Novel pentacoordinate silicon compounds bearing [Si-N-C-N-C-N] chelate ring derived from biguanide ligands

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Abstract

The reactions between secondary carbosilanes **1**–**3** and 1-propylbiguanide/1-phenylbiguanide, H_6bigR proceed via SiH/NH dehydrocoupling and afford 1,4-bis(silyl)-5-propyl/phenylbiguanides with the general formula $(R^1R_2^2SiCH_2CH_2SiMeH)_2 \cdot H_4bigR$, [$R^1 = Ph$, $R^2 = Me$, $R = {}^nPr$ (**4**), $R = Ph$ (**5**); $R^1 = Me$, $R^2 = Ph$, $R = {}^nPr$ (**6**), $R^1 = R^2 = Et$, $R = Ph$ (**7**)]. These compounds represent a new family of pentacoordinate silicon derivatives comprising of [Si-N-C-N-C-N] chelate ring and have been characterized by elemental analysis, FAB mass, IR and multinuclear (^1H, ^{13}C and ^{29}Si) NMR spectral studies.
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1. Introduction

Synthesis and structural studies of neutral pentacoordinate silicon compounds derived from ligands with strategically placed donor atoms (O, N and S) have received considerable attention in the past [1]. Major emphasis has been directed to understand the enhanced reactivity of these compounds towards nucleophiles and also their role in the mechanistic interpretation of nucleophilic substitution reactions at tetracoordinate silicon centers [1a,1b,1c]. While the majority of such compounds possess five- and six-membered chelate rings, a few reports on related hypercoordinate silicon derivatives containing higher-membered cyclic rings have also appeared [2]. Reductive coupling of pentacoordinate chlorosubstituted silicon precursors containing 8-dimethylamino-1-naphthyl group with magnesium is known to afford neutral hypercoordinate silicon compounds containing Si–Si bonds [3]. Recently, Tanaka et al. [4] have reported the synthesis and X-ray structure of pentacoordinate silicon compounds involving tri-, tetra- and pentasilane framework. These

studies are of relevance to understand the effect of pentacoordinate silicon on the electronic attributes and conformational behavior in these oligomers.

We have been interested in the study of SiN bonded derivatives containing biguanide ligands, hereafter abbreviated as H_6bigR (Chart 1). Although these ligands [5] have been extensively used in the coordination chemistry of transition metals [6], their potential in the main group chemistry is confined to only a few reported examples of tetracoordinate boron heterocycles (Chart 1). These have been synthesized by the reactions of amino boranes/boronic acid with biguanide [7] and are found to be stable towards hydrolysis. It is generally believed that the electronic effects arising from π-delocalized framework of biguanide ligand impart unusual stability to the metal chelates. It is thus desired to utilize the chelation property as well as the underlying electronic attributes of these ligands in the preparation of novel SiN bonded compounds.

In literature, SiH/NH dehydrocoupling reactions of diorganosilanes, R_2SiH_2 (R = alkyl, aryl) with nitrogen bases such as ammonia, amines or hydrazines are known to proceed efficiently only under transition metal/F^- ion catalyzed conditions [8,9]. We have recently reported that biguanide ligands as nitrogen precursors undergo SiH/NH dehydrocoupling reactions with methylphenylsilane/diphenylsilane at moderate

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Chart 1.

temperature in the absence of any external catalyst [10,11]. In order to understand the role of biguanide ligands in these uncatalyzed reactions as well as other factors affecting SiH/NH dehydrocoupling, these studies have been extended to a few alkylsubstituted secondary silanes. The carbosilanes $R^1R_2^2SiCH_2CH_2SiMeH_2$ **1–3** bearing terminal –SiH$_2$ groups serve as alkyl analogs to secondary silanes and thus have been chosen as the precursors owing to their ease of preparation and handling at elevated temperatures. In the absence of any external catalyst these carbosilanes react with 1-propylbiguanide/1-phenylbiguanide by SiH/NH dehydrocoupling pathway to afford the corresponding 1,4-bis(silyl)-5-propyl/phenylbiguanides **4–7** (Scheme 1) comprising of novel six-membered [Si-N-C-N-C-N] chelate ring with pentacoordinate silicon atom. The results obtained are reported in this communication.

