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Construction of Chiral Tetraorganosilicons by Tandem Desymmetrization of Silacyclobutanes/Intermolecular Dehydrogenative Silylation

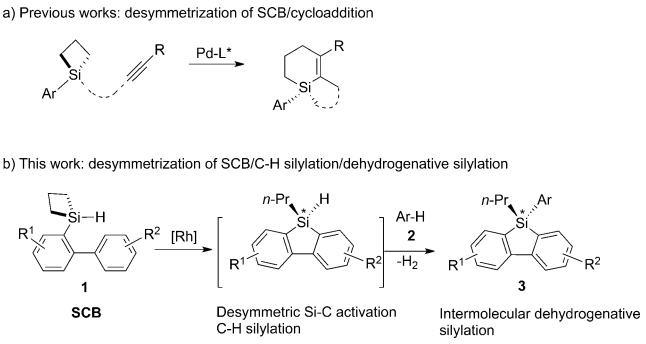
*Qing-Wei Zhang[+], Kun An[+], Li-Chuan Liu, Qi Zhang, Huifang Guo, and Wei He**

Abstract: *We report a method to construct chiral tetraorganosilicons by tandem silacyclobutane (SCB) desymmetrization–dehydrogenative silylations. A wide array of dibenzosiloles with stereogenic quaternary silicon centers were obtained in good yields and enantioselectivities up to 93 % ee. Chiral TMS-segphos was found to be a superior ligand in terms of reactivity and enantioselectivity.*

Organosilicon compounds have found wide applications in functional materials and pharmaceuticals.[1] Construction of silicon stereogenic centers has been a long-sought topic and is currently underdeveloped compared to chiral carbon centers.[2–4] A significant challenge in controlling the chirality of silicon resides in its tendency to form penta-covalent intermediates. While such intermediates can often lead to racemization via Berry pseudorotation,[5] they have also been cleverly exploited to construct silicon stereogenic centers via nucleophilic substitution by stoichiometric chiral reagents.[4]

Aside from the different bonding behavior of silicon, the general lack of strategies to construct silicon stereogenic centers could be understood by the fact that chiral carbon centers are often accessed by asymmetric addition to sp^2-hybridized carbons, whereas sp^2-hybridized silicons are not stable.[6] This simple fact has a very clear conceptual consequence: stereogenic silicons must come from tetrasubstituted silicon precursors. It is therefore not surprising that the catalytic construction of chiral silicons exclusively depends on desymmetrization of prochiral silicons. In this context, a number of prochiral silicons have been explored. Dihydrosilanes are the most common precursors owing to their versatile reactivity and wide availability. Desymmetrization based on the signature hydrosilylation reaction of alkynes,[7] ketones,[8] and alkenes[9] has been reported. Carbene insertion[10] and alcoholysis[11] are also very efficient and highly enantioselective. The more challenging cross-coupling reaction with aryl iodide has been described.[12] Asymmetric intramolecular dehydrogenative silylation reactions between Si–H and C–H have also been reported, with some intriguing mechanistic aspects unveiled very recently.[13] Other desymmetrization reactions that did not involve silicon atom in the bond formation, such as the [2+2+2] cycloaddition,[14] C–H bond activation,[15] and β-elimination of silacyclopentene oxides,[16] were also developed.

The advent of catalytic activation of inert Si–C bonds[17] provides a conceptually new strategy to access stereogenic silicon from Si–C precursors. Rh- or Ni-catalyzed desymmetrization of Si-aryl,[18] Si-alkynyl,[19] and Si-methyl bonds[20] were developed recently. Shintani, Hayashi, and co-workers have reported intriguing Pd-catalyzed desymmetric cycloadditions between silacyclobutane (SCB) and alkynes in both intra- and intermolecular fashions (Scheme 1 a).[21] Herein,



Scheme 1. Desymmetrization of SCB.

construction of chiral tetraorganosilicons via Rh-catalyzed tandem SCB desymmetrization/C–H silylation and intermolecular dehydrogenative silylation processes is reported (Scheme 1 b).[22] This method produced a wide array of dibenzosiloles with silicon stereogenic centers in good yield and high enantioselectivity. Of note, benzosiloles have been extensively studied owing to their promising optoelectronic properties.[1] However, to our knowledge, only three examples have been reported for the synthesis of dibenzosiloles with silicon stereogenic centers.[13–15]

