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# A Novel C-C Bond Forming Reaction of Aryl- and Alkenylsilanols. A Halogen-Free Mizoroki-Heck Type Reaction

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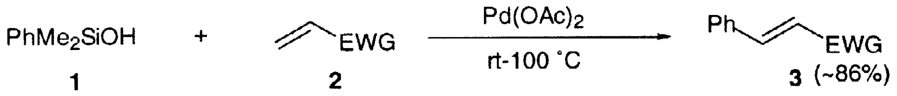
**Abstract:** *When dimethyl(phenyl)silanol is subjected to an electron-deficient olefin in the presence of a stoichiometric amount of Pd(OAc)$_2$, substitution of the C-H bond of the olefin by a phenyl group on the silanol occurs in 52-86% yields. The reactions of several aryl- and alkenylsilanols with several olefins are also found to proceed in the system of 10 mol% of Pd(OAc)$_2$, Cu(OAc)$_2$ (3 mol), LiOAc (2 mol) to give the corresponding products in up to 69% yield.* © 1998 Elsevier Science Ltd. All rights reserved.

We have recently reported a facile synthesis of silanol by alkylative cleavage of cyclic siloxanes with organolithium reagents.[1, 2] Several functional groups could be introduced into the silanol when the organolithium or the cyclic siloxane which possessed the functional groups was employed as the reagent or the substrate. The corresponding silanols with functional groups are, thereby, available for transformation reactions of their groups. In particular, the hydroxy group of the silanol plays an important role to effect reactions to neighboring functionalities such as cyclopropanation of an olefinic group of alkenylsilanol, for example, and several other reactions.[1, 3] Hence, transformation of the carbon-silicon bond of the silanol to a carbon-carbon bond or a carbon-heteroatom bond has increased its importance directed to the construction of backbones of complex organic molecules.[4] During the course of our studies based on the above strategy, we found a novel carbon-carbon bond forming reaction as shown in eq 1 when dimethyl(phenyl)silanol (**1**) was subjected to an α,β-unsaturated carbonyl compound **2** in the presence of palladium(II) acetate.



(1)

The reaction of PhMe$_2$SiOH (**1**) with methyl vinyl ketone (**2a**) is representative. A mixture of **1** (1 mmol), **2a** (1 mmol) and Pd(OAc)$_2$ (1 mmol) in 1,2-dimethoxyethane (0.25 M) was stirred at 60 °C for 13 h under an argon atmosphere and filtered through a short path silica gel column. Further purification by flush chromatography furnished 1-phenyl-1-buten-3-on (**3a**) in 64% yield.

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The reaction proceeded in a variety of solvents (MeCN: 66%, THF: 45%, DMF: 71%, hexane: 38%, AcOH: 77%) in moderate to excellent yields under similar conditions. Palladium(II) chloride also effected the reaction in 38% yield. However, the addition of triphenylphosphine to $Pd(OAc)_2$ poisoned the reaction to give no desired product. The reaction using 20 mol% of $Pd(OAc)_2$ afforded the product in 18% yield, showing good correspondence to the stoichiometry of the palladium species. On the other hand, a use of palladium(0) species such as $Pd(PPh_3)_4$ and $Pd_2(dba)_3$ resulted in no reaction.

The reaction was found less effective when other organosilicon derivatives such as $PhMe_2SiOMe$ (47%), $PhSiMe_3$ (8%) or $PhMe_2SiCl$ (6%) were employed. Accordingly, the silanol functionality appears to play an essential role to promote the smooth reaction. On the other hand, phenyltrifluorosilane (79%) exhibited reactivity comparable to that of silanol.[5, 6] Since the reactivity of the organic group of a silicon reagent generally increases with the number of the fluorine substituent on the silicon, as observed in the palladium-catalyzed cross-coupling reactions,[7] it should be pointed out that a single hydroxy group on silicon is as effective as three fluorine atoms of the trifluorosilane. The reactions similarly proceeded with several electron-deficient olefins such as $CH_2{=}CHCOMe$ (**2a**) (80%), $CH_2{=}CHCOOBu$ (**2b**) (76%), $CH_2{=}CHCN$ (**2c**) (86%, E/Z = ca 2:1), $CH_2{=}CHCHO$ (**2d**) (83%), and $CH_2{=}CHCOOH$ (52%) to furnish the corresponding phenylated products, respectively.[8] However, the use of styrene resulted in no reaction.

