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Scope and selectivity of $B(C_6F_5)_3$-catalyzed reactions of the disilane $(Ph_2SiH)_2$

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ABSTRACT

The diverse catalytic activity of the electrophilic borane $B(C_6F_5)_3$ in reactions of silanes with organic substrates has been exploited extensively in studies that mostly focus on very particular, useful functional group transformations in organic synthesis. This study examines the potential for harnessing the collective, broad scope of these transformations in the preparation of new oligosilane derivatives. Borane-catalyzed hydrosilation, heterodehydrogenative coupling, and dealkylative coupling reactions of a wide range of substrates with the disilane $(Ph_2SiH)_2$ were investigated. These allowed new mono- and disubstituted disilanes to be prepared that contain Si–O, Si–S, and Si–C linkages. Challenges and opportunities are described that arise from competing "over-reduction" chemistry, and the sensitivity of the catalysis to both the Lewis basicity and steric bulk of the substrates is examined.

1. Introduction

The vast majority of short-chain oligosilanes contain simple Si–Me or Si–Ar groups, and it can be challenging to introduce more varied or functional sidechains [1]. An appealing route to more structurally diverse oligosilanes involves modifying Si–H bonds in the all-silicon chains that result from metal-catalyzed dehydrocoupling of primary or secondary silanes [2]. However, as we have previously described [3], the Si–Si bonds in these catenates are susceptible to cleavage under "traditional" Si–H activation conditions, for example in the presence of transition metal catalysts, radical initiators, oxidative halogenating reagents, or strong base. We showed, for a limited number of O- and S-donor substrates, that the Lewis acid $B(C_6F_5)_3$ catalyzes Si–H activation reactions of the *sym*-dihydridodisilanes $(Ph_2SiH)_2$ and $(Me_2SiH)_2$ with absolute chemoselectivity, leaving the Si–Si bonds intact [3].

The chemistry of silanes mediated by $B(C_6F_5)_3$ is huge and growing [4]. Scheme 1 summarizes the wide variety of borane-catalyzed reactions of monosilanes that has been reported in the literature [5,6]. Of these, we exploited a) hydrosilation (of benzaldehyde, *p*-nitrobenzaldehyde, and thiobenzophenone) and b) heterodehydrocoupling (of catechol and aromatic and alkyl thiols) in our previous work, but we did not explore the utility of c) dealkylative coupling (primarily demethanative coupling). Here we report a wider survey of the scope of all three of these borane-catalyzed reactions of the disilane $(Ph_2SiH)_2$, which provides general insight into the use of this catalyst in the synthesis of structurally complex oligosilane materials. This work provides models for the potential post-polymerization modification of polysilanes containing Si–H bonds in the repeat unit [7]. Issues of selectivity for the degree of substitution at this disilane substrate also point to new strategies for the construction of unsymmetrically derivatized short-chain oligomers.

2. Results and discussion

2.1. New mono- and disilanes

We screened new substrates for the derivatization of $(Ph_2SiH)_2$ by first examining their reactivity with the monosilane Ph_2MeSiH, in which the Si–H bond should experience a similar steric and electronic environment to that in the disilane. The new monosilane derivatives we prepared are shown in Table 1. Products **1**–**8** are all colorless oils, which were characterized by ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR. The reactions proceed cleanly, except for the hydrosilation of propionaldehyde, for which competing "over-reduction" chemistry is observed: borane catalyzes the reaction of the hydrosilation product $Ph_2MeSiOPr^n$ (**1**) and a second equivalent of Ph_2MeSiH to give $(Ph_2MeSi)_2O$, presumably with loss of propane. This reaction is actually a subset of the dealkylative coupling illustrated in Scheme

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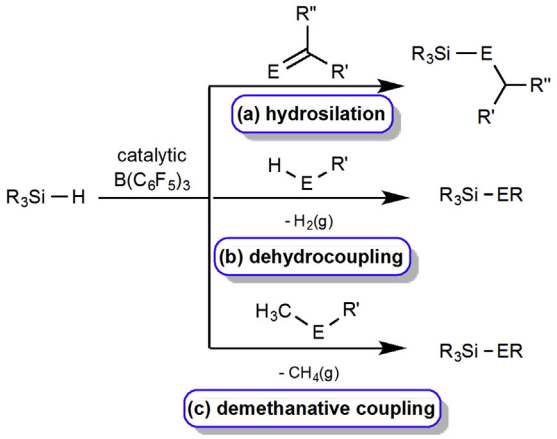


Scheme 1. Three general reactions of silanes catalyzed by $B(C_6F_5)_3$.

1c, and has been reported for other hydrosilation and dehydrocoupling reactions that install linear alkoxy sidechains at silicon [8]. We do not observe comparable over-reduction of 2-chloroethyl methyl ether in the synthesis of **6**, which we attribute to the much shorter reaction time required for this less Lewis basic substrate to react (*vide infra*).

Unlike the heteroatom-containing substrates, the reaction of 1-hexene to generate $Ph_2MeSiCH_2(CH_2)_4CH_3$ (**8**) required both an excess of substrate and a switch from toluene or benzene to the more polar solvent dichloromethane. We suspect that the reaction is sluggish due to poorer nucleophilicity of the C=C bond for the proposed silylium intermediate (*vide infra*), and that a polar solvent facilitates transient polarization of the double bond during this critical Si–C bond-forming step [9,10].

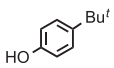
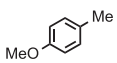
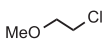
Tables 2 and 3 show the mono- and disubstituted disilanes we were able to prepare from the reactions of $(Ph_2SiH)_2$ with substrates from Table 1. We have also included products of thiol dehydrocoupling reactions that we previously reported [3b,7], for comparison of the requisite conditions. The products shown in Table 2 are colorless oils; those in Table 3 include both oils and solids as indicated. Competing over-reduction of propionaldehyde in reactions of $(Ph_2SiH)_2$ with this substrate led to complex mixtures from which we were unable to isolate discrete disilanes, so we have not included those reactions here. Surprisingly, the reaction of 2-chloroethyl methyl ether with $(Ph_2SiH)_2$ to give compound **18** (Table 3) proceeds cleanly, with no evidence for this over-reduction chemistry, despite being slower than the corresponding reaction with Ph_2MeSiH (*vide supra*). As discussed below, a monosubstituted complex could not be isolated via the hydrosilation of 1-hexene, disubstituted complexes could not be isolated for the hydrosilation reactions of acetone or cyclohexanone, and the disilane did not react at all with N-benzylideneaniline.

2.2. Issues affecting the generality of this route to functionalized disilanes

Our extension of the simple reactions of Ph_2MeSiH shown in Table 1 to the derivatization of $(Ph_2SiH)_2$ (Tables 2 and 3) highlights two issues that can affect strategies for this route to functionalized oligosilanes, in addition to the possibility of competing over-reduction reactions such as we described above [11]. First, the relative Lewis basicity of the substrate can have a large impact on the conversions obtained (or conditions required), due to potential catalyst inhibition. We [3] and others [8d,12b] have discussed the delicate balance of substrate basicity (its binding affinity for the borane) and nucleophilicity (its ability to attack the silylium-like intermediate generated through an η^1-silane-borane adduct, *vide infra*) in determining the activity of this borane catalyst in the reactions of silanes, and these studies provide new illustrations of this. Second, for silanes such as $(Ph_2SiH)_2$, which have more than one reactive Si–H bond, the selectivity for the degree of substitution (e.g. mono-vs disubstituted) is very sensitive to the steric bulk of the substrate. Below, we discuss both these issues in the context of the generally-accepted mechanism for $B(C_6F_5)_3$-catalyzed Si–H activation, which is shown in Scheme 2 for a carbonyl hydrosilation reaction [12].

