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# Preparation of a stable disilane amidinium heterocycle and attempted syntheses of an inorganic *N*-heterocyclic carbene

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#### ABSTRACT

The cyclic disilane amidinium salt [ $(Me_2SiNDipp)_2CH$ ]OTf (Dipp = 2,6-<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; OTf = OSO<sub>2</sub>CF<sub>3</sub>) was obtained in high yield, and attempts to generate the *N*-heterocyclic carbene [ $(Me_2SiNDipp)_2C$ :] via deprotonation with numerous bases exclusively gave ring-opened products of the general form: R -SiMe<sub>2</sub>-SiMe<sub>2</sub>N(Dipp)-CH=NDipp (R = carbon-, nitrogen- or oxygen-based nucleophiles). Although this approach was not directly successful in generating silicon-based *N*-heterocyclic carbenes, judicious manipulation of the ring-bound substituents might enable the future synthesis of new inorganic carbenes to transpire.

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#### 1. Introduction

Since their discovery [1], *N*-heterocyclic carbenes (NHCs) have adopted a prominent role as versatile ligands in coordination chemistry and are now replacing more traditional electron pair donors, such as phosphines, for various applications [2]. As a result, there has been considerable progress in modifying the electronic and steric properties of this general ligand class by changing the substituents at either the intraring carbon or nitrogen atoms, including the development of carbene systems where the  $\sigma$ -donor site is found at alternate positions along the *N*-heterocyclic carbene backbone [3].

A less explored method of tuning the  $\sigma$ -donor/ $\pi$ -acceptor strength of an *N*-heterocyclic carbene is to incorporate inorganic elements within an NHC framework. Important breakthroughs in this area include the synthesis of phosphorus-containing cyclic carbenes, such as heterocycle **A** by Grubbs et al. [4], and the preparation of boron-containing carbenes by the groups of Bertrand and Roesler (**B**–**D**) (Chart 1) [5]. Despite these advances, the development of new inorganic element-based NHCs has been somewhat slow due to the significant synthetic challenges stemming from the high degrees of reactivity inherent to many inorganic compounds.

0022-328X/\$ – see front matter @ 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jorganchem.2013.04.029 In this paper we describe our efforts to obtain an *N*-heterocyclic carbene with a disilane backbone (compound **E** in Chart 1). The initial goal of this project was to promote increased  $\sigma$ -donor ability relative to pre-existing NHCs via the placement of electron-donating silicon and tin atoms within a carbene heterocycle. Of note, we recently reported the heavier Group 14 element analogs of the target carbene **E**, wherein the carbene carbon in the heterocycle is replaced by Ge or Sn [i.e., (Me<sub>2</sub>SiNDipp)<sub>2</sub>E; E = Ge and Sn; Dipp = 2,6<sup>-i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] [6,7].

#### 2. Results and discussion

## 2.1. Preparation of an amidinium heterocycle containing a disilane backbone

The incorporation of inorganic elements within the backbone of an *N*-heterocyclic carbene (NHC) represents a relatively new concept, and provides an added dimension with respect to tuning the donor/acceptor properties of an *N*-heterocyclic carbene [4,5,8]. In order to progress toward a cyclic carbene with a tetramethyldisilane ( $-Me_2Si-SiMe_2-$ ) backbone, we modeled our synthetic strategy after a general method used previously to generate NHCs with heterocycles containing phosphorus and boron atoms [4,5].

The requisite disilane amidinium salt  $[(Me_2SiNDipp)_2CH]OTf$ (OTf = OSO\_2CF<sub>3</sub>) (**1**) was prepared from the cyclocondensation of ClSiMe\_2SiMe\_2Cl with the silylformamidine, DippN=CHN(Dipp)





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Chart 1. Various known inorganic element-containing NHCs (A–D) and the target species (E) discussed in this paper; Dipp = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>.

SiMe<sub>3</sub>, in the presence of Me<sub>3</sub>SiOTf (Eq. (1)). The potential NHC precursor, **1**, was isolated as a thermally stable white solid (Mp = 245-250 °C) in a nearly quantitative yield and was structurally authenticated by single-crystal X-ray crystallography (Fig. 1).



