

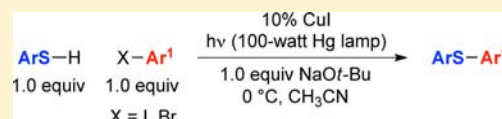
# A New Family of Nucleophiles for Photoinduced, Copper-Catalyzed Cross-Couplings via Single-Electron Transfer: Reactions of Thiols with Aryl Halides Under Mild Conditions (0 °C)

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**S** Supporting Information

**ABSTRACT:** Building on the known photophysical properties of well-defined copper–carbazolide complexes, we have recently described photoinduced, copper-catalyzed N-arylations and N-alkylations of carbazoles. Until now, there have been no examples of the use of other families of heteroatom nucleophiles in such photoinduced processes. Herein, we report a versatile photoinduced, copper-catalyzed method for coupling aryl thiols with aryl halides, wherein a single set of reaction conditions, using inexpensive CuI as a precatalyst without the need for an added ligand, is effective for a wide range of coupling partners. As far as we are aware, copper-catalyzed C–S cross-couplings at 0 °C have not previously been achieved, which renders our observation of efficient reaction of an unactivated aryl iodide at –40 °C especially striking. Mechanistic investigations are consistent with these photoinduced C–S cross-couplings following a SET/radical pathway for C–X bond cleavage (via a Cu(I)–thiolate), which contrasts with nonphotoinduced, copper-catalyzed processes wherein a concerted mechanism is believed to occur.

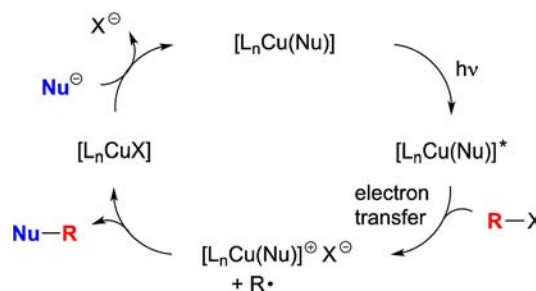


## INTRODUCTION

Transition-metal-catalyzed cross-coupling reactions that furnish carbon–heteroatom bonds are a powerful tool for the synthesis of fine chemicals, pharmaceuticals, and materials.<sup>1–3</sup> The use of thiols as the nucleophilic coupling partner affords access to sulfides (and therefore sulfoxides), important families of target molecules.<sup>4,5</sup> Cross-couplings catalyzed by palladium provide a useful approach to C–S bond construction,<sup>6</sup> although the cost of palladium and of the ligands that are typically required to achieve efficient catalysis has stimulated the development of complementary catalysts based on copper. Noteworthy progress has been described in copper-catalyzed C–S cross-couplings with aryl halides, although an elevated reaction temperature (≥50 °C) is almost always necessary.<sup>6a,b,7,8</sup>

We have recently reported photoinduced, copper-catalyzed C–N bond-forming reactions of carbazoles, specifically, N-phenylations and N-alkylations.<sup>9</sup> We hypothesize that these couplings may proceed via single electron transfer (SET) from an excited state of a Cu(I)–carbazolide complex to the organic electrophile (Figure 1).

One of the attractive features of photoinduced, copper-catalyzed C–N coupling reactions is that they can proceed at an unusually low temperature; for example, in the case of the phenylation of carbazole with iodobenzene, we observed several turnovers upon photolysis at –40 °C. In our initial investigations of photoinduced, copper-catalyzed cross-couplings, we focused on the use of carbazoles as nucleophiles, due to our knowledge of the photophysical properties of well-defined Cu(I)–carbazolide complexes.<sup>10</sup> Nevertheless, we hoped that this photoinduced SET strategy for copper-catalyzed cross-coupling might be generalizable to other nucleophiles for which



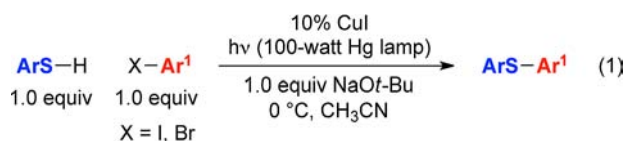
**Figure 1.** Outline of a possible mechanism for photoinduced, copper-catalyzed cross-coupling reactions. For the sake of simplicity, the copper complex that undergoes excitation ( $[L_nCu(Nu)]$ ) is depicted as uncharged.

an excited state of a Cu(I)–nucleophile adduct is accessible and sufficiently reducing to participate in SET with an electrophilic coupling partner.

