Palladium Complex Catalyzed Acylation of Allylic Esters with Acylsilanes

Yasushi Obora,‡ Yasuhiro Ogawa,† Yuji Imai,† Takashi Kawamura,† and Yasushi Tsuji*,‡

Contribution from the Catalysis Research Center and Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0811, Japan, and Department of Chemistry, Faculty of Engineering, Gifu University, Gifu 501-1893, Japan

Received March 13, 2001

Abstract: Acylation of allylic esters (**2**) with acylsilanes (**1**) in the presence of a catalytic amount (5 mol %) of a palladium complex is reported. The reaction proceeds selectively to afford β,γ-unsaturated ketones (**3**) in high yields. [Pd(η^3-$C_6H_5CH{=}CHCH_2$)(CF_3COO)]$_2$ (**4a**) showed the best catalytic activity. After the reaction, formation of $CF_3COOSiMe_3$ (**5a**) was confirmed by ^{29}Si NMR measurement of the resulting reaction mixture, indicating the trimethylsilyl moiety effectively traps the CF_3COO leaving group from **2**. The leaving group of the allylic esters affects the reaction considerably: allylic trifluoroacetate gave the best result, while the corresponding acetates and trichloroacetates did not afford any acylation products at all. Stoichiometric reaction of **4a** with **1** gave acylation product **3** with a formation of **5a** and Pd(0), whereas no acylation reaction took place with the corresponding acetate complex [Pd(η^3-$C_6H_5CH{=}CHCH_2$)(CH_3COO)]$_2$ (**4b**). A DFT calculation suggests that interaction of high-lying HOMO of **1** and low-lying LUMO of η^3-allylpalladium trifluoroacetate intermediate **4** would be indispensable in the catalytic cycle.

Introduction

The palladium(0)-catalyzed nucleophilic substitution of allylic esters[1] via η^3-allylpalladium intermediate is one of the most important homogeneous catalyses, since it has numerous applicabilities in synthetic organic chemistry.[2] So far, a number of nucleophiles such as stabilized carbanions,[3a,b] enolates,[3c,d] organotin compounds,[3e−g] and amines[3h,i] have been successfully employed in the reaction. However, functionality that can be directly introduced to the allylic system is still limited. Therefore, unexploited and capable functionalities should be explored to make the catalytic reaction more proficient.

β,γ-Unsaturated carbonyl compounds are versatile starting materials in a variety of synthetic reactions.[4] If acyl functionality can be introduced in the palladium-catalyzed nucleophilic substitution of allylic esters, the reaction will be a potent synthetic method. However, generation of nucleophilic acyl species[5] is usually difficult, since carbonyl functionality is found to be a good *electrophile*. Consequently, to realize the acylation reaction of allylic esters, carbonylative three-component coupling reactions with allylic benzoates, carbon monoxide, and organozinc compound were reported.[6,7] More recently, acylzirconocene chloride[8a] and chromium carbene complexes[8b] were employed in palladium-catalyzed acylation of allylic acetates or allylic bromide, respectively, but both of these reactions afforded acylation products only as a mixture of regioisomers.

We have developed palladium-catalyzed silylation[9] and cyanation[10] reactions of allylic esters using disilanes and silyl

‡ Hokkaido University.
† Gifu University.

(1) (a) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: Chichester, UK, 1995. (b) Harrington, P. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, UK, 1995; Vol. 12, pp 797−904. (c) Trost, B. M. *Acc. Chem. Res.* **1996**, *29*, 355. Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (d) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (e) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140. (f) Tsuji, J. *Pure Appl. Chem.* **1980**, *54*, 197. Tsuji, J. *Pure Appl. Chem.* **1980**, *58*, 869. (g) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361. (h) Matsuhashi, H.; Asai, S.; Hirabayashi, K.; Hatanaka, Y.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1943.

(2) (a) Godlesky, S. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, UK, 1991; Vol. 4, pp 585−661. (b) McQuillin, F. J.; Parker, D. G.; Stephenson, G. R. *Transition Metal Organometallics for Organic Synthesis*; Cambridge: New York, 1991; Chapter 6. (c) Harrington, P. J. *Transition Metals in Total Synthesis*; Wiley: New York, 1990; Chapter 3.

(3) (a) Tsuji, J.; Takahashi, H.; Morikawa, M. *Tetrahedron Lett.* **1965**, *21*, 4387. (b) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, UK, 1982; Vol. 8, Chapter 57, p 799. (c) Negishi, E.; Matsushita, H.; Chatterjee, S.; John, R. A. *J. Org. Chem.* **1982**, *47*, 3188. (d) Trost, B. M.; Self, C. R. *J. Org. Chem.* **1984**, *49*, 468. (e) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, *21*, 2595. (f) Godschalx, J. P.; Stille, J. K. *Tetrahedron Lett.* **1980**, *21*, 2599. (g) Gollaszewski, A.; Schwartz, J. *Organometallics* **1985**, *4*, 417. (h) Trost, B. M.; Genet, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 8516. (i) Trost, B. M.; Keinan, E. *J. Org. Chem.* **1979**, *44*, 3451.

