A model for homogeneous hydrodesulfurization. The importance of η2-coordination and sulfur coordination in C-H and C-S bond cleavage reactions of thiophene

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JANUARY 1992

Impact Factor: 12.11 · DOI: 10.1021/ja00027a022

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weak ligand is sufficient to have a major effect. As the monomer becomes more reactive, a stronger base is needed to lead to the required balancing of the rate constants. This living system has resulted in the preparation of perfectly linear and essentially monodispersed polybutadiene, which upon hydrogenation gives linear, nearly monodispersed polyethylene. These results provide a quantitative basis for the use of this technique in controlling the living polymerization of other strained, cyclic olefins.

Experimental Section

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out using standard Schlenk or vacuum-line techniques or in a N_2-filled drybox. Argon was purified by passage through a column of BASF RS-11 (Chemlog) and Linde 4Å molecular sieves. ^1H NMR spectra were recorded on a JEOL GX 400-MHz (399.65 MHz ^1H; 100.4 MHz ^{13}C; 61.25 MHz ^2H) spectrometer. Magnetization transfer experiments were performed according to published procedures.[16] Gel permeation chromatography (GPC) utilized Shodex KF-803, KF-804, and KF-805 columns and a Knauer differential refractometer. All GPC analyses were performed on a 0.5% w/v solution of polymer in dichloromethane. An injection volume of 0.1 mL and a flow rate of 1.5 mL/min were used. Calibration was based on narrow dispersity polystyrene standards (Polyscience) ranging from M_n = 3550 to 600000.

Materials. Cyclobutene,[17] $P(CD_3)_3$,[18] and $W(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2(NAr)$[6a,19b] (Ar = 2,6-diisopropylphenyl) were prepared according to literature procedures. $Mo(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2(NAr)$[13b] was kindly provided by Dr. Franz Stelzer. Dichloromethane-d_2 was dried over CaH_2. Benzene and toluene were distilled from sodium benzophenone ketyl. PMe_3 was distilled from Na. Acetone-d_6 was stirred over 4 Å molecular sieves. Benzaldehyde was washed with 10% Na_2CO_3 and saturated Na_2SO_3, dried over $MgSO_4$, and distilled under reduced pressure. Methanol was used without further purification. All of the purified solvents were stored under Ar in a flask with a Teflon valve.

Polymerization of Cyclobutene. A typical experiment was done in a small flask with a Teflon valve. The flask was charged with ~3 to 5 mg of catalyst dissolved in ~0.5 to 1.0 mL of benzene or toluene and ~5 to 10 equiv of phosphine in the drybox. The mixture was then degassed at liquid nitrogen temperature and cyclobutene was vacuum-transferred onto it. After being mixed well at −78 °C, the reactants were warmed up to room temperature and stirred for about an hour. The resulting polymer solution was added dropwise into rapidly stirring methanol containing a small amount of BHT. The precipitated polymer was collected and dried in vacuo overnight (87% yield).

Kinetics of the Polymerization with 1. A typical kinetic run consisted of the following: Stock solutions of 1.6 M cyclobutene, 4.112 M $P(CD_3)_3$, and 0.0907 M catalyst in toluene-d_8 were prepared. NMR tubes were charged with aliquots of the stock solutions, diluted with additional toluene-d_8 to provide 0.5 mL total volume. The tubes were kept at −78 °C before being rapidly transferred into the NMR probe. The spectra were recorded at the desired temperatures during certain time intervals. The disappearance of the olefinic protons of cyclobutene at 5.9 ppm was monitored with respect to the mesitylene internal standard at different phosphine and catalyst concentrations for over 3 half-lives ($\rho \geq 0.998$). Similarly, the disappearance of the bound-catalyst alkylidene proton resonance at 10.85 ppm was monitored at different phosphine and monomer concentrations over 3 half-lives. The first-order plots have $\rho \geq 0.996$. Least-squares analyses of first-order plots of ln ($[M]/[M_0]$) vs time and ln ($[C]/[C_0]$) vs time yielded $k_{obs(p)}$'s and $k_{obs(i)}$'s. Linear Erying plots for both propagation and inition have ρ = 0.996 and 0.997. Activation parameters were obtained from least-squares analyses of ln ($k_{app(p\text{ or }i)}/T$) vs $1/T$ plots.

Acknowledgment. We gratefully acknowledge NSF and Rohm & Haas for financial support of this work. We especially thank Lynda K. Johnson and Dr. R. A. Fisher for their help and advice in preparing this manuscript.

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A Model for Homogeneous Hydrodesulfurization. The Importance of η^2-Coordination and Sulfur Coordination in C–H and C–S Bond Cleavage Reactions of Thiophene

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Abstract: The reaction of $(C_5Me_5)Rh(PMe_3)PhH$ with thiophene at 60 °C produces the C–S cleavage adduct $(C_5Me_5)Rh(PMe_3)(SCH{=}CHCH{=}CH)$ in high yield. Irradiation of $(C_5Me_5)Rh(PMe_3)H_2$ at −20 °C in the presence of thiophene results in the formation of both the C–S insertion product and the new C–H addition adduct $(C_5Me_5)Rh(PMe_3)(2\text{-thienyl})H$. The latter can be independently prepared by the reaction of $(C_5Me_5)Rh(PMe_3)Cl_2$ with 2-thienyllithium, followed by $LiHBEt_3$. The 2-thienyl hydride rearranges intramolecularly to the C–S insertion adduct with activation parameters $\Delta H^* = 25.15$ (45) kcal/mol and $\Delta S^* = 3.0$ (2) eu. Preparation with $LiDBEt_3$ generates $(C_5Me_5)Rh(PMe_3)(2\text{-thienyl})D$, which rearranges to the C–S insertion product in which the deuterium is scrambled over both carbons that were originally adjacent to the sulfur atom. Similarly, the complex $(C_5Me_5)Rh(PMe_3)(3\text{-thienyl})H$ was prepared and observed to isomerize intramolecularly to the 2-thienyl derivative at 23 °C with a rate constant of 1.2 (1) × 10^{-3} s^{-1}. The corresponding deuteride complex $(C_5Me_5)Rh(PMe_3)(3\text{-thienyl})D$ was observed to rearrange selectively first to $(C_5Me_5)Rh(PMe_3)[2\text{-}(3\text{-deuteriothienyl})]H$ and then to a mixture of the C–S insertion adducts with deuterium attached to either the 3 or 4 carbon. The rearrangements of several methyl derivatives have also been studied and found to occur with similar regiospecificity. Heating of $(C_5Me_5)Rh(PMe_3)PhH$ in the presence of tetramethylthiophene results in the formation of the S-bound complex, $(C_5Me_5)Rh(PMe_3)(SC_4Me_4)$. The chloro derivative $(C_5Me_5)Rh(PMe_3)(2\text{-thienyl})Cl$ was found to crystallize in the monoclinic space group $P2_1/c$ with a = 8.992 (7) Å, b = 11.324 (10) Å, c = 18.480 (8) Å, β = 91.52 (6)°, V = 1881.0 (2.3), and Z = 4.

Introduction

The hydroprocessing of oil is a procedure in which a complex combination of chemical reactions are used to remove sulfur, nitrogen, and metals by reaction with hydrogen over a heterogeneous catalyst. In particular, the removal of sulfur (commonly referred to as hydrodesulfurization or HDS) from the less reactive aromatic sulfur-containing residues such as thiophene has been the subject of many studies.[1] While this process has been carried

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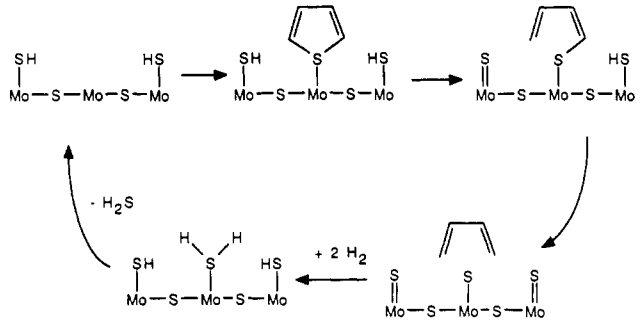
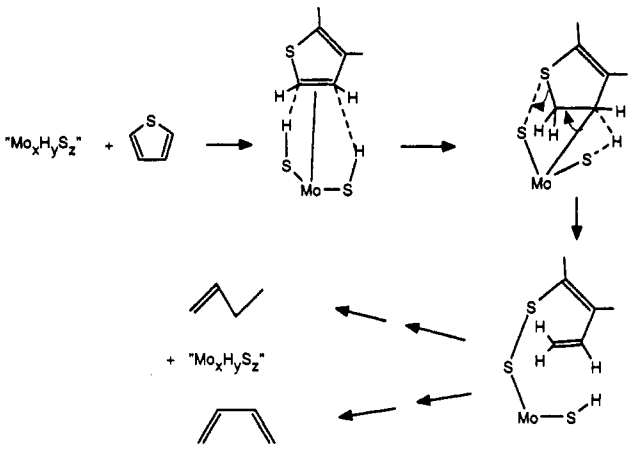
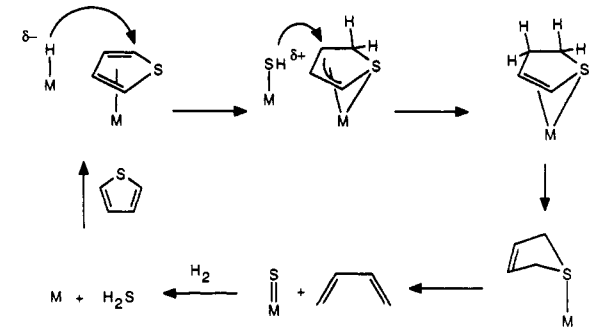
Scheme I



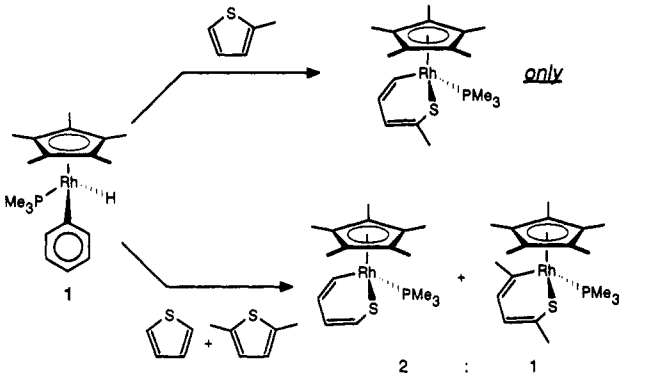
Scheme II



Scheme III



Scheme IV



out on an immense scale for many years, there is still debate over the mechanism(s) by which these reactions occur.

Much of the discussion of HDS deals with the initial mode by which molecules such as thiophene interact with the catalyst, which in the industrial case is a cobalt–molybdenum sulfide species supported on alumina. Many other metals also are active in HDS, and some are better than the commercially used catalyst.[2] Surface studies of metals and sulfided metals probably represent the most fundamental examinations of thiophene binding and provide evidence for π-bonding (η^5-C_4H_4S) as the dominant species on a surface such as Mo(100) or Ni(111).[3] Recent surface studies have also provided evidence for the cleavage of the C–S bond prior to hydrogenation of the unsaturated ring.[4] It is variations on these latter points that delineate the mechanisms that have been presented for HDS.