2. Results and discussion

The carbosilanes $R^1R_2^2SiCH_2CH_2SiMeH_2$ [$R^1 = Ph$, $R^2 = Me$ (**1**); $R^1 = Me$, $R^2 = Ph$ (**2**); $R^1 = R^2 = Et$ (**3**)] have been synthesized in two steps (Eq. (1)). The initial step involves hydrosilylation reaction between equimolar quantities of dichloromethylvinylsilane and the appropriate hydrosilane $R^1R_2^2SiH$ in presence of Karstedt's catalyst. Subsequent reaction of the resulting chlorocarbosilane with lithium aluminium hydride affords the corresponding carbosilane **1–3**, in ~70–75% yield. The carbosilane **3** is formed exclusively as the β-isomer, while **1** and **2** are isolated as a mixture of β-isomer (~95%) and minor amounts of α-isomer (~5%) as evident from HPLC data. Predominant formation of the β-isomer in these compounds is evident from ^1H and $^{13}C\{^1H\}$ DEPT-135 NMR spectra. ^{29}Si-NMR spectrum of compound **3** reveals two signals at δ 8.3 (s, Et$_3$Si) and -29.3 (t, SiMeH$_2$, $^1J_{SiH} = 189$ Hz) arising from the β-isomer. On the other hand, the presence of α- and β-isomeric mixture is discernable from $^{29}Si\{^1H\}$-NMR spectra of **1** and **2** (Section 3). The mass spectra (EI) reveal $[M - H]^+$ ion in each case. In addition, structurally significant ions are observed by the cleavage of SiC bonds and the relevant data are given in Section 3.

$$R^1R_2^2SiH + \text{(vinyl)}SiMeCl_2 \xrightarrow[\text{(ii) LiAlH}_4/ \text{Et}_2\text{O}]{\text{(i) Karstedt's catalyst}} R^1R_2^2SiCH_2CH_2SiMeH_2 + R^1R_2^2SiCH(CH_3)SiMeH_2$$

β – isomer   α – isomer

(major)   (minor)

$R^1 = Ph$, $R^2 = Me$ (**1**)

$R^1 = Me$, $R^2 = Ph$ (**2**)

$R^1 = R^2 = Et$ (**3**)

......equation 1

(1)

$R^1 = Ph$, $R^2 = Me$, $R = {}^nPr$ (**4**)

$R^1 = Ph$, $R^2 = Me$, $R = Ph$ (**5**)

$R^1 = Me$, $R^2 = Ph$, $R = {}^nPr$ (**6**)

$R^1 = R^2 = Et$, $R = Ph$ (**7**)

Scheme 1.

2.1. Reactions of the carbosilanes 1–3 with 1-propylbiguanide/1-phenylbiguanide- synthesis of 1,4-bis(silyl)-5-propyl/phenylbiguanides, 4–7

SiH/NH dehydrocoupling reactions between the carbosilanes 1–3 and biguanide ligands in a stoichiometric ratio of 2:1 in THF medium are extremely sluggish at room temperature. As evident from ^{1}H-NMR spectra of the reaction mixture at different time intervals, concentration of the SiH groups does not show a perceptible change with respect to the parent silane (δ 3.64–3.73). The unreacted silane was obtained in nearly quantitative yields after 96 h. However, at elevated temperatures (65–70 °C, 48 h) these reactions proceed efficiently in the absence of a catalyst to afford the corresponding 1,4-bis(silyl)-5-propyl/phenylbiguanides with the general formula $(R^1R_2^2SiCH_2CH_2SiMeH)_2 \cdot H_4bigR$, $[R^1 = Ph, R^2 = Me, R = {}^nPr$ (**4**), $R = Ph$ (**5**); $R^1 = Me, R^2 = Ph, R = {}^nPr$ (**6**), $R^1 = R^2 = Et, R = Ph$ (**7**)]. The silylbiguanides, thus isolated are hygroscopic, low melting solids and tend to decompose thermally above 100 °C. These compounds are soluble in common organic solvents such as CHCl$_3$, CH$_2$Cl$_2$, THF and DMSO.

All attempts to grow single crystals of **4**–**7** were unsuccessful. However, the structural identity of these compounds has been established by FAB mass, IR and multinuclear (^{1}H, ^{13}C, ^{29}Si) NMR studies. FAB mass spectra (3-nitrobenzylalcohol matrix) reveal the molecular ion peak, $[M]^+$ in each case and confirm the molecular nature of these compounds. The calculated isotopic distributions for the $[M]^+$ ions are in accord with the observed pattern. Structurally important fragment ions arise primarily from the cleavage of SiC, SiN and SiPh bonds. A representative FAB mass spectrum of **5** is given in Fig. 1 and the relevant data are summarized in Table 1. In the IR spectra (KBr pellet, Fig. 2), the absence of absorptions due to νNH$_2$ (3420

