Synthesis and Structure of *N*-(Silylalkyl)amides: Rhodium-Catalyzed Hydrosilylation of Enamides

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Rh(II) acetate effectively catalyzed the hydrosilylation of enamides, *N*-vinylurea, and imides to give *N*-(silylalkyl)amide derivatives in moderate to high yields. The silyl group was selectively introduced to the carbon atom adjacent to the nitrogen atom, whereas the efficiency and regioselectivity of the Rh-catalyzed hydrosilylation of vinyl carboxylates, thiocarboxylates, ethers, and thioethers were highly affected by the substitution patterns of the substrates and reaction conditions. The reaction of *N*-vinylphthalimide (**1f**) with deuteriosilane suggests that the catalytic process involving the oxidative addition of hydrosilane and migratory insertion of the alkenyl group of **1f** is reversible. The molecular structures of the *N*-(1-silylethyl)phthalimide **2f** and *N*-(1-silylethyl)acetamide **2k** species have been determined by X-ray analyses. The results show that there is no intramolecular interaction between the silicon atom and the oxygen atom of the carbonyl groups of **2f** and **2k**.

Introduction

The transition-metal-catalyzed hydrosilylation of olefins is one of the most important synthetic methods of alkylsilanes, and a variety of catalytic systems have been devised for simple olefins and olefins having carbonyl and cyano groups such as α,β-unsaturated ketones and nitriles so as to attain the regio- and stereoselective reactions.[1] In contrast, much less attention has been paid to the reaction of the olefins to which heteroatom-containing functional groups are directly attached. For example, little is known about hydrosilylation of olefins having nitrogen-containing functional groups such as enamines[2] and enamides.[4] Very recently, we found that Rh(II) acetate was effective for the hydrosilylation of *N*,*N*-divinylurea and that the reaction exhibited high regio-, and site selectivities.[5] These results prompted us to test the catalytic activity of a Rh catalyst in the hydrosilylation of functionalized olefins such as enamides and vinyl carboxylates.[6] In the present paper, the scope and limitation of the reactions have been studied. The successful hydrosilylation of enamides has provided a new synthetic route to *N*-silylalkylamides, which is one of the important synthetic intermediates.[7] X-ray molecular structure analyses of *N*-silylalkylamides are also disclosed.

Results and Discussion

Rhodium-Catalyzed Hydrosilylation of Functionalized Olefins. Initially, the reactions of *N*-benzyl enamide**1a** and dimethylphenylsilane (1.2 equiv) were examined in the presence of a catalytic amount of a variety of rhodium catalysts (eq 1, Table 1). In all cases the hydrosilylation of **1a** proceeded smoothly to give the

(1) (a) Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. Organometallic Chemistry Reviews. In *Journal of Organometallic Chemistry Library*; Seyferth, D., Davies, A. G., Fisher, E. O., Normant, J. F., Reutov, O. A., Eds.; Elsevier: Amsterdam, 1977; Vol. 5, p 1. (b) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (c) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoprt, Z., Eds.; John Wiley: Chichester, 1989; p 1479. (d) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 8, p 763.

(2) To our knowledge there have been two reports on the introduction of a silyl group to enamines with hydrosilane. One is the addition of trichlorosilane to the enamines derived from ketones and piperidine or pyrrolidine.[3a] Alternatively, Rh-catalyzed reaction of enamines with hydrosilane and CO has been reported to give α-(siloxymethylene)-amines.[3b]

(3) (a) Snyder, D. C. *J. Organomet. Chem.* **1986**, *301*, 137. (b) Ikeda, S.; Chatani, N.; Kajikawa, Y.; Ohe, K.; Murai, S. *J. Org. Chem.* **1992**, *57*, 2.

(4) The hydrosilylation of enamides are rare but known, see: (a) Skoda-Foldes, R.; Kollar, L.; Balint, H. *J. Organomet. Chem.* **1991**, *408*, 297. (b) Otiashvili, D.; Akhobadze, D.; Khananashvili, L. *Soobshch. Akad. Nauk. Gruz.* **1995**, *152*, 531.

(5) Murai, T.; Oda, T.; Kimura, F.; Onishi, H.; Kanda, T.; Kato, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2143.

(6) Although the hydrosilyation of vinyl carboxylates have been reported, only a limited number of the reactions proceeded with high efficiency; no example has been reported on the selective silylation at the internal carbon atoms of vinyl carboxylates. For example, see: (a) Marciniec, B.; Gulinski, J. *J. Mol. Catal.* **1981**, *10*, 123. (b) Lia, X.; Fan, Q.; Hong, M.; Cai, Q. *Xiamen Daxue Xuebao, Ziran Kexueban* **1989**, *28*, 158. (c) Kopping, B.; Chatgilialoglu, C.; Zehnder, M.; Giese B. *J. Org. Chem.* **1992**, *57*, 3994. (d) Celebuski, J. E.; Chan, C. *J. Org. Chem.* **1992**, *57*, 5535.

(7) The synthetic reactions of *N*-silylmethylamides and *N*-silylbenzylamides have been recently studied in great depth, see: (a) Jeon, Y. T.; Lee, C.-P.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 8847. (b) Ohno, M.; Komatsu, M.; Miyata, H.; Oshiro, Y. *Tetrahedron Lett.* **1991**, *32*, 5813. (c) Jung, Y. S.; Swartz, W. H.; Xu, W.; Mariano, P. S. *J. Org. Chem.* **1992**, *57*, 6037. (d) Comins, D. L.; Killpack, M. O. *J. Am. Chem. Soc.* **1992**, *114*, 10972. (e) Jung, Y. S.; Mariano, P. S. *Tetrahedron Lett.* **1993**, *34*, 4611. (f) Lee, Y. J.; Lee, C. P.; Jeon, Y. T.; Mariano, P. S.; Yoon, U. C.; Kim, D. U.; Kim, J. C.; Lee, J. G. *Tetrahedron Lett.* **1993**, *34*, 5855. (g) Yoon, U. C.; Kinm, D. K.; Kim, J. C.; Lee, J. G.; Mariano, P. S.; Lee, Y. J.; Ammon, H. L. *Tetrahedron Lett.* **1993**, *34*, 5859. (h) Sakuragi, A.; Shirai, N.; Sato, Y.; Kurono, Y.; Hatano, K. *J. Org. Chem.* **1994**, *59*, 148. (i) Pandey, G.; Lakshmaiah, G. *Synlett* **1994**, 277. (j) Yoon, U. C.; Kim, D. U.; Lee, C. W.; Choi, Y. S.; Lee, Y.-J.; Ammon, H. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1995**, *117*, 2698. (i) Yoon, U. C.; Cho, S. J.; Lee, Y.-J.; Mancheno, M. J.; Mariano, P. S. *J. Org. Chem.* **1995**, *60*, 2353. (j) Iyoda, M.; Sultana, F.; Komatsu, M. *Chem. Lett.* **1995**, 1133. (j) Lee, Y. J.; Ling, R.; Mariano, P. S.; Yoon, U. C.; Kim, D. U.; Oh, S. W. *J. Org. Chem.* **1996**, *61*, 3304.