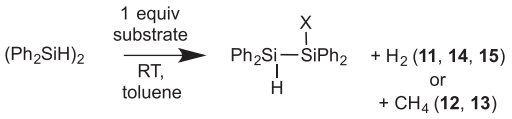
In **step a** of Scheme 2, the reversible formation of an η^1-silane-borane complex (**A**), gives the silicon strong "silylium" character and renders it highly susceptible to nucleophilic attack (**step b**). In

Table 1
New $B(C_6F_5)_3$-catalyzed reactions of Ph_2MeSiH (see Scheme 1 for reaction types).[a]

Substrate	Ph_2MeSiX X=	[Borane]/[Si–H]	Time (h)	Isolated yield (%)
	$O(CH_2)_2CH_3$ (**1**)	0.04	16	[b]
	$OCH(CH_3)_2$ (**2**)	0.04	12	73
	OC_6H_{11} (**3**)	0.05	16	[c]
	OC_6H_4-*p*-Bu^t (**4**)	0.05	1	99
	OC_6H_4-*p*-Me (**5**)	0.04	1	99
	$O(CH_2)_2Cl$ (**6**)	0.03	2	83
	$N(Ph)CH_2Ph$ (**7**)[d]	0.04	16	97
	$CH_2(CH_2)_4CH_3$ (**8**)[e]	0.04	16	74

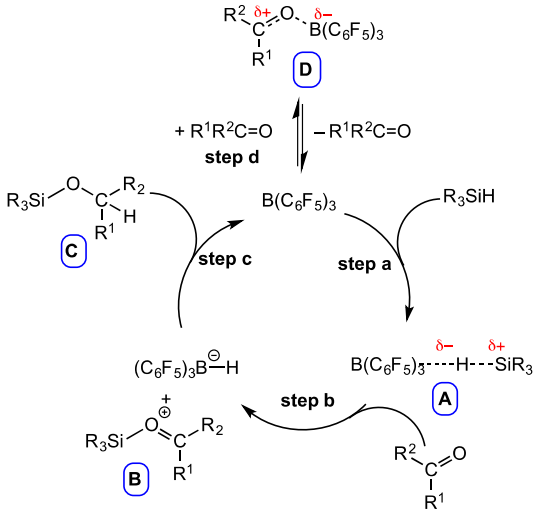
[a] Reactions carried out at RT in toluene, unless otherwise noted.
[b] Quantitative conversion (with respect to silane) to a 76:24 mixture of **1** and the over-reduction product $(Ph_2MeSi)_2O$.
[c] Obtained as an 86:14 mixture of **3** and unreacted Ph_2MeSiH.
[d] Reaction carried out in benzene.
[e] Reaction carried out in dichloromethane using a four-fold excess of 1-hexene.

Table 2
Monosubstituted disilanes prepared by $B(C_6F_5)_3$-catalyzed reactions of $(Ph_2SiH)_2$.



X=	[Borane]/[SiH]$_{total}$	Time (h)	Isolated yield (%)
$OCH(CH_3)_2$ (**9**)	0.05	16	86[a]
OC_6H_{11} (**10**)[b]	0.07	5	67
OC_6H_4-*p*-Bu^t (**11**)	0.05	16	[c]
OC_6H_4-*p*-Me (**12**)	0.05	16	99
$O(CH_2)_2Cl$ (**13**)[d]	0.07	144	[e]
$S(CH_2)_2CH_3$ (**14**)[f]	0.05	16	98
SC_6H_4-*p*-Me (**15**)[g]	0.02	1	90

[a] Product contained impurity (<10%) tentatively identified as disubstituted product $(Ph_2SiOCH(CH_3)_2)_2$.
[b] T = 55 °C, six-fold excess of substrate used.
[c] Isolated as a 26:67:7 mixture of unreacted $(Ph_2SiH)_2$, monosubstituted disilane **11**, and disubstituted disilane **16**, as determined by ^{1}H NMR.
[d] Reaction carried out in d_6-benzene.
[e] Isolated as a 15:75:10 mixture of unreacted $(Ph_2SiH)_2$, monosubstituted disilane **13**, and disubstituted disilane **18**, as determined by ^{1}H NMR.
[f] Ref. [7].
[g] Ref. [3b].



Scheme 2. Generally-accepted mechanism for hydrosilation of carbonyl groups catalyzed by $B(C_6F_5)_3$.

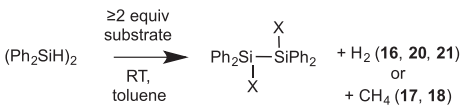
this case the nucleophile is the O of a generic carbonyl-containing substrate and the net reaction is an addition; other unsaturated substrates such as imines [13] and thioketones [3a] behave similarly. However this mechanism can be considered general also for other nucleophiles including alcohols [14] and silanols [15], methyl- and other linear alkyl ethers [8a,b], and silyl ethers (or alkoxysilanes) R'OSiR$_3$ [8d]. These reactions all involve the loss of either H_2 or alkane, RH, from the intermediate ion pair **B**, in addition to the silicon-containing product (**step c**).

2.2.1. Catalyst inhibition

The mechanism shown in Scheme 2 shows that the formation of traditional Lewis adducts can occur (off-cycle **step d**) in these borane-catalyzed reactions, but they generally provide a slower pathway than η^1-silane adduct formation (**step a**) and are not involved in productive catalysis [12d]. If this equilibrium lies sufficiently towards **D**, catalyst inhibition will occur, since the concentration of free borane available to activate the Si–H bond is significantly reduced. For example, primary alcohol substrates typically bind sufficiently strongly to the borane to inhibit catalytic dehydrogenative coupling with silanes [14,3b,16]. In this work, though, the borane catalyst exhibits relatively high activity for demethanative coupling of the methyl ether derivative of a primary alcohol, 2-chloroethyl methyl ether, with Ph_2MeSiH (Table 1, compound **6**) and $(Ph_2SiH)_2$ (Table 3, compound **18**). We attribute this activity to the lower Lewis basicity of the primary ROMe fragment, relative to primary ROH. The catalyst does not show such a pronounced difference in activities for the coupling reactions of aryl methyl ether $MeOC_6H_4$-*p*-Me and the phenol HOC_6H_4-*p*-Bu^t, although both O-donor substrates react more slowly, at higher catalyst loadings, than the softer S-donor thiocresol (e.g. compare entries in Table 2 for compounds **11** and **12** versus compound **15**) [17].

Catalyst inhibition was most pronounced for N-benzylideneaniline, which did not react at all with $(Ph_2SiH)_2$, even when mixtures were refluxed in toluene for up to 3 d [18]. This is consistent with the strong binding affinity of $B(C_6F_5)_3$ for this imine substrate reported by Piers et al.; they found that high temperatures, long reaction times, and/or relatively unhindered silanes were required to give hydrosilation products [13a]. Presumably nucleophilic attack of a bulky aryl imine at whatever small amount of activated silane forms under these conditions is greatly accelerated for less hindered silanes (*vide infra*) [19]. Thus the absence of catalytic activity for hydrosilation of N-benzylideneaniline by $(Ph_2SiH)_2$ not only highlights the issue of catalyst inhibition, but also indicates the

Table 3
Disubstituted disilanes prepared by $B(C_6F_5)_3$-catalyzed reactions of $(Ph_2SiH)_2$.



X=	[Borane]/[SiH]$_{total}$	Time	Product	Isolated yield (%)
OC_6H_4-*p*-Bu^t (**16**)[a]	0.10	16 h	white solid	21
OC_6H_4-*p*-Me (**17**)[a]	0.08	29 d	cloudy oil	[b]
$O(CH_2)_2Cl$ (**18**)	0.05	16 h	white solid	65
$CH_2(CH_2)_4CH_3$ (**19**)[c]	0.06	72 h	colorless oil	87
$S(CH_2)_2CH_3$ (**20**)[d]	0.04	144 h	colorless oil	[e]
SC_6H_4-*p*-Me (**21**)[d]	0.03	72 h	white solid	94

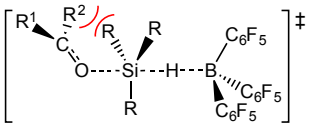
[a] T = 70 °C.
[b] Isolated as a 65:35 mixture of the monosubstituted disilane **12** and the disubstituted disilane **17**.
[c] Reaction carried out in a ten-fold excess of 1-hexene diluted with 10% dichloromethane (by volume).
[d] Ref. [3b].
[e] Four equivalents of *n*-propane thiol gave 1:1 mixture of monosubstituted disilane **14** and disubstituted disilane **20**.

higher steric hindrance associated with the Si–H bonds in $(Ph_2SiH)_2$ relative to our model monosilane Ph_2MeSiH, since hydrosilation of the same imine by the latter does occur at room temperature in the presence of the borane catalyst (Table 1, compound **7**).

