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Introduction

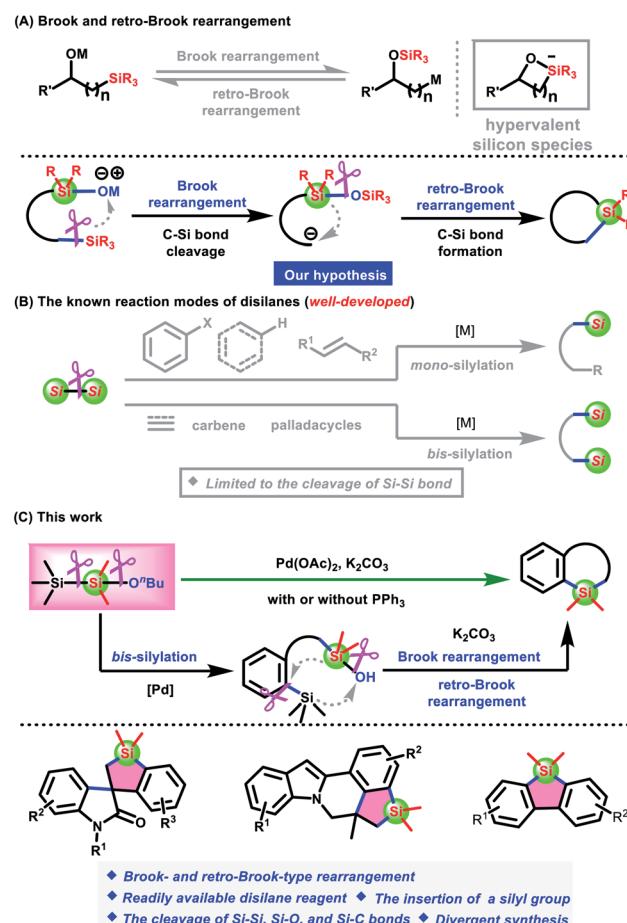
Silacycles have attracted increasing attention because they have shown unique physical, optoelectronic, and physiological properties in medicinal chemistry and materials science.¹ In this context, considerable efforts have been devoted to the development of synthetic methods for silacycles, which is a prerequisite for fully discovering their application potentials.^{2,3} Among them, of particular interest to synthetic chemists is the synthesis of silacycles *via* the cleavage of C-Si bonds.³ Typical strategies include direct annulation of silicon-based frameworks^{3a–n} and C-Si/C-C bond exchange reaction of small ring systems based on the existence of a high ring strain.^{3o–r} However, these methods generally require transition-metal catalysts to assist the activation of C-Si bonds. Transition-metal-free catalyzed annulation to assemble silacycles by cleaving C-Si bonds is still elusive so far.

The Brook rearrangement enables an intramolecular migration of a silyl group from carbon to oxygen atoms *via* a hypervalent silicon species,⁴ which was initially introduced by Brook⁵ and was demonstrated to be a reversible process.⁶ Its reverse process, namely retro-Brook rearrangement, can, in turn, be achieved by the transfer of a silyl group from oxygen to carbon atoms (Scheme 1A).⁷ Obviously, the Brook and retro-

Me₃SiSiMe₂(OⁿBu): a disilane reagent for the synthesis of diverse silacycles *via* Brook- and retro-Brook-type rearrangement†

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Herein, a readily available disilane Me₃SiSiMe₂(OⁿBu) has been developed for the synthesis of diverse silacycles *via* Brook- and retro-Brook-type rearrangement. This protocol enables the incorporation of a silylene into different starting materials, including acrylamides, alkene-tethered 2-(2-iodophenyl)-1H-indoles, and 2-iodobiaryls, *via* the cleavage of Si-Si, Si-C, and Si-O bonds, leading to the formation of spirobenzosiloles, fused benzosiloles, and π -conjugated dibenzosiloles in moderate to good yields. Preliminary mechanistic studies indicate that this transformation is realized by successive palladium-catalyzed bis-silylation and Brook- and retro-Brook-type rearrangement of silane-tethered silanols.



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Scheme 1 (A) Brook and retro-Brook rearrangement. (B) The Known reaction modes of disilanes. (C) Our work: a disilane reagent Me₃SiSiMe₂(OⁿBu) for the synthesis of diverse silacycles.