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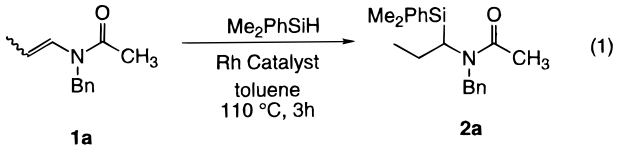
Table 1. Rh-Catalyzed Hydrosilylation of *N*-Benzyl-*N*-(1-propenyl)acetamide (1a)[a]

entry	Rh catalyst	yield (%)
1	$Rh_2(OAc)_4$	53[b]
2	$Rh_2(OAc)_4$[c]	50[b]
3	$[RhCl(CO)_2]_2$	37[d]
4	$RhH(PPh_3)_4$	21[d]
5	$Rh(acac)_3$	12[d]
6	$[RhCl(C_6H_{10})]_2$	33[d]
7	$RhCl(PPh_3)_3$	30[b]

[a] The reaction was carried out as follows unless otherwise noted: **1a** (1 mmol), Me_2PhSiH (1.2 equiv), Rh catalyst (2 mol %), toluene (10 mL) at 110 °C for 3 h. [b] Isolated yield. [c] $Rh_2(OAc)_4$ (1 mol %). [d] ^1H NMR yield.

product **2a** in which the silyl group was attached to the carbon adjacent to the nitrogen atom. Although a bulky

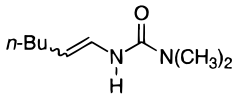
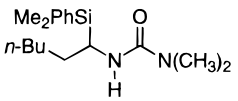
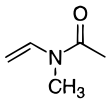
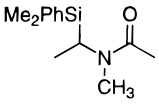
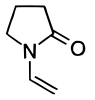
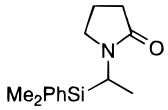
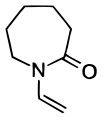
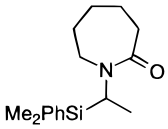
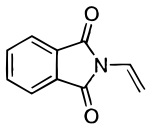
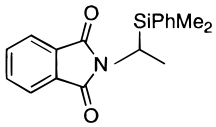
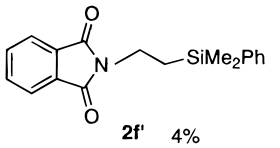


(1)

substituent group, such as a benzyl group, on the nitrogen atom was present in **1a**, the compound in which the silyl group was attached to the carbon atom β to the nitrogen atom was not observed. The use of $[RhCl(CO)_2]_2$, $[RhCl(C_6H_{10})]_2$, or $RhCl(PPh_3)_3$ as a catalyst gave **2a** in ca. 30% yields (entries 3, 6, and 7). Complexes $RhH(PPh_3)_4$ and $Rh(acac)_3$ exhibited lower catalytic activities, and the starting material was recovered (entries 4 and 5). Among the Rh catalysts, $Rh_2(OAc)_4$ was found to be the most effective, although it has not been used in the hydrosilylation of simple olefins and acetylenes as frequently.[8]

Second, Rh(II)-acetate-catalyzed hydrosilylation was applied to a range of *N*-vinylurea and enamides **1b**−**f** under reflux in toluene. The results are listed in Table 2. In the reaction of acyclic *N*-vinylurea (**1b**) and enamide (**1c**), the hydrosilylation took place selectively at the carbon atom attached to a nitrogen atom analogous to the reaction of **1a** (entries 1 and 2). The hydrogen atom on the nitrogen atom of **1b** does not affect the reaction course (entry 1), although Rh(II) acetate is known to react with acetamide to form a stable complex.[11] The addition of hydrosilane to 1-vinyl-2-pyrrolidinone (**1d**) also proceeded with high selectivity to give the product **2d** (entry 3), whereas the reaction of **1e** gave the product **2e** in a low yield (entry 4). As for the reaction of **1d**, the solvent effect was examined.

Table 2. Rh(II)-Acetate-Catalyzed Hydrosilylation of a Variety of Enamides[a]

entry	substrate	product yield [%][b]
1	 **1b**	 **2b** 78%
2	 **1c**	 **2c** 92%
3	 **1d**	 **2d** 90%[c] (93%)[d] (96%)[e] (58%)[f] (61%)[g]
4	 **1e**	 **2e** 15%
5	 **1f**	 **2f** 92%  **2f'** 4%

[a] The reaction was carried out as follow unless otherwise noted: Substrate (1.0 mmol), Me_2PhSiH (1.2 mmol), $Rh_2(OAc)_4$ (2.0 mol %), toluene (10 mL), at 110 °C for 3 h. [b] Isolated yield. [c] In benzene (10 mL) at 80 °C. [e] In THF (10 mL) at 66 °C for 24 h. [f] In CH_2Cl_2 (10 mL) at 40 °C. [g] In $(CH_3)_2CHOH$ (10 mL) at 82 °C for 6 h.

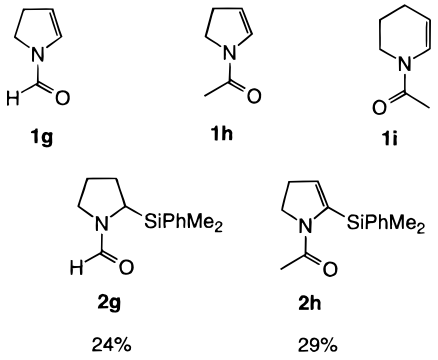
The longer reaction time was necessary in THF, but the silylated compound **2d** was quantitatively obtained. Dichloromethane and isopropyl alcohol could also be used as a solvent, although the yield of **2d** decreased. The silylated product of the alcohol was not detected in the latter case. The *N*-vinylphthalimide (**1f**) was also converted to *N*-(silylalkyl)imide **2f** in a high yield, although a small amount of the regioisomer **2f′** was formed. In contrast, Rh(II) acetate did not catalyze the hydrosilyation of *endo*-cyclic enamides **1g**−**i** as effectively. In the reaction of **1g**, the silyl group was selectively introduced to the carbon atom next to the nitrogen atom but the yield of the product **2g** was low. The 1-acetyl-2-pyrroline (**1h**) underwent dehydrosilyl-

(8) Rh(II) acetate has been reported to catalyze the silylation of an alcohol with low efficiency,[9a] although the Rh(II) perfluorobutyrate ($Rh_2(pfb)_4$) can be used as a catalyst for the hydrosilylation of 1-alkynes.[9b] In addition, the insertion of a rhodium carbenoid generated from diazoesters and $Rh_2(OAc)_4$ into the Si−H bond is known.[10]

(9) (a) Doyle, M. P.; High, K. G.; Bagheri, V.; Pieters, R. J.; Lewis, P. J.; Pearson, M. M. *J. Org. Chem.* **1990**, *55*, 6082. (b) Doyle, M. P.; High, K. G.; Nesloney, C. L.; Clayton, T. W., Jr.; Lin, J. *Organometallics* **1991**, *10*, 1225.

