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Synthesis and reactivity of novel oligosilanes bearing functional carbosilane side chains

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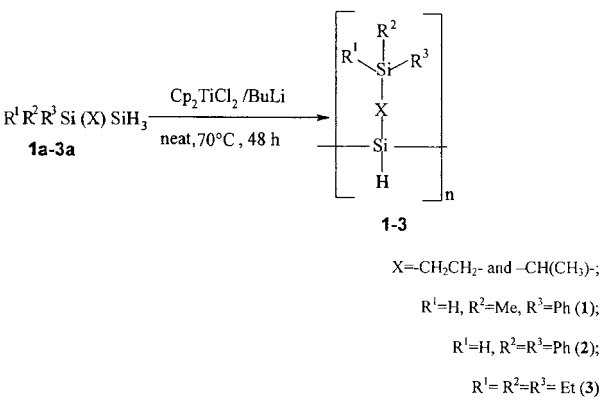
Abstract

New carbosilane monomers $R^1R^2R^3SiXSiH_3$ (X = $-CH_2CH_2-$ and $-CH(CH_3)$; R^1 = H, R^2 = Me, R^3 = Ph (**1a**); R^1 = H, R^2, R^3 = Ph (**2a**); R^1, R^2, R^3 = Et (**3a**) bearing primary and/or tertiary Si–H groups undergo Cp_2TiCl_2/*n*-BuLi catalyzed dehydropolymerization selectively at the primary Si–H site to afford the corresponding oligosilanes **1**–**3**, $[R^1R^2R^3SiXSiH]_n$ (n = 12–15). Treatment of the oligosilanes **1** and **2** with methanol in the presence of a catalytic amount of biguanide base results in the chemoselective transformation of the pendant carbosilyl Si–H to Si–OMe groups, yielding the methoxy- substituted oligosilanes **4** and **5** (R^1 = OMe), respectively. The reaction of **3** with methanol under a similar base catalyzed conditions reveals only 5% conversion of the skeletal Si–H to Si–OMe groups. The oligosilanes **1**–**5** are characterized by IR, UV, ^1H, ^{13}C, ^{29}Si, ($^1H-^{29}Si$) HSQC-NMR spectroscopy, GPC and TGA.

Keywords: Carbosilanes; Hydrosilylation; Dehydropolymerization; Chemoselectivity

1. Introduction

Polysilanes have emerged as an important class of organosilicon polymers due to their unique optical and electronic properties [1]. These properties have their origin due to σ bond delocalization in catenated silicon framework and are strongly influenced by the molecular weight [2], polymer conformation [3] and functional substituents attached to the silicon atoms [4]. Polysilanes have been of considerable interest as precursors for silicon carbide, a thermally stable ceramic material [5]. Though the classical Wurtz coupling reaction involving dichlorosilanes is extensively used for the preparation of alkyl/aryl substituted polysilanes, the method is of limited potential for functionally substituted analogs [1a,b]. With a few exceptions [6], the severe polymerization conditions in this approach impair the use of monomers with the functionalized groups. As an alternative, transition metal catalyzed dehydrocoupling of organosilanes [7,8] offer a useful route to polysilanes bearing the Si–H bonds. Similar catalytic dehydrocoupling reactions have been extended to a few primary or secondary silyl terminated carbosilane precursors [9]. Corriu et al. [5e,10] have reported the condensation reaction of 1,4-disilapentane, $H_2MeSiCH_2CH_2SiH_3$ in the presence of Cp_2TiMe_2 or Cp_2TiCl_2/2*n*-BuLi as catalyst. The studies reveal the initial formation of oligosilane, $[H_2MeSiCH_2CH_2SiH]_n$ by virtue of preferential reactivity of SiH_3 group. Thereafter side chain SiH_2 groups of the oligomer undergo condensation resulting in cross-linked polymer.



Scheme 1.

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A number of reports on the substitution chemistry of Si–Ph and Si–H bonds in polysilanes have appeared [11,12]. The chemical modification of preformed aryl substituted polysilanes has been employed to introduce heteroatom substituents on catenated silicon framework [11]. This synthetic strategy involves the dearylation of Si–Ph bond to generate the reactive Si–X groups (X = Cl, OTf etc.). Subsequent chemical transformation of these groups by nucleophilic reagents such as alcohols, amines or mercaptans affords the polysilanes with the desired functionality. However, the concomitant reactivity behavior of Si–H/Si–Ph groups in conjunction with silyl functionalities in the side chains has not been explored so far. Such studies would be of interest to expand the scope of substitution chemistry in the synthesis of functional polysilanes with interesting physical and chemical properties. In an attempt to address this issue, the oligosilanes **1**–**3**, bearing the functional carbosilane side chains has been synthesized (Scheme 1). These oligosilanes possess Si–H functional groups both in the skeletal and pendant carbosilyl units. Preliminary reactivity studies of these model oligosilanes with methanol under base catalyzed conditions provide evidence for chemoselective methanolysis of the Si–H groups associated with the pendant carbosilyl moieties. The details are reported herein.

