

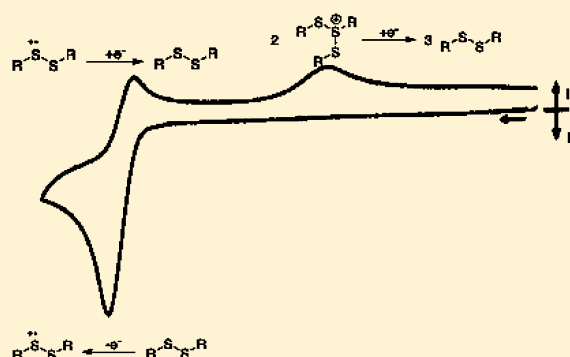
Anodic Oxidation of Disulfides: Detection and Reactions of Disulfide Radical Cations

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S Supporting Information

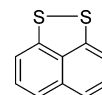
ABSTRACT: The anodic oxidation of five diaryldisulfides have been studied in a dichloromethane/[NBu₄][B(C₆F₅)₄] electrolyte. Cyclic voltammetry scans of (*p*-RC₆H₄)₂S₂ (R = Me, **1a**; R = F, **1b**; R = OMe, **1c**) show modest chemical reversibility for the 1^{0/+} couple (*E*_{1/2} values vs ferrocene: 1.04 V for **1a**, 1.21 V for **1b**, 0.92 V for **1c**), providing the first voltammetric evidence for the radical cation [Ar₂S₂]^{•+}. A dimer dication, [Ar₄S₄]²⁺, is proposed as an intermediate in the formation of the electrolysis product, the trisulfide [Ar₃S₃]⁺. The chemical reversibility of the one-electron oxidations of Ar₂S₂ vanishes in [PF₆]⁻-containing electrolytes. The radical cations of the more sterically constrained *ortho*-substituted analogues dimesityldisulfide (**2a**, *E*_{1/2} = 1.01 V) and bis(2,4,6-triisopropylphenyl)disulfide (**2b**, *E*_{1/2} = 0.98 V) show less tendency to dimerize. In all cases except **2b**, the bulk electrolysis product is [R₃S₃]⁺, consistent with earlier literature reports. A mechanism is proposed in which the trisulfide is formed by reaction of the dimer dication [Ar₄S₄]²⁺ with neutral Ar₂S₂ to afford the trisulfide in a net 2/3 e⁻ process. Oxidation of Ar₂S₂, either anodically or by a strong one-electron oxidant, in the presence of cyclohexene gives an efficient synthetic route to 1,2-substituted cyclohexyldisulfides.



INTRODUCTION

Owing, in part, to the importance of organic disulfides in structural biology,¹ the electrochemical oxidation of this class of compounds continues to draw study, adding to an already extensive body of papers.² For simple RSSR disulfides, the anodic electrolysis products and the (1 e⁻ vs 2 e⁻) electron-transfer stoichiometry depend principally on the nature of R and the temperature and chemical makeup of the solvent/supporting electrolyte system. An important general finding is that the radical cations of this series, [RSSR]^{•+}, have low kinetic stability. A few radical cations of cyclic disulfides (such as dithionaphthalene shown below) have been confirmed by optical or ESR spectroscopy.^{3,4} However, to the best of our knowledge, radical cations of the linear disulfides [RSSR]^{•+}, R = alkyl or aryl, although frequently invoked as intermediates, have not been confirmed even as a transient species by spectroscopy or cyclic voltammetry (CV). Rather, [RSSR]^{•+} has been reported to be kinetically unstable with respect to sulfur-sulfur cleavage,^{5–8} thereby initiating routes to formation of more stable in situ products, such as the sulfenium ion [RS]⁺^{5–13} or the trisulfide [R₃S₃]⁺.^{5,10,11,14} With the goals of finding direct electrochemical evidence for [RSSR]^{•+} and adding to the mechanistic understanding of the oxidatively induced conversion of disulfides to their cationic products, we have investigated the anodic oxidation of several diaryl disulfides and dimethyldisulfide in dichloromethane using the weakly coordinating anion (WCA) [B(C₆F₅)₄]⁻ as the supporting electrolyte anion. Although the low nucleophilicity of this

anion¹⁵ has been extremely valuable in promoting the stability of highly electrophilic organometallic systems,^{16,17} it has seen relatively few applications to organic redox chemistry.^{14,18} The present paper reports our findings on five diaryldisulfides (**1a–1c**, **2a**, and **2b**) and dimethyldisulfide. With the exception of the sterically hindered compound **2b**, the long-term (bulk electrolysis time scale) product is, in fact, the expected trisulfide [R₃S₃]⁺. However, some degree of chemical reversibility of the parent 0/+ couple was observed in each case for CV scans at modest scan rates, giving the first definitive voltammetric evidence for the radical cations of these compounds, and allowing a more detailed discussion of the mechanism of anodically induced formation of the trisulfide.

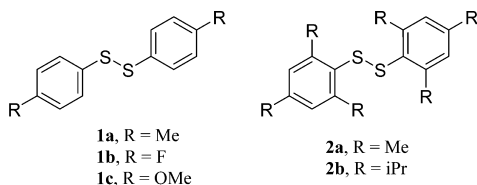


RESULTS AND DISCUSSION

The literature paper most relevant to our study is the communication by Matsumoto et al. in which catalytic amounts of [Ar₃S₃]⁺ were shown to initiate stereoselective addition of Ar₂S₂ to dienes.¹⁴ The authors generated the trisulfide cation in situ by bulk electrolysis of Ar₂S₂ in CH₂Cl₂/0.1 M [NBu₄][B-

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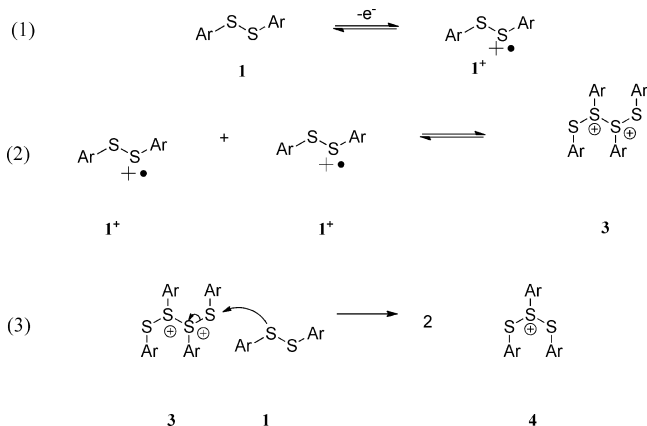
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(C₆F₅)₄], essentially the same medium as used in the present work. An important difference, however, is that the published work was carried out at low temperature (195 K), a factor that has an important effect on the ability to detect the primary radical cation [Ar₂S₂]^{•+}, **1**^{•+}. Although voltammograms of Ar₂S₂ were not shown or referred to in ref 14, CV scans of the diaryldisulfides under these low-temperature conditions are not likely to show any chemical reversibility for the [Ar₂S₂]^{0/+} couple (see below).