We commenced our study by using SCB[23,24] **1a** and 2-chlorothiophene **2a** as the model substrates under the catalysis of Rh(cod)Cl (10 mol %) (Table 1). No reaction took place in the absence of a ligand (entry 1). Because a pronounced ligand effect on the C–H silylation was observed in our earlier work,[25] a panel of ligands were screened (for ligand structures, see Figure S1 in the Supporting Information). When (*S*)-DTBM-BINAP was used, prod-

[*] Dr. Q.-W. Zhang,[+] K. An,[+] L.-C. Liu, Q. Zhang, Dr. H. Guo, Prof. Dr. W. He
School of Pharmaceutical Sciences, Tsinghua University
Beijing, 100084 (China)
E-mail: whe@mail.tsinghua.edu.cn
Homepage: http://www.sps.tsinghua.edu.cn/en/team/team/2016/0814/45.html
[+] These authors contributed equally to this work.
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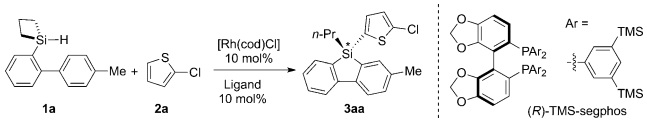
Table 1: Optimization of the reaction parameters.[a]



Entry	Ligand	Yield [%][b]	*ee* [%][c]
1	–	–	–
2	(*S*)-DTBM-BINAP	43	−64
3	(*S*)-MeO-Biphep	< 10	−66
4	(*R*)-DTBM-MeO-Biphep	21	60
5	(*S*)-TMS-MeO-Biphep	28	−86
6	(*R*)-Segphos	< 10	22
7	(*R*)-DM-Segphos	19	38
8	(*R*)-DTBM-Segphos	25	72
9	(*R*)-TMS-Segphos	35	86
10	(*S*)-DTBM-C1-Tunephos	< 10	−66
11[d]	(*R*)-TMS-Segphos	28	86
12[e]	(*R*)-TMS-Segphos	46, 44[h]	86, 85[h]
13[e,f]	(*R*)-TMS-Segphos	35	86
14[f]	(*R*)-TMS-Segphos	60	86
15[g]	(*S*)-TMS-Segphos	76	73

[a] Conditions: **1a** (0.1 mmol), **2a** (0.2 mmol) in *p*-xylene (1 mL) unless otherwise noted, 40 °C for 24 hrs. [b] Isolated yield. [c] Determined by HPLC. [d] In 1,4-dioxane. [e] In DCE. [f] [Rh(cod)OH] as the catalyst. [g] Triethylsilane (10 mol%) was added. [h] 3 mmol scale.

uct **3aa** was observed in 43% yield with excellent regioselectivity and moderate enantioselectivity (64% *ee*, entry 2). MeO-Biphep-type ligands, which possess narrower bite angles compared with BINAP, were screened (entries 3–5). Among this type of ligand, the reactivity improved as the stereohindrance increased, with yields ranging from < 10% to 28%. The (*S*)-TMS-MeO-Biphep gave a high enantioselectivity (−86% *ee*). Encouraged by these results, Segphos that have even narrower bite angles were then examined (entries 6–9). A similar correlation between the reactivity and the ligand steric hindrance was again noted. With the (*R*)-TMS-Segphos ligand, 86% *ee* was obtained, albeit with a lower 35% yield (entry 9).[26] Further increasing the stereohindrance by using (*S*)-DTBM-C1-Tunephos resulted in a further decreased yield of < 10% (entry 10).

