Electrophile-Promoted Carbon−Sulfur Bond Cleavage in η^2-Thiophene Complexes of Pentaammineosmium(II)

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Abstract: Several *S*-alkylthiophenium complexes of the type $[Os(NH_3)_5(4,5\text{-}\eta^2\text{-L})](OTf)_3$ (where L = *S*-alkylthiophenium, *S*-methylbenzo[*b*]thiophenium) are prepared by alkylation of the corresponding thiophene complexes. The *S*-alkylthiophenium species are proposed to undergo rapid and reversible cleavage of the C5−S bond, forming highly electrophilic metallacyclopropene intermediates. Although not directly observable, these *vinyl cation* intermediates may be trapped with both anionic and neutral nucleophiles affording η^2-4-(alkylthio)-1,3-butadiene complexes. Treatment of selected 4-(alkylthio)-1,3-butadiene complexes with an oxidant (e.g., DDQ) affords the organic ligand in good yield.

Introduction

Transition metal complexes of thiophenes have received considerable attention in recent years as homogeneous models for hydrodesulfurization (HDS) catalysis.[1] Studies on the inorganic and organometallic chemistry of coordinated thiophenes have focused mainly on reactions which lead to C−S activation, the key step in the catalytic hydrodesulfurization process. Consequently, there are numerous reports of C−S bond cleavage promoted by transition metals, and the most common of these involve direct insertion of the metal into a C−S bond[2] or nucleophile-induced C−S bond cleavage.[3]

In the course of our exploration of the ability of pentaammineosmium(II) to promote electrophilic addition reactions on η^2-bound arenes and aromatic heterocycles, we have initiated an investigation into the chemistry of η^2-thiophene complexes with electrophiles. Although η^2-coordination for thiophenes is rare,[4] such a species has been postulated as one of the intermediates in the hydrodesulfurization process,[5] and while the chemistry of coordinated thiophenes with nucleophiles has been extensively examined,[3] their reactivity toward electrophiles is much less developed.[6] Most thiophene complexes contain cationic metal centers (e.g., $Mn(CO)_3^+$, $RuCp^+$, Cp^*Rh^{2+}), and as such are best suited to participate in reactions with nucleophiles. We find that 4,5-η^2-thiophene complexes of osmium(II) react with carbon electrophiles at either C2, C3, or the sulfur depending on the electrophile and the substitution pattern of the thiophene.[7] Herein, we focus on the synthesis, characterization, and reactions of *S*-alkylated η^2-thiophenium complexes of pentaammineosmium(II).[8] We find that in the presence of a suitable nucleophile, *S*-alkylthiophenium complexes undergo cleavage of the C5−S bond to yield η^2-4-(alkylthio)-1,3-butadiene complexes which are readily demetalated to give the corresponding organic (alkylthio)butadienes (Scheme 1).

Results

***S*-Alkylation.** *S*-Alkylated thiophene complexes **8**−**16** and the 2,3-dihydrothiophenium complex **17** are prepared from the corresponding η^2-thiophene precursors **1**−**6** and the 2,3-dihydrothiophene precursor **7** through a direct *S*-alkylation (Table 1). Alkylation of each with methyl triflate provides the *S*-methylated compounds **8**−**13** and **17**; alkylation of the parent thiophene complex **1** with triethyloxonium hexafluorophosphate in acetonitrile provides the *S*-ethylated compound **14**, while benzylation of **1** with 3,5-dimethylbenzyl bromide in the presence of thallium triflate delivers **15** (Table 1). For all cases examined, the alkylation is regiospecific for sulfur and proceeds in 85−95% yield. *S*-Methylation occurs for a number of substituted thiophenes. Even methyl groups at the α-positions do not hinder the alkylation process (e.g., **11**). Benzo[*b*]-thiophene is readily methylated to form **13**, and the 3-methoxythiophene complex **5** combines with methyl triflate to form **12**. An excess of trimethyl orthoformate reacts with **1** in the presence of *tert*-butyldimethylsilyl triflate (TBSOTf) to afford the *S*-

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(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 recent examples of C−S insertion reactions, see: (a) Myers, A. W.; Jones, W. D. *Organometallics* **1996**, *15*, 2905. (b) Chen, J.; Young, V. G.; Angelici, R. J. *Organometallics* **1996**, *15*, 2727. (c) Chen, J.; Daniels, L. M.; Angelici, R. J. *Organometallics* **1996**, *15*, 1223. (d) Bianchini, C.; Meli, A. *J. Chem. Soc., Dalton Trans.* **1996**, 801. (e) Myers, A. W.; Jones, W. D.; McClements, S. M. *J. Am. Chem. Soc.* **1995**, *117*, 11704. (f) 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. (g) Bianchini, C.; Jimenez, M. V.; Meli, A.; Vizza, F. *Organometallics* **1995**, *14*, 4858.

(3) For examples of nucleophilic additions with or without C−S activation, see: (a) Krautscheid, H.; Feng, Q.; Rauchfuss, T. B. *Organometallics* **1993**, *12*, 3273. (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.

(4) To our knowledge, there are three known η^2-thiophene complexes. (a) For $\{2,3\text{-}\eta^2\text{-}[ReCp(NO)(PPh_3)]\text{-benzo}[b]\text{thiophene}\}^+$, see: Robertson, M. J.; Day, C. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1994**, *13*, 179. (b) For $\{2,3\text{-}\eta^2\text{-}[Os(NH_3)_5]\text{thiophene}\}^{2+}$, see: Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem.Soc.* **1989**, *111*, 5969. (c) For an example of a bridging η^2-thiophene in a triosmium cluster, see: Arce, A.; De Sanctis, Y. *J. Organomet. Chem.* **1986**, *311*, 371.

(5) (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) Luo, S.; Rauchfuss, T. B.; Gan, Z. *J. Am. Chem. Soc.* **1993**, *115*, 4943. (b) Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 8515.

(7) (a) Other electrophiles that react at C(2) include acetals and Michael acceptors: Spera, M. L.; Harman, W. D. Manuscript in preparation. (b) For an account describing the protonation of η^2-thiophene complexes, see: Spera, M. L.; Harman, W. D. *Organometallics* **1995**, *14*, 1559.

(8) For the synthesis and characterization of some *S*-alkylthiophenium salts, see: Acheson, R. M.; Harrison, D. R. *J. Chem. Soc. (C)* **1970**, 1764 and references therein.

S0002-7863(97)00941-4 CCC: $14.00

Scheme 1

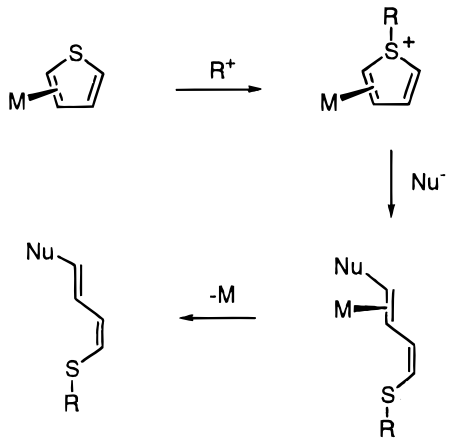
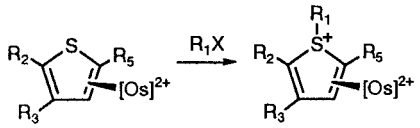


Table 1. Yield Data for *S*-Alkylthiophenium Complexes



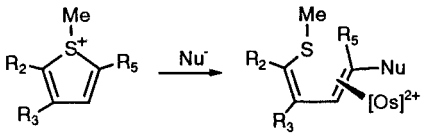
Product	%Yield	R_1	R_2	R_3	R_5
8	95	Me	H	H	H
9	90	Me	Me	H	H
10	91	Me	H	Me	H
11	85	Me	Me	H	Me
12	92	Me	H	OMe	H
13	93	Me	-	-	H
14	88	Et	H	H	H
15	88	Bn	H	H	H
16	87	DMM	H	H	H

Abbreviations: Bn = 3,5-dimethylbenzyl; DMM =1,1-dimethoxymethyl.

alkylated complex **16** in ~90% yield, but this reaction is sometimes compromised by trace amounts of 2*H*-thiophenium imputities.[7b] Running the reaction in the presence of a mild amine base (*i*-Pr_2EtN) and a large excess of electrophile minimizes this problem. The resulting product (**16**) fails to undergo hydrolysis when treated with water.[9] In contrast to what is known for η^2-pyrrole and furan complexes[10] of pentaammineosmium(II), there is no indication of a competing alkylation of the thiophene ring. But electrophilic addition at sulfur appears to be a general reaction only for certain alkylating reagents. While alkyl triflates undergo addition at the sulfur atom, acetals and Michael acceptors react with η^2-thiophene complexes at C(2).[7a]

As a class, the *S*-alkylated thiophenium complexes **8**−**17** show similar spectroscopic and electrochemical characteristics. The ^{1}H NMR spectrum of the *S*-methylthiophenium complex **8** in CD_3CN is similar to that of the thiophene complex **1** except that the four ring proton signals of **8** are shifted downfield ~0.5 to 1 ppm from those of **1**. The *cis*- and *trans*-ammine resonances are also shifted downfield, indicating the electron-deficient nature of the organic ligand. For **8**, a new singlet is observed at 3.22 ppm, corresponding to the *S*-methyl protons. The ^{13}C NMR and DEPT spectra (CD_3CN) show signals for two coordinated methine carbons at 61.75 ppm and 51.33 ppm, signals for two uncoordinated methine carbons at 155.69 and 113.76 ppm, as well as a new feature for the *S*-methyl carbon at 31.19 ppm. A cyclic voltammogram (CH_3CN/*n*-Bu_4PF_6/100 mV/s) for complex **8** exhibits a *reversible* oxidation wave at 1.37 V (NHE), ~800 mV more positive than for its precursor **1**. An irreversible ligand-centered reduction wave at −1.38 V is also observed.

