

Asymmetric Catalysis

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Regio- and Enantioselective Cobalt-Catalyzed Sequential Hydrosilylation/Hydrogenation of Terminal Alkynes

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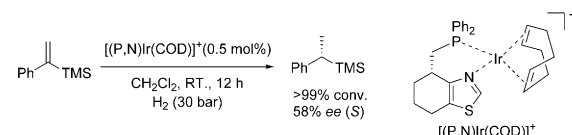
Abstract: A highly regio- and enantioselective cobalt-catalyzed sequential hydrosilylation/hydrogenation of alkynes was developed to afford chiral silanes. This one-pot method is operationally simple and atom economic. It makes use of relatively simple and readily available starting materials, namely alkynes, silanes, and hydrogen gas, to construct more valuable chiral silanes. Primary mechanistic studies demonstrated that highly regioselective hydrosilylation of alkynes with silanes occurred as a first step, and the subsequent cobalt-catalyzed asymmetric hydrogenation of the resulting vinyl-silanes showed good enantioselectivity.

Chiral organosilanes are important synthetic intermediates^[1] for chiral catalysts^[2] and silasubstitution in medicinal chemistry.^[3] Although several methods have been generally developed to prepare chiral organosilanes, such as asymmetric hydrosilylation of double bonds,^[4] desymmetrization of silanes,^[5] and asymmetric silicon-hydride bond insertions,^[6] the development of new strategies to efficiently construct chiral organosilanes is still highly desirable. Asymmetric hydrogenation of unsaturated carbon-carbon bonds^[7] is a useful reaction that has been widely used in organic synthesis, as well as in the chemical industry. Owing to the difficulty in differentiating the two enantiotopic faces in prochiral substrates,^[8] direct highly enantioselective hydrogenation of 1,1-disubstituted vinyl silanes has not so far been reported. In 2006, Andersson and co-workers^[9] reported an iridium-catalyzed asymmetric hydrogenation of vinyl silanes, however, only one example of asymmetric hydrogenation of 1,1-disubstituted vinyl silane was demonstrated, with 58 % *ee*.

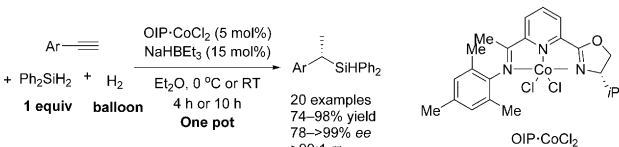
Sequential reactions are one of the most powerful synthetic methodologies, and they show unique step-economy features, decrease the cost of purifications, and improve the efficiency of synthesis.^[10] Inspired by previously reported work on the hydrosilylation of alkynes^[11] and asymmetric hydrogenation of alkenes,^[12] we developed a one-pot cobalt-catalyzed regio- and enantioselective sequential hydrosilylation/hydrogenation reaction of terminal alkynes to prepare chiral organosilanes (Scheme 1).

During our previous studies,^[11c] we found that the reaction of phenylacetylene **1a** with 3 equivalents of diphenylsilane

Anderson (2006)

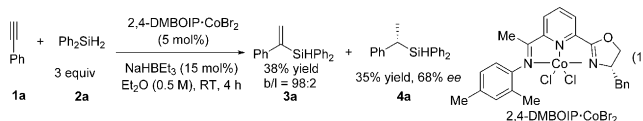


This work



Scheme 1. Transition-metal-catalyzed asymmetric hydrogenation for the synthesis of chiral silanes.

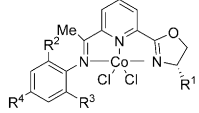
through asymmetric cobalt catalysis affords vinyl silane **3a** in 38 % yield, as well as the side product **4a** in 35 % yield with 68 % *ee* [Eq. (1)]. This initial result strongly encouraged us to optimize the reaction conditions for this unexpected chiral silane.



At the beginning of the optimization, hydrogen gas was selected as a more atom-economic hydrogenation reagent than hydrosilane. The reaction of **1a** with Ph_2SiH_2 in the presence of 5 mol % of cobalt precatalyst **L1a**- $CoCl_2$ ^[13] and 15 mol % of $NaBHET_3$ as a reductant in a solution of Et_2O (0.5 M) at room temperature using a balloon of hydrogen gas afforded the hydrosilylation product in 44 % yield (Table 1, entry 1) and a mixture of the branched and linear hydrogenation products **4a** and **5a** in 37 % yields with a 60:40 ratio of regioisomers (*rr*). When we changed the group on the oxazoline to an isopropyl group, hydrosilylation/hydrogenation products were afforded in 32 % yield with 93:7 *rr* (entry 2). When using less steric bulky 2,6-dimethyl imine (**L1c**), a significant improvement was observed, and the reaction afforded **4a** in 83 % yield with > 99:1 *rr* and 80 % *ee* (entry 3). When 2,4,6-trimethyl imine was used, the enantioselectivity of the reaction to give **4a** was increased to 88 % without any vinyl silanes (**L1d**, entry 4). The reaction with a ligand with a less sterically bulky methyl group on the oxazoline moiety afforded **4a** in 91 % yield and 88 % *ee* (entry 5). Various cobalt precatalysts, as well as reductants and solvents, were screened, but no better results were

