Pd-Catalyzed Intermolecular Si–O Formation via Si–C Activation

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Abstract: The development of efficient Si–O bond formation reaction with 100% atom-economy, excellent functional group tolerance and broad scope under mild conditions is highly desired due to the prevalence of silanol, silyl ether and their derivatives in synthetic chemistry and material science. Here, we have realized the Pd-catalyzed Si–O formation reaction via a Si–C activation approach with 100% atom-economy by employing silacyclobutanes (SCBs) and various hydroxy-containing substrates, including water, alcohols, phenols, and silanols. This protocol features a broad substrate scope, remarkable functional compatibility, and mild conditions, providing a series of silanols, silyl ethers in high efficiency. Notably, this protocol could also be used for selective protection of hydroxy functionalities, and for the access of a class of novel polymers containing Si–O main chain. Preliminary mechanistic studies unveiled that this reaction underwent a Pd-catalyzed concerted ring-opening mechanism.

Silicon-oxygen bond formation reactions have received tremendous attention due to the prevalence of silanol, silyl ether and their derivatives in organic chemistry, pharmaceuticals and material science.[1] Basically, the silicone industry is built upon the silicon-oxygen formation reactions, and the global silicone market size was valued at USD 18.59 billion in 2021. In addition, silyl groups (such as ^{i}Pr$_3$Si-, ^{t}BuMe$_2$Si-, ^{t}BuPh$_2$Si- etc.) are the valuable protecting groups of the hydroxyl functions in synthetic organic chemistry due to their good balance between the stability in the reaction procedure and easy removal afterwards.[2] Traditional construction of Si–O bond has been achieved by the reaction of hydroxy functionality with moisture-sensitive and corrosive chlorosilanes. This process normally requires the stoichiometric amount

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of a hydrochloric acid scavenger resulting in a large number of unwanted wastes, and is not compatible with the base-sensitive functional groups.[3] An alternative approach via the catalytic dehydrogenative coupling of alcohols with hydrosilanes has merged by virtue of the rapid development of the transition-metal catalysis, where H_2 is the only byproduct.[4] However, this process is still not 100% atom-economic and remains several limitations, including the less efficiency with the trisubstituted silanes which are normally introduced as the protecting groups, and the incompatibility of the functional groups, such as alkenyl and carbonyl groups due to the high reactivities of transition-metal catalyzed hydrosilylation event. Hence, to develop a general approach for the efficient construction Si–O bond with 100% atom-economy, excellent functional group tolerance and broad scope under mild conditions is highly desired in both industry and academic sectors.
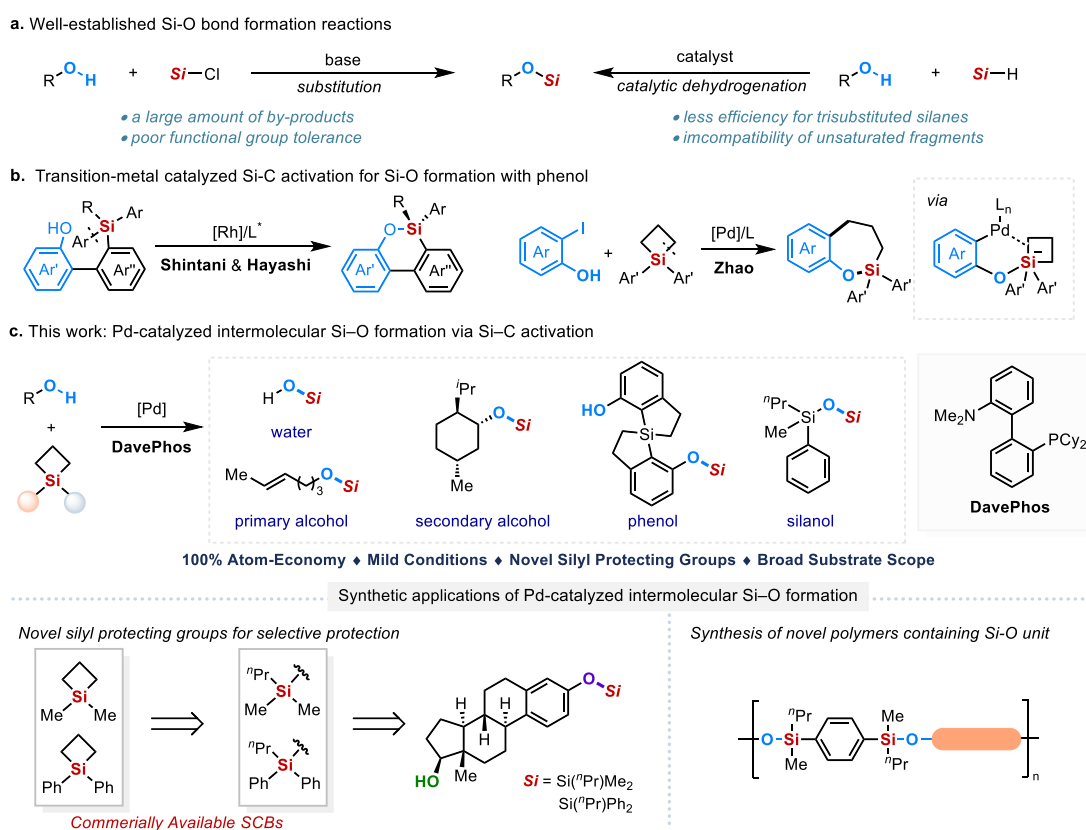
Scheme 1. Synopsis of Si–O bond formation.

