FG02-86ER13529). We also acknowledge Mr. William F. Schneider for modifications to the Xα-SW program and Dr. Melanie Pepper for helpful discussions. R.J.S. acknowledges Amoco for an Industrial Fellowship (1988) and The Ohio State University for a Presidential Fellowship (1989-1990).

**Supplementary Material Available:** Table IV, which contains the energy, electron occupancy, total metal participation, and relative participation of individual metal atomic orbitals for all valence orbitals discussed for each compound (9 pages). Ordering information is given on any current masthead page.

# Insertion of Rhodium into the Carbon-Sulfur Bond of Thiophene. Mechanism of a Model for the Hydrodesulfurization Reaction

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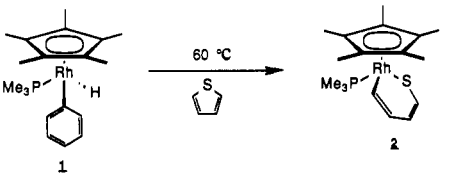
**Abstract:** The reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with thiophene leads to the elimination of benzene and oxidative addition of the thiophene C-S bond across the Rh(I) center, giving $(C_5Me_5)Rh(PMe_3)(SCH{=}CHCH{=}CH)$. Similar reactions occur with 2-methylthiophene, 3-methylthiophene, 2,5-dimethylthiophene, benzothiophene, and dibenzothiophene. Selectivity studies performed with these complexes are consistent with the coordination of sulfur to rhodium prior to C-S bond cleavage. Reversible reductive elimination of thiophene occurs at ~80 °C. The diene portion of the C-S insertion ligand undergoes a Diels-Alder reaction with dimethyl acetylenedicarboxylate to give dimethyl phthalate as a major product. The dimethylthiophene complex $(C_5Me_5)Rh(PMe_3)(SCMe{=}CHCH{=}CMe)$ was structurally characterized, crystallizing in the monoclinic space group $P\bar{1}$ with $a$ = 8.707 (8) Å, $b$ = 14.157 (15) Å, $c$ = 8.637 (5) Å, $\alpha$ = 100.90 (8)°, $\beta$ = 106.07 (6)°, $\gamma$ = 87.85 (8)°, $V$ = 1004 (3) Å$^3$, and $Z$ = 2.

## Introduction

Homogeneous modeling of the heterogeneous hydrodesulfurization (HDS) process[1] has focused upon reactions of metal complexes with thiophene and thiophene derivatives in an effort to elucidate the most important mechanistic pathways. Two general varieties of mechanisms have been proposed, one involving initial $\pi$ coordination of the thiophene either through one double bond[2] or through the entire $\pi$ system,[3] and the other invoking insertion of the metal into the carbon-sulfur bond through an S-bound complex.[4] While most of the homogeneous studies have pointed toward $\eta^4$- or $\eta^5$-thiophene intermediates,[5-11] evidence has also appeared for S-bound thiophene[12-19] and for metal insertion into the C-S bond.[20] We report here the evidence for insertion of a metal into the carbon-sulfur bond of thiophene by way of initial coordination through sulfur.

## Results

**Reactions with Thiophene Derivatives.** The complex $(C_5Me_5)Rh(PMe_3)(Ph)H$ (**1**) has been shown to behave as a thermal precursor for the generation of the unsaturated fragment $[(C_5Me_5)Rh(PMe_3)]$, which is active toward the oxidative addition of a variety of carbon-hydrogen bonds.[21] Recently, isolation of $\eta^2$-arene complexes was found to be possible with fused polycyclic aromatics.[22] In examining similar reactions with heterocyclic aromatics, we discovered that thiophene reacts with **1** at 60 °C in hexane solution to give benzene plus a single organometallic product in high yield in which all four of the thiophene hydrogens display distinct resonances in the $^1$H NMR spectrum (Table I). Furthermore, the $^{31}$P NMR spectrum shows a low-field doublet with $J_{Rh-P}$ = 160 Hz, indicative of a Rh(III) complex. The absence of a hydride resonance in the $^1$H NMR spectrum rules out a C-H bond oxidative addition adduct. The presence of a doublet of doublets in the $^{13}$C NMR spectrum provides strong evidence for the formulation of the product as the C-S insertion adduct, $(C_5Me_5)Rh(PMe_3)(SCH{=}CHCH{=}CH)$ (**2**) (eq 1).




1 2 (1)

A similar reaction of **1** with 2,5-dimethylthiophene led to the formation of the analogous insertion product, $(C_5Me_5)Rh$-

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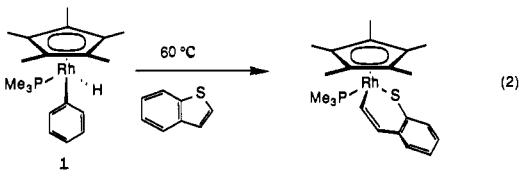
**Table I.** $^1$H NMR Spectral Data

