

# Zinc-Catalyzed Enantioselective Hydrosilylation of Ketones and Imines Under Solvent-Free Conditions

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#### Dedication ((optional))

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**Abstract:** Zinc acetate-promoted asymmetric hydrosilylation of various ketones and imines under solvent-free conditions is reported with unprecedented low catalyst loading. Exposure of ketones to 0.05 mol% Zn-based chiral diamine complex in the presence of triethoxysilane affords enantioenriched alcohols in excellent yields of isolated products (up to 98%) and *ee* (up to 97%). This methodology also allowed for chemoselective 1,2-reduction of  $\alpha$ , $\beta$ -unsaturated ketones and imines.

Catalytic reduction of prochiral ketones and imines is a valuable attempt to obtain enantiopure alcohols and amines. Among many various methods for the reduction of carbonheteroatom unsaturated bond, hydrosilylation promoted by chiral metal-based catalysts is especially attractive, due to its mild conditions and relatively low loadings of the chiral agent.<sup>[1]</sup> Platinum group metals-based catalysts are considered to be particularly effective for the stereoselective reduction of the carbonyl compounds even at low catalyst loading,<sup>[1,2]</sup> yet high toxicity and cost of platinum group metals seem to be substantial limitations, especially in the large-scale synthesis of bioactive compounds.

In respect to meet green chemistry approaches, consideration of environmental concerns must be addressed at early stages of product development. This is also important in the synthesis of optically pure alcohols and amines which are crucial building blocks for the synthesis of complex molecules. By doing so, firstly an application of highly efficient catalytic systems based on inexpensive, safer, non-noble metal sources and secondly excluding of unnecessary reagents and solvents should constitute the crucial development priorities. To meet these criteria, a number of iron<sup>[3,4]</sup> and zinc<sup>[5-6]</sup> complexes have been developed

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Scheme 1. Development of non-noble metal-based catalysis at low catalyst loadings.

as efficient catalysts for the asymmetric hydrosilylation of carbonyl substrates, recently.

The first example of zinc-based asymmetric hydrosilylation of ketones was reported by Mimoun in 1999 by using polymethylhydrosiloxane (Scheme 1a).<sup>[6a]</sup> Following this achievement, a number of protocols based on diethylzinc complexes was then developed,<sup>[6]</sup> but the most efficient examples require 1-2 mol% of a catalyst.<sup>[6a-f,h]</sup> Recent progress in this field concerns application of cheap, stable and non-hazardous zinc acetate<sup>[7,8]</sup> successfully replacing previously used diethylzinc complexes.<sup>[6]</sup> However, known Zn-based catalysts are still less efficient in comparison with platinum-group metals. In particular,

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hydrosilylation of carbonyl compounds employing low catalyst loadings (≤1%) are fairly limited.

Noteworthy progress have been observed in nonasymmetric hydrosilylation of ketones promoted by iron complexes.<sup>[4d,9]</sup> Basing on Tilley's work,<sup>[9a]</sup> Turculet reported the use of N-phosphinoamidine-based catalyst (Scheme 1b) at remarkably low loadings (down to 0.01 mol%).<sup>[9b]</sup> Recently, iron complexes with BIAN ligands were tested by Findlater.<sup>[9c]</sup> Interestingly, various ketones were reduced by using 1 mol% of catalyst under solvent-free conditions at elevated temperature (Scheme 1c). More efficient catalyst was presented by Chirik and co-workers who investigated the iron dialkyl complexes of pybox ligands for the hydrosilylation of acetophenone derivatives (Scheme 1d). The reactions were carried out under mild conditions with only 0.3 mol% of catalyst providing corresponding alcohols with moderate enantioselectivities (up to 50%), however.<sup>[4d]</sup> A significant example of more reactive and enantioselective hydrosilylation of ketones has been presented recently by Gade.<sup>[4k]</sup> The reaction scope was, however, demonstrated by using 5 mol% of iron complex with boxmi ligand.

Recently, we elaborated a convenient protocol for enantioselective hydrosilylation of prochiral ketones<sup>[8a,b]</sup> and imines<sup>[8c]</sup> by using readily available chiral  $Zn(OAc)_2$  complexes. However, the relatively high catalyst loading (5 mol%) was considered to be a potential limitation for industrial application of our methods.

