Pyridyl Group Assisted Deprotonation of a Methyl Group on Silicon: Complex Induced Proximity Effect and Novel Hydroxymethylation

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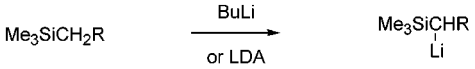
A novel methodology for the deprotonation of a methyl group on silicon has been developed. This newly developed α-lithiation protocol is based on the intramolecular pyridyl group coordination to stabilize the α-silyl carbanion together with the inherent silicon α effect. It was found that the deprotonation (*t*-BuLi/Et_2O/−78 °C) occurs with 2-pyridyltrimethylsilane but not with other related silanes such as phenyltrimethylsilane, 3-pyridyltrimethylsilane, and 4-pyridyltrimethylsilane. It seems that this deprotonation proceeded through the agency of the complex-induced proximity effect (CIPE) of a 2-pyridyl group on silicon. ^{1}H NMR analysis of (2-pyridyldimethylsilyl)methyllithium revealed the intramolecular coordination of a pyridyl group to lithium. (2-Pyridyldimethylsilyl)-methyllithium was found to react with chlorosilanes, hydrosilanes, chlorostannanes, bromine, iodine, organic bromides, aldehydes, and ketones in good to excellent yields. The resultant adducts were further oxidized with H_2O_2/KF to give the corresponding alcohols in excellent yields. Thus, this two-step transformation provides an efficient method for the nucleophilic hydroxymethylation.

Introduction

Since their introduction by Peterson in 1968,[1] the generation and the reactions of α-silyl carbanions is a subject of great interest in organic synthesis.[2] They have been widely used in Peterson-type olefination,[3] nucleophilic hydroxymethylation,[4] and their variants. α-Silyl carbanions are usually generated in four different ways: (1) Grignard reagent formation from the corresponding α-halosilane; (2) deprotonation by lithiating reagent such as butyllithium; (3) metal-heteroatom (S, Sn, Si, Se) exchange reaction; (4) addition of alkyllithium to vinylsilane. Among these α-silyl carbanion-generating methods, deprotonation by butyllithium is by far the most convenient way, since α-halosilanes, α-heteroatom substituted silanes, and vinylsilanes are not always readily available. In most cases, together with the stabilization of the carbanion by the α silyl group, additional stabilization effects by neighboring heteroatoms or electron-withdrawing groups have been exploited for their generation (eq 1).[5]

However, without such additional effects, the generation of α-silyl carbanion is known as a formidable task by means of hydrogen−metal exchange. For example, in the case of Me_4Si, the deprotonation (*n*-BuLi in TMEDA) is extremely slow and inefficient, giving the corresponding α-silyl carbanion in 36% yield after 4 days.[6] Presumably, this sluggish deprotonation stems from the lack of additional stabilization effects.[7]



(1)

R = $SiMe_3$, OMe, SMe, SPh, S(O)Ph, PPh_2, P(O)$(OEt)_2$, P(S)Ph_2, N_2, Cl, Ph, CO_2-*t*-Bu, CN, vinyl etc.

Thus, in silane deprotonation chemistry, a methyl group on silicon has been recognized as the most difficult group to deprotonate.[8] Nevertheless, there are several successes in the methyl group deprotonation including our recent work (Scheme 1).[9,10] Hosomi has reported that alkoxytrimethylsilane bearing a dimethylamino group can be easily deprotonated by *t*-BuLi to give the corresponding α-silyl carbanion.[9a] It has been mentioned that

(1) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780.
(2) For reviews, see: (a) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; John Wiley & Sons: New York, 2000. (b) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988. (c) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983. (d) Magnus, P. *Aldrichim. Acta* **1980**, *13*, 238.
(3) For a review, see: Ager, D. J. *Org. React.* **1990**, *38*, 1.
(4) Tamao, K.; Ishida, N.; Ito, Y.; Kumada, M. *Org. Synth.* **1990**, *69*, 96.
(5) (a) Chan, T. H.; Chang, E.; Vinokur, E. *Tetrahedron Lett.* **1970**, 1137. (b) Carey, F. A.; Court, A. S. *J. Org. Chem.* **1972**, *37*, 939. (c) Carey, F. A.; Hernandez, O. *J. Org. Chem.* **1973**, *38*, 2670. (d) Colvin, E. W.; Hamill, B. J. *Chem. Commun.* **1973**, 151. (e) Grobel, B.-T.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 83. (f) Ojima, I.; Kumagai, M.; Nagai, Y. *Tetrahedron Lett.* **1974**, 4005. (g) Hartzell, S. L.; Rathke, M. W. *Tetrahedron Lett.* **1976**, 2737. (h) Sachdev, K.; Sachdev, H. S. *Tetrahedron Lett.* **1976**, 4223. (i) Burford, C.; Cooke, F.; Ehlinger, E.; Magnus, P. *J. Am. Chem. Soc.* **1977**, *99*, 4536. (j) Ayalon-Chass, D.; Ehlinger, E.; Magnus, P. *Chem. Commun.* **1977**, 772. (k) Magnus, P.; Roy, G. *Chem. Commun.* **1979**, 822.
(6) Peterson, D. J. *J. Organomet. Chem.* **1967**, *9*, 373.
(7) For quantitative studies of α-silyl carbanion stabilization, see: (a) Wetzel, D.; Brauman, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 8333. (b) Brinkman, E. A.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1994**, *116*, 8304 and references therein. See also, (c) Damrauer, R.; Kass, S. R.; DePuy, C. H. *Organometallics* **1988**, *7*, 637. (d) Zhang, S.; Zhang, X. M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1995**, *117*, 602.
(8) (a) Gornowicz, G. A.; West, R. *J. Am. Chem. Soc.* **1968**, *90*, 4478. (b) Frye, C. L.; Salinger, R. M.; Fearon, F. W. G.; Klosowski, J. M.; DeYoung, T. *J. Org. Chem.* **1970**, *35*, 1308. (c) Pinkerton, F. H.; Thames, S. F. *J. Organomet. Chem.* **1971**, *29*, C4. (d) Bates, T. F.; Dandekar, S. A.; Longlet, J. J.; Wood, K. A.; Thomas, R. D. *J. Organomet. Chem.* **2000**, *595*, 87.

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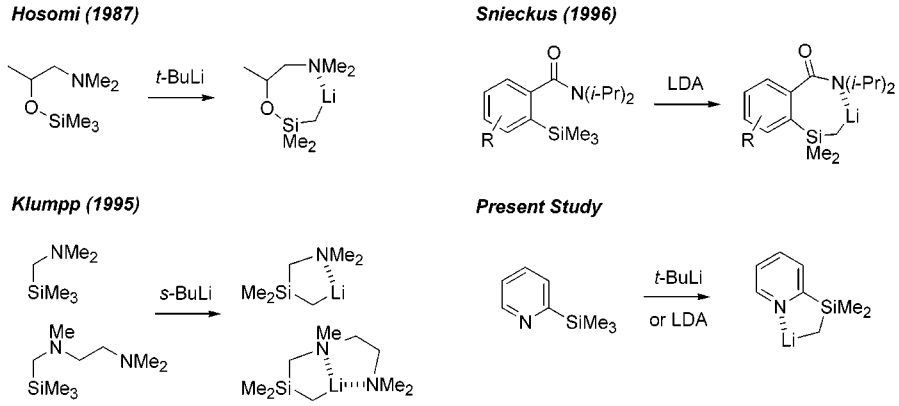
Scheme 1. Coordination-Assisted Deprotonation of Methyl Group on Silicon

