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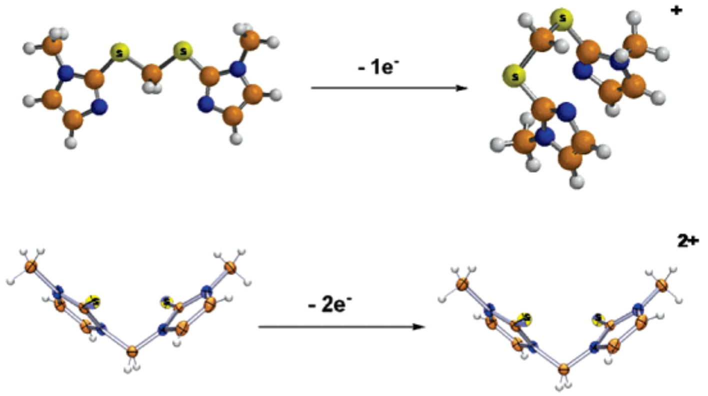
Unexpected New Chemistry of the Bis(thioimidazolyl)methanes

Rosalice M. Silva,[†] Mark D. Smith,[‡] and James R. Gardinier*[,†]

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53201-1881, and Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

james.gardinier@marquette.edu

Received June 1, 2005



The synthesis of the linkage isomers of the bis(thioimidazolyl)methane family of compounds, namely $CH_2(N\text{-tim})_2$ (**1**) and $CH_2(S\text{-tim})_2$ (**2**) (where tim = thio(methyl)imidazolyl) has been reinvestigated in order to optimize the yields, to complete the characterization of these known compounds, and also to ascertain the effect of varying heteroatom binding on their electrochemistry. During the course of these studies, the reactive intermediate $ClCH_2(S\text{-tim})$ (**3**) was isolated and characterized. The chloromethyl derivative **3** readily decomposes on warming to give the ionic compound $[CH_2\text{-}(\mu\text{-}C_4H_5N_2S)_2CH_2](Cl)_2$ (**4**), which was converted to the hexafluorophosphate salt (**5**) and then was characterized by single-crystal X-ray diffraction. It was also shown that $CH_2(S\text{-tim})_2$ (**2**) could be converted at temperatures greater than 120 °C to $CH_2(N\text{-tim})_2$ (**1**) by a thermal isomerization that proceeds via the remaining possible linkage isomer $CH_2(S\text{-tim})(N\text{-tim})$. Electrochemical studies on **1**−**3** in acetonitrile reveals that each undergoes irreversible (one electron per ring) oxidations above 0.7 V versus Ag/AgCl, while the ionic compound **5** shows an irreversible reduction wave centered at −1.09 V.

Introduction

Since their initial conception by Trofimenko in the mid 1960s, there has been an interest in the development of new scorpionate ligands for studies in diverse aspects of coordination chemistry.[1] Thus, research has spanned areas from catalyst development[2] to bioinorganic enzyme mimics[3] to the development of new spin crossover materials[4] and to fundamental studies on supramolecular chemistry.[5] These scorpionate ligands are typically either poly(pyrazolyl)borates or poly(pyrazolyl)methanes. In the last 20 years there has been an increasing interest in the development of scorpionates with "soft" Lewis donors such as sulfur groups that would presumably have a proclivity for binding softer metals. Pioneering work by the Reglinski[6] and Parkin[7] groups, continued by the

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[†] Marquette University.

[‡] University of South Carolina.

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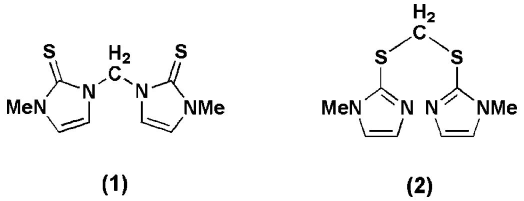
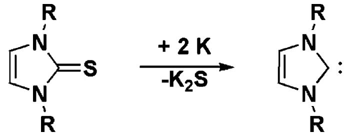


FIGURE 1. Isomeric bis(thioimidazolyl)methanes.

SCHEME 1. Reductive Desulfurization of the Thioimidazolyl Group To Yield a Carbene



Vahrenkamp,[8] Hill,[9] and Rabinovich[10] groups, is aimed toward using poly(thioimidazolyl)borates as spectator ligands for metal catalysis. Interestingly, the charge-neutral counterparts of these "soft" scorpionates, namely the poly(thioimidazolyl)methanes, have received relatively little attention. Only the bis(thioimidazolyl)methane linkage isomers[11,12] (Figure 1), the related C−N isomer of bis(thiobenzoimidazolyl)methane,[13] and a few of their metal complexes[14] have been reported. Our interest in poly(thioimidazolyl)alkanes has been fueled by our desire to prepare multitopic "soft" scorpionates for use in studying cooperativity in multimetallic catalyst systems, in the preparation of molecular wires, and in the development of new classes of functional redox-active coordination networks. Also, the known reductive desulfurization of thioimidazoline heterocycles with potassium metal to form imidazolium-based carbenes[15] (Scheme 1) makes linked poly(thioimidazolyl)alkanes an enticing class of compounds toward our group's research goals of developing "linked" geminal carbenes (Figure 2); thus, we have begun (re)examining the preparative routes and electrochemistry of the poly(thioimidazolyl)alkanes. During the course of our initial studies in this area, we made some surprising observations regarding the preparation, reactivity, and electrochemistry of the bis(thioimidazolyl)methane linkage isomers that we would like to share in this report. Future papers will address the coordination chemistry of these species with different metal compounds, and our efforts toward developing linked geminal carbenes will be reported in due course.

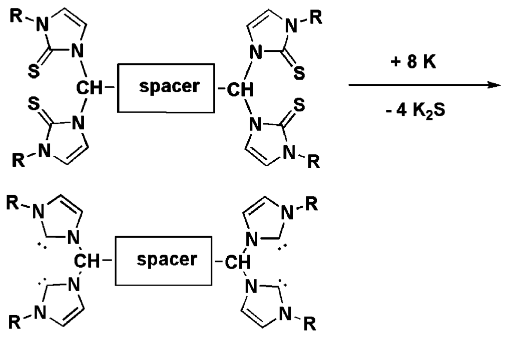


FIGURE 2. One synthetic approach to "linked" geminal carbenes.