2. Results and discussion

2.1. Synthesis and characterization of monomers, *1a*–*3a*

The carbosilanes **1a**–**3a** are synthesized in two steps (Eq. (1)). The initial step involves hydrosilylation reaction between equimolar quantities of trichlorovinylsilane and the hydrosilane $R^1R^2R^3SiH$ in presence of Speier's catalyst [13]. Subsequent reactions of the resulting chlorocarbosilane derivatives with $LiAlH_4$ afford the corresponding carbosilanes **1a**–**3a** as a mixture of α- and β-isomers in ~2:3 ratio

$$CH_2{=}CHSiCl_3 + R^1R^2R^3SiH \xrightarrow[\text{(ii) } LiAlH_4]{\text{(i) } H_2PtCl_6/70^\circ C} \underset{\textbf{1a-3a}}{R^1R^2R^3Si(X)\ SiH_3} \quad (1)$$

$$X = -CH_2CH_2-(\beta\text{-isomer});\ -CH(CH_3)-(\alpha\text{-isomer})$$

where $R^1 = H$, $R^2 = Me$, $R^3 = Ph$ (**1a**); $R^1 = H$, R^2, $R^3 = Ph$ (**2a**); R^1, R^2, $R^3 = Et$ (**3a**).

It is noteworthy that a change in vinylsilane/hydrosilane ratio to 2:1 does not alter the product composition, though concentration of α- and β-addition products is found to vary marginally with change in temperature and catalyst concentration.

The ^{1}H-NMR spectra of **1a**–**3a** allow the detection of both α- and β-isomers by simple inspection. For **1a**, the spectral pattern in C–CH_3 and Si–Me region is reminiscent of two diastereomers of the α-addition product (see Section 3). ^{13}C- and ^{29}Si-NMR spectra of **1a** also reveal well resolved signals arising from these diastereomers, in addition to the resonances of the β-isomer (Fig. 1). The ^{13}C- and ^{29}Si-NMR spectral data of the carbosilanes are given in Table 1. The detailed assignments of ^{13}C-NMR signals are made on the basis of DEPT $^{13}C\{^1H\}$135/90- and HSQC$\{^1H-^{13}C\}$-NMR studies, while those of ^{29}Si-NMR signals have been established using TOCSY and $\{^1H-^{29}Si\}$HSQC-NMR experiments.

2.2. Polymerization of *1a*–*3a*

The dehydrocoupling reactions of **1a**–**3a** were carried out neat at 70°C using the catalyst, Cp_2TiCl_2/BuLi [8e,f] with 1:2.2:40 catalyst to silane ratio. Although the monomers were consumed after 5–6 h (as evident from disappearance of νSiH frequency at 2145 cm^{-1}), the reactions were continued for 48 h to ensure the formation of enhanced molecular weight polymers. The crude polymer obtained in each case shows infrared frequency at 2118 (s) and 2078 (sh) cm^{-1} due to νSiH mode. By analogy with the similar spectral behavior reported earlier [14], the latter νSiH value is indicative of the formation of cyclic species. Separation of these cyclic and low molecular weight species is effected by repeated solvent extraction procedure using methanol and pentane mixture (see Section 3) and the oligosilanes **1**–**3** (Scheme 1) are obtained as pale yellow viscous gums in 40–53% isolable yield. These are soluble in common organic solvents such as dichloromethane, chloroform, hexane, toluene, THF etc. Table 2 summarizes the GPC data along with ^{1}H- and ^{29}Si-NMR chemical shift values of these oligomers. GPC data reveal a mono model molecular weight distribution with Dp ranging between 12 and 15 and polydispersity 1.28 and 1.78. The ^{1}H-NMR spectra of **1**–**3** show broad unresolved massifs in the regions characteristic of functional group protons (Fig. 2a). The integrated proton ratios of various groups are in accord with the idealized structure as shown in Scheme 1. For **1** and **2**, the spectra reveal two distinct resonances at δ 4.22–4.85 and 3.35–3.78 which are attributed to the Si–H protons linked with the carbosilane side chain and silicon backbone, respectively. The latter chemical shift region of skeletal Si–H groups is comparable with that observed for the oligomer **3** (δ 3.48–3.60) and also with those of the related alkyl substituted polysilanes $[RSiH]_n$ (where R = *n*-Pr, *n*-Bu) reported in literature [11a]. The 1:1 integral ratio of pendant and skeletally bound Si–H groups suggests the formation of linear oligosilanes. DEPT-135 $^{29}Si\{^1H\}$ spectra of **1** and **2** reveal complex pattern of signals in the region from δ −6.8 to −11.9