cm^{-1}) and δSiH$_2$ (945 cm^{-1}) modes provides a qualitative evidence for the occurrence of SiH/NH dehydrocoupling. The absorptions due to νNH mode (3350–3120 cm^{-1}) shift to lower frequency as compared to those observed in the parent biguanide (3370–3294 cm^{-1}) and suggests the coordinative association of imine NH with the silicon atom. The νC=N and νNCN absorptions appear at ca 1625 and 1560, 1426 cm^{-1} and remain practically unaltered. In the νSiH region, two medium intensity absorptions are observed at ca 2100 and 2200 cm^{-1} which persist in the solution state (CH$_2$Cl$_2$) as well. These results find an analogy with those of related silylbiguanides [10] as well as a few aminosilanes [12] and disilanes [13] reported earlier and suggest the existence of conformational mixtures. The presence of different conformers in **4**–**7** is also evident from ^{13}C{^{1}H}-NMR spectra in DEPT-135 mode which exhibit two signals for each of the methylene carbons as well as for the SiMe groups linked to the biguanide moiety (Section 3). In ^{1}H-NMR spectra, the resonances arising from the carbosilyl functionalities, $R^1R_2^2SiCH_2CH_2SiMeH$ are broad and devoid of J-coupling information, while NPr/NPh groups show their usual spectral characteristics. The integral intensities of various signals associated with the carbosilyl and NPr/NPh groups are in conformity with the proposed structure. In addition to a broad signal at δ 3.2–5.0 due to NH protons, a downfield resonance at δ 6.8–6.9 is attributed to the coordinated C=NH groups. The signal due to SiH protons appears at δ 4.6–4.7. However its appearance with the broad NH resonance makes a large uncertainty in the integrals. ^{29}Si{^{1}H}-NMR spectrum of each compound in CDCl$_3$ reveals signals at δ −1.3 (for **4**), −1.3 (for **5**), −4.8 (for **6**) and 8.2 (for **7**) and are assigned to $R^1R_2^2Si$ moiety of the carbosilyl side chain by comparison with ^{29}Si{^{1}H}-NMR spectra of the corresponding carbosilanes. Two
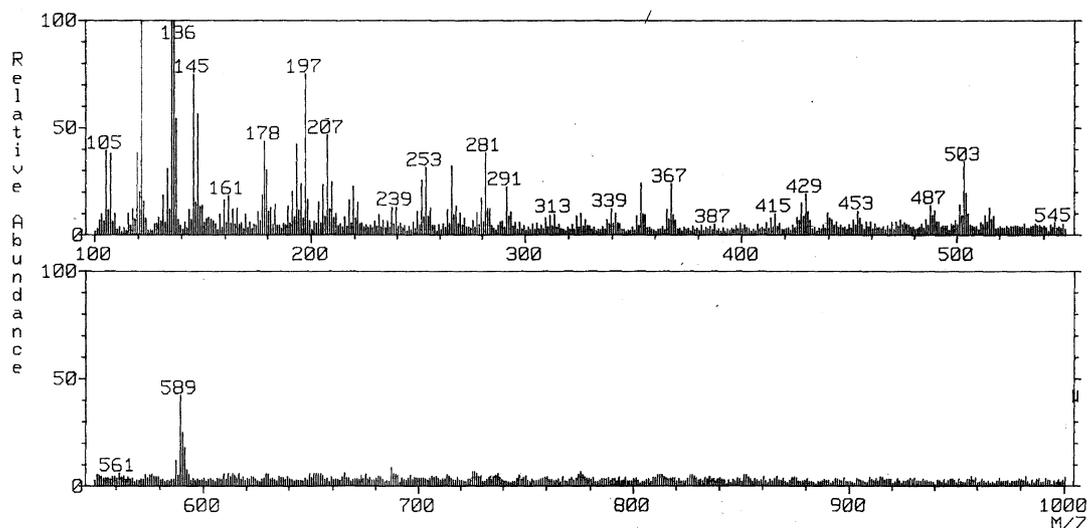
Fig. 1. FAB mass spectrum of (PhMe$_2$SiCH$_2$CH$_2$SiMeH)$_2$·H$_4$bigPh (**5**).

Table 1
FAB mass and ^{29}Si-NMR data of the compounds **4**–**7**

Compound	m/z [fragment ion]	δ ^{29}Si NMR		
		$R^1R_2^2Si$	$C_2Si(H)N$	$C_2Si(H)N_2$
4	555 [M]$^+$, 478 [M − C$_6$H$_5$]$^+$, 420 [M − PhMe$_2$Si]$^+$, 348 [M − PhMe$_2$SiCH$_2$CH$_2$SiMeH]$^+$, 285 [M − 2PhMe$_2$Si]$^+$, 197 [M − 2PhMe$_2$SiCH$_2$ − C$_3$H$_7$ − NH$_3$]$^+$, 144 [C$_5$H$_{13}$N$_5$]$^+$, 135 [PhMe$_2$Si]$^+$	−1.3	−7.8	−85.5
5	589 [M]$^+$, 514 [M − C$_6$H$_3$]$^+$, 453 [M − PhMe$_2$Si − H]$^+$, 367 [M − PhMe$_2$SiCH$_2$CH$_2$SiMeH − Me]$^+$, 353 [M − PhMe$_2$SiCH$_2$CH$_2$SiMe − 2Me]$^+$, 291 [M − 2PhMe$_2$SiCH$_2$]$^+$, 197 [M − 2PhMe$_2$SiCH$_2$ − Ph − NH$_3$]$^+$, 178 [C$_8$H$_{11}$N$_5$]$^+$, 135 [PhMe$_2$Si]$^+$	−1.3	−7.7	−86.5
6	623 [M]$^+$, 469 [M − 2C$_6$H$_5$]$^+$, 454 [M − Ph$_2$MeSi]$^+$, 398 [M − Ph$_2$MeSiCH$_2$CH$_2$]$^+$, 370 [M − Ph$_2$MeSiCH$_2$CH$_2$Si]$^+$, 229 [M − 2Ph$_2$MeSi]$^+$, 144 [C$_5$H$_{13}$N$_5$]$^+$	−4.8	−7.8	−85.5
7	549 [M]$^+$, 520 [M − Et]$^+$, 434 [M − Et$_3$Si]$^+$, 378 [M − Et$_3$SiCH$_2$CH$_2$Si]$^+$, 291 [M − 2Et$_3$SiCH$_2$]$^+$, 178 [C$_8$H$_{11}$N$_5$]$^+$	8.3	−7.5	−86.3

