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Synthesis of Copper(I) Thiolate Complexes in the Thioetherification of Aryl Halides

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Supporting Information

ABSTRACT: The copper(I) thiophenolato complexes 1–3 containing 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (Me₂phen) were isolated in excellent yields from reactions of $[CuOtBu]_4$ with the dative ligands and subsequent addition of 1 equiv of arenethiol. These complexes were characterized spectroscopically and crystallographically. X-ray structural analysis of a single crystal of $[(phen)Cu(\mu - SC_6H_5)]_2$ (1) revealed that this complex adopts a neutral



dimeric form with a weak Cu–Cu bonding interaction. These complexes were found to react with iodoarenes to form aryl sulfide products. The intermediacy of such complexes in copper-catalyzed thioetherification of aryl halides was demonstrated by the reactivity with p-tolyl iodide and o-tolyl iodide to form two aryl thioethers with selectivities similar to those of catalytic reactions conducted with the same two iodoarenes.

INTRODUCTION

Much research has focused on the development of copper catalysis in organic synthesis during the past decade.¹⁻¹² When simple ligands are used, the catalysts are inexpensive and less toxic than those based on precious metals. Copper-catalyzed coupling reactions to form C(aryl)-C, C(aryl)-N, and C(aryl)-O bonds starting from aryl halides and suitable reagents have been a particular focus of this work. Given the importance of aryl sulfides and their derivatives in numerous biologically and pharmaceutically active compounds,^{13–19} copper-catalyzed C(aryl)-S bond-forming reactions (eq 1)^{20–30} have been developed. However, this reaction has

$$R^{1} \xrightarrow{I_{1}} X + R^{2} \xrightarrow{I_{1}} SH \xrightarrow{[Cu]} R^{1} \xrightarrow{I_{1}} S \xrightarrow{I_{1}} R^{2}$$
(1)

been studied much less than other copper-catalyzed couplings.³¹ Most relevant to the work described here, no studies on the mechanism of copper-catalyzed coupling of thiol nucleophiles by ligated copper systems have been reported.

A series of ligands have been used with different copper precursors for the coupling of thiols with aryl halides, including ethylene glycol,³² neocuproine,³³ 1,2-diamine derivatives,³⁴ 1,1,1-tris(hydroxymethyl)ethane,³⁵ amino acids,³⁶ and β -keto esters.^{37,38} These ligands have been proposed to increase the catalyst solubility or stability and prevent aggregation of the metal, but the identity of thiolate complexes containing these ligands and the reactions of these complexes with haloareness have not been reported.

Liebeskind and co-workers proposed that the coupling of boronic acids and *N*-thioimides proceeded through a combination of Cu^I and Cu^{III} species.³⁹ More recently,

Liebeskind and Musaev et al. reported a density functional theory study on the mechanism of the CuI-templated aerobic cross-coupling of thiol esters with boronic acids to form ketones in which the nature of the active oxidized species $[LC(O)R^1]Cu-(O_2)-Cu[LC(O)R^1]^{2+}$ in these reactions was assessed.⁴⁰ In addition, Punniyamurthy and co-workers suggested that the C–S cross-coupling of thiols with aryl halides occurs by oxidative addition of RX to form the intermediate L_nRCuX followed by reductive elimination of $L_nRCuSAr$.⁴¹ However, the composition of the species that undergo these steps has not been established.

Recent contributions from our laboratory include the synthesis, characterization, and reactivity of a series of copper(I) imidate, amidate, amido, and phenoxide complexes that are chemically and kinetically competent to be intermediates in Ullmann reactions.^{42–44} This information has clarified several mechanistic questions about copper-catalyzed coupling reactions. In brief, the phenoxide and amidate complexes adopt ionic structures consisting of a copper cation containing two bidentate dative ligands and a copper anion containing two of the anionic ligands. These structures were shown to be the most stable form of these complexes in the solid state and in solution. Here, we report the preparation and isolation of copper(I) thiophenolato complexes, the structures of these species, and their reactions with aryl iodides. The structures of these species are distinct from those of the analogous copper(I) phenoxide complexes.

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RESULTS AND DISCUSSION

Synthesis of Copper(I) Thiophenolato and Alkanethiolate Complexes. A series of copper(I) thiophenolato complexes containing 1,10-phenanthroline (phen) and 2,9dimethyl-1,10-phenanthroline (Me₂phen) were prepared by the methods outlined in Scheme 1. Treatment of $[CuOtBu]_4$ with



the dative ligand and subsequent addition of 1 equiv of arenethiol resulted in the formation of complexes 1-3, containing phen and Me₂phen as the ancillary dative ligand. These complexes were isolated in excellent yields (81-86% yield). All these Cu(I) thiophenolates are diamagnetic and were characterized by NMR spectroscopy and elemental analysis.

