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Rhodium-catalyzed odorless synthesis of diaryl sulfides from borylarenes and *S*-aryl thiosulfonates

Various diaryl sulfides were efficiently prepared from readily available organoborons and *S*-aryl thiosulfonates using a rhodium catalyst. This simple and odorless method for sulfide synthesis has been achieved in the middle of Tokyo city.

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Cite this: *Chem. Commun.*, 2017, 53, 10640

Received 27th July 2017,
Accepted 23rd August 2017

DOI: 10.1039/c7cc05868c

rsc.li/chemcomm

Rhodium-catalyzed odorless synthesis of diaryl sulfides from borylarenes and *S*-aryl thiosulfonates†

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Various diaryl sulfides, including heteroaryl- and nitrogen-containing sulfides, have been efficiently prepared by rhodium-catalyzed odorless deborylative arylthiolation of organoborons with *S*-aryl thiosulfonates. The ready availability of starting materials and further transformation of sulfides have rendered a diverse range of organosulfur compounds easily accessible.

Aromatic sulfides represent a privileged class of compounds that exhibits broad applications in various research fields such as medicinal chemistry[1,2] and materials science[3] (Fig. 1). Thio group-guided transformations as well as the *ipso*-substitution reactions *via* the C–S bond cleavage of thioarenes have enhanced the utility of aromatic sulfides as synthetic intermediates.[4] Although recent developments in the transition-metal catalyzed C–S bond forming reactions have improved the accessibility of aromatic sulfides,[5,6] the types of sulfides that can be prepared are still limited and a novel method that enables the synthesis of a wide range of sulfides is still required.

In this context, we previously developed a facile synthetic route to aryl and alkenyl sulfides *via* the copper-catalyzed deborylthiolation of organoborons with thiosulfonates (Fig. 2A).[6h] The use of readily available thiosulfonates[7,8] as the source of the thio group rendered the entire transformation free of unpleasant odor and diverse sulfides easily accessible. However, while examining the substrate scope and limitation of this reaction, we found that the reaction between 2-thienylboronic acid (**1a**) and *S*-*p*-tolyl *p*-toluenethiosulfonate (**2a**) to prepare 2-thienyl 4-tolyl sulfide (**3a**) did not proceed under the standard copper-catalyzed conditions (Fig. 2B). This reaction possibly failed because of the deactivation of the catalyst, which is related to the strong coordination of the sulfur atom in **1a** to copper. Furthermore, thiolation of **1a** was not easy to achieve efficiently by the conventional catalytic thiolation methods using an easily available reagent, including thiol.[6d,f,g,9] To address this issue, we focused on a rhodium catalyst because rhodium is analogous to copper in terms of catalytic reactivity,[10] such as in 1,4-addition reactions, and several sulfides have been successfully prepared using a rhodium catalyst.[11] Based on this idea, we designed a catalytic cycle for the reaction between arylboronic acid and *S*-aryl thiosulfonate to afford the desired diaryl sulfide (Fig. 2C). This cycle involved the formal substitution reaction of a thiosulfonate with an arylrhodium intermediate **II**, which is generated from a rhodium catalyst **I** and arylboronic acid in the presence of a base. Herein, we report that a rhodium catalyst efficiently promoted the deborylthiolation of borylarenes with *S*-aryl thiosulfonates, including heteroaryl substrates such as **1a**, which enabled the synthesis of various diaryl sulfides.

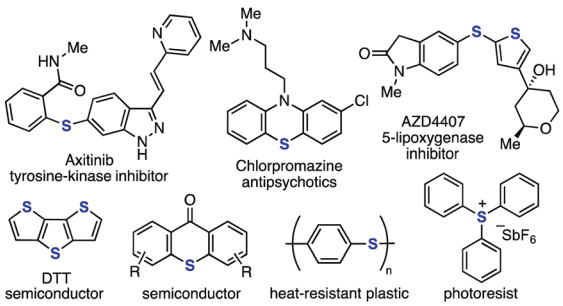

Fig. 1 Diverse diaryl sulfides applied in medicinal chemistry and materials science.