| compound | solvent | chem shift, $\delta$ (mult, $J$, area) |
|---|---|---|
| $(C_5Me_5)Rh(PMe_3)(SCH{=}CHCH{=}CH)$ | $C_6D_{12}$ | 1.246 (d, $J$ = 10.6 Hz, 9 H)<br>1.608 (d, $J$ = 2.7 Hz, 15 H)<br>5.558 (m, 1 H)<br>5.671 (m, 1 H)<br>6.424 (dt, $J$ = 7.4, 3.8 Hz, 1 H)<br>6.552 (dt, $J$ = 9.2, 3.7 Hz, 1 H) |
| $(C_5Me_5)Rh(PMe_3)SMe{=}CHCH{=}CMe)$ | $C_6D_6$ | 1.081 (d, $J$ = 9.9 Hz, 9 H)<br>1.606 (d, $J$ = 2.4 Hz, 15 H)<br>2.253 (s, 3 H)<br>2.389 (s, 3 H)<br>5.937 (d, $J$ = 6.7 Hz, 1 H)<br>6.351 (br s, 1 H) |
| $(C_5Me_5)Rh(PMe_3)[SCMe{=}CHCH{=}CH]$ | $C_6D_{12}$ | 1.611 (d, $J$ = 2.7 Hz, 15 H)<br>1.240 (d, $J$ = 10.2 Hz, 9 H)<br>1.916 (s, 3 H)<br>5.549 (d, $J$ = 6.6 Hz, 1 H)<br>6.367 (m, 2 H) |
| $(C_5Me_5)Rh(PMe_3)(SCH{=}CHC_6H_4)$ | $C_6D_6$ | 0.940 (d, $J$ = 10.9 Hz, 9 H)<br>1.475 (d, $J$ = 2.1 Hz, 15 H)<br>6.910 (t, $J$ = 7.1 Hz, 1 H)<br>6.990 (t, $J$ = 7.2 Hz, 1 H)<br>7.10 (m, 2 H)<br>7.375 (dd, $J$ = 9.0, 2.2 Hz, 1 H)<br>8.025 (d, $J$ = 8.0 Hz, 1 H) |
| $(C_5Me_5)Rh(PMe_3)(SC_{12}H_8)$ | $C_6D_6$ | 0.928 (d, $J$ = 10.3 Hz, 9 H)<br>1.357 (d, $J$ = 2.6 Hz, 15 H)<br>6.965 (m, 2 H)<br>7.025 (dt, $J$ = 7.5, 1.4 Hz, 1 H)<br>7.110 (dt, $J$ = 7.6, 0.8 Hz, 1 H)<br>7.380 (d, $J$ = 7.4 Hz, 1 H)<br>7.467 (d, $J$ = 7.6 Hz, 1 H)<br>7.636 (d, $J$ = 7.6 Hz, 1 H)<br>7.986 (d, $J$ = 7.6 Hz, 1 H) |

$(PMe_3)(SCMe{=}CHCH{=}CMe)$ (**3**). $J$-correlated $^{13}$C NMR spectroscopy again was consistent with C–S insertion, displaying an "up" polarized doublet of doublets for the carbon bound to rhodium. In this case, a single-crystal X-ray structural determination of the product was possible, confirming the insertion of the metal into the carbon–sulfur bond (Figure 1). The structure shows a planar geometry of the diene and sulfur atoms. The rhodium atom lies ~0.7 Å above this plane, giving rise to a slight puckering (26°) of the six-membered metallathiabenzene ring. The bond distances around the six-membered ring indicate a localized diene structure for the two C–C double bonds.

Complexes **2** and **3** slowly eliminate thiophene and dimethylthiophene, respectively, upon heating to 80 °C in the presence of $PMe_3$. The known complex $(C_5Me_5)Rh(PMe_3)_2$ is also formed.[23] From the half-life for the reaction of **2** with $PMe_3$, a value of $\Delta G^{\ddagger} \simeq 32$ kcal/mol is calculated by using the Eyring equation. **3** loses dimethylthiophene more rapidly at this temperature ($\tau_{1/2}$ = 4 days). Heating **2** to 110 °C in the presence of $H_2$ gives only thiophene and some of the bis-$PMe_3$ product, as described above.

Benzothiophene also undergoes C–S bond oxidative addition with **1** at 60 °C. A single product is formed, which is assigned as the complex in which the rhodium has inserted into the unsubstituted C–S bond away from the aromatic ring (eq 2). The




(2)

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assignment is made on the basis of the polarization of the Rh- and P-coupled resonance at $\delta$ 142.43 in the DEPT $^{13}$C NMR spectrum.

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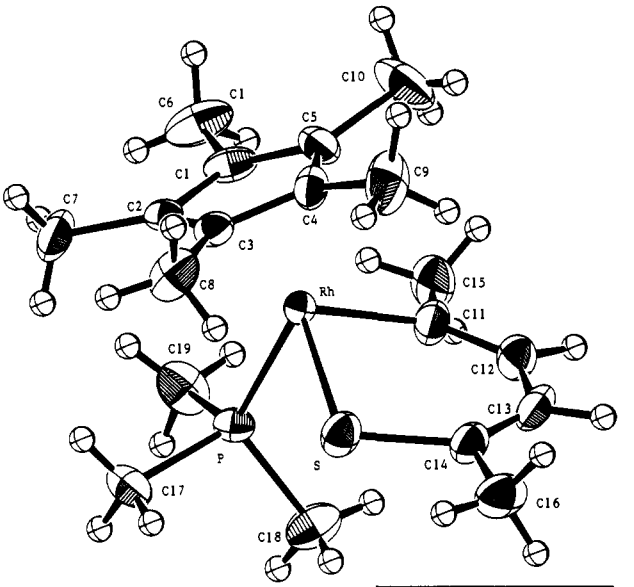
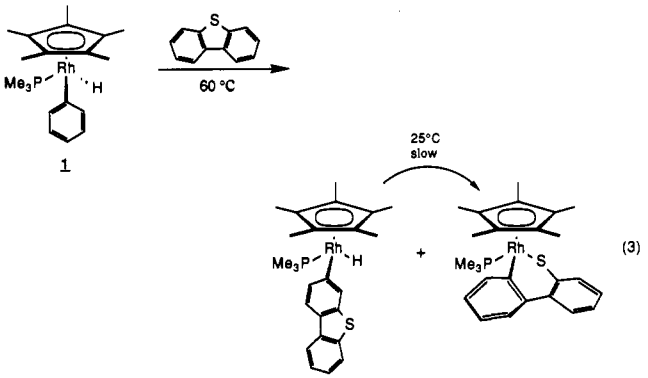



Figure 1. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(SCMe{=}CHCH{=}CMe)$. Ellipsoids are shown at the 50% probability level. Important bond distances (Å) and angles (deg): Rh–P, 2.243 (3); Rh–S, 2.336 (3); Rh–C11, 2.067 (8); C11–C12, 1.35 (1); C12–C13, 1.44 (1); C13–C14, 1.34 (1); C14–S, 1.741 (8); S–Rh–C11, 92.5 (2); S–Rh–P, 86.5 (1); P–Rh–C11, 92.5 (2); Rh–S–C14, 109.7 (3); S–C14–C13, 125.5 (6); C12–C13–C14, 128.3 (7); C11–C12–C13, 131.5 (7); Rh–C11–C12, 124.0 (6).

