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Carbon−Sulfur Bond Activation of Dibenzothiophenes and Phenoxythiin by $[Rh(dippe)(\mu\text{-}H)]_2$ and $[Rh_2(dippe)_2(\mu\text{-}Cl)(\mu\text{-}H)]$†

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The rhodium dimer $[Rh(dippe)(\mu\text{-}H)]_2$ (**1**) reacts with dibenzothiophene to form the C−S cleavage product $[Rh_2(dippe)_2(\mu\text{-}SC_{12}H_9)(\mu\text{-}H)]$ (**3**). Complex **1** also reacts with 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene to form $[Rh_2(dippe)_2(\mu\text{-}S\text{-}MeC_{12}H_8)(\mu\text{-}H)]$ (**4**) and $[Rh_2(dippe)_2(\mu\text{-}S\text{-}Me_2C_{12}H_7)(\mu\text{-}H)]$ (**6**), respectively. Reaction with phenoxythiin forms $[Rh_2(dippe)_2(\mu\text{-}S\text{-}C_6H_4OC_6H_5)(\mu\text{-}H)]$ (**8**). In **3**, rhodium addition to the ortho C−H bond of the β-ring of the biphenylthiolate substituent does not occur at 100 °C. The crystal structures of $[Rh_2(dippe)_2(\mu\text{-}Cl)(\mu\text{-}H)]$ (**2**), **4**, **6**, and **8** indicate that each complex contains a nearly planar $Rh_2(\mu\text{-}X)(\mu\text{-}H)$ core. The ^1H NMR spectra of **3**, **4**, and **6** suggest that the pyramidal geometry at the sulfur atom is maintained in solution and that sulfur inversion is absent. Unreacted **1** catalyzes H/D exchange between C_6D_6 and the biphenylate substituent of **3** faster than it cleaves the remaining C−S bond to make free biphenyl. Complex **3** is unreactive toward excess dibenzothiophene, while $[Rh_2(dippe)_2(\mu\text{-}Cl)(\mu\text{-}H)]$ cleaves a C−S bond of DBT to form $[Rh_2(dippe)_2(\mu\text{-}Cl)(\mu\text{-}SC_{12}H_9)]$ (**9**).

Introduction

In the past, the hydrodesulfurization of thiophenes using $[Ni(dippe)(\mu\text{-}H)]_2$ and systems that utilize the [M(dippe)] fragment (M = Pd, Pt) as a source of M(0) have been studied.[1−4] The former complex readily activates thiophenic carbon−sulfur bonds and, in the reaction with dibenzothiophene (DBT), eventually produces four metal complexes. Two of these complexes contain extracted sulfur. However, attempts to make the system catalytic have failed in that the regeneration of a reactive form of Ni(0) has proven to be elusive.[5] The latter systems that use palladium and platinum are highly reactive, but many of the Pd(0) and Pd(II) species easily degrade into colloidal metal and free ligand.

In light of the limitations of $[Ni(dippe)(\mu\text{-}H)]_2$ and [Pd(dippe)], a metal hydride was sought that was both reactive and capable of cycling between two stable oxidation states that are separated by two electrons. In regard to the homogeneous hydrodesulfurization of thiophenes, these two qualities are desirable, as evidenced by the many examples of thiophene C−S oxidative addition by complexes in which they are found. This search led to an investigation of $[Rh(dippe)(\mu\text{-}H)]_2$, which is one of a class of $[L_2Rh]_n(\mu\text{-}H)_n$ compounds that was developed by Fryzuk and co-workers in the 1980s.[6] They found that $[Rh(dippe)(\mu\text{-}H)]_2$ reacts with olefins to produce vinyl, alkenyl, dienyl, and diene hydride bridged dimers.[7,8] This complex also was observed to react with phenol, *N*-benzylideneaniline, H_2, aldimines, silanes, and other substrates to form a variety of products.[9]

$[Rh(dippe)(\mu\text{-}H)]_2$ offers several advantages. First, the rhodium centers can cycle between the stable Rh(+1) and Rh(+3) oxidation states, allowing $[Rh(dippe)(\mu\text{-}H)]_2$ to accommodate the two-electron oxidation that is necessitated by the activation of a carbon−sulfur bond in DBT. Second, $[L_2Rh]_n(\mu\text{-}H)_n$ compounds are electronically unsaturated, which aids their reactivity. Third, the smaller bite angle of dippe, relative to chelating phosphines with propyl and butyl backbones, forces the isopropyl moieties away from the Rh(μ-H) core. This reduces steric crowding around the rhodium centers to further improve reactivity. Finally, it was probable that $[Rh(dippe)(\mu\text{-}H)]_2$ would maintain itself as a dinuclear species in the presence of DBT, which is a desirable feature in a homogeneous system that attempts to model the bulk solids that are used in heterogeneous catalytic hydrodesulfurization. Indeed, evidence from the hydrogenation of 1-hexene

† Part of the Dietmar Seyferth Festschrift. This article is dedicated in honor of Professor Dietmar Seyferth for his special service and inspiration to organometallic chemists worldwide through his creation of this journal.

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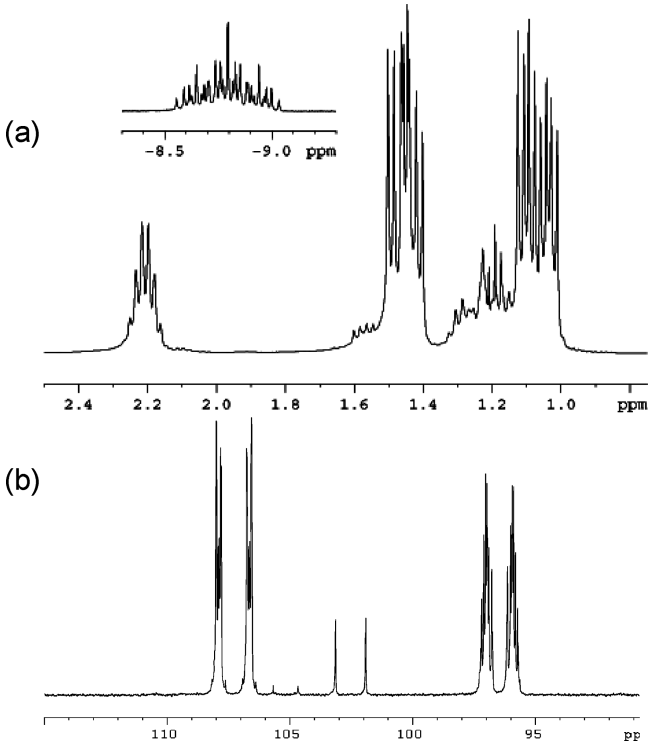


Figure 1. (a) ^{1}H NMR spectrum and (b) ^{31}P NMR spectrum of $[Rh_2(dippe)_2(\mu\text{-Cl})(\mu\text{-H})]$ (**2**). The doublet that is located around δ 102 corresponds to unreacted $[Rh(dippe)(\mu\text{-Cl})]_2$.

using $[Rh(^iPr_2P(CH_2)_nP^iPr_2)(\mu\text{-H})]_2$, where $n = 2, 3$, suggests that the smaller bite angle resulted in $[Rh(dippe)(\mu\text{-H})]_2$ interacting with substrate as a binuclear complex, whereas $[Rh(dippp)(\mu\text{-H})]_2$ fragmented into monomers.[10]

In the course of this study, $[Rh_2(dippe)_2(\mu\text{-Cl})(\mu\text{-H})]$ was also synthesized and its reactivity toward dibenzothiophene was investigated in conjunction with our study of $[Rh(dippe)(\mu\text{-H})]_2$. The ability of these complexes to insert into the carbon−sulfur bonds of dibenzothiophenes and phenoxythiin, to convert them into molecules easier to desulfurize, was determined. The results of this work are reported herein.

