Steric and Electronic Effects on the Insertion of a Rhodium Phosphine Complex into the C−S Bond of Substituted Dibenzothiophenes. Homogeneous Model for the Hydrodesulfurization Process

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The unsaturated 16e⁻ fragment [$(C_5Me_5)Rh(PMe_3)$] has been observed to insert into the sulfur−carbon bond in a variety of substituted dibenzothiophenes to give a six-membered metallacycle product. The regioselectivity of the C−S insertion was probed by varying the position and nature of substituents on dibenzothiophene, and selectivities were found to be directed by steric hindrance with a small electronic contribution. Insertion exclusively into the sterically less hindered C−S bond was found in 4-methyldibenzothiophene, 2,6-dimethyldibenzothiophene, and benzo[*b*]naphtho[2,1-*d*]thiophene. Insertion toward the unsubstituted ring was the major product of two C−S insertion isomers with 2-fluorodibenzothiophene and 2-methoxydibenzothiophene. Insertion toward the substituted ring was seen to be favored with 2-(trifluoromethyl)dibenzothiophene and 2-cyanodibenzothiophene. Unselective insertion into either C−S bond was found in 2-methyldibenzothiophene, 3-methyldibenzothiophene, 2,8-dimethyldibenzothiophene, 1,3,7-trimethyldibenzothiophene, and benzo[*b*]naphtho[1,2-*d*]thiophene. 2-Bromodibenzothiophene showed C−Br activation as well as two C−S insertion products (2:1), while 2-iododibenzothiophene showed C−I activation only. 4,6-Dimethyldibenzothiophene formed a labile S-bound complex which was observed to lose thiophene by substitution with free trimethylphosphine with $\Delta G^{\ddagger} = 24.5$ kcal/mol at 23 °C. X-ray structure determination of the products of reactions with 2-methyldibenzothiophene, 3-methyldibenzothiophene, 4-methyldibenzothiophene, 2,6-dimethyldibenzothiophene, 2,8-dimethyldibenzothiophene, benzo[*b*]naphtho[2,1-*d*]thiophene, 2-fluorodibenzothiophene, and 2-methoxydibenzothiophene confirmed the final identification of insertion selectivities. ^{1}H COSY and NOE difference experiments allowed assignment of regioselectivity with the products of 2-(trifluoromethyl)dibenzothiophene and 2-cyanodibenzothiophene by comparison with known samples.

Introduction

An advantage of studying model systems of industrial and catalytic processes is the ability to work with well-defined products and reactants under precisely controlled conditions, leading to mechanistic hypotheses unavailable from data collected under actual industrial conditions. The hydrodesulfurization (HDS) process is currently receiving attention from several research groups interested in applying homogeneous transition-metal model systems toward understanding the desulfurization of coal and petroleum feedstocks.[1] As it becomes necessary to employ heavier, more contaminated petroleum fractions and to remove a higher fraction of sulfur compounds (deep desulfurization), these studies offer the opportunity to discover more efficient or alternative methods for sulfur removal. Improved industrial conditions, prolonged catalyst life, and a decrease in air pollution from acid rain could be achieved through these investigations.[2]

Thiophene and thiophene-like molecules have been targeted as sulfur-containing molecules found in petroleum and coal which are difficult to desulfurize. Alkyl-substituted benzothiophenes and dibenzothiophenes have been found to be abundant but are more difficult to desulfurize than their unsubstituted parent derivatives using commercial heterogeneous catalysts.[3] Much of the recent chemistry with homogeneous transition-metal systems has been in the area of coordination modes of thiophenes,[4] reactivity of coordinated thiophenes,[5] and cleavage of the C−S bond.[6−11] Several binuclear[12] and cluster[13] systems have been examined as well in attempts to mimic surface interactions

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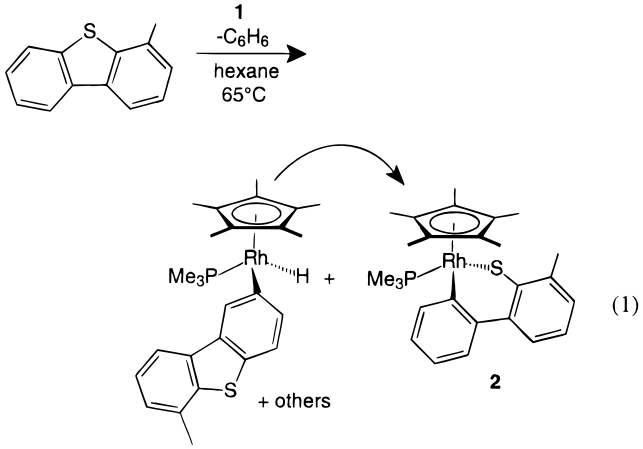
between sulfur impurities and silica-supported transition-metal sulfides currently used in the industrial HDS process.[14] Most of these studies have focused on the chemistry of monocyclic thiophene and its derivatives.

Recent studies in our laboratory with $(C_5Me_5)Rh(PMe_3)(Ph)H$ (**1**), known to reductively eliminate benzene at temperatures above 60 °C to generate the reactive 16e⁻ fragment $[(C_5Me_5)Rh(PMe_3)]$,[15] found that even the strong sulfur−aryl bonds of dibenzothiophene could be cleaved.[6] This led us to examine the reactivity and selectivity of a variety of substituted dibenzothiophenes, many of which have also been isolated from petroleum.[3a] The wide variety of substituted dibenzothiophenes that is accessible, coupled with their relative ease of synthesis, made these molecules attractive toward further investigations with our systems, especially since the reactivity of *substituted* dibenzothiophenes has not been examined with model systems. We were also interested in obtaining further mechanistic information on the C−S cleavage step leading to the six-membered metallacycle. As our results indicate, cleavage of the C−S bond by $[(C_5Me_5)Rh(PMe_3)]$ is best viewed as oxidative addition of a C−S bond to a rhodium center from an S-bound intermediate, while the selectivity of insertion is driven primarily by a steric factor with a smaller electronic effect.

Results

Reactions with Monomethyldibenzothiophenes. A similar sequence of observations was observed in all reactions of $(C_5Me_5)Rh(PMe_3)PhH$ (**1**) with dibenzothiophenes. Thermolysis of **1** with 4-methyldibenzothiophene[16] at 63 °C in C_6D_{12} solvent initially gives two major products resulting from activation of an aromatic C−H bond (^{31}P NMR (C_6D_{12}), δ 8.92, d, J = 150.6 Hz) and insertion into a C−S bond (δ 5.38, d, J = 161.8 Hz) (**2**) as evidenced by the magnitude of the J_{P-Rh} coupling constants in the ^{31}P spectrum. For the $[(C_5Me_5)Rh(PMe_3)]$ system, ^{31}P NMR spectroscopy has proved to be a valuable tool in the assignment of the formal oxidation state of rhodium (J_{Rh-P} = 200−230 Hz for Rh(I), J_{Rh-P} = 140−160 Hz for Rh(III)) and consequently the type of species formed (η^2-olefin, C−H activation, etc.).[6,17] Upon longer reaction times, **2** grows at the expense of the C−H activation products[18] until only the C−S-inserted complex remains (eq 1). C−H activation



(1)

was observed at early reaction times with every dibenzothiophene examined in this paper, although the specific sites of activation were not determined.

Due to difficulties in using NMR data to assign structures for the isomeric products of these reactions with substituted dibenzothiophenes, single-crystal X-ray structure determination was the most direct manner in which to correctly assign the site of insertion. X-ray studies of orange crystals of **2** identified the product as having arisen from C−S insertion away from the substituted ring (Figure 1). Selected bond distances and

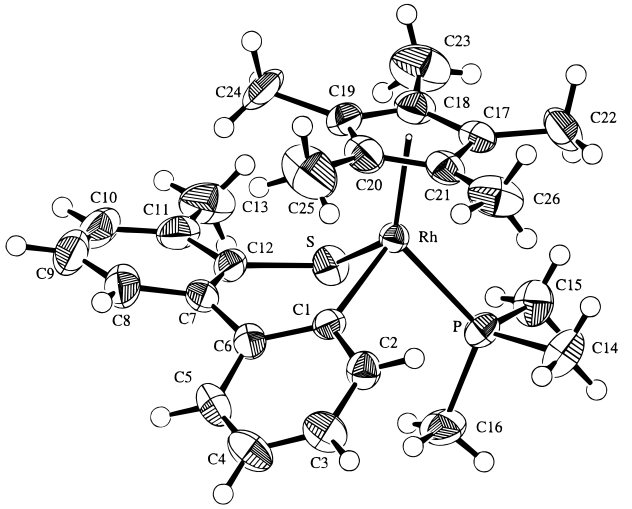


Figure 1. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(S\text{-}(4\text{-}Me\text{-}C_6H_3)\text{-}C_6H_4)$ (**2**). Ellipsoids are shown at the 50% probability level.

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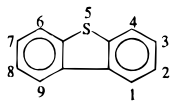
(16) The numbering scheme for dibenzothiophene is:



For metal-inserted complexes, the same numbering scheme is used with the metal inserted into the C−S bond nearest position 4.

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(18) In all thermal reactions of **1** with dibenzothiophenes, one or more C−H insertion products (5−30%) are seen in the ^1H or ^{31}P spectra at early reaction times. These species are only characterized on the basis of their ^{31}P chemical shifts and coupling constants (downfield, $J \approx 145$ Hz) and the appearance of new Cp*, PMe_3, and hydride resonances in the ^1H NMR spectrum. Coincidental overlap of resonances for these isomers has impeded full characterization of these intermediates. In all cases, the C−H activation products disappear over 20−40 h to give C−S insertion products.

Table 1. Selected Bond Distances (Å) for Compounds 2, 3a,b, 4a,b, 5, 6, 9, 11a, and 12a,b

	2	3a,b	4a,b	5	6	9	11a	12a,b
Rh−S	2.340(1)	2.35(1)	2.336(3)	2.335(2)	2.356(2)	2.327(1)	2.332(3)	2.333(2)
Rh−P	2.270(2)	2.24(2)	2.259(3)	2.267(2)	2.268(2)	2.264(2)	2.254(3)	2.272(2)
Rh−C(1)	2.034(5)	2.14(6)	2.02(1)	2.047(6)	2.038(6)	2.031(5)	2.037(8)	2.037(5)
S−C(12)	1.757(6)	1.73(5)	1.77(1)	1.754(7)	1.764(6)	1.748(5)	1.74(1)	1.740(6)
C(7)−C(12)	1.410(8)	1.50(5)	1.38(2)	1.42(1)	1.422(8)	1.399(7)	1.43(1)	1.406(8)
C(6)−C(7)	1.480(7)	1.54(5)	1.50(2)	1.493(9)	1.498(8)	1.483(7)	1.48(1)	1.492(8)
C(1)−C(6)	1.417(7)	1.23(6)	1.41(1)	1.414(9)	1.407(9)	1.397(7)	1.39(1)	1.411(7)

Table 2. Selected Bond Angles (deg) for Compounds 2, 3a,b, 4a,b; 5, 6, 9, 11a, and 12a,b

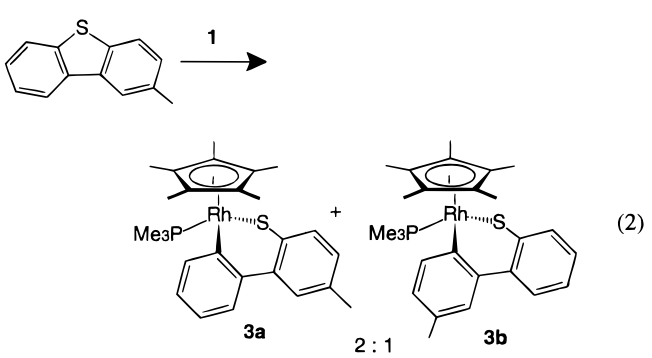
	2	3a,b	4a,b	5	6	9	11a	12a,b
S−Rh−P	85.03(5)	85.5(5)	85.4(1)	84.84(7)	84.90(8)	84.62(5)	84.2(1)	84.60(6)
S−Rh−C(1)	88.1(1)	82(2)	89.4(3)	88.4(2)	87.3(2)	88.1(1)	86.9(3)	88.7(2)
Rh−S−C(12)	104.8(2)	102(2)	100.7(4)	105.1(2)	102.5(2)	104.3(2)	100.7(3)	104.6(2)
Rh−C(1)−C(2)	118.8(4)	103(3)	119.7(8)	177.8(5)	120.9(5)	118.9(4)	119.8(7)	117.7(4)
P−Rh−C(1)	89.1(1)	89(2)	86.6(3)	88.8(2)	89.6(2)	88.3(1)	88.7(2)	89.3(1)
Rh−C(1)−C(6)	125.4(4)	145(5)	124.4(9)	124.7(5)	123.3(5)	124.5(4)	124.3(7)	125.3(4)
C(1)−C(6)−C(7)	124.2(4)	106(5)	123(1)	125.4(6)	123.9(6)	124.9(4)	124.4(8)	124.5(5)
S−C(12)−C(7)	122.2(4)	121(4)	121(1)	123.4(6)	121.2(5)	121.3(4)	123.4(8)	124.0(5)
C(6)−C(7)−C(12)	124.1(4)	127(4)	125(1)	123.4(7)	123.1(6)	123.8(4)	122(1)	124.1(5)
fold angle	47.3	48.9	47.7	46.4	53.2	60.8	52.5	60.83
biphenyl twist	37.0	40.0	42.4	32.7	42.5	36.6	38.2	30.95