In this report, we establish for the first time that photoinduced, copper-catalyzed cross-couplings can be accomplished with heteroatom nucleophiles other than carbazoles. Specifically, we demonstrate that C–S bond formation between thiols and aryl halides can be achieved using a simple method with an inexpensive precatalyst (CuI) under unusually mild conditions (0 °C or below) (eq 1). Our mechanistic observations are consistent with the pathway outlined in Figure 1, involving SET and a radical intermediate, thereby supporting the suggestion

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that this strategy for effecting cross-coupling may have substantial generality.

## RESULTS AND DISCUSSION

Under our standard conditions, thiophenol and 1-iodo-3,5-dimethylbenzene underwent C–S cross-coupling in good yield (85%) upon irradiation with a 100 W Hg lamp for 5 h at 0 °C in the presence of 10% CuI (Table 1, entry 1). A variety of

**Table 1. Photoinduced, Copper-Catalyzed C–S Couplings: Effect of Reaction Parameters**

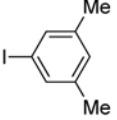
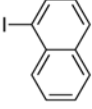


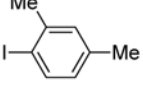
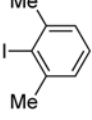
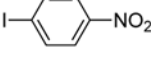
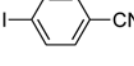
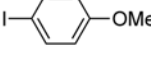
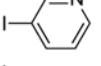
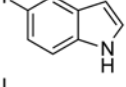


entry	variation from the standard conditions	yield (%) <sup>a</sup>
1	none	85
2	no CuI	10
3	no light	<1
4	no CuI and no light	<1
5	ambient light	<1
6	100 W Hg lamp, filtering out wavelengths <500 nm	<1
7	no NaOt-Bu	<1
8	LiOt-Bu instead of NaOt-Bu	69
9	KOt-Bu instead of NaOt-Bu	72
10	Cs <sub>2</sub> CO <sub>3</sub> instead of NaOt-Bu	39
11	CuCl <sub>2</sub> instead of CuI	65
12	Cu powder instead of CuI	25
13	[Cu <sub>5</sub> (SPh) <sub>7</sub> ][Na(12-crown-4)] <sub>2</sub> (1) <sup>b</sup> instead of CuI	80
14	5% CuI	57

<sup>a</sup>Yield obtained via calibrated GC analysis with the aid of an internal standard (average of two experiments). Scale of reaction: 0.33 mmol of each coupling partner. <sup>b</sup>10% loading of copper-atom equivalents.

control reactions established the importance of the copper catalyst and of the light (entries 2–6).<sup>11</sup> Essentially no cross-coupling was observed in the absence of NaOt-Bu (entry 7), whereas the identity of the alkali-metal cation associated with the *t*-butoxide base had a rather small impact on C–S bond formation (entries 8 and 9). Use of Cs<sub>2</sub>CO<sub>3</sub> as the Brønsted base resulted in a significant amount of the desired product (entry 10), although the coupling was less efficient than with NaOt-Bu. When CuCl<sub>2</sub> was employed in place of CuI, the formation of PhSSPh, possibly due to sacrificial oxidation of the thiolate to reduce the Cu(II) precatalyst, accompanied the generation of the diaryl sulfide (entry 11). Use of 5%, rather than 10%, CuI led to a lower yield of the coupling product (entry 14).

