

# Structure of Metallathiacycles: Planar vs Nonplanar Geometries. A Theoretical and Experimental Investigation

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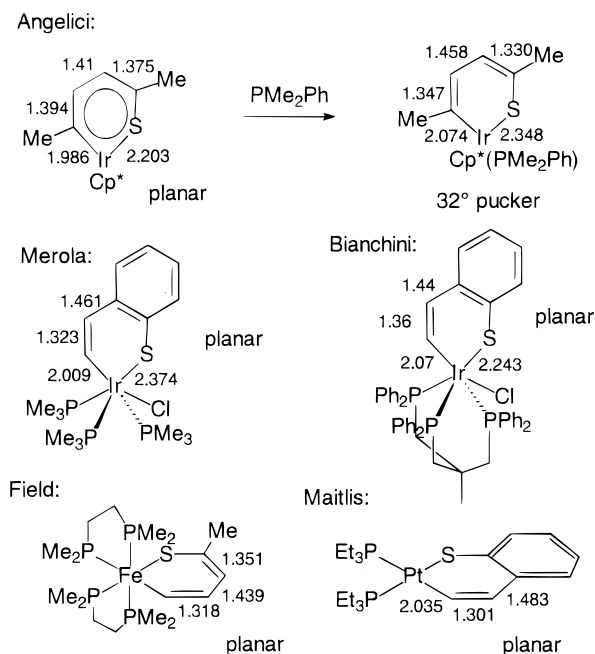
Since the previously reported results of Fenske–Hall molecular orbital calculations suggested that the bent metallacycle geometries observed in transition-metal-inserted thiophene complexes do not result from electronic properties, molecular mechanics calculations were employed to explore how steric factors could influence ring geometries. These calculations have identified steric factors responsible for the observed ring deformations in  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2,5-Me_2C_4H_2S)$  and benzothiophene and dibenzothiophene analogs. The results of the molecular mechanics calculations have been supported by X-ray structural characterization of the products formed via insertion of the reactive 16-electron metal fragment  $[(C_5Me_5)Rh(PMe_3)]$  into the C–S bonds of unsubstituted thiophene, benzothiophene, and dibenzothiophene. The parent thiophene complex, unlike the previously reported ring-substituted analog (and as predicted by the molecular mechanics calculations) is found to adopt a planar six-membered ring structure. The benzothiophene insertion product shows a moderate degree of bending of the metallathiacycle, whereas the dibenzothiophene molecule is strongly bent.

## Introduction

A number of mononuclear transition-metal complexes have been found to be capable of inserting into the C–S bonds of thiophenes, benzothiophenes, and dibenzothiophenes.<sup>1–7</sup> The products formed have been characterized as containing in some cases a delocalized metallathiabenzene ring and in others an isolated thiabutadiene fragment. In most examples, the six-membered ring formed upon metal insertion into the heterocycle is planar (Scheme 1). Ring planarity has been attributed to electronic factors in some cases and to steric factors in others.<sup>2,7,8</sup>

In one of the first examples of these complexes, Angelici found that insertion of iridium into 2,5-dimethylthiophene leads to the formation of the complex  $(C_5Me_5)Ir(\eta^2-C,S-2,5-Me_2C_4H_2S)$ . In this complex, the metallacycle adopts a planar geometry. In addition, the C–C bond distances around the ring are similar (1.375–

## Scheme 1



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(1) Jones, W. D.; Chin, R. M.; Crane, T. W.; Baruch, D. M. *Organometallics* **1994**, *13*, 4448–4452.

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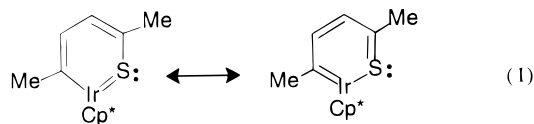
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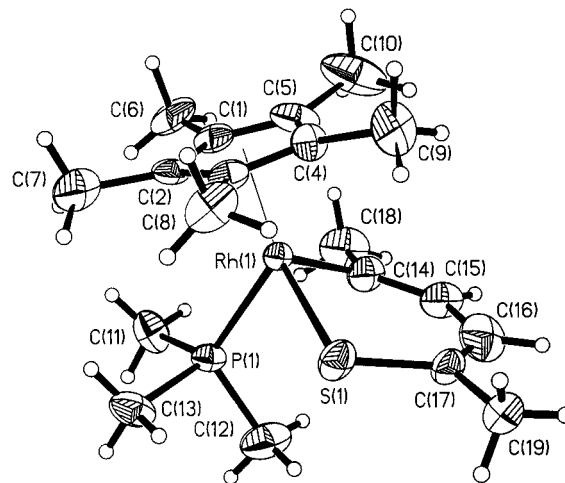
bonding. The planarity has been associated with delocalization of electron density from the ring system back onto the metal. This allows the molecule to adopt a pseudo 18-electron configuration, whereas the localized  $\pi$ -bonding structure would be only a 16-electron structure. The delocalization (eq 1) is reflected in the fact that the Ir–C, C–S, and C–C bond distances are intermediate between typical single and double bonds.<sup>3</sup> Molecular orbital calculations have also substantiated this ligand to metal electron transfer and have identified both the metal and ligand orbitals that are important



in this interaction.<sup>9</sup> Other electron deficient, 16-electron complexes prepared by Bianchini and co-workers also exhibit planar, delocalized ring systems for similar reasons.<sup>8</sup>

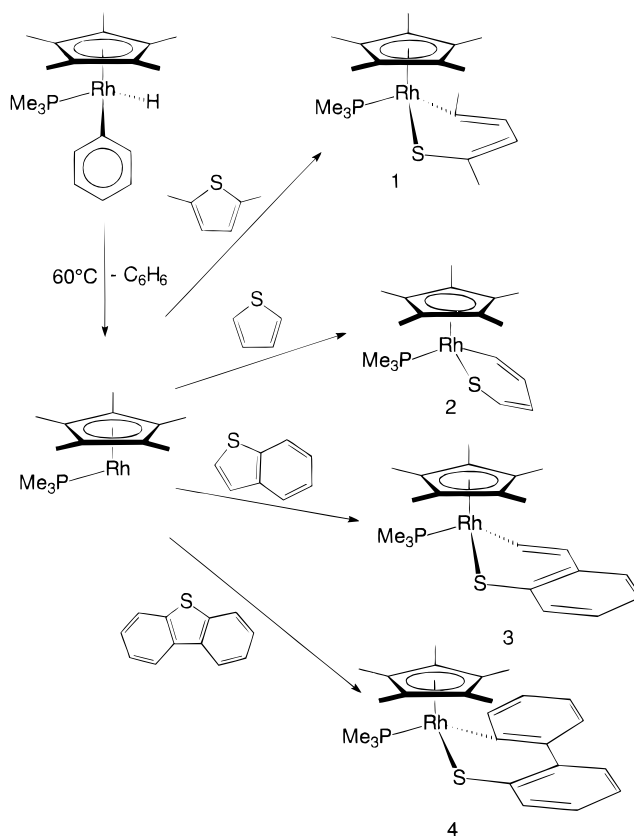
Angelici demonstrated the ability to add a number of ligands, most of which are donor in nature, to  $(C_5Me_5)Ir(\eta^2-C,S-2,5-Me_2C_4H_2S)$ . For example, reaction of this complex with  $PMe_2Ph$  results in the formation of  $(C_5Me_5)Ir(PMe_2Ph)(\eta^2-C,S-2,5-Me_2C_4H_2S)$ . X-ray structural examination of this compound shows two interesting features. The iridathiacycle is no longer planar, with the  $\alpha$ -carbon-iridium-sulfur plane bending  $32^\circ$  away from the plane of the thiophene. Also, the molecule shows a diene-like structure rather than a delocalized structure, with C-C distances around the ring from sulfur of 1.347(8), 1.458(8), and 1.330(6) Å. The C-S bond (1.741(5) Å) is primarily a single bond, as is the Ir-C bond (2.074(5) Å). Analogous structures have been observed in the  $PMePh_2$ - and CO-substituted analogs.<sup>2</sup>