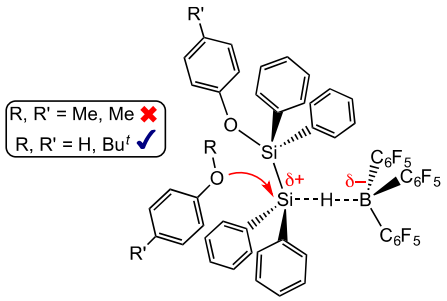
2.2.2. Steric bulk at the disilane and the substrate

The selectivity of these borane-catalyzed reactions of $(Ph_2SiH)_2$ for mono- or disubstituted products is sensitive to the bulk of the organic substrate. For example, substrates that give new Si-substituents that are branched beta to silicon (e.g. ketone, phenol, methyl phenyl ether, and thiophenol) favour formation of the monosubstituted disilane (compounds **9**–**12**, **15** in Table 2), and it is challenging to obtain the disubstituted product in these cases. Of these substrates, disubstituted compounds derived from acetone and cyclohexanone could not be prepared even with increased catalyst loadings and temperature, but those containing the (effectively branched but arguably less bulky) aryl substituents ($-OC_6H_4$-*p*-Bu^t (**16**) and $-SC_6H_4$-*p*-Me (**21**), Table 3) were accessible. These results can be rationalized in terms of the relative rates of nucleophilic attack of the substrate at the silylium centre (**step b** in the catalytic cycle in Scheme 2). Scheme 3 shows the proposed transition state structure for a carbonyl nucleophile, in which the incoming O-donor is *trans*-to the departing hydride at silicon [12b-d,13b]. The Scheme illustrates how the rate of this step will be sensitive to steric bulk of both the substituents at silicon *and* the nucleophile. For the relatively bulky $(Ph_2SiH)_2$ this nucleophilic attack is likely to be rate-determining even for the first substitution leading to monosubstituted product. Once a new substituent is installed at one of the two silicons in $(Ph_2SiH)_2$, 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 the methyl phenyl ether substrate, $CH_3OC_6H_4$-*p*-Me, the steric hindrance caused by the presence of the new phenoxy substituent in the monosubstituted "intermediate" **12**, is compounded by presence of the methyl group adjacent to the O-donor in the incoming second equivalent of substrate (Scheme 4). Thus, in contrast to the relatively facile preparation of the bisphenoxy derivative **16** (Table 3), the reaction of two (or more) equivalents of $CH_3OC_6H_4$-*p*-Me with $(Ph_2SiH)_2$ gave only partial conversion (35% estimated by ^1H NMR integration) to the disubstituted product $(Ph_2SiOC_6H_4$-*p*-$Me)_2$ (**17**), even under forcing conditions (Table 3). This is discussed further below, in the context of strategies for the synthesis of unsymmetrically substituted disilanes.

These steric arguments suggest that it should be relatively easy to access the disubstituted disilane $(Ph_2SiX)_2$ for substrates that lead to linear sidechains at Si. We did find that careful control of the stoichiometry in demethanative coupling reactions of 2-chloroethyl methyl ether is sufficient to allow isolation of either the monosubstituted product **12** (Table 2) or the disubstituted product **18** (Table 3). It is also straightforward to obtain the disubstituted product of hydrosilation of 1-hexene by $(Ph_2SiH)_2$ (Table 3, compound **19**). In this case, however, a high concentration of 1-hexene is required to give reasonable conversions (ten-fold excess of 1-hexene diluted in just 10% CH_2Cl_2 by volume). Under



Scheme 3. Transition state for nucleophilic attack of carbonyl at borane-activated silicon.



Scheme 4. Nucleophilic attack of aryloxy substrates at borane-activated, monosubstituted disilane.

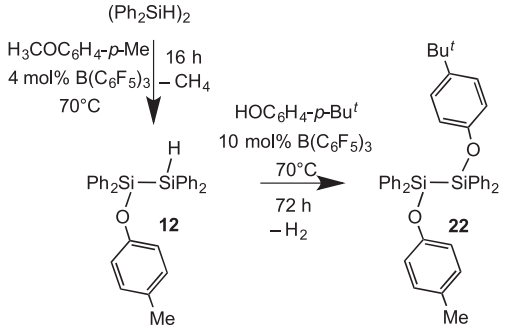
these conditions we observe almost quantitative conversion to disubstituted product **15**, with just trace amounts (~1% by ^1H NMR) of the monosubstituted product; we were unable to identify conditions to allow isolation of the monosubstituted product. These results point to a barrier to the second substitution that is actually lower than that for the first, despite the presence of the additional alkyl substituent in the monosubstituted product. This might be attributable to an inductive electronic effect of the new alkyl sidechain on the ease of borane activation of the second Si–H bond.

Curiously, in our previous studies of the dehydrogenative coupling of the linear substrate *n*-propylthiol by $(Ph_2SiH)_2$ we found conversion to the disubstituted disilane $(Ph_2SiSCH_2CH_2CH_3)_2$ to be very slow [3b]; even after 6 d reaction time at relatively high catalyst loading (for this substrate), we obtained 1:1 mixtures of the mono- and disubstituted disilanes. It seems unlikely that the slower second substitution in this case could be due to steric hindrance in the monosubstituted disilane **13**, despite the larger size of S relative to C or O, especially since we had no trouble preparing the analogous S-disubstituted disilane **19** *via* dehydrogenative coupling of HSC_6H_4-*p*-Me (thiocresol). This may point to a possible dampening electronic effect of the -SPr^n substituent on the borane activation of the residual Si–H bond in **13** [20]. We have not yet explored more forcing conditions such as increased temperature and catalyst loading in an attempt to push the second substitution reaction to completion.

3. Conclusions

Borane-catalyzed reactions of poly(hydrido)oligosilanes provide a wide scope of strategies for the construction of new, functional molecules containing Si–Si bonds. These studies delineate the issues that may arise in exploring new substrates; the isolation of pure, discrete products will almost inevitably require some careful optimization of catalyst loading, temperatures, and reaction times, especially when the products are oils instead of solids (see Section 4 and the Supporting Material).

The selectivity of these disilane derivatization reactions for mono- or disubstituted products provides an interesting opportunity to prepare novel, unsymmetrically substituted disilanes. We demonstrated this while assessing the low conversions we obtained for preparation of the disubstituted disilane $(Ph_2SiOC_6H_4$-*p*-$Me)_2$ (**17**). To show that the presence of one $-OC_6H_4$-*p*-Me group in the monosubstituted disilane **12** did not inherently deactivate the remaining Si–H bond in this molecule, we examined its reaction with HOC_6H_4-*p*-Bu^t in the presence of borane. The reaction required relatively high catalyst loading, and elevated temperatures, but we were able to isolate the mixed disilane **22** as a colorless oil in 84% yield (Scheme 5). We continue to explore the potential of this strategy in preparing new disilanes and larger, extended macromolecules with mixed substituents.



Scheme 5. Synthesis of a mixed bis(aryloxy)-substituted disilane.

4. Experimental

4.1. General details

All reactions and manipulations were performed under nitrogen using conventional glovebox or Schlenk techniques. Toluene, pentane, hexanes and dichloromethane were degassed by sparging with nitrogen and dried by passing through columns of activated alumina in a solvent purification system. d_6-Benzene (Aldrich) was degassed by one freeze-pump-thaw cycle, and vacuum transferred from sodium/benzophenone. Tris(pentafluorophenyl)borane (Alfa Aesar), was doubly sublimed. Triphenylphosphine (Alfa Aesar) was recrystallized from 95% ethanol and sublimed. Cyclohexanone, acetone (Caledon), and propionaldehyde (Aldrich) were distilled from anhydrous magnesium sulphate. 2-Chloroethyl methyl ether (Aldrich) was distilled from calcium hydride. *p*-Methylanisole (Aldrich) was sublimed. *p*-*t*-Butylphenol (Aldrich) was recrystallized from hexanes and sublimed. 1-Hexene (Aldrich) was distilled from sodium/benzophenone. N-Benzylideneaniline, prepared from the condensation of benzaldehyde and aniline in CH_2Cl_2, was recrystallized from CH_2Cl_2 and then sublimed (70 °C, dynamic vacuum) [21]. Diphenylmethylsilane (Aldrich) was used as received. $(Ph_2SiH)_2$ was prepared by a literature procedure [22].