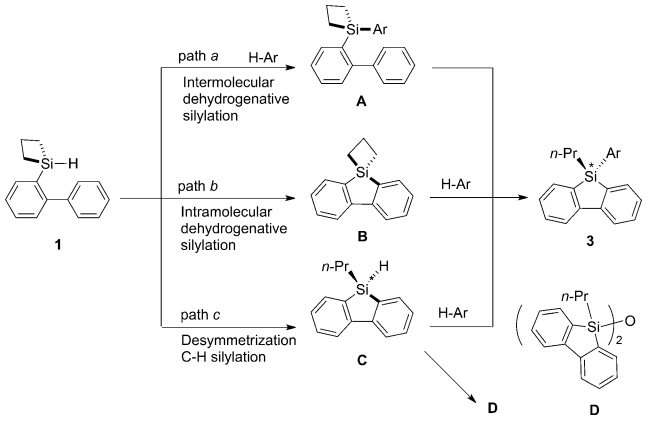
We then focused on optimizing the reaction using the (*R*)-TMS-Segphos ligand. The solvent had a significant effect on the yield, but not on the enantioselectivity. For example, the reaction gave the same 86% *ee* in 1,4-dioxane and in dichloroethane (DCE), but the yields were much higher in DCE (entry 11 versus 12). When the reaction was carried out on 3 mmol scale, product **3aa** could also be obtained in a comparable 44% yield and 85% *ee*. When [Rh(cod)OH] was used as the catalyst instead of [Rh(cod)Cl], a 35% yield was obtained for reaction in DCE (entry 13). Satisfyingly, the yield was improved to 60% with *p*-xylene as the solvent (entry 14). Disiloxane (see Scheme 2) and biphenyl side products accounted for the mass balance. The disiloxane can be effectively suppressed by adding triethylsilane at the cost of the enantioselectivity (entry 15 and Supporting Information).

The substrate scope was demonstrated using the optimized reaction conditions. We first examined the (hetero)-arene partner **2** using SCB **1a** (R = Me) and **1b** (R = Cl). The reaction between 2-chlorothiophene (**2a**) and **1a** gave dibenzosilole **3aa** in 60% yield and 86% *ee*, while the reaction between **2a** and **1b** afforded the desired product **3ba** in 63% yield and 93% *ee*. The silylation of 3-chlorothiophene (**2b**) took place exclusively at the 5-position but not at the competing 2-position, and the corresponding products **3ab** and **3bb** were obtained in 64% and 78% yields, with 91% and 88% *ee*, respectively. The more electron-rich 2-methylthiophene **2c** was also compatible with the reaction, producing only one constitutional product **3ac** in 65% yield. In this case, the enantioselectivity was lower (78% *ee*). The reactions involving 3-methylthiophene **2d** were also very regioselective, but the enantioselectivities varied significantly: 77% *ee* was observed for **3ad** and 92% *ee* was obtained for **3bd**.

The less reactive benzene (**1e**) and 3, 5-difluorobenzene (**1f**) were then employed. Owing to the lower reactivity, they were used as the solvent for the reaction (see footnote d). The reaction between benzene with SCB **1a** and **1b** successfully afford the desired products **3ae** and **3be** in a moderate yield (54%). The enantioselectivities were lower, however, with 65% *ee* for **3ae** and 68% *ee* for **3be**. The absolute configuration of **3ae** was unambiguously determined to be *S* by single-crystal X-ray spectroscopy.[27] 3,5-Difluorobenzene **1f** was slightly more reactive, and the reaction gave the corresponding product **3af** in a higher yield (63%) than that of **3ae** with similar enantioselectivity (67% *ee*).

A number of SCBs bearing different substituents on ring B were then tested using 2-chlorothiophene **2a** as the arene partner. SCB **1c** with an electron-withdrawing *para*-F substituent reacted smoothly with **2a** to give the product **3ca** in a good yield (70%) with a high enantioselectivity (91% *ee*). The electron-donating *para*-methoxyl group in SCB **1d** did not show an adverse effect, furnishing the product **3da** in a 67% yield with 93% *ee*. SCBs **1e**, **1f**, and **1g** bearing *meta*-substituents were also capable substrates. The reaction of SCB **1e** afforded the product **3ea** in 61% yield and 88% *ee*, while SCB **1f** gave the product **3fa** in an excellent enantioselectivity (90% *ee*). To test the limit of the reaction, SCB **1g** was reacted with the least active benzene **2e**. The desired product **3ge** was obtained in a 69% yield and a good enantioselectivity (80% *ee*). This method was successfully extended to the synthesis of bis-silole **3ha**, which was obtained in a 54% combined yield (**3ha** : racemate = 11:1 by HPLC, for details see page 29 in the Supporting Information) with 92% *ee*. When ring B of the substrate was changed into a ferrocene unit, the reaction showed a very high efficiency (88% yield). The desired product **3ie** was isolated as a single diastereomer in 91% *ee*.

The possible pathways of the current reaction are shown in Scheme 2, which involve different sequences of bond formation. In pathway *a*, the well-documented intermolecular dehydrogenative silylation[22] between the arene and the Si–H happens first, followed by asymmetric intramolecular C–H silylation of SCB. At face value, the latter step is a close analogue of the racemic reaction[25b] we reported recently (see below). Pathway *b* entails an intramolecular dehydrogenative silylation, which is also well established.[13] However, the intermolecular C–H silylation of SCB is not known to date.

