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Palladium-Catalyzed Oxidative Silylation of Simple Olefins To Give Allylsilanes Using Hexamethyldisilane and Molecular Oxygen as the Sole Oxidant

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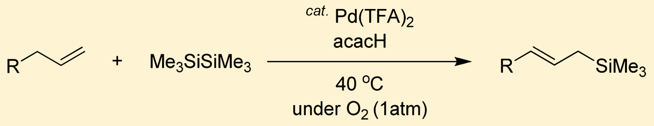
Supporting Information

ABSTRACT: A Pd-catalyzed oxidative silylation of simple olefins with hexamethyldisilane to give allylsilanes has been achieved using molecular oxygen as the sole oxidant. The reaction provides a useful protocol to access synthetically useful allylsilanes from easily accessible simple olefins and hexamethyldisilane without using any oxidants other than O_2.



Allylsilanes are regarded as important motifs because of their inherent reactivity, stability, and low toxicity. Therefore, allylsilanes have been used as building blocks for a range of organic transformations.[1] One well-known example is the allylation of electrophilic carbonyl compounds: the Hosomi–Sakurai reaction.[2]

The synthetic utility of allylsilanes has been developed over many decades. The conventional methods for the synthesis of allylsilanes include the reaction of allylmetal (Mg, Al, Cu, Sm) reagents[3] and hydrosilylation of 1,3-dienes.[4] Reagents containing silicon–metal bonds (e.g., Si–Cu, Si–Li, Si–Al, and Si–Mn bonds) have also been used for synthesizing allylsilanes.[5] Recently, allylsilanes have been prepared by Pd-catalyzed silyl-Heck reaction of olefins with Me_3SiI,[6] Co-catalyzed dehydrogenative silylation of olefins with hydrosilanes,[7] and Ni-catalyzed dealkoxylative cross-coupling from enol ethers.[8] In addition, Cu-catalyzed enantioselective synthesis of allylsilanes has also been developed.[9]

The formation of allylsilanes by allylic silylation of simple olefins via the formation of a π-allyl palladium intermediate is especially intriguing.[10] In general, allyl halides, allyl ethers, and allyl esters have been used as allyl sources.[11]

Hexamethyldisilane ($Me_3SiSiMe_3$) is a stable, commercially available organosilicon compound that has been widely employed as a silyl source in organosilicon chemistry.[12,13] Tsuji and co-workers reported allylic silylation of allylic acetates with $Me_3SiSiMe_3$ to form allylsilanes.[14] In this work, allylic trifluoroacetates gave the best yields. Furthermore, Lipshutz and co-workers reported silylation of allylic ethers and disilane in the presence of a Pd catalyst.[15] Quite recently, Szabó and co-workers reported the Pd-catalyzed allylic silylation of disilanes using allylic alcohols as allylation agents.[16]

Another topic of current interest is catalytic C–H functionalization by oxidative coupling as an environmentally friendly methodology.[17] Recently, our group reported Pd(II)-catalyzed intermolecular oxidative amination of olefins with amines using molecular oxygen as the oxidant.[18]

In light of recent developments in oxidative C–H functionalization chemistry, silylation by C–H activation would be highly beneficial as a synthetic process with minimal byproducts. To date, transition-metal-catalyzed aryl and alkyl C–H silylations have been reported.[19]

With regard to oxidative olefinic C–H silylation, Szabó and co-workers reported palladium-catalyzed synthesis of allylic silanes from olefins and disilane in the presence of a strong oxidant such as hypervalent iodines.[20] Being able to carry out this transformation using simple olefins and milder oxidants would be highly desirable.

In this paper, we report the Pd-catalyzed oxidative allylic silylation reaction of simple olefins and hexamethyldisilane using atmospheric oxygen as the sole oxidant.

Initially, we investigated various conditions to determine the optimal conditions for this reaction (Table 1). When 1-decene (**1a**) was reacted with hexamethyldisilane (**2**) in the presence of $Pd(OCOCF_3)_2$ under an oxygen atmosphere (1 atm, balloon), (*E*)-2-decenyltrimethylsilane (**3a**) was obtained in 49% yield (Table 1, entry 1). The reaction proceeded in a highly regio- and stereoselective manner and afforded the (*E*)-α-adduct exclusively. In the reaction, addition of acetylacetone (acacH) as an additive increases the yield of **3a** (63%, entry 2). We found that high yields were achieved when **2** was added portionwise to an excess of **1a**. The yield of **3a** was increased to 86% when **2** was added in three portions, one portion every 24 h over 72 h (entry 3). The best yields were obtained when $Pd(OCOCF_3)_2$ was used as the catalyst. The use of other selected Pd complexes showed low or no catalytic activity (entries 4–7). This suggests that the initial γ-hydrogen abstraction by the trifluoroacetate ligand forming a π-allylpalladium intermediate is a key step in the reaction (vide infra). Various other additives were examined (entries 8–10). The use of dibenzylideneacetone (dba) similarly gave the