The reaction of **1** with dibenzothiophene is slightly more complicated in that two organometallic products are formed, one of which has a hydride ligand. The $^{31}$P NMR spectrum of the mixture indicates that both are Rh(III) complexes, one of which has a rhodium–phosphorus coupling constant typical of a C–S insertion product ($J_{P-Rh}$ = 159 Hz) and the other with a coupling

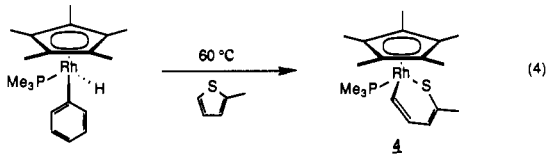
constant typical of a C–H activation product ($J_{P-Rh}$ = 149 Hz). $^1$H NMR data are consistent with the formulation of the products as the thiophene insertion product and an arene C–H bond activation product, although the site of C–H activation could not be ascertained (eq 3). Upon standing at 25 °C for several months




1 (3)

in $C_6D_{12}$ solution, the product containing the hydride resonance was slowly converted into the C–S insertion product.

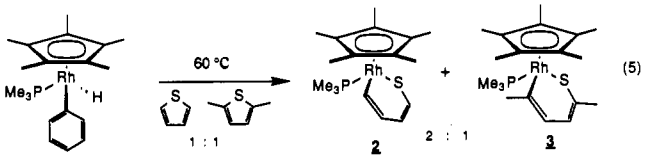
**Selectivity Studies.** The reaction of the unsymmetrically substituted 2-methylthiophene allowed the selectivity of the C–S insertion reaction to be probed. Reaction of **1** with 2-methylthiophene at 60 °C gives exclusively the product **4** resulting from rhodium insertion into the less hindered [1,5] C–S bond, as determined by *J*-correlated $^{13}$C NMR spectroscopy (eq 4). During




1 4 (4)

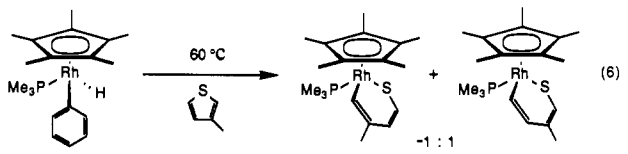
the course of the reaction, no evidence is seen for the presence of the other [1,2] insertion adduct.

In a related study, **1** was heated at 60 °C in hexane solution in the presence of a 1:1 mixture of thiophene and dimethylthiophene. The two C–S insertion products **2** and **3** were formed in a 2:1 ratio (eq 5).




1 2 3 (5)

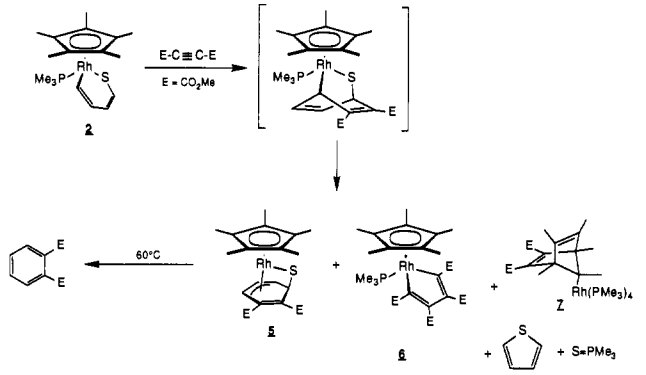
The reaction of **1** with 3-methylthiophene was also examined. Unlike the selective reaction seen with 2-methylthiophene, two products were observed in 1:1 ratio. These are assigned to the [1,2] and [1,5] C–S insertion isomers based upon NMR spectroscopy (eq 6).




1 (6)

**Reactions with Dimethyl Acetylenedicarboxylate (DMAD).** Neither complex **2** nor **3** react with hydrogen gas (1 atm) up to 110 °C; only $(C_5Me_5)Rh(PMe_3)_2$ forms slowly from decomposition. Preliminary studies, however, indicate that **2** reacts with DMAD in $C_6D_6$ solution at 80 °C to give the Diels–Alder product dimethyl phthalate as the major organic product (60%) as shown in Scheme I. An initial reaction with DMAD occurs at 25 °C, and the major product (60%) of the reaction is identified as the Diels–Alder adduct **5** in which $PMe_3$ has been displaced internally by an olefin. Other products identified in this reaction include

**Scheme I**




thiophene, the metallacyclopentadiene **6**, a complex that contains a Diels–Alder adduct of the $C_5Me_5$ ring (**7**), and $SPMe_3$. (See Experimental Section for details).

## Discussion

Several other studies have reported the cleavage of carbon–sulfur bonds of organosulfur substrates by metal complexes. Of those in which thiophene is involved, $Fe_3(CO)_{12}$ has often been used as a coordinating agent for sulfur in the form of FeS, forming clusters with metallacyclopentadiene rings.[24-28] In another case, a rhodium hydride was found to react with a variety of allylic sulfides to give propene and $Rh_2(\mu\text{-}SR)_2$ dimers.[29] Allylic sulfides are also cleaved by iron.[30] Cleavage of diaryl sulfides with nickel(0) has also been reported.[31,32] Angelici recently published a comprehensive account of the organometallic perspective of the HDS reaction.[33]

Very recently, two complexes similar to the ones described here have been reported, $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$[11] and $(C_5Me_5)Ir(\eta^4\text{-}2,5\text{-}C_4Me_2H_2S)$.[20] The latter complex has been found to rearrange to the C–S insertion adduct $(C_5Me_5)Ir(SCMe{=}CHCH{=}CMe)$ upon chromatography on basic alumina, or upon treatment with $NEt_3$. In comparison to complex **3** in the present work, the metallathiacyclohexane ring in $(C_5Me_5)Ir(SCMe{=}CHCH{=}CMe)$ was found to be fully resonance delocalized. The formation of an 18-electron Ir(III) metal complex provides the driving force for including the sulfur lone-pair electrons in the metal coordination sphere in the absence of another ligand. Angelici subsequently found that this complex coordinates $PMe_3$ to generate the iridium analogue of **3**.[34]