Results and Discussion

$[Rh(dippe)(\mu\text{-H})]_2$ and $[Rh_2(dippe)_2(\mu\text{-Cl})(\mu\text{-H})]$ Complexes. The complex $[Rh(dippe)(\mu\text{-H})]_2$ (**1**) has been synthesized by Fryzuk and co-workers by the reaction of $[Rh(COD)(\eta^3\text{-allyl})]$ with dippe and H_2.[7] We have found that **1** can also be synthesized directly by reaction of $[Rh(dippe)Cl]_2$ with 2 equiv of $LiHBEt_3$. The chloro−hydrido-bridged dimer $[Rh_2(dippe)_2(\mu\text{-Cl})(\mu\text{-H})]$ (**2**) forms if only $^1/_2$ equiv of $LiHBEt_3$ is employed.[11] The ^{1}H NMR spectrum of **2** (Figure 1a) indicates the presence of an asymmetric complex. There are a total of four different doublets of doublets that correspond to the dippe isopropyl substituents, and the hydride appears as a triplet of triplet of triplets. The ^{31}P NMR spectrum of **2** (Figure 1b) highlights the fact that a plane of symmetry is lost when one bridging hydride ligand in **1** is replaced with chloride. Whereas the phosphorus signal of **1** is a simple doublet, the signals for **2** are asymmetric. This is consistent with an AA′BB′XX′ spin

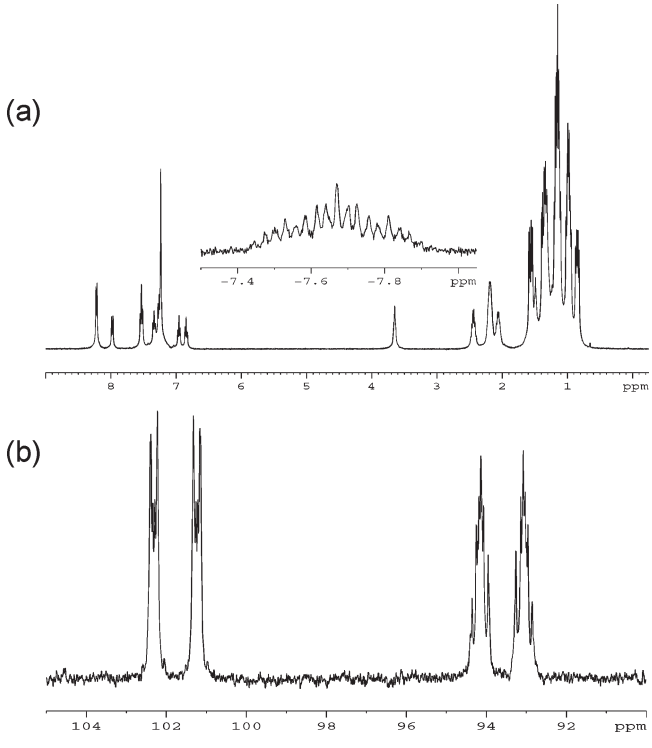
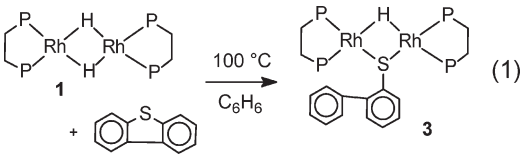


Figure 2. (a) ^{1}H NMR spectrum and (b) ^{31}P NMR spectrum of $[Rh_2(dippe)_2(\mu\text{-}SC_{12}H_9)(\mu\text{-H})]$ (**3**).

system, which results from the long-range coupling of phosphorus nuclei surrounding the asymmetric $Rh_2(\mu\text{-Cl})(\mu\text{-H})$ core.

Reaction between $[Rh(dippe)(\mu\text{-H})]_2$ and DBT. At 100 °C, the reaction between the rhodium hydride dimer **1** and 1 equiv of DBT goes to completion within ~10 days, to produce exclusively $[Rh_2(dippe)_2(\mu\text{-}SC_{12}H_9)(\mu\text{-H})]$ (**3**; eq 1). Activation of only one C−S bond of the organosulfur substrate is observed, despite the presence of a second metal and hydride ligand.



While a crystal structure of **3** could not be obtained, the ^{1}H and ^{31}P NMR spectra, as well as elemental analysis data, are consistent with a biphenylthiolato−hydrido-bridged rhodium dimer. In the ^{1}H NMR spectrum (Figure 2a), there is a complex multiplet at δ −7.88, which converts to a triplet upon broad-band phosphorus decoupling. This resonance is consistent with a hydride (J_{H-Rh} = 22.2 Hz) that occupies a bridging position between two identical rhodium centers. Evidence of the biphenylthiolato moiety is found in the aromatic region of the spectrum. Here, there are seven distinct resonances, with four α-ring protons and the para proton of the β-ring corresponding to 1 H, while the ortho and meta protons of the freely rotating β-ring correspond to 2 H. The aliphatic region of the spectrum indicates that a second plane of symmetry also has been lost and that sulfur inversion, which would restore that plane in solution, is absent. That is, there are four types of isopropyl substituents that are differentiated according to whether they are syn or anti to the

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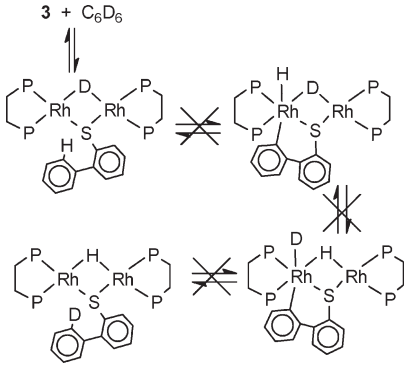
Scheme 1. Possible Mechanism for H/D Exchange

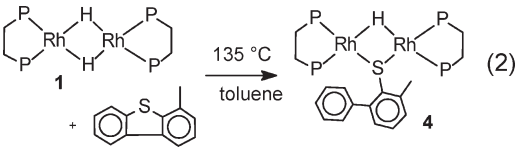


thiolato substituent, as well as to whether they are cis or trans to the bridging sulfur, resulting in the presence of eight different doublets of doublets for the isopropyl methyl groups. The ^{31}P NMR spectrum of **3** (Figure 2b) resembles the spectrum of **2**. It too consists of two differing sets of multiplets, consistent with an AA′BB′XX′ spin system that would result from the long-range coupling of phosphorus nuclei in a complex where one plane of symmetry has been lost upon the substitution of a bridging hydride ligand in **1** with a thiolato ligand.

In the same manner as reported for **1**,[7] complex **3** exchanges hydride for deuteride, which is obtained from the C_6D_6 solvent. The observed pseudo-first-order rate constant for this isotopic exchange process in C_6D_6 is 1.67×10^{-6} s^{-1} at 100 °C. However, there is *no* incorporation of deuterium at the ortho position of the biphenylate β-ring after 21 days at 100 °C, which indicates that **3** does *not* reversibly activate that C−H bond by the process that is shown in Scheme 1. This observation is of relevance to other H/D exchange reactions seen with **3** under different conditions (vide infra).

Reaction between [Rh(dippe)(μ-H)]$_2$ and 4-Methyldibenzothiophene. Experimental evidence[12] and theoretical calculations[13] from other studies indicate that the activation of a C−S bond of a thiophene by a metal center is preceded by the formation of an η^2(C,C)-bound thiophene−metal adduct, which leads to an η^2(C,S) adduct just prior to C−S addition. Consequently, dibenzothiophenes that are substituted with an alkyl group at the 4- or the 6-position, or both, are particularly refractory with respect to hydrodesulfurization—the alkyl substituent blocks dibenzothiophene precoordination in either in an η^2 fashion or via a sulfur lone pair of electrons.[14] Reaction of **1** with 4-methyldibenzothiophene (4-MeDBT) was therefore anticipated to be more difficult than reaction with dibenzothiophene.

