Regiochemical Selectivity in the Carbon−Sulfur Bond Cleavage of 2-Methylbenzothiophene: Synthesis, Characterization, and Mechanistic Study of Reversible Insertion into a C−S Bond

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Abstract: Thermolysis of $(C_5Me_5)Rh(PMe_3)(Ar)(H)$ (Ar = Ph or 3,5-xylyl) with 2-methylbenzothiophene at early reaction times yields a C−H activation compound and a single C−S insertion product resulting from insertion of rhodium into the S−C bond adjacent to the methyl substituent, **2k**. Prolonged heating results in the conversion of **2k** to the isomer in which the metal has inserted into the C−S bond adjacent to the aryl group via an intramolecular pathway, **2t**. Both **2k** and **2t** were characterized by ^1H, ^{31}P, and ^{13}C NMR spectroscopies and by single crystal X-ray diffraction. The kinetic product crystallized as a racemic twin in the orthorhombic space group $P2_12_12_1$, with $a = 8.5438(1)$ Å, $b = 12.8079(2)$ Å, $c = 19.3021(3)$ Å, $Z = 4$, and $V = 2112.19(5)$ Å^3, while the thermodynamic product crystallized in the triclinic space group $P\bar{1}$ with $a = 8.669(6)$ Å, $b = 8.86(1)$ Å, $c = 15.18(1)$ Å, $\alpha = 76.42(9)°$, $\beta = 86.66(7)°$, $\gamma = 74.46(9)°$, $Z = 2$, and $V = 1091.5(1.9)$ Å^3.

Introduction

Cleavage of the C−S bond is thought to be an important step in the removal of sulfur from thiophene in the hydrodesulfurization (HDS) process.[1] Thiophene and its benzo derivatives represent abundant sulfur-containing impurities in coal and petroleum feedstocks and are among the most difficult to desulfurize.[2,3] Homogeneous transition metal complexes are ideal for probing the mechanism for this process by allowing analysis of specific steps in the proposed HDS cycle.[4−6]

The activation of thiophene molecules upon coordination to a transition metal center has been the recent focus of many research groups.[7−9] Most of the reactivity reported to date of coordinated thiophenes falls into one of three areas: (1) the addition of a nucleophile or electrophile to the complexed thiophene,[8,10−12] (2) thermal or photochemical activation to dissociate an ancillary ligand to open an additional coordination site,[13,14] or (3) a change in the coordination mode of thiophene.[15,16] Reactions of the coordinated thiophene group itself without added reagents have been limited to desulfurization,[17] C−S insertion from an η^4-bound thiophene,[18] and the formation of trinuclear and dinuclear Rh complexes upon redistribution from an η^4-thiophene compound.[19]

The first example of insertion of a metal into the C−S bond of a thiophene was reported by King and co-workers in 1960.[20] The reaction of benzothiophene with $Fe_3(CO)_{12}$ resulted in the insertion of $Fe(CO)_3$ into the C−S bond away from the aryl substituent (Scheme 1). Thermolysis of this benzothiaferrole product at 175 °C in the presence of hydrogen produces ethylbenzene,[21] the major product of the HDS of benzo-

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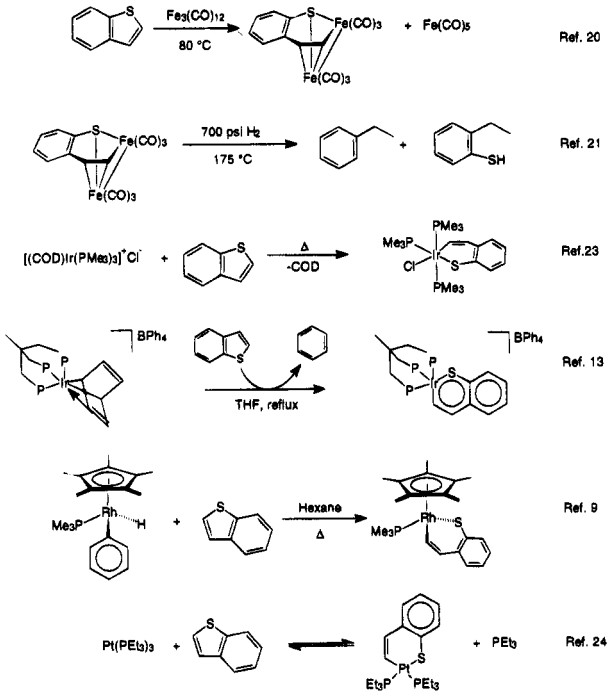
Scheme 1



thiophene,[22] which suggested that this homogeneous system could be a model for the industrial process.

Other insertion selectivities with benzothiophene also showed selective insertion away from the S−aryl bond. Selnau and Merola have structurally characterized the benzothiophene inserted compound *mer*-$(PMe_3)_3Ir(C_8H_6S)Cl$,[23] while Bianchini and co-workers reported insertion and hydrogenation of benzothiophene via $[(triphos)Ir(\eta^3\text{-}C,C,S\text{-}C_8H_6S)]^+$.[13] Both of these examples involve a metal surrounded by sterically hindering phosphine ligands, which could be argued to influence selective insertion into the less hindered S-vinyl bond of benzothiophene. More recent work by Bianchini with $(triphos)RhH_3$ has led to the ring opening and partial hydrogenation of the benzothiophene ring.[24] Work by Jones and Dong also showed the same selectivity toward C−S cleavage but with a less sterically hindered complex.[9] Maitlis and co-workers recently observed an equilibrium between uncomplexed and C−S inserted benzothiophene with an electron rich Pt^0 complex.[25] Again, selective insertion into the S−C(vinyl) bond was seen.

