ChemPubSoc Europe

DOI: 10.1002/chem.201303730

CHEMISTRY
A European Journal
Communication

C–H Activation

Rhodium-Catalyzed Directed Sulfenylation of Arene C–H Bonds

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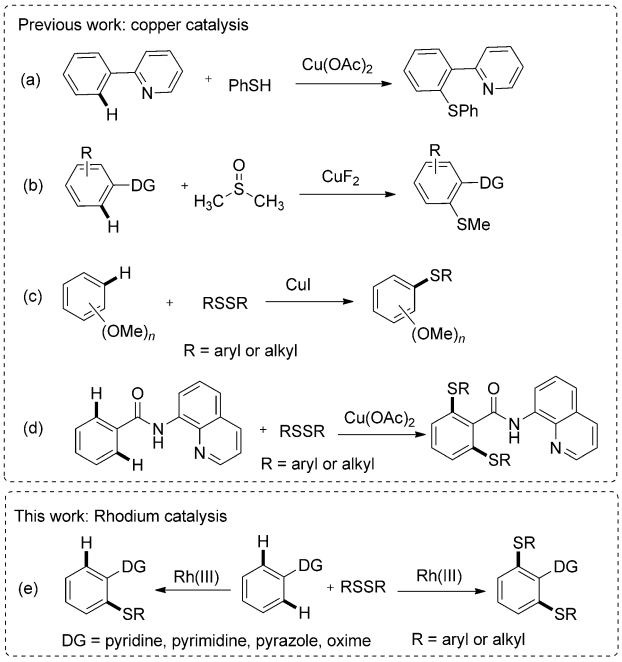
Abstract: The rhodium-catalyzed intermolecular direct C–H thiolation of arenes with aryl and alkyl disulfides was developed for the first time to provide a convenient route to aryl thioethers. This strategy is compatible with many different directing groups and exhibits excellent functional group tolerance. More significantly, mono- or dithiolation can be selectively achieved, thus providing a straightforward way for selective preparation of aryl thioethers and dithioethers.

Aryl sulfides are ubiquitous structural motifs in numerous biologically active natural products, pharmaceuticals, and materials.[1] Metal-mediated cross-coupling reactions of aryl (pseudo)-halides with sulfur nucleophiles, such as aryl thiols and aliphatic thiols, has been developed as a powerful tool to give aryl thioethers under a variety of conditions.[2] However, these methods require the prefunctionalization of substrates. With the increasing interest in transition-metal catalyzed C–H bond functionalization,[3] a direct thiolation of arene C–H bonds would provide an alternative method for the rapid preparation of aryl thioethers.

In the area of C–H bond functionalization, much attention has been paid to C–C, C–O, and C–N bond-forming reactions.[3] In sharp contrast, the formation of a C–S bond through transition-metal catalyzed C–H activation is rare and most examples have been limited to the formation of aryl sulfones[4] and benzothiazoles,[5] or the deprotonative sulfenylation of acidic heterocycles.[6] The more challenging preparation of aryl thioethers through non-acidic arene C–H activation are significantly rare,[7] presumably because the sulfur atom of thioethers can tightly bind to metals, leading to the deactivation of the metal catalyst.[8] Pioneering Cu-mediated direct thioetherification of the arene C–H bond was disclosed by Yu and co-workers (Scheme 1 a).[7a] Qing and co-workers developed a Cu^{II}-mediated methylthiolation of arene C–H bonds utilizing DMSO as the methylthiolation reagent (Scheme 1 b).[7b] Recently Cheng et al. reported a Cu^{I}-catalyzed thiolation of the di- or trimethoxybenzene C–H bond (Scheme 1 c).[7c] However, these methods suffer from low efficiency and a narrow scope of possible thiolation reagents or substrates. Very recently, Daugulis and co-workers reported a beautiful Cu^{II}-catalyzed thiolation of arene C–H bonds using bidentate directing groups (Scheme 1 d).[7d] However, in most cases, only dithioether products were obtained. Therefore, the development of a general non-acidic arene C–H thioetherification reaction (especially one using transition-metal catalysts other than Cu) that enables the selective preparation of valuable aryl thioethers and dithioethers, and is compatible with a broad scope of substrates and tolerant to a wide range of functional groups, would be of prime synthetic value.