As shown in Fig. 1,  $[(Me_2SiNDipp)_2CH]OTf(1)$  contains a cationic NSiSiNC heterocycle with a nearly planar arrangement of the constituent ring atoms. Interestingly, both SiMe<sub>2</sub> units within the tetramethyldisilane backbone in **1** are locked in mutually eclipsed



**Fig. 1.** Molecular structure (30% probability level) of the [(Me<sub>2</sub>SiNDipp)<sub>2</sub>CH]<sup>+</sup> cation in **1** with all hydrogen atoms except the imidazolium proton at C(1) omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)–Si(2) 2.2976(7), Si(1)–N(1) 1.8485(14), Si(2)–N(2) 1.8496(15), N(1)–C(1) 1.330(2), N(2)–C(1) 1.323(2), Si(1)···O(2) 2.8090(16), Si(1)···O(2) '2.8534(17); N(1)–C(1)–N(2) 120.46(14), N(1)–Si(2) 90.71(5), N(2)–Si(2)–Si(1) 90.34(5). O(2) is related to the triflate oxygen O(2)' by the symmetry operation –x, –y, 1 – z through the 0, 0, 1/2 inversion center.

geometries [N(1)-Si(1)-Si(2)-N(2) torsion angle = 5.08(6)° in 1] with narrow intraring N-Si-Si angles of ca. 90°. The adjacent N(1)-C(1)-N(2) angle in the imidazolium cation was determined to be 120.46(14)°, suggesting the presence of sp<sup>2</sup>-hybridization at C(1); significant N–C–N  $\pi$ -bonding is also present within this imidazolium heterocycle as manifested by average C-N bond lengths [1.326(3) Å] that are shorter than typical C–N single bonds. For comparison, the related intraring C–N bond lengths within the imidazolium triflate salt [(HCNDipp)<sub>2</sub>CH]OTf average to 1.329(5) Å [9]. Lastly, the aryl groups in **1** are significantly canted forward to form a steric pocket about the proximal imidazolium carbon centers, C(1). The  ${}^{19}F{}^{1}H{}$  NMR spectrum of **1** in CDCl<sub>3</sub> is consistent with the presence of a weakly interacting OTf anion in solution  $(\delta - 78.3 \text{ ppm}; c.f. [^{n}\text{Bu}_4\text{N}]\text{OTf}, \delta - 78.7 \text{ ppm})$  [10]. However significant Si…O contacts between the imidazolium ring in 1 and the OTf anion were detected in the solid state [2.8090(16) and 2.8534(17) Å] with the triflate anion located directly below the cationic ring; these Si-O distances lie within the sum of the van der Waals radii for O and Si (3.52 Å) [11]. The observed metrical parameters in 1 attest to a low degree of steric protection provided by the methyl substituents attached to the silicon atoms, thus enabling weak cation-anion contacts to exist.

### 2.2. Attempted deprotonation of **1** to afford an N-heterocyclic carbene

With the desired cyclic disilane amidinium salt 1 in hand, we explored various methods of accessing the target carbene [(Me<sub>2</sub>SiNDipp)<sub>2</sub>C:] via deprotonation of the ring-bound hydrogen atom at C(1) (Fig. 1). Our first deprotonation attempt involved treatment of **1** with the commonly used hindered base  $K[N(SiMe_3)_2]$ . This reaction vielded a new product as a colorless and moisturesensitive solid, however <sup>1</sup>H NMR spectroscopic analysis revealed that a downfield-positioned singlet at 7.39 ppm was present in  $C_6D_6$ , indicating that the N=CH-N unit remained intact. In addition, the expected resonance for a carbenic carbon of an NHC was not located in the  ${}^{13}C{}^{1}H$  NMR spectrum (>180 ppm) [1]. These data, in conjunction with the appearance of two inequivalent SiMe<sub>2</sub> environments in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, suggested that nucleophilic attack of the ring structure in **1** by the  $[N(SiMe_3)_2]$ anion had transpired. Single-crystal X-ray crystallography later identified the product as the ring-opened species (Me<sub>3</sub>Si)<sub>2</sub>NSiMe<sub>2</sub> SiMe<sub>2</sub>N(Dipp)C(H)=NDipp (2) (Scheme 1, Fig. 2).

The metrical parameters in **2** are consistent with the molecular structure presented in Scheme 1. Specifically, planar coordination environments are observed about N(1) and N(3) [angle sum = 359.0(3) and  $359.94(17)^\circ$ , respectively], while the Si–N



Scheme 1. Attempted deprotonation of [(Me<sub>2</sub>SiNDipp)<sub>2</sub>CH]OTf (1).

distances in **2** [1.7543(19) to 1.7999(18) Å] are in the typical range for single bonds with appreciable C–N bond length alternation noted along the chain [C(1)-N(1) = 1.368(2) Å; C(1)-N(2) = 1.274(3) Å]; the latter bond lengths correspond to localized C–N single and double bonds, respectively.

It appears from the above chemistry that the disilane backbone in **1** is prone to nucleophilic attack, thus posing a competing reaction pathway to the desired deprotonation of the imidazolium C–H group. Unfortunately we observed a similar ring-opening process when **1** was treated with the lithium amide Li[NHDipp] in

diethyl ether. As with K[N(SiMe<sub>3</sub>)<sub>2</sub>], nucleophilic ring-opening of the heterocycle in **1** by Li[NHDipp] occurred to give the *N*-disilylamino-substituted formamidine chain (DippNH)SiMe<sub>2</sub>Si-Me<sub>2</sub>N(Dipp)C(H)=NDipp (**3**) in nearly quantitative yield, with concomitant formation of LiOTf as a by-product (Scheme 1, Fig. 3). The refined metrical parameters for **3** derived by X-ray crystallography were similar to **2**, thus no further discussion will be made here.

