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Letter

Cobalt-Catalyzed Diastereoselective and Enantioselective Hydrosilylation of Achiral Cyclopropenes

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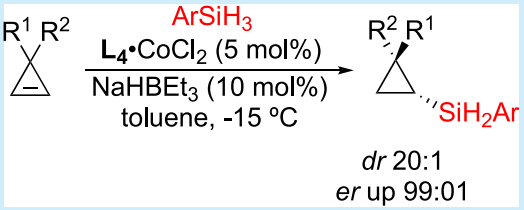
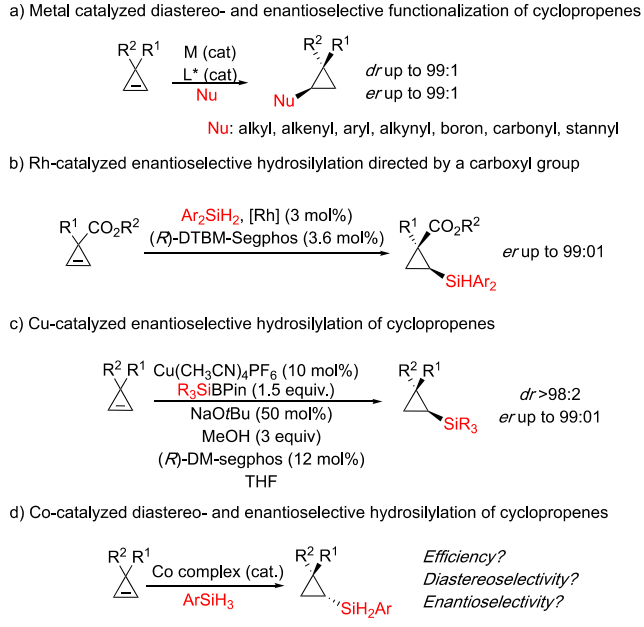
ABSTRACT: A mild diastereoselective and enantioselective cobalt-catalyzed hydrosilylation reaction of achiral cyclopropenes has been developed. In this protocol, various substituted cyclopropenes and arylsilanes were transformed, in the presence of readily available chiral cobalt complex, into silylcyclopropanes with high selectivities.



As three-membered carbocycle is a molecular backbone that frequently appears in natural products and related biologically active compounds,[1] the enantioselective preparation of polysubstituted cyclopropanes has extensively been investigated over the last few decades.[2] In addition, the inherent ring strain of three-membered rings promotes a series of easy transformations such as ring opening,[3] ring expansion,[4] cycloaddition,[5] rearrangement[6] toward the formation of more complex carbon skeletons. In the past few years, the catalytic diastereo- and enantioselective direct functionalization of achiral three-membered carbocycles,[7] as an alternative approach to the cyclopropanation of olefins,[8−10] has attracted significant attention as a new source of enantioenriched polysubstituted cyclopropanes from a common and unique starting material. Using such a direct functionalization strategy, a large variety of nucleophiles—alkyl,[11] alkenyl,[12] aryl,[13] alkynyl,[14] boronyl,[15] carbonyl,[16] stannyl[17] among others[18]—were selectively added on the three-membered ring (Scheme 1a). With the idea of extending the toolbox available to practitioners, we noticed that the catalytic and enantioselective preparation of silylcyclopropanes from unfunctionalized cyclopropenes was less developed until very recent reports from Oestreich[19] and Xu.[20] From the pioneering studies on enantioselective Simmons−Smith reaction of γ-silicon-substituted allylic alcohols using diethyl tartrate as chiral auxiliary[21] to the more recent directed Rh-catalyzed intramolecular enantioselective silylation of cyclopropyl methanol,[22] the pioneering report on Pt-catalyzed racemic hydrosilylation of achiral cyclopropenes was reported by Gevorgyan.[23] Based on this transformation and knowledge acquired for the catalytic functionalization of achiral 3,3-disubstituted cyclopropenes (Scheme 1a), recent enantioselective Rh-desymmetrization of cyclopropenyl ester (Scheme 1b)[20] and Cu-catalyzed enantioselective and diastereoselective addition of Si-nucleophiles to 3,3-disubstituted cyclopropenes (Scheme 1c)[19] were reported illustrating the power of these approaches to prepare silyl-substituted cyclopropanes.