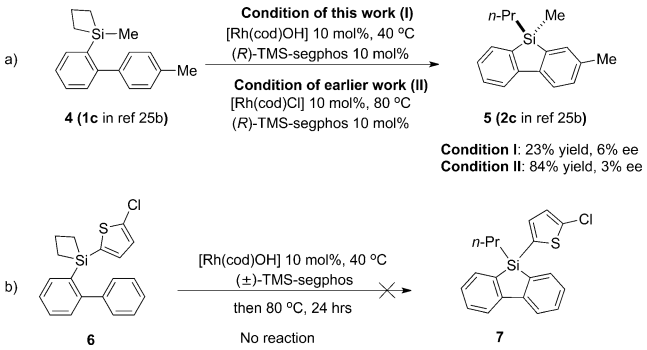


Scheme 2. Possible reaction pathways.

Pathway *c* requires that the SCB reacts prior to the commonly known reactive Si–H bond. A subsequent intermolecular dehydrogenative silylation that proceeded in either a stereospecific or a stereoconvergent fashion is necessary for the formation of the chiral product **3**.

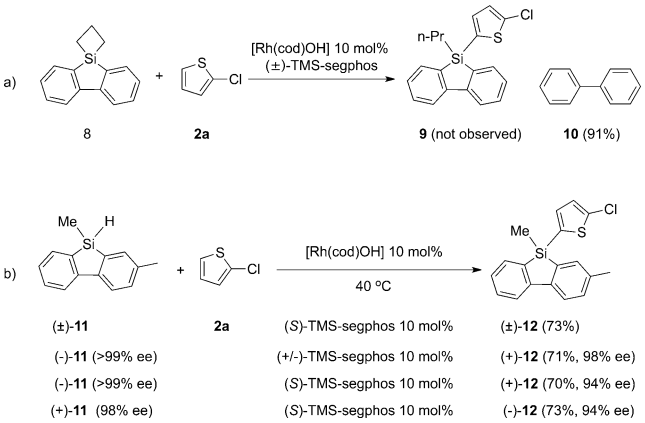
We attempted to isolate possible reaction intermediates (for example, **A**, **B**, or **C**) in reaction mixtures that were obtained by purposely stopping the reaction at low conversions. Except for the product **3** and disiloxane **D**, no other discernible compound was obtained. This observation is consistent with our NMR studies, which showed no signals corresponding to any of the proposed intermediates during the progression of the reactions. Therefore, we performed a number of control experiments to identify viable reaction intermediates.

Control experiments related to pathway *a* are shown in Scheme 3. Compound **4** (substrate **1c** in our previous racemic reaction[25b]) was converted to product **5** in a low yield (23%) under the conditions of this work, compared to 84% under previous conditions.[25b] However, almost no enantioselectivity was observed under both sets of conditions (6% and 3% *ee*, Scheme 3a). Compound **6** was then synthesized and subjected to the reaction conditions. In this case, no reaction was observed and substrate **6** was recovered even after extended heating at elevated temperature (80 °C) (Scheme 3b). These control experiments suggested that the present reaction is not a simple asymmetric version of our earlier report because the reaction did not proceed via the intermediacy of **A**. This phenomena could be attributed to less stereodifferentiation between methyl versus aryl groups, as compared to H versus aryl group in the oxidative insertion step.



Scheme 3. Control experiments on pathway *a*.

Further control experiments were then performed to distinguish pathways *b* and *c* (Scheme 4). First, reaction of independently synthesized spirosilole **8** (intermediate **B**) failed to give C–H silylation product **9**, while the desilylated side product **10** was obtained in a 91% yield (Scheme 4a).



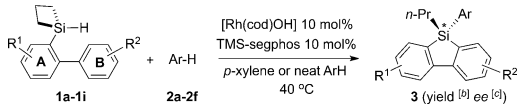
Scheme 4. Control experiments on pathways *b* and *c*.

