Silylation of Allylic Trifluoroacetates and Acetates Using Organodisilanes Catalyzed by Palladium Complex

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Silylation of allylic acetates (**1**) using organodisilanes (**2**) was carried out in the presence of a catalytic amount of $Pd(DBA)_2$−LiCl at 100 °C. The silylation proceeded smoothly without β-hydrogen elimination of a resulting (π-allyl)palladium intermediate. The added chloride salt such as LiCl or NaCl was indispensable for the catalytic activity. On the other hand, remarkable improvement of the silylation was realized by employing allylic trifluoroacetates (**4**) in place of the acetates (**1**) as the substrates. The silylation proceeded even at room temperature, and the added chloride salts was not necessary as the catalyst component. In the silylation, transmetalation of the disilanes (**2**) with (η^3-allyl)palladium intermediate (**7**) might be a critical step in the catalytic cycle. Model reactions for the transmetalation were carried out.

Introduction

The palladium(0)-catalyzed nucleophilic substitution of allylic esters has been used extensively in organic synthesis,[1−3] since it is truly one of the most useful and general transition-metal-catalyzed process. Allylic acetates and carbonates are by far the most often used allylic substrates. As for nucleophiles, stabilized carbanions[1−3] are mainly employed for alkylation, while other nucleophiles such as amines[4a,b] and zinc or boron enolates[4c,d] can be employed.

On the other hand, *silylation* of allylic esters must be a promising synthetic method of allylic silanes. The allylic silanes are highly versatile synthetic intermediates and have a large number of applications in organic synthesis.[5] Therefore, much attention has been paid to the preparation methods of allylic silanes, which include allylic Grignard reactions,[6] hydrosilylation of 1,3-dienes,[7] and Wittig reactions with (β-silylethylidene)phosphorane.[8] To date, however, only a few silylation reactions of allylic esters have been attempted. Fleming *et al.* reacted dimethylphenylsilyl cuprates with allylic acetates to obtain the corresponding allylic silanes.[9] Trost and co-workers attempted palladium-catalyzed silylations of allylic acetates with tris(trimethylsilyl)aluminum ($(Me_3Si)_3Al$·ether) as the silylating reagent.[10] However, the former reaction could not utilize other silyl moieties such as trimethylsilyl cuprate, and the latter often suffered from low regioselectivity. Furthermore, these silylating reagents must be prepared prior to the silylation. In contrast, hexamethyldisilane ($Me_3SiSiMe_3$, **2a**) is easily accessible and used in a wide variety of silylation reaction.[11] Suzuki *et al.* utilized **2a** in $Pd(PPh_3)_4$-catalyzed silylation of allylic acetates at 160 °C.[12] Unfortunately, for this potentially useful reaction, applicable substrates have severe limitation. In the reaction, (π-allyl)palladium intermediates generated by oxidative addition of allylic acetates to Pd(0) catalyst species readily decomposed by β-hydrogen elimination at the high reaction temperature.[13] Thus, allylic acetates that

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Table 1. Silylation of Allylic Acetates (1) in the Presence of LiCl[a]

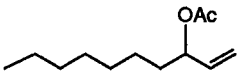
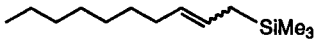
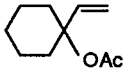
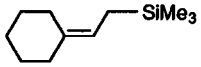
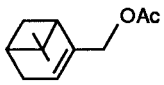
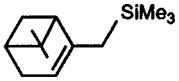
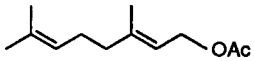
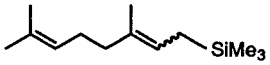
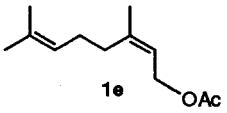
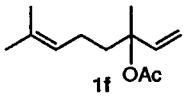
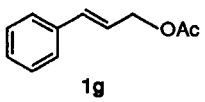
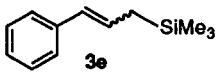
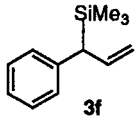
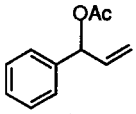
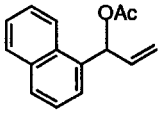
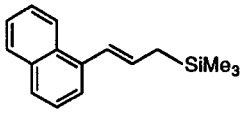
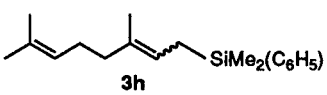
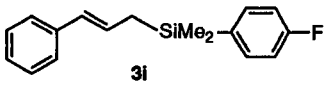
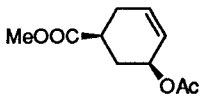
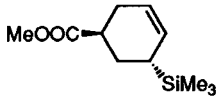
entry	allylic acetate (1)	product (3)	yield[b]/%	*E*/*Z* ratio
1	 **1a**	 **3a**	81	95 / 5
2[c]	 **1b**	 **3b**	62	-
3[d]	 **1c**	 **3c**	79	-
4	 **1d**	 **3d**	78	56 / 44
5	 **1e**	**3d**	74	55 / 45
6	 **1f**	**3d**	97	53 / 47
7	 **1g**	 **3e**	89 (92)	96 / 4
		 **3f**	(4)	-
8	 **1h**	**3e**	(81)	96 / 4
		3f	(3)	-
9	 **1i**	 **3g**	80	-
10[e]	**1f**	 **3h**	50	52 / 48

Table 1 (Continued)

entry	allylic acetate (1)	product (3)	yield[b]/%	*E*/*Z* ratio
11[f]	**1g**	 **3i**	98	-
12	 *cis*-**1j**[g]	 *trans*-**3j**[g]	67	-

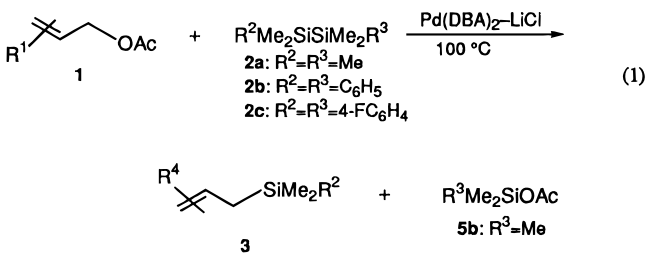
[a]Conditions: **1** (1.0 mmol), **2a** (2.0 mmol), LiCl (0.50 mmol), $Pd(DBA)_2$ (0.040 mmol), DMF (3.8 mL), at 100 °C for 40 h. [b]Isolated yields. Figures in parentheses show GLC yields determined by an internal standard method. [c]For 8h. [d]At 120 °C. [e]**2b** as the disilane. [f]**2c** as the disilane. [g]A 1:1 mixture of the two enantiomers.

have a primary or a secondary alkyl group at the α- or γ-position of the allylic moiety could not be used in the silylation.