(4) (a) Van Der Weerdt, A. J. A.; Cerfontain, H. *Tetrahedron* **1981**, *37*, 2121. (b) Ito, N.; Etoh, T.; Hagiwara, H.; Kato, M. *Synthesis* **1997**, 153. (c) Borecka, B.; Gudmundsdottir, A. D.; Olovsson, G.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1994**, *116*, 10322. (d) Banerjee, A. K.; Acevedo, J. C.; Gonzalez, R.; Rojas, A. *Tetrahedron* **1991**, *47*, 2081.

(5) (a) Lever, O. W., Jr. *Tetrahedron* **1976**, *32*, 1943 and references therein. (b) Seyferth, D.; Hui, R. C.; Wang, W.-L.; Archer, C. *J. Org. Chem.* **1993**, *58*, 5843. (c) Hanzawa, Y.; Narita, K.; Taguchi, T. *Tetrahedron Lett.* **2000**, *41*, 109.

(6) Tamaru, Y.; Yasui, K.; Takanabe, H.; Tanaka, S.; Fugami, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 645.

(7) For similar acylation of allylic chlorides by carbonylative three-component coupling reaction with allylic halides, carbon monoxide, and organotin, see: (a) Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833. (b) Merrifield, J. H.; Godschalx, J. P.; Stille, J. K. *Organometallics* **1984**, *3*, 1108.

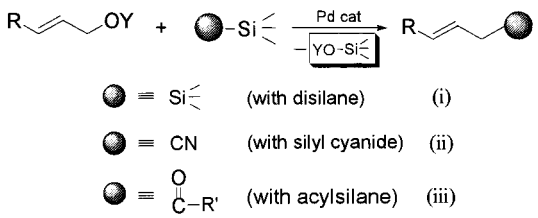
(8) (a) Hanzawa, Y.; Tabuchi, N.; Taguchi, T. *Tetrahedron Lett.* **1998**, *39*, 6249. (b) Sakurai, H.; Tanabe, K.; Narasaka, K. *Chem. Lett.* **1999**, 309.

(9) (a) Tsuji, Y.; Funato, M.; Ozawa, M.; Ogiyama, H.; Kajita, S.; Kawamura, T. *J. Org. Chem.* **1996**, *61*, 5779. (b) Tsuji, Y.; Kajita, S.; Isobe, S.; Funato, M. *J. Org. Chem.* **1993**, *58*, 3607.

(10) (a) Tsuji, Y.; Kusui, T.; Kojima, T.; Sugiura, Y.; Yamada, N.; Tanaka, S.; Ebihara, M.; Kawamura, T. *Organometallics* **1998**, *17*, 4835. (b) Tsuji, Y.; Yamada, N.; Tanaka, S. *J. Org. Chem.* **1993**, *58*, 16.

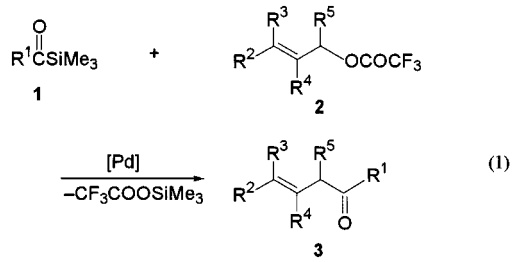
10.1021/ja010674p CCC: $20.00
Published on Web 10/09/2001

Scheme 1



cyanide as silylation and cyanation reagents, respectively (Scheme 1, i and ii). In these reactions, the silyl and the cyano functionalities were transferred from the silyl moieties of the reagents with concomitant formation of the Si−O bonds.

In this paper, we design the novel acylation reaction using acylsilanes (**1**)[11] as acylation reagents (Scheme 1, iii). A wide variety of acylsilanes are prepared readily, and these stable and easily accessible substrates are utilized in various organic syntheses.[12] Nevertheless, so far, there is only one example for the transition metal catalyzed reaction with **1** as a substrate, i.e., benzocyclobutanone synthesis from *o*-(α-phenylthio)alkylbenzoyltrimethylsilanes.[13] Herein, we report that **1** functions as a good acylation reagent for allylic trifluoroacetates in the presence of a palladium catalyst via Si−C *σ*-bond cleavage of **1** with formation of the Si−O bond (eq 1).