After the catalysts were extensively screened, several rhodium catalysts were found to promote the deborylative *p*-tolylthiolation of **1a** with **2a** (Table 1, entries 4–8). In particular, the desired sulfide **3a** was obtained efficiently when the reaction was conducted in methanol at 50 °C or room temperature using a rhodium catalyst coordinated with cyclooctadiene (5–10 mol% of Rh) in the presence of potassium phosphate (entries 5 and 8–10). Besides potassium phosphate, weaker bases, such as potassium

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† Electronic supplementary information (ESI) available: Experimental procedures, characterization for new compounds including NMR spectra. See DOI: 10.1039/c7cc05868c

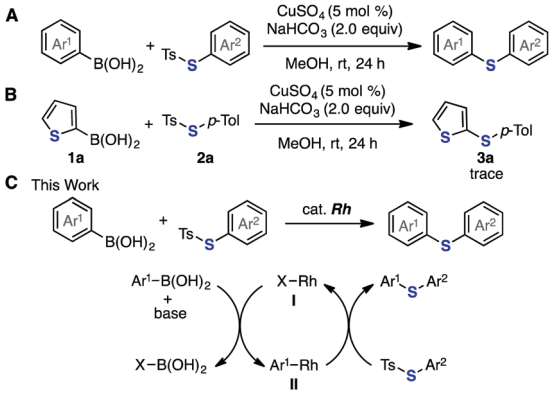
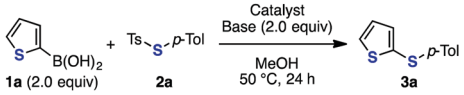


Fig. 2 Catalytic deborylthiolation of arylboronic acids with thiosulfonates. (A) Our previous work: copper-catalyzed deborylthiolation with thiosulfonates. (B) An attempt to prepare sulfide **3a** under copper-catalyzed conditions. (C) Designed catalytic cycle using a rhodium catalyst.

Table 1 Optimization of the reaction conditions



Entry	Catalyst (mol%)	Base	Yield[a] (%)
1	$[Rh(OCOCF_3)_2]_2$ (5)	K_3PO_4	Trace
2	$[RhCl(coe)_2]_2$ (5)	K_3PO_4	Trace
3	$[Rh(Cl)(1,5\text{-hexadiene})]_2$ (5)	K_3PO_4	Trace
4	$[RhCl(nbd)]_2$ (5)	K_3PO_4	36
5	$[RhCl(cod)]_2$ (5)	K_3PO_4	70
6	$Rh(cod)_2OTf$ (10)	K_3PO_4	27
7	$[Rh(cod)(MeCN)_2]BF_4$ (10)	K_3PO_4	34
8	$[Rh(OH)(cod)]_2$ (5)	K_3PO_4	71 (69)[b]
9	$[Rh(OH)(cod)]_2$ (2.5)	K_3PO_4	43
10[c]	$[Rh(OH)(cod)]_2$ (5)	K_3PO_4	62
11	$[Rh(OH)(cod)]_2$ (5)	K_2CO_3	55
12	$[Rh(OH)(cod)]_2$ (5)	CsF	65
13	$Rh(PPh_3)_3Cl$ (10)	K_3PO_4	Trace
14	$[IrCl(cod)]_2$ (5)	K_3PO_4	38

[a] Yields were determined by HPLC analysis. [b] Isolated yield shown in parentheses. [c] Reaction was conducted at room temperature.

carbonate and cesium fluoride, were also suitable (entries 11 and 12). The reactions using a rhodium catalyst coordinated with cyclooctene, 1,5-hexadiene, norbornadiene, or triphenylphosphine gave poor results (entries 2–4 and 13). These results suggested that cyclooctadiene with a suitable coordination ability to rhodium is crucial to efficiently achieve this transformation. In addition, an iridium catalyst was less effective for this transformation (entry 14). Similar to the copper-catalyzed reaction, the entire experimental process was free from unpleasant organosulfurous odor.