The present study focuses on three *para*-substituted arene derivatives, **1a–1c**, and the bis-*ortho*-substituted arene derivatives **2a** and **2b**. Measurements were also made on dimethyldisulfide. Results on **1a–1c** suggested that the overall anodic process proceeds by the mechanism given in Scheme 1,

Scheme 1. Proposed Mechanism for Anodic Oxidation of Diaryldisulfides



a key component being the dimer dication, [Ar₄S₄]²⁺, **3**. Subsequent preparation and electrochemical testing of the more sterically encumbered compounds **2a** and **2b** confirmed expectations based on this scheme.

Oxidation of *para*-Substituted Arene Disulfides, 1a–1c. At room temperature, all three of this group of disulfides displayed some degree of chemical reversibility with a CV scan rate of 0.2 V s⁻¹ in CH₂Cl₂/0.05 M [NBu₄][B(C₆F₅)₄], permitting assignment of the E_{1/2} values of their one-electron oxidations (Table 1). One millimolar solutions of **1a** and **1c** showed scan-rate-dependent chemical reversibility similar to

that shown in Figure 1, *i*_c/*i*_a ratios going from about 0.5 to 0.75 when scan rates were increased from 0.2 to 2 V s⁻¹. At a given

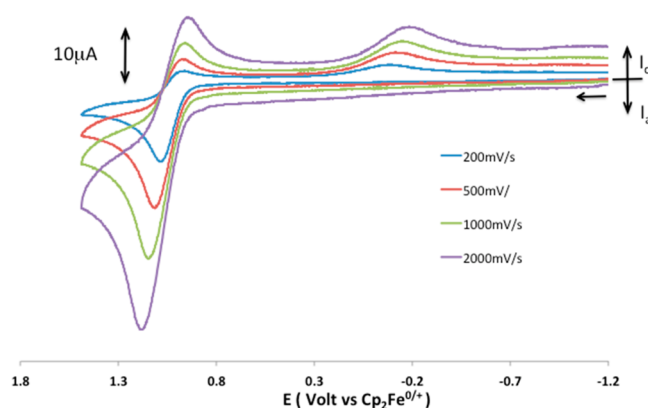


Figure 1. CV of **1a** (1.05 mM) in CH₂Cl₂/0.05 M [NBu₄][B(C₆F₅)₄] at different scan rates, 25 °C, 2 mm glassy carbon electrode.

concentration, anodic peak currents increased with the square root of the scan rate, confirming a diffusion-controlled anodic process. A diffusion coefficient of 1.73 × 10⁻⁵ cm² s⁻¹ was measured for **1a** by chronoamperometry on a 0.025 mM solution at 298 K. No matter what the degree of chemical reversibility of the **1**^{0/+} process, there were never more than two cathodic features: either that coupled to reduction of the radical cation at the appropriate E_{pc} or a totally irreversible peak (lacking a coupled anodic feature) appearing about 1 V or more negative of the E_{1/2} of the **1**^{0/+} couple. The potential of the irreversible wave varies with scan rate (*v*), appearing at the E_{pc} values given in Table 1 when *v* = 0.2 V s⁻¹. The *para*-substituted aryl derivatives will be discussed somewhat interchangeably owing to their similar overall anodic behavior.

A somewhat increased degree of chemical reversibility was observed for oxidation of the *p*-fluoroaryl derivative **1b** (solid line in Figure 2). In that case, there is only scant evidence of the follow-up product at E_{pc} ≈ 0 V. There are important variations that arise with changes in temperature and analyte concentration that will be described later. At this point, however, we bring attention to the complete *loss of reversibility* for **1b**^{0/+} if the electrolyte anion is [PF₆]⁻ rather than [B(C₆F₅)₄]⁻ (dashed line vs solid line in Figure 2). The fact that almost all of the earlier papers reporting voltammetry of diaryldisulfides^{5–12} were carried out using electrolytes having the traditional smaller anions, such as [PF₆]⁻ or [BF₄]⁻, accounts in great part for the absence of CV detection of [Ar₂S₂]^{•+} in the previous literature. It is also important to note that the follow-up product, identified as the trisulfide [(*p*-FC₆H₄)₃S₃]⁺ (see below), is still observed in the [PF₆]⁻-containing medium (E_{pc} ≈ 0.25 V).

Table 1. Potentials in CH₂Cl₂/0.05 M [NBu₄][B(C₆F₅)₄]^a

entry	compound	E _{1/2} (V vs FcH)	E _{pc} (V) of trisulfide product 4
1	(<i>p</i> -MeC ₆ H ₄) ₂ S ₂ , 1a	1.04	-0.03
2	(<i>p</i> -FC ₆ H ₄) ₂ S ₂ , 1b	1.21	0.02
3	(<i>p</i> -OMeC ₆ H ₄) ₂ S ₂ , 1c	0.92	-0.05
4	2a	1.01	-0.14
5	2b	0.98	not formed
6	Me ₂ S ₂	1.10	-0.43

^aE_{pc} was recorded at a scan rate of 0.2 V s⁻¹.

