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Highly Efficient and Chemoselective Ruthenium-Catalyzed Hydrosilylation of Aldehydes

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This paper is dedicated to Professor Eun Lee on the occasion of his honorable retirement and 65th birthday.

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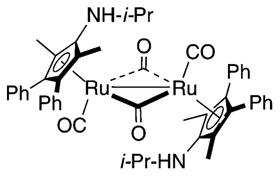
Abstract: The highly chemoselective hydrosilylation of aldehydes was achieved using a ruthenium catalyst activated by a household fluorescent light (30 W) at or below room temperature. The hydrosilylation was almost exclusive to aldehydes over ketones and olefins.

Keywords: aldehydes; chemoselectivity; hydrosilylation; photochemistry; ruthenium complexes

The hydrosilylation of carbonyl compounds is a fundamental transformation which has broad applications in organic synthesis and materials science.[1] This reaction is particularly attractive because it provides silyl-protected alcohols in a single step. A number of metal-catalyzed protocols have been developed,[2] all aiming at the hydrosilylation of ketones.[3] On the other hand, protocols for the selective hydrosilylation of aldehydes are limited. For example, the well-known Stryker's reagent $[Ph_3P(CuH)]_6$ shows a good selectivity for the hydrosilylation of aldehydes in the presence of ketones.[4] However, it has a strong preference for the competing 1,4-reductions in the hydrosilylation of α,β-unsaturated aldehydes. Recent studies on the chemoselective hydrosilylation of aldehydes using other metal catalysts also suffer from the low chemoselectivity, high catalyst loading, limited scope of the silanes, requirement of additives, and harsh conditions.[5]

Recently, we have reported the simple synthesis of an isolable diruthenium complex (**1**) and its conversion to a catalytic species that is active for the racemization of secondary alcohols simply by illuminating its solution.[6] We envisioned that the ruthenium hydride species, which has been proposed as a key catalytic species for the racemization, might also be active for the reduction of other functional groups. In this communication, we wish to report the utility of **1** for the chemoselective hydrosilylation of a wide range of aldehydes, which allows the use of various silanes under mild conditions and does not require additives.



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Initially, the reaction conditions were optimized in the hydrosilylation of benzaldehyde (Table 1). A fluorescent light (30 W) was needed to activate the ruthenium complex **1** (entry 1), because the reaction carried out without the fluorescent light showed no conversion (entry 2). Interestingly, however, illumination just for 30 min at the beginning of the reaction was enough to generate the catalytic species (entry 3). Lowering the temperature to 0 °C still maintained the catalytic activity (entry 4). Notably, the hydrosilylation showed complete conversion even at −78 °C with an extended reaction time (entry 5). Meanwhile, analogous diruthenium complexes such as $[Cp^*Ru(CO)_2]_2$ and $[CpRu(CO)_2]_2$ were practically ineffective for the hydrosilylation (entries 6 and 7).

Next, the scope of silanes was investigated in the hydrosilylation of benzaldehyde (Table 2). The reaction with *tert*-butyldimethylsilane was also successful to give the corresponding silyl ether in high yield, although it was slower than that with triethylsilane

Table 1. Catalytic hydrosilylation of benzaldehyde using **1**.[a]

$$\text{Ph-CHO} \xrightarrow[\text{HSiEt}_3\ (1.0\ \text{equiv})]{\mathbf{1}\ (0.50\ \text{mol\%}),\ h\nu} \text{Ph-CH}_2\text{OSiEt}_3$$

Entry	Ru	Temp.	Time [h]	Yield[b] [%]
1	**1**	r.t.	12[c]	>99
2	**1**	r.t.	12[d]	0
3	**1**	r.t.	12[e]	98
4	**1**	0 °C	12	94
5	**1**	−78 °C	48	90
6	$[Cp^*Ru(CO)_2]_2$	r.t.	24	3
7	$[CpRu(CO)_2]_2$	r.t.	24	0

[a] A solution of benzaldehyde (0.50 mmol), Et_3SiH (0.50 mmol), and **1** (0.50 mol%) in tetrahydrofuran (THF) (0.5 mL) was illuminated with a household fluorescent light (30 W) under an argon atmosphere.

[b] Measured by GC equipped with a TR-5 column using *trans*-stilbene as an internal standard.

[c] The reaction mixture was illuminated throughout the reaction (12 h).

[d] The reaction was carried out in the dark.

[e] The reaction mixture was illuminated for 30 min at the beginning of the reaction.