A wide range of arylboronic acids were efficiently deborylthiolated with thiosulfonate **2a** under the optimized conditions using 2.5 or 5.0 mol% of $[Rh(OH)(cod)]_2$ with potassium phosphate or potassium carbonate (Fig. 3). Various phenylboronic acids with either an electron-rich or electron-deficient substituent, such as methoxy, hydroxy, dimethylamino, bromo, and methoxycarbonyl groups, were efficiently thiolated to afford diaryl sulfides **3b–f**,

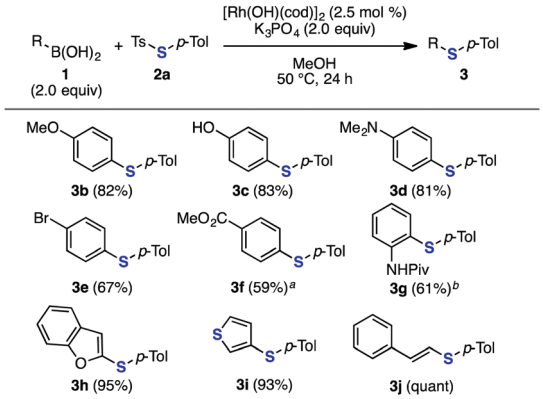


Fig. 3 Thiolation of various boronic acids with thiosulfonate **2a**. Isolated yields are shown. [a] K_2CO_3 was used instead of K_3PO_4. [b] 5 mol% of $[Rh(OH)(cod)]_2$ was used.

leaving these groups untouched. The deborylthiolation of a phenylboronic acid bearing a bulky group at the *ortho* position, such as 2-(pivaloylamino)phenylboronic acid, also occurred, affording 2-thioaniline derivative **3g**. Notably, substrates containing a group with an acidic proton, such as hydroxy and amide groups, tolerated the reaction. Moreover, the deborylthiolation of heteroaromatic substrates, such as 2-benzofuranyl- and 3-thienylboronic acids, smoothly proceeded to afford sulfides **3h** and **3i** in excellent yields. Besides the aromatic substrates, an alkenyl substrate such as β-styrylboronic acid also participated in this reaction to quantitatively afford alkenyl sulfide **3j**.

Various *S*-aryl thiosulfonates were also used to synthesize diaryl sulfides, as demonstrated in the reaction with 3-thienylboronic acid (**1i**) (Fig. 4). Thiosulfonates bearing an electron-donating or electron-withdrawing group successfully participated in this transformation to afford diaryl sulfides **3k–s**. Notably, the reactions with thiosulfonates bearing an unprotected amino or carbamate group, which were unfavorable substrates under copper-catalyzed conditions, also smoothly proceeded to afford diaryl sulfides **3n** and **3o** in high yields.

To gain insights into the mechanism of the rhodium-catalyzed deborylthiolation, we conducted several control experiments

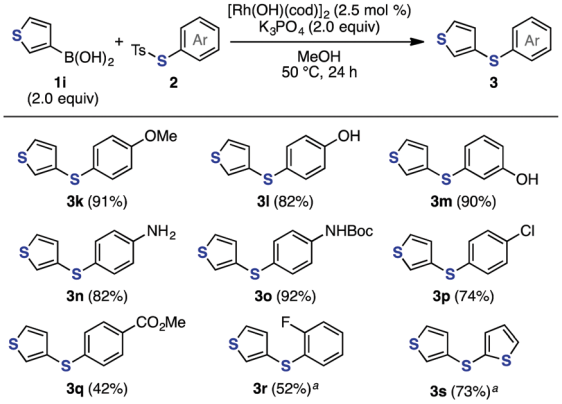


Fig. 4 Thiolation of arylboronic acid **1i** with various *S*-aryl thiosulfonates. Isolated yields are shown. [a] 5 mol% of $[Rh(OH)(cod)]_2$ was used.