In this paper, we report the first general silylation reactions of the allylic esters using organodisilanes (**2**). First, silylation of allylic acetates (**1**) using **2** is described, in which the $Pd(DBA)_2$−LiCl (DBA = dibenzylideneacetone) catalyst system showed good catalytic activity at 100 °C without the β-hydride elimination of the resulting (π-allyl)palladium intermediates. Furthermore, we have succeeded in remarkable improvement of the catalytic reaction by employing allylic trifluoroacetates (**4**) in place of the acetates (**1**) as the substrate. The improvement includes that (1) the reaction smoothly proceeds even at room temperature and (2) the added LiCl is not necessary in the catalytic system, *i.e.*, $Pd(DBA)_2$ alone shows high catalytic activity.

Results and Discussion

Silylation of Allylic Acetates in the Presence of LiCl. Allylic acetates (**1**) were smoothly silylated using organodisilanes (**2**) in the presence of the $Pd(DBA)_2$−LiCl catalyst system at 100 °C (eq 1).[14] The results are listed in Table 1. No reactions occurred at room temperature.



Aliphatic and alicyclic acetates (**1a**−**f**) were readily silylated with $Me_3SiSiMe_3$ (**2a**) and gave the corresponding allylic silanes (**3a**−**d**) in high isolated yields with good regioselectivity (entries 1−6). It is noteworthy that these substrates could not be silylated in the previous method using **2a**[12] because of the β-hydride elimination of the resulting (π-allyl)palladium intermediates (vide supra). Hence, the present reaction provides the first general method for the silylation of allylic acetates using organodisilanes. Aromatic allylic acetates (**1g**−**i**) also afforded the corresponding allylic silanes in high yields (entries 7−9). Substituted disilanes such as **2b** and **2c** also provided the corresponding allylic silanes (entries 10 and 11).

Lithium chloride was indispensable in the reaction. No reaction took place without the added salt. Varying the amount of LiCl had only a small effect: yields of **3e** from **1g** were 92% with 0.5 equiv of LiCl (entry 7), 86% with 1.0 equiv, and 83% with 5 equiv. Other salts (4 equiv) could replace LiCl in entry 7: yields of **3e** from **1g** were 92% with NaCl, 90% with KCl, 47% with KBr, and 15% with LiI. No allylic silanes were obtained with fluoride salts such as LiF, KF, and CsF. Thus, the chloride salts were the most effective as the additive. The reaction also proceeded in diglyme, but no reactions took place in toluene presumably due to low solubility of the added salts. As for the effect of the catalyst precursor, $Pd(DBA)_2$[15,16] showed high catalyst activity: yields of **3e** from **1g** were 92% with $Pd(DBA)_2$ (entry 7), 47% with $Pd(OAc)_2(PPh_3)_2$, 22% with $PdCl_2(PPh_3)_2$, and 11% with $Pd(PPh_3)_4$, respectively, under otherwise identical reaction conditions to those of entry 7.

One of the two silyl moieties of the disilanes (**2**) was incorporated in the product (**3**). The fate of the other silyl moiety was determined in the reaction using **2a** and **1g** (entry 7, with 0.5 equiv of LiCl) by taking a ^{29}Si NMR spectrum of the reaction mixture (locked with C_6D_6). After the reaction, the expected amount of Me_3SiOAc (**5b**, 21.5 ppm, lit.[17a] 22.0 ppm) was found along with (*E*)-**3e** (0.78 ppm) and excess **2a** (−20.5 ppm, lit.[17b] −20.5 ppm). However, no trace of Me_3SiCl (lit.[17c] 30.2 ppm) was detected in the reaction mixture. The same results were obtained even with 5 equiv of LiCl. Thus, one of the silyl moieties of **2** was trapped by the leaving acetate group effectively, not by the added chloride anion.

Silylation of Allylic Trifluoroacetates. Remarkable improvement of the silylation was realized by employing allylic trifluoroacetates (**4**) in place of the aecetates (**1**) as the substrate. The silylation proceeded even at room temperature. Furthermore, the added

(13) (a) Matsumoto *et al.* reported palladium-catalyzed silylation of allylic halides with **2a** at 120−170 °C.[13b] However, they only employed simple allylic halides having no possibility of the β-hydride elimination of resulting (π-allyl)palladium intermediates. (b) Matsumoto, H.; Yako, T.; Nagashima, S.; Motegi, T.; Nagai, Y. *J. Organomet. Chem.* **1978**, *148*, 97.

(14) For a preliminary account of this portion, see: Tsuji, Y.; Kajita, S.; Isobe, S.; Funato, M. *J. Org. Chem.* **1993**, *58*, 3607.

Table 2. Silylation of Allylic Trifluorocetates (4)[a]

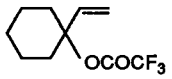
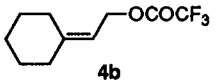
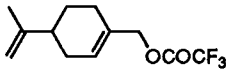
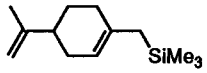
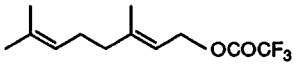
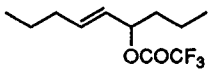
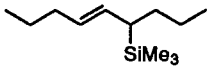
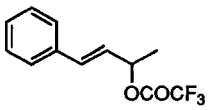
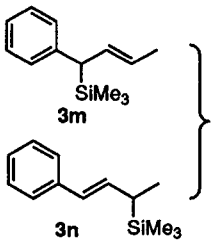
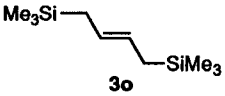
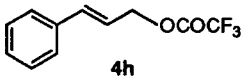
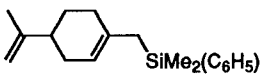
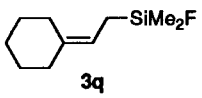
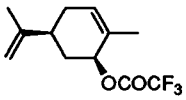
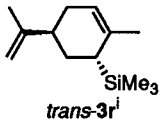
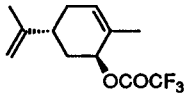
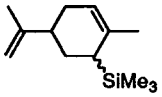
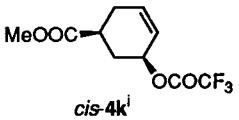
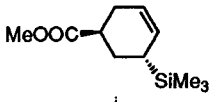
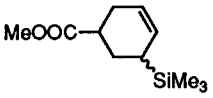
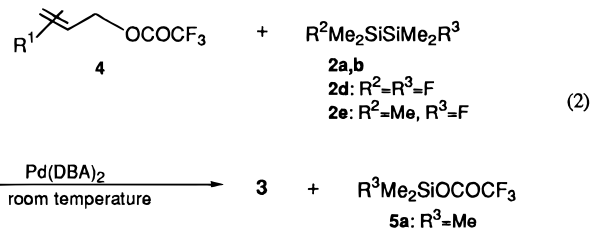
entry	allylic trifluoroacetate (1)	product (3)	yield[b]/%	*E*/*Z* ratio
13	 **4a**	**3b**	92	-
14	 **4b**	**3b**	89	-
15	 **4c**	 **3k**	80	-
16	 **4d**	**3d**	90	62 / 38
17	 **4e**	 **3l**	86	-
18	 **4f**[c]	 **3m** **3n**	72[d]	-
19	 **4g**	 **3o**	50	-
20	 **4h**	**3e**	94	99 / 1
21[e]	**4c**	 **3p**	50	-
22[f]	**4a**	 **3q**	96	-
23[g]	 *cis*-**4j**[h]	 *trans*-**3r**[i]	89	-

