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Rhodium-Catalyzed Dynamic Kinetic Asymmetric Hydrosilylation to Access Silicon-Stereogenic Center

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Dedicated to Prof. Chungu Xia on the occasion of his 60th birthday

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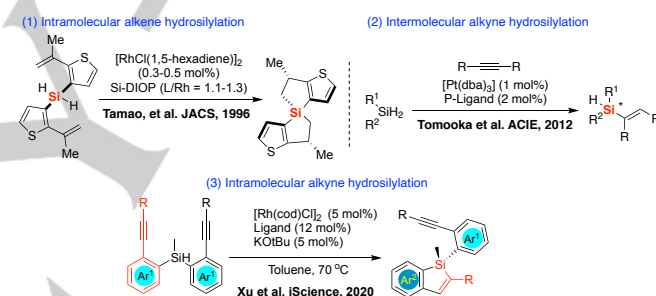
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Abstract: Strategies on the construction of enantiomerically pure silicon-stereogenic silanes generally relies on desymmetrization of prochiral and symmetric substrates. However, dynamic kinetic asymmetric transformations of organosilicon compounds have remained underdeveloped and unforeseen owing to a lack of an effective method for deracemization of the static silicon stereocenters. Here we report the first Rh-catalyzed dynamic kinetic asymmetric intramolecular hydrosilylation (DyKAH) with “silicon-centered” racemic hydrosilanes that enables the facile preparation of silicon-stereogenic benzosiloles in good yields and excellent enantioselectivities. The special rhodium catalyst controlled by non-diastereopure-type mixed phosphine-phosphoramidite ligand with axial chirality and multiple stereocenters can induce enantioselectivity efficiently in this novel DyKAH reaction. Density functional theory (DFT) calculations suggest that the amide moiety in chiral ligand plays important role in facilitating the S_N2 substitution of chloride ion to realize the chiral inversion of silicon center.

Hydrosilanes have long been the subject of intense study in organosilicon chemistry due to their unusual stability, considerable reactivity in functionalization and derivatization, physical or chemical properties and theoretical interest.^[1] And recent developments in hydrosilane chemistry shine a new light on the discovery and potential utility of the Si-H bond activation and its enantioselective Si-H functionalization.^[2] Especially, desymmetrization strategy of dihydrosilane has been widely applied in the synthesis of silicon-stereogenic silacycles since Tamao et al. reported the first Rh-catalyzed intramolecular hydrosilylation in 1996 (eq. 1 of Figure 1a)^[3]. In this context, the first example of platinum-catalyzed asymmetric intermolecular hydrosilylation of alkynes was reported by Tomooka and co-workers in 2012 (eq. 2 of Figure 1a).^[4] However, the catalytic asymmetric transformation with hydrosilanes and alkynes to access silicon-stereogenic center is still not easy and severely limited in comparison to that of carbon-stereocenter reactions.^[5] To the best of our knowledge, although the activation of Si-H bond of hydrosilanes by transition metal complexes provides fertile ground with a wide range of bonding scenarios,^[6] there is no reports for the catalytic asymmetric transformations of Si-H bonds based on kinetic resolution or dynamic kinetic asymmetric transformations (DyKATs) of “silicon-centered” racemic silanes to access silicon-stereogenic centers. In general, all the downstream transformations of “silicon-centered” chiral hydrosilanes resulted into the retention of configuration on the

silicon-stereogenic center,^[7] these chirality-reserved Si-H bond activation supported the difficulty of interconversion of configuration on the silicon center.^[8] Therefore, it is really challenging task for the stereoselective transformation of silicon-centered racemic hydrosilanes to silicon-stereogenic silanes.^[9]

a) Previous work on the synthesis of Si-stereogenic silanes via hydrosilylation:



b) This work:

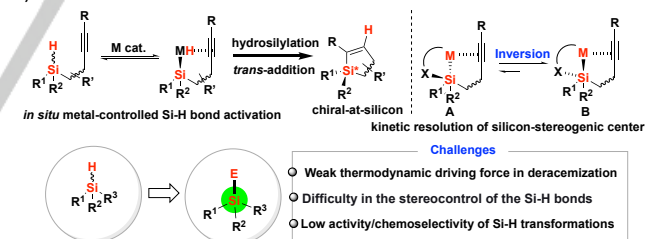


Figure 1. Inspiration for the development of a dynamic kinetic asymmetric hydrosilylation. a) Previous work on desymmetrization strategy for construction of Si-stereogenic center by hydrosilylation. b) New reaction design beyond desymmetrization in this work: Major challenges for the determination of the controllable DyKATs of Si-H bond.