The reaction of CuCl with KSBn, followed by addition of Me_2phen , produced complex 4, containing two K^+ ions ligated by six Me_2phen groups and an anionic tetranuclear copper(I) cluster ligated by six thiolates (Scheme 2). This Cu(I) alkylthio

Scheme 2



complex was obtained after crystallization from the reaction mixture in 92% yield. This result highlights that the site for binding of the dative ligand can be the countercation, as well as the copper reaction site.

To assess whether the arene thiolate complexes adopt ionic forms in solution or maintain the neutral forms observed in the solid state (vide infra), we measured the conductivity of 0.01 mM solutions containing complexes 1–4 in DMSO. The small values for the conductivity of solutions of 1–3 (2.55, 2.07, 7.89 Ω^{-1} cm² mol⁻¹, respectively) versus those of [NBu₄]Br (30.0 Ω^{-1} cm² mol⁻¹) imply that the neutral structure is the major form of the thiophenolato in solution, even in polar solvents. For reference, the conductivity of ferrocene was 0.09 Ω^{-1} cm² mol⁻¹. The higher conductivity value of 15.7 Ω^{-1} cm² mol⁻¹ for 4 is consistent with a structure in solution that is similar to the structure in the solid state.

X-ray Structure of $[(phen)Cu(\mu-SC_6H_5)]_2$ (1). Crystals of 1 suitable for X-ray diffraction were grown from CH₂Cl₂ at -30 °C. An ORTEP diagram of 1 is shown in Figure 1, and selected bond lengths and angles are summarized in Table 1. Related structures of ortho-substituted copper thiolates ligated by substituted phenanthrolines were reported previously.⁴⁵ In sharp contrast to the ionic phenoxide complexes of phenanthroline we isolated and characterized previously,^{42–44} complex 1 adopts a neutral dimeric structure in the solid state. The coordination geometry about the copper atom is



Figure 1. ORTEP drawing of **1** showing 40% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths and Angles of Complex 1

Bond Lengths (Å)					
Cu(1)-Cu(1A) Cu(1)-S(2) Cu(1)-N(2)	2.7207(4) 2.3400(5) 2.0710(14)	Cu(1)-S(1) Cu(1)-N(1)	2.2913(5) 2.0923(13)		
Bond Angles (deg)					
S(1)-Cu(1)-S(2) N(2)-Cu(1)-N(1) N(2)-Cu(1)-S(2)	108.011(14) 80.69(5) 114.31(4)	Cu(1)-S(1)-Cu(1A) N(1)-Cu(1)-S(1)	72.84(2) 122.30(4)		

pseudotetrahedral. Both Cu atoms are ligated by one phen ligand and bridged by the S atoms of the thiophenolato to form a planar Cu_2S_2 ring.

The Cu-Cu distance in 1 (2.7207(4) Å) is slightly longer than that observed in the related thiolato complexes [(phen)- $Cu(\mu - SC_6H_4CH_3 - o)]_2$ (2.613(3) Å)⁴⁶ and [(Me₂phen)Cu(μ - $SC_6H_4CH_3-0$]₂ (2.613 Å)⁴⁵ but is short enough to suggest that the complex contains a weak Cu-Cu bonding interaction. These Cu-Cu distances are much shorter than that in the complex $(Ph_3P)_2Cu(\mu-SPh)_2Cu(PPh_3)_2$ (3.662(2) Å).⁴⁷ The Cu-S distances are 2.2913(5) and 2.3400(5) Å, and these distances are slightly shorter than those found in $(Ph_3P)_2Cu(\mu$ -SPh)₂Cu(PPh₃)₂ (2.344(4) and 2.415(4) Å) and a thiolatebridged polymeric copper(I) compound, $[(Me_2phen)Cu-(SC_6H_5)]_n$ (average 2.319 Å).⁴⁸ However, all of these bond lengths are longer than those observed in the monomeric Cu(I) complex (tmphen)Cu(SAr) (2.1470(8) and 2.1687(14) Å).49 The Cu-S-Cu angle in 1 is only $72.84(2)^\circ$, and this angle is much smaller than that the 102.75(4) and 98.63(4)° Cu-S-Cu angles in $(Ph_3P)_2Cu(\mu-SPh)_2Cu(PPh_3)_2$. This small angle in 1 leads to the short Cu-Cu distance. The Cu-N distances (2.0923(13) and 2.0710(14) Å) are similar to those in the neutral and ionic compounds of phen-ligated copper(I) imidate, amidate, and aryloxide complexes.

X-ray Structure of $[(Me_2phen)_3K]_2[Cu_4(\mu-SCH_2C_6H_5)_6]$ (4). Single crystals of the tetranuclear copper complex 4 were grown by the diffusion of pentane into a THF solution of 4 at -30 °C. An ORTEP diagram is shown in Figure 2, and selected geometric parameters are given in Table 2. In contrast to the copper(I) thiophenolato complexes, complex 4 exists as an ionic form in the solid state. The anion cluster comprises a tetrahedral array of copper(I) centers ligated by six SBn ligands.



