (°)	0.00–55.00	2.08–25.03	2.11–23.25	2.58–24.99
Index range	$-11 \le h \le 11$, $0 \le k \le 13$, $-13 \le l \le 13$	$-23 \le h \le 23$, $-11 \le k \le 11$, $-27 \le l \le 19$	$-11 \le h \le 10$, $-11 \le k \le 5$, $-15 \le l \le 15$	$0 \le h \le 15$, $0 \le k \le 26$, $0 \le l \le 12$
Number of reflections collected	2485	8717	4557	2868
Number of independent reflections	2485 [R_{int}] = 0.0000	3861 [R_{int}] = 0.0000	1965 [R_{int}] = 0.0505	2868 [R_{int}] = 0.0000
R_1, wR_2 ($I > 2\sigma(I)$)	0.076, 0.099	0.0582, 0.1299	0.0745, 0.1832	0.0702, 0.2164
R_1, wR_2 (all data)	0.1197, 0.2556	0.0782, 0.1405	0.1449, 0.2138	0.1589, 0.2610
Goodness-of-fit F^2	1.09	1.110	1.081	1.037
Largest difference peak (e Å^{-3})	0.29 to −0.38	0.266 to −0.281	0.451 to −0.204	0.416 to −0.392

MHz, C_6D_6): δ 36.54 (s, NMe_2), 167.26 (s, *ipso*-C of ring).

4.4. 2,4,6-(tri)1-Piperidinyl-l,3,5-triazine (4)

$LiCHR_2$ (0.08 g, 4.70 mmol) was added to a stirred solution of 1-piperidinecarbonnitrile (0.55 cm^3, 4,75 mmol) in hexane (ca. 5 cm^3) at the r.t. After stirring for 6 h the mixture was filtered to give complex **4** as white precipitate (0.28 g, 55%), and then the filtrate was concentrated to give colorless crystalline **4** (0.19 g, 36%). The total yield was 89%. (Found: C, 65.40; H, 9.00; N, 24.17, $C_{18}H_{50}N_6$ requires C, 65.42; H, 9.15; N, 25.43%.) ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.25 (m, 6H,CH_2), 4.43 (s, 4H, NCH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 25.64 (s, $NCH_2CH_2CH_2CH_2CH_2$) δ 26.37 (s, NCH_2CH_2-$CH_2CH_2CH_2$) δ 44.59 (s, $NCH_2CH_2CH_2CH_2CH_2$), 165.97 (s, *ipso*-C of ring).

4.5. Li[N(R)C(Bu^t)C(H)C(NMe$_2$)NR]$_2$ (5) and2,4,-(bis)dimethylcyano-6-tertbutyl-l,3,5-triazine (6)

Dimethylcyanamide (0.58 cm^3, 7.22 mmol) in hexane (ca. 20 cm^3) was added dropwise to a stirred solution of [LiN(R)C(Bu^t)CHR]$_2$ (0.89 g, 3.61 mmol) in hexane (ca. 15 cm^3) at 0 °C. The mixture was allowed to warm r.t., and stirred for a further 12 h. The solvent was removed in vacua. The residue was sublimed at 80 °C, 4.3×10^{-4} pa to give a mixture of colorless crystals (0.16 g) of complexes **6** (74%,) and **3** (24%) analysted by HPLC. So the yield for **6** is 15%. The residue was extracted by hexane and concentrated to give crystalline complex of **5** (0.62 g, 54%). Complex **5**,^{1}H-NMR (C_6D_6, 300 Hz): δ 0.16 (s, 9H, $SiMe_3$), 0.50 (s, 9H, $SiMe_3$), 1.28 (s, 9H, CMe_3), 2.83 (s, 6H, NMe_2), 4.45 (s, 1H, CH); complex **6**, (Found: C, 59.31; H, 9.50; N, 31.22, $C_{11}H_{21}N_5$ requires C, 59.16; H, 9.71; N, 31.36%.) ^{1}H-NMR (C_6D_6, 300 Hz): δ 2.89 (s, 12H, NMe_2), 3.24 (s, 9H, CMe_3) ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 38.06$ (NMe_2) $\delta = 71.63$ (CMe_3) $\delta = 165.28$ (*ipso*-C of triazine ring) $\delta = 129.78$ (*ipso*-C of CMe_3).

