A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition GDCh Chemie

www.angewandte.org

Accepted Article

Title: Rh-Catalyzed Syntheses of Chiral Monohydrosilanes via Intramolecular C−H Functionalization of Dihydrosilanes

Authors: Wenpeng Ma, Li-Chuan Liu, Kun An, Tao He, and Wei He

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.202013041

Link to VoR: https://doi.org/10.1002/anie.202013041

WILEY-VCH

10.1002/anie.202013041

WILEY-VCH

RESEARCH ARTICLE

Rh-Catalyzed Syntheses of Chiral Monohydrosilanes via Intramolecular C−H Functionalization of Dihydrosilanes

Wenpeng Ma, Li-Chuan Liu, Kun An, Tao He and Wei He*

[a] Dr. W. Ma, L.-C. Liu, K. An, T. He and Prof. Dr. W. He
MOE Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology and School of Pharmaceutical Sciences & Tsinghua-Peking Joint Center for Life Sciences, Tsinghua University
Beijing, 100084 (P. R. China)
E-mail: whe@tsinghua.edu.cn

Supporting information for this article is given via a link at the end of the document.

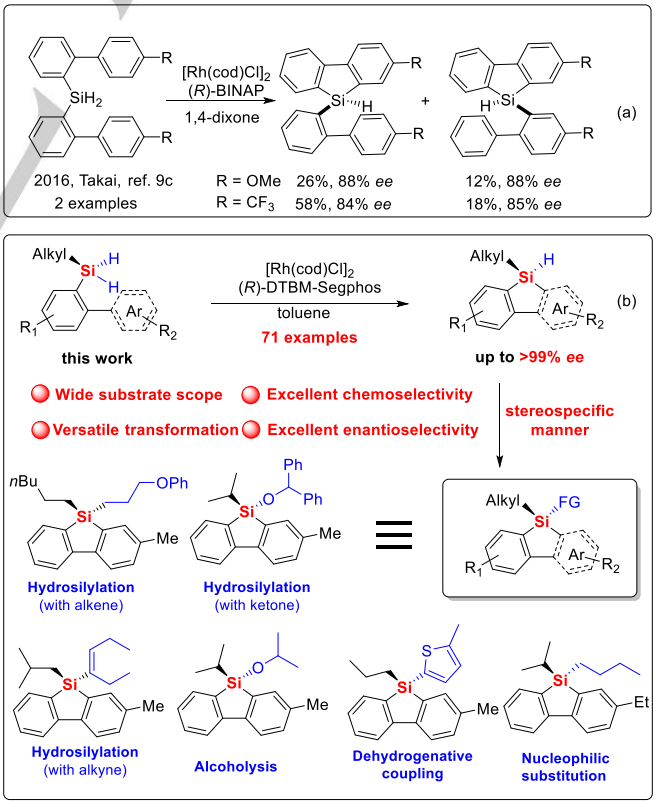
Abstract: The preparation of chiral monohydrosilanes remains a rarely achieved goal. To this end we developed a Rh catalyzed desymmetrization of dihydrosilanes by way of intramolecular C(sp^2)-H functionalization under simple and mild conditions. This method provides easy access to a broad range of chiral monohydrosilanes in good yields with excellent enantioselectivities (up to >99% *ee*). The monohydrosilanes constitute a good platform to access stereogenic silicons, as well as useful tool compounds to probe silicon stereochemistry.

Introduction

Stereogenic silicon compounds remain great synthetic challenges.[1, 2] The chiral monohydrosilanes are among the least accomplished goals in spite of their importance in material and organic chemistry. The desymmetrization of dihydrosilanes represents the most straightforward approach towards chiral monohydrosilanes given the wide availability of dihydrosilanes. However, the desymmetrization reactions are required to stop at the monohydrosilanes stage so as to avoid over-reactions leading to undesired tetrasubstituted silanes. To date, two types of reagents have been successfully engaged in the desymmetrization of dihydrosilanes: (1) π bonds such as ketones,[3] alkenes[4] and alkynes,[5] as in the well-known hydrosilylation reactions; (2) activated σ bonds such as carbenes,[6] alcohols[7] and aryliodides,[8] as in the formal dehydrogenative coupling reactions. Since these two types of reagents are of high reactivity, under carefully controlled conditions, the over-reactions (e.g., the second C-O or C-C bond formations) could be circumvented. As a result, desymmetrization of dihydrosilanes with these two types of reagents has shown good chemo- and enantio-selectivities.

The desymmetrization of dihydrosilanes using unactivated C-H bonds would be more attractive and ideal. The advantages would include: (1) the reaction utilizes widely available C-H bonds and is exempted from pre-functionalized reagents (e.g., π bonds, alcohols, carbenes, etc.); (2) the substrate scope could be significantly improved. We believe that the syntheses of chiral monohydrosilanes is a more fundamental question than the syntheses of tetrasubstituted silanes, since the further elaboration of the monohydrosilanes could provide any tetrasubstituted silanes products by virtue of the versatile reactivity of the Si-H bond in a stereospecific manner (*vide infra*).

The reaction involving unactivated C-H bonds are however much more demanding, since it requires harsher reaction conditions[9,2y,2z] due to the inert nature of the C-H bonds. This means that the monohydrosilanes could suffer a second C-H silylation, resulting in the undesired tetraorganosilanes as the thermodynamically favored products. This difficulty is supported by the only and few known examples reported to date. In 2016, Takai and his coworkers reported that the monohydrosilanes were only obtained when the reaction was stopped prematurely.[9c] Nonetheless, the enantioselectivities of the two reported examples were decent (Scheme 1a). In 2017, we reported that the chiral monohydrosilanes were probably produced in the Rh catalyzed dehydrogenative coupling between



Scheme 1. Asymmetric syntheses of monohydrosilanes.