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Table 1: Reaction optimization.^[a]


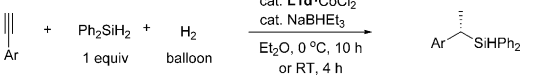
L1a·CoCl₂: R¹ = *i*Bu, R² = R³ = *i*Pr, R⁴ = H
L1b·CoCl₂: R¹ = *i*Pr, R² = R³ = *i*Pr, R⁴ = H
L1c·CoCl₂: R¹ = *i*Pr, R² = R³ = Me, R⁴ = H
L1d·CoCl₂: R¹ = *i*Pr, R² = R³ = R⁴ = Me
L1e·CoCl₂: R¹ = Me, R² = R³ = R⁴ = Me

Entry	Ligand	Yield 4a + 5a [%] ^[b] (b/l)	<i>ee</i> for 4a [%]	Yield of 3a [%] ^[b]
1	L1a	37 (60:40)	—	44
2	L1b	32 (93:7)	—	35
3	L1c	83 (>99:1)	80.4	<5
4	L1d	88 (>99:1)	88.0	0
5	L1e	91 (>99:1)	87.8	<5
6 ^[c]	L1d	80 (>99:1)	91.0	<5
7 ^[d]	L1d	72 (>99:1)	90.0	17

[a] **1a** (1.0 mmol), Ph₂SiH₂ (1 equiv), [Co] (0.05 equiv), NaBHET₃ (0.15 equiv), Et₂O (0.5 M), H₂ (balloon), RT, 4 h. [b] Yields were determined by ¹H NMR using TMSPh as an internal standard, and *ee* values were determined by HPLC. [c] Run at 0 °C, 10 h. [d] Run at –10 °C, 10 h.

obtained (see the Supporting Information). The reaction was carried out at 0 °C for 10 h to afford **4a** in 80 % yield with 91 % *ee* (entry 6). Upon further decreasing the reaction temperature to –10 °C, no improvement was observed (entry 7). The standard conditions were alkyne (0.5 mmol), Ph₂SiH₂ (1 equiv), **L1d**·CoCl₂ (0.05 equiv), and NaBHET₃ (0.15 equiv) in a solution of Et₂O (0.5 M) with a balloon of H₂ at 0 °C for 10 h or RT for 4 h.

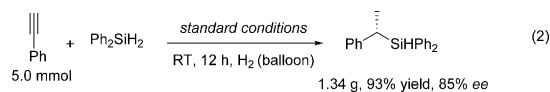
Having identified optimized reaction conditions, we investigated the scope with respect to the alkyne (Table 2). Unless otherwise noted, the *rr* values of all the reactions were greater than 50:1. Electron-donating or -withdrawing substituents on the phenyl ring were tolerated. TBS or benzyl protecting groups on a benzyl alcohol remained unchanged under the standard conditions. Interestingly, 3-chlorophenylacetylene and 3-bromophenylacetylene were converted into **4h** and **4i** in 83 % yield and greater than 99 % *ee*. More sterically hindered 3,5-dimethylphenylacetylene reacted to give **4j** in 80 % yield and 94 % *ee*. When a methyl group was placed at the 4-position of phenyl ring, introducing different substituents at the 3-position, such as methyl (**4k**, 93 % *ee*), ester (**4l**, 78 % *ee*), or chloro (**4m**, >99 % *ee*) groups, did affect the enantioselectivity of the reaction. 2-Naphthyl (**2n,o**), 9H-fluoren-2-yl (**2p**), 5-indyl (**2q**) groups were tolerated, with the chiral silane products produced in 84–86 % yield and 87–97 % *ee*. The reaction of alkyl acetylenes afforded the corresponding vinyl silanes **6** and **7** in only 70–80 % yield, but with high regioselectivity and without any hydrosilylation/hydrogenation products. Other diaryl silanes, such as di(3,5-dimethylphenyl) and di(2-naphthyl), could be also used as hydrosilylation reagents. The absolute configuration was verified by comparison of the optical rotation of 1-([1,1'-biphenyl]-4-yl)ethanol, which was obtained through oxidation of **4e**, with previously reported data.^[14]

Table 2: Substrate scope.^[a]


