

[Rh(OH)(cod)]₂ (cod = 1,5-Cyclooctadiene): A Highly Efficient Catalyst for 1,4-Hydrosilylation of α,β -Unsaturated Carbonyl Compounds

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Abstract: [Rh(OH)(cod)]₂ (cod: 1,5-cyclooctadiene) is found to be a highly efficient catalyst for 1,4-hydrosilylation of α,β -unsaturated carbonyl compounds leading to enolsilanes. The reaction of 2-cyclohexen-1-one with HSiMe(OEt)₂ in the presence of 0.005 mol% of the catalyst without solvent furnishes the corresponding enolsilane in 97% yield at room temperature within 10 min.

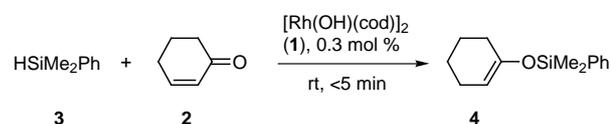
Key words: [Rh(OH)(cod)]₂, hydrosilylation, α,β -unsaturated carbonyl compounds, tertiary silanes, enolsilanes

Rhodium-catalyzed 1,4-selective hydrosilylation of α,β -unsaturated carbonyl compounds¹ is one of the facile method for the synthesis of enolsilanes, which have been widely used as a precursor of aldol condensation in the presence of Lewis Acid (Mukaiyama aldol) or transition metal catalyst.² Ojima and Chan reported that hydrosilylation of an α,β -unsaturated carbonyl compound using tertiary silanes (HSiR₃) with a rhodium catalyst, RhCl(PPh₃)₃ or RhH(PPh₃)₄, proceeded in a highly 1,4-selective manner, while the use of secondary silanes (H₂SiR₂) in the presence of the rhodium catalyst underwent selective 1,2-reduction.³

On the other hand, we recently reported several rhodium catalyzed carbon-carbon bond-forming reactions such as Mizoroki–Heck type reaction, 1,4-conjugate addition, 1,2-addition to aldehydes, and hydroarylation of alkynes with silanols and siloxanes, in which [Rh(OH)(cod)]₂ (cod = 1,5-cyclooctadiene) (**1**) was found to be an efficient catalyst.^{4,5} Further studies on the availability of the catalyst revealed that use of **1** was much effective for 1,4-hydrosilylation of α,β -unsaturated carbonyl compounds compared with the previously reported rhodium catalysts. Herein, we report conjugate hydrosilylation of α,β -unsaturated carbonyl compounds to afford enolsilanes in excellent yields under mild conditions.

The reaction of 2-cyclohexen-1-one (**2**) with phenyldimethylsilane (**3**) was carried out in the presence of 0.15 mol% of [Rh(OH)(cod)]₂ (**1**) at room temperature without solvent. The reaction was completed within 5 min and the corresponding enol silyl ether **4** was obtained in a quantitative yield (Equation 1). Activity of the hydroxrhodium complex **1** was revealed to be superior to other rhodium catalyst as shown in Table 1. The similar reaction with

several rhodium catalysts was carried out under diluted conditions with THF to compare relative activities. [Rh(OMe)(cod)]₂ and [Rh(OH)(nbd)]₂ (nbd: norbornadiene) were found to be equally effective to **1**. [RhCl(cod)]₂, [Rh(cod)₂]BF₄ and [RhI(cod)]₂⁶ also promoted the reaction but the activity as a catalyst was slightly lower than [Rh(OH)(cod)]₂. By contrast, the reaction using RhH(PPh₃)₄ or RhCl(PPh₃)₃ as a catalyst did not proceed under similar conditions.



Equation 1

Table 1 Rhodium-Catalyzed Hydrosilylation of **2** with **3**^a

Catalyst	Time, min	% Yield ^b
[Rh(OH)(cod)] ₂	10	89
	120	>99
[Rh(OMe)(cod)] ₂	10	95
[Rh(OH)(nbd)] ₂	10	84
[Rh(cod) ₂]BF ₄ ^c	120	79
[RhCl(cod)] ₂	10	56
	30	66
	120	93
[RhI(cod)] ₂	120	30
RhH(PPh ₃) ₄ ^c	120	0 ^d
RhCl(PPh ₃) ₃ ^c	120	0

^a The reaction was carried out with **2** (1.0 mmol) and **3** (1.1 mmol) in 3 mL of THF in the presence of 0.15 mol% of the rhodium catalyst.