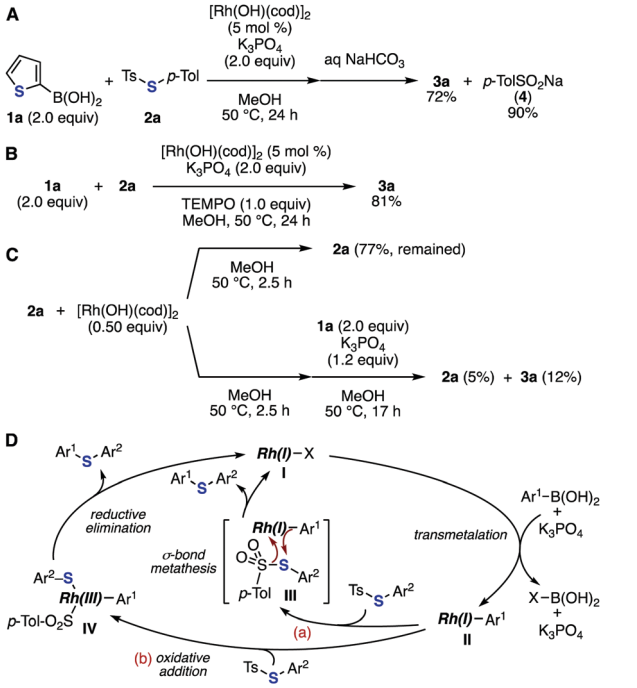
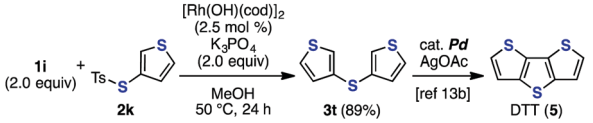
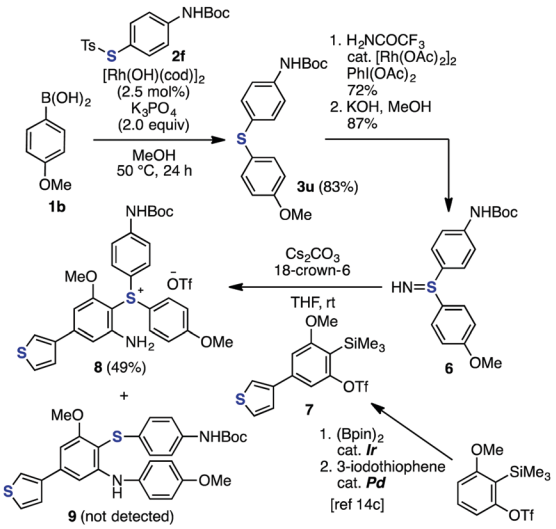


Fig. 5 Mechanistic studies. (A) Confirmation of the formation of sodium *p*-toluenesulfinate (**4**). (B) Reaction in the presence of TEMPO. (C) The effect of premixing thiosulfonate **2a** and an equimolar amount of rhodium salt on deborylthiolation. (D) Plausible reaction mechanism. Yields were determined by HPLC analysis.



Scheme 1 Formal synthesis of DTT.

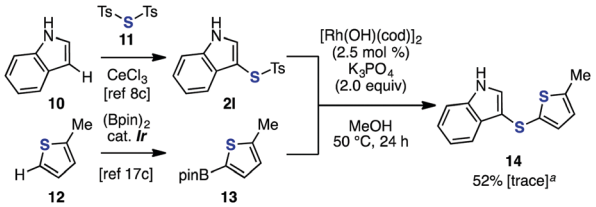


Scheme 2 Modular synthesis of a multisubstituted triaryl sulfonium salt.

(Fig. 5). From a comprehensive survey of the products formed in the reaction between **1a** and **2a**, the formation of a significant amount of sodium *p*-toluenesulfinate (**4**) along with sulfide **3a** was confirmed after the treatment with an aqueous solution of sodium bicarbonate (Fig. 5A).[12] The addition of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) did not inhibit the formation of sulfide **3a**, suggesting that radical intermediates were not involved in the reaction mechanism (Fig. 5B). The treatment of thiosulfonate **2a** with an equimolar amount of rhodium salt at 50 °C for 2.5 h led to the partial consumption (23%) of **2a**, and the subsequent addition of arylboronic acid **1a** and potassium phosphate to this mixture afforded only a small amount of sulfide **3a** (12% yield) (Fig. 5C). This result suggested that arylboronic acid and a base also play a significant role in generating an active catalytic species. Based on these results, the reaction was expected to start with transmetalation between the rhodium catalyst **I** and arylboronic acid in the presence of a base (Fig. 5D). Subsequent σ-bond metathesis of the arylrhodium intermediate **II** with thiosulfonate (path a) or the oxidative addition of thiosulfonate to the arylrhodium intermediate **II**, followed by reductive elimination (path b), afforded diaryl sulfide with the regeneration of rhodium sulfinate.

