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Rhodium-Catalyzed *ipso*-Borylation of Alkylthioarenes via C−S Bond Cleavage

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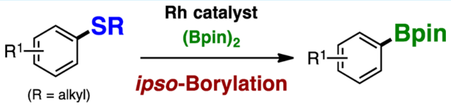
Supporting Information

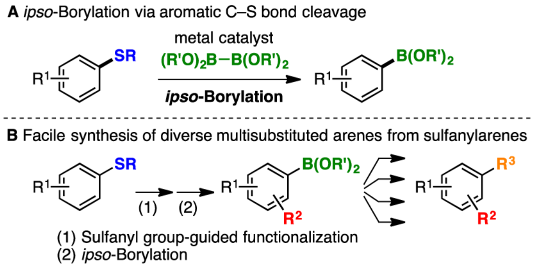
ABSTRACT: Rhodium-catalyzed transformation of alkyl aryl sulfides into arylboronic acid pinacol esters via C−S bond cleavage is reported. In combination with transition-metal-catalyzed sulfanyl group-guided regioselective C−H borylation reactions of alkylthioarenes, this method allows the synthesis of a diverse range of multisubstituted arenes.



Organoboron compounds are valuable synthetic intermediates used in a broad range of fields, including materials science and medicinal chemistry.[1] This is because versatile and reliable organoboron chemistries ensure a variety of further transformations.[1] In this context, many kinds of catalytic borylation reactions of arenes have been reported.[2−7] These include borylative cleavage of stable bonds, such as C−H,[3] C−O,[4] C−N,[5] C−CN,[6] and C−F[7] bonds, which considerably increased the number of available compounds. However, despite the supposed higher reactivity of C−S bonds than that of such stable bonds, borylative cleavage of aromatic C−S bonds has not been reported. Moreover, transformations via aromatic C−S bond cleavage are limited to C−C[8] and C−N[9] bond formations, although catalytic cleavage of C−S bonds has been well investigated for more than 80 years, especially for the hydrodesulfurization process in the petroleum industry.[10] One possible impediment to the achievement of catalytic C−S bond transformations is the high affinity of the sulfur atom for metal centers. This affinity is strong enough to stabilize the intermediates and terminate the catalytic cycle.[9a,11]

We envisioned that a screening of metal catalysts could lead to the realization of borylative C−S bond cleavage of sulfanylarenes (Scheme 1A). Also, increasing availability of thioarenes[12] and a number of reported sulfanyl group-directed functionalization methods[13] encouraged us to achieve this transformation. While a variety of regioselective functionalizations based on metal-mediated functional group-directed reactions via a C−H bond activation have been developed, further transformation of the directing group has not been fully explored;[14] this has restricted the synthetic applicability of these methods. We anticipated that *ipso*-borylation of sulfanylarenes could be one solution to this issue because the sulfanyl group could serve as both a directing and transformable group in this scheme, allowing facile synthesis of diverse, multisubstituted arenes (Scheme 1B). Herein, we report a transition-metal-catalyzed *ipso*-borylation of thioarenes via selective aromatic C−S bond cleavage; this enabled the versatile transformations of thioarenes guided by the sulfanyl group.