One of the earliest suggestions was that the thiophene bound to a vacant surface site produced by loss of an anion (sulfide or oxide).[5] Transfer of hydrogen from adjacent OH (or SH) groups leads to the production of butadiene and surface sulfides, which are hydrogenated to give H_2S (Scheme I). This mechanism adheres to the notion that butadiene is a primary product that is subsequently hydrogenated to butane in a separate catalytic reaction.[6] Theoretical studies have also provided support for the binding of thiophene through the sulfur as leading to the C–S cleavage reaction.[7]

More recently, however, it has been suggested that the C_1–C_2 double bond of thiophene interacts with an anion vacancy in the initial step[8] in order to account for the high reactivity of α-methyl-substituted thiophenes.[9] Following η^2-coordination, the thiophene is reduced by surface SH groups to give a σ-bonded species, which then cleaves the C–S bond in what appears to be similar to an elimination reaction (Scheme II). This model has also been stated as accommodating the observed preference for deuterium exchange into the α positions of the ring,[10] although migration of a hydrogen exo to the surface is required.

A third mechanism has been proposed in which a double β-elimination in a S-bound thiophene species leads to the extrusion of 1,3-butadiyne and the formation of surface bound H_2S.[11] This pathway is supported by the observation that deuterated thiophene leads to the production of some D_2S[12] but cannot account for the desulfurization of dibenzothiophene. Under typical HDS conditions, the diyne would be hydrogenated to butane.

Many studies of homogeneous reactions that model initial and subsequent steps in HDS reactions have also appeared in the literature. These include early reports of the insertion of iron into the C–S bond of thiophene[13] and extend to include π-complexes of thiophenes that can be reduced to partially hydrogenated or cleaved species.[14] Angelici has summarized many of these studies

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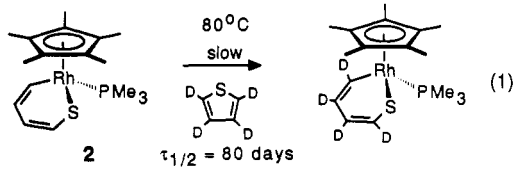
in a recent review and has proposed a mechanism for HDS that involves hydridic attack upon an η^5-bound thiophene followed by transfer of an acidic hydrogen to the 3-position of the thiophene ring (Scheme III).[15] Several other reviews are also appearing in which various homogeneous structural models for thiophene binding are compared.[16] Cluster models for thiophene HDS have also been reported, some of which produce the same active site on alumina as is found in commercial Mo/Co/S catalysts.[17]

In the current paper, we present evidence for a homogeneous model for the C–S bond cleavage of thiophene. A preliminary report of this work showed that the thermal reaction of the reactive fragment $[(C_5Me_5)Rh(PMe_3)]$ with thiophene leads to the C–S insertion product $(C_5Me_5)Rh(PMe_3)(SCH{=}CHCH{=}CH)$.[18] The reaction proceeds cleanly for 2-methylthiophene, 3-methylthiophene, 2,5-dimethylthiophene, benzothiophene, and dibenzothiophene, with a preference for insertion into the unsubstituted C–S bond when there is a choice. This report also presented competitive selectivity data, comparing the exclusive product formed with 2-methylthiophene with the 2:1 mixture of products seen with thiophene/2,5-dimethylthiophene (Scheme IV), as being most consistent with S-coordination of the thiophene prior to C–S cleavage. In the present series of studies, we present further evidence for the intermediacy of S-coordinated intermediates and also demonstrate that η^2-thiophene and σ-thienyl complexes play kinetically important roles leading to the S-bound thiophene complex prior to C–S insertion.

Results

As mentioned above, the complex $(C_5Me_5)Rh(PMe_3)PhH$ (**1**) was reported to react with thiophene at 60 °C in hexane solution to give the C–S cleavage product $(C_5Me_5)Rh(PMe_3)(SCH{=}CHCH{=}CH)$ (**2**) in high yield. This product is not as labile as the phenyl hydride complex **1**, as shown by heating a cyclohexane solution of **2** in the presence of a 10-fold excess of perdeuterothiophene. At 81 °C, the ^1H NMR spectrum shows the slow formation ($\tau_{1/2} \cong 80$ days) of free thiophene as **2-d_4** is formed (eq 1). The ^{31}P NMR spectrum displays the same doublet as seen for **2**.



(1)

The complex $(C_5Me_5)Rh(PMe_3)H_2$ was irradiated in the presence of thiophene in C_7D_{14} solution at −40 °C in order to look for intermediates in the C–S cleavage reaction. The major product observed was **2** (75%), although a second $(C_5Me_5)Rh(PMe_3)$-containing product was observed by ^1H NMR spectroscopy (25%). Three new olefinic resonances (δ 6.51, dq, J = 3.1, 1.0 Hz, 1 H; 6.76, dd, J = 5.1, 3.2 Hz, 1 H; 7.028, dd, J = 5.0, 0.5 Hz, 1 H) and a hydride resonance (δ −12.88, dd, J = 45, 28 Hz, 1 H) were seen for this compound. The ^{31}P NMR spectrum indicated that this compound was a Rh(III) complex (δ 6.56, d, J = 144.2 Hz) and led to its formulation as the C–H activation adduct $(C_5Me_5)Rh(PMe_3)(2\text{-thienyl})H$ (**3**) (eq 2). The ratio of products

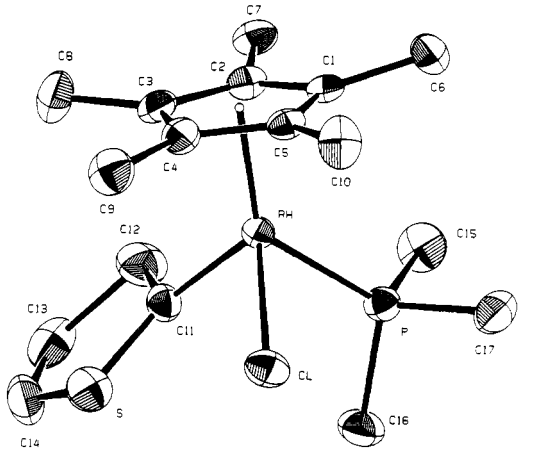


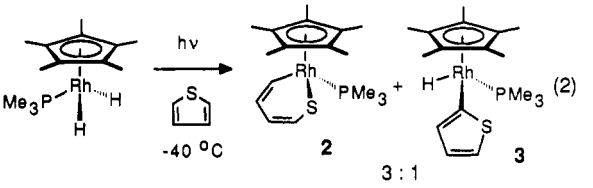
Figure 1. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(2\text{-thienyl})Cl$. Ellipsoids are shown at the 50% level.

Table I. Rate Data for the Conversion of 3 into 2 in Hexane Solvent[a]

temp, K	rate, s^{-1}	temp, K	rate, s^{-1}
301	1.40 (2) × 10^{-5}	321	2.56 (3) × 10^{-4}
307	3.50 (2) × 10^{-5}	325	3.83 (1) × 10^{-4}
307	3.54 (3) × 10^{-5}	330	7.16 (4) × 10^{-4}
310	5.45 (2) × 10^{-5}	330	7.12 (7) × 10^{-4}
313	9.98 (10) × 10^{-5}	335	1.114 (7) × 10^{-3}
317	1.474 (4) × 10^{-4}	335	1.17 (1) × 10^{-3}
317	1.405 (4) × 10^{-4}	325[b]	1.50 (2) × 10^{-4}
321	2.39 (1) × 10^{-4}	330[b]	2.92 (2) × 10^{-4}

[a] [3] ≅ 1 mM. [b] THF solvent.

2 and **3** remained 3:1 throughout the photolysis, suggesting that they are formed in parallel reactions rather than sequential reactions (e.g., $(C_5Me_5)Rh(PMe_3)H_2 \rightarrow 3 \rightarrow 2$).



(2)

The observation of the 2-thienyl derivative suggested that it might be prepared by the same route used for the synthesis of the phenyl hydride complex. Indeed, the reaction of $(C_5Me_5)Rh(PMe_3)Cl_2$ with 2-thienyllithium in THF solution led to the isolation of analytically pure yellow $(C_5Me_5)Rh(PMe_3)(2\text{-thienyl})Cl$ in 67% yield following chromatography and recrystallization. The bromo derivative was prepared in a similar fashion from $(C_5Me_5)Rh(PMe_3)Br_2$.

A crystal of the chloro derivative was subjected to single-crystal X-ray analysis. Following data collection in monoclinic space group $P2_1/c$, Patterson map solution and expansion of the structure proceeded routinely. It was noted, however, that the sulfur appeared to be disordered over the two possible rotamers (cf. hindered Rh–aryl rotation in $(C_5Me_5)Rh(PMe_3)PhCl$[19]). The structure was refined using a model in which the populations of the sulfur and the related ortho carbon atom (C12) were allowed to vary together in each rotamer. The refined populations (51.7% vs 48.3%) indicate little preference for either orientation. Final anisotropic refinement (isotropic on sulfur only) led to agreement values R = 0.036, R_w = 0.040. An ORTEP diagram of one rotamer is shown in Figure 1.

Reduction of $(C_5Me_5)Rh(PMe_3)(2\text{-thienyl})Cl$ with $LiHBEt_3$ followed by flash chromatography through silica gel results in the

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Table II. Summary of Crystallographic Data for $(C_5Me_5)Rh(PMe_3)(2\text{-thienyl})Cl$

formula	$RhPSClC_{17}H_{27}$
mol wt	432.79
space group	$P2_1/c$ (no. 14)
a, Å	8.992 (7)
b, Å	11.324 (10)
c, Å	18.480 (8)
β, deg	91.52 (6)
vol, Å^3	1881.0 (2.3)
ρ_{calc}, g cm^{-3}	1.528
Z	4
temp, °C	−75
radiation (monochromator)	Mo, 0.71073 Å (graphite)
μ cm^{-1}	12.20
range of trans factors	0.92–1.13
R (F_o)	0.0363
R_w (F_o)	0.0399

