Mechanistic Studies of Palladium(II)-Catalyzed Hydrosilation and Dehydrogenative Silation Reactions

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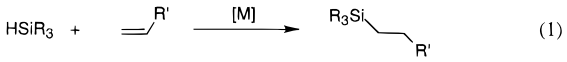
Received August 26, 1996[⊗]

Abstract: The cationic Pd(II) complexes, $[(phen)Pd(CH_3)(L)]^+[BAr'_4]^-$ phen = 1,10−phenanthroline; L = Et_2O, $Me_3SiC{\equiv}CSiMe_3$; Ar′ = 3,5-$(CF_3)_2C_6H_3$) catalyze the hydrosilation and dehydrogenative silation of olefins. Hydrosilation of ethylene, *tert*-butylethylene, 1-hexene, and cyclohexene by $HSiR_3$ (R = CH_2CH_3, C_6H_5) occurs in the presence of 1 mol % $[(phen)Pd(CH_3)(L)]^+[BAr'_4]^-$. The reaction of *tert*-butylethylene with $HSi(i\text{-}Pr)_3$ in the presence of $[(phen)Pd(CH_3)(L)]^+[BAr'_4]^-$ yields neohexane and *t*-BuCH=CHSi(*i*-Pr)$_3$. Low-temperature NMR experiments revealed that the catalyst resting state for the silations of ethylene and alkyl-substituted olefins is $[(phen)Pd(SiR_3)(\eta^2\text{-}H_2C{=}CHR')]^+[BAr'_4]^-$. Evidence for rapid, reversible silyl migration at −70 °C was observed by ^{1}H NMR spectroscopy. Deuterium labeling studies show that the intermediate Pd(II) alkyl complexes can isomerize via a series of β-hydride eliminations followed by reinsertions of olefin prior to reaction with $DSiEt_3$. Styrene undergoes both hydrosilation and dehydrogenative silation in the presence of $[(phen)Pd(CH_3)(L)]^+[BAr'_4]^-$ or $[(phen)Pd(\eta^3\text{-}CH(CH_3)C_6H_5)]^+[BAr'_4]^-$ yielding ethylbenzene, $R_3SiCH_2CH_2C_6H_5$ and *trans*-$R_3SiCH{=}CHPh$ (R = CH_2CH_3, $CH(CH_3)_2$). ^{1}H NMR spectroscopy revealed that the π-benzyl complexes $[(phen)Pd(\eta^3\text{-}CH(CH_2SiR_3)C_6H_5)]^+[BAr'_4]^-$ and $[(phen)Pd(\eta^3\text{-}CH(CH_3)C_6H_5)]^+[BAr'_4]^-$ are the catalyst resting states for the silation reactions of styrene.

Hydrosilation of olefins (eq 1) can be achieved either through



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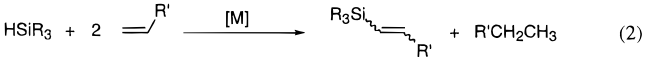
a free radical process or with the use of a transition metal catalyst, typically an electron-rich complex of a late transition metal such as Co, Rh, Pd, or Pt.[1,2] More recently, zirconocene derivatives,[3,4] lanthanide complexes,[5−7] and electrophilic late transition metal complexes[8] have been reported to catalyze the hydrosilation of olefins.

A variety of mechanisms have been proposed for this process. A widely accepted mechanism was first proposed by Chalk and Harrod (Scheme 1).[9,10] The key feature in the Chalk−Harrod mechanism is migratory insertion of an olefin hydride complex followed by reductive coupling of the alkyl and silyl fragments.[9,10] If the intermediate alkyl complex undergoes reversible β-hydride elimination and reinsertion with opposite regiochemistry, then the Chalk−Harrod mechanism provides an explanation for the olefin isomerization and deuterium scrambling observed in many hydrosilation reactions.[1]

However, many catalysts form vinylsilanes and alkanes in addition to the hydrosilation product (eq 2).[1,11−14] In some cases, dehydrogenative silation occurs more readily than



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hydrosilation.[13−15] Because of the utility of vinylsilanes in organic synthesis,[16] the dehydrogenative silation reaction is of interest. The Chalk−Harrod mechanism does not account for dehydrogenative silation, and a number of groups have proposed mechanisms based on silyl (rather than hydride) migration to olefin.[8,13,15,17−19]

One such possible mechanism is shown in Scheme 2. Silyl migration to olefin results in a β-silylalkyl intermediate, which can then undergo two possible reactions. The first possibility is β-hydride elimination to form an olefin−hydride complex. If reinsertion of the olefin with opposite regiochemistry occurs, isomerization of the alkyl complex results. Displacement of the olefin from the metal results in dehydrogenative silation. The second possibility is cleavage of the β-silylalkyl fragment by reaction by $HSiR_3$. This reaction may proceed via oxidative addition of silane followed by reductive elimination of the hydrosilated product or via a σ-bond metathesis reaction.

Efforts to detect intermediate species in many transition metal catalyzed hydrosilation reactions have been hindered by extremely high reaction rates[1] and heterogeneous systems.[20] In an earlier study from these laboratories, the cationic cobalt

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1997.

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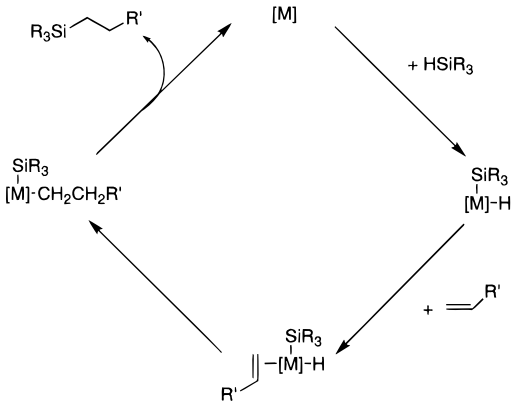
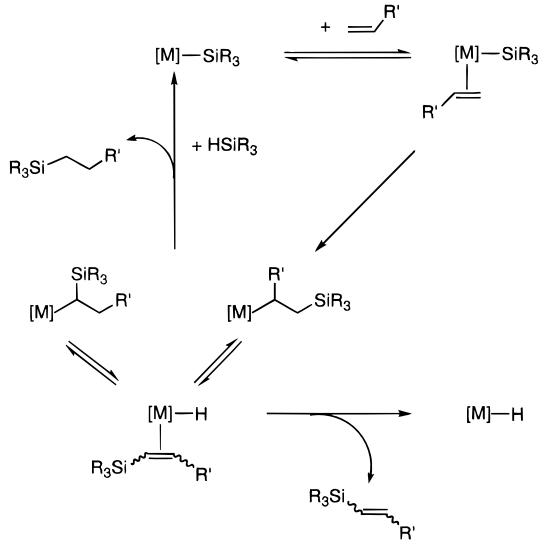
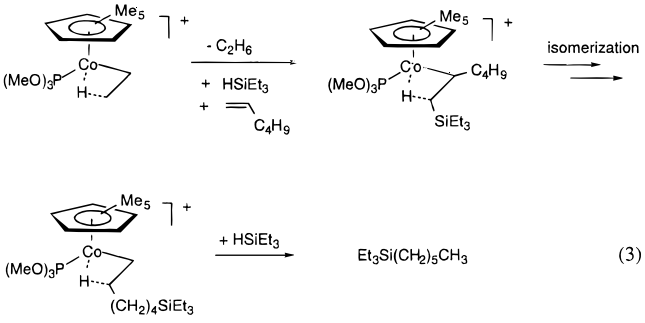
Scheme 1. Chalk−Harrod Mechanism for the Hydrosilation of Olefins



Scheme 2. Silyl Migration Mechanism for Hydrosilation and Dehydrogenative Silylation of Olefins



complex $[Cp^*Co(P(OMe)_3)(CH_2CH_2\text{-}\mu\text{-}H)]^+[BAr'_4]^-$ was found to be an efficient precatalyst for the hydrosilation of 1-hexene. Deuterium labeling studies and spectroscopic observation of intermediate species in this system suggested that the reaction proceeds by silyl migration to olefin followed by a series of β-hydrogen elimination and reinsertion reactions. The terminal cobalt alkyl complex $[Cp^*Co(CH_2CH\text{-}\mu\text{-}H(CH_2)_4SiEt_3)(P(OMe)_3)]^+[BAr'_4]^-$ then reacts with $HSiEt_3$ to form $Et_3Si(CH_2)_5CH_3$ (eq 3). Thus, silane adds with overall 1,6 regiochemistry.[8]



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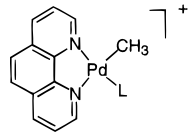
Cationic square-planar Pd(II) complexes have been found to be efficient catalysts for the formation of carbon−carbon bonds, including the dimerization[21,22] and polymerization of α-olefins[23] and the alternating co-polymerization of α-olefins with carbon monoxide.[24−28] We report here that the cationic Pd(II) complexes, $[(phen)Pd(CH_3)(L)]^+[BAr'_4]^-$ (phen = 1,10-phenanthroline; L = Et_2O (**1a**), $Me_3SiC{\equiv}CSiMe_3$ (**1b**); Ar′ = 3,5-$(CF_3)_2C_6H_3$) are efficient precatalysts for the formation of silicon−carbon bonds.

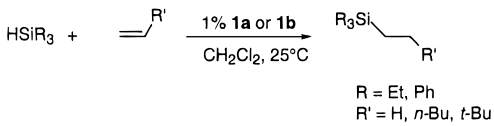


1a: L = Et_2O
1b: L = $Me_3SiC{\equiv}CSiMe_3$

Hydrosilation and dehydrogenative silation of olefins are achieved under mild conditions (25−85 °C, 0.1−2 mol % **1**). The mechanisms of the hydrosilation and dehydrgenative silation reactions were studied by a variety of low-temperature NMR experiments and deuterium labeling experiments. The results of these studies are presented below.

Results and Discussion

I. Survey of Silation Reactions. A. Silation of Ethylene and Alkyl-Substituted Olefins. In the presence of a catalytic amount of $[(phen)Pd(CH_3)(L)]^+[BAr'_4]^-$, hydrosilation of olefins proceeds at 25 °C in CH_2Cl_2 (eq 4). The addition of $HSiR_3$ to



(4)

α-olefins proceeds with a 1,2 regiochemistry. **1b** is a more convenient catalyst than the thermally unstable ether adduct **1a** since **1b** is thermally stable, moderately air- and water-stable, and stable at 25 °C in CH_2Cl_2. The results are summarized in Table 1.

When the reaction was conducted in Et_2O, lower yields were obtained. Likewise, only 5% yield is obtained when $[(phen)Pd(CH_3)(NCCH_3)(NCCH_3)]^+[BAr'_4]^-$ (**1c**) is used as the catalyst. The low yields are due to inhibition of the silation reaction rather than catalyst decomposition; NMR studies (see below) suggest that coordinating ligands such as acetonitrile or ether can compete with olefin or silane for the vacant coordination site and thus inhibit the hydrosilation reaction.

No dehydrogenative silation is observed in the reactions of ethylene, 1-hexene, or cyclohexene with $HSiR_3$ (R = Et, Ph). Some dehydrogenative silation (5%) is observed in the reaction of *tert*-butylethylene with $HSiEt_3$ in the presence of **1a** or **1b**. Efforts to increase the yield of *t*-BuCH=CHSiEt$_3$ by increasing the *t*-BuCH=CH_2/$HSiEt_3$ ratio were not successful.

The reaction of ethylene with $HSi(i\text{-}Pr)_3$ in the presence of 1 mol % **1a** yields the hydrosilation product, *i*-Pr_3SiEt (74% yield). In contrast, the reaction of *tert*-butylethylene with 0.5 equiv of $HSi(i\text{-}Pr)_3$ in the presence of 1% **1a** yields *trans*-*t*-BuCH=CHSi-

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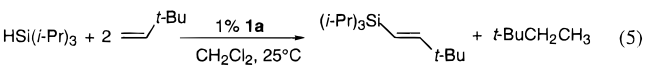
Table 1. Summary of Reaction Conditions[a,c] and Yields[b] for the Reaction of Ethylene and Alkyl-Substituted Olefins with $HSiR_3$ in the Presence of 1 mol % $[(phen)Pd(CH_3)(L)]^+[BAr'_4]^-$ (**1a**, L = Et_2O; **1b**, L = $Me_3CCSiMe_3$; **1c**, L = CH_3CN)

entry no.	$HSiR_3$ R =	olefin	catalyst	substrate ratio, $HSiR_3$/olefin	solvent	product	yield,[b] %
1	Et	ethylene	**1a**	*c*	CH_2Cl_2	$SiEt_4$	85
2	Et	1-hexene	**1b**	1.1	CH_2Cl_2	$Et_3Si(CH_2)_5CH_3$	88
3	Et	cyclohexene	**1b**	1.1	CH_2Cl_2	Et_3Si(Cy)	88
4	Et	*t*-BuCH=CH_2	**1b**	1.1	CH_2Cl_2	$Et_3SiCH_2CH_2$-*t*-Bu[d]	79
5	Et	*t*-BuCH=CH_2	**1b**	1.0	CH_2Cl_2	$Et_3SiCH_2CH_2$-*t*-Bu[d]	80
6	Et	*t*-BuCH=CH_2	**1b**	1.1	Et_2O	$Et_3SiCH_2CH_2$-*t*-Bu[d]	14
7	Et	*t*-BuCH=CH_2	**1c**	1.1	CH_2Cl_2	$Et_3SiCH_2CH_2$-*t*-Bu[d]	5
8	Ph	cyclohexene	**1b**	1.1	CH_2Cl_2	Ph_3Si(Cy)	78
9	Ph	*t*-BuCH=CH_2	**1b**	1.1	CH_2Cl_2	$Ph_3SiCH_2CH_2$-*t*-Bu	20[e]
10	*i*-Pr	ethylene	**1a**	*c*	CH_2Cl_2	$Si(i\text{-}Pr)_3Et$	75
11	*i*-Pr	*t*-BuCH=CH_2	**1a**	0.5	CH_2Cl_2	$(i\text{-}Pr)_3SiCH$=CH-*t*-Bu	82
12	*i*-Pr	*t*-BuCH=CH_2	**1a**	1.1	CH_2Cl_2	$(i\text{-}Pr)_3SiCH$=CH-*t*-Bu	94[f]

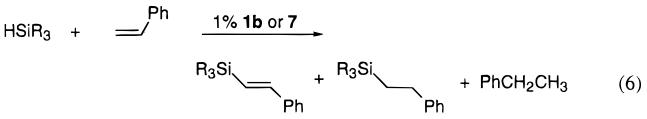
[a] 24 h, 25 °C. [b] Yields were calculated based on the limiting reagent. [c] C_2H_4 was bubbled through the solution until C_2H_4 uptake ceased. [d] Et_3SiCH=CH-*t*-Bu (5%) was also formed. [e] Recrystallized. [f] An equivalent amount of *t*-$BuCH_2CH_3$ was also produced.

