Tungsten(0) η^2-Thiophene Complexes: Dearomatization of Thiophene and Its Facile Oxidation, Protonation, and Hydrogenation

David A. Delafuente,[†] William H. Myers,[‡] Michal Sabat,[†] and W. Dean Harman*,[†]

Departments of Chemistry, University of Virginia, Charlottesville, Virginia 22904-4319, and University of Richmond, Richmond, Virginia 23173

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Complexes of the form TpW(NO)(PMe_3)(η^2-thiophene) have been synthesized in 31−40% yield by reduction of TpW(NO)(PMe_3)(Br) in the presence of the thiophene ligand. The dynamics of protonation and the subsequent deprotonation for the corresponding 2*H*-thiophenium complexes have been investigated. Hydrogenation of the uncoordinated double bond was accomplished, and sulfur−carbon, sulfur−oxygen, and carbon−carbon bond-forming reactions were explored with these complexes.

Introduction

Hydrodesulfurization (HDS) of petroleum streams has been described as the single most important industrial process involving transition metals.[1,2] Given that aromatic S-heterocycles are among the most difficult impurities to remove,[3] a large number of model studies concerning transition-metal thiophene complexes have appeared in the literature.[4−10] However, few reports have surfaced for group 6 metals, the most commonly employed transition metals in industrial processes.[1,2] While thiophene is typically observed to bind a transition metal in an η^5 or η^1 (through sulfur) manner, these binding modes are arguably not the most activating for the heterocycle. Intermediate hapticities (η^2−η^4), which result in a complete loss of the aromaticity,[11] would render the heterocycle more prone to reduction or other chemical alteration. For these reasons, we felt it would be instructive to explore the chemistry of η^2-coordinated thiophene complexes of tungsten, which would be analogous to the known complex TpW(NO)(PMe_3)(η^2-benzene) (Tp = hydridotris(pyrrazolyl)borate).[12] Herein, we report the synthesis and characterization of complexes having the form TpW(NO)(PMe_3)(4,5-η^2-L) (L = thiophene (**1**), 2-methylthiophene (**2**), and 2,5-dimethylthiophene (**3**)) and their elementary ligand-centered reactions with electrophiles.

Results

Compounds **1**−**3** were prepared in 31−40% yield by reduction of the W(I) precursor TpW(NO)(PMe_3)(Br)[12] with sodium, in the presence of the appropriate thiophene ligand. The spectroscopic and electrochemical properties of the three complexes are internally consistent and are similar to other known η^2-bound thiophene complexes.[13−16] Cyclic voltammograms for compounds **1**−**3** display irreversible oxidation waves between −0.1 and 0.1 V (NHE), and infrared absorptions corresponding to the nitrosyl ligand appear at 1564 cm^{-1}, a value similar to those observed for other η^2-aromatic complexes of {TpW(NO)(PMe_3)}.[12,17] FAB-MS data confirm the molecular formulas for **1**−**3**.

Given the stereogenic metal center in the complexing agent and the high rotational barrier for the thiophene−W bond (vide infra), four possible coordination stereoisomers are available for thiophene complexes **1**−**3**. Characterization for each of these isomers was carried out in consideration of the general observation that the phosphorous ligand strongly couples (8−11 Hz) with the proton of the bound carbon that extends into quadrant c shown in Figure 1. In addition, the bound methine group (or methyl, for the case of 2,5-dimethylthiophene) that extends into quadrant b experiences significant shielding from two pyrazole rings. These features, along with corroborating ^1H, ^{13}C, COSY,

* To whom correspondence should be addressed. E-mail: wdh5z@virigina.edu.
† University of Virginia.
‡ University of Richmond.

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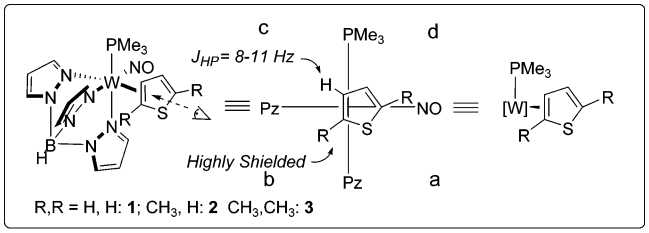

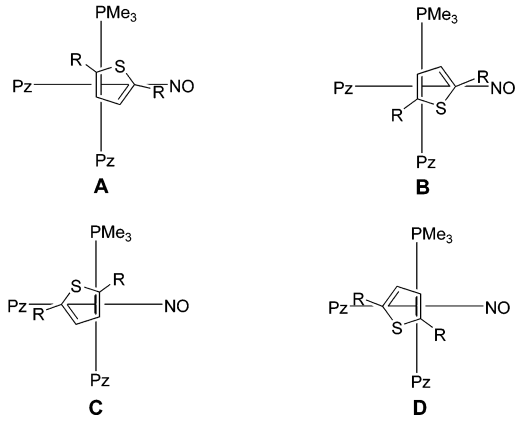

Figure 1. Coordination stereoisomers for thiophene complexes **1**−**3**.

Table 1. Proton Data for Thiophene Complexes 1−3 (ppm)

	compd					
position	**1A**	**1B**	**2A**	**2B**	**3B**	**3D**
2 (2-Me)	5.72	5.72	2.28	2.35	2.20	1.62
3	6.61	6.40	6.36	6.16	6.16	5.00
4	2.77	4.40	2.64	4.32	3.73	4.22
5 (5-Me)	5.10	3.36	5.05	3.31	1.00	2.24

Table 2. Carbon Data for Thiophene Complexes 1−3 (ppm)

	compd					
position	**1A**	**1B**	**2A**	**2B**	**3B**	**3D**
2	117.0	117.0				
3	130.3	130.0	127.3	127.5	128.5	126.4
4	65.9	67.2	66.6	66.3	72.5	77.8
5	67.5	65.7	67.7	66.0		

HSQC, HMBC, and NOESY data (Tables 1 and 2), provide the complete characterization of the major isomers of thiophene complexes **1**−**3**.

The ^{1}H NMR spectra for compounds **1** and **2** reveal two diastereomers (**A**:**B**) in a 1:1 ratio corresponding to those diastereomers in which the ring extends over the nitrosyl ligand (Figure 1). While compound **3** also exhibits two stereoisomers, the **A** isomer is no longer present, but its conformer **D** is observed in a 2:1 ratio (**B**:**D**). The methyl group for the purported isomer **3A** would extend into quadrant **c**, suffering a steric interaction with the pyrazole ring trans to the NO. This steric interaction has been previously documented for TpRe(CO)(L)(alkene) systems.[18] A single crystal of the dimethylthiophene complex **3** was subjected to X-ray diffraction analysis, and the resulting molecular structure diagram (**3B**) is shown in Figure 2, with the methyl group on the bound carbon oriented into quadrant b. Coordination of the thiophene across C5 and C4 results in a lengthening of this bond as well as the C5−S bond

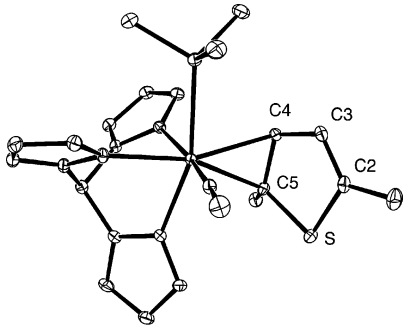

Figure 2. ORTEP diagram of compound **3B** (30% ellpisoids). Selected bond lengths (Å): W−C4, 2.256(2); W−C5, 2.224(2); C4−C5, 1.452(3); C5−S, 1.809(2); S−C2, 1.756(2); C3−C2, 1.341(3); C4−C3, 1.466(3).

as a result of the disruption of the partial π-bonding interaction between these pairs of atoms. Despite the methyl group on C5, the W−C5 bond distance (2.22 Å) is actually shorter than the corresponding value for W−C4 (2.26 Å), presumably as a result of a steric interaction with the phosphorus.[19] Judging from electrochemical and NMR data,[20] an S-bound isomer has never been detected for these complexes.

C2 Protonation. Compound **1** can be protonated using acids as weak as methylimidazolium triflate (MeImHOTf) (pK_a(H_2O) ≈ 7), indicating that in nonaqueous solvents the bound thiophene has a basicity much greater than that of the free heterocycle, which can be protonated only with superacids.[21] Diphenylammonium triflate (DPhAT; pK_a(H_2O) ≈ 1), was found to be a more efficient acid source, producing TpW(NO)(PMe_3)(*S*,5-η^2-thiophenium)(OTf) (**4**) in 91% yield. Protonation is reversible, and compound **4** can be deprotonated to return **1** with 1,8-diazobicyclo[5.4.0]undeca-7-ene ($DBUH^+$: pK_a(H_2O) ≈ 12). Thus, the basicity of the bound thiophene in **1** can be bracketed between methylimidazole and DBU in acetonitrile. Proton and carbon NMR data (including COSY and HMBC) indicate that protonation of **1** occurs at C2 (the uncoordinated α-carbon) and that the metal has changed its coordination position to C5−S. This is consistent with the osmium analogue $[Os(NH_3)_5(2H\text{-thiophenium})]^{3+}$.[14] Electrochemical analysis of compound **4** shows an irreversible reduction wave at −1.5 V and an irreversible oxidation at 1.1 V (NHE, 100 mV/s). The stretching frequency of the nitrosyl of **4** is shifted positively from 1564 to 1630 cm^{-1}, consistent with a loss of electron density at the metal. Mass spectral data show a peak at *m*/*z* 588, confirming the molecular formula of the 2*H*-thiophenium complex.