During the course of our studies on the mechanistic considerations of the C−S cleavage of thiophenes by homogeneous transition-metal systems, we became interested in the selectivities of the insertion step. Previous experiments with substituted thiophenes[9] and dibenzothiophenes[26] showed a preference for insertion based on steric constraints with a small electronic influence. In particular, reaction of $(C_5Me_5)Rh(PMe_3)(Ph)(H)$ with 2-methylthiophene leads only to insertion into the C−S bond away from the methyl substituent. Similarly, reaction of the same rhodium complex with benzothiophene gives only the C−S insertion product away from the aryl group. An S-bound intermediate has been shown to be consistent with experimental observations. The reactivity of 2-methylbenzothiophene was thought to be of interest in order to probe the selectivity between methyl or aryl substituents at the α position. Our investigations with this substrate unexpectedly revealed a facile, reversible C−S insertion step which led to observation and isolation of both kinetic and thermodynamic isomers.

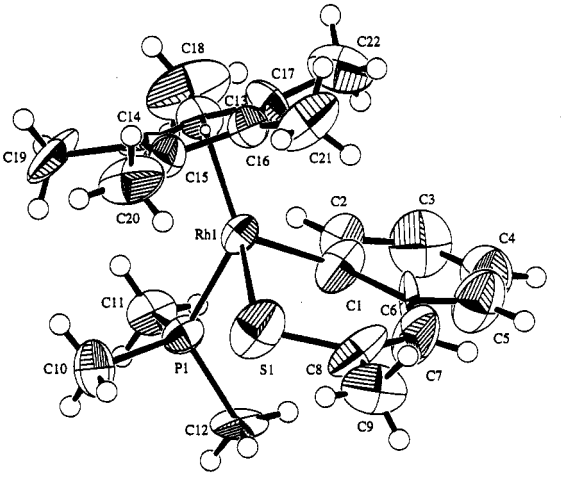


Figure 1. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)$(2-methylbenzothiophene)—thermodynamic product, **2t**. Ellipsoids are shown at the 50% probability level.

Table 1. Selected Bond Distances and Angles for 2t

Distances (Å)			
Rh(1)−S(1)	2.367(6)	C(3)−C(4)	1.34(3)
Rh(1)−P(1)	2.239(6)	C(4)−C(5)	1.43(3)
Rh(1)−C(1)	2.03(2)	C(5)−C(6)	1.33(3)
S(1)−C(8)	1.74(2)	C(6)−C(7)	1.45(3)
C(1)−C(2)	1.34(2)	C(7)−C(8)	1.36(3)
C(1)−C(6)	1.44(3)	C(8)−C(9)	1.50(3)
C(2)−C(3)	1.50(3)		
Bond Angles (deg)			
S(1)−Rh(1)−P(1)	85.8(2)	C(3)−C(4)−C(5)	116(2)
S(1)−Rh(1)−C(1)	93.5(8)	C(4)−C(5)−C(6)	123(2)
Rh(1)−S(1)−C(8)	109.5(9)	C(1)−C(6)−C(5)	120(2)
P(1)−Rh(1)−C(1)	85.8(6)	C(1)−C(6)−C(7)	127(2)
Rh(1)−C(1)−C(2)	112(2)	C(5)−C(6)−C(7)	113(2)
Rh(1)−C(1)−C(6)	126(2)	C(6)−C(7)−C(8)	130(2)
C(2)−C(1)−C(6)	121(2)	S(1)−C(8)−C(7)	126(2)
C(1)−C(2)−C(3)	116(2)	S(1)−C(8)−C(9)	111(2)
C(2)−C(3)−C(4)	123(2)	C(7)−C(8)−C(9)	123(2)

Results

$(C_5Me_5)Rh(PMe_3)(Ph)H$ (**1**) is known to reductively eliminate benzene to produce a highly reactive 16 electron intermediate capable of oxidatively adding a variety of C−X bonds.[27] Thermolysis of **1** with 2-methylbenzothiophene at 75 °C produced a C−H activation product (^{31}P NMR (C_6D_{12}) δ 9.01, d, J = 151 Hz), and what was assigned as a C−S insertion product, **2k** (^{31}P NMR δ 4.16, d, J = 164 Hz). The C−H activation product was observed to disappear upon prolonged heating; however, the C−S insertion product was also seen to decrease with concomitant formation of a new product, **2t** (^{31}P NMR δ 8.39, d, J = 159 Hz). Both the initial C−S inserted product and the final product had resonances with J_{Rh-P} in the range expected for a Rh(III) C−S insertion complex,[9,28] and both products contained a single 2-methylbenzothiophene molecule, as observed by ^1H NMR spectroscopy.

