Cluster

Pincer Ruthenium Catalyzed Intramolecular Silylation of C(sp²)–H Bonds

Α

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 B^2 , B^3 = alkyl, Ph R^4 , R^5 = Me, *i*Pr, *t*Bu

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Abstract Reported herein is a highly efficient intramolecular silylation of aromatic C-H bonds catalyzed by a pincer ruthenium complex, giving benzoxasiloles under relatively mild reaction conditions with broad substrate scope and low catalyst loadings. The silvlation product can be further converted into a biaryl product by Pd-catalyzed Hiyama-Denmark cross-coupling reactions.

Key words C-H bond functionalization, silylation, ruthenium, pincer ligand, C-C coupling

Transition-metal-catalyzed C-H bond functionalization is an efficient, straightforward, and powerful strategy for the synthesis of functionalized organic molecules.¹ Among various C-H functionalizations, silvlation of inert C-H bonds is particularly attractive because hydrosilanes are usually inexpensive, nontoxic, and stable for storage and handling.^{2,3} In addition, the resulting organosilicon compounds are valuable synthetic intermediates,⁴ which can undergo a variety of transformations to obtain useful derivatives and which have attracted wide interest in material sciences.⁵

Although the intermolecular silvlation of $C(sp^2)$ –H bonds has a long history beginning with the seminal work by Curtis in 1982,^{6,7} the intramolecular version has been reported much more recently. In 2005, Hartwig and co-workers⁸ reported the first Pt-catalyzed intramolecular silvlation of (2-phenylethyl)dimethylsilane and (3-phenylpropyl)diethylsilane to generate both five- and six-membered organosilicon products under harsh conditions (Scheme 1, a). Later, the same group found that a mild and efficient intramolecular silvlation of C(sp²)-H bonds could be accomplished by in situ introduction of a (hydrido)silyl group starting from ketones, alcohols, and amines.⁹ By using a similar strategy of generating the (hydrido)silyl group in situ, diverse structures of silacycles have been constructed by the work of Gevorgyan¹⁰ and Jeon.¹¹ The enantioselective intramolecular silvlations of $C(sp^2)$ -H bonds directed by a (hydrido)silyl group could also be achieved.¹² Moreover, Lin and co-workers¹³ developed highly active and recyclable single-site solid catalysts for intramolecular silvlation of C(sp²)-H bonds. Very recently, Xu and co-workers¹⁴ developed an Ir-catalyzed, silanol-directed intramolecular silylation of C(sp²)-H bonds. In addition, the group of Takai,¹⁵ He,¹⁶ Shibata,¹⁷ and Oestreich¹⁸ have independently applied intramolecular silvlations of C(sp²)-H bonds for the synthesis of silicon-containing π -conjugated molecules, which show promising potential in material sciences (Scheme 1, b).



Scheme 1 Transition-metal-catalyzed intramolecular silylation of C(sp²)-H bonds

Compared with the extensive studies on Pt, Ir, and Rh catalytic systems, the use of relatively inexpensive ruthenium catalysts for the intramolecular silylation of C(sp²)-H

bonds is much less developed.¹⁸ Recently, we reported the synthesis and characterization of a series of new hydrido ruthenium complexes bearing isopropyl-substituted pincer ligands,¹⁹ which exhibited excellent activity and selectivity for the intramolecular silylation of primary $C(sp^3)$ –H bonds and the undirected intermolecular silylation of heteroarenes.²⁰ These results encouraged us to further extend our work on pincer Ru catalyzed silylation to the intramolecular $C(sp^2)$ –H bond. We report herein that a bis(phosphine)-based pincer ruthenium complex is highly active for intramolecular silylations of primary (1°), secondary (2°), and tertiary (3°) (hydrido)silyl ethers to synthesize benzoxasilole products (Scheme 1, c).