Figure 2. ORTEP drawing of the dianion **4** showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths and Angles of Complex 4

Bond Lengths (Å) .					
Cu(1)-Cu(2)	2.7126(8)	Cu(1)-Cu(1A)	2.7273(7)		
Cu(1)-Cu(1B)	2.7273(7)	Cu(2)-Cu(1B)	2.7126(8)		
Cu(2)-Cu(1A)	2.7126(8)	Cu(1) - S(1)	2.2848(10)		
Cu(2) - S(1)	2.2651(8)	Cu(1) - S(2)	2.3044(8)		
Cu(1A)-S(2)	2.2706(8)	Cu(1)-S(2A)	2.2706(8)		
Bond Angles (deg)					
S(1)-Cu(1)-S(2)	110.06(3)	S(2A) - Cu(1) - S(1)	124.57(3)		
S(2A)-Cu(1)-S(2)	125.13(4)	S(1)-Cu(1)-Cu(2)	53.07(3)		
S(2)-Cu(1)-Cu(2)	103.69(2)	Cu(2)-Cu(1)- Cu(1B)	59.80(1)		
Cu(2)-Cu(1)- Cu(1A)	59.821(11)	Cu(1B)-Cu(1)- Cu(1A)	60.0		
Cu(2)-S(1)-Cu(1)	73.20(3)	Cu(1B)-S(2)-Cu(1)	73.18(3)		

Each copper atom is surrounded by three ligands to form a nearly trigonal planar geometry.

The Cu–Cu distances in 4 range from 2.7126(8) to 2.7273(7) Å and are comparable to the observed bond distances in 1 and the related thiolato tetranuclear Cu(I) complex $(Ph_4P)_2[Cu_4(SPh)_6]$ (a mean Cu–Cu distance of 2.76 (2) Å)⁵⁰ and also shows a weak bonding interaction. The Cu–S distances (average 2.2812 Å) are marginally shorter than those found in 1. The Cu–S–Cu angles (73.20(3) and 73.18(3)°) are also similar to those of complex 1.

Reactivity of 1–4 with Aryl lodides. These copper(I) thiophenolato complexes react with haloarenes to form aryl thioethers. The results of these experiments are summarized in eq 2. Reaction of the phen-ligated complex 2 with 5 equiv of p-



iodotoluene in DMSO- d_6 produced bis(4-methylphenyl) sulfide in 99% yield after 3 h at 110 °C, and reaction of the Me₂phen-ligated complex 3 with 5 equiv of *p*-iodotoluene in DMSO- d_6 formed bis(4-methylphenyl) sulfide in 83% yield after 6 h at 110 °C. These results indicate that complex 2,

containing the less sterically hindered phen ligand, reacts more quickly than complex 3, containing the more sterically hindered $o_{,o'}$ -dimethyl-disubstituted Me₂phen ligand. This observation parallels the relative reactions of aryl halides with copper(I) phenoxide complexes containing the same two ligands,⁴³ despite the difference in the ground-state structures. Complex 4 reacted with 5 equiv of *p*-tolyl iodide after 16 h at 110 °C in DMSO to afford the coupled product in 95% yield (eq 3).



To evaluate the intermediacy of the thiophenolato complexes in the copper-catalyzed etherification, we conducted the reactions of **2** with two iodoarenes and compared the ratio of the products of this reaction to that from a catalytic reaction between the arenethiol and the same two aryl halides. If complexes 1-3 are intermediates in the catalytic reaction, then the ratios of products from a single-turnover experiment and a catalytic reaction should be similar.

Isolated complex 2 reacted with a mixture of p-tolyl iodide and o-tolyl iodide to produce a 57:43 ratio of bis(4methylphenyl) sulfide and o-tolyl(p-tolyl)sulfide (eq 4). The



reaction of NaSC₆H₄Me-*p* with a 1:1 mixture of the two iodoarenes catalyzed by Cu/phen formed the same two aryl sulfides in a similar ratio (eq 5; Cu:phen = 1:1, (56 ± 1) :44;



Cu:phen = 1:2, (57 ± 1) :43; Cu:phen = 1:4, (57 ± 1) :43). The presence of the phen ligand affects the selectivity of the metal for the two haloarenes, although the effect was subtle. The reaction of a 1:1 ratio of the two iodoarenes catalyzed by CuI

alone gave a (51 ± 2) :49 ratio of the two aryl sulfides, rather than a (56-62):(38-44) ratio, and formed the two products in a lower combined yield (eq 5). In sharp contrast, in the absence of copper catalyst, the reaction afforded the two aryl sulfide products in a decreased yield with a (36 ± 3) :64 ratio.⁵¹ Thus, these data are at least consistent with the intermediacy of the isolated copper(I) thiophenolato complexes in the couplings of thiols with iodoarenes in the presence of CuI and phenanthroline as ligand.