additional resonances are observed at δ −7 to −8 and −85 to −87 in the spectrum of each compound. Based on DEPT-135 ^{29}Si{^{1}H}-NMR spectra, the former value is assigned to tetracoordinate silicon associated with $C_2Si(H)N$ while the latter is assigned to pentacoordinate $C_2Si(H)N_2$ moieties. These results are consistent with those of related tetra- and pentacoordinate silicon derivatives reported in literature [14]. The UV spectra of compounds **4**–**7** reveal an absorption characteristic of the biguanide functionality at 235–240 nm.

From the foregoing studies, it is apparent that molecular compounds **4**–**7** bearing [Si-N-C-N-C-N] chelate ring are accessible by adopting a straightforward synthetic protocol which involves SiH/NH dehydrocoupling between the carbosilanes **1**–**3** and biguanide ligands. A comparative assessment of these studies with those reported earlier [10] is significant in qualitative interpretation of the factors which govern SiH/NH dehydrocoupling phenomena involving biguanide ligands. A few significant conclusions which can be conceived are as follows.

(i) In contrast to the earlier reports [8,9], the reactions of secondary organosilanes $R^1R^2SiH_2$ (R^1 = Ph, R^2 = Ph, Me) [10] or carbosilanes **1**–**3** with biguanide ligands proceed at moderate temperature under uncatalyzed conditions. It is thus implied that strong chelating ability of biguanide ligand is the driving force for activation of SiH bonds in the precursor silanes via hypercoordinate silicon intermediate. This proposition is consistent with the literature report on SiH/NH dehydrocoupling reactions in presence of strong nucleophiles [9]. (ii) Presence of pentacoordinate silicon atom in compounds **4**–**7** is a unique feature not observed in their oligomeric analogs reported earlier [10]. In literature, a number of crystallographically authenticated examples of metal–biguanide chelates are known to
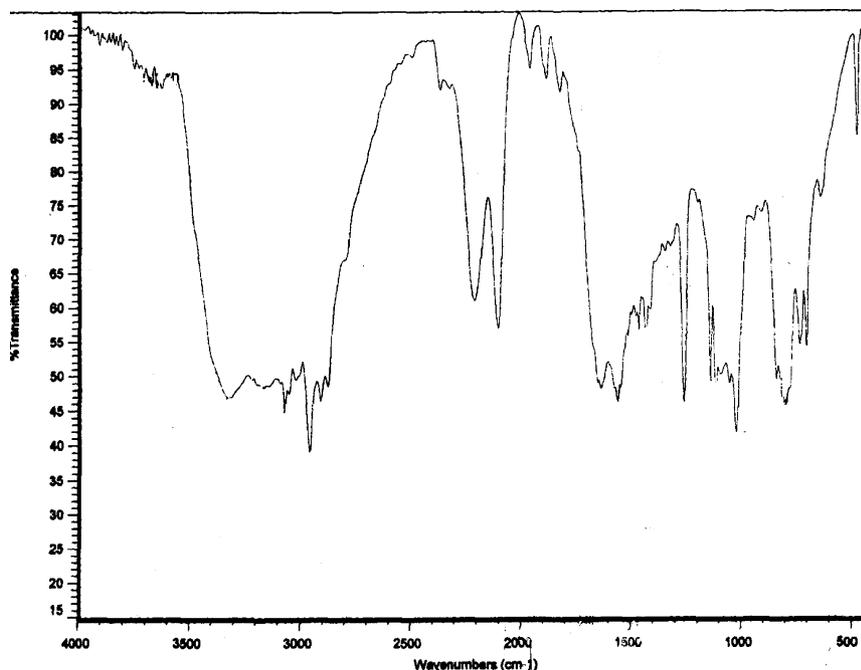
Fig. 2. IR spectrum (KBr pellet) of (PhMe$_2$SiCH$_2$CH$_2$SiMeH)$_2$·H$_4$bigPr (**4**).

possess planar structure [6c,6e,6f]. By analogy, it thus appears that the silicon atom in the vicinity of C=NH group in compounds **4**–**7** lies in the plane of biguanide ligand thereby favoring pentacoordination while any deviation from such planarity disfavors N→Si interaction as observed in the oligomeric silylbiguanides. (iii) Subtle difference in the rate of SiH/NH dehydrocoupling reactions has been observed depending upon the nature of substituents (alkyl or aryl) on silicon. Formation of monomeric compounds **4**–**7** derived from the carbosilanes may be attributed to slow rate of SiH/NH dehydrocoupling in comparison to that of aryl substituted secondary silanes which afford oligomers.

