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## Electrochemical and Structural Characterization of Tri- and Dithioether Copper Complexes

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Tri- and dithioethers tris(2-*tert*-butyl-4-methylphenylthiomethyl)amine (1), bis(2,4-dimethylphenylthio)methane (2), and bis(2-*tert*-butyl-4-methylphenylthio)methane (3) were developed to evaluate their coordination properties toward Cu<sup>+</sup>. The thioethers associate weakly with Cu<sup>+</sup> when ClO<sub>4</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup> are the counterions, while the reactions with CuI afford crystalline products in the case of nitrilotrithioether 1 and dithioether 2. The solid-state structures of the complexes [(1)CuI]<sub>2</sub> and [(2)(CuI)<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sub>2</sub>·2THF·4CH<sub>3</sub>CN are characterized by the chelating-bidentate coordination mode of 1 and the bridging nature of 2 spanning two Cu<sub>4</sub>I<sub>4</sub> cuboidal clusters. Electrochemical studies of the thioether/Cu<sup>+</sup> com-

### Introduction

Thioether ligands have been intensively studied in recent years because of their involvement in bioinorganic systems, particularly in the active sites of copper-containing metalloenzymes.<sup>[1]</sup> A growing number of copper complexes featuring thioether ligation have been developed, mainly aimed at understanding the role of sulfur-based donors in biological and chemical systems.<sup>[2]</sup> These include the exhaustively studied blue copper proteins,<sup>[1b,1c,3]</sup> in which the presence of thiolate and thioether donors play a key role in their characteristic fast electron-transfer kinetics. Thioether donors have recently been identified in copper trafficking,<sup>[1a,1j]</sup> in addition to the predominant thiolate-based Cu<sup>+</sup> metallochaperones. Moreover, the presence of methionine residues as thioether ligands in several types of copper monooxygenases,<sup>[1e,1f,1i,4]</sup> as well as the involvement of cysteine in the generation of the active site of galactose oxidase,<sup>[5]</sup> have further spurred the interest in copper-sulfur systems. The presence of sulfur donors around copper centers modulates the redox potential of the Cu2+/Cu+ couple, resulting in high plexes revealed that the sulfur-rich coordination environment results in high redox potentials for the  $Cu^{2+}/Cu^+$  couple, which is close to the first oxidation potential of the ligands. Thus, chemical ( $Cu^{2+}$ ) or electrochemical oxidation of the thioethers resulted in oxidative decomposition of the ligands with concomitant reduction to  $Cu^+$ , in agreement with the electrochemical results. Bulk electrolyses of the tri- and dithioethers **1–3** enabled us to confirm that the corresponding disulfides are the major oxidation products. The cathodic peak potentials for the  $Cu^+/Cu^0$  couple of the complexes allowed us to determine the relative stability of the thioether/  $Cu^+$  complexes.

redox potentials for sulfur-rich coordination environments. With regard to inorganic model systems, the ethylenebridged tripodal NS<sub>3</sub> ligands employed by the group of Rorabacher form stable  $Cu^+$  and  $Cu^{2+}$  complexes,<sup>[1c,6]</sup> and their electronic properties resemble those of type 1 copper sites in metalloenzymes with redox potentials in the order of 0.28 V relative to the ferrocinium/ferrocene (Fc<sup>+</sup>/Fc) couple. Related tripodal ligands with N<sub>2</sub>S<sub>2</sub> coordination environments have redox potentials as high as 0.54 V (vs. Fc<sup>+</sup>/ Fc).<sup>[7]</sup> In the case of methylene-bridged anionic and neutral tripodal trithioethers  $E(CH_2SR)_3$  (E = B, C, Si), reactions with Cu<sup>+</sup> afford monomeric, oligomeric, and polymeric complexes,<sup>[8]</sup> but attempts to prepare cupric analogues have been unsuccessful. This has prevented the determination of the Cu<sup>2+</sup>/Cu<sup>+</sup> redox potential in the latter systems; in addition, the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> has been observed with methylene-bridged tripodal ligands,<sup>[8b]</sup> which is coupled with ligand-based oxidation, indicating that there is an intrinsic reactivity of the  $E-CH_2$ -S linker.

In this context, we recently reported the synthesis of an nitrilotrithioether ligand ( $L^{Me}$  in Scheme 1), as well as its reactivity toward Cu<sup>+</sup> and Cu<sup>2+</sup>.<sup>[9]</sup> To further investigate the reactivity of methylene-bridged thioethers, we have prepared related sulfur-containing ligands. The nitrilotrithioether (1 in Scheme 1) allowed us to investigate the steric effects of the bulky *tert*-butyl groups in the *ortho* positions, while the dithioethers ArS-*CH*<sub>2</sub>-SAr that lack the potential nitrogen donor at the bridging position (2 and 3, Ar = substituted aromatic group) provided information on the effect of the heteroatom on the ease of oxidation of the ArS-

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Scheme 1. Tri- and dithioether ligands 1-3, and disulfides 4 and 5.

 $CH_2$ -E moiety (E = N, S). Thus, we report herein on the study of the electrochemical and structural properties of the ligands and their Cu<sup>+</sup> complexes. In addition, we also report on the chemical (Cu<sup>2+</sup>) and electrochemical oxidation reactions of the sulfur-containing ligands, which result mainly in the formation of the disulfides **4** and **5**, as well as minor amounts of C-C bond formation products.

#### **Results and Discussion**

The sterically encumbered nitrilotrithioether tris(2-tertbutyl-4-methylphenylthiomethyl)amine (1), which features tert-butyl groups in one of the ortho positions of the phenylthioether moieties, was prepared by acid-catalyzed condensation of 2-tert-butyl-4-methylbenzenethiol and hexamethylenetetramine (Scheme 2), in an analogous fashion to the previously reported L<sup>Me.[9]</sup> Compound 1 interacts weakly with Cu<sup>+</sup> centers in solution, as evidenced by <sup>1</sup>H NMR spectroscopy. The analyses of the <sup>1</sup>H NMR spectra of  $[D_3]$ acetonitrile solutions of 1 with varying amounts of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (0.5–2.0 equiv.) reveal only marginal changes in the signals corresponding to the ligand. Reactions of the related nitrilotrithioether L<sup>Me</sup> with equimolar amounts of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> and [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> had previously resulted in microcrystalline solids, but in the case of compound 1 isolation of the corresponding cuprous complexes appears to be precluded by the increased steric bulk of the ligand; attempts to precipitate or crystallize the complexes resulted in the recovery of the Cu<sup>+</sup> starting materials. Extended reaction times of 1 with the aforementioned copper salts results in ligand decomposition. Nonetheless, freshly prepared acetonitrile solutions allowed the detection of a peak at m/z = 657 by electrospray-ionization mass spectrometry (ESI-MS), which corresponds to a complex with a 1:1 stoichiometry  $[(1)Cu]^+$  (see Figure S1 in the Supporting Information); analysis of the same sample after 24 h of exposure to air revealed a new peak at m/z = 234, which could correspond to the product of oxidative C–C bond formation (see below).