To enable a dynamic kinetic asymmetric transformation of “silicon-centered” racemic organosilanes, we want to explore the deracemization of “silicon-centered” racemic hydrosilanes that bearing three different substituents through dynamic kinetic transformation of Si-H bonds. As presented in Figure 1b, we hypothesized that the racemic hydrosilane bearing an alkyne moiety could interact with transition metal catalyst via oxidative addition to give active intermediate, in which the dynamic kinetic interconversion between A and B would be beneficial to the formation of a silicon-stereogenic center. In this case, one of the chiral M-Si*-H species from the racemic hydrosilanes should exhibit much higher reactivity than that of another M-Si*-H

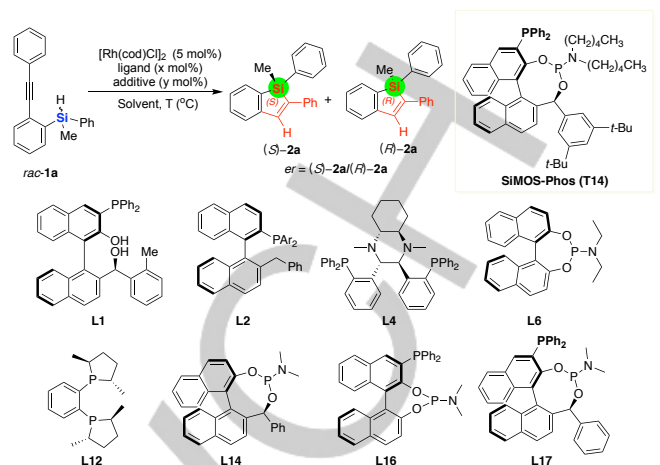
species, and an inert M-Si⁺-H species (for example, *R*-configuration at silicon center) can be converted into another active M-Si⁺-H species (for example, *S*-configuration at silicon center) with the aid of chiral ligand, so that the dynamic kinetic asymmetric hydrosilylation (DyKAH) can be successfully realized.

Herein, we report our effort to develop an unprecedented dynamic kinetic asymmetric hydrosilylation (DyKAH). Upon exposure to a novel rhodium catalyst with chiral P-ligand, the first example of dynamic kinetic asymmetric hydrosilylation of racemic hydrosilanes can be applied in the catalytic construction of silicon-stereogenic center, showing good to excellent enantioselectivities for a facile entry to silicon-stereogenic benzosiloles.

Initially, we investigated the rhodium-catalyzed intramolecular hydrosilylation of SiH-tethered monoalkyne **1a** in the presence of Ar-BINMOL-Phos (**L1**)^[10]. Reactions performed in toluene under mild conditions (50 °C) using [Rh(cod)Cl]₂ as precatalyst and KOtBu as additive proved to be operationally simple and highly efficient [95% nuclear magnetic resonance (NMR) yield] and with promising enantioselectivity as 55:45 *er* that impossibly obtained in the absence of KOtBu (Entry 1 of Table 1). Thus, the exciting finding in the Rh-controlled enantioselective control of racemic monohydrosilane promoted us to evaluate the possibility of dynamic kinetic asymmetric hydrosilylation by applying structurally diverse chiral phosphine ligands. By examining a set of chiral phosphine ligands and its analogues (See Scheme S1 of Supporting Information), we are pleased to find that several P-ligands, including several P-ligands (see the Scheme of Table 1) designed by our group,^[11] enabled enantioselective synthesis of enantiomeric excess of benzosilole bearing a silicon-stereogenic center (For representative results, see entries 2-9 of Table 1). However, most of P-ligands evaluated in this work have no ability in the dynamic kinetic control of enantioselective hydrosilylation in term of no *ee* value. It should be noted that the promising results of chiral phosphoramidite **L6** (60:40 *er*) and **L1** (55:45 *er*) inspired us to design a new ligand **L17** for this hydrosilylation reaction (Entry 8). Incredibly, we found the newly synthesized phosphine-phosphoramidite ligand exhibited moderate enantioselectivity (75:25 *er*) to give the desired product with excellent yield (Entry 9), which opens an entry to the structural modification of Ar-BINMOL-Phos -derived phosphine-phosphoramidite ligands for the Rh-catalyzed dynamic kinetic asymmetric hydrosilylation. We then investigated the newly designed phosphine-phosphoramidite ligands (simplified as SiMOS-Phos) for the improvement of enantioselectivity in this reaction.

Following an extensive survey of different SiMOS-Phos ligands (Figure S2), the best results were obtained when **T14** was used as a chiral ligand in this reaction, furnishing **2a** in 92% yield and 85:15 *er*. Of particular note for this screening, replacing **T14** with other SiMOS-Phos ligands afforded **2a** with low to moderate enantioselectivity as varied from 50:50 to 81:19 *er* (see Supplementary Information), albeit as most of SiMOS-Phos ligands resulted into good yields (70-95%). The implementation of this chiral ligand-controlled dynamic kinetic asymmetric hydrosilylation presents onerous challenges on the exploration of an effective P-ligands. In addition, the experimental data suggested that both the steric bulky group on aromatic ring of chiral Ar-BINMOL-Phos backbone and long-chain aliphatic substituent of amine moiety were important factors in the enhancement of dynamic kinetic asymmetric

Table 1. Optimization of the dynamic kinetic asymmetric hydrosilylation (DyKAH).^[a]