10.1002/anie.202013041

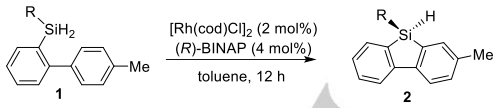
Si-H and C-H bonds. However, these monohydrosilanes were neither isolated in the premature reaction mixture, nor observed by NMR studies.[10d] They very likely underwent an *in-situ* Si-C bond formation in a stereospecific manner to afford the final tetraorganosilanes products. Very recently, He group reported two examples of intercepting the presumptive monohydrosilanes with alkenes.[2y,2z] Again, only one monohydrosilane was reported in a low yield in the mechanistic study. It is thus clear that the preparation of chiral monohydrosilanes by way of C-H functionalization is elusive.

Given our long standing interest[10] in silicon chemistry, herein we report the Rh catalyzed construction of a wide scope of chiral monohydrosilanes, with unprecedented chemo- and enantio-selectivity. We further illustrate that the chiral monohydrosilanes are indeed a versatile platform to access structurally diverse tetrasubstituted silanes (Scheme 1b), which are also of importance implication in terms of silicon stereochemistry.

Results and Discussion

We commenced our investigation by using dihydrosilanes substrates of type **1** as the substrate, (*R*)-BINAP as the chiral ligand and toluene as the solvent (Table 1). In accordance with Takai's report, when R was phenyl, the substrate decomposed[9c] (Table 1, entry 5). We thus shifted our attention to alkyl substituted substrates (Table 1, entries 1-4). These results compiled in Table 1 collectively showed that: (1) the chemo-selectivity to achieve monohydrosilanes was only possible with alkyl substituted dihydrosilanes. The bulkier R groups gave higher yields, but they required higher reaction temperatures (Table 1, entries 1-4); (2) only a moderate enantioselectivity could be obtained (Table 1, entry 3), suggesting that (*R*)-BINAP was not a competent ligand.

Table 1. Screening the proper dihydrosilanes substrates.

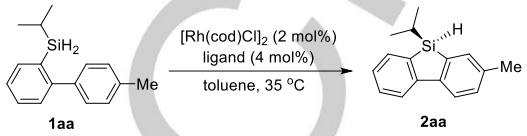


Entry	R	Temp.(°C)	Conv.[a]	Yiled[b]	*ee*[c]
1	Me	20	55%	50%	3%
2	*n*Pr	20	49%	41%	60%
3	*i*Pr	35	72%	61%	63%
4	*t*Bu	70	80%	69%	11%
5	Ph	20	>95%	-	-

Reaction conditions: substrate (0.2 mmol) in toluene (0.8 mL), $[Rh(cod)Cl]_2$ (2 mol%), (*R*)-BINAP (4 mol%), stirred for 12 h. [a] Determined by ^{1}H NMR spectroscopy of the crude reaction mixtures. [b] Isolated yields through silica chromatography. [c] Determined by HPLC with a chiral OD-H column.

We then set out to examine different diphosphine ligands by using **1aa** as the model substrate (Table 2), as our earlier work had demonstrated that ligands play a central role[10c] in related transformation. No reaction took place in the absence of a ligand (Table 2, entry 1), suggesting there was no background reaction. The less hindered ligand (*R*)-BINAP, (*R*)-MeO-Biphep, (*R*)-DTBM-Biphep, (*R*)-Segphos and (*R*)-DM-Segphos showed moderate reactivities and enantioselectivities (Table 2, entries 2-6). (*R*)-DTBM-Segphos, which possesses a wider dihedral angle and more hindered 3,5-di-*t*Bu-4-MeO-phenyl substituent, gave a 93% conversion with the highest 96% *ee* (Table 2, entry 7).

Table 2. Screening the optimal chiral ligands.



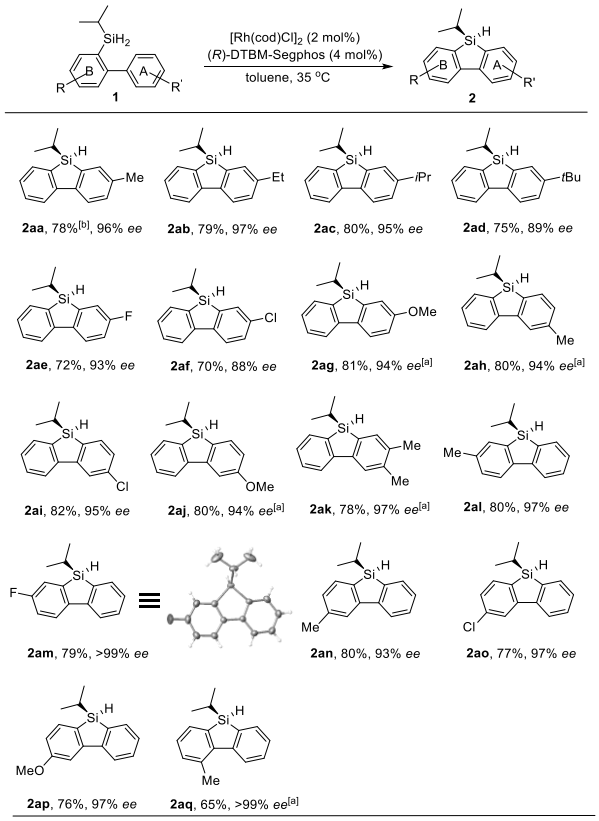
Entry	Ligand	Time(h)	Conv.[a]	*ee*[b]
1	-	12	-	-
2	(*R*)-BINAP	12	72%	63%
3	(*R*)-MeO-Biphep	12	75%	34%
4	(*R*)-DTBM-Biphep	12	89%	87%
5	(*R*)-Segphos	12	75%	51%
6	(*R*)-DM-Segphos	12	80%	36%
7	(*R*)-DTBM-Segphos	12	93%	96%

Reaction conditions: substrate (0.2 mmol) in toluene (0.8 mL), $[Rh(cod)Cl]_2$ (2 mol%), ligand (4 mol%), stirred at 35 °C for 12 h. [a] Determined by ^{1}H NMR spectroscopy of the crude reaction mixtures. [b] Determined by HPLC with a chiral OD-H column.