Scheme 1. Proposed Strategy


A *ipso*-Borylation via aromatic C–S bond cleavage

B Facile synthesis of diverse multisubstituted arenes from sulfanylarenes

(1) Sulfanyl group-guided functionalization
(2) *ipso*-Borylation

After extensive screening of the reaction conditions, we found that a preconditioned rhodium catalyst efficiently promoted *ipso*-borylation of 2-(methylsulfanyl)naphthalene (**1a**) via selective cleavage of the aromatic C−S bond (Table 1).[11b,15] After heating a mixture of $[RhCl(cod)]_2$ (2 mol %), PCy_3 (12 mol %), bis(pinacolato)diboron (**2a**, $(Bpin)_2$, 2 equiv), and CsF (3 equiv) in *n*-hexane at 80 °C for 1 h, **1a** was added to the mixture, which was then heated continuously at 80 °C for 12 h to afford the desired borylated product **3a** in quantitative yield (entry 1). The use of $[RhCl(coe)]_2$ instead of $[RhCl(cod)]_2$ gave a similar result (entry 2), whereas $[Rh(SMe)(cod)]_2$, a catalyst supposedly to be generated in situ, was ineffective (entry 3). The amount of CsF was reduced to 0.2 equiv (entry 4), which was essential (entry 5) for promoting the borylation (Table S1). This suggests that CsF contributed to the generation of an active catalyst such as a borylrhodium(I) species; the reaction using $[Rh(OH)(cod)]_2$ or $[Rh(OMe)(cod)]_2$ as the rhodium source, which are known to catalyze the reaction with borylarenes without adding an extra base,[16] proceeded efficiently in the absence of CsF (entries 6, 7; Table S2). The choice of PCy_3 as the ligand was crucial; other trialkylphosphines, triarylphosphines, or bidentate phosphine

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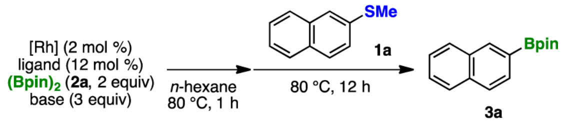
Table 1. Optimization of Reaction Conditions



entry	[Rh]	ligand	base	yield 3a (%)[a]
1	$[RhCl(cod)]_2$	PCy_3	CsF	>99
2	$[RhCl(coe)_2]_2$	PCy_3	CsF	>99
3	$[Rh(SMe)(cod)]_2$	PCy_3	CsF	0
4	$[RhCl(cod)]_2$	PCy_3	CsF[b]	>99
5	$[RhCl(cod)]_2$	PCy_3	–	0
6	$[Rh(OH)(cod)]_2$	PCy_3	–	>99 (89)[c]
7	$[Rh(OMe)(cod)]_2$	PCy_3	–	93
8	$[Rh(OH)(cod)]_2$	$P(c\text{-}C_5H_9)_3$	–	0
9	$[Rh(OH)(cod)]_2$	$P(n\text{-}Bu)_3$	–	4
10	$[Rh(OH)(cod)]_2$	PPh_3	–	4
11	$[Rh(OH)(cod)]_2$	dcpe[d]	–	0

[a] Yields determined by GC analysis, unless otherwise noted. [b] Reaction was conducted using 0.2 equiv of CsF. [c] Isolated yield in parentheses. [d] Reaction was conducted using 6 mol % of dcpe.

ligands gave poor results (entries 8–11 and Table S3). The reaction proceeded smoothly in nonpolar solvents. In particular, *n*-hexane gave a favorable result (Table S4). Using 2.0 equiv of $(Bpin)_2$ (**2a**) provided the best result (Table S5). The borylation of **1a** with bis(neopentyl glycolato)diboron (**2b**) instead of $(Bpin)_2$ (**2a**) under the optimal conditions (entry 6) did not proceed, and **1a** was recovered almost quantitatively.