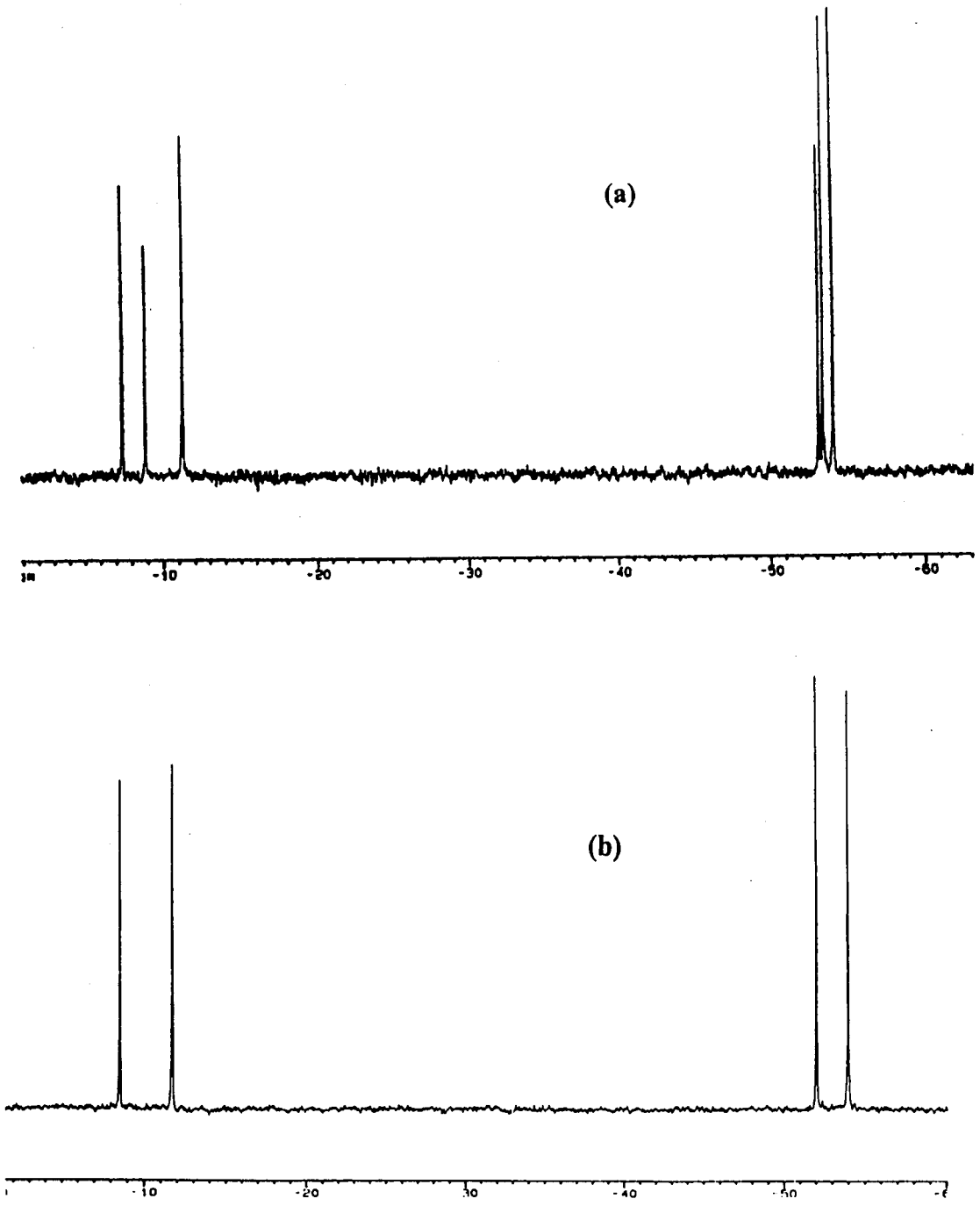


Fig. 1. $^{29}Si\{^{1}H\}$-NMR spectrum of: (a) carbosilane **1a**; (b) carbosilane **2a**.

and -57.0 to -67.0 (Fig. 3). The former chemical shift values are attributed to the silicon atoms of the pendant carbosilane units by comparison with those of the precursors while the latter values are ascribed to the skeletal silicon atoms. The terminal SiH_2 groups are identified by out of phase resonances in the region from δ -54.9 to -58.1. A comparison of the $^{29}Si\{^{1}H\}$-NMR spectra in DEPT-135 and normal mode reveals similar spectral characteristics. This implies that further cross-linking of the Si–H groups in the linear structure is either not present or is too weak to be detectable in $^{29}Si\{^{1}H\}$-NMR spectra. $\{^{1}H-^{29}Si\}$ HSQC-NMR spectrum of **2** (Fig. 4) reveals dominant cross peaks at δ -8.6 to $-11.2/4.2$–4.9 and -57.4 to $-64.4/3.5$–3.8 and furnishes additional evidence in support of the spectral assignments of the different Si–H groups. DEPT-135/90 $^{13}C\{^{1}H\}$ spectra of **1** and **2** identify complex pattern of signals for CH–CH_3 (δ 11.4–14.9) and