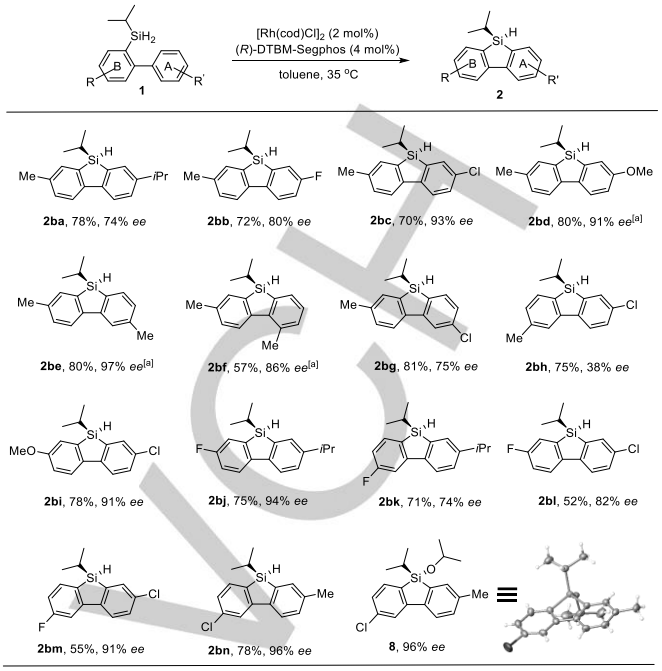
We demonstrated that the optimized reaction condition was applicable to isopropyl-Si substrates bearing different substituents on either of the **A** or the **B** ring (Scheme 2). A variety of substituents were well tolerated in general, giving good yields and excellent enantioselectivities. It was found that the enantioselectivity was insensitive to the steric hindrance of the alkyl side chain at 4-position of A ring (**2aa**-**2ad**). In addition, the electronic effect at 4-position of A ring (**2ae**-**2ag**) had no obvious impact on enantioselectivity. For substrates that had two possible reacting sites on **A** ring, the silylation took place exclusively on the less steric hindered site with excellent enantioselectivities (**2ah-2ak**). On the other hand, substituents of different electronic demands and on the different positions on **B** ring were compatible with the reaction. For example, electron neutral group (CH_3 in **2an**), electron withdrawing group (Cl in **2ao**) and electron donating group (OCH_3 in **2ap**) at the same position of **B** ring all witnessed the same level of good yields and excellent enantioselectivities. Notably, substrates **2am** and **2aq**, which were very different in substitution pattern and electronic features, both gave an impeccable enantioselectivity (>99% *ee*). The absolute configuration of **2am** was determined to be *S* based on single-crystal X-ray analysis (Scheme S1 in SI).[11]

Isopropyl-Si substrates bearing substituents on both the **A** and the **B** rings were also compatible with optimized reaction conditions (Scheme 3). In general, having substituents on both rings decreased the yields and enantioselectivities. Such an impact was very pronounced in the cases of **2ba**, **2bh** and **2bk**.

10.1002/anie.202013041



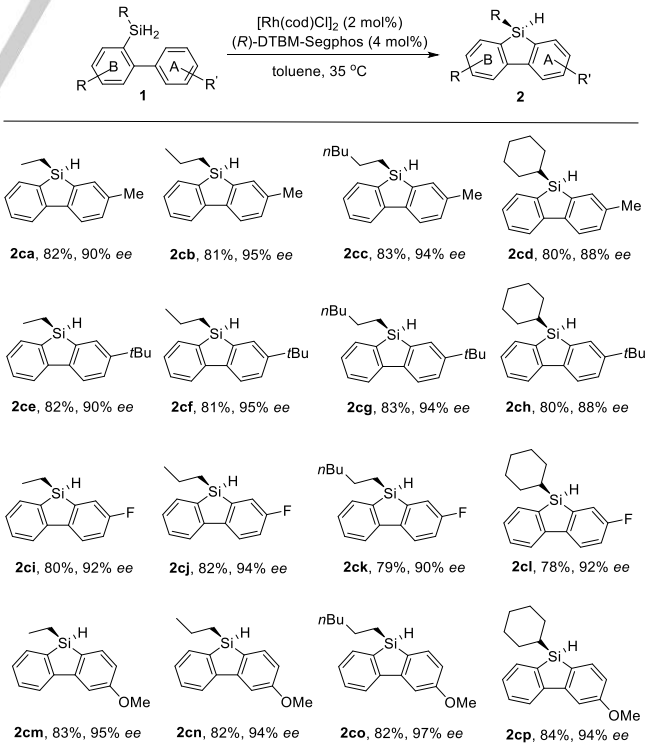
Scheme 2. General conditions: substrate (0.2 mmol) in toluene (0.8 mL), $[Rh(cod)Cl]_2$ (2.0 mol%), (*R*)-DTBM-Segphos (4.0 mol%), stirred at 35 °C for 12 h. Yields of isolated product were given. The *ee* values were determined by HPLC with chiral columns. [a] Stirred for 24 h. [b] On 4.5 mmol scale.



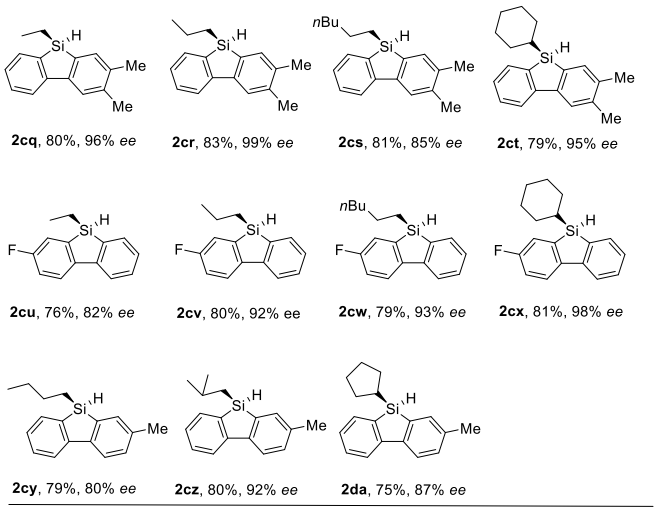
Scheme 3. General conditions: substrate (0.2 mmol) in toluene (0.8 mL), $[Rh(cod)Cl]_2$ (2.0 mol%), (*R*)-DTBM-Segphos (4.0 mol%), stirred at 35 °C for 12 h. Yields of isolated product were given. The *ee* values were determined by HPLC with chiral columns. [a] Stirred for 24 h.

