JOC Note

Zinc-Mediated Palladium-Catalyzed Formation of Carbon−Sulfur Bonds

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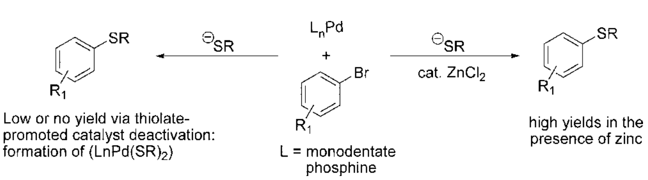

A catalytic amount of zinc chloride in combination with a palladium catalyst ligated by a monodentate phosphine allows the coupling of aryl and alkyl thiols with aryl bromides in high yields. The addition of zinc chloride to a palladium catalyst system that reportedly failed to promote sulfide formation allows this once ineffective catalyst system to provide the sulfide product in good yield. This paper describes a high-yielding and general monodentate phosphine-ligated palladium catalyst for biaryl and alkyl aryl sulfide formation.

Metal-catalyzed cross-coupling reactions have revolutionized how chemists synthesize small molecules. As evidence, a large number of reviews have been devoted to metal-catalyzed cross-coupling reactions.[1] Because of their ability to stabilize unsaturated metal complexes,[2] bulky monodentate phosphines are frequently used in combination with late transition metals as catalysts for many cross-coupling reactions.[1b] However, these catalysts typically do not promote the formation of carbon−sulfur bonds because of the displacement of these ligands by the thiolate coupling partners employed in these reactions.[3]

The challenge of finding a catalyst for the formation of carbon−sulfur bonds, as well as the presence of arylsulfides in drug candidates[4] has sparked the development of new technology to create this bond. A wide range of transition metals have been used to catalyze this coupling reaction, including palladium,[5] nickel,[6] copper,[7] cobalt,[8] and iron.[9] A highly general palladium catalyst to form biaryl sulfides and alkyl-aryl sulfides from aryl bromides and chlorides was reported recently by Hartwig.[5a] Hartwig's palladium catalyst is composed of a strongly coordinating bidentate ligand that resists displacement by the thiolate anion, likely the cause of catalyst deactivation in most of these reactions. For this reason, the use of palladium catalysts ligated by monodentate phosphine ligands to form these carbon−sulfur bonds has shown limited reaction scope, and in many cases, completely failed to promote this coupling reaction. The inefficiency of these catalysts to promote carbon−sulfur bond formation is likely caused by the displacement of the metal-bound phosphines by thiolates, producing an inactive catalyst.[5g] While preparing aryl ketones with the Fukuyama reaction,[10] the formation of an appreciable quantity of aryl sulfide in the presence of the palladium catalyst $[Pd(\mu\text{-}Br)(P^tBu_3)]_2$ (**1**) was observed (Scheme 1).[11] Because of the previously described failures of palladium complexes of monodentate phosphines to catalyze the formation of carbon−sulfur bonds from aryl halides and thiols, we decided to investigate the scope of this reaction and attempt to identify the factors that allow this transformation to occur.

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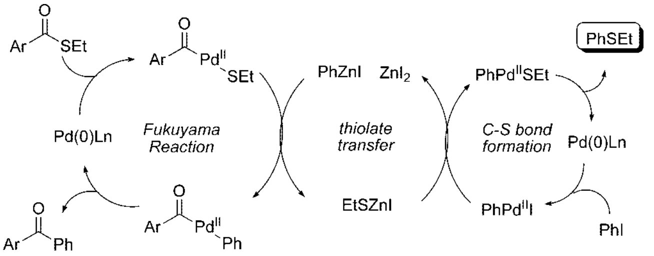
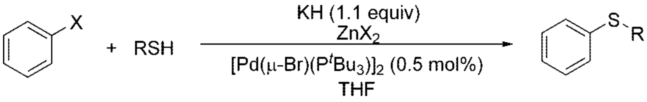
SCHEME 1. Potential Pathway for the Formation of Aryl Sulfides



The palladium-catalyzed Fukuyama reaction between a thioester and organozinc reagent produces the corresponding ketone with concomitant generation of a thiolate zinc halide, as shown in the proposed, generalized catalytic cycle. A possible role of the thiolate zinc halide may be to transfer the thiolate to palladium via transmetalation step under our Fukuyama conditions (Scheme 1). Under typical cross-coupling reaction conditions to form alkyl-aryl sulfides, the sodium or potassium thiolate is generated in situ from the corresponding base and thiol, exposing the palladium catalyst to a large excess of the thiolate. The zinc likely acts as an electrophilic buffer to protect the palladium center from attack by the thiol anions, because of the strong coordination between zinc and thiolate ligands.[12] However, the zinc−thiolate interaction is weak enough to allow transmetalation. Zinc metal has been employed in palladium-,[5c] nickel-,[6a] and cobalt-[8] catalyzed aryl sulfide syntheses; however, the role of zinc was to reduce the palladium(II), nickel(II), or cobalt(II) catalyst to palladium(0), nickel(0), and cobalt(I), respectively.