Table 3. Summary of Crystallographic Data for 2, 3a, 3b, 4a,b, and 5

	2	3a,b	4a,b	5
empirical formula	$RhPSC_{26}H_{34}$	$RhPSC_{26}H_{34}$	$RhPSC_{26}H_{34}$	$RhPSC_{27}H_{36}$
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1$ (No. 4)	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
Z	2	8	4	4
a, Å	8.320(2)	13.113(9)	11.974(4)	8.468(3)
b, Å	15.653(3)	16.34(2)	13.303(7)	23.907(8)
c, Å	9.460(3)	23.32(3)	15.377(7)	12.93(1)
β, deg	93.30(2)	90	90.91(3)	101.89(5)
V, Å^3	1230(1)	4996(15)	2449(3)	2561(4)
d_{calc}, g/cm^3	1.38	1.36	1.39	1.36
T, °C	−40	−20	−40	−40
radiation (monochrom)	Mo, 0.710 69 Å (graphite)	Mo, 0.710 69 Å (graphite)	Mo, 0.710 69 Å (graphite)	Mo, 0.710 69 Å (graphite)
scan rate, deg/min	2−16.5	2−16.5	2−16.5	2−16.5
scan range, deg	0.7 + 0.35 tan θ	0.7 + 0.35 tan θ	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
2θ range, deg	4−50	4−50	4−50	4−50
data collected	$+h,+k,\pm l$	$+h,+k,+l$	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of data collected	2418	4866	4727	5069
no. of unique data (>3σ)	2091	574	1922	2921
no. of params varied	258	132	261	271
abs coeff, cm^{-1}	8.37	8.25	8.41	8.06
systematic absences	0k0, k odd	0kl, k odd; h0l, l odd; hk0, h odd	0k0, k odd; h0l, $h + l$ odd	0k0, k odd; h0l, $h + l$ odd
abs cor	differential	differential	differential	differential
range of transmissn factors	0.90−1.05	0.66−1.07	0.73−1.15	0.68−1.24
R_1	0.0210	0.0789	0.0497	0.0438
R_2	0.0281	0.0714	0.0466	0.0489
goodness of fit	1.21	1.63	1.30	1.61

angles can be found in Tables 1 and 2, respectively. Table 3 contains a summary of crystallographic data.

When reacted with 2-methyldibenzothiophene at 70 °C in hexane, **1** gives two C−S insertion products in a 2:1 ratio (eq 2). As with the 4-methyldibenzothiophene case, several C−H activation products are observed at early reaction times and eventually disappear. Both products cocrystallized in overlapping positions in the unit cell, as determined by X-ray structural characterization, in a ratio of 57:43. The major isomer, **3a**, was identified as cleavage of the C−S bond *away* from the substituted ring, while the minor isomer, **3b**, reflected insertion into the opposite C−S bond (Figure 2). ^{31}P NMR spectroscopy of the single crystal used for X-ray structure determination confirmed that the crystallographic ratios mirrored those seen in the bulk solution.



(2)

To further analyze the effects of a monomethyl-substituted dibenzothiophene, the reactivity of 3-methyldibenzothiophene was examined. As with 2-methyldibenzothiophene, no selectivity was seen, as the final products after thermolysis with **1** in hexane were two C−S insertion products in a 1:1 ratio. X-ray structural characterization of the products **4a**,**b** revealed a disor-

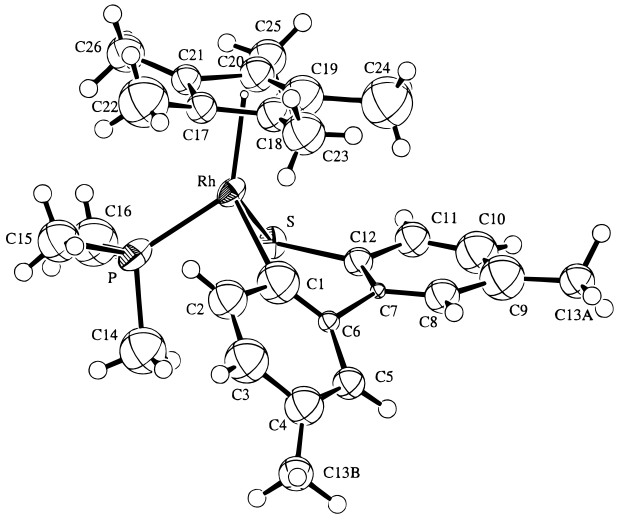


Figure 2. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)$(S-(2-Me-C_6H_3)-C_6H_4) (**3a**,**b**). Ellipsoids are shown at the 50% probability level. Only Rh, S, and P were refined anisotropically. Final population values are 0.57 for C(13A) and 0.43 for C(13B).

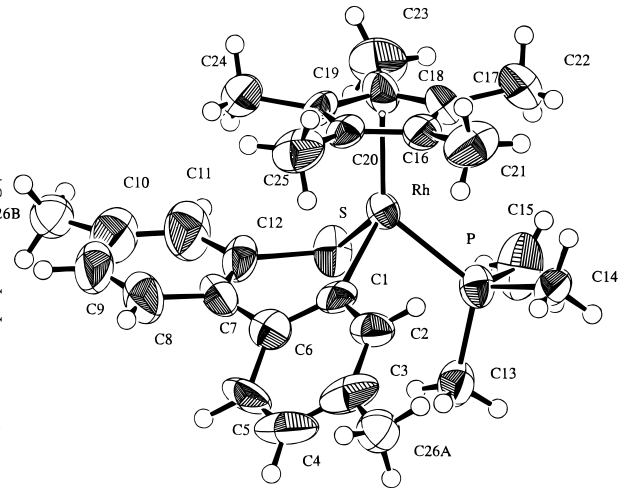


Figure 3. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)$(S-(3-Me-C_6H_3)-C_6H_4) (**4a**,**b**). Ellipsoids are shown at the 50% probability level. The methyl substituent was disordered and only refined isotropically. Final population values are 0.45 for C(26A) and 0.55 for C(26B).

dered crystal with both isomers crystallizing together, as with **3a**,**b** (Figure 3).

Reactions with Di- and Trimethyldibenzothiophenes. The insertion selectivities of several dimethyldibenzothiophenes were also examined. Reaction of **1** with the symmetrically substituted dimethyl isomer 2,8-dimethyldibenzothiophene in hexane gave the expected single C−S insertion product (**5**), characterized by ^{1}H and ^{31}P NMR spectroscopy and X-ray diffraction studies (Figure 4). Another dimethyl-substituted isomer, 2,6-dimethyldibenzothiophene, reacted with **1** in hexane to give a single C−S insertion product (**6**) (eq 3). Orange crystals of X-ray diffraction quality were used to identify **6** as having inserted into the C−S bond *away* from the sterically hindered methyl group (Figure 5), as seen in **2**. Crystallographic data can be found in Table 4.

An S-bound adduct (**7**) was formed when the sterically hindered 4,6-dimethyldibenzothiophene was reacted

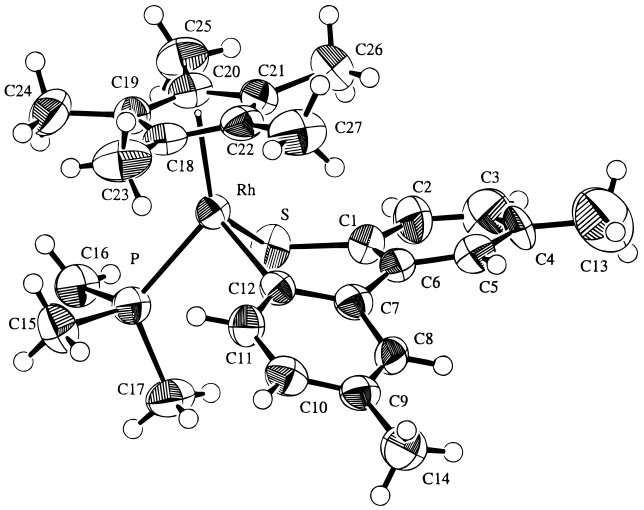


Figure 4. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)$(S-(8-Me-C_6H_3)-2-Me-C_6H_4) (**5**). Ellipsoids are shown at the 50% probability level.

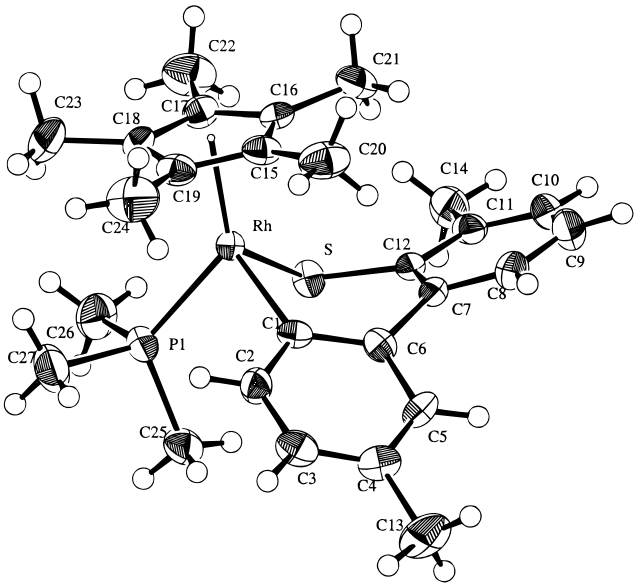
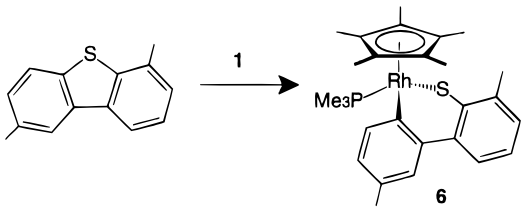


Figure 5. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)$(S-(6-Me-C_6H_3)-2-Me-C_6H_4) (**6**). Ellipsoids are shown at the 50% probability level.



