Electrophilic Additions to η^2-Thiophene Complexes: Synthesis of Novel Thiophenium and Thiafulvenium Species

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A series of complexes of the form $[Os(NH_3)_5(\eta^2\text{-L})](OTf)_2$ (where L = thiophene and OTf = trifluoromethanesulfonate, i.e., triflate) are synthesized and characterized and their reactivities with electrophilic reagents are examined. Depending on the electrophile and the substitution pattern of the coordinated thiophene, direct electrophilic addition occurs at either the sulfur, C2, or C3, affording thiophenium complexes. Some elementary transformations of selected thiophene complexes are exploited to prepare novel 1- and 2-thiafulvenium salts.

Introduction

The coordination chemistry of thiophenes has received considerable attention in recent years since transition metal thiophene complexes are potential homogeneous models for the surface intermediates observed on the heterogeneous hydrodesulfurization (HDS) catalysts employed in the petroleum industry.[1,2] The thiophene ligand can form coordination compounds with a variety of transition metals using one to all five of its atoms. While the first transition metal thiophene complex (η^5-thiophene)$Cr(CO)_3$ was reported by Fischer in 1958,[3] only within the past decade have examples of other coordination modes been prepared and their chemistry explored.[1,4,5] In the context of desulfurization, much of the early work regarding the coordination chemistry of thiophene has focused on C−S cleavage reactions. In contrast, little is known regarding the ability of a transition metal to activate a thiophene ligand toward organic reactions.[6]

The organic chemistry of thiophenes with electrophilic reagents parallels that of other five-membered aromatic heterocycles. Like both pyrroles and furans, thiophenes react with electrophiles via a substitution pathway primarily at the 2-position (i.e., the α-carbon).[7] In general, 2*H*- or 3*H*-thiophenium products of electrophilic addition are unstable and undergo rapid deprotonation to afford 2- and 3-substituted thiophenes. In addition, reactions with electrophiles often are compromised by polymerization or multiple electrophilic addition reactions. We hoped that, by stabilization of these thiophenium intermediates with the electron-rich pentaammineosmium(II) moiety,[8] thiophenes might participate in electrophilic addition reactions in a more controlled fashion, resulting in a greater degree of selectivity.

In a separate study, we have found that "hard" alkylating agents such as methyl triflate attack the sulfur of η^2-thiophene complexes such as $[Os(NH_3)_5(\eta^2\text{-thiophene})]^{2+}$, leading to cleavage of the C−S bond.[9] In this account we report the general reactivity of η^2-thiophene complexes of pentaammineosmium(II) toward electrophilic reagents (Figure 1) and focus primarily on reactions that form new carbon−carbon bonds with the heterocyclic ring. A portion of this account describing α-protonation of the coordinated thiophene ring has been previously communicated.[10]

Results

Synthesis and Characterization of η^2-Thiophene Complexes. Thiophene complexes **1**−**8** and **12**−**21** are prepared by the reduction of $[Os(NH_3)_5(OTf)](OTf)_2$ in the presence of the desired thiophene ligand in either

(1) For reviews of transition metal thiophene complexes, see (a) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61, and references therein. (b) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259.

(2) For reviews of the industrial HDS process, see (a) Girgis, M. J.; Gates, B. C. *Ind. Eng. Chem. Res.* **1991**, *30*, 2021. (b) Startsev, A. N. *Catal. Rev.—Sci. Eng.* **1995**, *37*, 353. (c) Wiegand, B. C.; Friend, C. M. *Chem. Rev.* **1992**, *92*, 491.

(3) Fischer, E. O.; Ölefe, K. *Chem. Ber.* **1958**, *91*, 2395.

(4) (a) For {2,3-η^2-[ReCp*$(CO)_2$]-benzo[*b*]thiophene}, see: Robertson, M. J.; Day, C. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1994**, *13*, 179. (b) For {2,3-η^2-[Os(NH_3)5]-thiophene}$^{2+}$, see: Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem Soc.* **1989**, *111*, 5969. (c) For an example of an η^2-thiophene in a triosmium cluster, see: Arce, Alejandro; De Sanctis, Y. *J. Organomet. Chem.* **1986**, *311*, 371. (d) For the synthesis of $Fe(CO)_2(POMe_3)(\eta^2$-thiophene-1,1-dioxide), see: Albrecht, R.; Weiss, E. *J. Organomet. Chem.* **1990**, *399*, 163.

(5) The η^2-coordination mode has been implicated in the HDS process. See: (a) Dong, L.; Duckett, S. B.; Ohnman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151. (b) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128.

(6) (a) Bianchini, C.; Frediani, P.; Herrera, V.; Jimenez, M. V.; Meli, A.; Rincon, L.; Sanchez-Delgado, R.; Vizza, F. *J. Am. Chem. Soc.* **1995**, *117*, 4333. (b). Bianchini, C.; Jimenez, M. V.; Meli, A.; Vizza, F. *Organometallics* **1995**, *14*, 4858.

(7) For reviews of the electrophilic chemistry of thiophenes, see: (a) Joule, J. A.; Mills, K.; Smith, G. F. *Heterocyclic Chemistry*, 3rd. ed.; Chapman & Hall: London, 1995; Chapter 15. (b) Taylor, R. In *Thiophene and its Derivatives, Part 2;* The Chemistry of Heterocyclic Compounds 44; John Wiley & Sons: New York, 1985.

(8) For recent applications of Os^{II} complexes to organic synthesis, see: (a) Hodges, L. M.; Spera, M. L.; Moody, M. W.; Harman, W. D. *J. Am. Chem. Soc.* **1996**, *118*, 7117. (b) Gonzalez, J.; Koontz, J. I.; Hodges, L. M.; Nilsson, K. R.; Neely, L. K.; Myers, W. M.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1995**, *117*, 3405. See also: Harman, W. D. *Chem. Rev.* **1997**, *97*, 1953.

(9) Spera, M. L.; Harman, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 8843.

(10) Spera, M. L.; Harman, W. D. *Organometallics* **1995**, *14*, 1559.

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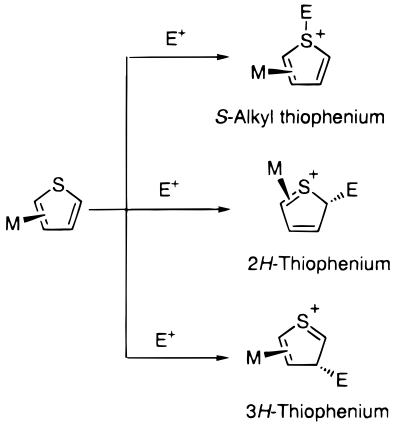
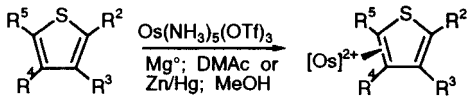


Figure 1. Electrophilic addition reactions of η^2-thiophene complexes.

Table 1. Yield Data for Selected η^2-Thiophene Complexes Where $[Os]^{2+}$ = the Cation $[Os(NH_3)_5]^{2+}$ and Triflate Counteranions Were Omitted for Clarity



compd	R^2	R^3	R^4	R^5	yield (%)
1	H	H	H	H	97
2	Me	H	H	H	94
3	H	Me	H	H	93
4	OMe	H	H	H	90
5	H	OMe	H	H	91
6	Me	H	H	Me	90
7	OAc	H	H	H	92
8	H	OAc	H	H	94
9	H	H	−	−	95
12	CHO	H	H	H	91
13	H	CHO	H	H	95
14	CH_2OH	H	H	H	89
15	H	CH_2OH	H	H	92
18	CO_2Me	H	H	H	91
20	$CH(OMe)_2$	H	H	H	89
21	$C(OMe)_2Me$	H	H	H	84

MeOH (Zn/Hg) or DMAc (Mg^0) (Table 1; yield >90%).[10] As a class, the η^2-thiophene complexes show similar spectroscopic and electrochemical characteristics. For all cases examined, an irreversible oxidation wave is observed between 0.5 and 0.7 V (NHE) in the cyclic voltammogram (MeCN/*n*-Bu_4NPF_6/100 mV/s). An irreversible reduction wave appears on return scan between +0.2 and −0.1 V (NHE) that corresponds to the oxidation product. Also observed on the return scan is a reversible couple at ~0.1 V (NHE) corresponding to $[Os(NH_3)_5(CH_3CN)]^{3+}$. For the thiophene complex **1**, the ^{1}H NMR spectrum (CD_3CN) exhibits two downfield resonances at 6.72 and 6.59 ppm, assigned as the uncoordinated protons H2 and H3, and two upfield resonances at 5.77 and 5.31 ppm, assigned as the coordinated protons H5 and H4.[11] For all η^2-thiophene complexes examined, $J_{H,H}$ is approximately 6 Hz between H2 and H3 as well as between H4 and H5; $J_{H,H}$ between H2 and H5 as well as between H3 and H4 is approximately 2 Hz. The ^{13}C NMR spectrum for **1** exhibits two downfield resonances at 130.8 and 121.7 ppm corresponding to the uncoordinated carbons C2 and C3 and two upfield methine resonances at 66.1 and 61.8 ppm corresponding to the coordinated carbons C5 and C4. Unlike η^2-pyrrole complexes, which decompose above 50 °C, η^2-thiophene complexes are stable up to 130 °C in CD_3CN or DMF-d_7 solution and do not exhibit fluxionality on the ^{1}H NMR time scale (300 MHz).

For monosubstituted thiophene ligands, only the 4,5-η^2 isomer is isolated upon complexation to Os^{II} at ambient (22 °C) temperature as the pentaammineosmium(II) fragment preferentially coordinates the unsubstituted double bond. For both the 2-methyl- and 3-methylthiophene complexes (**2** and **3**), a mixture of kinetic isomers is observed by ^{1}H NMR spectroscopy (CD_3OD, −40 °C), if the complexation is performed in CD_3OD at −40 °C. Even at this temperature, the 4,5-isomer is heavily favored (>95%), but a minor species, thought to be the 2,3-bound isomer, is observed and rapidly converts to the major isomer at −40 °C $t_{1/2} \sim 1$ min. Interestingly, the 2-deuteriothiophene complex **1-*d*** (prepared from 2-deuteriothiophene) is isolated as a ~1.5:1 mixture of 4,5-η^2 and 2,3-η^2-coordinated isomers, a ratio that represents a significant departure from the statistical distribution of 1:1.