The literature on hydrodesulfurization chemistry indicates that there is much debate over the mechanism(s) by which sulfur is removed from the thiophene moiety. Surface studies of thiophene have provided evidence for both $\eta^1$ and $\eta^5$ binding.[35] Many themes have arisen to explain the conversion of thiophene into butenes, butane, and hydrogen sulfide. In one path (with many variations)

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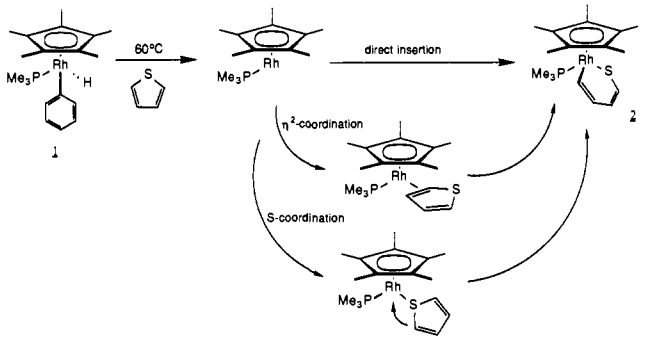
**Scheme II**




the initial steps involve $\pi$ coordination of the thiophene in an $\eta^2$, $\eta^4$, or $\eta^5$ fashion, followed by hydrogenation of a C–C double bond, after which further hydrogenation leads to C–S bond cleavage and formation of a metal–sulfur bond.[1,36] This pathway is supported by homogeneous modeling studies carried out by Angelici on $[(\eta^5\text{-}C_4H_4S)Mn(CO)_3]^+$[6] and $[CpRu(\eta^5\text{-}C_4H_4S)]^+$[8,9] and by Rauchfuss in reactions of $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$ with $Fe_3(CO)_{12}$.[11]

A second path proposed for thiophene HDS involves initial coordination of the sulfur atom in an $\eta^1$ fashion, followed by addition of hydrogen to the C–S bonds, thereby removing sulfur in one concerted step.[37] Harris examined this type of $\eta^1$ interaction theoretically and concluded that 4d metals can bind thiophene in this fashion more easily than 3d metals due to stronger metal–sulfur $\pi$ back-bonding.[38] Experimental evidence for thiophene binding through the sulfur atom indicates that in most cases this interaction is very weak. In a few cases, S-bound thiophene complexes have been isolated and structurally characterized. These examples include the Cp-teathered thiophene complex $[(C_5H_4CH_2C_4H_4S)Ru(PPh_3)_2]^+$,[13] the simple thiophene complex $(C_5Me_5)Re(\eta^1\text{-}C_4H_4S)(CO)_2$ and its binuclear adduct $(CO)_3Fe(\mu\text{-}\eta^4,\eta^1\text{-}C_4H_4S)Re(CO)_2(C_5Me_5)$,[12] $[Ru(NH_3)_5(C_4H_4S)]^{2+}$,[14] $CpFe(NCMe)_2(2,5\text{-}C_4H_2Me_2S)$,[18] $W(CO)_3(PCy_3)_2(C_4H_4S)$,[15] and thiophene complexes of the type $[CpFe(CO)_2(\eta^1\text{-thiophene})]^+$.[16,17]

In the present study, we put forth three possible mechanisms for formation of the C–S insertion adducts, as shown in Scheme II. The simplest mechanism involves no intermediate at all, and the 16-electron rhodium metal simply inserts directly into the C–S bond. The second pathway allows the thiophene to coordinate to the metal in an $\eta^2$ fashion prior to insertion. Our previous observation of $\eta^2$-arene complexes with this metal/ligand system requires strong consideration of this possibility. (An $\eta^4$-thiophene complex cannot be formed with a $PMe_3$ in the coordination sphere, since the 18-electron count of the metal would be exceeded.) The third pathway involves coordination of the thiophene through its sulfur atom. From this intermediate, intramolecular migration of the $\alpha$-carbon from sulfur to the metal accomplishes the desired insertion reaction.

The different selectivities observed in the reaction of 2-methylthiophene and thiophene/2,5-dimethylthiophene experiments provide a clue as to which of the above pathways is occurring with $[(C_5Me_5)Rh(PMe_3)]$. If the direct insertion pathway were operating, then the selective insertion of the rhodium into the unsubstituted C–S bond of 2-methylthiophene (eq 4) would have required that only product **2** be observed in the mixed thiophene/2,5-dimethylthiophene experiment (eq 5). Since very little selectivity was found in the latter competition experiment, direct insertion (an "$\eta^0$" pathway) seems unlikely.

If an $\eta^2$-thiophene complex were involved as an intermediate, then the selectivity with 2-methylthiophene would indicate that the rhodium prefers to bind to the unsubstituted double bond. Again, the mixed thiophene/2,5-dimethylthiophene experiment should have shown a preference for thiophene binding, which would have been reflected in the product distribution. Since no such preference was seen, the results are not consistent with an $\eta^2$ intermediate. Additional support for this conclusion is obtained in the experiment with 3-methylthiophene (eq 6). In this case, no preference is seen for either of the two insertion isomers. If $\eta^2$ binding were involved, one would expect to see a preference for coordination to the unsubstituted double bond, which in turn would favor one C–S insertion isomer over the other. Furthermore, the observation of insertion of rhodium into the C–S bond of dibenzothiophene virtually excludes $\eta^2$ coordination through the thiophene double bonds.