(i-Pr)$_3$ (82% yield) (eq 5). The hydrosilation product, *t*-$BuCH_2CH_2Si(i\text{-}Pr)_3$, is not observed. When a slight excess of $HSi(i\text{-}Pr)_3$ (1.1 equiv) was used, no hydrosilation is observed.



(5)

B. Silation Reactions of Styrene. The reaction of styrene with $HSiEt_3$ in the presence of **1b** or $[(phen)Pd(\eta^3\text{-}CH(CH_3)C_6H_5)]^+$ (**7**)[29] was investigated. The results are summarized in Table 2. Both hydrosilation and dehydrogenative silation of styrene occur, yielding a mixture of ethylbenzene, $Et_3SiCH_2CH_2Ph$, and *trans*-Et_3SiCH=CHC_6H_5 (eq 6). The product ratio $Et_3SiCH_2CH_2Ph$/*trans*-Et_3SiCH=CHC_6H_5 is dependent on the styrene/$HSiEt_3$ ratio. Hydrosilation predominates when styrene/$HSiEt_3$ < 1 (entry nos. 1 and 5). Dehydrogenative silation predominates when styrene/$HSiEt_3$ ≥ 1. At 85 °C, yields are higher.

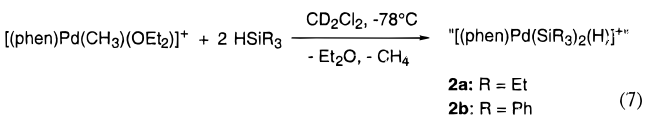


(6)

The reaction of $HSi(i\text{-}Pr)_3$ with styrene in the presence of 1 mol % **7** was investigated. Higher temperatures (85 °C) are required. Under identical conditions, the proportion of dehydrogenative silation observed is higher than in analogous reactions of $HSiEt_3$.

II. Silation of Ethylene and Alkyl-Substituted Olefins. A. NMR Studies. The hydrosilation and dehydrogenative silation reactions were investigated by low-temperature NMR spectroscopic methods in order to gain mechanistic insight. Complexes containing the $[BAr'_4]^-$ anion frequently exhibit enhanced stability and solubility and are well-suited for low-temperature NMR studies.[8,22,25,29,30]

The reaction of the precatalyst **1a** with 2 equiv of $HSiR_3$ (R = Et, Ph) at −78 °C in CD_2Cl_2 proceeds with loss of methane and formation of a new complex with the general formation $[(phen)Pd(SiR_3)_2(H)]^+[BAr'_4]^-$ (**2a**, R = Et; **2b**, R = Ph) (eq 7).



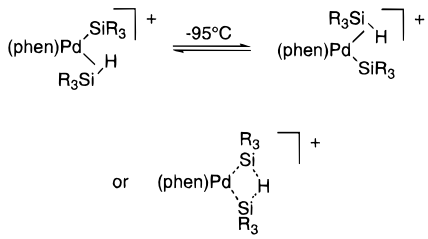
(7)

Table 2. Reaction Conditions[a,c] and Product Ratios[d] for the Reaction of Styrene with $HSiR_3$ (R = Et, *i*-Pr) in the Presence of 1 mol % $[(phen)Pd(\eta^3\text{-}CH(CH_3)C_6H_5)]^+[BAr'_4]^-$ (**7**)

entry no.	$HSiR_3$ R =	substrate ratio, styrene/$HSiR_3$	*T*, °C	solvent	yield,[b,d] %	product ratio, $PhCH_2CH_2SiR_3$/$PhCH$=$CHSiR_3$
1	Et	1:4	35	CH_2Cl_2	27	100:0
2	Et	1:1	35	CH_2Cl_2	50	45:55
3	Et	2:1	35	CH_2Cl_2	58	25:75
4	Et	4:1	35	CH_2Cl_2	77	13:87
5	Et	1:4	85	none[c]	85	96:4
6	Et	1:1	85	none[c]	65	43:57
7	Et	2:1	85	none[c]	84	32:68
8	Et	4:1	85	none[c]	88	21:79
9	*i*-Pr	1:4	85	none[c]	58	41:59
10	*i*-Pr	1:1	85	none[c]	52	13:87
11	*i*-Pr	2:1	85	none[c]	82	9:91
12	*i*-Pr	4:1	85	none[c]	97	0:100

[a] 24 hours. [b] Yield = ($PhCH_2CH_2SiR_3$ + $PhCH$=$CHSiR_3$). The yield is calculated based on the limiting reagent. For the reactions of equimolar amounts of $HSiR_3$ and styrene, the isolated yield will be <100% due to the conversion of styrene into ethylbenzene. [c] At 85 °C, **7** is soluble in neat $HSiR_3$/styrene and no additional solvent was used. [d] Ethylbenzene was removed *in vacuo* during product isolation. For this reason, the yield of ethylbenzene was not calculated but was assumed to be equal to the yield of $PhCH$=$CHSiR_3$.

Scheme 3. Possible Structures for **2**



In the presence of only 1 equiv of silane, a 1:1 mixture of **2** and **1a** is obtained. In **2a** the two $SiEt_3$ fragments are equivalent by ^1H and ^{13}C NMR spectroscopy at temperatures down to −95 °C. A singlet is observed at δ = −9.99 (**2a**) or −12.13 (**2b**) and is attributed to Si−H. At −95 °C no ^{29}Si satellites are observed, but the peak is quite broad and ^{29}Si−H coupling constants less than 40 Hz would not be detected. Based on the spectroscopic evidence **2a** and **2b** are either Pd(IV) hydrides with the general formula $[(phen)Pd(SiR_3)_2H]^+[BAr'_4]^-$ or a rapidly fluxional Pd(II) species which contains as η^1-silyl group and a η^2-silane (Scheme 3). A less likely possibility is that the hydride is symmetrically bridged between the silyl groups, as

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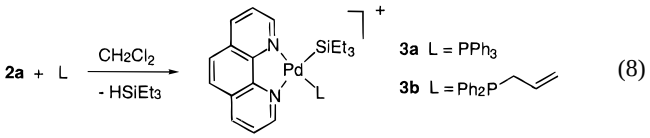
shown in Scheme 3. The reaction of **1a** with 2 equiv of HSi(*i*-Pr)$_3$ in CD_2Cl_2 at −78 °C does not yield any well-defined species, although CH_4 evolution is observed. It is possible that the larger steric requirements of Si(*i*-Pr)$_3$ prevent formation of a species with the general formula [(phen)Pd(Si(*i*-Pr)$_3$)$_2$(H)]$^+$[BAr′$_4$]$^-$.

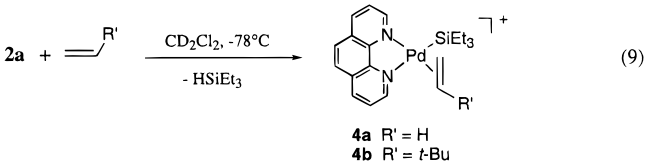
$HSiEt_3$ is readily displaced from **2a** by a variety of ligands, allowing the formation of a variety of cationic Pd(II) silyl complexes. Addition of triphenylphosphine to **2a** results in formation and isolation of [(phen)Pd($SiEt_3$)(PPh_3)]$^+$[BAr′$_4$]$^-$ (**3a**) (eq 8). When allyldiphenylphosphine is added to **2a** at



(8)

−78 °C, orange [(phen)Pd($SiEt_3$)($Ph_2PC_3H_5$)]$^+$[BAr′$_4$]$^-$ (**3b**) is isolated. ^{1}H and ^{31}P NMR spectroscopy suggest that in **3b** allyldiphenylphosphine is coordinated to palladium via phosphorus rather than through the olefin. The isolable Pd silyl complexes **3a**,**b** are not suitable hydrosilation precatalysts; no reaction of cyclohexene with $HSiEt_3$ was observed in the presence of 1 mol % **3a** or **3b** (CH_2Cl_2, 25 °C).

Addition of ethylene to a solution of **2a** at −78 °C results in displacement of $HSiEt_3$ and formation of [(phen)Pd($SiEt_3$)(η^2-C_2H_4)]$^+$[BAr′$_4$]$^-$ (**4a**) (eq 9). No hydrosilation is observed at −78 °C. In the presence of excess ethylene, exchange between free and bound ethylene is observed at −78 °C and only a single averaged signal can be observed (δ = 5.0 ppm). In the absence of excess ethylene, the coordinated ethylene ligand displays an AA′BB′ pattern centered at 4.9 ppm. The olefinic doublets collapse to a singlet as the temperature is raised. At the coalescence temperature, T_c = −70(1) °C, $k = 3.9 \times 10^2$ s^{-1}, $\Delta G^{\ddagger}$ = 9.2 kcal/mol. The fluxional behavior of **4a** is similar to that observed for the cationic alkyl complexes [(phen)Pd(R)(C_2H_4)]$^+$[BAr′$_4$]$^-$ (R = CH_3, $\Delta G^{\ddagger}$ = 9.2 (0.2) kcal/mol; R = C_2H_5, $\Delta G^{\ddagger}$ = 9.2 (0.2) kcal/mol).[21,25]



(9)

Addition of *tert*-butylethylene to a CD_2Cl_2 solution of **2a** at −78 °C results in displacement of $HSiEt_3$ and formation of [(phen)Pd($SiEt_3$)(η^2-CH_2CH-*t*-Bu)]$^+$[BAr′$_4$]$^-$ (**4b**). At −78 °C, no exchange is observed between free and bound *t*-butylethylene.

The reaction of **1a** with 1 equiv of $HSiEt_3$ followed by addition of H_2C═CHR′ (R′ = H, *t*-Bu) at −78 °C yields **4a** and **4b**, respectively. This method permits the generation of silane-free solutions of **4a**,**b** as well as the generation of tri(isopropyl)silyl analogues of **4**; the reaction of **1a** with 1 equiv of HSi(*i*-Pr)$_3$ at −78 °C followed by addition of *tert*-butylethylene results in formation of [(phen)Pd(Si(*i*-Pr)$_3$)(η^2-CH_2CH-*t*-Bu)]$^+$[BAr′$_4$]$^-$ (**4c**).

The rapid reaction of the precatalyst **1a** with 2 equiv of $HSiR_3$ to form **2** and the subsequent displacement of $HSiR_3$ by olefin to form **4** demonstrate how catalyst generation occurs in the silation reactions. Additionally, the reaction of **1a** with $HSiR_3$ suggests that alkyl complexes of the general formula [(phen)PdR″(L)]$^+$ (R″ = alkyl) react readily with silane to form alkane and regenerate a Pd(II) silyl complex; this reaction is a key step in the catalytic hydrosilation reaction (see below).

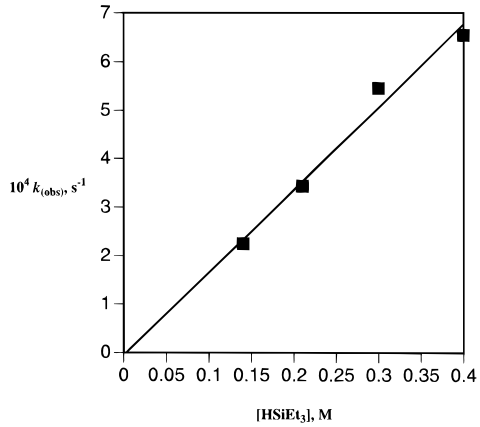
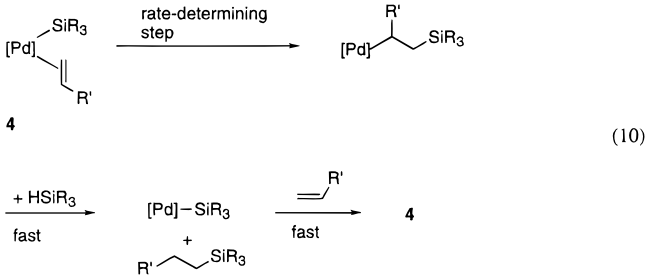


Figure 1. A plot for k_{obs} vs [$HSiEt_3$] for the reaction of [(phen)Pd($SiEt_3$)(H_2C═CH-*t*-Bu)]$^+$ (**4b**) with $HSiEt_3$ to form **2a** and *t*-BuCH_2-CH_2SiEt_3 (−38 °C; [**4b**] = 0.014 M; $k_{obs} = 1.7 \times 10^{-3}$ s^{-1} [$HSiEt_3$]).