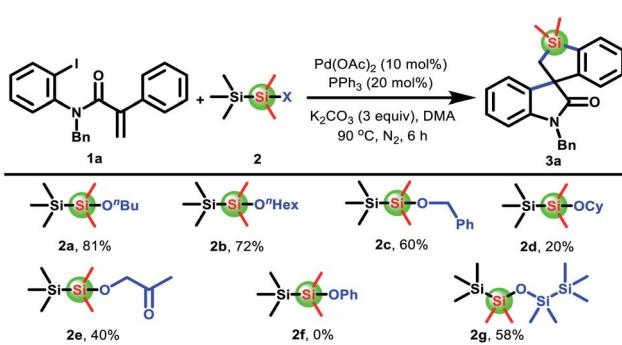


Brook rearrangements allow the cleavage of a C-Si bond and the formation of a C-Si bond under transition-metal-free catalysis.⁸ On the other hand, the existing studies are limited to the translocation of a single silyl group from the starting materials. The migration of two different silyl groups in one event has not been reported so far. In this context, we want to explore the synthesis of silacycles *via* the migration of two different silyl groups in the Brook and retro-Brook rearrangement. The design and synthesis of silane-tethered silanols is undoubtedly the primary task and challenge to achieve this hypothesis.

Disilanes have been among the most versatile silylation reagents in organic synthesis. Over the past few decades, a myriad of methods for accessing organosilanes from disilanes have focused on the activation of Si-Si bonds for the development of mono-silylation involving aryl halides or cyanides, alkenes, and C-H bonds and bis-silylation of alkynes, alkenes, carbenes, and palladacycles (Scheme 1B).^{9–13} Particularly, the pioneering work that realizes the bis-silylation of *in situ* generated palladacycles with hexamethyldisilane *via* the cleavage of Si-Si bonds has recently been reported by Zhang, Cheng, and us.^{12,13} These advances have inspired us to modify hexamethyldisilane, namely the replacement of the methyl group with an oxygen-containing group, for the synthesis of silane-tethered silanols, which were further converted into silacycles *via* Brook and retro-Brook-type rearrangement. Herein, we disclose a Brook and retro-Brook-type rearrangement strategy for the synthesis of diverse silacycles, including spirobenzosiloles, fused benzosiloles, and π -conjugated dibenzosiloles, by employing a readily available disilane reagent $\text{Me}_3\text{SiSiMe}_2(\text{O}^{\prime}\text{Bu})$ that could be prepared by a simple treatment of pentamethylchlorodisilane with *n*-butanol in the presence of NEt_3 at room temperature (Scheme 1C). Notably, the cleavage of Si-Si, Si-C, and Si-O bonds is involved in the transformation.

Results and discussion

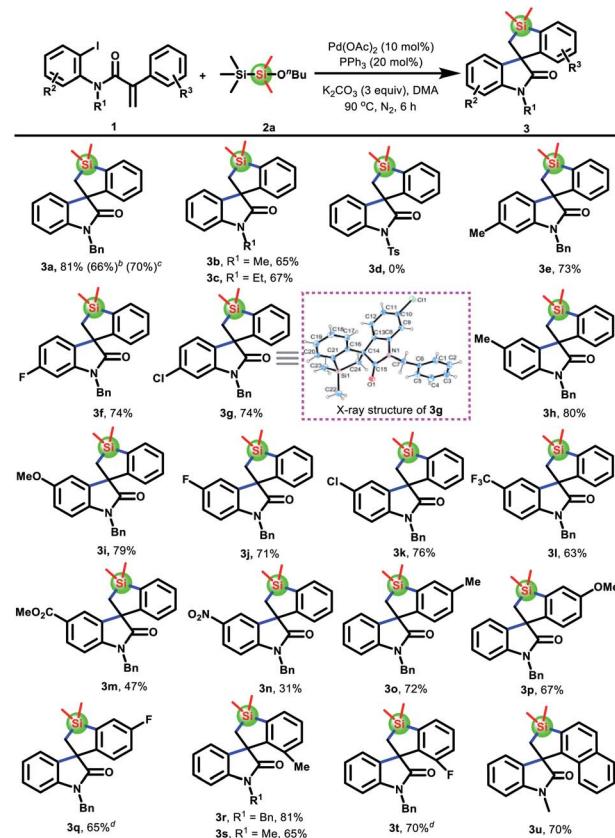
We initiated the studies by investigating the reaction of acrylamide **1a** with 1-butoxy-1,1,2,2,2-pentamethyldisilane **2a**. To our delight, the anticipated spirobenzosilole **3a** was indeed afforded in 66% yield by using a simple catalytic system composed of $\text{Pd}(\text{OAc})_2$ and K_2CO_3 in DMA at 90 °C. Encouraged by these initial results, various parameters were screened, and the optimized reaction conditions are as follows: **1a** (0.2 mmol),



Scheme 2 Screening of disilanes (2).