Florisil® (Aldrich or Caledon) was dried in an oven (135 °C, ≥16 h) and vacuum oven (~0.05 mm Hg, 45 °C, 6 h), before being taken into the glovebox for use. "Florisil column" refers to a Pasteur pipette plugged with oven-dried glass wool and filled with ~6 cm of Florisil® and ~1 cm of sand. Celite (AGP or Aldrich) was dried in an oven (135 °C, ≥16 h) and vacuum oven (~0.05 mm Hg, 45 °C, for at least 6 h). "Celite filter stick" refers to a Pasteur pipette, plugged with oven-dried glass wool and filled with ~1 cm of Celite and ~1 cm of sand. "Bomb flask" refers to thick-walled, cylindrical flask with a 4 mm Teflon needle valve and a side-arm.

NMR spectra were obtained on Bruker AVANCE 300 (^{1}H, ^{13}C), 500 (^{13}C, ^{29}Si), or 360 (^{29}Si) spectrometers. Chemical shifts are reported in ppm at ambient temperature. ^{1}H NMR spectra were referenced to residual protonated d_6-benzene (δ 7.16 ppm). ^{13}C NMR spectra (run as DEPT 135 experiments unless otherwise noted) were referenced to solvent peaks. ^{29}Si NMR spectra were referenced to external TMS at 0 ppm. Melting points were collected on a Gallenkamp melting point apparatus and are uncorrected.

Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, BC. Almost all products were obtained as oils, which contained trace unidentified impurities and/or small amounts of unreacted reagents or by-products. Microanalytical data is provided nonetheless for all products to give an indication of bulk purity; in some cases combined and weighted formulae were used to calculate expected %C, %H. NMR spectra for all samples are included in the Supplementary data.

4.2. Synthesis of monosilane derivatives

*General procedure for compounds **1-7**.* Substrate was added with stirring to a toluene or benzene solution of Ph_2MeSiH and $B(C_6F_5)_3$ in a Schlenk flask. The mixture was left stirring under N_2, either is a sealed flask or open to a Nujol bubbler. PPh_3 was added to quench the catalyst and the volatiles were removed under vacuum. Addition of hexanes or pentane to the resulting oily residue caused precipitation of the borane-phosphine adduct, which was removed by filtration through a Celite filter stick. Additional solvent was added to ensure elution of the product(s) from the filter stick, and volatiles were removed under vacuum from the combined washings to give the final isolated product(s).

$Ph_2MeSiOCH_2CH_2CH_3$ (**1**). Ph_2MeSiH (0.10 g, 0.52 mmol), $B(C_6F_5)_3$ (0.009 g, 0.02 mmol), toluene (1 mL), propionaldehyde (0.10 mL, 1.4 mmol); stirred under N_2 (closed flask) for 16 h PPh_3 (0.005 g, 0.02 mmol), hexanes (4 × 1 mL). Dried under vacuum at RT for 16 h. Clear, colorless oil (0.13 g, in 76% purity. The remaining 24% was the over-reduction product, $(Ph_2MeSi)_2O$). For **1**: ^{1}H NMR (300 MHz, C_6D_6) δ 0.58 (s, 3H), 0.84 (t, $^3J_{HH}$ = 6 Hz, 3H, CH_3), 1.46–1.57 (m, 2H, OCH_2CH_2) 3.57 (t, $^3J_{HH}$ = 6 Hz, 2H, OCH_2), 7.19–7.23 (overlapping m, 6H, $H_{m/p}$-$SiPh_2$), 7.64–7.69 (m, 4H, H_o-$SiPh_2$). ^{13}C NMR (75 MHz, C_6D_6) δ −2.9 ($SiCH_3$), 10.4 ($CH_2CH_2CH_3$), 26.1 (OCH_2CH_2), 65.1 (OCH_2), 128.0 (C_m-$SiPh_2$), 129.9 (C_p-$SiPh_2$), 134.6 (C_o-$SiPh_2$). ^{29}Si NMR (99 MHz, C_6D_6) δ −3.8. For **$(Ph_2MeSi)_2O$**: ^{1}H NMR (300 MHz, C_6D_6) δ 0.38 (s, 6H, CH_3), 7.19–7.23 (overlapping m, 12H, overlaps $H_{m/p}$-$SiPh_2$ in **1**, $H_{m/p}$-$SiPh_2$), 7.38 (d, 8H, H_o-$SiPh_2$). ^{13}C NMR (75 MHz, C_6D_6) δ 2.9 ($SiCH_3$, overlaps $SiCH_3$ in **2**–**3**), 128.2 (C_m-$SiPh_2$), 129.8 (C_p-$SiPh_2$), 134.3 (C_o-$SiPh_2$). DEPT30 ^{29}Si NMR (99 MHz, C_6D_6) δ −9.5 [23]. Anal. (calcd for 76% $C_{16}H_{20}OSi$ and 24% $C_{26}H_{26}OSi_2$): C 72.51 (75.31) H 6.99 (7.36) [24].

$Ph_2MeSiOCH(CH_3)_2$ (**2**). Ph_2MeSiH (0.13 g, 0.65 mmol), $B(C_6F_5)_3$ (0.012 g, 0.023 mmol), toluene (1 mL), acetone (0.10 mL, 1.4 mmol); stirred under N_2 (closed flask) for 12 h PPh_3 (0.006 g, 0.02 mmol), pentane (4 × 1 mL). Dried under vacuum at RT for 16 h. Clear, colorless oil (0.12 g, 73%). ^{1}H NMR (300 MHz, C_6D_6) δ 0.59 (s, 3H, CH_3) 1.11 (d, $^3J_{HH}$ = 6 Hz, 6H, $CH(CH_3)_2$), 4.00 (sept, 1H, OCH), 7.17–7.21 (overlapping m, 6H, $H_{m/p}$-SiPh), 7.65–7.70 (m, 4H, H_o-SiPh). ^{13}C NMR (75 MHz, C_6D_6) δ 0.0 ($SiCH_3$), 28.0 (OCH), 58.0 ($OCH(CH_3)_2$), 130.2 (C_m-$SiPh_2$), 132.0 (C_p-$SiPh_2$), 136.9 (C_o-$SiPh_2$). DEPT30 ^{29}Si NMR (99 MHz, C_6D_6) δ −6.1. Anal. (calcd for $C_{16}H_{20}OSi$): C 74.44 (74.95) H 7.72 (7.86).

$Ph_2MeSiOC_6H_{11}$ (**3**). Ph_2MeSiH (0.10 g, 0.50 mmol), $B(C_6F_5)_3$ (0.012 g, 0.023 mmol), toluene (1 mL), cyclohexanone (0.060 mL, 0.58 mmol); stirred under N_2 (closed flask) for 16 h PPh_3 (0.006 g, 0.02 mmol), hexanes (4 × 1 mL). Dried under vacuum at 70 °C for 2 h. Clear and colorless oil (0.12 g, in 86% purity. The remaining 14% was unreacted Ph_2MeSiH). ^{1}H NMR (300 MHz, C_6D_6) δ 0.61 (s, 3H, Si–CH_3), 1.01–1.13 (overlapping m, 3H, $OCHCH_2CH_{eq}$ and $OCHCH_2CH_2CH_{eq}$), 1.29 (m, 1H, $OCHCH_2CH_2CH_{ax}$), 1.41–1.54 (m, 2H, $OCHCH_{eq}$), 1.57–1.66 (m, 2H, $OCHCH_2CH_{ax}$), 1.71–1.80 (m, 2H, $OCHCH_{ax}$), 3.77 (quint, 1H, OeCH), 7.18e7.22 (overlapping m, 6H, $H_{m/p}$-$SiPh_2$), 7.69 (d, $^3J_{HH}$ = 7 Hz, 4H, H_o-$SiPh_2$). ^{13}C NMR (75 MHz, C_6D_6) −2.1 (Si–CH_3), 23.9 ($OCHCH_2CH_2$), 25.8 ($OCHCH_2CH_2CH_2$), 35.9 ($OCHCH_2$), 71.3 (O–CH), 128.0 (C_m-$SiPh_2$), 129.8 (C_p-$SiPh_2$), 134.6 (C_o-$SiPh_2$). DEPT30 ^{29}Si NMR (99 MHz, C_6D_6) δ −6.1. Anal. (calcd for 86% $C_{19}H_{24}OSi$ and 14% $C_{13}H_{14}Si$): C 74.94 (77.14) H 7.88 (8.06) [24].