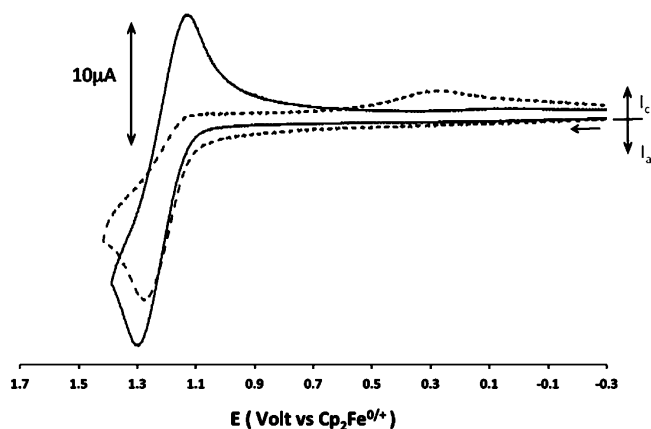


Figure 2. CV of **1b** (1.34 mM) in $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (solid line) and in $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{PF}_6]$ (dashed line), scan rate = 0.2 V/s, 25 °C, 2 mm glassy carbon electrode.

That the final oxidation product is the same in both $[\text{PF}_6]^-$ and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ electrolytes was confirmed by bulk anodic electrolysis of **1b** in $\text{CH}_2\text{Cl}_2/[\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ at $E_{\text{appl}} = 1.38 \text{ V}$. This reaction passed 1.03 F and gave a single electroactive product with $E_{\text{pc}} = -0.03 \text{ V}$ (Figure 3). The re-electrolysis

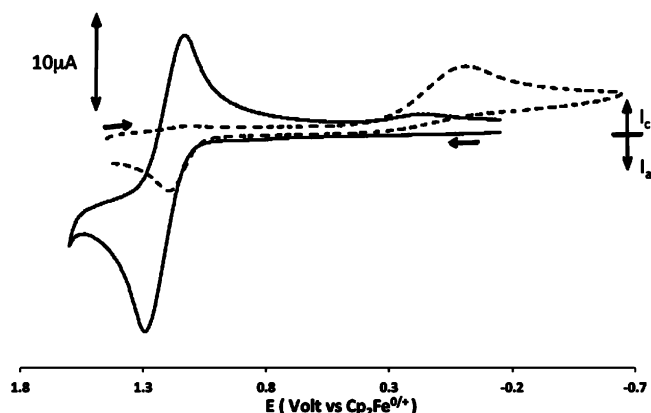


Figure 3. CV of **1b** (1.91 mM) in $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ before bulk electrolysis (solid line) and after bulk electrolysis at 1.38 V (dashed line), scan rate 0.2 = V/s, 25 °C, 2 mm glassy carbon electrode.

negative of the product wave ($E_{\text{appl}} = -0.70 \text{ V}$) consumed only 0.79 F and resulted in *quantitative* regeneration of the starting material (see comparative CVs in Figure SM1 of the Supporting Information). In a number of previous papers, including the electrolysis of Ar_2S_2 in a $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ electrolyte,¹⁴ the main product of the oxidation of Ar_2S_2 has been shown to be the trisulfide $[\text{Ar}_3\text{S}_3]^+$, **4**.^{5,10,11} This was confirmed in the present case by testing the voltammetric behavior of an authentic sample of $[\text{Ar}_3\text{S}_3]^+$ generated in situ by the reaction of **1a** with an equivalent of SbCl_5 .¹⁹ The resulting solution had an irreversible reduction wave near the E_{pc} value of -0.03 V observed after the bulk oxidation of **1a**. Consistent with this assignment, **1a** itself was formed when $[(p\text{-MeC}_6\text{H}_4)_3\text{S}_3]^+$ was reduced, either in CV scans or by bulk cathodic electrolysis. Although eq 4, therefore, describes the *gross* redox reaction, it is not informative about the mechanism of this chemically reversible process, especially on the nature of the



follow-up reactions beginning with the putative radical cation $[\text{Ar}_2\text{S}_2]^+$, **1**⁺. Molecular orbital theory predicts a relatively strong S–S bond in the radical cation $[\text{R}_2\text{S}_2]^+$, lowering the likelihood of simple S–S cleavage playing a role in the reaction.²⁰

Earlier work by Jouikov et al. reported a second-order dependence to the follow-up reactions of diaryldisulfide oxidations.²¹ Our increased ability to observe the disulfide radical cation allowed a more direct voltammetric study of analyte concentration effects, which are typified for **1a–1c** in Figure 4. At higher concentrations of **1a**, three important effects

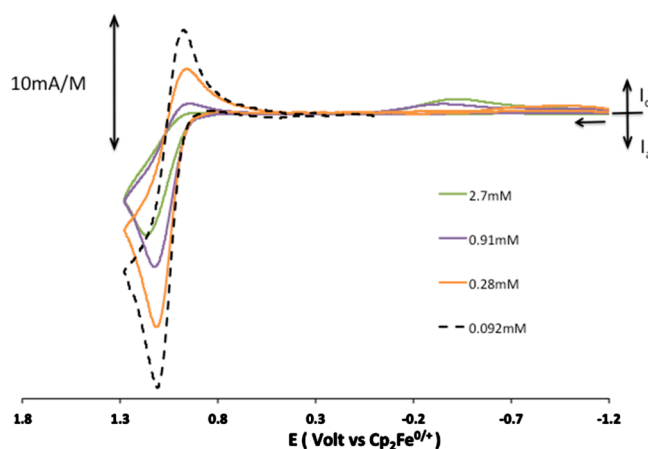
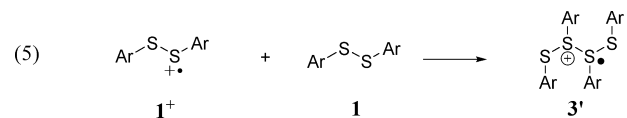


Figure 4. Background subtracted CV of **1a** at different concentrations in $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$, scan rate = 0.2 V/s, 25 °C, 2 mm glassy carbon electrode. Note that the ordinate has units of milliamp/molar.

are seen: (i) the oxidation of **1a** becomes less chemically reversible, (ii) the cathodic wave of the trisulfide product $[(p\text{-MeC}_6\text{H}_4)_3\text{S}_3]^+$ increases, and (iii) the concentration-normalized anodic peak current of **1a** decreases. As will be discussed, Scheme 1 is consistent with these experimental findings. A key element in the scheme is inclusion of the dimer dication, $[\text{Ar}_4\text{S}_4]^{2+}$, **3**, formed by radical–radical dimerization of **1**⁺ (eq 2). Nucleophilic attack on **3** by another mole of neutral **1** (eq 3) gives the final trisulfide **4** in a net 2/3 e^- process.

