Catalyzed Thiolation

Rhodium(III)-Catalyzed Thiolation of Azobenzenes

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Abstract: A rhodium(III)-catalyzed C–H activation and thiolation of azobenzene with disulfide was developed. A broad range of azobenzenes were thiolated with high regioselectivity to form mono-*ortho*-substituted products in moderate to excellent yields of up to 99%. The catalytic system could also be applied for the synthesis of a selenylated product and a benzothiophene.

Introduction

Azoarenes are ubiquitous structural motifs found in a multitude of natural products, and have significant value in materials science as rubber accelerators, organic dyes and molecular switches.^[1] They have also been used as directing groups in the metal-catalyzed formation of C–C,^[2] C–N,^[3] C–O bonds,^[4] and in cyclization^[5] and sulfonylation^[6] reactions. Aryl sulfides are also structural features commonly found in natural products with biological activity, and have been widely used in medicines and materials. The direct thiolation of C–H bonds represents an attractive strategy for the preparation of aryl sulfides.^[7]

Azoarenes bearing sulfide ether groups and their derivatives exist widely in natural products, functional materials and pharmaceuticals. For example, compounds A and $B^{[1g]}$ are inhibitors with kinesin activity (Figure 1); compound $C^{[1h]}$ is an inhibitor of human farnesyltransferase.

Previously, Wang and co-workers disclosed a highly selective C7-thiolation and selenation of indolines with disulfides and diselenides by Rh^{III}-catalyzed C–H bond activation (Scheme 1a).^[8a] Recently, Glorius et al. reported a cobalt-catalyzed C–H thiolation with thiophenol or disulfides (Scheme 1b).^[8b] Zhu and co-workers developed a methodology to achieve the direct *ortho*-functionalization of aromatic ketazines with aryl disulfides by Rh-catalyzed C–H activation in moderate yields (Scheme 1c).^[8c] Nevertheless, despite recent advances in this transformation, there is still a need for complementary methods in order to attain a broader utility of this reaction. In a continuation of our work and that of others on the catalytic synthesis of sulfur-containing compounds,^[9] we report here

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Figure 1. Selected examples of azoarenes bearing a sulfide ether group or related moiety.



Scheme 1. Selected examples of catalytic thiolation reactions.

our studies on thiolation of azobenzene by catalytic *ortho*-C–H activation (Scheme 1 d), which would overcome deactivation of the catalyst caused by sulfur.^[10] This method has the following advantages: high efficacy under standard conditions on a broad range of substrates with excellent functional group tol-

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erance in yields of up to 99%, and high regioselectivity with only mono-*ortho*-thiolated products.

Results and Discussion

We started our studies with the reaction between azobenzene (**1 a**, 0.3 mmol) and diphenyl disulfide (**2 a**, 0.05 mmol) in dichloroethane (DCE) at 110 °C for 24 h. Only a trace of the desired product **3 a** was obtained in the absence of catalyst or oxidant (Table 1, entries 1 and 2). In a screen of different metal catalysts, [Cp*RhCl₂]₂ (Cp*=pentamethylcyclopentadienyl; 0.005 mmol) gave the best result of 75% with AgBF₄ (0.2 mmol) as oxidant, whereas the others resulted in no desired product (Table 1, entries 3–7). Temperatures higher than 120 °C seemed to be unnecessary and even lead to lower yields at 140 °C (Table 1, entries 8–10). Other oxidants such as Cu(OAc)₂, AgOTf and AgSbF₆ were also tested, which gave lower yields than AgBF₄ (Table 1, entries 11–13). Further experi-