$Ph_2MeSiOC_6H_4$-p-Bu^t (**4**). Ph_2MeSiH (0.12 g, 0.58 mmol), $B(C_6F_5)_3$ (0.014 g, 0.027 mmol), toluene (1 mL), *p*-*t*-butylphenol (0.088 g, 0.59 mmol); stirred under N_2 (open to Nujol bubbler) for 1 h PPh_3 (0.007 g, 0.03 mmol), pentane (4 × 1 mL). Dried under vacuum at 70 °C for 2 h. Clear and colorless oil (0.20 g, 99%, containing a trace amount (<1%) of HOC_6H_4-*p*-Bu^t as determined by ^{1}H NMR). ^{1}H NMR (300 MHz, C_6D_6) δ 0.67 (s, 3H, $SiCH_3$), 1.16 (s, 9H, $C(CH_3)_3$),

6.92–6.97 (m, 2H, H_o-C_6H_4-*p*-Bu^t), 7.05–7.09 (m, 2H, H_m-C_6H_4-*p*-Bu^t), 7.17–7.20 (m, 6H, $H_{m/p}$-$SiPh_2$), 7.70 (d, 4H, $^3J_{HH}$ = 4 Hz, H_o-$SiPh_2$); ^{13}C NMR (75 MHz, C_6D_6) δ −2.6 ($SiCH_3$), 31.4 ($C(CH_3)_3$) 33.9 ($C(CH_3)_3$, identified from direct acquisition expt)), 119.6 (C_o-C_6H_4-*p*-Bu^t), 126.5 (C_m-C_6H_4-*p*-Bu^t), 128.7 (C_m-$SiPh_2$), 130.2 (C_p-$SiPh_2$), 134.7 (C_o-$SiPh_2$). DEPT30 ^{29}Si NMR (99 MHz, C_6D_6) δ −3.7. Anal. (calcd for $C_{23}H_{26}OSi$): C 81.8 (79.71) H 7.93 (7.56).

$Ph_2MeSiOC_6H_4$-p-Me (**5**). Ph_2MeSiH (0.13 g, 0.63 mmol), $B(C_6F_5)_3$ (0.014 g, 0.027 mmol), toluene (1 mL), *p*-methylanisole (0.083 g, 0.68 mmol); stirred under N_2 (open to Nujol bubbler) for 1 h PPh_3 (0.007 g, 0.03 mmol), pentane (4 × 1 mL). Dried under vacuum at RT for 16 h. Clear and colorless oil (0.19 g, 99%, contains trace unreacted $MeOC_6H_4$-*p*-Me). ^{1}H NMR (300 MHz, C_6D_6) δ 0.66 ($SiCH_3$), 2.02 (*p*-CH_3), 6.80 (d, 2H, $^3J_{HH}$ = 9 Hz, H_o-OC_6H_4-*p*-ME), 6.88 (d, 2H, $^3J_{HH}$ = 8 Hz, H_m-OC_6H_4-*p*-Me), 7.18 (m, 6H, $H_{m/p}$-$SiPh_2$), 7.69 (d, 4H, $^3J_{HH}$ = 4 Hz, H_o-$SiPh_2$); ^{13}C NMR (75 MHz, C_6D_6) δ −2.6 ($SiCH_3$), 20.4 (*p*-CH_3), 120.0 (C_o-OC_6H_4-*p*-Me), 128.1 (C_m-$SiPh_2$), 128.2 (C_m-OC_6H_4-*p*-Me), 130.2 (C_p-$SiPh_2$), 134.7 (C_o-$SiPh_2$). DEPT30 ^{29}Si NMR (99 MHz, C_6D_6) δ −3.6. Anal. (calcd for $C_{20}H_{20}OSi$): C 77.52 (78.90) H 6.49 (6.62).

$Ph_2MeSiOCH_2CH_2Cl$ (**6**). Ph_2MeSiH (0.16 g, 0.79 mmol), $B(C_6F_5)_3$ (0.011 g, 0.021 mmol), toluene (1 mL), 2-chloroethyl methyl ether (0.10 mL, 1.1 mmol); stirred under N_2 (open to Nujol bubbler) for 2 h PPh_3 (0.005 g, 0.02 mmol), pentane (6 × 1 mL). Dried under vacuum at RT for 16 h. Clear and colorless oil (0.18 g, 83%). ^{1}H NMR (300 MHz, C_6D_6) δ 0.52 (s, 3H, $SiCH_3$), 3.17 (t, $^3J_{HH}$ = 6 Hz, 2H, OCH_2CH_2Cl), 3.58 (t, 2H, OCH_2CH_2Cl), 7.17–7.21 (overlapping m, 6H, $H_{m/p}$-$SiPh_2$), 7.60 (d, $^3J_{HH}$ = 4 Hz, 4H, H_o-$SiPh_2$); ^{13}C NMR (75 MHz, C_6D_6) δ −3.1 ($SiCH_3$), 45.1 (OCH_2CH_2Cl), 63.8 (OCH_2CH_2Cl), 128.1 (C_m-$SiPh_2$), 130.1 (C_p-$SiPh_2$), 134.6 (C_o-$SiPh_2$). ^{29}Si NMR (99 MHz, C_6D_6) δ −1.9. Anal. (calcd for $C_{15}H_{17}OClSi$): C 64.98 (65.08) H 6.14 (6.19).

$Ph_2MeSiN(Ph)CH_2Ph$ (**7**). Ph_2MeSiH (0.11 g, 0.55 mmol), $B(C_6F_5)_3$ (0.012 g, 0.023 mmol), benzene (1 mL), N-benzylideneaniline (0.10 g, 0.55 mmol); used "bomb" flask (*vide supra*), degassed mixture by one freeze-pump-thaw cycle, heated flask in an oil bath (60 °C) for 48 h PPh_3 (0.006 g, 0.02 mmol), hexanes (4 × 1 mL). Dried under vacuum at 60 °C for 2 h. Clear and colorless oil (0.20 g, 97%, trace impurities were observed by ^{1}H NMR). ^{1}H NMR (300 MHz, C_6D_6) δ 0.71 (s, 3H, $SiCH_3$), 4.54 (s, 2H, NCH_2), 6.94 (t, 2H, $^3J_{HH}$ = 8 Hz, H_m-CH_2Ph), 7.00 (t, 2H, $^3J_{HH}$ = 7 Hz, H_m-NPh, overlaps H_o-CH_2Ph), 7.01 (d, 2H, $^3J_{HH}$ = 8 Hz, H_o-CH_2Ph, overlaps H_m-NPh), 7.04 (t, 1H, $^3J_{HH}$ = 8 Hz, H_p-CH_2Ph), 7.12–7.17 (overlapping m, 9H, H_p-NPh, H_m-$SiPh_2$, H_p-$SiPh_2$, H_o-NPh), 7.59 (d, 4H, $^3J_{HH}$ = 8 Hz, H_o-$SiPh_2$). ^{13}C NMR (75 MHz, C_6D_6) δ −1.1 ($SiCH_3$), 53.1 (NCH_2), 120.1 (C_p-CH_2Ph), 125.6 (C_p-$SiPh_2$), 126.7 (C_m-NPh), 126.8 (C_o-CH_2Ph), 128.4 (C_p-NPh), 128.6 (C_o-NPh), 129.0 (C_m-CH_2Ph), 130.1 (C_m-$SiPh_2$), 135.0 (C_o-$SiPh_2$). DEPT30 ^{29}Si NMR (99 MHz, C_6D_6) δ −5.3. Anal. (calcd for $C_{26}H_{25}NSi$): C 81.30 (82.27) H 7.20 (6.64).