Employment of CuI allowed the isolation of a complex upon treatment with 1 equiv. of 1; reactions with different Cu/ligand ratios resulted in the same product, the combustion analysis being consistent with a 1:1 stoichiometry. The ESI mass spectra of the complex contain peaks corresponding to copper-containing species at m/z = 1251 [(1)<sub>2</sub>Cu]<sup>+</sup>, fragmentation peaks at m/z = 1102 and 954, attributable to the sequential loss of 2-tBu-4-Me-C<sub>6</sub>H<sub>3</sub> groups, and the species  $[(1)Cu]^+$  at m/z = 657 (see Supporting Information Figure S2). Although <sup>1</sup>H and <sup>13</sup>C NMR spectra are characterized by small shifts of the signals corresponding to the ligand, confirmation of the formation of the copper complex was obtained by X-ray crystallography. Single crystals of [(1)CuI]<sub>2</sub> were obtained in the monoclinic space group  $P2_1/c$  by cooling concentrated acetonitrile solutions to -20 °C. A crystallographic inversion center generates the dimeric structure of the complex, which is characterized by bridging iodido ligands, defining a rhomboidal Cu<sub>2</sub>I<sub>2</sub> core with an average Cu-I distance of 2.625(1) Å and an I-Cu-I angle of 121.10(1)°. The deviation from an ideal tetrahedral geometry around Cu1 is also reflected in the compressed S1–Cu1–S2 angle of 90.15(2)°, as well as the corresponding S1-Cu1-I1 and S2-Cu1-I1 angles of 112.77(2) and 108.28(2)°, respectively. The average Cu-S bond length of 2.336(1) Å is within the range of related complexes (Figure 1);<sup>[10]</sup> a list of selected bond lengths and angles for all compounds is presented in Table 1. The crystallographically related copper centers are at a distance of 2.582(1) Å, which is considerably shorter than the sum of the van der Waals radii (2.80 Å),<sup>[11]</sup> and is only comparable to that reported



Scheme 2. Acid-catalyzed synthesis of tri- and dithioether ligands.

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by Hor and coworkers of 2.525(2) Å.<sup>[12]</sup> In the latter complex, the Cu<sup>+</sup> centers have amino and thioether ligands, and the Cu<sub>2</sub>I<sub>2</sub> cores differ from those of [(1)CuI]<sub>2</sub> in the triply bridging mode of the iodido ligands. In [(1)CuI]<sub>2</sub> the nitrogen atom on the ligand does not participate in bonding to copper, and the sum of the angles of 348.6° attests to its nearly planar geometry. In the related solid-state structure of [L<sup>Me</sup>(CuI)<sub>2</sub>(CH<sub>3</sub>CN)], all thioether groups of L<sup>Me</sup> coordinate to two independent Cu centers in a  $\mu$ - $\kappa$ <sup>1</sup>, $\kappa$ <sup>2</sup> fashion, while in the case of 1 only two of the thioether sulfur atoms coordinate to Cu1. We attribute this behavior to the increased steric hindrance conferred to the ligand by the *tert*-butyl groups in the *ortho* positions.



Figure 1. ORTEP diagram of  $[(1)CuI]_2$  at the 50% probability level; hydrogen atoms were removed for clarity.

Reaction of 1 with Cu<sup>2+</sup> salts resulted in oxidation of the ligand, with concomitant reduction to Cu<sup>+</sup>.<sup>[8b]</sup> For example, when 1-3 equiv. of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O were added to acetonitrile solutions of 1 the corresponding disulfide (2-tBu-4- $MeC_6H_3S_2$  (4) was detected by <sup>1</sup>H NMR spectroscopy; the solid-state structure of 4 characterized it unambiguously (see Figure S3 in the Supporting Information). An ESI-MS analysis of the samples revealed the presence of disulfidecopper complexes: when 2 equiv. of Cu<sup>2+</sup> were employed the species at m/z = 957, 779, and 599 were assigned to the complexes  $[(4)_2Cu(SC_6H_3-2-tBu-4-Me)]^+$ ,  $[(4)_2Cu]^+$ , and [(4)Cu(SC<sub>6</sub>H<sub>3</sub>-2-*t*Bu-4-Me)]<sup>+</sup>, respectively (see Supporting Information Figure S4). Repeated attempts to isolate the products resulted in the recovery of Cu<sup>+</sup> as [Cu(CH<sub>3</sub>CN)<sub>4</sub>]-ClO<sub>4</sub> and the disulfide 4. While ligand hydrolysis mediated by the Lewis-acidic cupric ion may be invoked, the oxidative degradation pathway proposed in Scheme 3 is supported by cyclic voltammetry measurements on solutions of 1 in the presence of Cu<sup>+</sup>, in which the first oxidation potential of 1 is below the value of the  $Cu^{2+}/Cu^{+}$  couple. This allows us to postulate that the interaction with  $Cu^{2+}$  would likely result in the oxidation of 1, with concomitant reduction of copper. Moreover, the electrochemical oxidation of 1 in the absence of copper affords the same products observed in

Table 1. Selected bond lengths [Å] and angles [°].

