Carbon—Sulfur Bond Cleavage in Thiophene by Group 6 Metallocenes

William D. Jones,* Robert M. Chin, Todd W. Crane, and David M. Baruch

Department of Chemistry, University of Rochester, Rochester, New York 14627

Photolysis of Cp_2MoH_2 in the presence of thiophene leads to the formation of the C—H insertion product $Cp_2Mo(2$-thienyl)H as the sole product, which was characterized by conversion to the chloro derivative $Cp_2Mo(2$-thienyl)Cl. Photolysis of Cp_2WH_2 in the presence of thiophene leads to the initial formation of the C—S insertion product $Cp_2\overline{WSCH{=}CHCH{=}\overline{C}H}$. Continued irradiation results in the conversion of this adduct to the C—H insertion product $Cp_2W(2$-thienyl)H. Thermal reaction of $Cp_2W(CH_3)H$ with thiophene gives both C—S and C—H insertion products in an 11:1 kinetic ratio. The complex $Cp_2\overline{WSCH{=}CHCH{=}\overline{C}H}$ crystallizes in orthorhombic space group *Pbca* (No. 61) with $a = 7.713(6)$ Å, $b = 13.636(5)$ Å, $c = 22.290(7)$ Å, $V = 2344.4(3.3)$ Å^3, $Z = 8$.

Introduction

The reactions of thiophenes with transition metal complexes has been under investigation recently as a means of modeling the initial steps in the hydrodesulfurization process. A variety of η^4 and η^5 complexes of thiophene have been prepared and structurally characterized,[1] some of which react with nucleophiles to give ring-opened products.[2] Several other metal complexes have been found to directly cleave the C—S bond, giving metallacycle products.[3–5]

The first such report involved the reaction of iron carbonyl with thiophene to give a dinuclear structure (Scheme 1a).[6] The reaction of $Cp^*Co(C_2H_4)_2$ with thiophene and dibenzothiophene gives similar dinuclear products (Scheme 1b).[7] The η^4-thiophene complex $Cp^*Ir(\eta^4$-$C_4H_2Me_2S)$ was found to rearrange to the C—S insertion product upon chromatography on basic alumina (Scheme 1c).[3] The reaction of the reactive fragment [Cp*Rh(PMe₃)] with thiophene was found to give

the C—S insertion product directly (Scheme 1d).[4] Thermolysis of the rhodium complex $Cp^*Rh(\eta^4$-$C_4Me_4S)$ leads to the formation of several products, one of which is a dinuclear rhodium complex in which the C—S bond has been cleaved (Scheme 1e).[8] Two related iridium complexes, [Ir(PMe₃)₃(COD)]Cl and [Ir(triphos)(η^4-C_6H_6)]-BPh₄, react with thiophene to give C—S insertion products (Scheme 1f,[5]g[9]). The group 10 complex Pt-(PEt₃)₃ has been shown to insert into the C—S bond of dibenzothiophene (Scheme 1h).[10] Recently, an iron complex has been reported that inserts into thiophene in a photochemical reaction (Scheme 1i).[11]

In this paper, the reactions of the reactive intermediates [Cp₂Mo] and [Cp₂W] with thiophene are investigated. These fragments are conveniently generated photochemically from their dihydride complexes and are known to undergo a wide variety of C—H insertion reactions with aromatic and benzylic but not alkane C—H bonds.[12] In the absence of a suitable oxidative addition substrate, reaction with the Cp C—H bonds leads to dimer formation.[13] An earlier report of the photochemical reaction of Cp_2WH_2 with thiophene and other heterocycles showed that C—H insertion could occur, among other products.[14]

Results and Discussion

Reaction of Cp_2MoH_2 with Thiophene. Photolysis of a thiophene solution of Cp_2MoH_2 for ~7.5 min led to