$Ph_2MeSiCH_2CH_2Bu^n$ (**8**). $PhMe_2SiH$ (0.21 g, 1.1 mmol) and $B(C_6F_5)_3$ (0.025 g, 0.049 mmol) were combined with 1-hexene (1.0 mL, 4.0 mmol) and CH_2Cl_2 (0.5 mL) in a Schlenk flask. The mixture was stirred under N_2 with the flask closed for 16 h. The volatiles were removed under vacuum, and the resulting oily residue was dissolved in pentane (1 mL) and filtered through a Florisil column to remove residual $B(C_6F_5)_3$ (a faint brown color was retained on the column). The column was washed with pentane (3 × 1 mL), and the volatiles were removed under vacuum from the combined filtrates to give a clear and colorless oil (0.22 g, 74%, trace impurities were observed by ^{1}H NMR). ^{1}H NMR (300 MHz, C_6D_6) δ 0.51 (s, 3H, Si–CH_3), 0.86 (t, $^3J_{HH}$ = 7 Hz, 3H, $(CH_2)_5CH_3$), 1.00–1.46 (overlapping m, 10H, Si–$CH_2CH_2CH_2CH_2CH_2$), 7.18–7.23 (overlapping m, 6H, $H_{m/p}$-SiPh2), 7.53 (d, $^3J_{HH}$ = 4 Hz, 4H, H_o-SiPh2); ^{13}C NMR (75 MHz, C_6D_6) δ −4.2 ($SiCH_3$), 14.3 ($Si(CH_2)_5CH_3$), 14.6 ($SiCH_2$), 23.0 ($Si(CH_2)_4CH_2$), 24.2 ($Si(CH_2)_3CH_2$), 31.8 ($Si(CH_2)_2CH_2$), 33.7 ($SiCH_2CH_2$) 128.2 (C_m-SiPh2), 129.4 (C_p-SiPh2), 134.9 (C_o-SiPh2). DEPT30 ^{29}Si NMR (99 MHz, C_6D_6) δ −7.1. Anal. (calcd for $C_{19}H_{26}Si$): C 80.68 (80.78) H 9.53 (9.28).

4.3. Synthesis of disilane derivatives

Ph_2SiH–$Si(OCH(CH_3)_2)Ph_2$ (**9**). Procedure was as described for monosilanes **1**–**7**. $(Ph_2SiH)_2$ (0.21 g, 0.58 mmol), $B(C_6F_5)_3$ (0.030 g, 0.059 mmol), toluene (2 mL), acetone (0.050 mL, 0.68 mmol); stirred under N_2 (closed flask) for 16 h PPh_3 (0.015 g, 0.057 mmol), pentane (6 × 1 mL). Dried under vacuum at RT for 16 h. Clear and colorless oil (0.23 g, 86% in >90% purity). A small amount of isopropoxy-containing impurity was observed by ^{1}H NMR, which may be the disubstituted product $(Ph_2SiHOCH(CH_3)_2)_2$. 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 equiv of acetone to isolated monosubstituted disilane product showed no reaction: the monosubstituted disilane with the same quantity of isopropoxy-containing impurity was recovered. ^{1}H NMR (300 MHz, C_6D_6) δ 1.08 (d, $^3J_{HH}$ = 6.0 Hz, 6H, $Si(CH(CH_3)_2)$), 4.18 (sept, ^{1}H, $Si(CH(CH_3)_2)$), 5.55 (s, $^1J_{SiH}$ = 183 Hz, 1H, Si–H), 7.08–7.16 (overlapping m, 12H, $H_{m/p}$-$SiPh_2$), 7.65–7.79 (m, 8H, H_o-$SiPh_2$); ^{13}C NMR (75 MHz, C_6D_6) δ 25.7 (CH_3), 67.4 (OCH), 127.9 (C_m-$HSiPh_2$), 128.1 (C_m-$OSiPh_2$), 128.2 (C_p-$HSiPh_2$), 130.0 (C_p-$OSiPh_2$), 135.4 (C_o-$HSiPh_2$), 136.5 (C_o-$OSiPh_2$). DEPT30 ^{29}Si NMR (99 MHz, C_6D_6) δ −38.2 (SiH), -8.1 ($SiOCH(CH_3)_2$). Anal. (calcd for $C_{27}H_{28}OSi_2$): C 75.88 (76.36) H 6.93 (6.65).

Ph_2SiH–$Si(OC_6H_{11})Ph_2$ (**10**). Procedure was as described for monosilanes **1**–**7**. $(Ph_2SiH)_2$ (0.10 g, 0.28 mmol), $B(C_6F_5)_3$ (0.019 g, 0.037 mmol), benzene (1 mL), cyclohexanone (0.20 mL, 1.9 mmol); used "bomb" flask (*vide supra*), degassed mixture by one freeze-pump-thaw cycle, heated sealed, evacuated flask in an oil bath (55 °C) for 5 h PPh_3 (0.010 g, 0.037 mmol), hexanes (5 × 1 mL). Dried under vacuum at 50 °C for 1 h. Clear and colorless oil (0.084 g, 67%). ^{1}H NMR (300 MHz, C_6D_6) δ 0.73–0.91 (overlapping m, 3H, $OCHCH_2CH_{eq}$ and $OCHCH_2CH_2CH_{eq}$), 1.02 (m, 1H, $OCHCH_2CH_2CH_{ax}$), 1.19–1.30 (m, 2H, $OCHCH_{eq}$), 1.30–1.41 (m, 2H, $OCHCH_2CH_{ax}$), 1.49–1.61 (m, 2H, $OCHCH_{ax}$), 3.93 (quintet, 1H, O–CH), 5.56 ppm (s, $^1J_{SiH}$ = 184 Hz, 1H, Si–H), 7.08–7.12 (overlapping m, 8H, H_m-SiPh and H_m-OSiPh2), 7.14–7.18 (m, 4H, H_p-SiPh and H_p-OSiPh2), 7.68 (d, $^3J_{HH}$ = 6 Hz, 4H, H_o-SiPh), 7.78 (d, $^3J_{HH}$ = 7 Hz, 4H, H_o-OSiPh2). ^{13}C NMR (75 MHz, C_6D_6) 23.9 ($OCHCH_2CH_2$), 25.7 ($OCHCH_2CH_2CH_2$), 35.9 ($OCHCH_2$), 73.0 (O–CH), 128.1 (C_m-SiPh), 128.2 (C_m-OSiPh2), 129.4 (C_p-SiPh), 130.0 (C_p-OSiPh2), 135.3 (C_o-SiPh), 136.5 (C_o-OSiPh2). DEPT30 ^{29}Si NMR (99 MHz, C_6D_6) δ −33.8 (SiH), -8.2 ($SiOC_6H_{11}$). Anal. (calcd for $C_{30}H_{32}OSi_2$): C 77.53 (77.53) H 6.80 (6.94).

Ph_2SiH–$Si(OC_6H_4$-p-$Bu^t)Ph_2$ (**11**). $(Ph_2SiH)_2$ (0.10 g, 0.27 mmol), HOC_6H_4-*p*-Bu^t (0.041 g, 0.27 mmol) and $B(C_6F_5)_3$ (0.015 g, 0.029 mmol) were combined in toluene (1 mL) in a Schlenk flask. The solution bubbled and frothed (elimination of H_2). The mixture was degassed with one freeze-pump-thaw cycle, then stirred under static vacuum at RT for 16 h. Volatiles were removed by evacuation to give a clear, faintly brown oil, which was washed through a Florisil column with hexanes (4 × 1 mL) to remove $B(C_6F_5)_3$ (and coloured impurity). Dried under vacuum at 60 °C for 1 h. Clear, colorless oil (0.095 g; shown by ^{1}H NMR to contain 67% **11**, along with 26% unreacted $(Ph_2SiH)_2$ and 7% disubstituted disilane **16**). For **11**: ^{1}H NMR (300 MHz, C_6D_6) δ 1.14 (s, 9H, overlaps $C(CH_3)_3$ from $(Ph_2SiOC_6H_4$-*p*-$Bu^t)_2$, $C(CH_3)_3$), 5.56 (s, 1H, $^1J_{SiH}$ = 188 Hz, Si–H), 6.98–7.00 (overlapping m, 4H, overlaps H_m-C_6H_4-*p*-Bu^t in $(Ph_2SiOC_6H_4$-*p*-$Bu^t)_2$, $H_{o/m}$-C_6H_4-*p*-Bu^t), 7.05–7.13 (overlapping m, 12H, overlaps $H_{m/p}$-$SiPh_2$ in $(Ph_2SiOC_6H_4$-*p*-$Bu^t)_2$ and $(Ph_2SiH)_2$, $H_{m/p}$-HSiPh and $H_{m/p}$-OSiPh), 7.57 (d, 4H, overlaps H_o-$SiPh_2$ in

($Ph_2SiH)_2$, $^3J_{HH}$ = 4 Hz, H_o-$HSiPh_2$), 7.56–7.83 (overlapping m, 4H, H_o-$OSiPh_2$). ^{13}C NMR (75 MHz, C_6D_6) δ 31.4 (CH_3), 33.9 (*C*(CH_3), from direct acquisition expt) 119.8 (C_o–C_6H_4-*p*-Bu^t), 126.4 (C_m-C_6H_4-*p*-Bu^t), 128.2 (C_m-$HSiPh_2$), 128.3 (C_m-$OSiPh_2$), 129.6 (C_p-$HSiPh_2$), 130.3 (C_p-$OSiPh_2$), 135.3 (C_o-$HSiPh_2$), 136.5 (C_o-$OSiPh_2$). DEPT30 ^{29}Si NMR (99 MHz, C_6D_6) δ −38.3 (SiH), -6.4 (SiAr). Anal. (calcd for 67% $C_{34}H_{34}OSi_2$ (**12**), 26% $C_{24}H_{22}Si_2$ (($Ph_2SiH)_2$), and 7% $C_{44}H_6H_6O_2Si_2$ (**16**)): C 79.36 (79.23) H 6.52 (6.57).