Table 2. Yield Data for 4-(Methylthio)-1,3-butadiene Complexes



Product	% Yield	R_2	R_3	R_5	Nu$^-$
18	77	H	H	H	H^-
19	91	H	H	H	CN^-
20	93	H	H	H	OAc^-
21	91	H	H	H	C_5H_5N
22	85	H	H	H	$PrNH_2$
23	82	H	H	H	N_3^-
24	58	H	H	H	PPh_3
25	83	H	H	H	PhO^-
26	55	H	H	H	PhS^-
27	64	Me	H	H	H^-
28	60	H	Me	H	H^-
29	71	Me	H	Me	H^-
30	71	-	-	H	H^-
31	89	-	-	H	CN^-
36	80	H	H	H	MeO^-

The *S*-alkylthiophenium complexes (**8**−**17**) are exceptionally stable compounds. While organic *S*-alkylthiophenium salts are strong alkylating agents and readily react with water and alcohols,[11] complexes **8**−**17** are stable in water and exhibit alkylating properties only in the presence of very polarizable nucleophiles such as PPh_3 (*vide infra*). For example, a solution of **8** is stable in D_2O for a week at 22 °C with no evidence of ring opening or hydrolysis. In CD_3CN in the absence of suitable nucleophiles, complex **8** is stable at elevated temperatures (80 °C) for as long as 24 h before decomposition products are detected.

Nucleophilic Additions. In contrast to the lack of reactivity between the η^2-thiophene complex **1** and nucleophiles, treatment of *S*-methylthiophenium complexes with nucleophiles affords 1-substituted η^2-4-(methylthio)-1,3-butadiene complexes in good yield (Table 2; 55−93%). The products, the net result of cleavage of the C5−S bond and nucleophilic addition to C5,

(9) In contrast, an η^3-allyl complex of pentaammineosmium(II) synthesized via the analogous electrophilic addition of trimethyl orthoformate to the *2,3*-η^2-cyclopentadiene complex readily undergoes hydrolysis in wet acetonitrile or acetone to afford the formyl-substituted allyl complex. Spera, M. L.; Lopez, K. W.; Harman, W. D. Unpublished results.

(10) For examples of electrophilic additions to analogous η^2-pyrrole complexes, see: Hodges, L. M.; Gonzales, J.; Myers, W. H.; Koontz, J. I.; Harman, W. D. *J. Org. Chem.* **1995**, *60*, 2125. For furan, see: (a) Chen, H.; Hodges, L. M.; Liu, R.; Stevens, W. C.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 5499. (b) Liu, R.; Chen, H.; Harman, W. D. *Organometallics* **1995**, *14*, 2861.

(11) For a review of thiophenium salts, see: Porter, A. E. A. *Adv. Heterocycl. Chem.* **1989**, *45*, 151 and references therein.

exhibit *cis*/*trans* ammine signals upfield from those of the starting thiophenium compounds; for the case of hydride additions, the resulting diene complexes show reversible oxidation couples near 0.60 V (NHE). For example, when the *S*-methylthiophenium complex **8** is treated with an acetonitrile solution of tetra-*n*-butylammoniumborohydride, a single new product, **18**, is formed. The ^{1}H NMR spectrum of **18** exhibits an upfield shifted methyl at 2.28 ppm, and signals corresponding to five olefinic protons ranging from 3.4 to 6.1 ppm. ^{13}C NMR and DEPT data indicate two uncoordinated methine carbons (135.28 and 123.28 ppm), one coordinated methine carbon (51.24 ppm), and a coordinated methylene (43.63 ppm). The cyclic voltammogram of the product exhibits a reversible oxidation wave at 0.65 V (NHE) which is characteristic of an η^2-bound olefin or diene.[12] On the basis of these data, we assign **18** to be a η^2-coordinated 4-(methylthio)-1,3-butadiene (Table 2).

Stereochemical Assignment of Dienes. For all cases examined, a *cis* vicinal coupling constant is observed ($J \sim 9$ Hz) for the uncoordinated protons H3 and H4 and establishes the geometry of this portion of the diene. A somewhat smaller vicinal coupling constant is observed ($J \sim 5-7$ Hz) for the coordinated olefinic protons H1 and H2. However, we have observed for Os(II)-η^2-olefin and vinyl ether complexes that the magnitude of both the *cis* and *trans* vicinal coupling constant on the coordinated olefin is often considerably *lower* than that of the uncoordinated olefin and varies depending on substitution.[12,13] Thus, we were unable to assign the geometry of the coordinated double bond using coupling constants alone. 1D-NOE and proton decoupling experiments on selected diene complexes (**20**, **21**, **25**, and **36**) allow full assignment of all proton resonances and stereochemistry. In each of the four cases that we investigated in detail, the coordinated olefin is *trans* while the uncoordinated olefin is *cis* (Figure 1). For example, with the pyridinium diene complex **21**, irradiation of the *ortho* ring protons (8.47 ppm) produces a 13.1% NOE enhancement for H1 and a 6.1% enhancement with H2. If the doublet (e.g., H1) at 6.92 ppm ($J = 7.3$ Hz) is irradiated, a 13% NOE is observed with the *ortho* protons of the pyridinium ring, as well as an 8.8% NOE with the doublet of doublets at 5.41 ppm (H3). Irradiation of H3 (5.41 ppm) causes an 11% enhancement with H(4). Irradiation of H4 (6.59 ppm; $J = 9.5$ Hz) causes an 9.1% enhancement with the doublet of doublets at 5.41 ppm (H3) and a 3.0% enhancement with the *S*-methyl protons at 2.40 ppm. Similar results are obtained for the other (e.g., **20**, **25**, and **36**) diene complexes. To further verify our claim, removal of the metal from two such diene complexes (**25** and **36**) affords the organic dienes **42** and **43** whose geometry is identical to that determined for the corresponding osmium(II) complexes. For example, treatment of **36** with 1.0 equiv of 2,3-dichloro-5,6-dicyanoquinone (DDQ) in acetone affords the free diene ligand **43** with the same *trans*,*cis* geometry ($J = 12.5$, 9.5 Hz) in good (80%) yield. The *trans* geometry of the coordinated olefin is observed even in the styrene derivative **31**. In this case a 9.0 Hz vicinal coupling constant is observed for the coordinated olefin while a 16.5 Hz coupling constant is observed for the free ligand.

The scope of nucleophilic addition with the osmium thiophenium complexes is broad (Table 2). In addition to hydride, nucleophiles that react at the α-carbon of η^2-thiophenium complexes include aliphatic and aromatic amines, alcohols, acetate ion, azide ion, triphenylphosphine, phenol, and thiophenol. However, the only carbon nucleophile which was successfully added was cyanide ion (**19**; 81%). In general, all nucleophilic addition reactions are carried out in an acetonitrile solution or slurry. Some reagents require the addition of a nonnucleophilic base (*i*-Pr_2EtN) to promote the reaction (e.g., methanol, phenol). Primary amines such as *n*-propyl amine require the addition of excess reagent to deprotonate the resulting *n*-propylammonium diene. In contrast to the single isomer observed for other nucleophilic additions, a mixture of *cis/trans* isomers results from methanol addition to **8**. Thiobutadiene **36** is isolated as a 7.5:1 mixture of *trans*,*cis* and *cis*,*cis* diene complexes. If **8** (0.061 M) is dissolved in CD_3OD in the absence of base and the solution monitored by ^{1}H NMR spectroscopy over several days, **36** is slowly formed as a 1:1 mixture of isomers. The reaction eventually reaches an equilibrium mixture of $\mathbf{8}$:$\mathbf{36}_{cis,cis}$:$\mathbf{36}_{trans,cis}$ of 1.2:1:1.

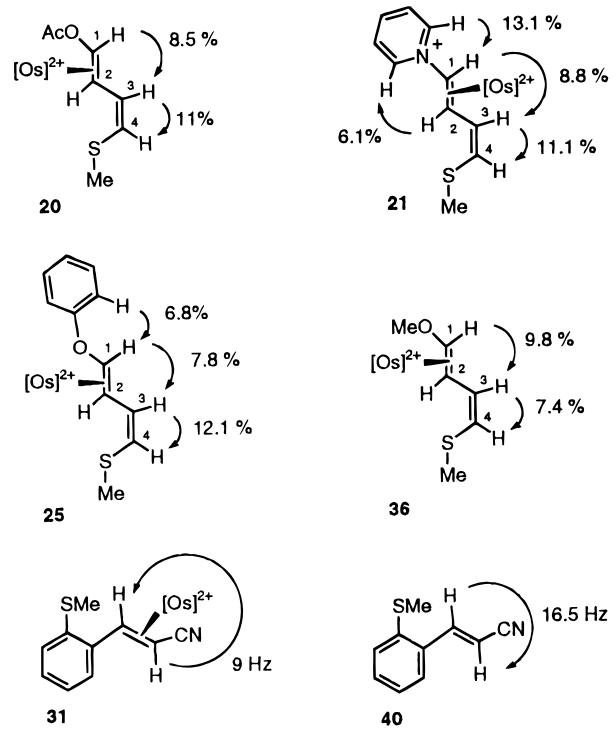


Figure 1. Establishment of diene geometry via 1D-NOE enhancements on selected 4-(methylthio)-1,3-butadiene complexes. $[Os]^{2+} = [Os(NH_3)_5]^{2+}$. Triflate counteranions omitted for clarity.