One would assume that the *iso*-propyl group on ring **A** had a negative impact on the enantioselectivity, but it did not hold true in the case of **2bj** that also has an *iso*-propyl group at the same position. The chlorine in **2bh** was seemingly smaller than *iso*-propyl group, yet it gave the lowest *ee* among all the cases. The absolute configuration of **2bn** was assigned as *R* by single-crystal X-ray analysis of the corresponding derivative compound **8** (Scheme S2 in SI).[11]

We showed that other alkyl substitutions on the Si atoms were also well tolerated (Scheme 4). Ethyl-Si substrates (i.e., **2ca**, **2ce**, **2ci**, **2cm**, **2cq** and **2cu**) gave good yields. The enantioselectivities were comparable to those of isopropyl-Si substrates, except that **2cu** saw a drastic decrease in enantioselectivity. *n*-Propyl-Si substrates (i.e., **2cb**, **2cf**, **2cj**, **2cn, 2cr** and **2cv**) were collectively superior than the ethyl-Si substrates and were more similar to that of the isopropyl-Si substrates. This trend again suggested that the steric hindrance was an important factor. *n*-Hexyl-Si substrates (i.e., **2cc**, **2cg**, **2ck**, **2co**, **2cs** and **2cw**) reacted smoothly to afford the corresponding chiral monohydrosilanes in consistently good yields (79-83%) and enantioselectivities (85-97%). In the cyclohexyl-Si substrates (i.e., **2cd**, **2ch**, **2cl**, **2cp, 2ct** and **2cx**), the more congested Si center did not compromise the yields and enantioselectivities. It was interesting to see that a 98% *ee* was obtained in the case of **2cx**. Furthermore, *n*-butyl-Si, *neo*-butyl-Si and cyclopentyl-Si (i.e., **2cy**, **2cz** and **2da**) were competent substrates under the optimized reaction conditions, giving the corresponding monohydrosilanes in good yields and enantioselectivities. Overall, the results in Scheme 4 suggested that all types of alkyl groups on the Si atoms should be viable and the enantioselectivities were influenced by the substitution patterns on both the Si atoms and the rings.



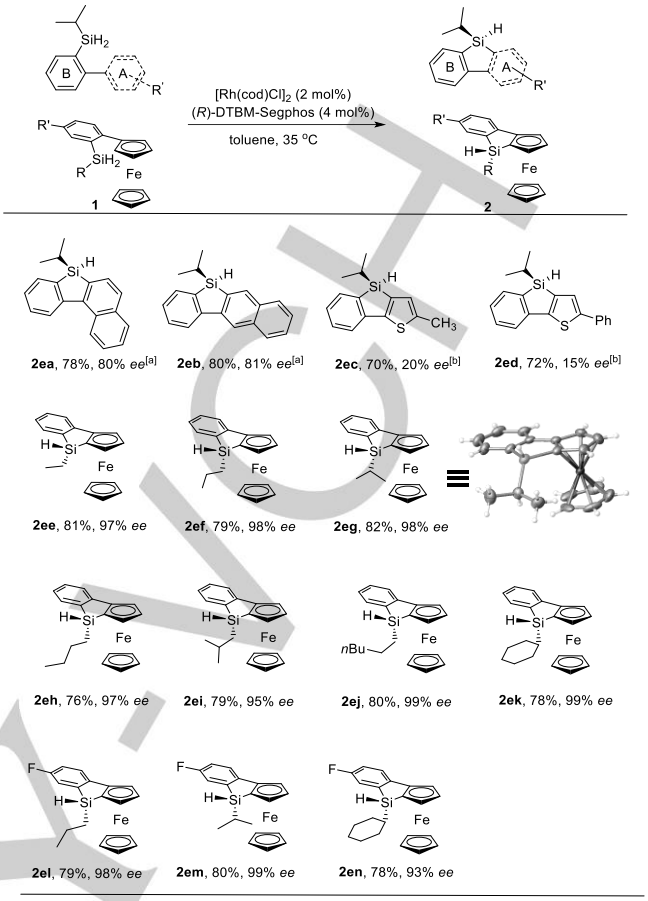
10.1002/anie.202013041



Scheme 4. General conditions: substrate (0.2 mmol) in toluene (0.8 mL), $[Rh(cod)Cl]_2$ (2.0 mol%), (*R*)-DTBM-Segphos (4.0 mol%), stirred at 35 °C for 12 h. Yields of isolated product were given. The *ee* values were determined by HPLC with chiral columns.

We demonstrated that our method also worked on non-biphenyl systems (Scheme 5). When A ring were naphthaline (**2da** and **2db**), the reactions gave good yields (78-80%) while the enantioselectivities saw a slight decrease (80-81%). Substituted thiophene[12] (**2dc** and **2dd**) afforded moderate yields (70-72%), however the enantioselectivities were poor (15-20%). Substrates bearing ferrocene skeleton on the A ring were shown to be efficient and highly enantioselective. On the 10 representative cases (e.g., **2ee**-**2en**), the yields were in the range of 76-82%, while the enantioselectivities were consistently high (93-99%). In all these examples, only one single diastereomer was obtained, featuring a planar chirality and a monohydrosilane functionality in the final products. Comparison among a panel of substrates bearing different alkyl groups on the Si atoms (cf., **2ee**-**2ek**), it was clear that for this type of substrates, the reaction yields and enantioselectivities were not sensitive to the steric and electronic demands of the alkyl groups (e.g., ethyl, *n*-propyl, isopropyl, *n*-butyl, *s*-butyl, hexyl and cyclohexyl). We also examined the ferrocene substrates with F-substitutions on the B ring (e.g., **2el**, **2em** and **2en**), which showed that the substitution on B ring were well tolerated with different alkyl-Si patterns. It was thus clear that our method should work well on various type of ferrocene substrates. The absolute configuration of the product **2eg** was determined to be $^{R/S}Si$, R_p according to single-crystal X-ray analysis (Scheme S3 in SI).[11]