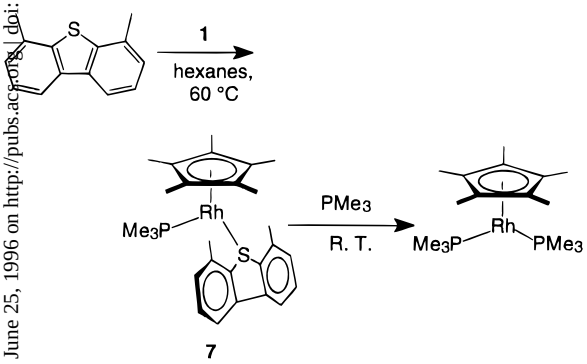
(3)

with **1** in hexane solvent. One methyl resonance, δ 2.831 (s, 6H), and three aromatic resonances, δ 7.04 (dd, 2H) 7.21 (t, 2H) and 7.76 (dd, 2H), were observed for the product by ^{1}H NMR spectroscopy. A doublet with a chemical shift and coupling constant characteristic of a Rh(I) σ-bound complex was also seen by ^{31}P NMR spectroscopy (δ −4.35, J = 226.9 Hz). The S-bound complex failed to insert upon further heating or upon reaction in different solvents but instead decomposed to $(C_5Me_5)Rh(PMe_3)_2$, which appears to be a thermodynamic sink for this system.[6] The lability of the S-bound complex was demonstrated by the addition of excess

Table 4. Summary of Crystallographic Data for 6, 9, 11a, and 12a,b

	6	9	11a	12a, 12b
empirical formula	$RhPSC_{27}H_{36}\cdot C_6H_6$	$RhPSC_{29}H_{34}$	$RhPSC_{26}H_{34}$	$RhFPSC_{25}H_{31}$
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Z	4	4	4	4
a, Å	10.780(7)	8.557(3)	10.197(8)	8.655(4)
b, Å	10.983(5)	15.446(5)	13.92(1)	21.24(1)
c, Å	26.048(5)	18.931(9)	17.74(1)	13.047(6)
β, deg	100.85(4)	90	96.03(4)	101.55(4)
V, Å^3	3029(5)	2502(3)	2503(4)	2349(4)
d_{calc}, g/cm^3	1.33	1.45	1.41	1.46
T, °C	−40	−40	−40	−20
radiation (monochrom)	Mo, 0.710 69 Å (graphite)	Mo, 0.710 69 Å (graphite)	Mo, 0.710 69 Å (graphite)	Mo, 0.710 69 Å (graphite)
scan rate, deg/min	2−16.5	2−16.5	2−16.5	2−16.5
scan range, deg	0.8 + 0.35 tan θ	0.7 + 0.35 tan θ	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
2θ range, deg	4−50	4−50	4−50	4−50
data collected	$+h,+k,\pm l$	$+h,+k,+l$	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of data collected	5932	2529	4829	4545
no. of unique data (>3σ)	2894	2288	2380	2872
no. of params varied	325	289	271	271
abs coeff, cm^{-1}	6.91	8.29	8.34	8.83
systematic absences	0k0, k odd; $h0l$ $h + l$ odd	h00, h odd; 0k0, k odd; 00l, l odd	0k0, k odd; $h0l$, $h + l$ odd	0k0, k odd; $h0l$, $h + l$ odd
abs corr	differential	differential	differential	differential
range of transmissn factors	0.86−1.07	0.87−1.29	0.73−1.12	0.85−1.15
R_1	0.0423	0.0260	0.0536	0.0366
R_2	0.0422	0.0324	0.0548	0.0427
goodness of fit	1.20	1.37	1.42	1.46

PMe_3 at room temperature. With a half-life of 36 h at room temperature ($\Delta G^{\ddagger} = 24.5$ kcal/mol), the S-bound complex was converted to $(C_5Me_5)Rh(PMe_3)_2$ (eq 4). An



(4)

7

unstable S-bound complex was previously observed when **1** was reacted with tetramethylthiophene.[6]

The influence of a trimethyl-substituted dibenzothiophene was then examined in order to probe the possibilities of an electronic effect from two methyl groups on one ring or the combined effect of three methyl groups on C−S insertion. 1,3,7-Trimethyldibenzothiophene was chosen on the basis of a lack of steric hindrance and ease of synthesis. No selectivity was seen when 1,3,7-trimethyldibenzothiophene was heated in the presence of **1** in C_6D_{12} solvent. Two C−S-inserted compounds (**8a**,**b**) were observed by ^{1}H and ^{31}P NMR spectroscopy in a 1.5:1 ratio.

Reactions with Benzonaphthothiophenes. Benzonaphthothiophenes have been identified in crude petroleum samples[19] and were also examined in this study. Benzodiphenylene sulfide (benzo[*b*]naphtho[2,1-*d*]thiophene) was reacted with **1** to give a single C−S insertion product, **9**. The product was structurally characterized, confirming that insertion had occurred away from the sterically hindered naphthyl side (Figure 6). Additional organometallic species were observed at

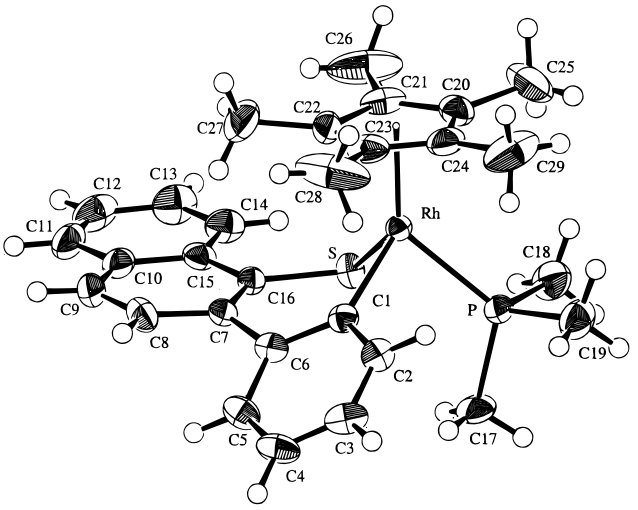
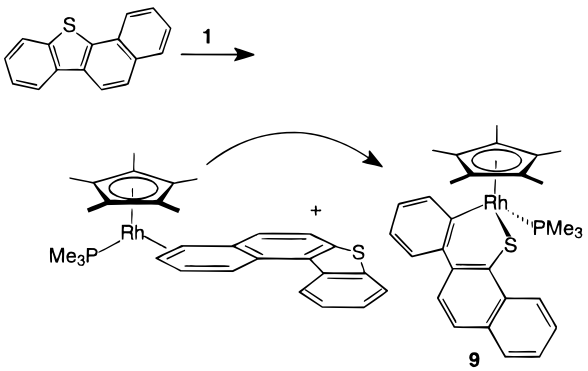


Figure 6. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(S\text{-}C_{10}H_6\text{-}C_6H_4)$ (**9**). Ellipsoids are shown at the 50% probability level.

early reaction times. In addition to the C−S-inserted compound **9** (^{31}P δ 4.28, d, J = 159.7 Hz), several C−H activation products and an η^2-coordinated product of the intact thiophene were also observed (eq 5). The latter



(5)

9

was identified by its characteristic ^{31}P NMR data (δ

(19) Willey, C.; Iwao, M.; Castle, R. N.; Lee, M. L. *Anal. Chem.* **1981**, *53*, 400−407.

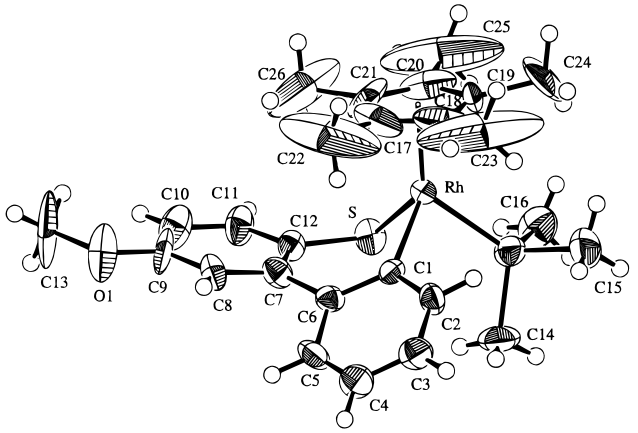
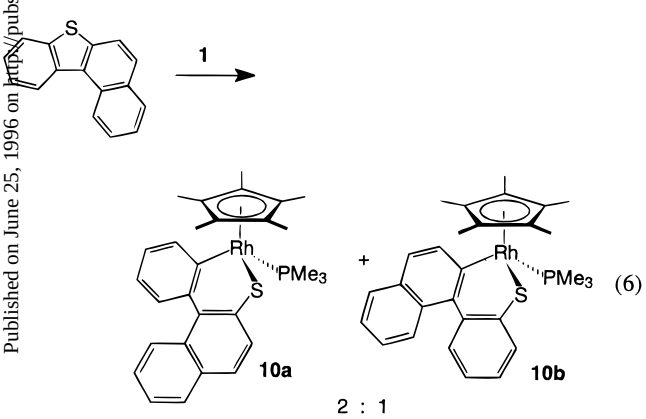


Figure 7. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(S\text{-}(2\text{-}MeO\text{-}C_6H_3)\text{-}C_6H_4)$ (**11a**). Ellipsoids are shown at the 50% probability level.

0.62, d, $J = 200.0$ Hz) and olefinic resonances in the ^1H NMR spectrum (δ 3.78, dt). This η^2 intermediate was short-lived under the reaction conditions, reflecting the reactivity of the naphthyl moiety rather than that of thiophene. Earlier studies of polycyclic aromatics with the $[(C_5Me_5)Rh(PMe_3)]$ fragment revealed extensive formation of η^2-arene complexes.[20] Ultimately, all of these species convert to **9** with continued heating.

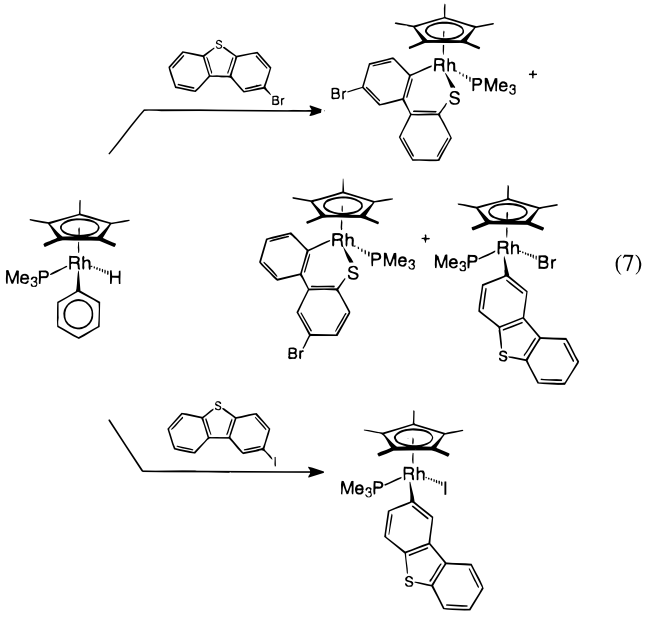
The electronic properties of the naphthyl group were further investigated with benzo[*b*]naphtho[1,2-*d*]-thiophene. With the steric bulk of the naphthyl rings directed away from sulfur, a 2:1 ratio of C−S-inserted products (**10a**,**b**) was seen upon reaction with **1** (eq 6).



(6)

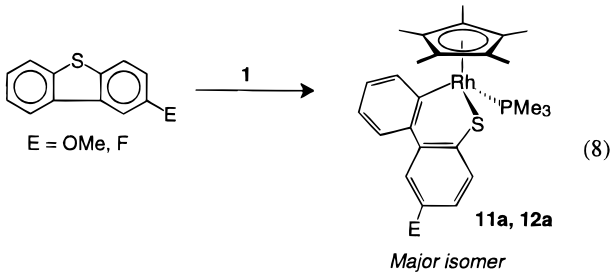
C−H activation and η^2 coordination were also seen at early reaction times. The site of insertion was not determined, as overlap in the aromatic region prevented application of useful NOE experiments, but the greater strength of a Rh−phenyl bond compared to a Rh−naphthyl bond would predict **10a** to be favored.[20]

Reactions with 2-Substituted Dibenzothiophenes. Contributions exclusively from electronic effects on dibenzothiophene C−S cleavage were examined by introducing heteroatom substitutions at the 2-position, para to the C−S bond. 2-Bromodibenzothiophene showed a 2:2:1 ratio of three organometallic compounds when heated with **1**. In addition to a 2:1 ratio of C−S-inserted products (^{31}P NMR: δ 4.49, d, $J = 158.8$ Hz and δ 3.90, d, $J = 157.0$ Hz), activation of the C−Br bond (^{31}P NMR: δ 5.26, d, $J = 154.2$ Hz) was seen as well. One product was seen in the reaction of **1** with 2-iododibenzothiophene. On the basis of ^1H and ^{31}P NMR data (δ 3.26, d, $J = 155.3$ Hz) the product was assigned as the activation of the C−I bond (eq 7).



(7)

Thermolysis of **1** at 67 °C in C_6D_{12} with 2-methoxydibenzothiophene gave two C−S-inserted products in a 4:1 ratio, as observed by ^1H and ^{31}P NMR spectroscopy (eq 8). The major product was crystallized and identified by X-ray diffraction as insertion *away* from the substituted ring, **11a** (Figure 7). 2-Fluorodibenzothiophene also gave two products in a 5:1 ratio when reacted with **1** at 66 °C (eq 8). Orange crystals of the mixture of products formed by slow diffusion of hexane into a benzene solution at −20 °C were analyzed by X-ray diffraction. The disordered structure showed that both isomers had cocrystallized. Least-squares refinement identified the major product as insertion *away* from the substituted ring, **12a**, by a ratio of 74:26 (Figure 8). Agreement between solution and crystallographic ratios was obtained by dissolving the X-ray crystal in C_6D_6 and comparing ^{31}P NMR data with those of the bulk solution.