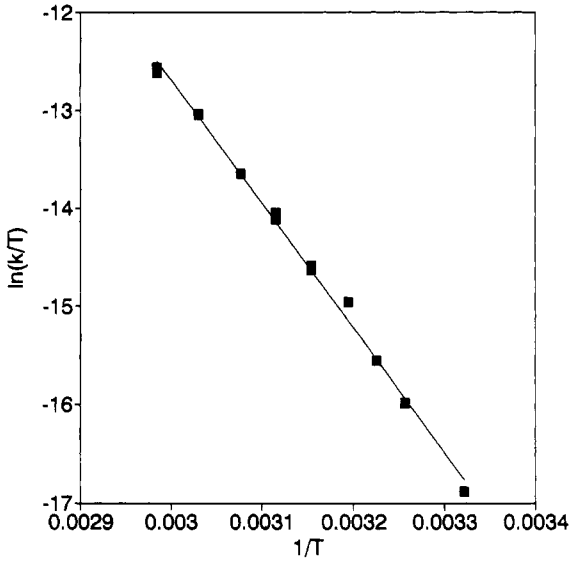


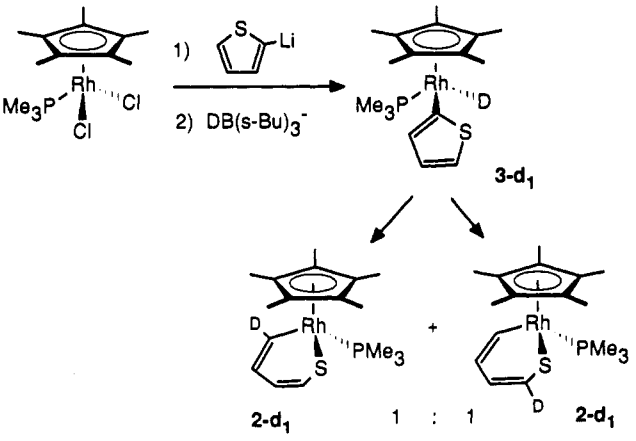
Figure 2. Eyring plot for the conversion of **3** into **2**.

formation of the 2-thienyl hydride complex, **3**. The derivative **3** was found to be unstable at room temperature and slowly converted to the more stable C–S insertion isomer **2** upon standing at room temperature. Since **2** is red and **3** is pale yellow, the rate of this interconversion can be measured conveniently by UV spectroscopy. Examination of the absorbance vs time behavior of **3** showed clean first-order behavior, giving the rate constants listed in Table I. By measuring the rate as a function of temperature, the activation parameters obtained from the Eyring plot shown in Figure 2 were found to be $\Delta H^{\ddagger} = 25.15$ (45) kcal/mol and $\Delta S^{\ddagger} = 3.0$ (2) eu. The rate in THF solvent was found to be slightly slower.

The conversion of **3** into **2** was found to be intramolecular. Monitoring the reaction at 81 °C by ^1H NMR spectroscopy in the presence of an excess (10×) of perdeuterothiophene showed no incorporation of the labeled substrate (as would be evidenced by the lack of appearance of the olefinic resonances of **2**). Monitoring the rearrangement in the presence of an excess of 2,5-dimethylthiophene also did not result in any incorporation of the dimethylthiophene into the C–S cleavage adduct.

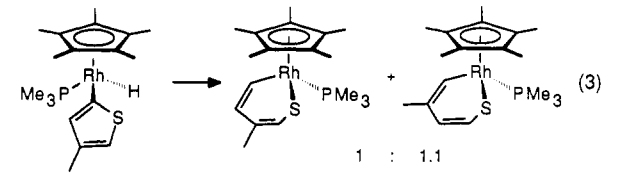
The ability to prepare **3** synthetically also allowed the generation of the isotopomer with deuterium specifically on the rhodium center. Reaction of $(C_5Me_5)Rh(PMe_3)(2\text{-thienyl})Cl$ with $LiDBEt_3$ permitted the generation of $(C_5Me_5)Rh(PMe_3)(2\text{-thienyl})D$. Flash chromatography through silica gel, however, resulted in extensive exchange of deuterium for hydrogen. Consequently, the deuterated reaction mixture was worked up by first dissolving in DMSO and extracting the neutral rhodium complex (**3-d_1**) into hexane. Examination of the reaction by ^{31}P NMR spectroscopy showed the formation of two Rh(III) species in a 1:1 ratio, identified as $(C_5Me_5)Rh(PMe_3)(2\text{-thienyl})H$ (δ 7.53, d, J = 148.8 Hz) and

Scheme V. 2-Thienyl Deuteride Rearrangement Is not Regiospecific



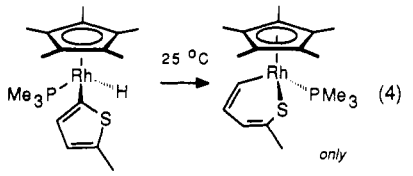
$(C_5Me_5)Rh(PMe_3)(2\text{-thienyl})D$ (δ 7.66, dt, J = 148.9, 6.8 Hz). The ^2H NMR spectrum shows the expected doublet of doublets at δ −12.53 for the Rh–D resonance. The Rh–D resonance was seen to decrease over a period of 48 h at room temperature as ^2H resonances at δ 6.54 and 5.54 grew in a 1:1 ratio, corresponding to deuterium incorporation into **2-d_1** at *both* the 2- and 5-positions (i.e., on carbons adjacent to either the sulfur or the rhodium). No deuterium resonance was seen corresponding to scrambling of deuterium in **3-d_1** between the Rh–D and the 5-position of the thienyl ligand *prior* to the rearrangement to **2-d_1** (Scheme V).

In a similar fashion, the rearrangement of the 4-methyl-2-thienyl derivative was monitored. Reaction of 4-methyl-2-thienyllithium with $(C_5Me_5)Rh(PMe_3)Cl_2$ gives analytically pure $(C_5Me_5)Rh(PMe_3)(4\text{-methyl-2-thienyl})Cl$ following chromatography. Reduction with $LiHBEt_3$ in THF solution followed by flash chromatography gives $(C_5Me_5)Rh(PMe_3)(4\text{-methyl-2-thienyl})H$ as the major product, as seen by ^{31}P and ^1H NMR spectroscopy. Over a period of several days at room temperature, the two C–S insertion products $(C_5Me_5)Rh(PMe_3)(SCH{=}CMeCH{=}CH)$ and $(C_5Me_5)Rh(PMe_3)(SCH{=}CHCMe{=}CH)$ grow in a ratio of 1:1.1, respectively (eq 3). At no time is the scrambling product of the 2-thienyl starting material, $(C_5Me_5)Rh(PMe_3)(3\text{-methyl-2-thienyl})H$, observed.



We have reported earlier that heating (60 °C) of **1** in the presence of 2-methylthiophene gives only one of two possible insertion products, in which the C–S bond away from the methyl group is selectively cleaved.[18] The above synthetic methods allow the preparation of possible precursors to this complex at lower temperatures. Reaction of $(C_5Me_5)Rh(PMe_3)Cl_2$ with 5-methyl-2-thienyllithium results in the formation of $(C_5Me_5)Rh(PMe_3)(5\text{-methyl-2-thienyl})X$ (X = Cl, Br) as above. (In this case, the halide derivative is a mixture of chloro and bromo derivatives due to the unavoidable presence of LiBr in the lithium reagent.) Reaction of this halide derivative with $LiHBEt_3$ as before gave only one major product, identified as $(C_5Me_5)Rh(PMe_3)(5\text{-methyl-2-thienyl})H$. This isomer then rearranged selectively to the previously observed isomer $(C_5Me_5)Rh(PMe_3)(SCMe{=}CHCH{=}CH)$ upon standing overnight at 25 °C (eq 4).

The preparation and rearrangement of the 3-thienyl derivatives was also examined. As above, reaction of 3-thienyllithium with the rhodium dibromide precursor yielded $(C_5Me_5)Rh(PMe_3)(3\text{-thienyl})Br$. Reaction of this complex with $LiHBEt_3$, followed by isolation using the DMSO/hexane extraction procedure described

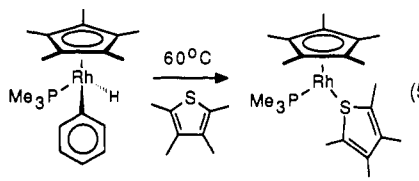


(4)

above, was found to give the rearranged product $(C_5Me_5)Rh(PMe_3)$(2-thienyl)H! Since about 1 h had elapsed between the time of the borohydride addition and the time that the first NMR analysis of the reaction could be performed, the reaction was repeated at low temperature. In this instance, the halide was first removed with Ag^+ in THF-d_8 in order to generate the more reactive species $[(C_5Me_5)Rh(PMe_3)(3\text{-thienyl})(THF\text{-}d_8)]^+$. Addition of $LiHBEt_3$ at −78 °C followed by ^1H and ^{31}P NMR analysis at −30 °C was found to be consistent with the formation of $(C_5Me_5)Rh(PMe_3)$(3-thienyl)H (**4**). The sample was warmed to 23 °C in the probe of the NMR spectrometer, at which temperature it slowly rearranged to the 2-thienyl derivative **3**. The rate of the reaction was estimated from a first-order plot of data obtained by integration of the ^{31}P resonances of a series of NMR spectra, with $k_{obs} = 1.2\ (1) \times 10^{-3}\ s^{-1}$ ($\tau_{1/2} \cong 10$ min).

The reaction of $(C_5Me_5)Rh(PMe_3)$(3-thienyl)Cl with $LiDBEt_3$ was also examined. Following workup with DMSO/hexane, the only product observed was the derivative with deuterium on the 3-position of the ring, $(C_5Me_5)Rh(PMe_3)$(3-deuterio-2-thienyl)H. The rearrangement from the 3- to the 2-position had occurred *regiospecifically* during the workup period. The subsequent rearrangement occurred upon standing at room temperature, to give both regioisomers of **2-d_1** with deuterium in either the 3- or 4-position (Scheme VI).

Direct evidence for the formation of a sulfur bound thiophene ligand was also obtained with this system. Thermolysis of **1** in the presence of an excess of tetramethylthiophene in hexane solution leads to the formation of a major new product (43%) whose ^{31}P NMR spectrum suggests a Rh(I) complex (δ −3.09, d, J = 222.2 Hz). Examination of the ^1H and ^{13}C spectra showed resonances consistent with the formation of the S-bound product $(C_5Me_5)Rh(PMe_3)(SC_4Me_4)$, in which pairs of thiophene methyl groups are rendered equivalent (eq 5). The complex proved too sensitive to isolate in pure form and showed no tendency for C–S bond cleavage as observed with all other thiophenes studied.



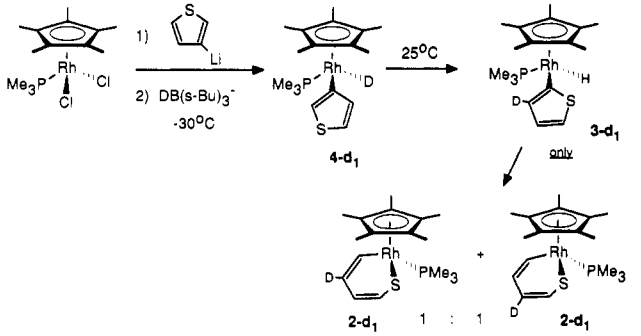
(5)

Discussion

The ability of $[(C_5Me_5)Rh(PMe_3)]$ to activate a variety of hydrocarbons has permitted detailed mechanistic studies of its interactions with many substrates. These studies provide strong evidence for the formation of an η^2-benzene complex as an intermediate in arene C–H bond activation.[20] The recent observations on the ability of fused polycyclic hydrocarbons to coordinate to this fragment and give stable η^2-complexes has led to the investigation of a number of new aromatic substrates.[21] It was these studies that prompted the investigation of reactions of thiophenes with rhodium.

