

## Communication

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J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.7b04137 • Publication Date (Web): 27 Jun 2017 Downloaded from http://pubs.acs.org on June 27, 2017

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# Highly Enantioselective Cobalt-Catalyzed Hydrosilylation of Alkenes

Biao Cheng, Peng Lu, Heyi Zhang, Xinpeng Cheng, Zhan Lu\*

Department of Chemistry, Zhejiang University, Hangzhou 310058, China

Supporting Information Placeholder

**ABSTRACT:** A cobalt-catalyzed highly Markovnikov-type and enantioselective hydrosilylation of alkenes is developed for the efficient synthesis of valuable chiral dihydrosilanes. This protocol is operationally simple and atom-economy, and using relatively simple and readily available starting materials. The reaction is suitable for both aryl and aliphatic alkenes with excellent functional group tolerability. The reaction could be easily carried out in a gram-scale. The TOF and TON is upto 1800 and 860, respectively.

Chiral organosilanes have gradually emerged their utilities in organic synthesis,<sup>1</sup> material science,<sup>2</sup> as well as silasubstitution in medicinal chemistry.<sup>3</sup> Several protocols have been generally developed to prepare highly enantiopure organosilanes, such as asymmetric hydrosilylation of double bond,<sup>4</sup> desymmetrization of silanes<sup>5</sup> and asymmetric silicon-hydride bond insertions.<sup>6</sup> To be an ideal synthetic strategy for the construction of carbon(sp<sup>3</sup>)silicon bonds, it shloud be enabled to tolerate various substitutents available for further derivatization. The hydrosilanes containing multiple hydrogen-silicon bonds have been proven as good candidates available for further elaboration. However, the previously reported methods were used to only afford chiral fully substituted silanes and few trisubstituted silanes whose potential utilities for silane drug-candidates, as well as modern materials and industrial processes were limited. The development of efficient methodologies for highly enantioselective construction of chiral silanes containing multiple hydrogen-silicon bonds is still highly desirable.

Noble transition metal-catalyzed hydrosilylation of alkenes is one of key methods to construct organosilanes.<sup>7</sup> In recent years, the useage of earth-abundant transition metals, such as chirik's iron catalysis,<sup>8</sup> leads to rapid growth of olefin hydrosilylation (**Scheme 1a**).<sup>9</sup> Very recently, Huang<sup>10</sup> and Ge<sup>11</sup> groups independently reported cobalt-catalyzed racemic Markovnikov hydrosilylation of alkenes in which the effects on regioselectivity were well studied on metals, ligands, substrates and silanes. However, in their studies, the corresponding multi-nitrogen dentated ligands proven to be not suitable for highly Markovnikov hydrosilylation of styrenes. To the best of our knowledge, the efficient earth-abundant transition metal catalysts Transition-metal-catalyzed hydrosilylation of alkenes



Previous works on highly enantioselective intermolecular hydrosilylation of olefins:



Scheme 1. Highly enantioselective intermolecular hydrosilylation of terminal olefins.

for enantioselective Markovnikov hydrosilylation of alkenes has not been well explored.

Hayashi and co-workers<sup>12</sup> found the MOP ligand could promote the palladium-catalyzed highly enantioselective hydrosilylation of alkenes (Scheme 1b). Then, various chiral phosphine ligands<sup>13</sup> have been applied for asymmetrichydrosilylation of alkenes, however, the silanes have to be polychloriznated or polyfluorinated silanes which limited functional group toleration. Tamao group<sup>14</sup> and Bosnich group<sup>15</sup> independently reported intramolecular asymmetric hydrosilylation of alkenes with silanes for synthesis of chiral cyclic silanes. In additionally, few examples on intermolecular highly enantioselective hydrosilylation of alkenes with non-halide silanes were described using cyclic vinyl esters or norbornene as substrates with anti-Markovnikov selectivity,<sup>16</sup> or using 1,1disubtituted alkenes with Markovnikov selectivity and moderate ee.<sup>17</sup> Nishiyama and co-workers reported a NCN-rhodiumcatalyzed asymmetric hydrosilylation of styrenes with trisubstituted hydrosilanes, however, the regioselectivity of this transformation is modest in many cases (30/70~91/9 b/l).<sup>18</sup> While this manuscript was in preparation, a copper-catalyzed asymmetric hydrosilylation of styrenes with silanes using chiral diphosphine ligand was reported by Buchwald group.<sup>19</sup> However, the reaction using superstoichiometric amount of silanes (1.5~5 equiv) should take 12~72 hours, and the chiral disubstituted hydrosilanes were synthesized only as intermediates for the preperation of chiral