Table 1
^{13}C and ^{29}Si spectral data δ (ppm) of carbosilanes **1a**–**3a** [a]

Compound	^{13}C-NMR				^{29}Si-NMR	
	C*CH*$_3$	Si*Me*	CH	CH_2	*Si*H/Et$_3$*Si*	*Si*H$_3$
PhMeHSiCH$_2^a$CH$_2^b$SiH$_3$		−6.03		−0.27[b] +9.33[a]	−11.2	−54.1
PhMeHSiCH(CH$_3$)SiH$_3$	12.01 12.62	−6.03 −6.87	−4.05 −4.31		−7.3 −8.8	−53.1 −53.3
Ph$_2$HSi CH$_2^a$CH$_2^b$SiH$_3$				0.00[b] 8.15[a]	−11.7	−53.9
Ph$_2$HSiCH(CH$_3$)SiH$_3$	12.75		−5.17		−8.4	−51.9
Et$_3$Si CH$_2^a$CH$_2^b$ SiH$_3$				3.32[b] 7.71[a]	8.1	−54.1
Et$_3$SiCH(CH$_3$)SiH$_3$	7.42		−0.69		8.9	−54.3

[a] a and b denote different carbon atoms as specified.

Table 2
^{1}H-, ^{29}Si-NMR and GPC data of oligomers **1**–**5**

Oligomer	δ ^{1}H-NMR (ppm)	δ ^{29}Si-NMR (ppm)	Mw	PD
1	7.31–7.54(Ph); 4.25–4.60(SiH pendant); 3.49–3.78(SiH backbone + SiH$_2$ end groups); 0.37–1.60(alkyl)	−6.8, −8.2, −8.8, −9.9, −10.2 −10.9, −11.5 (SiH pendant); −57.4 to −64.4 (SiH backbone + SiH$_2$ end groups)	2730	1.28
2	7.05–7.47(Ph); 4.22–4.85(SiH pendant); 3.35–3.69(SiH backbone + SiH$_2$ end groups);0.59–1.40(alkyl)	−8.6, −9.3, −10.7, −11.3, −11.9(SiH pendant); −57.9 to −66.7 (SiH backbone + SiH$_2$ end groups)	2860	1.65
3	3.48–3.68 (SiH backbone + SiH$_2$ end groups); 0.31–1.35(alkyl)	10.1, 9.4, 8.6, 8.3, 7.8 (Et$_3$Si); −52.5 to −61.6 (SiH backbone + SiH$_2$ end groups)	2120	1.78
4	7.21–7.59(Ph); 3.44–3.72(OMe + SiH backbone); 0.42–1.47(alkyl)	−8.2, −8.9, −10.2, −11.2, −11.7, −13.2, −15.0 (SiOMe); −57.1 to −63.7 (Si–H backbone)	2600	2.04
5	7.27–7.66(Ph); 3.43 –3.76(OMe + SiH backbone); 0.84 –1.46(alkyl)	−8.5, −9.3, −10.6, −10.9, −11.3, −12.0 (SiOMe); −56.3 to −65.9 (SiH backbone)	2780	1.82

CH–CH$_3$ (δ −0.9 to −4.9) groups arising from the carbosilanes side chains of α-isomer while the CH_2 groups of the β-isomer are found to resonate at δ 3.1–6.9 and 9.3–11.3. Quantitative ^{13}C-NMR spectra of these oligomers apparently reveal the presence of both α- and β-carbosilane side chains nearly in the same ratio ($\sim$2:3) as observed in the parent carbosilanes. This suggests similar reactivity of these isomers towards dehydropolymerization reactions. ^{13}C-NMR spectrum of **3** is less informative due to the overlap of signals of CH_2CH_2, CH and $SiEt_3$ groups. The infrared spectra of **1**–**3** display characteristic absorptions at 2117–18 (νSi–H) and 915–917 cm^{-1} (δ SiH$_2$) and are typical of linear oligosilanes [14]. The UV spectra of **1**–**3** in dichloromethane solution show absorptions at 263–264 nm due to σ bond delocalization in the skeletal framework. Though these absorptions are known to be quite sensitive to the polymer chain length as well as substitution on silicon atom [15], the values obtained herein are comparable with those of the alkyl substituted polysilanes [BuSiH]$_n$ [11a].

