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### Silylation products of cyclic tri-aminal carbanions and their lithiation<sup>†</sup>

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The structure of 1,3,5-trimethyl-1,3,5-triaza-cyclohexane (TMTAC) was determined by single crystal X-ray diffraction and compared with earlier gas-phase data. It shows a preference for an *aee*-conformation in all phases. Lithiated TMTAC, [(RLi)<sub>2</sub>·(RH)] (1) (R = 2,4,6-trimethyl-2,4,6-triaza-cyclohex-1-yl), was reacted with Et<sub>3</sub>SiCl, Ph<sub>3</sub>SiCl and PhMe<sub>2</sub>SiCl to afford the substituted silanes Et<sub>3</sub>SiR (1), Ph<sub>3</sub>SiR (2) and PhMe<sub>2</sub>SiR (3) in moderate yields. They were characterised by NMR spectroscopy (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si). 1 reacts with Me<sub>2</sub>SiCl<sub>2</sub> and Ph<sub>2</sub>SiCl<sub>2</sub> to give Me<sub>2</sub>SiR<sub>2</sub> (5) and Ph<sub>2</sub>SiR<sub>2</sub> (6) which were characterised by NMR spectroscopy. 5 was also identified by crystal structure determination. Analogous triple substitution could not be observed by employing trichlorosilanes. Quantumchemical calculations explain this by sterical overcrowding of the silicon atom. The reaction of 1 with SiCl<sub>4</sub> did not yield fourfold substitution but a formal insertion product of SiCl<sub>2</sub> into a C–N bond of the TMTAC ring (2,4,6-trimethyl-2,4,6-triaza-1,1-dichloro-1-sila-cycloheptane, 7) in very small quantities. It was identified by X-ray crystallography and shows an intramolecular Si ··· N dative bond. The reactions of (3) and (5) with *n*-butyl lithium afforded lithiation of the silicon bound methyl groups in both cases. The products, **8** and **9**, were characterised by NMR spectroscopy (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si), **8** was also characterised by X-ray crystallography.

#### Introduction

Known examples of the direct lithiation of amines are still scarce. This is due to the fact that they are formally non-stabilised or even destabilised lithium carbanions and thus one of the most favourable procedures to prepare such *a*-lithiated amines is still the transmetalation route developed by Seyferth *et al.*<sup>1</sup>

The few examples of direct deprotonation of amines include the lithiation of  $Me_2N(CH_2)_2NMe_2$  (TMEDA)<sup>2</sup> and  $MeN[(CH_2)_2NMe_2]_2$  (PMDTA).<sup>3</sup> These findings are important as these amines are often employed to increase the carbanion activity of the butyl lithiums. Other examples are (1,4,7-trimethyl-1,4,7-triazacyclononane,<sup>4</sup> *N*-methylpiperidine,<sup>5</sup> and (*R*,*R*)-tetramethyl-1,2-diaminocyclohexane<sup>6</sup>), which are always singly deprotonated at one of their terminal methyl positions. An exception in this context is the high-yield double deprotonation of aminals RMeNCH<sub>2</sub>NMeR to give LiCH<sub>2</sub>(Me)NCH<sub>2</sub>N(Me)CH<sub>2</sub>Li, again lithiated in terminal positions.<sup>7</sup>

We discovered recently that *n*BuLi metallates 1,3,5-trimethyl-1,3,5-triaza-cyclohexane (TMTAC) selectively at the methylene unit between two nitrogen atoms, leading to the first doubly amino-substituted carbanion, RLi ( $R = MeN(CH_2NMe)CH_{-}$ , used in this sense throughout this report),<sup>8</sup> and the product consists of an endless chain aggregate of a dimer of the metallated substrate molecules coordinated by the non-deprotonated substrate:  $[(RLi)_2 \cdot (RH)]_{--}$  (1). This reactivity pattern appears to be general for cyclic aminals,<sup>9,10</sup> and provides mechanistic insights into precoordination of the butyl lithium bases, which determine regioselectivity of metallation.<sup>9-11</sup> These compounds can serve as acylation agents for carbonyl compounds analogous to the Corey/Seebach reagents, but in contrast to the latter with the advantage of a heavy-metal-free workup procedure.<sup>8</sup>

Transmetallation of this lithiated TMTAC (1) is possible and a series of aluminium and gallium derivatives with MR'<sub>2</sub> groups replacing lithium (M = Al, Ga; R' = Me, Et) has been reported.<sup>12</sup> A trimethylsilyl derivative RSiMe<sub>3</sub> has also been reported and demonstrated to be capable again to serve as metallation substrate, however, then not at the aminal position but rather at the SiMe<sub>3</sub> group.<sup>12</sup> This carbanion was used again to generate aluminium and gallium derivatives.

Interestingly, the triaminal group R does not always stay intact when **1** is reacted with element halides. Bulkily substituted substrates lead to decomposition of **1** into MeN=CH<sub>2</sub> and MeN=CHLi fragments (TMTAC itself is a trimer of MeNCH<sub>2</sub>) and these fragments are then found included in the products.<sup>13</sup> Cp<sub>2</sub>YCl for instance reacts with RLi to give the complex Cp<sub>2</sub>Y[ $\eta^4$ (RCH<sub>2</sub>NMe)], with a new tetrapodal ligand and this monoanionic ligand is formed in one step (showing MeN=CH<sub>2</sub> reactivity). *t*-Bu<sub>2</sub>GaCl reacts with **1** to give *cyclo*-[*t*-Bu<sub>2</sub>GaCH==NMe]<sub>2</sub> (showing MeN==CHLi reactivity).

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It remained of interest whether more than one triaminal group R could be transferred to other elements and thus we explored this chemistry further with a range of silicon reagents and report here about the results. Prior to this we report the crystal structure of TMTAC for further comparison.