In the presence of **4a** and excess $HSiEt_3$ and ethylene (2−10 equiv), hydrosilation proceeds readily at −40 °C. During catalysis, **4a** is the only organometallic species observed by ^{1}H NMR spectroscopy. Upon complete consumption of ethylene, **2a** is regenerated. Similar results were obtained in the reaction of **4b** with excess *tert*-butylethylene and $HSiEt_3$. These results establish that the silyl−olefin complexes [(phen)Pd(SiR_3)(η^2-CH_2CHR′)]$^+$[BAr′$_4$]$^-$ are the catalyst resting state for the silation of olefins. This led us to propose a mechanism consisting of silyl migration to olefin followed by reaction of the β-silylethyl complex with $HSiR_3$ to form the hydrosilation product and regenerate [Pd]-SiR_3 (eq 10).

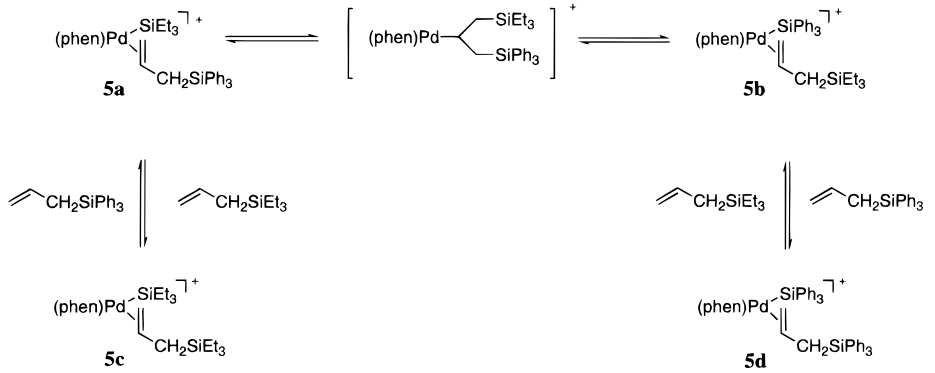


(10)

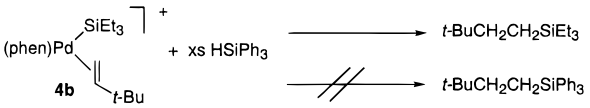
Based on the rapid reaction of **1a** with $HSiEt_3$ and the rapid formation of **4** from **2**, it was anticipated that the rate-determining step would be the silyl migration to olefin, and the hydrosilation reaction would be zero-order in [$HSiEt_3$]. CD_2Cl_2 solutions of **4a** and **4b** were monitored by ^{1}H NMR spectroscopy in the temperature range −60 to −20 °C. It was found that in the absence of $HSiEt_3$, complexes **4a**,**b** are *stable* in CD_2Cl_2 at temperatures up to ca. −20 °C. Neither the β-silylalkyl complexes [(phen)Pd($CHR'CH_2SiEt_3$)]$^+$ (R′ = H, *t*-Bu) nor any other species attributable to β-silyl migration was observed. This result suggested that β-silyl migration (**4** ⇌ [Pd]-R″) may be rapid and reversible, favoring **4** in the catalytic cycle. To examine this possibility, the kinetics of the reaction of **4b** with $HSiEt_3$ under pseudo-first-order conditions (10−30 equiv of $HSiEt_3$) was monitored at −38 °C. A first-order rate dependence on [$HSiEt_3$] was observed at all silane concentrations. ($k_{obs} = 1.7 \times 10^{-3}$ M^{-1} s^{-1} [$HSiEt_3$]) (Figure 1).

A crossover experiment was performed to determine whether the silyl and olefin fragments in complexes **4** are coupled in the hydrosilation product or if the bound olefin fragment is in some way attacked by free $HSiR_3$. **4b** was generated in CD_2Cl_2 at −78 °C; care was taken not to introduce excess $HSiEt_3$

Scheme 4. Nondegenerate Silyl Scrambling and Olefin Displacement Reactions in $[(phen)Pd(SiR_3)(\eta^2\text{-}CH_2{=}CHCH_2SiR'_3)]^+$



or *tert*-butylethylene. $HSiPh_3$ was added and the solution was allowed to warm to 25 °C. The hydrosilation product was analyzed by ^1H and ^{13}C NMR spectroscopy and found to be exclusively $t\text{-}BuCH_2CH_2SiEt_3$ (eq 11). The results of this



(11)

experiment suggest that intramolecular silyl migration to olefin occurs rather than an intermolecular reaction of bound *tert*-butylethylene with $HSiPh_3$.

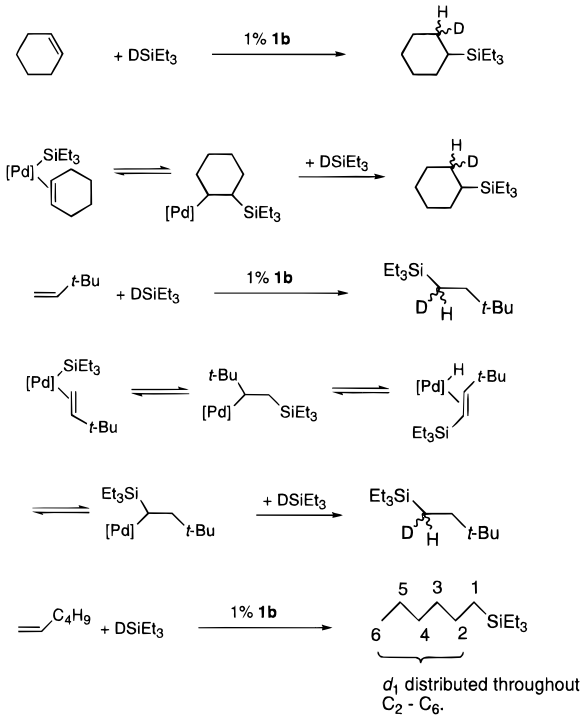
The results of the kinetics and crossover experiments strongly support rapid, *reversible* silyl migration. To test the reversibility of the silyl migration, a silyl scrambling experiment was performed (Scheme 4). $[(phen)Pd(SiEt_3)(\eta^2\text{-}H_2C{=}CHCH_2SiPh_3)]^+[BAr'_4]^-$ (**5a**) was generated in CD_2Cl_2 at −78 °C by addition of allyltriphenylsilane to a solution of **2a**. If silyl migration to olefin occurs with a 2,1 regiochemistry (as is suggested by the regiochemistry of the hydrosilated products), the Pd(II) alkyl intermediate would have two nonequivalent β-silyl substituents. If β-silyl elimination occurs it would be nondegenerate and would result in formation of a mixture of **5a** and a new complex, $[(phen)Pd(SiPh_3)(\eta^2\text{-}H_2C{=}CHCH_2SiEt_3)]^+[BAr'_4]^-$.

5a was generated at −78 °C and the NMR sample was inserted into a precooled (−78 °C) NMR probe. Initially, ≈95% **5a** was observed, but as the sample was allowed to warm to −60 °C, a mixture of **5a** (87%) and a new species **5b** (13%) whose ^1H NMR spectrum closely resembled that of **5a** was formed. $[(phen)Pd(SiPh_3)(\eta^2\text{-}H_2C{=}CHCH_2SiEt_3)]^+[BAr'_4]^-$ was independently generated at −78 °C and its NMR spectrum was identical with that of complex **5b**. At −60 °C, **5b** rapidly equilibrated to a mixture of **5a** (87%) and **5b** (13%). For the equilibrium **5a** ⇌ **5b**, $K(\text{eq}) = 0.15$ at −60 °C. These observations clearly establish that rapid and reversible silyl migration is occurring at −60 °C.

After an hour at −60 °C, two new species were also observed and identified as $[(phen)Pd(SiEt_3)(\eta^2\text{-}H_2C{=}CHCH_2SiEt_3)]^+[BAr'_4]^-$ (**5c**) and $[(phen)Pd(SiPh_3)(\eta^2\text{-}H_2C{=}CHCH_2SiPh_3)]^+[BAr'_4]^-$ (**5d**) (based on independent generation of these complexes).

The observed preference for **5a** may be due to preferential binding of the more electron-rich silyl fragment $SiEt_3$ to the electrophilic Pd(II) cation. The eventual formation of **5c** and **5d** results from nondegenerate exchange of allylsilane. The exchange may be explained by either an associative or dissociative mechanism in the presence of traces of free allylsilane. Mechanistic studies in related cationic Pd(II) systems suggest that olefin displacement proceeds by an associative mechanism.[23,29]

Scheme 5. Reactions of α-Olefins with $DSiEt_3$ in the Presence of **1b**



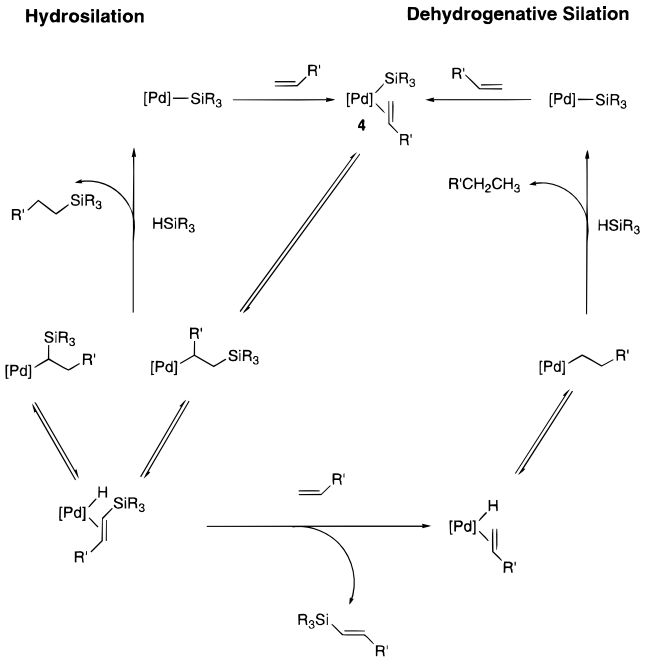
At −70 °C, the equilibration of **5a** and **5b** occurred competitively with the displacement of $HSiR_3$ from **2**. Accurate rate constants for the interconversion of **5a** and **5b** could not be obtained.

B. Deuterium Labeling Studies. Deuterium labeling studies were conducted to determine whether β-hydride elimination and reinsertion reactions occur in the β-silylalkyl intermediates prior to cleavage by silane. The reactions of cyclohexene, *tert*-butylethylene, and 1-hexene with $DSiEt_3$ in the presence of **1b** were investigated. The catalyst and substrate concentrations were similar to those used in the bulk hydrosilations. The deuteriosilated products were isolated and analyzed by ^{13}C NMR spectroscopy. The results are shown in Scheme 5.

For cyclohexene, deuteriosilation occurs, with a 1,2 regiochemistry and <5% deuterium incorporation is observed at any other position. These results are consistent with migratory insertion of cyclohexene followed by reaction of the Pd cyclohexyl intermediate with $DSiEt_3$, as shown in Scheme 5.

In contrast, the deuterosilation reaction of *tert*-butylethylene proceeds with a net 1,1 regiochemistry, and $t\text{-}BuCH_2CHDSiEt_3$ is the only product observed by ^{13}C NMR spectroscopy. A plausible mechanism is proposed consisting of migratory insertion of *tert*-butylethylene, followed by β-hydride elimina-

Scheme 6. Proposed Mechanism for the (phen)Pd^{+}-Catalyzed Hydrosilation and Dehydrogenative Silation of Alkyl-Substituted α-Olefins and Ethylene ([Pd] = [(phen)Pd]$^{+}$)



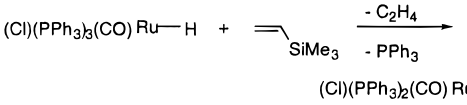
tion and reinsertion of *t*-BuCHCHSiEt_3 with opposite regiochemistry and subsequent cleavage by DSiEt_3.

The reaction of 1-hexene with DSiEt_3 in the presence of **1b** yields Et$_3$Si(C_6H_{12}D). Deuterium is incorporated at all positions along the *n*-hexyl chain except at *C*H_2SiEt_3. This result suggests that "chain-running" is facile. However, unlike the other examples shown in Scheme 5, the reaction is not regioselective.

The deuterium labeling studies suggest that reversible β-hydride elimination/olefin reinsertion reactions can occur prior to eventual cleavage of the Pd alkyl intermediate with HSiEt_3. Steric factors appear to predominate in these systems; e.g., the least congested alkyl intermediate is the most likely to react with silane. For *tert*-butylethylene and cyclohexene the difference in reactivity of the α- and β-silylalkyl intermediates is large enough that only the most accessible isomer reacts with HSiEt_3. For 1-hexene, there is not a significant steric difference between the various alkyl intermediates of the general formula [(phen)PdCH(C_nH_{2n+1})($C_{5-n}H_{2(5-n)}$)SiEt_3]$^{+}$ and thus the reaction of 1-hexene with DSiEt_3 is not regiospecific.

C. Mechanism of Silation Reactions of Ethylene and Alkyl-Substituted Olefins. A mechanistic scheme for the (phen)Pd(II)$^{+}$-catalyzed silation reactions of alkyl-substituted olefins and ethylene can be proposed based on the results of the low-temperature NMR studies, kinetics experiments, and deuterium labeling studies. This mechanism is shown in Scheme 6. The key features of this mechanism are (1) rapid, reversible silyl migration to olefin, (2) isomerization of the intermediate alkyl complexes through a series of β-hydride elimination reactions and reinsertion of the bound olefin with opposite regiochemistry, and (3) cleavage of the alkyl complex by HSiR_3.

