Metal-Catalyzed Hydrosilylation of Alkenes and Alkynes Using Dimethyl(pyridyl)silane

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Metal-catalyzed hydrosilylation of alkenes and alkynes using dimethyl(pyridyl)silane is described. The hydrosilylation of alkenes using dimethyl(2-pyridyl)silane (2-PyMe$_2$SiH) proceeded well in the presence of a catalytic amount of RhCl(PPh$_3$)$_3$ with virtually complete regioselectivity. By taking advantage of the phase tag property of the 2-PyMe$_2$Si group, hydrosilylation products were isolated in greater than 95% purity by simple acid−base extraction. Strategic catalyst recovery was also demonstrated. The hydrosilylation of alkynes using 2-PyMe$_2$SiH proceeded with a Pt(CH$_2$═CHSiMe$_2$)$_2$O/P(*t*-Bu)$_3$ catalyst to give alkenyldimethyl(2-pyridyl)silanes in good yield with high regioselectivity. A reactivity comparison of 2-PyMe$_2$SiH with other related hydrosilanes (3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH) was also performed. In the rhodium-catalyzed reaction, the reactivity order of hydrosilane was 2-PyMe$_2$SiH ≫ 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, PhMe$_2$SiH, indicating a huge rate acceleration with 2-PyMe$_2$SiH. In the platinum-catalyzed reaction, the reactivity order of hydrosilane was PhMe$_2$SiH, 3-PyMe$_2$SiH ≫ 4-PyMe$_2$SiH > 2-PyMe$_2$SiH, indicating a rate deceleration with 2-PyMe$_2$SiH and 4-PyMe$_2$SiH. It seems that these reactivity differences stem primarily from the governance of two different mechanisms (Chalk−Harrod and modified Chalk−Harrod mechanisms). From the observed reactivity order, coordination and electronic effects of dimethyl(pyridyl)silanes have been implicated.

Introduction

The transition metal-catalyzed hydrosilylation of carbon−carbon unsaturated molecules has proved to be an extremely valuable tool for the carbon−silicon bond formation by virtue of its high regio- and stereoselectivities.[1] There has been extraordinary progress in this hydrosilylation chemistry during the last two decades. For example, various types of cyclization/hydrosilylation are now viable when diene, enyne, and diyne are used as substrates.[2] Alternatively, intramolecular hydrosilylation of alkene can be used for the preparation of cyclic compounds with control of the relative and/or absolute stereochemistry.[3] The growing interest in the development of the metal-catalyzed cyclization/hydrosilylation process stems from the ability to assemble complex molecules from simple starting materials in a convergent and atom-economical manner.[4] Related carbonylative silylation reactions have also been developed.[5] Other seminal advances have been realized in the development of the general protocol for highly enantioselective hydrosilylation of alkenes, which has been an enduring problem for nearly 30 years.[6]

The value of this hydrosilylation has been further augmented by several protocols for converting the silyl group to other functional groups.[7] For example, certain silyl groups can be oxidatively converted to a hydroxyl group by hydrogen peroxide or peracids.[8] In recent years, the strategic use of the hydrosilylation/oxidation sequence has been well recognized as a powerful method for the diastereo- and enantioselective synthesis of various structurally diverse alcohols from structurally simple starting materials.[9]

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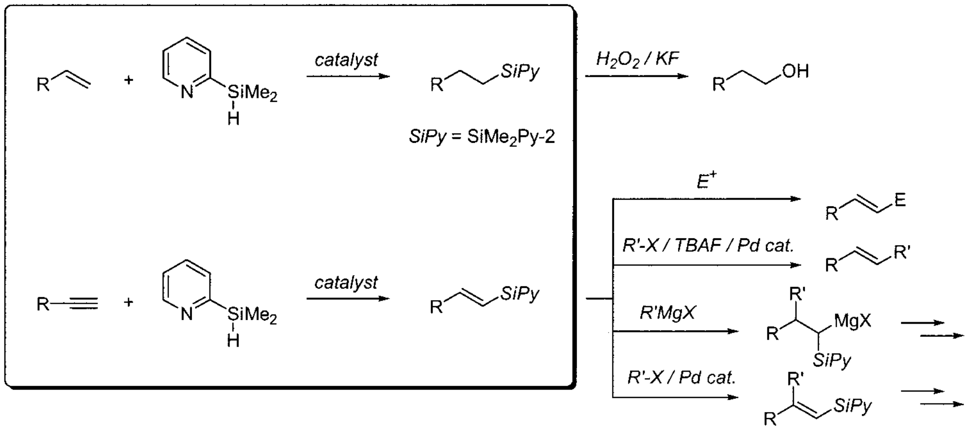
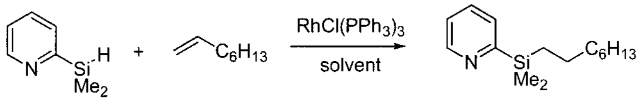
10.1021/jo0163389 CCC: $22.00

Scheme 1



Although there are many factors governing the hydrosilylation, most of the works in this area were devoted to a catalyst tuning for controlling the reactivity and selectivity of the reaction.[10] We envisioned that control of the reactivity and selectivity might be achieved by appending the secondary interaction moiety on the hydrosilane scaffold. During the course of a program directed at the development of removable directing groups, which control the metal-mediated and -catalyzed processes by complex-induced proximity effects,[11] we have found that a dimethyl(2-pyridyl)silyl (2-PyMe$_2$Si) group works well for such a purpose by taking advantage of the coordination of the pyridyl group to the metal.[12-24] This prompted us to investigate the behavior of dimethyl(2-pyridyl)silane (2-PyMe$_2$SiH) in the transition metal-catalyzed hydrosilylation of alkene and alkyne. Since we have already established that the resulting alkyl- and alkenyl(2-pyridyl)silanes can be subjected to further transformations such as oxidation,[13,14,18-21] electrophilic substitution,[15,19] Hiyama-type cross-coupling reaction,[17,23] carbomagnesation,[20] and Heck-type reaction,[16,23] an efficient procedure for the hydrosilylation of 2-PyMe$_2$SiH would be extremely worthwhile (Scheme 1). In this paper, we report the full details of this study.