While the thermal generation of $[(C_5Me_5)Rh(PMe_3)]$ by thermolysis of **1** leads to only C–S cleavage reactions with thiophenes, the photochemical generation of this fragment at low temperature gives a mixture of both C–H and C–S cleavage products (eq 2). In fact, based on the previous studies with benzene and naphthalene we expected that an η^2-thiophene complex would be formed initially, but that this would rapidly undergo intramolecular insertion into the C–H bond α to the sulfur. The observation of C–S cleavage was a surprise. Furthermore, since the ratio of the C–H and C–S insertion products does not change over the course of the low-temperature photolysis, they must be formed in parallel, rather than sequential reactions.

Scheme VI. 3-Thienyl Deuteride Rearrangement to 2-Thienyl Hydride Is Regiospecific



The rearrangement of **3** to **2** does occur, however, but only at higher temperatures. Since the lack of incorporation of free perdeuterothiophene into **2** rules out thiophene dissociation, the rearrangement must be intramolecular. The activation parameters are consistent with an intramolecular process ($\Delta S^{\ddagger} \cong 0$). The lack of regiochemical selectivity as revealed by the rearrangement of $(C_5Me_5)Rh(PMe_3)$(2-thienyl)D into **2-d_1** (Scheme V) indicates that a symmetrical intermediate (or an equilibrating one) must be involved. Scheme VII shows two possible pathways for this rearrangement.

In one pathway, the thiophene coordinates to the soft rhodium(I) center, and one of the α-carbons then undergoes a sulfur-to-metal migration. In the second pathway, the C–S insertion occurs by direct migration of the rhodium in an η^2-thiophene complex into the adjacent C–S bond. In the η^2-thiophene complex, the metal center is poised in just the proper position for this type of migration. Furthermore, an η^2-intermediate would nicely account for the parallel formation of the C–H insertion adduct, **3**. Since this pathway for C–S insertion would be expected to be selective and give only one regioisomer, a [1,3] shift of the rhodium around the thiophene is proposed to account for the mixture of isomers that is observed, despite the fact that this type of fluxional shift does not occur in the η^2-benzene complex.[22] In the absence of other data, these two mechanistic possibilities cannot be distinguished. It is also possible that both intermediates are involved in the rearrangement, with the formation of the η^2-complex preceding the formation of the S-bound complex (or vice versa).

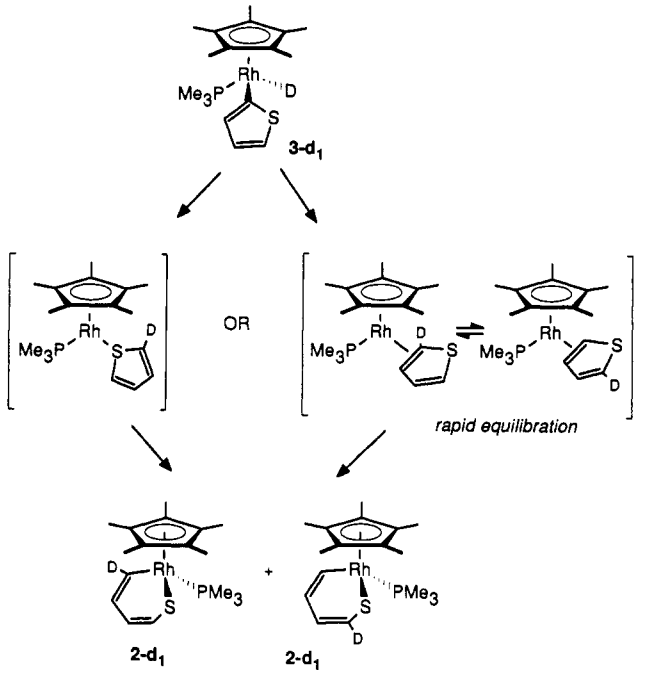
The rearrangement of the methyl derivative $(C_5Me_5)Rh(PMe_3)$(4-methyl-2-thienyl)H shown in eq 3 can also be explained with either of the above mechanistic pathways. An S-bound intermediate would give an ~1:1 mixture of the $(C_5Me_5)Rh(PMe_3)(SCH{=}CMeCH{=}CH)$ and $(C_5Me_5)Rh(PMe_3)(SCH{=}CHCMe{=}CH)$ C–S insertion products. An η^2-complex, however, would be anticipated to show a preference for the product $(C_5Me_5)Rh(PMe_3)(SCH{=}CMeCH{=}CH)$, since coordination of the rhodium to the unsubstituted double bond should be preferred, although the magnitude of this preference is difficult to predict. Likewise, the 5-methyl-2-thienyl hydride complex rearrangement (eq 4) can be fit into either pathway. Migration of the unsubstituted carbon would be preferred in the S-bound complex, or coordination of the unsubstituted double bond would be preferred in the η^2-complex.

The experiments with the 3-thienyl complexes were performed in order to address the possibility that the η^2-thiophene complex was fluxional. The rearrangement of the 3-thienyl complex **4-d_1** to the 2-thienyl complex **3-d_1** occurs regiospecifically, without scrambling of the deuterium into the 4-position of the 2-thienyl ring (Scheme VI). This result can be accounted for in terms of the 3- to 2-rearrangement occurring by way of the η^2-thiophene

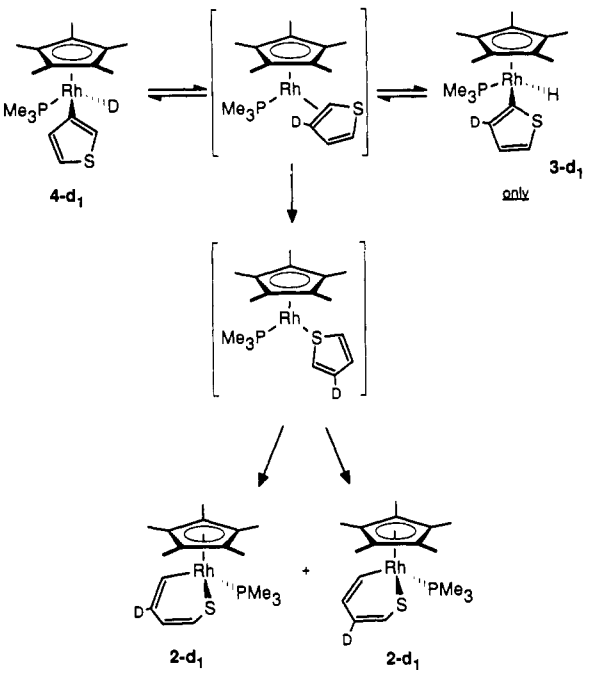
(21) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1989**, *111*, 8722–8723.

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

Scheme VII. Two Possibilities To Account for the Lack of Regiospecificity in the 2-Thienyl Deuteride Rearrangement



Scheme VIII. 3-Thienyl Deuteride Rearrangement Indicates that η^2-Intermediate Is not Fluxional



complex, *which cannot be fluxional* (Scheme VIII). This rearrangement is analogous to the hydrogen migration reported earlier in $(C_5Me_5)Rh(PMe_3)(C_6D_5)H$, in which a [1,2] migration around the phenyl ring was found to occur by way of a nonfluxional η^2-C_6D_5H complex.[23] If the aromatic thiophene molecule is indeed similar to benzene in its behavior when attached to $(C_5Me_5)Rh(PMe_3)$, then the 2-thienyl hydride to η^2-thiophene reaction should be rapid and reversible, with a reasonable thermodynamic preference for the C–H insertion product. The migration of the metal from the 2-thienyl complex to the C–S insertion adduct can then be accounted for in terms of a migration of rhodium from the double bond in the η^2-thiophene complex to the sulfur, followed by migration of carbon from the sulfur to the metal. In this way, the regiochemical selectivity is lost in the C–S cleavage reaction and not in the **4** to **3** rearrangement.

The ability to observe an S-bound complex with tetramethylthiophene (eq 5) offers support for the presence of this type of bonding with other thiophene derivatives. It is not clear at the present time why this tetrasubstituted substrate does not undergo the C–S cleavage reaction that has been seen with every other thiophene examined. The fact that 2,5-dimethylthiophene inserts pretty much rules out a steric barrier, although it is possible that the "buttressing effect" of forcing all four methyl groups on the six-membered ring into coplanarity destabilizes the insertion product. Similar steric problems are known to increase the racemization barriers in tetramethylphenanthrenes.[24] Another possibility is that the electron density in the ring is high enough that the C–S cleavage is no longer thermodynamically favorable. All other thiophenes that have been examined in this system are less electron rich. Angelici has noted that tetramethylthiophene is the best S-donor ligand among the methyl-substituted thiophenes.[25]

A recent observation by Angelici provides some support for the C–S cleavage mechanism cited here. Reaction of $CpRe(CO)_2$(THF) with thiophene gives an S-bound thiophene complex.[26] Further studies have shown that the $CpRe(CO)_2$ fragment binds to benzothiophene to give a mixture of η^2- and S-bound isomers, $CpRe(CO)_2(\eta^2$-benzothiophene) and $CpRe(CO)_2$(S-benzothiophene).[27] With the rhenium system, however, no C–H activation or C–S cleavage is observed. There are also several other examples of S-coordinated thiophene derivatives in the literature, but these are generally labile species.[28] Examples of other η^2-coordinated thiophenes are virtually nonexistent, with a single published report of such a complex by Taube.[29] It is also interesting to note that the reaction of $[(C_5Me_5)Rh(PMe_3)]$ with benzothiophene gives only the C–S insertion product, with no evidence for the formation of an η^2-complex as might have been expected based upon the equilibrium mixture of η^2 and C–H activation products seen with the related hydrocarbon, naphthalene.[21]

Consideration of the free energy requirements placed on the $[(C_5Me_5)Rh(PMe_3)]$ system by these studies provides an interesting overall view of the interactions of thiophene with the metal center, as shown in Scheme IX. The initial interaction with the 16-electron fragment shows a slight preference for C–S bond cleavage, which is accounted for by a preference for S-coordination over η^2-coordination. The C–S insertion product is the thermodynamically preferred compound. The η^2-thiophene complex can insert into either the 2- or 3-position of the ring, with the 2-thienyl isomer **3** being preferred kinetically (no **4** was seen at low temperature in eq 2). The 2-isomer is also preferred thermodynamically since the conversion of **4** to **3** was complete. The intramolecularity of the **3** to **2** conversion requires that a nondissociative

