

# Dehydrogenative coupling of primary alkyl silanes using Wilkinson's catalyst

Lisa Rosenberg\*, Danielle N. Kobus

Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, BC, Canada V8W 3V6

Received 24 March 2003; received in revised form 28 June 2003; accepted 28 June 2003

## Abstract

Primary alkyl silanes ( $\text{RSiH}_3$ , where  $\text{R} = n\text{-C}_{12}\text{H}_{25}$  or  $n\text{-C}_8\text{H}_{17}$ ) undergo dehydrogenative coupling in the presence of  $(\text{Ph}_3\text{P})_3\text{RhCl}$  (**1**) to give oligomeric products.  $^{29}\text{Si}\{^1\text{H}\}$ -NMR and gel permeation chromatography suggest that chains of up to 5–6 silicons are forming in these reactions. Variations in product distributions observed for these two substrates, of supposedly comparable Si–H reactivity, may be correlated with the relative rates of departure of hydrogen gas from the reaction mixtures. The sensitivity of this system to  $\text{H}_2(\text{g})$  concentrations may ultimately allow control over specific chain lengths formed.

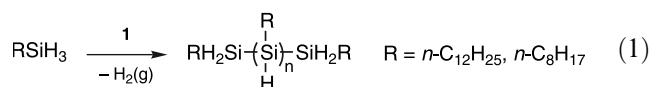
© 2003 Elsevier B.V. All rights reserved.

**Keywords:** Oligosilane; Alkyl silane; Dehydrogenative coupling; Rhodium catalyst

## 1. Introduction

Transition metal-catalyzed dehydrogenative coupling of silanes has been investigated primarily in the search for clean, high yield alternatives to Wurtz coupling for the production of high molecular weight (MW) polysilanes [1]. Most intensively studied have been the Group 4 metallocene catalyst systems, which can produce relatively high MW polymers (degree of polymerization (DP) as high as 70–100 monomer units) from primary aryl silanes [2]. Late transition metal complexes have received less attention in this context, since the coupling products resulting from late metal catalysis are almost invariably limited to short chains (2–5 silicons) [3]. Further, these catalysts typically exhibit competing catalytic activities for both dehydrocoupling and substituent redistribution reactions of hydrosilanes [4]. We recently showed that, for reactions of diaryl or mixed aryl–alkyl silanes with Wilkinson's catalyst,  $(\text{Ph}_3\text{P})_3\text{RhCl}$  (**1**), redistribution is actually slow relative to dehydrocoupling, allowing high chemoselectivity for the coupling reaction, under appropriate

conditions (vide infra) [5]. Furthermore, we observed *no* redistribution products in the coupling of *dialkyl* silanes, catalyzed by **1**, to di and trisilanes [6]. Given the typically enhanced reactivity of primary silanes in extended chain formation, relative to bulkier secondary or tertiary silanes [1], these results prompted us to examine the reactions of primary alkyl silanes in the presence of **1**, to probe the extent of dehydrocoupling in the (likely) absence of competing redistribution [7]. Established procedures for the zirconocene-catalyzed preparation of high MW poly(phenylsilane) hinge on pushing the reactions to extremely high monosilane conversion, since it is only under such conditions that the requisite coupling of intermediate-length chains to give long chains will occur [8]. Thus these methods employ high substrate concentrations and the removal of product dihydrogen under dynamic vacuum. For our studies, we therefore chose the relatively non-volatile substrates *n*-dodecylsilane,  $(\text{C}_{12}\text{H}_{25})\text{SiH}_3$ , and *n*-octylsilane,  $(\text{C}_8\text{H}_{17})\text{SiH}_3$ . We report here the dehydrocoupling reactions of these primary, alkylsilane substrates in the presence of catalytic amounts of **1** (Eq. (1)).



\* Corresponding author. Tel.: +1-250-721-7173; fax: +1-250-721-7147.

E-mail address: [lisarose@uvic.ca](mailto:lisarose@uvic.ca) (L. Rosenberg).

## 2. Results and discussion

### 2.1. Coupling reactions

Reactions were carried out in small glass vials open to the nitrogen atmosphere in a glovebox [9]. Bubbling, due to the loss of  $\text{H}_2(\text{g})$ , commenced immediately upon addition of neat *n*-dodecylsilane (clear liquid) to the solid catalyst, **1** (red, microcrystalline). This gas evolution was more dramatic for the analogous reaction of *n*-octylsilane (vide infra). Even with vigorous stirring, it took some minutes for the catalyst to completely dissolve in the silanes, at which point the mixture was typically a light golden-orange colour. The hydrogen evolution remained vigorous for up to half an hour, after which the bubbling gradually decreased, the mixtures became increasingly viscous, and the colour of the mixture also gradually darkened, ultimately to a dark rusty red–brown.