Table 1. Effect of Solvent in the Rhodium-Catalyzed Hydrosilylation of 1-Octene with 2-PyMe$_2$SiH[a]



1 **2a**

entry	solvent	yield (%)[b]
1	toluene	50
2	MeOH	0
3	DMF	42
4	CH_2Cl_2	71
5	$ClCH_2CH_2Cl$	78
6	THF	82
7	CH_3CN	88
8	CH_3CH_2CN	84

[a] All reactions were performed at room temperature for 30 min under argon using 2-PyMe$_2$SiH (0.5 mmol), 1-octene (1.5 mmol), and RhCl(PPh$_3$)$_3$ (5 mol %) in the indicated solvent (1 mL). [b] Determined by capillary GC analysis using pentadecane as an internal standard.

In addition, we have also found that the behavior of 2-PyMe$_2$SiH is quite different from those of other related hydrosilanes such as 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH.[25] The observation that the rate of hydrosilylation depends heavily on the choice of catalyst metal and hydrosilane implies the unusual mechanism-dependent acceleration and deceleration. These results are also discussed in this paper.

Results and Discussion

I. Catalytic Hydrosilylation of Alkenes Using 2-PyMe$_2$SiH. 1. Reaction Conditions. Preliminary screening of the catalysts, including palladium(0), platinum(0), and rhodium(I) complexes, revealed that RhCl(PPh$_3$)$_3$ was most effective in terms of the catalytic activity and regioselectivity for the hydrosilylation of alkenes using 2-PyMe$_2$SiH (**1**). For example, 1-octene can be hydrosilylated at room temperature in toluene to furnish **2a** in 50% yield (Table 1, entry 1). With this catalyst in hand, we have examined the effect of solvent in the reaction using 1-octene as a model substrate (Table

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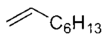
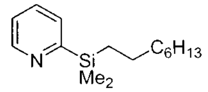
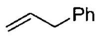
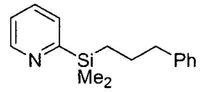
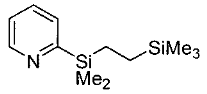
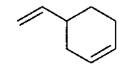
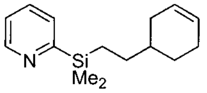
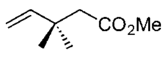
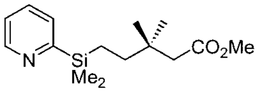
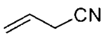
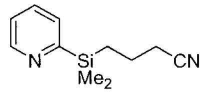
Table 2. Rhodium-Catalyzed Hydrosilylation of Alkenes with 2-PyMe$_2$SiH^a

entry	alkene	product (**2**)	yield (%)^b	purity (%)^c
1		 **2a**	86	>95
2		 **2b**	86	>95
3		 **2c**	93	>95
4		 **2d**	89	>95
5		 **2e**	83	>95
6		 **2f**	84	>95

^{a} All reactions were performed at room temperature under argon using 2-PyMe$_2$SiH (0.5 mmol), alkene (1.5 mmol), and RhCl(PPh$_3$)$_3$ (5 mol %) in CH$_3$CN (1 mL). ^{b} Isolated yield. ^{c} Determined by GC and ^{1}H NMR analysis.

1). The reaction proceeded with all the solvents examined except MeOH (entry 2). Interestingly, the reaction was completed within 30 min, regardless of the solvent employed. It was found that the use of CH$_3$CN resulted in 88% yield of **2a** with virtually complete regioselectivity (entry 7).

2. Hydrosilylation with Various Alkenes. Under the standard set of reaction conditions (5 mol % of RhCl(PPh$_3$)$_3$ at room temperature in CH$_3$CN), the hydrosilylation using 2-PyMe$_2$SiH occurred with various terminal alkenes (Table 2). It is possible to selectively hydrosilylate a terminal carbon−carbon double bond in the presence of an internal carbon−carbon double bond (entry 4). The reaction proceeded well without affecting the other functional groups such as ester and nitrile (entries 5 and 6). Unfortunately, internal alkene (2-octene, cyclohexene, norbornene), 1,1-disubstituted alkene (methylenecyclopentane), 1,3-diene (2-methyl-1,3-butadiene, 1,3-cyclohexadiene), and heteroatom-substituted alkene (butyl vinyl ether, 2,3-dihydrofuran, phenyl vinyl sulfide) were not applicable to the reaction.

3. Strategic Separation and Catalyst Reuse Utilizing the Acid−Base Phase-Switching Technique. As we recently reported, the additional bonus of using a 2-PyMe$_2$Si group is that it can also be utilized as a "phase tag",[26−28] which enables easy purification of the product.[12,16,22] By taking advantage of the phase tag property of the 2-PyMe$_2$Si group, all hydrosilylation products listed in Table 2 were isolated by the simple acid−base "phase-switching" technique. This phase tag property of the 2-PyMe$_2$Si group enables the use of excess alkene (3 equiv to **1** in this study) without having any difficulty at the purification stage. Importantly, the purities of the products are over 95% in all cases examined. This easy separation/purification protocol without using any chromatographic isolation technique is notable, and such strategic purification in solution-phase synthesis should become more and more important as an alternative to the solid-phase synthesis.[29]

Moreover, it was possible to recover the catalyst from the initial organic phase in the acid−base extraction purification process as described in the previous paper,[16] and the rhodium catalyst recovered in this manner could be used in the second, third, and forth runs in the hydrosilylation of **1** with 1-octene. When the reaction was carried out at room temperature for 1 h, **2a** was obtained in 86, 67, 59, and 50% yields, respectively. Although slight eroding of the catalytic activity was observed, these demonstrations indicate that the recovery of a metal catalyst does not necessarily have to rely on the polymer-supported catalyst and clearly pave the way for the strategic catalyst recovery in solution-phase synthesis.