Transition-metal catalyzed silicon-carbon activation has received increasing attention due to the efficient construction of various silicon-containing compounds with remarkable structure diversity.[5] For example, silacyclobutanes (SCBs) and their derivatives are known as versatile synthetic blocks to access

organosilane compounds via various ring-opening or ring expansion reactions.[6] However, the efficient formation of Si–O bond via the silicon-carbon activation approach is underdeveloped, and largely limited to silacycles formation.[7] For example, Hayashi and Shintani group reported a Rh-catalyzed synthesis of Si-stereogenic dibenzooxasilines via the Si–C(sp^2) activation.[7c] Recently, Zhao has developed Pd-catalyzed ring expansion process of SCBs to produce seven-membered cyclic silyl ether where the hydroxyl group in the substrate assists Si–C(sp^3) bond cleavage.[7f] The sole example for the preparation of acyclic silanols has been demonstrated by Gu group via a Rh-catalyzed aryl-Narasaka acylation of distorted five-membered silaflyoroenes, in which the chiral silanols were produced by the hydrolysis of the acylated cyclic intermediate.[7g] Here, we demonstrated the Pd-catalyzed intermolecular Si–O bond formation of various hydroxy-containing substrates via a Si–C bond activation approach for the first time[8] (Scheme 1c). A variety of hydroxy-containing compounds, including water, alcohols, phenols and silanols, could be silylated by SCBs with 100% atom-economy under mild conditions, thus providing a practical method for the preparation of silyl ethers and silanols. Given 1,1-dimethylsilacyclobutane and 1,1-diphenylsilacyclobutane are commercially available, this protocol provides a highly synthetic useful procedure with remarkable functional group tolerance for the installation of two novel silyl protection groups (^{n}PrMe$_2$Si-, and ^{n}PrPh$_2$Si-) for alcohols and phenols. Detailed studies on the reaction rates with different hydroxyl functionalities indicate our newly established protocol could be employed for selective protection of polyols bearing complex structures. Furthermore, the versatility of this reaction was demonstrated by the synthesis of a class of novel polymers containing Si–O units. The preliminary mechanistic studies revealed that a concerted ring-opening process might be involved in this reaction, and the kinetic studies indicate the concerted step is the rate-determining step for this reaction.