The third possible pathway involves coordination of the thiophene sulfur in the intermediate. Migration of the $\alpha$-carbon from the sulfur to the metal, facilitated by the p orbital on the carbon, then leads to the insertion product. In this mechanism, the 2-methylthiophene selectivity is accounted for in terms of the preferential migration of the unsubstituted $sp^2$-hybridized carbon. In the competition experiment between thiophene and dimethylthiophene, the insertion product selectivity is determined by whichever substrate sulfur first coordinates to the metal. Space-filling models show that either thiophene can coordinate easily, and the slight preference for the parent thiophene can be accommodated in terms of its less hindered ligating ability. The experiment with 3-methylthiophene, which gives insertion into both C–S bonds of the substrate, is easily explained with this intermediate since the methyl group in the 3-position does not interfere with either S coordination or sulfur-to-metal $\alpha$-carbon migration. This $\eta^1$-thiophene mechanism requires that the migration of carbon from sulfur to rhodium be more rapid than the rate of thiophene dissociation.

It is interesting to note that Harris and Chianelli predicted just this mechanism for the binding and C–S bond cleavage of thiophene by 4d metals.[38] The back-donation from the metal would populate the $3b_1$* orbital of thiophene, which is antibonding with respect to sulfur and the adjacent carbon atoms. The electron-rich $[(C_5Me_5)Rh(PMe_3)]$ fragment therefore ought to have been expected to be ideal for promoting C–S cleavage via sulfur coordination, based upon these predictions.

In light of our experiments with compounds like **2**, it is worthwhile to compare the current observations and mechanistic conclusions with those of Angelici.[20] In his experiments, the $\eta^4$-thiophene complex $(C_5Me_5)Ir(\eta^4\text{-}2,5\text{-dimethylthiophene})$ required basic conditions ($NEt_3$ or basic alumina) to insert into the C–S bond giving $(C_5Me_5)Ir(SCMe{=}CHCH{=}CMe)$. It is possible that the role of the base is to act as a weakly coordinating ligand for iridium, effectively producing $[(C_5Me_5)IrL]$ and thiophene, which then react to give the C–S insertion adduct.

Also of interest are the rhodium complexes prepared and studied by Rauchfuss, which are very similar to those described here. In his system, reduction of the dication $[(C_5Me_5)Rh(\eta^5\text{-}C_4Me_4S)]^{2+}$ also leads to a neutral $\eta^4$-thiophene complex.[11] Reaction with the two-electron ligand CO leads to displacement of thiophene, however, and no mention is made of the results of reaction with $PMe_3$ or $NEt_3$. Preliminary X-ray results also indicate that the thiophene ring is puckered with the sulfur away from the metal center. Rauchfuss has also reported that the sulfur in this complex can be *oxidized* to the $\eta^4$ *S*-oxide complex.[39]

In contrast to the above $\eta^4$-thiophene examples, Taube and co-workers have reported that thiophene forms an $\eta^2$ complex with $Os(NH_3)_5$. The product was characterized by $^1H$ NMR spectroscopy, and by analogy to similar $\eta^2$-arene and $\eta^2$-pyrrole derivatives. The reported NMR data, however, are also consistent with a C–S insertion adduct, since the hydrogens on the $\eta^2$ double bond fall in the $\delta$ 5.5–6.0 region of the $^1H$ NMR spectrum, although such a species would formally contain Os(IV).[40]

(36) Sauer, N. N.; Markel, E. J.; Schrader, G. L.; Angelici, R. J. *J. Catal.* **1989**, *117*, 295–297. Markel, E. J.; Schrader, G. L.; Sauer, N. N.; Angelici, R. J. *J. Catal.* **1989**, *116*, 11–22.
(37) Lipsch, J. M. J. G.; Schuit, G. C. A. *J. Catal.* **1969**, *15*, 179–189.
(38) Harris, S.; Chianelli, R. R. *J. Catal.* **1984**, *86*, 400–412.
(39) Skaugset, A. E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 2432–2433.
(40) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969–5970.

Finally, the attempts to cleave sulfur from the six-membered ring were less than satisfactory. Only a Diels–Alder reaction with the strong electrophile DMAD led to any organic products (dimethyl phthalate). The other compounds formed in this reaction attest to the high reactivity of DMAD.

## Conclusions

In conclusion, the observation of an oxidative addition of a carbon–sulfur bond to a metal center has been observed. Mechanistic studies are most consistent with an intermediate in which thiophene first coordinates to the metal via the sulfur atom, followed by migration of the $\alpha$-carbon to the metal center. Since sulfur can be extruded from thiophene following this initial step, the possibility of this pathway serving as an additional mechanism for petroleum hydrodesulfurization should not be neglected.

## Experimental Section

**General Procedures.** All manipulations were performed under an inert atmosphere of nitrogen or on a high-vacuum line with the use of Schlenk techniques. Reagent grade thiophene, 2-methylthiophene, 3-methylthiophene, benzothiophene, 2,5-dimethylthiophene, and dimethyl acetylenedicarboxylate (DMAD) were purchased from Aldrich Chemical Co. and were used without further purification, although each was freeze–pump–thaw degassed (three cycles) prior to use. Hexane was distilled according to our published procedures.

$^1$H (400 MHz) and $^{31}$P (162 MHz) NMR spectra were recorded on a Bruker AMX-400 spectrometer. $^{13}$C (75 MHz) NMR spectra were obtained on a GE QE-300 spectrometer. $^1$H NMR shifts were measured relative to residual $^1$H resonances in the deuterated solvents $C_6D_6$($\delta$ 7.15) and $C_6D_{12}$($\delta$ 1.38). $^{31}$P NMR spectra were reported in units of $\delta$ (chemical shifts are referred to external 10% $H_3PO_4$ at $\delta$ 0.0 ppm)). $^{13}$C NMR were measured relative to the deuterated solvent resonance ($C_6D_{12}$, $\delta$ 26.4 ppm). $C_6D_6$ and $C_6D_{12}$ were purchased from MSD Isotopes Merck Chemical Division Co. and were vacuum distilled from potassium–benzophenone prior to use. Elemental analyses were performed by Desert Analytics-Organic Microanalysis Laboratory. An Enraf-Nonius CAD4 diffractometer was used for X-ray crystal structure determination.

