

B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed reductions with hydrosilanes: Scope and implications to the selective modification of poly(phenylsilane)

by

Peter Tak Kwong Lee

Bachelors of Science, Simon Fraser University, 2006

Master of Science in Applied Science, Saint Mary's University, 2009

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of the Requirements for the Degree of

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in the Department of Chemistry

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University of Victoria

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## Supervisory Committee

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Dr. Jeremy Wulff, Department of Chemistry  
**Departmental Member**

Dr. Réal Roy, Department of Biology  
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## Abstract

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New complex silicon-containing molecules were made by  $B(C_6F_5)_3$ -catalyzed hydrosilation, dehydrocoupling, and dealkylative coupling reactions starting from Si-H reagents. The scope of reactions starting from disilane was expanded to include the formation of silicon-sulfur<sup>1</sup>, silicon-oxygen and silicon-alkyl side-chains. Reaction inhibition was found with some heteroatom substrates, such as phenols and imines, that strongly bound to  $B(C_6F_5)_3$ , and was consistent with the proposed mechanism (Chapter 2).  $B(C_6F_5)_3$  was found to be selective for Si-H activation in reactions of disilane and no competing Si-Si bond cleavage side-reactions were observed. This result will guide future studies and application of  $B(C_6F_5)_3$ -catalyzed reactions with polysilanes.

A different type of selectivity, the competing  $B(C_6F_5)_3$ -catalyzed over-reduction, is evaluated and discussed in Chapter 3. This over-reduction reaction was classified into two distinct cases: alkyl groups for which over-reduction reaction was dependent on the steric bulk of the alkyl group and benzylic groups for which over-reduction was dependent on having an  $\alpha$ -aryl group. These reactions are consistent with the proposed Piers-Oestreich mechanism (see Chapter 3) and suggest the rate-determining step for over-reduction is the nucleophilic attack of the alkoxy silane ( $R'-O-SiR_3$ ) to the

$R_3Si \cdots H \cdots B(C_6F_5)_3$  complex.<sup>2</sup> Benzylic side-chains were over-reduced regardless of the steric bulk of the aryl groups. Literature precedents suggest that benzyl over-reductions must undergo an alternative mechanism to the Piers-Oestreich mechanism. A number of mechanisms have been proposed in the literature and in Chapter 3, suggesting conventional heteroatom substrate-borane or silane-borane complexation.<sup>2</sup> Furthermore, over-reduction of benzylic sulfur-containing side-chains was found and this reaction was exploited in the  $B(C_6F_5)_3$ -catalyzed synthesis of unique silicon-sulfur-silicon-containing products. These over-reduction reactions highlighted the role of the silane for over-reduction and the challenges associated with the post-polymerization modification of poly(phenylsilane).

The advances in  $B(C_6F_5)_3$ -catalyzed synthesis of small silane molecules suggested reaction conditions and gave spectroscopic benchmarks that were applied to the post-polymerization modification of poly(phenylsilane) (Chapter 4). New X-modified poly(phenylsilane) derivatives with thiolato (sulfur), alkoxy/aryloxy (oxygen), amido (nitrogen) and alkyl (carbon) side-chains were prepared with 10-40% incorporation of the 'X' group into poly(phenylsilane). These new polysilanes were characterized by the following methods:  $^1H/^{13}C/^{29}Si$  NMR, IR, MALS-GPC, EA, and UV-vis absorption spectroscopy. Together, these characterization methods showed that the polysilane had not undergone Si-Si cleavage and thus demonstrated the utility of  $B(C_6F_5)_3$  for the selective activation of Si-H bonds. Thermal decomposition of X-modified poly(phenylsilane) derivatives and parent poly(phenylsilane) showed interesting redistribution pathways (Chapter 5). The thermal decomposition products of poly(phenylsilane) were identified: volatile monosilanes, a structurally complex not-yet-

identified phenylsilicon-containing material generated at 500 °C, and a mixture of silicon carbide (SiC) and elemental carbon generated at 800 °C.

The  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed post-polymerization method (Chapter 4) was evaluated based on the substitution percentage for X-functionalized poly(phenylsilane) derivatives. Reactions of highly electron-donating substrates gave a low amount of X incorporation (10%, e.g. aryloxy side-chains derived from phenol). Aryloxy groups were alternatively introduced via demethanative coupling, which gave a polymer with a greater substitution percentage (25%). The overall impact of the H-to-X substitution reactions was gauged by UV-vis absorption spectra and desirable UV absorption properties would require the modified poly(phenylsilane) to have a high degree of substitution.

## Table of Contents

Supervisory Committee .....	ii
Abstract .....	iii
Table of Contents .....	vi
List of Tables .....	ix
List of Figures .....	xi
List of Schemes .....	xxii
List of Equations .....	xxv
List of Abbreviations .....	xxvi
Acknowledgments .....	xxix
Dedication .....	xxx
1 Introduction .....	1
1.1 Routes to complex silicon-containing molecules .....	1
1.2 Alternative routes to complex silicon-containing molecules: hydrosilation, dehydrocoupling, and dealkylative coupling .....	4
1.3 Strategies for polysilane synthesis using B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> -catalyzed hydrosilation, dehydrocoupling, and dealkylative coupling reaction .....	9
2 B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> -catalyzed partial reduction of Ph <sub>2</sub> MeSiH and (Ph <sub>2</sub> SiH) <sub>2</sub> .....	15
2.1 Introduction .....	15
2.2 B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> -catalyzed synthesis of X-modified monosilanes .....	19
2.3 B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> -catalyzed synthesis of X-modified disilanes .....	23
2.3.1 Reaction mechanism and catalyst inhibition with basic substrates .....	26
2.3.2 Selectivity for monosubstituted versus disubstituted disilane products .....	31
2.3.3 Preparation of a mixed, unsymmetrically-disubstituted disilane .....	34
2.3.4 Competing over-reduction reactions .....	35
2.4 Summary .....	36
2.5 Impact and future work .....	37
2.6 Experimental .....	39
2.6.1 General details .....	39
2.6.2 Synthesis of X-modified monosilanes .....	41
2.6.3 Synthesis of monosubstituted disilanes .....	52
2.6.4 Synthesis of disubstituted disilanes .....	62
2.6.5 Synthesis of an unsymmetrically-disubstituted disilane .....	68
2.6.6 B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> -catalyzed reactions with <i>n</i> -propylidene- <i>n</i> -propylamine .....	70
3 Over-reduction of silanes catalyzed by B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> .....	73
3.1 Introduction .....	73
3.1.1 Reasons to study reduction .....	73
3.1.2 Reductions with hydrosilanes .....	75
3.1.3 Overview .....	77
3.2 Sensitivity of B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> -catalyzed reductions to the steric bulk of the silane ...	77
3.3 Facile over-reduction reactions with PhSiH <sub>3</sub> and Ph <sub>2</sub> SiH <sub>2</sub> .....	83
3.4 Over-reduction leads to polysiloxane by-products .....	89
3.5 Over-reduction of benzylic oxygen-containing substrates. ....	91
3.6 Selective partial reduction products from over-reducible substrates .....	103
3.7 Over-reduction in sulfur systems .....	105

3.8	Exploiting over-reduction for the synthesis of Si-S-Si-containing molecules	110
3.9	Partial reduction of nitrogen-containing substrates .....	114
3.10	Summary .....	116
3.11	Impact and future work .....	118
3.12	Experimental .....	121
3.12.1	General details .....	121
3.12.2	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> -mediated reactions of (Me <sub>2</sub> SiH) <sub>2</sub> or disilane 2-2 leading to over-reduction chemistry .....	122
3.12.3	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> -catalyzed reactions of oxygen-containing substrates with Ph <sub>2</sub> SiH <sub>2</sub> or PhSiH <sub>3</sub> , to identify possible over-reduction products .....	126
3.12.4	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> -catalyzed reactions of sulfur-containing substrates with Ph <sub>2</sub> SiH <sub>2</sub> or PhSiH <sub>3</sub> to identify possible over-reduction products .....	130
3.12.5	Synthesis of substituted disilanes .....	134
3.12.6	Preliminary attempts to make Si-S-containing oligomers and polymers .....	136
3.12.7	Reactions of small silanes (Ph <sub>2</sub> SiH <sub>2</sub> and PhSiH <sub>3</sub> ) with benzylideneaniline as determined by <sup>1</sup> H NMR .....	140
3.12.8	Synthesis of <i>N,N</i> -disilylamines (reactions with nitriles) .....	143
4	Post-polymerization modification of poly(phenylsilane) .....	146
4.1	Introduction .....	146
4.2	Synthesis of X-modified poly(phenylsilane) derivatives .....	151
4.3	Characterization of X-modified poly(phenylsilane) derivatives .....	153
4.3.1	Characterization by IR spectroscopy .....	153
4.3.2	Characterization by <sup>1</sup> H NMR .....	154
4.3.3	Characterization by DEPT135 <sup>13</sup> C NMR .....	157
4.3.4	Characterization by elemental analysis .....	158
4.3.5	Characterization by <sup>29</sup> Si NMR .....	165
4.3.6	Characterization by GPC and determination of B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> chemoselectivity .....	171
4.4	Challenges in post-polymerization modification .....	175
4.4.1	Catalyst inhibition by competing substrate coordination .....	175
4.4.2	Identification of competing over-reduction reactions .....	176
4.5	Properties of modified poly(phenylsilane) derivatives .....	184
4.6	Strategies for higher degree of modification .....	189
4.7	Impact and future work .....	191
4.8	Summary .....	196
4.9	Experimental .....	196
4.9.1	General details .....	196
4.9.2	Synthesis of parent poly(phenylsilane) [PhSiH] <sub>n</sub> (4-1) .....	197
4.9.3	Synthesis of modified poly(phenylsilane) .....	200
4.9.4	Identification of 1,1,2,2-tetraphenylethane (Ph <sub>2</sub> CH) <sub>2</sub> from 4-13 .....	224
4.9.5	Methods used to evaluate B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> selectivity for Si-H bond modification over Si-Si bond cleavage .....	226
4.9.6	Representative determination of the degree of Si-H substitution using <sup>1</sup> H NMR integration .....	227
4.9.7	Molecular weight analysis .....	227
4.9.8	UV-Vis absorption spectra .....	231
4.9.9	Thermogravimetric analysis (TGA) .....	232

5	Thermal degradation and redistribution of poly(phenylsilane) .....	234
5.1	Introduction.....	234
5.2	Thermogravimetric analysis (TGA) of poly(phenylsilane) .....	235
5.3	Identification of volatile thermolysis products .....	238
5.4	Identification of non-volatile partial thermolysis products.....	240
5.5	Summary .....	252
5.6	Impact and future work.....	253
5.7	Experimental .....	255
5.7.1	General.....	255
5.7.2	Thermolysis of poly(phenylsilane) (4-1) .....	255
5.7.3	Pyrolysis of poly(phenylsilane) (4-1) .....	257
	References.....	258

## List of Tables

Table 2.1. (a) Hydrosilation, (b) dehydrocoupling, and (c) demethanative coupling reactions of $\text{Ph}_2\text{MeSiH}$ (2-1) mediated by $\text{B}(\text{C}_6\text{F}_5)_3$ .....	19
Table 2.2. Monosubstituted disilanes prepared by $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reactions of disilane 2-2. ....	24
Table 2.3. Disubstituted disilanes prepared by $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reactions of disilane 2-2. ....	25
Table 3.1. Estimated cone angles for silanes, $\text{R}_3\text{Si-H}$ , based on established phosphine cone angles $\text{R}_3\text{P-M}$ . <sup>87</sup> .....	80
Table 3.2. Reactions of bulky O-containing substrates with smaller silanes $\text{Ph}_2\text{SiH}_2$ and $\text{PhSiH}_3$ to gauge susceptibility to over-reduction, as monitored by $^1\text{H}$ NMR. <sup>a</sup> .....	85
Table 3.3. Conditions used to avoid over-reduction in the synthesis of monosubstituted disilanes prepared by $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reactions of disilane 2-2 with benzophenone and thiobenzophenone. ....	104
Table 3.4. Reactions of S-containing substrates with smaller silanes $\text{Ph}_2\text{SiH}_2$ or $\text{PhSiH}_3$ to gauge susceptibility to over-reduction. <sup>a</sup> .....	107
Table 4.1. New X-modified poly(phenylsilane) derivatives (4-2 to 4-13) prepared by hydrosilation (Scheme 4.5a), dehydrocoupling (b), and demethanative coupling (c). ....	152
Table 4.2. Elemental analyses for parent poly(phenylsilane) (4-1) and X-modified poly(phenylsilane) derivatives (4-2 to 4-13), estimates for the degree of substitution %X based on elemental analyses, and comparison with elemental composition anticipated based on NMR estimates for %X. In some cases, elemental compositions corresponding to several %X are shown to illustrate sensitivity to the degree of substitution. Data for 4-11, 4-12, and 4-13 is used with permission (see note at beginning of Chapter 4). <sup>96</sup> .....	160
Table 4.3. $^{29}\text{Si}$ NMR DEPT experiments used for polysilanes (this Chapter) and disilanes (Chapter 2 and 3). ....	166
Table 4.4. Representative GPC (MALS) MW data for modified polysilanes, $-\text{PhSiH}/-\text{PhSiX}-$ , with corresponding data for the specific batches (4-1a-d) of parent poly(phenylsilane) used in each case. <sup>a,b</sup> Data for 4-11, 4-12, and 4-13 is used with permission (see note at beginning of Chapter 4). <sup>96</sup> .....	173
Table 4.5. Elemental analyses for modified polymers (4-5, 4-9, and 4-13) where over-reduction was observed. Data for 4-13 is used with permission (see note at beginning of Chapter 4). <sup>96</sup> .....	180

Table 4.6. Full GPC-MALS data sets collected for modified polymers and corresponding batches of parent poly(phenylsilane) (4-1). Data for 4-11, 4-12, and 4-13 is used with permission (see note at beginning of Chapter 4). <sup>96</sup> .....	227
Table 4.7. TGA inflection temperatures for parent poly(phenylsilane) (4-1) and modified poly(phenylsilane) derivatives (4-1 to 4-5, 4-7, 4-8, and 4-10 to 4-13). .....	232
Table 5.1. Characteristic data points for the TGA traces of 4-1, 5-1, and 5-2.....	244
Table 5.2. Molecular weights determined from GPC in CHCl <sub>3</sub> (1 mL/min). <sup>lxix</sup> .....	249

## List of Figures

- Figure 1.1. a)  $\eta^1$ -silane-borane complex and b) generic, strong  $\eta^1$ -silane-Lewis acid complex (LA = Lewis acid). ..... 11
- Figure 1.2.  $B(C_6F_5)_3$ -like catalysts a) 2- $B(C_6F_5)_2$ -2'-( $CH_3$ ) $C_{20}H_{12}$ ,<sup>43b</sup> b)  $B(C_6F_5)(2,2'-(CH_2)_2C_{20}H_{12})$ ,<sup>43c,d</sup> and c) 1,2-( $B(C_6F_5)_2$ ) $C_6H_4$ ,<sup>43a</sup> for catalytic hydrosilation, dehydrocoupling, or dealkylative coupling reactions. .... 12
- Figure 1.3. Rhenium-based catalysts a)  $Re(O)(PPh_3)_2Cl_3$ <sup>46a</sup> and b)  $Re(O)(CH_3)(N(C_6F_5)CH_2CH_2N(CH_3)CH_2CH_2N(C_6F_5))$ <sup>46b</sup> for catalytic hydrosilation reactions. .... 12
- Figure 1.4. Miscellaneous catalysts exhibiting  $\eta^1$ -H $\cdots$ SiR<sub>3</sub> activation for hydrosilation reactions a)  $Ir(P^tBu_3-OC_6H_3O-P^tBu_3)(H)(OC(CH_3)_2)$ ,<sup>30e</sup> b)  $Mo(O)_2Cl_2$ ,<sup>48</sup> c)  $[2,6-(CH_3)_2C_5H_3N-BC_{10}H_{18}]^+[NTf_2]^-$  (Tf =  $S(O)_2CF_3$ ),<sup>49</sup> d)  $MoTp(NDipp)(H)PMe_3$  (Tp =  $HB(C_3H_3N)_3^-$ , Dipp = 2,6- $^iPr_2C_6H_3$ ),<sup>50</sup> and e)  $Zn(DippNC(CH_3)CHC(CH_3)NDipp)H$ .<sup>51</sup> 12
- Figure 1.5. Lewis acidic phosphonium cations a)  $([P(C_6F_5)_3F]^+[B(C_6F_5)_4])$ ,<sup>53a</sup> b)  $[SIMesPPh_2F]^{2+}[(B(C_6F_5)_4)_2]^{2-}$  (SIMes = 1,3-Mes<sub>2</sub>C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>, Mes = 2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>),<sup>53c</sup> and c)  $([1,8-(PPh_2F)C_8H_{10}]^{2+}[(B(C_6F_5)_4)_2]^{2-})$ <sup>53b</sup> for Si-H activation and catalytic hydrosilation or dehydrocoupling. .... 13
- Figure 2.1. Si-H and Si-Si bonds in  $(Ph_2SiH)_2$  (2-2, disilane). ..... 15
- Figure 2.2. a) <sup>1</sup>H NMR (300 MHz) and b) DEPT135 <sup>13</sup>C NMR (75 MHz) of  $Ph_2MeSiOCH_2CH_2CH_3$  (2-3) in  $C_6D_6$ . The “ds” is disiloxane ( $Ph_2MeSi-O-SiMePh_2$ , 2-4) formed from the competing over-reduction reaction (See Chapter 3 for more details).... 43
- Figure 2.3. a) <sup>1</sup>H NMR (300 MHz) and b) DEPT135 <sup>13</sup>C NMR (75 MHz) of  $Ph_2MeSiOCH(CH_3)_2$  (2-5) in  $C_6D_6$ . ..... 44
- Figure 2.4. a) <sup>1</sup>H NMR (300 MHz) and b) DEPT135 <sup>13</sup>C NMR (75 MHz) of  $Ph_2MeSiOC_6H_{11}$  (2-6) in  $C_6D_6$ . The “v” is residual unreacted  $Ph_2MeSiH$ . The “#” is grease. .... 45
- Figure 2.5. a) <sup>1</sup>H NMR (300 MHz) and b) DEPT135 <sup>13</sup>C NMR (75 MHz) of  $Ph_2MeSiOC_6H_4-p-^tBu$  (2-7) in  $C_6D_6$ . The “p” is residual unreacted *p-t*-butylphenol ( $HOC_6H_4-p-^tBu$ ). ..... 47
- Figure 2.6. a) <sup>1</sup>H NMR (300 MHz) and b) DEPT135 <sup>13</sup>C NMR (75 MHz) of  $Ph_2MeSiOC_6H_4-p-CH_3$  (2-8) in  $C_6D_6$ . The “n” is residual unreacted *p*-methylanisole ( $CH_3OC_6H_4-p-CH_3$ ). ..... 48
- Figure 2.7. a) <sup>1</sup>H NMR (300 MHz) and b) DEPT135 <sup>13</sup>C NMR (75 MHz) of  $Ph_2MeSiOCH_2CH_2Cl$  (2-9) in  $C_6D_6$ . ..... 49

- Figure 2.8. a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{MeSiN}(\text{Ph})\text{CH}_2\text{Ph}$  (**2-10**) in  $\text{C}_6\text{D}_6$ . The “ds” is disiloxane ( $\text{Ph}_2\text{MeSi-O-SiMePh}_2$ ) formed from competing hydrolysis reactions. The “hx” is residual hexanes. .... 50
- Figure 2.9. a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{MeSiCH}_2\text{CH}_2\text{Bu}$  (**2-11**) in  $\text{C}_6\text{D}_6$ . The “#” is grease. .... 52
- Figure 2.10. a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{SiH-Si}(\text{OCH}(\text{CH}_3)_2)\text{Ph}_2$  (**2-12**) in  $\text{C}_6\text{D}_6$ . The “ $\epsilon$ ” is a Si-Ph/ $\text{OCH}(\text{CH}_3)_2$ -containing impurity, tentatively assigned as the disubstituted product  $[\text{Ph}_2\text{Si}(\text{OCH}(\text{CH}_3)_2)]_2$ . .... 54
- Figure 2.11. a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{SiH-Si}(\text{OC}_6\text{H}_{11})\text{Ph}_2$  (**2-13**) in  $\text{C}_6\text{D}_6$ . The “#” is grease. The “y” is *o*-SiPh-containing impurity, putatively assigned to the disubstituted product  $(\text{Ph}_2\text{SiOC}_6\text{H}_{11})_2$ . .... 55
- Figure 2.12.  $^1\text{H}$  NMR (300 MHz) of the crude mixture containing disilane **2-2** and  $\text{Ph}_2\text{SiH-Si}(\text{OC}_6\text{H}_4\text{-}i\text{Pr})\text{Ph}_2$  (**2-14**) in  $\text{C}_6\text{D}_6$ . .... 56
- Figure 2.13. a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{SiH-Si}(\text{OC}_6\text{H}_4\text{-}i\text{Pr})\text{Ph}_2$  (**2-14**) in  $\text{C}_6\text{D}_6$ . The “d” is the  $\text{C}(\text{CH}_3)_3$  in the disubstituted product  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}i\text{Pr})_2$  (**2-14**). The “#” is grease. .... 58
- Figure 2.14. a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{SiH-Si}(\text{OC}_6\text{H}_4\text{-}i\text{Pr}-\text{CH}_3)\text{Ph}_2$  (**2-15**) in  $\text{C}_6\text{D}_6$ . The “#” is grease. The “q” is disilane **2-2**. The “pt” is residual pentane. .... 60
- Figure 2.15. a)  $^1\text{H}$  NMR (300 MHz) of the reaction monitoring formation of  $\text{Ph}_2\text{SiH-Si}(\text{OCH}_2\text{CH}_2\text{Cl})\text{Ph}_2$  (**2-16**) in  $\text{C}_6\text{D}_6$ . The “s” is starting material  $(\text{Ph}_2\text{SiH})_2$ . The “m” is the monosubstituted product  $\text{Ph}_2\text{SiH-Si}(\text{OCH}_2\text{CH}_2\text{Cl})\text{Ph}_2$  (**2-16**). The “d” is the disubstituted product  $(\text{Ph}_2\text{SiOCH}_2\text{CH}_2\text{Cl})_2$  (**2-22**). .... 61
- Figure 2.16. a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $(\text{Ph}_2\text{SiCH}_2\text{CH}_2\text{Bu})_2$  (**2-19**) in  $\text{C}_6\text{D}_6$ . The “m” is a Si-Ph/ $\text{CH}_2\text{CH}_2\text{Bu}$ -containing compound, which is presumed to be <1% monosubstituted product  $(\text{Ph}_2\text{SiH-Si}(\text{CH}_2\text{CH}_2\text{Bu})\text{Ph}_2)$ . .... 63
- Figure 2.17. a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}i\text{Pr})_2$  (**2-20**) in  $\text{C}_6\text{D}_6$ . .... 65
- Figure 2.18. a)  $^1\text{H}$  NMR (300 MHz) and b)  $^{19}\text{F}$  ( $^1\text{H}$  decoupled) NMR (283 MHz) of the crude reaction mixture for the synthesis of  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}i\text{Pr})_2$  (**2-20**) in  $\text{C}_6\text{D}_6$ . The peaks designated “u” are for an unidentified  $\text{C}_6\text{F}_5$ -containing species that may be  $(\text{F}_5\text{C}_6)_2\text{-BOC}_6\text{H}_4\text{-}i\text{Pr}$  or  $\text{F}_5\text{C}_6\text{-B}(\text{OC}_6\text{H}_4\text{-}i\text{Pr})_2$  from the partial phenolysis of  $\text{B}(\text{C}_6\text{F}_5)_3$ . The peaks designated “p” are for the expected product  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}i\text{Pr})_2$  (**2-20**). .... 65
- Figure 2.19.  $^1\text{H}$  NMR (300 MHz) of a mixture of  $\text{Ph}_2\text{SiH-Si}(\text{OC}_6\text{H}_4\text{-}i\text{Pr}-\text{CH}_3)\text{Ph}_2$  (identified in the  $^1\text{H}$  NMR spectrum as “y”) and  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}i\text{Pr}-\text{CH}_3)_2$  (**2-21**) in  $\text{C}_6\text{D}_6$ . 67

- Figure 2.20. a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $(\text{Ph}_2\text{SiOCH}_2\text{CH}_2\text{Cl})_2$  (2-22) in  $\text{C}_6\text{D}_6$ . The “#” is grease. .... 68
- Figure 2.21. a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{Si}(\text{OC}_6\text{H}_4\text{-}i\text{Pr-CH}_3)\text{-Si}(\text{OC}_6\text{H}_4\text{-}i\text{Pr-}^t\text{Bu})\text{Ph}_2$  (2-24) in  $\text{C}_6\text{D}_6$ . The “z” is residual  $\text{Ph}_2\text{SiH-Si}(\text{OC}_6\text{H}_4\text{-}i\text{Pr-CH}_3)\text{Ph}_2$  (2-15). The “hx” is residual hexanes. .... 70
- Figure 2.22.  $^1\text{H}$  NMR (300 MHz) of a) crude reaction mixture of  $\text{Ph}_2\text{MeSiH}$ , *n*-propylidene-*n*-propylamine, and catalyst  $\text{B}(\text{C}_6\text{F}_5)_3$ , b) crude reaction mixture of  $(\text{Ph}_2\text{SiH})_2$ , *n*-propylidene-*n*-propylamine, and catalyst  $\text{B}(\text{C}_6\text{F}_5)_3$  showing no consumption of silane  $\text{Ph}_2\text{MeSiH}$  or  $(\text{Ph}_2\text{SiH})_2$  and similarity in product signals \*, likely coming from c) *n*-propylidene-*n*-propylamine- $\text{B}(\text{C}_6\text{F}_5)_3$  adduct and/or reaction of *n*-propylidene-*n*-propylamine with  $\text{B}(\text{C}_6\text{F}_5)_3$ , and d) *n*-propylidene-*n*-propylamine in  $\text{C}_6\text{D}_6$ . The a' and b' are signals for  $\text{Ph}_2\text{MeSiH}$  and  $(\text{Ph}_2\text{SiH})_2$  respectively. The “#” is residual grease. The “t” is toluene. .... 72
- Figure 3.1. Production of fine chemicals from either crude-oil-based or biomass building blocks. .... 74
- Figure 3.2. Relationship of the size of silyl group (y-axis) and alkyl group (x-axis) in its propensity for  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed over-reduction. .... 81
- Figure 3.3. Influence of steric bulk in  $\text{R}_3\text{SiH}$  and  $\text{R}_3\text{SiOCR}^1\text{R}^2\text{R}^3$  on the nucleophilic addition step (Scheme 3.3, step b) in the proposed mechanism for over-reduction. .... 85
- Figure 3.4. Representative  $^1\text{H}$  NMR (300 MHz) of the crude mixture from the reaction of phenylsilane ( $\text{PhSiH}_3$ ) with O-containing substrate (e.g. *t*-butanol) in  $\text{C}_6\text{D}_6$ . The “#” is grease. .... 88
- Figure 3.5.  $^1\text{H}$  NMR (300 MHz) (Si-H and benzylic region) of a) unreacted monosubstituted disilane  $\text{Ph}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Ph}_2$  (3-1), and the mixture of  $\text{Ph}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Ph}_2$  (3-1),  $\text{Ph}_2\text{SiH}_2$  (2-2), and  $\text{B}(\text{C}_6\text{F}_5)_3$  after b) 5 min, c) after 5 h in  $\text{C}_6\text{D}_6$ . Figure is adapted with permission (see note at the beginning of Chapter 3).<sup>96</sup> .... 106
- Figure 3.6. a)  $^1\text{H}$  NMR (300 MHz) of  $[\text{PhSiH-S}]_n$  (3-4) in  $\text{C}_6\text{D}_6$ . The “#” is grease. The “R” is residual partial reduction unit. This may be any of the following structural units: repeat unit,  $-\text{PhSi}(\text{SCH}_2\text{Ph})\text{S}-$ ; monosubstituted endcap,  $-\text{PhSi}(\text{H})\text{SCH}_2\text{Ph}$ ; or disubstituted endcap,  $-\text{PhSi}(\text{SCH}_2\text{Ph})_2$ . The intensity of the 3.0 to 8.0 ppm region has been magnified by a factor of four for clarity. .... 112
- Figure 3.7.  $^1\text{H}$  NMR (300 MHz) of oligomer mixture  $[\text{PhSiH-S}]$  (3-5) in  $\text{C}_6\text{D}_6$ . .... 114
- Figure 3.8.  $^1\text{H}$  NMR (250 MHz) of the crude reaction mixture in  $\text{C}_6\text{D}_6$  identifying major product  $\text{Me}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Me}_2$  and over-reduction minor products ( $\text{Ph}_2\text{CH}_2$  and  $\text{Me}_2\text{Si-S}$ -containing oligomers). .... 123

- Figure 3.9.  $^1\text{H}$  NMR (250 MHz) of the crude reaction mixture in  $\text{C}_6\text{D}_6$  showing major product  $\text{Ph}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Ph}_2$  and minor over-reduction products ( $\text{Ph}_2\text{CH}_2$  and Si-S-containing oligomers). ..... 124
- Figure 3.10.  $^1\text{H}$  NMR (300 MHz) of the crude reaction mixture in  $\text{C}_6\text{D}_6$  identifying major product  $\text{Ph}_2\text{SiH-Si}(\text{OCHPh}_2)\text{Ph}_2$  and over-reduction minor products ( $\text{Ph}_2\text{CH}_2$  and Si-O-containing oligomers). ..... 125
- Figure 3.11.  $^1\text{H}$  NMR (300 MHz) of the crude reaction mixture in  $\text{C}_6\text{D}_6$  showing multiple and/or broad Si-Ph, Si-H,  $\text{OCH}_2$ , or  $\text{CH}_2\text{CH}_3$ , peaks consistent with complex over-reduction reactions. .... 126
- Figure 3.12. a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{SiH-Si}(\text{OCHPh}_2)\text{Ph}_2$  (3-1) in  $\text{C}_6\text{D}_6$ . The “#” is grease. The “h” is hexanes. The “dpm” is diphenylmethane ( $\text{Ph}_2\text{CH}_2$ ) from over-reduction. The “d” and “L” are Si-H and OCH resonances respectively for longer Si-Si-O-containing chains from over-reduction/partial reduction reactions. .... 135
- Figure 3.13. a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $(\text{Ph}_2\text{SiH})_2\text{S}$  (3-3) in  $\text{C}_6\text{D}_6$ . The “o” is the phenyl groups belonging to a longer chain Si-S-containing oligomers, suspected to be  $\text{Ph}_2\text{SiH-S-Ph}_2\text{Si-S-Ph}_2\text{SiH}$ . The C/H ratios in 3-3 and suspected  $\text{Ph}_2\text{SiH-S-Ph}_2\text{Si-S-Ph}_2\text{SiH}$  are similar and contribute to the satisfactory elemental analysis result. .... 138
- Figure 3.14 a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H-}^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of  $[\text{PhSiH-S}]_n$  (3-4) in  $\text{C}_6\text{D}_6$ . The “#” is grease. The “R” is residual partial reduction unit. This may be any of the following structural units: repeat unit,  $-\text{PhSi}(\text{SCH}_2\text{Ph})\text{S-}$ ; monosubstituted endcap,  $-\text{PhSi}(\text{H})\text{SCH}_2\text{Ph}$ ; or disubstituted endcap,  $-\text{PhSi}(\text{SCH}_2\text{Ph})_2$ . 139
- Figure 3.3.15. a) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of the phenyl region (95-140 ppm) and b) DEPT90  $^{29}\text{Si}$  NMR (99 MHz) of  $[\text{PhSiH-S}]_n$  (3-4) in  $\text{C}_6\text{D}_6$ . .... 139
- Figure 3.16.  $^1\text{H}$  NMR (300 MHz) of  $\text{Ph}_2\text{SiH-N}(\text{Ph})\text{CH}_2\text{Ph}$  in  $\text{C}_6\text{D}_6$ . The “F” is residual free amine,  $\text{HN}(\text{Ph})\text{CH}_2\text{Ph}$ , formed from the hydrolysis of the Si-N bond in the product  $\text{Ph}_2\text{SiH-N}(\text{Ph})\text{CH}_2\text{Ph}$  (3-6). The “t” is toluene. The “#” is grease..... 141
- Figure 3.17.  $^1\text{H}$  NMR (300 MHz) of  $\text{PhSiH}_2\text{-N}(\text{Ph})\text{CH}_2\text{Ph} + \text{PhSiH}(\text{N}(\text{Ph})\text{CH}_2\text{Ph})_2$  in  $\text{C}_6\text{D}_6$ . The “a” is 3-8a. The “b” is 3-8b. The “F” is residual free amine,  $\text{HN}(\text{Ph})\text{CH}_2\text{Ph}$ , formed from the hydrolysis of the Si-N bond in the product in either 3-8a or 3-8b..... 143
- Figure 3.18.  $^1\text{H}$  NMR (300 MHz) of  $((n\text{-C}_6\text{H}_{13})_2\text{SiH})_2\text{NCH}_2\text{Ph}$  (3-8a) in  $\text{C}_6\text{D}_6$ . The “#” is grease. .... 144
- Figure 3.19.  $^1\text{H}$  NMR (300 MHz) of  $(\text{Ph}_2\text{SiH})_2\text{NCH}_2\text{Ph}$  (3-8b) in  $\text{C}_6\text{D}_6$ . The “#” is grease. .... 145
- Figure 3.20.  $^1\text{H}$  NMR (300 MHz) of  $-(\text{PhSiH})_2\text{NCH}_2\text{Ph-}$  (3-9) in  $\text{C}_6\text{D}_6$ . The “sms” indicates residual starting material,  $\text{PhSiH}_3$ ..... 145

Figure 4.1. The change in relative intensities of  $\nu_{\text{Si-H}}$  and  $\nu_{\text{C-H}}$  is particularly easy to see from comparison of the IR spectra (KBr) of a)  $\text{SCH}_2\text{CH}_2\text{CH}_3$  (4-11), b)  $\text{OCH}(\text{CH}_3)_2$ -modified poly(phenylsilane) derivatives (4-4), and c) parent poly(phenylsilane) (4-1). Peak intensities have been crudely normalized using signals in the  $2010\text{-}1790\text{ cm}^{-1}$  region ( $\delta/\rho_{\text{C-H}}$  (phenyl) overtones) to demonstrate the reduction in  $\nu_{\text{Si-H}}$  ( $\sim 2100\text{ cm}^{-1}$ ). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 154

Figure 4.2. Representative  $^1\text{H}$  NMR (300 MHz) of modified polysilanes  $-\text{[PhSiH]}-/-\text{[PhSiX]}-$  where X = a)  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$  (4-2), b)  $\text{OCH}(\text{CH}_3)_2$  (4-4), c)  $\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$  (4-7), d)  $\text{N}(\text{CH}_2\text{Ph})\text{Ph}$  (4-10), e)  $\text{SCH}_2\text{CH}_2\text{CH}_3$  (4-11). Spectrum f) shows the parent poly(phenylsilane) (4-1) in  $\text{C}_6\text{D}_6$ . In d) (4-10), the “•” highlights an impurity of free amine formed from the hydrolysis of  $-\text{N}(\text{Ph})\text{CH}_2\text{Ph}$  side-chains. The “#” is residual grease. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 156

Figure 4.3. DEPT135  $^{13}\text{C}$  NMR (75 MHz) of a)  $\text{CH}_2\text{CH}_2\text{Bu}$  (4-3), b)  $\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$  (4-7), c)  $\text{OCH}_2\text{CH}_2\text{Cl}$  (4-8) d)  $\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3$  (4-12)-modified polysilanes and d) parent poly(phenylsilane) (4-1) in  $\text{C}_6\text{D}_6$ . The “#” signal is due to residual grease. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 158

Figure 4.4.  $^{29}\text{Si}$  NMR (99 MHz) spectra obtained using short-range DEPT ( $^1J_{\text{SiH}} = 188\text{ Hz}$ ) for the representative modified polysilanes and the parent poly(phenylsilane) (4-1). This showed new signals for  $-\text{PhSiH}-$  groups that are adjacent to  $-\text{PhSiO}-$  and for  $\text{H-Si-O}$  endcaps, (a)  $-\text{OCH}(\text{CH}_3)_2$  (4-4), (b)  $-\text{OC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$  (4-6), (c)  $-\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$  (4-7), and (d)  $-\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3$  (4-12), and e) parent poly(phenylsilane) (4-1) in  $\text{C}_6\text{D}_6$ . Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 167

Figure 4.5.  $^{29}\text{Si}$  NMR chemical shifts of a)  $\text{Ph}_2\text{SiH-Si}(\text{OC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})\text{Ph}_2$  (2-7) and b)  $(\text{Ph}_2\text{Si}(\text{OC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}))_2$  (2-14) showing a chemical shift disparity in  $\text{Si}(\text{OAr})\text{Ph}_2$  unit depending on the adjacent “Si-H” or “Si-OAr” group. This suggests an endcap chemical shift disparity in 4-6 c)  $[\text{Si}]\text{-SiH}(\text{Ph})\text{-SiH}(\text{OC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})\text{Ph}$  and d)  $[\text{Si}]\text{-SiH}(\text{Ph})\text{-SiH}(\text{OC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})\text{Ph}$  with different adjacent group, “Si-H” or “Si-OAr”.  $[\text{Si}]$  = extended silicon chain.  $\text{Ar} = \text{C}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$ . ..... 169

Figure 4.6.  $^{29}\text{Si}$  NMR chemical shifts of a)  $\text{Ph}_2\text{SiH-Si}(\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3)\text{Ph}_2$  (2-18) and b)  $(\text{Ph}_2\text{Si}(\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3))_2$  (2-23) showing a chemical shift disparity in  $\text{Si}(\text{SAr})\text{Ph}_2$  unit depending on the adjacent “Si-H” or “Si-SAr” group. This suggests an endcap chemical shift disparity in 4-6 c)  $[\text{Si}]\text{-SiH}(\text{Ph})\text{-SiH}(\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3)\text{Ph}$  and d)  $[\text{Si}]\text{-SiH}(\text{Ph})\text{-SiH}(\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3)\text{Ph}$  with different adjacent group, “Si-H” or “Si-SAr”.  $[\text{Si}]$  = extended silicon chain.  $\text{Ar} = \text{C}_6\text{H}_4\text{-}p\text{-CH}_3$ . ..... 169

Figure 4.7.  $^{29}\text{Si}$  NMR (99 MHz) spectra obtained using a) long-range DEPT ( $^3J_{\text{SiH}} = 8\text{ Hz}$ ), b) short-range DEPT ( $^1J_{\text{SiH}} = 188\text{ Hz}$ ) for the  $\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$  (4-7) modified polysilane and c) short-range DEPT of parent poly(phenylsilane) (4-1) in  $\text{C}_6\text{D}_6$ . ..... 171

Figure 4.8. The aromatic region of representative DEPT135  $^{13}\text{C}$  NMR spectra (75 MHz) showing the high ratio of *o*-C signal due to -PhSiE- (E = O, S) units to *o*-C signal due to -PhSiH- units in modified polymers containing a)  $\text{OCH}_2\text{CH}_2\text{CH}_3$  (4-5), b)  $\text{OCHPh}_2$  (4-9), or c)  $\text{SCHPh}_2$  (4-13) groups, which have undergone over-reduction, relative to the spectra for d) for a “normal” modified polymer (4-7, 20%) and e) parent poly(phenylsilane) (4-1, “0%”) in  $\text{C}_6\text{D}_6$ . Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 178

Figure 4.9. a) UV-vis absorption spectra (in  $\text{CH}_2\text{Cl}_2$ , normalized at 260 nm) of X-modified poly(phenylsilane) derivatives (4-1 to 4-13), parent poly(phenylsilane) (4-1), and PMPS (4-14) a) showing similarity in shape of poly(phenylsilane) derivatives and b) illustrating the red shift of modified polymers with highest degree of substitution (X =  $\text{CH}_2\text{CH}_2\text{Bu}$  (4-3),  $\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3$  (4-12)), relative to parent poly(phenylsilane) (4-1) (“0%” degree of substitution, all tertiary-Si repeat units) and PMPS (4-14) (“100%” degree of substitution, all quaternary-Si repeat units). Legend for X: — CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph (4-2), — CH<sub>2</sub>CH<sub>2</sub>Bu (4-3), ..... OCH(CH<sub>3</sub>)<sub>2</sub> (4-4), ..... OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (4-5), — OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> (4-7), — OCH<sub>2</sub>CH<sub>2</sub>Cl (4-8), — N(Ph)CH<sub>2</sub>Ph (4-10), — SCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (4-11), — SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> (4-12), — SCHPh<sub>2</sub> (4-13) -modified poly(phenylsilane) derivatives, — parent poly(phenylsilane) (4-1) and — poly(methylphenylsilane) (4-14). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 187

Figure 4.10. TGA traces of modified polysilanes -[PhSiH]-/[PhSiX]-. Legend, for X: — CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph (4-2), — CH<sub>2</sub>CH<sub>2</sub>Bu (4-3), — OCH(CH<sub>3</sub>)<sub>2</sub> (4-4), ..... OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (4-5), — OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> (4-7), — OCH<sub>2</sub>CH<sub>2</sub>Cl (4-8), — N(Ph)CH<sub>2</sub>Ph (4-10), — SCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (4-11), — SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> (4-12), — SCHPh<sub>2</sub> (4-13), — parent poly(phenylsilane) (4-1)..... 189

Figure 4.11. UV-vis absorption spectra (in  $\text{CH}_2\text{Cl}_2$ , normalized at 260 nm) of — CH<sub>2</sub>CH<sub>2</sub>Bu (4-3-40%), — CH<sub>2</sub>CH<sub>2</sub>Bu (4-3-65%) modified polysilanes. — parent poly(phenylsilane) (4-1), and — poly(methylphenylsilane) (4-14)..... 191

Figure 4.12. Potential  $\text{B}(\text{C}_6\text{F}_5)_3$ -like catalysts available post-polymerization modification of poly(phenylsilane): a) Representative fluorophosphonium catalyst<sup>53</sup> and b) borenium catalyst.<sup>70</sup> ..... 195

Figure 4.13.  $^1\text{H}$  NMR (300 MHz) of poly(phenylsilane) (4-1) in  $\text{C}_6\text{D}_6$ . Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 199

Figure 4.14. DEPT135  $^{13}\text{C}$  NMR (75 MHz) of poly(phenylsilane) (4-1) in  $\text{C}_6\text{D}_6$ . Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 199

Figure 4.15. Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of poly(phenylsilane) (4-1) in  $\text{C}_6\text{D}_6$ . Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 200

Figure 4.16. IR spectrum (KBr) of poly(phenylsilane) (4-1). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 200

- Figure 4.17. a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ -modified poly(phenylsilane) (4-2) in  $\text{C}_6\text{D}_6$ . The “#” is grease. .... 201
- Figure 4.18. DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ -modified poly(phenylsilane) (4-2) in  $\text{C}_6\text{D}_6$ . For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 15 relative to the 100-160 ppm region. The “#” is grease. .... 202
- Figure 4.19. a) Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) and b) long-range DEPT45  $^{29}\text{Si}$  NMR (99 MHz,  $^3J_{\text{SiH}} = 8$  Hz) of  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ -modified poly(phenylsilane) (4-2) in  $\text{C}_6\text{D}_6$ . The “#” is grease. .... 202
- Figure 4.20. IR spectrum (KBr) of  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ -modified poly(phenylsilane) (4-2). 203
- Figure 4.21. a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of  $\text{CH}_2\text{CH}_2\text{Bu}$ -modified poly(phenylsilane) (4-3) in  $\text{C}_6\text{D}_6$ . The “#” is grease. .... 203
- Figure 4.22. DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{CH}_2\text{CH}_2\text{Bu}$ -modified poly(phenylsilane) (4-3) in  $\text{C}_6\text{D}_6$ . For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 5 relative to the 100-160 ppm region. The “#” is grease. .... 204
- Figure 4.23. a) Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) and b) long-range DEPT45  $^{29}\text{Si}$  NMR (99 MHz,  $^3J_{\text{SiH}} = 8$  Hz) of  $\text{CH}_2\text{CH}_2\text{Bu}$ -modified poly(phenylsilane) (4-3) in  $\text{C}_6\text{D}_6$ . The “#” is grease. .... 204
- Figure 4.24. IR spectrum (KBr) of  $\text{CH}_2\text{CH}_2\text{Bu}$ -modified poly(phenylsilane) (4-3). .... 205
- Figure 4.25. a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of  $\text{OCH}(\text{CH}_3)_2$ -modified poly(phenylsilane) (4-4) in  $\text{C}_6\text{D}_6$ . The “#” is grease. .... 206
- Figure 4.26. DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{OCH}(\text{CH}_3)_2$ -modified poly(phenylsilane) (4-4) in  $\text{C}_6\text{D}_6$ . For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 10 relative to the 100-160 ppm region. .... 206
- Figure 4.27. a) Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) and b) long-range DEPT45  $^{29}\text{Si}$  NMR (99 MHz,  $^3J_{\text{SiH}} = 8$  Hz) of  $\text{OCH}(\text{CH}_3)_2$ -modified poly(phenylsilane) (4-4) in  $\text{C}_6\text{D}_6$ . The “#” is grease. .... 207
- Figure 4.28. IR spectrum (KBr) of  $\text{OCH}(\text{CH}_3)_2$ -modified poly(phenylsilane) (4-4). .... 207
- Figure 4.29. a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of  $\text{OCH}_2\text{CH}_2\text{CH}_3$ -modified poly(phenylsilane) (4-5) in  $\text{C}_6\text{D}_6$ . The “#” is grease. .... 208
- Figure 4.30. DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{OCH}_2\text{CH}_2\text{CH}_3$ -modified poly(phenylsilane) (4-5) in  $\text{C}_6\text{D}_6$ . For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 10 relative to the 100-160 ppm region. .... 208

- Figure 4.31. Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of  $\text{OCH}_2\text{CH}_2\text{CH}_3$ -modified poly(phenylsilane) (4-5) in  $\text{C}_6\text{D}_6$ . ..... 209
- Figure 4.32. IR spectrum (KBr) of  $\text{OCH}_2\text{CH}_2\text{CH}_3$ -modified poly(phenylsilane) (4-5). 209
- Figure 4.33. a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of  $\text{OC}_6\text{H}_4$ -*p*- $^1\text{Bu}$ -modified poly(phenylsilane) (4-6) in  $\text{C}_6\text{D}_6$ . The “#” is grease..... 210
- Figure 4.34. a) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of the aryl region (100-160 ppm) and b)  $^{13}\text{C}$  NMR (75 MHz) of the alkyl region (0-80 ppm) of  $\text{OC}_6\text{H}_4$ -*p*- $^1\text{Bu}$ -modified poly(phenylsilane) (4-6) in  $\text{C}_6\text{D}_6$ . ..... 210
- Figure 4.35. a) Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of  $\text{OC}_6\text{H}_4$ -*p*- $^1\text{Bu}$ -modified poly(phenylsilane) (4-6) in  $\text{C}_6\text{D}_6$ . ..... 211
- Figure 4.36. a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of  $\text{OC}_6\text{H}_4$ -*p*- $\text{CH}_3$ -modified poly(phenylsilane) (4-7) in  $\text{C}_6\text{D}_6$ . ..... 211
- Figure 4.37. DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{OC}_6\text{H}_4$ -*p*- $\text{CH}_3$ -modified poly(phenylsilane) (4-7) in  $\text{C}_6\text{D}_6$ . For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 5 relative to the 100-160 ppm region. .... 212
- Figure 4.38. a) Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) and b) long-range DEPT45  $^{29}\text{Si}$  NMR (99 MHz,  $^3J_{\text{SiH}} = 8$  Hz) of  $\text{OC}_6\text{H}_4$ -*p*- $\text{CH}_3$ -modified poly(phenylsilane) (4-7) in  $\text{C}_6\text{D}_6$ . The “#” is grease..... 212
- Figure 4.39. IR spectrum (KBr) of  $\text{OC}_6\text{H}_4$ -*p*- $\text{CH}_3$ -modified poly(phenylsilane) (4-7).. 213
- Figure 4.40. a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of  $\text{OCH}_2\text{CH}_2\text{Cl}$ -modified poly(phenylsilane) (4-8) in  $\text{C}_6\text{D}_6$ . The “#” is grease. .... 213
- Figure 4.41. DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{OCH}_2\text{CH}_2\text{Cl}$ -modified poly(phenylsilane) (4-8) in  $\text{C}_6\text{D}_6$ . For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 10 relative to the 100-160 ppm region. The “#” is grease. .... 214
- Figure 4.42. a) Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) and b) long-range DEPT45  $^{29}\text{Si}$  NMR (99 MHz,  $^3J_{\text{SiH}} = 8$  Hz) of  $\text{OCH}_2\text{CH}_2\text{Cl}$ -modified poly(phenylsilane) (4-8) in  $\text{C}_6\text{D}_6$ . The “#” is grease..... 214
- Figure 4.43. IR spectrum (KBr) of  $\text{OCH}_2\text{CH}_2\text{Cl}$ -modified poly(phenylsilane) (4-8). ... 215
- Figure 4.44. a)  $^1\text{H}$  NMR (300 MHz) of  $\text{OCHPh}_2$ -modified poly(phenylsilane) (4-9) in  $\text{C}_6\text{D}_6$ . The “#” is grease..... 215
- Figure 4.45. DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{OCHPh}_2$ -modified poly(phenylsilane) (4-9) in  $\text{C}_6\text{D}_6$ . For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 10 relative to the 100-160 ppm region..... 216

- Figure 4.46. Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of OCHPh<sub>2</sub>-modified poly(phenylsilane) (4-9) in C<sub>6</sub>D<sub>6</sub>. ..... 216
- Figure 4.47. a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of N(Ph)CH<sub>2</sub>Ph-modified poly(phenylsilane) (4-10) in C<sub>6</sub>D<sub>6</sub>. The “#” is grease..... 217
- Figure 4.48. DEPT135  $^{13}\text{C}$  NMR (75 MHz) of N(Ph)CH<sub>2</sub>Ph-modified poly(phenylsilane) (4-10) in C<sub>6</sub>D<sub>6</sub>. For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 100 relative to the 100-160 ppm region..... 217
- Figure 4.49. a) Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of N(Ph)CH<sub>2</sub>Ph-modified poly(phenylsilane) (4-10) in C<sub>6</sub>D<sub>6</sub>..... 218
- Figure 4.50. IR spectrum (KBr) of N(Ph)CH<sub>2</sub>Ph-modified poly(phenylsilane) (4-10).. 218
- Figure 4.51. a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of SCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-modified poly(phenylsilane) (4-11) in C<sub>6</sub>D<sub>6</sub>. The “#” is grease. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 219
- Figure 4.52. DEPT135  $^{13}\text{C}$  NMR (75 MHz) of SCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-modified poly(phenylsilane) (4-11) in C<sub>6</sub>D<sub>6</sub>. For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 20 relative to the 100-160 ppm region. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 219
- Figure 4.53. Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of SCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-modified poly(phenylsilane) (4-11) in C<sub>6</sub>D<sub>6</sub>. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 220
- Figure 4.54. IR spectrum (KBr) of SCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-modified poly(phenylsilane) (4-11). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 220
- Figure 4.55.  $^1\text{H}$  NMR (300 MHz) of SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>-modified poly(phenylsilane) (4-12) in C<sub>6</sub>D<sub>6</sub>. The “#” is grease. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 221
- Figure 4.56. DEPT135  $^{13}\text{C}$  NMR (75 MHz) of SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>-modified poly(phenylsilane) (4-12) in C<sub>6</sub>D<sub>6</sub>. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 221
- Figure 4.57. Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>-modified poly(phenylsilane) (4-12) in C<sub>6</sub>D<sub>6</sub>. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 222
- Figure 4.58. IR spectrum (KBr) of SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>-modified poly(phenylsilane) (4-12). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 222
- Figure 4.59.  $^1\text{H}$  NMR (300 MHz) of Ph<sub>2</sub>CS-modified poly(phenylsilane) (4-13) in C<sub>6</sub>D<sub>6</sub>. The “#” is grease. The “o1” is diphenylmethane (Ph<sub>2</sub>CH<sub>2</sub>). The “o2” is 1,1,2,2-

tetraphenylethane ((Ph<sub>2</sub>CH)<sub>2</sub>). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 223

Figure 4.60. DEPT135 <sup>13</sup>C NMR (75 MHz) of SCHPh<sub>2</sub>-modified poly(phenylsilane) (4-13) in C<sub>6</sub>D<sub>6</sub>. The “o1” is diphenylmethane (Ph<sub>2</sub>CH<sub>2</sub>). The “o2” is 1,1,2,2-tetraphenylethane ((Ph<sub>2</sub>CH)<sub>2</sub>). For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 50 relative to the 100-160 ppm region. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 223

Figure 4.61. Short-range DEPT90 <sup>29</sup>Si NMR (99 MHz, <sup>1</sup>J<sub>SiH</sub> = 188 Hz) of SCHPh<sub>2</sub>-modified poly(phenylsilane) (4-13) in C<sub>6</sub>D<sub>6</sub>. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 224

Figure 4.62. IR spectrum (KBr) of SCHPh<sub>2</sub>-modified poly(phenylsilane) (4-13). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 224

Figure 4.63. Identification of (Ph<sub>2</sub>CH)<sub>2</sub> by GC-MS. Full CG trace (left) and MS for peak eluting at t = 14.184 min (right). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 225

Figure 4.64. <sup>1</sup>H NMR (300 MHz, D1 = 2s) of OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>-modified poly(phenylsilane) (4-7) in C<sub>6</sub>D<sub>6</sub> showing the method to obtain a degree of substitution (20%) by <sup>1</sup>H NMR integration. .... 227

Figure 4.65. Representative GPC M<sub>N</sub>/M<sub>W</sub> determination for a) parent poly(phenylsilane) (4-1) b) CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph-modified (4-2), c) CH<sub>2</sub>CH<sub>2</sub>Bu-modified (4-3), d) OCH(CH<sub>3</sub>)<sub>2</sub>-modified (4-4), e) OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-modified (4-5), f) OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>-modified (4-7), g) OCH<sub>2</sub>CH<sub>2</sub>Cl-modified (4-8), h) OCHPh<sub>2</sub>-modified (4-9), i) SCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-modified (4-11), j) SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>-modified (4-12), and k) SCHPh<sub>2</sub>-modified (4-13) poly(phenylsilane) derivatives in THF. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 230

Figure 4.66. UV-vis absorption spectra (in CH<sub>2</sub>Cl<sub>2</sub>, normalized at 260 nm) of modified poly(phenylsilane) derivatives (4-2 to 4-13) and parent poly(phenylsilane) (4-1) comparing a) C side chains 4-2 and 4-3, b) O side-chains 4-4, 4-5, 4-7, and 4-8, c) N side-chain 4-10, d) S side-chains 4-11, 4-12, and 4-13, e) aryl side-chains 4-2, 4-7, 4-10, 4-12, 4-13, f) branched side-chains 4-4, 4-10, 4-13, g) EC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> side-chains 4-7 and 4-12, h) straight side-chains 4-3, 4-5, 4-8, and 4-11 showing similarity to starting poly(phenylsilane) 4-1. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup> ..... 231

Figure 4.67. TGA traces (heating rate 10 °C/min) of modified poly(phenylsilane) derivatives (4-2 and 4-13) and parent poly(phenylsilane) (4-1) comparing a) C-side chains 4-2 and 4-3, b) O side-chains 4-4, 4-5, 4-7, and 4-8, c) N side-chains 4-10, d) S side-chains 4-11, 4-12, and 4-13, e) aryl side-chains 4-2, 4-7, 4-10, 4-12, 4-13, f) branched side-chains 4-4, 4-10, 4-13, g) EC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> side-chains 4-7 and 4-12, h) straight side-chains 4-3, 4-5, 4-8, and 4-11 showing similarity in shape and inflection temperature to starting poly(phenylsilane), 4-1. .... 233

Figure 5.1. TGA trace of **—** 4-1. Sample was heated at 10 °C/min from RT (approximately 20 °C) to 1000 °C. The inflection temperature is at  $320 \pm 10$  °C. A minimum mass was found at  $600 \pm 10$  °C (34% mass). The ceramic yield was 37%.... 236

Figure 5.2. IR spectrum of 5-3 showing diagnostic (5-3\*) absorption for SiC. .... 237

Figure 5.3. Identification of a)  $\text{PhSiH}_3$ , b)  $\text{Ph}_2\text{SiH}_2$ , c)  $\text{Ph}_3\text{SiH}$  by  $^1\text{H}$  NMR (300 MHz) of the crude mixture following thermolysis of poly(phenylsilane) (4-1) at 500 °C in  $\text{CDCl}_3$ . The “x” may be  $\text{Ph}_4\text{Si}$ . .... 239

Figure 5.4. Infrared spectrum of a) poly(phenylsilane) (4-1) and b) (5-1) showing similar  $\nu_{\text{Si-H}}$ ,  $\nu_{\text{C-H}}$ ,  $\nu_{\text{C-C}}$ ,  $\delta_{\text{C-H}}$ , and  $\rho_{\text{C-H}}$  and the absorption 5-1\* indicative of silica. .... 242

Figure 5.5. TGA traces of **- -** (5-1) and **...** (5-2) (**—** (4-1) taken from Figure 5.1). Samples were heated at 10 °C/min from RT (approximately 20 °C) to 1000 °C. The trace for 4-1 is included for comparison with 5-1 and 5-2. .... 243

Figure 5.6. First derivative of the TGA traces of **—** 4-1, **—** 5-1, and **—** 5-2. Samples were heated at 10 °C/min from RT (approximately 20 °C) to 1000 °C. .... 244

Figure 5.7. IR spectra of a) poly(phenylsilane) (4-1), b) 5-2, c) disilane 2-2 and d) propionaldehyde-modified poly(phenylsilane) (4-5) demonstrating that Si-chain length in 5-2 cannot be probed by IR spectroscopy and that 5-2 lacks Si-O bonds. .... 245

Figure 5.8.  $^1\text{H}$  NMR (300 MHz) of a) intermediate thermal decomposition poly(phenylsilane) (5-2) and b) poly(phenylsilane) (4-1) in  $\text{C}_6\text{D}_6$ . The “#” is grease and “h” is hexanes. The phenyl groups in  $\text{Ph}_3\text{SiH}$  are identified. .... 246

Figure 5.9. DEPT135  $^{13}\text{C}$  NMR (75 MHz) of a) intermediate thermal decomposition poly(phenylsilane) (5-2) and b) starting poly(phenylsilane) (4-1) in  $\text{C}_6\text{D}_6$  showing marginally broader peaks in 5-2, but a retention of the ratio of *o*-SiPh:*m/p*-SiPh. .... 247

Figure 5.10. Representative GPC trace of a) 5-2 and b) 4-1 in  $\text{CHCl}_3$  (1 mL/min) showing the disparity in LS (size) and dRI (concentration) in 5-2 and the comparable elution times in the short-chains in 5-2 (18.6 min elution) to parent poly(phenylsilane) (4-1). The “dRI” is differential refractive index. The “LS” is light scattering taken at 44.7°. .... 248

Figure 5.11. UV-vis absorption spectrum of a) **—** 4-1, b) **- -** 5-2, and c) **...**  $[\text{PhSiCH}_3]_n$  (4-14) in  $\text{CH}_2\text{Cl}_2$  normalized at 260 nm. .... 251

The identity of **5-2** deserves further investigation because it might be the polysilyne. In order to further evaluate **5-2**, the short chains must be removed by polymer precipitation. This would provide material that is more suitable for EA, GPC, and  $^{29}\text{Si}$  NMR because in the data presented here (Figure 5.12a), the short chains overwhelm the signal from **5-2**. Matching diagnostic data of the precipitated polymer from **5-2** to reported poly(phenylsilyne)<sup>164b,c,k,l</sup> would support the identification of polysilyne as the partial thermolysis product **5-2**. .... 254

**List of Schemes**

Scheme 1.1.....	2
Scheme 1.2.....	2
Scheme 1.3.....	3
Scheme 1.4.....	4
Scheme 1.5.....	5
Scheme 1.6.....	6
Scheme 1.7.....	6
Scheme 1.8.....	7
Scheme 1.9.....	8
Scheme 1.10.....	10
Scheme 1.11.....	13
Scheme 2.1.....	16
Scheme 2.2.....	17
Scheme 2.3.....	18
Scheme 2.4.....	22
Scheme 2.5. Here and below (Scheme 2.6 to Scheme 2.8) taken from Scheme 2.2. ....	26
Scheme 2.6.....	26
Scheme 2.7.....	27
Scheme 2.8.....	27
Scheme 2.9.....	31
Scheme 2.10.....	32
Scheme 2.11.....	34
Scheme 3.1.....	75
Scheme 3.2.....	76

Scheme 3.3. Over-reduction mechanism 1. ....	79
Scheme 3.4.....	82
Scheme 3.5.....	89
Scheme 3.6.....	91
Scheme 3.7.....	93
Scheme 3.8. Over-reduction mechanism 2. ....	95
Scheme 3.9. Over-reduction mechanism 3. ....	96
Scheme 3.10. Alternative proposal to over-reduction mechanism 3. ....	97
Scheme 3.11. Over-reduction mechanism 4. ....	98
Scheme 3.12. Over-reduction mechanism 5 ....	100
Scheme 3.13.....	102
Scheme 3.14.....	111
Scheme 3.15.....	111
Scheme 3.16.....	113
Scheme 3.17.....	115
Scheme 3.18.....	116
Scheme 3.19.....	120
Scheme 4.1. Reproduced from Scheme 1.4. ....	147
Scheme 4.2.....	148
Scheme 4.3.....	149
Scheme 4.4.....	150
Scheme 4.5.....	152
Scheme 4.6.....	176
Scheme 4.7. $[Si] = SiPh$ .....	183
Scheme 4.8.....	196

Scheme 5.1.....	239
Scheme 5.2.....	240
Scheme 5.3.....	250
Scheme 5.4.....	252

**List of Equations**

Equation 3.1 .....	90
Equation 3.2 .....	90
Equation 3.3 .....	90

**List of Abbreviations**

LED	light-emitting diode
Me	methyl
AIBN	2,2'-azobisisobutyronitrile
ACCN	1,1'-azobis(cyclohexane-carbonitrile)
Dipp	2,6-dimethylphenyl
Ph	phenyl
Bu	butyl
<sup>t</sup> Bu	<i>t</i> -butyl
<i>t</i>	tert
Tf	triflate
Tp	trispyrazolyl
IMes	1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene
Mes	2,4,6-trimethylphenyl
<i>n</i>	normal
<sup>n</sup> Pr	<i>n</i> -propyl
°C	degrees Celcius
NMR	nuclear magnetic resonance
<i>p</i>	para
h	hour
RT	room temperature
Ar	aryl
t	triplet
mmol	millimole
DEPT	distortionless enhancement polarization transfer

MHz	megahertz
s	singlet
t	triplet
m	multiplet
mL	milliliter
g	gram
<i>o</i>	ortho
<i>m</i>	meta
d	doublet
eq	equatorial
ax	axial
min	minute
Et	ethyl
TMDS	tetramethyldisiloxane
PMHS	poly(hydromethylsiloxane)
<sup>i</sup> Pr	isopropyl
GC-MS	gas chromatography mass spectrometry
<i>rac</i>	racemic
Hex	hexyl
br	broad
GPC	gel permeation chromatography
UV-vis	ultraviolet visible
UV	ultraviolet
IR	infrared
kDa	kiloDalton

EA	elemental analysis
PDI	polydispersity index
MALS-GPC	multiangle light scattering gel permeation chromatography
MW	molecular weight
$M_N$	number-average molecular weight
$M_w$	weight-average molecular weight
PDI	polydispersity or polydispersity index
THF	tetrahydrofuran
PMPS	poly(methylphenylsilane)
nm	nanometer
TGA	thermogravimetric analysis
m/z	mass-to-charge ratio
D1	delay time
XRD	X-ray diffraction
dRI	differential refractive index
LS	light scattering
$d\eta/dc$	refractive index increment
HMBC	heteronuclear multiple bond correlation
INADEQUATE	incredible natural abundance double quantum transfer experiment

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**Dedication**

To my family that has afforded me every opportunity to continue studying. My mother gave me love and compassion (and turned on the heat in my room at 11:00 pm every evening). My father taught me determination and will (and turned off the heat in my room at 7:00 am every morning).

# 1 Introduction

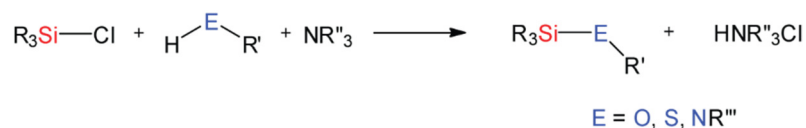
## 1.1 Routes to complex silicon-containing molecules

Silicon-containing molecules are desirable because of their utility for many diverse applications. Organic chemists often use silyl protecting groups derived from silicon-halide-containing reagents for complex organic synthesis.<sup>3</sup> Hydrosilanes are effective and efficient reducing agents, especially for oxygen-containing organic substrates.<sup>4</sup> Silicones are among the most used silicon-containing materials. In day-to-day chemistry applications, silicone grease is widely used as a lubricant for high vacuum applications.<sup>5</sup> Silicones are used in consumer products as anti-foaming agents, food additives, adhesives, sealants and more.<sup>6</sup> Silicones are considered chemically and biologically inert, making them desirable for a variety of food, medical, and construction applications (e.g. cooking equipment, medical implants, silicone rubber sealant).<sup>6</sup> Polysilanes, polymers with an all-silicon backbone, are molecules that can be used for lithographic applications as photoresists<sup>7</sup> and LED applications<sup>8</sup> for their absorption and emissive properties, respectively. Silicon carbide, which can be derived from the polysilane, dimethylpolysilane,<sup>9</sup> can be used as an abrasive or ceramic for high temperature applications.<sup>10</sup>

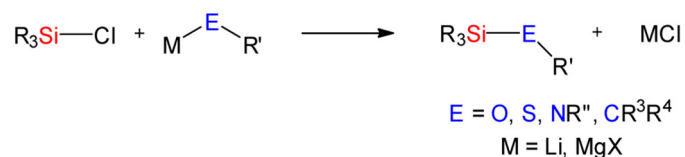
Most simple silicon-containing molecules are derived from starting materials with silicon-halogen bonds, Si-X (X = Cl, Br, usually Cl).<sup>11</sup> The Si-Cl reagents are primarily available from the direct synthesis process,<sup>11b,12</sup> but the subsequent reactions to make the desired product are inherently inefficient due to the elimination of the HCl (X = Cl) or metal salts. For example, heteroatom linkages (Si-E, E = O, S, NR') can be made using an

appropriate acid-base reaction, such as an alcohol, thiol, or amine (Scheme 1.1) with Si-X.<sup>11,13</sup> An accompanying base, such as trimethylamine (Et<sub>3</sub>N), is required to neutralize HCl and the resulting salt, e.g. Et<sub>3</sub>NH<sup>+</sup>Cl<sup>-</sup>, needs to be separated from the product. Alternatively, a metallated substrate (M-ER, M = Li, MgX, E = O, S, NR', CR'<sub>2</sub>) reacts directly with Si-Cl making new silicon-element bonds (Scheme 1.2) and a salt, MCl, which is removed by filtration.<sup>11b</sup> This method is used for the following reasons: (i) intuitiveness of combining the δ<sup>-</sup> E-substrate nucleophile with δ<sup>+</sup> silicon reagent electrophile to make the key Si-E bond; (ii) availability of reagents such as alcohols, amines, thiols, and metal-E-containing substrates (E = O, N, S, C); (iii) well-established precedents, particularly with silicon-chloride reagents; and (iv) thermodynamic driving force of salt elimination.<sup>11</sup> These following two reactions, either salt metathesis or acid-base, have high utility and ubiquity in organometallic chemistry.

**Scheme 1.1.**



**Scheme 1.2**

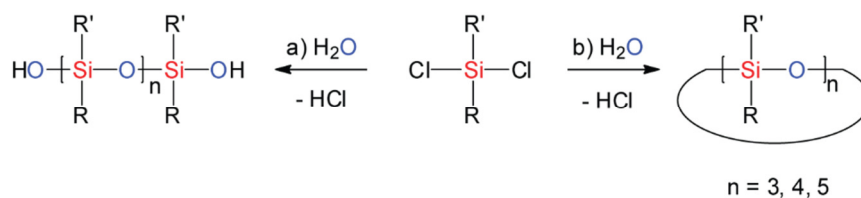


The syntheses shown in Scheme 1.1 and Scheme 1.2 have major disadvantages: extreme sensitivity to water, formation of corrosive by-products, and poor atom efficiency. Utilizing a silicon-halide bond does not incorporate the halogen into the structure. Furthermore, the acidic by-product, HX, from the reaction of alcohols, thiols, and amines, needs to be neutralized. This is typically done with an amine such as

triethylamine ( $\text{Et}_3\text{N}$ ). The problem is exacerbated if the nucleophile is metallated where the eliminated salt, MX (e.g. NaCl), generates excessive chemical waste.<sup>11a</sup>

An example of these challenges for the synthesis of everyday silicon-containing materials is the synthesis of polysiloxanes, commonly referred to as silicones. Controlled hydrolysis of dichlorosilanes is the industry standard for the preparation of short-chain (Scheme 1.3a) or cyclic (Scheme 1.3b) silicone oligomers.<sup>5,11b</sup> Hydrochloric acid (HCl) is eliminated from this reaction and neutralized with a base, usually  $\text{Et}_3\text{N}$ . The separation of  $\text{Et}_3\text{NH}^+\text{Cl}^-$  from the desired polysiloxane is cumbersome, yet tolerated because the silicone is very desirable. These short-chain (Scheme 1.3a) or cyclic (Scheme 1.3b) silicone oligomers are then polymerized by hydrolysis and condensation reactions to give the common silicones that are used on a day-to-day basis.<sup>6,11b</sup>

**Scheme 1.3.**

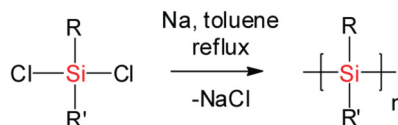


Another class of complex-silicon-containing molecules is the polysilane, which is an all silicon-backbone-containing polymer. Interest in polysilanes has been driven by their unique properties and potential applications.<sup>5,14</sup> Polysilanes absorb strongly in the ultraviolet spectrum and this property has been exploited in their use as a photoresist for lithographic applications. Polysilanes emit in the ultraviolet and visible region and could potentially be exploited for LED applications.<sup>8b,15</sup> In the presence of dopants, polysilanes are intrinsic semiconductors comparable to  $\pi$ -conjugated carbon polymers such as polyacetylene, poly(*p*-phenylene), poly(*p*-phenylene sulfide), and polypyrrole.<sup>16</sup>

Polysilanes are reported to have favorable third-order non-linear susceptibility properties; solubility of polysilanes in common solvents and stability to thermal and oxidative degradation suggests they can be exploited for non-linear optical applications.<sup>17</sup> However, developing new applications for polysilanes is a challenge due to the limited number of polysilanes available.<sup>14b,15</sup>

The preparation of the structurally complex polysilanes is typically done by reductive coupling (Wurtz coupling, Scheme 1.4) of the silicon-halide bond with an alkali metal, usually sodium metal. The removal of the stoichiometric by-product, NaCl, is an additional workup step for polysilanes prepared by this method. This common method for the preparation of polysilanes is limited to few monomers with formula  $RR'SiCl_2$ . Harsh and undesirable reaction conditions, refluxing toluene and sodium metal, are extreme safety hazards and preclude the generalization of R and R' groups in the synthesis, since many functional groups are unstable under these conditions.<sup>14b,c</sup> Furthermore, limited examples of heteroatom groups appended to polysilanes have been reported.<sup>14b,c</sup> In order to access a wide array of polysilanes for systematic testing, alternative and viable routes to them have to be developed.

**Scheme 1.4.**

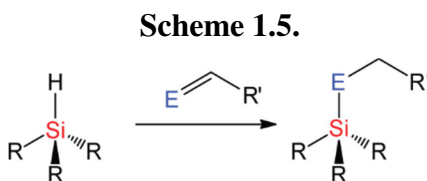


## 1.2 Alternative routes to complex silicon-containing molecules: hydrosilation, dehydrocoupling, and dealkylative coupling

Hydrosilation (Scheme 1.5), dehydrocoupling (Scheme 1.6), and dealkylative coupling (Scheme 1.7) are alternative and attractive routes to complex silicon-containing

molecules starting from silicon-hydrogen-containing molecules. The silicon-hydrogen bond (Si-H) is air- and water-stable, unlike silicon-chloride groups. Methods to initiate Si-H chemistry are often catalytic unlike the salt and acid elimination reactions described above.<sup>18</sup> The Si-H bond strength in  $R_3SiH$  is relatively invariant to the R groups and a wide array of hydrosilane reagents can undergo these reactions.<sup>19</sup> Many catalysts are available for Si-H bond activation, particularly transition metal catalysts.<sup>4c,d</sup> These reactions are more atom-efficient compared to the silicon-halide methods described above: hydrosilation produces no solid by-products, dehydrocoupling makes volatile hydrogen gas, and dealkylative coupling eliminates a small alkane, for example methane in demethanative coupling.

Hydrosilation (Scheme 1.5) is the formal addition of Si-H across an unsaturated bond, e.g.  $C=E$ , ( $E = O, S, CR_2, NR$ ). This is a common means of reducing unsaturated substrates in organic chemistry<sup>i</sup> and is also used industrially to cross-link silicones.<sup>20</sup>



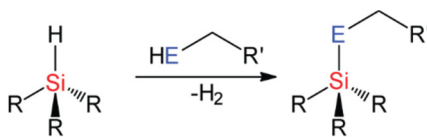
Dehydrocoupling (Scheme 1.6) is the reaction of Si-H with E-H to make a new Si-E bond. The sole by-product from this reaction, hydrogen gas ( $H_2$ ), is a low molecular weight volatile gas and its removal is straightforward. Common E-H substrates for dehydrocoupling are alcohols (O-H),<sup>21</sup> amines (N-H),<sup>22</sup> and thiols (S-H)<sup>23</sup> to make

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<sup>i</sup> Reduction of unsaturated substrates with hydrosilanes has been reviewed.<sup>4b-d</sup>

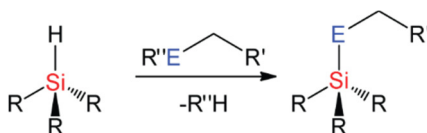
alkoxy, amido, or thiolato side-chains respectively.<sup>24</sup> Homodehydrocoupling to make Si-Si bonds has also been extensively studied and reviewed.<sup>25</sup>

**Scheme 1.6.**



Dealkylative coupling (Scheme 1.7) is the reaction of Si-H with R'CH<sub>2</sub>-E-R to make a new silicon-element bond while eliminating an alkane, R-H. This reaction is dependent on the size of the eliminating R group. Small groups, R = CH<sub>3</sub> > CH<sub>2</sub>CH<sub>3</sub> > CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> >> CH(CH<sub>3</sub>)<sub>2</sub> >>> C(CH<sub>3</sub>)<sub>3</sub>, eliminate more efficiently.<sup>26</sup> Dealkylative coupling is named after the eliminated alkane. For example, demethanative coupling eliminates CH<sub>4</sub> (methane) and deethanative coupling eliminates CH<sub>3</sub>CH<sub>3</sub> (ethane). The dealkylative coupling reactions described in this thesis primarily exploit demethanative coupling.

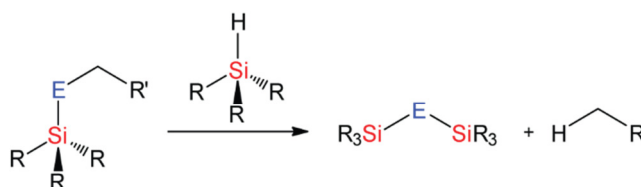
**Scheme 1.7.**



Hydrosilation is often referred to as a “partial reduction” reaction. This is because the “E” substrate has been reduced by Si-H. Dehydrocoupling and dealkylative coupling reactions are technically oxidation reactions. Yet dehydrocoupling and dealkylative coupling may be referred to as partial reductions because they form the same analogous products as hydrosilation, despite the absence of a comparable change in substrate oxidation state.

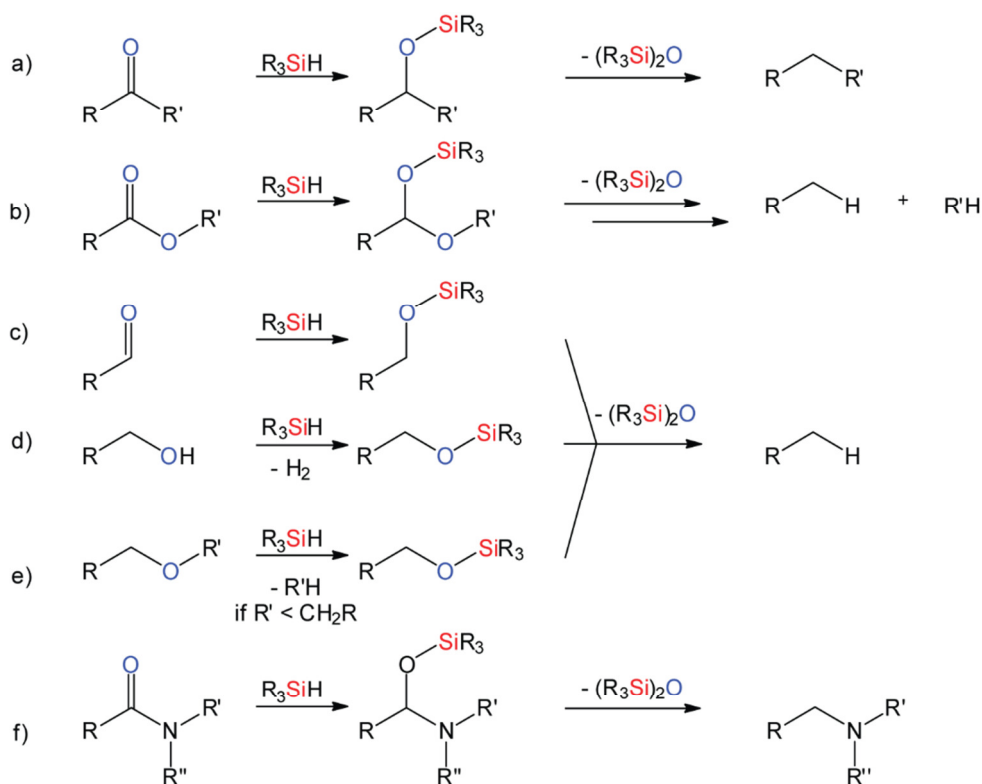
A special case of dealkylative coupling is an “over-reduction” reaction (Scheme 1.8). This is the case when the “E” substrate already contains a silicon-element bond, e.g.  $R_3SiOCH_2R'$ . Like dealkylative coupling, an alkane is eliminated, however, the element-containing product now has no silicon-to-carbon bonds and instead contains a silicon-element-silicon (Si-E-Si) linkage. Over-reduction can be a complicating factor in hydrosilation, dehydrocoupling, and dealkylative coupling reactions. Silicon-element bond-containing products from those reactions can undergo competing over-reduction reactions if another equivalent of Si-H is available. For example, the generalized silyl-containing product from dealkylative coupling (Scheme 1.7) can subsequently undergo an over-reduction reaction (Scheme 1.8) to eliminate  $R'CH_3$  and make the generalized silicon-element-silicon-containing product,  $R_3Si-E-SiR_3$ . The over-reduction reaction is common with oxygen-containing substrates (E = O), such as ketones (Scheme 1.9a),<sup>27</sup> esters (b),<sup>27</sup> aldehydes (c),<sup>27</sup> alcohols (d),<sup>2,28</sup> methyl ethers (e),<sup>2,28c</sup> and amides (f).<sup>29</sup> In these examples, a series of hydrosilation, dehydrocoupling, and dealkylative coupling reactions that terminates in an over-reduction reaction is often referred to simply as an over-reduction.<sup>ii</sup> Substantial interest in the hydrosilation and over-reduction of carbon dioxide has been reported in the recent literature.<sup>30</sup>

**Scheme 1.8.**



<sup>ii</sup> Full reduction and deoxygenation are also commonly used terms in the literature.

Scheme 1.9.



Hydrosilation, dehydrocoupling, and dealkylative coupling/over-reduction reactions have been exploited in the literature for the synthesis of complex silicon-containing molecules. The cross-linking of silicone polymers with Si-H and olefin groups is a well-established procedure.<sup>31</sup> As mentioned above, polysilane polymers can be prepared by homodehydrocoupling of monosilanes  $RSiH_3$ .<sup>25,32</sup> Dealkylative coupling has been exploited for attaching structurally complex aryloxy groups onto silicones starting from Si-H-containing polysiloxanes and these new silicones have shown interesting properties.<sup>33</sup> Synthesis of polysiloxanes via over-reduction was reported by Rubinsztajn starting from a Si-H-containing monomer with two Si-H units and a silicon-element-containing monomer with two Si-E-R units.<sup>34</sup> This polymerization was high-yielding, atom-efficient, and occurred at RT, and, suggested an alternative, attractive method

compared to the previously described hydrolysis of silicon-chloride-containing precursors.

### 1.3 Strategies for polysilane synthesis using $B(C_6F_5)_3$ -catalyzed hydrosilation, dehydrocoupling, and dealkylative coupling reaction

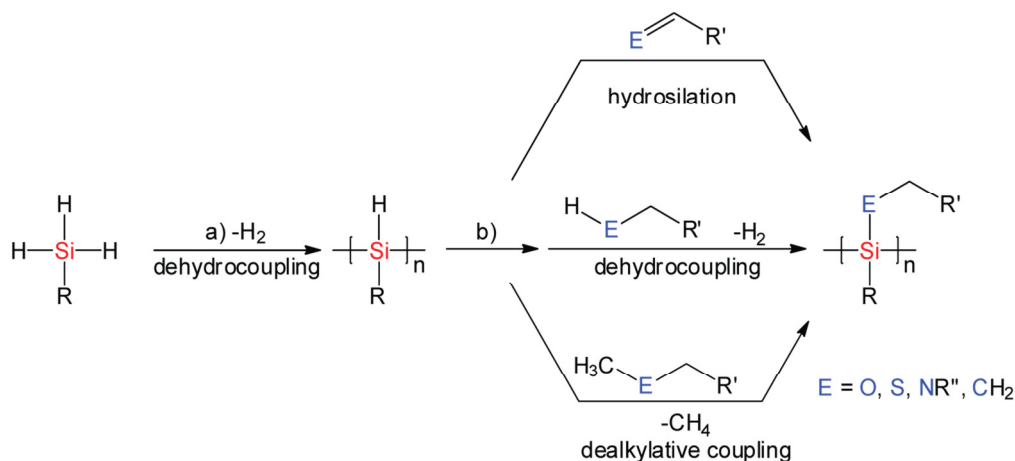
The primary goal of this thesis work was to use catalytic silane dehydrocoupling (Scheme 1.10a) to make polysilanes with repeat units  $-RSiH-$  and then apply hydrosilation, dehydrocoupling, or dealkylative coupling for the post-polymerization modification of these polysilanes (Scheme 1.10b). A significant literature detailing polysilanes prepared by dehydrocoupling has been published,<sup>5,14,25,32</sup> however general routes to polysilanes with the formula  $-RR'Si-$  have not yet been achieved by this method due to the low activity of secondary silanes in this reaction – they typically give short oligosilanes up to four silicon repeat units long. The post-polymerization route to  $-RR'Si-$  from  $-RSiH-$  has been achieved in some cases, but suffers from chemoselectivity problems. Reaction conditions amenable to, for example, hydrosilation (Scheme 1.5), often are the same as those used for silicon-silicon bond cleavage: typical transition metal catalysts such as Speier's catalyst ( $H_2PtCl_6$ )<sup>35</sup> or Karstedt's catalyst ( $[(CH_2=CHSiMe_2)_2O]Pt-\mu-(CH_2=CHSiMe_2)_2O-Pt[O(Me_2SiCH=CH_2)]$ )<sup>36</sup> are useful for hydrosilation chemistry; yet platinum complexes are commonly used for Si-Si bond cleavage<sup>iii</sup> and will likely degrade the polysilane oxidatively. This selectivity challenge has precluded the application of standard conditions and catalysts used for hydrosilation, dehydrocoupling, and dealkylative coupling to reactions with Si-H-containing

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<sup>iii</sup> There are many examples of late row transition metal complex cleaving Si-Si bonds and this has been reviewed.<sup>37</sup>

polysilanes. Some examples that have demonstrated efficient modification of silicon-hydride in polysilanes show some degree of silicon-silicon bond degradation.<sup>iv</sup>

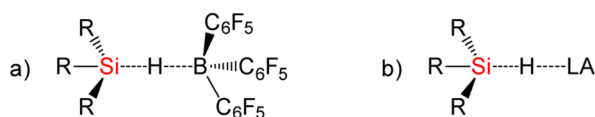
**Scheme 1.10.**



The Rosenberg group sought to address this selectivity problem by first studying the disilane  $(\text{Ph}_2\text{SiH})_2$  (**2-2**, hereafter referred to as disilane), which is a discrete small molecule model for a polysilane since it contains Si-Si and Si-H bonds. The desired selectivity was found using the borane catalyst,  $\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>1</sup>  $\text{B}(\text{C}_6\text{F}_5)_3$  had been established as a catalyst for the hydrosilation of carbonyls and imines and for the dehydrocoupling of alcohols with less complex monosilanes, bearing a single Si-H bond, but not for silanes containing Si-Si bonds.<sup>21,41</sup> The  $\text{B}(\text{C}_6\text{F}_5)_3$  catalyst has been shown to act differently toward Si-H bonds than traditional Lewis acids, including  $\text{BF}_3$ .<sup>42</sup> It was at the time anticipated that the classical substrate- $\text{B}(\text{C}_6\text{F}_5)_3$  complex, where the substrate is the

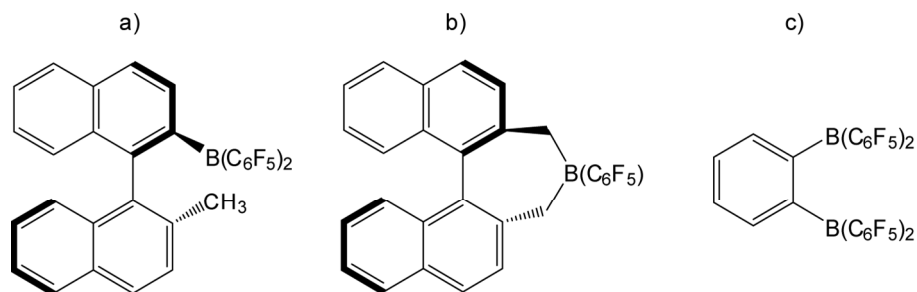
<sup>iv</sup> Waymouth reports that the halogenation of poly(phenylsilane) does not give shorter polymer, however reactions of poly(halophenylsilane) gave polymers with lower molecular weights (MWs) than the parent poly(phenylsilane), which is evident of Si-Si bond cleavage.<sup>38</sup> AIBN-initiated hydrosilation also gives polymers with lower-than-expected MWs.<sup>39</sup> Tanaka reports selectivity for the Si-Si bond in  $\text{AlCl}_3$ -catalyzed hydrosilation of alkynes with short-chain oligosilanes, however reactions of polysilanes gave some chain scission products.<sup>40</sup>

heteroatom reagent (e.g. carbonyl, alcohol, or alkyl ether) and hereafter referred to as such, was the key step in the reaction mechanism. Instead,  $B(C_6F_5)_3$  forms the  $\eta^1$ -silane-borane complex (Figure 1.1a) that leads to product formation while the aforementioned substrate- $B(C_6F_5)_3$  complex actually inhibited catalysis.

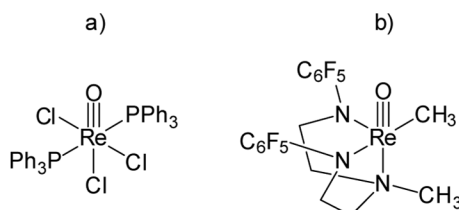


**Figure 1.1.** a)  $\eta^1$ -silane-borane complex and b) generic  $\eta^1$ -silane strong Lewis acid complex (LA = Lewis acid).

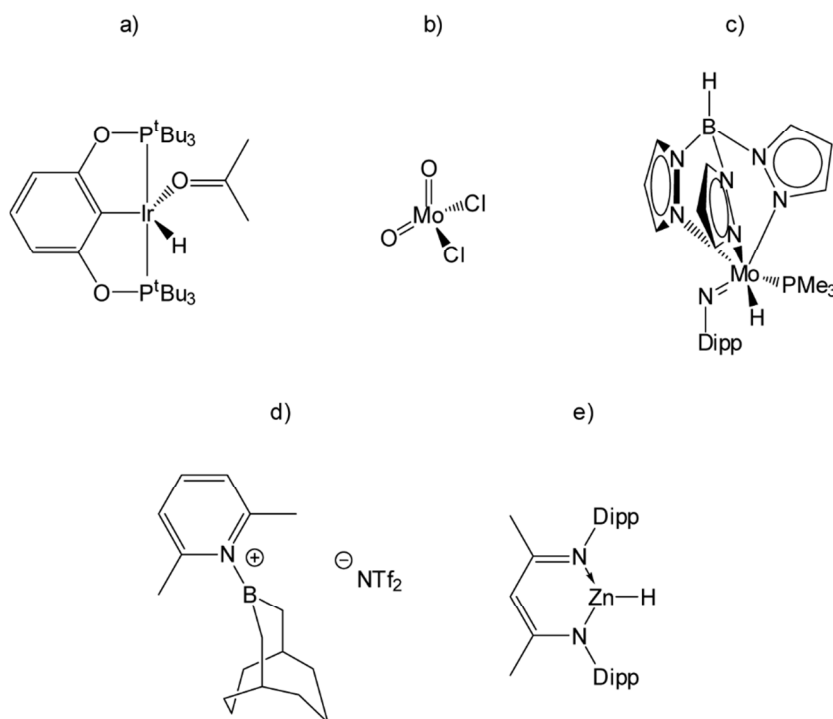
This type of  $\eta^1$ - $R_3Si\cdots H\cdots LA$  coordination complex (Figure 1.1b), where LA is a generalized Lewis acid, is reported with increasing frequency in the literature and will be discussed in greater detail in Chapter 2. Notable examples include the following: borane-based catalysts such as those shown in Figure 1.2a/b<sup>43</sup> and  $H_{o/p}$ - $B(C_6F_4H)$  (Figure 1.2c);<sup>44</sup>  $[R_3Si]^+[B(C_6F_5)_4]^-$ , silylium-ion mediated reactions;<sup>42b,45</sup> rhenium catalysts shown (Figure 1.3);<sup>46</sup>  $[Ph_3C]^+[B(C_6F_5)_4]^-$ , trityl cation-based reagents;<sup>47</sup> an iridium pincer complex (Figure 1.4a);<sup>30e</sup> molybdenum catalysts such as  $Mo(O)_2Cl_2$  (Figure 1.4b)<sup>48</sup> and  $MoTp(NDipp)(H)PMe_3$  (Figure 1.4c);<sup>49</sup> a borenium cation catalyst (Figure 1.4d);<sup>50</sup>  $\beta$ -diketiminato supported zinc catalyst (Figure 1.4e);<sup>51</sup> Stryker's reagent ( $[(PPh_3)CuH]_6$ );<sup>52</sup> and Lewis acidic phosphonium cations (Figure 1.5).<sup>53</sup>



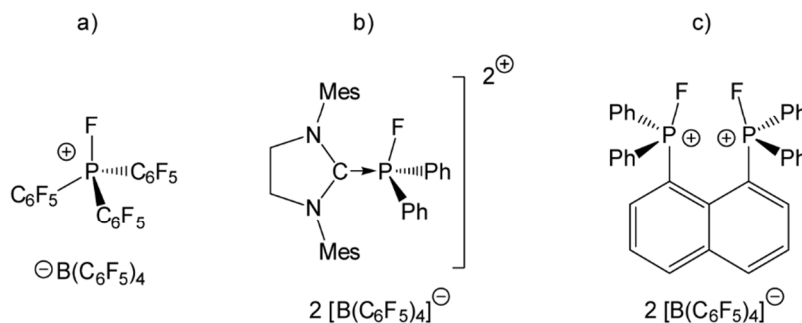
**Figure 1.2.**  $B(C_6F_5)_3$ -like catalysts a) 2- $B(C_6F_5)_2$ -2'-( $CH_3$ ) $C_{20}H_{12}$ ,<sup>43b</sup> b)  $B(C_6F_5)_2$ (2,2'-( $CH_2$ ) $_2C_{20}H_{12}$ ),<sup>43c,d</sup> and c) 1,2-( $B(C_6F_5)_2$ ) $C_6H_4$ ,<sup>43a</sup> for catalytic hydrosilation, dehydrocoupling, or dealkylative coupling reactions.



**Figure 1.3.** Rhenium-based catalysts a)  $Re(O)(PPh_3)_2Cl_2$ <sup>46a</sup> and b)  $Re(O)(CH_3)(N(C_6F_5)CH_2CH_2N(CH_3)CH_2CH_2N(C_6F_5))_2$ <sup>46b</sup> for catalytic hydrosilation reactions.



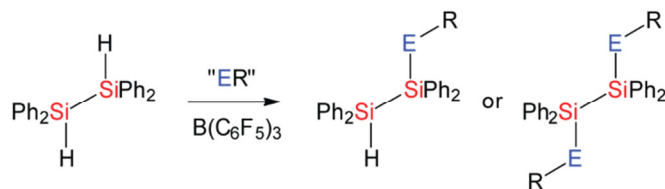
**Figure 1.4.** Miscellaneous catalysts exhibiting  $\eta^1-H \cdots SiR_3$  activation for hydrosilation reactions a)  $Ir(P^tBu_3-OC_6H_3O-P^tBu_3)(H)(OC(CH_3)_2)_2$ ,<sup>30e</sup> b)  $Mo(O)_2Cl_2$ ,<sup>48</sup> c)  $[2,6-(CH_3)_2C_5H_3N-BC_{10}H_{18}]^+[NTf_2]^-$  (Tf =  $S(O)_2CF_3$ ),<sup>49</sup> d)  $MoTp(NDipp)(H)PMe_3$  (Tp =  $HB(C_3H_3N)_3$ , Dipp = 2,6- $^iPr_2C_6H_3$ ),<sup>50</sup> and e)  $Zn(Dipp)NC(CH_3)CHC(CH_3)NDippH$ .<sup>51</sup>



**Figure 1.5.** Lewis acidic phosphonium cations a)  $([P(C_6F_5)_3F]^+[B(C_6F_5)_4]^-)$ ,<sup>53a</sup> b)  $[SIMesPPh_2F]^{2+}[B(C_6F_5)_4]_2^{2-}$  (SIMes = 1,3-Mes<sub>2</sub>C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>, Mes = 2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>),<sup>53c</sup> and c)  $([1,8-(PPh_2F)C_8H_{10}]^{2+}[B(C_6F_5)_4]_2^{2-})$ <sup>53b</sup> for Si-H activation and catalytic hydrosilation or dehydrocoupling.

Sulfur-containing substrates such as thiols and thioketones bind even more weakly to  $B(C_6F_5)_3$  than oxygen- or nitrogen-containing substrates described in the above studies and should therefore be more optimal for  $B(C_6F_5)_3$ -catalyzed reactions. Former Rosenberg group student Dan Harrison demonstrated that hydrosilation of thioketones and dehydrocoupling of thiols catalyzed by  $B(C_6F_5)_3$  proceeded with absolute selectivity for Si-H bond activation, giving the anticipated products,  $Ph_2SiH-Si(SR)Ph_2$  or  $(Ph_2SiSR)_2$  (monosubstituted or disubstituted, respectively, Scheme 1.11) with complete retention of the silicon-silicon bond.<sup>1</sup>

**Scheme 1.11.**



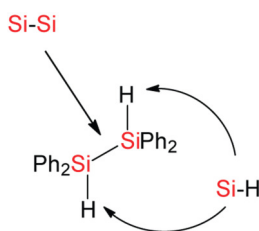
These important studies led to establishing the following goals: i) expanding the scope of  $B(C_6F_5)_3$ -catalyzed partial reduction reactions of oligosilanes (hydrosilation, dehydrocoupling, and dealkylative coupling) with new substrates encompassing S, O, N, and C-side-chains (Chapter 2) with a focus on understanding (and either avoiding or

exploiting) competing over-reduction reactions (Chapter 3); ii) applying  $B(C_6F_5)_3$ -catalyzed hydrosilation, dehydrocoupling, and dealkylative coupling to the post-polymerization modification of polysilanes with Si-H in the repeat unit (Chapter 4); and iii) investigating the selectivity of  $B(C_6F_5)_3$  catalysis for Si-H bond versus Si-Si bond scission in these long chains, which are less robust than the model disilane (**2-2**) (Chapter 4). A tangential study of the products from the thermal degradation of poly(phenylsilane) arose from a collaboration in 2013 with SeaStar Chemicals (Chapter 5). Together, the results of these experiments represent important steps towards expanding the variety of complex silicon-containing molecules that are available for potential use in synthesis and materials applications.

## 2 B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed partial reduction of Ph<sub>2</sub>MeSiH and (Ph<sub>2</sub>SiH)<sub>2</sub>

### 2.1 Introduction

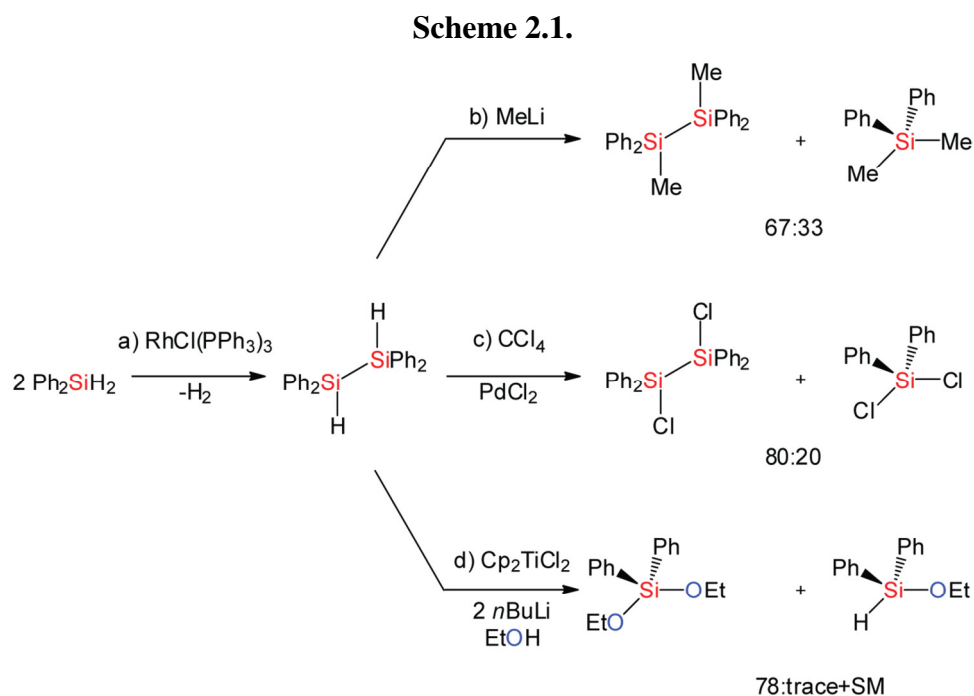
This chapter describes efforts to achieve selective Si-H activation and functionalization of oligosilanes bearing Si-H and Si-Si bonds, through catalysis with tris(pentafluorophenylborane), hereafter called B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. There is a wealth of literature reporting methods of activating silicon-hydrogen (Si-H) bonds, such as stoichiometric halogenation,<sup>54</sup> oxidation,<sup>4b</sup> deprotonation,<sup>55</sup> transition-metal catalysis,<sup>4c,d</sup> and Lewis-acid catalysis.<sup>40,42a,56</sup> However, these methods are incompatible with oligosilanes that contain both silicon-hydrogen (Si-H) and silicon-silicon (Si-Si) bonds since these reagents and catalysts activate Si-H bonds and cleave Si-Si bonds. Finding routes for the activation of Si-H bonds in the presence of Si-Si bonds is an ongoing challenge.