(10) (a) Bagheri, V.; Doyle, M. P.; Taunton, J.; Claxton, E. E. *J. Org. Chem.* **1988**, *53*, 6158. (b) Andrey, O.; Landais, Y.; Planchenault, D. *Tetrahedron Lett.* **1993**, *34*, 2927. (c) Landais, Y.; Planchenault, D. *Tetrahedron Lett.* **1994**, *35*, 4565. (d) Landais, Y.; Planchenault, D.; Weber, V. *Tetrahedron Lett.* **1994**, *35*, 9549. (e) Landais, V.; Parra-Rapado, L.; Planchenault, D.; Weber, V. *Tetrahedron Lett.* **1997**, *38*, 229. (f) Bulugahapitiya, P.; Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. *J. Org. Chem.* **1997**, *62*, 1630.

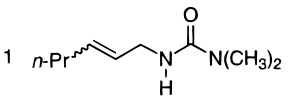
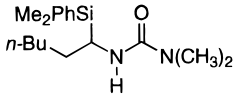
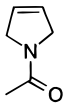
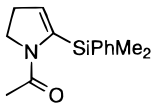
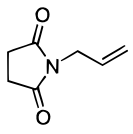
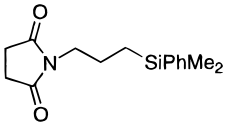
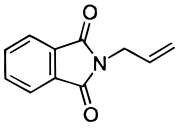
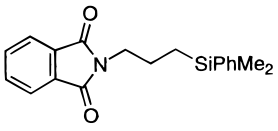
(11) Ahsan, M. Q.; Bernal, I.; Bear, J. L. *Inorg. Chem.* **1986**, *25*, 260.



ation to give **2h** in 29% yield. The $Rh_2(OAc)_4$-catalyzed reaction of **1i** with hydrosilane did not take place at all. These results imply the importance of the coordination of both the alkenyl and carbonyl groups to a catalytic species during the reactions.

Third, hydrosilylation of allylic amides **3** was carried out (Table 3). In the reaction of the urea **3a**, the introduction of the silyl group was accompanied with the isomerization of the alkenyl group to give **2b** in a low yield. As for **3b**, the alkenyl group was isomerized and dehydrosilylation took place similarly to the reaction of **1h**. On the contrary, the hydrosilylation of *N*-allyl imides **3c** and **3d** took place at the terminal carbon atoms of the alkenyl groups to give **2j** and **2i** in high yields. Even in these cases, the coordination of both the alkenyl and carbonyl groups to a catalytic species seems to play an important role in controlling the reactivity and regioselectivity since no hydrosilylation of 1-hexene proceeded under identical conditions.

Table 3. Rh(II)-Acetate-Catalyzed Hydrosilylation of Allylic Amides and Imides[a]

entry	substrate	product yield [%][b]
1	 **3a**	 **2b** 18%
2	 **3b**	 **2h** 36%
3	 **3c**	 **2i** 74%
4	 **3d**	 **2j** 96%

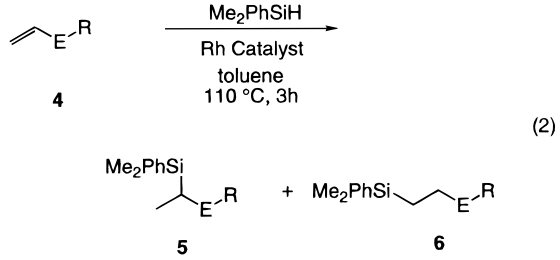
[a] The reaction was carried out as follows: Substrate (1.0 mmol), Me_2PhSiH (1.2 mmol), $Rh_2(OAc)_4$ (2.0 mol %), toluene (10 mL), at 110 °C for 3 h. [b] Isolated yield.

Table 4. Rh-Catalyzed Hydrosilylation of 4[a]

entry	substrate	E	R	Rh catalyst[b]	yield (%)	ratio[d] of **5**/**6**
1	**4a**	O	$C(O)CH_3$	**A**	62	72/28
2				**B**	46	55/45
3	**4b**	O	$C(O)C_6H_5$	**A**	64	85/15
4[e,f]				**A**	51	99/1
5				**B**	51	0/100
6				**C**	26	100/0
7[e]				**C**	100	94/6
8				**D**	35	0/100
9	**4c**	O	C(O)Bu-*t*	**A**	29	84/18
10				**D**	10	11/86
11	**4d**	O	Bu-*n*	**A**	100	0/100
12[f]	**4e**	S	$C(O)NMe_2$	**D**	40	100/0
13	**4f**	S	$C(O)C_6H_5$	**A**	20	91/9
14[g]	**4g**	S	$CH_2C_6H_5$	**A**	97	83/17
15[h]				**A**	84	91/9
16	**4h**	S	CH_2OCH_3	**A**	34	51/49
17[h]				**D**	67	10/90

[a] The reaction was carried out as follows unless otherwise noted: **4** (1 mmol), Me_2PhSiH (1.2 equiv), Rh catalyst (2 mol %), toluene (10 mL), at 110 °C for 6 h. [b] **A**: $Rh_2(OAc)_4$. **B**: $Rh(acac)_3$. **C**: $[RhCl(CO)_2]_2$. **D**: $[RhCl(C_6H_{10})]_2$. [c] Isolated yield. [d] The ratio of **5** and **6** was determined by ^1H NMR spectra. [e] In CH_3CN at 81 °C. [f] For 22 h. [g] In CH_2Cl_2 at 40 °C. [h] In C_6H_6 at 80 °C.

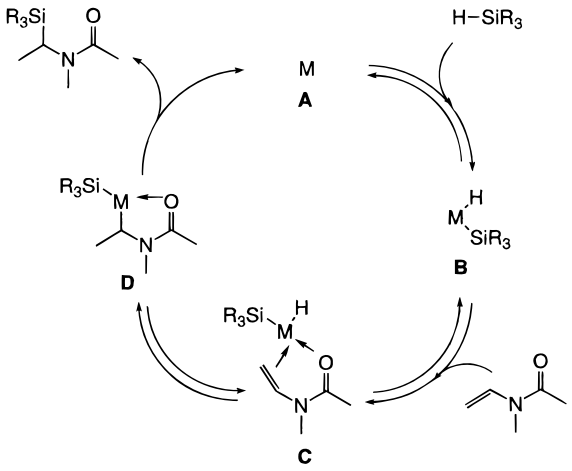
Finally, the Rh-catalyzed hydrosilyation of vinyl carboxylates, thiocarboxylates, ethers, and thioethers **4** was examined (eq 2, Table 4). The regioselectivity of the



