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Reactions of secondary silanes with biguanide bases: synthesis and characterization of oligomeric 1,4-bis(silyl)biguanides and 1-alkyl-2,5-bis(silyl)biguanides

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The reactions between diorganosilanes, $R^1R^2SiH_2$ (R^1 = Ph, R^2 = Ph or Me), and biguanide, 1-propylbiguanide or 1-cyclohexylbiguanide proceed *via* SiH/NH dehydrocoupling to afford the corresponding oligomeric 1,4-bis(silyl)-biguanides (**1**, **4**) and 1-alkyl-2,5-bis(silyl)biguanides (**2**, **3**, **5**) with the general formula $[R^1R^2SiNHC(NH)NC(NHSiR^1R^2H)NR^3]_n$ {where $R^1 = R^2$ = Ph; R^3 = H (**1**), Pr^n (**2**) or Cy (**3**). R^1 = Me, R^2 = Ph; R^3 = H (**4**) or Pr^n (**5**)}. These have been characterized by GPC, FAB mass, IR, multinuclear (^1H, ^{13}C, ^{29}Si) NMR data as well as TGA. The IR and NMR spectra suggest the presence of different conformers in these compounds.

Introduction

Recent interest in the Si–N bonded organosilicon derivatives stems from their potential applications in the preparation of high-tech ceramic materials.[1] This has led to the synthesis and characterization of a wide variety of such species ranging from molecular entities to oligomeric, polymeric and dendritic structures. Using silyl triflate as intermediate, Schmidbaur and co-workers[2] have reported cyclic and acyclic Si–N bonded compounds enriched in silicon and hydrogen contents, having potential applications in MOCVD processes. Transition metal catalyzed SiH/NH dehydrocoupling reactions between primary/secondary organosilanes and ammonia/hydrazine are known to yield oligomeric silazanes and aminosilanes.[3] The syntheses of high molar mass polysilazanes has been achieved by anionic/cationic ring opening polymerization of cyclodisilazanes.[4] Carbosilazane dendrimers containing Si–N–Si linkages have been prepared recently by adopting the divergent approach.[5] While the majority of these species are derived from ammonia or amines as N-ligands, analogous compounds with π-electron rich polyaza ligands in the structural framework are rare. The only example having close resemblance to this family is the poly(silylcarbodiimide)s,[6] $[RR'SiN{=}C{=}N]_n$. Potential application of these polymers in non-hydrolytic sol–gel processes has been demonstrated recently.[7]

We have focused our attention on the use of biguanide ligands (Chart 1) in the domain of Si–N chemistry. The choice of these ligands stems from their unique features such as the presence of a π-delocalized framework having both amine and imine functional groups[8] and also selective ability of the imine functions to bind transition metal ions.[9] These ligands are also of current interest owing to their medicinal properties[10] such as hypoglycemic, antimalarial activity and therapeutic treatment of pain, anxiety and memory disorders.

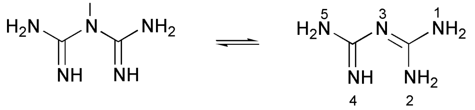
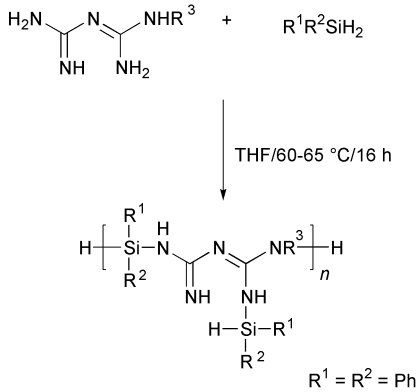


Chart 1

In the present study the reactivity of some secondary silanes, $R^1R^2SiH_2$ (R^1 = Ph; R^2 = Ph or Me), with biguanide, 1-propylbiguanide and 1-cyclohexylbiguanide has been investigated. These reactions proceed *via* SiH/NH dehydrocoupling resulting in the isolation of 1,4-bis(silyl)biguanides **1**, **4** and 1-alkyl-2,5-bis(silyl)biguanides **2**, **3**, **5** as a new class of –[Si–N–C–N–C–N]– based oligomers (Scheme 1). The details are reported herein.



