

Note

# The stable silylene $\text{Si}[(\text{NCH}_2\text{Bu}^t)_2\text{C}_6\text{H}_4-1,2]$ : Reactions with Group 14 element halides

Barbara Gehrhus\*, Peter B. Hitchcock, Helen Jansen

Department of Chemistry, School of Life Sciences, University of Sussex, Brighton BN1 9QJ, UK

Received 24 September 2005; received in revised form 15 October 2005; accepted 15 October 2005

Available online 29 November 2005

## Abstract

Reaction of the thermally stable silylene  $\text{Si}[(\text{NCH}_2\text{Bu}^t)_2\text{C}_6\text{H}_4-1,2]$  (**1**) [abbrev. as  $\text{Si}(\text{NN})$ ] with  $\text{SiX}_4$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) afforded the disilanes  $(\text{NN})\text{SiX}(\text{SiX}_3)$  and  $[(\text{NN})\text{SiX}]_2$  ( $\text{X} = \text{Br}$  only), the trisilane  $(\text{NN})\text{SiX}-(\text{SiX}_3)\text{Si}(\text{NN})$  and the monosilane  $(\text{NN})\text{SiX}_2$  ( $\text{X} = \text{Br}$  only), whereas treatment of **1** with  $\text{MCl}_4$  ( $\text{M} = \text{Ge}$  or  $\text{Sn}$ ) yielded  $(\text{NN})\text{SiCl}_2$  and  $\text{MCl}_2$ .  $[(\text{NN})\text{SiBr}]_2$  and  $(\text{NN})\text{SiBr}_2$  were also obtained by reaction of **1** with  $\text{Br}_2$ . Reaction of **1** with  $\text{PhSiCl}_3$  yielded the disilane  $(\text{NN})\text{SiCl}(\text{SiCl}_2\text{Ph})$  and trisilane  $[(\text{NN})\text{SiCl}]_2\text{SiClPh}$ , whereas the disilane  $(\text{NN})\text{SiCl}(\text{SiCl}_2\text{Me})$  was obtained with  $\text{MeSiCl}_3$ . The trisilane  $(\text{NN})\text{SiCl}-(\text{SiCl}_3)\text{Si}(\text{NN})$  was thermally labile and converted to  $[(\text{NN})\text{SiCl}]_2\text{SiCl}_2$ .

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**Keywords:** Silylene; Insertion; Group 14 halides; Disilane; Trisilane

## 1. Introduction

The chemistry of stable silylenes is now well established [1–3]. In recent years stable silylenes have been shown to extend the scope of insertion reactions of transient silylenes, including insertions into  $\text{M}-\text{N}$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) [4,5],  $\text{Li}-\text{C}$  [6],  $\text{Li}-\text{Si}$  [4],  $\text{B}-\text{C}$  [7],  $\text{C}-\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) [3,8,9],  $\text{M}(\text{II})-\text{N}$  ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ ) [10–13],  $\text{Sn}(\text{II})-\text{C}$  [14],  $\text{Sn}(\text{II})-\text{Cl}$  [15],  $\text{O}-\text{H}$  [16,17], and  $\text{Si}-\text{Cl}$  [18] bonds. The silylene  $\text{Si}[(\text{NCH}_2\text{Bu}^t)_2\text{C}_6\text{H}_4-1,2]$  [19] **1** [abbr.  $\text{Si}(\text{NN})$ ] also inserted into the  $\text{M}-\text{Cl}$  bond of  $[\text{MCl}_2(\text{PPh}_3)_2]$ , concomitant with  $\text{PPh}_3$  ligand replacement, leading to  $\text{trans}-[\text{M}\{\text{Si}(\text{NN})\}_2\{\text{Si}(\text{NN})\text{Cl}\}_2]$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) [20].

Reactions of stable silylenes with compounds containing a Group 14 element-halogen bond include the insertion into a  $\text{Si}-\text{Cl}$  [18] or  $\text{Sn}(\text{II})-\text{Cl}$  [15] bond (Scheme 1).