II. Catalytic Hydrosilylation of Alkynes Using 2-PyMe$_2$SiH. Having established the general protocol for the hydrosilylation of alkenes using 2-PyMe$_2$SiH (**1**), we next examined the hydrosilylation of alkynes. The use of RhCl(PPh$_3$)$_3$ resulted in a rapid consumption of **1** but gave a complex mixture of unidentified products. Since changing the solvent was found to be fruitless, catalyst

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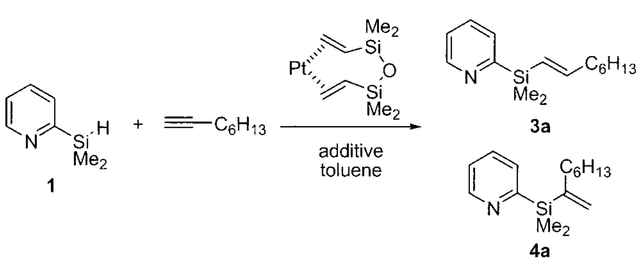
Table 3. Platinum-Catalyzed Hydrosilylation of 1-Octyne with 2-PyMe$_2$SiH^a



entry	Pt (mol %)	additive (mol %)	conditions	yield (%)^b	**3a**:**4a**^{b}
1	5	none	rt, 24 h	16	
2	5	PPh$_3$ (10)	40 °C, 24 h	62	84:16
3	5	P(C$_6$H$_4$F-*p*)$_3$ (10)	40 °C, 24 h	61	86:14
4	5	PPh$_3$ (5)	40 °C, 24 h	70	85:15
5	5	PPh$_3$ (5)	70 °C, 24 h	86	85:15
6	5	PPh$_3$ (5)	100 °C, 1 h	92	84:16
7	1	PPh$_3$ (1)	100 °C, 3.5 h	89	84:16
8	1	P(*t*-Bu)$_3$ (1)	100 °C, 15 h	89	99:1

^{a} All reactions were performed under argon using 2-PyMe$_2$SiH (0.5 mmol), 1-octyne (1.5 mmol), Pt(CH$_2$=CHSiMe$_2$)$_2$O, and additive in toluene (1 mL). ^{b} Determined by capillary GC analysis using pentadecane as an internal standard.

screening was again conducted. After many experiments, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex [Pt(CH$_2$=CHSiMe$_2$)$_2$O] was found to be a reasonable catalyst precursor for the hydrosilylation in toluene (Table 3, entry 1).[30] On the basis of this auspicious result, we have set out to investigate the effect of added ligand and reaction temperature (Table 3). Addition of PPh$_3$ (2 equiv to Pt) resulted in 62% yield of the desired hydrosilylation products (**3a** and **4a**) at 40 °C with 84% regioselectivity favoring the terminal silylated product **3a** (entry 2). Electronic tuning of PPh$_3$ did not improve the catalytic activity (entry 3). Reducing the amount of added PPh$_3$ (1 equiv to Pt) was found to be beneficial (entry 4). Raising the reaction temperature was even more beneficial without declining the regioselectivity (entries 5 and 6). In particular, the hydrosilylation products (**3a** and **4a**) were obtained in 92% yield after 1 h at 100 °C (entry 6). These conditions permit the hydrosilylation at low catalyst loadings without significant loss of the yield (entry 7). Moreover, we were delighted to find that the use of electron-rich and bulky P(*t*-Bu)$_3$ as a supporting ligand resulted in the production of **3a** with excellent regioselectivity (99%).[31]

Under the standard set of reaction conditions (1 mol % of Pt(CH$_2$=CHSiMe$_2$)$_2$O and 1 mol % of P(*t*-Bu)$_3$ at 100 °C in toluene), the hydrosilylation using 2-PyMe$_2$SiH occurred with various alkynes (Table 4). The regioselectivity was again excellent for various terminal alkynes (entries 2−5) when P(*t*-Bu)$_3$ was used as a ligand. When PPh$_3$ was used as a ligand, poorer regioselectivity (72−84%) was again observed. For the hydrosilylation of symmetrical internal alkynes, where the regioselectivity is no more an issue, we prefer to utilize PPh$_3$ instead of P(*t*-Bu)$_3$ because it is easier to handle and cheaper (entries 6 and 7).

III. Reactivity Comparison of 2-PyMe$_2$SiH with Other Related Hydrosilanes. 1. Rhodium-Catalyzed Hydrosilylation of 1-Octene with 2-PyMe$_2$SiH, 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH. Having observed the high reactivity of 2-PyMe$_2$SiH (**1**) in alkene hydrosilylation, we subjected other structurally and electronically related hydrosilanes (3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH) to the rhodium-catalyzed alkene hydrosilylation to assess the reactivity value. Thus, we examined the hydrosilylation of 1-octene with 2-PyMe$_2$SiH, 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH in the presence of RhCl(PPh$_3$)$_3$ (5 mol %) in CH$_3$CN. The mixture was stirred at 28 °C for from 15 min to 2 h, and the yield of hydrosilylated product was determined by GC analysis (Figure 1). The hydrosilylation using 2-PyMe$_2$SiH was completed within 30 min. On the other hand, hydrosilylation was extremely slow when using 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, or PhMe$_2$SiH.

2. Rhodium-Catalyzed Hydrosilylation of Vinyltrimethylsilane with 2-PyMe$_2$SiH, 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH. To see if the observed reactivity trend (2-PyMe$_2$SiH $\gg$ 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, PhMe$_2$SiH) was general or not with regard to alkene, we next investigated the use of vinyltrimethylsilane (Figure 2). Whereas the hydrosilylation using 2-PyMe$_2$SiH was completed within 30 min to afford the hydrosilylated product **2c** in greater than 90% yield, hydrosilylation using 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH was extremely sluggish under identical conditions. Thus, the reactivity trend (2-PyMe$_2$SiH $\gg$ 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, PhMe$_2$SiH) seems to be a universal phenomenon for the rhodium-catalyzed alkene hydrosilylation.