This mild, photoinduced method for C–S cross-coupling has broad scope. With respect to the aryl iodide, 1-iodonaphthalene and ortho-substituted electrophiles were suitable substrates (Table 2, entries 2–6), including a very hindered 2,6-disubstituted compound (entry 6). Furthermore, both activated and deactivated aryl iodides could be cross-coupled (entries 7–9). The method is compatible with a wide range of functional groups, including an aryl fluoride, a primary aniline,

**Table 2. Photoinduced, Copper-Catalyzed C–S Couplings: Scope with Respect to the Aryl Iodide**

entry	I–Ar <sup>1</sup>	yield (%) <sup>a</sup>
1		88
2		82
3		78
4		75
5		78
6		73
7		90
8		79
9		79
10		82
11		63
12		71
13		65

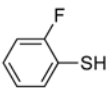
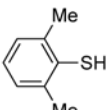
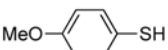
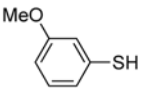
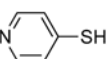
<sup>a</sup>Yield of purified product (average of two experiments). Scale of reaction: 1.0 mmol of each coupling partner.

a nitro group, a nitrile, an ether, a pyridine, an indole, and a thiophene.<sup>12</sup>

With respect to the aryl thiol, a diverse array of nucleophiles serves as suitable cross-coupling partners. Thus, hindered, electron-rich and electron-poor, and heterocyclic thiols reacted with an aryl iodide to generate a C–S bond in good yield (Table 3).

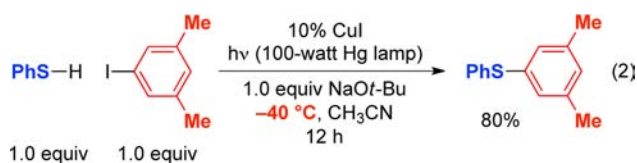
For the sake of convenience, we routinely conduct these photoinduced, copper-catalyzed cross-couplings of thiols with aryl iodides at 0 °C. However, we have determined that a very good yield of the desired product could also be obtained at –40 °C (eq 2). This observation stands in contrast to other

**Table 3. Photoinduced, Copper-Catalyzed C–S Couplings: Scope with Respect to the Aryl Thiol**

entry	ArS–H	yield (%) <sup>a</sup>
1		73
2		71
3		81
4		65
5		74



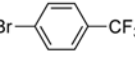
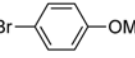
<sup>a</sup>Yield of purified product (average of two experiments). Scale of reaction: 1.0 mmol of each coupling partner.

copper-catalyzed C–S couplings, which are almost always carried out at  $\geq 50$  °C.<sup>6a,b,7,8</sup>



In copper-catalyzed cross-coupling reactions, aryl bromides are often significantly less reactive than the corresponding iodides.<sup>13</sup> Nevertheless, we have determined that, under the same conditions that we employed for aryl iodides, an array of bromides underwent photoinduced, CuI-catalyzed cross-coupling with aryl thiols (Table 4); not unexpectedly, the reaction times were somewhat longer for bromides than for iodides (12–24 versus 5–8 h). Hindered, electron-poor, and electron-rich

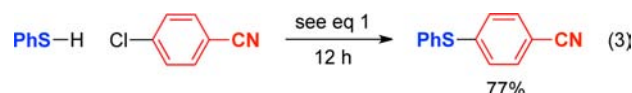
**Table 4. Photoinduced, Copper-Catalyzed C–S Couplings: Aryl Bromides as Coupling Partners**

entry	Br–Ar <sup>1</sup>	yield (%) <sup>a</sup>
1		73
2		59
3		70
4		64

<sup>a</sup>Yield of purified product (average of two experiments). Scale of reaction: 1.0 mmol of each coupling partner.

aryl bromides reacted with thiophenol upon irradiation at 0 °C. We are not aware of previous reports of copper-catalyzed couplings of thiols with aryl bromides that proceed below 60 °C.