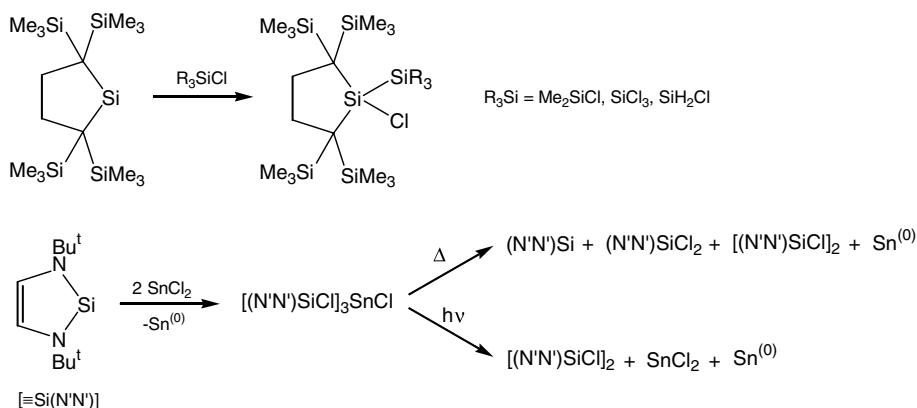
## 2. Results and discussion

The reaction of the silylene  $\text{Si}[(\text{NCH}_2\text{Bu}^t)_2\text{C}_6\text{H}_4-1,2]$  (**1**) [abbr. as  $\text{Si}(\text{NN})$ ] with  $\text{SiCl}_4$  proceeded under mild conditions and yielded as the main product the trisilane **2**, irrespective of the relative molar ratio of the reactants. Furthermore, in an NMR spectroscopic experiment, **1** was treated with an excess of  $\text{SiCl}_4$ ; the reaction mixture showed as the major component compound **2** but also of another product assigned as compound **3** on the basis of the  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectral data (Scheme 2). The trisilane **2** was thermally labile, being converted into the trisilane **4** upon heating.

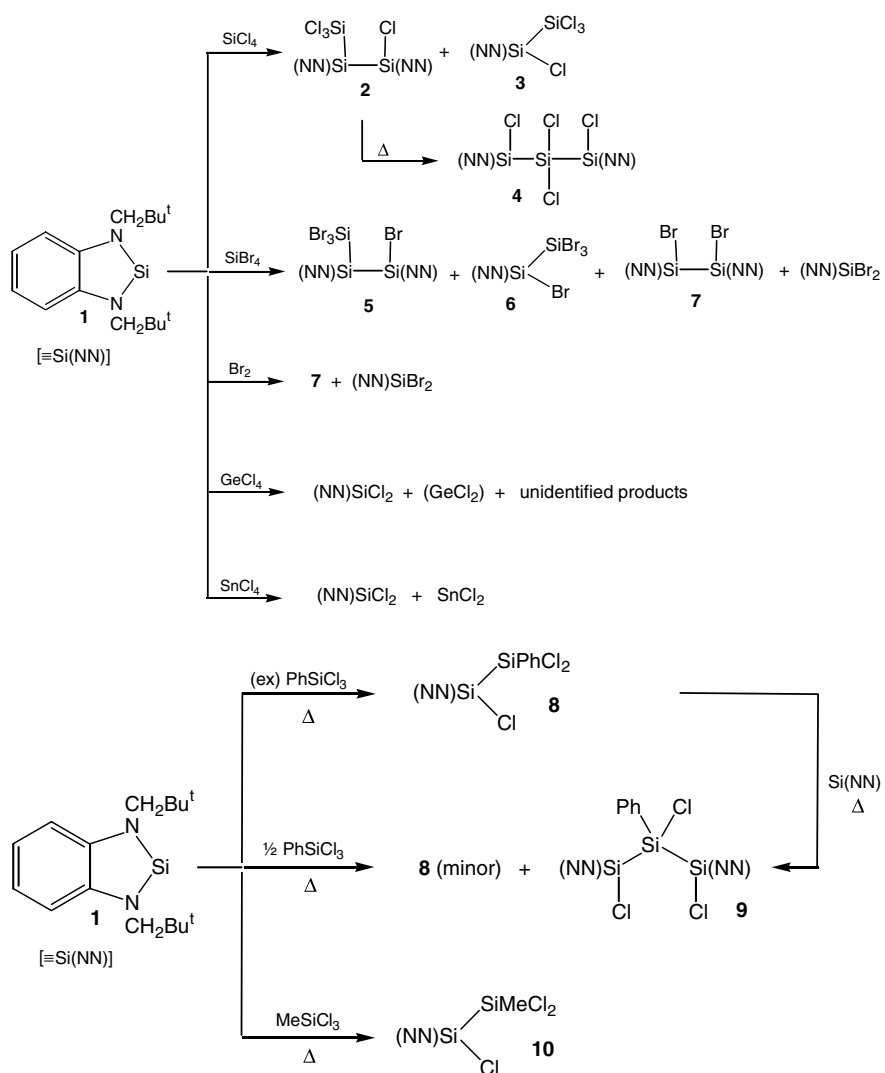
Treatment of a solution of **1** in  $\text{C}_6\text{D}_6$  with an excess of  $\text{SiBr}_4$  (NMR experiment) afforded a product mixture of the trisilane **5**, the disilanes **6** and **7** and the silane  $(\text{NN})\text{SiBr}_2$  in a ratio 1.5:2.1:1.0:2.2, respectively (Scheme 2). Alternatively, when a solution of **1** was slowly added to an excess of  $\text{SiBr}_4$  the ratio of **5**:**6**:**7**: $(\text{NN})\text{SiBr}_2$  was 1.7:1.1:1:5.5. Additionally, a  $^{29}\text{Si}$  NMR spectral signal at  $\delta -35.7$  showed the presence of  $(\text{SiBr}_3)_2$  [21]. Compound **5** was independently obtained by reaction of **1** with 1/2