Positing that amides such as the  $[N(SiMe_3)_2]^-$  and  $[NHDipp]^$ were too nucleophilic to participate in clean deprotonation chemistry with **1**, we attempted to prepare the disilane-bridged NHC



**Fig. 2.** Molecular structure of  $(Me_3Si)_2NSiMe_2SiMe_2N(Dipp)C(H)=NDipp (2) at a 30% probability level with all hydrogen atoms except for the formamidine proton at C(1) omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–N(1) 1.368(2), C(1)–N(2) 1.274(3), N(1)–Si(1) 1.799(18), Si(1)–Si(2) 2.3774(9), Si(2)–N(3) 1.7744(18), N(3)–Si(3) 1.7543(19), N(3)–Si(4) 1.7565(19); N(1)–C(1)–N(2) 122.18(18), C(1)–N(1)–Si(1) 119.70(14), N(1)–Si(2) 114.25(6), Si(1)–Si(2)–N(3) 107.89(6), Si(2)–N(3)–Si(3) 123.11(10), Si(2)–N(3)–Si(4) 118.80(10), Si(3)–N(3)–Si(4) 118.03(10).$ 



**Fig. 3.** Molecular structure of (DippNH)NSiMe<sub>2</sub>SiMe<sub>2</sub>N(Dipp)C(H)=NDipp (**3**) at a 30% probability level with all carbon-bound hydrogen atoms [except at C(5A)] and solvate molecules omitted for clarity. Selected bond lengths [Å] and angles [°] with values for the second molecule of **3** in the asymmetric unit listed in square brackets: Si(1)–Si(2) 2.3553(8) [2.3518(8)], Si(1)–N(1) 1.7728(19) [1.7792(19)], Si(2)–N(3) 1.7408(19) [1.7386(19)], N(1)–C(5) 1.376(3) [1.383(3)], N(2)–C(5) 1.287(3) [1.275(3)]; Si(2)–Si(1)–N(1) 114.94(6) [114.54(6)], Si(1)–Si(2)–N(3) 112.13(7) [112.06(7)], Si(1)–N(2)–C(5) 120.25(14) [120.61(12)], N(1)–C(5)–N(2) 122.6(2) [123.14(19)].

[(Me<sub>2</sub>SiNDipp)<sub>2</sub>C:] (**E**) from the reaction of **1** with the recently synthesized hindered base IPr= $CH_2$  (IPr = [(HCNDipp)<sub>2</sub>C]) [12–14]. Our studies were further motivated by the demonstrated role of IPr= $CH_2$  as a neutral Brønsted base in phosphazene [P(V)–N] chemistry [15]. When IPr= $CH_2$  was combined with a suspension of **1** in toluene, the immediate clearing of the mixture and the formation of a yellow solution was noted. Analysis of the reaction mixture revealed the presence of a new IPrCH<sub>2</sub>-containing product that had spectral properties inconsistent with the formation of an [IPr– $CH_3$ ]<sup>+</sup> salt [15]; one would expect [IPr– $CH_3$ ]OTf to be formed as a byproduct if successful deprotonation of **1** had occurred. Recrystallization of the solid from a THF/hexanes mixture at -35 °C afforded large colorless blocks that were identified as the ring-opened product [(IPrCH<sub>2</sub>)SiMe<sub>2</sub>SiMe<sub>2</sub>N(Dipp)C(H)=NDipp]OTf (**4**) (Scheme 1, Fig. 4).