3. Experimental

3.1. General comments

All operations were carried out using standard Schlenk line techniques under dry nitrogen atmosphere. Solvents were freshly distilled under inert atmosphere over sodium benzophenone (tetrahydrofuran, Et_2O) or phosphorous pentoxide (CH_2Cl_2, hexane) before use. Dichloromethylvinylsilane (Aldrich) was distilled over magnesium prior to use. Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex), dimethylphenylsilane, diphenylmethylsilane, Et_3SiH and lithium aluminium hydride (Aldrich) were used as procured. Infrared spectra were routinely obtained as thin films or KBr pellets on a Nicolet FT-IR 460 (Protégé) spectrometer. The UV spectra were obtained in THF solution on a Perkin–Elmer (Lambada Bio 20) spectrophotometer. ^{1}H-, ^{13}C-, and ^{29}Si- NMR spectra were obtained in Me_2SO-d_6, acetone-d_6 or $CDCl_3$ on a Bruker Spectrospin DPX 300MHz instrument. Chemical shifts are quoted relative to Me_4Si. ^{13}C{^{1}H}- and ^{29}Si{^{1}H}-NMR spectra in DEPT mode were obtained using standard pulse sequence with a J modulation time 3.7 ms and 5 s delay time. EI (70 eV) mass spectra were carried out on VG analytical (Model 70-s) mass spectrometer. The FAB mass spectra in 3-nitrobenzyl alcohol (NBA) matrix were recorded at room temperature on a JEOL SX 102/DA-6000 Mass Spectrometer/Data System using Argon/Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV. C, H and N analyses were carried out on a Perkin–Elmer 240-C rapid elemental analyzer. The HPLC data were obtained on Waters 1525 Binary HPLC fitted with Waters 2487 dual wavelength absorbance detector and a C-18 column. Hexane was used as the mobile phase. 1-Propylbiguanide and 1-phenylbiguanide were prepared following the methods known in literature [15,16] and were recrystallized from CH_2Cl_2 prior to use. In accord with the IUPAC nomenclature [17], the numbering scheme for these ligands is as shown in Chart 1.

3.2. Synthesis of the carbosilanes **1**–**3**

3.2.1. Preparation of **1**

To a stirred solution of dichloromethylvinylsilane (14.1 g, 13.0 ml, 0.10 mol) containing catalytic amount of Karstedt's catalyst (10^{-7} mol of Pt/mol of silane), dimethylphenylsilane (13.6 g, 15.3 ml, 0.10 mol) was added dropwise. Induction period was observed after a few milliliters of the silane was added. After the complete addition, the reaction mixture was heated at 70 °C for 7 h. The crude mixture was fractionally distilled (b.p. 95–97 °C/5 mmHg, yield 85%). The resulting chlorocarbosilane (23.5 g, 0.08 mole) in Et_2O was added dropwise to a dispersion of $LiAlH_4$ (3.5g, 0.09 mol) in ether at 0 °C. The contents were gently refluxed for 4–5 h and hydrolyzed with 1N HCl. Ether layer was extracted and dried over anhydrous Na_2SO_4. Thereafter the solvent was removed and the contents were distilled to yield **1** as a colorless liquid. (b.p. 130–135 °C, yield 75%). HPLC (hexane): β-isomer (95%), α-isomer (5%). EI mass: 208 $[M-H]^+$, 193 $[M-CH_3]^+$, 179 $[M-CH_3-CH_2]^+$, 135 $[PhMe_2Si]^+$. ^{1}H-NMR ($CDCl_3$): δ 7.60–7.35 (m, Si*Ph*), 3.72–3.68 (m, Si*H*), 0.72–0.70, 0.60–0.58 (m, SiC*H$_2$C*H$_2$, β), 0.24 (s, Ph*Me$_2$*Si, β), 0.11 (t, $^3J_{HH} = 4.0$ Hz, Si*Me*H$_2$, β), 1.00 (d, $^3J_{HH} = 7.4$ Hz, CHC*H$_3$*, α), 0.33–0.29 (m, SiC*H*, α), 0.22 (s, Ph*Me$_2$*Si, α), 0.02 (t, $^3J_{HH} = 4.0$ Hz, Si*Me*H$_2$, α). ^{13}C{^{1}H} DEPT-135 NMR ($CDCl_3$): δ 134.4 (*o*-SiPh), 129.7 (*p*-SiPh), 128.6 (*m*-SiPh), 9.4, 7.3 (Si*C*H$_2$*C*H$_2$, β), −0.7 (Ph*Me$_2$*Si, β), −2.5 (Si*Me*H$_2$, β), 11.6 (C*C*H$_3$, α), 2.4 (Si*C*H, α), 0.2 (Ph*Me$_2$*Si, α), −2.0 (Si*Me*H$_2$, α). ^{29}Si{^{1}H}-NMR ($CDCl_3$): δ −1.0 (Ph*Me$_2$Si*, β), −28.5 (*Si*MeH$_2$, β), 0.1 (Ph*Me$_2$Si*, α), −29.4 (*Si*MeH$_2$, α). IR (cm^{-1}): v(SiH) 2126, δ(SiH$_2$) 946, v(SiPh) 1114, v(SiMe) 1256. Anal. Calc. for $C_{11}H_{20}Si_2$: C, 63.46, H, 9.61. Found: C, 63.17, H, 9.52%.