**Preparation of $(C_5Me_5)\overline{Rh(PMe_3)(SCH{=}CHCH{=}CH)}$ (2).** $(C_5Me_5)Rh(PMe_3)(Ph)H$ (**1**) was prepared according to our published method.[41] A 0.20-g sample (0.51 mmol) of **1** was dissolved in 5 mL of hexane in a 10-mL beaker at room temperature and 0.050 mL (0.62 mmol) of thiophene added with a syringe. The mixed solution was transferred into a glass ampule fitted with a Teflon stopcock and stirred for 24 h under an $N_2$ atmosphere at 60 °C. The reaction was then cooled in an ice–water bath and the solvent removed on the vacuum line. The solid residue was dissolved in 2 mL of hexane. Concentration and cooling (−30 °C) afforded dark red crystals in high yield (93%). Anal. Calcd for $C_{17}H_{28}PRhS$: C, 51.26; H, 7.08; S, 8.05. Found: C, 51.01; H, 7.11; S, 8.06. $^{13}$C NMR ($C_6D_{12}$): $\delta$ 8.97 (s, $C_5Me_5$), 14.87 (d, $J$ = 34.9 Hz, $PMe_3$), 99.72 (t, $J$ = 3.6 Hz, $C_5Me_5$), 122.42 (t, $J$ = 2.8 Hz, SCH), 122.62 (s, CH), 126.49 (s, CH), 137.41 (dd, $J$ = 31.2, 23.0 Hz, RhCH). $^{31}$P NMR($C_6D_{12}$): $\delta$ 10.39 (d, $J$ = 160 Hz).

**$(C_5Me_5)\overline{Rh(PMe_3)(SCMe{=}CHCH{=}CMe)}$ (3).** The complex was prepared by the same method used for **2**. The dark red crystals were obtained from hexane (−30 °C) in 91% yield. An X-ray crystal structure of **3** was solved at −75 °C, which is shown in Figure 1. Anal. Calcd for $C_{19}H_{32}PRhS$: C. 53.52; H, 7.56; S, 7.52. Found: C, 53.72; H, 7.72; S, 7.62. MS (70 eV): 426 ($M^+$), 350 ($M^+ - PMe_3$). $^{13}$C NMR ($C_6D_{12}$): $\delta$ 9.41 (s, $C_5Me_5$), 16.00 (d, $J$ = 33.1 Hz, $PMe_3$), 27.67 (s, Me), 36.50 (d, $J$ = 8.5 Hz, $CH_3$), 99.72 (t, $J$ = 3.5 Hz, $C_5Me_5$), 120.35 (s, CH), 126.01 (s, CH), 129.18 (d, $J$ = 2.6 Hz, SC), 147.44 (dd, $J$ = 31.7, 17.1 Hz, RhC). $^{31}$P NMR($C_6D_6$): $\delta$ 6.49 (d, $J$ = 164 Hz).

**$(C_5Me_5)\overline{Rh(PMe_3)[SCMe{=}CHCH{=}CH]}$ (4).** A solution of **1** (21 mg, 0.051 mmol) in 4 mL of hexane was placed into a glass ampule with a Teflon stopcock and 0.050 mL of 2-methylthiophene added. The mixed solution was stirred at 60 °C for 22 h to give a dark red solution. Removal of the solvent yielded **4** as a dark red solid. $^{13}$C NMR ($C_6D_{12}$): $\delta$ 9.02 (s, $C_5Me_5$), 14.86 (d, $J$ = 34.7 Hz, $PMe_3$), 27.67 (d, $J$ = 1.8 Hz, $CH_3$), 99.64 (t, $J$ = 3.6 Hz, $C_5Me_5$), 120.63 (t, $J$ = 2.0 Hz, CH), 128.95 (s, CH), 131.04 (s. SC), 137.46 (dd, $J$ = 31.7, 23.4 Hz, RhC). $^{31}$P NMR($C_6D_{12}$): $\delta$ 10.56 (d, $J$ = 161 Hz).

**$(C_5Me_5)\overline{Rh(PMe_3)(SCH{=}CHC_6H_4)}$.** A 30-mg sample of **1** (0.076 mmol) reacted with 1 equiv of benzothiophene in hexane (4 mL) at 60 °C for 20 h to give a brown red solution. Removal of the solvent afforded the product as a dark red solid. $^{13}$C NMR ($C_6D_6$): $\delta$ 8.91 (s, $C_5Me_5$), 14.70 (d, $J$ = 34.1 Hz, $PMe_3$), 99.27 (t, $J$ = 3.5 Hz, $C_5Me_5$), 121.33 (s, CH), 125.93 (s, CH), 130.42 (s, CH), 131.34 (s, CH), 133.33 (S, CH), 137.62 (s, C), 140.64 (s, C), 144.44 (dd, $J$ = 31.5, 21.4 Hz, RhCH). $^{31}$P NMR($C_6D_6$): $\delta$ 7.75 (d, $J$ = 158 Hz).

**$(C_5Me_5)\overline{Rh(PMe_3)(SC_{12}H_8)}$.** Complex **1** (10 mg, 0.025 mmol) reacted with dibenzothiophene (28 mg, 0.152 mmol) in hexane (4 mL) at 60 °C for 18 h to give a ~1:1 mixture of a C–H activation product with the arene ring (as evidenced by the appearance of a hydride resonance in the $^1$H NMR spectrum) ($^{31}$P NMR: $\delta$ 7.55 (d, $J$ = 149 Hz)) and a C–S insertion product ($^{31}$P NMR: $\delta$ 3.86 (d, $J$ = 159 Hz)). Upon standing at 25 °C for several months, the amount of the hydride slowly diminished as the amount of the C–S insertion product increased. $^{13}$C NMR ($C_6D_{12}$): $\delta$ 9.13 (s, $C_5Me_5$), 14.61 (d, $J$ = 32.1 Hz, $PMe_3$), 98.87 (t, $J$ = 2.6 Hz, $C_5Me_5$), 123.29 (s, CH), 123.72 (s, CH), 124.70 (s, CH), 125.43 (s, CH), 129.77 (s, CH), 132.60 (s, CH), 139.95 (s, CH), 140.08 (s, CH), 143.73 (d, $J$ = 6.7 Hz, C), 145.83 (s, C), 147.00 (s, C), 159.92 (dd, $J$ = 34.2, 13.5 Hz, RhC). $^{31}$P NMR($C_6D_6$): $\delta$ 3.86 (d, $J$ = 159 Hz). Anal. Calcd for $C_{25}H_{32}PRhS$: C, 60.24; H, 6.47. Found: C, 60.15; H, 6.45.