In light of electrochemical data, the reactivity of **1** with weak one-electron oxidants supports the notion that the η^2-thiophene species has access to its sulfur bound isomer. Dialkyl sulfide complexes of pentaammineosmium(II) typically have oxidation potentials near 0 V (NHE) and as such are easily oxidized by permethylferrocenium ion ($E_{1/2} = 0.04$ V (NHE)). When a stoichiometric amount of $Cp_2^*Fe^+$ is added to a MeCN solution of the thiophene complex **1**, the osmium complex is immediately oxidized to the $[Os(NH_3)_5(CH_3CN)]^{3+}$ complex as evidenced by cyclic voltammetry. The η^2 isomer of **1** has a reduction potential that is far too positive to be oxidized by $Cp_2^*Fe^+$. In addition, Angelici and co-workers have observed an equilibrium mixture of η^1- and η^2-benzothiophenes for the system $CpRe(CO)_2$.[4a] For η^2-furan complexes of pentaammineosmium(II), the rate of 2,3-η^2 to 4,5-η^2 isomerization is significantly lowered by an alkyl group in the 3-position. We have concluded from this observation that these η^2-furan ligands, like their nitrogen counterparts, undergo this isomerization via the 3,4-η^2 intermediate. However, for 3-substituted thiophenes, the corresponding 2,3-η^2 to 4,5-η^2 isomerization occurs at a rate similar to that for the 2-methylated analogue. This observation further supports the putative presence of S-bound intermediates.

If other unsaturated functional groups are present in the thiophene ligand, kinetic mixtures of regioisomers are often produced at fast complexation times (<5 min) but convert to the most thermodynamically stable isomer.[12] For example, the benzo[*b*]thiophene complex **9** is formed as a ~4:1:1 mixture of regioisomers corresponding to the 2,3-η^2, 4,5-η^2, and 6,7-η^2 isomers, respectively. Two sets of *cis*- and *trans*-ammine resonances (2.89, 4.19 ppm and 2.77, 4.12 ppm) are observed in a 2:1 ratio as are six coordinated olefin signals. A cyclic voltammogram of this initial product shows two

(11) Throughout this manuscript we show the osmium coordinated to the 4,5-position of the thiophene ring in order to utilize the standard thiophene nomenclature (i.e., C2-protonation, etc.)

(12) Using a large (e.g., ~10 w/w equiv) excess of reducing agent to Os^{III} ensures that the reduction is essentially complete <15 min. Typically, Zn/Hg reductions are complete by CV (e.g., no OsIII) within 30 min and Mg^0 reductions are complete within 1 h.

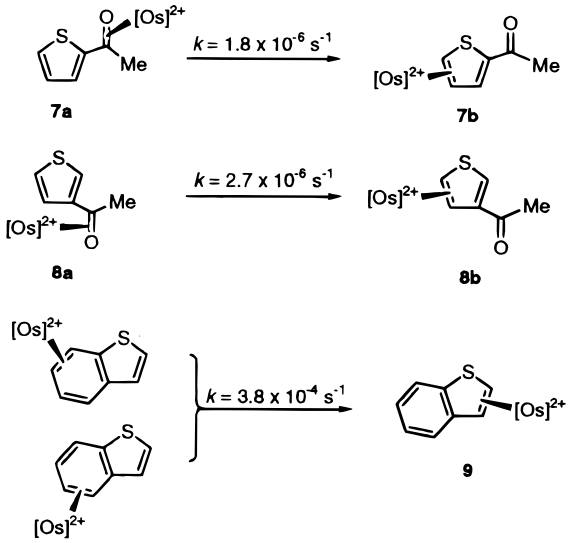


Figure 2. Linkage isomerization of η^2-thiophene complexes.

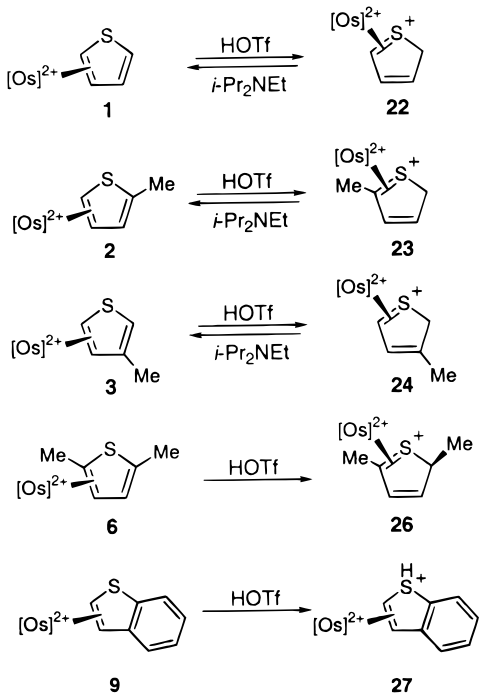


Figure 3. Synthesis of 1,5-η^2-2*H*-thiophenium complexes.

reversible oxidation waves at 0.37 and 0.51 V. If a CD_3CN solution of freshly prepared **9** is monitored by ^1H NMR spectroscopy (60 °C), the 4,5-η^2 and 6,7-η^2 isomers convert to the 2,3-η^2 isomer with a specific rate of $k = 3.8 \times 10^{-4}$ s^{-1} (Figure 2).[13] This migration also occurs at ambient temperature in the solid state over a period of 2 weeks.[14]

For the 2- and 3-acetylthiophene complexes **7** and **8**, a mixture of η^2-carbonyl and 4,5-η^2 isomers is initially formed (**7a,b** and **8a,b**; ~3:2 η^2-CO:η^2-ring) which convert to the η^2-ring-bound isomers **7b** and **8b** upon standing in solution (CD_3CN, 22 °C, $k = \sim 10^{-6}$ s^{-1}) or warming to 60 °C (Figure 2). This behavior is in marked contrast to that observed for the 2-acetyl-1-methylpyrrole complex, where an initial 3:1 mixture of η^2-CO:η^2-ring-bound isomers undergoes a linkage isomerization to afford an entirely carbonyl-bound complex.[8a]

The thiophenecarboxaldehydes also afford kinetic mixtures upon complexation to pentaammineosmium(II) (**12a,b**; 3:1 η^2-CO:η^2-ring and **13a,b**; 7:1 η^2-CO:η^2-ring). However, in contrast to the linkage isomerizations observed for acetylthiophene complexes **7** and **8**, neither *C,O*-η^2-aldehyde complex isomerizes to its ring bound isomer when heated. The ratio of carbonyl to ring bound isomers remains unchanged when CD_3CN solutions of each are monitored by ^1H NMR spectroscopy from 22 to 90 °C. Endeavoring to explore the reactivity of the ring-bound aldehyde complexes, we prepared the 4,5-η^2-2-thiophenecarboxaldehyde complex **12b** via acid hydrolysis of the dimethyl acetal complex **20**. When a solution of **20** in MeCN is treated with excess H_2O and HOAc, the 4,5-η^2-2-thiophenecarboxaldehyde complex **12b** is isolated after ~6 h. This complex, like the ring-bound acetylthiophene complexes, does not undergo isomerization to the carbonyl complex, even upon moderate heating (50−70 °C, CD_3CN, 6 h); instead, substitution by solvent occurs, affording the $[Os(NH_3)_5(CD_3CN)]^{3+}$ complex.

The coordination of both benzo[*b*]thiophene and benzofuran to the weaker π-base $Ru(NH_3)_5^{2+}$ affords stable 2,3-η^2species **10** and **11** upon isolation. In contrast, indole does not form a stable η^2-complex with pentaammineruthenium(II). Pentaammineruthenium(II) has been reported to form an η^2:η^2-binuclear complex with furan but does not form a stable η^2-complex with thiophene.[15] Kuehn and Taube have reported electrochemical evidence for an unstable S-bound thiophene complex with $Ru(NH_3)_5^{2+}$.[16]

C2 Protonation.[10] Treatment of complexes **1**−**3**, **5**, and **6** with 1.1 equiv of HOTf in either CH_3CN or MeOH affords novel η^2-coordinated 2*H*-thiophenium complexes **22**−**26** in high (>85%) yield (Figure 3). For the protonated thiophene complex **22**, the ^1H NMR (CD_3CN) spectrum exhibits a broad singlet at 7.96 ppm (1H) and two sets of doublets of doublets at 6.90 and 6.76 ppm (J = 5.9, 1.9 Hz, 1H for both protons), as well as two upfield doublets of doublets at 3.08 and 2.62 ppm (J = 20.7, 1.9 Hz, 1H for both protons). The *cis*- and *trans*-ammine resonances are shifted considerably downfield, to 3.71 and 5.21 ppm, compared to the precursor. 1D-NOE data indicate a significant enhancement (14.6%) for the proton at 7.96 ppm (H5) upon irradiation of the *cis*-ammines. Additional NOE enhancements are observed for the proton at 6.90 ppm (10.5%, H4) and the doublet of doublets at 3.08 ppm (5.8%, $H2_{endo}$). ^{13}C NMR and DEPT (CD_3CN) spectra for **22** exhibit two uncoordinated methine carbons at 136.8 and 131.3 ppm, a methine carbon at 71.3 ppm, and a methylene carbon at 43.5 ppm. For each complex, an irreversible oxidation wave is observed in the cyclic voltammogram between

(13) An identical isomerization is observed for the η^2-benzofuran complex. Spera, M. L. Ph.D. Dissertation, University of Virginia, January, 1998.

(14) We have also observed stable 2,3-η^2-bound benzo[*b*]thiophene and benzofuran complexes of pentaammineruthenium(II). While a stable η^2-thiophene complex of $Ru(NH_3)_5^{2+}$ has not been observed, Taube reports observing a short-lived S-bound complex upon reduction of $[Ru(NH_3)_5OTf](OTf)_2$ in the presence of excess thiophene. See: Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689.

(15) Chen, H. Ph.D. Dissertation, University of Virginia, January, 1997.

(16) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689.