Results and Discussion

As our continuous interests on developing efficient approaches for the construction of functional organosilanes[9], we wondered the silanols and silyl ethers could be efficiently prepared with 100% atom economy via the coupling of SCBs with hydroxy-containing substrates. Hence, we first explored the feasibility of the Si–O formation reaction by conducting the reaction with commercially available 1,1-diphenylsiletane (**2**) and water as the model substrate, due to the importance of silanols in synthetic

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chemistry[10]. After systematic evaluation of the catalyst system, we found a Pd(OAc)$_2$/DavePhos combination was efficient for this Si–O formation reaction, giving the targeted silanol **3a** in 80% ^{1}H NMR yield (entry 1, Table 1), while other transition metal catalysts were inefficient under current conditions (For details, see the Supporting Information). The efficiency of the reaction was decreased when more bulky mono-phosphine ligands (SPhos or [t]BuDavePhos) were used (entries 9-10). Bidentate ligands, such as diphosphine ligands and 1,10-phenanthroline ligand, were also investigated, affording silanol in low to moderate yields (entries 11-14). The screening of the solvents indicated both nonpolar and polar solvents provided the target product **3a** in acceptable yields except for dichloromethane (entries 2-4). The yield was further improved to 94% in a higher concentration with a shorter reaction time (entry 5). Notably, the control experiments indicate both palladium catalyst and DavePhos are essential to the reaction. Without the assistance of monophosphine ligand, only 6% ^{1}H NMR yield of desired product was obtained (entries 6-7).

Table 2. Evaluation of reaction parameters.[a,b]

entry	Deviation from conditions	Yield (%)	entry	Ligand	Yield (%)
1	none	80	8	PCy$_3$	36
2	Hexane instead of Toluene	44	9	SPhos	18
3	DMA instead of Toluene	71	10	[t]BuDavePhos	42
4	DCM instead of Toluene	7	11[c]	dppe	61
5	Toluene (0.2 M), 6 h	94	12[c]	dppf	20
6	No Pd(OAc)$_2$	<1	13[c]	XantPhos	6
7	No DavePhos	6	14[c]	Phenanthroline	37

[a] Reaction conditions: **1a** (1.0 mmol, 10 equiv), **2** (0.1 mmol), Pd(OAc)$_2$ (1.1 mg, 5.0 mol%), DavePhos (7.9 mg, 10 mol%), Toluene (1.0 mL), 60 °C, 12 h. [b] Yield was determined by ^{1}H NMR using CH$_2$Br$_2$ as the internal standard. [c] Ligand (5.0 mol%) was used.

Under the optimal reaction conditions, the generality of this Pd-catalyzed Si–O formation reaction via Si–C activation was evaluated regarding the hydroxy-containing substrates (Table 2). In general, this

protocol was suitable for a wide range of the substrates containing hydroxy functionality, affording the desired silanols and silyl ethers in good to excellent yields. The reaction of 1,1-diphenylsiletane (**2**) with water gave the corresponding silanol **3a** in 85% yield. A variety of alcohols, including primary and secondary alcohols (**1b-k** and **1l-p**), underwent this Si–O formation process to afford the corresponding silyl ethers in 70-97% yields. Although the reaction with tertiary alcohols is not efficient, this protocol could tolerate tertiary silanols (**1q-r**), probably because the silanols have a loosen steric environment in comparison to tertiary alcohols due to the longer Si–C bond (Si–C vs C–C, ca. 1.87 Å vs ca. 1.53 Å). It is noteworthy that this protocol is also suitable for the alcohols bearing basic heterocycles and functionalities, including pyridine (**1j**) and tertiary amine (**1k**), which normally resulted in the corresponding salts under typical silyletherification reaction with silyl chlorides. Both various electron-rich and electron-deficient phenols were evaluated, and the electronic properties of phenol derivatives didn't significantly affect the reactivity of this reaction. The desired silyl ethers (**3t-3aa**) were yielded in 82-96% yields. With regarding the bulky ortho-disubstituted phenols (**1ab** and **1ac**), a higher temperature was required for maintaining the high reactivity. It should be pointed out that the reactions of the bisphenols (**1ae-1ah**), including BINOL (**1ag**) and SPSiOL (spirosilabiindane diol, **1ah**)[9a], afforded the monosilylated products in 82-85% yields using 1.0 equivalent of **2**, indicating the high potency for selective protection of symmetric diphenols. Under the established mild conditions, this reaction also shows good functional group compatibility, where the substrates containing methoxy (**1b**, **1ac**), chloro- (**1d**, **1u**), alkenyl (**1e**), benzyl (**1g**), amino (**1v**, **1y**), naphthalene (**1z**) or pyren (**1aa**) were all tolerated. The generality of the protocol was further demonstrated by conducting this reaction with complex natural products. The silylation of *L*-menthol (**1ai**), (-)-Corey lactone benzoate (**1aj**), cholesterol (**1ak**), *L*-tyrosinate derivative (**1al**) and estrone (**1am**) proceeded smoothly to provide the corresponding products in high efficiency.