To investigate the scope of **1** as a catalyst for the formation of aryl sulfides, different reaction conditions were evaluated by modifying the identity and amount of the zinc reagent. Aryl and alkyl thiols were reacted in the presence of iodobenzene, base, and **1**. Upon initial investigations, it became apparent that the order of addition was extremely important. The thiol was added to a THF solution of aryl halide, base, zinc chloride, and **1**, and then reacted for 12 h. The results stemming from these reaction conditions were inconsistent. Reproducible results were obtained from the addition of thiol to a solution of the base in THF, followed by introduction of the zinc salt into this mixture with stirring, for 10 min. After this time, aryl halide was added to the reaction, followed by catalyst **1**, as a solution of THF (Table 1). Using these general reaction conditions, we discovered that zinc iodide and zinc chloride provided similar results, and that the optimum amount of zinc was slightly higher than 0.5 equiv. The reactions of iodobenzene and ethanethiol proceeded at ambient temperature, while reactions of iodobenzene and benzenethiol required warming to 60 °C. Similar reactions of bromobenzene and ethanethiol or benzenethiol required heating to 60 and 90 °C, respectively. In the absence of the zinc reagent, the reaction of bromobenzene and ethanethiol under our optimized conditions did not yield product. Interestingly, the corresponding reaction of bromobenzene and benzenethiol in the absence of zinc chloride did completely convert the starting materials to product. When zinc chloride was employed in the reaction of bromobenzene and benzenethiol, a catalytic amount of lithium iodide was necessary to increase the rate of the reaction. These results will be discussed in later sections (vide infra). Using the conditions described above and outlined in Table 1, several organic and inorganic bases that are commonplace in metal-catalyzed cross-coupling reactions were tested. The use of potassium hydride, sodium bis(trimethylsilyl) amide, or sodium *tert*-butoxide was found to give the highest yields of product among the bases screened. We chose to employ sodium *tert*-butoxide as base in these reactions because of its ease of handling.

TABLE 1. Screening Conditions for the Palladium-Catalyzed Arylation of Aryl and Alkyl Thiols[a]



entry	PhX	RSH	ZnX$_2$ (equiv)	*T* (°C)	*t* (h)	P:SM[b]
1	PhI	EtSH	ZnI$_2$ (1.1)	23	12	80:20
2	PhI	EtSH	ZnI$_2$ (0.5)	23	12	10:90
3	PhI	EtSH	ZnI$_2$ (0.64)	23	12	100:0
4	PhI	EtSH	ZnCl$_2$ (0.64)	23	12	100:0
5	PhI	PhSH	ZnCl$_2$ (0.64)	23	2	46:54
6	PhI	PhSH	ZnCl$_2$ (0.64)	60	2	100:0
7	PhBr	EtSH	ZnCl$_2$ (0.64)	23	2	4:96
8	PhBr	EtSH	ZnCl$_2$ (0.64)	60	2	98:2
9	PhBr	PhSH	ZnCl$_2$ (0.64)	60	2	24:76
10	PhBr	PhSH	ZnCl$_2$ (0.64)	90	2	100:0[c]
11	PhBr	PhSH	no zinc	90	2	100:0
12	PhBr	EtSH	no zinc	60	2	0:100

[a] See the Supporting Information for complete experimental procedures. [b] P:SM is the ratio of the sulfide product to starting aryl halide according to GC analysis. [c] LiI (0.5 equiv) was added.