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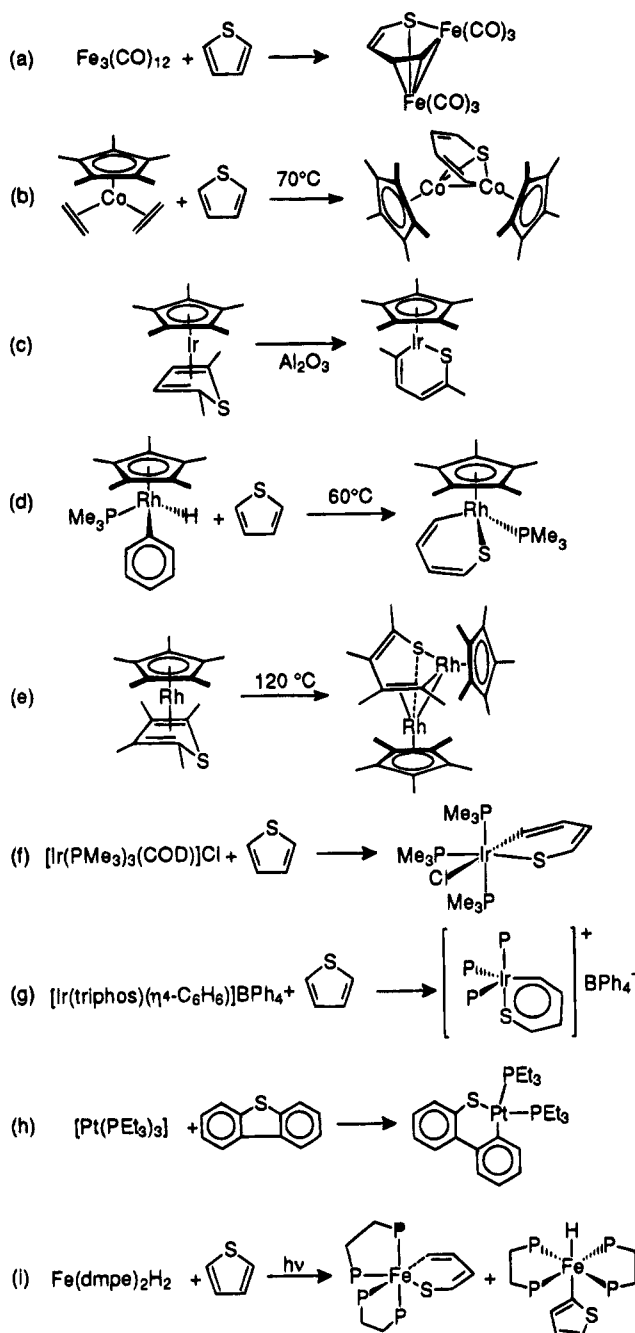
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Scheme 1

(a) $Fe_3(CO)_{12}$ + [thiophene] →

(b) [Cp*Co] + [thiophene] $\xrightarrow{70°C}$

(c) [Cp*Ir] $\xrightarrow{Al_2O_3}$

(d) Me_3P—[Cp*Rh]—H + [thiophene] $\xrightarrow{60°C}$

(e) [Cp*Rh] $\xrightarrow{120°C}$

(f) $[Ir(PMe_3)_3(COD)]Cl$ + [thiophene] →

(g) $[Ir(triphos)(\eta^4\text{-}C_6H_6)]BPh_4^+$ + [thiophene] →

(h) $[Pt(PEt_3)_3]$ + [dibenzothiophene] →

(i) $Fe(dmpe)_2H_2$ + [thiophene] $\xrightarrow{h\nu}$

a new product which had proton resonances at δ 7.09, 6.67, 6.60, 4.61, and −7.19 in the ^{1}H NMR spectrum. The product was assigned as the C—H bond activated product, $CpMo(C_4H_3S)(H)$ (eq 1). The C—H activation

$$[Cp_2MoH_2] + [thiophene] \xrightarrow[\lambda > 300 \text{ nm}]{h\nu} [Cp_2Mo(H)(thienyl)] \quad (1)$$
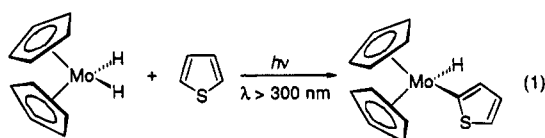
occurs at the α position of the thiophene, based on decoupling experiments and the absence of a singlet proton resonance which would be expected if C—H activation had occurred at the β position. Irradiation

at −20 °C in methylcyclohexane-d_{14} also gave only the C—H insertion product.

