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# Condensation of primary silanes in the presence of $Cp_2MCl_2/{}^nBuLi$ (M = Ti, Zr, Hf)

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## Abstract

The condensation of $RSiH_3$ (R = Ph, $^n$Bu, $^n$Hex) to silicon oligomers in the presence of the catalyst precursor combination $Cp_2MCl_2/2{}^nBuLi$ (M = Ti, Zr, Hf) has been monitored by gas chromatography and the intermediate oligomers characterized by GC-MS. The average molecular weights of the isolated products from $PhSiH_3$ depend on the catalyst and increase through the sequence, Hf < Ti < Zr, to a maximum of about 1800 for reactions conducted at room temperature. In the condensation of alkylsilanes linear oligomers are produced in the initial stages of the reaction and as the reaction continues cyclic polysilanes are formed with increasing numbers of isomers as the number of silicon atoms increases. A large rate difference is observed in the formation of the diastereomers of the tetrasilane produced from $PhSiH_3$ for all three catalysts. For reactions conducted at 50°C both diastereomers of $H({}^nBuSiH)_4H$ are produced in equal amounts throughout the reaction period for M = Ti but at different rates for M = Zr and only one diastereomer is observed for M = Hf. The observations are discussed in terms of chain growth through sigma-bond metathesis processes.

## Introduction

Polysilanes exhibit extensive sigma-electron delocalization along the silicon backbone which gives rise to unusual physical and electronic properties that may find commercial applications [1]. The ultraviolet and electronic properties appear to be a function of both the chain length and the conformation of the silicon backbone [2]. Most polysilanes are generated by a Wurtz-type coupling reaction. The resulting polymers usually exhibit polydispersity and are polymodal [1]. The utility of well-defined materials for applications of polysilanes in microelectronics has prompted the search for alternative synthetic methods such as dehydrocoupling [3], ring-opening polymerization [4] and anionic polymerization of masked disilenes [5].

The dehydrocoupling of primary silanes by a metallocene from the titanium triad was first reported by Harrod in 1985 [6]. The coupling products of $PhSiH_3$ with average degree of polymerization ($D_p$) of 10 from $Cp_2TiMe_2$ [7] and up to 20

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for $Cp_2ZrMe_2$ [8] have been reported. However, with $Cp_2TiPh_2$ under more forcing conditions an average $D_p$ value of only 7 was observed [9]. The alkylsilane $^nBuSiH_3$ provided linear and cyclic products with $D_p$ values from 2 through 8 in the presence of $Cp_2ZrMe_2$ [10]. Although aspects of the dehydrocoupling of hydrosilanes have recently been reviewed the mechanistic details of the condensation process are not yet resolved [3,11].

We recently reported that the catalyst generated from the combination of the commercially available reagents $Cp_2ZrCl_2$ and $^nBuLi$ can provide oligomers with $D_p$ values from 2 through 8 from the secondary silane $PhMeSiH_2$ [12]. The studies have been extended and we report here our results of the condensation of primary silanes with both alkyl and phenyl substituents in the presence of all three of the titanium triad metals in the combination of $Cp_2MCl_2$ and $^nBuLi$.

## Results

The coupling reactions of primary silanes were conducted in toluene at room temperature with a silane to metallocene ratio usually between 50 and 70 and monitored by gas chromatography from the time of addition of the silane to the catalyst system to the termination of the reaction. Oligomer assignments were verified by GC-MS but the maximum chain length observed under these conditions was shorter than those observed on the GC columns employed. In general the parent ions are observed through the linear tetrasilane although very weak parent ions were observed for the pentasilane and hexasilane from $BuSiH_3$. Parent ions for the cyclopolysilanes were observed through the $Si_7$ system.

The approximate conversion of starting silane to oligomers was determined by removal of volatile material under vacuum when the reactions were terminated. Under the conditions used to monitor oligomer formation starting silane appeared in the solvent front therefore the data are summarized in the Tables as distribution of oligomers.

*Condensation of $PhSiH_3$.* Oligomers of $H(PhSiH)_xH$ from disilane ($x = 2$) through pentasilane ($x = 5$) were observable under the GC and GC-MS conditions employed, although the molecular ion of the pentasilane was not observed. An additional oligomer or oligomers was observed in the GC trace which was assumed to be at least the hexasilane. Phenylsilane condenses rapidly in the presence of $Cp_2MCl_2/^nBuLi$ (M = Ti, Zr) but more slowly with $Cp_2HfCl_2/^nBuLi$ as illustrated in Table 1. The percent conversion of starting material was not determined until reactions were terminated and volatile material was removed. On this basis, consumption of starting silane occurs more rapidly in the zirconium system. Essentially quantitative conversion of $PhSiH_3$ with the zirconium catalyst occurs after 1 h whereas longer than 5 h is required for titanium. With hafnium only about 25% conversion to oligomers occurs after 24 h.

The initial products of condensation are linear oligomers and cyclic products would not be expected until the chain length contained five and/or six silicon atoms. The molecular weight of the oligomers present in the product mixture after 24 h was measured by GPC against a polystyrene standard and showed a bimodal distribution with $M_w = 1775$ ($M_w/M_n = 1.17$) and 614 ($M_w/M_n = 1.01$) from the zirconium catalyst and $M_w = 1308$ ($M_w/M_n = 1.09$) and 600 ($M_w/M_n = 1.03$) from the titanium catalyst. When the reaction of $PhSiH_3$ with $Cp_2ZrCl_2/^nBuLi$ was

Table 1

Condensation of $PhSiH_3$ in the presence of $Cp_2MCl_2/{}^{n}BuLi$

| $Cp_2MCl_2$ M | Temp. [a] (°C) | Time (h) | Distribution of oligomers [b] | | | | |
|---|---|---|---|---|---|---|---|
| | | | $Si_2$ | $Si_3$ | $Si_4$ | $Si_5$ | $Si_x$ |
| Ti | 20 | 0 [c] | 100 | – | – | – | – |
| | | 0.5 | 79 | 21 | – | – | – |
| | | 1 | 62 | 27 | 8.5 | 2.5 | – |
| | | 5 | 25 | 26 | 21 | 16 | 9.1 [d] |
| | | 24 [e] | | | | | |
| Zr | 20 | 0 [c] | – | – | – | – | – |
| | | 0.25 | 38 | 28 | 19 | 12 | 2.9 |
| | | 0.50 | 33 | 28 | 22 | 14 | 3.7 |
| | | 1 | 29 | 24 | 24 | 17 | 4.5 [f] |
| | | 5 [e] | | | | | |
| | 0 | 0 [c] | – | – | – | – | – |
| | | 0.5 | 64 | 36 | – | – | – |
| | | 2.5 | 52 | 33 | 15 | – | – |
| | | 5 [g] | | | | | |
| Hf | 20 | 0 [c] | 0 | – | – | – | – |
| | | 1 | 100 | – | – | – | – |
| | | 3 | 73 | 21 | 5.2 | – | – |
| | | 5 | 61 | 26 | 9.1 | 4.0 | – |
| | | 24 [h] | 44 | 29 | 14 | 10 | 2.3 |
| | 50 | 0 [c] | – | – | – | – | – |
| | | 0.25 | 67 | 25 | 7.3 | – | – |
| | | 0.5 | 50 | 30 | 14 | 6.2 | – |
| | | 1.0 | 40 | 29 | 17 | 11 | 3.0 |
| | | 3.0 | 29 | 25 | 22 | 16 | 7.8 [i] |
| | | 5.0 | 28 | 26 | 23 | 17 | 6.4 [j] |
| | | 24 [k] | | | | | |

[a] Reactions performed in toluene with $Cp_2MCl_2/2{}^{n}BuLi$ with a Si/M mole ratio between 50 and 70. [b] Distribution determined from uncorrected GC data: [oligomer/sum of oligomers]×100. $Si_2 = H(PhSiH)_2H$, *etc.* [c] First aliquot after addition of silane. [d] Additional component, 2.9% $Ph_2SiH_2$. [e] 100% mass recovery after removal of volatiles. [f] Additional components, 9.8% of oligomers with $Ph_2Si$ unit. [g] 46% mass recovery. [h] 27% mass recovery. [i] Additional components, 8.9% of oligomers with $Ph_2Si$ units. [j] Additional components, 13% of oligomers with $Ph_2Si$ units. [k] 59% mass recovery.

determined after 9.5 h a bimodal distribution was also observed with $M_w = 1677$ ($M_w/M_n = 1.12$) and 678 ($M_w/M_n = 1.02$). The observation of the lower molecular weight material suggests the presence of cyclopentasilane and/or cyclohexasilane.