Identification of the thermodynamic product **2t** was initially obtained by ^1H NOE experiments. Irradiation of the (C_5Me_5)

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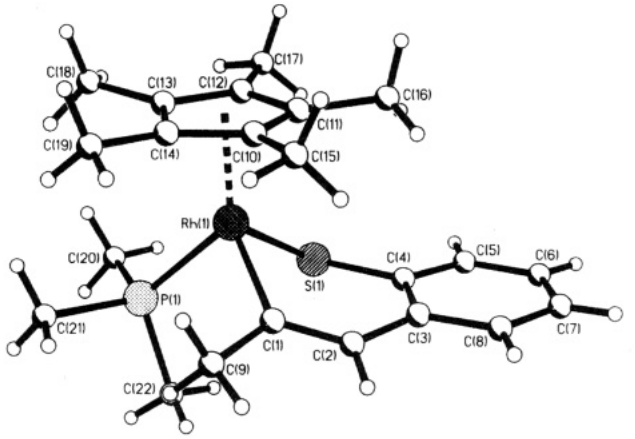
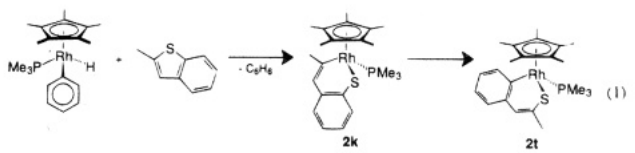


Figure 2. Drawing of $(C_5Me_5)Rh(PMe_3)$(2-methylbenzothiophene)—kinetic product, **2k**.

resonance of **2t** enhanced the benzothiophene methyl resonance as well as a doublet at δ 7.3 in the aromatic region. Irradiation of the phosphine methyl resonance enhanced the δ 7.3 resonance only. This peak was assigned as H-7 through ^{1}H COSY and ^{1}H−^{1}H homonuclear decoupling experiments.[29] Consistent with insertion of Rh into the S−C(aryl) bond, this assignment was confirmed by a single crystal X-ray structure of **2t**, shown in Figure 1. Table 1 contains selected bond distances and angles. The six-membered ring is slightly puckered, with an angle of 24.6° between the Rh−S−C1 and S1−C8−C7−C6−C1 planes.

In order to isolate the kinetic product for characterization, conditions were sought under which formation of the kinetic product was optimized. This was accomplished by using the more labile complex $(C_5Me_5)Rh(PMe_3)$(3,5-xylyl)H (**3**) which loses arene readily at 50 °C.[30] Thermolysis of **3** with 2-methylbenzothiophene at 47 °C for 9 h in C_6D_{12} solution gave a ~36:1 ratio of **2k** to **2t**. NOE experiments with **2k** identified the structure as arising from insertion of rhodium into the C−S bond *adjacent to the methyl substituent* (eq 1). Irradiation of the



(1)

(C_5Me_5) resonance of **2k** gave enhancement of the benzothiophene methyl resonance, as did irradiation of the PMe_3 resonance. In addition, fine structure in the benzothiophene methyl resonance was observed from coupling of phosphorus and rhodium to the methyl hydrogens at δ 2.202 (br t, J_{P-H} = 1.2 Hz, C_6D_{12} solution), as identified through a ^{1}H{^{31}P} spectrum in which the methyl resonance collapsed to doublet (J = 1.2 Hz). Confirmation of this assigned structure was also obtained with a single crystal X-ray structure of **2k**, shown in Figure 2. Selected bond distances and angles are located in Table 2, while a summary of X-ray data parameters for both isomers are in Table 3. The puckering of the six-membered ring is 42.5° in **2k**, substantially larger than in **2t**.

(29) Numbering scheme for benzothiophene is

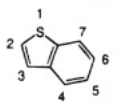


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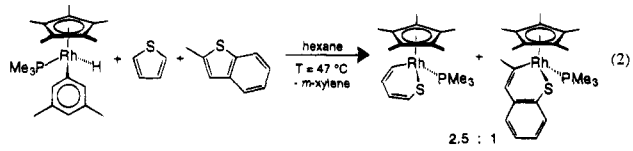
Table 2. Selected Bond Distances and Angles for 2k

	Distances (Å)		
Rh(1)−S(1)	2.3429(13)	C(3)−C(4)	1.416(7)
Rh(1)−P(1)	2.2657(12)	C(4)−C(5)	1.396(8)
Rh(1)−C(1)	2.048(5)	C(5)−C(6)	1.375(8)
S(1)−C(4)	1.748(6)	C(6)−C(7)	1.382(8)
C(1)−C(9)	1.492(7)	C(7)−C(8)	1.380(8)
C(1)−C(2)	1.338(7)	C(8)−C(3)	1.406(7)
C(2)−C(3)	1.465(8)		
	Intramolecular Bond Angles (deg)		
S(1)−Rh(1)−P(1)	87.70(5)	C(2)−C(1)−C(9)	119.6(5)
S(1)−Rh(1)−C(1)	88.5(2)	C(2)−C(3)−C(4)	122.8(5)
P(1)−Rh(1)−C(1)	90.94(13)	C(3)−C(4)−C(5)	118.3(5)
Rh(1)−S(1)−C(4)	106.4(2)	C(4)−C(5)−C(6)	122.3(6)
Rh(1)−C(1)−C(2)	123.1(4)	C(4)−C(3)−C(8)	118.1(5)
Rh(1)−C(1)−C(9)	116.6(4)	C(3)−C(8)−C(7)	122.2(5)
S(1)−C(4)−C(5)	118.4(4)	C(5)−C(6)−C(7)	120.0(6)
S(1)−C(4)−C(3)	123.3(4)	C(6)−C(7)−C(8)	119.1(5)
C(1)−C(2)−C(3)	131.7(5)	C(2)−C(3)−C(8)	119.0(5)