Taken together, the reaction scope studies have demonstrated that our method can produce a wide variety of chiral monohydrosilanes. The reaction worked well on bi-phenyl skeletons, tolerating many types of substitution patterns on either phenyl ring or on the bi-phenyls (Scheme 2 and 3). The substitutions the Si could be selected from at least 7 different alkyl groups (Scheme 4). The method could be extended to non-bi-phenyl skeletons and was especially successful on the ferrocene substrates (Scheme 5). With a few exceptions, our reactions were usually efficient and highly enantioselective. This work represents the first viable and general syntheses of the highly desired chiral monohydrosilanes.



Scheme 5. General conditions: substrate (0.2 mmol) in toluene (0.8 mL), $[Rh(cod)Cl]_2$ (2.0 mol%), (*R*)-DTBM-Segphos (4.0 mol%), stirred at 35 °C for 12 h. Yields of isolated product were given. The *ee* values were determined by HPLC with chiral columns. [a] Stirred for 24 h. [b] Stirred at 50 °C for 24 h.

We believed that the reaction mechanism should involve a dehydrogenative pathway, as first proposed by Kuninobu and Takai[9a] and then by Mitsudo and Suga.[12] We used **1aa** as the example (Figure 1) to illustrate such a pathway based on the main ideas of the earlier reports.[9a,12] First, [Rh(cod)Cl] coordinated with (*R*)-DTBM-Segphos, and the active catalytic species Rh^{I}-H was generated. Oxidative addition of Rh-H with Si-H **1aa** gave a Rh^{III} species **I**, followed by reductive elimination to afford Rh^{I} species **II**. A second sequence of oxidative addition/reductive elimination would produce the product **2aa** and regenerated the active catalytic species Rh-H. It was very likely the first oxidative addition was the enantioselective step. The difference between our reaction and that of Kuninobu and Takai was that one hydrogen was preserved, probably due to choose of an alkyl group instead of an aryl group and the relative mild reaction condition. The difference between our reaction and that of Mitsudo and Suga was that a hydrogen atom but not a R group was a spectator. In the latter case, there was chemo- and enantio-selectivity concerns.

We illustrated that our method could serve as a platform to access various stereogenic silicon compounds (Scheme 6). To showcase the general reactivity, we chose different chiral monohydrosilanes as the starting points. First, alcoholysis[7] of **2aa** with isopropanol afforded the corresponding siloxane **3a** under the ambient condition [Eq. (a)]. The hydrosilylation with π

10.1002/anie.202013041

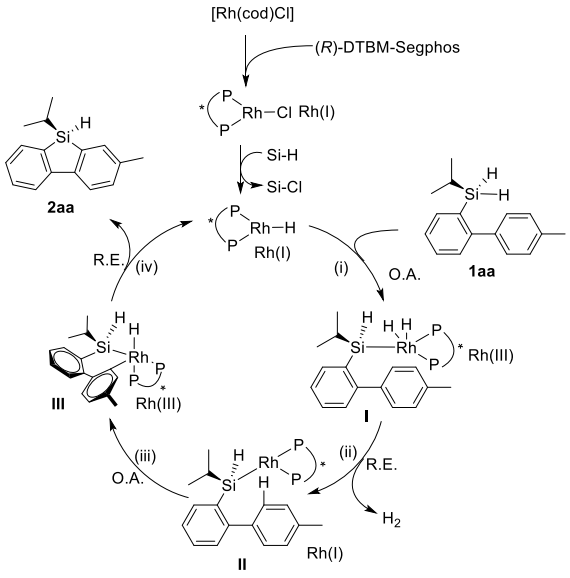
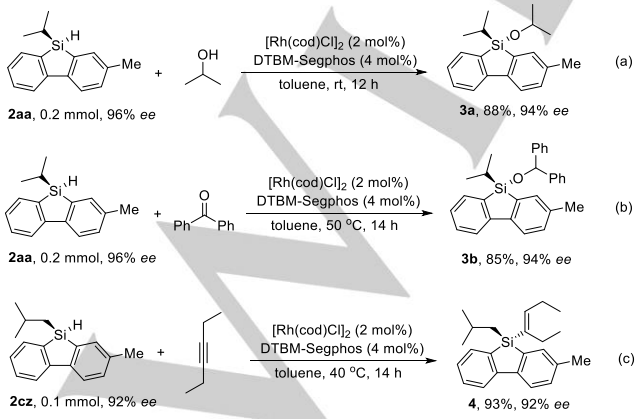
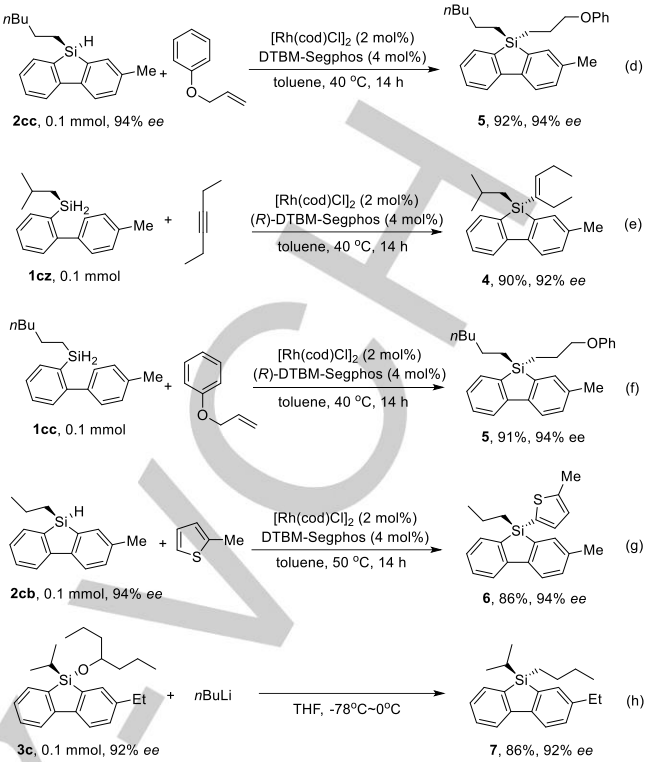


Figure 1. Proposed mechanism.