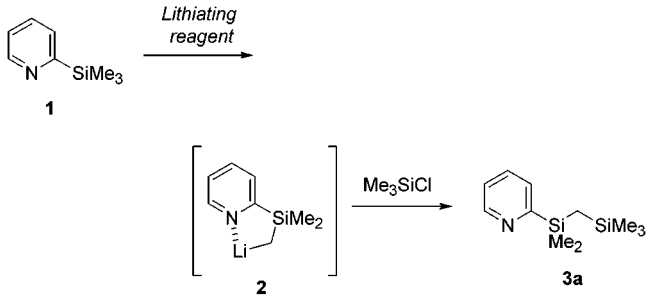


both oxygen and nitrogen atoms are necessary for the deprotonation, indicating the importance of both the inductive effect of oxygen and the coordination effect of nitrogen. Friesen[9b] and Quayle[9c] also observed similar effects in the deprotonation of a *tert*-butyldimethylsilyl group. Snieckus has reported that an aryltrimethylsilane-bearing amido group undergoes facile deprotonation by lithium diisopropylamide (LDA).[9d] Klumpp[9e] and Strohmann[9f] have also reported the methyl group deprotonation by taking advantage of the intramolecular amino group coordination. We have recently developed the extremely facile deprotonation of methyl group on silicon by virtue of intramolecular assistance of 2-pyridyl group.[10,11] Herein, we describe the full details of our studies for the efficient deprotonation of methyl group on silicon based on the intramolecular pyridyl group coordination. Related deprotonation of 2-pyridylsilanes and novel nucleophilic hydroxymethylation are also described.

Results and Discussion

Deprotonation of 2-Pyridyltrimethylsilane. We envisioned that the methyl group of 2-pyridyltrimethylsilane (**1**)[12] should be easily deprotonated based on the efficient coordination of the intramolecular pyridyl group. Thus, we examined the reagent for the deprotonation, and its efficiency was evaluated by the reaction of thus-generated (2-pyridyldimethylsilyl)methyllithium (**2**) and trimethylsilyl chloride (Table 1). The deprotonation of **1** did not occur with *n*-BuLi at −78 °C (Table 1, entry 1). Raising the temperature to 0 °C seemed to generate some anionic species but gave a complex mixture of unidentified products after the treatment with Me_3SiCl (Table 1, entry 2). Presumably, *n*-BuLi attacked the pyridine ring as a nucleophile. On the other hand, the deprotonation proceeded with *s*-BuLi at −78 °C and **3a** was isolated in 60% yield together with some unidentified products (Table 1, entry 3). The use of *t*-BuLi gave rise to the quantitative deprotonation of **1**, and **3a** was isolated in 93% yield (Table 1, entry 4). Lithium diisopropylamide (LDA) was also found to be effective for the deprotonation at 0 °C (Table 1, entry 5). When we added more LDA and Me_3SiCl in the reaction mixture, the doubly silylated product became the major product because **3a** is more acidic than starting material **1**. Premixing of LDA and Me_3SiCl prior to the addition of **1** also resulted in the production of considerable doubly silylated product.

Table 1. Conditions for the Deprotonation of 1



entry	lithiating reagent (equiv)	solvent	conditions	result (yield, %)
1	*n*-BuLi (1.1)	Et_2O	−78 °C, 30 min	no reaction
2	*n*-BuLi (1.1)	Et_2O	0 °C, 30 min	complex mixture
3	*s*-BuLi (1.1)	Et_2O	−78 °C, 30 min	**3a** (60)
4	*t*-BuLi (1.1)	Et_2O	−78 °C, 30 min	**3a** (93)
5	LDA (1.1)	Et_2O	0 °C, 2 h	**3a** (69)

Complex Induced Proximity Effect. We assume that the deprotonation of **1** proceeded through the agency of what Beak and Meyers have termed "complex induced proximity effect (CIPE)".[13] In the reaction, there must be a preequilibrium complex (**A**) of **1** and *t*-BuLi prior to the subsequent deprotonation (Scheme 2).[14] As a result, the formation of **A** renders the deprotonation event

(9) (a) Hosomi, A.; Kohra, S.; Tominaga, Y.; Shoji, M.; Sakurai, H. *Chem. Pharm. Bull.* **1987**, *35*, 1663. (b) Friesen, R. W.; Sturino, C. F.; Daljeet, A. K.; Kolaczewska, A. *J. Org. Chem.* **1991**, *56*, 1944. (c) Imanieh, H.; Quayle, P.; Voaden, M.; Conway, J.; Street, S. D. A. *Tetrahedron Lett.* **1992**, *33*, 543. (d) Brough, P. A.; Fisher, S.; Zhao, B.; Thomas, R. C.; Snieckus, V. *Tetrahedron Lett.* **1996**, *37*, 2915. (e) Luitjes, H.; de Kanter, F. J. J.; Schakel, M.; Schmitz, R. F.; Klumpp, G. W. *J. Am. Chem. Soc.* **1995**, *117*, 4179. (f) Abele, B. C.; Strohmann, C. In *Organosilicon Chemistry III*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, 1998; p 206.

(10) (a) Itami, K.; Mitsudo, K.; Yoshida, J. *Tetrahedron Lett.* **1999**, *40*, 5533. (b) Itami, K.; Mitsudo, K.; Yoshida, J. *Tetrahedron Lett.* **1999**, *40*, 5537.

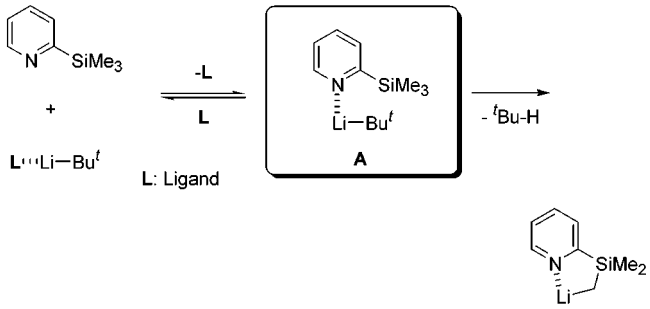
(11) For other related chemistry of 2-pyridylsilanes, see: (a) Yoshida, J.; Itami, K.; Mitsudo, K.; Suga, S. *Tetrahedron Lett.* **1999**, *40*, 3403. (b) Itami, K.; Mitsudo, K.; Yoshida, J. *J. Org. Chem.* **1999**, *64*, 8709. (c) Itami, K.; Nokami, T.; Yoshida, J. *Org. Lett.* **2000**, *2*, 1299. (d) Itami, K.; Mitsudo, K.; Kamei, T.; Koike, T.; Nokami, T.; Yoshida, J. *J. Am. Chem. Soc.* **2000**, *122*, 12013. (e) Itami, K.; Nokami, T.; Yoshida, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1074.

(12) Anderson, D. G.; Bradney, M. A. M.; Webster, D. E. *J. Chem. Soc. B* **1968**, 450.

(13) For reviews on CIPE, see: (a) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356. (b) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879. (c) Beak, P.; Basu, A.; Gallagher, D. J.; Park, Y. S.; Thayumanavan, S. *Acc. Chem. Res.* **1996**, *29*, 552.