\* Corresponding author.

E-mail address: [b.gehrhus@sussex.ac.uk](mailto:b.gehrhus@sussex.ac.uk) (B. Gehrhus).



Scheme 1.



Scheme 2.

an equivalent of  $\text{SiBr}_4$ . Compounds **7** and  $(\text{NN})\text{SiBr}_2$  were identified by comparison of spectral data with those of the products from the reaction of **1** with bromine (Scheme 2).

Reaction of **1** with the heavier Group 14 metal chlorides  $\text{MCl}_4$  ( $\text{M} = \text{Ge}$  or  $\text{Sn}$ ) afforded as the major compound the

dichlorosilane  $(\text{NN})\text{SiCl}_2$  [19] and a precipitate which from  $\text{GeCl}_4$  is believed to have been  $\text{GeCl}_2$  by analogy with the formation of  $\text{SnCl}_2$  in the reaction of **1** with  $\text{SnCl}_4$  (Scheme 2).

Reaction of **1** with the chlorosilane  $\text{PhSiCl}_3$  or  $\text{MeSiCl}_3$  (Scheme 2) needed more vigorous conditions. Thus, the

disilane **8** or the trisilane **9** were formed at 100 °C over a period of two days. The formation of **8** or **9** was dependent on the relative ratios of the reactants. Silylene **1** gave **8** with an excess of PhSiCl<sub>3</sub>, but compound **9** was the major product from **2**(**1**) + PhSiCl<sub>3</sub>. Additionally, it was shown that **8** is a precursor for **9** in the reaction of **8** with **1**. The reaction of **1** with MeSiCl<sub>3</sub> afforded the disilane **10**. Attempted purification of **10** by distillation led to its partial decomposition to H(Cl)Si[(NCH<sub>2</sub>Bu')<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-1,2] **10a**. No reaction was observed between **1** and Me<sub>3</sub>SiCl.

Compounds **2–10** have been fully characterised by multinuclear NMR spectroscopy. The structure of **2** was also confirmed by X-ray structural analysis (Fig. 1). Viewing the molecule along the Si–Si bond shows the Cl and SiCl<sub>3</sub>

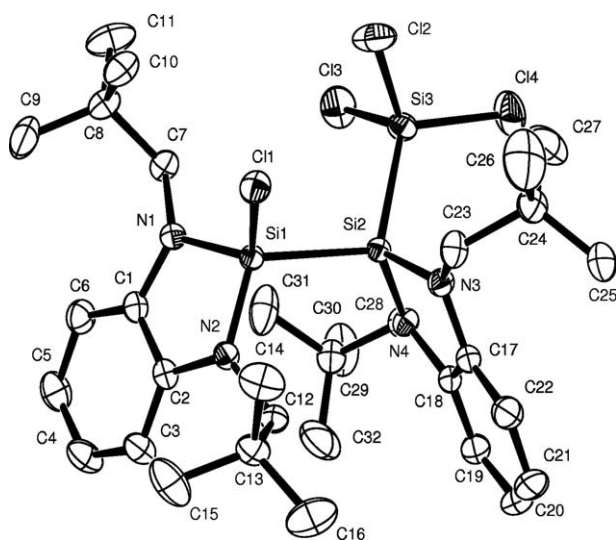


Fig. 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Si(1)–Si(2) 2.4025(6), Si(2)–Si(3) 2.3817(6), N(1)–Si(1)–N(2) 94.00(6), N(4)–Si(2)–N(3) 93.46(6).