Table 3. Summary of Crystallographic Data for 2k and 2t

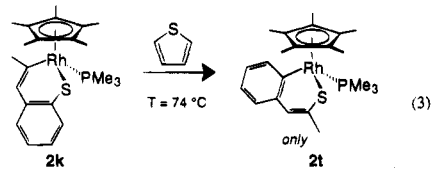
crystal parameters	kinetic isomer	thermodynamic isomer
chemical formula	$RhPSC_{22}H_{32}$	$RhPSC_{22}H_{32}$
formula weight	462.43	462.43
cryst syst	orthorhombic	triclinic
space group (no.)	$P2_12_12_1$	$P\bar{1}$ (no. 2)
Z	4	2
a, Å	8.5438 (1)	8.669 (6)
b, Å	12.8079 (2)	8.86 (1)
c, Å	19.3021 (3)	15.18 (1)
α, deg	90	76.42 (9)
β, deg	90	86.66 (7)
γ, deg	90	74.46 (9)
vol., Å^3	2112.19 (5)	1091.5 (1.9)
ρ_{calc}, g cm^{-3}	1.454	1.41
cryst dimens, mm	0.03 × 0.04 × 0.06	0.09 × 0.07 × 0.05
temp, °C	−100	−40
measurement of intensity data	kinetic isomer	thermodynamic isomer
diffractometer	Siemans SMART	Enraf-Nonius CAD4
radiation (monochrom)	Mo, 0.71073 Å (graphite)	Mo, 0.71073 Å (graphite)
scan rate, deg/min	0.6	2−16.5
scan range, deg		0.7 + 0.35 tan θ
2θ range, deg	0−46.5	4−50
data collected	$-6 \leq h \leq 9$, $-12 \leq k \leq 14$, $-20 \leq l \leq 21$ (1.3 hemispheres	$+h,\pm k,\pm l$
no. of data collected	8487	4123
no. of unique data	2788 [$F^2 > 4\sigma(F^2)$]	1477 [$F^2 > 3\sigma(F^2)$]
no. of params varied	269	226
μ, cm^{-1}	9.86	9.52
systematic absences	$h00$, h odd; $0k0$, k odd; $00l$, l odd	none
abs cor	SHELXA	differential
range of trans. factors		0.58−1.00
$R(F_o)$	0.034	0.0737
$R_w(F_o)$	0.058	0.0643
goodness of fit	1.11	2.15

To probe the mechanism of this transformation, we first sought to determine whether the **2k** to **2t** isomerization was an intra- or intermolecular conversion. First, the competitive barriers for thiophene vs 2-methylbenzothiophene activation were measured by heating a solution of **3** and a 10:3.5 mixture of thiophene:2-methylbenzothiophene (eq 2). After thermolysis at 47 °C for 19 h a ratio of 7.14:1 was observed for thiophene:2-methylbenzothiophene C−S inserted products. The corrected ratio of 2.5:1 corresponds to ~0.6 kcal/mol preference for thiophene over 2-methylbenzothiophene indicating a small



(2)

kinetic difference in reactivity between the two thiophenes. Second, the conversion from the kinetic isomer **2k** to the thermodynamic isomer **2t** was monitored in the presence of a large excess of thiophene (30 equiv). No thiophene insertion product was seen when **2k** was converted to **2t** by heating at 74 °C for 38 h, indicating an *intramolecular* mechanism for the isomerization (eq 3).



(3)

Conversion of **2k** to **2t** followed first order kinetics, but analysis of final product concentrations after heating the kinetic product for 102 h at 85 °C (~13 half-lives) revealed an approximate equilibrium ratio of 21:1 for **2t**:**2k**. The large value of K_{eq} allowed treatment of data as a simple first order process over the first three half-lives. Rate constants were calculated from data collected from 47−85 °C, as shown in Table 4.

The kinetic preference for formation of **2k** over **2t** can be estimated as ~2.3 kcal/mol at 47 °C by analysis of product concentrations at early reaction times. Attempts to accurately measure the barrier for loss of 2-methylbenzothiophene from **2t** were unsuccessful as thermolysis in the presence of excess PMe_3 at 106 °C for 66 h showed no sign of thiophene loss, a reflection of the high thermal stability believed characteristic of all these $(C_5Me_5)Rh$ C−S inserted products.[9]

Discussion

Earlier studies in our laboratory show that the reactive fragment $[(C_5Me_5)Rh(PMe_3)]$, formed thermally from benzene loss from **1**, inserts into a wide variety of thiophene C−S bonds.[9] Evidence has been provided that C−H insertion occurs by way of initial η^2-coordination to the thiophene, whereas C−S insertion occurs by way of a symmetrical S-bound adduct. In looking at selectivities in C−S bond cleavage by these types of low oxidation state systems, it is important therefore to consider the choices available to the S-bound complex of the thiophene. Bianchini has characterized a pseudoallylic η^3-benzothiophene complex as an immediate precursor to C−S insertion,[13] but in the present system, the occurrence of such an η^3-species is unlikely as it would be a 20-electron compound (PMe_3 is not labile in these C−S cleavage adducts).