2a (0.3 mmol), $\text{Pd}(\text{OAc})_2$ (10 mol%), PPh_3 (20 mol%), and K_2CO_3 (0.6 mmol) in DMA (2 mL) at 90 °C under N_2 for 6 h (see the ESI† for details). Next, several disilanes **2b–h** were tested. As shown in Scheme 2, when the *n*-butyl group of disilane **2a** was replaced by other functional groups such as *n*-hexyl, benzyl, cyclohexyl, and 2-oxopropyl, all of them could afford the desired product **3a**, albeit in a lower yield. Unexpectedly, disiloxane **2g** was unreactive. Finally, disiloxane **2g** was found to produce product **3a** in 58% yield.

With the optimal reaction conditions and disilane reagent confirmed, the scope of acrylamides **1** was subsequently examined. Gratifyingly, this protocol was applicable to a large variety of acrylamides **1** to afford spiro[benzo[*b*]silole-3,3'-indolin]-2'-ones **3a–u** in moderate to good yields (Scheme 3). Note that the replacement of iodine atoms with bromine atoms on the acrylamide showed good reactivity, delivering the product **3a** in 66% yield. Moreover, the three substructures of acrylamides **1** were systematically investigated. Regarding different substituents on the nitrogen atom, methyl or ethyl group substituted acrylamides **1b** and **1c** were competent substrates, while acrylamide **1d** with a Ts group could not give the target product **3d** under the standard conditions. For the 2-iodoaniline fragment, a broad range of functional groups on the

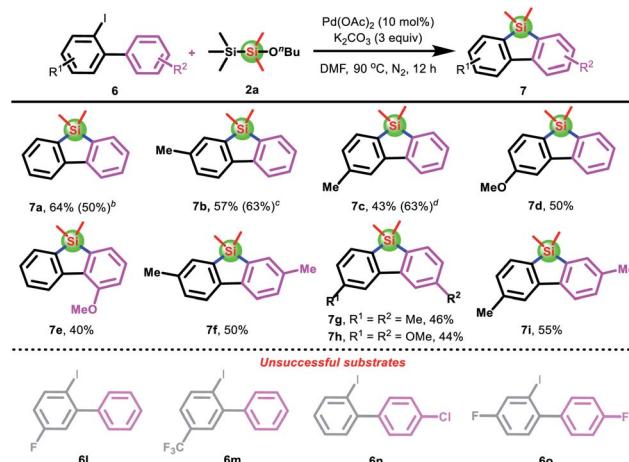


Scheme 3 Variations of the acrylamides (1). ^aReaction conditions: **1** (0.2 mmol), **2a** (0.3 mmol), $\text{Pd}(\text{OAc})_2$ (10 mol%), PPh_3 (20 mol%), K_2CO_3 (3 equiv.), and DMA (2 mL) at 90 °C under a N_2 atmosphere for 6 h. ^b*N*-Benzyl-*N*-(2-bromophenyl)-2-phenylacrylamide. ^c**1a** (1 mmol). ^d70 °C and 1 h.

