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Homogeneous models of thiophene HDS reactions. Selectivity in thiophene C—S cleavage and thiophene reactions with dinuclear metal complexes

William D. Jones,* David A. Vicic, R. Martin Chin, James H. Roache and Andy W. Myers

Department of Chemistry, University of Rochester, Rochester, NY 14627, U.S.A.

Abstract—The reactive 16 e^- metal fragment $[(C_5Me_5)Rh(PMe_3)]$ inserts into a wide variety of thiophene C—S bonds. The structures of the thiophene, benzothiophene and dibenzothiophene insertion complexes have been determined. While the thiophene complex adopts a planar six-membered ring structure the other metallacycles are bent and all molecules possess localized diene structures. The mechanism of C—S cleavage was found to proceed by way of initial sulfur coordination. 2-Methylbenzothiophene gives a kinetic product resulting from cleavage of the sulfur–vinyl bond, but then rearranges to cleave the sulfur–aryl bond. A number of substituted dibenzothiophenes were examined, showing little electronic effect of substituents, but showing a large steric effect of substituents at the 4 and 6 positions. 4,6-Dimethyldibenzothiophene does not undergo cleavage, but instead forms an S-bound complex. Reactions of a cobalt analog, $(C_5Me_5)Co(C_2H_4)_2$ with thiophenes also lead to C—S cleaved products and the use of a dinuclear iridium system produces a butadiene complex in which both C—S bonds have been cleaved. © 1997 Elsevier Science Ltd

Keywords: HDS; hydrodesulfurization; modelling; homogeneous catalysis.

The hydrodesulfurization of petroleum is one of several steps in the hydrotreating of oil in which sulfur is removed from thiols and thiophenes as H_2S [1]. The process uses a supported molybdenum sulfide catalyst containing cobalt and operates under pressures of 150–600 psi hydrogen at 300–450°C. The sulfur content in oil of 1–5% is reduced to 0.1% in gasoline and future sulfur limits may be reduced to as little as 0.003–0.04%.

Important studies performed by Kabe, Ishihara and Tajima using a mixture of polyaromatic sulfur-containing compounds in light oil with a commercial HDS catalyst under typical operating conditions show the limitations of the current generation of catalysts [2]. Figure 1 shows a GC trace of these sulfur containing compounds prior to treatment. Figure 2 shows how this original mixture of compounds is changed upon HDS treatment at temperatures of 350–390°C. While all of the benzothiophenes are removed, it can be observed that specific dibenzothiophenes are difficult to desulfurize. These include 4-methyldibenzothiophene, 4,6-dimethyldibenzothiophene and other polyalkylated dibenzothiophenes.

Work in our laboratory has focused upon homogeneous models for the desulfurization of thiophenes [3–12]. Mechanistic studies might provide insights into the workings of the heterogeneous catalyst systems that could lead to new catalyst developments with improved desulfurization characteristics. In this manuscript, results with homogeneous systems that cleave the C—S bonds of thiophenes are summarized.

RESULTS AND DISCUSSION

The reactive fragment $[(C_5Me_5)Rh(PMe_3)]$ produced by heating solutions of $(C_5Me_5)Rh(PMe_3)$ (Ph)H has been found to insert into a wide variety of thiophene C—S bonds (Scheme I) [3]. One of the first products to be structurally characterized was the adduct formed with 2,5-dimethylthiophene. This

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*Author to whom correspondence should be addressed.