Table 2 (Continued)

entry	allylic trifluoroacetate (1)	product (3)	yield[b]/%	*E*/*Z* ratio
24	*cis*-**4j**[h]	*trans*-**3r**[i]	83	-
25	 *trans*-**4j**[j]	 *trans*- and *cis*-**3r**	88	-
26[g]	 *cis*-**4k**[i]	 *trans*-**3j**[i]	89	-
27	*cis*-**4k**[i]	 *cis*- and *trans*-**3j**	85	-

[a]Conditions: **4** (1.0 mmol), **2a** (2.0 mmol), $Pd(DBA)_2$ (0.030 mmol), and THF (5.5 mL), at room temperature for 12 h. [b]Isolated yields. [c]Used as an ether solution (0.16 moldm^{-3}). [d]Total yield; **3p**:**3q** = 3:1. [e]**2b** as the disilane. [f]**2d** as the disilane. [g]In THF-acetonitrile (4:1 in volume) at 40 °C. [h](1*R*,5*R*) or (1*S*,5*S*). [i]A 1:1 mixture of the two enantiomers. [j](1*S*,5*R*) or (1*R*,5*S*).

chloride salt is not necessary, *i.e.*, $Pd(DBA)_2$ alone showed high catalyst activity (eq 2). The results are shown in



(2)

Table 2. Various allylic trifluoroacetates (**4a**−**h**) were silylated smoothly to the corresponding allylic silanes at room temperature (entries 13−20). The acetates corresponding to **4c**, *cis*-**4j**, and *trans*-**4j** afforded the silylated products in low yields (<10%) under the same reaction conditions as those in eq 1. The reaction proceeded in the presence of a catalytic amount (3 mol %) of $Pd(DBA)_2$ in various solvents: yields of **3e** from **4h** were 94% in THF (entry 20), 92% in toluene, and 61% in DMF, respectively. As the catalyst precursor, $Pd(DBA)_2$[15,16] showed high catalytic activity. Surprisingly, $Pd(OAc)_2$ also had high catalytic activity: the yields of **3e** from **4h** were 99% in toluene and 96% in THF. In these cases, $Pd(OAc)_2$ must be reduced to Pd(0) species in situ by **2a**. Actually, an NMR tube reaction of $Pd(OAc)_2$ (1 equiv) with **2a** (50 equiv) at room temperature in toluene-d_8 afforded the expected amount of Me_3SiOAc (**5b**: ^{29}Si NMR 22.0 ppm; lit.[17a] 22.0 ppm) with concomitant formation of palladium black powder in 5 min. In contrast, $Pd(OAc)_2-PPh_3$ (P/Pd = 2 or 3), $PdCl_2$, $PdCl_2$(COD), and $PdCl_2(PhCN)_2$ did not show any catalytic activity as the catalyst precursor. Similar NMR tube reaction of these catalyst precursors with excess **2a** at room temperature or at 40 °C did not show any sign of reactions (monitored with ^{29}Si NMR), indicating no in situ reduction to catalytically active Pd(0). Moreover, $Pd(PPh_3)_4$ showed no catalytic activity, either. Hence, for the present silylation reaction of **4**, palladium(0) complex without coordinating ligands, naked Pd(0), is most favorable as the catalyst precursor. Phenyl- and fluoro-substituted disilanes (**2b** and **2d**) also reacted with **4** to afford the corresponding allylic silanes (entries 21 and 22).

After the reaction, the formation of $Me_3SiOCOCF_3$ (**5a**) was confirmed in entry 20 by taking a ^{29}Si NMR spectrum of the filtered reaction mixture: **5a** appeared at 33.1 ppm (lit.[17a] 33.1 ppm) as well as (*E*)-**3e** (at 0.78 ppm) and excess **2a** (at −20.5 ppm[17b]) with the expected intensities. Similar to the reaction using allylic acetates (**1**), the leaving trifluoroacetate group effectively trapped one silyl moiety, with the other silyl group being incorporated in the products. In both cases, strong oxophilicity of the silicon (bond dissociation energy: Si−O 430−530 kJ mol^{-1})[18] may facilitate the silylation reaction.

Recently, Vitagliano *et al.* examined the stereochemistry of the oxidative addition of *trans*-4-acetoxy-2-

(15) (a) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065. (b) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1977**, *17*, 134.

(16) (a) $Pd_2(DBA)_3 \cdot CHCl_3$[16b] showed similar catalytic activity. (b) Ukai, T.; Kawazuka, H.; Ishii, Y.; Bonnett, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

(17) (a) Bassingdale, A. R.; Posnan, T. B. *J. Organomet. Chem.* **1979**, *175*, 273. (b) Hunter, B. K.; Reewes, L. W. *Can. J. Chem.* **1967**, *46*, 1399. (c) Van den Berghe, E. V.; Van der Kelen, G. P. *J. Organomet. Chem.* **1973**, *59*, 175.

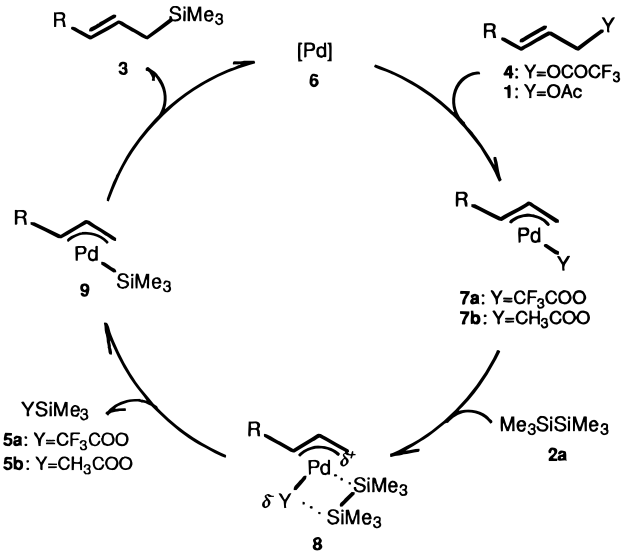
(18) Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, pp 5−10.