At low concentrations, the one-electron oxidation of **1** dominates (eq 1), accounting for the close-to-reversible CV behavior at or below approximately 10^{-4} M concentrations of **1**. If the only effect of higher concentrations of analyte was to favor the dimer dication in the chemically reversible process of eq 2, the measured $E_{1/2}$ would simply shift negative without changing the chemical reversibility of the anodic reaction. A further follow-up reaction must be invoked to account for the observed loss of reversibility (point (i) in the preceding paragraph) and the appearance of the cathodic wave for reduction of **4** (point (ii)).

In principle, the additional follow-up reaction could be of neutral **1** with either the monomer radical cation $[\text{Ar}_2\text{S}_2]^+$ (eq 5) or the dimer dication $[\text{Ar}_4\text{S}_4]^{2+}$ (eq 3). Although the



radical–substrate reaction of eq 5 cannot be ruled out, since subsequent S–S cleavage would give the observed trisulfide

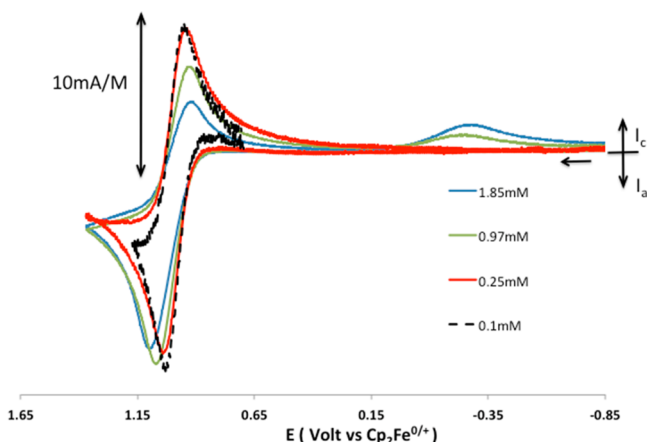


Figure 6. Background subtracted CV of **2a** at different concentrations in $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$, scan rate = 0.2 V/s , $25 \text{ }^\circ\text{C}$, 2 mm glassy carbon electrode. Note that the ordinate has units of milliamperes/molar. A higher noise level restricted analysis in the range of -0.85 to 0.65 V for 0.1 mM solution.

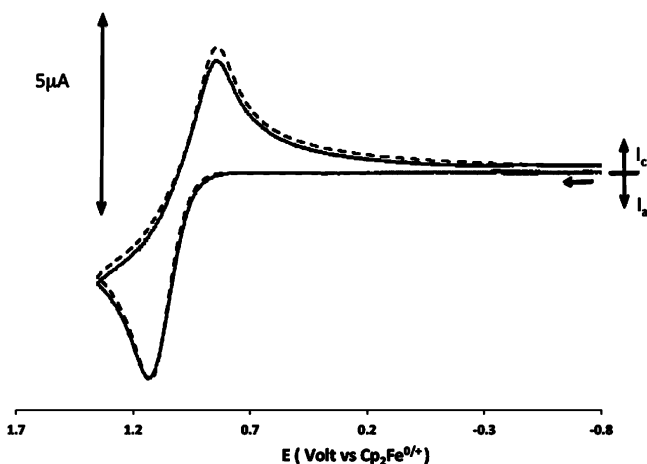


Figure 7. Background subtracted CV of **2b** (0.057 mM) in $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (solid line) and digital simulation (dashed line), scan rate = 0.2 V/s , $25 \text{ }^\circ\text{C}$, 2 mm glassy carbon electrode.

arise from slow heterogeneous electron transfer (ET) for the $\mathbf{2b}^{0/+}$ couple rather than from chemical follow-up reactions. Digital simulations (dashed line in Figure 7) confirm this, being consistent with a standard heterogeneous rate constant, k_s , of $7.4 \times 10^{-4} \text{ cm s}^{-1}$. Whereas the reason(s) for the slow ET for this compound cannot be delineated without further study, we refer the interested reader to more in-depth studies on how steric effects may influence k_s values for other organic redox couples.³¹

Oxidation of Dimethyldisulfide. CV scans of 1.5 mM Me_2S_2 showed only the barest of evidence for the radical cation $[\text{Me}_2\text{S}_2]^+$ at scan rates of 1 V s^{-1} or less (Figure S5, Supporting Information). This is consistent with our model in which a second-order follow-up reaction occurs more readily when dimerization of the radical cation is favored. The major product for the oxidation of Me_2S_2 , responsible for a cathodic wave near -0.43 V , is almost certainly the trisulfide $[\text{Me}_3\text{S}_3]^+$.

Reactivity of the Trisulfide Cation. A number of authors have investigated the reactivities of trisulfide cations, $[\text{R}_3\text{S}_3]^+$, with olefins,^{5,14} alkynes,⁹ and compounds with other functional groups.^{6,10,32,33} We thought it useful to carry out similar

reactions between the trisulfides $[\text{Ar}_3\text{S}_3]^+$ and a weak nucleophile such as an olefin in the present $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ -containing medium. As expected, addition of olefin led to a decrease in the chemical reversibility of the $[\text{Ar}_2\text{S}_2]^{0/+}$ couple and the disappearance of the trisulfide reduction peak (see Figure 8 for **1a** in the presence of cyclohexene). Although a

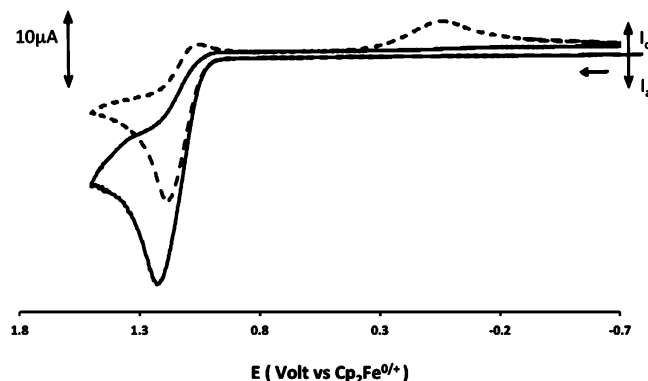
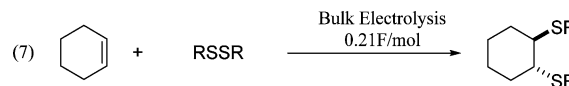


Figure 8. Cyclic voltammogram of **1a** (1.05 mM) in $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$, scan rate = 0.2 V/s , 2 mm diameter glassy carbon electrode, $25 \text{ }^\circ\text{C}$, without cyclohexene (dashed line), and with 1 equiv of cyclohexene (solid line).

reaction between the radical cation $[\text{Ar}_2\text{S}_2]^+$ and the olefin cannot be ruled out, it seems more likely that the trisulfide cation is undergoing a rapid reaction with the olefin.

