Reduction of α,β-Unsaturated Ketones with Diphenylsilanes Bearing Several Substituents on Their Phenyl Moiety Catalyzed by Rhodium–Phosphine Complexes

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(Received October 25, 2006; CL-061258; E-mail: tota@mail.doshisha.ac.jp)

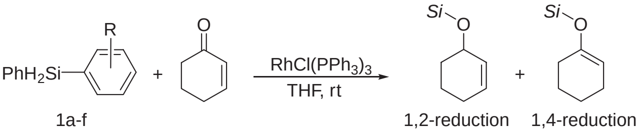
1,4-Addition product was afforded exclusively by rhodium–phosphine complex-catalyzed hydrosilylation by using 2-cyclohexen-1-one and a dihydrosilane bearing an ether substituent in spite of the fact that dihydrosilanes were believed to give 1,2-addition product selectively.

It is known that Rh-catalyzed hydrosilylation of α,β-unsaturated ketones brings about 1,2-reduction by using dihydrosilanes, forming allylic alcohols. In contrast, it is also known that the same reaction brings about 1,4-reduction by using monohydrosilanes,[1] forming silyl enol ethers, which can be used as powerful synthons in Mukaiyama aldol reaction.[2] Although these mechanisms are yet unknown, it is believed that the number of hydrogen on silicon atom dominates these regioselectivities.[1] In spite of this belief, there were several examples which disobeyed this rule. For example, Ojima and Kogure reported that low concentration of dihydrosilane caused increase of 1,4-addition product,[1b] so we assumed there must be another hidden regioselecting factor especially related to some property of silane itself. In 1995, Zheng and Chan proposed a unique mechanism in which ketone coordinates to silane rather than rhodium in silyl–$\text{Rh}^{\text{III}}\text{H}$ complex to form alkoxysilyl–$\text{Rh}^{\text{III}}\text{H}$ species, though, they could find no clear evidence for this mechanism.[1c] If their mechanism is true, the silane could be considered as a Lewis acid in the catalyses.

At the same time, there have been a lot of reports dedicated to understanding the nature of silicon hypervalency by introducing many kinds of functional groups to substituents of silicon which can form intramolecular dative bonds.[3] This means these reports took Lewis acidity of silanes for granted. To our knowledge, there has been no report of catalysis using hydrosilanes with hypervalency for Rh-catalyzed reduction of α,β-unsaturated ketones. Here, we report catalysis using a dihydrodiphenylsilane with a dative ether group at an appropriate position inverted its regioselectivity completely.

Encouraged by a report in which a methoxymethyl ether group has worked as a dative ligand to silane,[4] we first envisaged that the application of dihydrosilane **1b** would have some influence on the selectivity in catalysis. 2-Cyclohexen-1-one and $\text{RhCl(PPh}_3)_3$ were used as a substrate and a catalyst. Results are summarized in Table 1. The catalysis using dihydrosilane **1b** inverted its regioselectivity completely to afford 1,4-addition product exclusively (Entry 2). To elucidate the role of an oxygen atom of an ether group more clearly, several alkylated dihydrosilanes were also tested. Entries 3–5 indicates that steric effect of alkyl groups had small influence on regioselectivity and gave regioisomer mixtures. Interestingly, MesPhSiH_2 **1f**, with which Fu and Tao has obtained higher enantioselectivity than with **1a** in asymmetric hydrosilylation of ketones using planer-chiral P,N ligand, showed considerably high 1,4-selectivity.[5]

Table 1. Regioselectivity of Rh-catlayzed hydrosilylation of 2-cyclohexen-1-one with a variety of dihydrosilanes[a]



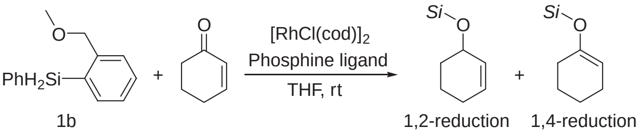
Entry	Silane	R	Yield/%[b]	1,2-/1,4-[b]
1	**1a**	H	100	100/0
2	**1b**	$2\text{-CH}_2\text{OCH}_3$	95	0/100
3	**1c**	2-Me	100	90/10
4	**1d**	2-Et	76	83/17
5	**1e**	2-*n*-Pr	71	79/21
6	**1f**	2,4,6-triMe	37	27/73

[a]Substrate (1 mmol), silane (1.5 equiv.), and catalyst (0.5 mol %) were used for 3 h. [b]Determined by ^{1}H NMR internal standard method.

Sevearl phosphine ligands were tested in Table 2. Among Entries 1–3 ortho-substituted monodentate ligand was found to cause 1,2-fashion reduction. Catalyses using dppf, dppe, and (*S*)-binap afforded 1,2-/1,4-fashion reduction mixtures. 1,2-Fashion reduction product was exclusively afforded by catalyses using dppp or xantphos. From these results (Tables 1 and 2) an ether group on **1b** was found to be effective for reducing the substrate in 1,4-fashion; though, congestion around metal center reverses the regioselectivity to 1,2-fashion.