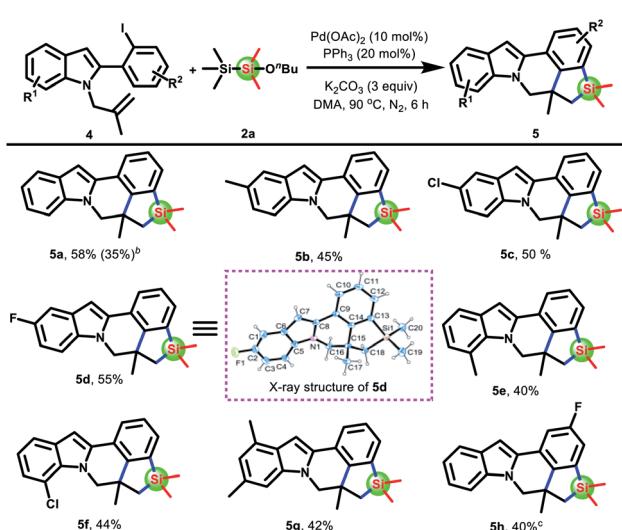


benzene ring, including electron-donating groups (Me and OMe), modifiable halogen groups (F and Cl), and even strong electron-withdrawing groups (CF₃, CO₂Me, and NO₂), were well tolerated (3e–n). Meanwhile, the structure of 3g was unambiguously confirmed by X-ray crystallography. Their electronic properties seem to affect the reactivity, since substrates 1l–n with strong electron-withdrawing groups, especially CO₂Me and NO₂ groups, resulted in a diminished yield. Finally, the compatibility was further demonstrated by testing the key 2-phenylalkene moiety. Both the benzene ring containing *ortho* or *para* substituents and the naphthalene ring could survive, affording spirobenzosilole 3o–u in moderate to good yields. Nevertheless, a slight modification of the reaction conditions was required when substrates bearing F groups were used (3q and 3t). When the reaction was scaled up to 1 mmol, 70% spirocyclic product 3a could also be obtained.

To highlight the generality of this domino Heck/silacyclization, we envision that fused benzosiloles can be synthesized by a domino Heck/*ortho* C–H functionalization of aryl iodides. Therefore, 2-(2-iodophenyl)-1-(2-methylallyl)-1*H*-indole was employed to react with disilane 2a under the above reaction conditions. To our delight, indolo[2,1-*a*]silolo[4,3,2-*de*]isoquinolines 5a could smoothly be produced in 58% yield by the cleavage of Si–Si and Si–O bonds. Encouraged by these results, the scope of 2-(2-halophenyl)-1-(2-methylallyl)-1*H*-indoles was then explored (Scheme 4). Bromine atoms instead of iodine atoms on the substrate 4a' were subjected to the standard conditions, which could give product 5a, albeit in a lower yield. Satisfactorily, substrates 4b–g being diversely substituted (Me, F, and Cl) on the indole ring were able to undergo this domino Heck/silacyclization with disilane 2a to provide the desired products 5b–g in moderate yields. Differently, using substrate 4h required relatively mild conditions.



Scheme 5 Variations of the 2-iodobiphenyls (6). ^aReaction conditions: 6 (0.2 mmol), 2a (0.24 mmol), Pd(OAc)₂ (10 mol%), K₂CO₃ (3 equiv.), and DMF (2 mL) at 90 °C under a N₂ atmosphere for 12 h. ^b2-Bromobiphenyl was used. ^c2-Iodo-4'-methyl-1,1'-biphenyl was used. ^d2-Iodo-3'-methyl-1,1'-biphenyl was used.

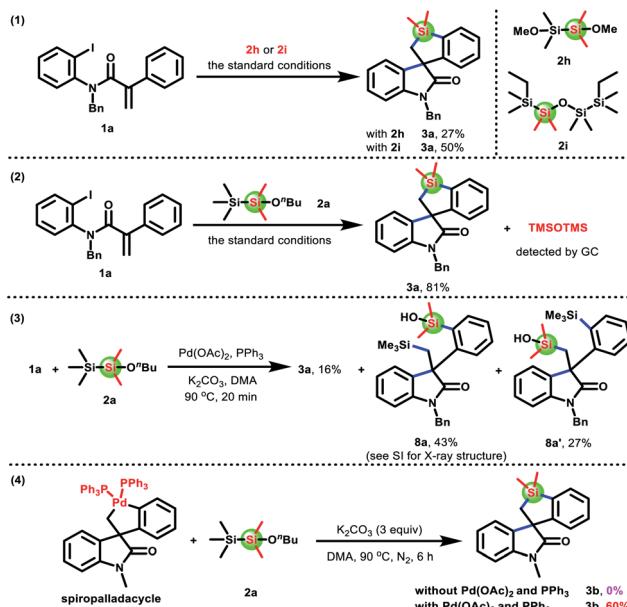


Scheme 4 Variations of the 2-(2-iodophenyl)-1*H*-indoles chlorides (4). ^aReaction conditions: 4 (0.2 mmol), 2a (0.3 mmol), Pd(OAc)₂ (10 mol%), PPh₃ (20 mol%), K₂CO₃ (3 equiv.), and DMA (2 mL) at 90 °C under a N₂ atmosphere for 6 h. ^b2-(2-Bromophenyl)-1-(2-methylallyl)-1*H*-indole. ^c70 °C and 1 h.