Although there have been several examples of silyl migration to olefins,[18,19] including the cobalt-based hydrosilation catalyst described above,[8] there have been only a few well-defined examples of β-silyl elimination reactions. Wrighton and coworkers observed reversible insertion of ethylene into the Fe-Si bond upon photolysis of (Cp)Fe(CO)$_2$SiMe_3 under ethylene.[17] In an example of an irreversible β-silyl elimination reaction, a ruthenium silyl complex is formed via extrusion of ethylene from a β-silylethyl intermediate (eq 12).[31]

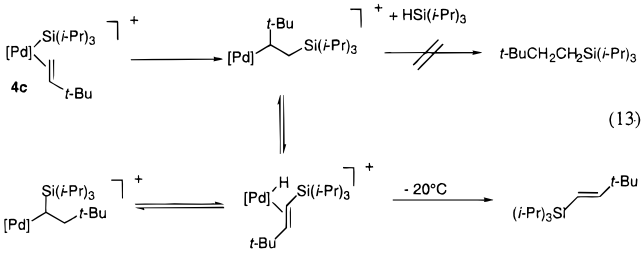


(12)

The deuterium labeling studies suggest that [Pd]−R″ (R″ = alkyl) can undergo rapid β-hydride elimination reactions. Reinsertion of the bound olefin with opposite regiochemistry results in isomerization of the Pd(II) alkyl intermediate. At −38 °C, the reaction of **4b** with HSiEt_3 proceeds fairly rapidly (k_{obs} = 1.6×10^{-3} M^{-1} s^{-1} [HSiEt_3]); the deuterium labeling studies suggest that isomerization of the alkyl fragment occurs prior to reaction with HSiR_3. The isomerization of the Pd(II) alkyl intermediate must therefore be occurring quite rapidly even at low temperatures. Similar evidence for rapid "chain-running" reactions has been observed in Pd(II)- and Ni(II)-catalyzed polymerization of α-olefins.[23]

The final step in the proposed catalytic cycle is the cleavage of [Pd]−R″ with HSiR_3. The deuterium labeling studies suggest that the regiochemistry of this reaction is dependent on the steric demands of both HSiR_3 and [Pd]−R″; typically, the least hindered isomer of [Pd]−R″ reacts with HSiR_3.

In the reaction of *tert*-butylethylene with HSi(*i*-Pr)$_3$, both possible isomers of [Pd]−R″ have bulky substituents α to Pd (eq 13); in this situation, the reaction of [Pd]−R″ with HSi(*i*-Pr)$_3$ is predicted to be disfavored, in agreement with the experimental results. To test this hypothesis, a CD_2Cl_2 solution of **4c** was prepared at −78 °C and the solution was warmed to −20 °C. Dissociation of *trans*-(*i*-Pr)$_3$SiCH═CH-*t*-Bu occurs both in the presence and absence of HSi(*i*-Pr)$_3$. No hydrosilation is observed. The results of this NMR experiment are consistent with both the proposed mechanism and the results of the catalytic silation of *tert*-butylethylene by HSi(*i*-Pr)$_3$. The dehydrogenative silation reaction will be discussed in greater detail in the next section.

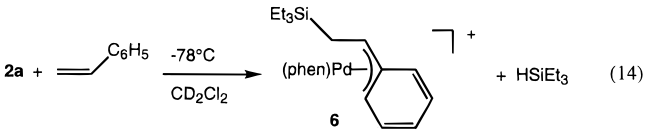


(13)

III. Silation Reactions of Styrene. The silation reactions of styrene were investigated by low-temperature NMR spectroscopy and deuterium labeling studies in an attempt to gain a mechanistic understanding of this system. To our knowledge, no mechanistic studies on dehydrogenative silation have been reported. We were particularly interested in determining why dehydrogenative silation occurs much more readily for styrene than for alkyl-substituted olefins such as cyclohexene or *tert*-butylethylene.

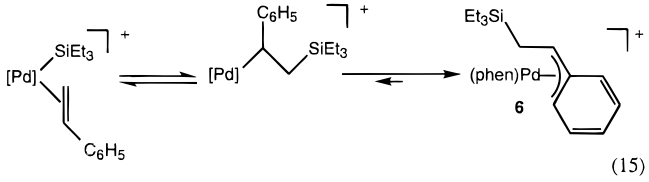
A. NMR Studies. The reaction of **2a** with styrene in CD_2Cl_2 at −78 °C yields a new complex, **6** (eq 14). ^{1}H and ^{13}C NMR data for **6** are consistent with the formulation [(phen)Pd(η^3-CH(CH_2SiEt_3)C_6H_5)]$^{+}$[BAr′$_4$]$^{-}$ based on comparisons with the related, structurally characterized π-benzyl complex [(phen)Pd(η^3-CH(CH_2CH_3)C_6H_5)]$^{+}$[BAr′$_4$]$^{-}$ which is formed in the reaction of **1a** with styrene.[29] In the absence of HSiEt_3 or

(31) Wakatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703.



styrene, CD_2Cl_2 solutions of **6** are stable for several days at 25 °C; however, when solutions of **6** were concentrated, decomposition to palladium black and *trans*-$Et_3SiCH{=}CHC_6H_5$ occurred.

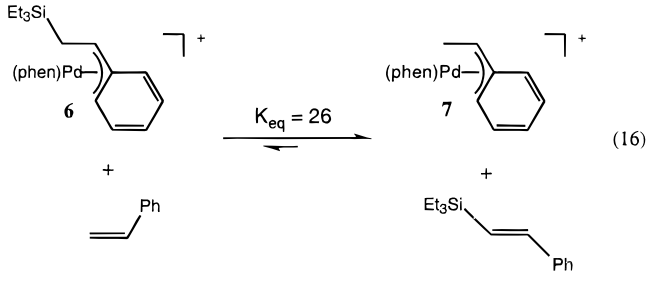
The η^2-styrene complex, $[(phen)Pd(SiEt_3)(\eta^2\text{-}H_2C{=}CHC_6H_5)]^+[BAr'_4]^-$, was not observed in the reaction of **2a** with styrene at −78 °C. Thus, silyl migration is quite rapid even at low temperatures. This result is in agreement with the results from the silyl scrambling experiments described above. Following silyl migration to styrene, isomerization of the initially formed σ-benzyl intermediate to the more stable π-benzyl complex **6** occurs (eq 15). Qualitatively, the silyl migration to styrene is



faster than the analogous methyl migration to styrene in $[(phen)Pd(CH_3)(\eta^2\text{-}H_2C{=}CHC_6H_5)]^+[BAr'_4]^-$ ($\Delta H^{\ddagger} = 16.6 \pm 1.3$ kcal/mol, $\Delta S^{\ddagger} = -6.6 \pm 5.4$ eu).[29]

The reaction of **6** with excess $HSiEt_3$ results in formation of $PhCH_2CH_2SiEt_3$ and regeneration of **2a**. The rate was measured under pseudo-first-order conditions (10−30 equiv of $HSiEt_3$) at 13 °C and found to be first order in $HSiEt_3$ ($k_{obs} = 1.1 \times 10^{-4}$ M^{-1} s^{-1} [$HSiEt_3$] (Figure 2). The rate is much slower than that observed for the reaction of **4b** with $HSiEt_3$ (−38 °C; $k_{obs} = 1.7 \times 10^{-3}$ M^{-1} s^{-1} [$HSiEt_3$]). Since the steric demands of a *tert*-butyl group are actually greater than that of a phenyl group, the low reactivity of **6** with $HSiEt_3$ must be attributed to the equilibrium between the σ- and π-benzyl isomers of **6**, which strongly favors the π-benzyl isomer.

In the presence of excess styrene at 25 °C, **6** reacts with styrene to produce *trans*-$Et_3SiCH{=}CHC_6H_5$ and $[(phen)Pd(\eta^3\text{-}CH(CH_3)C_6H_5)]^+[BAr'_4]^-$ (**7**), (eq 16). The displacement of



trans-$Et_3SiCH{=}CHC_6H_5$ is reversible, but the equilibrium lies in favor of the less-crowded π-benzyl complex **7** (25 °C; $K_{eq} = 26$). In a related reaction, $[(phen)Pd(\eta^3\text{-}CH(CH_2CH_3)C_6H_5)]^+[BAr'_4]^-$ reacts with excess styrene to produce **7** (25 °C; $K_{eq} = 249$) and *trans*-methylstyrene.[29] Mechanistic studies for this process suggest that the benzyl transfer reaction proceeds via β-hydride elimination followed by associative displacement of *trans*-$CH_3CH{=}CHPh$ by styrene. β-Hydride migration and rapid isomerization produces the new π-benzyl complex **7**. Based on the kinetics experiments (see below) and the similarities between the two systems, it is likely that the interconversion of **6** and **7** proceeds through a similar series of reactions (Scheme 7).

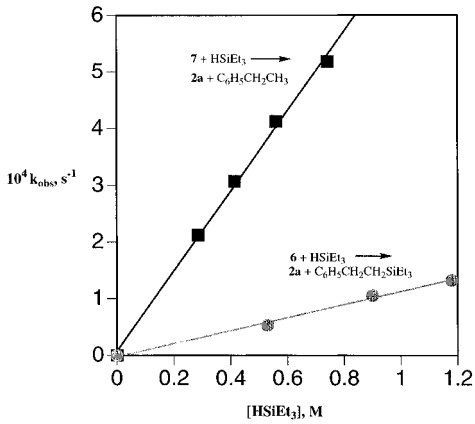
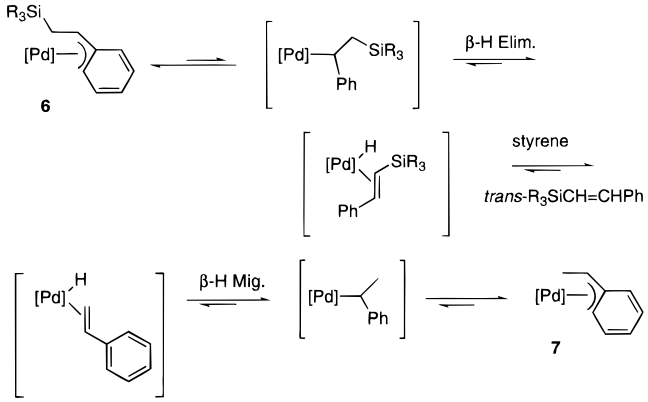


Figure 2. Plots of k_{obs} vs [$HSiEt_3$] for the reaction of $[(phen)Pd(\eta^3\text{-}CH(CH_2SiEt_3)C_6H_5)]^+$ (**6**) and $[(phen)Pd(\eta^3\text{-}CH(CH_3)C_6H_5)]^+$ (**7**) ([**6** or **7**] = 0.027 M) with $HSiEt_3$ at 13 °C. (**6** + $HSiEt_3$ → **2a** + $PhCH_2CH_2SiEt_3$; $k_{obs} = 1.1 \times 10^{-4}$ s^{-1} [$HSiEt_3$]; $R^2 = 0.995$.) (**7** + $HSiEt_3$ → **2a** + $PhCH_2CH_3$; $k_{obs} = 7.1 \times 10^{-4}$ s^{-1} [$HSiEt_3$]; $R^2 = 0.998$.)

Scheme 7. Proposed Associative Benzyl Exchange Mechanism for the Reaction of $[(phen)Pd(\eta^3\text{-}CH(CH_2SiR_3)C_6H_5)]^+$ (**6**) and Styrene ([Pd] = $(phen)Pd^+$)



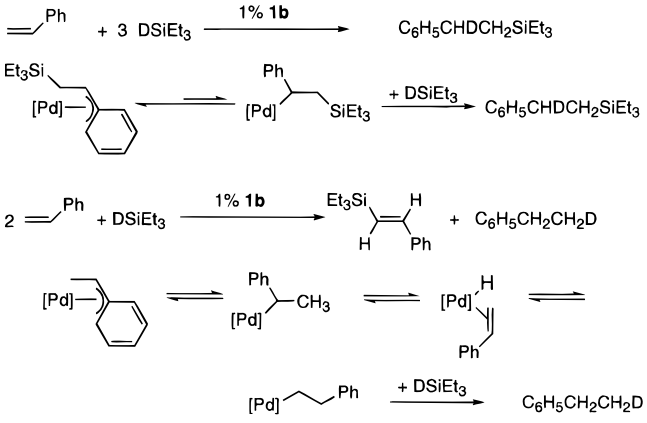
The kinetics of the reaction of **6** with excess styrene were measured at 13 °C. The results are shown in Figure 3. The system approached saturation at higher styrene concentrations. The saturation rate constant was obtained as the reciprocal of the intercept of the plot of $1/k_{obs}$ vs 1/[styrene] ($k_{sat} = 1.1 \times 10^{-4}$ s^{-1}). The rate dependence on [styrene] suggests that displacement of *trans*-$Et_3SiCH{=}CHPh$ occurs via an associative mechanism. Similar kinetic behavior was observed in the reaction of $[(phen)Pd(\eta^3\text{-}CH(CH_2CH_3)C_6H_5)]^+[BAr'_4]^-$ with styrene.[29] In a typical catalytic reaction (Table 2), $[styrene]_{initial} > 2$ M, so saturation behavior is assumed.

The π-benzyl complex **7** reacts with $HSiEt_3$ to produce ethylbenzene and **2a**. The reaction of **7** with $HSiEt_3$ was monitored under pseudo-first-order conditions (0.027 M **7**, 10−30 equiv of $HSiEt_3$) at 13 °C. The reaction of **7** with $HSiEt_3$ was found to be first order in both **7** and $HSiEt_3$ ($k_{obs} = 7.1 \times 10^{-4}$ M^{-1} s^{-1} [$HSiEt_3$]) (Figure 2).

