ORGANOMETALLICS

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Hydrosilylation of Aldehydes and Ketones Catalyzed by a Terminal Zinc Hydride Complex, [κ^3-Tptm]ZnH

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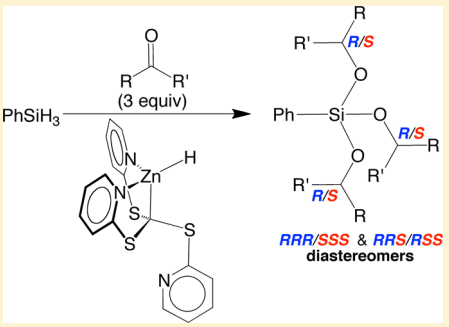
Supporting Information

ABSTRACT: Tris(2-pyridylthio)methyl zinc hydride, [κ^3-Tptm]ZnH, is an effective catalyst for multiple insertions of carbonyl groups into the Si−H bonds of Ph_xSiH_{4-x} (x = 1, 2). Specifically, [κ^3-Tptm]ZnH catalyzes the insertion of a variety of aldehydes and ketones into the Si−H bonds of $PhSiH_3$ and Ph_2SiH_2 to afford $PhSi[OCH(R)R']_3$ and $Ph_2Si[OCH(R)R']_2$, respectively. The mechanism for hydrosilylation is proposed to involve insertion of the carbonyl group into the Zn−H bond to afford an alkoxy species, followed by metathesis with the silane to release the alkoxysilane and regenerate the zinc hydride catalyst. Multiple insertion of prochiral ketones results in the formation of diastereomeric mixtures of alkoxysilanes that can be identified by NMR spectroscopy.



INTRODUCTION

Catalytic hydrosilylation of carbonyl compounds to afford alkoxysilanes is an area of interest in that it provides a method to achieve the overall reduction to the alcohol *via* subsequent hydrolysis of the alkoxysilane.[1,2] Furthermore, alkoxysilanes[3,4] have applications in organic synthesis[5] and materials chemistry (including stone consolidation,[6] the synthesis of mesoporous silica nanoparticles,[7] and silsesquioxane derivatives[8]). In addition to obtaining improved catalysts for this transformation, it is important to develop effective catalysts that are based on abundant non-precious metals.[9] Zinc is one such metal,[10] and we have recently demonstrated that the tris(2-pyridylthio)methyl zinc hydride complex, [κ^3-Tptm]ZnH (Figure 1),[11] can serve as an effective catalyst for the hydrosilylation of aldehydes, ketones, and carbon dioxide.[12−14] Here, we extend the scope of the catalytic hydrosilylation transformations that are mediated by [κ^3-Tptm]ZnH.

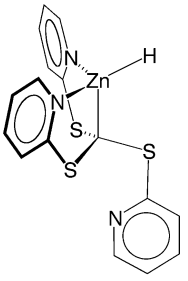
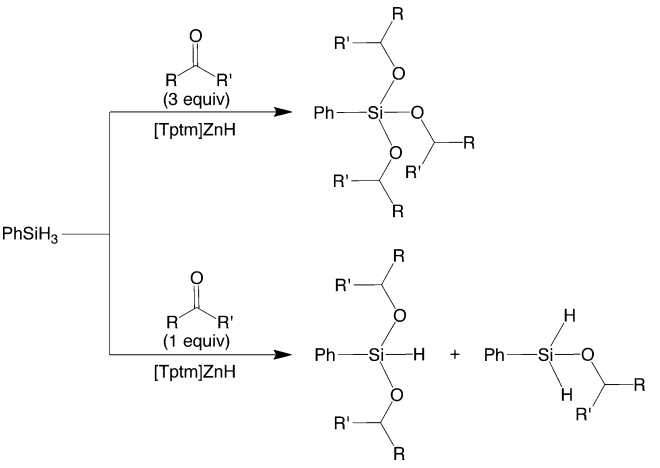


Figure 1. [κ^3-Tptm]ZnH, a mononuclear zinc hydride catalyst.

RESULTS AND DISCUSSION

We have previously reported that [κ^3-Tptm]ZnH is capable of catalyzing insertion of both acetaldehyde and acetone into all three of the Si−H bonds of $PhSiH_3$ to afford $PhSi(OEt)_3$ and $PhSi(OPr^i)_3$, respectively (Scheme 1).[12,15,16] Such compounds are of interest because aryltrialkoxysilanes have applications in cross-coupling reactions,[4] but are traditionally synthesized *via* the reaction of Grignard or lithium reagents with $Si(OR)_4$.[17]

Scheme 1. Zinc-Catalyzed Insertion of Carbonyl Compounds into the Si−H Bonds of $PhSiH_3$[a]



[a]See Table 1 for conditions.

Special Issue: Gregory Hillhouse Issue

Received: June 15, 2015

DOI: 10.1021/acs.organomet.5b00506
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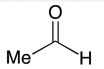
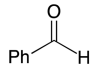
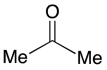
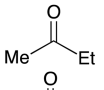
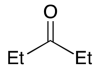
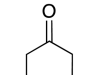
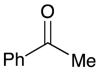
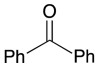
Table 1. [κ^3-Tptm]ZnH-Catalyzed Insertion of Aldehydes and Ketones into the Si−H Bonds of $PhSiH_3$

aldehyde/ketone	$PhSiH_3$:RR′CO ratio					
	1:1[a]			1:3.3[b]		
	distribution	time (h:m)	TOF (h^{-1})	distribution	time (h:m)	TOF (h^{-1})
	$PhSiH_2[OCH(R)R']$ (20%), $PhSiH[OCH(R)R']_2$ (80%)	0:05	1200[c]	$PhSi[OCH(R)R']_3$ (100%)	0:10	542[c]
	$PhSiH[OCH(R)R']_2$ (90%), $PhSi[OCH(R)R']_3$ (10%)	0:10	600[c]	$PhSi[OCH(R)R']_3$ (100%)	0:20	271
	$PhSiH_2[OCH(R)R']$ (24%), $PhSiH[OCH(R)R']_2$ (76%)	3:00	33	$PhSi[OCH(R)R']_3$ (100%)	2:10	42
	$PhSiH_2[OCH(R)R']$ (11%), $PhSiH[OCH(R)R']_2$ (89%)	6:00	17	$PhSi[OCH(R)R']_3$ (100%)	3:30	26
	$PhSiH_2[OCH(R)R']$ (24%), $PhSiH[OCH(R)R']_2$ (76%)	18:00	6	$PhSi[OCH(R)R']_3$ (100%)	12:00	8
	$PhSiH_2[OCH(R)R']$ (21%), $PhSiH[OCH(R)R']_2$ (79%)	2:10	46	$PhSi[OCH(R)R']_3$ (100%)	22:00	4
	$PhSiH_2[OCH(R)R']$ (3%), $PhSiH[OCH(R)R']_2$ (97%)	0:45	133	$PhSi[OCH(R)R']_3$ (100%)	1:10	77
	$PhSiH_2[OCH(R)R']$ (5%), $PhSiH[OCH(R)R']_2$ (95%)	0:10	600[c]	$PhSi[OCH(R)R']_3$ (100%)	0:10	542[c]

[a]1.0 mol % catalyst based on $PhSiH_3$; reactions performed at room temperature in C_6D_6, and conversions determined by ^1H NMR spectroscopy; TON = 100; product mixture contains excess $PhSiH_3$. [b]3.3 mol % catalyst based on $PhSiH_3$; reactions performed at room temperature in C_6D_6, and conversions determined by ^1H NMR spectroscopy; TON = 90. [c]In view of the high activity, these values represent the minimum TOF.

Thus, even though metal-catalyzed insertion of aldehydes and ketones into Si−H bonds is well established,[2,18] the insertion of carbonyl groups into three Si−H bonds had not been reported as a general synthetic method for $PhSi(OR)_3$ derivatives.

For example, catalysts such as $[(C_6H_3Pr^i_2)N]Mo(PMe_3)_3(Cl)H$,[19] $[Tp][(C_6H_3Pr^i_2)N]Mo(PMe_3)H$,[20] $[Tp][(C_6H_3Pr^i_2)N]Mo(PMe_3)H$,[21] $[\{\kappa^2\text{-}Ph_2PC_6H_4)_2O\}Mo(NO)(NCMe)_3][BAr^F_4]$,[22] $[Fe\{N(SiMe_3)_2\}_2]$,[2f] and $Et_2OFe(CATPOP)$[23] only efficiently insert aldehydes and ketones into two of the Si−H bonds of $PhSiH_3$, with insertion into all three Si−H bonds occurring only to a small extent.[24] Compounds that catalyze the insertion of aldehydes and ketones into all three Si−H bonds of $PhSiH_3$ have, nevertheless, been described[25,26] subsequent to our report.[12,27] Thus, in view of the fact that triple insertion of carbonyl compounds into $PhSiH_3$ is not well established, we have examined further the ability of [κ^3-Tptm]ZnH to catalyze such transformations.

Multiple Insertion of RC(O)R′ into $PhSiH_3$. Illustrative examples of aldehydes and ketones that undergo [κ^3-Tptm]ZnH-catalyzed insertion into the Si−H bonds of $PhSiH_3$ are summarized in Table 1. In each case, treatment of a 1:3.3 mixture of $PhSiH_3$ and RC(O)R′ with 3.3 mol % of catalyst (relative to $PhSiH_3$) results in the quantitative formation of the triple insertion product, $PhSi[OCH(R)R']_3$. Aldehydes are the most active, and the reactions proceed to completion in less than 20 min, with turnover frequencies (TOFs) > 200 h^{-1} over this period.[28] Dialkyl ketones are the slowest but proceed smoothly to completion over a period of 1 day. In contrast to dialkyl ketones, however, the diaryl ketone Ph_2CO is very reactive, and the reaction proceeds to completion in less than 10 min at room temperature. The reactions can also be performed in the absence of solvent. For example, addition of PhC(O)Me (3.3 equiv) to $PhSiH_3$ in the presence of [κ^3-Tptm]ZnH (3.3 mol %) results in the rapid formation of $PhSi[OCH(Me)Ph]_3$. The effectiveness of [κ^3-Tptm]ZnH as a catalyst to achieve triple insertion of a ketone into $PhSiH_3$ is made evident by the fact that the TOF (77 h^{-1}) for insertion of acetophenone in benzene solution at room temperature is greater than that for the manganese catalyst, (^{Ph_2PPr}PDI)Mn (47 h^{-1}).[25b] Furthermore, a heterogeneous cesium catalyst possessed a TOF of only 1.7 h^{-1} at an elevated temperature (80 °C).[27]

While selective triple insertion is observed upon treatment of $PhSiH_3$ with 3 equiv of RC(O)R′, a mixture of single, double, and triple insertion products, $PhSiH_2[OCH(R)R']$, $PhSiH[OCH(R)R']_2$, and $PhSi[OCH(R)R']_3$, is observed upon treatment of $PhSiH_3$ with fewer equivalents of RC(O)R′. For example, a 1:1 mixture of PhC(O)Me and $PhSiH_3$ gives a mixture that contains predominantly $PhSiH[OCH(Me)Ph]_2$, together with a small amount of $PhSiH_2[OCH(Me)Ph]$ (3%) and unreacted $PhSiH_3$ (Table 1), while a 2:1 mixture of PhC(O)Me and $PhSiH_3$ gives a mixture that contains $PhSi[OCH(Me)Ph]_3$ and $PhSiH[OCH(Me)Ph]_2$. The observation that both 1:1 and 2:1 mixtures of PhC(O)Me and $PhSiH_3$ give primarily the double insertion product indicates that, whereas incorporation of one alkoxy group significantly promotes the insertion into the remaining Si−H bonds, the effect is less pronounced upon incorporation of a second alkoxy substituent.

A noteworthy feature of the reactions of prochiral ketones is that the triple insertion products, $PhSi[OCH(R)R']_3$, display interesting spectroscopic properties. For example, rather than exhibiting in the ^1H NMR spectrum a simple doublet that is often associated with the methyl group of a [CH(Me)] moiety, the methyl groups of $PhSi[OCH(Me)Ph]_3$ are characterized by *eight* signals in a *ca.* 1:1:1:1:1:1:1:1 ratio (Figure 2).

DOI: 10.1021/acs.organomet.5b00506
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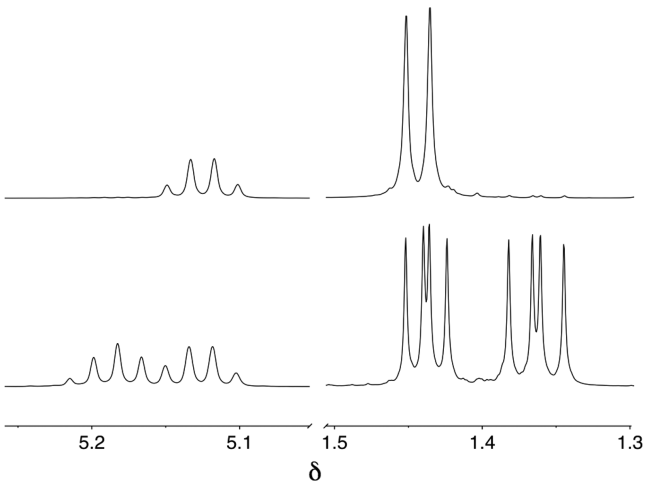

Figure 2. ^{1}H NMR spectra (C_6D_6) of methine (left) and methyl (right) regions for enantiopure (*S,S,S*)-PhSi[OCH(Me)Ph]$_3$ (top) and the mixture of isomers of PhSi[OCH(Me)Ph]$_3$ (bottom).

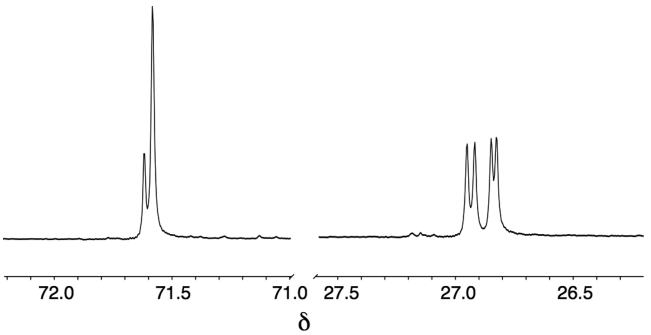

Figure 3. ^{13}C{^{1}H} NMR spectra (C_6D_6) of methine (left) and methyl (right) signals for the mixture of *RRR/SSS* and *RSS/RRS* isomers of PhSi[OCH(Me)Ph]$_3$.

Correspondingly, the ^{13}C{^{1}H} NMR spectrum of PhSi[OCH(Me)Ph]$_3$ exhibits four signals for the methyl groups (Figure 3). Thus, both the ^{1}H and ^{13}C{^{1}H} NMR spectra indicate that, in solution, the methyl groups of PhSi[OCH(Me)Ph]$_3$ are in *four* equally populated unique chemical environments.