Ph_2SiH–Si(OC_6H_4-p-Me)Ph_2 (**12**). Procedure was as described for **1**–**7**. ($Ph_2SiH)_2$ (0.30 g, 0.82 mmol), $B(C_6F_5)_3$ (0.042 g, 0.082 mmol), toluene (2 mL), *p*-methylanisole (0.10 g, 0.82 mmol); stirred under N_2 (open to Nujol bubbler) for 16 h PPh_3 (0.021 g, 0.080 mmol), pentane (6 × 1 mL). Dried under vacuum at 70 °C for 2 h. Clear, colorless, viscous oil (0.38 g, 99%) in >97% purity. A small amount (~3%) of unreacted ($Ph_2SiH)_2$ was detected by ^1H NMR. ^1H NMR (300 MHz, C_6D_6) δ 1.99 (s, 3H, *p*-CH_3), 5.56 (s, 1H, $^1J_{SiH}$ = 187 Hz, Si–H), 6.74 (dt, 2H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, H_o-OC_6H_4-*p*-Me), 6.92 (dt, 2H, $^3J_{HH}$ = 9 Hz, $^4J_{HH}$ = 1 Hz, H_m-OC_6H_4-*p*-Me), 7.04–7.12 (m, 12H, $H_{m/p}$-$SiPh_2$), 7.57–7.79 (m, 8H, H_o-$SiPh_2$); ^{13}C 20.4 (*p*-CH_3), 120.1 (C_o-OC_6H_4-*p*-Me), 128.2 (C_m-Si(H)Ph_2), 128.3 (C_m-$OSiPh_2$), 129.6 (C_m-OC_6H_4-*p*-Me), 130.1 (C_p-$HSiPh_2$), 130.3 (C_p-$OSiPh_2$), 135.3 (C_o-$HSiPh_2$), 136.5 (C_o-$OSiPh_2$). DEPT30 ^{29}Si NMR (99 MHz, C_6D_6) δ −38.4 (SiH), -6.3 (SiAr). Anal. (calcd for 97% $C_{31}H_{28}OSi_2$ (**12**) and 3% $C_{24}H_{22}Si_2$ (($Ph_2SiH)_2$)): C 76.93 (78.75) H 6.09 (5.97).

*Formation of Ph_2SiH–Si(OCH_2CH_2Cl)Ph_2 (**13**) monitored by ^1H NMR.* ($Ph_2SiH)_2$ (0.050 g, 0.14 mmol), $CH_3OCH_2CH_2Cl$ (0.013 g, 0.14 mmol), $B(C_6F_5)_3$ (0.010 g, 0.020 mmol), and C_6D_6 (1 mL) were combined in an NMR tube equipped with a J-Young valve. The NMR tube was shaken and vented periodically (to release CH_4 pressure) on the vacuum line under N_2. ^1H NMR signal for the OCH_3 group in $CH_3OCH_2CH_2Cl$ disappeared after 4 h, at which point the relative ratios of ($Ph_2SiH)_2$, **13**, and ($Ph_2SiOCH_2CH_2Cl)_2$ (**18**) were 15:75:10 respectively. For **13**: ^1H NMR (300 MHz, C_6D_6) δ 3.11 (t, $^3J_{HH}$ = 6 Hz, 2H, CH_2CH_2Cl), 3.71 (t, 2H, CH_2CH_2Cl), 5.55 (s, $^1J_{SiH}$ = 186 Hz, 1H, Si–H), 7.04–7.19 (overlapping m, 12H, $H_{m/p}$-$SiPh_2$ and $H_{m/p}$-$OSiPh_2$), 7.63–7.71 (overlapping m, 8H, H_o-$SiPh_2$ and H_o-$OSiPh_2$).

($Ph_2SiOC_6H_4$-p-$Bu^t)_2$ (**16**). ($Ph_2SiH)_2$ (0.10 g, 0.27 mmol), *p*-*t*-butylphenol (0.11 g, 0.71 mmol), and $B(C_6F_5)_3$ (0.028 g, 0.055 mmol) were combined with toluene (1 mL) in a "bomb" flask. The mixture was degassed with one freeze-pump-thaw cycle, then heated under static vacuum to 70 °C for 16 h, after which the flask was cooled to RT and toluene was removed under vacuum to give a light brown, viscous oil. A ^1H NMR spectrum taken at this point shows 100% conversion to disubstituted product (see Fig. S15a in the SI). The mixture was washed through a Florisil column with hexanes (6 × 1 mL) to remove $B(C_6F_5)_3$ and B-OC_6H_4-*p*-Bu^t-containing byproducts [25]. Volatiles were removed under vacuum with heating to 60 °C, to give a white oily solid. Pentane (1 mL) was added to dissolve the crude product, then the volatiles were removed under vacuum to give a white, powdery solid (0.038 g, 21%). ^1H NMR (300 MHz, C_6D_6) δ 1.13 (s, 18H, -*C*e(CH_3)), 6.98–7.01 (overlapping m, 8H, $H_{o/m}$-C_6H_4-*p*-Bu^t), 7.07–7.13 (overlapping m, 12H, $H_{m/p}$-Ph), 7.81 (d, $^3J_{HH}$ = 7 Hz, 8H, H_o-Ph); ^{13}C NMR (75 MHz, C_6D_6) δ 31.4 (CH_3), 33.9 (−*C*−(CH_3) from ^{13}C NMR), 119.8 (C_o-C_6H_4-*p*-Bu^t), 126.37 (C_m-C_6H_4-*p*-Bu^t), 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) δ −11.1. Anal. (calcd for 81% $C_{44}H_{46}O_2Si_2$ (**16**) and 19% C_2H_6OSi (grease)): C 78.47 (78.50) H 6.95 (7.02).

($Ph_2SiOC_6H_4$-p-Me)$_2$ (**17**). ($Ph_2SiH)_2$ (0.20 g, 0.55 mmol), *p*-methylanisole (0.19 g, 0.20 mL, 1.6 mmol), and $B(C_6F_5)_3$ (0.024 g, 0.047 mmol) were combined with toluene (2 mL) in a "bomb" flask. The mixture was degassed using one freeze-pump-thaw cycle, then stirred and heated under static vacuum to 70 °C for 16 h, then cooled to RT. 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*-Me)Ph_2 (**12**). More $B(C_6F_5)_3$ (0.022 g, 0.043 mmol) and toluene (1 mL) were added, the flask was degassed with one freeze-pump-thaw cycle, and the mixture was again heated to 70 °C under static vacuum for 28 d, after which the flask was cooled to RT and toluene was removed under vacuum to give a light brown, viscous oil. The oil was washed through a Florisil column with hexanes (4 × 1 mL) to remove $B(C_6F_5)_3$. Volatiles were removed under vacuum with heating to 60 °C, to give 0.13 g of a cloudy oil that was a 65:35 mixture of **12** and **17.** For **17**: ^1H NMR (300 MHz, C_6D_6) δ 1.97 (s, 6H, *p*-CH_3, overlaps *p*-CH_3 in **12**), 6.73 (d, 4H, H_m-OC_6H_4-*p*-Me, overlaps H_m-OC_6H_4-*p*-Me in **12**), 6.93 (d, 4H, H_o-OC_6H_4-*p*-Me, overlaps H_o-OC_6H_4-*p*-Me in **12**), 7.06–7.12 (overlapping m, 6H, $H_{m/p}$-$SiPh_2$, overlaps $H_{m/p}$-$SiPh_2$ in **12**), 7.76–7.82 (overlapping m, 8H, H_o-$SiPh_2$, overlaps H_o-$SiPh_2$ in **12**). Mixture was not submitted for microanalysis.