Heating promotes the formation of longer oligomers with the $Cp_2HfCl_2/{}^{n}BuLi$ combination. After 1 h at room temperature only disilane was observed but heating at 50°C produced disilane through pentasilane in the same time period. Heating also increases the percent conversion of the starting silane. These observations parallel those reported for the condensation of $PhMeSiH_2$ [12]. Small amounts of oligomer products with $Ph_2Si$ units are observed with the hafnium catalyst when mixtures are heated. Such oligomers were also found with the zirconium catalyst.

Table 2

Condensation of $^n$BuSiH$_3$ in the presence of Cp$_2$MCl$_2$ / $^n$BuLi

| Time (h) | Cp$_2$MCl$_2$ [a] M | Distribution of oligomers [b] | | | | | |
|---|---|---|---|---|---|---|---|
| | | Si$_2$ | Si$_3$ | Si$_4$(a/b) [c] | Si$_5$($l$/c) [d] | Si$_6$($l$/c) [d] | Si$_x$($x$) [e] |
| 0.0 [f] | Ti [g] | [100] | – | – | – | – | – |
| | Zr [h] | [100] | – | – | – | – | – |
| | Hf [g] | 0 | – | – | – | – | – |
| 0.5 | Ti [g] | 44 | 25 | 22 (1/0.95) | 9 (1/0) | – | – |
| | Zr [h] | 68 | 26 | 6 (0/6) | – | – | – |
| | Zr [g] | 39 | 32 | 16 (1/5.5) | 12 (1/0.4) | – | – |
| | Hf [g] | 79 | 20 | – | – | – | – |
| 1.0 | Ti [g] | 24 | 18 | 24 (1/0.9) | 20 (1/0) | 9 (1/0) | 5 (7–8) |
| | Zr [h] | 54 | 30 | 10 (0/10) | 6 (1/0) | – | – |
| | Zr [g] | 30 | 29 | 18 (1/4) | 14 (1/0.3) | 8 (1/0.7) | 2 (7) |
| | Hf [g] | 74 | 26 | – | – | – | – |
| 3.0 | Ti [g] | 10 | 9 | 15 (1/0.9) | 18 (1/0.08) | 16 (1/0.65) | 33 (7–10) |
| | Zr [h] | 45 | 32 | 13 (1/41) | 15 (1/0.31) | – | – |
| | Zr [g] | 18 | 19 | 17 (1/1.8) | 16 (1/0.40) | 18 (1/1.5) | 12 (7–8) |
| | Hf [g] | 62 | 27 | 6 (0/6) | 2 (1/0) | – | – |
| 8.0 | Ti [g] | 5 | 5 | 7 (1/0.9) | 8 (1/0.20) | 11 (1/1.3) | 65 (7–11) |
| | Zr [h] | 27 | 25 | 15 (1/4.7) | 14 (1/0.43) | 11 (1/0.9) | 8 (7) |
| | Hf [g] | 61 | 32 | 8 (0/8) | 2 (1/0) | – | – |
| 24 | Ti [g,i] | 3 | 2 | 3 (1/0.9) | 4 (1/0.8) | 9 (1/7) | 78 (7–11) |
| | Zr [h,j] | 8 | 7 | 9 (1/0.8) | 8 (1/0.5) | 25 (1/4) | 42 (7–10) |
| | Hf [g,k] | 53 | 32 | 9 (0/10) | 6 (1/0.6) | – | – |

[a] Reactions performed in toluene with Cp$_2$MCl$_2$/2$^n$BuLi with a Si/M mole ratio between 50 and 60. [b] Distribution determined from uncorrected GC data: [oligomer/sum of oligomers]×100. Si$_2$ = H(BuSiH)$_2$H, *etc.* [c] Two diastereomers, a = isomer with shorter retention time with value set to 1 when both diastereomers are present. [d] Linear ($l$) and cyclic (c) oligomers. Linear isomer taken as 1. [e] Longer oligomers; range of $x$ in H($^n$BuSiH)$_x$H given. [f] First aliquot taken just after addition of $^n$BuSiH$_3$ to catalyst precursor. [g] Reactions run at 50°C. [h] Reactions run at 20°C. [i] Workup after 48 h gave 75% mass recovery. [j] Workup after 48 h gave 76% mass recovery. [k] Workup after 48 h gave 29% mass recovery.

*Condensation of RSiH$_3$ (R = $^n$Bu, $^n$Hex).* The condensation of alkylsilanes takes place at a slower rate than that exhibited by PhSiH$_3$. The results for $^n$BuSiH$_3$ are summarized in Table 2 and indicate a step growth nature for the condensation process. Oligomers containing up to 11 silicon atoms were observed in the GC traces and oligomers with up to seven silicon atoms could be characterized by GC-MS. The MS-data are similar to those reported by Hilty [10] for the condensation of $^n$BuSiH$_3$. With longer reaction periods cyclic products with five and more silicon atoms are formed although more slowly with titanium than with zirconium. The reactions of Cp$_2$HfCl$_2$/$^n$BuLi are quite slow even at 50°C where only 29% conversion of starting silane is observed after 48 h.

Table 3 details the Si–H region of the IR spectra of isolated reaction mixtures. Hilty has suggested [10] that linear oligomers usually exhibit an Si–H band > 2100$^{-1}$ and the corresponding cyclosilanes exhibit a band < 2100 cm$^{-1}$. The oligomers from condensation of n-BuSiH$_3$ with hafnium (run 5) contain only minor amounts

Table 3

IR data (SiH region) for coupling products of $^{n}BuSiH_3$

| Run | $Cp_2MCl_2$ M | Temp./Time (°C/h) | Conversion [a] | IR: SiH [b] ($cm^{-1}$) |
|---|---|---|---|---|
| 1 | Ti | 50/48 | 75 | 2102(st)<br>2079(sh) |
| 2 | Zr | 20/24 | 62 | 2108(st)<br>2084(sh) |
| 3 | | 20/48 | 75 | 2102(sh)<br>2080(st) |
| 4 | | 50/24 | 76 | 2098(sh)<br>2078(st) |
| 5 | Hf | 50/48 | 29 | 2114(st) |

[a] Based on the weight recovered after removal of volatile materials. [b] Thin film, KBr disk.

of cyclics and exhibit an Si–H band at 2114 $cm^{-1}$. All other samples exhibit a principal band either above or below 2100 $cm^{-1}$ as well as a shoulder below or above 2100 $cm^{-1}$ which most likely reflects the proportion of cyclic relative to linear products. This can be seen by comparing runs 2 and 4 (Table 3) for Zr where the linear products predominate for the room temperature run and cyclics dominate at the higher temperature run.

In the condensation of $^{n}BuSiH_3$ the two diastereomers of the tetrasilane are clearly discernible. Once formed the ratio of diastereomers produced in the presence of titanium remains constant throughout the time period and the ratio is approximately 1. In the case of the zirconium catalyzed condensation the two diastereomers are formed at different rates and the diastereomer with the longer retention time is formed initially and is also consumed more rapidly. With hafnium, only one diastereomer is observed from 3 h through 48 h. In the condensation of $^{n}HexSiH_3$ with the zirconium catalyst the diastereomer with the shorter retention time is also the slowest to form.