[(1)CuI] <sub>2</sub>						
Cu1–I1	2.658(1)	I1-Cu1-I1*	121.10(1)			
Cul-I1*	2.591(1)	S1-Cu1-S2	90.15(2)			
Cu1–S1	2.334(1)	I1-Cu1-S1	112.77(2)			
Cu1–S2	2.338(1)	I1-Cu1-S2	108.28(2)			
Cu1…Cu1*	2.582(1)	Cu1–I1–Cu1*	58.90(1)			
[(2)(CuI) <sub>4</sub> (CH <sub>3</sub> CN) <sub>2</sub> ] <sub>2</sub> ·2THF·4CH <sub>3</sub> CN						
Cu1–I1	2.760(1)	I1–Cu1–I2	113.40(2)			
Cu1–I2	2.660(1)	I1-Cu1-I3	113.00(2)			
Cu1–I3	2.592(1)	I2-Cu1-I3	113.42(2)			
Cu2–I1	2.687(1)	I1-Cu2-I2	115.36(2)			
Cu2–I2	2.674(1)	I1-Cu2-I4	112.49(2)			
Cu2–I4	2.615(1)	I2-Cu2-I4	111.67(2)			
Cu3–I1	2.689(1)	I1–Cu3–I3	110.73(2)			
Cu3–I3	2.736(1)	I1–Cu3–I4	110.10(2)			
Cu3–I4	2.688(1)	I3-Cu3-I4	116.37(2)			
Cu4–I2	2.690(1)	I2-Cu4-I3	109.40(2)			
Cu4–I3	2.689(1)	I2-Cu4-I4	108.80(2)			
Cu4–I4	2.692(1)	I3–Cu4–I4	117.87(2)			
Cu1–S1	2.304(1)	S1–Cu1–I1	93.10(3)			
Cu2–S2	2.327(1)	S1–Cu1–I2	109.54(3)			
Cu3–N1	1.972(4)	S1–Cu1–I3	112.71(4)			
Cu4–N2	1.985(5)	S2-Cu2-I1	100.41(3)			
Cu1···Cu2	2.679(1)	S2–Cu2–I2	104.63(3)			
Cu1…Cu3	2.697(1)	S2–Cu2–I4	111.40(3)			
Cu1···Cu4	2.687(1)	N1–Cu3–I1	109.1(1)			
Cu2····Cu3	2.689(1)	N1–Cu3–I3	102.9(1)			
Cu2····Cu4	2.737(1)	N1–Cu3–I4	107.2(1)			
Cu3····Cu4	2.650(1)	N2-Cu4-I2	114.0(1)			
		N2-Cu4-I3	103.0(1)			
	-	N2-Cu4-I4	103.8(1)			

the chemical oxidation by  $Cu^{2+}$  (see Electrochemical Studies section).



Scheme 3. Proposed mechanism for the formation of the C–C coupling product by oxidation of  $1.^{[9]}$ 

In contrast to the reported Cu<sup>2+</sup> oxidation of L<sup>Me</sup>, no C–C bond formation products were isolated from the chemical or electrochemical oxidations of 1. Nonetheless, FAB<sup>+</sup> mass spectra of the reaction mixtures are characterized by the presence of a peak at m/z = 234 (see Supporting Information Figure S5), which could arise from the Mannich-type attack of one of the electrochemically active N–*CH*<sub>2</sub>–



S groups on the *ortho* position of the thioether generated according to Scheme 3.

The different reactivities of the trithioethers 1 and L<sup>Me</sup> could in principle be ascribed to the steric effect exerted by the ortho tert-butyl groups in the former, compared to that of the ortho methyl groups in the latter. For example, substitution of a tert-butyl for a methyl group in related ligands has resulted in higher oxidation potentials for the corresponding Cu complexes.<sup>[7]</sup> An additional feature of the nitrilotrithioethers 1 and  $L^{Me}$  is the presence of the central nitrogen atom, which may direct the oxidative decomposition by stabilizing the resulting iminium cations. In order to verify the role of the N atom we prepared dithioethers that can potentially act as ligands toward copper ions, but that lack the central nitrogen atom. The study of the electrochemical properties of the dithioether/Cu<sup>+</sup> systems, as well as their chemical (Cu<sup>2+</sup>) and electrochemical oxidation processes by cyclic voltammetry, revealed that the N-CH<sub>2</sub>-S moiety in the nitrilotrithioethers is characterized by lower oxidation potentials than that of the S-CH<sub>2</sub>-S groups in the dithioethers.

Thus, we explored the coordination properties of the dithioether compounds bis(2,4-dimethylphenylthio)methane (2), and bis(2-*tert*-butyl-4-methylphenylthio)methane (3) toward Cu<sup>+</sup> salts. As in the case of 1, <sup>1</sup>H NMR spectroscopic analyses of solutions of 2 with various amounts of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> and [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> revealed small displacements of the ligand-derived signals. Although the association of 2 with Cu<sup>+</sup> appears to be weak, ESI-MS revealed the presence of Cu<sup>+</sup> complexes of 2: the base peak at m/z = 639 was assigned to the species  $[(2)_2Cu]^+$ , while the peak at m/z = 351 corresponds to the complex [(2)Cu]<sup>+</sup> (see Supporting Information Figure S6). Despite these observations we were unable to isolate the copper complexes of 2 present in solution, and resorted to cyclic voltammetry measurements to confirm complex formation by monitoring the addition of Cu<sup>+</sup> to solutions of 2 (see Electrochemical Studies section).

Reactions of 2 with CuI resulted in the formation of two products with different stoichiometries, based on combustion analysis; when relatively high ligand to copper ratios were employed (from 2:1 to 1:1), the solid isolated was consistent with the empirical formula  $[(2)(CuI)_2(CH_3CN)_2]$ . While the structures of CuI/thioether complexes are hard to predict, a tentative proposal would correspond to a coordination polymer with bridging dithioethers, akin to those reported with bis(arylthio)methanes (aryl = phenyl, ptolyl).<sup>[13]</sup> The steric hindrance exerted by the additional methyl groups in the *ortho* position of the aromatic groups of 2 may preclude the extended ordering required for the formation of adequate crystals. When the ratio of 2 to copper was low (from 1:2 to 1:4), the product isolated corresponded to the formula [(2)(CuI)<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>]; the yield of this product was optimized by using 4 equiv. of CuI per ligand. Colorless X-ray quality crystals of [(2)(CuI)<sub>4</sub>-(CH<sub>3</sub>CN)<sub>2</sub>]<sub>2</sub>·2THF·4CH<sub>3</sub>CN were obtained by cooling a concentrated solution in 1:1 acetonitrile/THF to -20 °C. The complex crystallizes in the monoclinic space group  $P2_1/n$ , with compound 2 bridging two distorted cuboidal Cu<sub>4</sub>I<sub>4</sub> moieties, in an analogous fashion to the macrocyclic structures reported with bridging bidentate amines.<sup>[14]</sup> The iodido ligands coordinate the Cu<sup>+</sup> ions in a µ<sub>3</sub> fashion, with Cu1 and Cu2 having additional thioether ligands from the S1 and S2 atoms, respectively. The sulfur donors correspond to two molecules of the ligand 2, which are related by a crystallographic inversion center; this symmetry element also generates the second Cu<sub>4</sub>I<sub>4</sub> fragment. Cu3 and Cu4 have additional nitrogen donors from molecules of acetonitrile, so that all Cu<sup>+</sup> ions have pseudo-tetrahedral coordination geometries, with I<sub>3</sub>S and I<sub>3</sub>N donor sets; an OR-TEP diagram of [(2)(CuI)<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sub>2</sub>·2THF·4CH<sub>3</sub>CN is presented in Figure 2, and selected bond lengths and angles are given in Table 1. The complex is characterized by average bond lengths of Cu-I 2.681(1) Å, Cu-S 2.316(1) Å, and Cu-N 1.979(5) Å, all of which are within the range of reported values;[10d,10f,10g,15] the bond angles around the copper centers vary from 93.10(3) to 117.87(2)°. The four Cu and four I atoms define distorted tetrahedra within the Cu<sub>4</sub>I<sub>4</sub> units, with average distances for Cu–Cu of 2.690(1) and I–I of 4.463(1) Å. Although the luminescent properties of the complex are beyond the scope of this work, in related systems a Cu–Cu distance in the range of 2.77–2.80 A appears to be required for luminescence.<sup>[10g,13,15b,15c,16]</sup>