3.2.2. Preparation of **2**

The reaction between diphenylmethylsilane (19.8 g, 20.0 ml, 0.1 mol) and dichloromethylvinylsilane (14.1 g, 13.0 ml, 0.1 mol) was carried out in a manner similar to that described for **1**. The chlorocarbosilane thus obtained (b.p. 140–145 °C/5 mmHg, 0.09 mol) was treated with $LiAlH_4$ (3.4 g, 0.09 mol) to afford the carbosilane **2** as a colorless liquid (b.p. 90–93 °C/5 mmHg, yield 70%). HPLC (hexane): β-isomer (96%), α-isomer (4%). EI mass: 269 $[M-H]^+$, 255 $[M-CH_3]^+$, 241 $[M-CH_3-CH_2]^+$, 197 $[Ph_2MeSi]^+$, 192 $[M-C_6H_6]^+$. ^{1}H-NMR ($CDCl_3$): δ 7.50–7.30 (m, Si*Ph*), 3.68–3.64 (m, Si*H*), 1.04–1.00, 0.63–0.61 (m, SiC*H$_2$C*H$_2$, β), 0.50 (s, Ph$_2$*Me*Si, β), 0.07 (t, $^3J_{HH} = 3.9$ Hz, Si*Me*H$_2$, β), 0.99 (d, $^3J_{HH} = 7.5$ Hz, CHC*H$_3$*, α), 0.22–0.18 (m, SiC*H*, α), 0.54 (s, Ph$_2$*Me*Si, α), 0.02 (t, $^3J_{HH} = 4.0$ Hz, Si*Me*H$_2$, α). ^{13}C{^{1}H} DEPT-135 NMR ($CDCl_3$): δ 134.8 (*o*-SiPh), 129.4 (*p*-SiPh), 128.8 (*m*-SiPh), 10.6, 7.6 (Si*C*H$_2$*C*H$_2$, β), −1.0 (Ph$_2$*Me*Si, β), −2.3 (Si*Me*H$_2$, β), 11.3 (C*C*H$_3$,

α), 2.2 (Si*C*H, α), 1.2 (Ph$_2$Me*Si*, α), −2.2 (Si*Me*H$_2$, α). ^{29}Si{^{1}H}-NMR (CDCl$_3$): δ −4.9 (Ph$_2$Me*Si*, β), −28.8 (*Si*MeH$_2$, β), −4.0 (Ph$_2$Me*Si*, α), −29.5 (*Si*MeH$_2$, α). IR (cm^{-1}): ν(SiH) 2125, δ(SiH$_2$) 945, ν(SiPh) 1113, ν(SiMe) 1256. Anal. Calc. for C$_{16}$H$_{22}$Si$_2$: C, 71.11, H, 8.15. Found: C, 70.94, H, 8.02%.

3.2.3. Preparation of 3

The reaction between Et$_3$SiH (14.0 g, 19.0 ml, 0.12 mol) and dichloromethylvinylsilane (16.9 g, 16.0 ml, 0.12 mol) was carried out following the procedure described for **1**. The resulting chlorocarbosilane was distilled (b.p. 95–100 °C/5 mmHg, 0.10 mol) and treated with LiAlH$_4$ (4.26 g, 0.11 mol) in Et$_2$O. The carbosilane **3** was obtained as a colorless liquid (b.p. 60–65 °C/5 mmHg, yield 75%). EI mass: 187 [M − H]$^+$, 173 [M − CH$_3$]$^+$, 159 [M − Et]$^+$, 115 [Et$_3$Si]$^+$. ^{1}H-NMR (CDCl$_3$): δ 3.73–3.69 (m, Si*H*), 0.52–0.48 (m, SiC*H$_2$*C*H$_2$*), 0.95 (t, $^3J_{HH}$ = 7.6 Hz, C*H$_3$*–Et), 0.12 (t, $^3J_{HH}$ = 4.0 Hz, SiMe*H$_2$*). ^{13}C{^{1}H} DEPT-135 NMR (CDCl$_3$): δ 7.1 (*C*H$_3$–Et), 7.0, 2.5 (Si*C*H$_2$*C*H$_2$), 0.6 (Si*Me*H$_2$). ^{29}Si-NMR (CDCl$_3$): δ 8.3 (Et$_3$*Si*), −26.2, −29.3, −32.5 (*Si*MeH$_2$, $^1J_{SiH}$ = 189 Hz). IR (cm^{-1}): ν(SiH) 2124, δ(SiH$_2$) 946, ν(SiMe) 1257. Anal. Calc. for C$_9$H$_{24}$Si$_2$: C, 57.45, H, 12.77. Found: C, 57.36, H, 12.64%.