The same reaction conditions used for the reaction of DBT with **1** were employed for 4-MeDBT activation (C_6D_6, 100 °C, 1 equiv of 4-MeDBT). After more than 3 months the reaction had not gone to completion, and several unidentified resonances were present by ^{31}P NMR spectroscopy (vide infra). When the reaction was carried out in toluene at 135 °C with an excess of 4-methyldibenzothiophene (3 equiv), however, the reaction went to completion within 1 week to give the product [Rh$_2$(dippe)$_2$(μ-S-MeC$_{12}$H$_8$)(μ-H)] (**4**) (eq 2). An atmosphere of hydrogen was also found to accelerate the hydrogenolysis reaction.



The use of excess 4-MeDBT is problematic, since commercial sources typically contain about 4% dibenzothiophene as an impurity. Use of commercial 4-MeDBT resulted in a mixture of **3** and **4**, since **1** reacts rapidly with the sterically unhindered DBT.[15] 4-MeDBT was therefore synthesized in pure form by an alternative method that did not use DBT as a precursor.[16] Reaction of **1** with 4-MeDBT was carried to completion in 6.5 days. **4** was purified by eluting the sample through silica with pentane and then with 20/80 THF/pentane. This allowed **4** to be cleanly separated from the excess 4-MeDBT as a golden yellow solid in 80% yield.

The ^{31}P NMR spectrum of **4** is nearly identical with that of **3**, with a set of doublets of multiplets similar to those seen in Figure 2b. The ^{1}H NMR spectra of **3** and **4** are also very similar. The aryl methyl peak in **4** is observed as a singlet at δ 2.93, and one less resonance was present in the aromatic region. The hydride resonance of **4** shows the same splitting as that observed in **3** but is shifted slightly upfield and is centered at δ −8.29. A small impurity (approximately 2%) was present in the isolated product and was determined by independent synthesis to be the complex [Rh$_2$(dippe)$_2$(μ-S-2-MeC$_6$H$_4$)(μ-H)]. The origin of this impurity derives from reaction of **1** with di-*o*-tolyl disulfide, which is present as an impurity in the synthesized 4-MeDBT (approximately 1%).

Crystals of **4** suitable for X-ray diffraction were grown from a saturated solution of hexanes at −30 °C (see Figure 3). The crystal structure shows that cleavage of the C−S bond occurs exclusively at the less hindered side of 4-MeDBT. **4** consists of a nearly planar Rh$_2$(μ-S)(μ-H) core with a pyramidal geometry at sulfur. Each Rh(I) center has a slightly distorted square planar geometry. The hydride is bridging between both Rh centers, and the distance between the Rh centers is 2.89 Å, close enough to assume that bonding between the Rh centers is occurring. The average Rh−P distance is 2.21 Å.

The progress of the reaction was followed by ^{31}P NMR spectroscopy, during which time several intermediates were observed. The identity of these intermediates could not be determined, except for one. The disubstituted product [Rh(dippe)(μ-S-MeC$_{12}$H$_8$)]$_2$ (**5**) was found to form rapidly in the reaction with impure 4-MeDBT (10 equiv). It consisted of 14% of the reaction mixture (determined by integration of the ^{31}P NMR spectrum). In the reaction with purified 4-MeDBT (99%) it was sometimes observed in trace amounts. The path for formation of **5** using the less pure 4-MeDBT remains uncertain but does not appear to form from a secondary reaction of **4** with excess 4-MeDBT. [Rh(dippe)(μ-S-MeC$_{12}$H$_8$)]$_2$ is an orange crystalline solid

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(14) Myers, A. W.; Jones, W. D. *Organometallics* **1996**, *15*, 2905.
(15) Commercial routes involve 4-lithiation of DBT followed by methylation; either incomplete deprotonation or the presence of water during the methylation can easily lead to DBT contamination of the 4-MeDBT produced by this route.
(16) Tedjamulia, M. L.; Tominaga, Y.; Castle, R. N.; Lee, M. L. *J. Heterocycl. Chem.* **1983**, *20*, 1485–95.

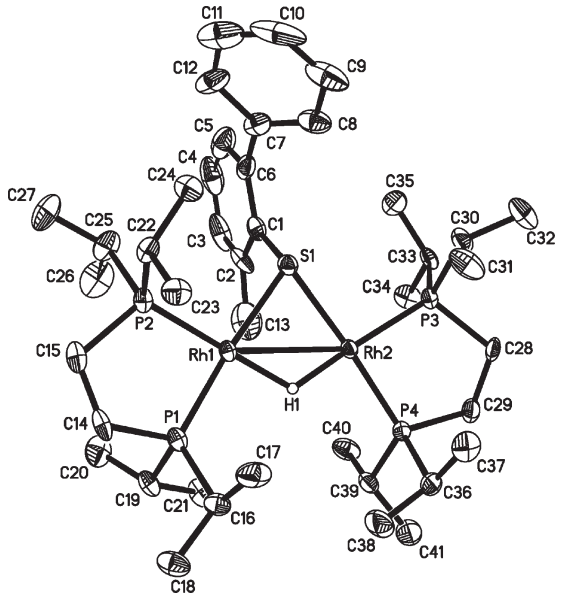


Figure 3. ORTEP drawing of $[Rh_2(dippe)_2(\mu\text{-S-MeC}_{12}H_8)(\mu\text{-H})]$ (**4**). Ellipsoids are shown at the 30% probability level. All hydrogens except for the bridging hydride are omitted for clarity.

that is insoluble in hydrocarbons and was isolated by extracting the reaction product with hexanes, leaving behind **5**. The ^{31}P NMR shows a doublet centered at δ 89.93 (J_{Rh-P} = 175 Hz). The ^{1}H NMR shows an aryl methyl resonance at δ 4.68. A crystal structure of **5** was obtained, as shown in Figure 4. The structure belongs to the space group $P2_1/c$ and consists of a planar Rh_2S_2 core. The geometry around the two Rh(I) centers is distorted square planar, with the two bridging biphenyl thiolate ligands orientated anti to one another. The Rh−P bond lengths in **5** are identical with those found in **4** (2.21 Å); however, the Rh−S bond lengths in **5** are elongated in comparison to those in **4** (2.47 vs 2.34 Å). The Rh−Rh distance (3.694 Å) is much longer than in the μ-H compound **4**, indicative of no Rh−Rh interaction.

Reaction between [Rh(dippe)(μ-H)]$_2$ and 4,6-Dimethyldibenzothiophene. The activation of 4,6-dimethyldibenzothiophene (4,6-Me$_2$DBT) remains a considerable challenge in HDS chemistry. The two methyl groups on the ring are well positioned to sterically block a metal surface from interacting with the C−S bonds, making it the most difficult thiophene to activate.[17] There are few examples in the literature which have shown activation of 4,6-Me$_2$DBT by a metal complex.[18]

1 was found to react with 4,6-Me$_2$DBT in a fashion similar to that for DBT and 4-MeDBT (eq 3). For a typical reaction 17−20 equiv of 4,6-Me$_2$DBT was used, and 1 atm of hydrogen was added to the reaction vessel. Hydrogen, as in the case of 4-MeDBT, was found to accelerate the reaction. The C−S bond activation of 4,6-Me$_2$DBT was complete in 8.5 days,

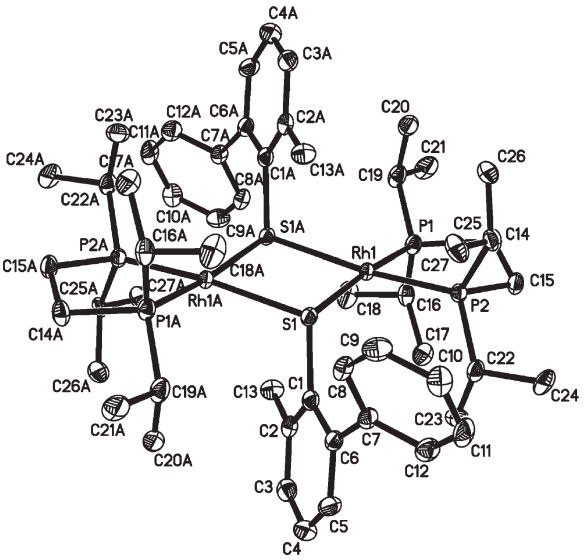
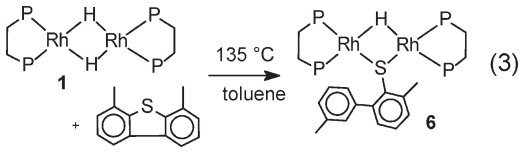


Figure 4. ORTEP drawing of $[Rh(dippe)(\mu\text{-S-MeC}_{12}H_8)]_2$ (**5**). Ellipsoids are shown at the 30% probability level. All hydrogen atoms are omitted for clarity.

forming $[Rh_2(dippe)_2(\mu\text{-SMe}_2C_{12}H_7)(\mu\text{-H})]$ (**6**), characterized by an almost identical set of doublet of multiplet resonances centered at δ 99 and 93 in the ^{31}P NMR spectrum.