Since separating the mixture of $CpMo(C_4H_3S)(H)$ and Cp_2MoH_2 proved difficult, the product mixture was reacted with CCl_4 to convert the hydride complexes to their chloro derivatives. After the mixture was stirred with CCl_4 for 14 h at 25 °C, the ^{1}H NMR spectrum showed no hydrides present and the formation of three new thienyl resonances and a new Cp resonance, as well as resonances for Cp_2MoCl_2. The spectrum was consistent with the formulation $CpMo(C_4H_3S)(Cl)$ (eq 2), which was isolated in 17% yield by recrystallization from a toluene/hexanes mixture.

$$[Cp_2Mo(H)(thienyl)] \xrightarrow{CCl_4} [Cp_2Mo(Cl)(thienyl)] \quad (2)$$
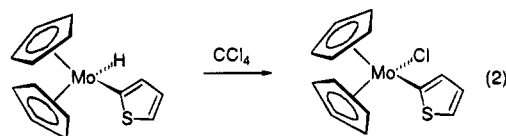
The thermal reaction of Cp_2MoH_2 with isoprene was used as a nonphotochemical source of the $[Cp_2Mo]$ fragment.[15] Reaction of Cp_2MoH_2 with thiophene in the presence of isoprene gives two products in a 0.77:1 ratio, the C—H insertion product observed above and the η^2-isoprene complex $Cp_2Mo(\eta^2\text{-}3,4\text{-isoprene})$.[16]

Photolysis of Cp_2WH_2 with Thiophene. Photolyzing a mixture of Cp_2WH_2, thiophene, and hexanes (λ > 300 nm) for 14 h led to the formation of two products, assigned as $(C_5H_5)_2W(CH=CHCH=CHS)$, 1, and $Cp_2W(C_4H_3S)(H)$, 2, based on the ^{1}H NMR spectrum, in a 1:1 ratio (eq 3; cf. ref 14). If a shorter irradiation time is used (2 h), then a 4:1 ratio of 1:2 is produced. Longer irradiations lead to almost complete conversion to 2 (>95%).

$$[Cp_2WH_2] \xrightarrow{h\nu} [Cp_2W(CH=CHCH=CHS)] + [Cp_2W(H)(thienyl)] \quad (3)$$

1   2
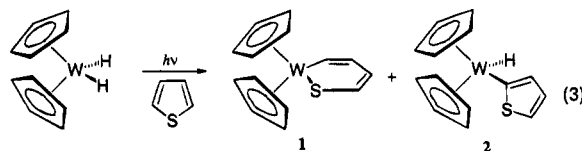
A single crystal X-ray diffraction study of 1 confirmed the structure to be that of a C—S bond cleaved thiophene complex (Figure 1). Bond distances and angles for 1 are given in Table 1. The metallathiacycle six-membered ring of $(C_5H_5)_2W(CH=CHCH=CHS)$ is puckered slightly by 23°. The puckering of the metallacycle is comparable to that in the complex $(C_5Me_5)Rh(PMe_3)$-$(CH=CHCH=CHS)$, which has a puckering of 26° in the metallacycle.[4] The bonds of the metallacycle in $(C_5H_5)_2W(CH=CHCH=CHS)$ are believed to be localized due to the nonplanarity of the ring, the upfield shift of the proton resonances in the ^{1}H NMR spectrum, and the alternating bond lengths in the butadiene fragment. The localized nature of the bonding in the metallathiacycle differs from that in $(C_5Me_5)Ir[C(Me)=CHCH=C-(Me)S]$ and $[(triphos)Ir(SCH=CHCH=CH)]^+$, in which the bonding in the metallacycle is believed to be delo-

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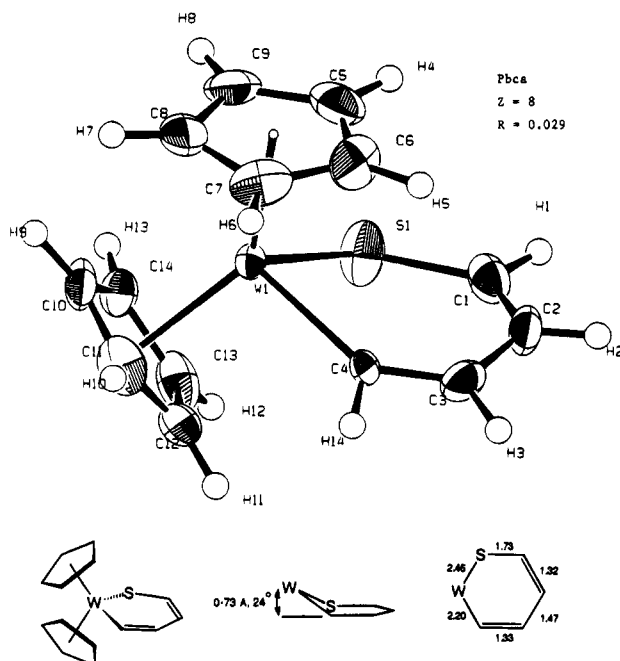(16) Thomas, J. L. J. Am. Chem. Soc. **1973**, 95, 1838–1848.