3.3. Synthesis of 1,4-bis(silyl)-5-propylbiguanides, 4-7

3.3.1. Synthesis of (PhMe$_2$SiCH$_2$CH$_2$SiMeH)$_2$· H$_4$bigPr (4)

To a clear solution of 1-propylbiguanide (0.32 g, 2.2 mmol) in dry THF (15 ml) was added PhMe$_2$-SiCH$_2$CH$_2$SiMeH$_2$ (**1**) (0.93 g, 4.5 mmol) with the help of a hypodermic syringe. The contents were heated at 65–70 °C for ~48 h. The solvent was stripped off under vacuum resulting in a sticky mass. Repeated washings with hexane afford a white solid which was filtered and dried under vacuum (yield: 1.1 g, 95%, m.p. 63–65 °C). ^{1}H-NMR (Me$_2$SO-d$_6$): δ 7.62–7.31 (Si*Ph*, 10H), 6.89–6.87 (C=N*H*, 1H), 4.82–3.20 (br, N*H*+Si*H*, 5H), 2.90 (t, $^3J_{HH}$ = 7.4 Hz, NC*H$_2$*, 2H), 1.40–1.36 (m, NCH$_2$C*H$_2$*, 2H), 0.83 (t, $^3J_{HH}$ = 7.4 Hz, C*H$_3$*–Pr, 3H), 0.64–0.60, 0.40–0.36 (SiC*H$_2$*C*H$_2$*, 8H), 0.17–0.15 (Ph*Me$_2$*Si, 12H), 0.03–0.01 (Si*Me*H, 6H). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 162.4, 162.2 (*C*=N), 136.2 (*i*-SiPh), 132.3 (*o*-SiPh), 127.6 (*p*-SiPh), 126.5 (*m*-SiPh), 41.3 (N*C*H$_2$), 22.1 (NCH$_2$*C*H$_2$), 10.5 (*C*H$_3$-Pr), 10.1, 9.7, 5.5, 5.3 (Si*C*H$_2$*C*H$_2$), −2.4, −2.5 (Si*Me*), −4.5 (Ph*Me$_2$*Si). IR (KBr pellet, cm^{-1}): 3340, 3160 (νNH), 2206, 2099 (νSiH), 1625 (νCN), 1560, 1426 (νNCN), 1257 (νSiMe), 1113 (νSiPh). Anal. Calc. for C$_{27}$H$_{49}$N$_5$Si$_4$: C, 58.38, H, 8.83, N, 12.61, Si, 20.18. Found: C, 58.20, H, 8.64, N, 12.43, Si, 19.98%.

3.3.2. Synthesis of (PhMe$_2$SiCH$_2$CH$_2$SiMeH)$_2$· H$_4$bigPh (5)

The reaction between 1-phenylbiguanide (0.26 g, 1.5 mmol) and PhMe$_2$SiCH$_2$CH$_2$SiMeH$_2$ (**1**) (0.61 g, 2.9 mmol) was performed in a similar manner as described for **4**. After the usual workup the compound **5** was obtained as a white solid (yield: 0.8 g, 90%, m.p. 68–70 °C). ^{1}H-NMR (Me$_2$SO-d$_6$): δ 7.61–7.30 (Si*Ph*, 10H), 7.20–6.82 (m, N*Ph*, 5H), 6.94–6.90 (C=N*H*, 1H), 4.80–3.64 (br, N*H*+Si*H*, 5H), 0.65–0.61, 0.47–0.43 (SiC*H$_2$*C*H$_2$*, 8H), 0.21–0.19 (Ph*Me$_2$*Si, 12H), −0.08 to −0.06 (Si*Me*H, 6H). ^{13}C-NMR (Me$_2$SO-d$_6$): δ 159.4, 159.2 (*C*=N), 136.4 (*i*-SiPh), 133.4 (*o*-SiPh), 129.8 (*p*-SiPh), 127.5 (*m*-SiPh), 149.9 (*i*-NPh), 128.3 (*m*-NPh), 123.9 (*p*-NPh), 120.6 (*o*-NPh), 9.8, 9.5, 5.7, 5.5 (Si*C*H$_2$*C*H$_2$), −2.3, −2.5 (Si*Me*H), −4.5 (Ph*Me$_2$*Si). IR (KBr pellet, cm^{-1}): 3348, 3150 (νNH), 2198, 2099 (νSiH), 1625 (νCN), 1559, 1426 (νNCN), 1257 (νSiMe), 1113 (νSiPh). Anal. Calc. for C$_{30}$H$_{47}$N$_5$Si$_4$: C, 61.12, H, 7.98, N, 11.88, Si, 19.01. Found: C, 61.10, H, 7.92, N, 11.80, Si, 18.52%.