**Reaction of $(C_5Me_5)Rh(PMe_3)PhH$ with 3-Methylthiophene.** Complex **1** (0.027 g, 0.064 mmol) was dissolved in 5 mL of hexane and 6 equiv of 3-methylthiophene (0.040 mL, 0.41 mmol) added. The reaction was carried out in a glass ampule with a Teflon stopcock at 60 °C for 23 h. The two C–S insertion products obtained were characterized by $^{31}$P NMR spectroscopy, forming in a 1.2:1 ratio ($\delta$ 9.59 (d, $J$ = 154.4 Hz), 10.65 (d, $J$ = 154.5 Hz)). The individual isomers were not assigned.

**Reaction of 2 with $PMe_3$.** A solution of **2** (25 mg, 0.063 mmol) in $C_6D_{12}$ (0.5 mL) was prepared in a resealable NMR tube and $PMe_3$ (0.25 mmol) added on the vacuum line. The solution was heated to 80 °C in an oil bath and removed periodically to monitor the reaction by $^{31}$P NMR spectroscopy. As the resonances for **2** decreased, the resonances for thiophene and $(C_5Me_5)Rh(PMe_3)_2$ increased. The half-life for the reaction was estimated at ~72 days based upon the rate of reaction over the first 2 weeks.

**Intermolecular Competition Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with Thiophene and 2,5-Dimethylthiophene.** A 20-mg sample of **1** (0.051

**Table II.** Summary of Crystallographic Data for $(C_5Me_5)\overline{Rh(PMe_3)(SCMe{=}CHCH{=}CMe)}$

| | |
|---|---|
| **Crystal Parameters** | |
| formula | $RhPSC_{19}H_{32}$ |
| form wt | 426.40 |
| cryst syst | triclinic |
| space group | $P\bar{1}$ |
| $Z$ | 2 |
| $a$, Å | 8.707 (8) |
| $b$, Å | 14.157 (15) |
| $c$, Å | 8.637 (5) |
| $\alpha$, deg | 100.90 (8) |
| $\beta$, deg | 106.07 (2) |
| $\gamma$, deg | 87.85 (8) |
| vol, Å$^3$ | 1004 (3) |
| $d_{calc}$, g/cm$^3$ | 1.41 |
| cryst dimens, mm | 0.30 × 0.34 × 0.56 |
| temp, °C | −75 |
| **Measurement of Intensity Data** | |
| diffractometer | Enraf-Nonius CAD4 |
| radiation (monochromator) | Mo, 0.710 69 Å (graphite) |
| scan type | $2\theta/\omega$ |
| takeoff angle, deg | 2.6 |
| total bkgd time | (scan time)/2 |
| scan rate, deg/min | 2–16.5 |
| scan range, deg | 0.7 + 0.35 tan $\theta$ |
| $2\theta$ range, deg | 2–50 |
| data collected | $-h,\pm k,\pm l$ |
| no. of data collected | 3783 |
| no. of unique data $>3\sigma$ | 2898 |
| no. of params varied | 199 |
| abs coeff, cm$^{-1}$ | 10.02 |
| systematic absences | none |
| abs cor | differential |
| range of transmission factors | 0.835–1.397 |
| equiv data | $0kl = 0\bar{k}\bar{l}$ |
| agreement between equiv data ($F_o$) | 0.01 |
| $R_1$ | 0.046 |
| $R_2$ | 0.058 |
| goodness of fit | 4.60 |

(41) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650–1663.

mmol) was dissolved in 4 mL of hexane. An 8.0-μL aliquot of thiophene (0.10 mmol) and 12.0 μL of 2,5-dimethylthiophene (0.10 mmol) were added to this solution via syringe. The reaction solution was stirred in a glass ampule fitted with a Teflon stopcock for 20 h at 60 °C. The solvent was removed and the product was dissolved in 0.5 mL of $C_6D_6$. The products observed were **2** (67%) and **3** (33%) by $^1H$ NMR spectroscopy.

**Reaction of 2 with DMAD.** A solution of **2** (10 mg, 0.025 mmol) in $C_6D_6$ (0.5 mL) was treated with DMAD (5 μL, 0.041 mmol) at 25 °C. Complete reaction occurred over 24 h, giving a mixture of four products. These species were characterized by $^1H$ NMR, $^{31}P$ NMR, and mass spectroscopies, but could not be easily separated. In addition to thiophene (40%) ($^1H$ NMR: δ 6.920 (d, $J$ = 4.6 Hz, 2 H), 6.815 (d, $J$ = 4.6 Hz, 2 H)), the major organometallic product (60%) was assigned structure **5**. For **5**, $^1H$ NMR ($C_6D_6$): δ 1.636 (s, 15 H), 1.224 (d, $J$ = 10.5 Hz, 9 H), 3.498 (s, 3 H), 3.485 (s, 3 H), 3.531 (t, $J$ = 8 Hz, 1 $H_b$), 4.355 (dd, $J$ = 7.7, 1.4 Hz, 1 $H_a$), 5.872 (dd, $J$ = 9.8, 8.7 Hz, 1 $H_c$), 6.104 (d, $J$ = 9.9 Hz, 1 $H_d$). Homonuclear decoupling indicates connectivity $Rh—CH_a—CH_b=CH_c—CH_d—S$. MS (75 eV) $m/e$ 464 ($M^+$), 463 ($M^+$ - H), 269 ($[(C_5Me_5)Rh(S)]^+$ - H). The remaining two products were assigned structures **6** and **7**, formed in 25% and 20% yields, respectively. **6** can be independently synthesized by the reaction of DMAD with $(C_5Me_5)Rh(PMe_3)(\eta^2$-phenanthrene).[22] For $(C_5Me_5)Rh(PMe_3)[C_4(COOMe)_4]$ (**6**), $^1H$ NMR ($C_6D_6$): δ 1.853 (d, $J$ = 2.5 Hz, 15 H), 0.947 (d, $J$ = 9.0 Hz, 9 H), 3.46 (s, 6 H), 3.39 (s, 6 H). $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ -1.06 (d, $J$ = 188 Hz). MS (75 eV): 598 ($M^+$), 522 ($M^+$ - $PMe_3$). For $(PMe_3)_4Rh[C_5Me_5C_2(COOMe)_2]$ (**7**), $^1H$ NMR ($C_6D_6$): δ 1.224 (virtual q, $J$ = 10.4 Hz, 36 H), 1.345 (s, 6 H), 1.557 (s, 6 H), 1.866 (s, 3 H), 3.641 (s, 3 H), 3.661 (s, 3 H). $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ 4.08 (d, $J$ = 145 Hz). Upon heating to 80 °C for 40 h, compounds **5** and **6** were observed to go away and dimethyl phthalate was formed ($^1H$ NMR: δ 6.876 (dd, $J$ = 5.6, 3.3 Hz, 2 H), 7.512 (dd, $J$ = 5.6, 3.3 Hz, 2 H), 3.499 (s, 6 H); 60% based on **2**). This product was confirmed by GC-MS comparison with an authentic sample. In addition, formation of $S=PMe_3$ ($^{31}P$ NMR: δ 30.45 (br s)) was evident and **7** was the only significant organometallic complex remaining.