Scheme 1. Enantioselective Preparation of Cyclopropylsilanes



In light of these last reports, we would like to disclose the Co-catalyzed diastereoselective and enantioselective hydrosilylation of achiral cyclopropenes (Scheme 1d). When our model substrate, cyclopropene **1a**, was subjected to the

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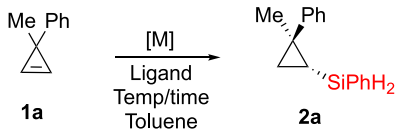
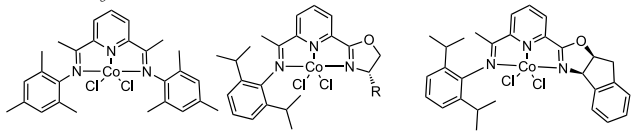
Table 1. Co-catalyzed Diastereoselective and Enantioselective Hydrosilylation of Cyclopropene 1a[a]



entry[b]	[M]	ligand/additive	temperature, T (°C)	diastereomeric ratio, dr[c]	enantiomeric ratio, er[d]
1	L_1·$CoCl_2$	$NaBHEt_3$	−15	20:1	NA
2	L_2·$CoCl_2$	$NaBHEt_3$	−15	ND	NA
3	L_3·$CoCl_2$	$NaBHEt_3$	−15	10:1	86:14
4	L_4·$CoCl_2$	$NaBHEt_3$	−15	20:1	96:04
5	L_5·$CoCl_2$	$NaBHEt_3$	−15	7.3:1	96:04
6[e]	L_4·$CoCl_2$	$NaBHEt_3$	−15	20:1	96:04
7	L_4·$CoCl_2$	–	−15	ND	NA
8	–	$NaBHEt_3$	−15	ND	NA



[a]The reactions were run on a 0.10 mmol scale, [Co] (10 mol %), ligand or additive (20 mol %) in toluene (0.1 M) and the reaction mixture was stirred at the indicated temperature for 5 h. NA, not analyzed; ND, no detection of the desired product. [b]Entries 1, 3, 4, and 6: full conversion; entry 2: 10% conversion; entries 7 and 8: no conversion. [c]Determined by GC analysis of hydrolyzed aliquots. [d]Determined by chiral HPLC. [e]5 mol % cobalt complex (L_4·$CoCl_2$) and 10 mol % $NaBHEt_3$ were used in the reaction.

diastereoselective hydrosilylation reaction with commercially available phenylsilane as a silylating reagent in the presence of palladium or rhodium salts with chiral ligands, no or racemic desired cyclopropylsilane **2a** was detected (see the Supporting Information (SI) for all tested transition metals and conditions). However, inspired by the recent report on cobalt-catalyzed hydrosilylation reaction of double bonds,[24] we first tested the racemic Co-catalyzed hydrosilylation reaction of **1a** with the precatalyst L_1·$CoCl_2$, and we were delighted to observe a very diastereoselective hydrosilylation reaction of **1a** (diastereomeric ratio (dr) = 20:1; see Table 1, entry 1).

Having in hand this precatalyst that smoothly afforded silylcyclopropane as a single diastereoisomer, we concentrated our first efforts to underline the scope of this reaction by varying the nature of the cyclopropenes and the silane, as described in Scheme 2. Cyclopropenes bearing various different substituents on the aromatic ring smoothly undergo the hydrosilylation reaction with $PhSiH_3$ to produce the corresponding silyl-substituted cyclopropanes (**2b**−**2f**; see Scheme 2) in good yield and high diastereoselectivity. Different silanes could also be introduced on the three-membered ring possessing either substituents of different electronic properties on the aromatic ring (**2g**−**2n** in Scheme 2) or by using diphenylsilane Ph_2SiH_2 (**2o**−**2r** in Scheme 2).