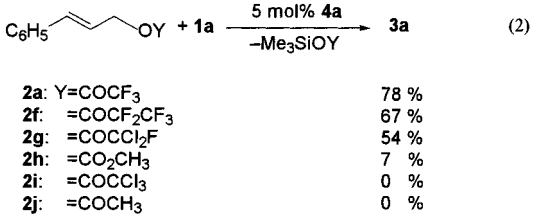


Results and Discussion

Results are listed in Table 1. When the reaction of 3-phenylpropionyltrimethylsilane (**1a**) with cinnamyl trifluoroacetate (**2a**) was carried out in the presence of a catalytic amount of $[Pd(\eta^3\text{-}C_6H_5CH{=}CHCH_2)(CF_3COO)]_2$ (**4a**) (5 mol %), the acylation product (**3a**) was obtained regio- and stereoselectively in high yield (entry 1). The product is only *β*,*γ*-unsaturated ketone, and no α,*β*-unsaturated isomers were detected. ^{29}Si NMR measurement of the resulting reaction mixture after the reaction confirmed a comparable formation of $CF_3COOSiMe_3$ (**5a**: 33.6 ppm, lit.[14] 33.1 ppm), indicating the Me_3Si moiety of **1a** effectively trapped the CF_3COO leaving group from **2a**. The reaction of **1a** with **2a** was carried out under various conditions. As a catalyst precursor, **4a** gave the best result (entry 1). Other palladium complexes showed lower catalytic activities: the yield of **3a** was 53% with $Pd(OCOCF_3)_2$, 27% with $Pd(DBA)_2$, 12% with $Pd(OCOCH_3)_2$, and 0% with $Pd(OSO_2CF_3)_2$. Palladium complexes with phosphine ligands such as $PdMe_2(PMePh_2)_2$, $PdCl_2(PPh_3)_2$, $Pd(DBA)_2$ combined with P(*n*-Bu)$_3$ (P/Pd = 3), and $Pd(DBA)_2$ combined with $P(OCH_2)_3CC_2H_5$ (P/Pd = 3) totally suppressed the catalytic activity. Addition of CsF or *n*-Bu_4NF to the catalyst system lowered the yield to <5%.[15] Other metal complexes such as $Pt(DBA)_2$ and (C_5Me_5)-RuCl(COD) did not show any catalytic activity at all. As for the solvent, THF gave the best result. Toluene and dioxane could be used similarly. However, strongly coordinated solvents such as CH_3CN and DMF lowered the yields considerably.

The acylation reaction of **2a** with acylsilanes such as nonanoyl- (**1b**), butyryl- (**1c**), 4-methylvaleryl- (**1d**), and 3-methylbutyrylsilane (**1e**) gave the corresponding (*E*)-*β*,*γ*-unsaturated ketones regio- and stereoselectively in good yields (entries 2−5). Various allylic trifluoroacetates (**2b**−**e**) can be employed in the reaction affording the corresponding acylation products regioselectively (entries 6−10).[16] However, the reaction of benzoyltrimethylsilane ($C_6H_5(C{=}O)SiMe_3$) with **2a** was sluggish and not stereoselective to afford the corresponding ketone in 26% yield with stereoisomers (*E*:*Z* = 88:12).

Noteworthy is that leaving groups of the allylic esters affect the reaction considerably (eq 2). The trifluoroacetate (**2a**) gave



the highest yield. The corresponding pentafluoropropionate (**2f**) and dichlorofluoroacetate (**2g**) gave **3a** in 67% and 54% yields, respectively. The carbonate (**2h**) only afforded **3a** in 7% yield. Further, the corresponding trichloroacetate (**2i**) and acetate (**2j**) did not afford any acylation product at all.[17] Among the acetates, esters of stronger acid seem to have higher reactivity.

In the previous silylation[9] and cyanation[10] reaction of allylic esters, the silyl moiety effectively trapped the oxygen-containing leaving groups by forming the Si−O bond (Scheme 1). Strong oxophilicity of the silicon atom may be an important driving force for these successful reactions. In the present acylation reaction, a comparable formation of $CF_3COOSiMe_3$ (**5a**) was confirmed after the reaction by ^{29}Si NMR (vide supra), suggesting the strong oxophilicity of the silicon atom might operate similarly. For the marked effect of the trifluoroacetate moiety (**2a**) as compared with acetate (**2j**) in eq 2, the stronger Si−O bond of **5a** than that of $CH_3COOSiMe_3$ (**5b**), which should have been obtained in the reaction with **2j**, might be responsible. Thus, to estimate bond dissociation energies of the Si−O bonds of **5a** and **5b**, ab initio molecular orbital calculation with the MP4/6-31+G(2d,p)//B3LYP/6-31G(d) method[19] was

(11) (a) Page, P. C. B.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147. (b) Qi, H.; Curran, D. P. In *Comprehensive Organic Functional Group Transformations*; Katrinsky, A. R., Meth-Cohn, O., Rees, C. W., Moody, C. J., Eds.; Pergamon: Oxford, UK, 1995; pp 409−431. (c) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; John Wiley & Sons: New York, 2000. (d) Cirillo, P. F.; Panek, J. S. *Org. Prep. Proc. Int.* **1992**, *24*, 553.

(12) (a) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic: London, UK, 1988; Chapter 12. (b) Ricci, A.; Degl'Inniocenti, A. *Synthesis* **1989**, 647. (c) Cheng, S.-y.; Jiaang, W.-f.; Cherng, C.-d.; Tang, K.-h.; Huang, C.-h.; Tsai, Y.-m. *J. Org. Chem.* **1997**, *62*, 9089. (d) Bonini, B. F.; Comes-Franchini, M.; Fochi, M.; Mazzanti, G.; Ricci, A. *J. Organomet. Chem.* **1998**, *567*, 181. (e) Sakurai, H.; Yamane, M.; Iwata, M.; Saito, N.; Narasaka, K. *Chem. Lett.* **1996**, 841.

(13) Kang, J.; Choi, Y. R.; Kim, B. J.; Jeong, J. U.; Lee, S.; Lee, J. H.; Pyun, C. *Tetrahedron Lett.* **1990**, *31*, 2713.