3. Platinum-Catalyzed Hydrosilylation of 1-Octene with 2-PyMe$_2$SiH, 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH. Having established the unusual reactivity trend in the rhodium-catalyzed alkene hydrosilylation, we next examined platinum-catalyzed alkene hydrosilylation using 2-PyMe$_2$SiH, 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH. First, we examined the hydrosilylation of 1-octene with 2-PyMe$_2$SiH, 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH in the presence of Pt[(CH$_2$=CHSiMe$_2$)$_2$O] (1 mol %) and PPh$_3$ (1 mol %) in EtCN. The mixture was stirred at 80 °C for from 30 min to 2 h, and the yield of hydrosilylated product was determined by GC analysis (Figure 3). Quite interestingly, the reactivity trend was completely different from that observed in the rhodium-catalyzed reaction (Figure 1). Whereas the hydrosilylation using 3-PyMe$_2$SiH and PhMe$_2$SiH proceeded smoothly, the hydrosilylation was much slower when using 2-PyMe$_2$SiH and 4-PyMe$_2$SiH (Figure 3).

4. Platinum-Catalyzed Hydrosilylation of Vinyltrimethylsilane with 2-PyMe$_2$SiH, 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH. To investigate in more depth the reactivity difference of hydrosilanes in the platinum-catalyzed alkene hydrosilylation, we next investigated the use of vinyltrimethylsilane (Figure 4). It was found that the reaction using 4-PyMe$_2$SiH was slower than that using 3-PyMe$_2$SiH or PhMe$_2$SiH but sufficiently faster than that using 2-PyMe$_2$SiH. Exhibition of the reactivity difference between 2-PyMe$_2$SiH and 4-PyMe$_2$SiH may be due to the higher reactivity of vinyltrimethylsilane toward hydrosilylation.

5. Platinum-Catalyzed Hydrosilylation of 1-Octyne with 2-PyMe$_2$SiH, 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH. We next examined the platinum-

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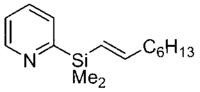
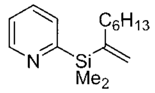
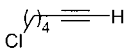
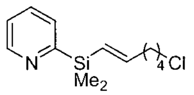
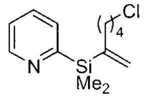
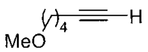
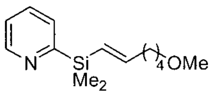
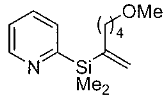
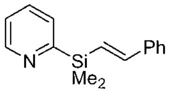
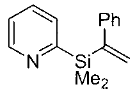
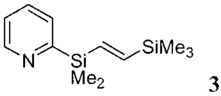
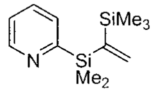
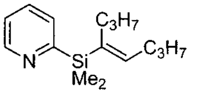
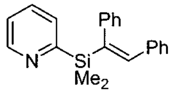
[30] (a) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998. (b) Lewis, L. N.; Sy, K. G.; Bryant, G. L., Jr.; Donahue, P. E. *Organometallics* **1991**, *10*, 3750.

[31] (a) Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1987**, *6*, 191. (b) Denmark, S. E.; Wang, Z. *Org. Lett.* **2001**, *3*, 1073.

Table 4. Platinum-Catalyzed Hydrosilylation of Alkynes Using 2-PyMe$_2$SiH

entry	alkyne	products (3 and 4)		yield (%)[c]	3 : 4[d]
1[a]	C_6H_{13}—≡—H	 3a	 4a	89	99 : 1
2[a]		 3b	 4b	84	>99 : <1
3[a]		 3c	 4c	75	>99 : <1
4[a]	Ph—≡—H	 3d	 4d	93	>99 : <1
5[a]	Me_3Si—≡—H	 3e	 4e	63	90 : 10
6[b]	C_3H_7—≡—C_3H_7	 3f		85	-
7[b]	Ph—≡—Ph	 3g		86	-

[a] Reactions were performed under argon using 2-PyMe$_2$SiH (0.5 mmol), alkyne (1.0 mmol), Pt(CH$_2$=CHSiMe$_2$)$_2$O (1 mol %), and P(t-Bu)$_3$ (1 mol %) in toluene (1.5 mL) at 100 °C. [b] Reactions were performed under argon using 2-PyMe$_2$SiH (0.5 mmol), alkyne (1.0 mmol), Pt(CH$_2$=CHSiMe$_2$)$_2$O (1 mol %), and PPh$_3$ (1 mol %) in toluene (1 mL) at 100 °C. [c] Isolated yield. [d] Determined by GC and ^{1}H NMR analysis.

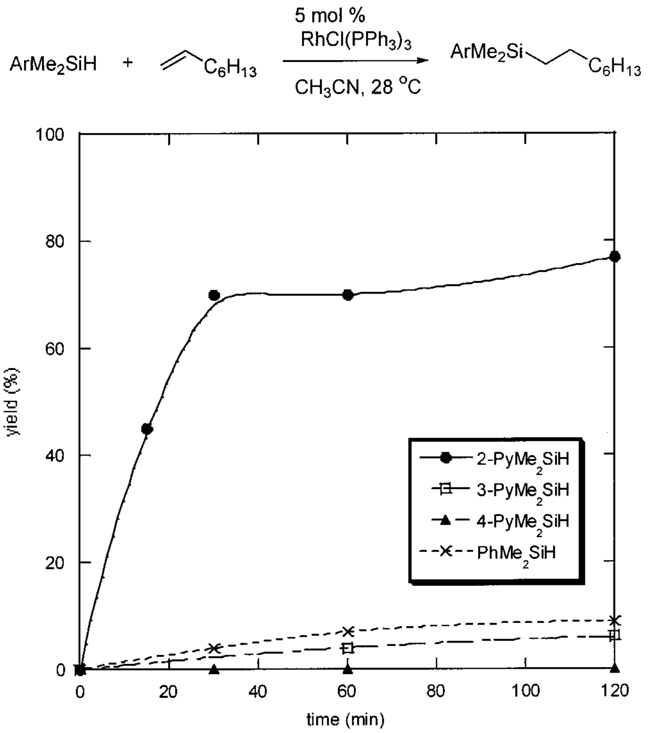


Figure 1. Rh-catalyzed hydrosilylation of 1-octene.