Albeit unusual, the spectroscopic patterns are, nevertheless, easily rationalized by recognizing that PhSi[OCH(Me)Ph]$_3$ exists as two diastereomers by virtue of the fact that the molecule contains three chiral centers. Specifically, a molecule with three chiral centers can have a maximum of 8 (*i.e.*, 2^3) stereoisomers, which are determined by the *R* and *S* configurations at each center; however, in view of the local three-fold symmetry of PhSi[OCH(Me)Ph]$_3$, the number of isomers is reduced to four. Thus, PhSi[OCH(Me)Ph]$_3$ consists of two diastereomers, each of which exists as an enantiomeric pair, *i.e.*, *RRR/SSS* and *RRS/SSR*, as illustrated in Figure 4. Statistically, however, the *RRS/SSR* set of isomers are a factor of 3 more prevalent than the *RRR/SSS* isomers, evidence for which is provided by the fact that the ^{29}Si{^{1}H} NMR spectrum exhibits two signals at −59.85 and −59.92 ppm in a 3:1 ratio (Figure 5), while the enantiopure compound shows only a signal at −59.92 ppm. Both of these chemical shifts are consistent with a PhSi(OR)$_3$ species, as illustrated by the data for PhSiH$_{3-x}$(OR)$_x$ (x = 0−3) in Table 2.[29]

In view of the fact that the *RRR/SSS* isomers possess a C_3 axis, the three methyl groups of these isomers are chemically

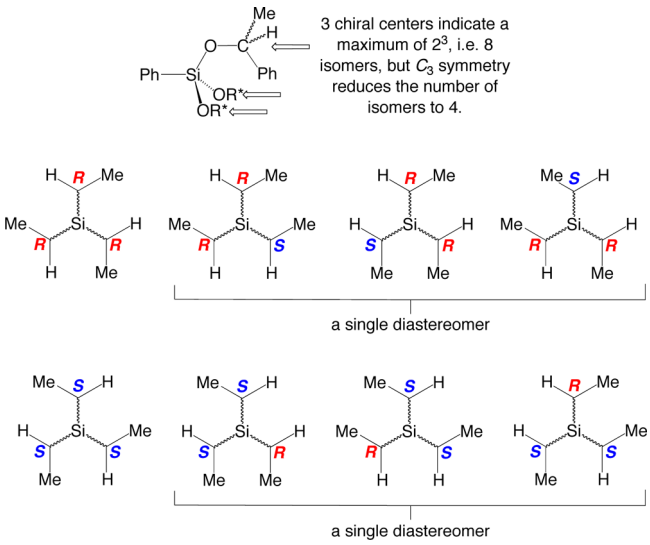

Figure 4. Stereoisomers of PhSi[OCH(Me)Ph]$_3$ (the phenyl groups and oxygen atoms attached to the asymmetric carbon centers are omitted for clarity). Molecules with either *RRS* or *SSR* configurations are statistically a factor of 3 more prevalent than those with either *RRR* or *SSS* configurations.

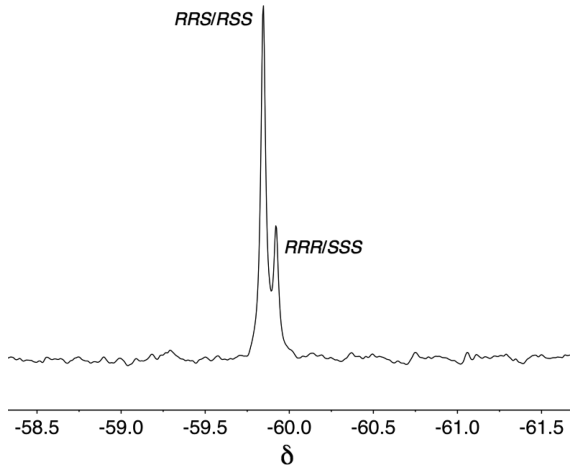

Figure 5. ^{29}Si{^{1}H} NMR spectrum of PhSi[OCH(Me)Ph]$_3$ illustrating a 3:1 ratio of diastereomers in C_6D_6.

equivalent.[36] On the other hand, the *RRS/SSR* isomers are devoid of symmetry, with the result that the three methyl groups are chemically inequivalent. As such, a 1:3 statistical mixture of *RRR/SSS* and *RRS/SSR* isomers of PhSi[OCH(Me)Ph]$_3$ would give rise to spectroscopic signals associated with *four equally abundant* sets of methyl groups (Figure 6). Thus, the ^{13}C{^{1}H} NMR spectrum exhibits four signals in a 1:1:1:1 ratio, while the ^{1}H NMR spectrum exhibits eight signals in a 1:1:1:1:1:1:1:1 ratio, corresponding to four doublets. Similar patterns are also observed for the methine and phenyl groups, although they are less easily identified due to overlap.

Evidence that the above assignment is correct is provided by the synthesis of enantiopure (*R,R,R*)-PhSi[OCH(Me)Ph]$_3$ and (*S,S,S*)-PhSi[OCH(Me)Ph]$_3$ by the [κ^3-Tptm]ZnH-catalyzed alcoholysis of PhSiH$_3$ with (*R*)-(+)-1-phenylethanol and (*S*)-(−)-1-phenylethanol, respectively (Scheme 2). For example, the ^{1}H NMR spectrum of (*S,S,S*)-PhSi[OCH(Me)Ph]$_3$ exhibits a simple doublet for the methyl groups (Figure 2), while the ^{13}C{^{1}H} NMR spectrum exhibits a singlet. Comparison of the

DOI: 10.1021/acs.organomet.5b00506
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Table 2. $^{29}Si\{^1H\}$ NMR Chemical Shift Data for $PhSiH_{3-x}(OR)_x$

$PhSiH_{3-x}(OR)_x$	δ (ppm)	ref
x = 0		
$PhSiH_3$	−60.1[a]	29b
x = 1		
$PhSiH_2(OEt)$	−28.6[a]	30, 31
$PhSiH_2(OPr^i)$	−22.5[a]	30, 31
$PhSiH_2[OCH(Me)Ph]$	−20.4[a]	30, 31
x = 2		
$PhSiH(OEt)_2$	−30.53[a]	this work
	−30.8[a]	30
$PhSiH(OPr^i)_2$	−34.58[a]	this work
	−34.8[a]	30
	−34.3[b]	32
$PhSiH[OCH(Me)Et]_2$	−33.24 (*RsS*), −33.66 (*RR/SS*), −34.18 (*RrS*)[a]	this work
$PhSiH(OCHEt_2)_2$	−32.55[a]	this work
$PhSiH(OCy)_2$	−34.63[a]	this work
$PhSiH[OCH(Me)Ph]_2$	−32.15 (*RR/SS*), −32.25 (*RsS*), −32.41 (*RrS*)[a]	this work
	−32.6[a]	19, 30, 31
$PhSiH(OCHPh_2)_2$	−30.09[a]	this work
x = 3		
$PhSi(OEt)_3$	−57.9[a]	this work
	−60.3[b]	32
	−60.5[c]	33
	−58.2[b]	34
$PhSi(OCH_2Ph)_3$	−56.4[a]	this work
	−55.7[b]	35
$PhSi(OPr^i)_3$	−61.8[a]	this work
$PhSi[OCH(Me)Et]_3$	−62.26 (*RRR/SSS*), −62.30 (*RSS/RRS*)[a]	this work
$PhSi(OCHEt_2)_3$	−63.04[a]	this work
$PhSi(OCy)_3$	−61.62[a]	this work
$PhSi[OCH(Me)Ph]_3$	−59.85 (*RRR/SSS*), −59.92 (*RSS/RRS*)[a]	this work
	−32.7[a,d]	19, 30
$PhSi(OCHPh_2)_3$	−58.1[a]	this work

[a]C_6D_6. [b]$CDCl_3$. [c]Neat. [d]This value is not characteristic of $PhSi(OR)_3$ compounds and is presumably erroneous.

^1H and $^{13}C\{^1H\}$ NMR spectra of (*R,R,R*)-$PhSi[OCH(Me)Ph]_3$ and (*S,S,S*)-$PhSi[OCH(Me)Ph]_3$ with the statistical mixture of *RRR/SSS* and *RRS/SSR* isomers thus enables the spectral assignment for the *RRS/SSR* diastereomers.

Interestingly, although $PhSi[OCH(Me)Ph]_3$ has been previously reported, the occurrence of isomers has not been explicitly discussed. In this regard, it is pertinent to note that the original report actually describes the ^1H NMR spectroscopic signals of methyl groups as a doublet at δ 1.36 ppm (J = 6 Hz) in C_6D_6,[19,37] which is not consistent with the interpretation described herein.[38−40]

As discussed above for $PhSi[OCH(Me)Ph]_3$, the bis(alkoxy) compound $PhSiH[OCH(Me)Ph]_2$ also exists as a mixture of diastereomers resulting from the different *R* and *S* configurations of the alkoxy groups, with the result that the methyl groups do not appear as a simple doublet in the ^1H NMR spectrum (Figure 7). Specifically, $PhSiH[OCH(Me)Ph]_2$ consists of a mixture of *RR/SS*, *RrS*, and *RsS* diastereomers (Figure 8), each of which has a unique ^1H NMR spectrum.

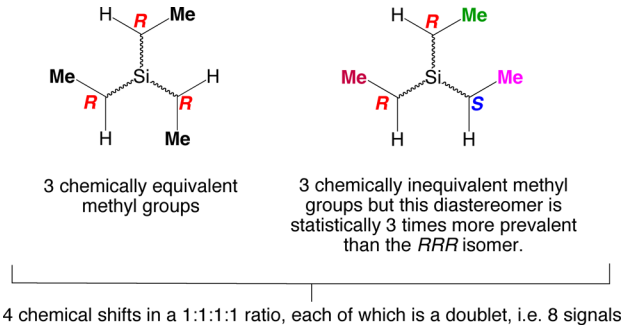
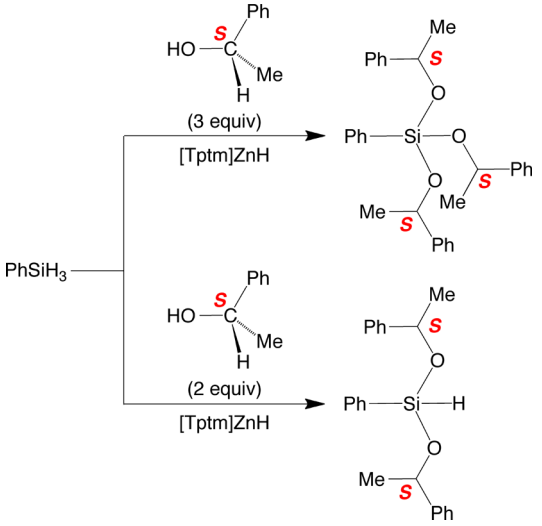


Figure 6. Origin of eight signals for the methyl groups of $PhSi[OCH(Me)Ph]_3$ in the ^1H NMR spectrum, with chemically equivalent methyl groups coded by color. The methyl groups of the *RRR* isomer are chemically equivalent, whereas the methyl groups of the *RRS* isomer are chemically inequivalent; however, since the *RRS* isomer is statistically a factor of 3 more prevalent than the *RRR* isomer, four equally abundant methyl groups are observed. A similar argument pertains to comparison of their enantiomers, *i.e.*, *SSS* and *SSR*.

Scheme 2. Synthesis of (*S,S,S*)-$PhSi[OCH(Me)Ph]_3$ and (*S,S*)-$PhHSi[OCH(Me)Ph]_2$ *via* Alcoholysis



The existence of the *RrS* and *RsS* diastereomers is a consequence of the fact that the silicon in (*R,S*)-$PhSiH[OCH(Me)Ph]_2$ is a "pseudoasymmetric center",[41] a term that is used to describe a stereogenic center in an achiral molecule, and is given the notation *r* and *s*. Since the *RR* and *SS* isomers are enantiomers, there are three sets of diastereomers, namely *RR/SS*, *RrS*, and *RsS*, each of which has a unique spectral signature, as clearly indicated by the observation of three signals in the $^{29}Si\{^1H\}$ NMR spectrum (Figure 9) and three signals associated with the [SiH] moieties in the ^1H NMR spectrum (Figure 10). The distribution of *RR/SS*, *RrS*, and *RsS* isomers is 2:1.06:0.93,[42,43] which corresponds closely to the statistical distribution of 2:1:1.

However, while the spectral features of $PhSiH[OCH(Me)Ph]_2$ associated with the [SiH] moieties provide evidence for the three chemical environments that are consistent with the presence of three diastereomers, the methyl region of the ^1H NMR spectrum exhibits signals due to *four* chemically inequivalent methyl groups. The observation of four different

DOI: 10.1021/acs.organomet.5b00506
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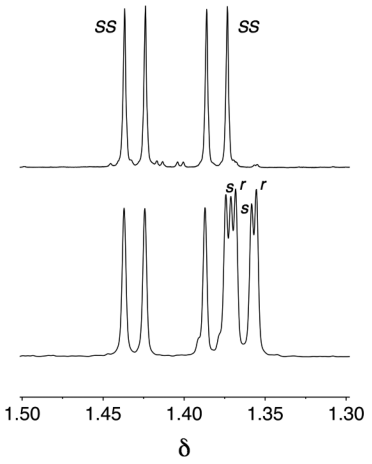

Figure 7. Methyl region of the ^{1}H NMR spectrum of PhSiH[OCH(Me)Ph]$_2$ illustrating four doublets associated with the three *RR*/*SS*, *RrS* ("*r*"), and *RsS* ("*s*") diastereomers (bottom) and two doublets associated with (*S*,*S*)-PhSiH[OCH(Me)Ph]$_2$ (top). Note that of the *RrS* and *RsS* diastereomers, *RrS* is arbitrarily assigned to the more abundant isomer.

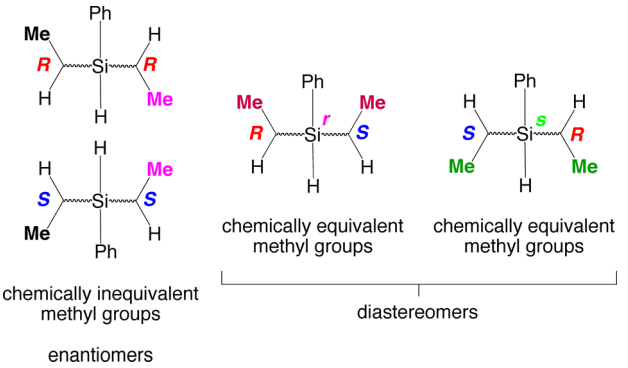

Figure 8. Isomers of PhSiH[OCH(Me)Ph]$_2$, with chemically equivalent methyl groups coded by color (the phenyl groups and oxygen atoms attached to the asymmetric carbon centers are omitted for clarity). While the methyl groups of the *RR* and *SS* isomers are chemically inequivalent, the methyl groups of the *RrS* and *RsS* isomers are chemically equivalent due to the presence of a mirror plane. As such, the methyl region of the ^{1}H NMR spectrum consists of four doublets in a ratio that reflects the relative abundance of the *RR*/*SS*, *RrS*, and *RsS* diastereomers.