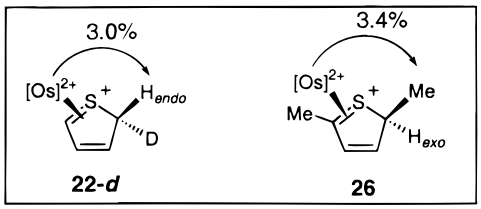
1.17 and 1.59 V (NHE) as is an irreversible reduction wave between 0.12 and 0.25 V (NHE). These data are consistent with protonation occurring at the uncoordinated α-carbon (C2) with migration of the metal to the newly formed C5−S double bond. For both the 3-methylthiophene **3** and 3-methoxythiophene complexes **5**, protonation occurs at the α-carbon adjacent to the substituent, i.e., C2. In contrast, protonation of the 2-methylthiophene complex occurs at the former coordinated α-carbon such that the metal is now coordinated on the double bond containing the methyl substituent (Figure 3). Both the 2-methoxythiophene and 2-carbomethoxythiophene complexes **4** and **18** decompose to unidentified products upon treatment with HOTf in CD_3CN at 22 °C. If the protonation of either complex is performed at −40 °C (HOTf/CD_3CN), no intermediates are observed by ^1H NMR spectroscopy (−40 °C).

The α-protonation of η^2-thiophene complexes is with one exception reversible. Treatment of complexes **22**−**25** with an amine base (pyridine, *i*-Pr_2NEt) results in the regeneration of the thiophene conjugate bases **1**−**3** and **5** as well as traces (<5%) of $[Os(NH_3)_5(CH_3CN)]^{3+}$ (Figure 3). Precipitation of the protonated 2,5-dimethylthiophene complex **26** in either diethyl ether or methylene chloride, with or without a base quench, affords a complicated mixture of products including ammonium and $[Os(NH_3)_5(CH_3CN)]^{3+}$ ions. No bound thiophene resonances are observed for this mixture.

In contrast to the facile nucleophilic additions observed for other cationic ligands of pentaammineosmium(II),[8] the 2*H*-thiophenium complexes fail to undergo nucleophilic addition reactions with heteroatom or carbon nucleophiles. While **22** is unreactive in the presence of silanes, silyl enol ethers, and silyl ketene acetals, deprotonation of the 2*H*-thiophenium species **22** occurs when basic nucleophiles such as H^-, CN^-, or enolates are used. The pK_a of **1** in MeCN is 2 ± 1, based on bracketing experiments using various organic bases (i.e., diphenylamine and 2,6-di-*tert*-butylpyridine).

While 2*H*-thiophenium complexes are observed to form by ^1H NMR spectroscopy even at −80 °C, the benzo[*b*]thiophene complex **9** affords an S-protonated species at ambient temperature (22 °C) with excess HOTf in CD_3CN. Treatment of **9** with HOTf (∼3.1 × 10^{-4} M) in CD_3CN affords only unreacted **9** even after several hours. However, if the concentration of acid is substantially increased (2.6 × 10^{-3} M), a new product **27** is observed after 1 h by NMR spectroscopy. The ^1H and ^{13}C NMR data for **27** are consistent with protonation occurring at the sulfur atom. ^1H NMR (CD_3CN) data indicate a set of downfield shifted *cis*- and *trans*-ammine resonances at 3.78 and 5.36 ppm, as well as signals corresponding to an η^2-coordinated benzo[*b*]-thiophene ligand. This product is stable in acidic CD_3CN, but decomposes upon isolation, and has not been further characterized.

Endeavoring to determine the stereoselectivity of the protonation reaction, we examined the protonation of the 2,5-dimethylthiophene complex **6** with HOTf to yield **26**, as well as thiophene complexes **1** and **3** with triflic acid-d_1 affording **22-*d*** and **24-*d*** respectively (Figure 4). A weak NOE enhancement (3.4%) is measured between the *cis*-ammines and the methyl substituent at the site of protonation (i.e., C2) in complex **26**. When triflic



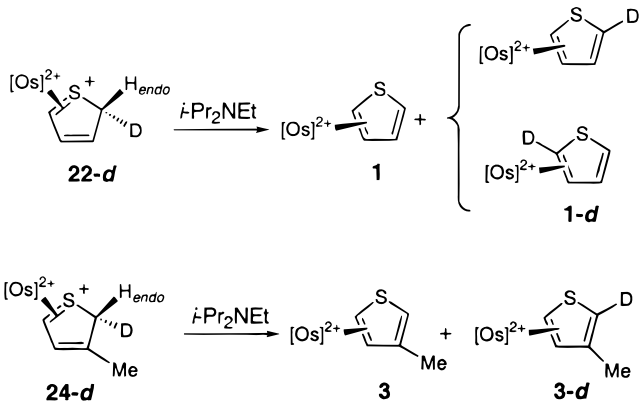


Figure 4. Determination of stereochemistry of H^+/D^+-addition to thiophene complexes **1**, **3**, and **6**.

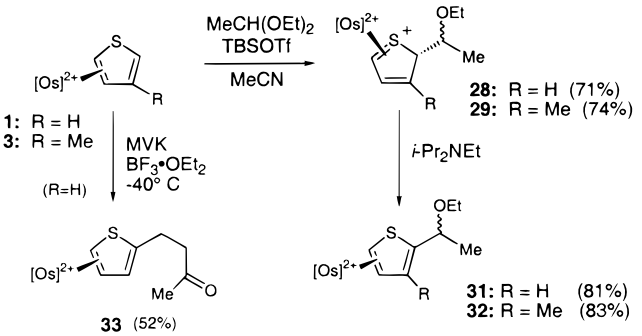


Figure 5. C2-alkylation of 2-unsubstituted thiophene complexes.

acid-*d* is added to a solution of **1**, the upfield methylene resonance (2.62 ppm, $H2_{exo}$) has disappeared, and the downfield methylene resonance (3.08 ppm, $H2_{endo}$) is now a broad singlet, but at full intensity. When the *cis*-ammines of **22-*d*** are irradiated, a small enhancement (∼3.0%) is measured for $H2_{endo}$. If compound **22-*d*** is treated with the base *i*-Pr_2NEt, the ^1H NMR spectrum (CD_3CN) of the resulting product (a mixture of **1** and **1-*d***) exhibits signals for both H2 and H5 that are reduced by ∼67% relative to either H3 or H4. A similar result is observed when the 3-methylthiophene complex **3** is treated successively with DOTf and *i*-Pr_2NEt affording **3-*d***. The ^1H NMR spectrum of the resulting product exhibits a resonance for C2 which integrates for ∼50% of either C4 or C5. This suggests a 1:1 mixture of **3** and a 3-methylthiophene complex incorporating deuterium at C2. Taken together, these data support a stereoselective *exo* protonation for these thiophene complexes, but a nonselective deprotonation.

C2 Alkylation. η^2-Thiophene complexes lacking substituents at the α-carbons undergo Lewis acid-promoted *addition* reactions with acetals at C2 to afford 2-substituted-2*H*-thiophenium species (**28** and **29**, Figure 5). Treatment of a solution of **1** in MeCN with 1.2 equiv of distilled acetaldehyde diethyl acetal and 1.1 equiv of

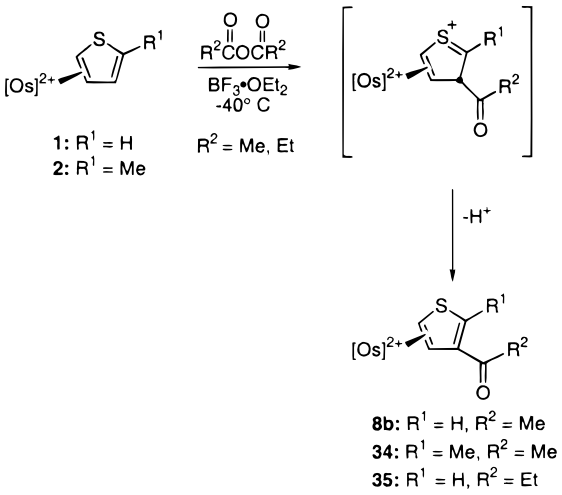


Figure 6. β-Acylation reaction of η^2-thiophene complexes **1** and **2**.

tert-butyldimethylsilyl triflate (TBSOTf) affords a new product whose NMR spectral features are very similar to those of the 2*H*-thiophenium species resulting from the protonation of **1**. The deep purple 2-substituted thiophenium complex **28** is isolated in 71% yield. In a similar fashion, the 3-methylthiophene complex **3** reacts with acetaldehyde diethyl acetal to afford the 2,3-disubstituted thiophenium complex **29** in 74% yield. For both **28** and **29**, the complexes are isolated as 1:1 mixtures of diastereomers. 1D-NOE enhancement studies undertaken on **28** verify that the electrophile attacks from the *exo* face. Upon irradiation of the *cis*-ammines, NOE enhancements for H5 (15.5%) and $H2_{endo}$ (7.5%) were measured.

The 2-substituted 2*H*-thiophenium complexes **28** and **29** undergo deprotonation at C2 upon treatment with base (*i*-Pr_2NEt, MeCN) to afford the 2-substituted and the 2,3-disubtituted thiophene complexes **31** and **32**, respectively, in >80% yield as 1:1 mixtures of diastereomers (Figure 5). In contrast, if the 2-position is alkylated (e.g., **2** and **6**), the C2-alkylation reaction fails and only the protonated product **23** is observed.

When a CH_3CN solution of **1** is treated with 1.1 equiv of distilled MVK and 1.1 equiv of TBSOTf at −40 °C in the absence of base, a new product, **33**, is isolated after 5 min in moderate yield (51%). The *cis*- and *trans*-ammine resonances at 2.96 (12H) and 4.19 ppm (3H) and the absence of $H2_{endo}$ are consistent for a neutral substituted thiophene complex. Other Michael acceptors, including the highly reactive maleimides, fail to undergo Lewis acid promoted additions with thiophene complexes and instead afford either starting material or thiophenium complexes.

C3 Acylation. In marked contrast to the facile 2-acylation of free thiophenes, the thiophene complex **1** reacts with acid anhydrides in the presence of a Lewis acid to afford *β-substituted* thiophene complexes in high yield (Figure 6). For example, complex **1** reacts with 1.2 equiv of acetic anhydride in the presence of $BF_3{\cdot}OEt_2$ (1.1 equiv) at −40 °C in a 2:1 cosolvent mixture of acetonitrile and propionitrile to afford the 3-acetylthiophene complex **8b** after 24 h in high yield (93%). The ^1H NMR spectrum and electrochemical data for this product are identical to those for the complex obtained from authentic 3-acetylthiophene, although traces (<5%) of the 2*H*-thiophenium complex **22** are present. In a similar fashion, propionic anhydride is observed to react at C3 to afford the 3-propionylthiophene complex **35** along with ∼25% of the 2*H*-thiophenium **22** as an impurity.[17] When cyclic anhydrides such as maleic or succinic anhydride are used, only the protonated thiophenium complex **22** is observed. Anhydrides also fail to react if C3 is alkylated, as in the case of the 3-methylthiophene complex **3**, where reaction with acetic anhydride affords only the 2*H*-3-methylthiophenium complex **24**.