In the condensation of $^{n}HexSiH_3$ in the presence of $Cp_2ZrCl_2/^{n}BuLi$ the tetrasilane was the limit determined by GC-MS, however, GC data suggest that up to heptamer is observed and that both cyclic and linear products are formed. As with the previous cases the condensation occurs more rapidly at higher temperatures. For the reaction conducted at 50°C when volatile material was removed under vacuum up to 200°C a residue that probably contains mainly cyclics (Si–H, 2068 $cm^{-1}$) was obtained.

## Discussion

The formation of disilane and trisilane from $PhSiH_3$ in the presence of $Cp_2TiMe_2$ (DMT) or $Cp_2ZrMe_2$ (DMZ) has been monitored over short time periods by $^1H$ NMR spectroscopy [13] and similar measurements have been employed to follow the slow condensation over several weeks of $PhSiH_3$ to disilanes through tetrasilanes with $CpCp^*Hf(Cl)SiH_2Ph$ [14]. Overlap of the Si–H

Table 4

Dehydrocoupling of primary silanes: comparison of $Cp_2MMe_2$ and $Cp_2MCl_2$/$^n$BuLi

$RSiH_3 \xrightarrow{\text{toluene}} H(RSiH)_xH + (RSiH)_y$

| R | $Cp_2MMe_2$ M | $M_w$ or $x$, $y$ | Method [a] | $Cp_2MCl_2$/$^n$BuLi M | $M_w$ or $x$, $y$ | Method [a] |
|---|---|---|---|---|---|---|
| Ph | Ti | 950 [b] | VPO | Ti | 1300 [c] | GPC |
| | | | | | 600 | |
| | Zr | 1850 [d] | VPO | Zr | 1780 [c] | GPC |
| | | $x = 10$ [e] | GPC | | 614 | |
| | | $y = 5$ | | | | |
| | Zr | 2500 [f] | GPC | Zr | 1860 [g] | GPC |
| | | 5230 [h] | GPC | | 4300 [h] | GPC |
| | Hf | – [i] | | Hf | $x = 2–6$ [c] | GCMS |
| Bu | Zr | $x = 2–8$ [j] | GCMS | Zr | $x = 2–10$ [c] | GC/GCMS |
| | | $y \geq 5$ | | | $y \geq 5$ | |
| Hex | Ti | 984 [k] | VPO | – | – | – |
| | Zr | $x \sim 13$ [l] | GPC | Zr | $x = 2–7$ [c] | GC/GCMS |
| | | | | | $y \geq 5$ | |

[a] Method of measurement of $M_w$. [b] Calculated from data given in ref. 15, [cat] = 0.033 $M$, [$PhSiH_3$] = 1.6 $M$; 60°C; time period not specified. [c] This work. [d] Conditions unknown [16]. [e] [cat] = 0.075 $M$, [$PhSiH_3$] = 4.0 $M$; 1 d [13]. [f] [cat] = 0.012 $M$, [$PhSiH_3$] = 5.63; 41 h; GPC measurement on raw polymer [10]. [g] [cat] = 0.016; [$PhSiH_3$] = 5.59; 7 h. GPC measurement on raw polymer [17]. [h] GPC measurement of fractionated polymer (after removal of cyclics) [17]. [i] [cat] = 0.10; [$PhSiH_3$] = 0.20; 20–90°C; 12 h, no reaction [18]. [j] [cat] = 0.080; [$BuSiH_3$] = 5.2 $M$, 1 d [19]. [k] Calculated from data given in ref. 15, [cat] = 0.014 $M$; [$HexSiH_3$] = 1.4 $M$, 20°C, time period not specified. [l] [cat] = 0.075 M; [$HexSiH_3$] = 3.1 $M$, 20 d [13].

signals for oligomers higher than the trisilane appears to preclude accurate analyses of reaction mixtures by $^1H$ NMR [13]. The average molecular weights or chain lengths of oligomer mixtures produced from $PhSiH_3$ in the presence of DMT, DMZ and from $^nBuSiH_3$ and $^nHexSiH_3$ in the presence of DMZ have been reported and the results are summarized in Table 4 and compared with data for the combined catalyst system employed in this study. Molecular weights have been determined by various methods and the reactions are not all performed under the same conditions of time, concentration and silane/catalyst ratio. Therefore comparisons of the preformed catalyst precursors, $Cp_2MMe_2$, with the combination catalyst precursor, $Cp_2MCl_2$/$^n$BuLi, are not readily made.

All reactions of the catalyst precursor combination $Cp_2MCl_2$/$^n$BuLi were carried out in toluene and results for zirconium differ from those for titanium both with respect to rate of consumption of the primary silane and the chain length of the oligomer formed. Rates are faster and chain lengths are longer with $Cp_2ZrCl_2$/$^n$BuLi. In addition, both catalyst systems appear to produce the same cyclic products. Earlier reports suggested that the products from $PhSiH_3$ were linear oligomers in which the chain lengths from $Cp_2ZrMe_2$ and $Cp_2TiMe_2$ differed on the basis of VPO measurements [16]. More recently the molecular weight and molecular weight distributions are described as essentially the same for the two catalysts and, in addition, cyclic oligomers are produced with both catalysts [13]. Waymouth and coworkers have presented data which suggest that the $M_w$

values for the oligomers increase with increasing concentration of $PhSiH_3$ [17]. Therefore the similarity of product mixtures produced from $Cp_2TiMe_2$ and $Cp_2ZrMe_2$ could occur in the more dilute solutions studied by Harrod [15,16]. Waymouth has also shown that when the cyclic products formed in the condensation of $PhSiH_3$ with DMZ are removed, the $M_w$ of the fractionated oligomers can double or triple that of the raw polymer [17]. The results obtained by Waymouth for the unfractionated polymer produced with $Cp_2ZrCl_2/{}^nBuLi$ and the results we obtained for the same catalyst system are similar.

Although $Cp_2HfMe_2$ does not promote the condensation of primary silanes the combination of $Cp_2HfCl_2/{}^nBuLi$ produces oligomers but at reasonable rates only above room temperature. Under similar conditions the average chain length of the oligomers formed increases through the sequence: $Hf < Ti < Zr$.

Only one set of reaction conditions was reported for the coupling of ${}^nBuSiH_3$ with DMZ and products were characterized only after a 24 h reaction period at room temperature by a combination of GCMS and GC/FT-IR [10]. The results with $Cp_2MCl_2/{}^nBuLi$ are similar to those observed with DMZ. However slightly longer oligomers are observed with $Cp_2MCl_2/{}^nBuLi$ for $M = Zr$. The condensation of $nBuSiH_3$ by DMT has not been reported but $Cp_2TiCl_2/{}^nBuLi$ is an effective catalyst although formation of oligomers is slower than with the zirconium system. With longer reaction times and/or higher temperatures cyclic oligomers are formed with both Zr and Ti systems. The condensation of ${}^nHexSiH_3$ occurs in a similar manner as that of ${}^nBuSiH_3$ but cannot be monitored for chain lengths longer than 7. As observed with DMT and DMZ the rate of coupling of primary alkylsilanes with $Cp_2MCl_2/{}^nBuLi$ is slower than that observed for phenylsilane.

If two different primary silanes are cocondensed, oligomers with mixed substituents should form. The coupling reaction of a mixture of ${}^nBuSiH_3$ and ${}^nHexSiH_3$ in a 1:1 molar ratio catalyzed by $Cp_2ZrCl_2/{}^nBuLi$ at 20°C was monitored by GC and the products were identified by GC/MS. The results are summarized in Table 5. The two monosilane products that incorporate a butyl group, $Bu_2SiH_2$ and $BuHexSiH_2$, are observed. In addition three disilanes HAAH, HABH, HBBH, and four trisilanes, HAAAH, HAABH (or HABAH), HABBH (or HBABH) and HBBBH ($A = {}^nBuSiH$; $B = {}^nHexSiH$) are observed in close to statistical amounts. All five of the tetrasilanes could be identified by GC-MS although $HAB_3H$ and $HB_4H$ did not exhibit parent ions. Overlap of higher oligomers of $HA_xH$ with the lower oligomer of $HB_{x-1}H$ precluded additional assignments in both GC and GC-MS data.