Table 1. Optimization of reaction conditions ^[a]						
N:N + PhSSphCp*Rh						
	1a	2a	3a			
Entry	Catalyst	Oxidant	T [°C]	Yield [%]		
1	_	_	110	Tr		
2	[Cp*RhCl ₂] ₂	-	110	Tr		
3	[Cp*RhCl ₂] ₂	AgBF ₄	110	75		
4	Pd(OAc) ₂	AgBF ₄	110	ND		
5	$Rh_2(OAc)_4$	AgBF ₄	110	ND		
6	Ni(OAc) ₂	AgBF₄	110	ND		
7	Co(OAc) ₂	AgBF ₄	110	ND		
8	[Cp*RhCl ₂] ₂	AgBF₄	120	86		
9	[Cp*RhCl ₂] ₂	AgBF₄	130	86		
10	[Cp*RhCl ₂]	AgBF ₄	140	47		
11	[Cp*RhCl ₂] ₂	Cu(OAc) ₂	120	45		
12	[Cp*RhCl ₂]	AgOTf	120	29		
13	[Cp*RhCl ₂] ₂	AgSbF ₄	120	ND		
14 ^[b]	[Cp*RhCl ₂] ₂	AqBF₄	120	57		
15 ^[c]	[Cp*RhCl ₂]	AqBF₄	120	59		
16 ^[d]	[Cp*RhCl ₂] ₂	AgBF₄	120	78		
17 ^[e]	[Cp*RhCl_]	AgBF₄	120	19		
18 ^[f]	[Cp*RhCl_]	AgBF.	120	12		
19 ^[g]	[Cp*RhCl_]	AgBF.	120	67		
20 ^[h]	[Cp*RhCl_]	AgBF.	120	63		
21 ^[i]	[Cn*RhCl_]	AgBF.	120	61		
22 ^[j]	[Cp*RhCl_]	AgBF.	120	66		
23 ^[k]	[Cn*RhCl_]	AgBF.	120	ND		
24 ^[I]	[Cp*RhCl_]	AgBF.	120	ND		
25 ^[m]	[Cn*RhCl_]	AgBF.	120	ND		
26 ^[n]	[Cp*RhCl ₂] ₂	AgBF.	120	ND		
27 ^[0]	[Cp*RhCl ₂] ₂	AgBF ₄	120	ND		
[a] Reaction conditions: 1a (0.3 mmol), 2a (0.05 mmol), $[Cp*RhCl_2]_2$ (0.005 mmol), AgBF ₄ (0.2 mmol), DCE (1 mL), 24 h, air. [b] AgBF ₄ (0.8 mmol). [c] AgBF ₄ (0.6 mmol). [d] AgBF ₄ (0.4 mmol). [e] AgBF ₄ (0.1 mmol). [f] AgBF ₄ (0.04 mmol). [g] CH ₂ Cl ₂ (1 mL). [h] EtOAc (1 mL). [j] EtOH (1 mL). [j] MeOH (1 mL). [k] Dioxane (1 mL). [l] CH ₃ CN (1 mL). [m] HFIP (1 mL). [n] Acetone (1 mL). [o] Toluene (1 mL). Tr = trace amounts detected; ND = not detected.						

ments indicated that 0.2 mmol AgBF₄ was sufficient for the reaction (Table 1, entries 14–18). Finally, the reaction proceeded smoothly in the solvents CH_2Cl_2 , ethyl acetate, EtOH, MeOH (Table 1, entries 19–22), whereas other solvents, including dioxane, CH_3CN , hexafluoroisopropanol (HFIP), acetone, and toluene were unsuitable for the reaction (Table 1, entries 23–27). The optimized reaction conditions were azobenzene (0.3 mmol) and diphenyl disulfide (0.05 mmol), $[Cp*RhCl_2]_2$ (0.005 mmol), AgBF₄ (0.2 mmol) in DCE at 120°C for 24 h (Table 1, entry 8).

With the established optimal conditions in hand, the scope of the azobenzene substrate was investigated. As shown in Scheme 2, azobenzenes bearing either electron-donating or withdrawing groups were coupled with disulfides smoothly in moderate to good yields. Electron-donating groups seemed to favor the reactions. For example, *para*-methyl- (**3 d**) or ethyl-(**3 e**) substituted azobenzene gave 80% and 84% yields products, respectively, whereas only around 50% yields were obtained in the case of fluoro-, chloro-, or bromo-substituted analogues (**3 i**-**3 k**, respectively). Steric hindrance was also an important factor that affected the results. *Ortho*-substituted substrates (product **3 h**) gave obviously lower yields than *para* or *meta*-substituted analogues (products **3 d** and **3 b**). Further-



 $\label{eq:Scheme 2. Screening of azoarenes. Reaction conditions: 1 (0.3 mmol), 2a (0.05 mmol), [Cp*RhCl_2]_2 (0.005 mmol), AgBF_4 (0.2 mmol), DCE (1 mL), 120 °C, 24 h, air; isolated yields in parentheses.$

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Scheme 3. Screening of disulfides. Reaction conditions: 1 a (0.3 mmol), 2 (0.05 mmol), [Cp*RhCl₂]₂ (0.005 mmol), AgBF₄ (0.2 mmol), DCE (1 mL), 120 $^{\circ}$ C, 24 h; isolated yields in parentheses.

more, the catalytic system is compatible with alkoxy (3z) and ester (3ab) groups.