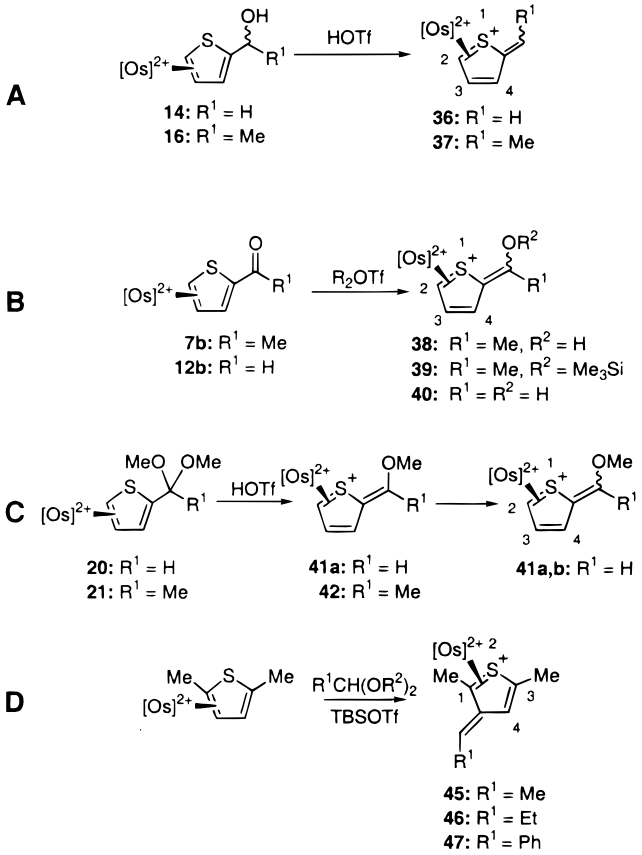


Figure 7. Synthesis of 1,2-η^2-1-thiafulvenium and 1,2-η^2-2-thiafulvenium complexes from 2-substituted and 2,5-disubstituted thiophene complexes.

Formation of Thiafulvenium Complexes.[18] Pentaammineosmium(II) complexes of formyl- and acetylthiophenes as well as their alcohol derivatives are readily converted into novel thiafulvenium complexes using the appropriate electrophiles (Figure 7). For example, if the 2-hydroxymethylthiophene complex **14** is treated with 1.1 equiv of HOTf in either CH_3CN or MeOH, protonation occurs not at C2 but on the hydroxy substituent, which after elimination of water affords the 1,2-η^2-1-thiafulvenium species **36** in excellent yield (A, Figure 7). The spectroscopic data for **36** support a structure similar to that of a 2*H*-thiophenium complex, with an additional feature corresponding to an exocyclic methylene group. The ^1H NMR spectrum (CD_3CN) of **36** includes a doublet at 8.35 ppm (J = 2.9 Hz, 1H) assigned to the proton at C2, a doublet at 7.31 ppm

(17) If the reaction is quenched with an amine base, the thiophene complex **1** is the observed impurity.

(18) We have named these compounds such that the quaternary carbon from which the exocyclic double bond extends is C5. See Figure 7.

(J = 2.9 Hz, 1H), a doublet of doublets at 7.18 ppm (J = 5.9 Hz, 2.9 Hz, 1H), and two doublets (J = 2.9 Hz, 1H each) at 7.07 and 7.04 ppm assigned as the exocyclic methylene protons. The ^{13}C NMR and DEPT spectra confirm the presence of a methylene carbon at 124.14 ppm, two uncoordinated methine resonances (145.12, 129.91 ppm), a quaternary carbon (144.07 ppm), and a coordinated methine carbon (64.65 ppm). If the 2-(2-hydroxy)ethylthiophene complex **16**, prepared as a 1:1 mixture of diastereomers, is treated under similar conditions, the 6-methyl-1-thiafulvenium complex **37** forms as a 7:1 mixture of isomers about C6 in 82% yield.

Hydroxy- or silyloxythiafulvenium complexes are also formed when the 2-acetylthiophene complex **7b** or the 2-formylthiophene complex **12b** are either protonated or treated with TMSOTf in CH_3CN (B, Figure 7). Treatment of **7b** in MeCN with 1.2 equiv of HOTf affords upon isolation the 6-hydroxy-6-methyl-1-thiafulvenium complex **38** in 90% yield as a 6:1 mixture of diastereomers. 1D-NOE data indicate that the major isomer has the methyl substituent oriented away from the sulfur, as depicted in Figure 7. If the protonation of **7b** is performed in methanol ($\sim 1.8 \times 10^{-4}$ M HOTf), then a 1:1 mixture of thiafulvenium to acetylthiophene complexes results. The ring-bound 2-formylthiophene complex **12b** undergoes protonation at the carbonyl oxygen to afford a 1-thiafulvenium complex, **40**, similar to that observed for the protonation of 2-acetylthiophene. This product is isolated as a 3:2 mixture of diastereomers.

Methoxy-substituted thiafulvenium complexes are prepared via elimination of a methoxy group from either a dimethyl acetal or a dimethyl ketal complex (C, Figure 7). While methoxy-substituted 2-azafulvenium complexes are readily prepared from the 2-acetylpyrrole complex and methyl triflate, the 2- and 3-acetylthiophene complexes under similar conditions undergo S-methylation exclusively.[19] The dimethyl acetal and dimethyl ketal substituted complexes **20** and **21** both afford 6-methoxy-1-thiafulvenium complexes (**41** and **42**) upon treatment with HOTf. The protonation of the 2-thiophenecarboxaldehyde dimethyl acetal complex **20** initially affords **41a** as one isomer: however, this product slowly equilibrates to a 2:1 ratio of isomers (**41a,b**; Figure 7). In contrast, protonation of the 2-acetylthiophene dimethyl ketal complex **21** affords only one isomer, **42**.

The formation of 1,2-η^2-2-thiafulvenium complexes (**45**−**47**) is possible from an η^2-thiophene when both α-positions of thiophene are blocked (D, Figure 7). For example, when a solution of **6** in MeCN is treated with acetal (1.2 equiv) and TBSOTf (1.1 equiv) at 22 °C, a new product **45** precipitates as a *single* isomer in 87% isolated yield. The ^{1}H NMR spectrum (CD_3CN) of **45** contains a downfield singlet at 7.41 ppm, a quartet at 6.88 ppm, J = 7.3 Hz, 1H), *cis*- and *trans*-ammine resonances at 3.86 and 5.39 ppm, two ring methyl resonances at 2.40 and 1.97 ppm, and a doublet at 1.65 ppm (J = 7.3 Hz, 3H). ^{13}C NMR data indicate two olefinic methine signals (131.35 and 129.31 ppm) as well as a coordinated methine (68.71 ppm). Other acetals

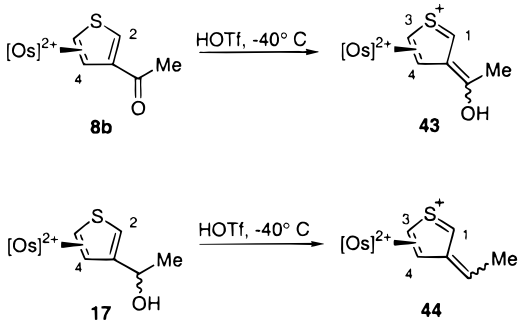


Figure 8. Synthesis of 3,4-η^2-2-thiafulvenium complexes from 3-substituted thiophene complexes.

(propionaldehyde dimethyl acetal, benzaldehyde dimethyl acetal) readily react in the presence of TBSOTf with complex **6** to afford the thiafulvenium analogues **46** and **47**, respectively. For all cases examined, the reaction proceeds to afford only one isomer, in contrast to what is commonly observed for the α-addition of acetals. 1D-NOE enhancement studies of **46** support a structural assignment with the substituent on C6 directed away from the sulfur. Attempts to prepare the parent 1,2-η^2-2-thiafulvenium species from either dimethoxy- or diethoxymethane and **6** failed.

3,4-η^2-2-Thiafulvenium complexes may be prepared starting from 3-acyl- or 3-(hydroxyalkyl)thiophenes (Figure 8). In contrast to the remarkable room-temperature stability of the 1,2-η^2-1- and 1,2-η^2-2-thiafulvenium complexes, 3,4-η^2-2-thiafulvenium complexes are stable in acidic acetonitrile only at low temperature (−40 °C, Figure 8). When the 3-substituted complexes **8b, 15**, and **17** are treated with HOTf in MeCN at 22 °C, no stable diamagnetic species are observed by ^{1}H NMR spectroscopy. For both **8b** and **17**, a deep-red solution forms upon addition of HOTf at 22 °C which decomposes over a period of seconds. A cyclic voltammogram of the final solution indicates the presence of a significant amount of $[Os(NH_3)_5(CH_3CN)]^{3+}$. However, if the same reactions are performed at −40 °C, new products are observed by low-temperature ^{1}H NMR spectroscopy (CD_3CN, −40 °C). The protonation of either **8** or **17** affords the 3,4-η^2-2-thiafulvenium complexes **43** and **44** whose ^{1}H NMR exhibits signals corresponding to H1 (i.e., on the uncoordinated C−S double bond) between 9.5 and 10.5 ppm, approximately 2 ppm further downfield than that observed in 1,2-η^2-coordinated thiafulvenium complexes. ^{13}C NMR data (CD_3CN, −40 °C) have been obtained for **44**, in which the resonance for C1 appears at 160.1 ppm. The 3-acetylthiophene complex **8b** and the 2-thiafulvenium complex **43** derived from it have limited solubility in CD_3CN at −40 °C; thus, **43** has not been characterized by ^{13}C NMR spectroscopy. When solutions of these 2-thiafulvenium complexes are allowed to warm to ambient temperature, uncharacterized paramagnetic products are formed. The 3-(hydroxymethyl)thiophene complex **15** does not form a stable diamagnetic product upon treatment with HOTf, even at −40 °C.

Nucleophilic Addition to Thiafulvenium Complexes. Nucleophiles react with 1-thiafulvenium complexes at the exocyclic methylene carbon to afford substituted thiophene complexes **2**, **48**, and **49** in good yield (Figure 9). When the 1-thiafulvenium complex **36** is treated with *n*-Bu_4NBH_4 (1.2 equiv) in MeCN, the

(19) These S-alkylated complexes do not undergo *C,S*-cleavage in the presence of nucleophiles. Spera, M. L. Ph.D. Dissertation, University of Virginia, January, 1998.