Like its conjugate base, the 2*H*-thiophenium complex **4** is produced initially as two isomers, **4B** and **4C** (Figure 3). This diastereomer ratio is determined by kinetic factors and varies depending on the method of protonation. The ratio of **4B**:**4C** is initially 6:1 when formed from **1** and an excess of TFA (d_6-acetone), while this ratio is 1:1 when the Brønsted acid is DPhAT (MeOH). Over a period of several days, the formation of **4A** is observed, concurrent with the disappearance

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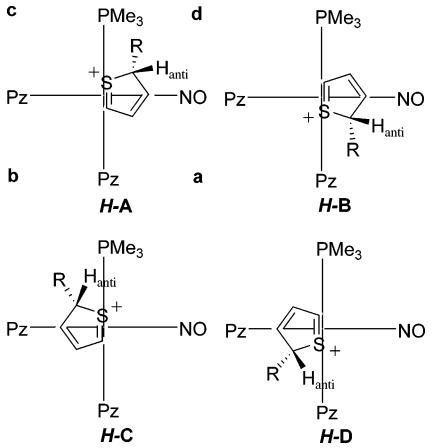

Figure 3. Stereoisomers for 2*H*-thiophenium complexes **4** and **5** (R = H, **4**; R = CH_3, **5**).

Table 3. Proton Data for 2*H*-Thiophenium Complexes 4−6 (ppm)

	compd						
position	**4A**	**4B**	**4C**	**5B**	**5D**	**6E**	**6F**
H2 (anti)	4.91	4.38	4.87	3.39	5.03	6.73	4.92
H2 (syn)	4.29	2.91	4.38				
(2-Me)				1.54	0.16	1.82	1.75
H3	5.55	5.69	5.39	5.63	5.59	5.00	3.98
H4	7.00	7.09	**5.59**	7.03	6.94	4.06	4.85
H5 (5-Me)	**4.44**	6.58	6.15	6.50	6.50	2.48	2.64

Table 4. Carbon Data for 2*H*-Thiophenium Complexes 4−6 (ppm)

	compd						
position	**4A**	**4B**	**4C**	**5B**	**5D**	**6E**	**6F**
C2	47.0	40.8	44.3	53.1	53.9	62.4	61.4
C3	119.9	132.5	125.6	132.5	133.4	81.7	86.8
C4	135.3	136.5	135.1	134.9	134.7	92.6	86.1
C5	82.1	89.0	82.8	88.6	90.2	218.1	216.6

of **4C**. Heating the mixture to 80 °C facilitates this process, and the final equilibrium ratio of **4A**:**4B** is determined to be 1:1.

Key to the stereochemical assignment of **4C** is the ^{1}H NMR signal that shows H4 at 5.59 ppm (Table 3, in boldface), dramatically shifted upfield from its position in **4A** and **4B** due to the shielding effect of quadrant b (vide supra). Other data for **4C** closely match those of isomers **4A** and **4B** (Tables 3 and 4). By similar logic, the stereochemistry of isomer **4A** is assigned on the basis of its C5 proton at 4.44 ppm. This value deviates significantly from those reported for the other isomers (bold in Table 3) and indicates its projection into quadrant b. In contrast to the large deviations in proton data for different isomers, carbon chemical shifts (Table 4), assigned by HSQC data, are in close agreement, regardless of the isomer stereochemistry.

Compound **2** can be protonated to form TpW(NO)(PMe$_3$)(*S*,5-η^2-2-methylthiophenium)(OTf) (**5**) in 79% yield. Unlike its osmium counterpart, [14] protonation of the 2-methylthiophene complex occurs at the substituted α-carbon, C2, generating a quaternary carbon. The 2-methylthiophene complex **2** can be protonated with DPhAT but fails to react after 1 h with the weaker acid pyridinium triflate (pK_a(H_2O) ≈ 5). The thiophenium complex **5** can be deprotonated using lithium diisopropylamide (LDA; pK_a of conjugate acid: ≈ 36), but it resists deprotonation by DBU or potassium *tert*-butoxide (KO-*t*-Bu) (for *tert*-butyl alcohol, pK_a(H_2O) ≈ 19) after 1 h. Taken together, these observations indicate that the bound 2-methylthiophene is slower to protonate *and* that its conjugate acid is slower to deprotonate, compared to the respective thiophene analogues. These observations indicate a substantial kinetic barrier for either process (vide infra).

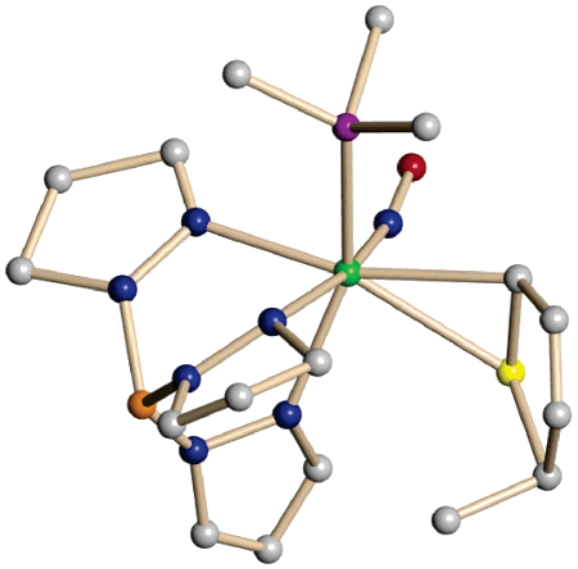

Figure 4. Molecular model of 2*H*-thiophenium complex **5D** based on X-ray data.

When the 2*H*-thiophenium complex **2** is protonated with DPhAT in methylene chloride, two diastereomers are formed, in a **5B**:**5D** ratio ranging from 1:1 to 1:3. When **2** is protonated at −40 °C in acetone with HOTf, this ratio increases to 4:1. Heating **5** at 40 °C over a period of 3 days results in significant decomposition, thus preventing the determination of an equilibrium constant.

The stereochemistry at C2 of the 2*H*-thiophenium complex **5** is consistent with the proton adding to the face of the thiophene opposite to the metal. This is most evident in compound **5D**. Single crystal X-ray diffraction data indicate that the methyl group of C2 is pushed in toward the metal (Figure 4). The crystal structure was found to be internally disordered, and as a result, meaningful bond lengths and angles could not be obtained. However, the basic stereochemical features illustrated in Figure 3 are unmistakable, the most significant feature being the syn relationship of the metal and C2 methyl group. The chemical shift of this methyl group (0.16 ppm) is unusually low, a characteristic of substituents in quadrant b (vide supra). That the methyl is oriented toward the metal in solution is suggested also by NOESY interactions between the **5D** methyl and two pyrazole peaks at 8.57 and 8.18 ppm. The methyl group in **5B** is also assigned to be syn to the metal on the basis of proton−proton coupling and NOE data. In particular, the methyl group of **5B** (1.54 ppm) shows an NOE interaction with a pyrazole proton (8.30 ppm), and the H2 proton for **5B** (3.39 ppm) couples with H3 (J = 6 Hz), the same coupling constant observed for **5D.** Additionally, chemical shifts for **5B** and **5D** (Table 4) are very similar, confirming that these two species are stereoisomers, not constitutional isomers.

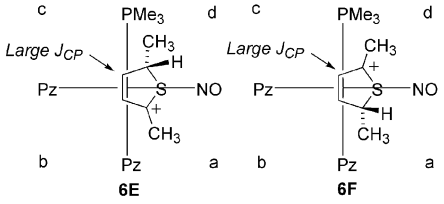

Figure 5. 2*H*-Thiophenium complexes **6E** and **6F**.

The compound **4**-*d* was prepared by treating the thiophene complex **1** with DPhAT in CH_3OD. Early ^1H NMR spectra of the resulting solution confirmed that protonation occurred selectively at what is assumed to be the anti position ($H2_{anti}$). However, upon isolation of this compound, the deuterium had scrambled with an undetermined proton source. A similar result occurred with the preparation of **5**-*d*.

Compound **3** can be protonated using DPhAT to form **6** in 82% yield. Although mass spectral data support the molecular formula for the intended thiophenium complex, proton and carbon NMR data differ dramatically from those reported for **4** and **5**. Compound **6** is formed as a mixture of two diastereomers, **6E** and **6F**, in a kinetic ratio ranging from 15:1 to 1.5:1 depending on reaction conditions (Figure 5). Protonating compound **3** in acetonitrile delivers a 1.5:1 ratio of **6E** to **6F**, and in methanol, the ratio rises to 15:1. The identification of the diastereomers was accomplished using 1D and 2D NMR experiments. The C3 carbon in **6E** has a ^{13}C doublet at 81.7 ppm, and the C4 carbon in **6F** has a ^{13}C doublet at 86.1 ppm. Both of these resonances are split into doublets by ^{13}P, indicating that the corresponding carbons are positioned toward the PMe_3 ligand.

However, the most strikingly unusual resonance is C5, which is considerably downfield (C5 at 218.1 and 216.6 ppm for **6E** and **6F**, respectively) from the resonance for other 2*H*-thiophenium complexes. A detailed NMR analysis suggests that the two isomers of thiophenium **6** are bound through C3 and C4, but *not* C5, which has a chemical shift which approximates that of an uncoordinated carbocation.[22] For comparison, two η^2-benzenium complexes have previously been reported: the η^2-*m*-xylenium complex of osmium(II)[23] (two diastereomers, with the cationic carbon at 190.9 and 170.4 ppm) and TpRe(CO)(L)(η^2-naphthalenium) (L = pyridine, DMAP) (105.4 ppm).[24,25] In contrast, the analogous rhenium fragment TpRe(PMe_3) forms η^3-naphthalenium complexes in which the NMR data for all three bound carbons are about equal (73−78 ppm).[25]

Reduction of the bound thiophene was achieved by catalytic hydrogenation. A solution of thiophene complex **1** was subjected to an atmosphere of hydrogen (1 atm; 20 °C) in the presence of an equal mass of Pd/C (10%). NMR data for the product (**7**; 22%) indicate a mixture of two coordination diastereomers in a 1:1 ratio. ^{13}C NMR and $^{13}C-^1H$ correlation data confirm the assignment of the two dihydrothiophene isomers (**7A** and **7B**)

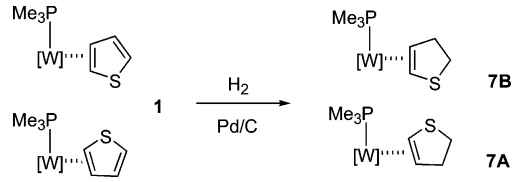

Figure 6. Hydrogenation of thiophene bound to tungsten.