The stepgrowth formation of silicon chains from $PhSiH_3$ as described by both Tilley [14] and Harrod [13] in $^1H$ NMR experiments is also reflected in the GC-data summarized in Tables 1 and 2. However, the GC data also reveal additional details concerning the linear and cyclic products that are formed. In the condensation of ${}^nBuSiH_3$ the two diastereomers of the tetrasilane, $H({}^nBuSiH)_4H$ are formed in equal proportions with the titanium catalyst but only one diastereomer is observed with the hafnium system. With zirconium, one diastereomer is formed more rapidly with both ${}^nBuSiH_3$ and ${}^nHexSiH_3$ and also consumed more rapidly (see Table 2). When the reaction is conducted at higher temperatures (50°C) both diastereomers are formed in almost equal amounts. In the condensation of $PhSiH_3$ only one diastereomer is observed in the early stages of the

Table 5

Coupling of a mixture of $^{n}BuSiH_3$ (A) and $^{n}HexSiH_3$ (B) catalyzed by $Cp_2ZrCl_2$ / $^{n}BuLi$

| Time | Product distribution [a] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Si(R) | | $Si_2$ | | | $Si_3$ | | | | $Si_4$ | | |
| | A(R) [b] | B(R) [c] | $A_2$ | AB | $B_2$ | $A_3$ | $A_2B$ | $B_2A$ | $B_3$ | $A_4$ | $A_3B$ | $A_2B_2$ |
| 1.0 | 1.5 | 3.4 | 8.6 | 20 | 13 | 3.5 | 11 | 12 | 4.5 | 0.8 | 4.0 | 2.5 |
| 6.0 | 6.3 | 2.3 | 5.6 | 15 | 9.3 | 2.7 | 11 | 11 | 4.3 | 0.9 | 6.0 | – |
| 24.0 | 7.3 | 2.9 | 6.0 | 16 | 10 | 2.8 | 10 | 11 | 4.1 | 0.9 | 5.6 | – |

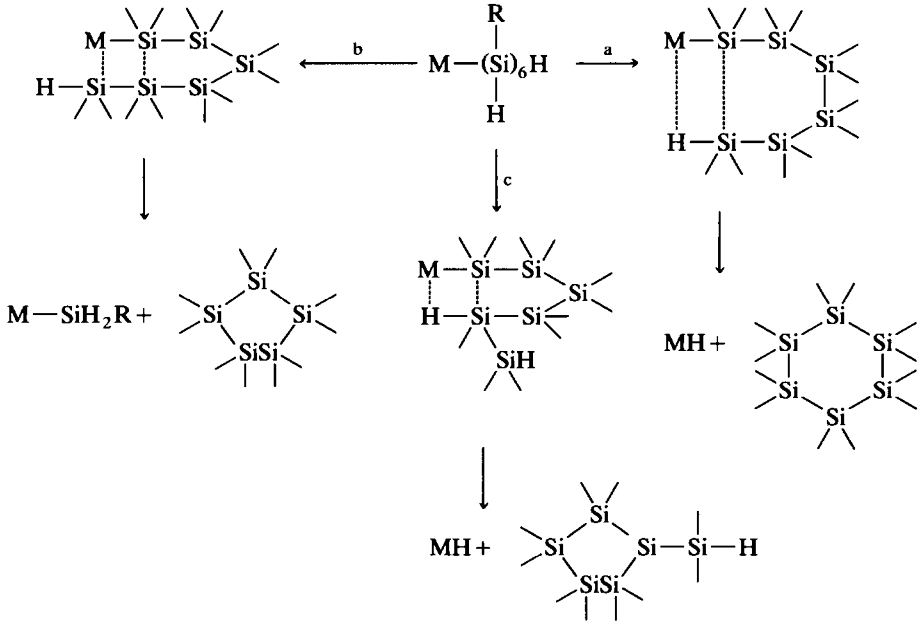
[a] Based on raw GC area%. Symbols $Si_2$ = disilane; $Si_3$ = trisilane, $Si_4$ = tetrasilane. A = derived from $BuSiH_3$; B = derived from $^{n}HexSiH_3$. [b] A(R) = $Bu_2SiH_2$.
[c] B(R) = $Bu(Hex)SiH_2$.

reaction but the second diastereomer is observed in trace amounts after 30 min in the case of zirconium and after 3 h in the case of titanium. Empirical force field calculations demonstrate that there are no conformational differences in the trimer and/or tetramer from $^{n}BuSiH_3$ and therefore the nonstatistical distribution appears to arise from the intermediate transition metal complex [19]. The observation of essentially one diastereomer in the condensation of $PhSiH_3$ (approximately 3 *M* silane solutions) is consistent with the formation of stereoregular polymers as reported in the condensation of $PhSiH_3$ with $Cp_2ZrMe_2$ and $Cp_2ZrHCl$ catalysts by Waymouth [17a] and with bis(indenyl)dimethylzirconium complexes by Harrod [17b]. When the condensation of $PhSiH_3$ is conducted in more dilute solutions the difference in rate of formation of the two diastereomers of the tetrasilane decreases [20].

With alkyl-substituted primary silane the presence of two diastereomers at the tetrasilane stage suggests the formation of mixtures of oligomers that may be atactic. Some evidence for this suggestion comes from the GC-MS analysis of the longer oligomers. Under the conditions used in these experiments two linear and two cyclic pentasilanes, two linear and three cyclic hexasilanes and two linear and five cyclic heptasilanes are observed. The larger number of cyclic polysilanes may be due to the formation of geometrical isomers but could also be due to the formation of silyl-substituted cyclopolysilanes, for example, the cycloheptasilanes could also contain silylcyclohexasilanes. The ratio of cyclic/linear polysilanes increases faster for the $Si_6$ system than for the $Si_5$ which may imply more facile formation of the six-membered ring. Although the GC data show the presence of higher cyclic (and linear) oligomers it seems less likely that ring sizes would continue to increase since intermediate ring sizes are thermodynamically less stable [1b].

The currently accepted mechanism for the dehydrocoupling of hydrosilanes by metallocene-based catalysts involves a series of sigma-bond metatheses as originally described by Tilley and coworkers [3a,21]. The formation of cyclic oligomers may result from an intramolecular metathesis reaction of $M(RSiH)_xH$ where $x = 5$. Scheme 1 illustrates possible metathesis reactions of a six-atom chain bound to a metal center. Reaction with a terminal Si–H (route a) or a terminal Si–Si bond (route b) leads to a six-membered ring and five-membered rings respectively. Reaction of an internal Si–H bond (route c) would provide silyl-substituted cyclics. A reaction of an internal Si–Si bond would lead to a four-membered ring for which there is no experimental evidence, although this process is possible for longer chains and could account for the observation that depolymerization occurs to convert linears to cyclics [11]. If the configuration at the silicon centers are random in $M(RSiH)_xH$ then different geometrical isomers would be expected for the cyclics that are formed. The tendency towards depolymerization and/or cyclic formation may be determined in the transition state that leads to the metathesis reaction. It is the formation of cyclics and/or the reaction of silicon–silicon bonds of oligomers that may result in the limitation of the current metallocene complexes for building polysilanes.

The condensation of $H_2PhSiSiPhH_2$ and $H_2PhSiSiPhHSiPhH_2$ with DMZ and DMT occurs stepwise when the reactions are carried out under conditions where the reactions are slow enough to monitor and oligomers with degrees of polymerization of 4, 6, 8..., or 6, 9, 12... respectively are formed [11]. The condensation



Scheme 1.

of $MeH_2SiSiH_2Me$ with DMT provided chains with three to eight silicon atoms in the early stages of reaction which suggests that reaction of silicon-silicon bonds occurs. The condensation of 1,2-dimethyldisilane with DMZ appears to give branched products which would occur if internal Si–H bonds in chains react [22].