(3)

However, an additional product formed competitively with **6** and also displayed the familiar AA′BB′XX′ splitting pattern with resonances centered at δ 110 and 91 in the ^{31}P NMR spectrum. The product was assigned as $[Rh_2(dippe)_2(\mu\text{-SH})(\mu\text{-H})]$ (**7**). **7** formed as the major product initially, but as **1** was consumed an approximately 50:50 ratio of **6** and **7** formed. The ^{1}H NMR spectrum of the mixture showed the hydride resonance of **7** at δ −7.84 and the S−H resonance at δ −0.02. A disordered X-ray structure of **7** was obtained (see the Supporting Information for structure details). **7** was generated independently when **3** was reacted with **1** without the presence of dibenzothiophene.

The much slower rate of activation of 4,6-Me$_2$DBT explains the appearance of **7**. **7** was observed by ^{31}P NMR spectroscopy in the reaction of 4-MeDBT (1 equiv) with **1**. Formation of **7** in reactions of **1** with 4-MeDBT (excess) and DBT does not occur, due to the much faster consumption of **1** in these reactions compared to the reaction with 4,6-Me$_2$DBT. **7** is apparently formed from reaction of **1** with μ-SR complexes such as **3**, **4**, and **6**.

7 was found to decompose after several days of heating after the consumption of **1**, leaving **6** as the main product of the reaction. **6** was isolated in a manner similar to that for **4** by using silica gel to separate it from the excess thiophene. An impurity was present that was consistent with a $[Rh_2(dippe)_2(\mu\text{-SAr})(\mu\text{-H})]$ (Ar = aryl) complex (approximately 10% by ^{31}P NMR spectroscopy). This species likely arose from a small impurity present in the 4,6-Me$_2$DBT and then was magnified due to the large excess of 4,6-Me$_2$DBT used in the reaction. The isolated yield of **6** was 24%. The low yield was attributed to the slow formation of **6** and an increase in

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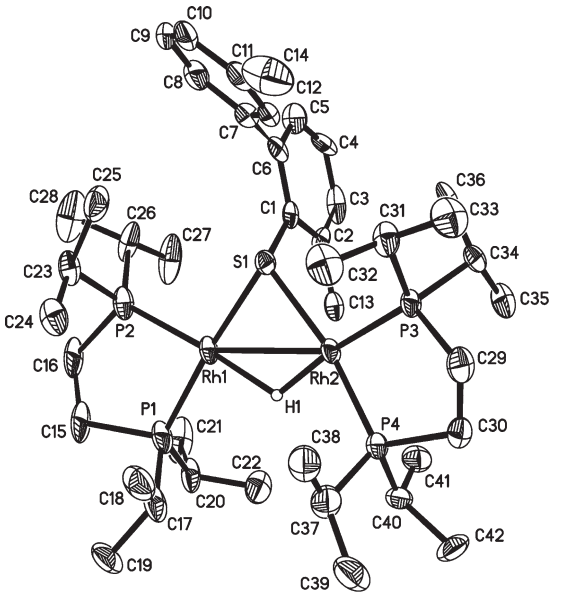


Figure 5. ORTEP drawing of $[Rh_2(dippe)_2(\mu\text{-}SMe_2C_{12}H_7)(\mu\text{-}H)]$ (**6**). Ellipsoids are shown at the 30% probability level. All hydrogens except for the bridging hydride are omitted for clarity.

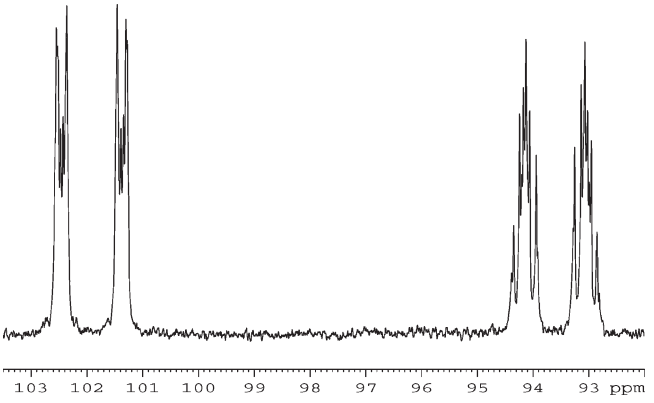


Figure 6. ^{31}P NMR spectrum of $[Rh_2(dippe)_2(\mu\text{-}S\text{-}C_6H_4OC_6H_5)(\mu\text{-}H)]$ (**8**).

decomposition (via **7**) compared to **3** and **4**. A crystal suitable for X-ray diffraction was grown from slow evaporation of a hexanes solution, and the structure is shown in Figure 5.

To the best of our knowledge, this is the first X-ray structure obtained of a C−S activated 4,6-Me_2DBT metal complex showing complete C−S bond cleavage and hydrogenation (the earlier platinum examples formed a metallacycle[18b−d]). The structure is nearly identical with that shown for **4**, with the key structural difference being the presence of the second methyl group on the bridging biphenyl thiolate. The Rh−Rh distance (2.859 Å) is almost identical with that in **4**. The ^1H NMR spectrum of **6** shows the two methyl resonances present at δ 2.94 and 2.44 (C_6D_6). The resonance at δ 2.94 is attributed to the methyl group attached to the phenyl thiolate ring, since the resonance is identical with the aryl methyl resonance found for **4**.

Reaction between [Rh(dippe)(μ-H)]$_2$ and Phenoxythiin. Complex **1** was treated with phenoxythiin in order to determine its preference for activating C−S versus C−O bonds in thiophenic molecules. As eq 4 illustrates, over 8 days at 82 °C in C_6D_6, the rhodium hydride dimer is completely consumed to produce exclusively the phenoxythiolato-bridged dimer

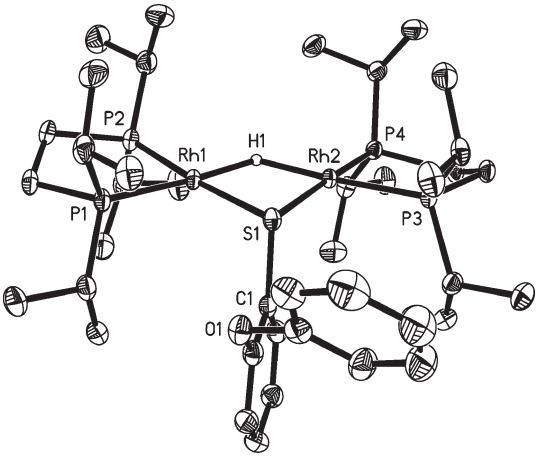
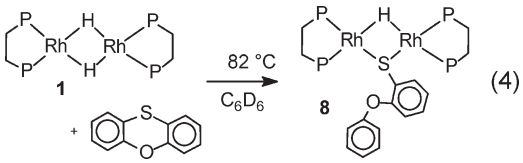


Figure 7. ORTEP drawing of $[Rh_2(dippe)_2(\mu\text{-}S\text{-}C_6H_4OC_6H_5)(\mu\text{-}H)]$ (**8**). Ellipsoids are shown at the 30% probability level. All hydrogens, except for the bridging hydride, are omitted for clarity.