Figure 1. ORTEP drawing of $Cp_2W(C_4H_4S)$, 1. Ellipsoids are shown at the 50% probability level.

Table 1. Selected Distances and Angles for $Cp_2W(C_4H_4S)$, 1

Distances (Å)			
W1−S1	2.461(3)	C1−C2	1.32(2)
W1−C4	2.20(1)	C2−C3	1.47(2)
S1−C1	1.73(1)	C3−C4	1.33(1)

Angles (deg)			
S1−W1−C4	85.4(3)	C1−C2−C3	126(1)
W1−S1−C1	111.7(4)	C2−C3−C4	129(1)
S1−C1−C2	128(1)	W1−C4−C3	130.7(7)

calized.[3,9] Other examples of metallathiacycles which display localized bonding as indicated by the ¹H NMR resonances are *mer*-(Me₃P)₃Ir(Cl)[SCH=CHCH=CH][5] and *mer*-(Et₃P)₃Ir(H)[SCH=CHCH=CH].[17] The benzothiophene analog of the former complex was structurally characterized as having a planar metallacycle structure, despite the fact that it can achieve an 18e configuration without delocalization. The steric demands of the phosphine groups were cited as the probable cause of this observation. A similar observation was made in the structural characterization of (DMPE)₂Fe(SCH=CHCH=CH), which also has a planar geometry and a nondelocalized structure.[11]

Photolysis of Cp_2WH_2 is known to generate the unsaturated 16e metallocene, $[Cp_2W]$, which can then insert into the C−S bond of thiophene to give complex 1.[12] The initial binding mode of the thiophene to tungstenocene is unknown since no intermediates are observed by ¹H NMR spectroscopy, but earlier studies with [(C₅Me₅)Rh(PMe₃)] indicated that S-binding precedes C−S insertion.[4] 1 then apparently undergoes a photochemical rearrangement to yield the C−H activated adduct, 2. The viability of this pathway was demonstrated by the photolysis of an isolated sample of 1, which led to the formation of 2. The photochemical rearrangement of 1 to 2 was found to be intramolecular.

Photolysis of 1 in the presence of thiophene-d_4 led to no incorporation of thiophene-d_4 into 2, as determined by ²H NMR spectroscopy. It is not clear why the C−S inserted adduct 1 is the photochemical kinetic product whereas 2 is the thermodynamic product (*vide infra*).

The kinetic selectivity of the $[Cp_2W]$ fragment for C−S vs C−H bond cleavage was examined by thermal elimination of methane from $Cp_2W(CH_3)H$ in neat thiophene at 80 °C. The reaction was complete in 3 h, giving a 10:1 ratio of 1:2. The ratio did not change upon further heating for 6 h, indicating that this represents the kinetic selectivity of the $[Cp_2W]$ fragment.[18] The C−S insertion complex is labile, however, at 135 °C. Heating a solution of 1 in C_6D_6 at 135 °C produces $Cp_2W(C_6D_5)D$ with a half life of 42 h.[19]

In the only other photochemical system reported for thiophene C−S cleavage, irradiation of Fe(dmpe)H₂ at low temperature leads to the formation of a mixture of C−H insertion products as well as C−S insertion products, tentatively assigned as cis and trans isomers with both α and β C−H insertion. Warming to 0 °C led to the formation of only one C−H and one C−S insertion product (ratio not indicated). Further photolysis did not change this ratio, suggesting that the compounds were not photolabile.[11]

Conclusions

Group 6 metal complexes have been found to react with thiophene in two ways. The molybdenocene fragment reacts with the α-C−H bonds to give a thienyl hydride complex. The tungstenocene fragment reacts by preferential insertion into the C−S bond, and this species is then photochemically converted into the C−H insertion product by an intramolecular pathway.