**Figure 2.1.** Si-H and Si-Si bonds in (Ph<sub>2</sub>SiH)<sub>2</sub> (**2-2**, disilane).

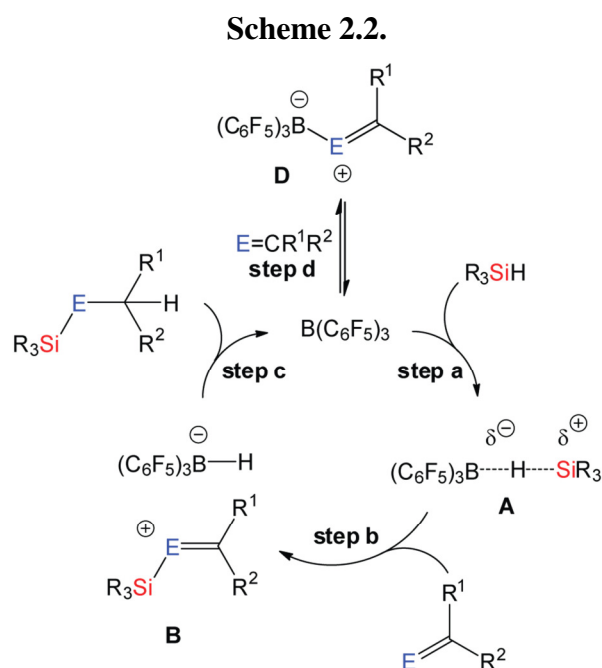
The Rosenberg group has previously studied the selectivity for Si-H activation and Si-Si bond cleavage using the disilane (Ph<sub>2</sub>SiH)<sub>2</sub> (**2-2**),<sup>1c</sup> which has two Si-H units and one Si-Si bond (Figure 2.1); the disilane **2-2** serves as a small-molecule chemoselectivity-model substitute for polysilane. Many reagents and conditions were screened with disilane **2-2**, including reactions with strong bases (Scheme 2.1b), halogenation reactions (Scheme 2.1c), and transition-metal catalyzed reactions (Scheme

2.1d). Some of these reactions had purported selectivity for poly(phenylsilane) modification, particularly halogenation<sup>38</sup> and transition metal catalyzed methods.<sup>57</sup> However, reactions of disilane (e.g. Scheme 2.1b-d) consistently generated a mixture of products exhibiting various degrees of desirable Si-H activation and undesirable Si-Si cleavage.<sup>1c</sup>



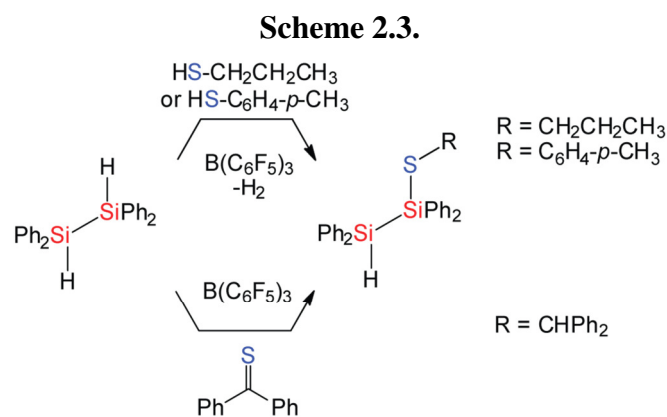
Prior to these studies in the Rosenberg group, the strong Lewis acid,  $\text{B}(\text{C}_6\text{F}_5)_3$  was demonstrated to be a catalyst for hydrosilation, dehydrocoupling, and dealkylative coupling.<sup>41b,42a,58</sup> These reactions were demonstrated to have three beneficial features: mild reaction conditions (most examples were done at RT);<sup>21</sup> low catalyst loading (1-4 mol%  $\text{B}(\text{C}_6\text{F}_5)_3$ );<sup>41b</sup> and applicability to a wide range of substrates such as aldehydes/ketones/esters,<sup>41b</sup> alcohols/phenols,<sup>21</sup> and alkyl ethers.<sup>33c</sup> Lewis acid activation of the heteroatom substrate, e.g. a carbonyl group, should be the key step according to traditional Lewis acid catalysis. However, strongly basic substrates, which were expected

to coordinate well with  $B(C_6F_5)_3$ , were actually found to inhibit catalysis. The investigators found that  $B(C_6F_5)_3$  forms an important silane-borane complex  $((C_6F_5)_3B \cdots H \cdots SiR_3$ , **A** in Scheme 2.2) and this key association is the important step for Si-E formation. This is known as the Piers-Oestreich mechanism, which is shown for hydrosilation in Scheme 2.2.<sup>41b,42a,b,d,e,59</sup> Similar and analogous steps are involved in the heterodehydrocoupling and dealkylative coupling reaction mechanisms with E-H- or E-alkyl substrates.<sup>21,60</sup>



This unique hydrosilation/dehydrocoupling/dealkylative coupling method was recognized by the Rosenberg group for its potential application to the catalytic activation of Si-H in  $(Ph_2SiH)_2$ . Silane-borane complex (**A**) formation was encouraged by selecting sulfur substrates, such as *n*-propylthiol, thiobenzophenone, and *p*-thiocresol, or oxygen substrates, such as *p*-nitrobenzaldehyde and catechol, which have weaker Lewis base interaction with  $B(C_6F_5)_3$ .<sup>61</sup> Efficient and selective routes to new Si-Si-E-containing

molecules were developed using the  $B(C_6F_5)_3$ -catalyzed method (Scheme 2.3). Identified products from these reactions were either the monosubstituted disilane ( $Ph_2SiH-Si(X)Ph_2$ ) or disubstituted disilane ( $(Ph_2SiX)_2$ ) ( $X = E$ -containing side-chain). Most importantly, in all examples and trials, these reactions showed absolute selectivity for Si-H activation with no competing Si-Si bond cleavage.<sup>1</sup>



This work begins with the expansion of the previously established<sup>1</sup> scope of reactions to include a wider array of substrates. In this chapter,  $B(C_6F_5)_3$ -catalyzed reactions with oxygen-, nitrogen-, sulfur- and olefin-containing substrates are reported. These reactions were initially evaluated with a monosilane,  $Ph_2MeSiH$  (**2-1**, in Section 2.2), to establish reactivity and benchmarks for subsequent reactions with the disilane, (**2-2**,  $(Ph_2SiH)_2$ , in Section 2.3). The subtle differences in substrate that give either monosubstituted (formula  $Ph_2SiH-Si(X)Ph_2$ ) or disubstituted (formula  $(Ph_2SiX)_2$ ) disilane products where 'X' is the appended group are described. These studies led to the synthesis of a unique, unsymmetrically-disubstituted disilane (formula  $Ph_2SiX-Si(X')Ph_2$ , Section 2.3.3), and suggest the potential for other unsymmetrically-substituted disilanes to be formed by a similar method.


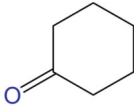
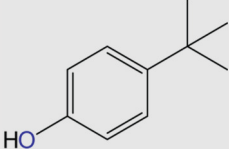
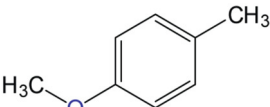
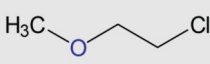
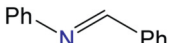
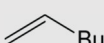
## 2.2 B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed synthesis of X-modified monosilanes

A variety of substrates was initially evaluated by screening their reactivity with Ph<sub>2</sub>MeSiH, a monosilane in which the Si-H bond has a similar steric environment to that in the disilane. The resulting X-functionalized monosilanes (**2-3** to **2-11**) are shown in Table 2.1. The reactions are straightforward, except for the hydrosilation of propionaldehyde (to form **2-3**). Over-reduction chemistry was detected in the hydrosilation of propionaldehyde: B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyzes the reaction of the hydrosilation product Ph<sub>2</sub>MeSiO<sup>n</sup>Pr (**2-3**) and a second equivalent of Ph<sub>2</sub>MeSiH (**2-1**) to give Ph<sub>2</sub>MeSi-O-SiMePh<sub>2</sub> (**2-4**)<sup>v</sup>, presumably with loss of propane. The B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed over-reduction reaction will be discussed in greater detail in Chapter 3.

**Table 2.1.** (a) Hydrosilation, (b) dehydrocoupling, and (c) demethanative coupling reactions of Ph<sub>2</sub>MeSiH (**2-1**) mediated by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.

#	Substrate	Product <sup>a</sup>	catalyst loading, reaction time <sup>b</sup>	<sup>29</sup> Si NMR <sup>c</sup> (ppm)	% Yield
<b>2-3</b>		Ph <sub>2</sub> MeSiOCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	4 mol%, 16 h	-3.8	<sup>d</sup>

<sup>v</sup> The disiloxane product, (Ph<sub>2</sub>MeSi)<sub>2</sub>O (**2-4**), has been identified and characterized in the literature.<sup>62</sup> Examples of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed reactions leading to general disiloxane structures have also been identified in the literature.<sup>2,27a,28c,42b,60,63</sup>

2-5		$\text{Ph}_2\text{MeSiOCH}(\text{CH}_3)_2$	4 mol%, 12 h	-6.1	73
2-6		$\text{Ph}_2\text{MeSiOC}_6\text{H}_{11}$	5 mol%, 16 h	-6.1	<sup>e</sup>
2-7		$\text{Ph}_2\text{MeSiOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$	5 mol%, 1 h	-3.7	99
2-8		$\text{Ph}_2\text{MeSiOC}_6\text{H}_4\text{-}p\text{-CH}_3$	4 mol%, 1 h	-3.6	99
2-9		$\text{Ph}_2\text{MeSiOCH}_2\text{CH}_2\text{Cl}$	3 mol%, 2 h	-1.9	83
2-10		$\text{Ph}_2\text{MeSiN}(\text{Ph})\text{CH}_2\text{Ph}$	4 mol%, 60 °C, 16 h in $\text{C}_6\text{H}_6$	-5.3	97
2-11		$\text{Ph}_2\text{MeSiCH}_2\text{CH}_2\text{Bu}$	4 mol%, 16 h in 1-hexene/ $\text{CH}_2\text{Cl}_2^f$	-7.1	74

<sup>a</sup>Other functionalized monosilanes containing Si-S bonds made by  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysis have been previously reported.<sup>1a,b</sup> <sup>b</sup>Reactions were carried out at RT and the solvent was toluene, unless otherwise specified. <sup>c</sup>In  $\text{C}_6\text{D}_6$ . <sup>d</sup>The  $^1\text{H}$  NMR showed complete conversion of  $\text{Ph}_2\text{MeSiH}$  to products with 76% converted to alkoxy silane ( $\text{Ph}_2\text{MeSiOCH}_2\text{CH}_2\text{CH}_3$ , **2-3**) and 24% converted to disiloxane ( $\text{Ph}_2\text{MeSi-O-SiMePh}_2$ , **2-4**). <sup>e</sup>The  $^1\text{H}$  NMR showed a mixture of  $\text{Ph}_2\text{MeSiOC}_6\text{H}_{11}$  (**2-6**, 86%) and unreacted  $\text{Ph}_2\text{MeSiH}$  (**2-1**, 14%). <sup>f</sup>An excess of 1-hexene was used (4:1 1-hexene: $\text{Ph}_2\text{MeSiH}$ ). Partial conversion to **2-11** was observed when a 1:1 stoichiometry was used.

Hydrolysis is a persistent problem in reactions with imines and olefins.

Hydrosilation of benzylideneaniline (and likely other imines) gave the hydrosilation

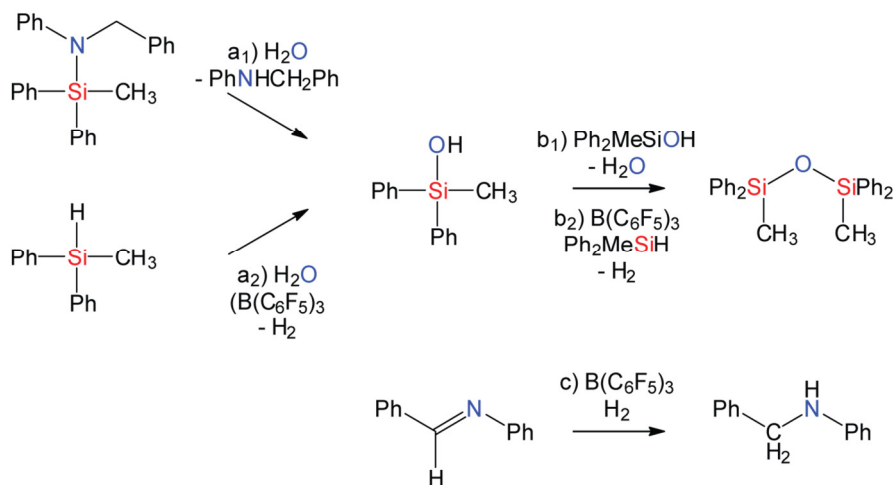
product,  $\text{Ph}_2\text{MeSiN(Ph)CH}_2\text{Ph}$  (**2-10**), free amine,  $\text{PhNHCH}_2\text{Ph}$ , and disiloxane,  $\text{Ph}_2\text{MeSi-O-SiMePh}_2$  (**2-4**). The two by-products formed on hydrolysis of the Si-N bond in **2-10** (Scheme 2.4a<sub>1</sub>) or of the monosilane (Scheme 2.4a<sub>2</sub>) via  $\text{B(C}_6\text{F}_5)_3$  catalysis. In either case, this gives the silanol, which is susceptible to condensation (Scheme 2.4b<sub>1</sub>) or dehydrocoupling (Scheme 2.4b<sub>2</sub>). The free amine,  $\text{HN(Ph)CH}_2\text{Ph}$ , forms either from hydrolysis of the Si-N bond (Scheme 2.4a<sub>1</sub>) or from  $\text{B(C}_6\text{F}_5)_3$ -catalyzed hydrogenation (Scheme 2.4c). The competing hydrolysis reaction was minimized (trace disiloxane detected by  $^1\text{H NMR}$ , see Section 2.6.2, Figure 2.8) by changing the reaction solvent from toluene to benzene, which was rigorously dried by distillation over sodium metal.<sup>vi</sup> Likewise, reactions of silanes with allylbenzene (not included in Table 2.1) gave undesirable hydrolysis by-products to give the disiloxane,  $(\text{Ph}_2\text{MeSi})_2\text{O}$  **2-4**. Allylbenzene and trace water compete for nucleophilic attack of  $(\text{C}_6\text{F}_5)_3\text{B}\cdots\text{H}\cdots\text{SiR}_3$  (**A**, Scheme 2.2). Some residual water likely remained in allylbenzene even after distillation over magnesium sulfate (see experimental Section 2.6.1), and the problem was magnified when an excess of allylbenzene was added.<sup>vii</sup>

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<sup>vi</sup> Benzene was used because it was previously distilled it for the synthesis and workup of poly(phenylsilane) (**4-1**, see Chapter 4). Toluene was obtained from the solvent purification system and was found to be insufficiently dry for extremely water sensitive syntheses, such as the synthesis of **2-10**.

<sup>vii</sup> Used 15 equivalents of allylbenzene, 90% by volume.

Scheme 2.4



$\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed hydrosilation of olefins, either allylbenzene, 1-hexene, or attempts with propylene, are more challenging than ones with heteroatoms, such as phenols, ketones, and thiols. It was determined that the addition of a small amount of dichloromethane (~10% by volume) is also necessary for these olefin hydrosilation reactions, probably to facilitate transient polarization of the double bond during nucleophilic attack at the silylium intermediate (**step b**, Scheme 2.2). More relevant to the issue of trace moisture leading to competing catalytic hydrolysis of silane, the reaction of 1:1 olefin-to-silane stoichiometry resulted in very low product conversions (<1%, estimated by  $^1\text{H}$  NMR) and an excess of olefin substrate (e.g. 4 equivalents) was required for complete conversion. Reactions of monosilane with propylene showed only partial conversion (<1% by  $^1\text{H}$  NMR, not included in Table 2.2) because gaseous propylene could not be added and condensed into a solution of  $\text{CH}_2\text{Cl}_2$  and **2-1** in a high enough quantity for complete conversion. An allylbenzene-to-silane stoichiometry that affords high conversion to  $\text{Ph}_2\text{MeSiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$  has not yet been found, but  $^1\text{H}$  NMR signals consistent with its formation in low conversion have been identified. It is likely that allylbenzene- $\text{B}(\text{C}_6\text{F}_5)_3$  complexation (Scheme 2.2, **D**) inhibits catalysis. Similar non-


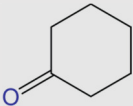
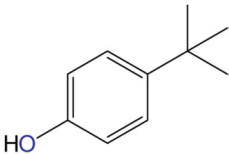
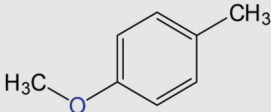
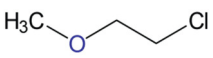
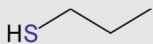
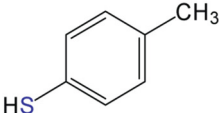
heteroatom sequestration of  $B(C_6F_5)_3$  by phenylacetylene has been found, which forms a deep red solution in  $C_6D_6$ , toluene, or  $CDCl_3$ . This completely inhibits Si-H reactivity with  $Ph_2MeSiH$ ,  $Ph_2SiH_2$ , and  $PhSiH_3$ . Olefin- $B(C_6F_5)_3$  binding is suspected to be weaker in reactions of 1-hexene, leading to complete conversion to **2-11**.

The identification and preparation of these diverse monosilanes illustrates the wide scope of all reaction types, hydrosilation, dehydrocoupling, and dealkylative coupling with sulfur, oxygen, nitrogen, or carbon-containing substrates, and the resulting Si-X compounds (Table 2.1) that are achievable under mild conditions.

### 2.3 $B(C_6F_5)_3$ -catalyzed synthesis of X-modified disilanes

The extension of the simple reactions of  $Ph_2MeSiH$  shown in Table 2.1 to the derivatization of disilane **2-2** highlighted three issues that can affect the results of this synthetic route to the formation of functionalized disilanes: (i) low conversions for more basic substrates due to catalyst inhibition (i.e. binding of substrate to  $B(C_6F_5)_3$ ) and/or catalyst poisoning, which sometimes occurs following substrate-to- $B(C_6F_5)_3$  binding (Section 2.3.1)); (ii) a sensitivity to the steric bulk of the substrate for the selectivity to give mono- or disubstituted products (Section 2.3.2 and 2.3.3); and (iii) competing over-reduction reactions that occur with straight-chain alkoxy groups, eliminating alkyl-H and forming Si-O-Si (Section 2.3.4 and in more detail in Chapter 3). Below, the reactions of disilane with a variety of substrates are reported and discussed in the context of the generally-accepted mechanism for  $B(C_6F_5)_3$ -catalyzed Si-H activation (Scheme 2.2).

**Table 2.2.** Monosubstituted disilanes prepared by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed reactions of disilane 2-2.

#	Substrate	X =	Conditions <sup>a</sup> : catalyst loading <sup>b</sup> , temperature, time	<sup>29</sup> Si NMR (ppm)	% Yield
$  \begin{array}{ccc}  \begin{array}{c} \text{H} \\   \\ \text{Ph}_2\text{Si}-\text{SiPh}_2 \\   \\ \text{H} \\ \mathbf{2-2} \end{array} & \xrightarrow[\text{B(C}_6\text{F}_5)_3, -\text{H}_2/\text{CH}_4]{\begin{array}{c} \text{E=CRR}^1 \text{ or RE-H/CH}_3 \\ 1 \text{ equiv} \\ \text{E = O, S} \end{array}} & \begin{array}{c} \text{X} \\   \\ \text{Ph}_2\text{Si}-\text{SiPh}_2 \\   \\ \text{H} \end{array}  \end{array}  $					
2-12		OCH(CH <sub>3</sub> ) <sub>2</sub>	5 mol%, RT, 16 h	δ -8.1 (Si-O), -38.2 (Si-H)	86
2-13		OC <sub>6</sub> H <sub>11</sub>	7 mol%, 55 °C, 5 h	δ -8.2 (Si-O), -33.8 (Si-H)	67
2-14		OC <sub>6</sub> H <sub>4</sub> - <i>p</i> - <sup>t</sup> Bu	5 mol%, 70 °C, 32 h	δ -6.4 (Si-O), -38.3 (Si-H)	<i>d</i>
2-15		OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	5 mol%, RT, 16 h	δ -6.3 (Si-O), -38.4 (Si-H)	99
2-16		OCH <sub>2</sub> CH <sub>2</sub> Cl	C <sub>6</sub> D <sub>6</sub> , 7 mol%, RT, 144 h	<i>e</i>	<i>f</i>
2-17 <sup>g</sup>		SCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	5 mol%, RT, 15 h	δ -9.8 (Si-S), -35.9 (Si-H)	98
2-18 <sup>g</sup>		SC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	2 mol%, RT, 1 h	δ -8.9 (Si-S), -35.1 (Si-H)	90

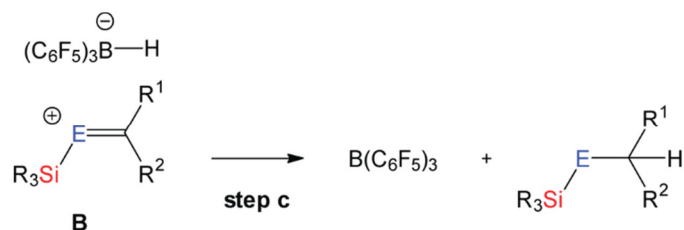
<sup>a</sup>Solvent was toluene, unless otherwise noted. <sup>b</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyst loading reported in mol% relative to mole equivalents of Si-H in silane substrate (two equivalents of Si-H in **2-2**). <sup>c</sup>NMR solvent was C<sub>6</sub>D<sub>6</sub>. <sup>d</sup>Reaction proceeded until all disilane reacted, which gave the desired product along with approximately 15% (estimated by <sup>1</sup>H NMR integration) of the disubstituted disilane (**2-20**). <sup>e</sup>This reaction was monitored by <sup>1</sup>H NMR. No <sup>13</sup>C or <sup>29</sup>Si NMR was collected because a complex mixture was found. <sup>f</sup>Reactions of carefully controlled 1:1 (Ph<sub>2</sub>SiH)<sub>2</sub>:CH<sub>3</sub>-O-CH<sub>2</sub>CH<sub>2</sub>Cl stoichiometry gave a mixture of starting disilane **2-2**, monosubstituted disilane (**2-16**), and disubstituted disilane (**2-22**) (15:75:10% estimated by <sup>1</sup>H NMR integration) <sup>g</sup>Previously reported in the literature.<sup>1a</sup>

**Table 2.3.** Disubstituted disilanes prepared by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed reactions of disilane **2-2**.

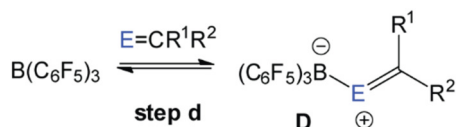
#	Substrate	X =	Conditions <sup>a</sup> : catalyst loading <sup>b</sup> , temperature, time	<sup>29</sup> Si NMR (ppm)	% Yield
<b>2-19</b>		CH <sub>2</sub> CH <sub>2</sub> Bu <sup>c</sup>	1-hexene/ CH <sub>2</sub> Cl <sub>2</sub> , 6 mol%, RT, 72 h	-20.3	87
<b>2-20</b>		OC <sub>6</sub> H <sub>4</sub> - <i>p</i> - <sup>t</sup> Bu	10 mol%, 70 °C, 16 h	-11.1	21
<b>2-21</b>		OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	8 mol%, 70 °C, 29 d	<sup>d</sup>	35 <sup>e</sup>
<b>2-22</b>		OCH <sub>2</sub> CH <sub>2</sub> Cl	5 mol%, RT, 16 h	-7.7	65
<b>2-23<sup>f</sup></b>		SC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	4 mol%, RT, 72 h	-10.6	94



Scheme 2.7.



Scheme 2.8.



As mentioned in Section 2.1, when originally formulated, the Piers-Oestreich mechanism shown in Scheme 2.2 (steps shown again in Scheme 2.5 to Scheme 2.8) presented a departure from the “classic” mode of Lewis acid activation of, for example, carbonyl groups, which relies on  $\text{B}(\text{C}_6\text{F}_5)_3$  binding to the, e.g. O-donor, inducing C-O bond polarization and subsequently facilitating a reaction of the organic substrate. The formation of such traditional Lewis adducts can occur in reactions of silane with  $\text{B}(\text{C}_6\text{F}_5)_3$  (see **step d** in Scheme 2.8), but generally provides a slower pathway than the silane adduct formation.<sup>42c</sup> In Scheme 2.2, this is illustrated by showing the formation of the  $\text{B}(\text{C}_6\text{F}_5)_3$ -carbonyl adduct, **D**, as an off-cycle event. If this equilibrium lies sufficiently towards **D**, catalyst inhibition will occur, since the concentration of free  $\text{B}(\text{C}_6\text{F}_5)_3$  available to activate the Si-H bond will be significantly reduced. Accordingly, very low turnovers are reported in the attempted  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed dehydrocoupling reactions of silanes with small primary alcohols such as *n*-propanol and ethanol,<sup>21</sup> and no dehydrocoupling of *n*-propanol with disilane **2-2** is observed in the presence of up to 10 mol%  $\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>1a,c</sup> Evidently, the primary alcohol substrates bind to  $\text{B}(\text{C}_6\text{F}_5)_3$  sufficiently to inhibit the catalytic reaction, due to their basic nature. The Rosenberg group previously

exploited the lower  $B(C_6F_5)_3$  binding affinity of thiols, relative to alcohols, in the facile incorporation of both  $-SCH_2CH_2CH_3$  and  $-SC_6H_4-p-CH_3$  sidechains via dehydrocoupling reactions of *n*-propylthiol (**2-17**) and *p*-thiocresol (monosubstituted **2-18**, disubstituted **2-23**) at low catalyst loadings.<sup>1a</sup>

Catalyst inhibition and/or poisoning was noted in the reaction of *p-t*-butylphenol or *p*-methylanisole with disilane **2-2**. A low conversion to the monosubstituted disilane **2-14** was found at RT (32% conversion, estimated by  $^1H$  NMR integration, see experimental Section 2.6.3). Moving to a less Lewis basic source of OAr, the methyl ether substrate *p*-methylanisole, which can participate in demethanative coupling, near-complete conversion was obtained under mild conditions and catalyst loading comparable to the loading used for the monosubstituted disilane **2-14**. This result suggested that less catalyst inhibition occurred with *p*-methylanisole compared to *p-t*-butylphenol. The synthesis of the disubstituted product (**2-20**) showed evidence for the poisoning of catalyst  $B(C_6F_5)_3$ :  $^1H$  and  $^{19}F$  NMR spectra showed signals that were attributable to products of the decomposition to the putative  $B(C_6F_5)_3$ -phenolysis products  $B(OC_6H_4-p-^tBu)_3$  and  $HC_6F_5$ , (experimental Section 2.6.3, see Figure 2.19). The reaction to give the disubstituted product derived from *p*-methylanisole (**2-21**) did not give poisoning products,  $B(OC_6H_4-p-CH_3)_3$  and  $CH_3-C_6F_5$ , even after heating the reaction for days.

These aryloxy examples also demonstrate the role of the silane's steric bulk that impacts the nucleophilic attack (Figure 2.7) of the substrate at silicon in the  $(C_6F_5)_3B \cdots H \cdots SiR_3$  complex (A). Computations on  $R_3SiH$  and  $B(C_6F_5)_3$  showed that the LUMO of the Lewis adduct  $(C_6F_5)_3B \cdots H \cdots SiR_3$  (Scheme 2.2, A) had a large lobe on

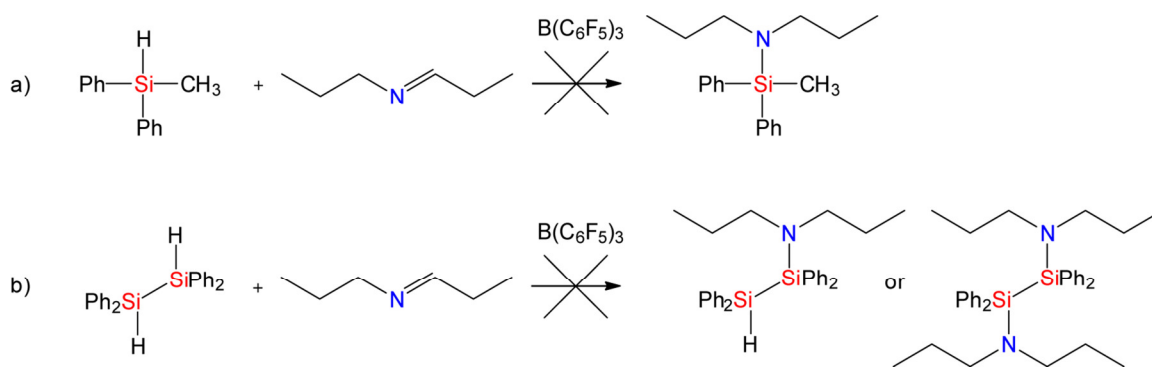
silicon trans to the Si•••H•••B bond, which suggested the preferred site of nucleophilic attack to occur *trans*- to the departing H•••B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>42b</sup> Additionally, studies using a resolved, stereogenic silane reagent showed inversion at the silicon stereocenter in hydrosilation products, which is consistent with the attack of the nucleophile occurring at the “back” of the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-complexed silane, giving a transition state structure in which the incoming O-donor is *trans*- to the departing hydride at silicon (e.g. as shown in Scheme 2.10).<sup>43c,59a</sup> Chojnowski’s studies of the dealkylative coupling of silanes with alkoxy silanes likewise indicate that this transition state is critical to the reaction.<sup>60</sup> This Si-O bond-forming step is probably rate-limiting and is clearly going to be sensitive to steric bulk at both the silane and the nucleophile. In the case of reactions to make substituted monosilanes and disilanes, rapid conversion to product occurred in the reaction of the less bulky monosilane after only 1 h while similar catalyst loadings and reaction temperatures with the bulkier disilane **2-2** led to either a slow conversion (16 h, complete conversion, **2-15**) or partial conversion (1 h, 32% conversion, **2-14**). These results suggest that the rate-determining step of the reaction is sterically dependent and is consistent with the nucleophilic attack at the silane-borane complex (**A**, Figure 2.7).

Low B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed reactivity of **2-1** and **2-2** with benzylideneaniline was observed and is consistent with the Lewis basicity of imines. No immediate reaction occurs between disilane **2-2** and benzylideneaniline at RT with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyst. A noticeable feature is the formation of an imine-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> complex, which shows a small downfield <sup>1</sup>H NMR signal due to the iminyl proton (N=CH δ 8.14 ppm in C<sub>6</sub>D<sub>6</sub>, δ 8.11 ppm in C<sub>6</sub>D<sub>6</sub> with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>).<sup>41a</sup> This strong imine-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> association has been reported by Piers for the same and similar-sized imines and is overcome by one or more of the

following methods: heating the reaction mixture up to 110 °C; choosing a smaller silane, typically PhMe<sub>2</sub>SiH; or extended reaction times up to three days.<sup>41a</sup> A mixture of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, disilane **2-2** and benzylideneaniline (imine substrate) was heated to 110 °C in toluene for three days. The solution turned to a dark brown and an aliquot removed for <sup>1</sup>H NMR showed no apparent consumption of silane. It is suspected that the steric hindrance of benzylideneaniline prevents hydrosilation with the equally sterically hindered disilane **2-2**. Reducing the steric hindrance of the silane to Ph<sub>2</sub>MeSiH (**2-1**) led to the complete conversion to imine hydrosilation product (**2-10**, Table 2.1).

Alternative reactions of **2-1** or disilane **2-2** with the less bulky imine, *n*-propylidene-*n*-propylamine (Scheme 2.9a and b respectively), gave a clear and colorless oil; <sup>1</sup>H NMR showed complete consumption of the imine with no apparent consumption of silane (see experimental Section 2.6.6, Figure 2.22). Diagnostic <sup>1</sup>H NMR signals in both reactions of this imine showed the same unidentified imine-converted product, which does not appear to be the imine-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adduct. It is suspected that *n*-propylidene-*n*-propylamine and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> reacted independently of either silane and did not give the anticipated hydrosilation products (Scheme 2.9a/b). B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed imine hydrosilation and related B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed hydrogenations have consistently used bulkier imines, particularly those with phenyl/aryl, isopropyl, *t*-butyl, or sulfonato groups bonded to the nitrogen.<sup>41a,59a,68</sup> These attempted reactions and those of others in the literature show the challenge of introducing amino substituents via B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed imine hydrosilation, due to the strongly Lewis basic imines inhibiting the catalysis. The role of steric bulk will be discussed in greater detail in Chapter 3.

Scheme 2.9.

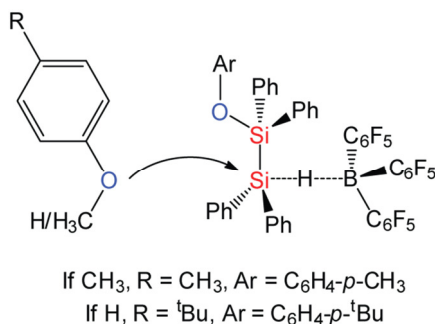


### 2.3.2 Selectivity for monosubstituted versus disubstituted disilane products

The degree of selectivity for mono- (Table 2.2) or disubstituted (Table 2.3) products in these derivatization reactions is highly sensitive to the bulk of both the organic substrate and the disilane. The disilane **2-2** used in these reactions is quite bulky; earlier studies using  $(\text{Me}_2\text{SiH})_2$  showed that it reacts at much lower catalyst loadings than disilane **2-2** for any given substrate.<sup>1a,b</sup> Accordingly, substrates that lead to side-chains with branching at the  $\alpha$ -to-E position (e.g. ketone, phenyl methyl ether, phenol, thiophenol, (**2-12** to **2-15**, **2-18**) favour formation of the monosubstituted disilane, and it is challenging to obtain the disubstituted product in these cases. However, disubstituted compounds containing the two (effectively branched but arguably less bulky) aryl substituents ( $-\text{OC}_6\text{H}_4\text{-}i\text{-Bu}$  (**2-14**) and  $-\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3$  (**2-23**)<sup>1a</sup>) were prepared after optimization of the reaction time, catalyst loading, and temperature. It was anticipated that the disubstituted product  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}p\text{-CH}_3)_2$  (**2-15**) could be prepared by similar reaction conditions as for **2-14** because of the weaker Lewis basicity of *p*-methylanisole compared to *p*-*t*-butylphenol. However, this reaction gave only partial conversion (35% estimated by  $^1\text{H}$  NMR integration) to the disubstituted product, even after increasing catalyst loading, temperature, and reaction time (10 mol%  $\text{B(C}_6\text{F}_5)_3$ , 70 °C for 28 d (670

h)). The increased steric hindrance of the methyl ether likely contributes to a poorer nucleophilicity of *p*-methylanisole (Scheme 2.10, showing **step b** from the catalytic cycle in Scheme 2.2 modified for these reactions), making a second substitution extremely slow.

**Scheme 2.10.**



Substrates giving less bulky, straight-chain side-groups favour the disubstituted products (**2-19**, **2-22**). Again, these observations are consistent with the mechanism for B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed Si-H activation shown in Scheme 2.2. Once a new substituent is installed at one of the two silicons, the steric encumbrance at the remaining Si-H bond is certainly enhanced, and much more so for the branched, relative to the linear, side-chains introduced.

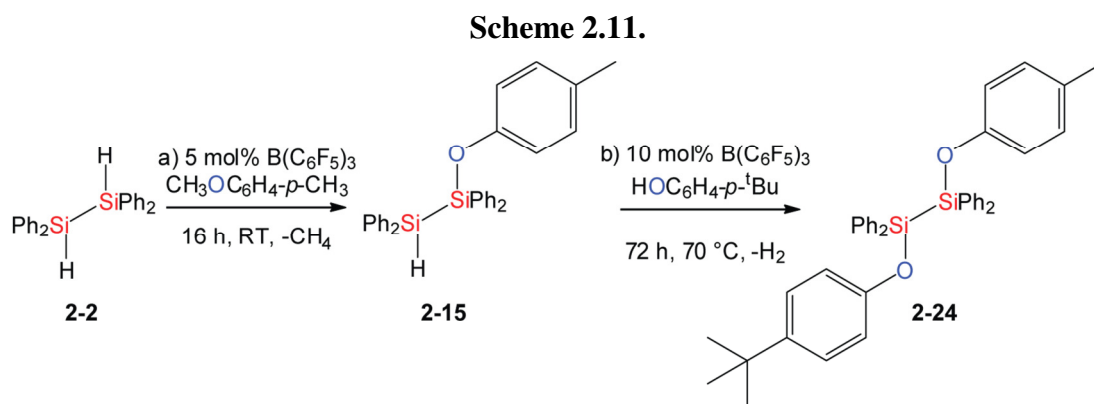
For substrates that lead to linear sidechains at Si (2-chloroethyl methyl ether and 1-hexene), isolating the monosubstituted products was challenging. Attempts to do so by carefully controlled 1:1 stoichiometry of disilane and 2-chloroethyl methyl ether gave good conversion (75% estimated by <sup>1</sup>H NMR integration). However, this also showed disubstituted product (10%) and disilane starting material (15%) in a mixture that was difficult to separate (Table 2.2). Similarly for the 1-hexene reaction, conditions allowing selective production of the monosubstituted product in useful amounts have not yet been

identified. The reaction is sluggish in the presence of 1-5 equivalents of 1-hexene, giving only a trace amount (<1% estimated by  $^1\text{H}$  NMR integration, Figure 2.17) of the suspected monosubstituted product ( $\text{Ph}_2\text{SiH-Si}(\text{CH}_2\text{CH}_2\text{Bu})\text{Ph}_2$ ). Near-complete conversion was achieved using 10 equivalents of 1-hexene, giving the disubstituted product with just trace amounts (<1% by  $^1\text{H}$  NMR) of the suspected monosubstituted product. Further increasing the 1-hexene loading to 20 equivalents resulted in a mixture of products: major product unreacted disilane **2-2**, minor product disubstituted disilane **2-19**, and a trace of monosubstituted disilane. This lack of product conversion is probably due to the doubled volume of the reaction when increasing the 1-hexene loading, which effectively decreases the concentration of catalyst and disilane **2-2**. These results suggest that the barrier to the second substitution is actually lower than the barrier for the first, which may indicate some inductive electronic effect of the new alkyl sidechain on the ease of activation of the second Si-H bond. Preparation of disubstituted products with substrates *n*-propylthiol and allylbenzene was (surprisingly) challenging. Attempts to prepare the disubstituted *n*-propylthiolato product gave monosubstituted product (**2-17**) and  $(\text{Ph}_2\text{SiSCH}_2\text{CH}_2\text{CH}_3)_2$  in a 1:1 mixture (estimated by  $^1\text{H}$  NMR integration) and unreacted *n*-propylthiol, even after 144 h reaction time.<sup>1a,c</sup> Higher reaction temperatures or increased catalyst loading have not yet been tried, yet are expected to allow for greater conversions to the disubstituted product. No reaction between allylbenzene and disilane **2-2** has been observed as of yet, even after applying the same conditions as used for 1-hexene: 10 equivalents of allylbenzene and elevated temperatures. This may be due to a possible higher affinity of allylbenzene for binding to  $\text{B}(\text{C}_6\text{F}_5)_3$  compared to 1-hexene, as discussed above in Section 2.2. In general,  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed olefin hydrosilation has

been less studied compared to heteroatom counterparts.<sup>ix</sup> Ongoing optimizations for these olefin hydrosilation reactions remain a challenge, as discussed above for allylbenzene.

### 2.3.3 Preparation of a mixed, unsymmetrically-disubstituted disilane

This knowledge of the selectivity for monosubstituted and disubstituted disilanes presented a unique opportunity to prepare unsymmetrically-disubstituted derivatives of disilane. The product  $\text{Ph}_2\text{SiH-Si}(\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3)\text{Ph}_2$  (**2-15**) was examined in this context because it exclusively forms the monosubstituted product (Scheme 2.11a). The  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reaction of **2-15** with *p-t*-butylphenol gave the mixed disubstituted disilane in 84% yield (Scheme 2.11b, **2-24**).



Based on the lack of reaction of **2-15** with a second equivalent of *p*-methylanisole, **2-24** is not expected to form from the reverse order of reactions: dehydrocoupling of *p-t*-butylphenol ( $\text{HOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$ ) to give **2-14**, followed by demethanative coupling of *p*-methylanisole ( $\text{CH}_3\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$ ). Reactions of disilane **2-2** with *p-t*-butylphenol have thus far shown poor selectivity for the monosubstituted product. Product **2-14** has not yet

<sup>ix</sup> Only one literature example has reported  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed olefin hydrosilation and the authors did not include a detailed mechanistic study.<sup>66</sup>

been obtained exclusively without some conversion to disubstituted product (**2-20**, Scheme 2.11c); recall that this reaction was challenging because of the substrate- $\text{B}(\text{C}_6\text{F}_5)_3$  inhibition at RT and the poisoning of  $\text{B}(\text{C}_6\text{F}_5)_3$  via phenolysis reactions. More systematic synthesis with phenol loadings that account for  $\text{B}(\text{C}_6\text{F}_5)_3$  phenolysis and conditions such as temperature optimized to limit the disubstituted product formation may indeed yield exclusively the monosubstituted product **2-14**. Even if exclusive **2-14** could be obtained, reaction of **2-14** with *p*-methylanisole would not give **2-24** efficiently. The partial conversion to **2-21** showed that the methyl ether is a poor nucleophile compared to *p*-*t*-butylphenol for making its respective symmetrical disubstituted product. Regardless of the para-substituent on the aromatic side-chain in the monosubstituted disilanes (<sup>t</sup>Bu in **2-14** or CH<sub>3</sub> in **2-15**), the attack of methyl ether is slow to make either the previously discussed disubstituted product **2-21** or the unsymmetrical disilane **2-24** by the opposite order of reactions in Scheme 2.11.

### 2.3.4 Competing over-reduction reactions

Competing  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed over-reduction chemistry is a persistent problem when the substrate for reaction will introduce a short, straight-chain alkoxy substituent at silicon. Initial reactions of disilane **2-2** with propionaldehyde did not show any conversion, even to the monosubstituted product. This is attributed to the higher aldehyde Lewis basicity compared to ketones, which leads to the sequestration and inhibition of  $\text{B}(\text{C}_6\text{F}_5)_3$  (Scheme 2.2, C), in concert with the higher bulk of the disilane relative to  $\text{Ph}_2\text{MeSiH}$ . Only after heating the reaction for 16 h (5 mol%  $\text{B}(\text{C}_6\text{F}_5)_3$ , sealed tube) did hydrosilation products form. The isolated mixture showed broad Si-H, Si-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>,

and Si-Ph peaks in its  $^1\text{H}$  NMR spectrum.<sup>x</sup> This is consistent with oligomerization via multiple hydrosilation and over-reduction reactions. The scope and implications of  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed over-reduction of various substrates with silanes will be discussed in greater detail in Chapter 3.

## 2.4 Summary

A wide scope of  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed hydrosilation, dehydrocoupling, and demethanative coupling reactions with either the monosilane,  $\text{Ph}_2\text{MeSiH}$  (**2-1**) or disilane (**2-2**), was demonstrated. These provided new X-modified silanes such as the monosubstituted disilane and disubstituted disilane.  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reactions of disilane proceeded with absolute chemoselectivity for Si-H bond transformations and no products showing Si-Si bond cleavage were identified or isolated. Over-reduction reactions were identified in reactions of silane with the substrate propionaldehyde and this will be discussed in greater detail in Chapter 3.

The reactions of disilane **2-2** demonstrated some interesting substitutional selectivity, with the tendency to form the monosubstituted (**2-12** to **2-18**) or disubstituted disilane (**2-19** to **2-24**) depending on the properties of the substrate. Lewis basic substrates such as phenols and imines showed poor or no conversion respectively to dehydrocoupling or hydrosilation products. Modified reaction conditions such as increased catalyst loading, reaction time, and temperature could be applied to give disubstituted products in some cases. Bulkier branched substrates were found to give mainly the monosubstituted products,  $\text{Ph}_2\text{SiH-Si}(\text{X})\text{Ph}_2$ . Less bulky substrates gave

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<sup>x</sup> See Section 3.12.2 for experimental details.

disubstituted products,  $(\text{Ph}_2\text{SiX})_2$ . These substrates showed poor selectivity for the monosubstituted product. In-depth knowledge of substrate selectivity above enabled the preparation of  $\text{Ph}_2\text{Si}(\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3)\text{-Si}(\text{OCH-}p\text{-}^t\text{Bu})\text{Ph}_2$ , an unsymmetrically-substituted disilane starting from the symmetric disilane **2-2**.

## 2.5 Impact and future work

The synthesis of a new mixed disilane (**2-24**) suggests that more examples of unsymmetrically-substituted disilanes can be prepared. Reactivity of disilanes with transition metals has been extensively studied and reviewed;<sup>37</sup> these new disilanes may be incorporated into larger, more complex structures for continued studies. The selectivity for monosubstituted versus disubstituted products (summarized in Table 2.2 and Table 2.3, respectively) indicates which substrate pairs are compatible for synthesizing new unsymmetrical disubstituted disilanes. Substrates such as 1-hexene, *p-t*-butylphenol, and 2-chloroethyl methyl ether that are selective for the disubstituted product (**2-19**, **2-20**, **2-22**) are appropriate for the second substitution for the unsymmetrically-disubstituted disilane, but not for the monosubstituted intermediate product. Substrates acetone, cyclohexanone, *p*-methylanisole, *n*-propylthiol, and *p*-thiocresol selectively form their respective monosubstituted products, but do not readily form symmetric disubstituted products. These cannot be reliably used as the second substrate in unsymmetrical reactions but are recommended candidates for installing the first substituent. Many possible combinations of substrates for modifying disilanes can be envisioned to make unique mixed disilanes. These potential unsymmetrically substituted disilanes may even contain two different heteroatoms, for example aryloxy/alkoxy and thiolato side-chains.

Although a variety of functional groups can be appended onto disilanes, one functional group that has not undergone straightforward  $B(C_6F_5)_3$ -catalyzed reactivity with silanes is the alkyne. These substrates are interesting for two reasons: their resulting olefin side-chains are  $\pi$ -conjugated from the substrate to the oligosilane; and interesting possible products are imaginable since the hydrosilation product is an olefin and is available for a second  $B(C_6F_5)_3$ -catalyzed hydrosilation. However, no hydrosilation reactivity is observed and instead  $B(C_6F_5)_3$ -acetylene complexation occurs as described in Section 2.2. Additional research into the olefin reaction mechanism is required to unlock potential  $B(C_6F_5)_3$ -catalyzed alkyne hydrosilation.

A critical result of this study is the lack of silicon-silicon bond cleavage products in reactions of disilane **2-2**. This was initially observed for silicon-sulfur bond forming reactions.<sup>1</sup> Likewise, reactions of disilane with oxygen and olefin-containing substrates show that  $B(C_6F_5)_3$  is a chemoselective catalyst for Si-H bond activation and does not lead to Si-Si cleavage. Reactions of poly(phenylsilane) that are catalyzed by  $B(C_6F_5)_3$  are not expected to give Si-Si cleavage products.

The new X-modified monosilanes and disilanes are benchmarks for the post-polymerization modification of poly(phenylsilane). The reaction conditions used, such as catalyst loading, solvent, stoichiometry, and temperature, suggest starting points for reactions of poly(phenylsilane). X-modified polysilanes are expected to have complex NMR spectra based on the structural complexity of poly(phenylsilane). NMR characterization of the monosilanes and disilanes gives appropriate spectroscopic benchmarks for the anticipated polymer products to be synthesized in Chapter 4.

## 2.6 Experimental

### 2.6.1 General details

Unless otherwise noted, all reactions and manipulations were performed under N<sub>2</sub> in an MBraun Unilab 1200-780 glovebox or using conventional Schlenk techniques. Toluene, pentane, hexanes and dichloromethane were degassed by sparging with N<sub>2</sub> and dried using an MBraun solvent purification system. Benzene was purchased from Caledon and purified by distillation from sodium/benzophenone. Deuterated benzene was purchased from Aldrich, freeze-pump-thaw degassed and vacuum transferred from sodium/benzophenone. Disilane ((Ph<sub>2</sub>SiH)<sub>2</sub>, **2-2**) was prepared according to literature procedures.<sup>69</sup> Methylphenylsilane (**2-1**), *n*-propylthiol, and *n*-propylamine were purchased from Aldrich and used without further purification. 2-Chloroethyl methyl ether and *p*-methylanisole (CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>) were purchased from Aldrich and dried by distillation from calcium hydride. Propionaldehyde was purchased from Aldrich and dried by distillation from magnesium sulphate, except for the synthesis of *n*-propylidene-*n*-propylamine, for which drying was not necessary. Acetone and cyclohexanone were purchased from Caledon and dried by distillation from magnesium sulfate. *p*-*t*-Butylphenol (HOC<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu) was purchased from Aldrich and purified by recrystallization in hexanes and then sublimation (50 °C, dynamic vacuum). 1-Hexene was purchased from Aldrich and dried by distillation from sodium/benzophenone under nitrogen. Allylbenzene was purchased from Aldrich and dried by distillation from magnesium sulfate. Tris(pentafluorophenyl)borane, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, was purchased from Alfa Aesar and purified by double sublimation (110 °C, dynamic vacuum). Triphenylphosphine was purchased from Alfa Aesar and was purified by recrystallization

in 95% ethanol and then sublimation (70 °C, dynamic vacuum). Diphenylsilane was purchased from Aldrich and dried by vacuum distillation over calcium hydride. Calcium hydride was purchased from Aldrich or ACP and used without further purification. Benzaldehyde and aniline were purchased from Anachemia and used without further purification. Benzylideneaniline was prepared by condensing benzaldehyde and aniline in CH<sub>2</sub>Cl<sub>2</sub> and was purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub> and then sublimation (70 °C, dynamic vacuum). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of benzylideneaniline closely matched literature spectra.<sup>70</sup> Anhydrous magnesium sulfate was purchased from Caledon and used without further purification. Florisil® was purchased from Aldrich or Caledon and was dried in an oven (135 °C, for at least 16 h) and vacuum oven (~0.05 mm Hg, 45 °C, 6 h). A Florisil column (used for the removal of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in cases where the addition of PPh<sub>3</sub> to precipitate the borane-phosphine adduct is not practical) was constructed in a Pasteur pipette, plugged with dried glass wool, filled with ~6 cm of Florisil® and ~1 cm of sand. Celite was purchased from AGP or Aldrich and was dried in an oven (135 °C, for at least 16 h) and vacuum oven (~0.05 mm Hg, 45 °C, for at least 6 h). A Celite filter stick was constructed in a Pasteur pipette, plugged with dried glass wool, filled with ~1 cm of Celite and ~1 cm of sand. The “bomb” flask was a one-piece, thick-walled, cylindrical flask with a 4 mm Kontes valve equipped with a side-arm. Substituted disilanes **2-18** (Ph<sub>2</sub>SiH-Si(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)Ph<sub>2</sub>) and **2-23** ((Ph<sub>2</sub>SiSC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>)<sup>1a</sup> were prepared according to literature procedures. Microanalysis was performed by Canadian Microanalytical Service Ltd., Delta, BC, Canada. Melting temperatures were collected on a Gallenkamp melting point apparatus and are uncorrected.

NMR spectra were obtained on a Bruker AC 250 spectrometer ( $^1\text{H}$ ), Bruker AVANCE 300 spectrometer ( $^1\text{H}$  and  $^{13}\text{C}$ ), Bruker AVANCE 500 spectrometer ( $^{13}\text{C}$  and  $^{29}\text{Si}$ ), or a Bruker AVANCE 360 spectrometer ( $^{29}\text{Si}$ ).  $^1\text{H}$  NMR spectra were referenced to the residual proton peak in benzene- $d_6$  ( $\delta$  7.16 ppm) relative to tetramethylsilane (TMS) at 0 ppm.  $^{13}\text{C}$  NMR spectra were referenced to solvent peaks relative to tetramethylsilane (TMS) at 0 ppm.  $^{29}\text{Si}$  NMR spectra were obtained using DEPT30 or direct acquisition methods.<sup>xi</sup>  $^{29}\text{Si}$  NMR spectra were referenced to external TMS at 0 ppm. Chemical shifts are reported in ppm at ambient temperature.

Most products described below are oils. Trace unidentified impurities, or small amounts of unreacted reagents or by-products, are observed in some cases. Microanalytical data is provided in all cases, as well as  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for samples submitted for microanalysis, to indicate purity obtained.

## 2.6.2 Synthesis of X-modified monosilanes

### *General procedure for synthesis of monosilanes, except for n-hexyl derivative 2-11*

In a Schlenk flask equipped with a stir bar,  $\text{Ph}_2\text{MeSiH}$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  were combined with toluene or benzene. To this stirring mixture, substrate was added (dropwise if a liquid). The contents were left stirring under  $\text{N}_2$  (closed flask or open to a Nujol bubbler). After stirring for the time specified,  $\text{PPh}_3$  was added and the volatiles were removed by evacuation to give an oily residue. Hexanes or pentane was added to dissolve the oily residue and the cloudy solution was filtered through a Celite filter stick (to remove precipitated phosphine-borane adduct). Hexanes or pentane was added to

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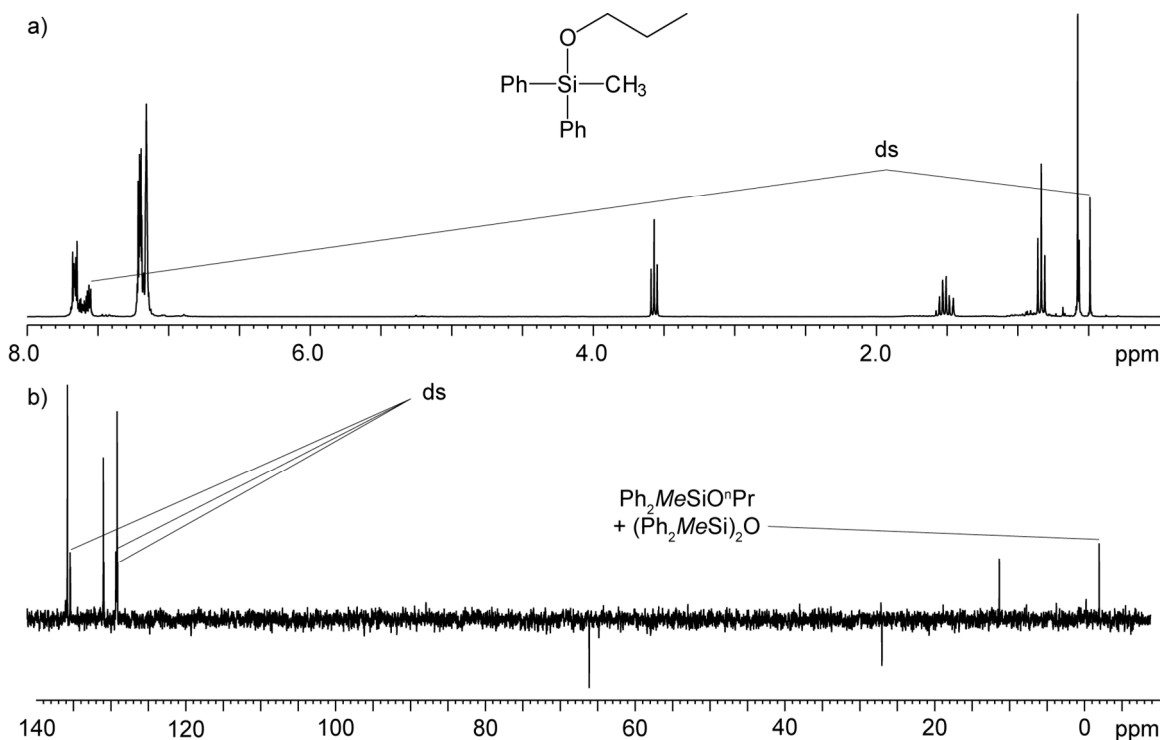
<sup>xi</sup> See Section 4.3.5, Table 4.3 for more detail on DEPT  $^{29}\text{Si}$  NMR experiments.

wash the Celite filter stick to give a clear and colorless combined filtrate. Volatiles were removed by evacuation at RT or other temperature as specified, for the time specified to give the described product.

*Ph<sub>2</sub>MeSiOCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (2-3):*

**2-1** (0.10 g, 0.52 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.009 g, 0.02 mmol), toluene (1 mL), propionaldehyde (0.10 mL, 1.4 mmol), PPh<sub>3</sub> (0.005 g, 0.02 mmol), hexanes (4 x 1 mL). Procedural notes: stirred under N<sub>2</sub> in a closed flask for 16 h; volatiles removed under dynamic vacuum at RT for 16 h. A clear and colorless oil was isolated (0.13 g, in 76% purity). The remaining 24% was the over-reduction product, (Ph<sub>2</sub>MeSi)<sub>2</sub>O (**2-4**). Ph<sub>2</sub>MeSiOCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (**2-3**): <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 0.58 (s, 3H, CH<sub>3</sub>), 0.84 (t, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 3H, CH<sub>3</sub>), 1.52 (sextet, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>) 3.57 (t, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 2H, OCH<sub>2</sub>), 7.19-7.23 (overlapping m, 6H, overlapping with H<sub>m/p</sub>-SiPh<sub>2</sub> in **2-4**, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.64-7.69 (m, 4H, H<sub>o</sub>-SiPh<sub>2</sub>). DEPT135 <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ -2.9 (SiCH<sub>3</sub>, overlapping with SiCH<sub>3</sub> in **2-4**), 10.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 26.1 (OCH<sub>2</sub>CH<sub>2</sub>), 65.1 (OCH<sub>2</sub>), 128.0 (C<sub>m</sub>-SiPh<sub>2</sub>), 129.9 (C<sub>p</sub>-SiPh<sub>2</sub>), 134.6 (C<sub>o</sub>-SiPh<sub>2</sub>). DEPT30 <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>) δ -3.8. (Ph<sub>2</sub>MeSi)<sub>2</sub>O (**2-4**): <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 0.38 (s, 6H, CH<sub>3</sub>), 7.19-7.23 (overlapping m, 12H, overlapping with H<sub>m/p</sub>-SiPh<sub>2</sub> in **2-3**, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.38 (overlapping d, 8H, H<sub>o</sub>-SiPh<sub>2</sub>). DEPT135 <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 2.9 (SiCH<sub>3</sub>, overlapping with SiCH<sub>3</sub> in **2-3**), 128.2 (C<sub>m</sub>-SiPh<sub>2</sub>), 129.8 (C<sub>p</sub>-SiPh<sub>2</sub>), 134.3 (C<sub>o</sub>-SiPh<sub>2</sub>).

DEPT30  $^{29}\text{Si}$  NMR (99 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -9.5. Anal. Calc. for 24%  $\text{C}_{26}\text{H}_{26}\text{OSi}_2$  and 76%  $\text{C}_{16}\text{H}_{20}\text{OSi}$ : C 75.31 H 7.36. Found: C 72.51 H 6.99.<sup>xii</sup>



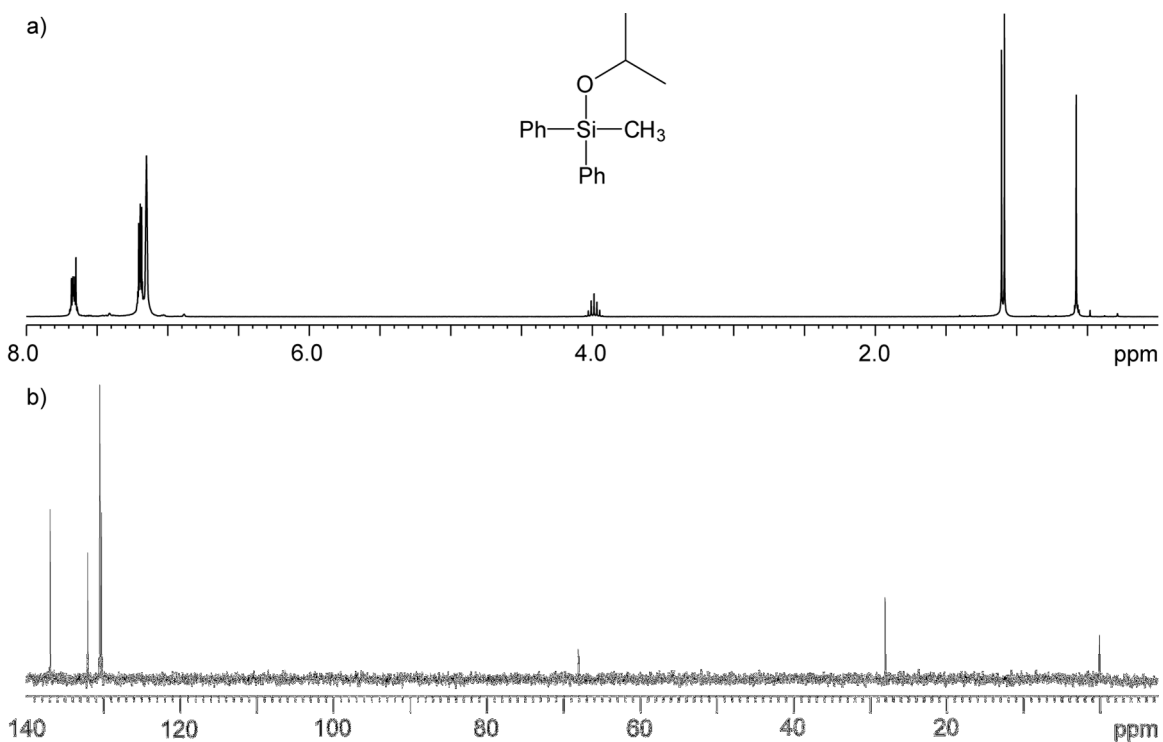
**Figure 2.2.** a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{MeSiOCH}_2\text{CH}_2\text{CH}_3$  (**2-3**) in  $\text{C}_6\text{D}_6$ . The “ds” is disiloxane ( $\text{Ph}_2\text{MeSi-O-SiMePh}_2$ , **2-4**) formed from the competing over-reduction reaction (See Chapter 3 for more details).

*Ph<sub>2</sub>MeSiOCH(CH<sub>3</sub>)<sub>2</sub>* (**2-5**):

**2-1** (0.13 g, 0.65 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.012 g, 0.023 mmol), toluene (1 mL), acetone (0.10 mL, 1.4 mmol),  $\text{PPh}_3$  (0.006 g, 0.02 mmol), pentane (4 x 1 mL). Procedural notes: stirred under  $\text{N}_2$  (closed flask) for 12 h; volatiles removed under dynamic vacuum at RT for 16 h. A clear and colorless oil was isolated (0.12 g, 73%, trace impurities were observed by  $^1\text{H}$  NMR (see spectrum below)).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.59 (s, 3H,

<sup>xii</sup> Even when the molar ratio of silane and disiloxane products are adjusted in an attempt to fit this microanalytical data, these results are consistent with the presence of one or more impurities in this oil that are not readily identified by NMR.

CH<sub>3</sub>) 1.11 (d,  $^3J_{\text{HH}} = 6$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.00 (m,  $^3J_{\text{HH}} = 6$  Hz, 1H, OCH), 7.17-7.70 (overlapping m, 6H, H<sub>m</sub>-SiPh<sub>2</sub>, H<sub>p</sub>-SiPh<sub>2</sub>), 7.65-7.21 (m, 4H, H<sub>o</sub>-SiPh<sub>2</sub>). DEPT135 <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 0.0 (SiCH<sub>3</sub>), 28.0 (OCH), 58.0 (OCH(CH<sub>3</sub>)<sub>2</sub>), 130.2 (C<sub>m</sub>-SiPh<sub>2</sub>), 132.0 (C<sub>p</sub>-SiPh<sub>2</sub>), 136.9 (C<sub>o</sub>-SiPh<sub>2</sub>). DEPT30 <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>) δ -6.1. Anal. Calc. for C<sub>16</sub>H<sub>20</sub>OSi: C 74.95 H 7.86. Found: C 74.44 H 7.72.

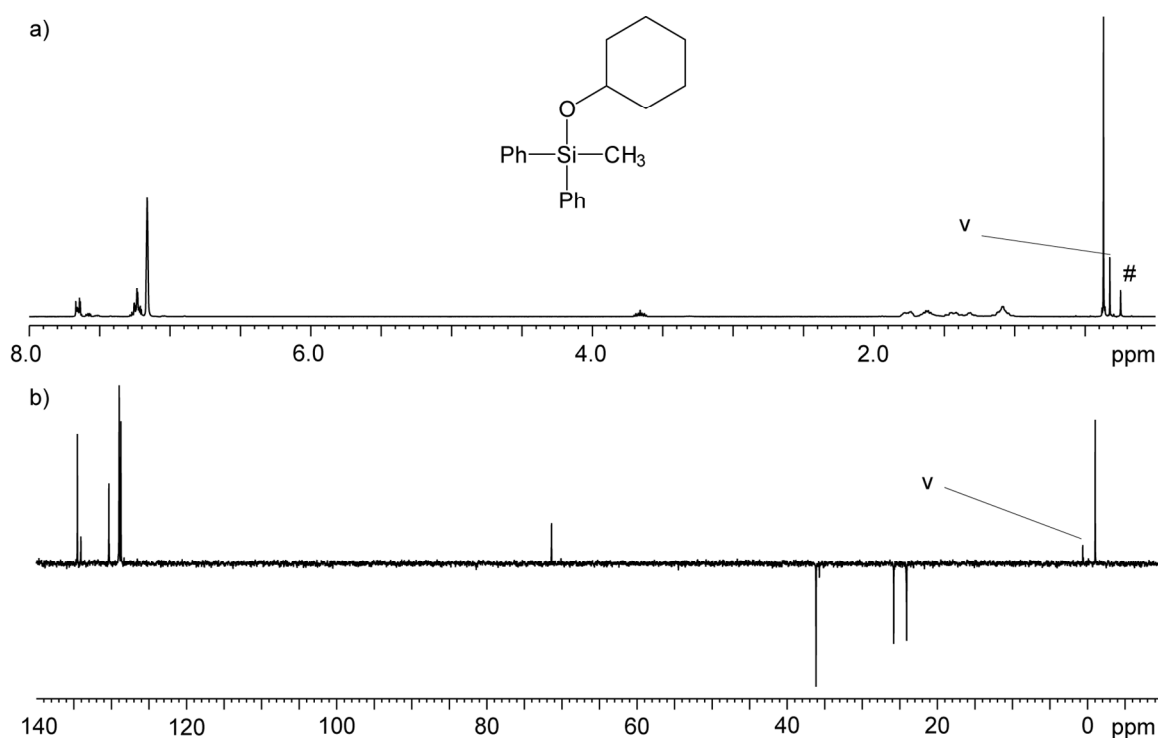


**Figure 2.3.** a) <sup>1</sup>H NMR (300 MHz) and b) DEPT135 <sup>13</sup>C NMR (75 MHz) of Ph<sub>2</sub>MeSiOCH(CH<sub>3</sub>)<sub>2</sub> (**2-5**) in C<sub>6</sub>D<sub>6</sub>.

*Ph<sub>2</sub>MeSiOC<sub>6</sub>H<sub>11</sub>* (**2-6**):

**2-1** (0.10 g, 0.50 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.012 g, 0.023 mmol), toluene (1 mL), cyclohexanone (0.060 mL, 0.58 mmol), PPh<sub>3</sub> (0.006 g, 0.02 mmol), hexanes (4 x 1 mL). Procedural notes: stirred under N<sub>2</sub> (closed flask) for 16 h; volatiles removed under dynamic vacuum at 70 °C for 2 h. A clear and colorless oil was isolated (0.12 g, in 86% purity). The remaining 14% was unreacted Ph<sub>2</sub>MeSiH, see spectrum below). <sup>1</sup>H NMR

(300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.61 (s, 3H, Si-CH<sub>3</sub>), 1.01-1.13 (overlapping m, 3H, OCHCH<sub>2</sub>CH<sub>eq</sub> and OCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>eq</sub>), 1.29 (m, 1H, OCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>ax</sub>), 1.41-1.54 (m, 2H, OCHCH<sub>eq</sub>), 1.57-1.66 (m, 2H, OCHCH<sub>2</sub>CH<sub>ax</sub>), 1.71-1.80 (m, 2H, OCHCH<sub>ax</sub>), 3.77 (quintet, 1H, OCH), 7.18-7.22 (overlapping m, 6H, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.69 (overlapping d, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 4H, H<sub>o</sub>-SiPh<sub>2</sub>). DEPT135 <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) -2.1 (Si-CH<sub>3</sub>), 23.9 (OCHCH<sub>2</sub>CH<sub>2</sub>), 25.8 (OCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 35.9 (OCHCH<sub>2</sub>), 71.3 (O-CH), 128.0 (C<sub>m</sub>-SiPh<sub>2</sub>), 129.8 (C<sub>p</sub>-SiPh<sub>2</sub>), 134.6 (C<sub>o</sub>-SiPh<sub>2</sub>). DEPT30 <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  -6.1. Anal. Calc. for 86% C<sub>19</sub>H<sub>24</sub>OSi and 14% C<sub>13</sub>H<sub>14</sub>Si: C 77.14 H 8.06. Found: C 74.94 H 7.88.<sup>xiii</sup>



**Figure 2.4.** a) <sup>1</sup>H NMR (300 MHz) and b) DEPT135 <sup>13</sup>C NMR (75 MHz) of Ph<sub>2</sub>MeSiOC<sub>6</sub>H<sub>11</sub> (**2-6**) in C<sub>6</sub>D<sub>6</sub>. The “v” is residual unreacted Ph<sub>2</sub>MeSiH. The “#” is grease.

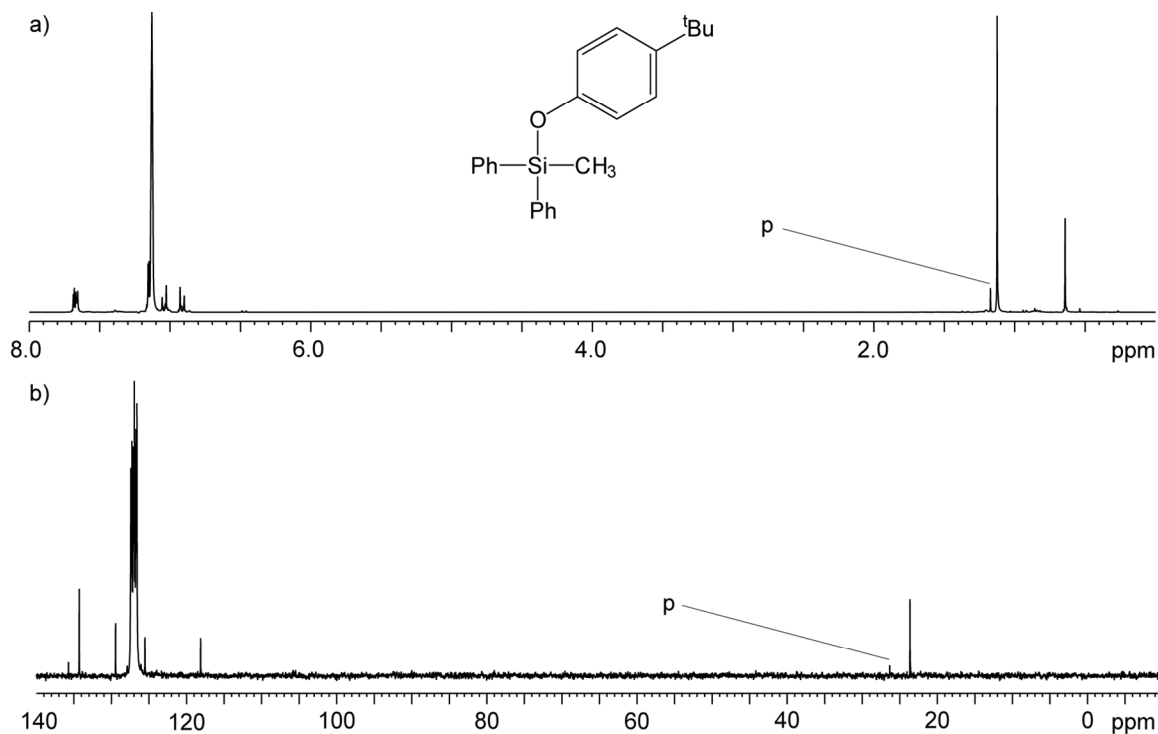
<sup>xiii</sup> Even when the molar ratio of silane and starting material are adjusted in an attempt to fit this microanalytical data, these results are consistent with the presence of one or more impurities in this oil that are not readily identified by NMR.

*Ph<sub>2</sub>MeSiOC<sub>6</sub>H<sub>4</sub>-p<sup>-</sup>Bu (2-7):*

**2-1** (0.12 g, 0.58 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.014 g, 0.027 mmol), toluene (1 mL), *p-t*-butylphenol (0.088 g, 0.59 mmol), PPh<sub>3</sub> (0.007 g, 0.03 mmol), pentane (4 x 1 mL). Procedural notes: stirred under N<sub>2</sub> (open to Nujol bubbler) for 1 h; volatiles removed under dynamic vacuum at 70 °C for 2 h. A clear and colorless oil was isolated (0.20 g, 99%, a trace amount (<1%) of *p-t*-butylphenol was detected by <sup>1</sup>H NMR (see below for spectrum)). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 0.67 (s, 3H, SiCH<sub>3</sub>), 1.16 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 6.94 (m, 2H, H<sub>o</sub>-C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu), 7.07 (m, 2H, H<sub>m</sub>-C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu), 7.17-7.20 (m overlapping with C<sub>6</sub>D<sub>5</sub>H, 6H, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.70 (overlapping d, 4H, <sup>3</sup>J<sub>HH</sub> = 4 Hz, H<sub>o</sub>-SiPh<sub>2</sub>); DEPT135 <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ -2.6 (SiCH<sub>3</sub>), 31.4 (C(CH<sub>3</sub>)<sub>3</sub>) 33.9 (-C-(CH<sub>3</sub>)<sub>3</sub> by <sup>13</sup>C NMR), 119.6 (C<sub>o</sub>-C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu), 126.5 (C<sub>m</sub>-C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu), 128.7 (C<sub>m</sub>-SiPh<sub>2</sub>), 130.2 (C<sub>p</sub>-SiPh<sub>2</sub>), 134.7 (C<sub>o</sub>-SiPh<sub>2</sub>). DEPT30 <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>) δ -3.7. Anal. Calc. for C<sub>23</sub>H<sub>26</sub>OSi: 79.71 H 7.56. Found: C 81.8 H 7.93.<sup>xiv</sup>

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<sup>xiv</sup> %C values are not drastically changed when including the molar ratio of **2-7** and *p-t*-butylphenol suggested by <sup>1</sup>H NMR. %C content in **2-7** and *p-t*-butylphenol are similar (79.79 and 79.96, respectively). These results are consistent with the presence of one or more impurities in this oil that are not readily identified by NMR.

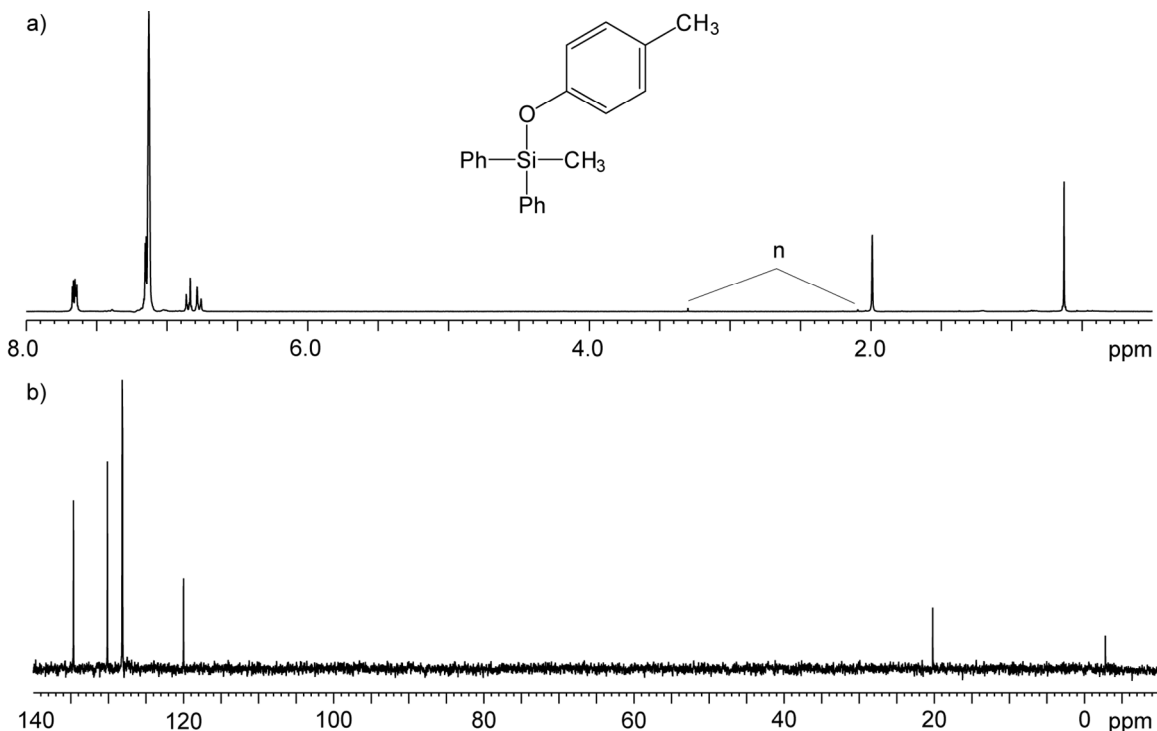


**Figure 2.5.** a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{MeSiOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$  (**2-7**) in  $\text{C}_6\text{D}_6$ . The “p” is residual unreacted  $p\text{-}t$ -butylphenol ( $\text{HOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$ ).

*Ph<sub>2</sub>MeSiOC<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>* (**2-8**):

**2-1** (0.13 g, 0.63 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.014 g, 0.027 mmol), toluene (1 mL),  $p$ -methylanisole (0.083 g, 0.68 mmol),  $\text{PPh}_3$  (0.007 g, 0.03 mmol), pentane (4 x 1 mL). Procedural notes: stirred under  $\text{N}_2$  (open to Nujol bubbler) for 1 h; volatiles removed under dynamic vacuum at RT for 16 h. A clear and colorless oil was isolated (0.19 g, 99%, a trace amount (<1%) of  $p$ -methylanisole was detected by  $^1\text{H}$  NMR (see below for spectrum)).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.66 (SiCH<sub>3</sub>), 2.02 ( $p$ -CH<sub>3</sub>), 6.80 (dt, 2H,  $^3J_{\text{HH}} = 9$  Hz,  $\text{H}_o\text{-OC}_6\text{H}_4\text{-}p\text{-CH}_3$ ), 6.88 (d, 2H,  $^3J_{\text{HH}} = 8$  Hz,  $\text{H}_m\text{-OC}_6\text{H}_4\text{-}p\text{-CH}_3$ ), 7.18 (m, overlapping with  $\text{C}_6\text{D}_5\text{H}$ , 6H,  $\text{H}_{mp}\text{-SiPh}_2$ ), 7.69 (overlapping d, 4H,  $^3J_{\text{HH}} = 4$  Hz,  $\text{H}_o\text{-SiPh}_2$ ); DEPT135  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -2.6 (SiCH<sub>3</sub>), 20.4 ( $\text{C}_p\text{-CH}_3$ ), 120.0 ( $\text{C}_o\text{-OC}_6\text{H}_4\text{-}p\text{-CH}_3$ ), 128.1 ( $\text{C}_m\text{-SiPh}_2$ ), 128.2 ( $\text{C}_m\text{-OC}_6\text{H}_4\text{-}p\text{-CH}_3$ ), 130.2 ( $\text{C}_p\text{-SiPh}_2$ ), 134.7

(C<sub>o</sub>-SiPh<sub>2</sub>). DEPT30 <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>) δ -3.6. Anal. Calc. for C<sub>20</sub>H<sub>20</sub>OSi: C 78.90 H 6.62. Found: C 77.52 H 6.49.



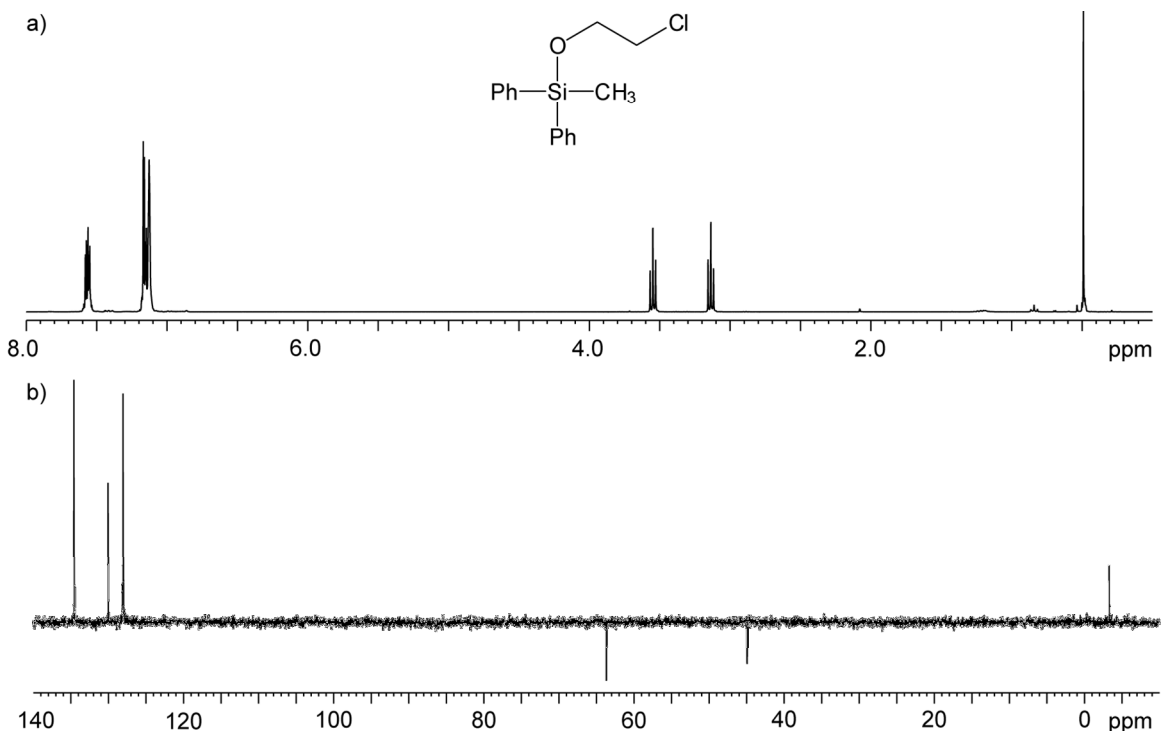
**Figure 2.6.** a) <sup>1</sup>H NMR (300 MHz) and b) DEPT135 <sup>13</sup>C NMR (75 MHz) of Ph<sub>2</sub>MeSiOC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> (**2-8**) in C<sub>6</sub>D<sub>6</sub>. The “n” is residual unreacted *p*-methylanisole (CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>).

*Ph<sub>2</sub>MeSiOCH<sub>2</sub>CH<sub>2</sub>Cl (2-9):*

**2-1** (0.16 g, 0.79 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.011 g, 0.021 mmol), toluene (1 mL), 2-chloroethyl methyl ether (0.10 mL, 1.1 mmol), PPh<sub>3</sub> (0.005 g, 0.02 mmol), pentane (6 x 1 mL). Procedural notes: stirred under N<sub>2</sub> (open to Nujol bubbler) for 2 h; volatiles removed under dynamic vacuum at RT for 16 h. A clear and colorless oil was isolated (0.18 g, 83%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 0.52 (s, 3H, SiCH<sub>3</sub>), 3.17 (t, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>Cl), 3.58 (t, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>Cl), 7.17-7.21 (overlapping m, 6H, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.60 (overlapping d, <sup>3</sup>J<sub>HH</sub> = 4 Hz, 4H, H<sub>o</sub>-SiPh<sub>2</sub>); DEPT135 <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ -3.1 (SiCH<sub>3</sub>), 45.1 (OCH<sub>2</sub>CH<sub>2</sub>Cl), 63.8 (OCH<sub>2</sub>CH<sub>2</sub>Cl), 128.1 (C<sub>m</sub>-SiPh<sub>2</sub>),

130.1 ( $C_p$ -SiPh<sub>2</sub>), 134.6 ( $C_o$ -SiPh<sub>2</sub>); DEPT30  $^{29}\text{Si}$  NMR (99 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -1.9. Anal.

Calc. for  $\text{C}_{15}\text{H}_{17}\text{OCISi}$ : C 65.08 H 6.19. Found: C 64.98 H 6.14.

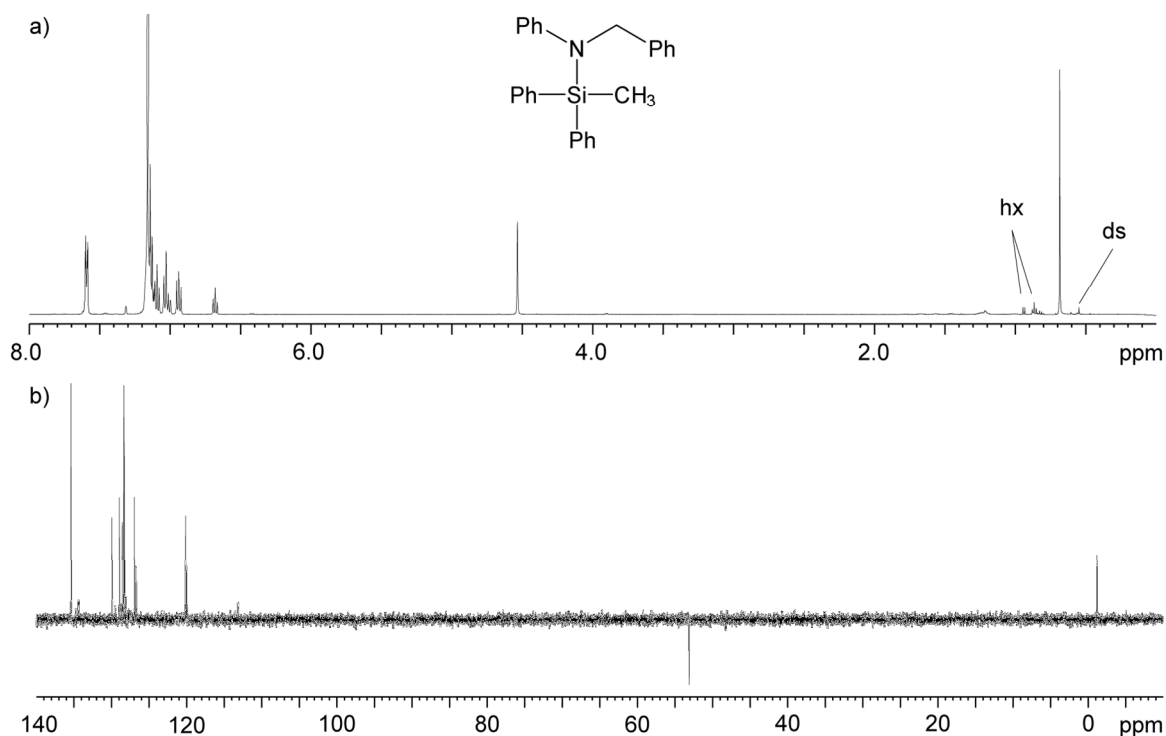


**Figure 2.7.** a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{MeSiOCH}_2\text{CH}_2\text{Cl}$  (**2-9**) in  $\text{C}_6\text{D}_6$ .

*Ph<sub>2</sub>MeSiN(Ph)CH<sub>2</sub>Ph* (**2-10**):

**2-1** (0.11 g, 0.55 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.012 g, 0.023 mmol), benzene (1 mL), benzylideneaniline (0.10 g, 0.55 mmol),  $\text{PPh}_3$  (0.006 g, 0.02 mmol), hexanes (4 x 1 mL). Procedural notes: a one-piece “bomb” flask was used instead of a Schlenk flask; subjected to one-freeze-pump-thaw cycle; heated flask in an oil bath (60 °C) for 48 h, volatiles removed under dynamic vacuum and heating to 60 °C for 2 h. A clear and colorless oil was isolated (0.20 g, 97%, trace impurities, such as  $(\text{Ph}_2\text{MeSi})_2\text{O}$  (**2-4**), were observed by  $^1\text{H}$  NMR (see spectrum below)).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.71 (s, 3H, SiCH<sub>3</sub>), 4.54 (s, 2H, NCH<sub>2</sub>), 6.94 (t, 2H,  $^3J_{\text{HH}} = 8$  Hz,  $\text{H}_m$ -CH<sub>2</sub>Ph), 7.00 (t, 2H,  $^3J_{\text{HH}} = 7$

Hz,  $H_m$ -NPh, overlapping with  $H_o$ -CH<sub>2</sub>Ph), 7.01 (d, 2H,  $^3J_{HH} = 8$  Hz,  $H_o$ -CH<sub>2</sub>Ph, overlapping with  $H_m$ -NPh), 7.04 (t, 1H,  $^3J_{HH} = 8$  Hz,  $H_p$ -CH<sub>2</sub>Ph), 7.12-7.17 (overlapping m, 9H,  $H_p$ -NPh,  $H_m$ -SiPh<sub>2</sub>,  $H_p$ -SiPh<sub>2</sub>,  $H_o$ -NPh), 7.59 (d, 4H,  $^3J_{HH} = 8$  Hz,  $H_o$ -SiPh<sub>2</sub>). DEPT135 <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ -1.1 (SiCH<sub>3</sub>), 53.1 (NCH<sub>2</sub>), 120.1 (C<sub>p</sub>-CH<sub>2</sub>Ph), 125.6 (C<sub>p</sub>-SiPh<sub>2</sub>), 126.7 (C<sub>m</sub>-NPh), 126.8 (C<sub>o</sub>-CH<sub>2</sub>Ph), 128.4 (C<sub>p</sub>-NPh), 128.6 (C<sub>o</sub>-NPh), 129.0 (C<sub>m</sub>-CH<sub>2</sub>Ph), 130.1 (C<sub>m</sub>-SiPh<sub>2</sub>), 135.0 (C<sub>o</sub>-SiPh<sub>2</sub>). DEPT30 <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>) δ -5.3. Anal. Calc. for C<sub>26</sub>H<sub>25</sub>NSi: C 82.27 H 6.64. Found: C 81.30 H 7.20.

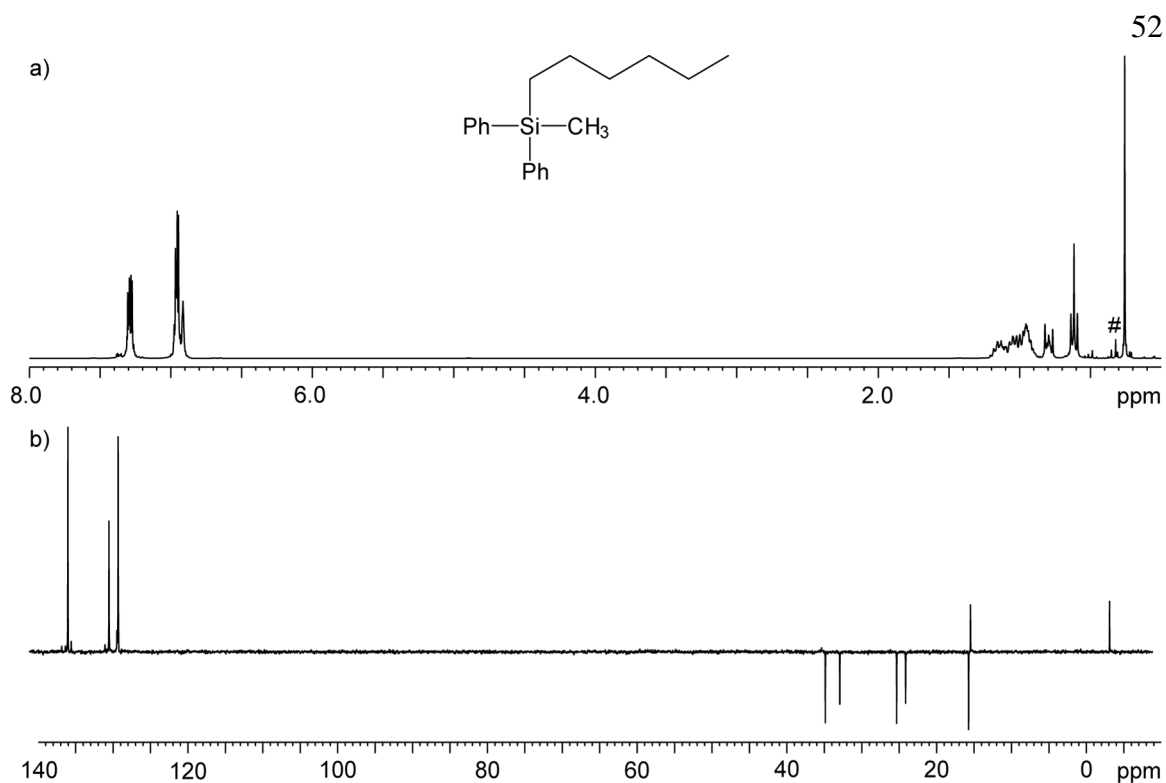


**Figure 2.8.** a) <sup>1</sup>H NMR (300 MHz) and b) DEPT135 <sup>13</sup>C NMR (75 MHz) of Ph<sub>2</sub>MeSiN(Ph)CH<sub>2</sub>Ph (2-10) in C<sub>6</sub>D<sub>6</sub>. The “ds” is disiloxane (Ph<sub>2</sub>MeSi-O-SiMePh<sub>2</sub>) formed from competing hydrolysis reactions. The “hx” is residual hexanes.

*Ph<sub>2</sub>MeSiCH<sub>2</sub>CH<sub>2</sub>Bu (2-11):*

In a Schlenk flask equipped with a stir bar, **2-1** (0.21 g, 1.1 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.025 g, 0.049 mmol) were combined in 1-hexene (1.0 mL, 4.0 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL). The contents were left stirring under N<sub>2</sub> (closed flask). After 16 h, volatiles

were removed by evacuation to give an oily residue. Pentane (1 mL) was added to dissolve the oily residue and the solution was filtered through a Florisil column (to remove residual  $B(C_6F_5)_3$  catalyst, a faint brown color was retained on the column). Pentane (1 mL) was added to wash the Florisil column and this was repeated two more times with pentane (2 x 1 mL) to give a clear and colorless combined filtrate. Volatiles were removed by dynamic vacuum at RT for 16 h. A clear and colorless oil was isolated (0.22 g, 74%, trace impurities were observed by  $^1H$  NMR (see spectrum below)).  $^1H$  NMR (300 MHz,  $C_6D_6$ )  $\delta$  0.51 (s, 3H, Si-CH<sub>3</sub>), 0.86 (t,  $^3J_{HH} = 7$  Hz, 3H, (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.00-1.46 (overlapping m, 10H, Si-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 7.18-7.23 (overlapping m, 6H, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.53 (overlapping d,  $^3J_{HH} = 4$  Hz, 4H, H<sub>o</sub>-SiPh<sub>2</sub>); DEPT135  $^{13}C$  NMR (75 MHz,  $C_6D_6$ )  $\delta$  -4.2 (SiCH<sub>3</sub>), 14.3 (Si(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 14.6 (SiCH<sub>2</sub>), 23.0 (Si(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>), 24.2 (Si(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>), 31.8 (Si(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 33.7 (SiCH<sub>2</sub>CH<sub>2</sub>) 128.2 (C<sub>m</sub>-SiPh<sub>2</sub>), 129.4 (C<sub>p</sub>-SiPh<sub>2</sub>), 134.9 (C<sub>o</sub>-SiPh<sub>2</sub>); DEPT30  $^{29}Si$  NMR (99 MHz,  $C_6D_6$ )  $\delta$  -7.1. Anal. Calc. for C<sub>19</sub>H<sub>26</sub>Si: C 80.78 H 9.28. Found: C 80.68 H 9.53.



**Figure 2.9.** a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{MeSiCH}_2\text{CH}_2\text{Bu}$  (**2-11**) in  $\text{C}_6\text{D}_6$ . The “#” is grease.

### 2.6.3 Synthesis of monosubstituted disilanes

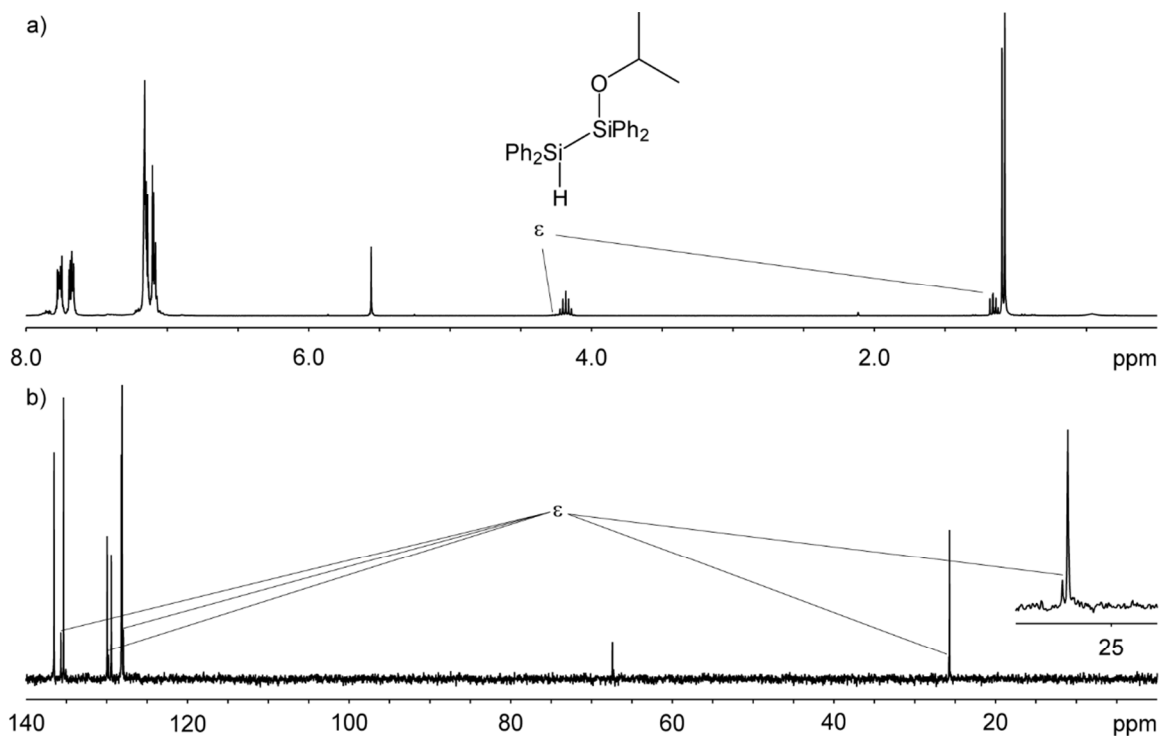
*General procedure for synthesis of monosubstituted disilanes, except for 2-14 (method B) and 2-16:*

The general procedure is the same as for monosilanes (described above in Section 2.6.2) except the silane, **2-1**, was substituted for **2-2** ( $(\text{Ph}_2\text{SiH})_2$ ).