$R^1 = R^2$ = Ph; R^3 = H **1**, Pr^n **2**, Cy **3**
R^1 = Me, R^2 = Ph; R^3 = H **4**, Pr^n **5**

Scheme 1

Results and discussion

Syntheses

Addition of two equivalents of diphenylsilane/methylphenylsilane to either a suspension of biguanide or to a clear solution of 1-propylbiguanide/1-cyclohexylbiguanide in THF medium results in brisk effervescence in each case that apparently slows after a period of time. Refluxing for 15–16 h and subsequent work-up of the concentrated reaction mixture with n-hexane afford the corresponding silylated biguanides **1**–**5**. Carrying out the reaction with an excess (3 equivalents) of the diorganosilane does not alter the product composition and the unchanged silanes can be recovered.

Characterization

The oligomers **1**–**5** are white, moderately air sensitive solids soluble in solvents such as CH_2Cl_2, $CHCl_3$, THF, dmf, dmso, *etc.* These have been characterized by a combination of

Table 1 FAB mass spectral data (commonly observed fragment ions) for **1**–**3**

m/*z*	**1** (M^+, 928)	**2** (M^+, 1012)	**3** (M^+, 1092)
895	$[M - NH_3 - NH_2]^+$	$[M - NHPr - NH_2Pr]^+$	$[M - NHCy - NH_2Cy]^+$
835	$[M - C_6H_5 - NH_2]^+$	$[M - C_6H_5 - NPr - Pr]^+$	$[M - C_6H_5 - NCy - Cy]^+$
757	$[M - 2C_6H_5 - NH_3]^+$	$[M - 2C_6H_5 - NHPr - Pr]^+$	$[M - 2C_6H_5 - NHCy - Cy]^+$
697	$[M - 3C_6H_5]^+$	$[M - 2C_6H_4 - C_6H_5 - 2Pr]^+$	$[M - 2C_6H_4 - C_6H_5 - 2Cy]^+$
637	$[M - Ph_2SiH(NH) - NH_2 - C_6H_5]^+$	$[M - Ph_2SiH(NH) - NH_2 - C_6H_5 - 2C_3H_6]^+$	$[M - Ph_2SiH(NH) - NH_2 - C_6H_5 - 2C_6H_{10}]^+$
259	$[M - 2Ph_2Si - 3C_6H_4 - C_6H_5]^+$	$[M - 2Ph_2Si - 4C_6H_4 - C_3H_6 - Pr]^+$	$[M - 2Ph_2Si - 4C_6H_4 - C_6H_{10} - Cy]^+$

Other significant ions observed are as follows: for **1**, *m*/*z* 929, $[M + H]^+$, 775, $[M - C_6H_5 - C_6H_4]^+$, 101, $[C_2N_5H_7]^+$; for **2**, *m*/*z* 955, $[M - NPr]^+$, 143, $[C_5N_5H_{13}]^+$; for **3**, *m*/*z* 1094, $[M + 2H]^+$, 1075, $[M - NH_3]^+$, 1015, $[M - C_6H_5]^+$, 981, $[M - C_6H_5 - 2NH_3]^+$, 937, $[M - C_6H_6 - C_6H_5]^+$, 183, $[C_8N_5H_{17}]^+$.

Table 2 FAB mass spectral data (commonly observed fragment ions) for **4** and **5**

m/*z*	**4** (M'^+, 1358)	**5** (M'^+, 1526)
1167	$[M' - 2C_6H_6 - 2NH_3 - H]^+$	$[M' - C_6H_5 - C_6H_4 - 2NH_3 - 4Pr]^+$
1130	$[M' - 2C_6H_6 - 2CH_3 - CH_4 - C_2H_2]^+$	$[M' - C_6H_5 - C_6H_4 - 3CH_3 - C_2H_2 - 4Pr]^+$
1045	$[M' - 4C_6H_6 - H]^+$	$[M' - 4C_6H_5 - 4Pr - H]^+$
908	$[M' - 5C_6H_6 - 4CH_3]^+$	$[M' - C_6H_6 - 4C_6H_5 - 4CH_3 - 4Pr]^+$
893	$[M' - 5C_6H_6 - 5CH_3]^+$	$[M' - C_6H_6 - 4C_6H_5 - 5CH_3 - 4Pr]^+$
772	$[M' - 2C_6H_6 - 5C_6H_5 - 3CH_3]^+$	$[M' - 5C_6H_5 - 2C_6H_4 - 3CH_3 - 4Pr]^+$
603	$[M' - 2PhMeSiH - 6C_6H_6 - 3CH_3]^+$	$[M' - 2PhMeSiH - 3CH_3 - 2C_6H_6 - 4C_6H_5 - 4Pr]^+$
586	$[M' - 2PhMeSiH - 6C_6H_6 - 3CH_3 - NH_3]^+$	$[M' - 2PhMeSiH - 2C_6H_6 - 4C_6H_5 - 3CH_3 - NH_3 - 4Pr]^+$
389	$[M' - 5PhMeSiHNH_2 - 3C_6H_6 - 3CH_4 - H_2]^+$	$[M' - 5PhMeSiHNH_2 - C_6H_6 - 2C_6H_5 - 3CH_4 - 4Pr]^+$