substituents in a gauche relationship. The Si(1)–Si(2) [2.4025(6) Å] is slightly longer than the Si(2)–Si(3) [2.3817(6) Å] bond; these data may be compared with the Si–Si bonds in related (NN)Si(R<sup>1</sup>)–(R<sup>2</sup>)Si(NN) compounds {R<sup>1</sup> = R<sup>2</sup> = Bu<sup>t</sup> 2.465(7) Å [6]; R<sup>1</sup> = Cl, R<sup>2</sup> = Pr 2.3652(7) Å [9]; R<sup>1</sup> = Cl, R<sup>2</sup> = CH<sub>2</sub>Cl 2.362(2) Å [9]}.

The formation of the disilanes **2** and **5** is believed to proceed by a similar radical pathway that led to the disilanes (NN)Si(X)–(R)Si(NN) (X = Cl or Br, R = alkyl) from **1** and an alkyl halide [3,9]. Scheme 3 shows this pathway, adapted from the proposal by McKee et al. [22] for the reaction of a bis(amino)silylene with an alkyl halide.

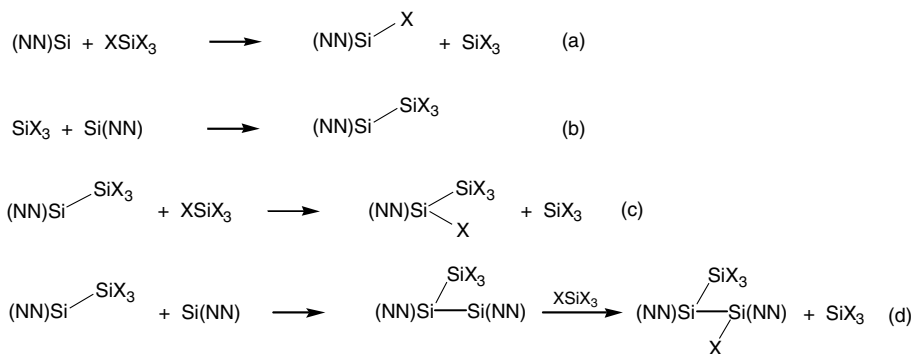
The formation of **7** and (SiBr<sub>3</sub>)<sub>2</sub> can be explained by dimerisation of the (NN)Si(Br) and the SiBr<sub>3</sub> radical generated in path (a), (c) or (d), respectively, in Scheme 3. (NN)SiBr<sub>2</sub> is proposed to form by the halogen abstraction of (NN)Si(Br) from SiBr<sub>4</sub>.

The pathway to the trisilane **4** is believed to proceed by extrusion of **1** from **2** ( $\alpha$ -elimination [23,24]) and concomitant insertion of **1** into the Si–Cl bond of the intermediate (NN)Si(Cl)–SiCl<sub>3</sub> (Scheme 4). Similar silylene extrusions were observed when the disilanes (NN)Si(X)–(R)Si(NN) (X = Cl or Br, R = alkyl) where heated [9].

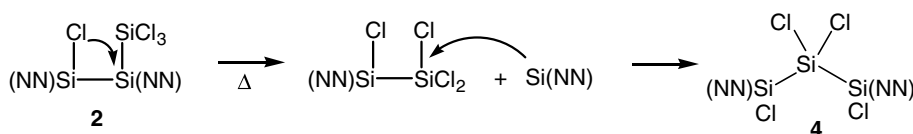
### 3. Experimental

#### 3.1. General procedures

All operations and manipulations were carried out under purified argon, by conventional Schlenk techniques. Solvents were dried and degassed before use. Microanalyses were carried out at the University of North London. The NMR spectra were recorded (at 298 K) using Bruker instruments: Bruker DPX 300 [<sup>1</sup>H (300.13 MHz), <sup>13</sup>C (75.42 MHz)] and AMX 500 [<sup>29</sup>Si (99.36 MHz), <sup>119</sup>Sn]



Scheme 3.