*$\text{Ph}_2\text{SiH}-\text{Si}(\text{OCH}(\text{CH}_3)_2)\text{Ph}_2$  (**2-12**):*

**2-2** (0.21 g, 0.58 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.030 g, 0.059 mmol), toluene (2 mL), acetone (0.050 mL, 0.68 mmol),  $\text{PPh}_3$  (0.015 g, 0.057 mmol), pentane (6 x 1 mL). Procedural notes: stirred under  $\text{N}_2$  (closed flask) for 16 h; volatiles removed under dynamic vacuum at RT for 16 h. A clear and colorless oil was isolated (0.23 g, 86% in >90% purity). A small amount of isopropoxy-containing impurity was observed by  $^1\text{H}$  NMR, which may

be the disubstituted product  $(\text{Ph}_2\text{SiOCH}(\text{CH}_3)_2)_2$ . When the experiment was repeated using two equivalents of acetone, the same ratio of monosubstituted product to isopropoxy-containing impurity was obtained. Likewise, the addition of a second equivalent of acetone to isolated monosubstituted disilane product showed no reaction: the monosubstituted disilane with the same quantity of isopropoxy-containing impurity was recovered.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.08 (d,  $^3J_{\text{HH}} = 6.0$  Hz, 6H,  $\text{Si}(\text{CH}(\text{CH}_3)_2)$ ), 4.18 (m,  $^3J_{\text{HH}} = 6.0$  Hz, 1H,  $\text{Si}(\text{CH}(\text{CH}_3)_2)$ ), 5.55 (s,  $^1J_{\text{SiH}} = 183$  Hz, 1H, Si-H), 7.08-7.16 (overlapping m, 12H,  $\text{H}_{m/p}$ -SiPh<sub>2</sub>), 7.65-7.79 (m, 8H,  $\text{H}_o$ -SiPh<sub>2</sub>); DEPT135  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  25.7 (CH<sub>3</sub>), 67.4 (OCH), 127.9 ( $\text{C}_m$ -HSiPh<sub>2</sub>), 128.1 ( $\text{C}_m$ -OSiPh<sub>2</sub>), 128.2 ( $\text{C}_p$ -HSiPh<sub>2</sub>), 130.0 ( $\text{C}_p$ -OSiPh<sub>2</sub>), 135.4 ( $\text{C}_o$ -HSiPh<sub>2</sub>), 136.5 ( $\text{C}_o$ -OSiPh<sub>2</sub>). DEPT30  $^{29}\text{Si}$  NMR (99 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -8.1 (Si-O), -38.2 (Si-H). Anal. Calc. for  $\text{C}_{27}\text{H}_{28}\text{OSi}_2$ : C 76.36 H 6.65. Found: C 75.88 H 6.93.

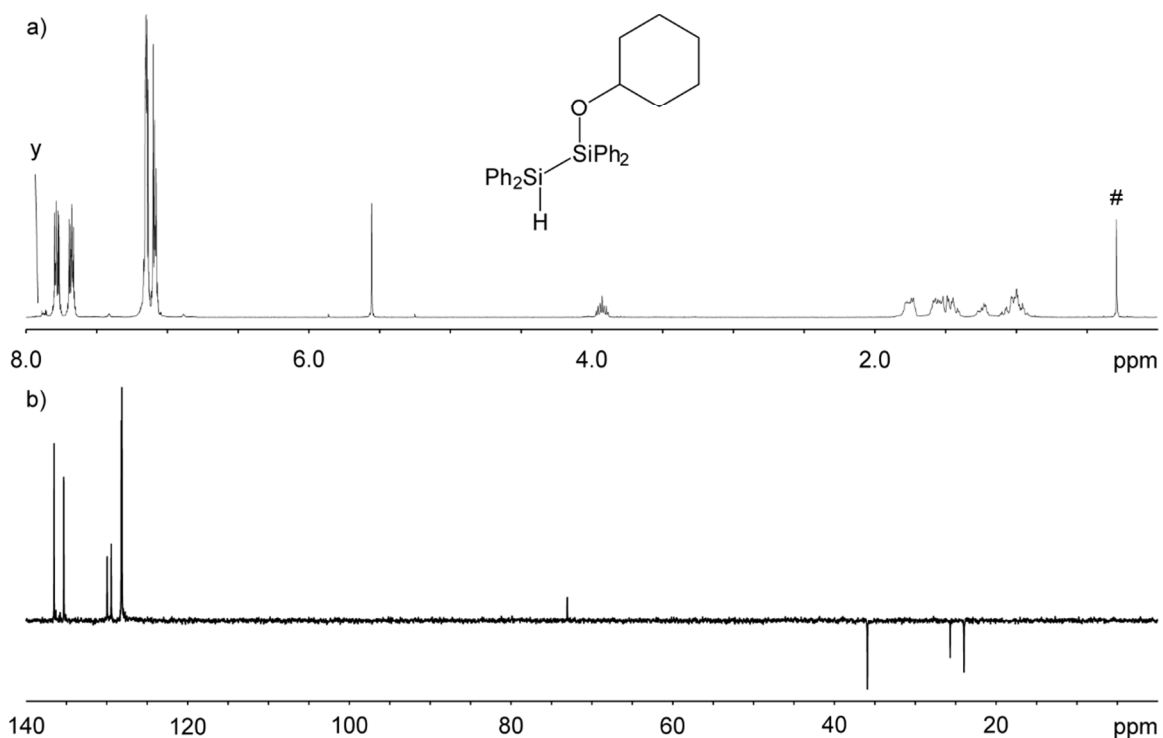


**Figure 2.10.** a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{SiH-Si}(\text{OCH}(\text{CH}_3)_2)\text{Ph}_2$  (**2-12**) in  $\text{C}_6\text{D}_6$ . The “ $\epsilon$ ” is a Si-Ph/ $\text{OCH}(\text{CH}_3)_2$ -containing impurity, tentatively assigned as the disubstituted product  $[\text{Ph}_2\text{Si}(\text{OCH}(\text{CH}_3)_2)]_2$ .

*$\text{Ph}_2\text{SiH-Si}(\text{OC}_6\text{H}_{11})\text{Ph}_2$  (**2-13**):*

**2-1** (0.10 g, 0.28 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.019 g, 0.037 mmol), benzene (1 mL), cyclohexanone (0.20 mL, 1.9 mmol),  $\text{PPh}_3$  (0.010 g, 0.037 mmol), hexanes (5 x 1 mL). Procedural notes: a one-piece “bomb” flask was used instead of a Schlenk flask; subjected to one-freeze-pump-thaw cycle; heated flask in an oil bath (55 °C) for 5 h, volatiles removed under dynamic vacuum at 50 °C for 1 h. A clear and colorless oil was isolated (0.084 g, 67%).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.73-0.91 (overlapping m, 3H,  $\text{OCHCH}_2\text{CH}_{\text{eq}}$  and  $\text{OCHCH}_2\text{CH}_2\text{CH}_{\text{eq}}$ ), 1.02 (m, 1H,  $\text{OCHCH}_2\text{CH}_2\text{CH}_{\text{ax}}$ ), 1.19-1.30 (m, 2H,  $\text{OCHCH}_{\text{eq}}$ ), 1.30-1.41 (m, 2H,  $\text{OCHCH}_2\text{CH}_{\text{ax}}$ ), 1.49-1.61 (m, 2H,  $\text{OCHCH}_{\text{ax}}$ ), 3.93 (quintet, 1H, O-CH), 5.56 ppm (s,  $^1J_{\text{SiH}} = 184$  Hz, 1H, Si-H), 7.08-7.12 (overlapping m, 8H,  $\text{H}_m\text{-SiPh}_2$  and  $\text{H}_m\text{-OSiPh}_2$ ), 7.14-7.18 (m overlapping with  $\text{C}_6\text{D}_5\text{H}$ , 4H,  $\text{H}_p\text{-SiPh}_2$  and

$H_p$ -OSiPh<sub>2</sub>), 7.68 (overlapping d,  $^3J_{HH} = 6$  Hz, 4H,  $H_o$ -SiPh<sub>2</sub>), 7.78 (overlapping d,  $^3J_{HH} = 7$  Hz, 4H,  $H_o$ -OSiPh<sub>2</sub>). DEPT135  $^{13}C$  NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) 23.9 (OCHCH<sub>2</sub>CH<sub>2</sub>), 25.7 (OCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 35.9 (OCHCH<sub>2</sub>), 73.0 (O-CH), 128.1 (C<sub>m</sub>-SiPh<sub>2</sub>), 128.2 (C<sub>m</sub>-OSiPh<sub>2</sub>), 129.4 (C<sub>p</sub>-SiPh<sub>2</sub>), 130.0 (C<sub>p</sub>-OSiPh<sub>2</sub>), 135.3 (C<sub>o</sub>-SiPh<sub>2</sub>), 136.5 (C<sub>o</sub>-OSiPh<sub>2</sub>). DEPT30  $^{29}Si$  NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>) -8.2 (Si-O), -33.8 (Si-H). Anal. Calc. for C<sub>30</sub>H<sub>32</sub>OSi<sub>2</sub>: C 77.53 H 6.94. Found: C 87.36 H 8.23.<sup>xv</sup>

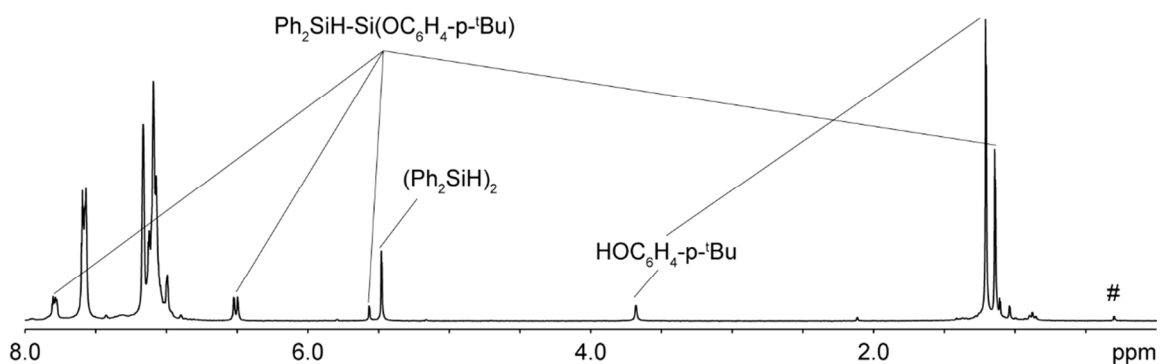


**Figure 2.11.** a)  $^1H$  NMR (300 MHz) and b) DEPT135  $^{13}C$  NMR (75 MHz) of  $Ph_2SiH-Si(OC_6H_{11})Ph_2$  (**2-13**) in C<sub>6</sub>D<sub>6</sub>. The “#” is grease. The “y” is *o*-SiPh-containing impurity, putatively assigned to the disubstituted product ( $Ph_2SiOC_6H_{11}$ )<sub>2</sub>.

<sup>xv</sup> Including vacuum grease (as suggested by the identification of “#” in  $^1H$  NMR in Figure 2.11) gives %C/%H values in poorer agreement with experimental. The “y” identified in the  $^1H$  NMR suggests either over-reduction products (e.g.  $(Ph_2SiH-SiPh_2)_2O$ ,  $Ph_2SiH-SiPh_2-O-SiPh_2-Si(OC_6H_{11})Ph_2$ ,  $(Ph_2Si(OC_6H_{11})-SiPh_2)_2O$ , or longer oligomers) or disubstituted product  $(Ph_2SiOC_6H_{11})_2$  are present in the mixture.

*Ph*<sub>2</sub>SiH-Si(OC<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)Ph<sub>2</sub> (**2-14**), Method A:

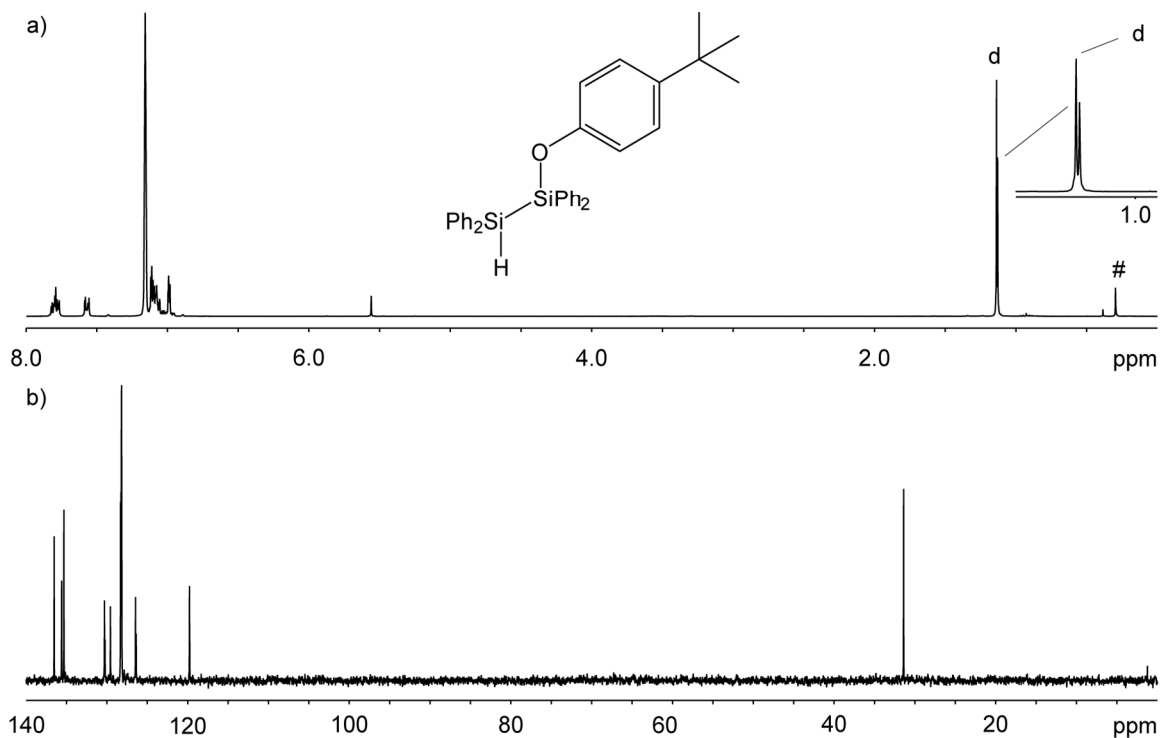
**2-2** (0.10 g, 0.27 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.012 g, 0.023 mmol), toluene (1 mL), *p*-*t*-butylphenol (0.041 g, 0.27 mmol), PPh<sub>3</sub> (0.007 g, 0.03 mmol), pentane (6 x 1 mL). Procedural notes: stirred under N<sub>2</sub> (open to Nujol bubbler) for 1 h. White oily solid. <sup>1</sup>H NMR showed approximately 32% conversion to Ph<sub>2</sub>SiH-Si(OC<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)Ph<sub>2</sub> based on the relative integrals for Si-H peaks due to disilane **2-2** and product Ph<sub>2</sub>SiH-Si(OC<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)Ph<sub>2</sub> (**2-14**). Longer reaction times (up to 16 h) showed only marginal increase in conversion, approximately 34% estimated by <sup>1</sup>H NMR. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.14 (s, 9H, -CH<sub>3</sub>), 5.56 (s, 1H, <sup>1</sup>J<sub>SiH</sub> = 188 Hz, Si-H), 6.98-7.00 (overlapping m, 4H, H<sub>o/m</sub>-C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu), 7.05-7.13 (overlapping m, 12H, H<sub>m/p</sub>-HSiPh and H<sub>m/p</sub>-OSiPh), 7.57 (overlapping d, 4H, <sup>3</sup>J<sub>HH</sub> = 4 Hz, H<sub>o</sub>-HSiPh<sub>2</sub>), 7.56-7.83 (overlapping m, 4H, H<sub>o</sub>-OSiPh<sub>2</sub>). DEPT135 <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 31.4 (CH<sub>3</sub>), 33.9 (-C-(CH<sub>3</sub>) by <sup>13</sup>C NMR) 119.8 (C<sub>o</sub>-C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu), 126.4 (C<sub>m</sub>-C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu), 128.2 (C<sub>m</sub>-HSiPh<sub>2</sub>), 128.3 (C<sub>m</sub>-OSiPh<sub>2</sub>), 129.6 (C<sub>p</sub>-HSiPh<sub>2</sub>), 130.3 (C<sub>p</sub>-OSiPh<sub>2</sub>), 135.3 (C<sub>o</sub>-HSiPh<sub>2</sub>), 136.5 (C<sub>o</sub>-OSiPh<sub>2</sub>); DEPT30 <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>) δ -6.4 (Si-O), -38.3 (Si-H).



**Figure 2.12.** <sup>1</sup>H NMR (300 MHz) of the crude mixture containing disilane **2-2** and Ph<sub>2</sub>SiH-Si(OC<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)Ph<sub>2</sub> (**2-14**) in C<sub>6</sub>D<sub>6</sub>.

*Ph<sub>2</sub>SiH-Si(OC<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)Ph<sub>2</sub> (2-14) Method B:*

In a “bomb” flask equipped with a stir bar, **2-2** (0.10 g, 0.27 mmol), *p-t*-butylphenol (0.041 g, 0.27 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.014 g, 0.027 mmol) were combined in toluene (1 mL). The solution bubbled and frothed (elimination of H<sub>2</sub>). The mixture was degassed with one freeze-pump-thaw cycle. The mixture was heated in an oil bath (70° C) for 16 h. Volatiles were removed by evacuation to give a white oily material and an aliquot removed for <sup>1</sup>H NMR showed partial (90%) conversion to monosubstituted disilane. To this mixture, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.017 g, 0.033 mmol) *p-t*-butylphenol (0.007 g, 0.047 mmol), and toluene (1 mL) were added. The clear and colorless solution was degassed by one freeze-pump thaw cycle. The mixture was heated in an oil bath (70 °C) for 16 h. Volatiles were removed by evacuation to give a yellow-brown oil. The mixture was dissolved in hexanes (1 mL) and eluted through a Florisil column to give a clear and colorless filtrate (brown color retained on the column). Hexanes (3 x 1 mL) was used to wash the column. Volatiles were removed by evacuation and the residue was heated to 70 °C to give a clear, colorless oil (0.086 g, 61% in >85% purity). No unreacted **2-2** was present; the other product was (Ph<sub>2</sub>SiOC<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)<sub>2</sub> (**2-20**, 15%, estimated by <sup>1</sup>H NMR integration). <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR assignments are listed in Method A, above. Mixture was not submitted for microanalysis. The lack of selectivity for **2-14** led to this mixture being used to make the disubstituted product **2-20**.

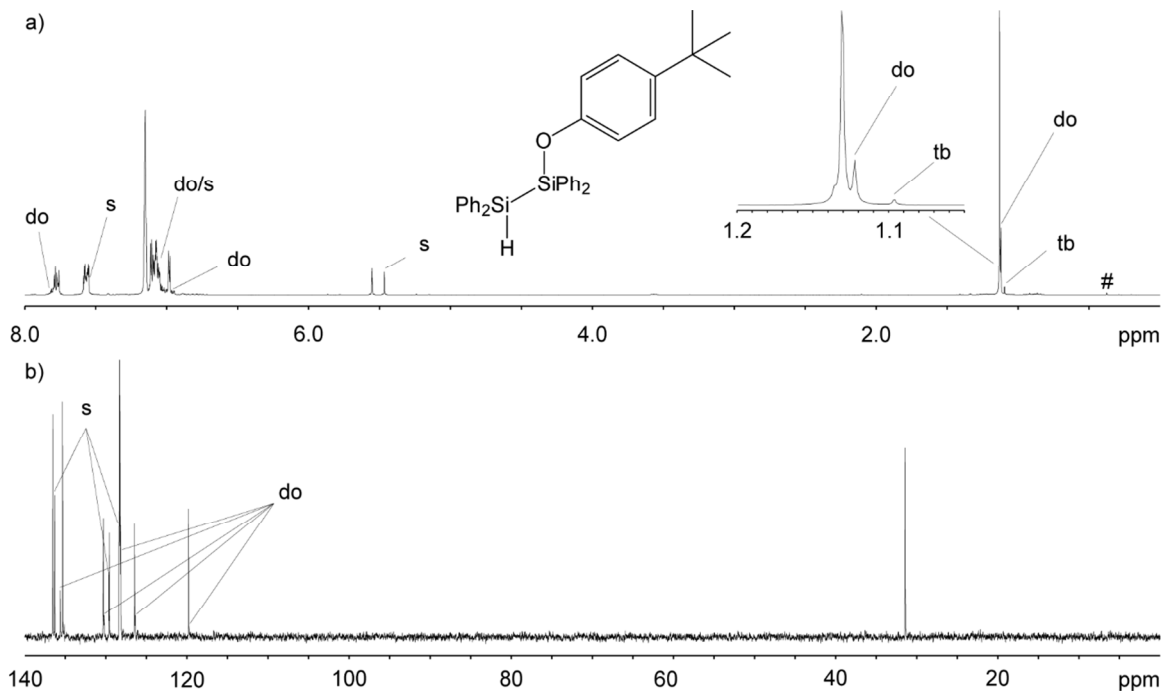


**Figure 2.13.** a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{SiH-Si}(\text{OC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})\text{Ph}_2$  (**2-14**) in  $\text{C}_6\text{D}_6$ . The “d” is the  $\text{C}(\text{CH}_3)_3$  in the disubstituted product  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})_2$  (**2-14**). The “#” is grease.

*$\text{Ph}_2\text{SiH-Si}(\text{OC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})\text{Ph}_2$  (**2-14**) Method C (added post defense):*

Disilane (0.10 g, 0.27 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.015 g, 0.029 mmol), toluene (1 mL), *p*-*t*-butylphenol (0.041 g, 0.27 mmol), hexanes (4 x 1 mL). Procedural notes: subjected to one freeze-pump-thaw cycle; stirred for 16 h at RT;  $\text{PPh}_3$  was not added; the crude mixture was dissolved in hexanes and was eluted through a Florisil column. Clear and colorless oil (0.095 g;  $^1\text{H}$  NMR (see spectrum below) showed a mixture of disilane (26%), **11** (67%), and **16** (7%).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.14 (s, 9H, overlapping with  $-\text{CH}_3$  in  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})_2$ ,  $-\text{CH}_3$ ), 5.56 (s, 1H,  $^1J_{\text{SiH}} = 188$  Hz, Si-H), 6.98-7.00 (overlapping m, 4H, overlapping with  $\text{H}_m\text{-C}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$  in  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})_2$ ,  $\text{H}_{o/m}\text{-C}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$ ), 7.05-7.13 (overlapping m, 12H, overlapping with  $\text{H}_{m/p}\text{-SiPh}_2$  in  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})_2$  and  $(\text{Ph}_2\text{SiH})_2$ ,  $\text{H}_{m/p}\text{-HSiPh}$  and  $\text{H}_{m/p}\text{-OSiPh}$ ), 7.57 (overlapping d,

4H, overlapping with  $H_o$ -SiPh<sub>2</sub> in (Ph<sub>2</sub>SiH)<sub>2</sub>,  $^3J_{HH} = 4$  Hz,  $H_o$ -HSiPh<sub>2</sub>), 7.56-7.83 (overlapping m, 4H,  $H_o$ -OSiPh<sub>2</sub>). DEPT135 <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 31.4 (CH<sub>3</sub>), 33.9 (-C-(CH<sub>3</sub>) by <sup>13</sup>C NMR) 119.8 (C<sub>o</sub>-C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu), 126.4 (C<sub>m</sub>-C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu), 128.2 (C<sub>m</sub>-HSiPh<sub>2</sub>), 128.3 (C<sub>m</sub>-OSiPh<sub>2</sub>), 129.6 (C<sub>p</sub>-HSiPh<sub>2</sub>), 130.3 (C<sub>p</sub>-OSiPh<sub>2</sub>), 135.3 (C<sub>o</sub>-HSiPh<sub>2</sub>), 136.5 (C<sub>o</sub>-OSiPh<sub>2</sub>). DEPT30 <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>) δ -6.4 (Si-O), -38.3 (Si-H).

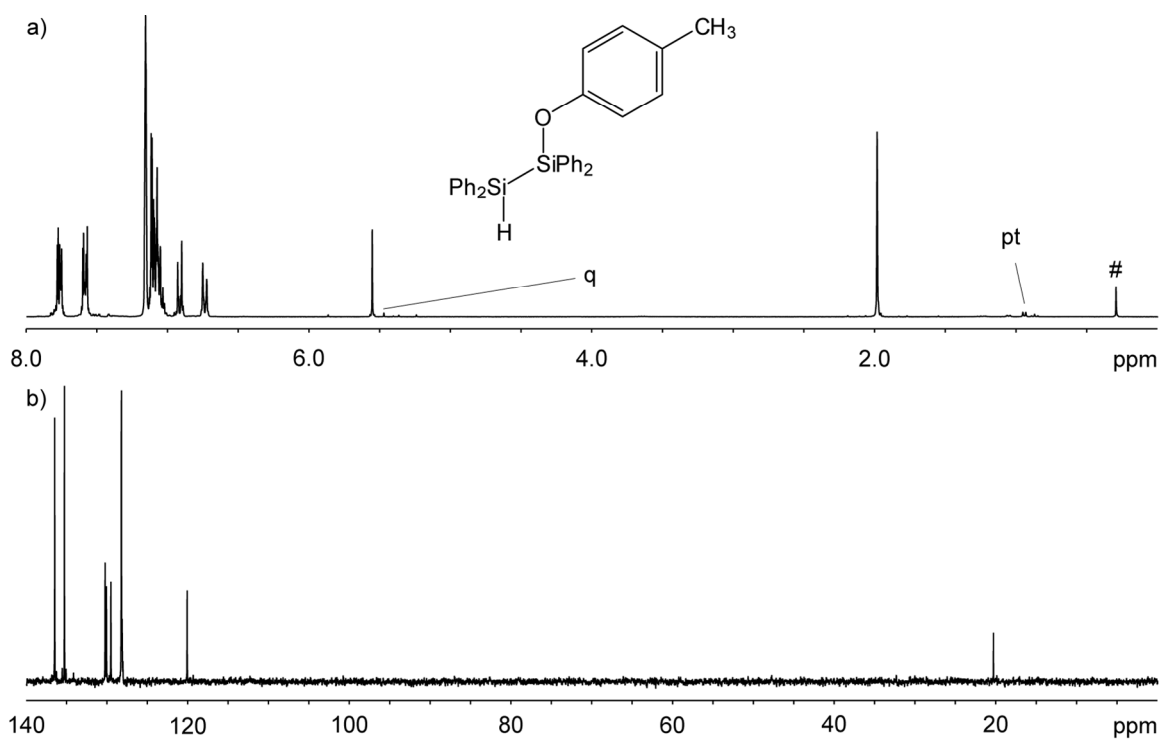


**Figure 2.14.** a) <sup>1</sup>H NMR (300 MHz) and b) DEPT135 <sup>13</sup>C NMR (75 MHz) of Ph<sub>2</sub>SiH-Si(OC<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)Ph<sub>2</sub> (11) in C<sub>6</sub>D<sub>6</sub>. The “s” is unreacted disilane. The “do” is the disubstituted product (Ph<sub>2</sub>SiOC<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)<sub>2</sub> (**2-14**). The “tb” is an unidentified signal likely from a C(CH<sub>3</sub>)<sub>3</sub> group. The “#” is grease.

*Ph*<sub>2</sub>SiH-Si(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)Ph<sub>2</sub> (**2-15**):

**2-2** (0.30 g, 0.82 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.042 g, 0.082 mmol), toluene (2 mL), *p*-methylanisole (0.10 g, 0.82 mmol), PPh<sub>3</sub> (0.021 g, 0.080 mmol), pentane (6 x 1 mL). Procedural notes: stirred under N<sub>2</sub> (open to Nujol bubbler) for 16 h. The product was heated to 70 °C under dynamic vacuum for 2 h to remove volatiles. A clear, colorless,

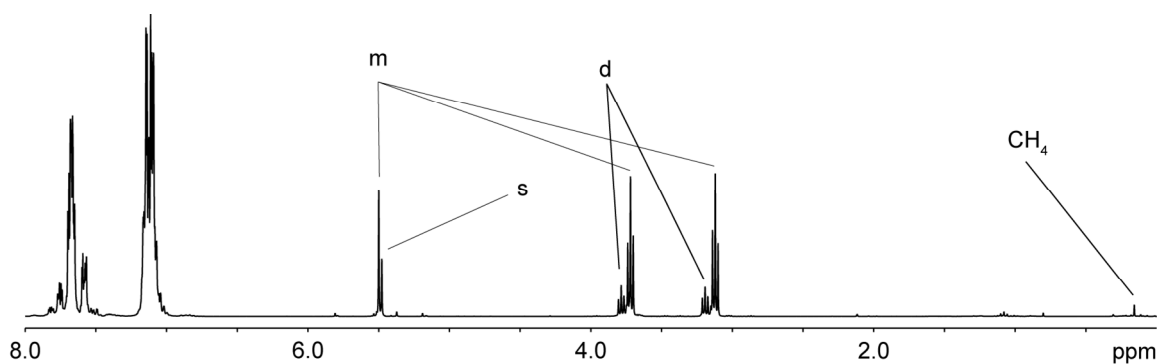
viscous oil was isolated (0.38 g, 99% in >97% purity. A trace amount of unreacted  $(\text{Ph}_2\text{SiH})_2$  was detected by  $^1\text{H}$  NMR (see spectrum below)).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.99 (s, 3H,  $p\text{-CH}_3$ ), 5.56 (s, 1H,  $^1J_{\text{SiH}} = 187$  Hz, Si-H), 6.74 (dt, 2H,  $^3J_{\text{HH}} = 8$  Hz,  $^4J_{\text{HH}} = 1$  Hz,  $\text{H}_o\text{-OC}_6\text{H}_4\text{-}p\text{-CH}_3$ ), 6.92 (dt, 2H,  $^3J_{\text{HH}} = 9$  Hz,  $^4J_{\text{HH}} = 1$  Hz,  $\text{H}_m\text{-OC}_6\text{H}_4\text{-}p\text{-CH}_3$ ), 7.04-7.12 (m, 12H,  $\text{H}_{m/p}\text{-SiPh}_2$ ), 7.57-7.79 (m, 8H,  $\text{H}_o\text{-SiPh}_2$ ); DEPT135  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  20.4 ( $p\text{-CH}_3$ ), 120.1 ( $\text{C}_o\text{-OC}_6\text{H}_4\text{-}p\text{-CH}_3$ ), 128.2 ( $\text{C}_m\text{-Si(H)Ph}_2$ ), 128.3 ( $\text{C}_m\text{-OSiPh}_2$ ), 129.6 ( $\text{C}_m\text{-OC}_6\text{H}_4\text{-}p\text{-CH}_3$ ), 130.1 ( $\text{C}_p\text{-HSiPh}_2$ ), 130.3 ( $\text{C}_p\text{-OSiPh}_2$ ), 135.3 ( $\text{C}_o\text{-HSiPh}_2$ ), 136.5 ( $\text{C}_o\text{-OSiPh}_2$ ); DEPT30  $^{29}\text{Si}$  NMR (99 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -6.3 (Si-O), -38.4 (Si-H). Anal. Calc. for  $\text{C}_{31}\text{H}_{28}\text{OSi}_2$ : C 78.76 H 5.97. Found: C 76.93 H 6.09.



**Figure 2.15.** a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{SiH-Si}(\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3)\text{Ph}_2$  (**2-15**) in  $\text{C}_6\text{D}_6$ . The “#” is grease. The “q” is disilane **2-2**. The “pt” is residual pentane.

Monitoring formation of  $\text{Ph}_2\text{SiH-Si}(\text{OCH}_2\text{CH}_2\text{Cl})\text{Ph}_2$  (**2-16**) by  $^1\text{H}$  NMR

**2-2** (0.050 g, 0.14 mmol), 2-chloroethyl methyl ether (0.013 g, 0.14 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.010 g, 0.020 mmol), and  $\text{C}_6\text{D}_6$  (1 mL) were combined in an NMR tube equipped with a J-Young valve. The solution was mixed by shaking the NMR tube and was vented periodically (to release  $\text{CH}_4$  pressure) on the vacuum line under  $\text{N}_2$ . The reaction was monitored by  $^1\text{H}$  NMR over 6 days. Complete consumption of 2-chloroethyl methyl ether was evident (lack of O- $\text{CH}_3$  group in  $^1\text{H}$  NMR) after 4 h. Relative ratios of  $(\text{Ph}_2\text{SiH})_2$ ,  $\text{Ph}_2\text{SiH-Si}(\text{OCH}_2\text{CH}_2\text{Cl})\text{Ph}_2$ , and  $(\text{Ph}_2\text{SiOCH}_2\text{CH}_2\text{Cl})_2$  were 15:75:10% respectively (estimated by  $^1\text{H}$  NMR integration).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  3.11 (t,  $^3J_{\text{HH}} = 6$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{Cl}$ ), 3.71 (t,  $^3J_{\text{HH}} = 6$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{Cl}$ ), 5.55 (s,  $^1J_{\text{SiH}} = 186$  Hz, 1H, Si-H), 7.04-7.19 (overlapping m, 12H,  $\text{H}_{m/p}\text{-SiPh}_2$  and  $\text{H}_{m/p}\text{-OSiPh}_2$ ), 7.63-7.71 (overlapping m, 8H,  $\text{H}_o\text{-SiPh}_2$  and  $\text{H}_o\text{-OSiPh}_2$ ).



**Figure 2.16.** a)  $^1\text{H}$  NMR (300 MHz) of the reaction monitoring formation of  $\text{Ph}_2\text{SiH-Si}(\text{OCH}_2\text{CH}_2\text{Cl})\text{Ph}_2$  (**2-16**) in  $\text{C}_6\text{D}_6$ . The “s” is starting material  $(\text{Ph}_2\text{SiH})_2$ . The “m” is the monosubstituted product  $\text{Ph}_2\text{SiH-Si}(\text{OCH}_2\text{CH}_2\text{Cl})\text{Ph}_2$  (**2-16**). The “d” is the disubstituted product  $(\text{Ph}_2\text{SiOCH}_2\text{CH}_2\text{Cl})_2$  (**2-22**).

$\text{Ph}_2\text{SiH-Si}(\text{SCH}_2\text{CH}_2\text{CH}_3)\text{Ph}_2$  (**2-17**):

**2-2** (0.51 g, 1.4 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.068 g, 0.13 mmol), solution of benzene/*n*-propylthiol (5 mL benzene, 0.14 g, 1.8 mmol *n*-propylthiol),  $\text{PPh}_3$  (0.035 g,

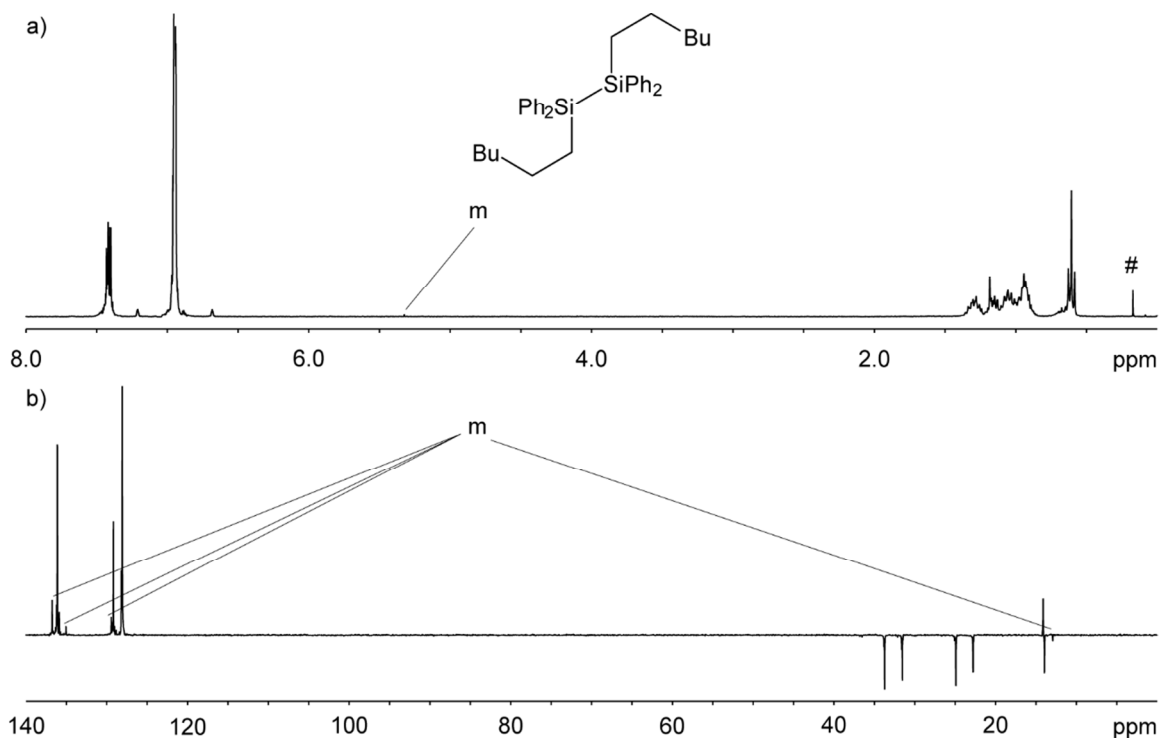
0.13 mmol), hexanes (11 x 1 mL). Procedural notes: stirred under N<sub>2</sub> (open to Nujol bubbler) for 1 min, then under N<sub>2</sub> (closed flask) for 15 h. Clear, colorless, viscous oil (0.60 g, 98%) <sup>1</sup>H NMR of the product was the same as previously reported,<sup>1a</sup> with no observable unreacted starting material. DEPT30 <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>) δ -9.8 (Si-S), -35.9 (Si-H).

#### 2.6.4 Synthesis of disubstituted disilanes

*(Ph<sub>2</sub>SiCH<sub>2</sub>CH<sub>2</sub>Bu)<sub>2</sub> (2-19):*

In a Schlenk flask equipped with a stir bar, **2-2** (0.30 g, 0.82 mmol) and B(C<sub>6</sub>F<sub>3</sub>)<sub>3</sub> (0.053 g, 0.10 mmol) were combined with 1-hexene (1.0 mL, 8.0 mmol) and dichloromethane (0.1 mL). The mixture was stirred in a closed flask for 72 h under N<sub>2</sub>, after which the volatiles were removed under vacuum to give a cloudy oily residue. The resulting residue was dissolved in hexanes (1 mL) and eluted through a Florisil column (to remove B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>). The column was rinsed with hexanes (5 x 1 mL), and the volatiles of the combined fractions were removed under vacuum. A clear, colorless, viscous oil was isolated (0.38 g, 87% in ~99% purity). <sup>1</sup>H/<sup>13</sup>C NMR spectra showed minor peaks presumed to be the monosubstituted product Ph<sub>2</sub>SiH-Si(CH<sub>2</sub>CH<sub>2</sub>Bu)Ph<sub>2</sub>, estimated <1% by <sup>1</sup>H NMR integration (see spectrum below). Increased reaction time (up to 3 d) and additional catalyst (up to 0.20 mmol) did not result in this impurity being converted to (Ph<sub>2</sub>Si(CH<sub>2</sub>CH<sub>2</sub>Bu))<sub>2</sub>. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 0.82 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 6H, CH<sub>3</sub>), 1.07-1.62 (m, 20H, CH<sub>2</sub>), 7.12-7.21 (overlapping m, 12H, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.59-7.67 (m, 8H, H<sub>o</sub>-SiPh<sub>2</sub>); DEPT135 <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 14.0 (CH<sub>3</sub>), 14.1 (SiCH<sub>2</sub>), 22.8 (Si(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>), 24.9 (Si(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>), 31.6 (Si(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 33.7 (SiCH<sub>2</sub>CH<sub>2</sub>), 128.1 (C<sub>m</sub>-

SiPh<sub>2</sub>), 129.2 (C<sub>p</sub>-SiPh<sub>2</sub>), 136.1 (C<sub>o</sub>-SiPh<sub>2</sub>); direct acquisition <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>) δ -20.3 (Si-CH<sub>2</sub>). Anal. Calc. for C<sub>36</sub>H<sub>46</sub>Si<sub>2</sub>: C 80.83 H 8.67. Found: C 80.97 H 9.04.



**Figure 2.17.** a) <sup>1</sup>H NMR (300 MHz) and b) DEPT135 <sup>13</sup>C NMR (75 MHz) of (Ph<sub>2</sub>SiCH<sub>2</sub>CH<sub>2</sub>Bu)<sub>2</sub> (**2-19**) in C<sub>6</sub>D<sub>6</sub>. The “m” is a Si-Ph/ CH<sub>2</sub>CH<sub>2</sub>Bu-containing compound, which is presumed to be <1% monosubstituted product (Ph<sub>2</sub>SiH-Si(CH<sub>2</sub>CH<sub>2</sub>Bu)Ph<sub>2</sub>).

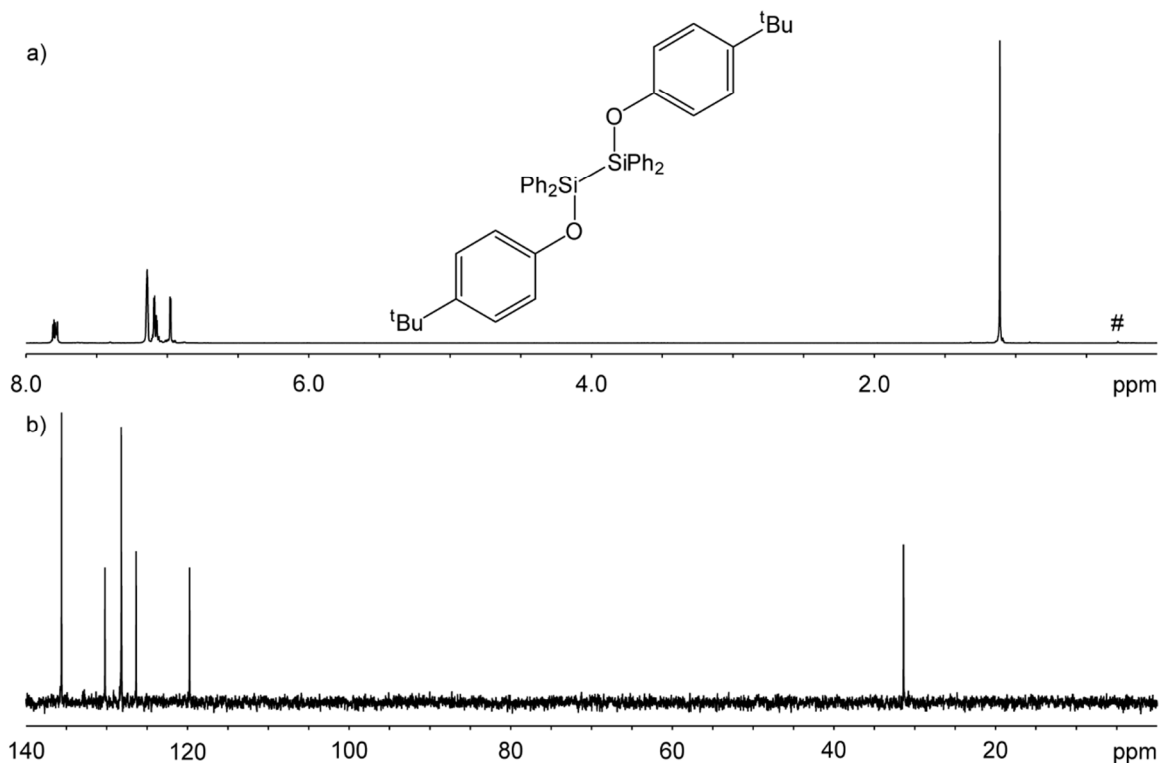
(Ph<sub>2</sub>SiOC<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)<sub>2</sub> (**2-20**):

In a “bomb” flask equipped with a stir bar, **2-2** (0.10 g, 0.27 mmol), *p-t*-butylphenol (0.11 g, 0.71 mmol), and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.028 g, 0.055 mmol) were combined with toluene (1 mL). Flask contents were degassed using one freeze-pump-thaw cycle. The mixture was stirred and heated in an oil bath (70 °C) for 16 h, after which the sealed flask was cooled to RT and toluene was removed under vacuum to give a light brown, viscous oil. A <sup>1</sup>H NMR spectrum taken at this point shows 100% conversion to disubstituted product (see Figure 2.19a). The mixture was dissolved in hexanes (1 mL)

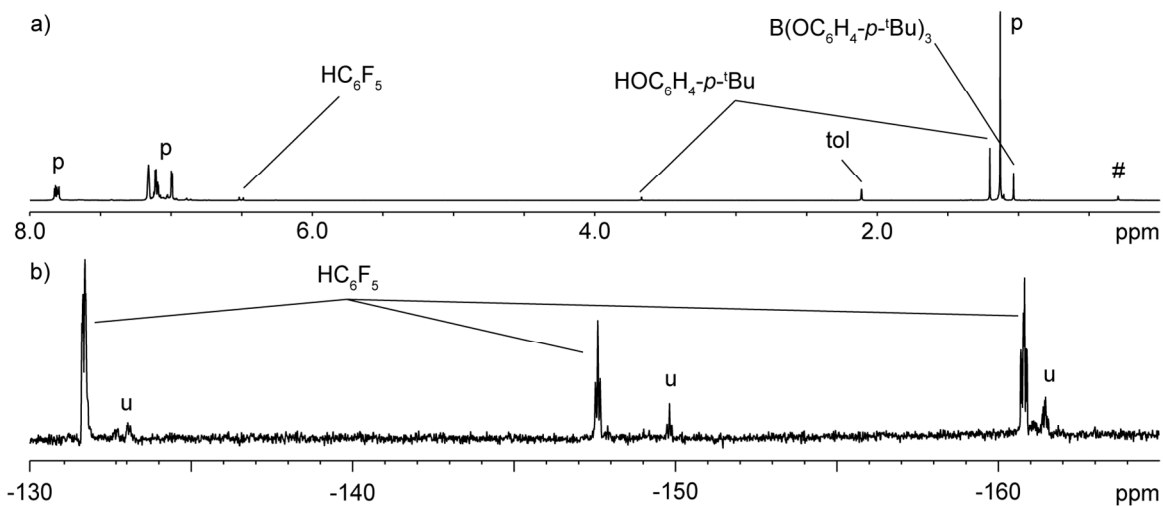
and eluted through a Florisil column (to remove  $B(C_6F_5)_3$  and  $B-OC_6H_4-p-tBu$ -containing by products) and a clear colorless filtrate was collected (the brown color of the starting solution was retained on the Florisil column). The column was rinsed with hexanes (5 x 1 mL) and the fractions were combined in a Schlenk flask. Volatiles were removed under dynamic vacuum at 60 °C for 2 h to give an oily, white solid. Pentane (1 mL) was added and the solid dissolved to give a clear and colorless solution. Volatiles were removed under dynamic vacuum at RT for 1 h to give a white, powdery solid (0.038 g, 21%<sup>xvi</sup>).  $^1H$  NMR (300 MHz,  $C_6D_6$ )  $\delta$  1.13 (s, 18H,  $-C-(CH_3)$ ), 6.98-7.01 (overlapping m, 8H,  $H_{o/m}-C_6H_4-p-tBu$ ), 7.07-7.13 (overlapping m, 12H,  $H_{m/p}-Ph$ ), 7.81 (overlapping d,  $^3J_{HH} = 7$  Hz, 8H,  $H_o-Ph$ )  $\delta$ ; DEPT135  $^{13}C$  NMR (75 MHz,  $C_6D_6$ )  $\delta$  31.4 ( $CH_3$ ), 33.9 ( $-C-(CH_3)$  by  $^{13}C$  NMR), 119.8 ( $C_o-C_6H_4-p-tBu$ ), 126.37 ( $C_m-C_6H_4-p-tBu$ ), 128.2 ( $C_m-SiPh_2$ ), 130.2 ( $C_p-SiPh_2$ ), 135.6 ( $C_o-SiPh_2$ ); DEPT30  $^{29}Si$  NMR (99 MHz,  $C_6D_6$ )  $\delta$  -11.1 (Si-O). M.p. 81-82 °C. Anal. Calc. for  $C_{44}H_{46}O_2Si_2$  (**2-20**) and 19%  $C_2H_6OSi$  (grease): C 78.50 H 7.02. Found: C 78.47 H 6.95.

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<sup>xvi</sup> For comparison, synthesis of **2-14** (Method B) gave a mixture of major product  $Ph_2SiH-Si(OC_6H_4-p-tBu)Ph_2$  (84%) and minor product  $(Ph_2SiOC_6H_4-p-tBu)_2$  (16%)



**Figure 2.18.** a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})_2$  (**2-20**) in  $\text{C}_6\text{D}_6$ .

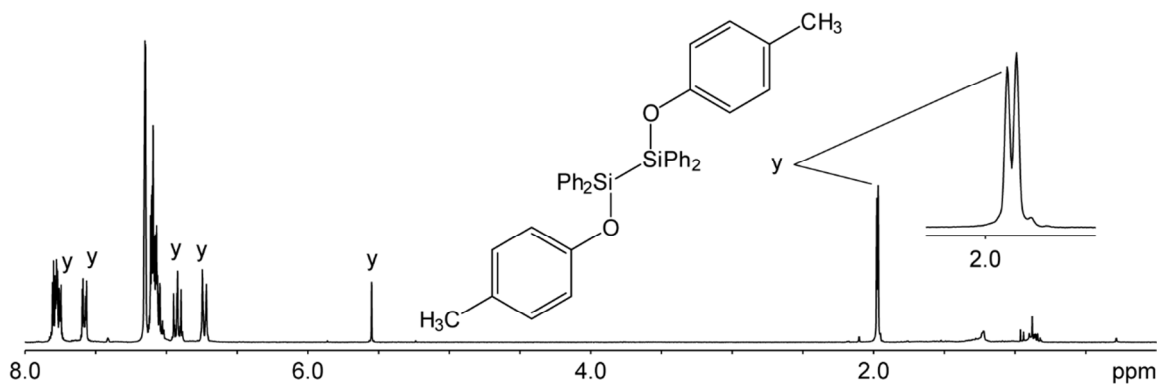


**Figure 2.19.** a)  $^1\text{H}$  NMR (300 MHz) and b)  $^{19}\text{F}$   $\{^1\text{H}\}$  NMR (283 MHz) of the crude reaction mixture for the synthesis of  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})_2$  (**2-20**) in  $\text{C}_6\text{D}_6$ . The peaks designated "u" are for an unidentified  $\text{C}_6\text{F}_5$ -containing species that may be  $(\text{F}_5\text{C}_6)_2\text{-BOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$  or  $\text{F}_5\text{C}_6\text{-B(OC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})_2$  from the partial phenolysis of  $\text{B(C}_6\text{F}_5)_3$ . The peaks designated "p" are for the expected product  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})_2$  (**2-20**).

$(Ph_2SiOC_6H_4-p-CH_3)_2$  (**2-21**):

In a “bomb” flask equipped with a stir bar, **2-2** (0.20 g, 0.55 mmol), *p*-methylanisole (0.19 g, 1.6 mmol), and  $B(C_6F_5)_3$  (0.024 g, 0.047 mmol) were combined with toluene (2 mL). Flask contents were degassed using one freeze-pump-thaw cycle. The mixture was stirred and heated in an oil bath (70 °C) for 16 h, after which the sealed flask was cooled to RT and toluene was removed under vacuum to give a light brown, viscous oil. An aliquot removed for  $^1H$  NMR showed complete conversion to the monosubstituted product,  $Ph_2SiH-Si(OC_6H_4-p-CH_3)Ph_2$  (**2-15**). Toluene (1 mL) and  $B(C_6F_5)_3$  (0.022 g, 0.043 mmol) were added, and then the flask was degassed with one freeze-pump-thaw cycle. The mixture was stirred and heated in an oil bath (70 °C) for 28 d, after which the sealed flask was cooled to RT and toluene was removed under vacuum to give a light brown, viscous oil. Hexanes (1 mL, then 3 x 1 mL) was added and the solution was eluted through a Florisil column (to remove  $B(C_6F_5)_3$ , the brown color was retained on the Florisil column). A clear colorless filtrate was collected and the fractions were combined. Volatiles were removed under dynamic vacuum at 60 °C for 2 h. A cloudy oil that was a mixture of the mono- and disubstituted products (**2-15** and **2-21**) in a 65:35 ratio (estimated from  $^1H$  NMR integration) was isolated.  $^1H$  NMR (300 MHz,  $C_6D_6$ )  $\delta$  1.97 (s, 6H, *p*-CH<sub>3</sub>, overlapping with *p*-CH<sub>3</sub> in  $Ph_2SiH-Si(OC_6H_4-p-CH_3)Ph_2$ ), 6.73 (d, 4H,  $H_m-OC_6H_4-p-CH_3$ , overlapping with  $H_m-OC_6H_4-p-CH_3$  in  $Ph_2SiH-Si(OC_6H_4-p-CH_3)Ph_2$ ), 6.93 (d, 4H,  $H_o-OC_6H_4-p-CH_3$ , overlapping with  $H_o-OC_6H_4-p-CH_3$  in  $Ph_2SiH-Si(OC_6H_4-p-CH_3)Ph_2$ ), 7.06-7.12 (overlapping m, 6H,  $H_{m/p}-SiPh_2$ , overlapping with  $H_{m/p}-SiPh_2$  in  $Ph_2SiH-Si(OC_6H_4-p-CH_3)Ph_2$ ), 7.76-7.82 (overlapping m, 8H,  $H_o-SiPh_2$ , overlapping with  $H_o-SiPh_2$  in  $Ph_2SiH-Si(OC_6H_4-p-CH_3)Ph_2$ ). Mixture was not

submitted for microanalysis. Product decomposed to a cloudy white, viscous insoluble oil of undetermined identity over 72 h. It was decided that it was unnecessary to repeat this experiment given the reaction time (28 d) and lack of selectivity for desired product, **2-21**.

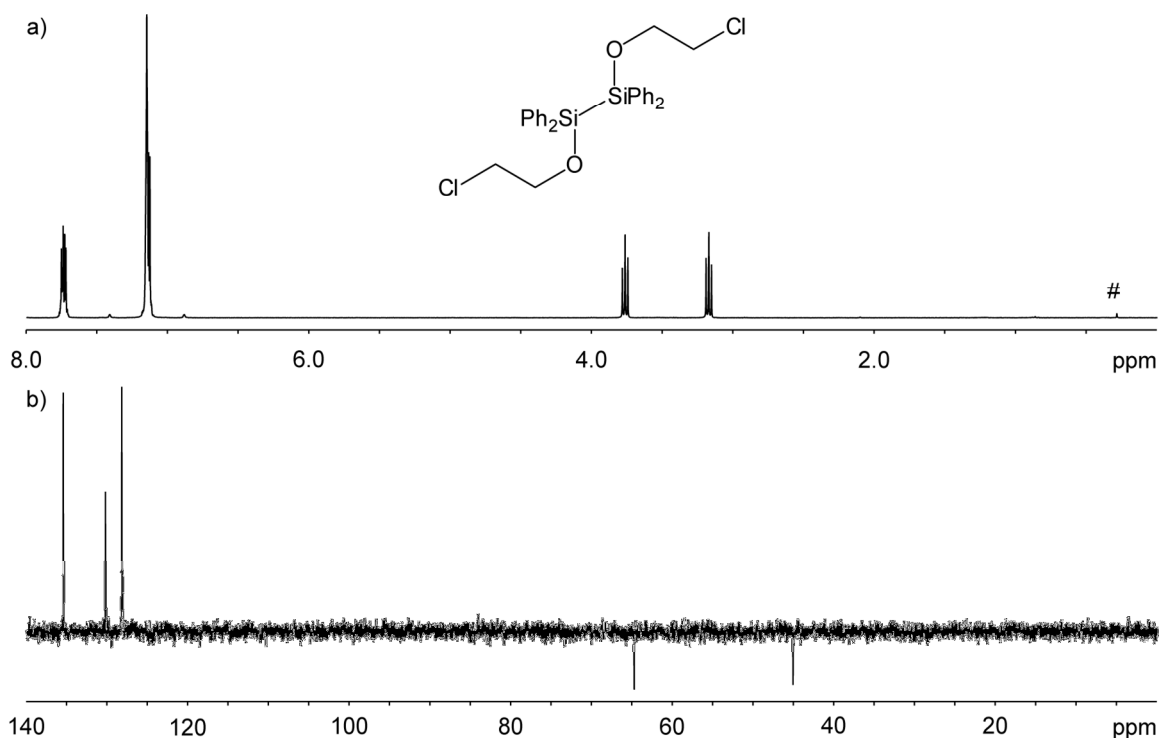


**Figure 2.20.**  $^1\text{H}$  NMR (300 MHz) of a mixture of  $\text{Ph}_2\text{SiH-Si}(\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3)\text{Ph}_2$  (identified in the  $^1\text{H}$  NMR spectrum as “y”) and  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}p\text{-CH}_3)_2$  (**2-21**) in  $\text{C}_6\text{D}_6$ .

$(\text{Ph}_2\text{SiOCH}_2\text{CH}_2\text{Cl})_2$  (**2-22**):

In a Schlenk flask equipped with a stir bar, **2-2** (0.10 g, 0.27 mmol) and  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.015 g, 0.029 mmol) were combined with toluene (1 mL). To this stirring mixture, 2-chloroethyl methyl ether (0.050 mL, 0.55 mmol) was added dropwise. The contents were left stirring under  $\text{N}_2$  (open to the Nujol bubbler). After 16 h, the mixture became cloudy white and toluene was removed under vacuum. Cold pentane (2 mL) was added and a white precipitate formed. The precipitate was collected by filtration on a sintered glass frit under vacuum to give a white powdery solid. The product was washed with cold pentane (4 mL), dried under vacuum for 2h at  $50\text{ }^\circ\text{C}$ , to give a white powdery solid (0.094 g, 65%).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  3.17 (t,  $^3J_{\text{HH}} = 6\text{ Hz}$ , 4H,  $\text{OCH}_2\text{CH}_2\text{Cl}$ ), 3.77 (t,  $^3J_{\text{HH}} = 6\text{ Hz}$ , 4H,  $\text{OCH}_2\text{CH}_2\text{Cl}$ ), 7.14 (m, 12H,  $\text{H}_{m/p}\text{-SiPh}_2$ ), 7.75 (m, 8H,  $\text{H}_o\text{-SiPh}_2$ ); DEPT135  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  45.1 ( $\text{OCH}_2\text{CH}_2\text{Cl}$ ), 64.8 ( $\text{OCH}_2\text{CH}_2\text{Cl}$ ),

128.2 ( $C_m$ -SiPh<sub>2</sub>), 130.3 ( $C_p$ -SiPh<sub>2</sub>), 135.4 ( $C_o$ -SiPh<sub>2</sub>); direct acquisition <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>) δ -7.7 (Si-O). M. p. 138-140 °C. Anal. Calc. for 93% C<sub>28</sub>H<sub>28</sub>O<sub>2</sub>Cl<sub>2</sub>Si<sub>2</sub> (**2-22**) and 7% C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>Si (grease): C 63.23 H 5.36. Found: C 63.28 H 5.17.



**Figure 2.21.** a) <sup>1</sup>H NMR (300 MHz) and b) DEPT135 <sup>13</sup>C NMR (75 MHz) of (Ph<sub>2</sub>SiOCH<sub>2</sub>CH<sub>2</sub>Cl)<sub>2</sub> (**2-22**) in C<sub>6</sub>D<sub>6</sub>. The “#” is grease.

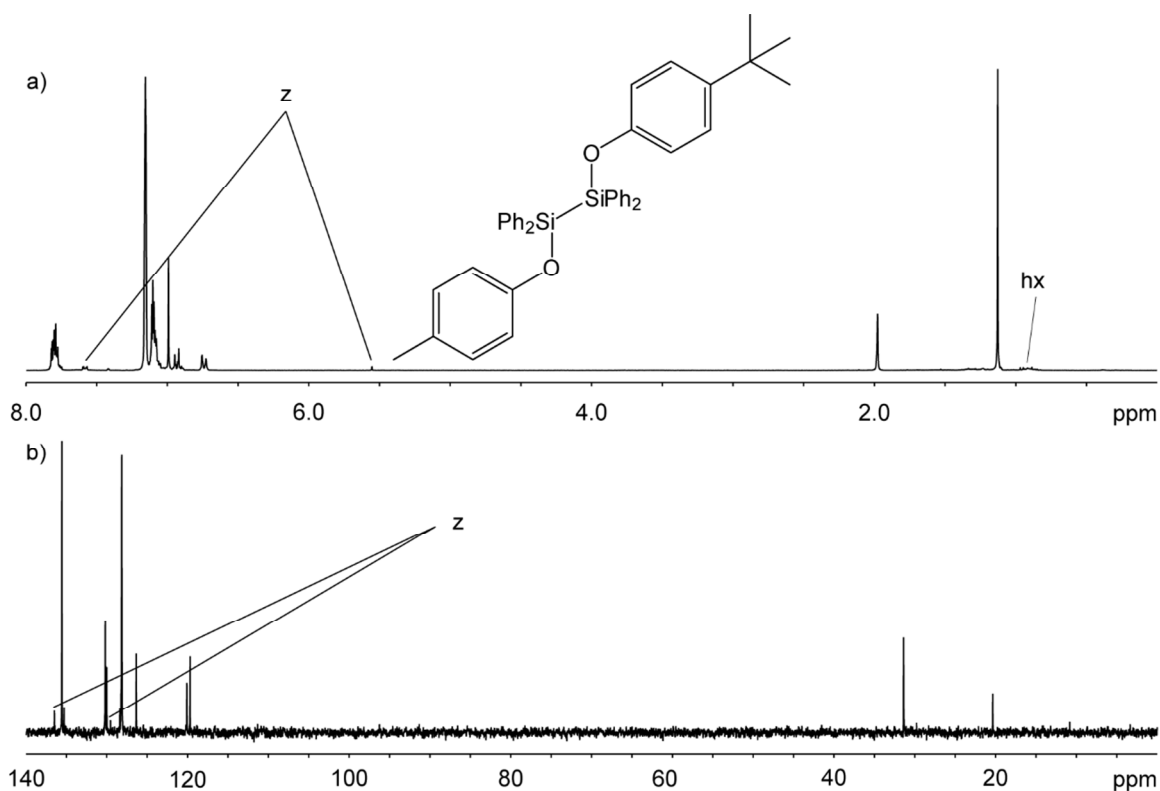
### 2.6.5 Synthesis of an unsymmetrically-disubstituted disilane

*Ph*<sub>2</sub>Si(*OC*<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)-Si(*OC*<sub>6</sub>H<sub>4</sub>-*p*-*t*Bu)Ph<sub>2</sub> (**2-24**):

Procedure was the same as **2-21** up to the identification of Ph<sub>2</sub>SiH-Si(*OC*<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)Ph<sub>2</sub> (**2-15**) by <sup>1</sup>H NMR. Procedural notes: **2-2** (0.10 g, 0.27 mmol), *p*-methylanisole (0.040 g, 0.33 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.015 g, 0.029 mmol), toluene (1 mL). Toluene (1 mL), *p*-*t*-butylphenol (0.044 g, 0.29 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.22 g, 0.043 mmol) were added to the flask. Flask contents were degassed using one freeze-pump-thaw cycle. The mixture was stirred and the flask was heated in an oil bath (70 °C)

for 72 h, after which the sealed flask was cooled to RT and toluene was removed under vacuum to give a light brown, viscous oil. Hexanes (1 mL) was added to give a light brown solution. The solution was eluted through a Florisil column (to remove  $B(C_6F_5)_3$  and  $B-OC_6H_4-p-tBu$ -containing by-products, the brown color was retained on the Florisil column) and a clear colorless filtrate was collected. The column was washed with hexanes (4 x 1 mL) and the fractions were combined in a Schlenk flask. Volatiles were removed under dynamic vacuum at 70 °C for 2 h (to remove residual *p-t*-butylphenol and  $C_6F_5H$ ), and then cooled to RT. A viscous cloudy oil was isolated (0.14 g, 84%, >99% purity, <1% residual  $Ph_2SiH-Si(OC_6H_4-p-CH_3)Ph_2$  (**2-15**) estimated by  $^1H$  NMR integration, see spectrum below).  $^1H$  NMR: 1.13 (s, 9H,  $C(CH_3)_3$ ), 1.98 (s, 9H, *p*- $CH_3$ ), 6.74 (dt,  $^3J_{HH} = 8$  Hz,  $^4J_{HH} = 2$  Hz, 2H,  $H_m-OC_6H_4-p-CH_3$ ), 6.94 (dt,  $^3J_{HH} = 8$  Hz,  $^4J_{HH} = 2$  Hz, 2H,  $H_o-OC_6H_4-p-CH_3$ ), 6.98-7.00 (overlapping m, 4H,  $H_o-OC_6H_4-p-tBu$ ,  $H_m-OC_6H_4-p-tBu$ ), 7.07-7.12 (overlapping m, 12H,  $H_m-OC_6H_4-p-tBu$ ,  $H_p-OC_6H_4-p-tBu$ ,  $H_m-OC_6H_4-p-CH_3$ ,  $H_p-OC_6H_4-p-CH_3$ ), 7.77-7.83 (overlapping m, 8H,  $H_o-SiPh_2OC_6H_4-p-tBu$ ,  $H_o-SiPh_2OC_6H_4-p-CH_3$ ). DEPT135  $^{13}C$  NMR 20.4 ( $-C(CH_3)_3$ ), 31.4 (*p*- $CH_3$ ), 119.7 ( $C_m-OC_6H_4-p-tBu$ ), 120.1 ( $C_m-OC_6H_4-p-CH_3$ ), 126.4 ( $C_o-C_6H_4-p-tBu$ ), 128.2 (overlapping,  $C_p-SiPh_2OC_6H_4-p-tBu$ ,  $C_p-SiPh_2OC_6H_4-p-CH_3$ ), 130.0 ( $C_o-OC_6H_4-p-CH_3$ ), 130.2 (overlapping,  $C_m-SiPh_2OC_6H_4-p-tBu$ ,  $C_m-SiPh_2OC_6H_4-p-CH_3$ ), 135.6 (overlapping,  $C_o-SiPh_2OC_6H_4-p-tBu$ ,  $C_o-SiPh_2OC_6H_4-p-CH_3$ ). DEPT30  $^{29}Si$  (500 MHz,  $C_6D_6$ ) -10.9 ( $SiOC_6H_4-p-CH_3$ ), -11.1 ( $SiOC_6H_4-p-tBu$ ). Anal. Calc. for  $C_{41}H_{40}O_2Si_2$ : C 79.31 H 6.49. Found: C 77.59 H 6.40.<sup>xvii</sup>

<sup>xvii</sup> %C values are not drastically changed when including the molar ratio of **2-15** and **2-24** suggested by  $^1H$  NMR. These results are consistent with the presence of one or more impurities in this oil that are not readily identified by NMR.



**Figure 2.22.** a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{Ph}_2\text{Si}(\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3)\text{-Si}(\text{OC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})\text{Ph}_2$  (**2-24**) in  $\text{C}_6\text{D}_6$ . The “z” is residual  $\text{Ph}_2\text{SiH-Si}(\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3)\text{Ph}_2$  (**2-15**). The “hx” is residual hexanes.

### 2.6.6 $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reactions with *n*-propylidene-*n*-propylamine

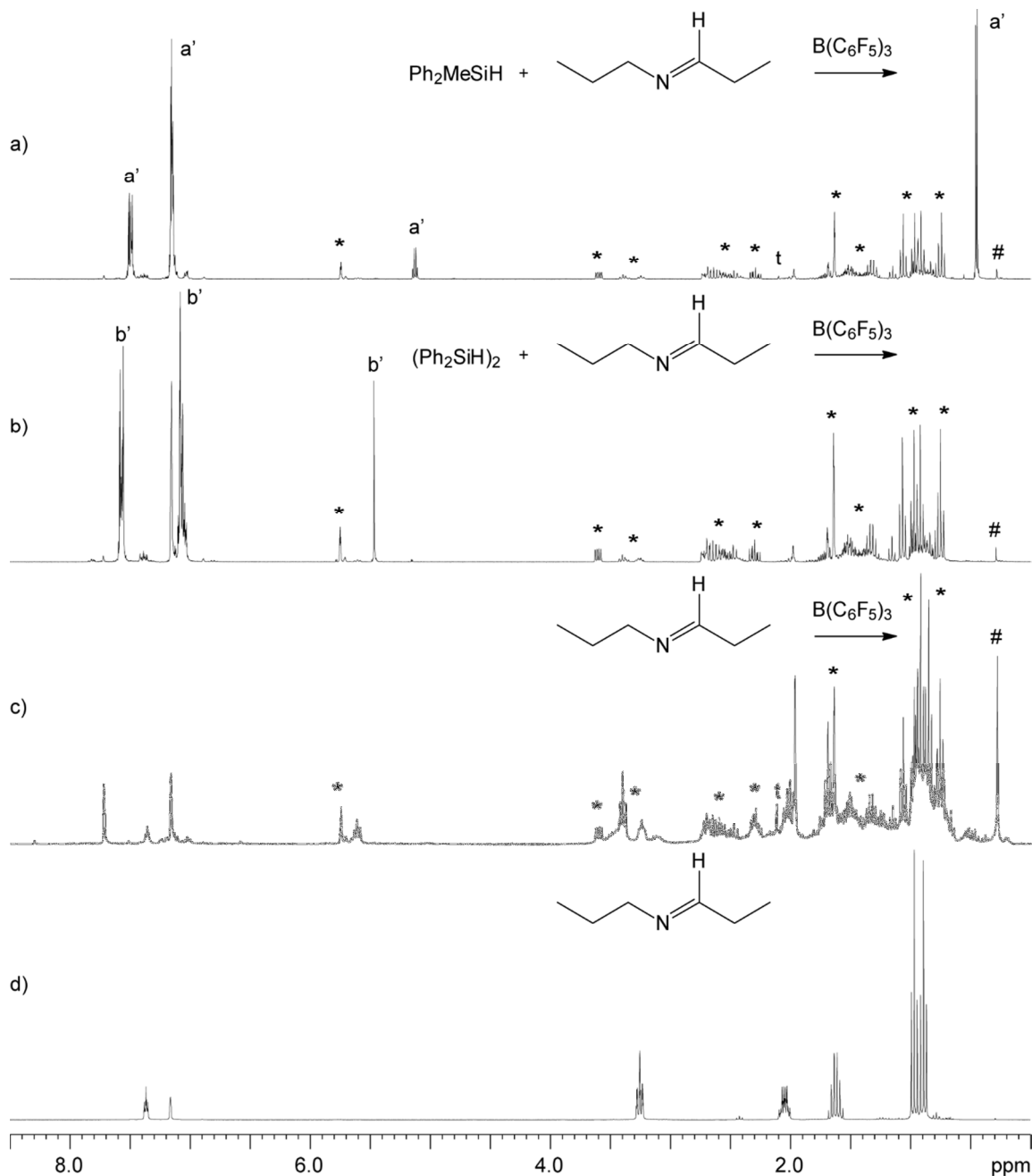
#### *Synthesis of n-propylidene-n-propylamine:*

Synthesis of *n*-propylidene-*n*-propylamine was adapted from a literature preparation.<sup>71</sup> Propionaldehyde (14.5 mL, 11.7 g, 202 mmol) was added to a three-neck flask equipped with a stir bar, and the flask was cooled to 0 °C in an ice bath. The propionaldehyde was stirred and *n*-propylamine (16.5 mL, 11.9 g, 201 mmol) was added dropwise over 1.5 h. KOH (~10 pellets) was added and the mixture was cooled to -18 °C (freezer). After 24 h, the solution formed two layers and the top layer (organic, clear yellow liquid, crude *n*-propylidene-*n*-propylamine) was decanted by Pasteur pipette. The

crude product was purified by distillation with KOH (~5 g) as the drying agent to give a clear and colorless liquid (5.7 g, 29%).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.89 (t, 3H,  $^3J_{\text{HH}} = 7$  Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_3$ ), 0.92 (t, 3H,  $^3J_{\text{HH}} = 7$  Hz,  $\text{N}=\text{CHCH}_2\text{CH}_3$ ), 1.62 (sextet,  $^3J_{\text{HH}} = 7$  Hz,  $\text{NCH}_2\text{-CH}_2$ ), 2.05 (qt, 2H,  $^3J_{\text{HH}} = 4$  Hz,  $^4J_{\text{HH}} = ^5J_{\text{HH}} = 1$  Hz,  $\text{N}=\text{CH-CH}_2$ ), 3.25 (tq, 2H,  $^3J_{\text{HH}} = 7$  Hz,  $^4J_{\text{HH}} = 1$  Hz,  $\text{N-CH}_2$ ), 7.37 (tt, 1H,  $^3J_{\text{HH}} = 4$  Hz,  $^4J_{\text{HH}} = 1$  Hz,  $\text{H-C=N}$ ); DEPT135  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  10.1 ( $\text{NCH}_2\text{CH}_2\text{CH}_3$ ), 11.8 ( $\text{N}=\text{CHCH}_2\text{CH}_3$ ), 24.3 ( $\text{NCH}_2\text{-CH}_2$ ), 29.0 ( $\text{NCH}_2\text{-CH}_2$ ), 63.3 ( $\text{N-CH}_2$ ), 163.7 ( $\text{C=N}$ ).

*Reaction of  $\text{Ph}_2\text{MeSiH}$  (2-1) or  $(\text{Ph}_2\text{SiH})_2$  (2-2) and *n*-propylidene-*n*-propylamine:*

This procedure is representative for the reaction of  $\text{Ph}_2\text{MeSiH}$  (2-1) or  $(\text{Ph}_2\text{SiH})_2$  (2-2). In a Schlenk flask equipped with a stir bar, 2-2 (0.10 g, 0.27 mmol) and *n*-propylidene-*n*-propylamine (0.10 mL, 0.75 mmol) were combined with toluene (1 mL).  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.014 g, 0.027 mmol) was added and the mixture turned slightly cloudy. The mixture was stirred at RT. After 16 h,  $\text{PPh}_3$  (0.007 g, 0.03 mmol) was added and the mixture was stirred for 1 min. Volatiles were removed by evacuation leaving a white solid. The solid mixture was dissolved in pentane (1 mL) and eluted through a Florisil column. Pentane (1 mL) was used to wash the Florisil column and this process was repeated four times to collect a clear and colorless eluent. Volatiles were removed by evacuation to give a cloudy white oil. An aliquot was removed for  $^1\text{H}$  NMR (Figure 2.23b). The NMR spectra for the reaction of  $(\text{Ph}_2\text{SiH})_2$  and  $\text{Ph}_2\text{MeSiH}$  both show a lack of consumption of the silane and the conversion of *n*-propylidene-*n*-propylamine to unidentified products (\*) (Figure 2.23a/b). These similar “\*” signals suggest a reaction between *n*-propylidene-*n*-propylamine and  $\text{B}(\text{C}_6\text{F}_5)_3$  is occurring independent of the added silane.



**Figure 2.23.**  $^1\text{H}$  NMR (300 MHz) of a) crude reaction mixture of  $\text{Ph}_2\text{MeSiH}$ , *n*-propylidene-*n*-propylamine, and catalyst  $\text{B}(\text{C}_6\text{F}_5)_3$ , b) crude reaction mixture of  $(\text{Ph}_2\text{SiH})_2$ , *n*-propylidene-*n*-propylamine, and catalyst  $\text{B}(\text{C}_6\text{F}_5)_3$  showing no consumption of silane  $\text{Ph}_2\text{MeSiH}$  or  $(\text{Ph}_2\text{SiH})_2$  and similarity in product signals \*, likely coming from c) *n*-propylidene-*n*-propylamine- $\text{B}(\text{C}_6\text{F}_5)_3$  adduct and/or reaction of *n*-propylidene-*n*-propylamine with  $\text{B}(\text{C}_6\text{F}_5)_3$ , and d) *n*-propylidene-*n*-propylamine in  $\text{C}_6\text{D}_6$ . The  $\text{a}'$  and  $\text{b}'$  are signals for  $\text{Ph}_2\text{MeSiH}$  and  $(\text{Ph}_2\text{SiH})_2$  respectively. The “#” is residual grease. The “t” is toluene.

### 3 Over-reduction of silanes catalyzed by $\text{B}(\text{C}_6\text{F}_5)_3$

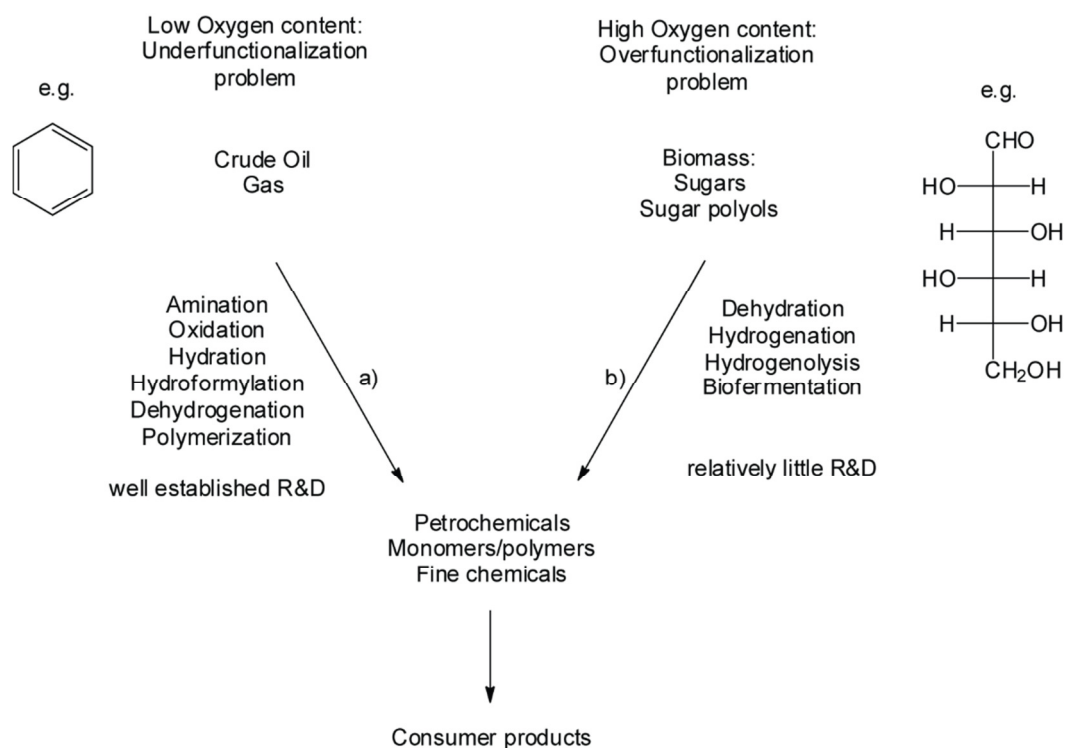
**Note:** Some of this material has been published in “Borane-Catalyzed Si-H Activation Routes to Polysilanes Containing Thiolato Side Chains”, Lee, P. T. K.; Skjel, M. K.; Rosenberg, L. *Organometallics* 2013, 32, 1575-1578. Copyright 2013 American Chemical Society (adapted with permission). Some of the experiments in Section 3.12.2 were done by former Rosenberg group member Dan Harrison.

#### 3.1 Introduction

##### 3.1.1 Reasons to study reduction

Resources from the petrochemical industry have had a major impact on the world. A major source of energy is derived from crude oil supplies. Beyond that and more directly important to the chemical industry is the synthesis and development of chemical building blocks. These molecules, derived from hydrocarbons containing only C and H atoms, must first be functionalized to add a useful functional group, such as an oxygen-containing alcohol (OH), before they can be used as chemical building blocks or for further functional group transformations (Figure 3.1a). With increasing energy and consumer demands, new sources of chemical building blocks must be found to ensure an adequate supply. An opposite and alternative approach to such chemicals is from C/H/O-containing biomass molecules (Figure 3.1b), where a deoxygenation, defunctionalisation, or reduction reaction is required to simplify the molecule to contain fewer, manageable functional groups.<sup>28a,72</sup> Some chemical building blocks already come from reduction routes. Biomass molecules such as glycerol (three carbon chain/C3), erythritol (C4), xylitol (C5), and glucitol/sorbitol (C6) come from important reduction/deoxygenation

pathways.<sup>28a</sup> The link between the non-functionalized crude oil products and the highly functionalized biomass molecules (Figure 3.1b) has not yet been bridged. It is thus a challenge to selectively reduce biomass molecules, such as the C3-C6 molecules described above, into important chemical building blocks that resemble hydrocarbon-like functionalized molecules.



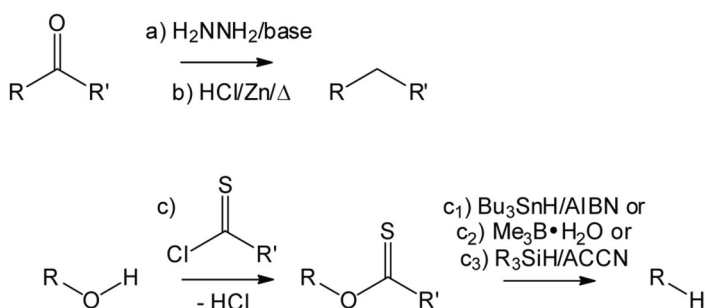
**Figure 3.1.** Production of fine chemicals from either crude-oil-based or biomass building blocks.

Hydrogenation is the preferred method for defunctionalizing oxygen-containing molecules to form saturated hydrocarbons based on cost and atom economy.<sup>73,xviii</sup>

<sup>xviii</sup> If the starting substrate is an alcohol, removal of the OH group requires first a dehydration to give an olefin, followed by a hydrogenation to give the saturated alkane. If the starting substrate contains a carbonyl (aldehyde or ketone), this involves first a hydrogenation to give an alcohol (OH) and then the above reactions to give the deoxygenated product. Even though dehydration is a required step, the overall process is often simply referred to as a hydrogenation.

However, hydrogenation has some limitations and challenges: flammability of H<sub>2</sub> gas, necessity of specialized equipment to handle H<sub>2</sub>, and non-reactivity with some O-containing functional groups, such as carboxylic acids, esters, and amides.<sup>74</sup> Other methods to deoxygenate O-containing molecules are common in the laboratory: two commonly cited methods are the Barton-McCombie deoxygenation of alcohols (Scheme 3.1c),<sup>28b,75</sup> and the Wolff-Kishner/Clemmensen (Scheme 3.1a/b) reduction of carbonyls.<sup>76</sup> A number of problems inhibit their large-scale application including low atom-economy, harsh reaction conditions, and lack of generality of the reaction.

**Scheme 3.1.**

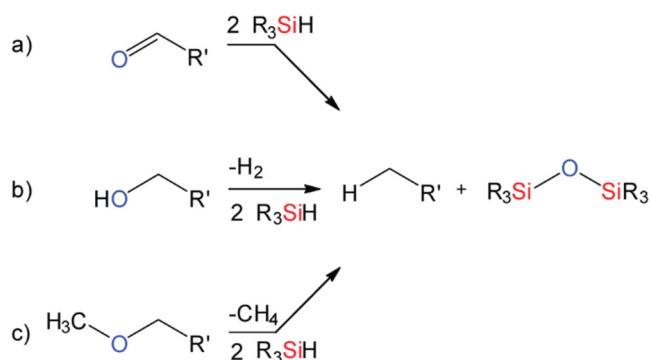


### 3.1.2 Reductions with hydrosilanes

An increasingly attractive and studied method for deoxygenation suitable for the laboratory scale involves using hydrosilanes as reducing agents (Scheme 3.2). The reaction is driven by the formation of a strong disiloxane bond, Si-O-Si<sup>4b</sup> and is applicable to a wide variety of functional groups: alcohol/ether deoxygenation,<sup>26a,77</sup> ketone/aldehyde/carbonyl deoxygenation,<sup>27a,63,78</sup> acid/ester/amide deoxygenation,<sup>27b,29a,b,e,79</sup> CO<sub>2</sub> reduction,<sup>30b,c,30f-h,80</sup> and there are some related desulfurizations reactions.<sup>81</sup> The “over-reduction” of alcohols, ethers, ketones/aldehydes, and carboxylic acids/esters to saturated hydrocarbons with hydrosilanes can be catalyzed

by  $\text{B}(\text{C}_6\text{F}_5)_3$ . These reactions have been shown to proceed under mild conditions (mostly occurring at RT) and to be applicable to a wide array of O-containing functional groups.<sup>2,27a,60,82</sup> The over-reduction process catalyzed by  $\text{B}(\text{C}_6\text{F}_5)_3$  has been investigated in some detail in the contexts of (i) avoiding over-reduction in the pursuit of partially-reduced organic substrates,<sup>79b</sup> (ii) deliberately defunctionalizing organic substrates by removing oxygen in the form of disiloxanes,<sup>2,28c,77a,83</sup> and (iii) building macromolecular structures based on repeat Si-O-Si units by facile removal of straight-chain alkanes.<sup>26b,33c,58,77b</sup>

**Scheme 3.2.**



These  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed examples of over-reduction are part of a larger resurgence of interest in the use of catalytic reactions of silanes, especially those catalyzed by transition metals, to defunctionalize oxygen-rich substrates.<sup>xix</sup> Studies include a number of transition metal systems that catalyze, for example, the over-reduction of C=O in carboxylic acid derivatives, such as esters or amides, to  $\text{CH}_3$  or  $\text{CH}_2$  using silanes.<sup>29e,79g,j,85</sup> These mild catalytic reactions provide useful functional group transformations. Metal-mediated over-reduction of  $\text{CO}_2$  to methane by silanes has found increasing prominence in the literature.<sup>30b,c,30f-h,80a</sup> The utility of this chemistry in

<sup>xix</sup> Transition-metal catalyzed over-reduction with silanes has been reviewed recently.<sup>27b,84</sup>

defunctionalizing organic substrates typically overshadows interest in the Si-O-Si by-product; their formation is implicit and is rarely described in detail. A notable exception is an in-depth study of the transition metal-catalyzed over-reduction of DMF with Et<sub>3</sub>SiH to give Me<sub>3</sub>N and Et<sub>3</sub>SiOSiEt<sub>3</sub>.<sup>79i-k</sup>

### 3.1.3 Overview

In this chapter, the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed over-reduction of substrates leading to silane intermediates containing straight-chain alkoxy or S/O-benzylic substrates, is reported. The parameters affecting the tendency for partial versus over-reduction (e.g. bulk of silyl and substrate groups) were investigated in detail. The discovery of the over-reduction of S-containing substrates was exploited to synthesize new and interesting Si-S-Si-containing dimers and polymers. These over-reduction reactions have been reported in detail for E = O, but are completely novel for E = S using B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>xx</sup> and rare in general among transition-metal catalyzed reactions<sup>81</sup>. Possible reaction mechanisms that would account for the facile over-reduction of benzylic substrates are discussed.

## 3.2 Sensitivity of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed reductions to the steric bulk of the silane

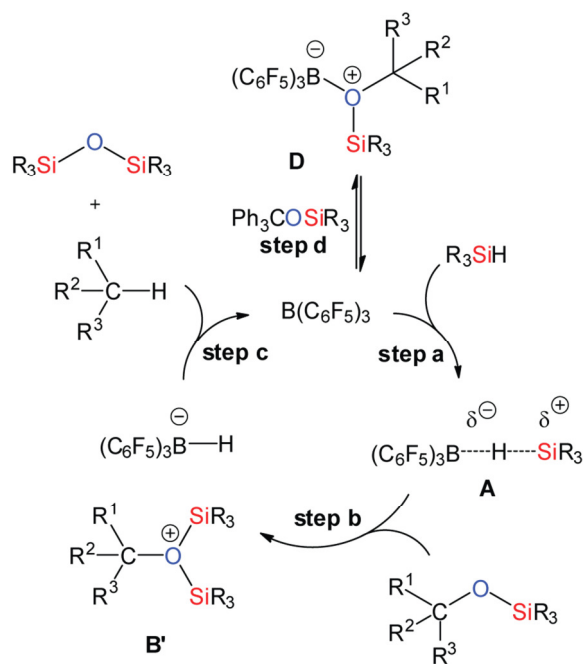
This focus on the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed over-reduction reactions of hydrosilanes stems from ongoing studies of partial reduction reactions described in Chapter 2. Substrate-screening reactions using the monosilane Ph<sub>2</sub>MeSiH showed an issue of selectivity in these reactions: the steric properties of the substrate the relative amounts of partial and over-reduction that occurs. For example, ketones such as cyclohexanone react

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<sup>xx</sup> Similar results were published by other researchers (Saito, K.; Kondo, K.; Akiyama, T. *Organic Letters* **2015**, *17*, 3366. Publication date (Web): June 23, 2015)<sup>86</sup> during the final revisions of this thesis.

with the silane to give exclusively the branched “partial reduction” products via hydrosilation ( $\text{Ph}_2\text{MeSiOC}_6\text{H}_{11}$  (**2-6**)), while the linear propionaldehyde gives a mixture of partial- and over-reduction products (**2-3** and **2-4**) under comparable conditions. For propionaldehyde, the partial reduction product,  $\text{Ph}_2\text{MeSiOCH}_2\text{CH}_2\text{CH}_3$  (**2-3**), is less bulky, enabling it to react with a second equivalent of silane in the presence of  $\text{B}(\text{C}_6\text{F}_5)_3$  catalyst to release propane and form the disiloxane,  $\text{Ph}_2\text{MeSi-O-SiMePh}_2$  (**2-4**).

This relationship between the degree of branching in the alkoxy silane partial reduction products and the tendency for over-reduction to compete with partial reduction has been identified previously. Gevorgyan and Yamamoto’s studies on the use of  $\text{Et}_3\text{SiH}$  to over-reduce alcohols and ethers to alkanes showed the fastest rates and highest yields for linear substrates yielding primary C-H bonds, while branched substrates reacted more slowly.<sup>2,27a,28c,63</sup> These results can be rationalized in the context of a mechanism for over-reduction that parallels the generally-accepted mechanism(s) for carbonyl hydrosilation, dehydrocoupling, and demethanative coupling as proposed by Piers and Oestreich.<sup>42a,b,d,e</sup> In Scheme 3.3 the mechanism has been redrawn for the particular case of over-reduction, to highlight the details of **step b**, in which an alkoxy silane (resulting from any of a number of “partial reduction” reactions of the silane) plays the role of the nucleophile. Gevorgyan and Yamamoto invoke the reversible formation of  $\text{R}_3\text{Si}\cdots\text{H}\cdots\text{B}(\text{C}_6\text{F}_5)_3$  (**A**, **step a**) and the bulk of the alkoxy silane nucleophile (**step b**) to rationalize their observed selectivity.

**Scheme 3.3.** Over-reduction mechanism 1.

The rate of the over-reduction reaction should be sensitive to the size of the alkyl group that is eliminated and also to the size of the silyl group(s) involved in the reaction. In fact, the steric influence of  $-\text{SiR}_3$  should be a compounding issue in the rates of over-reduction reactions, since it affects both access of the nucleophile to the electrophilic silylium centre in **A** (Scheme 3.3) and the bulk of the incoming nucleophilic silyl ether (**step b**, Scheme 3.3). If the silane is very bulky, it can effectively prohibit both partial reduction *and* over-reduction, apparently by preventing the formation of  $\text{R}_3\text{Si} \cdots \text{H} \cdots \text{B}(\text{C}_6\text{F}_5)_3$  (**A**). For example, Piers showed that  ${}^i\text{Pr}_3\text{SiH}$ , a bulky silane with a Tolman cone angle of  $160^\circ$  (Table 3.1), does not participate in  $\text{B}(\text{C}_6\text{F}_5)_3$ -mediated reactions with any organic substrates.<sup>42b</sup> A former student in the Rosenberg group, Dan Harrison, found the same to be true for the extremely bulky  $({}^i\text{Pr}_2\text{SiH})_2$ .<sup>1b,c</sup> Piers has attributed this non-reactivity to the “front strain” provided by the bulky isopropyl groups, which prevents the approach of  $\text{B}(\text{C}_6\text{F}_5)_3$  to make **A**.<sup>42b</sup> A recent study assessing suitable

conditions for the  $B(C_6F_5)_3$ -catalyzed reduction of carboxylic acids to aldehydes found that bulkier silanes ( $Ph_3SiH$ ,  $Et_3SiH$ ; see Table 3.1 for a ranking of the relative bulk of some common silanes) resulted in more of the desired partial reduction products, while less hindered sources of Si-H bonds ( $Et_2SiH_2$ , 1,1,2,2-tetramethyldisiloxane (TMDS), and the polymeric poly(methylhydrosiloxane) (PMHS)) gave more over-reduction products.<sup>79h</sup> Another study found that the complete deoxygenation of glucose (five branched (secondary) OH groups, one unbranched (primary) OH group) could be effected via  $B(C_6F_5)_3$ -mediated over-reduction with  $Et_2SiH_2$ .<sup>77a</sup> The same authors have recently showed that moving to non-bulky tertiary silanes can actually allow useful chemoselectivity in these reductions for primary vs. secondary -OH sites in the substrate sugars.<sup>83</sup> Other examples of using smaller silanes to affect the  $B(C_6F_5)_3$ -catalyzed over-reduction of oxygen-containing substrates include the over-reduction of  $R-OSiMe_2Ph$  ( $R = 2-(SiMe_2Ph)C_6H_{10}$ ) by  $PhMe_2SiH$  to give  $2-(SiMe_2Ph)C_6H_{11}$  and  $(PhMe_2Si)_2O$ ,<sup>82,xxi</sup> and the over-reduction by PMHS of ketones<sup>78a</sup> that were only partially reduced by the bulkier  $Et_3SiH$ .<sup>2,27a,28c,63</sup> The combined effect of the silyl and alkyl group size on the propensity for over-reduction is depicted and summarized in Figure 3.2.

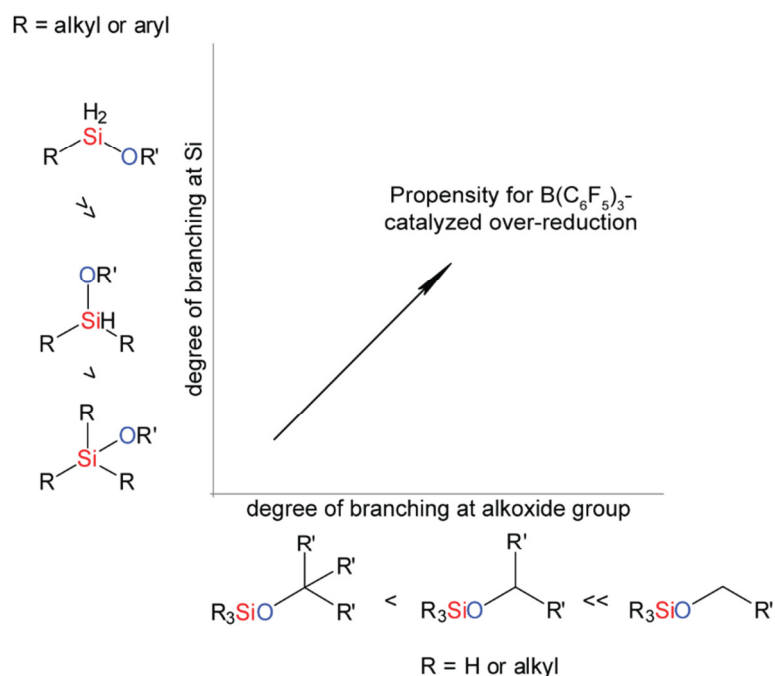
**Table 3.1.** Estimated cone angles for silanes,  $R_3Si-H$ , based on established phosphine cone angles  $R_3P-M$ .<sup>87</sup>

Entry	Silane, $R_3Si-H$	Tolman cone angle ( $^\circ$ )
1	$BuSiH_3^a$	$92^\circ$
2	$PhSiH_3$	$101^\circ$
3	$Et_2SiH_2^b$	$117^\circ$
4	$Me_2PhSiH$	$122^\circ$

<sup>xxi</sup> This reaction did not proceed when  $Ph_3SiH$  was used as the reductant.<sup>21</sup>

5	Ph <sub>2</sub> SiH <sub>2</sub>	128°
6	Et <sub>3</sub> SiH/Bu <sub>3</sub> SiH	132°
7	Ph <sub>2</sub> MeSiH	136°
8	Ph <sub>3</sub> SiH	145°
9	<sup>i</sup> Pr <sub>3</sub> SiH	160°

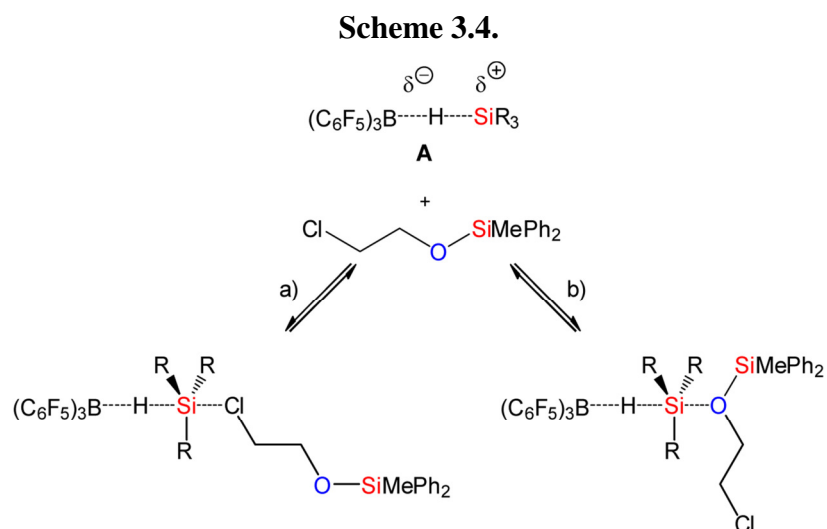
<sup>a</sup>Estimate based on a linear extrapolation of the ratio of the published cone angles of the relevant tertiary phosphines, PBu<sub>3</sub>/PPh<sub>3</sub> to the ratio of angles of primary phosphines PH<sub>2</sub>Bu(unknown)/PH<sub>2</sub>Ph(known). <sup>b</sup>Estimate based on weighted average of those for PH<sub>3</sub> (1/3) and PEt<sub>3</sub> (2/3).



**Figure 3.2.** Relationship of the size of silyl group (y-axis) and alkyl group (x-axis) in its propensity for B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed over-reduction.

Interestingly, the demethanative coupling of Ph<sub>2</sub>MeSiH (**2-1**) or disilane (**2-2**, (Ph<sub>2</sub>SiH)<sub>2</sub>) with CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>Cl did not lead to over-reduction products, yet similar conditions used to make Ph<sub>2</sub>MeSiOCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (**2-3**) gave minor over-reduction product (Ph<sub>2</sub>MeSi)<sub>2</sub>O (**2-4**) (24% estimated by <sup>1</sup>H NMR integration, see experimental Section 2.6.1, Figure 2.2). Partial reduction products Ph<sub>2</sub>MeSiOCH<sub>2</sub>CH<sub>2</sub>Cl (**2-9**) and

Ph<sub>2</sub>MeSiOCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (**2-3**) have comparable steric bulk (size difference of a chloride versus a methyl is inconsequential). Nucleophilic attack of the alkoxy silane, ClCH<sub>2</sub>CH<sub>2</sub>OSiR<sub>3</sub>, at (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B<sup>δ-</sup>•••H<sup>δ+</sup>•••SiR<sub>3</sub> (**A** in Scheme 3.3) is expected to proceed similarly to CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OSiR<sub>3</sub> because they are both primary alkoxy groups. The chloro substituent may interact with Si<sup>δ+</sup>: a defined model for the interaction of a chloro substituent with R<sub>3</sub>Si<sup>δ+</sup>•••H<sup>δ-</sup>•••B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> has not yet been formalized in the literature, but Oestreich suggests a solvent-X<sup>δ-</sup>•••Si<sup>δ+</sup> interaction (X = F, Cl) may be present in B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed reactions of a chiral silane with imines.<sup>67</sup> It is uncertain how “Cl” in **2-9** behaves in the reaction mechanism to dissuade over-reduction, but one possibility is that Cl competitively binds to silicon in (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B<sup>δ-</sup>•••H<sup>δ+</sup>•••SiR<sub>3</sub> (Scheme 3.4a), therefore limiting the “O” in **2-9** to attack silane-borane complex (Scheme 3.4b).



Reactions of disilane **2-2** with propionaldehyde or 2-chloroethyl methyl ether showed a greater disparity in their tendency to give over-reduction products. Partial and over-reduction reactions were evident in the reaction of disilane **2-2** with propionaldehyde. The reaction of disilane **2-2** with 2-chloroethyl methyl ether gave

exclusively the partial reduction product, **2-22**; this result suggests that conditions were found serendipitously that gave the product without competing over-reduction reactions. Although full optimization has not yet been pursued for some of these reactions with propionaldehyde, a systematic analysis of reaction conditions, including catalyst loading, temperature and reaction time, may enable the isolation of the following molecules, free of over-reduction products:  $\text{Ph}_2\text{MeSiOCH}_2\text{CH}_2\text{CH}_3$  (**2-3**); the monosubstituted disilane  $\text{Ph}_2\text{SiH-Si(OCH}_2\text{CH}_2\text{CH}_3)\text{Ph}_2$ ; and the disubstituted disilane,  $(\text{Ph}_2\text{SiOCH}_2\text{CH}_2\text{CH}_3)_2$ .