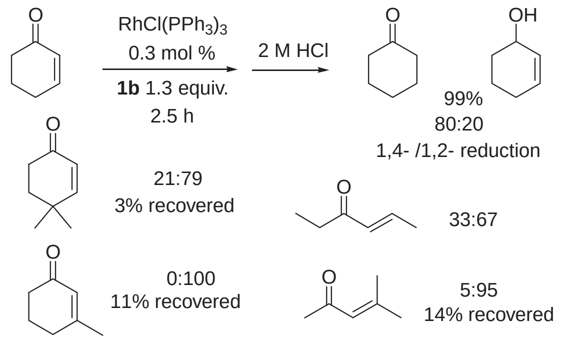
Next, we applied the other α,β-unsaturated ketones to this catalysis using **1b**. During the investigation under several reac-

Table 2. Effect of ligands on regioselectivity[a]

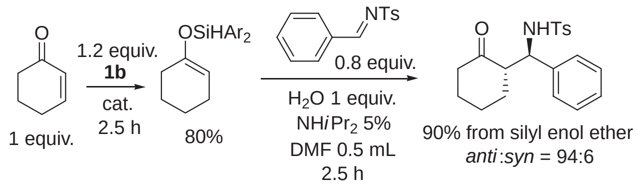


Entry	Ligand (mol %)	Yield/%[b]	1,2-/1,4-[b]
1	PPh_3 (3)	39	0/100
2	(*o*-anisyl)PPh_2 (3)	20	100/0
3	(*p*-anisyl)$_3$P (3)	53	0/100
4	dppf (1)	65	38/62
5	(*S*)-binap (1)	61	74/26
6	dppe (1)	75	87/13
7	dppp (1)	65	100/0
8	xantphos (1)	50	100/0

[a]Substrate (1 mol %) and $[\text{RhCl(cod)}]_2$ (0.5 mol %) was used (24 h). [b]Determined by ^{1}H NMR internal standard method.



Scheme 1. Regioselectivities of several α,β-unsaturated ketones using **1b** with no solvent.



Scheme 2. One-pot synthesis procedure for a β-amino ketone.

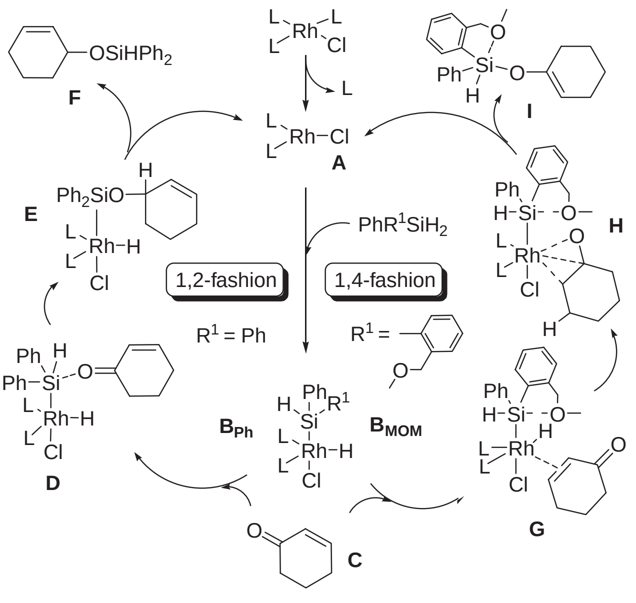
tion conditions, we noticed that catalyses using some ketones produced 1,2-/1,4-reduction mixtures by using H_2SiPh_2. Reaction conditions reported by Ojima and Kogure[1b] where no solvent was used is considered to be the most effective conditions for dihydrosilanes to demonstrate high 1,2-reduction selectivity. The results with several α,β-unsaturated ketones by using no solvent are summarized in Scheme 1. The result with 2-cyclohexen-1-one showed worse selectivity; though, it still remained high 1,4-selectivity. Catalyses with the other ketones under the same conditions resulted in dramatic decrease the ratios of their 1,4-selectivity due probably to the steric hindrance around their β-carbon.

As a supporting evidence for the 1,4-reduction, we carried out one-pot Mannich-type reaction depicted in Scheme 2. We anticipated that the silyl enol ether catalytically generated in situ with **1b** should remain a hydride ligand on a silicon atom. These kind of silyl enol ethers have been known to exhibit high reactivity in base-catalyzed Mannich-type reaction in the presence of water and diisopropylamine as a base.[6]

As expected, a β-amino ketone was obtained in 72% (90% from a silyl enol ether) with high anti-selectivity in one-pot synthetic procedure. In contrast, less than 5% of the same product was obtained by using $HSiMe_2Ph$ in the same procedure. This result would clearly support that a silyl enol ether bearing a hydride ligand on its silicon is involved in this reaction.

From these results, we postulated mechanisms of rhodium-catalyzed hydrosilylation of 2-cyclohexen-1-one as depicted in Scheme 3. In 1,2-fashion, our results could be explained by the idea of Zheng and Chan in which a carbonyl oxygen atom would coordinate to Si rather than Rh, depicted as **D**.

When **1b** is used, its ethereal oxygen atom would coordinate at its silicon Lewis acid orbital intramolecularly, drawn as **G**. Therefore, the rhodium metal would predominantly behave as a Lewis acid to give 1,4-addition product probably through π-coordination by the C=C double bond of the substrate.[7] 1,2-Fashion reduction was exhibited by a Rh–xantphos catalyst and **1b** presumably because the Rh has no vacant orbital due to the extremely wide bite angle of bidentate xantphos.[8] Substrates with steric hidrance around their β-carbon would probably disfavored the π-coordination interaction with the complex, causing 1,2-reduction preferentially.



Scheme 3. Plausible Rh-catalyzed hydrosilylation mechanisms with 2-cyclohexen-1-one using diphenylsilane and **1b**.

In summary, we found that 1,4-addition product was exclusively afforded by rhodium-catalyzed hydrosilylation of 2-cyclohexen-1-one by using dihydrosilane bearing an ether substituent in spite of the fact that dihydrosilanes were believed to give 1,2-addition product selectively.

This work was partially supported by a grant to RCAST at Doshisha University from the Ministry of Education, Culture, Sports, Science and Techonlogy, Japan.

This paper is dedicated to the heartfelt memory of the late Professor Yoshihiko Ito of Doshisha University.

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) February 3, 2007; doi:10.1246/cl.2007.366