Results and Discussion

Syntheses. The linkage isomers depicted in Figure 1, which for brevity we shall refer to as CH_2(N-tim)$_2$ (**1**) and CH_2(S-tim)$_2$ (**2**), respectively (tim = thioimidazolyl), have been prepared by the multiple routes as summarized in Scheme 2. We found that we could isolate analytically pure compound **1** in greater than 75% yield based on 2-mercapto-1-methylimidazole by using absolute methanol as a solvent for crystallization of [CH_2(imidazolyl)$_2$](I)$_2$ and compound **1**. The literature reports only a 50% overall yield using ethanol as a solvent for crystallization; unfortunately, the grade of ethanol was not reported. We found [CH_2(imidazolyl)$_2$](I)$_2$ to be insoluble in refluxing absolute ethanol, but this compound had appreciable solubility in 95% ethanol. Thus, the loss encountered in the original report might be attributed to the greater solubility of the former compound in 95% ethanol compared to that in methanol (reported here). The characterization data of compound **1** agreed well with literature data.[11] The crystal structure of the free ligand **1** was unknown before this report and can be found in the Supporting Information.

While it has been reported that 2-mercapto-1-methylimidazole exists as predominantly the NH rather than SH tautomer in solution (bottom left of Scheme 2),[16] the greater acidity of the thiol moiety results in the formation of thiolate species on reaction with Brønsted bases. This reaction was taken advantage of in the original literature preparation of CH_2(S-tim)$_2$ (**2**);[12] however, neither a yield nor complete characterization data were reported for this compound. We encountered difficulties when attempting to scale the literature preparation near and above the 5 g scale, as a solid mass is formed on adding CH_2Cl_2 to the NaS-tim salt (formed from NaOMe and 2-mercapto-1-methylimidazole). This solid mass prevented adequate mixing, especially at room temperature; thus, we found it necessary to add copious solvent and heat the reaction mixture at reflux for 1 week (rather than stirring at room temperature for 9 days followed by 12 h reflux as in the literature). The crude product obtained in this way was a nearly colorless or pale yellow oil (rather than the

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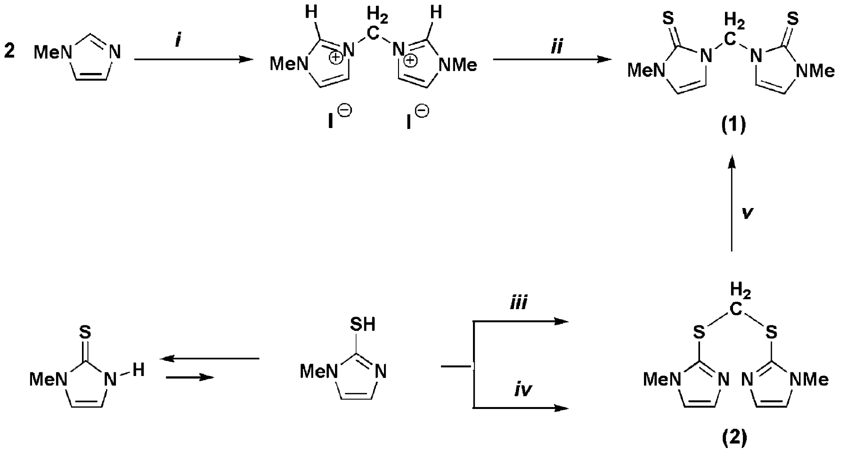
SCHEME 2. Preparative Routes to Bis(thioimidazolyl)methanes[a]



[a] Legend: (i) CH_2I_2, EtOAc, reflux; (ii) 2 K_2CO_3, 1/4 S_8, MeOH, reflux; (iii) (a) NaOMe, HOMe; (b) CH_2Cl_2, reflux, 1 week; (iv) K_2CO_3, KOH, H_2O, CH_2Cl_2, $[NBu_4](Br)$, reflux, 1 week; (v) neat, 180 °C, 14 h.

reported orange oil) and was found to be a mixture by NMR (vide infra) of $CH_2(S\text{-tim})_2$ (**2**) and the monosubstituted compound $ClCH_2(S\text{-tim})$ (**3**). After separating the mixture by chromatography, we obtained a 76% yield of pure **2** and less than 10% of **3** based on the starting heterocycle. We found that pure **2** is a colorless, low-melting crystalline solid, in contrast to the literature, which reported **2** as an orange oil. It is noted that melts of **2** supercool readily and that **2** has a significant freezing point depression constant, as even the smallest quantity (<ca. 0.5%) of impurity (by NMR) will render **2** (or more accurately, the mixture) a liquid. Unfortunately, it has not yet been possible to grow suitable single crystals for X-ray structural analysis. The NMR spectrum of a $CDCl_3$ solution of **2** agrees with the proposed formula and with the literature data.[12] It is important to note that resonances for the imidazolyl ring hydrogens in **2** (which occur as doublets) have smaller coupling constants (of 1 Hz) than those of the C−N isomer (2.4 Hz) **1**. In addition, the resonance for methylene hydrogens occurs further upfield in **2** (δ 4.64) than in **1** (δ 6.31). Thus, the coupling constants and chemical shifts of the methylene resonance can be used to distinguish between a C−S- versus a C−N-bonded isomer in this family of compounds. The identity of **3** was established by elemental analysis and by its NMR spectrum. The NMR spectrum of a $CDCl_3$ solution of **3** consists of a pair of doublets at δ_H 7.14 and 6.99 (with small coupling constant of 1 Hz) for thioimidazolyl ring hydrogens, a singlet at δ_H 4.96 for the methylene hydrogens, and a singlet at δ_H 3.71 for methyl hydrogens. The relative integrations and chemical shifts of the methylene hydrogen resonances are consistent with the presence of only one sulfur-bonded thioimidazolyl group per methylene moiety.

Since it is known in related poly(pyrazolyl)methane chemistry that the use of a phase transfer catalyst and a refluxing aqueous/organic biphase system can greatly enhance product yields and decrease reaction times,[17] we explored this synthetic methodology to compounds **2** and **3**. The biphasic route using a KOH/K_2CO_3 mixed base system produced mixtures of $CH_2(S\text{-tim})_2$ (**2**), the monosubstituted compound $ClCH_2(S\text{-tim})$ (**3**), and unidentified decomposition products where the relative amounts of the components depended mainly on the time allowed for the reaction. The optimum reaction time for the formation of **2** (65% based on NMR and mass measurements; vide infra) is 7 days, whereas that for **3** (22%) is 24 h. We are currently investigating the role of the base in the preferential formation of either **2** or **3**.

During an initial attempt to purify compound **3** by vacuum distillation, it was found that the liquid decomposed to $[CH_2(\mu\text{-}C_4H_5N_2S)_2CH_2](Cl)_2$ (**4**), a solid that was soluble only in very polar solvents such as either methanol or water. In separate experiments, DTA measurements showed that the conversion occurs between 47 and 50 °C at atmospheric pressure, albeit slowly, but heating samples of pure **3** in a sealed tube to 140 °C for 30 min repeatedly afforded 80% yields of pure **4**. The ionic nature and formula of $[CH_2(\mu\text{-}C_4H_5N_2S)_2CH_2](Cl)_2$ (**4**) was supported by its solubility properties, by elemental analytical data, and by the observation that aqueous solutions gave positive tests for chloride ions with $AgNO_3$. Also, the NMR spectrum of a methanol solution of the ionic solid (Supporting Information) showed only one set of signals for the methyl−thioimidazolyl group at δ 8.37, 7.90, and 3.98 in a 2:2:3 ratio, respectively, in addition to two sets of AB signals centered at δ 6.94 and 5.03 for methylene hydrogens (two hydrogens each). A cyclic structure with CH_2N_2 and CH_2S_2 fragments can be deduced from both the chemical shifts of the two AB methylene resonances (that are consistent with those of compounds **1** and **2**, respectively) and the expected magnetic nonequivalence of the methylene hydrogens in a cyclic structure. Unfortunately, it has not yet been possible to grow single crystals for X-ray structural analysis.