#### **Results and discussion**

#### Crystal structure of TMTAC

Due to the growing importance of the chemistry of TMTAC, it is desirable to determine the molecular structure in the crystal. TMTAC was reported to have a preference for the axial orientation of the methyl substituents, as was also found in other hexahydros-triazines.14 TMTAC exists in the liquid as a 1:1 mixture of the diaxial and monoaxial conformers, with no molecules having the triequatorial conformation.<sup>14b</sup> In contrast, the gas-phase conformer composition and structure has been reported earlier by Vilkov et al.<sup>15</sup> TMTAC vapour contains a sole conformer with one axially oriented and two equatorially methyl substituents (aeeconfiguration). Its main structural parameters (only mean values determined) were reported to be  $r_{g}$ (C–N) = 1.463(3) Å,  $r_{g}$  (C–H) = 1.117(5) Å,  $\angle$  (C–N–C) = 110.91(1)° and  $\angle$  (N–C–N) = 111.1(1)°.<sup>15</sup> The reason for this conformational behaviour is the electrostatic repulsion between the lone pairs of electrons at the nitrogen atoms and also anomeric contributions.14

We have now succeeded in growing a single crystal of TMTAC for X-ray diffraction in a sealed capillary on an X-ray diffractometer by generating manually a crystal seed at 247 K and cooling down slowly to 100 K. It belongs to the monoclinic system, space group  $P2_1/n$ . The asymmetric unit contains four molecules, three of which are oriented with their N<sub>3</sub> planes parallel and one with an angle of 65° between it and the average N<sub>3</sub> planes of the other molecules (Fig. 1).

> mean parameters assuming an idealised molecular  $C_{\rm s}$  symmetry. This allows also a comparison with the values determined by gas electron diffraction (GED).<sup>15</sup> In this GED refinement, N-C distances and all angles of the same type (N–C–N and C–N–C) were assumed to be equal. Consequently, this gas-phase structure has been derived with only three parameters defining the heavy atom skeleton. Our new crystal structure parameters suggest that this assumption is only of limited validity. For instance, the largest C–N–C angle is that describing the position of the axial methyl group (C(1)–N(1)–C(4) etc.) with an average of  $112.4^{\circ}$ ; the smallest C-N-C angle is the endocyclic one involving the nitrogen atom with the equatorial methyl group (C(1)-N(2)-C(2) etc.) with an average of 109.1°. The reported very high precision of the gas electron diffraction parameter for C-N-C at 110.91(1)° reflects the value for an average, but does not reflect the spread in chemically distinguishable parameters; as with more parameters refining and closely related distances leading to correlation the provided error is probably misleading in terms of absolute accuracy.

> The chemical meaningful information to be extracted from the new crystal structure determination is that there is a systematic and significant difference between C–N bond lengths, N–C–N and C– N–C bond angles of the same type relating to the distinguishable chemical surrounding of the contributing atoms. The differences

	XRD mol 1		XRD average all mols	GED <sup>16</sup>
N(1)-C(1)	1.454(2)	)		]
N(1)-C(3)	1.452(2)	}	1.453	
N(2)-C(1)	1.475(2)	]	1 472	
N(3)-C(3)	1.475(2)	Ĵ	1.4/3	
N(2)-C(2)	1.457(2)	]	1 458	1.463(3)
N(3)-C(2)	1.455(2)	]	1.450	
N(1)-C(4)	1.465(2)	}	1.468	
N(2)–C(5)	1.456(2)	Ì	1 456	
N(3)-C(6)	1.457(2)	ſ	1.150	J
C(1)-N(1)-C(3)	109.0(1)	}	108.7	]
C(1)-N(1)-C(4)	112.4(1)	l	112.4	
C(3)-N(1)-C(4)	112.5(1)	ſ	112.1	110.01(1)
C(1)-N(2)-C(2)	109.0(1)	]	100.1	{ 110.91(1)
C(2)-N(3)-C(3)	109.0(1)	Ì	109.1	
C(2)-N(2)-C(5)	110.1(1)	]	110.0	
C(2)-N(3)-C(6)	110.1(1)	}	110.0	J
N(1)-C(1)-N(2)	111.8(1)	]	1117	]
N(1)-C(3)-N(3)	111.7(1)	ſ	111./	111.1(1)
N(2)-C(2)-N(3)	110.4(1)	}	110.4	

(1)

Fig. 1 Asymmetric unit of the crystal structure of TMTAC with four molecules. Hydrogen atoms omitted for clarity.

All four independent molecules adopt the *aee*-configuration – as in the gas-phase – and only marginally different structures. Table 1 lists the parameters of one molecule together with the

in angles have already been mentioned, for the three existing types of N–C bonds, the group including C(1)–N(2) has much longer values (1.473 Å on average) than the two other groups (1.453 and 1.458 Å on average).

In order to establish a parameter describing the conformation of TMTAC concerning the positions of the methyl groups, we introduce the angle  $\chi$  defined as depicted in Fig. 2 as the angle between the N–C vector of the corresponding bond and the plane defined by the three nitrogen atoms.  $\chi$ [C(4)<sub>ax</sub>] is 98.1° for the axial methyl group in the molecule shown in Fig. 2 and 97.4° on average for the four independent molecules in the unit cell. The exocyclic methyl group about C(5) adopts a corresponding angle of  $\chi$ [C(5)<sub>eq</sub>] = -19.4°.



Fig. 2 Molecular structure of one molecule of TMTAC with definition of the angle X describing the orientation of the axial methyl group relative to the  $N_3$  plane. This angle is 97.4° on average for the four independent molecules. Hydrogen atoms omitted for clarity.

**Reaction of lithiated TMTAC (1) with monochlorosilanes.** We reacted lithiated TMTAC, 1, with various trialkylsilanes, namely  $Et_3SiCl$ ,  $Ph_3SiCl$  and  $Me_2PhSiCl$  (Scheme 1). In all cases the single substitution could be achieved without greater difficulties, yielding  $R-SiEt_3$  (2),  $R-SiPh_3$  (3) and  $R-SiMe_2Ph$  (4).



Scheme 1 Reaction of 1 with trialkylchlorosilanes.

Purification of **2** and **3** was possible by distillation and crystallisation, respectively, but these techniques were not applicable to **4** due to glassy solidification and decomposition before reaching the boiling temperature. The preparative yields were always moderate (**2** 69%, **3** 78%, **4** 69%). Compounds **2** and **3** were characterised by elemental analyses and NMR spectroscopy of the nuclei <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si. As most of these data deserve no detailed comments, we refer to the experimental part.