($Ph_2SiOCH_2CH_2Cl)_2$ (**18**). ($Ph_2SiH)_2$ (0.10 g, 0.27 mmol) and $B(C_6F_5)_3$ (0.015 g, 0.029 mmol) were combined with toluene (1 mL) in a Schlenk flask. 2-Chloroethyl methyl ether (0.050 mL, 0.55 mmol) was added dropwise with stirring, and the resulting mixture was stirred under N_2 (open to the nujol bubbler) for 16 h, by which time it was cloudy white. The toluene was removed under vacuum and cold pentane (2 mL) was added, giving a white precipitate. The precipitate was collected by filtration, washed with cold pentane (4 mL), and dried under vacuum, giving a white powdery solid (0.094 g, 65%). ^1H NMR (300 MHz, C_6D_6) δ 3.17 (t, $^3J_{HH}$ = 6 Hz, 4H, OCH_2CH_2Cl), 3.77 (t, 4H, OCH_2CH_2Cl), 7.14 (m, 12H, $H_{m/p}$-$SiPh_2$), 7.75 (m, 8H, H_o-$SiPh_2$); ^{13}C NMR (75 MHz, C_6D_6) δ 45.1 (OCH_2CH_2Cl), 64.8 (OCH_2CH_2Cl), 128.2 (C_m-$SiPh_2$), 130.3 (C_p-$SiPh_2$), 135.4 (C_o-$SiPh_2$). ^{29}Si NMR (99 MHz, C_6D_6) δ −7.7. M.p. 138–140 °C. Anal. (calcd for 93% $C_{28}H_{28}O_2Cl_2Si_2$ (**18**) and 7% C_2H_6OSi (grease)): C 63.28 (63.23) H 5.17 (5.36).

($Ph_2SiCH_2CH_2Bu)_2$ (**19**). ($Ph_2SiH)_2$ (0.30 g, 0.82 mmol) and $B(C_6F_3)_3$ (0.053 g, 0.10 mmol) were combined with 1-hexene (1.0 mL, 8.0 mmol) and CH_2Cl_2 (0.1 mL) in a Schlenk. The mixture was stirred under N_2 in a closed flask for 72 h, after which the volatiles were removed under vacuum. The resulting cloudy oily residue was washed through a Florisil column with hexanes (6 × 1 mL) to remove $B(C_6F_5)_3$. The volatiles were removed under vacuum, giving a clear, colorless, viscous oil (0.38 g, 87% in ~99% purity). ^1H/^{13}C NMR spectra showed minor peaks presumed to be due to the monosubstituted product Ph_2SiH–Si(CH_2CH_2Bu)Ph_2 (<1%). However increased reaction time (up to 3 d) and additional catalyst (up to 0.20 mmol) did not result in this impurity being converted to **19.** ^1H NMR (300 MHz, C_6D_6) δ 0.82 (t, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.07–1.62 (m, 20H, CH_2), 7.12–7.21 (overlapping m, 12H, $H_{m/p}$-$SiPh_2$), 7.59–7.67 (m, 8H, H_o-$SiPh_2$); ^{13}C NMR (75 MHz, C_6D_6) δ 14.0 (CH_3), 14.1 ($SiCH_2$), 22.8 ($Si(CH_2)_4CH_2$), 24.9 ($Si(CH_2)_3CH_2$), 31.6 ($Si(CH_2)_2CH_2$), 33.7 ($SiCH_2CH_2$), 128.1 (C_m-$SiPh_2$), 129.2 (C_p-$SiPh_2$), 136.1 (C_o-$SiPh_2$). ^{29}Si NMR (99 MHz, C_6D_6) δ −20.3. Anal. (calcd for $C_{36}H_{46}Si_2$): C 80.97 (80.83) H 9.04 (8.67).

$Ph_2Si(OC_6H_4$-p-Me)-Si(OC_6H_4-p-$Bu^t)Ph_2$ (**22**). Compound **12** was generated *in situ* as described above for the attempted prep of **17**, using ($Ph_2SiH)_2$ (0.10 g, 0.27 mmol), *p*-methylanisole (0.040 g, 0.33 mmol), $B(C_6F_5)_3$ (0.015 g, 0.029 mmol), and toluene (1 mL). The toluene was removed under vacuum to give an oily residue, to which *p*-*t*-butylphenol (0.44 g, 0.29 mmol), $B(C_6F_5)_3$ (0.22 g, 0.043 mmol) and toluene (1 mL) were added. The flask was degassed with one freeze-pump-thaw cycle, and the mixture was again heated to 70 °C under static vacuum. After 72 h the flask was cooled to RT and toluene was removed under vacuum to give a light brown, viscous oil. The oil was washed through a Florisil column with hexanes (5 × 1 mL) to remove $B(C_6F_5)_3$ and coloured impurities. The hexanes was removed under vacuum, and the resulting residue was heated to 70 °C for 2 h under dynamic vacuum to

remove volatiles including residual $CH_3OC_6H_4$-*p*-Me, HOC_6H_4-*p*-Bu^t, and C_6F_5H, giving a viscous cloudy oil. (0.14 g, 84%, >99% purity, <1% residual $Ph_2SiHeSi(OC_6H_4$-*p*-Me$)Ph_2$ (**12**)). ^{1}H 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*-Me), 6.94 (dt, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 2$ Hz, 2H, H_o-OC_6H_4-*p*-Me), 6.98–7.00 (overlapping m, 4H, H_o-OC_6H_4-*p*-Bu^t, H_m-OC_6H_4-*p*-Bu^t), 7.07–7.12 (overlapping m, 12H, H_m-OC_6H_4-*p*-Bu^t, H_p-OC_6H_4-*p*-Bu^t, H_m-OC_6H_4-*p*-Me, H_p-OC_6H_4-*p*-Me), 7.77–7.83 (overlapping m, 8H, H_o-$SiPh_2OC_6H_4$-*p*-Bu^t, H_o-$SiPh_2OC_6H_4$-*p*-Me). ^{13}C NMR 20.4 ($C(CH_3)_3$), 31.4 (*p*-CH_3), 119.7 (C_m-OC_6H_4-*p*-Bu^t), 120.1 (C_m-OC_6H_4-*p*-Me), 126.4 (C_o-C_6H_4-*p*-Bu^t), 128.2 (overlapping, C_p-$SiPh_2OC_6H_4$-*p*-Bu^t, C_p-$SiPh_2OC_6H_4$-*p*-Me), 130.0 (C_o-OC_6H_4-*p*-Me), 130.2 (overlapping, C_m-$SiPh_2OC_6H_4$-*p*-Bu^t, C_m-$SiPh_2OC_6H_4$-*p*-Me), 135.6 (overlapping, C_o-$SiPh_2OC_6H_4$-*p*-Bu^t, C_o-$SiPh_2OC_6H_4$-*p*-Me). DEPT30 ^{29}Si (99 MHz, C_6D_6) −10.9 ($SiOC_6H_4$-*p*-Me), -11.1 ($SiOC_6H_4$-*p*-Bu^t). Anal. (calcd for 99% $C_{41}H_{40}O_2Si_2$ (**22**) and 1% $C_{31}H_{28}OSi_2$ (**12**): C 77.59 (79.30) H 6.40 (6.49)).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2016.02.035.

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[18] Mixtures resulting from the attempted hydrosilation of N-benzylideneaniline showed a downfield ^{1}H NMR signal attributable the iminyl proton (N=*CH*) of a putative imine-borane complex at 8.57 ppm in d_6-benzene and 8.59 ppm in d_8-toluene, relative to the analogous signal for the free imine, which appears at 8.14 ppm and 8.08 ppm respectively (see Supplementary data). However, Piers reports a high field shift of 7.89 ppm for the iminyl proton of the isolated borane adduct in d_8-toluene. J.M. Blackwell, W.E. Piers, M. Parvez, R. McDonald, Organometallics 21 (2002) 1400.
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[25] See Supplementary data for ^{1}H and ^{19}F NMR spectra obtained for an aliquot of the crude reaction mixture, indicating the presence of these species.