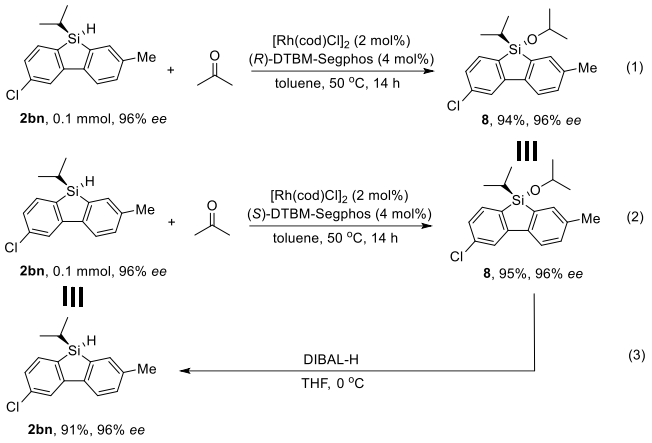
bond compounds such as ketone,[3] alkene[4] and alkyne[5] were also successful [Eq. (b), (c) and (d)], affording different stereogenic tetraorganosilanes containing Si-O, Si-C(sp^2) and Si-C(sp^3) bonds. In all cases, the corresponding tetraorganosilanes products were prepared in high yields without erosion of the enantioselectivities. Notably, we showed that the Si-H bond formation-hydrosilylation could be carried out in a tandem fashion with high yields and enantioselectivity [Eq. (e) and (f)], of which of the full accounts were reported separately. Intermolecular C−H functionalization of **2cb** with 2-methylthiophene[10d] provided the tetraorganosilanes product **6** with high yield and enantioselectivity [Eq. (g)]. Moreover, oxa-benzosilole **3c** was converted to tetraorganosilole **7** by nucleophilic substitution[13] of *n*-BuLi, of which the enantiomerically-pure reaction has not been reported before [Eq. (h)]. These examples, together with the versatile reactivity of Si-H bonds, illustrated the ample potential of the chiral monohydrosilanes. This method of chiral monohydrosilane syntheses will serve as a platform technology to access other stereogenic silicons, either in a step-wise manner or in a tandem fashion.





Scheme 6. Derivatization of monohydrosilanes.

Our method also provided chiral monohydrosilanes as probing compounds to investigate the stereochemistry concerning Si centers. For example, we studied stereochemistry concerning the hydrosilylation of the chiral monohydrosilane **2bn** with acetone (Scheme 7). A pair of reactions with either the (*R*)-DTBM-Segphos [Eq. (1)] or the (*S*)-DTBM-Segphos [Eq. (2)] afforded the identical siloxane product **8**, according to NMR spectra and HPLC chromatograms. The absolute configuration of the siloxane **8** was determined to be *S* according to single-crystal X-ray analysis (Scheme S2 in SI). DIBAL-H reduction of the siloxane **8** produced the initial chiral monohydrosilane **2bn**, which was confirmed by comparing the NMR spectra and HPLC chromatograms. This interesting sequences of reactions indicated that: (1) the stereochemistry of hydrosilylation reactions between the chiral Si-H and the acetone was substrate controlled but not ligand controlled, which was in accordance with our earlier report of the intermolecular C-H/Si-H dehydrogenative coupling;[10d] (2) the DIBAL-H reduction of the siloxane was stereospecific, which was consistent with the report of Oestreich.[14] As Oestreich's work proposed that during the DIBAL-H reduction, the Si center had >99% retention, it was clear that in the first hydrosilylation step [Eq. (1) and (2)], the Si center also had >99% retention. This observation was very different than the $B(C_6F_5)_3$ catalyzed hydrosilylation reaction.[14] This example showed that the chiral monohydrosilanes were useful tools to probe stereochemistry questions that might seem intuitive but remain vague [e.g., Scheme 6, Eq. (c) and (d)].



Scheme 7. Determination of the chirality.

Conclusion

In conclusion, we have developed the first viable and general method for the construction of chiral monohydrosilanes, via Rh catalyzed dehydrogenative coupling between dihydrosilane Si-H bond and C(sp^2)-H bonds. This method provided a wide scope of chiral monohydrosilanes, with broad choices of substituents on the Si centers, especially alkyl-substituted stereogenic silicons that could not be made otherwise. The chiral monohydrosilanes were a powerful platform to access chiral tetraorganosilanes by virtue of the versatile reactivity of the remaining Si-H bonds, in either a step-wise manner or a tandem fashion. It also can be used as ~~a~~ valuable tool in probing the silicon stereochemistry. Mechanistic studies as well as intermolecular variants of this method are under investigation in our laboratory and will be reported in due case.

Acknowledgements

We thank the National Natural Science Foundation of China (Nos. 21625104 and 21971133), National Key Research & Development Program of China (Nos. 2017YFA0505203), and the General Financial Grant from the China Postdoctoral Science Foundation (2017M610074).

Keywords: monohydrosilane • dihydrosilanes • desymmetrization • enantioselectivity

[1] For reviews, see: a) L.-W. Xu, L.Li, G.-Q. Lai, J.-X. Jiang, *Chem. Soc. Rev.*, **2011**, *40*, 1777; b) R. Shintani, *Asian J. Org. Chem.* **2015**, *4*, 510; c) C. Cheng, J. F. Hartwig, *Chem. Rev.* **2015**, *115*, 8946; d) L. Li, Y. Zhang, L. Gao, Z. Song, *Tetrahedron Lett.* **2015**, *56*, 1466; e) J. O. Bauer, C. Strohmann, *Eur. J. Inorg. Chem.* **2016**, *2868*; f) Y.-M. Cui, Y. Lin, L.-W. Xu, *Coord. Chem. Rev.* **2017**, *330*, 37; g) R. Shintani, *J. Synth. Org. Chem. Jpn*. **2018**, *76*, 1163; h) R. Shintani, *Synlett* **2018***, 29, 388*.