Although significant steps toward sustainability can be made by decreasing of the catalyst loading, another environmentally benign strategy is to conduct the reactions under solvent-free conditions.<sup>[10]</sup> To our best knowledge such a protocol has never been used for Zn-catalyzed enantioselective hydrosilylation,<sup>[9,11]</sup> and some previously reported studies required application of protic solvent as a crucial reaction component.<sup>[6]</sup>

Now, we present an improved protocol for the asymmetric hydrosilylation where only 0.05-0.1 mol% of zinc acetate complexes has been applied for the reduction of various ketones and imines. Moreover, presented stable zinc complexes bearing convenient (*R*,*R*)-1,2-diphenylethylene-1,2-diamine-derived ligands can be employed at room temperature not only with unprecedented activity but also selectivity for the 1,2-reduction of  $\alpha$ , $\beta$ -unsaturated ketones under solvent-free conditions.

Based on previous studies in our group<sup>[8]</sup> we selected  $(EtO)_2MeSiH$  (DEMS) and  $(EtO)_3SiH$  (TES) as the most promising silanes allowing to obtain enantioenriched (S)-1-phenylethanol

Table 1. Asymmetric hydrosilylation of 1a under various conditions.<sup>[a]</sup>

O 1) Zn(OAc) <sub>2</sub> :L1 (1:2) OH silane (2 equiv.), 24 h 2) TBAF 1a 2a						
Entry	Silane	Solvent	Temp.	Cat. loading [mol%]	Conv. [%] <sup>[b]</sup>	ee [%] <sup>[b]</sup>
1	DEMS	THF	rt	1	-	-
2	TES	THF	rt	1	99	93
3	TES	THF	rt	0.3	99	94
4	TES	THF	-30 °C	0.3	-	-
5 <sup>[c,d]</sup>	TES		rt	0.3	99	89
<b>6</b> <sup>[c,e]</sup>	TES	-	rt	0.05	99	94
7	TES	-	-30 °C	0.05	-	-

[a] Reactions were carried out by stirring zinc acetate with L1 (1:2 molar ratio) in THF (1 mL) at room temperature under argon. Silane (1 mmol) and acetophenone (0.5 mmol) were added and the reaction mixture was stirred at the mentioned temperature for 24 h. [b] Conversions and *ees* were determined by HPLC methods. [c] Reaction was carried out by stirring acetophenone (5 mmol) with zinc acetate and L1 (1:2 molar ratio) in TES (10 mmol) at room temperature under argon. [d] Reaction was completed after 40 min. [e] Reaction was completed after 6 h.

(2a) as a model product. The reaction carried out in THF with 5 mol% of the catalyst resulted in the formation of desired alcohol with 94% ee when DEMS was used as a hydrogen source and 93% ee in the case of TES. Further reduction of the catalyst loading was unfortunately not possible in the case of DEMS (Table 1, entry 1), but to our delight TES remained a useful hydrogen source even at low catalyst loading (entries 2 and 3). Given the considerable efficiency of Fe-based catalytic system under solvent-free conditions reported previously<sup>[9c,11]</sup> we decided to exclude solvent from the reaction. Such protocol resulted in dramatic reduction of the reaction time from about 24 hours (entry 3) to 40 minutes (entry 5). High concentration of the reagents, however, caused heat evolution and the resulting product was obtained with lower enantioselectivity. Further decrease of the amount of the catalyst to 0.05 mol% provided the desired product with 94% ee and quantitative conversion of the substrate (entry 6). The catalytic activity of our system declines at low temperatures (entries 4 and 7) while an excellent catalytic activity was maintained for the reaction carried out at room temperature.

After choosing the best silane and with the reaction conditions optimized, several alkyl-aryl ketones have been investigated as useful carbonyl substrates. In all cases, the

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promoted by zinc acetate-L1 complex.[a] 1) 0.05 mol% Zn(OAc)<sub>2</sub> 0.1 mol% L1 ŌН 2 equiv. (EtO)<sub>3</sub>SiH 25 °C, 6 h  $R_2$ 2) TBAF 1a-I 2a-I ОН OН OН 2c 2b 79% yield, 96% ee<sup>[b]</sup> 81% yield, 94% ee 75% yield, 96% ee<sup>[b]</sup> OMe OH OH MeO MeO 2d 2e 2f 85% yield, 90% ee 90% yield, 95% ee 88% yield, 90% ee OH CI CI **2g** 92% yield, 90% ee 94% yield, 90% ee 93% yield, 87% ee OH OH OH O<sub>2</sub>N 02N 2k 21 2 79% yield, 92% ee<sup>[b,c]</sup> 93% yield, 81% ee 98% yield, 93% ee