Except above ligands, all the ligands **L1-L17** and **T1-T17** were showed in Figure S1-S2 and Scheme S1 of ESI

Entry	Ligand	Additive	T (°C)	Solvent	Yield (%) ^[b]	<i>er</i> ^[c]
1	L1	KOtBu	50	Toluene	95	55:45
2	L2	-	50	Toluene	64	60:40
3	L4	-	50	Toluene	81	60:40
4	L6	-	50	Toluene	94	60:40
5	L12	-	50	Toluene	87	67:33
6	L14	-	50	Toluene	<10	50:50
7	L16	-	50	Toluene	95	50:50
8	L17	-	50	Toluene	99	75:25
9	T14	-	50	Toluene	92	85:15
10	T14	-	50	THF	95	77:23
11	T14	-	50	DMF	99	83:17
12	T14	-	50	DCE	95	71:29
13	T14	-	50	MTBE	79	57:43
14	T14	-	40	Toluene	78	85:15
15	T14	-	70	Toluene	80	72.5:27.5
16 ^[d]	T14	-	50	Toluene	78	95:5
17	T14	NaBr	50	Toluene	70	87.5:12.5
18	T14	CuF ₂	50	Toluene	70	81:19
19	T14	KF	50	Toluene	76	66.5:33.5
20	T14	TMSCl	50	Toluene	<10	85:15

[a] Reaction conditions: **1a** (0.2 mmol), [Rh(cod)Cl]₂ (5 mol%), ligand (12 mol%) for entries 1-15 or ligand (24 mol%) for entries 16-20, additive (10 mol%), solvent (1.2 mL), for 12-16 h. [b] NMR yield. [c] The *er* values were determined by HPLC using chiral columns. [d] Isolated yield by flash column chromatography.

hydrosilylation. Encouraged by the above results, we subsequently investigated the solvent effect and other reaction parameters, such as temperature and additives (Entries 10-20 of Table 1). Fortunately, when the amount of non-diastereopure

SiMOS-Phos (**T14**) was increased to 24 mol% because of the racemic P-center of phosphoramidite moiety, the *er* value of **2a** was obtained as 96:4 *er*.

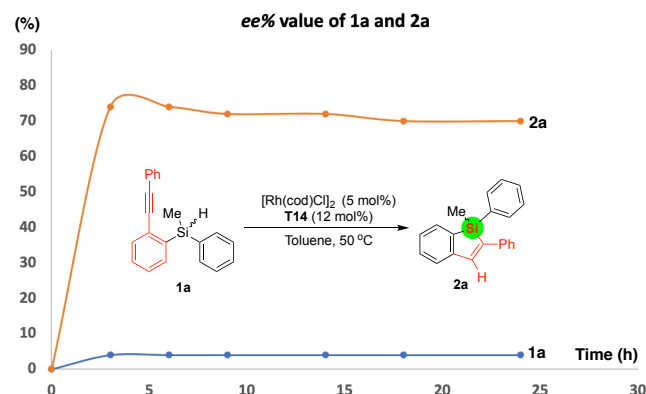
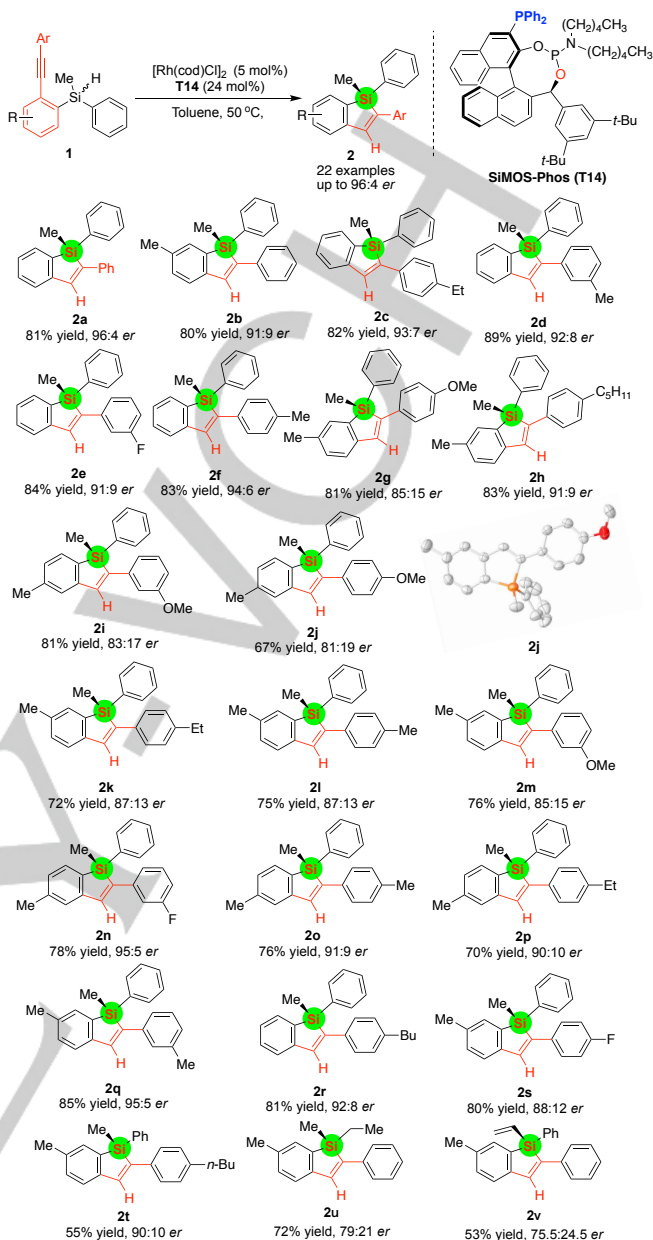