The optimal conditions (Table 1, entry 6) were applicable to the borylation of a wide range of alkylthioarenes **1** (Figure 1). Thioanisole (**1b**) and its derivatives substituted with an electron-withdrawing group, such as **1c**–**e**, or an electron-donating group such as **1f**–**p**, were smoothly transformed into the corresponding borylarenes **3b**–**p** in moderate to excellent yields (Figure 1A). Under these conditions, borylative cleavage of C–F or C–O bond was not observed. Although aryl acetates are prone to hydrolysis upon treatment with a weak base,[17] the borylation of thioanisyl acetate **1k** proceeded efficiently, demonstrating the mildness of the reaction conditions.[18] The reaction was scalable without further optimization, as demonstrated in the gram-scale synthesis of **3l**. A substrate having an acidic methylene group such as **1q** also participated in this reaction. Although aryl tosylates are potentially activated by low-valent transition metals such as a rhodium(I) complex,[19] selective C–S bond cleavage was observed for thioanisyl tosylate **1r**, leaving the tosyloxy group untouched, which is applicable for further transformations via conventional cross-coupling reactions.[20] In contrast, attempts to borylate 4-chlorothioanisole resulted in formation of a complex mixture (Figure S1). Borylation proceeded uneventfully, even for the substrates with a sterically hindered methylthio group such as **1t**. Moreover, *ipso*-borylation of *ortho*- or *para*-borylthioanisole afforded diborylbenzenes **3u** and **3v**, respectively. The borylation of heteroarylthioanisoles such as thienylthioanisole **1w** also took place, providing **3w** in good yield. Thioanisole **1x** bearing an *N*-sulfonylated indole moiety was borylated with low efficiency under the optimal conditions. In this case, alternative conditions using $[RhCl(cod)]_2$ in the presence of CsF (Table 1, entry 1) were more effective, yielding the borylated product **3x** in high yield. Unfortunately, borylation of substrates that bear a reactive site, such as an acidic proton, halide, or formyl group, gave no desired products (Figure S1). The method was also applicable to the borylation of alkylthioarenes other than methylthio substrates (Figure 1B); 2-(alkylsulfanyl)naphthalenes **4a**–**c** bearing an ethyl, an isopropyl, or a benzyl group on the sulfur atom were transformed to **3a** in excellent yields. The reaction with diphenyl sulfide (**4d**) afforded the desired product **3b** in a lower yield than alkylthioarenes. Although the borylation of 2-naphthalenethiol or methyl phenyl sulfone did not furnish the corresponding borylarenes (Figure S1), methyl phenyl sulfoxide (**4e**) participated in the reaction via cleavage of the aromatic C–S(O) bond and afforded **3b** in moderate yield. While borylative cleavage of benzylic $C(sp^3)$–S bond of methyl 2-methylbenzyl sulfide (**4f**) was not observed under the same conditions, borylarene **5** was obtained in moderate yield, indicating that borylation via thioether-directed *ortho*-C–H activation[21] proceeded instead (Figure 1C).

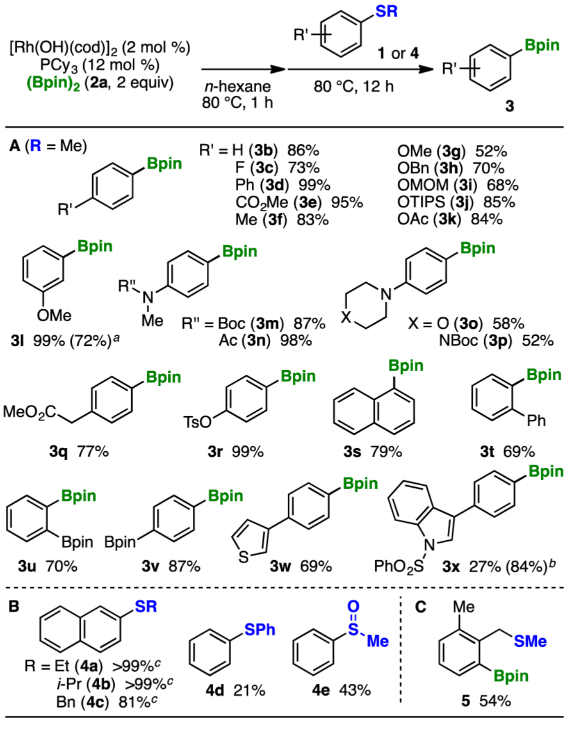


Figure 1. *ipso*-Borylation of alkylthioarenes. Isolated yields are shown, unless otherwise noted. [a] Yield for the reaction using 7.00 mmol of **1l** (1.08 g) in parentheses. [b] Yield for the reaction using $[RhCl(cod)]_2$/CsF system (Table 1, entry 1) in parentheses. [c] Yields determined by GC analysis.

