

# A Triruthenium Carbonyl Cluster Bearing a Bridging Acenaphthylene Ligand: An Efficient Catalyst for Reduction of Esters, Carboxylic Acids, and Amides by Trialkylsilanes

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Received March 18, 2002

**Abstract:** An efficient reduction of carboxylic acids, esters, and amides with trialkylsilanes is accomplished using a triruthenium carbonyl cluster bearing a bridging acenaphthylene ligand, ( $\mu_3, \eta^2: \eta^3: \eta^5$ -acenaphthylene)Ru<sub>3</sub>(CO)<sub>7</sub>, as the catalyst. Preactivation of the catalyst by hydrosilanes accelerates the reactions. Sterically small trialkylsilanes are effective in these reactions. Reduction of carboxylic acids and amides efficiently produces the corresponding silyl ethers and amines, respectively. Reduction of esters gives a mixture of silyl and alkyl ethers, but can be controlled by changing the silanes and solvents.

Reduction of carboxylic acids, esters, and amides is an important synthetic method of synthesizing aldehydes, alcohols, or amines; however, reduction of these substrates is generally more difficult than that of ketones and aldehydes, and further investigation is required to develop efficient protocols to reduce them under mild conditions.<sup>1</sup> In contrast to well-investigated catalytic hydrosilylation of ketones and aldehydes,<sup>2</sup> transition-metal-catalyzed reduction of carboxylic acids, esters, and amides with silanes has not been reported until recently.<sup>3–8</sup> Buchwald and co-workers reported titanocene-

catalyzed reduction of esters and amines with HSi(OEt)<sub>3</sub>,<sup>4</sup> whereas Ohta<sup>5</sup> and Ito<sup>6</sup> published Rh-catalyzed hydrosilylation of esters or reduction of amides with Ph<sub>2</sub>SiH<sub>2</sub> or PhSiH<sub>3</sub>. Selective reduction of esters to ethers was developed by Cutler *et al.* by the manganese-catalyzed reaction with PhSiH<sub>3</sub>.<sup>7</sup> Fuchikami and co-workers have recently demonstrated that Ru<sub>3</sub>(CO)<sub>12</sub> and other ruthenium complexes are active catalysts for the hydrosilylation of esters to silyl acetals and for the reduction of amides.<sup>8</sup> Although these ruthenium-catalyzed reactions are attractive as synthetic methods to obtain aldehydes or amines, the high reaction temperature (~100 °C) necessary to accomplish these reactions is a drawback. We recently reported that a triruthenium carbonyl cluster bearing a  $\mu_3$ -acenaphthylene ligand, ( $\mu_3, \eta^2: \eta^3: \eta^5$ -acenaphthylene)Ru<sub>3</sub>(CO)<sub>7</sub> (**1**), is an active catalyst for the hydrosilylation of ketones and aldehydes, the reduction of acetals and cyclic ethers, and the ring-opening polymerization of cyclic ethers.<sup>9</sup> The catalytic activity of **1** in these reactions is much higher than that of Ru<sub>3</sub>(CO)<sub>12</sub> under the same conditions;<sup>9</sup> this prompted us to examine reduction of carboxylic acids, esters, and amides with trialkylsilanes using **1** as the catalyst. In this paper, we wish to report that reduction of these compounds is efficiently achieved by the catalysis of **1** preactivated by hydrosilanes. By an appropriate choice of the hydrosilanes, the production of silyl ethers from carboxylic acids, that of silyl and alkyl ethers from esters, and that of amines from amides proceed even at room temperature within several hours, providing efficient methods to prepare alcohols, alkyl ethers, and amines.