Figure 2. ORTEP diagram of  $[(2)(CuI)_4(CH_3CN)_2]_2$ ·2THF·4CH<sub>3</sub>CN at the 50% probability level, hydrogen atoms and the solvate molecules of CH<sub>3</sub>CN and THF were removed for clarity.

In an analogous fashion to the reactions of the nitrilotrithioethers  $L^{Me}$  and 1 with  $Cu^{2+}$ , treatment of 2 with  $Cu^{2+}$ salts resulted in oxidation of the ligand and reduction of copper. Addition of 2 equiv. of  $Cu(ClO_4)_2 \cdot 6H_2O$  to acetonitrile solutions of 2 resulted in the formation of the disulfide (2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>S)<sub>2</sub> (5) as the only organic product, as detected by <sup>1</sup>H NMR spectroscopy. [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> was recovered in nearly quantitative yield, based on the amount of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O employed. When only 1 equiv. of Cu-(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O was employed, ESI-MS analyses of the samples allowed the detection of mixed dithioether (ArSCH<sub>2</sub>-

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SAr)/disulfide (ArSSAr)–copper complexes; for example, the species at m/z = 761, 639, 625, 611, and 351 were assigned to the complexes  $[(2)(5)Cu(SC_6H_3-2,4-Me_2)]^+$ ,  $[(2)_2Cu]^+$ ,  $[(2)(5)Cu]^+$ ,  $[(5)_2Cu]^+$ , and  $[(2)Cu]^+$ , respectively (see Supporting Information Figure S7). Among the species detected, the peaks at m/z = 501, 487, and 473 can be assigned to the successive loss of methylene groups, and the tentative formulae  $[(2)Cu(SC_6H_3-2,4-Me_2)]^+$  and [(5)Cu-(SC<sub>6</sub>H<sub>3</sub>-2,4-Me<sub>2</sub>)]<sup>+</sup> for the latter two species. Intriguingly, the peak at m/z = 501 would correspond to the species [(2) $Cu(SC_6H_3-2,4-Me_2)]^+$  plus the mass of an additional methylene group; while the coordination of the very reactive carbosulfonium ion  $[2,4-Me_2C_6H_3S=CH_2]^+$  as ligand appears unlikely <sup>[17]</sup> an alternative formulation would correspond to

yiene group; while the coordination of the very feactive carbosulfonium ion  $[2,4-Me_2C_6H_3S=CH_2]^+$  as ligand appears unlikely,<sup>[17]</sup> an alternative formulation would correspond to a product of C–C bond formation between the latter fragment and an aromatic ring of the dithioether **2** (see Scheme 4). This would clearly represent a minor reaction manifold, since no products of this type could be isolated or detected by <sup>1</sup>H NMR spectroscopy. Oxidative C–C bond formation starting from **2** (or **3**) would be disfavored by the intermolecular nature of the reaction, compared to the intramolecular reaction starting from **1**, outlined in Scheme 3.



Scheme 4. Proposed mechanism of oxidative C–C bond formation from **2**.

The sterically hindered dithioether bis(2-tert-butyl-4methylphenylthio)methane (3) appears to behave as 2 in its interaction with Cu<sup>+</sup> ions, based on spectroscopic evidence. Thus, <sup>1</sup>H NMR spectra of mixtures of 3, and either  $[Cu(CH_3CN)_4]PF_6$  or  $[Cu(CH_3CN)_4]ClO_4$  in acetonitrile are characterized by small changes in the chemical shifts of the ligand-derived signals. Mass spectra contain peaks ascribed to Cu<sup>+</sup> complexes of 3, including those at m/z =807 and 435, which were assigned to  $[(3)_2Cu]^+$  and  $[(3)_2Cu]^+$ Cu]<sup>+</sup>, respectively. The base peak at m/z = 823 corresponds to the product of air oxidation of  $[(3)_2Cu]^+$ , namely  $[(3)_2 CuO]^+$ . Fragmentation of the latter complex gives rise to  $[(3)CuO]^+$ , detected at m/z = 451 (see Supporting Information Figure S8). Thus, the cuprous complexes of 3 are more easily oxidized by dioxygen in the ionization chamber than those of 2.

In contrast to the behavior of **1** and **2** toward CuI, no crystalline products were obtained in the reactions with **3**, even when the less sterically demanding CuBr and CuCl were employed. Two factors can be identified in the stability of the complexes: the degree of steric hindrance exerted by the *ortho* substituents of the arylthioethers, and the size of the chelate that may be formed upon complexation of Cu<sup>+</sup>. In the case of **3**, both considerations appear to disfavor thioether coordination to the copper centers: the steric influence of the bulky *ortho tert*-butyl groups as well as the proximity of the sulfur atoms, which do not allow the formation of a four-member chelate in  $[(2)(CuI)_4(CH_3CN)_2]_2$ .