Table 1. Optimization for asymmetric hydrosilylation of styrene.<sup>*a*</sup>



Pł	ר + PhSiH₃	cat. OIP <sup>.</sup> CoCl <sub>2</sub> cat. NaO <sup>r</sup> Bu	SiH <sub>2</sub> Ph	SiHaPh	
		N <sub>2</sub> , solvent, rt, 1 h	Pn		
	1a 2a		3a 4a		
entry	$L \cdot CoCl_2$	ashumt (M)	yield of $3a+4a (\%)^b$	<i>ee</i> of <b>3a</b>	
	(mol %)	solvent (NI)	(b/l)	$(\%)^{c}$	
1	La (5)	THF (0.25)	73 (95/5)	72	
2	Lb (5)	THF (0.25)	74 (92/8)	88	
3	Lc (5)	THF (0.25)	63 (93/7)	98.6	
4	Ld (5)	THF (0.25)	66 (95/5)	98.7	
5	Le (5)	THF (0.25)	56 (97/3)	98.8	
6	Lf (5)	THF (0.25)	71 (>98/2)	98.5	
7	Lg (5)	THF (0.25)	75 (>98/2)	97.9	
8	Lh (5)	THF (0.25)	18 (34/66)	-	
$9^d$	<b>Lf</b> (1)	THF (0.25)	80 (>98/2)	98.6	
$10^{d}$	<b>Lf</b> (1)	toluene (0.25)	73 (>98/2)	99.3	
$11^{d}$	<b>Lf</b> (1)	dioxane (0.25)	82 (>98/2)	99.0	
$12^{d}$	<b>Lf</b> (1)	Et <sub>2</sub> O (0.25)	83 (>98/2)	99.2	
$13^{d}$	<b>Lf</b> (1)	Et <sub>2</sub> O (0.5)	89 (>98/2)	99.4	
$14^d$	<b>Lf</b> (1)	Et <sub>2</sub> O (1.0)	88 (>98/2)	99.2	
15 <sup>d,e</sup>	<b>Lf</b> (1)	Et <sub>2</sub> O (0.5)	83 (98/2)	99.7	
$16^{d,e,f}$	<b>Lf</b> (1)	Et <sub>2</sub> O (0.5)	84 (>98/2)	99.3	
$17^{e,f,g}$	Lf (0.3)	Et <sub>2</sub> O (0.5)	90 (>98/2)	99.0	
18 <sup>e, h</sup>	<b>Lf</b> (1)	Et <sub>2</sub> O (0.5)	84 (>98/2)	99.3	
$19^{e}$	-	Et <sub>2</sub> O (0.5)	0	-	
<sup>a</sup> The reaction was conducted using styrene (0.6 mmol), phenvlsilane (0.5					

<sup>a</sup>The reaction was conducted using styrene (0.6 mmol), phenylsilane (0.5 mmol), cobalt complex and NaO'Bu (3 equiv to cobalt precatalyst) in a solution at room temperature for 1 hour. <sup>b</sup> Determined by <sup>1</sup>H NMR using TMSPh as an internal standard. <sup>c</sup> Determined by chiral HPLC. <sup>d</sup>1.5 mmol scale. <sup>e</sup> 1a/2a = 1/1. <sup>f</sup> 10 min. <sup>g</sup> 3 mmol scale. <sup>h</sup> With 1 equiv. of water.

alcohols via Tamao oxidation. Additionally, the reaction of aliphatic alkenes was not described.