The structure of the cationic silvlamine chain [(IPrCH<sub>2</sub>)SiMe<sub>2-</sub>  $SiMe_2N(Dipp)C(H)=NDipp]^+$  in **4** is shown in Fig. 4, and as in the ring-opened products 2 and 3, an intact intrachain N-C(H)=N unit is present. The nucleophilic IPrCH<sub>2</sub> group is terminally bound to a SiMe<sub>2</sub>-residue via C(5), and the corresponding Si-C distance [1.935(3) Å] is considerably longer than the Si-C bond lengths involving the methyl groups in the adjacent Me<sub>2</sub>SiSiMe<sub>2</sub> array [e.g., Si(1)-C(1) = 1.869(4) Å]. Notably, the  $-SiMe_2-N(Dipp)C(H)=$ NDipp unit is crystallographically disordered over two positions and thus a higher degree of error is associated with the refined metrical parameters involving this segment. Upon binding of the IPr=CH<sub>2</sub> donor to a Si center to form **4**, a substantial lengthening of the  $C_{IPr}$ -CH<sub>2</sub> bond [C(6)-C(5) = 1.472(4) Å] occurs relative to the free *N*-heterocyclic olefin IPr=CH<sub>2</sub> which contains a *bona fide* C=C double bond [1.331(8) Å] [14]. Moreover, the analogous C<sub>IPr</sub>--CH<sub>2</sub> bond in the IPrCH<sub>2</sub> adduct IPrCH<sub>2</sub>·SnH<sub>2</sub>·W(CO)<sub>5</sub> [14] is slightly shorter [1.446(2) Å] than the related linkage in 4, but points toward a similar bonding environment within the IPrCH<sub>2</sub> donors in each complex. The structural data for 4 is in line with the donation of  $\pi$ -electron density from the terminal olefin group in IPr=CH<sub>2</sub> to silicon, with a concomitant increase in N–C  $\pi$ -bonding within the central heterocycle of the IPrCH<sub>2</sub> donor (as evidenced by shortening



**Fig. 4.** Molecular structure of the [(IPrCH<sub>2</sub>)SiMe<sub>2</sub>SiMe<sub>2</sub>N(Dipp)C(H)=NDipp]<sup>+</sup> cation in **4** at a 30% probability level. All hydrogen atoms except for the formamidine proton at C(9A) have been omitted for clarity. Selected bond lengths [Å] and angles [°] with values belonging to a disordered  $-SiMe_2-N(Dipp)=CHN(Dipp)$  unit in square brackets: Si(1)-Si(2A) 2.357(7) [2.346(15)], Si(1)-C(5) 1.935(3), Si(2A)-N(3A) 1.800(12) [1.76(2)], N(3A)-C(9A) 1.376(17) [1.34(4)], N(4A)-C(9A) 1.281(17) [1.22(4)]; Si(2A)-Si(1)-C(5) 98.84(19) [102.0(4)], Si(1)-Si(2A)-N(3A) 113.4(4) [118.0(10)], Si(2A)-N(3A)-C(9A) 119.7(8) [115.8(17)], N(3A)-C(9A)-N(4A) 121.5(12) [125(3)].

of the intraring N–C bonds in **4**). The OTf counteranion in **4** is well separated from the cationic chain in the solid state with no Si–OTf contacts noted within 6 Å.

Given the widespread use of K[O<sup>t</sup>Bu] to deprotonate imidazolium cations and form stable *N*-heterocyclic carbenes [16], compound **1** was combined with an equivalent of KIO<sup>t</sup>Bul. A white, free flowing solid was obtained upon work-up which gave <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>29</sup>Si{<sup>1</sup>H} NMR data consistent with the formation of the ringproduct  $[(^{t}BuO)SiMe_2SiMe_2N(Dipp)C(H)=NDipp]$  5 opened (Scheme 1). Specifically, two distinct SiMe<sub>2</sub> environments were located by NMR spectroscopy and characteristic <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR resonances for the <sup>t</sup>BuO residue were also detected. Moreover, an intact formamidine CH group was found at 7.32 ppm in the <sup>1</sup>H NMR spectrum of **5** along with an accompanying imine  ${}^{13}C{}^{1}H$ NMR resonance at 157.1 ppm (in  $C_6D_6$ ). Unfortunately attempts to obtain crystals of **5** of suitable guality for single-crystal X-ray crystallography were unsuccessful [17], however satisfactory elemental analyses (C, H and N) were obtained. Lastly, attempts to deprotonate 1 using stoichiometric quantities of sodium metal or sodium naphthalenide gave the known aryl-substituted formamidine DippN=C(H)-NH(Dipp) [5a] along with unknown SiMe<sub>2</sub>-containing products.

The above reactions indicate a high propensity of the Si-N linkages in 1 to undergo nucleophilic cleavage. The significant steric pocket created by the flanking Dipp groups about the imidazolium proton at C(1) in 1 (Fig. 1) likely directs the reactivity away from this unit and toward the electron deficient silicon centers positioned at the opposite end of the CN<sub>2</sub>Si<sub>2</sub> ring. Another factor likely promoting ring-opening versus deprotonation is the ring strain in the imidazolium precursor **1** as illustrated by the *N*(Dipp)-*Si*–*Si* angles of *ca*. 90°; these angles become much wider in the ring-opened products **2–4** where angles in the range of  $113.4(4) - 118.0(10)^{\circ}$  are observed. Thus it appears that either less encumbered groups will be have to present at the nitrogen atoms in the disilane amidinium ring, and/or that increased steric bulk will have to be incorporated along the disilane backbone in order to induce successful deprotonation chemistry. We are currently exploring the synthesis of the hindered analogs of 1 which contain increased steric bulk at silicon in order suppress the ring-opening chemistry [18] (e.g., in the form of a tetraisopropyldisilane group,  $-iPr_2SiSi^iPr_2-$ , as part of an NHC unit).