Scheme 1. Different approaches toward C–S bond formation through non-acidic arene C–H activation.

Recently, {Cp^*Rh^{III}} complexes have emerged as very useful and efficient catalysts for C–H bond activation[3a–c,i,m] and subsequent C–halogen,[9] C–N,[10] and especially C–C bond-forming reactions,[11–14] including alkynylation, olefination,[11] nucleophilic additions,[12] and coupling with carbene precursors[13] and aziridines.[14] Indeed, it was also found that Rh^{III} catalysts could complement other transition metals in the functionalization of C–H bonds in terms of activity, substrate scope, selectivity, and functional-group tolerance.[9–14] However, to the best of our knowledge, there is no report on the more challenging

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201303730.

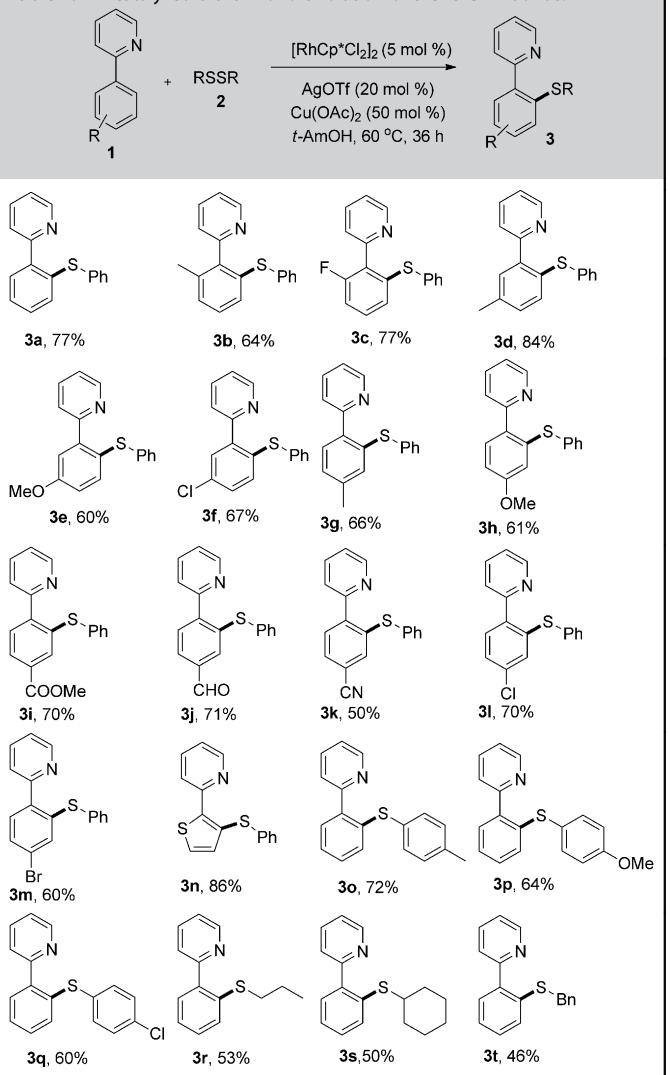
C–S bond formation by Rh-catalyzed transformations. Given the prevalence of aryl thioethers in medicinal chemistry and pharmaceutical industries, here we describe the first example of Rh-catalyzed arene C–H thioetherification (Scheme 1e). Significantly, this new C–H thioetherification reaction is compatible with many different directing groups (e.g., pyridine, pyrimidine, pyrazole, and oxime) and tolerates various synthetically useful functional groups, selectively providing mono- or dithioethers by simply changing the reaction conditions.