To emphasize the versatility of the disilane reagent Me₃SiSiMe₂(O^tBu), we next attempted to synthesize π -conjugated dibenz[*b,d*]siloles by performing the reaction of 2-iodo-1,1'-biphenyl with Me₃SiSiMe₂(O^tBu) 2a. However, no anticipated product was observed under the above standard conditions. Subsequently, PPh₃ was found to suppress the reaction, since dibenz[*b,d*]siloles 7a could be afforded in 52% yield by the removal of PPh₃. Encouraged by these results, the optimal reaction conditions that could furnish 64% of 7a were established by the screening of various parameters (see the ESI† and Scheme 5). Afterward, a series of substituted 2-iodobiphenyls were examined. Delightfully, the electron-donating group (Me and OMe) on the benzene ring could be tolerated for the silacyclization reaction with disilane 2a, thus delivering the desired products 7b–k in moderate yields. Unfortunately, this protocol was not applicable to substrates 6l–o bearing an electron-withdrawing group. The possible reason is that the protonation of palladacycles formed by substrates 6l–o is easier than bis-silylation (see the ESI†).

To gain insight into the reaction mechanism, a range of control experiments were performed (Scheme 6). The reaction of acrylamides 1a with disiloxane 2h or 2i could afford product 3a in 27% and 50% yields, respectively, under the optimal reaction conditions (eqn (1)†). Moreover, hexamethyldisiloxane (TMSOTMS) was detected by gas chromatography in the model reaction of 1a with 2a (eqn (2), see the ESI†). These results indicated that the silicon source of product 3a came from the dimethylsilyl group generated by disilane 2a via the cleavage of Si–Si and Si–O bonds. Interestingly, two disilylated products 8a and 8a' as well as product 3a were isolated in 43%, 27%, and 16% yields when 1a and 2a were reacted under the standard conditions for 20 minutes (eqn (3)†). Therefore, we speculated that two disilylated products 8a and 8a' were the reaction intermediates (the structure of 8a was absolutely confirmed by X-ray crystallography). Finally, a spiropalladacycle¹⁴ that could

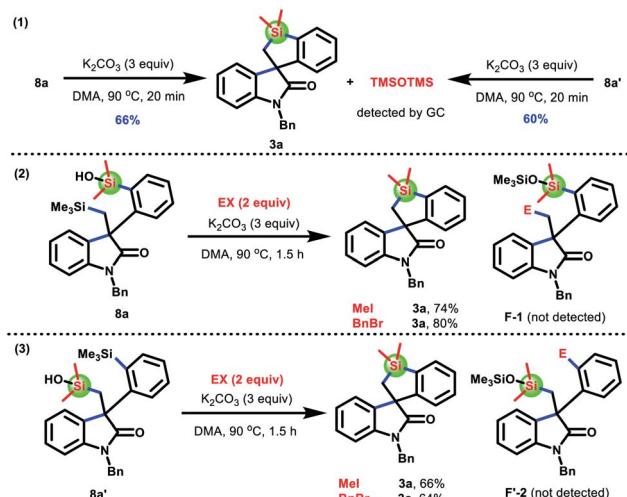




Scheme 6 Mechanistic experiments.

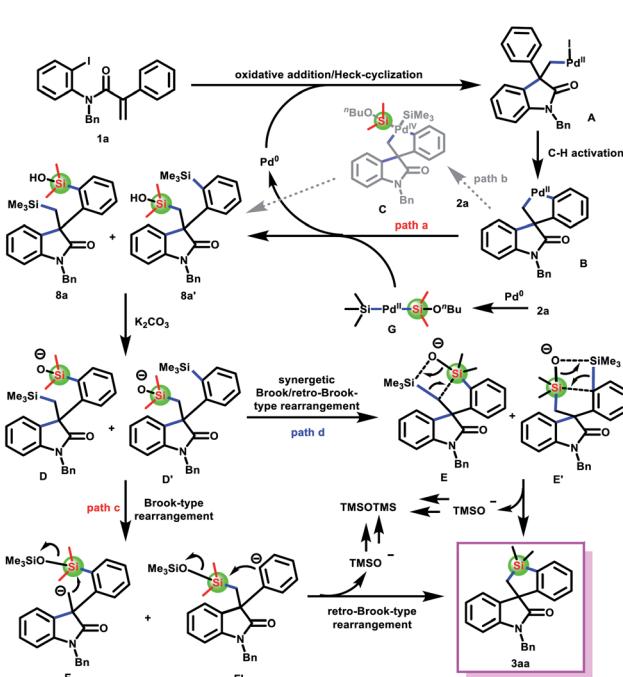
be prepared from acrylamides and stoichiometric $\text{Pd}(\text{PPh}_3)_4$ was employed for the reaction with disilane **2a** (eqn (4) \dagger). Unexpectedly, no product **3b** was observed in the absence of $\text{Pd}(\text{OAc})_2$ and PPh_3 . Surprisingly, extra addition of $\text{Pd}(\text{OAc})_2$ and PPh_3 could give product **3b** in 60% yield. These results suggested that the spiropalladacycle as a reaction intermediate underwent transmetalation with intermediate **G**, rather than direct oxidative addition with disilane **2a**, to furnish disilylated products **8a** and **8a'**, which were then converted into the desired product **3a**.