$[Rh_2(dippe)_2(\mu\text{-}S\text{-}C_6H_4OC_6H_5)(\mu\text{-}H)]$ (**8**) in 31% isolated yield. The selectivity of **1** for C−S bond activation may be due to the greater strength of the C−O bond, the lesser ability of oxygen to precoordinate to a rhodium center, or both. Each factor arises from the greater lone electron pair delocalization into the phenyl rings from oxygen as opposed to sulfur, which is indicated by the crystal structure of phenoxythiin. Its C−O−C angle is around 117.4°, while its C−S−C angle is around 97.7°.[19]



The ^{31}P NMR spectrum of **8** consists of a set of complex multiplets that are centered around δ 102 and 93.5 (Figure 6) and that have the same pattern as the signals that correspond to **2**−**4**. Its ^1H NMR spectrum indicates that, like **3** and **4**, it is a thiolato−hydrido-bridged dimer. The aromatic region consists of five separate signals from δ 7.76 to 6.59, which each integrate for one proton, and overlapping multiplets that are centered around δ 7.23, which together integrate for four protons. The hydride region consists of a multiplet that is centered at δ −7.81. The aliphatic proton region of the spectrum is somewhat broad. However, the appearance of more than one isopropyl methine signal indicates that, as in **3**, there is more than one type of isopropyl group in the dippe ligand.

A single-crystal X-ray structure of **8** is shown in Figure 7 and resembles the structure of **4** in that, while the $Rh_2(\mu\text{-}S)(\mu\text{-}H)$ core is nearly planar, the bridging sulfur atom is pyramidal with an exo-oriented phenoxythiolato substituent. Both C−O bond lengths and the C−O−C angle in that substituent are similar to those in the parent phenoxythiin.[19]

Sulfur tends to be highly pyramidalized, relative to oxygen, in both XR_3^+ and M_2XR groups, where X = O, S and R = H, alkyl, because its bonding molecular orbitals have

(19) Fitzgerald, L. J.; Gallucci, J. C.; Gerkin, R. E. *Acta Crystallogr., Sect. C* **1991**, *47*, 381.

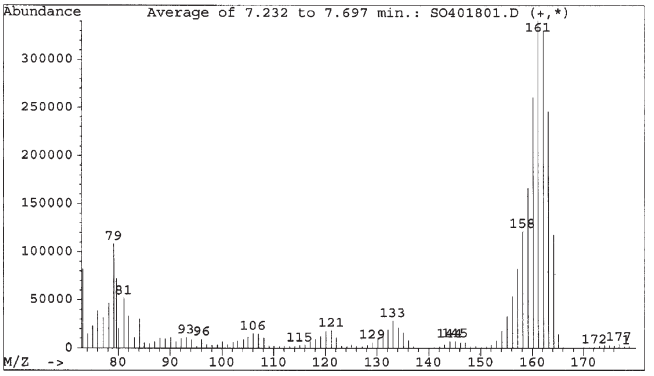


Figure 8. GC-MS of the C_6D_6 solution from the reaction between **1** and 2 equiv of DBT.

more p-orbital character. For instance, the distribution of the sum of the bond angles about the X atom, $\sum$, in M_2XR groups is centered near 315° for sulfur, while it is centered around 360° for oxygen.[20] The bridging sulfur atoms in both **4** and **8** demonstrate this tendency. With a $\sum$ value of approximately 306.8°, the 4-methylbiphenylthiolato sulfur of **4** is slightly more pyramidalized than the average M_2SR sulfur. Remarkably, $\sum$ for the phenoxythiolato sulfur of **8** is 284.9°, which is smaller than the calculated value of 286° for SH_3^+.[20]

Production of Free Biphenyl. The analysis by GC-MS of the C_6D_6 solution from the reaction between **1** and 2 equiv of DBT indicated the presence of nondeuterated (*m*/*z* 154), monodeuterated, multideuterated, and perdeuterated biphenyl. As Figure 8 shows, highly deuterated biphenyls predominate over mono-, di-, tri-, and tetradeuterated biphenyl, with hepta- and octadeuterated biphenyls being the most prevalent.

To determine if the biphenyl originated from DBT or if it resulted from the coupling of solvent molecules, **1** was heated at 100 °C for 26 days in C_6H_6, in C_6D_6, and in toluene. Analysis of all three solutions by GC-MS and ^{1}H NMR spectroscopy demonstrated that no biphenyl was formed. In contrast, a C_6D_6 solution of approximately a 2:1 mixture of **1** and **3** was heated for 4 days at 100 °C, and analysis by GC-MS indicated that biphenyl was present. Moreover, after **1** and **8** were heated together at 100 °C in C_6D_6 for 5 days, free diphenyl ether was detected by GC-MS. This time tri- and tetradeuterated products were predominant. The reactions between the hydride dimer and **3** and **8** indicate that the completely desulfurized organic product most likely is produced via the cleavage of the C−S bond of the thiolato-bridged rhodium complex by unreacted **1**. The binuclear rhodium complex $[Rh_2(dippe)_2(\mu\text{-SH})(\mu\text{-H})]$ (**7**) can be identified in these reactions by ^{31}P NMR spectroscopy.

$[Rh(dippe)(\mu\text{-H})]_2$ H/D Exchange of the Thiolato Substituent of $[Rh_2(dippe)_2(\mu\text{-SC}_{12}H_9)(\mu\text{-H})]$. The fact that the biphenyl produced is deuterated to varying stages in the reaction between **1** and **3** indicates that the former, which is known to exchange hydride for deuteride with benzene solvent, must undergo reversible C−H activation of the biphenyl thiolate substituent and C_6D_6 solvent before cleaving the C−S bond in a manner that is described in Scheme 2. Effectively, **3** undergoes H/D exchange prior to the second C−S cleavage. The distribution of deuterated biphenyls that is observed by GC-MS suggests that **1** prefers to initiate H/D exchange at the freely rotating β-ring as opposed to the α-ring.

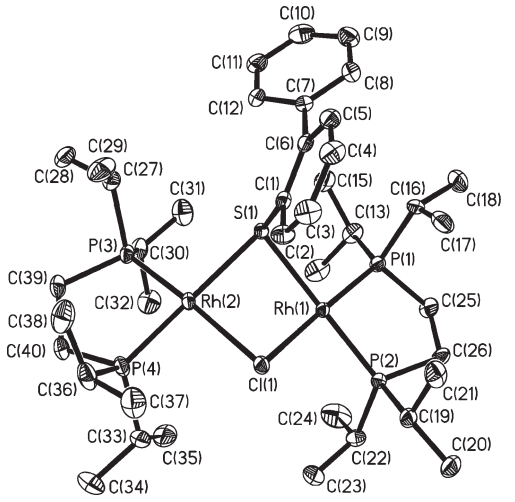
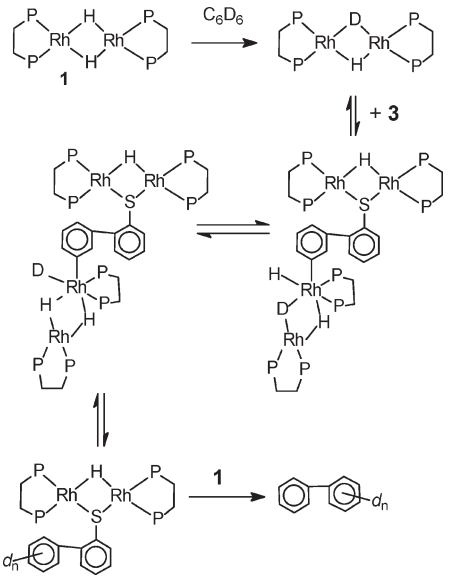


Figure 9. ORTEP drawing of $[Rh_2(dippe)_2(\mu\text{-Cl})(\mu\text{-SC}_{12}H_9)]$ (**9**). Ellipsoids are shown at the 30% probability level. All hydrogens, except for the bridging hydride, are omitted for clarity.

