Communication

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Synthesis of Benzosiloles by Intramolecular *anti*-Hydroarylation via *ortho*-C–H Activation of Aryloxyethynyl silanes

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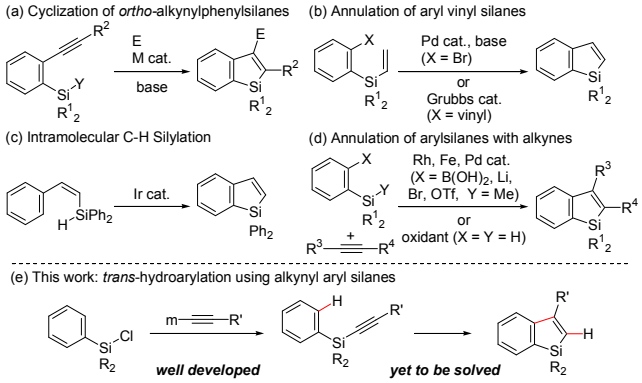
Supporting Information Placeholder

ABSTRACT: Straightforward synthesis of benzosiloles was achieved by the invention of Pd/acid-catalyzed intramolecular *anti*-hydroarylation of aryloxyethynyl(aryl)silanes via *ortho*-C–H bond activation. The aryloxy group bound to the ethynyl carbon is the key factor for this transformation.

Siloles and silole-based condensed aromatics have attracted increasing attention due to their potential applications, e.g., building blocks for organic synthesis and π-conjugated functional materials as high electron-affinity, hole-blocking and solid-state luminescence.[1,2] For the synthesis of a benzosilole, metal-catalyzed annulation protocols are available. A typical example is the annulation of *o*-alkynyl(aryl)silanes with additives such as electrophiles (Scheme 1a).[1g,2c,2d,3] Intramolecular Mizoroki-Heck reaction, olefin metathesis, and *ortho*-silylation of (Z)-phenylvinylsilane also lead to benzosilole formation (Scheme 1b, c).[4,5,6] Recently, annulations of alkynes with arylsilanes via Si–Me or Si–H bond cleavage have been reported (Scheme 1d).[7] However, as compared to dibenzosiloles, synthetic methods to access benzosiloles are less developed. In light of the fact that alkynyl(aryl)silanes can be easily prepared by the reaction of chlorosilanes with terminal alkynes and used widely in organic synthesis, e.g., to protect terminal alkynes, straightforward *trans*-insertion using alkynyl(aryl)silanes via *ortho*-C–H bond activation is an ideal synthetic method for benzosiloles (Scheme 1e). However, this sort of transformation has remained unexplored, in contrast to indene synthesis which starts with propargylarenes.[8] Thus, development of an annulation strategy using alkynyl(aryl)silanes is critical for achieving synthetic diversity toward the enhancement of the chemistry of siloles. Herein we report a straightforward synthesis of benzosiloles by palladium/acid-catalyzed intramolecular *anti*-hydroarylation of alkynyl(aryl)silanes via C–H bond activation.

To achieve the metal-catalyzed annulation using alkynyl(aryl)silanes, *ortho*-C–H bond activation directed by an alkynyl group is absolutely required. However, it is difficult to use an alkynyl group as a directing group for C–H bond activation.[9] We previously disclosed that aryl silylethynyl ethers underwent Pd-catalyzed annulation with alkynes and alkenes via *ortho*-C–H bond activation to construct various complex oxacycles.[10,11] Based on these findings, we envisaged that an aryl C–H bond *ortho* to an oxyethynylsilyl group can be activated and undergo *trans*-addition to the alkynyl moiety to form benzosiloles.

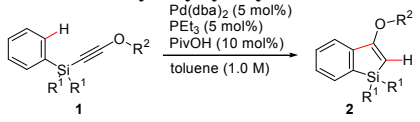
Scheme 1. Metal-catalyzed annulation for the synthesis of benzosiloles