Bulk electrolysis at room temperature in the presence of 1 equiv of olefin led to rapid consumption of the disulfide after only 0.21 F per olefin, indicative of an electrocatalytic mechanism leading to the formation of the corresponding vicinal disulfide (eq 7) in high yield, consistent with the



previous literature.¹⁴ To the best of our knowledge, only aromatic disulfides have been reported to undergo a catalytic addition to olefin under oxidative conditions.³⁴ In the present case, however, as denoted in Table 2, electron-rich and

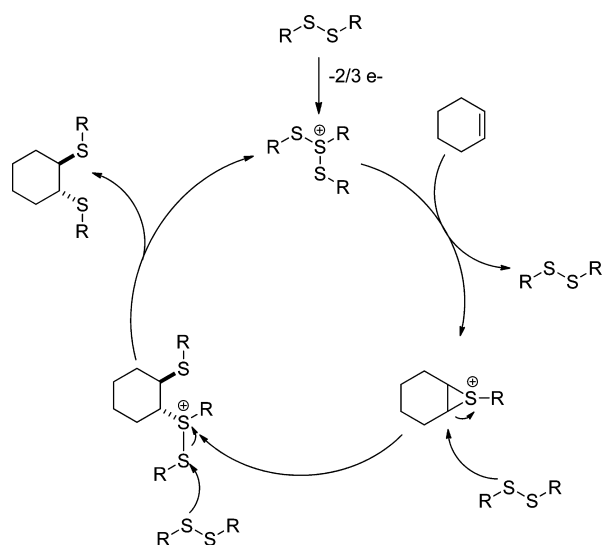
Table 2. Electrochemical Disulfurization at Room Temperature in $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$

entry	disulfide	1,2-disulfide yield (%)
1	(<i>p</i> -MeC ₆ H ₄) ₂ S ₂ , 1a	97, 7a
2	(<i>p</i> -FC ₆ H ₄) ₂ S ₂ , 1b	91, 7b
3	(<i>p</i> -OMeC ₆ H ₄) ₂ S ₂ , 1c	78, 7c
4	Me ₂ S ₂	94, 8

electron-poor aromatic disulfides as well as aliphatic disulfides are compatible with the reaction conditions. Moreover, the reaction could be performed at room temperature rather than at $-78 \text{ }^\circ\text{C}$. When $[\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ was replaced by $[\text{NBu}_4][\text{PF}_6]$, only traces of the corresponding 1,2-disulfide were observed.³⁵ Scheme 2 accounts for the disulfurization reaction.

Finally, the chemical and photochemical oxidation of disulfides, at room temperature, in the presence of 1 equiv of olefin and a catalytic amount of either $[(2,4\text{-Br}_2\text{C}_6\text{H}_3)_3\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**5**) (Magic Green) or 2,4,6-triphenylpyrrium

Scheme 2. Proposed Mechanism for the Anodically-Initiated Disulfurization of Cyclohexene



$[B(C_6F_5)_4]$ (**6**) and UV light led smoothly, within less than 15 min, to the formation of the expected 1,2-disulfide in high yield (eq 8). This would be a versatile alternative to the low-temperature electrolysis and, in some cases, might have practical advantages. See Table 3 for yields.

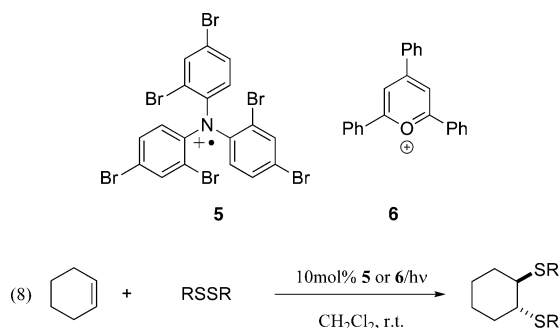


Table 3. Chemical and Photochemical Disulfurization at Room Temperature

entry	disulfide	[Cat][$B(C_6F_5)_4$]	1,2-disulfide yield (%) ^a
1	(<i>p</i> -MeC ₆ H ₄) ₂ S ₂ , 1a	5	99, 7a
2	(<i>p</i> -FC ₆ H ₄) ₂ S ₂ , 1b	5	92, 7b
3	(<i>p</i> -OMeC ₆ H ₄) ₂ S ₂ , 1c	5	75, 7c
4	Me ₂ S ₂	5	95, 8
5	(<i>p</i> -MeC ₆ H ₄) ₂ S ₂ , 1a	6	91, 7a
6	(<i>p</i> -FC ₆ H ₄) ₂ S ₂ , 1b	6	79, 7b
7	(<i>p</i> -OMeC ₆ H ₄) ₂ S ₂ , 1c	6	61, 7c
8	Me ₂ S ₂	6	90, 8

^aYields are reported for isolated pure compounds.

SUMMARY AND CONCLUSIONS

The anodic oxidation of five different diaryldisulfides has been studied in a dichloromethane/ $[NBu_4][B(C_6F_5)_4]$ electrolyte. With one exception, namely, the sterically encumbered bis-*ortho*-substituted triisopropyl compound **2b**, bulk oxidation furnishes a quantitative yield of the triaryltrisulfide $[Ar_3S_3]^+$, in agreement with the previous literature.^{5,10,11,14} By controlling

the concentration of the disulfide, new cyclic voltammetry evidence has emerged, providing the first verification of the radical cation $[Ar_2S_2]^+$ and allowing a more detailed mechanistic analysis than previously possible.