(8)

Slight selectivity was seen in the reactions of 2-(trifluoromethyl)dibenzothiophene and 2-cyanodibenzothiophene (eq 9). Two C−S-inserted products were observed in a ratio of 5:1 when 2-cyanodibenzothiophene was reacted with **1**. While crystallization attempts of the products were unsuccessful, the major isomer, **15a**, was identified as insertion *toward* the substituted ring as described below. A 5:1 ratio of C−S insertion products

(20) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1989**, *111*, 8722−8723. Belt, S. T.; Dong, L.; Duckett, S. B.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 266−269. Chin, R. M.; Dong, L.; Duckett, S. B.; Jones, W. D. *Organometallics* **1992**, *11*, 871−876. Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685−7695.

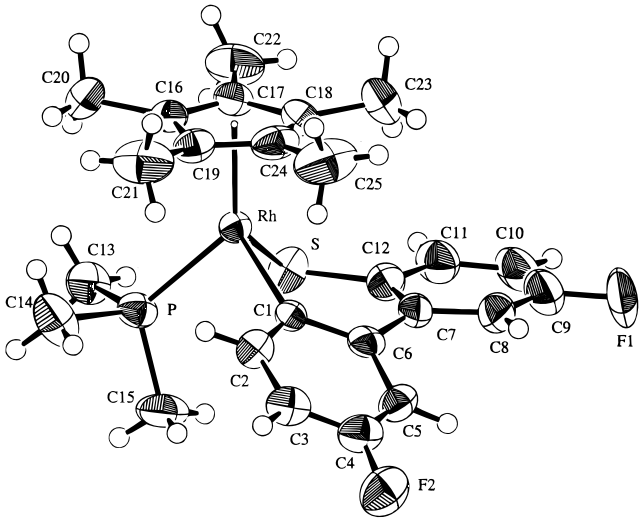
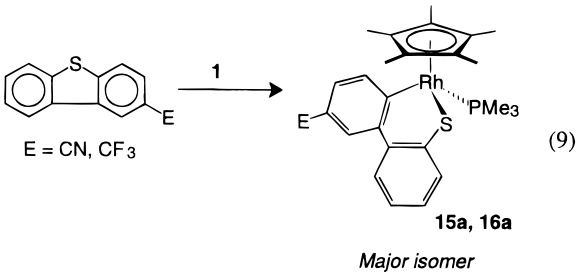


Figure 8. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(S\text{-}(2\text{-}F\text{-}C_6H_3)\text{-}C_6H_4)$ (**12a**,**b**). Ellipsoids are shown at the 50% probability level. All atoms were refined anisotropically. Final population values are 0.74 for F and 0.26 for F(2).



(9)

was also observed when **1** was reacted with 2-(trifluoromethyl)dibenzothiophene. The major isomer was also assigned as **16a**, insertion *toward* the substituted ring, as described below.

Nuclear Overhauser Effect Difference Experiments. Due to difficulty in forming X-ray-quality crystals, the insertion selectivities of the 2-cyanodibenzothiophene- and the 2-(trifluoromethyl)dibenzothiophene-inserted products were assigned on the basis of ^1H COSY and NOE difference NMR experiments. Assignments of the aromatic resonances of **15a** were first made with a 2D $^1H-^1H$ COSY experiment, shown in Figure 9. NOE difference spectra were obtained using a pulse program employing consecutive on, and off-resonance selective irradiation pulses of opposite transmitter phase. The FID was transformed to give a single difference spectrum showing only the irradiated peak and peaks enhanced by NOE. $(C_5Me_5)Rh(PMe_3)(S\text{-}(6\text{-}Me\text{-}C_6H_3)\text{-}2\text{-}Me\text{-}C_6H_4)$ (**6**) was examined first, as its geometry had been established by X-ray diffraction. When the aromatic proton H-4 was irradiated, both the C_5Me_5 and the PMe_3 resonances showed enhancement of 2.5% and 2.9%, respectively; however, when the methyl group in the 6-position was irradiated, an NOE of 1.4% was seen only to the C_5Me_5 resonance (Figure 10a). The inverse experiments supported these results. Irradiation of the C_5Me_5 resonance showed enhancement to H-4 and Me-6, while irradiating the PMe_3 methyl resonance showed enhancement to H-4 only. This difference in enhancement reveals information on the environment of the proton resonances in the 4- and 6-positions, i.e. those groups adjacent to sulfur in the parent thiophene.

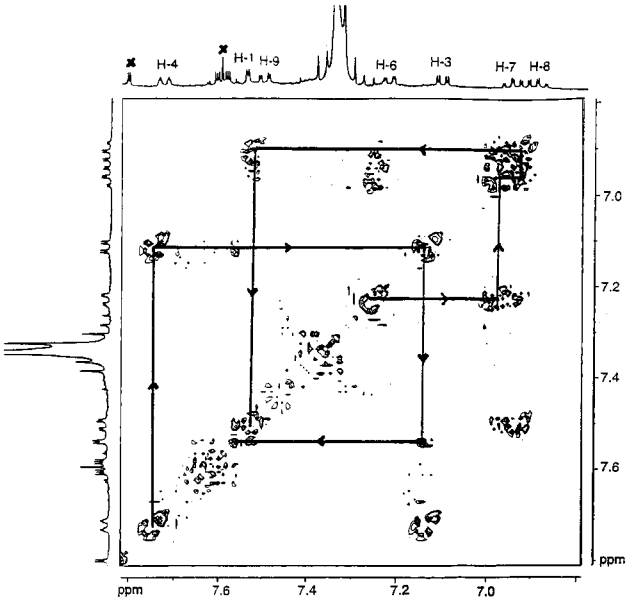


Figure 9. $^1H-^1H$ COSY spectrum of $(C_5Me_5)Rh(PMe_3)(S\text{-}C_6H_4\text{-}2\text{-}CN\text{-}C_6H_3)$ (**15a**). Unreacted 2-cyanodibenzothiophene peaks are marked with ×.

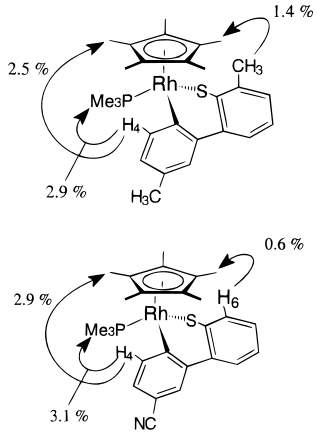


Figure 10. Through-space NOE pathways and enhancement percentages in (a, top) **6** and (b, bottom) **15a**.

When the major isomer of $(C_5Me_5)Rh(PMe_3)(S\text{-}C_6H_4\text{-}2\text{-}CN\text{-}C_6H_3)$, **15a**, was examined with NOE difference NMR experiments, the aromatic resonance at δ 7.72 showing enhancement to both the C_5Me_5 (2.9%) and the PMe_3 (3.1%) was assigned as H-4, shown in Figures 10b and 11. This result verifies that insertion *toward* the substituted ring is the major product in this case. Insertion toward the substituted ring is also observed with 2-(trifluoromethyl)dibenzothiophene, verified by similar ^1H COSY and NOE experiments. Irradiation of the resonance identified as H-4 (δ 7.7) showed enhancement to both C_5Me_5 and PMe_3 resonances, while irradiation of H-6 showed enhancement to the C_5Me_5 resonance only.

Competition Studies. Several mechanistic studies were carried out to examine kinetic selectivities of different thiophenes. When $(C_5Me_5)Rh(PMe_3)(Ph)H$ was heated at 66 °C with a 10-fold excess of a 1:1 mixture of thiophene and dibenzothiophene for 18 h, a 5:1 ratio (by NMR integration) of thiophene- to dibenzothiophene-inserted complexes was found. When $(C_5Me_5)Rh(PMe_3)(Ph)H$ was heated at 66 °C with a 5-fold excess of a 1:1 mixture of dibenzothiophene and 4-methyldiben-

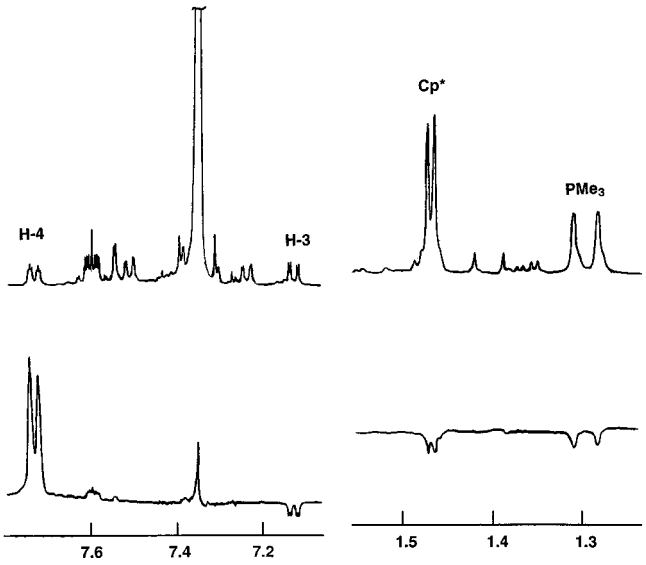
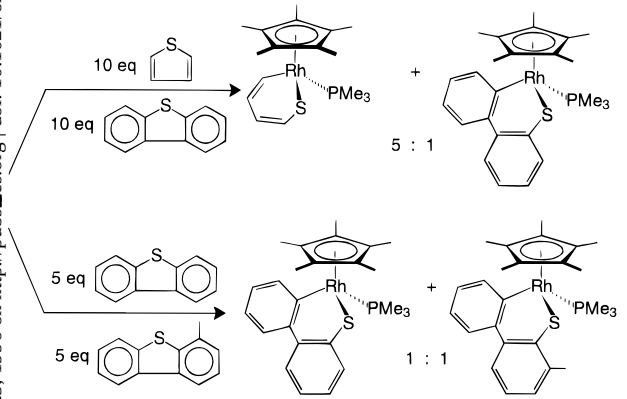


Figure 11. Normal ^{1}H NMR spectra (top traces) and NOE difference spectra when H-4 is irradiated (bottom traces) for **15a**. Anti-phase peaks reveal NOE enhancement to C_5Me_5 and PMe_3, as well as enhancement through coupling to neighboring H-3.

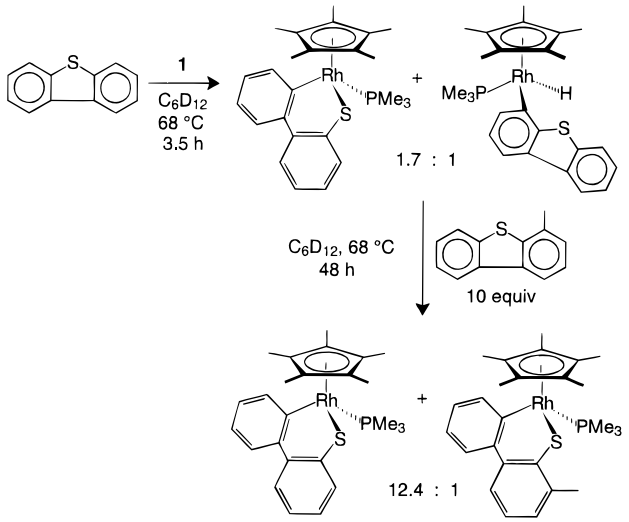
Scheme 1



Zothiophene for 39.5 h, a 1:1 ratio of inserted products was observed (Scheme 1).

To address the question of intramolecular versus intermolecular C−S insertion from a C−H-activated dibenzothiophene complex, **1** was heated at 68 °C with 1 equiv of dibenzothiophene for 3.5 h, until all of **1** had been converted to a 63:37 ratio of C−S insertion to C−H activation products. At this time, 10 equiv of 4-methyldibenzothiophene was added and the mixture heated again. After 48 h the reaction was complete and a 92:8 ratio of dibenzothiophene- to 4-methyldibenzothiophene-inserted inserted compounds was found (Scheme 2).