We initiated our investigations using 2,6-diisopropylphenoxy(*tert*-butyldiphenylsilyl)ethyne (**1a**) based on our previously reported hydroalkylation conditions[10f] and gratifyingly found that an intramolecular *anti*-hydroarylation proceeded smoothly under $Pd(dba)_2$/PEt_3/PivOH catalytic conditions to form product **2a** in 95% yield (Table 1, Entry 1).[12] A preparative gram-scale reaction using **1a** (1.20 g) was carried out, and **2a** was successfully obtained in 93% yield (1.11 g, Entry 2). The other carbonaceous groups such as 3,5-xylyl (**1b**) and neopentyl (**1c**) on oxygen gave products in lower yields (Entries 3 and 4). These results show that the diisopropylphenyl group on oxygen is the most suitable for this annulation due likely to its bulkiness and lack of hydrogen atoms at the *ortho*-positions. The reaction using various phenylsilylalkynes **1d**-**1h** was carried out. Substrates **1d** and **1e** having less bulky methyl groups on silicon gave the corresponding products (**2d** and **2e**) under suitable conditions, however, with diminished stability of the substrates and decreased reaction rates (Entries 5 and 6). On the other hand, carbonaceous substituents bulkier than methyl groups led to an increase in product yield. Triphenylsilylalkyne **1f** also afforded product **2f** at a higher temperature due to its lower reactivity (Entry 7). In the case of two *n*-butyl groups on silicon, annulation proceeded to give **2g** in a high yield although high catalyst loading was required (Entry 8). More bulky isopropyl-substituted substrate **1h** resulted in the best yield of **2h** (98%, Entry 9). Such bulky effects may be the result of the Thorpe-Ingold effect, which pushes the phenyl group closer to the

alkynyl group and stabilizes the silyl group. Of note, the aryloxy group is crucial for this annulation: *t*BuPh$_2$Si(C≡CPh) (**3**) did not undergo the annulation at all, indicating that an electron-deficient alkynyl group derived from oxygen promotes the hydroarylation due to an effective interaction with the palladium(0) complex.

Table 1. Reaction of oxyethynylsilylarenes[a]



1 2

Entry	1	R^1	R^2	Temp (°C)	Time	2 (%)[b]
1	**1a**	*t*Bu, Ph	Dipp	100	10 h	**2a**, 95
2[c]	**1a**	*t*Bu, Ph	Dipp	100	46 h	**2a**, 93
3[d]	**1b**	*t*Bu, Ph	3,5-Xyl	120	24 h	**2b**, 30
4[d]	**1c**	*t*Bu, Ph	CH_2tBu	140	13 h	**2c**, 10[e]
5[d]	**1d**	Me, Ph	Dipp	90	7 d	**2d**, 80
6[d,f]	**1e**	Me_2	Dipp	90	9 d	**2e**, 54
7	**1f**	Ph_2	Dipp	140	22 h	**2f**, 89
8[d]	**1g**	Bu_2	Dipp	100	40 h	**2g**, 86
9	**1h**	*i*Pr_2	Dipp	120	22 h	**2h**, 98

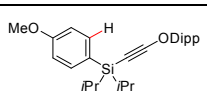
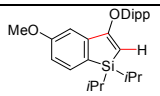
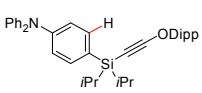
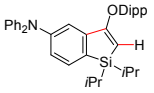
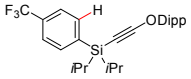
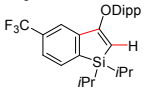
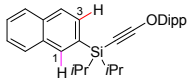
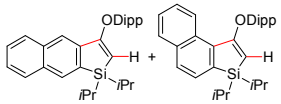
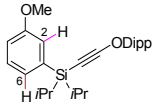
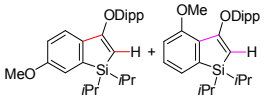
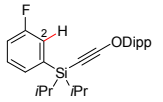
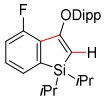
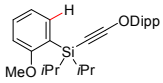
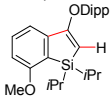
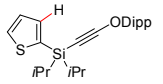
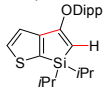
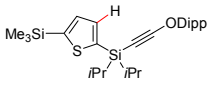
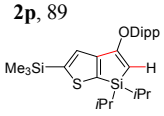
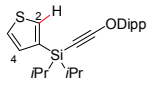
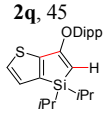
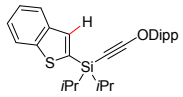
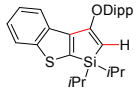
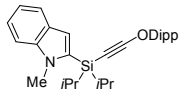
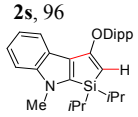
[a] **1**, Pd(dba)$_2$ (5 mol%), PEt$_3$ (5 mol%), PivOH (10 mol%), in toluene (1.0 M). [b] Isolated yield. [c] **1a** (1.20 g, 2.72 mmol) was used to give **2a** (1.11 g, 2.52 mmol). [d] Pd(dba)$_2$/PEt$_3$ (10 mol%). [e] NMR yield. [f] P*n*Bu$_3$ as a ligand. PivOH = *t*BuCO$_2$H, Dipp = 2,6-*i*Pr$_2$-C$_6$H$_3$, 3,5-Xyl = 3,5-Me$_2$-C$_6$H$_3$.