### 2.2. Oligomer product analysis

Although the relatively low volatility of the substrates employed in these dehydrocoupling reactions allowed us to efficiently remove  $\text{H}_2(\text{g})$ , without carrying off monosilane, during catalytic runs, it has hampered our ability to fully characterize the resulting, oligomeric products. Routine mass spectrometric (MS) and GC–MS techniques do not provide useful data for these extremely high-boiling oils. However,  $^{29}\text{Si}\{^1\text{H}\}$ -NMR spectra (71.55 MHz) of product mixtures for both *n*-dodecyl- and *n*-octylsilane suggest the DP is low. Sharp, discrete signals are observed in the range of  $-56$  to  $-72$  ppm, as shown for *n*-octylsilane in Fig. 1a. The total number of signals is small, relative to  $^{29}\text{Si}\{^1\text{H}\}$  spectra reported for high MW poly(arylsilanes), [10a,b] and even relative to spectra reported for linear, low MW oligo(phenylsilane) ( $\text{DP} = 2\text{--}5$ ), [10c] systems with analogous distributions of stereogenic centres, as a function of chain length, to our product oligomers. This is consistent with the presence of a small number of inequivalent types of Si centre in the mixture (i.e. a small range of shorter chain lengths and hence limited stereochemical variations). The low number of  $^{29}\text{Si}$ -NMR signals might also be attributable to the presence of many coincidental peaks (i.e. small or negligible chemical shift distinctions for silicons in similar environments for many different chain lengths), but we feel this is unlikely, since spectra of our samples exhibit a relatively wide chemical shift window, with peaks distributed over about 17 ppm, versus the 10 ppm window observed for di- through penta(phenylsilane)s [10c]. We have made tentative assignments for the monosilane through tetrasilane (two diastereomers) [11]. The remaining, unassigned peaks are presumably due to higher oligomers, and possibly cyclic oligomers. Gel permeation

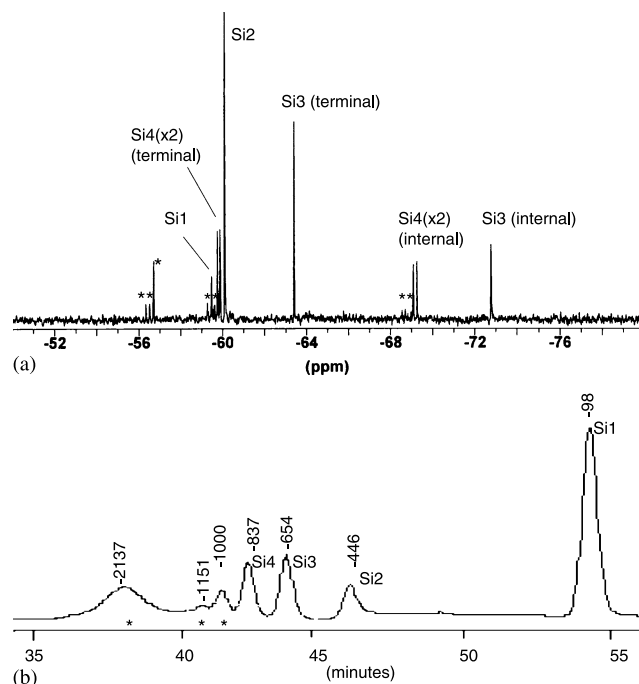


Fig. 1. (a) 71.5 MHz  $^{29}\text{Si}\{^1\text{H}\}$ -NMR spectrum ( $\text{C}_6\text{D}_6$ ) and (b) GPC trace for a sample of oligo(*n*-octylsilane), obtained from an experiment using 0.5 mol.% catalyst and a reaction time of 4 h, carried out in an open reaction vial in the glovebox (see Section 4). Peaks/regions marked with \* are not yet conclusively assigned. In the GPC trace, mass (relative to polystyrene) is indicated for each peak maximum (m.p.).  $M_w$  and  $M_n$  values are shown for this sample in Table 2, in Section 4. GPC relative integrals (shown in Table 2) are uncorrected.

chromatography (GPC) also suggests the products of dehydrocoupling are discrete oligomers. A typical GPC trace, with seven distinct integration regions, is shown for an oligo(*n*-octylsilane) sample in Fig. 1b. Four monodisperse peaks with longer elution times may be attributed to monosilane through tetrasilane. The three peaks with shorter elution times include two monodisperse peaks and one slightly broader peak (polydispersity (PD) = 1.05), which is probably correspond to chains of 5–6 silicons, which may exist in either cyclic or linear form [12]. We are currently exploring the use of MALDI MS experiments to more definitively characterize these oligomers.