Anion exchange with KPF_6 afforded $[CH_2(\mu\text{-}C_4H_5N_2S)_2CH_2](PF_6)_2$ (**5**), a derivative that was insoluble in either water or methanol but had solubility in less polar solvents such as acetone (moderately soluble) and acetonitrile (very soluble) that facilitated the growth of single crystals for X-ray diffraction studies. The crystal structure of the dication in **5** is given in Figure 3. This eight-membered-ring dication is nearly isostructural with the

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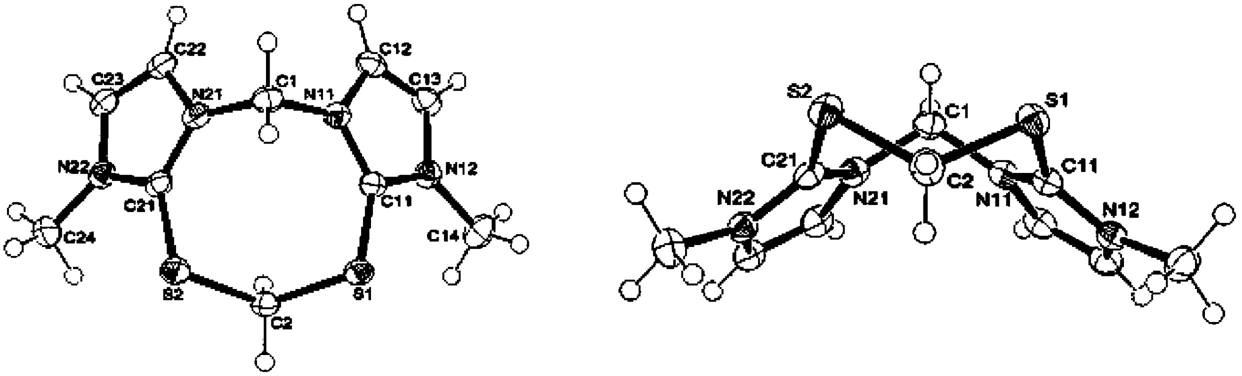

FIGURE 3. Two views of the $[CH_2(\mu\text{-}C_4H_5N_2S)_2CH_2]$ dication. Displacement ellipsoids are drawn at the 50% probability level.

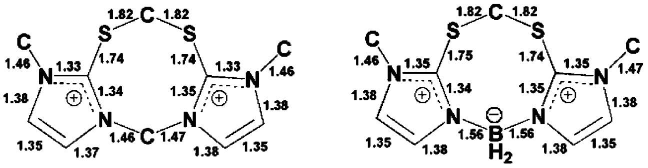

FIGURE 4. Comparison of the bond distances in the $[CH_2(\mu\text{-}C_4H_5N_2S)_2CH_2]$ dication (left) and the $[BH_2(\mu\text{-}C_4H_5N_2S)_2CH_2]$ monocation (right).

monocationic borate derivative $[BH_2(\mu\text{-}C_4H_5N_2S)_2CH_2](Cl)\cdot H_2O$,[9] which is formed via the slow decomposition of $Na[H_2B(N\text{-tim})_2]$ in methylene chloride. That is, the dication adopts a chair conformation, where the only significant difference between its structure and that of the monocationic borate is the average sp^3-element−nitrogen bond distance for the $N-CH_2-N$ (1.47 Å) and $N-BH_2-N$ (1.56 Å) fragments (Figure 4). There is a slight shortening of the N−C−N bonds in both **5** and the borate complex, which average 1.34 and 1.35 Å, respectively, relative to the free ligand **1** (average 1.36 Å; Supporting Information) but these are comparable to those in metal complexes of either **1** or **2** (average 1.35 Å).[11,12,14] The NMR spectra of **5** in acetone or acetonitrile (Supporting Information) are similar to the spectra of **4** in CD_3OD (**5** is insoluble in CD_3OD), with two sets of AB signals for methylene hydrogens, indicating that the cationic structure was not greatly affected by anion exchange. These data, combined with the structural study on **5**, further support the notion that **4** also exists as the cyclic $[CH_2(\mu\text{-}C_4H_5N_2S)_2CH_2](Cl)_2$ species.

During initial attempts to prepare the dication, it was found that when mixtures of $ClCH_2$(S-tim) and CH_2(S-tim)$_2$ (i.e., the crude product mixture from the preparations of $ClCH_2$(S-tim)) were heated to about 180 °C, some CH_2(N-tim)$_2$ could be detected as an organic-soluble byproduct of reaction. This prompted investigations into the thermal stabilities of each *pure* compound, where it was found that CH_2(N-tim)$_2$ was formed by the thermal isomerization of only CH_2(S-tim)$_2$ in this temperature range. Admittedly, traces of CH_2(N-tim)$_2$ are formed along with numerous other decomposition products by the thermal decomposition of **4**, but only at temperatures greater than about 250 °C. It is also noted that similar C−S to C−N isomerizations have been previously observed in simple alkylated thioimidazolyls, but to our knowledge the kinetics of such rearrangements were not fully investigated.[19]