We commenced our studies by investigating the reaction conditions for silvlation of dimethyll(2-phenylpropan-2-yl)oxy]silane (**2a**, Table 1). With *tert*-butylethylene (TBE, 1 equiv) as the hydrogen acceptor, the reaction of **2a** in the presence of 1 mol% of **1a** at 120 °C generated the desired product **3a** in 73% yield (Table 1, entry 1), along with the side products generated by hydrosilylation of TBE (4%) and dehydrogenative silvlation of TBE (17%). By employing an internal olefin, cis-cyclooctene (COE), as the hydrogen acceptor, 3a was formed in 89% yield without any detectable product of hydrosilylation or dehydrogenative silylation of COE (Table 1, entry 2). The silvlation of 2a catalyzed by the more electron-rich complex **1b** (1 mol%) with COE (1 equiv) gave **3a** in a quantitative yield after 12 h at 120 °C (Table 1, entry 3). Lowering the temperature to 80 °C generated 3a in 86% yield (Table 1, entry 4), and prolonging the reaction time to 24 h afforded 3a in 99% yield (Table 1, entry 5). Reducing the catalyst loading to 0.5 mol% was detrimental to the conversion (Table 1, entry 6). The intramolecular C-H bond silvlation did not proceed in the absence of the Ru catalyst (Table 1, entry 7). In another control experiment, the desired product **3a** was produced in 8% yield without the hydrogen acceptor (Table 1, entry 8). The reactions with several common ruthenium complexes were also examined, however, none of them work (Table 1, entries 9–13).

Having established the optimal reaction conditions, we next explored the substrate scope of the silylation reaction (Scheme 2).²¹ It was found that tertiary, secondary, and primary (hydrido)silyl ethers **2** bearing electron-donating or electron-withdrawing groups in *para*, *meta*, and *ortho* position were well tolerated to give the corresponding benzoxasilole products in high isolated yields. It should be noted that the cyclization of tertiary (hydrido)silyl ethers via $C(sp^2)$ –H functionalization has been rarely reported.^{9a} Various types of functionalities, including ether (**3d, j, j', l**), amine (**3e**), fluoro (**3f, o, x**), trifluoromethyl (**3g**), and heterocyclic (**3m**) groups, were compatible with the reaction conditions. The substrate **2i** possessing a methyl in the *meta* position of the phenyl group underwent silylation at the less sterically



Entry	[Ru] (mol%)	H Acceptor	Temp (°C)) Time (h)	Yield (%) ^b
1	1a (1)	TBE	120	12	73°
2	1a (1)	COE	120	12	89
3	1b (1)	COE	120	12	99
4	1b (1)	COE	80	12	86
5	1b (1)	COE	80	24	99
6	1b (0.5)	COE	80	24	43
7	none	COE	80	24	0
8	1b (0.5)	none	80	24	8
9	Ru ₃ (CO) ₁₂ (1)	COE	80	24	0
10	$[Cp^*RuCl_2]_2(1)$	COE	80	24	0
11	(cod)Ru(2-methylallyl) ₂ (1)	COE	80	24	0
12	Ru(acac) ₃ (1)	COE	80	24	0
13	[RuCl ₂ (p-cymene)] ₂ (1)	COE	80	24	0

^a Reaction conditions: **2a** (0.5 mmol), [Ru] (0.5-2.5 mol%), TBE (1 equiv) or COE (1 equiv).

^b Determined by ¹H NMR analysis of the crude reaction mixture using mesitylene as an internal standard.

^c Hydrosilylation of TBE (4%) and dehydrogenative silylation of TBE (17%) were also observed by GC–MS and ¹H NMR.