Similar to the ligand-substituted iridium compounds, a number of other structurally characterized transition-metal-inserted thiophene complexes contain metallathiacycles which deviate significantly from planarity. The majority of these bent systems are derived from the reactive 16-electron metal fragment  $[(C_5Me_5)Rh(PMe_3)]$ , which has been shown to insert into a wide variety of thiophenes, benzothiophenes, and dibenzothiophenes (Scheme 2).<sup>10-13</sup> In all 11 of the X-ray structures examined to date, the molecules display a strong puckering of the metallacycle in which the four thiophene carbon atoms and the sulfur atom are essentially coplanar but the rhodium lies several tenths of an Angstrom out of the plane. The first such complex to be structurally characterized was that produced by insertion into the C-S bond of 2,5-dimethylthiophene,  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2,5-Me_2C_4H_2S)$ , **1** (Figure 1). Examination of this ordered structure shows features common to all of the bent thiophene insertion derivatives. The rhodathiacycle in **1** is puckered at  $26^\circ$ . The bond distances around the ring in **1** for C14-C15, C15-C16, and C16-C17 are 1.35(1), 1.44(1), and 1.34(1) Å, respectively, showing the same bond alternation observed in Angelici's iridium analogs. Angelici explained these structural data in terms of the  $\eta^2-C,S-2,5-Me_2C_4H_2S$  ligand acting strictly as a formal 2-electron donor with no ring delocalization.<sup>2</sup> That is, bending of the metallacycle eliminates back-donation of the ligand  $\pi$  electrons onto an already saturated (18-electron) metal center. It is important to note that all of the rhodium-inserted complexes which have been structurally characterized contain *derivatized* thiophenes, benzothiophenes, or dibenzothiophenes.



**Figure 1.** ORTEP drawing of  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2,5-Me_2C_4H_2S)$ , **1**, with ellipsoids shown at the 50% probability level.

### Scheme 2



The structures of other electron-precise, metal-inserted thiophene complexes, however, exhibit metallacycle rings which are both planar *and* localized.<sup>6,7</sup> The localized, diene-like structure of these complexes is reflected in the observed M-S, M-C, and C-C bond distances and the upfield  $^1H$  resonances of the ring protons. The ring planarity observed in these molecules has generally been associated with the metallacycle being positioned in a steric "pocket" within a molecule, which restricts ring deformations.<sup>7</sup> It is apparent, however, that a sterically restrictive environment is not necessary for a complex to exhibit a planar ring system (e.g., square-planar  $(PEt_3)_2Pt(\eta^2-C,S-C_8H_6S^5)$ ).

Although ring planarity in electron-deficient metal-inserted complexes can be explained in terms of delo-

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(12) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559-564.

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calization, the above observations suggest that there is not a correlation between the flattening of the ring and the delocalization of the bonds within the ring for the coordinatively saturated 18-electron complexes. We first began to address questions concerning the different ring geometries by investigating the fundamental electronic structure of these molecules using Fenske–Hall molecular orbital calculations.<sup>8</sup> The emphasis of the initial studies was to determine the effects that different metal centers, ancillary ligands, and thiophenic moieties have on the electronic structures of the complexes. An additional focus of that initial investigation involved identifying bonding characteristics among the different complexes which could be directly related to their observed metallacycle geometry. Interestingly, calculations on the 18-electron complexes containing localized ring systems revealed that the highest occupied ligand  $\pi$ -orbital interacts with a “metal  $\pi$ -orbital” to produce an antibonding HOMO (highest occupied molecular orbital) in the complex. The presence of this unstable, high-energy orbital suggested to us that bending the metallacycle in these complexes might alleviate, to some extent, this unfavorable interaction. For example, bending the metallacycle could reorient the sulfur electron lone pairs so as to reduce some of the antibonding nature of the HOMO. To test this hypothesis, the metallacycles in the bent systems were artificially flattened and calculations on the planar isomers were compared to the calculations on the original, known structures. We found that the electronic structures of the 18-electron complexes are relatively unperturbed by changes in metallacycle geometry, i.e., no difference in the antibonding character of the HOMO is observed in complexes containing either a planar or bent metallacycle. In addition, no other bonding characteristic could be identified which would indicate a preference for a particular ring geometry. These observations are consistent with the fact that several 18-electron complexes have been reported which contain planar *localized* structures. These planar structures suggest that localized bonding does not require metallacycle bending.

Both the fact that electronic properties do not distinguish between the two ring conformations in 18-electron compounds and the fact that planar localized systems have been reported suggest that steric rather than electronic interactions may be responsible for ring deformations. In order to identify steric interactions which could lead to ring distortions, molecular mechanics calculations were performed on several metal-inserted complexes containing bent ring systems. The results of the molecular mechanics calculations for  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2,5-Me_2C_4H_2S)$  are discussed in detail in the first section of this report. In addition, qualitative results of the molecular mechanics calculations on the benzothiophene and dibenzothiophene analogs to the rhodium thiophene species are discussed.