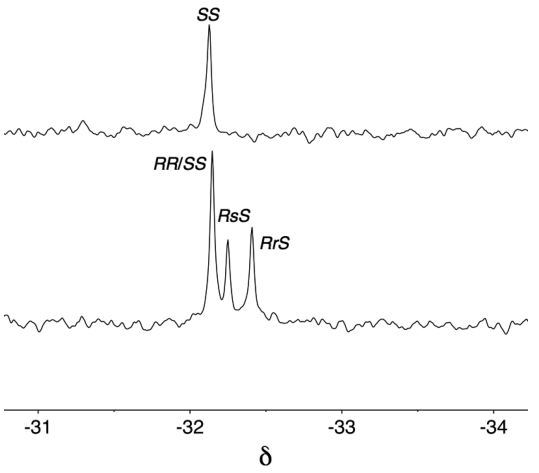

Figure 9. ^{29}Si{^{1}H} NMR spectrum illustrating the three *RR*/*SS*, *RrS*, and *RsS* diastereomers of PhSiH[OCH(Me)Ph]$_2$ (bottom), and enantiopure (*S*,*S*)-PhSiH[OCH(Me)Ph]$_2$ (top).

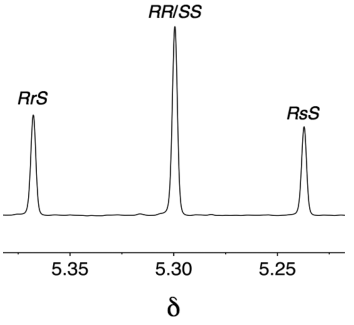

Figure 10. Si−H region of the ^{1}H NMR spectrum of PhSiH[OCH(Me)Ph]$_2$ illustrating the three *RR*/*SS*, *RrS*, and *RsS* diastereomers.

chemical environments for the methyl groups of three diastereomers is a consequence of the fact that the *RR* and *SS* enantiomers do not possess a mirror plane, thereby resulting in diastereotopic methyl groups. In contrast, both the *RrS* and *RsS* diastereomers exhibit chemically equivalent methyl groups because the molecules possess a mirror plane. The methyl region of the ^{1}H NMR spectrum of PhSiH[OCH(Me)Ph]$_2$ thus exhibits eight signals (*i.e.*, four doublets) with an intensity distribution that is consistent with the 2:1.06:0.93 diastereomeric composition as indicated by the SiH signals.

Support for this assignment is provided by the synthesis of the *SS* isomer by the [κ^3-Tptm]ZnH-catalyzed alcoholysis of PhSiH$_3$ with 2 equiv of (*S*)-(−)-1-phenylethanol (Scheme 2), thereby demonstrating that (*S*,*S*)-PhSiH[OCH(Me)Ph]$_2$ is characterized by two doublets in the methyl region of the ^{1}H NMR spectrum. Furthermore, the synthesis of (*S*,*S*)-PhSiH[OCH(Me)Ph]$_2$ allows identification of the signals associated with the [SiH] moiety in both the ^{29}Si{^{1}H} and ^{1}H NMR spectra.

As noted above for PhSi[OCH(Me)Ph]$_3$, the NMR data presented for PhSiH[OCH(Me)Ph]$_2$ in the literature are highly varied. For example, the appearance of the methyl groups has been described in terms of a doublet,[44] three doublets,[45] a multiplet,[25b] and a "few" overlapping doublets,[46] with there being no report of which we are aware that refers to the pattern as four doublets. The SiH region of the ^{1}H NMR spectrum has been described as comprising three singlets,[45,46] which is consistent with our observations, but has also been described as a singlet.[44] Finally, the ^{29}Si{^{1}H} NMR spectrum has been described as a singlet,[44] in contrast to the three signals that we observe.

Multiple Insertion of RC(O)R′ into Ph$_2$SiH$_2$. Ph$_2$SiH$_2$ is also a commonly used reagent for the hydrosilylation of aldehydes and ketones, although it often exhibits reduced reactivity compared to PhSiH$_3$.[47] Therefore, it is significant that [κ^3-Tptm]ZnH is also an effective catalyst for room temperature hydrosilylation reactions employing Ph$_2$SiH$_2$, affording products derived from both single and double insertion (Scheme 3 and Tables 3 and 4). The ability of [κ^3-Tptm]ZnH to achieve double insertion of ketones into Ph$_2$SiH$_2$ is of note since only the monoinsertion product is typically observed.[48] The reactivity of Ph$_2$SiH$_2$ towards insertion is, nevertheless, lower than that of PhSiH$_3$, as illustrated by the fact that the zinc-catalyzed reaction of PhC(O)Me with an excess of a *ca.* 1:1 mixture of PhSiH$_3$ and Ph$_2$SiH$_2$ results in the formation of a

DOI: 10.1021/acs.organomet.5b00506
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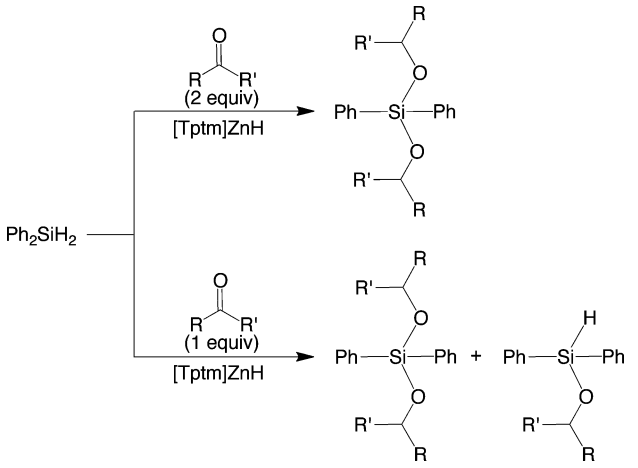
Scheme 3. Zinc-Catalyzed Insertion of Carbonyl Compounds into the Si−H Bonds of $PhSiH_3$[a]



[a]See Table 3 for conditions.

mixture of monophenylsilane derivatives, $PhSiH_2[OCH(Me)Ph]$ and $PhSiH[OCH(Me)Ph]_2$, and the diphenylsilane derivative, $Ph_2SiH[OCH(Me)Ph]$, of which the latter is a minor component with a mole fraction of 0.19.

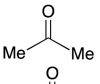
As observed for hydrosilylation involving $PhSiH_3$, the double insertion of prochiral ketones into the two Si−H bonds of Ph_2SiH_2 results in the formation of diastereomeric mixtures. Thus, $Ph_2Si[OCH(Me)Ph]_2$ exists as a mixture of *RR*/*SS* and *RS* diastereomers (Figure 11), which can be distinguished by $^{29}Si\{^1H\}$ NMR spectroscopy (Figure 12).

In contrast to $PhSiH[OCH(Me)Ph]_2$, however, in which the methyl groups of the *RR*/*SS* isomers are diastereotopic, the methyl groups of the *RR*/*SS* isomers of $Ph_2Si[OCH(Me)Ph]_2$ are chemically equivalent by virtue of a C_2 axis and thus give rise to a single doublet in the ^1H NMR spectrum. Likewise, the methyl groups of the *RS* isomer are rendered equivalent by a mirror plane, and therefore also give rise to a doublet. As such, the diastereomeric mixture of $Ph_2Si[OCH(Me)Ph]_2$ exhibits two doublets (with ratios that correspond to the relative abundance of the *RR*/*SS* and *RS* diastereomers) in the methyl region of the ^1H NMR spectrum (Figure 13).[54]

The signals attributable to (*S*,*S*)-$Ph_2Si[OCH(Me)Ph]_2$ (δ = 1.40, J = 7 Hz) have been assigned by its independent synthesis *via* the zinc-catalyzed reaction between Ph_2SiH_2 and (*S*)-(−)-1-phenylethanol (Figure 13). On the basis of this assignment, it is evident that the *RR*/*SS* and *RS* diastereomers are formed in a ratio of 1:0.62,[55] which is significantly different to the statistical ratio of 1.0:1.0. It is, therefore, evident that the diastereoselectivity for double insertion of a prochiral ketone into Ph_2SiH_2 is greater than that for insertion into $PhSiH_3$.

3. Mechanism of Hydrosilylation. A large variety of mechanisms for hydrosilylation of carbonyl compounds has been discussed in the literature.[56] For example, two of the earliest proposed mechanisms involve sequential *(i)* oxidative addition of a Si−H bond, *(ii)* coordination of the carbonyl compound, *(iii)* insertion of the carbonyl moiety into either the M−H or M−Si bond, and *(iv)* Si−O or C−H bond reductive elimination.[1,57,58] A variant for silanes that have more than one hydride involves, after oxidative addition of the Si−H bond: *(i)* coordination of the carbonyl group to silicon, *(ii)* transfer of a silicon hydride to carbon, and *(iii)* Si−H bond reductive elimination.[59] Another class of proposed mechanisms involves the attack of a carbonyl oxygen upon a coordinated silicon species (*e.g.*, silylene moieties,[58,60] silane adducts,[56a,61−64] and hypervalent silyl groups).[65,66] Mechanisms that involve σ-bond

Table 3. [κ^3-Tptm]ZnH-Catalyzed Insertion of Aldehydes and Ketones into the Si−H Bonds of Ph_2SiH_2

aldehyde/ ketone	Ph_2SiH_2:RR′CO ratio 1:1[a] distribution	time (h:m)	TOF (h^{-1})	1:2.2[b] distribution	time (h:m)	TOF (h^{-1})
	$Ph_2Si[OCH(R)R']_2$ (54%), $Ph_2SiH[OCH(R)R']$ (46%)	0:05	1200[c]	$Ph_2Si[OCH(R)R']_2$ (100%)	0:10	545[c]
	$Ph_2Si[OCH(R)R']_2$ (93%), $Ph_2SiH[OCH(R)R']$ (7%)	0:45	133	$Ph_2Si[OCH(R)R']_2$ (100%)	1:50	49
	$Ph_2SiH[OCH(R)R']$ (100%)	4:15	24	$Ph_2Si[OCH(R)R']_2$ (100%)	24:00	4
	$Ph_2SiH[OCH(R)R']$ (100%)	13:00	8	$Ph_2Si[OCH(R)R']_2$ (100%)	17:00	5
	$Ph_2SiH[OCH(R)R']$ (100%)	23:00	4	$Ph_2Si[OCH(R)R']_2$ (100%)	21:00	4
	$Ph_2SiH[OCH(R)R']$ (100%)	12:00	8	$Ph_2Si[OCH(R)R']_2$ (100%)	29:00	3
	$Ph_2SiH[OCH(R)R']$ (100%)	1:30	67	$Ph_2Si[OCH(R)R']_2$ (100%)	24:00	4
	$Ph_2SiH[OCH(R)R']$ (100%)	0:25	240	$Ph_2Si[OCH(R)R']_2$ (100%)	4:00	23

[a]1.0 mol % catalyst based on Ph_2SiH_2; reactions performed at room temperature in C_6D_6, and conversions determined by ^1H NMR spectroscopy; TON = 100; product mixture contains excess Ph_2SiH_2. [b]2.2 mol % catalyst based on Ph_2SiH_2; reactions performed at room temperature in C_6D_6, and conversions determined by ^1H NMR spectroscopy; TON = 91. [c]In view of the high activity, these values represent the minimum TOF.

DOI: 10.1021/acs.organomet.5b00506
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Table 4. $^{29}Si\{^1H\}$ NMR Data for $Ph_2SiH_{2-x}(OR)_x$

$Ph_2SiH_{2-x}(OR)_x$	δ (ppm)	ref
***x* = 0**		
Ph_2SiH_2	−33.4[a]	49
	−35.7	50
***x* = 1**		
$Ph_2SiH(OEt)$	−11.98[a]	this work
	−17.6[b]	51
$Ph_2SiH(OPr^i)$	−14.81[a]	this work
	−20.5[b]	51
$Ph_2SiH(OCH_2Ph)$	−10.27[a]	this work
	−16.1[b]	51
$Ph_2SiH[OCH(Me)Et]$	−14.14[a]	this work
$Ph_2SiH(OCHEt_2)$	−13.38[a]	this work
$Ph_2SiH(OCy)$	−15.03[a]	this work
	−20.9[b]	51
$Ph_2SiH[OCH(Me)Ph]$	−12.94[a]	this work
$Ph_2SiH(OCHPh_2)$	−11.52[a]	this work
	−19.30[c]	52
***x* = 2**		
$Ph_2Si(OEt)_2$	−32.11[a]	this work
	−32.6[b]	32
$Ph_2Si(OCH_2Ph)_2$	−30.02[a]	this work
	−30.0[b]	53
$Ph_2Si(OPr^i)_2$	−35.53[a]	this work
$Ph_2Si[OCH(Me)Et]_2$	−35.65, −35.69[a]	this work
$Ph_2Si(OCHEt_2)_2$	−35.55[a]	this work
$Ph_2Si(OCy)_2$	−35.65[a]	this work
$Ph_2Si[OCH(Me)Ph]_2$	−33.30, −33.23[a]	this work
	−33.91, −33.97[b]	this work
	−39.45, −33.77[b,d]	27
$Ph_2Si(OCHPh_2)_2$	−30.71[a]	this work

[a]C_6D_6. [b]$CDCl_3$. [c]CD_2Cl_2. [d]The reported value of −39.45 is very different from the value that we observe in the same solvent.

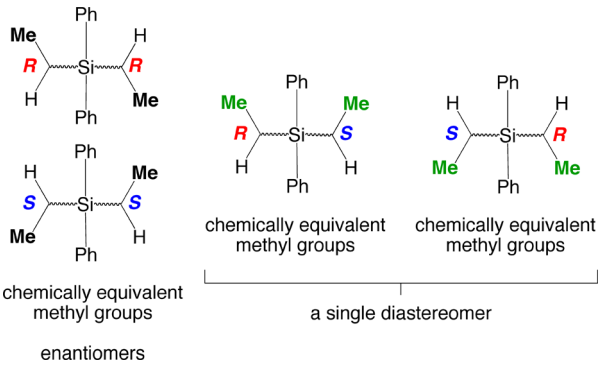

Figure 11. Isomers of $Ph_2Si[OCH(Me)Ph]_2$, with chemically equivalent methyl groups coded by color (the phenyl groups and oxygen atoms attached to the asymmetric carbon centers are omitted for clarity). The methyl groups of the *RR* and *SS* isomers are chemically equivalent due to the presence of a C_2 axis, while the methyl groups of the *RS* isomer are chemically equivalent due to the presence of a mirror plane. As such, the ^1H NMR spectrum consists of two doublets in a ratio that reflects the relative abundance of the *RR*/*SS* and *RS* diastereomers.

metathesis processes have been proposed for both early[67] and late[68,69] transition metals, and also main group metals.[70] The active catalytic species for such mechanisms is a terminal

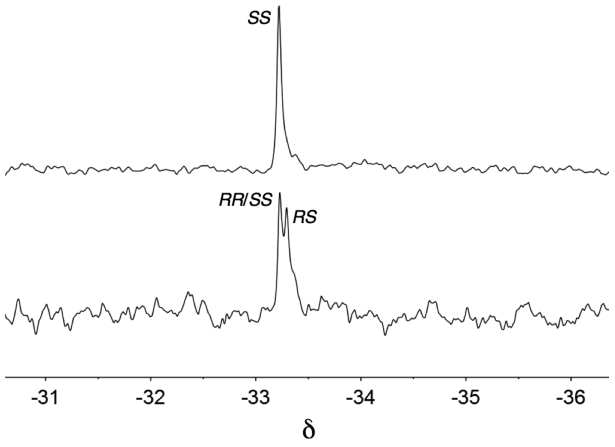

Figure 12. $^{29}Si\{^1H\}$ NMR spectrum illustrating the *RR*/*SS* and *RS* diastereomers of $Ph_2Si[OCH(Me)Ph]_2$ in C_6D_6 (bottom) and (*S*,*S*)-$Ph_2Si[OCH(Me)Ph]_2$ (top).