cyclohexenyl trifluoroacetate (**4i**) to $Pd(DBA)_2$.[19] With this particular trifluoroacetate, they found that the stereochemistry of the oxidative addition was affected by the nature of the solvent in the reaction. They reported that the stereochemistry of the oxidative addition was inversion (85% selectivity) in THF−acetonitrile mixed solvent (4:1 in volume), but retention (90% selectivity) in THF. In order to investigate stereochemistry of the present silylation reaction, *cis*-**4j** was subjected to the reaction. The reaction proceeded smoothly and afforded the *trans*-isomer (*trans*-**3r**) exclusively in the THF−acetonitrile mixed solvent (4:1 in volume) (entry 23).[20] The same clean overall inversion was also observed in THF to afford only *trans*-**3r** (entry 24). Thus, in the case of *cis*-**4j**, the nature of the solvent did not affect the stereocourse of the silylation. On the other hand, the silylation of *trans*-**4j** afforded a 1:1 mixture of *trans*- and *cis*-**3r** in THF (entry 25), while the conversion was very low in the THF−acetonitrile mixed solvent. Furthermore, the silylation of *cis*-**4k** provided only *trans*-**3j** in the THF−acetonitrile mixed solvent (entry 26), while a 1:1 mixture of *trans*- and *cis*-**3j** was obtained in THF (entry 27). The oxidative addition reaction of **4i** to $Pd(DBA)_2$ in THF is reported to be very slow as compared with that in THF−acetonitrile mixed solvent.[19] Therefore, in the silylation of *trans*-**4j** and *cis*-**4k** carried out in THF (entries 25 and 27), the (π-allyl)palladium intermediate might undergo *trans*−*cis* isomerization,[21] and this will cause the formation of stereoisomers as the products. Concerning allylic acetates, the stereochemistry of the oxidative addition to Pd(0) complexes is known to be inversion.[22] In the silylation of allylic acetate, *cis*-**1j** afforded only *trans*-**3j** with the $Pd(DBA)_2$−LiCl catalyst system in DMF at 100 °C: again clean overall inversion (entry 12, Table 1). Accordingly, at least when the silylation is stereospecific (entries 12, 23, 24, and 26), the stereochemistry of the oxidative addition of the allylic esters must be inversion and the silyl moiety attacks the π-allyl face from the palladium side. Disilanes (**2**) alone are not good nucleophiles. Therefore, **2** should be activated on the Pd catalyst center prior to the silylation and, as a result, one of the silyl moieties of **2** will attack the π-allyl plane from the palladium side.

Catalytic Cycle. A possible catalytic cycle is shown in Scheme 1. The catalytic cycle begins with oxidative addition of **4** or **1** to Pd(0) active catalyst species (**6**) and gives a (π-allyl)palladium trifluoroacetate (**7a**) or acetate (**7b**) intermediate. Transmetalation of disilane (**2**) with **7** might afford (π-allyl)silyl species (**9**) with concomitant formation of silyl trifluoroacetate (**5a**) or acetate (**5b**); the formations of **5a** and **5b** has been confirmed by ^{29}Si NMR spectra of the resulting reaction mixtures (vide supra). Finally, reductive elimination of **9** can provide the allylic silanes (**3**) as the product and regenerates the active catalyst species (**6**).

With regard to the catalyst cycle, the oxidative addition of allylic trifluoroacetate (**4**) to Pd(0) is well-known.[19] Indeed, reaction of **4h** (1 equiv) with $Pd(DBA)_2$ (1 equiv) proceeded smoothly at room temperature to afford (π-allyl)palladium trifluoroacetate dimer (**10a** in Scheme 2) as yellow crystals in 55% yield, while the corresponding acetate (**1g**) apparently did not react with $Pd(DBA)_2$ under similar reaction conditions. In order to determine the rate-determining step, the silylation rates of **4a** and **4b** were compared. Both substrates afforded the same

Scheme 1

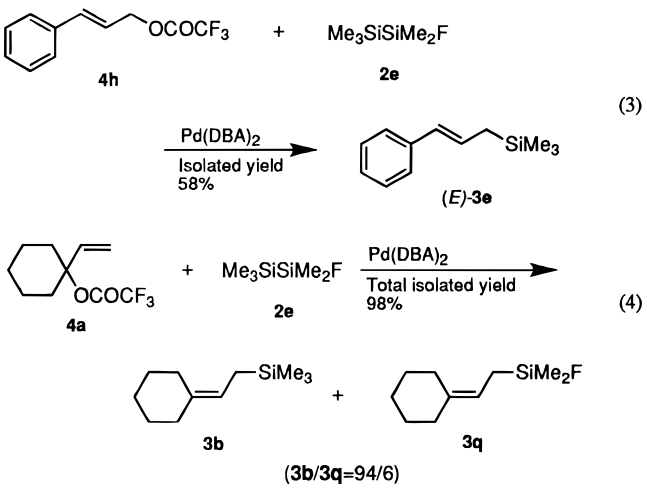


product (**3b**) in high yields (entries 13 and 14) via a common palladium intermediate. However, the reaction of **4a** is much faster than that of **4b**: 80 times faster on the basis of their initial rates. Hence, the rate-determining step in the catalytic cycle must be the oxidative addition stage, since the following catalytic steps are the same between these two substrates.

There is no precedent for the transmetalation of disilanes (**2**) with (π-allyl)palladium trifluoroacetate (**7a**) or acetate (**7b**) complexes (**7** + **2** → **9** + **5**; Scheme 1). Therefore, a model reaction of the transmetalation step was carried out. As a model complex for **7a**, **10a** was employed. In the reaction of **10a** (1 equiv) with **2a** (10 equiv) in toluene-d_8 at room temperature (Scheme 2), a clear yellow solution turned black within a few seconds and a palladium black powder appeared. A ^{29}Si NMR spectrum of the colorless filtrate showed that **5a** and **3e** were formed in equal amounts; the yield of **3e** was 55% by GC (with heptadecane as an internal standard on Apieson grease L). The transmetalation might proceed via π-allyl silyl palladium intermediate (**9**, Scheme 2) with a transition state such as **8**[23] (Scheme 1). We attempted to trap the intermediate **9** by adding phosphines (PPh_3, PMe_3) or other ligands to the reaction mixture. However, these added ligands often hindered the transmetalation. Any silyl species such as **9** could not be detected by ^{29}Si, ^{1}H, and ^{13}C NMR spectra in these reactions. As soon as an intermediate such as **9** is formed, very fast reductive elimination of this highly unsaturated species (14-electron species) may afford **3** and **6**. Moreover, to see how the transmetalation is influenced electronically, the silylation of **4h** was carried out with unsymmetrical fluoropentamethyldisilane ($FMe_2SiSiMe_3$, **2e**) under the standard reaction conditions. In the reaction, the silylation exclusively afforded a trimethylsilylated product ((*E*)-**3e**) and a fluorodimethylsilylated product was not detected (eq 3). Similar results were obtained in the reaction of **4a** with **2e**, in which the trimethylsilylated product (**3b**) was obtained as a major isomer and the fluorodimethylsilylated product (**3q**, cf. entry 22) as a minor one (eq 4). Hence, in the transmetalation stage, the more nucleophilic silyl moiety, $SiMe_3$ rather than $SiMe_2F$,[26] attacked the π-allyl moiety.