### 3.3 Facile over-reduction reactions with $\text{PhSiH}_3$ and $\text{Ph}_2\text{SiH}_2$

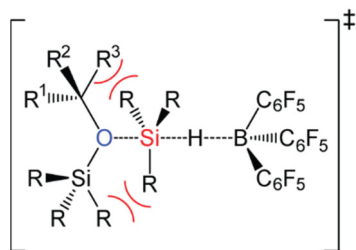
Further investigations found that the size of the silane has a strong influence on the propensity for over-reduction of oxygen-containing substrates. These substrates showed no tendency for over-reduction with the bulkier tertiary silane,  $\text{Et}_3\text{SiH}$ .<sup>2,27a,28c,63</sup> Screening reactions of some branched and aryl oxygen-containing substrates with the secondary silane,  $\text{Ph}_2\text{SiH}_2$ , or the primary silane,  $\text{PhSiH}_3$ , were undertaken to assess the ease of over-reduction.  $\text{PhSiH}_3$  is smaller than  $\text{Et}_2\text{SiH}_2$ , whereas  $\text{Ph}_2\text{SiH}_2$  is bigger than  $\text{Et}_2\text{SiH}_2$  but smaller than  $\text{Et}_3\text{SiH}$  (Table 3.1). A similar study of  $\text{B(C}_6\text{F}_5)_3$ -catalyzed over-reduction reactions with silanes has been reported in the literature, in which *n*-butylsilane (*n*- $\text{BuSiH}_3$ ) or diethylsilane ( $\text{Et}_2\text{SiH}_2$ ) were used to reduce a wide variety of oxygen-containing substrates: primary, secondary, and tertiary alcohols, methyl aryl ethers, phenols, aldehydes, ketones, and carboxylic acids.<sup>88</sup> This study found increasing likelihood for over-reduction with less bulky *n*- $\text{BuSiH}_3$  compared to  $\text{Et}_2\text{SiH}_2$ . Substrates that gave exclusive partial reductions products with  $\text{Et}_3\text{SiH}$  as the reductant<sup>2,27a,28c,63</sup>

could be over-reduced with moderate to high conversions with  $\text{Et}_2\text{SiH}_2$  or  $n\text{-BuSiH}_3$ , respectively.<sup>88,xxii</sup>

In these studies, reactions of  $\text{Ph}_2\text{SiH}_2$  or  $\text{PhSiH}_3$  gave results that are consistent with the above mentioned report of over-reduction using smaller silanes. Unlike McRae's study,<sup>88</sup> the Si-containing products were identified as well as the alkanes produced; these are shown in Table 3.2 and in Section 3.4. For branched alkyl substrates derived from acetone (entry 1), cyclohexanone (entry 3), and *t*-butanol (entry 5), reactions of  $\text{Ph}_2\text{SiH}_2$  showed minor amounts of over-reduction products within minutes; in contrast,  $\text{Et}_3\text{SiH}$  was reported to give exclusively partial reduction products for comparably-sized substrates in the presence of  $\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>2,27a,28c,63</sup> The reactions of the same three bulky substrates (Table 3.2, entries 2, 4, and 6) with  $\text{PhSiH}_3$  resulted in complete consumption of the substrate within minutes (see Figure 3.4 for  $^1\text{H}$  NMR example) to yield mostly over-reduction products (e.g. Table 3.2, 100% in entry 4) along with minor amounts of partial reduction products (e.g. Table 3.2, < 20% in entry 2). The increasing ease of over-reduction with diminishing size of the silane reductant ( $\text{Et}_3\text{SiH} < \text{Ph}_2\text{SiH}_2 < \text{Et}_2\text{SiH}_2 < \text{PhSiH}_3 < n\text{-BuSiH}_3$ ), to allow the participation even of substrates that give very bulky alkoxy silane partial reduction products, further demonstrates the likely importance of the transition state shown in Figure 3.3.


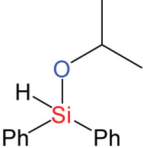
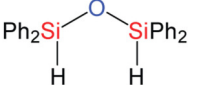
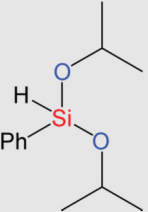
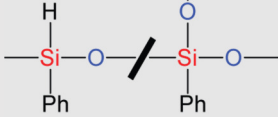
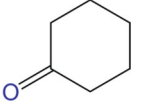
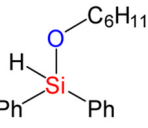
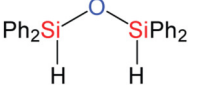
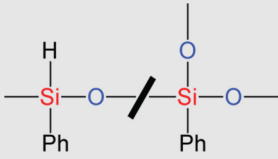
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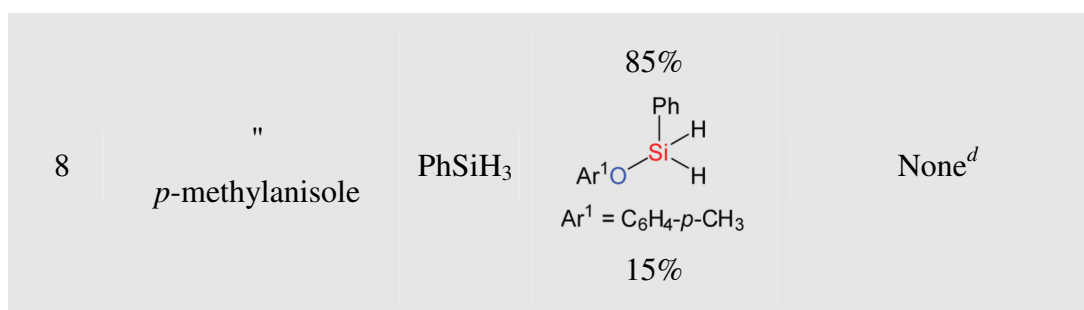
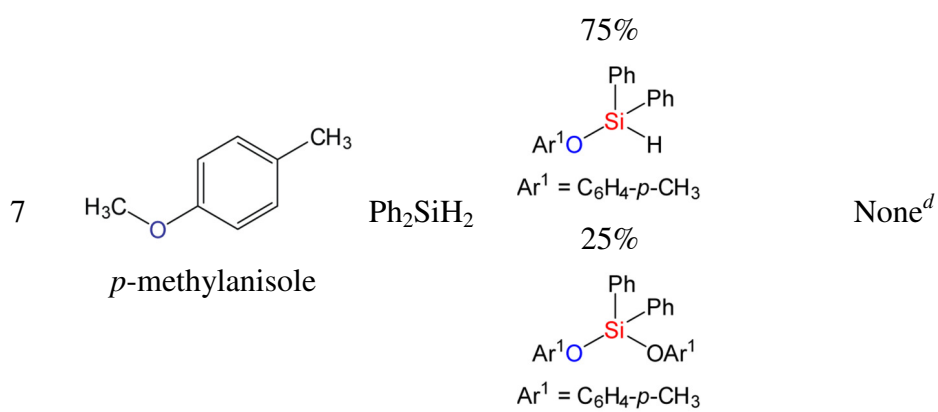
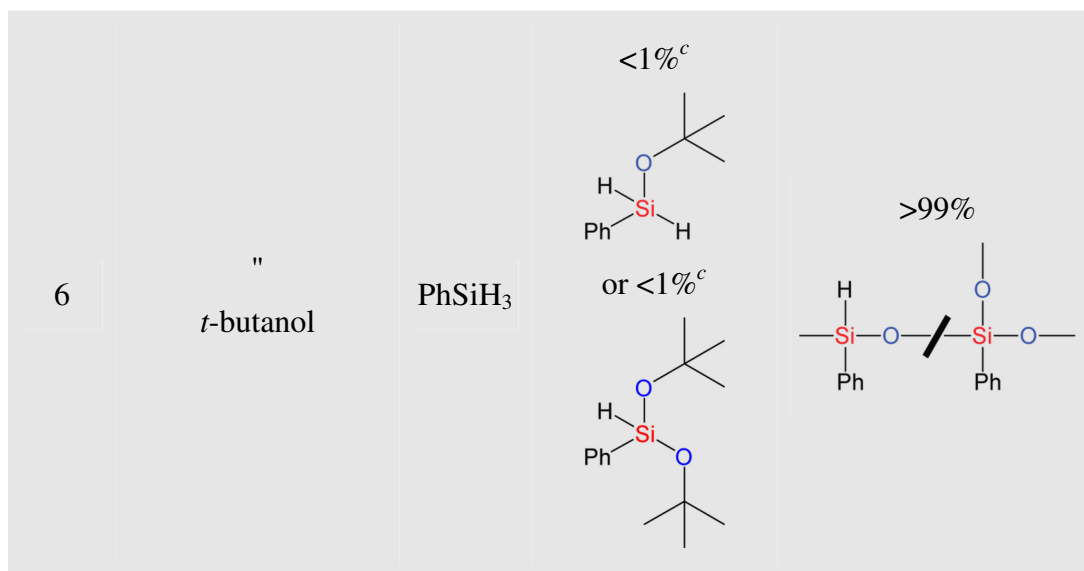
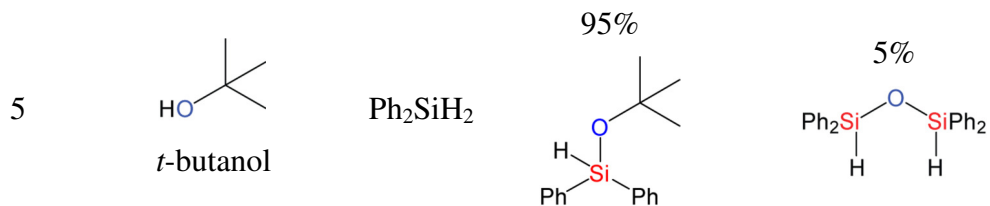
<sup>xxii</sup> Some interesting selectivity was reported in reactions of  $n\text{-BuSiH}_3$  or  $\text{Et}_2\text{SiH}_2$  with  $\alpha,\beta$ -unsaturated ketones. These reductions gave products where only the  $\text{C}=\text{O}$  is reduced to a  $\text{CH}_2$  and the olefin is unchanged.<sup>88</sup> This is unlike other reported  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed partial reduction and over-reduction reactions of  $\alpha,\beta$ -unsaturated ketones and  $\text{PhMe}_2\text{SiH}$ , which found products consistent with 1,4-addition, then olefin hydrosilation, then over-reduction: the product retained a Si-C bond at C2.<sup>82</sup>

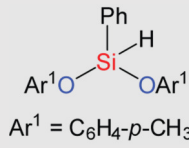
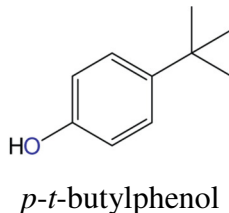
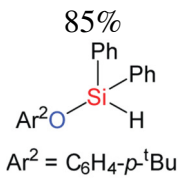
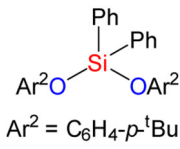
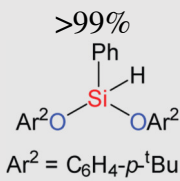


**Figure 3.3.** Influence of steric bulk in  $R_3SiH$  and  $R_3SiOCR^1R^2R^3$  on the nucleophilic addition step (Scheme 3.3, **step b**) in the proposed mechanism for over-reduction.

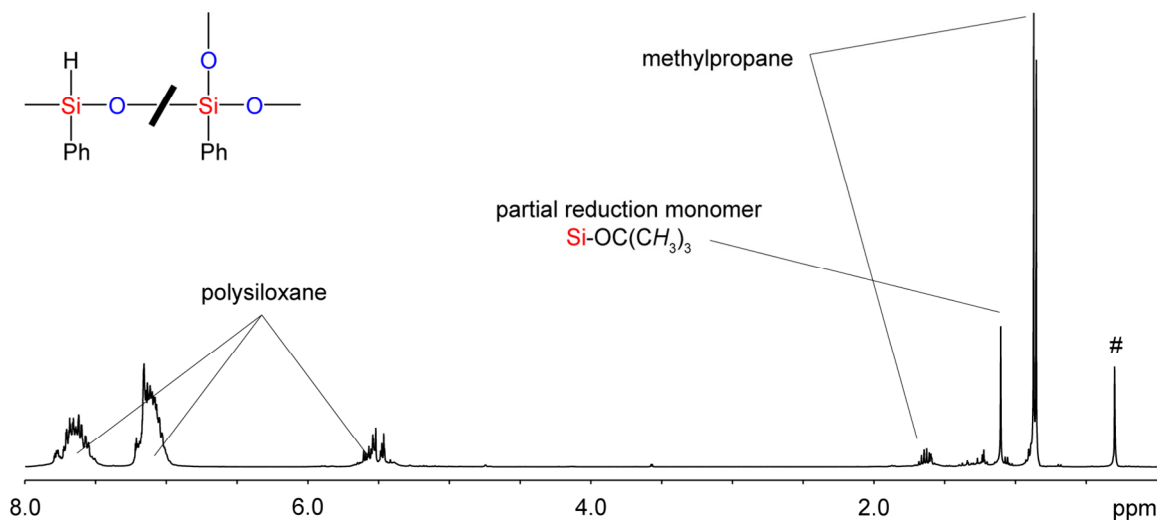
**Table 3.2.** Reactions of bulky O-containing substrates with smaller silanes  $Ph_2SiH_2$  and  $PhSiH_3$  to gauge susceptibility to over-reduction, as monitored by  $^1H$  NMR.<sup>a</sup>

Entry	Substrate <sup>b</sup>	Silane	Partial reduction <sup>b</sup>	Over-reduction <sup>b</sup>
1	 acetone	$Ph_2SiH_2$	<1% 	99% 
2	" acetone	$PhSiH_3$	5% 	95% 
3	 cyclohexanone	$Ph_2SiH_2$	70% 	30% 
4	" cyclohexanone	$PhSiH_3$		>99% 



			 $\text{Ar}^1 = \text{C}_6\text{H}_4\text{-}p\text{-CH}_3$	
9 <sup>e</sup>	 <i>p-t</i> -butylphenol	Ph <sub>2</sub> SiH <sub>2</sub>	85%  $\text{Ar}^2 = \text{C}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$ 15%  $\text{Ar}^2 = \text{C}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$	None
10 <sup>e</sup>	" <i>p-t</i> -butylphenol	PhSiH <sub>3</sub>	>99%  $\text{Ar}^2 = \text{C}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$	None

<sup>a</sup>Conditions: 10:1 silane:substrate; 5 mol% B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>; in C<sub>6</sub>D<sub>6</sub> unless otherwise noted; 5-15 min reaction time unless otherwise noted. <sup>b</sup>In all cases, the substrate was completely consumed in the presence of excess silane. Percentages are relative amounts of products based on <sup>1</sup>H NMR integrations. <sup>c</sup>Unable to determine if monosubstituted or disubstituted. <sup>d</sup>Methane produced, not toluene. <sup>e</sup>Reaction done in CDCl<sub>3</sub>.

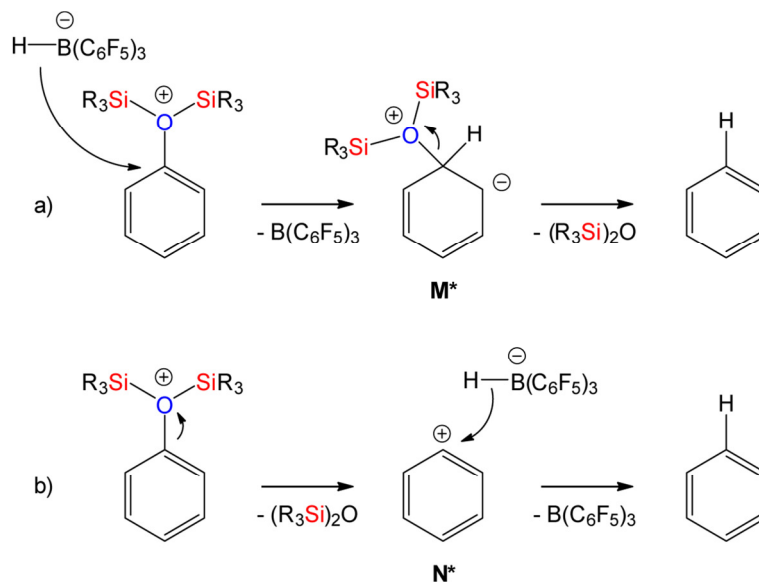


**Figure 3.4.** Representative  $^1\text{H}$  NMR (300 MHz) of the crude mixture from the reaction of phenylsilane ( $\text{PhSiH}_3$ ) with O-containing substrate (e.g. *t*-butanol) in  $\text{C}_6\text{D}_6$ . The “#” is grease.

As shown in entries 7-10 in Table 3.2, the aryl alcohol and aryl methyl ether substrates give exclusively partial reduction products in these screening reactions. The bulk of the aryl group is arguably less than that of the bulkiest alkyl groups examined, which suggests that over-reduction should occur. However, even reactions of *p*-*t*-butylphenol or *p*-methylanisole with  $\text{PhSiH}_3$  did not produce alkylbenzenes, nor by  $\text{Et}_3\text{SiH}$ ,<sup>2,28c</sup>  $\text{Et}_2\text{SiH}_2$  or *n*- $\text{BuSiH}_3$ .<sup>88</sup> This result can be explained by evaluating the requisite nucleophilic substitution step shown in Scheme 3.3, **step c**, which is similar to nucleophilic aromatic substitution: the two commonly acknowledged mechanisms for nucleophilic aromatic substitution are the  $\text{S}_{\text{N}}\text{Ar}$  or  $\text{S}_{\text{N}}1$  mechanism (Scheme 3.5a or b, respectively).<sup>89</sup> In the  $\text{S}_{\text{N}}\text{Ar}$  mechanism, the nucleophile,  $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ , must attack the aryl ring; yet the hydride is a poor nucleophile and it is thus unfavourable to make the addition intermediate  $\mathbf{M}^*$  in Scheme 3.5a, particularly without an electron withdrawing group on the aryl ring. In the  $\text{S}_{\text{N}}1$  mechanism, elimination of the disiloxane product requires the development of at least a partial positive charge at the  $\text{sp}^2$  carbon bound to

the oxygen in  $N^*$  (Scheme 3.5b), which then becomes the site of hydride delivery from the  $[HB(C_6F_5)_3]^-$  counterion. Relative to  $sp^3$ -hybridized alkyl carbons, aryl carbons are notoriously poor at bearing such positive charge due to their participation in delocalized  $\pi$ -bonding.

**Scheme 3.5.**

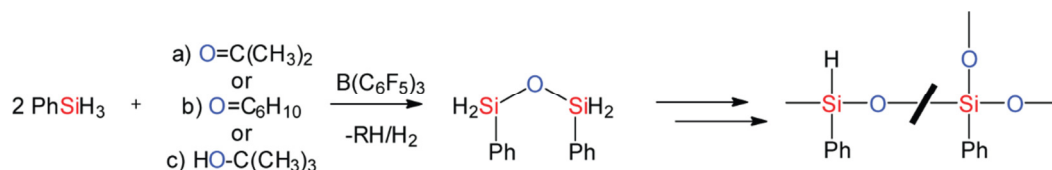


### 3.4 Over-reduction leads to polysiloxane by-products

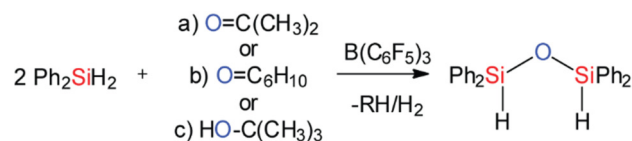
The reactivity of multiple Si-H bonds in  $PhSiH_3$  can lead to complex over-reduction product mixtures.  $^1H$  NMR spectra of these reaction mixtures showed broad aromatic and Si-H signals consistent with the presence of relatively long polysiloxane chains containing both Si-Ph and Si-H groups in the repeat unit (see  $^1H$  NMR spectrum Figure 3.4 above). The presence of the Si-H bond in the repeat unit likely also leads to the introduction of additional side-groups (i.e. H replaced with OR), branching, and cross-linking. Conclusive diagnoses of these structural features were challenging because of the complexity of the NMR spectra. Some sharp signals correspond to some simple partial reduction products or discrete short-chain oligomers, such as  $(PhSiH_2)_2O^{90}$

(Equation 3.1); these are either low intensity or overlapping with broad peaks, precluding assignments. The screening reactions of the bulkier  $\text{Ph}_2\text{SiH}_2$  shown in Equation 3.2 largely halted at the partial reduction products, giving only trace amounts of the disiloxane,  $(\text{Ph}_2\text{SiH})_2\text{O}$ ,<sup>91</sup> although presumably under more forcing conditions further reaction of the tertiary Si-H bonds in this compound could allow the preparation of longer siloxane chains or cyclic oligomers. Rubinsztajn has effectively exploited similar over-reduction chemistry (Equation 3.3) to make more defined, linear, polysiloxane structures using the O-containing substrate  $\text{Ph}_2\text{Si}(\text{OCH}_3)_2$  and the rigid silane reagent  $\text{HSiMe}_2\text{-C}_6\text{H}_4\text{-p-SiMe}_2\text{H}$ , with two *para*-disposed, reasonably unhindered Si-H bonds (comparable in steric bulk to  $\text{PhMe}_2\text{SiH}$  ( $122^\circ$ , Table 3.1)) as condensation monomers.<sup>34b,58,92</sup>

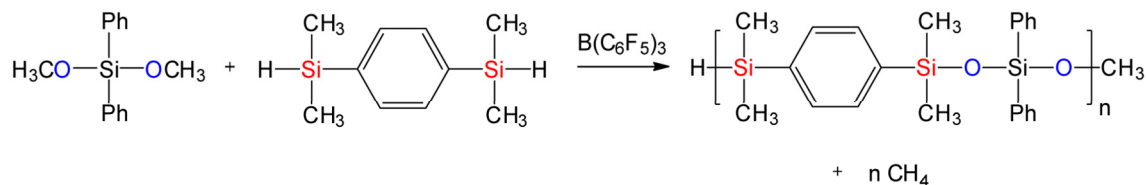
Equation 3.1



Equation 3.2

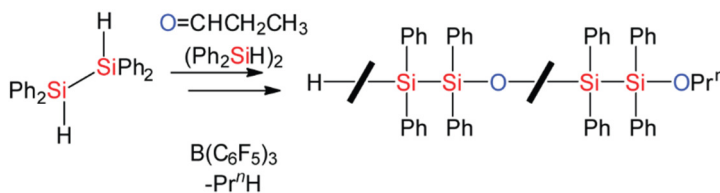


Equation 3.3



Interestingly, as mentioned above, over-reduction of some substrates with reducing agent disilane **2-2** gives structurally unique Si-Si-O-oligomers. This was diagnosed by broadened signals for the Si-Ph, Si-H, and Si-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> groups in the <sup>1</sup>H NMR (see experimental Section 3.12.2, Figure 3.11), which indicated multiple iterations of intermolecular over-reduction reactions giving a mixture of oligomeric products (Scheme 3.6). The degree of oligomerization obtained in this mixture has not yet been determined, but a generic “disilane-siloxane” structure (Scheme 3.6) would include Si-Si-O repeat units with H and/or O<sup>n</sup>Pr end-groups. The mixture could also contain products resulting from “backbiting”: cyclic oligomerization that can form eight- or ten-membered rings, by analogy to the favoured D4 or D5 rings known in siloxane chemistry.<sup>93</sup>

Scheme 3.6

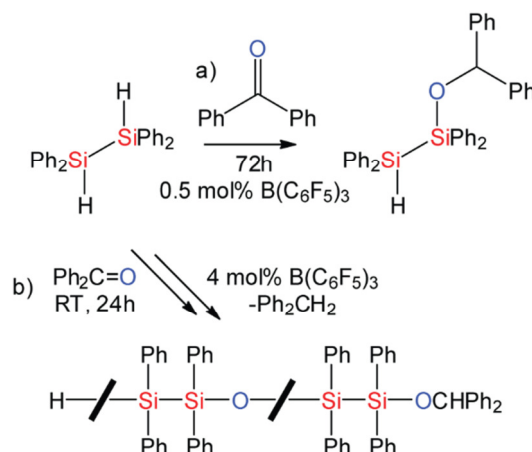


### 3.5 Over-reduction of benzylic oxygen-containing substrates.

B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed over-reduction of benzophenone to diphenylmethane occurs at RT even with the bulky reductant disilane **2-2**. Initial efforts to make the monosubstituted disilane Ph<sub>2</sub>SiH-Si(OCHPh<sub>2</sub>)Ph<sub>2</sub> (**3-1**, Scheme 3.7a), using comparable conditions to other B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed functionalization reactions of the disilane (see Chapter 2), gave reaction mixtures that showed sharp <sup>1</sup>H NMR signals for the over-reduction product Ph<sub>2</sub>CH<sub>2</sub> and broad signals for Si-Ph (see experimental Section 3.12.2, Figure 3.10) indicating the probable oligomerization of the disilane fragment to one or more variants

of an interesting “disilane-siloxane” (Si-Si-O, Scheme 3.6b), similar to that was discussed above for the over-reduction of propionaldehyde by the disilane. The number of Si-Si-O repeat units and the ratio of end units Si-H:Si-OCHPh<sub>2</sub> has not yet been evaluated and this mixture may even contain cyclic structures. The over-reduction of benzophenone is surprising in the context of the proposed mechanism for over-reduction of propionaldehyde, since it implies involvement of the alkoxy silane intermediate, Ph<sub>2</sub>SiH-Si(OCHPh<sub>2</sub>)Ph<sub>2</sub> (Scheme 3.7), which is a bulky nucleophile. However, this is not an isolated example: there are other reports of facile over-reduction of branched and bulky O-donor substrates containing benzylic substituents. For example, acetophenone and 1-phenylethanol undergo partial reduction with Et<sub>3</sub>SiH and then over-reduction using Me<sub>3</sub>SiH in the presence of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>2,27a</sup> Piers reported over-reduction of acetophenone by the bulky silane Ph<sub>3</sub>SiH in the presence of catalytic amounts of [Ph<sub>3</sub>C]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>, [Ph<sub>3</sub>Si]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>, and 1,2-[B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>F<sub>4</sub>, although not with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>42b</sup> The “branch bulk” provided by the alpha methyl group on acetophenone should inhibit over-reduction based on the mechanism shown in Scheme 3.3, but apparently the presence of the carbocation-stabilizing α-phenyl group overrides this steric discouragement. Even substrates that would lead to heavily branched benzylic silyl ethers (e.g. R<sub>3</sub>SiOCHPh<sub>2</sub>, R<sub>3</sub>SiOCPh<sub>3</sub>) can be over-reduced with Et<sub>3</sub>SiH, demonstrating far less sensitivity to the degree of bulk at the organic substrate than the non-benzylic, alkoxy examples described above.<sup>2,27a,28c,63</sup>

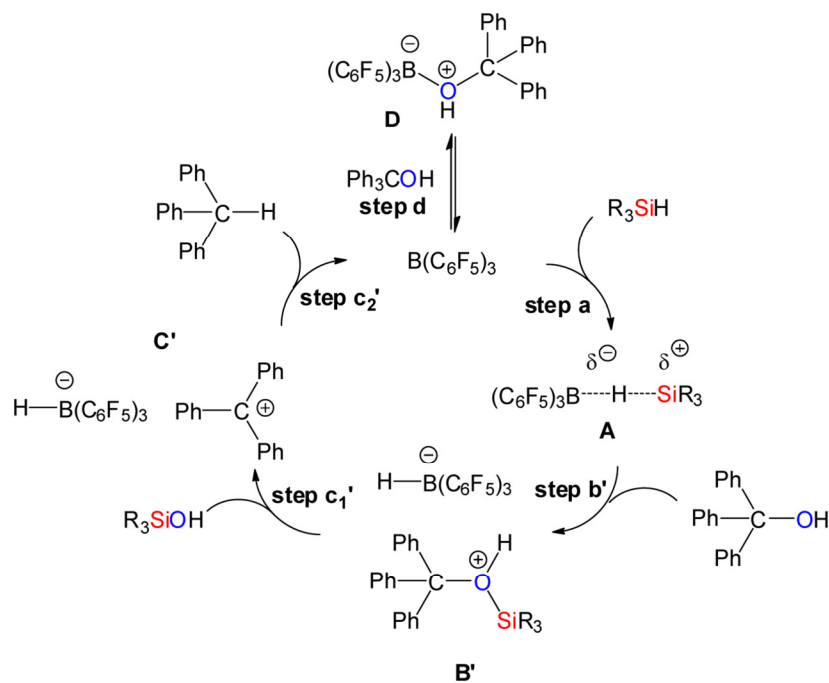
Scheme 3.7



Gevorgyan and Yamamoto note this apparent steric discrepancy in trityl alcohol (Ph<sub>3</sub>COH) reactions that led to facile production of triphenylmethane (Ph<sub>3</sub>CH), which based on the above discussion of branched versus unbranched substrates should not undergo over-reduction. They propose two mechanisms to account for these results: mechanism 2 (Scheme 3.8), which is similar to Piers-Oestreich mechanism shown in Scheme 3.3; and mechanism 3 (Scheme 3.9), which invokes E-substrate•••B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> complexation. However, these proposed mechanisms cannot be adapted to the over-reduction of benzophenone without first invoking a hydrosilation reaction, which leads to yet two other proposed mechanisms 4 and 5 (Scheme 3.11 and Scheme 3.12). Below, these mechanistic possibilities are surveyed and substrate scenarios are suggested for which each mechanism is probably valid.

One of Gevorgyan and Yamamoto's proposed mechanisms for the over-reduction of benzylic alcohols (over-reduction mechanism 2, Scheme 3.8) is modified from over-reduction mechanism 1 (Scheme 3.3) to rationalize the sensitivity of benzylic substrates to over-reduction.<sup>2</sup> In this mechanism the key step remains B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> activation of silane (**A** in Scheme 3.8) and nucleophilic attack of the alcohol (**step b'** in Scheme 3.8) to give a

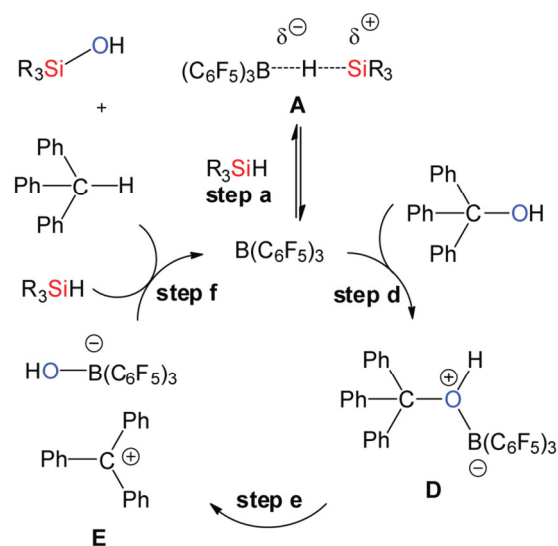
cationic adduct,  $[\text{Ph}_3\text{C-O(H)SiR}_3]^+$ , (**B'** in Scheme 3.8, similar to **B'** in Scheme 3.3). Instead of losing  $\text{H}_2$  (to give a silyl ether as might be expected from studies in Chapter 2), this intermediate makes silanol,  $\text{HOSiR}_3$ , and benzylic carbocation (**C'**, **step c<sub>1</sub>'** in Scheme 3.8). The elimination of silanol was confirmed when the addition of one equivalent of silane led to the production of one equivalent of silanol, which was detected by GC-MS. This cycle is appealing because any feature of the O-donor substrate that enhances the stability of the carbocation in **C'** (i.e. adjacent phenyl rings) should contribute to an increase in the rate of over-reduction, as is observed experimentally. While this mechanism is plausible based on the mounting evidence<sup>41b,42,67</sup> for  $(\text{C}_6\text{F}_5)_3\text{B}\cdots\text{H}\cdots\text{SiR}_3$  formation (Scheme 3.8, **A**), there remains a drawback of this mechanism: the two bulky reagents, silane and alcohol, come into close proximity, which was shown above with bulky nucleophiles to discourage over-reduction; if that step remains the key rate-determining over-reduction step, then the stabilization of benzylic carbocation (**C'** in Scheme 3.8) should not contribute greatly to an overall relative rate increase compared to equally branched, yet not benzylic examples.

**Scheme 3.8.** Over-reduction mechanism 2.

An alternative proposal, mechanism 3/Scheme 3.9, invokes a more traditional Lewis acid/base interaction: the alcohol substrate binds to the  $\text{B}(\text{C}_6\text{F}_5)_3$  (**step d**), giving an oxonium-type intermediate (**D**) that then undergoes C-O bond cleavage (**step e**) to generate the ion pair **E** consisting of a benzylic carbocation and a hydroxyborate anion. Finally, the benzylic cation abstracts a hydride from the silane (**step f**) and the resulting silylium is “trapped” by the  $\text{OH}^-$  anion, releasing free  $\text{B}(\text{C}_6\text{F}_5)_3$ . As for mechanism 2, this proposal is appealing because any feature of the O-donor substrate that enhances the stability of the carbocation in **E** (i.e. adjacent phenyl rings) should contribute to an increase in the rate of over-reduction, as is observed experimentally. Also, the intermediates do not require the close approach of bulky alcohol substrate to bulky silane, which is consistent with the low sensitivity of the rate of over-reduction to these steric features. Support for this putative cycle includes the fact that trityl cation has been shown to be capable of abstracting hydrides from silanes<sup>45</sup> (**step f**). Both mechanism 2 and 3 are

consistent with the formation of silanol ( $\text{HOSiR}_3$ , also referred to as a hydroxysilane) when the reaction is carried out using just a single equivalent of silane<sup>2</sup> and both bypass an initial dehydrocoupling step. Mechanism 3 is best suited for branched benzylic alcohol substrates such as trityl alcohol and diphenylmethanol ( $\text{Ph}_2\text{CHOH}$ ) where nucleophilic attack is not favorable. The unbranched benzylic substrates, such as benzyl alcohol ( $\text{PhCH}_2\text{OH}$ ) or dibenzyl ether ( $\text{PhCH}_2\text{OCH}_2\text{Ph}$ ) could show first dehydrocoupling or dealkylative coupling products, respectively, which then undergo over-reduction reactions, as for typical Piers-Oestreich over-reduction mechanisms (Scheme 3.3).<sup>2,28c</sup>

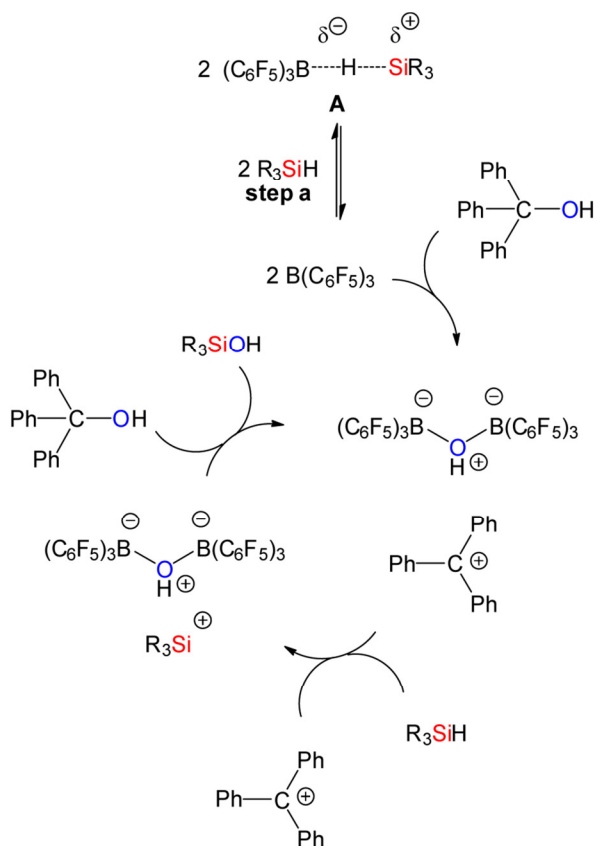
**Scheme 3.9.** Over-reduction mechanism 3.



A variation on Gevorgyan and Yamamoto's over-reduction mechanism 3 for the over-reduction of trityl alcohol ( $\text{Ph}_3\text{COH}$ ) has been proposed that invokes dehydroxylation with two equivalents of  $\text{B}(\text{C}_6\text{F}_5)_3$  (Scheme 3.10).<sup>94</sup> Like mechanism 3, this proposal is dependent on having an OH-containing substrate as opposed to a carbonyl-containing substrate and the dehydroxylation is supported by GC-MS observed silanol when using 1:1 substrate-to-silane stoichiometry. The same suggested substrates,

HOCHPh<sub>2</sub> and HOCPh<sub>3</sub> may undergo this over-reduction mechanism instead of mechanism 3. Yet, as for the above mechanisms, this proposed mechanism cannot be applied directly to benzophenone because it does not contain an OH group.

**Scheme 3.10.** Alternative proposal to over-reduction mechanism 3.

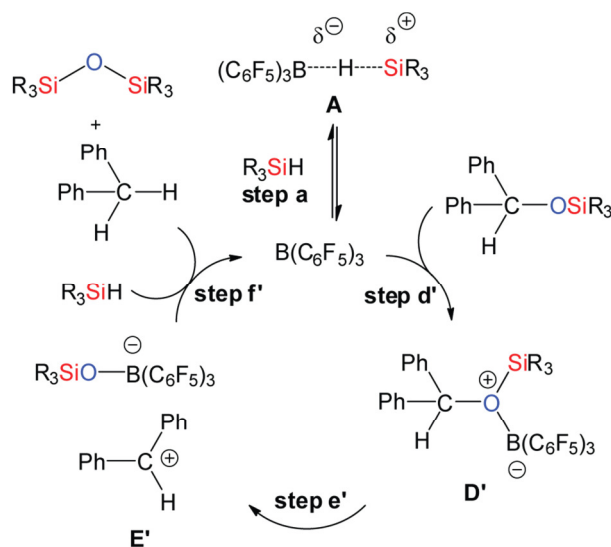


It is difficult to imagine a pathway to over-reduction of carbonyl-containing substrates that does not involve preliminary formation of the intermediate silyl ether (alkoxysilane) that results from carbonyl hydrosilylation. Invoking pathways that directly remove “O” from benzophenone suggests either carbene (Ph-(C:)-Ph) or dicationic (Ph-C<sup>2+</sup>-Ph) intermediates. Mechanisms proposing the carbene or dicationic intermediates have not been suggested for any B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed reactions and are

unlikely due to the higher energy intermediates than the proposed silyl ether intermediate,  $\text{Ph}_2\text{CH-O-SiR}_3$ .

Benzophenone and acetophenone are over-reduced far more easily and quickly than comparably bulky hydrosilation substrates that do not lead to benzyloxy substituents on Si. Mechanism 4 (Scheme 3.11) shows another possible alternative cycle for the over-reduction of benzophenone and related aryl carbonyl substrates. If a hydrosilation reaction occurs first, then the intermediate silyl ether itself is activated by the  $\text{B}(\text{C}_6\text{F}_5)_3$  (**step d'** in Scheme 3.11) leading to dissociation (**step e'**) into the ion pair **E'**. The intermediate "siloxaborane" anion (**E'**) picks up a silylium ion to give a disiloxane product. Once again, if **step e'** (Scheme 3.11) is rate-determining, any feature of the aryl groups that enhances the stability of the carbocation should contribute to an increase in the rate of the over-reduction reaction, relative to the partial reduction reaction that generates the silyl ether.

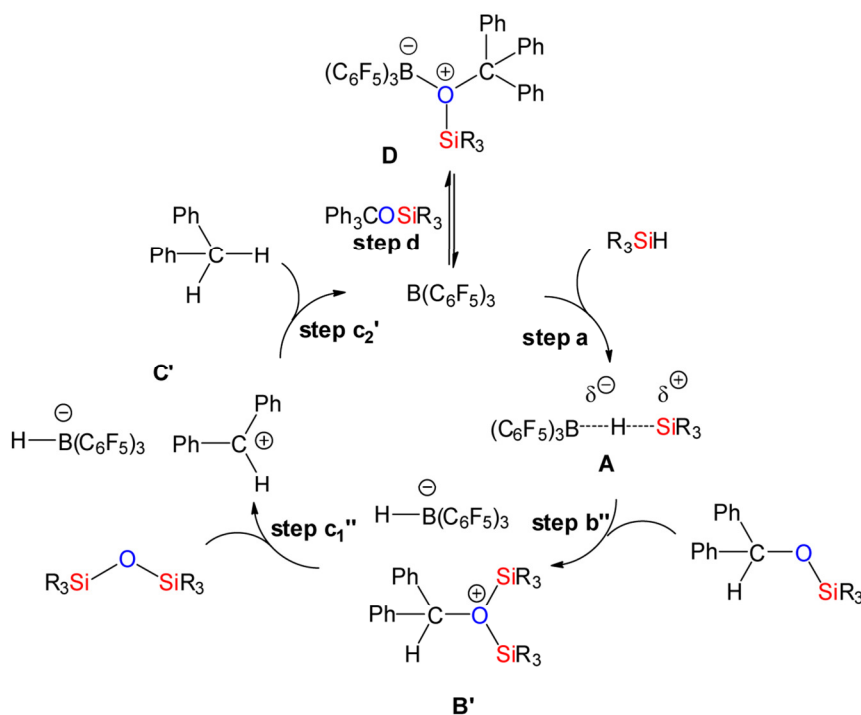
**Scheme 3.11.** Over-reduction mechanism 4.



A more conventional Piers-Oestreich mechanism, over-reduction mechanism 5 (Scheme 3.12), could be proposed for the over-reduction of benzophenone, which also requires formation of the benzyloxysilane that comes from a preceding hydrosilation reaction. This proposal is reminiscent of mechanism 1 (Scheme 3.3), except a benzylic carbocation intermediate ( $C'$ , Scheme 3.12) is invoked, similar to mechanism 2 (Scheme 3.8). It is not obvious which of these mechanisms (mechanism 4 and 5) is occurring based on the above experiments and examples in the literature. Support for an initial hydrosilation reaction occurring for benzophenone comes from the ability to modify reaction conditions to allow selective preparation of the hydrosilation product,  $Ph_2SiH-Si(OCHPh_2)Ph_2$ , as discussed below.<sup>xxiii</sup>

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<sup>xxiii</sup> The fact that exclusively partial reduction products can be isolated from the hydrosilation of acetophenone and the dehydrocoupling of 1-phenylethanol under some conditions also shows that the initial partial reduction may precede over-reduction for these benzylic carbonyl substrates.<sup>2,21,41b</sup>

**Scheme 3.12.** Over-reduction mechanism 5

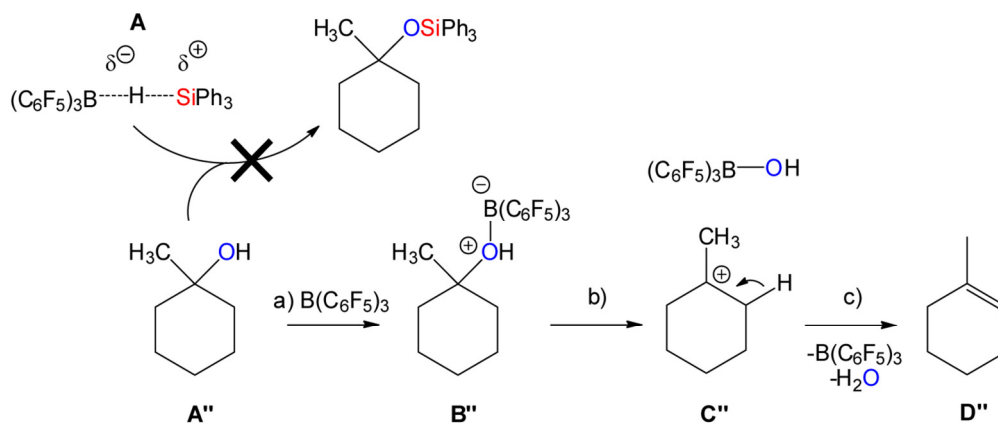
Mechanisms 4 and 5 require that the bulky silyl ether either coordinate to  $\text{B}(\text{C}_6\text{F}_5)_3$  (Scheme 3.11, **step d'**) or attack  $(\text{C}_6\text{F}_5)_3\text{B}^{\delta-} \cdots \text{H}^{\delta+} \cdots \text{SiR}_3$  (Scheme 3.12, **step b''**), neither of which is favorable for the bulky branched substrate with a diphenylmethyl side-chain and particularly if the silyl group is also bulky. Whichever mechanism is actually occurring, these proposals suggest that the subsequent over-reduction is dependent on steric bulk of the substrate and silyl group whereas the initial hydrosilylation reaction does not have as great a size-of-substrate dependency since the nucleophile (e.g. benzophenone) does not have an added bulky silyl group. Support for these carbocation-forming mechanisms described above (mechanisms 1-5) comes from  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reactions of 1-methylcyclohexanol with  $\text{Ph}_3\text{SiH}$  (Scheme 3.13).<sup>21</sup> This produced minor partial reduction (dehydrocoupling) and major olefin-containing products. This appears to be an example of potential carbocation formation. For example the mechanism in Scheme

3.9 (mechanism 3) suggests substrate- $\text{B}(\text{C}_6\text{F}_5)_3$  coordination and dehydroxylation, which is shown for 1-methylcyclohexanol in Scheme 3.13a/b. The olefinic products likely come from an elimination reaction (Scheme 3.13c) that occurs via a tertiary carbocation intermediate,  $\text{CH}_3\text{C}^+(\text{CH}_2)_5$  ( $\text{C}''$  in Scheme 3.13), which has presumably comparable stability to proposed benzyl cations ( $\text{E}$ , Scheme 3.9).<sup>xxiv</sup> This elimination reaction occurs instead of an over-reduction, as suggested and described in detail above for trityl and diphenylmethyl cations, which lack the necessary  $\beta$ -CH to participate in elimination chemistry. The silane reagent,  $\text{Ph}_3\text{SiH}$ , is extremely bulky ( $145^\circ$ , Table 3.1), which inhibits both  $(\text{C}_6\text{F}_5)_3\text{B}\cdots\text{H}\cdots\text{SiR}_3$  ( $\text{A}$ , Scheme 3.3) formation for dehydrocoupling reactivity and over-reduction via Si-H abstraction by the putative carbocation  $\text{C}''$  (Scheme 3.13) to give methylcyclohexane ( $\text{CH}_3\text{C}_6\text{H}_{11}$ ), as would be expected for the over-reduction reaction. Complete conversion to the partial reduction (dehydrocoupling) product is found when the less bulky  $\text{Et}_3\text{SiH}$  is the reductant, suggesting that silane-borane complex activation is more favored. The authors of this work noted a discrepancy getting to olefin-containing products using  $\text{Ph}_3\text{SiH}$  versus dehydrocoupling products using  $\text{Et}_3\text{SiH}$ , but did not provide a rationale for this disparity.

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<sup>xxiv</sup> More complex olefin by-products observed are likely the result of olefin oligomerization catalyzed by  $\text{B}(\text{C}_6\text{F}_5)_3$ . A control reaction of styrene with  $\text{B}(\text{C}_6\text{F}_5)_3$  gave insoluble product mixtures consistent with olefin polymerization.  $\text{B}(\text{C}_6\text{F}_5)_3$  as a co-catalyst for metal-catalyzed olefin polymerization is well established.<sup>95</sup>

Scheme 3.13



Further evidence for the importance of carbocation intermediates in these reactions comes from the  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed over-reduction reaction of *S*-(-)- $\text{PhC}(\text{OR})(\text{CH}_3)\text{H}$  ( $\text{R} = \text{H}, \text{SiEt}_3$ ) with  $\text{Et}_2\text{MeSiD}$ . Gevorgyan and Yamamoto report the over-reduction of this substrate to give a racemic mixture, *rac*- $\text{PhCD}(\text{CH}_3)\text{H}$ , despite starting from a pure stereoisomer.<sup>2</sup> This result posits the formation of a benzyloxy carbocation that mediates the over-reduction process. When the planar carbocation forms, the stereochemical information is lost and leads to a racemic mixture.

Regardless of the reaction mechanisms in these systems, it is clear that some deviation from the more general Si-H activation mechanism for these systems shown in Scheme 3.3 (mechanism 1) is possible for the benzylic substrates in these over-reduction reactions, and the particular stability afforded to benzylic carbocations does suggest the likely importance of such an intermediate or transition state. Despite the diminished sensitivity of these over-reduction reactions to substrate bulk, Piers describes successfully limiting over-reduction of acetophenone, benzaldehyde, and ethylbenzoate through a combination of a bulky silane ( $\text{Ph}_3\text{SiH}$ ), carefully controlled 1:1 substrate to silane stoichiometry, and low catalyst loading<sup>41b</sup>, and Gevorgyan and Yamamoto have also

reported limiting the over-reduction of benzaldehyde and benzoic acid by  $\text{Et}_3\text{SiH}$  through control of the stoichiometry of the added silane.<sup>27a,63</sup>

### 3.6 Selective partial reduction products from over-reducible substrates

In some cases, over-reduction can be curtailed by carefully controlling reaction time and catalyst loading. For example, in this work, under typical reaction conditions (4 mol%  $\text{B}(\text{C}_6\text{F}_5)_3$ , 16 h, RT), the reaction of disilane **2-2** and benzophenone gives a complex mixture of partial and over-reduction products (see experimental Section 3.12.2). However, the partial reduction product,  $\text{Ph}_2\text{SiH-Si}(\text{OCHPh}_2)\text{Ph}_2$  (**3-1**) was exclusively isolated under optimized reaction conditions (0.5 mol%, 72 h, RT).

Another example of modified conditions discouraging over-reduction chemistry relates to the observation of over-reduction of the sulfur-containing substrate, thiobenzophenone (*vide infra*). Former group member Dan Harrison reported reaction conditions for the synthesis of  $\text{Ph}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Ph}_2$  (**3-2**) and  $(\text{Me}_2\text{SiSCHPh}_2)_2$ <sup>1b,c</sup> that were inadvertently optimized: he was trying to ensure complete conversion of starting silane and minimize formation of an unidentified by-product, which is now identified as the over-reduction product, diphenylmethane. Likewise, a forensic analysis of spectra run by Dan Harrison when he was optimizing  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reactions of monosilanes,  $\text{Ph}_3\text{SiH}$ ,  $\text{Ph}_2\text{MeSiH}$ ,  $\text{Et}_3\text{SiH}$ , or  $\text{PhMe}_2\text{SiH}$  with thiobenzophenone showed diagnostic  $^1\text{H}$  and  $^{13}\text{C}$  signals due to diphenylmethane: an indication that over-reduction of this S-containing substrate was occurring, presumably producing interesting “disilthiane” products containing Si-S-Si linkages.<sup>1</sup> Exceeding reported conditions (e.g. increased catalyst loading or reaction time) led to competing over-reduction products, namely

diphenylmethane and longer Si-S-Si-containing oligomers, as diagnosed from broad signals in the  $^1\text{H}$  NMR spectra (see experimental Section 3.12.2 for examples).

**Table 3.3.** Conditions used to avoid over-reduction in the synthesis of monosubstituted disilanes prepared by  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reactions of disilane **2-2** with benzophenone and thiobenzophenone.

#	Substrate	X =	Conditions <sup>a</sup> : catalyst loading <sup>b</sup> , temperature, time	$^{29}\text{Si}$ NMR (ppm) <sup>c</sup>	% Yield
3-1		OCHPh <sub>2</sub>	0.5 mol%, RT, 72 h	$\delta$ -4.1 (Si-O), -39.1 (Si-H)	93
3-2 <sup>d</sup>		SCHPh <sub>2</sub>	4 mol%, RT, 3 h	$\delta$ -9.9 (Si-S), -36.3 (Si-H)	95

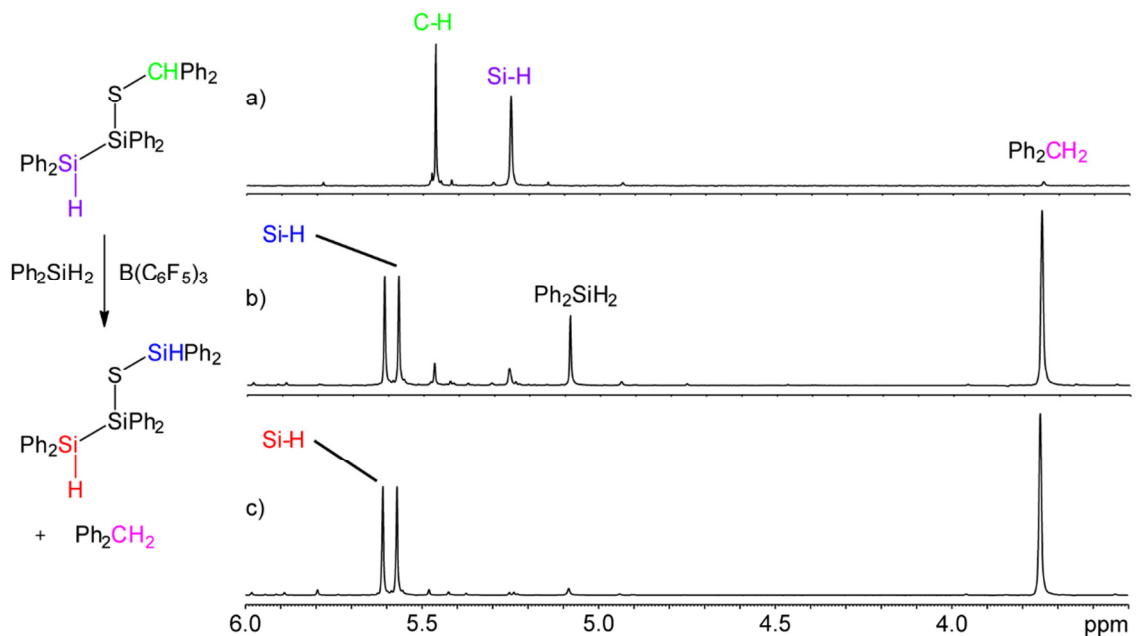
<sup>a</sup>Solvent was toluene. <sup>b</sup> $\text{B}(\text{C}_6\text{F}_5)_3$  catalyst loading reported in mol% relative to mol equivalents of Si-H in silane substrate (i.e. two equivalents of Si-H in **2-2**). <sup>c</sup>NMR solvent was  $\text{C}_6\text{D}_6$ . Reported in ppm. <sup>d</sup>Reported in the literature.<sup>1b</sup>

A consistently higher over-reduction reactivity of oxygen-containing substrates, either aliphatic or benzylic, was found compared to sulfur-substrates. The disilane/benzophenone reaction had a stronger propensity for over-reduction, compared to the sulfur analogue, thiobenzophenone, since an even lower catalyst (0.5 compared to 4 mol%, Table 3.3) was required to avoid over-reduction, and yet still gave complete

conversion from starting disilane **2-2**. No over-reduction was observed under any conditions with *n*-propylthiol, while propionaldehyde is challenging to prevent over-reduction from occurring. Attempts to optimize the reaction of disilane **2-2** with propionaldehyde have not yet yielded exclusively either of the expected possible partial reduction product,  $\text{Ph}_2\text{SiH-Si}(\text{O}^n\text{Pr})\text{Ph}_2$  or  $(\text{Ph}_2\text{SiO}^n\text{Pr})_2$ .

### 3.7 Over-reduction in sulfur systems

As noted above, benzylic sulfur substrates were discovered to be susceptible to over-reduction. Control reactions of thiobenzophenone with reductants  $\text{PhSiH}_3$  or  $\text{Ph}_2\text{SiH}_2$  produced diphenylmethane and  $^1\text{H}$  NMR spectra of these reaction mixtures showed signals consistent with the corresponding disilthiane products,  $(\text{PhSiH}_2)_2\text{S}$  and  $(\text{Ph}_2\text{SiH})_2\text{S}$ , respectively. Furthermore, the isolated monosubstituted disilane,  $\text{Ph}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Ph}_2$  (**3-1**), reacted with  $\text{Ph}_2\text{SiH}_2$  over 5 h to give the unsymmetrical disilthiane,  $\text{Ph}_2\text{SiH-Si}(\text{SSiHPh}_2)\text{Ph}_2$ , and diphenylmethane (Figure 3.5).



**Figure 3.5.**  $^1\text{H}$  NMR (300 MHz) (Si-H and benzylic region) of a) unreacted monosubstituted disilane  $\text{Ph}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Ph}_2$  (**3-1**), and the mixture of  $\text{Ph}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Ph}_2$  (**3-1**),  $\text{Ph}_2\text{SiH}_2$  (**2-2**), and  $\text{B}(\text{C}_6\text{F}_5)_3$  after b) 5 min, c) after 5 h in  $\text{C}_6\text{D}_6$ . Figure is adapted with permission (see note at the beginning of Chapter 3).<sup>96</sup>

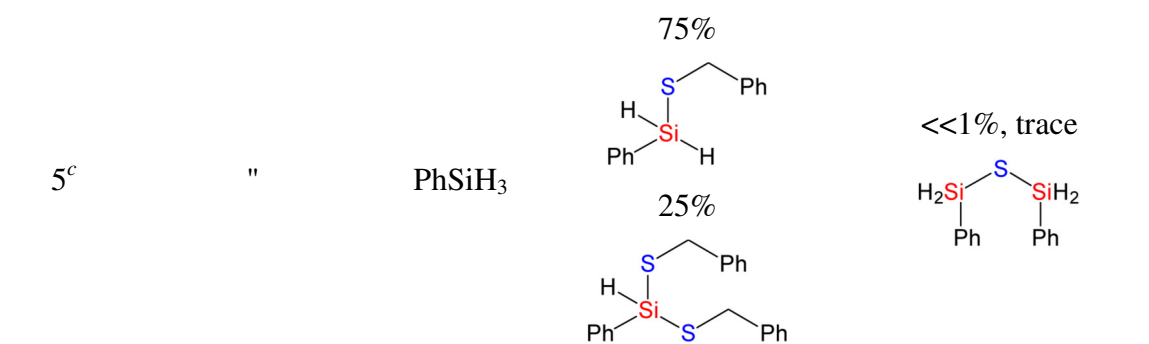
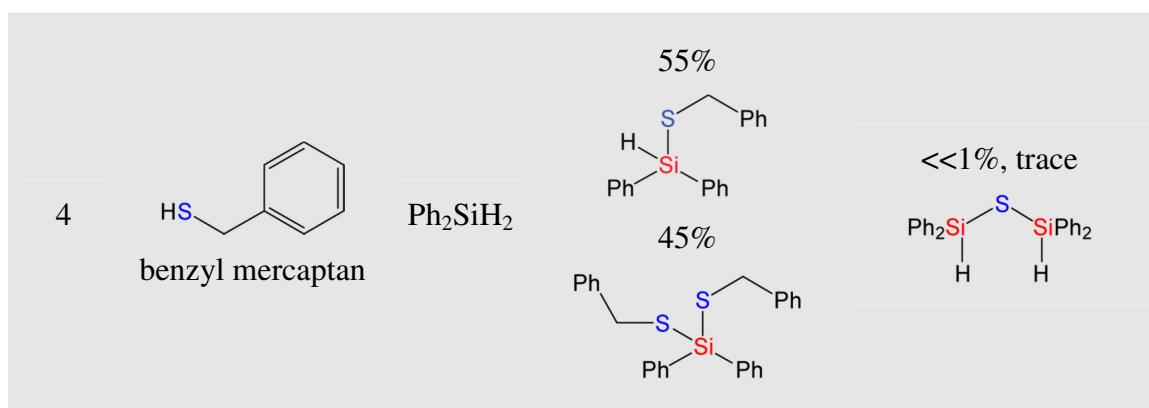
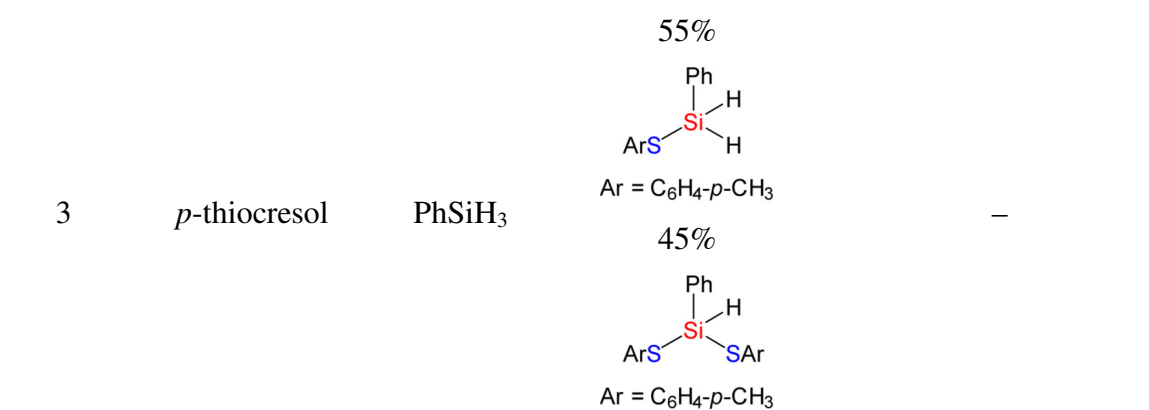
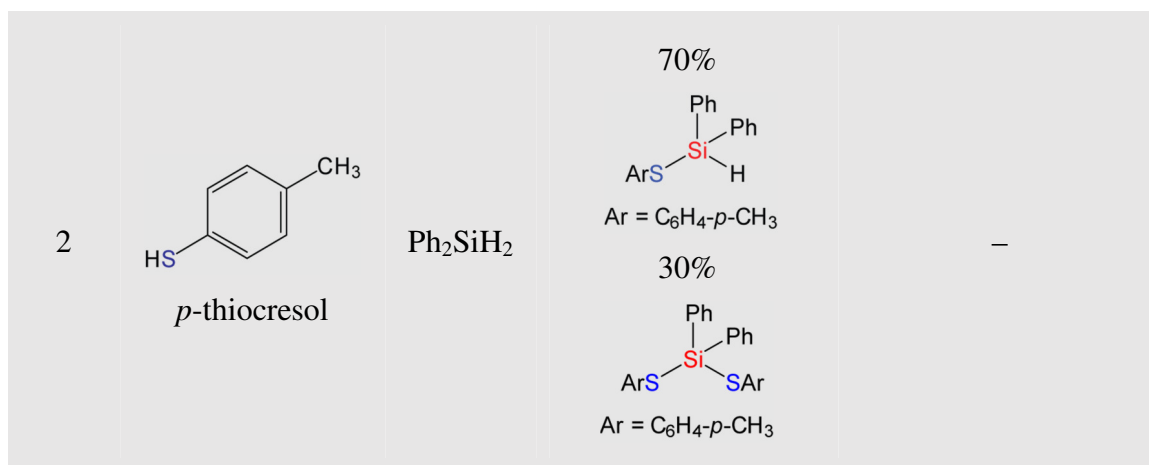
Reduction and over-reduction of thiobenzophenone with the bulky disilane **2-2**, was relatively slow, allowing selective isolation of partial reduction products (see Section 3.6). Previous studies confirm the steric hindrance of the silane critically affects this  $\text{B}(\text{C}_6\text{F}_5)_3$  catalysis: the hydrosilylation of thiobenzophenone by  $(\text{Me}_2\text{SiH})_2$  to give disubstituted  $(\text{Me}_2\text{SiSCHPh}_2)_2$  requires just 0.004 mol%  $\text{B}(\text{C}_6\text{F}_5)_3$ , while a catalyst loading of 4 mol% is required to obtain only the monosubstituted product,  $\text{Ph}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Ph}_2$  (**3-1**).<sup>1b</sup> Catalyst loading impacts the outcome of the partial and over-reduction reactions. Finding a catalyst loading that encourages partial reduction, yet does not lead to competing over-reduction, was challenging for these reactions of disilane, as well as for reactions of monosilanes reported in the literature.<sup>1a,b</sup>

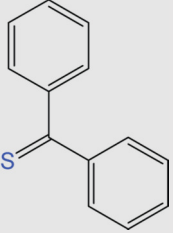
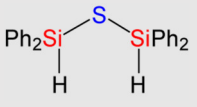
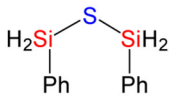
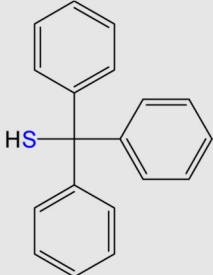
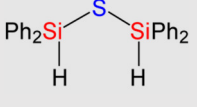
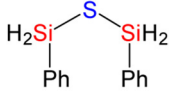

The extent of  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed desulfurization was investigated using  $\text{Ph}_2\text{SiH}_2$  and  $\text{PhSiH}_3$  (Table 3.4). The alkyl substrate, *n*-propylthiol was not desulfurized and gave

exclusively partial reduction products. Evidently the sterically unhindered phenylsilyl propyl thioether product (e.g.  $\text{PhH}_2\text{Si-S-CH}_2\text{CH}_2\text{CH}_3$ ) does not act as a nucleophile toward the silylium centre in the  $(\text{C}_6\text{F}_5)_3\text{B}\cdots\text{H}\cdots\text{SiR}_3$  adduct (A, Scheme 3.3) as do the analogous O-donor silyl ethers formed from hydrosilation of propionaldehyde. Reactions of *p*-thiocresol, an aryl-SH, with  $\text{Ph}_2\text{SiH}_2$  or  $\text{PhSiH}_3$  did not yield the desulfurization product, toluene. This was unsurprising given the lack of over-reduction observed for comparable aryloxy-containing substrates (see above Table 3.2). No reaction of thiophene with these silanes occurs. However, all the substrates that contain benzylic sulfur substituents can be over-reduced by  $\text{Ph}_2\text{SiH}_2$  or  $\text{PhSiH}_3$  (Table 3.4 entries 4 to 9), although the over-reduction of benzyl mercaptan is very slow relative to that of thiobenzophenone or trityl mercaptan. With the exception of transition-metal catalyzed over-reductions of thioamides,<sup>81b,97</sup> there are no other examples of silane over-reduction of S-containing substrate described in the literature aside from the very recent report by Akiyama.<sup>86,xx</sup> The thioamide substrate in these reports has an adjacent amino group that may provide a similar cation-stabilizing effect similar to a benzyl-stabilized cation that ultimately facilitates Si-S-Si leaving (*vide infra*).

**Table 3.4.** Reactions of S-containing substrates with smaller silanes  $\text{Ph}_2\text{SiH}_2$  or  $\text{PhSiH}_3$  to gauge susceptibility to over-reduction.<sup>a</sup>

Entry	Substrate	Silane	Partial reduction <sup>b</sup>	Over-reduction <sup>b</sup>
1	<i>n</i> -propylthiol	$\text{PhSiH}_3$	$  \begin{array}{c}  >99\% \\  \text{S-CH}_2\text{CH}_2\text{CH}_3 \\    \\  \text{H-Si} \\    \\  \text{Ph-S-CH}_2\text{CH}_2\text{CH}_3  \end{array}  $	–



6 <sup>d</sup>		Ph <sub>2</sub> SiH <sub>2</sub>	–	>99% 
7 <sup>d</sup>	"	PhSiH <sub>3</sub>	–	>99% 
8		Ph <sub>2</sub> SiH <sub>2</sub>	–	>99% 
9 <sup>c</sup>	"	PhSiH <sub>3</sub>	–	>99% 
10		PhSiH <sub>3</sub>	–	–

<sup>a</sup>Conditions: 10:1 silane:substrate ratio; 5 mol% B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>; in C<sub>6</sub>D<sub>6</sub> unless otherwise noted; 5-15 min reaction time unless otherwise noted. <sup>b</sup>In all cases, the substrate was completely consumed in the presence of excess silane. Percentages are relative amounts of products based on <sup>1</sup>H NMR integrations. <sup>c</sup>When this reaction was done on a preparative scale, longer Si-S-containing oligomers were obtained (see next Section 3.8). <sup>d</sup>Reaction done in CDCl<sub>3</sub> instead of C<sub>6</sub>D<sub>6</sub>.

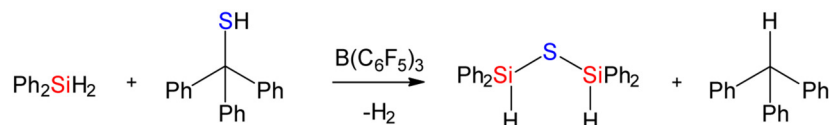
This tendency of benzylic S-donor substrates to be over-reduced seems to support the notion of distinct pathways for the over-reduction of linear alkyl and benzylic O-donor substrates presented earlier in Section 3.5; perhaps the benzylic substrates (both S- and O-donor) all participate in the alternative cycles shown in Scheme 3.9 and Scheme 3.11. This result is somewhat unexpected because Scheme 3.9 and Scheme 3.11 rely on the formation of E-B adducts (E = O, S), and because the binding affinities of the soft S-donors for  $B(C_6F_5)_3$  are lower<sup>61</sup> than those of the harder O-donors. This result again emphasizes the importance of the benzyl substituents: the polarization and ultimate cleavage of the E-C bond is so facile that significant rates of over-reduction are achieved even at very low adduct concentrations. As for the benzylic O-donor substrates, over-reduction is efficient for thiobenzophenone and trityl mercaptan despite their increased steric bulk.

### 3.8 Exploiting over-reduction for the synthesis of Si-S-Si-containing molecules

The  $B(C_6F_5)_3$ -catalyzed over-reduction chemistry of benzylic S-donor substrates presents some interesting possibilities for the synthesis of new molecules containing Si-S-Si linkages, as an alternative to traditional routes involving stoichiometric reactions of Si-Cl bonds with  $H_2S$ .<sup>98</sup> Discrete Si-S-Si-containing  $(Ph_2SiH)_2S$  (**3-3**, Scheme 3.14) can be prepared from  $Ph_2SiH_2$  and trityl mercaptan ( $Ph_3CSH$ ) with catalyst  $B(C_6F_5)_3$  (1 mol%). Reactions of  $Ph_2SiH_2$  or  $PhSiH_3$  with benzyl mercaptan ( $PhCH_2SH$ ) were attempted because the possibility of “toluene elimination” chemistry was appealing due to the ease of removal of toluene by evacuation from disilthiane products compared to the sublimation techniques used to remove triphenylmethane. However, this resulted in a mixture of partial and over-reduction products (e.g.  $Ph_2SiH-SCH_2Ph$ ,  $Ph_2SiH-S-SiHPh_2$

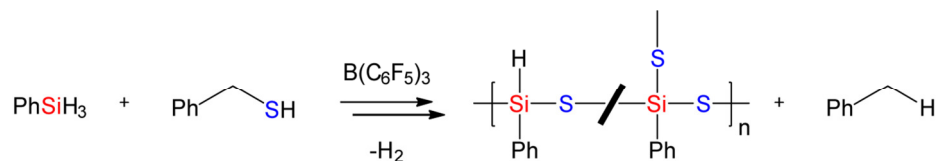
(**3-3**), and longer oligomers with or without SCH<sub>2</sub>Ph side-chains); the rate of over-reduction using a substrate with only one  $\alpha$ -phenyl group seems to be prohibitively low for synthetic utility compared to a more “activated” substrate with additional  $\alpha$ -phenyl groups.<sup>xxv</sup>

**Scheme 3.14**

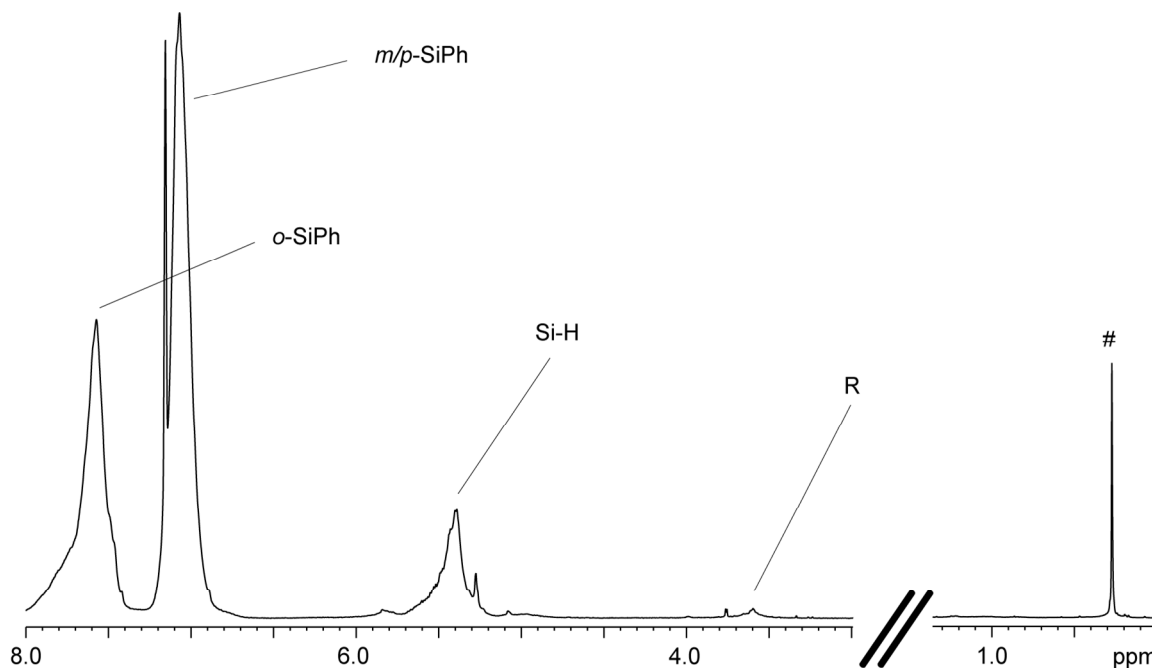


Reaction of PhSiH<sub>3</sub> with benzyl mercaptan showed rapidly occurring over-reduction to make longer Si-S-Si-containing oligomers or polymers, but still some partial reduction products remained in the mixture. This reaction (Scheme 3.15) produced oligomer/polymer poly(hydridophenylsilthiane), [PhSiH-S]<sub>n</sub> (**3-4**), as evidenced by broad Si-H and Si-Ph peaks in the <sup>1</sup>H NMR (Figure 3.6). Yet a broad peak was found (‘R’ in Figure 3.6) indicative of remaining SCH<sub>2</sub>Ph side-chains that had not yet undergone over-reduction.

**Scheme 3.15**



<sup>xxv</sup> Over-reduction of the more “activated” substrate thiobenzophenone is more efficient - complete conversion to disilthiane, **3-3**, occurred within minutes - but separation of the highly soluble **3-3** from by-product Ph<sub>2</sub>CH<sub>2</sub> (boiling point 264 °C) is problematic.



**Figure 3.6.** a)  $^1\text{H}$  NMR (300 MHz) of  $[\text{PhSiH-S}]_n$  (**3-4**) in  $\text{C}_6\text{D}_6$ . The “#” is grease. The “R” is residual partial reduction unit. This may be any of the following structural units: repeat unit,  $-\text{PhSi}(\text{SCH}_2\text{Ph})\text{S}-$ ; monosubstituted endcap,  $-\text{PhSi}(\text{H})\text{SCH}_2\text{Ph}$ ; or disubstituted endcap,  $-\text{PhSi}(\text{SCH}_2\text{Ph})_2$ . The intensity of the 3.0 to 8.0 ppm region has been magnified by a factor of four for clarity.

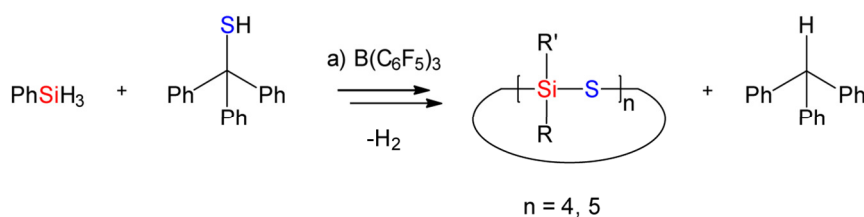
The polymerization of  $\text{PhSiH}_3$  with a more “activated” sulfur substrate, trityl mercaptan ( $\text{HSCPh}_3$ ) was attempted to obtain a polymer free of residual, partial reduction groups  $-\text{SCPh}_3$ . The rapid production of triphenylmethane and a lack of identifiable S-H signals in the  $^1\text{H}$  NMR<sup>xxvi</sup> suggested that efficient Si-S-Si formation had occurred, however, this gave a mixture of short/cyclic oligomers, **3-5** (Scheme 3.16). The  $^1\text{H}$  NMR (Figure 3.7) showed many discrete Si-H and Si-Ph signals. This was unlike the broad Si-H and Si-Ph regions in the  $^1\text{H}$  NMR above (Figure 3.6) and suggested that the product formed short chain oligomers instead of the longer chains that were desired. These sharp signals have not yet been assigned; cyclic oligomers are proposed based on the relatively

<sup>xxvi</sup>  $^1\text{H}$  NMR signals for the putative partial reduction product,  $\text{PhSiH}_2-\text{SCPh}_3$ , were not readily identified, if present, by  $^1\text{H}$  NMR due to complex and overlapping signals in the aromatic region.

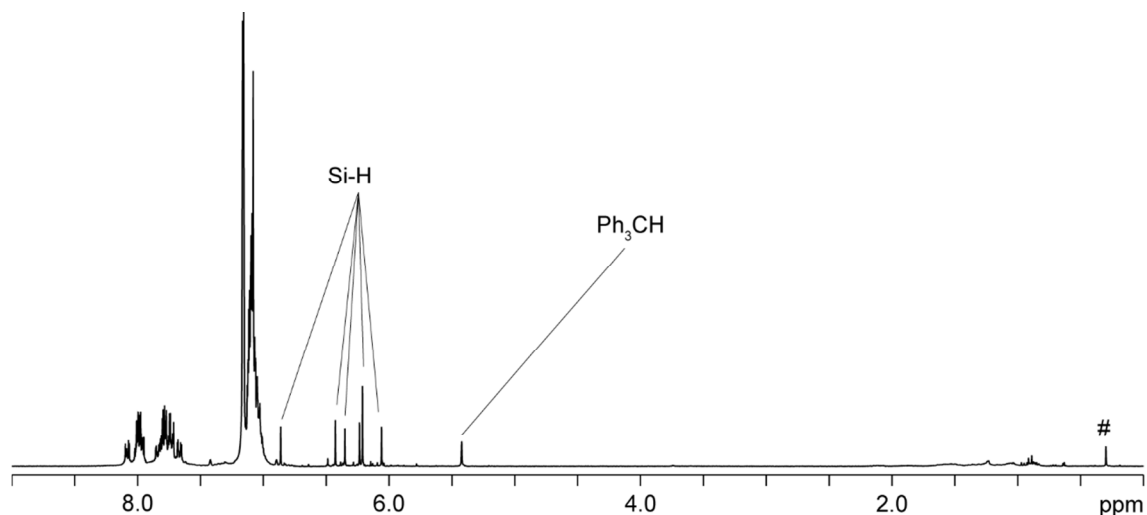
simple Si-H region in the  $^1\text{H}$  NMR. The ring sizes, eight- and ten-membered rings or four and five  $-\text{PhSiH-S}-$  repeat units are suggested based on the common ring sizes for silicones.<sup>93</sup> Diastereomers of the eight and ten-membered rings are likely present and contribute to the number of sharp signals in the  $^1\text{H}$  NMR.<sup>93,xxvii</sup> The downfield shift at  $\delta$  6.87 ppm suggests a more strained ring size in four-membered ring,  $[\text{PhSiH-S}]_2$ , based on the  $^1\text{H}$  NMR chemical shifts of H in cyclobutane compared to the less strained cyclopentane or cyclohexane.

These synthetic methods and those reported in the literature for the analogous formation of Si-O-Si-containing polymers<sup>26a,58,92</sup> are encouraging signs that these new and interesting Si-S-Si-containing molecules can be prepared. While the trityl mercaptan method was unable to obtain longer oligomers or polymers, desulfurization of benzyl mercaptan with  $\text{PhSiH}_3$  led to polymers with only minor amounts of  $-\text{SCH}_2\text{Ph}$  side-chains. Optimized reaction conditions that encourage over-reduction/desulfurization, such as elevated temperatures and increased catalyst loading, may give Si-S-Si-containing polymers that are free of partial reduction side-chains.

**Scheme 3.16**



<sup>xxvii</sup>  $[\text{PhSiH-S}]_4$  and  $[\text{PhSiH-S}]_5$  have four unique diastereomers each. No oligomer  $(\text{PhSiH}_2)_2\text{S}$ , which has been characterized above and in the literature<sup>90</sup>, shown in Table 3.4 entries 7/9, was found.



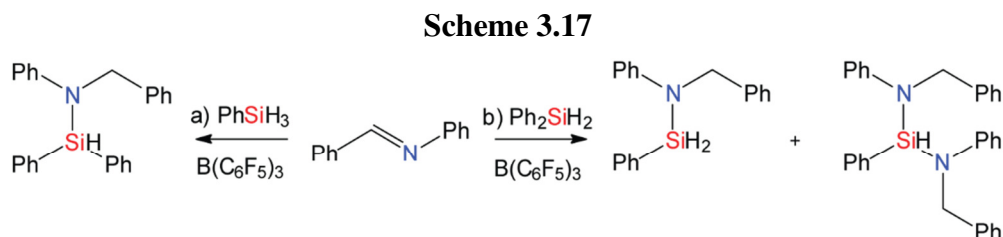
**Figure 3.7.**  $^1\text{H}$  NMR (300 MHz) of oligomer mixture [PhSiH-S] (**3-5**) in  $\text{C}_6\text{D}_6$ .

### 3.9 Partial reduction of nitrogen-containing substrates

The production of disilthianes via catalytic “desulfurization” of organic substrates by silanes is unusual and intriguing. The over-reduction of O-donor substrates by silanes was originally presumed to be driven by the strength of the Si-O-Si bonds (569 kJ/mol for  $\text{Me}_3\text{Si-O-SiMe}_3$ )<sup>19b</sup> formed in these reactions, but this is not the case for Si-S-Si bonds (414 kJ/mol for  $\text{Me}_3\text{Si-SBu}$ ).<sup>19a</sup> This result encouraged evaluation of other possible heteroatoms substrates, such as nitrogen sourced from imines or nitriles (408 kJ/mol for  $\text{Me}_3\text{Si-NMe}_2$ )<sup>19b</sup> for possible over-reduction due to their reported  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reactions.<sup>41a,59a,67,99</sup> However, as described below, even with the smallest silanes,  $\text{Ph}_2\text{SiH}_2$  and  $\text{PhSiH}_3$ , only partial reduction products are found for these substrates with no elimination of alkane by-products.

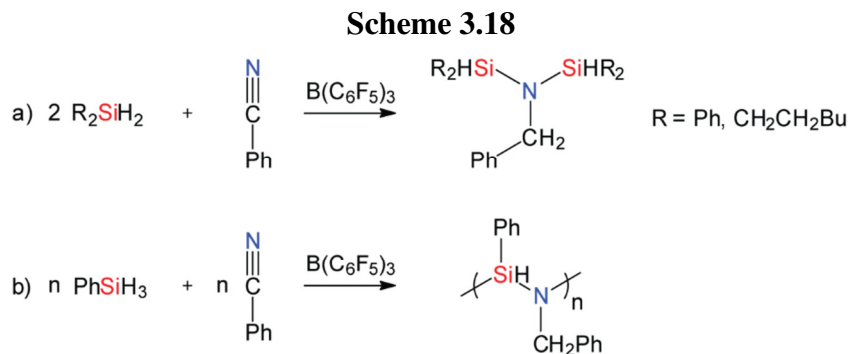
Screening reactions of  $\text{Ph}_2\text{SiH}_2$  or  $\text{PhSiH}_3$  with benzylideneaniline (Scheme 3.17a/b respectively) gave no over-reduction; instead these gave *N*-silylamine products quantitatively over 1 h. These included  $\text{Ph}_2\text{SiH}(\text{N}(\text{Ph})\text{CH}_2\text{Ph})$  (**3-5**, Scheme 3.17a) with  $\text{Ph}_2\text{SiH}_2$  or a mixture of monohydrosilation (**3-7a**) and dihydrosilation (**3-7b**) products

with  $\text{PhSiH}_3$  (Scheme 3.17b). The absence of over-reduction products in reactions of nitrogen-containing substrates is attributable to three factors: the Lewis basicity of the nitrogen substrate/product, the poor leaving-group ability of the  $\text{NRR}'$  amino group, and steric bulk at the nitrogen. Off-cycle complexation of  $\text{B}(\text{C}_6\text{F}_5)_3$ , as discussed in Section 2.3.1, is an even greater problem with highly Lewis basic imine or product silylamine. Over-reduction of the silylamine product would require the  $\text{NR}(\text{SiR}'_3)$  to bear at least a partial negative charge and behave as a leaving group, which is generally not favored.<sup>89</sup> The trivalent nitrogen is inherently bulkier than divalent O/S-silyl derivatives, which also discourages over-reduction.



Similarly, reactions of  $n\text{-Hex}_2\text{SiH}_2$ ,  $\text{Ph}_2\text{SiH}_2$  or  $\text{PhSiH}_3$  with nitriles led to  $N,N$ -disilylamines and no over-reduction products. These reactions gave either a discrete monomer  $(\text{R}_2\text{SiH})_2\text{NCH}_2\text{Ph}$  (**3-8a**,  $\text{R} = \text{Ph}$  and **3-8b**,  $\text{R} = n\text{-Hex}$ , Scheme 3.18a) with  $\text{R}_2\text{SiH}_2$  or the oligomer polysilazane  $[\text{PhSiH}-\text{NCH}_2\text{Ph}]_n$  (**3-9**, Scheme 3.18b) with  $\text{PhSiH}_3$ . The reaction proceeds cleanly for benzonitrile, but gives product mixtures with  $\text{Ph}_2\text{SiH}_2$  for the other nitriles examined: acetonitrile and acrylonitrile. The reaction of  $\text{Ph}_2\text{SiH}_2$  with acetonitrile gave partial conversion to the dihydrosilation product,  $(\text{Ph}_2\text{SiH})_2\text{NCH}_2\text{CH}_3$  as determined by  $^1\text{H}$  NMR. This result suggested some  $\text{B}(\text{C}_6\text{F}_5)_3$  catalyst inhibition from either acetonitrile or the product disilylamine. The  $^1\text{H}$  NMR of an

aliquot from the reaction of  $\text{Ph}_2\text{SiH}_2$  with acrylonitrile showed a mixture of hydrosilation products with either two or three silyl groups incorporated into the product.



These reactions are interesting because  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reactions of nitriles with silanes have been less explored<sup>xxviii</sup> than other oxygen-, nitrogen-, sulfur-, or olefin-containing substrates; the recently developed fluorophosphonium catalyst,  $[\text{FP}(\text{C}_6\text{F}_5)_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , which exhibits  $\text{B}(\text{C}_6\text{F}_5)_3$ -like activity, catalyzes hydrosilation of nitriles<sup>53a</sup> even with the larger silane,  $\text{Et}_3\text{SiH}$ . Examples of transition-metal catalyzed nitrile hydrosilation typically show complex reaction pathways typically leading to a mixture of products<sup>101</sup>, yet these  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reactions are straightforward and rapid; and hydrolysis of these *N*-silylamines gives amines, which are desirable products.

### 3.10 Summary

Competing  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed over-reduction reactions were identified and products were characterized for a number of model hydrosilation and dehydrocoupling reactions. Substrates for this reaction were classified in two distinct groups: straight-chain alkoxy groups and *S*/*O*-benzylic groups. Steric bulk of the substrate was shown to be a

<sup>xxviii</sup> The  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed hydrosilation of conjugated nitriles, such as cinnamionitrile, with  $\text{Et}_2\text{SiH}_2$  has been recently published.<sup>100</sup>

major factor affecting the propensity for alkoxy chains to undergo over-reduction. Bulkier branched substrates, e.g. acetone and cyclohexanone, did not undergo over-reduction with silanes such as  $\text{Ph}_2\text{MeSiH}$  (**2-1**) and disilane **2-2**. Steric bulk at the silane was shown to be an important factor affecting over-reduction. Extensive screening reactions demonstrated that the smaller silanes,  $\text{PhSiH}_3$  and  $\text{Ph}_2\text{SiH}_2$ , could over-reduce bulkier substrates, including acetone, cyclohexanone, and *t*-butanol.

Benzylic substrates behaved differently from those leading to linear alkoxy chains: even for sterically hindered substrates such as benzophenone and triphenylmethyl mercaptan, over-reduction was possible. A mechanism invoking a  $\text{B}(\text{C}_6\text{F}_5)_3$ -substrate adduct has been proposed (Scheme 3.9 and Scheme 3.11)<sup>2</sup> to rationalize this change in selectivity, however, this mechanism is only valid for OH, SH, and OR-containing substrates. Over-reduction also occurs with benzophenone and thiobenzophenone, containing C=O and C=S groups, respectively, where  $\text{B}(\text{C}_6\text{F}_5)_3$ -coordination and elimination of OH/SH groups is not possible and so alternative mechanisms that first involve hydrosilation then over-reduction have been proposed. These mechanisms feature either substrate- $\text{B}(\text{C}_6\text{F}_5)_3$  (**D'**) or  $(\text{C}_6\text{F}_5)_3\text{B}\cdots\text{H}\cdots\text{SiR}_3$  (**A**) complexation routes and it is thus far undetermined which route is actually occurring with diphenylmethoxy or diphenylmethylthiolato substrates silane intermediates.

Facile S-benzylic over-reduction was exploited to make Si-S-Si-containing molecules. Reactions of different sulfur substrates, triphenylmethyl mercaptan ( $\text{Ph}_3\text{CSH}$ ), thiobenzophenone ( $\text{Ph}_2\text{CS}$ ), and benzyl mercaptan ( $\text{PhCH}_2\text{SH}$ ), indicated that over-reduction was favored for the substrate with the most phenyl groups, trityl mercaptan. This is the most sterically bulky of the three substrates, but it also leads to the most

stabilized putative carbocation intermediate. New Si-S-Si-containing molecules were made from  $\text{Ph}_2\text{SiH}_2$  or  $\text{PhSiH}_3$  from the over-reduction of benzyl mercaptan or triphenylmethyl mercaptan: dimer  $(\text{Ph}_2\text{SiH})_2\text{S}$  (**3-3**), polymer  $[\text{PhSi}(\text{H})\text{S}]_n$  (**3-4**), and cyclic oligomer  $[\text{PhSi}(\text{H})\text{S}]_n$  (**3-5**). The synthesis of these molecules is a new, catalytic method of preparing disilthiane products without the need for undesirable  $\text{H}_2\text{S}$  gas or corrosive silicon-chloride-containing starting materials.

### 3.11 Impact and future work

The studies of  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed over-reduction with S-containing substrates point to many readily available silicon-sulfur-containing oligomers, beyond the molecules synthesized and characterized here. Preliminary results indicate that this method is viable, however there are challenges associated with the substrates investigated to date. The most promising results in terms of over-reduction capability were achieved using trityl mercaptan ( $\text{Ph}_3\text{CSH}$ ), which eliminates triphenylmethane, although this by-product is difficult to remove. Reactions of silanes with benzyl mercaptan ( $\text{PhCH}_2\text{SH}$ ), which gave the most easily removed by-product, toluene, showed the least efficient over-reduction. Performing the less efficient reactions at elevated temperatures is an important next step. Elevated temperatures would be expected to force over-reduction due to increased Si-H to Si-E conversion at higher temperatures, which was demonstrated in the synthesis of substituted disilanes  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})_2$  (**2-20**) and  $\text{Ph}_2\text{Si}(\text{OC}_6\text{H}_4\text{-}p\text{-}\text{CH}_3)\text{-Si}(\text{OC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})\text{Ph}_2$  (**2-24**) (see Chapter 2). Thus far, silicon-sulfur-containing oligomers and polymers have not yet been utilized for applications, in part because the currently recognized route to these molecules uses

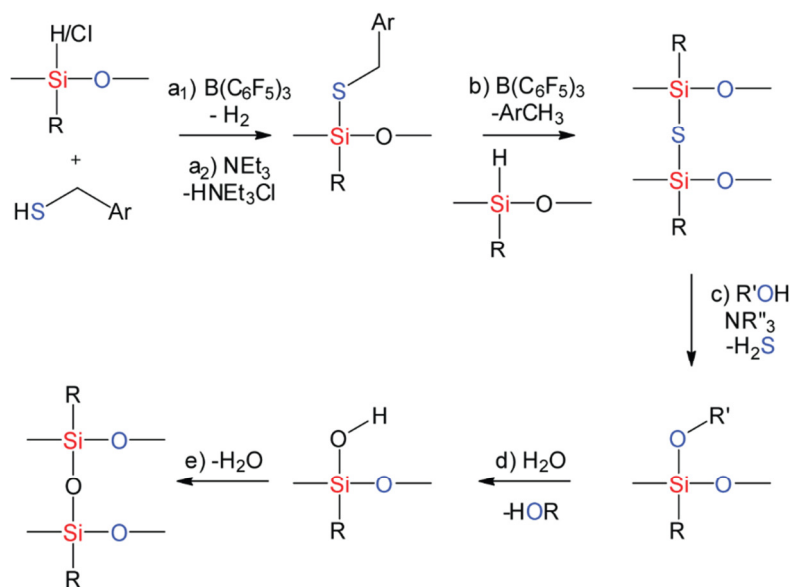
undesirable starting materials,  $R_2SiCl_2$  and  $H_2S$ .<sup>xxix</sup> Continued efforts to make these poly(silthianes) must include a more extensive characterization, including GPC, IR, and EA. The MWs of these new polymers are particularly interesting to compare the number of Si-S repeat units against the well-characterized polysiloxanes synthesized by  $B(C_6F_5)_3$ -catalyzed methods.

A Si-S-polymer property that may be exploited is its sensitivity to hydrolysis or alcoholysis. Degradation of Si-S bonds occurs rapidly at RT in water, methanol, ethanol, and other alcohols.<sup>1c,102</sup> Cross-linked polysiloxanes have found widespread applications.<sup>5-6,11b</sup> These polymers are a mobile, shapeable viscous liquid when applied to a surface. When exposed to air over time, the polymer eliminates  $H_2O$  irreversibly to give a hydrophobic surface or sealant. If an application can be found that requires a silicone to cross-link (Scheme 3.19b), revert to linear chain (Scheme 3.19c), and then cross-link again (Scheme 3.19c/d), then  $B(C_6F_5)_3$ -catalyzed over-reduction of sulfur substrates may be exploited. The first step is the reaction of the polysiloxane with sulfur substrate to form thiolato side-chains with an appropriate benzyl group. Thiolato side-chains may be derived from  $B(C_6F_5)_3$  catalyzed dehydrocoupling or by classical nucleophilic substitution at silicon mediated by Si-Cl (Scheme 3.19a). A sulfur cross-link can then be introduced by  $B(C_6F_5)_3$ -catalyzed over-reduction to make the Si-S-Si linkage ((Scheme 3.19b). Cross-linking can be reversed by alcoholysis leaving a polymer that is not cross-linked ((Scheme 3.19c). The disadvantage to this method is the elimination of  $H_2S$ , which has an undesirable odor. Therefore, this method may be only applicable or desirable if a low quantity of  $H_2S$  is generated and/or if the odor is not an issue.

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<sup>xxix</sup> Few examples of Si-S-Si-containing oligomers and polymers are found in the literature.<sup>83,91a,96</sup>

Scheme 3.19



$\text{B(C}_6\text{F}_5)_3$ -catalyzed reactions of nitrogen-containing substrates have been thus far challenging due to substrate inhibition. Limited literature examples of  $\text{B(C}_6\text{F}_5)_3$ -catalyzed hydrosilation of imines show competing undesirable reactivity.<sup>42b,43d,59a</sup>  $\text{B(C}_6\text{F}_5)_3$ -catalyzed hydrosilation of nitriles has been largely unexplored despite similar  $\text{B(C}_6\text{F}_5)_3$ -catalyzed hydrogenation reactions<sup>53a,68</sup> in the literature.<sup>xxx</sup> Screening reactions of  $\text{Ph}_2\text{SiH}_2$  or  $\text{PhSiH}_3$  with imines or nitriles show that reduction is relatively facile compared to bulkier silanes such as disilane **2-2**. In general, these smaller silanes may be applied to reduction processes where other, more commonly used silanes for reduction, such as  $\text{Et}_3\text{SiH}$  and poly(methylhydrosiloxane) (PMHS), are less effective, especially for the highly Lewis basic N-donor substrates.

In the context of the  $\text{B(C}_6\text{F}_5)_3$ -catalyzed post-polymerization modification of poly(phenylsilane), reactions of poly(phenylsilane) with substrates that lead to *n*-alkoxy,

<sup>xxx</sup> Recently,  $\text{B(C}_6\text{F}_5)_3$ -catalyzed hydrosilation of conjugated nitriles has been reported using the small silane,  $\text{Et}_2\text{SiH}_2$ .<sup>100</sup>

benzyloxy, or thiobenzyloxy side-chains may exhibit complex over-reduction chemistry. These reactions need to be assessed for possible over-reduction by checking the modified polysilane's  $^1\text{H}$  NMR spectrum for over-reduction products (alkanes) and/or analyzing its molecular weight for a substantial increase (a substantial increase in MW would be indicative of cross-linking and therefore over-reduction).

## 3.12 Experimental

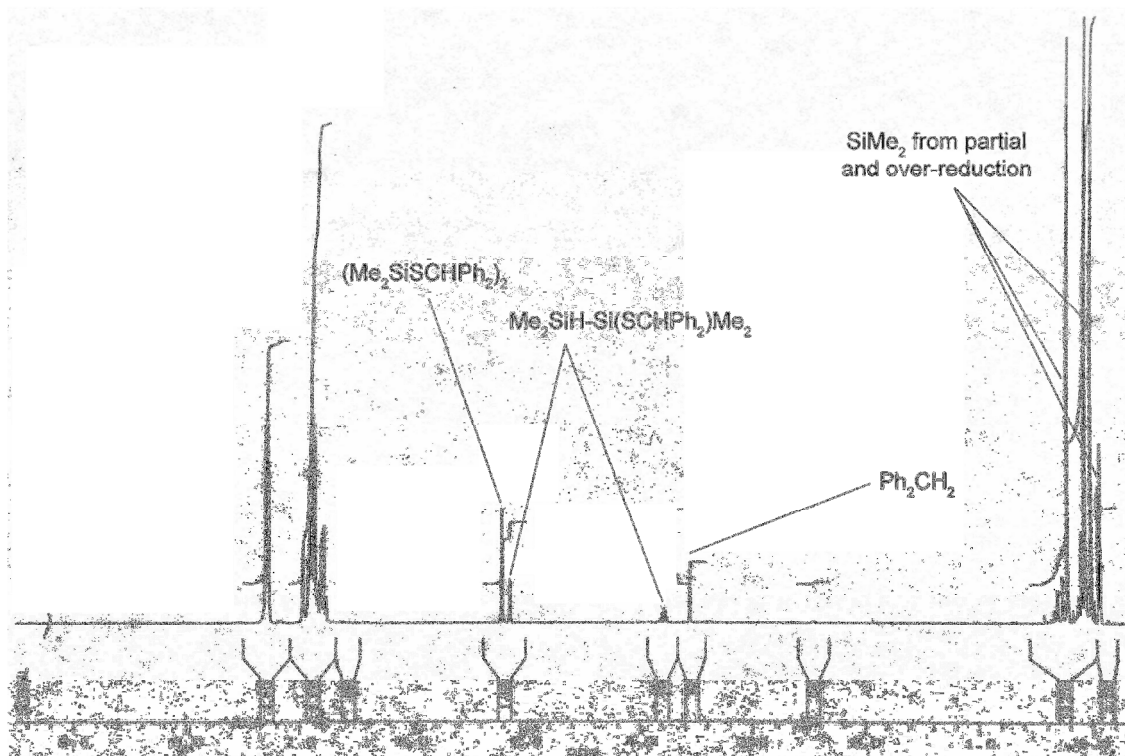
### 3.12.1 General details

General details described in Chapter 2, Section 2.5 are valid in this chapter unless otherwise noted. Deuterated chloroform was purchased from Aldrich, freeze-pump-thaw degassed and vacuum transferred from calcium hydride. *t*-Butanol was purchased from Aldrich and purified by distillation from calcium hydride. Benzophenone ( $\text{Ph}_2\text{CO}$ ) was purchased from Caledon and purified by recrystallization from anhydrous ethanol and then sublimation (50 °C, dynamic vacuum). *p*-Thiocresol ( $\text{HSC}_6\text{H}_4\text{-}p\text{-CH}_3$ ) and dihexylsilane were purchased from Aldrich and used without further purification. Benzyl mercaptan ( $\text{PhCH}_2\text{SH}$ ) was purchased from Aldrich and dried by vacuum distillation from 4 Å molecular sieves. Thiobenzophenone ( $\text{Ph}_2\text{CS}$ ) was synthesized according a literature procedure.<sup>103</sup> Trityl mercaptan ( $\text{Ph}_3\text{CSH}$ ) was purchased from Acros and purified by sublimation (90 °C, dynamic vacuum). Phenylsilane was prepared by literature procedures and was dried by distillation over calcium hydride.<sup>104</sup> Benzonitrile was purchased from Alfa Aesar and purified by vacuum distillation over potassium carbonate.  $\text{Ph}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Ph}_2$  (**3-2**)<sup>1a,b</sup> was prepared according to literature procedures.