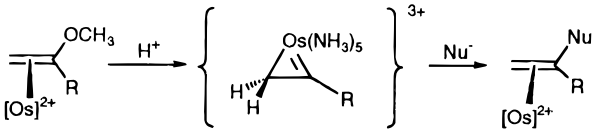
A competing demethylation reaction is observed upon treatment of **8** with PPh_3. Triphenylphosphine reacts with **8** in CD_3CN to afford a mixture of **1**, diene **24**, and methyltriphenylphosphonium triflate. The ratio of **1** to diene **24** varies with reaction conditions. Treatment of a CD_3CN solution of **8** with 2.0 equiv of PPh_3 affords a 4:1 mixture of **1** and diene **24** after 36 h at 22 °C. Repeating this reaction at 70 °C results in only a minor change in the product ratio (5:1). However, we find that by increasing the concentration of nucleophile to ~1 M (10 equiv; 22 °C), an increase in the production of the phosphonium diene complex occurs such that the ratio of **1** to **24** is 1.9:1. If the order of addition is switched such that the thiophenium complex **8** is *added slowly to* a high concentration of PPh_3 in CD_3CN, then the diene complex **24** becomes the dominant product (4:1). Workup of the reaction mixture affords pure **24** in 58% isolated yield. In no case does the ratio of thiophene complex to diene complex change over time.

Similar to the reaction with PPh_3, the rate of pyridine addition is sufficiently slow that it may be monitored by ^{1}H NMR spectroscopy or cyclic voltammetry (CV). The reaction half-life is found to vary with concentration of pyridine. For

(12) Chen, H.; Harman, W. D. *J. Am. Chem. Soc.* **1996**, *118*, 5672.

(13) The *trans*- $^3J_{H,H}$ for several η^2-olefin and vinyl ether complexes of pentaammineosmium(II) vary from 6.0 to 10.2 Hz. *Cis*-coupling constants vary from 4.8 to 9.0 Hz.

Scheme 2



example, for a pyridine concentration of 1.2 M, the half-life is ~24 min; if the concentration of nucleophile is decreased to 0.12 M, the half-life shows a corresponding increase to ~2.8 h. At very high pyridine concentrations (e.g., 3.5 M), the reaction is complete within 1 min, judging by a cyclic voltammogram. No reaction is observed when **8** is treated with an excess (10−20 equiv) of the silyl ketene acetal 1-methoxy-2-methyl-1-(trimethylsiloxy)propene (MMTP),[14] or vinyl ethers such as 1-ethoxypropene or 2-(trimethylsiloxy)propene. Enolates such as potassium acetylacetonate and sodium diethylmalonate are also unreactive at 22 °C over a period of 1 day and moderate heating (80 °C) results in intractable mixtures of paramagnetic products. Dimethylzinc fails to react with **8** after 1 day in acetonitrile solution, even at 80 °C and in the presence of $CuOTf_2$.[15]

We have recently shown that η^2-vinyl ether complexes of pentaammineosmium(II) react with nucleophiles via an S_N1-type elimination−addition mechanism involving a metallacyclopropene intermediate (i.e. an η^2-vinyl cation; Scheme 2).[12] Consequently, we explored the possibility of using the alkoxy-substituted diene complex **20** as a precursor to functionalized dienes. However, treatment of a solution of **20** and MMTP (~3 equiv) with TBSOTf in acetonitrile at either −40° or 22 °C affords only thiophenium complex **8**. Increasing the concentration of nucleophile to ~1.5 M does not affect these results. For diene **21**, the pyridinium substituent may also be eliminated at elevated temperatures. Although the pyridinium diene complex (**21**) does not undergo exchange in the presence of pyridine-d_5 at 22 °C, heating a CD_3CN solution of **21** at 80 °C affords a mixture of free pyridine and *S*-methylthiophenium **8**. If the reaction is repeated at 80 °C in the presence of a large excess of pyridine-d_5 (6.09 M), complex **8** is not observed, but the pyridine substituent is exchanged by pyridine-d_5 without any change in olefin geometry. At 22 °C in CD_3CN, no such exchange is detected after 24 h.

As part of our investigation into the mechanism of the nucleophilic addition to thiophenium complexes, the reaction of both 1-(dimethylsulfonio)propene (**32**) and *S*-methyl-2,3-dihydrothiophenium (**17**) complexes with pyridine was also explored under conditions similar to those reported above for **8**. Complex **32** (8:1 *trans/cis*) reacts immediately ($t_{1/2}$ < 1 s) with pyridine in CD_3CN at 22 °C under dilute conditions ([Nu] = 0.073 M) to give the pyridinium-substituted propene complex **33** as an 8:1 mixture of geometric isomers (Figure 2). These reaction conditions were similar to those of the reaction of the thiophenium complex **8** with pyridine except that the latter reaction proceeded more slowly with a reaction half-life of over 8 h at similar pyridine concentrations (Figure 2). For the *S*-methyl-2,3-dihydrothiophenium complex **17**, the reaction with pyridine ([Nu] = 0.078 M) affords the pyridinium adduct **35** with a half-life of 8 h, a reaction rate that is similar to that seen for the thiophenium complex **8**.

Ring Opening/Desulfurization by Raney Nickel. Raney nickel is known to desulfurize and hydrogenate a variety of

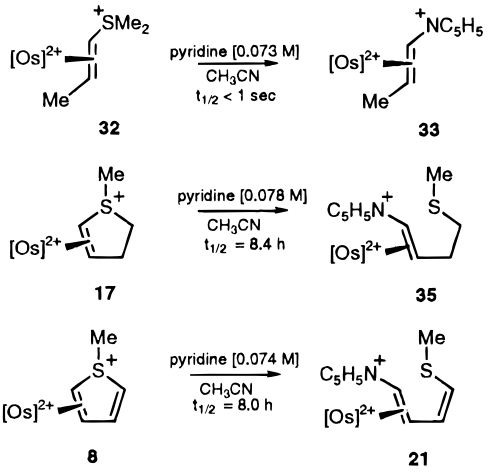


Figure 2. Reactivity of 1-(dimethylsulfonio)-3-propene vs *S*-methyl-2,3-dihydrothiophenium and *S*-methylthiophenium complexes with pyridine.

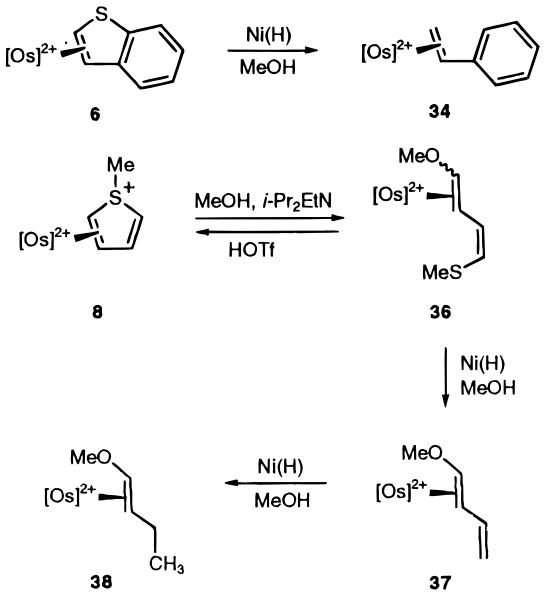


Figure 3. Desulfurization of η^2-benzothiophene and η^2-*S*-methylthiophenium complexes.

organosulfur compounds.[16] Thiophenes are desulfurized with difficulty and the resulting products undergo rapid hydrogenation to various hydrocarbons. The η^2-thiophene complex **1** is unreactive toward Raney nickel in MeOH (45 °C).[17] However, the η^2-benzo[*b*]thiophene complex **6** is readily desulfurized to form the olefin-bound η^2-styrene complex **34** (Figure 3).[18] The thiophenium complex **8** also readily reacts with Raney nickel in MeOH to give two different C−S cleavage products depending on reaction time. Treatment of **8** with a MeOH slurry of Raney nickel affords after 30 min **37** as a pale yellow solid (59%), the product of addition of methoxide to **8** followed by

(14) This silyl ketene acetal undergoes facile nucleophilic addition to various pentaammineosmium(II) areneium complexes.

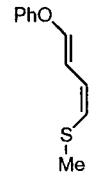
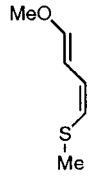
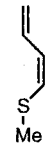
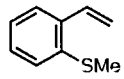
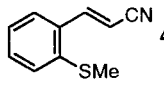
(15) Copper triflate promotes the addition of dimethyl zinc to an η^3-allyl species derived from an η^2-naphthalene complex. Winemiller, M. D.; Harman, W. D. Unpublished results.

(16) Mozingo, R. *Org. Syn.* **1941**, *21*, 15. For a review describing the synthetic applications of Raney Nickel, see: Pizey, J. S. *Synthetic Reagents*; Wiley: New York, 1974; Vol 2, pp 175−311.