Although the focus of this discussion has been on a comparison of the results of $Cp_2MMe_2$ and $Cp_2MCl_2/{}^nBuLi$ for the condensation of primary silanes data on a few other catalysts have also been reported. Tilley and coworkers have developed the catalyst system $CpCp^*M(SiR_3)R'$ ($M = Zr, Hf$; $R = SiMe_3$; $R' = Me, Cl$) where activity of the catalyst can be varied by changing R′ and M [23]. With $M = Zr$, $R' = Me$, the $M_w$ of the product obtained from $PhSiH_3$ (in toluene) after 40 h is ~ 1450 but contains 50% cyclics whereas a similar condensation with $M = Hf$, $R' = Cl$ at 90–100°C for 48–72 h gave a $M_w$ of 2733 [24]. However, Tilley has successfully built longer oligomers through a two step process by reacting $H(PhSiH)_xH$ (formed from the Hf catalyst) with $CpCp^*[SiR_3]Me$ to achieve $M_w$ close to 10,000 [23b]. This approach to building higher oligomers involves the use of a catalyst that minimizes cyclic formation followed by a catalyst that is effective for condensing secondary silanes (the chain end of the oligomers). Other catalyst systems based on the titanium triad such as $LTiMe_2$ (L = 1,2-bis(indenyl)ethane), $LZrCl_2/MeLi$ [L = 1,2-bis(tetrahydroindenyl)ethane] [25], $Cp_2ZrHCl$ [17] and $Cp_2TiPh_2$ [9] produce oligomers with $M_w$ usually lower than 1200 as do the recently reported organolanthanide catalysts, $Cp^*_2LnR$ [Ln = La, Nd, Sm, Y, Lu; R = H, $CH(SiMe_3)_2$] [26,27].

The purpose of this study was to monitor the condensation reaction at the early stages of the reaction. The results support the step-growth process for the condensation of primary silanes which occurs for all three catalysts systems,

$Cp_2MCl_2/2^nBuLi$ with some diastereomeric induction for M = Zr and Hf with both alkyl- and phenylsilane but not for Ti with alkylsilanes. Varying the concentration of the starting silane appears to affect the rate of formation of the diastereomers of the tetrasilane although there is no obvious explanation for this effect. In addition, GC-MS analysis has shown that both cyclic and linear products with the same number of silicon atoms contain more than one isomer. This observation suggests that if sigma-bond metathesis is the operative reaction pathway, catalysts that discriminate between the growing end of the chain and internal Si–H and Si–Si bonds will be required to construct longer oligomers.

## Experimental

### *General*

All reactions were carried out under an inert atmosphere of dry nitrogen or argon. Solvents were dried by standard techniques, and all glassware was dried in an oven at 110–120°C prior to use. Toluene and diglyme were purified by distillation and stored over molecular sieves.

The GC data were collected on a Varian Aerograph Series 1400 Gas Chromatograph with a 15 m × 0.54 mm i.d., 1.5 m film DB-5 column (J & W Scientific) [column A] at a flow rate of 6 mL/min helium, temperature programming 50–320°C (20°C/min) and recorded on a HP3394A integrator. The injection temperature was 200°C and detector was set at 320°C. Alternatively data were collected on a Shimadzu GC-14A Gas Chromatograph with column A or a DB-5 capillary column [column B] at the same flow rate and temperature programming but with different injector (275°C) and detector (350°C) temperatures and recorded on a Shimadzu CR601 integrator. Mass spectral data were collected on a Hewlett–Packard 5988A GC/MS instrument with an RTE-A data system with gas chromatographic separations in split injection mode using a 12.5 m (HP-1) capillary column. In most cases all fragments $> 10\%$ of the base peak and $m/e > 100$ are included. Infrared spectra were determined on a Perkin–Elmer model 1600 FT-IR spectrophotometer as thin films.

The following compounds were commercially available: $PhSiCl_3$, $^nBuSiCl_3$, $^nHexSiH_3$, $Cp_2ZrCl_2$, $Cp_2TiCl_2$, $Cp_2HfCl_2$, $LiAlH_4$. Commercial $^nBuLi$ (1.6 *M* in hexane) was periodically titrated to determine the active organolithium content. Concentrations used are 1.6 *M* unless specified otherwise. The hydrosilanes $PhSiH_3$ [28], $^nBuSiH_3$ [10] were prepared by literature methods from the chlorosilane and $LiAlH_4$.

### *Condensation of $PhSiH_3$*

*$Cp_2ZrCl_2/^nBuLi$.* In the drybox, $Cp_2ZrCl_2$ (87 mg, 0.30 mmol) was transferred into a preweighed 10 ml round-bottom flask and capped tightly. Degassed toluene (4.2 mL) was injected into the flask under nitrogen and the slurry was cooled in an ice-bath. The $^nBuLi$ (0.37 mL, 0.59 mmol) was injected by syringe. The colorless mixture turned yellow immediately and darkened to yellow-purple after stirring for 5 min at 0°C. Then $PhSiH_3$ (2.17 g, 20.0 mmol) was injected into the reaction flask, forming a light yellow clear solution, and bubbling occurred immediately. After removal of the ice-bath, vigorous bubbling was observed and the reaction mixture changed to orange within 15 min at room temperature.

Aliquots were removed periodically to prepare the GC samples by adding hexane followed by filtering through celite. The first aliquot was taken immediately after the silane was added. Analysis of the aliquots provided the following integration data (uncorrected) [time (min), area% of dimer, trimer, tetramer, pentamer, longer oligomers, {oligomers with $Ph_2Si$ units}]: 0.0 (no oligomers observed); 15.0 (36.8, 27.2, 19.0, 11.5, 2.8, 0, {0}); 30.0 (31.1, 26.8, 20.8, 13.1, 3.5, 0, {0}); 60 (24, 20, 20, 14, 3.7, {9.2}). The starting silane is coincident with the solvent front and after 1 h most of the short oligomers were converted to longer oligomers which could not be detected by GC.

$H(PhSiH)_2H$ (*m/e*): 214 ($M^+$, 5.8), 183 (100), 107 (19), 106 (13), 105 (54). $H(PhSiH)_3H$ (*m/e*): 320 ($M^+$, 1.1), 289 (10), 259 (12), 213 (15), 212 (37), 211 (24), 210 (30), 183 (35), 181 (14), 134 (11), 107 (15), 106 (13), 105 (100).

$H(PhSiH)_4H$ (*m/e*): 426 ($M^+$, 1.7), 319 (15), 318 (24), 288 (13), 287 (40), 259 (10), 240 (22), 212 (18), 211 (50), 210 (43), 209 (28), 208 (20), 207 (14), 183 (25), 181 (17), 107 (15), 106 (14), 105 (100). A trace of $PhSi(Bu)H_2$ [(*m/e*): 164 ($M^+$), 107 (100)] was observed.

The reaction mixture was stirred for 24 h at room temperature before removal of volatile material under vacuum. Hexanes (3 mL) and toluene (2 mL) were added and the resultant slurry was filtered through celite. After removal of the solvent at RT/0.6 mmHg for 20 min, a yellow colored gum (1.91 g) was obtained. IR: 2098 $cm^{-1}$ (SiH, strong). GPC data (THF, polystyrene standard): $M_w$, 1775 ($M_w/M_n$) = 1.17); 614 ($M_w/M_n = 1.01$) [29*].

In a second reaction, $Cp_2ZrCl_2$ (87 mg, 0.30 mmol) in toluene (4.2 mL) and $^nBuLi$ (0.38 mL, 0.60 mmol) were allowed to react with $PhSiH_3$ (2.24 g, 18 mmol) for 9.5 h before removal of catalyst and volatile material. GPC data (THF, polystyrene standard): $M_w$, 1680 ($M_w/M_n = 1.12$); 680 ($M_w/M_n = 1.02$) [29].