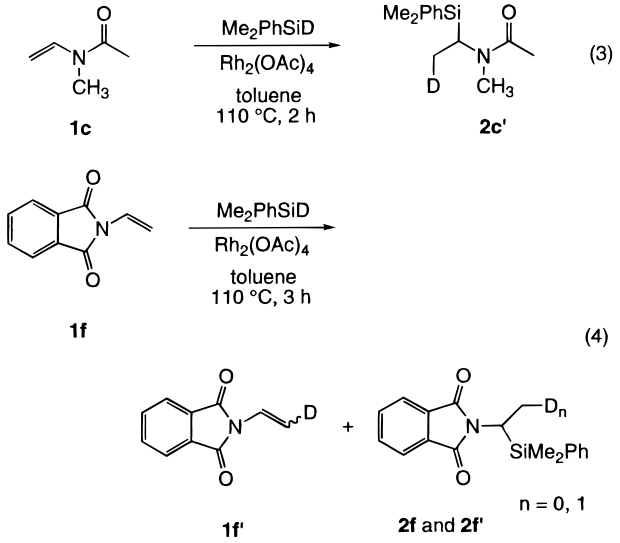
reaction of **4** was highly dependent on the substrates, solvents, and catalysts used unlike the hydrosilylation of **1**. For example, in the reaction of vinyl acetate (**4a**), the use of $Rh_2(OAc)_4$ as the catalyst gave **5a** predominantly, whereas the $Rh(acac)_3$-catalyzed reaction showed no regioselectivity (entries 1 and 2). Noteworthy is that both regioisomers were obtained from **4b** with high selectivity by changing the catalyst (entries 3−8). The reaction of **4b** with hydrosilane in CH_3CN in the presence of a catalytic amount of $[RhCl(CO)_2]_2$ gave **5b** exclusively (entry 7), whereas the use of $Rh(acac)_3$ gave only **6b** (entry 5). In the $Rh_2(OAc)_4$-catalyzed hydrosilylation of vinyl ether **4d**, the silyl group was completely introduced to the terminal carbon atom to give **6d** quantitatively (entry 11). On the other hand, in a similar reaction of vinyl thioether **4g**, the product **5g** where the silyl group was attached to the internal carbon atom of **4g** (entries 14 and 15) predominated. To obtain the product of type **6** (E = S) the combination of **4h** and $[RhCl(C_6H_{10})]_2$ was effective (entry 17).

The reaction pathway of the present reactions is outlined in Scheme 1 on the basis of the Chalk−Harrod mechanism proposed for hydrosilylation of the olefins,[12] although an alternative pathway involving silyl migra-

Scheme 1



tion[13] should not be excluded. The present reaction may begin with the oxidative addition of hydrosilane to a low-valent transition metal complex **A** to generate a hydrido−silyl complex **B**. Then, the migratory insertion of the olefin moiety into the metal−hydride bond via **C** may form an alkyl-metal species **D**. Finally, the reductive elimination of an alkyl and silyl group from **D** would result in the formation of the product and the regeneration of **A**. The high selectivity of the reaction using **1** may be ascribed to the efficient coordination of both an alkenyl group and an oxygen atom of the carbonyl group of **1** to the metal center as in **C**, which has been assumed in the Rh-catalyzed hydrogenation of enamides.[14] The regioselectivity of the reaction may also be controlled by the formation of five-membered cyclic complex **D**. To elucidate the reaction pathway the reaction using deuteriosilane has been carried out (eqs 3 and 4). The



(12) (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16. (b) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; p 1415.

(13) (a) Corey, J. Y. In *Advances in Silicon Chemistry*; Larson, G. L., Ed.; JAI Press: Greenwich, CT, 1991; Vol. 1, p 355. (b) Brown, J. M.; Lloyd-Jones, G. C. *J. Am. Chem. Soc.* **1994**, *116*, 866.

(14) (a) Brown, J. M.; Chaloner, F. A. *Tetrehedron Lett.* **1978**, 1877. (b) Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 838. (c) Landis, C. R.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1746. (d) Bakos, J.; Karaivanov, R.; Laghmari, M.; Sinou, D. *Organometallics* **1994**, *13*, 2951.

Table 5. Crystal Data and Data Collection Parameters for 2f and 2k

	2f	2k
mol formula	$C_{18}H_{19}NO_2Si$	$C_{13}H_{21}NOSi$
cryst syst	prismatic	prismatic
cryst color	colorless	colorless
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	9.377(2)	10.545(1)
b (Å)	6.619(2)	9.728(2)
c (Å)	26.904(6)	14.599(1)
β(deg)	99.32(2)	91.953(9)
V (Å^3)	1496.8(3)	1647.7(7)
Z value	4	4
D_c (g/cm^3)	1.247	1.045
μ(Mo Kα) (cm^{-1})	1.49	1.40
cryst dimens (mm)	0.30 × 0.40 × 0.30	0.48 × 0.22 × 0.57
max 2θ (deg)	55.0	55.0
radiation, λ (Å)	Mo Kα, 0.7109	Mo Kα, 0.7109
scan mode	ω-2θ	ω-2θ
temp (°C)	23.0	23.0
hkl range	$h = 0-12$	$h = 0-14$
	$k = 0-9$	$k = 0-13$
	$l = -35$ to 35	$l = -19$ to 19
scan width (deg)	1.21 + 0.30 tan θ	1.84 + 0.30 tan θ
no. of reflns		
total	4363	3835
unique	4117	3647
with $l \geq 3\sigma(l)$	2254	1978
no. of variables	200	146
residuals: R,[a] R_w[b]	0.056, 0.044	0.066, 0.076
p value[b]	0.003	0.04
goodness of fit	3.09	2.23
max shift/error in final cycle	3.03	6.58
min, max peaks, e$^-$/Å^3	−0.34, 0.33	−0.23, 0.34

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = [\sigma^2(F_o) + p^2(F_o)^2/4]^{-1}$.

deuterium was cleanly incorporated to the terminal carbon atom of **1c** to give **2c′** in a high yield. On the contrary, the reaction of **1f** gave the mixture of undeuterated and deuterated products **2f** and **2f′**. Furthermore, deuterium was incorporated into the terminal carbon atom of recovered **1f′**. These results have suggested that the catalytic cycle from **A** to **D** in Scheme 1 appears to be reversible and that the reductive elimination from **D** is the rate-determining step as far as **1f** is concerned.