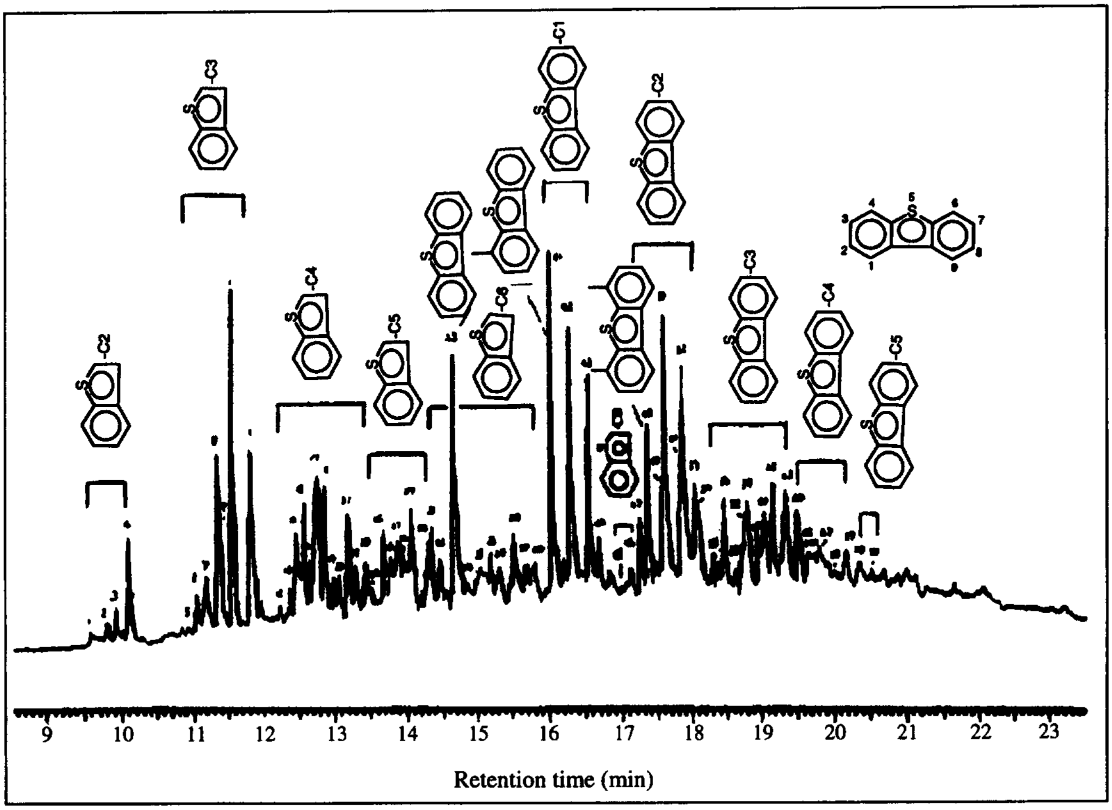
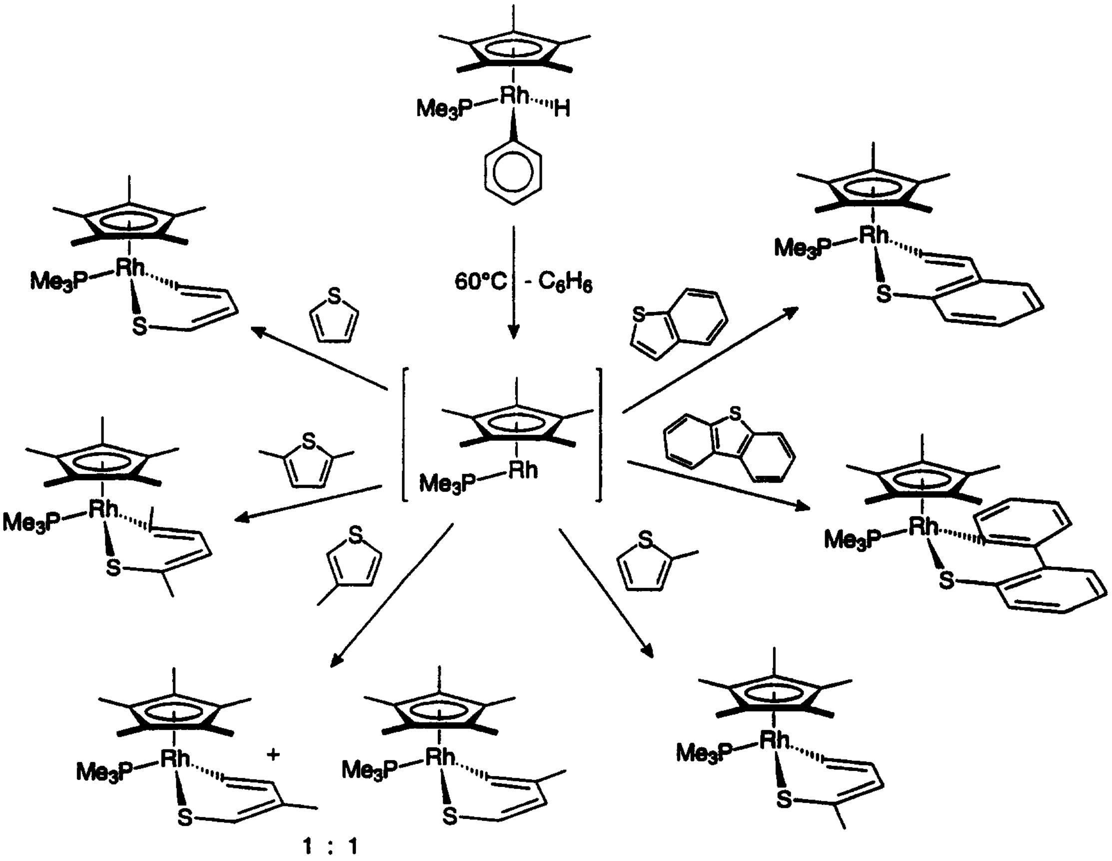


Fig. 1. GC trace of polyaromatic sulfur containing compounds in light oil (reproduced with permission from [2]).