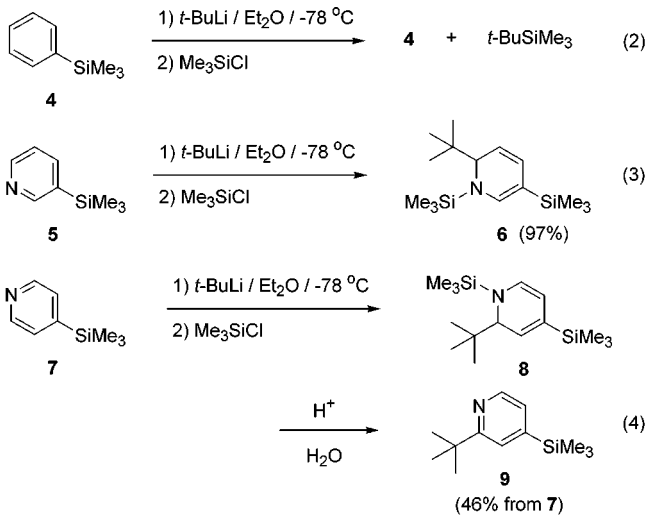
(14) Trost has reported a similar coordination effect in the deprotonation of imino thioethers. Trost, B. M.; Vaultier, M.; Santiago, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 7929.

Scheme 2. Complex Induced Proximity Effect in the Deprotonation of 1



intramolecular in nature. The importance of this preequilibrium complex formation was further supported by the observation of dramatic solvent and additive effects in this deprotonation. When the reaction of **1** and *t*-BuLi was performed in THF instead of Et_2O or in the presence of an equimolar amount of TMEDA in Et_2O, the desired deprotonation did not occur at all, giving a complex mixture after the treatment with Me_3SiCl. These results may be attributed to the inhibition of preequilibrium complex formation by the external coordinating solvent (THF) or additive (TMEDA).[15]

To substantiate that the facile deprotonation of **1** is attributed to the CIPE together with an inherent silicon α effect, we next examined the deprotonation of phenyltrimethylsilane (**4**), 3-pyridyltrimethylsilane (**5**),[12] and 4-pyridyltrimethylsilane (**7**),[12] where the CIPE cannot be expected as in the case of **1**. In the case of **4**, no reaction occurred with the addition of *t*-BuLi. Upon treatment with *t*-BuLi, neither **5** nor **7** generated the desired α-silyl carbanion, and in both cases, nucleophilic attack of *t*-BuLi to the pyridine ring occurred (eqs 3 and 4). This pronounced difference between **1** and **4**, **5**, or **7** implies the governance of CIPE in the deprotonation of **1**.



Coordination of the Pyridyl Group in 2-PyMe_2-SiCH_2Li. In addition to the kinetic preference for the deprotonation of **1** by CIPE, we presume that the stabilization of generated organolithium **2** by the intramolecular pyridyl group coordination is also responsible for the efficiency of this deprotonation process.

(15) For the BuLi/TMEDA complex, see: Chadwick, S. T.; Rennels, R. A.; Rutherford, J. L.; Collum, D. B. *J. Am. Chem. Soc.* **2000**, *122*, 8640 and references therein.

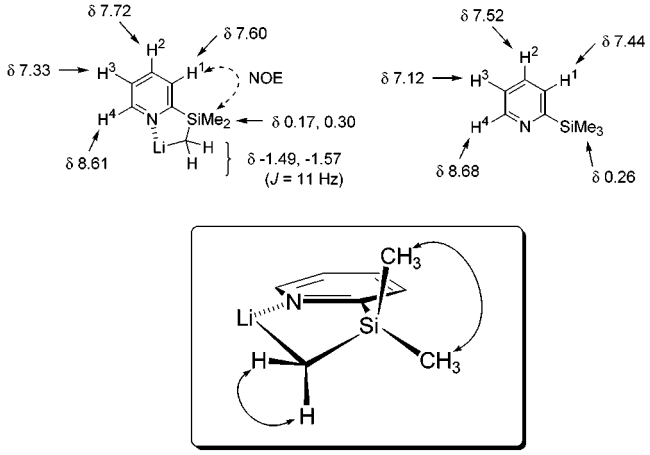


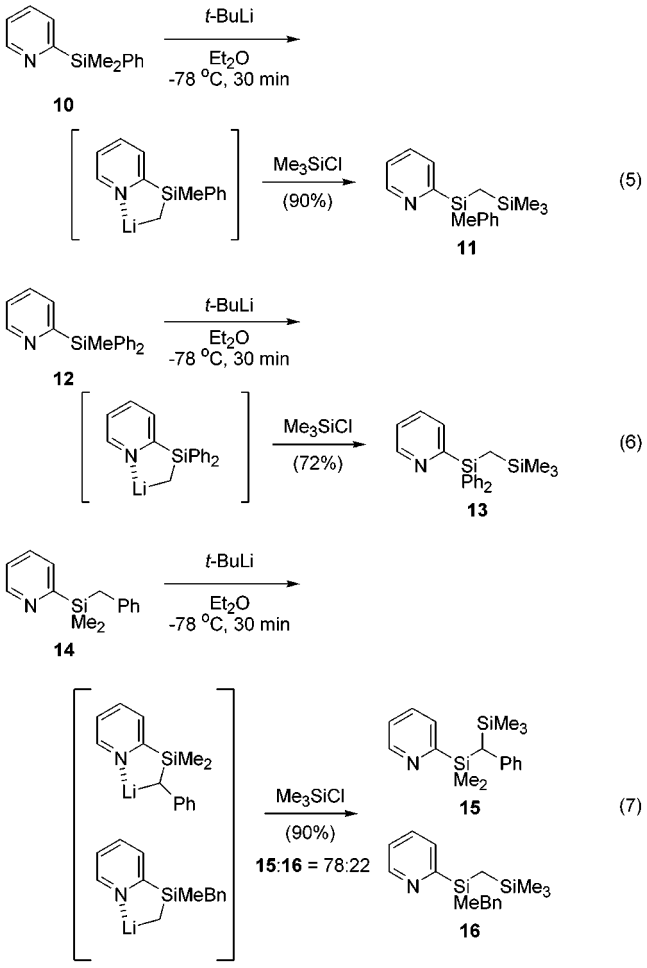
Figure 1. Comparison of ^1H NMR of **1** and **2** in Et_2O-d_{10} at −78 °C.

Although the structure of **2** has not been determined by X-ray crystallography,[16] we examined the structure of **2** in solution using ^1H NMR spectroscopy in Et_2O-d_{10} at −78 °C. For comparison, ^1H NMR spectroscopy was also taken for the parent **1** under identical conditions (Figure 1). When compared to **1**, noticeable changes in the pyridine ring chemical shift were observed for **2**. Downfield shifts were observed for H^1, H^2, and H^3, which indicate the intramolecular pyridyl group coordination to lithium. In addition,^1H NMR spectrum of **2** showed two singlets due to the two methyl groups on silicon and two sets of doublet (J = 11.0 Hz) due to the two protons on α-carbon, which coalesced at 0 °C. The observed nonequivalence of these protons is most likely attributed to the coordination induced rigid five-membered cyclic structure of **2**.

Related Pyridyl Group Assisted Deprotonation. Next, we investigated the deprotonation of other related 2-pyridylsilanes. As in the case of **1**, 2-pyridyl(phenyl)-dimethylsilane (**10**) and 2-pyridyldiphenylmethylsilane (**12**) were easily deprotonated by *t*-BuLi in Et_2O. After treatment with Me_3SiCl, **11** and **13** were isolated in 90% and 72% yields, respectively (eqs 5 and 6). When 2-pyridyl(benzyl)dimethylsilane (**14**) was subjected to the standard conditions, deprotonation occurred at two different positions. The deprotonation at the benzylic proton led to **15** and the deprotonation at the methyl proton led to **16** after quenching with Me_3SiCl (eq 7). It may be reasonable to assume that the mainly generated (silyl)-benzyllithium is thermodynamically more stable than the (silyl)methyllithium.