Although the molecular mechanics calculations on  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2,5-Me_2C_4H_2S)$  point to several structural features responsible for its observed bent metallacycle geometry, we conclude that the most influential group appears to be the methyl substituent on the  $\alpha$ -carbon. In order to validate this conclusion, the parent, unsubstituted complex,  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-C_4H_4S)$ , as well as the parent benzothiophene and dibenzothiophene complexes,  $(C_5Me_5)Rh(PMe_3)(\eta^2-$

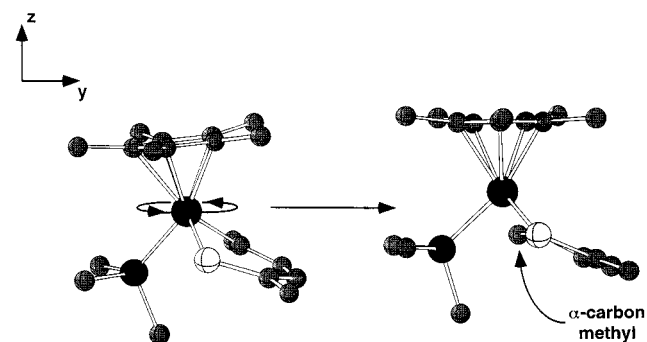
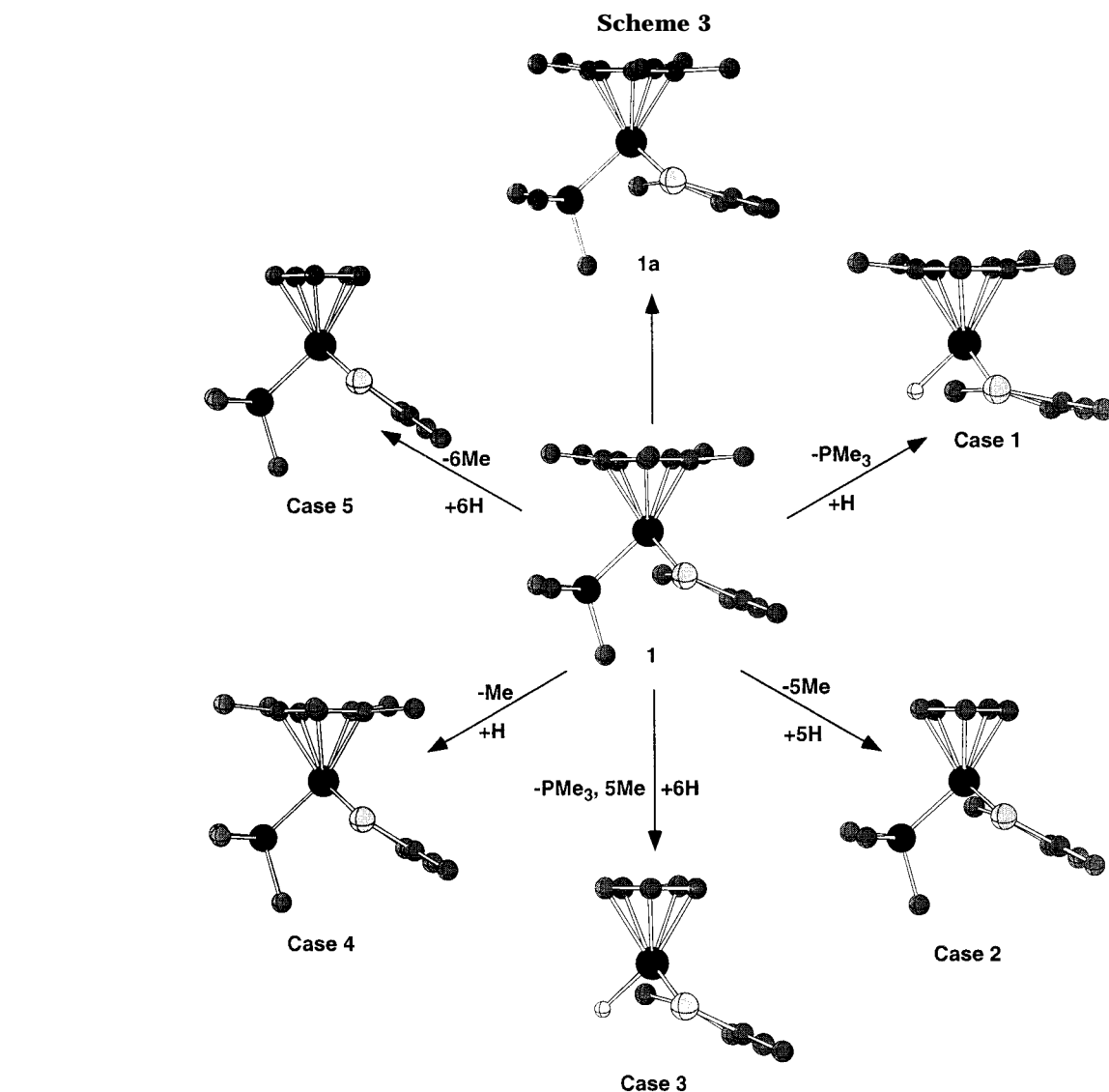
$C,S-C_8H_6S)$  and  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-C_{12}H_8S)$ , respectively, were structurally characterized. The structural features of the three unsubstituted complexes are reported in the final section of the paper, and comparisons are made between these structures and those predicted by molecular mechanics.

## Results and Discussion

**Molecular Mechanics Calculations. Thiophene Complexes.** The results of the molecular mechanics calculations on  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2,5-Me_2C_4H_2S)$  are shown in Scheme 3. The orientation of the molecules shown in the scheme is such that the sulfur and  $\alpha$ -carbon lie along a line perpendicular to the plane of the paper (along the  $x$ -axis in Figure 2). That is, the  $\alpha$ -carbon lies directly behind the sulfur atom; the methyl on the  $\alpha$ -carbon is visible just to the left of the sulfur atom. The hydrogen atoms have been omitted for clarity. The known structure (**1**), determined via X-ray diffraction, is shown at the center of the scheme. The structure resulting from the molecular mechanics minimization of **1** is shown at the top of the scheme (**1a**). Upon minimization of **1**, the rhodium–sulfur and sulfur–carbon bond lengths decrease from 2.34 to 2.20 Å and 1.74 to 1.66 Å, respectively, while the rhodium–carbon bond length increases from 2.07 to 2.13 Å. The sulfur–rhodium–carbon bond angle increases slightly from 92.3° to 93.6°. Structurally, the metallacycles in both **1** and **1a** lie in a pocket formed by the pentamethylcyclopentadienyl ( $Cp^*$ ) and the trimethylphosphine ligands. The most notable movement in **1a** is that of the methyl on the  $\alpha$ -carbon shifting down and away from the  $Cp^*$  methyls. Because of inherent hybridization requirements at the  $\alpha$ -carbon ( $sp^2$ ), the thiabutadiene portion of the ring is concomitantly affected. The result is a slight increase in the bend angle from 26.0° in **1** to 27.1° in **1a**. Despite the small changes in structure, **1a** is very similar to the known crystal structure and thus provides additional support that the bend in the metallacycle is indeed related to steric factors.

In order to determine the molecular subunits on  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2,5-Me_2C_4H_2S)$  responsible for the bent geometry of its metallacycle, various ligands on the molecule were replaced by smaller, less sterically demanding ligands. The results of the molecular mechanics calculations of these modified structures are discussed in the following six case studies:

**Case 1.** The trimethylphosphine moiety on **1** was replaced by a smaller hydride ligand. Minimization results in movement of the sulfur and  $\alpha$ -carbon away from the  $Cp^*$  methyls and toward the smaller hydride ligand. In addition, the  $\alpha$ -methyl moves down and away from the  $Cp^*$  methyls. When present, the bulky phosphine ligand restricts the degree of these movements by effectively reducing the area available to the thiophene moiety. The large phosphine ligand forces the sulfur,  $\alpha$ -carbon, and the  $\alpha$ -methyl close to  $Cp^*$ . With the much smaller hydride ligand, on the other hand, these particular groups are not forced into such a “tight” pocket and the ring system moves accordingly. The diene portion of the metallacycle, however, remains out of the S–Rh–C plane. When the  $\alpha$ -methyl group moves down and away from  $Cp^*$ , the  $sp^2$  hybridization at the  $\alpha$ -carbon forces the ring to remain puckered. The combination of these movements leads to a notable increase in the thiophene bend angle to 40.6°.