Figure 2. The determination of a DyKAH process by monitoring of progress of the Rh-catalyzed intramolecular hydrosilylation of racemic **1a**.

Furthermore, to clarify the reality of Rh-catalyzed dynamic kinetic asymmetric hydrosilylation in the presence of SiMOS-Phos (**T14**), we monitored the progress of this reaction by the determination of *er* value of **2a**. As depicted in Figure 2, the *er* values of desired product **2a** remained unchanged during the reaction process and the residual substrate **1a** was still determined as an almost racemic molecule. These results directly indicated that the Rh-catalyzed hydrosilylation of a racemic monohydrosilane is likely to occur as a dynamic kinetic asymmetric transformation (DyKATs).

With the success of the stereoselective dynamic kinetic asymmetric hydrosilylation (DyKAH) of the racemic hydrosilane based on SiMOS-Phos (**T14**), we then examined the substrate scope for this reaction. We prepared a series of “silicon-centered” racemic hydrosilanes bearing electron-withdrawing fluorine- and electron-donating methyl- or other alkyl groups for this DyKAH reaction. As shown in Scheme 1, the dynamic kinetic asymmetric hydrosilylation of various substrates took place stereoselectively to give the desired silicon-stereogenic benzosiloles with good yields and excellent enantioselectivities (up to 96:4 *er*). The structure and absolute configuration of **2j** was unambiguously confirmed by single-crystal X-ray analysis.^[12] The methyl substituents on *meta*- or *para*-position of phenyl ring were compatible with this catalyst system in this reaction, giving the corresponding DyKAH products in 75–89% yields and good enantioselectivities varied from 87:13 to 96:4 *er*. Moreover, the racemic hydrosilanes bearing ethyl, butyl, or pentyl group were also suitable for this dynamic kinetic asymmetric hydrosilylation, affording the desired silicon-stereogenic benzosiloles, in good yields and excellent enantioselectivities, such as **2r** with 81% yield and 92:8 *er*. In addition, we also checked the enantioselective synthesis of **2m**, **2q**, and **2s** in the DMF and the same level of conversion and enantioselectivity was achieved in this DyKAH reaction.



Scheme 1. Substrate scope for Rh-catalyzed dynamic kinetic asymmetric hydrosilylation of racemic hydrosilanes to access silicon-stereogenic benzosiloles.

Largely different from the well-recognized desymmetrization strategy for synthesis of silicon-stereogenic silanes,^[13] our experimental results supported that present dynamic kinetic asymmetric hydrosilylation (DyKAH) of racemic hydrosilanes provided an unprecedented method for the highly enantioselective synthesis of silicon-stereogenic organosilicon compounds.^[14] It should be noted that, similar to previously reported finding that enantioselective hydrogenation or hydroformylation of olefins could be completed by self-adaptable tropos catalysts or achieved from a mixture of non-diastereopure ligands,^[15] it is reasonable that only one diastereomer of SiMOS-Phos with suitable steric repulsion and molecular recognition (For related spectra analysis, see Figure S5 of Supporting Information) can assist the Rh-catalyzed DyKAH. In this case, we believe that one of the chiral Rh-Si*–H species from a diastereomer of

SiMOS-Phos should exhibit much higher reactivity than that of another Rh-Si*-H species, and an inert Rh-Si*-H species (for example, *R*-configuration at silicon center) can be converted into

another active Rh-Si*-H species (for example, *S*-configuration at silicon center) with the aid of chiral SiMOS-Phos ligand.