We chose the reaction of 2-phenylpyridine (**1a**) with diphenyl disulfide (**2a**) as a model reaction (see Table S1 in the Supporting Information). Although no coupling occurred when using $[RhCp^*Cl_2]_2$ (5 mol%) as a catalyst, addition of $AgSbF_6$ (20 mol%) catalyzed the reaction to give the desired product **3a** (for structure, see Table 1), albeit with low conversion. Addition of an oxidant (150 mol%) significantly affected this C–S coupling reaction and the use of Ag_2CO_3 as an oxidant gave improved conversion and yield, providing dithioether **4a** (for structure, see Table 4) as a main product. Other halide-abstracting reagents were also tested and AgOTf proved to be particularly effective, giving a sharp increase in the conversion and yield. Dithioether **4a** was obtained in the greatest yield by using Rh/AgOTf as the catalyst, Ag_2CO_3 as the oxidant, and toluene as the solvent, heated to 150 °C for 36 h. Selective monothioetherification was achieved by using Rh/AgOTf as the catalyst, $Cu(OAc)_2$ as the oxidant, and *t*-AmOH (*t*-AmOH = 2-methyl-2-butanol) as the solvent, heated to 60 °C for 36 h. Control experiments revealed that the rhodium(III) complex is essential.

With the optimal reaction conditions in hand, substrate scope with respect to mono-thiolation was then surveyed (Table 1). The reaction did not show pronounced electronic preference, and introduction of various electron-rich (**3b**, **3d**, **3e**, **3g**, **3h**), electron-poor (**3i–k**), and halogen (**3c**, **3f**, **3l**, **3m**) groups at the *ortho* (**3b**, **3c**), *meta* (**3d–f**), and *para* (**3g–m**) positions of the phenyl ring were all well tolerated. The *meta*-substituted derivatives showed excellent regioselectivity in C–H activation to give the less sterically crowded isomers (**3d–f**). In particular, the 2-methyl derivative (**3b**) exhibited good reactivity, thus showing high tolerance for steric hindrance. Furthermore, ester (**3i**), nitrile (**3k**), halogen (**3f**, **3l** and **3m**), and even electrophilic carboxaldehyde (**3j**) groups were compatible with this C–S bond-forming reaction, making further functionalization possible. Notably, the reaction was able to thiolate the C–H bond of heterocyclic substrates (**3n**). The substrate scope was further extended to disulfides. To our delight, various diaryl disulfides showed good reactivities, irrespective of the electronic nature of the substituents on the phenyl ring (**3o–q**). Fortunately, the alkyl (**3r** and **3s**) and benzyl (**3t**) disulfides were also compatible with the conditions and afforded the corresponding thiolation products in good yields, thus allowing for high diversity in the synthesis of aryl thioethers.

To demonstrate the scope of other possible directing groups, various pyridine directing groups were investigated (Table 2). Pyridine rings functionalized with electron-donating (**3aa–ad**) or -withdrawing (**3ae**) groups were tolerated well

Table 1. Rh-catalyzed *ortho* mono-thiolation of arene C–H bonds.[a]

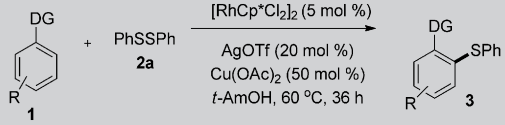


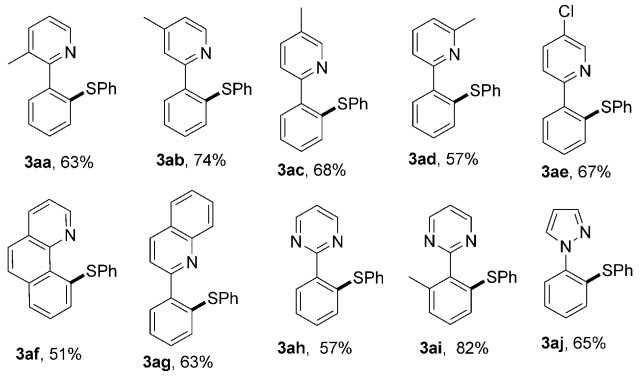
[a] 0.2 mmol scale; yield of isolated products shown.