Reactions of 2 with Various Electrophiles. Having established the facile deprotonation of **1**, we subsequently embarked on the reaction of thus-generated **2** with various electrophiles, and the results are listed in Table 2. Not only chlorosilanes (Table 2, entries 1 and 2) but also hydrosilane were effective in this reaction (Table 2, entry 3). Chlorostannanes also work as excellent electrophiles (Table 2, entries 4 and 5). The reaction with bromine and iodine gave the synthetically useful silylmethyl halides (Table 2, entries 6 and 7). Allyl, benzyl,

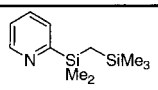
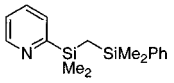
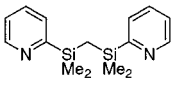
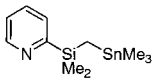
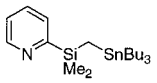
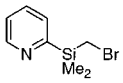
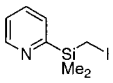
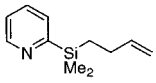
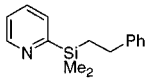
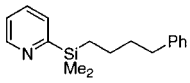
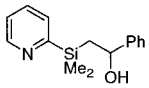
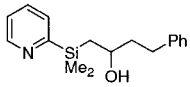
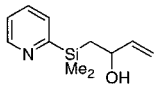
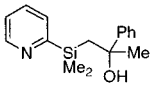
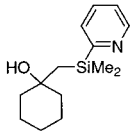
(16) Very recently, Eaborn and Smith have established the pyridyl group coordination to lithium in the very similar 2-$PyMe_2SiC(SiMe_3)_2$-Li·THF complex by X-ray crystal structure analysis. Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; Hill, M. S.; Smith, J. D. *Organometallics* **2000**, *19*, 3224.



and alkyl bromides were also found to be excellent electrophiles (Table 2, entries 8−10). Unfortunately, secondary and tertiary alkyl halides were not applicable in this reaction, partially due to the high basicity of **2**. Aromatic and aliphatic aldehydes were also found to be applicable (Table 2, entries 11−13). Ketones also gave their adducts, albeit with lower yields (Table 2, entries 14 and 15).

Nucleophilic Hydroxymethylation. Recently,[10,11] we have found that the 2-pyridyldimethylsilyl (2-PyMe$_2$-Si) group is a versatile silyl group that is convertible to the hydroxyl group with much milder conditions compared to the well-known PhMe$_2$Si group.[17,18] We envisioned that, when connected with our previous findings of the oxidative cleavage of 2-PyMe$_2$Si group, **2** can be regarded as a novel nucleophilic hydroxymethylating agent (Scheme 3).[4,19] This procedure may be complementary to the conventional electrophilic hydroxymethylation using formaldehyde.

Table 2. Reactions of 2 with Various Electrophiles

entry	electrophile	product		yield (%)
1	Me_3SiCl		**3a**	93
2	$PhMe_2SiCl$		**3b**	99
3	2-$PyMe_2SiH$		**3c**	63
4	Me_3SnCl		**3d**	83
5	Bu_3SnCl		**3e**	76
6	Br_2		**3f**	65
7	I_2		**3g**	84
8	CH_2=$CHCH_2Br$		**3h**	95
9	$PhCH_2Br$		**3i**	99
10	$Ph(CH_2)_3Br$		**3j**	84
11	PhCHO		**3k**	85
12	$PhCH_2CH_2CHO$		**3l**	63
13	CH_2=CHCHO		**3m**	62
14	PhC(O)Me		**3n**	55
15	Cyclohexanone		**3o**	64

Thus, we examined the oxidative cleavage of carbon−silicon bonds of (2-pyridyldimethylsilyl)methylated products in Table 2. Listed in Table 3 are the representative results for the H_2O_2 oxidation. The oxidations were performed by modified Tamao procedure[11b] using 30%

(17) For a review on PhMe$_2$Si group oxidation, see: Fleming, I.; Henning, R.; Parker, D. C.; Plaut. H. E.; Sanderson, P. E. J. *J. Chem. Soc., Perkin Trans. 1* **1995**, 317.

(18) For excellent reviews on oxidative cleavage of carbon−silicon bonds, see: (a) Tamao, K. In *Advances in Silicon Chemistry*, Larson, G. L., Ed.; JAI Press Inc., 1996; Vol. 3, p 1. (b) Fleming, I. *ChemTracts: Org. Chem.* **1996**, 1. (c) Jones, G. R.; Landais, Y. *Tetrahedron* **1996**, *52*, 7599.

(19) (a) Rathke, M. W.; Kow, R. *J. Am. Chem. Soc.* **1972**, *94*, 6854. (b) Beak, P.; McKinnie, B. G. *J. Am. Chem. Soc.* **1977**, *99*, 5213. (c) Stille, W. C.; Mitra, A. *J. Am. Chem. Soc.* **1978**, *100*, 1929. (d) Wissner, A. *Tetrahedron Lett.* **1978**, 2749. (e) Meyer, N.; Seebach, D. *Chem. Ber.* **1980**, *113*, 1290. (f) Pelter, A. *Chem. Soc. Rev.* **1982**, *11*, 191. (g) Kosugi, M.; Sumiya, T.; Ohhashi, K.; Sano, H.; Migita, T. *Chem. Lett.* **1985**, 997.

Scheme 3. (2-Pyridyldimethylsilyl)methyllithium (2) as a Novel Hydroxymethylating Reagent

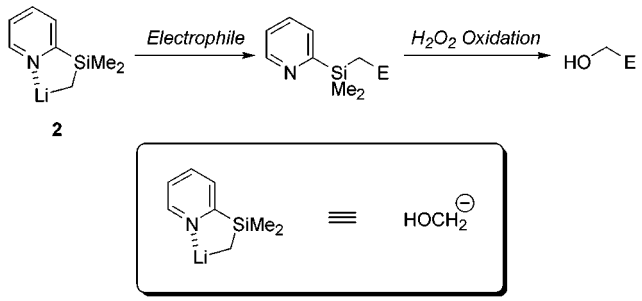
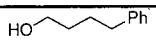
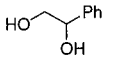
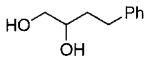
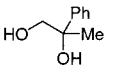
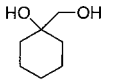


Table 3. H_2O_2 Oxidation of (2-Pyridyldimethylsilyl)methylated Products

entry	substrate	product	yield (%)
1	**3j**		98
2	**3k**		96
3	**3l**		90
4	**3n**		93
5	**3o**		95

H_2O_2 (30 equiv), KF (2.0 equiv), and $KHCO_3$ (2.0 equiv) in MeOH/THF (1/1) at 50 °C. In all cases, the oxidation proceeded well to give the corresponding alcohols, which are regarded as overall hydroxymethylated products of the electrophiles.[20] Noteworthy was that these oxidative conditions were also applicable to β-hydroxysilanes, which are prone to undergo Peterson-type elimination to form alkenes.[3]

Conclusion

In conclusion, we have developed a novel methodology for the deprotonation of a methyl group on silicon. This protocol is based on the intramolecular pyridyl group coordination to stabilize the α-silyl carbanion together with the inherent silicon α effect. It is suggested that this deprotonation proceeded through the agency of complex induced proximity effect (CIPE) of 2-pyridyl group on silicon. (2-Pyridyldimethylsilyl)methyllithium (**2**) was found to react with various electrophiles, and the resultant adducts were further oxidized with H_2O_2/KF to give the corresponding alcohols in good to excellent overall yields. This two-step transformation provides an efficient method for the nucleophilic hydroxymethylation.