The thermal isomerization of neat CH_2(S-tim)$_2$ at temperatures between 120 and 180 °C was monitored by NMR spectroscopy. The thermal isomerization reactions were performed in closed (evacuated) thick-walled glass vessels suspended in the middle of a preheated oil bath by copper wire. Attempts to use more typical apparatus (round-bottomed flasks and reflux condensers) gave poorly reproducible results, due to distillation of CH_2(S-tim)$_2$ into the cooler parts of the apparatus. An NMR spectrum of the mixture obtained after heating a pure sample of CH_2(S-tim)$_2$ to 150 °C for 16 h (Supporting Information) is typical of all others obtained in the kinetic study. Resonances for three different species can be identified: the most intense set of four resonances (triangles, Figure S5) is for the hydrogens of CH_2(S-tim)$_2$ (the CS_2 isomer) while those four resonances of medium intensity (circles, Figure S5) are for CH_2(N-tim)$_2$ (the CN_2 isomer). There is a final set of seven resonances (squares, Figure S5) that occurs in a 1:1:1:1:2:3:3 ratio and is assigned to the remaining possible linkage isomer CH_2(S-tim)(N-tim), the CNS isomer. This assignment was made since the resonance of the methylene hydrogens of this last isomer occurs at δ 5.56, a value intermediate between δ 6.31 for the CN_2 isomer and δ 4.64 for the CS_2 isomer. Also, one pair of the thioimidazolyl hydrogen doublet resonances at δ 7.08 and 6.95 has a smaller coupling constant (of 1 Hz) than the second pair of doublet resonances at δ 6.86 and 6.58 (with a coupling of 2.4 Hz), indicative of C−S- and C−N-bonded thioimidazolyls, respectively. Unfortunately, we were unsuccessful at isolating pure samples of the CNS isomer. Over time, the signals for the C−N isomer **1** grew at the expense of those for **2** and of those for the minor CNS isomer. These observations indicate that CH_2(N-tim)$_2$ is thermodynamically the most stable isomer (as expected from a comparison of bond dissociation enthalpies),[18] while the mixed CNS isomer, which never comprises more than 10% of the mixture in the 120−180 °C temperature range, is an intermediate in the isomerization reaction. Relative integrations of the three sets of resonances showed that rate of the disappearance of **2** over time was constant, indicating that the isomerization

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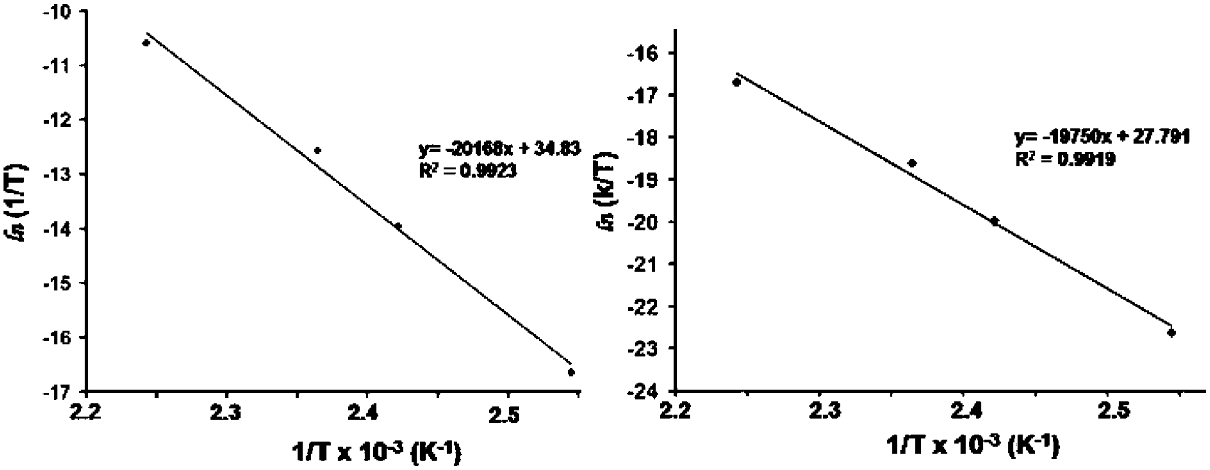

FIGURE 5. Arrhenius (left) and Eyring (right) plots for the thermal isomerization of $CH_2(S\text{-tim})_2$.

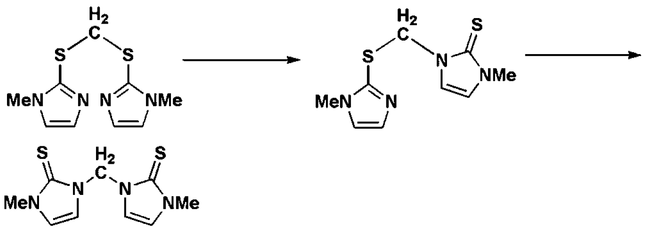

FIGURE 6. Proposed mechanism for the thermal isomerization of $CH_2(S\text{-tim})_2$.

TABLE 1. Kinetic Parameters for the Thermal Isomerization of $CH_2(S\text{-tim})_2$ (2)

temp (K)	$t_{1/2}$ (h)	k (s^{-1})
446	7.64	2.52×10^{-5}
423	54.7	3.52×10^{-6}
413	220	8.75×10^{-7}
393	32447	5.93×10^{-8}

was first order in $CH_2(S\text{-tim})_2$. A summary of the results of the kinetic study of the isomerization reactions is provided in Table 1. Both Arrhenius and Eyring plots are given in Figure 5. From these data the following activation parameters were obtained: $E_a = 175.2$ kJ/mol, $\Delta H^{\ddagger} = 164.2$ kJ/mol, and $\Delta S^{\ddagger} = 33.5$ J/(K mol). From these data we propose an intramolecular mechanism for rearrangement based on sequential 1,3-sigmatropic shifts, as in Figure 6. This proposed mechanism is based on the observations that the activation enthalpy is significantly smaller than the bond dissociation energies of the (Me)C−S bond in Me−SPh, a reference compound whose bond dissociation energy has been determined to be around 265 kJ/mol theoretically and 287 kJ/mol experimentally.[18] Also, the observed activation entropy is small but positive, consistent with the proposed mechanism. Also, the activation energy of the first and second steps of the reaction in Figure 6 should be comparable, in agreement with the observation that only a small fraction of the CNS isomer is observed over the temperature range of the kinetic study.

The electrochemistry of the derivatives **1**−**3** and **5** (summarized in Table 2 and in the Supporting Information) was initially investigated in order to determine if any potentially more attractive reducing agents (other than potassium metal) could be used to generate carbenes from the geminal thioimidazolyls, but only in the case of **5** was an irreversible reduction wave clearly observed (−1.17 V versus Ag/AgCl) in the potential window of CH_3CN in the voltammetric experiments. The singular reduction behavior of **5** compared to that of the remaining derivatives is likely a result of its dicationic nature and of the constrained proximity of its two thioimidazolyl rings. Interestingly, the other thiomidazolyl derivatives exhibit irreversible oxidation waves at potentials greater than about 0.7 V versus Ag/AgCl. The isomers with sulfur bonded to the methylene moiety (**2** and **3**) are more difficult to oxidize than the carbon−nitrogen derivative **1**, as can be seen from the first oxidation waves of each (1.19, 1.07, and 0.72 V versus Ag/AgCl, for **2**, **3**, and **1**, respectively). Moreover, the thioether derivatives **2** and **3** each have a second oxidation wave at 1.51 and 1.44 V, respectively, where the shapes of the waves are reminiscent of ECE reactions.