Table 2. Yields and ee values of acetophenone derivatives hydrosilylation

[a] Reactions were carried out by stirring ketone (5 mmol) with zinc acetate and **L1** (1:2 molar ratio) in TES (10 mmol) at room temperature under argon atmosphere for 6 h. The resulting silyl ethers were hydrolyzed with TBAF. After purification by column chromatography *ee* values were determined by HPLC methods. [b] 0.3 mol% of catalyst were used. [c] Reaction was completed after 10 h.

reactions proceeded efficiently with only 2 equivalents of the silane. The results are summarized in Table 2 with given yields of the final products isolated by column chromatographic purification. An increase of steric bulkiness of an alkyl chain heightened *ee* values to 96% (**2b**, **2c**), however, these substrates required increasing catalyst loading to 0.3 mol% for the reactions to proceed.

The hydrosilylation reactions of acetophenone derivatives bearing various electron donating (2d-2i) and electronwithdrawing groups (2j-2k) were also carried out with very good yields. While for most substrates the efficiency of our catalytic system did not depend on the type of the substituent and alcohols were obtained with slightly lower enantioselectivities compared with acetophenone (about 90%), for 2e bearing *m*-MeO group a slight increase of ee value was observed, whereas **2k** with an electron-withdrawing substituent at *para* position was reduced with a low level of enantioselectivity (81%). The hydrosilylation of 2-acetonaphthone was also carried out with very good *ee* value (**2I**).

Based on the literature and our own studies, we postulate a tentative mechanism for the hydrosilylation of acetophenone by using [Zn]-DPEDA catalytic system as depicted in Scheme 2. Previously, Kwit<sup>[12]</sup> suggested that formation of a hydrogen bond between the proton of the amino group and the oxygen atom of the carbonyl group is crucial for spatial arrangement of both a catalyst and a ketone. Moreover, the pathway assuming formation of a Zn-hydride species was reported to be the most favorable. We indeed observed a Zn-H at  $\delta$  = 4.55 ppm (see Supporting Information). Thus, based on <sup>1</sup>H NMR spectra analysis, we suggested two possible transition states explaining observed enantioselectivity (Scheme 2). The key step of the reaction involves formation of a hydrogen bond between the amino group

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Scheme 2. Proposed transition states explaining observed stereoselevtivity.

of the activated Zn-H catalyst and the carbonyl group of the ketone. Relative orientation of the substrate is determined by the steric repulsion between bulky 3,5-di-*tert*-butylbenzene moiety and larger substituent adjacent to the carbonyl group. In the favored approach zinc hydride attacks acetophenone from the *Re* face resulting in the formation of (*S*)-configuration product.

Having in hand this efficient catalyst, we decided to test also its applicability to the hydrosilylation of unsaturated ketones and imines. In contrast to hydrosilylation of alkyl-aryl ketones and imines relatively few reports were quoted involving selective 1,2reduction of  $\alpha$ , $\beta$ -unsaturated compounds promoted by non-noble metals, in most cases focusing only on reduction of 4-phenylbut-3-en-2-one.<sup>[4a,4f-g,6a,6d,6n,7a-b,13]</sup> However, the reaction deserves special attention since so-obtained allyl alcohols and amines may

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be used for a wide range of subsequent diastereoselective transformations.<sup>[14]</sup> Recently, Lipshutz provided protocols for the CuH-catalyzed 1,2-reduction of  $\beta$ , $\beta$ - and  $\alpha$ -substituted enones

leading to secondary allyl alcohols (Scheme 1c).<sup>[13b,c]</sup> High enantioselectivities (up to 95%) were induced by expensive and difficult to obtain SEGPHOS and BIPHEP ligands.

Thus, the Zn-L1 catalyzed enantioselective hydrosilylation was extended to various enones and biaryl ketones (Table 3). It should be noted that an optimal catalyst loading strongly depends on type of substrate and was carefully determined for each example. We started our substrate screening with 4-phenylbut-3-en-2-one (**3a**) which resulted in the chemoselective 1,2-reduction providing corresponding product (**4a**) with moderate yield and **Table 3.** Yields and *ee* values of various ketones hydrosilylation promoted

by zinc acetate-L1 complex.[a]