Next, we turned our attention to check the substrate scope of SCBs with water as the model substrate, which could open a new avenue for efficient preparation of silanols. As showed in Table 3, various 1,1-diarylsiletanes with either electron-rich (**4a-b**, **4f**) or electron-deficient (**4c-e**) aryl group all successfully participated in this Pd-catalyzed Si–O formation reaction in up to 95% yields. The reaction also proceeded smoothly with 1-methyl-1-arylsiletanes (**4h-l**), affording the corresponding silanols containing diverse

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functional groups such as dibenzo[*b*,*d*]furan (**5k**) and indole (**5l**). 1,1-Dibenzylsiletane (**5m**) was also also compatible with this Pd-catalyzed process. It is noteworthy that the C–Si activation happened solely on the

Table 2. Pd-Catalyzed coupling 1,1-diphenylsiletane of with water, alcohols, phenols, and silanols.[a,b]
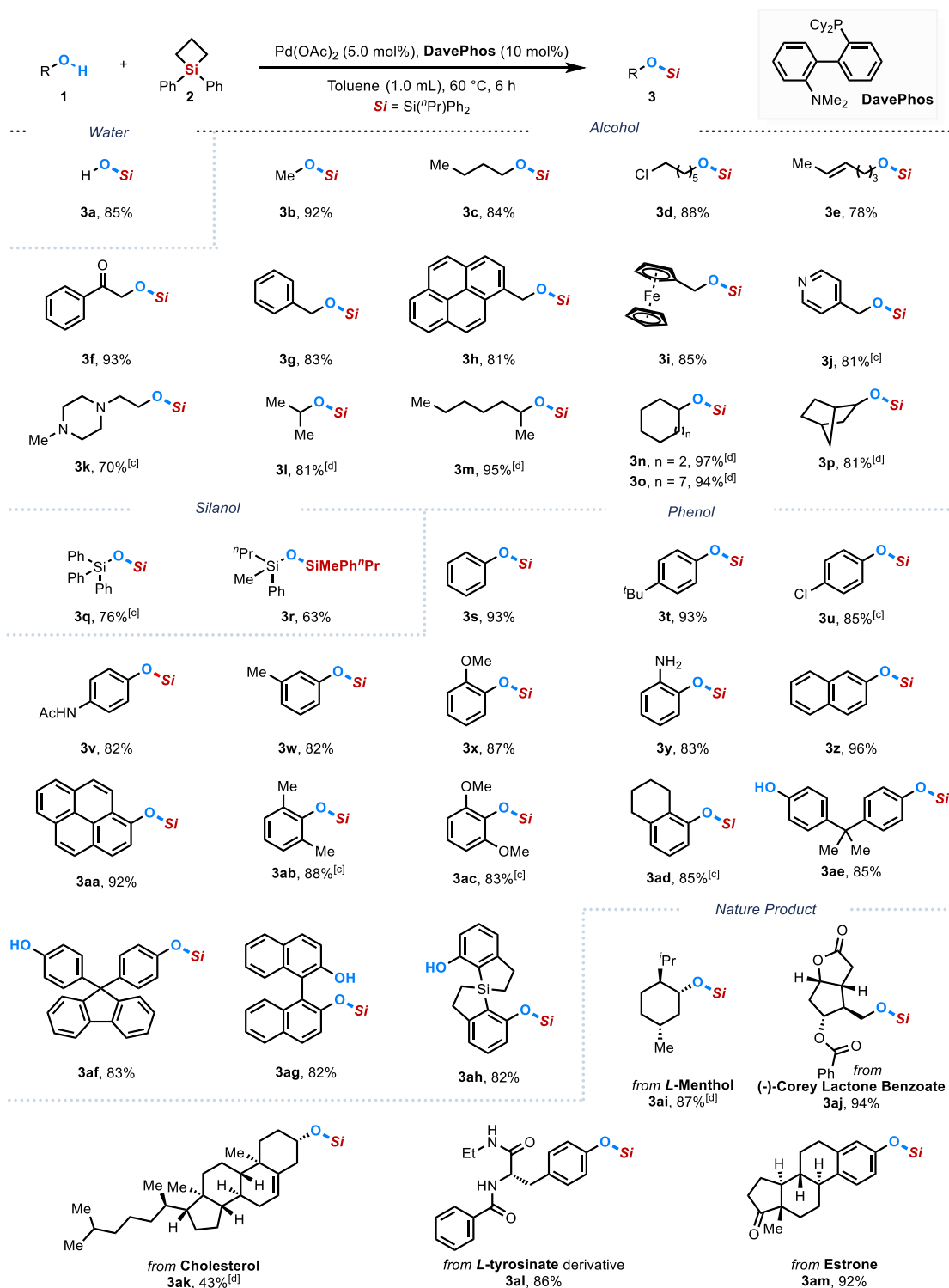
[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.2 mmol, 1.0 equiv), Pd(OAc)$_2$ (2.2 mg, 5.0 mol%), DavePhos (7.9 mg, 10 mol%), Toluene (1.0 mL), 60 °C, 6 h. [b] Isolated yield. [c] 100 °C, 12 h. [d] Pd(MeCN)$_2$Cl$_2$ (2.6 mg, 5.0 mol%), 100 °C, 12 h.