and the tolerance of halide groups (**3ae**) offers the opportunity for further functionalization. The steric bulk on the pyridine ring had a limited effect on the reaction. Good reactivities were seen when a methyl group was present on the pyridine ring (**3aa–ad**), regardless of whether it was at the 3-, 4-, 5-, or 6-position. Multicyclic pyridine derivatives were also found to be useful in this thiolation reaction, with tricyclic benzo[*h*]quinoline and bicyclic quinolone both giving the corresponding products (**3af** and **3ag**, respectively) in good yields. Notably, other *N*-based groups could also serve as effective directing groups. For example, by using pyrimidine or pyrazole as the directing group, the reaction provided the corresponding thiolation products (**3ah–aj**) and also showed high tolerance for steric hindrance (**3ai**), thus expanding the scope of the present thiolation method.

In addition to heterocycles, ketoximes also worked well as a directing group to facilitate the thiolation reaction (Table 3). Notably, no product was observed in the absence of Rh catalyst, indicating that the rhodium(III) complex is essential.[15]

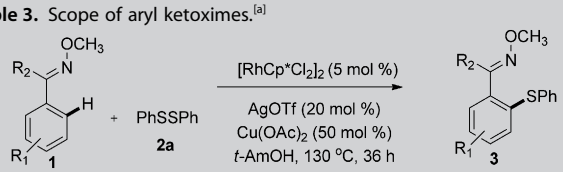
Table 2. Scope of other directing groups.[a]

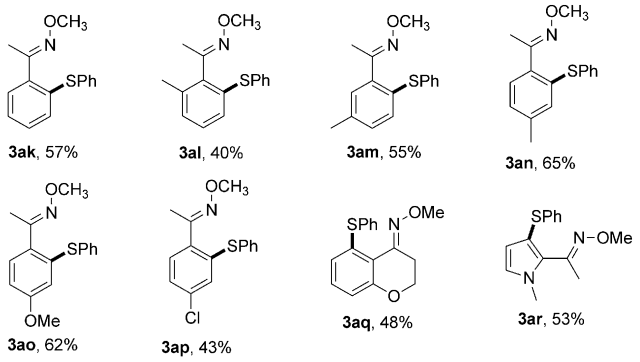




[a] 0.2 mmol scale; yield of isolated products shown.

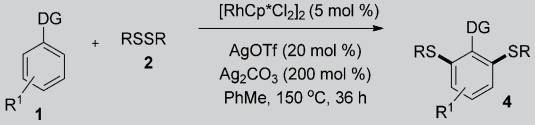
Table 3. Scope of aryl ketoximes.[a]

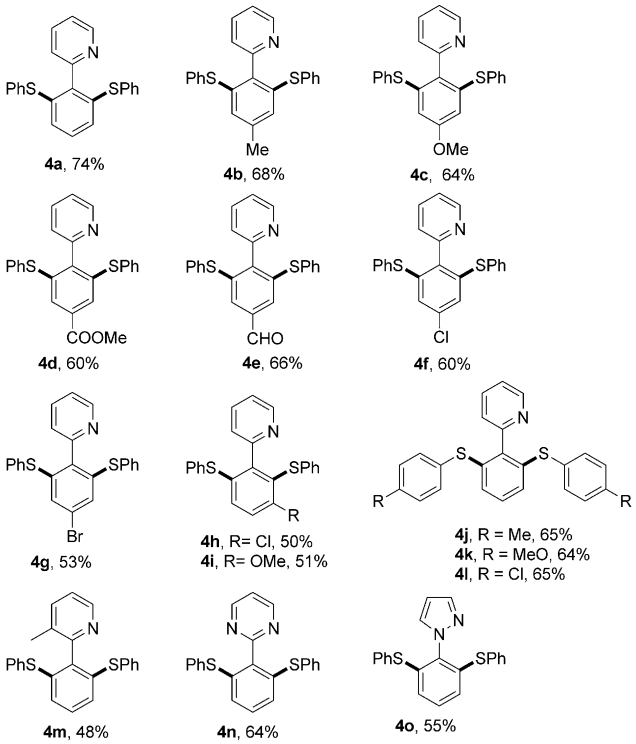




[a] 0.2 mmol scale; yield of isolated products shown.