Experimental Section

General Information. All operations and routine manipulations were performed under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corp. dri-lab. 1,2-Dimethoxyethane (DME) was dried over KOH pellets and distilled from a sodium dispersion under a nitrogen atmosphere. Tetrahydrofuran, benzene, and toluene were distilled from dark purple solutions of benzophenone ketyl. Benzene-d_6, THF-d_8, and methylcyclohexane-d_{14} were distilled under vacuum from dark purple solutions of benzophenone ketyl and stored in ampules with Teflon-sealed vacuum line adapters. CD_2Cl_2 was dried over CaH_2. NaCp·DME was prepared as described in the literature.[20] Thiophene (99+%) was purchased from Aldrich Chemical Co. and purified as previously reported.[21] Isoprene was purchased from Aldrich and degassed prior to use. Thiophene-d_4 was prepared as previously described.[22] $MoCl_5$, WCl_6, and $NaBH_4$ were obtained from Aldrich Chemical Co. and used as received. Cp_2MoH_2 and Cp_2-

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(18) Attempts to prepare the fragment from Cp_2WH_2 and isoprene in neat thiophene at 135 °C gave a 6:1 ratio of 1 and 2 after 3 days (80% conversion). However, complex 1 is labile under these reaction conditions, so that this ratio does not represent the true kinetic selectivity of the fragment.

(19) The disappearance of 1 follows first-order kinetics with $k = 4.6$-(1) × 10⁻⁶ s⁻¹. Traces (1−2%) of 2 are also seen in the reaction, and probably form via intramolecular rearrangement rather than in a competitive reaction of $[Cp_2W]$ with the large excess of benzene-d_6.

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WH$_2$ were prepared using modified literature preparations.[23] Cp$_2$W(CH$_3$)H was prepared as described previously.[24]

All ^{1}H NMR spectra were recorded on a Bruker AMX400 NMR spectrometer. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced to the chemical shifts of residual solvent resonances (C$_6$H$_6$, δ 7.15). Data were typically recorded with a digital resolution of 0.3 Hz. Photolysis was done using an Ace-Hanovia UV lamp Model 6515 or an Oriel 200 W Hg/Xe lamp. The preparative photolysis tube was a Pyrex cylindrical tube with a length of 11.5 cm, an inner diameter of 6.0 cm, an outer diameter of 7.0 cm, and a total volume of ~35 cm^3. Analyses were obtained from Desert Analytics.

Preparation of Cp$_2$MoH$_2$. This preparation avoids the lengthy workup and filtrations employed in the earlier preparation.[25] NaCp·DME (13.0 g, 0.073 mol) and NaBH$_4$ (2.6 g, 0.069 mol) were placed into a three neck flask, and 250 mL of dry THF was added to the mixture. MoCl$_5$ (4.0 g, 0.015 mol) was added very slowly over a 20 min period. The mixture was allowed to stir at 25 °C for 20 min under N$_2$. The flask was then fitted with a reflux condenser and a Teflon sealable stopcock, and the solution was refluxed for 10 h. After the solution was cooled to 0 °C, 20 mL of degassed MeOH was added dropwise. The solution was allowed to warm to 25 °C and stirred for an additional 40 min. The solvent was then removed under reduced pressure and the residue extracted with benzene (3 × 60 mL). The extract was filtered through neutral alumina and the benzene removed under reduced pressure. The residue was sublimed (90–95 °C, 10^{-5} mmHg) onto a cold finger to give 910 mg of product (27%).

Preparation of Cp$_2$WH$_2$. This preparation avoids the lengthy acidic workup and filtration employed in the earlier preparation.[26] NaCp·DME (10.0 g, 0.056 mol) and NaBH$_4$ (1.09 g, 0.029 mol) were placed into a three neck flask, and 150 mL of dry THF was added. WCl$_6$ (3.58 g, 0.009 mol) was slowly added over a 20 min period to the mixture. The resulting mixture was stirred for 40 min at 25 °C. The flask was fitted with a condenser and a Teflon sealable stopcock and the solution refluxed for 20 h. The solution was cooled to 0 °C and 8 mL of degassed H$_2$O added dropwise. The solution was then warmed to room temperature and stirred for an additional 40 min, the solvent was removed under reduced pressure, and the residue was extracted with benzene (3 × 40 mL). The extract was filtered through neutral alumina and the benzene removed under reduced pressure. Sublimation (100 °C, 10^{-5} Torr) gave 1.19 g of pure Cp$_2$WH$_2$ (42%).