3.3.3. Synthesis of (Ph$_2$MeSiCH$_2$CH$_2$SiMeH)$_2$· H$_4$bigPr (6)

The reaction between 1-propylbiguanide (0.30 g, 2.1 mmol) and Ph$_2$MeSiCH$_2$CH$_2$SiMeH$_2$ (**2**) (1.13 g, 4.2 mmol) was performed by following the procedure as described for **4**. The compound **6** was obtained as a white solid (yield: 1.2 g, 95%, m.p. 70–72 °C). ^{1}H-NMR (Me$_2$SO-d$_6$): δ 7.51–7.20 (Si*Ph*, 20H), 6.90–6.86 (C=N*H*, 1H), 6.22–4.20 (br, N*H*+Si*H*, 5H), 2.96 (t, $^3J_{HH}$ = 7.6 Hz, NC*H$_2$*, 2H), 1.48–1.46 (m, NCH$_2$C*H$_2$*, 2H), 0.90 (br, C*H$_3$*–Pr+SiC*H$_2$*, 7H), 0.50–0.46 (SiC*H$_2$*C*H$_2$*+Ph$_2$*Me*Si, 10H), −0.09 to −0.07 (Si*Me*H, 6H). ^{13}C{^{1}H}-NMR (Me$_2$SO-d$_6$): δ 162.2, 162.1 (*C*=N), 136.4 (*i*-SiPh), 134.2 (*o*-SiPh), 129.4 (*p*-SiPh), 128.2 (*m*-Si*Ph*), 41.5 (N*C*H$_2$), 22.2 (NCH$_2$*C*H$_2$), 10.3 (*C*H$_3$–Pr), 10.5, 9.8, 6.4, 6.2 (Si*C*H$_2$*C*H$_2$), −2.4, −2.5 (Si*Me*H), −1.6 (Ph$_2$*Me*Si). IR (KBr pellet, cm^{-1}): 3330, 3154 (νNH), 2190, 2099 (νSiH), 1625 (νCN), 1560, 1427 (νNCN), 1256 (νSiMe), 1110 (νSiPh). Anal. Calc. for C$_{37}$H$_{53}$N$_5$Si$_4$: C, 71.27, H, 8.51, N, 11.24, Si, 17.98. Found: C, 71.02, H, 8.23, N, 11.03, Si, 17.58%.

3.3.4. Synthesis of (Et$_3$SiCH$_2$CH$_2$SiMeH)$_2$·H$_4$bigPh (7)

The synthesis of compound **7** was achieved by the reaction of 1-phenylbiguanide (0.35 g, 2.0 mmol) with Et$_3$SiCH$_2$CH$_2$SiMeH$_2$ (**3**) (0.75 g, 4.0 mmol). The reaction conditions employed are similar to those described for **4** (yield: 1.0 g, 95%, m.p. 58–60 °C). ^{1}H-NMR (Me$_2$SO-d$_6$): δ 7.22–6.80 (m, N*Ph*, 5H), 6.97–6.94 (C=N*H*, 1H), 6.21–4.20 (br, N*H*+Si*H*, 5H), 0.86–0.82 (C*H$_3$*–Et, 9H), 0.45–0.41 (Si*CH$_2$*, 20H), 0.03–0.01 (Si*Me*H, 6H). ^{13}C{^{1}H}-NMR (dmso-d$_6$): δ 159.0, 158.3 (*C*=N), 149.8 (*i*-NPh), 128.9 (*m*-NPh),

122.8 (*p*-NPh), 120.1 (*o*-NPh), 7.1 (*CH$_3$*–Et), 2.5, 2.7 (Si*CH$_2$*), 0.6 (Si*Me*H). IR (KBr pellet, cm^{-1}): 3343, 3120 (*v*NH), 2203, 2099 (*v*SiH), 1620 (*v*CN), 1560, 1427 (*v*NCN), 1257 (*v*SiMe). Anal. Calc. for C$_{26}$H$_{55}$N$_5$Si$_4$: C, 56.83, H, 10.02, N, 12.23, Si, 20.12. Found: C, 56.64, H, 9.86, N, 11.98, Si, 20.04%.

Acknowledgements

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