4.6. [Li{N(R)C(Bu^t)C(H)C(o-pyridyl)NR}]$_2$ (7)

o-Cyanopyridine (0.47 cm^3, 4.88 mmol) was added dropwise to a stirred solution of [LiN(R)C(Bu^t)CHR]$_2$ (1.25 g, 5.02 mmol) in diethyl ether (ca. 20 cm^3) at −78 °C and the mixture was stirred for 30 min. and then allowed to warm r.t. for another 12 h. The mixture was filtered to give complex **7** as yellow precipitate (0.51 g, 29%); and the filtrate was concentrated to get crystalline **7** (0.64 g, 37%). The total yield was 66%. ^{1}H-NMR

(C_6D_6, 300 Hz): δ 0.07(s, 9H, $SiMe_3$), 0.49(s, 9H, $SiMe_3$), 1.16 (s, 9H, CMe_3), 5.69 (s, 1H, CH) 7.54–8.56 (m, 4H,pyridyl).

4.7. $[Li\{N(R)C(Bu^t)C(H)C(p\text{-}pyridyl)NR\}]_2$ (**8**)

As same procedures for complex **7** thus *p*-Cyanopyridine (0.81 g, 7.78 mmol) $[LiN(R)C(Bu^t)CHR]_2$ (1.93 g, 7.78 mmol) in diethyl ether (ca. 25 cm^3) gave yellow precipitate (1.31 g, 48%, analyzed as **8**), and the filtrate was concentrated to get another part of crystalline complex **8** (0.57 g, 21%), the total yield was 79%. ^{1}H-NMR (C_6D_6, 300 Hz): δ 0.07 (s, 9H, $SiMe_3$), 0.51 (s, 9H, $SiMe_3$), 1.49 (s, 9H, CMe_3), 5.49 (s, 1H, CH) 6.43–8.56 (m, 4H, pyridyl).

4.8. 2,4,-(bis)*o*-Pyridyl-6-tertbutyl-1,3,5-triazine (**9**)

o-Cyanopyridine (0.939 g, 9.01 mmol) was added to a stirred solution of $[LiN(R)C(Bu^t)CHR]_2$ (2.36 g, 9.49 mmol) in diethyl ether (ca. 20 cm^3) at 0 °C for 30 min. The mixyure was stirred for 12 h at r.t. and filtered. The air-stable yellow preciptate of compound **9** was obtained (0.52 g, 41%). ^{1}H-NMR (C_6D_6, 300 Hz): δ 1.33 (s, 9H, CMe_3), 6.92–6.99 (m, 2H, pyridyl), 7.30 (s, 1H, pyridyl), 8.17 (m, 1H, pyridyl), 8.72–8.88 (m, 2H, pyridyl) 9.50 (s, 1H, pyridyl), 10.36 (s, 1H, pyridyl).

4.9. 2,4,-(bis)*p*-Pyridyl-6-tertbutyl-1,3,5-triazine (**10**)

p-Cyanopyridine (0.61 g, 6.48 mmol) was added to a stirred solution of $[LiN(R)C(Bu^t)CHR]_2$ (0.81 g, 3.24 mmol) in diethyl ether (ca. 20 cm^3) at 0 °C for 30 min. The mixture was stirred for 12 h at r.t. and filtered.

The air-stable precipitate of compound **10** was obtained (0.72 g, 76%) and a suitable single crystal was obtained by recrystallization in Et_2O. (Found: C, 70.28; H, 6.12; N, 23.34, $C_{17}H_{117}N_5$ requires C, 70.08; H, 5.88; N, 24.04%.) ^{1}H-NMR ($CDC1_3$, 300 Hz): δ 1.73 (s, 9H, CMe_3), 8.02–9.08 (m, $8H_5$ pyridyl).

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 151058 for complex **1**, no. 151057 for complex **7**, no. 151059 for complex **6** and no. 151056 for complex **10.** Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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