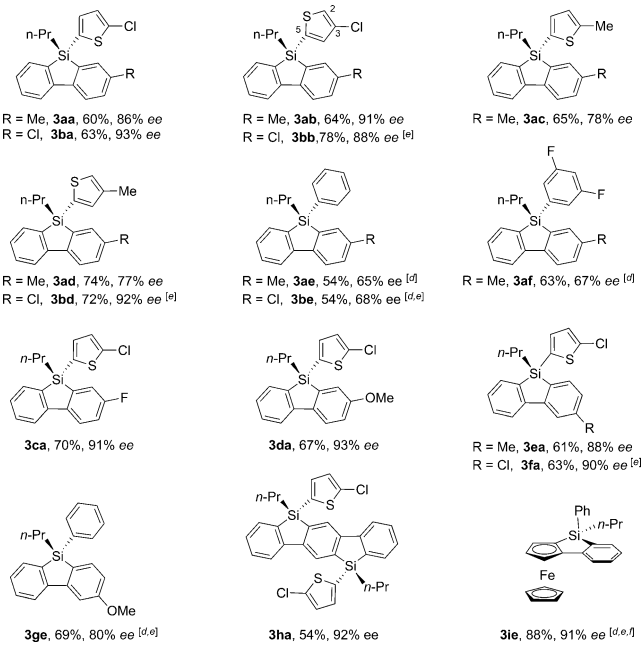
This experiment suggested that the final product **3** was not formed via pathway *b*. However, given the observation that biphenyl side products were observed in many of the reactions reported in Table 2, it is likely that pathway *b* is a counterproductive competing pathway.

Despite numerous attempts, we failed to isolate intermediate **C** in the reaction of **1** in absence of the arene partner **2** even under stringent glovebox conditions. Therefore, intermediate **C** (tertiary silane **11**) was prepared in both racemic and enantio-enriched forms. A series of control reactions substantiated that the stereo-determining step is the SCB opening/intramolecular C–H silylation process in pathway *c* (Scheme 4b). It is clear that the intermolecular dehydrogenative coupling between **11** and **2a** is stereospecific and independent of the chirality of the ligand. Interestingly, such types of stereospecific intermolecular Si–H/C–H dehydrogenative coupling is rarely reported.[13c]

In conclusion, we reported a method to construct dibenzosiloles with silicon stereogenic centers, which hinged on the newly discovered C–H silylation reactivity of SCB. In this reaction, SCB undergoes desymmetric C–H silylation in the presence of a reactive Si–H bond, producing a chiral silane intermediate that ultimately furnished the dibenzosilole product. This works unveils a number of surprising reactivity features that warrant further investigation.

Table 2: Substrate scope.[a]





[a] Conditions: **1** (0.1 mmol), **2** (0.2 mmol, 0.4 mmol for **3 ha**) in *p*-xylene (1 mL) at 40 °C; [b] Isolated yield. [c] Determined by HPLC. [d] neat ArH (1 mL) instead of *p*-xylene. [e] (*S*)-TMS-segphos was used as ligand, reversed configuration and *ee* were shown. [f] [Rh(cod)Cl] (10 mol%) as the catalyst.

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Keywords: dibenzosiloles · enantioselectivity · silacyclobutanes · tetraorganosilicons

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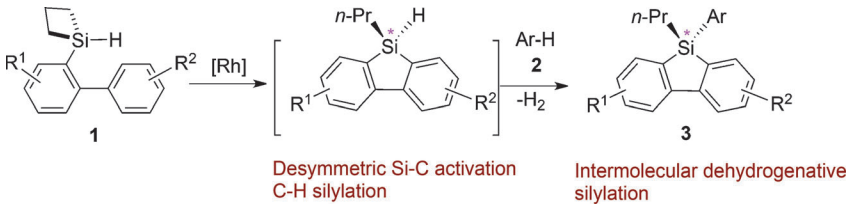
Communications

Asymmetric Catalysis

Q.-W. Zhang, K. An, L.-C. Liu, Q. Zhang, H. Guo, W. He* ———— ■■■■–■■■■

Construction of Chiral Tetraorganosilicons by Tandem Desymmetrization of Silacyclobutanes/ Intermolecular Dehydrogenative Silylation



Chiral silicon: A Rh-catalyzed reaction between silacyclobutane and (hetero)-arenes in the presence of (*R*)- or (*S*)-TMS-segphos provides access to a wide array of chiral dibenzosiloles in good yields and enantioselectivities (up to 93% *ee*). The reaction proceeds through a rarely documented desymmetrization of silacyclobutane, followed by intra- and intermolecular dehydrogenative silylation processes.