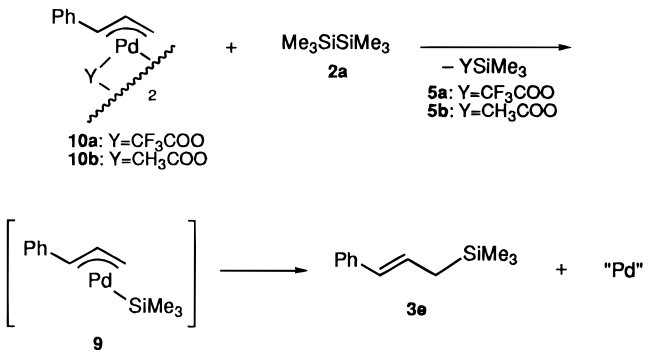
As for the oxidative addition of allylic acetates (**1**), the (π-allyl)palladium acetate complex (**10b** in Scheme 2) could not be prepared by direct oxidative addition of **1g**

(19) Vitagliano, A.; Åkermark, B.; Hansson, S. *Organometallics* **1991**, *10*, 2592.



to $Pd(DBA)_2$: apparently no reactions occurred. Therefore, **10b** was prepared by reaction of the corresponding chloro dimer (**10c**: Y = Cl) with CH_3COOAg.[27] The complex **10b** (1 equiv) also reacted with **2a** (10 equiv) in toluene-d_8 at room temperature (Scheme 2). The reaction afforded trimethylsilyl acetate (**5b**, ^{29}Si resonance at 22.1 ppm[17a]), (*E*)-**3e** (^{29}Si resonance at 0.78 ppm, 30% yield by GC), and palladium metal (black powder) within a few seconds. Thus, this model reaction might suggest that each catalytic step can proceed even without added LiCl, if the (π-allyl)palladium acetate intermediate (**7b**) is formed in the catalytic cycle (Scheme 1). These results may imply that the added LiCl is indispensable only in oxidative addition stage. The added chloride salt can react with a palladium complex

Scheme 2

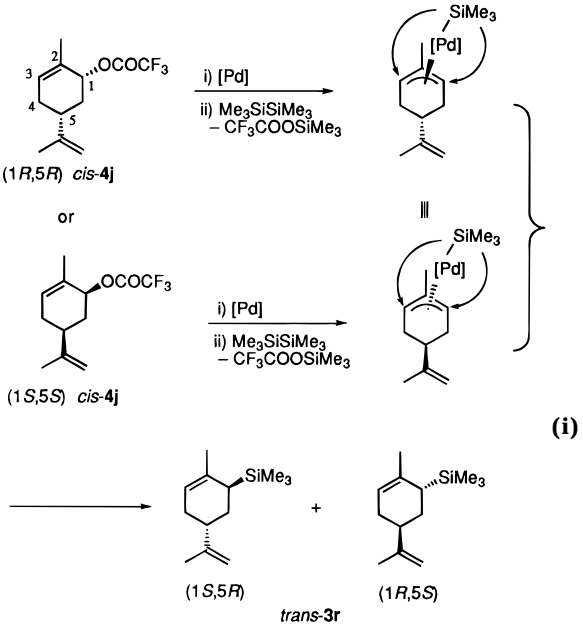


to give a chloropalladate species (eq 5).[28] Such a palladate species would be nucleophilic enough to oxidatively add to **1** at 100 °C and initiate the catalytic cycle (Scheme 1).

$$PdL_n + LiCl \xrightarrow{-L} Li^+[PdL_{n-1}Cl]^- \qquad (5)$$

Silylation of Allylic Acetates in the Presence of Trifluoroacetic Acid. It has been reported that (π-allyl)palladium acetate complexes such as **10b** can be converted into the corresponding trifluoroacetate complexes such as **10a** by reaction with CF_3COOH.[19] This result and the above investigation on the catalytic cycle will strongly suggest that silylation of allylic acetates (**1**) can proceed in the presence of a stoichiometric amount of added CF_3COOH under reaction conditions similar to those of eq 2. Indeed, this is the case. When **1g** was reacted with **2a** in the presence of 2 equiv of CF_3COOH at room temperature in toluene, **3e** (*E*/*Z* = 99/1) was obtained in 92% yield (entry 28, Table 3). In the absence of the CF_3COOH, no reactions occurred. The reaction proceeded smoothly in toluene, while the catalyst was decomposed into insoluble materials in THF or diglyme. The reaction did not proceed via the corresponding

(20) A chiral gas chromatography analysis (on CP-Chirasil Dex CB, CHROMPACK) showed the product was a 1:1 mixture of two enantiomers, even if an optically pure *cis*-**4j** ((1*R*,5*R*) or (1*S*,5*S*)) was employed. If stereochemistry of oxidative addition of *cis*-**4j** to Pd(0) is stereoselectively inversion (or even retention), each optically pure *cis*-**4j** affords the same optically inactive (π-allyl)palladium species (i). Since regioselectivity of the silylation cannot be regulated without a chiral auxiliary ligand, the present silylation inevitably affords *trans*-**3r** as a 1:1 mixture of the two enantiomers ((1*S*,5*R*) or (1*R*,5*S*)).



(21) (a) Granberg, K. L.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1992**, *114*, 6858. (b) MacKenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046.

(22) (a) Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767. (b) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730.

(23) Oxidative addition of disilane to Pd(0)[24a] or Pt(0)[24b] complexes containing basic phosphines has been reported. However, for these oxidative addition reactions, the Si−Si bond must be activated by a substituent such as F or Cl on the silicon. In these cases, a simple disilane such as **2a** was totally inert toward the oxidative addition. Even if oxidative addition of **2a** to **7** was considered, some Pd(IV) intermediates must be presumed in the catalytic cycle. However, such a catalytic cycle including a Pd(0)−Pd(II)−Pd(IV) four-electron redox system should be highly unlikely, especially for those active even at room temperature. Hence, the transmetalation might proceed via a four-centered σ-metathesis[25] transition state such as **8** rather than the oxidative addition−reductive elimination sequence.

(24) (a) Ozawa, F.; Sugawara, M.; Hayashi, T. *Organometallics* **1994**, *13*, 3237. (b) Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447.

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(26) (a) Populations of the HOMO on each Si atom of **2e** were calculated with the Gaussian 92 program.[26b] Geometrical parameters were optimized under the C_s symmetry with the STO-3G basis set, and molecular orbitals were calculated with 3-21G*. The contour map indicates that the HOMO spreads slightly more over the trimethylsilyl Si(2) atom than the Si(1) atom attached to F: Mulliken point charge population of the HOMO on the Si(1) is 0.266 and 0.322 on the Si(2). Therefore, the calculation suggested that more nucleophilic silyl moiety attacks the allyl system. (b) Frisch, M. J.; Gordon, M. H.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian 92; Gaussian, Inc., Pittsburgh, PA, 1992.