Experimental Section

General Methods. Unless otherwise noted, all reactions were carried out under argon atmosphere. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were freshly distilled under argon from sodium benzophenone ketyl prior to use. 2-Pyridyltrimethylsilane (**1**),[12] 3-pyridyltrimethylsilane (**5**),[12] and 4-pyridyltrimethylsilane (**7**)[12] were prepared according to the literature procedures. NMR spectra were recorded on a Varian GEMINI-2000 (^{1}H 300 MHz, ^{13}C 75 MHz) spectrometer in $CDCl_3$ with internal standards (7.26 ppm ^{1}H, 77.0 ppm ^{13}C). EI mass spectra were recorded on a JMS-SX102A spectrometer. FAB mass spectra were recorded on a JMS-HX110A spectrometer. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer.

(2-Pyridyldimethylsilyl)methyllithium (2). To a solution of 2-pyridyltrimethylsilane (**1**) (151 mg, 1.0 mmol) in dry Et_2O (2 mL) was added dropwise a solution of *t*-BuLi (1.16 mmol, 1.64 M solution in pentane) at −78 °C under argon. The mixture was stirred for additional 30 min to afford an orange ether solution of (2-pyridyldimethylsilyl)methyllithium (**2**).

[(2-Pyridyldimethylsilyl)methyl]trimethylsilane (3a). To a solution of **2** (1.0 mmol) in Et_2O (2 mL) was added chlorotrimethylsilane (130 mg, 1.2 mmol) at −78 °C. After the reaction mixture was stirred at 0 °C for 3 h, 1 N aqueous HCl (5 mL) was added to the mixture, and the aqueous phase was separated. The organic phase was extracted with 1 N aqueous HCl (4 × 5 mL). The combined aqueous phase was neutralized by the addition of $NaHCO_3$ and was extracted with Et_2O (3 × 10 mL). Drying over $MgSO_4$ and removal of solvent under reduced pressure afforded **3a** (208 mg, 93%, >95% pure as judged by ^{1}H NMR and capillary GC analysis) as a colorless oil: ^{1}H NMR δ −0.05 (s, 9 H), 0.07 (s, 2 H), 0.33 (s, 6 H), 7.14 (ddd, J = 7.5, 5.1, 1.5 Hz, 1 H), 7.48 (ddd, J = 7.5, 1.5, 1.2 Hz, 1 H), 7.54 (td, J = 7.5, 1.8 Hz, 1 H), 8.75 (ddd, J = 5.1, 1.8, 1.2 Hz, 1 H); ^{13}C NMR δ −1.0, 1.0, 2.1, 122.5, 128.6, 133.9, 150.1, 169.2. IR (neat) 1576, 1559, 1451, 1418, 1248, 1138, 1053 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{11}H_{21}NSi_2$ 223.1213, found 223.1211. Anal. Calcd for $C_{11}H_{21}NSi_2$: C, 59.12; H, 9.47; N, 6.27. Found: C, 59.35; H, 9.53; N, 6.22.

2-*tert*-Butyl-1,5-bis(trimethylsilyl)-1,2-dihydropyridine (6): ^{1}H NMR δ 0.02 (s, 9 H), 0.19 (s, 9 H), 0.79 (s, 9 H), 3.44 (dd, J = 6.0, 0.9 Hz, 1 H), 5.13 (ddd, J = 9.0, 6.0, 1.2 Hz, 1 H), 6.05 (dd, J = 9.0, 0.9 Hz, 1 H), 6.31 (d, J = 1.2 Hz, 1 H); ^{13}C NMR δ −1.5, −0.1, 25.3, 39.8, 60.1, 109.7, 112.6, 126.2, 141.6; IR (neat) 1619, 1541, 1252 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{14}H_{28}NSi_2$ (M − CH_3)$^+$ 266.1760, found 266.1755. Anal. Calcd for $C_{15}H_{31}NSi_2$: C, 63.98; H, 11.10; N, 4.97. Found: C, 63.79; H, 11.32; N, 4.75.

2-*tert*-Butyl-1,4-bis(trimethylsilyl)-1,2-dihydropyridine (8): ^{1}H NMR δ 0.07 (s, 9 H), 0.16 (s, 9 H), 0.81 (s, 9 H), 3.38 (dd, J = 6.0, 0.9 Hz, 1 H), 5.09 (dd, J = 6.9, 0.9 Hz, 1 H), 5.28 (dt, J = 6.0, 0.9 Hz, 1 H), 6.14 (dt, J = 6.9, 0.9 Hz, 1 H); ^{13}C NMR δ −1.8, −0.2, 25.5, 39.8, 60.1, 106.1, 120.4, 133.6, 134.4.

2-*tert*-Butyl-4-trimethylsilylpyridine (9): ^{1}H NMR δ 0.28 (s, 9 H), 1.38 (s, 9 H), 7.18 (dd, J = 4.8, 0.9 Hz, 1 H), 7.43 (t, J = 0.9 Hz, 1 H), 8.52 (dd, J = 4.8, 0.9 Hz, 1 H); ^{13}C NMR δ −1.7, 30.3, 37.3, 123.1, 125.0, 147.4, 150.1, 167.8. IR (neat) 1584, 1252, 1156 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{12}H_{21}NSi$ 207.1443, found 207.1446.

2-Pyridyl(phenyl)dimethylsilane (10): ^{1}H NMR δ 0.63 (s, 6 H), 7.19 (ddd, J = 7.5, 4.8, 1.5 Hz, 1 H), 7.35−7.40 (m, 3 H), 7.44 (dm, J = 7.5 Hz, 1 H), 7.55 (td, J = 7.5, 1.5 Hz, 1 H), 7.59−7.64 (m, 2 H), 8.81 (dm, J = 4.8 Hz, 1 H); ^{13}C NMR δ −3.3, 122.8, 127.9, 129.3, 129.7, 134.0, 134.3, 137.3, 150.3, 166.7. IR (neat) 1574, 1559, 1453, 1428, 1246, 1109 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{13}H_{15}NSi$ 213.0974, found 213.0975. Anal. Calcd for $C_{13}H_{15}NSi$: C, 73.18; H, 7.09; N, 6.57. Found: C, 73.44; H, 7.18; N, 6.63.

[[2-Pyridyl(phenyl)methylsilyl]methyl]trimethylsilane (11): ^{1}H NMR δ −0.10 (s, 9 H), 0.37 (d, J = 14.1 Hz, 1 H), 0.48 (d, J = 14.1 Hz, 1 H), 0.67 (s, 3 H), 7.18 (ddd, J = 7.5, 4.8, 1.5 Hz, 1 H), 7.32−7.37 (m, 3 H), 7.44 (dt, J = 7.8, 1.5 Hz, 1 H), 7.53 (td, J = 7.5, 1.5 Hz, 1 H), 7.59 (dd, J = 7.2, 2.1 Hz, 2 H), 8.79 (ddd, J = 4.8, 1.8, 1.2 Hz, 1 H); ^{13}C NMR δ −2.8, 0.6, 1.1, 122.6, 127.7, 129.0, 129.5, 133.8, 134.2, 138.0, 150.0, 167.3; IR (neat) 1574, 1427, 1250, 1049 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{16}H_{23}NSi_2$ 285.1369, found 285.1370.

(20) In the oxidation, an equimolar amount of pyridine, which is derived from the pyridyl group on silicon, is formed. See ref 11b.