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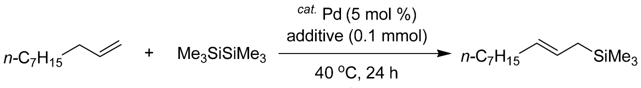
Table 1. Pd-Catalyzed Oxidative Silylation of 1-Decene (**1a**) with Hexamethyldisilane (**2**)[a]



1a **2** **3a**

entry	catalyst	additive	solvent	yield[b] (%)
1	$Pd(TFA)_2$	none	none	49
2	$Pd(TFA)_2$	acacH	none	63
3[c]	$Pd(TFA)_2$	acacH	none	86 (80)
4	$Pd(OAc)_2$	acacH	none	3
5	$Pd(dba)_2$	acacH	none	nd
6	$Pd(acac)_2$	acacH	none	nd
7	$PdCl_2$	acacH	none	nd
8	$Pd(TFA)_2$	dba	none	57
9	$Pd(TFA)_2$	DMSO	none	28
10	$Pd(TFA)_2$	PPh_3	none	3
11	$Pd(TFA)_2$	acacH	$PhCF_3$	69
12	$Pd(TFA)_2$	acacH	toluene	62
13	$Pd(TFA)_2$	acacH	mesitylene	48
14[d]	$Pd(TFA)_2$	acacH	DMF	6
15[d]	$Pd(TFA)_2$	acacH	DMA	2
16[e]	$Pd(TFA)_2$	acacH	decane	nd
17[f]	$Pd(TFA)_2$	acacH	none	25
18[g]	$Pd(TFA)_2$	acacH	none	nd
19[h]	$Pd(TFA)_2$	acacH	none	49
20[i]	$Pd(TFA)_2$	acacH	none	30

[a] Reaction conditions: **1a** (20 mmol) was reacted with **2** (0.5 mmol) in the presence of a Pd catalyst (0.05 mmol) and additive (0.10 mmol) at 40 °C for 24 h under an atmosphere of oxygen. TFA = trifluoroacetate, acacH = acetylacetone, dba = dibenzylideneacetone. [b] GC yields based on **2** except the values in the parentheses. The selectivity of the (*E*)-*α*-adduct is >95%. [c] **2** was added in three portions (0.2, 0.2, and 0.1 mmol) every 24 h for 72 h. [d] Solvent (1 mL) was used. [e] Reaction was performed using **1a** (0.5 mmol), **2** (0.5 mmol), and solvent (20 mmol). [f] Reaction performed under air. [g] Reaction performed under Ar. [h] Reaction temperature was room temperature. [i] Reaction temperature was 60 °C.

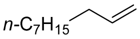
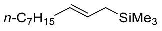
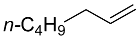
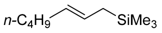
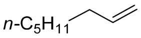
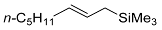
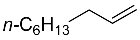
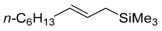
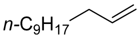
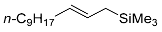
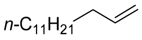
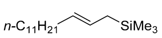
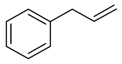
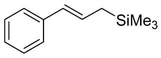
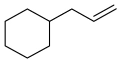
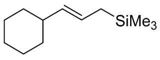
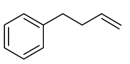
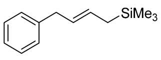
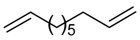
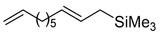
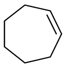
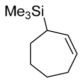
product in good yield (entry 8). However, when DMSO and PPh_3 were used as additives, the catalytic activity considerably deteriorated (entries 9 and 10) compared with the reaction carried out in absence of additive (entry 1). The reaction effectively proceeded by using olefin (1-decene) as both solvent and substrate. The use of solvents such as DMF, DMA, and decane resulted in lower yields (entries 11−16). Excess 1-decene can be recovered in 84% yield after the reaction, and no isomerization of 1-decene was observed by GC analysis.

The reaction required molecular oxygen as oxidant, and low or no coupling product was obtained when the reaction was carried out under an atmosphere of air or Ar (entries 17 and 18). The reaction at room temperature (entry 19) and the reaction at 60 °C only afforded the product in moderate yield (entry 20).