The results of the thermogravimetric analysis (TGA) studies of the oligomers **1**–**3** are shown in Fig. 5. It is evident that the onset of thermal decomposition of the least stable oligosilane **3** begins at 110°C while the oligomer **2** is stable up to 350°C. The thermal stability of **1** lies between these two extremes. The decomposition of **1** is gradual, indicating 48% weight loss after heating the sample up to 1000°C in nitrogen atmosphere. The oligomer **2** shows two successive thermal decomposition steps at temperature ranging between 350–580 and 600–800°C with 36 and 18% weight loss, respectively. Similarly oligomer **3** exhibits weight loss of 21 and 34% in the temperature range between 110–220 and 350–580°C, respectively. Although detailed study of the thermal decomposition pathway is warranted, high residual yield indicates the potential of these oligomers as preceramic precursors.

2.3. Reactivity studies of *1*–*3*

In our endeavor to understand the reaction chemistry of these oligosilanes, base-catalyzed methanolysis of the Si–H functional groups has been examined. Since the use of classical organic bases in the transformation of Si–H to Si–OR bonds is well known at the molecular

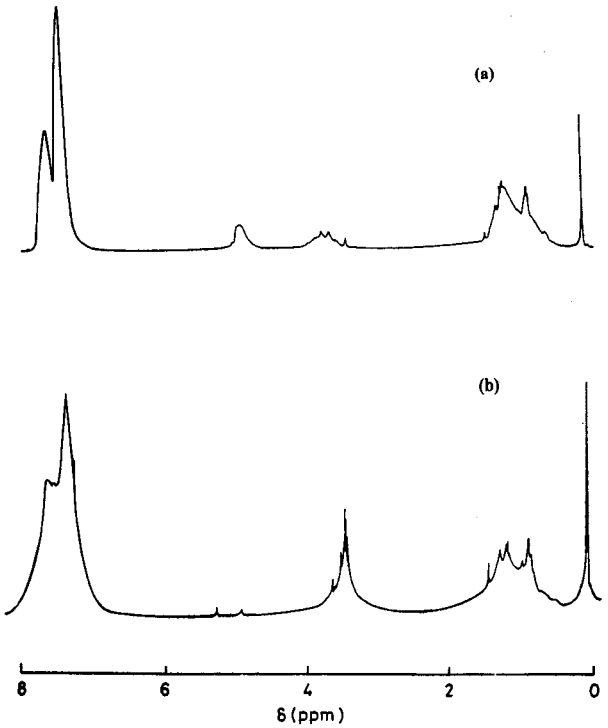


Fig. 2. (a) ^{1}H-NMR spectrum of: (a) oligomer **2**; (b) oligomer **5**.

level [16], the feasibility of such transformation in the oligosilanes **1** and **2** has been initially studied using methanol and catalytic amount of triethylamine as a base. ^{1}H-NMR spectra of the resulting oligomers reveal that the methanolysis occurs chemoselectively at the carbosilyl Si–H groups, with no apparent reactivity of the skeletal Si–H bonds being observed under these conditions. After 24 h nearly 25% conversion of the carbosilyl Si–H to SiOMe groups has been observed. Similar reactions when performed using a biguanide base [17] as catalyst proceeds at a much faster rate. The progress of these reactions has been monitored by ^{1}H-NMR spectroscopy at different time intervals. It is

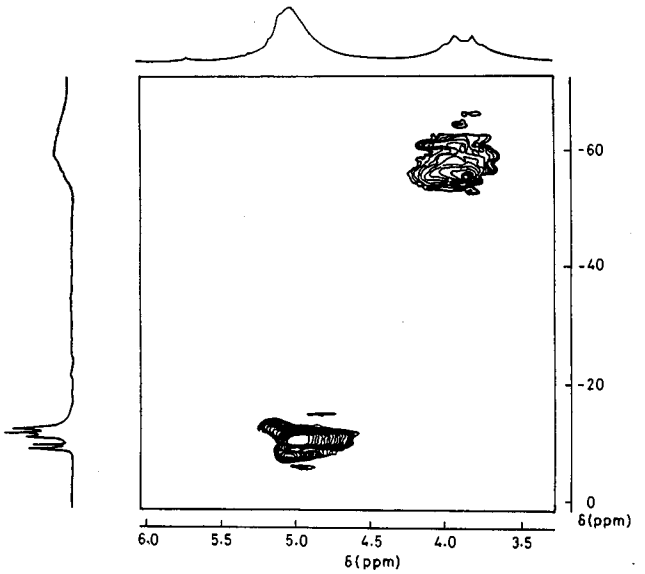


Fig. 4. (^{1}H–^{29}Si) HSQC-NMR spectrum of oligomer **2**.