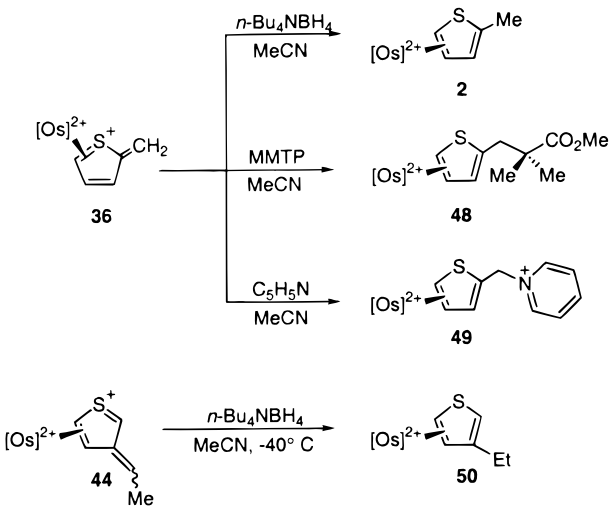


Figure 9. Reactivity of thiafulvenium complexes **36** and **44** with nucleophiles.

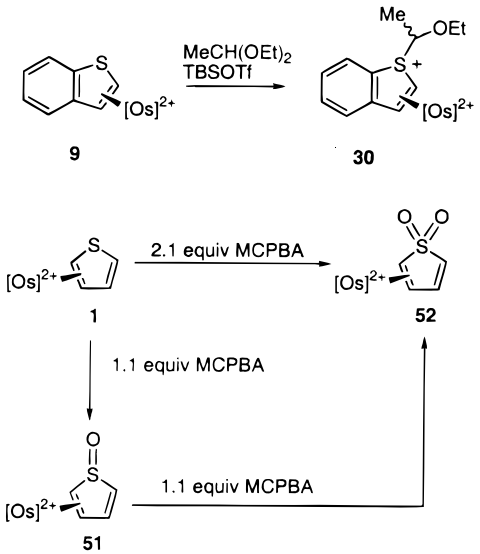


Figure 10. Reactivity of sulfur atom in η^2-benzo[*b*]-thiophene complex **9** and η^2-thiophene complex **1**.

2-methylthiophene complex is isolated in 86% yield. Other nucleophiles such as 1-methoxy-2-methyl-1-trimethylsiloxy-1-propene (MMTP) and pyridine add to C6 to afford 2-substituted thiophene complexes **48** and **49**, respectively. Similarly, when a MeCN/EtCN solution of **44** is treated with *n*-Bu_4NBH_4 at −40 °C, the 3-ethylthiophene complex **50** results in an 87% isolated yield.

Reactions at Sulfur. We have recently reported the synthesis of a variety of S-alkylated thiophenium complexes via direct S-alkylation with carbon electrophiles.[9] In a similar manner, the benzo[*b*]thiophene complex **9** appears to undergo S-alkylation with acetaldehyde diethyl acetal judging from ^{1}H NMR data. Note that this is in contrast to the C2-alkylations normally observed with this electrophile for simple thiophene complexes (Figure 10). This reaction requires the use of a large excess (∼5 equiv) of both the acetal (acetaldehyde diethyl acetal) and TBSOTf. The product isolated after 24 h is, at best, a 1:1 mixture of starting material **9** and the S-alkylated benzo[*b*]thiophenium **30**. Increasing the concentration of both electrophile and Lewis acid results in an intractable polymer.

The oxidant *m*-chloroperoxybenzoic acid (MCPBA) reacts with the thiophene complex **1** to afford S-oxidized thiophene complexes in good yield (Figure 10). When the thiophene complex is treated with ∼1.0 equiv of MCPBA,[20] a new product, **51,** is isolated in 95% yield, along with traces (5−10%) of a second product, **52**. Complex **51** reacts with excess MCPBA to afford **52** in 95% yield. The ^{1}H NMR spectra of **50** and **51** are identical to that of **1** except that the *cis*- and *trans*-ammine resonances of **51** and **52** are shifted approximately 0.5 ppm downfield from those of **1**. The resonance for the uncoordinated α-proton, H2, is sensitive to the increasing electron-withdrawing effects on the sulfoxide and sulfone functionalities in **51** and **52**, respectively. For the *S*-oxide **51**, H2 resonates approximately 0.2 ppm further downfield (6.96 ppm) than in the thiophene complex **1**. In the *S*-dioxide **52**, H2 resonates even further downfield at 7.36 ppm. Surprisingly, this trend is not observed for the other ring protons. The electrochemistry (CV) of both **51** ($E_{1/2}$ = 1.09 V) and **52** ($E_{1/2}$ = 1.15 V) is consistent with an olefin-like ligand that is more electron-deficient than thiophene. Other examples of transition metal complexes of thiophene 1-oxides and 1,1-dioxides, including an η^2-complex of the latter, have been reported.[21,22]

Decomplexation of η^2-Thiophene Ligands. Ligands are removed from the pentaammineosmium(II) metal center either by oxidizing the metal to Os^{III} or heating the complex in a coordinating solvent such as MeCN, acetone, or DMAc. When an acetone solution of the 3-ethylthiophene complex **50** is treated with 1 equiv of AgOTf, the 3-ethylthiophene ligand **53** is recovered in good yield (83%) upon workup. Similarly, when the 2,3-disubstituted thiophene complex **32** is heated in MeCN (80 °C, 26 h), the free ligand **54** is recovered in 76% yield upon workup.

Discussion

The organometallic chemistry of transition metal thiophene complexes as well as other sulfur-containing ligands is most often applied to providing homogeneous models for surface species implicated in the heterogeneous HDS process.[1,2] Aside from reactions leading to C−S cleavage, few reports exist specifically describing synthetically useful transformations of bound thiophenes. Although carbon nucleophiles have been observed to add to both the carbon and sulfur atoms,[23] there are no reports describing the formation of 2*H*- or 3*H*-thiophenium complexes resulting from the addition of carbon electrophiles.

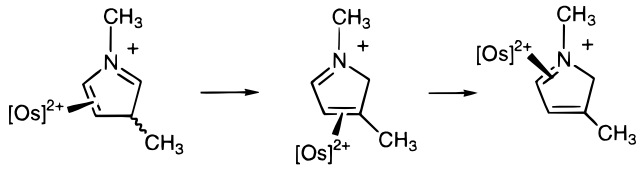
(20) The reagent was purchased from Lancaster with a minimum purity of 70−75% and used as received. Equivalents of this reagent are calculated on an assumed purity of 70%.

(21) Skaugset, A. E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 2432.

(22) For an η^2-complex, see ref 4d. For an η^4-complex of cobalt, see: Albrecht, R.; Weiss, E. *J. Organomet. Chem.* **1991**, *413*, 355.

(23) (a) Lee, S. S.; Lee, T. Y.; Choi, D. S.; Lee, J. S.; Chung, Y. K.; Lee, S. W.; Lah, M. S. *Organometallics* **1997**, *16*, 1749. (b) Hachgenei, J. W.; Angelici, R. J. *J. Organomet. Chem.* **1988**, *355*, 359. (c) Hachgenei, J. W.; Angelici, R. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 909. (d) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897.

Comparison of η^2-Heterocycle Reactivity.[24] The uncoordinated portion of an η^2-pyrrole or η^2-furan chemically resembles an enamine or vinyl ether, respectively. As such, both η^2-furan and η^2-pyrrole complexes of pentaammineosmium(II) preferentially undergo β- electrophilic addition reactions.[8] The weaker π-donor properties of sulfur compared to nitrogen or oxygen greatly reduce the nucleophilicity of the β-position. Only for the case of acylation with anhydrides is a β-carbon preferentially attacked over an α-carbon. The general 4,5-η^2 to 1,5-η^2 rearrangement of the metal center observed for thiophenium complexes has at least one parallel in pentaammineosmium(II) chemistry. When the η^2-1,3-dimethylpyrrole complex is protonated, several Os^{II}−pyrrolium isomers are formed that all convert to a 2*H*-pyrrolium complex in which the metal is coordinated to C3 and C4. This species, although stable enough to isolate, ultimately isomerizes to a 1,5-η^2-2*H*-pyrrolium complex analogous to the 2*H*-thiophenium species described herein. However, this isomerization is only seen in the nitrogen heterocycle when a methyl group at C3 forces the metal away from the C3−C4 bond.



The increased basicity of the η^2-thiophene complexes relative to the uncoordinated ligand has been observed for other η^2-heterocycle complexes of pentaammineosmium(II) and is attributed to the increased electron density imparted by the electron-rich metal center to the ligand.[8,24] While polymerization has hampered the measurement of the pK_a's of many uncoordinated thiophenes, the pK_a of 2*H*-2,5-di-*tert*-butylthiophenium has been determined to be −10.2.[25] By treating the 2*H*-thiophenium complex **22** with organic bases in acetonitrile, we have estimated the pK_a of **22** to be between 1 and 3. Thus, η^2-coordination of thiophene to pentaammineosmium(II) renders the coordinated thiophene ligand 11−13 orders of magnitude *more basic* than an uncoordinated thiophene. Remarkably, the conjugate acid 2*H*-thiophenium complexes are stable at 20 °C, even in water.

Mechanism and Selectivity of Electrophilic Addition. Electrophilic addition to η^2-thiophene complexes occurs with high regioselectivity (i.e., sulfur vs C2 vs C3 addition), and stereoselectivity (*exo*/*endo* electrophilic addition), although the former is not as easily predictable as with furans and pyrroles.[24] Although η^2-thiophene complexes have been observed to react with electrophiles at all positions of the heterocycle depending on reagent, in no case studied have mixtures of regioisomers been produced. Hard carbon electrophiles

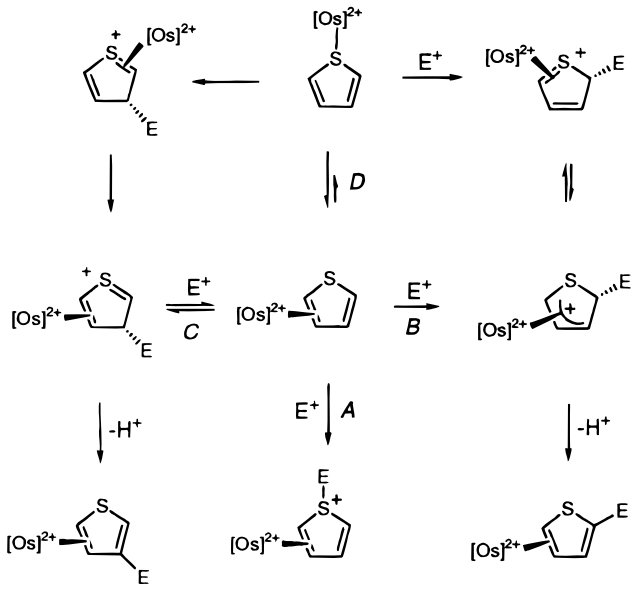


Figure 11. Mechanistic pathways for electrophilic addition/substitution reactions of η^2-thiophene complexes.

and the electrophilic oxygen source MCPBA react exclusively at the sulfur (path A, Figure 11) to form either *S*-alkylthiophenium or S-oxidized thiophenes. Conversely, α- or β-addition is more commonly observed for the reactions of an η^2-thiophene with softer carbon electrophiles such as acetals and Michael acceptors.