**Figure 2.** Orientation of  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2,5-Me_2C_4H_2S)$  for discussion of molecular mechanics calculations.

The results of case 1 indicate that complexes containing substituents smaller than  $PMe_3$  should exhibit greater bend angles while ones with larger substituents exhibit contracted bend angles. This conclusion is supported by the bend angles in several complexes that incorporate the analogous  $(C_5Me_5)Ir(\eta^2-C,S-2,5-Me_2C_4H_2S)$  fragment. For example,  $(C_5Me_5)(CO)Ir(\eta^2-C,S-2,5-Me_2C_4H_2S)$ , which contains a small carbonyl ligand, exhibits a bend angle of  $35.7^\circ$  while the  $PMePh_2$  analog has a bend angle of only  $14^\circ$ . The  $PMe_2Ph$  analog has a bend angle of  $26.3^\circ$ , which is approximately equivalent to the rhodium  $PMe_3$  complex. This is due to the fact

that the one phenyl group on  $PMe_2Ph$  is directed away from the thiophene moiety and results in a ligand which closely resembles  $PMe_3$  in apparent size.<sup>2</sup>

**Case 2.** Each methyl on the  $Cp^*$  ligand was replaced with a hydrogen atom to form a cyclopentadienyl ( $Cp$ ) ligand. When the altered structure is minimized, the thiophene ring remains in the pocket formed by the phosphine and  $Cp$  ligands. The  $\alpha$ -methyl, however, not influenced as greatly by the smaller, less sterically demanding  $Cp$  ligand, moves closer to the  $Cp$  ligand and away from the bulky phosphine group. Again, because of the  $sp^2$  hybridization at the  $\alpha$ -carbon, the movement of the methyl group on the  $\alpha$ -carbon leads to a smaller bend angle of  $14.0^\circ$ .

**Case 3.** In accordance with cases 1 and 2, hydrogen atoms were substituted for both the phosphine ligand and the  $Cp^*$  methyls. Minimization results in a structural "average" of the two individual cases. Specifically, the sulfur and  $\alpha$ -carbon move away from the bulkier  $Cp$  group and toward the smaller hydride ligand. The  $\alpha$ -methyl also moves slightly away from the  $Cp$  and toward the hydride. None of these interactions, however, are as pronounced as when there are methyl groups on the cyclopentadienyl ring. The metallacycle bend angle, the approximate average of the case 1 and case 2 bend angles, is  $25.6^\circ$ .

**Case 4.** The  $\alpha$ -methyl was substituted with a hydrogen atom. The hydrogen atom was initially placed on the original C–C bond axis at a distance of 0.950 Å. Although a methyl group in the  $\alpha$  position interacts strongly with the Cp\* methyls, a hydrogen at this location does not interact to any extent. In each of the three previous cases, most atomic movement was determined by the motion of the  $\alpha$ -methyl toward less congested areas. The geometry of the ring was dictated by the  $sp^2$  hybridization requirements of the  $\alpha$ -carbon. With the smaller hydrogen, the correct hybridization can be retained even if the ring achieves planarity. Consequently, it should not be surprising that the thiophene ring for this structure is relatively planar. In fact, the bend angle for this structure is only 11.8°. It is worth mentioning that substitution of the methyl group on the  $\delta$ -carbon with hydrogen rather than the methyl on the  $\alpha$ -carbon contracts the bend angle by only 1°. Although small, the reduction in bend angle suggests an interaction of the  $\delta$ -methyl with the  $PMe_3$  ligand. Substitution of both thiophenic methyls (positions 2 and 5) with hydrogen atoms results in a slightly more planar ring (bend angle = 11.3°).

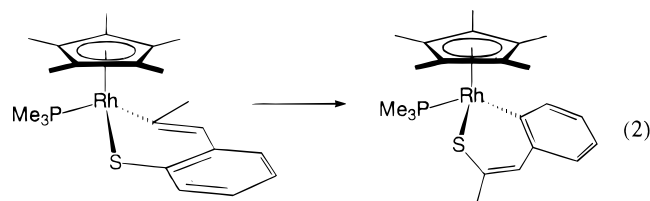
**Case 5.** The Cp\* methyls and  $\alpha$ -methyl were substituted with hydrogen atoms similar to cases 2 and 4. Without the Cp\* methyls or  $\alpha$ -methyl present, the metallacycle can lie in the phosphine–Cp pocket with virtually no ring distortion. Again, planarity is expected since the driving force for ring distortion is highly dependent on the location of the  $\alpha$ -methyl group. That is, the position of the  $\alpha$ -methyl dictates the ring geometry because of imposed hybridization requirements of the  $\alpha$ -carbon. In this hydrogen-substituted complex, the same hybridization requirements are still present but the ring can achieve planarity because the hydrogen atom on the  $\alpha$ -carbon is small enough that it does not interact to any extent with the Cp ring. As a result, the bend angle for this structure is 6.8°. If both thiophene methyls are substituted with hydrogen atoms, the bend angle is further reduced to 5.5°.

**Case 6.** The sulfur atom in each of the structures described in cases 1–5 was replaced with a smaller oxygen atom. (Note that one example of the insertion of a transition metal into furan does exist).<sup>14</sup> In all cases, the bend angle is contracted in the oxygen-containing system from that of the corresponding sulfur-containing metallacycle. The reduction in the bend angle for each case is between 20 and 45%.

In summary, four factors influence the degree to which the thiophenic moiety on  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2,5-Me_2C_4H_2S)$  is bent: the presence of Cp\* methyls, the  $\alpha$ -carbon methyl, the presence of the large phosphine ligand, and the bulky sulfur atom. Of these, as illustrated by a majority of the cases, the most sterically influential component on the heterocycle of  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2,5-Me_2C_4H_2S)$  is the methyl on the  $\alpha$ -carbon. That is, when no methyl group is present on the  $\alpha$ -carbon, the metallacycle achieves an almost planar geometry. It is important to note that the ring never achieves complete planarity. This is probably due to the large size of the sulfur atom. Evidence for this exists in the structure of  $(PEt_3)_2Pt(\eta^2-C,S-C_8H_6S)$  in which the metallacycle is slightly bent

despite the absence of any bulky ligands that could influence its geometry.