The scope of the present annulation was examined (Table 2). Electron-donating groups such as methoxy and diphenylamino at the *para*-position did not affect the reactivity, giving **2i** and **2j** quantitatively, whereas the electron-withdrawing trifluoromethyl group had moderate reactivity and required a high catalyst loading for a good yield of **2k** (Entries 1-3). The reaction of 2-naphthyl(ethynyl)silane **1l** underwent the hydroarylation to give linear naphthosilole **2l** as the main product via less-hindered C3–H bond activation in **1l** together with the generation of bent naphthosilole **2'l** via C1–H bond activation (Entry 4). When **1m** bearing a methoxy group at C3 was used in the reaction at 100 °C, the C2–H bond *ortho* to the methoxy group was more reactive, giving rise to **2'm** as the major product (Entry 5). In the case of 3-fluorinated **1n**, the C2–H bond was selectively activated and **2'n** was obtained in good yield (Entry 6).[13] The *ortho*-methoxy group in **1o** did not interfere with the hydroarylation to form **2o** (Entry 7). Heteroarylated alkynylsilanes could be applied to this annulation reaction. Substrates **1p-s** having 2- and 3-thienyl and 2-benzothienyl groups on silicon were transformed to the corresponding thienosiloles **2p-s** (Entries 8-11). In the case of 3-thienyl isomer **1r**, the C2–H bond was solely activated without cleavage of the C4–H bond. The TMS group on the thieno group was tolerated (Entry 9). *N*-Methylindole **1t** could be used in the annulation reaction and the corresponding tricycle **2t** was obtained in a high yield (Entry 12).

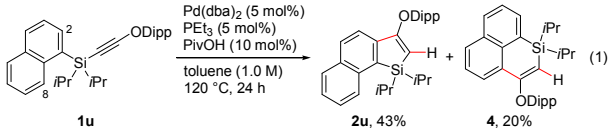
When 1-naphthyl(ethynyl)silane **1u** was used in this hydroarylation under optimized conditions, C2–H bond activation occurred to give naphthosilole **2u** in conjunction with C8–H bond activation to form 1-silaphenalene **4** (eq 1).[14] The observed selectivity may be attributed to the steric influence.

The successful reaction was applied to the double annulation of 4,4'-bis(oxyethynylsilyl)biphenyl **5**. The reaction underwent double hydroarylation using the same molar ratios of the catalysts as in the single annulation to give 5,5'-bibenzosilole **6** (eq 2).

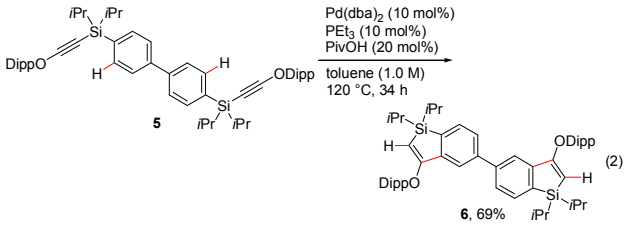
Table 2. Synthesis of condensed siloles[a]

Entry	1	Time (h)	2 (%)[b]
1	 **1i**	20	 **2i**, 98
2	 **1j**	20	 **2j**, 99
3[c]	 **1k**	60	 **2k**, 85
4	 **1l**	24	 **2l** + **2'l**, 73 (71:29)
5[d]	 **1m**	26	 **2m** + **2'm**, 86 (33:67)
6	 **1n**	24	 **2'n**, 82
7	 **1o**	24	 **2o**, 80
8	 **1p**	20	 **2p**, 89
9[c]	 **1q**	24	 **2q**, 45
10	 **1r**	24	 **2r**, 98
11	 **1s**	24	 **2s**, 96
12	 **1t**	24	 **2t**, 73

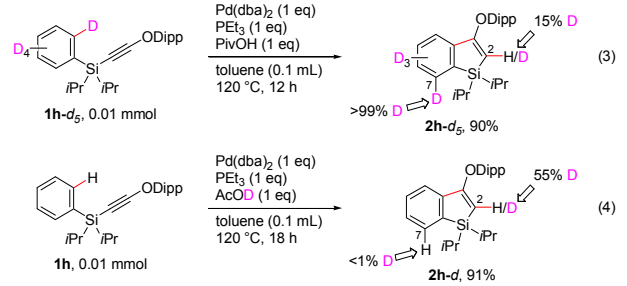
[a] **1**, Pd(dba)$_2$ (5 mol%), PEt$_3$ (5 mol%), PivOH (10 mol%), in toluene (1.0 M), at 120 °C. [b] Isolated yield. [c] Pd(dba)$_2$/PEt$_3$ (10 mol%). [d] 100 °C.