Other significant ions observed are as follows: for **4**, *m*/*z* 1204, $[M' - 2C_6H_5]^+$, 1174, $[M' - 2C_6H_5 - 2CH_3]^+$, 740, $[M' - 4C_6H_6 - 3C_6H_5 - 5CH_3]^+$, 681, $[M' - 2PhMeSiH - 5C_6H_6 - 3CH_3]^+$; for **5**, *m*/*z* 1463, $[M' - 2CH_4 - 2CH_3]^+$, 1438, $[M' - 2C_3H_8]^+$, 1374, $[M' - 2C_6H_4]^+$, 1316, $[M' - 2C_6H_4 - CH_3 - C_3H_7]^+$.

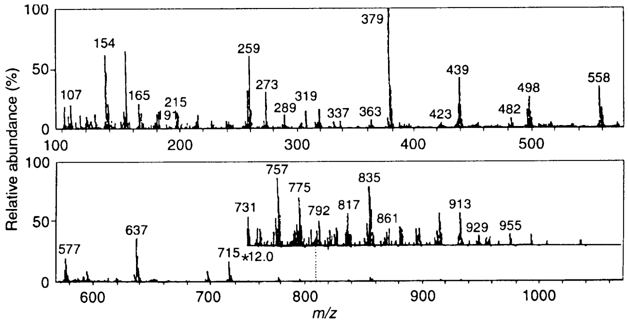


Fig. 1 FAB mass spectrum of **1**.

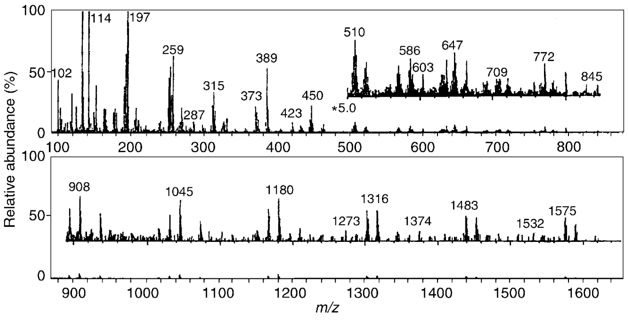


Fig. 2 FAB mass spectrum of **5**.

analytical and spectroscopic techniques including elemental analyses, GPC, FAB mass, IR, multinuclear (^1H, ^{13}C and ^{29}Si) NMR spectroscopy and thermogravimetry analyses. The analytical data (see Experimental section) are consistent with the ideal structure as shown in Scheme 1. Evidence in support of the oligomeric structures of these compounds comes from FAB mass spectral studies in 3-nitrobenzyl alcohol (NBA) matrix (Figs. 1, 2). Under the FAB mass conditions, **1**–**3** display the highest ions at *m*/*z* 929, $[M + H]^+$, 955, $[M - NPr]^+$, and 1094, $[M + 2H]^+$, respectively, which are attributed to dimeric entities $[M]^+$. For **4** and **5** the highest ions at *m*/*z* 1204, $[M' - 2C_6H_5]^+$, and 1463, $[M' - 2CH_4 - 2CH_3]^+$, respectively are assigned based on a tetrameric structural unit $[M']^+$. The structurally important fragment ions arising from these oligomers are given in Tables 1 and 2. The data reveal a number of commonly observed fragment ions that are associated primarily with the skeletal backbone units. In addition, the calculated isotopic distributions for the fragment ions at *m*/*z* 835, 757, 697 for **1**–**3** and 1130, 1045, 893, 772 for **4** and **5** are in accord with the observed pattern. GPC analyses of these oligomers reveal weight average molecular weights (M_w) ranging between 1380 and 1690 with polydispersity 1.06–1.15 (see Experimental section). For **1**–**3** the M_w values are found to be much higher (≈38–49%) than the proposed dimeric structures obtained from the FAB mass data. However for **4** and **5** a fortuitous close proximity of the M_w values to those of the tetrameric units was observed. The simple FAB mass behavior coupled with the low molecular weight and narrow polydispersity (M_w/M_n) in the GPC all point towards the products being simple oligomeric species. IR spectra of these oligomers obtained as KBr pellets reveal a few notable features. While the absorption at *ca.* 3420 cm^{-1} due to νNH_2 mode is appreciably reduced in intensity as compared to that of the parent ligands, the characteristic absorptions of the δSiH_2 mode at 930–920 cm^{-1} is completely absent. These observations clearly suggest that the oligomers **1**–**5** are formed by a SiH/NH dehydrocoupling pathway involving the NH_2 sites of the biguanide ligands. Interestingly, the spectrum of each oligomer shows two medium intensity absorptions in the νSiH region at *ca.* 2200 and 2130 cm^{-1}. These absorptions are also found to persist in solution (THF, CH_2Cl_2, dmso) though the intensity of the bands varies with time (Fig. 3). Such spectral behavior is thought to arise due to the existence of two (or more) conformers, which undergo slow interconversion in the solution state. Similar behavior has been reported for conformational mixtures in unsymmetrically substituted aminosilanes[11] as well as disilanes.[12]