The choice of hexamethyldisilane as a silyl source is crucial for an efficient reaction. We found that using other disilanes such as $PhMe_2SiSiMe_2Ph$ and $PhMe_2SiSiMe_3$ led no reaction at all.

Next we investigated a range of olefins under the optimized conditions (Table 2). A variety of olefins, including simple *α*-olefins and allylbenzene, can be used in the reaction and afford the corresponding (*E*)-*α*-allylsilanes (**3a**−**3i**) in good to excellent yields with high selectivity (entries 1−9). Allylbenzene (**1g**), allylcyclohexane (**1h**), and 4-phenyl-1-butene (**1i**) are tolerated in the reaction to afford corresponding allylsilanes (**3g**−**i**) in good yields (entries 7−9). When the reaction was performed with 1,10-decadiene (**1j**) as an *α*,*ω*-diene, selective monoallylic silylation took place on one side of the *α*,*ω*-diene and afforded allylsilane (**3j**) in good yield with high selectivity (entry 10). The reactivity of internal olefins was sluggish in the allylic silylation with **2**. The reaction with cycloheptene (**1k**) gave the product in 15% yield (entry 11). Unfortunately, the use of functionalized olefins such as allyl butylether, allyl phenylether, and allyl phenylacetate did not afford any allylsilane.

Table 2. Pd-Catalyzed Oxidative Silylation of Various Olefins (**1**) with **2**[a]

entry	Olefin	Product	yield (%)
1	 **1a**	 **3a**	80
2	 **1b**	 **3b**	63
3	 **1c**	 **3c**	84
4	 **1d**	 **3d**	53
5	 **1e**	 **3e**	73
6	 **1f**	 **3f**	83
7	 **1g**	 **3g**	76
8	 **1h**	 **3h**	57
9	 **1i**	 **3i**	58
10	 **1j**	 **3j**	76
11[b]	 **1k**	 **3k**	15

[a] Reaction conditions: **1a** (20 mmol) was reacted with **2** (0.5 mmol) in the presence of $Pd(TFA)_2$ (0.05 mmol) and acetylacetone (0.10 mmol) at 40 °C under an atmosphere of oxygen and **2** was added in three portions (0.2, 0.2, and 0.1 mmol, respectively) every 24 h over the 72 h. [b] Reaction time was 24 h.

It is reported that the reaction of olefins with Pd(II) generates an η^3-allyl palladium intermediate by means of allylic C−H bond activation.[21,22] Therefore, (η^3-cinnamyl)palladium trifluoroacetate dimer (**4**) and (η^3-cinnamyl)palladium acetate dimer (**5**) were prepared independently, and the stoichiometric reaction with **2** was carried out (Scheme 1).[18a,23] This study showed that the reaction of **4** with **2** gave corresponding allylsilane **3g** in 23% yield, but the reaction with **5** was sluggish

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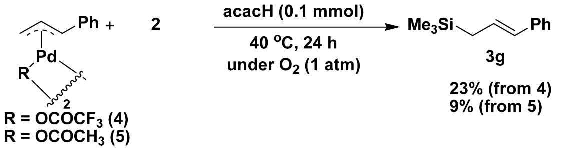
Scheme 1. Stoichiometric Reaction of η^3-Allyl Palladium Acetate Dimers (4 and 5) with 2



and gave **3g** in only 9% along with hexamethydisiloxane as byproduct. This implies that the transformation of the η^3-allyl palladium intermediate with disilane is the key rate-determining step in this reaction. In addition, the use of **4** as catalyst under the conditions shown in entry 2, Table 1, afforded **3a** in 7% yield.

A plausible reaction mechanism for the transformation is shown in Figure 1. Initially, Pd(II) reacts with olefin **1** to form η^3-allyl palladium intermediate **A** through allylic hydrogen abstraction.[18a,22,23] Next, **A** is subjected transmetalation with $Me_3SiSiMe_3$ (**2**) to form silyl(η^3-allyl)palladium intermediate **B**, followed by the production of allylsilane **3** with Pd(0). Then, Pd(0) is reoxidized by dioxygen to generate Pd(II).[24] The key to achieving high yields is the portionwise addition of hexamethyldisilane due to the formation of hexamethyldisiloxane ($Me_3SiOSiMe_3$) under the oxygen atmosphere. The formation of hexamethyldisiloxane (7.87 ppm)[25] and $Me_3SiOCOCF_3$ (33.11 ppm)[26] was observed when the reaction mixture was monitored by ^{29}Si NMR. In addition, it is difficult to rationalize the role of acetylacetone as an efficient additive in the reaction. However, the positive effect of the acacH additive in the direct C−H activation has been reported.[27]