Scheme 4.

and referenced internally to residual solvent resonances, or externally for  $^{29}\text{Si}$  and  $^{119}\text{Sn}$  and referenced to  $\text{SiMe}_4$  and  $\text{SnMe}_4$ , respectively (data in  $\delta$ ). Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected.

### 3.2. Reaction of **1** with $\text{SiCl}_4$

In an NMR spectroscopic experiment, a solution of **1** in  $\text{C}_6\text{D}_6$  was treated with an excess of  $\text{SiCl}_4$ . The resulting mixture was shown to consist of **2** and **3** in a ratio 2.3:1.  $^1\text{H}$  NMR for **3**:  $\delta$  0.95 (s, 18H,  $\text{Bu}^t$ ), 3.24, 3.26, 3.28 and 3.3 (AB-type, 4H,  $\text{CH}_2$ ), 6.68–6.80 (m, together with signals of **2**, phenyl).  $^{29}\text{Si}$  NMR:  $\delta$  –20.1 (SiN) and –4.4 (SiCl).

### 3.3. $[1,2\text{-C}_6\text{H}_4(\text{NCH}_2\text{Bu}^t)_2]\text{Si}(\text{SiCl}_3)\text{-Si}(\text{Cl})\text{-}[(\text{NCH}_2\text{Bu}^t)_2\text{C}_6\text{H}_4\text{-}1,2]$ (**2**)

$\text{SiCl}_4$  (1.25 ml, 10.94 mmol) was added to a solution of the silylene **1** (1.00 g, 3.65 mmol) in hexane (40 ml). The mixture was stirred for 16 h. The solvent was removed in vacuo and the resulting solid was extracted into hexane. The extract was filtered and cooled at  $-25^\circ\text{C}$  yielding yellow crystals of **2** (1 g, 76%) (Found: C, 53.7; H, 7.38; N, 7.73%.  $\text{C}_{32}\text{H}_{52}\text{Cl}_4\text{N}_4\text{Si}_3$ : requires C, 53.5; H, 7.29; N, 7.80%), m.p. 173–175  $^\circ\text{C}$ .

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.85 (s, 18H,  $\text{CH}_3$ ) 0.96 (s, 18H,  $\text{CH}_3$ ), 2.99, 3.02, 3.11 and 3.14 (AB-type, 4H,  $\text{CH}_2$ ), 3.24, 3.27, 3.33 and 3.36 (AB-type, 4H,  $\text{CH}_2$ ), 6.68–6.80 (m, 8H, phenyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  29.2 ( $\text{CMe}_3$ ), 29.6 ( $\text{CMe}_3$ ), 33.9 ( $\text{CMe}_3$ ), 34.1 ( $\text{CMe}_3$ ), 55.5 ( $\text{CH}_2$ ), 56.5 ( $\text{CH}_2$ ), 110.7, 111.7, 118.7, 119.1, 140.2 and 141.1 (phenyl).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  –17.3 (SiCl), –14.2 (SiN) and –2.8 (SiN). EIMS;  $m/z = 718$  ( $[\text{M}]^+$ , 20%), 583 ( $[\text{M} - \text{SiCl}_3]^+$ , 14%). X-ray suitable crystals were grown at room temperature from a concentrated hexane solution.

### 3.4. $[1,2\text{-C}_6\text{H}_4(\text{NCH}_2\text{Bu}^t)_2]\text{Si}_2\text{SiCl}_2$ (**4**)

A sample of **2** was heated in  $\text{C}_6\text{D}_6$  in a sealed NMR tube at  $100^\circ\text{C}$  for 16 h. NMR spectroscopic analysis revealed the complete rearrangement to compound **4**. Alternatively, a solution of **2** (0.36 g, 0.42 mmol) in toluene (5 ml) was refluxed for 2 days. The solvent was removed in vacuo and the residue was crystallised from hexane to afford **4** as a yellow solid (0.26 g, 87%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.87 (s, 36H,  $\text{CH}_3$ ), 3.02 (br, s, 8H,  $\text{CH}_2$ ), 6.60–6.63 and 6.69–6.73 (m, 8H, phenyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  29.4 ( $\text{CMe}_3$ ), 33.9 ( $\text{CMe}_3$ ), 55.8 ( $\text{CH}_2$ ), 110.9, 119.1 and 140.1 (phenyl).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  –14.2 (SiN) and –10.0 (SiCl). EIMS;  $m/z = 718$  ( $[\text{M}]^+$ , 43%).