***N*-(Silylalkyl)amides: X-ray Molecular Structure Analysis and Hydrolysis.** The structures of *N*-(silylalkyl)amides are of great interest, in particular, whether there is an interaction between the silyl group and the oxygen atom of the carbonyl group or not.[15] After several disappointing results, the single crystal of **2f** and *N*-(1-dimethylphenylsilyl)propylacetamide **2k**[5] was successfully obtained. The crystal data and data-collection parameters are collected in Table 5. ORTEP drawings of **2f** and **2k** are shown in Figures 1 and 2, respectively. The selected bond distances and angles are listed in Tables 6 and 7. The torsion angles between the carbonyl oxygen and the alkylsilyl or the methyl group are 145.7(2)° and 84.0(4)°, respectively, in **2f**, as shown in

(15) (a) Macharashvili, A. A.; Shklover, V. E.; Struchkov, Y. T.; Oleneva, G. I.; Kramarova, E. P.; Shipov, A. G.; Baukov, Y. I. *J. Chem. Soc., Chem. Commun.* **1988**, 683. (b) Macharashvili, A. A.; Shklover, V. E.; Chernikova, N. Y.; Antipin, M. Y.; Struchkov, Y. T.; Baukov, Y. I.; Oleneva, G. I.; Kramarova, E. P.; Shipov, A. G. *J. Organomet. Chem.* **1989**, *359*, 13. (c) Shklover, V. E.; Ovchinnikov, Y. E.; Struchov, Y. T.; Kopilov, V. M.; Kovyazine, T. G.; Voronkov, M. G. *Akad. Nauk SSSR* **1985**, *548*, 131. (c)Artamkina, O. B.; Shipov, A. G.; Mohammed, N.; Krut'ko, D. P.; Zaitseva, G. S.; Baukov, Y. I. *Metalloorg. Khim.* **1991**, *4*, 694.

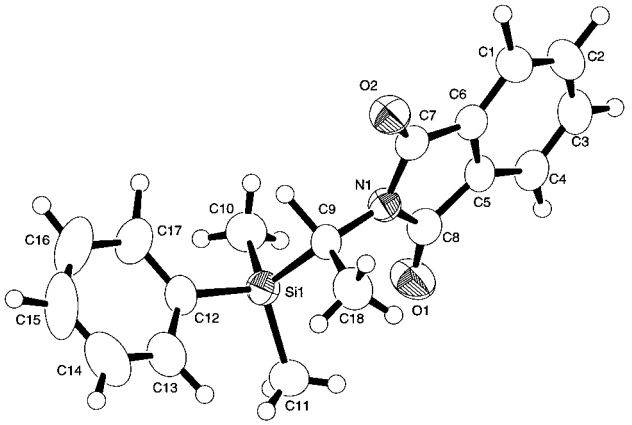


Figure 1. Molecular structure of **2f**.

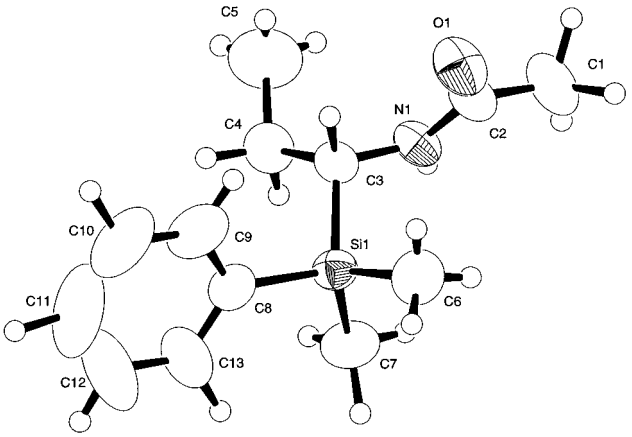


Figure 2. Molecular structure of **2k**.

Table 6. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for 2f

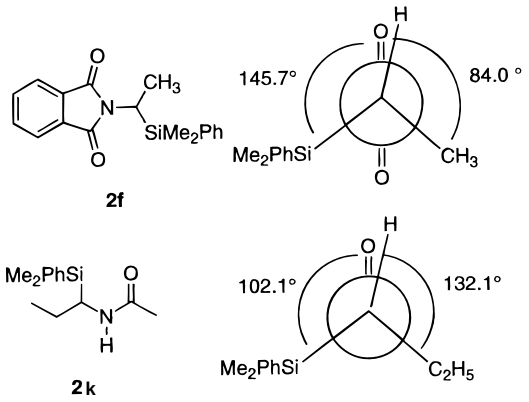
Bond Distances			
Si(1)−C(9)	1.910(3)	C(9)−C(18)	1.514(4)
N(1)−C(9)	1.474(4)	C(9)−H(5)	1.22
Bond Angles			
C(8)−N(1)−C(9)	127.2(3)	O(2)−C(9)−N(1)	124.2(3)
O(1)−C(8)−N(1)	124.1(4)	Si(1)−C(9)−N(1)	115.9(2)
Si(1)−C(9)−C(18)	113.6(2)	N(1)−C(9)−C(18)	109.8(3)
C(7)−N(1)−C(9)	122.0(3)		
Torsion Angles			
Si(1)−C(9)−N(1)−C(7)	145.7(2)	C(7)−N(1)−C(9)−H(5)	53.7
O(1)−C(8)−N(1)−C(9)	4.3(6)	C(8)−N(1)−C(9)−H(5)	132.5
O(2)−C(7)−N(1)−C(9)	−1.1(5)	C(7)−N(1)−C(9)−C(18)	−84.0(4)
Si(1)−C(9)−N(1)−C(8)	−40.4(4)	C(8)−N(1)−C(9)−C(18)	89.9

Table 7. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for 2k

Bond Distances			
Si(1)−C(3)	1.893(3)	C(3)−C(4)	1.539(4)
N(1)−C(3)	1.470(4)	N(1)−H(4)	1.05
Bond Angles			
C(3)−N(1)−H(4)	115.6	N(1)−C(3)−H(5)	103.8
O(1)−C(2)−C(1)	121.7	N(1)−C(2)−C(1)	115.7(3)
Si(1)−C(3)−N(1)	109.8(2)	O(1)−C(2)−N(1)	122.6(3)
Si(1)−C(3)−H(5)	109.1	C(4)−C(3)−H(5)	110.0
Torsion Angles			
Si(1)−C(3)−N(1)−C(2)	−102.4(3)	C(2)−N(1)−C(3)−C(4)	132.1(3)
O(1)−C(2)−N(1)−C(3)	0.5(5)	C(1)−C(2)−N(1)−C(3)	−179.2(3)

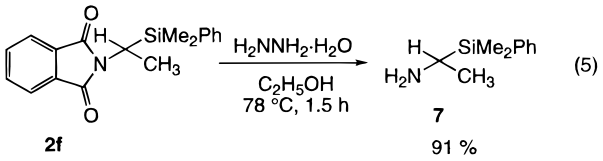
Scheme 2. As for **2k**, the torsion angles between the carbonyl group and the alkylsilyl or the ethyl group are 102.4(3)° and 132.1(3)°, respectively. These results show that the intramolecular interaction between the silicon atom and the oxygen atom does not exist in the

Scheme 2



solid state despite the high affinity of the silicon atom to the oxygen atom. The hydrogen atom in **2f** and **2k** is rather close to the oxygen atom. This is in marked contrast to the case of the *N*-(silylmethyl)amides having the electron-withdrawing groups such as fluorine and chlorine on the silyl atom.[15] It is probably because the energy level of the σ^* orbital of the silicon−carbon bond is not low enough to interact with the lone-pair electrons on the carbonyl group, and the steric factor may be a dominant factor to control the conformations.