Photolysis of Cp$_2$MoH$_2$ with Thiophene. Cp$_2$MoH$_2$ (77 mg, 0.334 mmol) and 35 mL of thiophene were placed into a photolysis tube. The pale yellow solution was photolyzed for 4 min (Pyrex filter, λ > 300 nm). Then the lamp was turned off and a 0.5 mL aliquot withdrawn from the reaction mixture. The ^{1}H NMR spectrum of the aliquot showed a 3:2 mixture of CpMo(2-thienyl)H:Cp$_2$MoH$_2$. The reaction mixture was photolyzed for an additional 3.5 min. The ^{1}H NMR spectrum of an aliquot now showed a 2:1 ratio of CpMo(2-thienyl)H:Cp$_2$MoH$_2$. For CpMo(2-thienyl)H: ^{1}H NMR (400 MHz, 25 °C, C$_6$D$_{12}$) δ 7.09 (dd, J = 0.8, 5.0 Hz, 1 H), 6.67 (dd, J = 3.2, 5.0 Hz, 1 H), 6.60 (dd, J = 0.8, 3.2 Hz, 1 H), 4.61 (d, J = 0.7 Hz, 5 H), -7.19 (m, 1 H).

Preparation of Cp$_2$Mo(C$_4$H$_3$S)(Cl). A reaction mixture of Cp$_2$Mo(2-thienyl)H and Cp$_2$MoH$_2$ was prepared as described above and transferred to a 250 mL flask. The solvent was removed under reduced pressure and 40 mL of hexanes added to the brown residue. CCl$_4$ (0.532 g, 3.46 mmol) was added and the solution allowed to stir in the dark for 14 h at 22 °C. The hexanes were removed under reduced pressure, and the product was recrystallized from a toluene/hexanes (1:4) mixture at -30 °C to give 13 mg (17%) of pure product. ^{1}H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$): δ 7.44 (dd, J = 1.0, 4.9 Hz, 1 H), 7.08 (dd, J = 1.0, 3.3 Hz, 1 H), 7.01 (dd, J = 3.3, 4.9 Hz, 1 H), 5.23 (s, 10 H). ^{13}C{^{1}H} JMOD NMR (100 MHz, 25 °C, CD$_2$-Cl$_2$): δ 143.02 (s, C), 141.87 (s, CH), 131.88 (s, CH), 127.94 (s, CH), 83.95 (s, CH) Anal. Calcd (found) for C$_{14}$H$_{13}$ClMoS: C, 48.78 (49.90); H, 3.80 (3.94).

Preparation of (C$_5$H$_5$)$_2$W̅(CH=CHCH=CH̅S̅). Cp$_2$WH$_2$ (80 mg, 0.253 mmol), thiophene (16 mL, 0.200 mol), and 20 mL of hexanes were placed into a photolysis tube. The pale yellow solution was photolyzed (Pyrex filter, λ > 300 nm) for 2 h. A ^{1}H NMR spectrum of the crude reaction mixture showed a 4:1 ratio of **1:2**. The reaction mixture was filtered to remove any decomposition products, and the solvent was removed from the filtrate. The brown residue that remained was recrystallized from a toluene/hexanes (1:4) mixture at -30 °C. The product was collected on a frit and washed (3 × 1 mL) with hexanes to give 30 mg of pure product (37%). For (C$_5$H$_5$)$_2$W̅-(CH=CHCH=CH̅S̅): ^{1}H NMR (400 MHz, 25 °C, THF-d_8) δ 7.67 (d, J = 11.8 Hz, 1 H), 6.13 (dd, J = 11.8, 6.8 Hz, 1 H), 5.91 (dd, J = 6.9, 9.9 Hz, 1 H), 5.30 (d, J = 9.9 Hz, 1 H), 4.98 (s, 10 H); JMOD ^{13}C{^{1}H} NMR (100 MHz, 25 °C, THF-d_8) δ 136.1 (s), 127.5 (s), 1222.63 (s), 116.2 (m), 92.4 (s). Anal. Calcd (found) for C$_{14}$H$_{14}$SW: C, 42.23 (42.48); H, 3.54 (3.60). For Cp$_2$W(C$_4$H$_3$S)(H): ^{1}H NMR (400 MHz, 25 °C, C$_6$D$_6$) δ 7.37 (d, J = 5.0 Hz, 1 H), 7.06 (d, J = 3.1 Hz, 1 H), 6.99 (dd, J = 3.1, 5.0 Hz, 1H), 4.20 (s, 10 H), -10.71 (s, 1 H).