## Reaction of lithiated TMTAC (1) with the dichlorosilanes $Me_2SiCl_2$ and $Ph_2SiCl_2$

**Reaction with Me<sub>2</sub>SiCl<sub>2</sub>.** The reaction of lithiated TMTAC (1) with dichlorodimethylsilane,  $Me_2SiCl_2$  (Scheme 2) afforded the formation of dimethyl-bis(2,4,6-trimethyl-2,4,6-triaza-cyclohex-1-yl)silane (5) in relatively low yields of 35% after recrystallisation. This is due to the presence of free TMTAC in 1, which complicates purification by recrystallisation. Compound 5 is a colourless (slightly yellowish) solid and is soluble in hydrocarbons. It was characterised by NMR spectroscopy and its crystal structure was determined.



Scheme 2 Reaction of 1 with Me<sub>2</sub>SiCl<sub>2</sub>.

The <sup>1</sup>H NMR spectrum of a C<sub>6</sub>D<sub>6</sub> solution shows broad signals for the hydrogen atoms attached to the rings at 3.37 and 3.02 ppm. The methyne proton results in a resonance at 3.26 ppm. The exocyclic methyl groups are detected as two singlets at 2.69 and 1.80 ppm, the methyl groups at silicon at 0.43 ppm. The <sup>13</sup>C NMR spectrum shows peaks 79.4 and 75.2 ppm for the ring carbon atoms, at 43.9 and 39.9 ppm for the *N*-methyl groups and at –1.1 ppm for the methyl groups at the silicon atom. The {<sup>1</sup>H}<sup>29</sup>Si NMR spectrum contains a single resonance at 0.0 ppm. The molecular structure of **5** in the crystal is shown in Fig. 3.



Fig. 3 Molecular structure of 5 in the crystal. Hydrogen atoms have been omitted for clarity. Selected distances and angles [Å, deg]: Si(1)–C(1) 1.923(2), Si(1)–C(7) 1.929(2), Si(1)–C(13) 1.882(2), Si(1)–C(14) 1.878(2), N(1)–C(1) 1.462(2), N(1)–C(3) 1.451(2), N(1)–C(4) 1.472(2), C(1)–Si(1)–C(7) 106.6(1), C(13)–Si(1)–C(14) 111.2(1), Si(1)–C(1)–N(2) 114.6(2), N(1)–C(1)–N(2) 110.2(2); tilt angles:  $\chi$ [C(4)<sub>ax</sub>] 97.0°,  $\chi$ [C(5)<sub>eq</sub>] –19.4°,  $\chi$ [C(11)<sub>ax</sub>] 98.2°.

The Si–C bonds to the methyl groups (1.882(1) and 1.878(1))Å) in compound **5** are shorter than those to the carbon atoms of the triazacyclohexyl rings (1.923(2) and 1.929(2) Å). The latter are larger than in the trimethylsilylated TMTAC, R–SiMe<sub>3</sub>, at 1.918(2) Å.<sup>12</sup> The reason is probably due to steric factors, as the H···H distances between the two R substituents are as close as 2.48 Å. A distorted tetrahedral coordination geometry characterises the bonding situation of the silicon atom; there are compressed angles like  $\angle$ (C(1)–Si(1)–C(7)) at 106.6°, while others are larger than the tetrahedral angle, such as  $\angle$ (C(13)–Si(1)–C(14)) at 111.2°. Both *N*,*N*,*N*-trimethyl-triazacyclohexyl units in **5** adopt the *aee*-configuration, alike to free TMTAC. The angle  $\chi$  characterising the tilt of the axial methyl group measures 97.6° on average, which is almost identical to TMTAC (97.4°).

**Reaction with Ph<sub>2</sub>SiCl<sub>2</sub>.** Analogous to the reaction described above, that of lithiated TMTAC (1) with dichlorodiphenylsilane,  $Ph_2SiCl_2$  afforded  $Ph_2SiR_2$  (6), but only in very low isolated yield of 4%. Characterisation of the compound was effected by spectroscopic means and is in general analogous to that of 5. The data are listed in the experimental section.

## Reaction of lithiated TMTAC (1) with trichlorosilanes and tetrachlorosilane, ${\rm SiCl}_4$

We have undertaken various attempts to isolate triply Rsubstituted silanes by reactions of 1 with MeSiCl<sub>3</sub> and HSiCl<sub>3</sub>, but failed to isolate new products. Attempts to achieve partially substituted products like R-SiCl<sub>3</sub>, R<sub>2</sub>SiCl<sub>2</sub> etc. from the reactions of 1 with excess of SiCl<sub>4</sub> were also unsuccessful. A possible explanation is that reactions of TMTAC (included in 1) or the substitution products with SiCl<sub>4</sub> occur leading to ionic products of the type  $[(\eta^3-TMTAC)SiCl_3]^+$ .<sup>16</sup> We could only isolate some crystalline material in one experiment; however, the amount was so small that identification of this product (7) was solely possible on the basis of X-ray diffraction and we report this structure displayed in Fig. 4 to show that quite unexpected chemical processes occur within such mixtures. Compound 7 is the product of a formal insertion of a SiCl<sub>2</sub> unit into the TMTAC ring, widening it from six to seven ring members. The Lewis acidity of the silicon atom with a substituent pattern SiCNCl<sub>2</sub> is sufficient to induce the formation of a dative bond to the nitrogen atom N(2) within the ring. This leads to a bicyclic system comprising a four- and a five-membered ring. Ring strain leads to deformation of the coordination spheres of the involved atoms. The coordination geometry at silicon is that of a strongly distorted trigonal pyramid with the dative bonds and one Cl substituent adopting the axial positions (angle Cl(2)-Si(1)···N(2) 166.7(1)°). The equatorial substituents are Cl(1), N(1) and C(3); their angles involving the silicon atom are C(3)-Si(1)-N(1) 125.2(2), Si(1)-N(1)-C(1) 104.7(2) and C(3)-Si(1)-Cl(1) 110.7(1)°, clearly showing the strong deviation from a trigonal planar arrangement.