(17) The Raney nickel was purchased as a 50% wt/wt slurry in water from Aldrich. The water was removed (in a glovebox under nitrogen!) by repeatedly washing with anhydrous methanol and drying under a stream of nitrogen. The material should be used immediately since its activity decreases rapidly when stored as a dry solid. The slurry is usually stable for ~6 months. Unwanted portions of this highly pyrophoric material may be conveniently destroyed by refluxing in a large volume of acetone overnight followed by dilution with water.

(18) When **34** is prepared from styrene, a mixture of linkage isomers results which favors the olefin. Upon warming to 80 °C in CD_3CN, the metal migrates to the olefin.

Table 3. Yield Data for Functionalized 4-(Methylthio)-1,3-butadienes and 2-(Methylthio)styrenes

Product		Conditions	%Yield[a]
	**42**	1.2 equiv AgOTf acetone	58 (44)
	**43**	1.0 equiv DDQ acetone	80 (59)
	**41**	1.0 equiv DDQ CH_3CN	55 (39)
	**39**	0.6 equiv DDQ CH_3CN	78 (50)
	**40**	1.0 equiv DDQ 2.0 equiv HOTf CH_3CN	82 (66)

[a] Yield data is for the decomplexation step. Yield data in parentheses are overall yields calculated from thiophene or benzo[*b*]thiophene.

desulfurization. If the reaction is carried out for longer reaction times (> 3h), the only product isolated is the desulfurized and hydrogenated 1-methoxybutene complex **38** as an off-white solid in 52% yield. The residual base (NaOH) used during preparation of the commercial nickel catalyst generates the methoxide nucleophile.[16] The resulting methoxy diene **36** undergoes rapid desulfurization to **37** and eventual hydrogenation to **38**. The analogous reaction of **8** with methanol in the presence of strong bases such as NaOMe or DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) affords an uncharacterized paramagnetic brown solid.

Decomplexation of 4-(Methylthio)-1,3-butadienes. Liberation of the organic product is achieved by oxidation of the pentaammineosmium(II) moiety with a suitable oxidant (Table 3). For complexes **18** and **30**, the half-wave oxidation potentials are 0.65 and 0.72 V (NHE), respectively, and are readily oxidized by DDQ.[19] For the styrene derivative **30**, addition of 0.6 equiv of the two electron oxidant DDQ immediately forms a dark brown precipitate, and $[Os(NH_3)_5(CH_3CN)]^{3+}$ is observed by electrochemistry as an oxidation product ($E_{1/2} \approx -0.10$ V).[20] Workup of the solution affords 2-(methylthio)styrene (**39**) as a yellow oil in 78% isolated yield. For complex **18**, addition of 1.2 equiv of DDQ to an acetonitrile solution precipitates an osmium salt, and free (methylthio)butadiene **41** is obtained in 55% isolated yield. For the [2-(methylthio)phenyl]cyanoethene complex **31** ($E_{p,a} = 1.23$ V), stronger oxidizing conditions are required. Addition of triflic acid (~2 equiv) to a solution of **31** in CH_3CN followed by addition of 1.1 equiv of DDQ affords the organic **40** in 82% isolated yield.

For some of the dienes a decomplexation procedure was required that was nonacidic in order to prevent polymerization of the organic product. While the potential of AgOTf in CH_3CN is only ~0.59 V (NHE),[21] in acetone it is ~0.73 V, which makes it a practical oxidant for several of the diene complexes described herein. For example, addition of 1.2 equiv of AgOTf in acetone to a solution of **25** affords the phenoxythiobutadiene **42** in 58% yield. Dienes **39**−**43** are stable toward polymerization in dilute $CDCl_3$ solution for several hours at 22 °C, allowing ^{1}H NMR characterization; however, attempts to purify these materials for microanalysis resulted in polymerization.

Discussion

Examples of C−S activation that do not involve direct insertion of the metal into the carbon−heteroatom bond[2] have been generally limited to nucleophilic addition reactions.[3] For example, Angelici has shown that the complex CpRu(η^5-thiophene)$^+$ undergoes C−S cleavage upon hydride addition to the α-carbon via an associative mechanism.[3d] The nucleophile attacks the heterocycle directly at an α-carbon affording an unobserved allyl sulfide intermediate, which then undergoes C−S cleavage to afford the observed ring-opened product. In contrast, the reaction of $Mn(CO)_3(\eta^5$-thiophene)$^+$ and hydride affords only the corresponding allyl intermediate;[3a,d] the lack of C−S activation in this complex is in agreement with the much lower activity of Mn as an HDS catalyst as compared to Ru.[22]

Rauchfuss *et al*. have demonstrated that the electron-rich thiophene complex (η^6-C_6Me_6)Ru(η^4-thiophene) reacts with protons at an α- carbon to form a ring-opened complex, but this process has been shown to occur by protonation *at the metal* followed by hydride transfer to the α-carbon.[6b] In contrast to most of the transition metal fragments that coordinate thiophene, the pentaammineosmium(II) moiety is strongly electron-donating but yet it resists oxidative addition reactions. Thus, pentaammineosmium(II) complexes of unsaturated organic molecules such as heterocycles, arenes, and dienes undergo electrophilic addition reactions *directly* on the ligand.[23] In contrast to pyrrole or furan complexes, the η^2-thiophene systems show reactivity with hard electrophiles primarily at the heteroatom. While other electrophiles (e.g., protons,[24a] anhydrides, acetals, and Michael acceptors[24b]) react at C(2) or C(3), trialkyloxonium salts, orthoesters, and alkyl triflates react to form *S*-alkylated products. Whereas pyridine, water, and alcohols are readily alkylated by *S*-alkylthiophenium salts, the pentaammineosmium(II) complexes of these ligands exhibit completely different reactivity

(19) DDQ is a two-electron oxidant whose potential is 0.71 V (NHE) for the first electron transfer. In theory, only 0.5 equiv of oxidant is required to oxidize Os(II) to Os(III), however, we have found that ~1.0 equiv is required for many Os(II) oxidations.

(20) Observation of this product indicates solvent substitution on Os(III) for the desired ligand.

(21) The oxidation potential of many oxidants, particularly small cations, varies considerably with the coordinating ability of the solvent. For a review of the use of various redox reagents in organometallic chemistry, see: Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

(22) For a comparison the activity of several transition metals in HDS catalysis, see Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1981**, *67*, 430.

(23) For examples of activation of arenes and heterocycles toward electrophilic additions, see for phenol: Kopach, M. E.; Gonzalez, J.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *56*, 4321. For aniline, see: Kolis, S. P.; Gonzalez, J.; Bright, L. M.; Harman, W. D. *Organometallics* **1996**, *15*, 245. For activation of pyrrole and furan, see ref 10.

(24) (a) Protonation is believed to occur initially at sulfur, followed by rearrangement of the metal and transfer of the proton to C(2). See ref 7b. (b) Both substitution and addition products are observed at either C(2) or C(3) depending on the electrophile and substitution pattern of the thiophene ring. Spera, M. L.; Harman., W. D. Preliminary results.

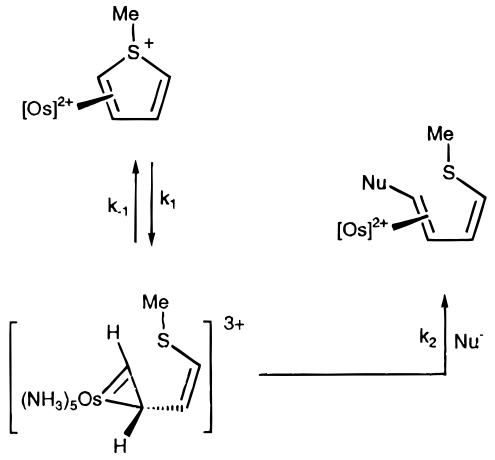


Figure 4. Proposed "vinyl cation" (metallacyclopropene) intermediate from $Os(NH_3)_5(2,3\text{-}\eta^2\text{-1-methylthiophenium})^{3+}$.

toward these reagents. The general increase in stability of these η^2-*S*-alkylthiophenium complexes most likely results from a π-back-bonding interaction with the metal, similar to how organic *S*-alkylthiophenium salts are stabilized by addition of electron-donating alkyl groups to the thiophene ring.[11]

Pioneering work by Angelici *et al*. has shown that highly reducing η^4-thiophene complexes exhibit increased nucleophilicity at the heteroatom, and the complex $Cp^*Ir(\eta^4\text{-2,5-dimethylthiophene})$ has been shown to displace dimethyl sulfide from $Me_2S{\cdot}BH_3$ to afford a BH_3-thiophene adduct.[25] An example of chalcogen *alkylation* in a coordinated heteroaromatic complex has also been reported[26] where treatment of $Cp^*(CO)_2Re(2,3\text{-}\eta^2\text{-selenophene})$ with $Me_3O[BF_4]$ affords the 1-methylselenophenium complex. Most recently, the addition of a Grignard reagent to the sulfur atom in $[(\eta^5\text{-thiophene})Mn(CO)_3]^+$ has been reported to afford η^4-*S*-alkylthiophenium complexes.[27] To our knowledge, a link between any of these thiophenium complexes and carbon−chalcogen bond activation has not been shown,[28] although Rauchfuss *et al*. have demonstrated reversible C−S activation in $\{(ring)\text{-}Ru(\eta^5\text{-tetramethylthiophene})\}^{2+}$ complexes by a nucleophilic attack at sulfur.[3a] Thus, the present study establishes an important link between electrophilic addition to sulfur and C−S activation for thiophenes. Furthermore, the participation of an η^2-thiophene in C−S activation has been demonstrated for the first time.