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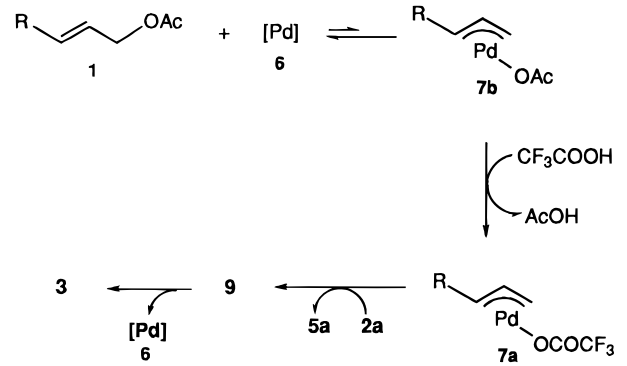
Table 3. Silylation of Allylic Acetates in the Presence of CF_3COOH[a]

entry	substrate	added acid (equiv)[b]	solvent	yield/%[c]	relative rate[d]
28	**1g**	CF_3COOH (2)	toluene	92	2.36
29	**1b**	CF_3COOH (1)	toluene	99	
30	**1f**	CF_3COOH (1)	toluene	(52)[e]	
31	**1g**	CF_3COOH (0.7)	toluene	4	0.07
32	**1g**	CF_3COOH (1.4)	toluene	40	0.92
33	**1g**	$CF_2ClCOOH$ (2)	toluene	40	1.18
34	**4h**	none	THF	(94)	1.00
35	**4h**	none	toluene	92	1.59
36[f]	**4h**	CF_3COOH (2)	toluene	82	28.0

[a] Conditions: **1** (1.0 mmol), **2a** (2.0 mmol), $Pd(DBA)_2$ (0.030 mmol), toluene (5.5 mL) at room temperature for 12 h. [b] Amount of the added acid based on **1** or **4**. [c] GC yields determined by the internal standard method. Numbers in parentheses show isolated yields. [d] Determined by initial rates. [e] E/Z = 54/46. [f] For 1 h.

Scheme 3



trifluoroacetate (**4h**), since reaction between **1g** and CF_3COOH in toluene at room temperature did not afford **4h** at all in the presence or absence of $Pd(DBA)_2$ as the catalyst precursor. Other allylic acetates such as **1b** and **1f** were also smoothly silylated with **2a** into **3b** and **3d**, respectively, in the presence of 1 equiv of CF_3COOH at room temperature (entries 29 and 30). Again, no reaction occurred in the absence of the added CF_3COOH. In order to get good conversion of **1**, a stoichiometric amount of CF_3COOH is required (entries 28, 31, and 32). However, a large amount of the acid caused a protodesilylation reaction.[29] With **1b** and **1f**, the protodesilylation is predominant and even 2 equiv of CF_3COOH lowered the yields considerably. As for the added acid, $CF_2ClCOOH$ in place of CF_3COOH reduced the yield and relative rate considerably (entry 33), while the addition of CCl_3COOH, TsOH, or H_2SO_4 did not afford the allylic silane (**3**) at all. Interestingly, even in the silylation of the allylic trifluoroacetate (**4h**), the addition of CF_3COOH enhanced the reaction rate considerably (entries 34−36).

A plausible reaction path is shown in Scheme 3. The oxidative addition of **1** with $Pd(DBA)_2$ would afford the (π-allyl)palladium acetate intermediate (**7b**), but in a very low equilibrium concentration.[30] The concentration must be so low that the reaction with **2** will not proceed with a reasonable reaction rate. However, in the presence of CF_3COOH, the acid can protonate **7b** to the corresponding **7a**.[19] Once **7a** is formed, transmetalation followed by reductive elimination as shown in Scheme 1 will follow.

Conclusion

Allylic acetates (**1**) were silylated with organodisilanes (**2**) in the presence of a catalytic amount of $Pd(DBA)_2$−LiCl at 100 °C. The silylation proceeded even at room temperature by employing allylic trifluoroacetates (**4**) as the substrate in place of **1**, in which the added LiCl was not necessary as the catalyst component.

Experimental Section

Materials. The reagents and the solvents were dried and purified before use by usual methods.[31] Hexamethyldisilane (**2a**) was purchased from Aldrich. 1,2-Difluorotetramethyldisilane (**2d**),[32a] fluoropentamethyldisilane (**2e**),[32a] and dichlorotetramethyldisilane (**2f**)[32b] were prepared by the methods reported by Kumada. Other disilanes (**2b** and **2c**) were synthesized from **2f** using the corresponding organolithiums. Allylic esters such as **1j**,[33] **4j**,[34] and **4k**[33] were prepared from the corresponding alcohols with acetyl chloride or trifluoroacetic anhydride. The following catalyst precursors were prepared by the published methods: $Pd(DBA)_2$,[15] $Pd(PPh_3)_4$,[35a] $PdCl_2(PhCN)_2$,[35b] $Pd(OAc)_2(PPh_3)_2$,[35c] $PdCl_2(PPh_3)_2$,[35d] and $PdCl_2$(COD).[35e] Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Silylation of Allylic Acetates (1) in the Presence of LiCl. A typical procedure is as follows (entry 4): $Pd(DBA)_2$ (23 mg, 0.040 mmol) and dry LiCl (21 mg, 0.50 mmol) were placed in a 20 mL flask equipped with a three-way stopcock, and the whole system was evacuated for 30 min. Then, DMF (3.8 mL), geranyl acetate (**1d**; 196 mg, 1.0 mmol), and hexamethyldisilane (**2a**; 293 mg, 2.0 mmol) were added in this order under argon flow. The color of the solution changed from reddish brown to yellow upon the addition of **1d**. The homogeneous solution was stirred for 40 h at 100 °C. The mixture was then passed through a short Florisil column (8 mm i.d. × 70 mm) to give a clear pale yellow solution. Kugelrohr distillation (Büchi) gave a mixture of geranyl- and neryltrimethylsilanes (**3d**) in 78% yield (164 mg, 0.78 mmol; pot temperature 100 °C/8 mmHg). ^{13}C NMR and GC analyses showed the E/Z ratio to be 56/44.