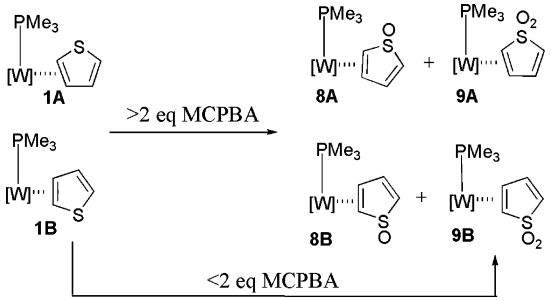

Figure 7. Oxidation of the thiophene complex to form oxo- and dioxothiophene complexes.

shown in Figure 6. The low yield was attributed to absorption of the product by the carbon support. While using a lower catalyst loading improved the recovery of mass (80% yield at 50 mg of Pd−C/200 mg of complex), the reaction was observed repeatedly to stop at about 50% completion, presumably as a result of poisoning. Although the yield is low, we note that hydrogenation of thiophene itself typically requires elevated temperatures and pressures or strongly acidic solutions.[26,27]

Remarkably, the thiophene in compound **1** can be oxidized to a 1,1-dioxide complex (**9**) with 3-chloroperbenzoic acid (MCPBA) *without oxidizing the metal*. Similar findings were reported for the pentaammineosmium(II) analogue.[10] When 100 mg of compound **1** was reacted with 0.8 equiv of MCPBA, 90 mg of TpW(NO)(PMe_3)(η^2-4,5-thiophene-1-oxide) (**8**) and TpW(NO)(PMe_3)(η^2-4,5-thiophene-1,1-dioxide) (**9**) was obtained in a 4:2:1 ratio of **8B** to **8A** to **9B** (Figure 7). The major product is that of single oxidation (**8A** and **8B**), while the minor product is the dioxide **9B**, with the SO_2 group oriented away from the phosphine. When only 0.5 equiv of MCPBA is used, a small quantity of the sulfoxide **8B** was precipitated from solution (hexanes) in sufficient purity to allow its partial characterization.[28] When over 2 equiv of MCPBA was used with **1**, then only **9B** was formed in 46% yield. The weaker oxidant 4-methylmorpholine *N*-oxide was unreactive with compound **1**. Although thiophene itself can readily be oxidized to a dioxide, the resulting dioxide is unstable and rapidly undergoes dimerization.[29]

Alkylation Reactions. Compounds **1** and **2** can be alkylated at sulfur with methyl triflate to form the *S*-methylthiophenium complexes **10** and **11** in 79−88% yield (Figure 8). Methylation occurs rapidly at room temperature, and the formation of diastereomers is observed for both complexes in a 1:2.5 ratio for **A**:**B**. This

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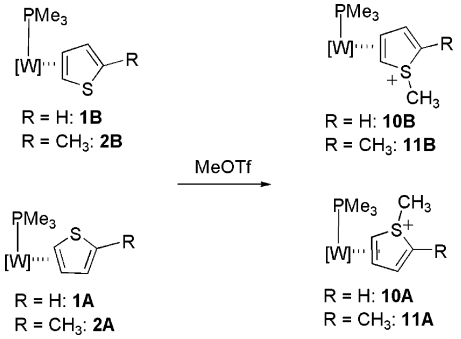

Figure 8. Methylation of η^2-thiophene complexes **1** and **2**.

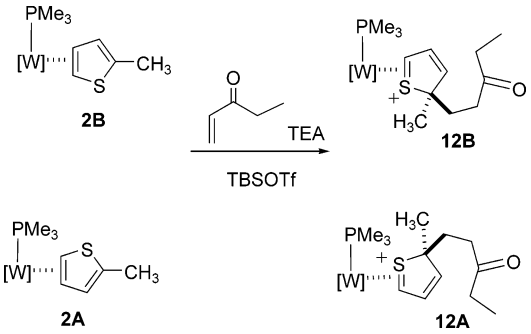

Figure 9. Thiophene alkylation at C2 with Michael acceptors.

A:**B** ratio, when the solution was allowed to equilibrate (3 days, 20 °C), reaches 1:4. Similar S-methylation can be accomplished with the osmium(II) thiophene analogues,[9] and the resulting thiophenium complexes are susceptible to nucleophilic addition at C5, producing 1-substituted η^2-4-(methylthio)-1,3-butadiene complexes in good yields. Attempts to add nucleophiles to compounds **10** and **11** were unsuccessful. Hydride additions to **10** were attempted with $NaBH_4$ and $LiAlH_4$, but the former resulted in no reaction, while the latter resulted in decomposition. Bases such as pyridine, DBU, and KO-*t*-Bu were also unreactive with **10**; however, when DBU or KO-*t*-Bu was added to a CD_3OD solution of **10**, the exchange of the *S*-methyl protons was observed, suggesting the formation of a sulfur ylide intermediate. When benzaldehyde was added to a mixture of base and **10**, compound **1** was recovered in good yield. 1-Phenyl-1-benzothiophenium salts undergo cycloaddition with both cyclopentadiene and 1,3-diphenylisobenzofuran in refluxing methylene chloride.[30] Each of the dienes were combined with the *S*-methylthiophenium complex **10**, but cycloaddition was not observed (16 h, 40 °C).

C2 Alkylation. For softer carbon electrophiles, alkylation can take place at carbon. Methyl vinyl ketone (MVK) and ethyl vinyl ketone (EVK) undergo reactions with thiophene complexes **1** and **2** to give 2*H*-thiophenium complexes analogous to **4** and **5** (Figure 9). The reaction was best accomplished in methylene chloride, with 2 equiv of *tert*-butyldimethylsilyl triflate (TBSOTf), 2 equiv of the ketone, and 1 drop of triethylamine (TEA). A number of reaction conditions were tested in an attempt to improve the electrophilic addition of enones to thiophene. Changing the solvent was among the first variables tested. In THF, a polymer is formed under the

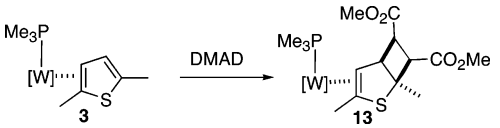

Figure 10. [2 + 2] cycloaddition of DMAD and η^2-thiophene.

acid conditions, and in acetonitrile, there was a loss of the thiophene ligand, which was replaced by an η^2-bound acetonitrilium ligand.[31] TBSOTf was the only Lewis acid to promote Michael addition but did so with poor reproducibility under similar conditions. The addition of a base, to prevent the side reaction of protonation,[32] was also important in the successful addition of an electrophile. TEA produced the best results, whereas DBU caused the reaction to oil upon isolation, and lutidine was not a strong enough base to deprotonate the thiophenium. Reactions with other Michael acceptors (cyclopent-2-en-1-one, methyl acrylate, methyl propiolate, butyn-2-one) were attempted but were unsuccessful under even the best conditions for EVK and MVK.

Alternatively, when the 2,5-dimethylthiophene compound **3** is combined with DMAD (no additional promotor is needed), a net [2 + 2] cycloaddition occurs, forming TpW(NO)(PMe_3)(3,4-η^2-3-dimethyl-2-thiabicyclo-[3.2.0]hepta-3,6-diene-6,7-dicarboxylic acid dimethyl ester) (**13**; Figure 10). Compound **13** was isolated as one diastereomer in low yields, due to a competing oxidation of the metal. A similar [2 + 2] cycloaddition had been observed with the TpRe(CO)(MeIm)(4,5-η^2-2,5-dimethylfuran) and DMAD.[33] Compound **13** was oxidized with AgOTf and heated in an attempt to liberate the bicyclic ligand, but the reaction was unsuccessful. Other alkenes or alkynes (butyn-2-one, methyl propiolate) were found to not participate in the [2 + 2] cycloaddition with **3**.

Discussion

Although thiophenes have been observed to form complexes with hapticities ranging from 1 to 5, very few examples exist in which the thiophene is η^2 coordinated.[14,15,34,35] Complexes of rhenium, osmium, and molybdenum are known, but significantly, virtually nothing has been reported about the reactivity of η^2-coordinated thiophene other than for the complex $[Os(NH_3)_5(\eta^2\text{-thiophene})]^{2+}$.[9,10] Given the important role that Mo and W play in the HDS process,[1,2] it is particularly important to map out the fundamental reaction chemistry for different coordination modes with these metals.

The η^2 coordinate binding mode is less common for 16-electron metal complexes than is the η^1, or S-bound, form.[4] While not observed for the tungsten complexes reported herein, the S-bound isomer has been observed in equilibrium with the η^2-bound isomer for the related complexes TpRe(CO)(^{t}BuNC)(thiophene) and TpRe(CO)-

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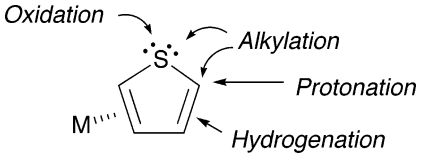
(PMe_3)(thiophene), which exist as η^2/η^1 mixtures in 1.2:1 and 5.2:1 ratios, respectively.[15,36] The more electron-rich TpRe(CO)(MeIm)[37] fragment has a reduction potential similar to that of the TpW(NO)(PMe_3) system and only forms η^2 isomers (cf. TpRe(CO)(^{t}BuNC)(η^2-thiophene), $E_{p,a}$ = 0.55 V; TpRe(CO)(PMe_3)(η^2-thiophene), $E_{1/2}$ = 0.01 V; TpRe(CO)(MeIm)(η^2-thiophene), $E_{p,a}$= −0.03 V; **1**, $E_{p,a}$ = −0.02 V).[16,19]

By disrupting the aromatic stabilization of thiophene, coordination of the heterocycle enhances the reactivity pattern of the native heterocycle.