**Screening of the Reaction Conditions.** As reported previously, the hydrosilylation of ketones or aldehydes with trialkylsilanes proceeds at room temperature in the presence of **1**.<sup>9</sup> In a typical example, hydrosilylation of acetophenone with EtMe<sub>2</sub>SiH (1.5 equiv) in the presence of **1** (1 mol %) afforded the corresponding silyl ether in over 95% yield after 18 h (method A, Scheme 1, eq 1). By screening the reaction conditions, we have found that prior activation of **1** with EtMe<sub>2</sub>SiH in dioxane followed by addition of acetophenone in a benzene solution resulted in the production of a highly active catalyst species, which promoted rapid hydrosilylation of acetophenone with EtMe<sub>2</sub>SiH leading to the quantitative formation of the silyl ether within 1 h (method B, Scheme 1,

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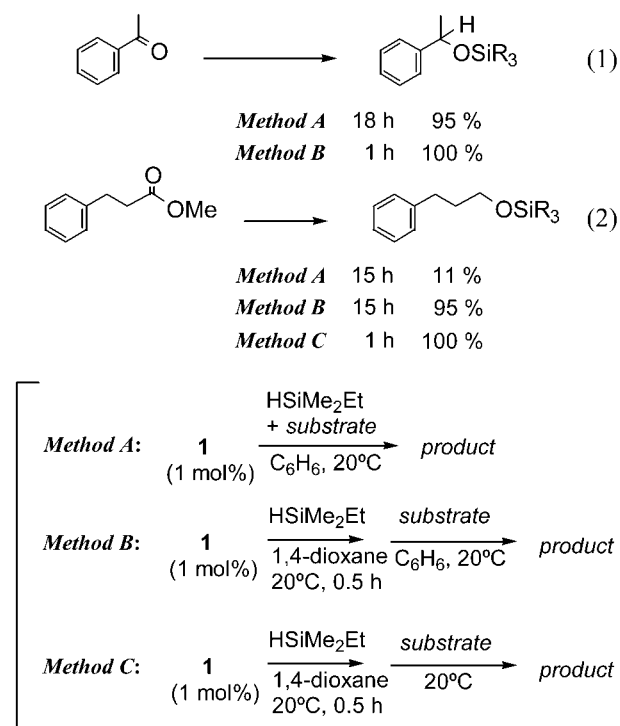
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## SCHEME 1



eq 1). Similarly, reduction of methyl hydrocinnamate with  $\text{EtMe}_2\text{SiH}$  (2.5 equiv) under the conditions of method A resulted in formation of the ethyldimethylsilyl ether of 3-phenylpropanol (11%) after 15 h with recovery of the starting material (Scheme 1, eq 2). Application of method B to the reduction of methyl hydrocinnamate with  $\text{EtMe}_2\text{SiH}$  accelerated the reaction leading to complete consumption of the ester after 15 h (Scheme 1, eq 2). Furthermore, the reaction was over within 1 h when neat methyl hydrocinnamate instead of its benzene solution was added to the solution of the activated catalyst as shown in Scheme 1, eq 2 (method C). These results showed that method C can be the most efficient method for the hydrosilylation of methyl hydrocinnamate and can be applicable to the reduction of carboxylic acids, esters, and amides at room temperature.

As described later, the reduction of carboxylic acids, esters, and amides is actually accomplished by  $\text{EtMe}_2\text{SiH}$  according to method C. The reaction of carboxylic acids affords the corresponding silyl ethers as a single product, whereas that of amides gives amines. In contrast, the reaction of esters generally gives two products, silyl ethers and alkyl ethers. Alkyl silyl acetals were detected at the initial stage of the reaction as intermediates, and the selectivity of the subsequent reductive cleavage of either the C–OR bond or the C–OSi bond in the silyl acetal determines the ratio of the silyl ether and the alkyl ether in the products. In contrast to the fact that the reaction of methyl hydrocinnamate with  $\text{EtMe}_2\text{SiH}$  gave the corresponding silyl ether as the single product, ethyl hydrocinnamate gave a 4:1 mixture of the silyl ether and the ethyl ether under the same reaction conditions. To understand the effect of silanes, catalysts, and the activation methods of the catalyst on the rate and the selectivity of the reaction, the reaction of ethyl hydrocinnamate with various organosilanes was inves-