We monitored the diagnostic Si–H region, from 3.5–6.0 ppm, in  $^1\text{H}$ -NMR spectra of catalytic reaction mixtures for *n*-dodecylsilane, to gauge the conversion of monomer to coupled products, and to assess the relative amounts of disilane and longer oligomers formed as a function of overall conversion. The highest field signals, due to terminal Si–H bonds, shift downfield for longer chains (Fig. 2). The mono and disilane show distinct multiplets in this region, corresponding to terminal  $\text{SiH}_3$  and  $\text{SiH}_2$  groups, respectively. The complexity of overlapping peaks at lower field, attributable to trisilane and longer chains, has so far precluded complete assignment of Si–H signals to specific oligo-

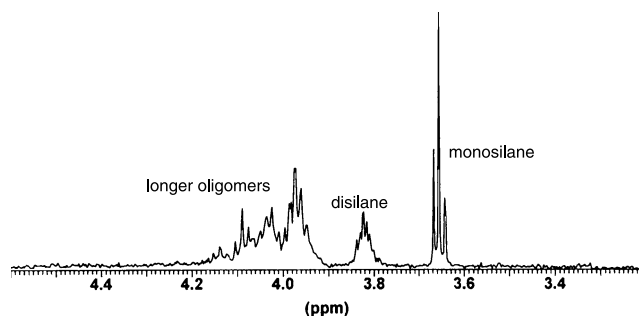


Fig. 2. Si–H region of the 500 MHz  $^1\text{H-NMR}$  spectrum of oligo( $n$ -dodecylsilane) in  $\text{C}_6\text{D}_6$ . The sample was obtained from an experiment using 0.5 mol.% catalyst and a reaction time of 4 h, carried out under dynamic vacuum (see Section 4).

mers. This region is complicated by the presence of both terminal and internal Si–H groups, and of multiple stereoisomers for chains of four or more silicons. Nevertheless, based on total Si–H relative integrals in this region of the  $^1\text{H-NMR}$  spectrum, we estimated crude values for (a) the conversion of monosilane to products and (b) the ratio of disilane to longer chains (Table 1, entries 1–4) [13]. The extent of oligomerization of  $n$ -dodecylsilane clearly increases with conversion, typical of the stepwise chain growth seen for condensation polymerization [8].

### 2.3. Sensitivity of catalyst system to removal of $\text{H}_2(\text{g})$

For reactions of  $n$ -dodecylsilane in the presence of **1** carried out for 4 h under dynamic vacuum, instead of at ambient glovebox pressure, crude conversions increased to an average of 80%. The disilane remained at about 30% (entry #5 in Table 1) of the product distribution under these conditions, but the amount of disilane gradually diminished over longer reaction times, to a minimum of  $\sim 20\%$  of the product distribution, at the highest conversions ( $\sim 95\%$ , at 13 h). The higher

Table 1  
Crude product distributions estimated from 300 MHz  $^1\text{H-NMR}$  spectra of oligo( $n$ -alkylsilane) mixtures

Entry	Substrate	Reaction time (h)	Conversion (%)	Ratio of $\text{Si}_2:\text{Si}_{n>2}$
1	$n$ -Dodecylsilane	1	20	72:28
2	$n$ -Dodecylsilane	2	36	42:58
3	$n$ -Dodecylsilane	3	44	32:68
4	$n$ -Dodecylsilane	4	59	29:71
5	$n$ -Dodecylsilane <sup>a</sup>	4	80	28:72
6	$n$ -Octylsilane	2	94 <sup>b</sup>	21:79
7	$n$ -Octylsilane	4	95 <sup>b</sup>	19:81

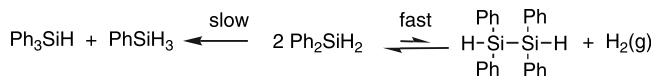
All reactions carried out with vigorous stirring of 0.5 mol.% **1** in neat substrate at room temperature, in vials open to the glovebox atmosphere, unless otherwise specified.

<sup>a</sup> Reaction carried out under dynamic vacuum.