The most fundamental reaction explored in this context was protonation, which occurs at C2, similar to that found for η^4-thiophenes[4] and for thiophene itself.[21] What is remarkable is the degree to which the basicity is enhanced. The back-bonding resulting from tungsten coordination stabilizes the thiophenium ligand to the point that its acidity is similar to that of an ammonium salt (pK_a estimated between 7 and 12). In contrast, thiophene itself can only be protonated with superacids.[21] Furthermore, whereas η^4-thiophene complexes undergo endo protonation, the tungsten thiophene complexes discussed herein undergo exo protonation (vide supra), similar to the case for the pentaammineosmium(II) analogue.[14]

The asymmetric metal center and high rotational barrier of the thiophenium and thiophene complexes provide insight into the mechanism of protonation. Given that the initial ratio of coordination diastereomers for thiophene complex **1** is 1:1 (A:B) (see Figure 1), a similar ratio of corresponding thiophenium complexes would be expected (i.e., the ratio **4A**:**4B**; see Figure 2), *provided* that protonation occurred directly to the 4,5-η^2 isomers. Instead of **4A**, the diastereomer that appears with **4B** is **4C** (1:1 ratio), the thermodynamically unstable rotamer of **4B**. While it is possible that the thiophene diastereomer **C** is present at low (but undetectable) concentrations at equilibrium, it would have to have a specific rate of protonation over 20 times greater than that of diastereomer **B** in order to explain the kinetic ratio of thiophenium isomers (given that by NMR [**C**] < 0.05[**B**]). More likely is the possibility that protonation occurs from a more reactive constitutional isomer such as the S-bound isomer (Figure 11). Studies with other metals indicate that the kinetic barrier for η^2-coordinated thiophene conversion to its S-bound isomer is low (cf. 15−18 kcal/mol for TpRe(CO)(^{t}BuNC)-(η^2-thiophene)).[36] We propose not only that the sulfur-bound intermediate is not only energetically accessible and more basic but also that it exists as a mixture of rotamers, which are not as sensitive to the steric influence of the ligand set as suggested in Figure 11. Upon protonation, the 2*H*-thiophenium ligand returns to η^2 coordination (bound across C5 and sulfur). The

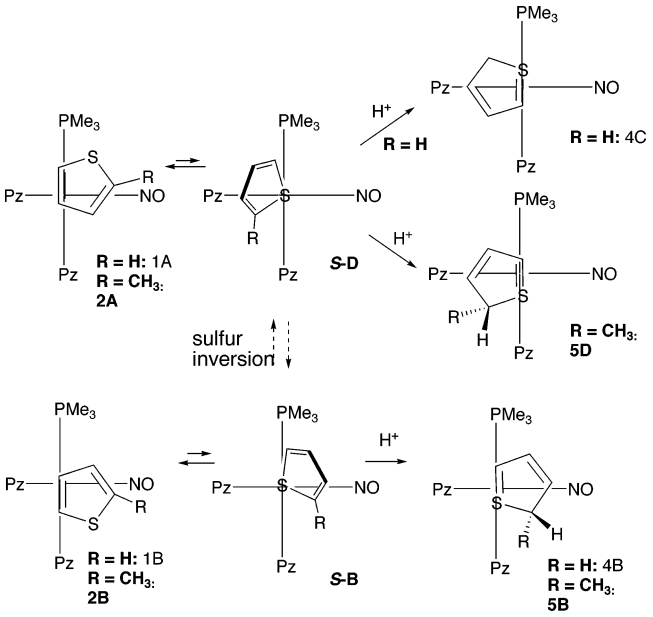
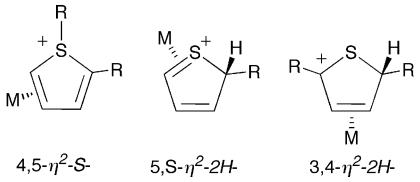


Figure 11. Proposed mechanism of bound thiophene protonation.

Chart 1



observation that deuteration is initially stereoselective would be consistent with either η^2-thiophene or η^1-thiophene protonation. In the latter case, the metal does not lie in the plane of the heterocycle but is canted, and this is consistent with sp^3 hybridization of the heteroatom.[38] Angelici has reported the structure of Cp*Re-(CO)$_2$(*S*-η^1-thiophene),[39,40] confirming this geometry.

The 2-methylated analogue **2** likely has rotamers in which the methyl groups are directed away from the phosphine ligands (see Figure 9). The two 2*H*-thiophenium isomers initially formed from **2** (**5B** and **5D**) conform to these expectations (see Figure 9). In addition, the methyl group at C2 would be expected to lower the concentration of the purported S-bound isomer, and thus the rate of protonation would be slower (observed to be true). Furthermore, according to the principle of microscopic reversibility, deprotonation would be slower for the 2-methylthiophenium complex than for the thiophene analogue because, as with protonation, the first step would be an η^2-to-sulfur linkage isomerization.

Of the three unusual thiophenium constitutional isomers observed (Chart 1), the 3,4-η^2-2*H* form is the most remarkable, and to our knowledge, its structure is unprecedented. According to ^{13}C NMR data for **6**, the C5 carbons of **6E** and **6F** approximate uncoordinated carbocations. Apparently, the C5 methyl group stabilizes

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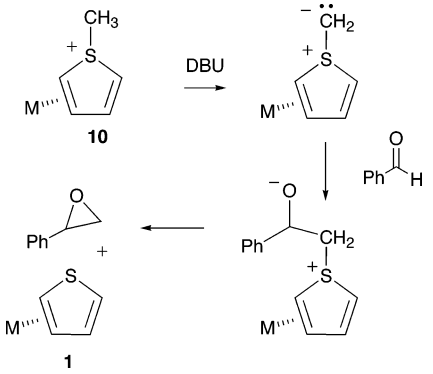

Figure 12. Proposed mechanism of demethylation of thiophenium **10**.

this carbocation through hyperconjugation while also destabilizing the C5−S linkage isomer (cf. **4** or **5**), as a result of its steric interaction with the metal fragment. Its formation could come about either by a linkage isomerization of the 5,S-2H isomer or directly from the protonation of the 4,5-η^2 thiophene isomer. Our limited observations for this process do not favor one mechanism over the other.

Beyond protonation, several other reactivity patterns emerge for η^2-coordinated thiophenes. Similar to what is observed for the complex $[Os(NH_3)_5(\eta^2\text{-thiophene})]^{2+}$,[10] the nucleophilic sulfur can be both alkylated and oxidized. Treatment with MCPBA forms both the monooxo (**8**) and dioxo (**9**) complexes directly from the η^2-thiophene precursor **1**. Weiss et al. have reported the thiophene dioxide complex $Fe(CO)_2(P(OMe)_3)_2(\eta^2\text{-}C_4H_4SO_2)$, prepared directly from the dioxide ligand.[41] Thiophene dioxide itself is stable in solution for only brief periods.[29] Angelici and Chen have reported the reaction of IrCp*(η^4-2,5-dimethylthiophene) with $(CH_3)_3O^+$ to form the corresponding *S*-thiophenium complex,[42] but nothing was reported about the reactivity of the resulting complex. In the case of the methylthiophenium complex **10** the complex is remarkably stable, even in the presence of water and base. Rather than demethylate, a solution of **10** in methanol-d_4 and DBU undergoes deuterium exchange. This suggests that the sulfur ylide is accessible, as shown in Figure 12. To test for this intermediate, the reaction was repeated with benzaldehyde. Peralkylated thiophene ylides have been reported to form epoxides from aryl aldehydes, and the reaction of **10** with benzaldehyde to return **1** is suspected to occur by a similar mechanism (Figure 12).

Perhaps the most significant reaction observed for the thiophene complex **1** is its reaction with H_2 in the presence of a Pd catalyst. η^2-Coordinated thiophene complexes have long been postulated as key intermediates in the HDS process,[43] but the dearth of model η^2-thiophene complexes, especially for group 6, has prevented confirmation that this coordination mode activates the heterocycle toward hydrogenation. Coordination by the heteroatom, while not a serious problem for the tungsten, does apparently cause problems with the palladium, at least under our experimental conditions. As a result of this Pd poisoning, large catalyst loadings (10 mg of Pd/100 mg of **1**) were required to complete the reaction. The only other example of hydrogenation reported for an η^2-thiophene complex is for $[Os(NH_3)_5(\eta^2\text{-thiophene})]^{2+}$.[44]

Conclusion

The η^2 coordination of thiophenes by tungsten renders the heterocyclic ligand susceptible to mild hydrogenation, protonation, and oxidation at sulfur. In addition, both the sulfur and ring carbons can be alkylated, even in the case where a quaternary carbon is created. Presumably, similar chemical pathways become available with molybdenum coordination as well, and we are currently pursuing this possibility.