In a third reaction, $Cp_2ZrCl_2$ (57 mg, 0.20 mmol) in 2.8 mL toluene and $^nBuLi$ (0.25 ml, 0.40 mmol) were allowed to react with $PhSiH_3$ (1.47 g, 13.6 mmol) at 0°C. A bright yellow solution formed and bubbling lasted for almost 5 h. Analysis of aliquots showed the following composition [time (h), area% of dimer, trimer, tetramer]: 0.0 (0, 0, 0), 0.5 (64, 36, 0), 2.5 (52, 33, 15). Workup in a similar fashion after 5 h provided a light yellow thick oil (0.67 g, 46% mass recovery).

*$Cp_2TiCl_2/{}^nBuLi$.* In a similar fashion, the $Cp_2TiCl_2$ (44 mg, 0.18 mmol) in 2.5 mL toluene and $^nBuLi$ (0.22 mL, 0.35 mmol) were allowed to react with $PhSiH_3$ (1.22 g, 11.3 mmol) at 0°C to give a dark-green colored slurry. After removal of the ice-bath, slow bubbling was observed and lasted for several hours. Analysis of the aliquots showed the following oligomer composition [time (h), wt.% dimer, trimer, tetramer, pentamer]: 0.0 (100, 0, 0, 0), 0.5 (79, 21, 0, 0), 1.0 (62, 27, 8.5, 2.5), 5.0 (24, 24, 20, 15, {9.1% longer oligomers; 2.9% $Ph_2SiH_2$}). After 5 h most products are longer oligomers which were not detectable. Workup in the same manner, after 24 h at room temperature, provided a brown-red colored, viscous oil (1.23 g, 100% mass recovery). IR: 2110 $cm^{-1}$ (SiH, strong). GPC data (THF, polystyrene standard): $M_w = 1308$ ($M_w/M_n = 1.09$); 600 ($M_w/M_n = 1.03$) [29].

*$Cp_2HfCl_2/{}^nBuLi$.* In a similar fashion, $Cp_2HfCl_2$ (87 mg, 0.23 mmol) in toluene (3.2 mL) and $^nBuLi$ (0.31 mL, 1.5 *M*, 0.46 mmol) were reacted with

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* Reference number with an asterisk indicates a note in the list of references.

$PhSiH_3$ (1.51 g, 14.0 mmol) at room temperature (20°C) whereupon a light yellow colored slurry formed. Analysis of aliquots showed the following oligomer composition [time (h), area% of dimer, trimer, tetramer, pentamer]: 0.0 (no oligomers observed), 1.0 (100, 0, 0, 0), 3.0 (73, 21, 5.2), 5.0 (61, 26, 9, 4), 24 (44, 29, 14, 10, {2% hexamer}). Workup in the same manner after 24 h provided a colorless cloudy oil (0.41 g, 27% mass recovery). $^1$H NMR ($\delta$, $CDCl_3$): 4.38 (s, Si–H), 4.41 (m, Si–H), 7–7.6 (brd m, arom).

In a second run, $Cp_2HfCl_2$ (66 mg, 0.17 mmol) in 2.5 mL toluene and $^n$BuLi (0.23 mL, 1.5 $M$, 0.35 mmol) were allowed to react with $PhSiH_3$ (1.21 g, 11.2 mmol) at 50°C. A light yellow slurry formed and slow bubbling was observed for 3 h. Analysis of aliquots showed the following composition of oligomers [time (h), wt.% of dimer, trimer, tetramer, pentamer, longer oligomers, {$Ph_2Si$-containing oligomers}]: 0.0 (no oligomers observed), 0.25 (67, 25, 7.3, 0, 0 {0}), 0.5 (50, 30, 14, 6.2, 0, {0}), 1.0 (40, 29, 17, 11, 3, {0}), 3.0 (26, 23, 20, 14, 7.2, {8.9%}), 5.0 (23, 22, 19, 14, 5.4 {13%}). Workup in the same manner after 24 h provided a light yellow viscous oil (0.71 g, 59% mass recovery). IR: 2107 cm$^{-1}$ (Si–H), strong). $^1$H NMR ($\delta$, $CDCl_3$): 4.0–4.45 (brd, featureless, SiH), 4.38 (s, Si–H), 6.8–7.6 (brd, featureless, arom).

### *Condensation of $^n$BuSiH$_3$*

*$Cp_2ZrCl_2$/$^n$BuLi.* A slurry of $Cp_2ZrCl_2$ (53 mg, 0.18 mmol) in toluene (2.1 mL) was allowed to react with $^n$BuLi (0.30 mL, 1.2 $M$, 0.36 mmol) at 0°C before addition of $^n$BuSiH$_3$ (0.77 g, 8.7 mmol) to give an orange-colored solution. After removal of the ice-bath, the solution turned to a brown-red color and slow bubbling was observed which lasted for 3 h. Analysis of aliquots showed the following composition of oligomers [time (h), area% of $Bu_2SiH_2$, dimer, trimer, tetramer (two isomers), pentamer (linear/cyclic), hexamer (linear/cyclic), longer oligomers, {$Bu_2Si$ containing oligomers)]: 0.0 (94.4, 5.5, 0..), 0.5 (44, 34, 13, 0/2.8, 0, 0, 0, {6.5}), 1.0 (33, 32, 18, 0/6, 3.8(1), 0, 0, {6.1}), 3.0 (28, 29, 21, 0.2/8.2, 4.8/1.5, 0, 0, {5.2}), 8.0 (20, 21, 19, 2/9.4, 7.8/3.4, 4.3/4.0, 6.4, {3.7%}), 24 (15, 7, 6, 4.0/3.3, 4.4/2.2, 4.1/16.6, 35, {2.2}), 48 (12, 2, 2, 1.3/0.7, 0.6/0.9, 1.8/13, 62, {1.7}). The starting silane appears in the solvent front. The fragments generated from the oligomers contain clusters which differ in the number of hydrogens with a range that can be up to 8 mass units. For data enclosed in brackets only the most intense ion in such clusters is provided.

($^n$Bu)$_2$SiH$_2$ ($m/e$): 144 ($M^+$, 1.9), 143 (2.3), 142 (6.9), 114 (14), 87 (39), 86 (16), 73 (57), 59 (100), 58 (33).

H($^n$BuSiH)$_2$H ($m/e$): 174 ($M^+$, 22), 117 ($M^+$-Bu, 14) [89 (26), 88 (13), 87 (61), 86 (96), 85 (32), 75 (16), 71 (12), 59 (89), 58 (100), 57 (17)].

H($^n$BuSiH)$_3$H ($m/e$): 260 ($M^+$, 4.3), 172 ($M^+$-BuSiH$_3$, 100), 144 (22), 141 (84) [117 (33), 116 (69), 114 (23), 89 (25), 85 (72), 84 (75), 59 (20)].

H($^n$BuSiH)$_4$H, two isomers ($m/e$): 346 ($M^+$, absent), 258 ($M^+$-BuSiH$_3$, 14), 202 ($M^+$ – Bu$_2$SiH$_2$, 56), 171 (19), 170 (18), [146 (52), 141 (20), 121 (38), 115 (80), 114 (100), 105 (24), 85 (54)]; 346 ($M^+$, 0.3), 258 (48), 202 ($Bu_2Si_3H_4$, 100), 171 (28), 170 (25) [146 (64), 115 (54), 114 (88), 85 (34)].

H($^n$BuSiH)$_5$H ($m/e$): 432 ($M^+$, absent), 344 ($M^+$ – BuSiH$_3$, 31), 288 (47), 258 (22), 256 (20), 233 (57), 232 (100), 202 (62), 200 (93) [177 (62), 176 (61), 175 (41), 147 (67), 146 (56), 145 (84), 144 (89), 121 (70), 119 (77), 117 (69), 115 (83), 114 (71), 113 (62), 85 (55)].