2-Pyridyldiphenylmethylsilane (12): ^{1}H NMR δ 0.91 (s, 3 H), 7.24 (ddd, J = 7.5, 4.8, 1.5 Hz, 1 H), 7.33−7.41 (m, 6 H), 7.45 (dt, J = 7.2, 1.2 Hz, 1 H), 7.54−7.60 (m, 5 H), 8.86 (ddd, J = 4.8, 1.8, 1.2 Hz, 1 H); ^{13}C NMR δ −4.1, 122.9, 127.8, 129.4, 130.9, 134.0, 135.2, 135.3, 150.4, 164.7; IR (neat) 1427, 1113, 793, 731 cm^{-1}; HRMS (EI) m/z calcd for $C_{18}H_{17}NSi$ 275.1130, found 275.1129.

[(2-Pyridyldiphenylsilyl)methyl]trimethylsilane (13): ^{1}H NMR δ −0.17 (s, 9 H), 0.71 (s, 2 H), 7.20 (ddd, J = 7.5, 4.8, 1.5 Hz, 1 H), 7.32−7.40 (m, 6 H), 7.46 (dt, J = 7.5, 1.5 Hz, 1 H), 7.53 (td, J = 7.5, 1.5 Hz, 1 H), 7.62−7.66 (m, 4 H), 8.84 (ddd, J = 4.8, 1.8, 1.5 Hz, 1 H); ^{13}C NMR δ −0.6, 1.2, 122.8, 127.7, 129.3, 130.9, 133.9, 135.6, 136.0, 150.1, 165.6; IR (neat) 1428, 1248, 1109, 835, 700 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{25}NSi_2$ 347.1526, found 347.1534.

2-Pyridyl(benzyl)dimethylsilane (14): ^{1}H NMR δ 0.31 (s, 6 H), 2.42 (s, 2 H), 6.97 (dm, J = 7.5 Hz, 2 H), 7.02−7.09 (m, 1 H), 7.12−7.24 (m, 3 H), 7.40 (dm, J = 7.5 Hz, 1 H), 7.55 (td, J = 7.5, 1.5 Hz, 1 H), 8.82 (dm, J = 5.1 Hz, 1 H); ^{13}C NMR δ −4.2, 24.8, 122.9, 124.1, 128.2, 128.3, 129.4, 134.0, 139.6, 150.2, 166.8; IR (neat) 1599, 1574, 1493, 1451, 1418, 1248, 1208 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{17}NSi$ 227.1130, found 227.1129. Anal. Calcd for $C_{14}H_{17}NSi$: C, 73.95; H, 7.54; N, 6.16. Found: C, 74.05; H, 7.61; N, 6.10.

[(2-Pyridyldimethylsilyl)benzyl]trimethylsilane (15): ^{1}H NMR δ −0.13 (s, 9 H), 0.25 (s, 3 H), 0.47 (s, 3 H), 2.01 (s, 1 H), 6.94−7.03 (m, 3 H), 7.12−7.19 (m, 3 H), 7.38 (dt, J = 7.5, 1.5 Hz, 1 H), 7.52 (td, J = 7.5, 1.5 Hz, 1 H), 8.78 (ddd, J = 4.5, 1.5, 1.2 Hz, 1 H); ^{13}C NMR δ −2.14, −2.07, −0.2, 27.5, 122.7, 123.4, 128.0, 129.0, 129.4, 133.8, 142.2, 149.9, 167.5; IR (neat) 1248, 1199, 1034 cm^{-1}; HRMS (EI) m/z calcd for $C_{17}H_{25}NSi_2$ 299.1526, found 299.1525.

[[2-Pyridyl(benzyl)methylsilyl]methyl]trimethylsilane (16): ^{1}H NMR δ −0.10 (s, 9 H), 0.01 (d, J = 13.8 Hz, 1 H), 0.18 (d, J = 13.8 Hz, 1 H), 0.34 (s, 3 H), 2.36 (d, J = 13.5 Hz, 1 H), 2.43 (d, J = 13.5 Hz, 1 H), 6.87 (d, J = 6.9 Hz, 2 H), 7.01−7.05 (m, 1 H), 7.10−7.16 (m, 2 H), 7.20 (ddd, J = 7.5, 4.8, 1.5 Hz, 1 H), 7.33 (dt, J = 7.8, 1.2 Hz, 1 H), 7.53 (td, J = 7.5, 1.8 Hz, 1 H), 8.80 (ddd, J = 4.8, 1.8, 1.2 Hz, 1 H); ^{13}C NMR δ −3.8, 0.0, 1.2, 26.3, 122.8, 123.9, 128.0, 128.3, 129.5, 133.8, 139.6, 150.0, 166.9. IR (neat) 1493, 1250, 1049, 837 cm^{-1}; HRMS (EI) m/z calcd for $C_{17}H_{25}NSi_2$ 299.1526, found 299.1520.

Reactions of 2 with Various Electrophiles. In all cases, **2** was generated in situ by the procedure described above, and the electrophiles were added to the solution of **2**. Unless otherwise noted, reactions were performed at −78 °C to room temperature for several hours. Purification of the products was done by acid−base extraction or by typical silica gel chromatography.

[(2-Pyridyldimethylsilyl)methyl]dimethylphenylsilane (3b): ^{1}H NMR δ 0.23 (s, 6 H), 0.27 (s, 6 H), 0.35 (s, 2 H), 7.16 (ddd, J = 7.5, 4.8, 1.5 Hz, 1 H), 7.29−7.33 (m, 3 H), 7.42−7.49 (m, 3 H), 7.54 (td, J = 7.5, 1.8 Hz, 1 H), 8.76 (ddd, J = 4.8, 1.8, 1.2 Hz, 1 H); ^{13}C NMR δ −1.1, −0.5, 1.1, 122.6, 127.7, 128.68, 128.71, 133.4, 134.0, 140.9, 150.1, 168.9; IR (neat) 3067, 2955, 1576, 1559, 1428, 1248, 1113 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{23}NSi_2$ 285.1369, found 285.1358.

Bis(2-pyridyldimethylsilyl)methane (3c): ^{1}H NMR δ 0.22 (s, 12 H), 0.38 (s, 2 H), 7.08 (ddd, J = 7.5, 4.8, 1.5 Hz, 2 H), 7.38 (ddd, J = 7.5, 1.5, 1.2 Hz, 2 H), 7.46 (td, J = 7.5, 1.8 Hz, 2 H), 8.68 (ddd, J = 4.8, 1.8, 1.2 Hz, 2 H); ^{13}C NMR δ −1.2, 0.1, 122.5, 128.6, 133.8, 150.0, 168.7; IR (neat) 2955, 1576, 1559, 1451, 1418, 1248, 1051 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{19}N_2Si_2$ $(M - CH_3)^+$ 271.1087, found 271.1079. Anal. Calcd for $C_{15}H_{22}N_2Si_2$: C, 62.88; H, 7.74; N, 9.78. Found: C, 62.61; H, 7.78; N, 9.79.

[(2-Pyridyldimethylsilyl)methyl]trimethylstannane (3d): ^{1}H NMR δ 0.01 (s, J_{Sn-H} = 54.0 Hz, 9 H), 0.06 (s, 2 H), 0.31 (s, 6 H), 7.16 (ddd, J = 7.5, 5.1, 1.8 Hz, 1 H), 7.49 (ddd, J = 7.5, 1.8, 1.5 Hz, 1 H), 7.56 (td, J = 7.5, 1.8 Hz, 1 H), 8.75 (ddd, J = 5.1, 1.8, 1.5 Hz, 1 H); ^{13}C NMR δ −8.0, −6.4, −0.6, 122.5, 128.4, 133.8, 149.9, 169.3; IR (neat) 1576, 1246 cm^{-1}; HRMS (FAB) m/z calcd for $C_{11}H_{22}NSiSn$ $(M + H)^+$ 316.0537, found 316.0547.