### 3.12.2 B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-mediated reactions of (Me<sub>2</sub>SiH)<sub>2</sub> or disilane 2-2 leading to over-reduction chemistry

#### *Reaction of (Me<sub>2</sub>SiH)<sub>2</sub> with thiobenzophenone:*

This experiment and the following one were performed by Dan Harrison during his M.Sc. They are included here because the unidentified peak in Dan's <sup>1</sup>H NMR spectra (labeled "dyn peak" in original spectra, but now removed because of proper assignment) was identified as the over-reduction product, diphenylmethane (Ph<sub>2</sub>CH<sub>2</sub>). In a Schlenk flask equipped with a stir bar, (Me<sub>2</sub>SiH)<sub>2</sub> (0.075 g, 0.65 mmol), thiobenzophenone (0.25 g, 1.3 mmol), and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.003 g, 0.006 mmol) were combined with 1 mL of toluene. The blue solution turned clear and colorless and was stirred for 1 h under N<sub>2</sub> in a glove box. An aliquot was removed for <sup>1</sup>H NMR. The <sup>1</sup>H NMR spectrum (Figure 3.8) showed monosubstituted (Me<sub>2</sub>SiH-Si(SCHPh<sub>2</sub>)Me<sub>2</sub>) and disubstituted ((Me<sub>2</sub>SiSCHPh<sub>2</sub>)<sub>2</sub>) products, as well as over-reduction products (Ph<sub>2</sub>CH<sub>2</sub> and multiple Me<sub>2</sub>SiS-containing oligomers).

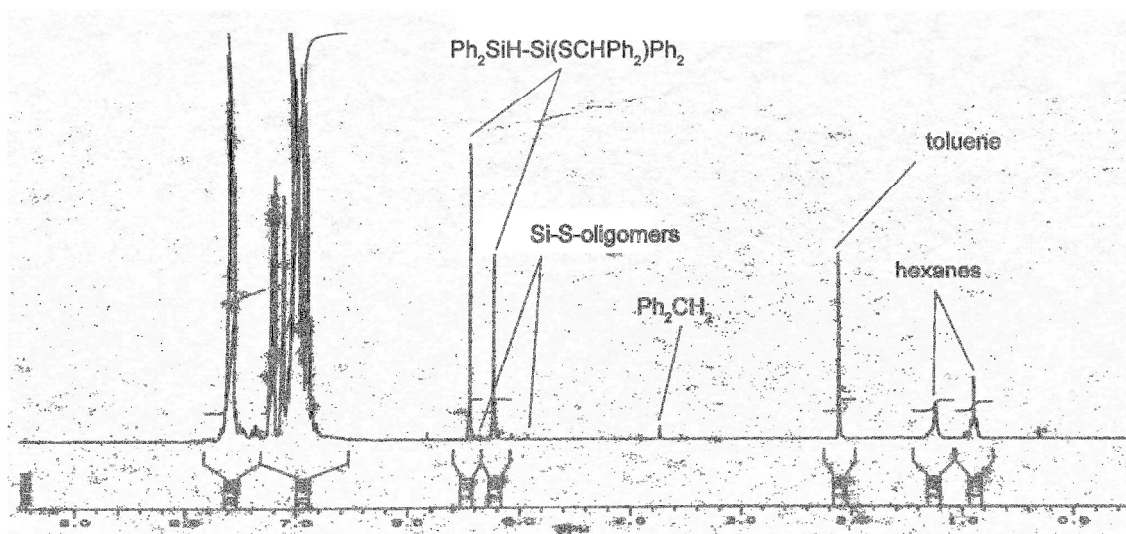


**Figure 3.8.**  $^1\text{H}$  NMR (250 MHz) of the crude reaction mixture in  $\text{C}_6\text{D}_6$  identifying major product  $\text{Me}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Me}_2$  and over-reduction minor products ( $\text{Ph}_2\text{CH}_2$  and  $\text{Me}_2\text{Si-S}$ -containing oligomers).

*Reaction of disilane 2-2 with thiobenzophenone:*

This experiment (see above notes) was performed by Dan Harrison. In a Schlenk flask equipped with a stir bar, disilane (0.19 g, 0.50 mmol), thiobenzophenone (0.10 g, 0.50 mmol), and  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.020 g, 0.040 mmol) were combined with 4 mL of toluene. The blue solution turned green and was stirred for 1.5 h under  $\text{N}_2$  (closed flask). After 2.5 h, the solution was clear and slightly yellow, almost colorless. The volume of the solvent was reduced to approximately  $\frac{1}{3}$  of its starting volume by evacuation.  $\text{PPh}_3$  (0.011 g, 0.041 mmol) and pentane (2 mL) were added. A cloudy white precipitate formed. The mixture was filtered through a Celite filter stick and a clear and colorless eluent was collected. Volatiles were removed under vacuum for 3 h. A viscous, clear, colorless oil was isolated. An aliquot was removed for  $^1\text{H}$  NMR (Figure 3.9). The  $^1\text{H}$  NMR spectrum

showed the major product ( $\text{Ph}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Ph}_2$ ) as well as over-reduction products (diphenylmethane, Si-S-containing oligomers).

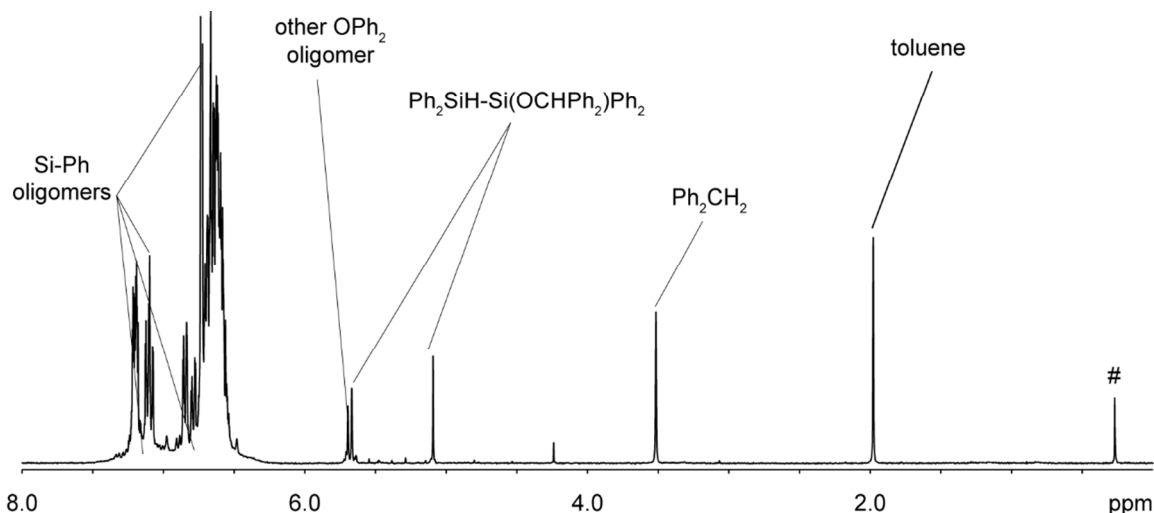


**Figure 3.9.**  $^1\text{H}$  NMR (250 MHz) of the crude reaction mixture in  $\text{C}_6\text{D}_6$  showing major product  $\text{Ph}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Ph}_2$  and minor over-reduction products ( $\text{Ph}_2\text{CH}_2$  and Si-S-containing oligomers).

*Reaction of disilane 2-2 with benzophenone:*

In a Schlenk flask equipped with a stir bar, **2-2** (0.10 g, 0.27 mmol), benzophenone (0.050 g, 0.27 mmol), and  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.014 g, 0.027 mmol) were combined with 1 mL of toluene. The solution was stirred for 16 h under  $\text{N}_2$  (closed flask).  $\text{PPh}_3$  (0.007 g, 0.03 mmol) was added and the mixture was stirred for 5 min. The solvent was removed by evacuation to give a cloudy viscous oil. Hexanes (1 mL) was added and a cloudy white precipitate formed. The mixture was filtered through a Celite filter stick (to remove precipitated phosphine-borane). Hexanes (1 mL x 5) was added to wash the filter stick. A clear and colorless filtrate was collected and the fractions were combined. Volatiles were removed under dynamic vacuum at RT for 3 h. A viscous, clear, colorless oil was isolated. An aliquot was removed for  $^1\text{H}$  NMR (Figure 3.10). The  $^1\text{H}$  NMR

spectrum showed the major product ( $\text{Ph}_2\text{SiH-Si}(\text{OCHPh}_2)\text{Ph}_2$ ) as well as over-reduction products (diphenylmethane and Si-O-containing oligomers).



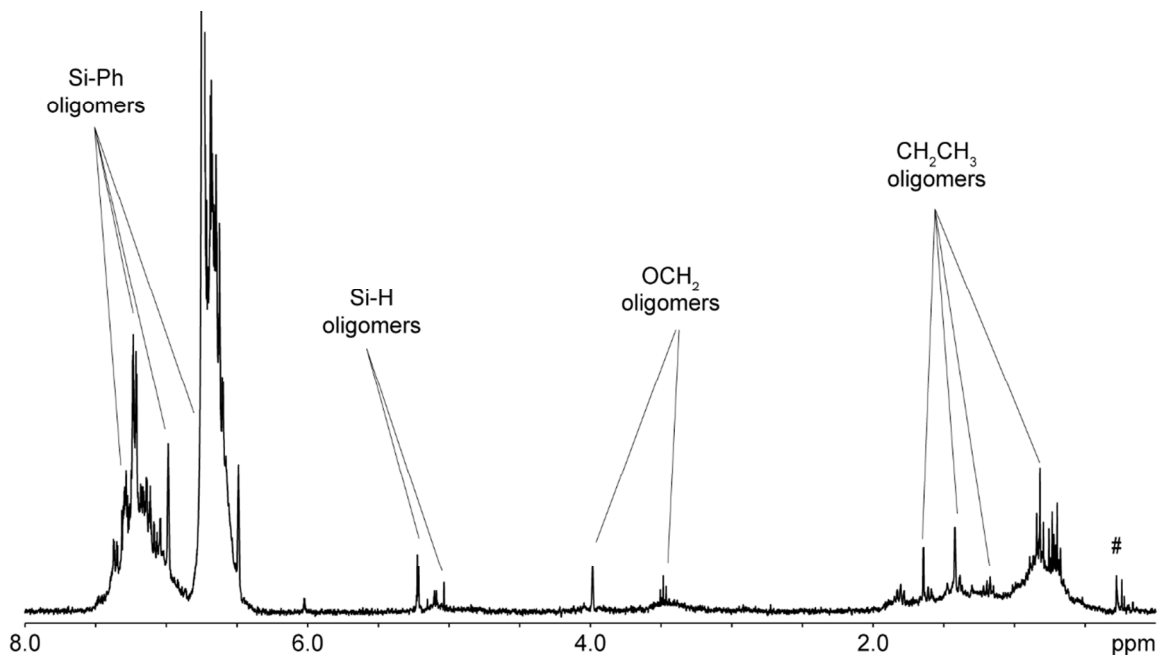
**Figure 3.10.**  $^1\text{H}$  NMR (300 MHz) of the crude reaction mixture in  $\text{C}_6\text{D}_6$  identifying major product  $\text{Ph}_2\text{SiH-Si}(\text{OCHPh}_2)\text{Ph}_2$  and over-reduction minor products ( $\text{Ph}_2\text{CH}_2$  and Si-O-containing oligomers).

*Reaction of disilane 2-2 with propionaldehyde:*

In a “bomb” flask equipped with a stir bar, **2-2** (0.199 g, 0.54 mmol) and  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.029 g, 0.057 mmol) were combined with propionaldehyde (1.0 mL, 14 mmol). The mixture was degassed by one freeze-pump-thaw cycle and then was stirred and heated to  $70\text{ }^\circ\text{C}^{\text{xxxi}}$  in a sealed flask under static vacuum. After 16 h, volatiles were removed by evacuation giving a clear, slightly-yellow oil. Hexanes (1 mL) was added to dissolve the residual oil and the solution was eluted through a Florisil column (to remove  $\text{B}(\text{C}_6\text{F}_5)_3$ ). The column was washed with hexanes (4 x 1 mL). Volatiles were removed from the combined washings under dynamic vacuum at  $70\text{ }^\circ\text{C}$  for 1 h. A clear, yellow oil was

<sup>xxxi</sup> No reaction of **2-2** with propionaldehyde occurs at RT over 72 h.

isolated (0.055 g).  $^1\text{H}$  NMR (Figure 3.11) showed sharp and broad peaks attributed to  $\text{OCH}_2\text{CH}_2\text{CH}_3$ , Si-H, and Si-Ph groups in multiple products.



**Figure 3.11.**  $^1\text{H}$  NMR (300 MHz) of the crude reaction mixture in  $\text{C}_6\text{D}_6$  showing multiple and/or broad Si-Ph, Si-H,  $\text{OCH}_2$ , or  $\text{CH}_2\text{CH}_3$ , peaks consistent with complex over-reduction reactions.

### 3.12.3 $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reactions of oxygen-containing substrates with $\text{Ph}_2\text{SiH}_2$ or $\text{PhSiH}_3$ , to identify possible over-reduction products

#### *Representative procedure:*

In a Schlenk flask equipped with a stir bar, the following were combined:  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.005 g, 0.01 mmol), silane (0.037 g, 0.10 mmol of  $\text{Ph}_2\text{SiH}_2$  or 0.022 g, 0.20 mmol of  $\text{PhSiH}_3$ ), O/S-substrate (0.020 mmol), and  $\text{C}_6\text{D}_6$  (1 mL) (unless otherwise noted). The mixture was stirred for 5 to 10 min (unless otherwise noted) then transferred to an NMR tube and a  $^1\text{H}$  NMR spectrum was obtained. Substrate was completely consumed in all examples below. Reported percentages are relative amounts of Si-containing products based on  $^1\text{H}$  NMR integration.

*Ph<sub>2</sub>SiH<sub>2</sub> + acetone:*

<sup>1</sup>H NMR (300 MHz) **propane** (trace): δ 0.86 (t, 6H, CH<sub>3</sub>), 1.26 (septet, 2H, CH). **Ph<sub>2</sub>SiH(OCH(CH<sub>3</sub>)<sub>2</sub>)** (<1%): δ 1.00 (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 6H, CH<sub>3</sub>), 4.05 (septet, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 1H, CH), 5.49 (s, <sup>1</sup>J<sub>SiH</sub> was not detected due to its low concentration, 1H, Si-H), 7.18-7.23 (m, 6H, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.75-7.81 (m, 4H, H<sub>o</sub>-SiPh<sub>2</sub>). **(Ph<sub>2</sub>SiH)<sub>2</sub>O** (99%): δ 5.91 (s, <sup>1</sup>J<sub>SiH</sub> = 218 Hz, 2H, Si-H), 7.08-7.21 (m, overlapping with C<sub>6</sub>D<sub>5</sub>H, 12H, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.63 (d, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 8H, H<sub>o</sub>-SiPh<sub>2</sub>).

*PhSiH<sub>3</sub> + acetone:*

<sup>1</sup>H NMR (300 MHz) **propane** (trace): *vide supra*. **PhSiH(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>** (5%): δ 1.13 (d, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 12H, CH<sub>3</sub>), 2.71 (m, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 2H, CH), Si-H and Si-Ph signals were difficult to distinguish from broad and sharp signals in polysiloxane and short-chain oligomers. **Polysiloxane** (95%): δ 5.36-5.70 (br m, FWHM = 70 Hz, overlapping with Si-H in PhSiH(OCH(CH<sub>3</sub>)<sub>2</sub>), Si-H), 6.97-7.22 (br m, FWHM = 50 Hz, overlapping with C<sub>6</sub>D<sub>5</sub>H, overlapping with H<sub>m/p</sub>-SiPh in PhSiH(OCH(CH<sub>3</sub>)<sub>2</sub>), H<sub>m/p</sub>-SiPh), 7.49-7.82 (br m, FWHM = 50 Hz, overlapping with H<sub>o</sub>-SiPh in PhSiH(OCH(CH<sub>3</sub>)<sub>2</sub>), H<sub>o</sub>-SiPh).

*Ph<sub>2</sub>SiH<sub>2</sub> + cyclohexanone:*

<sup>1</sup>H NMR (300 MHz) **cyclohexane**: δ 1.41 (s, 12H, CH<sub>2</sub>). **Ph<sub>2</sub>SiH(OC<sub>6</sub>H<sub>11</sub>)** (70%): δ 1.01-1.13 (m, 3H, OCHCH<sub>2</sub>CH<sub>eq</sub> and OCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>eq</sub>), 1.23-1.34 (m, 1H, OCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>ax</sub>), 1.44-1.55 (m, 2H, OCHCH<sub>eq</sub>), 1.55-1.67 (m, 2H, OCHCH<sub>2</sub>CH<sub>ax</sub>), 1.79-1.89 (m, 2H, OCHCH<sub>ax</sub>), 3.81-3.90 (m, 1H, OCH), 5.78 (s, <sup>1</sup>J<sub>SiH</sub> = 210 Hz, 1H, Si-H). 7.13-7.22 (m, overlapping with H<sub>m/p</sub>-SiPh<sub>2</sub> in (Ph<sub>2</sub>SiH)<sub>2</sub>O, 6H, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.72-7.76 (m, 4H, H<sub>o</sub>-SiPh<sub>2</sub>). **(Ph<sub>2</sub>SiH)<sub>2</sub>O** (30%): *vide supra*.

*PhSiH<sub>3</sub> + cyclohexanone:*

<sup>1</sup>H NMR (300 MHz) **cyclohexane**: *vide supra*. **Polysiloxane** (>99%): δ 1.08-1.95 (m, cyclohexyl groups appended to polysiloxane, OC<sub>6</sub>H<sub>11</sub>), 5.26-5.72 (br m, FWHM = 80 Hz, 2H, Si-H), 6.95-7.23 (br m, FWHM = 60 Hz, overlapping with C<sub>6</sub>D<sub>5</sub>H and H<sub>*m/p*</sub>-SiPh in (PhSiH<sub>2</sub>)<sub>2</sub>O, H<sub>*m/p*</sub>-SiPh), 7.44-7.86 (br m, FWHM = 80 Hz, overlapping with H<sub>*o*</sub>-SiPh in (PhSiH<sub>2</sub>)<sub>2</sub>O, H<sub>*o*</sub>-SiPh).

*Ph<sub>2</sub>SiH<sub>2</sub> + t-butanol:*

<sup>1</sup>H NMR (300 MHz) **methylpropane** (trace): δ 0.86 (d, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 9H, CH<sub>3</sub>), 1.55-1.71 (m, 1H, CH). **Ph<sub>2</sub>SiH(OC(CH<sub>3</sub>)<sub>3</sub>)** (95%): δ 0.95 (s, 9H, CH<sub>3</sub>), 5.81 (s, 1H, <sup>1</sup>J<sub>SiH</sub> = 208 Hz, Si-H), 7.15-7.22 (m, overlapping with C<sub>6</sub>D<sub>5</sub>H, 6H, H<sub>*m/p*</sub>-SiPh<sub>2</sub>), 7.68-7.74 (m, 4H, H<sub>*o*</sub>-SiPh<sub>2</sub>). **(Ph<sub>2</sub>SiH)<sub>2</sub>O** (5%): *vide supra*.

*PhSiH<sub>3</sub> + t-butanol:*

<sup>1</sup>H NMR (300 MHz) **methylpropane** (trace): *vide supra*. **PhSiH<sub>2</sub>OC(CH<sub>3</sub>)<sub>3</sub>** or **PhSiH(OCH(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>**<sup>xxxii</sup> (<1%): δ 1.10 (s, 9H or 18H, C(CH<sub>3</sub>)<sub>3</sub>), Si-H and Si-Ph signals were difficult to distinguish from broad and sharp signals in polysiloxane and short-chain oligomers. **Polysiloxane** (99%): δ 5.39-5.67 (br m, FWHM = 70 Hz, Si-H), 6.97-7.23 (br m, FWHM = 60 Hz, overlapping with C<sub>6</sub>D<sub>5</sub>H, H<sub>*m/p*</sub>-SiPh), 7.49-7.82 (br m, FWHM = 70 Hz, H<sub>*o*</sub>-SiPh).

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<sup>xxxii</sup> Assignment of the monosubstituted or disubstituted product could not be made because of the overlapping polysiloxane peaks in the Si-H and Si-Ph region.

*Ph<sub>2</sub>SiH<sub>2</sub> + p-methylanisole:*

Reaction time was 1 h. <sup>1</sup>H NMR (300 MHz) **methane** (trace): δ 0.16 (s, 4H, CH<sub>4</sub>). **Ph<sub>2</sub>SiH(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)** (75%): δ 1.96 (s, 3H, *p*-CH<sub>3</sub>), 5.08 (br s<sup>xxxiii</sup>, FWHM = 20 Hz, 1H, Si-H), 6.78 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2H, H<sub>o</sub>-OC<sub>6</sub>H<sub>4</sub>), 6.97 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, overlapping with H<sub>m</sub>-OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> in Ph<sub>2</sub>Si(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>, 2H, H<sub>m</sub>-OC<sub>6</sub>H<sub>4</sub>), 7.07-7.18 (m, overlapping with H<sub>m/p</sub>-SiPh<sub>2</sub> in Ph<sub>2</sub>Si(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>, 6H, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.68-7.72 (d, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 4H, H<sub>o</sub>-SiPh<sub>2</sub>). **Ph<sub>2</sub>Si(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>** (25%): δ 2.02 (s, 6H, *p*-CH<sub>3</sub>), 6.82 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 4H, H<sub>o</sub>-OC<sub>6</sub>H<sub>4</sub>), 6.97 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, overlapping with H<sub>m</sub>-OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> in Ph<sub>2</sub>SiH(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 4H, H<sub>m</sub>-OC<sub>6</sub>H<sub>4</sub>), 7.10-7.15 (m, overlapping with H<sub>m/p</sub>-SiPh<sub>2</sub> in Ph<sub>2</sub>SiH(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 6H, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.80-7.94 (m, 4H, H<sub>o</sub>-SiPh<sub>2</sub>).

*PhSiH<sub>3</sub> + p-methylanisole:*

Reaction time was 1 h. <sup>1</sup>H NMR (300 MHz) **methane** (trace): *vide supra*. **PhSiH<sub>2</sub>(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)** (85%): δ 2.01 (s, 3H, CH<sub>3</sub>), 4.32 (br s, <sup>xxxiii</sup> FWHM = 90 Hz, 2H, Si-H), 6.80 (d, <sup>3</sup>J<sub>HH</sub> = 5 Hz, 2H, H<sub>m</sub>-OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.02 (d, <sup>3</sup>J<sub>HH</sub> = 5 Hz, overlapping with H<sub>o</sub>-OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> in PhSiH(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>, 2H, H<sub>m</sub>-OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.06-7.15 (m, overlapping with H<sub>m/p</sub>-OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> in PhSiH(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>, 3H, H<sub>m/p</sub>-OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.79 (d, <sup>3</sup>J<sub>HH</sub> = 5 Hz, 2H, H<sub>o</sub>-SiPh). **PhSiH(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>** (15%): δ 1.99 (s, 6H, CH<sub>3</sub>), 4.32 (br s, <sup>xxxiii</sup> FWHM = 90 Hz, 1H, Si-H), 6.83 (d, <sup>3</sup>J<sub>HH</sub> = 5 Hz, 4H, H<sub>m</sub>-OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.02 (d, <sup>3</sup>J<sub>HH</sub> = 5 Hz, overlapping with H<sub>o</sub>-OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> in PhSiH<sub>2</sub>(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 4H, H<sub>m</sub>-OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.06-7.15 (m, overlapping with H<sub>m/p</sub>-OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> in PhSiH<sub>2</sub>(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 3H, H<sub>m/p</sub>-OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.94 (d, <sup>3</sup>J<sub>HH</sub> = 5 Hz, 2H, H<sub>o</sub>-SiPh).

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<sup>xxxiii</sup> This Si-H broadening has been reported previously with Et<sub>3</sub>SiH.<sup>42b</sup>

*Ph<sub>2</sub>SiH<sub>2</sub> + p-t-butylphenol:*

Reaction and <sup>1</sup>H NMR done in CDCl<sub>3</sub>. <sup>1</sup>H NMR (300 MHz) **Ph<sub>2</sub>SiH(OC<sub>6</sub>H<sub>4</sub>-p-<sup>t</sup>Bu)** (85%): δ 1.26 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 5.12 (br s, <sup>xxxiii</sup> FWHM = 40 Hz, 1H, Si-H), 6.85-6.90 (m, 2H, H<sub>m</sub>-OC<sub>6</sub>H<sub>4</sub>-p-<sup>t</sup>Bu), 7.18-7.23 (m, 2H, H<sub>o</sub>-OC<sub>6</sub>H<sub>4</sub>-p-<sup>t</sup>Bu), 3.34-7.44 (m, overlapping with H<sub>m/p</sub>-SiPh<sub>2</sub> in Ph<sub>2</sub>SiH<sub>2</sub> and Ph<sub>2</sub>Si(OC<sub>6</sub>H<sub>4</sub>-p-<sup>t</sup>Bu)<sub>2</sub>, 6H, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.66-7.70 (m, 4H, H<sub>o</sub>-SiPh<sub>2</sub>). **Ph<sub>2</sub>Si(OC<sub>6</sub>H<sub>4</sub>-p-<sup>t</sup>Bu)<sub>2</sub>** (15%): δ 1.23 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 7.12-7.18 (m, 4H, H<sub>o</sub>-OC<sub>6</sub>H<sub>4</sub>-p-<sup>t</sup>Bu), 7.21-7.25 (m, overlapping with H<sub>m</sub>-OC<sub>6</sub>H<sub>4</sub>-p-<sup>t</sup>Bu in Ph<sub>2</sub>SiH(OC<sub>6</sub>H<sub>4</sub>-p-<sup>t</sup>Bu), 4H, H<sub>m</sub>-OC<sub>6</sub>H<sub>4</sub>-p-<sup>t</sup>Bu), 7.34-7.44 (m, overlapping with H<sub>m/p</sub> in Ph<sub>2</sub>SiH(OC<sub>6</sub>H<sub>4</sub>-p-<sup>t</sup>Bu), 6H, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.74-7.78 (m, 4H, H<sub>o</sub>-SiPh<sub>2</sub>).

*PhSiH<sub>3</sub> + p-t-butylphenol:*

Reaction and <sup>1</sup>H NMR done in CDCl<sub>3</sub>. <sup>1</sup>H NMR (300 MHz) **PhSiH(OC<sub>6</sub>H<sub>4</sub>-p-<sup>t</sup>Bu)<sub>2</sub>** (99%): δ 1.35 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 5.50 (s, 1H, Si-H), 6.98-7.04 (m, 4H, H<sub>o</sub>-OC<sub>6</sub>H<sub>4</sub>-p-<sup>t</sup>Bu), 7.23-7.25 (m, 4H, H<sub>m</sub>-OC<sub>6</sub>H<sub>4</sub>-p-<sup>t</sup>Bu), 7.40-7.56 (overlapping m, 3H, H<sub>m/p</sub>-SiPh), 7.84-7.89 (m, 2H, H<sub>o</sub>-SiPh).

### 3.12.4 B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed reactions of sulfur-containing substrates with Ph<sub>2</sub>SiH<sub>2</sub> or PhSiH<sub>3</sub> to identify possible over-reduction products

*Representative procedure was identical to that described above for O-substrates:*

*PhSiH<sub>3</sub> + n-propylthiol:*

<sup>1</sup>H NMR (300 MHz) **PhSiH(SCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>** (>99%): δ 0.74 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 6H, CH<sub>3</sub>), 1.44 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 4H, SiSCH<sub>2</sub>CH<sub>2</sub>), 2.31 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 4H, SiSCH<sub>2</sub>), 5.88 (s, <sup>1</sup>J<sub>SiH</sub> = 235 Hz, 1H, Si-H), 7.05-7.17 (m, overlapping with C<sub>6</sub>D<sub>5</sub>H, 3H, H<sub>m/p</sub>-SiPh), 7.82 (d, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 2H, H<sub>o</sub>-SiPh).

*Ph<sub>2</sub>SiH<sub>2</sub> + p-thiocresol:*

<sup>1</sup>H NMR (300 MHz) **Ph<sub>2</sub>SiH(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)** (70%): δ 1.88 (s, 3H, CH<sub>3</sub>), 5.87 (s, <sup>1</sup>J<sub>HH</sub> = 221 Hz, 1H, Si-H), 6.67 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, H<sub>o</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>, 2H), 7.06-7.15 (m, overlapping with H<sub>m/p</sub>-SiPh<sub>2</sub> in Ph<sub>2</sub>Si(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>, 6H, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.36 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2H, H<sub>m</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.65-7.69 (m, 4H, H<sub>o</sub>-SiPh<sub>2</sub>). **Ph<sub>2</sub>Si(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>** (30%): δ 1.92 (s, 6H, CH<sub>3</sub>), 6.73 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 4H, H<sub>o</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.06-7.15 (m, overlapping with H<sub>m/p</sub>-SiPh<sub>2</sub> in Ph<sub>2</sub>SiH(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 6H, H<sub>m/p</sub>-SiPh<sub>2</sub>), 7.40 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 4H, H<sub>m</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.71-7.75 (m, 4H, H<sub>o</sub>-SiPh<sub>2</sub>).

*PhSiH<sub>3</sub> + p-thiocresol:*

Reaction and <sup>1</sup>H NMR done in CDCl<sub>3</sub>. <sup>1</sup>H NMR (300 MHz) **PhSiH<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)** (55%): δ 2.33 (s, overlapping with *p*-CH<sub>3</sub> in PhSiH(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>, 3H, CH<sub>3</sub>), 5.17 (s, <sup>1</sup>J<sub>SiH</sub> = 221 Hz, 2H, Si-H), 7.06 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, overlapping with H<sub>m</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> in PhSiH(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>, 2H, H<sub>m</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.06 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, overlapping with H<sub>m</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> in PhSiH(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>, 2H, H<sub>m</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.30 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, overlapping with H<sub>o</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> in PhSiH(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>, 2H, H<sub>o</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.33-7.50 (m, overlapping with H<sub>m/p</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> in PhSiH(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>, 3H, H<sub>m/p</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.62-7.67 (m, overlapping with H<sub>o</sub>-SiPh in PhSiH(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>, 2H, H<sub>o</sub>-SiPh). **PhSiH(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)<sub>2</sub>** (45%): δ 2.33 (s, overlapping with *p*-CH<sub>3</sub> in PhSiH<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 6H, CH<sub>3</sub>), 5.77 (s, <sup>1</sup>J<sub>SiH</sub> = 249 Hz, 1H, Si-H), 7.06 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, overlapping with H<sub>m</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> in PhSiH<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 4H, H<sub>m</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.30 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, overlapping with H<sub>o</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> in PhSiH<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 4H, H<sub>o</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>), 7.33-7.50 (m, overlapping with H<sub>m/p</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> in

$\text{PhSiH}_2(\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3)$ , 3H,  $\text{H}_{m/p}\text{-SC}_6\text{H}_4\text{-}p\text{-CH}_3$ ), 7.62-7.67 (m, overlapping with  $\text{H}_o\text{-SiPh}$  in  $\text{PhSiH}_2(\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3)$ , 2H,  $\text{H}_o\text{-SiPh}$ ).

*Ph<sub>2</sub>SiH<sub>2</sub> + benzyl mercaptan:*

Reaction time was 30 min.  $^1\text{H}$  NMR (300 MHz) **toluene** (trace):  $\delta$  2.11 ppm (3H,  $\text{CH}_3$ ), aromatic signals overlapped by  $(\text{Ph}_2\text{SiH})_2\text{S}$ ,  $\text{Ph}_2\text{SiH}(\text{SCHPh}_2)$ , and  $\text{Ph}_2\text{Si}(\text{SCH}_2\text{Ph})_2$ . **Ph<sub>2</sub>SiH(SCH<sub>2</sub>Ph)** (55%):  $^1\text{H}$  NMR  $\delta$  3.58 (s, 2H,  $\text{SCH}_2$ ), 5.68 (s,  $^1J_{\text{SiH}} = 218$  Hz, 1H, Si-H), 6.95-7.09 (m, overlapping with  $\text{H}_{o/m/p}\text{-Ph}$  in toluene and  $\text{H}_{o/m/p}\text{-SCH}_2\text{Ph}$  in  $\text{Ph}_2\text{Si}(\text{SCH}_2\text{Ph})_2$ , 5H,  $\text{H}_{o/m/p}\text{-SCH}_2\text{Ph}$ ), 7.10-7.15 (m, overlapping with  $\text{H}_{m/p}\text{-SiPh}_2$  in  $\text{Ph}_2\text{Si}(\text{SCH}_2\text{Ph})_2$ , 6H,  $\text{H}_{m/p}\text{-SiPh}_2$ ), 7.64-7.69 (m, 4H,  $\text{H}_o\text{-SiPh}_2$ ). **Ph<sub>2</sub>Si(SCH<sub>2</sub>Ph)<sub>2</sub>** (45%):  $\delta$  3.78 (s, 4H,  $\text{SCH}_2\text{Ph}$ ), 6.95-7.09 (m, overlapping with  $\text{H}_{o/m/p}\text{-Ph}$  in toluene and  $\text{H}_{m/p}\text{-SiPh}_2$  in  $\text{Ph}_2\text{SiH}(\text{SCH}_2\text{Ph})$ , 6H,  $\text{H}_{m/p}\text{-SiPh}_2$ ), 7.83-7.89 (m, 4H,  $\text{H}_o\text{-SiPh}_2$ ). **(Ph<sub>2</sub>SiH)<sub>2</sub>S** (trace):  $\delta$  5.78 (s,  $^1J_{\text{SiH}} = 221$  Hz, 2H, Si-H), 7.02-7.11 (m, 12H,  $\text{H}_{m/p}\text{-SiPh}$ ), 7.59-7.63 (m, 8H,  $\text{H}_o\text{-SiPh}$ )

*PhSiH<sub>3</sub> + benzyl mercaptan:*

Reaction time was 30 min.  $^1\text{H}$  NMR (500 MHz) **toluene** (trace) *vide supra*. **PhSiH<sub>2</sub>(SCH<sub>2</sub>Ph)** (75%):  $\delta$  3.50 (s, 2H,  $\text{SCH}_2$ ), 5.00 (br s, <sup>xxxiii</sup> FWHM = 30 Hz, 2H, Si-H), 6.97-7.14 (m, overlapping with  $\text{H}_{o/m/p}\text{-SCH}_2\text{Ph}$  and  $\text{H}_{m/p}\text{-SiPh}$  in  $\text{PhSiH}(\text{SCH}_2\text{Ph})_2$ , 8H,  $\text{H}_{o/m/p}\text{-SCH}_2\text{Ph}$  and  $\text{H}_{m/p}\text{-SiPh}$ ), 7.45-7.54 (m, 2H,  $\text{H}_o\text{-SiPh}$ ). **PhSiH(SCH<sub>2</sub>Ph)<sub>2</sub>** (25%):  $\delta$  3.66 (d,  $^2J_{\text{HH}} = 13$  Hz, 2H,  $\text{SCH}_2\text{Ph}$ ), <sup>xxxiv</sup> 3.74 (d,  $^2J_{\text{HH}} = 13$  Hz, 2H,  $\text{SCH}_2\text{Ph}$ ), <sup>xxxiv</sup> 5.72 (s,  $^1J_{\text{SiH}} = 240$  Hz, 1H, Si-H), 6.97-7.14 (m, overlapping with  $\text{H}_{o/m/p}\text{-$

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<sup>xxxiv</sup> The geminal protons on  $\text{SCH}_2\text{Ph}$  in  $\text{PhSiH}(\text{SCH}_2\text{Ph})_2$  are unique in the  $^1\text{H}$  NMR, suggesting some restricted rotation of the  $\text{SCH}_2\text{Ph}$  group in  $\text{PhSiH}(\text{SCH}_2\text{Ph})_2$ .

SCH<sub>2</sub>Ph and H<sub>*m/p*</sub>-SiPh in PhSiH<sub>2</sub>(SCH<sub>2</sub>Ph), 13H, H<sub>*o/m/p*</sub>-SCH<sub>2</sub>Ph and H<sub>*m/p*</sub>-SiPh), 7.69 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2H, H<sub>*o*</sub>-SiPh). (**PhSiH<sub>2</sub>**)<sub>2</sub>S (trace): 5.13 (br s, <sup>xxxiii</sup> 4H, Si-H), 7.01-7.13 (m, overlapping with H<sub>*o/m/p*</sub>-SCH<sub>2</sub>Ph and H<sub>*m/p*</sub>-SiPh in PhSiH<sub>2</sub>(SCH<sub>2</sub>Ph) and PhSiH(SCH<sub>2</sub>Ph)<sub>2</sub>, 3H, H<sub>*m/p*</sub>-SiPh), 7.46-7.50 (m, 2H, H<sub>*o*</sub>-SiPh).

*Ph<sub>2</sub>SiH<sub>2</sub> + thiobenzophenone:*

Reaction and <sup>1</sup>H NMR done in CDCl<sub>3</sub> to compare to <sup>1</sup>H NMR of the anticipated disilthiane reported in the literature.<sup>105,xxxv</sup> <sup>1</sup>H NMR (300 MHz) **diphenylmethane**: δ 4.04 (s, 2H, CH<sub>2</sub>), aromatic signals overlapped by (Ph<sub>2</sub>SiH)<sub>2</sub>S. (**Ph<sub>2</sub>SiH**)<sub>2</sub>S (>99%): δ 5.57 (s, <sup>1</sup>J<sub>SiH</sub> = 223 Hz, 2H, Si-H), 7.31-7.47 (m, overlapping with H<sub>*o/m/p*</sub>-Ph in Ph<sub>2</sub>CH<sub>2</sub> and residual CHCl<sub>3</sub>, 12H, H<sub>*m/p*</sub>-SiPh<sub>2</sub>), 7.66 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 8H, H<sub>*o*</sub>-SiPh<sub>2</sub>).

*PhSiH<sub>3</sub> + thiobenzophenone:*

Reaction and <sup>1</sup>H NMR done in CDCl<sub>3</sub> to compare to <sup>1</sup>H NMR of anticipated disilthiane reported in the literature.<sup>90,xxxv</sup> <sup>1</sup>H NMR (300 MHz) **diphenylmethane**: *vide supra*, aromatic signals overlapped by (PhSiH<sub>2</sub>)<sub>2</sub>S and [PhSiH-S]<sub>n</sub>. Over-reduction product was initially detected (**PhSiH<sub>2</sub>**)<sub>2</sub>S (>99%): δ 5.11 (br s, <sup>xxxiii</sup> <sup>1</sup>J<sub>SiH</sub> = 223 Hz, 4H, Si-H), 7.22-7.47 (m, overlapping with H<sub>*m/p*</sub>-SiPh in PhSiH<sub>3</sub>, overlapping with residual CHCl<sub>3</sub>, 6H, H<sub>*m/p*</sub>-SiPh), 7.65 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 4H, H<sub>*o*</sub>-SiPh).

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<sup>xxxv</sup> Other reactions were done in CDCl<sub>3</sub> to compare diagnostic <sup>1</sup>H NMR signals with initially anticipated over-reduction products.

*Ph<sub>2</sub>SiH<sub>2</sub> + trityl mercaptan:*

Mixture immediately became a clear yellow solution, then became clear and colorless after 15 s. <sup>1</sup>H NMR (300 MHz) **triphenylmethane**: δ 5.42, aromatic signals overlapped by (Ph<sub>2</sub>SiH)<sub>2</sub>S. **(Ph<sub>2</sub>SiH)<sub>2</sub>S** (>99%): *vide supra*.

*PhSiH<sub>3</sub> + trityl mercaptan:*

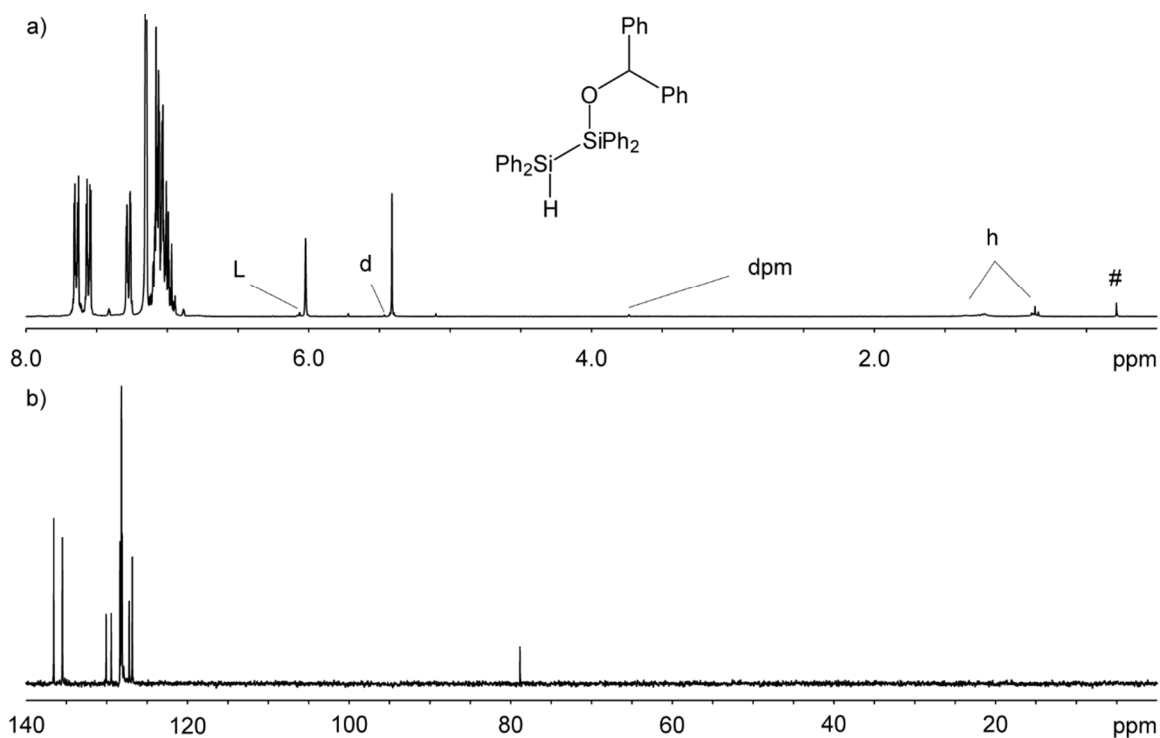
Mixture immediately became a clear yellow solution, then turned to clear and colorless after 5 s. <sup>1</sup>H NMR (300 MHz) **triphenylmethane**: *vide supra*, aromatic signals overlapped by (PhSiH<sub>2</sub>)<sub>2</sub>S. **(PhSiH<sub>2</sub>)<sub>2</sub>S** (>99%): *vide supra*.

### 3.12.5 Synthesis of substituted disilanes

*Ph<sub>2</sub>SiH-Si(OCHPh<sub>2</sub>)Ph<sub>2</sub> (3-1):*

In a Schlenk flask equipped with a stir bar, **2-2** (0.10 g, 0.27 mmol) and benzophenone (0.050 g, 0.27 mmol) were combined with toluene (1 mL). To this mixture a solution of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (1.4 mg, 0.0027 mmol) in toluene (1.0 mL) was added dropwise with stirring. The contents were left stirring under N<sub>2</sub> (closed flask) at RT. After 72 h, a solution of PPh<sub>3</sub> (0.7 mg, 0.003 mmol) in toluene (1.0 mL) was added. After 5 min of stirring, volatiles were removed under vacuum to give a clear viscous oil. The oil was dissolved in pentane (1 mL) and the solution was filtered through a Celite column (to remove precipitated phosphine-borane adduct). The Celite column was washed three times with pentane (3 x 1 mL). Volatiles were removed under dynamic vacuum at RT for 2 h. A clear and colorless oil was isolated (0.14 g, 93%. Trace impurities detected by <sup>1</sup>H NMR, see below). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 5.41 (s, <sup>1</sup>J<sub>SiH</sub> = 186 Hz, 1H, Si-H), 6.02

(s, 1H, OCH), 6.96-7.05 (overlapping m, 18H,  $H_{m/p}$ -HSiPh<sub>2</sub>,  $H_{m/p}$ -OSiPh<sub>2</sub>, and  $H_{m/p}$ -OCHPh<sub>2</sub>) 7.27 (d,  $^3J_{HH} = 8$  Hz, 4H,  $H_o$ -OCHPh<sub>2</sub>), 7.56 (d,  $^3J_{HH} = 8$  Hz, 4H,  $H_o$ -HSiPh), 7.64 (d,  $^3J_{HH} = 7$  Hz, 4H,  $H_o$ -O-SiPh); DEPT135 <sup>13</sup>C DEPT NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 78.9 (OCH), 126.8 (C<sub>p</sub>-OCHPh<sub>2</sub>), 127.2 (C<sub>o</sub>-OCHPh<sub>2</sub>), 128.1 (C<sub>m</sub>-OSiPh<sub>2</sub>), 128.2 (C<sub>m</sub>-OSiPh<sub>2</sub>), 128.4 (C<sub>m</sub>-OCHPh<sub>2</sub>), 129.4 (C<sub>p</sub>-HSiPh<sub>2</sub>), 130.1 (C<sub>p</sub>-OSiPh<sub>2</sub>), 135.5 (C<sub>o</sub>-HSiPh<sub>2</sub>), 136.6 (C<sub>o</sub>-OSiPh<sub>2</sub>). DEPT30 <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>) δ -4.1 (Si-O), -39.1 (Si-H). Anal. Calc. for C<sub>37</sub>H<sub>32</sub>OSi<sub>2</sub>: C 80.97 H 5.88. Found: C 86.73 H 6.56.<sup>xxxvi</sup>



**Figure 3.12.** a) <sup>1</sup>H NMR (300 MHz) and b) DEPT135 <sup>13</sup>C NMR (75 MHz) of Ph<sub>2</sub>SiH-Si(OCHPh<sub>2</sub>)Ph<sub>2</sub> (**3-1**) in C<sub>6</sub>D<sub>6</sub>. The “#” is grease. The “h” is hexanes. The “dpm” is diphenylmethane (Ph<sub>2</sub>CH<sub>2</sub>) from over-reduction. The “d” and “L” are Si-H and OCH resonances respectively for longer Si-Si-O-containing chains from over-reduction/partial reduction reactions.

<sup>xxxvi</sup> Trace impurities were detected by <sup>1</sup>H NMR, such “h”, “dpm”, “d”, and “L” shown in Figure 3.12. The presence of longer chains “d” and “L” suggests longer chains arising from over-reduction reactions may be present in quantities that are not readily identified by <sup>1</sup>H NMR.

*Identification of  $\text{Ph}_2\text{SiH-Si}(\text{SiHPh}_2)\text{Ph}_2$  from the reaction of  $\text{Ph}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Ph}_2$  with  $\text{Ph}_2\text{SiH}_2$*

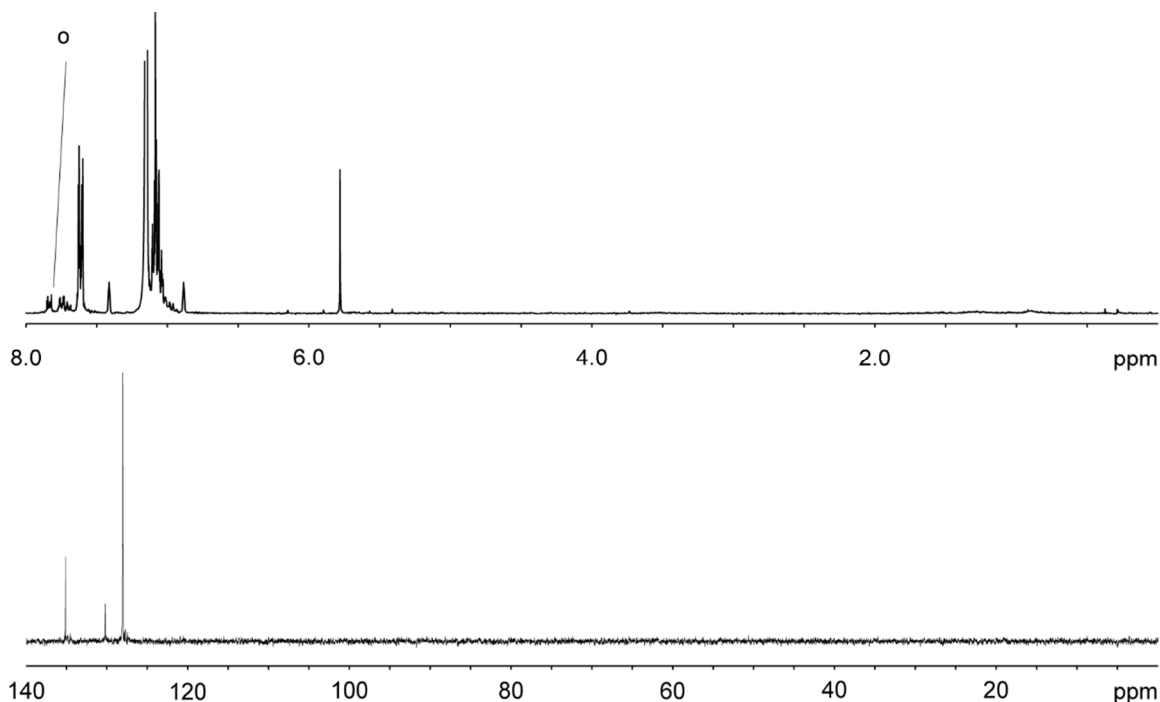
$\text{B}(\text{C}_6\text{F}_5)_3$  (0.003 g, 0.006 mmol),  $\text{Ph}_2\text{SiH}_2$  (0.010 g, 0.054 mmol),  $\text{Ph}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Ph}_2$  (0.032 g, 0.055 mmol), and  $d_6$ -benzene (1 mL) were combined in a sealable J-Young NMR tube for monitoring by  $^1\text{H}$  NMR. After 5 h, Si-H and C-H signals due to the starting  $\text{Ph}_2\text{SiH-Si}(\text{SCHPh}_2)\text{Ph}_2$  had disappeared, and signals due to two new Si-H moieties had appeared, attributable to  $\text{Ph}_2\text{SiH-Si}(\text{SSiHPh}_2)\text{Ph}_2$ , along with the  $\text{CH}_2$  peak corresponding to diphenylmethane. See Figure 3.5 for  $^1\text{H}$  NMR progress.

### 3.12.6 Preliminary attempts to make Si-S-containing oligomers and polymers

*Synthesis of  $(\text{Ph}_2\text{SiH})_2\text{S}$  (3-3):*

In a Schlenk flask equipped with a stir bar,  $\text{Ph}_2\text{SiH}_2$  (0.21 g, 1.1 mmol), trityl mercaptan (0.22 g, 0.79 mmol), and benzene (2 mL) were combined, giving a clear light brown solution. To the stirring solution,  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.017 g, 0.033 mmol) was added and the mixture bubbled and frothed vigorously. The solution was stirred under  $\text{N}_2$  (open to a Nujol bubbler). After 1 h, the solution turned to clear and colorless and the stirring was continued under  $\text{N}_2$  (closed flask). After 16 h, volatiles were removed by evacuation to give a white oily residue. The residue was dissolved in toluene (1 mL) to give a clear and colorless solution. The solution was passed through a Florisil column (to remove  $\text{B}(\text{C}_6\text{F}_5)_3$ ) and the column was rinsed with toluene (3 x 1 mL) to collect a clear and colorless filtrate. Volatiles were removed by evacuation to give a white oily residue. Hexanes (1 mL) was added to give a cloudy white solution (precipitating  $\text{Ph}_3\text{CH}$ ). This solution was cooled to  $-18\text{ }^\circ\text{C}$  (freezer) and then filtered on a sintered glass frit and washed with hexanes (2 x 1 mL). The clear and colorless filtrate was cooled to  $-18\text{ }^\circ\text{C}$

and white precipitate formed ( $\text{Ph}_3\text{CH}$ ). The mother liquor was decanted and filtered through a Celite filter stick. The Celite filter stick was washed with cold hexanes (2 x 1 mL). The fractions were combined and volatiles were removed by evacuation to give a cloudy oil. A Schlenk flask containing this oil was heated to 80 °C under dynamic vacuum to sublime residual  $\text{Ph}_3\text{CH}$ . The residual oil was dissolved in hexanes (1 mL) and decanted. Volatiles were removed under dynamic vacuum for 1 h. A clear and colorless oil was isolated (0.030 g, 13%)  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  5.78 (s,  $^1J_{\text{SiH}} = 221$  Hz, 2H, Si-H), 7.02-7.11 (m, 12H,  $\text{H}_{m/p}$ -SiPh), 7.59-7.63 (m, 8H,  $\text{H}_o$ -SiPh); DEPT135  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  128.1 ( $\text{C}_m$ -SiPh), 130.3 ( $\text{C}_p$ -SiPh), 135.2 ( $\text{C}_o$ -SiPh). DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -9.3. Anal. Calc. for  $\text{C}_{24}\text{H}_{22}\text{SSi}_2$ : C 72.31 H 5.56. Found: C 72.30 H 5.51.

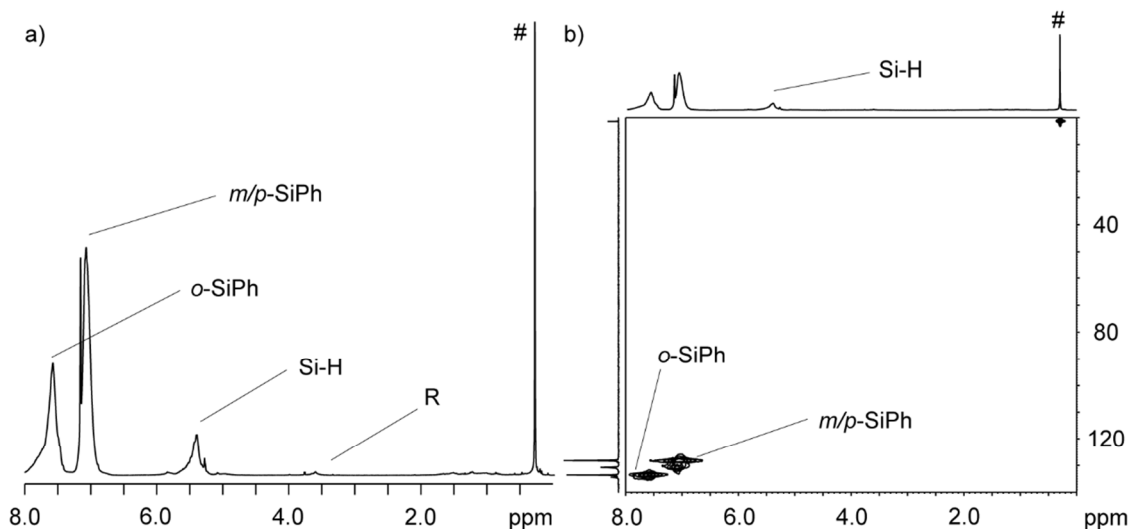


**Figure 3.13.** a)  $^1\text{H}$  NMR (300 MHz) and b) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $(\text{Ph}_2\text{SiH})_2\text{S}$  (**3-3**) in  $\text{C}_6\text{D}_6$ . The “o” is the phenyl groups belonging to a longer chain Si-S-containing oligomers, suspected to be  $\text{Ph}_2\text{SiH-S-Ph}_2\text{Si-S-Ph}_2\text{SiH}$ . The C/H ratios in **3-3** and suspected  $\text{Ph}_2\text{SiH-S-Ph}_2\text{Si-S-Ph}_2\text{SiH}$  are similar and contribute to the satisfactory elemental analysis result.

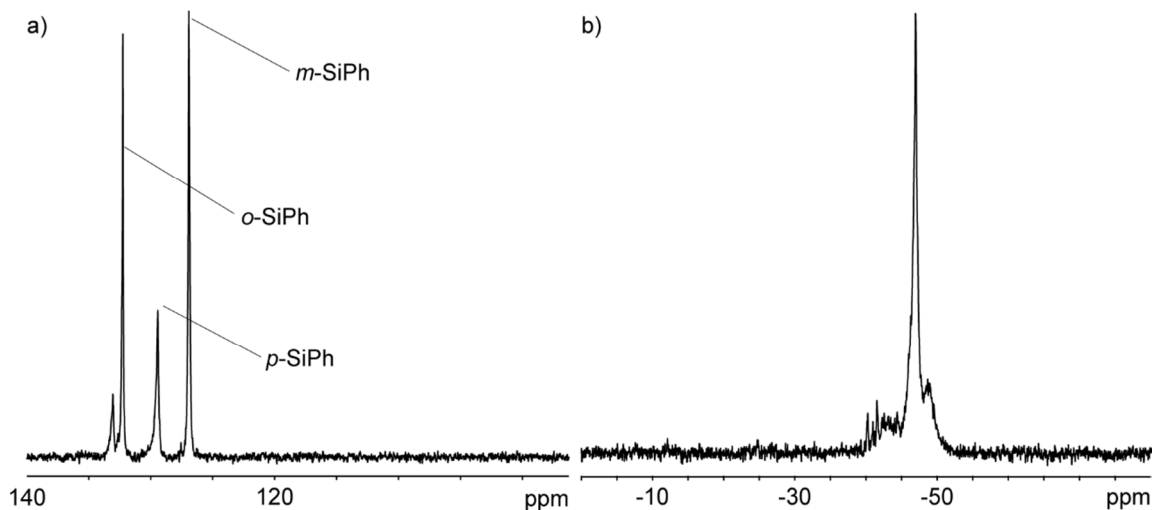
*Synthesis of  $[\text{PhSiH-S}]_n$  (**3-4**):*

In a Schlenk flask equipped with a stir bar,  $\text{PhSiH}_3$  (0.20 mL, 1.6 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.025 g, 0.15 mmol), and benzyl mercaptan (0.18 mL, 1.5 mmol) were combined in a neat mixture. The solution immediately bubbled ( $\text{H}_2$ ) for 1-2 minutes. The solution was stirred at RT for 16 h in a closed flask. Volatiles were removed by evacuation to give a clear and colorless oil. Hexanes (1 mL) was added to give a cloudy white solution. The mixture was eluted through a Florisil column and a clear and colorless filtrate was collected. The Florisil column was washed with hexanes (5 x 1 mL), and the fractions were combined. Volatiles were removed by evacuation and a crude  $^1\text{H}$  NMR showed sharp signals indicative of short-chain oligomers and partial reduction products all in trace quantities. The column was then washed with toluene (5 mL) and a

clear and colorless extract was collected, separately from the hexanes extracts. Volatiles were removed from the toluene extract by evacuation for 16 h to give a white, oily solid (0.21 g).



**Figure 3.14** a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of  $[\text{PhSiH-S}]_n$  (**3-4**) in  $\text{C}_6\text{D}_6$ . The “#” is grease. The “R” is residual partial reduction unit. This may be any of the following structural units: repeat unit,  $-\text{PhSi}(\text{SCH}_2\text{Ph})\text{S}-$ ; monosubstituted endcap,  $-\text{PhSi}(\text{H})\text{SCH}_2\text{Ph}$ ; or disubstituted endcap,  $-\text{PhSi}(\text{SCH}_2\text{Ph})_2$ .



**Figure 3.15.** a) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of the phenyl region (95-140 ppm) and b) DEPT90  $^{29}\text{Si}$  NMR (99 MHz) of  $[\text{PhSiH-S}]_n$  (**3-4**) in  $\text{C}_6\text{D}_6$ .

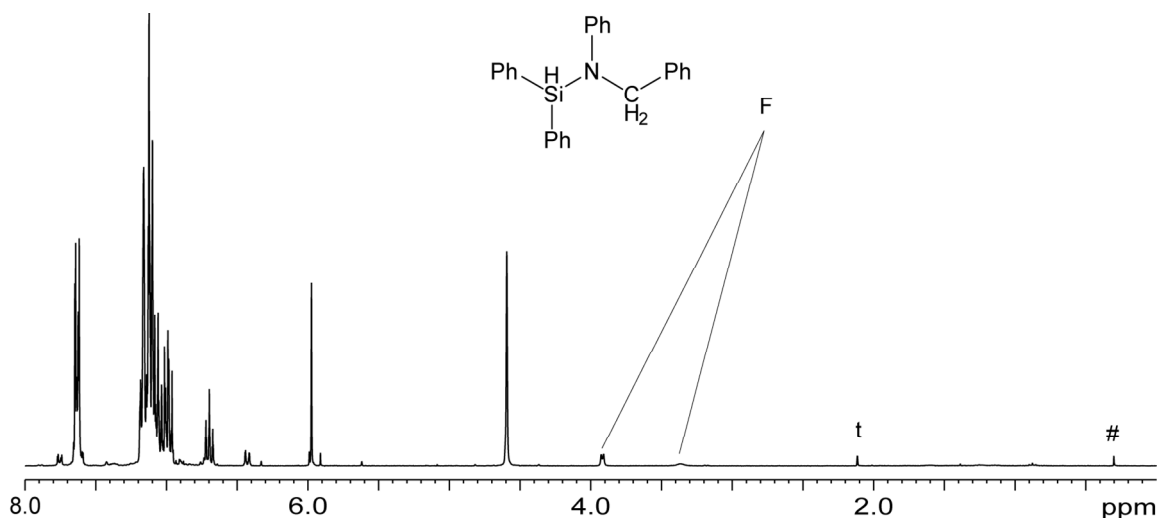
*Synthesis of oligomer mixture [PhSiH-S] (3-5):*

In a Schlenk flask equipped with a stir bar, PhSiH<sub>3</sub> (0.21 g, 1.9 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.013 g, 0.025 mmol), and trityl mercaptan (0.51 g, 1.8 mmol) were combined in benzene (1 mL). The solution immediately bubbled (H<sub>2</sub>) for 1-2 minutes and turned to a clear slightly-orange solution. The orange color faded over 1 h and a white precipitate formed. The mixture was stirred for 16 h in a closed flask. After 16 h, the solution was cloudy and white. Volatiles were removed by evacuation to give an oily white residue. The residue was dissolved in benzene (5 mL) and the solution was passed through a Florisil column (some of the Ph<sub>3</sub>CH precipitated on the column and was removed). The column was washed with additional benzene (10 x 1 mL) to give a clear and colorless filtrate. Volatiles were removed by evacuation to give a clear and colorless oil. The oil was heated to 90 °C under vacuum and a white solid (Ph<sub>3</sub>CH) collected on the sublimation cold finger. The residual oil was dissolved in benzene and then transferred to a new flask. Volatiles were removed under dynamic vacuum for 1 h to give a clear and colorless oil (0.017 g). See <sup>1</sup>H NMR (Figure 3.7).

**3.12.7 Reactions of small silanes (Ph<sub>2</sub>SiH<sub>2</sub> and PhSiH<sub>3</sub>) with benzylideneaniline as determined by <sup>1</sup>H NMR***Ph<sub>2</sub>SiH-N(Ph)CH<sub>2</sub>Ph (3-6):*

In a Schlenk flask equipped with a stir bar, Ph<sub>2</sub>SiH<sub>2</sub> (0.20 g, 1.1 mmol), benzylideneaniline (0.20 g, 1.1 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.019 g, 0.037 mmol) were combined with toluene (1 mL) to give a clear yellow solution. The contents were stirred under N<sub>2</sub> (closed flask). After 2 h, PPh<sub>3</sub> (0.010 g, 0.038 mmol) was added. The solution immediately turned to clear and colorless. Volatiles were removed by evacuation to give

an oily residue. Pentane (1 mL) was added and the cloudy white solution was filtered through a Celite column (to remove precipitated phosphine-borane adduct). The column was washed with pentane (5 x 1 mL) to give a clear and colorless combined filtrate. Volatiles were removed under dynamic vacuum for 2 h. A clear and colorless oil was isolated (0.29 g, 73%).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  4.59 (s, 2H,  $\text{NCH}_2$ ), 5.98 (s,  $^1J_{\text{SiH}} = 213$  Hz, 1H, Si-H), 6.70 (t,  $^3J_{\text{HH}} = 7$  Hz, 1H,  $\text{H}_p\text{-NPh}$ ), 6.94-7.20 (m, overlapping with  $\text{C}_6\text{D}_5\text{H}$ , 15H,  $\text{H}_{m/p}\text{-SiPh}_2$ ,  $\text{H}_{o/m}\text{-NPh}$ ,  $\text{H}_{o/m/p}\text{-NCH}_2\text{Ph}$ ), 7.63 (d,  $^3J_{\text{HH}} = 7$  Hz, 4H,  $\text{H}_o\text{-SiPh}_2$ ).

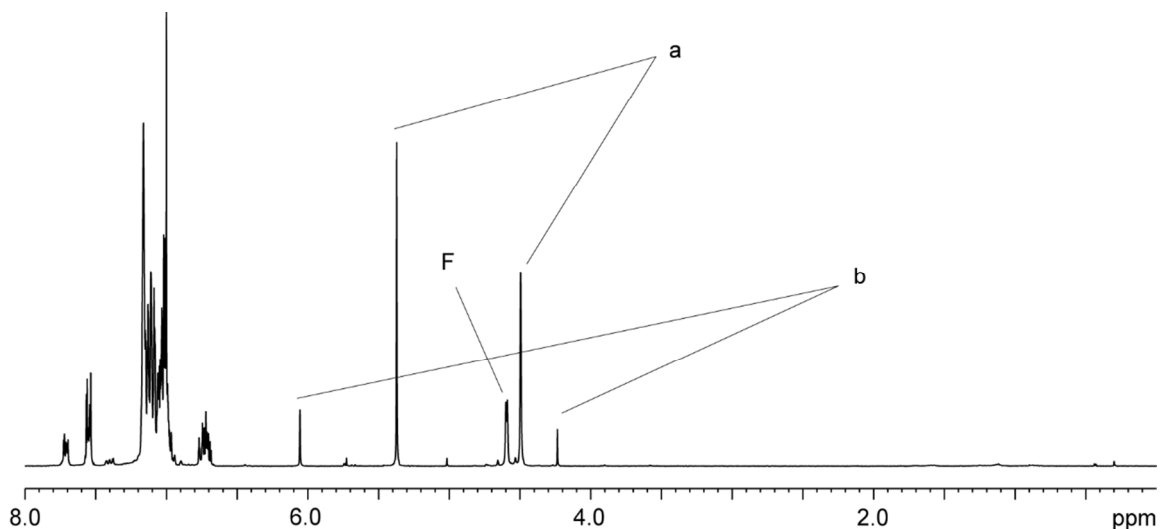


**Figure 3.16.**  $^1\text{H}$  NMR (300 MHz) of  $\text{Ph}_2\text{SiH-N(Ph)CH}_2\text{Ph}$  in  $\text{C}_6\text{D}_6$ . The “F” is residual free amine,  $\text{HN(Ph)CH}_2\text{Ph}$ , formed from the hydrolysis of the Si-N bond in the product  $\text{Ph}_2\text{SiH-N(Ph)CH}_2\text{Ph}$  (**3-6**). The “t” is toluene. The “#” is grease.

*$\text{PhSiH}_2\text{-N(Ph)CH}_2\text{Ph}$  (**3-7a**) +  $\text{PhSiH(N(Ph)CH}_2\text{Ph)}_2$  (**3-7b**) (Reaction of  $\text{PhSiH}_3$  with benzylideneaniline (imine)):*

In a Schlenk flask equipped with a stir bar,  $\text{PhSiH}_3$  (0.14 g, 1.3 mmol), benzylideneaniline (0.20 g, 1.1 mmol) and  $\text{B(C}_6\text{F}_5)_3$  (0.010 g, 0.020 mmol) were combined with toluene (1 mL) to give a clear yellow solution. The contents were stirred under  $\text{N}_2$  (closed flask). After 1 h,  $\text{PPh}_3$  (0.005 g, 0.019 mmol) was added. The solution immediately turned clear and colorless. Volatiles were removed by evacuation to give an

oily residue. Pentane (1 mL) was added and the cloudy white solution was filtered through a Celite column (to remove precipitated phosphine-borane adduct). The column was washed with pentane (5 x 1 mL) to give a clear and colorless combined filtrate. Volatiles were removed under dynamic vacuum at RT for 2 h. A clear and colorless oil was isolated, which showed a mixture of the monohydrosilation and dihydrosilation products (95% monohydrosilation ( $\text{PhSiH}_2\text{-N(Ph)CH}_2\text{Ph}$ ) and 5% dihydrosilation ( $\text{PhSiH(N(Ph)CH}_2\text{Ph)}_2$ ) products. Free amine was also detected, which may result from the hydrolysis of either product. Product **3-7a** is likely more susceptible to hydrolysis because it has less steric bulk around silicon. Neither product's sensitivity to hydrolysis or alcoholysis has been evaluated deliberately yet. For  $\text{PhSiH}_2\text{-N(Ph)CH}_2\text{Ph}$  (70%, **3-7a**):  $^1\text{H NMR}$  (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  4.50 (s, 2H,  $\text{NCH}_2$ ), 5.38 (s,  $^1J_{\text{SiH}} = 213$  Hz, 2H, Si-H), 6.68-6.78 (m, overlapping with  $\text{H}_p\text{-NPh}$  in  $\text{PhSiH(N(Ph)CH}_2\text{Ph)}_2$  and  $\text{HN(Ph)CH}_2\text{Ph}$ , 1H,  $\text{H}_p\text{-NPh}$ ), 6.97-7.14 (m, 12H,  $\text{H}_{m/p}\text{-SiPh}$ ,  $\text{H}_{o/m}\text{-NPh}$ ,  $\text{H}_{o/m/p}\text{-NCH}_2\text{Ph}$ ), 7.55 (d,  $^3J_{\text{HH}} = 7$  Hz, 2H,  $\text{H}_o\text{-SiPh}$ ). For  $\text{PhSiH(N(Ph)CH}_2\text{Ph)}_2$  (30%, **3-7b**):  $^1\text{H NMR}$  (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  4.24 (s, 4H,  $\text{NCH}_2$ ), 6.06 (s,  $^1J_{\text{SiH}} = 230$  Hz, 1H, Si-H), 6.68-6.78 (m, overlapping with  $\text{H}_p\text{-NPh}$  in  $\text{PhSiH}_2\text{-N(Ph)CH}_2\text{Ph}$  and  $\text{HN(Ph)CH}_2\text{Ph}$ , 2H,  $\text{H}_p\text{-NPh}$ ), 6.97-7.14 (m, 21H,  $\text{H}_{m/p}\text{-SiPh}$ ,  $\text{H}_{o/m/p}\text{-NPh}$ ,  $\text{H}_{o/m/p}\text{-NCH}_2\text{Ph}$ ), 7.71 (d,  $^3J_{\text{HH}} = 7$  Hz, 2H,  $\text{H}_o\text{-SiPh}$ ).

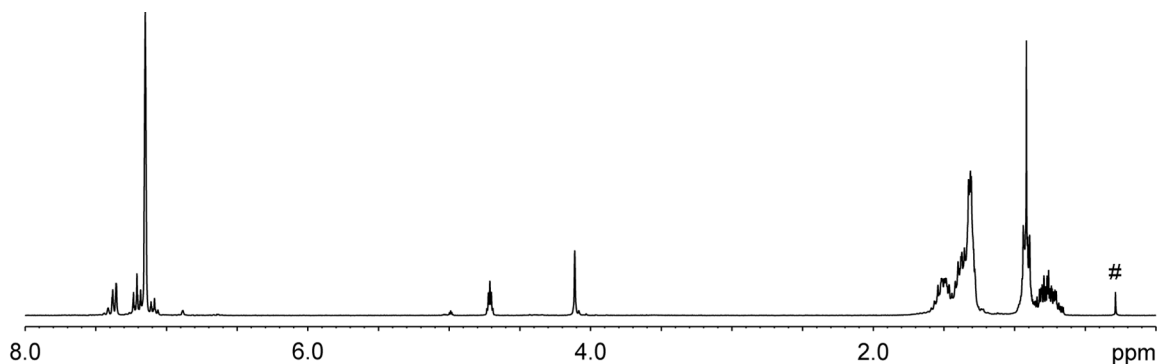


**Figure 3.17.**  $^1\text{H}$  NMR (300 MHz) of  $\text{PhSiH}_2\text{-N(Ph)CH}_2\text{Ph} + \text{PhSiH(N(Ph)CH}_2\text{Ph)}_2$  in  $\text{C}_6\text{D}_6$ . The “a” is **3-8a**. The “b” is **3-8b**. The “F” is residual free amine,  $\text{HN(Ph)CH}_2\text{Ph}$ , formed from the hydrolysis of the Si-N bond in the product in either **3-8a** or **3-8b**.

### 3.12.8 Synthesis of *N,N*-disilylamines (reactions with nitriles)

#### *((n-C\_6H\_{13})\_2SiH)\_2NCH\_2Ph* (**3-8a**)

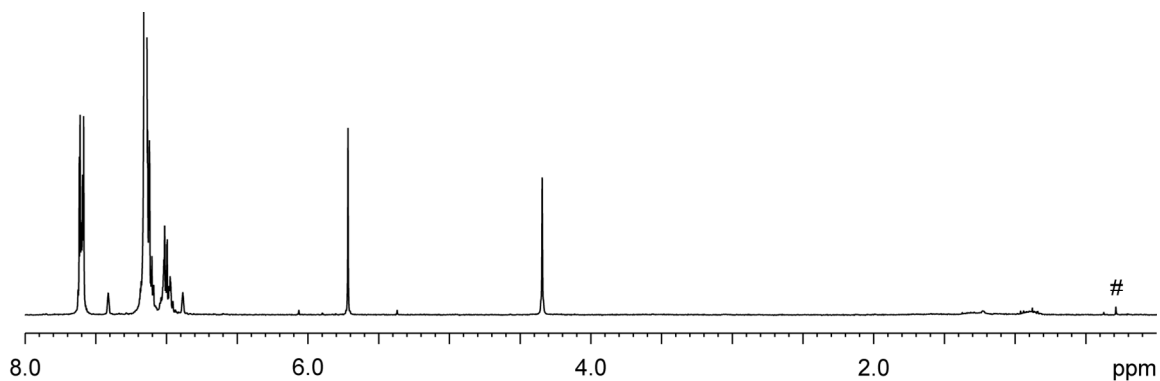
In a Schlenk flask equipped with a stir bar, *n*-Hex<sub>2</sub>SiH<sub>2</sub> (0.20 g, 0.97 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.020 g, 0.039 mmol), benzonitrile (0.058 g, 0.56 mmol) and toluene (1 mL) were combined to give a clear and colorless solution. The mixture was stirred at RT. After 16 h, volatiles were removed by evacuation to leave a clear and colorless oil. The mixture was dissolved in hexanes (1 mL) and eluted through a Florisil column. The column was washed with hexanes (3 x 1 mL) and a clear and colorless filtrate was collected. Volatiles were removed under dynamic vacuum at 70 °C for 1 h. A clear and colorless oil was isolated (0.13 g, 54%).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.65-0.85 (m, 8H, SiCH<sub>2</sub>), 0.91 (t,  $^3J_{\text{HH}} = 6$  Hz, 12H, CH<sub>3</sub>), 1.27-1.59 (m, 36H, SiCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 4.11 (s, 2H, NCH<sub>2</sub>), 4.71 (quint,  $^1J_{\text{SiH}} = 3$  Hz, 2H, Si-H), 7.09 (t,  $^3J_{\text{HH}} = 7$  Hz, 1H, H<sub>p</sub>-CH<sub>2</sub>Ph), 7.21 (t,  $^3J_{\text{HH}} = 7$  Hz, 2H, H<sub>m</sub>-CH<sub>2</sub>Ph), 7.37 (d,  $^3J_{\text{HH}} = 8$  Hz, 2H, H<sub>o</sub>-CH<sub>2</sub>Ph).



**Figure 3.18.**  $^1\text{H}$  NMR (300 MHz) of  $((n\text{-C}_6\text{H}_{13})_2\text{SiH})_2\text{NCH}_2\text{Ph}$  (**3-8a**) in  $\text{C}_6\text{D}_6$ . The “#” is grease.

*(Ph<sub>2</sub>SiH)<sub>2</sub>NCH<sub>2</sub>Ph* (**3-8b**)

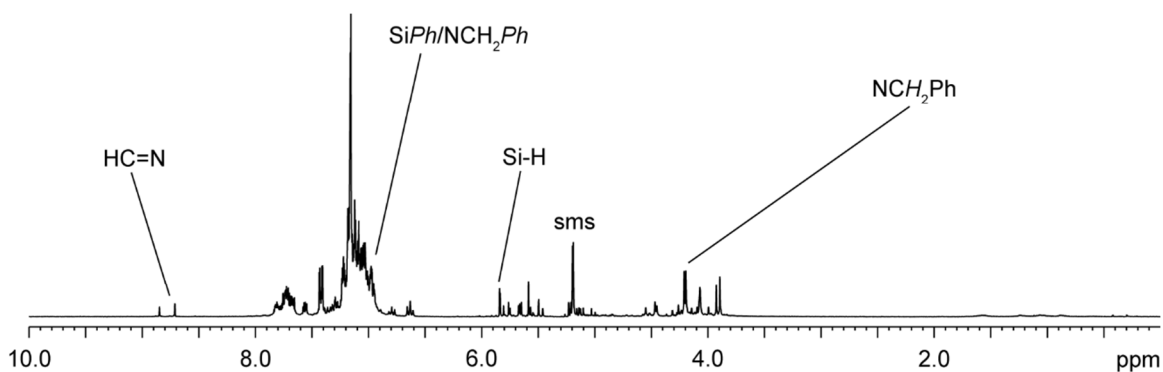
In a Schlenk flask equipped with a stir bar,  $\text{Ph}_2\text{SiH}_2$  (0.20 g, 1.1 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.020 g, 0.039 mmol), benzonitrile (0.061 g, 0.59 mmol) and toluene 1 mL were combined to give a clear and colorless solution. The mixture was stirred at RT. After 16 h, volatiles were removed by evacuation to leave a clear and colorless oil. The mixture was dissolved in hexanes (1 mL) and eluted through a Florisil column. The column was washed with hexanes (3 x 1 mL) to give clear and colorless combined fractions. Volatiles were removed under dynamic vacuum at 70 °C for 1 h. A clear and colorless oil was isolated (0.12 g, 45%).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  4.34 (s, 2H,  $\text{NCH}_2$ ), 5.72 (s,  $^1J_{\text{SiH}} = 209$  Hz, 2H, SiH), 6.96-7.04 (m, 5H, *o*- $\text{CH}_2\text{Ph}$ , *m*- $\text{CH}_2\text{Ph}$ , *p*- $\text{CH}_2\text{Ph}$ ), 7.10-7.16 (m, overlapping with  $\text{C}_6\text{D}_5\text{H}$ , 12H, *m*-SiPh, *p*-SiPh), 7.60 (d,  $^3J_{\text{HH}} = 4$  Hz, 8H, *o*-SiPh).



**Figure 3.19.**  $^1\text{H}$  NMR (300 MHz) of  $(\text{Ph}_2\text{SiH})_2\text{NCH}_2\text{Ph}$  (**3-8b**) in  $\text{C}_6\text{D}_6$ . The “#” is grease.

*-PhSiH-NCH<sub>2</sub>Ph- oligosilazane (3-9)*

In a Schlenk flask equipped with a stir bar,  $\text{PhSiH}_3$  (0.22 g, 2.0 mmol), benzonitrile (0.21 g, 2.0 mmol), and  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.012 g, 0.023 mmol) were combined in a neat mixture. After 6 d stirring, the mixture turned from clear and colorless solution to thick, viscous, clear and orange mixture. An aliquot removed for  $^1\text{H}$  NMR showed a complex mixture of signals indicative of short-chain oligomers containing  $-\text{PhSiH}-\text{NCH}_2\text{Ph}-$  repeat units.



**Figure 3.20.**  $^1\text{H}$  NMR (300 MHz) of  $-(\text{PhSiH})_2\text{NCH}_2\text{Ph}-$  (**3-9**) in  $\text{C}_6\text{D}_6$ . The “sms” indicates residual starting material,  $\text{PhSiH}_3$ .

## 4 Post-polymerization modification of poly(phenylsilane)

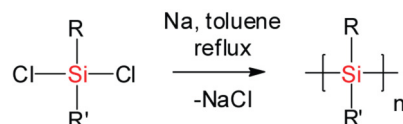
**Note:** Some of this material has been published in “Borane-Catalyzed Si-H Activation Routes to Polysilanes Containing Thiolato Side Chains”, Lee, P. T. K.; Skjel, M. K.; Rosenberg, L. *Organometallics* **2013**, 32, 1575-1578. Copyright 2013 American Chemical Society (adapted with permission). Miranda Skjel initiated the synthesis and characterization by  $^1\text{H}$  and  $^{29}\text{Si}$  NMR and GPC for **4-1**, **4-11**, **4-12**, and **4-13**.

### 4.1 Introduction

Polysilanes are polymers featuring an all-Si backbone. They have attracted widespread interest due to the  $\sigma$ -conjugation they exhibit along their all-Si chain, which affords a number of interesting properties.<sup>5,14a,c,d,106</sup> These “inorganometallic” polymers undergo facile photochemical decomposition to silyl radicals and silylenes.<sup>107</sup> Their UV-vis absorption spectra have been studied in depth: their strong absorptions in the UV region ( $\lambda_{\text{max}}(\sigma\text{-}\sigma^*) = 300\text{-}350\text{ nm}$ )<sup>108</sup> (and, critically, not in the visible region) have been shown to vary with temperature (thermochromism),<sup>108e,109</sup> solvent (solvatochromism),<sup>109a,110</sup> chain conformation,<sup>111</sup> and side-chain composition<sup>112</sup>. Emissive properties (emission and fluorescence spectra)<sup>108b,d,e,111a,112-113</sup> have also been reported for polysilanes. These decomposition, absorption, and emission properties have been exploited for a number of applications: in lithography as a photoresist,<sup>7,114</sup> in the photoinitiation of radical-initiated and cationic polymerizations,<sup>115</sup> in semiconducting<sup>16</sup> and photoconducting polymer solid state layers,<sup>116</sup> in charge-transport as a hole-conducting medium,<sup>15,117</sup> in non-linear optical devices as thin film-absorbing media,<sup>17</sup> and in the emissive and hole-transporting layer of LED devices.<sup>8</sup>

To date, most reported studies of polysilanes have been limited to poly(methylphenylsilane) and a few derivatives with dialkylsilane/alkylarylsilane repeat units, which can be prepared from chlorosilane precursors using Wurtz/reductive coupling methods (Scheme 4.1).<sup>118</sup> Problems accompanying this conventional polysilane synthesis<sup>xxxvii</sup> include: safety issues associated with sodium metal and harsh reaction conditions; large-scale separations due to stoichiometric elimination of sodium chloride; and control over the degree of polymerization, which leads to polydisperse samples or vastly different molecular weights from different batches.<sup>119</sup> Furthermore, Wurtz coupling does not allow systematic, broad variation of side-chains R/R' in polysilanes of formula [SiRR']<sub>n</sub>.<sup>14b,c</sup> In particular, the introduction of heteroatom-containing derivatives is challenging under the harsh reductive coupling conditions.

**Scheme 4.1.** Reproduced from Scheme 1.4.

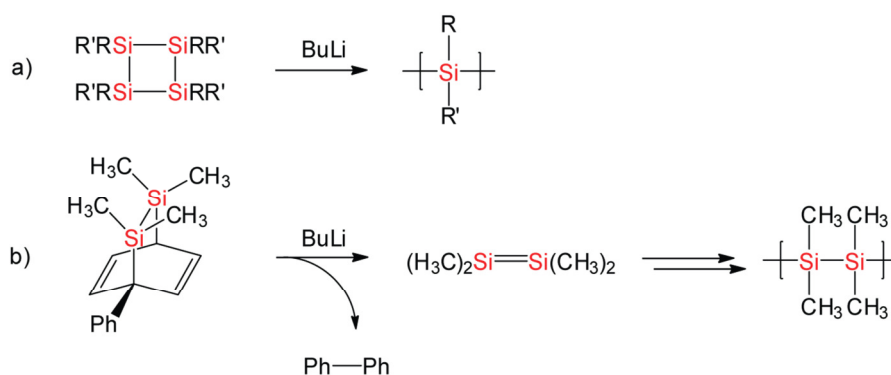


Limited studies have described the effects of side-chains on the properties of polysilanes. These include the following: aryl groups,<sup>120</sup> hydrides,<sup>121</sup> alkyl side-chains,<sup>110</sup> alkoxy groups,<sup>112b</sup> and aryl side-chains that contain azobenzene<sup>111a</sup> or alkoxy<sup>122</sup> groups. Each of these examples show important side-chain effects for these specific examples. However, a general understanding of the side-chain effects has yet to be formulated. This is difficult to attain because the current methods to prepare polysilanes do not lead to a wide selection of polysilanes. Studies constructing devices incorporating polysilanes have

<sup>xxxvii</sup> The synthesis of polysilanes by reductive coupling (Wurtz coupling) has been reviewed recently.<sup>14b</sup>

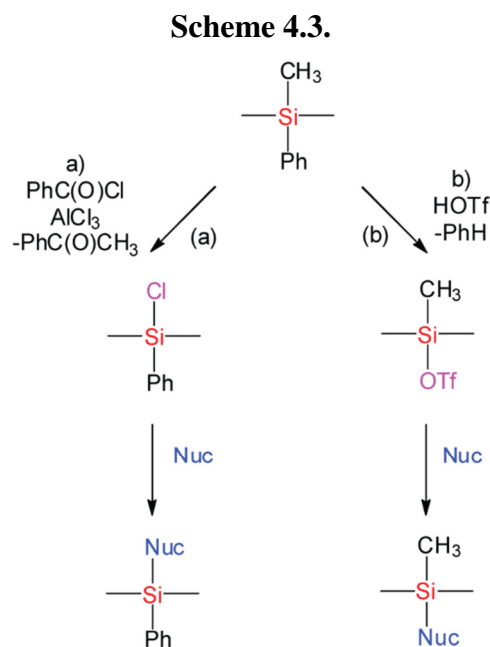
noted this limitation and suggested their ongoing issues may be offset by more available polysilane derivatives.<sup>8b,15</sup> Other routes to polysilanes, such as anionic ring-opening polymerization (Scheme 4.2a) and polymerization of masked disilenes (Scheme 4.2b), start from structurally unique monomers, so these methods have a limited scope for introducing side-chain complexity. Both of these rely on the preparation of complex monomers. Monomers for anionic ring-opening polymerization are ring-strained cyclic oligosilanes.<sup>123</sup> Wurtz coupling is the preferred method for building cyclic oligosilanes, which are subject to the same limited scope and undesirable reaction conditions as Wurtz coupling polymerization. Olefin-like monomers derived from structurally complex 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-dienes (masked disilenes) may also be monomers for polysilane polymerization (Scheme 4.2b), yet their synthesis and scope is limited to a few examples.<sup>124</sup> Challenges of generalizing polysilane polymerization and complex monomers for polymerization have led to alternative synthetic methods of modifying existing polysilanes.

**Scheme 4.2.**



Post-polymerization modification of Wurtz-coupled polysilanes (Scheme 4.3.) has been suggested as a systematic route to polysilanes with a wider side-chain scope. The combination of Lewis acid, trichloroaluminum ( $\text{AlCl}_3$ ), and benzoyl chloride ( $\text{PhC}(\text{O})\text{Cl}$ )

has been used to cleave Si-Me bonds in poly(methylphenylsilane) (Scheme 4.3a).<sup>125</sup> The protic acid, triflic acid (HOTf), modifies Si-Ph bonds in poly(methylphenylsilane) (Scheme 4.3b).<sup>126,xxxviii</sup> In both cases, the side-chains can then be modified through subsequent reactions, for example butyl groups delivered using *n*-butyllithium or *n*-propoxy groups from *n*-propanol/Et<sub>3</sub>N. Inevitably, these methods show less than ideal chemoselectivity, with variable amounts of competing Si-Si bond cleavage that can diminish polymer molecular weights (MWs).<sup>40,125,128,xxxix</sup>



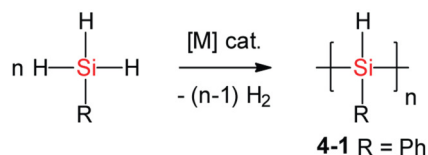
Another post-polymerization modification approach to the preparation of a wider variety of polysilanes capitalizes on the reactivity of Si-H bonds in the repeat units of poly(hydrosilane) polymers prepared via catalytic homodehydrocoupling of primary silanes (Scheme 4.4).<sup>18b,c,32,129</sup> Examples of Si-H modification of poly(phenylsilane) (**4-1**)

<sup>xxxviii</sup> Reactions of polysilanes with triflic acid has been reviewed.<sup>127</sup>

<sup>xxxix</sup> Uhlig<sup>127</sup> reports chemoselectivity for triflic acid methods, however, Corey<sup>128</sup> notes that the selectivity is in question. The selectivity of AlCl<sub>3</sub>-catalyzed reactions was discussed in footnote iv in Chapter 1 and will be discussed below.

include AlCl<sub>3</sub>-catalyzed hydrosilation of alkynes,<sup>40</sup> radical-based halogenation using CX<sub>4</sub> (X = Cl, Br),<sup>38</sup> AIBN-initiated hydrosilation of olefins and ketones via a radical-based mechanism,<sup>39,130</sup> titanocene-catalyzed heterodehydrocoupling with alcohols,<sup>57</sup> and platinum-catalyzed, microwave-assisted hydrosilation of olefins.<sup>131</sup>

**Scheme 4.4.**



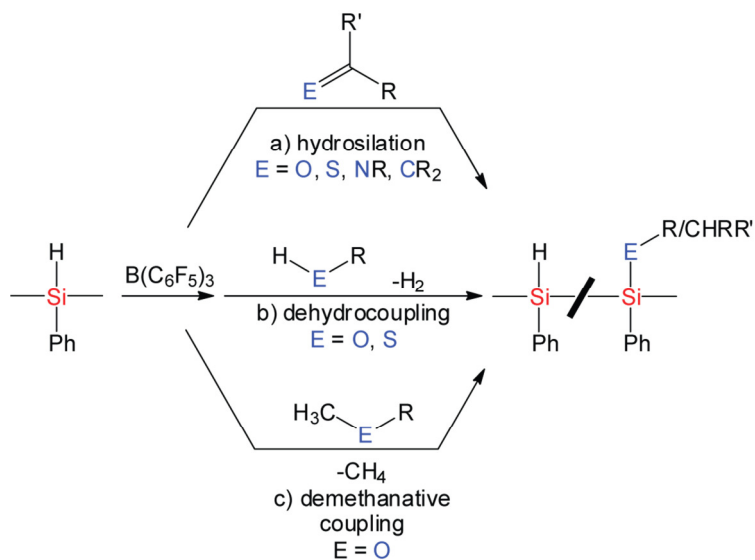
Earlier studies in the Rosenberg group screened many of these reported Si-H modification conditions, and other classic monosilane Si-H activation reactions, using the model disilane (**2-2**, (Ph<sub>2</sub>SiH)<sub>2</sub>): oxidation/halogenation using Br<sub>2</sub>, Cl<sub>2</sub>, *N*-bromosuccinimide, thionyl chloride, or catalytic PdCl<sub>2</sub> with CCl<sub>4</sub>; strong bases such as MeLi; transition-metal catalyzed routes using Cp<sub>2</sub>TiCl<sub>2</sub>/*n*-BuLi, Speier's catalyst, H<sub>2</sub>PtCl<sub>6</sub>, or Wilkinson's catalyst, Rh(PPh<sub>3</sub>)<sub>3</sub>Cl; and AIBN radical-initiated methods. These reactions exhibited varying degrees of Si-Si bond scission in disilane, even when the desired Si-H to Si-X transformation occurred in high yield.<sup>1</sup> Evidence for this competing Si-Si bond cleavage was also reported for longer oligo- and polysilane substrates for both the AlCl<sub>3</sub>-catalyzed hydrosilation chemistry<sup>40</sup> and the AIBN-initiated radical hydrosilation<sup>39</sup> reactions. The catalytic route with AlCl<sub>3</sub> was reported only for alkyne substrates with limited success for oligosilanes and complex redistribution products for polysilanes.<sup>40</sup> The AIBN radical-initiated method attached alkyl and alkoxy side-chains on poly(phenylsilane) derived from olefins, ketones, and aldehydes, and the modified polymers had a slight reduction in molecular weight compared to its parent poly(phenylsilane) (**4-1**).

Clearly, limiting Si-Si bond scission and expanding substrate scope should be goals of future methods for the post-polymerization modification of polysilanes. One promising method uses  $\text{B}(\text{C}_6\text{F}_5)_3$  to catalyze Si-H bond activation for hydrosilation, dehydrocoupling, and dealkylative coupling as described in Chapter 1.<sup>21,41b,42b,60</sup> The Rosenberg group previously showed that this method allows the introduction of new Si-S,<sup>1a,b</sup> Si-O, and Si-C bonds from disilane **2-2** without concomitant Si-Si cleavage. This chapter reports the application of  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed Si-H activation chemistry to poly(phenylsilane); the characterization of new X-modified poly(phenylsilane) derivatives by  $^1\text{H}/^{13}\text{C}/^{29}\text{Si}$  NMR, IR, EA, GPC, TGA, and UV-vis absorption spectroscopy; an assessment of the chemoselectivity of  $\text{B}(\text{C}_6\text{F}_5)_3$  catalysis; and an evaluation of the challenges and limitations of the  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed method.

## 4.2 Synthesis of X-modified poly(phenylsilane) derivatives

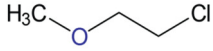
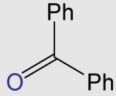
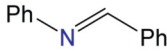
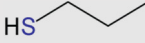
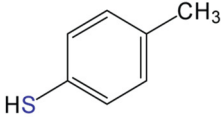
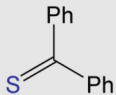
New X-modified poly(phenylsilane) derivatives (**4-2** to **4-13**, Table 4.1) were prepared via three different  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed transformations of the Si-H bonds in poly(phenylsilane) (**4-1**): hydrosilation of aldehydes, ketones, thioketones, imines, and olefins (route a); dehydrocoupling of phenols, and thiols (route b); and demethanative coupling of aryl methyl ethers, and alkyl methyl ethers (route c). Reactions of the model disilane (described in Chapter 2 and in the literature<sup>1</sup>) helped to establish appropriate reaction conditions (solvent, catalyst loading, anticipated reaction time, and temperature), and provided benchmarks for spectroscopic characterization ( $^1\text{H}/^{13}\text{C}/^{29}\text{Si}$  NMR spectra) of the modified polymers.

Scheme 4.5.



**Table 4.1.** New X-modified poly(phenylsilane) derivatives (**4-2** to **4-13**) prepared by hydrosilation (Scheme 4.5a), dehydrocoupling (b), and demethanative coupling (c).

Polymer	Substrate	New side-chain X	modification method <sup>a</sup>	degree of Si-H substitution <sup>b</sup>
<b>4-2</b>		CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Ph	(a)	20
<b>4-3</b>		CH <sub>2</sub> CH <sub>2</sub> Bu	(a)	40
<b>4-4</b>		OCH(CH <sub>3</sub> ) <sub>2</sub>	(a)	25
<b>4-5</b>		OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	(a)	70 <sup>c</sup>
<b>4-6</b>		OCH <sub>2</sub> CH <sub>2</sub> Cl	(b)	10
<b>4-7</b>		OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	(c)	25

4-8		OCH <sub>2</sub> CH <sub>2</sub> Cl	(c)	25
4-9		OCHPh <sub>2</sub>	(a)	70 <sup>c</sup>
4-10		N(Ph)CH <sub>2</sub> Ph	(a)	10
4-11		SCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	(b)	20
4-12		SC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	(b)	40
4-13		SCHPh <sub>2</sub>	(a)	35 <sup>c</sup>

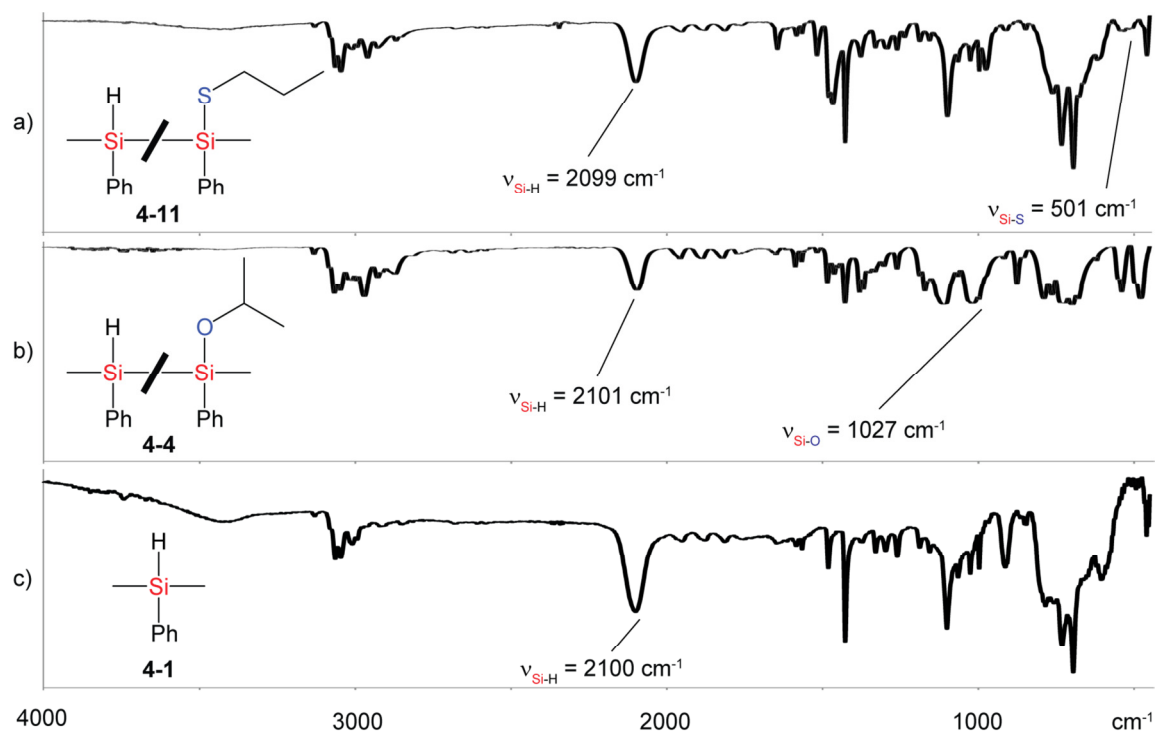
<sup>a</sup>Refers to methods illustrated in Scheme 4.5. (a) hydrosilation, (b) dehydrocoupling, (c) demethanative coupling. <sup>b</sup>Determined by <sup>1</sup>H NMR, highest observed conversions given. <sup>c</sup>These reactions were accompanied by competing side reactions with by-products whose structures cause NMR analysis of conversions to deviate as will be discussed in 2.3.4

### 4.3 Characterization of X-modified poly(phenylsilane) derivatives

#### 4.3.1 Characterization by IR spectroscopy

A wide range of analytical methods was employed to characterize the new modified polysilanes, and to assess the chemoselectivity and activity of the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyst in these reactions. The simplest qualitative confirmation of the success of the modifications comes from IR analysis of KBr pellets of the solid polymer samples (Figure 4.1 and experimental Section 4.9.2). In general, the complexity of the spectra increases following modification, which is consistent with a loss of symmetry arising from partial replacement of the Si-H bonds along the polymer chains. An observed reduction in the intensity of  $\nu_{\text{Si-H}}$  (~2100 cm<sup>-1</sup>) relative to  $\nu_{\text{C-H}}$  (~3000 cm<sup>-1</sup>) following modification is also consistent with the replacement of Si-H bonds in the parent polymers

with new C-H containing side-chains. For the putative alkoxy- and thioalkoxy-containing polysilanes, absorptions corresponding to  $\nu_{\text{Si-O}}$  (1000-1100  $\text{cm}^{-1}$ , **4-4** to **4-9**) and  $\nu_{\text{Si-S}}$  (489-501  $\text{cm}^{-1}$ , **4-11** to **4-13**) were observed (Figure 4.1).