Our group has recently developed a cobalt-catalyzed asymmetric sequential hydrosilylation/hydrogenation of alkynes with diphenyl hydrosilane for the preperation of chiral benzylic silanes containing single carbon(sp<sup>3</sup>)-silicon bond.<sup>20</sup> However, either chiral disubstituted hydrosilanes or nonbenzylic silanes could not be obtained. As a continuation of our interest in earth-abundant transition metal-catalyzed asymmetric reactions, herein, we report a highly enantioselecetive cobalt-catalyzed Markovnikov hydrosilylation of both aromatic and aliphatic alkenes with silanes for the synthesis of chiral dihydrosilanes (Scheme 1c).

In our previous studies, we found that chiral oxazoline iminopyridine (OIP) cobalt complex could catalyze hydrosilylation of styrene with diphenylsilane, however, to afford the linear product as a major one. At the beginning of screening, simple styrene and phenylsilane were chosen as model substrates, and sodium *tert*-butoxide<sup>21</sup> was used as a mild activator. Encouragingly, the hydrosilylation of styrene (0.6 mmol) with phenylsilane (0.5 mmol) using La CoCl<sub>2</sub> (5 mol%) as a precatalyst afforded the desired products in 73% yield with a ratio of 95/5 b/l (entry 1, table 1). Compared to our previous studies, the Markovnikov selectivity was significantly improved using phenylsilane as a silane source. Impressively, when the more



<sup>*a*</sup> The reaction was conducted using styrene (1 mmol), phenylsiliane (1 mmol), cobalt complex (0.01 mmol) and NaO'Bu (0.03 mmol) in a solution of Et<sub>2</sub>O (0.5 M) at room temperature for 1 h. Isolated yield. Without note,  $b/l \ge 98/2$ . <sup>*b*</sup> b/l = 97/3. <sup>*c*</sup> b/l = 96/4. <sup>*d*</sup> 2 mol% of cobalt complex. <sup>*e*</sup> 0 °C. <sup>*f*</sup> Using (*R*)-Lf as a ligand.

sterically hindered imine with 2,6-di(diphenyl)methyl group (Lc) was introduced, the enantioselectivity was dramatically increased up to 98.6% (entries 1-3). The regioselectivity varied with change in different electronic properties on imino group. The reaction using the electron-withdrawing ligand (Ld) afforded products in a slightly low yield with a slightly better regioselectivity compared with the reaction using electron-donating ligands (Le-f) (entries 3-5). Notably, the regioselectivity was also sensitive to substitutents on oxazoline in which a better selectivity was observed using less sterically hindered ozazolines (enties 5-8). The reaction in 1.5 mmol scale could be carried out using 1 mol% of  $Lf CoCl_2^{22}$  to afford 3a in 80% yield with 98.6% ee. Among various screened solvents, such as toluene, dioxane, and diethyl ether (entries 10-12), diethyl ether is the best solvent in which 3a was observed in 82% yield with >98/2 b/l and >99% ee (entry 12). A slightly better yield and enantioselectivity were observed under higher concentration conditions (entries 13 and 14). Using one equivlent of phenylsilane, the reaction underwent smoothly to afford 3a in 83% yield with 98/2 b/l and extremely high ee (99.7%) (entry 15). The reaction could be done in 10 min to afford 3a in 84% yield

Table 2. Scope of chiral silanes.<sup>a</sup>

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59 60 (entry 16). It is worthy to note that the reaction with 0.3 mol% catalyst loading in 3 mmol scale could complete in 10 min, delivering to **3a** in 90% yield with >98/2 b/l and 99% ee (entry 17). The turnover frequency is upto 1800. To our suprise, the reaction could undergo smoothly with one additional equivlent of water which demonstrated that this was not moisture sensitive protocol (entry 18). The reaction did not occur in the absence of precatalyst (entry 19).<sup>23</sup> The standard conditions were chosen as using olefin (1 mmol), phenylsiliane (1 equiv), Lf·CoCl<sub>2</sub> (1 mol%) and NaO'Bu (3 mol%) in a solution of Et<sub>2</sub>O (0.5 M) at room temperature for 1 h.