[2] For examples for chiral tetraorganosilanes, see: a) R. Shintani, K. Moriya, T. Hayashi, *J. Am. Chem. Soc.* **2011***, 133,* 16440; b) R. Shintani, H. Otomo, K. Ota, T. Hayashi, *J. Am. Chem. Soc.* **2012***, 134,* 7305; c) R. Shintani, E. E. Maciver, F. Tamakuni, T. Hayashi, *J. Am. Chem. Soc.* **2012***, 134,* 16955; d) M. Onoe, K. Baba, Y. Kim, Y. Kita, M. Tobisu, N. Chatani, *J. Am. Chem. Soc.* **2012***, 134,* 19477; e) R. Shintani, K. Moriya, T. Hayashi, *Org. Lett.* **2012**, *14*, 2902; f) Y. g) X. Lu, L. Li, W. Yang, K. Jiang, K.-F. Yang, Z.-J. Zheng, L.-W. Xu, *Eur. J. Org. Chem.* **2013**, 5814; g) R. Shintani, C. Takagi, T. Ito, M. Naito, K. Nozaki, *Angew. Chem. Int. Ed.* **2015**, *54*, 1616; *Angew. Chem.* **2015**, *127*,1636; h) R. Shintani, H. Kurata, K. Nozaki, *Chem. Commun.* **2015**, *51*, 11378; i) Y. Naganawa, T. Namba, M. Kawagishi, H. Nishiyama, *Chem. Eur. J.* **2015**, *21*, 9319; j) R. Kumar, Y. Hoshimoto, H. Yabuki, M. Ohashi, S. Ogoshi, *J. Am. Chem. Soc.* **2015***, 137,* 11838; k) M. Murai, H. Takeshima, H. Morita, Y. Kuninobu, K. Takai, *J. Org. Chem.* **2015**, *80*, 5407; l) M. Murai, K. Matsumoto, Y. Takeuchi, K. Takai, *Org. Lett.* **2015**, *17*, 3102; m) K. Igawa, D. Yoshihiro, Y. Abe, K. Tomooka, *Angew. Chem. Int. Ed.* **2016**, *55*, 5814; *Angew. Chem.* **2016**, *128*, 5908; n) R. Shintani, R. Takano, K. Nozaki, *Chem. Sci.* **2016**, *7*, 1205; o) J. Zhang, J.-Z. Xu, Z.-J. Zheng, Z. Xu, Y.-M. Cui, J. Cao, L.-W. Xu, *Chem. Asian J.* **2016**, *11*, 2867; p) M. Murai, Y. Takeuchi, K. Yamauchi, Y. Kuninobu, K. Takai, *Chem. Eur. J.* **2016**, *22*, 6048; q) M. Murai, R. Okada, A. Nishiyama, K. Takai, *Org. Lett.* **2016**, *18*, 4380; r) M. Murai, Y. Takeuchi, K. Yamauchi, Y. Kuninobu, K. Takai, *Chem. Eur. J.* **2016**, *22*, 6048; s) Y. Sato, C. Takagi, R. Shintani, K. Nozaki, *Angew. Chem. Int. Ed.* **2017**, *56*, 9211; *Angew. Chem.* **2017**, *129*, 9339; t) R. Shintani, N. Misawa, R. Takano, K. Nozaki, *Chem. Eur. J.* **2017**, *23*, 2660; u) P.-W. Long, X.-F. Bai, F. Ye, L. Li, Z. Xu, K.-F. Yang, Y.-M. Cui, Z.-J. Zheng, L.-W. Xu, *Adv. Synth. Catal.* **2018**, *360*, 2825; v) H. Chen, Y. Chen, X. Tang, S. Liu, R. Wang, T. Hu, L. Gao, Z. Song, *Angew. Chem. Int. Ed.* **2019**, *58*, 4695; *Angew. Chem.* **2019**, *131*, 4743; w) Y. Lin, W.-Y. Ma, Z. Xu, Z.-J. Zheng, J. Cao, K.-F. Yang, Y.-M. Cui, L.-W. Xu, *Chem. Asian J.* **2019**, *14*, 2082; x) G. Zhang, Y. Li, Y. Wang, Q. Zhang, T. Xiong, Q. Zhang, *Angew. Chem. Int. Ed.* **2020**, *59*, 11927, *Angew. Chem.* **2020**, *132*, 12025; while our manuscript is under review, He group reported the syntheses of tetraorganosilicons: y) D. Mu, W. Yuan, S. Chen, N. Wang, B. Yang, L. You, B. Zu, P. Yu, C. He, *J. Am. Chem. Soc.* **2020**, *142*, 13459; z) B. Yang, W. Yang, Y. Guo, L. You, C. He, *Angew. Chem. Int. Ed*. **2020**, 10.1002/anie.202009912.

[3] a) R. J. P. Corriu, J. J. E. Moreau, *J. Organomet. Chem.* **1974**, *64*, C51; b) T. Hayashi, K. Yamamoto, M. Kumada, *Tetrahedron Lett*. **1974**, *15*, 331; c) T. Ohta, M. Ito, A. Tsuneto, H. Takaya, *J. Chem. Soc. Chem. Commun*. **1994**, 2525.