Treatment of 3 with 1–2 equiv. of  $Cu(ClO_4)_2 \cdot 6H_2O$  for ESI-MS analysis revealed a different behavior from that of 2. In this case an unidentified species was detected at m/z = 1501, with a poorly defined isotopic pattern. Fragmentation of this species gives rise to two peaks at m/z = 679 and 971; the latter was assigned to the mixed dithioether/ disulfide complex  $[(3)(4)Cu(SC_6H_3-2-tBu-4-Me)]^+$  (see Figure S9 in the Supporting Information). The absence of other peaks corresponding to Cu complexes of 3 or 4 is consistent with the low stability determined by cyclic voltammetry.

#### **Electrochemical Studies**

Further evidence of the oxidative nature of the ligand decomposition reactions was obtained from cyclic voltammetry measurements and bulk electrolysis experiments. Compounds 1-3 were characterized electrochemically in an acetonitrile solution at a concentration of 1 mM and a scan rate of 0.100 V s<sup>-1</sup>. Under these conditions the observed oxidation signals behave irreversibly, and therefore most of the cathodic peaks are not well defined. In the case of 1 five oxidation processes were identified as Iap, IIap, IIIap, IVap, and  $V^{ap}$  (see Table 2), with anodic peak potentials ( $E^{ap}$ ) at 0.65, 1.04, 1.42, 1.61, and 1.96 V relative to the Fc<sup>+</sup>/Fc couple, respectively. Compound 2 presented four oxidative processes at 0.92, 1.08, 1.63, and 2.02 V, while 3 is characterized by only three oxidation processes, with  $E^{ap}$  at 0.95, 1.53, and 1.92 V. With regard to the interaction of the thioethers with Cu<sup>+</sup>, comparison of the voltammograms of an acetonitrile solution of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub>, and 2 plus 2 equiv. of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub>, reveals that the potential peak reduction process from Cu<sup>+</sup> to Cu<sup>0</sup> is shifted from -0.97 to -1.07 V ( $\Delta E = 105$  mV, see Figure 3). We attribute this behavior to the coordination of 2 to  $Cu^+$ , which results in the stabilization of the cuprous complex, and hence a

Table 2. Redox potentials of the compounds  $L^{Me}$  and 1–3 (V,  $\it E$  vs. Fc+/Fc).

	Iap	II <sup>ap</sup>	$III^{ap}$	IV <sup>ap</sup>	Vap
L <sup>Me</sup>	0.56 <sup>[a]</sup>	_	_	_	_
1	0.65	1.04	1.42	1.61	1.96
2	0.92	1.08	1.63	2.02	_
3	0.95	1.53	1.92	-	_

[a] Taken from ref.<sup>[9]</sup>

more negative reduction potential. Solutions of 1 and 3 with 2 equiv. of Cu<sup>+</sup> also presented a shift in the reduction peak potentials from Cu<sup>+</sup> to Cu<sup>0</sup> ( $\Delta E = 202 \text{ mV}$  for 1, and  $\Delta E = 14 \text{ mV}$  for 3, see Supporting Information Figures S10 and S11), suggesting that the complex 1/Cu is the most stable, while 3/Cu presents the weakest thioether/Cu interaction, in agreement with the inaccessibility of isolable cuprous complexes of 3. Attempts to characterize the CuI complexes of 1–3 electrochemically were precluded by the complexity of the anodic region of the voltammograms.



Figure 3. Cyclic voltammograms of **2** plus 2 equiv. of  $[Cu(CH_3-CN)_4]ClO_4$  (black line) and  $[Cu(CH_3CN)_4]ClO_4$  (gray line).

Comparison of the products of the chemical oxidation of the thioethers with Cu<sup>2+</sup>, with those of the electrochemical oxidation of 1-3 was achieved by chronopotentiometry. The compounds were electrolyzed by applying a current of  $100 \,\mu\text{A}$  to  $1 \,\text{mm}$  solutions of the thioethers in a  $0.1 \,\text{m}$  $(C_4H_9)_4NPF_6$  acetonitrile solution. The effectiveness of this method was confirmed by measuring the voltammograms of the solutions before and after electrolysis, which revealed close to 90% completion. Figure 4 shows a representative example of the cyclic voltammograms obtained for 2; the first oxidation corresponds to 1e<sup>-</sup> processes for 1 and 2. In the case of 3, the first oxidation wave decreases by 47%after electrolysis, and the fact that only three anodic peaks are observed for this compound suggests that the peak at  $E^{\rm ap} = 0.95$  V involves more than one oxidative process (see Figures S12 and S13, Supporting Information).

Upon electrolysis the products of oxidation of the thioethers were analyzed by mass spectrometry and <sup>1</sup>H NMR spectroscopy. The high concentration of the supporting electrolyte in the solutions gave rise to spectra partially obscured by the signals corresponding to the  $[(C_4H_9)_4N]^+$  cation at m/z = 242 in all mass spectra (see Figure S14, Supporting Information). The low abundance of the other peaks in the spectra did not allow the identification of ligand-derived fragments. Nonetheless, the <sup>1</sup>H NMR spectra



Figure 4. Cyclic voltammograms of **2** before (gray line) and after (black line) electrolysis.

revealed the peaks corresponding to the disulfides 4 and 5 as the main products of the electrochemical oxidation, and the disappearance of the characteristic  $E-CH_2$ -S singlets (E = N, S) between  $\delta$  = 4.29 and 4.49 ppm of 1–3 (see Figures S15 and S16, Supporting Information). Thus, ligand decomposition to the corresponding disulfides is an oxidative process, which can be carried out by chemical (Cu<sup>2+</sup>) or electrochemical methods.

Comparison of the first anodic peak potentials (I<sup>ap</sup>, Table 2) of compounds  $L^{Me}$  and 1–3 reveals that the nitrilotrithioethers are more easily oxidized than the dithioethers. This can be attributed to the presence of the central nitrogen atom in  $L^{Me}$  and 1, which upon oxidation results in the formation of iminium ions. In contrast, the oxidation of 2 and 3 gives rise to the less stable carbosulfonium ions. Thus, it seems plausible to propose that the nitrogen-stabilized iminium species are more easily generated due to their relative stability, resulting in lower oxidation potentials for the nitrilotrithioethers.