Scheme 2



Discussion

Steric Effects. The selective formation of one C−S-inserted product in the case of 4-methyldibenzothiophene suggested that a steric effect was driving the insertion of rhodium into the C−S bond. This hypothesis was supported by the results of unselective C−S insertion in other monomethyl-substituted dibenzothiophenes in which the steric hindrance had been removed and by the formation of a single isomer in the case of 2,6-dimethyldibenzothiophene, which had competitive steric but balanced electronic effects. The observation of a single C−S-inserted isomer corresponding to insertion away from the sterically hindered side revealed that *steric effects override electronic effects* in these systems. The results with the two benzonaphthothiophenes also delineate the importance of steric factors, as benzo[*b*]-naphtho[2,1-*d*]thiophene gave one C−S-inserted product (*away* from the hindering naphtho group) while no selectivity was seen when that hindrance was removed with benzo[*b*]naphtho[1,2-*d*]thiophene.

The sterically hindered 4,6-dimethyldibenzothiophene forms a labile S-bound complex when heated with **1**. The half-life for the S-bound compound was measured as 36 h at 23 °C ($\Delta G^{\ddagger}$ = 24.9 kcal/mol) by observing the formation of $(C_5Me_5)Rh(PMe_3)_2$ upon addition of trimethylphosphine. Angelici has observed stronger bonding in methylated dibenzothiophenes.[21] It is possible that the lack of C−S insertion can be attributed to a stronger binding of 4,6-dimethyldibenzothiophene than in the other dibenzothiophenes. The observation of C−S insertion in 2,8-dimethyldibenzothiophene, however, argues against this as a reason for not observing C−S insertion.

Electronic Effects. Electron-donating and electron-withdrawing substituents on the dibenzothiophene ring were observed to have modest effects upon the C−S insertion selectivity. Both 2-methoxydibenzothiophene and 2-fluorodibenzothiophene showed a preference (∼5:1) for insertion away from the substituted side. Both the methoxy and fluorine groups can act as π-donors in these compounds,[20] deactivating the ring to which they are attached toward C−S cleavage. The methoxy substituent can deactivate ortho or para positions by resonance, while fluorine can deactivate the π-system of the ring through inductive effects. A small insertion selectivity in the opposite direction (∼5:1), favoring insertion into the C−S bond of the substituted ring, was seen with dibenzothiophenes with strong π- or σ-withdrawing groups, i.e. 2-cyanodibenzothiophene and 2-(trifluoromethyl)dibenzothiophene.

The observed selectivities can be interpreted in terms of the options available to the S-bound dibenzothiophene complex with Rh(I). Insertion into the C−S bond can be depicted as going through the process indicated in Figure 12. The electron-rich rhodium(I) metal donates electron density into the dibenzothiophene LUMO,

(21) White, C. J.; Wang, T.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1994**, *13*, 4474−4480.

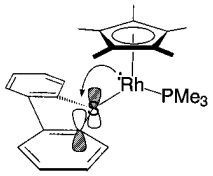


Figure 12. Molecular orbital depiction of the transition state leading to C−S cleavage in substituted dibenzothiophenes.

which is C−S antibonding in character, leading to cleavage of that C−S bond, a model which has been suggested previously by Harris and Chianelli.[22] Substituents at the 2-position would be expected to have only a minor effect on final selectivities of C−S insertion by variation of the coefficient of the LUMO on the carbon adjacent to sulfur. Further investigations into the molecular orbital character of substituted dibenzothiophenes may shed more light on this mechanism.[23]

The unselective behavior seen in the monomethyl-substituted dibenzothiophenes (2-methyldibenzothiophene and 3-methyldibenzothiophene) is a reflection of the lack of steric constraints and the weak σ-donor properties of the methyl group. In fact, the combined presence of two or three methyl groups does not provide enough of an electronic influence to substantially alter the insertion selectivity.

Competition Studies. In the competition reaction of **1** with thiophene and dibenzothiophene, the 5:1 insertion product ratio corresponds to a $\Delta\Delta G^{\ddagger} = 1.1$ kcal/mol difference in activation barriers at 66 °C between thiophene and dibenzothiophene, revealing that the insertion of **1** into dibenzothiophene is readily accomplished, even in the presence of excess thiophene. No difference exists between the observed barriers for activation of dibenzothiophene and 4-methyldibenzothiophene. These conclusions reasonably assume that the observed product ratios are kinetic ratios. Prior studies of the compound arising from C−S insertion into thiophene show that exchange of inserted thiophene is exceedingly slow ($\tau_{1/2} \approx 80$ days at 81 °C) under these conditions.[6] The similar competitive reactivity of such a variety of thiophenes is consistent with the proposed model of irreversible sulfur coordination to rhodium followed by a rapid insertion into the C−S bond.

The observation of a C−S insertion product of 4-methyldibenzothiophene when a 1.7:1 C−S:C−H activation mixture of dibenzothiophene was reacted with free 4-methyldibenzothiophene indicates that *some* of the C−H-activated species undergoes reductive elimination back to the 16e$^-$ intermediate [$(C_5Me_5)Rh(PMe_3)$]. If 100% of the C−H-activated species reductively eliminated to give the 16e$^-$ intermediate [$(C_5Me_5)Rh(PMe_3)$], we would expect the same 63:37 ratio of dibenzothiophene to 4-methyldibenzothiophene C−S-inserted products as seen in the initial C−S:C−H activation ratios. 4-Methyldibenzothiophene is in a large excess (10 equiv) and can be assumed to react completely with any [$(C_5Me_5)Rh(PMe_3)$] formed from loss of dibenzothiophene. The ratio found reflects that approximately 80% of the *C−H-activated species* reacts in an *intramolecular* fashion while 20% reacts through an intermolecular pathway, observed by formation of **2**.

(22) Harris, S.; Chianelli, R. R. *J. Catal.* **1984**, *86*, 400−412.
(23) Harris, S.; Palmer, M. Department of Chemistry, University of Wyoming, personal communication.

Comparison with Commercial HDS. Laboratory studies of real heterogeneous HDS systems under industrial conditions[24] provide for an interesting comparison with these homogeneous bond cleavage studies. The commercial catalyst readily desulfurizes alkylated thiophenes and benzothiophenes. Even dibenzothiophene itself is desulfurized, as are 1-methyl-, 2-methyl-, and 3-methyldibenzothiophene. The catalyst requires more forcing deep HDS conditions to desulfurize 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene as well as polymethylated dibenzothiophenes remain unreactive.[3a]

The observations as to the ease of C−S bond cleavage by our rhodium complex parallel these observed reactivities, although in the present study sulfur is not completely removed from any dibenzothiophene. Our studies show that only in the 4- or 6-position does an alkyl group inhibit C−S bond cleavage by the reactive Rh(I) metal fragment. When both positions are blocked, then a labile S-bound dibenzothiophene complex is formed. But are these mononuclear metal complexes even related to the commercial systems? It is possible that under the strongly reducing conditions of the commercial HDS system (heat + H_2 pressure), some low-oxidation-state metal centers are produced and function in a fashion similar to that observed here. Our studies with an iridium dimer show indeed that thiophene at least can be desulfurized by low-oxidation-state metals.[25] In this model, the high temperatures and H_2 pressures of commercial HDS systems would then be required to reduce the μ-sulfido ligand from the metal center.

X-ray Crystal Structures. Crystallographic data for all X-ray crystal structures in this paper can be found in Tables 3 and 4. Tables 1 and 2 illustrate several physical features of C−S-inserted dibenzothiophenes and point out several common features. Sulfur has a pyramidal geometry in every example. The rhodium atom lies above the plane of the SC_4 fragment from the original thiophene ring, displaying a fold angle of ∼50−60°. A twist of 30−40° between the two phenyl rings is evident, as cleavage of the C−S bond has disrupted the planar geometry of the uncomplexed dibenzothiophene.

Conclusions

The versatility of $(C_5Me_5)Rh(PMe_3)PhH$ toward cleaving carbon−sulfur bonds has been examined with many substituted dibenzothiophenes. C−S cleavage is controlled by steric factors in an S-bound intermediate, with electronic factors playing a minor role. Strong π-donating groups in the "2" position favor cleavage of the C−S bond away from the substituted ring, while strongly electron withdrawing groups favor cleavage of the C−S bond of the substituted ring.

Experimental Section

General Procedures. All manipulations were carried out under an N_2 atmosphere or on a high-vacuum line using Schlenk techniques. All solvents were distilled from dark purple solutions of sodium benzophenone ketyl under a

(24) As described in ref 3a, a $Co-Mo/Al_2O_3$ catalyst is pre-sulfided under a flow of 3% H_2S/H_2 at 400 °C and then used for desulfurization of the petroleum fraction under ∼400 psi of H_2 at 350−390 °C.
(25) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1994**, *116*, 198−203.

nitrogen atmosphere. Reagent grade thiophene, dibenzothiophene, benzo[*b*]naphtho[2,1-*d*]thiophene, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were purchased from Aldrich Chemical Co. and were used without further purification, although each liquid was freeze−pump−thaw degassed (three cycles) prior to use. $(C_5Me_5)Rh(PMe_3)(Ph)H$ was synthesized as previously reported.[26]

^1H (400 MHz), ^{31}P (162 MHz), and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AMX-400 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; $(CD_3)_2CO$, δ 2.04). ^{31}P NMR chemical shifts were measured in ppm relative to 10% H_3PO_4 (δ 0.0). Chemical shifts for ^{13}C NMR were measured in ppm relative to the deuterated solvent resonance (C_6H_6, δ 128.0; C_6H_{12}, δ 26.4 ppm). Elemental analyses were performed by Desert Analytics. An Enraf-Nonius CAD4 diffractometer was used for X-ray crystal structure determination.

Synthesis of Substituted Dibenzothiophenes. 4-Methyldibenzothiophene, 2-methyldibenzothiophene, 2,6-dimethyldibenzothiophene, 2,8-dimethyldibenzothiophene, 4,6-dimethyldibenzothiophene, 3-methyldibenzothiophene, 1,3,7-trimethyldibenzothiophene, benzo[*b*]naphtho[1,2-*d*]thiophene, and 2-fluorodibenzothiophene were prepared by the method of Castle, Lee, and co-workers[27] with one modification. The aromatization procedure was revised by replacing use of Se at 300 °C with use of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing benzene for 2 h.[28] This modification eliminates contact with and disposal of toxic selenium, effectively suppresses rearrangements of substituents in the aromatization step, and decreases reaction times. 2-Bromodibenzothiophene,[29] 2-iododibenzothiophene,[30] 2-hydroxydibenzothiophene,[31] 2-methoxydibenzothiophene,[32] and 2-cyanodibenzothiophene[33] were prepared as previously described. Synthesis of 2-(trifluoromethyl)dibenzothiophene from 2-iododibenzothiophene followed the method of Burton and co-workers.[34] Detailed procedures for syntheses of all substituted dibenzothiophenes in this paper can be found in the Supporting Information.

Reaction of 1 with 4-Methyldibenzothiophene. A solution of **1** (10 mg, 0.03 mmol) in 1 mL of dry C_6D_{12} reacted with 4-methyldibenzothiophene (5 mg, 0.028 mmol) at 63 °C for 17 h to give one C−S insertion product (**2**: (^{31}P NMR δ 4.38 (J = 161.8 Hz)) and one major C−H activation product (^{31}P NMR δ 8.92 (J = 150.6 Hz); ^1H NMR δ 1.767 (d, J = 1.6 Hz, Cp*) 1.074 (d, J = 10.0 Hz, PMe_3), −12.622 (dd, J = 49.8, 32.1 Hz, RhH), aromatic resonances obscured). The C−H activation product disappears upon further heating at 63 °C for 40 h more to produce **2** cleanly. After removal of solvent the residue was extracted with hexanes. Orange crystals formed from recrystallization from C_6D_6/hexanes at −20 °C. X-ray structural determination identified the product as insertion away from the substituted ring (91% yield). Anal. Calcd for $RhSPC_{26}H_{34}$: C, 60.93; H, 6.69. Found: C, 60.99; H, 6.60. ^1H NMR (C_6D_6): δ 0.951 (d, J = 9.8 Hz, PMe_3), 1.340 (d, J = 2.8 Hz, Cp*), 2.876 (s, Me), 6.977 (td, J = 7.4, 1.6 Hz, H-7), 7.012 (t, J = 7.5 Hz, H-2), 7.084 (dq, J = 7.0, 0.9 Hz, H-6), 7.112 (td, J = 7.6, 1.4 Hz, H-8), 7.355 (dd, J = 7.63, 1.0 Hz, H-3), 7.380 (dd, J = 7.6, 1.2 Hz, H-1), 7.640 (dd, 7.8, 1.6 Hz, H-9). ^{13}C NMR (C_6D_6): δ 9.10 (s, C_5Me_5), 14.43 (d, 32.0 Hz, PMe_3), 23.30 (s, Me), 98.93 (t, J = 4.1 Hz, C_5Me_5), 122.38 (s, CH), 123.69 (s, CH), 125.25(s, CH), 126.57 (s, CH), 127.32 (s, CH), 139.29 (s, CH), 143.92 (d, J = 7.1 Hz, C), 146.69 (s, C), 147.50 (s, C), 159.74 (dd, J = 34.0, 13.5 Hz, Rh−C). Other resonances were obscured by the solvent peak.