**X-ray Structural Characterization of 3.** Well-formed dark red crystals of the compound were prepared by slow evaporation of a hexane solution. The lattice constants were obtained from 25 centered reflections with values of χ between 5 and 70°. Cell reduction with the program TRACER revealed only a primitive triclinic crystal system. Data were collected on the crystal at -75 °C in accord with the parameters in Table II. The space group was assigned as the centric choice $P\bar{1}$ on the basis of N($z$) statistics and $Z_{calc}$. The correctness of this choice was confirmed by successful solution of the Patterson map, showing a rhodium atom in a general position. The structure was expanded by using the DIRDIF program supplied by the Molecular Structure Corp., whose programs were used for further refinement of the structure.[42] Following full isotropic refinement of the structure containing the non-hydrogen atoms, an absorption correction was applied with the DIFABS absorption correction program. Full least-squares anisotropic refinement of the structure with hydrogens placed in idealized positions based upon a difference Fourier map converged with $R_1$ = 0.0457 and $R_2$ = 0.0583.

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**Supplementary Material Available:** Tables (S-I-S-V) of bond distances and angles, anisotropic thermal parameters, and coordinates of hydrogen atoms (7 pages); listings of calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

(42) $R_1 = (\sum||F_o| - |F_c||)/(\sum|F_o|)$; $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}(\sum wF_o^2)$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors $f_o$, $f'$, $f''$: Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

# Stereoselective α-Alkylation of Metallacyclic Zirconoxycarbene Complexes—A Case of Asymmetric 1,5-Induction

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**Abstract:** Coupling of $W(CO)_6$, butadiene, and pinacolone or acetone at the $Cp_2Zr$ template yields the chiral nine-membered metallacyclic zirconoxycarbene complexes $Cp_2ZrOC[=W(CO)_5]CH_2CH=CHCH_2CR^1R^2O$ (**3a**) ($R^1$ = $CH_3$, $R^2$ = $C(CH_3)_3$) and (**3b**) ($R^1$ = $R^2$ = $CH_3$), respectively, exhibiting a trans C=C double bond in the ring. Complex **3b** is deprotonated by the ylide $Ph_3P=CH_2$ at the α-position to the carbene carbon center to yield the chiral unconjugated metallacyclic carbene complex anion **5b**. Ylide deprotonation of **3a** gives the carbanion **5a** which is stereoselectively alkylated at C6 to yield predominately the (2*R**,6*S**)(4,5,6-p*S**) configurated carbene complexes $Cp_2ZrOC[=W(CO)_5]CR^3R^4CH=CHCH_2CR^1R^2O$ (e.g., **6a**, $R^3$ = H, $R^4$ = $CH_3$, 70% de). Repetition of the deprotonation/alkylation reaction sequence stereoselectively yields doubly α-alkylated carbene complexes (e.g., **10**, $R^3$ = $CH_3$, $R^4$ = $CD_3$, 86% de or **15**, $R^3$ = $C_2H_5$, $R^4$ = $CH_2CH=CH_2$, >96% de). The stereo- and regiochemical assignments are based on X-ray crystal structure analyses of the representative complexes **6a** and **9**. Complex **6a** crystallizes in the space group $P\bar{1}$ with cell parameters $a$ = 11.036 (2) Å, $b$ = 12.998 (3) Å, $c$ = 13.259 (3) Å, α = 97.59 (1)°, β = 103.88 (1)°, γ = 107.59 (1), $Z$ = 2, $R$ = 0.058, $R_w$ = 0.058. Complex **9** crystallizes in the space group $Pna2_1$ with cell parameters $a$ = 15.779 (2) Å, $b$ = 13.736 (3) Å, and $c$ = 13.311 (3) Å, $Z$ = 4, $R$ = 0.050, $R_w$ = 0.027. Hydrolysis of the α-methylated zirconoxycarbene complex **6a** in the presence of diazomethane gives the enol ether $HOC(CH_3)(CMe_3)$-$CH_2CH=CHCH(CH_3)C(OCH_3)=CH_2$ with conservation of the stereochemistry introduced at the metallacyclic starting material. Similarly, treatment of **6a** with water/pyridine *N*-oxide produces (2*R**,6*S**)-*trans*-6-hydroxy-2,6,7,7-tetramethyl-3-octenoic acid (**19**).

## Introduction

We have recently introduced a novel method for converting metal carbonyls to transition-metal carbene complexes.[1] The key step of this procedure is the addition of the very reactive ($\eta^2$-olefin) group 4 metallocene type reagents to the M—C≡O moiety, followed by a (probably concerted) ring closure reaction to yield, e.g., metallacyclic zirconoxycarbene complexes. Starting from the readily available (butadiene)zirconocene reagent (**1**) one

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