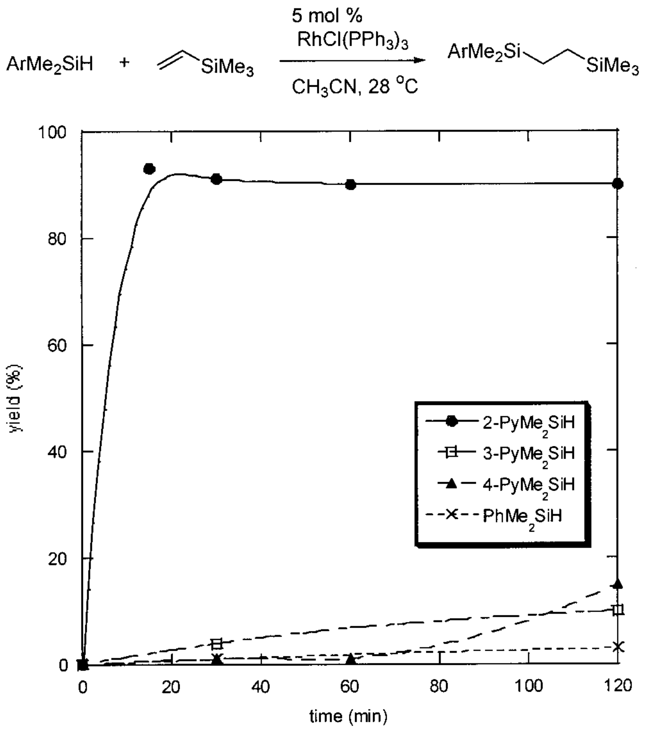


Figure 2. Rh-catalyzed hydrosilylation of vinyltrimethylsilane.

catalyzed hydrosilylation of 1-octyne with 2-PyMe$_2$SiH, 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH in the presence of Pt[(CH$_2$=CHSiMe$_2$)$_2$O] (1 mol %) and PPh$_3$ (1 mol %) in EtCN. The mixture was stirred at 80 °C for from 30

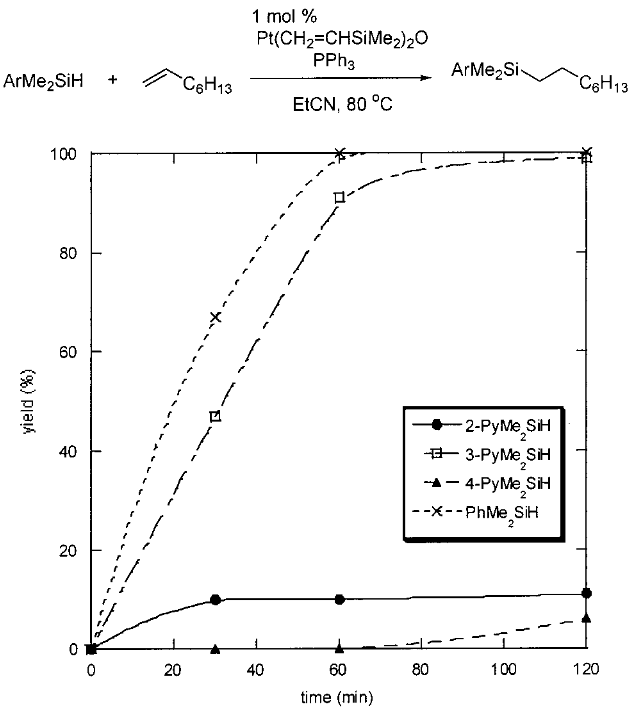


Figure 3. Pt-catalyzed hydrosilylation of 1-octene.

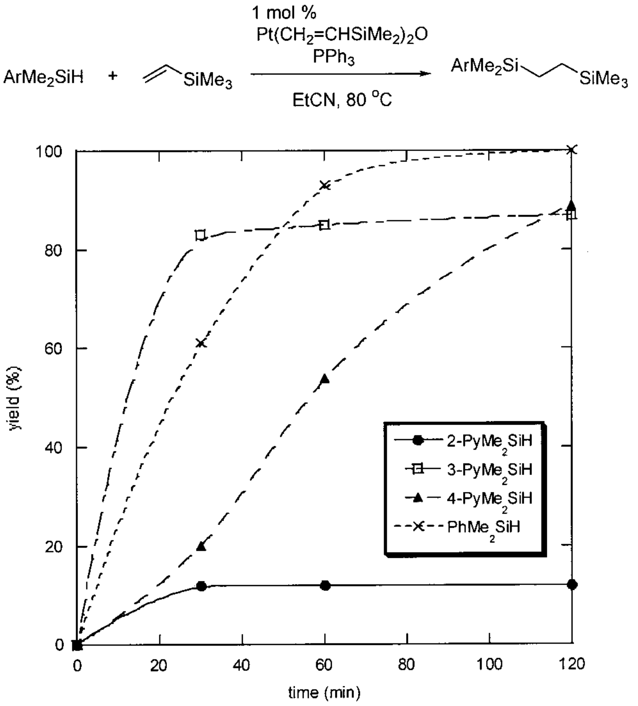


Figure 4. Pt-catalyzed hydrosilylation of vinyltrimethylsilane.