(23) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240–4242.
(24) Armstrong, R. N.; Ammon, H. L.; Darnow, J. N. *J. Am. Chem. Soc.* **1987**, *109*, 2077–2082.
(25) Choi, M.-G.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 1417–1419.
(26) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 8753–8754. Choi, M.-G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2436–2442.
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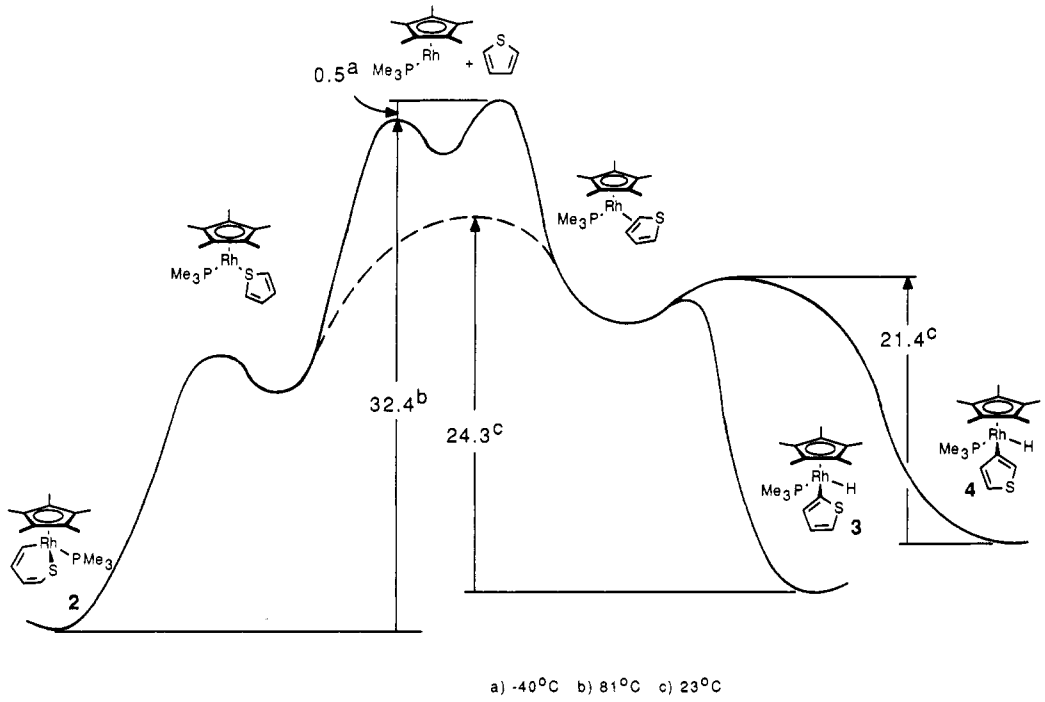
(30) Cowley, S. W., Ph.D. Thesis, Southern Illinois University, 1975. See also ref 8.
(31) Gaertner, R.; Tonkyn, R. G. *J. Am. Chem. Soc.* **1951**, *73*, 5872.
(32) $R_1 = |\sum||F_o| - |F_c||/\sum|F_o||$; $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}/[\sum wF_o^2]$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{1/2}$ 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.

Scheme IX



pathway join one side of this diagram to the other. This is shown by the dotted line, which represents the migration of the metal from the double bond to the sulfur. The integrity of the complex **3-d_1** prior to C–S cleavage requires that this migration be irreversible, which can be accommodated as long as the barrier to C–S insertion from the S-bound intermediate is lower than the barrier to reverse migration back to the C–C double bond. The transition state for the C–S insertion is envisioned as involving an η^2-geometry of the lengthened thiophene C–S bond.

Conclusions

In summary, the observation of an oxidative addition of a carbon–sulfur bond to a metal center has allowed a series of detailed mechanistic studies to be performed. These experiments are consistent with an intermediate in which thiophene first coordinates to the metal via the sulfur atom, followed by migration of the α-carbon to the metal center. In addition, η^2-complexation to a thiophene C–C double bond leads to the production of C–H activation products, which are thermodynamically less favored but kinetically significant. Since sulfur can be extruded from thiophene following this initial step, as demonstrated previously, the possibility of this pathway serving as an additional mechanism for petroleum hydrodesulfurization should not be neglected.

Finally we note that an early postulation for the mechanism of HDS was put forth suggesting that thiophene equilibrated between a π complex and a σ complex with the α carbon, prior to forming the S-bound complex that was responsible for the C–S cleavage reaction.[30] This picture of the species involved in HDS agrees quite well with that painted by the homogeneous modelling studies presented here.

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, and 2-lithiothiophene were purchased from Aldrich Chemical Co. and were used without further purification, although each was freeze–pump–thaw degassed (three cycles) prior to use. Perdeuterothiophene was obtained from MSD Isotopes Merck Chemical Division Company. Hexane was distilled according to our published procedures. $(C_5Me_5)Rh(PMe_3)PhH$ and $(C_5Me_5)Rh(PMe_3)H_2$ were prepared as previously described.[22]

^1H (400 MHz), ^{13}C (100 MHz), and ^{31}P (162 MHz) NMR spectra were recorded on a Bruker AMX-400 spectrometer. ^1H NMR shifts were measured relative to residual ^1H resonances in the deuterated solvents: C_6D_6 (δ 7.15) and C_6D_{12} (δ 1.38). ^{31}P NMR spectra are reported in units of δ (chemical shifts are referred to external 10% H_3PO_4 at δ 0.0 ppm). ^{13}C NMR were measured relative to the deuterated solvent resonance (C_6D_{12}, δ 26.4 ppm). C_6D_6 and C_6D_{12} were purchased from MSD Isotopes Merck Chemical Division Company 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. UV spectra were recorded on a HP Diode Array UV–vis spectrophotometer.

Photochemical Reaction of $Cp^*Rh(PMe_3)H_2$ with Thiophene. A C_7D_{14} solution of $(C_5Me_5)Rh(PMe_3)H_2$ (0.020 g, 0.0632 mmol) was placed in an NMR tube. To this solution was added 30.0 μL of thiophene (0.379 mmol). The sample was cooled to −40 °C with a 45/55 (v/v) of methanol/H_2O/liquid-nitrogen bath and irradiated through a quartz window in a glass dewar. The reaction was monitored by ^1H and ^{31}P NMR spectroscopies with the probe of the NMR spectrometer cooled to −40 °C. Following several hours of irradiation, two products were observed in a ratio of 3:1. The major product was identified as the C–S insertion product **2** and the second product was identified as a C–H bond activation product $(C_5Me_5)Rh(PMe_3)(2\text{-thiophenyl})H$ by comparing with the authentic samples (see below). No evidence for an S-bound (or any other) species was observed. The conversion of the hydride to the C–S insertion product was observed upon warming to room temperature for several hours. This conversion was easily determined from the integrated intensities of the PMe_3 resonances of the C–S insertion product and the C–H activation product in the ^{31}P NMR spectrum. For $(C_5Me_5)Rh(PMe_3)H_2$: ^1H NMR (C_7D_{14}) δ −13.982 (dd, J = 42.7, 29.7 Hz, 2 H), 1.340 (dd, J = 9.7, 1.2 Hz, 9 H), 2.100 (t, J = 1.0 Hz, 15 H); ^{31}P NMR δ 7.19 (d, J = 152.6 Hz). For $(C_5Me_5)Rh(PMe_3)(SCH{=}CHCH{=}CH)$: ^1H NMR (C_7D_{14}) δ 1.312 (dd, J = 10.3, 1.3 Hz, 9 H), 1.696 (d, J = 2.7 Hz, 15 H), 5.703 (d, J = 3.8 Hz, 1 H), 5.728 (t, J = 3.8 Hz, 1 H), 5.828 (dd, J = 7.7, 0.5 Hz, 1 H), 5.852 (dd, J = 7.8, 0.5 Hz, 1 H); ^{31}P NMR δ 10.64 (d, J = 161.8 Hz). For $(C_5Me_5)Rh(PMe_3)(2\text{-thiophenyl})H$: ^1H NMR (C_7D_{14}) δ −12.722 (dd, J = 48.0, 29.2 Hz, 1 H), 1.229 (dd, J = 10.0, 1.0 Hz, 9 H), 1.918 (d, J = 2.3 Hz, 15 H). Other proton resonances were obscured by free thiophene resonances: ^{31}P NMR δ 7.71 (d, J = 148.5 Hz).

Synthesis of $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)Br$. A sample of $Cp^*Rh(PMe_3)Br_2$ (0.15 g, 0.3 mmol) was dissolved in 5 mL of dry THF in a Schlenk tube in the glovebox. After the addition of 0.32 mL of a 1 M THF solution of 2-thienyllithium (2-ThLi) (0.32 mmol) the solution's color changed slowly from deep red to a pale red/yellow. After 30 min the sample was attached to a high vacuum line, and the solvent removed was under vacuum. The resulting solid was dissolved in a minimal volume of CH_2Cl_2 and introduced onto a thin-layer silica chromatography plate. Elution with CH_2Cl_2/THF (98/2) yielded two yellow bands. The first is due to the disubstituted product $Cp^*Rh(PMe_3)(C_4H_3S)_2$, which is produced in low yield and decomposes slowly on the plate. The second fraction was extracted from the plate with CH_2Cl_2. After removal

of the solvent, 0.12 g of a yellow solid, identified as $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)(Br)$, was obtained: yield 80%. For $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)_2$: ^1H NMR ($CDCl_3$) δ 1.34 (dd, J = 10.0, 0.8 Hz, 9 H, PMe_3), 1.71 (d, J = 2.8 Hz, 15 H, Cp^*), 7.03 (dq, J = 3.6, 0.8 Hz, 2 H), 7.11 (dd, J = 2.4, 4 Hz, 2 H), 7.38 (d, J = 2.8 Hz, 2 H); ^{31}P NMR ($CDCl_3$) δ 2.83 (d, J = 145 Hz); ^{13}C NMR ($CDCl_3$) δ 146.83 (dd, J = 23.4, 43.6 Hz), 134.2 (s), 126.75 (t, J = 2.1 Hz), 126.4 (s), 16.25 (dd, J = 32.8, 1.2 Hz, PMe_3), 9.93 (t, J = 0.85 Hz, Cp^*). C_5Me_5 carbon not observed. For $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)Br$: ^1H ($CDCl_3$) δ 1.42 (dd, J = 10.7, 0.8 Hz, 9 H, PMe_3), 1.70 (dd, J = 3.0, 0.4 Hz, 15 H, Cp^*), 6.84 (br, 1 H), 7.0 (dd, J = 5.0, 3.2 Hz, 1 H), 7.30 (d, J = 5.0 Hz, 1 H); ^{31}P ($CDCl_3$) δ 6.56 (d, J = 144.2 Hz); ^{13}C ($CDCl_3$) 147.8 (dd, J = 42.8, 23.4 Hz), 131.7 (s), 127.68 (s), 127.27 (s), 99.5 (dd, J = 3.3, 4.9 Hz), 15.74 (dd, J = 32.2, 1.0 Hz, PMe_3), 9.47 (d, J = 1.2 Hz, Cp^*); MS, 70 eV [m/e (%)] 159 (100), 237 (7), Cp^*Rh^+; 314 (4), $Cp^*Rh(PMe_3)^+$; 317 (3), $M^+ - Th - PMe_3$; 319 (3), $M^+ - Th - PMe_3$; 393 (1), $M^+ - Th$; 395 (1), $M^+ - Th$; 476/478 (0.5) M^+.