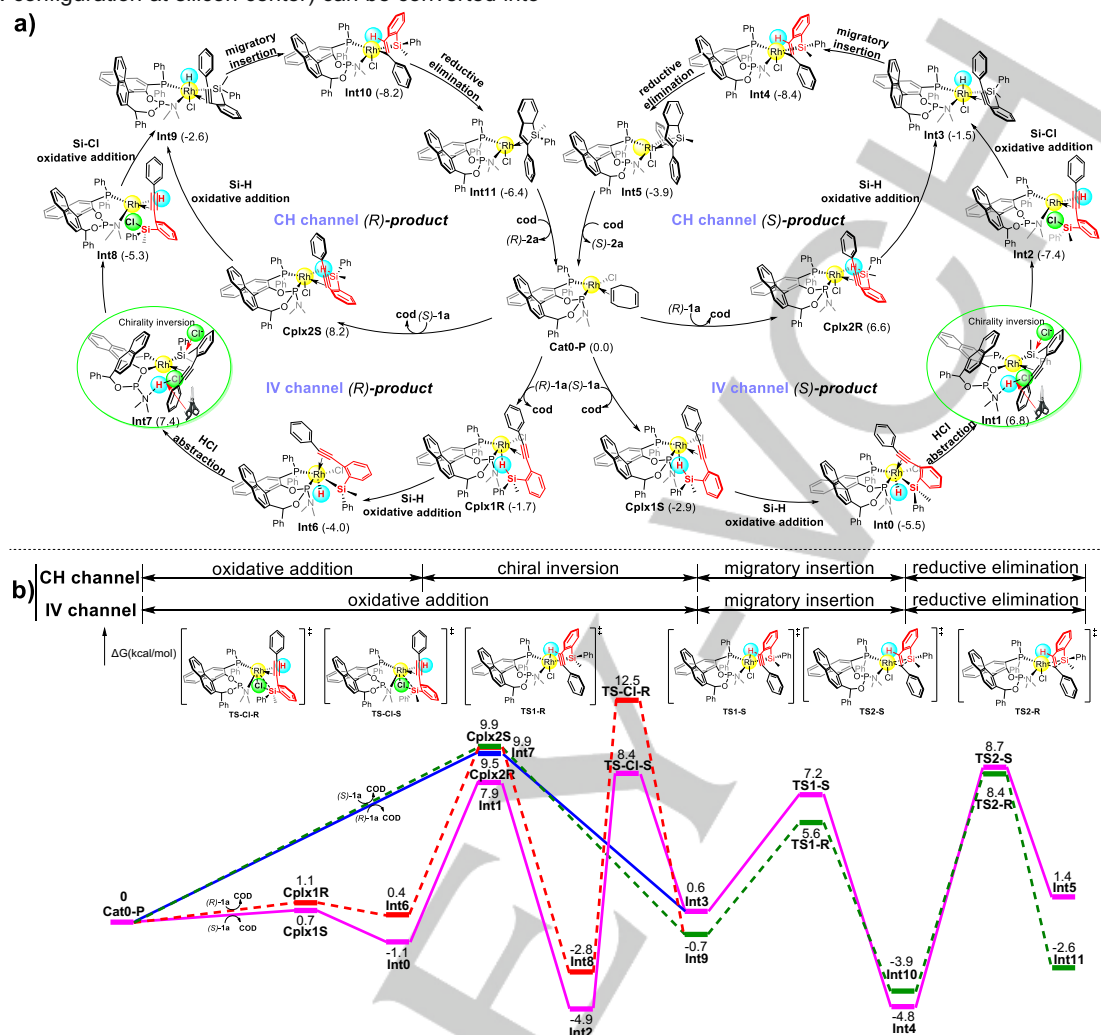


Figure 3. (a) Computed catalytic cycle with relative energy in parenthesis (Chalk-Harrod channel and the chiral inversion channel) and (b) Gibbs energy profile for Rh/(*R,S,S*)-L17 intramolecular hydrosilylation of (*S*)-1a and (*R*)-1a calculated at the SMD(toluene) M06L/def2TZVP//M06L/6-31G(d,p)-SDD(Rh) level of theory. The energy values are given in kcal/mol.

To rationalize the new chemistry of rhodium-catalyzed dynamic kinetic asymmetric alkyne hydrosilylation of "silicon-centered" racemic hydrosilanes, density functional theory (DFT) calculations have been carried out for Rh/(*R,S,S*)-L17-catalyzed intramolecular hydrosilylation of (*S*)-1a and (*R*)-1a to elucidate the reaction mechanism and stereo-control mode. Two reaction channels including the traditional Chalk-Harrod mechanism (*CH* channel) and an unprecedented ligand-assisted chiral inversion channel (*IV* channel) have been identified and the catalytic cycle together with the free energy profile is shown in Figure 3. The reaction begins with the pre-activation of [Rh(cod)Cl]₂ with ligand to generate the active catalyst species Cat0-P that can recognize the substrate 1a through ligand exchange.

In the *CH* channel, both the Si-H bond and C≡C triple bond of 1a coordinate to the Rh center of Cat0-P from the radial direction, forming Cplx2R and Cplx2S respectively. 1a within this precursor complex directly undergoes Si-H oxidative addition reaction with no energy barrier to generate Int3 and Int9 (See Figure S7 of ESI), which is followed by the migratory insertion of C≡C triple bond via TS1-S and TS1-R, leading to

Int4 and Int10. Then the Si-C reductive elimination proceeds via TS2-S and TS2-R to generate the coordinated Int5 and Int11. Finally, the resulting product (*S*)-2a and (*R*)-2a are released from the Rh center, regenerating the catalytic active species. In this reaction channel, the configuration of the silicon atom is preserved and the precursor complex is the highest free energy point, indicating substrate recognition is the rate-determining step. Cplx2R is slightly lower in free energy than Cplx2S by 0.4 kcal/mol.