Studies of the reaction of **1** with 2-methylthiophene showed only insertion into the C−S bond away from the methyl substituent, an observation interpreted in terms of the choices open to the S-bound precursor complex. The C−S bond adjacent to the methyl group presents an additional steric barrier to the insertion, giving rise to the observed selectivity. In the reaction of **1** with benzothiophene, the S-bound complex now "sees" a choice between a C−S bond stemming from an aromatic ring or an unhindered C−S bond. Insertion into the latter is preferred, again presumably on steric grounds, since one would have anticipated a preference for insertion into the S−aryl bond with formation of the stronger metal−aryl bond.[27]

Table 4. Rate Constants and Activation Parameters for the Conversion of 2k to 2t

T, K	k,[a] s^{-1}	$\Delta G^{\ddagger}$ (kcal/mol)
320	$(2.38 \pm 0.11) \times 10^{-7}$	28.47 ± 0.06
335	$(4.34 \pm 0.04) \times 10^{-6}$	27.90 ± 0.01
348	$(6.36 \pm 0.5) \times 10^{-6}$	28.75 ± 0.03
358	$(2.36 \pm 0.08) \times 10^{-5}$	28.66 ± 0.06

[a] Errors are expressed in terms of 95% confidence levels as determined by Student's t−test.

Further heating of the observed product does not result in an isomerization.

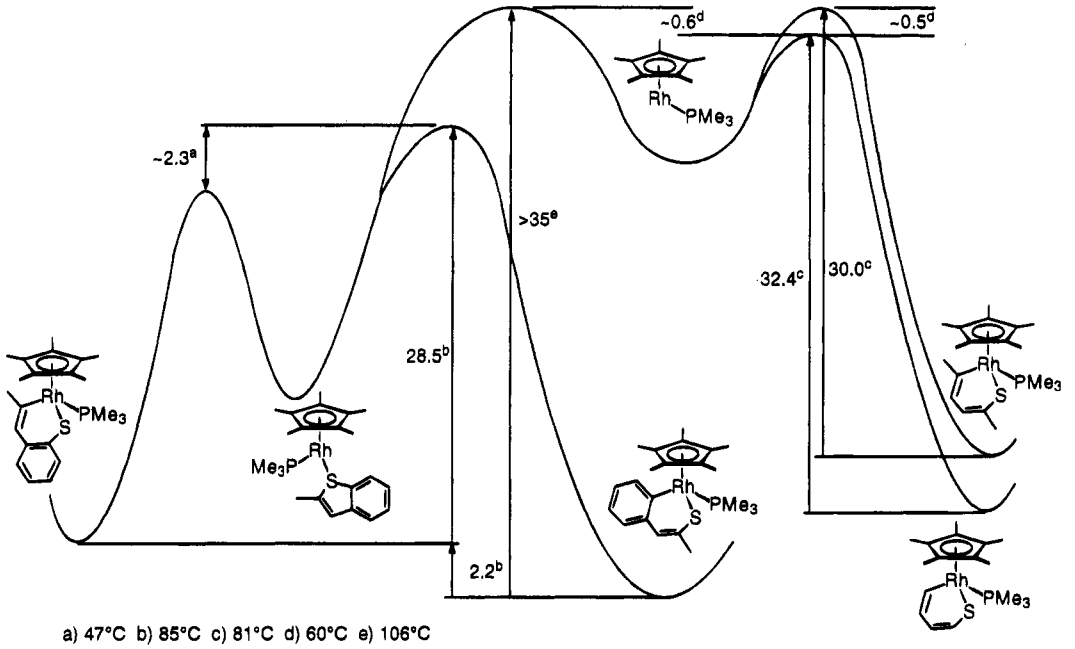
The reaction of 2-methylbenzothiophene was examined to determine which of the above effects would dominate the C−S cleavage selectivity. It was anticipated that the presence of a methyl group in the 2-position might change the selectivity from that observed with benzothiophene, but the formation and interconversion of kinetic and thermodynamic isomers in the reaction of 2-methylbenzothiophene was somewhat surprising. The kinetic preference in the S-bound complex for insertion into the C−S bond adjacent to the methyl group can be interpreted in terms of the LUMO of benzothiophene, which has a large coefficient on the carbon to which the methyl group is attached.[31] The thermodynamic preference for isomer **2t** can be readily interpreted in terms of a preference for the stronger metal−carbon bond, i.e., metal−aryl vs metal−vinyl.[27]