Mechanism. Heteroatom-substituted olefins (e.g., vinyl ethers) coordinated to pentaammineosmium(II) readily undergo nucleophilic substitution in acid.[12] This substitution proceeds through an elimination−addition sequence where the reactive intermediate is an η^2-vinyl cation (i.e., a metallacyclopropene) which has been observed and characterized by NMR spectroscopy for selected cases (Scheme 2). Noting similarities in both the regiochemistry and stereochemistry in the nucleophilic substitution reactions of η^2-vinyl ether[12] and the η^2-thiophenium complexes examined in this account, we propose that the nucleophilic additions observed at C5 for these η^2-thiophenium complexes occur through a similar reaction mechanism (Figure 4). Our rationale for a dissociative C5 substitution mechanism follows. We have recently reported that vinylsulfonium complexes such as **32** undergo nucleophilic substitution at the bound α-carbon via a metallacyclopropene intermediate that behaves functionally as a metal-stabilized vinyl cation.[12] The thiophenium complex **8** can be considered an analog of **32** except that the sulfide leaving group is now tethered to the coordinated olefin (e.g., C4). In a similar manner, cleavage of the C5−S bond of a thiophenium complex such as **8** would afford an η^2-vinyl cation species similar to that observed for vinyl ethers[12] (Figure 4). The implications of this tethered leaving group manifest themselves in the reactivity of the complex. We have found the rate of nucleophilic addition to be considerably faster for the sulfonium substituted olefin **32** than that for the thiophenium complex **8** (Figure 2) at the same temperature, but this difference can be attributed to a competition in the latter case between the rates of external nucleophilic addition (i.e., k_2 in Figure 4) and reversible addition of the tethered sulfur (i.e., k_{-1}). The failure to directly observe the proposed vinyl cation intermediate for the thiophenium complexes, even at low temperatures (e.g., −80 °C), or to carry out substitution reactions at C5 with mild carbon nucleophiles that were successfully added to simple substituted olefins is also likely due to this competing back rate (k_{-1}). We have shown that for the analogous reaction with the dihydrothiophenium complex **17**, the rate of pyridine substitution is also considerably more sluggish than the simple vinylsulfonium complex **32** (Figure 2), yet, this rate is virtually identical to that of the thiophenium system (**8**). This observation suggests that the uncoordinated double bond of the η^2-thiophenium has a minimal bearing on the nucleophilic substitution chemistry at C5. For an associative C5 substitution mechanism, the substitution rates for the olefin complex **32**, and the dihydrothiophenium complex **17** should be similar since there are no steric or electronic differences in the proximity of C5.

For most of the reaction products listed in Table 2, the *trans* stereochemistry observed for the coordinated double bond is proposed to be the result of a significant kinetic preference for β-alkylated η^2-vinyl cations to add a nucelophile *trans* to the alkyl substituent (Figure 4), and this stereochemical feature was recently identified for nucleophilic substitutions of η^2-coordinated furan as well as η^2-vinyl ether complexes.[12] For the reaction of **8** with methanol in which acid is a byproduct, the formation of *both* isomers is observed. Consistent with this observation, acid is known to catalyze a similar *cis/trans* equilibration in vinyl ether complexes,[12] and when a moderate base (i-Pr_2EtN) is included in the reaction between **8** and methanol to neutralize the acid, the *trans* isomer is the dominant product (7.5:1). Isomerization is also observed when the methoxy-substituted 4-(alkylthio)-1,3-butadiene complex **36** is treated with 0.1 equiv of HOTf: here, compound **8** is slowly regenerated, along with a 1:1 mixture of *cis/trans* isomers of **36**. The formation of thiophenium complex **8** from a ring-opened product (e.g., **20**, **21**, and **36**) demonstrates the reversibility of the reaction. When the 4-(alkylthio)-1,3-butadiene complex contains a good leaving group (e.g., pyridine) ring closure of the tethered sulfide nucleophile occurs via elimination of the leaving group, the microscopic reverse of the initial ring opening reaction.

Route to 4-(Alkylthio)-1,3-butadienes. (Alkylthio)butadienes are useful intermediates for organic synthesis but are difficult to prepare via traditional organic methods.[2f] Bianchini and co-workers recently prepared a series of (alkylthio)-butadienes from the reaction of the $16e^-$ fragment (triphos)-RhH with various thiophenes.[2f] Rhodium-promoted C−S insertion followed by electrophilic addition at the sulfur and subsequent removal of the metal affords the thiobutadiene

(25) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199.
(26) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 5651.
(27) 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.
(28) An Os(II)-η^2-selenophene complex has been *Se*-alkylated in our laboratories in high (>95%) yield and undergoes a similar C−Se bond cleavage in the presence of nucleophiles. Spera, M. L.; Harman, W. D. Unpublished results.

ligands in good yield. The osmium methodology described herein is complementary to this approach in that it provides a general route to functionalized thiobutadienes in which functionality can be adjusted at virtually all positions by choice of electrophile, substituted thiophene, *and* nucleophile. Thus, thiobutadienes may be prepared with both electron-donating and electron-withdrawing substituents (Table 3), and the metal may be recovered as the solvent−pentaammineosmium(III) complex.

Concluding Remarks

Central to the coordination chemistry of thiophenes is the search for a discrete homogeneous model for the mechanism of catalytic hydrodesulfurization, where the two main unresolved issues regard the initial coordination of the thiophene to the catalyst surface and whether the initial step is hydrogenation of the ligand or C−S cleavage.[5b] This account illustrates for the first time chemistry associated with the η^2-coordination mode of thiophenes (a coordination mode implicated in the heterogeneous HDS process),[5b] novel reactions of bound thiophenes with electrophiles, and a general nucleophilic addition process for *S*-alkyl-η^2-thiophenium species involving a proposed metallacyclopropene intermediate. Although this intermediate is only postulated in the thiophenium system, a close analog has been recently characterized.[12] More importantly, we have demonstrated the first example of *electrophile* initiated C−S activation in an η^2-thiophene complex using a metal known to form an highly reactive heterogeneous HDS catalyst.[22,29] An increased understanding of the interactions of thiophene with transition metals will ultimately further the development of more efficient HDS systems.

Experimental Section

General. The synthesis and characterization of the thiophene **(1)**, 2-methylthiophene **(2)**, 3-methylthiophene **(3)**, 2,5-dimethylthiophene **(4)**, 3-methoxythiophene (**5**), and benzo[*b*]thiophene (**6**) complexes have been reported previously.[7b] 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. 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). Thiophene ligands were purchased from Aldrich, distilled from CaH_2, and deoxygenated prior to use with the exception of benzo[*b*]thiophene which was used as received. All other reagents were purchased from Aldrich and used as received unless otherwise noted, with the exception of $[Os(NH_3)_5OTf](OTf)_2$, which was synthesized as described by Lay et al.[30]

{4,5-η^2-[Os(NH$_3$)$_5$]-2,3-dihydrothiophene}(OTf)$_2$ (7). Pd (10% on carbon, 36 mg) was suspended in 865 mg of MeOH in a 50 mL round bottom flask fitted with a gas inlet and balloon. The flask was charged with hydrogen (∼1 atm) and the suspension was stirred vigorously for 1 h. The flask was vented, and a solution of **1** (211 mg, 0.321 mmol) in 1.1 g of MeOH was added. The flask was again charged with hydrogen and stirred vigorously for 12 h. The flask was vented, and the solvent was concentrated under reduced pressure and filtered through a bed of Celite into 100 mL of stirring diethyl ether. The resulting ivory precipitate was filtered, washed with ether (3 × 10 mL), and dried *in vacuo*, affording 175 mg (0.266 mmol) of an pale yellow powder, 83%: ^{1}H NMR (CD_3CN) δ 4.75 (d, J = 5.9 Hz, 1H), 4.09 (br s, 3H), 3.89 (m, 1H), 3.01 (br s, 12H), 2.89 (m, 2H), 2.22 (m, 1H), 1.80 (m, 1H).

{4,5-η^2-[Os(NH$_3$)$_5$]-1-methylthiophenium}(OTf)$_3$ (8). Procedure A. To a solution of **1** (397 mg, 0.604 mmol) in 1.97 g of CH_3CN was added a solution of CH_3OTf (297 mg, 1.81 mmol) and the reaction was monitored by CV. After 1 h, the solution was precipitated into 50 mL of stirring diethyl ether and filtered through a fine fritted funnel, yield 455 mg (92%) of a yellow-orange solid: ^{1}H NMR (CD_3CN) δ 7.59 (dd, J = 5.4 Hz, 2.6 Hz, 1H), 6.60 (dd, J = 5.4 Hz, 1.6 Hz, 1H), 6.09 (dd, J = 4.5 Hz, 1.6 Hz, 1H), 5.52 (dd, J = 4.5 Hz, 2.6 Hz, 1H), 4.67 (br s, 3H), 3.39 (br s, 12H), 3.22 (s, 3H); ^{13}C NMR (CD_3CN) δ 155.69 (CH), 113.67 (CH), 61.75 (CH), 51.33 (CH), 31.19 (CH_3); CV $E_{1/2}$ = 1.37 V (NHE); $E_{p,c}$ = −1.38 V (NHE). Anal. Calcd for $C_7H_{22}N_5S_4O_9F_9Os$: C, 11.69; H, 2.70; N, 7.52. Found: C, 11.90; H, 2.63; N, 7.51. **Procedure B:** To a vigorously stirred slurry of **1** (508 mg, 0.773 mmol) in 1.43 g of DME was added methyl triflate (330 mg, 2.32 mmol). After 12 h, the resulting dark-brown slurry was added to 100 mL of stirring diethyl ether and filtered through a 15 mL medium frit. The filter cake was washed with ether (2 × 10 mL) and dried *in vacuo* to afford 599 mg (0.730 mmol) of a golden-brown powder, 95%.