[a] Reactions were carried out by stirring ketone (0.5 mmol) with zinc acetate and **L1** (1:2 molar ratio) in TES (10 mmol) at room temperature under argon atmosphere for 6 h. The resulting silyl ethers were hydrolyzed with TBAF. After purification by column chromatography ee values were determined by HPLC methods. [b] Hydrolysis was carried out using  $K_2CO_3$  in MeOH. [c] 0.3 mol% cat. [d] Reaction time 8 h. [e] 0.1 mol% cat. [f] 0.2 mol% cat. [g] Starting material was retrieved. [h] 1M HCI was used for hydrolysis of silyl ether. 
 Table 4. Conversion and ee values of various ketimines hydrosilylation

 promoted by zinc acetate-L2 complex.<sup>[a]</sup>



[a] Reaction was carried out by stirring *N*-phosphinylimine (0.44 mmol) with zinc acetate (0.022 mmol) and **L2** (0.022 mmol) in TES (0.88 mmol) at room temperature under argon atmosphere for 24 h. The reactions were then quenched by addition of NaOH in MeOH. After purification by column chromatography *ee* values were determined by HPLC methods.

81% ee. Then we tested the impact of further changes of αsubstitution on the outcome of the reaction. a-Substitution with a methyl (4b) or a benzyl group (4d) led to the desired products with very good enantioselectivities (89% for both examples), whereas phenyl group (4c) decreased enantioselectivity down to 75%. This tendency was previously reported by Lipshutz.<sup>[13b]</sup> Modification of the length of an alkyl chain at  $\beta$  (4e) or  $\alpha$ ' position (4f) did not affect the stereoselectivity of the reaction leading to the corresponding alcohols with 81% and 88% ee respectively. The hydrosilylation reactions of substrates with two sp<sup>2</sup> carbon atoms adjacent to carbonyl group (4g-i) resulted in either obtaining good yield but products with poor, close-to-racemic enantioselectivity (4g, 4h) or no conversion in case of substrate 3i. The reductions of substrates with various conjugated systems were also carried out. Interestingly, the reduction of the substrate bearing ynone moiety gave a corresponding propargyl alcohol (4j) with excellent enantioselectivity. Finally,  $\alpha$ , $\beta$ , $\gamma$ , $\delta$ -unstaturated systems were tested leading to quantitative conversion of dienons

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after only 6 hours with 0.1 mol% catalyst loading providing products of 1,2-addition with good ees. Noteworthy,  $\alpha$ -substitution slightly increased stereoselectivity (4I) compared with unsubstituted product (4k).

Lastly, we applied our methodology for the reduction of various *N*-phosphinylimines. This requited however 5 mol% of zinc acetate-(1*R*,2*R*)-*N*,*N*-dibenzyl-1,2-diphenylethane-1,2-diamine (**L2**) with (1:1) [Zn]:**L2** molar ratio (Table 4). As collected data show solvent-free conditions had only a slight influence on enantioselectivity of preformed reactions (**6a-6e**) compared with those carried out in dry THF.<sup>[Bf]</sup> Conjugated *N*-phosphinylenimines gave corresponding products with very good ees (**6f**, **6g**), which are similar to the values obtained when ZnEt<sub>2</sub> was used as a zinc source.<sup>[6n]</sup>

In summary, a zinc acetate-diamine complex has been proven to catalyze hydrosilylation of various ketones under solvent-free conditions with remarkably low catalyst loadings (0.05-0.3 mol%). The reductions of substrates with various conjugated systems resulted in formation of products of 1,2addition. The enantioenriched alcohols were obtained with very good yields (up to 98% of isolated product) and stereoselectivities (ees up to 97%). The mechanistic aspect of our method has been studied by <sup>1</sup>H NMR spectra analysis proving formation of the Zn-H species. In general, enantioenriched *N*-Dpp amines were also obtained with good yields and very good enantioselectivities, although the catalyst loading necessary for the reactions to proceed still remains relatively high (5 mol%).

#### **Experimental Section**

#### General procedure for asymmetric hydrosilylation of ketones

 $Zn(OAc)_2$  and L1 samples were prepared using microbalance. To a 5 ml vial equipped with a magnetic stir bar were subsequently added: 0.46 mg (0.0025 mmol)  $Zn(OAc)_2$ , 3.06 mg (0.005 mmol) L1, ketone (0.833–5 mmol, 1 equiv.) and triethoxysilane (1.67–10 mmol, 2 equiv.). The vial was flushed with Ar and sealed. The completion of the reaction was monitored by TLC. After specified time the reaction was cooled to 0 °C, quenched with tetrabutylammonium fluoride solution 1.0 M in THF. After stirring for 5 minutes the mixture was then subjected to a silica gel column and eluted with a mixture of hexane and ethyl acetate (6:1). The ee values were then determined by HPLC methods.

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