Table 2. Hydrosilylation of benzaldehyde with various silanes.[a]

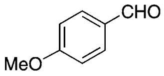
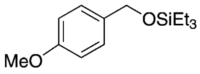
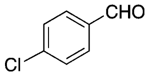
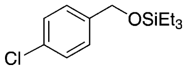
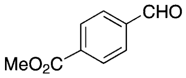
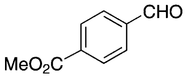
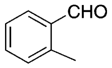
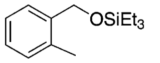
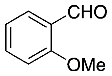
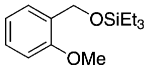
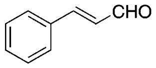
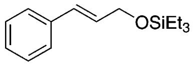
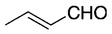
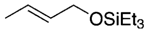
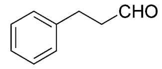
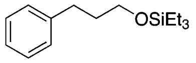
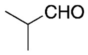
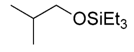
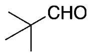
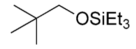
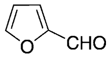
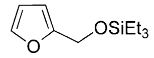
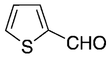
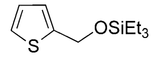
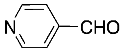
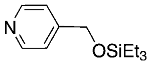
Entry	Silane	Time [h]	Yield[b] [%]
1	$t\text{-BuMe}_2\text{SiH}$	24	93
2	Ph_3SiH	24	90
3	Ph_2MeSiH	24	90
4	$(i\text{-Pr})_3\text{SiH}$	24	13[c]

[a] A solution of benzaldehyde (0.50 mmol), a silane (0.50 mmol), and **1** (0.50 mol%) in THF (0.5 mL) was illuminated with a household fluorescent light (30 W) for 1 h at room temperature under an argon atmosphere.

[b] Isolated yield of silyl ether.

[c] Measured by ^{1}H NMR using 1,2-dichloroethane as an internal standard.

Table 3. Hydrosilylation of various aldehydes.[a]

Entry	Aldehyde	Time [h]	Product	Yield[b,c] [%]
1		10		>99 (97)
2		10		96 (94)
3		12		98 (96)
4		17		98 (96)
5		10		95 (95)
6		24		90 (88)
7		24		96[d] (94)
8		24		96 (92)
9	$CH_3(CH_2)_6$—CHO	24	$CH_3(CH_2)_7$—$OSiEt_3$	94[e] (91)
10		24		96[d] (83)
11		24		85 (75)
12		12		98 (93)
13		24		81[d,f] (76)
14		36		85[d,f] (83)

[a] *Typical procedure:* A solution of aldehyde (0.50 mmol), Et_3SiH (0.50 mmol), and **1** (0.50 mol%) in THF (0.5 mL) was illuminated with a fluorescent light (30 W) at room temperature.

[b] Measured by GC equipped with a TR-5 column using *trans*-stilbene as an internal standard.

[c] Numbers in the parenthesis are isolated yields.

[d] Measured by ^{1}H NMR using 1,2-dichloroethane as the internal standard.

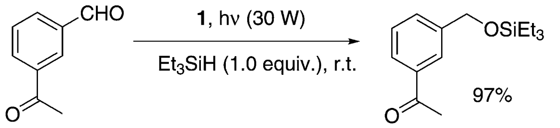
[e] 1.0 mol% of **1** was used.

[f] Two equivalents of Et_3SiH and 2 mol% of **1** were used at 80 °C.

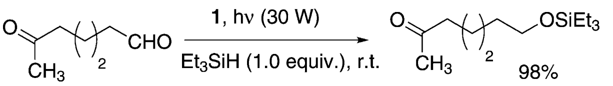
(entry 1). The reactions with triphenylsilane and methyldiphenylsilane were comparable to that with *tert*-butyldimethylsilane (entries 2 and 3), while the reaction with triisopropylsilane was much less efficient (entry 4).[2b]

Under the optimized conditions, the hydrosilylation using the ruthenium complex **1** and triethylsilane was tested for various aldehydes (Table 3). The hydrosilylation of aromatic aldehydes was not affected significantly by the ring substituents except for a nitro group (entries 1–5).[7] Chloro and ester groups remained intact during the hydrosilylation (entries 2 and 3). *ortho*-Methyl groups appeared to slow the hydrosilylation, while *ortho*-methoxy groups did not show retarding effect (entries 4 and 5). Notably, only 1,2-addition was observed in the hydrosilylation of α,β-unsaturated aldehydes (entries 6 and 7).[7] Aliphatic aldehydes were also good substrates for the hydrosilylation, although the reactions were slower than those of aromatic ones (entries 8–11). Interestingly, the steric effect of the alkyl groups was not significant, as shown by the effective reaction of isobutyraldehyde (entry 10) and pivalaldehyde (entry 11). The furan ring did not interfere with the catalytic hydrosilylation (entry 12). Also, the hydrosilylation of thiophenyl- and pyridylaldehydes was successful with a higher catalyst loading under elevated temperature (entries 13 and 14).