{4,5-η^2-[Os(NH$_3$)$_5$]-1-ethylthiophenium}(OTf)$_3$ (14). To a solution of **1** (125 mg, 0.19 mmol) in CH_3CN (279 mg) was added solid triethyloxonium hexafluorophosphate (71 mg, 0.29 mmol). The resulting red-brown solution was allowed to stand for 12 h, and then triflic acid (38 mg, 0.25 mmol) was added.[31] After 10 min, the solution was added to 40 mL of stirring diethyl ether, the resulting precipitate was filtered, washed with ether (2 × 5 mL), and dried *in vacuo* to afford 139 mg of a red-brown powder, 88%: ^{1}H NMR (CD_3CN) δ 7.57 (dd, J = 5.1 Hz, 2.9 Hz, 1H), 6.35 (dd, J = 5.1 Hz, 2.2 Hz, 1H), 5.84 (dd, J = 4.8 Hz, 2.9 Hz, 1H), 5.45 (dd, J = 4.8 Hz, 2.2 Hz, 1H), 3.64 (m, 1H), 3.51 (m, 1H), 4.52 (br s, 3H), 3.24 (br s, 12H), 1.25 (t, J = 7.3 Hz, 3H); ^{13}C NMR (CD_3CN) δ 157.02 (CH), 109.67 (CH), 57.70 (CH), 52.56 (CH_2), 37.29 (CH), 7.90 (CH_3); CV $E_{1/2}$ = 1.34 V (NHE); $E_{p,a}$ = −1.62 V (NHE). Anal. Calcd for $C_9H_{24}N_5S_4O_9F_9Os$: C, 12.93; H, 2.89; N, 8.38. Found: C, 12.63; H, 2.73; N, 8.38.

{4,5-η^2-[Os(NH$_3$)$_5$]-1-(3,5-dimethylbenzyl)thiophenium}(OTf)$_3$ (15). To a solution of **1** (163 mg, 0.25 mmol) in CH_3CN (402 mg) was added solid 3,5-dimethylbenzyl bromide (247 mg, 1.24 mmol) and thallium triflate (437 mg, 1.24 mmol). The resulting slurry was stirred for 12 h and filtered through a 15 mL fine porosity frit into 50 mL of stirring diethyl ether to afford a golden brown precipitate. The precipitate was filtered, washed with ether, and dried *in vacuo* to afford 203 mg (88%) of crude **15**: ^{1}H NMR (CD_3CN) δ 7.42 (m, 1H), 7.10 (s, 1H), 7.03 (s, 2H), 6.29 (m, 1H), 6.10 (m, 1H), 5.13 (m, 1H), 5.01 (d, J = 12.5 Hz, 1H), 4.69 (br s, 3H), 4.65 (d, J = 12.5 Hz, 1H), 3.39 (br s, 12H), 2.31 (s, 6H); ^{13}C NMR (CD_3CN) δ 157.48 (C), 139.45 (CH), 131.94 (CH), 129.66 CH), 128.04 (CH), 128.04 (CH), 127.63 (C), 110.16 (CH), 58.42 (CH_2), 48.46 (CH), 21.06 (CH_3); CV $E_{1/2}$ = 1.30 V (NHE). A sample of **15** was recrystalized from acetonitrile/ether prior to microanalysis. Anal. Calcd for $C_{16}H_{30}N_5O_9S_4F_9Os$: C, 20.76; H, 3.27; N, 7.56. Found: C, 20.70; H, 3.25; N, 7.54.

{4,5-η^2-[Os(NH$_3$)$_5$]-1-(1,1-dimethoxymethyl)thiophenium}-(OTf)$_3$ (16). To a solution of **1** (218 mg, 0.226 mmol) in 1.71 g CH_3-CN was added trimethylorthoformate (218 mg, 2.26 mmol, dried, and distilled from Na°) and TBSOTf (594 mg, 2.26 mmol). After 1 h the resulting red-brown solution was added to ether (50 mL), and the precipitate was filtered, washed with Et_2O (2 × 10 mL) and dried *in vacuo* to afford an intractable tacky brown solid consisting of approximately 5:1 of *S*-alkylated to ring protonated material: ^{1}H NMR (CD_3CN) δ 7.56 (dd, J 5.9 Hz, 2.2 Hz, 1H), 6.56 (dd, J = 5.9 Hz, 1.5 Hz, 1H), 6.07 (dd, J = 4.5 Hz, 1.5 Hz, 1H), 5.51 (dd, J = 4.5 Hz, 2.2 Hz, 1H), 4.65 (br s, 3H), 4.16 (s, 1H), 3.38 (br s, 12H), 3.20 (s, 6H); ^{13}C NMR (CD_3CN) δ 155.59 (CH), 113.62 (CH), 61.74 (CH_3 X 2), 61.08 (CH), 51.34 (CH), 27.92 (CH); CV $E_{1/2}$ = 1.31 V (NHE); $E_{p,c}$ = −1.33 V (NHE). This is a mixture of *S*-acetal and 2*H*-thiophenium complexes.

{1,2-η^2-[Os(NH$_3$)$_5$]-(*Z*)-4-(methylthio)-1,3-butadiene}(OTf)$_2$ (18). To a solution of **8** (232 mg, 0.282 mmol) in 342 mg of acetonitrile was added a solution of tetra-*n*-butylammonium borohydride (80 mg, 0.310 mmol) in 190 mg of acetontrile. After 5 min, the reaction mixture was added to stirring CH_2Cl_2, and the precipitate was filtered, washed

(29) Mitchell, P. C. H. *Catalysis (London)* **1981**, *4*, 175.

(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.

(31) Addition of excess triflic acid exchanges the PF_6 counteranion for triflate.

with CH_2Cl_2 (2 × 5 mL), and dried *in vacuo* affording 146 mg (0.217 mmol) of a yellow powder, 77%: ^{1}H NMR (CD_3CN) δ 6.09 (d, J = 9.5 Hz, 1H), 5.18 (overlapping m, 2H), 4.25 (m, buried, 1H), 4.20 (br s, 3H), 3.43 (dd, J = 8.1 Hz, 1.8 Hz, 1H). 3.16 (br s, 12H), 2.29 (s, 3H). ^{13}C NMR (CD_3CN): δ 135.28 (CH), 123.28 (CH), 51.24 (CH), 43.63 (CH_2), 17.3 (CH_3); CV $E_{1/2}$ = 0.65 V (NHE). Anal. Calcd for $C_7H_{23}N_5S_3O_6F_6Os$: C, 12.48; H, 3.44; N, 10.40. Found: C, 12.36; H, 3.40; N, 10.69.

{1,2-η^2-[Os(NH$_3$)$_5$]-(1*E*,3*Z*)-1-acetoxy-4-(methylthio)-1,3-butadiene}(OTf)$_2$ (20). To a solution of **8** (255 mg, 0.311 mmol) in 677 mg acetonitrile was added solid ammonium acetate (29 mg, 0.370 mmol), and the resulting slurry was stirred vigorously for 15 min. The slurry was filtered through 15 mL fine porosity frit into 50 mL of stirring diethyl ether affording a yellow-orange precipitate. The precipitate was filtered, washed with ether, and dried *in vacuo* to afford 211 mg (0.289 mmol) of a yellow-orange powder, 93%: ^{1}H NMR (CD_3CN) δ 7.09 (d, J = 5.9 Hz, 1H), 6.28 (d, J = 9.5 Hz, 1H), 5.17 (dd, J = 10.3 Hz, 9.5 Hz, 1H),4.63 (dd, J = 9.5 Hz, 5.9 Hz, 1H), 4.19 (br s, 3H), 3.17 (br s, 12H), 2.31 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (CD_3CN) δ 173.26 (CO), 131.27 (CH), 124.81 (CH), 88.74 (CH), 42.29 (CH), 20.88 (CH_3), 17.06 (CH_3); CV $E_{p,a}$ = 1.10 V (NHE). Anal. Calcd for $C_9H_{25}N_5S_3O_8F_6Os$: C, 14.77; H, 3.44; N, 9.57. Found: C, 14.42; H, 3.68; N, 9.39.