#### 3. Conclusions

The potential *N*-heterocyclic carbene precursor  $[(HCNDipp)_2CH]$ OTf (1) was prepared and structurally characterized. Attempts to generate a new inorganic carbene via deprotonation of the disilanecontaining precursor 1 with a variety of common sterically encumbered bases invariably led to nucleophilic attack of the base on the ring backbone to form ring-opened species with intact formamidine C–H groups (compounds 2–5). Despite the lack of successful deprotonation in this study, the preparation of a new class of imidazolium rings with inorganic backbones is significant as future modification of the steric bulk at the backbone-positioned Si centers might still allow for access to new carbene derivatives with considerably altered electronic properties relative to their ubiquitous organic counterparts.

#### 4. Experimental

#### 4.1. General procedures

All reactions were performed using standard Schlenk techniques under an atmosphere of nitrogen or in a nitrogen-filled glove box (Innovative Technology, Inc.). Solvents were dried using a Grubbs-type solvent purification system [19] manufactured by Innovative Technology, Inc., and degassed (freeze-pump-thaw method) and stored under an atmosphere of nitrogen prior to use. Dichlorotetramethyldisilane and trimethylsilyl triflate were purchased from Gelest and used as received. Potassium bis(trimethylsilyl)amide, potassium *tert*-butoxide, and sodium metal were purchased from Aldrich and used as received. DippN=  $C(H)NDipp(SiMe_3)$  (Dipp =  $2,6^{-i}Pr_2C_6H_3$ ) [4a], Li[NHDipp] [20], and IPr= $CH_2$  (IPr = [(HCNDipp)\_2C]) [14] were prepared according to literature procedures. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>19</sup>F{<sup>1</sup>H} and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra were recorded on a Varian iNova-400 spectrometer and referenced externally to SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>29</sup>Si{<sup>1</sup>H}) and CFCl<sub>3</sub> (<sup>19</sup>F{<sup>1</sup>H}). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Melting points were obtained in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected.

#### 4.2. X-ray crystallography

Crystals of appropriate quality for X-ray diffraction studies were removed from a vial in a glove box and immediately covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then selected, attached to a glass fiber, and quickly placed in a lowtemperature stream of nitrogen [21]. All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo K $\alpha$  (1 and 2) and Cu K $\alpha$  (3 and 4) radiation with the crystals cooled to  $-100 \,^{\circ}C$ (Table 1). The data were corrected for absorption through Gaussian integration from indexing of the crystal faces. Structures were solved using direct methods with the programs SHELXS-97 [22] (1), SHELXD [23] (2–4), and refinements were completed using SHELXL-97 [22]. Hydrogen atoms were assigned positions based on the sp<sup>2</sup> or sp<sup>3</sup> hybridization geometries of their attached carbon or nitrogen atoms, and were given thermal parameters 20% greater than those of their parent atoms.

#### 4.2.1. Special refinement conditions

*Compound* **4**: Attempts to refine peaks of residual electron density as disordered or partial-occupancy tetrahydrofuran solvent molecules were unsuccessful. The data were corrected for disor-dered electron density through use of the SQUEEZE procedure [24] as implemented in *PLATON* [25]. A total solvent accessible void volume of 2237.1 Å<sup>3</sup> with a total electron count of 555 (consistent with 12 molecules of solvent THF, or 3 molecules per asymmetric unit) was found in the unit cell. Moreover, the distances within two of the disordered isopropyl groups were restrained during the refinement as:  $d(C57A-C58A) = d(C57A-C59A) = d(C77A-C79A) = d(C77B-C79B) = d(C77B-C79B) = d(C77B-C79B) = d(C78B\cdotsC59B) = d(C78B\cdotsC79A) = d(C78A\cdotsC79A) = d(C58B\cdotsC59B) = d(C78B\cdotsC79B) = 2.49(1) Å.$ 