Addition at either C2 or C3 can occur by two different pathways depending on the position of the metal at the moment of electrophilic attack. In path B (Figure 11), the η^2-thiophene complex undergoes a direct electrophilic addition at the α-carbon in a manner similar to η^2-diene complexes of pentaammineosmium(II).[26] The latter complexes were found to undergo protonation at the terminal uncoordinated carbon to afford stable η^3-allyl systems. Donation of an electron pair by the sulfur into the allyl system and migration of the metal from the 3,4-position to the 1,5-position would afford the observed 2*H*-thiophenium structure. Precedent for a 3,4-η^2 to 1,5-η^2 migration has been observed for the protonation of 3-methylpyrrole derivatives.[24a] Deprotonation at the tetrahedral ring carbon would generate the corresponding 2-substituted thiophene complex. Electrophilic addition at the β position could hypothetically occur directly at C3 with the metal bound across C4 and C5, and the corresponding 3*H*-thiophenium could then deprotonate to give 3-substituted thiophenes (path C).

An alternative pathway leading to either α- or β-electrophilic addition would require an initial linkage isomerization to form an S-bound intermediate (path D, Figure 11). With the metal coordinating the sulfur, the heterocycle would retain aromatic character with the metal substituent functioning as a π-donor and could react much as an uncoordinated thiophene does by an α-electrophilic addition mechanism. The 2*H*-thiophenium resulting from α-addition could undergo a sulfur to 1,5-η^2 isomerization to form the observed 2*H*-thiophenium products. Although electrochemical data for **1** support the notion that the η^2-thiophene species has access to its sulfur bound isomer (vide supra), the

(24) (a) For general β-electrophilic additions to η^2-pyrrole complexes, see: Hodges, L. M.; Gonzalez, J.; Koontz, J. I.; Myers, W. H.; Harman, W. D. *J. Org. Chem.* **1995**, *60*, 2125. (b) For general β-electrophilic additions to η^2-furan complexes, see: Chen, H.; Hodges, L. M.; Liu, R. L.; Stevens, W. C., Jr.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 5499.

(25) Carmody, M. P.; Cook, M. J.; Dassanayake, N. C.; Katritzky, A. R.; Linda, P.; Tack, R. D. *Tetrahedron* **1976**, *32*, 1767.

(26) Spera, M. L.; Chin, R. M.; Winemiller, M. D.; Lopez, K. W.; Sabat, M.; Harman, W. D. *Organometallics* **1996**, *15*, 5447.

regiochemistry observed for both acylations and alkylations of monoalkylated η^2-thiophene complexes makes the hypothesized electrophilic addition to an S-bound intermediate (path D) highly improbable. Acylation of **2** to form **33** (Figure 6), alkylation of **3** to form **29** (Figure 5), and deuteration of **3** followed by deprotonation all result in 2,3-disubstituted thiophene ligands exclusively, observations that are significantly different from what would be expected if path D were dominant.

The observed β-acylation reaction is in stark contrast to the α-selectivity found with acetals and Michael acceptors. It is possible that for an η^2-thiophene complex, the β-carbon may be *kinetically* more accessible to electrophilic addition than the α-position. For the acylation reaction, the acidity of H3 of the hypothetical 3*H*-thiophenium intermediate is expected to be greatly enhanced by the close proximity of the carbonyl group (*E* in path C; Figure 11). Thus, rapid deprotonation is likely to occur by solvent (CH_3CN) trapping the electrophile at C3. With other electrophiles (i.e., acetals, Michael acceptors, H^+) it is possible that the combination of the lower acidity of H3 and its more hindered nature make spontaneous deprotonation at C3 less likely. Thus, the hypothesized electrophilic addition at C3 would ultimately reverse and C2 addition could eventually occur.

Electrophilic additions to η^2-arene, diene, and other heterocycle systems examined have all exhibited exclusive *exo* addition.[8] Similarly, *exo* addition to η^2-thiophene complexes occurs for the addition of both hydrogen and carbon electrophiles. A weak NOE enhancement (3.0%) is observed for H_{endo} in **22-*d***upon irradiation of the *cis*-ammines. The ^{1}H NMR spectrum of this product clearly indicates deuterium incorporation occurs exclusively at $H2_{exo}$. The deuterium scrambling observed when either **22-*d*** or **24-*d*** is treated with base indicates a nonselective deprotonation of either $H2_{exo}$ or $H2_{endo}$; however, we note that there is no scrambling in **22-*d*** prior to the addition of base. In accordance with the principle of microscopic reversability, protonation and deprotonation of these thiophene complexes must be occurring by separate mechanisms. In addition to the steric and electronic differences between a triflate anion (i.e. the conjugate base of triflic acid) and an amine (e.g., Hünig's base), it is possible that the acidic ammine ligands play a role in the deprotonation mechanism.[27] For example, the coordinated ammines may undergo deprotonation in the presence of Hünig's base and then serve to intramolecularly deprotonate the thiophenium ligand. The latter proposal suggests an attractive mechanism to explain how *endo* deprotonation could compete with the expected *exo* deprotonation mechanism, but participation by the ammines cannot be confirmed without further investiagtion.

Thiafulvenium Complexes. We are unaware of any reports describing the synthesis of thiafulvenium salts or complexes.[28] However, a dicationic tetrathiaporphyrin ligand has been synthesized which contains two 1-thiafulvenium units.[29] The methine carbon adjacent to the positively charged sulfur (i.e., C2 in the thiafulvenium unit) resonates at 163.9 ppm consistent with that reported for C2 in the 3,4-η^2-1-thiafulvenium complex **40**. The synthesis of 1,2-η^2-1-thiafulvenium and 3,4-η^2-2-thiafulvenium complexes resulting from the protonation of a basic substituent (complexes **36**−**44**) was anticipated given the precedent with the η^2-1-methylpyrrole system.[24a] However, the formation of 1,2-η^2-2-thiafulvenium complexes **45**−**47** from 2,5-dimethylthiophene was surprising. While protonation of the 2,5-dimethylthiophene complex **6** occurs at C2, the TBSOTf-promoted alkylation with acetals occurs at a β-carbon. It is likely that this addition is reversible, as we have hypothesized for other acetal additions to β-carbons, the rapid elimination of alcohol locks the new substituent in the β-position.

Concluding Remarks. We have demonstrated several novel pathways for the addition of electrophiles to an η^2-thiophene ligand. The π-basic osmium(II) metal center helps to stabilize the electron deficient products of these reactions (i.e., 2*H*-thiophenium, *S*-alkylthiophenium, thiafulvenium, and S-oxidized thiophenes), thus inhibiting rearomatization in many cases. Given the coordination geometry (1,5-η^2) of the 2*H*-thiophenium intermediates, it is attractive to invoke the possibility that the electrophilic addition might occur to an undetected intermediate where the metal is bound (η^1) to sulfur. However, the regiochemistry observed for electrophilic additions to 2- or 3-alkylated thiophene complexes is inconsistent with this notion. In several instances, the observed chemistry deviates significantly from that seen with other η^2-coordinated five-member heterocycles of pentaammineosmium(II) as well as from that of the uncoordinated heterocycle itself.

Experimental Section

General Data. All ^{1}H NMR spectra were recorded at 300 MHz and are referenced vs TMS using residual CD_2HCN, acetone-d_5, or $CHCl_3$ as an internal standard. All ^{13}C NMR spectra were recorded at 75 MHz and are referenced vs TMS using the same internal standards. The ^{13}C NMR (CD_3CN) resonance for the triflate anion (~122 ppm, q, J = 316 Hz) was not always observed due to its low intensity and thus is not reported. All cyclic voltammograms were recorded in CH_3CN using n-Bu_4PF_6 as electrolyte with a scan rate of 100 mV/s and are referenced to the normal hydrogen electrode (NHE) using an internal standard (Cp_2Fe ($E_{1/2}$ = 0.55 V (NHE) or $[Cp_2Co][PF_6]$, $E_{1/2}$ = −0.78 V (NHE)). 2-Deuteriothiophene was prepared by D_2O quenching of 2-thienyllithium prepared in situ from thiophene and *n*-butyllithium.[24] Magnesium powder (Aldrich, 50 mesh) was activated by treating with iodine in DME under nitrogen, stirring for 1 h, filtering, and washing with DMAc, acetone, and Et_2O. All other reagents were purchased from Aldrich and used as received, with the exception of $[Os(NH_3)_5OTf](OTf)_2$, which was synthesized as described by Lay et al.[30] All reactions were performed under nitrogen in a glovebox (Vacuum Atmospheres Co.) equipped with an electronic balance. Masses instead of volumes are reported for solvents and liquid reagents out of convenience.

(27) Pentaammineosmium(II) complexes (e.g. **1**) dissolved in MeOH-*d* in the presence of an amine base rapidly undergo proton/deuterium exchange on the ammine ligands.

(28) For a review, see: Sammes, M. P., in *Pyrroles, Part 1;* The Chemistry of Heterocyclic Compounds 48, Jones, R. A., Ed.; John Wiley & Sons: New York, 1990; Chapter 4.

(29) Vogel, E.; Röhrig, P.; Sicken, M.; Knipp, B.; Herrmann, A.; Pohl, M.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1651.

(30) (a) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Chem.* **1989**, *28*, 3001. (b) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Synth.* **1986**, *24*, 269. For an improved detailed procedure for the synthesis of this reagent, see: Gonzalez, J., Ph.D. Dissertation, University of Virginia, May, 1995. This compound is currently available from Aldrich.