Finally, hydrolysis of *N*-(silylethyl)phthalimide **2f** with hydrazine was examined (eq 5) since the general synthetic method of (silylethyl)amine **7** is still lacking.[16]



(5)

N-(Silylethyl)imide **2f** and hydrazine monohydrate were stirred under reflux in ethyl alcohol for 1.5 h. The reaction mixture was extracted with ether and saturated sodium hydrogen carbonate aqueous solution to give α-(silylethyl)amine **7** in 91% yield.

In summary, Rh-catalyzed hydrosilylation of the olefins attached to nitrogen-, oxygen-, and sulfur-containing functional groups has been demonstrated. The highly regioselective addition of hydrosilane to *N*-vinylurea, enamides, and *N*-vinylimides was attained by using $Rh_2(OAc)_4$ as the catalyst. In the reaction of vinyl carboxylates, thiocarboxylates, vinyl ether, and vinyl sulfides, the catalytic activity and regioselectivity of the reaction were highly dependent on the substrates, catalysts, and solvents. The results using deuteriosilane have suggested that the reductive elimination may be the rate-determining step as far as **1f** is concerned. X-ray molecular structure analyses of *N*-(silylalkyl)-imide and -amide have shown no intramolecular coordination of the oxygen atom toward the silicon atom.

Experimental Section

General Comments. The ^1H NMR spectra were measured on a JEOL α-400 (400 MHz) in $CDCl_3$. Chemical shifts of the

(16) (a) Fessenden, R. J.; Coon, M. D. *J. Med. Chem.* **1964**, *7*, 561. (b) Hengelsberg, H.; Tacke, R.; Fritsche, K.; Syldatk, C.; Wagner, F. *J. Organomet. Chem.* **1991**, *415*, 39. (c) Constantieux, T.; Picard, J.-P. *Organometallics* **1996**, *15*, 1604.

protons are reported in δ values, referenced to tetramethylsilane as an internal standard. The ^{13}C NMR spectra were measured on a JEOL α-400 (100 MHz). The mass spectra (MS) were taken on Shimadzu GCMS QP-1000(a) (EI mode). Melting points were determined using a Yanagimoto melting point apparatus and are uncorrected. Elemental analyses were carried out by the Elemental Analysis Center in Kyoto University. Silica gel 60 (particle size 63−200 μm (70−230 mesh ASTM)) from Kanto Chemical Co. Ltd. was used. *N*-Vinylamides and -imides **1c**−**f**, dimethylphenylsilane, $Rh_2(OAc)_4$, $Rh_2[(CO)_4Cl]_2$, $Rh(acac)_3$, $RhH(PPh_3)_4$, and $[RhCl(C_6H_{10})]_2$ were purchased from Aldrich or Chisso Co. Ltd. Enamides **1b**,[17] **1g**,[18] **1h**,[19] and **1i**[19] and allylic amides **3a**,[20] **3b**,[21] **3c**,[22] and **3d**[22] were prepared as reported previously. $RhCl(PPh_3)_3$[23] was prepared by a published procedure. *N*-(Silylalkyl)amide **2k** was prepared by a reaction similar to that in eq 1.[5]

***N*-(1-(Dimethylphenylsilyl)propyl)-*N*-(phenylmethyl)acetamide (2a).** In a 20 mL two-necked flask fitted with a reflux condenser were placed *N*-benzyl-*N*-(1-propenyl)acetamide (**1a**) (0.198 g, 1.0 mmol) and toluene (10 mL) under a nitrogen atmosphere. To this solution were added $Rh_2(OAc)_4$ (0.008 g, 0.02 mmol) and dimethylphenylsilane (0.19 mL, 1.2 mmol), and the reaction was stirred under reflux for 3 h. Then, the reaction mixture was cooled and concentrated in vacuo. The oil was purifed through column chromatography on silica gel by using ethyl acetate/*n*-hexane (1:2) as the eluent to give *N*-(1-(dimethylphenylsilyl)propyl)-*N*-(phenylmethyl)acetamide (**2a**) (0.164 g, 50% yield) as a colorless oil: IR (neat) 1634 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.20 (s, 3H, −Si−CH_3), 0.41 (s, 3H, −Si−CH_3), 0.89 (t, 3H, J = 7.4 Hz, C−CH_3), 1.72 (m, 2H, −CH_2−), 2.12 (s, 3H, (C═O)CH_3), 2.90 (s, 2H, −CH_2−Ph), 4.22 (m, 1H, CH), 7.15−7.36 (m, 10H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.3, −2.4, 13.2, 22.0, 25.2, 51.9, 127.5, 127.7, 127.8, 128.5, 128.5, 133.9, 137.1, 140.2, 170.3; MS *m*/*z* 325 (M^+). Anal. Calcd for $C_{20}H_{27}NOSi$: C, 73.79; H, 8.36. Found: C, 73.49; H, 8.12.

***N*′-(1-(Dimethylphenylsilyl)hexyl)-*N*,*N*-dimethylurea (2b):** white solid (mp 86−87 °C); IR (KBr) 1621 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.34 (s, 6H, CH_3), 0.83 (t, 3H, J = 6.9 Hz, CH_3), 1.23 (m, 8H, CH_2), 2.81 (s, 6H, $N(CH_3)_2$), 3.58 (m, 1H, CH), 3.88 (br, 1H, NH), 7.37−7.55 (m, 5H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.8, −4.4, 14.1, 22.6, 26.9, 31.9, 32.2, 36.3, 40.2, 127.9, 129.3, 134.1, 136.9, 158.6; MS *m*/*z* 291 (M^+ − 1). Anal. Calcd for $C_{17}H_{30}N_2OSi$: C, 66.61; H, 9.86. Found: C, 66.80; H, 10.02.

***N*-(1-(Dimethylphenylsilyl)ethyl)-*N*-methylacetamide (2c):** colorless oil; IR (neat) 1639 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.33 (s, 3H, CH_3), 0.41 (s, 3H, CH_3), 1.18 (d, 2.1H, J = 7.3 Hz, *trans*-CH_3), 1.25 (d, 0.9H, J = 7.6 Hz, *cis*-CH_3), 1.98 (s, 2.1H, *trans*-(O═C)CH_3), 2.03 (s, 0.9H, *cis*-(O═C)CH_3), 2.76 (s, 2.1H, *cis*-N−CH_3), 2.79 (s, 0.9H, *trans*-N−CH_3), 3.45 (q, 0.27H, J = 7.5 Hz, *cis*-CH), 3.98 (q, 0.73H, J = 7.5 Hz, *trans*-CH), 7.34−7.52 (m, 5H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 21.9, 24.8, 25.6, 37.9, 41.7, 43.2, 45.5, 123.2, 124.5, 124.8, 126.5, 169.5; MS *m*/*z* 235 (M^+). Anal. Calcd for $C_{13}H_{21}NOSi$: C, 66.33; H, 8.99. Found: C, 66.12; H, 9.29.