<sup>b</sup> Conversions may be overestimated, due to volatility of substrate.

conversions we observe for dehydrocoupling of  $n$ -dodecylsilane under dynamic vacuum are consistent with the fact that this is a condensation reaction: removal of  $\text{H}_2(\text{g})$  should drive the reaction toward coupled product(s). This factor becomes more important in the context of the probable thermochemistry of silane coupling, since bond dissociation energies available for Si–H, H–H and Si–Si bonds suggest that the dehydrocoupling reactions may be close to thermoneutral [1c]. Indeed, we previously showed that the equilibrium for dehydrogenative coupling of diphenylsilane to 1,1,2,2-tetraphenyldisilane, which is very fast in the presence of **1**, lies heavily toward monosilane, and that disturbing this equilibrium by rapid removal of  $\text{H}_2(\text{g})$  is key to selectivity for coupling over redistribution in this system (Scheme 1) [5]. For  $n$ -dodecylsilane, we see no evidence of redistribution, but the increased conversions resulting from efficient  $\text{H}_2(\text{g})$  removal under vacuum suggests that similarly small, yet rapid, coupling equilibria may be in effect for this system. That longer times were then required to shift the product distribution from disilane to longer chains indicates that, at the rate of  $\text{H}_2(\text{g})$  removal from the mixtures achieved under dynamic vacuum, formation of trisilane is rate determining.

The extreme sensitivity of alkyl silane dehydrocoupling, in the presence of **1**, to the concentration of  $\text{H}_2(\text{g})$  is evident from the effect of even subtle changes in the viscosity of the substrate. For comparable reactions carried out in open vials, with stirring, in the glovebox, we observed a dramatic increase in coupling activity on switching from  $n$ -dodecylsilane to the slightly less viscous  $n$ -octylsilane as substrate. The  $n$ -octylsilane reactions show a striking amount of foaming and bubbling, immediately upon addition of the silane to solid **1**. Values for crude conversions, based on  $^1\text{H-NMR}$  spectroscopy, are apparently high (entries 6 and 7, Table 1), but are not entirely reliable indicators of the extent of consumption of monosilane, due to the relative volatility of residual  $n$ -octylsilane (b.p. 162–163 °C). A better indication of the greater coupling activity of this substrate, and an implicit indicator of high monosilane conversion (vide supra), is the low ratio of disilane to longer chains (21:79), observed after only 2 h reaction at ambient pressure (entry 6, Table 1). Clearly,  $\text{H}_2(\text{g})$  is leaving the reaction mixtures at a greater rate for  $n$ -octylsilane than for  $n$ -dodecylsilane, for reactions carried out in open vessels at ambient pressure. The relatively slow growth of longer oligo( $n$ -dodecylsilane) chains under conditions of dynamic vacuum, even at high conversions of monosilane to disilane, further



Scheme 1.

illustrates the impact of the higher viscosity of the *n*-dodecylsilane reaction mixtures: the resulting increase in local concentrations of H<sub>2</sub>(g) evidently affects the kinetics of the entire catalytic oligomerization reaction manifold [14].

### 3. Conclusions

We have shown that Wilkinson's catalyst is active, under mild conditions and at low catalyst concentration, for the dehydrogenative oligomerization of primary alkyl silanes to chains of up to 5–6 silicons. We continue to investigate this system, to identify conditions allowing quantitative conversions of monosilanes, and perhaps the formation of longer chain lengths. Regardless of whether high MW polysilanes are accessible for these substrates, however, the sensitivity of this catalysis to the rate of removal of H<sub>2</sub>(g) is of great interest. It points to the possibility of deliberate manipulation of product distribution, via careful balance of catalyst and substrate concentrations, and overall reaction conditions. We are currently exploring this promising route to the preparation of oligosilanes of discrete chain lengths.

### 4. Experimental

#### 4.1. General conditions, reagents, and instruments

Unless otherwise noted, all reactions and manipulations were done under an N<sub>2</sub>(g) atmosphere in an MBraun Unilab 1200/780 glovebox or using conventional Schlenk techniques. Hexanes, ether, and THF were purified by distillation from sodium/benzophenone under argon. Deuterated benzene, purchased from Cambridge Isotopes or CIL, was degassed and vacuum transferred from sodium/benzophenone. Wilkinson's catalyst, **1**, gave similar results whether prepared by the literature method [15] or purchased from Aldrich. *n*-Dodecyltrichlorosilane was purchased from United Chemical Technologies (UTC) and used without further purification. *n*-Octylsilane was purchased from UTC and distilled under nitrogen from CaH<sub>2</sub>. LiAlH<sub>4</sub> was purchased from ACP Chemicals, Inc. Florisil was purchased from Aldrich and placed in tapered glass columns (1 cm i.d. × 20 cm), plugged with cotton wool. The packed columns were dried for at least 16 h in an oven at 110–120 °C, then cooled overnight under vacuum in the glovebox antechamber.