Nitrogen atom N(1) is planar coordinated and placed at a distance of 1.705(2) Å to the silicon atom; this is longer than in Me<sub>2</sub>N-SiHCl<sub>2</sub> [1.664(2) Å]<sup>17</sup> and Me<sub>2</sub>N-SiCl<sub>3</sub> [1.665(3) Å],<sup>18</sup> as is expected from the involvement of the bond within a strained four-membered ring. The two Si–Cl distances are different (Si(1)–Cl(1) 2.102(1), Si(1)–Cl(2) 2.144(1) Å) due to their different roles in the coordination sphere of silicon.

This result demonstrates that it is obviously not possible to achieve a fourfold substitution at silicon with 2,4,6-trimethyl-2,4,6-triaza-cyclohex-1-yl groups R – this is most likely to be due to steric reasons. Without going into details we observed similar problems with attempts to prepare triply substituted compounds, *e.g.* using MeSiCl<sub>3</sub> as a substrate. These attempts



Fig. 4 Molecular structure of product 7 isolated in minor quantities from the reaction of 1 with SiCl<sub>4</sub>. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles [Å,deg] Si(1)–N(1) 1.705(2) Si(1)–Cl(1) 2.102(1) Si(1)–C(3) 1.876(2) N(1)–C(1) 1.444(3) N(1)–C(4) 1.449(2) N(2)–C(2) 1.480(2) N(3)–C(3) 1.463(3), Si(1)  $\cdots$  N(2) 2.115(2); C(3)–Si(1)–N(1) 125.2(2), N(2)  $\cdots$  Si(1)–Cl(2) 166.7(1), C(3)–Si(1)  $\cdots$  N(2) 85.0(1), N(1)–Si(1)  $\cdots$  N(2) 70.0(1), Si(1)–N(1)–C(1) 104.7(2).

remained unsuccessful. However, note that the loosely related tri(cyclohexyl)silanes are known compounds.<sup>19</sup>

# Quantumchemical estimation of possible limitations for the substitution grade with 2,4,6-trimethyl-2,4,6-triaza-cyclohex-1-yl groups at silicon

Due to the experimental observation, that a higher substitution grade than two with 2,4,6-trimethyl-2,4,6-triaza-cyclohex-1-yl groups could not be achieved, we tried to estimate the feasibility of such attempts on the basis of quantum chemical calculations on the M05-2X/6-311G(dp) level (and 6-311(2df) for silicon).

Two isodesmic reactions were investigated. The first is the reaction of a silane with two 2,4,6-trimethyl-2,4,6-triaza-cyclohex-1-yl groups R,  $R_2SiMe_2$ , which exchanges formally an R group with R-H = TMTAC.

#### $R_2MeSi-Me + R-H \rightarrow R_2MeSi-R + Me-H$

While breaking and forming the same number of Si–C and C– H bonds, this reaction is calculated to be endothermic by 46 kJ mol<sup>-1</sup>. As electronic effects can be assumed to be less important, this number mainly reflects the energy increase by steric crowding. The second reaction investigated by this method is one involving an overcrowded silane with three R groups. The steric stress is somewhat released by exchanging the fourth substituent Me by H by a formal exchange reaction with trimethylsilane.

#### $R_3Si-Me + Me_3Si-H \rightarrow R_3SiH + Me_3Si-Me$

The calculations predict this reaction to release 15 kJ mol<sup>-1</sup>, again demonstrating the importance of steric effects. It is important to note that these values were calculated for components with the lowest energies conformers, *i.e.* the *aee*-conformers. The calculated minimum structure of  $R_3$ SiMe is shown in Fig. 5. It also shows the short distance between hydrogen atoms exemplified by the distance between the Si bound methyl group and the axially positioned methyl group of one R substituent.

Table 2 lists energies calculated for the change between two of the conformational possibilities of some compounds, TMTAC itself,  $R_2SiMe_2$  (2),  $R_3SiMe$  and  $R_3SiH$ , in each case for the ground

 $\Delta E [kJ mol^{-1}]$ 

20

47

89

58

Me

2

#### Table 2 Energy differences for different conformers of TMTAC, R<sub>2</sub>SiMe<sub>2</sub> (2), R<sub>3</sub>SiMe and R<sub>3</sub>SiH. The conformation assignment is for all R groups

Me

Conformational change	e
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Fig. 5 Molecular structure of R<sub>3</sub>SiMe calculated on the M05-2X/6-311G(d,p) level (and 6-311(2df) for silicon) of theory. Only selected hydrogen atoms are shown for clarity. Selected bond lengths and angles [Å,deg] Si(1)-C(1) 1.945, Si(1)-C(7) 1.937, N(1)-C(1) 1.455, N(1)-C(2) 1.444, N(1)-C(4) 1.465, H(42) ··· H(44) 2.102, C(1)-Si(1)-C(7) 124.4, C(1)-Si(1)-C(13) 105.8, C(1)-Si(1)-C(19) 105.4, C(1)-N(1)-C(4) 113.0,  $\chi[C(4)_{ax}]$  98.0,  $\chi[C(5)_{eq}]$  -19.7.

state aee-conformations and the eee-conformation (for all R substituents). The values demonstrate that the conformation-based energies are coarsely additive. R<sub>2</sub>SiMe<sub>2</sub> (2) with two R groups needs about two times the energy needed for the conformational change in TMTAC, while R<sub>3</sub>SiMe and R<sub>3</sub>SiH with three groups require about three times that value.

#### Lithiation of R<sub>2</sub>SiMe<sub>2</sub> (5) and RSiMe<sub>2</sub>Ph (4)

Lithiated  $R_2SiMe_2$  (5). It was earlier shown that the trimethylsilyl derivative of TMTAC, R-SiMe<sub>3</sub>, can be metallated with butyl lithium. This metallation takes place at the siliconbound methyl groups rather than at the nitrogen heterocycle. The question arose, whether it would be possible to metallate  $R_2SiMe_2$  (5) and if so, where the metallation would take place. We reacted 5 with *n*-butyl lithium at -78 °C in hexane and obtained a product, metallated at the silicon bound methyl group:  $[{MeN(CH_2NMe)_2CH}SiMe(CH_2Li)]_2$  (8) (Scheme 3). Compound 8 was characterised by <sup>1</sup>H, <sup>7</sup>Li, <sup>13</sup>C and <sup>29</sup>Si NMR spectroscopy in  $C_6D_6$  solution.