The mechanism of the reactions of these complexes with iodoarenes was evaluated by conducting experiments that probe the potential for initial electron transfer and the potential intermediacy of free aryl radical intermediates. To probe the potential of an initial, outer-sphere electron-transfer mechanism, we compared the reactivity of the copper(I) thiopheno-lato with 4-chlorobenzonitrile to the reactivity of this complex with 1-bromonaphthalene. The chloroarene is more easily reduced than the bromoarene, and the resulting aryl radical anions undergo dissociation of halide at the same fast rates.^{52,53} However, concerted oxidative additions of chloroarenes are typically much slower than concerted oxidative additions of bromoarenes.

In the event, the reaction of **2** in DMSO at 110 °C with 4chlorobenzonitrile and 1-bromonaphthalene in separate vessels for 12 h produced the corresponding aryl sulfides **5** and **6** in 0% and 69% yields, respectively. Consistent with this observation, the reaction of **2** with a mixture of 4-chlorobenzonitrile and 1bromonaphthalene in DMSO at 110 °C after 12 h generated **5** and **6** in 0% and 32% yields, respectively (eq 6). This lack of reaction with the chloroarene but reaction with the less readily reduced bromoarene argues against a mechanism involving initial, outer-sphere electron transfer.



The intermediacy of an aryl radical formed by another mechanism was probed by conducting reactions with *o*-(allyloxy)iodobenzene. This aryl radical corresponding to this iodoarene is known to undergo cyclization to yield the 2,3-(dihydrobenzofuranyl)methyl radical with a rate constant of 9.6 $\times 10^9$ s⁻¹ in DMSO with subsequent formation of 2-methyldihydrobenzofuran. Thus, if the copper complex led to generation of a free aryl radical from the iodoarene, the reaction of **2** with *o*-(allyloxy)iodobenzene would generate cyclized products.

The reaction of **2** with *o*-(allyloxy)iodobenzene in DMSO- d_6 at 110 °C 28 h gave the product 7 from C–S coupling at the aryl group in 54% yield, along with phenyl allyl ether **8** in 1% yield from hydrodehalogenation (eq 7). The catalytic reaction



of *p*-toluenethiol with *o*-(allyloxy)iodobenzene, in the presence of 10 mol % CuI and 20 mol % phen in DMSO solvent at 110 °C, produced 7 and 8 in 62% and 5% yields, respectively (eq 8). No cyclized product 3-methyl-2,3-dihydrobenzofuran was



formed in either of these reactions. This absence of products from cyclization in the stoichiometric or catalytic reactions implies that the C-S coupling process occurs without the intermediacy of aryl radicals.

CONCLUSION

In conclusion, we have prepared copper(I) thiophenolato complexes that are kinetically and chemically competent to be intermediates in the copper-catalyzed thioetherification of aryl halides. The arenethiolate complexes exist in a neutral dimeric form in the solid state, whereas the benzenethiolate complex adopts a tetranuclear ionic structure with the dative phenanthroline ligand bound to the potassium cation and the tetranuclear copper species possessing a dianionic charge. The reactivity of the complexes with two haloarenes that probe for electron transfer processes and the reactivity of an aryl iodide that probes for the intermedicy of aryl radicals provide evidence against electron transfer to form free or caged aryl radicals. Further investigations on the mechanisms of copper-catalyzed coupling reactions are currently being conducted.

EXPERIMENTAL SECTION

General Experimental Procedure and Reagent Availability. All manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques. All glassware was oven- or flame-dried immediately prior to use. Solvents were freshly dried and degassed according to the procedures in ref 56 prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., and were degassed and stored over activated 4 Å molecular sieves. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. Copper tert-butoxide ([CuO-tBu]₄) was prepared using the reported procedures.^{54,55} The ${}^{1}H$ and ${}^{13}C{}^{1}H$ } NMR spectra were obtained at 293 K on a Bruker Avance 400 spectrometer, and chemical shifts were recorded relative to the solvent resonance. GC-MS measurements were conducted on a Shimadzu QP2010SE instrument. GC measurement was conducted on a Shimadzu 2010Plus with an FID detector. Elemental analyses were performed at the Microanalytical Laboratory of the Fujian Institute of Research on the Structure of Matter.

Preparation of [(phen)Cu(μ-SC₆H₅)]₂ (1). A solution of 1,10phenanthroline (18.0 mg, 0.100 mmol) in 1 mL of THF was added dropwise to a solution of $[CuOtBu]_4$ (13.6 mg, 0.0250 mmol) in 5 mL of THF. The resulting reddish brown solution was stirred at room temperature for 30 min. To this mixture was added a solution of thiophenol (11.0 mg, 0.100 mmol) in 1 mL of THF. The product precipitated from the reaction mixture immediately as a red-brown precipitate. The mixture was stirred for an additional 1 h at room temperature, at which time pentane (12 mL) was added to precipitate the remaining product. The product was separated by filtration through a fine-fritted funnel and washed with pentane to afford 28.5 mg (81% yield) of 1 that was analytically pure after recrystallization from CH₂Cl₂/Et₂O. ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.09 (s, 2H), 8.48 (s, 4H), 7.96 (s, 4H), 7.65 (s, 4H), 6.90 (s, 4H), 6.46 (s, 2H), 6.34 (s, 4H). ¹³C{¹H} (101 MHz, DMSO-*d*₆): δ 149.69, 142.91, 136.58, 131.88, 129.93, 128.07, 127.73, 127.03, 124.96, 122.14. Anal. Calcd for $C_{36}H_{26}Cu_2N_4S_2\cdot 0.25CH_2Cl_2:$ C, 59.88; H, 3.67; N, 7.71. Found: C, 60.24; H, 3.71; N, 8.03. Conductivity (34 °C, 0.01 mM in DMSO): 2.55 Ω cm² mol^{-1}.