Synthesis of $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)(Cl)$. $Cp^*Rh(PMe_3)Cl_2$ (0.41 g, 1.06 mmol) was dissolved in 5 mL of dry degassed THF in a Schlenk tube. A 1 M solution (1.32 mL) of 2-thienyllithium in THF (1.32 mmol) was added over 5 min, while the solution was stirred. After 30 min the solvent was removed, and the residue was introduced onto a TLC plate. Elution with CH_2Cl_2/THF (98/2) yielded two yellow bands. The second band was extracted from the plate with CH_2Cl_2, the solvent was then removed under reduced pressure, and 0.3 g of $Cp^*Rh(PMe_3)(C_4H_3S)Cl$ was collected as a yellow solid: yield 67%. Anal. Calcd (Found) for $RhClPSC_{17}H_{27}$: 47.18 (48.08) C, 6.29 (6.44) H. For $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)Cl$: ^1H ($CDCl_3$) δ 1.37 (dd, J = 10.9, 0.8 Hz, 9 H, PMe_3), 1.66 (dd, J = 3.0, 0.4 Hz, 15 H, Cp^*), 6.80 (br, 1 H), 7.03 (dd, J = 5.0, 3.3 Hz, 1 H), 7.34 (d, J = 5.0 Hz, 1 H); ^{31}P ($CDCl_3$) 8.42 (d, J = 144.2 Hz); ^{13}C ($CDCl_3$) 149.43 (dd, J = 41.8, 25.5 Hz), 130.53 (s), 127.68 (s), 127.22 (s), 99.3 (dd, J = 3.2, 5.1 Hz), 14.67 (dd, 33.2, 1.0 Hz, PMe_3), 9.18 (d, J = 1.2 Hz, Cp^*). MS, 70 eV [m/e (%)] 159 (100), 238 (10), Cp^*Rh^+; 273 (3), Cp^*RhCl^+; 314 (2), $Cp^*Rh(PMe_3)^+$; 356 (2), $M^+ - PMe_3$; 432 (1), M^+. The synthesis of $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)Cl$ is carried out with commercially obtained LiTh. The product, however, is commonly contaminated with the bromide, i.e., exchange has occurred with free bromide, probably from LiBr in the lithium reagent.

Reduction of $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)Cl$ with Superhydride ($LiHBEt_3$). $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)Cl$ (65 mg, 0.15 mmol) was dissolved in 5 mL of dry THF and 0.45 mL of a 1 M solution of superhydride (3-fold excess) in THF added. After 30 min at room temperature the solvent was removed, and the residue was dissolved in 1 mL of hexane. The resulting solution was introduced onto a 3-cm long silica column and flash chromatographed with 20 mL of a hexane/THF mixture (98/2). The eluent was collected in a small Schlenk flask. After the removal of the solvent a white solid with a pale red tinge was obtained. Multinuclear NMR spectroscopy confirmed that the major component of this solid was $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)(H)$. This product rearranges thermally to $Cp^*Rh(PMe_3)(SCH{=}CHCH{=}CH)$, the C–S insertion adduct, over several days at room temperature. The rate of this rearrangement was determined by UV monitoring of a hexane stock solution of **3** as a function of temperature. The absorbance of a shoulder at 344 nm with absorbance close to 1 was used for the rate analysis. Data are collected in Table I. For $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)H$: ^1H (C_6D_{12}) δ −12.88 (dd, J = 45, 28 Hz, 1 H), 1.159 (ddd, J = 10.0, 1.2, 0.2 Hz, 9 H, PMe_3), 1.82 (ddd, J = 2.4, 1.1, 0.2 Hz, 15 H, Cp^*), 6.51 (dq, J = 3.1, 1.0 Hz, 1 H), 6.76 (dd, J = 5.1, 3.2 Hz, 1 H), 7.028 (dd, J = 5.0, 0.4 Hz, 1 H); ^{31}P (C_6D_{12}) δ 7.53 (d, J = 148.8 Hz); ^{13}C (C_6D_{12}) δ 146.26 (dd, J = 40.7, 21.5 Hz), 132.74 (s) CH, 127.11 (d, J = 2.8 Hz, CH), 126.5 (s, CH), 98.2 (t, J = 3.3 Hz, Cp^*), 19.22 (dd, J = 32.5, 1.5 Hz, PMe_3), 10.77 (dd, J = 2.5, 1.0 Hz, Cp^*).

Preparation of $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)(D)$. $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)(Cl)$ (100 mg, 0.23 mmol) was dissolved in 3 mL of dry THF. Three equivalents of superdeuteride were then added (0.69 mL of a 1 M solution in THF). After 30 min at room temperature the solvent was removed, and the resulting oil was dissolved in 0.1 mL of dry DMSO. Approximately 5 mL of hexane was added, and the resulting two-component system stirred for 5 min. The top hexane layer was then carefully transferred into a Schlenk tube, and the extraction procedure was repeated twice more. The resulting hexane fraction was pumped to dryness, and 0.4 mL of hexane was added. The solution was then transferred into a resealable 5-mm NMR tube. $^{31}P\{^1H\}$ NMR spectroscopy confirmed the production of two Rh(III) species, identified as $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)(H)$ and $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)(D)$ in the ratio 1:1. A ^2H NMR spectrum was then recorded, showing a single major resonance at −12.5 ppm of area 100 units, corresponding to the expected metal deuteride resonance of $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)(D)$. Additional resonances were visible at δ 6.54 and 5.54 ppm (area 15 and 14 units). After 48 h, the metal deuteride resonance was no longer evident, but the resonances at δ 6.54 and 5.54 ppm had grown equally in intensity, and their ratio was still 1:1. These chemical shifts correspond to the two proton resonances in the C–S insertion product which were assigned to hydrogen atoms adjacent to the rhodium and sulfur centers. There was no evidence for scrambling of the deuterium into the 5-position to give $Cp^*Rh(PMe_3)(5\text{-deutero-2-thienyl})(H)$.

Rearrangement of $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)(H)$ (10 mg) at 81 °C in a solution of C_6D_{12} containing a 4-fold excess of 2,5-dimethylthiophene or C_6H_{12} containing a 10-fold excess of perdeuterothiophene, C_4D_4S, yields only $Cp^*Rh(PMe_3)(SCH{=}CHCH{=}CH)$. No exchange products are observed, which would have been clearly be seen in both the ^1H and ^2H NMR spectra obtained after reaction.

Synthesis of $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}4\text{-}Me)Cl$. Preparation of the 4-methylthienyl-2-lithiate was achieved by placing 2.6 g of 3-methylthiophene in 20 mL of dry THF and adding 15 mL of a 1.7 M solution of LiBu in THF at room temperature. Titration with diphenylacetic acid showed the solution to be 0.63 M in 4-methylthienyl-2-lithiate. A Schlenk tube was then prepared which contained 0.3 g of $Cp^*Rh(PMe_3)Cl_2$ in 10 mL of dry degassed THF. Two milliliters of the 3-methylthienyl-1-lithiate solution was then added dropwise over 5 min. The solution was stirred for 2 h at room temperature before the solvent was removed. Purification of the residue was achieved by TLC. A single yellow band was obtained which yielded 0.1 g of $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}4\text{-}Me)Cl$: yield 31%. For $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}4\text{-}Me)Cl$: ^1H ($CDCl_3$) δ 1.37 (d, J = 10.9 Hz, 9 H, PMe_3), 1.65 (d, J = 2.9 Hz, 15 H, Cp^*), 2.23 (s, 3 H), 6.62 (br s, 1 H), 6.84 (s, 1 H); ^{31}P ($CDCl_3$) δ 8.3 (d, J = 144 Hz); ^{13}C ($CDCl_3$) δ 149.5 (br), 138.00 (s), 133.63 (d, J = 2.7 Hz), 122.42 (s), 99.3 (dd, J = 3.3, 5.0 Hz, Cp^*), 15.62 (d, J = 0.8 Hz), 14.72 (dd, J = 34.1, 2.6 Hz, PMe_3), 9.2 (dd, J = 2.8, 1.2 Hz, Cp^*); MS, 70 eV [m/e (%)] 173 (100), 237 (7), Cp^*Rh^+; 273 (3); 314 (2) $Cp^*Rh(PMe_3)^+$; 370 (0.6), $M^+ - PMe_3$; 446 (1), M^+. Anal. Calcd (Found) for $RhPSClC_{18}H_{29}$: 48.39 (48.02) C; 6.54 (6.57) H.

Reduction of $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}4\text{-}Me)Cl$ with Superhydride. A sample of $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}4\text{-}Me)Cl$ (30 mg) was dissolved in dry THF, and 0.2 mL of a 1 M THF solution of superhydride was added. The solution was left stirring for 30 min before the solvent was removed in vacuo. The residue was introduced onto a short silica gel column and flashed through with a hexane/THF (98:2) solvent system. The eluent was reduced to dryness yielding a pale red solid. Multinuclear NMR revealed that the major component was $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}4\text{-}Me)H$. $Cp^*Rh(PMe_3)(2\text{-}C_4H_2MeS)H$: ^1H (C_6D_{12}) δ −12.94 (dd, J = 29.7, 48.0 Hz, 1 H), 1.17 (dd, J = 10.0, 1.1 Hz, 9 H, PMe_3), 1.82 (ddd, J = 2.4, 1.1, 0.4 Hz, 15 H, Cp^*), 2.11 (d, J = 1.1 Hz, 3 H, Me), 6.3 (m, 1 H), 6.58 (m, 1 H); ^{31}P (C_6D_{12}) δ 7.46 (d, J = 149.3 Hz); ^{13}C (C_6D_{12}) δ 137.12 (s, C), 135.9 (s, CH), 123.5 (s, CH), 98.2 (t, J = 3.4 Hz, Cp^*), 19.21 (dd, J = 32.4, 1.5 Hz, PMe_3), 15.64 (s, Me), 10.79 (d, J = 1.1 Hz, Cp^*).

Over a period of several days the two C–S insertion products, $Cp^*Rh(PMe_3)(SCH{=}CMeCH{=}CH)$ and $Cp^*Rh(PMe_3)(SCH{=}CHCMe{=}CH)$, grow in a ratio of 1:1.1, respectively. At no time was the isomer $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}3\text{-}Me)H$ observed. For $Cp^*Rh(PMe_3)(SCH{=}CMeCH{=}CH)$: ^1H NMR δ 1.217 (dd, J = 0.9, 10.2 Hz, PMe_3), 1.612 (d, J = 2.4 Hz, Cp^*), 1.66 (d, J = 1.2 Hz, Me), 5.22 (tq, J = 3.6, 1.3 Hz, RhSCH), 6.31 (dd, J = 8.0, 2.5 Hz, CH), 6.67 (dt, J = 3.8, 8.6 Hz, RhCH); ^{13}C NMR δ 139.5 (dd, J = 31.1, 24.1 Hz, CH), 136.06 (s, CMe), 130.72 (s, CH), 116.70 (s, CH), 99.72 (t, J = 3.9 Hz, Cp^*), 29.07 (d, J = 1.5 Hz, Me), 14.82 (dd, J = 34.8, 1.0 Hz, PMe_3), 9.01 (d, J = 1.4 Hz, Cp^*); ^{31}P NMR δ 10.24 (d, J = 161.3 Hz).

For $Cp^*Rh(PMe_3)(SCH{=}CHCMe{=}CH)$: ^1H NMR δ 1.217 (dd, J = 0.9, 10.2 Hz, PMe_3), 1.605 (d, J = 2.6 Hz, Cp^*), 1.87 (t, J = 1.2 Hz, Me), 5.54 (dd, J = 9.9, 1.8 Hz), 5.59 (dt, J = 3.5, 9.9 Hz, RhSCH), 6.05 (ddqu, J = 3.9, 9.5, 2.0 Hz, RhCH); ^{13}C NMR δ 128.96 (dd, J = 32.2, 23.1 Hz, CH), 127.54 (s, CMe), 126 (s, CH), 124.6 (s, CH), 99.65 (t, J = 3.8 Hz, Cp^*), 29.05 (d, J = 1.5 Hz, Me), 14.78 (dd, J = 1.0, 34.9 Hz, PMe_3), 8.95 (d, J = 1.5, Cp^*); ^{31}P NMR δ 8.99 (d, J = 161.3 Hz).