A broad resonance in the <sup>1</sup>H NMR spectrum at 0.14 ppm represents the lithiated SiCH<sub>2</sub> unit, while a signal at 0.46 ppm corresponds to the unchanged SiCH<sub>3</sub> group. The <sup>7</sup>Li NMR spectrum contains a resonance at 1.2 ppm. A <sup>13</sup>C NM resonance at -2.8 ppm corresponds to the carbanionic function SiCH<sub>2</sub>Li, while a signal at -1.1 ppm represents the Si-bound methyl group and one at 77.5 ppm, the ring carbon atom attached to silicon (SiCHN<sub>2</sub>). The methylene NCH<sub>2</sub>N units give a signal at 79.3 ppm. Resonances



Me

Me

*n*BuLi

<sup>29</sup>Si NMR spectrum at 0.0 ppm completes the spectroscopic data. The result of a crystal structure determination of 8 is shown

in Fig. 6. The compound crystallises in the triclinic space group P1. Despite several attempts of crystallisation and examination of various crystals, the crystal quality of the best measurement was still limited. There is an inversion centre lying in the middle of the  $C_2Li_2$  ring, formed by dimerisation of two units of monomeric 8. The coordination spheres of the two lithium atoms are completed



Fig. 6 Molecular structure of 8 in the solid state. Selected bond lengths and angles [Å, deg]: Li(1)-C(13) 2.210(7), Li(1)-N(1) 2.168(7), Li(1')-N(4) 2.181(8), Si(1)-C(1) 1.956(3), Si(1)-C(13) 1.803(4), Si(1)-C(14) 1.887(3), N(1)-C(1) 1.492(4), N(1)-C(4) 1.477(4), Li(1)-Li(1') 2.542(13), Li(1)-C(13)-Li(1') 70.4(3), Li(1)-C(13)-Si(1) 98.4(2), C(13)-Li(1)-C(13') 109.6(3), C(13)-Si(1)-C(1) 109.7(2), N(1)-C(1)-Si(1) 111.6(2), N(1)–C(1)–N(2) 115.4(3),  $\chi$ [C(4)<sub>ax</sub>]C 95.0,  $\chi$ [C(5)<sub>ax</sub>] 108.0,  $\chi[C(6)_{eq}] - 20.4.$ 

by two contacts each to nitrogen atoms of the 2,4,6-trimethyl-2,4,6-triaza-cyclohex-1-yl rings.

Most of the bond lengths in **8** are relatively similar to the corresponding ones in **5**. The bonds between the silicon atom and the ring carbon atoms at 1.956(3) to C(1) and 1.930(4) Å to C(7) are slightly longer than in **5** (1.923(2) Å). Close are the distances to the methyl group in **8** (1.887(3) Å) and in **5** (1.882(2) Å). Shorter though is the bond Si(1)–C(13) to the carbanion at 1.803(4) Å. This is the structural proof of the concept of anion stabilisation by adjacent silicon atoms through hyperconjugation.

The distance Li(1)–C(13) is 2.210(7) Å and that to the lithium symmetry equivalent, Li(1)'–C(13), 2.200(8) Å. The coordinative bonds between lithium and nitrogen atoms are shorter than these: N(1)–Li(1) 2.168(7) N(4')–Li(1) 2.181(8) Å. Despite the relative close proximity of the two lithium atoms at 2.542(13) Å, they are pushed apart from one another as becomes obvious from the deformation of the Li<sub>2</sub>C<sub>2</sub> ring; the C–Li–C angles are widened to 109.6(3)°, whereas the Li–C–Li angles are compressed to 70.4(3)°; this leads to an Li<sub>2</sub>C<sub>2</sub> rhomb.

The conformation of the 2,4,6-triaza-cyclohex-1-yl groups is unusual. As shown above, the preferred conformation is *aee*. In **8** one of the rings and its substituents adopts the *aee*- (bound to C(7)) while the other has the *aae*-conformation (involving C(1)). This is presumably due to the spatial preorgansisation by  $Li \cdots N$ interactions which leads to steric repulsion between the methyl groups at the nitrogen and silicon atoms C(14) and C(5).

**Lithiated RSiMe<sub>2</sub>Ph (4).** A similar reactivity pattern towards metallation with butyl lithium is observed when  $RSiMe_2Ph$  is employed as a substrate (Scheme 4).



Scheme 4 Lithiation of RSiMe<sub>2</sub>Ph (4)

Product **9** is obtained in 33% yield directly, as it precipitates after addition of butyl lithium to a cold solution of **4**. Despite various attempts, obtaining crystals suitable for structural analysis was not possible. Compound **4** was characterised by NMR spectroscopy.

Fig. 7 shows the <sup>1</sup>H NMR spectrum recorded from a d<sup>8</sup>-thf solution of **4**. Despite there being no information about the degree of aggregation in this donor solvent, the data suggest an *aee*-conformation, because there are three signals for the *N*-bound methyl groups. This is unusual as in many other cases we observed only two signals for these methyl groups in TMTAC derivatives indicating rapid exchange. The non-metallated methyl group at silicon and the Li–CH<sub>2</sub>–Si unit can easily be distinguished by their integrals and their chemical shifts of 0.29 and –1.91 ppm.

Consistently, the <sup>13</sup>C NMR spectrum also contains three resonances for the methyl groups at nitrogen at 41.2, 40.5 and 39.3 ppm. The Si-bound methyl group causes a resonance at 2.0, the carbanionic group at -12.1 ppm. The <sup>29</sup>Si NMR shows a single peak at -2.3 ppm.



**Fig. 7** <sup>1</sup>H NMR spectrum of a solution of compound **9** in  $d^8$ -THF (\* denotes a resonance due to silicone grease).