Preparation of $[(phen)Cu(\mu-SC_6H_4CH_3-p)]_2$ (2). A solution of 1,10-phenanthroline (18.0 mg, 0.100 mmol) in 1 mL of THF was added dropwise to a solution of [CuOtBu]₄ (13.6 mg, 0.0250 mmol) in 5 mL of THF. The resulting reddish brown solution was stirred at room temperature for 30 min. To this mixture was added a solution of p-thiocresol (12.4 mg, 0.100 mmol) in 1 mL of THF. The product precipitated from the reaction mixture immediately as a red-brown precipitate. The mixture was stirred for an additional 1 h at room temperature, at which time pentane (12 mL) was added to precipitate the remaining product. The product was separated by filtration through a fine-fritted funnel and washed with pentane to afford 31.5 mg (86% yield) of 2 that was analytically pure after recrystallization from CH₂Cl₂/Et₂O. ¹H NMR (400 MHz, DMSO- d_6): δ 9.07 (s, 4H), 8.51 (s, 4H), 7.99 (s, 4H), 7.71 (s, 4H), 6.76 (s, 4H), 6.18 (s, 4H), 1.91 (s, 6H). ${}^{13}C{}^{1}H{}$ (101 MHz, DMSO-d6): δ 149.78, 143.42, 139.41, 131.69, 130.58, 128.79, 127.75, 126.91, 124.79, 20.70. Anal. Calcd for C38H30Cu2N4S2 CH2Cl2 Et2O: C, 57.84; H, 4.74; N, 6.27. Found: C, 57.91; H, 4.28; N, 6.09. Conductivity (34 °C, 0.01 mM in DMSO): 2.07 Ω cm² mol⁻¹

Preparation of [(Me₂phen)Cu(µ-SC₆H₄CH₃-p)]₂ (3). A solution of 2,9-dimethyl-1,10-phenanthroline (21.7 mg, 0.100 mmol) in 1 mL of THF was added dropwise to a solution of [CuOtBu]₄ (13.6 mg, 0.0250 mmol) in 5 mL of THF. The resulting reddish brown solution was stirred at room temperature for 30 min. To this mixture was added a solution of p-thiocresol (12.4 mg, 0.100 mmol) in 1 mL of THF. The product precipitated from the reaction mixture immediately as a redbrown precipitate. The mixture was stirred for an additional 1 h at room temperature, at which time pentane (12 mL) was added to precipitate the remaining product. The product was separated by filtration through a fine-fritted funnel and washed with pentane to afford 33.0 mg (83% yield) of 3 that was analytically pure after recrystallization from CH₂Cl₂/Et₂O. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.75 (d, J = 8.3 Hz, 4H), 8.21 (s, 4H), 7.96 (d, J = 8.3 Hz, 4H), 7.00 (s, 4H), 6.44 (s, 4H), 2.39 (s, 12H), 2.06 (s, 6H). ¹³C{¹H} (101 MHz, DMSO-d₆): δ 158.18, 147.74, 137.95, 136.97, 132.45, 128.04, 127.69, 126.43, 126.20, 125.79, 25.70, 20.89. Anal. Calcd for C42H38Cu2N4S2.0.5CH2Cl2: C, 61.32; H, 4.72; N, 6.73. Found: C, 61.12; H, 5.00; N, 6.62. Conductivity (34 °C, 0.01 mM in DMSO): 7.89 Ω cm² mol⁻¹