Synthesis of $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}5\text{-}Me)Cl$. Preparation of the 5-methythienyl-2-lithiate was achieved by placing 1.00 g of 2-methylthiophene in 20 mL of dry THF and adding 6.0 mL of a 1.7 M solution of LiBu in THF at room temperature. Titration with diphenylacetic acid showed the solution to be 0.41 M in 5-methylthienyl-2-lithiate. A Schlenk tube was then prepared which contained 0.2 g of $Cp^*Rh(PMe_3)Cl_2$ in 10 mL of dry degassed THF. The 5-methylthienyl-2-lithiate solution (0.63 mL) was added dropwise over 5 min. The solution was stirred for 2 h at room temperature before the solvent was removed. Purification of the residue was achieved by TLC. A single yellow band was obtained which yielded $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}5\text{-}Me)Cl$ and $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}5\text{-}Me)Br$ in equal amounts: yield 0.09 g. For

$Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}5\text{-}Me)Cl$: ^1H NMR ($CDCl_3$) δ 1.24 (dd, J = 10.9, 0.6 Hz, 9 H, PMe_3), 1.67 (d, J = 2.9 Hz, 15 Hz, Cp^*); ^{31}P NMR δ 8.46 (d, J = 144.8 Hz); ^{13}C NMR δ 99.3 (dd, J = 3.2, 5.0 Hz, Cp^*), 15.78 (dd, J = 33.8, 2.6 Hz, PMe_3), 15.51 (s, Me), 9.27 (s, Cp^*). For $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}5\text{-}Me)Br$ ^1H NMR ($CDCl_3$) δ 1.44 (dd, J = 10.7, 0.7 Hz, 9 H, PMe_3), 1.72 (d, J = 3.0 Hz, 15 H, Cp^*); ^{31}P NMR δ 6.61 (d, J = 144.9 Hz); ^{13}C NMR δ 99.4 (dd, J = 3.2, 5.0 Hz, Cp^*), 15.54 (s, Me), 14.78 (dd, J = 33.4, 2.6 Hz, PMe_3), 9.27 (s, Cp^*).

Reduction of $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}5\text{-}Me)Cl$ and $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}5\text{-}Me)Br$ with Superhydride. The $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}5\text{-}Me)Br/Cl$ mixture was dissolved in THF, and 0.6 mL of a M solution of superhydride was added. After 30 min the solvent was removed, and the residue was flash chromatographed through a short silica column with a hexane/THF solvent system (98:2). An off-white solid was collected prior to removal of the solvent. ^1H NMR spectroscopy showed that one major product was formed, which subsequently rearranged upon standing overnight in C_6D_{12} at 25 °C to form the C–S insertion product $Cp^*Rh(PMe_3)(SCMe{=}CHCH{=}CH)$. For $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}5\text{-}Me)H$: ^1H NMR (C_6D_{12}) δ −12.99 (dd, J = 28.4, 48.4 Hz, 1 H), 1.169 (ddd, J = 10.0, 1.1, 0.2 Hz, 9 H, PMe_3), 1.82 (ddd, J = 2.5, 1.2, 0.5 Hz, 15 H, Cp^*), 2.325 (ddd, J = 1.1, 0.5, 0.4 Hz, Me), 6.26 (dtt, J = 3.1, 1.2, 0.3 Hz, 1 H), 6.39 (ddq, J = 3.1, 1.1, 0.3 Hz, 1 H); ^{31}P NMR (C_6D_{12}) δ 7.67 (d, J = 149.5 Hz); ^{13}C NMR (C_6D_{12}) δ 144.4 (dd, J = 43.1, 21.4 Hz, C), 132.67 (s, CH), 130.08 (s, C), 126.04 (s, CH), 98.11 (t, J = 3.8 Hz, Cp^*), 14.44 (s, Me), 19.27 (dd, J = 32.6, 1.5 Hz, PMe_3), 10.82 (s, Cp^*).

Synthesis of $Cp^*Rh(PMe_3)(3\text{-thienyl})Br$. Approximately 0.6 g of 3-bromothiophene was dissolved in 10 mL of diethyl ether, and the solution was then degassed and cooled to −78 °C. A 1.7 M solution (1.8 mL) of BuLi in THF was then added dropwise. The solution turned pale yellow and was left for 2 h at −78 °C to ensure complete reaction had occurred. The metal complex $Cp^*Rh(PMe_3)Cl_2$ (0.3 g) was then added, and the solution was left for 3 h at −78 °C. The solution was then allowed to warm to room temperature over a further 2-h period. The solution was then quenched with 1 mL of H_2O. A precipitate formed at this stage. All the volatiles were then removed under reduced pressure, and the residue was placed on a TLC plate. Elution with CH_2Cl_2/THF (96/4) yielded a broad yellow fraction followed by a sharp yellow band. The first band contained no rhodium species; however, collection of the second band with CH_2Cl_2 yielded $Cp^*Rh(PMe_3)(3\text{-}C_4H_3S)Br$, isolated as a red microcrystalline solid in 30% yield (0.102 g). Anal. Calcd (Found) for $RhBrPSC_{17}H_{27}$: 42.78 (42.72) C, 5.70 (5.63) H. For $Cp^*Rh(PMe_3)(3\text{-}C_4H_3S)Br$: ^1H NMR ($CDCl_3$) δ 1.38 (dd, J = 10.5, 0.8 Hz, 9 H, PMe_3), 1.68 (d, J = 2.9 Hz, 15 H, Cp^*), 6.82 (br, 1 H), 7.1 (br, 1 H), 7.22 (dd, J = 4.6, 2.7 Hz, 1 H); ^{31}P ($CDCl_3$) δ 7.69 (d, J = 148.5 Hz); ^{13}C ($CDCl_3$, 210 K) δ 146.5 (dd, J = 36.2, 25.8 Hz, C), 143.45 (dd, J = 32.5, 21.8 Hz), 126.1 (s), 123.7 (s), 122.3 (s), 121.5 (s), 118.6 (s), 98.5 (dd, J = 3.3, 5.0 Hz, Cp^*), 15.3 (d, J = 33.9 Hz, PMe_3), 10.6 (s, Cp^*); MS, 70 eV [m/e, (%)] 159 (100); 237 (43), Cp^*Rh^+; 314 (16), $Cp^*Rh(PMe_3)^+$; 317 (21), $M^+ - Th - PMe_3$; 319 (21), $M^+ - Th - PMe_3$; 393 (4), $M^+ - Th$; 395 (4), $M^+ - Th$; 397 (0.6), $M^+ - Br$; 400/402 (4) $M^+ - PMe_3$; 476/478 (1), M^+.

Reduction of $Cp^*Rh(PMe_3)(3\text{-thienyl})Br$ with Superhydride. A sample of $Cp^*Rh(PMe_3)(3\text{-}C_4H_3S)(Cl)$ (~10 mg) was reduced with superhydride in THF. The residue was pumped to dryness, and the solid obtained was dissolved in DMSO. After three extractions into hexane the combined fraction was pumped to dryness. The residue was dissolved in C_6D_{12}, and a ^1H NMR spectrum was recorded. The only visible product was $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)(H)$. This product subsequently rearranged to the expected C–S insertion adduct.

Low-Temperature Reduction of $Cp^*Rh(PMe_3)(3\text{-thienyl})Br$ with Superhydride. A sample of $Cp^*Rh(PMe_3)(3\text{-}C_4H_3S)Cl$ (10 mg) was dissolved in THF-d_8, and $AgPF_6$ was added. The solution was immediately frozen in liquid nitrogen. A 1 M solution (0.2 mL) of superhydride was then added at −78 °C. An NMR spectrum was then recorded at 210 K, revealing that the 3-thienylhydride was formed. Subsequently the sample was warmed to 296 K, at which point it isomerised to the 2-thienylhydride with a rate constant of 1.2×10^{-3} s^{-1}. For $Cp^*Rh(PMe_3)(3\text{-}C_4H_3S)H$: ^1H NMR (THF-d_8, 240 K) Cp^* obscured by THF δ −13.29 (dd, J = 47.6, 31 Hz, 1 H), 1.08 (dd, J = 10.0, 0.9 Hz, 9 H, PMe_3), 6.37 (dt, J = 2.6, 1.0 Hz, 1 H), 6.72 (d, J = 4.7 Hz, 1 H), 6.96 (dd, J = 4.6, 2.6 Hz, 1 H); ^{31}P NMR (THF-d_8, 240 K) δ 6.29 (d, J = 144.9 Hz). For $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)H$: ^1H NMR (THF-d_8, 296 K): δ −13.02 (dd, J = 47, 29 Hz, 1 H), 1.21 (ddd, J = 10.0, 1.1, 0.2 Hz, 9 H, PMe_3), 1.84 (ddd, J = 0.4, 1.1, 2.4 Hz, 15 H, Cp^*), 6.54 (dq, 3.3, 0.9 Hz, 1 H), 6.77 (dd, J = 3.5, 5.0 Hz, 1 H), 7.06 (dq, J = 5.0, 0.5 Hz, 1 H); ^{31}P (THF-d_8, 296 K) 5.22 (d, J = 146.6 Hz).

Reduction of $Cp^*Rh(PMe_3)(3\text{-thienyl})Br$ with Superdeuteride. A sample of $Cp^*Rh(PMe_3)(3\text{-}C_4H_3S)Cl$ (30 mg) was reduced with superdeuteride (2.4 mL, 1 M solution) in THF. The residue was pumped to dryness, and the crude product obtained was dissolved in 0.1 mL of DMSO. After four extractions into 2 mL of hexane the combined hexane residue was pumped to dryness, and the off-white solid obtained was dissolved in cyclohexane. ^{31}P, ^1H, and ^2H NMR spectra confirmed that only one product was formed, $Cp^*Rh(PMe_3)(2\text{-}C_4H_2D)H$, in which the deuterium label was specifically located at the 3-position. Thus, the only product resonance visible in the ^2H spectrum occurred at 6.49 ppm. Using presaturation to remove the large solvent signal in the ^1H spectrum, it could be seen that the resonance at 6.49 ppm was only 50% of the expected intensity. The overall deuteration was therefore ~50%. Thermal rearrangement led to the formation of the C–S insertion product. The resonances observed at δ 5.67 and 6.43 ppm in the ^2H and ^1H spectra were consistent with this fact. Interestingly, the ^1H resonances were now 75% of their expected intensity, confirming the absence of a large kinetic isotope effect and the symmetrical nature of the intermediate leading to the C–S insertion product.