**TABLE 1. Hydrosilylation of Ethyl Hydrocinnamate with  $\text{EtMe}_2\text{SiH}$  under Various Conditions**

**cat.:**  $\mathbf{1}$   $\mathbf{2}$   $\mathbf{3}$   $\mathbf{4}$

entry	catalyst	$\text{R}_3\text{SiH}$	solvent <sup>a</sup>	temp (°C)	time (h)	conv. (%)	product-ratio (%) <sup>b</sup>		
							A <sub>alcohol</sub>	B <sub>ether</sub>	C <sub>aldehyde</sub>
1	$\mathbf{1}$	$\text{EtMe}_2\text{SiH}$	1,4-dioxane	20	1	100	80	20	0
2	$\mathbf{1}$	$\text{HSi(CH}_2)_2\text{SiH}$	1,4-dioxane	20	2	100	84	16	0
3	$\mathbf{1}$	$\text{Et}_2\text{MeSiH}$	1,4-dioxane	20	5	100	24	76	0
4	$\mathbf{1}$	$\text{PhMe}_2\text{SiH}$	1,4-dioxane	20	21	95	83	17	1
5	$\mathbf{1}$	$\text{Ph}_2\text{MeSiH}$	1,4-dioxane	20	21	74	84	16	0
6	$\mathbf{1}$	$\text{Et}_3\text{SiH}$	1,4-dioxane	20	21	7	0	0	100
7	$\mathbf{1}$	$^i\text{Pr}_3\text{SiH}$	1,4-dioxane	20	24	0	0	0	0
8	$\mathbf{2}$	$\text{EtMe}_2\text{SiH}$	1,4-dioxane	20	24	56	0	100	0
9	$\mathbf{3}$	$\text{EtMe}_2\text{SiH}$	1,4-dioxane	20	24	34	0	99	1
10	$\mathbf{4}$	$\text{EtMe}_2\text{SiH}$	1,4-dioxane	20	24	40	0	98	2
11	$\text{Ru}_1(\text{CO})_{12}$	$\text{EtMe}_2\text{SiH}$	1,4-dioxane	20	24	0	0	0	0
12	$\mathbf{1}$	$\text{EtMe}_2\text{SiH}$	benzene	20	1	100	58	42	0
13	$\mathbf{1}$	$\text{EtMe}_2\text{SiH}$	diethyl ether	20	2	100	39	45	16
14	$\mathbf{1}$	$\text{EtMe}_2\text{SiH}$	tetrahydropyran	20	2	94	47	53	0
15	$\mathbf{1}$	$\text{EtMe}_2\text{SiH}$	oxepane	20	8	69	39	61	0
16	$\mathbf{1}$	$\text{EtMe}_2\text{SiH}$	pyridine	20	22	0	0	0	0
17	$\mathbf{1}$	$\text{EtMe}_2\text{SiH}$	1,4-dioxane	10	1	100	72	28	0
18	$\mathbf{1}$	$\text{EtMe}_2\text{SiH}$	1,4-dioxane	40	<1	100	79	21	0
19	$\mathbf{1}$	$\text{EtMe}_2\text{SiH}$	1,4-dioxane	60	<1	100	85	15	0

<sup>a</sup> Concentration of  $\mathbf{1}$  was 0.05 mol/L. <sup>b</sup> The ratio of the products was determined on the basis of integral ratios of the  $^1\text{H}$  NMR spectra of the crude mixture using dichloroethane as an internal standard.

tigated. In Table 1 are summarized the results obtained by changing the reaction conditions when using ethyl hydrocinnamate. The yields and the ratios of the products were determined after hydrolysis of the formed silyl ethers or of the alkyl silyl acetals. As shown in entries 1–7 (Table 1), the rate and the product ratio are dependent on the hydrosilane used. The rate is in the order  $\text{EtMe}_2\text{SiH} > \text{HSiMe}_2(\text{CH}_2)_2\text{SiMe}_2\text{H} > \text{Et}_2\text{MeSiH} > \text{PhMe}_2\text{SiH} > \text{Ph}_2\text{MeSiH} \gg \text{Et}_3\text{SiH} > ^i\text{Pr}_3\text{SiH}$ . The ratio of the alcohol to the alkyl ether is 80:20–83:17 with  $\text{EtMe}_2\text{SiH}$ ,  $\text{HSiMe}_2(\text{CH}_2)_2\text{SiMe}_2\text{H}$ ,  $\text{PhMe}_2\text{SiH}$ , and  $\text{Ph}_2\text{MeSiH}$ , whereas the ethyl ether predominantly forms when  $\text{Et}_2\text{MeSiH}$  is used as the silane. Monitoring the reaction by NMR revealed that the reaction is stepwise; the silyl acetal is formed first, followed by the production of a mixture of the silyl ether and the alkyl ether. In fact, slow hydrosilylation with  $\text{Et}_3\text{SiH}$  gave the silyl acetal as a single product in low yield, which in turn gave hydrocinnamaldehyde after hydrolysis.