Preparation of $[(Me_2phen)_3K]_2[Cu_4(\mu-SCH_2C_6H_5)_6]$ (4). A solution of KSCH2C6H5 (16.2 mg, 0.100 mmol) in 1 mL of THF was added to a suspension of CuCl (9.9 mg, 0.10 mmol) in 5 mL of THF. The resulting mixture was stirred at room temperature for 1 h. To this yellow mixture was added a solution of 2,9-dimethyl-1,10phenanthroline (21.7 mg, 0.100 mmol) in 1 mL of THF. The resulting solution turned reddish brown immediately and was further stirred at room temperature for 30 min. The resulting reaction mixture was filtrated through a layer of Celite. Pentane (12 mL) was added to the filtrate to precipitate the product. The product was separated by filtration through a fine-fritted funnel and washed with pentane to afford 35.6 mg (92% yield) of 4. ¹H NMR (400 MHz, DMSO- d_6): δ 8.35 (d, J = 8.2 Hz, 12H), 7.87 (s, 12H), 7.63 (d, J = 8.2 Hz, 12H), 7.43 (d, J = 7.2 Hz, 12H), 7.14 (t, J = 7.2 Hz, 12H), 7.05 (t, J = 6.7 Hz, 6H), 3.90 (s, 12H), 2.80 (s, 36H). ¹³C{1H} (101 MHz, DMSO- d_6): δ 157.57, 142.14, 137.35, 128.07, 127.33, 127.09, 125.84, 125.61, 124.94, 124.01, 37.01, 25.11. Conductivity (34 °C, 0.005 mM in DMSO): 15.7 $\Omega \text{ cm}^2 \text{ mol}^{-1}$

Representative Procedure for Measuring the Yield of $[(phen)Cu(\mu-SC_6H_4CH_3-p)]_2$ (2) with *p*-lodotoluene. Complex 2 (7.3 mg, 0.020 mmol) and 1,3,5-trimethoxybenzene (3.4 mg, 0.020 mmol) as internal standard were weighed into a vial and dissolved in 0.6 mL of DMSO- d_6 . The contents of the vial were agitated and then transferred to an NMR tube containing a septum-lined screw cap. An initial ¹H NMR spectrum was acquired. *p*-lodotoluene (21.8 mg, 0.100 mmol, 5.0 equiv) was then added as a DMSO- d_6 solution (0.1 mL), and the resulting mixture was heated at 110 °C in an oil bath. The

NMR tube was removed at regular intervals, and ¹H NMR spectra were acquired at 25 °C until the yield did not change. The yield of the *p*-tolyl phenyl sulfide was calculated to be 99%.

Representative Procedure for Measuring the Yield of $[(Me_2phen)Cu(\mu-SC_6H_4CH_3-p)]_2$ (3) with *p*-lodotoluene. Complex 3 (7.9 mg, 0.020 mmol) and 1,3,5-trimethoxybenzene (3.4 mg, 0.020 mmol) as internal standard were weighed into a vial and dissolved in 0.6 mL of DMSO- d_6 . The contents of the vial were agitated and then transferred to an NMR tube containing a septum-lined screw cap. An initial ¹H NMR spectrum was acquired. *p*-Iodotoluene (21.8 mg, 0.100 mmol, 5.0 equiv) was then added as a DMSO- d_6 solution (0.1 mL), and the resulting mixture was heated at 110 °C in an oil bath. The NMR tube was removed at regular intervals, and ¹H NMR spectra were acquired at 25 °C until the yield did not change. The yield of the *p*-tolyl phenyl sulfide was calculated to be 83%.

Representative Procedure for Measuring the Yield of $[(Me_2phen)_3K]_2[Cu_4(\mu-SCH_2C_6H_5)_6]$ (4) with *p*-lodotoluene. Into a small vial was placed 4 (7.7 mg, 0.0033 mmol), *p*-iodotoluene (21.8 mg, 0.100 mmol), and 0.6 mL of DMSO. The vial was sealed with a Teflon-lined screw cap, and the mixture was stirred at 110 °C for 16 h. The resulting solution was warmed to room temperature, and 100 μ L of diphenyl disulfide (0.20 mmol/mL in DMSO) was added as internal standard. The mixture then was filtered through a layer of Celite. The filtrate was analyzed by GC/MS. The yield was calculated to be 95%.

Competition Reaction of $[(phen)Cu(\mu-SC_6H_4CH_3-p)]_2$ (2) with *p*-lodotoluene and *o*-lodotoluene. Into a small vial was placed 2 (7.3 mg, 0.020 mmol), *p*-iodotoluene (21.8 mg, 0.100 mmol), *o*-iodotoluene (21.8 mg, 0.100 mmol), and 0.6 mL of DMSO-*d*₆. The vial was sealed with a Teflon-lined screw cap, and the mixture was stirred at 110 °C for 3 h. The resulting solution was warmed to room temperature, and 100 μ L of a solution of 1,3,5-trimethoxybenzene (0.20 mmol/mL in DMSO-*d*₆) was added as internal standard. The mixture then was filtered through a layer of Celite. The filtrate was analyzed by ¹H NMR spectroscopy. The yields of *p*-tolyl phenyl sulfide and *o*-tolyl phenyl sulfide were calculated to be 57% and 43%, respectively.