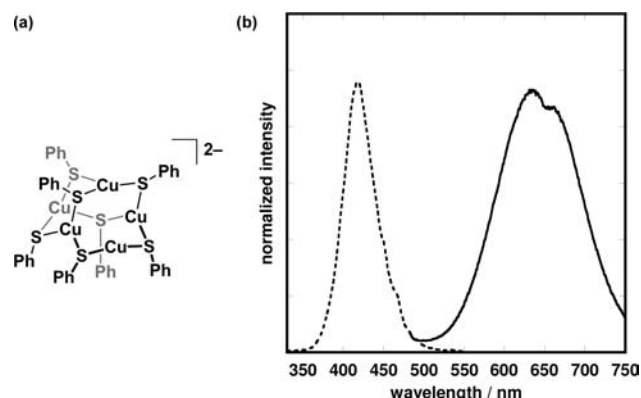
Furthermore, photoinduced coupling of a thiol with an activated aryl chloride could be achieved at 0 °C (eq 3). To the best of our knowledge, such electrophiles have not been reported to participate in copper-catalyzed C–S cross-couplings at a temperature below 60 °C.



As discussed above, from the outset we were interested in determining the generality of the proposed SET/radical-based pathway for photoinduced, copper-catalyzed cross-couplings (Figure 1) in the case of nucleophiles other than carbazoles. For the C–S couplings described herein, our working hypothesis is that a Cu(I)–thiolate is likely undergoing excitation. In fact, the photophysical properties of Cu(I)–thiolates have previously been explored by others, due in part to the occurrence of such motifs in metal-binding proteins;<sup>14</sup> furthermore, polynuclear copper clusters bearing anionic sulfur ligands have been observed to exhibit luminescence that is susceptible to quenching by outer-sphere oxidants.<sup>15</sup>

In order to identify copper species that might be relevant to the mechanism of photoinduced C–S cross-couplings, an aliquot from the reaction of thiophenol with 1-iodo-3,5-dimethylbenzene was analyzed by ESI–MS after 1 h of irradiation at 0 °C. Two prominent negatively charged ion signals, corresponding to  $[\text{Cu}(\text{SPh})_2]^-$  and  $[\text{Cu}_2(\text{SPh})_3]^-$ , were observed.<sup>16</sup>

By combining equimolar amounts of CuI, PhSH, and NaOt-Bu in  $\text{CH}_3\text{CN}$ , followed by filtration and the addition of excess 12-crown-4, we were able to obtain pale-yellow crystals of a Cu(I)–thiolate complex,  $[\text{Cu}_5(\text{SPh})_7][\text{Na}(12\text{-crown-4})_2]_2$  (**1**). The X-ray crystal structure revealed a distorted tetrahedral arrangement of four Cu centers, with a fifth Cu inserted along one edge (Figure 2a).<sup>17</sup> All of the thiolates occupy bridging positions.



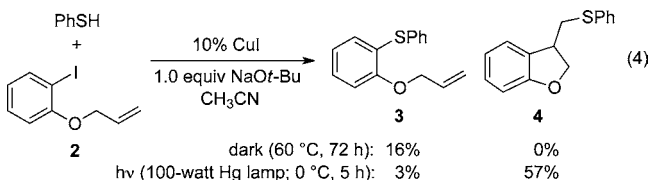
**Figure 2.** (a) Representation of the solid-state structure of  $[\text{Cu}_5(\text{SPh})_7][\text{Na}(12\text{-crown-4})_2]_2$  (**1**). (b) Excitation spectrum at 635 nm emission (dotted line) and emission spectrum at 418 nm excitation (solid line) for **1** in  $\text{CH}_3\text{CN}$  at room temperature.

Solutions of copper complex **1** in  $\text{CH}_3\text{CN}$  exhibited the same two predominant ESI–MS signals ( $[\text{Cu}(\text{SPh})_2]^-$  and  $[\text{Cu}_2(\text{SPh})_3]^-$ ) as observed under the catalytic reaction conditions, suggestive of solution equilibria that lead to a Cu(I)–thiolate

speciation that differs from the solid-state structure. Although solutions of complex **1** in CH<sub>3</sub>CN were not visibly luminescent, an emissive state is accessible upon excitation at short wavelengths in the visible spectrum (excitation maximum at 418 nm; Figure 2b). Consistent with these photophysical properties, no C–S coupling was observed when a filter that blocked wavelengths <500 nm was applied to the light source (Table 1, entry 6).