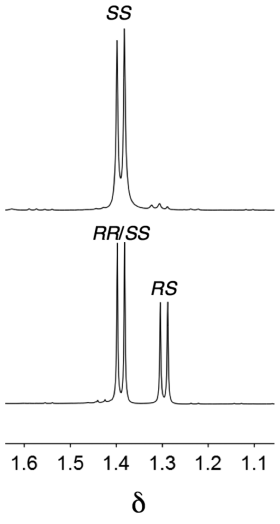

Figure 13. Methyl region of the ^1H NMR spectrum of $Ph_2Si[OCH(Me)Ph]_2$ illustrating two doublets associated with the *RR*/*SS* and *RS* diastereomers (bottom), and enantiopure (*S*,*S*)-$Ph_2Si[OCH(Me)Ph]_2$ (top).

hydride complex, [M]−H, that undergoes insertion of the carbonyl compound to generate an alkoxide species, [M]−OC(H)(R)R′, which undergoes metathesis with a silane to release the alkoxysilane and thereby regenerate the hydride catalyst, [M]−H.

In view of the presence of the hydride ligand, a reasonable mechanism for the [κ^3-Tptm]ZnH-catalyzed hydrosilylation of carbonyl compounds is illustrated in Scheme 4, and consists of two principal steps, namely *(i)* insertion of the carbonyl group into the Zn−H bond of [κ^3-Tptm]ZnH to form an alkoxide, [Tptm]ZnOCH(R)R′, and *(ii)* metathesis of the Zn−O and H−Si bonds to regenerate [κ^3-Tptm]ZnH and release the alkoxysilane, $PhSiH_2[OCH(R)R']$.[70] Additional cycles allow for the subsequent formation of the double and triple insertion products, $PhSiH[OCH(R)R']_2$ and $PhSi[OCH(R)R']_3$. A similar mechanism would also apply for the insertion of the carbonyl group into the Si−H bonds of Ph_2SiH_2. Precedent for these steps is provided by the observations that *(i)* CO_2 inserts into the Zn−H bond of [κ^3-Tptm]ZnH,[11,71] and *(ii)* silanes are capable of reacting with the Zn−O bonds of [Tptm]ZnOR and $[Tptm]ZnO_2CH$ to form [κ^3-Tptm]ZnH.[11,12]

DOI: 10.1021/acs.organomet.5b00506
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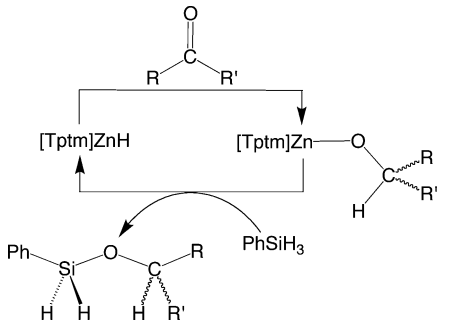
Scheme 4. Possible Mechanism for the Zinc-Catalyzed Insertion of a Carbonyl Group into Si−H Bonds, As Illustrated for $PhSiH_3$



However, while compounds that contain a terminal hydride ligand are potential candidates for a catalytic cycle involving σ-bond metathesis pathways, it must be noted that the hydride ligand need not be directly involved in the mechanism; rather, it is possible that the hydride remains on the metal center during the course of the transformation and serves a role as a spectator ligand.[21,72−74] Several pieces of evidence, however, indicate that the hydride ligand of [κ^3-Tptm]ZnH plays a critical role in the mechanism.

As an illustration, ^{1}H NMR spectroscopy demonstrates that insertion of the carbonyl group into the Zn−H bond of [κ^3-Tptm]ZnH to form an alkoxide, [Tptm]ZnOCH(R)R′, is facile, and that subsequent treatment with $PhSiH_3$ regenerates [κ^3-Tptm]ZnH and liberates an alkoxysilane. For example, treatment of [κ^3-Tptm]ZnH with Ph_2CO generates [Tptm]-$ZnOCHPh_2$, of which the alkoxy group is identified by a singlet at δ 6.28 in the ^{1}H NMR spectrum. The corresponding reaction of [κ^3-Tptm]ZnD results in the formation of the isotopologue, $[Tptm]ZnOCDPh_2$, as indicated by ^{1}H NMR spectroscopy. Furthermore, the deuterium incorporation into the alkoxide ligand is maintained upon release of the alkoxysilane when treated with $PhSiH_3$. Likewise, treatment of [κ^3-Tptm]ZnH with PhC(O)Me generates [Tptm]ZnOCH(Me)Ph,[75] of which the alkoxy group is identified by a quartet at δ 5.41 and a doublet at δ 1.59 in the ^{1}H NMR spectrum. The corresponding reaction of [κ^3-Tptm]ZnD results in the formation of the isotopologue, [Tptm]ZnOCD(Me)Ph, and deuterium incorporation into the alkoxide ligand is maintained upon release of the alkoxysilane when treated with $PhSiH_3$.

[κ^3-Tptm]ZnH also reacts with PhCHO to generate $[Tptm]ZnOCH_2Ph$, and the corresponding reaction of [κ^3-Tptm]ZnD generates [Tptm]ZnOCD(H)Ph, but does not result in deuterium incorporation into excess PhCHO. This observation demonstrates that insertion of the carbonyl compound into the Zn−H bond is irreversible on the time scale of the experiments.

With respect to the final step, *i.e.*, cleavage of the Zn−OR bond by the silane to regenerate [κ^3-Tptm]ZnH, recent theoretical calculations have demonstrated that this reaction is facile and that the transformation involves a 4-centered transition state in which the silicon has an approximately trigonal bipyramidal geometry.[76] Thus, the data are consistent with a general mechanism for hydrosilylation of aldehydes and ketones that involves carbonyl insertion into the Zn−H bond to form a alkoxide species, [Tptm]ZnOCH(R)R′, followed by metathesis with either $PhSiH_3$ or Ph_2SiH_2 to liberate the alkoxysilane and regenerate the zinc hydride catalyst.

It is also worth discussing the observation that the ratio of the *RRR*/*SSS* and *RRS*/*SSR* diastereomers of $PhSi[OCH(Me)Ph]_3$ is close to statistical (*i.e.*, 1:3), as is the ratio of the *RR*/*SS*, *RrS*, and *RsS* diastereomers of $PhSiH[OCH(Me)Ph]_2$ (*i.e.*, 2:1:1), whereas the *RR*/*SS* and *RS* diastereomers of $Ph_2Si[OCH(Me)Ph]_2$ are formed in a 1:0.62 ratio that is distinctly different than the statistical value (*i.e.*, 1:1).

In order to examine whether it is feasible for isomer interconversion to occur under the reaction conditions, we investigated the possibility that a mixture of (*R*,*R*,*R*)-$PhSi[OCH(Me)Ph]_3$ and (*S*,*S*,*S*)-$PhSi[OCH(Me)Ph]_3$ enantiomers could convert to the *RRS* and *RSS* diastereomers. Significantly, ^{1}H NMR spectroscopy demonstrated that isomer interconversion did not occur at room temperature (or at 100 °C), either in the presence or absence of the zinc catalyst, [κ^3-Tptm]ZnH. Thus, it is evident that the approximately statistical distribution of *RRR*/*SSS* and *RRS*/*SSR* diastereomers of $PhSi[OCH(Me)Ph]_3$ represents a kinetic distribution, although this distribution may also be coincidentally the same as the thermodynamic distribution.

With respect to the formation of $Ph_2Si[OCH(Me)Ph]_2$, we note that monitoring of the zinc-catalyzed reaction between Ph_2SiH_2 and PhC(O)Me as a function of the extent reaction indicates that the ratio of *RR*/*SS* and *RS* diastereomers is constant throughout the reaction. Since the ratio is constant, the observation indicates that the distribution either reflects the kinetic selectivity or the thermodynamic selectivity if isomer interconversion is facile. On the basis that the *RRR* and *SSS* isomers of $PhSi[OCH(Me)Ph]_3$ do not redistribute readily (*vide supra*), it is most likely that the 1:0.62 ratio of *RR*/*SS* and *RS* diastereomers of $Ph_2Si[OCH(Me)Ph]_2$ corresponds to a kinetic selectivity. We have also observed that a different diastereomeric ratio (1:0.87) is obtained employing a cesium catalyst,[18] and that the 1:0.62 ratio does not change upon heating at 100 °C, an observation which indicates that isomer interconversion is not facile under these conditions.

In addition to probing for isomer interconversion, we have also examined the possibility of alkoxide exchange between different pairs of molecules, namely *(i)* $PhSi(OPr^i)_3$ and (*S*,*S*,*S*)-$PhSi[OCH(Me)Ph]_3$, and *(ii)* $Ph_2Si(OPr^i)_2$ and (*S*,*S*)-$Ph_2Si[OCH(Me)Ph]_2$. Significantly, no scrambling of alkoxide ligands is observed under the reaction conditions, or upon heating,[77] which also supports the above observation that isomer interconversion does not occur readily.

CONCLUSIONS

In summary, the zinc hydride complex, [κ^3-Tptm]ZnH, is an effective catalyst for the multiple insertion of carbonyl compounds into the Si−H bonds of $PhSiH_3$ and Ph_2SiH_2, *via* a mechanism that is proposed to involve insertion of the carbonyl group into the Zn−H bond to afford an alkoxy species, followed by metathesis with the silane to release the alkoxysilane and regenerate the zinc hydride catalyst. Multiple insertion of prochiral ketones results in the formation of diastereomeric mixtures of alkoxysilanes that can be identified by NMR spectroscopy. Since the alkoxysilanes can also be obtained *via* the zinc-catalyzed dehydrocoupling of alcohols with silanes, the reactions with (*R*)-(+)-1-phenylethanol and (*S*)-(−)-1-phenylethanol provide a means of identifying the diastereomers that result from the hydrosilylation of acetophenone.

DOI: 10.1021/acs.organomet.5b00506
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EXPERIMENTAL SECTION

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques under an argon atmosphere unless otherwise specified.[78] Solvents were purified and degassed by using standard procedures. ^{1}H NMR spectra were measured on Bruker 300 DRX, Bruker 300 DPX, Bruker 400 Avance III, Bruker 400 Cyber-enabled Avance III, and Bruker 500 DMX spectrometers. ^{1}H chemical shifts are reported in ppm relative to internal $SiMe_4$ (δ = 0). ^{13}C NMR spectra are reported in ppm relative to internal $SiMe_4$ (δ = 0). ^{29}Si chemical shifts are reported in ppm and were referenced internally with respect to $SiMe_4$ (δ = 0). Coupling constants are given in hertz. [κ^3-Tptm]ZnH was prepared by the literature method,[11] $PhSiH_3$, PhCHO, PhC(O)Me, Ph_2CO, Me_2CO, MeC(O)H, MeC(O)Et, Et_2CO, cyclohexanone, 1-phenylethanol, (*R*)-(+)-1-phenylethanol, and (*S*)-(+)-2-butanol were obtained from Sigma-Aldrich, Ph_2SiH_2 was obtained from Alfa Aesar, and (*S*)-(−)-1-phenylethanol was obtained from Fluka. PhCHO was distilled prior to use.

General Procedure for Catalytic Comparisons of Hydrosilylation Reactions. *1:1 $PhSiH_3$:RC(O)R′.* A solution of $PhSiH_3$ (79 mg, 0.73 mmol) and RC(O)R′ (0.73 mmol) in C_6D_6 (0.7 mL) was treated with [κ^3-Tptm]ZnH (3 mg, 0.0073 mmol) in an NMR tube equipped with a J. Young valve. The catalytic reactions were monitored by ^{1}H NMR spectroscopy and the products were identified by a combination of ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (see below).

1:3.3 $PhSiH_3$:RC(O)R′. A solution of $PhSiH_3$ (24 mg, 0.22 mmol) and RC(O)R′ (0.73 mmol) in C_6D_6 (0.7 mL) was treated with [κ^3-Tptm]ZnH (3 mg, 0.0073 mmol) in an NMR tube equipped with a J. Young valve. The catalytic reactions were monitored by ^{1}H NMR spectroscopy, and the products were identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (see below).

1:1 Ph_2SiH_2:RC(O)R′. A solution of Ph_2SiH_2 (134 mg, 0.73 mmol) and RC(O)R′ (0.73 mmol) in C_6D_6 (0.7 mL) was treated with [κ^3-Tptm]ZnH (3 mg, 0.0073 mmol) in an NMR tube equipped with a J. Young valve. The catalytic reactions were monitored by ^{1}H NMR spectroscopy, and the products were identified by a combination of ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (see below).

1:2.2 Ph_2SiH_2:RC(O)R′. A solution of Ph_2SiH_2 (61 mg, 0.33 mmol) and RC(O)R′ (0.73 mmol) in C_6D_6 (0.7 mL) was treated with [κ^3-Tptm]ZnH (3 mg, 0.0073 mmol) in an NMR tube equipped with a J. Young valve. The catalytic reactions were monitored by ^{1}H NMR spectroscopy, and the products were identified by a combination of ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (see below).

Synthesis of $PhSi(OPr^i)_3$. A suspension of [κ^3-Tptm]ZnH (6 mg, 0.015 mmol) in C_6D_6 (*ca.* 1.5 mL) in an NMR tube equipped with a J. Young valve was treated with $PhSiH_3$ (48 mg, 0.44 mmol). Acetone (85 mg, 1.46 mmol) was added, and the solution was allowed to stand at room temperature for a period of *ca.* 12 h. After this period, the volatile components were removed *in vacuo*, and the oily residue was dissolved in benzene (*ca.* 1 mL). The solution was passed through a short plug of silica, and the volatile components were removed *in vacuo* to yield $PhSi(OPr^i)_3$ as a colorless oil (78 mg, 57% yield).

Catalytic Hydrosilylation of PhC(O)Me by $PhSiH_3$ in the Absence of a Solvent. A suspension of [κ^3-Tptm]ZnH (6 mg, 0.015 mmol) in $PhSiH_3$ (48 mg, 0.44 mmol) was treated with PhC(O)Me (175 mg, 1.5 mmol) in a vial. The mixture was shaken, and an exothermic reaction ensued. An aliquot was removed after 2 min and analyzed by ^{1}H NMR spectroscopy, thereby showing complete conversion of $PhSiH_3$ to a 0.53:1 mixture of $PhSiH[OCH(Me)Ph]_2$ and $PhSi[OCH(Me)Ph]_3$ (TON = 78, TOF = 2310 h^{-1}). Another aliquot was removed after 1 h and analyzed by ^{1}H NMR spectroscopy, thereby demonstrating that the mixture had converted completely to $PhSi[OCH(Me)Ph]_3$ (TON = 88, TOF = 88 h^{-1}).