Experimental Section

General Methods. NMR spectra were obtained on a 300 or 500 MHz Varian INOVA spectrometer or a Bruker 300 or 500 MHz Avance spectrometer. All chemical shifts are reported in ppm and are referenced to tetramethylsilane (TMS) utilizing residual ^1H and ^{13}C signals of the deuterated solvents as internal standards. Coupling constants (*J*) are reported in hertz (Hz). Infrared spectra (IR) were recorded on a MIDAC Prospect Series (Model PRS) spectrometer as a glaze on a horizontal attenuated total reflectance (HATR) accessory (Pike Industries). Electrochemical experiments were performed under a dinitrogen atmosphere using a BAS Epsilon EC-2000 potentiostat. Cyclic voltammograms (CV) were recorded at 100 mV/s (25 °C) (unless otherwise specified) in a standard three-electrode cell from +1.7 to −1.7 V with a glassy-carbon working electrode, *N*,*N*-dimethylacetamide (DMA) solvent, and tetrabutylammoniumhexaflurophosphate (TBAH) electrolyte (∼0.5 M). All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = −0.78 V) or ferrocene ($E_{1/2}$ = 0.55 V) as an internal standard. The peak-to-peak separation was less than 100 mV for all reversible couples. Elemental analysis (EA) was obtained from Atlantic Microlabs, Inc. or with a Perkin-Elmer 2400 Series II CHNS/O analyzer. Unless otherwise noted, all synthetic reactions and electrochemical experiments were performed under a dry nitrogen atmosphere. Mass spectra were obtained on a JEOL JMS600 using FAB+ or a Shumadzu GCMS QP5050 by direct inlet; no counterions were observed. CH_2Cl_2, benzene, THF (tetrahydrofuran), and hexanes were purged with nitrogen and purified by passage through a column packed with activated alumina. Other solvents and liquid reagents were thoroughly purged with nitrogen prior to use. Deuterated solvents were used as received from Cambridge Isotopes.

TpW(NO)(PMe$_3$)(4,5-η^2-thiophene) (1A and 1B). TpW(NO)(PMe$_3$)(Br)[17] (9.85 g, 16.9 mmol) was dissolved in thiophene (100 mL). Sodium metal (11.8 g) was added, and the solution was stirred for 18 h. The solution was placed on 2.5 cm of Celite, wetted with benzene, in a 350 mL glass filter. The Celite was washed with 500 mL of benzene. The filtrate was then purified on a 5 cm silica plug, wetted with benzene on a 600 mL glass filter. The product, a bright yellow band, was eluted with diethyl ether (2 L) followed by a 1/1 diethyl ether/THF mixture (300 mL). The filtrate was evaporated to 200 mL and diluted with pentane (1 L), and the precipitate was collected on a 60 mL medium-porosity glass filter and dried in vacuo. The previous step was repeated using the filtrate, and an orange-yellow solid (3.10 g 31.2% yield) was obtained of **1A** and **1B** (1:1 ratio). ^1H NMR (acetone-d_6): δ 8.69 (d, J = 1.8 Hz, 1H, Tp B), 8.29 (d, J = 1.8 Hz, 1H, Tp A), 8.04 (d, J = 2.0 Hz, 1H, Tp), 7.99 (d, J = 2.0 Hz, 1H, Tp), 7.96 (dd, J = 2.4, 2.4 Hz, 2H, Tp, Tp), 7.91 (dd, J = 1.8, 2.2 Hz, 2H, tp, Tp),

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7.85 (d, J = 2.4 Hz, 1H, Tp), 7.81 (d, J = 2.4 Hz, 1H, Tp), 7.54 (d, J = 2.2 Hz, 1H, Tp), 7.42 (d, J = 2.0 Hz, 1H, Tp), 6.61 (dd, J = 5.3, 2.6 Hz, 1H, 3A), 6.40 (dd, J = 5.3, 2.6 Hz, 1H, 3B), 6.37 (q, J = 2.2, 2.0, 4.2 Hz, 2H Tp), 6.31 (t, J = 2.2, 2.2 Hz, 2H, Tp), 6.26 (q, J = 2.2, 2.4, 4.6 Hz, 2H, Tp), 5.72 (dd, J = 5.7, 5.7 Hz, 2H, 2A, 2B), 5.10 (ddd, J = 0.9, 8.1, 4.1 Hz, 1H, 5A), 4.40 (dddd, J = 2.6, 2.9, 8.1, 12.8 Hz, 1H, 4B), 3.36 (ddd, J = 0.9, 2.9, 5.3 Hz, 1H, 5B), 2.77 (dt, J = 2.6, 5.3 Hz, 1H, 4A), 1.34, (d, J = 8.1 Hz, 9H, PMe_3 B), 1.32 (d, J = 8.4 Hz, 9H, PMe_3 A). ^{13}C NMR (acetone-d_6): δ 144.7, 143.6, 142.0, 139.6, 137.5, 136.9, 136.4, 136.1 (Tp 3- and 5-positions), 130.3 (3A), 130.0 (3B), 117.0 (2A and 2B), 107.1, 107.0, 106.8, 106.7, 106.2 (Tp 4-positions), 67.5 (5B), 67.2 (4B), 65.9 (4A), 65.7 (5A), 13.9 (d, PMe_3 B), 13.4 (d, PMe_3 A). Anal. Calcd: C, 33.97; H, 4.19; N, 16.31. Found: C, 33.66, H, 4.18; N, 16.95. CV: E_{pa} = −0.02 V, E_{pa} = 0.50 V. IR: $\nu_{N\equiv O}$ 1564 cm^{-1}. Low-resolution mass spectrometry (LRMS): calcd, 587.1; found, 587.1.

TpW(NO)(PMe_3)(4,5-η^2-2-methylthiophene) (2A and 2B). TpW(NO)(PMe_3)(Br) (2.92 g, 5.0 mmol) was dissolved in 2-methylthiophene (10 mL). Sodium amalgam (11.5 g, 1 wt %) was added, and the solution was stirred for 18 h. The solution was placed on 2.5 cm of Celite, wetted with benzene, in a 150 mL medium-porosity glass filter. The Celite was washed with benzene (200 mL). The filtrate was then placed on a 5 cm silica plug, wetted with benzene, in a 150 mL glass filter. A yellow product band was eluted with diethyl ether (1 L). The filtrate was evaporated to dryness, and the residue was dissolved in methylene chloride (2 mL) and then precipitated from pentane (200 mL), collected on a fine-porosity glass filter, and dried in vacuo. Compound **2** was isolated (1.20 g, 39.9% yield) as a yellow solid in a 1.5:1 ratio of **2A** to **2B**. ^1H NMR (acetone-d_6): δ 8.74 (d, J = 2.0 Hz, 1H, Tp), 8.33 (d, J = 1.7 Hz, 1H, Tp), 8.01 (d, J = 1.7 Hz, 1H, Tp), 7.99 (d, J = 1.7 Hz, 1H, Tp), 7.94 (t, J = 2.4, 2.0 Hz, 2H, Tp), 7.88 (t, J = 2.4, 2.4 Hz, 2H, Tp), 7.83 (d, J = 2.4 Hz, 1H, Tp), 7.80 (d, J = 2.3 Hz, 1H, Tp), 7.50 (d, J = 2.0 Hz, 1H, Tp), 7.37 (d, J = 2.0 Hz, 1H, Tp), 6.36 (t, J = 2.3, 2.0 Hz, 3H, 3A, Tp4, Tp4), 6.31 (q, J = 2.0, 2.4, 4.4 Hz, 2H, Tp4, Tp4), 6.25 (p, J = 2.0, 2.4, 3.4, 4.4 Hz, 2H, Tp4, Tp4), 6.16 (s(br), 1H, 3A), 5.05 (dd, J = 3.7, 8.4 Hz, 1H, 5B), 4.32 (m, 1H, 4A), 3.31 (dd, J = 2.7, 8.4 Hz, 1H, 5A), 2.64 (m, 1H, 4B), 2.28 (s, 3H, 2Me-B), 2.25 (s, 3H, 2Me-A), 1.47 (d, J = 8.1 Hz, 9H, PMe_3-A), 1.32 (d, J = 8.4 Hz, 9H, PMe_3-B). ^{13}C NMR (acetone-d_6): δ 144.1, 143.0, 141.2, 141.2, 139.2, 136.7, 136.1, 135.7 (Tp 3- and 5-positions), 127.5 (3B), 127.3 (3A), 106.4, 106.1, 105.5 (Tp 4-positions), 67.7 (5A), 66.6 (4A), 66.3 (4B), 66.0 (5B), 13.8 (PMe_3 B), 13.5 (PMe_3 A), 13.0 (2-MeB), 12.7 (2-Me A). CV: $E_{p,a}$ = 0.04 V, $E_{p,a}$ = 0.46 V. IR: $\nu_{N\equiv O}$ =1565 cm^{-1}. Anal. Calcd: C, 33.97; H, 4.19; N, 16.31. Found: C, 33.66; H, 4.18; N, 16.95. LRMS: calcd, 601.1; found, 600.9.