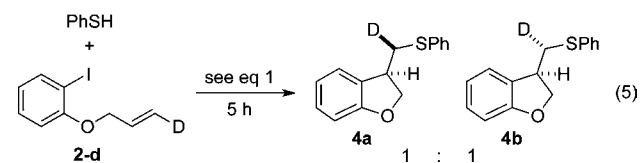
Under our standard C–S cross-coupling conditions, copper complex **1** served as a competent precatalyst (Table 1, entry 13). Furthermore, upon irradiation at 0 °C, it reacted directly with 1-iodo-3,5-dimethylbenzene (7.0 equiv with respect to **1**) to provide 2.5 equiv of the coupled product.

The possible intermediacy of an aryl radical (R· in Figure 1) in these photoinduced C–S couplings was assessed with the aid of an aryl iodide bearing a pendant olefin (eq 4).<sup>7a,9a</sup> The radical



generated by cleavage of the C–I bond of compound **2** has been reported to rapidly cyclize to the dihydrobenzofuran with a unimolecular rate constant of  $9.6 \times 10^9 \text{ s}^{-1}$  in DMSO.<sup>18</sup> Whereas reaction of aryl iodide **2** with PhSH in the dark at 60 °C for 72 h furnished only the uncyclized product (**3**) in low yield,<sup>19</sup> the photoinduced coupling provided cyclized product **4** with high selectivity. The observation of cyclization under photochemical conditions not only has mechanistic implications but also underscores the potential of SET-initiated reactions to access tandem processes that complement non-photoinduced pathways.

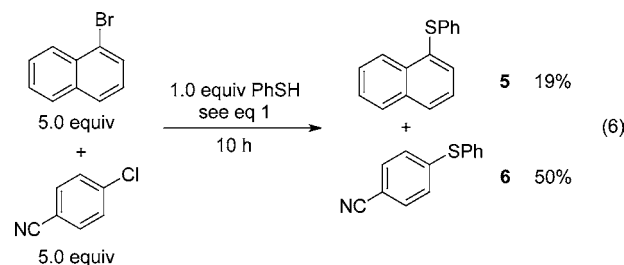
Aryl iodide **2-d**, a monodeuterated variant of **2**, reacted to form a 1:1 mixture of diastereomeric dihydrobenzofurans **4a** and **4b** (eq 5), as expected for the putative radical intermediate



generated upon addition of the aryl radical to the pendant olefin. On the other hand, a pathway involving only concerted oxidative addition, *syn*  $\beta$ -migratory insertion, and then reductive elimination would be expected to yield a single diastereomer (**4a**).<sup>9a</sup>

Further support for a mechanism involving one-electron reduction of the aryl halide, as opposed to concerted oxidative addition, was obtained from a competition experiment between 1-bromonaphthalene and 4-chlorobenzonitrile. While selective activation of the weaker C–Br has been viewed as supporting a concerted mechanism for oxidative addition, the opposite selectivity is expected for an SET pathway, based on the relative outer-sphere reduction potentials (–2.03 V for 4-chlorobenzonitrile and –2.17 V for 1-bromonaphthalene vs SCE in DMF).<sup>20</sup>

Under our conditions for photoinduced C–S coupling, the ratio of products in this competition experiment was 2.6:1 in



favor of activation of the C–Cl bond (eq 6), consistent with the expectation for an SET mechanism.<sup>21</sup> In a previous report of a nonphotoinduced, copper-mediated C–S cross-coupling (DMSO, 110 °C), exclusive reaction of 1-bromonaphthalene was observed in the presence of 4-chlorobenzonitrile.<sup>7a</sup>