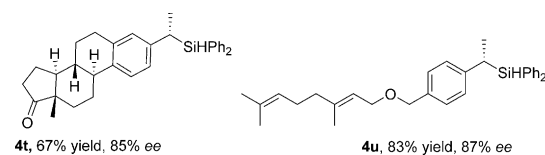
4b , 84%, 92% <i>ee</i>	4c , 87%, 92% <i>ee</i>	4d , 95%, 92% <i>ee</i>	4e , 86%, 85% <i>ee</i>
4f , 97%, 90% <i>ee</i> ^[b]	4g , 82%, 91% <i>ee</i>	4h , 83%, >99% <i>ee</i> ^[b]	4i , 83%, >99% <i>ee</i> ^[b]
4j , 80%, 94% <i>ee</i>	4k , 75%, 93% <i>ee</i>	4l , 91%, 78% <i>ee</i> ^[b]	4m , 91%, >99% <i>ee</i> ^[b]
4n , 84%, 87% <i>ee</i>	4o , 86%, 97% <i>ee</i>	4p , 85%, 87% <i>ee</i>	4q , 85%, 91% <i>ee</i> ^[b]
6 , 70%, >99/1 ^[b]	7 , 80%, >99/1 ^[b]	4r , 79%, 85% <i>ee</i> ^[b]	4s , 74%, 90% <i>ee</i> ^[b]

[a] Alkynes (0.5 mmol), Ph₂SiH₂ (1 equiv), [Co] (0.05 equiv), NaBHET₃ (0.15 equiv), Et₂O (0.25 M), 0 °C, 10 h. [b] 1 mmol scale, Et₂O (0.5 M), RT, 4 h. [c] With 0.2 equiv of [Co].

The reaction could be carried out on a gram scale at room temperature to afford **4a** in 93 % yield and 85 % *ee* [Eq. (2)].



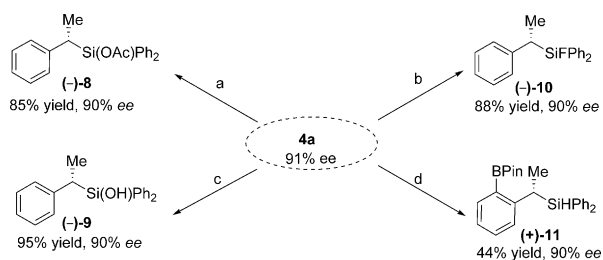
Alkynes contained in bioactive molecules could also be converted into corresponding chiral silanes (Scheme 2). Functional groups such as ketones, alkenes, and ethers were also tolerated, which suggests that the reaction has the potential to be a good late-stage functionalization strategy for complicated molecules.



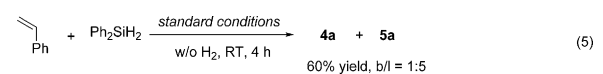
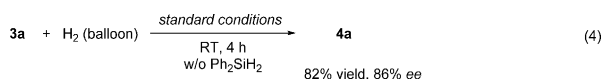
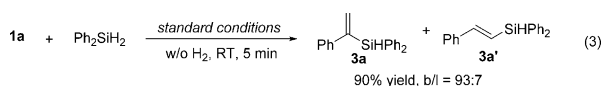
Scheme 2. Late-stage functionalization of complex molecules.

The chiral silanes could be further functionalized to give silanols, silyl esters, silyl fluorides, and C–H boration products under suitable conditions (Scheme 3).^[15]

Control experiments were carried out to elucidate the reaction pathway. In the absence of H₂ gas, the reaction of **1a** with Ph₂SiH₂ afforded **3a** in 90 % yield with 93:7 *rr* [Eq. (3)]. The hydrogenation of **3a** afforded **4a** in 82 % yield and 86 % *ee* [Eq. (4)]. The hydrogenation reaction of the linear silane **3a'** afforded the linear product **5a** with full conversion, albeit in a low yield, which might be additional evidence for the high

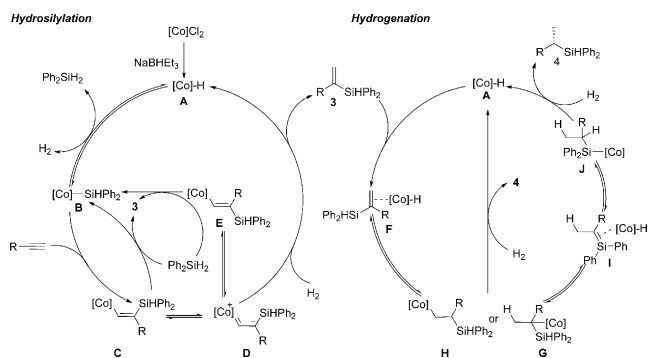
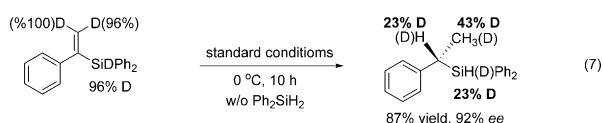
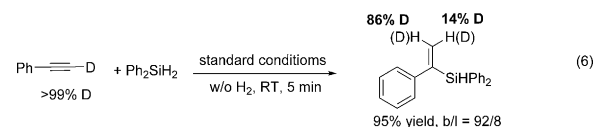


regioselectivity of this sequential reaction. The hydrosilylation of styrene gave a mixture of branched and linear products with a b/l ratio of 1:5 [Eq. (5)]. These two reactions suggest that the reaction most likely occurs through hydrosilylation followed by hydrogenation.