#### Conclusion

The above experimental results show, that up to two 2,4,6-trimethyl-2,4,6-triaza-cyclohex-1-yl groups can easily be introduced into the coordination sphere of silicon by reacting chlorosilanes with lithiated TMTAC. However, threefold substitution provokes a problem due to steric overcrowding. This was confirmed by quantumchemical calculations. Upon attempts to achieve fourfold substitution of silicon in SiCl<sub>4</sub> with 2,4,6-trimethyl-2,4,6-triaza-cyclohex-1-yl groups by lithiated TMTAC, the system swerved and in small quantities a product of a formal insertion of SiCl<sub>2</sub> into the C–N bonds of the TMTAC ring was observed. In most of the compounds the 2,4,6-trimethyl-2,4,6-triaza-cyclohex-1-yl units adopt the same conformation as in free TMTAC, the *aee*-conformation.

Systems containing methyl groups at silicon, like  $R_2SiMe_2$  and  $RSiMe_2Ph$  (R = 2,4,6-trimethyl-2,4,6-triaza-cyclohex-1-yl) can be deprotonated by butyl lithium. The lithiation does not take place at the heterocyclic unit, but at the Si–Me groups.

#### Experimental

#### General methods

All manipulations were carried out under an atmosphere of dry nitrogen in anhydrous and degassed solvents (distilled before use from standard drying agents) using Schlenk vacuum-line techniques or an MBRAUN UNILAB glovebox. NMR spectra were recorded in  $C_6D_6$ ,  $d_8$ -toluene and  $d_8$ -THF on a BRUKER AVANCE DRX 500 and a BRUKER AVANCE 600 spectrometer. All NMR chemical shifts were referenced to the residual peaks of the protons of the used solvents. Elemental analyses were performed using an ELEMENTAR VARIO EL III CHNS and a LECO CHNS 932 (the carbon contents of silicon compounds are systematically low due to carbide formation).<sup>9</sup> Bis[(2,4,6-trimethyl-2,4,6-triazacyclo-hex-1-yl)-lithium]-(1,3,5-trimethyl-1,3,5-triaza-cyclohexane)-adduct ([(RLi)<sub>2</sub>·(RH)]) (1) was prepared as previously described by us.<sup>1</sup>

#### Preparations

[MeN(CH<sub>2</sub>NMe)<sub>2</sub>CH]-SiEt<sub>3</sub> (2). 2.0 g (5.0 mmol) lithiated TMTAC (1) are placed in a vessel and 20 mL diethyl ether were added at -78 °C. Chlorotriethylsilane (1.7 mL, 1.5 g,

10 mmol) diluted with 10 mL diethyl ether added dropwise. The resulting suspension was allowed to warm to ambient temperature overnight. The precipitated lithium chloride was filtered off and washed three times with 5 mL of diethyl ether. After removal of the volatile solvent, the product was yielded as yellowish liquid. The pure product was yielded by distillation at 80–84 °C and 0.1 mbar. Yield 1.79 g (7.36 mmol, 73%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  3.41 (d, 2H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 10 Hz), 3.02 (s, 1H, SiCH), 2.92 (d br, 2H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 10 Hz), 2.59 (s, 6H, 2-NCH<sub>3</sub>), 1.80 (s, 3H, 4-NCH<sub>3</sub>), 0.97 (t, 12H, SiCH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz), 0.65 (q, 6H, SiCH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  79.7 (br, NCH<sub>2</sub>N), 75.5 (SiCH), 43.9 (br, 2-NCH<sub>3</sub>), 39.8 (4-NCH<sub>3</sub>), 7.5 (CH<sub>2</sub>CH<sub>3</sub>), 2.9 (CH<sub>2</sub>CH<sub>3</sub>); <sup>29</sup>Si-NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  3.5 (s). Found: C, 59.20; H, 12.01; N, 17.26. Calc. for C<sub>12</sub>H<sub>29</sub>N<sub>3</sub>Si (243.21): C, 57.62; H, 11.75; N, 17.09%.

[MeN(CH<sub>2</sub>NMe)<sub>2</sub>CH]-SiPh<sub>3</sub> (3). The procedure was the same as described above for 2. Employed reagents: 1 (3.99 g, 10.0 mmol, 40 mL Et<sub>2</sub>O), chlorotriphenylsilane (5.90 g 20.0 mmol, 20 mL Et<sub>2</sub>O). The compound was isolated by reducing the volume of the raw solution after filtration and crystallisation. Yield 3.02 g (7.80 mmol, 78%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.88 (m, 6H, SiPh), 7.19 (m, 9H, SiPh), 3.98 (s, 1H, SiCH), 3.42 (d, 2H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 10.1 Hz), 2.90 (d, br, 2H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 10.0 Hz), 2.64 (s, 6H, *o*-NCH<sub>3</sub>), 1.68 (s, 3H, 4-NCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>) δ 136.9 (SiPh), 136.0 (SiPh), 129.6 (SiPh), 128.0 (SiPh), 79.0 (br, NCH<sub>2</sub>N), 76.9 (SiCH), 44.9 (br, 2-NCH<sub>3</sub>), 39.7 (4-NCH<sub>3</sub>); <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>) δ –20.7 (s) Found: C, 74.37; H, 7.54; N, 10.84. Calc. for C<sub>24</sub>H<sub>29</sub>N<sub>3</sub>Si (387.21): C, 72.39; H, 7.79; N, 9.83%.