[(2-Pyridyldimethylsilyl)methyl]tributylstannane (3e): ^{1}H NMR δ −0.01 (s, J_{Sn-H} = 65.1 Hz, 2 H), 0.31 (s, 6 H), 0.70−0.78 (m, 6 H), 0.85 (t, J = 7.2 Hz, 9 H), 1.18−1.50 (m, 12 H), 7.15 (ddd, J = 7.5, 5.1, 1.8 Hz, 1 H), 7.49 (dm, J = 7.5 Hz, 1 H), 7.55 (td, J = 7.5, 1.5 Hz, 1 H), 8.75 (dm, J = 5.1 Hz, 1 H); ^{13}C NMR δ −9.5, −0.5, 10.2, 13.5, 27.3, 29.0, 122.5, 128.6, 133.9, 150.1, 169.9; IR (neat) 1576, 1559, 1464, 1456, 1418, 1375, 1246, 1138 cm^{-1}; HRMS (FAB) m/z calcd for $C_{20}H_{40}NSiSn$ $(M + H)^+$ 440.1952, found 440.1955. Anal. Calcd for $C_{20}H_{39}NSiSn$: C, 54.55; H, 8.93; N, 3.18. Found: C, 54.39; H, 9.20; N, 3.25.

(2-Pyridyldimethylsilyl)methyl bromide (3f): ^{1}H NMR δ 0.48 (s, 6 H), 2.75 (s, 2 H), 7.24 (ddd, J = 7.5, 4.8, 1.5 Hz, 1 H), 7.55 (dt, J = 7.5, 1.5 Hz, 1 H), 7.62 (td, J = 7.5, 1.5 Hz, 1 H), 8.77 (ddd, J = 4.8, 1.5, 1.2 Hz, 1 H); ^{13}C NMR δ −4.3, 16.1, 123.3, 129.4, 134.1, 150.2, 164.5; IR (neat) 1576, 1250, 839 cm^{-1}; HRMS (EI) m/z calcd for $C_8H_{12}NSiBr$ 228.9922, found 228.9920.

(2-Pyridyldimethylsilyl)methyl iodide (3g): ^{1}H NMR δ 0.48 (s, 6 H), 2.28 (s, 2 H), 7.23 (ddd, J = 7.5, 4.8, 1.5 Hz, 1 H), 7.54 (dt, J = 7.8, 1.5 Hz, 1 H), 7.61 (td, J = 7.5, 1.5 Hz, 1 H), 8.77 (ddd, J = 4.8, 1.5, 1.2 Hz, 1 H); ^{13}C NMR δ −14.6, −3.4, 123.3, 129.4, 134.1, 150.2, 164.9; IR (neat) 1574, 1419, 1248, 839 cm^{-1}; HRMS (EI) m/z calcd for $C_8H_{12}NSiI$ 276.9784, found 276.9789.

2-Pyridyldimethyl(3-butenyl)silane (3h): ^{1}H NMR δ 0.29 (s, 6 H), 0.86−0.94 (m, 2 H), 2.00−2.12 (m, 2 H), 4.83 (ddd, J = 10.2, 4.8, 1.5 Hz, 1 H), 4.94 (ddd, J = 17.1, 3.6, 1.5 Hz, 1 H), 5.82 (ddd, J = 17.1, 10.2, 6.3 Hz, 1 H), 7.13 (ddd, J = 7.5, 4.8, 1.5 Hz, 1 H), 7.45 (ddd, J = 7.5, 1.5, 1.2 Hz, 1 H), 7.53 (td, J = 7.5, 1.8 Hz, 1 H), 8.74 (ddd, J = 4.8, 1.8, 1.2 Hz, 1 H); ^{13}C NMR δ −3.8, 13.7, 27.7, 112.9, 122.7, 129.0, 133.9, 141.3, 150.2, 167.6; IR (neat) 1640, 1576, 1418, 1248 cm^{-1}; HRMS (EI) m/z calcd for $C_{11}H_{17}NSi$ 191.1130, found 191.1135.

2-Pyridyldimethyl(phenethyl)silane (3i): ^{1}H NMR δ 0.36 (s, 6 H), 1.20−1.27 (m, 2 H), 2.66−2.74 (m, 2 H), 7.10−7.35 (m, 6 H), 7.50 (ddd, J = 7.5, 1.5, 1.2 Hz, 1 H), 7.58 (td, J = 7.5, 1.5 Hz, 1 H), 8.81 (ddd, J = 4.8, 1.5, 1.2 Hz, 1 H); ^{13}C NMR δ −3.9, 16.7, 29.7, 122.7, 125.5, 127.8, 128.3, 129.1, 133.9, 144.9, 150.2, 167.4; IR (neat) 1574, 1495, 1453, 1418, 1246 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{19}NSi$ 241.1287, found 241.1281.

2-Pyridyldimethyl(4-phenylbutyl)silane (3j): ^{1}H NMR δ 0.33 (s, 6 H), 0.86−0.94 (m, 2 H), 1.36−1.49 (m, 2 H), 1.60−1.72 (m, 2 H), 2.60 (t, J = 7.8 Hz, 2 H), 7.13−7.22 (m, 4 H), 7.23−7.30 (m, 2 H), 7.49 (ddd, J = 7.5, 1.5, 1.2 Hz, 1 H), 7.57 (td, J = 7.5, 1.8 Hz, 1 H), 8.80 (ddd, J = 4.5, 1.8, 1.2 Hz, 1 H); ^{13}C NMR δ −3.8, 14.5, 23.3, 35.1, 35.4, 122.7, 125.5, 128.2, 128.4, 129.1, 133.9, 142.8, 150.2, 167.9; IR (neat) 1576, 1454, 1246 cm^{-1}; HRMS (EI) m/z calcd for $C_{17}H_{23}NSi$ 269.1600, found 269.1609.

2-Pyridyldimethyl(2-hydroxy-2-phenyl)ethylsilane (3k): ^{1}H NMR δ 0.27 (s, 3 H), 0.38 (s, 3 H), 1.39 (dd, J = 14.7, 3.3 Hz, 1 H), 1.57 (dd, J = 14.7, 10.2 Hz, 1 H), 5.05 (dd, J = 10.2, 3.3 Hz, 1 H), 7.16−7.26 (m, 2 H), 7.31 (t, J = 7.8 Hz, 2 H), 7.44 (d, J = 7.8 Hz, 2 H), 7.54 (dm, J = 7.8 Hz, 1 H), 7.63 (tm, J = 7.8 Hz, 1 H), 8.70 (dm, J = 5.1 Hz, 1 H); ^{13}C NMR δ −3.0, −2.7, 28.1, 70.0, 123.1, 125.2, 126.4, 128.0, 129.3, 135.0, 148.0, 148.9, 166.5; IR (neat) 1580, 1455, 1420, 1250 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{19}NOSi$ 257.1236, found 257.1226.