#### 4.3. Synthetic procedures

#### 4.3.1. [(Me<sub>2</sub>SiNDipp)<sub>2</sub>CH]OTf (**1**)

DippN=CH–N(SiMe<sub>3</sub>)(Dipp) (5.409 g, 12.38 mmol) was mixed with ClSiMe<sub>2</sub>SiMe<sub>2</sub>Cl (2.30 mL, 2.31 g, 12.4 mmol) in 60 mL of CH<sub>2</sub>Cl<sub>2</sub> at room temperature. After 1 h, Me<sub>3</sub>SiOTf (2.24 mL, 2.75 g, 12.4 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added to the reaction mixture dropwise at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 2 h, and the volatiles were removed under dynamic vacuum to yield pure **1** as a fine white powder. Yield: 7.41 g, 95%. Recrystallization of the product from toluene/CH<sub>2</sub>Cl<sub>2</sub> yielded **1** as colorless crystals of suitable quality for X-ray crystallographic analysis. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.67 (s, 12H, Si(CH<sub>3</sub>)<sub>2</sub>), 1.12 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.35 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 2.91 (septet, 4H, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, ArH), 7.59 (s, 1H, N=CH–N).  ${}^{13}C{}^{1}H{}$  NMR (CDCl<sub>3</sub>):  $\delta$  –2.9 (SiCH<sub>3</sub>), 23.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 125.2 (ArC), 129.9 (ArC), 133.1 (ArC), 145.5 (ArC), 168.9 (N=CH–N).  ${}^{19}F{}^{1}H{}$  NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  –78.3 (br). Mp (°C): 245–250. Anal. Calcd. for C<sub>30</sub>H<sub>47</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>SSi<sub>2</sub>: C, 57.29; H, 7.53; N, 4.45; S, 5.10. Found: C, 57.14; H, 7.13; N, 4.35; S, 4.49.

#### 4.3.2. $(Me_3Si)_2NSiMe_2SiMe_2N(Dipp)C(H)=NDipp$ (2)

To a mixture of K[N(SiMe<sub>3</sub>)<sub>2</sub>] (73 mg, 0.37 mmol) and **1** (173 mg, 0.275 mmol) was added 10 mL of benzene. A yellow mixture formed within a few minutes and the mixture was stirred for 1 h. Filtration of the mixture through Celite followed by removal of the volatiles afforded a white solid that was recrystallized from a toluene/hexanes mixture  $(-35 \degree C)$  to give 2 as colorless crystals of suitable quality for X-ray crystallography. Yield: 129 mg, 73%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.28 (s, 18H, N(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>), 0.48 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.69  $(s, 6H, Si(CH_3)_2), 1.08 (d, 12H, {}^3J_{HH} = 6.8 Hz, CH(CH_3)_2), 1.27 (d, 12H, 12H)$  ${}^{3}J_{\text{HH}} = 6.8 \text{ Hz}, \text{CH}(\text{CH}_{3})_{2}$ ), 3.42 (septet, 2H,  ${}^{3}J_{\text{HH}} = 6.8 \text{ Hz}, \text{CH}(\text{CH}_{3})_{2}$ ), 3.58 (septet, 2H,  ${}^{3}J_{HH} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 7.03–7.17 (m, 6H, ArH), 7.39 (s, 1H, N=CH-N).  ${}^{13}C{}^{1}H$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.1 (N(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>), 6.4 (Si(CH<sub>3</sub>)<sub>2</sub>), 6.9 (Si(CH<sub>3</sub>)<sub>2</sub>), 23.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 123.5 (ArC), 123.9 (ArC), 124.2 (ArC), 140.8 (ArC), 147.6 (ArC), 157.6 (N=CH-N). HR-MS, EI (m/z): Calcd. for [M<sup>+</sup>]: 639.42554. Found: 639.42471  $(\Delta ppm = 1.3 ppm)$ . Mp (°C): 168–172. Anal. Calcd. for C<sub>35</sub>H<sub>65</sub>N<sub>3</sub>Si<sub>4</sub>: C, 65.66; H, 10.23; N, 6.56. Found: C, 65.28; H, 10.34; N, 6.76.

#### 4.3.3. $(DippNH)SiMe_2SiMe_2N(Dipp)C(H)=NDipp(3)$

To a slurry of **1** (100 mg, 0.159 mmol) in 6 mL of toluene was added a cold (-35 °C) solution of Li[NHDipp] (29 mg, 0.16 mmol) in 5 mL of Et<sub>2</sub>O. A pale yellow mixture was formed immediately and the reaction mixture was stirred overnight at room temperature and filtered through Celite. Removal of the volatiles from the filtrate followed by washing of the product with 3 mL of hexanes gave 3 as a white powder. Yield: 103 mg, 98%. Crystals suitable for X-ray crystallography were grown from a saturated THF solution layered with hexanes at -35 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.38 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.39 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 1.09 (d, 6H,  ${}^{3}J_{HH} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (d, 12H,  ${}^{3}J_{HH} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.22 (d, 12H,  ${}^{3}J_{HH} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.24 (d, 6H,  ${}^{3}J_{HH} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.39 (s, 1H, NH), 3.48 (septet, 2H,  ${}^{3}J_{HH} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.61 (septet, 4H,  ${}^{3}J_{HH} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 7.02–7.13 (m, 9H, ArH), 7.42 (s, 1H, N=CH–N). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, peak assignment based on gHSQC and <sup>13</sup>C{<sup>1</sup>H} DEPT experiments):  $\delta$  -1.4 (Si(CH<sub>3</sub>)<sub>2</sub>), 0.7 (Si(CH<sub>3</sub>)<sub>2</sub>), 23.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 123.4 (ArC), 123.7 (ArC), 124.2 (ArC), 124.3 (ArC), 124.4 (ArC), 127.8 (ArC), 138.4 (ArC), 139.5 (ArC), 140.7 (ArC), 145.3 (ArC), 146.3 (ArC), 147.9 (ArC), 158.2 (N=CH-N). Mp (°C): 119–121. Anal. Calcd. for C<sub>41</sub>H<sub>65</sub>N<sub>3</sub>Si<sub>2</sub>: C, 75.05; H, 9.98; N, 6.40. Found: C, 75.33; H, 10.18; N, 6.26.