Under the optimized conditions, the substrate scope is explored in Table 2. 1) Without any note, the regioseleectivity is better than 98/2; 2) The ee values for all benzylic silanes are better than 98%, in most cases, higher than 99% ee; 3) Various electron-donating and electron-withdrawing functional groups are well tolerated, such as phenyl group, ethers, thioethers, trifluoromethyl group, halides, ketal, ester, amides, amines, ketone, silyl group, free alcohol; 4) The substituents at ortho-, meta- and para-position on phenyl group of styrene are also tolerated; 5) The 1-naphethyl, 2-naphthyl and 5-(N-methyl)indyl ethylenes could be delivered to 3s-u in 68-85% yield with 98-99% ee; 6) In particularly, the reaction of sulphur-containing compounds, such as 2-vinyl thiophene and 3-vinyl benzothiophene, afforded the corresponding chiral silanes 3v with 98% and 3w with 98.5% ee, respectively, which is much better than the result using asymmetric Cu-catalyzed reaction (57-66% ee for (3w);<sup>19</sup> This protocol is a good method for suppressing deactivation by coordination with sulphur compounds, which are often used in the rubber industry;7c 7) The reaction of pyridinecontaining alkene afforded 3x in 74% yield with 99% ee; 8) The simple terminal alkyl alkenes or containing functional groups, such as halide, silyl, amide, ketone, and free alcohol, were also compatible with this reaction under 0 °C, delivering 3y-ad in 53-91% yield with 81-87% ee; 9) Notably, various phenylsilanes with electron-donating or electron-withdrawing groups, such as methoxy (2b) and chloro (2c) groups, proved to be suitable for this catalytic system, giving the corresponding products **3ae-af** in 80-97% yields with >99% ee; 10) The opposite enantiomer (R)-3a could be easily obtained using (R)-Lf as a ligand; 10) The absolute configuration was confirmed by X-ray diffraction of (S)-3t<sup>24</sup> 11) The reaction of styrene with strically bulky (MeO)<sub>3</sub>SiH did not occur. The reaction of styrene with Ph<sub>2</sub>SiH<sub>2</sub> afforded the Heck-type linear vinylsilane in 43% yield. This indicated that a sterically demanding silyl group disfavored Markovnikov selectivity due to strong steric repulsion between alkene and silyl group;<sup>11</sup> 12) The reactions of 1,1-disubtituted alkenes (such as 2-(4'-methoxyphenyl)butene) or 1,2-disubstituted alkenes (such as trans-anethole) with PhSiH<sub>3</sub> did not occur.

The gram scale reaction using 0.1 mol% catalyst loading could be smoothly performed to afford **3a** in 86% yield with 98% ee (eq. 1). The turnover number is upto 860.

The chiral silanes could be further derivatized (Scheme 2). The corresponding chiral alcohol **5d** could be easily obtained via Fleming-Tamao oxidation.<sup>25</sup> The silane **3a** could also be controllably oxidized to monohydroxysilane **6a** in 70% yield and dihydroxysilanes **7** in 67-92% yield.<sup>26</sup> There is an interesting sequential strategy for the synthesis of polysubstituted silane **8a** by emerging cobalt-catalyzed Markovnikov selective hydrosilylation of styrene with iron-catalyzed *anti*-Markovnikov selective hydrosilylation of styrene.<sup>27</sup> The cobalt-catalyzed



Scheme 2. Further Derivatizations. a) i) HBF<sub>4</sub>·Et<sub>2</sub>O (5 equiv), DCM (0.02 M), rt, 3 h; ii) KF/KHCO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, MeOH/THF (1/1), rt, 15 h; b) BCl<sub>3</sub> (1 equiv), DCM (0.25 M), 6 h, then H<sub>2</sub>O, overnight; c) Pd/C (0.1 equiv), Et<sub>2</sub>O (0.3 M), H<sub>2</sub>O, rt, overnight; d) styrene (1 equiv), Lb·FeCl<sub>2</sub> (5 mol%), NaBHEt<sub>3</sub> (15 mol%), neat, rt, 12h; e) phenylacetylene (2 equiv), Xantphos·CoBr<sub>2</sub> (10 mol%), NaBHEt<sub>3</sub> (30 mol%), THF (0.5 M), rt, 5 h; f) phenylacetylene (1.2 equiv),  $^{2.4-}_{DMBn}$ OJP·CoBr<sub>2</sub> (5 mol%), NaBHEt<sub>3</sub> (15 mol%), THF (1 M), rt, 3 h. The detail could be found in supporting information.

regioselectivity-controllable hydrosilylation of alkynes could be achieved using Xantphos and OIP ligands<sup>20a</sup> to afford *anti*-Markovnikov and Markovnikov selective products **9a** and **10a** in 59% and 63% yield, respectively.