{1,2-η^2-[Os(NH$_3$)$_5$]-(1*E*,3*Z*)-4-(methylthio)-1-(propylamino)-1,3-butadiene}(OTf)$_2$ (22). Propylamine (59 mg, 0.360 mmol) was added to a solution of **8** (134 mg, 0.163 mmol) in 399 mg of CH_3CN. After 1 h, the reaction mixture was added to 50 mL of stirring CH_2Cl_2, the precipitate was collected on a fine frit, and washed with CH_2Cl_2 (2 × 10 mL) to afford 101 mg (0.138 mmol) of a yellow powder, 85%: ^{1}H NMR (acetone-d_6) δ 6.10 (d, J = 9.5 Hz, 1H), 5.29 (dd, J = 7.3 Hz, 10.3 Hz, 1H), 5.18 (d, J = 7.3 Hz, 1H), 4.73 (br s, 3H), 4.28 (dd, J = 10.3 Hz, 9.5 Hz, 1H), 3.79 (br s, 12H), 2.88 (m, 2H), 2.28 (s, 3H), 1.58−1.51 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H), N−H not assigned; ^{13}C NMR (acetone-d_6) δ 134.65 (CH), 121.85 (CH), 75.86 (CH), 55.41 (CH_2), 43.85 (CH), 24.13 (CH_2), 17.13 (CH_3), 11.92 (CH_3); CV $E_{p,a}$ = 0.57 V (NHE). Anal. Calcd for $C_{10}H_{30}N_6S_3F_6O_6Os$: C, 16.44; H, 4.14; N, 11.50. Found: C, 16.45; H, 4.20; N, 11.47.

{1,2-η^2-[Os(NH$_3$)$_5$]-(1*E*,3*Z*)-1-azido-4-(methylthio)-1,3-butadiene}(OTf)$_2$ (23). Solid sodium azide (30 mg, 0.461 mmol) was added to a solution of **8** (192 mg, 0.234 mmol) in 773 mg of acetonitrile. Water (~5 drops) was added to help solubilize the azide salt. The slurry was stirred vigorously for 2 h, filtered through a 15 mL fine frit to remove undisolved sodium azide, and precipitated in ether to afford 137 mg (0.192 mmol) of a tan solid, 82%; ^{1}H NMR (CD_3CN) δ 6.18 (d, J = 9.2 Hz, 1H), 5.82 (d, J = 6.6 Hz, 1H), 5.09 (overlapping dd, J = 10.2 Hz, 9.2 Hz, 1H), 4.41 (dd, J = 6.6 Hz, 10.2 Hz, 1H), 4.32 (br s, 3H), 3.22 (br s, 12H), 2.84 (s, 3H); ^{13}C NMR (CD_3CN) δ 130.78 (CH), 125.62 (CH), 71.73 (CH), 43.88 (CH), 17.01 (CH_3); CV $E_{p,a}$ = 0.91 V (NHE). Anal. Calcd for $C_7H_{22}N_8O_6F_6S_3Os$: C, 11.76; H, 3.10; N, 15.68. Found: C, 12.09; H, 3.19; N, 15.41.

{1,2-η^2-[Os(NH$_3$)$_5$]-(1*E*,3*Z*)-4-(methylthio)-1-(triphenylphosphonio)-1,3-butadiene}(OTf)$_3$ (24). A solution of **8** (118 mg, 0.143 mmol) in 365 mg of CH_3CN was added to a solution of triphenylphosphine (302 mg, 1.14 mmol) in 968 mg of CH_3CN. After 30 min, the reaction mixture was added to 50 mL of CH_2Cl_2, the resulting thiophene complex impurity was removed by filtration, and the filtrate diluted with 50 mL of diethyl ether. The resulting yellow precipitate was filtered, washed with ether, and dried *in vacuo*, affording 90 mg (0.083 mmol) of a yellow powder, 58%: ^{1}H NMR (CD_3CN) δ 7.91−7.68 (m, 15H), 6.68 (d, J = 9.5 Hz, 1H), 5.60 (overlapping dd, J = 9.5 Hz, 10.5 Hz, 1H), 5.23 (m, 1H), 5.00 (overlapping dd, J = 9.5 Hz, 9.5 Hz, 1H), 4.57 (br s, 3H), 3.15 (br s, 12H), 2.36 (s, 3H); ^{13}C NMR (CD_3CN) δ 135.96 (CH), 134.39 (d, J = 9.2 Hz, CH), 131.51 (d, J = 12.8 Hz, CH), 129.95 (d, J = 5.5 Hz, C), 133.47 (CH), 123.02 (CH), 49.99 (CH), 20.41 (CH), 17.36 (CH_3); CV $E_{p,a}$ = 1.39 V (NHE); $E_{p,c}$ = −1.45 V (NHE). Anal. Calcd for $C_{27}H_{37}N_5O_9F_9PS_4Os$: C, 28.81; H, 3.44; N, 6.46. Found: C, 28.80; H, 3.60; N, 6.58.

{1,2-η^2-[Os(NH$_3$)$_5$]-(1*E*,3*Z*)-4-(methylthio)-1-phenoxy-1,3-butadiene}(OTf)$_2$ (25). Phenol (36 mg, 0.380 mmol) was added to a solution of **8** (104 mg, 0.127 mmol) in 608 mg of CH_3CN. *i*-Pr_2EtN (49 mg, 0.381 mmol) was added, and the reaction mixture allowed to stand for 10 min. The workup for **24** was followed: yield 80 mg (0.105 mmol), 83%; ^{1}H NMR (CD_3CN) δ 7.31 (m, 1H), 7.06 (d, J = 8.1 Hz, 2H), 6.96 (m, 2H), 6.57 (d, J = 5.9 Hz, 1H), 6.33 (d, J = 9.5 Hz, 1H), 5.30 (dd, J = 10.5 Hz, 9.5 Hz, 1H), 4.53 (dd, J = 5.9 Hz, 10.5 Hz, 1H), 4.30 (br s, 3H), 3.27 (br s, 12H), 2.31 (s, 3H); ^{13}C NMR (CD_3CN) δ 162.40 (C), 130.17 (CH), 129.95 (CH), 126.39 (CH), 122.03 (CH), 116.17 (CH), 91.23 (CH), 44.83 (CH), 17.23 (CH_3); CV $E_{p,a}$ = 1.05 V (NHE). Anal. Calcd for $C_{13}H_{27}N_5O_7F_6S_3Os$: C, 20.54; H, 3.37; N, 9.13. Found: C, 20.39; H, 3.55; N, 9.15.

***trans*-{η^2-[Os(NH$_3$)$_5$]-1-(dimethylsulfonio)-propene}(OTf)$_3$ (32).** To a solution of the ethyl propenyl ether complex[12] (296 mg, 0.448 mmol) in 535 mg of CH_3CN was added dimethyl sulfide (62 mg, 0.987 mmol) and TBSOTf (130 mg, 0.493 mmol). After 5 min the reaction mixture was added to 50 mL of diethyl ether under stirring, and the resulting yellow precipiate was filtered, washed with ether (2 × 10 mL), and dried *in vacuo* to afford 324 mg (0.393 mmol) of a yellow powder, 88%: ^{1}H NMR (CD_3CN) δ 4.66 (d, J = 7.3 Hz, 1H), 4.55 (q, J = 6.7 Hz, 1H), 4.45 (br s, 3H), 3.38 (br s, 12H), 3.06 (s, 3H), 2.92 (s, 3H), 1.50 (d, J = 6.7 Hz, 3H). Anal. Calcd for $C_8H_{26}N_5O_9F_9S_4Os$: C, 11.64; H, 3.17; N, 8.48. Found: C, 11.71; H, 3.22; N, 8.49.

***cis*-{η^2-[Os(NH$_3$)$_5$]-3-pyridinio-2-propene}(OTf)$_3$ (33).** Pyridine (8 mg, 0.101 mmol) was added to a solution of **32** (56 mg, 0.067 mmol) in 489 mg CH_3CN causing an immediate color change from golden brown to red. The solution was immediately added to 50 mL of CH_2Cl_2 under stirring, filtered, washed with CH_2Cl_2 (2 × 5 mL), and dried *in vacuo* to afford 41 mg (0.049 mmol) of a pink powder, 72%: ^{1}H NMR (CD_3CN) δ 8.67 (d, J = 6.5 Hz, 2H), 8.52 (d, J = 6.9 Hz, 1H), 7.94 (t, J = 7.1 Hz, 2H), 6.61 (d, J = 7.3 Hz, 1H), 5.43 (m, 1H), 4.46 (br s, 3H), 3.29 (br s, 12H), 1.49 (d, J = 6.0 Hz, 3H). Anal. Calcd for $C_{11}H_{25}N_6O_9S_3F_9Os$: C, 15.68; H, 2.99; N, 9.97. Found: C, 15.76; H, 3.03; N, 10.01.

***cis*-{η^2-[Os(NH$_3$)$_5$]-1-(methylthio)-4-pyridinio-3-butene}(OTf)$_3$ (35).** To a solution of **17** (32 mg, 0.039 mmol) in CH_3CN (416 mg) was added pyridine (17 mg, 0.215 mmol). After 16 h, the resulting red solution was added to 50 mL of CH_2Cl_2 under stirring, filtered, washed with CH_2Cl_2 (2 × 5 mL), and dried *in vacuo* to afford 29 mg (0.032) of a pink powder, 81%: ^{1}H NMR (CD_3CN) δ 8.72 (d, J = 5.9 Hz, 2H), 8.53 (d, J = 8.1 Hz, 1H), 7.87 (t, J = 7.3 Hz, 2H), 6.72 (d, J = 7.4 Hz, 1H), 5.45 (m, 1H), 4.54 (br s, 3H), 3.36 (br s, 12H), 2.84 (m, 2H), 2.07 (s, 3H), 1.47 (m, 2H). Anal. Calcd for $C_{13}H_{29}O_9S_4F_9N_6Os$: C, 17.30; H, 3.24; N, 9.31. Found: C, 17.33; H, 3.00; N, 9.70.