As mentioned earlier, the NOE experiments are in complete support of the structures found by X-ray studies. A substituent bound to the α carbon bound to rhodium lies closer in space to both the phosphine *and* (C_5Me_5) methyl groups and exhibits an NOE enhancement when those methyl groups are irradiated (and *vice versa*). A substituent bound to the α carbon bound to sulfur also lies close to the (C_5Me_5) methyl groups but not as close to the phosphine methyl hydrogens. Observation of an enhanced thiophene aromatic resonance (δ 7.3) when the phosphine and (C_5Me_5) resonances of **2t** were irradiated led us to assign this isomer as insertion of rhodium into the S−C(aryl) bond. Conversely, assignment of **2k** as insertion adjacent to the benzothiophene methyl substituent was made after that methyl group was enhanced due to irradiation of the PMe_3 and (C_5Me_5) resonances. The ^{31}P data for complexes **2k** and **2t** also provide evidence for the assigned structures. The doublet resonance for **2k** is both upfield (by over 4.5 ppm) and has a larger Rh−P coupling constant (by 7 Hz) than that for **2t**. These observations are consistent with a kinetic isomer that has a more electron rich rhodium center, characteristic of the electron donating properties of the methyl substituent on the carbon bound to the metal. The Rh−C bond in **2k** is also slightly longer (2.048(5) Å) than in **2t** (2.03(2) Å), even though both bonds involve sp^2 carbon, again pointing to a weaker Rh−C interaction in **2k**.

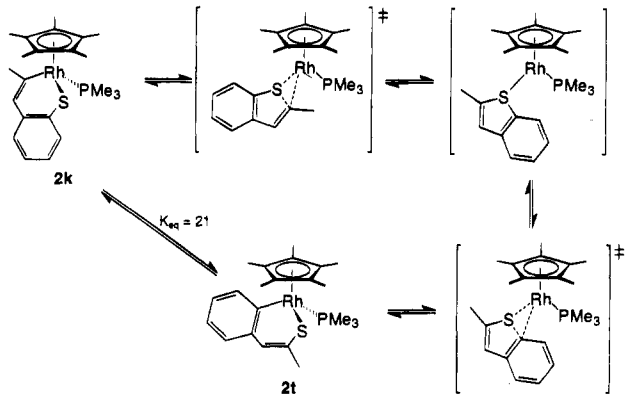
Scheme 2 shows a free energy profile for formation of **2k** and **2t** as well as relative values for thiophene and 2,5-dimethylthiophene activation at ~80 °C. The kinetic selectivity for formation of **2k** vs **2t** is estimated at ~2.3 kcal/mol, based upon the nearly exclusive formation of **2k** at early reaction times. The structures involved in the interconversion are viewed in terms of the intermediates and transition states shown in Scheme 3. The final equilibrium concentrations of 21:1 for **2t**:**2k** were measured near the limit of sensitivity of NMR and thus give only an approximate $\Delta G°$ value of 2.2 kcal/mol. Attempts to

(31) Preliminary geometrical optimization calculations were carried out on benzothiophene and 2-methylbenzothiophene using the program PM3 in the Hyperchem calculation package. In both cases, the phenyl α-carbon had a coefficient of −0.30, while the vinyl α-carbon showed a coefficient of −0.5.

Scheme 2



Scheme 3



measure the activation barrier for loss of 2-methylbenzothiophene from the thermodynamic isomer **2t** were unsuccessful, but the conditions under which no reaction was observed (106 °C, 66 h) allow calculation of a minimum activation barrier, had thiophene loss only just begun. The minimum barrier of 35 kcal/mol reflects the increased strength of the Rh−aryl bond as compared with the Rh−C (vinyl) bonds in (C_5Me_5)Rh(PMe$_3$)(S-CH=CH-CH=CH) ($\Delta G^{\ddagger}$ = 32.4 kcal/mol) and (C_5Me_5)Rh(PMe$_3$)(S-CMe=CH-CH=CMe) ($\Delta G^{\ddagger}$ = 30.0 kcal/mol).

While the half-life for thiophene-d_4 exchange with (C_5Me_5)Rh(PMe$_3$)(S-CH=CH-CH=CH) at 80 °C was ~72 days, the half-life for thiophene exchange for the 2,5-dimethylthiophene derivative was only 4 days at this temperature.[9] Presumably a result of increased steric interactions, or a destabilizing effect of the electron donating ability of the methyl group, the ground state energy of the C−S inserted adduct is raised. Competition experiments of **1** with thiophene and 2,5-dimethylthiophene showed only a ~0.6 kcal/mol preference toward activation of thiophene vs 2,5-dimethylthiophene.[9] This observation provides an insight into explaining the behavior of 2-methylbenzothiophene.

Conclusions

Kinetic and thermodynamic isomers are found when (C_5Me_5)Rh(PMe$_3$)(3,5-xylyl)H is reacted with 2-methylbenzothiophene. The reversible insertion into the S−C(Me) bond, unique to these (C_5Me_5)Rh C−S inserted systems, is a reflection of a high energy kinetic product relative to the benzothiophene analog as a result of increased steric factors.