^1H NMR spectroscopy of a working catalyst solution revealed the presence of both **6** and **7** in the presence of excess styrene and $HSiEt_3$. Thus, the π-benzyl complexes **6** and **7** are the catalyst resting state for the silation reactions of styrene. **7** can be recovered in >90% yield (based on **1b**) from the reaction mixture by precipitation with hexane upon completion of the catalytic reaction.

B. Deuterium Labeling Studies. The hydrosilation and dehydrogenative silation reactions of styrene with $DSiEt_3$ were

Scheme 8. Reactions of Styrene with $DSiEt_3$ in the Presence of **1b**



investigated (Scheme 8). The reaction of a 3-fold molar excess of $DSiEt_3$ with styrene in the presence of 1% **1b** yielded $C_6H_5CHDCH_2SiEt_3$. In contrast, the reaction of excess styrene with $DSiEt_3$ in the presence of 1% **1b** yielded $C_6H_5CH_2CH_2D$ as the only deuterated product. No evidence for deuterium incorporation into *trans*-$C_6H_5CHCHSiEt_3$ was observed. The reaction of **7** with 4 equiv of $DSiEt_3$ in CD_2Cl_2 yielded $C_6H_5CH_2CH_2D$. Once again, steric factors appear to govern the regiochemistry of cleavage by silane.

C. Mechanism of Hydrosilation and Dehydrogenative Silation of Styrene. A mechanistic scheme can be proposed based on the results of the NMR experiments and the deuterium labeling studies. This mechanism is shown in Scheme 9. As was the case with the hydrosilation, silyl migration to coordinated olefin is a key feature in the silation reactions of styrene. However, rapid isomerization to the π-benzyl complex **6** occurs, so that the complexes $[(phen)Pd(SiEt_3)(\eta^2\text{-}CH_2CHPh)]^+$ and $[(phen)Pd(\eta^1\text{-}CH(CH_2SiEt_3)(C_6H_5)]$, which are plausible intermediates in the conversion of **2a** to **6**, are not observed.

The concentration-dependent rate constants for the conversion of **6** to **7** and the reaction of **6** and **7** with $HSiEt_3$ at 13 °C can be compared directly (Scheme 10). The reaction of the π-benzyl complexes **6** and **7** with excess $HSiEt_3$ show a first-order dependence on $[HSiEt_3]$ and no evidence of saturation kinetics under the reaction conditions (Figure 2). In contrast, saturation

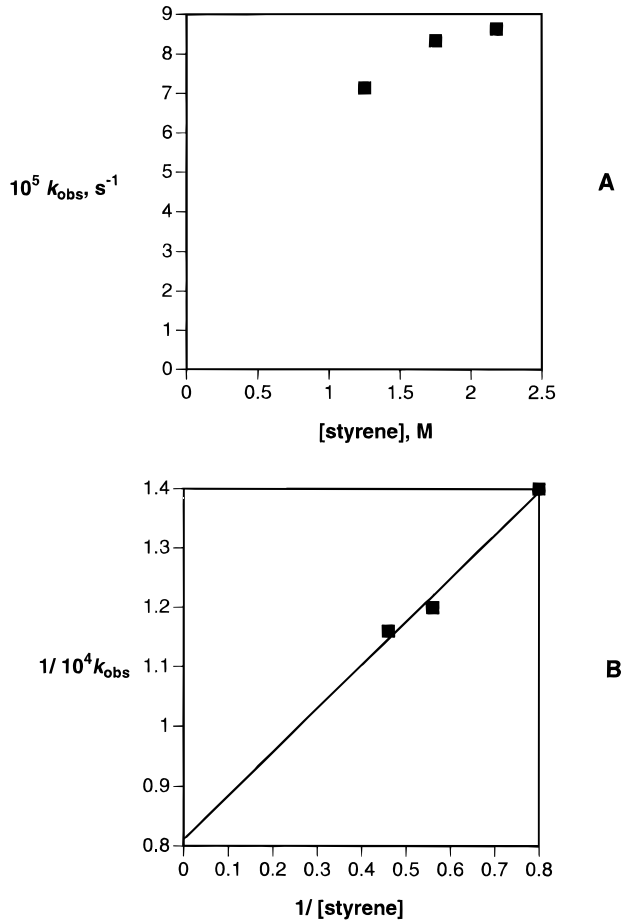
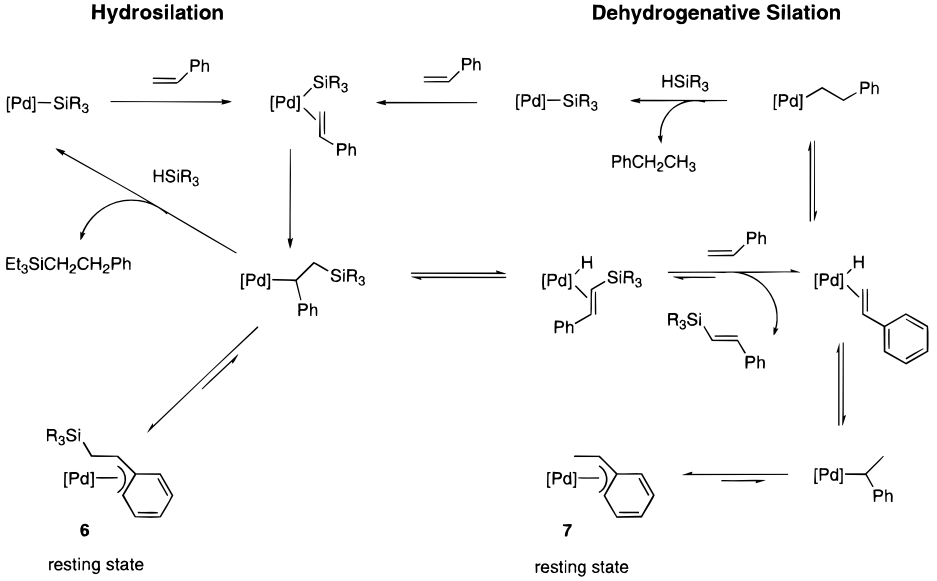


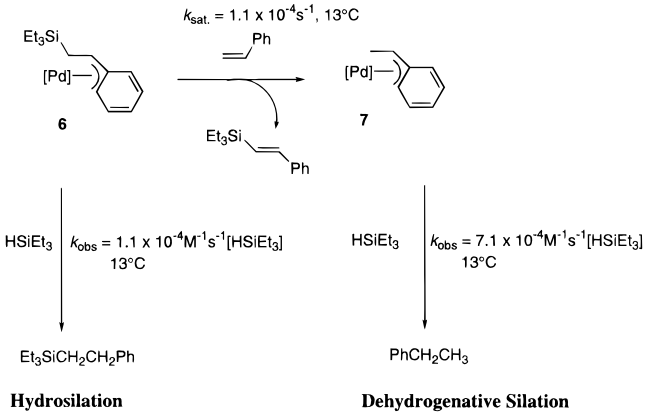
Figure 3. (A) A plot of k_{obs} vs [styrene] for the reaction of $[(phen)Pd(\eta^3\text{-}CH(CH_2SiEt_3)C_6H_5)]^+$ (**6**) ([**6**] = 0.027 M) and styrene yielding $[(phen)Pd(\eta^3\text{-}CH(CH_3)C_6H_5)]^+$ (**7**) and *trans*-PhCH=CHSiEt$_3$. (B) A plot of $1/k_{obs}$ vs 1/[styrene] for the conversion of **6** to **7**. The k_{sat} was determined from the inverse of the intercept of the inverse plot ($k_{sat} = 1.1 \times 10^{-4}$ s^{-1}). See ref 29 for the derivation of the kinetic expression for the benzyl exchange reaction.

behavior is observed in the conversion of **6** to **7**. For the conversion of **6** to **7**, $k_{sat} = 1.1 \times 10^{-4}$ s^{-1}. In a typical catalytic reaction (Table 2), the initial styrene concentration >2 M and saturation is assumed.

Scheme 9. Proposed Mechanism for the $[(phen)Pd]^+$-Catalyzed Hydrosilation and Dehydrogenative Silation of Styrene ([Pd] = $(phen)Pd^+$)



Scheme 10. Comparison of the Concentration-Dependent Rate Constants for the Rate-Determining Steps of the Hydrosilation and Dehydrogenative Silation Reactions of Styrene with $HSiEt_3$ at 13 °C



As shown in Scheme 10, the displacement of *trans*-C_6H_5-CH═CHSiEt$_3$ from **6** results in dehydrogenative silation of styrene, and the reaction of **6** with $HSiEt_3$ results in hydrosilation. The similarities in the rates of the two processes and the fact that the rate of displacement of *trans*-C_6H_5CH═CHSiEt$_3$ saturates at high styrene concentration suggest that the distribution of hydrosilation and dehydrogenative silation in the catalytic reactions might be significantly altered by changing the relative ratios of styrene and $HSiEt_3$. This was observed in the catalytic silations of styrene (Table 2), in agreement with the proposed mechanism. No quantitative predictions of product distributions were possible since the rates were determined at 13 °C in CD_2-Cl_2 and the preparative scale silations were conducted at higher temperature (35−85 °C).

The difference in the rate constants for the reactivity of the π-benzyl complexes **6** and **7** with $HSiEt_3$ may be due to steric factors. If this is the case, then it suggests that the reaction of the π-benzyl complexes **6** or **7** with a bulkier silane (such as HSi(*i*-Pr)$_3$) would be even slower. This was confirmed qualitatively by noting that no reaction was observed between **7** and excess HSi(*i*-Pr)$_3$ in CD_2Cl_2 at 25 °C. Since the rate of associative displacement of styrene would be unlikely to change as much, the use of bulkier silanes should favor the dehydrogenative silation reaction rather than the hydrosilation reaction. This was observed in the reactions of styrene with HSi(*i*-Pr)$_3$ (Table 2). Similar results were recently observed in a Rh-catalyzed dehydrogenative silation of styrene.[13]

Even when steric factors are taken into account, the silation reactions of styrene proceed much more slowly than the silation reactions of alkyl-substituted olefins. It is likely that this difference results from the high stability of the π-benzyl intermediates **6** and **7**. The relatively low reactivity of **6** toward $HSiR_3$ allows an alternate reaction, the displacement of *trans*-R_3SiCH═CHPh by styrene, to occur at a similar rate. Thus, dehydrogenative silation is competitive with hydrosilation in this system.

Conclusions

Several conclusions can be drawn from the results of the mechanistic studies and deuterium labeling studies.

(1) In the silation reactions of alkyl-substituted α-olefins and ethylene, the catalyst resting state is the η^2-olefin complex, [(phen)Pd(SiR$_3$)(η^2-H$_2$C═CHR′)]$^+$. This is true for both hydrosilation and dehydrogenative silation.

(2) *Silyl migration to olefin is rapid and reversible at −60 °C.* The ease of β-silyl elimination reactions in this system suggests that β-silyl elimination may be a facile reaction of other transition metal β-silyl(alkyl) complexes. The silyl migration and elimination reactions are similar to hydride and alkyl migration reactions and β-hydrogen and β-methyl abstraction reactions, respectively.[2]

(3) The deuterium labeling studies and formation of vinyl silanes suggest that in addition to the rapid, the degenerate β-silyl migrations, β-hydrogen elimination and reinsertion reactions are operative in this system. Both the β-silyl migrations and the β-hydride migrations are operative at low temperatures (<−40 °C).

(4) The eventual reaction of the Pd(II) alkyl intermediate ([Pd]−R″) with $HSiR_3$ appears to be governed by steric factors, with the most accessible isomer reacting the fastest. If intermediate [Pd]−R″ and/or the silane $HSiR_3$ are too bulky, the cleavage of [Pd]−R″ by $HSiR_3$ is disfavored and associative displacement of vinylsilane by alkene can occur, resulting in dehydrogenative silation. In this system, *dehydrogenative silation results when the reaction with HSiR$_3$ is inhibited*, rather than when associative displacement is promoted (e.g., by addition of a coordinating ligands such as PPh_3).

(5) The proposed mechanism of styrene hydrosilation and dehydrogenative silation is similar to that proposed for the silation reactions of ethylene and alkyl-substituted olefins. The main difference is that in the silation reactions of styrene, the catalyst resting states are the π-benzyl complexes **6** and **7** rather than the η^2-olefin complexes, [(phen)Pd(SiR$_3$)(η^2-H$_2$C═CHR′)]$^+$. The stability of the π-benzyl complexes results in a slow reaction with $HSiR_3$. As a result of the low reactivity of **6** with $HSiR_3$, the associative displacement of vinylsilane by styrene becomes competitive with cleavage by $HSiR_3$, and significant amounts of dehydrogenative silation are observed, despite the relatively low steric demands of $SiEt_3$ and phenyl groups.

(6) It should be emphasized that the catalysts used in this study are highly electrophilic, cationic Pd(II) complexes. The Pd(II)-catalyzed hydrosilation and dehydrogenative silation reactions reported here may proceed by a different mechanism than Pd(0)-catalyzed hydrosilation of olefins, in which dehydrogenative silation is not observed and hydrosilation of styrene occurs with silation of the benzylic carbon.

The results reported here contribute to an understanding of the factors that govern hydrosilation and dehydrogenative silation reactions. Using the mechanistic information obtained in this study, we are currently investigating the development of new catalysts that are highly selective for dehydrogenative silation.