Since the racemic L_1·$CoCl_2$ complex was the best combination for a diastereoselective hydrosilylation reaction, a series of cobalt complexes possessing similar structures but with different chiral backbones were prepared and submitted to the hydrosilylation reaction on our model substrate **1a** (see Table 1, entries 2−6). Although the benzyl-substituted precatalyst L_2·$CoCl_2$ did not produce the hydrosilylated product **2a** (see Table 1, entry 2), the cobalt complex L_3·$CoCl_2$ containing an *iso*-propyl moiety smoothly led to **2a** with decent diastereomeric ratio (dr = 10:1) and enantiomeric ratio (er = 86:14) values (see Table 1, entry 3). The best combination was found when the chiral cobalt complex L_4·$CoCl_2$ was engaged in our model reaction and afforded the corresponding product **2a** with high diastereoselectivity and enantioselectivity (dr = 20:1, er = 96:04), demonstrating that the nature of the chiral ligand also significantly influences the diastereoselectivity of the reaction (Table 1, entry 4). To further confirm this steric effect of the chiral ligand on the diastereoselectivity of the hydrosilylation reaction, a more sterically hindered chiral complex (L_5·$CoCl_2$) was synthesized and tested under our standard conditions. In this case, the enantioselectivity was the same but the diastereoselectivity decreased to 7.3:1. Further study showed that the catalyst loading of the complex (L_4·$CoCl_2$) could be decreased to 5 mol %, while preserving the efficiency of the transformation (see Table 1, entry 6). Control experiments indicate that both the cobalt complex and reducing agent ($NaBHEt_3$) were necessary for the enantioselective catalytic hydrosilylation reaction, as no desired product **2a** was observed in their absence (see Table 1, entries 7 and 8, respectively). Having established the best experimental conditions for a mild cobalt-catalyzed diastereoselective and enantioselective hydrosilylation reaction of achiral cyclopropene **1a** (5 mol % cobalt complex L_4·$CoCl_2$, 10 mol % $NaBHEt_3$ in toluene at −15 °C for 5 h), we then have investigated the scope of this transformation. Cyclopropenes having various aromatic substituents undergo similar enantioselective hydrosilylation reaction with phenylsilane to provide the corresponding enantiomerically enriched silylcyclopropanes **2a**−**2e** in good yields with excellent diastereoselectivities and enantioselectivities (see Scheme 3). Different substituted aryl silanes reagents were prepared and tested in our transformation. *para*-Methoxyphenylsilane and tolylsilane, as well as *ortho*-methoxyphenylsilane, were added, with excellent selectivities to various cyclopropenes (**2g**−**2x** in Scheme 3).

Spirocyclopropene also undergoes the Co-catalyzed diastereoselective and enantioselective hydrosilylation reaction with