We currently consider that the active catalyst responsible for the borylative C–S bond cleavage of **1** is a borylrhodium(I) species such as **C1**, which was generated by preheating the mixture of $[Rh(OH)(cod)]_2$, PCy_3, and $(Bpin)_2$ (**2a**) (Scheme 2). The same species **C1** is likely to be formed by the addition of CsF when $[RhCl(cod)]_2$ was used in place of $[Rh(OH)(cod)]$ (Table 1, entries 1 and 4). In this scheme, borylarene **3** is formed via oxidative addition[22] of **1** to **C1** followed by reductive elimination or σ-bond metathesis between **1** and **C1**.[23] The whole catalytic cycle is completed by regeneration of **C1** via transmetalation of low-valent methylthiorhodium(I) species **C2** with diboron **2a**. Because the electron density of the rhodium center of **C2** is increased, due to the highly σ-donating phosphine ligands, the strong Rh–S bond is rendered easily cleavable under the mild conditions.[24]

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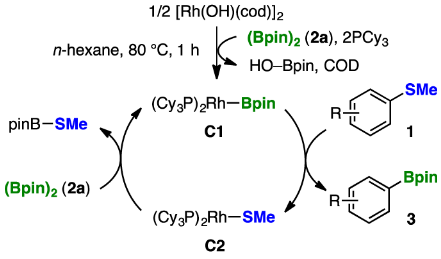
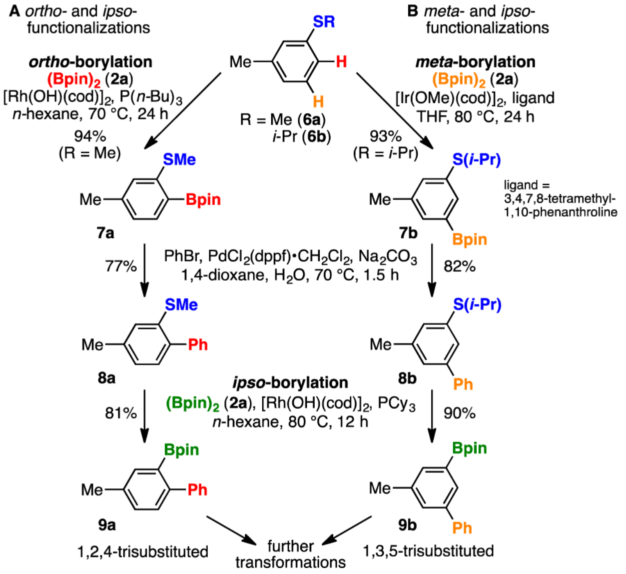
Scheme 2. Plausible Reaction Mechanism



The proposed mechanism is supported by spectroscopic analyses. The ^{31}P NMR analysis of a mixture of [Rh(OH)(cod)]$_2$, PCy$_3$, and (Bpin)$_2$ (**2a**) in cyclohexane-d_{12} before heating showed a major doublet signal at δ 43.2 ($J_{\mathrm{P-Rh}}$ = 179 Hz) (Figure S2), indicating the coordination of PCy$_3$ to the rhodium center. This signal disappeared after heating the solution at 80 °C for 1 h, and instead, two doublet signals appeared at δ 45.0 ($J_{\mathrm{P-Rh}}$ = 169 Hz) and δ 59.7 ($J_{\mathrm{P-Rh}}$ = 152 Hz) (Figure S4). ESI-MS analysis of this heated mixture showed major peaks with the m/z values of 791.47 and 533.62 that correspond to [**C1** + H]$^+$ and [**C1** − PCy$_3$ + Na]$^+$, respectively (Figure S5).[25] These results indicate that preheating of the mixture contributed to the generation of the borylrhodium(I) species **C1** (Scheme 2). Finally, addition of methylthioarene **1f** to the mixture with continuous heating at 80 °C for 1 h quantitatively afforded the borylarene **3f** (Figure S6), confirming the catalytic activity of this mixture for borylation. Even after completion of the borylation, the major signals in the ^{31}P NMR and ESI-MS spectra were observed (Figures S7 and S8), suggesting that the active borylrhodium(I) species **C1** still existed in the reaction mixture. Conversely, spectroscopic signals corresponding to **C2**, which is likely to be more stable than **C1**,[26] were not observed throughout the reaction; this indicates that borylative C−S bond cleavage is the rate-determining step (**C1** + **1** to **C2** + **3** in Scheme 2).[27]