Reaction of 1 with 2-Methyldibenzothiophene. In an ampule fitted with a Teflon valve a 55 mg (0.14 mmol) sample of **1** in ∼5 mL of hexane was heated with 63 mg (0.32 mmol) of 2-methyldibenzothiophene at 70 °C for 15 h, after which two C−S insertion products (**3a**,**b**): ^{31}P NMR (C_6D_{12}) **3a** δ 4.84 (J = 161.1 Hz), **3b** δ 4.91 (J = 161.2 Hz)) and several C−H activation products were observed. The two C−S-inserted products were the only remaining organometallic species after continued heating for 72 h. Solvent was removed and the residue extracted with hexanes. A $^1H-^1H$ 2D NMR TOCSY experiment allowed assignment of the proton resonances for **3a**,**b**. X-ray diffraction quality crystals formed from slow evaporation of hexane solution, revealing that both C−S-inserted isomers cocrystallized and electron density for each methyl group was found at the 2- and 8-positions (80% yield). Anal. Calcd for $RhSPC_{26}H_{34}$: C, 60.93; H, 6.69. Found: C, 60.05; H, 6.59. **3a:** ^1H NMR (C_6D_{12}) δ 1.172 (d, J = 9.6 Hz, PMe_3), 1.447 (s, Cp*), 2.197 (s, Me), 6.580 (dd, J = 7.7, 1.8 Hz, H-3), 6.710 (td, J = 7.3, 1.6 Hz, H-7), 6.860 (td, J = 7.2, 1.4 Hz, H-8), 6.996 (d, J = 1.4 Hz, H-1), 7.299 (dd, J = 6.28, 1.7 Hz, H-6), 7.317 (dd, J = 7.8, 1.5 Hz, H-9), 7.342 (d, J = 7.8 Hz, H-4); ^{13}C NMR (C_6D_{12}) δ 9.34 (s, C_5Me_5), 15.11 (d, J = 31.8 Hz, PMe_3), 21.28 (s, Me), 99.27 (t, J = 4.0 Hz, C_5Me_5), 123.82 (s, CH), 125.39 (s, CH), 126.87 (s, CH), 128.15 (s, CH), 129.48 (s, CH), 130.27 (s, CH), 131.90 (s, CH), 139.88 (d, J = 7.1 Hz, C), 146.24 (s, C), 146.91 (s, C), 159.40 (dd, J = 34.5, 13.5 Hz, Rh−C). **3b:** ^1H NMR (C_6D_{12}) δ 1.182 (d, J = 9.6 Hz, PMe_3), 1.453 (s, Cp*), 2.230 (s, Me), 6.591 (dd, J = 7.7, 2.0 Hz, H-3), 6.720 (td, J = 7.4, 1.4 Hz, H-8), 6.798 (td, J = 7.3, 1.4 Hz, H-7), 7.145 (dd, J = 7.8, 1.5 Hz, H-6), 7.166 (dd, J = 8.9, 1.5 Hz, H-4), 7.186 (d, J = 2.1 Hz, H-1), 7.454 (dd, J = 7.6, 1.5 Hz, H-9); ^{13}C NMR (C_6D_{12}) δ 9.34 (s, C_5Me_5), 15.19 (d, J = 32.3 Hz, PMe_3), 21.07 (s, Me), 99.27 (t, J = 4.0 Hz, C_5Me_5), 123.82 (s, CH), 125.39 (s, CH), 126.87 (s, CH), 128.15 (s, CH), 129.48 (s, CH), 130.27 (s, CH), 132.62 (s, CH), 143.70 (d, J = 7.1 Hz, C), 145.86 (s, C), 147.07 (s, C), 154.36 (dd, J = 33.6, 13.6 Hz, Rh−C).

Reaction of 1 with 3-Methyldibenzothiophene. Thermolysis of **1** (50 mg, 0.12 mmol) with 3-methyldibenzothiophene (26 mg, 0.13 mmol) in ∼5 mL of hexane at 66 °C for 67.5 h in an ampule with a Teflon valve gives two C−S-inserted products (**4a**,**b**) in a 1:1 ratio. The products were isolated by removing solvent and extracting with hexanes. Orange crystals formed from slow diffusion of hexane into a benzene solution at −20 °C. X-ray structural analysis showed crystallization of both **4a** and **4b**. Least-squares refinement indicated a 55:45 ratio (71% yield). Anal. Calcd for $RhSPC_{26}H_{34}$: C, 60.93; H, 6.69. Found: C, 60.08; H, 7.06. **4a:** ^1H NMR (C_6D_6) δ 0.959 (dd, J = 9.8, 0.9 Hz, PMe_3), 1.377 (dd, 2.4, 0.4 Hz, Cp*), 2.281 (s, Me); ^{31}P NMR (C_6D_6) δ 4.498 (d, J = 160.0 Hz); ^{13}C NMR (C_6D_6) δ 9.11 (s, C_5Me_5), 14.58 (J = d, 32.0 Hz, PMe_3), 20.92 (s, Me), 98.79 (t, J = 2.2 Hz, C_5Me_5), 159.61 (dd, J = 33.9, 13.6 Hz, Rh−C). **4b:** ^1H NMR (C_6D_6) δ 0.938 (dd, J = 9.7, 0.9 Hz, PMe_3), 1.377 (dd, J = 2.4, 0.4 Hz, Cp*), 2.198 (s, Me); ^{31}P NMR (C_6D_6) δ 4.380 (d, J = 159.6 Hz); ^{13}C NMR (C_6D_6) δ 9.13 (s, C_5Me_5), 14.58 (d, J = 32.0 Hz, PMe_3), 21.42 (s, Me), 98.84 (t, J = 2.6 Hz, C_5Me_5), 159.34 (dd, J = 33.4, 13.6 Hz, Rh−C). Due to overlap, aromatic resonances were not assigned.

Reaction of 1 with 2,8-Dimethyldibenzothiophene. A 50 mg (0.13 mmol) sample of **1** was heated at 67 °C in an ampule sealed with a Teflon valve with 25.7 mg (0.12 mmol) of 2,8-dimethyldibenzothiophene in ∼5 mL of hexane for 51 h. Solvent was removed under vacuum and a light orange solution extracted with hexanes. One C−S-inserted product

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(**5**) was observed, as expected with a symmetrically substituted dibenzothiophene. Slow evaporation of a benzene solution gave orange crystals which were used for X-ray structure determination (89% yield). Anal. Calcd for $RhSPC_{27}H_{36}$: C, 61.59; H, 6.89. Found: C, 61.34; H, 6.64. ^{1}H NMR (C_6D_6): δ 0.970 (dd, J = 9.8, 0.4 Hz, PMe_3), 1.403 (d, J = 2.8 Hz, Cp*), 2.230 (s, 2-Me), 2.332 (s, 8-Me), 6.827 (dd, J = 7.9, 1.9 Hz, H-3), 6.884 (dd, J = 7.6, 1.9 Hz, H-7), 7.317 (d, J = 7.4 Hz, H-6), 7.411 (d, J = 1.5 Hz, H-1), 7.560 (d, 1.6 Hz, H-9), 7.919 (d, J = 7.76 Hz, H-4). ^{31}P NMR (C_6D_6): δ 4.36 (d, J = 160.0 Hz). ^{13}C NMR (C_6D_6): δ 9.20 (d, J = 1.1 Hz, C_5Me_5), 14.51 (d, J = 32.0 Hz, PMe_3), 21.05 (s, Me), 21.29 (s, Me), 98.75 (t, J = 4.1 Hz, C_5Me_5), 131.98 (s, CH), 132.11 (s, CH), 132.50 (s, CH), 139.70 (s, CH), 139.96 (s, CH), 145.71 (s, C), 146.83 (s, C), 155.2 (dd, J = 34.0, 13.2 Hz, Rh−C). The remaining aromatic peaks were obscured by solvent.

Reaction of 1 with 2,6-Dimethyldibenzothiophene. One C−S-inserted product (**6**: ^{31}P NMR (C_6D_6) δ 4.813 (d, J = 160.2 Hz)) was found after 55 mg (0.14 mmol) of **1** was heated with 36 mg (0.17 mmol) of 2,6-dimethyldibenzothiophene in ~5 mL of hexane at 70 °C for 40 h. Orange crystals formed upon standing in hexane solution at room temperature for several weeks. Single-crystal X-ray structure determination identified **6** as insertion on the less sterically hindered side cocrystallized with one molecule of benzene (85% yield). Anal. Calcd for $RhSPC_{33}H_{42}$: C, 65.55; H, 7.00. Found: C, 64.68; H, 6.91. ^{1}H NMR (C_6D_6): δ 0.978 (d, J = 9.8 Hz, PMe_3), 1.356 (d, J = 2.8 Hz, Cp*), 2.300 (s, 2-Me), 2.88 (s, 6-Me), 6.870 (dd, J = 7.5, 1.6 Hz, H-3), 7.033 (t, J = 7.4 Hz, H-8), 7.091 (d, J = 1.2 Hz, H-7), 7.271 (dd, J = 7.6 Hz, H-4), 7.432 (dd, J = 7.4, 2.0 Hz, H-9), 7.507 (d, J = 1.7 Hz, H-1). ^{13}C NMR (C_6D_6): δ 9.50 (s, C_5Me_5), 15.15 (d, J = 32.5 Hz, PMe_3), 22.11 (s, Me), 24.50 (s, Me), 98.87 (t, J = 3.6 Hz, C_5Me_5), 122.29 (s, CH), 126.52 (s, CH), 129.91 (s, CH), 132.16 (s, CH), 139.14 (s, CH), 139.17 (s, CH), 139.30 (s, C), 145.40 (s, C), 146.46 (d, 7.1 Hz, C), 147.55 (s, C), 153.50 (s, C), 154.8 (dd, J = 33.4, 13.0 Hz, Rh−C).

Reaction of 1 with 4,6-Dimethyldibenzothiophene. A 10 mg (0.030 mmol) sample of **1** was heated at 68 °C in a resealable NMR tube with a Teflon valve with 10 mg (0.050 mmol) of 4,6-dimethyldibenzothiophene in 0.5 mL of C_6D_{12} for 7 h. A dark green solution resulted. An S-bound complex (**7**) was the major product, accompanied by small amounts of C−H activation products and the known decomposition complex $(C_5Me_5)Rh(PMe_3)_2$. Continued heating saw a decrease in both the C−H activation product and the S-bound complex, leading to conversion to the bis(phosphine) complex. **7:** ^{1}H NMR (C_6D_{12}) δ 1.244 (d, J = 1.8 Hz, Cp*), 1.414 (d, J = 7.8 Hz, PMe_3), 2.831 (s, Me), 7.038 (dd, J = 8.0, 3.3 Hz, H-3,7), 7.212 (t, J = 4.1 Hz, H-2,8), 7.763 (dd, J = 8.0, 3.9 Hz, H-1,9); ^{31}P NMR (C_6D_{12}) δ −4.35 (d, J = 226.9 Hz).

Lability Study with PMe_3. To a 10 mg sample of the S-bound complex $(C_5Me_5)Rh(PMe_3)$(4,6-dimethyldibenzothiophene) (**7**) in dry C_6D_{12} (0.5 mL) in a resealable NMR tube was added 10 equiv of PMe_3. The loss of coordinated thiophene and the appearance of $(C_5Me_5)Rh(PMe_3)_2$ was monitored at room temperature by ^{31}P NMR spectroscopy. Compound **7** had a half-life of ~36 h at room temperature, corresponding to a $\Delta G^{\ddagger}$ value of 24.5 kcal/mol at 23 °C.