Experimental Section

General Methods. All operations and routine manipulations were performed under a nitrogen atmosphere, either on a high vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corporation dri-lab. All solvents were distilled from dark purple solutions of benzophenone ketyl. Benzene-d_6 and cyclohexane-d_{12} were distilled under vacuum from dark purple solutions of benzophenone ketyl and stored in ampules with Teflon sealed vacuum line adapters. Thiophene and benzothiophene were purchased from Aldrich Chemical Company and used without further purification. Trimethylphosphine was purchased from Strem Chemicals, Inc. The preparation and characterization of **1** and **3** have been previously reported.[30]

^{1}H (400 MHz), ^{31}P (162 MHz), and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AMX400 NMR spectrometer. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced to the chemical shifts of residual solvent resonances (C_6H_6, δ 7.15; C_6H_{12}, δ 1.38; acetone, δ 2.04). ^{31}P NMR chemical shifts were measured in ppm relative to 30% H_3PO_4 (δ 0.0), while ^{13}C NMR shifts were calibrated to the chemical shift of the solvent (C_6D_6, δ 128.0). All kinetics plots and least squares error analysis of rate data was done using Microsoft Excel. Analyses were obtained from Desert Analytics. An Enraf-Nonius CAD4 diffractometer and Siemans SMART CCD area detector were used for X-ray crystal structure determination.

Synthesis of 2-Methylbenzothiophene. Benzothiophene (5.0 g, 0.037 mol) was dissolved in 70 mL of dry diethyl ether and cooled to −78 °C in a dry-ice/acetone bath. A THF solution of *n*-butyllithium (0.074 mol) was added dropwise under a nitrogen atmosphere and stirred for 45 min at −78 °C. The solution was gradually warmed to room temperature and stirred for an additional 45 min. Slow addition of degassed dimethyl sulfate (0.111 mol) at −78 °C was followed by stirring for 30 min. After warming to room temperature the solution was quenched with an aqueous solution of NaOH (0.7 g, 0.134 mol), washed with water, dried with $MgSO_4$, and reduced in volume to produce a white solid. Recrystallization in CH_2Cl_2/hexanes produced

4.80 g (0.032 mol) of white needles of 2-methylbenzothiophene (86% yield). The compound sublimes readily at ambient temperature under vacuum: ^{1}H NMR (C_6D_6) δ 2.141 (s, 3 H, Me), 6.624 (s, 1 H, H-3), 7.033 (td, J = 7.0, 1.1 Hz, 2 H), 7.484 (d, J = 8.0 Hz, 1 H), 7.530 (d, J = 8.0 Hz, 1 H); ^{13}C NMR (C_6D_6) δ 15.72 (s), 122.042 (s, C), 122.27 (s, C−H), 122.83 (s, C−H), 123.72 (s, C−H), 124.34 (s, C−H), 140.22 (s, C), 140.74 (s, C), 140.97 (s, C).

Preparation of (C_5Me_5)Rh(PMe_3)(2-methylbenzothiophene)—Kinetic Product, 2k. A hexane solution (5 mL) of (C_5Me_5)Rh(PMe_3)-(3,5-xylyl)H (0.50 g, 0.12 mmol) and 2-methylbenzothiophene (0.020 g, 0.14 mmol) was heated at 47 °C for 9 h in an ampule with a Teflon adapter. The solvent and excess 2-methylbenzothiophene were removed in vacuo and the brown solid was extracted with hexanes. Evaporation of the hexanes solution yielded an orange solid consisting of a 35.6:1 ratio of **2k**:**2t**. Resonances of **2k** were assigned by ^{1}H COSY NMR spectroscopy: ^{1}H NMR (C_6D_6) δ 1.039 (dd, J = 9.7, 0.8 Hz, 9 H, PMe_3), 1.501 (d, J = 2.7 Hz, 15 H, C_5Me_5), 2.229 (br t, J_{P-H} = 1.2 Hz, 3 H, Me), 6.889 (br s, 1 H, H-3), 6.959 (m, 2 H, H-5, H-6), 7.125 (m, 1 H, H-7), 7.950 (m, 1 H, H-4); ^{31}P NMR (C_6D_6) δ 4.00 (d, J = 162 Hz); ^{13}C NMR (C_6D_6) δ 9.23 (d, J = 1.1 Hz, C_5Me_5), 15.15 (d, J = 32.0 Hz, PMe_3), 21.57 (s, Me), 99.20 (t, J = 3.7 Hz, C_5Me_5), 122.26, 123.95, 130.86, 130.56, 130.12, 134.29, 137.29 (br d, Rh-*C*). Remaining peak was obscured by solvent.

Preparation of (C_5Me_5)Rh(PMe_3)(2-methylbenzothiophene)—Thermodynamic Product, 2t. (C_5Me_5)Rh(PMe_3)(Ph)H (0.020 g, 0.051 mmol) and 2-methylbenzothiophene (0.0075g, 0.051 mmol) were heated at 65 °C in 0.5 mL of C_6D_{12} in a resealable NMR tube with Teflon stopcock for 3 days. Solvent was removed in vacuo, and the solid was redissolved in fresh hexanes. Orange crystals formed after sitting in the freezer at −20 °C for several days: ^{1}H NMR (acetone-d_6) δ 1.260 (dd, J = 9.4, 0.8 Hz, 9 H, PMe_3), 1.615 (d, J = 2.7 Hz, 15 H, C_5Me_5), 2.051 (s, 3 H, Me), 5.998 (s, 1 H, H-3), 6.582 (td, J = 7.3, 1.7 Hz, 1 H, H-5), 6.644 (dd, J = 7.4, 1.8 Hz, 1 H, H-4), 6.704 (td, J = 6.9, 1.3 Hz, 1 H, H-6), 7.306 (d, J = 7.6 Hz, 1 H, H-7); ^{31}P NMR (acetone-d_6) δ 8.77 (d, J = 157 Hz); ^{13}C NMR (C_6D_{12}) δ 6.51 (s, C_5Me_5), 14.41 (d, J = 24.7 Hz, PMe_3), 28.68 (s, Me), 105.10 (t, J = 3.7 Hz, C_5Me_5), 128.52 (s), 131.55 (s), 131.66 (s), 134.37 (s), 135.19 (br s), 140.32 (s), 141.51 (s), 148.16 (s).