observed that the Si–H signal (δ 4.25–4.85) arising from pendant carbosilanes in **1** and **2** slowly decreases in intensity with time and finally disappears completely within 3–4 h (Fig. 2b). The resulting viscous gums isolated from these reactions are identified as **4** and **5** $[(MeO)R^{2}R^{3}Si(X)SiH]_{n}$ (Scheme 2). Table 2 summarizes the GPC, ^{1}H- and ^{29}Si-NMR data of these oligomers. A comparison of the GPC data with those of the parent oligomers **1** and **2** suggest that the catenated silicon framework remains apparently unaffected during the chemical transformation. ^{1}H-NMR spectra of **4** and **5** are in accord with the suggested composition. The ^{29}Si{^{1}H}-NMR chemical shifts of these oligosilanes show a close resemblance with those of the parent oligomers **1** and **2**. Although spectral similarity for the skeletal silicon atoms in the region from δ −56.3 to −65.9 is expected, the observed parity in δ ^{29}Si for the

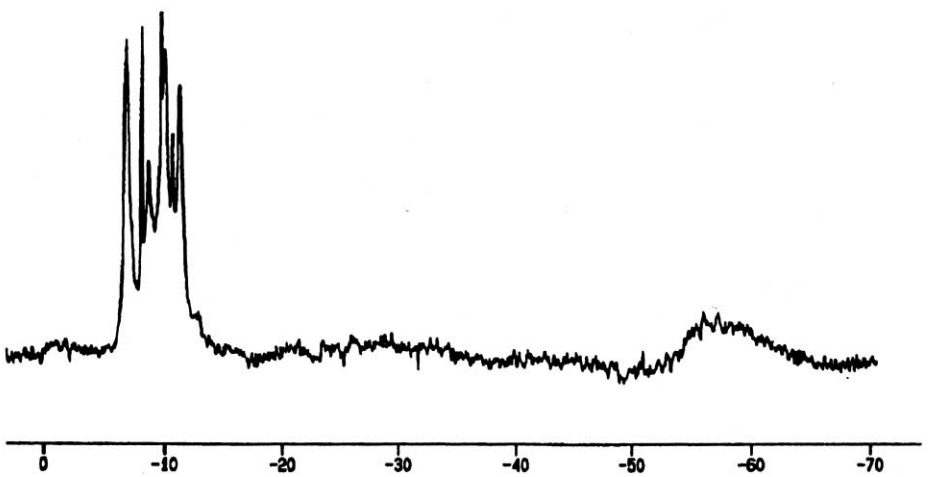


Fig. 3. ^{29}Si{^{1}H}DEPT 135°-NMR spectrum of oligomer **1**.

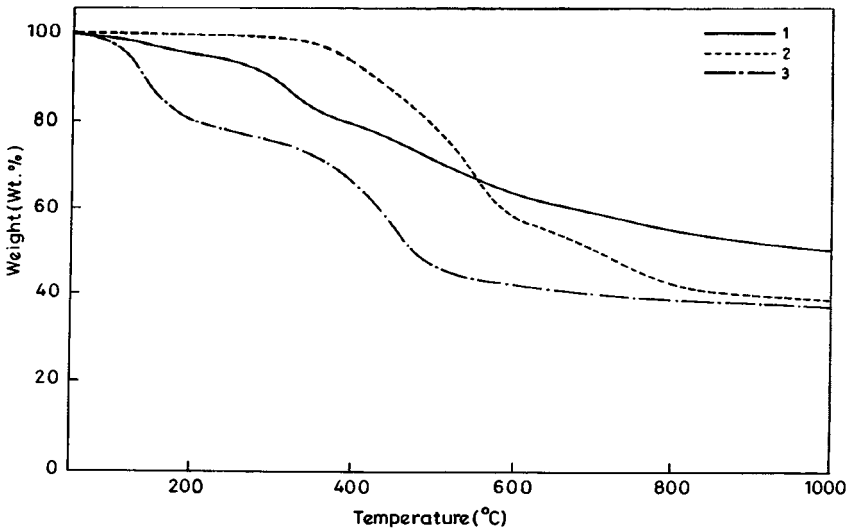


Fig. 5. Thermogravimetric analysis (TGA) of oligosilanes **1**–**3**.

$MeOSiR^2R^3$ (in **4** and **5**) and $HSiR^2R^3$ (in **1** and **2**) moieties need special mention. A justification to these assignments is sought by comparing the δ ^{29}Si-NMR values of the carbosilane monomers, **1a** and **2a** and their methoxy derivatives which show close resemblance in their chemical shifts [18]. Additionally, {^{1}H–^{29}Si} HSQC-NMR spectra of the oligomers **4** and **5** reveal only one cross peak in each case in the region from -56.3 to $-65.9/3.4$–3.8 suggesting the retention of skeletal Si–H groups in these oligomers. The chemoselective methanolysis of the pendant carbosilane Si–H groups in **1** and **2** is further supported by a similar reaction of **3** with methanol. ^{1}H-NMR spectrum of the oligomer obtained after 24 h reveals that approximately 5% of SiOMe groups are formed.