**Benzothiophene Complexes.** Insertion of the  $(C_5Me_5)Rh(PMe_3)$  fragment into the thiophene ring of 2-methylbenzothiophene has been shown to lead to two isomers, both of which have been structurally characterized.<sup>11</sup> As illustrated in eq 2, the first or kinetic isomer is the bent benzothiophene analog to **1** in which the methyl group resides on the  $\alpha$ -carbon of the metallacycle. This isomer readily rearranges to a thermody-



amic product which places the methyl substituent farther away from the other ligands. Molecular mechanics calculations were carried out on the kinetic isomer of  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2-MeC_8H_5S)$ . Despite limitations in accurately modeling the benzothiophene ring system (see Experimental Section), the results indicate that similar interactions to those observed in **1** contribute to the bent conformation of the metallacycle. Specifically, the methyl group on the  $\alpha$ -carbon appears to be primarily responsible for the 42.5° bend in the ring system. Substitution of this methyl group with a smaller hydrogen atom leads to a significant flattening of the metallacycle. The calculations predict the bend angle in the unsubstituted complex to be approximately 12°. Once again, this demonstrates the effect that the  $\alpha$ -methyl has on the ring conformation. In fact, the influence of the  $\alpha$ -methyl on the ring system is significant enough to suggest that isomerization to the thermodynamic product may well be related to steric interactions of the methyl group on the  $\alpha$ -carbon with the methyl groups on Cp\*. Although in both the thermodynamic and kinetic products the  $\alpha$ -carbon of the metallacycle ring is also bonded to another carbon, the thermodynamic product is not as sterically bulky at that position as is the kinetic isomer (a planar C–H versus a methyl group); this not only leads to a steric stabilization of the thermodynamic isomer but also to a decrease in bend angle (the bend angle in the thermodynamic product is 24.6°).

**Dibenzothiophene Complexes.** Limitations in modeling the ring systems of the rhodium-inserted dibenzothiophene analogs<sup>10</sup> once again only allow for a qualitative discussion of the results of the molecular mechanics calculations. It is clear, however, that the structures of these complexes are dependent on several factors. One of the most important factors is the tendency for the phenyl rings in these complexes to mimic biphenyl in that they exhibit a twist about the C–C bond connecting them. (This characteristic of the phenyl rings should not be surprising since the aromaticity of the dibenzothiophene moiety is broken immediately upon metal insertion, and there is no longer a driving force to remain planar.) Although the twist angles do vary between different substituted dibenzothiophene complexes, they all lie in the range of the 44° twist angle observed in biphenyl.<sup>15</sup> Because of this tendency for the phenyl rings to twist, it is clear that

(14) Bleeker, J. R.; Haile, T.; New, P. R.; Chiang, M. Y. *Organometallics* **1993**, *12*, 517–528.

**Table 1. Summary of Crystallographic Data for 2, 3, and 4**

	2	3	4
Crystal Parameters			
chem form	RhPSC <sub>17</sub> H <sub>28</sub>	RhPSC <sub>21</sub> H <sub>30</sub>	RhPSC <sub>25</sub> H <sub>32</sub>
fw	398.33	448.39	498.45
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	<i>Pca</i> 2 <sub>1</sub> (No. 29)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>Pca</i> 2 <sub>1</sub> (No. 29)
<i>Z</i>	8	8	4
<i>a</i> , Å	19.7409(6)	17.7781(3)	9.7151(2)
<i>b</i> , Å	9.4823(3)	8.7959(1)	14.3632(1)
<i>c</i> , Å	19.6504(6)	27.9997(4)	16.5451(3)
$\beta$ , deg	90	105.50(10)	90
vol, Å <sup>3</sup>	3678.3(2)	4219.3(1)	2308.7(7)
$\rho_{\text{calcd}}$ , g cm <sup>-3</sup>	1.439	1.412	1.434
cryst dims, mm <sup>3</sup>	0.35 × 0.22 × 0.22	0.60 × 0.20 × 0.04	0.26 × 0.20 × 0.12
temp, °C	-50	-50	-50
Measurement of Intensity Data			
diffractometer	Siemens SMART	Siemens SMART	Siemens SMART
radiation	Mo K $\alpha$ , 0.710 73 Å	Mo K $\alpha$ , 0.710 73 Å	Mo K $\alpha$ , 0.710 73 Å
frame range/time, deg/s	0.3/10	0.3/30	0.3/10
2 $\theta$ range, deg	4-50	4-50	4-56
data collected	-19 ≤ <i>h</i> ≤ 23, -11 ≤ <i>k</i> ≤ 11, -22 ≤ <i>l</i> ≤ 21	-23 ≤ <i>h</i> ≤ 19, -11 ≤ <i>k</i> ≤ 11, -36 ≤ <i>l</i> ≤ 31	-12 ≤ <i>h</i> ≤ 12, -19 ≤ <i>k</i> ≤ 15, -21 ≤ <i>l</i> ≤ 20
no. of data collected	15 791	21 186	13 542
no. of unique data	5831	7424	5183
no. of obsd data ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	5435	5435	4140
agreement between equivalent data ( <i>R</i> <sub>int</sub> )	0.022	0.078	0.041
no. of params varied	471	531	262
$\mu$ , cm <sup>-1</sup>	11.19	9.84	9.08
systematic absences	0 <i>kl</i> , <i>l</i> odd; <i>h</i> 0 <i>l</i> , <i>h</i> odd; 00 <i>l</i> , <i>l</i> odd	0 <i>k</i> 0, <i>k</i> odd; <i>h</i> 0 <i>l</i> , <i>h</i> + <i>l</i> odd	0 <i>kl</i> , <i>l</i> odd; <i>h</i> 0 <i>l</i> , <i>h</i> odd; 00 <i>l</i> , <i>l</i> odd
abs corr	empirical	empirical	empirical
range of transmission factors	0.68-0.81	0.65-0.90	0.68-0.79
<i>R</i> <sub>1</sub> ( <i>F</i> <sub>o</sub> <sup>2</sup> , <i>I</i> > 2 $\sigma$ )	0.0260	0.0604	0.0417
w <i>R</i> <sub>2</sub> ( <i>F</i> <sub>o</sub> <sup>2</sup> , <i>I</i> > 2 $\sigma$ )	0.0571	0.1325	0.0693
goodness of fit	1.15	1.15	1.10

planarity of a dibenzothiophene moiety in a metal-inserted complex would be unexpected regardless of ring substituents and ligand environment.

In summary, the results of the molecular mechanics calculations show that certain substituents exert a strong steric influence on the conformation of the metallacycle in these metal-inserted systems. Specifically, for both the rhodium-inserted thiophene and benzothiophene complexes, the  $\alpha$ -methyl group appears to be the primary factor responsible for the observed ring geometries.

Upon completion of the molecular mechanics calculations, it was clear that our conclusions could only be confirmed through structural characterizations of unsubstituted complexes. Although preparation of unsubstituted analogs to the rhodium-inserted complexes have already been reported,<sup>12</sup> structural characterization has previously not been attainable. Given the results of the molecular mechanics calculations, however, considerable effort was made to characterize the structures of the unsubstituted, rhodium-inserted thiophene, benzothiophene, and dibenzothiophene complexes. These structures are discussed below.