The improvement in the reaction efficiency for the deborylthiolation of heteroatom-containing substrates rendered the synthesis of diverse sulfur-containing molecules easily achievable (Schemes 1–3). For example, the formal synthesis of dithienothiophene (DTT, **5**)[13] was achieved *via* the rhodium-catalyzed coupling between 3-thienylboronic acid (**1i**) and 3-thienyl thiosulfonate **2k**, affording di(3-thienyl)sulfide (**3t**), which has been reported as the precursor of DTT (**5**)[13b] (Scheme 1). Furthermore, in combination with our aryne chemistry,[14] the short synthesis of a highly functionalized triaryl sulfonium salt **8** was accomplished (Scheme 2). The rhodium-catalyzed thiolation of *p*-anisylboronic acid (**1b**) with thiosulfonate **2f** afforded the corresponding diaryl sulfide **3u** in high yield. Subsequently, **3u** was transformed to sulfilimine **6** based on a reported method.[15] The generation of 3-methoxy-5-(3-thienyl)benzyne from the precursor **7**[14c] in the presence of sulfilimine **6** by the treatment of the mixture with cesium carbonate and 18-crown-6 at room temperature[14a] unexpectedly afforded multisubstituted triaryl sulfonium salt **8** as the major product. The formation of 2-sulfanylaniline derivative **9**, which was assumed to be obtained *via* the direct thioamination of aryne and subsequent migratory *N*-arylation,[14c] was not observed.

The utility of the rhodium-catalyzed deborylthiolation reaction was further demonstrated in the synthesis of diheteroaryl sulfide **14** from simple starting materials, which were easily prepared using the recently emerging C–H functionalization chemistry[16,17] (Scheme 3). According to the reported method,[8c] thiosulfonate **2l** was prepared by the cerium trichloride-mediated electrophilic *p*-toluenesulfonylthiolation of indole (**10**) using di(*p*-toluenesulfonyl)sulfide (**11**) that proceeded in a regioselective manner at the C3-position. Meanwhile, the C5-borylated 2-methylthiophene **13** was prepared regioselectively by the iridium-catalyzed C–H borylation of 2-methylthiophene (**12**) according to the reported method.[17c] The rhodium-catalyzed coupling between **2l** and **13** successfully proceeded to afford diaryl sulfide **14**. In contrast, an attempt of the same transformation under copper-catalyzed



Scheme 3 Formal C–H arylthiolation of indole. [a] Yield of **14** when the reaction was performed under copper-catalyzed conditions ($CuSO_4$ (5 mol%), $NaHCO_3$ (2.0 equiv.), MeOH, rt, 24 h) in brackets.

conditions resulted in the formation of only a trace amount of the desired product **14**. These results clearly highlighted the advantage of rhodium-catalyzed conditions for synthesizing various di(hetero)aryl sulfides.

In summary, we have developed an odorless synthetic route to diaryl sulfides by the rhodium-catalyzed deborylthiolation of borylarenes using thiosulfonates. Because of the mild reaction conditions, a wide range of substrates could be used, which significantly expanded the scope of the diaryl sulfides that could be synthesized, including heteroaryl- and nitrogen-containing compounds. Further studies of this reaction in terms of the application to the synthesis of bioactive compounds and the detailed mechanism are currently underway.

This work was supported by the Platform Project for Supporting Drug Discovery and Life Science Research funded by AMED; P-CREATE from AMED; JSPS KAKENHI Grant Numbers 15H03118 (B; T. H.), 16H01133 (Middle Molecular Strategy; T. H.), 26350971 (C; S. Y.); Naito Foundation (S. Y.).

Conflicts of interest

There are no conflicts to declare.

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