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Rhodium-Catalyzed Coupling of 2-Silylphenylboronic Acids with Alkynes Leading to Benzosiloles: Catalytic Cleavage of the Carbon−Silicon Bond in Trialkylsilyl Groups

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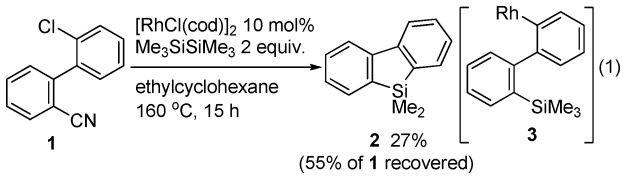
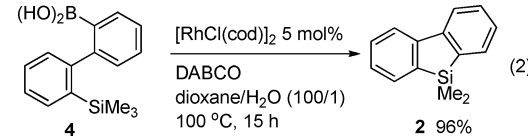
We report herein a rhodium-catalyzed benzosilole synthesis that involves the cleavage of a C−Si bond of a trialkylsilyl group as a key step. Apart from allyl- and benzylsilanes[1] and strained silanes,[2] transformation via the cleavage of C(sp^3)−Si bonds without the use of a discrete penta- or hexacoordinate silicon species[3] normally requires extremely vigorous conditions.[4] Notable exceptions to this are as follows. Intramolecular nucleophilic substitution at a silicon center to cleave C(sp^3)−Si bonds has been reported, but the reaction requires the use of a stoichiometric amount of either organomagnesium[5a] or -lithium reagent.[5b−f] Palladium-catalyzed oxidative methylation of olefins using a trimethylsilyl group as a methyl source has also been reported. In this reaction, the use of organotrimethylsilanes bearing an amide group at an appropriate position is essential for the activation of Me−Si bonds.[6] One isolated example of cleavage of a C(sp^3)−Si bond under rhodium-catalyzed conditions has been reported,[7] but, as of this writing, this intriguing reaction has never been investigated in detail.

In the course of our studies of rhodium-catalyzed cleavage of C−CN bonds assisted by silicon-based reagents,[8] we investigated the reaction of nitrile **1** in the hope of trapping an iminoacylrhodium intermediate with the aryl chloride moiety. To our surprise, however, the only product obtained was dibenzosilole **2** (27% yield), in which one of the Me−Si bonds derived from hexamethyldisilane was cleaved (eq 1).



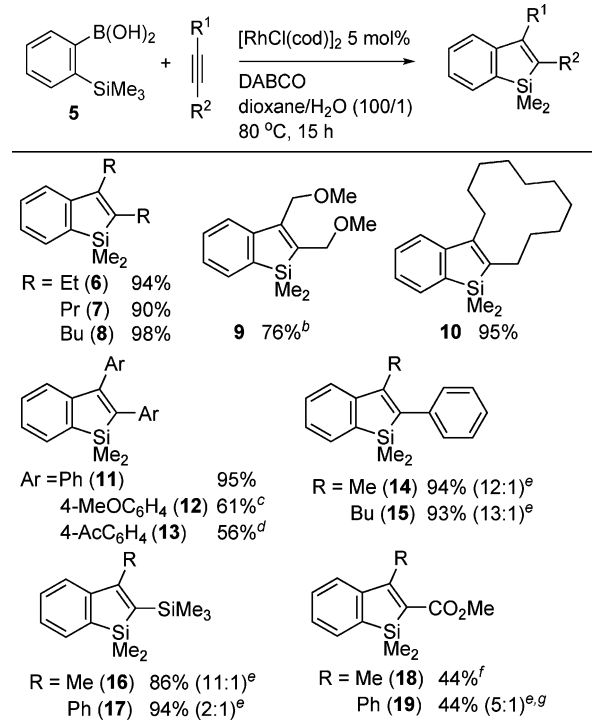
On the basis of our previous finding that a cyano group can be replaced with a trimethylsilyl group under these conditions,[8a,b] a feasible explanation for the formation of **2** involves the intramolecular cyclization of an arylrhodium species **3**, although, to the best of our knowledge, such a displacement at a silicon center by an arylrhodium complex has never been reported. To test this hypothesis, we set out to investigate the rhodium-catalyzed reaction of boronic acid **4**, which should be a more suitable precursor for the postulated intermediate **3**. Gratifyingly, the expected benzosilole **2** was indeed formed under conditions typical for generating an arylrhodium species from arylboronic acids.[9] After brief optimization studies [see the Supporting Information (SI) for details], the yield of this catalytic cyclization reaction via Me−Si bond cleavage was increased to 96% (eq 2).

Encouraged by these successful results, we next intended to extend the catalytic Me−Si bond cleavage reaction to a two-component coupling



using 2-(trimethylsilyl)phenylboronic acid (**5**) and alkynes, expecting that the vinylrhodium intermediate formed by addition of the arylrhodium to the alkyne[9c,10] would undergo a similar displacement at the silicon center. The reaction of **5** with 3-hexyne under optimal conditions for an intramolecular cyclization reaction furnished the expected benzosilole **6** in excellent yield (Table 1). Aliphatic internal alkynes bearing other alkyl groups (leading to **7** and **8**) and alkoxy groups (yielding **9**) also efficiently

Table 1. Rh-Catalyzed Benzosilole Synthesis by the Reaction of **5** with Various Alkynes[a]



[a] Reaction conditions: **5** (0.5 mmol), [RhCl(cod)]$_2$ (0.025 mmol), and DABCO (1.0 mmol) in 100:1 dioxane/H_2O (1 mL) at 80 °C for 15 h. Isolated yields based on **5** are shown. [b] Run using alkyne (2.0 mmol) and [RhCl(cod)]$_2$ (0.050 mmol). [c] Run using alkyne (0.6 mmol) in DMF. [d] Run using alkyne (0.6 mmol) and NEt_3 (1.0 mmol) in place of DABCO. [e] Values in parentheses refer to the ratio of regioisomers, which was determined by NMR. [f] Run at 100 °C using alkyne (2.0 mmol), [RhCl(cod)]$_2$ (0.050 mmol), and Na_2CO_3 (1.0 mmol) in place of DABCO. [g] Run at 130 °C using alkyne (2.0 mmol), [RhCl(cod)]$_2$ (0.050 mmol), and Na_2CO_3 (1.0 mmol) in place of DABCO.