#### Conclusions

In summary, the thioether/Cu<sup>+</sup> systems derived from ligands 1–3 and different cuprous salts are present in solution as a rapidly interconverting mixture of complexes with different stoichiometries. The chelate ring size of four does not support copper complexation and gives rise instead to a sixmembered ring in  $[(1)CuI]_2$ , with 1 acting as a bidentate thioether. The instability of four-membered chelates renders 2 as a bridging ligand toward CuI clusters, although extended bridging to generate coordination polymers appears to be restricted by the steric influence of the *ortho* methyl groups. Dithioether 3 appears to be both restricted to form chelates and too sterically congested to afford isolable Cu<sup>+</sup> complexes, either as discrete or polymeric species. Chemical or electrochemical oxidation of 1 results mainly in the disul-

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fide 4, although a small amount of intramolecular C-C bond formation appears to take place. Compounds 2 and 3 are also oxidized to the disulfides 5 and 4, respectively. These observations are supported by bulk electrolysis of the ligands, which also results in the formation of the disulfides. Mass spectrometry appears to indicate that intermolecular C-C bond formation occurs in the oxidation of 2, as proposed in Scheme 4, although the amount of product formed would be negligible. This is probably because of the instability of the reactive [ArS=CH<sub>2</sub>]<sup>+</sup>, which would readily decompose in the presence of nucleophiles. The oxidation potentials determined for the thioether/Cu<sup>+</sup> complexes are high (see Table 2), as expected for copper centers in sulfur-rich coordination environments. Furthermore, the thioethers employed do not support cupric complexes, since reactions with  $Cu^{2+}$  lead to the oxidation of 1–3. Thus, in thioether coordination environments Cu<sup>+</sup> is favored over Cu<sup>2+</sup>, and it is likely that ligand-promoted reduction of the metal center can occur in these systems.

### **Experimental Section**

**General:** Compounds were manipulated under an atmosphere of dinitrogen in a glovebox or by vacuum-line and Schlenk techniques. Solvents were dried by standard methods and distilled under N<sub>2</sub> prior to use. CuI, [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub>, Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, hexamethy-lenetetramine, 2,4-dimethylthiophenol, *para*-formaldehyde, and *p*-toluenesulfonic acid were used as received from commercial suppliers. [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> and 2-*tert*-butyl-4-methylthiophenol were prepared according to literature procedures.<sup>[18,19]</sup> Melting points were determined with an Electrothermal Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded with a Bruker Tensor 27 spectrophotometer in the 4000–400 cm<sup>-1</sup> region as CH<sub>2</sub>Cl<sub>2</sub> solutions or by using KBr disks. NMR spectra were recorded with

Table 3. Summarized crystallographic data.

a JEOL Eclipse 300 spectrometer in  $CDCl_3$  with tetramethylsilane as an internal standard, or in  $CD_3CN$  referenced relative to the residual solvent protons at 300 (<sup>1</sup>H) or 75 MHz (<sup>13</sup>C). Mass spectra were obtained with a JEOL JMS-SX-102A mass spectrometer at an accelerating voltage of 10 kV, with a nitrobenzyl alcohol matrix and Xenon atoms at 6 keV (FAB<sup>+</sup>), or a Bruker Daltonics Esquire 6000 spectrometer with ion trap (Electrospray). Elemental analyses were performed at the microanalytical facility of the Instituto de Química.

**Warning!** Metal perchlorates are potentially explosive and should be handled with extreme care.

Electrochemical Studies: Measurements were made under N2 in anhydrous acetonitrile with a potentiostat-galvanostat EG&G PAR model 263A with a glassy carbon working electrode and a platinum wire auxiliary electrode. Potentials were recorded vs. a pseudo-reference electrode of AgBr(s)/Ag(wire) immersed in a 0.1 M (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>-NBr acetonitrile solution. The working electrode was polished with alumina and washed with acetonitrile prior to measurements. All voltammograms were started from the current null potential ( $E_i$  = 0) and were scanned in both directions, positive and negative, and obtained at a scan rate of 0.100 Vs<sup>-1</sup>. In agreement with IUPAC convention, the voltammogram of the Fc<sup>+</sup>/Fc system was obtained to establish the values of the anodic  $(E^{ap})$ , and cathodic  $(E^{cp})$  peak potentials. The electrolytic domain under the working conditions was -2.2 to 3.2 V relative to AgBr(s)/Ag(wire). Bulk electrolyses were performed with a high-surface platinum wire as the auxiliary electrode and a platinum minigrid as the working electrode.

**X-ray Crystallography:** Selected crystallographic data are presented in Table 3. Single crystals were mounted at 173 K on a Bruker SMART diffractometer equipped with an Apex CCD area detector. Frames were collected by omega scans, and integrated with the Bruker SAINT software package using the appropriate unit cell.<sup>[20]</sup> The structures were solved using the SHELXS-97 program,<sup>[21]</sup> and refined by full-matrix least-squares on  $F^2$  with SHELXL-97.<sup>[22]</sup> Weighted *R* factors,  $R_{w}$ , and all goodness of fit indicators, *S*, were

	[(1)CuI] <sub>2</sub>	[( <b>2</b> )(CuI) <sub>4</sub> (CH <sub>3</sub> CN) <sub>2</sub> ] <sub>2</sub> ·2THF·4CH <sub>3</sub> CN	4
Empirical formula	$C_{72}H_{102}Cu_2I_2N_2S_6$	$C_{58}H_{80}Cu_8I_8N_8O_2S_4$	C <sub>22</sub> H <sub>30</sub> S <sub>2</sub>
$M_{\rm r}$ [gmol <sup>-1</sup> ]	1568.80	2573.06	358.58
Temperature [K]	100(2)	100(2)	298(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_{1}2_{1}2_{1}$
Crystal size [mm]	$0.132 \times 0.258 \times 0.348$	$0.102 \times 0.196 \times 0.242$	$0.190 \times 0.200 \times 0.380$
<i>a</i> [Å]	16.630(2)	16.434(2)	8.567(1)
b [Å]	14.794(2)	14.014(2)	12.899(1)
c [Å]	15.185(2)	18.041(2)	37.925(2)
β[°]	95.394(2)	97.336(s)	90
γ [°]	90	90	90
V[Å <sup>3</sup> ]	3719.3(8)	4121.1(8)	4190.8(4)
Z	2	2	8
$\mu$ (Mo- $K_a$ ) [mm <sup>-1</sup> ]	1.610	5.161	0.255
$\theta$ range	1.85 to 25.42	1.79 to 25.38	1.67 to 25.00
hkl range	$-20 \le h \le 19$	$-18 \le h \le 19$	$-10 \le h \le 10$
	$-17 \le k \le 17$	$-16 \le k \le 16$	$-15 \le k \le 15$
	$-18 \le l \le 18$	$-21 \le l \le 21$	$-45 \le l \le 45$
$D_{\rm calc}  [\rm kg  m^{-3}]$	1.401	2.074	1.137
Refined parameters	391	451	449
Total reflections	29845	33441	34044
Unique reflections	6832	7547	7400
$R_1 [\hat{I} > 2\sigma(I)]$	0.0286	0.0306	0.0463
$wR_2$	0.0680	0.0643	0.0730
Goodness of fit	1.063	1.049	0.913