Silylation of Allylic Trifluoroacetates (4). The silylation of **4a** is typical (entry 13). A 20 mL flask was charged with $Pd(DBA)_2$ (17 mg, 0.030 mmol) and THF (5.5 mL) under an argon atmosphere. The palladium complex was dissolved with stirring to afford a deep purple solution. Then, **2a** (293 mg, 2.0 mmol) and **4a** (222 mg, 1.0 mmol) were added in this order. The reaction mixture turned pale yellow, and the reaction was carried out at room temperature for 12 h. After the reaction, the reaction mixture was diluted with diethyl

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(30) (a) Yamamoto *et al*. reported oxidative addition reaction of allyl acetate with several Pd(0) complexes.[30b,c] With $Pd(PPh_3)_4$, no apparent changes were observed at room temperature or even at 80 °C. However, when deuterium-labeled CH_2=$CHCD_2OAc$ was used as the substrate in the reaction, the recovered allyl acetate consisted of CD_2=$CHCH_2OAc$ and CH_2=$CHCD_2OAc$, indicating that equilibrium between the substrate and oxidative addition product did exist, but the concentration of the adduct was too low to be detected. In order to isolate the oxidative adducts, more basic phosphine is required. Thus, with $Pd(PCy_3)_2$ (PCy_3 = tricyclohexylphosphine), the oxidative addition afforded yellow isolable $Pd(\eta^3\text{-}C_3H_5)(OAc)(PCy_3)$. In the present silylation reaction, the catalyst species (**6**) does not contain any phosphines or other donating ligands. Therefore, concentration of the oxidative addition species (**7b**) must be much lower (Scheme 3). (b) Yamamoto, T.; Saito, O.; Yamamoto, A. *J. Am. Chem. Soc.* **1981**, *103*, 5600. (c) Yamamoto, T.; Akimoto, M.; Saito, O.; Yamamoto, A. *Organometallics* **1986**, *5*, 1559.

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ether (20 mL), washed with saturated $NaHCO_3$ aqueous solution (20 mL), and dried over anhydrous $MgSO_4$. Kugelrohr distillation afforded **3b** in 92% yield (168 mg, 0.92 mmol; pot temperature 80 °C/1 mmHg).

Silylation of Allylic Acetates (1) in the Presence of CF_3COOH. A typical procedure is described for the silylation of **1g** (entry 28). Toluene (5.5 mL) and $Pd(DBA)_2$ (17 mg, 0.030 mmol) were placed in a 20 mL flask under argon atmosphere. To the stirred deep purple solution were added heptadecane (180 mg, 0.75 mmol; as an internal standard for GC analysis), **1g** (176 mg, 1.0 mmol), **2a** (293 mg, 2.0 mmol), and CF_3COOH (228 mg, 2.0 mmol) in this order. The solution was stirred at room temperature for 12 h. Gas chromatograph analysis showed that **3e** was obtained in a 92% yield (*E*/*Z* = 99/1).

Reaction of 10a or 10b with 2a. In a 5 mm i.d. NMR tube, **10a** (20 mg, 0.03 mmol) or **10b** (17 mg, 0.03 mmol) was dissolved in argon-degassed toluene-d_8 (0.5 mL). Hexamethyldisilane (**2a**) (88 mg, 0.6 mmol) was added into the solution at room temperature. Within a few seconds, a black powder appeared. The liquid part was transferred through a short Celite plug into another NMR tube. The formation of **3e** was confirmed by ^1H, ^{13}C, and ^{29}Si NMR spectra. The yield of **3e** was determined by GC using heptadecane as an internal standard on Apieson grease L. The ^{29}Si NMR spectrum is most diagnostic of the formation of **5a** (33.1 ppm; lit.[17a] 33.1 ppm) or **5b** (22.1 ppm, lit.[17a] 22.0 ppm).

Some products have been identified by comparison with published spectral data; **3b**,[36] **3c**,[37] **3d**,[38] **3e**,[39,40] **3f**,[40] and **3o**.[41]

***(E)*-3a:**[42] ^1H NMR δ −0.01 (s, 9H), 0.89 (t, J = 7.4 Hz, 3H), 1.28 (m, 10H), 1.40 (d, J = 8 Hz, 2H), 1.97 (q, J = 7.4 Hz, 2H), 5.24 (dt, J = 15 Hz, 7.4 Hz, 1H), 5.37 (dt, J = 15 Hz, 8 Hz, 1H); ^{13}C NMR δ −1.94 (q), 14.2 (q), 22.7 (t), 22.8 (t), 29.2 (t), 29.3 (t), 30.2 (t), 32.0 (t), 32.9 (t), 126.0 (d), 129.2 (d); MS *m*/*e* 212 (M^+).

***(Z)*-3a:**[42] ^{13}C NMR δ −1.72 (q), 14.2 (q), 18.5 (t), 22.7 (t), 27.2 (t), 29.3 (t), 30.2 (t), 32.0 (t), 32.9 (t), 125.2 (d), 127.9 (d); MS *m*/*e* 212 (M^+).

3g: ^1H NMR δ 0.01 (s, 9H), 1.68 (dd, J = 7.7 Hz, 1 Hz, 2H), 6.11 (dt, J = 15 Hz, 7.7 Hz, 1H), 6.85 (d, J = 15 Hz, 1H), 7.25−8.05 (m, 7H); ^{13}C NMR δ −1.74 (q), 24.5 (t), 123.2 (d), 124.1 (d), 125.5 (d), 125.6 (d), 125.70 (d), 125.73 (d), 128.5 (d), 131.1 (d), 131.2 (s), 133.7 (s), 136.4 (s); MS *m*/*e* 240 (M^+). Anal. Calcd for $C_{16}H_{20}Si$: C, 79.93; H, 8.38. Found: C, 79.80; H, 8.45.

***(E)*-3h:** ^{13}C NMR δ −3.21 (q), 15.8 (q), 17.70 (q), 17.8 (t), 25.8 (q), 26.9 (t), 40.0 (t), 119.7 (d), 124.7 (d), 127.7 (d), 128.9 (d), 131.0 (s), 133.0 (s), 133.6 (d), 139.3 (s). Anal. Calcd for $C_{18}H_{28}Si$: C, 79.34; H, 10.36. Found: C, 79.21; H, 10.49.

***(Z)*-3h:** ^{13}C NMR δ −3.12 (q), 17.4 (t), 17.67 (q), 23.4 (q), 25.7 (q), 26.5 (t), 31.8 (t), 119.9 (d), 124.7 (d), 127.7 (d), 128.9 (d), 131.2 (s), 133.0 (s), 133.6 (d), 139.2 (s). Anal. Calcd for $C_{18}H_{28}Si$: C, 79.34; H, 10.36. Found: C, 79.19; H, 10.40.

3i: ^1H NMR δ −0.01 (s, 6H), 1.55 (d, J = 6.8 Hz, 2H), 5.79−5.94 (m, 2H), 6.64−6.86 (m, 3H), 6.91−6.94 (m, 2H), 7.11−7.20 (m, 4H). ^{13}C NMR δ −3.15 (q), 23.1 (t), 114.9 (d, $^2J_{C-F}$ = 20 Hz), 125.6 (d), 126.4 (d), 126.8 (d), 128.5 (d), 129.2 (d), 133.9 (s, $^4J_{C-F}$ = 4.4 Hz), 135.6 (d, $^3J_{C-F}$ = 7.3 Hz), 138.3 (s), 163.9 (s, $^1J_{C-F}$ = 246 Hz).