**Structures of the Unsubstituted Complexes. (C<sub>5</sub>Me<sub>5</sub>)Rh(PMe<sub>3</sub>)( $\eta^2$ -C,S-C<sub>4</sub>H<sub>4</sub>S).** The complex (C<sub>5</sub>Me<sub>5</sub>)Rh(PMe<sub>3</sub>)(Ph)H serves as a useful thermal precursor of the reactive 16-electron fragment. As described earlier,<sup>12</sup> heating this compound in the presence of thiophene in hydrocarbon solution results in the near quantitative formation of (C<sub>5</sub>Me<sub>5</sub>)Rh(PMe<sub>3</sub>)( $\eta^2$ -C,S-C<sub>4</sub>H<sub>4</sub>S), **2**. While the compound crystallized readily, a

satisfactory solution of the structure required substantial effort.

The molecule crystallizes in orthorhombic space group *Pca*2<sub>1</sub> with *Z* = 8, which requires that there be two independent molecules within the asymmetric unit. Collection of 1.3 hemispheres of highly redundant data using a Siemens SMART CCD area detector system allowed a successful solution and refinement of the structure. Each molecule is disordered with respect to the orientation of the metallathiacycle. A successful refinement of each molecule was accomplished in SHELX using bond distance restraints to make the rings similar. This type of refinement gives excellent agreement between equivalent bond distances in all disordered components. In the final model, all non-hydrogen atoms could be refined anisotropically and reasonable thermal parameters were obtained. The metallathiacycle occupancy was refined in each of the molecules, with a 78/22 occupancy ratio in one molecule (**A/B**) and a 84/16 occupancy ratio in the other (**C/D**). In addition, the molecule refined as a 66/34 racemic twin in this polar space group. A list of crystal data is given in Table 1. Selected bond distances and angles are listed in Table 2.

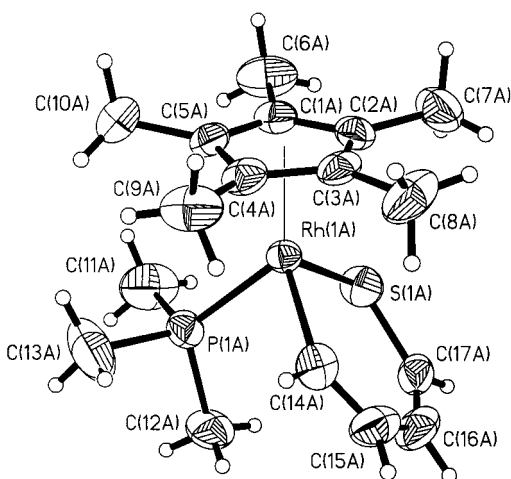
Examination of the structure of **2** (molecule **A** is typical) shows a virtually planar ring system, with an average pucker of only 4° between the C14-Rh1-S1 and S1-C17-C16-C15-C14 planes (Figure 3). The C-C distances for C14-C15, C15-C16, and C16-C17 refined as 1.34(2), 1.45(1), and 1.31(1) Å, showing bond alternation for a localized diene structure. The Rh1-C14 distance of 2.013(13) Å is typical of that for a rhodium to sp<sup>2</sup> hybridized carbon distance (cf. 2.054(9) Å in (C<sub>5</sub>Me<sub>5</sub>)Rh(PMe<sub>3</sub>)(Ph)Br<sup>16</sup>). The C17-S1 distance

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**Table 2. Selected Bond Distances (Å) and Pucker Angles of Planes (deg) for 1–4**

compound <sup>a</sup>	Rh–S	Rh–C14	C14–C15	C15–C16	C16–C17	S–C17	pucker angle
<b>1</b>	2.336(3)	2.067(8)	1.35(1)	1.44(1)	1.34(1)	1.741(8)	26
<b>2A</b>	2.346(3)	2.013(13)	1.34(2)	1.451(11)	1.308(12)	1.748(9)	4
<b>2B</b>	2.354(14)	2.02(2)	1.35(2)	1.45(2)	1.31(2)	1.73(2)	4
<b>2C</b>	2.330(2)	2.017(12)	1.317(14)	1.460(9)	1.327(10)	1.731(9)	2
<b>2D</b>	2.26(2)	2.01(2)	1.32(2)	1.46(2)	1.32(2)	1.73(2)	8
<b>3A</b>	2.325(2)	2.032(6)	1.263(9)	1.467(9)	1.410(9)	1.761(7)	14
<b>3B</b>	2.375(6)	2.08(2)	1.33(2)	1.46(2)	1.41(2)	1.75(2)	33
<b>3C</b>	2.324(7)	2.06(2)	1.30(2)	1.45(2)	1.41(2)	1.77(2)	33
<b>4</b>	2.318(6)	2.01(2)	1.44(2)	1.47(2)	1.43(2)	1.77(2)	41

<sup>a</sup> For disordered molecules, the letter denotes the disorder component. In **2**, there are two molecules in the asymmetric unit and **2A/2B** and **2C/2D** each represent a disordered pair. In **3**, there are two molecules in the asymmetric unit. **3A** is not disordered, and **3B/3C** represent a disordered pair.



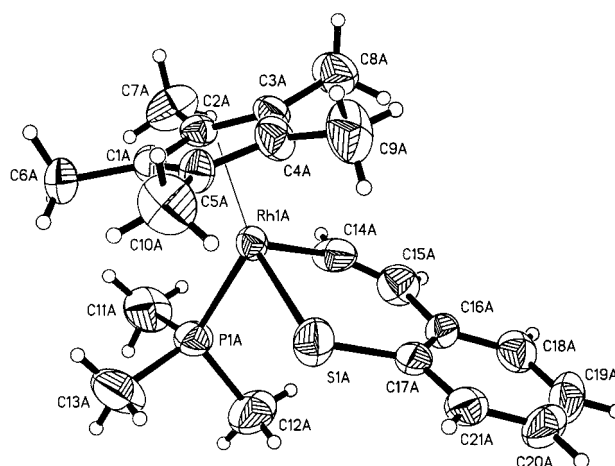
**Figure 3.** ORTEP drawing of  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-C_8H_6S)$ , **2**, with ellipsoids shown at the 50% probability level.

of 1.748(9) Å is comparable to that seen in  $Ir(PMe_3)_3Cl(\eta^2-C,S-C_8H_6S)$  (1.763(7) Å)<sup>7</sup> and  $(C_5Me_5)Ir(PMe_2Ph)(\eta^2-C,S-2,5-Me_2C_4H_2S)$  (1.741(5) Å).<sup>2</sup>

The nearly planar metallacycle in this unsubstituted complex differs significantly from the puckered ring of the corresponding 2,5-methyl-substituted complex (bend angles of 4° and 26.0°, respectively). The different structures are consistent with the results of the molecular mechanics calculations, which predicted that removal of the two methyl groups would result in a bend angle of 11.8°. The fact that the angle is even smaller than predicted is most likely due to the non-metallacycle portion of the complex being “frozen” in the molecular mechanics calculations (see Experimental Section).