### 3.5. Reaction of **1** with $\text{SiBr}_4$

In an NMR spectroscopic experiment, a solution of **1** in  $\text{C}_6\text{D}_6$  was treated with an excess of  $\text{SiBr}_4$ . The mixture was

shown to consist of **5**, **6**, **7** and (NN) $\text{SiBr}_2$  in a ratio 1.5:2.1:1.0:2.2. Alternatively, a solution of **1** (0.59 g, 2.15 mmol) in benzene (20 ml) was slowly added to a solution of  $\text{SiBr}_4$  (1.3 ml, 10.76 mmol) in benzene (10 ml). The mixture was stirred for 16 h and then a sample was taken for NMR spectral analysis. The mixture contained **5**, **6**, **7** and (NN) $\text{SiBr}_2$  in a ratio 1.7:1.1:1:5.5, and  $(\text{SiBr}_3)_2$  [21]. Signals assigned to **6**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.0 (s, 18H,  $\text{CH}_3$ ), 3.15 (br. s, 4H,  $\text{CH}_2$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR:  $\delta$  –26.5 (SiBr) and –20.0 (SiN). Signal assignment could not be verified by independent synthesis. For NMR spectral assignments of **5**, **7** and (NN) $\text{SiBr}_2$ , see below.

### 3.6. Reaction of **1** with $\text{Br}_2$

In an NMR spectroscopic experiment, a solution of **1** in  $\text{C}_6\text{D}_6$  was treated with an excess of  $\text{Br}_2$ . The mixture was shown to consist of **7** and (NN) $\text{SiBr}_2$  in a ratio 1.5:1.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) of **7**:  $\delta$  0.84 (s, 18H,  $\text{Bu}^t$ ), 3.05, 3.08, 3.11 and 3.14 (AB-type, 4H,  $\text{CH}_2$ ) and 6.71–6.98 (m, together with signals for (NN) $\text{SiBr}_2$ , phenyl).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ) of **7**:  $\delta$  –23.5.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) of (NN) $\text{SiBr}_2$ :  $\delta$  0.97 (s, 18H,  $\text{Bu}^t$ ), 3.22 (s, 4H,  $\text{CH}_2$ ) and 6.71–6.98 (m, together with signals for **7**, phenyl).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ) of (NN) $\text{SiBr}_2$ :  $\delta$  –40.8.

### 3.7. $[1,2\text{-C}_6\text{H}_4(\text{NCH}_2\text{Bu}^t)_2]\text{Si}(\text{SiBr}_3)\text{-Si}(\text{Br})[(\text{NCH}_2\text{Bu}^t)_2\text{C}_6\text{H}_4\text{-}1,2]$ (**5**)

$\text{SiBr}_4$  (0.14 ml, 1.09 mmol) was added to a solution of **1** (0.6 g, 2.19 mmol) in hexane (40 ml) and stirred for 16 h. The solvent was removed in vacuo yielding **5** as a yellow viscous oil, which was contaminated with traces of (NN) $\text{SiBr}_2$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.98 (br. s, 36H,  $\text{Bu}^t$ ), 3.14, 3.19, 3.26 and 3.30 (AB-type, 4H,  $\text{CH}_2$ ), 3.31, 3.35, 3.41 and 3.46 (AB-type, 4H,  $\text{CH}_2$ ) and 6.72–6.82 (m, 8H, phenyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  29.6 and 29.8 ( $\text{CMe}_3$ ), 34.0 ( $\text{CMe}_3$ ), 55.6 and 55.9 ( $\text{CH}_2$ ), 111.1, 111.4, 119.1, 119.5, 139.6 and 140.2 (phenyl).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  –30.8 (SiBr), –27.9 (SiN) and –21.4 (SiN).