NMR spectra were obtained on a Bruker AC300 instrument operating at 300.133 MHz (<sup>1</sup>H), a Bruker AC360 instrument operating at 360.136 MHz (<sup>1</sup>H), 90.565 MHz (<sup>13</sup>C DEPT), or 71.547 MHz (<sup>29</sup>Si DEPT), or a Bruker AV500 instrument operating at 500.133 MHz (<sup>1</sup>H) or 99.358 MHz (<sup>29</sup>Si). <sup>1</sup>H chemical

shifts are referenced to residual protonated solvent peaks at 7.15 ppm (C<sub>6</sub>D<sub>5</sub>H), relative to tetramethylsilane (TMS), <sup>13</sup>C chemical shifts are referenced to C<sub>6</sub>D<sub>6</sub> at 128 ppm relative to TMS, and <sup>29</sup>Si chemical shifts are referenced to external TMS. UV spectra were recorded for samples in cyclohexane on an Ultraspec 2100 instrument. IR spectra were recorded for neat samples between NaCl plates using a Perkin–Elmer FT-IR spectrometer (Spectrum 1000). GPC data was collected for samples dissolved in THF at 30 °C, using a Waters 515 HPLC pump equipped with Styragel<sup>®</sup> HR columns (3, 1, and 0.5 in series) and a Waters 2410 differential refractometer detector. MS was carried out using electron impact ionization (70 eV), on a Kratos Concept H instrument equipped with a non-polar GC column (oven temperature 100–250 °C). Elemental analysis was performed by Canadian Microanalytical Service, Ltd, Delta, BC, Canada.

#### 4.2. Synthesis of *n*-dodecylsilane, (C<sub>12</sub>H<sub>25</sub>)SiH<sub>3</sub>

This synthesis was adapted from a literature preparation of phenylsilane, PhSiH<sub>3</sub> [16]. *n*-Dodecyltrichlorosilane, (C<sub>12</sub>H<sub>25</sub>)SiCl<sub>3</sub> (24.5 ml, 25 g, 0.082 mmol), was added dropwise, with stirring, to LiAlH<sub>4</sub> (4.6 g, 0.12 mmol) in 200 ml diethyl ether, in a 500-ml round-bottom flask cooled in an ice bath. After the addition was complete, the resulting mixture was allowed to warm to room temperature, and was heated to reflux overnight. The resulting white precipitate was then allowed to settle, and the supernatant ether solution was decanted by cannula to a beaker containing HCl(aq) (3 M, 400 ml), cooled in an ice bath. The mixture was allowed to stir for 45 min, then the organic layer was extracted. The aqueous layer was washed with diethyl ether (3 × 100 ml), and the combined organic fractions were dried over MgSO<sub>4</sub> and filtered. Most of the ether was removed by rotary evaporation, and the resulting concentrate was distilled under vacuum (85 °C, 0.005 mmHg) to yield a clear liquid (13.3 g, 81% yield).

<sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, δ): 0.51–0.60 (m, 2H, CH<sub>3</sub>C<sub>10</sub>H<sub>20</sub>CH<sub>2</sub>SiH<sub>3</sub>); 0.92 (t, 3H, <sup>3</sup>J<sub>H–H</sub> = 7.5 Hz, CH<sub>3</sub>C<sub>10</sub>H<sub>20</sub>CH<sub>2</sub>SiH<sub>3</sub>); 1.25–1.35 (br overlapping m, 10H, CH<sub>3</sub>C<sub>10</sub>H<sub>20</sub>CH<sub>2</sub>SiH<sub>3</sub>); 3.66 (t, 3H, CH<sub>3</sub>C<sub>10</sub>H<sub>20</sub>CH<sub>2</sub>SiH<sub>3</sub>, <sup>1</sup>J<sub>Si–H</sub> = 192 Hz (from <sup>29</sup>Si satellites)). <sup>13</sup>C{<sup>1</sup>H}-NMR (90.5 MHz, C<sub>6</sub>D<sub>6</sub>, δ): 6.2 (terminal CH<sub>3</sub>, C12); 14.4 (Cα to Si, C1); 23.1 (C11); 26.7 (C2); 29.7–30.1 (C4–9); 32.4 (C10), 32.9 (C3). <sup>29</sup>Si{<sup>1</sup>H}-NMR (71.5 MHz, C<sub>6</sub>D<sub>6</sub>, δ): –59.5. Mass spectrum *m/z* (% abundance): 200(8) [M], 172(9) [M–(CH<sub>2</sub>)<sub>2</sub>], 144(4) [M–(CH<sub>2</sub>)<sub>4</sub>], 113(8) [M–(CH<sub>2</sub>)<sub>4</sub>SiH<sub>3</sub>], 99(27) [M–(CH<sub>2</sub>)<sub>5</sub>SiH<sub>3</sub>], 85(8) [(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>], 71(10) [(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>], 59(100) [CH<sub>2</sub>CH<sub>2</sub>SiH<sub>3</sub>], 43(25) [(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>]. High resolution mass spectrum Calc. for C<sub>12</sub>H<sub>28</sub>Si (monoisotopic): 200.1960. Found 200.1953 ± 0.0003. Anal. Calc. C<sub>12</sub>H<sub>28</sub>Si: C, 71.91; H, 14.08. Found: C, 71.28; H,