If the aryl groups contain only a *para* substituent, the chemical reversibility of the $[Ar_2S_2]^{0/+}$ couple is rather modest at CV scan rates of 0.2–0.5 V s⁻¹, with only minor changes occurring with alterations in the *para* substituent. The reversibility of $1^{0/+}$ is increasingly disfavored at higher concentrations of disulfide and at lower temperatures, conditions that favor a second-order follow-up reaction of the radical cation $[Ar_2S_2]^+$, almost certainly forming the dimer dication $[Ar_4S_4]^{2+}$. A further follow-up reaction must then occur, most likely between $[Ar_4S_4]^{2+}$ and the neutral starting material, to provide the trisulfide final product, $[Ar_3S_3]^+$. Under conditions favoring the follow-up reactions, the anodic electron-transfer stoichiometry is reduced from the one electron needed for formation of $[Ar_2S_2]^+$ to the two-thirds electron needed to form the trisulfide $[Ar_3S_3]^+$. Replacement of the $[PF_6]^-$ supporting electrolyte anion by the weakly coordinating $[B(C_6F_5)_4]^-$ anion is key to permitting detection of the radical cations. It is likely that weaker ion-pairing between the dimer dication and $[B(C_6F_5)_4]^-$ imparts thermodynamic stability to the monomeric radical cation, thereby disfavoring the follow-up reactions required to obtain the long term electrolysis product $[Ar_3S_3]^+$.

Efficient disulfurization is observed when the oxidation of Ar_2S_2 is carried out in the presence of cyclohexene. Initiation of the disulfurization can be carried out either anodically or by use of a catalytic amount of a sufficiently strong one-electron oxidizing agent.

Finally, we note that the anodic behavior of diphenyldiselenide, Ph_2Se_2 , was briefly investigated. CV scans between 0.2 and 1 V s⁻¹ for 0.88 mM Ph_2Se_2 in $CH_2Cl_2/0.05$ M $[NBu_4][B(C_6F_5)_4]$ showed only a chemically irreversible anodic wave at $E_{pa} \approx 1.05$ V and a single cathodic product wave near -0.1 V.

EXPERIMENTAL SECTION

Electrochemical procedures were carried out under dry nitrogen, using either Schlenck techniques or a drybox maintained at 1–3 ppm oxygen. Solvents were dried and distilled as previously described.³⁶ Ditylidydisulfide and dimethyldisulfide were obtained commercially. Di-*p*-fluorophenyldisulfide, di-*p*-methoxyphenyldisulfide, dimesityldisulfide, and di(2,4,6-triisopropylphenyl)disulfide were prepared by reduction of the corresponding sulfonyl chloride with triphenylphosphine.³⁷ $[NBu_4][PF_6]$ (Tokyo Chemical Industry) was recrystallized from absolute ethanol and vacuum-dried for at least 24 h at 100 °C. $[NBu_4][B(C_6F_5)_4]$ was prepared as described earlier³⁸ and also vacuum-dried at 100 °C. A full description of the electrochemical procedures is available.³⁶ Among the most important features is that a traditional three-electrode cell setup was employed for voltammetry, with the reference electrode separated by a fine frit from the working electrode solution. For bulk electrolyses, a fine frit was also used to separate the working and auxiliary compartments. The working electrodes were 2 mm glassy carbon disks for voltammetry and platinum gauze for bulk electrolyses. The experimental reference electrode was a homemade Ag/AgCl wire, but all potentials in this paper are referred to the ferrocene/ferrocenium potential,³⁹ obtained using the *in situ* method^{39b} to track the experimental potential versus ferrocene. NMR data were obtained using a 500 MHz instrument.

Preparation of $[N(2,4-C_6H_3Br_2)_3][B(C_6F_5)_4]$, [5][TFAB]. $[5-][SbCl_6]^{40}$ (15g, 14.2 mmol) and $K[TFAB]$ (Boulder Scientific Co.) (11.3 g, 15.7 mmol) were dissolved in 700 mL of dry dichloroethane and stirred at room temperature for 30 min. The reaction was cooled

at $-20\text{ }^{\circ}\text{C}$ for 45 min and then filtered. The solvent was removed under reduced pressure, and the resulting green solid was dissolved in 700 mL of dry dichloromethane. The solution was filtered again to remove residual $\text{K}[\text{SbCl}_6]$. The filtrate was concentrated to 100 mL and then added to 700 mL of dry hexane, leaving a green amorphous solid. The liquid was decanted off, another 100 mL of dichloromethane was added, and the resulting solution was again added to 700 mL of hexanes (the redissolving process gave a purer final product). After cooling the solution to $-20\text{ }^{\circ}\text{C}$ for 30 min, followed by filtration and overnight vacuum drying of the deep green precipitate, 19.9 g (85%) of the desired product was obtained as a deep green powder. Anal. Calcd for $\text{C}_{42}\text{H}_9\text{BBr}_6\text{F}_{20}\text{N}$: C, 36.09; H, 0.65; N, 1.00. Found: C, 35.79; H, 0.79; N, 1.13

Preparation of [2,4,6-Triphenylpyrriium][B(C₆F₅)₄], [6]-[TFAB]. [6][BF₄] (1.2g, 3.04 mmol) and K[TFAB] (Boulder Scientific Co.) (2.18 g, 3.04 mmol) were suspended in 60 mL of dry diethylether and stirred at room temperature for 12 h. The solution was then filtered, and the solvent was removed under reduced pressure. A 2.82g (94%) amount of the desired product was obtained as a bright yellow powder. ¹H NMR (500 MHz, CDCl₃): 7.70–7.77 (m, 6H), 7.8 (qt, 3H, $J = 7.5\text{ Hz}$, 1.2 Hz), 7.98–8.00 (m, 2H), 7.20–7.22 (m, 4H), 8.38 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): 114.3, 128.0, 128.2, 128.8, 130.7, 130.9, 132.3, 136.5, 136.6. ¹⁹F NMR (470 MHz, CDCl₃): -166.7 , -162.8 , -132.6 . IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$: 660, 681, 767, 975, 1081, 1458, 1620. Anal. Calcd for $\text{C}_{47}\text{H}_{17}\text{BF}_{20}\text{O}$: C, 57.11; H, 1.73. Found: C, 57.24; H, 2.01.