^1H NMR spectra of **1**–**5** show a complex pattern of resonances (wherever applicable) in the region δ 7.7–7.1 (Si–Ph) and 0.5–0.1 (Si–Me), while n-propyl (in **2**, **5**) and cyclohexyl (in **3**) groups associated with the biguanide ligands show the normal NMR pattern. The NH protons are observed as a broad signal at δ 6.5–4.8 and show concentration dependent chemical shifts

Table 3 ^{29}Si NMR values for compounds **1**–**5**

Compound	Chromophore	δ ^{29}Si, *J*/Hz
1	Ph_2SiN_2, $Ph_2Si(H)N$	−46.0, −42.6 *J*(SiH) 188
2	Ph_2SiN_2, $Ph_2Si(H)N$	−41.7, −38.1 *J*(SiH) 190
3	Ph_2SiN_2, $Ph_2Si(H)N$	−46.4, −42.8
4	$PhMeSiN_2$, $PhMeSi(H)N$	−32.7, −33.6, −30.1, −30.4 *J*(SiH) 190, 196
5	$PhMeSiN_2$, $PhMeSi(H)N$	−32.5, −33.2, −30.1, −30.4

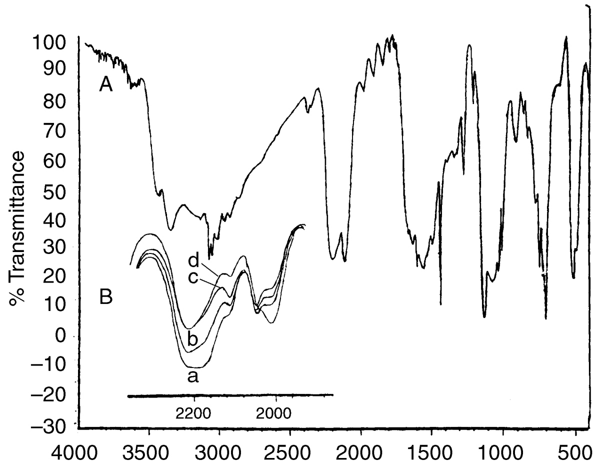


Fig. 3 (A) IR spectrum of **1** (KBr pellet). (B) Partial spectrum of **1** in THF showing the SiH region: (a) fresh sample, (b) after 30 min, (c) 60 min and (d) 90 min.