Comparison of Hydrosilylation by $PhSiH_3$ and Ph_2SiH_2. A solution (0.3 mL) of a *ca.* 1:1 mixture of $PhSiH_3$ (0.15 M) and Ph_2SiH_2 (0.15 M) in C_6D_6 was diluted with C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve and was treated sequentially with [κ^3-Tptm]ZnH (3 mg, 0.0073 mmol) and PhC(O)Me (0.8 μL, 0.0066 mmol). The sample was monitored by ^{1}H NMR spectroscopy, which demonstrated the formation of a mixture of monophenyl derivatives, $PhSiH_2[OCH(Me)Ph]$ and $PhSiH[OCH(Me)Ph]_2$, and the diphenyl derivative, $Ph_2SiH[OCH(Me)Ph]$, of which the latter is a minor component, with a mole fraction of 0.19.

Spectroscopic Evidence for an Alkoxide Intermediate, [Tptm]ZnOCH(R)R′. (i) A suspension of [κ^3-Tptm]ZnH (5 mg, 0.012 mmol) in C_7D_8 (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with PhC(O)Me and monitored by ^{1}H NMR spectroscopy, thereby demonstrating the immediate formation of an alkoxide compound, [Tptm]Zn[OCH(Me)Ph], as indicated by the observation of a quartet signal at δ 5.41 assignable to [Tptm]Zn-[OC<u>H</u>(Me)Ph] and a doublet at δ 1.59 assignable to [Tptm]Zn-[OCH(<u>Me</u>)Ph]. Addition of an excess of $PhSiH_3$ to the intermediate results in the formation of a mixture of alkoxysilanes and [κ^3-Tptm]ZnH.

(ii) A suspension of [Tptm]ZnD (5 mg, 0.012 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with PhC(O)Me and monitored by ^{1}H NMR spectroscopy, thereby demonstrating the immediate formation of an alkoxide compound, [Tptm]Zn[OCD(Me)Ph], as indicated by the observation of a singlet signal at δ 1.65 assignable to [Tptm]Zn[OCD(<u>Me</u>)Ph]. Addition of an excess of $PhSiH_3$ to the intermediate results in the formation of a mixture of deuterated alkoxysilanes and [κ^3-Tptm]ZnH.

(iii) A suspension of [κ^3-Tptm]ZnH (5 mg, 0.012 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Ph_2CO and monitored by ^{1}H NMR spectroscopy, thereby demonstrating the immediate formation of an alkoxide compound, $[Tptm]Zn[OCHPh_2]$, as indicated by the observation of a singlet at δ 6.28 assignable to $[Tptm]Zn[OC\underline{H}Ph_2]$. Addition of an excess of $PhSiH_3$ to the intermediate results in the formation of a mixture of alkoxysilanes and [κ^3-Tptm]ZnH.

(iv) A suspension of [Tptm]ZnD (5 mg, 0.012 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Ph_2CO and monitored by ^{1}H NMR spectroscopy, thereby demonstrating the immediate formation of an alkoxide compound, $[Tptm]Zn[OCDPh_2]$, with the site of deuterium incorporation being demonstrated by the absence of a signal at δ 6.28. Addition of an excess of $PhSiH_3$ to the intermediate results in the formation of a mixture of deuterated alkoxysilanes and [κ^3-Tptm]ZnH.

(v) A suspension of [κ^3-Tptm]ZnH (5 mg, 0.012 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with PhCHO and monitored by ^{1}H NMR spectroscopy, thereby demonstrating the immediate formation of an alkoxide compound, $[Tptm]Zn[OCH_2Ph]$, as indicated by the observation of a singlet at δ 5.39 assignable to $[Tptm]Zn[OC\underline{H}_2Ph]$. Addition of an excess of $PhSiH_3$ to the intermediate resulted in the formation of a mixture of alkoxysilanes and [κ^3-Tptm]ZnH.

(vi) A suspension of [κ^3-Tptm]ZnD (5 mg, 0.012 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with PhCHO and monitored by ^{1}H NMR spectroscopy, thereby demonstrating the immediate formation of an alkoxide compound, [Tptm]Zn[OCH(D)Ph], with the site of deuterium incorporation being demonstrated by reduction in the intensity of the signal at δ 5.39 (there is no observable incorporation of deuterium into the aldehyde site on the basis of integration). Addition of an excess of $PhSiH_3$ to the intermediate resulted in the formation of a mixture of deuterated alkoxysilanes and [κ^3-Tptm]ZnH.

[κ^3-Tptm]ZnH-Catalyzed Alcoholysis of $PhSiH_3$ with 1-Phenylethanol To Give $PhSi[OCH(Me)Ph]_3$. *Racemic 1-Phenylethanol.* A suspension of [κ^3-Tptm]ZnH (8 mg, 0.02 mmol) in C_6D_6 (*ca.* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with $PhSiH_3$ (88 mg, 0.81 mmol). 1-Phenylethanol (393 μL, 3.26 mmol) was added, thereby resulting in evolution of H_2 over a period of *ca.* 2.5 h. The sample was analyzed by ^{1}H NMR spectroscopy, thereby demonstrating the conversion to $PhSi[OCH(Me)Ph]_3$ as a statistical mixture of *RRR*/*SSS* and *RRS*/*RSS* diastereomers. Mass spectrum: m/z = 467.3 $\{M-1\}^+$.

(S)-(−)-1-Phenylethanol. A suspension of [κ^3-Tptm]ZnH (3 mg, 0.0073 mmol) in C_6D_6 (*ca.* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with $PhSiH_3$ (24 mg, 0.22 mmol). (*S*)-

DOI: 10.1021/acs.organomet.5b00506
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(−)-1-Phenylethanol (89 mg, 0.73 mmol) was added, thereby resulting in evolution of H_2 over a period of *ca.* 2 h. The sample was analyzed by ^{1}H NMR spectroscopy, thereby demonstrating the conversion to (*S,S,S*)-PhSi[OCH(Me)Ph]$_3$. ^{1}H NMR (C_6D_6): δ 1.44 [d, J = 6 Hz, 9H, PhSi[OCH(C$\underline{H}_3$)Ph]$_3$], 5.13 [q, J = 6 Hz, 3H, PhSi([OC$\underline{H}$(CH$_3$)Ph]$_3$], 7.04−7.24 [m, 18H, $\underline{Ph}$Si[OCH(CH$_3$)$\underline{Ph}$]$_3$], 7.82−7.84 [m, 2H, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): δ 26.93 [s, 3C, PhSi[OCH(C$\underline{H}_3$)Ph)]$_3$], 71.62 [s, 3C, PhSi[OC$\underline{H}$(CH$_3$)Ph]$_3$], 125.66 [s, 6C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 127.17 [s, 3C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 128.06 [s, 2C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 128.39 [s, 6C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 130.56 [s, 1C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 132.24 [s, 1C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 135.36 [s, 2C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 146.09 [s, 3C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$]. ^{29}Si{^{1}H} NMR (C_6D_6): δ −60.01 (*SSS*).

(R)-(+)-1-Phenylethanol. A suspension of [κ^3-Tptm]ZnH (8 mg, 0.02 mmol, 0.8 mol %) in C_6D_6 (*ca.* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with $PhSiH_3$ (88 mg, 0.81 mmol). (*R*)-(+)-1-Phenylethanol (393 μL, 3.26 mmol) was added, thereby resulting in evolution of H_2 over a period of *ca.* 2.5 h. The sample was analyzed by ^{1}H NMR spectroscopy, thereby demonstrating the conversion to (*R,R,R*)-PhSi[OCH(Me)Ph]$_3$. The volatile components were removed *in vacuo*, and the colorless oil obtained was redissolved in CH_2Cl_2 (*ca.* 1 mL) and purified by flash column chromatography (silica gel, *ca.* 3 mL) to give (*R,R,R*)-PhSi[OCH(Me)Ph]$_3$ as a colorless oil after removal of the solvent *in vacuo*.

[κ^3-Tptm]ZnH-Catalyzed Alcoholysis of $PhSiH_3$ with (*S*)-(−)-1-Phenylethanol To Give (*S,S*)-PhSiH[OCH(Me)Ph]$_2$. A suspension of [κ^3-Tptm]ZnH (3 mg, 0.0073 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with $PhSiH_3$ (24 mg, 0.22 mmol). (*S*)-(−)-1-Phenylethanol (52 μL, 0.43 mmol) was added, thereby resulting in evolution of H_2 over a period of *ca.* 20 min. The sample was analyzed by ^{1}H NMR spectroscopy, thereby demonstrating the conversion to (*S,S*)-PhSiH[OCH(Me)Ph]$_2$. ^{1}H NMR (C_6D_6, selected resonances): δ 1.38[d, J = 6 Hz, 3H, PhSiH[OCH($\underline{Me}$)Ph]$_2$], 143 [d, J = 6 Hz, 3H, PhSiH[OCH($\underline{Me}$)Ph]$_2$], 4.991 [q, J = 6 Hz, 1H, PhSiH[OC$\underline{H}$(Me)Ph]$_2$, 4.987 [q, J = 6 Hz, 1H, PhSiH[OC$\underline{H}$(Me)Ph]$_2$, 5.29 [s, 1H, PhSi$\underline{H}$[OCH(Me)Ph]$_2$. ^{13}C{^{1}H} NMR: δ 26.68 [s, 1C, PhSiH[OCH($\underline{Me}$)Ph]$_2$], 26.74 [s, 1C, PhSiH[OCH($\underline{Me}$)Ph]$_2$], 72.32 [s, 1C, PhSiH[O$\underline{C}$H(Me)Ph]$_2$], 72.36 [s, 1C, PhSiH[O$\underline{C}$H(Me)Ph]$_2$]. ^{29}Si{^{1}H} NMR (C_6D_6): δ −32.13.

[κ^3-Tptm]ZnH-Catalyzed Alcoholysis of Ph_2SiH_2 with (*S*)-(−)-1-Phenylethanol To Give (*S,S*)-Ph_2Si[OCH(Me)Ph]$_2$. A suspension of [κ^3-Tptm]ZnH (7 mg, 0.017 mmol, 2.5 mol %) in C_6D_6 (*ca.* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Ph_2SiH_2 (61 mg, 0.33 mmol) and (*S*)-(−)-1-phenylethanol (89 mg, 0.73 mmol). The sample was analyzed by ^{1}H NMR spectroscopy, thereby demonstrating the conversion to (*S,S*)-PhSiH[OCH(Me)Ph]$_2$ over a period of 45 min. ^{1}H NMR (C_6D_6, selected resonances): δ 1.39 [d, J = 6 Hz, 6H, Ph_2Si[OCH($\underline{Me}$)Ph]$_2$, 5.05 [q, J = 6 Hz, 2H, Ph_2Si[OC$\underline{H}$(Me)Ph]$_2$. ^{13}C{^{1}H} NMR (C_6D_6, selected resonance): δ 27.08 [s, 2C, Ph_2Si[OCH($\underline{Me}$)Ph]$_2$], 71.61 [s, 2C, Ph_2Si[O$\underline{C}$H(Me)Ph]$_2$]. ^{29}Si{^{1}H} NMR (C_6D_6): δ −33.23.

Investigation of Potential Scrambling in $PhSi(OR)_3$ and $Ph_2Si(OR)_2$. (i) A mixture of (*S,S,S*)-PhSi[OCH(Me)Ph]$_3$ (*ca.* 10 mg) and (*R,R,R*)-PhSi[OCH(Me)Ph]$_3$ (*ca.* 10 mg) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was allowed to stand at room temperature for 12 h and was then heated at 100 °C. The sample was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the absence of scrambling.

(ii) A mixture of (*S,S,S*)-PhSi[OCH(Me)Ph]$_3$ (*ca.* 10 mg), (*R,R,R*)-PhSi[OCH(Me)Ph]$_3$ (*ca.* 10 mg), and [κ^3-Tptm]ZnH (3 mg, 0.0073 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was allowed to stand at room temperature for 12 h and was then heated at 100 °C. The sample was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the absence of scrambling.

(iii) A mixture of (*S,S,S*)-PhSi[OCH(Me)Ph]$_3$ (*ca.* 10 mg) and PhSi(OPr^i)$_3$ (*ca.* 10 mg) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was allowed to stand at room temperature for 12 h and then heated at 100 °C. The sample was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the absence of scrambling.

(iv) A mixture of (*S,S,S*)-PhSi[OCH(Me)Ph]$_3$ (*ca.* 10 mg), PhSi(OPr^i)$_3$ (*ca.* 10 mg), and [κ^3-Tptm]ZnH (3 mg, 0.0073 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was allowed to stand at room temperature for 12 h and was then heated at 100 °C. The sample was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the absence of scrambling.

(v) A mixture of Ph_2Si(OPr^i)$_2$ (*ca.* 10 mg) and (*S,S*)-Ph_2Si[OCH(Me)Ph]$_2$ (*ca.* 10 mg) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was allowed to stand at room temperature for 12 h and was then heated at 100 °C. The sample was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the absence of scrambling.

(vi) A mixture of Ph_2Si(OPr^i)$_2$ (*ca.* 10 mg), (*S,S*)-Ph_2Si[OCH(Me)Ph]$_2$ (*ca.* 10 mg), and [κ^3-Tptm]ZnH (3 mg) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was allowed to stand at room temperature for 12 h and was then heated at 100 °C. The sample was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the absence of scrambling.

NMR Spectroscopic Data for $PhSiH_{3-x}$[OCH(R)R′]$_x$ and Ph_2SiH_{2-x}[OCH(R)R′]$_x$. The alkoxysilanes PhSi(OCH$_2$Ph)$_3$,[35] PhSiH(OCH$_2$Ph)$_2$,[79] PhSi[OCH(Me)Ph]$_3$,[19,25b,79] PhSiH[OCH(Me)Ph]$_2$,[19,25b] PhSi(OCHPh$_2$)$_3$,[19] PhSiH(OCHPh$_2$)$_2$,[19] PhSiH$_2$(OCHPh$_2$),[80] PhSi(OEt)$_3$,[25b,32] PhSiH(OEt)$_2$,[25b,30] PhSiH$_2$(OEt),[30] PhSi(OPr^i)$_3$,[19] PhSiH(OPr^i)$_2$,[25b,30,32] PhSiH$_2$(OPr^i)$_2$,[30] PhSi[OCH(Me)Et]$_3$,[81] PhSiH$_2$[OCH(Me)Et],[82] PhSi(OCy)$_3$,[83] PhSiH(OCy)$_2$,[83] PhSiH$_2$(OCy),[83] Ph_2Si(OCH$_2$Ph)$_2$,[15b] Ph_2SiH(OCH$_2$Ph),[2f,51] Ph_2Si[OCH(Me)Ph]$_2$,[18,27] Ph_2SiH[OCH(Me)Ph],[2f] Ph_2Si(OCHPh$_2$)$_2$,[18] Ph_2SiH(OCHPh$_2$),[18] Ph_2Si(OEt)$_2$,[32,84−86] Ph_2SiH(OEt),[51,87] Ph_2Si(OPr^i)$_2$,[15b] Ph_2SiH(OPr$^i_2$),[15b,51] Ph_2SiH[OCH(Me)Et],[88] Ph_2SiH(OCHEt$_2$),[2f] Ph_2Si(OCy)$_2$,[18] and Ph_2SiH(OCy)[2f,18,51] have been previously described, and NMR spectra for these compounds have been listed for a variety of solvents. Additional data obtained here for solutions in C_6D_6 are provided below.