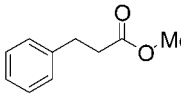
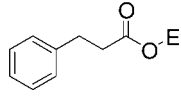
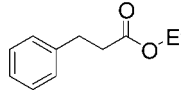
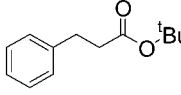
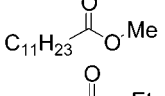
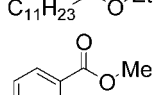
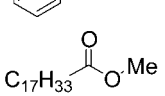
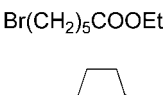
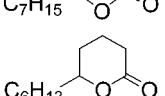
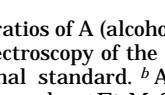
The factors determining the rate and the selectivity other than the structure of the silanes described above are the catalyst used, the activation method of the catalyst, and the reaction temperature. The ruthenium complexes,  $(\mu_2, \eta^2: \eta^3\text{-}4,6,8\text{-trimethylazulene})\text{Ru}_3(\text{CO})_7$  ( $\mathbf{2}$ ),  $(\mu_2, \eta^2: \eta^3\text{-}4,6,8\text{-trimethylazulene})\text{Ru}_2(\text{CO})_5$  ( $\mathbf{3}$ ), and  $(\mu_2, \eta^2: \eta^3\text{-}4,6,8\text{-trimethylazulene})\text{Ru}_4(\text{CO})_9$  ( $\mathbf{4}$ )<sup>10</sup> were found to be catalytically active in the reduction of ethyl hydro-

cinnamate with  $\text{EtMe}_2\text{SiH}$ . Although the reactions were slower than that of **1**, the ethyl ether was obtained as a single product.  $\text{Ru}_3(\text{CO})_{12}$  used for the Fuchikami hydrosilylation was totally inactive at room temperature. As solvent for the activation of **1**, benzene,  $\text{Et}_2\text{O}$ , and tetrahydropyran can be used instead of dioxane. The activation of **1** in oxepane is less effective, whereas pyridine causes deactivation of the catalyst. Use of THF resulted in its polymerization.<sup>8</sup> Interestingly, the ratios of ether to silyl ether were somewhat higher in these solvents than in dioxane. At higher reaction temperature, the reaction was more rapid, but the alcohol/alkyl ether ratio did not differ much with temperature. All of these results suggest that the reduction of ethyl hydrocinnamate is achieved successfully under mild conditions by using **1**, preactivated by hydrosilanes and sterically small hydrosilanes as the catalyst and the reducing reagents. The ratio of the silyl ether to the alkyl ether is affected by various factors; however, good to high selectivity can be attained by an appropriate choice of the hydrosilanes as described below.

**The Reduction of Esters, Carboxylic Acids, and Amides.** In Tables 2 and 3 are summarized the reduction of esters, lactones, carboxylic acids, and amides with  $\text{EtMe}_2\text{SiH}$  using **1** as the catalyst. As shown in entries 1, 2, and 4 in Table 2, the reaction rate with  $\text{EtMe}_2\text{SiH}$  is sensitive to the bulkiness of the alkyl group of the ester:  $\text{Me} > \text{Et} \gg \text{tBu}$ . The product ratios also depend on the alkyl group of the esters; the ethyl and *tert*-butyl esters gave the corresponding alkyl ethers as byproducts. Aromatic and aliphatic esters including those containing a Br atom or a carbon-carbon double bond underwent the reaction with  $\text{EtMe}_2\text{SiH}$  as shown in entries 7–9 (Table 2), in which a mixture of alcohols and ethers was obtained after hydrolysis of the reaction mixture in ratios of 93:7–59:41. Improvement of the selectivity to form the alkyl ether as a single product is possible by appropriate choice of the silane and the solvent used for the activation of **1**. As typical examples, ethyl hydrocinnamate or ethyl laurate was reduced to the corresponding ethyl ether as the major product by  $\text{Et}_2\text{MeSiH}$ , when **1**, activated by  $\text{Et}_2\text{MeSiH}$  in tetrahydropyran, was used as the catalyst as shown in entries 3 and 6 (Table 2). Selective formation of cyclic ethers was achieved from lactones with  $\text{EtMe}_2\text{SiH}$  as shown in entries 10 and 11 (Table 2).