{3,4-η^2-[Os(NH$_3$)$_5$]-(1*E*,3*Z*)-4-methoxy-1-(methylthio)-1,3-butadiene}(OTf)$_2$ (36). To a solution of **8** (160 mg, 0.195 mmol) in methanol (916 mg) was added *i*-Pr_2EtN (27 mg, 0.209 mmol). The solution was allowed to stand for 1 h and added to 50 mL of CH_2Cl_2, the precipitate (**1**) was removed by filtration, and the filtrate diluted with diethyl ether. The resulting yellow precipitate was filtered, washed with Et_2O, and dried *in vacuo* to afford 104 mg, 76%, of a yellow powder, as a 7.5:1 mixture of geometric isomers: ^{1}H NMR (CD_3CN) δ 6.16 (d, J = 9.5 Hz, 1H), 6.01 (d, J = 5.5 Hz, 1H), 5.07 (dd, J = 10.3 Hz, 9.5 Hz, 1H), 4.37 (dd, J = 10.3 Hz, 5.5 Hz, 1H), 4.13 (br s, 3H), 3.55 (s, 3H), 3.11 (br s, 12H), 2.31 (s, 3H); ^{13}C NMR (CD_3CN) δ 130.12 (CH), 122.61 (CH), 94.94 (CH), 62.01 (CH_3), 42.16 (CH), 15.85 (CH_3); CV $E_{p,a}$ = 0.79 V (NHE). Anal. Calcd for $C_{10}H_{25}N_5O_7F_6S_3Os$: C, 16.51; H, 3.46; N, 9.62. Found: C, 16.51; H, 3.44; N, 9.70.

{3,4-η^2-[Os(NH$_3$)$_5$]-(*E*)-4-methoxy-1,3-butadiene}(OTf)$_2$ (37). Procedure A: Under an inert atmosphere, dry Raney nickel[32] (600 mg, ~5 wt/wt equiv, Aldrich, W-2) was added to a solution of **8** (120 mg, 0.146 mmol) in methanol and the resulting slurry was vigorously stirred for 30 min. The slurry was filtered through a 15 mL fine frit and added to 50 mL of ether to afford a pale yellow precipitate which was filtered, washed with diethyl ether (2 × 5 mL) and dried *in vacuo* affording 72 mg (0.110 mmol) of a pale yellow powder, 75%: ^{1}H NMR (CD_3CN) δ 6.03 (d, J = 5.9 Hz, 1H), 5.28−5.11 (m, 3H), 4.13 (br s, 3H), 4.02 (dd, J = 9.5 Hz, 5.9 Hz, 1H), 3.57 (s, 3H), 2.99 (br s, 12H). Anal. Calcd for $C_7H_{23}N_5O_7F_6S_2Os$: C, 13.09; H, 1.26; N, 10.90. Found: C, 13.00; H, 1.27; N, 11.18. **Procedure B:** Under an inert atmosphere, 716 mg of dry Raney nickel (Aldrich, W-2) was added to a solution of **36** (141 mg, 0.201 mmol) in 2.71 g methanol. The slurry was stirred vigorously for 1h and the workup from proceudre A was followed: yield 96 mg, 72%.

(32) This operation is most easily carried out under dry nitrogen in a glovebox.

{η^2-[Os(NH$_3$)$_5$]-(*E*)-4-methoxy-3-butene}(OTf)$_2$ (38). Procedure A: Under an inert atmosphere, dry Raney nickel (Aldrich, W-2) was added to a solution of **8** in methanol and the resulting slurry was vigorously stirred for 10 h. The slurry was filtered through a 15 mL fine frit and added to 50 mL of ether to afford a yellow precipitate: ^{1}H NMR (CD$_3$CN) δ 5.62 (d, J = 5.9 Hz, 1H), 4.02 (br s, 3H), 3.53 (s, 3H), 3.39 (m, 1H), 3.01 (br s, 12H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (CD$_3$CN) δ 96.03 (CH), 63.03 (CH$_3$), 47.40 (CH), 22.99 (CH$_2$), 18.56 (CH$_3$); CV $E_{p,a}$ = 0.83 V (NHE); $E_{p,c}$ = 0.54 V (NHE). Anal. Calcd for C$_7$H$_{25}$N$_5$O$_7$F$_6$S$_2$Os: C, 13.05; H, 1.56; N, 10.87. Found: C, 12.96; H, 1.51; N, 10.97. **Procedure B:** Under an inert atmosphere, 362 mg dry Raney nickel (Aldrich, W-2) was added to a solution of **36** (71 mg, 0.101 mmol) in 1.97 g of methanol. The slurry was stirred vigourously for 8h and the workup from procedure A was followed: yield 35 mg of ivory powder, 52%.

2-(Methylthio)styrene (39).[33] A solution of DDQ (103 mg, 0.46 mmol) in CH$_3$CN (252 mg) was added to a solution of **30** (549 mg, 0.76 mmol) in 1.12 g CH$_3$CN. After 5 min, the dark reaction mixture was added to 50 mL of CH$_2$Cl$_2$. The resulting slurry was filtered through a pad of silica gel, and the frit was washed with CH$_2$Cl$_2$ (2 × 10 mL). The solvent was removed under reduced pressure affording 88 mg of a golden-brown oil, 88%.

(*E*)-1-[2-(Methylthio)phenyl]-2-cyanoethene (40). To a solution of **31** (200 mg, 0.267 mmol) in 1.01 g CH$_3$CN was added HOTf (120 mg, 0.80 mmol) and DDQ (67mg, 0.294 mmol). After 15 min, DBU (130 mg, 0.086 mmol) was added affording a dark gummy precipitate. The reaction mixture was added to 50 mL of diethyl ether and filtered through a pad of silica gel. The silica was washed with ether (3 × 10 mL), and the solvent removed under reduced pressure to afford 38 mg (0.217 mmol) of a yellow oil, 82%: ^{1}H NMR (CDCl$_3$) δ 7.91 (d, J = 16.5 Hz, 1H), 7.45−7.21 (m, 4H), 5.83 (d, J = 16.5 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 147.54 (CH), 139.08 (C), 133.22 (C), 131.08 (CH), 127.72 (CH), 126.31 (CH), 125.78 (CH), 116.28 (CN), 97.75 (CH), 16.79 (CH$_3$).

(*Z*)-1-(Methylthio)butadiene[34] **(41).** A solution of DDQ (88 mg, 0.387 mmol) was added to a solution of **18** (237 mg, 0.352 mmol) in 290 mg of CH$_3$CN. The dark slurry was stirred for 5 min and then filtered through a bed of basic alumina. The solvent was removed under reduced pressure, affording **41** as a yellow oil, 19 mg, 55%.

(1*E*,3*Z*)-4-(Methylthio)-1-phenoxy-1,3-butadiene (42). To a solution of **25** (315 mg, 0.412 mmol) in acetone (1.3 g) was added solid AgOTf (127 mg, 0.490 mmol), and the slurry was stirred at ambient temperature for 15 min. The slurry was added to 30 mL of diethyl ether and filtered through a plug of silica gel. The filtrate was removed under reduced pressure to afford 46 mg of a yellow oil, 58%: ^{1}H NMR (CDCl$_3$) δ 7.33 (t, J = 8.5 Hz, 2H), 7.07 (t, J = 8.5 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 11.9 Hz, 1H), 6.26 (dd, J = 11.9 Hz, 10.1 Hz, 1H), 6.08 (dd, J = 10.1 Hz, 9.5 Hz, 1H), 5.84 (d, J = 9.5 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 156.71 (C), 146.13 (CH), 129.56 (CH), 125.71 (CH), 123.14 (CH), 122.00 (CH), 116.74 (CH), 109.93 (CH), 17.32 (CH$_3$).

(1*E*,3*Z*)-4-(Methylthio)-1-methoxy-1,3-butadiene (43). To a solution of **36** (245 mg, 0.349 mmol) in acetone (800 mg) was added a solution of DDQ (0.349 mmol) in 896 mg of acetone. The resulting slurry was stirred for 15 min and filtered through a bed of basic alumina, and the filtrate was evaporated to a red-brown residue. The residue was partitioned between 10% Na$_2$CO$_{3(aq)}$ and CH$_2$Cl$_2$ and extracted with CH$_2$Cl$_2$, and the organic layers was dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure to afford **43** as a yellow oil, (36 mg, 0.277 mmol), 80%: ^{1}H NMR (CDCl$_3$) δ 6.64 (d, J = 12.5 Hz, 1H), 6.02 (dd, J = 10.2 Hz, 9.5 Hz, 1H), 5.72 (dd, J = 12.5 Hz, 10.2, 1H), 5.63 (d, J = 9.5 Hz, 1H), 2.28 (s, CH$_3$).

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Supporting Information Available: Text giving experimental procedures and characterizations for all compounds described in this account (15 pages). See any current masthead page for ordering and Internet access instructions.

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(33) This compound has been previously reported. See Crow, W. D.; McNab, H. *Aust. J. Chem.* **1979**, *32*, 123.

(34) This compound has been previously reported. See: (a) Everhardus, R. H.; Gräfing, R.; Brandsma, L. *Synth. Commun.* **1983**, 623. (b) Crumbie, R. L.; Ridley, D. D. *Aust. J. Chem.* **1981**, *34*, 1017.