***N*-(1-(Dimethylphenylsilyl)ethyl)-2-pyrrolidinone (2d):** colorless oil; IR (neat) 1682 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.37 (s, 6H, CH_3), 1.20 (d, 3H, J = 7.8 Hz, CH_3), 1.83 (m, 2H, CH_2), 2.28 (m, 2H, CH_2), 3.10 (m, 2H, CH_2), 3.97 (q, 1H, J = 7.6 Hz, CH), 7.36−7.53 (m, 5H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.22, −4.16, 13.2, 18.0, 30.8, 37.7, 54.4, 127.8, 129.3, 133.8, 137.1, 173.9; MS *m*/*z* 247 (M^+). Anal. Calcd for $C_{14}H_{21}NOSi$: C, 67.97; H, 8.55. Found: C, 67.73; H, 8.12.

***N*-(1-(Dimethylphenylsilyl)ethyl)hexahydro-2-azepinone (2e):** colorless oil; IR (neat) 1635 (C═O), cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.27 (s, 3H, CH_3), 0.29 (s, 3H, CH_3), 1.12 (d, 3H, J = 7.6 Hz, CH_3), 1.53 (m, 6H, CH_2), 2.36 (m, 2H, CH_2), 3.11 (m, 2H, CH_2), 3.85 (q, 1H, CH), 7.27−7.46 (m, 5H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.70, 13.9, 23.3, 29.2, 30.0, 37.3, 44.2, 48.4, 127.7, 129.0, 134.0, 138.5, 175.0; MS *m*/*z* 275 (M^+); HRMS calcd for $C_{16}H_{25}NOSi$ 275.17042, found 275.17311.

2-(1-(Dimethylphenylsilyl)ethyl)-1*H*-isoindole-1,3-(2*H*)-dione (2f): white solid (mp 90−92 °C); IR (KBr) 1706 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.39 (s, 3H, CH_3), 0.53 (s, 3H, CH_3), 1.39 (d, 3H, J = 7.8 Hz, CH_3), 3.99 (q, 1H, J = 7.6 Hz, CH), 7.26−7.74 (m, 9H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.10, −3.72, 14.5, 35.8, 122.8, 127.8, 129.3, 132.1, 133.6, 133.8, 137.0, 168.7; MS *m*/*z* 308 (M^+ − 1). Anal. Calcd for $C_{18}H_{19}NO_2Si$: C, 69.87; H, 6.19. Found: C, 69.64; H, 8.12.

1-Formyl-2-(dimethylphenylsilyl)pyrrolidine (2g): colorless oil; IR (neat) 1668 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.37 (s, 6H, CH_3), 1.79 (m, 2H, CH_2), 2.06 (m, 2H, CH_2), 3.38 (m, 2H, CH_2), 3.68 (m, 1H, CH), 7.34−7.53 (m, 5H, C_6H_5), 8.03 (s, 1H, (C═O)−H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.68, −4.37, 24.4, 27.8, 44.5, 47.6, 128.1, 129.7, 133.8, 136.7, 160.7; MS *m*/*z* 233 (M^+). Anal. Calcd for $C_{13}H_{19}NOSi$: C, 66.90; H, 8.21. Found: C, 67.09; H, 8.49.

1-Acetyl-2-(dimethylphenylsilyl)-2-pyrroline (2h): white solid; IR (KBr) 1582 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.49 (s, 6H, CH_3), 2.03 (s, 3H, CH_3), 2.73 (ddd, 2H, J = 2.7, 2.7, 2.7 Hz, CH_2), 3.81 (t, 2H, J = 9.0 Hz, CH_2), 5.24 (t, 1H, J = 2.8 Hz, CH═), 7.32−7.58 (m, 5H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.03, 22.5, 31.0, 48.1, 126.8, 127.5, 128.5, 134.1, 140.1, 144.5, 166.3; MS *m*/*z* 245 (M^+). Anal. Calcd for $C_{14}H_{19}NOSi$: C, 68.52; H, 7.80. Found: C, 68.51; H, 8.06.

2-(3-(Dimethylphenylsilyl)propyl)-1*H*-imidazole-1,3-(2*H*)-dione (2i): colorless oil; IR (neat) 1694 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.26 (s, 6H, CH_3), 0.72 (t, 2H, J = 8.7 Hz, CH_2), 1.56 (m, 2H, CH_2), 2.67 (s, 4H, CH_2), 3,47 (t, 2H, J = 7.4 Hz, CH_2), 7.33−7.49 (m, 5H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.2, 12.9, 22.3, 28.1, 41.7, 127.8, 129.0, 133.5, 138.7, 177.3; MS *m*/*z* 275 (M^+). Anal. Calcd for $C_{15}H_{21}NOSi$: C, 65.41; H, 7.68. Found: C, 65.61; H, 7.65.

2-(3-(Dimethylphenylsilyl)propyl)-1*H*-isoindole-1,3-(2*H*)-dione (2j): pale yellow oil; IR (neat) 1714 (C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.26 (s, 6H, CH_3), 0.77 (t, 2H, J = 8.7 Hz, CH_2), 1.67 (m, 2H, CH_2), 3.65 (t, 2H, J = 7.3 Hz, CH_2), 7.32−7.83 (m, 9H, C_6H_5, C_6H_4); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.2, 0.01, 12.9, 23.2, 40.9, 123.2, 127.8, 129.0, 132.1, 133.5, 133.8, 138.7, 168.4; MS *m*/*z* 323 (M^+). Anal. Calcd for $C_{19}H_{21}NO_2Si$: C, 70.55; H, 6.54. Found: C, 70.28; H, 6.50.

Mixture of Benzoic Acid 1-(Dimethylphenylsilyl)propyl Ester (5b) and Benzoic Acid 2-(Dimethylphenylsilyl)-propyl Ester (6b): colorless oil; IR (neat) 1723 (C═O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): **5b** δ 0.33 (s, 6H, CH_3), 1.28 (d, J = 7.3 Hz, 3H, CH_3), 5.11 (q, J = 7.3 Hz, 1H, CH), 7.30−7.94 (m, 10H, C_6H_5); **6b** δ 0.29 (s, 6H, CH_3), 1.29 (t, J = 7.3 Hz, 2H, CH_2), 4.29 (t, J = 8.13 Hz, 2H, CH_2), 7.29−7.96 (m, 10H, C_6H_5); MS *m*/*z* 284 (M^+). Anal. Calcd for $C_{17}H_{20}O_2Si$: C, 71.79; H, 7.09. Found: C, 72.00; H, 9.21.