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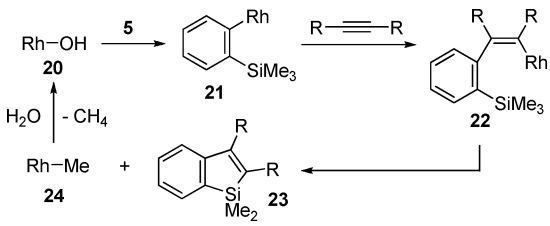
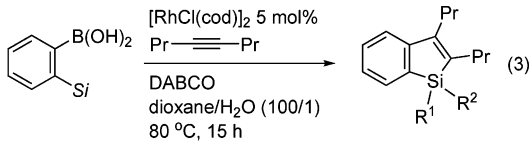
Scheme 1. Possible Mechanism



afforded the corresponding benzosiloles. Benzosilole **10**, which contains a fused 12-membered cycloalkane ring, was synthesized using cyclododecyne as the alkyne component. Diarylalkynes also served as good coupling partners in the present catalysis, furnishing densely arylated benzosilole derivatives **11**−**13**, which constitute an important class of compounds in the context of organic electronic materials.[11] Unsymmetrical alkynes proved to be applicable as well. Arylalkylacetylenes underwent a two-component annulation to form benzosiloles **14** and **15**, which bear an aryl group at the 2-position in the major isomer. Although an attempt to use terminal alkynes was unsuccessful,[12] silyl-protected alkynes can be efficiently assembled into the benzosilole ring with the silyl group predominantly located at the 2-position, as in **16** and **17**. Benzosiloles bearing ester functionality, such as **18** and **19**, are also accessible through this reaction. It should be noted that the regioselectivity observed with unsymmetrical alkynes is consistent with that previously reported for catalytic reactions involving addition of arylrhodium to alkynes.[9,10]

A possible mechanism is depicted in Scheme 1. Arylrhodium intermediate **21**, generated by the transmetalation of **5** to rhodium hydroxide **20**, adds across alkynes to form the vinylrhodium intermediate **22**,[9,10] which subsequently undergoes formal substitution at a trimethylsilyl group to afford the benzosilole product **23** and methylrhodium **24** via the cleavage of a Me−Si bond. Finally, protonolysis of **24** regenerates the catalytically active rhodium hydroxide **20**. Although the elucidation of a more detailed mechanism, especially that for the cleavage of a Me−Si bond, must await further studies, we have preliminary experimental support for the involvement of methylrhodium **24**. When the rhodium-catalyzed reaction of **5** with diphenylacetylene was conducted in the absence of added H_2O, then GC−MS and ^{1}H NMR analyses detected the desired benzosilole **11** along with 1,2-diphenyl-1-propene, which is presumably formed by the addition of **24** to diphenylacetylene (see the SI for details).

To better understand this unprecedented catalytic C−Si bond cleavage reaction, the effect of the substituent of the silicon moiety was examined (eq 3).



Si = $SiEt_3$ (**25**) — $R^1 = R^2 = Et$ (**26**) 46%

$SiMe_2(i\text{-Pr})$ (**27**) — $R^1 = Me$, $R^2 = i\text{-Pr}$ (**28**) 82%

$SiMe_2Ph$ (**29**) — $R^1 = R^2 = Me$ (**7**) 36%; $R^1 = Me$, $R^2 = Ph$ (**30**) 25%

The reaction proved to be sensitive to steric demand, as exemplified by a diminished yield in the reaction of triethylsilyl derivative **25**. This reactivity difference can be applied to selective cleavage of Me−Si over *i*-Pr−Si bonds in **27**, resulting in the formation of benzosilole **28**. In the case of a boronic acid bearing a dimethylphenylsilyl group, siloles **7** and **30** were obtained in 36 and 25% yield, respectively. This result highlights the unique feature of the rhodium-catalyzed C−Si bond cleavage reaction whereby the reactivity of Me−Si and Ph−Si bonds are relatively close. This is in sharp contrast to intramolecular substitution by the organolithium nucleophile, in which the Ph−Si bond in the dimethylphenylsilyl group is exclusively cleaved via pentaorganosilicate.[5b] This clearly indicates that the displacement at a silicon center by the arylrhodium species proceeds through an intermediate (or transition state) possessing a nature that differs completely from pentaorganosilicate.

In summary, a rhodium-catalyzed benzosilole synthesis via the cleavage of a C−Si bond has been disclosed. Conventional C−Si bond formation reactions basically require reactive silicon reagents such as halo- and hydrosilanes, which often hampers their application to elaborate systems. The method described herein has demonstrated that a robust trialkylsilyl group can be utilized as a synthetic intermediate for the formation of a new C−Si bond. Current efforts directed toward exploration of the full synthetic potential of this methodology, including catalytic asymmetric syntheses of siloles containing silicon-centered chirality, and elucidation of the mechanism are ongoing in our laboratory.

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Supporting Information Available: Detailed experimental procedures and characterization of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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