Synthesis of Ligands. The esterification of 2-thiophenecarboxylic acid, the reduction of formyl and acetylthiophene to their corresponding alcohols, and the acetalization of 2-formylthiophene are standard literature procedures. The ketalization of 2-acetylthiophene is a modification of the acetalization procedure and is described below.

Synthesis of Complexes. The synthesis and characterization of several of the thiophene complexes described in this account have been previously reported.[10] Representative syntheses for the two methods employed are given. Full experimental procedures and characterization for all compounds may be found in the Supporting Information.

2-Acetylthiophene Dimethyl Ketal. This compound was prepared using a slight modification of a standard ketalization procedure. Solid *p*-TsOH·H_2O (760 mg, 4 mmol) was added to a solution of 2-acetylthiophene (5.03 g, 40 mmol) and anhydrous trimethyl orthoformate (9.32 g, 0.088 mmol) in ~100 mL of anhydrous methanol. The reaction solution was allowed to stand at 22 °C for 30 min and then quenched with Et_3N (565 mg, 5.59 mmol). The reaction mixture was partitioned between H_2O and Et_2O, and the aqueous layer extracted with Et_2O (3 × 50 mL). The combined organic layers were dried (Na_2SO_4) and the solvent removed under reduced pressure to afford 6.21 g (36.1 mmol) of the title compound as a pale yellow oily liquid, 91% which was used without further purification.

{4,5-η^2-[Os(NH_3)$_5$]-thiophene}(OTf)$_2$ (1). Activated magnesium powder (1.84 g) was added to a solution of thiophene (3.50 g, 41.6 mmol) in *N*,*N*-dimethylacetamide (DMAc; 2.12 g). Solid [Os(NH_3)$_5$(OTf)](OTf)$_2$ (3.00 g, 4.16 mmol) was added slowly while the slurry was stirred vigorously. The slurry was stirred for an additional 1 h upon completion of osmium addition. The DMAc solution is decanted into a 150 mL fine porosity frit. The remaining Mg^0 is washed with several portions of 1,2-dimethoxyethane (DME), and the solution was added to the frit with stirring. The solution is filtered into 300 mL of stirring CH_2Cl_2 and the resulting yellow precipitate is filtered, washed with CH_2Cl_2 (3 × 30 mL), and dried in vacuo affording 2.48 g (91%) of yellow powder. ^{1}H NMR (CD_3CN): δ 6.72 (dd, J = 5.4, 1.6 Hz, 1H), 6.59 (dd, J = 5.4 Hz, 2.6 Hz, 1H), 5.77 (dd, J = 5.4, 1.6 Hz, 1H), 5.31 (dd, J = 5.4, 2.6 Hz, 1H), 4.19 (br s, 3H), 2.91 (br s, 12H). ^{13}C NMR (CD_3CN): δ 130.76 (CH), 121.67 (CH), 66.13 (CH), 61.80 (CH). CV: $E_{p,a}$ = 0.55 V, $E_{p,c}$ = 0.12 V (NHE).

{*C,O*-η^2-[Os(NH_3)$_5$]-2-acetylthiophene}(OTf)$_2$ (7a). Solid [Os(NH_3)$_5$(OTf)](OTf)$_2$ (507 mg, 0.702 mmol) was added slowly to a vigorously stirred slurry of 2-acetylthiophene (900 mg, 7.14 mmol) and zinc amalgam (1.89 g) in methanol (2.58 g). After 45 min, the slurry was filtered into 100 mL of Et_2O. The resulting tacky red precipitate was filtered, washed with Et_2O, and dried in vacuo affording 451 mg (0.645 mmol) of a red powder as a mixture of 2:1 mixture of isomers **7a** and **7b**, 92%. ^{1}H NMR (CD_3CN): δ 7.20 (m, 2H), 7.02 (m, 1H), 4.95 (br s, 3H), 3.36 (br s, 12H), 1.74 (s, 3H).

{4,5-η^2-[Os(NH_3)$_5$]-2-acetylthiophene}(OTf)$_2$ (7b). The crude mixture consisting of **7a** and **7b** (2:1) was disolved in either ~2 g of acetone or acetonitrile and warmed to ~60 °C for 5 h and then precipitated into 150 mL of diethyl ether affording the ring-bound complex **7b** in virtually quantitative yield. ^{1}H NMR (CD_3CN): δ 7.59 (d, J = 2.9 Hz, 1H), 5.89 (d, J = 5.9 Hz, 1H), 5.41 (dd, J = 5.9 Hz, 2.9 Hz, 1H), 4.22 (br s, 3H), 2.99 (br s, 12H), 2.37 (s, 3H). ^{13}C NMR (CD_3CN): δ 192.88 (CO), 146.77 (CH), 140.06 (C), 67.51 (CH), 61.55 (CH), 27.04 (CH_3). CV: $E_{p,a}$= 0.69 V (NHE); $E_{p,c}$ = 0 V (NHE). Anal. Calcd for $C_8H_{21}N_5O_7F_6S_3Os$: C, 13.73; H, 3.03; N, 10.01. Found: C, 13.93; H, 3.23; N, 9.90.

{2,3-η^2-[Os(NH_3)$_5$]-benzo[*b*]thiophene}(OTf)$_2$ (9). The crude product was warmed in either acetone or acetonitrile for ~10 min at 70 °C to afford the *2,3*-η^2 isomer; yield: 95%. ^{1}H NMR (CD_3CN): δ 7.61 (m, 1H), 7.41 (m, 1H), 7.25 (m, 2H), 5.80 (d, J = 5.8 Hz, 1H), 5.43 (d, J = 5.8 Hz, 1H), 4.19 (br s, 3H), 2.89 (br s, 12H). ^{13}C NMR (CD_3CN): δ 146.49 (C) 139.66 (C), 126.74 (CH), 125.79 (CH), 124.21 (CH), 123.15 (CH), 62.47 (CH), 55.61 (CH). CV: $E_{p,a}$ = 0.51 V (NHE).

{1,5-η^2-[Os(NH_3)$_5$]-2*H*-thiophenium}(OTf)$_3$ (22). A solution of 206 mg of HOTf (1.37 mmol) in 120 mg of CH_3CN was added to a solution of 229 mg (0.349 mmol) of **1** in 878 mg of CH_3CN. The resulting deep red solution was added to 150 mL of stirring diethyl ether; the precipitate was filtered, washed with ether (3 × 20 mL), and dried in vacuo, affording 257 mg (91%) of a pink powder. ^{1}H NMR (CD_3CN): δ 7.96 (br s, 1H), 6.90 (dd, J = 5.9 Hz, 1.9 Hz, 1H), 6.76 (dd, J = 5.9 Hz, 1.9 Hz, 1H), 5.21 (br s, 3H), 3.71 (br s, 12H), 3.08 (dd, J = 20.7 Hz, 1.9 Hz, 1H), 2.62 (dd, J = 20.7 Hz, 1.9 Hz, 1H). ^{13}C NMR (CD_3CN): δ 136.81 (CH), 131.35 (CH), 71.29 (CH), 43.47 (CH_2). CV: $E_{p,a}$ = 1.59 V (NHE); $E_{p,c}$ = 0.25 V (NHE). Anal. Calcd for $C_7H_{20}N_5O_9F_9S_4Os$: C, 10.41; H, 2.50; N, 8.67. Found: C, 10.54; H, 2.73; N, 8.94.

{1,5-η^2-[Os(NH_3)$_5$]-2-(1-ethoxyethyl)thiophenium}(OTf)$_3$ (28). A solution of **1** (238 mg, 0.362 mmol) and acetaldehyde diethyl acetal (55 mg, 0.466 mmol) in 1.42 g of a 2:1 cosolvent mixture of acetonitrile and proprionitrile was cooled to −40 °C. TBSOTf (119 mg, 0.451 mmol) was added, and the resulting dark violet solution was allowed to stand for 15 min. The solution was added to 50 mL of stirring diethyl ether, and the precipitate was filtered, washed with diethyl ether (2 × 10 mL), and dried in vacuo, affording 225 mg (0.257 mmol) of a dark violet powder, 71%, as a 1:1 mixture of diastereomers. ^{1}H NMR (CD_3CN, both isomers): δ 7.99 (d, J = 2.2 Hz, 1H), 7.92 (d, J = 2.2 Hz, 1H), 6.89 (m, 2H), 6.65 (m, 2H), 5.37 (br s, 6H), 3.89 (br s, 24H), 3.78−3.26 (m, 8H), 1.38 (d, J = 6.6 Hz, 3H), 1.29 (d, J = 6.6 Hz, 3H), 1.17 (overlapping m, 6H). Anal. Calcd for $C_{11}H_{28}N_5O_{10}S_4F_9Os$: C, 15.02; H, 3.21; N, 7.96. Found: C, 15.31; H, 3.30; N, 8.18.

{4,5-η^2-[Os(NH_3)$_5$]-2-(1-ethoxyethyl)thiophene}(OTf)$_2$ (31). A solution of **28** (212 mg, 0.237 mmol) in 930 mg MeCN was treated with *i*-Pr_2NEt (39 mg, 0.302 mmol) and allowed to stand for 5 min. The reaction mixture was added to 50 mL of CH_2Cl_2, and the precipitate was filtered, washed with CH_2Cl_2 (2 × 10 mL), and dried in vacuo, affording 143 mg (0.193 mmol) of a tan powder, 81%, as a 1:1 mixture of diastereomers. ^{1}H NMR (CD_3CN, both isomers): δ 6.52 (d, overlapping, 2H), 5.71 (d, J = 5.9 Hz, 2H), 5.21 (overlapping dd, 2H), 4.19 (br s, 6H), 4.32 (q, J = 6.6 Hz, 2H), 3.52−3.36 (m, 4H), 2.97 (br s, 24H), 1.39 (d, J = 5.9 Hz, 3H), 1.31 (d, J = 5.9 Hz, 3H), 1.11 (t, J = 6.6 Hz, 3H), 1.06 (t, J = 6.6 Hz, 3H). ^{13}C NMR (CD_3CN, both isomers): δ 145.24 (C), 144.88 (C), 127.94 (CH), 127.58 (CH), 74.71 (CH), 74.27 (CH), 65.43 (CH), 65.18 (CH), 64.60 (CH_2), 64.34 (CH_2), 61.21 (CH), 61.19 (CH), 23.75 (CH_3), 21.59 (CH_3), 15.75 (CH_3), 15.63 (CH_3). Anal. Calcd for $C_{10}H_{27}N_5O_7F_6S_3Os$: C, 16.46; H, 3.73; N, 9.60. Found: C, 16.89; H, 3.84; N, 10.00.