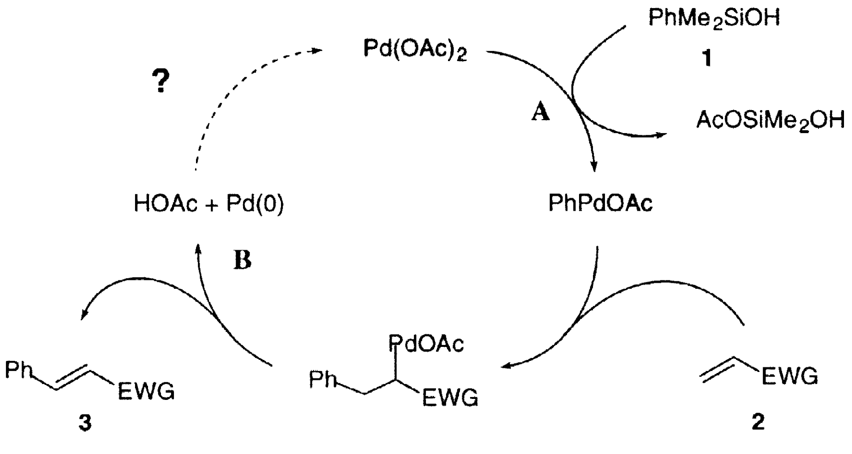
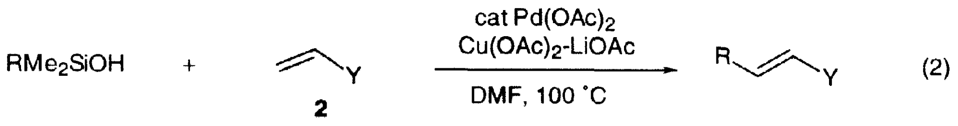


Fig 1. The reaction of a silanol and an electron deficient olefin with $Pd(OAc)_2$

Since the product in the present reaction is identical with that of the Mizoroki-Heck reaction,[9] the reaction can be recognized to be a halogen-free Mizoroki-Heck type reaction using silanol as a metalloid.[10] In contrast to the fact that the Mizoroki-Heck reactions generally employ a Pd(0) species as a catalyst, the silanol reaction appears to proceed mediated by Pd(II).[11] We, thus, consider the initial stage of our silanol reaction is migration of the phenyl group of **1** to palladium, a transmetalation which occurs by the use of Pd(II) (See **A** in Fig 1). Since the transmetalation has not been achieved, to the best of our knowledge, without addition of a fluoride ion which forms a pentacoordinate organosilicate, the migration is remarkably unexpected.[6, 12] Indeed, subsequent generation of Pd(0) as shown in **B** of Fig 1 would account for the failure of the attempted catalytic reaction.

In light of the presumed mechanistic aspect, we were intrigued to perform the reaction of silanol using a catalytic amount of a palladium species. Since Pd(0) is formed along with desired product **3**, regeneration of the Pd(II) species should be promising to complete the catalytic cycle in Fig 1 (the step shown as dotted arrow).

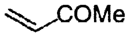
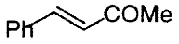
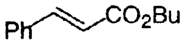
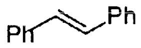
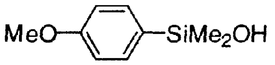
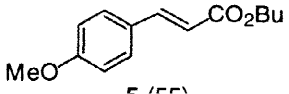
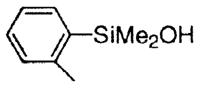
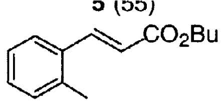
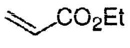
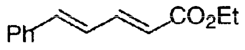
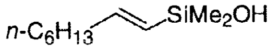
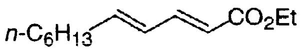
The reaction of silanol and an olefin in the presence of a catalytic amount of $Pd(OAc)_2$ with a wide variety of oxidants was examined. We found that the catalytic process was achieved by using $Cu(OAc)_2$-LiOAc as a re-oxygenation system. (eq 2) The reaction of dimethyl(phenyl)silanol (**1**) with butyl acrylate (**2b**) proceeded by the catalysis of 10 mol% of $Pd(OAc)_2$ in the presence of copper(II) acetate (3 mol) and lithium acetate (2 mol) in DMF. The corresponding product **3b** was obtained in 69% yield after the reaction at 100 °C for 24 h. As summarized in Table 1, the reaction proceeded with a variety of olefins. It is remarkable that a catalytic reaction with styrene proceeded to give 63% yield, although the stoichiometric reaction failed. In addition, the use of alkenylsilanols also effected the reaction in moderate yields to afford the corresponding dienes, respectively.