As shown in Table 3, similar to the reduction of esters, carboxylic acids were easily reduced to the corresponding silyl ethers in the presence of 3.5 equiv of  $\text{EtMe}_2\text{SiH}$  based on the carboxylic acid, subsequent hydrolysis of which afforded the corresponding alcohols as a single product in good yields (Table 3, entries 1–3). The initial step of the reaction is a dehydrogenative silylation of the carboxylic acids to the corresponding silyl esters, which could be confirmed by spectral data of the products formed in the reaction of hydrocinnamic acid with 1.2 equiv of  $\text{EtMe}_2\text{SiH}$ . Application of method C to the reduction of tertiary amides also proceeded smoothly to give the corresponding amines in good yields (Table 3, entries 4–6). Reaction of secondary amides only resulted in dehydrogenative silylation to give the corre-

**TABLE 2. Hydrosilylation of Esters with  $\text{EtMe}_2\text{SiH}$  Catalyzed by **1****

entry	ester	time (h)	conv. (%)	NMR ratio		yield (%) <sup>b</sup>	
				A: B <sup>a</sup>	A	B	
1		0.5	100	100: 0	97	0	
2		1	100	80: 20	55	11	
3 <sup>c</sup>		1	100	0: 100	0	87	
4 <sup>d</sup>		12	100	89: 11	80	7	
5	$\text{C}_{11}\text{H}_{23}$ 	3	100	82: 18	69	17	
6 <sup>c</sup>	$\text{C}_{11}\text{H}_{23}$ 	22	100	20: 80	17	75	
7		24	80	93: 7	52	0	
8	$\text{C}_{17}\text{H}_{33}$ 	6	73	64: 36	32	22	
9	$\text{Br}(\text{CH}_2)_5\text{COOEt}$	2	100	59: 41	47	40	
10	$\text{C}_7\text{H}_{15}$ 	3	100	0: 100	0	79	
11	$\text{C}_6\text{H}_{13}$ 	2	100	0: 100	0	73	

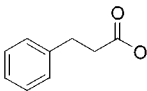
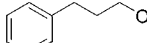
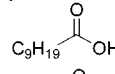
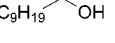
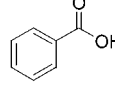
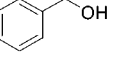
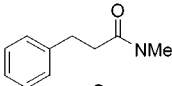
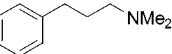
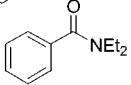
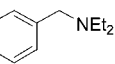
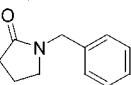
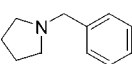
<sup>a</sup> The ratios of A (alcohol) and B (ether) were determined by <sup>1</sup>H NMR spectroscopy of the crude mixture using dichloroethane as an internal standard. <sup>b</sup> All products were purified by column chromatography. <sup>c</sup>  $\text{Et}_2\text{MeSiH}$  and tetrahydropyran were used as the silane and solvent. <sup>d</sup>  $\text{HSiMe}_2\text{Et}$  (4 equiv) was used.

sponding silyl amides, and addition of the H–Si bond of  $\text{EtMe}_2\text{SiH}$  to the C=O group did not take place under the conditions used.