$(^n\text{BuSiH})_5$ (*m/e*): 430 ($M^+$, 51), 344 (14), 343 (21), 342 ($M^+ - \text{BuSiH}_3$, 56), 286 ($M^+ - \text{Bu}_2\text{SiH}_2$, 100), 230 (89) [174 (51), 143 (21), 117 (13)].

A total of five $\text{Si}_6$-containing species was observed. Data for two examples are provided.

$\text{H}(^n\text{BuSiH})_6\text{H}$ (*m/e*): 518 ($M^+$, absent), 430 (2.3), 344 (10), 342 (8), 288 (16), 286 (25), 232 (28), 230 (32) [205 (25), 202 (29), 200 (28), 177 (33), 175 (52), 171 (31), 147 (64), 145 (67), 144 (56), 143 (55), 133 (25), 121 (49), 119 (58), 117 (64), 115 (80), 113 (63), 85 (65), 59 (100)].

$(^n\text{BuSiH})_6$ (*m/e*): 516 ($M^+$, 10), 428 (67), 372 (66), 316 (79), 286 (13), 262 (25), 261 (51), 260 (82), 235 (20), 230 (19), 229 (20), 218 (20) [205 (43), 204 (50), 203 (47), 201 (20), 199 (23), 179 (37), 175 (63), 173 (55), 171 (55), 149 (41), 147 (63), 145 (47), 143 (64), 117 (45), 115 (49), 113 (46), 87 (28), 85 (40), 59 (100)].

A total of six $\text{Si}_7$-containing species was observed. Data for two examples are given.

$\text{H}(^n\text{BuSiH})_7\text{H}$ (*m/e*): 604 ($M^+$, absent), 517 (6) [430 (55), 373 (38), 344 (35), 342 (70), 319 (28), 317 (43), 288 (40), 287 (40), 286 (75), 261 (44), 231 (47), 230 (58), 205 (51), 203 (45), 199 (30), 177 (42), 175 (100), 173 (62), 149 (43), 147 (78), 145 (70), 143 (70), 119 (43), 117 (51), 115 (50), 113 (39), 89 (29), 87 (25), 85 (42), 59 (65).

$(^n\text{BuSiH})_7$ (*m/e*): 602 ($M^+$, 6.3) [515 (58), 514 (69), 459 (37), 458 (32), 428 (55), 403 (36), 372 (48), 347 (40), 316 (52), 291 (32), 289 (32), 260 (42), 233 (75), 229 (29), 205 (70), 203 (80), 201 (76), 199 (71), 197 (40), 179 (36), 177 (60), 175 (71), 173 (83), 171 (67), 147 (49), 145 (52), 143 (88), 140 (80), 117 (33), 115 (43), 113 (30), 87 (37), 85 (38), 59 (100)].

After 48 h at room temperature, volatile material was removed under vacuum. Hexanes (5 mL) were added to the residue and the mixture was filtered through celite. Removal of the solvent from the filtrate at room temperature (0.3 mmHg) for 20 min, provided a yellow oil (0.58 g, 75% mass recovery).

In a second reaction, $\text{Cp}_2\text{ZrCl}_2$ (100 mg, 0.37 mmol) in 2.5 mL toluene and $^n\text{BuLi}$ (0.57 mL, 1.3 *M*, 0.74 mmol) were allowed to react with $^n\text{BuSiH}_3$ (2.23 g, 25.3 mmol) at room temperature for 24 h. After workup in the same manner, a bright yellow clear oil (1.38 g, 62% mass recovery) was obtained. Product mixture, IR: 2108 $\text{cm}^{-1}$ (Si–H, strong) and 2084 $\text{cm}^{-1}$ (Si–H, sh).

In a third reaction, $\text{Cp}_2\text{ZrCl}_2$ (157 mg, 0.54 mmol) in 3.7 mL toluene and $^n\text{BuLi}$ (0.67 mL, 1.07 mmol) were allowed to react with $^n\text{BuSiH}_3$ (3.14 g, 35.5 mmol) at 50°C for 24 h. Analysis of aliquots showed the following composition of oligomers [time (h), area% of $\text{Bu}_2\text{SiH}_2$, dimer, trimer, tetramer (two isomers), pentamer (linear/cyclic), hexamer (linear/cyclic), longer oligomers, {$\text{Bu}_2\text{Si}$ containing oligomers}]: 0.5 (13, 34, 28, 2.2/12, 7.7/2.7, 0, 0, {0}), 1.0 (11, 26, 25, 3.1/12.4, 9.0/2.8, 4.1/3.0, 1.5, {1.1}), 3.0 (9.8, 16, 17, 5.6/10.1, 10.5/4.2, 6.5/10, 10.9), 5.0 (9.0, 8.8, 9.1, 6.1/5.9, 7.9/2.8, 5.8/16, 27), 24 (11, 2.5, 1.8, 1.1/0.9, 2/1, 1/11, 66 {0.7}). After workup in a similar manner a yellow oil (2.38 g, 76% mass recovery) was obtained. IR: 2078 $\text{cm}^{-1}$ (Si–H, strong), 2098 $\text{cm}^{-1}$ (Si–H, shoulder). An attempt to distil the short oligomers from the product mixture was not successful.

*$\text{Cp}_2\text{TiCl}_2$/$^n$BuLi.* In similar fashion, the $\text{Cp}_2\text{TiCl}_2$ (61 mg, 0.25 mmol) in toluene (2.8 mL) and $^n\text{BuLi}$ (0.41 mL, 0.49 mmol) were allowed to react with $^n\text{BuSiH}_3$ (1.13 g, 12.8 mmol) at 0°C and formed a dark brown slurry. The ice-bath

was removed and the flask placed into a 50°C oil bath where the reaction mixture turned to blue-black. Analysis of aliquots showed the following distribution of oligomers [time (h), wt.% of $Bu_2SiH_2$, dimer, trimer, tetramers (two isomers), pentamers (linear/cyclic), hexamers (linear/cyclic), longer oligomers]: 0.0 (73, 22, 0...), 0.5 (26, 32, 18, 8.5/8.1, 6.8 (1/0), 0, 0, 0], 1.0 (17, 20, 15, 11/9.4, 17/0, 7.7/0, 4.4), 3.0 (13, 8.3, 7.7, 6.6/5.9, 14/1.1, 8.5/5.5, 28), 8.0 (13, 4.5, 4.0, 3.0/2.7, 5.9/1.2, 4.1/5.4, 56), 24 (12, 2.5, 2.2, 1.5/1.4, 1.9/1.4, 1.0/7.3, 69). Workup after 48 h provided a dark brown oil (0.85 g, 75% mass recovery). IR: 2102 $cm^{-1}$ (Si–H, strong) and 2079 $cm^{-1}$ (Si–H, sh).

*$Cp_2HfCl_2$/$^n$BuLi.* A slurry of $Cp_2HfCl_2$ (72 mg, 0.19 mmol) in toluene (2.2 mL) and $^n$BuLi (0.33 mL, 1.2 *M*, 0.39 mmol) were allowed to react with $^nBuSiH_3$ (0.83 g, 9.4 mmol) in an ice-bath. After a few minutes, the reaction flask was placed into a 50°C oil-bath and a cream-colored cloudy solution formed. Analysis of the aliquots showed the following distribution of oligomers [time (h), wt.% of $Bu_2SiH_2$, dimer, trimer, tetramer, pentamer]: 0 (79, oligomers absent), 0.5 (28, 57, 15, 0), 1.0 (23, 57, 20, 0, 0) 3.0 (18, 51, 22, 5.1, 3.9), 8.0 (17, 48, 25, 6.3, 2.0(1)), 24 (16, 45, 27, 7.5, 3.3), 48 (14, 39, 28, 8.2, 4.0/2.8). Workup after 48 h provided a light yellow oily material (0.24 g, 29% mass recovery).