TpW(NO)(PMe_3)(4,5-η^2-2,5-dimethylthiophene) (3B and 3D). TpW(NO)(PMe_3)(Br) (3.04 g, 5.2 mmol) was dissolved in 20 mL of 2,5-dimethylthiophene. Sodium amalgam (51 g, 1 wt %) was added, and the solution was stirred for 18 h. The solution was placed on 2.5 cm of Celite, wetted with benzene in a 60 mL glass filter. The Celite was washed with benzene (200 mL). The filtrate was then placed on a 5 cm silica plug, that was wetted with benzene, in a 150 mL glass filter. A yellow product band was eluted with 2/1 benzene/diethyl ether (50 mL) followed by 100% diethyl ether (300 mL). The solution was evaporated to dryness, and the remaining residue was dissolved in THF (6 mL), precipitated in pentane (200 mL), collected on a 60 mL fine-porosity glass filter, and dried in vacuo. Compound **22** was isolated (1.121 g, 35.4% yield) as a yellow solid in a 3:1 ratio of B to D. ^1H NMR (acetone-d_6) for isomer B: δ 8.75 (d, J = 2.0 Hz, 1H, Tp), 7.94 (d, J = 2.0 Hz, 1H, Tp), 7.90 (d, J = 2.4 Hz, 2H, Tp), 7.87, (d, J = 2.4 Hz, 1H, Tp), 7.58 (d, J = 2.0 Hz, 1H, Tp), 6.36 (t, J = 2.0, 2.4 Hz, 1H, Tp4), 6.33 (t, J = 2.0, 2.4 Hz, 1H, Tp4), 6.28 (t, J = 2.0, 2.4 Hz, 1H, Tp4), 6.2 (m, 1H, 3), 3.73 (dd, J = 1.3, 11.4 Hz, 1H, 4), 2.20 (s, 3H, 2-Me), 1.36 (d, J = 8.1 Hz, 9H, PMe_3), 1.00 (s, 3H, 5-Me). ^{13}C NMR (acetone-d_6) for isomer B: δ 143.7, 142.2, 139.2, 136.6, 135.9 (Tp 3- and 5-positions), 128.5 (3), 106.2, 106.1, 105.9 (Tp 4-positions), 72.5 (4), 24.7 (5-Me), 13.7 (2-Me), 13.3 (PMe_3). ^1H NMR for isomer D (acetone-d_6): δ 8.30 (d, J = 2.0 Hz, 1H, Tp), 8.07 (d, J = 2.0 Hz, 1H, Tp), 8.03 (d, J = 2.4 Hz, 1H, Tp), 7.87 (d, buried 1H, Tp), 7.81 (d, J = 2.0 Hz, 1H, Tp), 7.79 (d, J = 2.4 Hz, 1H, Tp), 6.37 (t, buried, 1H, Tp), 6.4 (t, buried, 1H, Tp), 6.15 (t, J = 2.4 Hz, 1H, Tp), 5.00 (s, 1H, 3), 4.22 (s, 1H, 4), 2.42 (s, 3H, 5-Me), 1.62 (t, J = 1.0, 1.3 Hz, 3H, 2-Me), 1.30 (d, J = 8.4 Hz, PMe_3). ^{13}C NMR for isomer D (acetone-d_6): δ 144.2, 142.7, 141.6, 135.6, 135.5, 135.5 (Tp 3- and 5-positions), 107.0, 106.2, 104.7 (Tp 4-positions), 126.4 (3), 77.8 (4), 31.0 (5-Me), 15.0 (2-Me), 12.3 (PMe_3). CV: $E_{p,a}$ = 0.13 V. IR: $\nu_{N\equiv O}$ 1564 cm^{-1}. LRMS: calcd, 615.1; found, 615.0.

TpW(NO)(PMe_3)(*S*,5-η^2-thiophenium)(OTf) (4A, 4B, and 4C). Compound **1** (100 mg, 0.17 mmol) and DPhAT (55 mg, 0.17 mmol) were mixed in acetone (2 mL). After a few minutes the solution was added slowly to pentane (50 mL) and the precipitate was collected on a 15 mL fine-porosity glass filter and dried in vacuo. Compound **4** was collected (114 mg, 90.8% yield) as a peach-colored solid. ^1H NMR (acetone-d_6) of isomer A: δ 8.43, (d, J = 2.0 Hz, 1H, Tp), 8.22 (d, J = 2.4 Hz, 1H, Tp), 8.18 (d, J = 2.4 Hz, 1H, Tp), 8.16, (d, J = 2.4 Hz, 1H, Tp), 7.98 (d, J = 2.4 Hz, 1H, Tp), 7.65 (d, J = 2.4 Hz, 1H, Tp), 7.00 (ddd, J = 2.7, 3.4, 5.7 Hz, 1H, 4), 6.53, (t, J = 2.4, 2.4 Hz, 1H, Tp4), 6.49 (t, J = 2.0, 2.7 Hz, 1H, Tp4), 6.43 (t, J = 2.0, 2.7 Hz, 1H, Tp4), 5.55 (m, J = 2.7, 3.4, 5.7 Hz, 1H, 3), 4.91 (m, J = 18.1, 2.0, 3.7 Hz, 1H, 2), 4.44 (s (br), 1H, 5), 4.29 (ddd, J = 2.7, 2.4, 17.5 Hz, 1H, 2), 1.50 (d, J = 9.7 Hz, 9H, PMe_3). ^{13}C NMR (acetone-d_6) of isomer A: δ 146.1, 143.6, 138.2 (Tp 3- and 5-positions), 109.2, 108. (Tp 4-positions), 135.3 (4), 119.9 (3), 82.1 (5), 47.0 (2), 12.88 (PMe_3). ^1H NMR (acetone-d_6) of isomer B: δ 8.58 (d, J = 2.2 Hz, 1H, Tp5), 8.30 (d, J = 1.9 Hz, 1H, Tp), 8.20 (d, J = 2.2 Hz, 1H, Tp), 8.14 (d, J = 2.2 Hz, 1H, Tp3), 8.06 (t, J = 3.4, 2.5 Hz, 2H, Tp3, Tp3), 7.09 (m, J = 2.2, 2.5 Hz, 1H, 4), 6.60 (t, J = 2.2, 2.5 Hz, 1H, Tp4), 6.58 (buried, 1H, 5), 6.54 (t, J = 2.2, 2.5 Hz, 1H, Tp4), 6.40 (t, J = 2.2, 2.5 Hz, 1H, Tp4), 5.69 (ddd, J = 3.1, 2.8, 2.5 Hz, 1H, 3), 4.38 (dd, J = 18.1 Hz, 2), 2.91 (d, J = 20.0, 2.8, 2.5 Hz, 1H, 2), 1.47 (d, J = 9.7 Hz, 9H, PMe_3), ^{13}C NMR (acetone-d_6) of isomer B: δ 147.8, 147.1, 145.7, 139.8, 139.6, 138.7 (Tp 3- and 5-positions), 136.5 (4), 128.7 (3), 109.2, 108.7, 107.7 (Tp 4-positions), 89.0 (d, 5), 40.8 (2), 13.3 (d, PMe_3). ^1H NMR (acetone-d_6) of isomer C: δ 8.54 (d, J = 2.2 Hz, 1H, Tp3), 8.36 (d, J = 2.2 Hz, 1H, Tp), 8.17 (d, J = 2.2 Hz, 1H, Tp), 8.09 (d, J = 2.2 Hz, 1H, Tp5), 8.03 (d, J = 2.2 Hz, 1H, Tp5), 7.48 (d, J = 2.2 Hz, 1H, Tp3), 6.58 (t, J = 2.5, 2.2 Hz, 1H, Tp4), 6.51 (t, J = 2.5, 2.2 Hz, 1H, Tp4), 6.37 (t, J = 2.5, 2.2 Hz, 1H, Tp4), 6.15 (m, 1H, 5), 5.59 (ddd, J = 2.9, 1.9, 3.8 Hz, 1H, 4), 5.39 (dd, J = 2.5, 3.4 Hz, 1H, 3), 4.87 (dd, J = 19.1, 2.2 Hz, 1H, 2), 4.38 (dd, J = 18.1, 2.2 Hz, 1H, 2), 1.54 (d, J = 9.7 Hz, 9H, PMe_3), ^{13}C NMR (acetone-d_6) of isomer C: δ 145.7, 143.9, 143.6, 139.2, 139.0, 138.2 (Tp 3- and 5-positions), 135.1 (4), 125.6 (3), 108.9, 108.7, 108.3 (Tp 4-positions), 82.8 (5), 44.3 (2), 12.4 (PMe_3). CV: $E_{p,a}$ = −1.47 V, $E_{p,a}$ = 1.07 V. IR: $\nu_{N\equiv O}$ 1630 cm^{-1}. LRMS: calcd, 588.1; found, 588.3. Anal. Calcd: C, 28.78; H, 3.49; N, 13.05. Found: C, 28.80; H, 3.54; N, 13.05.

TpW(NO)(PMe_3)(*S*,5-η^2-2-methylthiophenium)(OTf) (5B and 5D). Compound **2** (500 mg, 0.83 mmol) was dissolved in CH_2Cl_2 (5 mL) followed by addition of DPhAT (291 mg, 0.91 mmol) and the solution stirred for 2 min. The solution was then added to ether (100 mL), and the precipitate was collected as an orange solid on a 30 mL fine-porosity glass filter and dried in vacuo. Compound **5** was obtained in a 3:1 ratio of B to D (495 mg, 79.3% yield). ^1H NMR (acetone-d_6) of isomer B: δ 8.64 (d, J = 1.7 Hz, 1H, Tp), 8.30 (d, J = 1.7 Hz, 1H, Tp), 8.21 (d, J = 2.4 Hz, 1H, Tp), 8.14 (d, J = 2.0 Hz, 1H, Tp), 8.07 (t, J = 2.7, 2.7 Hz, 2H, Tp, Tp), 7.03 (m, J = 3.4, 2.7, 2.7, 6.0 Hz, 1H, 4), 6.60 (t, J = 2.4, 2.4 Hz, 1H, Tp4), 6.55 (t, J = 2.4, 2.4 Hz, 1H, Tp4), 6.50 (buried, 1H, 5), 6.40 (t, J = 2.4, 2.4 Hz, 1H, Tp4), 5.63 (dd, J = 1.7, 6.0 Hz, 1H, 3), 3.39 (buried, 1H,

2), 1.54 (d, J = 7.3 Hz, 3H, 2-Me), 1.46 (d, J = 10.1 Hz, 9H, PMe_3). ^{13}C NMR (acetone-d_6) of isomer B: δ 147.5, 145.6, 140.0, 139.7, 138.9 (Tp 3- and 5-positions), 134.9 (4), 132.5 (3), 88.6 (5), 53.1 (2), 22.7 (2-Me), 12.3 (d, J = 32.6 Hz, PMe_3). ^1H NMR (acetone-d_6) of isomer D: δ 8.57 (d, J = 1.7 Hz, 1H, Tp), 8.30 (d, J = 1.7 Hz, 1H, Tp), 8.19 (d, J = 2.0 Hz, 1H, Tp), 8.18 (d, J = 2.4 Hz, 1H, Tp), 8.07 (d, J = 2.4 Hz, 2H, Tp), 6.94 (d, J = 6.0 Hz, 1H, 4), 6.60 (t, J = 2.4, 2.4 Hz, 1H, Tp4), 6.52 (t, J = 2.4, 2.0 Hz, 1H, Tp4), 6.50 (d, J = 2.4 Hz, 1H, 5), 6.44 (t, J = 2.4, 2.4 Hz, 1H, Tp4), 5.59 (dd, J = 2.4, 6.0 Hz, 1H, 3), 5.03 (d, J = 6.4 Hz, 1H, 2), 1.50 (d, J = 9.7 Hz, 9H, PMe_3), 0.16 (d, J = 7.1 Hz, 1H, 2-Me), ^{13}C NMR (acetone-d_6) of isomer D: δ 148.6, 145.5, 139.6, 139.4, 138.4 (Tp 3- and 5-positions), 134.7 (4), 133.4 (3), 109.0, 108.2, 107.6 (Tp 4-positions), 90.2 (5), 53.9 (2), 15.7 (2-Me), 13.1 (d, J = 31.8 Hz, PMe_3). CV: $E_{p,c} = -1.67$ V, $E_{p,a}$ = 0.78 V, $E_{p,a}$ = 1.11 V. IR: $\nu_{N\equiv O}$ 1632 cm^{-1}. LRMS: calcd, 602.1; found, 601.9.