[MeN(CH<sub>2</sub>NMe)<sub>2</sub>CH]-SiMe<sub>2</sub>Ph (4). The procedure was similar to that described for 2. Employed reagents: 1 (2.0 g, 5.0 mmol, 20 mL hexane), chlorodimethylphenylsilane (1.77 mL, 1.71 g, 10.0 mmol, 20 mL hexane). The compound was isolated by reducing the volume of the raw solution after filtration and crystallisation. Yield 3.02 g (7.80 mmol, 78%). The volatile solvent was removed by application of reduced pressure. The product remains as an orange oil, which contained some impurities and was not purified, as distillation led to decomposition and crystallisation was not possible. It was employed as such in further reactions. Yield 1.84 g (6.98 mmol, 69%). <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ )  $\delta$  7.67 (d, 2H, SiPh,  ${}^3J_{HH}$  = 7.8 Hz), 7.20 (m, 3H, SiPh), 3.46 (d, 2H, NC $H_2$ N,  ${}^2J_{HH}$  = 10.0 Hz), 3.14 (s, 1H, SiCH), 2.80 (d, 2H, NC $H_2$ N,  ${}^2J_{HH}$  = 10.0 Hz), 2.48 (s, 6H, 2-NC $H_3$ ), 1.79 (s, 3H, 4-NCH<sub>3</sub>), 0.43 (s, 6H, SiCH<sub>3</sub>); <sup>13</sup>C NMR  $\delta$  (125 MHz, C<sub>6</sub>D<sub>6</sub>) 139.7 (SiPh), 134.5 (SiPh), 129.1 (SiPh), 80.2 (br, NCH<sub>2</sub>N), 77.8 (SiCH), 42.9 (2-NCH<sub>3</sub>), 39.9 (4-NCH<sub>3</sub>), -1.8 (SiCH<sub>3</sub>); <sup>29</sup>Si NMR  $(99 \text{ MHz}, C_6 D_6) \delta - 6.8 \text{ (s)}; \text{ MS} (\text{EI}, 70 \text{ eV}, \text{liquid}) 176 (M^+-\text{Ph-Me}, 176 \text{ eV})$ 66%), 162 (M+-PhMe2, 30%), 135 (SiMe2Ph, 100%), 128 (TMTAC, 100%), 121 (SiMePh, 12%), 105 (SiPh, 13%), 85 (TMTAC-Me<sub>3</sub>, 19%), 42 (SiMe, 49%).

[MeN(CH<sub>2</sub>NMe)<sub>2</sub>CH]<sub>2</sub>SiMe<sub>2</sub> (5). A stirred suspension of lithiated TMTAC (1 3.0 g, 7.5 mmol) in 20 mL pentane was dropped into a solution of dichlordimethylsilane (0.90 mL, 1.0 g, 7.5 mmol) in 30 mL pentane at -78 °C. The resulting suspension was allowed to warm to ambient temperature overnight. The precipitated lithium chloride was filtered off. The solvent was removed under reduced pressure, which yielded crystalline material in the last stages of concentration. Yield 0.84 g (2.7 mmol, 35%). <sup>1</sup>H

NMR (500 MHz,  $C_6D_6$ )  $\delta$  3.37 (d, br, 4H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 8.7 Hz), 3.26 (s, 2H, SiCH), 3.02 (s, br, 4H, NCH<sub>2</sub>N), 2.69 (s, 12H, 2-NCH<sub>3</sub>), 1.80 (s, 6H, 4-NCH<sub>3</sub>), 0.43 (s, 6H, SiCH<sub>3</sub>); <sup>13</sup>C-NMR (125 MHz,  $C_6D_6$ )  $\delta$  79.4 (br, NCH<sub>2</sub>N), 75.2 (br, SiCH), 43.9 (br, 2-NCH<sub>3</sub>), 39.9 (4-NCH<sub>3</sub>), -1.1 (SiCH<sub>3</sub>); <sup>29</sup>Si-NMR (99 MHz,  $C_6D_6$ )  $\delta$  0.0 (s); MS (EI, 70 eV) *m*/*z* 128 (TMTAC, 100%), 101 (TMTAC-(Me)<sub>2</sub>, 19%), 85 (TMTAC-(Me)<sub>3</sub>, 51%), 59 (SiMe<sub>2</sub>, 26%), 44 (SiMe, 90%).

[MeN(CH<sub>2</sub>NMe)<sub>2</sub>CH]<sub>2</sub>-SiPh<sub>2</sub> (6). The procedure was similar to that described for **5**. Employed reagent: dichlorodiphenylsilane (1.03 mL, 1.26 g, 5.00 mmol, 20 mL hexane), **1** (2.0 g, 5.0 mmol, 20 mL hexane). After filtration and concentration of the solution under reduced pressure, the product precipitated as fine powder upon cooling to 4 °C and was yielded by filtration. Yield 0.1 g (0.2 mmol, 4%). <sup>1</sup>H-NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.83 (d, 2H, Si*Ph*, <sup>3</sup>J<sub>HH</sub> = 6.3 Hz), 7.21 (m, 10H, Si*Ph*), 3.77 (s, 2H, Si*CH*), 3.44 (d, 4H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 10.3 Hz), 2.91 (d, 4H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 10.3 Hz), 2.91 (d, 4H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 10.3 Hz), 2.63 (s, 12H, 2-NCH<sub>3</sub>), 1.72 (s, 6H, 4-NCH<sub>3</sub>); <sup>13</sup>C-NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  137.7 (Si*Ph*), 137.6 (Si*Ph*), 135.0 ((Si*Ph*), 129.5 (Si*Ph*), 78.9 (br, NCH<sub>2</sub>N), 74.0 (Si*CH*), 44.7 (br, 2-NCH<sub>3</sub>), 39.8 (4-NCH<sub>3</sub>); <sup>29</sup>Si-NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  -23.3 (s).

**2,4,6-Trimethyl-2,4,6-triaza-1,1-dichloro-1-sila-cycloheptane** (7). A few tiny crystals of this compound were obtained in the following way. Freshly distilled tetrachlorosilane (0.14 mL, 0.20 g, 1.2 mmol) were condensed onto freshly prepared **1** (1.0 g, 2.5 mmol) under vacuum at liquid nitrogen temperature. The mixture was warmed to -78 °C and allowed to slowly warm to ambient temperature overnight. The lithium chloride was filtered off and the obtained clear solution cooled to 30 °C, whereby a few crystals of **7** precipitated within one week. Characterisation was undertaken solely by X-ray diffraction.