Reaction of 1 with 1,3,7-Trimethyldibenzothiophene. In a resealable NMR tube with Teflon stopcock, 15 mg (0.04 mmol) of **1** was heated at 68 °C in dry C_6D_{12} (0.5 mL) with 1 equiv (9 mg, 0.04 mmol) of 1,3,7-trimethyldibenzothiophene. Two C−S-inserted products (**8a**,**b**) in a 1.5:1 ratio were seen after heating for 31.5 h (85% yield). **8a:** ^{1}H NMR (C_6D_6) δ 1.142 (dd, J = 9.7, 0.9 Hz, PMe_3), 1.453 (d, J = 2.8 Hz, Cp*), 2.126 (s, Me), 2.142 (s, Me), 2.190 (s, Me); ^{31}P NMR (C_6D_6) δ 5.27 (d, J = 162.3 Hz). **8b:** ^{1}H NMR (C_6D_6) δ 1.074 (dd, J = 9.7, 0.9 Hz, PMe_3), 1.452 (d, J = 2.8 Hz, Cp*), 2.140 (s, Me), 2.147 (s, Me), 2.157 (s, Me); ^{31}P NMR (C_6D_6): δ 5.13 (d, J = 161.4 Hz). Aromatic resonances were not assigned.

Reaction of 1 with Benzo[*b*]naphtho[2,1-*d*]thiophene. A 10 mg (0.026 mmol) sample of **1** and 5.2 mg (0.022 mmol) of benzo[*b*]naphtho[2,1-*d*]thiophene were heated at 68 °C in dry C_6D_{12} (0.5 mL) in an ampule with a Teflon valve. After 5 h, three organometallic species were observed, corresponding to several C−H activation products (^{31}P NMR δ 8.43 (d, J = 155.3 Hz)), an η^2 coordination adduct (δ 0.62 (d, J = 200.0 Hz)), and one C−S-inserted compound, **9** (δ 4.28 (d, J = 159.7 Hz)). Continued heating for an additional 65 h saw a decrease in all three products until no signal was observed by ^{31}P NMR spectroscopy and an orange solid formed on the sides of the NMR tube. Cyclohexane solvent was removed, and the orange solid was dissolved in C_6D_6, which showed the characteristic resonance by ^{31}P NMR of one C−S-inserted product. Slow evaporation of benzene solvent gave orange crystals of **9** of X-ray diffraction quality, indicating the product was inserted away from the sterically hindered side (75% yield). Anal. Calcd for $RhSPC_{29}H_{34}$: C, 63.50; H, 6.25. Found: C, 63.72; H, 6.10. ^{1}H NMR (C_6D_6): δ 0.979 (d, J = 9.8 Hz, PMe_3), 1.257 (d, J = 2.7 Hz, Cp*), 6.987 (td, J = 7.2, 1.5 Hz), 7.313 (td, J = 7.0, 1.3 Hz), 7.398 (d, J = 7.5 Hz), 7.508 (td, J = 6.1, 1.5 Hz), 7.511 (d, J = 8.3 Hz), 7.658 (d, J = 8.6 Hz), 7.709 (t, J = 8.5 Hz), 9.690 (d, J = 8.5 Hz). ^{31}P NMR (C_6D_6): δ 4.28 (d, J = 159.7 Hz). ^{13}C NMR (C_6D_6): δ 9.18 (d, J = 1.6 Hz, C_5Me_5), 14.73 (d, J = 32.0 Hz, PMe_3), 99.02 (t, J = 3.6 Hz, C_5Me_5), 122.94 (s, CH), 123.79 (s, CH), 125.14 (s, CH), 132.35 (s, CH), 137.55 (s, CH), 139.53 (s, CH), 142.31 (d, J = 7.69, C), 143.60 (s, C), 146.83 (s, C), 160.65 (dd, J = 33.0, 13.2 Hz, Rh−C). The remaining aromatic peaks were obscured by solvent.

Reaction of 1 with Benzo[*b*]naphtho[1,2,-*d*]thiophene. Thermolysis of a 5 mg (0.013 mmol) sample of **1** with 10 mg (0.04 mmol) of benzo[*b*]naphtho[1,2-*d*]thiophene in dry C_6D_{12} (0.5 mL) in a resealable NMR tube at 70 °C for 18 h also gave C−H activation products and η^2 coordination adducts, as seen with the reaction of benzo[*b*]naphtho[2,1-*d*]thiophene. In this case, two C−S insertion isomers (**10a**,**b**) in a 2:1 ratio were observed. After 5 days some C−H activation products and η^2 coordination adducts still remained, but the ratio of **10a** to **10b** was unchanged. Only **10a** and **10b** remained after continued heating. The site of insertion for the major isomer was undetermined (70% yield). ^{1}H NMR (C_6D_6) δ 1.189 (d, J = 9.6 Hz, PMe_3), 1.463 (d, J = 2.8 Hz, Cp*); ^{31}P NMR (C_6D_6) δ 5.20 (d, J = 161.8 Hz). **10b**: ^{1}H NMR (C_6D_6) δ 1.032 (d, J = 9.7 Hz, PMe_3), 1.463 (d, J = 2.8 Hz, Cp*); ^{31}P NMR (C_6D_6) δ 3.80 (d, J = 160.3 Hz). Aromatic resonances were not assigned.

Reaction of 1 with 2-Methoxydibenzothiophene. A 10 mg (0.026 mmol) sample of **1** was heated at 67 °C with 5 mg (0.023 mmol) of 2-methoxydibenzothiophene in a resealable NMR tube with dry C_6D_{12} (0.5 mL). After 25 h two C−S insertion products (**11a**,**b**) in a 4.2:1 ratio and several C−H activation products were seen. The solvent and unreacted thiophene were removed under vacuum, and new C_6D_{12} was condensed onto the sample. Further heating saw the disappearance of the C−H activation product until only **11a**,**b** remained. A larger scale reaction (60 mg of **1**) produced orange crystals of **11a** after slow evaporation of benzene solvent. X-ray structural analysis indicated the major isomer was insertion away from the substituted ring. The X-ray crystal was dissolved in C_6D_6 and its ^{31}P NMR spectrum compared to that of the bulk product to confirm that the major product had indeed been crystallized (65% yield). Anal. Calcd for $RhSPOC_{26}H_{34}$: C, 59.09; H, 6.48. Found: C, 58.99; H, 6.40. **11a**: ^{1}H NMR (C_6D_6) δ 0.934 (d, J = 9.8 Hz, PMe_3), 1.381 (d, J = 2.8 Hz, Cp*), 3.412 (s, −OMe), 6.630 (dd, J = 8.4, 2.8 Hz, H-3), 6.974 (td, J = 7.3, 1.5 Hz, H-7 or H-8), 7.102 (td, J = 7.5, 1.3 Hz, H-7 or H-8), 7.217 (d, J = 2.7 Hz, H-1), 7.402 (d, J = 7.6 Hz, H-6), 7.657 (dd, J = 7.7, 1.2 Hz, H-9), 7.865 (d, J = 8.4 Hz, H-4); ^{31}P NMR (C_6D_6) δ 4.30 (d, J = 159.8 Hz); ^{13}C NMR (C_6D_6) δ 9.18 (d, J = 1.6 Hz, C_5Me_5), 14.55 (d, J = 31.9 Hz, PMe_3), 54.89 (s, -OMe), 98.8 (t, J = 3.6 Hz, C_5Me_5), 110.89 (s, CH), 115.64 (s, CH), 123.67 (s, CH), 125.51 (s, CH), 127.80 (s, CH), 133.01 (s, CH), 134.29 (dd, J = 7.1, 1.3 Hz, C), 140.13 (dd, J = 13.7, 1.5 Hz, C), 147.88 (t, J = 1.5 Hz, C), 157.21 (s, CH), 160.94 (dd, J = 35.0, 13.7 Hz, Rh−C). **11b**: ^{1}H NMR

(C_6D_6) δ 0.948 (d, J = 9.6 Hz, PMe_3), 1.372 (d, J = 2.8 Hz, Cp*), 3.486 (s, −OMe), 6.798 (dd, J = 8.2, 2.9 Hz, H-3), 7.021 (td, J = 7.5, 1.2 Hz, H-7 or H-8), 7.353 (d, J = 2.8 Hz, H-1), 7.510 (d, J = 7.5, 1,2 Hz, H-6), 7.980 (dd, J = 8.0, 1.5 Hz, H-9); ^{31}P NMR (C_6D_6) δ 4.41 (d, J = 160.1 Hz); ^{13}C NMR (C_6D_6) δ 9.14 (d, J = 1.0 Hz, C_5Me_5), 14.70 (d, J = 31.9 Hz, PMe_3), 54.62 (s, -OMe), 100.08 (t, J = 3.6 Hz, C_5Me_5), 113.49 (s, CH), 116.19 (s, CH), 121.86 (s, CH), 124.77 (s, CH), 129.69 (s, CH), 132.73 (s, CH), 139.66 (dd, J = 13.7, 1.5 Hz, C), 145.89 (d, J = 1.1 Hz, C), 146.98 (t, J = 1.5 Hz, C), 157.91 (s, CH), 161.04 (dd, J = 35.0, 13.7 Hz, Rh−C). Some aromatic resonances were obscured by other product peaks.

Reaction of 1 with 2-Fluorodibenzothiophene. A 10 mg (0.026 mmol) sample of **1** was heated at 66 °C with 4 mg (0.020 mmol) of 2-fluorodibenzothiophene in a resealable NMR tube with dry C_6D_{12} (0.5 mL) for 20.5 h. Two C−S insertion products (**12a**,**b**) were observed in a 5:1 ratio as well as several C−H activation products. After solvent was removed and fresh C_6D_{12} was condensed onto the sample, heating was continued for an additional 4.75 h until all C−H activation products had disappeared. A larger scale (50 mg, 0.13 mmol of **1**) reaction gave orange crystals by slow diffusion of hexanes into a benzene solution of the product at −20 °C. X-ray structural analysis showed that **12a**,**b** had cocrystallized (65% yield). Anal. Calcd for $RhSPFC_{25}H_{31}$: C, 58.14; H, 6.05. Found: C, 57.06; H, 6.21. **12a**: ^{1}H NMR (C_6D_6) δ 0.887 (d, J = 9.8 Hz, PMe_3), 1.309 (d, J = 2.7 Hz, Cp*); ^{31}P NMR (C_6D_6) δ 4.16 (d, J = 158.9 Hz). **12b**: ^{1}H NMR (C_6D_6) δ 0.879 (d, J = 9.8 Hz, PMe_3), 1.300 (d, J = 2.6 Hz, Cp*); ^{31}P NMR (C_6D_6) δ 4.07 (d, J = 158.0 Hz). Aromatic resonances were not assigned.

Reaction of 1 with 2-Bromodibenzothiophene. Thermolysis of 40 mg (0.10 mmol) of **1** in dry C_6D_{12} (~1 mL) with 50 mg (0.20 mmol) of 2-bromodibenzothiophene at 65 °C for 36 h in an ampule fitted with a Teflon valve gave a dark red solution containing three organometallic products in a 2:2:1 ratio. The two major products were assigned as one C−S insertion isomer (**13a**: ^{31}P NMR (C_6D_6) δ 4.49 (d, J = 158.8 Hz)) and a C−Br activation compound (**13c**: ^{31}P NMR (C_6D_6) δ 5.26 (d, J = 154.2 Hz)). The remaining product was assigned as the other C−S insertion isomer (**13b**: ^{31}P NMR (C_6D_6) δ 3.90 (d, J = 157.0 Hz)). Additional heating did not change the product composition or ratios. **13a**: ^{1}H NMR (C_6D_6) δ 0.864 (d, J = 7.2 Hz, PMe_3), 1.393 (d, J = 2.8 Hz, Cp*). **13b:** ^{1}H NMR (C_6D_6) δ 1.086 (d, J = 10.4 Hz, PMe_3), 1.276 (d, J = 2.8 Hz, Cp*). **13c:** ^{1}H NMR (C_6D_6) δ 0.952 (d, J = 10.1 Hz, PMe_3), 1.349 (d, J = 2.8 Hz, Cp*). Aromatic resonances were not assigned.

Reaction of 1 with 2-Iododibenzothiophene. In a resealable NMR tube with Teflon stopcock, 10 mg (0.030 mmol) of **1** was heated at 67 °C in dry C_6D_{12} (0.5 mL) with 8 mg (0.030 mmol) of 2-iododibenzothiophene. After 20 h one organometallic product (**14**) was seen by ^{1}H and ^{31}P NMR spectroscopy, corresponding to a C−I activation adduct (90% yield, NMR). ^{1}H NMR (C_6D_{12}): δ 1.436 (d, J = 10.1 Hz, PMe_3), 1.673 (d, J = 2.8 Hz, Cp*), 8.05 (m, 2 H), 7.69 (m, 2 H), 7.31 (m, 3 H). ^{31}P NMR (C_6D_{12}): δ 3.26 (d, J = 155.3 Hz).