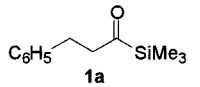
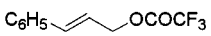
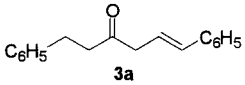
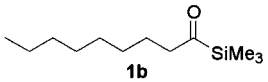
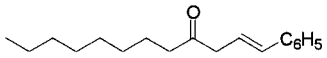
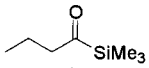
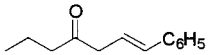
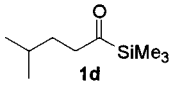
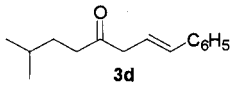
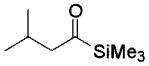
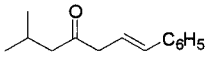
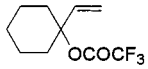
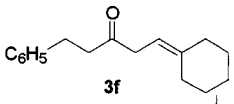
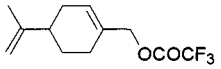
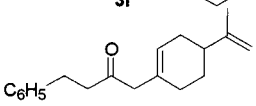
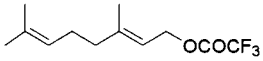
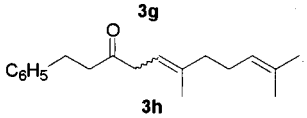
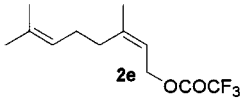
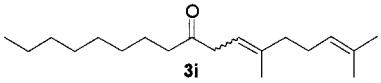
(14) Bassingdale, A. R.; Posnan, T. B. *J. Organomet. Chem.* **1979**, *175*, 273.

(15) (a) Degl'Inniocenti, A.; Ricci, A.; Mordini, A.; Reginato, G.; Colotta, V. *Gazz. Chim. Ital.* **1987**, *117*, 645. (b) Ricci, A.; Degl'Innocenti, A.; Chimichi, S.; Fiorenza, M.; Rossini, G.; Bestmann, H. J. *J. Org. Chem.*, **1985**, *50*, 130.

(16) Allylic trifluoroacetates with substituents at the α-position such as 2-cyclohexenyl trifluoroacetate did not give any acylation products at all.

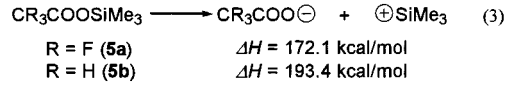
(17) In eq 2, only allylic esters containing a fluorine atom (**2a**, **2f**, and **2g**) afford the acylation product. It is well-known that a fluoride anion strongly interacts with a silicon atom of silanes.[18] However, there will be no direct interaction between the fluorine atom of **2** and the silicon atom of **1** in eq 2, since ^{29}Si NMR measurement of a mixture of **1a** and **2a** in the absence of a palladium catalyst at 70 °C in toluene-d_8 showed the ^{29}Si resonance of **1a** at 9.73 ppm did not change.

Table 1. Palladium-Complex-Catalyzed Acylation of Allylic Trifluoroacetates[a]

	1	2	3	yield/%[b]
1	 **1a**	 **2a**	 **3a**	(78)60
2	 **1b**	**2a**	 **3b**	63
3	 **1c**	**2a**	 **3c**	(65)55
4	 **1d**	**2a**	 **3d**	56
5	 **1e**	**2a**	 **3e**	43
6	**1a**	 **2b**	 **3f**	46
7	**1a**	 **2c**	 **3g**	(49)36
8	**1a**	 **2d**	 **3h**	(75)58[c]
9	**1a**	 **2e**	**3h**	44[d]
10	**1b**	**2d**	 **3i**	60[e]

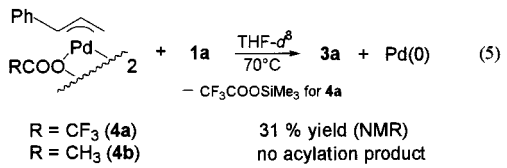
[a] Conditions: **1** (0.50 mmol), **2** (1.0 mmol), **4a** (0.025 mmol), and THF (0.5 mL) under reflux for 16 h. [b] Isolated yields. Numbers in parentheses show GLC yield determined by the internal standard method. [c] *E*:*Z* = 71:29. [d] *E*:*Z* = 63:37. [e] *E*:*Z* = 68:32.

carried out for the heterolytic (eq 3) and the homolytic cleavage (eq 4). However, in both cases, lower (by ca. 20 kcal/mol) Si−O



bond dissociation energy was calculated for **5a** than for **5b**. Consequently, simple comparison of the Si−O bond dissociation energies between **5a** and **5b** could not explain the distinct effect of the trifluoroacetate moiety of **2a** in eq 2.

The most plausible catalytic cycle for the present acylation is shown in Scheme 2. The catalytic cycle will be initiated by the oxidative addition of allylic ester (**2**) to Pd(0) to give an η^3-allylpalladium intermediate (**4**) (step a). This step has been well-studied.[20] Subsequently **4** reacts with acylsilane (**1**) to afford **5** and the acylation product (**3**), possibly via **6**. There is, however, no precedent for the reactions of η^3-allylpalladium species with **1**.[21] Therefore, a model reaction for step b was carried out. As model compounds of **4** for the reaction of **2a** and **2j**, **4a** and (η^3-cinnamyl)palladium acetate dimer (**4b**) were prepared, respectively. Then, stoichiometric reaction of **4a** and **4b** with **1a** was carried out at 70 °C as the model for step b (eq 5). As a result, **4a** provided **3a** with a concomitant formation