**$(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-C_8H_6S)$ .** The synthesis of the benzothiophene insertion complex  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-C_8H_6S)$ , **3**, was also described earlier<sup>12</sup> by the reaction of  $(C_5Me_5)Rh(PMe_3)(Ph)H$  with benzothiophene. A single product was obtained and crystallized. Once again, solution of the structure was not trivial due to disorder problems, but a suitable model and restrained refinement give excellent results.

The molecule crystallizes in space group  $P2_1/n$  with  $Z = 8$ , indicating the presence of 2 molecules per asymmetric unit. In modeling the solution, one of the unique molecules was ordered (**A**) and the second showed the same type of insertion orientation disorder as was seen with thiophene (**B/C**, 50/50). The six-membered ring distances in the two overlapping rings



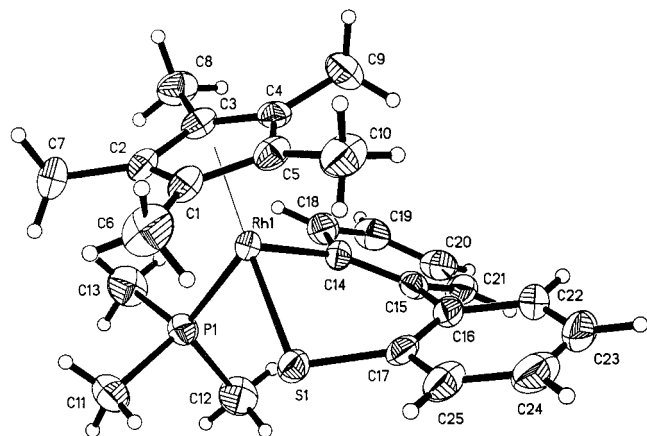
**Figure 4.** ORTEP drawing of  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-C_8H_6S)$ , **3**, with ellipsoids shown at the 50% probability level.

in the **B/C** molecule were restrained to similar distances as in the ordered **A** molecule, allowing a complete anisotropic refinement of the model. The agreement between equivalent bond distances in the distinct ordered and disordered molecules provides support for the accuracy of the disorder model.

Molecule **A** of complex **3** shows a slight puckering of the metallathiacycle of 14° (Figure 4). Molecules **B/C** show greater puckering (33°), but the overlap of the two groups makes the evaluation of this angle less reliable. Bond distances for molecule **A** are again consistent with a localized bonding picture, with C14–C15, C15–C16, and C16–C17 distances of 1.263(9), 1.467(9), and 1.410(9) Å. The Rh1–C14 distance of 2.032(6) Å is again typical of rhodium to  $sp^2$  hybridized carbon bond distances.

Again, the predicted value for the metallacycle bend angle of this complex was found to be approximately 12° and is in good agreement with the determined value. Even the two disordered molecules (**B/C**) exhibit a reduction (although much smaller) in bend angle compared to the methyl-substituted benzothiophene. Also note that only one product (vinyllic C–S cleavage) is observed for the unsubstituted complex. This suggests the importance the  $\alpha$ -methyl group plays in the observed rearrangement of the substituted complex.

**$(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-C_{12}H_8S)$ .** The third compound in this series is formed by the reaction of  $(C_5Me_5)Rh(PMe_3)(Ph)H$  with dibenzothiophene to give  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-C_{12}H_8S)$ , **4**.<sup>12</sup> This molecule crystallizes in orthorhombic space group  $Pca2_1$  with  $Z = 4$ .



**Figure 5.** ORTEP drawing of  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-C_{12}H_8S)$ , **4**, with ellipsoids shown at the 50% probability level.

Only one ordered molecule is observed in the asymmetric unit (Figure 5). The metallacycle is strongly puckered, with a  $41^\circ$  angle between the Rh1–S1–C14 and the S1–C14–C15–C16–C17 planes. In this case, however, there is a twisting along the biphenyl C15–C16 bond of  $32^\circ$  which makes the latter plane less well-defined than in compounds **2** and **3**. The bond distances for C14–C15, C15–C16, and C16–C17 are 1.44(2), 1.47(2), and 1.43(2) Å, the similarity of which probably reflects delocalization within the biphenyl unit rather than the rhodathiacycle. The Rh1–C14 distance of 2.01(2) Å is similar to that seen in the other compounds. These structural results demonstrate the persistence of a significant twist angle even in *unsubstituted* metal-inserted dibenzothiophene complexes.

### Conclusions

Because molecular orbital calculations suggested that electronic factors are not responsible for the metallacycle geometry (planar versus bent) in 18-electron transition-metal-inserted thiophene complexes, molecular mechanics calculations were performed on several bent-ring systems in order to determine whether steric factors are in fact responsible for the ring conformations. Molecular mechanics calculations on  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2,5-Me_2C_4H_2S)$  and the 2-methyl benzothiophene analog indicate that the methyl group on the  $\alpha$ -carbon of the thiophenic ligand is the primary factor responsible for the observed bent geometry of the metallacycle. These results led us to predict that removal of this methyl group would lead to a significantly more planar ring system. This prediction was confirmed by structural characterization of unsubstituted analogs. Structural characterization of the parent, unsubstituted complex,  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-C_4H_4S)$  reveals the presence of a nearly planar metallacycle. In addition, the predicted bend angle for the unsubstituted benzothiophene analog is comparable to that of the actual structure (molecule **3A**). Although predictions were not made for angles in the unsubstituted dibenzothiophene product, the structure shows a bend angle and a twist angle comparable to other substituted analogs. This suggests that the "biphenyl twist" is the primary factor responsible for the bent metallacycles observed in both substituted and unsubstituted metal-inserted dibenzothiophene complexes.

The results from our earlier electronic structure calculations combined with the molecular mechanics calculations and structure determinations reported here suggest that the geometries observed in other 18-electron metal-inserted systems are also highly dependent on steric factors. Any small electronic preference for a particular geometry is probably overshadowed by steric preferences. Consequently, one expects to find planar metallacycles in complexes which do not contain sterically bulky groups that can influence the metallacycle.

### Experimental Section

**Molecular Mechanics Calculations.** The results of the molecular mechanics calculations were obtained using the 1.01 Universal Force Field<sup>17–19</sup> as implemented through Cerius<sup>2,20</sup>. For the calculations on  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2,5-Me_2C_4H_2S)$ , the known, experimental structure for the complex was used as the starting point. To simplify the calculation, the entire molecule, except the metallacycle, was frozen in space so that movement upon minimization was limited to the thiophene ring system. Pure steric interactions between the metallacycle and the rest of the molecule were desired so as to determine conformational preferences based solely on spatial arguments, i.e., minimization should result in the metallacycle being positioned at maximal distances from other substituents. To achieve this, only the following energy terms were employed: bond stretching, torsion, inversion, van der Waals. Other properties of the molecule, for example the  $\pi$  system in the metallacycle, were simulated through atom typing, i.e., by typing the ring carbon as C\_2, twisting about the C–C bonds was restricted. The other atoms were typed, in accordance with the force field, as follows: rhodium, Rh6+3; sulfur, S\_2; phosphorus, P\_3; thiophene carbon, C\_2 or C\_R; alkyl carbon, C\_3; hydrogen, H\_.