^b The yield was estimated by ¹H NMR using trichloroethylene as an internal standard.

^c The catalyst loaded was 0.3 mol%.

^d The yield reported in ref.^{3b} is 84% after stirring at room temperature for 12 h with 0.3 mol % of the catalyst without solvent.

The reaction with several tertiary silanes was examined as shown in Table 2. In addition to phenyldimethylsilane (**3**), a variety of tertiary silanes affected the hydrosilylation to give the corresponding enol silyl ethers of **2**. The similar

trialkylsilane, HSiEt_3 , also affected the reaction in excellent yields. Disiloxane, $\text{HSiMe}_2\text{OSiMe}_3$ and alkoxy-silanes, $\text{HSiMe}_2(\text{OEt})$, $\text{HSiMe}(\text{OEt})_2$, and $\text{HSi}(\text{OEt})_3$ were found similarly effective. The hydrosilylation with cyclic tetrasiloxanes (HSiMeO)₄ and polysiloxane (HSiMeO)_n (PMHS; $n = \text{ca. } 45\text{--}50$)⁷ also afforded the corresponding enolsilanes although it took longer reaction periods at 60 °C.

Table 2 Hydrosilylation of 2-Cyclohexen-1-one with Various Tertiary Silanes^a

Silane	Solvent	Temp., °C	Time	% Yield
HSiEt_3	THF	60	4 h	>99
	none	r.t.	3 h	>99
$\text{HSiMe}_2\text{OSiMe}_3$	THF	r.t.	10 min	>99
HSiMe_2OEt	THF	r.t.	30 min	82
	none	r.t.	10 min	>99
$\text{HSiMe}(\text{OEt})_2$	THF	r.t.	30 min	92
$\text{HSi}(\text{OEt})_3$	THF	r.t.	13 h	>99
	none	r.t.	3 h	>99
(HSiMeO) ₄	THF	60	4 h	>99
(HSiMeO) _n	THF	60	6 days	85

^a The reaction was carried out with 2-cyclohexen-1-one (1.0 mmol) and a tertiary silane (1.1 mmol) in the presence of $[\text{Rh}(\text{OH})(\text{cod})]_2$ (0.15 mol %) in 3 mL of THF or neat. The yield was estimated by ¹H NMR analysis using trichloroethylene as an internal standard.

The reaction was examined with further smaller catalyst loading. Hydrosilylation of 2-cyclohexen-1-one (**2**) with ethoxydimethylsilane was carried out in the presence of 0.005 mol% of the rhodium catalyst **1** at room temperature without solvent. After stirring for 20 min the corresponding enolsilane was produced quantitatively (confirmed by ¹H NMR) and isolated in 97% yield by bulb-to-bulb distillation.⁸

Next, hydrosilylation with various α,β -unsaturated carbonyl compounds was carried out. The results are summarized in Table 3. The five-membered cyclic ketone, 2-cyclopenten-1-one, and **3** underwent the hydrosilylation similarly to give the enolsilane in 86% isolated yield. The reaction with an acyclic enone, (*E*)-*n*-C₅H₁₁CH=CHCOMe also proceeded although the obtained product was a mixture of stereoisomers. A trisubstituted enone, Me₂C=CHCOMe could affect the reaction at a slightly higher reaction temperature or a longer reaction period. In addition to ketones, α,β -unsaturated ester and aldehyde such as methyl methacrylate, CH₂=C(Me)COOMe and crotonaldehyde, (*E*)-MeCH=CHCHO afforded the corresponding enolsilanes in excellent yields.

Table 3 Rhodium-Catalyzed Hydrosilylation with Various α,β -Unsaturated Carbonyl Compounds^a

Substrate	Temp., °C	Time, min	% Yield (ratio) ^b
2-cyclopenten-1-one	r.t.	10	86
(<i>E</i>)- <i>n</i> -C ₅ H ₁₁ CH=CHCOMe	r.t.	10	93 ^{c,d} (<i>E</i> / <i>Z</i> =35:65)
Me ₂ C=CHCOMe	60	30	87 (<i>E</i> / <i>Z</i> =26:74)
	r.t.	12 h	95 ^d (<i>E</i> / <i>Z</i> =21:79)
CH ₂ =C(Me)COOMe	r.t.	10	87 ^d
(<i>E</i>)-MeCH=CHCHO	r.t.	10	80 ^{c,d} (<i>E</i> / <i>Z</i> =19:81)

^a Unless otherwise noted the reaction was carried out with α,β -unsaturated carbonyl compound (1.0 mmol) and phenyldimethylsilane (1.1 mmol) in the presence of $[\text{Rh}(\text{OH})(\text{cod})]_2$ (0.15 mol %) in 3 mL of THF.