In the *IV* channel (Figure 3), the Si-H bond coordinates to the Rh center from the axial direction, forming Cplx1R and Cplx1S instead of the radial direction as that in Cplx2R and Cplx2S. Similarly, the Si-H oxidative addition follows with no energy barrier to form Rh(III)(H)(silyl)(Cl) complex (Int0 and Int4) (See Figure S7 of ESI). Then an interesting configuration inversion on the silicon center occurs. With the assistance of adjacent amine moiety in the ligand, HCl is released from the Rh center and generates the Rh(I) silyl complex (Int1 and Int7), in which the released HCl is coordinated to the amine nitrogen atom. It's noteworthy that this process will be unavailable with the chiral P in (*R*)-configuration (Figure S10 of ESI). In this case, Int1 and

Int7 act as a springboard for the complete dissociation of Cl⁻ from the Rh center. Then S_N2-type substitution of Cl⁻ toward the silicon center of **Int1** or **Int7** follows, leading to Rh(I) hydride complex (**Int2** and **Int8**). In the next step, **Int2** and **Int8** undergo a Si-Cl oxidative addition reaction via **TS-CI-R** and **TS-CI-S** to generate much more stable **Int3** and **Int9**. Under this reaction channel, the Rh(III) silyl hydride complex **Int0** and **Int6** generated in the first Si-H oxidative addition step are nicely transformed to its' enantiomers **Int3** and **Int9** respectively. The Si-Cl oxidative addition is the rate-determining step in this pathway.

Just as expected, we were delighted to found that the Rh/SiMOS-Phos catalyst can selectively lower the inter-conversion free energy barrier for (*S*)-**1a** (**TS-CI-S**) by 4.1 kcal/mol with respect to that for (*R*)-**1a** (**TS-CI-R**). Compared with the *CH* channel, the **TS-CI-S** is lower in free energy than **Cplx2S** by 1.5 kcal/mol, while the **TS-CI-R** is higher in free energy than **Cplx2R** by 3.0 kcal/mol. These results clearly indicate that (*S*)-**1a** tends to follow the *IV* channel, whereas (*R*)-**1a** tends to follow the traditional *CH* channel, which accord well with our experimental findings.

In summary, we have achieved a novel dynamic kinetic asymmetric hydrosilylation of "silicon-centered" racemic hydrosilanes by using a newly developed SiMOS-Phos as a chiral ligand. A wide range of "silicon-centered" racemic alkyne-containing hydrosilanes are applicable for this reaction, giving the silicon-stereogenic benzosiloles with good enantioselectivities (up to 96:4 *er*). This protocol offers an unprecedented access to silicon-stereogenic organosilicon compounds from racemic substrates and will inspire synthetic chemists to explore new multiple stereogenic and tropos ligands for asymmetric catalysis. The DFT studies showed that the dynamic kinetic asymmetric hydrosilylation is realized by a chiral inversion process with the silyl Rh(III) hydride complex as a conversion platform, in which the Rh/SiMOS-Phos catalyst can selectively lower the transition state energy of (*R*)-**1a** in the Chalk-Harrod channel and that of (*S*)-**1a** in the inversion channel.

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Conflicts of interest

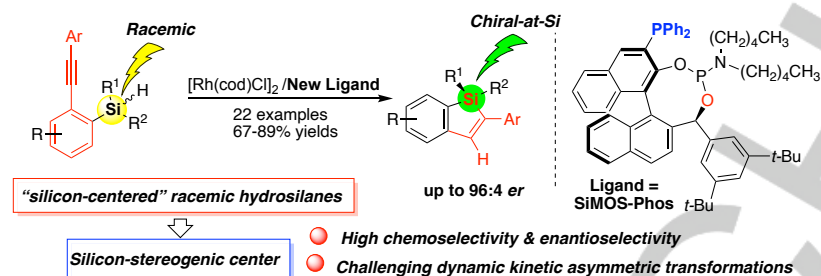
There are no conflicts to declare.

Keywords: Asymmetric catalysis; organosilicon; silicon-stereogenic; silacycle; dynamic kinetic resolution