**Figure 4.1.** The change in relative intensities of  $\nu_{\text{Si-H}}$  and  $\nu_{\text{C-H}}$  is particularly easy to see from comparison of the IR spectra (KBr) of a)  $\text{SCH}_2\text{CH}_2\text{CH}_3$  (**4-11**), b)  $\text{OCH}(\text{CH}_3)_2$ -modified poly(phenylsilane) derivatives (**4-4**), and c) parent poly(phenylsilane) (**4-1**). Peak intensities have been crudely normalized using signals in the 2010-1790  $\text{cm}^{-1}$  region ( $\delta/\rho_{\text{C-H}}$  (phenyl) overtones) to demonstrate the reduction in  $\nu_{\text{Si-H}}$  ( $\sim 2100 \text{ cm}^{-1}$ ). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

### 4.3.2 Characterization by $^1\text{H}$ NMR

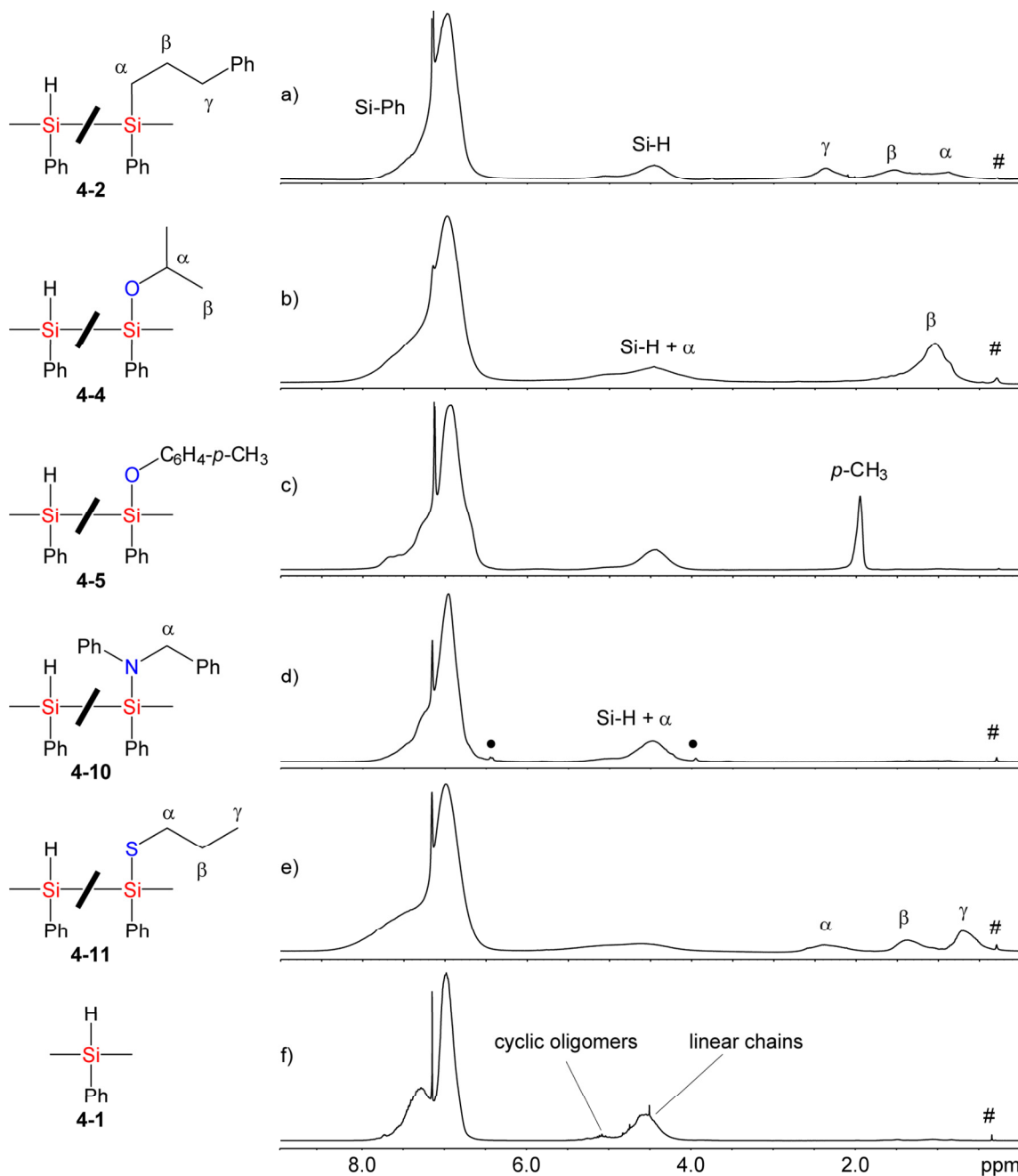
Further confirmation of the polymer modifications comes from  $^1\text{H}$  NMR spectroscopy (Figure 4.2): from these spectra the degree of substitution is estimated for each new polymer. For example, the isopropoxy side-chains in poly(phenylsilane) modified via the catalytic hydrosilation of acetone (**4-4**, Figure 4.2b) gives rise to signals

corresponding to  $\alpha$ -CH and  $\beta$ -CH<sub>3</sub> groups, as well as signals corresponding to the Si-Ph repeat units, and residual Si-H signals that are broadened relative to the analogous signals for the parent polysilane. Signals in the aryl region (6.5-8.0 ppm) increase in complexity following modification due to the introduction of new Ph-Si-O environments. For this example, the degree of substitution was determined by comparing the relative integrals for the signals due to the Si-H,  $\alpha$ -CH, and  $\beta$ -CH<sub>3</sub> groups: these indicate that 25% modification of Si-H to Si-OCH(CH<sub>3</sub>)<sub>2</sub> groups has occurred.<sup>x1</sup>

The <sup>1</sup>H NMR spectrum of **4-10** (N(Ph)CH<sub>2</sub>Ph side-chains) illustrates the extreme sensitivity of the Si-N bond to hydrolysis. The “•” in Figure 4.2d is residual free amine eliminated from **4-10** in the presence of residual water. When the <sup>1</sup>H NMR sample is left exposed to air, the free amine peak intensity increases over time. Even experiments minimizing exposure to air showed a very small amine peak “•” (~1%) in the <sup>1</sup>H NMR. This indicates that **4-10** must contain some Si-OH or Si-O-Si linkages.

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<sup>x1</sup> See experimental Section 4.9.6, Figure 4.64, for representative detailed determination of %X by <sup>1</sup>H NMR integrations.

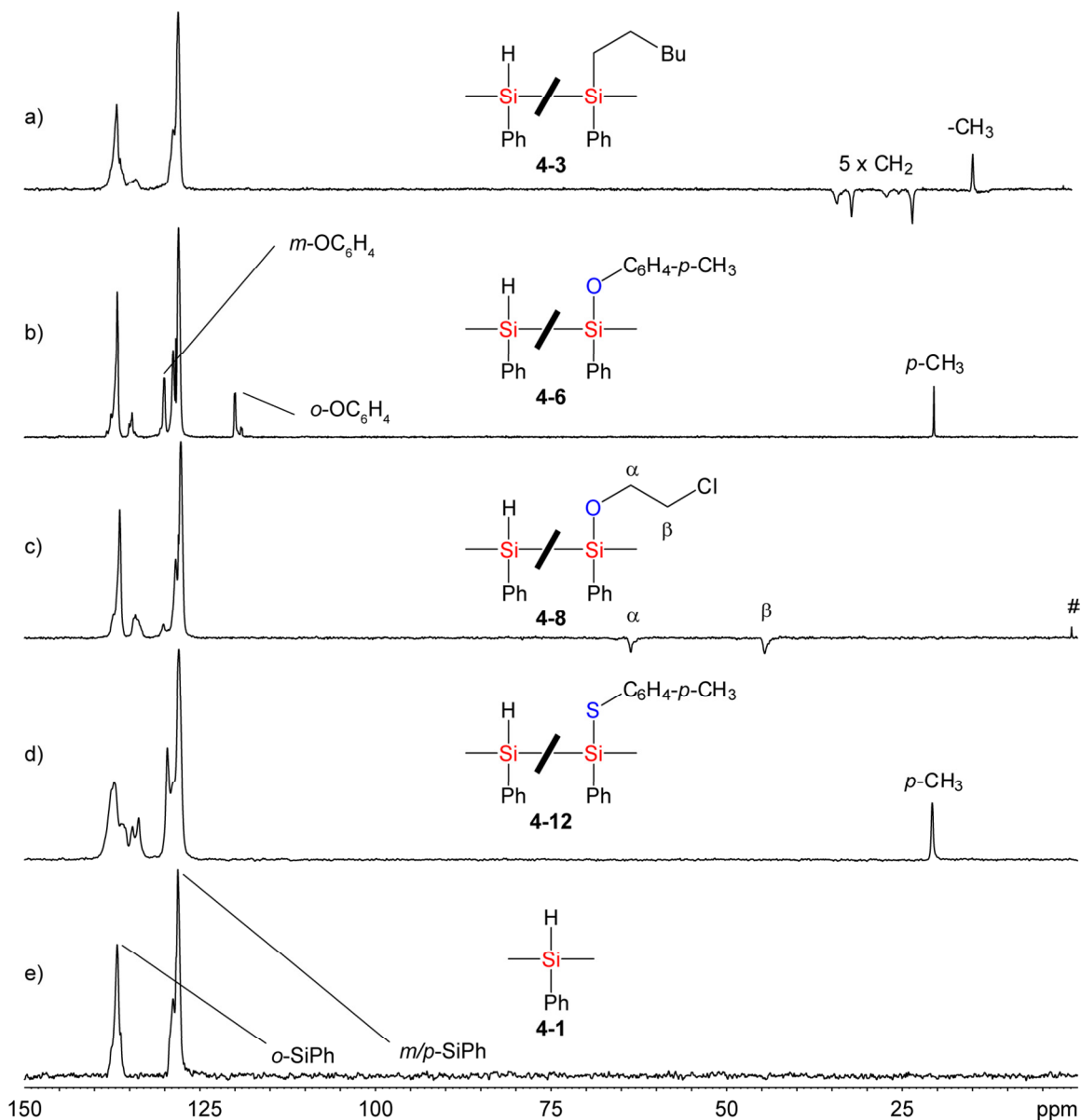


**Figure 4.2.** Representative  $^1\text{H}$  NMR (300 MHz) of modified polysilanes  $-\text{[PhSiH]}-/-\text{[PhSiX]}-$  where X = a)  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$  (**4-2**), b)  $\text{OCH}(\text{CH}_3)_2$  (**4-4**), c)  $\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$  (**4-7**), d)  $\text{N}(\text{CH}_2\text{Ph})\text{Ph}$  (**4-10**), e)  $\text{SCH}_2\text{CH}_2\text{CH}_3$  (**4-11**). Spectrum f) shows the parent poly(phenylsilane) (**4-1**) in  $\text{C}_6\text{D}_6$ . In d) (**4-10**), the “•” highlights an impurity of free amine formed from the hydrolysis of  $-\text{N}(\text{Ph})\text{CH}_2\text{Ph}$  side-chains. The “#” is residual grease. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

### 4.3.3 Characterization by DEPT135 $^{13}\text{C}$ NMR

DEPT135  $^{13}\text{C}$  NMR of the modified polymers provides diagnostic information complementary to that obtained from the  $^1\text{H}$  NMR spectra. For example, polymer **4-8** ( $\text{OCH}_2\text{CH}_2\text{Cl}$  side-chains, Figure 4.3c), gives DEPT135  $^{13}\text{C}$  signals with phases corresponding to the  $\alpha\text{-CH}_2$  and  $\beta\text{-CH}_2$  groups. The  $\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$ -modified poly(phenylsilane) (**4-7**) shows an increase in complexity in the aromatic region, which includes new signals for (Figure 4.3b) *ortho*- $\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$  (120 ppm) and *meta*- $\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$  (130 ppm) corresponding to the phenoxy group. Modified polymers **4-3**, **4-7**, **4-8** and **4-12** also show increased complexity (Figure 4.1a-d) in the aromatic region (137 ppm *o*-SiPh and 128 ppm *m/p*-SiPh).

The broad peaks in the  $^1\text{H}$  (describe above),  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMRs (described in Section 4.3.5) suggest a variety of chemical and spatial environments along the all-silicon chains in these samples: the peaks are a distribution of chemical shifts as opposed to resolvable peaks. Each silicon in the chain is a stereocenter, which contributes to the broad NMR peaks. Additionally, the large size of the molecules and possible slow rotation of their bonds may affect the isotropy of these molecules and therefore contribute to the broad signals. However, some examples of polymers with comparable molecular weights (1-100 kDa, measured by GPC relative to polystyrene standards) show sharp  $^1\text{H}^{132}$  and  $^{13}\text{C}^{133}$  NMR signals.



**Figure 4.3.** DEPT135  $^{13}\text{C}$  NMR (75 MHz) of a) CH<sub>2</sub>CH<sub>2</sub>Bu (**4-3**), b) OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> (**4-7**), c) OCH<sub>2</sub>CH<sub>2</sub>Cl (**4-8**) d) SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> (**4-12**)-modified polysilanes and d) parent poly(phenylsilane) (**4-1**) in  $\text{C}_6\text{D}_6$ . The “#” signal is due to residual grease. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

#### 4.3.4 Characterization by elemental analysis

There were some difficulties associated with integrating broad  $^1\text{H}$  NMR peaks (see Table 4.1 and Section 4.9.6, Figure 4.64 for  $^1\text{H}$  NMR integration example). Integration of broad and overlapping peaks (in phenyl regions in all examples, and in Si-

H or alkyl regions for **4-4**, **4-5**, **4-8**, and **4-10**) often gave variations between different batches, for different samples prepared from the same batch, and even for replicate  $^1\text{H}$  NMR spectra run on the same sample. Based on these challenges, an error of  $\pm 5\%$  was estimated from this method. The X-modified polysilanes were also characterized by elemental analysis (EA) as a potentially orthogonal quantitative method (Table 4.2).

Both the  $^1\text{H}$  NMR integration and EA methods only account for polymer repeat units  $\text{PhSi-H}$  or  $\text{PhSi-X}$  and do not account for the existence of endcaps  $-\text{Si(Ph)H}_2$ ,  $-\text{Si(Ph)HX}$ , or  $-\text{Si(Ph)X}_2$ . The estimated endcap-to-repeat-unit ratio is 1:7 to 1:16 based on GPC  $M_N/M_W$  of parent poly(phenylsilane) (**4-1**, see Section 4.3.6), and the mass of repeat units. Short polymer chains will account for larger contributions to the estimated %X when endcaps have been 'X' modified. The characterization of endcaps in X-modified poly(phenylsilane) derivatives using  $^{29}\text{Si}$  NMR is discussed in more detail in Section 4.3.5. It is not straightforward to account for the impact of substituted endcaps on the EA results. More generally, ascribing a bulk formula, as for  $-\text{PhSiH-/-PhSiX-}$  in %X, to a polydisperse and chemically non-uniform polymer sample may have inherent limitations. Nevertheless, these formulas have elemental compositions that are sensitive to %X content.

A survey of the polysilane literature indicates that elemental analysis is an infrequently used method to characterize polysilanes. Only a limited number of examples report consistency between %C/%H/%E (E = N or Cl) found by elemental analysis and that calculated from the proposed polysilane repeat unit.<sup>65a,134</sup> The combustion analysis of

polysilanes may be inefficient since a by-product may be silicon carbide (SiC) instead of the expected oxidation product, SiO<sub>2</sub>.<sup>xli</sup>

As shown in Table 4.2, elemental composition for X-modified poly(phenylsilane) polymers containing heteroatoms adjacent to Si (**4-7**, **4-8**, **4-10**, **4-11**, and **4-12**) matches reasonably well with the calculated element percentages based on <sup>1</sup>H NMR integrations, i.e. within the estimated ± 5% deviation, a reassuring affirmation of the validity of the <sup>1</sup>H NMR integration estimates.<sup>xlii</sup> Such satisfactory elemental analysis has similarly been reported for other oligo/polysilanes with Si-H/Si-Cl/Si-N repeat units.<sup>134d</sup>

**Table 4.2.** Elemental analyses for parent poly(phenylsilane) (**4-1**) and X-modified poly(phenylsilane) derivatives (**4-2** to **4-13**), estimates for the degree of substitution %X based on elemental analyses, and comparison with elemental composition anticipated based on NMR estimates for %X. In some cases, elemental compositions corresponding to several %X are shown to illustrate sensitivity to the degree of substitution. Data for **4-11**, **4-12**, and **4-13** is used with permission (see note at beginning of Chapter 4).<sup>96</sup>

#	X =	Found CH/N or S	Calc'd for %X (best fit in bold)		Calc'd for %X based on <sup>1</sup> H NMR	
			%X	C/H/N or S	%X	C/H/N or S
<b>4-1</b>	H	67.99/5.69	<b>0</b>	<b>67.86/5.69</b>	0	67.86/5.69
			10	70.22/5.98		
<b>4-2</b>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Ph	68.51/5.35	<b>5</b>	<b>69.10/5.84</b>	20	72.16/6.21
			0	67.86/5.69		
<b>4-3</b>	CH <sub>2</sub> CH <sub>2</sub> Bu	68.82/7.24	20	70.29/6.88	40	72.14/7.78
			<b>15</b>	<b>69.75/6.62</b>		

<sup>xli</sup> Literature correlating low %C from combustion analysis of polysilanes with silicon carbide has not been found, however, anecdotal evidence suggests this is a commonly held position among polysilane chemists.

<sup>xlii</sup> %S for **4-11** was an overestimate compared to <sup>1</sup>H NMR integrations. However, the ± 5% estimates in Table 4.2 suggest a high sensitivity of %S to %X. The %X determined from <sup>1</sup>H NMR integration may be an overestimate.

			10	69.16/6.33		
			95	65.87/7.31		
<b>4-4</b>	OCH(CH <sub>3</sub> ) <sub>2</sub>	60.31/6.25	<b>25</b>	<b>67.16/6.26</b>	25	67.16/6.26
			5	67.70/5.82		
<b>4-5</b>	OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	62.65/5.18	<sup>a</sup>		70	66.65/7.00
			25	66.45/5.46		
<b>4-7</b>	OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	68.42/5.58	<b>20</b>	<b>69.75/5.70</b>	20	69.75/5.70
			15	73.05/5.93		
			35	60.20/21.01		
<b>4-8</b>	OCH <sub>2</sub> CH <sub>2</sub> Cl	61.20/4.92	<b>30</b>	<b>61.10/5.36</b>	25	62.05/5.41
			25	62.05/5.41		
<b>4-9</b>	OCHPh <sub>2</sub>	64.21/4.31	<sup>a</sup>		100 <sup>b</sup>	84.51/ 6.22
			10	70.53/5.76/ 1.40		
<b>4-10</b>	N(Ph)CH <sub>2</sub> Ph	66.49/5.93/ 0.70	<b>5</b>	<b>69.30/5.73/ 0.61</b>	5	69.30/5.73/ 0.61
			0	67.86/5.69/0		
			25 <sup>c</sup>	64.92/6.05/ 6.54		
<b>4-11</b>	SCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	60.23/4.82/ 5.76	<b>20</b>	<b>65.43/5.99/ 5.39</b>	20	65.43/5.99/ 5.39
			15	65.98/5.92/ 4.17		

				68.00/5.52/ 5.96		
			25	<b>67.97/5.55/</b>		
<b>4-12</b>	SC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	66.88/5.44/ 5.78	<b>20</b>	<b>4.99</b>	25	68.00/5.52/ 5.96
			15	67.95/5.58/ 3.93		
			5	67.89/5.65/ 1.45		
<b>4-13</b>	SCHPh <sub>2</sub>	67.91/4.74/ 7.99	<i>a</i>		<b>40</b>	72.42/5.43/ 7.03

<sup>a</sup>These examples showed over-reduction chemistry (Chapter 3). These EA results are discussed in more detail in Section 4.4.2 (see Table 4.5). <sup>b</sup>Actual calculations gave a negative value for %Si-H due to the non-inclusion of PhSiO<sub>1/2</sub> repeat units (see Section 4.4.2). For comparison, %Si-H was assumed to be zero to show %C/%H values. <sup>c</sup>As %X is increased, %H/%S increase, but %C decreases.

Polymers **4-2** and **4-3**, which contain CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph and CH<sub>2</sub>CH<sub>2</sub>Bu side-chains, respectively, give %C (and %H) values that are low relative to the values calculated from <sup>1</sup>H NMR integrations (Table 4.1). Polymer **4-4**, with OCH(CH<sub>3</sub>)<sub>2</sub> side-chain, gave %C value that was low, however its %H value was consistent with <sup>1</sup>H NMR integrations. The <sup>1</sup>H NMR integration is presumed to be a satisfactory method for quantifying the degree of substitution in these polymers based on the correlation between <sup>1</sup>H NMR integrations and elemental analysis established above for the heteroatom polysilanes. The low %C/%H values for some of the polymers may be attributed to three possible issues: hydrolysis of small alkoxy side-chains (e.g. **4-4**); high inhomogeneity of the polymer sample (e.g. **4-2** and **4-3**) compared to heteroatom examples; and incomplete combustion that leads to silicon carbide (SiC) (e.g. for **4-2** and **4-3**).<sup>xliii</sup>

<sup>xliii</sup> Deviations in elemental analysis are considered by Canadian Microanalytical to be ± 0.3% for all elements analyzed.<sup>135</sup> These can contribute to the variance described above, but these estimates are too small compared to the variances in Table 4.2.

Hydrolysis of polysilanes was apparent for only a select few polysilanes: **4-4**, **4-5**, **4-10**, and **4-11**. If left dissolved in NMR solvent ( $C_6D_6$ ), most of these polymers examples showed resistance to hydrolysis and no change in the  $^1H$  NMR, even after prolonged exposure (3-5 days) to air except for **4-4**, **4-5**, **4-10**, and **4-11**.<sup>xliv</sup> These samples showed  $^1H$  NMR detectable quantities of their protonolyzed free H-containing side-chain, isopropanol, 2-chloroethanol, benzylphenylamine, and *n*-propylthiol, respectively. It is possible that incorporation of “O” content by hydrolysis into these polymers occurred prior to their combustion analysis, which would contribute to the lower %C, %H, and %N results for these examples, particularly **4-10**<sup>xlv</sup> where Si-O bonds are implied because of the detected free amine.

Polymers **4-2** and **4-3** had particularly poor agreement compared to heteroatom derivatives. As will be discussed further below (Section 4.3.6), GPC analysis shows that polydispersity (PDI) values (2.8 and 3.1 respectively (*vide infra*)) were significantly higher than parent poly(phenylsilane) (1.6-1.8) and other modified poly(phenylsilane) examples (2.0-2.2). The high PDI values for **4-2** and **4-3** suggest an even greater inhomogeneity for these samples. A literature established route to SiC is the pyrolysis of the polysilane, poly(dimethylsilane), in the absence of air/O<sub>2</sub>.<sup>9</sup> The alkyl group CH<sub>3</sub>, or more generally CH<sub>n</sub>, adjacent to Si is important to the mechanism of SiC formation,

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<sup>xliv</sup> Most polysilanes will degrade when exposed UV light,  $\lambda = 300$  to  $360$  nm, and in ambient light.<sup>107b</sup> However, modified polysilanes (**4-1** to **4-13**) can be exposed to ambient light for days with no changes to their  $^1H$  NMR or UV-vis absorption spectra. Poly(phenylsilane) (**4-1**) degrades at very low wavelengths ( $\lambda < 260$  nm) but not at higher wavelengths. Because of the presence of the repeat Si-H along the polysilane backbone, parent poly(phenylsilane) and modified poly(phenylsilane) examples (**4-1** to **4-13**) exhibit different properties than most commonly studied polysilanes. This relationship will be discussed in greater detail in Section 4.5.

<sup>xlv</sup> See “•” in Figure 4.2d in Section 4.3.2

which leads to polycarbosilane,  $[(\text{CH}_3)\text{SiH}-\text{CH}_2]_n$ , before becoming SiC.<sup>xlvi</sup> Polymers **4-2** and **4-3** have adjacent  $\text{CH}_2$  groups and may have unexpectedly pyrolyzed during analysis. This form of silicon with adjacent  $-\text{CH}_2-$  groups may combust inefficiently instead of oxidizing to  $\text{SiO}_2$  as desired.<sup>xlvii</sup>

There have been some reports of satisfactory elemental analysis with alkyl polysilanes between %C/%H from EA and values calculated from expected repeat units.<sup>134a,c</sup> These literature examples are relatively simple polysilanes  $-\text{RR}'\text{Si}-$  prepared by Wurtz coupling and it was unnecessary to reconcile proportions of repeat units from  $^1\text{H}$  NMR as done above (Table 4.1 and Table 4.2).

Few polysilane studies attempt to correlate  $^1\text{H}$  NMR integrations and EA results. Qin has reported satisfactory  $^1\text{H}$  NMR/EA results from modified poly(cyclohexylmethylsilane)-*co*-poly(hydridomethylsilane)<sup>17e</sup> and poly(methylphenylsilane)-*co*-poly(dimethylsilane)<sup>134e</sup>. In these cases, post-polymerization modification gave polysilanes with three to four distinct repeat units. The aggressive reaction conditions led to polymers that had a high proportion of modified repeat units (>80%). However this also drastically reduced the molecular weight of the modified polysilane compared to its parent polysilane (e.g. functionalized polysilane,  $M_N = 2500$  to  $3500$ ,  $M_W = 8900$  to  $12000$  compared to starting polysilane  $M_N = 9396$ ,  $M_W =$

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<sup>xlvi</sup> Some unusual transformation of **4-5** and **4-11** ( $\text{OCH}_2\text{CH}_2\text{CH}_3$  and  $\text{SCH}_2\text{CH}_2\text{CH}_3$  side-chains, respectively) was found when these polymers were heated above  $50^\circ\text{C}$  under vacuum. This gave products that were insoluble in common NMR solvents ( $\text{C}_6\text{D}_6$ ,  $\text{CDCl}_3$ , and  $\text{D}_2\text{O}$ ). No mass loss occurs for these polymers (see Section 4.5 and Figure 4.10 for more detail) at this temperature under TGA conditions ( $\text{N}_2$  atmosphere,  $+10^\circ\text{C}/\text{min}$ ). This transformation may be due to cross-linking or a precursor to silicon carbide, both of which suspected to be insoluble in common solvents. This process was not further evaluated for either polymer.

<sup>xlvii</sup> Combustion analysis of SiC is discussed in more detail in Chapter 5.

39340 (all molecular weights relative to polystyrene standards) and consistently a lower polydispersity (3.56 to 3.42 for functionalized polysilane compared to 4.19 for starting polysilane), which suggested a higher homogeneity following modification.<sup>17e</sup>

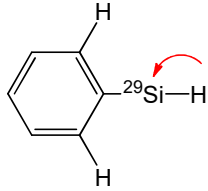
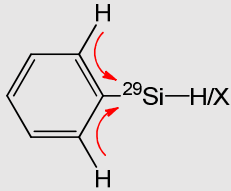
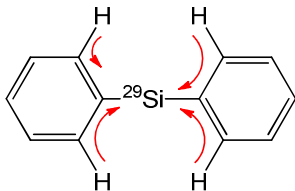
The low values for %C and %H for **4-5**, **4-9** and **4-13** will be discussed in greater detail in Section 4.4.2. These results can be reconciled with cross-linking as a result of over-reduction (Chapter 3), which leads to the formation of new Si-E-Si bonds (E = O, S).

#### 4.3.5 Characterization by <sup>29</sup>Si NMR

Characterization of the modified polysilanes by <sup>29</sup>Si NMR presents some interesting challenges. Inherently, the <sup>29</sup>Si nuclei is difficult to observe, due to the low sensitivity of the nucleus (natural abundance 4.67% <sup>29</sup>Si and small, negative magnetogyric ratio ( $-5.32 \times 10^{-7} \text{ T}^{-1} \text{ s}^{-1}$ )). Broad <sup>29</sup>Si peaks are expected based on the broad <sup>1</sup>H and <sup>13</sup>C spectra shown above. These problems were first approached through increased sample concentrations. Solution concentrations of 100 mg/mL were routinely used in these <sup>29</sup>Si NMR experiments. However, this could not address another problem: borosilicate glass appears as a broad peak centered at -80 to -100 ppm in the direct acquisition <sup>29</sup>Si NMR and this can overlap with the broad <sup>29</sup>Si peaks due to the PhSiH repeat unit, which are expected to be a broad massif at -60 ppm. Polarization transfer (DEPT) methods were applied to avoid this borosilicate signal overlap. DEPT methods were used to enhance signal to noise ratios and the DEPT parameters were modified for the number of H-atoms available for the experiment, which was either short range

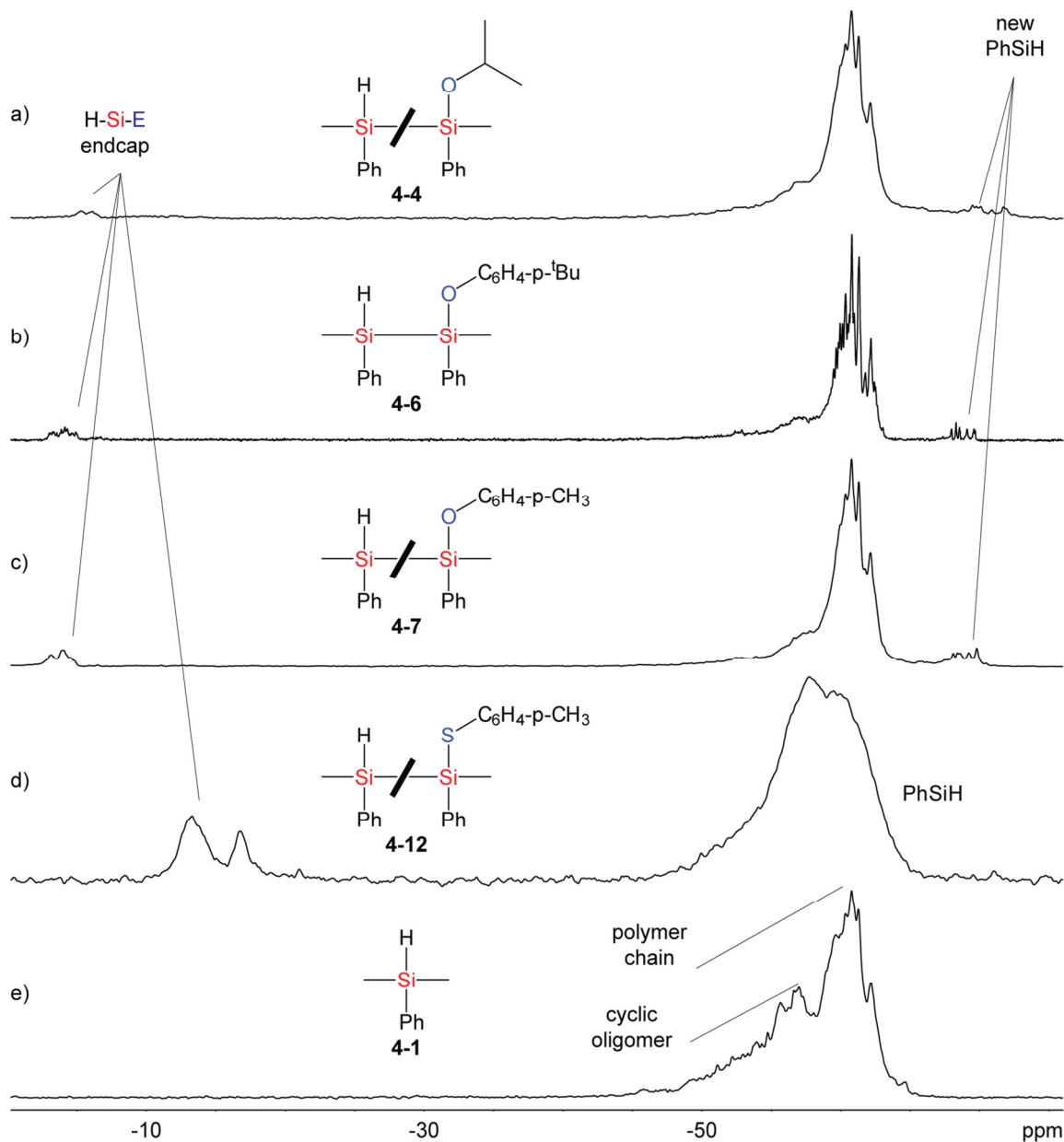
(DEPT90 for 1H,  $^1J_{\text{SiH}} = 188$  Hz, Table 4.3a) or long-range (DEPT45 for 2H,  $^3J_{\text{SiH}} = 8$  Hz, Table 4.3b or DEPT30 for 4H,  $^3J_{\text{SiH}} = 8$  Hz, Table 4.3c) DEPT.<sup>136</sup>

**Table 4.3.**  $^{29}\text{Si}$  NMR DEPT experiments used for polysilanes (this Chapter) and disilanes (Chapter 2 and 3).

Entry	Silane	Polarization transfer experiment	$\approx J_{\text{Si-H}}$
a		DEPT90, 1H	188 Hz
b		DEPT45, 2H	8 Hz
c		DEPT30, 4H	8 Hz

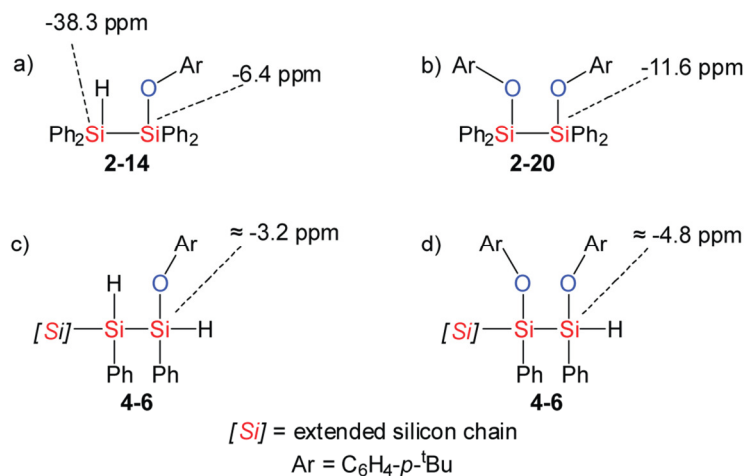
The short-range DEPT method (Table 4.3a) allows relatively facile observation of the repeat Si-H in the parent poly(phenylsilane) in the range 45-65 ppm (Figure 4.4b), as well as residual Si-H bonds in the modified polymers in the same region. The signals due to  $-\text{Si}(\text{Ph})\text{H}_2$  endcaps are presumed to be included in this region and  $^{29}\text{Si}$  NMR experiments to distinguish them from the bulk  $-\text{Si}(\text{Ph})\text{H}-$  signals were attempted. An experiment optimized for observing  $-\text{Si}(\text{Ph})\text{H}_2$  endcaps gave a spectrum that had the same shape and showed a decrease in signal-to-noise compared to the optimal method (DEPT90  $^1J_{\text{SiH}} = 188$  Hz). No distinct changes in the  $^{29}\text{Si}$  NMR spectrum were observed that would indicate the enhancement and presence of  $-\text{SiH}_2\text{Ph}$  over  $-\text{PhSiH}-$ . A broad

signal for the cyclic oligomers has been identified in the literature and is labeled in Figure 4.4e.<sup>137</sup>

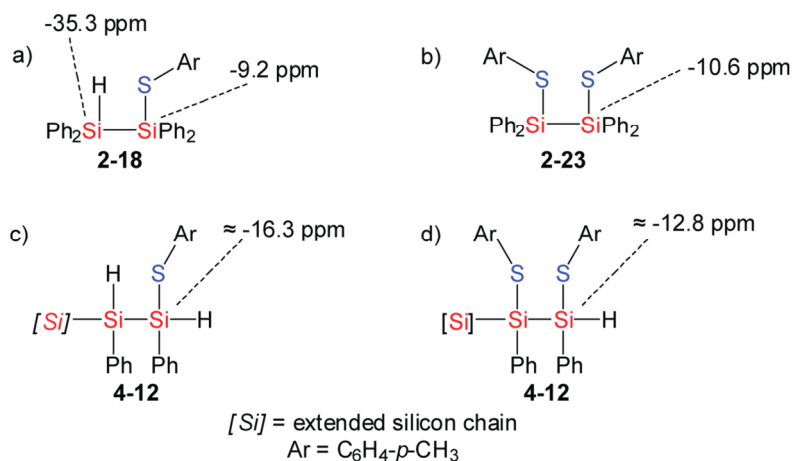


**Figure 4.4.**  $^{29}\text{Si}$  NMR (99 MHz) spectra obtained using short-range DEPT ( $^1J_{\text{SiH}} = 188$  Hz) for the representative modified polysilanes and the parent poly(phenylsilane) (**4-1**). This showed new signals for -PhSiH- groups that are adjacent to -PhSiO- and for H-Si-O endcaps, (a) -OCH(CH<sub>3</sub>)<sub>2</sub> (**4-4**), (b) -OC<sub>6</sub>H<sub>4</sub>-p-<sup>t</sup>Bu (**4-6**), (c) -OC<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub> (**4-7**), and (d) -SC<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub> (**4-12**), and (e) parent poly(phenylsilane) (**4-1**) in C<sub>6</sub>D<sub>6</sub>. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

In contrast, for some of the Si-O modified polymers, this short-range DEPT experiment does show new signals attributable to H-SiPh-O endcaps, with chemical shifts (-3.7 ppm) consistent with Si-O environments (e.g. Table 4.3b). Two distinct peaks for -PhSi(H)X endcaps (X = C, S) were detected (**4-2**, **4-3**, **4-11** in experimental Section 4.9.2, **4-12** in Figure 4.4d), which are assigned to endcap environments  $[Si]-PhSiH-PhSi(H)X$  or  $[Si]-PhSiX-PhSi(H)X$  ( $[Si]$  is an extended silicon chain), where the adjacent Si has an X or H group. Some evidence for this disparity in endcap chemical shifts ( $\pm 1$  to 5 ppm) leading to two peaks is found in the  $^{29}Si$  NMR of the substituted disilanes **2-14** and **2-18** described in Chapter 2. A difference in  $^{29}Si$  chemical shift is noted for the “Si-X” unit in the monosubstituted disilanes (-6.4 ppm in  $Ph_2SiH-Si(OC_6H_4-p-^tBu)Ph_2$  (**2-14**) and -9.2 ppm in  $Ph_2SiH-Si(SC_6H_4-p-CH_3)Ph_2$  (**2-18**)) versus the disubstituted disilanes (-11.6 ppm in  $(Ph_2SiOC_6H_4-p-^tBu)_2$  (**2-20**) and -10.6 ppm in  $(Ph_2SiSC_6H_4-p-CH_3)_2$  (**2-23**)). This indicates the “Si-X” chemical shift in disilane shifts upfield if the adjacent silicon has an aryloxy or thiolato group. Thus different peaks in the  $^{29}Si$  NMR of their analogous X-modified polysilanes (Figure 4.4b/d) can be attributed to different endcap substitution possibilities. The downfield peak is a silicon adjacent to an H (Figure 4.5c or Figure 4.6c) and the upfield peak is adjacent to an aryloxy (Figure 4.5d) or thiolato (Figure 4.6d).



**Figure 4.5.** <sup>29</sup>Si NMR chemical shifts of a) Ph<sub>2</sub>SiH-Si(OC<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)Ph<sub>2</sub> (**2-7**) and b) (Ph<sub>2</sub>Si(OC<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu))<sub>2</sub> (**2-14**) showing a chemical shift disparity in Si(OAr)Ph<sub>2</sub> unit depending on the adjacent “Si-H” or “Si-OAr” group. This suggests an endcap chemical shift disparity in **4-6** c) [Si]-SiH(Ph)-SiH(OC<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)Ph and d) [Si]-SiH(Ph)-SiH(OC<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)Ph with different adjacent group, “Si-H” or “Si-OAr”. [Si] = extended silicon chain. Ar = C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu.

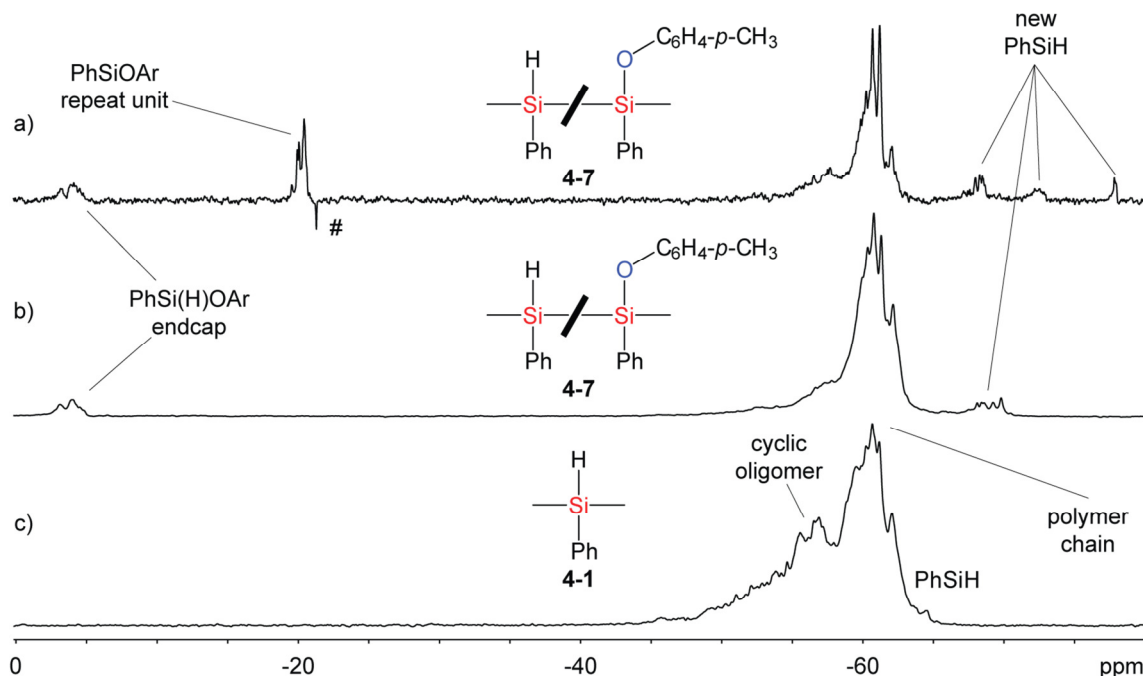


**Figure 4.6.** <sup>29</sup>Si NMR chemical shifts of a) Ph<sub>2</sub>SiH-Si(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)Ph<sub>2</sub> (**2-18**) and b) (Ph<sub>2</sub>Si(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>))<sub>2</sub> (**2-23**) showing a chemical shift disparity in Si(SAr)Ph<sub>2</sub> unit depending on the adjacent “Si-H” or “Si-SAr” group. This suggests an endcap chemical shift disparity in **4-6** c) [Si]-SiH(Ph)-SiH(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)Ph and d) [Si]-SiH(Ph)-SiH(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>)Ph with different adjacent group, “Si-H” or “Si-SAr”. [Si] = extended silicon chain. Ar = C<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>.

Assignments for additional new peaks denoted “new PhSiH” (Figure 4.4a-c) have not yet been determined. They are presumed to be -PhSiH- repeat units based on their

being near to, but upfield from the main -PhSiH- peak, and are possibly adjacent to one or two “PhSiOR” groups.

The long-range DEPT30 (4H transfer, Table 4.3c) experiment works well for diagnosing the model disilanes Ph<sub>2</sub>SiH-Ph<sub>2</sub>SiX and (Ph<sub>2</sub>SiX)<sub>2</sub> (see Chapter 2), but application of the corresponding long-range DEPT45 (2H transfer, Table 4.3b) experiment to poly(phenylsilane) (**4-1**) and its derivatives (**4-2** to **4-13**) was not always successful. For some polysilanes new Si-O environments can be detected using this long-range experiment, such as for the OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>-modified polymer (Figure 4.7), but quaternary silicons in -PhSiX- repeat units are not consistently detected in all of the modified polysilanes. The reasons for success or lack thereof, of the long-range experiment are not immediately apparent, however, it must be related to %X incorporation and orientation of the phenyl group with respect to the polysilane chain. For polymers with lower %X, the -PhSiX- repeat units are inherently harder to detect by these DEPT <sup>29</sup>Si NMR experiments. A variety of phenyl group orientations along the polysilane chain may each have different optimized DEPT transfer conditions, such as coupling constants; coupling constant for <sup>3</sup>J<sub>SiH</sub> = 6, 7, 9, and 10 Hz were also tested in many examples, still showing no <sup>29</sup>Si signals.



**Figure 4.7.**  $^{29}\text{Si}$  NMR (99 MHz) spectra obtained using a) long-range DEPT ( $^3J_{\text{SiH}} = 8$  Hz), b) short-range DEPT ( $^1J_{\text{SiH}} = 188$  Hz) for the  $\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$  (**4-7**) modified polysilane and c) short-range DEPT of parent poly(phenylsilane) (**4-1**) in  $\text{C}_6\text{D}_6$ .

#### 4.3.6 Characterization by GPC and determination of $\text{B}(\text{C}_6\text{F}_5)_3$ chemoselectivity

Polymer modification reactions were initially modeled by the disilane (**2-2**, Chapter 2), which gave a good indication of the probable selectivity of these  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reactions for Si-H versus Si-Si activation. Molecular weight, GC-MS, and  $^1\text{H}$  NMR experiments verified that no Si-Si bonds were being cleaved in the reactions of the less robust poly(phenylsilane) (**4-1**).<sup>xlvi</sup> Molecular weight analysis using multiangle light scattering gel permeation chromatography (MALS-GPC, hereafter referred to as GPC) was used to assess conservation of the polymer chain lengths following polymer modification. The molecular weight (MW) of the polymers was measured before and after modification. As shown in Table 4.4 (full experimental GPC results are in Table 4.6,

<sup>xlvi</sup> The weakness and lability of polysilane Si-Si linkages and those of other group 14 polycatenates is described by Hill<sup>22</sup> as well as in polysilane reviews<sup>5,14a,c</sup>.

experimental Section 4.9.7), the MWs for each modified polysilane are larger than those for the specific parent poly(phenylsilane) (**4-1**), and polydispersities ( $PDI = M_w/M_n$ ) also increase with polymer modification. This is consistent with intact polymer “skeletons” having undergone variable degrees of substitution with side-chains considerably heavier than the hydrogens they replaced. Polymers **4-5** and **4-9** are notable for their large MW relative to PDI. Over-reduction (Chapter 3) occurred for these functional groups and this process will be described and discussed further in the Section 4.4.

**Table 4.4.** Representative GPC (MALS) MW data for modified polysilanes, -PhSiH-/PhSiX-, with corresponding data for the specific batches (**4-1a-d**) of parent poly(phenylsilane) used in each case.<sup>a,b</sup> Data for **4-11**, **4-12**, and **4-13** is used with permission (see note at beginning of Chapter 4).<sup>96</sup>

polymer	X =	M <sub>N</sub> (kDa)	M <sub>W</sub> (kDa)	PDI
<b>4-1a</b>	H	2.3 ± 0.2	4.0 ± 0.3	1.7
			↓	
<b>4-2</b>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Ph	13.1 ± 1.9	36.6 ± 4.0	2.8
<b>4-1b</b>	H	1.9 ± 0.2	3.0 ± 0.3	1.6
			↓	
<b>4-3</b>	CH <sub>2</sub> CH <sub>2</sub> Bu	5.1 ± 0.2	15.5 ± 0.4	3.0
<b>4-7</b>	OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	2.8 ± 0.3	5.1 ± 0.5	1.8
<b>4-8</b>	OCH <sub>2</sub> CH <sub>2</sub> Cl	8.9 ± 0.4	17.6 ± 0.5	2.0
<b>4-1c</b>	H	1.8 ± 0.2	2.4 ± 0.3	1.3
			↓	
<b>4-4</b>	OCH(CH <sub>3</sub> ) <sub>2</sub>	5.8 ± 0.2	13.0 ± 1.8	2.2
<b>4-5</b>	OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	21.3 ± 1.4	42.2 ± 5.5	2.0
<b>4-1d</b>	H	2.2 ± 0.2	3.5 ± 0.3	1.6
			↓	
<b>4-9</b>	OCHPh <sub>2</sub>	4.8 ± 0.3	15.0 ± 1.2	3.1
<b>4-11</b>	SCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	2.8 ± 0.5	4.8 ± 0.7	1.7
<b>4-12</b>	SC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	3.4 ± 0.2	5.4 ± 0.4	1.6
<b>4-13</b>	SCHPh <sub>2</sub>	2.6 ± 0.2	5.4 ± 0.4	2.0

<sup>a</sup>Error estimated based on deviations for samples run in triplicate. <sup>b</sup>The full GPC data set (replicate batches of each modified polymers) is shown in Section 4.9.7, Table 4.6.

The degree of increase in molecular weight, both number averaged molecular weight (M<sub>N</sub>) and weight-averaged molecular weight (M<sub>W</sub>), but particularly M<sub>W</sub>, is higher

than expected based on the extent of substitution of X side-chains estimated by  $^1\text{H}$  NMR. This can be rationalized by a number of observations. Most of the X-modified polymers were moisture-sensitive and possible hydrolysis and cross-linking might have increased the molecular weight. When polymers were dissolved in THF and allowed to stand in solution before injection into the GPC, increasing molecular weight was found when the time between dissolution and injection was increased. This observation was most evident with small alkoxy groups (**4-4/4-8**) and thiolato groups (**4-11/4-12**) for which the Si-E bond is less protected by bulky groups. Corroborating the possibility of hydrolysis during GPC analysis is the error in MW estimates for the X-modified poly(phenylsilane) derivatives, which were generally larger those for the parent polymer (**4-1**).

Polymers **4-2/4-3** do not have side-chains sensitive to hydrolysis. These polymers showed vastly increased  $M_N$  and  $M_W$ , but also a larger increase in PDI (2.8 for **4-2**, 3.0 for **4-3**, Table 4.4) compared to standard O/S modifications (1.8-2.2, Table 4.4). GPC traces for **4-2/4-3** are much broader (see Figure 4.65b/c). These results suggest that  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed olefin hydrosilation favors two possibilities: Si-H groups in longer Si-chains and/or Si-H groups on chains that already contain X substituents. This tendency for higher *n*-hexyl incorporation is similar reactions of disilane **2-2** ( $(\text{Ph}_2\text{SiH})_2$ ) with 1-hexene, which mostly gave disubstituted product (**2-19**). In either case, this leads to a degree of substitution that is higher for longer chains, which gives disproportionately higher  $M_W$  values for the sample as a whole.

To further test for possible competing Si-Si scission reactions, pentane/hexanes washings of the isolated polymers (see experimental Section 4.9.5) were collected to search for evidence of short chain, silicon-containing products, which should be more

soluble than the polymers. Most of the modified polymers are powdered solids that can be washed repeatedly with either pentane or hexanes. GC-MS traces of these washings did not show any signs of possible cleavage products, even at long elution times (30 min). Additionally, the non-volatile components of these polymer washings were analyzed by  $^1\text{H}$  NMR: the solvent and volatiles were removed from aliquots under vacuum, and samples were prepared by dissolving the resulting residues in  $\text{C}_6\text{D}_6$ . No sharp signals attributable to small oligosilanes or monosilanes were observed by this method.

#### 4.4 Challenges in post-polymerization modification

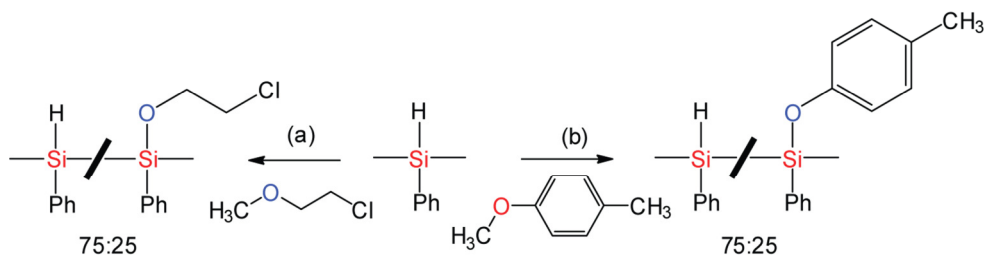
Two classes of substrate have been identified that do not react optimally during the  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed polymer modification. These include substrates for which catalyst inhibition was observed due to substrate- $\text{B}(\text{C}_6\text{F}_5)_3$  adduct formation (Section 4.4.1), and substrates for which the  $\text{B}(\text{C}_6\text{F}_5)_3$  catalyzes competing Si-H reactions, leading to “over-reduction” chemistry (4.4.2).

##### 4.4.1 Catalyst inhibition by competing substrate coordination

As discussed in depth in Chapter 2, sequestration of catalyst  $\text{B}(\text{C}_6\text{F}_5)_3$  via its competitive coordination with strongly electron-donating substrates, such as imines or alcohols/phenols, inhibits conversion of the Si-H repeat units, leading to lower degrees of polymer modification. Comparable  $\text{B}(\text{C}_6\text{F}_5)_3$  adduct formation is suspected to be responsible for the low conversions found for the dehydrocoupling reactions of *p-t*-butylphenol ( $\text{HOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$ ) with poly(phenylsilane) (10% substitution of Si-H bonds). For such challenging Lewis basic substrates an alternative route to comparable

aryloxy- or alkoxy-substituted silanes and polymers is available:  $B(C_6F_5)_3$ -catalyzed demethanative coupling (Scheme 4.6a/b) of the corresponding methyl ethers. This route has been exploited to prepare the two Si-O-containing polymers **4-7** (from *p*-methylanisole, Scheme 4.6b) and **4-8** (from 2-chloroethyl methyl ether, Scheme 4.6a), both with approximately 25% incorporation of side-chains under mild conditions.

Scheme 4.6.



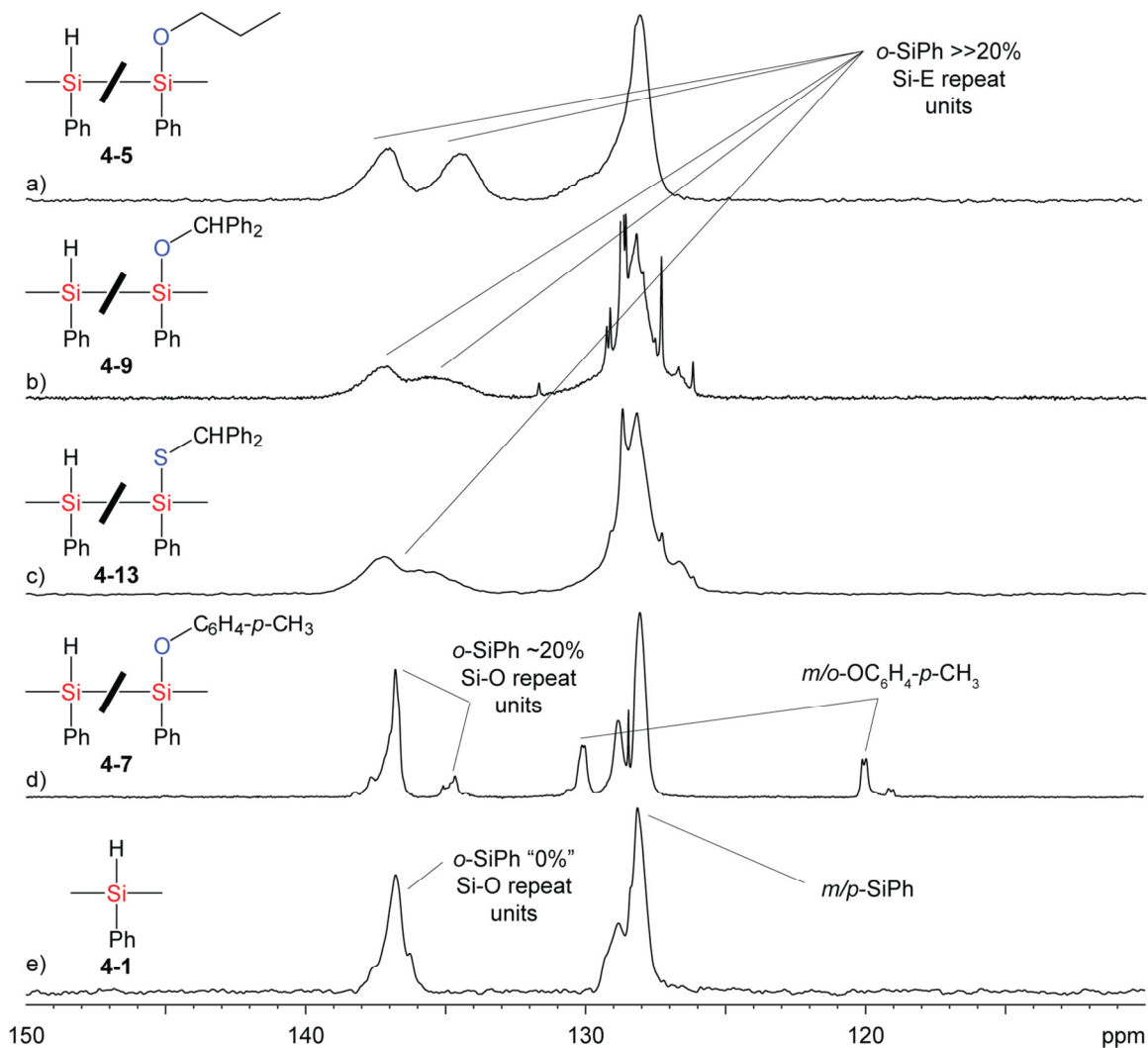
#### 4.4.2 Identification of competing over-reduction reactions

Competing over-reduction reactions (Chapter 3) have been identified and characterized in polymers **4-5**, **4-9**, and **4-13**. The propensity for over-reduction can be divided into two cases, benzylic side groups (benzyloxy **4-9** and thiobenzyloxy **4-13**) and straight-chain alkyl groups (alkoxy, **4-5**), as described previously (Chapter 2 and 3). The over-reduction product  $Ph_2CH_2$ , diphenylmethane, was detected by  $^1H/^{13}C$  NMR in reactions of benzophenone (**4-9**) and thiobenzophenone (**4-13**).  $(Ph_2CH)_2$ , 1,1,2,2-tetraphenylethane, was also detected as a by-product in the preparation of **4-13** only.<sup>xlix</sup> Propane, from over-reduction of propionaldehyde (during the synthesis of **4-5**), was not detected due to its volatility.  $^1H$  NMR integration of **4-5** seemed to indicate an

<sup>xlix</sup> See experimental Figure 4.63 for detailed identification. A mechanism explaining the formation of 1,1,2,2-tetraphenylethane has not yet been determined. A control reaction of  $Ph_2CH_2$  and  $B(C_6F_5)_3$  showed no reaction. 1,1,2,2-tetraphenylethane is not observed in reactions of thiobenzophenone with mono- or disilanes.

unexpectedly high degree of incorporation of Si-O<sup>n</sup>Pr groups (70%, i.e. very low intensity  $\delta$ Si-H relative to  $\delta$ CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). In fact, this NMR integration was misleading because the residual Si-H bonds in the modified polymer were consumed by the competing over-reduction reaction during the preparation of this polymer.

In addition to the very low relative integration for Si-H in the <sup>1</sup>H NMR, crude integration of peaks in the aromatic region of the DEPT135 <sup>13</sup>C NMR spectrum of **4-5** (Figure 4.8a) showed a much higher intensity of the ortho CH signal from -PhSiO- (modified) units relative to that from -PhSiH- units than is observed for other modified polymers that did not exhibit over-reduction (Figure 4.8d/e). This is consistent with the “insertion” of a high proportion of Si-O-Si linkages, at the expense of Si-H bonds, in the modified polymer. The <sup>29</sup>Si NMR spectra for **4-5**, **4-9**, and **4-13** (see experimental Figure 4.31, Figure 4.46, and Figure 4.61, respectively) show signals due to residual PhSiH repeat units that are broader and quite featureless compared to other O-modified poly(phenylsilane) derivatives (**4-4**, **4-6**, **4-7**, and **4-8**). This indicated a structural similarity among the three over-reduction polymers compared to those not exhibiting over-reduction. The broadness is attributed to new PhSiH repeat unit environments, where the Si-H may be adjacent to one or two Si-H, SiOR, or Si-O-Si units.



**Figure 4.8.** The aromatic region of representative DEPT135  $^{13}\text{C}$  NMR spectra (75 MHz) showing the high ratio of *o*-C signal due to -PhSiE- (E = O, S) units to *o*-C signal due to -PhSiH- units in modified polymers containing a) OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (**4-5**), b) OCHPh<sub>2</sub> (**4-9**), or c) SCHPh<sub>2</sub> (**4-13**) groups, which have undergone over-reduction, relative to the spectra for d) for a “normal” modified polymer (**4-7**, 20%) and e) parent poly(phenylsilane) (**4-1**, “0%”) in C<sub>6</sub>D<sub>6</sub>. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

The EA results for these polymers indicate a substantial contribution of the Si-E-Si repeat unit in the polymer structure. As already shown in Table 4.2, for polymers **4-5**, **4-9**, and **4-13** there was poor agreement between  $^1\text{H}$  NMR and EA estimates of %X incorporation. Consider the first example, polymer **4-5**. The over-reduction repeat unit, -PhSiO<sub>1/2</sub>-, was included in the calculation shown in Table 4.5. Attempts to reconcile

elemental analysis data with the degree of over-reduction occurring were made by trial-and-error calculations. Even when assuming the exclusive presence of the  $\text{-PhSiO}_{1/2}\text{-}$  repeat unit gave  $\%C/\%H$  values that were in better agreement with the experimental EA than the calculated values shown previously in Table 4.2. This calculation was optimized by the following method: first by constraining the ratio of  $\text{PhSiH}:\text{PhSiO}^n\text{Pr}$  to 30:70 determined from  $^1\text{H}$  NMR integrations,<sup>1</sup> then by trial-and-error estimates for the presence of additional  $\%PhSiO_{1/2}$  to give the best estimate of repeat unit proportions. A similar trial-and-error calculation for polymer **4-9** showed a high proportion of  $\text{-PhSiO}_{1/2}\text{-}$ .<sup>li</sup>

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<sup>1</sup>  $^1\text{H}$  NMR integration method does not account for possible  $\text{-PhSiO}_{1/2}\text{-}$  repeat units. See experimental Figure 4.64 in experimental Section 4.9.6 for calculation example.

<sup>li</sup> Relative quantities of  $\text{PhSiH}$  and  $\text{PhSiOCHPh}_2$  could not be determined in polymer **4-9** because of a lack of identifiable side-chains in the  $^1\text{H}$  NMR spectrum. Broad and overlapping polymer signals, and sharp  $\text{Ph}_2\text{CH}_2$  signals precluded straightforward integration analysis. A 1:1 ratio was assumed in the calculation. Changes in this ratio do not significantly affect  $\%C/\%H$  calculations because of the relatively low overall combined quantity of combined  $\text{PhSiH}$  and  $\text{PhSiOCHPh}_2$  suggested by this calculation.  $^1\text{H}$  NMR integration showed a quantity of  $\text{Ph}_2\text{CH}_2$  relative to the combined quantity of  $\text{PhSiH} + \text{PhSiOCHPh}_2$  (1:1). This is represented in the calculations for **4-9** in Table 4.5.

**Table 4.5.** Elemental analyses for modified polymers (**4-5**, **4-9**, and **4-13**) where over-reduction was observed. Data for **4-13** is used with permission (see note at beginning of Chapter 4).<sup>96</sup>

Found		Composition calc'd for %X degree of substitution; best fit in bold. %Si-H/%SiER = 0/0% included for comparison			Calc'd based on <sup>1</sup> H NMR integrations
#	%C/%H/ %S	%Si-H/ %Si-ER/ %PhSi-E <sub>1/2</sub> / %Ph <sub>2</sub> CH <sub>2</sub> <sup>a</sup> / %(Ph <sub>2</sub> CH) <sub>2</sub> <sup>b</sup>	%C/%H/ %S	%X	%C/%H
<b>4-5</b>	62.65/5.18	<b>2/5/93</b> 0/0/100	<b>63.90/4.68</b> 63.37/4.45	70	66.65/7.00
<b>4-9</b>	64.21/4.31	0/0/100/0 <b>0.5<sup>c</sup>/0.5<sup>c</sup>/98/1</b>	63.67/4.45 <b>64.21/4.50</b>	100 <sup>d</sup>	84.51/6.22
<b>4-13</b>	67.91/4.74/7.99	0/0/100/0/0 <b>0.71/8.49/73.56/ 11.49/5.75</b>	60.32/4.04/13.10 <b>67.90/5.45/10.36</b>	40	72.42/5.43/7.03

<sup>a</sup>%Ph<sub>2</sub>CH<sub>2</sub> only relevant for **4-9** and **4-13**. Relative residual %Ph<sub>2</sub>CH<sub>2</sub> estimated by <sup>1</sup>H NMR. <sup>b</sup>(Ph<sub>2</sub>CH)<sub>2</sub> only relevant for **4-13**. Relative residual %(Ph<sub>2</sub>CH)<sub>2</sub> <sup>1</sup>H NMR integration. <sup>c</sup>%Si-H:%Si-OR was assumed to be 0.5%:0.5%. Overlapping Si-H/Si-OR/CH<sub>2</sub>Ph<sub>2</sub> signals precluded estimation %Si-H:%Si-OR by <sup>1</sup>H NMR. Values high in %Si-H or %Si-OR only greatly affected %C/%H calculations if their sum was greater than 1%. <sup>d</sup>Actual calculations determined a non-real/negative number for %Si-H due to the non-inclusion of PhSiO<sub>1/2</sub> repeat units. Its absolute value was small (10%) compared to %Si-OCHPh<sub>2</sub>. Assumed %Si-H to be zero to compare %C/%H values to those including %PhSiO<sub>1/2</sub>.

An optimized ratio of repeat units was more difficult to determine for **4-13**. The initial calculation assuming exclusively -PhSiS<sub>1/2</sub>- unit (Table 4.5, entry **4-13**) did not give satisfactory %C/%H/%S values as it had with O-derivatives **4-5** and **4-9**. This suggested a higher relative proportion of %PhSiH and %PhSiE units in polymer **4-13** compared to the above examples and substantially complicated the trial-and-error determination. The results of the trial-and-error calculation reported Table 4.5 for **4-13** gives

$\% \text{PhSiH} / \% \text{PhSiSCHPh}_2 / \% \text{PhSiS}_{1/2}$  in very approximate agreement with EA results<sup>lii</sup>, however markedly less so than **4-5** and **4-9**. Specifically, the estimate for %S is high (%S: Exp 7.99, Calc'd 10.36, Table 4.5). Further trial-and-error analysis might give a better estimate for  $\% \text{PhSiH} / \% \text{PhSiSCHPh}_2 / \% \text{PhSiS}_{1/2}$ . These calculations show that the repeat units in **4-13** are not as straightforward as **4-5** and **4-9** since a relatively low quantity of over-reduction repeat unit,  $-\text{PhSiS}_{1/2}-$ , is present, compared to the degree of  $-\text{PhSiO}_{1/2}-$  in **4-5** and **4-9**.

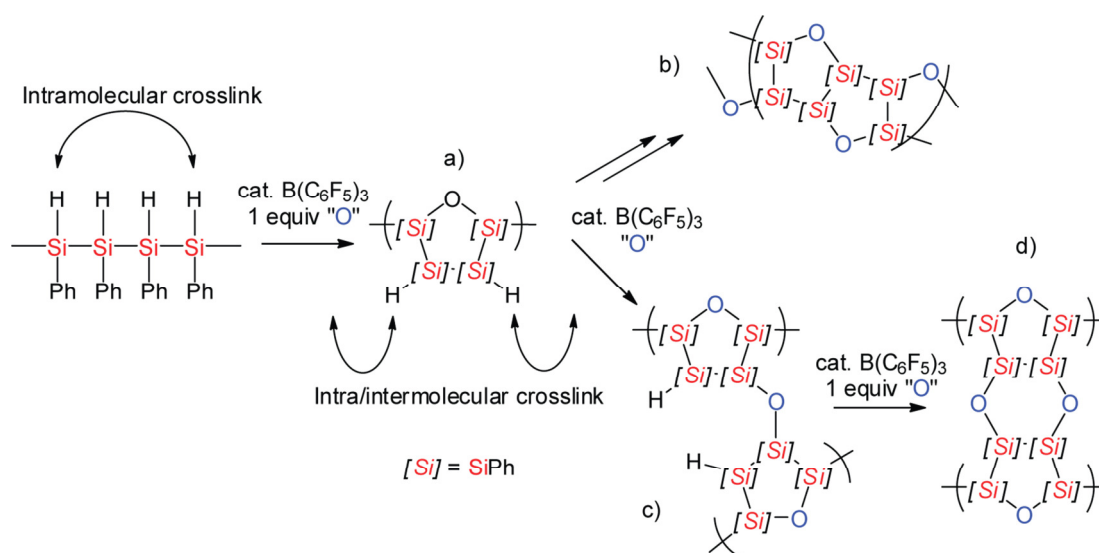
The GPC data obtained for polymers **4-5**, **4-9**, and **4-13** is consistent with the incorporation of a high proportion of Si-E-Si linkages, although the three polymers give quite different results (see Table 4.4 MWs, and Table 4.6 in experimental Section 4.9.7, Table 4.6). First, examples **4-9** and **4-13**, which were prepared through the introduction of ECHPh<sub>2</sub> side-chains, showed residual Ph<sub>2</sub>CH<sub>2</sub> in the mixture by <sup>1</sup>H/<sup>13</sup>C NMR (see Figure 4.44, Figure 4.45, Figure 4.59, and Figure 4.60 in experimental Section 4.9.2). Although these polymers did not have significantly higher MWs than the rest of the modified polymers, the MW measurement was likely offset by this residual, low-MW Ph<sub>2</sub>CH<sub>2</sub>, which could not be removed even after repeated washings with pentane or hexanes. Consistent with this, PDI values of **4-9** and **4-13** of 3.1 and 2.2, respectively, are also greater than for the other heteroatom-modified polymers where over-reduction is not observed (**4-4**, **4-7**, **4-8**, **4-11**, **4-12**), which show a comparatively modest increase in PDI

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<sup>lii</sup> Relative quantities of PhSiH and PhSiECHPh<sub>2</sub> could not be determined in this sample because of a lack of identifiable side-chains in the <sup>1</sup>H NMR spectrum, broad/overlapping signals, and sharp Ph<sub>2</sub>CH<sub>2</sub> and (Ph<sub>2</sub>CH)<sub>2</sub> signals, all of which precluded straightforward integration analysis. Integration of the broad PhSiH and PhSiECHPh<sub>2</sub> regions gave an indication of their combined relative intensity  $\%(\text{PhSiH} + \text{PhSiECHPh}_2)$ . A crude estimate of  $\% \text{Ph}_2\text{CH}_2$  and  $\%(\text{Ph}_2\text{CH})_2$  was made relative to  $\%(\text{PhSiH} + \text{PhSiECHPh}_2)$  and this was included in the trial-and-error calculation in Table 4.5.

from 1.6-1.8 (in the parent poly(phenylsilane) (**4-1**)) to 1.6-2.2. This suggests that some long chains are formed from over-reduction at the high MW end, with the  $\text{Ph}_2\text{CH}_2$  (and, for **4-13**,  $(\text{Ph}_2\text{CH})_2$ ) impurities broadening the distribution at the low end of the MW scale. The other example, **4-5**, showed data directly evident of over-reduction occurring. Its MW was found to be much higher than other modified polymers (Table 4.4, e.g.  $M_N/M_W = 21.3/42.2$  kDa for **4-5** compared to  $M_N/M_W = 1.8/2.4$  kDa for **4-1**, increased by a factor of 10-20 times and at least double in other examples, see Table 4.6 in experimental Section 4.9.7), consistent with a substantial amount of cross-linking.

Despite the suspected cross-linking, polymers **4-5**, **4-9**, and **4-13** are soluble in common organic solvents, which suggests the degree of intermolecular cross-linking in these examples is still somewhat low. The high degree of cross-linking determined by EA results above suggests heavily cross-linked polysiloxane-like insolubility. Indeed, the solubility yet high degree of cross-linking determined for these polymers seems to be contradictory. To account for these results, a structure is envisioned that consists of a lightly cross-linked, yet heavily oxygenated, polymer, as illustrated in Scheme 4.7. The formation of small polysilicon-siloxane rings via intramolecular over-reduction is proposed and these may be incorporated into a variety of “linear” (e.g. Scheme 4.7c) or “fused” structures (e.g. Scheme 4.7b/d) via further over-reduction by residual Si-H bonds. These structures are consistent with a polysilane that has undergone many over-reduction reactions, yet is not as heavily cross-linked as common insoluble polysiloxanes.<sup>5,138</sup>

Scheme 4.7.  $[Si] = SiPh$ .

A similar intra/intermolecular cross-linking with sulfur is presumed for polymer **4-13**, however to a lesser degree compared to **4-5** and **4-9**. This is based on lower  $^1H$  NMR integrations for  $Ph_2CH_2$  and  $(Ph_2CH)_2$  relative to broad polymer signals, and on EA results pointing to lower  $\%PhSi-S_{1/2}$  in **4-13** relative to  $\%PhSi-O_{1/2}$  in **4-5/4-9**. Overall, these reactions show that over-reduction readily occurs in polysilanes  $OCH_2CH_2CH_3$  (**4-5**) and  $ECHPh_2$  (**4-9**, **4-13**) particularly for the bulkier, benzylic,  $OCHPh_2$  (**4-9**) and  $SCHPh_2$  (**4-13**), side-groups as discussed previously in Chapter 3.

These substrates and analogous ones that lead to O/S-benzylic or primary alkoxy side-chains need to be avoided for post-polymerization modification of poly(phenylsilane) because of the inevitability of over-reduction. Benzylic substrates, in particular, are extremely prone to over-reduction. An experiment reducing the catalyst loading (from 4 or 5 mol% to 0.5 mol%) for reactions of benzophenone or thiobenzophenone with poly(phenylsilane) was attempted to eliminate competing over-reduction reactions. Lower catalyst loadings have been previously exploited to make **3-1** ( $Ph_2SiH-Si(OCHPh_2)Ph_2$ ) and **3-2** ( $Ph_2SiH-Si(SCHPh_2)Ph_2$ ). However, this did not result

in a decrease in over-reduction in reactions of poly(phenylsilane) (**4-1**). No changes in the  $^1\text{H}$  NMR of **4-13** were observed in runs with either 5 or 0.5 mol%  $\text{B}(\text{C}_6\text{F}_5)_3$ : broad Si-H/Si-Ph signals and discrete  $\text{Ph}_2\text{CH}_2$  or  $(\text{Ph}_2\text{CH})_2$  had the same relative intensity in the  $^1\text{H}$  NMR regardless of the catalyst loading.

#### 4.5 Properties of modified poly(phenylsilane) derivatives

UV-vis spectroscopic analysis allows for the speculation of the conformational preferences of these modified polymers in relation to the parent poly(phenylsilane). The important absorption of interest arises from the sigma conjugation along the all-Si backbone of polysilanes, the  $\sigma$ - $\sigma^*$  transition.<sup>liii</sup> The energy of this transition depends on the persistence length of  $\sigma$ -conjugated chromophore(s) in the polymer sample, i.e. the number of silicon atoms included in stretches of all-*anti* configurations along the polysilane chain.<sup>121,140</sup> Any *gauche* arrangement along a given four-silicon unit within the chain will interrupt the chromophore. In general, higher MW samples show more intense, red-shifted  $\sigma$ - $\sigma^*$  absorptions.<sup>liv</sup> Presumably this reflects a higher proportion of longer chromophores in these samples. However, the nature of the polymer side-chains also plays a critical role in the number and length of chromophores in the sample, since the size of the side-chain affects the conformational preferences of the polysilicon chain and the barriers to rotation around the relatively long Si-Si bonds.

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<sup>liii</sup> Although commonly believed to be the  $\sigma$ - $\sigma^*$  transition, the actual description<sup>139</sup> is more complex. For the purposes of a basic interpretation and description, it will continue to be referred to as  $\sigma$ - $\sigma^*$  in this work.

<sup>liv</sup> For oligomers with two to six repeat units  $\lambda_{\text{max}} = 236\text{-}265$ ,  $\epsilon = 18200 - 30500$ .<sup>108a</sup> The dependence of  $\lambda_{\text{max}}$  on polysilane chain length is described in the literature (e.g. for [(*n*-dodecyl)( $\text{CH}_3$ )Si] $_n$ , if  $n = 50$  then  $\lambda_{\text{max}} = 300$  nm, if  $n = 1350$  then  $\lambda_{\text{max}} = 350$ ).<sup>107b</sup>

The UV-vis spectra (shown in Figure 4.9a) illustrates the impact of these features. Both poly(phenylsilane) (**4-1**, black line) and poly(methylphenylsilane)<sup>lv</sup> (**4-14**, PMPS, grey line), in CH<sub>2</sub>Cl<sub>2</sub>, show reasonably intense absorptions in the 250-300 nm region. This absorption has been attributed to  $\sigma$ - $\sigma^*$  for short Si-chain oligomers and/or  $\pi$ - $\pi^*$  for the phenyl group.<sup>108a,b,140-141</sup> Literature discussions of the electronic spectra of polysilanes have focused far less on this higher energy region<sup>39,125,141-142</sup> than on the 300-400 nm region where the intense  $\sigma$ - $\sigma^*$  absorption is typically found. For PMPS, **4-14**, an intense, red-shifted  $\sigma$ - $\sigma^*$  absorption at 337 nm is the main distinguishing feature, while for poly(phenylsilane) (**4-1**) the corresponding  $\sigma$ - $\sigma^*$  absorption is far less red-shifted, observed as a weak, low-energy shoulder to the Ph-based absorption in the 250-300 nm region. These results are consistent both with the higher MW of the PMPS (**4-14**)<sup>125,lv</sup> and a much higher abundance of all-*anti* conformations in the PMPS sample, a result of the greater steric influence of the CH<sub>3</sub> group at each repeat unit, relative to the H in poly(phenylsilane). In poly(phenylsilane) (**4-1**), the small hydrogen side-chain allows the polysilane to “kink” (adopt *gauche* conformations) and therefore reduces the chromophore length(s).<sup>39,121,130a</sup>

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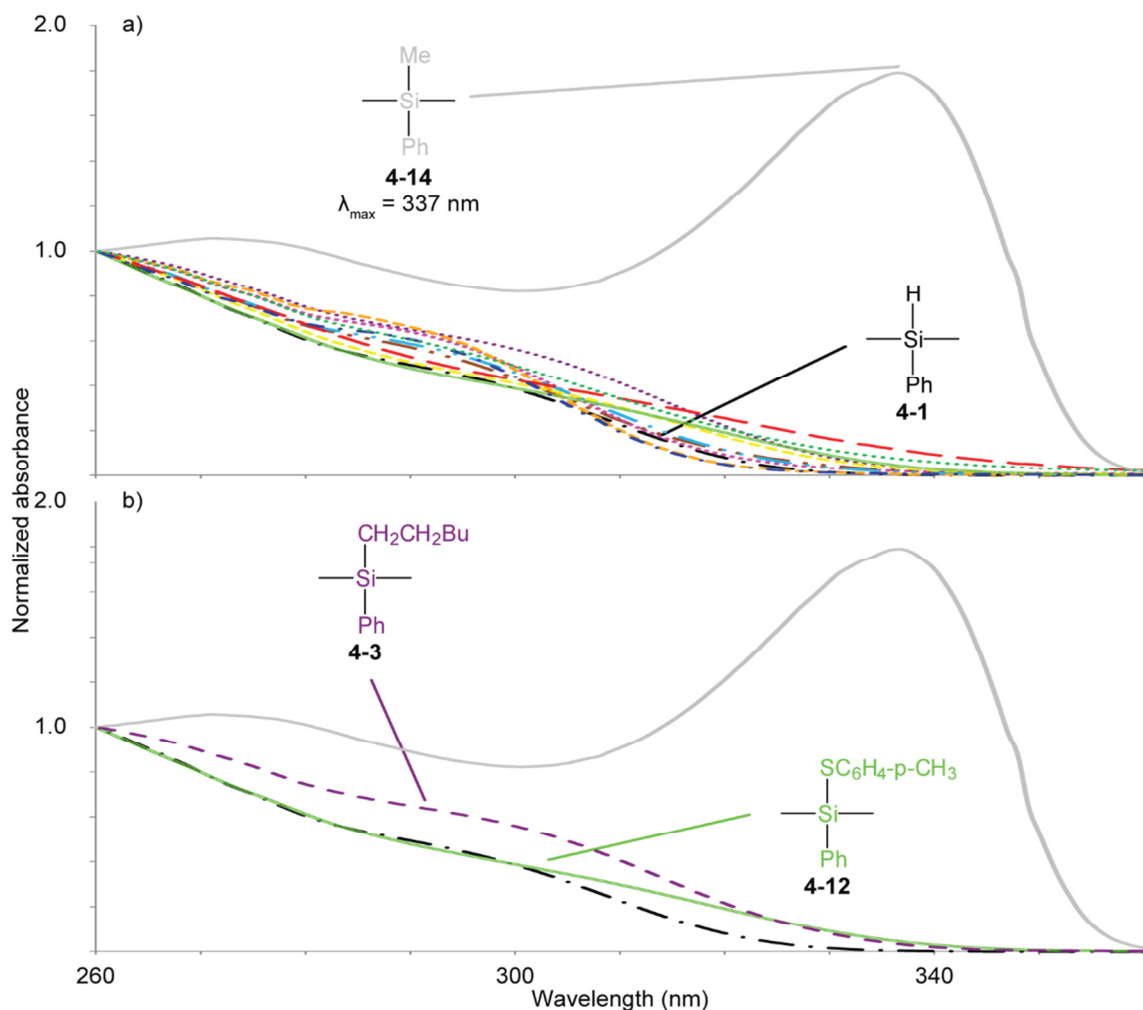
<sup>lv</sup> Prepared by reductive Wurtz coupling using the method reported in the literature<sup>125</sup> (grey line).

<sup>lvi</sup> MW of  $M_N = 5.0$  (85%), 300 (15 kDa) determined by GPC relative to polystyrene standards was originally reported by the authors of reference 118 (endnote).<sup>125</sup> MWs of PMPS (**4-14**) were measured using the random coil model ( $M_N = 5.6$  kDa,  $M_W = 16.9$  kDa). However, it has been suggested that for PMPS (**4-14**), and other all-quaternary-Si polymers, the rigid rod calculation may be a more suitable model.<sup>121</sup>

The UV-vis spectra of modified polysilanes (Figure 4.9a) are very similar to that of poly(phenylsilane) (**4-1**).<sup>lvii</sup> This result is consistent with the relatively high number of residual Si-H units in these polysilanes (60-90%, based on <sup>1</sup>H NMR and elemental analyses). The modified polymers with the highest degrees of substitution (40%, X = CH<sub>2</sub>CH<sub>2</sub>Bu (**4-3**) or SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> (**4-12**)) gave the largest red shifts in their  $\sigma$ - $\sigma^*$  transitions (Figure 4.11b), an indication that the nature of the new side-chain has less influence on Si-chain lengths of the  $\sigma$ -conjugated chromophores than does the number of -H groups that are replaced. Studies of other X-modified poly(phenylsilane) derivatives,<sup>39,130a</sup> X-modified poly(hexylsilane) derivatives,<sup>130b</sup> and -RR'Si-/RSiH- polysilanes derived from Wurtz coupling<sup>130a,141</sup> have identified similar trends for the impact of the degree of Si-H substitution on their UV-Vis absorption spectra.

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<sup>lvii</sup> See experimental Figure 4.66 for UV-vis absorption spectra of polymers in different groups, for the comparison of similarly modified poly(phenylsilane) derivatives (**4-2** to **4-13**) and parent poly(phenylsilane) (**4-1**).



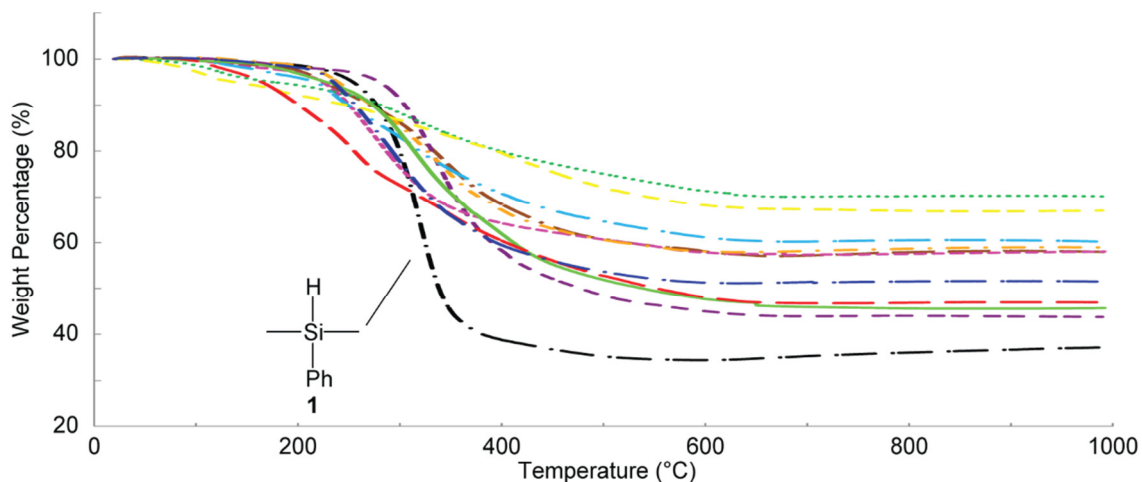
**Figure 4.9.** a) UV-vis absorption spectra (in  $\text{CH}_2\text{Cl}_2$ , normalized at 260 nm) of X-modified poly(phenylsilane) derivatives (**4-1** to **4-13**), parent poly(phenylsilane) (**4-1**), and PMPS (**4-14**) a) showing similarity in shape of poly(phenylsilane) derivatives and b) illustrating the red shift of modified polymers with highest degree of substitution (X =  $\text{CH}_2\text{CH}_2\text{Bu}$  (**4-3**),  $\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3$  (**4-12**)), relative to parent poly(phenylsilane) (**4-1**) (“0%” degree of substitution, all tertiary-Si repeat units) and PMPS (**4-14**) (“100%” degree of substitution, all quaternary-Si repeat units). Legend for X: —•—  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$  (**4-2**), —•—  $\text{CH}_2\text{CH}_2\text{Bu}$  (**4-3**), —•—  $\text{OCH}(\text{CH}_3)_2$  (**4-4**), —•—  $\text{OCH}_2\text{CH}_2\text{CH}_3$  (**4-5**), —•—  $\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$  (**4-7**), —•—  $\text{OCH}_2\text{CH}_2\text{Cl}$  (**4-8**), —•—  $\text{N}(\text{Ph})\text{CH}_2\text{Ph}$  (**4-10**), —•—  $\text{SCH}_2\text{CH}_2\text{CH}_3$  (**4-11**), —•—  $\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3$  (**4-12**), —•—  $\text{SCHPh}_2$  (**4-13**) -modified poly(phenylsilane) derivatives, —•— parent poly(phenylsilane) (**4-1**) and —•— poly(methylphenylsilane) (**4-14**). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

As for the electronic absorption spectra described above, thermal gravimetric analysis (TGA) of the modified polysilanes gave thermal decomposition curves and transition temperatures very similar to those for the parent poly(phenylsilane) (**4-1**) and

other reported polysilanes,<sup>130b,134a,143</sup> both with and without Si-H groups. In all cases, the TGA traces show classic “S-shape” curves,<sup>144</sup> which indicate a relatively straightforward decomposition mechanism,<sup>lviii</sup> with inflection temperatures distributed within a fairly narrow range (240-340°C, see Table 4.7 in Section 4.9.9 for table of inflection temperatures) and similar to that for the parent poly(phenylsilane) (320 ± 10°C). A similar decomposition process is presumed for all samples, which is related to skeletal fragmentation.<sup>145</sup> Although there is an apparent trend toward smaller mass reduction with increasing degree of substitution, a real physical meaning cannot be inferred without a normalization of degree-of-substitution-to-mass that requires many assumptions: mass of the side-chains and parent polymer; the degree of substitution; the average chain length; and a uniform mass loss based on the assumed polymer structure. A detailed comparison of all X-modified poly(phenylsilane) derivatives with appropriate groupings based on side-chains is given in the experimental Section 4.9.9. The products and mechanism of thermolysis of the parent polymer (**4-1**) are identified and discussed, respectively, more thoroughly in Chapter 5.

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<sup>lviii</sup> See Chapter 5 for more detail on the mechanism of thermal decomposition.



**Figure 4.10.** TGA traces of modified polysilanes  $-\text{[PhSiH]}/-\text{[PhSiX]}-$ . Legend, for X:  $\text{---}$   $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$  (**4-2**),  $\text{---}$   $\text{CH}_2\text{CH}_2\text{Bu}$  (**4-3**),  $\text{---}$   $\text{OCH}(\text{CH}_3)_2$  (**4-4**),  $\text{---}$   $\text{OCH}_2\text{CH}_2\text{CH}_3$  (**4-5**),  $\text{---}$   $\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$  (**4-7**),  $\text{---}$   $\text{OCH}_2\text{CH}_2\text{Cl}$  (**4-8**),  $\text{---}$   $\text{N}(\text{Ph})\text{CH}_2\text{Ph}$  (**4-10**),  $\text{---}$   $\text{SCH}_2\text{CH}_2\text{CH}_3$  (**4-11**),  $\text{---}$   $\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3$  (**4-12**),  $\text{---}$   $\text{SCHPh}_2$  (**4-13**),  $\text{---}$  parent poly(phenylsilane) (**4-1**).

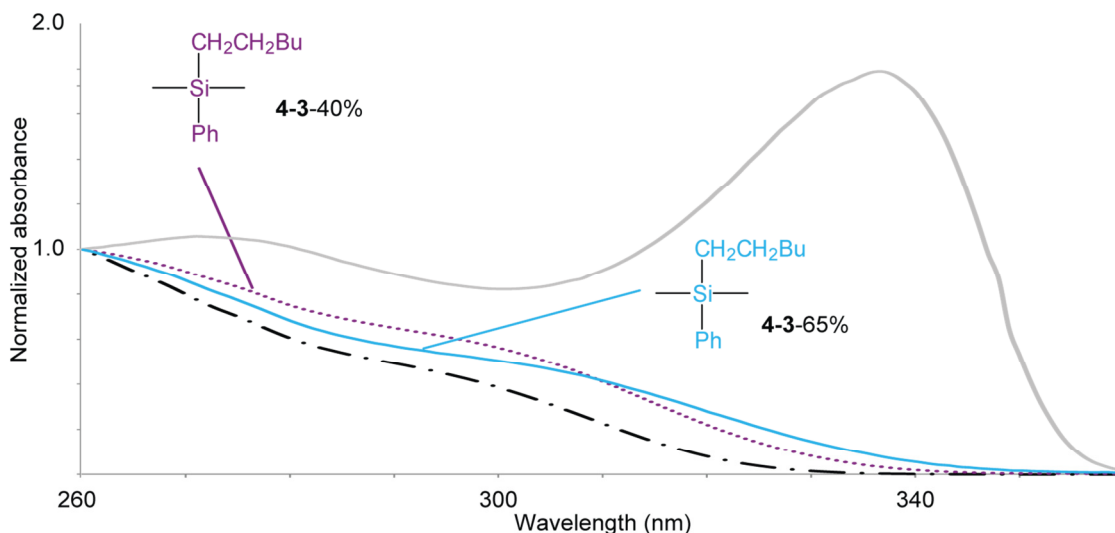
#### 4.6 Strategies for higher degree of modification

A relatively high degree of substitution (84%) for a polymer containing the same side-chains as those introduced in **4-3** was reported using AIBN-radical-initiated hydrosilation of 1-hexene by poly(phenylsilane).<sup>39</sup> These results are consistent with the discussion above of the impact on UV-vis  $\sigma\text{-}\sigma^*$  absorption when replacing  $-\text{H}$  in poly(phenylsilane) with  $-\text{R}$ : this literature version of **4-3** with 84% substitution (**4-3-84%**) showed an intense  $\sigma\text{-}\sigma^*$  absorption with  $\lambda_{\text{max}} = 325$  nm, supporting its increased Si-backbone rigidity relative to **4-3** with 40% substitution (**4-3-40%**) prepared by the  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed method. The non-H groups, in this example *n*-hexyl groups, prevent rotation of the Si-Si bond to a *gauche* orientation and enforce a preferentially *anti* silicon backbone that is optimal for a strong  $\sigma\text{-}\sigma^*$  absorption.

The degree of substitution of **4-3** was increased by heating the  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reaction of the parent polymer with 1-hexene to reflux (70 °C) in a sealed tube. Polymer **4-3** was chosen for reaction optimization because of its already high X-incorporation in

RT reactions (40%) and its well behaved non-hydrolytically sensitive side-group. This experiment gave a polymer with a 65% *n*-hexyl incorporation (**4-3**-65%) compared to 40% at RT. However, this did not significantly affect the  $\sigma$ - $\sigma^*$  absorption for the polymer, which had a UV-vis absorption spectrum with similar shape to other B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-modified poly(phenylsilane) derivatives (10-40% substitution, Figure 4.9a). A slight red shift in the spectrum of **4-3**-65% (3 to 5 nm in the 310-350 nm region) is consistent with an increased degree of substitution but also suggests a higher “critical” degree of substitution is required for a significant increase in the average persistence lengths in the polymer.

The next immediate goal is to achieve a comparably high degree of substitution to the *n*-hexyl modified poly(phenylsilane) reported by Waymouth ( $\geq 84\%$  for **4-3**), but perhaps another important and interesting goal is to find the degree of substitution that impacts the conformation of poly(phenylsilane) (**4-1**) that shows a distinct  $\sigma$ - $\sigma^*$ . This might be achieved by systematically investigating reaction conditions, catalyst loading and temperature, to find suitable parameters for different %X *n*-hexyl incorporations, e.g. 70, 75, and 80% *n*-hexyl groups. These conformation changes may occur at lower than 84% substitution. The only examples of 1-hexene-poly(phenylsilane) modification are 84%, for which the desired structural changes occur<sup>39</sup>, and 65%, for which the desired structural changes do not occur. A suggests a necessary degree of substitution required for post-polymerization of poly(phenylsilane) in order to obtain desirable polysilane properties.



**Figure 4.11.** UV-vis absorption spectra (in  $\text{CH}_2\text{Cl}_2$ , normalized at 260 nm) of  $\text{CH}_2\text{CH}_2\text{Bu}$  (4-3-40%),  $\text{CH}_2\text{CH}_2\text{Bu}$  (4-3-65%) modified polysilanes.  $\text{parent poly(phenylsilane) (4-1)}$ , and  $\text{poly(methylphenylsilane) (4-14)}$ .

#### 4.7 Impact and future work

An important goal of future work is achieving desirable properties for X-modified polysilanes: an intense  $\sigma\text{-}\sigma^*$  UV absorption that can be exploited for either absorption or emission applications. These properties may be achieved using three general methods: optimizing reaction conditions, making appropriate substrate choices, and applying new catalysts.

It is anticipated that optimizing reaction conditions (increasing heat and catalyst loading) will lead to higher %X incorporation into the poly(phenylsilane) chain. The synthesis of 4-3-65% demonstrates that increased temperature will result in more Si-H to *n*-hexyl group conversion. Higher catalyst loadings have not yet been tested in this and similar reactions. If both increased temperature and catalyst loading are applied, even higher X incorporation than 65% is anticipated. For example, in the reactions of disilane 2-2 described in Chapter 2, synthesis of  $(\text{Ph}_2\text{SiOC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})_2$  (2-20) required both an

increase in temperature and a higher catalyst loading (10 mol%  $B(C_6F_5)_3$ ) to append two aryloxy groups.

Appropriate substrate selection is necessary for achieving higher %X incorporation. Substrates that are prone to over-reduction, such as primary alkoxy and O/S-benzylic groups should be avoided. Likewise, O- or S-containing benzylic substrates, such as benzophenone and thiobenzophenone, also lead to over-reduction reactions and should be avoided. Substrates giving a low degree of catalyst inhibition by adduct formation and having a low degree of steric hindrance are optimal for nucleophilic attack at the  $R_3Si\cdots H\cdots B(C_6F_5)_3$  complex. Promising substrates evaluated thus far are 1-hexene and *p*-thiocresol ( $HSC_6H_4-p-CH_3$ ); both show low affinities for coordination and sequestration of  $B(C_6F_5)_3$  whereas benzylideneaniline (imine) and *p-t*-butylphenol ( $HOC_6H_4-p-t-Bu$ ) showed a high binding affinity for  $B(C_6F_5)_3$  and gave modified poly(phenylsilane) derivatives with relatively low amounts of incorporated side-chain. The steric bulk of the substrate is also critical as seen in reactions of disilane **2-2**, which showed preferential monosubstituted or disubstituted products based on substrate size.

It has been challenging thus far to prepare nitrogen-containing poly(phenylsilane) derivatives by these methods. However, a literature example suggests substrate possibilities have not yet been exhausted, particularly for HN-containing heterocycles; recently, the straightforward  $B(C_6F_5)_3$ -catalyzed silane dehydrocoupling with pyrroles, indoles, and anilines, was reported.<sup>99</sup> The less Lewis-basic HN-containing heterocycles gave complete conversions to aminosilane products at RT with low-to-moderate catalyst loadings (1-5 mol%  $B(C_6F_5)_3$ ).<sup>lix</sup> These reactions attach interesting side-chains that are

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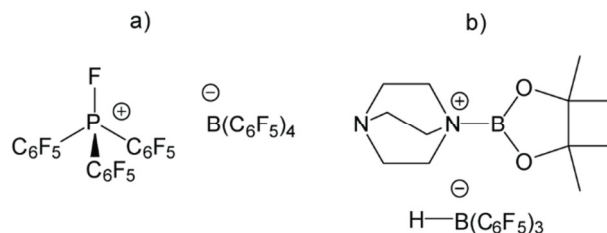
<sup>lix</sup> Most examples used 1 mol%  $B(C_6F_5)_3$ .

chromophores with desirable absorption properties, which may lead to emissive properties. Using current  $B(C_6F_5)_3$ -catalyzed methods, it is challenging to directly append  $\pi$ -conjugated side-groups to the all-Si  $\sigma$ -conjugated system. Hydrosilation of olefins, carbonyls, and thiocarbonyls inevitably leads to side-chains with  $sp^3$  carbons separating the  $\sigma$ -conjugated polymer chain from the  $\pi$ -conjugated side-chain. The nitrogen-containing substrates described above should be the next substrate class evaluated for post-polymerization modification, given the vast availability of HN-containing heterocycles (e.g. pyrroles, indoles, and anilines) and the apparent efficiency of these dehydrocoupling reactions. In addition, although UV-absorbing side-chains containing phenolate (**4-6**, **4-7**) and thiophenolate (**4-12**) have been appended, substrates with extended chromophores such as naphthyloxy groups have not yet been tested. These would also be interesting to investigate, particularly in the context of developing new, potentially emissive materials.