C(sp^3)–Si bond when spiro silacyclobutanes containing both C(sp^3)–Si and C(sp^2)–Si bonds (**4n-o**), giving the cyclic silanols in moderate to good yields. Polyaromatic pyrene and tetraphenylethylene (TPE) fragments are key scaffolds widely presented in organic optoelectronic materials. The introduction of the Si–O unit in such molecules might alter the photophysical properties. SCBs attached with pyrene (**4p**) or the tetraphenylethylene (TPE) (**4q**) reacted with water efficiently, providing a new approach for the construction of silicon-oxygen containing optoelectronic materials.

Table 3. Scope of SCBs.[a,b]
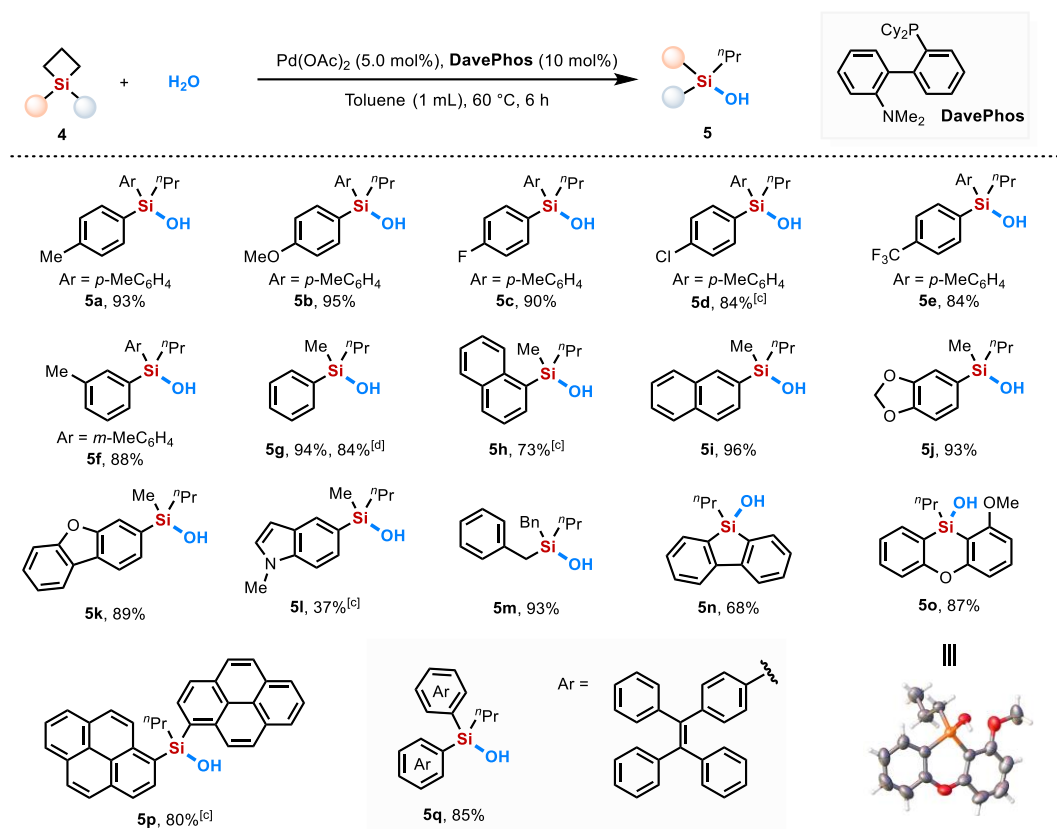
[a] Reaction conditions: **4** (0.2 mmol, 1.0 equiv), water (0.2 mmol, 1.0 equiv), Pd(OAc)2 (2.2 mg, 5.0 mol%), DavePhos (7.9 mg, 10 mol%), Toluene (1.0 mL), 60 °C, 6 h. [b] Isolated yield. [c] 100 °C, 12 h. [d] The reaction was conducted on 10 mmol scale.
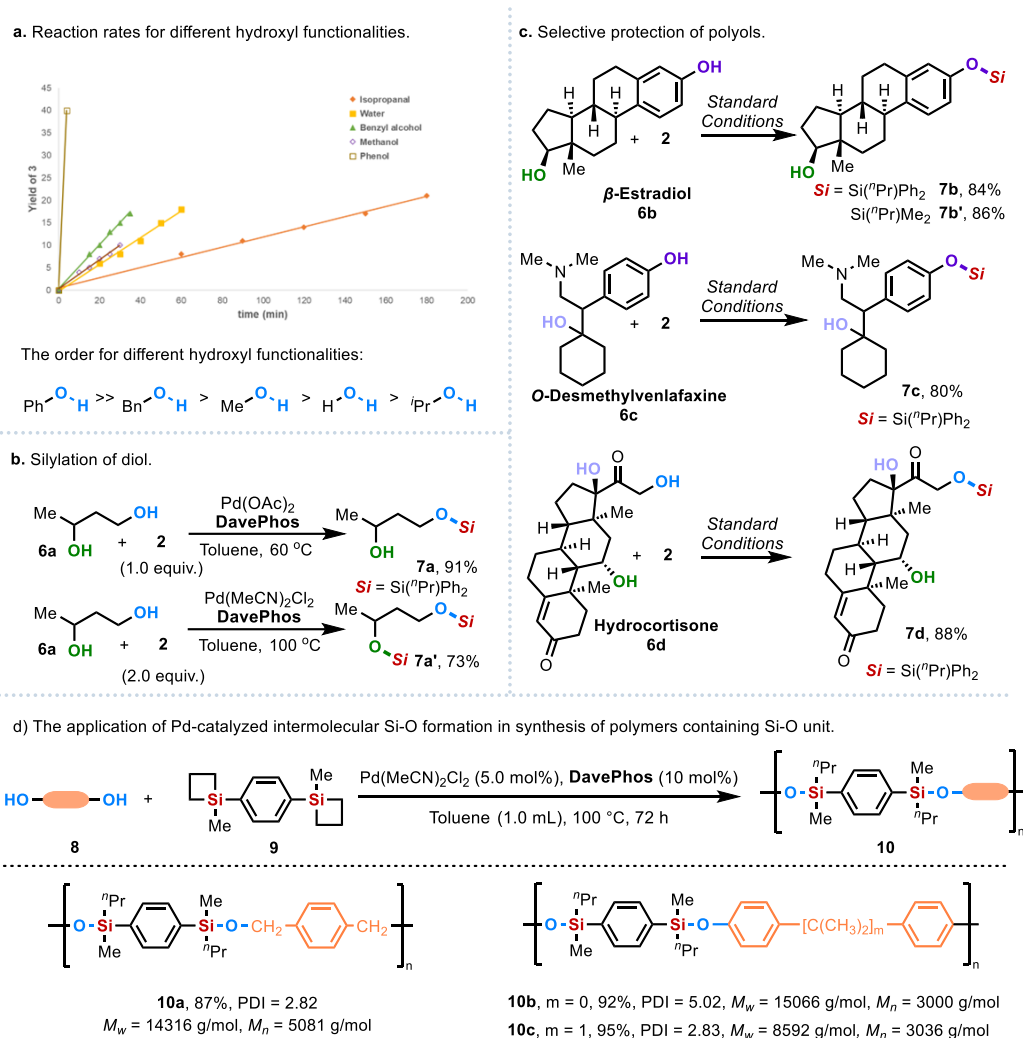
Figure 1. Applications of Pd-catalyzed intermolecular Si–O formation.