TABLE 2. Electrochemical Properties of Compounds 1−3 and 5 in Acetonitrile[a]

compd	$E_{1/2}$ (V)[b]	no. of e[c]
$CH_2(N\text{-tim})_2$ (**1**)	0.72 (anodic)	2
$CH_2(S\text{-tim})_2$ (**2**)	1.51 (anodic), 1.19 (anodic)	1 each
$ClCH_2(S\text{-tim})$ (**3**)	1.44, 1.07	1 each
$CH_2(\mu\text{-}C_4H_5N_2S)_2CH_2](PF_6)_2$ (**5**)	−1.17 (cathodic)	na[d]

[a] NBu_4PF_6 as electrolyte. [b] $E_{1/2} = (E_a - E_c)/2$. [c] From redox titrations in CH_2Cl_2. [d] na = not available due to insolubility in CH_2Cl_2.

Redox titrations of **1**−**3** in CH_2Cl_2 (**5** is insoluble) with the cation radical 9,10-dimethoxyoctahydro-1,4:5,8-dimethanoanthracenium hexachloroantimonate,[20] a moderately strong oxidant ($E_{1/2}$(red) = 1.08 V versus Ag/AgCl), monitored by UV−vis spectroscopy (Figure 7) established that oxidation occurred and provided the stoichiometry of the electrochemical reactions. After the addition of 1/2 equiv of $CH_2(N\text{-tim})_2$ to the oxidant, the absorption band for the cation radical oxidant disappeared, concomitant with the formation of an uncharacterized precipitate. This precipitate is the reason for the slight increase in absorbance after 1/2 equiv of **1** is added, as seen in Figure

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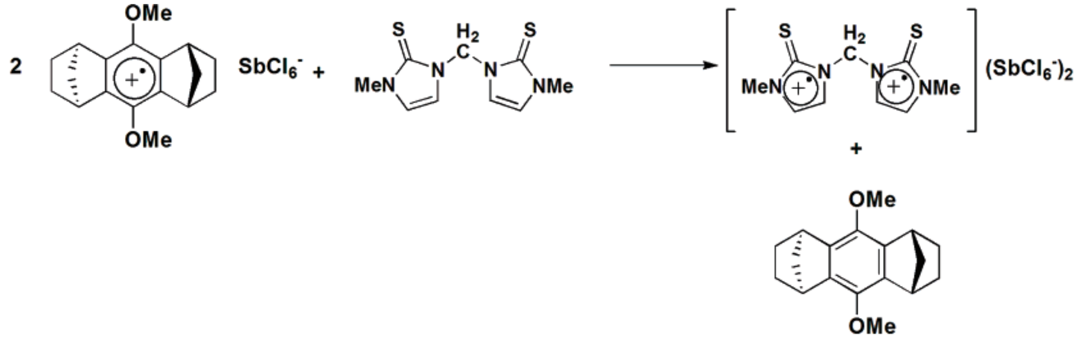

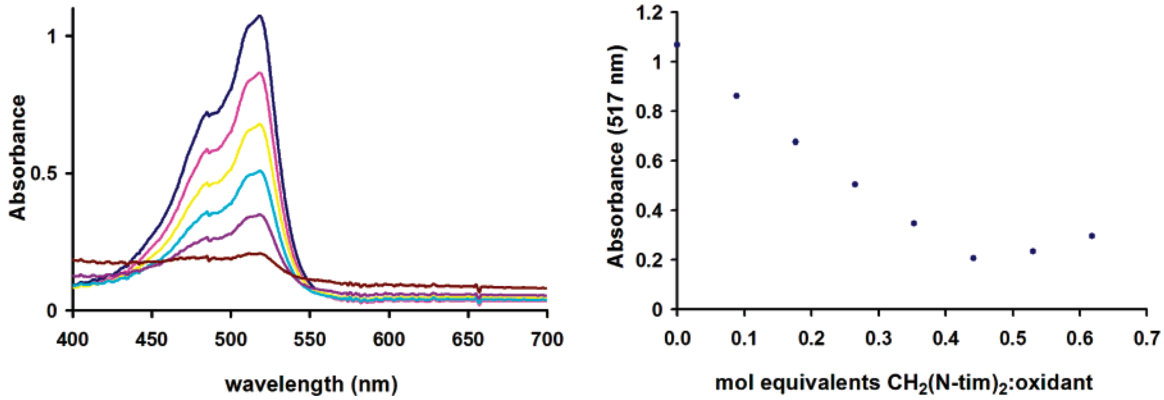

FIGURE 7. UV−visible spectral overlay for the titration of the cation radical 9,10-dimethoxyoctahydro-1,4:5,8-dimethanoanthracenium hexachloroantimonate with $CH_2(N\text{-tim})_2$. Bottom right: Plot of absorbance versus moles of added $CH_2(N\text{-tim})_2$.

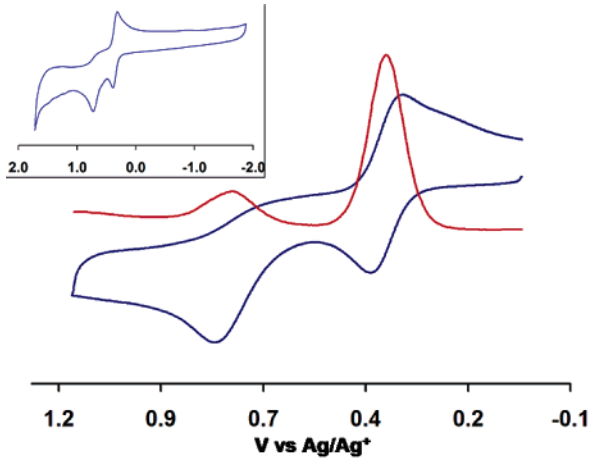

FIGURE 8. Cyclic and square wave voltammograms of an equimolar mixture of $CH_2(N\text{-tim})_2$ and ferrocene.

7. The stoichiometry of the oxidation of **1** corresponded to a two-electron process. These results are in *contrast* with those calculated from the ratio of current intensities of the square wave and cyclic voltammograms for an equimolar mixture of **1** and ferrocene, as shown in Figure 8. That only one oxidation wave is observed for **1** indicates that there is no electron communication between the oxidized geminal thioimidazolyl groups in solution. This is consistent with what would be expected on the basis of the solid-state structure of the unoxidized derivative **1**, where no $\pi-\pi$ interactions are observed. The intramolecular centroid−centroid distance of 4.35 Å and the dihedral angle, α, of 79° between geminal thioimidazolyl planes are much larger than the values of 3.6 Å and $\alpha = 0-4°$ for prototypical $\pi-\pi$ interactions.[21]