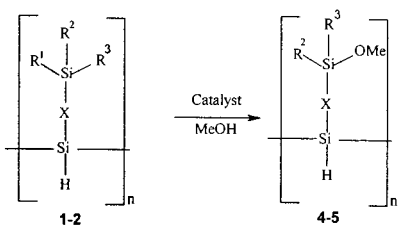
In summary, the synthesis of new oligosilanes **1**–**3** bearing functional carbosilane pendant groups has been achieved by the titanium catalyzed condensation reactions of the carbosilane monomers, $R^1R^2R^3Si(X)SiH_3$. These oligosilanes serve as useful models to unfold the chemical behavior of Si–H groups associated with the pendant carbosilane unit and the skeletal framework. In contrast to the observed slow rate of methanolysis of the pendant carbosilyl Si–H groups in presence of triethylamine base, a quantitative and chemoselective conversion of the pendant carbosilyl Si–H to Si–OMe group is achieved using catalytic amount of biguanide base. Detailed studies on the reaction chemistry on these oligosilanes are in progress.

3. Experimental

3.1. General comments

All reactions were carried out under dry nitrogen atmosphere using Schlenk techniques. Solvents were dried by standard methods. All glassware were thoroughly dried in an oven at 110–120°C and flame dried under a stream of dry nitrogen, prior to use. Trichlorovinylsilane, dichloromethylphenylsilane and dichlorodiphenylsilane (Aldrich) were distilled over Mg prior to use. Et_3SiH, lithium aluminum hydride and Cp_2TiCl_2 (Aldrich) were used as received. Diphenylsilane and methylphenylsilane were prepared from the corresponding chlorosilanes by following the known method [19]. The molarity of hexane solution of *n*-BuLi (Aldrich) was confirmed by a titration method [20].

^{1}H- , ^{13}C- and ^{29}Si-NMR spectra were recorded in $CDCl_3$ on a Bruker 300DPX spectrometer at frequency of 300, 75.5 and 59.6 MHz, respectively. ^{13}C- and ^{29}Si-NMR spectra in DEPT mode were obtained using a standard pulse sequence with a *J* modulation time 3.7 ms and 2 s delay time. ^{1}H–^{13}C and ^{1}H–^{29}Si (HSQC) spectra were recorded using standard pulse sequence with a relaxation delay of 2 s for each of the $512t_1$ experiments [21]. The chemical shifts are quoted with



Where X=-CH_2CH_2-and -$CH(CH_3)$-;

R^1=H, R^2= Me, R^3= Ph;

R^1= H, R^2, R^3= Ph.

Scheme 2.

respect to TMS. Infrared and UV spectra were obtained in dichloromethane solution on a Nicolet FTIR 460 (Protégé) and Perkin–Elmer (Lambada Bio 20) spectrophotometer, respectively. Gel permeation chromatography of the oligosilanes 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. TGA was carried out under a nitrogen atmosphere (30–1000°C, heating rate 10°C min^{-1}) on Perkin–Elmer, TGA-7, thermogravimetric analyzer.

3.2. Preparation of $PhMeHSi(X)SiH_3$ ($X = -CH_2CH_2-$, $-CH(CH_3)-$), **1a**

To the stirred solution of trichlorovinylsilane (6.26 g, 4.9 ml, 38.5 mmol) containing catalytic amount of H_2PtCl_6 (solution in 2-propanol, 10^{-7} mol of Pt/mol of silane used), methylphenylsilane (4.27 g, 4.8 ml, 35.0 mmol) was added dropwise. Induction period was observed after a few ml of the silane was added. After the complete addition, the reaction mixture was heated to 70°C for 7 h. The crude mixture was fractionally distilled (b.p. 90–95°C/5 mm Hg, yield 85%). The resulting chlorocarbosilane (8.43 g, 29.8 mmol) in Et_2O was added dropwise to a dispersion of $LiAlH_4$ (1.81g, 47.6 mmol) in ether at 0°C. The contents were gently refluxed for 5–6 h and then hydrolyzed with 1 N HCl. Ether layer was extracted and dried over anhydrous Na_2SO_4. Thereafter, the solvent was removed and the contents were distilled under vacuum to yield **1a** as a colorless liquid (b.p. 40–42°C/5 mm Hg, yield 67%). ^{1}H-NMR ($CDCl_3$): δ 0.35 (d, $^3J_{HH} = 3.78$ Hz, Si*Me*,β), 0.39 (dd, $^3J_{HH} = 3.66$ Hz, Si*Me*,α), 0.41–0.46 (m, CH), 0.71–0.77 (m, PhMeSiCH_2), 0.86–0.94 (m, CH_2SiH_3), 1.15 (dd, $^3J_{HH} = 7.43$ Hz, CH_3), 4.35–4.41 (m, Si*H*), 3.51–3.56 (m, SiH_3), 7.31–7.54 (m, Ph). IR (cm^{-1}) ν(SiH) 2143.