The reaction of deuterated **1a** afforded deuterated **3a** with an *E/Z* ratio of 86:14 [Eq. (6)], which demonstrates that more than one intermediate exists during the alkyne addition. To explain the details of this transformation, the reaction of deuterated **3a** in the presence of H₂ gas at 0 °C was conducted to afford deuterated **4a** in 87% yield and 92% *ee* [Eq. (7)]. Deuteration at the benzyl position and the partial absence of deuteration at the silicon atom and methyl group show that alkene insertion into the cobalt hydride bond is reversible. However, a direct H–D exchange pathway^[16] could not be ruled out.

The proposed reaction mechanism is shown in Scheme 4. The cobalt precursor is reduced by NaBHET₃ to cobalt



Scheme 4. Proposed mechanism for the hydrosilylation/hydrogenation of alkynes.

hydride species **A**, which is silylated by Ph₂SiH₂ to generate cobalt silyl species **B**. The alkyne is inserted into the active cobalt silyl species **B** to afford cobalt vinyl species **C**, which undergoes Crabtree–Ojima-type^[17] isomerization to form intermediates **D** and **E**. All of the intermediates (**C**–**E**) can undergo hydrogen exchange with Ph₂SiH₂ or H₂ to give vinyl silane **3** and regenerate the cobalt silyl species or cobalt hydride species. The hydrogenation reaction^[12h,18] starts with coordination of the vinyl silane to cobalt hydride species **A**, followed by alkene insertion into the cobalt hydrogen bond to form cobalt carbon species **H** and **G**. Both cobalt species can be directly reacted with H₂ to provide the product and regenerate the cobalt hydride species. β-Hydrogen elimination of **G** may occur to give **I**, which may quickly undergo C=Si double-bond insertion to generate cobalt silyl species **J**.^[19] **J** is then quenched with H₂ to form the product and regenerate cobalt hydride species **A**. It should be noted that most of reaction steps are reversible. Further mechanistic studies will be required to elucidate the details of the enantioselective.

In summary, we have developed a novel regio- and enantioselective cobalt-catalyzed sequential hydrosilylation/hydrogenation of alkynes. This one-pot method is operationally simple and atom economic; it uses relatively simple and readily available starting materials to construct more valuable chiral silanes, which can be further functionalized to give diverse silicon-containing chiral compounds. Primary mechanistic studies demonstrated that the regioselectivity is controlled by the alkyne hydrosilylation step and the enantioselectivity is generated through asymmetric hydrogenation of the resulting vinyl silanes. Although enantioselective hydrogenation reactions of 1,1-disubstituted alkenes containing carbon, nitrogen, oxygen, or boron have been successfully achieved, this is a first reported highly enantioselective hydrogenation of 1,1-disubstituted vinyl silanes. Further studies in our laboratory will be focused on base-metal-catalyzed asymmetric sequential reactions.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alkynes · cobalt · hydrogenation · hydrosilylation · silanes

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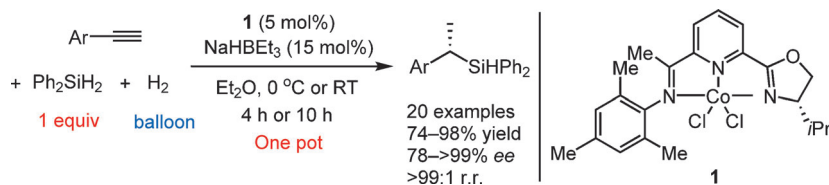
Communications



Asymmetric Catalysis

J. Guo, X. Shen, Z. Lu* — ■■■■-■■■■

Regio- and Enantioselective Cobalt-Catalyzed Sequential Hydrosilylation/Hydrogenation of Terminal Alkynes



We're in this together: A novel regio- and enantioselective cobalt-catalyzed sequential hydrosilylation/hydrogenation of alkynes was developed. This one-pot method is operationally simple and atom economic. It makes use of relatively

simple and readily available starting materials to construct more valuable chiral silanes, which can be further functionalized to diverse silicon-containing chiral compounds.