Given the importance of silyl protection group in organic synthesis, the development of efficient Si–O formation reaction with remarkable functional group tolerance under mild conditions might also lead to the development novel silyl protection groups.[2] With commercially available 1,1-diphenylsilacyclobutane as the silyl source, we first investigated the reaction rates with regarding various hydroxy functionalities. The exploration of the order of the reaction rates with different alcohols and phenols will provide a guiding principle for selective protection using our newly developed Si–O formation reaction. As listed in Figure 1a, the sequence of the reaction rates for difference hydroxy functionalities with 1,1-diphenylsilacyclobutane **2** is PhOH >> BnOH > MeOH > H_2O > ^{i}PrOH. Based on this principle, the selective protection of polyols containing different hydroxy functionalities has been achieved (Figure 1b and 1c). With β-estradiol (**6b**) containing both phenolic hydroxy and alcoholic hydroxy groups as substrate,

the silylations with either commercially available SCBs (1,1-diphenylsiletane or 1,1-dimethylsiletane) were occurred selectively on phenolic hydroxy, delivering the corresponding products (**7b** and **7b'**) in high selectivity. The similar selective protection of O-desmethylvenlafaxine (**6c**) has also been realized using our protocol. For the polyols including different alkyl hydroxy groups, the less steric hindered hydroxy group could be selectively protected (**6d**). Moreover, the silylation on the primary alcohol of **7a** was realized in high yield with the secondary alcohol untouched under the standard conditions using 1.0 equiv. of 1,1-diphenylsiletane **2**, and the full protection could also be achieved by slightly modifying the reaction conditions using $Pd(MeCN)_2Cl_2$ as catalyst at higher temperature.

To further demonstrate the synthetic utility of this newly developed methodology, we further performed the polymerization reaction by using diols and bis-SCBs, which could provide a novel polymer containing the Si–O units. The polymerization reaction was conducted between **9** containing two SCB fragments and the diol (**8**), and the high conversions were reached under our reaction conditions at a higher temperature (100 °C). The high M_W values (14316 g/mol and 15066 g/mol) were reached when 1,4-benzenedimethanol (**8a**) or (1,1'-biphenyl)-4,4'-diol (**8b**) was used as the hydroxyl source. The Si–O–C linkages in the polymers are susceptive in acidic condition which has potential utilization for triggered degradation in biomedicine.[11]

To better understand the reaction mechanism, the reaction was first performed with CD_3OD under the standard reaction conditions (Figure 2a). The deuterium on the product **3b**-*d* only appeared at the terminal position of ^{n}Pr group, revealing no β-H elimination occurred during the ring-opening process. The parallel kinetic isotope effect (KIE) experiments indicated that the O–H cleavage might be involved in the rate-determining step ($k_H/k_D = 2.61/1.0$) (Figure 2b). Furthermore, the kinetic studies were conducted, showing that this reaction is first order to alcohol, SCB and palladium catalyst, which indicated that both substrates and catalyst were all involved in the rate-determining step (Figure 2c). The reaction process was also monitored by ^{1}H NMR. The fact that no detection of Si–Pd–C species when the reaction was heated at 60 °C without alcohol and Pd–H species after addition of alcohol might rule out that the reaction was initiated by oxidative addition of Pd(0) to SCB[6n,6p] or alcohol. According to the aforementioned mechanistic