TpW(NO)(PMe_3)(3,4-η^2-2,5-dimethylthiophenium)-(OTf) (6E and 6F). Compound **3** (105 mg, 0.170 mmol) was placed into acetonitrile (1.5 mL) with DPhAT (60 mg, 0.188 mmol) and the solution stirred for 5 min. The solution was added to ether (80 mL), and the precipitate was collected on a fine-porosity glass filter. To the solution was added hexanes (40 mL), and the precipitate was collected on a fine-porosity glass filter and dried in vacuo. Compound **6** was obtained (107 mg, 81.9% yield) as a bright orange solid in a 2:1 ratio of E to F. ^1H NMR (acetone-d_6) of isomer E: δ 8.26 (d, J = 1.8 Hz, 1H, Tp), 8.22 (d, J = 2.2 Hz, 1H, Tp), 8.15 (d, J = 2.2 Hz, 1H, Tp), 8.08 (d, J = 2.0 Hz, 1H, Tp), 8.05 (d, J = 2.2 Hz, 1H, Tp), 7.93 (d, J = 1.8 Hz, 1H, Tp), 6.73 (m, 1H, 2), 6.61 (t, J = 2.2, 2.2 Hz, 1H, Tp4), 6.56 (t, J = 2.2, 2.2 Hz, 1H, Tp4), 6.43 (t, J = 2.2, 2.2 Hz, 1H, Tp4), 5.00 (m, 1 Hz, 3), 4.06 (d, J = 4.2 Hz, 1H, 4), 2.48 (s, 3H, 5-Me), 1.82 (d, J = 6.8 Hz, 3H, 2-Me) 1.24 (d, J = 9.2 Hz, 9H, PMe_3). ^{13}C NMR of isomer E (acetone-d_6): δ 218.1 (5), 146.0, 145.8, 143.0, 139.5, 139.4, 139.2 (Tp 3- and 5-positions), 109.0, 108.8, 107.8 (Tp 4-positions), 92.6 (4), 81.7 (d, J = 14.5 Hz, 3), 62.4 (2), 25.3 (5-Me), 21.2 (2-Me), 14.0 (d, J = 31.6 Hz, PMe_3). ^1H NMR (acetone-d_6) of isomer F: δ 8.31 (d, J = 2.1 Hz, 1H, Tp), 8.29 (d, J = 1.8 Hz, 1H, Tp), 8.20 (d, J = 2.1 Hz, 1H, Tp), 8.14 (d, J = 2.5 Hz, 1H, Tp), 8.02 (d, J = 2.1 Hz, 1H, Tp), 7.93 (d, J = 2.1 Hz, 1H, Tp), 6.59 (t, J = 2.1, 2.4 Hz, 1H, Tp 4), 6.54 (t, J = 2.1, 2.5 Hz, 1H, Tp 4), 6.42 (buried, 1H, Tp 4), 4.92 (dd, J = 6.7, 7.0 Hz, 1H, 2), 4.85 (dd, J = 14.0, 4.0 Hz, 1H, 4), 3.98 (dd, J = 4.0, 1.84 Hz, 1H, 3), 2.64 (s, 3H, 5-Me), 1.75 (d, J = 6.7 Hz, 3H, 2-Me), 1.35 (d, J = 9.5 Hz, 9H, PMe_3). ^{13}C NMR of isomer F (acetone-d_6): δ 216.6 (5), 146.3 (Tp), 146.1 (Tp), 143.5 (Tp), 139.5 (Tp), 139.1 (Tp), 139.0 (Tp), 109.0 (Tp 4), 108.5 (Tp 4), 107.8 (Tp 4), 86.8 (d, J = 15.8 Hz, 3), 86.1 (4), 61.4 (2), 27.9 (5-Me), 24.5 (2-Me), 12.8 (d, J = 31.6 Hz, PMe_3), IR: $\nu_{N\equiv O}$ 1614 cm^{-1}. LRMS: calcd, 616.1; found, 616.1.

TpW(NO)(PMe_3)(4,5-η^2-2,3-dihydrothiophene) (7A and 7B). To a MeOH (10 mL) solution was added 10% Pd−C (113 mg), and the reaction mixture was stirred under a balloon of H_2 gas for 30 min. Then compound **1** (100 mg) was added and stirred under a balloon of H_2 for 2.5 h. The Pd−C was filtered off, and the filtrate was evaporated to dryness. The residue was dissolved in THF (2 mL) and precipitated from pentane (50 mL), and the product was collected on a fine-porosity glass filter and dried in vacuo. The compound **7** was isolated (22 mg, 22% yield) as a white powder. ^1H NMR (acetone-d_6): δ 8.89 (d, J = 2.0 Hz, 1H, Tp), 8.26 (d, J = 1.8 Hz, 1H, Tp), 8.13 (d, J = 2.0 Hz, 1H, Tp), 8.07 (d, J = 2.0 Hz, 1H, Tp), 7.95 (d, J = 2.3 Hz, 1H, Tp), 7.93 (d, J = 2.4 Hz, 1H, Tp), 7.89 (d, J = 2.3 Hz, 2H, Tp, Tp), 7.78 (t, J = 2.6, 2.4 Hz, 2H, Tp, Tp), 7.62 (d, J = 2.0 1H, Hz, Tp), 7.53 (d, J = 2.0 Hz, 1H, Tp), 6.40 (q, J = 1.7, 1.98, 2.3, 2H, Tp 4, Tp 4), 6.27 (m, J = 2.3, 2.0, 2.1, 2.3, 2.3, 2.4 Hz, 4H, Tp 4, Tp 4, Tp 4, Tp 4), 3.98 (dd, J = 8.6, 11.8 Hz, 1H, 5A), 3.70 (m, 1H, 2B), 3.67 (m, 2H, 2A, 2), 3.30−3.03 (m, 4H, 4B, 2,3,3), 2.61 (m, 2H, 5B, 3), 2.54 (m, 1H, 3), 1.68 (ddd, J = 5.5, 2.7, 8.4 Hz, 1H, 4A), 1.32 (d, J = 8.6 Hz, 9H, PMe_3 A), 1.28 (d, J = 8.2 Hz, 9H, PMe_3 B). ^{13}C NMR (acetone-d_6): δ 144.2 (s, Tp), 143.9 (s, Tp), 143.1 (s, Tp), 142.3 (s, Tp), 142.2 (s, Tp), 141.8 (s, Tp), 137.5 (s, Tp), 137.0 (s, Tp), 136.8 (s, Tp), 136.3 (s, Tp), 136.2 (s, Tp), 107.1 (s, Tp 4), 107.0 (s, Tp 4), 106.0.7 (s, Tp 4), 106.4 (s, Tp 4), 106.1 (s, Tp 4), 65.8 (s, 5B), 63.9 (d, J = 14.66 Hz, 5A), 57.7 (d, J = 13.287 Hz, 4B), 57.2 (s, 4A), 42.8 (s, 2), 41.5 (s, 2), 31.8 (s, 3), 31.4 (s, 3), 13.6 (d, J = 15.96 Hz, PMe_3), 13.2 (d, J = 16.10 Hz, PMe_3). IR: $\nu_{N\equiv O}$ 1551 cm^{-1}.

TpW(NO)(PMe_3)(η^2-dioxidethiophene) (9B). Compound **1** (100 mg, 0.17 mmol) and MCPBA (65 mg at 68 wt %, 0.37 mmol) were added to acetonitrile (4 mL) and the solution was stirred for 10 min. The solution was evaporated until a white precipitate was formed, which was then collected on a fine-porosity glass filter. The filtrate was tripled in volume with THF, and the product was precipitated from pentane (100 mL), collected on a fine-porosity glass filter, and dried in vacuo. Compound **9** was isolated (48 mg, 46% yield) as a light brown solid. ^1H NMR (acetone-d_6): δ 8.23 (1H, d, J = 2.01 Hz, Tp), 8.11 (1H, d, J = 2.01 Hz, Tp), 8.04 (1H, d, J = 2.35 Hz, Tp), 8.00 (1H, d, J = 2.35 Hz, Tp), 7.92 (1H, d, J = 2.35 Hz, Tp), 7.84 (1H, d, J = 2.35 Hz, Tp), 7.44 (1H, ddd, J = 1.01, 3.01, 0.67 Hz, 2), 6.50 (1H, t, J = 2.01, 2.35 Hz, Tp 4), 6.39 (1H, t, J = 2.01, 2.35 Hz, Tp 4), 6.33 (1H, t, J = 2.01, 2.35 Hz, Tp 4), 5.42 (1H, dt, J = 1.01, 0.67, 5.70 Hz, 3), 3.80 (1H, dd, J = 1.01, 7.39 Hz, 4), 2.40 (1H, m, 5), 1.27 (9H, d, J = 9.40 Hz, PMe_3). ^{13}C NMR (acetone-d_6): δ 145.5 (Tp), 145.4 (2), 144.6 (Tp), 142.7 (Tp), 138.2 (Tp), 137.9 (Tp), 136.7 (Tp), 117.9 (3), 108.0 (Tp 4), 107.4 (Tp 4), 107.2 (Tp 4), 71.0 (d, J = 15.5, 4), 54.8 (5), 13.5 (d, J = 29.6, PMe_3). IR: $\nu_{N\equiv O}$ 1597 cm^{-1}. LRMS: calcd, 619.1; found, 619.