Competition Reaction of NaSC₆H₄Me-*p* with *p*-lodotoluene and *o*-lodotoluene Catalyzed by Cul/phen (1:2). Into a small vial was placed CuI (1.0 mg, 0.0050 mmol, 10 mol %), 1,10phenanthroline (1.8 mg, 0.010 mmol, 20 mol %), NaSC₆H₄Me-*p* (7.3 mg, 0.050 mmol), *p*-iodotoluene (54.5 mg, 0.250 mmol), *o*iodotoluene (54.5 mg, 0.250 mmol), and 0.6 mL of DMSO-*d*₆. The vial was sealed with a Teflon screw cap, and the reaction mixture was stirred at 110 °C for 24 h. The resulting mixture was warmed to room temperature, and 100 μ L of 1,3,5-trimethoxybenzene (0.20 mmol/mL in DMSO-*d*₆) was added as internal standard. The mixture then was filtered through a layer of Celite. The filtrate was analyzed by ¹H NMR spectroscopy. The yields of *p*-tolyl phenyl sulfide and *o*-tolyl phenyl sulfide were calculated to be 54% and 34%, respectively.

Competition Reaction of NaSC₆H₄Me-*p* with *p*-lodotoluene and *o*-lodotoluene Catalyzed with Cul/phen (1:1). Into a small vial was placed CuI (1.0 mg, 0.0050 mmol, 10 mol %), 1,10phenanthroline (0.9 mg, 0.005 mmol, 10 mol %), NaSC₆H₄Me-*p* (7.3 mg, 0.050 mmol), *p*-iodotoluene (54.5 mg, 0.250 mmol), *o*iodotoluene (54.5 mg, 0.250 mmol), and 0.6 mL of DMSO. The vial was sealed with a Teflon-lined screw cap, and the reaction mixture was stirred at 110 °C for 24 h. The resulting mixture was warmed to room temperature, and 100 μ L of diphenyl disulfide (0.20 mmol/mL in DMSO) was added as internal standard. The mixture then was filtered through a layer of Celite. The filtrate was analyzed by GC/MS. The yields of *p*-tolyl phenyl sulfide and *o*-tolyl phenyl sulfide were calculated to be 54% and 41%, respectively.

Competition Reaction of NaSC₆H₄Me-*p* with *p*-lodotoluene and *o*-lodotoluene Catalyzed with Cul/phen (1:4). Into a small vial was placed CuI (1.0 mg, 0.0050 mmol, 10 mol %), 1,10phenanthroline (3.6 mg, 0.020 mmol, 40 mol %), NaSC₆H₄Me-*p* (7.3 mg, 0.050 mmol), *p*-iodotoluene (54.5 mg, 0.250 mmol), *o*iodotoluene (54.5 mg, 0.250 mmol), and 0.6 mL of DMSO. The vial was sealed with a Teflon-lined screw cap, and the reaction mixture

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was stirred at 110 °C for 24 h. The resulting mixture was warmed to room temperature, and 100 μ L of diphenyl disulfide (0.20 mmol/mL in DMSO) was added as internal standard. The mixture then was filtered through a layer of Celite. The filtrate was analyzed by GC/MS. The yields of *p*-tolyl phenyl sulfide and *o*-tolyl phenyl sulfide were calculated to be 56% and 41%, respectively.

Competition Reaction of NaSC₆H₄Me-*p* with *p*-lodotoluene and *o*-lodotoluene Catalyzed by Cul. Into a small vial was placed CuI (1.0 mg, 0.0050 mmol, 10 mol %), NaSC₆H₄Me-*p* (7.3 mg, 0.050 mmol), *p*-iodotoluene (54.5 mg, 0.250 mmol), *o*-iodotoluene (54.5 mg, 0.250 mmol), and 0.6 mL of DMSO-*d*₆. The vial was sealed with a Teflon-lined screw cap, and the reaction mixture was stirred at 110 °C for 24 h. The resulting mixture was warmed to room temperature, and 100 μ L of 1,3,5-trimethoxybenzene (0.20 mmol/mL in DMSO-*d*₆) was added as internal standard. The mixture then was filtered through a layer of Celite. The filtrate was analyzed by ¹H NMR spectroscopy. The yields of *p*-tolyl phenyl sulfide and *o*-tolyl phenyl sulfide were calculated to be 42% and 37%, respectively.

Competition Reaction of NaSC₆H₄Me-*p* with *p*-lodotoluene and *o*-lodotoluene without Cul/phen. Into a small vial was placed NaSC₆H₄Me-*p* (7.3 mg, 0.050 mmol), *p*-iodotoluene (54.5 mg, 0.250 mmol), *o*-iodotoluene (54.5 mg, 0.250 mmol), and 0.6 mL of DMSO. The vial was sealed with a Teflon-lined screw cap, and the reaction mixture was stirred at 110 °C for 24 h. The resulting mixture was warmed to room temperature, and 100 μ L of diphenyl disulfide (0.20 mmol/mL in DMSO) was added as internal standard. The mixture then was filtered through a layer of Celite. The filtrate was analyzed by GC/MS. The yields of *p*-tolyl phenyl sulfide and *o*-tolyl phenyl sulfide were calculated to be 23% and 40%, respectively.