With our optimized conditions in hand, we investigated the scope of the coupling reaction of aryl bromides and alkyl thiols using the monodentate phosphine ligated palladium catalyst **1**. As shown in Table 1, zinc chloride was necessary to allow the formation of the alkyl aryl sulfide. Unlike the reactions of aryl thiolates and aryl bromides, the addition of lithium iodide was not necessary, likely due to the increased nucleophilicity of the alkyl thiolates with respect to the aryl thiolates. Most all of the alkyl thiols employed were coupled with aryl bromides in excellent yields (Table 2). The use of ZnCl$_2$ (0.64 equiv) was necessary to ensure catalyst activity. The catalyst loading of **1** was low (0.5−2.0 mol %) and demonstrates the impressive ability of ZnCl$_2$ to keep the alkyl thiolate from decomposing the palladium catalyst. Most of the reactions were complete within 1−2 h. Unactivated aryl halides (entries 1 and 2) and aryl halides containing electron-withdrawing groups (entries 3−5) or electron-donating groups (entries 6−9) were competent partners in this coupling reaction. The use of hindered aryl bromides (entries 7−9) or heterocyclic aryl bromides (entries 10 and 11) also formed the corresponding sulfide product in good yields. Although seemingly unaffected by the presence of the indole, the interaction of 2-pyridyl bromide and zinc chloride under our standard conditions failed to produce the corresponding aryl sulfide product. The affinity of the zinc reagent toward the pyridyl group may allow faster decomposition of the palladium catalyst because of the formation of pyridyl complexes of zinc.[13] In the absence of zinc and at a higher catalyst loading, *tert*-butyl-2-pyridyl sulfide was formed in 46% yield.

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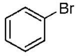
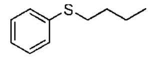
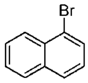
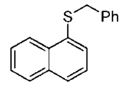
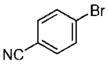
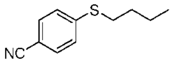
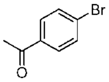
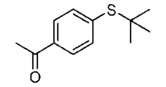
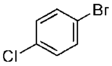
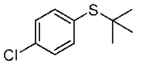
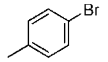
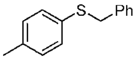
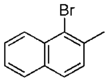
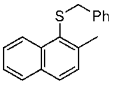
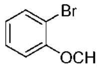
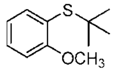
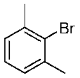
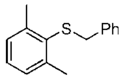
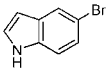
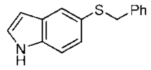
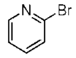
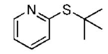
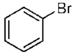
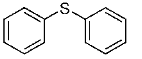
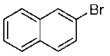
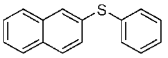
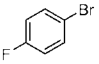
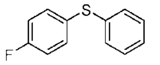
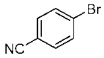
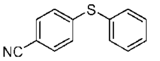
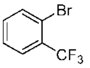
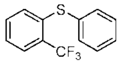
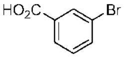
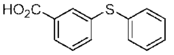
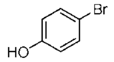
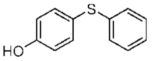
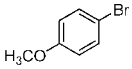
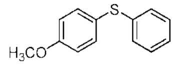
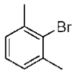
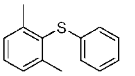
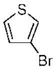
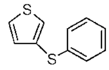
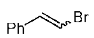
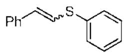
TABLE 2. Palladium-Catalyzed Arylation of Alkyl Thiols

entry	RBr	product	cat. (mol %)	yield[b]
1			1	99
2			1	99
3			1	99
4[c]			0.5	99[d]
5[c]			1	97[d]
6			1	94
7			1	99
8[c]			1	84[d]
9			2	99
10			1	99
11[c]			2	46[d]

[a] See the Supporting Information for complete experimental procedures. [b] Yield is an average of two reactions. [c] KH (1.1 equiv) was used as base. [d] Yield was determined by ^{1}H NMR spectroscopy.