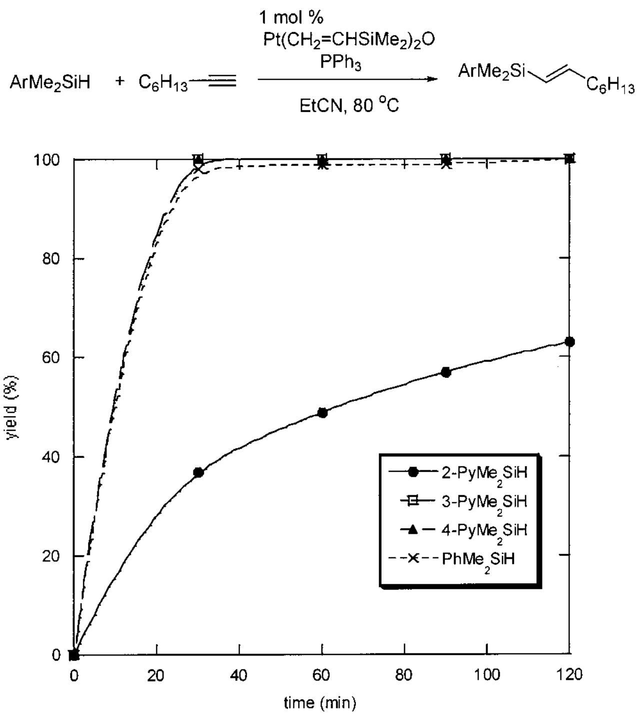
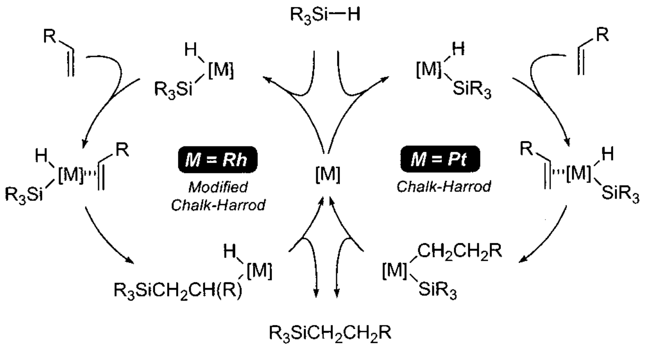


Figure 5. Pt-catalyzed hydrosilylation of 1-octyne.

Scheme 2



min to 2 h, and the yield of hydrosilylated product was determined by GC analysis (Figure 5). Whereas the hydrosilylation using 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH proceeded smoothly and was completed within 30 min, the hydrosilylation was substantially slower when using 2-PyMe$_2$SiH (63% yield after 2 h). These results are slightly different from those we observed in the platinum-catalyzed hydrosilylation of 1-octene (the rate deceleration was observed with 2-PyMe$_2$SiH and 4-PyMe$_2$SiH). We assume that the reactivity difference between 2-PyMe$_2$SiH and 4-PyMe$_2$SiH in this case may be due to the higher reactivity of alkynes than that of alkenes toward hydrosilylation.

IV. Mechanism and Possible Explanation for the Rate Acceleration and Deceleration. We have observed unusual rate acceleration and deceleration in hydrosilylation using 2-PyMe$_2$SiH, 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH. We envisioned that these remarkable reactivity differences might be closely related to the mechanism of metal-catalyzed hydrosilylation.[1] It has been well documented that there are two mechanistically different pathways for metal-catalyzed hydrosilylation. The Chalk–Harrod mechanism is proposed for the platinum-catalyzed hydrosilylation of alkenes, in which alkene is inserted into the Pt–H bond (generated by the oxidative addition of Si–H to Pt) (Scheme 2).[32] On the other hand, a modified Chalk–Harrod mechanism is proposed for the rhodium-catalyzed hydrosilylation, in which alkene insertion takes place at the Rh–Si bond (Scheme 2).[33] Recent theoretical studies support the

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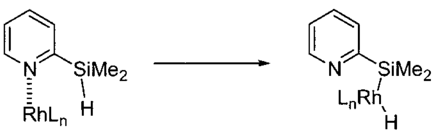
(32) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.

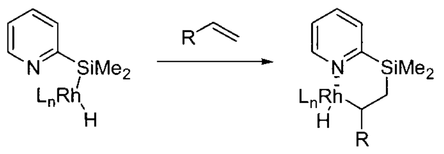
(33) (a) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345. (b) Millan, A.; Towns, E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 673. (c) Ojima, I.; Fuchikami, T.; Yatabe, M. *J. Organomet. Chem.* **1984**, *260*, 335. (d) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366.

Scheme 3

(a) Coordination-Induced Facile Oxidative Addition



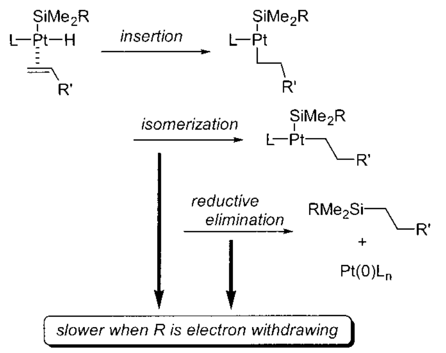
(b) Coordination-Induced Facile Alkene Insertion



occurrence of these two reaction pathways.[34,35] Alkyne hydrosilylation has been proposed to occur via a mechanism similar to that of alkene hydrosilylation.[36]

1. Possible Explanation for the Reactivity Difference of Hydrosilanes in the Rhodium-Catalyzed Hydrosilylation. The mechanistic rationale for this unusual metal-dependent acceleration and deceleration is of special interest. In the case of rhodium-catalyzed hydrosilylation, the electronic nature of 2-PyMe$_2$SiH cannot be a decisive factor for its high reactivity since neither 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, or PhMe$_2$SiH rivals 2-PyMe$_2$SiH in terms of reactivity (Figures 1 and 2). The coordination of the pyridyl group on silicon might have some accelerating effects at a certain stage of the reaction. Previously,[12] we presumed that the acceleration might be attributed to the facile oxidative addition of Si−H to Rh on the basis of the precoordination effect (Scheme 3a).[37] Alternatively, it is also plausible to surmise that the pyridyl group on silicon coordinates to the catalyst rhodium after the insertion of olefin, thereby stabilizing the olefin-inserted intermediate (Scheme 3b). This coordination might enhance the olefin insertion process that has been theoretically uncovered as the rate-determining step in the rhodium-catalyzed hydrosilylation of ethylene.[35] It is noteworthy that the latter coordination effect (Scheme 3b) can only be expected in the rhodium-catalyzed reaction, which proceeds with the modified Chalk−Harrod mechanism.[33]

Scheme 4



2. Possible Explanation for the Reactivity Difference of Hydrosilanes in the Platinum-Catalyzed Hydrosilylation. In the case of platinum-catalyzed hydrosilylation, the electronic effect of the aryl group on silicon should have played the key role since rate deceleration was observed with 2-PyMe$_2$SiH and 4-PyMe$_2$SiH. It is well-known that 2- and 4-pyridyl groups are better electron-withdrawing groups than 3-pyridyl and phenyl groups because of a resonance-oriented reason. Reactivity differences between 2-PyMe$_2$SiH and 4-PyMe$_2$SiH (4-PyMe$_2$SiH > 2-PyMe$_2$SiH) observed in the hydrosilylation of vinyltrimethylsilane and 1-octyne may be due to the stronger electron-withdrawing ability of the 2-pyridyl group than that of the 4-pyridyl group.