similar to those observed in the case of the parent biguanides. The identity of the SiH signals could not be established unequivocally, presumably due to overlap of the signals with that of NH protons. Nevertheless, the integrated proton ratios of various groups are in agreement with the proposed composition. ^{13}C NMR spectra also reflect the complexity in the SiPh and SiMe signals, while the n-propyl and cyclohexyl groups associated with the biguanide ligand (in **2**, **3** and **5**) show their usual characteristics. These results are thought to arise from the conformational changes in the solution state and are in accord with the IR spectral analysis. The ^{29}Si-{^{1}H} NMR chemical shift data of **1**–**5** are summarized in Table 3. The close resemblance of ^{29}Si chemical shifts for **1**–**3** as well as for **4** and **5** clearly suggest their structural similarities. A noteworthy feature is the close proximity of the ^{29}Si chemical shift values to those of analogous siloxanes (Ph_2SiO_2 δ −46.1, $PhMeSiO_2$ δ −32.4, −34.9).[13] A similar analogy in δ ^{29}Si values has been reported for poly(silylcarbodiimide)s[6] and an argument to this effect has been put forth based on similarities in electronegativities of N=C=N and O_2^- species. The appearance of four distinct resonances for **4** and **5** (Fig. 4) is thought to be due to adjacent stereogenic silicon and nitrogen centers. Additional evidence in support of these spectral assignments (for **1**, **2** and **4**) has been obtained from DEPT-135 ^{29}Si NMR (proton coupled) spectra. The spectra reveal a distinct doublet at δ −41.0, −44.2 ($J_{Si\text{-}H}$ = 188 Hz) for **1** and −36.5, −39.7 ($J_{Si\text{-}H}$ = 190 Hz) for **2** while the signals due to the Ph_2SiN_2 moiety are not observed. Similarly for **4** the spectrum shows two closely spaced doublets at δ −28.8, −32.0 (J_{SiH} = 190 Hz) and −28.5, −31.8 (J_{SiH} = 196 Hz). The data support the ^{29}Si spectral assignments given in Table 3 and thus rule out the possibility of further SiH/NH coupling in these oligomers.

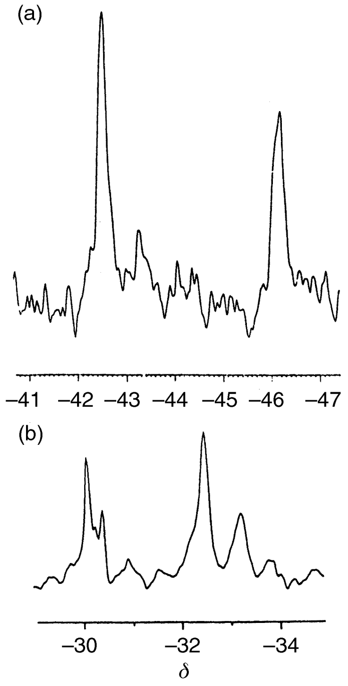


Fig. 4 ^{29}Si NMR spectrum of (a) **1** and (b) **5**.

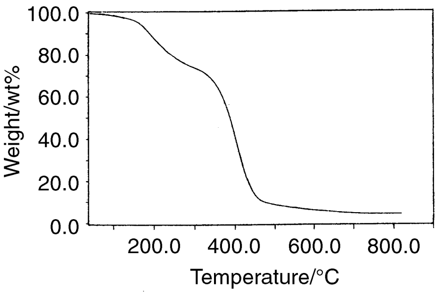


Fig. 5 Thermogravimetric analysis (TGA) of **2**.

The TGA profiles for all the oligomers are essentially similar (Fig. 5) showing no significant weight loss until 150–160 °C. Thermal degradation occurs predominantly in two stages. In the first step nearly 30% of the weight loss occurs between 150 and 300 °C followed by a catastrophic loss of about 60–65% between 340 and 550 °C. Although a detailed study of the thermal decomposition pathway is warranted, the low residual yield is suggestive of extensive breakdown of the oligomeric structures under thermal conditions.

Conclusion

The silylbiguanides **1**–**5** reported herein are a new class of SiN bonded oligomers containing π delocalized biguanide ligands in the structural framework. These are synthesized by the SiH/NH dehydrocoupling reactions between secondary silanes and biguanide/1-propylbiguanide/1-cyclohexylbiguanide bases. IR and NMR spectroscopic data suggest the existence of different conformers in these oligomeric products.

Experimental

General details

All operations were carried out using standard Schlenk line techniques under a dry nitrogen atmosphere. Solvents were freshly distilled under an inert atmosphere over sodium–benzophenone (tetrahydrofuran, diethyl ether) or phosphorus pentaoxide (n-hexane) before use. Dichloromethylphenylsilane, dichlorodiphenylsilane 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, ^{1}H, ^{13}C, ^{29}Si NMR spectra in dmso-d$_6$ (for **1**, **4**) and $CDCl_3$ (for **2**, **3**, **5**) on a Bruker Spectrospin DPX 300MHz instrument. Chemical shifts are quoted relative to TMS. ^{29}Si NMR spectra in DEPT mode were obtained using a standard pulse sequence with a J modulation time of 3.7 ms and 5 s delay time. 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. Gel permeation chromatography of the oligomers were carried out in THF solutions on a Waters Associated Liquid Chromatograph comprising Ultrastyragel permeation columns, a 501 HPLC solvent delivery system and R-400 refractive index detector. Polystyrene standards were used for calibration. C, H and N analyses were carried out on a Perkin-Elmer 240-C rapid elemental analyzer. The thermogravimetric analyses were carried out in a N_2 atmosphere between 30 and 1000 °C (heating rate 10 °C min^{-1}) on a Perkin-Elmer 7 Series Thermal Analysis System.