{*4,5*-η^2-[Os(NH_3)$_5$]-3-acetyl-2-methylthiophene}(OTf)$_2$ (34). A solution of **2** (127 mg, 0.189 mmol) and Ac_2O (26 mg, 0.255 mmol) in 1.2 g of a 2:1 cosolvent mixture of acetonitrile and propionitrile was cooled to −40 °C. BF_3·OEt_2 (35 mg, 0.248 mmol) was added dropwise and the reaction mixture allowed to stand for ~24 h. The reaction mixture was added directly to 100 mL of diethyl ether, affording a brown precipitate which was filtered, washed with Et_2O (2 × 10 mL), and dried in vacuo affording 125 mg (0.175 mmol) of a brown powder, 93%. ^{1}H NMR (CD_3CN): δ 5.54 (d, J = 6.3 Hz, 1H), 5.41 (d, J = 6.3 Hz, 1H), 4.20 (br s, 3H), 3.03 (br s, 12H), 2.52 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (CD_3CN): δ 196.49 (CO), 151.29 (C), 141.05 (C), 60.77 (CH), 60.58 (CH), 30.56 (CH_3), 17.16 (CH_3). Anal. Calcd for $C_9H_{23}N_5O_7F_6S_3Os$: C, 15.15; H, 3.25; N, 9.81. Found: C, 15.41; H, 3.08; N, 10.01.

{*1,2*-η^2-[Os(NH_3)$_5$]-1-thiafulvenium}(OTf)$_3$ (36). To a slurry of **14** (187 mg, 0.272 mmol) in 389 mg of CH_3CN was added 53 mg (0.354 mmol) of HOTf. The resulting dark purple slurry was stirred for 5 min and then added to 50 mL of diethyl ether. The precipitate was filtered, washed with ether (2 × 10 mL), and dried in vacuo, affording 211 mg (0.258 mmol) of

a dark purple powder, 95%. ^{1}H NMR (CD_3CN): δ 8.35 (d, J = 2.9 Hz, 1H), 7.31 (d, J = 2.9 Hz, 1H), 7.18 (dd, J = 5.9 Hz, 2.9 Hz, 1H), 7.07 (d, J = 5.9 Hz, 1H), 7.04 (dd, J = 2.9 Hz, 1H). 5.42 (br s, 3H), 3.93 (br s, 12H). ^{13}C NMR (CD_3CN): δ 145.12 (CH), 144.07 (C), 129.91 (CH), 124.14 (CH_2), 64.65 (CH). CV: $E_{p,c}$ = −0.61 V (NHE). Anal. Calcd for $C_8H_{20}N_5O_9F_9S_4Os$: C, 11.72; H, 2.46; N, 8.54. Found: C, 11.36; H, 2.67; N, 8.80.

{*1,2*-η^2-[Os(NH$_3$)$_5$]-1,3,6-trimethyl-2-thiafulvenium}(OTf)$_3$ (45). A solution of **6** (100 mg, 0.145 mmol) in 751 mg of CH_3CN was treated with acetaldehyde diethyl acetal (21 mg, 0.176 mmol) and TBSOTf (52 mg 0.196 mmol). After 5 min, the solution was added to 50 mL of diethyl ether, and the precipitate was filtered, washed with ether (2 × 10 mL), and dried in vacuo, affording 109 mg (0.127 mmol) of a powder, 87%. ^{1}H NMR (CD_3CN): δ 7.41 (s, 1H), 6.88 (q, J = 7.3 Hz, 1H), 5.39 (br s, 3H), 3.86 (br s, 12H), 2.40 (s, 3H), 1.97 (s, 3H), 1.65 (d, J = 7.3 Hz, 3H). ^{13}C NMR (CD_3CN): δ 150.71 (C), 135.17 (C), 131.35 (CH), 129.31 (CH), 68.71 (C), 19.88 (CH_3), 16.01 (CH_3), 10.60 (CH_3). CV: $E_{p,c}$ = −0.69 V (NHE). Anal. Calcd for $C_{11}H_{26}N_5S_4O_9F_9Os$: C, 15.33; H, 3.04; N, 8.13. Found: C, 15.41; H, 2.90; N, 8.37.

{*4,5*-η^2-[Os(NH$_3$)$_5$]-2-(1-carbomethoxy-1-methylpropyl)-thiophene}(OTf)$_2$ (48). MMTP (58 mg, 0.333 mmol) was added to a solution of **36** (142 mg, 0.173 mmol) in 1.01 g MeCN causing an immediate color change to golden-brown. After 5 min, the reaction mixture was added to 50 mL of Et_2O, the precipitate filtered, washed with Et_2O, and dried in vacuo affording 106 mg (0.137 mmol) of a golden brown powder, 79%. ^{1}H NMR (CD_3CN): δ 6.27 (d, J = 2.3 Hz, 1H), 5.62 (d, J = 5.2 Hz, 1H), 5.14 (dd, J = 5.2 Hz, 2.3 Hz, 1H), 4.29 (br s, 3H), 3.63 (s, CH_3), 3.00 (br s, 14H), 1.20 (s, 6H). ^{13}C NMR (CD_3CN): δ 178.05 (CO), 137.05 (C), 129.97 (CH), 65.50 (CH), 61.67 (CH_3), 52.32 (CH_2), 41.70 (CH), 43.98 (C), 15.23 (2 × CH_3). CV: $E_{p,a}$ = 0.57 V (NHE); $E_{p,c}$ = 0.13 V (NHE). Anal. Calcd for $C_{12}H_{29}N_5O_8F_6S_3Os$: C, 18.68; H, 3.79; N, 9.07. Found: C, 18.72; H, 3.88; N, 9.11.

{*4,5*-η^2-[Os(NH$_3$)$_5$]-thiophene-1-oxide}(OTf)$_2$ (51). MCPBA (74 mg, 0.300 mmol based on 70% purity) was added to a solution of **1** (196 mg, 0.298 mmol) in 1.35 g of CH_3CN. After 30 min, the reaction mixture was added to 50 mL of Et_2O. The precipitate was filtered, washed with Et_2O (2 × 10 mL), and dried in vacuo, affording 190 mg (0.282 mmol) of a yellow-orange solid, 95%.^{1}H NMR (CD_3CN): δ 6.96 (dd, J = 5.9 Hz, 2.2 Hz, 1H), 6.58 (d, J = 5.9 Hz, 1H), 5.57 (dd, J = 4.4 Hz, 2.2 Hz, 1H), 4.92 (d, J = 4.4 Hz, 1H), 4.44 (br s, 3H), 3.42 (br s, 12H). ^{13}C NMR (CD_3CN): δ 143.06 (CH), 130.41 (CH), 55.27 (CH), 52.66 (CH). CV: $E_{1/2}$ = 1.09 V (NHE). Anal. Calcd for $C_6H_{19}N_5S_3O_7F_6Os$: C, 10.70; H, 2.84; N, 10.40. Found: C, 11.13; H, 2.96; N, 10.56.

{*4,5*-η^2-[Os(NH$_3$)$_5$]-thiophene-1,1-dioxide}(OTf)$_2$ (52). MCPBA (156 mg, mmol based on 70% purity) was added to a solution of **1** (189 mg, 0.288 mmol) in 1.21 g of CH_3CN. After 30 min, the reaction mixture was added to 50 mL of Et_2O. The precipitate was filtered, washed with Et_2O (2 × 10 mL), and dried in vacuo, affording 189 mg (0.274 mmol) of a yellow-orange solid, 95%.^{1}H NMR (CD_3CN): δ 7.36 (dd, J = 6.4 Hz, 2.9 Hz, 1H), 6.41 (d, J = 6.4 Hz, 1H), 5.42 (dd, J = 5.9 Hz, 2.9 Hz, 1H), 5.08 (d, J = 5.9 Hz, 1H), 4.62 (br s, 3H), 3.39 (br s, 12H). ^{13}C NMR (CD_3CN): δ 147.67 (CH), 123.69 (CH), 53.82 (CH), 44.47 (CH). CV: $E_{1/2}$ = 1.15 V (NHE). Anal. Calcd for $C_6H_{19}N_5S_3O_8F_6Os$: C, 10.45; H, 2.78; N, 10.16. Found: C, 10.22; H, 2.95; N, 10.34.

3-Ethylthiophene (53).[31] A solution of **50** (370 mg, 0.540 mmol) in 1.56 g of acetone was added to a solution of AgOTf (162 mg, 0.633 mmol) in 452 mg of acetone. After 15 min, the reaction mixture was added to 50 mL of diethyl ether and filtered through a bed of silica gel. The solvent was removed under vacuum, affording 58 mg (0.518 mmol) of a pale yellow oil, 83%.

2-(1-Ethoxyethyl)-3-methylthiophene (54). A solution of **32** (457 mg, 0.615 mmol) in 1.27 g MeCN was heated at 80 °C in a sealed pressure tube for 26 h. The solvent was removed under vacuum, affording a dark tacky residue which is partitioned between 10% $Na_2CO_{3\,(aq)}$ and diethyl ether. The ether layers were combined, dried ($MgSO_4$), and filtered through a bed of silica gel to remove residual metallic impurities. The ether was removed under vacuum, affording 79 mg of a golden-brown oil, 76%. This material was characterized without further purification. ^{1}H NMR ($CDCl_3$): δ 7.13 (d, J = 5.2 Hz, 1H), 6.77 (d, J = 5.1 Hz, 1H), 4.73 (q, J = 6.6 Hz, 1H), 3.41 (m, 2H), 2.21 (s, 3H), 1.50 (d, J = 6.6 Hz, 3H), 1.19 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 141.38 (C), 133.26 (C), 129.68 (CH), 122.73 (CH), 71.35 (CH), 63.75 (CH_2), 23.91 (CH_3), 15.36 (CH_3), 13.71 (CH_3). Anal. Calcd for $C_9H_{14}SO$: C, 63.49; H, 8.29; N, 0.00. Found: C, 63.53; H, 7.96; N, 0.40.

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Supporting Information Available: Text giving full experimental procedures and characterizations for all compounds described in this account. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) This is a known compound. Galpern, G. D. In *Thiophene and its Derivatives, Part I;* The Chemistry of Heterocyclic Compounds 44; John Wiley & Sons: New York, 1985; Chapter 4.