If the proposed polysilane preparation method (dehydrocoupling polymerization followed by  $B(C_6F_5)_3$ -catalyzed post-polymerization modification) is to replace the Wurtz coupling synthesis as the standard method for preparing polysilanes, then it needs to have most, or preferably all, of the following traits: catalytic; atom-efficient; scalable to high quantities; safe, where all potential safety considerations have been addressed; applicable to many substrates to give a wide variety of side-chains; and efficient at appending near 100% X groups, which is the key ongoing challenge. Wurtz coupled polymers inherently have 100% X groups, since they are formed from  $RR'SiCl_2$  monomers. In order to get to desirable absorption/emission properties like those shown in polysilanes derived from Wurtz coupling, X-modified poly(phenylsilane) derivatives

need to have high degrees of X groups. An evaluation of the role of different side-chains cannot be made until the substitution percentages are higher. Until this is achieved, all of the element-side-chain poly(phenylsilane) derivatives will appear similar to parent poly(phenylsilane) due to the relatively high residual Si-H content. Continued work to achieve higher %X incorporations is necessary before the absorption properties of the X side-chains on poly(phenylsilane) can be studied.

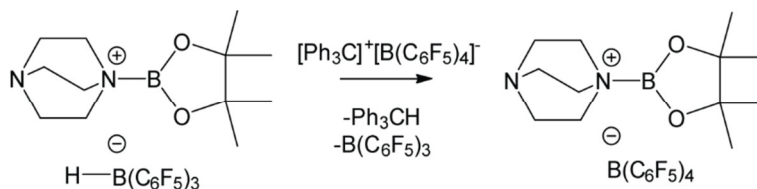
A number of different catalysts have been found that mimic the  $\eta^1\text{-H}\cdots\text{SiR}_3$  complexation described in Chapters 2 and 3, which is the key step of  $\text{B}(\text{C}_6\text{F}_5)_3$  catalyzed Si-H activation. These include modified  $\text{B}(\text{C}_6\text{F}_5)_3$  catalysts reported by Piers<sup>43a,44</sup> and Oestreich<sup>43c,67</sup> and fluorophosphonium catalysts prepared by Stephan<sup>53</sup> (Figure 4.12a) as well as an interesting variety of Lewis acidic transition metal complexes.<sup>30e,48,50-51</sup> These catalysts may have distinct advantages compared to  $\text{B}(\text{C}_6\text{F}_5)_3$  such as higher activity for Si-H activation and/or lower steric bulk around the Lewis acidic center. Fluorophosphonium catalysts have shown remarkable activity for hydrosilation and dehydrocoupling reactions using catalyst loadings as low as 1.5 mol%<sup>53a</sup> Applying these catalysts to reactions of poly(phenylsilane) could result in greater side-chain incorporation. Furthermore, fluorophosphonium catalysis has an even greater substrate scope than  $\text{B}(\text{C}_6\text{F}_5)_3$ , including well-established reactivity with alkynes<sup>146</sup> and nitriles.<sup>53a</sup> The downside to these fluorophosphonium catalysts is their extreme sensitivity to residual moisture.<sup>146</sup>



**Figure 4.12.** Potential  $B(C_6F_5)_3$ -like catalysts available post-polymerization modification of poly(phenylsilane): a) Representative fluorophosphonium catalyst<sup>53</sup> and b) borenium catalyst.<sup>70</sup>

Other potential candidates for Si-H activation catalysts come from the more general field of frustrated Lewis pairs (FLPs), of which  $B(C_6F_5)_3$ -catalyzed Si-H activation is a subset.<sup>42a,147</sup> Many reactions have shown hydrogenation mechanisms that are akin to the key  $\eta^1\text{-H}\cdots\text{SiR}_3$  chemistry described and exploited in Chapters 2 to 4.<sup>70,147b,148</sup> For example, borenium-based catalysts have been shown to activate  $H_2$ , but analogous Si-H chemistry has not yet been reported.<sup>70</sup> The Lewis acidic borenium centre may be less bulky compared to  $B(C_6F_5)_3$  due to the smaller adjacent alkoxy ligands on boron. A challenge to applying this catalyst for Si-H activation chemistry is replacing the counterion typically found in these complexes,  $HB(C_6F_5)_3^-$  (Scheme 4.8, left). This counterion may compete for nucleophilic attack at Si with the intended substrate, which would lead to H exchange at Si and no net reaction occurring. A reaction pathway for counterion exchange is proposed in Scheme 4.8. Reaction of the borenium catalyst with trityl tetrafluoroborate ( $[Ph_3C]^+[B(C_6F_5)_4]^-$ ) exchanges the counterion from  $HB(C_6F_5)_3^-$  to  $B(C_6F_5)_4^-$ . This subsequent cationic complex has a highly electrophilic boron center that should be capable of  $\eta^1\text{-H}\cdots\text{SiR}_3$  coordination similar to  $B(C_6F_5)_3$ , as well as reduced steric bulk around borenium allowing for more facile silane-B complexation.

Scheme 4.8.



## 4.8 Summary

New X-modified poly(phenylsilane) derivatives (**4-2** to **4-13**) were made with a variety of side-chains including thiolato, alkoxy, aryloxy, amido, and alkyl side-chains and have been rigorously characterized. These examples provide proof of concept for chemoselective modification of polysilanes by  $\text{B(C}_6\text{F}_5\text{)}_3$ -catalyzed hydrosilation, dehydrocoupling, or demethanative coupling and represent mostly entirely new polymer structures. This work has highlighted challenges in this approach, which include catalyst inhibition by competing substrate coordination and possible over-reduction of side-chains either small, primary alkoxy groups or benzylic groups. Interesting opportunities for future work include increasing the %X incorporation onto poly(phenylsilane). Suggested methods include changing reaction conditions or using a more active catalyst. Desirable properties, namely the UV-vis absorption for  $\sigma\text{-}\sigma^*$  will be more prominent and important for poly(phenylsilane) derivatives with higher X incorporation.

## 4.9 Experimental

### 4.9.1 General details

General details listed in Section 2.6.1 and 3.12.1 are valid in this Section unless otherwise noted. Allylbenzene was purchased from Aldrich and dried by distillation from magnesium sulfate.

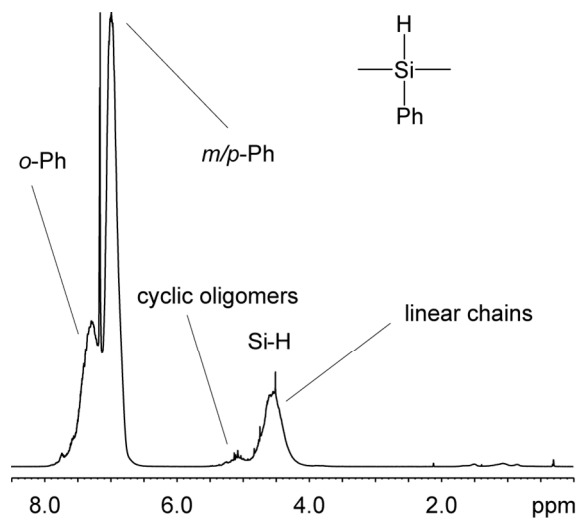
UV-vis spectra were acquired for samples in spectroscopic grade dichloromethane, at RT on a Varian Cary-1 or Cary-5 spectrophotometer. GC-MS chromatograms/spectra were obtained on a Polaris Trace Q-DSQ (GC column was DB5-MS 15 m length, 0.25 mm inner diameter, 25  $\mu\text{m}$  coating; temperature was increased from 50 to 250  $^{\circ}\text{C}$  at 25  $^{\circ}\text{C}/\text{min}$  and then held for 22 min for a total 30 min chromatogram; flow rate was 1 mL/min; MS: EI 70 eV ionization). Thermogravimetric analysis (TGA) was carried out on a TA Instruments SDT Q600 in a  $\text{N}_2$  atmosphere with temperature increased from 20 to 1000  $^{\circ}\text{C}$  at a rate of 10  $^{\circ}\text{C}/\text{min}$ . Infrared spectra were obtained for KBr pellets on a Perkin-Elmer Spectrum One FT-IR spectrometer.

Molecular weights were determined from triple detection gel permeation chromatography (MALS-GPC), carried out in the laboratory of Prof. Derek Gates or Prof. Parisa Mehrkhodavandi at the University of British Columbia, using an Agilent liquid chromatograph equipped with an Agilent 1200 series isocratic pump, Agilent 1200 series standard autosampler, Phenomenex Phenogel 5  $\mu\text{m}$  narrow bore columns (4.6 x 300 mm)  $10^4 \text{ \AA}$  (1000-75000), Wyatt OptilabrEx differential refractometer ( $\lambda = 658 \text{ nm}$ , 40  $^{\circ}\text{C}$ ), Wyatt TriStar miniDAWN (laser light scattering detector at  $\lambda = 690 \text{ nm}$ ), and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL/min was used and samples were dissolved in THF or  $\text{CHCl}_3$  (ca. 2-3 mg/mL). The  $d\eta/dc$  values of all polymers were calculated using 100% mass recovery methods using the ASTRA software version 5.

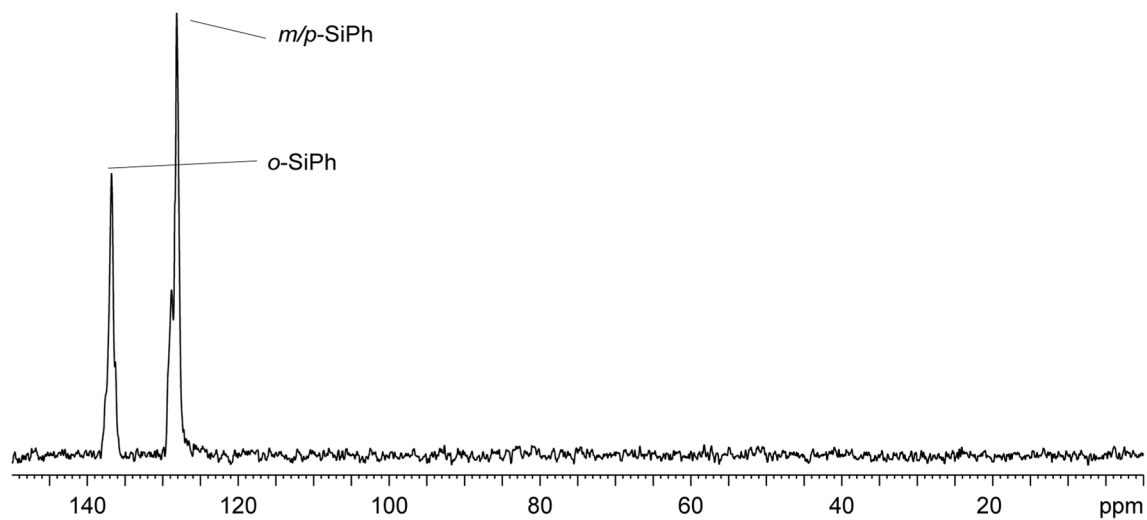
#### **4.9.2 Synthesis of parent poly(phenylsilane) $[\text{PhSiH}]_n$ (4-1)**

This procedure was reported in the literature and is used with permission (see note at the beginning of Chapter 4).<sup>96</sup> To a Schlenk tube equipped with a stir bar,  $\text{PhSiH}_3$  (5.8 g, 54 mmol) and  $\text{Cp}_2\text{ZrHCl}$  (0.047 g, 0.18 mmol) were combined. After 10 min of

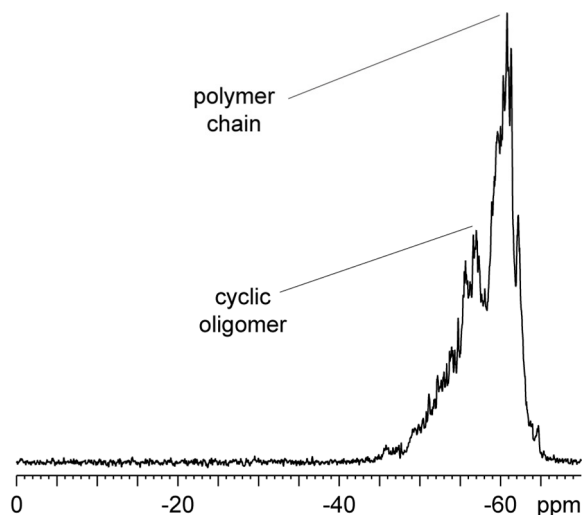
stirring, the mixture turned cloudy and slightly yellow and slowly evolved gases. The mixture was stirred under  $N_2$  (open to the glovebox atmosphere to allow for  $H_2$  to be released). After 24 h, stirring ceased and the mixture became viscous and orange. The contents were mixed by tilting the flask to allow the contents to run along the side of the flask and then the flask was returned to its upright condition and the contents were allowed to settle. After 48 h, the same mixing procedure was applied. With the polymer mixture moving slowly along the sides of the flask, benzene (0.5 mL) was added and mixed by agitating the flask. The contents were then allowed to stand overnight. After 72 h, the mixing procedure was performed again and ~10 mL of benzene was added to dissolve the contents. The solution was then passed through a ~7 cm column of Florisil® (10 cm height, 1.5 cm inner diameter, plugged with glass wool). Additional benzene (2 x 10 mL) was used to wash the column. The fractions were combined and volatiles were removed by evacuation. Residual  $PhSiH_3$  was removed by adding benzene to dissolve the contents, then removing volatiles under vacuum (5 x 30 mL). Yield: 5.6 g (98%) of sticky, pale yellow gum.



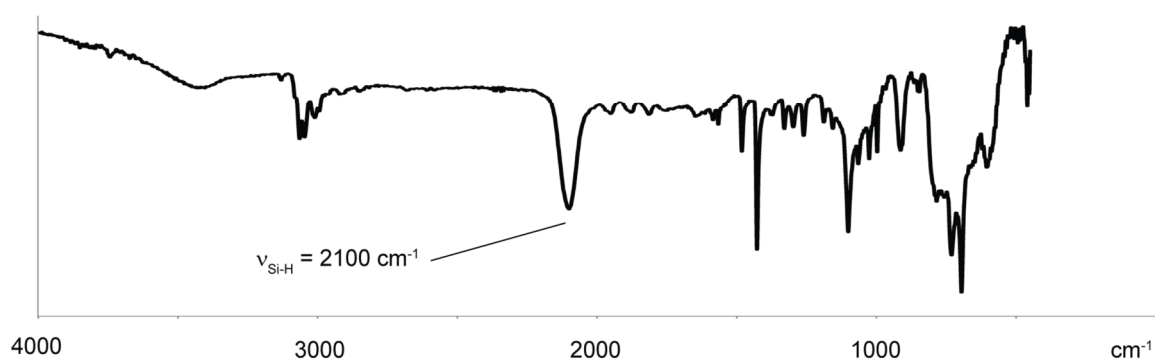
**Figure 4.13.**  $^1\text{H}$  NMR (300 MHz) of poly(phenylsilane) (**4-1**) in  $\text{C}_6\text{D}_6$ . Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>



**Figure 4.14.** DEPT135  $^{13}\text{C}$  NMR (75 MHz) of poly(phenylsilane) (**4-1**) in  $\text{C}_6\text{D}_6$ . Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>



**Figure 4.15.** Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of poly(phenylsilane) (**4-1**) in  $\text{C}_6\text{D}_6$ . Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>



**Figure 4.16.** IR spectrum (KBr) of poly(phenylsilane) (**4-1**). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

### 4.9.3 Synthesis of modified poly(phenylsilane)

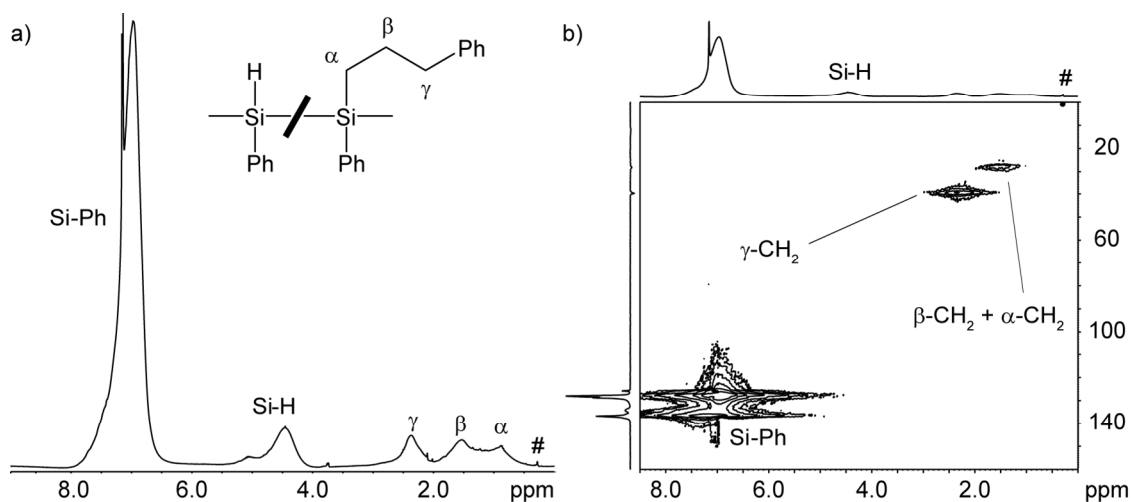
#### *General procedure for modified polysilanes, olefinic substrates*

In a Schlenk flask equipped with a stir bar, **4-1**,  $\text{B}(\text{C}_6\text{F}_5)_3$ , and substrate were combined with  $\text{CH}_2\text{Cl}_2$ . The mixture was stirred under  $\text{N}_2$  (closed flask) for 16 h, and then the volatiles were removed under vacuum. The mixture was dissolved in benzene and eluted through a Florisil column with benzene, to remove  $\text{B}(\text{C}_6\text{F}_5)_3$ . Volatiles were

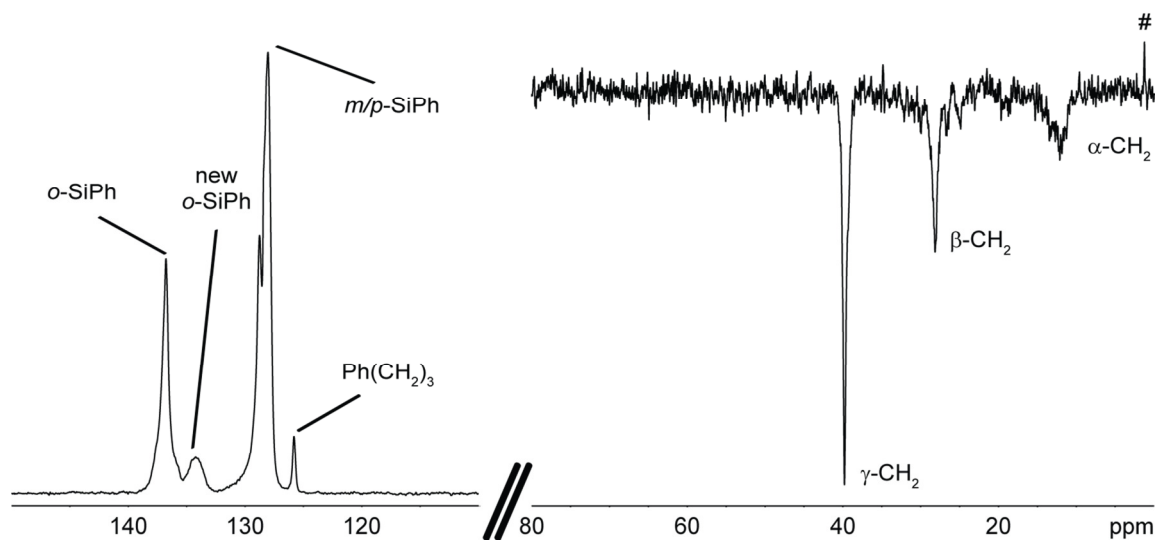
removed under dynamic vacuum at RT or other temperature as specified, for time specified to give the described product.

*[PhSiH]-/[PhSiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph] – allylbenzene-modified poly(phenylsilane) (4-2):*

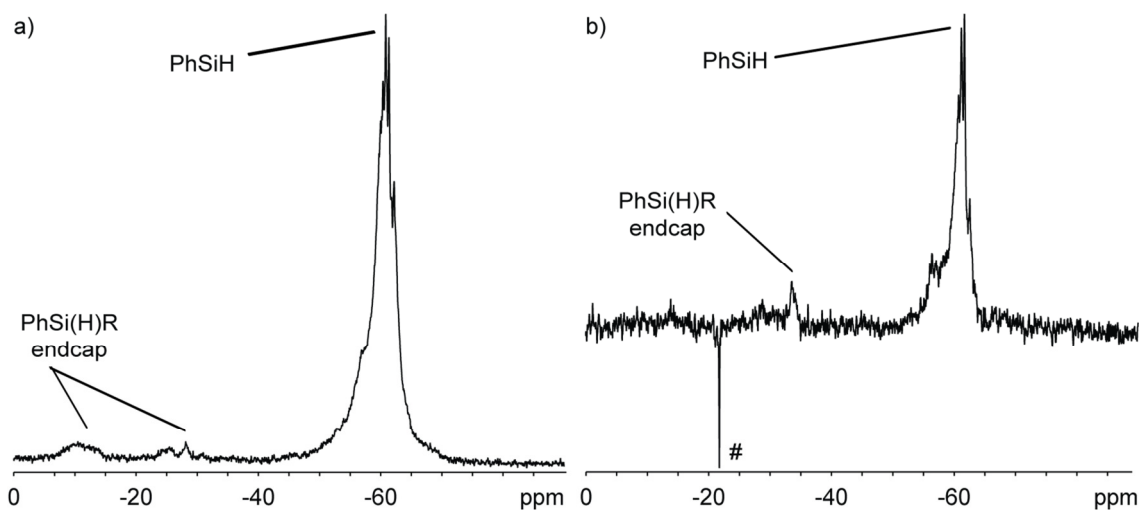
**4-1** (0.32 g, 2.9 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.070 g, 0.13 mmol), allylbenzene (1.0 mL, 7.6 mmol), CH<sub>2</sub>Cl<sub>2</sub> (0.1 mL), benzene (10 x 1 mL). Procedural notes: residual allylbenzene was removed from the mixture by dissolving it in benzene (1 mL) and then removing volatiles under vacuum and this process was repeated nine times; then volatiles were removed under dynamic vacuum for 16 h at RT. An off-white solid was isolated (0.20 g).



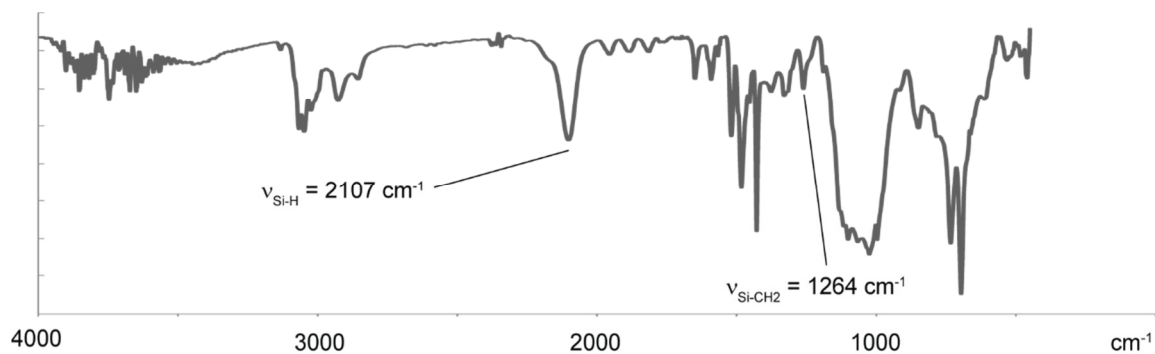
**Figure 4.17.** a) <sup>1</sup>H NMR (300 MHz) and b) <sup>1</sup>H-<sup>13</sup>C HSQC (<sup>1</sup>H 300 MHz, <sup>13</sup>C 75 MHz) of CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph-modified poly(phenylsilane) (**4-2**) in C<sub>6</sub>D<sub>6</sub>. The “#” is grease.



**Figure 4.18.** DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ -modified poly(phenylsilane) (**4-2**) in  $\text{C}_6\text{D}_6$ . For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 15 relative to the 100-160 ppm region. The “#” is grease.



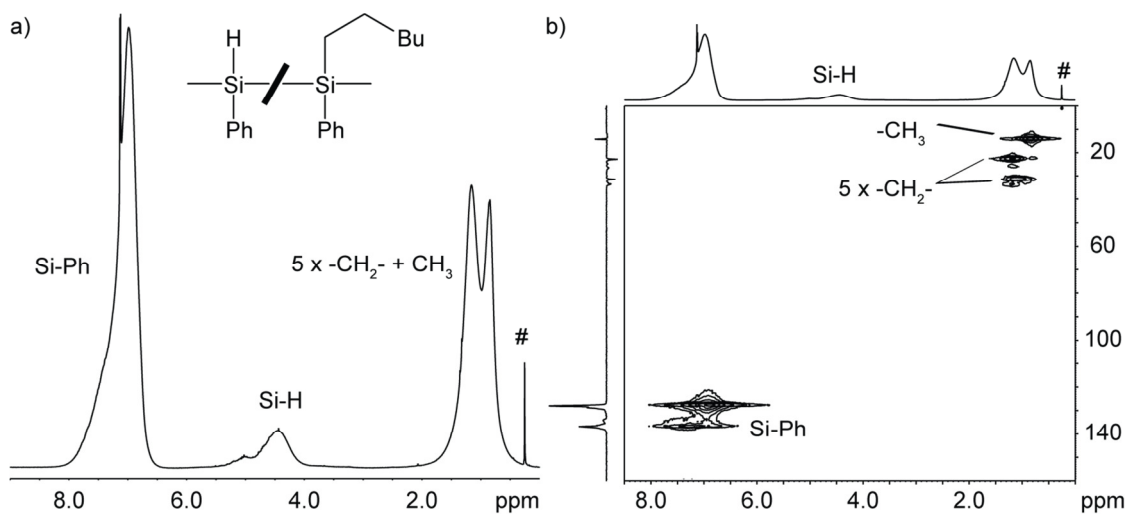
**Figure 4.19.** a) Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) and b) long-range DEPT45  $^{29}\text{Si}$  NMR (99 MHz,  $^3J_{\text{SiH}} = 8$  Hz) of  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ -modified poly(phenylsilane) (**4-2**) in  $\text{C}_6\text{D}_6$ . The “#” is grease.



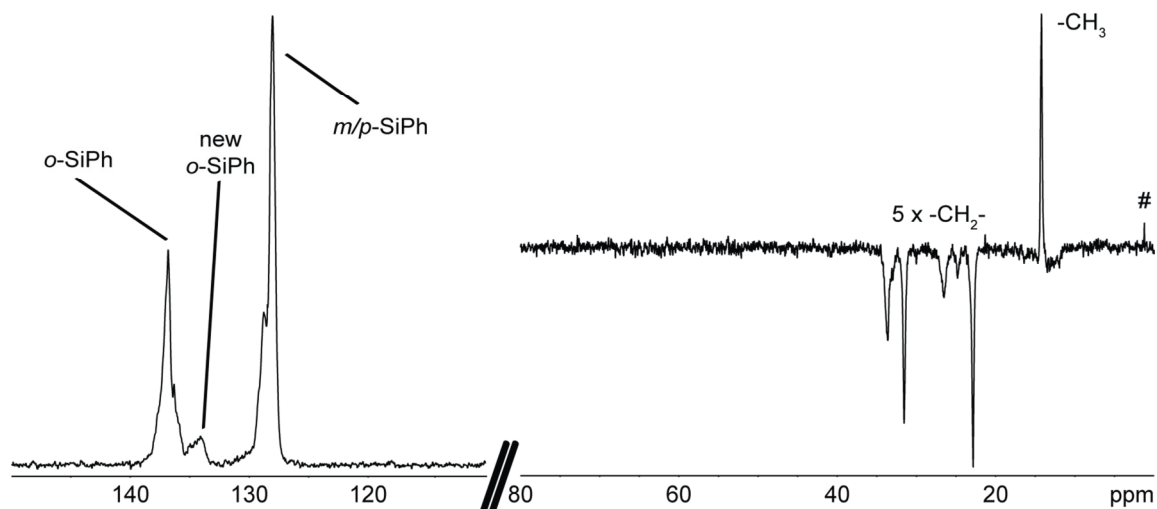
**Figure 4.20.** IR spectrum (KBr) of  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ -modified poly(phenylsilane) (**4-2**).

*[PhSiH]-/[PhSiCH<sub>2</sub>CH<sub>2</sub>Bu] – 1-hexene-modified poly(phenylsilane) (4-3):*

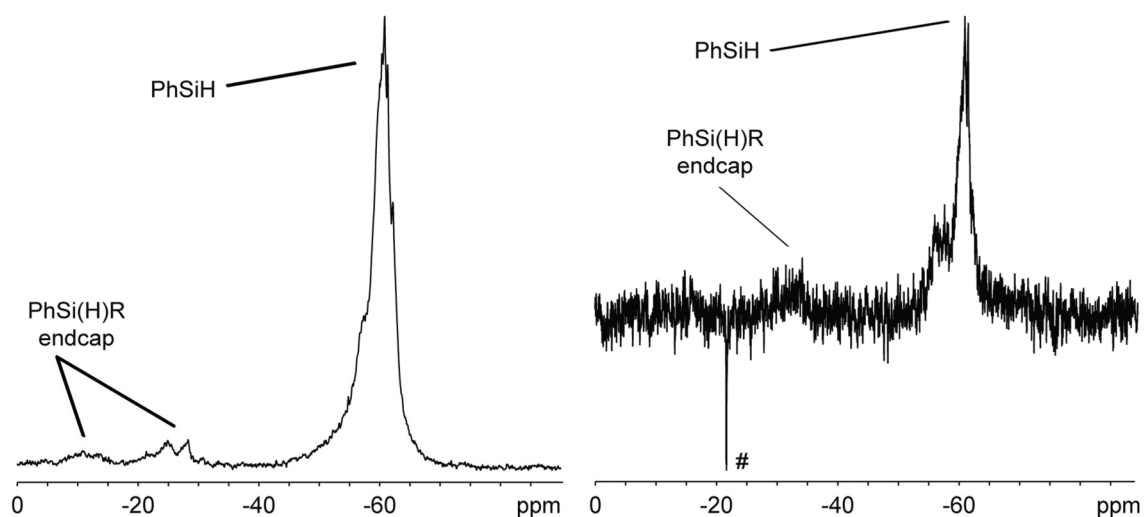
**4-1** (0.21 g, 2.0 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.050 g, 0.098 mmol), 1-hexene (2.0 mL, 16 mmol),  $\text{CH}_2\text{Cl}_2$  (0.1 mL), benzene (6 x 1 mL). Procedural notes: volatiles were removed under dynamic vacuum at 40 °C for 2 h. A clear yellow (or colorless in other batches); a viscous oil was isolated (0.27 g, yellow color may be residual zirconium catalyst from the preparation of  $[\text{PhSiH}]_n$ , see synthesis of **4-1**).



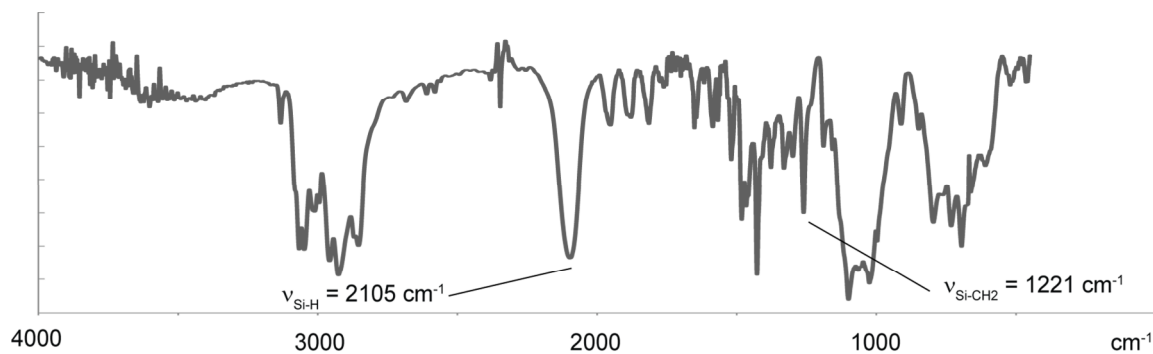
**Figure 4.21.** a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of  $\text{CH}_2\text{CH}_2\text{Bu}$ -modified poly(phenylsilane) (**4-3**) in  $\text{C}_6\text{D}_6$ . The “#” is grease.



**Figure 4.22.** DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{CH}_2\text{CH}_2\text{Bu}$ -modified poly(phenylsilane) (**4-3**) in  $\text{C}_6\text{D}_6$ . For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 5 relative to the 100-160 ppm region. The “#” is grease.



**Figure 4.23.** a) Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) and b) long-range DEPT45  $^{29}\text{Si}$  NMR (99 MHz,  $^3J_{\text{SiH}} = 8$  Hz) of  $\text{CH}_2\text{CH}_2\text{Bu}$ -modified poly(phenylsilane) (**4-3**) in  $\text{C}_6\text{D}_6$ . The “#” is grease.



**Figure 4.24.** IR spectrum (KBr) of CH<sub>2</sub>CH<sub>2</sub>Bu-modified poly(phenylsilane) (**4-3**).

*[PhSiH]-/[PhSiCH<sub>2</sub>CH<sub>2</sub>Bu] – 1-hexene-modified poly(phenylsilane) (4-3-65%):*

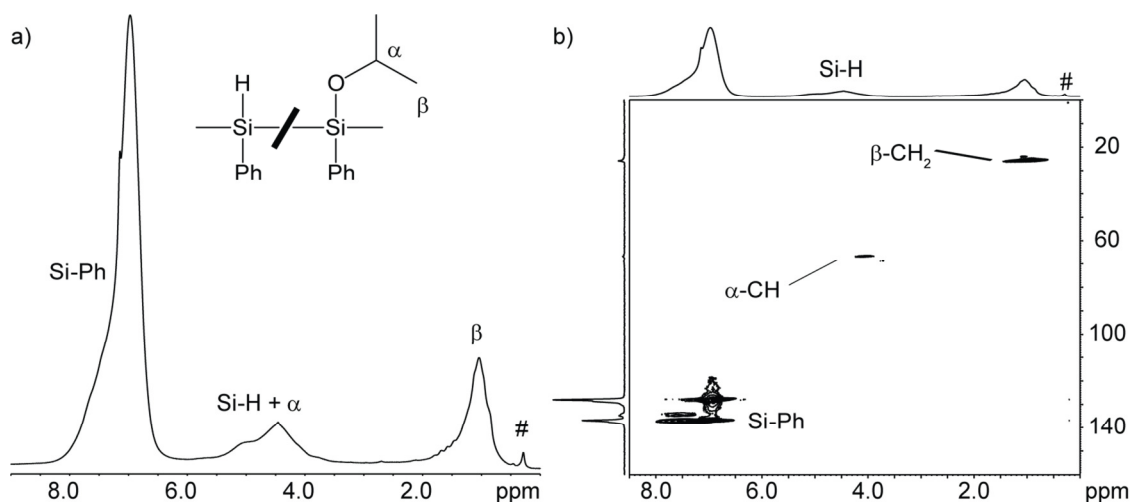
**4-1** (0.11 g, 1.0 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.024 g, 0.047 mmol), 1-hexene (1.0 mL, 8.0 mmol), CH<sub>2</sub>Cl<sub>2</sub> (0.1 mL), benzene (1 mL, then 5 x 1 mL). Procedural notes: reaction was done in a “bomb” flask equipped with a stir bar; flask contents were degassed using one freeze-pump-thaw cycle. The mixture was heated in an oil bath (70° C) for 16 h and then cooled to RT; volatiles were removed under dynamic vacuum at 45 °C for 2 h. A clear, colorless, viscous oil was isolated (0.071 g).

*General procedure for modified polysilanes, non-olefinic substrates:*

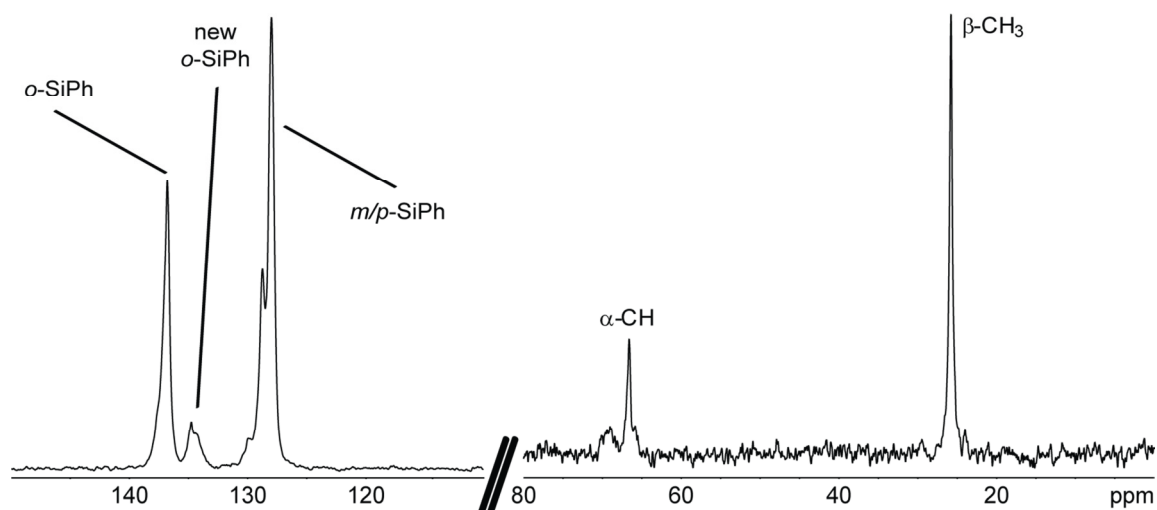
In a Schlenk flask equipped with a stir bar, [PhSiH]<sub>n</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> were combined in toluene or benzene. Substrate was added with stirring (dropwise if a liquid). The mixture was stirred under N<sub>2</sub> (open to Nujol bubbler or closed flask) at RT for the time specified. Volatiles were removed under vacuum. The polymer was triturated with hexanes or pentane and then the solvent was removed by decanting. This process was repeated two more times hexanes or pentane. The resulting powder was dissolved in 5 mL of benzene. Volatiles were removed under dynamic vacuum at RT or other temperature as specified, for the time specified to give the described product.

*[PhSiH]-/[PhSiOCH(CH<sub>3</sub>)<sub>2</sub>] – acetone-modified poly(phenylsilane) (4-4):*

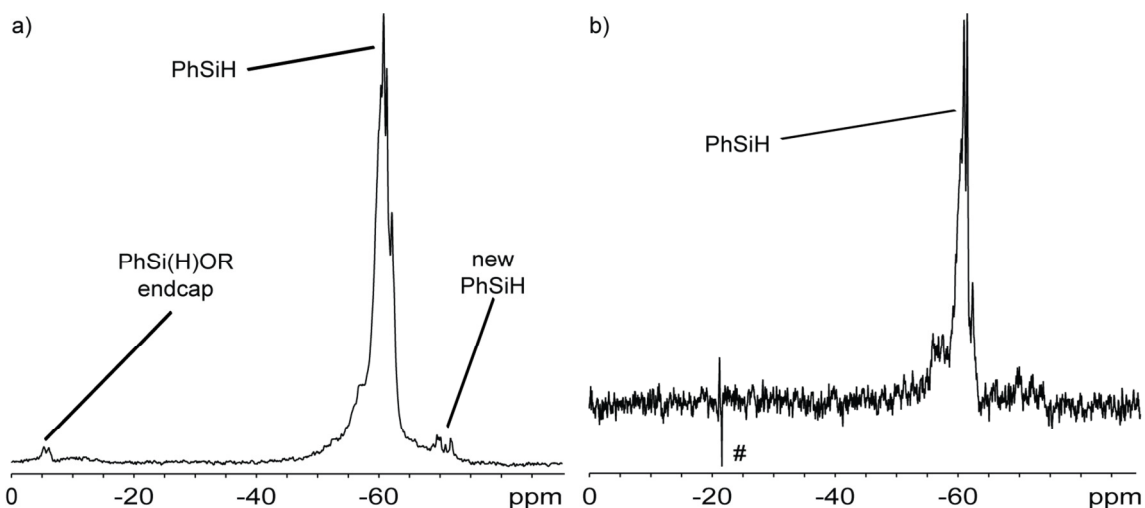
**4-1** (0.55 g, 5.2 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.13 g, 0.25 mmol), toluene (5 mL), acetone (0.40 mL, 5.5 mmol), hexanes (3 x 20 mL), benzene (5 mL). Procedural notes: stirred under N<sub>2</sub> (closed flask) for 16 h; volatiles were removed under dynamic vacuum at RT for 16 h. An off-white solid was isolated (0.15 g).



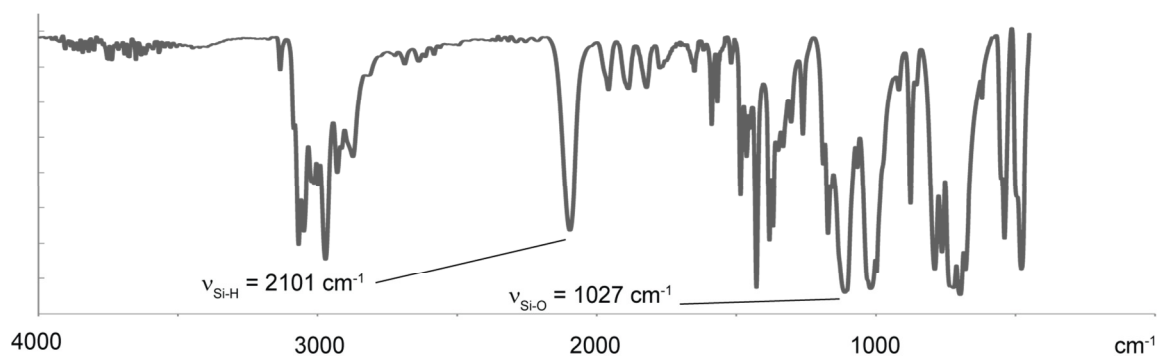
**Figure 4.25.** a) <sup>1</sup>H NMR (300 MHz) and b) <sup>1</sup>H-<sup>13</sup>C HSQC (<sup>1</sup>H 300 MHz, <sup>13</sup>C 75 MHz) of OCH(CH<sub>3</sub>)<sub>2</sub>-modified poly(phenylsilane) (**4-4**) in C<sub>6</sub>D<sub>6</sub>. The “#” is grease.



**Figure 4.26.** DEPT135 <sup>13</sup>C NMR (75 MHz) of OCH(CH<sub>3</sub>)<sub>2</sub>-modified poly(phenylsilane) (**4-4**) in C<sub>6</sub>D<sub>6</sub>. For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 10 relative to the 100-160 ppm region.



**Figure 4.27.** a) Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) and b) long-range DEPT45  $^{29}\text{Si}$  NMR (99 MHz,  $^3J_{\text{SiH}} = 8$  Hz) of  $\text{OCH}(\text{CH}_3)_2$ -modified poly(phenylsilane) (**4-4**) in  $\text{C}_6\text{D}_6$ . The “#” is grease.

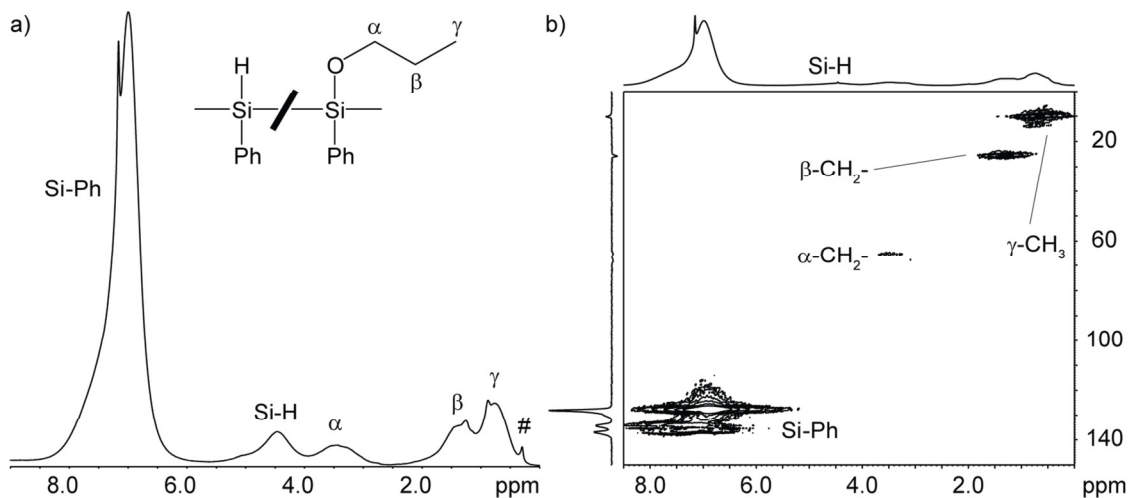


**Figure 4.28.** IR spectrum (KBr) of  $\text{OCH}(\text{CH}_3)_2$ -modified poly(phenylsilane) (**4-4**).

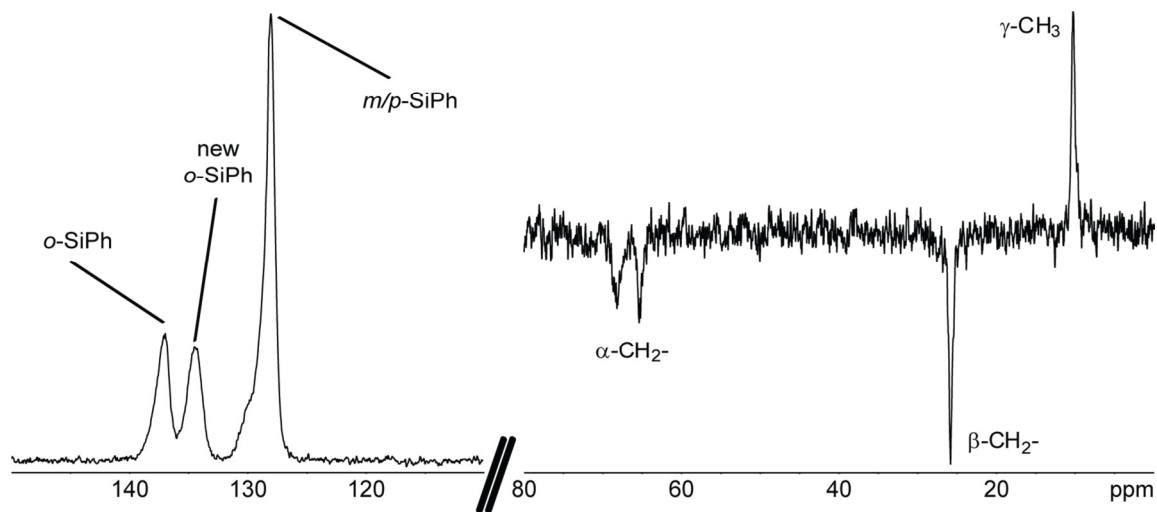
*[PhSiH]-/[PhSiOCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>] – propionaldehyde-modified poly(phenylsilane) (**4-5**):*

**4-1** (0.50 g, 4.7 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.12 g, 0.23 mmol), toluene (3 mL), propionaldehyde (0.30 mL, 4.2 mmol), pentane (3 x 10 mL). Procedural notes: stirred under  $\text{N}_2$  (closed flask); product was collected by vacuum filtration of the

pentane/product mixture; the product was not dissolved in benzene; volatiles were removed under dynamic vacuum at RT for 16 h.<sup>lx</sup> A white solid was isolated (0.41 g).

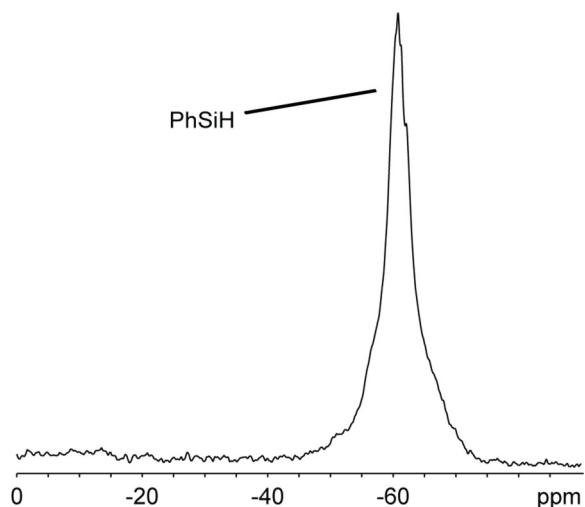


**Figure 4.29.** a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of  $\text{OCH}_2\text{CH}_2\text{CH}_3$ -modified poly(phenylsilane) (**4-5**) in  $\text{C}_6\text{D}_6$ . The “#” is grease.

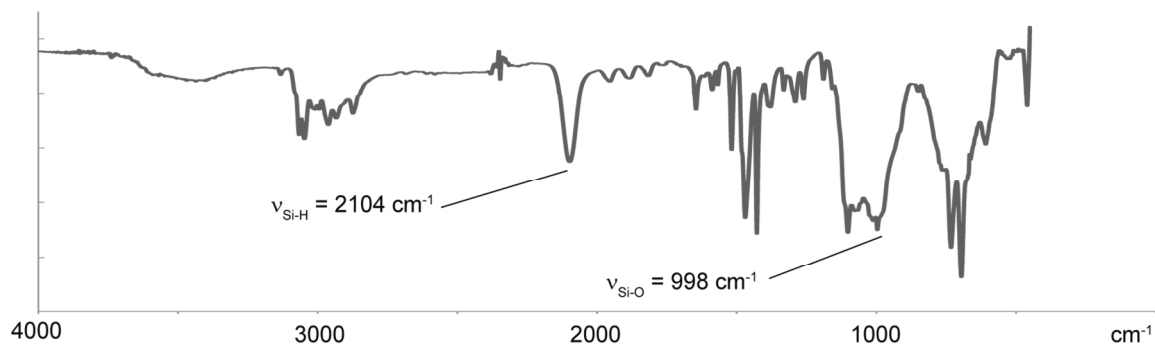


**Figure 4.30.** DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{OCH}_2\text{CH}_2\text{CH}_3$ -modified poly(phenylsilane) (**4-5**) in  $\text{C}_6\text{D}_6$ . For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 10 relative to the 100-160 ppm region.

<sup>lx</sup> If this polymer is heated to over  $50^\circ\text{C}$  under vacuum, the resulting material becomes insoluble in common solvents (benzene, toluene, dichloromethane, chloroform, hexane, pentane, water, ether, THF). The mechanism of decomposition has not yet been probed.



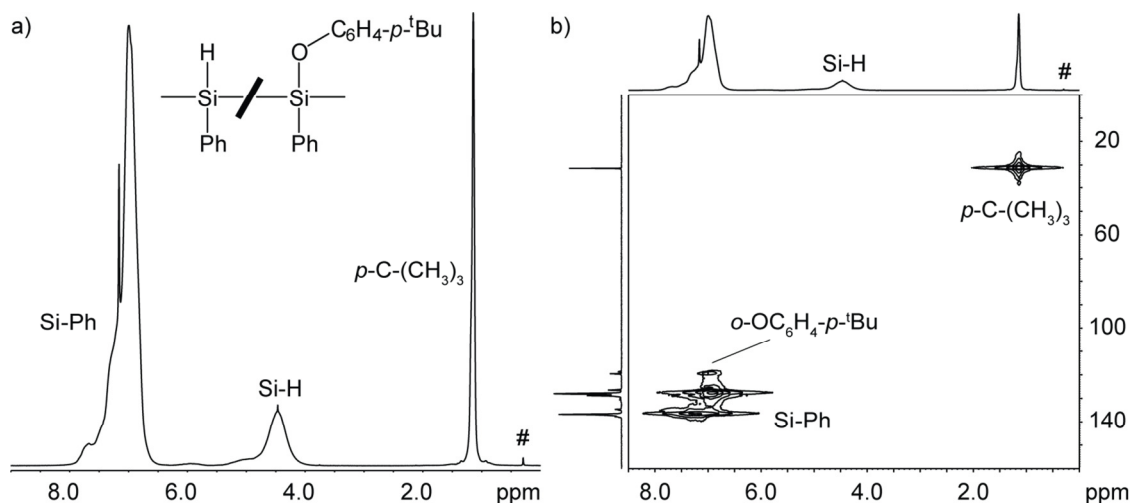
**Figure 4.31.** Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of  $\text{OCH}_2\text{CH}_2\text{CH}_3$ -modified poly(phenylsilane) (**4-5**) in  $\text{C}_6\text{D}_6$ .



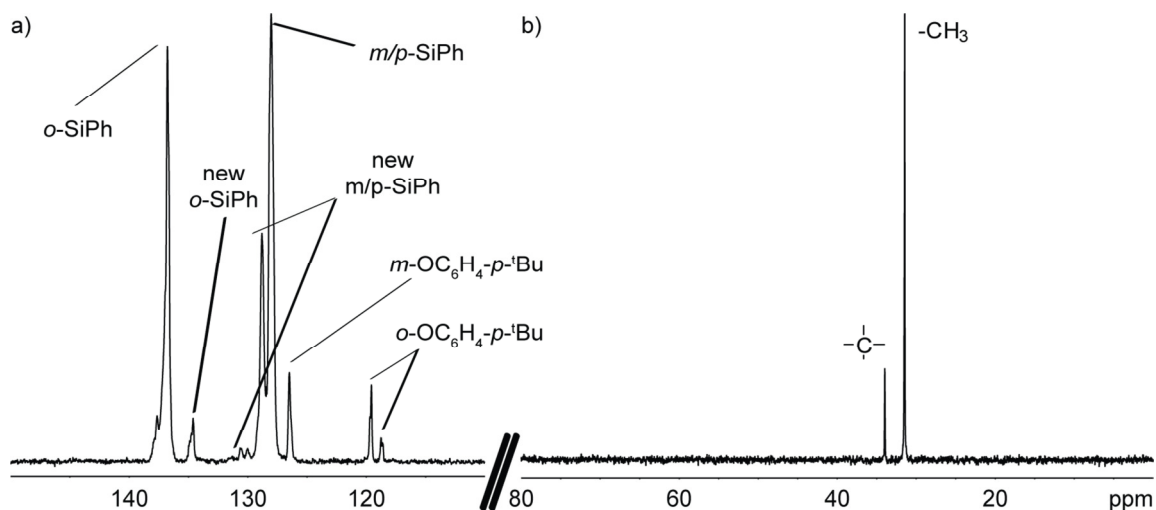
**Figure 4.32.** IR spectrum (KBr) of  $\text{OCH}_2\text{CH}_2\text{CH}_3$ -modified poly(phenylsilane) (**4-5**).

*[PhSiH]-/[PhSiOC<sub>6</sub>H<sub>4</sub>-*p*-Bu] - *p*-*t*-butylphenol-modified poly(phenylsilane) (**4-6**):*

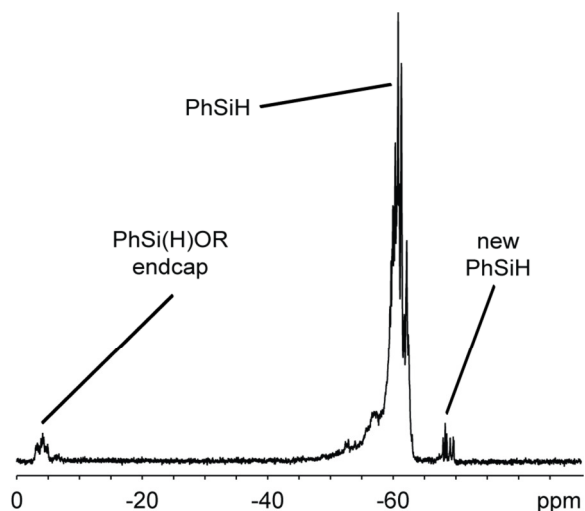
**4-1** (0.23 g, 2.2 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.052 g, 0.10 mmol), toluene (2 mL), *p*-*t*-butylphenol (0.17 g, 1.1 mmol), pentane (6 x 10 mL). Procedural notes: stirred under  $\text{N}_2$  (open to Nujol bubbler) for 1 h; volatiles were removed under dynamic vacuum at  $60^\circ\text{C}$  for 2 h. An off-white solid was isolated (0.11 g).



**Figure 4.33.** a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of  $\text{OC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$ -modified poly(phenylsilane) (**4-6**) in  $\text{C}_6\text{D}_6$ . The “#” is grease.



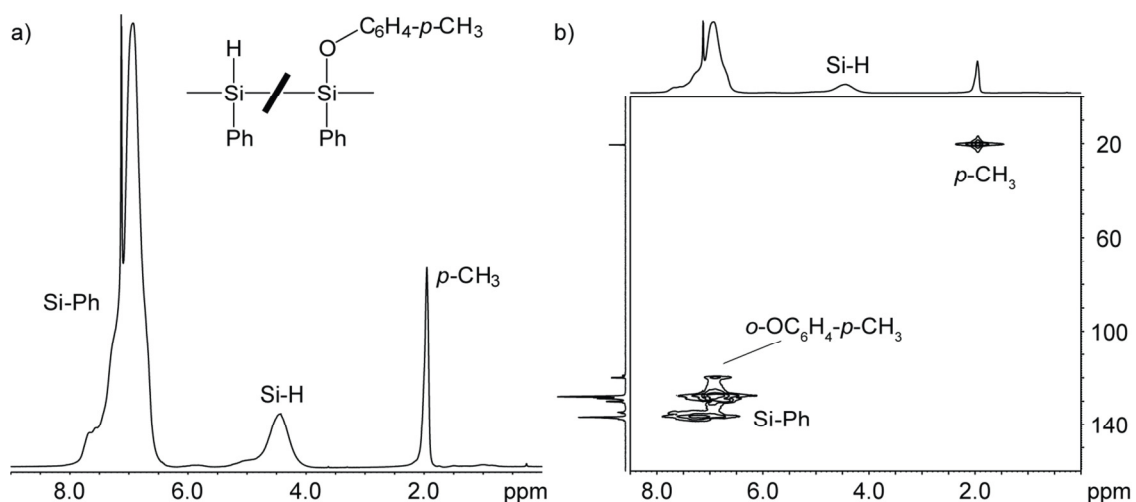
**Figure 4.34.** a) DEPT135  $^{13}\text{C}$  NMR (75 MHz) of the aryl region (100-160 ppm) and b)  $^{13}\text{C}$  NMR (75 MHz) of the alkyl region (0-80 ppm) of  $\text{OC}_6\text{H}_4\text{-}p\text{-}^t\text{Bu}$ -modified poly(phenylsilane) (**4-6**) in  $\text{C}_6\text{D}_6$ .



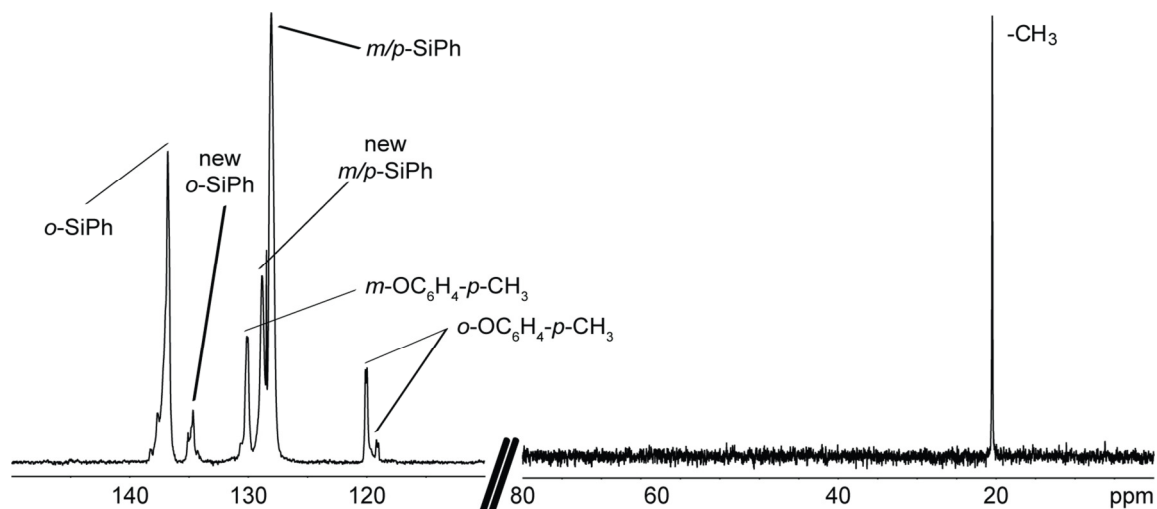
**Figure 4.35.** a) Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of  $\text{OC}_6\text{H}_4$ - $p$ - $^t\text{Bu}$ -modified poly(phenylsilane) (**4-6**) in  $\text{C}_6\text{D}_6$ .

*[PhSiH]-/[PhSiOC<sub>6</sub>H<sub>4</sub>- $p$ -CH<sub>3</sub>]* – *p*-methylanisole-modified poly(phenylsilane) (**4-7**):

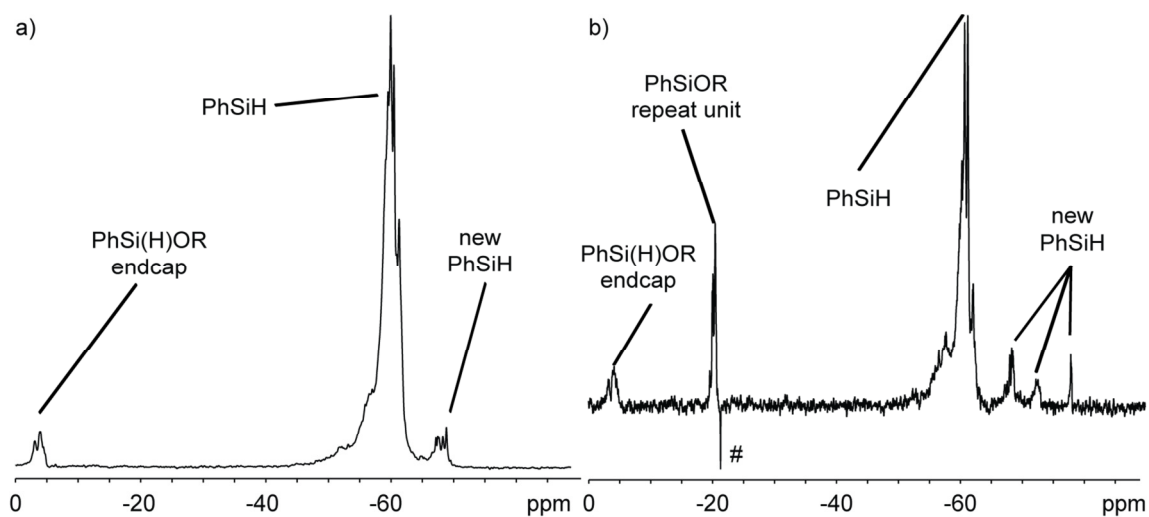
**4-1** (0.53 g, 5.0 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.12 g, 0.24 mmol), toluene (3 mL), *p*-methylanisole (0.31 g, 2.5 mmol), pentane (20 mL, then 2 x 20 mL). Procedural notes: stirred under  $\text{N}_2$  (open to Nujol bubbler) for 16 h; volatiles were removed under dynamic vacuum at 50 °C for 16 h. An off-white solid was isolated (0.25 g).



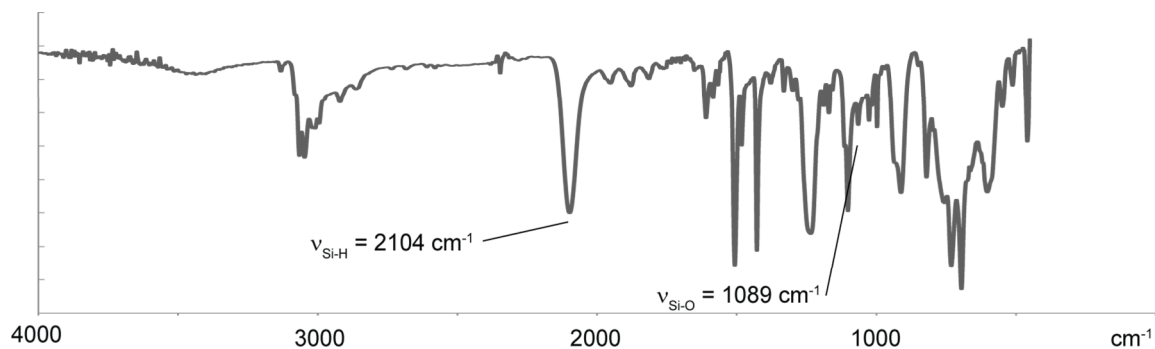
**Figure 4.36.** a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of  $\text{OC}_6\text{H}_4$ - $p$ - $\text{CH}_3$ -modified poly(phenylsilane) (**4-7**) in  $\text{C}_6\text{D}_6$ .



**Figure 4.37.** DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{OC}_6\text{H}_4$ -*p*- $\text{CH}_3$ -modified poly(phenylsilane) (**4-7**) in  $\text{C}_6\text{D}_6$ . For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 5 relative to the 100-160 ppm region.



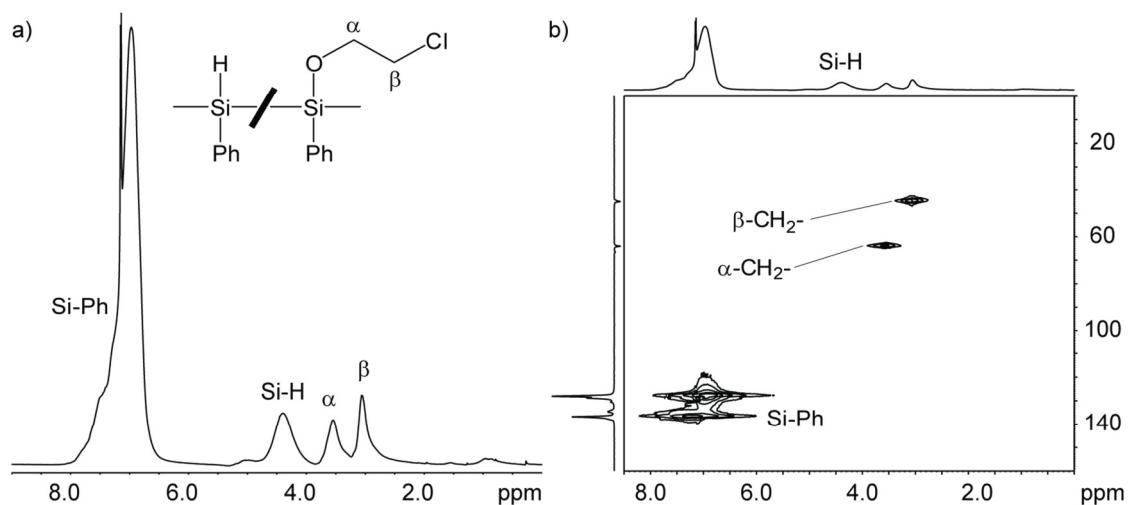
**Figure 4.38.** a) Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) and b) long-range DEPT45  $^{29}\text{Si}$  NMR (99 MHz,  $^3J_{\text{SiH}} = 8$  Hz) of  $\text{OC}_6\text{H}_4$ -*p*- $\text{CH}_3$ -modified poly(phenylsilane) (**4-7**) in  $\text{C}_6\text{D}_6$ . The “#” is grease.



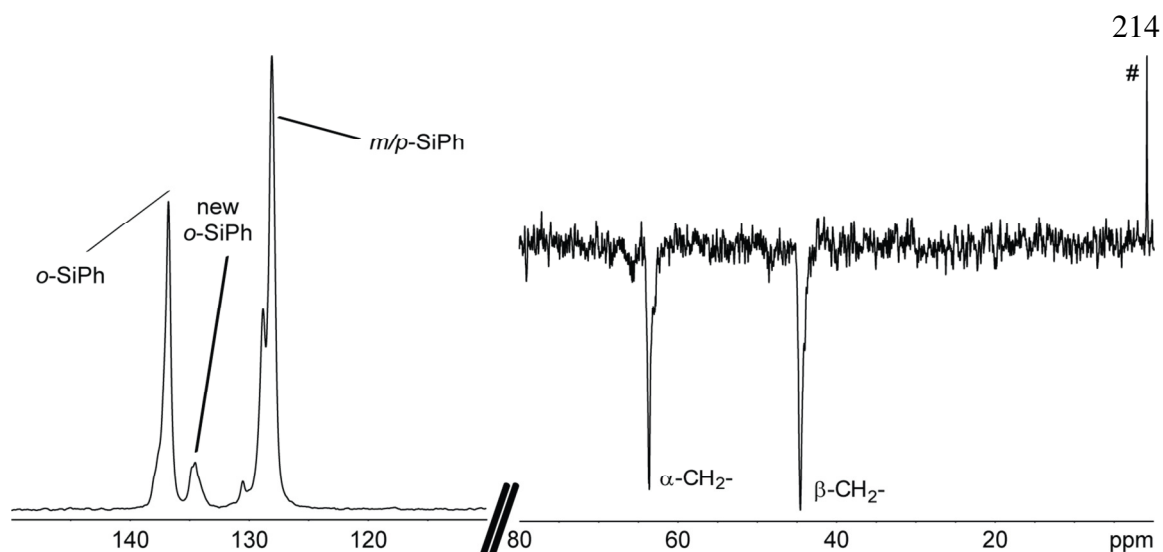
**Figure 4.39.** IR spectrum (KBr) of OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>-modified poly(phenylsilane) (**4-7**).

[PhSiH]-/[PhSiOCH<sub>2</sub>CH<sub>2</sub>Cl] – 2-chloroethyl methyl ether-modified poly(phenylsilane) (**4-8**):

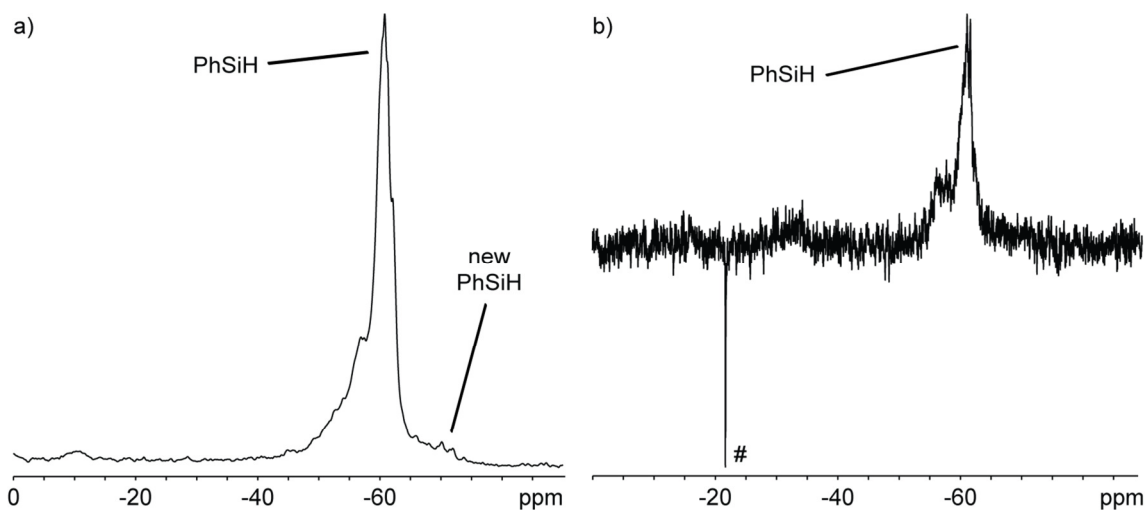
**4-1** (0.30 g, 2.8 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.071 g, 0.14 mmol), toluene (3 mL), pentane (3 x 10 mL), 2-chloroethyl methyl ether (0.30 mL, 3.3 mmol). Procedural notes: stirred under N<sub>2</sub> (open to Nujol bubbler) for 16 h; volatiles were removed under dynamic vacuum at RT for 16 h. An off-white solid was isolated (0.17 g).



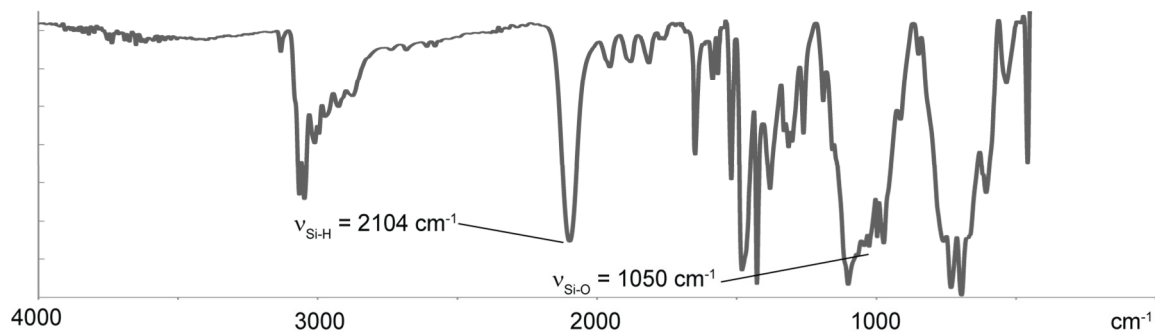
**Figure 4.40.** a) <sup>1</sup>H NMR (300 MHz) and b) <sup>1</sup>H-<sup>13</sup>C HSQC (<sup>1</sup>H 300 MHz, <sup>13</sup>C 75 MHz) of OCH<sub>2</sub>CH<sub>2</sub>Cl-modified poly(phenylsilane) (**4-8**) in C<sub>6</sub>D<sub>6</sub>. The “#” is grease.



**Figure 4.41.** DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{OCH}_2\text{CH}_2\text{Cl}$ -modified poly(phenylsilane) (**4-8**) in  $\text{C}_6\text{D}_6$ . For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 10 relative to the 100-160 ppm region. The “#” is grease.



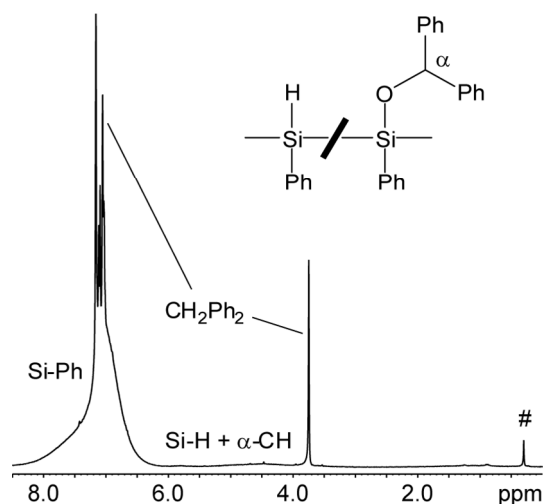
**Figure 4.42.** a) Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) and b) long-range DEPT45  $^{29}\text{Si}$  NMR (99 MHz,  $^3J_{\text{SiH}} = 8$  Hz) of  $\text{OCH}_2\text{CH}_2\text{Cl}$ -modified poly(phenylsilane) (**4-8**) in  $\text{C}_6\text{D}_6$ . The “#” is grease.



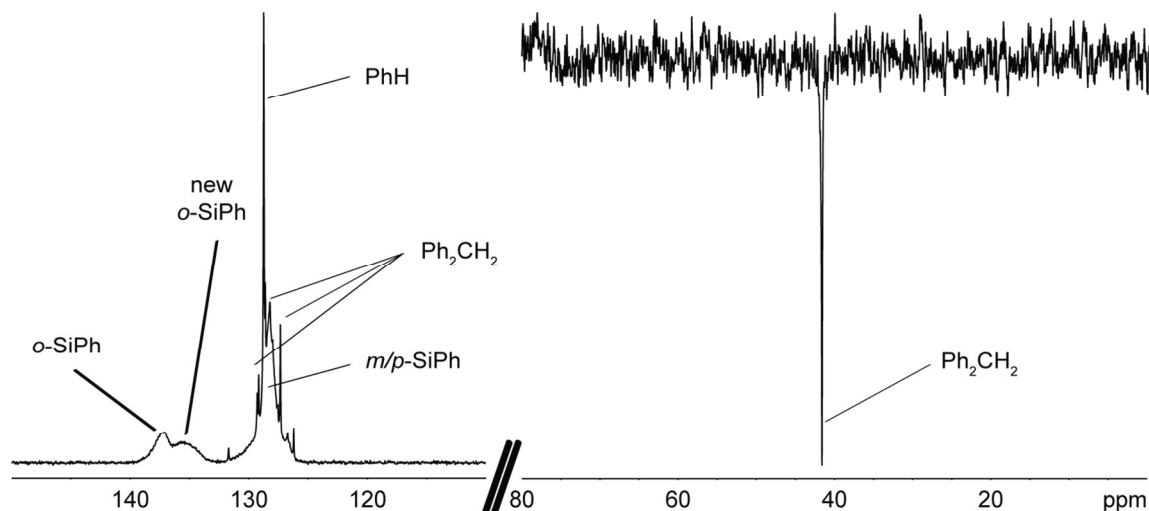
**Figure 4.43.** IR spectrum (KBr) of OCH<sub>2</sub>CH<sub>2</sub>Cl-modified poly(phenylsilane) (**4-8**).

*[PhSiH]-/[PhSiOCHPh<sub>2</sub>] – benzophenone-modified poly(phenylsilane) (4-9):*

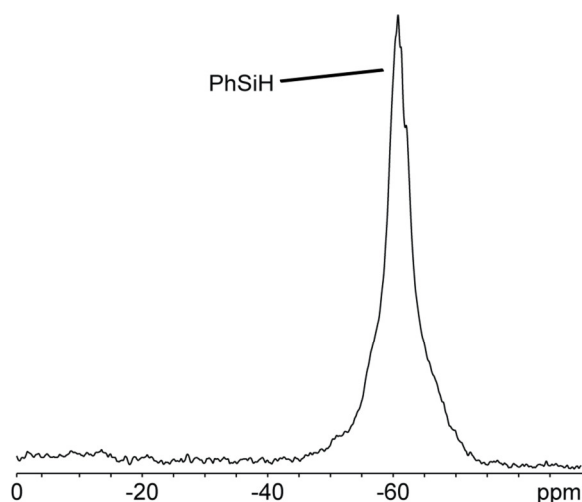
**4-1** (0.30 g, 2.9 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.074 g, 0.14 mmol), toluene (2 mL), benzophenone (0.27 g, 1.5 mmol), pentane (20 mL, then 2 x 20 mL). Procedural notes: stirred under N<sub>2</sub> (closed flask) for 16 h; started as a clear and colorless solution, and then turned to a clear brown solution during the 16 h stirring period; product was not dissolved in benzene; volatiles were removed under vacuum at 50 °C for 2h. A brown solid was isolated (0.22 g).



**Figure 4.44.** a) <sup>1</sup>H NMR (300 MHz) of OCHPh<sub>2</sub>-modified poly(phenylsilane) (**4-9**) in C<sub>6</sub>D<sub>6</sub>. The “#” is grease.



**Figure 4.45.** DEPT135  $^{13}\text{C}$  NMR (75 MHz) of OCHPh<sub>2</sub>-modified poly(phenylsilane) (**4-9**) in C<sub>6</sub>D<sub>6</sub>. For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 10 relative to the 100-160 ppm region.

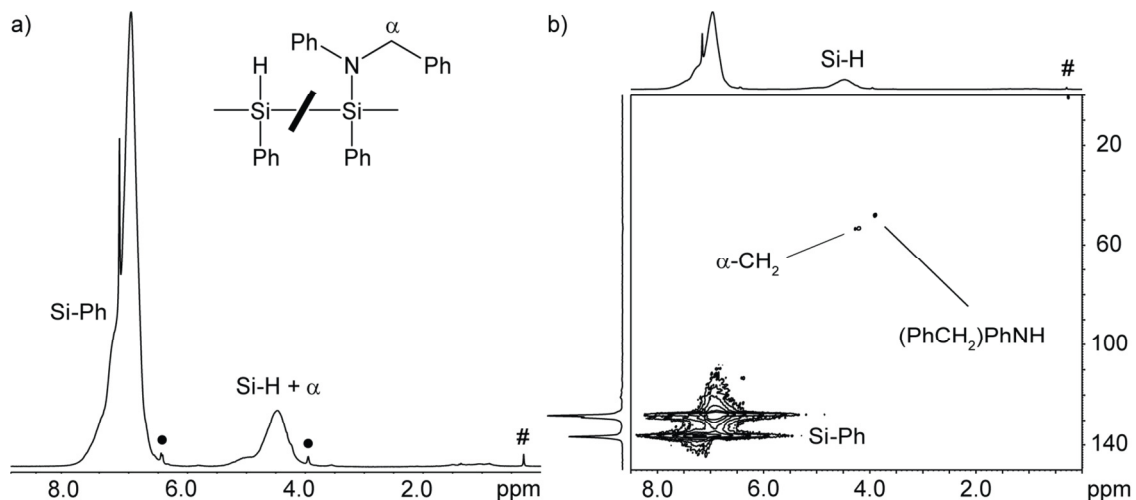


**Figure 4.46.** Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of OCHPh<sub>2</sub>-modified poly(phenylsilane) (**4-9**) in C<sub>6</sub>D<sub>6</sub>.

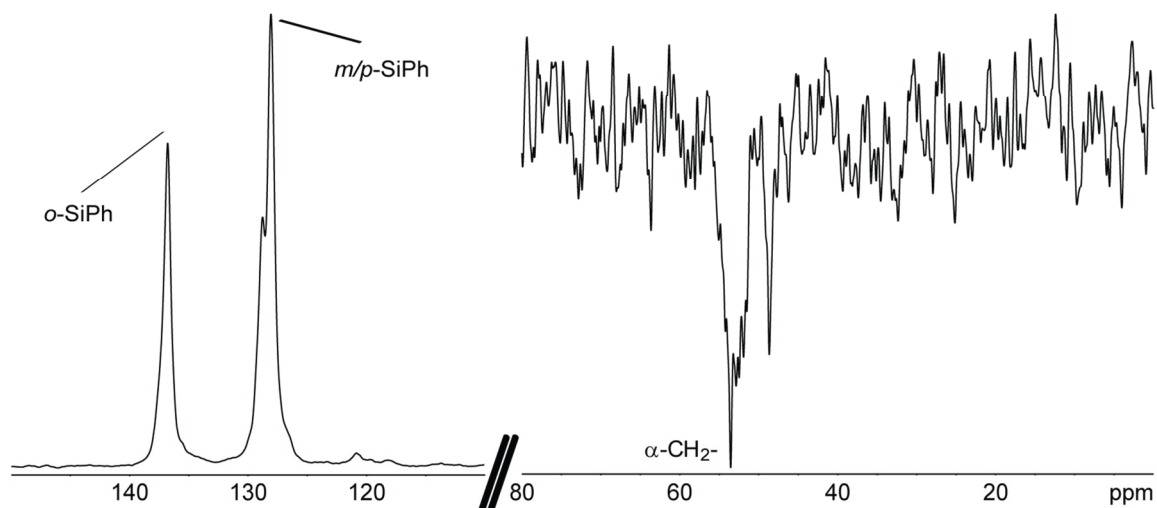
*[PhSiH]-/[PhSiNPhCH<sub>2</sub>Ph] – benzylideneaniline-modified poly(phenylsilane) (**4-10**):*

**4-1** (0.207 g, 1.9 mmol), benzylideneaniline (0.17 g, 0.94 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.044 g, 0.086 mmol), toluene (1 mL), pentane (3 x 10 mL), benzene (5 mL). Procedural notes: reaction was done in a “bomb” flask equipped with a stir bar; flask contents were degassed using one freeze-pump-thaw cycle. The mixture was heated in an oil bath (70°

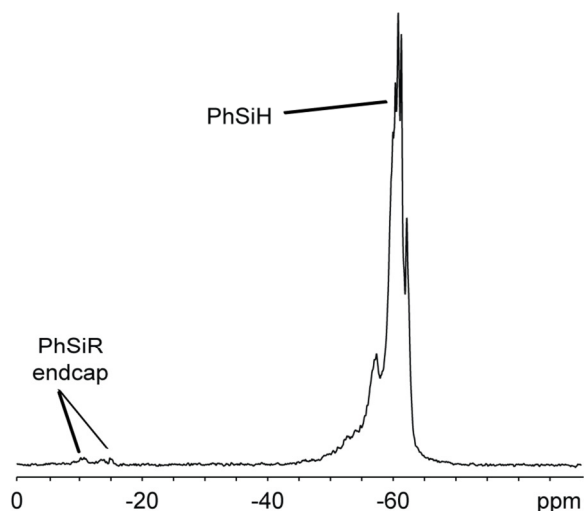
C) for 16 h and then cooled to RT; volatiles were removed under dynamic vacuum at 45°C for 2 h. A yellow solid was isolated (0.069 g).



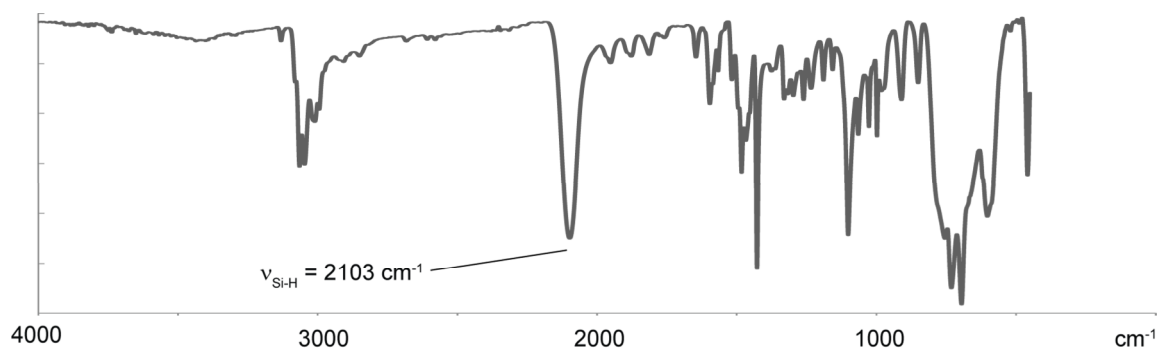
**Figure 4.47.** a)  $^1\text{H}$  NMR (300 MHz) and b)  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) of N(Ph)CH $_2$ Ph-modified poly(phenylsilane) (**4-10**) in  $\text{C}_6\text{D}_6$ . The “#” is grease.



**Figure 4.48.** DEPT135  $^{13}\text{C}$  NMR (75 MHz) of N(Ph)CH $_2$ Ph-modified poly(phenylsilane) (**4-10**) in  $\text{C}_6\text{D}_6$ . For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 100 relative to the 100-160 ppm region.



**Figure 4.49.** a) Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of N(Ph)CH<sub>2</sub>Ph-modified poly(phenylsilane) (**4-10**) in C<sub>6</sub>D<sub>6</sub>.

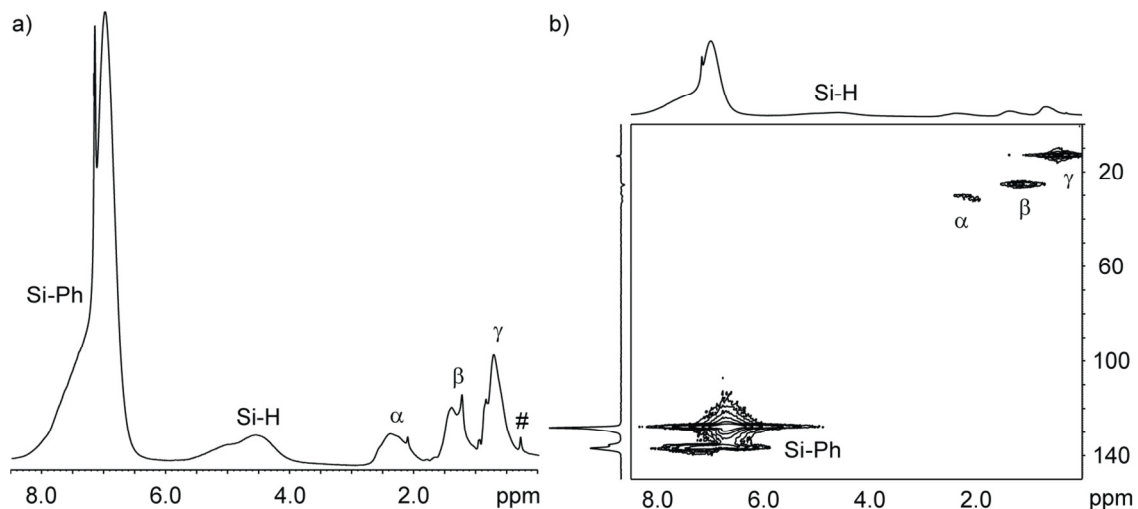


**Figure 4.50.** IR spectrum (KBr) of N(Ph)CH<sub>2</sub>Ph-modified poly(phenylsilane) (**4-10**).

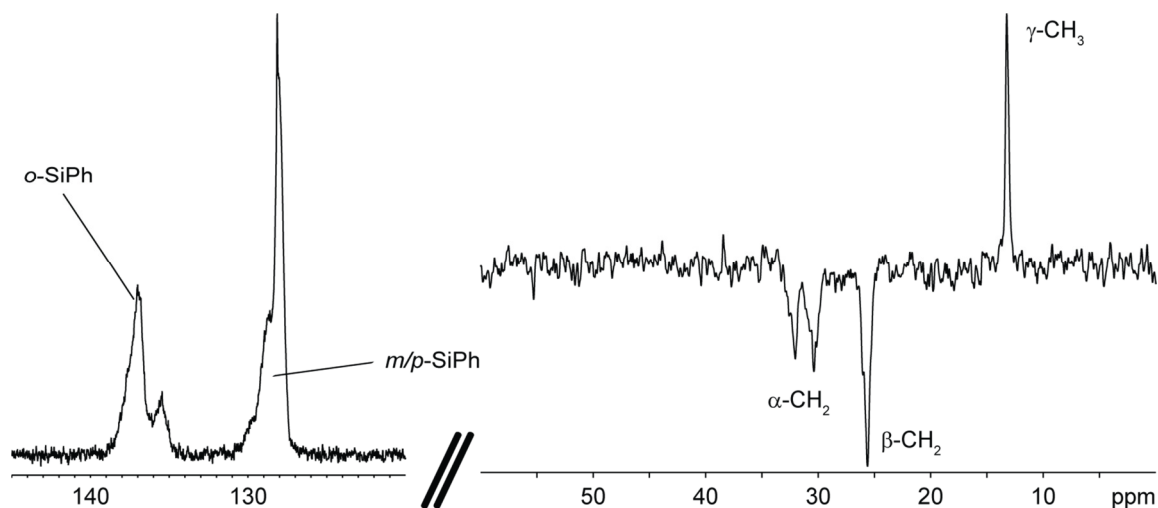
*[PhSiH]-/[PhSiSCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>] – n-propylthiol modified-poly(phenylsilane) (**4-11**):*

This procedure was reported in the literature and is used with permission (see note at the beginning of Chapter 4).<sup>96</sup> **4-1** (0.12, 1.6 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.030 g, 0.059 mmol), *n*-propylthiol (0.12 g, 1.6 mmol), toluene (1 mL), hexanes (3 x 20 mL). Procedural notes: stirred under N<sub>2</sub> (open to Nujol bubbler) for 1 h; the product was not dissolved in benzene;  $^1\text{H}$  NMR of these washings indicate the polymer may be slightly soluble in

hexane; volatiles were removed under dynamic vacuum at RT for 16 h<sup>lxi</sup>. A fine white powder was isolated (0.096 g).

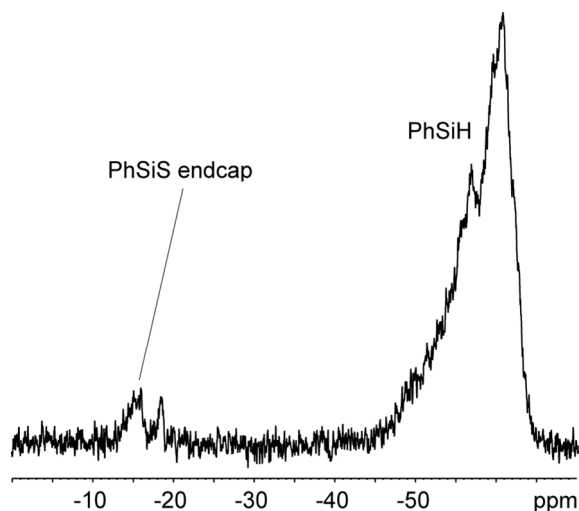


**Figure 4.51.** a) <sup>1</sup>H NMR (300 MHz) and b) <sup>1</sup>H-<sup>13</sup>C HSQC (<sup>1</sup>H 300 MHz, <sup>13</sup>C 75 MHz) of SCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-modified poly(phenylsilane) (**4-11**) in C<sub>6</sub>D<sub>6</sub>. The “#” is grease. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

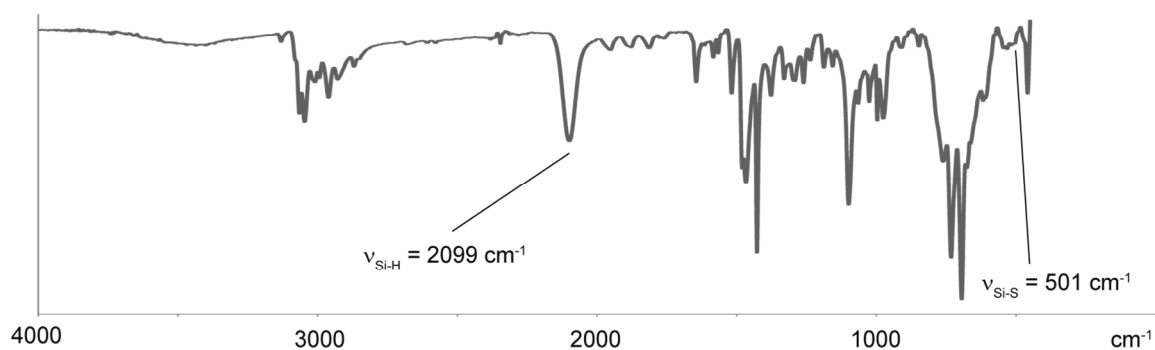


**Figure 4.52.** DEPT135 <sup>13</sup>C NMR (75 MHz) of SCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-modified poly(phenylsilane) (**4-11**) in C<sub>6</sub>D<sub>6</sub>. For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 20 relative to the 100-160 ppm region. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

<sup>lxi</sup> If this polymer is heated to over 50 °C under vacuum, the resulting material becomes insoluble in common solvents (benzene, toluene, dichloromethane, chloroform, hexane, pentane, water, ether, THF). The mechanism of decomposition has not yet been probed.



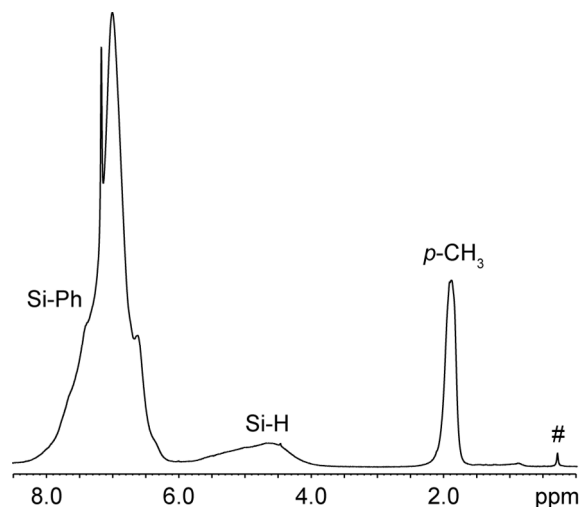
**Figure 4.53.** Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of  $\text{SCH}_2\text{CH}_2\text{CH}_3$ -modified poly(phenylsilane) (**4-11**) in  $\text{C}_6\text{D}_6$ . Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>



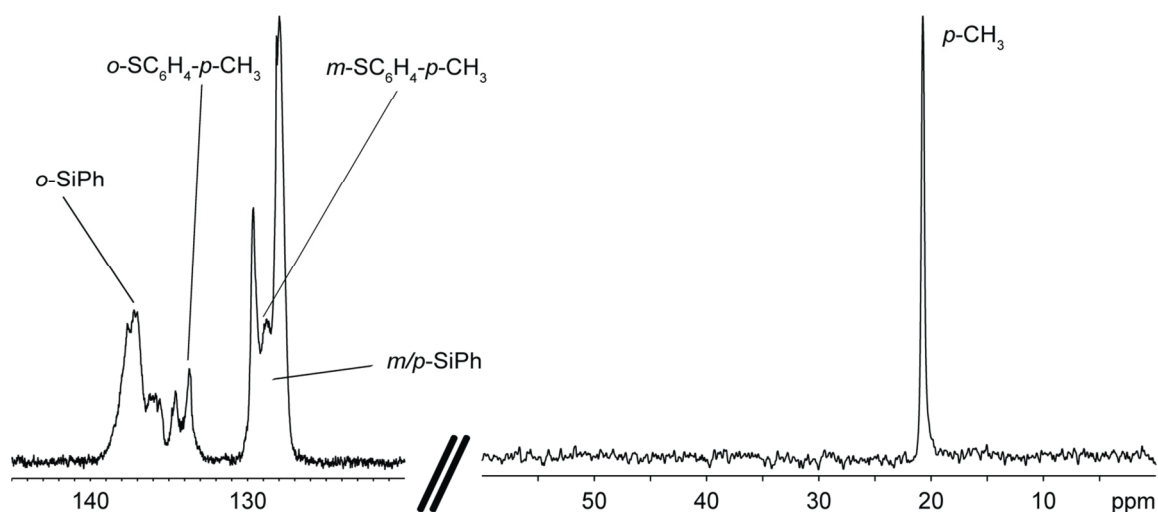
**Figure 4.54.** IR spectrum (KBr) of  $\text{SCH}_2\text{CH}_2\text{CH}_3$ -modified poly(phenylsilane) (**4-11**). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

*[PhSiH]-/[PhSiSC<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>] - p-thiocresol-modified-poly(phenylsilane) (**4-12**):*

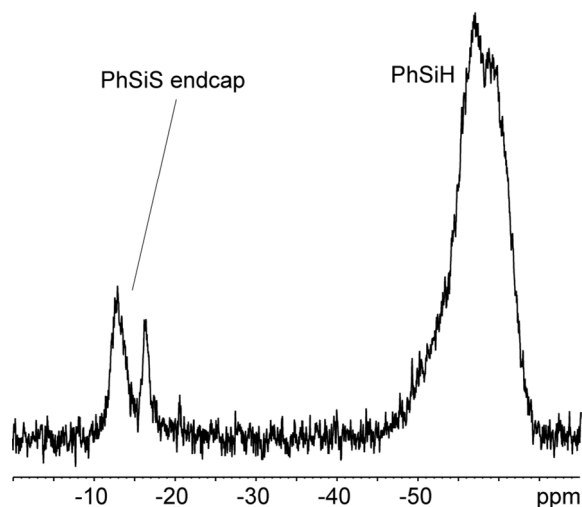
This procedure was reported in the literature and is used with permission (see note at the beginning of Chapter 4).<sup>96</sup> **4-1** (0.18 g, 1.7 mmol), *p*-thiocresol (0.12 g, 0.98 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.028 g, 0.055 mmol), toluene (2 mL), pentane (3 x 10 mL). Procedural notes: stirred under  $\text{N}_2$  (open to Nujol bubbler) for 1 h; product was collected by vacuum filtration; benzene was not added to dissolve the product; volatiles were removed under dynamic vacuum at 50 °C 1 h. A white powder was isolated (0.12 g).