An investigation of different disulfides was then performed. As shown in Scheme 3, the reaction could tolerate a wide range of substituted disulfides. However, no systematic influence of the substituents was found, which was similar to the results of Glorius and co-workers.^[8b] The highest yield (99%) was obtained in the case of the *para*-fluoro disulfide substrate (product **3 u**). In addition, this catalytic system could also be applied for diphenyl diselenide, which afforded the corresponding product **3 y** in moderate yield 59% (Scheme 4).

Further experimentation confirmed that the azobenzene-directing group could be easily removed under acidic conditions to generate the thiolated free aniline, as exemplified by reaction of **3a** with 90% yield.^[11] Next, we envisaged the synthesis of a benzothiophene **4**, an important moiety present in many organic semiconductors, through intramolecular C–H/C–Br activation and cyclization in a two-step reactions with a total yield of 54%.^[12] Also, the sulfide group of **3m** could be oxidized to the sulfonyl group in 82% yield (Scheme 5).

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Scheme 4. Catalytic selenylation reaction.

To gain insight into the possible catalytic pathway of this reaction, a series of experiments were performed. Firstly, a hydrogen-deuterium exchange experiment was performed. Treatment of azobenzene (**1 a**) with D₂O led to significant deuterium scrambling (Scheme 6a), indicating that the cleavage of the *ortho*-C–H bond would be a reversible process. Then, the kinetic isotope effect values ($k_{\rm H}/k_{\rm D}$) for the parallel and intermolecular competitive reactions were determined to be 2.2 and 2.3, indicating that the arene C–H bond cleavage might be the rate-determining step (Scheme 6 b and c).

In addition, the five-membered rhodacycle complex I was successfully isolated by the reaction of **1a** with [Cp*RhCl₂]₂ (Scheme 7a); its structure was determined by X-ray crystallographic analysis, which suggested the catalytic process involves C–H activation.^[13] Further experiments confirmed the complex I was an efficient catalyst to promote the thiolation of **1a** with **2a**, giving the corresponding product **3a** in 86% yield (Scheme 7b). Meanwhile, the complex I could also be reacted with **2a** to give the desired product **3a** in 81% yield. These results indicated the five-membered rhodacycle complex I to be an intermediate in the catalytic cycle.

On the basis of our work and literature reports,^[8] a plausible reaction pathway is proposed (Scheme 8). First, the active $[Cp*Rh^{III}CI]^+$ species II is generated by the anion exchange of AgBF₄ with the starting material $[Cp*RhCI_2]_2$.^[10] Then, the central metal coordinates with the azo group, the ligand undergoing a directed reversible *ortho*-C–H bond activation to form the five-membered rhodacycle intermediate I, which then



Scheme 5. Derivatization reactions.

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Scheme 6. Preliminary mechanistic study.





[Cp*RhCl₂]₂

Scheme 8. Proposed catalytic pathway.

and catalysis by the intermediate Rh^{III} complex. The features of this reaction include exclusive regioselectivity and broad functional group tolerance. Further studies on other valuable synthetic reactions starting from azobenzene compounds are now in progress.



reacts with the disulfide, forming **3a** and the intermediate III. The product **3a** might also be obtained from III through reductive elimination. Cp*Rh¹ is formed, which was then oxidized to Rh^{III} by AgBF₄ to complete the catalytic cycle.

Conclusions

In summary, we developed a concise and effective methodology to achieve the direct Rh-catalyzed *ortho*-C–H activation and functionalization of azobenzenes with diaryl disulfides. The reaction mechanism was studied by H–D exchange experiments

Experimental Section

Typical procedure for the thiolation of C-H bonds

A Schlenk tube with a magnetic stirrer bar was charged with $[Cp*RhCl_2]_2$ (0.005 mmol), AgBF₄ (0.2 mmol), azobenzene (1 a, 0.3 mmol), diphenyl disulfide (2 a, 0.05 mmol) and DCE (1 mL). The resulting solution was stirred at the selected temperature. After 24 h, the mixture was diluted with dichloromethane and washed by water. The resulting organic layer was then concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1:100 v/v) to provide 3 a.

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Conflict of interest

The authors declare no conflict of interest.

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