[{MeN(CH<sub>2</sub>NMe)<sub>2</sub>CH}<sub>2</sub>-SiMe(CH<sub>2</sub>Li)]<sub>2</sub> (8). *n*-Butyl lithium (1.6 M in hexane, 1.0 mL, 1.6 mmol) was dropped into a solution of [MeN(CH<sub>2</sub>NMe)<sub>2</sub>CH]<sub>2</sub>SiMe<sub>2</sub> (5) (0.43 g, 1.4 mmol) in 10 mL hexane at -78 °C. Warming the reaction mixture to ambient temperature resulted in precipitation of a colourless solid, which was filtered and washed three times with 5 mL of hexane and dried in vacuum. Yield 0.21 g (0.33 mmol, 46%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  3.52 (d, 8H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 9.9 Hz), 3.04 (br, 4H, SiCH), 2.96 (d, 8H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 10.0 Hz), 2.71 (s, 24H, 2-NCH<sub>3</sub>), 2.21 (12H, 4-NCH<sub>3</sub>), 0.46 (s, 6H, SiCH<sub>3</sub>), 0.14 (s, 4H, SiCH<sub>2</sub>Li); <sup>7</sup>Li NMR (194 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.2 (s); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$ 79.3 (NCH<sub>2</sub>N), 77.5 (SiCH), 40.5 (2-NCH<sub>3</sub>), 39.9 (4-NCH<sub>3</sub>), -1.1 (SiCH<sub>3</sub>), -2.8 (SiCH<sub>2</sub>Li); <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.0 (s).

[MeN(CH<sub>2</sub>NMe)<sub>2</sub>CH]-SiMePh(CH<sub>2</sub>Li) (9). The procedure was similar to that described for **8**. Employed reagents: *n*-butyl lithium (1.6 M in hexane, 2.2 mL, 3.5 mmol), [MeN(CH<sub>2</sub>NMe)<sub>2</sub>CH]<sub>2</sub>SiMePh (6) (0.94 g, 3.3 mmol). Yield 0.30 g (1.1 mmol, 33%). <sup>1</sup>H NMR (500 MHz, d<sub>8</sub>-THF)  $\delta$  7.77 (d, 2H, SiPh, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz), 7.16 (m, 3H, SiPh, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz), 3.65 (d, 1H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 9.2 Hz), 3.60 (d, 1H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 9.3 Hz), 2.85 (s, 1H, SiCH), 2.72 (d, 1H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 8.9 Hz), 2.68 (d, 1H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 8.3 Hz), 2.51 (s, 3H, NCH<sub>3</sub>), 2.29 (s, 3H, NCH<sub>3</sub>), 2.02 (s, 3H, NCH<sub>3</sub>), 0.30 (s, 3H, SiCH<sub>3</sub>), -1.91 (s, 2H, CH<sub>2</sub>Li); <sup>13</sup>C NMR (125 MHz, d<sub>8</sub>-THF)  $\delta$  148.2 (SiPh), 133.9 (SiPh), 126.5 (SiPh), 126.3 (SiPh), 80.7 (NCH<sub>2</sub>N), 80.5 (NCH<sub>2</sub>N), 80.3 (SiCH), 41.2 (NCH<sub>3</sub>), 40.5 (NCH<sub>3</sub>), 39.3 Table 3Crystal and refinement data for the structure determinations of compounds 1, 5, 7 and 8

Compound	TMTAC	5	7	8
Formula	$C_6H_{15}N_3$	$C_{14}H_{34}N_6Si$	$C_6H_{15}Cl_2N_2Si$	$C_{28}H_{66}Li_2N_{12}Si_2$
M <sub>r</sub>	129.21	314.56	228.20	640.99
cryst. size [mm]	$0.25 \times 0.25 \times 0.25$ (Capillary)	$0.06 \times 0.16 \times 0.28$	$0.24 \times 0.28 \times 0.30$	$0.16 \times 0.28 \times 0.30$
cryst. syst.	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	Pbca	$P\overline{1}$
a/Å	11.5902(2)	8.2646(5)	6.7426(2)	7.0976(11)
b/Å	18.9804(3)	13.3023(8)	15.1934(3)	12.225(2)
c/Å	14.0480(2)	16.6558(7)	21.4697(5)	12.2926(17)
α (°)	90	90	90	61.357(6)
$\beta$ (°)	95.5696(9)	96.950(4)	90	77.351(7)
$\gamma$ (°)	90	90	90	86.350(6)
V/Å <sup>3</sup>	3075.78(8)	1817.65(17)	2199.42(9)	912.3(2)
Z	16	4	8	1
$D_{\rm c}/{\rm Mg}~{\rm m}^{-3}$	1.116	1.149	1.378	1.167
$\mu/\text{mm}^{-1}$	0.071	0.134	0.656	0.134
θ-range [°]	3.0-30.0	3.0-27.5	3.3-27.5	3.0-27.5
reflns collected	78902	17917	20157	10304
unique reflns	8927	4048	2505	3755
R <sub>int</sub>	0.041	0.039	0.031	0.146
Reflections $I > 2\sigma(I)$	6917	3211	2428	1688
refined param.	565	198	169	214
$R_1, WR_2 [I > 2\sigma(I)]$	0.041/0.103	0.0428/0.1038	0.0327/0.0709	0.0658/0.1196
$R_1$ , w $R_2$ [all data]	0.057/0.116	0.0600/0.1150	0.0339/0.0714	0.1894/0.1512
$\Delta \rho_{\rm max/min}/e {\rm \AA}^{-3}$	0.251/-0.202	0.362/-0.280	0.314/-0.252	0.032/-0.339
CCDC no.	821375	821376	821377	821378

(NCH<sub>3</sub>), 2.0 (SiCH<sub>3</sub>), -12.1 (CH<sub>2</sub>Li); <sup>29</sup>Si NMR (99 MHz, d<sub>8</sub>-THF)  $\delta$  -2.3 (s).

**Crystallographic structure determinations.** The crystallographic data sets for TMTAC, **5**, **6** and **8** were collected on a Bruker Nonius Kappa CCD, operated with monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Structure solutions and refinements were undertaken with the programs SHELXS-97<sup>20</sup> and SHELXL-97.<sup>20</sup> The crystal quality of **8** was limited. The low scattering power of the crystal is the reason for the relative small number of reflections with  $I > 2\sigma(I)$ . We used data up to  $\theta_{max} = 27.5^{\circ}$ and thereby could include some 50 reflections (between  $\theta = 25$ and 27°) to improve the validity of structural information. This leads to a lower completeness and worse *R* and  $R_{int}$  factors, but increases the amount of information and thus the validity of the structure. Experimental details are listed in Table 3. CCDC reference numbers 821375 (TMTAC), 821376 (**5**), 821377 (**6**), 821378 (**8**). For crystallographic data see ESI.†

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