Sakaki recently determined by theoretical calculations that the platinum-catalyzed hydrosilylation proceeds with the Chalk−Harrod mechanism, and the overall rate is determined by the isomerization of the olefin-inserted intermediate and subsequent reductive elimination.[34] According to their report, the isomerization of the olefin-inserted intermediate occurs readily when the silyl group exhibits strong trans influence. Eaborn has reported that the trans influence of the silyl group becomes weaker when electron-withdrawing group is attached onto silicon.[38] Thus, the 4-pyridyl group and, more efficiently, the 2-pyridyl group on silicon are expected to decelerate the isomerization step (Scheme 4).

Electronic properties of silyl groups might have influenced the reductive elimination step as well. Ozawa has reported that the reductive elimination from the (alkyl)(silyl)platinum complex is slower when a electron-withdrawing group is attached onto silicon.[39] Sakaki also observed the same trend in theoretical calculations.[34] Therefore, one might expect that the reductive elimination is slower when 2- and 4-pyridyl groups, which are better electron-withdrawing groups than the 3-pyridyl or phenyl group, are attached onto silicon. However, since there are many factors governing this elemental step,[40] it is impossible to conclude any clear rationale at this stage.

Conclusion

In conclusion, we have established the efficient rhodium- and platinum-catalyzed hydrosilylation of alkenes and alkynes by utilizing 2-PyMe$_2$SiH as a new silylating agent. The phase tag property of the 2-PyMe$_2$Si group enabled the simple acid−base extraction as a product purification method. Moreover, unusual metal- and hydrosilane-dependent acceleration and deceleration were found during the reactivity comparison using 2-PyMe$_2$SiH, 3-PyMe$_2$SiH, 4-PyMe$_2$SiH, and PhMe$_2$SiH. It seems that these reactivity differences stem primarily from the governance of two different mechanisms (Chalk−Harrod and modified Chalk−Harrod mechanisms). Coordination of the 2-pyridyl group might have accelerated the rate-determining olefin insertion process in the rhodium-catalyzed reaction. The electron-withdrawing ability of 2- and 4-pyridyl groups might have decelerated the rate-

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(34) (a) Sakaki, S.; Mizoe, N.; Sugimoto, M. *Organometallics* **1998**, *17*, 2510. (b) Sakaki, S.; Mizoe, N.; Sugimoto, M.; Musashi, Y. *Coord. Chem. Rev.* **1999**, *192*, 933.

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(36) Sugimoto, M.; Yamasaki, I.; Mizoe, N.; Anzai, M.; Sakaki, S. *Theor. Chem. Acc.* **1999**, *102*, 377.

(37) (a) Auburn, M. J.; Holmes-Smith, R. D.; Stobart, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 1314. (b) Djurovich, P. I.; Safir, A. L.; Keder, N. L.; Watts, R. J. *Inorg. Chem.* **1992**, *31*, 3195.

(38) Chatt, J.; Eaborn, C.; Ibekwe, S. D.; Kapoor, P. N. *J. Chem. Soc. A* **1970**, 1343.

(39) Ozawa, F. *J. Organomet. Chem.* **2000**, *611*, 332.

(40) Hasebe, K.; Kamite, J.; Mori, T.; Katayama, H.; Ozawa, F. *Organometallics* **2000**, *19*, 2022.

determining isomerization and/or reductive elimination steps in the platinum-catalyzed reaction. Although further investigation is needed to settle the precise mechanism for metal- and hydrosilane-dependent acceleration and deceleration, the present study clearly implies alternative controlling factors in the metal-catalyzed hydrosilylation chemistry.

Experimental Section

Dimethyl(2-pyridyl)silane (1). To a solution of 2-bromopyridine (40.4 g, 255.5 mmol) in Et_2O (80 mL) was added dropwise a hexane solution of butyllithium (255 mmol) at −78 °C under argon. The mixture was stirred at −78 °C for an additional 2 h. The resultant solution of 2-pyridyllithium was added to a solution of chlorodimethylsilane (23.2 g, 245.6 mmol) in Et_2O (60 mL) at −78 °C. After being stirred at room temperature for 1 h, the mixture was washed with H_2O (4 × 100 mL), and then the organic phase was dried over Na_2SO_4. Removal of the solvent under reduced pressure and subsequent distillation afforded the title compound in 86% purity as judged by capillary GC. A second distillation afforded **1** (12.1 g, 36%) as a colorless liquid in a pure form: bp 68−72 °C/20 mmHg; ^{1}H NMR (300 MHz) δ 0.40 (d, $J = 3.9$ Hz, 6 H), 4.46 (septet, $J = 3.9$ Hz, 1 H), 7.22 (ddd, $J = 7.5$, 4.8, 1.2 Hz, 1 H), 7.54 (ddd, $J = 7.5$, 1.8, 1.2 Hz, 1 H), 7.60 (td, $J = 7.5$, 1.8 Hz, 1 H), 8.77 (ddd, $J = 4.8$, 1.8, 1.2 Hz, 1 H); ^{13}C NMR (75 MHz) δ −4.8, 123.1, 129.8, 134.2, 150.4, 165.8; IR (neat) 2124, 1576, 1559, 1420, 1248 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_7H_{11}NSi$ 137.0661, found 137.0658.