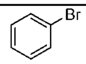
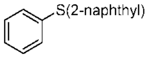
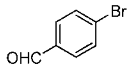
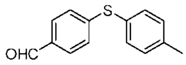
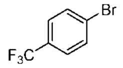
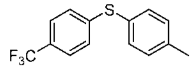
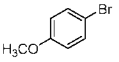
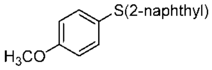
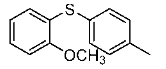
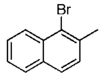
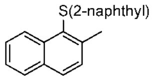
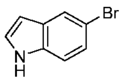
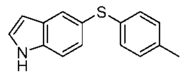
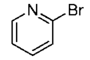
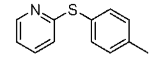
We have established our current catalyst and conditions to promote the coupling of aryl bromides and alkyl thiols in high yields and with low catalyst loading. To examine the broad applicability of this catalyst system in the formation of carbon−sulfur bonds, we next examined reactions of aryl bromides and aryl thiols. The conditions described in Table 2 (cat. **1**, $ZnCl_2$, NaO^{t}Bu) were applied to the palladium-catalyzed cross-coupling reactions of aryl bromides and benzenethiol. In the absence of lithium iodide, most of the reactions were quite sluggish and provided low yields. However, the addition of a substoichiometric amount of lithium iodide increased the rate of the reaction dramatically. The beneficial effect of LiI may be explained by the previously described anionic effects that are observed in related palladium-catalyzed reactions.[14] With these modified conditions, a number of diverse bromide coupling partners were employed (Table 3). Once again, electronic or steric factors of the aryl bromide did not greatly influence the yields of these reactions. This catalyst system also tolerated the presence of functional groups, such as cyano (entry 4), carboxylic acid (entry 6), and hydroxy (entry 7), without a significant loss in overall yield. The reactions of substrates that contained acidic functional groups were conducted in the presence of 2.3 equiv of NaO^{t}Bu. 3-Bromothiophene reacted with benzenethiol to give the corresponding sulfide in 96% yield (entry 10). These reaction conditions also catalyzed the coupling of β-bromostyrene and benzenethiol in high yield and without erosion of the double-bond stereoisomeric ratio (entry 11).

TABLE 3. Palladium-Catalyzed Arylation of Benzenethiol[a]

entry	RBr	product	cat. (mol %)	yield[b]
1			0.5	97
2			0.9	99
3			1	94
4			0.9	99
5			0.9	99
6[c]			1	77
7[c]			1	95
8			0.5	99
9			1.3	99
10			1	96
11			1	96[d]

[a] See the Supporting Information for complete experimental procedures. [b] Yield is an average of two reactions. [c] 2.3 equiv of NaO^{t}Bu was used. [d] E:Z = 85:15 for starting material and product.

TABLE 4. Palladium-Catalyzed Arylation of Thiocresol and 2-Naphthalenethiol[a]

entry	RBr	product	cat. (mol %)	yield[b]
1			0.6	96
2			0.5	92
3			0.6	94
4			0.6	98
5			0.5	99
6			0.6	99
7			0.5	97
8[c]			2.0	47[d]

[a] See the Supporting Information for complete experimental procedures. [b] Yield is an average of two reactions. [c] KH (1.1 equiv) used as base, $ZnCl_2$ and LiI were not used. [d] Yield determined by ^{1}H NMR spectroscopy.

This chemistry was then extended to palladium-catalyzed arylations of thiocresol and 2-naphthalenethiol (Table 4). As expected, the reactions proceeded smoothly to the desired products with low loadings of palladium catalysts. Most all of the substrates that were examined are listed in Table 4, as

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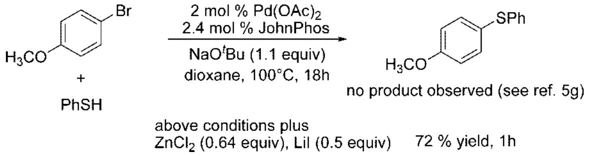
(14) Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 5–314.

catalyst **1** is general in scope. The rapid and relatively mild reaction conditions allowed the reaction of 4-bromobenzaldehyde and thiocresol to proceed in almost quantitative yield. As seen in the cross-coupling reaction of 2-bromopyridine and *tert*-butyl thiol in Table 2, the reaction of 2-bromopyridine and thiocresol provided mediocre yields of the desired product, even in the presence of 2 mol % of palladium catalyst **1**.

We were interested to see if the benefit of zinc to keep the thiolate away from the palladium until the transmetalation step had the same effect on previous catalysts employed in the palladium-catalyzed formation of carbon−sulfur bonds. Therefore, we examined a result reported by Buchwald and coworkers in 2004 (eq 1). Buchwald reported that the reaction of 4-bromoanisole and benzenethiol in the presence of a catalytic amount of palladium acetate and the monodentate ligand, JohnPhos (2-(di-*tert*-butylphosphino)biphenyl, failed to produce the corresponding diaryl sulfide. Presumably, benzenethiolate is deactivating the palladium catalyst via displacement of the monodentate phosphine ligand. Indeed, the addition of 0.64 equiv of zinc chloride and 0.5 equiv of lithium iodide to the catalyst generated from palladium acetate and JohnPhos afforded the desired product in 72% yield. The addition of lithium iodide (0.5 equiv) to the reaction mixture described in eq 1, in the absence of zinc chloride, failed to provide any biaryl sulfide product after 4 h.