Most notably, this catalytic system showed remarkable chemoselectivity towards aldehydes over ketones. For example, 3-acetylbenzaldehyde was almost exclusively transformed into the corresponding primary silyl ether in the reaction with an equimolar amount of triethylsilane under the optimized conditions [Eq. (1)].[8] Moreover, only the formyl group was reacted in the hydrosilylation of 6-oxoheptanal [Eq (2).][9]



(1)



(2)

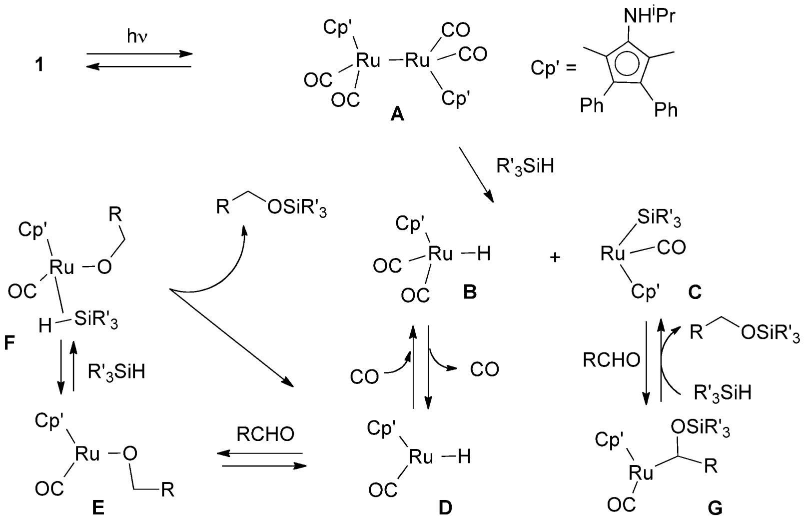
Although further studies are required to elucidate the mechanism of the catalytic hydrosilyliation, probable pathways are proposed in Scheme 1 on the basis of the chemistry known for ruthenium complexes related to **1** and the results described above.[10] The low energy light ($\lambda > 400$ nm) transforms the bridged form into a terminal form (**A**).[10a,b] This initial step would be followed by the cleavage of the Ru–Ru bond and the subsequent reaction with a trialkylsilane to form a ruthenium hydride (**B**) and a silyl ruthenium species (**C**).[10c,11] The reaction of **B** with an aldehyde to form a ruthenium alkoxide **E** would occur after the liberation of CO from **B** to generate a low-coordinate ruthenium hydride (**D**). The reaction of a trialkylsilane with **E** produces the silyl ether product with regeneration of **D**. In fact, the ruthenium hydride **B** was observed in the reaction mixture during the hydrosilylation.[12,13] In a separate experiment, we confirmed that the catalytic hydrosilylation can be effected using the ruthenium hydride **B** with comparable efficiency to that under the optimized conditions.[14] The intermediacy of **E** is also supported by the recent reports that suggest an analogous ruthenium alkoxide species as the key intermediate for the catalytic racemization of alcohols.[15] Meanwhile, the direct reaction of **C** with an aldehyde to give the intermediate **G** cannot be ruled out, which can react with a silane to give the silyl ether product with regeneration of **C**.

In summary, we have demonstrated a highly efficient and practical hydrosilylation of aldehydes using a readily available and isolable diruthenium complex (1) under mild conditions without any additives. The reaction is applicable to a wide range of aldehydes, and is exclusively selective for the aldehydes over ketones and olefins.

Experimental Section

General Procedure of the Hydrosilyation of Benzaldehyde

In a J-Young flask a mixture of benzaldehyde (50 μL, 0.50 mmol), $SiEt_3H$ (80 μL, 0.50 mmol), and Ru complex **1** (2.3 mg, 0.0025 mmol) in THF (0.5 mL) was illuminated with fluorescent light (30 W) at room temperature under argon atmosphere. After the reaction mixture had been concentrated, the crude product was purified by column chromatography (silica gel; hexane: ethyl acetate = 20:1) to give $PhCH_2OSiEt_3$; yield: 110 mg (96%).



Scheme 1. Proposed pathway for the photoinduced hydrosilylation of aldehydes.

Acknowledgements

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[7] *p*-Nitrobenzaldehyde, styrene, and phenylacetylene were unreactive under the silylation conditions; more than 96% of the starting aldehydes remained in reaction mixture after 12 h.

[8] The use of two equivalents of triethylsilane gave the same product selectively in 95% yield.

[9] 6-Oxoheptanal was prepared from 1-methylcyclohexene according to a known procedure: K. C. Nicolaou, V. A. Adsool, C. R. H. Hale, *Org. Lett.* **2010**, *12*, 1552.

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[12] The characteristic hydride peak for **B** was observed at −9.6 ppm in the reaction mixture (C_6D_6) by ^{1}H NMR.

[13] The ruthenium hydride **B** was recovered in the form of the corresponding chloride complex in 94% yield by treating the reaction mixture with chloroform, which can be reconverted to **B** through the reaction with 2-propanol in the presence of sodium carbonate. See: J. H. Choi, Y. K. Choi, Y. H. Kim, E. S. Park, E. J. Kim, M.-J. Kim, J. Park, *J. Org. Chem.* **2004**, *69*, 1972.

[14] The hydrosilylation of benzaldehyde (0.50 mmol) using 1 mol% of **B** gave benzyloxytriethylsilane in 80% yield under the optimized conditions.

[15] a) J. Nyhlen, T. Privalov, J.-E. Bäckvall, *Chem. Eur. J.* **2009**, *15*, 5220; b) J. B. Åberg, J. Nyhlén, B. Martín-Matute, T. Privalov, J.-E. Bäckvall, *J. Am. Chem. Soc.* **2009**, *131*, 9500.