The synthetic utility of the *ipso*-borylation reaction was enhanced by using it in combination with catalytic *ortho*- and *meta*-selective C−H borylation methods for alkylthioarenes; this enabled the facile synthesis of diverse multisubstituted arenes (Scheme 3). For example, rhodium-catalyzed borylation of methyl 3-tolyl sulfide (**6a**) performed under the reported conditions[13c] with some modification afforded the 2-borylated product **7a** (Scheme 3A). This reaction proceeded regioselectively at the sterically less hindered *ortho*-position of the methylthio group, which served as a directing group. Subsequent Suzuki−Miyaura cross-coupling[28] of **7a** with bromobenzene followed by *ipso*-borylation smoothly afforded **9a**, which is further transformable to various 1,2,4-trisubstituted benzene derivatives. Moreover, iridium-catalyzed borylation of isopropyl 3-tolyl sulfide (**6b**) selectively afforded the *meta*-borylated product **7b** in excellent yield (Scheme 3B).[29] Contrary to the case for *ortho*-borylation of **6a** with a methylthio group, the bulkiness of the isopropylthio group effectively prevented the deactivation of catalysis through coordination of the sulfur atom to the iridium center, thereby enabling the efficient conversion.[30] Further functionalization involving the cross-coupling reaction followed by *ipso*-borylation efficiently afforded the 1,3,5-trisubstituted compound **9b**. These results demonstrate that *ipso*-borylation is useful for preparing a broad range of multisubstituted arenes from alkylthioarenes in a regioselective manner based on the combined use of several organoboron chemistries.

Scheme 3. Synthesis of Trisubstituted Arenes via Alkylthio Group-Guided Regioselective Borylation and *ipso*-Borylation



In summary, we have achieved efficient *ipso*-borylation of alkylthioarenes via rhodium-catalyzed aromatic C−S bond cleavage. Transition-metal-catalyzed regioselective C−H borylation of an alkylthioarene followed by transformation of the boryl group and subsequent *ipso*-borylation has enabled a variety of multisubstituted arenes to be easily accessible. Furthermore, borylation of methylthioarenes followed by deborylthiolation[12] enables facile switching of the methyl group on the sulfur atom to other groups. This is a powerful approach to synthesize a wide range of thiolated compounds efficiently with a common skeleton. Applications of the method to the synthesis of a diverse variety of arenes and further mechanistic studies are currently underway in our group.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01250.

> Experimental procedures, characterization for new compounds including copies of NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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(23) *ipso*-Borylation of **1a** was significantly inhibited when the reaction was performed in the presence of radical scavengers such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) or a Galvinoxyl free radical (Table S6). These results suggested involvement of a one-electron transfer mechanism for C−S bond cleavage, although further mechanistic studies are required.

(24) Although electron-rich thioanisoles were also borylated by this method, a possibility that the *ipso*-borylation proceeded via the mechanism based on S$_N$Ar-type reaction could not be excluded.

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(27) Rh-catalyzed borylation of a mixture of **1b** (0.1 mmol) and **1e** (0.1 mmol) with **2a** (0.1 mmol) at 80 °C for 30 min afforded **3b** (1.7% GC yield) and **3e** (51% GC yield), respectively. This result indicated that this borylation reaction favors electron-deficient thioarenes and supports that C−S bond cleavage is the rate-determining step. See the Supporting Information for details.

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(30) Ir-catalyzed C−H borylation of **6a** afforded the desired *meta*-borylated product in 37% yield, and a large amount of **6a** was recovered.