#### 4.3.4. $[(IPrCH_2)SiMe_2SiMe_2N(Dipp)C(H)=NDipp]OTf(4)$

To a mixture of **1** (100 mg, 0.159 mmol) and IPr=CH<sub>2</sub> (64 mg, 0.16 mmol) was added 10 mL of toluene to give a pale yellow solution that was stirred overnight at room temperature. Removal of the volatiles from the reaction mixture gave a white solid (137 mg, 84%) which was then recrystallized from a THF/hexanes mixture at  $-35 \,^{\circ}$ C to afford **4** as colorless blocks suitable for X-ray crystallography. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -0.14 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.02 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.90 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.03 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.09 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.13 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 2.15 (s, 2H, IPrCH<sub>2</sub>-), 2.46 (septet, 4H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.05 (septet, 2H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.13 (septet, 2H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 6.90 (d, 4H, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, ArH), 7.04 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, ArH), 7.07 (s, 1H, N=CH-N), 7.11 (d, 4H, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz,

Table 1			
Crystallographic	data fo	or compo	unds <b>1–4</b>

	1	2	<b>3</b> <sup>b</sup>	<b>4</b> ·3THF
Empirical formula	C <sub>37</sub> H <sub>55</sub> F <sub>3</sub> N <sub>2</sub> O <sub>3</sub> SSi <sub>2</sub>	C <sub>35</sub> H <sub>65</sub> N <sub>3</sub> Si <sub>4</sub>	C <sub>41</sub> H <sub>65</sub> N <sub>3</sub> Si <sub>2</sub>	C <sub>70</sub> H <sub>109</sub> F <sub>3</sub> N <sub>4</sub> O <sub>6</sub> SSi <sub>2</sub>
fw	721.07	640.26	656.14	1247.85
Cryst. dimens. (mm <sup>3</sup> )	$0.41 \times 0.17 \times 0.10$	$0.47\times0.32\times0.20$	$0.42 \times 0.16 \times 0.10$	$0.22 \times 0.19 \times 0.04$
Cryst. syst.	Triclinic	Triclinic	Orthorhombic	Monoclinic
Space group	P1	P1	Pca2 <sub>1</sub>	$P2_1/c$
Unit cell dimensions				
a (Å)	12.0453(6)	12.608(2)	21.2311(3)	22.8618(4)
b (Å)	12.9148(6)	12.784(3)	19.8205(3)	15.9609(3)
<i>c</i> (Å)	14.8650(7)	13.411(3)	19.3515(3)	20.8615(4)
α (°)	107.5129(6)	85.364(2)	90	90
β(°)	90.7948(6)	74.799(2)	90	98.9915(9)
γ (°)	113.3687(5)	73.697(2)	90	90
V (Å <sup>3</sup> )	2000.79(17)	2002.2(7)	8143.3(2)	7518.7(2)
Ζ	2	2	8	4
ho (g cm <sup>-3</sup> )	1.197	1.062	1.070	1.102
Abs. coeff. (mm <sup>-1</sup> )	0.190	0.174	1.001	1.132
T (K)	173(1)	173(1)	173(1)	173(1)
$2\theta_{\max}$ (°)	55.10	53.00	140.10	135.98
Total data	17873	16260	53094	49,007
Unique data (R <sub>int</sub> )	9151 (0.0256)	8274 (0.0276)	15096 (0.0317)	13,063 (0.0420)
Obs. data $[I > 2\sigma(I)]$	6856	6141	14,242	10,225
Params	490	389	838	809
$R_1 \left[ I > 2\sigma(I) \right]^{\mathrm{a}}$	0.0474	0.0492	0.0431	0.0883
$wR_2$ [all data] <sup>a</sup>	0.1382	0.1509	0.1230	0.2456
Max/min $\Delta \rho$ (e <sup>-</sup> Å <sup>-3</sup> )	0.488/-0.487	0.539/-0.444	0.784/-0.267	0.377/-0.390

<sup>a</sup>  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; wR_2 = [\Sigma w (F_o^2 - F_c^2)_2 / \Sigma w (F_o^4)]^{1/2}.$ 

<sup>b</sup> Flack parameter = 0.264(17).