13.88%. UV:  $\lambda_{\max}$  (nm) = 196. IR ( $\text{cm}^{-1}$ ) 2141 (s) Si–H<sub>stretch</sub>; 925 (s) Si–H<sub>bend</sub>.

### 4.3. Oligomerization reactions

#### 4.3.1. Reactions performed in open vials in the glovebox

In a typical experiment, the catalyst **1** (2.5 mg, 0.0027 mmol) was weighed, outside the glovebox, into 1 dram, flat-bottomed vials, which were then taken into the glovebox. Substrate, either *n*-C<sub>12</sub>H<sub>25</sub>SiH<sub>3</sub> (108 mg, 0.539 mmol) or *n*-C<sub>8</sub>H<sub>17</sub>SiH<sub>3</sub> (78 mg, 0.54 mmol), and a flea stir bar were added to each vial, and the vials were placed on a stir plate, where vigorous stirring was established. After an allotted time period (1–18 h), hexane solutions (5 ml) of the reaction mixtures were filtered through florisil to quench the reactions and remove the catalyst. An extra 5 ml of hexanes was used to remove the Si-containing products from the columns. The hexanes was removed under vacuum from aliquots (~2 ml) of these solutions, and the residues were dissolved in benzene-*d*<sub>6</sub> for NMR analysis.

#### 4.3.2. Reactions performed under dynamic vacuum

These reactions were carried out for *n*-dodecylsilane, C<sub>12</sub>H<sub>25</sub>SiH<sub>3</sub>, on the same scale as described above. The catalyst was weighed into 5-ml round-bottom flasks and stir-bars were added. The flasks were attached to a Schlenk line via teflon needle-valve adaptors (Kontes, 4 mm), evacuated, and back-filled with nitrogen. Stir plates were placed underneath the flasks. The silane monomer was weighed in the glovebox, then transferred to 1.0-ml syringes equipped with short lengths of intramedic tubing. The syringes were removed from the glovebox with knots tied at the end of the tubing. The knots were clipped off with scissors, immediately before adding the silane to the catalyst via the needle valve, under a strong flow of nitrogen. The flasks were then evacuated, and were left under dynamic vacuum. Reaction start times were recorded as the time at which each flask was opened to full vacuum and vigorous stirring was established. To stop the reactions, the flasks were sealed under vacuum, taken into the glovebox, and quenched on florisil columns as described above.

#### 4.3.3. Characterization of oligomer product mixtures

The data shown below corresponds to the samples whose NMR spectra and GPC analyses are presented in Figs. 1 and 2 and Table 2.

For *n*-dodecylsilane: <sup>1</sup>H-NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>,  $\delta$ ): (See Fig. 2) 0.75–0.81 (overlapping m, CH<sub>3</sub>C<sub>10</sub>H<sub>20</sub>CH<sub>2</sub>Si); 0.86–1.00 (overlapping t, CH<sub>3</sub>C<sub>10</sub>H<sub>20</sub>CH<sub>2</sub>Si); 1.25–1.655 (br overlapping m, CH<sub>3</sub>C<sub>10</sub>H<sub>20</sub>CH<sub>2</sub>Si); 3.66 (t, SiH<sub>3</sub>, monosilane); 3.83 (m, SiH<sub>2</sub>, disilane); 3.97 (m, SiH<sub>2</sub>, trisilane); 3.92–4.20 (overlapping m, SiH and SiH<sub>2</sub>, trisilane and higher oligomers). <sup>29</sup>Si{<sup>1</sup>H}-NMR (71.5 MHz, C<sub>6</sub>D<sub>6</sub>,  $\delta$ ):