***trans*-3j:**[10] ^1H NMR δ 0.01 (s, 9H), 1.55−1.64 (m, 1H), 1.84 (dt, J_{gem} = 14 Hz, J_{eq-ax} = J_{eq-eq} = 4.2 Hz, 1H), 1.97 (ddd, J_{gem} = 14 Hz, J_{ax-ax} = 9.2 Hz, J_{ax-eq} = 6.6 Hz), 2.13−2.33 (m, 2H), 2.56−2.63 (m, 1H), 3.65 (s, 3H), 5.54−5.66 (m, 2H); ^{13}C NMR δ −2.82 (q), 25.1 (d), 25.7 (t), 26.9 (t), 37.6 (d), 51.6 (q), 122.5 (d), 127.8 (d), 176.1 (s).

***cis*-3j:**[10] ^1H NMR δ −0.03 (s, 9H), 1.41 (q, J_{gem} = J_{ax-ax} = 12 Hz, 1H), 1.52−1.62 (m, 1H), 1.97−2.07 (m, 1H), 2.12−2.34 (m, 2H), 2.38−2.47 (m, 1H), 3.66 (s, 3H), 5.55−5.66 (m, 2H); ^{13}C NMR δ −3.82 (q), 25.9 (d), 27.0 (t), 27.7 (t), 40.1 (d), 123.5 (d), 127.3 (d), 175.9 (s).

3k: ^1H NMR δ −0.01 (s, 9H), 1.40 (s, 2H), 1.39−1.66 (m, 2H), 1.71 (s, 3H), 1.70−1.75 (m, 1H), 1.85−1.96 (m, 2H), 1.96−2.12 (m, 2H), 4.69 (s, 2H), 5.19 (m, 1H); ^{13}C NMR δ −1.19 (q), 20.8 (q), 27.6 (t), 28.1 (t), 30.9 (t), 31.5 (t), 41.2 (d), 108.3 (t), 118.3 (d), 135.1 (s), 150.3 (s). Anal. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found: C, 74.84; H, 11.67.

3l: ^1H NMR δ 0.00 (s, 9H), 0.91 (t, J = 7.4 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H), 1.17−1.56 (m, 9H), 1.98−2.06 (m, 2H); ^{13}C NMR δ −3.17 (q), 13.6 (q), 13.9 (q), 22.3 (t), 23.2 (t), 31.2 (t), 32.8 (t), 35.1 (d), 128.0 (d), 131.7 (d). Anal. Calcd for $C_{12}H_{26}Si$: C, 72.64; H, 13.21. Found: C, 72.69; H, 13.48.

3m:[43,44] ^1H NMR δ 0.00 (s, 9H), 1.74 (ddd, J = 6.4 Hz, 1.8 Hz, 0.8 Hz, 3H), 2.92 (d, J = 10 Hz, 1H), 5.45 (dqd, J = 15 Hz, 6.4 Hz, 0.8 Hz, 1H), 5.85 (ddq, J = 15 Hz, 10 Hz, 1.6 Hz, 1H), 7.08−7.46 (m, 5H); ^{13}C NMR δ −3.00 (q), 18.1 (q), 42.8 (d), 123.5 (d), 125.6 (d), 127.1 (d), 128.2 (d), 130.2 (d), 138.6 (s).

3n:[44] ^1H NMR δ 0.07 (s, 9H), 1.22 (d, J = 7.6 Hz, 3H), 1.83 (pd, J = 7.6 Hz, 0.8 Hz, 1H), 6.25 (d, 16 Hz, 1H), 6.35 (dd, J = 16 Hz, 7.6 Hz, 1H), 7.06−7.44 (m, 5H); ^{13}C NMR δ −3.39 (q), 13.5 (q), 27.3 (d), 124.4 (d), 125.7 (d), 126.2 (d), 128.4 (d), 134.4 (d), 143.1 (s).

3p: ^1H NMR δ 0.00 (s, 3H), 0.01 (s, 3H), 1.02−1.81 (m, 7H), 1.37 (s, 2H), 1.43 (s, 3H), 4.39−4.32 (m, 2H), 4.90−4.96 (m, 1H), 7.04−7.07 (m, 3H), 7.20−7.27 (m, 2H); ^{13}C NMR δ −2.73 (q), 20.8 (q), 26.6 (t), 28.0 (t), 30.9 (t), 31.5 (t), 41.0 (d), 108.3 (t), 119.1 (d), 127.6 (d), 128.8 (d), 133.0 (s), 133.6 (d), 134.4 (s), 150.2 (s). Anal. Calcd for $C_{18}H_{26}Si$: C, 79.93; H, 9.69. Found: C, 80.22; H, 9.66.

3q: ^1H NMR δ 0.22 (s, 6H), 1.45−1.59 (m, 5H), 1.60 (dd, J_{H-H} = 8.4 Hz, $^3J_{H-F}$ = 5.2 Hz, 2H), 2.04−2.12 (m, 5H), 5.07 (tp, J = 8.4 Hz, 1.2 Hz, 1H); ^{13}C NMR δ −1.66 (q, $^2J_{C-F}$ = 15 Hz), 17.5 (t, $^2J_{C-F}$ = 13 Hz), 26.9 (t), 27.5 (t), 28.4 (t), 28.7 (t), 37.3 (t), 113.5 (d, $^3J_{C-F}$ = 1.6 Hz), 139.1 (s). Methylation of **3q** with MeLi in THF at −40 °C afforded **3b** quantitatively.

***trans*-3r:** ^1H NMR δ 0.06 (s, 9H), 1.53−1.57 (m, 1H), 1.66 (td, J_{gem} = 12 Hz, J_{ax-ax} = 12 Hz, J_{ax-ex} = 5.7 Hz, 1H), 1.65−1.67 (m, 3H), 1.71 (t, J = 1.1 Hz, 3H), 1.84 (ddd, J_{gem} = 12 Hz, J_{ex-ax} = 4.0 Hz, J_{ex-ex} = 1.8 Hz, 1H), 1.90−2.18 (m, 3H), 4.66−4.70 (m, 2H), 5.27−5.31 (m, 1H); ^{13}C NMR δ −0.50 (q), 20.5 (q), 24.77 (q), 30.5 (t), 30.74 (t), 31.8 (d), 39.4 (d), 108.3 (t), 118.5 (d), 135.7 (s), 150.3 (s). Anal. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found: C, 74.96; H, 11.59.

***cis*-3r** (obtained as a 1:1 mixture of the *cis*- and *trans*-isomers): ^{13}C NMR δ −2.33 (q), 21.0 (q), 24.67 (q), 30.68 (t), 30.9 (t), 31.4 (d), 41.8 (d), 108.1 (t), 120.8 (d), 135.0 (s), 150.8 (s). Anal. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found (as a 1:1 mixture of the *cis*- and *trans*-isomers): C, 74.89; H, 11.62.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of **3i**, **3q**, and *cis*-**3r** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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