2-Methyl-2-phenyl-5-oxa-2-silanonane (5d): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.21 (s, 6H, CH_3), 0.80 (t, 3H, J = 7.3 Hz, CH_3), 1.10 (t, 2H, J = 7.3 Hz, CH_2), 1.25 (m, 2H, CH_2), 1.43 (m, 2H, CH_2), 3.25 (t, 2H, J = 6.7 Hz, CH_2), 3.40 (t, 2H, J = 8.1 Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ −2.7, 13.9, 17.4, 19.4, 31.9, 67.6, 70.2, 76.7, 127.7, 128.9, 133.5, 138.9; MS *m*/*z* 236 (M^+). Anal. Calcd for $C_{14}H_{24}OSi$: C, 71.11; H, 10.23. Found: C, 70.86; H, 10.24.

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2,3-Dimethyl-2,5-diphenyl-4-thia-2-silapentane (5g): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.43 (s, 6H, CH_3), 1.38 (d, 2H, J = 7.1 Hz, CH_3), 2.14 (q, 2H, J = 7.2 Hz, CH), 3.81 (s, 2H, CH_2), 7.32−7.60 (m, 10H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.8, 16.3, 26.7, 36.0, 126.8, 127.9, 128.4, 128.8, 129.1, 133.5, 138.3, 138.5; MS m/z 286 (M^+). Anal. Calcd for $C_{17}H_{22}SSi$: C, 71.27; H, 7.74. Found: C, 71.03; H, 7.70.

2-Methyl-2,6-diphenyl-5-thia-2-silahexane (6g): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 6H, CH_3), 1.02 (sex, 2H, J = 1.7, 5.6 Hz, CH_2), 2.70 (sex, 2H, J = 1.0, 1.7, 2.7, 3.9 Hz, CH_2), 3.61 (s, 2H, CH_2), 7.13−7.39 (m, 10H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.1, 16.3, 26.7, 36.0, 126.8, 127.9, 128.4, 128.8, 129.1, 133.5, 138.3, 138.5; MS m/z 286 (M). Anal. Calcd for $C_{17}H_{22}SSi$: C 71.27, H 7.74, Found: C 71.14, H 7.86.

2,3-Dimethyl-2-phenyl-6-oxa-4-thia-2-silaheptane (5h): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.37 (s, 6H, CH_3), 1.31 (d, 3H, J = 7.3 Hz, CH_3), 2.33 (q, 1H, J = 7.2 Hz, CH), 3.27 (s, 3H, CH_3), 4.61 (d, 2H, J = 11.5 Hz, CH_2), 7.35−7.57 (m, 5H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.9, −4.4, 16.9, 22.9, 55.4, 74.5, 127.7, 129.2, 134.0, 136.9; MS m/z 240 (M^+). Anal. Calcd for $C_{12}H_{20}OSSi$: C, 59.94; H, 8.38. Found: C, 60.01; H, 8.54.

2-Methyl-2-phenyl-7-oxa-5-thia-2-silaoctane (6h): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.36 (s, 6H, CH_3), 1.15 (q, 2H, J = 3.7, 5.8, 8.3 Hz, CH_2), 2.63 (q, 2H, J = 3.9, 5.6, 8.1 Hz, CH_2), 3.31 (s, 3H, CH_3), 4.61 (s, 2H, CH_2), 7.34−7.50 (m, 5H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.1, 16.8, 26.5, 55.8, 75.2, 127.9, 129.1, 133.5, 138.2; MS m/z 240 (M^+). Anal. Calcd for $C_{12}H_{20}OSSi$: C, 59.94; H, 8.38 Found: C, 59.84; H, 8.56.

Deuteriosilylation of *N*-Vinylphthalimide (1f). In a 20 mL two-necked flask fitted with a reflux condenser were placed *N*-vinylphthalimide (0.346 g, 2.0 mmol) and toluene (10 mL) under a nitrogen atmosphere. To this solution were added $Rh_2(OAc)_4$ (0.016 g, 0.04 mmol) and deuteriodimethylphenylsilane (0.19 mL, 1.2 mmol), and the mixture was stirred under reflux. After 3 h, the reaction mixture was cooled and concentrated in vacuo. The oil was chromatographed on a silica gel column by using ethyl acetate/*n*-hexane (1:2) as the eluent to give the deuterio starting material **1f** (0.091 g) as a white solid and the deuterio-silylated compounds **2f** and **2f′** (0.344 g) as a white solid.

Hydrolysis of *N*-1-(Dimethylphenylsilyl)phthalimide (2f). In a 50 mL three-necked flask fitted with a reflux condenser were placed *N*-1-(dimethylphenylsilyl)phthalimide (**2f**) (3.708 g, 12.0 mmol) and ethyl alcohol (40 mL). To this solution was added hydrazine monohydrate (5.55 mL, 120 mmol), and the mixture was stirred under reflux for 1.5 h. The reaction mixture was cooled and extracted with ether and a saturated sodium hydrogen carbonate aqueous solution. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$ and concentrated to give 1-(dimethylphenylsilyl)-ethylamine (**7**) (1.956 g, 91%) as an oil with purity higher than 95%. IR (neat) 3069, 3021, 2957, 2806, 1709, 1589, 1427, 1249, 1114, 815 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.32 (s, 6H, CH_3), 1.14 (d, 3H, J = 7.3 Hz, CH_3), 1.39 (br, 2H, NH_2), 2.49 (q, 1H, J = 7.4 Hz, CH), 7.34−7.61 (m, 5H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ −6.05, −5.51, 20.1, 36.1, 127.9, 129.2, 134.1, 137.1; MS m/z 179 (M^+).

X-ray Molecular Structure Analysis. All measurements were carried out on a Rigaku AFC7R diffractomater with graphite-monochromated Mo Kα radiation (λ = 0.7109 Å). All of the structures were solved and refined using the TeXsan crystallographic software package on an IRIS Indigo computer. X-ray-quality crystals of **2f** and **2k** were obtained by slow diffusion of dichloromethane into hexane solutions of each of the samples. The crystals were cut from the grown needles. All of the samples were stable in air. The cell dimensions were determined by a least-squares refinement of the diffractmeter angles for 25 automatically centered reflections. Two standard reflections were measured every 150 reflections, and no decay was deteted. The linear absorption coefficiencies, μ, for Mo Kα radiation are 1.4 (**2f**) and 1.5 cm^{-1} (**2k**). Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization factors. The structure was solved by direct methods and expanded using Fourier techniques. Neutral-atom scattering factors were taken from Cromer and Waber.[24] Anomalous dispersion effects were indicated in F_{calc}; the value for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[25] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[26] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The weighting scheme was based on counting statistics and included factors (p = 0.040 (**2f**), 0.003 (**2k**)) to downweight the intense reflections. Plots of $\sum\omega(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices show no unusual trends. Crystal data and measurement description are summarized in Table 5.

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Supporting Information Available: Tables giving positional and thermal parameters, bond distances and angles, and torsion angles and figures giving additional views of **2f** and **2k** (8 pages). Ordering information is given on any current masthead page.

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