In summary, an efficient catalytic reduction of carboxylic acids, esters, and amides with trialkylsilanes could be established by using **1** as the catalyst. Prior activation of **1** by hydrosilanes dramatically accelerated the reactions. The reaction rate and selectivity of the products are dependent on hydrosilanes, solvents, substrates, and catalysts. Sterically small trialkylsilanes, such as  $\text{HSiMe}_2\text{Et}$ ,  $\text{HMe}_2\text{Si}(\text{CH}_2)_2\text{SiMe}_2\text{H}$ , and  $\text{HSiMeEt}_2$ , are effective in the catalytic reduction of the carboxylic acid derivatives, whereas bulky hydrosilanes and dihydro- and trihydrosilanes were ineffective. Reduction of esters generally gives a mixture of silyl and alkyl ethers. The product ratios are mainly dependent on the structure of the esters, but can be controlled by changing the silanes and solvents in some cases. Reduction of carboxylic acids and amides efficiently produce the corresponding

(10) (a) Nagashima, H.; Suzuki, A.; Nobata, M.; Aoki, K.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2441. (b) Matsubara, K.; Ryu, K.; Maki, T.; Iura, T.; Nagashima, H. *Organometallics*, in press.

**TABLE 3. Catalytic Reduction of Carboxylic Acids and Amides with EtMe<sub>2</sub>SiH Catalyzed by **1****

entry	substrate	time (h)	product	yield (%)
1		0.5		72 (isolated) 89 (NMR)
2		6		80 (isolated) 100 (NMR)
3		18		46 (isolated) 62 (NMR)
4		0.5		75 (isolated) 100 (NMR)
5		0.5		56 (isolated) 98 (NMR)
6		2		45 (isolated) 90 (NMR)

<sup>a</sup> HSiMe<sub>2</sub>Et (4 equiv) was treated with carboxylic acids.

<sup>b</sup> HSiMe<sub>2</sub>Et (2.5 equiv) was treated with amides.

silyl ethers and amines, respectively, in good yields. By means of preactivation of **1** with hydrosilanes to produce the highly active catalyst species, the reactions apparently proceed at lower temperatures compared with the conventional ruthenium-catalyzed reduction of esters and amides which proceeds at 100 °C to afford alkyl silyl acetals and amines, respectively.<sup>8</sup> Application of this highly catalytic active species to the reduction of other organic substrates with hydrosilanes is actively in progress.

## Experimental Section

All manipulations were carried out under a dinitrogen atmosphere unless otherwise noted. The solvents, benzene, diethyl ether, tetrahydropyran, oxepane, and benzene-*d*<sub>6</sub> were distilled from benzophenone ketyl and stored under a dinitrogen atmosphere. Dioxane and pyridine were dried over CaH<sub>2</sub> and distilled before use. The hydrosilanes HSiMe<sub>2</sub>Et, Me<sub>2</sub>HSi(CH<sub>2</sub>)<sub>2</sub>-SiHMe<sub>2</sub>, HSiMeEt<sub>2</sub>, HSiMe<sub>2</sub>Ph, HSiEt<sub>3</sub>, and HSiPr<sub>3</sub> were distilled just before use. Other reagents were used as received. Column chromatography was carried out using silica gel (Merck No. 1.07734.9025). The ruthenium complexes **1**–**4** were prepared according to published methods.<sup>9,10</sup> In the reduction of esters and carboxylic acids, silyl ethers were produced. These could be isolated as shown below as the representative. However, in most of the cases, the product determination was carried out after hydrolysis of the silyl ethers. The products were identified by comparison of their spectral data with those of authentic samples or published data. Spectral data of these products are in the Supporting Information.

**Typical Procedure To Synthesize Silyl Ethers.** To a solution of **1** (6.0 mg, 9.3 μmol) in dioxane (0.18 mL) was added dimethylethylsilane (0.30 mL, 2.3 mmol). The mixture was stirred for 0.5 h at room temperature, and methyl hydrocinnamate (0.16 mL, 0.91 mmol) was added dropwise at ambient