Table 4. Rh-catalyzed *ortho* dithiolation of arene C–H bonds.[a]



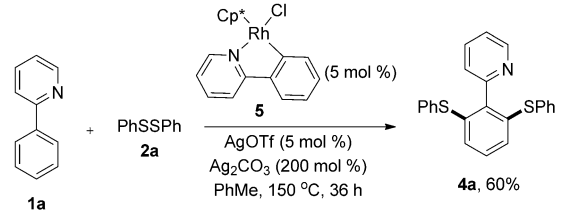


[a] Reaction conditions: 0.2 mmol of **1**, 0.5 mmol of **2**, 0.01 mmol $[RhCp^*Cl_2]_2$, 0.04 mmol of AgOTf, 0.4 mmol of Ag_2CO_3 and 0.3 mL of PhMe at 150 °C for 36 h. Yield of isolated products shown.

Electronically modified aryl ketoximes were viable for this thiolation reaction (**3ak**–**ap**) and a bicyclic ketoxime also successfully underwent thiolation to give **3aq**. More gratifyingly, aromatic heterocycles were also successfully reacted (**3ar**). The above features indicate that the present method is a general reaction that can be extended to more directing groups and it is complementary to previous Cu-catalyzed C–H thiolation reactions.[7]

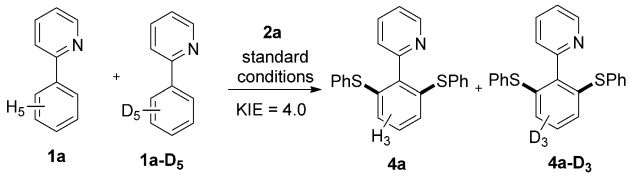
Next, the scope of the double C–H activation/thioetherification reaction was examined (Table 4). Various substrates containing both electron-donating and electron-withdrawing groups at the *para*-position of the phenyl ring were successfully coupled with **2a**, providing dithioether products in moderate to good yields (**4a**–**g**). Notably, ester (**4d**), carboxaldehyde (**4e**), and halogen (**4f** and **4g**) groups were tolerated, offering the opportunity for further functionalization. Contrasting with previous Rh-catalyzed C–H functionalization reactions,[9–14] *meta*-substituted substrates successfully provided difunctionalized products, enabling the preparation of 1,2,3,4-tetrasubstituted benzene derivatives (**4h** and **4i**). Both electron-rich and electron-poor diaryl disulfides were successfully coupled with 2-phenylpyridine to give products **4j**–**l** in good yields. More gratifyingly, the present dithiolation reaction tolerated other N-based directing groups (**4m**–**o**) even when 6-methylpyridine was used as the directing group (**4m**), indicating the high level of steric tolerance of this system. Notably, double activation of arene C–H bonds is rare with rhodium catalysis,[9,16] and most reported examples involved C–C bond formation as well.[16]

To probe the catalytic mechanism, we carried out several experiments: First, cyclometalated Rh^{III} complex **5** was found to successfully catalyze the thiolation reaction of 2-phenylpyridine to give dithiolation product **4a** in 60% yield, indicating the plausible intermediacy of a rhodacycle complex in the catalytic cycle (Scheme 2). A significant primary kinetic isotope effect ($k_H/k_D = 4.0$) was observed for an intermolecular competitive



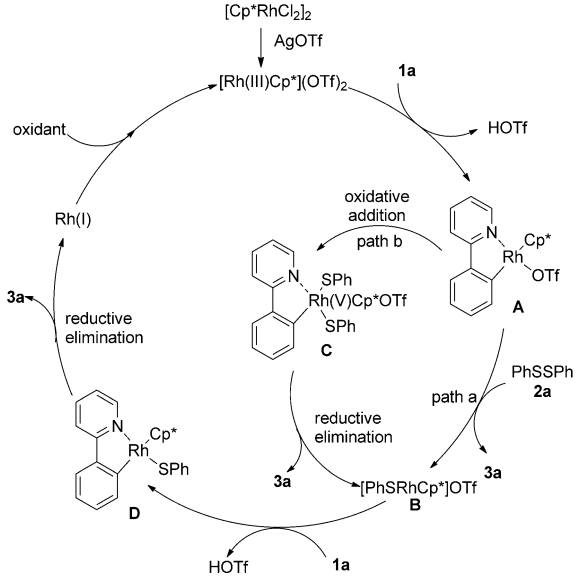
Scheme 2. Preliminary mechanistic study.