## CONCLUSION

We have described a mild and versatile photoinduced, copper-catalyzed method for cross-coupling aryl thiols with aryl halides. This study provides the first evidence that the approach that we have recently reported for photoinduced N-phenylation and N-alkylation of carbazoles is viable for other nucleophiles. Key features of the present method include the use of a single set of reaction conditions for the efficient coupling of a broad range of aryl thiols with a wide array of functionalized aryl halides (iodides and bromides), including hindered, electron-poor and electron-rich, and heterocyclic partners, at 0 °C with a 1:1:1 stoichiometry of thiol:halide:base. To the best of our knowledge, copper-catalyzed C–S cross-couplings at 0 °C have not previously been described; in this respect, our observation that we can achieve a photoinduced reaction of an unactivated aryl iodide at –40 °C is especially striking. A simple and inexpensive precatalyst (CuI) is employed, and no ligand coadditive is necessary. A series of mechanistic studies are consistent with these photoinduced C–S couplings proceeding through the proposed SET/radical pathway (via a Cu(I)–thiolate), in contrast with previously reported nonphotoinduced reactions, wherein C–X bond cleavage is generally believed to occur via concerted oxidative addition to copper. Ongoing studies are directed at developing other photoinduced coupling reactions and elucidating the mechanism of these processes.

## EXPERIMENTAL SECTION

**Representative Procedure.** Under an atmosphere of N<sub>2</sub>, a borosilicate glass tube was charged in turn with CuI (0.10 mmol, 10%), NaOt-Bu (1.0 mmol, 1.0 equiv), CH<sub>3</sub>CN (3.0 mL), the aryl halide (1.0 mmol, 1.0 equiv), and the aryl thiol (1.0 mmol, 1.0 equiv). The tube was sealed with a rubber septum, and then the heterogeneous reaction mixture was stirred at 0 °C, irradiating with a 100 W Hg lamp. After 5–24 h, the volatiles were removed under reduced pressure. The residue was suspended in Et<sub>2</sub>O, and the mixture was filtered through a short plug of Celite. The filtrate was concentrated, and the residue was purified by column chromatography.

## ASSOCIATED CONTENT

### Supporting Information

Experimental procedures and product characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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(9) (a) Creutz, S. E.; Lotito, K. J.; Fu, G. C.; Peters, J. C. *Science* **2012**, *338*, 647–651. (b) Bissember, A. C.; Lundgren, R. J.; Creutz, S. E.; Peters, J. C.; Fu, G. C. *Angew. Chem., Int. Ed.* **2013**, *52*, 5129–5133.

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(11) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173–3174.

(12) (a) On a gram-scale (1.40 g of product), the coupling illustrated in entry 1 of Table 2 proceeded in 82% yield. (b) In preliminary experiments under our standard conditions, a ketone was compatible with the reaction conditions, but an ester and an aldehyde were not.

(13) For leading references, see: Beletskaya, I. P.; Cheprakov, A. V. *Organometallics* **2012**, *31*, 7753–7808.

(14) For example, see: (a) Beltrami, M.; Lerch, K. *FEBS Lett.* **1981**, *127*, 201–203. (b) Li, Y. J.; Weser, U. *Inorg. Chem.* **1992**, *31*, 5526–5533. (c) Green, A. R.; Presta, A.; Gasyna, Z.; Stillman, M. J. *Inorg. Chem.* **1994**, *33*, 4159–4168.

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(16) [Cu(SPh)<sub>2</sub>]<sup>−</sup> has also been detected in ESI–MS studies of the nonphotoinduced, CuI/1,10-phenanthroline-catalyzed C–S cross-coupling of thiophenol with iodobenzene (120 °C in toluene): Cheng, S.-W.; Tseng, M.-C.; Lii, K.-H.; Lee, C.-R.; Shyu, S.-G. *Chem. Commun.* **2011**, *47*, 5599–5601.

(17) While the X-ray data were of sufficient quality to establish the connectivity of copper complex **1**, the structure suffered from a high degree of disorder in one of the thiolate ligands and in the encapsulated sodium cations. A directly analogous [Cu<sub>5</sub>(SPh)<sub>7</sub>]<sup>2−</sup> complex has been structurally characterized with Me<sub>4</sub>N<sup>+</sup> counterions: Dance, I. G. *J. Chem. Soc., Chem. Commun.* **1976**, 103–104.

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(19) Similarly, Hartwig has reported that the reaction of a Cu(I)–thiolate with aryl iodide **2** in DMSO at 110 °C afforded only acyclic products, suggesting that an aryl radical is not an intermediate (ref 7a).

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