PhSi[OCH(Me)Ph]$_3$. PhSi[OCH(Me)Ph]$_3$ exists as a statistical mixture of *RRR/SSS* and *RRS/RSS* diastereomers. ^{1}H NMR ($CDCl_3$): (a) *RRR/SSS*: δ 1.42 [d, J = 6 Hz, 9H, PhSi[OCH(C$\underline{H}_3$)Ph]$_3$], 4.99 [q, J = 6 Hz, 3H, PhSi[OC$\underline{H}$(CH$_3$)Ph]$_3$, overlapping with *RRS/RSS*], 7.16−7.39 [m, 18H, $\underline{Ph}$Si[OCH(CH$_3$)$\underline{Ph}$]$_3$, overlapping with *RRS/RSS*], 7.57−7.60 [m, 2H, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$, overlapping with *RRS/RSS*]. (b) *RRS/RSS*: δ 1.30 [d, J = 6 Hz, 3H, PhSi[OCH(C$\underline{H}_3$)Ph]$_3$], 1.32 [d, J = 6 Hz, 3H, PhSi[OCH(C$\underline{H}_3$)Ph]$_3$], 1.39 [d, J = 6 Hz, 3H, PhSi[OCH(C$\underline{H}_3$)Ph]$_3$], 4.95−5.08 [m, 3H, PhSi(OC$\underline{H}$(CH$_3$)Ph)$_3$, overlapping with *RRR/SSS*], 7.16−7.39 [m, 18H, $\underline{Ph}$Si[OCH(CH$_3$)$\underline{Ph}$]$_3$, overlapping with *RRR/SSS*], 7.53−7.56 [m, 2H, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$]. ^{1}H NMR (C_6D_6): (a) *RRR/SSS*: δ 1.45 [d, J = 6 Hz, 9H, PhSi[OCH(C$\underline{H}_3$)Ph]$_3$], 5.12 [q, J = 6 Hz, 3H, PhSi[OC$\underline{H}$(CH$_3$)Ph]$_3$, overlapping with *RRS/RSS*], 7.04−7.32 [m, 18H, $\underline{Ph}$Si(OCH(CH$_3$)$\underline{Ph}$)$_3$, overlapping with *RRS/RSS*], 7.82−7.85 [m, 2H, $\underline{Ph}$Si(OCH(CH$_3$)Ph)$_3$]. (b) *RRS/RSS*: δ 1.35 [d, J = 6 Hz, 3H, PhSi[OCH(C$\underline{H}_3$)Ph]$_3$], 1.37 [d, J = 6 Hz, 3H, PhSi[OCH(C$\underline{H}_3$)Ph]$_3$], 1.44 [d, J = 6 Hz, 3H, PhSi[OCH(C$\underline{H}_3$)Ph]$_3$], 5.10−5.21 [m, 3H, PhSi[OC$\underline{H}$(CH$_3$)Ph]$_3$, overlapping with *RRR/SSS*], 7.05−7.30 [m, 18H, $\underline{Ph}$Si(OCH(CH$_3$)$\underline{Ph}$)$_3$, overlapping with *RRR/SSS*], 7.78−7.81 [m, 2H, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$]. ^{13}C{^{1}H} NMR ($CDCl_3$): (a) *RRR/SSS*: δ 26.76 [s, 3C, PhSi[OCH(C$\underline{H}_3$)Ph]$_3$], 71.28 [s, 3C, PhSi[OC$\underline{H}$(CH$_3$)Ph]$_3$, overlapping with *RRS/RSS*], 125.54 [s, 6C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 127.04 [s, 3C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 127.78 [s, 2C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 128.23 [s, 6C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 130.33 [s, 1C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 131.72 [s, 1C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 135.08 [s, 2C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$, overlapping with *RRS/RSS*], 145.80 [s, 3C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$]. (b) *RRS/RSS*: δ 26.60 [s, 1C, PhSi[OCH(C$\underline{H}_3$)Ph]$_3$], 26.62 [s, 1C, PhSi[OCH(C$\underline{H}_3$)Ph]$_3$], 26.72 [s, 1C, PhSi[OCH(C$\underline{H}_3$)Ph]$_3$], 71.25 [s, 2C, PhSi[OC$\underline{H}$(CH$_3$)Ph]$_3$], 71.28 [s, 1C, PhSi[OC$\underline{H}$(CH$_3$)Ph]$_3$, overlapping with *RRR/SSS*], 125.47 [s, 6C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 126.96 [s, 3C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 127.80 [s, 2C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 128.18 [s, 6C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 131.56 [s, 1C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 135.08 [s, 2C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$, overlapping with *RRR/SSS*], 145.84 [s, 1C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 145.90 [s, 1C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 145.93 [s, 1C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): (a) *RRR/SSS*: δ 26.95 [s, 3C, PhSi[OCH-

DOI: 10.1021/acs.organomet.5b00506
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($\underline{C}H_3$)Ph]$_3$], 71.58 [s, 3C, PhSi[O$\underline{C}$H(CH$_3$)Ph]$_3$, overlapping with *RRS/RSS*], 125.65 [s, 6C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 127.24 [s, 3C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$, overlapping with *RRS/RSS*], 128.06 [s, 2C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 128.39 [s, 6C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$, overlapping with *RRS/RSS*], 130.56 [s, 1C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 132.18 [s, 1C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 135.36 [s, 2C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$, overlapping with *RRS/RSS*], 146.07 [s, 3C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$]. (b) *RRS/RSS*: δ 26.83 [s, 1C, PhSi[OCH($\underline{C}$H$_3$)Ph]$_3$], 26.85 [s, 1C, PhSi[OCH($\underline{C}$H$_3$)Ph]$_3$], 26.92 [s, 1C, PhSi[OCH($\underline{C}$H$_3$)Ph]$_3$], 71.58 [s, 2C, PhSi[O$\underline{C}$H(CH$_3$)Ph]$_3$, overlapping with *RRR/SSS*], 71.61 [s, 1C, PhSi[O$\underline{C}$H(CH$_3$)Ph]$_3$], 125.63 [s, 3C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 125.68 [s, 3C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 127.17 [s, 2C, PhSi[OCH-(CH$_3$)$\underline{Ph}$]$_3$, overlapping with *RRR/SSS*], 127.24 [s, 1C, PhSi[OCH-(CH$_3$)$\underline{Ph}$]$_3$], 127.25 [s, 1C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 128.06 [s, 6C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 128.39 [s, 2C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$, overlapping with *RRR/SSS*], 128.45 [s, 2C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 130.56 [s, 1C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$ overlapping with *RRR/SSS*], 132.00 [s, 2C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 135.35 [s, 2C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$], 135.36 [s, 2C, $\underline{Ph}$Si[OCH(CH$_3$)Ph]$_3$, overlapping with *RRR/SSS*], 146.13 [s, 1C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$], 146.17 [s, 1C, PhSi[OCH-(CH$_3$)$\underline{Ph}$]$_3$], 146.20 [s, 1C, PhSi[OCH(CH$_3$)$\underline{Ph}$]$_3$]. ^{29}Si{^{1}H} NMR (CDCl$_3$): δ −60.59 (*RRR/SSS*), −60.50 (*RRS/SRR*). ^{29}Si{^{1}H} NMR (C_6D_6): δ −59.92 (*RRR/SSS*), −59.85 (*RRS/RSS*).

PhSiH[OCH(Me)Ph]$_2$.[89] The compound exists as a mixture of the *RR/SS*, *RrS*, and *RsS* diastereomers in a 2:1.06:0.93 ratio. ^{1}H NMR (C_6D_6, selected resonances): (a) *RrS*: δ 1.36 [d, J = 6 Hz, 6H, PhSiH[OCH($\underline{Me}$)Ph]$_2$], 4.97−5.06 [m, 2H, PhSiH[O$\underline{C}$H(Me)Ph]$_2$, overlap with *RsS* and *RR/SS*], 5.37 [s, 1H, PhSi$\underline{H}$[OCH(Me)Ph]$_2$]. (b) *RsS*: δ 1.36 [d, J = 6 Hz, 6H, PhSiH[OCH($\underline{Me}$)Ph]$_2$], 4.97−5.06 [m, 2H, PhSiH[O$\underline{C}$H(Me)Ph]$_2$, overlap with *RrS* and *RR/SS*], 5.24 [s, 1H, PhSi$\underline{H}$[OCH(Me)Ph]$_2$]. (c) *RR/SS*: δ 1.38 [d, J = 6 Hz, 3H, PhSiH[OCH($\underline{Me}$)Ph]$_2$], 1.43 [d, J = 6 Hz, 3H, PhSiH[OCH($\underline{Me}$)-Ph]$_2$],], 4.97−5.06 [m, 2H, PhSiH[O$\underline{C}$H(Me)Ph]$_2$, overlap with *RrS* and *RsS*], 5.30 [s, 1H, PhSi$\underline{H}$[OCH(Me)Ph]$_2$]. ^{13}C{^{1}H} NMR (C_6D_6, selected resonances): (a) *RrS*: δ 26.16 [s, 2C, PhSiH[OCH($\underline{Me}$)Ph]$_2$], 72.27 [s, 2C, PhSiH[O$\underline{C}$H(Me)Ph]$_2$]. (b) *RsS*: δ 26.07 [s, 2C, PhSiH[OCH($\underline{Me}$)Ph]$_2$], 72.31 [s, 2C, PhSiH[O$\underline{C}$H(Me)Ph]$_2$]. (c) *RR/SS*: δ 26.68 [s, 2C, PhSiH[OCH($\underline{Me}$)Ph]$_2$], 26.74 [s, 2C, PhSiH[OCH($\underline{Me}$)Ph]$_2$], 72.33 [s, 2C, PhSiH[O$\underline{C}$H(Me)Ph]$_2$], 72.37 [s, 2C, PhSiH[O$\underline{C}$H(Me)Ph]$_2$]. ^{29}Si{^{1}H} NMR (C_6D_6): δ −32.15 (*RR/SS*), −32.25 (*RsS*), −32.41 (*RrS*).

PhSiH$_2$[OCHPh$_2$).[90] ^{1}H NMR (C_6D_6, selected resonances): δ 5.20 [s, 2H, PhSi$\underline{H}_2$(OCHPh$_2$)], 5.81 [s, 1H, PhSiH$_2$(O$\underline{C}$HPh$_2$)]. ^{13}C{^{1}H} NMR (C_6D_6, selected resonances): δ 79.50 [s, 1C, PhSi-H$_2$(O$\underline{C}$HPh$_2$)].

PhSi[OCH(Me)Et]$_3$.[91] The compound exists as a statistical mixture of the *RRR/SSS* and *RSS/SRR* diastereomers in a 1:3 ratio. ^{1}H NMR (C_6D_6): (a) *RRR/SSS*: δ 0.914 [t, J = 7 Hz, 9H, PhSi[OCH(Me)-CH$_2$C$\underline{H}_3$]$_3$], 1.236 [d, J = 6 Hz, 9H, PhSi[OCH($\underline{Me}$)Et]$_3$], 1.45−1.66 [m, 6H, PhSi[OCH(Me)C$\underline{H}_2$CH$_3$]$_3$, overlapping with *RRS/RSS*], 4.13−4.19 [m, 3H, PhSi[O$\underline{C}$H(Me)Et]$_3$, overlapping with *RRS/RSS*], 7.21−7.28 [m, 3H, $\underline{Ph}$Si[OCH(Me)Et]$_3$, overlapping with *RRS/RSS*], 7.90 [m, 2H, $\underline{Ph}$Si[OCH(Me)Et]$_3$, overlapping with *RRS/RSS*]. (b) *RRS/RSS*: δ 0.916 [t, J = 7 Hz, 3H, PhSi[OCH(Me)CH$_2$C$\underline{H}_3$]$_3$], 0.918 [t, J = 7 Hz, 3H, PhSi[OCH(Me)CH$_2$C$\underline{H}_3$]$_3$], 0.920 [t, J = 7 Hz, 3H, PhSi[OCH(Me)CH$_2$C$\underline{H}_3$]$_3$], 1.230 [d, J = 6 Hz, 3H, PhSi[OCH-($\underline{Me}$)Et]$_3$], 1.233 [d, J = 6 Hz, 3H, PhSi[OCH($\underline{Me}$)Et]$_3$], 1.234 [d, J = 6 Hz, 3H, PhSi[OCH($\underline{Me}$)Et]$_3$], 1.45−1.66 [m, 6H, PhSi[OCH-(Me)C$\underline{H}_2$CH$_3$]$_3$, overlapping with *RRR/SSS*], 4.12−4.19 [m, 3H, PhSi[O$\underline{C}$H(Me)Et]$_3$, overlapping with *RRR/SSS*], 7.21−7.28 [m, 3H, $\underline{Ph}$Si[OCH(Me)Et]$_3$, overlapping with *RRR/SSS*], 7.90 [m, 2H, $\underline{Ph}$Si[OCH(Me)Et]$_3$, overlapping with *RRR/SSS*]. ^{13}C{^{1}H} NMR (C_6D_6): (a) *RRR/SSS*: δ 9.99 [s, 3C, PhSi[OCH(Me)CH$_2$$\underline{C}H_3$]$_3$, overlapping with *RRS/RSS*], 23.11 [s, 3C, PhSi[OCH($\underline{Me}$)Et]$_3$], 32.51 [s, 3C, PhSi[OCH(Me)$\underline{C}$H$_2$CH$_3$]$_3$, overlapping with *RRS/RSS*], 70.60 [s, 3C, PhSi[O$\underline{C}$H(Me)Et]$_3$, overlapping with *RRS/RSS*], 127.97 [s, 2C, $\underline{Ph}$Si[OCH(Me)Et]$_3$, overlapping with *RRS/RSS*], 130.15 [s, 1C, $\underline{Ph}$Si[OCH(Me)Et]$_3$, overlapping with *RRS/RSS*], 134.08 [s, 1C, $\underline{Ph}$Si[OCH(Me)Et]$_3$, overlapping with *RRS/RSS*], 135.29 [s, 2C, $\underline{Ph}$Si[OCH(Me)Et]$_3$, overlapping with *RRS/RSS*]. (b) *RRS/RSS*: δ 9.98 [s, 2C, PhSi[OCH(Me)CH$_2$$\underline{C}H_3$]$_3$], 9.99 [s, 1C, PhSi[OCH-(Me)CH$_2$$\underline{C}H_3$]$_3$, overlapping with *RRR/SSS*], 23.07 [s, 1C, PhSi-[OCH($\underline{Me}$)Et]$_3$], 23.08 [s, 1C, PhSi[OCH($\underline{Me}$)Et]$_3$], 23.10 [s, 1C, PhSi[OCH($\underline{Me}$)Et]$_3$], 32.51 [s, 3C, PhSi[OCH(Me)$\underline{C}$H$_2$CH$_3$]$_3$, overlapping with *RRR/SSS*], 70.60 [s, 3C, PhSi[O$\underline{C}$H(Me)Et]$_3$, overlapping with *RRR/SSS*], 70.61 [s, 6C, PhSi[O$\underline{C}$H(Me)Et]$_3$], 127.97 [s, 2C, $\underline{Ph}$Si[OCH(Me)Et]$_3$, overlapping with *RRR/SSS*], 130.15 [s, 1C, $\underline{Ph}$Si[OCH(Me)Et]$_3$, overlapping with *RRR/SSS*], 134.08 [s, 1C, $\underline{Ph}$Si[OCH(Me)Et]$_3$, overlapping with *RRR/SSS*], 135.29 [s, 2C, $\underline{Ph}$Si[OCH(Me)Et]$_3$, overlapping with *RRR/SSS*]. ^{29}Si{^{1}H} NMR (C_6D_6): δ −62.26 (*RRR/SSS*), −62.30 (*RSS/SRR*).