Interestingly, the stoichiometry of the first oxidation wave of **2** ($E_{1/2} = 1.19$ V) with the cation radical was consistent with a one-electron process, as in Figure 9a. These data are in *contrast* with those calculated from the ratio of current intensities of the square wave and cyclic voltammograms for an equimolar mixture of **2** and ferrocene, which range from 0.25 to 4 electrons, depending on the sample, concentration, and scan rate. This apparent contrast between the titration and voltammetric experiments is likely due to a large difference in diffusion rates (coefficients) between ferrocene and the oxidized form of **2**.[22] Similar discrepancies between titration and voltammetric data have been reported recently during attempts to characterize the electrochemical behavior of $C_6(C_6H_4\text{-}[4\text{-Me-}2,5\text{-}(MeO)_2C_6H_2])_6$.[23] Thus, caution should be employed when using comparisons of current intensities from voltammograms to determine the stoichiometry of redox reactions. It should be emphasized that the use of the cation radical salts in redox titrations provides a simpler and more convenient alternative to the tedious coulometric methods traditionally used to accurately determine the number of electrons involved in redox reactions. Compound **3**, with oxidation waves similar to those for **2** (Supporting Information), also does not appear to survive electrochemical reactions. The redox titration data shown in Figure 9b demonstrate

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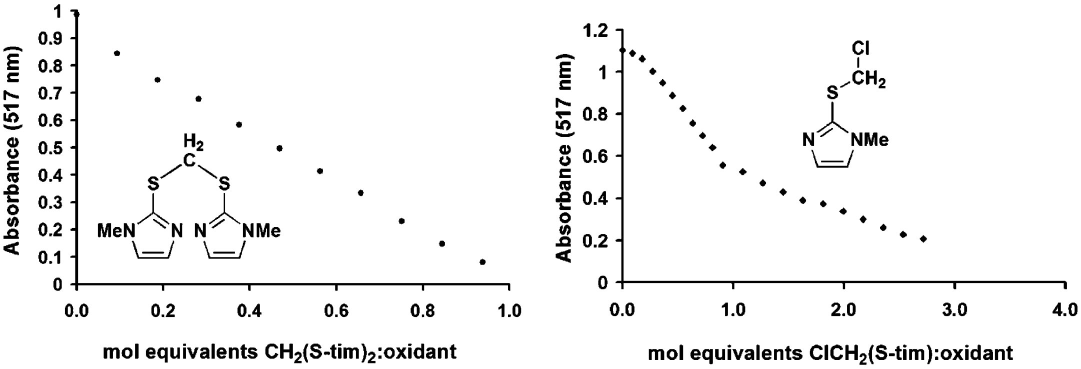
[21] (a) Takahashi, H.; Tsuboyama, S.; Umezawa, Y.; Honda, K.; Nishio, M. *Tetrahedron* **2000**, *56*, 6185 (b) Janiak, C. *Dalton Trans.* **2000**, 3885.

[22] Flanigan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

[23] Rathore, R.; Burns, C. L.; Deselinescu, M. I. *Org. Lett.* **2001**, *3*, 2887.



(A) (B)

FIGURE 9. Redox titration plots of (a, left) **2** and (b, right) **3** with the cation radical 9,10-dimethoxyoctahydro-1,4:5,8-dimethanoanthracenium hexachloroantimonate.

that a new species is formed after 1 equiv of **3** is added to the oxidant but only half of the original oxidant is consumed. Studies on the unusual chemical and electrochemical reactivity of **3** are an active area of research in our group.

We are tentatively attributing the difference in the electrochemical behavior between **1** and **2** to be due to the relative conformational flexibility of the latter compound, which allows for an intramolecular π-stacking interaction that would either stabilize a one-electron cation thioimidazolium radical or would promote intramolecular bond formation via proximal imidazoline rings. An intramolecular π-stacked geometry is not possible for the former compound (**1**) with a very short methylene linkage. This difference in geometry of **1** and **2** would be akin to the known capability of bis(pyrenyl)propane and the known inability of bis(pyrenyl)methane to form intramolecular excimers, the so-called $n = 3$ rule, where n is the three methylene groups needed for two alkane-linked chromophores to achieve planplanar sandwich conformation.[24] Efforts are underway to isolate and further identify the oxidized forms of **1**−**3** by chemical oxidations and to further investigate the electrochemical behavior of these thioimidazolyls.

Summary and Conclusions

We have optimized the synthetic conditions for the formation of the two bis(thioimidazolyl)methane linkage isomers $CH_2(N\text{-tim})_2$ (**1**) and $CH_2(S\text{-tim})_2$ (**2**) in *pure form* by choosing the appropriate solvent for crystallizations in both cases and by heating the reaction mixture for a sufficient time period in the latter case. We have shown that the CS_2-bonded isomer is thermodynamically less stable than the CN_2-bonded isomer. Heating a pure sample of the CS_2 isomer results in the conversion to the CN_2 isomer via the intermediate $CH_2(S\text{-tim})(N\text{-tim})$, the remaining possible linkage isomer. If the preparative reaction to form the CS_2 isomer is not allowed to go to completion, it is possible to isolate $ClCH_2(S\text{-tim})$ (**3**) as a temperature-sensitive colorless oil. This chloromethyl derivative decomposes above about 50 °C to give $[CH_2(\mu\text{-}C_4H_5N_2S)_2CH_2](Cl)_2$ (**4**) as an organic-insoluble ionic solid that can be converted to the organic-soluble $[CH_2(\mu\text{-}C_4H_5N_2S)_2CH_2](PF_6)_2$ (**5**) by ion exchange. Current studies are underway to determine whether it will be possible to use this facile reaction to prepare a new class of ionic liquid by appropriate substitutions on either the thioimidazolyl rings or anions. Surprisingly, compounds **1**−**3** were found to undergo irreversible oxidations above 0.7 V versus Ag/AgCl; thus, while the nature of the oxidized form of this class of compounds has not yet been elucidated, compounds **1**−**3** may be useful electroactive ligands for incorporation into future functional coordination compounds and networks.

Experimental Section

Syntheses. Bis(2-thione-3-methylimidazolyl)methane, $CH_2(N,N\text{-}C_4H_5N_2S)_2$ (1). This compound was best prepared on a 25−50 g scale by the literature route[11] by reacting $[CH_2(\text{imidazolyl})_2](I)_2$ with sulfur in the presence of K_2CO_3. An important modification was that hot (boiling) anhydrous methanol solutions of either $[CH_2(\text{imidazolyl})_2](I)_2$ (ca. 1.5 g/100 mL) or **1** (ca. 5 g/100 mL) were filtered (while hot) and then cooled to −20 °C overnight to give the respective pure compounds as colorless needles. The crystals of each compound were isolated by filtration, washed with 20 mL of cold MeOH and 20 mL of Et_2O, and then dried in an oven for 30 min. If necessary, the pure compound **1**, as a colorless solid, can also be obtained by column chromatography on silica gel with ethyl acetate as the eluent ($R_f = 0.72$, silica plate) followed by recrystallization, as above. The following data are for **1**. Mp: 201−202 °C (lit.[11] mp 202−203 °C). Anal. Calcd (found) for $C_9H_{12}N_4S_2$: C, 44.97 (45.20); H, 5.03 (5.25); N, 23.31 (23.02). ^1H NMR (δ, $CDCl_3$): 7.61 (d, 2H, $J = 2.4$ Hz), 6.61 (d, 2H, $J = 2.4$), 6.31 (s, 2H), 3.58 (s, 6H). ^{13}C NMR (δ, $CDCl_3$): 163.7, 118.7, 117.8, 56.3, 35.4. UV/vis (nm, CH_3CN) λ_{max} (log ϵ): 211 (2.36), 240 (3.58), 266 (2.79). IR (KBr, cm^{-1}): 3165, 3127, 3098, 2972, 2943, 1653 (w, C=C), 1229 (m, C=S).