based on  $F^2$ . The observed criterion of  $(F^2 > 2\sigma F^2)$  was used only for calculating the *R* factors. All non-hydrogen atoms were refined with anisotropic thermal parameters in the final cycles of refinement. Hydrogen atoms were placed in idealized positions, with C– H distances of 0.93 and 0.98 Å for sp<sup>2</sup>- and sp<sup>3</sup>-hybridized carbon atoms, respectively. The isotropic thermal parameters of the hydrogen atoms were assigned the values of  $U_{\rm iso} = 1.2$  times the thermal parameters of the parent non-hydrogen atom.

CCDC-782635 (for  $[(1)CuI]_2$ ), -782636 (for  $[(2)(CuI)_4(CH_3-CN)_2]_2$ ), -782637 (for 4) contain the crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

Tris(2-tert-butyl-4-methylphenylthiomethyl)amine (1): 2-tert-Butyl-4-methylthiophenol (0.60 g, 3.33 mmol), hexamethylenetetramine (0.09 g, 0.63 mmol), and p-toluenesulfonic acid (0.02 g) were placed in a sealed vessel under N<sub>2</sub>, and then heated to 115–120 °C for 2 d. After cooling to room temperature and removing volatile materials (primarily NH<sub>3</sub>) under vacuum, another portion of 2-tert-butyl-4methylthiophenol (0.20 g, 1.11 mmol) was added, and the mixture was heated to 115-120 °C for a further 18 d. The yellow oil obtained was washed with MeOH, dissolved in hexanes, and filtered. The components were separated by flash column chromatography on silica gel, eluting with hexanes followed by 9:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub> afforded 1 (0.25 g, 33.4%) as a colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.27$  (d,  ${}^{3}J = 7.70$  Hz, 3 H, Ar), 7.16 (d,  ${}^{4}J = 1.52$  Hz, 3 H, Ar), 6.86 (dd,  ${}^{3}J$  = 7.70,  ${}^{4}J$  = 1.52 Hz, 3 H, Ar), 4.49 (s, 6 H, NCH<sub>2</sub>S), 2.29 (s, 9 H, ArCH<sub>3</sub>), 1.48 [s, 27 H, ArC(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.71 (Ar), 136.60 (Ar), 135.17 (Ar), 131.28 (Ar), 127.68 (Ar), 127.39 (Ar), 62.18 (NCH<sub>2</sub>), 36.66 (ArCH<sub>3</sub>), 30.90 [ArC(CH<sub>3</sub>)<sub>3</sub>], 21.54 [ArC(CH<sub>3</sub>)<sub>3</sub>] ppm. IR (KBr): ṽ = 2961, 2920, 2869, 1726, 1690, 1597, 1453, 1395, 1261, 1213, 1100, 1043, 919, 878, 810, 688, 636, 475 cm<sup>-1</sup>. FAB<sup>+</sup> MS:  $m/z = 592 (1^+)$ , 536 ( $[1 - tBu]^+$ ), 414 ( $[ArSCH_2]_2NCH_2^+$ ). C<sub>36</sub>H<sub>51</sub>NS<sub>3</sub> (593.99): calcd. C 72.79, H 8.65; found C 72.59, H 8.90.

Bis(2,4-dimethylphenylthio)methane (2): 2,4-Dimethylthiophenol (2.00 g, 14.47 mmol), para-formaldehyde (0.22 g, 7.23 mmol), and p-toluenesulfonic acid (0.05 g) were heated to reflux in toluene (20 mL) for 14 h. After cooling to room temperature, the solution was washed with a saturated aqueous Na<sub>2</sub>CO<sub>3</sub> solution (20 mL), and twice with brine (20 mL). The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure, and the solid obtained was crystallized from hexanes to afford of 2 (1.71 g, 82.2%) as a colorless solid; m.p. 29-30 °C. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN):  $\delta$  = 7.31 (d, <sup>3</sup>J = 7.95 Hz, 2 H, Ar), 7.06 (s, 2 H, Ar), 7.01 (d, <sup>3</sup>J = 7.95 Hz, 2 H, Ar), 4.29 (s, 2 H, SCH<sub>2</sub>S), 2.28 (s, 12 H, ArCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 140.20 (Ar), 138.65 (Ar), 132.47 (Ar), 132.32 (Ar), 131.82 (Ar), 128.59 (Ar), 40.33 (SCH<sub>2</sub>S), 21.35 (ArCH<sub>3</sub>), 20.94 (ArCH<sub>3</sub>) ppm. IR (KBr):  $\tilde{v}$  = 2971, 2922, 2863, 1602, 1479, 1448, 1403, 1380, 1225, 1202, 1055, 1036, 878 cm<sup>-1</sup>. C<sub>17</sub>H<sub>20</sub>S<sub>2</sub> (288.47): calcd. C 70.78, H 6.99; found C 70.52, H 6.91.

**Bis(2**-*tert*-**butyl-4**-**methylphenylthio)methane** (3): 2-*tert*-Butyl-4methylthiophenol (0.52 g, 2.88 mmol), *para*-formaldehyde (43 mg, 1.44 mmol), and *p*-toluenesulfonic acid (10 mg) were heated to reflux in toluene (10 mL) for 14 h. After cooling to room temperature the solution was washed with a saturated aqueous Na<sub>2</sub>CO<sub>3</sub> solution (10 mL) and twice with brine (10 mL). The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure, and the product obtained was purified by flash column chromatography on silica gel. Eluting with hexanes afforded 3 (0.34 g, 63.5%) as a colorless oil. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN):  $\delta$  = 7.44 (d, <sup>3</sup>J = 7.98 Hz, 2 H, Ar), 7.24 (d,  ${}^{4}J$  = 1.38 Hz, 2 H, Ar), 7.01 (m, 2 H, Ar), 4.39 (s, 2 H, SCH<sub>2</sub>S), 2.29 (s, 6 H, ArCH<sub>3</sub>), 1.42 [s, 18 H, ArC-(CH<sub>3</sub>)<sub>3</sub>] ppm.  ${}^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.20 (Ar), 138.26 (Ar), 134.71 (Ar), 132.19 (Ar), 129.02 (Ar), 128.64 (Ar), 44.04 (SCH<sub>2</sub>S), 37.42 (ArCH<sub>3</sub>), 31.36 [ArC(CH<sub>3</sub>)<sub>3</sub>], 21.67 [ArC-(CH<sub>3</sub>)<sub>3</sub>] ppm. IR (KBr):  $\tilde{v}$  = 2972, 2924, 2874, 1592, 1454, 1395, 1364, 1248, 1242, 1193, 1046, 904, 879 cm<sup>-1</sup>. C<sub>23</sub>H<sub>32</sub>S<sub>2</sub> (372.63): calcd. C 74.14, H 8.66; found C 74.28, H 8.72.