PhSiH[OCH(Me)Et]$_2$.[89] The compound exists as a mixture of the *RR/SS*, *RrS*, and *RsS* diastereomers in a 2:1.10:0.93 ratio. ^{1}H NMR (C_6D_6, selected resonances): (a) *RrS*: δ 0.892 [t, J = 7 Hz, 6H, PhSiH[OCH(Me)CH$_2$C$\underline{H}_3$]$_2$], 1.169 [d, J = 6 Hz, 6H, PhSiH[OCH-($\underline{Me}$)Et]$_2$], 1.39−1.47 [m, 8H, PhSiH[OCH(Me)C$\underline{H}_2$CH$_3$]$_2$, overlapping *RrS* and *RsS*], 3.94−4.00 [m, 2H, PhSiH[O$\underline{C}$H(Me)Et]$_2$, overlapping *RrS*, *RsS*, and *RR/SS*], 5.30 [s,1H, PhSi$\underline{H}$[OCH(Me)-Et]$_2$]. (b) *RsS*: δ 0.890 [t, J = 7 Hz, 6H, PhSiH[OCH(Me)-CH$_2$C$\underline{H}_3$]$_2$], 1.167 [d, J = 6 Hz, 6H, PhSiH[OCH($\underline{Me}$)Et]$_2$], 3.94−4.00 [m, 2H, PhSiH[O$\underline{C}$H(Me)Et]$_2$, overlapping *RrS*, *RsS*, and *RR/SS*], 5.29 [s, 1H, PhSi$\underline{H}$[OCH(Me)Et]$_2$]. (c) *RR/SS*: δ 0.87 [t, J = 7 Hz, 6H, PhSiH[OCH(Me)CH$_2$C$\underline{H}_3$]$_2$], 1.18 [d, J = 6 Hz, 3H, PhSiH[OCH($\underline{Me}$)Et]$_2$], 1.19 [d, J = 6 Hz, 3H, PhSiH[OCH($\underline{Me}$)-Et]$_2$], 1.52−1.60 [m, 4H, PhSiH[OCH(Me)C$\underline{H}_2$CH$_3$]$_2$], 3.94−4.00 [m, 2H, PhSiH[O$\underline{C}$H(Me)Et]$_2$, overlapping with *RrS* and *RsS*], 5.29 [s, 1H, PhSi$\underline{H}$[OCH(Me)Et]$_2$]. ^{13}C{^{1}H} NMR (C_6D_6, selected resonances): (a) *RrS*: δ 10.07 [s, 2C, PhSiH[OCH(Me)CH$_2$$\underline{C}H_3$]$_2$, overlapping with *RsS* and *RR/SS*], 23.20 [s, 2C, PhSiH[OCH($\underline{Me}$)-Et]$_2$], 32.44 [s, 2C, PhSiH[OCH(Me)$\underline{C}$H$_2$CH$_3$]$_2$, overlapping with *RsS*], 71.29 [s, 2C, PhSiH[O$\underline{C}$H(Me)Et]$_2$]. (b) *RsS*: δ 10.07 [s, 2C, PhSiH[OCH(Me)CH$_2$$\underline{C}H_3$]$_2$, overlapping with *RrS* and *RR/SS*], 23.12 [s, 2C, PhSiH[OCH($\underline{Me}$)Et]$_2$], 32.44 [s, 2C, PhSiH[OCH-(Me)$\underline{C}$H$_2$CH$_3$]$_2$ overlapping with *RrS*], 71.57 [s, 2C, PhSiH[O$\underline{C}$H-(Me)Et]$_2$]. (c) *RR/SS*: δ 10.07 [s, 2C, PhSiH[OCH(Me) CH$_2$$\underline{C}H_3$]$_2$, overlapping with *RrS* and *RrS*], 23.16 [s, 2C, PhSiH[OCH($\underline{Me}$)Et]$_2$], 32.41 [s, 2C, PhSiH[OCH(Me) $\underline{C}$H$_2$CH$_3$]$_2$], 71.24 [s, 1C, PhSiH-[O$\underline{C}$H(Me)Et]$_2$], 71.62 [s, 1C, PhSiH[O$\underline{C}$H(Me)Et]$_2$]. ^{29}Si{^{1}H} NMR (C_6D_6): δ −33.24 (*RsS*), −34.18 (*RrS*), −33.66 (*RR/SS*).

PhSiH$_2$[OCH(Me)Et].[90] ^{1}H NMR (C_6D_6, selected resonances): δ 0.82 [t, J = 7 Hz, 3H, PhSiH$_2$[OCH(Me)CH$_2$C$\underline{H}_3$]], 1.08 [d, J = 6 Hz, 3H, PhSi$\underline{H}_2$[OCH($\underline{Me}$)Et]], 3.66−3.72 [m, 1H, PhSiH$_2$[O$\underline{C}$H(Me)-Et]], 5.24 [s, 2H, PhSi$\underline{H}_2$[OCH(Me)Et]]. ^{13}C{^{1}H} NMR (C_6D_6, selected resonances): δ 22.61 [s, 1C, PhSiH$_2$[OCH(Me)CH$_2$C$\underline{H}_3$]], 32.13 [s, 1C, PhSiH$_2$[OCH($\underline{Me}$)Et]], 73.20 [s, 1C, PhSiH$_2$[O$\underline{C}$H-(Me)Et]].

PhSi(OCHEt$_2$)$_3$.[90] ^{1}H NMR (C_6D_6): δ 0.93 [t, J = 7 Hz, 18H, PhSi[OCH(CH$_2$C$\underline{H}_3$)$_2$]$_3$], 1.55−1.67 [m, 12H, PhSi[OCH-(C$\underline{H}_2$CH$_3$)$_2$]$_3$], 4.03 [quint, J = 6 Hz, 3H, PhSi(O$\underline{C}$HEt$_2$)$_3$], 7.21 [m, 3H, $\underline{Ph}$Si(OCHEt$_2$)$_3$], 7.90−7.92 [m, 2H, $\underline{Ph}$Si(OCHEt$_2$)$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): δ 9.72 [s, 6C, PhSi[OCH(CH$_2$$\underline{C}H_3$)$_2$]$_3$], 29.21 [s, 6C, PhSi[OCH(C$\underline{H}_2$CH$_3$)$_2$]$_3$], 75.58 [s, 3C, PhSi-(O$\underline{C}$HEt$_2$)$_3$], 127.93 [s, 1C, $\underline{Ph}$Si(OCHEt$_2$)$_3$], 130.09 [s, 1C, $\underline{Ph}$Si(OCHEt$_2$)$_3$], 134.21 [s, 1C, $\underline{Ph}$Si(OCHEt$_2$)$_3$], 135.33 [s, 1C, $\underline{Ph}$Si(OCHEt$_2$)$_3$]. ^{29}Si{^{1}H} NMR (C_6D_6): δ −63.04.

PhSiH$_2$(OCHEt$_2$).[90] ^{1}H NMR (C_6D_6, selected resonances): δ 0.85 [t, J = 7 Hz, 6H, PhSiH$_2$[OCH(CH$_2$C$\underline{H}_3$)$_2$]], 1.37−1.60 [m, 4H, PhSiH$_2$[OCH(C$\underline{H}_2$CH$_3$)$_2$]], 3.51 [tt, J = 5 Hz, J = 7 Hz, 1H, PhSiH$_2$(O$\underline{C}$HEt$_2$)], 5.27 [s, 2H, PhSi$\underline{H}_2$(OCHEt$_2$)]. ^{13}C{^{1}H} NMR (C_6D_6, selected resonances): δ 10.06 [s, 2C, PhSiH$_2$[OCH-(CH$_2$$\underline{C}H_3$)$_2$]], 29.55 [s, 2C, PhSiH$_2$[OCH(C$\underline{H}_2CH_3$)$_2$]], 78.62 [s, 1C, PhSiH$_2$(O$\underline{C}HEt_2$)].

PhSiH(OCHEt$_2$)$_2$.[89] ^{1}H NMR (C_6D_6, selected resonances): δ 0.88 [t, J = 7 Hz, 6H, PhSiH[OCH(CH$_2$C$\underline{H}_3$)$_2$]$_2$], 0.93 [t, J = 7 Hz, 6H, PhSiH[OCH(CH$_2$C$\underline{H}_3$)$_2$]$_2$], 1.37−1.60 [m, 8H, PhSiH[OCH-(C$\underline{H}_2$CH$_3$)$_2$]$_2$], 3.80 [tt, J = 5 Hz, J = 7 Hz, 2H, PhSiH(O$\underline{C}$HEt$_2$)$_2$], 5.33 [s, 1H, PhSi$\underline{H}$(OCHEt$_2$)$_2$]. ^{13}C{^{1}H} NMR (C_6D_6, selected resonances): δ 9.95, [s, 2C, PhSiH[OCH(CH$_2$$\underline{C}H_3$)$_2$]$_2$], 9.96 [s, 2C, PhSiH[OCH(CH$_2$$\underline{C}H_3$)$_2$]$_2$], 29.60 [s, 4C, PhSiH[OCH-

DOI: 10.1021/acs.organomet.5b00506
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($\underline{C}H_2CH_3)_2]_2$], 76.56 [s, 2C, PhSiH($O\underline{C}HEt_2)_2$]. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −32.55.

PhSi(OCy)$_3$. ^1H NMR (C_6D_6): δ 1.13−1.25 [m, 4H, PhSi[OCH-($C_5\underline{H}_{10})]_3$], 1.31−1.39 [m, 4H, PhSi[OCH($C_5\underline{H}_{10})]_3$], 1.53−1.62 [m, 4H, PhSi[OCH($C_5\underline{H}_{10})]_3$], 1.66−1.73 [m, 4H, PhSi[OCH($C_5\underline{H}_{10})]_3$], 1.92−1.95 [m, 4H, PhSi[OCH($C_5\underline{H}_{10})]_3$], 4.14 [tt, J = 4 Hz, J = 9 Hz, 3H, PhSi[OCH($C_5H_{10})]_3$], 7.23−7.29 [m, 3H, $\underline{Ph}Si(OCy)_3$], 7.94−7.97 [m, 2H, $\underline{Ph}Si(OCy)_3$]. $^{13}C\{^1H\}$ NMR: δ 24.13 [s, 6C, PhSi[OCH($\underline{C}_5H_{10})]_3$], 26.01 [s, 3C, PhSi[OCH($\underline{C}_5H_{10})]_3$], 35.88 [s, 6C, PhSi[OCH($\underline{C}_5H_{10})]_3$], 71.13 [s, 3C, PhSi[O$\underline{C}$H($C_5H_{10})]_3$], 130.21 [s, 1C, $\underline{Ph}Si(OCy)_3$], 134.13 [s, 1C, $\underline{Ph}Si(OCy)_3$], 135.24 [s, 2C, $\underline{Ph}Si(OCy)_3$]. $^{29}Si\{^1H\}$ NMR: δ −61.62.

PhSiH(OCy)$_2$.[89] ^1H NMR (C_6D_6, selected resonances): δ 3.97 [tt, J = 9 Hz, J = 4 Hz, 2H, PhSiH[O$\underline{C}$H($C_5H_{10})]_2$], 5.34 [s, 1H, PhSi$\underline{H}$($OCy)_2$]. $^{13}C\{^1H\}$ NMR: δ 72.01 [s, 2C, PhSiH[O$\underline{C}$H-($C_5H_{10})]_2$]. $^{29}Si\{^1H\}$ NMR: δ −34.63.

PhSiH$_2$(OCy).[90] ^1H NMR (C_6D_6, selected resonances): δ 3.68 [tt, J = 9 Hz, J = 4 Hz, 1H, $PhSiH_2$[O$\underline{C}$H($C_5H_{10})$]], 5.26 [s, 2H, $PhSi\underline{H}_2$(OCy)]. $^{13}C\{^1H\}$ NMR (C_6D_6, selected resonances): δ 73.69 [s, 1C, $PhSiH_2$[O$\underline{C}$H($C_5H_{10})$]].

Ph$_2$Si[OCH(Me)Ph]$_2$. The compound exists as a mixture of the two diastereomers, *RR/SS* and *RS*, in a 1:0.62 ratio. ^1H NMR (C_6D_6, selected resonances): (a) *RR/SS*: δ 1.39 [d, J = 6 Hz, 6H, Ph_2Si[OCH($\underline{Me}$)Ph]$_2$], 5.05 [q, J = 6 Hz, 2H, Ph_2Si[O$\underline{C}$H(Me)Ph]$_2$, overlapping with *RS*] (b) *RS*: δ 1.30 [d, J = 6 Hz, 6H, Ph_2Si[OCH($\underline{Me}$)Ph]$_2$], 5.08 [q, J = 6 Hz, 2H, Ph_2Si[O$\underline{C}$H(Me)Ph]$_2$, overlap with *RR/SS*]. $^{13}C\{^1H\}$ (C_6D_6, selected resonances): (a) *RR/SS*: δ 27.06 [s, 2C, Ph_2Si[OCH($\underline{Me}$)Ph]$_2$], 71.60 [s, 2C, Ph_2Si[O$\underline{C}$H-(Me)Ph]$_2$]. (b) *RS*: δ 26.86 [s, 2C, Ph_2Si[OCH($\underline{Me}$)Ph]$_2$], 71.64 [s, 2C, Ph_2Si[O$\underline{C}$H(Me)Ph]$_2$]. $^{29}Si\{^1H\}$ (C_6D_6): −33.30 (*RS*), −33.23 (*RR/SS*).

Ph$_2$Si(OCHPh$_2$)$_2$. ^1H NMR (C_6D_6, selected resonances): δ 6.02 [s, 2H, Ph_2Si(O$\underline{C}$H$Ph_2)_2$]. $^{13}C\{^1H\}$ NMR (C_6D_6, selected resonances): δ 77.53 [s, 2C, Ph_2Si(O$\underline{C}$H$Ph_2)_2$]. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −30.71.

Ph$_2$SiH(OCHPh$_2$). ^1H NMR (C_6D_6, selected resonances): δ 5.98 [s, 1H, Ph_2SiH(O$\underline{C}$H$Ph_2)$], 5.67 [s, 1H, $Ph_2Si\underline{H}$(O$CHPh_2)$]. $^{13}C\{^1H\}$ NMR (C_6D_6, selected resonances): δ 78.62 [s, 1C, Ph_2SiH-(O$\underline{C}$H$Ph_2)$]. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −11.52.

Ph$_2$Si(OEt)$_2$. ^1H NMR (C_6D_6): δ 1.15 [t, J = 7 Hz, 6H, Ph_2Si(OCH$_2$C$\underline{H}_3)_2$], 3.79 [q, J = 7 Hz, 4H, Ph_2Si(OC$\underline{H}_2$C$H_3)_2$]. 7.21 [m, 6H, $\underline{Ph}_2Si$(OCH_2C$H_3)_2$], 7.80 [m, 4H, $\underline{Ph}_2Si$(OCH_2C$H_3)_2$]. $^{13}C\{^1H\}$ NMR (C_6D_6, selected resonances): δ 18.48 [s, 2C, Ph_2Si(OCH$_2$C$\underline{H}_3)_2$], 58.97 [s, 2C, Ph_2Si(O$\underline{C}$H$_2$C$H_3)_2$]. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −32.11.