TpW(NO)(PMe_3)(4,5-η^2-*S*-methylthiophenium)(OTf) (10A and 10B). Compound **1** (300 mg, 0.51 mmmol) was dissolved in acetonitrile (5 mL). Methyl triflate (125 mg, 0.76 mmol) was added, and the solution was evaporated to dryness. The residue was dissolved in THF (2 mL) and then precipitated into ether (100 mL), collected on a fine-porosity glass filter, and dried in vacuo. Compound **10** was obtained (340 mg, 88.8% yield) as an orange solid in a 1:2.5 ratio of A to B. ^1H NMR (acetone-d_6) of isomer A: δ 8.23 (1H, d, buried, Tp), 8.21 (1H, d, buried, Tp), 8.13 (1H, d, buried, Tp), 8.06 (1H, d, J = 2.49 Hz, Tp), 8.02 (1H, d, J = 2.29 Hz, Tp), 7.89 (1H, d, J = 2.49 Hz, Tp), 7.85 (1H, dd, J = 2.90, 4.89 Hz, 3), 6.53 (1H, t, buried, Tp 4), 6.42 (1H, t, buried, Tp 4), 6.36 (1H, t, J = 2.29, 2.14 Hz, Tp 4), 5.83 (1H, d, J = 4.73 Hz, 2), 4.91 (1H, ddd, J = 1.37, 6.10, 8.85, Hz, 5), 3.16 (3H, s, Me), 2.70 (1H, m, 4), 1.37 (9H, d, J = 9.00 Hz, PMe_3). ^1H NMR (acetone-d_6) of isomer B: δ 8.23 (1H, d, J = 1.84 Hz, Tp), 8.21 (1H, d, J = 2.14 Hz, Tp), 8.12 (1H, d, J = 2.28 Hz, Tp), 8.08 (1H, d, J = 2.28 Hz, T7.95 (1H, d, J = 2.49 Hz, Tp), 7.81 (1H, d, J = 2.14 Hz, Tp), 7.67 (1H, dd, J = 2.75, 5.04 Hz, 3), 6.53 (1H, t, J = 2.29, 2.29 Hz, Tp 4), 6.43 (1H, t, J = 2.14, 2.29 Hz, Tp 4), 6.39 (1H, t, J = 2.29, 2.29 Hz, Tp 4), 5.88 (1H, 5.04, 2), 4.20 (1H, ddd, J = 0.91, 2.75, 8.85, Hz, 4), 3.47 (1H, dt, J = 1.60, 1.30, 5.96 Hz, 5), 3.06 (3H, s, Me), 1.34 (9H, d, J = 9.15, PMe_3). CV: $E_{p,a}$ = 0.02 V. IR: $\nu_{N\equiv O}$ 1595 cm^{-1}. LRMS: calcd, 602.1; found, 602.0.

TpW(NO)(PMe_3)(4,5-η^2-2,*S*-dimethylthiophenium)-(OTf) (11A and 11B). Compound **2** (100 mg, 0.17 mmmol) was dissolved in acetonitrile (4 mL). Methyl triflate (33 mg, 0.20 mmol) was added, and the solution was evaporated to dryness. The residue was dissolved in THF (1 mL) and then precipitated from pentane (100 mL), collected on a fine-porosity glass filter, and dried in vacuo. Compound **11** was obtained (100 mg, 78.7% yield) as a pale brown solid in a 1:2.5 ratio of A to B. ^1H NMR (acetone-d_6): δ 8.10 (1H, d, J = 2.29 Hz, Tp (B)), 8.06 (1H, d, J = 2.29 Hz, Tp (B)), 8.04 (1H, d, J = 2.29 Hz, Tp (A)), 7.95 (1H, d, J = 2.29 Hz, Tp (A)), 7.94 (1H, d, J = 2.49 Hz, Tp (B)), 7.73 (1H, d, J = 2.49 Hz, Tp (B)), 7.58 (1H, s, br, 3A), 7.39 (1H, s, br, 3B), 6.62 (1H, t, J = 2.29, 2.44 Hz, Tp4 (A)), 6.52 (1H, t, J = 2.29, 2.13 Hz, Tp4 (B)), 6.40 (1H, t, J = 2.29, 2.44 Hz, Tp4 (B)), 6.38 (1H, t, J = 2.29, 2.44 Hz,

Tp4 (B)), 6.37 (1H, t, J = 2.29, 2.44 Hz, Tp4 (A)), 4.88 (1H, dd, J = 6.87, 8.40 Hz, 4A), 4.08 (1H, m, 4B), 3.42 (1H, dd, J = 1.68, 6.41 Hz, 5B), 3.23 (3H, s, S-Me A), 3.14 (3H, s, S-Me B), 2.55 (3H, s, 2-Me A), 2.52 (3H, s, 2-Me B), 1.38 (9H, d, J = 9.01 Hz, PMe_3 A), 1.35 (9H, d, J = 9.15 Hz, PMe_3 B).

TpW(NO)(PMe_3)(*S,C(5)*-η^2-2-methyl-2-(3-oxopentyl)-2*H*-thiophenium)(OTf) (12B). Compound **2** (100 mg, 0.17 mmol) was dissolved in CH_2Cl_2 (1.5 mL), and TEA (1 drop), EVK (89 mg, 0.33 mg), and TBSOTf (269 mg, 0.33 mmol) were added. The solution was stirred for 18 h. The reaction mixture was added to ether (25 mL), which produced an oil. After the ether was decanted, the oil was dissolved in THF (2 mL) and precipitated into ether (100 mL). The precipitate was collected on a fine-porosity glass filter and dried in vacuo. Compound **12** was isolated (71 mg, ~90% clean by NMR) as a brown solid. ^{1}H NMR (acetone-d_6): δ 8.62 (1H, d, J = 2.20 Hz, Tp), 8.30 (1H, d, J = 2.20 Hz, Tp), 8.20 (1H, d, J = 2.20 Hz, Tp), 8.18 (1H, d, J = 2.42 Hz, Tp), 8.11 (1H, d, J = 2.20 Hz, Tp), 8.08 (1H, d, J = 2.42 Hz, Tp), 6.94 (1H, dd, J = 2.41, 6.15 Hz, 4), 6.60 (1H, t, J = 2.42, 2.20 Hz, Tp 4), 6.54 (1H, t, J = 2.42, 2.20 Hz, Tp 4), 6.48 (1H, dd (br) J = 2.42, 3.96 Hz, 5), 6.46 (1H, t, J = 2.42, 2.42 Hz, Tp 4), 5.44 (1H, d, J = 6.15 Hz, 3), 2.72 (2H, q, J = 6.81, 8.79, 6.81 Hz, 7), 2.50 (2H, q, J = 7.25, 7.47, 7.25 Hz, 8), 1.51 (9H, d, J = p.67 Hz, PMe_3), 1.37 (2H, t, J = 7.25, 7.47 Hz, 6), 0.98 (3H, t, J = 7.25, 7.25 Hz, 9), 0.25 (3H, s, 2-Me).

TpW(NO)(PMe_3)(η^2-1,3-Dimethyl-2-thiabicyclo[3.2.0]-hepta-3,6-diene-6,7-dicarboxylic acid dimethyl ester) (13). Compound **3** (100 mg, 0.16 mmol) was dissolved in CH_3-CN (1 mL) with DMAD (102 mg, 0.72 mmol) and stirred for 18 h. The solution was evaporated to dryness, and the residue was dissolved in CH_2Cl_2 (1 mL). The solution was placed on a 500 μm silica gel plate and eluted with a 3:7 mixture of hexanes and ethyl acetate. An orange band was isolated from the top of the silica plate, which contained compound **13**. ^{1}H NMR (acetone-d_6): δ 8.64 (1H, d, J = 1.92 Hz, Tp), 8.08 (1H, d, J = 1.93 Hz, Tp), 7.94 (1H, d, J = 2.31 Hz, Tp), 7.91 (1H, d, J = 2.30 Hz, Tp), 7.84 (1H, d, J = 2.30 Hz, Tp), 7.57 (1H, d, J = 2.31 Hz, Tp), 6.40 (1H, t, J = 2.30, 2.31 Hz, Tp 4), 6.32 (1H, t, J = 2.30, 1.93 Hz, Tp 4), 6.30 (1H, t, J = 1.92, 2.30 Hz, Tp 4), 4.08 (1H, s, 3), 3.83 (3H, s, CO_2Me), 3.77 (3H, s, CO_2Me), 2.80 (1H, d, J = 9.22 Hz, 4), 1.81 (3H, s, 2-Me), 1.34 (9H, d, J = 8.07 Hz, PMe_3), 0.99 (3H, s, 5-Me). ^{13}C NMR (acetone-d_6): δ 143.5 (Tp), 142.7 (Tp), 137.4 (Tp), 136.8 (Tp), 129.7 (Tp), 126.1 (Tp), 107.1 (Tp 4), 106.8 (Tp 4), 106.5 (Tp 4), 70.9 (3), 61.3 (4), 51.7 (CO_2Me), 51.7 (CO_2Me), 28.0 (5-Me), 21.5 (2-Me), 13.6 (d, PMe_3). CV: $E_{p,c}$ = −1.58 V, $E_{p,a}$ = 0.43 V.

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Supporting Information Available: Crystallographic details for compound **3B** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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