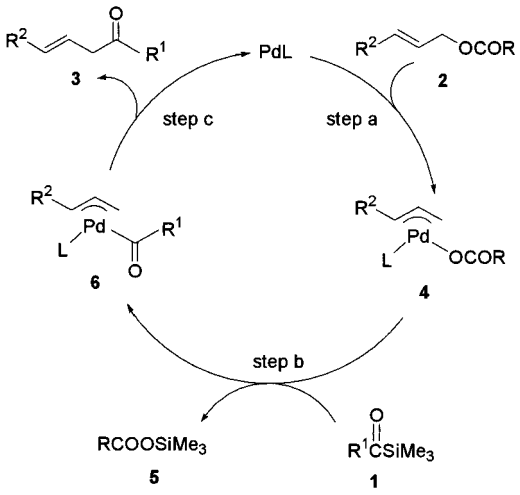


of $CF_3COOSiMe_3$ (**5a**) and Pd (0),[22] while no acylation product

(18) (a) Damrauer, R.; O'Connell, B.; Danahey, S. E.; Simon, R. *Organometallics* **1989**, *8*, 1167. (b) Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490.

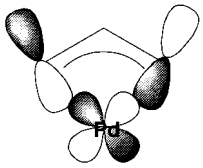
(19) The Gaussian 98 package: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gompartz, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian: Pittsburgh, PA, 1988.

Scheme 2



was obtained at all by the reaction of **4b** with **1a**. This observation is very consistent with the catalytic reaction (eq 2), in which **2a** gave the acylated product, while **2j** did not.

One of the most characteristic feature of acylsilanes (**1**) is their much lower oxidation potentials than those of the corresponding ketones and aldehydes[23a,b] which induce unique spectroscopic behavior.[23c,d] This is due to higher HOMO[24a] levels caused by strong mixing of the Si−CO σ-orbital and the localized oxygen lone pair.[24b,c] Thus, electrochemical oxidation of acylsilanes occurs easily with a facile cleavage of the Si−CO σ-bonds.[23a,b] As shown in eq 5, the reactivity of **4a** and **4b** is quite different. To gain further insight into this different reactivity, DFT calculation was performed on $[Pd(\eta^3\text{-}C_3H_5)(CF_3COO)]_2$ (**4c**) and $[Pd(\eta^3\text{-}C_3H_5)(CH_3COO)]_2$ (**4d**), models for **4a** and **4b**, with the B3LYP/LANL2DZ method.[19] LUMOs of **4c** and **4d** look very similar, consisting of antibonding interaction between nonbonding π (nπ) of the η^3-C_3H_5 and the palladium d orbital (**8**, see Supporting Information). However, LUMO



8

energy of **4c** (−2.537 eV) is much lower than that of **4d** (−1.628 eV). It might be conceivable that HOMO-LUMO interaction[25] (one-electron transfer or concerted) between **1** and **4** is requisite in eq 5 and the catalytic cycle (step b, Scheme 2). To realize such interaction with the high-lying HOMO of **1**, the lower lying LUMO of **4** containing the CF_3COO moiety would be indispensable.

Experimental Section

Materials. The reagents and the solvents were dried and purified before use by the usual procedures.[26] The following catalyst precursors and complexes were prepared by the published methods: **4a**,[27] **4b**,[28] $Pd(OCOCF_3)_2$,[29] $Pd(OCOCH_3)_2$,[30] $Pd(OSO_2CF_3)_2$,[30] $Pd(DBA)_2$,[31] $PdCl_2(PMePh_2)_2$,[32] and $Pd(PPh_3)_4$.[33] Acylsilanes **1** were prepared according to published methods.[12a−d] Allylic trifluoroacetates were obtained with the corresponding alcohols.

Analytical and Computational Procedures. All manipulations were performed under argon atmosphere in conventional Schlenk-type glassware on a dual-manifold Schlenk line. NMR spectra were recorded on a Bruker ARX-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{29}Si, 79.3 MHz). The mass spectra were measured on a Shimadzu QP-5050A (EI) and a JEOL JMS-700TZ (HRMS, EI). The GC analysis was made on a Shimadzu GC-8APF equipped with an integrator (C-R6A) with a column (3 mm i.d. × 3 m) packed with Silicon OV-17 (2% on Uniport HP, 60/80 mesh) or Apiezon Grease L (5% on Uniport HP, 60/80 mesh). IR spectra were measured on a Shimadzu FT-IR-8300. Elemental analysis was preformed at the Center for Instrumental Analysis of Hokkaido University. Molecular orbital calculations were performed with the Gaussian 98 package[19] on an HP Exemplar V2500 at the Computing Center of Hokkaido University.

Acylation Procedure. A typical procedure is described for the synthesis of **3a**. A mixture of **1a** (103 mg, 0.5 mmol), **2a** (230 mg, 1.0 mmol), **4a** (14 mg, 0.025 mmol), and THF (0.5 mL) and a magnetic stirring bar were placed under an argon flow in a 20 mL round-bottomed flask with stirring for 16 h under reflux. After the reaction, the whole mixture was passed through a short Florisil column (8 mm i.d. × 50 mm) to afford a clear yellow solution. GLC analysis (OV-17) with eicosane as an internal standard showed **3a** was formed in 78% yield. The product (**3a**) was isolated by medium-pressure column chromatography (silica gel with hexane/EtOAc = 98/2) followed by Kugelrohr distillation in 60% yield (pot temperature 180 °C/1 mmHg).