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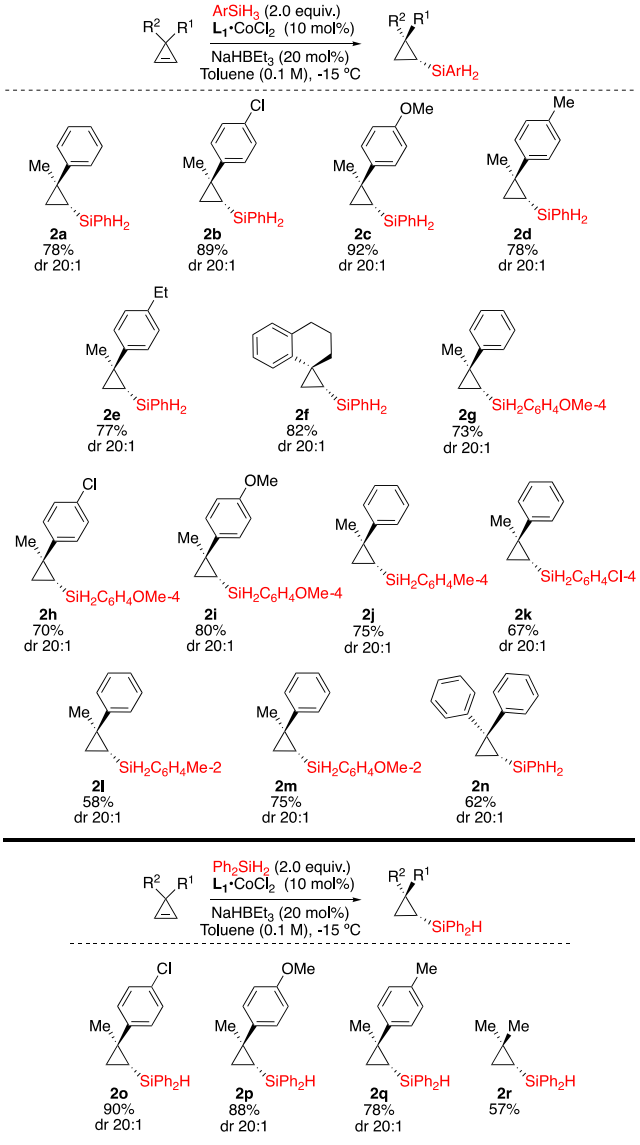
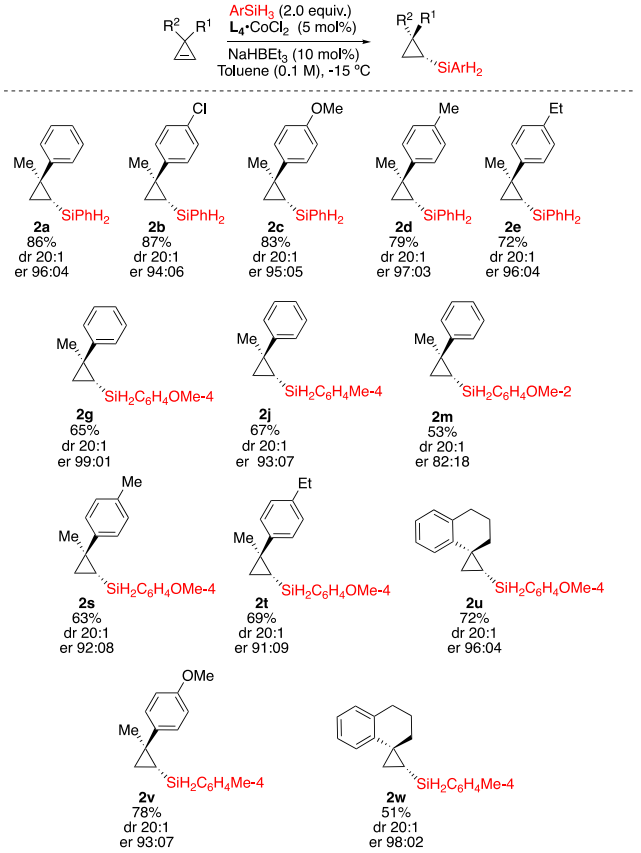
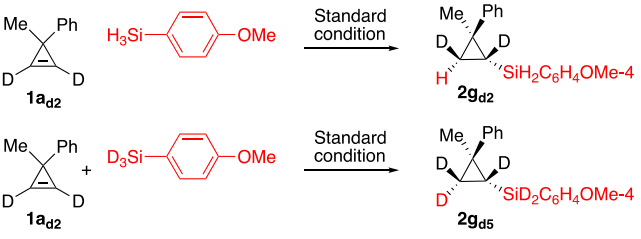
Scheme 2. Diastereoselective Co-catalyzed Hydrosilylation of Cyclopropenes



Scheme 3. Co-catalyzed Diastereoselective and Enantioselective Hydrosilylation of Cyclopropenes



Scheme 4. Labelling Experiments



high efficiency (**2u** and **2w** in Scheme 3). Note that increased steric hindrance around the reactive site of the silane decreases the enantioselectivities (compare **2g** and **2m** in Scheme 3), which was further confirmed when no hydrosilylation reaction was detected when more sterically hindered 1,3,5-trimethylphenylsilane or diphenylsilane was used as a silane reagent (not reported in Scheme 3). The absolute configuration of the cyclopropylsilanes was determined after oxidation of **2a** to cyclopropanol[25] and comparison with literature data.[15b] All other configurations were determined by analogy.

To gain further understanding on the nature of the hydrosilylation reaction, two deuterium labeling experiments were performed. As shown in Scheme 4, when deuterated cyclopropene $\mathbf{1a}_{d2}$ was used as a substrate, $\mathbf{2g}_{d2}$ was isolated. On the other hand, when cyclopropene $\mathbf{1a}_{d2}$ and deuterated silane were used, fully deuterated cyclopropane $\mathbf{2g}_{d5}$ was obtained, suggesting that the cyclopropylcobalt intermediate was protonated by the silane to regenerate the active catalytic species (see the Supporting Information for all analysis and NMR data).

In summary, a mild diastereoselective and enantioselective cobalt-catalyzed hydrosilylation reaction of achiral cyclopropenes has been developed. In this protocol, various substituted cyclopropenes and arylsilanes were transformed, in the presence of readily available chiral cobalt complex, into silylcyclopropanes with high selectivities. This atom-economy approach to silylated saturated three-membered rings constitute an additional tool for the direct functionalization of three-membered carbocyclic skeleton.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01833.

Experimental procedures, characterization data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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