coupling of **2a** with a 1:1 mixture of **1a** and **1a-D_5** at a low conversion (Scheme 3). This KIE value of 4 is typical for the C–H activation processes.[17]



Scheme 3. Intermolecular KIE experiment.

Although the mechanism of the reaction is unclear at this moment, we tentatively propose the following mechanistic pathway on the basis of the above data (Scheme 4). First, the $[RhCp^*Cl_2]_2$ precursor reacts with the AgOTf additive to provide a cationic Rh^{III} species, which facilitates the C–H bond activation of substrate **1a** to form an Ar–Rh^{III} rhodacycle (**A**). Intermediate **A** can undergo a nucleophilic-addition-type reaction with diphenyl disulfide to afford the desired product **3a** and $PhSRh^{III}$ species **B** (path a). Alternatively, oxidative addition of the disulfide bond to the Rh^{III} center could occur to give a Rh^{V} intermediate (**C**),[18] followed by reductive elimination to give product **3a** and Rh^{III} **B** (path b). Intermediate **B** can continue to react with substrate **1a** through a C–H activation step to form a five-membered rhodacycle intermediate (**D**), which would undergo reductive elimination to afford **3a** together with a rhodium(I) species. Oxidation of Rh^{I} gives Rh^{III} to complete the catalytic cycle.



Scheme 4. Proposed mechanism.

In summary, we have reported the first example of Rh-catalyzed direct C–H thiolation by using readily available disulfides as thiolation reagents. This protocol shows a broad substrate scope and many different directing groups can be used in the C–H thiolation reaction. More significantly, this method allows for selective mono- or dithiolation and exhibits excellent tolerance of functional groups, enabling the straightforward and selective preparation of valuable and versatile aryl thioethers and dithioethers. Owing to its high selectivity and broad substrate scope, this C–H thiolation reaction should be of high synthetic value. Detailed mechanistic studies and synthetic applications of the Rh-catalyzed thiolation reaction are underway.

Experimental Section

General Procedure

An oven-dried reaction vessel was charged with $[Cp^*RhCl_2]_2$ (6.1 mg, 0.01 mmol), AgOTf (10.2 mg, 0.04 mmol), 2-phenylpyridine (**1a**; 31 mg, 0.2 mmol), diphenyl disulfide (**2a**; 43 mg, 0.2 mmol), $Cu(OAc)_2$ (20 mg, 0.1 mmol), and 2 mL of *t*-AmOH (0.1 M). The vessel was sealed and heated at 60 °C (oil bath) for 36 h. The resulting mixture was cooled to room temperature, filtered through a Celite pad and then transferred directly to an alumina column and eluted with petroleum ether and acetone (15:1) to give products **3a** (40.5 mg, 77% yield).

Acknowledgements

Support of this work by the National Natural Science Foundation of China (No. 21302200) is gratefully acknowledged.

Keywords: arenes · C–H activation · C–S bond formation · rhodium · thiolation

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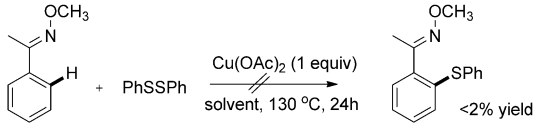
[15] We have tried to catalyze the thiolation reaction by using copper catalysts in the absence of Rh complexes under a lot of conditions, including different temperature and various solvents such as DMSO, CH_3CN, DCE. However, no product was observed, indicating the necessity of Rh complexes.



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Received: September 24, 2013
Published online on November 28, 2013