- [1] a) S. Pati, Z. Rappoport, Eds., *The Chemistry of Organic Silicon Compounds*, Vol. 1; Wiley: Chichester, U.K., **1989**; Vol. 2; Z. Rappoport, Y. Apeloig, Eds., **1998**; b) M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, **2000**; c) K. Motokura, R. A. Pramudita, *Chem. Rev.* **2019**, *19*, 1199-1209; d) M. Iglesias, F. J. Fernandez-Alvarez, L. A. Oro, *Coord. Chem. Rev.* **2019**, *386*, 240-266; e) L. Li, Y. L. Wei, L. W. Xu, *Synlett* **2020**, *31*, 21-34; f) J. Walkowiak, J. Szyling, A. Franczyk, R. L. Melen, *Chem. Soc. Rev.* **2022**, *51*, 869-994.
- [2] a) M. C. Lipke, A. L. Liberman-Martin, T. D. Tilly, *Angew. Chem. Int. Ed.* **2017**, *56*, 2260-2294; b) V. M. Uvarov, D. A. de Vekki, *J. Organomet. Chem.* **2020**, *923*, 121415; c) P. He, M. Y. Hu, X. Y. Zhang, S. F. Zhu, *Synthesis* **2021**, *54*, 49-55; d) J. Guo, Z. Cheng, J. Chen, X. Chen, Z. Lu, *Acc. Chem. Res.* **2021**, *54*, 2701-2716; e) F. Ye, L. W. Xu, *Synlett*, **2021**, *32*, 1281-1288; f) K. Kucinski, H. Stachowiak-Dluzynska, G. Hreczycho, *Coord. Chem. Rev.* **2022**, *459*, 214456; g) Y. Kong, D. Mu, *Chem. Asian J.* **2022**, *17*, e202200104.
- [3] a) K. Tamao, K. Nakamura, H. Ishii, S. Yamaguchi, M. Shiro, *J. Am. Chem. Soc.* **1996**, *118*, 12469-12470; b) Y. Naganawa, T. Namba, M. Kawagishi, *Chem. Eur. J.* **2015**, *21*, 9319-9322; c) X. Chang, P. L. Ma, H. C. Chen, C. Y. Li, P. Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 8937-8940; d) Y. H. Huang, Y. Wu, Z. Zhu, S. Zheng, Z. Ye, Q. Peng, P. Wang, *Angew. Chem. Int. Ed.* **2022**, *61*, e202113052; e) R.-H. Tang, Z. Xu, Y.-X. Nie, X.-Q. Xiao, K.-F. Yang, J.-L. Xie, B. Guo, G.-W. Yin, X.-M. Yang, L.-W. Xu, *iScience* **2020**, *23*, 101268.
- [4] K. Igawa, D. Yoshihiro, N. Ichikawa, N. Kokan, K. Tomooka, *Angew. Chem. Int. Ed.* **2012**, *51*, 12745-12748.
- [5] a) M. Oestreich, *Synlett*, **2007**, 1629-1643; b) L.-W. Xu, L. Li, G.-Q. Lai, J.-X. Jiang, *Chem. Soc. Rev.* **2011**, *40*, 1777-1790; c) L. W. Xu, *Angew. Chem. Int. Ed.* **2012**, *51*, 12932-12934; d) R. Shintani, *Asian J. Org. Chem.* **2015**, *4*, 510-514; e) J. O. Bauer, C. Strohmman, *Eur. J. Org. Chem.* **2016**, 2868-2881; f) Y. M. Cui, Y. Lin, L. W. Xu, *Coord. Chem. Rev.* **2017**, *330*, 37-52; g) R. Shintani, *Synlett*, **2018**, *29*, 388-396; h) L. Zheng, X.-X. Nie, Y. Wu, P. Wang, *Eur. J. Org. Chem.* **2021**, 6006-6014; i) K. Igawa, K. Tomooka, in *Organosilicon Chemistry: Novel Approaches and Reactions*; T. Hiyama, M. Oestreich, Eds. Wiley-VCH Verlag GmbH & Co. KGaA, **2020**; Chapter 14, PP 495-532.
- [6] J. Y. Corey, *Chem. Rev.* **2016**, *116*, 11291-11435.
- [7] a) J. R. Jagannathan, J. C. Fetting, J. T. Shaw, A. K. Franz, *J. Am. Chem. Soc.* **2020**, *142*, 11674-11679; b) H. Wen, X. Wan, Z. Huang, *Angew. Chem. Int. Ed.* **2018**, *57*, 6319-6323.
- [8] Y. Wu, P. Wang, *Angew. Chem. Int. Ed.* **2022**, *61*, e202205382.
- [9] a) S. Bähr, A. Simonneau, E. Irran, M. Oestreich, *Organometallics*, **2016**, *35*, 925-928; b) C. Xu, Z. Ye, L. Xiang, S. Yang, Q. Peng, X. Leng, Y. Chen, *Angew. Chem. Int. Ed.* **2021**, *60*, 3189-3195.
- [10] X. Wang, S. S. Huang, F. J. Zhang, J. L. Xie, Z. Li, Z. Xu, F. Ye, L. W. Xu, *Org. Chem. Front.* **2021**, *8*, 6577-6584.
- [11] F. Ye, Z. Xu, L. W. Xu, *Acc. Chem. Res.* **2021**, *54*, 452-470.
- [12] Deposition number for product **2j** is 2076805. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.
- [13] For recent examples, see: a) S. Chen, J. Zhu, J. Ke, Y. Li, C. He, *Angew. Chem. Int. Ed.* **2022**, *61*, e202117820; b) W. Lu, Y. Zhao, F. Meng, *J. Am. Chem. Soc.* **2022**, *144*, 5233-5240; c) K. An, W. P. Ma, L. C. Liu, T. He, G. Y. Guan, Q. W. Zhang, W. He, *Nat. Commun.* **2022**, *13*, 847; d) L. Wang, W. Lu, J. Zhang, Q. Chong, F. Meng, *Angew. Chem. Int. Ed.* **2022**, e202205624; e) L. Zhang, K. An, Y. Wang, Y. D. Wu, X. Zhang, Z. X. Yu, W. He, *J. Am. Chem. Soc.* **2021**, *143*, 3571-3582; f) W. T. Zhao, Z. Q. Lu, H. Zheng, X. S. Xue, D. Zhao, *ACS Catal.* **2018**, *8*, 7997-8005; g) J. Zhang, N. Yan, C. W. Ju, D. Zhao, *Angew. Chem. Int. Ed.* **2021**, *60*, 25723-25728; h) H. Zhang, D. Zhao, *ACS Catal.* **2021**, *11*, 10748-10753; i) Y. Guo, M. M. Liu, X. Zhu, L. Zhu, C. He, *Angew. Chem. Int. Ed.* **2021**, *60*, 13887-13891; j) Y. You, S. Ge, *Angew. Chem. Int. Ed.* **2021**, *60*, 12046-12052; k) J. Zhu, S. Chen, C. He, *J. Am. Chem. Soc.* **2021**, *143*, 5301-5307; l) X. Bi, J. Feng, X. Xue, Z. Gu, *Org. Lett.* **2021**, *23*, 3201-3206; m) J. L. Xie, Z. Xu, H. Q. Zhou, Y. X. Nie, J. Cao, G. W. Yin, J. P. Bouillon, L. W. Xu, *Sci. China Chem.* **2021**, *64*, 761-769; n) S. Chen, D. Mu, P. L. Mai, J. Ke, Y. Li, C. He, *Nat. Commun.* **2021**, *12*, 1249; o) W. Ma, L. C. Liu, K. An, T. He, W. He, *Angew. Chem. Int. Ed.* **2021**, *60*, 4245-4251; p) B. Yang, W. Yang, Y. Guo, L. You, C. He, *Angew. Chem. Int. Ed.* **2020**, *59*, 22217-22222; q) X. B. Wang, Z. J. Zheng, J. L. Xie, X. W. Gu, Q. C. Mu, G. W. Yin, F. Ye, Z. Xu, L. W. Xu, *Angew. Chem. Int. Ed.* **2020**, *59*, 790-797; r) D. Mu, W. Yang, S. Chen, N. Wang, B. Yang, L. You, B. Zu, P. Zu, P. Yu, C.