General Procedure for Oxidatively Catalyzed Disulfurization of Olefins. Cyclohexene (58 μL , 0.57 mmol) and the disulfide (0.57 mmol) were dissolved in 0.6 mL of dry dichloromethane. [S][TFAB] or [6][TFAB] (0.057 mmol) was then added, and the solution was stirred (and photolyzed when [6][TFAB] was used) for 15 min at room temperature, after which 0.2 mL of triethylamine was added to quench the reaction. The solvent was removed under reduced pressure, and the crude product was then purified by chromatography over silica gel using diethyl ether/hexane (1/9) as eluent.

1,2-Bis(*p*-tolylthio)cyclohexane 7a. ¹H NMR (500 MHz, CDCl₃): 1.45–1.48 (m, 2H), 1.67–1.76 (m, 4H), 2.29–2.34 (m, 2H), 2.41 (s, 6H), 3.26–3.29 (m, 2H), 7.14 (d, 4H, $J = 8.09\text{ Hz}$), 7.34 (d, 4H, $J = 8.11\text{ Hz}$). ¹³C NMR (125 MHz, CDCl₃): 20.9, 23.4, 29.8, 49.8, 129.4, 130.7, 132.8, 136.9. IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$: 810, 1018, 1090, 1445, 1491, 2856, 2932, 3019. MSEI+ m/z (%): 329.3 (0.4) (MH⁺), 328.1 (1), 327.2 (5), 205.5 (16), 204.8 (100). HRMSEI+ for $\text{C}_{20}\text{H}_{22}\text{S}_2$: calculated = 329.13922, found = 329.13922.

1,2-Bis((4-fluorophenyl)thio)cyclohexane 7b. ¹H NMR (500 MHz, CDCl₃): 1.35–1.39 (m, 2H), 1.54–1.60 (m, 2H), 1.63–1.68 (m, 2H), 2.16–2.20 (m, 2H), 3.05–3.08 (m, 2H), 6.96–6.99 (m, 4H), 7.34–7.37 (m, 4H). ¹³C NMR (125 MHz, CDCl₃): 23.7, 30.4, 50.6, 115.9 (d, $J = 21.7\text{ Hz}$), 129.2 (d, $J = 3.4\text{ Hz}$), 135.3 (d, $J = 8.1\text{ Hz}$), 162.3 (d, $J = 247.9$). ¹⁹F NMR (470 MHz, CDCl₃): -113.9 . IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$: 635, 830, 1013, 1155, 1225, 1489, 1589, 2858, 2934. MSEI+ m/z (%): 336.2 (1) (MH⁺), 335.2 (5), 210.5 (5), 209.5 (13), 208.7 (100), 81.1 (10). HRMSEI+ for $\text{C}_{18}\text{H}_{18}\text{F}_2\text{S}_2\text{Na}$: calculated = 359.07102, found = 359.07102.

1,2-Bis((4-methoxy)thio)cyclohexane 7c. ¹H NMR (500 MHz, CDCl₃): 1.31–1.35 (m, 2H), 1.52–1.55 (m, 2H), 1.63–1.66 (m, 2H), 3.80 (s, 6H), 6.81 (d, 4H, $J = 8.75\text{ Hz}$), 7.34 (d, 4H, $J = 8.75\text{ Hz}$). ¹³C NMR (125 MHz, CDCl₃): 23.9, 50.7, 55.2, 114.3, 124.5, 135.5, 159.3. IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$: 827, 1031, 1171, 1245, 1284, 1492, 1591, 2836, 2931. MSEI+ m/z (%): 361.2 (1) (MH⁺), 360.7 (1), 359.1 (5), 223.0 (6), 222.0 (15), 221.0 (100), 139.0 (1). HRMSEI+ for $\text{C}_{20}\text{H}_{24}\text{S}_2\text{Na}$: calculated = 383.11099, found = 383.11099.

1,2-Bis(methylthio)cyclohexane 8. ¹H NMR (500 MHz, CDCl₃): 1.28–1.32 (m, 2H), 1.44–1.49 (m, 2H), 1.66–1.70 (m, 2H), 2.08 (s, 6H), 2.09–2.16 (m, 2H), 2.58–2.61 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): 13.9, 24.5, 31.6, 49.1. IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$: 737, 905, 1008, 1201, 1439, 2834, 2931, 2974. MSEI+ m/z (%): 177.5 (5) (MH⁺), 176.5 (6), 175.5 (58), 174.6 (9), 129.8 (10), 128.8 (100), 127.8 (10), 81.0 (3). HRMSEI+ for $\text{C}_8\text{H}_{16}\text{S}_2\text{Na}$: calculated = 199.05856, found = 199.0586.

■ ASSOCIATED CONTENT

📄 Supporting Information

Cyclic voltammograms, an analysis of the dependence of anodic peak current as a function of analyte concentration, and NMR spectra. 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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■ REFERENCES