Scheme 2. Pathway for H/D Exchange in the Biphenylate Substituent of 3 by 1 before Cleaving the Second C−S Bond



Reaction between $[Rh_2(dippe)_2(\mu\text{-Cl})(\mu\text{-H})]$ and DBT. Complex **2** activates the C−S bond in DBT to form $[Rh_2(dippe)_2(\mu\text{-Cl})(\mu\text{-SC}_{12}H_9)]$ (**9**) as the major product. The chloro−hydrido-bridged rhodium dimer is less reactive than **1**. For instance, the reaction between **2** and 10 equiv of DBT in C_6D_6 at 100 °C takes 51 days to reach 97% completion. Moreover, there is evidence of partial decomposition at that temperature and duration of time. **9** can be prepared independently from the reaction of **2** with 2-(phenylthio)phenol at 20 °C. A crystal structure of **9** was obtained and is shown in Figure 9. The complex is bent along the S−Cl axis with a dihedral angle θ of 134.9°, and the angle between the Rh_1−S−Rh_2 and Rh_1−Cl−Rh_2 planes, ϕ, is 135.7°. The ^{31}P NMR spectrum indicates the presence of long-range coupling through the sulfur and chloride bridges, as the phosphorus signals of **9** consist of two doublets of doublets of doublets.

(20) Aullón, G.; Ujaque, G.; Lledós, A.; Alvarez, S. *Chem. Eur. J.* **1999**, *5*, 1391.

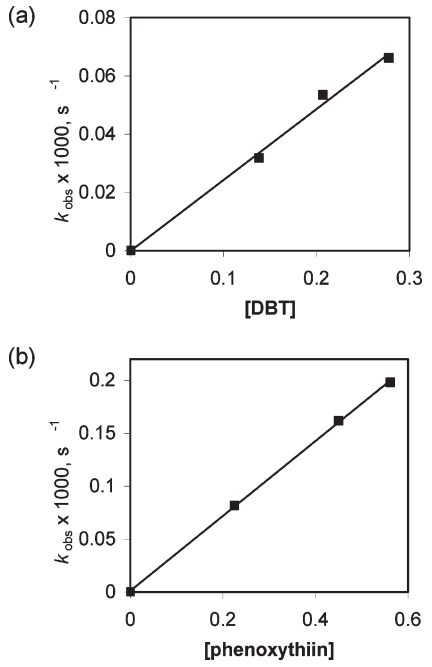
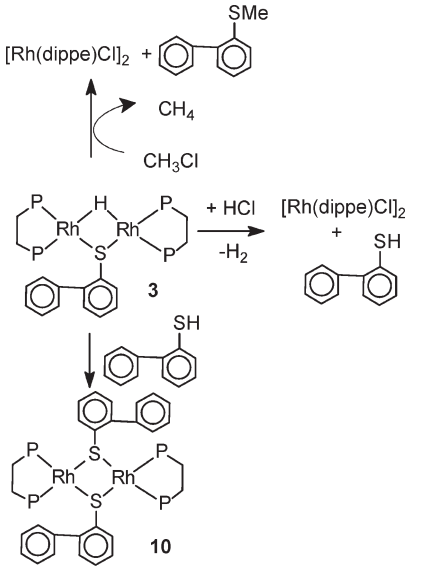


Figure 10. Plots of (a) k_{obs} versus [DBT] and (b) k_{obs} versus [phenoxythiin] for the reactions between **1** and DBT and phenoxythiin, respectively.

Scheme 3. Reactivity of $[Rh_2(dippe)_2(\mu\text{-}SC_{12}H_9)(\mu\text{-}H)]$ (3)



Kinetic Studies. Kinetic studies were conducted on the reactions between **1** and DBT, between **1** and phenoxythiin, and between **2** and DBT. However, good-quality data were obtained only for the reactions that involved **1**. The experiments were conducted under pseudo-first-order conditions in C_6D_6 at 100 °C, and all plots of $\ln([\mathbf{1}]_0/[\mathbf{1}])$ were linear, which is consistent with **1** reacting as a dimer with the substrate. The plots of [DBT] versus k_{obs} and [phenoxy] versus k_{obs} are shown in parts a and b of Figure 10, respectively. The second-order rate constants for the reactions with DBT and phenoxythiin are $[2.43(13)] \times 10^{-4}$ and $[3.54(5)] \times 10^{-4}$ M^{-1} s^{-1}, respectively.

Comparison of $[Rh_2(dippe)_2(\mu\text{-}Cl)(\mu\text{-}H)]$ (2) and $[Rh_2(dippe)_2(\mu\text{-}SC_{12}H_9)(\mu\text{-}H)]$ (3). Despite the fact that **3** is isoelectronic with **2**, it does not activate a C−S bond of DBT. Only decomposition occurs when it is exposed to prolonged heating at 100 °C in C_6D_6 in the presence of DBT. However, **3** does form products with other substrates, which is illustrated by Scheme 3. It reacts with 2 equiv of CH_3Cl to produce $[Rh(dippe)(\mu\text{-}Cl)]_2$, 2-biphenyl methyl sulfide, and CH_4. The addition of approximately 2 equiv of HCl to **3** also results in the formation of $[Rh(dippe)(\mu\text{-}Cl)]_2$, but it is now accompanied by H_2 and 2-phenylthiophenol. Finally, while it is unable to cleave a second C−S bond of DBT, **3** activates the thiol bond of 2-phenylthiophenol to make $[Rh(dippe)(\mu\text{-}SC_{12}H_9)]_2$ (**10**) and H_2. **10** has been synthesized independently from **1** plus 2-phenylthiophenol or from $[Rh(dippe)Cl]_2$ and lithium 2-phenylthiophenolate, and as expected, its single-crystal X-ray structure is very similar to that of the methyl derivative **5**.[21]

Conclusion

This study has demonstrated the ability of **1** to activate C−S bonds in dibenzothiophenes and phenoxythiin. **3** is unable to either activate a second molecule of DBT or completely extract sulfur from the substrate without the participation of additional **1**. Hydrogen (1 atm) was found to accelerate reactions with 4-MeDBT and 4,6-DMDBT, although it is not required by the reaction stoichiometry, and catalytic sulfur removal is not observed. In a competition between aryl-S and aryl-O cleavage, only the former is observed.

Experimental Section

All operations were performed under a nitrogen atmosphere unless otherwise stated. Benzene, THF, and hexanes were distilled from dark purple solutions of sodium benzophenone ketyl. $[Rh(COD)(\mu\text{-}Cl)]_2$ was purchased from Strem Chemical Co., dibenzothiophene and sodium hydrosulfide were purchased from Aldrich Chemical Co., and 2-phenylthiophenol was obtained from the laboratory of John C. DiCesare, University of Tulsa. All of these reagents were kept under vacuum overnight before using. Chloromethane was purchased from Aldrich Chemical Co., and dihydrogen was purchased from Air Products Co. 1,2-Bis(diisopropylphosphino)ethane was synthesized according to a literature method.[22] $[Rh(dippe)(\mu\text{-}H)]_2$ (**1**) and $[Rh_2(dippe)_2(\mu\text{-}Cl)(\mu\text{-}H)]$ (**2**) were synthesized as previously reported.[11] Neutral silica, 80−200 mesh, was heated to 200 °C under vacuum for 2 days and stored under nitrogen. A Siemens-SMART three-circle CCD diffractometer was used for X-ray crystal structure determinations. Elemental analyses were obtained by Desert Analytics or Robertson Microlit. All ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer. ^1H chemical shifts are reported relative to the residual proton resonance in the deuterated solvent. ^{31}P chemical shifts are reported relative to the signal of external 85% H_3PO_4. Mass spectra were recorded using a Shimadzu LCMS-2010 instrument.