Diphenylsilane and methylphenylsilane were prepared by reduction of the respective dichlorosilanes with lithium aluminium hydride in dry diethyl ether.[14] Biguanide was prepared according to the literature method,[15] as were 1-propylbiguanide sulfate and 1-cyclohexylbiguanide sulfate.[16] The corresponding bases were obtained by treating the sulfates with alcoholic NaOH. Recrystallization of the resulting compounds from dichloromethane gave analytically pure ligands. In accord with the IUPAC nomenclature[17] the numbering Scheme for the ligands is as shown in Chart 1.

Syntheses of compounds 1–5

1,4-Bis(diphenylsilyl)biguanide 1. To a stirred suspension of biguanide (0.317 g, 3.14 mmol) in dry THF (60 ml) was added diphenylsilane (1.155 g, 6.28 mmol) with the help of a hypodermic syringe. A brisk effervescence was observed immediately on mixing the two reactants. Slow dissolution of the solid occurs upon heating (60–62 °C) for 3–4 h. The mixture was refluxed for 16 h at 60–65 °C, then concentrated under vacuum and n-hexane added. A curdy white precipitate was obtained which was filtered off, washed with n-hexane and dried under vacuum (1.25 g, 85%) (Found: C, 67.05; H, 5.58; N, 15.02; Si, 11.98. $C_{26}H_{25}N_5Si_2$ requires C, 67.38; H, 5.40; N, 15.11; Si, 12.09%). $\tilde{\nu}_{max}$/cm^{-1}: (KBr pellet) 3417 (νNH_2), 3347, 3268 (νNH), 2194, 2104 (νSiH), 1635 (νCN), 1540, 1470 (νNCN), 1119 (νSiPh), 995 (νSiNC); (THF) 2182, 2124 (νSiH). δ_H(dmso-d$_6$) 7.66–7.18 (20H, m, C_6H_5); 6.52–5.47 (5H, br, NH + SiH). δ_C(dmso-d$_6$) 159.6, 158.7 (C=N), 133.5–127.4 (C_6H_5). GPC: $M_w = 1386$, $M_w/M_n = 1.06$.

1,4-Bis(diphenylsilyl)-5-propylbiguanide 2. To a clear solution of 1-propylbiguanide (0.284 g, 1.99 mmol) in dry THF (50 ml) was added diphenylsilane (0.734 g, 3.98 mmol) with the help of a hypodermic syringe. A brisk effervescence was observed on mixing the two reactants. The reaction was carried out in a manner similar to that described for **1**. Compound **2** was isolated as a white solid (0.81 g, 80%) (Found: C, 67.46; H, 6.15; N, 13.38; Si, 10.93. $C_{29}H_{31}N_5Si_2$ requires C, 68.91; H, 6.14; N, 13.86; Si, 11.09%); $\tilde{\nu}_{max}$/cm^{-1}: (KBr pellet) 3440 (νNH_2), 3334, 3124 (νNH), 2183, 2111 (νSiH), 1623 (νCN), 1558 (νNCN), 1117 (νSiPh), 995 (νSiNC); (CH_2Cl_2) 2192, 2110 (νSiH). δ_H($CDCl_3$) 7.58–7.12 (20H, m, C_6H_5), 6.15–4.84 (4H, br, NH + SiH), 2.94 (2H, t, NCH_2), 1.43 (2H, m, CH_2), 0.87 (3H, t, CH_3). δ_C($CDCl_3$) 167.0, 160.5 (C=N), 134.2–127.4 (C_6H_5), 41.9 (NCH_2), 22.4 (CH_2), 11.0 (CH_3). GPC: $M_w = 1476$, $M_w/M_n = 1.12$.