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experiments, a proposed reaction pathway was depicted in Figure 2e. The Pd(0) species was formed by the in-situ reduction of Pd(OAc)$_2$ in the presence of phosphine ligand, which could coordinate with both alcohol and SCB. Next, the concerted ring-opening process was proceeded to deliver the intermediate **II**, which underwent reductive elimination to give the final product **3** and release Pd(0) species. Given the observation of secondary kinetic effect in alcoholic O–H cleavage, the concerted hydroxy group assisted ring-opening process was the rate-determining step in this reaction.
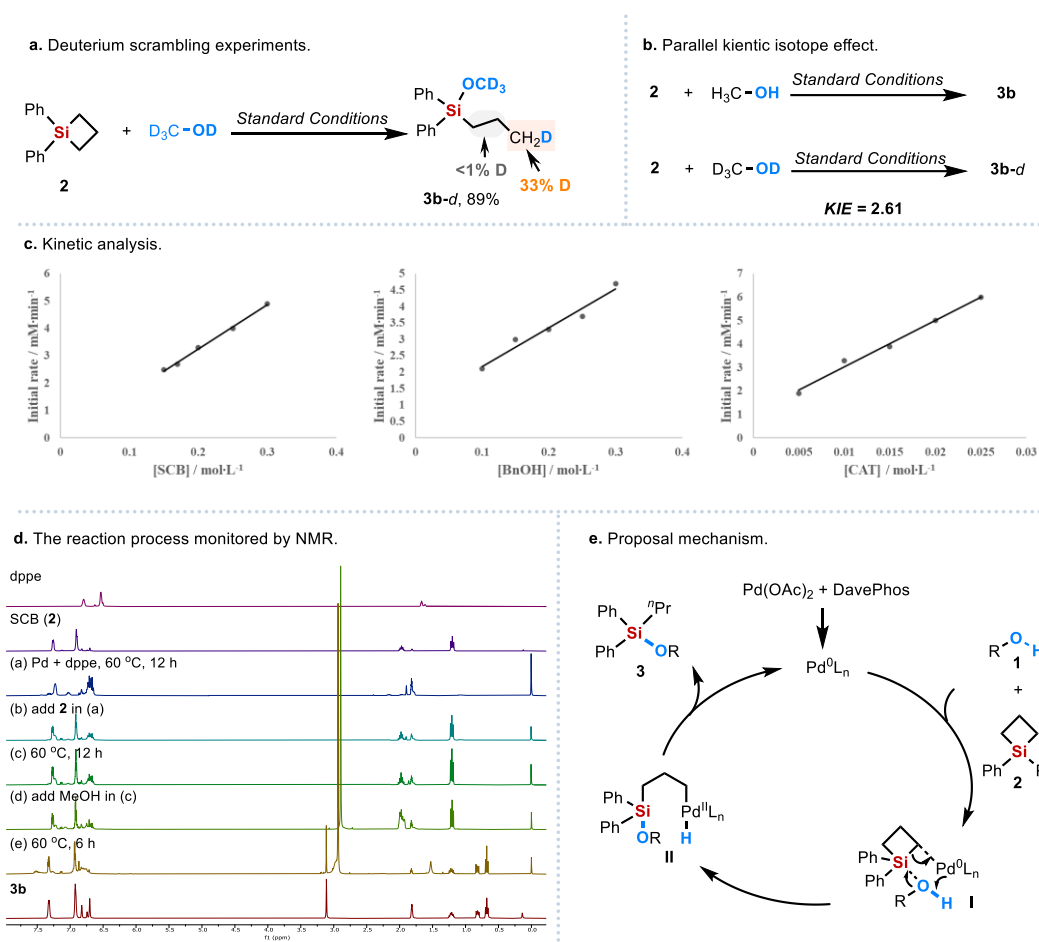

Figure 2. Mechanistic Studies.

Conclusion

In summary, we have demonstrated a Pd-catalyzed intermolecular Si–O bond formation reaction via a C–Si activation approach using silacyclobutanes as silicon source. The present catalytic system is compatible with various types of hydroxy functionalities, including water, alcohols, silanols and phenols. This reaction features 100% atom-economy, a broad substrate scope and mild conditions. Moreover,

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selective protection of complex compounds containing multiple types of hydroxy functionalities has been realized with commercially available SCBs, providing a synthetic useful protecting strategy with novel silyl protecting groups in organic synthetic chemistry. This protocol has also been valued in the synthesis of the novel polymers bearing Si–O units, indicating the potential utilization in material science.

Supplementary Information is available in the online version of the paper.

Acknowledgements

Keywords: Si–O formation • Si–C activation • palladium • silacyclobutane • silanol • silyl ether

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