Dimethyl(3-pyridyl)silane. By a procedure similar to that used to prepare dimethyl(2-pyridyl)silane, the title compound was obtained from 3-bromopyridine (78%) as a pale yellow liquid: bp (bulb-to-bulb distillation) 120−150 °C/20 mmHg; ^{1}H NMR (300 MHz) δ 0.38 (d, $J = 3.9$ Hz, 6 H), 4.46 (septet, $J = 3.9$ Hz, 1 H), 7.30 (dd, $J = 7.5$, 4.8 Hz, 1 H), 7.85 (dt, $J = 7.5$, 1.8 Hz, 1 H), 8.60 (dd, $J = 4.8$, 1.8 Hz, 1 H), 8.71 (t, $J = 1.8$ Hz, 1 H); ^{13}C NMR (75 MHz) δ −4.3, 123.3, 132.4, 141.7, 150.3, 154.5; IR (neat) 2124, 1574, 1557, 1395, 1252 cm^{-1}. Anal. Calcd for $C_7H_{11}NSi$: C, 61.25; H, 8.08; N, 10.20. Found: C, 61.05; H, 8.18; N, 10.00.

Dimethyl(4-pyridyl)silane. By a procedure similar to that used to prepare dimethyl(2-pyridyl)silane, the title compound was obtained from 4-bromopyridine hydrochloride (78%) as a pale yellow liquid: bp (bulb-to-bulb distillation) 120−150 °C/20 mmHg; ^{1}H NMR (300 MHz) δ 0.34 (d, $J = 3.9$ Hz, 6 H), 4.38 (septet, $J = 3.9$ Hz, 1 H), 7.38 (dd, $J = 4.5$, 1.5 Hz, 2 H), 8.54 (dd, $J = 4.5$, 1.5 Hz, 2 H), ^{13}C NMR (75 MHz) δ −4.6, 128.7, 147.3, 148.6; IR (neat) 2128, 1402, 1129, 880 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_7H_{11}NSi$ 137.0661, found 137.0660. Anal. Calcd for $C_7H_{11}NSi$: C, 61.25; H, 8.08; N, 10.20. Found: C, 61.05; H, 8.18; N, 10.00.

Typical Procedure for the Rhodium-Catalyzed Hydrosilylation of Alkenes with 2-PyMe$_2$SiH (Table 2, Entry 1). To a solution of $RhCl(PPh_3)_3$ (23.1 mg, 5 mol %) in CH_3CN (1.0 mL) were added 1-octene (168 mg, 1.5 mmol) and dimethyl(2-pyridyl)silane (**1**) (69 mg, 0.5 mmol) under argon. After the mixture was stirred at room temperature for 30 min, toluene (0.5 mL) was added to the mixture. This mixture was extracted with 1 N aqueous HCl (6 × 5 mL). The combined aqueous phase was neutralized by adding $NaHCO_3$ and then extracted with EtOAc (3 × 10 mL). Drying over Na_2SO_4 and removal of the solvents under reduced pressure afforded **2a** (107 mg, 86%) as a colorless oil. The purity of **2a** was determined to be over 95% by capillary GC and ^{1}H NMR analysis.

Typical Procedure for the Platinum-Catalyzed Hydrosilylation of Alkynes with 2-PyMe$_2$SiH (Table 4, Entry 1). To a solution of $Pt(CH_2{=}CHSiMe_2)_2O$ (0.005 mmol, 1 mol %, 0.1 M solution in poly(dimethylsiloxane)) and P(*t*-Bu)$_3$ (1.0 mg, 0.005 mmol, 1 mol %) in toluene (1.5 mL) were added 1-octyne (110 mg, 1.0 mmol) and **1** (69 mg, 0.5 mmol) under argon. After the mixture was stirred at 100 °C for 15 h, toluene (0.5 mL) was added. This mixture was extracted with 1 N aqueous HCl (5 × 5 mL). The combined aqueous phase was neutralized by adding $NaHCO_3$ and then extracted with EtOAc (3 × 10 mL). Drying over Na_2SO_4 and removal of the solvents under reduced pressure afforded a mixture of **3a** and **4a** (110 mg, 89%) as a colorless oil. The ratio of **3a**/**4a** was determined to be 99:1 by capillary GC and ^{1}H NMR analysis. Regioisomers **3a** and **4a** were separated by gel permeation chromatography.

Procedure for the Reactivity Comparison Experiments for Rhodium-Catalyzed Reactions (Figures 1 and 2). To a solution of $RhCl(PPh_3)_3$ (23.1 mg, 5 mol %) in CH_3CN (1.0 mL) were added alkene (1.5 mmol) and hydrosilane (0.5 mmol) under argon. The mixture was stirred at 28 °C for from 15 min to 2 h, and the yield of hydrosilylated product was determined by GC analysis.

Procedure for the Reactivity Comparison Experiments for Platinum-Catalyzed Reactions (Figures 3−5). To a solution of $Pt(CH_2{=}CHSiMe_2)_2O$ (0.005 mmol, 1 mol %, 0.1 M solution in poly(dimethylsiloxane)) and PPh_3 (1.3 mg, 0.005 mmol, 1 mol %) in EtCN (1.0 mL) were added alkene or alkyne (1.0 mmol) and hydrosilane (0.5 mmol) under argon. The mixture was stirred at 80 °C for from 15 min to 2 h, and the yield of hydrosilylated product was determined by GC analysis.

Supporting Information Available: Spectroscopic data for all products, ^{13}C NMR spectra of **2b**, **2d**, **3c**, **4a**, **4d**, **4e**, (*E*)-1-dimethyl(3-pyridyl)silyl-1-octene, 2-dimethyl(3-pyridyl)silyl-1-octene, (*E*)-1-dimethyl(4-pyridyl)silyl-1-octene, and 2-dimethyl(4-pyridyl)silyl-1-octene, and the procedure for the consecutive use of recovered rhodium catalyst. This material is available free of charge via the Internet at http://pubs.acs.org.

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