[4] a) K. Tamao, K. Nakamura, H. Ishii, S. Yamaguchi, M. Shiro, *J. Am. Chem. Soc.* **1996**, *118*, 12469; b) Y. Naganawa, T. Namba, M. Kawagishi, H. Nishiyama, *Chem. Eur. J.* **2015**, *21*, 9319; c) G. Zhan, H.-L. Teng, Y. Luo, S.-J. Lou, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed.* **2018**, *57*, 12342; *Angew. Chem.* **2018**, *130*, 12522; d) X Chang, P.-L Ma, H.-C. Chen, C.-Y. Li, P. Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 8937; *Angew. Chem.* **2020**, *132*, 9022; e) Z.-Y. Zhao, Y.-X. Nie, R.-H. Tang, G.-W. Yin, J. Cao, Z. Xu, Y.-M. Cui, Z.-J. Zheng, L.-W. Xu, *ACS Catal.* **2019**, *9*, 9110.

[5] a) K. Igawa, D. Yoshihiro, N. Ichikawa, N. Kokan, K. Tomooka, *Angew. Chem. Int. Ed.* **2012**, *51*, 12745; *Angew. Chem.* **2012**, *124*, 12917; b) H. Wen, X. Wan, Z. Huang, *Angew. Chem. Int. Ed.* **2018**, *57*, 6319; *Angew. Chem.* **2018**, *130*, 6427.

[6] Y. Yasutomi, H. Suematsu, T. Katsuki, *J. Am. Chem. Soc.* **2010**, *132*, 4510.

[7] a) R. J. P. Corriu, J. J. E. Moreau, *Tetrahedron Lett.* **1973**, *14*, 4469; b) R. J. P. Corriu, J. J. E. Moreau, *J. Organometallic Chem.* **1976**, *120,* 337; c) D. R. Schmidt, S. J. O'Malley, J. L. Leighton, *J. Am. Chem. Soc.* **2003**, *125*, 1190.

[8] a) Y. Kurihara, M. Nishikawa, Y. Yamanoi, H. Nishihara, *Chem. Commun.* **2012**, *48*, 11564; b) L. Chen, J.-B. Huang, Z. Xu, Z.-J. Zheng, K.-F. Yang, Y.-M. Cui, J. Cao, L.-W. Xu, *RSC Adv.* **2016**, *6*, 67113; c) S. Koga, S. Ueki, M. Shimada, R. Ishii, Y. Kurihara, Y. Yamanoi, J. Yuasa, T. Kawai, T. Uchida, M. Iwamura, K. Nozaki, H. Nishihara, *J. Org. Chem.* **2017**, *82*, 6108.

[9] a) Y. Kuninobu, K. Yamauchi, N. Tamura, T. Seiki, K. Takai, *Angew. Chem. Int. Ed.* **2013**, *52*, 1520; *Angew. Chem.* **2013**, *125*, 1560; b) M. Murai, H. Takeshima, H. Morita, Y. Kuninobu, K. Takai, *J. Org. Chem.* **2015**, *80*, 5407; c) M. Murai, Y. Takeuchi, K. Yamauchi, Y. Kuninobu, K. Takai, *Chem. Eur. J.* **2016**, *22*, 6048.

[10] a) Q-W Zhang, K. An, W He, *Angew. Chem. Int. Ed.* **2014**, *53*, 5667; *Angew. Chem.* **2014***, 126,* 5773; b) Q. W. Zhang, K. An, L. C. Liu, Y. Yue, W. He, *Angew. Chem. Int. Ed.* **2015**, *54*, 6918; *Angew. Chem.* **2015**, *127*, 7022; c) Q.-W. Zhang, K. An, L.-C. Liu, S. Guo, C. Jiang, H. Guo, W. He, *Angew. Chem. Int. Ed.* **2016**, *55*, 6319; *Angew.Chem.* **2016**, *128*, 6427; d) Q.-W. Zhang, K. An, L.-C. Liu, Q. Zhang, H. Guo, W. He, *Angew.*

Chem. Int. Ed. **2017**, *56*, 1125; *Angew. Chem.* **2017**, *129*,1145; e) T He, L.-C. Liu, L. Guo, B. Li, Q.-W. Zhang, W. He, *Angew. Chem. Int. Ed.* **2018**, *57*, 10868; *Angew. Chem.* **2018**, *130*, 11034. f) T. He, L.-C. Liu, W.-P. Ma, B. Li, Q.-W. Zhang, W. He, *Chem. Eur. J.* **2020**, 10.1002/chem.202003506.

[11] CCDC 1975576 (**2am**), 2032647 (**8**) and 2032648 (**2eg**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

[12] K. Mitsudo, S. Tanaka, R. Isobuchi, T. Inada, H. Mandai, T. Korenaga, A. Wakamiya, Y. Murata, S. Suga, *Org. Lett.* **2017**, *19*, 2564.

[13] T. Fallon, M. Oestreich, *Angew.Chem. Int. Ed.* **2015***, 54,* 12488; *Angew. Chem.* **2015***, 127,* 12666.

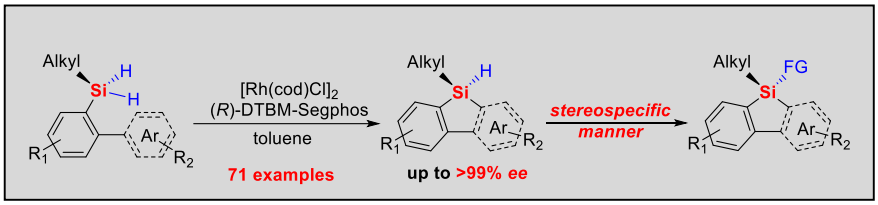
[14] D. T. Hog, M. Oestreich, *Eur. J. Org. Chem.* **2009***, 5047*.

10.1002/anie.202013041

WILEY-VCH

RESEARCH ARTICLE

Rh-Catalyzed Syntheses of Chiral Monohydrosilanes via Intramolecular C−H Functionalization of Dihydrosilanes



Chiral Silanes! A Rh-chiral diphosphine complex catalyzed desymmetrization of dihydrosilanes were achieved via formal intramolecular Si-H/C-H dehydrogenative coupling reactions. This simple, mild and practical method enjoys a unprecedently high enantioselectivity and a unprecedently wide substrate scope. These chiral monohydrosilanes could be further elaborated into various stereogenic silicons in a stereospecific manner.