Synthesis of $[Rh_2(dippe)_2(\mu\text{-}SC_{12}H_9)(\mu\text{-}H)]$ (3). DBT (55.8 mg, 0.303 mmol) was dissolved in a 25 mL C_6H_6 solution along with $[Rh(dippe)(\mu\text{-}H)]_2$ (0.222 g, 0.303 mmol). The reaction mixture was placed in a 50 mL ampule that was sealed with a Teflon valve and heated at 100 °C for approximately 10 days. The solution was transferred to a 50 mL round-bottom flask, and the solvent was removed under vacuum to leave a golden yellow solid. The solid was dissolved in a minimal amount of hexanes, and the solution was chilled to −30 °C to yield pure product (0.188 g, 67.8%). ^1H

(21) Oster, S. S.; Jones, W. D. *Inorg. Chim. Acta* **2004**, *357*, 1836.
(22) Cloke, F. G. N.; Gibson, V. C.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1988**, 2227.

NMR (C_6D_6, 25 °C): δ 8.22 (d, *o*-phenyl, J = 7.7 Hz, 2H), 7.97 (d, *m*-thiophenol, J = 7.7 Hz, 1H), 7.53 (t, *m*-phenyl, J = 7.5 Hz, 2H), 7.33 (t, *p*-phenyl, J = 7.3 Hz, 1H), 7.26 (m, *o*-thiophenol, 1H), 6.95 (t, *m*-thiophenol, J = 7.3 Hz, 1H), 6.84 (t, *p*-thiophenol, J = 7.4 Hz, 1H), 2.44 (m, $(CH_3)CH$, J = 6.9 Hz, 2H), 2.19 (bm, $(CH_3)CH$, 4H), 2.06 (m, $(CH_3)CH$, J = 7.1 Hz, 2H), 1.59−0.96 (m, $(CH_3)_2CH$, 48H), 1.39−1.32 (m, $P(CH_2)_2P$, 8H), −7.88 (m, Rh−*H*−Rh, J = 22.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 144.75 (m, *m*-thiophenol), 131.02 (s, *o*-phenyl), 129.52 (s, *o*-thiophenol), 127.13 (s, *m*-phenyl), 126.22 (s, *p*-phenyl), 124.43 (s, *p*-thiophenol), 123.90 (s, *m*-thiophenol), 28.49−27.47 (m, $(CH_3)_2CH$), 22.77 (m, $P(CH_2)_2P$), 22.13 (m, $P(CH_2)_2P$), 21.63 (d, $(CH_3)_2CH$, J = 7.8 Hz), 21.35 (d, $(CH_3)_2CH$, J = 6.9 Hz), 20.66 (s, $(CH_3)_2CH$), 20.02 (d, $(CH_3)_2CH$, J = 19.9 Hz), 19.47 (d, $(CH_3)_2CH$, J = 7.7 Hz), 19.34 (d, $(CH_3)_2CH$, J = 3.9 Hz), 18.65 (s, $(CH_3)_2CH$), 17.88 (d, $(CH_3)_2CH$), J = 21.1 Hz). Accidental overlap results in fewer signals than types of carbons. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 102.47 (m), 101.40 (m), 94.30 (m), 93.20 (m). Anal. Calcd (found) for $C_{40}H_{74}Rh_2P_4S$: C, 52.40 (52.03); H, 8.14 (8.09). APCI-MS (+): m/z 915.15 ($[M - H]^+$), 916.15 ($[M]^+$)

Synthesis of [Rh$_2$(dippe)$_2$(μ-S-MeC$_{12}$H$_8$)(μ-H)] (4). 4-Methyldibenzothiophene (0.0117 g, 0.0590 mmol) and [Rh(dippe)(μ-H)]$_2$ (0.0144 g, 0.0197 mmol) were dissolved in 1 mL of toluene and placed in a J. Young NMR tube. The reaction mixture was heated at 135 °C and monitored periodically by ^{31}P NMR spectroscopy. The reaction was complete after 6.5 days, as the solution color changed from emerald green to dark red. The toluene was removed by vacuum. The solid was dissolved in pentanes and eluted through a Pasteur pipet containing glass wool and 2 in. of silica. A 10 mL portion of pentanes eluent was collected as a fraction, containing the excess thiophene. A 20/80 THF/pentanes solution was used to elute **4**, which was then evaporated to dryness to leave a golden yellow solid (0.0147 g, 80%). ^1H NMR (C_6D_6, 25 °C): δ 8.12 (d, J = 7.3 Hz, 2 H), 7.45 (t, J = 7.6 Hz, 2 H), 7.29 (t, J = 7.4 Hz, 1 H), 7.24 (m, 1 H), 7.03 (m, 2 H), 2.94 (s, CH_3, 3 H), 2.38 (m, $(CH_3)CH$, 2 H), 2.14 (bm, $(CH_3)CH$, 4 H), 1.97 (m, $(CH_3)CH$, 2 H), 1.49−0.61 (m, 56 H), −8.29 (m, Rh−*H*−Rh, 1 H). $^{13}C\{^1H\}$ NMR (THF-d_8, 25 °C): δ 147.17 (s), 145.76 (s), 145.63 (s), 142.97(s), 132.34 (s), 130.28 (s), 128.21 (s), 127.51 (s), 126.64 (s), 124.36 (s), 29.77−28.79 (m), 23.18 (m), 22.60 (d, J = 7.8 Hz), 21.54 (d, J = 6.9 Hz), 20.68 (d, J = 5.3 Hz), 20.38 (s), 19.74 (s), 19.17 (m), 18.36 (d, J = 3.2 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 99.41 (dd, J = 175, 27 Hz), 94.08 (m), 93.21 (m). Anal. Calcd (found) for $C_{41}H_{76}Rh_2P_4S$: C, 52.90 (53.14); H, 8.23 (8.07). APCI-MS (+): m/z 929.15 ($[M - H]^+$), 930.15 ($[M]^+$).

Synthesis of [Rh(dippe)(μ-S-MeC$_{12}$H$_8$)]$_2$ (5). The complex was formed using an excess of 4-methyldibenzothiophene (10 equiv, 96% purity) relative to [Rh(dippe)(μ-H)]$_2$, when heated in C_6D_6 at 100 °C for 1 week. The solid is formed as a minor product (approximately 14% by ^{31}P NMR). Due to its low solubility in hydrocarbons, it can be isolated by extracting out **4** with hexanes. ^1H NMR (THF-d_8, 25 °C): δ 7.97 (d, J = 7.5 Hz, 4 H), 7.29 (m, 4 H), 7.19 (t, J = 7.4 Hz, 4 H), 7.03 (d, J = 7.3 Hz, 2 H), 6.94 (t, J = 7.4 Hz, 2 H), 4.68 (s, 6 H), 1.43 (m, 4 H), 1.19 (dd, J = 7.2, 14.5 Hz, 12 H), 1.13 (m, 4 H), 1.02 (dd, J = 7.0, 11.8 Hz, 12 H), 0.87 (m, 8 H), 0.66 (t, J = 7.5, 8.3 Hz, 12 H), 0.31 (dd, J = 7.0, 14.9 Hz, 12 H). $^{31}P\{^1H\}$ NMR (THF-d_8, 25 °C): δ 89.93 (d, J_{Rh-P} = 175 Hz).