**[(1)Cul]<sub>2</sub>:** CuI (91 mg, 0.48 mmol) was added to a solution of **1** (285 mg, 0.48 mmol) in CH<sub>3</sub>CN (10 mL) and the mixture was stirred under N<sub>2</sub> for 12 h. The solution was concentrated to ca. 4 mL, and cooling to  $-25 \,^{\circ}$ C afforded [(1)Cul]<sub>2</sub> (243 mg, 83.6%) as colorless crystals; m.p. 196–199 °C (dec). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN):  $\delta = 7.27$  (d, <sup>3</sup>*J* = 7.80 Hz, 3 H, Ar), 7.22 (d, <sup>4</sup>*J* = 1.80 Hz, 3 H, Ar), 6.89 (m, 3 H, Ar), 4.50 (s, 6 H, NCH<sub>2</sub>S), 2.27 (s, 9 H, ArCH<sub>3</sub>), 1.45 [s, 27 H, ArC(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 151.43$  (Ar), 137.81 (Ar), 135.93 (Ar), 131.96 (Ar), 128.70 (Ar), 128.33 (Ar), 62.85 (NCH<sub>2</sub>S), 37.26 (ArCH<sub>3</sub>), 31.20 [ArC(CH<sub>3</sub>)<sub>3</sub>], 21.41 [ArC(CH<sub>3</sub>)<sub>3</sub>] ppm. IR (KBr):  $\tilde{\nu} = 3039$ , 2960, 2918, 2867, 1597, 1562, 1468, 1447, 1394, 1359, 1332, 1257, 1210, 1125, 1090, 1041, 924, 876, 810, 705, 665, 631, 471 cm<sup>-1</sup>. C<sub>72</sub>H<sub>102</sub>Cu<sub>2</sub>I<sub>2</sub>N<sub>2</sub>S<sub>6</sub> (1568.87): calcd. C 55.12, H 6.55, N, 1.79; found C 54.83, H 6.32, N 1.93.

**[(2)(CuI)<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sub>2</sub>:** CuI (276 mg, 1.44 mmol) was added to a solution of **2** (105 mg, 0.36 mmol) in CH<sub>3</sub>CN (10 mL) and the mixture was stirred under N<sub>2</sub> for 12 h. The solution was concentrated to ca. 2 mL, and cooling to -25 °C afforded [(2)(CuI)<sub>4</sub>(CH<sub>3</sub>CN)<sub>4</sub>]<sub>2</sub> (236 mg, 57.9%) as a colorless crystalline product. M.p. > 300 °C. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN):  $\delta$  = 7.32 (d, <sup>3</sup>*J* = 7.95 Hz, 2 H, Ar), 7.06 (s, 2 H, Ar), 7.02 (d, <sup>3</sup>*J* = 7.95 Hz, 2 H, Ar), 4.30 (s, 2 H, SCH<sub>2</sub>S), 2.28 (s, 12 H, ArCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 139.86 (Ar), 138.32 (Ar), 132.08 (Ar), 131.99 (Ar), 131.43 (Ar), 128.28 (Ar), 40.08 (SCH<sub>2</sub>S), 21.02 (ArCH<sub>3</sub>), 20.62 (ArCH<sub>3</sub>) ppm. IR (KBr):  $\bar{\nu}$  = 3008, 2971, 2945, 2915, 2857, 2731, 1599, 1478, 1447, 1378, 1278, 1230, 1195, 1149, 1050, 874, 830, 803, 724, 652, 617, 540, 441 cm<sup>-1</sup>. C<sub>42</sub>H<sub>52</sub>Cu<sub>8</sub>I<sub>8</sub>N<sub>4</sub>S<sub>4</sub> (2264.74): calcd. C 22.27, H 2.31, N 2.47; found C 22.65, H 2.50, N 2.12.

**Bis(2**-*tert*-**Butyl-4**-methylphenyl) Disulfide (4): On a preparative scale, the disulfide is best synthesized by air oxidation of the corresponding arylthiol. A CH<sub>2</sub>Cl<sub>2</sub> solution of the thiol<sup>[19]</sup> is left standing exposed to air for 72 h, and the sole product is the disulfide in quantitative yield. The compound was crystallized by slow evaporation of a concentrated hexane solution at 4 °C; the solid melts readily on handling. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN):  $\delta$  = 7.55 (d, <sup>3</sup>*J* = 7.98 Hz, 2 H, Ar), 7.15 (d, <sup>4</sup>*J* = 1.35 Hz, 2 H, Ar), 6.92 (d, <sup>3</sup>*J* = 7.98 Hz, 2 H, Ar), 2.29 (s, 6 H, ArCH<sub>3</sub>), 1.48 (s, 18 H, ArCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 148.95 (Ar), 137.00 (Ar), 132.80 (Ar), 131.68 (Ar), 127.58 (Ar), 127.51 (Ar), 36.54 (ArCH<sub>3</sub>), 31.08 [ArC(CH<sub>3</sub>)<sub>3</sub>], 21.46 [ArC(CH<sub>3</sub>)<sub>3</sub>] ppm. IR (KBr):  $\tilde{v}$  = 2963, 2927, 2871, 1593, 1460, 1398, 1364, 1344, 1300, 1239, 1193, 1162, 1096, 1056, 1018, 902 cm<sup>-1</sup>.

**Supporting Information** (see also the footnote on the first page of this article): Additional spectroscopic and mass spectrometry data, cyclic voltammograms, and an ORTEP diagram of **4**.

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