temperature. Stirring was continued for 1 h. The <sup>1</sup>H NMR measurement of the crude mixture showed the quantitative formation of 3-phenylpropyl dimethylethylsilyl ether. After the solvent was removed in vacuo, distillation of the residual liquid under reduced pressure (70 °C, 10<sup>2</sup> Pa) gave the silyl ether in 57% yield (115 mg, 0.52 mmol). Alternatively, silyl ethers were prepared in high yields by reduction of the carboxylic acids with dimethylethylsilane. In a typical example, a solution of the mixture of **1** (7.5 mg, 11.5 μmol) and dimethylethylsilane (0.62 mL, 4.7 mmol) in dioxane (0.20 mL) was stirred for 0.5 h at room temperature, and hydrocinnamic acid (172.6 mg, 1.15 mmol) was added. The solution was stirred for 1 h, and the desired 3-phenylpropyl dimethylethylsilyl ether was subsequently purified by distillation at 150 °C (215 mg, 0.96 mmol, 84% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.18–7.31 (m, 5H), 3.62 (t, *J* = 6.4 Hz, 2H), 2.67 (dd, *J* = 7.6, 7.9 Hz, 2H), 1.85 (m, 2H), 0.96 (t, *J* = 7.9 Hz, 3H), 0.58 (q, *J* = 7.9 Hz, 2H), 0.09 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 142.1, 128.4, 128.3, 125.7, 62.0, 34.3, 32.1, 8.0, 6.7, –2.7; <sup>29</sup>Si NMR (CDCl<sub>3</sub>) δ 18.5; EI-MS *m/z* 222 [M<sup>+</sup>], 223 [M<sup>+</sup> + 1], 224 [M<sup>+</sup> + 2], 225 [M<sup>+</sup> + 3]; HRMS calcd for C<sub>13</sub>H<sub>22</sub>OSi 222.1440, found 222.1447.

**Typical Procedure for the Reduction of Esters.** To a solution of **1** (7.7 mg, 12 μmol) in dioxane (0.20 mL) was added dimethylethylsilane (0.38 mL, 2.9 mmol). The mixture was stirred for 30 min at room temperature, and the color of the solution turned from red to dark brown. Methyl hydrocinnamate (0.185 mL, 1.2 mmol) was added dropwise at ambient temperature, and an exothermic reaction took place. The mixture was stirred for 0.5 h. The reaction was quenched by adding aqueous hydrochloric acid. Then, the mixture was extracted with ether. The combined organic layers were washed with aqueous NaHCO<sub>3</sub> and brine and dried over MgSO<sub>4</sub>. After the solvent was removed in vacuo, the residual mixture was purified by column chromatography by eluting with 7–10% ethyl acetate in hexane to give 3-phenylpropyl alcohol (128 mg, 0.94 mmol, 97%).

**Typical Procedure for the Reduction of Carboxylic Acids.** To a solution of **1** (16.5 mg, 25.2 μmol) in dioxane (0.45 mL) was added dimethylethylsilane (0.84 mL, 6.3 mmol). The mixture was stirred for 30 min at room temperature. Hydrocinnamic acid (380 mg, 2.55 mmol) was added at ambient temperature. Then, stirring continued for 0.5 h. A vigorous gas evolution occurred. The reaction was quenched by adding aqueous hydrochloric acid, and then the mixture was extracted with ether. The combined organic layers were washed with aqueous NaHCO<sub>3</sub> and brine, and dried over MgSO<sub>4</sub>. After the solvent was removed in vacuo, the residual mixture was separated by column chromatography by eluting with 7–10% ethyl acetate in hexane to give 3-phenylpropyl alcohol (248 mg, 1.82 mmol, 72%).

**Typical Procedure for the Reduction of Amides.** To a solution of **1** (6.4 mg, 9.8 μmol) in dioxane (0.18 mL) was added dimethylethylsilane (0.32 mL, 2.4 mmol). The mixture was stirred for 30 min at room temperature. *N,N*-diethylhydrocinnamamide (0.168 mL, 0.99 mmol) was added at ambient temperature. Stirring was continued for 1 h. The <sup>1</sup>H NMR measurement of the crude mixture showed the quantitative formation of *N,N*-diethyl-2-phenylpropylamine. After removal of the solvent in vacuo, distillation of the residual liquid gave *N,N*-diethyl-2-phenylpropylamine (121 mg, 0.74 mmol, 75%).

**Acknowledgment.** A part of this study was financially supported by the Japan Society for the Promotion of Science (Grants-In-Aid for Scientific Research 12750768, 13450374).

**Supporting Information Available:** <sup>1</sup>H and <sup>13</sup>C NMR spectra of 3-phenylpropyl dimethylethylsilyl ether and the NMR spectral data of the alcohols, ethers, and amines. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO025726N