3a: white solid; mp 56−57 °C; ^{1}H NMR ($CDCl_3$) δ 2.83 (t, J = 7 Hz, 2H), 2.95 (t, J = 7 Hz, 2H), 3.31 (d, J = 7 Hz, 2H), 6.31 (dt, J = 16 Hz, 7 Hz, 1H), 6.47 (d, J = 16 Hz, 1H), 7.21−7.39 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 29.8 (CH_2), 44.0 (CH_2), 47.2 (CH_2), 121.9 (CH), 126.2 (CH), 126.3 (CH), 127.6 (CH), 128.4 (CH), 128.57 (CH), 128.60 (CH), 133.9 (CH), 136.9 (C), 141.0 (C), 207.7 (C); IR (neat, cm^{-1}) 1713 ($\nu_{C=O}$); MS (relative intensity) m/z 250 (M^+, 6), 134 (3), 117 (19), 105 (100), 91 (95); HRMS calcd for $C_{18}H_{18}O$ 250.1358, found 250.1360. Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.07; H, 7.31.

3b:[34] colorless oil; 148 °C(pot)/0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7 Hz, 3H), 1.20−1.36 (m, 10H), 1.54−1.63 (m, 2H), 2.48 (t, J = 7 Hz, 2H), 3.31 (d, J = 7 Hz, 2H), 6.32 (dt, J = 16, 7 Hz, 1H), 6.47

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

(21) For reactions of η^3-allylpaladium chloride with acyl transition metal complexes, see: Hegedus, L. S.; Tamura, R. *Organometallics* **1982**, *1*, 1188.

(22) The reaction would proceed via (η^3-allyl)(acyl)palladium species **6**. However, we could not isolate or even detect **6**, which may be unstable under the reaction conditions to afford **3** and Pd(0) black or mirror.

(23) (a)Yoshida, J.-i.; Itoh, M.; Matsunaga, S.-i.; Isoe, S. *J. Org. Chem.* **1992**, *57*, 4877. (b) Yoshida, J.-i.; Matsunaga, S.-i.; Isoe, S. *Tetrahedron Lett.* **1989**, *30*, 5293. (c) Brook, A. G.; Quigley, M. A.; Peddle, G. J. D.; Schwartz, N. V.; Warner, C. M. *J. Am. Chem. Soc.* **1960**, *82*, 102. (d) Harnish, D. F.; West, R. *Inorg. Chem.* **1963**, *2*, 1082.

(24) (a) Since there has been no explicit comparison of HOMO energy between acylsilanes (**1**) and the corresponding ketones, it was calculated for $Me(C{=}O)SiMe_3$ (**1f**) and $Me(C{=}O)CMe_3$ (**7**): HOMO energy, −9.747 (**1f**) and −10.580 eV (**7**) by HF/6-31G(2d, p); −5.940 (**1f**) and −6.463 eV (**7**) by B3LYP/6-31G(d). (b) Bock, H.; Seidl, H. *J. Am. Chem. Soc.* **1969**, *91*, 355. (c) Ramsey, B. G.; Brook, A.; Bassindale, A. R.; Bock, H. *J. Organomet. Chem.* **1974**, *74*, C41.

(25) (a) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985. (b) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976. (c) Rauk, A. *Orbital Interaction Theory of Organic Chemistry*, 2nd ed.; Wiley: New York, 2001.

(26) Armagego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, UK, 1997.

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

(28) (a) Robinson, S. D.; Shaw, B. L. *J. Organomet. Chem.* **1965**, *3*, 367. (b) Takahashi, Y.; Tsukiyama, K.; Sakai, S.; Ishii, Y. *Tetrahedron Lett.* **1970**, 1913.

(29) Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.

(30) Murata, S.; Ido, Y. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1746.

(31) (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.

(32) Jenkins, J. M.; Verkade, J. G. *Inorg. Synth.* **1968**, *11*, 108.

(33) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(34) Yasui, K.; Fugami, K.; Tanaka, S.; Tamaru, Y. *J. Org. Chem.* **1995**, *60*, 1365.

(d, J = 16 Hz, 1H), 7.20−7.43 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.1 (CH_3), 22.7 (CH_2), 23.7 (CH_2), 29.16 (CH_2), 29.22 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 42.5 (CH_2), 47.0 (CH_2), 122.2 (CH), 126.3 (CH), 127.5 (CH), 128.6 (CH), 133.6 (CH), 136.9 (C), 209.0 (C); IR (neat, cm^{-1}) 1717 ($\nu_{C=O}$); MS (relative intensity) m/z 258 (M^+, 5), 141 (63), 123 (5), 117 (26), 116 (8), 115 (26), 91 (14), 81 (15), 71 (75), 67 (10), 57 (100), 55 (23).

3c:[35] colorless oil; 154 °C (pot) /0.5 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 7 Hz, 3H), 1.63 (sex, J = 7 Hz, 2H), 2.47(t, J = 7 Hz, 2H), 3.31 (d, J = 7 Hz, 2H), 6.33 (dt, J = 16, 7 Hz, 1H), 6.47 (d, J = 16 Hz, 1H) 7.21−7.41 (m, 5H); ^{13}C NMR ($CDCl_3$) 13.8 (CH_3), 17.2 (CH_2), 44.4 (CH_2), 47.0 (CH_2), 122.2 (CH), 126.3 (CH), 127.5 (CH), 128.7 (CH), 133.6 (CH), 136.9 (C), 209.0 (C); IR (neat, cm^{-1}) 1715 ($\nu_{C=O}$); MS (relative intensity) m/z 188 (5), 117 (20), 115 (22), 91 (11), 71 (100).