Synthesis of [Rh$_2$(dippe)$_2$(μ-S-Me$_2$C$_{12}$H$_7$)(μ-H)] (6). 4,6-Dimethyldibenzothiophene (0.0545 g, 0.257 mmol) and [Rh(dippe)-(μ-H)]$_2$ (0.0108 g, 0.0147 mmol) were placed in a J. Young NMR tube, and 1 mL of toluene was added. The sample was freeze−pump−thaw degassed (3×) to remove nitrogen, and 1 atm of hydrogen was then added. The reaction mixture was heated to 135 °C and monitored periodically by ^{31}P NMR spectroscopy. The reaction was complete after 8.5 days, as the solution color changed from emerald green to dark red. The toluene was removed by vacuum, and the dark red-gray residue was extracted with hexanes (3 × 1 mL) and concentrated to dryness. The solid was dissolved in a minimum amount of hexanes and eluted through a Pasteur pipet containing glass wool and 2 in. of silica. A 20 mL portion of hexanes eluent was collected as a fraction, containing the excess thiophene. Benzene (5 mL) was used to elute **6**, which was then evaporated to dryness to leave a dark yellow solid (0.0033 g, 24%). ^1H NMR (THF-d_8, 25 °C): δ 7.73 (m, 1 H), 7.47 (d, J = 7.5 Hz, 1 H), 7.19 (t, J = 7.4 Hz, 1 H), 7.01 (d, J = 7 Hz, 1 H), 6.89 (d, J = 7 Hz, 2 H), 6.83 (m, 2 H), 2.62 (s, CH_3, 3 H), 2.37 (s, CH_3, 3 H), 2.34 (m, $(CH_3)CH$, 2 H), 2.16 (m, $(CH_3)CH$, 4 H), 1.98 (m, $(CH_3)CH$, 2 H), 1.51−0.62 (m, 56 H), −8.24 (m, Rh−*H*−Rh, 1 H). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 146.92 (s), 145.70 (s), 145.50 (s), 142.57(s), 136.40 (s), 133.17 (s), 132.66 (s), 132.26 (s), 127.84 (s), 127.56 (s), 127.24 (s), 124.45 (s), 29.70−28.46 (m), 22.84 (m), 22.44 (d, J = 7.2 Hz), 22.04 (s), 21.38 (s), 20.69 (s), 20.35 (s), 19.62 (s), 19.23 (s), 19.07 (s), 18.38 (s). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 99.16 (dd, J = 173, 28 Hz), 93.94 (m), 92.83 (m). APCI-MS (+): m/z 943.25 ($[M - H]^+$), 944.20 ($[M]^+$).

Synthesis of [Rh$_2$(dippe)$_2$(μ-SH)(μ-H)] (7). **7** could not be isolated in pure form; all relevant data are taken from a mixture of **7**, **6**, and 4,6-Me$_2$DBT. ^1H NMR (C_6D_6, 25 °C): δ −0.02 (s, 1 H), −7.84 (m, 1 H). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 110.08 (dd, J = 181, 29 Hz), 91.52 (m), 90.56 (m). An X-ray structure (disordered, modeled as a 50/50 cocrystallization of **1** and **7**) is reported in the Supporting Information.

Synthesis of [Rh$_2$(dippe)$_2$(μ-S-C$_6$H$_4$OC$_6$H$_5$)(μ-H)] (8). Phenoxythiin (40.3 mg, 0.20 mmol) and Rh(dippe)(μ-H)]$_2$ (147.4 mg, 0.20 mmol) were dissolved in 25 mL of C_6H_6 and placed in a 50 mL Schlenk flask. The reaction mixture was heated to 80 °C for 14 days. The solution was transferred to a 50 mL round-bottom flask, and the solvent was removed under vacuum to leave a dark yellow solid. The solid was dissolved in a minimal amount of hexanes, and the solution was chilled to −30 °C to yield pure product (58.2 mg, 31.0%). ^1H NMR (C_6D_6, 25 °C): δ 7.74 (dd, J = 7.7, 1.2 Hz, 1H), 7.26−7.19 (m, 4H), 6.93−6.90 (m, 1H), 6.87−6.85 (m, 1H), 6.73 (td, J = 7.1, 1.2 Hz, 1H), 6.62 (td, J = 7.1, 1.2 Hz, 1H), 2.46−1.80 (bm, 8H), 1.66−0.60 (m, 56H), −7.81 (m, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 144.81 (s), 129.29 (s), 124.32 (s), 121.83 (s), 121.59 (s), 119.66 (s), 117.65 (s), 28.28 (s), 28.08 (s), 26.38 (s), 22.83 (m), 21.87 (m), 21.47 (s), 21.41 (s), 19.66 (s), 18.71 (s), 15.73 (s), 15.46 (s). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 102.54−102.36 (m), 101.46−101.30 (m), 94.34−93.84 (m), 93.25−92.85 (m). Anal. Calcd (found) for $C_{40}H_{74}Rh_2P_4OS$: C, 51.50 (51.44); H, 8.00 (8.32).

Synthesis of [Rh$_2$(dippe)$_2$(μ-Cl)(μ-SC$_{12}$H$_9$)] (9). Lithium 2-(phenylthio)phenolate (0.095 g, 0.490 mmol) in THF was transferred by cannula to a stirred THF suspension of [Rh(dippe)(μ-Cl)]$_2$ (0.392 g, 0.489 mmol). After approximately 0.5 h, the solvent was reduced under vacuum and the solution was vacuum-filtered through neutral alumina. The solution was chilled to −30 °C to yield a yellow precipitate. The precipitate was separated from the supernatant by vacuum filtration, washed three times with hexanes, and then dried under vacuum (218.9 mg, 47.0%). ^1H NMR (C_6D_6, 25 °C): δ 9.98 (d, J = 7.9 Hz, 1H), 8.04 (d, J = 7.6 Hz, 2H), 7.33 (bt, J = 7.6 Hz, 2H), 7.26 (d, J = 7.3 Hz, 1H), 7.19−7.13 (m, 2H), 7.00 (t, J = 7.2 Hz, 1H), 2.53−0.46 (bm, 64H). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 140.06 (s), 131.14 (s), 130.37(s), 126.79 (s), 125.77 (s), 125.72 (s), 123.83 (s), 27.36 (s), 27.14 (s), 22.93 (m), 21.03 (m), 18.70 (s). Accidental overlap results in fewer signals than types of carbons. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 99.61 (ddd, $J_{P-Rh(1)}$ = 200.2 Hz, J_{P-P} = 28.1 Hz, $J_{P-Rh(2)}$ = 5.5 Hz), 92.50 (ddd, $J_{P-Rh(1)}$ = 172.9 Hz, J_{P-P} = 28.1 Hz, $J_{P-Rh(2)}$ = 4.0 Hz). Anal. Calcd (found) for $C_{40}H_{73}Rh_2P_4SCl$: C, 50.50 (50.42); H, 7.74 (7.81).

Alternative Synthesis of [Rh$_2$(dippe)$_2$(μ-Cl)(μ-SC$_{12}$H$_9$)] (9). Approximately 5 equiv of 2-(phenylthio)phenol (9.7 mg, 0.053 mmol) was dissolved in a C_6D_6 solution of **2** (8.1 mg, 0.011 mmol). The resulting mixture was placed in a resealable NMR tube for analysis. **9** forms immediately (43%) as the major product.

Alternative Synthesis of [Rh$_2$(dippe)$_2$(μ-Cl)(μ-SC$_{12}$H$_9$)] (9). Approximately 10 equiv of dibenzothiophene (19 mg, 0.10 mmol) in C_6D_6 was added to a resealable NMR tube that contained a C_6D_6 solution of **2** (8.0 mg, 0.010 mmol). The contents of the

tube were heated at 100 °C for 55 days to completely consume **2** and produce **9** in approximately 28% yield by integration of ^{31}P NMR signals.

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Supporting Information Available: Text, tables, and CIF files giving details of the X-ray structure determinations and crystal data for **4**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org. The structures are available in the Cambridge Crystallographic Database as CCDC #748860−748863, 767419, and 767420.