Photolysis of (C$_5$H$_5$)$_2$W̅(CH=CHCH=CH̅S̅) in the Presence of Thiophene-d_4. (C$_5$H$_5$)$_2$W̅(CH=CHCH=CH̅S̅) (5 mg, 0.013 mmol), thiophene-d_4 (20 ?L, 0.25 mmol), and 0.5 mL of C$_6$H$_6$ were placed into a Teflon-capped resealable NMR tube. The solution was photolyzed (Pyrex filter, λ > 300 nm) at 70 °C for 3 days. The ^{1}H NMR spectrum showed a 50% conversion to Cp$_2$W(C$_4$H$_3$S)H, **2-d_0**. No Cp$_2$W(C$_6$H$_5$)H was detected. The ^{2}H NMR spectrum showed no evidence for incorporation of thiophene-d_4.

Thermal Reaction of Cp$_2$W(CH$_3$)H with Thiophene. Cp$_2$W(CH$_3$)H (6 mg, 0.018 mmol) and 0.5 mL of thiophene were placed into a Teflon-capped resealable NMR tube and heated at 80 °C for 3 h. The volatiles were removed under reduced pressure, and C$_6$D$_6$ was condensed into the NMR tube. The ^{1}H NMR spectrum showed a 10:1 ratio of C–S inserted complex **1** to C–H bond activated product **2**. The product ratio was unchanged after an additional 6 h of heating at 80 °C.

Thermal Decomposition of (C$_5$H$_5$)$_2$W̅(CH=CHCH=CH̅S̅). (C$_5$H$_5$)$_2$W̅(CH=CHCH=CH̅S̅) (2 mg, 0.005 mmol) and 0.5 mL of C$_6$D$_6$ were placed into a Teflon-capped resealable NMR tube. The solution was heated at 135 °C for 70 h. ^{1}H NMR spectra were recorded every 12 h and showed the presence of free thiophene, Cp$_2$W(C$_6$D$_5$)D, Cp$_2$W(C$_4$H$_3$S)H, and (C$_5$H$_5$)$_2$W̅-(CH=CHCH=CH̅S̅), as described in the text.

Thermal Reaction of Cp$_2$WH$_2$ with Thiophene in the Presence of Isoprene. Cp$_2$WH$_2$ (10 mg, 0.032 mmol), 0.5 mL of thiophene, and 0.1 mL of isoprene were placed into a Teflon-capped resealable NMR tube and heated at 135 °C for 3 days. The thiophene and other organic volatiles were removed under reduced pressure, and C$_6$D$_6$ was condensed into

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Table 2. Data Collection Parameters for Cp₂W(C₄H₄S), 1

chem formula	$WSC_{14}H_{14}$
fw	398.18
cryst syst	orthorhombic
space group (No.)	*Pbca* (No. 61)
Z	8
a, Å	7.713(6)
b, Å	13.636(5)
c, Å	22.290(7)
vol, Å³	2344.4(3.3)
d_{calc}, g cm⁻³	2.26
temp, °C	−20
no. of unique data, $F^2 > 3\sigma(F^2)$	1375
no. of params varied	145
μ, cm⁻¹	102.04
range of transm factors	0.83−1.52
$R(F_o)$	0.029
$R_w(F_o)$	0.0329
goodness of fit	1.165