### 3.8. Reaction of **1** with $\text{GeCl}_4$

A solution of **1** (0.27 g, 0.98 mmol) in hexane (20 ml) was slowly added to a solution of  $\text{GeCl}_4$  (0.34 ml, 2.95 mmol) in hexane (20 ml) at  $-78^\circ\text{C}$ . The mixture was allowed to come to ambient temperature and was stirred for 16 h during which a pale yellow precipitate had formed. An  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) spectral sample was taken from the reaction mixture and showed major signals corresponding to (NN) $\text{SiCl}_2$  [19], accompanied by unidentified products.

### 3.9. Reaction of **1** with $\text{SnCl}_4$

A solution of **1** (0.3 g, 1.09 mmol) in hexane (20 ml) was slowly added to a solution of  $\text{SnCl}_4$  (0.64 ml, 5.47 mmol) in hexane (20 ml). The mixture was stirred for 16 h during

which time a pale green precipitate had formed. The mixture was filtered and the remaining solid was dried in vacuo. A signal at  $\delta$  [ $^{119}\text{Sn}\{^1\text{H}\}$ ]  $-211$  (THF/ $\text{C}_6\text{D}_6$ ) confirmed the formation of  $\text{SnCl}_2$  (independently verified by  $^{119}\text{Sn}\{^1\text{H}\}$  NMR analysis of a sample of  $\text{SnCl}_2$  in THF/ $\text{C}_6\text{D}_6$ ). All volatiles were removed from the filtrate in vacuo resulting in a pale yellow oil which was confirmed to be (NN) $\text{SiCl}_2$  by  $^1\text{H}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectroscopy [19].

### 3.10. $[1,2\text{-C}_6\text{H}_4(\text{NCH}_2\text{Bu}^t)_2]\text{Si}(\text{Cl})\text{Si}(\text{Ph})\text{Cl}_2$ (**8**)

Silylene **1** (0.42 g, 1.53 mmol) was dissolved in  $\text{PhSiCl}_3$  (5 ml, 31.2 mmol) and the solution was heated at  $100^\circ\text{C}$  for two days. The excess  $\text{PhSiCl}_3$  was removed in vacuo ( $10^{-3}$  Torr,  $80^\circ\text{C}$ ) yielding a yellow, highly viscous oil, which was identified as compound **8**.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.87 (s, 18H,  $\text{Bu}^t$ ), 3.17, 3.23, 3.26 and 3.31 (AB-type, 4H,  $\text{CH}_2$ ), 6.81–6.86 (m, 4H, phenyl), 7.00–7.02 (m, 3H, phenyl), 7.71–7.74 (m, 2H, phenyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  29.2 ( $\text{CMe}_3$ ), 33.8 ( $\text{CMe}_3$ ), 55.9 ( $\text{CH}_2$ ), 111.0, 119.1, 128.9, 132.3, 133.1, 134.2 and 140.1 (phenyl).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-15.9$  and  $-1.4$  ( $\text{SiPhCl}_2$ ). EIMS;  $m/z = 486$  ( $[\text{M}]^+$ , 20%).

### 3.11. $[\{1,2\text{-C}_6\text{H}_4(\text{NCH}_2\text{Bu}^t)_2\}\text{Si}_2]\text{Si}(\text{Ph})\text{Cl}$ (**9**)

A mixture of **1** and  $\text{PhSiCl}_3$  in a ratio 2:1 was heated in  $\text{C}_6\text{D}_6$  in a sealed NMR tube at  $100^\circ\text{C}$  for two days. NMR spectroscopic analysis revealed the presence of compound **9** and small amounts of **8**.  $^1\text{H}$  NMR for **9**:  $\delta$  0.80 (s, 18H,  $\text{Bu}^t$ ),  $\delta$  0.97 (s, 18H,  $\text{Bu}^t$ ), 2.86, 3.91, 3.02 and 3.07 (AB-type, 4H,  $\text{CH}_2$ ), 3.20, 3.25, 3.28 and 3.33 (AB-type, 4H,  $\text{CH}_2$ ), 6.71–6.74 (m, 2H, phenyl), 6.74–6.84 (m, 6H, phenyl), 6.94–7.01 (m, 3H, phenyl), 7.64–7.67 (m, 2H, phenyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR for **9**:  $\delta$  29.2 ( $\text{CMe}_3$ ), 29.5 ( $\text{CMe}_3$ ), 33.7 ( $\text{CMe}_3$ ), 33.9 ( $\text{CMe}_3$ ), 56.0 ( $\text{CH}_2$ ), 56.2 ( $\text{CH}_2$ ), 110.6, 110.8, 118.9, 128.7, 128.9, 131.4, 133.2, 135.2, 140.4 and 140.8 (phenyl).  $^{29}\text{Si}\{^1\text{H}\}$  NMR for **9**:  $\delta$   $-24.2$  ( $\text{SiClPh}$ ) and  $-8.7$  ( $\text{SiN}$ ). Alternatively, a mixture of **8** and excess of **1** was heated in  $\text{C}_6\text{D}_6$  in a sealed NMR spectral tube at  $100^\circ\text{C}$  for two days. The spectrum revealed the presence of compound **9** together with small amounts of unreacted **8** and **1**.