*Condensation of ($^n$Hex)$SiH_3$ catalyzed by $Cp_2ZrCl_2$/$^n$BuLi*

The $Cp_2ZrCl_2$ (48 mg, 0.16 mmol) in 1.5 mL toluene and $^n$BuLi (0.21 mL, 0.33 mmol) were allowed to react with $^nHexSiH_3$ (1.29 g, 11.1 mmol) at 20°C in a manner similar to the $^nBuSiH_3$ case. Analysis of aliquots showed the following distribution of oligomers [time (h), wt.% of (Hex)$BuSiH_2$, dimer, trimer, tetramers (two isomers), pentamer (linear/cyclic)]: 0 (57, 39, 0, 0, 0, 0), 1.0 (22, 49, 23, 1.2/4.7, 0, 0, 0), 2.0 (20, 42, 24, 3.3/6.6, 4.2, 0), 24 (41, 24, 13, 9.1/4.8, 8.3/3.3). The starting material n-$HexSiH_3$ appeared in the solvent front. Workup after 48 h provided a light yellow oil (1.06 g, 0.94 g of oligomers, 73% mass recovery).

(Hex)(Bu)$SiH_2$ (*m/e*): 172 ($M^+$, 0.7), 171 (1.4), 170 (3.1), 142 (8.4), [115 (49), 87 (40), 73 (85), 59 (100)].

H($^n$HexSiH)$_2$H (*m/e*): 230 ($M^+$, 1.2), [115 (32), 114 (24), 99 (23), 86 (100), 73 (32), 59 (40)].

H($^n$HexSiH)$_3$H (*m/e*): 344 ($M^+$, 0.2), 228 (14), 197 (16), [145 (13), 115 (34), 114 (47), 113 (100), 112 (100), 97 (41), 85 (64)].

H($^n$HexSiH)$_4$H (two isomers; *m/e*): 458 ($M^+$, absent), 342 (26), 258 (17), 227 (30), 226 (24), 197 (20), [175 (21), 143 (53), 142 (55), 115 (64), 113 (100), 112 (70), 111 (87), 85 (74)]; second isomer (*m/e*): 458 ($M^+$, absent), 342 (26), 258 (14); 227 (25), 226 (26), [197 (18), 143 (46), 142 (57), 121 (43), 115 (43), 114 (32), 113 (100), 112 (78), 111 (76), 85 (61)].

In a second reaction, the $Cp_2ZrCl_2$ (72 mg, 0.24 mmol) in toluene (3.6 mL) and $^n$BuLi (0.41 mL, 1.2 *M*, 0.49 mmol) were allowed to react with ($^n$Hex)$SiH_3$ (1.49 g, 12.9 mmol) in a similar fashion at 0°C. A yellow-orange, clear solution formed. After removal of the ice-bath the reaction flask was placed into a 50°C oil-bath whereupon a dark brown slurry formed and bubbling occurred vigorously for about 2 h. Analysis of aliquots showed the following composition of oligomers [time (h), wt.% of (Hex)$BuSiH_2$, dimer, trimer, tetramer (two isomers), pentamers (linear/cyclic), longer oligomers]: 0 (45, 36, 0..), 0.5 (6.7, 31, 22, 3.8/9.2, 7.9/2.0, 14.9), 1.0 (4.9, 22, 16, 4.6/7.4, 8.9/2.7, 30), 3.0 (5.2, 16, 12, 5.8/5.6, 7.6/2.4, 40), 8.0 (3.7, 5.4, 3.7, 2.1/1.6, 3.8/1.8, 74), 24 (4.2, 2.0, 1.0, 1.1/0.5, 1.7/1.3, 87). Workup after 24 h gave a yellow oil (1.32 g, 89% mass recovery).

In a third reaction, the $Cp_2ZrCl_2$ (139 mg, 0.47 mmol) in 3.3 mL toluene and $^{n}$BuLi (0.60 mL, 0.95 mmol) were allowed to react with ($^{n}$Hex)$SiH_3$ (2.13 g, 18.4 mmol) at 20°C for 24 h. Workup in a similar fashion provided a yellow cloudy oil (1.42 g, 67% mass recovery). Kugelrohr distillation provided a fraction (0.03 g) with b.p. up to 210°C/0.03 mmHg [IR: 2125 $cm^{-1}$ (SiH)] and an undistilled residue (1.32 g) [IR: 2068 $cm^{-1}$ (SiH)].

In another reaction, $Cp_2ZrCl_2$ (166 mg, 0.57 mmol) in toluene (3.9 mL) and $^{n}$BuLi (0.71 mL, 1.14 mmol) were allowed to react with ($^{n}$Hex)$SiH_3$ (2.03 g, 17.6 mmol) at 20°C for 5 h. Workup in the same manner provided a yellow oil (0.53 g, 26% mass recovery). IR: 2114 $cm^{-1}$ (Si–H).

### *Condensation of a n-BuSiH$_3$/n-HexSiH$_3$ mixture catalyzed by Cp$_2$ZrCl$_2$/$^{n}$BuLi*

A sample of $Cp_2ZrCl_2$ (75 mg, 0.26 mmol) was transferred to a preweighed 10 ml round-bottomed flask and degassed toluene (2.0 mL) and $^{n}$BuLi (0.32 mL, 0.51 mmol) were added with cooling at 0°C. A brown-reddish colored slurry formed. Addition of $^{n}$BuSiH$_3$ (0.81 g, 9.2 mmol) and $^{n}$HexSiH$_3$ (1.08 g, 9.4 mmol) produced an orange-colored solution which changed to a brown color when removed from the ice-bath. Slow bubbling was observed which disappeared after 5 h. Analysis of aliquots showed the following distribution of products (GC area% are summarized in Table 5):

($^{n}$Hex)BuSiH$_2$, (*m*/*e*): 172 ($M^+$, 0.1), 170 (6.2), 142 (9.1), [115 (65), 87 (43), 73 (82), 59 (100)].

H($^{n}$HexSiH)($^{n}$BuSiH)H, *m*/*e*: 202 ($M^+$, 3.6), [115 (42), 114 (31), 99 (24), 89 (16), 87 (27), 86 (100), 85 (32), 73 (32), 59 (61)].

H($^{n}$BuSiH)$_2$($^{n}$HexSiH)H, (*m*/*e*): 288 ($M^+$, 1.3), 200 (23), [172 (47), 141 (49), 116 (49), 113 (79), 112 (74), 85 (100), 84 (97), 59 (42)].

H($^{n}$BuSiH)($^{n}$HexSiH)$_2$H, (*m*/*e*): 316 ($M^+$, 1.1), 228 (12), [200 (19), 197 (10), 169 (16), 145 (12), 113 (92), 112 (100), 97 (36), 85 (63), 84 (54)].

H($^{n}$BuSiH)$_3$($^{n}$HexSiH)H, (*m*/*e*): 374 ($M^+$, absent), 286 ($M^+-$ BuSiH$_3$, 58), 230 (47), [202 (62), 198 (34), 174 (13), 172 (19), 169 (21), 167 (19), 146 (61), 142 (60), 121 (55), 114 (100), 85 (81).

H($^{n}$BuSiH)$_2$($^{n}$HexSiH)$_2$H, (*m*/*e*): 402 ($M^+$, absent), 314 ($M^+-$ BuSiH$_3$, 48), 286 ($M^+-$ HexSiH$_3$, 37), 258 (10), [230 (50), 198 (51), 169 (31), 142 (81), 113 (100)].

After 24 h at room temperature, the volatile material was removed under vacuum and hexanes (5 mL) were added to the mixture. The slurry was then filtered through celite to produce a bright yellow colored filtrate. Evacuation of the filtrate at room temperature (2.5 mmHg) for 20 min gave a yellow oily material (0.88 g, 47% mass recovery). IR: 2110 $cm^{-1}$ (Si–H, strong), 2083 $cm^{-1}$ (Si–H, sh).

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