Bis(1-methyl-1*H*-imidazol-2-ylthio)methane, $CH_2(S,S\text{-}C_4H_5N_2S)_2$ (2). Method A. A modification of the literature route was followed.[12] Thus, 5.00 g (43.8 mmol) of 2-mercapto-1-methylimidazole was dissolved in 100 mL of methanol and 1.67 g (43.8 mmol) of powdered NaOMe was added in one portion. The mixture was heated to reflux for 30 min, and then solvent was removed by rotary evaporation to leave a colorless solid, presumably Na(S-tim). Next 250 mL of CH_2Cl_2 was added to the flask containing Na(S-tim), whereupon a solid mass formed. The flask was fitted with a condenser, and the

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(24) DeSchryver, F. C.; Collart, P.; Vandendriessche, J.; Goedeweeck, R.; Swinnen, A.; Van der Auwaer, M. *Acc. Chem. Res.* **1987**, *20*, 159.

(25) SMART Version 5.625, SAINT+ Version 6.22, and SADABS Version 2.05; Bruker Analytical X-ray Systems, Inc., Madison, WI, 2001.

(26) Sheldrick, G. M. SHELXTL Version 6.1; Bruker Analytical X-ray Systems, Inc., Madison, WI, 2000.

reaction mixture was heated at reflux for 1 week. Water was added to the resulting colorless suspension; the phases were separated, and the aqueous phase was extracted with three 50 mL portions of CH_2Cl_2. The organics were dried over Na_2SO_4 and filtered, and solvent was removed by rotary evaporation (care being taken not to heat the mixture above about 35 °C; vide infra) to leave 4.93 g of a nearly colorless to pale yellow oil that was identified as a 4:1 mixture of **2** and $ClCH_2$(S-tim) (**3**; vide infra) (determined by NMR). The mixture was separated by passing the mixture through a silica gel plug, first using Et_2O to elute 0.55 g of $ClCH_2$(S-tim) ($R_f = 0.4$, same solvent, silica plate) and then methanol to elute 4.00 g (76%) of pure **2** (R_f 0.6, same solvent silica plate) as a pale yellow oil that crystallized on standing. Small portions of **2** (up to ca. 150 mg/10 mL) may be recrystallized by cooling a Et_2O solution to −30 °C in a freezer for a few hours. The mother liquor was decanted, and the colorless crystals were dried under vacuum. Mp: 51−52 °C. Anal. Calcd (found) for $C_9H_{12}N_4S_2$: C, 44.97 (45.07); H, 5.03 (5.02); N, 23.31 (23.29). ^{1}H NMR (δ, $CDCl_3$): 6.99 (d, 2H, $J = 1$ Hz), 6.86 (d, 2H, $J = 1$ Hz), 4.64 (s, 2H), 3.61 (s, 6H). ^{13}C NMR (δ, $CDCl_3$): 140.2, 129.9, 123.1, 40.2, 33.6. UV/vis (nm, CH_3CN) λ_{max} (log ϵ): 206 (3.90), 226 (4.27), 264 (4.03). IR (KBr, cm^{-1}): 3133, 3093, 3003, 2939, 1683 (w, C=C), 1510 (m, C=N), 752 (C−S).

Method B. A mixture of 5.00 g (43.8 mmol) of 2-mercapto-3-methylimidazole, 1.15 g (3.56 mmol) of tetrabutylammonium bromide, 35.5 g (1.58 mol) of KOH, 100 mL of H_2O, 7.00 g (50.5 mmol) of K_2CO_3, and 40 mL of CH_2Cl_2 were heated at reflux for 7 days. After heating, the phases were separated. The aqueous layer was extracted with two 50 mL portions of CH_2Cl_2, and the original organic layer was washed with eight 100 mL portions of H_2O. The combined organics were dried over $MgSO_4$ and filtered, and solvent was removed under vacuum to leave 3.57 g of a mixture of $ClCH_2$(Stim) (**3**; vide infra) and **2** (determined by NMR). Purification was achieved by column chromatography on silica gel, using a 50% hexanes/50% Et_2O to pure Et_2O gradient to remove **3**; then elution with absolute methanol (R_f 0.6, silica plate, same solvent) afforded 2.17 g (65%) of **2** as a viscous yellow oil that crystallized on standing. The characterization data are identical with those described above.

^{1}H NMR Spectroscopic Investigation of the Thermal Isomerization of 2. Glass ampules containing 25 mg portions of **2** were flame-sealed under vacuum (0.1 mmHg) such that a glass loop was formed on the top of the ampule. Copper wire was threaded through the glass loop, and the ampules were suspended but completely immersed in a preheated oil bath (temperatures between 120 and 175 °C were investigated) for various amounts of time, typically 1, 2, 3, 4, 8, 16, and 24 h and longer for the lower temperature runs. The ampules were removed from the oil bath, and the isomerization reactions were quenched by immersing the ampules in a room-temperature water bath. The contents of the ampule were dissolved in $CDCl_3$, and the ^{1}H NMR spectrum was acquired. The percentages of **2**, **3**, and CH_2(S-tim)(N-tim) were determined by using the average values obtained by comparing the relative integrations for each type of aromatic and methylene hydrogen signal for **2** and **3** in the ^{1}H NMR spectrum of the mixture. In addition, the *N*-methyl hydrogen signals for each compound in the mixture are not well resolved; thus, reliable integrations could not be made for these signals.