3d: colorless oil; 178 °C (pot)/0.5 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.88 (d, J = 7 Hz, 6H), 1.44−1.62 (m, 3H), 2.48 (t, J = 7 Hz, 2H), 3.32 (d, J = 7 Hz, 2H), 6.32 (dt, J = 16, 7 Hz, 1H), 6.48 (d, J = 16 Hz, 1H), 7.28−7.41 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 22.4 (CH_3), 27.7 (CH), 32.5 (CH_2), 40.6 (CH_2), 46.9 (CH_2), 122.3 (CH), 126.3 (CH), 127.5 (CH), 128.6 (CH), 133.6 (CH), 137.0 (C), 209.2 (C); IR (neat, cm^{-1}) 1715 ($\nu_{C=O}$); MS (relative intensity) m/z 216 (M^+, 6), 145 (3), 117 (31), 115 (29), 99 (73), 91 (19), 81 (100), 71 (38), 57 (11), 55 (16). HRMS calcd for $C_{15}H_{20}O$ 216.1514, found 216.1508.

3e: colorless oil; 165 °C (pot)/0.5 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.94 (d, J = 7 Hz, 6H), 2.15−2.25 (m, 1H), 2.39 (d, J = 7 Hz, 2H), 3.32 (d, J = 7 Hz, 2H), 6.32 (dt, J = 16, 7 Hz, 1H), 6.48 (d, J = 16 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 23.0 (CH_3), 25.0 (CH), 47.8 (CH_2), 51.9 (CH_2), 122.5 (CH), 126.7 (CH), 127.9 (CH), 129.0 (CH), 134.1 (CH), 137.3 (C), 209.4 (C); IR (neat, cm^{-1}) 1713 ($\nu_{C=O}$); MS (relative intensity) m/z 202 (M^+, 4), 117 (15), 115 (16), 91 (9), 85 (62), 57 (100); HRMS calcd for $C_{14}H_{18}O$ 202.1358, found 202.1352.

3f: colorless oil; 180 °C (pot)/1 mmHg; ^{1}H NMR ($CDCl_3$) δ 1.43−1.62 (m, 6H), 2.06−2.16 (m, 4H), 2.74 (t, J = 7 Hz, 2H), 2.89 (t, J = 7 Hz, 2H), 3.09 (d, J = 7 Hz, 2H), 5.21 (t, J = 7 Hz, 1H), 7.15−7.22 (m, 3H), 7.25−7.31 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 26.7 (CH_2), 27.6 (CH_2), 28.4 (CH_2), 29.0 (CH_2), 29.8 (CH_2), 37.1 (CH_2), 42.1 (CH_2), 43.6 (CH_2), 112.4 (CH), 126.1 (CH), 128.3 (CH), 128.5 (CH), 141.2 (C), 143.9 (C), 208.7 (C); IR (neat, cm^{-1}) 1715 ($\nu_{C=O}$); MS (relative intensity) m/z 242 (M^+, 9), 133 (14), 109 (11), 105 (100), 91 (63), 79 (24), 77 (19), 67 (59), 65 (15), 55 (23); HRMS calcd for $C_{17}H_{22}O$ 242.1671, found 242.1662.

3g: ^{1}H NMR ($CDCl_3$) δ 1.38−1.52 (m, 1H), 1.74 (s, 3H), 1.87−2.02 (m, 3H), 2.06−2.22 (m, 3H), 2.78 (t, J = 7 Hz, 2H), 2.90 (t, J = 7 Hz, 2H), 3.02 (s, 2H), 4.72 (s, 1H), 4.74 (s, 1H), 5.51−5.57 (m, 1H), 7.17−7.23 (m, 3H), 7.26−7.32 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.2 (CH_3), 28.0 (CH_2), 29.5 (CH_2), 30.2 (CH_2), 31.2 (CH_2), 41.0 (CH_2), 43.6 (CH_2), 52.7 (CH), 109.5 (CH_2), 126.3 (CH), 128.7 (CH), 128.9 (CH), 129.3 (CH), 131.7 (C), 141.6 (C), 150.1 (C), 209.0 (C); IR (neat, cm^{-1}) 1715 ($\nu_{C=O}$); MS (relative intensity) m/z 268 (M^+, 3), 135 (9), 133 (19), 120 (12), 105 (100), 93 (10), 92 (9), 91 (96), 79 (18), 77 (17), 65 (12), 55 (9); HRMS calcd for $C_{19}H_{24}O$ 268.1827, found 268.1826.

(35) Shono, T.; Nishiguchi, I.; Ohmizu, H. *Chem. Lett.* **1977**, 1321.