- He, *J. Am. Chem. Soc.* **2020**, *142*, 13459-13468; s) G. Zhang, Y. Li, Y. Wang, Q. Zhang, T. Xiong, Q. Zhang, *Angew. Chem. Int. Ed.* **2020**, *59*, 11927-11931; t) P. W. Long, J. L. Xie, J. J. Yang, S. Q. Lu, Z. Xu, F. Ye, L. W. Xu, *Chem. Commun.*, **2020**, 56, 4188-4191; u) Q. Wang, F. Ye, J. Cao, Z. Xu, Z. J. Zheng, L. W. Xu, *Catal. Commun.* **2020**, *138*, 105950; v) 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*, 2082-2085.
- [14] We have also checked the intermolecular hydrosilylation of 1,2-diphenylethyne with racemic hydrosilane and found that the desired product could be obtained with 53% yield and 54.5:45.5 *er* (see Supporting Information).
- [15] Due to the existence of a P-stereogenic center on SiMOS-Phos, this ligand is a mixture of two diastereomers, also see: a) M. T. Reetz, J.-A. Ma, R. Goddard, *Angew. Chem. Int. Ed.* **2005**, *44*, 412-415; b) D. G. Blackmond, T. Rosner, T. Neugebauer, M. T. Reetz, *Angew. Chem. Int. Ed.* **1999**, *38*, 2196-2199; c) M. T. Reetz, *Angew. Chem. Int. Ed.* **2008**, *47*, 2556-2588; d) D. Chen, M. Schmitkamp, G. Franciò, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* **2008**, *47*, 7339-7341; e) J. Jia, D. Fan, J. Zhang, Z. Zhang, W. Zhang, *Adv. Synth. Catal.* **2018**, *360*, 3793-3800; f) M. Diéguez, O. Pàmies, C. Moberg, *Acc. Chem. Res.* **2021**, *54*, 3252-3262; g) W. Faller, A. R. Lavoie, J. Parr, *Chem. Rev.* **2003**, *103*, 3345-3367.

Table of Contents



An unprecedented (SiMOS-Phos) ligand-controlled Rh-catalyzed hydrosilylation of "silicon-centered" racemic hydrosilanes was developed for the highly efficient and enantioselective construction of silicon-stereogenic centers of benzosiloles (up to 96:4 *er*). This achievement was obtained by using an original synthetic strategy involving dynamic kinetic asymmetric transformations.