Procedure for the Reaction of $[(phen)Cu(\mu-SC_6H_4CH_3-p)]_2$ (2) with 4-Chlorobenzonitrile. Into a small vial was placed 2 (7.3 mg, 0.020 mmol), 4-chlorobenzonitrile (14.0 mg, 0.100 mmol), and 0.6 mL of DMSO. The vial was sealed with a Teflon-lined screw cap, and the mixture was stirred at 110 °C for 48 h. The resulting solution was warmed to room temperature, and 100 μ L of 1,3,5-trimethoxybenzene (0.20 mmol/mL in DMSO) was added as internal standard. The mixture then was filtered through a layer of Celite. The filtrate was analyzed by GC/MS. Formation of *p*-tolyl thiophenyl benzonitrile product was not detected.

Procedure for the Reaction of $[(phen)Cu(\mu-SC_6H_4CH_3-p)]_2$ (2) with 1-Bromonaphthalene. Into a small vial was placed 2 (7.3 mg, 0.020 mmol), 1-bromonaphthalene (21 mg, 0.10 mmol), and 0.6 mL of DMSO. The vial was sealed with a Teflon-lined screw cap, and the mixture was stirred at 110 °C for 48 h. The resulting solution was warmed to room temperature, and 100 μ L of 1,3,5-trimethoxybenzene (0.20 mmol/mL in DMSO) was added as internal standard. The mixture then was filtered through a layer of Celite. The filtrate was analyzed by GC/MS. The yield of the 1-*p*-tolyl thiophenyl naphthalene was calculated to be 69%.

Competition Reaction of $[(phen)Cu(\mu-SC_6H_4CH_3-p)]_2$ (2) with 4-Chlorobenzonitrile and 1-Bromonaphthalene. Into a small vial was placed 2 (7.3 mg, 0.020 mmol), 4-chlorobenzonitrile (14 mg, 0.10 mmol), 1-bromonaphthalene (21 mg, 0.10 mmol), and 0.6 mL of DMSO. The vial was sealed with a Teflon-lined screw cap, and the mixture was stirred at 110 °C for 48 h. The resulting solution was warmed to room temperature, and 100 μ L of a solution of 1,3,5trimethoxybenzene (0.20 mmol/mL in DMSO) was added as internal standard. The mixture then was filtered through a layer of Celite. The filtrate was analyzed by GC/MS. The yield of 1-*p*-tolyl thiophenyl naphthalene was calculated to be 32%. The *p*-tolyl thiophenyl benzonitrile product was not detected.

Procedure for the Reaction of $[(phen)Cu(\mu-SC_6H_4CH_3-p)]_2$ (2) with *o*-(Allyloxy)iodobenzene. Into a small vial was placed complex 2 (7.3 mg, 0.020 mmol), *o*-(allyloxy)iodobenzene (26.0 mg, 0.100 mmol), and 0.6 mL of DMSO-*d*₆. The mixture was agitated and transferred to a Teflon-lined screw-capped NMR tube. The NMR tube was heated at 110 °C in a constant-temperature bath for 24 h. The resulting solution was warmed to room temperature, and 100 μ L of 1,3,5-trimethoxybenzene (0.20 mmol/mL in DMSO-*d*₆) was added as internal standard. A 0.1 mL aliquot of the solution was withdrawn and

diluted with ethyl acetate, and the resulting solution was filtered through a layer of Celite. The mixture was analyzed by GC/MS. The yields determined by GC/MS of phenyl allyl ether and the *p*-tolyl aryl thioether versus the 1,3,5-trimethoxybenzene internal standard were calculated to be 1% and 54%, respectively.

Procedure for the Reaction of NaSC₆H₄Me-p with o-(Allyloxy)iodobenzene Catalyzed by Cul/phen. Into a small vial was placed CuI (1.0 mg, 0.0050 mmol, 10 mol %), 1,10phenanthroline (1.8 mg, 0.010 mmol, 20 mol %), NaSC₆H₄Me-p (7.3 mg, 0.050 mmol), o-(allyloxy)iodobenzene (130.0 mg, 0.2500 mmol), and 0.6 mL of DMSO-d₆. The mixture was agitated and transferred to a Teflon-lined screw-capped NMR tube. The NMR tube was heated at 110 °C in a constant-temperature bath for 24 h. The resulting solution was warmed to room temperature, and 100 μ L of a solution of 1,3,5trimethoxybenzene $(0.20 \text{ mmol/mL} \text{ in DMSO-}d_6)$ was added as internal standard. A 0.1 mL aliquot of the solution was withdrawn and diluted with ethyl acetate, and the resulting solution was filtered through a layer of Celite. The mixture was analyzed by GC/MS. The yields determined by GC/MS of phenyl allyl ether and the *p*-tolyl aryl thioether versus the 1,3,5-trimethoxybenzene internal standard were calculated to be 5% and 62%, respectively.

ASSOCIATED CONTENT

S Supporting Information

CIF files giving details of the X-ray structures of 1 and 4. 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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