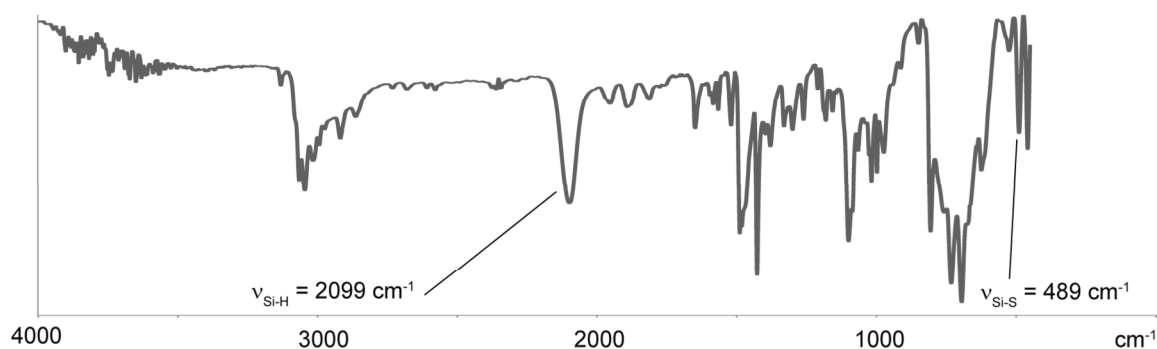
**Figure 4.55.**  $^1\text{H}$  NMR (300 MHz) of  $\text{SC}_6\text{H}_4$ - $p$ - $\text{CH}_3$ -modified poly(phenylsilane) (**4-12**) in  $\text{C}_6\text{D}_6$ . The “#” is grease. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>



**Figure 4.56.** DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{SC}_6\text{H}_4$ - $p$ - $\text{CH}_3$ -modified poly(phenylsilane) (**4-12**) in  $\text{C}_6\text{D}_6$ . Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>



**Figure 4.57.** Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of  $\text{SC}_6\text{H}_4$ -*p*- $\text{CH}_3$ -modified poly(phenylsilane) (**4-12**) in  $\text{C}_6\text{D}_6$ . Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

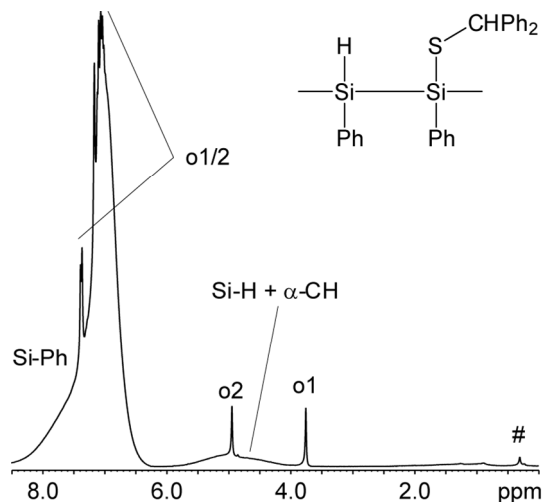


**Figure 4.58.** IR spectrum (KBr) of  $\text{SC}_6\text{H}_4$ -*p*- $\text{CH}_3$ -modified poly(phenylsilane) (**4-12**). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

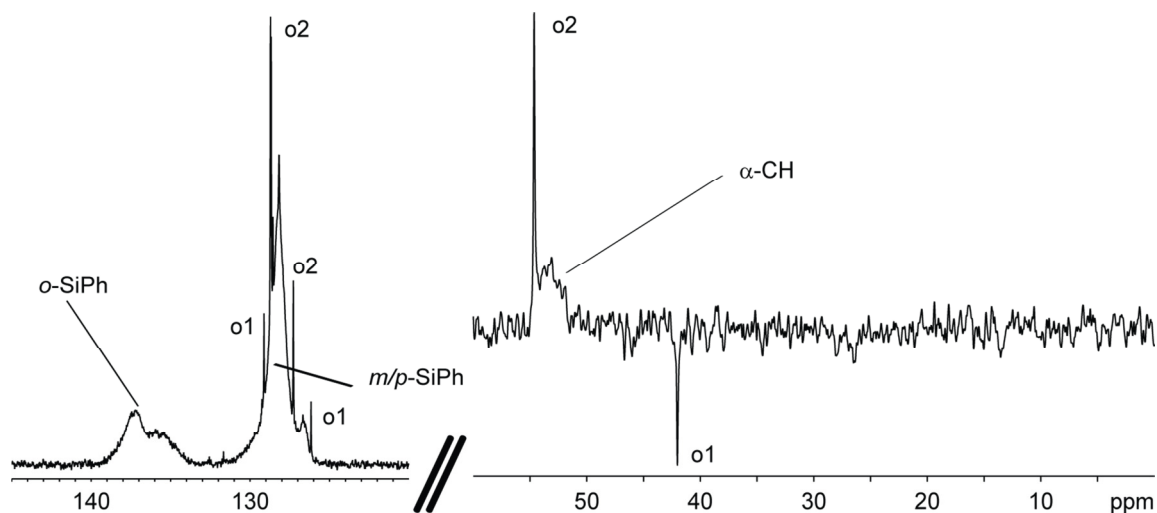
*[PhSiH]-/[PhSiSCHPh<sub>2</sub>] – thiobenzophenone-modified-poly(phenylsilane) (4-13)*

This procedure was reported in the literature and is used with permission (see note at the beginning of Chapter 4).<sup>96</sup> **4-1** (0.12 g, 1.2 mmol), thiobenzophenone (0.11 g, 0.57 mmol),  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.028 g, 0.055 mmol), toluene (2 mL), pentane (10 mL, then 2 x 10 mL). Procedural notes: stirred under  $\text{N}_2$  (closed flask) for 24 h; product was collected by vacuum filtration; product was not dissolved in benzene; volatiles were removed under dynamic vacuum at 50 °C for 1 h; A pale yellow powder was isolated (0.12 g).  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR samples for the SCHPh<sub>2</sub>-modified polymer consisted of a saturated solution in

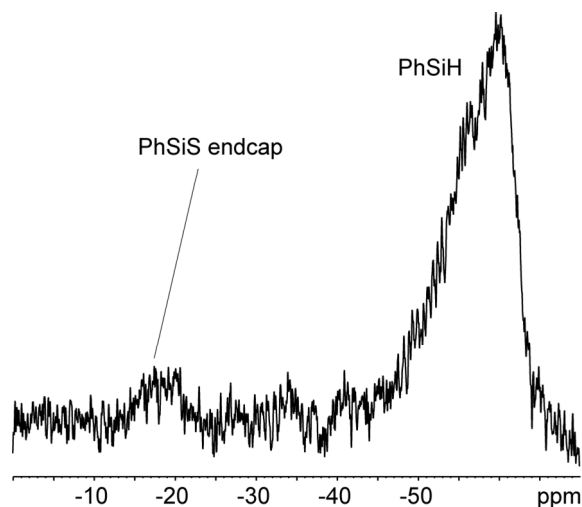
$d_6$ -benzene, which was filtered through a Pasteur pipette plugged with glass wool into the NMR tube.



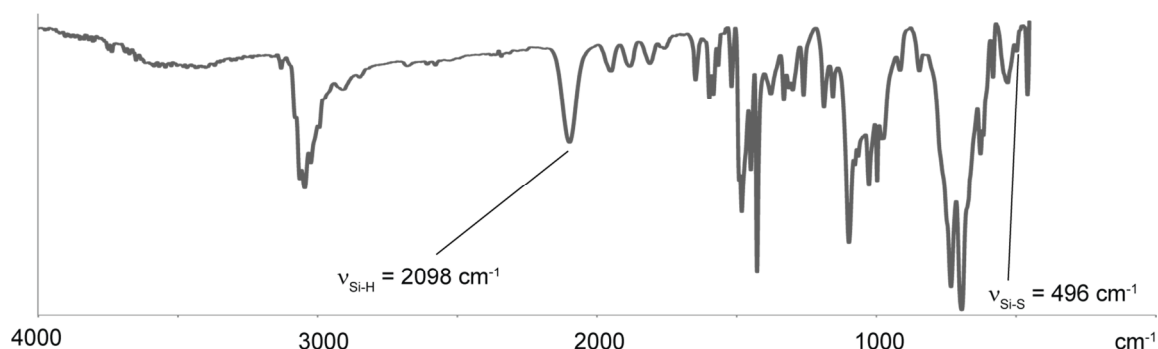
**Figure 4.59.**  $^1\text{H}$  NMR (300 MHz) of  $\text{Ph}_2\text{CS}$ -modified poly(phenylsilane) (**4-13**) in  $\text{C}_6\text{D}_6$ . The “#” is grease. The “o1” is diphenylmethane ( $\text{Ph}_2\text{CH}_2$ ). The “o2” is 1,1,2,2-tetraphenylethane ( $(\text{Ph}_2\text{CH})_2$ ). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>



**Figure 4.60.** DEPT135  $^{13}\text{C}$  NMR (75 MHz) of  $\text{SCHPh}_2$ -modified poly(phenylsilane) (**4-13**) in  $\text{C}_6\text{D}_6$ . The “o1” is diphenylmethane ( $\text{Ph}_2\text{CH}_2$ ). The “o2” is 1,1,2,2-tetraphenylethane ( $(\text{Ph}_2\text{CH})_2$ ). For clarity, the 0-80 ppm region has been vertically expanded by a factor of about 50 relative to the 100-160 ppm region. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>



**Figure 4.61.** Short-range DEPT90  $^{29}\text{Si}$  NMR (99 MHz,  $^1J_{\text{SiH}} = 188$  Hz) of SCHPh<sub>2</sub>-modified poly(phenylsilane) (**4-13**) in C<sub>6</sub>D<sub>6</sub>. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>



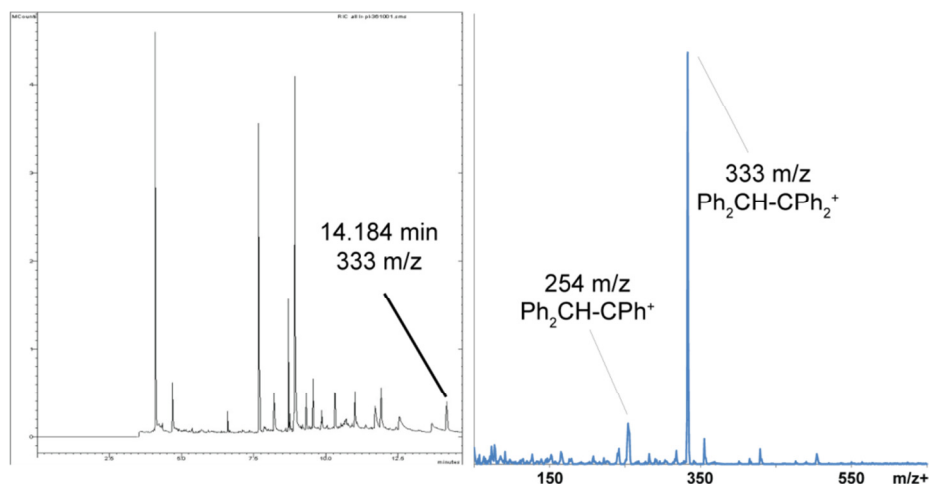
**Figure 4.62.** IR spectrum (KBr) of SCHPh<sub>2</sub>-modified poly(phenylsilane) (**4-13**). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

#### 4.9.4 Identification of 1,1,2,2-tetraphenylethane (Ph<sub>2</sub>CH)<sub>2</sub> from 4-13

The 1,1,2,2-tetraphenylethane by-product in hydrosilation of thiobenzophenone by poly(phenylsilane) was identified by multiple methods. First, the experimental benzylic  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were compared with previously reported spectra. The experimental  $\delta$  ( $^1\text{H}$  300 MHz, CDCl<sub>3</sub>) was 4.88 ppm and  $\delta$  ( $^{13}\text{C}$  75 MHz, CDCl<sub>3</sub>) 54.7 ppm; both were close to the literature  $\delta$  ( $^1\text{H}$  400 MHz, CDCl<sub>3</sub>) 4.76 ppm and  $\delta$  ( $^{13}\text{C}$  100 MHz, CDCl<sub>3</sub>) 56.32 ppm.<sup>149</sup> A DEPT90  $^{13}\text{C}$  experiment showed enhancement for the

peak suspected to belong to 1,1,2,2-tetraphenylethane, thus confirming this was a C-H methine species.

This procedure was reported in the literature and is used with permission (see note at the beginning of Chapter 4).<sup>96</sup> An aliquot of this polymer was then intentionally decomposed/hydrolyzed in order to obtain a sample suitable for GC-MS. A sample of polymer (0.3 g) was dissolved in dichloromethane (5 mL) and water (0.5 mL). The mixture was stirred in an open flask until the solvent evaporated. The light-brown residue was dissolved in hexanes (5 mL) and then filtered through a Pasteur pipette plugged with glass wool. A clear and colorless filtrate was collected and solvent was removed on the rotary evaporator. A  $^1\text{H}$  NMR spectrum of the crude material showed it still contained diphenylmethane, 1,1,2,2-tetraphenylethane, and a small amount of PhSi-containing polymer. The residue was dissolved in dichloromethane (5 mL) and then used for a GC-MS sample. The GC chromatogram showed a small peak corresponding to  $m/z^+ = 333$ , the parent ion for 1,1,2,2-tetraphenylethane.



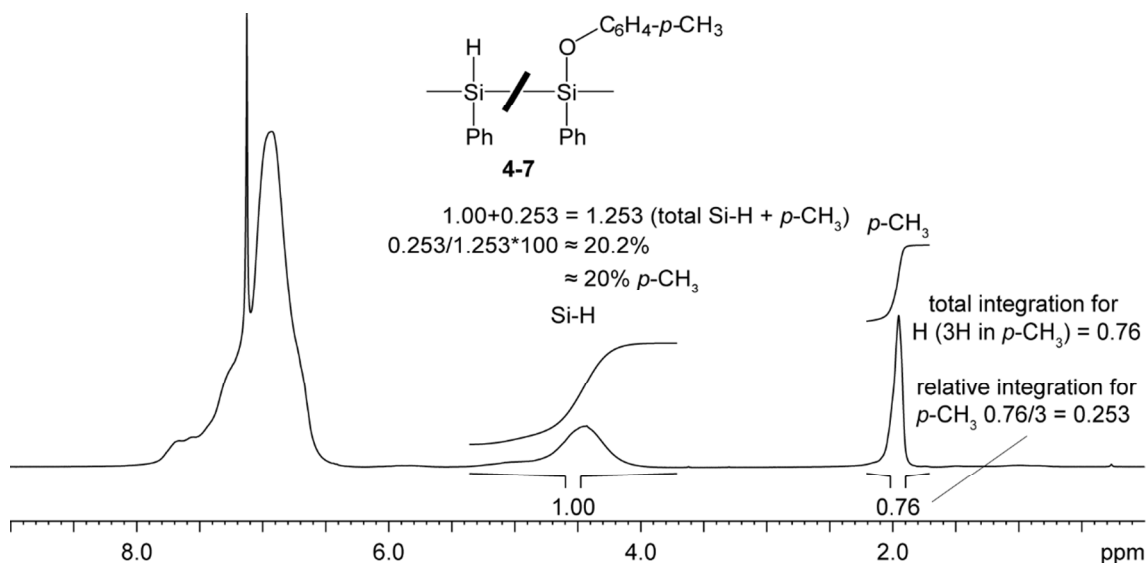
**Figure 4.63.** Identification of  $(\text{Ph}_2\text{CH})_2$  by GC-MS. Full CG trace (left) and MS for peak eluting at  $t = 14.184$  min (right). Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

#### 4.9.5 Methods used to evaluate $B(C_6F_5)_3$ selectivity for Si-H bond modification over Si-Si bond cleavage

The pentane or hexanes washings obtained during the syntheses of **4-4** to **4-13** were diluted with pentane or hexane, respectively, to approximately 100 mL total volume. An aliquot (1.5-2 mL) of solution was removed and this was analyzed by GC-MS. The major chromatogram trace peaks were unreacted substrate (non-volatile substrates in **4-6**  $m/z = 150$ , **4-7**  $m/z = 122$ , **4-9**  $m/z = 182$ , **4-10**  $m/z = 181$ , **4-12**  $m/z = 124$ , and **4-13**  $m/z = 198$ ) and  $B(C_6F_5)_3$  catalyst (usually detected as hydrolyzed/degraded by-product, pentafluorobenzene ( $C_6HF_5$ )  $m/z = 168$ ).

The remainder of each ~100 mL solution was evacuated to remove solvent (pentane or hexanes), leaving a white or slightly-yellow residue. The residue was dissolved in  $C_6D_6$  and was analyzed by  $^1H$  and  $^{19}F$  NMR. In the  $^1H$  NMR spectra, unreacted/removed substrate (for polymers **4-6**, **4-7**, **4-9**, **4-10**, **4-12**, and **4-13**) and/or trace amounts (signals just above the  $^1H$  NMR baseline) of the X-modified poly(phenylsilane) (**4-4** to **4-13**) were detected. No discrete or sharp signals in the Si-H region (4-6 ppm) or elsewhere were detected. In the  $^{19}F$  NMR, either  $B(C_6F_5)_3$  and/or substrate-coordinated  $B(C_6F_5)_3$  were identified (three  $^{19}F$  peaks slightly displaced from free  $B(C_6F_5)_3$ ).

#### 4.9.6 Representative determination of the degree of Si-H substitution using $^1\text{H}$ NMR integration



**Figure 4.64.**  $^1\text{H}$  NMR (300 MHz, D1 = 2s) of  $\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$ -modified poly(phenylsilane) (**4-7**) in  $\text{C}_6\text{D}_6$  showing the method to obtain a degree of substitution (20%) by  $^1\text{H}$  NMR integration.

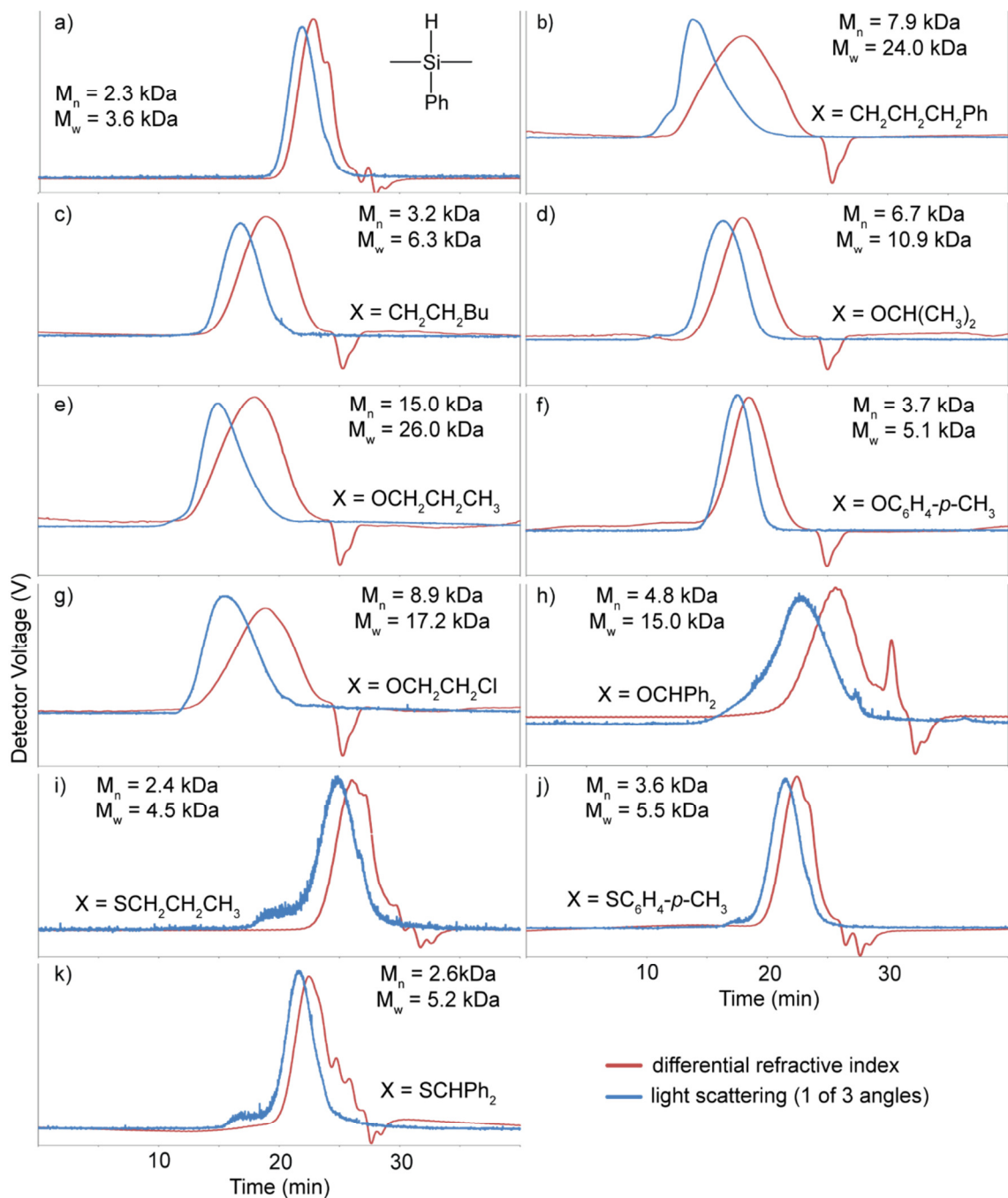
#### 4.9.7 Molecular weight analysis

**Table 4.6.** Full GPC-MALS data sets collected for modified polymers and corresponding batches of parent poly(phenylsilane) (**4-1**). Data for **4-11**, **4-12**, and **4-13** is used with permission (see note at beginning of Chapter 4).<sup>96</sup>

Polymer	Batch	X =	$M_N$ (kDa)	$M_W$ (kDa)	PDI
<b>4-1</b>	<b>a</b>	H	$2.3 \pm 0.2$	$4.0 \pm 0.3$	1.7
				↓	
<b>4-2</b>	<b>a</b>	$\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$	$13.0 \pm 1.9$	$37.0 \pm 4.0$	2.8
<b>4-1</b>	<b>b</b>	H	$1.9 \pm 0.2$	$3.0 \pm 0.3$	1.6
				↓	
<b>4-2</b>	<b>b</b>	$\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$	$2.2 \pm 0.3$	$4.6 \pm 0.7$	2.1
<b>4-1</b>	<b>e</b>	H	$0.89 \pm 0.2$	$1.5 \pm 0.3$	1.7
				↓	
<b>4-2</b>	<b>c</b>	$\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$	$7.7 \pm 0.3$	$22.0 \pm 1.4$	2.9
<b>4-1</b>	<b>a</b>	H	$2.3 \pm 0.2$	$4.0 \pm 0.3$	1.7
				↓	
<b>4-3</b>	<b>a</b>	$\text{CH}_2\text{CH}_2\text{Bu}$	$4.4 \pm 0.5$	$12.0 \pm 1.1$	2.7

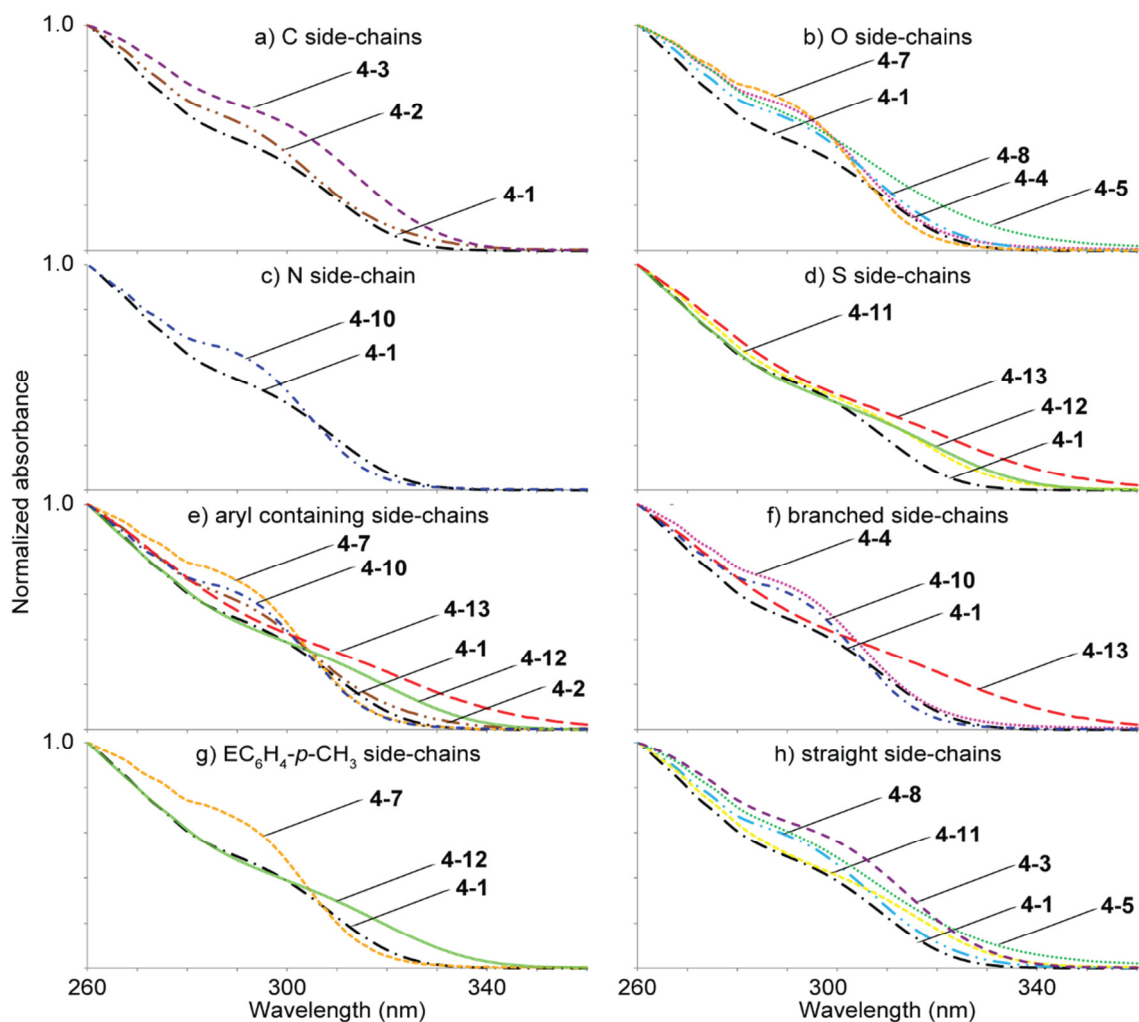
4-1	b	H	$1.9 \pm 0.2$	$3.0 \pm 0.3$	1.6
				↓	
4-3	b	CH <sub>2</sub> CH <sub>2</sub> Bu	$5.1 \pm 0.2$	$15.0 \pm 0.4$	3.0
4-1	c	H	$1.8 \pm 0.2$	$2.4 \pm 0.3$	1.3
				↓	
4-3	c	CH <sub>2</sub> CH <sub>2</sub> Bu	$3.3 \pm 0.1$	$6.5 \pm 0.3$	2.0
4-1	b	H	$1.9 \pm 0.2$	$3.0 \pm 0.3$	1.6
				↓	
4-4	a	OCH(CH <sub>3</sub> ) <sub>2</sub>	$7.4 \pm 1.0$	$12.0 \pm 1.5$	1.6
4-1	c	H	$1.8 \pm 0.2$	$2.4 \pm 0.3$	1.3
				↓	
4-4	b	OCH(CH <sub>3</sub> ) <sub>2</sub>	$5.8 \pm 0.2$	$13.0 \pm 1.8$	2.2
4-1	c	H	$1.8 \pm 0.2$	$2.4 \pm 0.3$	1.3
				↓	
4-4	c	OCH(CH <sub>3</sub> ) <sub>2</sub>	$17.0 \pm 2.8$	$34.0 \pm 5.0$	2.1
4-1	a	H	$2.3 \pm 0.2$	$4.0 \pm 0.3$	1.7
				↓	
4-5	a	OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	$12.0 \pm 2.4$	$23.0 \pm 3.1$	1.9
4-1	b	H	$1.9 \pm 0.2$	$3.0 \pm 0.3$	1.6
				↓	
4-5	b	OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	$18.0 \pm 0.5$	$36.0 \pm 0.9$	1.9
4-1	b	H	$1.9 \pm 0.2$	$3.0 \pm 0.3$	1.6
				↓	
4-5	c	OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	$8.4 \pm 1.2$	$16.0 \pm 2.7$	1.9
4-1	c	H	$1.8 \pm 0.2$	$2.4 \pm 0.3$	1.3
				↓	
4-5	d	OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	$21.0 \pm 1.4$	$42.0 \pm 5.5$	2.0
4-1	b	H	$1.9 \pm 0.2$	$3.0 \pm 0.3$	1.6
				↓	
4-7	a	OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	$2.8 \pm 0.3$	$5.1 \pm 0.6$	1.8
4-1	c	H	$1.8 \pm 0.2$	$2.4 \pm 0.3$	1.3
				↓	
4-7	b	OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	$3.0 \pm 0.2$	$5.5 \pm 0.3$	1.8
4-1	c	H	$1.8 \pm 0.2$	$2.4 \pm 0.3$	1.3
				↓	
4-7	c	OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	$3.7 \pm 0.1$	$5.2 \pm 0.1$	1.4
4-1	b	H	$1.9 \pm 0.2$	$3.0 \pm 0.3$	1.6
				↓	
4-8	a	OCH <sub>2</sub> CH <sub>2</sub> Cl	$8.9 \pm 0.4$	$18.0 \pm 0.5$	2.0

4-1	c	H	$1.8 \pm 0.2$	$2.4 \pm 0.3$	1.3
				↓	
4-8	b	OCH <sub>2</sub> CH <sub>2</sub> Cl	$12.0 \pm 0.9$	$24.0 \pm 1.6$	2.1
4-1	e	H	$0.89 \pm 0.2$	1.5	1.7
				↓	
4-8	c	OCH <sub>2</sub> CH <sub>2</sub> Cl	$2.5 \pm 0.1$	$4.4 \pm 0.1$	1.8
4-1	d	H	$2.2 \pm 0.2$	$3.5 \pm 0.3$	1.6
				↓	
4-9	a	OCHPh <sub>2</sub>	$4.8 \pm 0.3$	$15.0 \pm 1.2$	3.1
4-1	d	H	$2.2 \pm 0.2$	$3.5 \pm 0.3$	1.6
				↓	
4-10	a	SCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	$4.0 \pm 0.3$	$6.9 \pm 0.6$	1.7
4-1	d	H	$2.2 \pm 0.2$	$3.5 \pm 0.3$	1.6
				↓	
4-10	b	SCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	$2.5 \pm 0.2$	$4.5 \pm 0.1$	1.8
4-1	d	H	$2.2 \pm 0.2$	$3.5 \pm 0.3$	1.6
				↓	
4-11	a	SC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	$3.4 \pm 0.2$	$5.4 \pm 0.2$	1.6
4-1	f	H	$1.7 \pm 0.2$	$2.6 \pm 0.3$	1.6
				↓	
4-11	b	SC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	$3.1 \pm 0.1$	$5.0 \pm 0.1$	1.6
4-1	d	H	$2.2 \pm 0.2$	$3.5 \pm 0.3$	1.6
				↓	
4-13	a	SCHPh <sub>2</sub>	$2.6 \pm 0.3$	$5.7 \pm 0.4$	2.2
4-1	d	H	$2.2 \pm 0.2$	$3.5 \pm 0.3$	1.6
				↓	
4-13	b	SCHPh <sub>2</sub>	$2.5 \pm 0.3$	$5.1 \pm 0.4$	2.0



**Figure 4.65.** Representative GPC  $M_N/M_W$  determination for a) parent poly(phenylsilane) (**4-1**) b)  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ -modified (**4-2**), c)  $\text{CH}_2\text{CH}_2\text{Bu}$ -modified (**4-3**), d)  $\text{OCH}(\text{CH}_3)_2$ -modified (**4-4**), e)  $\text{OCH}_2\text{CH}_2\text{CH}_3$ -modified (**4-5**), f)  $\text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$ -modified (**4-7**), g)  $\text{OCH}_2\text{CH}_2\text{Cl}$ -modified (**4-8**), h)  $\text{OCHPh}_2$ -modified (**4-9**), i)  $\text{SCH}_2\text{CH}_2\text{CH}_3$ -modified (**4-11**), j)  $\text{SC}_6\text{H}_4\text{-}p\text{-CH}_3$ -modified (**4-12**), and k)  $\text{SCHPh}_2$ -modified (**4-13**) poly(phenylsilane) derivatives in THF. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

## 4.9.8 UV-Vis absorption spectra

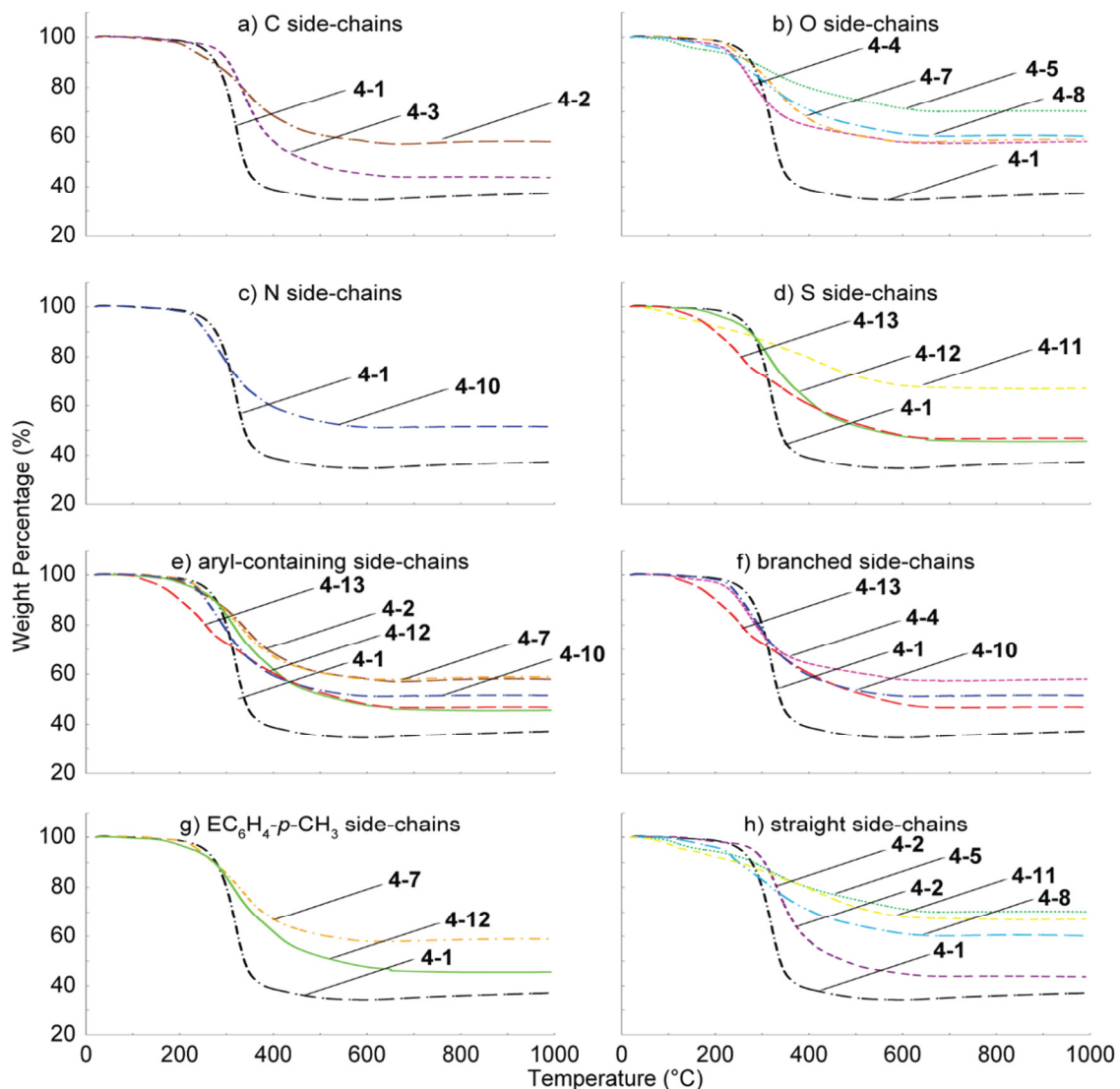


**Figure 4.66.** UV-vis absorption spectra (in  $\text{CH}_2\text{Cl}_2$ , normalized at 260 nm) of modified poly(phenylsilane) derivatives (**4-2** to **4-13**) and parent poly(phenylsilane) (**4-1**) comparing a) C side chains **4-2** and **4-3**, b) O side-chains **4-4**, **4-5**, **4-7**, and **4-8**, c) N side-chain **4-10**, d) S side-chains **4-11**, **4-12**, and **4-13**, e) aryl side-chains **4-2**, **4-7**, **4-10**, **4-12**, **4-13**, f) branched side-chains **4-4**, **4-10**, **4-13**, g)  $\text{EC}_6\text{H}_4$ -*p*- $\text{CH}_3$  side-chains **4-7** and **4-12**, h) straight side-chains **4-3**, **4-5**, **4-8**, and **4-11** showing similarity to starting poly(phenylsilane) **4-1**. Figure is adapted with permission (see note at the beginning of Chapter 4).<sup>96</sup>

#### 4.9.9 Thermogravimetric analysis (TGA)

**Table 4.7.** TGA inflection temperatures for parent poly(phenylsilane) (**4-1**) and modified poly(phenylsilane) derivatives (**4-1** to **4-5**, **4-7**, **4-8**, and **4-10** to **4-13**).

Polymer	X =	Inflection Temperature ( $\pm 10$ °C)	Ceramic Yield (%)
<b>4-1</b>	Si-H	320	37
<b>4-2</b>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Ph	340	58
<b>4-3</b>	CH <sub>2</sub> CH <sub>2</sub> Bu	340	44
<b>4-4</b>	OCH(CH <sub>3</sub> ) <sub>2</sub>	280	58
<b>4-5</b>	OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	310	70
<b>4-7</b>	OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	340	59
<b>4-8</b>	OCH <sub>2</sub> CH <sub>2</sub> Cl	320	60
<b>4-10</b>	N(Ph)CH <sub>2</sub> Ph	300	52
<b>4-11</b>	SCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	270	67
<b>4-12</b>	SC <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub>	310	46
<b>4-13</b>	SCHPh <sub>2</sub>	240	47



**Figure 4.67.** TGA traces (heating rate 10 °C/min) of modified poly(phenylsilane) derivatives (**4-2** and **4-13**) and parent poly(phenylsilane) (**4-1**) comparing a) C-side chains **4-2** and **4-3**, b) O side-chains **4-4**, **4-5**, **4-7**, and **4-8**, c) N side-chains **4-10**, d) S side-chains **4-11**, **4-12**, and **4-13**, e) aryl side-chains **4-2**, **4-7**, **4-10**, **4-12**, **4-13**, f) branched side-chains **4-4**, **4-10**, **4-13**, g)  $\text{EC}_6\text{H}_4\text{-}p\text{-CH}_3$  side-chains **4-7** and **4-12**, h) straight side-chains **4-3**, **4-5**, **4-8**, and **4-11** showing similarity in shape and inflection temperature to starting poly(phenylsilane), **4-1**.

## 5 Thermal degradation and redistribution of poly(phenylsilane)

This chapter describes a tangential project that resulted from a collaboration between the Rosenberg group and SeaStar Chemicals Inc. This included work by Dr. Cunhai Josh Dong (pyrolysis of poly(phenylsilane) (**4-1**, Section 5.7.3) and XRD of **5-3**), and Dr. Raj Odedra. Jon Clarke, an undergraduate student in the Rosenberg group, did the thermogravimetric analysis of poly(phenylsilane) (**4-1**, Section 5.2), the identification of volatile thermolysis products (Section 5.3), and the initial characterization of **5-2** (Section 5.4) under my supervision.

### 5.1 Introduction

The goal of the collaboration was to investigate the preparation of titanium disilicide ( $\text{TiSi}_2$ ) from the thermal degradation of a mixture of poly(phenylsilane) (**4-1**) and titanium dihydride ( $\text{TiH}_2$ ). A sol-gel method for the preparation of titanium disilicide starting from an air/water stable mixture that can be effectively “shaped” for deposition using the sol-gel’s fluid-like mobility was proposed. Thermal elimination of all of the carbons and hydrogens from the **4-1**/ $\text{TiH}_2$  mixture was anticipated and desired, leaving only silicon and titanium in the desired stoichiometry. However, preliminary thermolysis experiments with exclusively poly(phenylsilane) did not give silicon metal as originally desired and indicated a complex thermal degradation process had occurred to give principally silicon carbide with carbon of some form and volatile by-products.

Silicon carbide (SiC) is an interesting and well-studied material. Its numerous properties are exploited in the manufacture of abrasives,<sup>10</sup> heat-resistant materials,<sup>150</sup> lightning arresters in electric power systems,<sup>151</sup> semiconductors for electronic devices,<sup>152</sup>

and LEDs.<sup>153</sup> One well-established method for preparing SiC is from the thermolysis of poly(dimethylsilane).<sup>9a,c,154</sup> A unique feature of this thermolysis is the initial formation of a poly(carbosilane),  $[(\text{CH}_3\text{SiH})\text{CH}_2]_n$  at 500 °C.<sup>9c</sup> Higher temperatures (>1000 °C) are used to transform the poly(carbosilane) “intermediate” into SiC. In contrast, polysilane (**4-1**) does not have an adjacent methyl or alkyl group and cannot decompose via the same proposed pathway as poly(dimethylsilane).

This chapter reports the interesting thermal decomposition of poly(phenylsilane). The products were identified as SiC and discrete monosilanes, which are formed via a complex series of redistribution reactions. A partial thermolysis experiment was undertaken to isolate and characterize an intermediate thermolysis product.

## 5.2 Thermogravimetric analysis (TGA) of poly(phenylsilane)

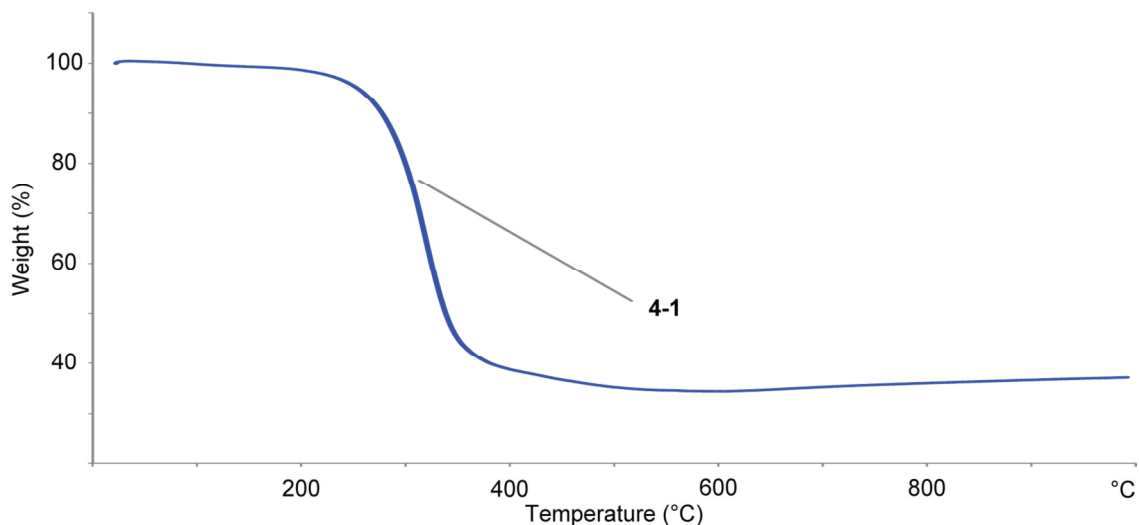
The TGA trace of poly(phenylsilane) (**4-1**) showed a characteristic S-curve (Figure 5.1),<sup>144</sup> with a ceramic yield of 37%, and a temperature of inflection at 320 °C. This data suggests that thermolysis produced SiC, as the expected ceramic yield of **4-1** to SiC is 38%.<sup>lxii</sup> Upon closer inspection of the TGA, two unique features were found: a minimum mass percentage (34%) at 600 °C and a gradual increase in mass (3%) from 600 to 1000 °C, which suggests the remaining solid silicon-containing residue was being oxidized (likely surface oxidation to  $\text{SiO}_2$ )<sup>lxiii</sup> over time at higher temperatures. The experiment was done under  $\text{N}_2$  to avoid oxygen and subsequent oxidation. However, this was done crudely by flushing the TGA oven with  $\text{N}_2$ . It is conceivable that at high

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<sup>lxii</sup> Ceramic yield is the ratio of the mass of product formed from heating to the mass of its precursor used for the TGA process expressed as a percentage.

<sup>lxiii</sup> Expected ceramic yield of **4-1** to  $\text{SiO}_2$  is 57%.

temperatures oxidation may have occurred. This Si or SiO<sub>2</sub> ambiguity led to repeating the thermal decomposition experiment on a larger scale and under a rigorously inert atmosphere to obtain an adequate quantity of the final product for characterization.

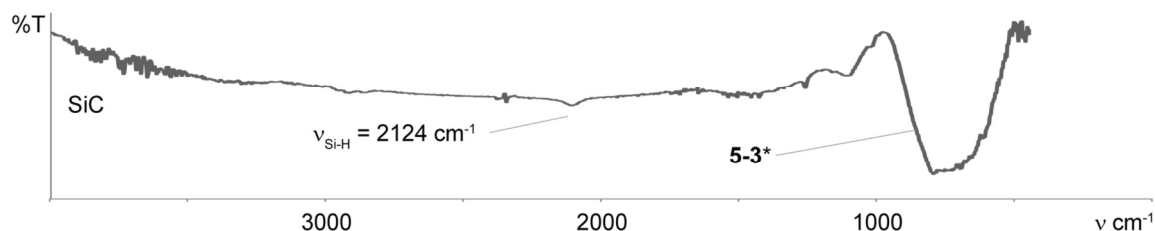


**Figure 5.1.** TGA trace of — **4-1**. Sample was heated at 10 °C/min from RT (approximately 20 °C) to 1000 °C. The inflection temperature is at  $320 \pm 10$  °C. A minimum mass was found at  $600 \pm 10$  °C (34% mass). The ceramic yield was 37%.

A sample of **4-1** in a quartz tube was heated to 800 °C under an atmosphere of argon and hydrogen (95:5)<sup>lxiv</sup> to give **5-3**. Its physical appearance was similar to the literature description<sup>9c</sup> of SiC made from the thermolysis of poly(dimethylsilane), a “black and metallic luster fiber”. However, the primary method of identifying SiC, X-ray diffraction (XRD), showed **5-3** to be amorphous: an inconclusive test for SiC. Product **5-3** was initially challenging to characterize by conventional methods such as NMR because of its insolubility in common solvents. This led to analyzing the solid in the IR

<sup>lxiv</sup> Studies on polysiloxanes,<sup>156</sup> polycarbosilanes,<sup>157</sup> and hydrogenated silicon carbide<sup>158</sup> have used an atmosphere of argon and hydrogen in their pyrolysis procedures. Systematic studies on the pyrolysis atmosphere have demonstrated that the hydrogen suppresses H<sub>2</sub> elimination from the product. This encourages excess carbon to be eliminated as CH<sub>4</sub>.<sup>157,159</sup>

spectrometer as a KBr pellet. The IR spectrum shows few distinct features, except for a broad, intense peak at 550-900  $\text{cm}^{-1}$  (**5-3\*** in Figure 5.2) and is consistent with published IR spectra of SiC.<sup>160</sup>



**Figure 5.2.** IR spectrum of **5-3** showing diagnostic (**5-3\***) absorption for SiC.

Further evidence that sample **5-3** was SiC was found by elemental analysis. This analysis was initially expected to be inconclusive for SiC because of its perceived inability to oxidize to  $\text{SiO}_2$  and  $\text{CO}_2$  under standard combustion analysis conditions. This should give low values of %C, but instead, the %C/%H obtained was higher than expected for complete combustion of material of the formula “SiC” (calculated: %C/%H 29.95/0, found: 41.80/0.50). A formula of  $\text{SiC}_{1.7}\text{H}_{0.2}$  was invoked to obtain a %C/%H consistent with experimental results (calculated: 41.92/0.5). The higher Si:C ratio than expected (1:1 Si:C) suggests additional carbon content, which is probably residual elemental carbon.<sup>lxv</sup> The low %H value indicates residual Si-H on the surface, which is consistent with the observation of a weak IR absorption  $\nu_{\text{Si-H}} = 2124 \text{ cm}^{-1}$  (Figure 2). It may be assumed that silicon carbide and elemental carbon did not combust completely in the elemental analyzer, since the method used is optimized for organic molecules and not

<sup>lxv</sup> The elemental analysis of silicon carbide from the pyrolysis of other polysilanes, fully and partially substituted, has been reported in the literature. These examples show that a higher Si:C ratio in the starting polysilane leads to a greater elemental carbon content in the pyrolyzed product.<sup>155</sup>

inorganic solids that are known for their stability at high temperature. Thus the proposed formula ( $\text{SiC}_{1.7}\text{H}_{0.2}$ ) may be an underestimate for the true %C.

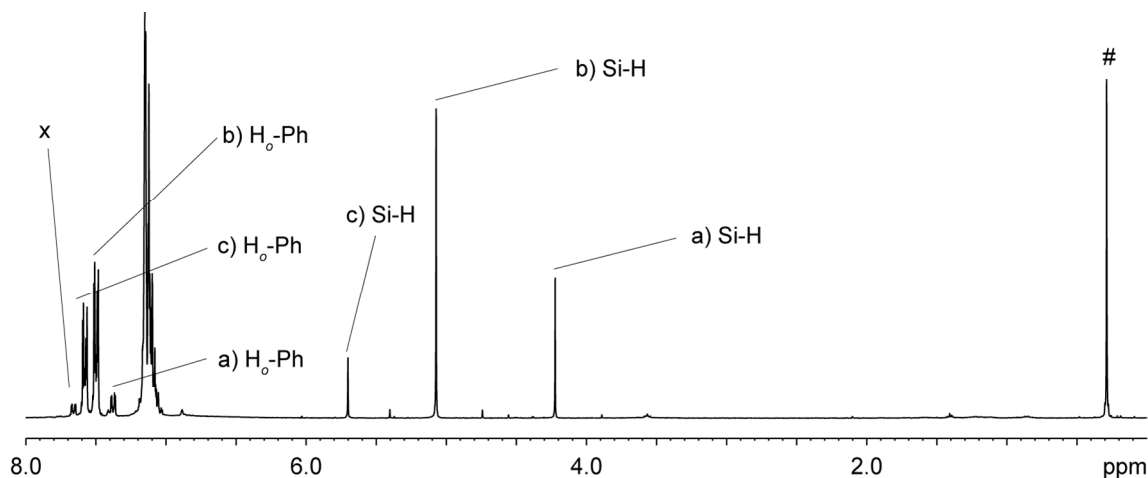
### 5.3 Identification of volatile thermolysis products

The formulaic complexity of thermolysis product **5-3** encouraged the investigation of the volatile by-product or by-products, which were found to be monosilanes  $\text{PhSiH}_3$ ,  $\text{Ph}_2\text{SiH}_2$ , and  $\text{Ph}_3\text{SiH}$ . A partial thermolysis experiment was performed in a one-piece closed flask to a maximum temperature of 500 °C,<sup>lxvi</sup> which was above the inflection temperature observed in the TGA trace of **4-1** (Figure 5.1). After reaching 500 °C and holding for 30 min, the flask was cooled to RT. An aliquot was removed from the crude mixture for  $^1\text{H}$  and  $^{29}\text{Si}$  NMR analysis. This unambiguously showed monosilanes,  $\text{Ph}_3\text{SiH}$ ,  $\text{Ph}_2\text{SiH}_2$ , and  $\text{PhSiH}_3$  (Figure 5.3), by comparison with spectra of authentic samples.  $^1\text{H}$  NMR of the crude thermolysis mixture did not show the presence of longer oligomers (disilanes, trisilanes, etc.) or benzene.<sup>lxvii</sup> After extraction and isolation of these monosilanes, they accounted for approximately 50% of the starting poly(phenylsilane) mass. Thus,  $\text{Ph}_3\text{SiH}$ ,  $\text{Ph}_2\text{SiH}_2$ , and  $\text{PhSiH}_3$  are apparently the major volatile by-products eliminated in thermal decomposition and the TGA experiment.

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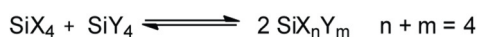
<sup>lxvi</sup> Temperature was measured with a thermocouple placed outside the flask. The actual temperature inside the flask may be lower than 500 °C.

<sup>lxvii</sup> A  $^1\text{H}$  NMR was also run of the crude sample in  $\text{CDCl}_3$  to confirm a lack of signal due to  $\text{C}_6\text{H}_6$ .



**Figure 5.3.** Identification of a)  $\text{PhSiH}_3$ , b)  $\text{Ph}_2\text{SiH}_2$ , c)  $\text{Ph}_3\text{SiH}$  by  $^1\text{H}$  NMR (300 MHz) of the crude mixture following thermolysis of poly(phenylsilane) (**4-1**) at  $500^\circ\text{C}$  in  $\text{CDCl}_3$ . The “x” may be  $\text{Ph}_4\text{Si}$ .

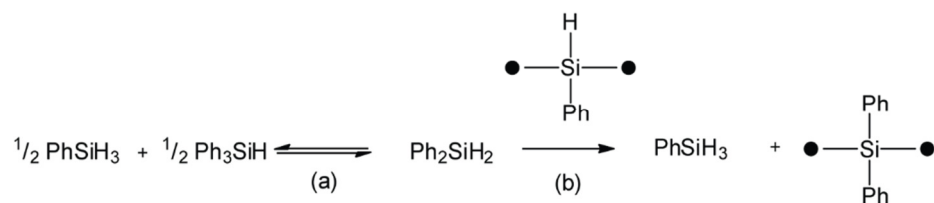
### Scheme 5.1.



These monosilanes eliminated during the thermolysis of poly(phenylsilane) (**4-1**) must have formed as a result of redistribution reactions. Redistribution is the intra- or intermolecular exchange of ligands, i.e. X and Y ligands on Si as shown in Scheme 5.1, and there is extensive literature describing both the catalytic<sup>161</sup> and thermal<sup>161a,162</sup> redistribution of di- and oligosilanes. All of the bonds in poly(phenylsilane), Si-Si, Si-Ph and Si-H, can undergo thermal and catalytic redistribution reactions.<sup>lxviii</sup> Free monosilanes likely also undergo redistribution with **4-1** or another monosilane. For example,  $\text{Ph}_2\text{SiH}_2$  can redistribute with another polysilane chain (Scheme 5.2b) to exchange an H or Ph substituent, or with another equivalent of  $\text{Ph}_2\text{SiH}_2$  (Scheme 5.2a) to give  $\text{PhSiH}_3$  and  $\text{Ph}_3\text{SiH}$ . These related redistribution reactions illustrate that a high degree of product complexity is possible for the thermal redistribution of **4-1**.

<sup>lxviii</sup> The relative redistribution reactivity for general silanes has been found to be  $\text{Cl} \approx \text{Br} \approx \text{OR} \approx \text{NR}_2 \approx \text{SR} > \text{H} \approx \text{silyl} > \text{Ph} \approx \text{alkyl}$ . For relevant reviews on redistribution at silicon and group 14 homologues, see the following literature references.<sup>13c,163</sup>

Scheme 5.2.



Another possible monosilane redistribution product,  $\text{SiH}_4$  was not detected. Silane gas ( $\text{SiH}_4$ ) may be anticipated if the redistribution reaction occurs with  $\text{PhSiH}_3$ . Only 90% mass was recovered following thermolysis and the remaining 10% mass initially was conceived to be  $\text{SiH}_4$ . However,  $\text{SiH}_4$  is extremely combustible, and its generation would have been immediately observed during the thermolysis or workup. The partial thermolysis experiment was safely scaled to 5 and 6 g of starting poly(phenylsilane) (**4-1**) without any combustible material forming.

Tetraphenylsilane,  $\text{Ph}_4\text{Si}$ , may have been identified by  $^1\text{H}$  NMR (“x” in Figure 5.3). No  $^{29}\text{Si}$  NMR signal for  $\text{Ph}_4\text{Si}$  using direct acquisition experiments was observed and the putative  $^1\text{H}$  NMR signal suggests it is in low concentration compared to other monosilanes. If  $\text{Ph}_4\text{Si}$  does form, subsequent redistribution of  $\text{Ph}_4\text{Si}$  with an equivalent of any Si-H-containing species in the mixture, e.g.  $\text{Ph}_2\text{SiH}_2$ ,  $\text{PhSiH}_3$ , or **4-1**, to give  $\text{Ph}_3\text{SiH}$  may be favored under these conditions.

#### 5.4 Identification of non-volatile partial thermolysis products

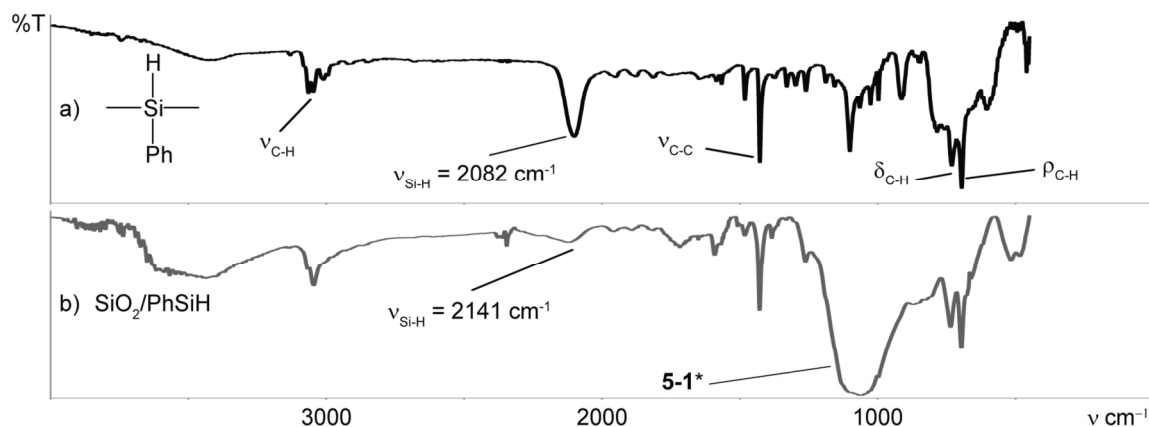
Two solid products, **5-1** and **5-2**, make up the remaining approximately 50% mass recovered from the partial thermolysis experiment. Benzene was added to the crude thermolysis mixture, which mostly dissolved except for a crystalline orange solid, **5-1**, which was then separated by filtration. As described below, ultimately this solid was

found to be a mixture of poly(phenylsilane) (**4-1**) and silica ( $\text{SiO}_2$ ). Benzene was removed from the filtrate by evacuation leaving a yellow oily residue. Hexanes was added to the oily mixture and a yellow solid (**5-2**) precipitated, the major product, which was collected by filtration. This intermediate thermolysis product is characterized later in this Section.

Solid product **5-1**, the mixture of **4-1** and silica, was isolated in low yield (2% of mass of **4-1** used in partial thermolysis experiment). A TGA trace of **5-1** (Figure 5.1) showed an S-curve with a high ceramic yield (88%, Table 5.1). Its IR spectrum showed similar absorptions to **4-1**, i.e.  $\nu_{\text{Si-H}}$ ,  $\nu_{\text{C-H}}$ ,  $\nu_{\text{C-C}}$ ,  $\delta_{\text{C-H}}$ , and  $\rho_{\text{C-H}}$ , due to residual poly(phenylsilane) (Figure 5.4). In addition, a broad absorption (900-1200  $\text{cm}^{-1}$ ) correlated well with literature IR spectra for silica.<sup>160b</sup> The ratio of poly(phenylsilane) to silica in **5-1** was quantified by elemental analysis. Experimental %C/%H values support a mixture of PhSiH and  $\text{SiO}_2$  (calculated %C/%H 41.75/3.50 for 47.5% PhSiH, 52.5%  $\text{SiO}_2$ , found: 41.81/3.61).

$\text{SiO}_2$  might have formed if there was some trace water in the thermolysis experiment. Water may have come from repeated washings of **4-1** with benzene during its synthesis and workup. Polymer **4-1** was washed with a large volume of benzene (180 mL per 5 g of polymer prepared and used for thermolysis experiment). Additional benzene (20 mL) was used to dissolve and transfer **4-1** to the reaction flask to ensure quantitative and straightforward transfer. Benzene was dried and distilled over sodium metal, however if a trace amount of water is present in the benzene solvent, using a high quantity of benzene could have led to more water being introduced to the polymer. The low quantity obtained (2% of mass of **4-1** used in partial thermolysis experiment) and a

lack of oxidation of the monosilanes indicates that oxidation of **4-1** by residual water or oxygen is relatively minor.

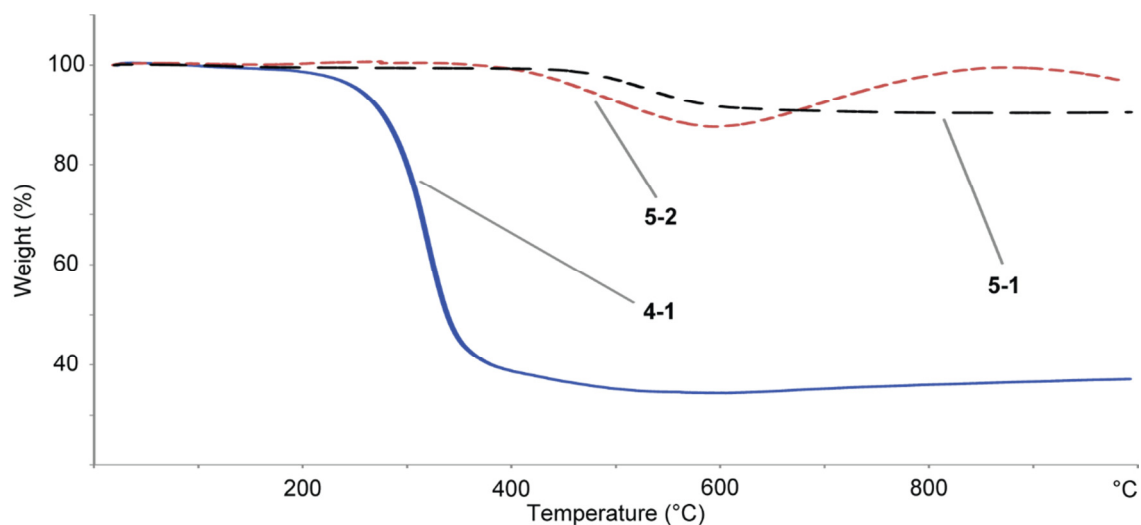


**Figure 5.4.** Infrared spectrum of a) poly(phenylsilane) (**4-1**) and b) (**5-1**) showing similar  $\nu_{\text{Si-H}}$ ,  $\nu_{\text{C-H}}$ ,  $\nu_{\text{C-C}}$ ,  $\delta_{\text{C-H}}$ , and  $\rho_{\text{C-H}}$  and the absorption **5-1\*** indicative of silica.

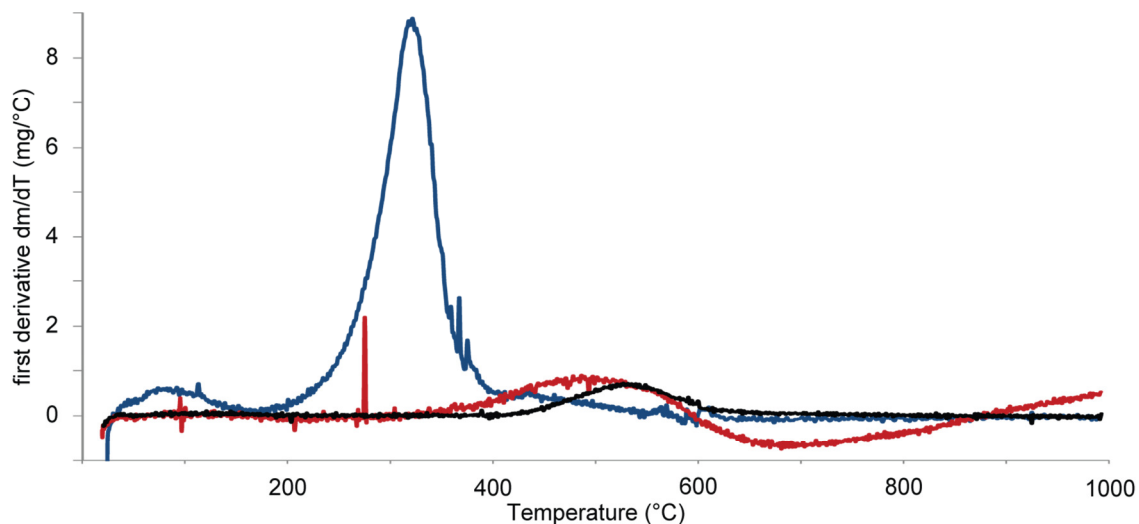
The major (44%) partial thermolysis product, **5-2**, was a bright yellow solid that was soluble in common solvents such as benzene, THF, diethyl ether, and dichloromethane. The solubility allowed for the characterization of **5-2** by multiple methods, including TGA, spectroscopy (IR, NMR, UV-vis) and GPC, which showed a partially thermolyzed material with some longer Si-Si chains compared to poly(phenylsilane) (**4-1**).

The TGA trace of **5-1** and **5-2** are shown in Figure 5.5 (with **4-1** taken from Figure 5.1 for comparison). Data for all compounds is collected in Table 5.1. The TGA trace of **5-2** has some similar features to its parent polymer (**4-1**): a minimum mass percentage at 600 °C (dashed red trace in Figure 5.1 and entry **5-2** in Table 5.1) and a relatively small mass increase from 600 to 1000 °C, which indicates partial oxidation to  $\text{SiO}_2$ . The inflection temperature and ceramic yield for **5-2**, 480 °C and 88% respectively, were higher than in **4-1**. This is because the TGA of **5-2** is the Section of the TGA trace

of **4-1** at greater than 500 °C.<sup>lxvi</sup> Above 500 °C, there is less remaining mass to lose, hence the higher ceramic yield. The inflection point is higher because it represents only the mass loss at greater than 500 °C, instead of the entire range of temperatures. The first derivative plot for the TGA of **4-1**, **5-1**, and **5-2** (Figure 5.6) showed that the inflection temperature for **5-2** (520 °C) does not correspond to a point of interest in the TGA of **4-1**, such as an inflection temperature or temperature at minimum mass.



**Figure 5.5.** TGA traces of **5-1** (---) and **5-2** (---) (**4-1**) taken from Figure 5.1). Samples were heated at 10 °C/min from RT (approximately 20 °C) to 1000 °C. The trace for **4-1** is included for comparison with **5-1** and **5-2**.



**Figure 5.6.** First derivative of the TGA traces of **4-1**, **5-1**, and **5-2**. Samples were heated at 10 °C/min from RT (approximately 20 °C) to 1000 °C.

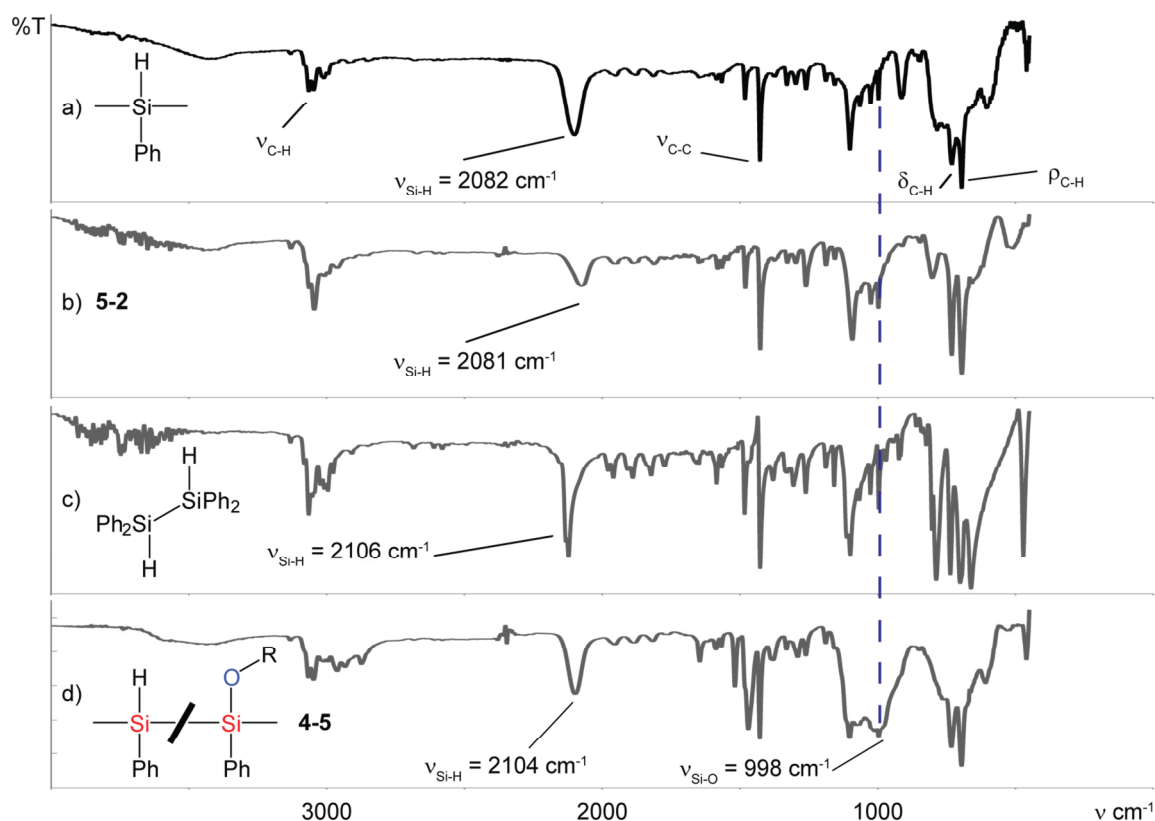
**Table 5.1.** Characteristic data points for the TGA traces of **4-1**, **5-1**, and **5-2**.

Sample	Inflection temperature ( $\pm 10$ °C)	Temperature at mass minimum ( $\pm 10$ °C) <sup>a</sup>	Ceramic Yield (%)
<b>4-1</b>	320	600	34% <sup>b</sup> , 37%
<b>5-1</b>	520	n/a	91%
<b>5-2</b>	480	600	88% <sup>a</sup> 97%

<sup>a</sup>A minimum mass that does not correspond to the ceramic yield is a common feature in TGA curves, but it is not observed in all TGA spectra. This is likely due to oxidation of remaining Si material to SiO<sub>2</sub> based on literature examples.<sup>144</sup> <sup>b</sup>At 600 °C.

Further insight into the structure of **5-2** comes from its IR spectrum. A decrease in  $\nu_{\text{Si-H}}$  intensity relative to  $\nu_{\text{C-H}}$  indicated a net loss of Si-H following thermolysis. Diagnostic IR absorptions for  $\nu_{\text{Si-H}}$ ,  $\nu_{\text{C-H}}$ ,  $\nu_{\text{C-C}}$ ,  $\delta_{\text{C-H}}$ , and  $\rho_{\text{C-H}}$  (Figure 5.7a/b) in both **4-1** and **5-2** suggest the presence of similar groups, Si-Ph and Si-H. A comparison to the spectrum of 1,1,2,2-tetraphenyldisilane ((Ph<sub>2</sub>SiH)<sub>2</sub>, **2-2**) (Figure 5.7c), shows that these diagnostic fingerprint absorptions are present in even the shortest possible Si-Si

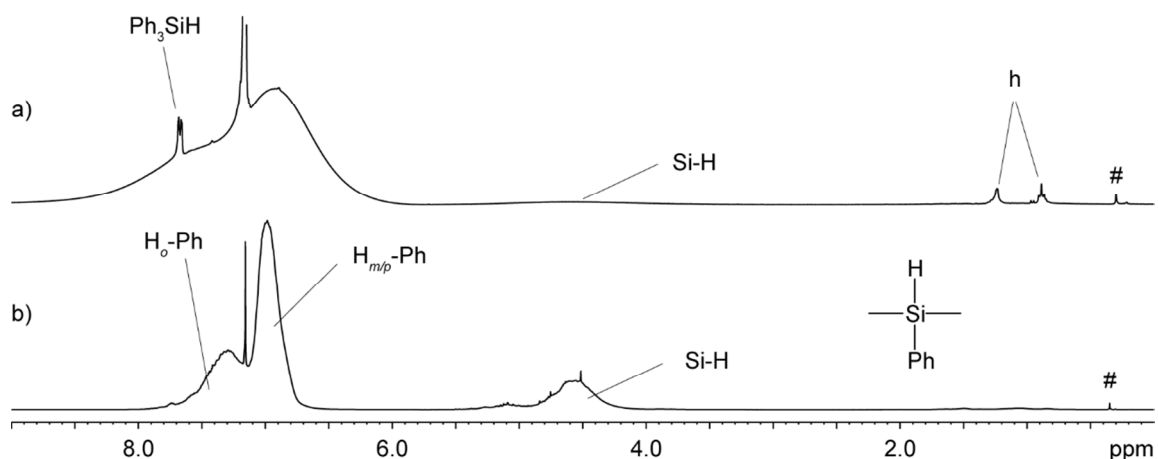
containing molecule and thus no significant changes in the extended Si-Si system could be detected by this method. The absence of Si-O linkages in **5-2** was confirmed when comparing its IR spectrum to **4-5** (Figure 5.7d), which had significant quantities of Si-O groups due to partial and over-reduction reactions (see Section 4.4.2); the broad, intense, and diagnostic Si-O absorption at  $\sim 1000\text{ cm}^{-1}$  is mostly absent in the IR spectrum of **5-2** (Figure 5.7b).



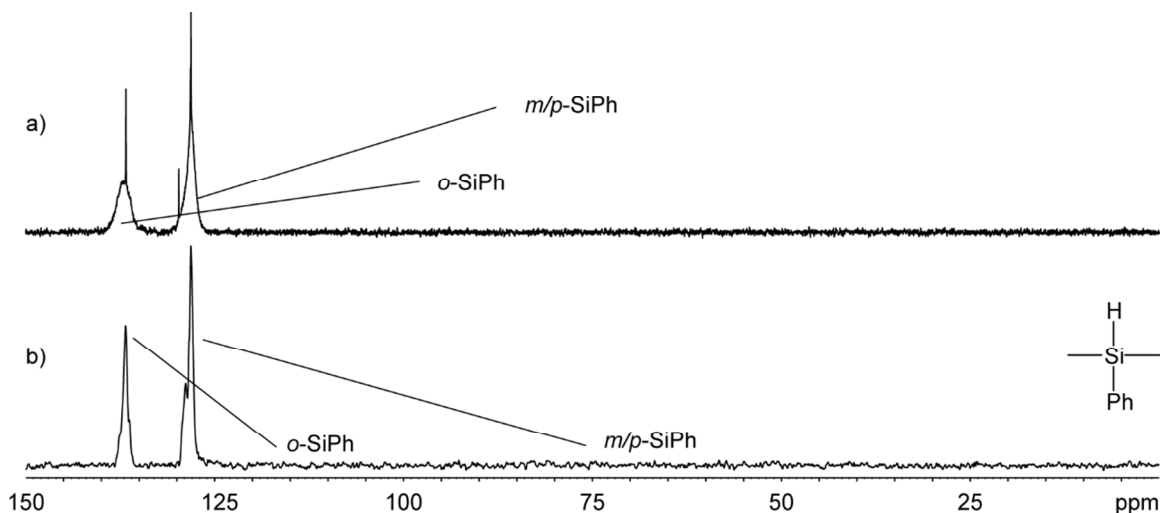
**Figure 5.7.** IR spectra of a) poly(phenylsilane) (**4-1**), b) **5-2**, c) disilane **2-2** and d) propionaldehyde-modified poly(phenylsilane) (**4-5**) demonstrating that Si-chain length in **5-2** cannot be probed by IR spectroscopy and that **5-2** lacks Si-O bonds.

The  $^1\text{H}$  and DEPT135  $^{13}\text{C}$  NMR spectra of **5-2** showed that **4-1** had undergone significant redistribution, yet retained an intact phenyl group. The  $^1\text{H}$  NMR of **5-2** showed a broad, weak Si-H peak(s) relative to the Si-Ph region (Figure 5.8a). More complex Si-Ph and Si-H environments were apparent based on broader Si-Ph and Si-H

signals in the  $^1\text{H}$  NMR spectrum for **5-2** compared to that for **4-1** (Figure 5.8b). This was partially evident in the DEPT135  $^{13}\text{C}$  NMR (Figure 5.9), which showed slightly-broader peaks associated with  $\text{C}_o\text{-SiPh}$  and  $\text{C}_{m/p}\text{-SiPh}$ . The relative intensities and chemical shifts for  $\text{C}_o\text{-SiPh}:\text{C}_{m/p}\text{-SiPh}$  are largely unchanged from a 2:3 ratio expected for a monosubstituted aryl group. If thermolysis had caused reactions of Si with a C-H in the phenyl group, e.g. to make a Si-1,4- $\text{C}_6\text{H}_4\text{-Si}$  linkage, this would be indicated by an increased ratio of  $\text{C}_o\text{-SiPh}:\text{C}_{m/p}\text{-SiPh}$  due to more C-H bonds being adjacent to the silyl group, and might have led to larger molecules via cross-linking.



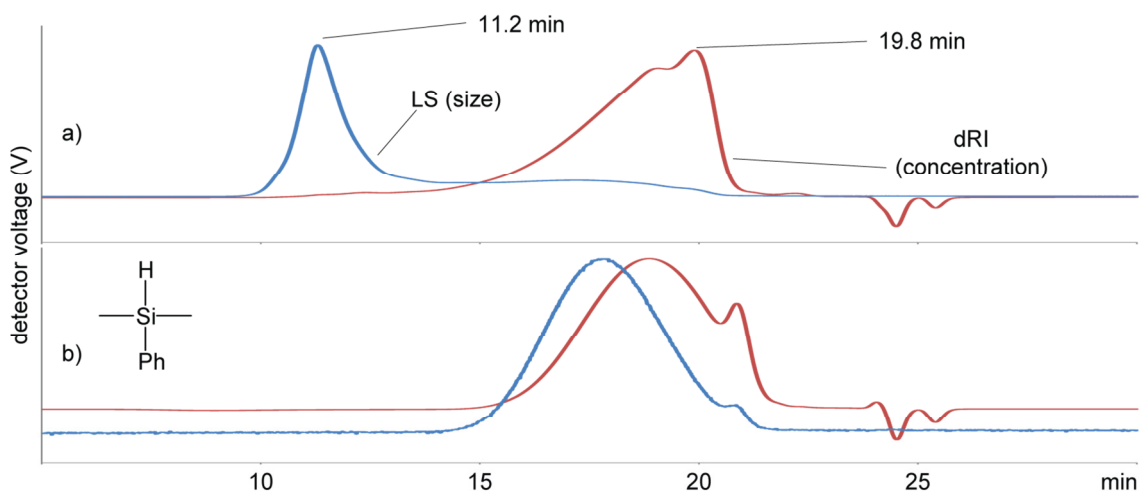
**Figure 5.8.**  $^1\text{H}$  NMR (300 MHz) of a) intermediate thermal decomposition poly(phenylsilane) (**5-2**) and b) poly(phenylsilane) (**4-1**) in  $\text{C}_6\text{D}_6$ . The “#” is grease and “h” is hexanes. The phenyl groups in  $\text{Ph}_3\text{SiH}$  are identified.



**Figure 5.9.** DEPT135 <sup>13</sup>C NMR (75 MHz) of a) intermediate thermal decomposition poly(phenylsilane) (**5-2**) and b) starting poly(phenylsilane) (**4-1**) in C<sub>6</sub>D<sub>6</sub> showing marginally broader peaks in **5-2**, but a retention of the ratio of *o*-SiPh:*m/p*-SiPh.

GPC analysis of **5-2** indicates that longer chains are present, however, the majority of the sample retains a similar chain length to the starting material poly(phenylsilane) (**4-1**). The light scattering trace for the GPC of **5-2** (Figure 5.10a, blue trace) shows a strong peak at an early elution time (11.2 min) suggesting high mass molecules. This elution coincides with a relatively weak dRI (differential refractive index) signal, which indicates a low concentration of the injected mass. Based on the refractive index detector response (dRI), the majority of the injected sample appeared at a longer elution time (19.8 min) with corresponding weak LS intensity suggesting short, low mass chains. The short-chain elution time approximately coincided with the peak maximum of parent poly(phenylsilane) (**4-1**) (18.6 min). The estimated molecular weight (MW) of **4-1** is similar to that of the short chains in **5-2** based on the differential refractive index peak elution times (dRI, red curves in Figure 5.10). These conclusions were supported by molecular weight estimates (Table 5.2) calculated from the GPC

data.<sup>lxix</sup> The polydispersity of **5-2** was very high (PDI = 6.1), confirming this is a mix of very long and relatively short chains. MW studies suggest that polymer **5-2** contains some unusual and interesting all-Si-containing chains in polymer **5-2**.



**Figure 5.10.** Representative GPC trace of a) **5-2** and b) **4-1** in  $\text{CHCl}_3$  (1 mL/min) showing the disparity in LS (size) and dRI (concentration) in **5-2** and the comparable elution times in the short-chains in **5-2** (18.6 min elution) to parent poly(phenylsilane) (**4-1**). The “dRI” is differential refractive index. The “LS” is light scattering taken at  $44.7^\circ$ .

<sup>lxix</sup> The LS/dRI traces in Figure 5.10a show that **5-2** has a bimodal (or polymodal) size distribution. The average MW description of the high and low MW regimes for **5-2a/b** (Table 5.2) does not accurately describe either region well. Regardless, the values show a high PDI as suggested by the GPC traces in Figure 5.10.

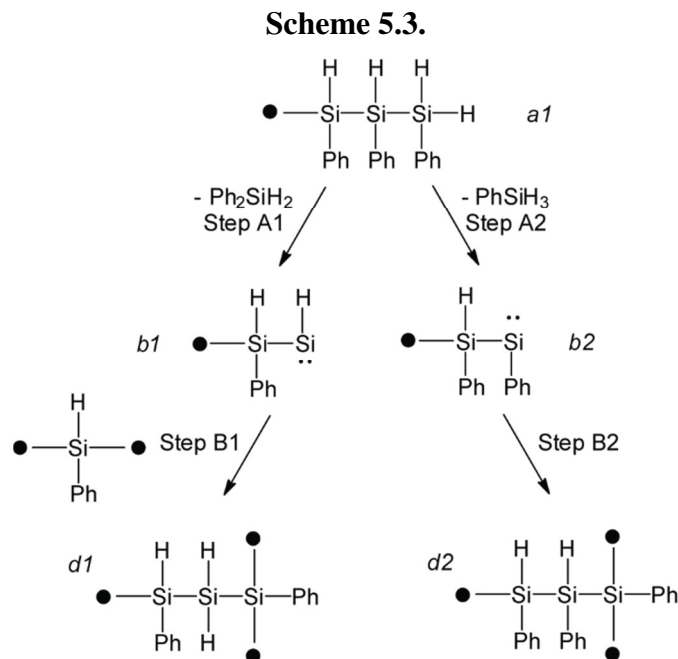
**Table 5.2.** Molecular weights determined from GPC in CHCl<sub>3</sub> (1 mL/min).<sup>lxix</sup>

#	dη/dc (mL/g) <sup>a</sup>	M <sub>N</sub> (kDa)	M <sub>W</sub> (kDa)	PDI
<b>4-1</b>	0.29	2.0 ± 0.2	3.3 ± 0.3	1.6
			↓	
<b>5-2a<sup>b</sup></b>	0.38	6.0 ± 0.1	37 ± 6	6.1
<b>5-2b<sup>b</sup></b>	0.35	5.7 ± 0.3	30 ± 1	5.3

<sup>a</sup>This dη/dc calculation assumes a constant differential refractive index over the entire elution period (8-20 min). This is true only if the endcaps of the polymer are the same throughout the distribution. The endcaps in **5-2** have not yet been identified, but they are assumed to be the same for the long and short chain fractions. <sup>b</sup>The partial thermolysis experiment was performed twice. GPC was done on both batches, giving **5-2a** and **5-2b**.

The results described above show two key steps during thermolysis of **4-1** to the thermolysis intermediate **5-2**: elimination of monosilane by-products and elongation of some all-Si chains. A possible reaction scheme for the redistribution of poly(phenylsilane) that could lead to the observed product mixture is proposed in Scheme 5.3. Volatile monosilane by-products must come from the formal reductive elimination of endcap (Steps A1/2). Elimination of monosilane endcaps is proposed because <sup>1</sup>H/<sup>13</sup>C signals consistent with shorter Si-chain, such as disilanes, trisilanes, or longer oligosilanes, were not found. Elimination of disilanes and longer oligosilanes might also occur, however, they must subsequently decompose to monosilanes or react with polymer to make elongated chains or branches. The new silylene endcap in the proposed intermediate *b1/2* undergoes a formal oxidative addition with Si-H (Step B2), which elongates the all-Si chain. The simple, straightforward sequence of events proposed in Scheme 5.3 is likely more complicated in the actual sample due to possible side-chain redistribution reactions, such as those shown in Scheme 5.2, and the inherent

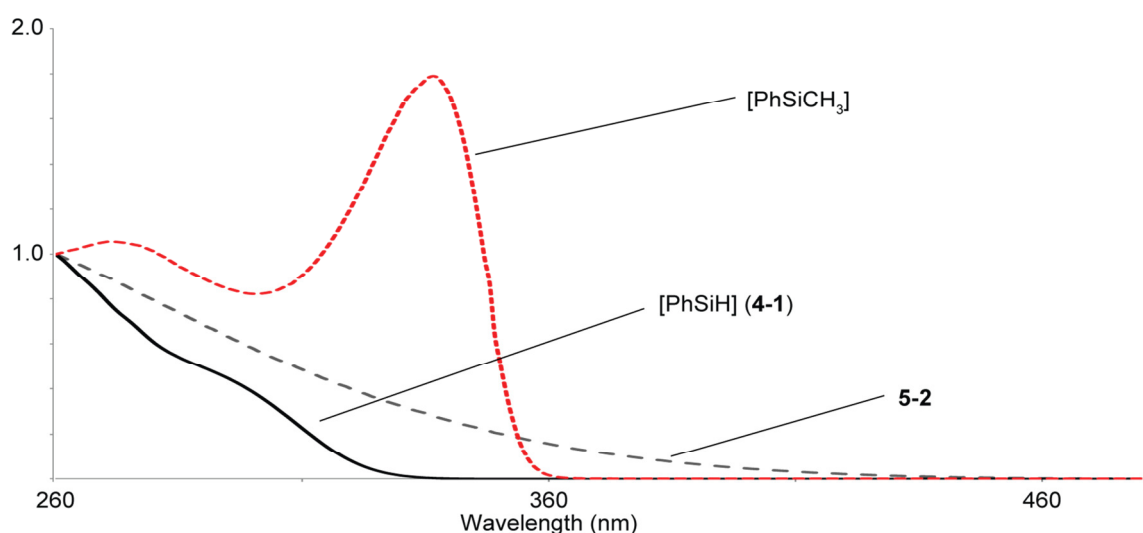
polydispersity of poly(phenylsilane), which contains polymers of many different Si-chain lengths.



Elongated all-Si chains could potentially be observed in the UV-vis absorption spectrum: longer Si-Si chains are expected to cause a red shift in the UV-vis absorption spectrum of **5-2**.<sup>107b,lxx</sup> The absorption spectrum of **5-2** (Figure 5.11) shows signal intensity over a wider range that includes much longer wavelengths than for **4-1** suggesting longer Si chains are present in **5-2**. Both **4-1** and **5-2** lack an intense  $\lambda_{\max}$  feature and have similar overall shapes. The role of residual Si-H compared to a Si-CH<sub>3</sub> group in determining chain conformation, and hence the UV-vis absorption spectrum was previously discussed in detail in Chapter 4. In brief, the methyl group leads to longer Si chains in an *anti* conformation and a distinct  $\lambda_{\max}$  feature. The Si-H group allows for the Si chain to adopt *gauche* conformations more easily and on average shortens the length of

<sup>lxx</sup> Molar extinction coefficients and  $\lambda_{\max}$  increase with Si-chain length, however this is proposed to reach a maximum at 40-50 repeat Si units.<sup>14a,107b</sup>

the Si chromophore leading to a blue shift and decreased intensity of the  $\lambda_{\max}$  feature. The lack of a  $\lambda_{\max}$  in the absorption spectrum of **5-2** (Figure 5.11) indicates two possibilities: the long Si chains are low in concentration, which is supported by  $M_N/M_W$  values and GPC analysis, and do not give an obvious increase in intensity at the red end of the spectrum; or Si-H groups persist even in the newly formed the long chains, which leads to a decrease in the length of the Si chromophore in the *anti* conformation.

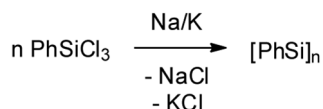


**Figure 5.11.** UV-vis absorption spectrum of a) — **4-1**, b) - - **5-2**, and c) ...  $[\text{PhSiCH}_3]_n$  (**4-14**) in  $\text{CH}_2\text{Cl}_2$  normalized at 260 nm.

Currently a structural formula for **5-2** has not yet been proposed, but based on the above data and redistribution possibilities the following structural components must be considered: endcap units  $-\text{SiH}_3$ ,  $-\text{SiH}_2\text{Ph}$ ,  $-\text{SiHPh}_2$ , and  $-\text{SiPh}_3$ , and repeat units  $-\text{SiH}_2-$ ,  $-\text{PhSiH}-$ ,  $-\text{SiPh}_2-$ ,  $-\text{PhSi}[\text{Si}]-$ ,  $-\text{[Si]SiH}-$ , and  $-\text{[Si]Si[Si]}-$ , where  $[\text{Si}]$  is an extended polysilane chain that may be linear or branched. If there are many branching repeat units, such as  $-\text{PhSi}[\text{Si}]-$ , in **5-2**, its identity may be a polysilyne. Polysilynes have been prepared in the literature using Wurtz coupling (Scheme 5.4) and characterized extensively by NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$ ), IR, and UV-vis absorption spectroscopy.<sup>164</sup> The

reported synthesis of poly(phenylsilylene) shows  $^1\text{H}$  NMR and IR spectra that are comparable to the spectra shown in Figure 5.8a and Figure 5.7b, respectively, for **5-2**.<sup>164b,c,g</sup> Furthermore, UV-vis absorption spectra of reported polysilylenes have a similar shape to that shown in Figure 5.11b, in particular a characteristic decaying broad shoulder from 200 to 400 nm.<sup>164a,k,l</sup> Likewise, continued heating of polysilylenes up to 1000 °C gives SiC.<sup>164b,c,e</sup>  $^{29}\text{Si}$  NMR spectra of polysilylenes reported in the literature have a broad signal at -50 to -60 ppm.<sup>164c,k,l</sup>  $^{29}\text{Si}$  NMR experiments (HMBC, DEPT, direct acquisition) were attempted on **5-2** to probe the silicon-chain environment, but no  $^{29}\text{Si}$  signals were detected. This result suggests that  $^{29}\text{Si}$  peaks may be too broad to observe and it is an ongoing challenge to characterize the Si environments in **5-2**.

#### Scheme 5.4



## 5.5 Summary

The initial goal of making titanium disilicide by thermal decomposition of a sol-gel mixture of poly(phenylsilane) and titanium dihydride ( $\text{TiH}_2$ ) was not achieved. Instead, TGA, IR, and EA indicated that SiC, C, and trace  $\text{SiO}_2$  formed from the thermal decomposition of poly(phenylsilane), which precluded the formation of Ti:Si material from this process.

The thermal degradation process was investigated in greater detail and a partial thermolysis experiment was conceived to identify volatile and non-volatile products resulting from heating to 500 °C. This experiment identified formation of monosilanes as volatile by-products.  $\text{PhSiH}_3$ ,  $\text{Ph}_2\text{SiH}_2$ , and  $\text{Ph}_3\text{SiH}$  were observed as the major volatiles

generated during thermal decomposition. Partial thermolysis afforded two other products: an insoluble mixture (**5-1**) of poly(phenylsilane) and SiO<sub>2</sub>, the latter forming in low conversion from the thermal hydrolysis; and a polydisperse silane polymer (**5-2**). The remaining silane polymer was analyzed in depth by <sup>1</sup>H/<sup>13</sup>C NMR, IR, elemental analysis, GPC, and UV-vis absorption spectroscopy. These methods collectively showed evidence for the thermal redistribution of Si-H, Si-Ph, and Si-Si bonds. The identity of **5-2** may be a polysilyne, however, further research is required to confirm its presence and ultimately propose a structure.

## 5.6 Impact and future work

Systematic control of the partial thermolysis of poly(phenylsilane) is desired in order to standardize the thermolysis experiment. Controlled partial thermolysis by the described method was problematic due to the experimental setup. While a temperature of 500 °C was reached, this was crudely approximated with a thermocouple placed between the heating mantle and the flask.<sup>lxxi</sup> Mixing was not possible during the experiment so a lack of homogeneity during thermolysis was expected. It was difficult to control the rate of temperature increase, particularly at high temperature. The following steps could be taken to standardize the partial thermolysis experiment: uniform temperature around the reaction flask as it is heated up to 500 °C, digital control of the rate of temperature increase, and mechanical mixing or stirring of the contents. Such an apparatus is not currently commercially available, but may be constructed from a vacuum oven properly

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<sup>lxxi</sup> The temperature likely does not have to reach 500 °C in order to initiate redistribution. TGA studies (Section 5.2, Figure 5.1) show that the onset temperature is around 300 °C. If the temperature is held at 320 °C (inflection point), this should be sufficient thermal energy for redistribution to give **5-2**.

adapted with a mechanical stirrer. These conditions would ensure uniformity and reproducibility in the experiment and would allow accurate quantification of the individual monosilane products, which was roughly estimated thus far. Relative abundances of  $\text{Ph}_3\text{SiH}$ ,  $\text{Ph}_2\text{SiH}_2$ , and  $\text{PhSiH}_3$  at a given temperature setting could be determined if temperature, time, and homogeneity were adequately controlled. A calculation for the proportion of phenyl versus hydrido groups in the monosilane mixture versus the starting poly(phenylsilane) (**4-1**, 50:50) would then inform the proportion of phenyl/hydrido groups that remain in polymer **5-2** based on a simple mass balance calculation.

Confirmation of the branching repeat units in **5-2** could be assessed by  $^{29}\text{Si}$  NMR. A branched poly(phenylsilane) has been recently reported and its structure was confirmed by  $^1\text{H}$ - $^{29}\text{Si}$  HMBC NMR.<sup>165</sup>  $^{29}\text{Si}$  NMR experiments have not yet identified any signals in samples of **5-2**, despite trying HMBC, DEPT, and direct acquisition methods. A possible solution is the  $^{29}\text{Si}$ - $^{29}\text{Si}$  INADEQUATE experiment, which exploits the  $^{29}\text{Si}$ - $^{29}\text{Si}$  one-bond coupling.<sup>166</sup> However, this experiment requires making a version of **5-2** that is doped with  $^{29}\text{Si}$  (approximately 50% required<sup>166</sup>), which would be extremely costly. If the short and long chains in **5-2** can be separated, a more concentrated sample of the long chains in **5-2** can be prepared and may be suitable for  $^{29}\text{Si}$  NMR experiments.

The identity of **5-2** deserves further investigation because it might be the polysilyne. In order to further evaluate **5-2**, the short chains must be removed by polymer precipitation.<sup>lxxii</sup> This would provide material that is more suitable for EA, GPC, and  $^{29}\text{Si}$  NMR because in the data presented here (Figure 5.12a), the short chains overwhelm the

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<sup>lxxii</sup> The low molecular weight fractions in **5-2** should be removed and this might be possible by precipitation in methanol, which is a standard method of purifying polymers.

signal from **5-2**. Matching diagnostic data of the precipitated polymer from **5-2** to reported poly(phenylsilyne)<sup>164b,c,k,l</sup> would support the identification of polysilyne as the partial thermolysis product **5-2**.

This putative method for synthesizing polysilynes impacts their usage. Polysilynes absorb strongly in the UV region; unlike polysilanes, they are much more resistant to photolytic decomposition.<sup>164l</sup> The straightforward preparation of poly(phenylsilane) and the suspected poly(phenylsilyne) described in Chapter 4 and this chapter, respectively, can likely be done on a large scale. The fact that longer chains in **5-2** are soluble suggests that thin films can be made from solution casting methods and they would be superior to those made from parent polysilane **4-1**. Short chain polysilanes make poor films, giving crystals or weak conglomerates.<sup>167</sup> This avenue for identifying the structure of **5-2**, by polymer precipitation and then characterization, should be evaluated in order to determine the impact of this material.

## **5.7 Experimental**

### **5.7.1 General**

General details listed in Section 2.6.1, 3.12.1, and 4.9.1 are valid in this section unless otherwise noted. X-ray diffraction (XRD) patterns with a resolution of 0.05° (2 $\theta$ ) and a scan speed of 1 °/min, were collected using a Rigaku Miniflex diffractometer with a Cr source (K $\alpha$  radiation,  $\lambda = 2.2890 \text{ \AA}$ ) operating at 30 kV and 15 mA.

### **5.7.2 Thermolysis of poly(phenylsilane) (4-1)**

A solution of poly(phenylsilane) (**4-1**) in benzene (approximately 1 g in 1 mL) was added to a pre-weighed “bomb” flask. Volatiles were removed by heating the flask to 125 °C under dynamic vacuum for 30 minutes. The residual material was a high-

viscosity, cloudy oil. The flask and its contents were weighed again. This process was repeated two more times until a constant weight was obtained (1.05 g of **4-1**) and then the flask was closed under static vacuum. The sealed flask was heated to 50 °C. The temperature was increased progressively in 50 °C increments over 2 h 15 min (50 °C every 15 min) until the temperature reached 500 °C. The temperature was held at 500 ± 5 °C. After 30 minutes, the heat was turned off and the flask was allowed to cool to RT to give a dark brown/red viscous, cloudy mixture. Three freeze-pump-thaw cycles were applied and the flask was weighed (recovered 0.84 g, 90% recovery). An aliquot was removed for  $^1\text{H}/^{29}\text{Si}$  NMR (Figure 5.3). Benzene (10 mL) was added to give a clear, yellow solution with an orange precipitate. The solution was filtered under vacuum to collect an orange precipitate and a clear, yellow filtrate. The orange precipitate was washed with hexanes (10 x 5 mL). Volatiles were removed under dynamic vacuum at 50 °C for 1 h. An orange, crystalline solid was isolated (**5-1**, 0.021 g, 3% of recovery of crude material, 2% of starting poly(phenylsilane) (**4-1**)).<sup>lxxiii</sup> The clear, yellow filtrate was treated separately. Volatiles were removed under vacuum to give a yellow, oily mixture. Hexanes (5 mL) was added. The mixture turned cloudy yellow and an orange precipitate formed. The top yellow layer was decanted and then filtered under vacuum to collect a yellow powdery solid and a clear and colorless filtrate. The yellow solid was washed with hexanes (10 x 5 mL). The solid was collected and volatiles were removed under dynamic vacuum at 50 °C for 1 h. A yellow powdery solid was isolated (**5-2**, 0.37 g, 44% recovery of crude material, 42% of starting poly(phenylsilane) (**4-1**)).

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<sup>lxxiii</sup> **5-1** did not dissolve in common solvents, dichloromethane, chloroform, benzene, toluene, diethyl ether, THF, hexanes, or pentane.

### 5.7.3 Pyrolysis of poly(phenylsilane) (4-1)

Poly(phenylsilane) (**4-1**, ~1 g) was dissolved in toluene and then added to a quartz boat. The quartz boat was placed in a furnace tube. The tube was evacuated and heated to 55-70 °C for 30 min, then cooled to RT and refilled with argon. This process was repeated four times. The tube was evacuated and then refilled with argon/hydrogen gas (argon with 5% H<sub>2</sub>). The temperature was then increased by 5 °C/min up to 800 °C and then held for 14 h. The tube was then cooled to RT and a shiny flakey black material was obtained. An XRD spectrum showed no peaks indicating there was no crystalline material present.

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