### 3.12. $[1,2\text{-C}_6\text{H}_4(\text{NCH}_2\text{Bu}^t)_2]\text{Si}(\text{Cl})\text{Si}(\text{Me})\text{Cl}_2$ (**10**) and $[1,2\text{-C}_6\text{H}_4(\text{NCH}_2\text{Bu}^t)_2]\text{Si}(\text{Cl})\text{H}$ (**10a**)

$\text{MeSiCl}_3$  (1.43 ml, 12.22 mmol) was added to a solution of **1** (0.66 g, 2.44 mmol) in benzene (20 ml). The mixture was heated at reflux for 2 days. All volatiles were removed in vacuo yielding **10** as a yellow oil. Attempted purification by distillation led to its partial decomposition affording a 2:1 mixture of **10** and **10a**.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) of **10**:  $\delta$  0.70 (s, 3H,  $\text{CH}_3$ ), 0.95 (s, 18H,  $\text{Bu}^t$ ), 3.30 (br. s, 4H,  $\text{CH}_2$ ), 6.82–6.88 (m, 4H, phenyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ) of **10**:  $\delta$  8.3 ( $\text{CH}_3$ ), 29.3 ( $\text{CMe}_3$ ), 33.9 ( $\text{CMe}_3$ ), 55.6 ( $\text{CH}_2$ ), 111.0, 119.1 and 139.9 (phenyl).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )

of **10**:  $\delta$   $-16.5$  and  $-14.2$  ( $\text{SiMeCl}_2$ ). EIMS;  $m/z = 424$  ( $[\text{M}]^+$ , 30%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) of **10a**:  $\delta$  0.87 (s, 18H,  $\text{Bu}^t$ ), 3.08 (s, 4H,  $\text{CH}_2$ ), 6.42 (s, 1H, SiH), 6.79–6.81 (m, 4H, phenyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ) of **10a**:  $\delta$  28.4 ( $\text{CMe}_3$ ), 34.0 ( $\text{CMe}_3$ ), 54.5 ( $\text{CH}_2$ ), 109.8, 118.7 and 131.9 (phenyl).  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ) of **10a**:  $\delta$   $-19.7$  (d,  $^2J(\text{H},\text{Si}) = 318$  Hz).

### 3.13. X-ray structure determination for complex **2**

Data for the crystal structure determination were collected on a Kappa CCD diffractometer at 173(2) K using monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda$  0.71073 Å). The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  using SHELXL 97 [25], with all non-H atoms anisotropic. Crystal data and refinement details for  $\text{C}_{32}\text{H}_{52}\text{Cl}_4\text{N}_4\text{Si}_3$ :  $M_r$  718.85, orthorhombic, space group  $P2_12_12_1$  (No. 19),  $a = 9.7274(1)$ ,  $b = 18.8759(2)$ ,  $c = 20.7539(3)$  Å,  $U = 3810.69(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu = 0.43$  mm<sup>-1</sup>, 6914 unique reflections collected,  $R_1 = 0.023$  for 6720 reflections with  $I > 2\sigma(I)$ ,  $wR_2 = 0.057$  for all reflections.

## 4. Supplemental material

Crystallographic data for the structural analysis for compound **2** have been deposited with the Cambridge Crystallographic Data centre, CCDC No. 284464. 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>).

## Acknowledgements

We thank the EPSRC for the award of an Advanced Fellowship for B.G. and the Free University of Amsterdam for support for H.J.

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