Ligand substitutions were made to determine the steric influences on the geometry of the metallacycles. For example, the phosphine group on  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2,5-Me_2C_4H_2S)$  was replaced with a hydrogen atom in order to identify the effect that a large ligand in that spatial position had on the ring geometry. When substituting ligands in this manner, the new, smaller ligand was placed coincident with the original ligand at an appropriate bond distance (e.g., in substituting the trimethylphosphine on  $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S-2,5-Me_2C_4H_2S)$  for a hydrogen atom, the hydrogen atom was positioned on the axis formed between the metal and the original phosphorus atom). Bond distances for the substitute atoms were estimated via an initial molecular mechanics calculation. The C–H and the Rh–H bond distances were estimated to be 0.950 and 1.690 Å, respectively. (Although the Rh(III)–H bond length is longer than expected,<sup>21,22</sup> the length is not important in the sense that hydrogen was chosen as an alternate ligand simply because it is smaller than  $PMe_3$ . That is, the observed trends in bend angles would be similar despite the rhodium–ligand bond distance.) Molecular mechanics calculations on all other complexes discussed were carried out in a similar manner.

It is important to note that the ring systems in the metal-inserted benzo- and dibenzothiophene complexes are difficult

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to model using molecular mechanics. For the rhodium-inserted thiophene complex, the carbon backbone of the ring system could be modeled simply as a conjugated  $\pi$ -system. This particular model is in good agreement with the experimental data which shows a short–long–short alternation in the C–C bond lengths. Experimental data on the benzothiophene complex, however, suggests that the  $\alpha$ – $\beta$  double bond of the metallacycle ring is not conjugated with the  $\pi$  system of the attached benzene ring. Bonding within the carbon backbone of the ligand must, thus, be modeled as a (double bond)–(single bond)–(aromatic ring). Similar complications arise when modeling the metal-inserted dibenzothiophene ring systems. Consequently, only qualitative comments on the calculated ring bend angles (and phenyl twist angles in the dibenzothiophene complexes) produced by various perturbations of the molecule are made.

**General Procedures.** All operations and routine manipulations were performed under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corp. Dri-Lab. The preparation and characterization of **1**, **2**, **3**, and **4** have been previously reported.<sup>12</sup> A Siemens SMART CCD area detector diffractometer equipped with an LT-2 low-temperature unit was used for the X-ray crystal structure determinations.

**X-ray Structural Determination of (C<sub>5</sub>Me<sub>5</sub>)Rh(PMe<sub>3</sub>)( $\eta^2$ -C,*S*-C<sub>4</sub>H<sub>4</sub>S), **2**.** Slow evaporation of a cyclohexane solution of **2** produced small, orange prisms. A single crystal of dimensions 0.35 × 0.22 × 0.22 mm<sup>3</sup> was mounted on a glass fiber with epoxy. Data were collected at –50 °C on a Siemens SMART CCD area detector system employing a 3 kW sealed tube X-ray source operating at 1.5 kW. Data (1.3 hemispheres) were collected over 7 h, yielding 15 791 data after integration using SAINT (see Table 1). Laue symmetry revealed an orthorhombic crystal system, and cell parameters were determined from 5934 unique reflections<sup>23</sup> with 5831 unique data (93% with  $I > 2\sigma(F)$ ,  $R_{\text{int}} = 0.022$ ). The space group was assigned as *Pca*2<sub>1</sub> on the basis of systematic absences using XPREP, and the structure was solved and refined using direct methods included in the SHELX package. For a *Z* value of 8, there are two independent molecules of **2** within the asymmetric unit. Examination of a difference map following isotropic refinement of the (C<sub>5</sub>Me<sub>5</sub>)Rh(PMe<sub>3</sub>) fragment showed evidence for an orientation disorder of the metallacycle group for each of the two independent molecules. In the refinement model, the two different orientations were allowed to refine independently while restraining intra-ring distances to be similar using the SHELX SAME instruction. The occupancies of the two orientations were also refined. In the final model, non-hydrogen atoms were refined anisotropically (on  $F^2$ ), with hydrogens included in idealized locations. The structure was

refined as a 67:33 racemic twin, with  $R_1 = 0.026$  and  $wR_2 = 0.057$ .<sup>24</sup> Fractional coordinates and thermal parameters are given in the Supporting Information.

**X-ray Structural Determination of (C<sub>5</sub>Me<sub>5</sub>)Rh(PMe<sub>3</sub>)( $\eta^2$ -C,*S*-C<sub>8</sub>H<sub>6</sub>S), **3**.** Slow evaporation of a cyclohexane solution of **3** produced small, orange plates. The data collection and reduction was conducted as for complex **2**, with details given in Table 1. For space group *P*2<sub>1</sub>/*n* with *Z* = 8, there must be two independent molecules within the asymmetric unit. Solution with the SHELX package again showed disorder in the metallathiacycle following isotropic refinement of the (C<sub>5</sub>Me<sub>5</sub>)Rh(PMe<sub>3</sub>) fragment for one of the two independent molecules. In the refinement model, the two different orientations were allowed to refine independently while restraining intra-ring distances to be similar to those of the ordered molecule using the SHELX SAME instruction. The occupancies of the two orientations was fixed at 50/50, since the thermal parameters appeared equal for the two rings. In the final model, non-hydrogen atoms were refined anisotropically (on  $F^2$ ), with hydrogens included in idealized locations with  $R_1 = 0.060$  and  $wR_2 = 0.132$ . Fractional coordinates and thermal parameters are given in the Supporting Information.

**X-ray Structural Determination of (C<sub>5</sub>Me<sub>5</sub>)Rh(PMe<sub>3</sub>)( $\eta^2$ -C,*S*-C<sub>12</sub>H<sub>8</sub>S), **4**.** Slow evaporation of a cyclohexane solution of **4** produced small, orange prisms. The data collection and reduction was conducted as for complex **2**, with details given in Table 1. For space group *Pca*2<sub>1</sub> with *Z* = 4, there is only one independent molecule within the asymmetric unit. Routine solution with the SHELX package and full anisotropic refinement of the structure with hydrogen atoms included in idealized positions refined to  $R_1 = 0.0417$  and  $wR_2 = 0.0693$ . 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<sub>5</sub>Me<sub>5</sub>)Rh(PMe<sub>3</sub>)(thiophene), (C<sub>5</sub>Me<sub>5</sub>)Rh(PMe<sub>3</sub>)(benzothiophene), and (C<sub>5</sub>Me<sub>5</sub>)Rh(PMe<sub>3</sub>)(dibenzothiophene) and drawings of disordered molecules of **2a–d** and **3b,c** (21 pages). Ordering information is given on any current masthead page.

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(23) It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since the systematic error is not included. More reasonable errors might be estimated at 10× the listed values.

(24) Using the SHELX95 package,  $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$ ,  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ , where  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$  and  $P = [I(\text{Max of } 0 \text{ or } F_o^2) + (1 - f)F_c^2]$ .