Reaction of 1 with 2-Cyanodibenzothiophene. In an ampule with a Teflon stopcock, 50 mg (0.13 mmol) of **1** was heated at 73 °C in dry hexanes (~5 mL) with 27 mg (0.13 mmol) of 2-cyanodibenzothiophene. After 20 h two organometallic products (**15a**,**b**) were seen by ^{1}H and ^{31}P NMR spectroscopy in a 5.3:1 ratio (65% yield). **15a**: ^{1}H NMR ($(CD_3)_2CO$) δ 1.293 (d, J = 9.0, Hz, PMe_3), 1.463 (d, J = 2.8 Hz, Cp*), 6.905 (td, J = 7.2, 1.5 Hz, H-8), 6.966 (td, J = 7.2, 1.7 Hz, H-7), 7.113 (dd, J = 7.8, 2.0 Hz, H-3), 7.229 (dd, J = 7.9, 1.5 Hz, H-6), 7.502 (dd, J = 7.8, 1.6 Hz, H-9), 7.536 (d, J = 1.9 Hz, H-1), 7.720 (dt, J = 7.8, 1.0 Hz, J_{P-H} = 1.0 Hz, H-4); ^{31}P NMR ($(CD_3)_2CO$) δ 4.14 (d, J = 155.2 Hz); ^{13}C NMR (C_6D_6) δ 9.11 (s, C_5Me_5), 14.72 (d, J = 32.6 Hz, PMe_3), 99.88 (t, J = 3.6 Hz, C_5Me_5), 107.21 (s, CN), 120.79 (s, CH), 123.91 (s, CH), 125.78 (s, CH), 126.85 (s, C), 127.16 (s, CH), 128.30 (s, CH), 128.55 (s, CH), 130.01 (s, C), 132.90 (s, CH), 142.26 (d, J = 13.0 Hz, Rh−C), 145.61 (s, C), 147.28 (s, C). **15b**: ^{1}H NMR (C_6D_6) δ 0.827 (dd, J = 9.1, 0.9 Hz, PMe_3), 1.211 (d, J = 2.8 Hz, Cp*); ^{31}P NMR (C_6D_6) δ 4.10 (d, J = 157.8 Hz). Aromatic peaks for **15b** were obscured.

Reaction of 1 with 2-(Trifluoromethyl)dibenzothiophene. A 10 mg (0.03 mmol) sample of **1** was heated with 6.3 mg (0.03 mmol) of 2-(trifluoromethyl)dibenzothiophene at 68 °C for 55 h in dry C_6D_{12} (0.5 mL). Two C−S-inserted compounds (**16a**,**b**) were observed in a ratio of 5:1. **16a**: ^{1}H NMR ($(CD_3)_2CO$) δ 1.309 (d, J = 10.1 Hz, 1H, PMe_3), 1.491 (d, J = 2.8 Hz, 15H, Cp*), 6.888 (td, J = 7.5, 1.6 Hz, 1H, H-7), 6.954 (td, J = 7.3, 1.4 Hz, 1H, H-8), 7.101 (dd, J = 7.9, 2.0 Hz, 1H, H-3), 7.221 (dd, J = 7.7, 1.4 Hz, 1H, H-9), 7.489 (dd, J = 7.5, 1.3 Hz, 1H, H-6), 7.519 (br s, 1H, H-1), 7.717 (br d, J = 7.9 Hz, 1H, H-4); ^{31}P NMR ($(CD_3)_2CO$) δ 4.48 (d, J = 155.7 Hz). **16b**: ^{1}H NMR (C_6D_6) δ 0.827 (dd, J = 9.1, 0.9 Hz, PMe_3), 1.211 (d, J = 2.8 Hz, Cp*). Aromatic peaks were not assigned. ^{31}P NMR (C_6D_6): δ 4.80 (d, J = 160.0 Hz).

Competition Experiments. In dry hexane solvent (1.0 mL) with 0.1 mL of C_6D_{12} added for deuterium lock, 10 mg (0.03 mmol) of **1** was heated at 66 °C with a 1:1 ratio of thiophene (10 equiv, 0.3 mmol) and dibenzothiophene (10 equiv, 0.3 mmol) for 18 h. An inverse gated ^{31}P pulse program allowed accurate integration of the phosphorus resonances to give a 5.07:1 ratio of thiophene to dibenzothiophene C−S-inserted products. Periodic ^{31}P NMR spectra were recorded to verify that this 5:1 ratio did not change throughout the reaction.

When **1** (10 mg, 0.03 mmol) was heated at 66 °C with a 5-fold excess of a 1:1 ratio of dibenzothiophene and 4-methyldibenzothiophene (0.13 mmol) in mesitylene solvent for 39.5 h, a 1:1 ratio of C−S-inserted products was observed.

Intramolecular vs Intermolecular Study. In a resealable NMR tube, 10 mg (0.03 mmol) of **1** was heated at 68 °C with 1 equiv (5 mg, 0.03 mmol) of dibenzothiophene in C_6D_{12} (0.5 mL). After 3.5 h, all **1** had been converted to a 1.7:1 ratio of C−S- to C−H-inserted compounds. A 10 equiv (50 mg, 0.3 mmol) amount of 4-methyldibenzothiophene was added under nitrogen and the sample heated at 68 °C for an additional 48 h. ^{31}P NMR spectroscopy revealed a 92:8 ratio of C−S-inserted dibenzothiophene to **2**. This ratio reveals that 80% of the C−H-activated dibenzothiophene complex had reacted through an intramolecular pathway to insert into the C−S bond while 20% had reductively eliminated and then reacted with the excess 4-methyldibenzothiophene in solution.

X-ray Structural Determination of $(C_5Me_5)Rh(PMe_3)$-(S-(4-Me-C_6H_3)-C_6H_4) (2). Orange crystals of **2** were formed from slow evaporation of a benzene solution at room temperature. A single crystal of approximate dimensions 0.10 × 0.14 × 0.05 mm^3 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 Corp. TEXSAN analysis software package was used for data reduction and solution.[35] A 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 anisotropic refinement of the non-hydrogen atoms (with hydrogen atoms attached to carbons in idealized positions) was carried out to convergence. Fractional coordinates are given in the Supporting Information.

X-ray Structural Determination of $(C_5Me_5)Rh(PMe_3)$-(S-(2-Me-C_6H_3)-C_6H_4) (3a,b). An orange crystal of approximate dimensions 0.16 × 0.14 × 0.04 mm^3 was attached to a

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

glass fiber with epoxy. Data collection and reduction were as for **2**, but with an orthorhombic crystal system, in accord with parameters in Table 3. The space group was assigned as *Pbca*; however, electron density for methyl groups was found at the 2- and 8-positions, revealing that both isomers had cocrystallized. The methyl groups were constrained with a total population of 1 and with identical *B* values. Least-squares refinement indicated a final population ratio of 57.7% to 42.3%, with the major product being insertion away from the substituted ring. This ratio was consistent with solution ratios, and confirmation was obtained by redissolving the X-ray crystal and comparing ^{31}P spectra. Only Rh, P, and S were refined anisotropically, while the C_5Me_5 and dibenzothiophene moieties were refined isotropically with hydrogens in fixed, idealized positions. Fractional coordinates are given in the Supporting Information.

X-ray Structural Determination of $(C_5Me_5)\overline{Rh(PMe_3)\text{-}(S\text{-}(3\text{-}Me\text{-}C_6H_3)\text{-}C_6H_4)}$ (4a,b). An orange crystal of approximate dimensions 0.08 × 0.06 × 0.04 mm^3 was mounted on a glass fiber with epoxy. Data collection and reduction were as for **2** with a monoclinic crystal system, in accord with parameters in Table 3. The space group was assigned as $P2_1/c$. As in compounds **3a**,**b**, both isomers of **4** cocrystallized. Similar population and thermal parameter constraints were applied, and final populations of the methyl groups on the dibenzothiophene fragment were calculated by least-squares refinement to be 55% to 45%. All non-hydrogen atoms were refined anisotropically except for the methyl substituents, which were only refined isotropically. Fractional coordinates are given in the Supporting Information.

X-ray Structural Determination of $(C_5Me_5)\overline{Rh(PMe_3)\text{-}(S\text{-}(8\text{-}Me\text{-}C_6H_3)\text{-}2\text{-}Me\text{-}C_6H_4)}$ (5). An orange crystal of approximate dimensions 0.08 × 0.06 × 0.04 mm^3 was mounted on a glass fiber with epoxy. Data collection and reduction were as for **2** with a monoclinic crystal system, in accord with parameters in Table 3. The space group was identified as $P2_1/n$. All non-hydrogen atoms were refined anisotropically with hydrogen atoms attached to carbons in fixed, idealized positions. Fractional coordinates are given in the Supporting Information.

X-ray Structural Determination of $(C_5Me_5)\overline{Rh(PMe_3)\text{-}(S\text{-}(6\text{-}Me\text{-}C_6H_3)\text{-}2\text{-}Me\text{-}C_6H_4)}$ (6). An orange crystal of approximate dimensions 0.11 × 0.09 × 0.08 mm^3 was mounted on a glass fiber with epoxy. Data collection and reduction were as for **2** with a monoclinic crystal system, in accord with parameters in Table 4. The space group was identified as $P2_1/n$ and a single molecule of benzene found to crystallize with compound **6**. All non-hydrogen atoms were refined anisotropically with hydrogen atoms attached to carbons in fixed, idealized positions. Fractional coordinates are given in the Supporting Information.

X-ray Structural Determination of $(C_5Me_5)\overline{Rh(PMe_3)\text{-}(S\text{-}C_{10}H_6\text{-}C_6H_4)}$ (9). An orange crystal of approximate dimensions 0.18 × 0.08 × 0.03 mm^3 was mounted on a glass fiber with epoxy. Data collection and reduction were as for **2**, but with an orthorhombic crystal system, in accord with parameters in Table 4. The space group was identified as $P2_12_12_1$. All non-hydrogen atoms were refined anisotropically with hydrogen atoms attached to carbons in fixed, idealized positions. Fractional coordinates are given in the Supporting Information.

X-ray Structural Determination of $(C_5Me_5)\overline{Rh(PMe_3)\text{-}(S\text{-}(2\text{-}MeO\text{-}C_6H_3)\text{-}C_6H_4)}$ (11a). An orange crystal of approximate dimensions 0.08 × 0.06 × 0.04 mm^3 was mounted on a glass fiber with epoxy. Data collection and reduction were as for **2** with a monoclinic crystal system, in accord with parameters in Table 4. The space group was identified as $P2_1/n$. All non-hydrogen atoms were refined anisotropically with hydrogen atoms attached to carbons in fixed, idealized positions. Fractional coordinates are given in the Supporting Information.

X-ray Structural Determination of $(C_5Me_5)\overline{Rh(PMe_3)\text{-}(S\text{-}(2\text{-}F\text{-}C_6H_3)\text{-}C_6H_4)}$ (12a,b). An orange crystal of approximate dimensions 0.16 × 0.15 × 0.08 mm^3 was mounted on a glass fiber with epoxy. Data collection and reduction were as for **2** with a monoclinic crystal system, in accord with parameters in Table 4. The space group was identified as $P2_1/n$. As with compound **3,** however, both isomers of **12** had cocrystallized. Both 2- and 8-sites were labeled as fluorines and were connected with a total population constraint of 1 with identical *B* values. After least-squares refinement, a ratio of 74.3% to 25.7% was found for the two fluorine positions, the major product (**12a**) being insertion away from the substituted ring. This ratio mirrored solution ratios, as confirmed by comparing the ^{31}P NMR spectrum of the X-ray crystal with that of the parent solution. All non-hydrogen atoms were refined anisotropically, with hydrogen atoms attached to carbons in fixed, idealized positions. Fractional coordinates are given in the Supporting Information.

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Supporting Information Available: Text giving detailed synthetic procedures for synthesis of the substituted dibenzothiophenes and tables of data collection parameters, bond lengths, bond angles, fractional atomic coordinates, and anisotropic thermal parameters for compounds **2**, **3a**,**b**, **4a**,**b**, **5**, **6**, **9**, **11a**, **12a**,**b**, and **15a** (86 pages). Ordering information is given on any current masthead page.

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