- (1) Fass, D. *Annu. Rev. Biophys.* **2012**, *41*, 63.
- (2) Vertler, H.; Grubner, J.; Pardini, V. L. In *Organic Electrochemistry*, 4th ed.; Lund, H., Hammerich, O., Eds.; Marcel Dekker, Inc.: New York, 2001; pp 623–638.
- (3) (a) Naphthalene disulfide: Zweig, A.; Hoffmann, A. K. *J. Org. Chem.* **1965**, *30*, 3997. (b) Tetrathiotetracene (TTT): Geiger, W. E. *J. Phys. Chem.* **1973**, *77*, 1862. (c) Tetrathionaphthalene (TTN): Wudl, F.; Schafer, D. E.; Miller, B. *J. Am. Chem. Soc.* **1976**, *98*, 253. (d) TTT and TTF: Nogami, T.; Tanaka, H.; Ohnishi, S.; Tasaka, Y.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 22.
- (4) Bock, H.; Stein, A.; Semkow, A. *Chem. Ber.* **1980**, *113*, 3208.
- (5) Matsumoto, K.; Suga, S.; Yoshida, J. *Org. Biomol. Chem.* **2011**, *9*, 2586.
- (6) Do, Q. T.; Elothmani, D.; Simonet, J.; Le Guillanton, G. *Electrochim. Acta* **2005**, *50*, 4792.
- (7) Elothmani, D.; Do, Q. T.; Simonet, J.; Le Guillanton, G. *J. Chem. Soc., Chem. Commun.* **1993**, 715.
- (8) Tsuchida, E.; Nishide, H.; Park, Y.-S. *J. Electrochem. Soc.* **1992**, *139*, 2401.
- (9) Boryczka, S.; Elothmani, D.; Do, Q. T.; Simonet, J.; Leguillanton, G. *J. Electrochem. Soc.* **1996**, *143*, 4207.
- (10) Suga, S.; Matsumoto, K.; Ueoka, K.; Yoshida, J. *J. Am. Chem. Soc.* **2006**, *128*, 7710.
- (11) Matsumoto, K.; Ueoka, K.; Suzuki, S.; Suga, S.; Yoshida, J. *Tetrahedron* **2009**, *65*, 10901.
- (12) Do, Q. T.; Elothami, D.; Le Guillanton, G. *Tetrahedron Lett.* **1998**, *39*, 4657.
- (13) Glass, R. S.; Jouikov, V. *Tetrahedron Lett.* **1999**, *40*, 6357.
- (14) Matsumoto, K.; Fujie, S.; Suga, S.; Nokami, T.; Yoshida, J. *Chem. Commun.* **2009**, 5448.
- (15) (a) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (b) Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066.
- (16) Camire, N.; Nafady, A.; Geiger, W. E. *J. Am. Chem. Soc.* **2002**, *124*, 7260.
- (17) Barrière, F.; Geiger, W. E. *Acc. Chem. Res.* **2010**, *43*, 1030.
- (18) (a) Woods, J. E.; Ge, Y.; Smith, D. K. *J. Am. Chem. Soc.* **2008**, *130*, 10070. (b) Matsumoto, K.; Fujie, S.; Suga, S.; Nokami, T.; Yoshida, J. *Chem. Commun.* **2009**, 5448. (c) Chong, D.; Stewart, M. P.; Geiger, W. E. *J. Am. Chem. Soc.* **2009**, *131*, 7968.
- (19) The reaction of SbCl_5 with Ar_2S_2 to give in situ $[\text{Ar}_3\text{S}_3]^+$ is well-documented. See references: (a) Weiss, R.; Schlierf, C. *Synthesis* **1976**, 323. (b) Grewal, G.; Kaila, N.; Franck, R. W. *J. Org. Chem.* **1992**, *57*, 2084. (c) Gybin, A. S.; Smit, W. A.; Bogdanov, V. S. *Tetrahedron Lett.* **1980**, *21*, 383.

- (20) Bonifačić, M.; Asmus, K.-D. *J. Chem. Soc., Perkins Trans. II* **1986**, 1805.
- (21) (a) Latypova, V. Z.; Chichirov, A. A.; Jouikov, V. V.; Yakovleva, O. G.; Vinokurova, R. I.; Ustyugova, I. A.; Kargin, Yu. M. *Zh. Obshch. Khim. (Engl. Transl.)* **1989**, *59*, 1190. (b) Latypova, V. Z.; Jouikov, V. V.; Kargin, Yu. M. *Zh. Obshch. Khim. (Engl. Transl.)* **1990**, *60*, 2473. (c) Jouikov, V. V.; Simonet, J. Organic Electrochemistry. In *Encyclopedia of Electrochemistry*; Bard, A. J., Stratmann, M., Schäfer, H.-J., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 8, pp 232–276.
- (22) Nafady, A.; Costa, P. J.; Calhorda, M. J.; Geiger, W. E. *J. Am. Chem. Soc.* **2006**, *128*, 16587.
- (23) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; John Wiley & Sons: New York, 2001; pp 234–239.
- (24) Details of this voltammetric analysis are available in the Supporting Information. It assumes that the anodic current function at the lowest concentration is that of a one-electron process. The anodic peak current for a totally irreversible oxidation having a transfer coefficient of 0.48 (measured from the anodic peak width) and an electron-transfer stoichiometry of 0.67 should be 50% of that of a reversible one-electron process. Values of about 45% are measured from Figure 4.
- (25) Barrière, F.; Camire, N.; Geiger, W. E.; Mueller-Westerhoff, U.; Sanders, R. *J. Am. Chem. Soc.* **2002**, *124*, 7262.
- (26) Beck, W.; Stükel, K. *Chem. Rev.* **1988**, *88*, 1405.
- (27) Laws, D. R.; Chong, D.; Nash, K.; Rheingold, A. L.; Geiger, W. E. *J. Am. Chem. Soc.* **2008**, *130*, 9859.
- (28) Stone, N. J.; Sweigart, D. A.; Bond, A. M. *Organometallics* **1986**, *5*, 2553.
- (29) Hill, M. G.; Lamanna, W. M.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 4687.
- (30) ¹⁹F NMR spectra of the oxidized solution showed no fluorine-containing products besides [PF₆]⁻.
- (31) (a) Kraiya, C.; Evans, D. H. *J. Electroanal. Chem.* **2004**, *565*, 29. (b) Evans, D. H. *Chem. Rev.* **2008**, *108*, 2111.
- (32) Bewick, A.; Coe, D. E.; Mellor, J. M.; Owton, W. M. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1033.
- (33) Glass, R. S.; Jouikov, V. V.; Bojkova, N. V. *J. Org. Chem.* **2001**, *66*, 4440.
- (34) Matsumoto, K.; Sanada, T.; Shimazaki, H.; Shimada, K.; Hagiwara, S.; Fujie, S.; Ashikari, Y.; Suga, S.; Kashimura, S.; Yoshida, J. *Asian J. Org. Chem.* **2013**, *2*, 325.
- (35) Fujie, S.; Mastumoto, K.; Suga, S.; Yoshida, J. *Chem. Lett.* **2009**, *12*, 1188.
- (36) Chong, D.; Laws, D. R.; Nafady, A.; Costa, P. J.; Rheingold, A. L.; Calhorda, M. J.; Geiger, W. E. *J. Am. Chem. Soc.* **2008**, *130*, 2692.
- (37) Kabalka, G. W.; Reddy, M. S.; Yao, M.-L. *Tetrahedron Lett.* **2009**, *50*, 7340.
- (38) LeSuer, R. J.; Buttolph, C.; Geiger, W. E. *Anal. Chem.* **2004**, *76*, 6395.
- (39) (a) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461. (b) Gagne, R. E.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854. (c) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.
- (40) Schmidt, W. E.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577.