Experimental Section

General. Unless otherwise noted, all reactions were conducted under an atmosphere of dry, deoxygenated argon or nitrogen using standard Schlenk techniques or in a Vacuum Atmospheres glovebox. Pentane, hexane, ether, toluene, and tetrahydrofuran were distilled from sodium benzophenone ketyl under a nitrogen atmosphere prior to use. Dichloromethane was distilled from P_4O_{10} under a nitrogen atmosphere. CD_2Cl_2 (CIL) was dried over CaH_2 under argon and was degassed and vacuum transferred. $CDCl_3$ was used as received. (phen)PdMe$_2$,[29] H(OEt$_2$)$_2$BAr′$_4$,[30] [(phen)Pd(CH$_3$)(OEt$_2$)]$^+$[BAr′$_4$]$^-$ (**1a**),[29] [(phen)Pd(CH$_3$)(NCCH$_3$)]$^+$[BAr′$_4$]$^-$ (**1c**),[26] and [(phen)Pd(η^3-CH(CH$_3$)C$_6$H$_5$)]$^+$[BAr′$_4$]$^-$ (**7**)[29] were prepared according to reported procedures. Ethylene (polymer grade) was purchased from Matheson Gases. Unless otherwise noted, silanes, chlorosilanes, and olefins were purchased from Aldrich and used without further purification. Et_3SiD was prepared from Et_3SiCl and $LiAlD_4$ in Et_2O.[8] ^{1}H NMR of the product revealed <5% H incorporation. Allyltriethylsilane was prepared from allylmagnesium bromide and Et_3SiCl in THF.

^{1}H and ^{13}C chemical shifts were referenced to residual protio solvent peaks and solvent ^{13}C peaks, respectively. Coupling constants are

reported in hertz; routine coupling constants are not listed. Elemental analyses were performed by Oneida Laboratories.

Atom labeling schemes for the phenanthroline and $((CF_3)_2C_6H_3)_4B^-$ counterion resonances are as follows:

The ^{1}H NMR resonances were assigned into groups of a, b, c, d or a, a′, b, b′, c, c′, d, d′ according to their characteristic coupling patterns. The ^{13}C NMR resonances were assigned in pairs such as C_a or $C_{a'}$ and $C_{a'}$ or C_a, based on their chemical shifts and $^1J_{CH}$. The relation between the ^{1}H and ^{13}C assignments and the stereochemistry with respect to the ligands X and Y has not been ascertained.

^{1}H and ^{13}C data attributed to the counterion $BAr'_4{}^-$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$) follow. These are consistent for all examined cationic complexes and are not included in each compound characterized below. ^{1}H NMR (CD_2Cl_2) δ 7.72 (s, 8, H_o), 7.56 (s, 4, H_p). ^{1}H chemical shifts are accurate to within ±0.02 ppm. ^{13}C NMR (CD_2Cl_2) δ 162.1 (q, $J_{C\text{-}B}$ = 50 Hz, C_i), 135.2 (C_o), 129.3 (q, $^2J_{C\text{-}F}$ = 31 Hz, C_m), 125.0 (q, $J_{C\text{-}F}$ = 272 Hz, *C*F$_3$), 117.8 (C_p). ^{13}C NMR chemical shifts and coupling constants are consistent to within ±1 ppm and ±2 Hz, respectively.

[(phen)Pd(CH$_3$)(Me$_3$SiC≡CSiMe$_3$)]$^+$[BAr′$_4$]$^-$ (1b). Solid (phen)Pd$(CH_3)_2$ (116 mg, 0.37 mmol) and $[H(OEt_2)_2]^+[BAr'_4]^-$ (365 mg, 0.37 mmol) were combined. The reaction flask was cooled to −30 °C and Et_2O (10 mL) and CH_2Cl_2 (5 mL) were added. The resulting slurry was allowed to warm to 25 °C to dissolve solid (phen)Pd$(CH_3)_2$, and then the solution was cooled to −30 °C. Bis(trimethylsilyl)acetylene (85 μL, 0.37 mmol) was added and colorless microcrystals formed. The mixture was allowed to warm to room temperature, and the solid dissolved. The mixture was stirred for 1 h and then the volume was reduced to 5 mL *in vacuo* and cooled slowly to −78 °C. Colorless needles formed and were washed with 10 mL of cold Et_2O, collected, and dried (yield 285 mg, 59%). ^{1}H NMR (CD_2Cl_2, 20 °C) δ 8.95 (d, 1, phen H_a), 8.71 (d, 1, phen H_a), 8.59 (dd, 1, phen H_c), 8.54 (dd, 1, phen H_c), 8.05 (s, 2, phen H_d), 8.00 (dd, 1, phen H_b), 7.92 (dd, 1, phen H_b), 1.06 (s, 3, PdC*H*$_3$), 0.32 (s, 18, Si(C*H*$_3$)$_3$). ^{13}C NMR (CD_2Cl_2, 20 °C) δ 147.2, 145.2 (C_a, $C_{a'}$), 146.2, 143.2 (C_e, $C_{e'}$), 139.7, 138.4 (C_c, $C_{c'}$), 129.9, 129.3 (C_f, $C_{f'}$), 126.8, 126.5 (C_d, $C_{d'}$), 124.6, 124.4 (C_b, $C_{b'}$), 103.6 (Me$_3$Si*C*≡*C*SiMe$_3$), 7.9 (Pd*C*H$_3$), −1.7 (Si*Me*$_3$). Anal. Calcd for $C_{53}H_{41}N_2BF_{24}PdSi_2$: C, 47.67; H, 3.09; N, 2.10. Found: C, 47.83; H, 3.04; N, 1.94.

Hydrosilation with HSiEt$_3$. General Procedure. In a glovebox, solid [(phen)Pd(CH$_3$)(Me$_3$SiCCSiMe$_3$)]$^+$[BAr′$_4$]$^-$ (150 mg, 0.10 mmol) was loaded into a Schlenk flask. The flask was removed from the glovebox and 5 mL of CH_2Cl_2 was added. Olefin (10.0 mmol) was added to the solution and $HSiEt_3$ (1.80 mL, 11.2 mmol) was then added. The yellow solution was stirred overnight. CH_2Cl_2, $HSiEt_3$, and olefin were removed in vacuo, leaving a clear oil and a precipitate of Pd black and deactivated catalyst residue. The oil was dissolved in hexane (5 mL) and passed through alumina (4 × 1 cm). Hexane was removed in vacuo, leaving a colorless oil which was pure by ^{1}H NMR. Yields and NMR data for the hydrosilation products are given below.

SiEt$_3$Cy. Yield = 88%. ^{1}H NMR ($CDCl_3$, 20 °C) δ 1.70 (m, 6), 1.17 (m, 4, C*H*$_2$CHSiEt$_3$), 0.92 (t, 9, SiCH$_2$C*H*$_3$), 0.7 (t, 1, C*H*SiEt$_3$), 0.49 (q, 6, SiC*H*$_2$CH$_3$). ^{13}C NMR ($CDCl_3$, 20 °C) δ 28.4, 27.9, 27.2, 23.6 (C_6H_{11}), 7.7 (SiCH$_2$*C*H$_3$), 2.0 (SiC*H*$_2$CH$_3$).

SiEt$_3$(CH$_2$CH$_2$-*t*-Bu). Yield = 79%. ^{1}H NMR ($CDCl_3$, 20 °C) δ 1.1 (m, 2, C*H*$_2$-*t*-Bu), 0.90 (t, 9, SiCH$_2$C*H*$_3$), 0.82 (s, 9, *t*-Bu) 0.5 (m, 2, C*H*$_2$SiEt$_3$), 0.47 (q, 6, SiC*H*$_2$CH$_3$). ^{13}C NMR ($CDCl_3$, 20 °C) δ 37.8 (*C*H$_2$-*t*-Bu), 31.1 (*C*Me$_3$), 28.8 (C*Me*$_3$), 7.47 (SiCH$_2$*C*H$_3$), 5.05 (*C*H$_2$-SiEt$_3$), 3.20 (SiCH$_2$CH$_3$).

SiEt$_3$([CH$_2$]$_5$CH$_3$). Yield = 88%. NMR data matched reported data.[8]

SiEt$_4$. In a modification of the above procedure, **1a** (0.1 mmol) was generated from (phen)PdMe$_2$ and $[H(OEt_2)_2][BAr'_4]$ at −78 °C in 10 mL of CH_2Cl_2. $HSiEt_3$ (1.55 mL, 9.8 mmol) was added. Ethylene was bubbled through the solution and the mixture was allowed to warm to room temperature. After 20 min, a precipitate of Pd black had formed and ethylene addition was stopped. Solvent was removed in vacuo, yielding a colorless oil that was pure $SiEt_4$ by ^{1}H NMR (1.20 g, 85%).

Si(*i*-Pr)$_3$(Et). Si(*i*-Pr)$_3$(Et) was prepared in a procedure similar to that used for $SiEt_4$. The resulting colorless oil was pure by ^{1}H and ^{13}C NMR (yield 75%). ^{1}H NMR ($CDCl_3$, 20 °C) δ 1.0 (m, 24, *i*-Pr + SiCH$_2$C*H*$_3$), 0.82 (q, 2, SiC*H*$_2$CH$_3$). ^{13}C NMR ($CDCl_3$, 20 °C) δ 18.0 (CH*Me*$_2$), 10.0 (*C*HMe$_2$), 7.33, 0.0 (SiEt). Anal. Calcd for $C_{11}H_{26}Si$: C, 70.87; H, 14.06. Found: C, 70.66; H, 14.63.

SiPh$_3$Cy. In a drybox, solid $HSi(C_6H_5)_3$ (1.37 g, 5.27 mmol) and **1b** (76 mg, 0.05 mmol) were loaded into a Schlenk flask. The solids were then dissolved in 10 mL of CH_2Cl_2 at −78 °C and cyclohexene (500 μL, 5.0 mmol) was added. The solution was warmed to room temperature and allowed to stir overnight. Solvent was removed in vacuo, yielding a gray solid. The solid was dissolved in 50 mL of hot hexane and filtered. The volume of the filtrate was reduced to 20 mL, at which point crystals began to form. Colorless crystals were collected and dried (1.37 g, 78%) ^{1}H NMR ($CDCl_3$, 20 °C) δ 7.3−7.5 (m, 15, $SiPh_3$), 1.94 (br d, 2, C*H*$_2$), 1.7 (br s, 2, C*H*$_2$), 1.6 (t, 1, C*H*SiPh$_3$), 1.4−1.1 (br m, 6, C*H*$_2$). ^{13}C NMR ($CDCl_3$, 20 °C) δ 136.0, 134.6, 129.2, 122.7 (Ph), 28.2, 28.1, 26.8 (*C*H$_2$), 24.1 (*C*HSiPh$_3$).

SiPh$_3$(CH$_2$CH$_2$-*t*-Bu). $Si(C_6H_5)_3(CH_2CH_2$-*t*-Bu) was prepared using the same procedure described for $Si(C_6H_5)_3(C_6H_{11})$. A colorless oil was obtained which crystallized from hexane at −30 °C after 2 months (recrystallized yield 20%). ^{1}H NMR ($CDCl_3$, 20 °C) δ 7.3−7.5 (m, 15, $SiPh_3$), 1.55 (br s, 2, C*H*$_2$-*t*-Bu), 1.32 (br s, 2, C*H*$_2$SiPh$_3$), 0.85 (s, 9, *t*-Bu). ^{13}C NMR ($CDCl_3$, 20 °C) δ 135.7, 135.4, 129.3, 127.8 (Ph), 37.6 (*C*H$_2$-*t*-Bu), 31.3 (*C*Me$_3$), 28.8 (C*Me*$_3$), 7.5 (*C*H$_2$SiPh$_3$). Anal. Calcd for $C_{24}H_{28}Si$: C, 83.66; H, 8.19. Found: C, 83.07; H, 7.92.

***t*-BuCH═CHSi(*i*-Pr)$_3$. 1a** was generated in situ at −78 °C from phenPdMe$_2$ (31 mg, 0.1 mmol) and $[H(OEt_2)_2]^+[BAr'_4]^-$ (101 mg, 0.1 mmol) in CH_2Cl_2. $HSi(i\text{-}Pr)_3$ (2.0 mL, 10 mmol) and *t*-BuCH═CH$_2$ (2.6 mL, 20 mmol) were added via syringe. The mixture was allowed to warm to room temperature and stir for 24 h. CH_2Cl_2 and *t*-BuCH$_2$-CH$_3$ were removed in vacuo. The resulting oil was dissolved in hexane (10 mL) and filtered through a pipet of alumina (4 × 1 cm). Hexane was removed in vacuo, leaving a colorless oil that was pure *t*-BuCH═CHSi(*i*-Pr)$_3$ by ^{13}C NMR spectroscopy (1.97 g, 82%). ^{1}H NMR ($CDCl_3$) δ 6.07 (d, 1, $J_{H\text{-}H}$ = 19 Hz, C*H*-*t*-Bu), 5.37 (d, 1, $J_{H\text{-}H}$ = 19 Hz, C*H*Si(*i*-Pr)$_3$), 1.0 (br m, 30 total, Si(*i*Pr)$_3$ + *t*-Bu). ^{13}C NMR ($CDCl_3$) δ 159.9 ($J_{C\text{-}H}$ = 145 Hz, *C*H-*t*-Bu), 115.7 ($J_{C\text{-}H}$ = 134 Hz, *C*HSi(*i*-Pr)$_3$), 35.4 (*C*Me$_3$), 29.1 (C*Me*$_3$), 18.6 (CH(*Me*)$_2$), 10.9 (*C*H-(Me)$_2$). Anal. Calcd for $C_{15}H_{32}Si$: C, 74.91; H, 13.41. Found: C, 74.16; H, 13.24.