3.3. Preparation of $Ph_2SiH(X)SiH_3$ ($X = -CH_2CH_2-$, $-CH(CH_3)-$), **2a**

The reaction was carried out in a manner similar to that described for **1a** using diphenylsilane (4.97 g, 5.0 ml, 27.0 mmol) and trichlorovinylsilane(4.83 g, 3.8 ml, 29.7 mmol). No induction period was observed. The contents were heated at 70°C for 12 h and distilled (b.p. 138–142°C/5 mm Hg, yield 88%). The chlorocarbosilane (8.21 g, 23.8 mmol) thus obtained was treated with $LiAlH_4$ (1.44 g, 38.0 mmol) to afford the product as a colorless liquid (b.p. 115–117°C/5 mm Hg, yield 78%). ^{1}H-NMR ($CDCl_3$): δ 0.71–0.77 (m, CH_2SiH_3), 1.14–1.22 (m, Ph_2SiCH_2), 1.23 (d, $^3J_{HH} = 7.41$ Hz, CH_3), 4.85–4.93 (m, Si*H*), 3.53 (t, $^3J_{HH} = 3.72$ Hz, SiH_3), 3.57 (d, $^3J_{HH} = 3.84$ Hz, SiH_3), 7.31–7.54 (m, Ph). IR (cm^{-1}) ν(SiH) 2145.

3.4. Preparation of $Et_3Si(X)SiH_3$ ($X = -CH_2CH_2-$, $-CH(CH_3)-$), **3a**

The reaction between Et_3SiH (3.65 g; 5 ml; 31.5 mmol) and vinyltrichlorosilane (5.54 g, 4.3 ml; 34.0 mmol) was carried out following the procedure described for **1a**. Strong induction period was observed during the addition. The contents were heated for 70°C for 5 h and distilled (b.p. 85–88°C/5 mm Hg, yield 91%). The distillate (7.92 g, 28.5 mmol) was treated with $LiAlH_4$ (1.73 g, 45.6 mmol) in Et_2O. The product was obtained as a colorless liquid (b.p. 47–49°C/5 mm Hg, yield 82%). ^{1}H-NMR ($CDCl_3$): δ 0.21–0.23 (m, *CH*), 0.48–0.70 (m, $CH_2SiH_3 + CH_2$(Et)), 0.90–0.98 (m, $Et_3SiCH_2 + CH_3$(Et)), 1.13 (d, $^3J_{HH} = 7.54$ Hz, CH_3), 3.53 (t, $^3J_{HH} = 3.61$ Hz, SiH_3), 3.56 (d, $^3J_{HH} = 3.32$ Hz, SiH_3). IR (cm^{-1}) ν(SiH) 2144.

3.5. Polymerization reactions

In a typical procedure, the carbosilane **1a** (0.80 g; 4.44 mmol) was charged with Cp_2TiCl_2 (0.28 g; 0.11 mmol) and *n*-BuLi (0.20 ml, 1.30 M in hexane) under dry N_2 conditions. The solution immediately turned blue in color. The reaction mixture was heated at 70°C for 48 h. Thereafter, *n*-hexane ($\sim$30 ml) was added and dry air was bubbled in the solution to deactivate the catalyst. The solid residue was filtered through a short column of celite and clear filtrate was kept under vacuum for several hours to remove the volatile materials. The resulting gummy residue was dissolved in minimum amount of pentane and MeOH was added dropwise until the oligosilane was obtained in a separate layer as an oily viscous gum. The dissolution/separation procedure was repeated three times to remove the catalyst and decomposition products, yielding the oligosilane **1** (Yield 53%). Following the similar procedure as above, the oligomers **2** and **3** were obtained using the monomers **2a** and **3a**, respectively. Yield (40–43%).

3.6. Reactions of **1–3** with MeOH

In a typical experiment, MeOH (3.0 ml; 59.4 mmol) and biguanide base (0.025 g; 0.25 mmol) were added to a stirred solution of the oligosilane **1** (1.0 g; Mw = 2690) in CH_2Cl_2 (15 ml). The reaction mixture was allowed to stir at room temperature and an aliquot of the above reaction was removed with the help of a cannula at one-hour time intervals. The solvent was evaporated under vacuum and *n*-hexane was added to precipitate biguanide catalyst, which was filtered. Removal of *n*-hexane from the filtrate gave a yellow viscous gum, which was subjected to ^{1}H-NMR studies. After 4 h of stirring, the bulk reaction mixture was treated similarly as above to afford the oligomer **4**. The

reactions of **2** and **3** with MeOH were performed by following the similar procedure.

The oligosilanes **1** and **2** (1 g) in CH_2Cl_2 (10 ml) were reacted separately with MeOH (2.0 ml; 39.5 mmol) in presence of Et_3N (5.0 mmol). After stirring the reaction mixture for 24 h, volatiles were removed under vacuum and the resulting viscous gum was subjected to ^{1}H-NMR studies.

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