hindered aryl C-H bond exclusively. However, cyclization of the 3-methoxy derivative 2i gave two isomers (3i and 3i') in a 1.18:1 ratio, resulting from the silvlation of $C(sp^2)$ -H bonds ortho and para to the methoxy group, respectively. Surprisingly, the reaction of (hydrido)silyl ether **2k** with an ortho-methyl substituent produced benzoxasiline **3k'** as the major product, which was generated from the silvlation of C(sp³)–H bond of the methyl group. Besides **3k'**, a 26% yield of benzoxasilole 3k was also observed by GC-MS and ¹H NMR analysis. In the case of a (hydrido)silyl ether **2l** with a methoxy group at the *ortho* position, the corresponding benzoxasilole 31 was obtained in high yield. This reaction was also found to be applicable to heteroaromatic (hydrido)silyl ether substrate 3m. The benzylic position of the tertiary (hydrido)silyl ether was not limited to dimethyl substituents, and substitution of one methyl by *n*-propyl (**3n**,**o**), isopropyl (**3p**), phenyl (**3q**), benzyl (**3r**), diethyl (**3s**), or diphenyl (3u) was tolerated. The (hydrido)silyl ether 2t underwent C-H silylation smoothly to generate spirocyclic benzoxasilole **3t** in 94% yield.

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Scheme 2 Substrate scope of the intramolecular arene *ortho*-silylation of (hydrido)silyl ether. *Reagents and conditions*: 2 (0.5 mmol), 1b (1 mol%), and COE (1 equiv) at 80 °C for 24 h. Yields shown are of isolated products. ^a 1b (2.5 mol%). ^b 100 °C. ^c A 26% yield of benzoxasilole 3k was also observed by GC–MS and ¹H NMR analysis.^d 48 h.^e 120 °C for 12 h. ^f TBE (1 equiv).^g 1b (5 mol%).

The steric circumstance around the silicon atom and ether group has a pronounced influence on the reactivity of the (hydrido)silyl ethers. The tertiary (hydrido)silyl ethers containing dimethyl groups at the Si atom underwent annulation efficiently, while the cyclization of secondary and primary (hydrido)silyl ethers bearing dimethyl groups at the Si atom gave a complex mixture. For example, secondary (hydrido)silyl ether **2v** reacted rather sluggish under standard conditions, producing 1-phenylethanol and some other unidentified side products. When the methyl groups on the silicon atom were replaced by two isopropyl substituents, excellent reactivities and high yields were obtained with relatively higher catalyst loadings (2.5–5 mol%) at 120 °C for both secondary (**3w–z**) and primary (hydrido)silyl ethers (**3aa**). The silylation reaction also proceeded smoothly for a primary (hydrido)silyl ether with one methyl and one *tert*-butyl group on the Si atom (**3ab**). Thus, high activity could be achieved for sterically hindered tertiary (hydrido)silyl ethers with small substituents on the Si atom, or less sterically crowded secondary and primary (hydrido)silyl ethers with large substituents on the Si atom.²²

The presence of a Si–O bond in benzoxasilole products render them suitable for further transformations, such as Hiyama–Denmark cross-coupling (Scheme 3).^{9a,23,24} After screening a variety of reaction conditions, we found that by using Pd(OAc)₂/PPh₃ (5 mol%) as the catalyst and CH₃ONa (5 equiv) as the base, the coupling between benzoxasilole **3a** with iodobenzene in *p*-xylene occurred smoothly at 80 °C to generate biaryl product **4a** in 78% yield after a basic workup. The reaction conditions were also effective for the coupling of **3a** with bromobenzene, giving 73% yield of **4a**.



Scheme 3 Pd-catalyzed Hiyama–Denmark coupling 3a with aryl halides

A plausible reaction mechanism is proposed based on our previous work on Ru-catalyzed intramolecular silylation of primary $C(sp^3)$ –H bonds (Scheme 4).^{20a} Initially, the active catalytic species **A** reacts with the hydrogen acceptor, COE, to produce the cyclooctyl-Ru(II) species **B**, which undergoes σ -bond metathesis with Si–H bond in the substrate via intermediate **C** affording intermediate **D**. Subsequently, intramolecular σ -bond metathesis between Ru–Si bond and C–H bond takes place to produce the desired product **3a** and regenerate the active catalytic species **A**. The steric hindrance on either the C or Si atom in the substrates may facilitate the interaction between the Ru–Si bond and the intramolecular C–H bond, probably due to the Thorpe–Ingold effect.