2-Pyridyldimethyl(2-hydroxy-4-phenyl)butylsilane (3l): ^{1}H NMR δ 0.32 (s, 3 H), 0.38 (s, 3 H), 1.12 (ddd, J = 15.0, 3.0, 0.9 Hz, 1 H), 1.24 (dd, J = 15.0, 10.2 Hz, 1 H), 1.72−2.00 (m, 2 H), 2.73 (ddd, J = 13.5, 10.5, 6.0 Hz, 1 H), 2.89 (ddd, J = 13.5, 10.5, 5.7 Hz, 1 H), 3.93−4.04 (m, 1 H), 7.13−7.32 (m, 6 H), 7.55 (ddd, J = 7.5, 2.4, 0.9 Hz, 1 H), 7.64 (tdd, J = 7.5, 1.5, 0.9 Hz, 1 H), 8.09 (dm, J = 4.8 Hz, 1 H); ^{13}C NMR δ −2.9, −2.2, 25.2, 32.5, 43.0, 67.1, 123.2, 125.5, 128.2, 128.5, 129.4, 135.0, 142.9, 149.0, 166.8; IR (neat) 1580, 1455, 1250 cm^{-1}; HRMS (EI) m/z calcd for $C_{17}H_{23}NOSi$ 285.1549, found 285.1551.

2-Pyridyldimethyl(2-hydroxy-3-butenyl)silane (3m): ^{1}H NMR δ 0.32 (s, 3 H), 0.34 (s, 3 H), 1.15 (dd, J = 14.7, 3.6 Hz, 1 H), 1.26 (dd, J = 14.7, 9.9 Hz, 1 H), 4.35−4.44 (m, 1 H), 4.96 (ddd, J = 10.5, 2.1, 1.5 Hz, 1 H), 5.19 (ddd, J = 17.4, 1.8, 1.5 Hz, 1 H), 5.95 (ddd, J = 17.4, 10.5, 6.0 Hz, 1 H), 7.21 (ddd,

J = 7.5, 4.8, 1.5 Hz, 1 H), 7.52 (ddd, J = 7.5, 1.8, 1.5 Hz, 1 H), 7.62 (td, J = 7.5, 1.5 Hz, 1 H), 8.64 (ddd, J = 4.8, 1.8, 1.5 Hz, 1 H); ^{13}C NMR δ −2.7, −2.0, 25.4, 68.9, 112.0, 123.1, 129.3, 135.0, 144.2, 148.9, 166.4; IR (neat) 1580, 1420, 1250 cm^{-1}; HRMS (EI) m/z calcd for $C_{10}H_{14}NOSi$ $(M - CH_3)^+$ 192.0845, found 192.0847.

2-Pyridyldimethyl(2-hydroxy-2-phenyl)propylsilane (3n): ^{1}H NMR δ −0.26 (s, 3 H), 0.28 (s, 3 H), 1.64 (s, 3 H), 1.76 (s, 2 H), 7.10−7.23 (m, 2 H), 7.26 (tm, J = 7.2 Hz, 2 H), 7.43 (dm, J = 7.8 Hz, 1 H), 7.53 (dm, J = 7.2 Hz, 2 H), 7.59 (tdm, J = 7.8, 1.5 Hz, 1 H), 7.89 (brs, 1 H), 8.70 (dm, J = 5.1 Hz, 1 H); ^{13}C NMR δ −2.2, −1.2, 33.8, 35.0, 72.6, 123.1, 124.7, 125.8, 127.8, 129.4, 135.0, 148.6, 151.1, 167.1; IR (neat) 1580, 1445, 1250 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{18}NOSi$ $(M - CH_3)^+$ 256.1158, found 256.1164.

1-[(2-Pyridyldimethylsilyl)methyl]cyclohexanol (3o): ^{1}H NMR δ 0.30 (s, 6 H), 1.18−1.50 (m, 6 H), 1.30 (s, 2 H), 1.55−1.72 (m, 4 H), 6.53 (brs, 1 H), 7.18 (ddd, J = 7.2, 5.1, 1.5 Hz, 1 H), 7.51 (ddd, J = 7.8, 1.5, 1.2 Hz, 1 H), 7.60 (ddd, J = 7.8, 7.2, 1.8 Hz, 1 H), 8.64 (ddd, J = 5.1, 1.8, 1.2 Hz, 1 H); ^{13}C NMR δ −0.7, 22.8, 25.6, 31.2, 41.4, 70.3, 123.0, 129.5, 134.9, 148.9, 167.6; IR (neat) 1578, 1453, 1420, 1248 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{23}NOSi$ 249.1549, found 249.1551.

Typical Procedure for H_2O_2 Oxidation (Table 3, Entry 1). To a mixture of KF (24 mg, 0.41 mmol) and $KHCO_3$ (41 mg, 0.41 mmol) in MeOH (1 mL) and THF (1 mL) was added **3j** (55 mg, 0.20 mmol) and then aqueous 30% H_2O_2 (0.70 g, 6.12 mmol). The mixture was stirred at 50 °C for 6 h. After being cooled at room temperature, the reaction mixture was treated with water (10 mL). The mixture was extracted with Et_2O (4 × 10 mL), and the combined organic phase was washed successively with 15% aqueous $Na_2S_2O_3$ (10 mL). Drying over $MgSO_4$ and subsequent silica gel chromatography (hexane/EtOAc = 1/1 to 1/2) afforded 4-phenylbutanol[21] (30 mg, 96%) as a colorless solid: ^{1}H NMR δ 1.50−1.75 (m, 4 H), 2.25 (brs, 1 H), 2.64 (t, J = 7.2 Hz, 2 H), 3.60 (t, J = 6.3 Hz, 2 H), 7.00−7.30 (m, 5 H); ^{13}C NMR δ 27.3, 32.2, 35.7, 62.5, 125.7, 128.5, 128.6, 142.3.

1-Phenyl-1,2-ethanediol (Table 3, entry 2):[22] ^{1}H NMR δ 3.55 (dd, J = 13.8, 8.4 Hz, 1 H), 3.63 (dd, J = 13.8, 2.7 Hz, 1 H), 3.95 (brs, 1 H), 4.27 (brs, 1 H), 4.70 (dd, J = 8.4, 2.7 Hz, 1 H), 7.20−7.30 (m, 5 H); ^{13}C NMR δ 67.6, 74.6, 126.1, 127.8, 128.4, 140.5.

4-Phenyl-1,2-butanediol (Table 3, entry 3):[22] ^{1}H NMR δ 1.65−1.85 (m, 2 H), 2.60−2.90 (m, 2 H), 3.40−3.55 (m, 3 H), 3.60−3.80 (m, 2 H), 7.15−7.25 (m, 3 H), 7.25−7.35 (m, 2 H); ^{13}C NMR δ 31.7, 34.5, 66.6, 71.5, 126.0, 128.4, 128.5, 141.8.

2-Phenyl-1,2-propanediol (Table 3, entry 4):[22] ^{1}H NMR δ 1.48 (s, 3 H), 2.78 (brs, 1 H), 3.21 (brs, 1 H), 3.56 (d, J = 11.1 Hz, 1 H), 3.71 (d, J = 11.1 Hz, 1 H), 7.22−7.45 (m, 5 H); ^{13}C NMR δ −0.7, 22.8, 25.6, 31.2, 41.4, 70.3, 123.0, 129.5, 134.9, 148.9, 167.6.

1-(Hydroxymethyl)cyclohexanol (Table 3, entry 5):[4] ^{1}H NMR δ 1.20−1.70 (m, 10 H), 2.67 (brs, 1 H), 3.10 (brs, 1 H), 3.41 (s, 2 H); ^{13}C NMR δ 21.7, 25.8, 33.9, 69.9, 71.9.

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Supporting Information Available: ^{13}C NMR spectra for compounds **3b**,**d**,**f**−**o**, **9**, **11**−**13**, **15**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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