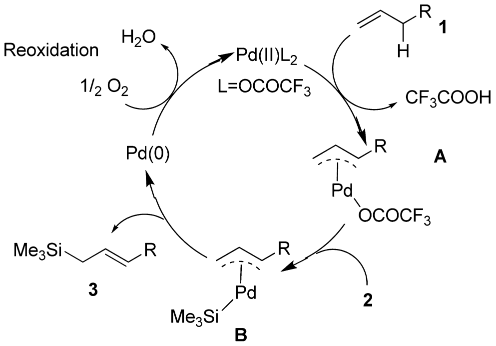


Figure 1. Plausible reaction mechanism for the oxidative allylsilylation of disilane with olefins.

In conclusion, we have demonstrated the $Pd(OCOCF_3)_2$-catalyzed oxidative silylation of simple olefins with hexamethyldisilane, using atmospheric oxygen as the sole oxidant.

EXPERIMENTAL SECTION

General. GC analysis was performed with a flame ionization detector using a 0.22 mm × 25 m capillary column (BP-5). ^{1}H and ^{13}C NMR were measured at 400 MHz in $CDCl_3$ with Me_4Si as the internal standard.

Compounds except for **3a**,[6b] **3b**,[28a] **3c**,[28a] **3d**,[28a] **3e**,[28b] **3f**,[28b] **3g**,[15] **3h**,[28c] **3i**,[4] **3k**[28] were reported previously.

Experimental Procedure. *Typical Procedure for the Preparation of **3a** (entry 3, Table 1).* To a mixture of Pd $(OCOCF_3)_2$ (17 mg, 0.05 mmol) and acetylacetone (10 mg, 0.1 mmol) were added **1a** (2.8 g, 20 mmol) and **2** (73 mg, 0.5 mmol) under O_2 in a 30 mL round-bottomed flask. The reaction mixture was stirred at 40 °C for 72 h. Compound **2** was added in three batches, one every 24 h over a period of 72 h (first time, 0.2 mmol (29 mg); second time, 0.2 mmol (29 mg); third time, 0.1 mmol (15 mg)). The product (**3a**) was isolated by column chromatography (silica gel, *n*-hexane) in 80% yield (85 mg).

*Procedure for the Preparation of **3a** (entry 1, Table 1).* To a mixture of Pd $(OCOCF_3)_2$ (17 mg, 0.05 mmol) were added **1a** (2.8 g, 20 mmol) and **2** (73 mg, 0.5 mmol) under O_2 in a 30 mL round-bottomed flask. The reaction mixture was stirred at 40 °C for 24 h. The yield of product was estimated from peak areas based on an internal standard (tridecane) using GC, and the product (**3a**) was obtained in 49% yield.

*Reaction of **4/5** with **2** (Scheme 1).* To a mixture of **4**/**5** (0.05 mmol) and acetylacetone (10 mg, 0.1 mmol) was added **2** (73 mg, 0.5 mmol) under O_2 in a 30 mL round-bottomed flask. The reaction mixture was stirred at 40 °C for 24 h. The yields of products were estimated from peak areas based on an internal standard (tridecane) using GC, and product **3g** was obtained in 23 and 9% yield, respectively.

3j: 76% yield (80 mg), colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.88−5.78 (m, 1H), 5.42−5.21 (m, 2H), 5.04−4.93 (m, 2H), 2.08−1.96 (m, 4H), 1.42−1.28 (m, 8H), 0.00 (s, 9H); ^{13}C{^{1}H}NMR ($CDCl_3$, 400 MHz) δ 139.2 (CH), 128.9 (CH), 126.0 (CH), 114.1 (CH_2), 33.8 (CH_2), 32.7 (CH_2), 29.8 (CH_2), 28.8 (CH_2), 28.6 (CH_2), 22.6 (CH_2), −2.00 (CH_3); IR (neat, cm^{-1}) ν 3005, 2954, 2926, 2854, 1641, 1248, 1155, 964, 910, 850, 696; GC-MS (EI) *m/z* (relative intensity) 210 (1) [M$^+$], 139(3), 136(4), 114(2), 99(2), 73(100), 59(5), 45(6); HRMS (EI-TOF) *m/z* calcd for $C_{13}H_{26}Si$ [M$^+$] 210.1804, found 210.1803.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Original NMR spectra for products **3**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01216.

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Notes

The authors declare no competing financial interest.

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