To verify our hypothesis and propose the possible formation process of **3a** from **8a** or **8a'**, we conducted several control experiments (Scheme 7). The silacyclization of disilylated products **8a** and **8a'**, respectively, was conducted in the absence

Scheme 7 Mechanistic experiments. The possible process for the transformation of **8a** and **8a'** into **3a**.

of $\text{Pd}(\text{OAc})_2$ and PPh_3 , and the product **3a** was obtained in 66% and 60% yields as expected (eqn (1) \dagger). Besides, TMSOTMS was also detected (see the ESI \dagger). These results demonstrated that the transformation of **8a** and **8a'** into **3a** involved the cleavage of the $\text{Me}_3\text{Si}-\text{C}$ bond, which did not require the assistance of palladium catalysts. On the basis of these results from eqn (1) \dagger and previous work reported by Smith and Takeda,¹⁵ we speculated that **8a** and **8a'** undergo a Brook- and retro-Brook-type rearrangement to afford **3a** (path c and path d). To capture carbanion species **F** and **F'**, two common electrophilic reagents, such as iodomethane and benzyl bromide, were added for the silacyclization of **8a** and **8a'** (eqn (2) and (3) \dagger). However, the corresponding products **F-1** and **F'-2** were not observed. Therefore, these results are more favorable to this pathway involving synergistic Brook/retro-Brook-type rearrangement (path d).

Based on the results of mechanistic experiments as well as reported work,^{12,13,15} a plausible mechanism for the synthesis of silacycles was proposed (Scheme 8). Initially, oxidative addition followed by intramolecular Heck-cyclization of acrylamides **1a** to $\text{Pd}(0)$ species forms intermediate **A**, which then undergoes a C-H activation to afford spiropalladacycle **B**. Next, spiropalladacycle **B** produces disilylated products **8a/8a'** and regenerates $\text{Pd}(0)$ by sequential transmetalation with intermediate **G** generated by disilane **2a**, reductive elimination and further hydrolysis (path a). **8a** and **8a'** then undergo a synergistic Brook/retro-Brook-type rearrangement to afford **3a** and a trimethylsiloxy anion, which could be converted into TMSOTMS (path d).¹⁶ Notably, another possible pathway that synthesizes disilylated products **8a/8a'** by direct oxidative addition of spiropalladacycle **B** with disilane **2a** is ruled out by the results of eqn (4) \dagger (path b).



Scheme 8 Possible reaction mechanism.

Conclusions

In conclusion, we have disclosed the first example of divergent synthesis of silacycles *via* a Brook- and retro-Brook-type rearrangement strategy by employing a readily accessible disilane reagent $\text{Me}_3\text{SiSiMe}_2(\text{O}^{\text{t}}\text{Bu})$. In this novel transformation, divergent silacycles, such as spirobenzosiloles, fused benzosiloles, and π -conjugated dibenzosiloles, can be produced in moderate to good yields by an unprecedented complex process composed of a bis-silylation of a palladacycle and a Brook- and retro-Brook-type rearrangement. Notably, mechanistic studies reveal that bis-silylation of the palladacycle is completed by a transmetalation process. Further applications of the disilane reagent $\text{Me}_3\text{SiSiMe}_2(\text{O}^{\text{t}}\text{Bu})$ and the rearrangement are still in progress in our laboratory.

Data availability

All experimental procedures and spectroscopic data can be found in the ESI.[†]

Author contributions

Y. X. designed and performed the experiments and analysed the data. W. X., X. C., X. L., H. L., M. Z., X. Y. and G. D. contributed to data analysis and scientific discussion. Y. Y. and Y. L. supervised the project, analyzed the results and wrote the manuscript.

Conflicts of interest

The authors declare no competing interests.

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