1-Cyclohexyl-2,5-bis(diphenylsilyl)biguanide 3. This compound was prepared by a procedure analogous to that described for **2** using 1-cyclohexylbiguanide (0.149 g, 0.81 mmol) and diphenylsilane (0.298 g, 1.62 mmol). A curdy white precipitate was obtained which was filtered off, washed with n-hexane and dried under vacuum (0.40 g, 85%) (Found: C, 69.79; H, 6.45; N, 12.51; Si, 10.23. $C_{32}H_{35}N_5Si_2$ requires C, 70.45; H, 6.42; N, 12.84; Si, 10.28%). $\tilde{\nu}_{max}$/cm^{-1}: (KBr pellet) 3450 (νNH_2), 3365, 3250 (νNH), 2197, 2108 (νSiH), 1613 (νCN), 1552 (νNCN), 1117 (νSiPh), 994 (νSiNC); (CH_2Cl_2) 2198, 2110 (νSiH). δ_H($CDCl_3$) 7.53–7.06 (20H, m, C_6H_5); 6.10–5.44 (4H, br, NH + SiH); 3.09 (H, m, NCH); 1.48 (10H, m, CH_2). δ_C($CDCl_3$) 160.5, 159.9 (C=N), 134.4–127.3 (C_6H_5), 49.9 (NCH), 33.0, 24.7 (CH_2). GPC: $M_w = 1513$, $M_w/M_n = 1.08$.

1,4-Bis(methylphenylsilyl)biguanide 4. The reaction between methylphenylsilane (1.181 g, 9.68 mmol) and biguanide (0.489 g, 4.84 mmol) in dry THF was performed under similar conditions as described for **1**. The compound **4** was obtained as a white solid (1.34 g, 80%) (Found: C, 56.25; H, 6.02; N, 20.46; Si, 15.74. $C_{16}H_{21}N_5Si_2$ requires C, 56.63; H, 6.19; N, 20.64; Si, 16.51%). $\tilde{\nu}_{max}$/cm^{-1}: (KBr pellet) 3420 (νNH_2), 3337, 3208 (νNH), 2189, 2112 (νSiH), 1635 (νCN), 1558 (νNCN), 1124 (νSiPh), 997 (νSiNC); (THF) 2170, 2116 (νSiH). δ_H (dmso-d$_6$) 7.40–7.27 (10H, m, C_6H_5), 6.42–5.27 (5H, br, NH + SiH), 0.38–0.12 (6H, m, $SiCH_3$). δ_C(dmso-d$_6$) 162.4, 161.4 (C=N), 134.4–126.7 (C_6H_5), 1.2 to −0.4 (CH_3). GPC: $M_w = 1536$, $M_w/M_n = 1.11$.

1,4-Bis(methylphenylsilyl)-5-propylbiguanide 5. The reaction between methylphenylsilane (0.327 g, 2.68 mmol) and 1-propylbiguanide (0.191 g, 1.34 mmol) in dry THF was performed under similar conditions as described for **2**. The compound **5** was obtained as a white solid (0.43 g, 83%) (Found: C, 58.49; H, 7.05; N, 17.81; Si, 14.43. $C_{19}H_{27}N_5Si_2$ requires C, 59.84; H, 7.08; N, 18.37; Si, 14.69%). $\tilde{\nu}_{max}$/cm^{-1}: (KBr pellet) 3450 (νNH_2), 3327, 3250 (νNH), 2190, 2102 (νSiH), 1646 (νCN), 1544 (νNCN), 1124 (SiPh), 997 (νSiNC); (CH_2Cl_2) 2205, 2105 (νSiH). δ_H($CDCl_3$) 7.58–7.31 (10H, m, C_6H_5); 6.15–4.88 (4H, br, NH + SiH); 2.90 (2H, t, NCH_2); 1.41 (2H, m, CH_2), 0.85 (3H, t, CH_3); 0.51–0.05 (6H, m, $SiCH_3$). δ_C($CDCl_3$) 161.1, 162.1 (C=N), 133.6–127.8 (C_6H_5), 1.0 to −0.4 ($SiCH_3$), 42.5 (NCH_2), 22.7 (CH_2), 11.4 (CH_3). GPC: $M_w = 1689$, $M_w/M_n = 1.14$.

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References

1 D. Seyferth, *ACS Symp. Ser.*, 1988, **360**, 143 and references therein; R. M. Laine, Y. D. Blum, D. S. Tse and R. Glaser, *ACS Symp. Ser.*, 1988, **360**, 124 and references therein; M. Birot, J. P. Pillot and J. Dunogues, *Chem. Rev.*, 1995, **95**, 1443; Y. D. Blum, K. B. Schwartz and R. M. Laine, *J. Mater. Sci.*, 1989, **24**, 1707; M. Peuckert, T. Vaahs and M. Bruick, *Adv. Mater.*, 1990, **2**, 398; N. S. C. K. Yive, R. J. P. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *Chem. Mater.*, 1992, **4**, 1263; N. S. C. K. Yive, R. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *New J. Chem.*, 1991, **15**, 85.