Table 3. Fractional Atomic Coordinates for Cp₂W(C₄H₄S), 1

atom	x	y	z	B_{eq} (Å²)
W(1)	0.82728(4)	0.42581(3)	0.12101(1)	1.63(2)
S(1)	0.9886(4)	0.3053(2)	0.0609(1)	3.8(2)
C(1)	1.124(1)	0.2343(9)	0.1050(5)	3.2(5)
C(2)	1.112(1)	0.2150(9)	0.1631(6)	3.4(5)
C(3)	0.972(1)	0.2489(8)	0.2032(4)	3.1(5)
C(4)	0.858(1	0.3208(7)	0.1953(4)	1.8(4)
C(5)	1.112(1)	0.494(1)	0.1162(6)	3.9(6)
C(6)	1.067(2)	0.483(1)	0.1761(5)	3.9(6)
C(7)	0.920(2)	0.5395(9)	0.1872(5)	3.7(6)
C(8)	0.874(1)	0.5868(9)	0.1317(6)	3.9(6)
C(9)	0.9942)	0.5560(9)	0.0879(5)	3.7(6)
C(10)	0.581(1)	0.4983(8)	0.0906(6)	3.4(6)
C(11)	0.545(2)	0.447(1)	0.14525)	3.8(6)
C(12)	0.559(1)	0.346(1)	0.1298(6)	3.7(6)
C(13)	0.607(1)	0.335(1)	0.0721(6)	3.6(6)
C(14)	0.627(1)	0.428(1)	0.0471(4	3.0(5)

the NMR tube. The ¹H NMR spectrum showed $(C_5H_5)_2\overline{W(C-H=CHCH=CHS)}$ (69%), Cp₂WH₂ (20%), and Cp₂W(C₄H₃S)H (11%).

Thermal Reaction of Cp₂MoH₂ with Thiophene in the Presence of Isoprene. Cp₂MoH₂ (3 mg, 0.013 mmol), 0.5 mL thiophene, and 0.1 mL of isoprene were placed into a Teflon-capped resealable NMR tube and heated at 100 °C for 12 h. The thiophene and other volatiles were removed under reduced pressure, and C₆D₆ was condensed into the NMR tube. The ¹H NMR spectrum showed Cp₂Mo(C₄H₃S)H and Cp₂Mo(η^2-3,4-isoprene) in a 0.77:1 ratio. Cp₂Mo(η^2-3,4-isoprene): ¹H NMR (400 MHz, 25 °C, C₆D₆) δ 4.56 (d, J = 19.2 Hz, 1 H), 3.91 (s, 5 H), 3.85 (s, 5 H), 2.56 (dd, J = 12.6, 9.3 Hz, 1 H), 1.64 (dd, J = 12.6, 5.2 Hz, 1 H), 1.43 (dd, J = 9.1, 5.2 Hz, 1 H), 2.00 (s, 3 H).

Low-Temperature Photolysis of Cp₂MoH₂ in the Presence of Thiophene. Cp₂MoH₂ (3 mg, 0.013 mmol), thiophene (8.5 mg, 0.10 mmol), and 0.5 mL of methylcyclohexane-d_{14} were placed into a Teflon-capped NMR tube and photolyzed (λ > 300 nm) at −20 °C for 20 min. The ¹H NMR spectrum, recorded at −20 °C, showed Cp₂Mo(C₄H₃S)H and starting material. No resonances corresponding to a C−S bond cleaved product were detected.

X-ray Structure Determination of Cp₂W(C₄H₄S). A single black crystal of the complex was mounted with epoxy on a glass fiber, and cell constants were obtained from 25 centered reflections with values of χ between 0 and 70°. Routine data collection of one octant of data was undertaken on the primitive orthorhombic cell, as indicated in Table 2. The Molecular Structure Corp. TEXSAN analysis software package was used for data reduction and solution. A Patterson map solution of the structure to locate the tungsten atom, followed by expansion of the structure with the program DIRDIF, revealed all non-hydrogen atoms. Following refinement, an absorption correction was applied using the program DIFABS. Full matrix least squares anisotropic refinement of all non-hydrogen atoms (with hydrogens attached in idealized positions) was carried out to convergence. Selected intramolecular bond distances and angles are given in Table 1and fractional atomic coordinates in Table 1.

Supplementary Material Available: Tables of crystal data, calculated atomic coordinates, anisotropic thermal parameters, and interatomic distances and angles (7 pages). Ordering information is given on any current masthead page.

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