To demonstrate the possible mechanism of the asymmetric hydrosilylation of olefins, the reaction of D<sub>8</sub>-styrene with 4methoxyphenylsilane was performed under standard conditions to afford D-3ae in 97% yield and 98% ee within a clean regiochemistry transfer of hydrogen on silane into the methyl group on the hydrosilylation product (eq. 2). Based on the of the pyridine diimine-coblat-catalyzed mechanisms hydrosilylation,<sup>28</sup> the alkene insertion to cobalt-hydride bond pathway exists an equilibrium between the alkene insertion to cobalt-hydride bond and  $\beta$ -hydride elimination. Additionally, the low-valent cobalt hydride species is used to be sensitive to moisture. Under this catalytic conditions, water could be tolerated. Based on this, we proposed that the long existence of cobalt hydride species is less possible. Although the alkene insertion to cobalt-hydride bond could not be exclusively ruled out, it should suggest that carbon-carbon double bond insertion into cobaltsilicon intermediate might be a prior step in the reaction.<sup>29</sup> According the previously reported mechanisms of hydrosilvlation of alkenes,<sup>28</sup> the proposed mechanism for asymmetric hydrosilylation of olefin was shown in Scheme 3. The cobalt silicon species (A) obtained from reducing OIP·CoCl<sub>2</sub> by NaO'Bu and PhSiH<sub>3</sub> could undergo alkene insertion to generate cobalt alkyl species (B) which reacted with PhSiH<sub>3</sub> to regenerate cobalt-silicon species and afford the hydrosilylation product. More experimental and computational studies should be further performed to gain an accurate understanding of the origin of the high regio- and enantioselectivity.



Scheme 3. Proposed Mechanism

In summary, we develop a cobalt-catalyzed highly enantioselective Markovnikov-type hydrosilylation of olefins with silanes to construct more valuable chiral dihydrosilanes. The reaction is operationally simple and atom-economy with excellent functional group tolerability. For the vinylarenes, the chiral benzyl silanes are obtained with 82% average yields and better than 98% ee. The aliphatic alkenes are also suitable under optimized conditions to afford the chiral aliphatic dihydrosilanes in 81-87% ee. The opposite enantiomer of silanes could be easily obtained using the opposite enantiomer ligand. The reaction could be easily carried out in a gram-scale using 0.1 mol% of catalyst loading. The TOF and TON is upto 1800 and 860, respectively. Further studies on the utility of chiral dihydrosilanes will be explored in our laboratory.

### ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures, characterization data for all compounds (PDF). X-ray diffraction of Lf·CoCl<sub>2</sub> (cif). X-ray diffraction of **3t** (cif).

# AUTHOR INFORMATION

### Corresponding Author

\*E-mail: luzhan@zju.edu.cn

### Notes

The authors declare no competing financial interests.

## ACKNOWLEDGMENT

Financial support was provided by the National 973 Program (2015CB856600), NSFC (21472162) and Zhejiang University.

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- (23) Although these reactions were carried out in our laboratories without incident, the reaction of alkoxides with PhSiH<sub>3</sub> is known to liberate pyro-phoric SiH<sub>4</sub>. Therefore, all appropriate safety precautions should be taken when carrying out large-scale reactions.
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(29) A primary model to predict the regio- and stereochemical outcome is shown in supporting information.

R 🔨 +	OIP•CoCl <sub>2</sub> (0.1-2 mol NaO <sup>t</sup> Bu (0.5-6 mol%	%) 5) SiH <sub>2</sub> Ar	
ArSiH <sub>3</sub>	$N_2$ , Et <sub>2</sub> O, rt or 0 <sup>o</sup> C, 1	h R Me	
( <i>Tequiv</i> )	ON upto 860	33 examples	
TOF upto 1800 good toleration of various functional groups		53-97 % yields	
		>96/4 b/l	
		81->99 % ee	