Reactions of Styrene. In a typical procedure, **1b** or **7** (0.05 mmol) was loaded into a flask that was fitted with a Teflon plug. For the reactions conducted at 35 °C, CH_2Cl_2 (1 mL) was added to dissolve the catalyst. For the reactions conducted at 85 °C, the catalyst was soluble in styrene/silane and no solvent was added. Styrene and $HSiR_3$ (R = C_2H_5, $CH(CH_3)_2$) were then added and the reaction was allowed to stir for 24 h. CH_2Cl_2, ethylbenzene, and unreacted styrene and $HSiR_3$ were then removed in vacuo, leaving a pale yellow oil and a yellow solid. The oil was dissolved in hexane and passed through a pipet full of alumina (4 × 1 cm) to remove any remaining **7**. Hexane was then removed in vacuo, leaving a colorless oil that was a mixture of C_6H_5-$CH_2CH_2SiR_3$ and *trans*-C_6H_5CH═$CHSiR_3$. ^{1}H and ^{13}C NMR data matched reported values.[13] Yields and product distribution are given in Table 1. The hexane-insoluble yellow solid isolated from the reaction mixture was washed with hexane and dried. ^{1}H NMR data for the solid matched that of **7**.

[(phen)Pd(SiEt$_3$)(HSiEt$_3$)]$^+$[BAr′$_4$]$^-$ (2a). [(phen)Pd(CH$_3$)(OEt$_2$)]$^+$-[BAr′$_4$]$^-$ (53 mg, 0.042 mmol) was loaded into a NMR tube. CD_2Cl_2 (700 μL) was added at −78 °C, the mixture was shaken to dissolve the solid, and $HSiEt_3$ (14 μL, 0.11 mmol) was added. The sample was inserted into a precooled NMR probe. ^{1}H NMR (CD_2Cl_2, −60 °C) δ 9.05 (d, 2, phen), 8.54 (d, 2, phen), 7.96 (br. s, 4, phen), 1.00 (m, 30, SiC*H*$_2$CH$_3$ + SiCH$_2$C*H*$_3$), −9.99 (s, 1, Si-*H*-Si). ^{13}C NMR (CD_2Cl_2, −60 °C) δ 151.8, 144.4, 140.3, 130.0, 127.6, 125.8 (phen) 9.2 (SiCH$_2$CH$_3$), 8.5 (SiCH$_2$*C*H$_3$). ^{1}H and ^{13}C NMR revealed that the two silyl groups were equivalent at −80 °C.

[(phen)Pd(SiPh$_3$)(HSiPh$_3$)]$^+$[BAr′$_4$]$^-$ (2b). Solid [(phen)Pd(CH$_3$)(OEt$_2$)]$^+$[BAr′$_4$]$^-$ (30 mg, 0.024 mmol) and HSiPh$_3$ (18 mg, 0.069 mmol) were combined in an NMR tube. CD_2Cl_2 (700 μL) was added at −78 °C and the tube was shaken briefly to dissolve the solids. The sample was inserted into a precooled NMR probe. ^{1}H NMR (CD_2Cl_2, −80 °C) δ 10.2 (br s, 2, phen H$_{a,a'}$) 8.2−7 (36, phen + SiPh$_3$), −12.13 (s, 1, Si-*H*).

[(phen)Pd(SiEt$_3$)(PPh$_3$)]$^+$[BAr′$_4$]$^-$ (3a). Solid (phen)Pd(CH$_3$)$_2$ (64 mg, 0.20 mmol) and [H(OEt$_2$)$_2$]$^+$[BAr′$_4$]$^-$ (210 mg, 0.21 mmol) were combined. CH_2Cl_2 (10 mL) was added at −78 °C and the mixture was stirred until the solids had dissolved and methane evolution ceased. HSiEt$_3$ (65 μL, 0.40 mmol) was added to generate **2a**. A solution of PPh$_3$ (62 mg, 0.20 mmol) in CH_2Cl_2 (3 mL) was added to the solution of **2a** at −78 °C. The mixture became orange and was stirred for 20 min. The volume was reduced to 3 mL and pentane (5 mL) was added. An orange microcrystalline solid formed. The solid was collected, washed with 5 mL of pentane and dried (145 mg, 48%). ^{1}H NMR (CD_2Cl_2) δ 7.2−9.0 (m, 23 total, phen + phenyl), 0.82 (t, 9, SiCH$_2$C*H*$_3$), 0.65 (q, 6, SiC*H*$_2$CH$_3$). ^{31}P NMR (CD_2Cl_2) δ 37.8. Anal. Calcd for $C_{68}H_{50}N_2BF_{24}PPdSi$: C, 53.47; H, 3.30; N, 1.83. Found: C, 53.03; H, 2.89; N, 0.75.

[(phen)Pd(SiEt$_3$)(Ph$_2$PCH$_2$CH═CH$_2$)]$^+$[BAr′$_4$]$^-$ (3b). **3b** was prepared in a manner similar to that described for **3a** (yield 74%). ^{1}H NMR (CD_2Cl_2) δ 8.52, 8.50 (br s, 4 tot., phen + Ph), 7.99 (s, 2, phen), 7.1−7.8 (m, 12, phen + Ph), 5.93 (m, 1, CH$_2$═C*H*CH$_2$PPh$_2$), 5.20 (dd, 1, C*H*$_a$H$_b$═CHCH$_2$PPh$_2$), 5.07 (dd, 1, CH$_a$H$_b$═CHCH$_2$PPh$_2$), 3.42 (m, 2, C*H*$_2$PPh$_2$), 0.95 (m, 15, SiEt$_3$). ^{31}P NMR (CD_2Cl_2) δ 29.3. Anal. Calcd for $C_{65}H_{50}N_2BF_{24}PPdSi$: C, 52.35; H, 3.38; N, 1.87. Found: C, 52.12; H, 3.20; N, 0.98.

[(phen)Pd(SiEt$_3$)(η^2-C$_2$H$_4$)]$^+$[BAr′$_4$]$^-$ (4a). [(phen)Pd(CH$_3$)(OEt$_2$)]$^+$-[BAr′$_4$]$^-$ (10.2 mg, 0.08 mmol) was loaded into a NMR tube. CD_2Cl_2 (700 μL) was added at −78 °C, the mixture was shaken to dissolve the solid, and HSiEt$_3$ (2.0 μL, 0.015 mmol) was added. Ethylene (0.50 mL, 0.022 mmol) was added via syringe. The sample was inserted into a precooled (−90 °C) NMR probe. ^{1}H NMR (CD_2Cl_2, −90 °C) δ 8.74, 8.37 (d, 1 each, phen H$_{a,a'}$), 8.65, 8.51 (d, 1 each, phen H$_{c,c'}$), 8.05, 7.88 (dd, 1 each, phen H$_{b,b'}$), 7.99 (s, 2, phen H$_{d,d'}$), 5.12, 4.70 (br d, 2 each, C$_2$H$_4$), 0.88 (t, 9, SiCH$_2$C*H*$_3$), 0.55 (q, 6, SiC*H*$_2$CH$_3$). In the presence of excess ethylene, exchange between free and bound ethylene occurs and only a single averaged resonance is observed at 5.0 ppm.

[(phen)Pd(SiEt$_3$)(η^2-CH$_2$═CH-*t*-Bu)]$^+$[BAr′$_4$]$^-$ (4b). [(phen)Pd-(SiEt$_3$)(η^2-CH$_2$═CH-*t*-Bu)]$^+$[BAr′$_4$]$^-$ was generated at −78 °C using a procedure similar to that described for [(phen)Pd(SiEt$_3$)(C$_2$H$_4$)]$^+$[BAr′$_4$]$^-$. ^{1}H NMR (CD_2Cl_2, −80 °C) δ 9.33, 9.25 (d, 1 each, phen H$_{a,a'}$), 8.50 (m, phen H$_{c,c'}$), 9.93 (phen H$_{b,b'}$ and H$_{d,d'}$), 4.17 (dd, 1, H$_2$C═C*H*-*t*-Bu), 3.63 (d, 1, *H*$_a$H$_b$C═CH-*t*-Bu), 3.12 (d, 1, H$_a$*H*$_b$C═CH-*t*-Bu), 1.02 (s, 9, *t*-Bu), 0.78 (t, 9, SiCH$_2$C*H*$_3$), 0.61 (q, 6, SiC*H*$_2$CH$_3$). ^{13}C NMR (CD_2Cl_2, −60 °C) δ 152.2, 151.5 (phen C$_{a,a'}$), 144.1, 143.2 (phen C$_{e,e'}$), 139.8, 139.5 (phen C$_{c,c'}$), 130.0, 129.7 (phen C$_{f,f'}$), 127.7, 127.5 (phen C$_{d,d'}$), 125.9, 125.85 (phen C$_{b,b'}$), 94.2 (H$_2$C═*C*H-*t*-Bu), 55.0 (H$_2$*C*═CH-*t*-Bu), 35.8 (*C*Me$_3$), 30.1 (C*Me*$_3$), 15.5, 9.9 (Si*Et*$_3$).

[(phen)Pd(Si(*i*-*Pr*)$_3$)(η^2-CH$_2$═CH-*t*-Bu)]$^+$[BAr′$_4$]$^-$ (4c). In a 5-mm NMR tube, **1a** (52 mg, 0.042 mmol) was dissolved in CD_2Cl_2 (700 μL) at −78 °C. HSi(*i*-Pr)$_3$ (8.5 μL, 0.042 mmol) was added and the mixture was shaken once to mix. *tert*-Butylethylene (6 μL, 0.046 mmol) was added, yielding a yellow solution. The sample was inserted into a precooled (−65 °C) NMR probe. ^{1}H NMR (CD_2Cl_2, −65 °C) δ 9.28, 9.00 (d, 1 each, phen H$_{a,a'}$) 8.55 (overlapping doublets, 2 total, phen H$_{c,c'}$), 9.95 (s, 2, phen H$_{d,d'}$), 7.86 (m, 2, phen H$_{b,b'}$), 3.68 (d, 1, *H*$_a$H$_b$═CH-*t*-Bu), 1.2 (br s, 30 total, *i*-Pr + *t*-Bu). Note: the peaks associated with H$_a$*H*$_b$═CH-*t*-Bu and H$_2$C═C*H*-*t*-Bu were not located and were assumed to be obscured by the free ether peak at 3.4 ppm. ^{13}C NMR (CD_2Cl_2, −65 °C) δ 154.3, 152.4 (C$_{a,a'}$) 146.2, 144.3 (C$_{e,e'}$), 139.5, 139.1 (C$_{c,c'}$), 130.2, 129.8 (C$_{f,f'}$), 127.4, 127.3 (C$_{d,d'}$), 126.1, 125.5 (C$_{b,b'}$), 72.0 (H$_2$C═*C*H-*t*-Bu), 37.5 (H$_2$*C*═CH-*t*-Bu), 30.2 (*C*Me$_3$), 29.4 (C*Me*$_3$), 18.3, 18.2 (CH*Me*$_2$), 11.3 (*C*HMe$_2$). Free *t*-BuCH═CHSi(*i*-Pr)$_3$ was observed when a solution of **4c** was warmed to −20 °C.

Kinetic Study of the Reaction of 4b with HSiEt$_3$. **1a** (12 mg, 0.01 mmol) was loaded into a 5-mm NMR tube and dissolved in 700 μL of CD_2Cl_2 at −78 °C. HSiEt$_3$ was added via syringe to generate **2a**; *t*-BuCH═CH$_2$ (1.2 μL, 0.009 mmol) was added and the NMR tube was shaken briefly and inserted into a precooled (−38 ± 1 °C) NMR probe. The concentration of **4b** was monitored as a function of time; the Ar′ H$_{para}$ resonance at 7.25 ppm was used as an internal standard. Rate constants were obtained from a plot of ln [**4b**] vs time. Reaction conditions and observed rate constants are shown in Table 3. The rate dependence on [HSiEt$_3$] was determined from the slope of the line obtained from a plot of k_{obs} vs [HSiEt$_3$] (Figure 1) ($k_{obs} = 1.7 \times 10^{-3}$ M^{-1} s^{-1} [HSiEt$_3$], $R^2 = 0.979$).

Table 3

[**4a**], M	[HSiEt$_3$], M	vol of HSiEt$_3$, μL	10^4 k_{obs}, s^{-1}
0.014	0.14	15.6	2.25
0.014	0.21	24	3.43
0.014	0.30	35	5.46
0.013	0.40	48	6.54

Reaction of 4b with HSiPh$_3$. A CD_2Cl_2 solution (700 μL) of **4b** was generated from **1a** (52 mg, 0.042 mmol), HSiEt$_3$ (7 μL, 0.043 mmol), and *tert*-butylethylene (6 μL, 0.046 mmol) at −78 °C. A solution of HSiPh$_3$ (24 mg, 0.09 mmol) in 300 μL of CD_2Cl_2 was then added and the solution was allowed to warm to room temperature. *t*-BuCH$_2$CH$_2$SiEt$_3$ was observed by ^{1}H and ^{13}C NMR spectroscopy; *t*-BuCH$_2$CH$_2$SiPh$_3$ was not detected.