2 M. Soldner, A. Schier and H. Schmidbaur, *Inorg. Chem.*, 1997, **36**, 1758; M. Soldner, A. Schier and H. Schmidbaur, *Inorg. Chem.*, 1998, **37**, 510; N. W. Mitzel, H. Schmidbaur, D. W. H. Rankin, B. A. Smart, M. Hofmann and P. R. Schleyer, *Inorg. Chem.*, 1997, **36**, 4360; M. Soldner, J. Riede, A. Schier and H. Schmidbaur, *Chem. Ber.*, 1998, **37**, 601.

3 H. Q. Liu and J. F. Harrod, *Organometallics*, 1992, **11**, 822; J. He, H. Q. Liu, J. F. Harrod and R. Hynes, *Organometallics*, 1994, **13**, 336; Y. Blum and R. M. Laine, *Organometallics*, 1986, **5**, 2081; W. D. Wang and R. Eisenberg, *Organometallics*, 1991, **10**, 2222.

4 E. Duget, M. Schappacher and A. Soum, *Macromolecules*, 1992, **25**, 4835.

5 J. Hu and D. Y. Son, *Macromolecules*, 1998, **31**, 8644; M. Veith, R. Elasser and R.-P. Kruger, *Organometallics*, 1999, **18**, 656.

6 J. Schuhmacher, M. Weinmann, J. Bill, F. Aldinger and K. Muller, *Chem. Mater.*, 1998, **10**, 3913.

7 R. Riedel, E. Kroke, A. Greiner, A. O. Gabriel, L. Ruwisch and J. Nicolich, *Chem. Mater.*, 1998, **10**, 2964; R. Rovai, C. W. Lehmann and J. S. Bradley, *Angew. Chem., Int. Ed.*, 1999, **38**, 2036.

8 S. R. Ernst and F. W. Cagle, Jr., *Acta Crystallogr., Sect. B*, 1977, **33**, 235; B. Clement and U. Girreser, *Magn. Reson. Chem.*, 1999, **37**, 662.

9 A. Syamal, *J. Sci. Ind. Res.*, 1978, **37**, 661; R. O. C. Hart, S. G. Bott, J. L. Atwood and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 1992, 894; A. Marchi, L. Marvelli, M. Cattabriga, R. Rossi, M. Neves, V. Bertolasi and V. Ferretti, *J. Chem. Soc., Dalton Trans.*, 1999, 1937.

10 F. Kurzer and E. D. Pitchfork, *Top. Curr. Chem.*, 1968, **10**, 446; C. R. Sirtori and C. Pasik, *Pharmacol. Res.*, 1994, **30**, 187; J. E. Gerich, *N. Engl. J. Med.*, 1989, **321**, 1231; W. M. Watkins, J. D. Chulay, D. G. Sixsmith, H. C. Spencer and R. E. Howells, *J. Pharm. Pharmacol.*, 1987, **39**, 261; P. Morain, C. Abraham, B. Portevin and G. De Nanteuil, *Mol. Pharmacol.*, 1994, **46**, 732.

11 H. Fleischer, D. C. McKean, C. R. Pulham and M. Bühl, *J. Chem. Soc., Dalton Trans.*, 1998, 585.

12 S. L. Hinchley, B. A. Smart, C. A. Morrison, H. E. Robertson, D. W. H. Rankin, R. Zink and K. Hassler, *J. Chem. Soc., Dalton Trans.*, 1999, 2303; C. A. Morrison, D. W. H. Rankin, H. E. Robertson, P. D. Lickiss and P. C. Masangane, *J. Chem. Soc., Dalton Trans.*, 1999, 2293.

13 G. Engelhardt, M. Magi and E. Lippmaa, *J. Organomet. Chem.*, 1973, **54**, 115.

14 R. A. Benkeser, M. Landeaman and D. Foster, *J. Am. Chem. Soc.*, 1952, **74**, 648.

15 D. Karipides and W. C. Fernelius, *Inorg. Synth.*, 1963, **7**, 56.

16 N. Rajan and S. Gupta, *Z. Anorg. Allg. Chem.*, 1962, **315**, 2000.

17 *Nomenclature of Organic Chemistry*, Pergamon, Oxford, 1979, Rule C-962.1.