–72.8 (SiH trisilane); –69.3, –69.1 (SiH tetrasilane diastereomers); –65.8 (unassigned); –63.4 (SiH<sub>2</sub> trisilane); –60.1 (SiH<sub>2</sub> disilane); –59.9, –59.8 (SiH<sub>2</sub> tetrasilane diastereomers); –59.6 (unassigned); –59.5 (SiH<sub>3</sub> monosilane); –59.3, –56.7, –56.5, –56.4 (unassigned). UV (nm):  $\lambda_{\max}$  = 211. IR ( $\text{cm}^{-1}$ ): Si–H<sub>stretch</sub>, 2110 (m-s) Si–H<sub>bend</sub> 923 (m). GPC: see Table 2.

For *n*-octylsilane: <sup>1</sup>H-NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>,  $\delta$ ): 0.80–0.90 and 1.10–1.20 (overlapping m, CH<sub>3</sub>C<sub>10</sub>H<sub>20</sub>CH<sub>2</sub>Si); 0.90–1.10 (overlapping t, CH<sub>3</sub>C<sub>10</sub>H<sub>20</sub>CH<sub>2</sub>Si); 1.30–1.80, 1.90–2.15 (br overlapping m, CH<sub>3</sub>C<sub>10</sub>H<sub>20</sub>CH<sub>2</sub>Si); 3.74 (t, <sup>3</sup>J<sub>H-H</sub> = 3.0 Hz, SiH<sub>3</sub>, monosilane); 3.90 (m, SiH<sub>2</sub>, disilane); 4.05 (m, SiH<sub>2</sub>, trisilane); 4.00–4.30 (overlapping m, SiH and SiH<sub>2</sub>, trisilane and higher oligomers). <sup>29</sup>Si{<sup>1</sup>H}-NMR (99.4 MHz, C<sub>6</sub>D<sub>6</sub>,  $\delta$ ): (see Fig. 1a) –72.8 (SiH trisilane); –69.3, –69.1 (SiH tetrasilane diastereomers); –68.7, –65.8 (unassigned); –63.4 (SiH<sub>2</sub> trisilane); –60.1 (SiH<sub>2</sub> disilane); –59.9, –59.8 (SiH<sub>2</sub> tetrasilane diastereomers); –59.7 (unassigned); –59.5 (SiH<sub>3</sub> monosilane); –59.3, –56.7, –56.5, –56.4 (unassigned). UV (nm):  $\lambda_{\max}$  = 213. IR ( $\text{cm}^{-1}$ ) Si–H<sub>stretch</sub>, 2147, 2110 (s), Si–H<sub>bend</sub> 923 (s) GPC: see Fig. 1b and Table 2.

### Acknowledgements

We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for financial support, and D.J. Harrism for carrying out GPC analyses.

Table 2  
Examples of GPC data <sup>a</sup> for oligo(*n*-alkylsilane)s

Oligo( <i>n</i> -dodecylsilane) <sup>b</sup>				Oligo( <i>n</i> -octylsilane) <sup>c</sup>			
%Area	<i>M</i> <sub>w</sub>	<i>M</i> <sub>n</sub>	PD	%Area	<i>M</i> <sub>w</sub>	<i>M</i> <sub>n</sub>	PD
43	3435	3335	1.03	20	2184	2089	1.05
7	1894	1878	1.01	4	1211	1206	1.00
10	1498	1494	1.00	5	1002	1000	1.00
16	1242	1239	1.00	10	835	834	1.00
15	971	969	1.00	12	653	651	1.00
4	662	660	1.00	7	439	438	1.00
5	318	317	1.00	42	97	97	1.00

<sup>a</sup> *M*<sub>w</sub> relative to polystyrene standards. Relative integrals (% area) are uncorrected.

<sup>b</sup> Data for sample giving <sup>1</sup>H-NMR spectrum in Fig. 2. A baseline jump occurred as the first peak (*M*<sub>w</sub> = 318) was eluting, making integration of this signal unreliable. It is smaller than expected, so the other peak areas, calculated as a percentage of the total area, are somewhat higher than they should be.

<sup>c</sup> Data for sample giving <sup>29</sup>Si{<sup>1</sup>H}-NMR spectrum and GPC trace in Fig. 1.