Observation of [(phen)Pd(SiEt$_3$)(η^2-H$_2$C═CHCH$_2$SiPh$_3$)]$^+$[BAr′$_4$]$^-$ (5a). **1a** (33 mg, 0.027 mmol) was loaded into a 5-mm NMR tube and dissolved in CD_2Cl_2 (400 μL) at −78 °C. HSiEt$_3$ (8 μL, 0.05 mmol) was added and the mixture was shaken briefly to generate **2a**. Allyltriphenylsilane (10 mg, 0.033 mmol) was dissolved in 300 μL of CD_2Cl_2 and added to the solution of **2a** at −78 °C. The sample was inserted into a precooled (−78 °C) NMR probe. ^{1}H NMR (CD_2Cl_2, −60 °C) δ 5.85 (br m, 1, H$_2$C═C*H*CH$_2$SiPh$_3$), 4.22, 3.43 (d, 1 each, *H*$_2$C═CHCH$_2$SiPh$_3$), 2.20 (dd, C*H*$_a$H$_b$SiPh$_3$), 1.62 (t, 1, CH$_a$*H*$_b$SiPh$_3$). Because of the equilibrium between **5a** and **5b**, the resonances associated with SiPh$_3$, phen, and SiEt$_3$ are quite complicated and are not listed here.

Observation of [(phen)Pd(SiPh$_3$)(η^2-H$_2$C═CHCH$_2$SiEt$_3$)]$^+$[BAr′$_4$]$^-$ (5b). A solution of **5b** in CD_2Cl_2 was prepared in a manner similar to that described for **5a**. ^{1}H NMR (CD_2Cl_2, −60 °C) δ 4.8 (br m, 1, H$_2$C═C*H*CH$_2$SiEt$_3$), 4.05, 3.67 (d, 1 each, *H*$_2$C═CHCH$_2$SiEt$_3$), 2.32 (dd, C*H*$_a$H$_b$SiEt$_3$), 1.78 (t, 1, CH$_a$*H*$_b$SiEt$_3$). Because of the equilibrium between **5a** and **5b**, the resonances associated with SiPh$_3$, phen, and SiEt$_3$ are quite complicated and are not listed here.

[(phen)Pd(SiEt$_3$)(η^2-H$_2$C═CHCH$_2$SiEt$_3$)]$^+$[BAr′$_4$]$^-$ (5c). **1a** (33 mg, 0.027 mmol) was loaded into a NMR tube. CD_2Cl_2 (700 μL) was added at −78 °C, the mixture was shaken to dissolve the solid, and HSiEt$_3$ (4.2 μL, 0.036 mmol) was added. The mixture was shaken briefly and allyltriethylsilane (5.4 μL, 0.27 mmol) was added via syringe. The NMR sample was then inserted into a precooled (−78 °C) NMR probe and the spectra were acquired. ^{1}H NMR (CD_2Cl_2, −78 °C) δ 9.17 (d, 2, phen), 8.49 (d, 2, phen) 7.92 (s, 2, phen) 7.90 (m, 2, phen), 4.8 (br m, 1, H$_2$C═C*H*$_2$CH$_2$SiEt$_3$), 3.64, 3.36 (d, 1 each, *H*$_2$C═CH$_2$CH$_2$SiEt$_3$), 1.74 (d, 1, H$_2$C═CH$_2$C*H*$_a$H$_b$SiEt$_3$), 1.20 (t, 1, H$_2$C═CH$_2$CH$_a$*H*$_b$SiEt$_3$), 0.86 (t, 18, SiCH$_2$C*H*$_3$; note that the two SiEt$_3$ resonances are apparently coincident), 0.63, 0.55 (q, 6 each, SiCH$_2$-CH$_3$); ^{13}C NMR (CD_2Cl_2) δ 150.7 (phen C$_{a,a'}$), 136.3 (phen C$_{e,e'}$), 139.4 (phen C$_{c,c'}$), 129.6 (phen C$_{f,f'}$), 125.4 (phen C$_{b,b'}$), 90.0 (H$_2$C═*C*HCH$_2$-SiEt$_3$), 61.8 (H$_2$*C*═CHCH$_2$SiEt$_3$), 21.0 (H$_2$C═CH*C*H$_2$SiEt$_3$), 8.3, 8.2 (SiCH$_2$*C*H$_3$), 6.9 (SiCH$_2$CH$_3$); note that the two SiEt$_3$ resonances are apparently coincident).

[(phen)Pd(SiPh$_3$)(η^2-H$_2$C═CHCH$_2$SiPh$_3$)]$^+$[BAr′$_4$]$^-$ (5d). Solid HSiPh$_3$ (15 mg, 0.05 mmol) and **1a** (33 mg, 0.027 mmol) were loaded into a NMR tube. The solids were dissolved in 400 μL of CD_2Cl_2 at −78 °C. Allyltriphenylsilane (20 mg, 0.067 mmol) was dissolved in 400 μL of CD_2Cl_2 and added via syringe to the cold solution of [(phen)Pd(SiPh$_3$)(HSiPh$_3$)]$^+$[BAr′$_4$]$^-$. The NMR tube was shaken briefly to mix the solution and then inserted into a precooled (−78 °C) NMR probe. ^{1}H NMR (CD_2Cl_2, −60 °C) δ 4.08, 3.42 (d, 1 each, *H*$_2$C═CHCH$_2$SiPh$_3$), 4.0 (br m, 1, H$_2$C═C*H*CH$_2$SiPh$_3$), 3.08 (d, 1, C*H*$_a$H$_b$SiPh$_3$), 2.35 (t, 1, CH$_a$*H*$_b$SiPh$_3$). The peaks associated with phenyl, Ar′, and phen are not listed.

[(phen)Pd(η^3-CH(CH$_2$SiEt$_3$)C$_6$H$_5$)]$^+$[BAr′$_4$]$^-$ (6). [(phen)Pd(CH$_3$)-(OEt$_2$)]$^+$[BAr′$_4$]$^-$ (60 mg, 0.049 mmol) was loaded into a NMR tube. CD_2Cl_2 (700 μL) was added at −78 °C. HSiEt$_3$ (13 μL, 0.081 mmol)

Table 4

[**6**], M	[$HSiEt_3$], M	vol of $HSiEt_3$, μL	$10^4 k_{obs}$, s^{-1}
0.0263	0.49	60	0.53
0.0286	0.87	98	1.05
0.0273	1.18	141	1.30

was added via syringe to the cold solution. The mixture was shaken briefly to dissolve the solid and generate [(phen)Pd($SiEt_3$)(HSi-Et_3)]$^+$[BAr′$_4$]$^-$. Styrene (6 μL, 0.0525 mmol) was added. ^{1}H NMR (CD_2Cl_2, −60 °C) δ 9.02, 8.56, 8.45, 8.41, 7.38, 7.22, 6.38 (d, 1 each, phen + C_6H_5), 7.97 (dd, 1, phen), 7.93 (d, 2, phen), 7.56 (m, 2 phen), 7.29 (t, 1, phen), 4.11 (dd, 1, C*H*CH_2SiEt_3), 1.32 (m, 2, C*H*$_2$$SiEt_3$), 0.93 (t, 9, $SiCH_2CH_3$), 0.60 (q, 6, $SiCH_2CH_3$). ^{13}C NMR (CD_2Cl_2, −60 °C) δ 150.0, 149.9, 148.9, 147.7, 147.6, 146.5, 145.4, 144.0, 140.9, 140.8, 139.5, 139.2, 135.3, (phen + C_6H_5), 64.2 (*C*HCH_2SiEt_3), 14.6 (CH*C*H_2SiEt_3), 7.13 ($SiCH_2CH_3$), 2.64 ($SiCH_2CH_3$). Note: [(phen)Pd(η^3-$CH(CH_2SiEt_3)(C_6H_5)$)]$^+$[BAr′$_4$]$^-$ is stable at 25 °C in CD_2Cl_2 solution, but in the solid state it decomposes to form Pd black and (2-triethylsilyl)styrene. For this reason it could not be isolated in analytically pure form.

Kinetic Study of the Reaction of 6 with $HSiEt_3$. **6** (0.02 mmol) was generated *in situ* as described above. When the total volume of $HSiEt_3$ to be added was <100 μL, 700 μL of CD_2Cl_2 was added; when the volume of $HSiEt_3$ was >100 μL, 600 μL of CD_2Cl_2 was added. Mesitylene (0.5 μL) was added as an internal standard and the solution was cooled to −78 °C. $HSiEt_3$ was added via a gas-tight syringe and the sample was inserted into a precooled (13 ± 1 °C) NMR probe. The concentration of **6** was monitored as a function of time. Rate constants were obtained as the slope of the line −ln [**6**] vs time. Two runs were performed at each $HSiEt_3$ concentration and the rates were averaged. The results are shown in Table 4 and in Figure 2. The rate dependence on [$HSiEt_3$] was determined from the slope of the line obtained from a plot of k_{obs} vs [$HSiEt_3$] ($k_{obs} = 1.1 \times 10^{-4}$ M^{-1} s^{-1} [$HSiEt_3$]).

Kinetic Study of the Reaction of 7 with $HSiEt_3$. **7** (25 mg, 0.02 mmol) was loaded into a 5-mm NMR tube. Mesitylene (0.5 μL) was added as an internal standard. When the total volume of $HSiEt_3$ to be added was <100 μL, 700 μL of CD_2Cl_2 was added; when the volume of $HSiEt_3$ was >100 μL, 600 μL of CD_2Cl_2 was added. The solution was cooled to −78 °C and $HSiEt_3$ was added via gas-tight syringe. The sample was inserted into a precooled (13 ± 1 °C) NMR probe. The concentration of **7** was monitored as a function of time. Rate constants were obtained as the slope of the line −ln [**7**] vs time. Two runs were performed at each $HSiEt_3$ concentration and the rates were averaged. The results are shown in Table 5 and in Figure 2. The rate dependence on [$HSiEt_3$] was determined from the slope of the line obtained from a plot of k_{obs} vs [$HSiEt_3$] ($k_{obs} = 7.1 \times 10^{-4}$ M^{-1} s^{-1} [$HSiEt_3$].)

Kinetic Study of the Reaction of 6 with Styrene. **6** (0.02 mmol) was generated *in situ* from **1a** (25 mg, 0.02 mmol), $HSiEt_3$ (3.5 μL, 0.022 mmol), and styrene (2.5 μL, 0.022 mmol) in CD_2Cl_2 (600 μL). Mesitylene (0.5 μL) was added as an internal standard and the solution was cooled to −78 °C. Styrene was added via gas-tight syringe and the sample was inserted into a precooled (13 ± 1 °C) NMR probe. The methine signals of **6** and **7** were monitored. Rate constants were obtained as the slope of the line of −ln ([**6**]/[**6**]+[**7**]) vs time. Two runs were performed at each styrene concentration and the rates were averaged. The results are shown in Table 6 and in Figure 3. The limiting rate constant (k_{sat}) was obtained as the inverse of the intercept of the plot of $1/k_{obs}$ vs 1/[styrene]. $k_{sat} = 1.1 \times 10^{-4}$ s^{-1}.

Table 5

[**7**], M	[$HSiEt_3$], M	vol of $HSiEt_3$, μL	$10^4 k_{obs}$, s^{-1}
0.0272	0.287	34	2.12
0.0267	0.414	50	3.07
0.026	0.560	70	4.12
0.0252	0.742	95	5.18

Table 6

[**6**], M	[styrene], M	vol of styrene, μL	$10^5 k_{obs}$, s^{-1}
0.0286	1.25	100	7.14
0.0266	1.75	150	8.33
0.025	2.18	200	8.62

Determination of the Equilibrium Constant for 6 + Styrene ⇌ 7 + *trans-β*-Triethylsilylstyrene (20 °C). A 5-mm NMR tube was charged with **7** (21.5 mg, 0.0171 mmol), *trans-β*-triethylsilylstyrene (45 mg, 0.204 mmol), and CD_2Cl_2 (700 μL). The tube was subjected to three freeze−pump−thaw cycles and then flame-sealed under vacuum. The ^{1}H NMR spectrum was monitored until equilibrium was reached (ca. 7 days). The equilibrium constant was calculated from K_{eq} = [*trans-β*-triethylsilylstyrene][**7**]/[styrene][**6**]; the concentrations were determined by the relative integrals. $K_{eq} = 26$.

Reactions of RCH=CH_2 with $DSiEt_3$: General Procedure. **1b** (15 mg, 0.01 mmol) was dissolved in 1 mL of CH_2Cl_2. Olefin (1 mmol) and $DSiEt_3$ (1.2 mmol) were added and the reaction was allowed to stir overnight at 25 °C (1-hexene, cyclohexene, and *tert*-butylethylene). When styrene was used as the substrate, the stoichiometry was varied (styrene/$DSiEt_3$ = 0.33 and 2) and the reaction was stirred at 35 °C overnight. CH_2Cl_2 was removed in vacuo and the resulting oil was analyzed by ^{13}C NMR spectroscopy. The results are shown below (only the peaks showing D incorporation are listed).

Cyclohexene/$DSiEt_3$. ^{13}C NMR ($CDCl_3$) δ 27.8 (t, $J_{C\text{-}D}$ = 19, *C*HDCHSiEt_3).

***t*-BuCH=CH_2/$DSiEt_3$.** ^{13}C NMR ($CDCl_3$) δ 4.78 (t, $J_{C\text{-}D}$ = 17, *t*-$BuCH_2$*C*HDSiEt_3).

1-Hexene/$DSiEt_3$. ^{13}C NMR (C_6D_6) δ 34.6, 32.6, 24.9, 15.0 (t).

Styrene (2 equiv)/$DSiEt_3$. ^{13}C NMR ($CDCl_3$) δ 26.5 (t, $J_{C\text{-}D}$ = 19 Hz, $PhCH_2CH_2D$).

Styrene (1 equiv) $DSiEt_3$ (3 equiv). ^{13}C NMR ($CDCl_3$) δ 11.9 (t, $J_{C\text{-}D}$ = 19, PhC*H*D$CH_2Si Et_3$).

Acknowledgment. We thank the National Institutes of Health for funding (GM 28938). A.M.L. thanks the National Science Foundation for a postdoctoral fellowship.

JA962979N