2-((Chloromethyl)thio)-1-methylimidazole, $ClCH_2(S\text{-}C_4H_5N_2S)$ (3). A mixture of 5.00 g (43.8 mmol) of 2-mercapto-3-methylimidazole, 1.15 g (3.56 mmol) of tetrabutylammonium bromide, 35.5 g (1.58 mol) of KOH, 100 mL of H_2O, 7.00 g (50.5 mmol) of K_2CO_3, and 40 mL of CH_2Cl_2 were heated at reflux for 24 h. (Immediately after the addition of the reagents the reaction mixture was pale blue, but after a few minutes it turned yellow.) After heating, the phases were separated. The aqueous layer was extracted with two 50 mL portions of CH_2Cl_2, and the original organic layer was washed with eight 100 mL portions of H_2O. The combined organics were dried over $MgSO_4$ and filtered, and solvent was removed under vacuum (0.05 mmHg, without external heating, vide infra) to leave impure **3** as a temperature-sensitive yellow oil. Column chromatography on silica gel using a 5:1 to 2:1 gradient of hexane/Et_2O afforded 1.58 g (22%) of **3** as a temperature-sensitive colorless oil in the first band (R_f 0.15, SiO_2 plate, 2:1 hexane/Et_2O). Anal. Calcd (found) for $C_5H_7ClN_2S$: C, 36.91 (37.07); H, 4.34 (4.29); N, 17.23 (16.91). ^{1}H NMR (δ, acetone-d_6): 7.14 (d, 2H, $J = 1$ Hz), 6.99 (d, 2H, $J = 1$ Hz), 4.96 (s, 2H), 3.71(s, 3H). ^{13}C NMR (δ, $CDCl_3$): 138.1, 130.6, 123.8, 51.1, 34.3. UV/vis (nm, CH_3CN) λ_{max} (log ϵ): 206 (3.90), 226 (4.27), 264 (4.03). IR (KBr, cm^{-1}): 3128, 3108, 3019, 2947, 2943, 1652 (w, C=C), 1508 (m, C=N), 754 (C−S), 718 (C−Cl).

Diimidazolium[2,1-d:1′2′-g][1,3,5,7]dithiadiazocine Chloride, $[CH_2(\mu\text{-}C_4H_5N_2S)_2CH_2][Cl]_2$ (4). A glass ampule fitted with a glass loop and copper wire was charged with 0.110 g of **3** and was flame-sealed under vacuum. The ampule was suspended by the copper wire in a preheated 140 °C oil bath so that it was completely immersed for 30 min, during which time a crystalline solid formed. After the ampule was cooled to room temperature by an external water bath and was opened, the solid was washed with CH_2Cl_2 and acetone and then dried under vacuum to give 91 mg (83%) of **4** as a hygroscopic colorless solid. The following analytical data are for a dried sample not exposed to atmospheric moisture. Mp: 224 °C dec to a brown solid, 246 °C liquifies. Anal. Calcd (found) for $C_{10}H_{14}Cl_2N_4S_2$: C, 36.91 (36.77); H, 4.34 (4.26); N, 17.23 (16.88). ^{1}H NMR (δ, CD_3OD): 8.41 (d, $J = 2.4$ Hz, 2H), 7.90 (d, $J = 2.4$ Hz, 2H), 6.94 (AB multiplet, J_{AB} =14.7 Hz, $\Delta\nu$ = 40.6 Hz, 2H), 5.03 (AB multiplet, J_{AB} =14.7 Hz, $\Delta\nu$ = 115.5 Hz, 2H), 3.98 (s, 6H). ^{13}C NMR (δ, CD_3OD): 141.5, 126.8, 124.5, 59.3, 40.9, 36.9. IR (KBr, cm^{-1}): 3143, 3111, 3034, 2962, 2893, 1652 (w, C=C), 1569 (m, C=N), 781 (C−S). The samples readily pick up water from the atmosphere. A sample exposed to laboratory air for 2 h had the following analyses: Anal. Calcd (found) for $C_{10}H_{18}Cl_2N_4O_2S_2$, **4**·$2H_2O$: C, 33.24 (33.00); H, 5.02 (4.85), N, 15.51 (15.09).

Diimidazolium [2,1-d:1′2′-g] [1,3,5,7]dithiadiazocine Hexafluorophosphate, $[CH_2(\mu\text{-}C_4H_5N_2S)_2CH_2][PF_6]_2$ (5). A suspension of 0.150 g (0.461 mmol) of **4** and 2.28 g (12.4 mol) of KPF_6 in 15 mL of CH_3CN was stirred at room temperature for 1 h and filtered. Solvent was removed by rotary evaporation to leave a light yellow solid. The solid was washed with two 10 mL portions of water and one 10 mL portion of Et_2O and then was dried under vacuum (0.1 mmHg) for 2 h to leave 0.224 g (90%) of **5** as a colorless solid. Mp: 234 °C dec to brown solid, 246 °C liquifies. Anal. Calcd (found) for $C_{10}H_{14}F_{12}N_4P_2S_2$: C, 22.07 (21.99); H, 2.59 (2.61), N, 10.29 (10.12). ^{1}H NMR (δ, CD_3CN): 7.96 (d, 2H, $J = 2.4$ Hz), 7.62 (d, 2H, $J = 2.4$ Hz), 6.64 (AB multiplet, $J_{AB} = 14.9$ Hz, $\Delta\nu = 14.6$ Hz, 2H), 4.49 (AB multiplet, $J_{AB} = 15.0$ Hz, $\Delta\nu = 53.8$ Hz, 2H), 3.86 (s, 6H). ^{13}C NMR (δ, CD_3CN): 127.6, 125.3, 60.0, 40.8, 37.6; SCN not observed. UV/vis (nm, CH_3CN) λ_{max} (log ϵ): 204 (5.42), 214 (5.36), 262 (4.41), 268 (4.24). IR (KBr, cm^{-1}): 3178, 3152, 3077, 3044, 2966, 1627 (w, C=C), 1575 (m, C=N), 832 (s, P−F), 757 (C−S). Single crystals of an acetonitrile solvate suitable for a diffraction study were obtained by allowing a layer of Et_2O to slowly diffuse into an acetonitrile solution over 3 days while being stored in a refrigerator.

Cyclic Voltammetry. Electrochemical measurements were collected under a nitrogen atmosphere at a scan rate of 200 mV/s for samples as 0.1 mM CH_3CN solutions with 0.1 M NBu_4PF_6 as the supporting electrolyte. A three-electrode cell comprised of an Ag/AgCl electrode, a platinum working electrode, and a glassy-carbon counter electrode was used for the voltammetric measurements. The data were calibrated by using an equimolar quantity of ferrocene (with respect to the analyte) as an internal standard (Fc/Fc$^+$ 0.35 V versus Ag/AgCl). Data obtained for samples without added ferrocene were identical with those with ferrocene.

Redox Titration Experiments Monitored by UV−Vis Spectroscopy. Standard solutions of the cation radical 9,10-dimethoxyoctahydro-1,4:5,8-dimethanoanthracenium hexachloroantimonate[23] were prepared by dissolving the cation radical in freshly distilled methylene chloride and diluting until the absorbance measured at 517 nm was about 1.0, corresponding to a concentration of 1.37×10^{-4} M (ϵ 7300). For the titrations, 4 mL of this standard solution was used and the spectrum was acquired before and after the addition of 10 μL aliquots of 0.005 48 M solutions of **1**, **2**, or **3**.

Acknowledgment. We thank Marius Costache for assistance with DTA measurements and Prof. Rajendra Rathore for samples of the cation radical and for helpful suggestions. J.R.G. thanks Marquette University and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support.

Supporting Information Available: Text, tables, and figures giving full experimental details, spectral and electrochemical characterization data, crystallographic data; crystal data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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