Ar*H*), 7.23 (t, 2H,  ${}^{3}J_{HH} = 8.0$  Hz, Ar*H*), 8.40 (s, 2H, N–CH– in IPrCH<sub>2</sub>).  ${}^{13}C{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>, peak assignment based on gHSQC and  ${}^{13}C{}^{1}H{}$ DEPT experiments):  $\delta$  –2.6 (coincidental Si(CH<sub>3</sub>)<sub>2</sub> groups), 14.4 (IPrCH<sub>2</sub>–), 22.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 123.5 (–N–CH– in IPrCH<sub>2</sub>), 124.3 (ArC), 124.4 (ArC), 125.9 (ArC), 127.2 (ArC), 130.4 (ArC), 132.7 (ArC), 137.1 (ArC), 140.3 (ArC), 145.6 (ArC), 147.4 (ArC), 150.2 (ArC), 157.4 (N=CH–N).  ${}^{19}F{}^{1}H{}$ NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  –77.5 (s, –CF<sub>3</sub>). Mp (°C): 193–195. Anal. Calcd. for C<sub>58</sub>H<sub>85</sub>F<sub>3</sub>N<sub>4</sub>O<sub>3</sub>SSi<sub>2</sub>: C, 67.53; H, 8.31; N, 5.43; S, 3.11. Found: C, 67.10; H, 8.24; N, 5.22; S, 2.68.

#### 4.3.5. $[(^{t}BuO)SiMe_{2}SiMe_{2}N(Dipp)C(H)=NDipp](5)$

To a mixture of **1** (100 mg, 0.158 mmol) and K[O<sup>t</sup>Bu] (18 mg, 0.161 mmol) was added 6 mL of THF. The reaction mixture was stirred overnight at room temperature to give a clear solution. Removal of the volatiles from the resulting solution afforded a white solid, which was then extracted with 6 mL of toluene and filtered through Celite to obtain a colorless filtrate. Removal of the volatiles from the filtrate yielded **5** as a white solid. Yield: 94 mg, 90%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.43 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.55 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 1.10 (d, 6H,  ${}^{3}J_{\text{HH}} = 7.0$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.17 (s, 9H, OC(CH<sub>3</sub>)<sub>3</sub>), 1.26 (d, 9H,  ${}^{3}J_{\text{HH}} = 7.0 \text{ Hz CH}(CH_{3})_{2}), 1.27 \text{ (d, 9H, } {}^{3}J_{\text{HH}} = 7.0 \text{ Hz, CH}(CH_{3})_{2}), 3.51$ (septet, 4H,  ${}^{3}J_{HH} = 7.0$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 7.02–7.17 (m, 6H, ArH), 7.32 (s, 1H, N=CH-N). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -1.8 (Si(CH<sub>3</sub>)<sub>2</sub>), 3.8 (Si(CH<sub>3</sub>)<sub>2</sub>), 23.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.9 (OC(CH<sub>3</sub>)<sub>3</sub>), 28.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 32.3 (OC(CH<sub>3</sub>)<sub>3</sub>), 123.4 (ArC), 123.5 (ArC), 124.2 (ArC), 127.9 (ArC), 128.1 (ArC), 128.3 (ArC), 140.6 (ArC), 147.8 (ArC), 157.1 (N=CH-N). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -8.4 (s, Si(CH<sub>3</sub>)<sub>2</sub>), 3.5 (s, Si(CH<sub>3</sub>)<sub>2</sub>). Mp (°C): 96–98. Anal. Calcd. for C<sub>35</sub>H<sub>65</sub>N<sub>3</sub>Si<sub>4</sub>: C, 71.68; H, 10.21; N, 5.07. Found: C, 71.94; H, 10.18; N, 5.38.

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#### Appendix A. Supplementary material

CCDC 931778–931782, NMR spectra for all reported compounds (1–5) along with crystallographic details for **6**, X-ray data (compounds 1–4 and **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac. uk/data\_request/cif.

#### Appendix B. Supplementary material

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.04.029.

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- Occasionally during the synthesis of 5, single crystals of a byproduct [17] DippN=CHN(Dipp)-SiMe<sub>2</sub>SiMe<sub>2</sub>-N(Dipp)CH=NDipp **6** could be isolated from the reaction mixture (few mg). This product was identified by X-ray crystallography (see Fig. S6 and Table S1 in the Supporting information) however attempts to directly prepare **6** via the reaction of Li[(Dipp) NC(H)=NDipp] [5a] with 1 yielded no discernable reaction; thus at this time we are unsure how trace quantities of 6 are formed during the synthesis of 5.
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