Ph$_2$SiH(OEt).[92] ^1H NMR (C_6D_6, selected resonances): δ 1.11 [t, J = 6 Hz, 3H, Ph_2SiH(OCH$_2$C$\underline{H}_3)$], 3.71 [q, J = 6 Hz, 2H, Ph_2SiH-(OC$\underline{H}_2$C$H_3)$], 5.66 [s, 1H, $Ph_2Si\underline{H}$(OCH_2C$H_3)$]. $^{13}C\{^1H\}$ NMR (C_6D_6, selected resonances): δ 18.29 [s, 1C, Ph_2SiH(OCH$_2$C$\underline{H}_3)$], 60.53 [s, 1C, Ph_2SiH(O$\underline{C}$H$_2$C$H_3)$]. ^{29}Si NMR (C_6D_6): δ −11.98.

Ph$_2$Si(OPr^i)$_2$. ^1H NMR (C_6D_6, selected resonances): δ 1.16 [d, J = 6 Hz, 12H, Ph_2Si(OCH$\underline{Me}_2)_2$], 4.22 [hept, J = 6 Hz, 2H, Ph_2Si-(OC$\underline{H}$M$e_2)_2$]. $^{13}C\{^1H\}$ NMR (C_6D_6, selected resonances): δ 25.78 [s, 4C, Ph_2Si(OCH$\underline{Me}_2)_2$], 65.80 [s, 2C, Ph_2Si(O$\underline{C}$HM$e_2)_2$]. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −35.53.

Ph$_2$SiH(OPr^i$_2$). ^1H NMR (C_6D_6, selected resonances): δ 1.14 [d, J = 6 Hz, 6H, Ph_2SiH(OCH$\underline{Me}_2)$], 4.07 [hept, J = 6 Hz, 1H, Ph_2SiH(OC$\underline{H}$M$e_2)$], 5.70 [s, 1H, $Ph_2Si\underline{H}$(OCHM$e_2)$]. $^{13}C\{^1H\}$ NMR (C_6D_6 selected resonances): δ 25.40 [s, 2C, Ph_2SiH-(OCH$\underline{Me}_2)$], 67.37 [s, 1C, Ph_2SiH(O$\underline{C}$HM$e_2)$]. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −14.81.

Ph$_2$Si[OCH(Me)Et]$_2$.[93] The compound exists as a mixture of two diastereomers, *RR/SS* and *RS*, in a 1:1 ratio. ^1H NMR (C_6D_6, selected resonances): (a) *RS*: δ 0.87 [t, J = 7 Hz, 6H, Ph_2Si[OCH(Me)-CH$_2$C$\underline{H}_3]_2$, overlapping with *RR/SS*], 1.158 [d, J = 6 Hz, 6H, Ph_2Si[OCH($\underline{Me}$)Et]$_2$], 1.40−1.65 [m, 4H, Ph_2Si[OCH(Me)-C$\underline{H}_2$CH$_3]_2$, overlapping with *RR/SS*], 3.98−4.06 [m, 2H, Ph_2Si-[OC$\underline{H}$(Me)Et]$_2$, overlapping *RR/SS*]. (b) *RR/SS*: δ 0.87 [t, J = 7 Hz, 6H, Ph_2Si[OCH(Me)CH$_2$C$\underline{H}_3]_2$, overlapping with *RS*], 1.165 [d, J = 6 Hz, 6H, Ph_2Si[OCH($\underline{Me}$)Et]$_2$], 1.40−1.65 [m, 4H, Ph_2Si[OCH(Me)-C$\underline{H}_2$CH$_3]_2$, overlapping with *RS*], 4.02 [m, 2H, Ph_2Si[O$\underline{C}$H(Me)Et]$_2$, overlapping with *RS*]. $^{13}C\{^1H\}$ NMR (C_6D_6, selected resonances): (a) *RR/SS*: δ 9.92 [s, 2C, Ph_2Si[OCH(Me)$\underline{C}H_2$C$H_3]_2$, overlapping with *RS*], 23.13 [s, 2C, Ph_2Si[OCH($\underline{Me}$)Et]$_2$], 32.49 [s, 4C, Ph_2Si[OCH-(Me)$\underline{C}H_2$C$H_3]_2$, overlapping with *RS*], 70.77 [s, 2C, Ph_2Si[O$\underline{C}$H-(Me)Et]$_2$, overlapping with *RR/SS*]. (b) *RS*: δ 9.91 [s, 2C, Ph_2Si[OCH(Me)$\underline{C}H_2$C$H_3]_2$], 9.92 [s, 2C, Ph_2Si[OCH(Me)-$CH_2\underline{C}H_3]_2$, overlapping with *RR/SS*], 23.06 [s, 2C, Ph_2Si[OCH($\underline{Me}$)-Et]$_2$], 32.49 [s, 4C, Ph_2Si[OCH(Me)$\underline{C}H_2$C$H_3]_2$ overlapping with *RR/SS*], 70.77 [s, 2C, Ph_2Si[O$\underline{C}$H(Me)Et]$_2$, overlapping with *RR/SS*]. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −35.65 (*RR/SS*), −35.69 (*RS*).

Ph$_2$SiH[OCH(Me)Et]. ^1H NMR (C_6D_6): δ 0.85 [t, J = 7 Hz, 3H, Ph_2SiH[OCH(Me)CH$_2$C$\underline{H}_3$]], 1.13 [d, J = 6 Hz, 3H, Ph_2SiH[OCH-($\underline{Me}$)Et]], 1.34−1.60 [m, 2H, Ph_2SiH[OCH(Me)C$\underline{H}_2$CH$_3$]], 3.85 [m, 1H, Ph_2SiH[OC$\underline{H}$(Me)CH$_2$CH$_3$]], 5.71 [s, 1H, $Ph_2Si\underline{H}$[OCH(Me)-CH$_2$CH$_3$]], 7.18 [m, 6H, $\underline{Ph}_2SiH$[OCH(Me)Et]], 7.70 [m, 4H, $\underline{Ph}_2SiH$[OCH(Me)Et]]. $^{13}C\{^1H\}$ NMR (C_6D_6, selected resonances): δ 10.12 [s, 1C, Ph_2SiH[OCH(Me)CH$_2\underline{C}H_3$]], 22.9 [s, 1C, Ph_2SiH-[OCH($\underline{Me}$)Et]], 32.29 [s, 1C, Ph_2SiH[OCH(Me)$\underline{C}H_2$CH$_3$]], 72.33 [s, 1C, Ph_2SiH[O$\underline{C}$H(Me)Et]]. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −14.14.

Ph$_2$Si(OCHEt$_2$)$_2$. ^1H NMR (C_6D_6, selected resonances): δ 0.87 [t, J = 8 Hz, 12H, Ph_2Si[OCH(CH$_2$C$\underline{H}_3)_2]_2$], 1.55 [m, 8H, Ph_2Si[OCH-(C$\underline{H}_2$CH$_3)_2]_2$], 3.83 [quintet, J = 6 Hz, 2H, Ph_2Si[OC$\underline{H}$-(CH$_2$CH$_3)_2]_2$]. $^{13}C\{^1H\}$ NMR (C_6D_6, selected resonances): δ 9.74 [s, 4C, Ph_2Si[OCH(CH$_2\underline{C}H_3)_2]_2$], 29.24 [s, 4C, Ph_2Si[OCH-($\underline{C}$H$_2$CH$_3)_2]_2$], 75.84 [s, 2C, Ph_2Si(O$\underline{C}$HEt$_2)_2$]. $^{29}Si\{^1H\}$ NMR-(C_6D_6): δ −35.55.

Ph$_2$SiH(OCHEt$_2$). ^1H NMR (C_6D_6, selected resonances): δ 0.85 [t, J = 8 Hz, 6H, Ph_2SiH[(OCH(CH$_2$C$\underline{H}_3)_2$]], 1.49 [m, 4H, Ph_2SiH-[OCH(C$\underline{H}_2$CH$_3)_2$]], 3.68 [tt, J = 5 Hz, J = 6 Hz, 1H, Ph_2SiH-(OC$\underline{H}$Et$_2)$], 5.73 [s, 1H, $Ph_2Si\underline{H}$(OCHEt$_2)$]. $^{13}C\{^1H\}$ NMR (C_6D_6, selected resonances): δ 9.98 [s, 2C, Ph_2SiH[OCH(CH$_2\underline{C}H_3)_2$]], 29.46 [s, 2C, Ph_2SiH[OCH($\underline{C}$H$_2$CH$_3)_2$]], 77.42 [s, 1C, Ph_2SiH(O$\underline{C}$HEt$_2)$]. $^{29}Si\{^1H\}$ NMR(C_6D_6): δ −13.38.

Ph$_2$Si(OCy)$_2$. ^1H NMR (C_6D_6, selected resonances): δ 1.49 [m, 20H, Ph_2Si[OCH($\underline{C}_5H_{10})]_2$], 4.02 [tt, J = 4 Hz, J = 9 Hz, 2H, Ph_2Si[O$\underline{C}$H($C_5H_{10})]_2$]. $^{13}C\{^1H\}$ NMR (C_6D_6, selected resonances): δ 24.01 [s, 4C, Ph_2Si[OCH($\underline{C}_5H_{10})]_2$], 25.94 [s, 2C, Ph_2Si[OCH-($\underline{C}_5H_{10})]_2$], 35.88 [s, 4C, Ph_2Si[OCH($\underline{C}_5H_{10})]_2$], 71.21 [s, 2C, Ph_2Si[O$\underline{C}$H($C_5H_{10})]_2$]. $^{29}Si\{^1H\}$ NMR: δ −35.65.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00506.

^1H NMR spectra (PDF)

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Notes

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DOI: 10.1021/acs.organomet.5b00506
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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (DE-FG02-93ER14339). Aaron Sattler is thanked for helpful discussions.

■ DEDICATION

This paper is dedicated to the memory of Gregory L. Hillhouse, an inspirational chemist, friend, and colleague.

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(36) A reviewer questioned the use of the term "chemically equivalent" rather than "isochronous", since the latter refers to signals possessing the same chemical shift. In this regard, while "chemically equivalent" and "isochronous" are sometimes used interchangeably, it is important to note that there is an important distinction between the two terms.[a,b] Two nuclei (or sets of nuclei) are classified as chemically equivalent if they are related by a symmetry operation.[c] Such nuclei would experience equal magnetic shielding and would thus have identical chemical shifts; *i.e.*, they are isochronous. However, while chemically equivalent nuclei must be isochronous, the converse is not necessarily true, such that two nuclei that are isochronous need not be chemically equivalent. Thus, nuclei may be isochronous either due to chemical equivalence (*i.e.*, symmetry), fast exchange, or a coincidentally identical magnetic environment.[d] For example, consider an ether with different long-chain alkyl groups, $Me(CH_2)_xO(CH_2)_yMe$: the two methyl groups on each end of the chains are clearly chemically inequivalent because they are not related by a symmetry operation, but could still coincidentally have the same chemical shift and, therefore, be isochronous. Another illustration is provided by $[Tp^{Me_2}]Pt(H)_2Si(CH_2CH_3)_3$, for which the ethyl groups appear as a *singlet*.[e] Obviously, the CH_2 and CH_3 groups cannot be classified as being chemically equivalent but, because they are coincidentally isochronous, the ethyl group appears as a singlet. A related example is provided by the observation of a singlet for the ethyl group corresponding to one set of ^{199}Hg satellite signals of EtHgCl.[f] Other issues concerned with the inappropriate use of these terms have also been discussed.[g] (a) van Gorkom, M.; Hall, G. E. *Q. Rev., Chem. Soc.* **1968**, *22*, 14−29. (b) *Spectroscopy: An Interdisciplinary Integral Description of Spectroscopy from UV to NMR*; Skrabal, P. M., Ed.; vdf Hochschulverlag AG: Zürich, 2012. (c) Silverstein, R. M.; Lalonde, R. T. *J. Chem. Educ.* **1980**, *57*, 343−344. (d) Structural Analysis of Organic Compounds Combined Application of Spectroscopic Methods. *Studies in Analytical Chemistry*; Clerc, J. T., Pretsch, E., Seibl, J., Eds.; Elsevier: Amsterdam, 1981; Vol. *1*, p 25. (e) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2000**, *19*, 3748−3750. (f) Sattler, W.; Yurkerwich, K.; Parkin, G. *Dalton Trans.* **2009**, 4327−4333. (g) Fulea, A. O. *Rev. Roum. Chim.* **1988**, *33*, 39−52.
(37) Furthermore, it was also described as a doublet in $CDCl_3$ (δ = 1.53, J = 6.5 Hz). See ref 27.
(38) Subsequent reports on $PhSi[OCH(Me)Ph]_3$ have likewise not discussed the spectroscopic features of $PhSi[OCH(Me)Ph]_3$ in terms of the diastereomeric mixture. For example, the methyl group has been described as an unspecified multiplet (ref 25b), and as a range of chemical shifts (ref 25c). Of these varied descriptions, it is not clear how the eight-line pattern that we observe for the methyl region of $PhSi[OCH(Me)Ph]_3$ in the ^1H NMR spectrum (Figure 2) could be described as a single doublet (refs 19, 27, and 30).
(39) Also inconsistent is the observation of a single ^{29}Si NMR chemical shift of −32.7 ppm (ref 19) which differs markedly from the values of −59.84 and −59.92 ppm that we have observed for the two diastereomers. The value of −32.7 ppm reported for $PhSi[OCH(Me)Ph]_3$ is also much more in accord with that expected for a species of composition $PhSiH(OR)_2$, rather than that for $PhSi(OR)_3$, as discussed above (Table 2).
(40) We also note that we have prepared a sample of $PhSi[OCH(Me)Ph]_3$ by a literature method (ref 27), and the ^1H NMR spectrum of the product obtained corresponds to that reported here.
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(42) Of the pair of *RrS* and *RsS* diastereomers, the *RrS* isomer is arbitrarily assigned as the one that is more abundant.
(43) A similar ratio of diastereomers is observed upon zinc-catalyzed dehydrocoupling of a 2:1 mixture of PhCH(Me)OH and $PhSiH_3$.
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(90) Minor component of a mixture with $PhSiH(OR)_2$.
(91) Assignment for the *RRR*/*SSS* isomers confirmed by the synthesis of (*S*,*S*,*S*)-$PhSi[OCH(Me)Et]_3$ *via* dehydrocoupling of $PhSiH_3$ with (*S*)-Et(Me)CHOH as catalyzed by [κ^3-Tptm]ZnH.
(92) Minor component of a mixture with $Ph_2Si(OR)_2$.
(93) Assignment for the *RR*/*SS* isomers confirmed by the synthesis of (*S*,*S*)-$Ph_2Si[OCH(Me)Et]_2$ *via* dehydrocoupling of Ph_2SiH_2 with (*S*)-Et(Me)CHOH as catalyzed by [κ^3-Tptm]ZnH.

DOI: 10.1021/acs.organomet.5b00506
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