In summary, we have developed a highly efficient ruthenium catalyst for the intramolecular silylation of $C(sp^2)$ – H bonds of 1°, 2°, and 3° (hydrido)silyl ethers. Featuring broad substrate scope, relatively mild reaction conditions, and low catalyst loadings, this transformation provides a highly attractive route for the synthesis of benzoxasiloles. Moreover, the synthetic utility of the benzoxasilole product was demonstrated by Pd-catalyzed Hiyama–Denmark cross-coupling with aryl halides.

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Supporting Information

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- (21) **General Procedure for Silylation of (Hydrido)silyl Ethers 2** A 5 mL dried Schlenk tube was charged with **1b**, (hydrido)silyl ether **2** (0.5 mmol), and hydrogen acceptor (TBE or COE, 1 equiv) under Ar atmosphere. Then the flask was sealed tightly with a Teflon plug and stirred at 80–120 °C for complete conver-

sion. After that, the reaction mixture was cooled to room temperature. Mesitylene (0.5 equiv, 0.25 mmol) was added as an internal standard, and the yield was determined by ¹H NMR spectroscopy. The crude mixture was purified by flash column chromatography (silica gel, PE/EtOAc = 100:1 as eluent) to obtain the benzoxasilole product **3**. Data for **3a** are given here as an example.

The general procedure was followed with Ru complex **1b** (2.7 mg, 5.0 µmol), (hydrido)silyl ether **2a** (97.2 mg, 0.5 mmol), and COE (65.0 µL, 0.5 mmol) at 80 °C for 24 h. The benzoxasilole product **3a** was afforded as a colorless liquid (95.0 mg, 99% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.56 (d, *J* = 8.0 Hz, 1 H), 7.43 (t, *J* = 8.0 Hz, 1 H), 7.32 (t, *J* = 8.0 Hz, 1 H), 7.25 (d, *J* = 8.0 Hz, 1 H), 1.58 (s, 6 H), 0.42 (s, 6 H). ¹³C NMR (101 MHz, CDCl₃): δ = 158.0, 134.5, 130.8, 129.8, 126.9, 122.2, 83.5, 32.2, 1.4. These spectroscopic data correspond to reported data.^{5d}

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- (24) General Procedure for Hiyama-Denmark Coupling 3a with PhI

In an Ar-filled glovebox, a 5 mL dried Schlenk tube was charged with Pd(OAc)₂ (3.4 mg, 15.0 µmol, 5 mol%), PPh₃ (8.6 mg, 33.0 µmol, 11.0 mol%), CH₃ONa (81.0 mg, 1.5 mmol), and *p*-xylene (1 mL). Then, benzoxasilole 3a (57.8 mg, 0.3 mmol) and PhI (0.60 mmol) were added. The tube was sealed tightly with a Teflon plug under Ar atmosphere. The reaction mixture was stirred at room temperature for 1 h, and subsequently heated at 80 °C for 12 h. Then the reaction mixture was cooled to room temperature, and MeOH (1.5 mL) and 10% NaOH (2 mL) were added under vigorous stirring at 50 °C for 48 h. The resulting solution was extracted with EtOAc and washed with brine (15 mL), dried over anhydrous Na₂SO₄. After filtration and evaporation of the solvent, the crude mixture was purified by flash column chromatography (silica gel, EtOAc/PE = 1:50) to obtain the desired product 4a as a white solid (49.5 mg, 78%, m.p. 68-70 °C). ¹H NMR (400 MHz, CDCl₃): δ = 7.67 (d, J = 8.0 Hz, 1 H), 7.38 (m, 6 H), 7.26 (t, J = 8.0 Hz, 1 H), 7.10 (d, J = 8.0 Hz, 1 H), 1.89 (s, 1 H), 1.49 (s, 6 H). ¹³C NMR (101 MHz, CDCl₃): δ = 146.2, 143.9, 140.0, 132.2, 129.6, 127.9, 127.5, 127.2, 126.2, 125.9, 74.2, 32.7. Spectral data are in agreement with published data.²⁵

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