Thiophene/2-Methylbenzothiophene Competition. (C_5Me_5)Rh-(PMe_3)(3,5-xylyl)H (0.010 g, 0.02 mmol) was heated in hexanes (0.5 mL) at 47 °C with a mixture of 2-methylbenzothiophene (0.010 g, 0.07 mmol) and thiophene (0.020 g, 0.2 mmol) for 19 h in a resealable NMR tube. The hexanes were removed under vacuum, and C_6D_6 was added. Analysis of the final product mixture showed thiophene insertion (^{31}P NMR δ 10.97, d, J = 158 Hz, 87.7%) and 2-methylbenzothiophene insertion (^{31}P NMR (C_6D_6) δ 4.00, d, J = 162 Hz, 12.3%). This ratio, after correcting for initial thiophene and 2-methylthiophene concentrations, corresponds to a final ratio of 2.5:1 thiophene:2-methylthiophene insertion products.

Product Conversion in the Presence of Thiophene. A C_6D_{12} solution (0.5 mL) of **2k** (0.010 g, 0.022 mmol) was heated at 74 °C for 38 h with 30 equiv of thiophene (0.054 g, 0.65 mmol). The thermodynamic product, **2t** (^{31}P NMR: δ 8.39, d, J = 159 Hz), was the exclusive product, as observed by ^{1}H and ^{31}P NMR spectroscopy.

Thermolysis of the Thermodynamic Product with PMe_3. The thermodynamic product, **2t** (0.011 g, 0.022 mmol), was heated in a resealable NMR tube in C_6D_6 with 50 equiv of PMe_3 (1.1 mmol) at 106 °C for 66 h. No loss of thiophene or formation of (C_5Me_5)Rh-(PMe_3)$_2$ was observed.

Kinetic Studies of 2k to 2t Isomerization. Degassed C_6D_6 solutions of **2k** in a resealable NMR tube were monitored by ^{1}H and ^{31}P spectroscopy to follow the conversion to **2t**. Integration of methyl resonances of each product were used to measure concentrations, and data were plotted as ln (% **2k**) against time to obtain rate constants for each temperature.

X-ray Structural Determination of (C_5Me_5)Rh(PMe_3)(2-methylbenzothiophene)—Kinetic Isomer, 2k. Slow evaporation of a benzene solution of **2k** produced small, orange crystals. A single crystal of dimensions 0.03 × 0.04 × 0.06 mm was mounted on a glass fiber with epoxy. Data were collected at −100 °C on a Siemans SMART CCD area detector system employing a 2kW sealed tube X-ray source. Hemispheres (1.3) of data were collected over 13 h, yielding 8487 observed data (see Table 3). Laue symmetry revealed an orthorhombic crystal system, with 2788 unique data (92% with $I > 4\sigma(F)$, R_{int} = 0.070). The space group was assigned as $P2_12_12_1$ on the basis of systematic absences, and the structure was solved and refined using direct methods included in the SHELXA package. All non-hydrogen atoms were refined anisotropically (on F^2), with hydrogens included in idealized locations. In the final model, the structure was refined as a 67:33 racemic twin, with R_1 = 0.034 and wR_2 = 0.064. Fractional coordinates and thermal parameters are given in the supporting information.

X-ray Structural Determination of (C_5Me_5)Rh(PMe_3)(2-methylbenzothiophene)—Thermodynamic Isomer, 2t. Light orange crystals formed from a hexane solution cooled to −20 °C for several days. A small single crystal with dimensions 0.09 × 0.07 × 0.05 mm was mounted on a glass fiber with epoxy. Lattice constants were obtained from 25 centered reflections with values of χ between 5 and 70°. Data were collected at −40 °C in accord with parameters in Table 3. The Molecular Structure Corporation TEXSAN analysis software package was used for data reduction and solution.[32] Patterson map solution of the structure to locate the rhodium atom, followed by expansion of the structure with the program DIRDIF, revealed all non-hydrogen atoms. Following isotropic refinement, an absorption correction was applied using the program DIFABS. Full matrix, least squares refinement of the non-hydrogen atoms (with hydrogens attached to carbons in idealized positions) was carried out to convergence, with R_1 = 0.0737 and R_2 = 0.0643. Fractional coordinates and thermal parameters are given in the supporting information.

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Supporting Information Available: Tables of data collection parameters, bond lengths, bond angles, fractional atomic coordinates, anisotropic thermal parameters, and least squares planes for (C_5Me_5)Rh(PMe_3)(2-methylbenzothiophene), and kinetic and thermodynamic products (14 pages); tables of calculated and observed structure factors (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(32) $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$, $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}/\sum w|F_o|^2$, 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*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.