3h (as a mixture of E and Z)**:** ^{1}H NMR ($CDCl_3$) δ 1.57−1.77 (m, 9H), 1.99−2.12 (m, 4H), 2.65−2.77 (m, 2H), 2.87−2.98 (m, 2H), 3.09 (d, J = 7 Hz, 2H), 5.07 (t, J = 6 Hz, 1H), 5.29 (t, J = 7 Hz, 1H), 7.14−7.22 (m, 3H), 7.24−7.31 (m, 2H); ^{13}C NMR (E isomer) δ 16.4 (CH_3), 17.7 (CH_3), 25.7 (CH_3), 26.5 (CH_2), 29.8 (CH_2), 39.6 (CH_2), 42.9 (CH_2), 43.8 (CH_2), 115.6 (CH), 123.8 (CH), 126.4 (CH), 128.3 (CH), 128.5 (CH), 131.7 (C), 139.5 (C), 141.1 (C), 208.7 (C); ^{13}C NMR (Z isomer) δ 17.7 (CH_3), 23.5 (CH_3), 25.7 (CH_3), 26.3 (CH_2), 29.8 (CH_2), 32.8 (CH_2), 42.6 (CH_2), 43.7 (CH_2), 116.3 (CH), 123.9 (CH), 126.4 (CH), 128.3 (CH), 128.5 (CH), 132.0 (C), 139.4 (C), 141.1 (C), 208.7 (C); IR (neat, cm^{-1}) 1715 ($\nu_{C=O}$); GC/MS (E isomer), (relative intensity) m/z 270 (M^+, 1), 227 (6), 201 (5), 133 (16), 122 (17), 107 (12), 105 (100), 91 (76), 79 (10), 77 (12), 69 (63), 67 (13); GC/MS (Z isomer) (relative intensity) m/z 270 (M^+, 1), 227 (4), 201 (14), 133 (14), 122 (29), 107 (17), 105 (100), 95 (13), 91 (76), 81 (19), 79 (15), 77 (16), 71 (13), 69 (62), 65 (11), 57 (25), 55 (23); GC/HRMS (E isomer) calcd for $C_{19}H_{26}O$ 270.1984, found 270.1978; GC/HRMS (Z isomer) calcd for $C_{19}H_{26}O$ 270.1984, found 270.1979.

3i (as a mixture of E and Z)**:** ^{1}H NMR δ 1.01 (t, J = 7 Hz, 3H), 1.22−1.41 (m, 12H), 1.60−1.67 (m, 6H), 1.76 (s, 3H), 2.10−2.26 (m. 6H), 2.95−3.02 (m, 2H), 5.23−5.31 (m, 1H), 5.52−5.61 (m, 1H); ^{13}C NMR (E isomer) δ 14.5 (CH_3), 16.6 (CH_3), 17.9 (CH_3), 23.2 (CH_2), 24.3 (CH_2), 26.0 (CH_3), 27.1 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 30.0 (CH_2), 32.4 (CH_2), 40.2 (CH_2), 42.2 (CH_2), 42.9 (CH_2), 117.3 (CH), 124.8 (CH), 131.6 (C), 138.6 (C), 207.2 (C); ^{13}C NMR (Z isomer) δ 14.5 (CH_3), 16.6 (CH_3), 23.2 (CH_2), 23.7 (CH_3), 24.3 (CH_2), 26.0 (CH_3), 26.9 (CH_2), 29.78 (CH_2), 29.80 (CH_2), 30.0 (CH_2), 32.4 (CH_2), 32.6 (CH_2), 42.4 (CH_2), 42.6 (CH_2), 118.1 (CH), 124.7 (CH), 131.9 (C), 138.6 (C), 207.2 (C); IR (neat, cm^{-1}) 1717 ($\nu_{C=O}$); GC/MS (E isomer) 278 (M^+, 0.2), 23 (1), 209 (3), 141 (16), 123 (8), 122 (17), 107 (14), 81 (22), 71 (60), 68 (20), 67 (29), 57 (100); GC/MS (Z isomer) 278 (M^+, 0.3), 235 (1), 209 (17), 141 (23), 137 (5), 123 (12), 122 (34), 107 (34), 95 (10), 81 (35), 71 (7), 69 (74), 68 (15), 67 (27), 57 (100), 55 (29); GC/HRMS (E isomer) calcd for $C_{19}H_{34}O$ 278.2610, found 278.2615; GC/HRMS (Z isomer) calcd for $C_{19}H_{34}O$ 278.2610, found 278.2615.

Reaction of [Pd(η^3-PhCH═CHCH$_2$)(CF$_3$COO)]$_2$ (4a) with 1a (eq 5). In a 5 mm i.d. NMR tube, **4a** (30 mg, 0.04 mmol) and mesitylene (20 μL, an internal standard for ^{1}H NMR spectroscopy) were dissolved in degassed THF-d_8 (0.3 mL). Then, 3-phenylpropionyltrimethylsilane (**1a**) (9 mg, 0.04 mmol) was added into the solution at room temperature. The reaction was carried out at 70 °C for 16 h.

Acknowledgment. The authors are grateful to Professor K. Hori of Yamaguchi University for useful discussion. This work was supported by Grant-in-Aid for Scientific Research on Priority Area "Molecular Physical Chemistry" (No. 11166202) from the Ministry of Education, Science and Culture, Japan. Financial support from the Asahi Glass Foundation is also gratefully acknowledged.

Supporting Information Available: Optimized structures, their Cartesian coordinates, and LUMOs for **4c** and **4d** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA010674P