(2)

R = Aryl, Alkenyl
Y = COMe, $CO_2R$, CN, Ph, etc.

Table 1. Reactions of organosilanols with olefins in the presence of catalyticPd$(OAc)_2$ with $Cu(OAc)_2$/LiOAc.[a]

| Silanol | Olefin **2** | Time/h | Product (Yield/%) |
|---|---|---|---|
| Ph–$SiMe_2OH$<br>**1** | <br>**2a** | 24 | <br>**3a** (48) |
| | <br>**2b** | 24 | <br>**3b** (69) |
| | <br>**2c** | 24 | <br>**3c** (34)[b] |
| | <br>**2d** | 24 | <br>**3d** (37) |
| | <br>**2e** | 24 | <br>**3e** (63) |
| <br>**4** | **2b** | 24 | <br>**5** (55) |
| <br>**6** | **2b** | 24 | <br>**7** (54) |
| <br>**8** | <br>**2f** | 44 | <br>**9** (41) |
| <br>**10** | **2f** | 44 | <br>**11** (52)[c] |

[a] Reaction conditions (unless otherwise specified): solvent DMF (3 mL), temp 100 °C, silanol (0.5 mmol), olefin (0.5 mmol), $Pd(OAc)_2$ (10 mol%), $Cu(OAc)_2$ (1.5 mmol), LiOAc (1.0 mmol). [b] *E/Z*=ca. 2/1 by $^1H$ NMR. [c] The product contains a small amount of stereoisomers (not identified).

In summary, the carbon-silicon bond of silanol was transformed to a carbon-carbon bond through the reaction with olefins mediated by palladium(II) acetate or the catalytic use of $Pd(OAc)_2$ with $Cu(OAc)_2$/LiOAc. The reaction serves as a *halogen-free Mizoroki-Heck type reaction with silanol,* which would be a potential environmentally benign synthetic process. Taken together with our facile synthesis of the silanol as reported previously,[1] the present transformation demonstrates a high synthetic utility of silanols.

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4 Colvin, E. W. *Silicon Reagents in Organic Synthesis*, Academic Press: London, 1988; *Organosilicon Chemistry*, ed. Auner, N.; Weis, J., VCH, WeinHeim, 1994.

5 Similar reactions with difluoro(methyl)phenylsilane and fluoro(dimethyl)phenylsilane resulted in giving the corresponding product in 32% yield and a trace amount, respectively.

6 Organopentafluorosilicates are reported to undergo the reaction with electron-deficient olefins. See: Yoshida, J.; Tamao, K.; Yamamoto, H.; Kakui, T.; Uchida, T.; Kumada, M. *Organometallics* **1982**, *1*, 542-549.

7 Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471-1478.

8 Reaction conditions: dimethyl(phenyl)silanol (0.5 mmol); olefin (0.5 mmol); Pd(OAc)$_2$ (0.5 mmol); DMF (2 mL); 13 h; 100 °C.

9 Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581; Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1505-1508; Heck, R. F.; Nolley Jr, J. P. *J. Org. Chem.* **1972**, *37*, 2320-2322; Dieck, H. A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1133-1136; Heck, R. F. *Org. React.* **1982**, *27*, 345-390; Tsuji, J. *Palladium Reagents and Catalysts; Innovations in Organic Synthesis*, Wiley, 1996, p 127-163.

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12 Related transmetalation of an organosilicon compound was also observed by the use of copper(I): Ikegashira, K.; Nishihara, Y.; Hirabayashi, K.; Mori, A.; Hiyama, T. *Chem. Commun.* **1997**, 1039-1040; Ito, H.; Sensui, H.; Arimoto, K.; Miura, K.; Hosomi, A. *Chem. Lett.* **1997**, 639-670.