1u **2u**, 43% **4**, 20% (1)

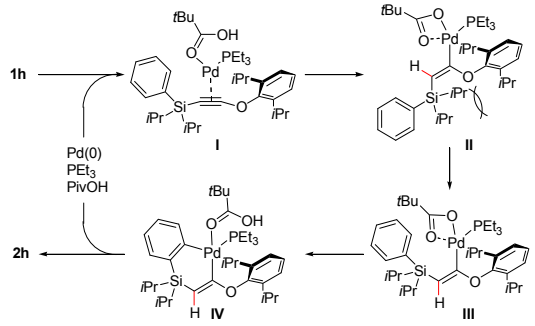


To gain an insight into the mechanism, pentadeuterated-phenyl substrate **1h**-d_5 was used in the annulation in the presence of stoichiometric amounts of Pd(0)/PEt_3/PivOH. The 2-hydrogenated product **2h**-d_5 was mainly obtained in 90% yield (15% D at C2; eq 3). Moreover, **1h** underwent this reaction with 1 equiv of Pd(0)/PEt_3 and AcOH-*d* to form the 2-deuterated product **2h**-*d* with 55% deuterium incorporation at C2 (eq 4). The fact that the deuteration ratio by use of AcOH-*d* was higher than that using **1h**-d_5 clearly indicated that the 2-hydrogen in the product was derived from the acid. Of note, no H/D scrambling at C7 suggested that C–H cleavage was irreversible. The kinetic isotope effect (KIE) observed was 2.83, indicating that the rate-limiting step was the C–H cleavage step which proceeded via a concerted-metalation-deprotonation pathway.



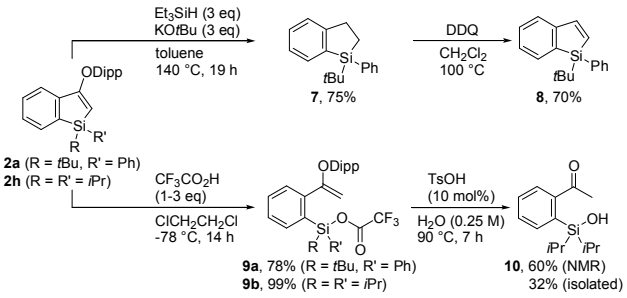
A probable reaction mechanism is shown in Scheme 2 using **1h** as a representative substrate. First, a pivalic acid-coordinated palladium complex **I** with an η^2-alkyne is generated, which then undergoes *syn*-hydropalladation[15] to provide vinyl palladium pivalate **II**. An alternative pathway leading to **II** could be assumed: oxidative addition of pivalic acid to palladium(0) can give hydridopivaloxypalladium(II), which reacts with **1h** to generate **II**. Dipp and two isopropyl groups on silicon accelerate the stereoisomerization[16] due to steric repulsion, forming *Z*-complex **III**. It is also assumed that the oxygen atom assists the isomerization by the donation of its lone pair electron to the C–C double bond. Subsequent C–H activation via the CMD pathway[17] gives palladacycle **IV** followed by reductive elimination to furnish the product **2h** and regenerate palladium(0) and pivalic acid.[18]

Scheme 2. Proposed mechanism



Finally, the synthetic transformation of the products was examined (Scheme 3). Reduction of **2a** took place with Et_3SiH under KO*t*Bu conditions[19] to provide silaindanes **7**. Subsequent oxidation by DDQ gave **8**.[20] Furthermore, trifluoroacetic acid attacked the C–Si bond in **2** at -78 °C to form a silyl esters **9** due to the high electron-donating ability of C2. Subsequent treatment with TsOH catalyst gave a 2-acetylphenylsilanol **10** with elimination of the Dipp group.

Scheme 3. Synthetic transformation



In conclusion, the present study presents an unprecedented straightforward synthesis of benzosiloles by the intramolecular *trans*-insertion of alkynylsilyl groups into an *ortho*-C–H bond. This method is widely applicable toward a broad range of products from readily available alkynyl(aryl)silanes. The Pd(0)/pivalic acid catalytic conditions are effective for the hydroarylation, by initially activating the alkynyl group, followed by C–H activation. Current efforts are directed toward the development of similar hydroarylation reactions for straightforward formation of various condensed (hetero)aromatics.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and characterization data of new compounds are available free of charge *via* the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

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Notes

The authors declare no competing financial interests.

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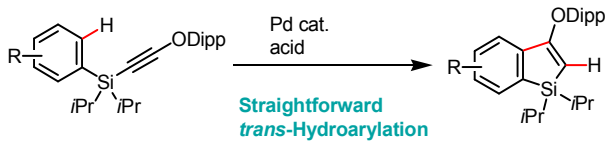
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