(1)

From the observations of the reactions presented, we believe that zinc is moderating the reactivity of the thiolate anion to ensure that the palladium catalyst is not deactivated. Below is a summary of the findings in this study:

(1) Reactions with alkyl thiolates: The addition of an excess of alkyl thiolate to **1** causes catalyst deactivation. The addition of a zinc salt, such as zinc chloride, prevents catalyst deactivation, most likely due to the strong affinity that zinc has for thiolate anion. Importantly, the thiolate complex is still allowed to participate in the transmetalation step, and the addition of lithium iodide is not needed in these reactions.

(2) Reactions with aryl thiolates: The addition of most aryl thiolates to **1** does not appear to deactivate the catalyst. However, the use of zinc in these reactions allows for cleaner, higher yielding transformations. Furthermore, we observed that some aryl bromides, such as 3-bromothiophene and 4-bromobenzaldehyde, absolutely required the addition of zinc chloride and lithium iodide. Lithium iodide was always necessary when zinc chloride was used in reactions of arylthiolates. Under these reaction conditions, lithium iodide may likely undergo a halogen exchange reaction with the arylpalladium(II) bromide that is generated from the oxidative addition of aryl bromide to the unsaturated palladium(0) complex; however, this newly formed arylpalladium(II) iodide complex might undergo a slower transmetalation with the zinc thiolate complex.[15] Therefore, the lithium salt may promote the reaction via anionic effect, or somehow increase the rate of transmetalation by interaction with the zinc thiolate. As expected, the thiolate anion is less reactive, relative to potassium or sodium thiolates, when zinc is the counterion.

In summary, we have reported a monodentate-ligated palladium catalyst that promotes the formation of alkyl-aryl and biaryl sulfides from the corresponding aryl halides and alkyl or aryl thiolates. The previous catalytic deactivation pathway observed when using catalysts of this type in palladium-catalyzed carbon−sulfur bond formations is avoided by employing a substoichiometric amount of zinc chloride. The zinc acts to shield the palladium center from direct attack by the thiolate anion, which ultimately would lead to catalyst deactivation via displacement of the monodentate phosphine ligand. The benefit of zinc in this chemistry is not limited to catalyst **1**, but can also allow palladium-catalyzed carbon−sulfur bond formations of previously reported unreactive catalysts. These newly developed catalytic conditions provide an alternative to the use of bidentate phosphine ligands for these reactions, demonstrate the importance of zinc thiolate interactions in organometallic chemistry,[12a] as well as present an alternative strategy that employs a catalytic amount of zinc to combat catalyst deactivation via nucleophilic reagents.

Experimental Section

Typical Procedure. Under an inert atmosphere, THF (0.4 mL) is added to a septum-capped vial containing NaO^tBu (106 mg, 1.10 mmol) and a stir bar. Benzylthiol (118 μL, 1.00 mmol) is added and the reaction mixture is stirred for 10 min. At this time, $ZnCl_2$ (87 mg, 0.64 mmol) in THF (0.4 mL) is added and the reaction mixture is stirred for 10 min. To this reaction mixture was added 1-bromonaphthalene (139 μL, 1.00 mmol) followed by $[Pd(\mu\text{-}Br)(P^tBu_3)]_2$ (**1**) (7.7 mg, 0.0099 mmol) in THF (0.4 mL). The reaction is stirred at 60 °C for 1 h. At this time, silica gel is added to the reaction and the solvent is removed under vacuum. Purification by column chromatography yields the sulfide (250 mg, 1.00 mmol, 100% yield) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 4.15 (s, 2H), 7.19−7.27 (m, 5H), 7.32−7.36 (m, 1H), 7.47−7.56 (m, 3H), 7.73 (d, $J = 8$ Hz, 1H), 7.84 (d, $J = 8$ Hz, 1H), 8.42 (d, $J = 8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.5, 125.2, 125.7, 126.3, 126.6, 127.3, 128.6, 128.7, 129.1, 129.4, 133.2, 133.5, 134.0, 137.6; HRMS (ESI) calcd for $C_{17}H_{14}S$ $[M + Na]^+$ 273.0708, found 273.0712.

Acknowledgement. This work was generously supported by Ohio State University. We also thank Johnson-Matthey for the generous gift of $[Pd(\mu\text{-}Br)(P^tBu_3)]_2$.

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

JO900385D

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[15] Casado, A. L.; Espinet, P. *J. Am. Chem. Soc.* **1998**, *120*, 8978.