Preparation of Tetramethylthiophene (C_4Me_4S). Preparation of C_4Me_4S was achieved by reducing 3,4-bis(chloromethyl)-2,5-dimethylthiophene with $LiAlH_4$. The following procedure for preparing 3,4-bis(chloromethyl)-2,5-dimethylthiophene was adapted from Gaertner and Tonkyn.[31] Thirty milliliters of concentrated hydrochloric acid was placed in a 125-mL Erlenmeyer flask and saturated with hydrogen chloride gas. Trioxane (12.0 g) was added to the solution and stirred for 10 min. To this clear solution was added 2,5-dimethylthiophene (4.2 g, 37.4 mmol), dropwise. The blue mixture was stirred for 2.5 h, diluted with 120 mL of water, and extracted with 50 mL of ether and 50 mL of petroleum ether. The extracts were washed with dilute HCl acid, H_2O, 5% sodium bisulfite, H_2O, dilute NaOH, and H_2O. Pale yellow crystals were obtained by evaporation of the solvents. Recrystallization from hexane at −30 °C afforded 3,4-bis(chloromethyl)-2,5-dimethylthiophene as colorless crystals in 45% yield (2.36 g): ^1H NMR (C_6D_6) δ 1.903 (s, 6 H), 4.258 (s, 4 H); ^{13}C NMR (C_6D_6) δ 135.92 (s, C), 132.54 (s, C), 37.31 (s, CH_2Cl), 12.36 (s, CH_3).

3,4-Bis(chloromethyl)-2,5-dimethylthiophene (1.10 g, 5.26 mmol) was dissolved in 15 mL of THF under an N_2 atmosphere. Ten milliliters of a THF suspension of 0.47 g of $LiAlH_4$ (grey powder) was added very slowly to the solution, which effervesced. The mixture was stirred for 1 h at room temperature and refluxed for 2 h at 65 °C and then cooled to 10 °C. A mixture of approximately 15 mL of THF/H_2O, 3:2 by volume, was added very cautiously with stirring, while keeping the temperature below 10 °C (ice–water bath). The mixture was transferred slowly with stirring into a 250-mL beaker containing 10 mL of sulfuric acid in ice and water. The product was extracted by ether and washed twice with water (50 mL each time). Following removal of the solvent in vacuo (20 mmHg), a pale yellow liquid was obtained. Vacuum distillation gives tetramethylthiophene as a colorless liquid in 50% yield (0.36 g): ^1H NMR (C_6D_6) δ 1.785 (s, 6 H), 2.091 (s, 6 H); ^{13}C NMR (C_6D_6) δ 132.80 (s, C), 12.94 (s, CH_3), 12.64 (s, CH_3). Another quaternary carbon was not observed which might be obscured by C_6D_6 peaks.

Preparation of $Cp^*Rh(PMe_3)(S\text{-}C_4Me_4S)$. To a hexane solution of **1** (0.030 g, 0.076 mmol) was added ~0.1 mL of TMT (large excess). After being stirred at 60 °C for 20 h the resulting solution was evaporated to dryness in vacuo. A ^{31}P NMR spectrum revealed the presence of four complexes in which three minor complexes were identified as $Cp^*Rh(PMe_3)_2$ (33%), $Cp^*Rh(PMe_3)H_2$ (7%), and $Cp^*Rh(PMe_3)(Ph)H$ (17%). The major product (43%) of this reaction has a large coupling constant $J_{P\text{-}Rh}$ of 222 Hz in the high field region (^{31}P NMR δ −3.09). This complex has the formulation $(C_5Me_5)Rh(PMe_3)(SC_4Me_4)$ which was confirmed by its ^1H and ^{13}C NMR spectroscopy: ^1H NMR (C_6D_6) δ 1.139 (d, J = 8.0 Hz, 9 H), 1.845 (s, 6 H), 1.891 (d, J = 1.9 Hz, 15 H), 2.161 (s, 6 H); ^{31}P NMR (C_6D_6) δ −3.09 (d, J = 222.2 Hz); ^{13}C NMR (C_6D_6) δ 137.56 (s, C), 132.24 (s, C), 94.43 (t, J = 3.5 Hz, C_5Me_5), 21.09 (d, J = 24.2 Hz, PMe_3), 13.38 (s, CH_3), 12.19 (s, CH_3), 11.42 (s, C_5Me_5).

X-ray Structural Characterization of $(C_5Me_5)Rh(PMe_3)(2\text{-thienyl})Cl$. Well-formed dark yellow 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 X between 5 and 70°. Cell reduction with the program TRACER revealed only a primitive monoclinic 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 unique choice $P2_1/c$ on the basis of systematic absences. 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 using the DIRDIF program supplied by the Molecular Structure Corporation, whose programs were used for further refinement of the structure.[32] Following full isotropic refinement of the structure containing the non-hydrogen atoms, it was noted that the thermal parameters for the sulfur and C12 suggested that the thienyl ligand was disordered

over the two possible rotamers. Following isotropic refinement and pairwise constrained refinement of the sulfur and C12 populations, an absorption correction was applied using the DIFABS absorption correction program. Full least-squares anisotropic refinement (except for sulfur, which was isotropic) of the structure with hydrogens placed in idealized positions based upon a difference Fourier map converged with R_1 = 0.0363 and R_2 = 0.0399.

Acknowledgment. Support by the National Science Foundation, Grant CHE-9102318, is gratefully acknowledged for the studies leading to this work. S.B.D. also thanks the Exxon Education Foundation for support.

Registry No. 1, 81971-46-2; **2**, 131323-30-3; **3**, 136953-53-2; $Cp^*Rh(PMe_3)H_2$, 84624-03-3; $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)Br$, 136953-54-3; $Cp^*Rh(PMe_3)Br_2$, 88704-26-1; $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)_2$, 136953-55-4; $Cp^*Rh(PMe_3)(2\text{-}C_4H_3)(Cl)$, 136953-56-5; $Cp^*Rh(PMe_3)Cl_2$, 80298-79-9; $Cp^*Rh(PMe_3)(2\text{-}C_4H_3S)(D)$, 136953-57-6; $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}4\text{-}Me)Cl$, 137038-74-5; $Cp^*Rh(PMe_3)(2\text{-}C_4H_2S\text{-}4\text{-}Me)H$, 136953-58-7; $Cp^*Rh(PMe_3)(SCH{=}CMeCH{=}CH)$, 136953-59-8; $Cp^*Rh(PMe_3)(SCH{=}CHCMe{=}CH)$, 136953-60-1; $Cp^*Rh(PMe_3)(2\text{-}C_4H_2\text{-}5\text{-}Me)Cl$, 136953-61-2; $Cp^*Rh(PMe_3)(2\text{-}C_4H_2\text{-}5\text{-}Me)Br$, 136953-62-3; $Cp^*Rh(PMe_3)(SCMe{=}CHCH{=}CH)$, 131323-32-5; $Cp^*Rh(PMe_3)(3\text{-}C_4H_3S)Br$, 136953-63-4; $Cp^*Rh(PMe_3)(3\text{-}C_4H_3S)H$, 136953-64-5; $Cp^*Rh(PMe_3)(2\text{-}C_4H_2DS)H$, 136953-65-6; 2-ThLi, 2786-07-4; C_4Me_4S, 14503-51-6; thiophene, 110-02-1; 3-methylthiophene, 616-44-4; 2-methylthiophene, 554-14-3; 3-bromothiophene, 872-31-1; 3,4-bis(chloromethyl)-2,5-dimethylthiophene, 5368-70-7; 2,5-dimethylthiophene, 638-02-8.

Supplementary Material Available: Tables S-I-S-VI of bond distances and angles, coordinates of atoms, and anisotropic thermal parameters (7 pages); listing of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

Calorimetric Studies of the Heats of Protonation of the Metal in $Fe(CO)_3$(bidentate phosphine, arsine) Complexes: Effects of Chelate Ligands on Metal Basicity

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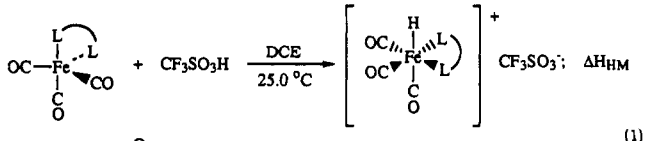
Abstract: Titration calorimetry has been used to determine the heats of protonation (ΔH_{HM}) of $Fe(CO)_3(L\frown L)$ complexes ($L\frown L$ = dppm, dppe, dppp, dppb, dppbz, *cis*-dppv, arphos, dmpm, dcpe, and diars) with CF_3SO_3H in 1,2-dichloroethane solution at 25.0 °C. Spectroscopic studies show that protonation occurs at the metal center to form *fac*-$[Fe(H)(CO)_3(L\frown L)]CF_3SO_3$. For the series $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$, n = 1-4, ΔH_{HM} becomes less exothermic as the chelate size increases from n = 1 (−24.0 ± 0.2 kcal mol^{-1}) to n = 4 (−20.1 ■ 0.2 kcal mol^{-1}). Moreover, the chelate complexes are substantially more basic than the related nonchelate complex $Fe(CO)_3(PPh_2Me)_2$ (ΔH_{HM} = −17.6 ± 0.4 kcal mol^{-1}). Likewise, $Fe(CO)_3$(dmpm) is much more basic (ΔH_{HM} = −30.2 ± 0.4 kcal mol^{-1}) than $Fe(CO)_3(PMe_3)_2$ (ΔH_{HM} = −23.3 ± 0.3 kcal mol^{-1}). The higher basicities of complexes with small chelate ligands are ascribed to distortions imposed on the $Fe(CO)_3(L\frown L)$ complexes by the chelate ligand. Basicities of several other $Fe(CO)_3(L\frown L)$ complexes are also discussed.

Introduction

Bidentate phosphines and arsines are commonly used chelating ligands in transition-metal complex chemistry.[1] The effects of the chelates on the properties and reactivities of metal complexes have been the subject of several investigations.[2] However, little is known of the effects of bidentate phosphine and arsine ligands on the basicities of such complexes.[3]

In this paper, we examine how chelate size and basicity controls the basicities of $Fe(CO)_3(L\frown L)$ complexes, as measured by their heats of protonation (ΔH_{HM}) with CF_3SO_3H in 1,2-dichloroethane (DCE) solvent at 25.0 °C (eq 1). Comparisons are made with ΔH_{HM} values of analogous monodentate phosphine complexes



(1)

where $L\frown L$ is

$Ph_2P(CH_2)PPh_2$ (dppm)
$Ph_2P(CH_2)_2PPh_2$ (dppe)
$Ph_2P(CH_2)_3PPh_2$ (dppp)
$Ph_2P(CH_2)_4PPh_2$ (dppb)
$Ph_2P(1,2\text{-}C_6H_4)PPh_2$ (dppbz)
cis-$Ph_2P(CH{=}CH)PPh_2$ (cis-dppv)
$Ph_2P(CH_2)_2AsPh_2$ (arphos)
$Me_2P(CH_2)PMe_2$ (dmpm)
$Cy_2P(CH_2)_2PCy_2$ (dcpe)
$Me_2As(1,2\text{-}C_6H_4)AsMe_2$ (diars)

$Fe(CO)_3(L)_2$. In previous calorimetric studies of basicities were reported the heats of protonation of monophosphines (PR_3),[4a] diphosphines,[4b] and a series of methylcyclopentadienyl complexes

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