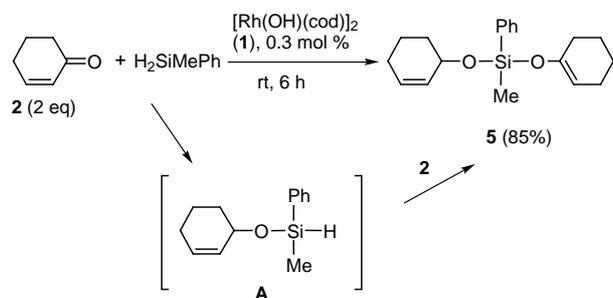
^b The isomer ratio was determined by ¹H NMR analysis.

^c The rhodium catalyst loading was 0.005 mol %.

^d The reaction was carried out without solvent.

On the other hand, 1,2-hydrosilylation with secondary silanes (R_2SiH_2) was found to be less selective when $[\text{Rh}(\text{OH})(\text{cod})]_2$ was employed as a catalyst. When the reaction was carried out with a secondary silane, H₂SiPhMe, and twice molar amounts of 2-cyclohexen-1-one (**2**) in the presence of 0.15 mol% of **1**, alkoxyenolsilane **5** was obtained in 85% yield as shown in Scheme suggesting to afford 1:1 mixture of 1,2- and 1,4-hydrosilylation products, respectively. The result suggests that the secondary silane would undergo the 1,2-hydrosilylation leading to a possible intermediate **A**, which is a tertiary silane. Hence, **A** would then affect 1,4-hydrosilylation of **2** to afford **5**. This would be due to the relatively slower 1,2-hydrosilylation toward 1,4-reaction with $[\text{Rh}(\text{OH})(\text{cod})]_2$ as a catalyst, which enables the rapid 1,4-reaction of **A**. In the reaction with $\text{RhH}(\text{PPh}_3)_4$ or $\text{RhCl}(\text{PPh}_3)_3$, by contrast, sluggish hydrosilylation of the formed tertiary silane that corresponds to the intermediate **A** would result in the 1,2-selective reaction.³ Consequently, the reaction with the hydroxorhodium catalyst afforded the mixture of 1,2- and 1,4-products despite high selectivity of both 1,2-hydrosilylation with a secondary silane and 1,4-reaction of the formed tertiary silane.

In conclusion, we have shown that a rhodium complex, $[\text{Rh}(\text{OH})(\text{cod})]_2$ is a highly efficient catalyst for the synthesis of enolsilanes from α,β -unsaturated carbonyl compounds. Since the reaction can be carried out under mild conditions without solvent and with a small amount (0.005–0.15 mol%) of the catalyst loading, the product could be isolated by direct distillation of the reaction mixture. The present process, therefore, would be a practical synthetic method for the precursor of Mukaiyama aldol reactions.



Scheme

References

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 - (6) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 4735.
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 - (8) The mixture of 2-cyclohexen-1-one (**2**, 10 mmol) and HSi(OEt)Me₂ (11 mmol) in the presence of [Rh(OH)(cod)]₂ (1 mg, 0.005 mol%) was stirred at room temperature for 10 min under an argon atmosphere. The resulting mixture was subjected to bulb-to-bulb distillation under 0.5 Torr at 55 °C (bath temp) to afford 1.95 g of (1-cyclohexenyl)ethoxy(dimethyl)silane (97%) as a colorless liquid. ¹H NMR (CDCl₃, 300 MHz) δ 0.18 (s, 6 H), 1.22 (t, *J* = 7.2 Hz, 3 H), 1.42–1.60 (m, 2 H), 1.61–1.76 (m, 2 H), 1.94–2.14 (m, 4 H), 3.79 (q, *J* = 7.2 Hz, 2 H), 4.94–4.98 (m, 1 H).