## References

- [1] (a) T.D. Tilley, *Comments Inorg. Chem.* 10 (1990) 37; (b) J.Y. Corey, *Adv. Silicon Chem.* 1 (1991) 327; (c) F. Gauvin, J.F. Harrod, H.G. Woo, *Adv. Organomet. Chem.* 42 (1998) 363; (d) J.A. Reichl, D.H. Berry, *Adv. Organomet. Chem.* 43 (1999) 197.
- [2] (a) T. Imori, T.D. Tilley, *Polyhedron* 13 (1994) 2231; (b) V.K. Dioumaev, J.F. Harrod, *J. Organomet. Chem.* 521 (1996) 133.
- [3] See, for example (a) M.D. Fryzuk, L. Rosenberg, S.J. Rettig, *Inorg. Chim. Acta* 222 (1994) 345, and references therein. There are very few examples of late metal activities for the production of longer silicon chains ( $DP \geq 6$ ). These include (b) B.P.S. Chauhan, T. Shimizu, M. Tanaka, *Chem. Lett.* (1997) 785; (c) F.-G. Fontaine, T. Kadkhodazadeh, D. Zargarian, *Chem. Commun.* (1998) 1253.
- [4] M.D. Curtis, P.S. Epstein, *Adv. Organomet. Chem.* 19 (1981) 213.
- [5] L. Rosenberg, C.W. Davis, J. Yao, *J. Am. Chem. Soc.* 123 (2001) 5120.
- [6] Precedent for the lower migratory aptitude of Si-alkyls relative to Si-aryls in the presence of late transition metals includes [3a,b], and (a) P. Burger, R.G. Bergman, *J. Am. Chem. Soc.* 115 (1993) 10462.
- [7] Dehydrocoupling of primary alkyl silanes to low MW oligosilanes has previously been reported for Group 4 metallocene catalysts; see Ref. [2b] and (a) W.H. Campbell, T.K. Hilty, L. Yurga, *Organometallics* 8 (1989) 2615; (b) J.Y. Corey, X.-H. Zhu, *J. Organomet. Chem.* 439 (1992) 1; (c) H.-G. Woo, S.-Y. Kim, M.-K. Han, E.J. Cho, I.N. Jung, *Organometallics* 14 (1995) 2415; (d) R.M. Shaltout, J.Y. Corey, *Organometallics* 15 (1996) 2866.
- [8] T.D. Tilley, *Acc. Chem. Res.* 26 (1993) 22.
- [9] The high activity of this e-rich Rh catalyst for catalytic heterodehydrocoupling of Si–H bonds with H<sub>2</sub>O, ultimately leading to the formation of oligosiloxanes, necessitates rigorously dry conditions for these homodehydrocoupling reactions and their workup. L.S. Chang, J.Y. Corey, *Organometallics* 8 (1989) 1885.
- [10] (a) B.J. Grimmond, J.Y. Corey, *Organometallics* 18 (1999) 2223; (b) B.J. Grimmond, J.Y. Corey, *Organometallics* 19 (2000) 3776; (c) V.K. Dioumaev, K. Rahimian, F. Gauvin, J.F. Harrod, *Organometallics* 18 (1999) 2249.
- [11] (a) The progression of  $\delta^{29}\text{Si}$  for these products is consistent with assignments for terminal and internal Si's made previously for the  $^{29}\text{Si}\{^1\text{H}\}$ -NMR spectra of oligo(di-*n*-hexylsilane); (b) K. Obata, M. Kira, *Organometallics* 18 (1999) 2216.
- [12] GPC-derived MWs, relative to polystyrene standards (Table 2, Section 4), are considerably higher than expected for these small oligomers. In the absence of conclusive MS data, we cannot be certain of our assignments. However, we anticipate considerable discrepancy between absolute and calculated MWs, given the structural differences between polystyrene and our samples containing long alkyl side chains.
- [13] Since longest oligomers result from the *loss* of H<sub>2</sub> from shorter chains, these calculations are biased toward the shorter, more Si–H rich chains, and underestimate the amounts of longer chains. They serve only to establish trends in relative amounts, not absolute product distributions.
- [14] This is consistent with reports of the dehydropolymerization of phenylsilane in the presence of group 4 metallocene catalysts, where the addition of toluene to viscous reaction mixtures under dynamic vacuum is necessary to obtain high polymer. See Ref. [2a].
- [15] J.A. Osborn, G. Wilkinson, *Inorg. Synth.* 10 (1967) 68.
- [16] R.A. Benkeser, H. Landesman, D.J. Foster, *J. Am. Chem. Soc.* 74 (1952) 648.