Scheme I.

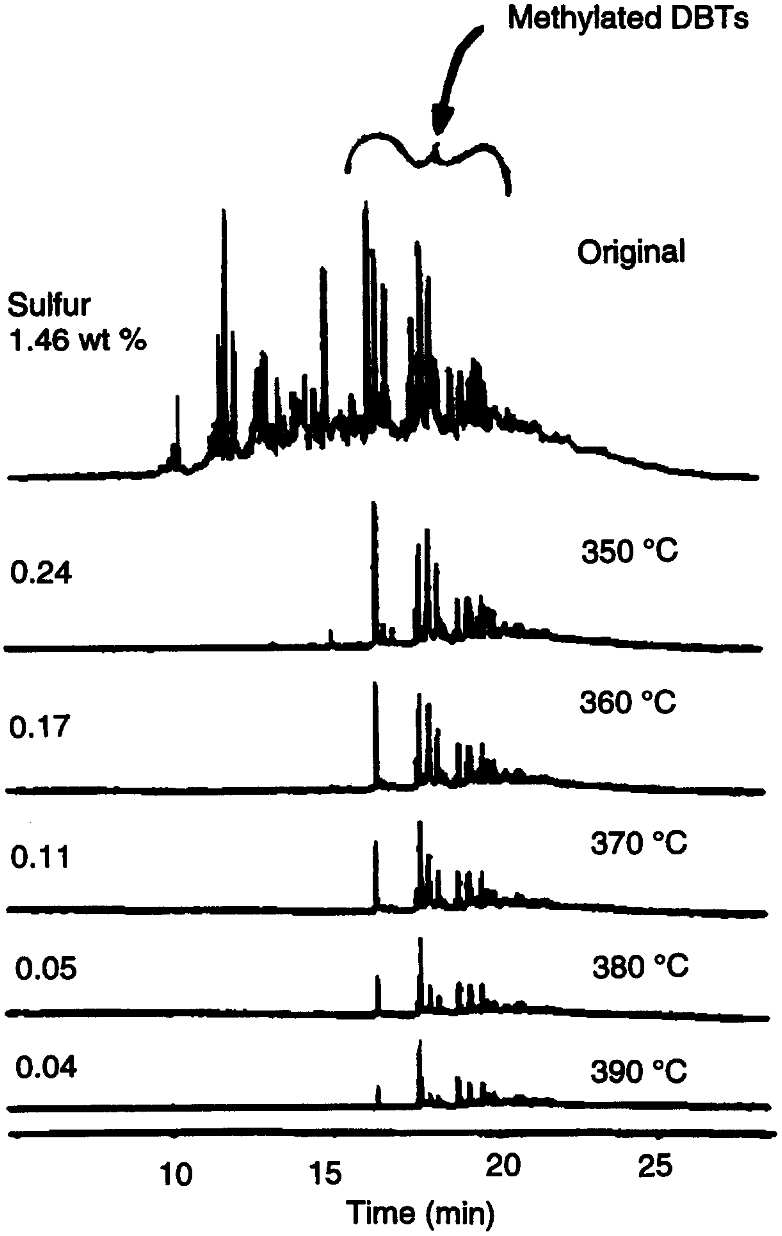


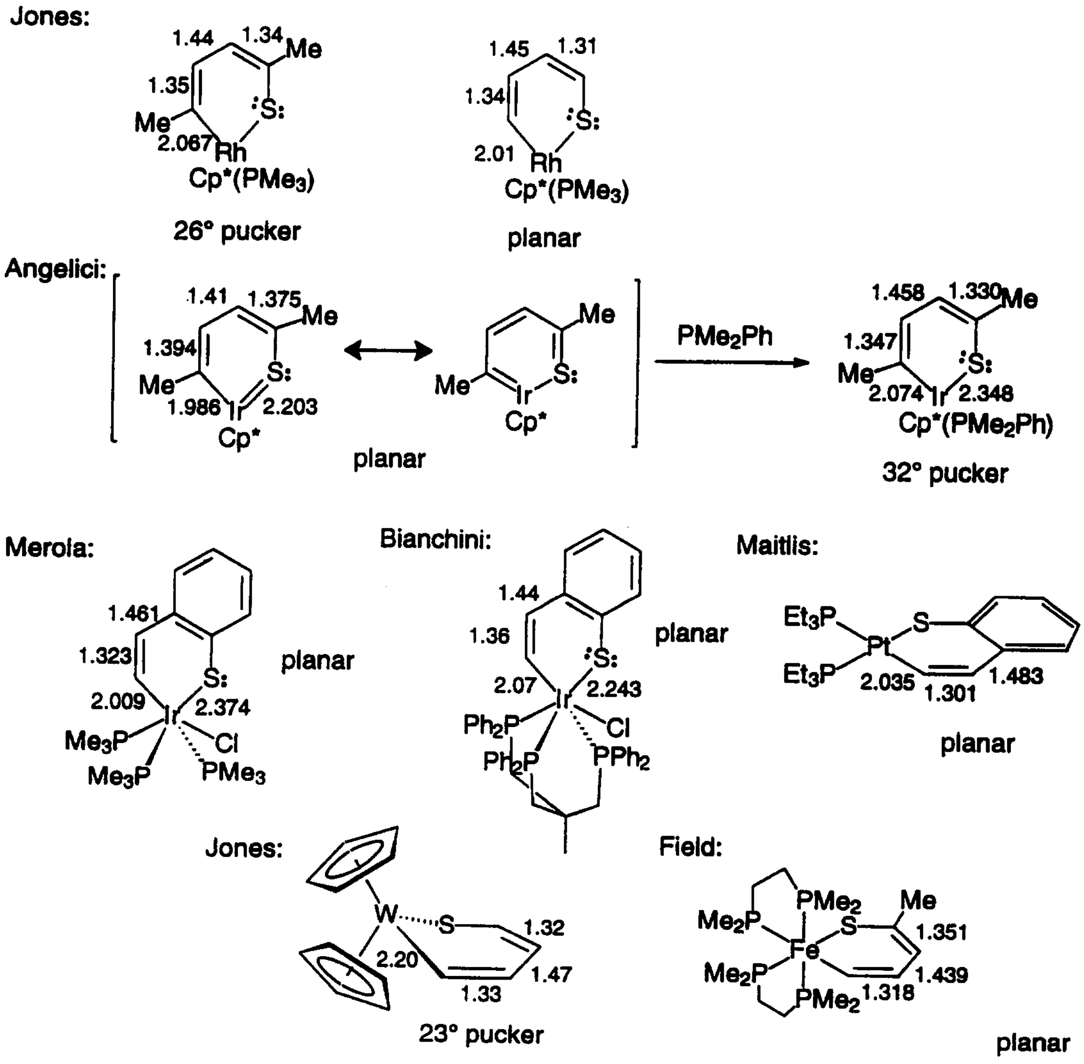
Fig. 2. GC trace of desulfurized oil at each temperature (reproduced with permission from [2]).

C—S insertion product shows a bent six-membered ring in which the sulfur and butadiene portion of the ring form a plane that is oriented at an angle of 26° to the rhodium–sulfur–C_α plane. The distances around the ring are consistent with a localized bonding structure (Scheme II). In contrast, the structure of the parent thiophene insertion product displays a planar metallathiabenzene ring, although once again bond length alternation is seen in the diene portion of the ring [13].

A number of other mononuclear transition metal complexes have been found to be capable of inserting into the C—S bonds of thiophenes, benzothiophenes and dibenzothiophenes [14–20]. As shown in Scheme II, the products formed have been characterized as containing in some cases a delocalized metallathiabenzene ring and in others as an isolated thiobutadiene fragment. In most examples, the six-membered ring formed upon insertion is planar. Delocalization of the π-electrons into an electron deficient metal has been cited as a reason for the molecule adopting a planar geometry, although steric factors seem to be more important in determination of the planarity [14,16].

The mechanism of insertion of $[(C_5Me_5)Rh(PMe_3)]$ into the C—S bond of thiophene has been investigated using a variety of labeling techniques [4]. Attempts to directly observe an intermediate in the reaction at low temperature failed. Irradiation of $(C_5Me_5)Rh(PMe_3)H_2$ in the presence of thiophene at −40°C results in the formation of a 3:1 ratio of $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-C,S-}C_4H_4S)$ and $(C_5Me_5)Rh(PMe_3)(2\text{-thienyl})H$. Upon warming the sample, the 2-thienyl hydride complex converts to the C—S insertion complex. If this rearrangement is carried out in the presence of an excess of thiophene-d_4, no incorporation of the deuterated thiophene into the product is observed, indicating that the rearrangement takes place without dissociation of the thiophene from the metal center.

The rearrangement of the 2-thienyl deuteride complex was examined by the reaction of $(C_5Me_5)Rh(PMe_3)Cl_2$ with 2-thienyllithium followed



Scheme II.

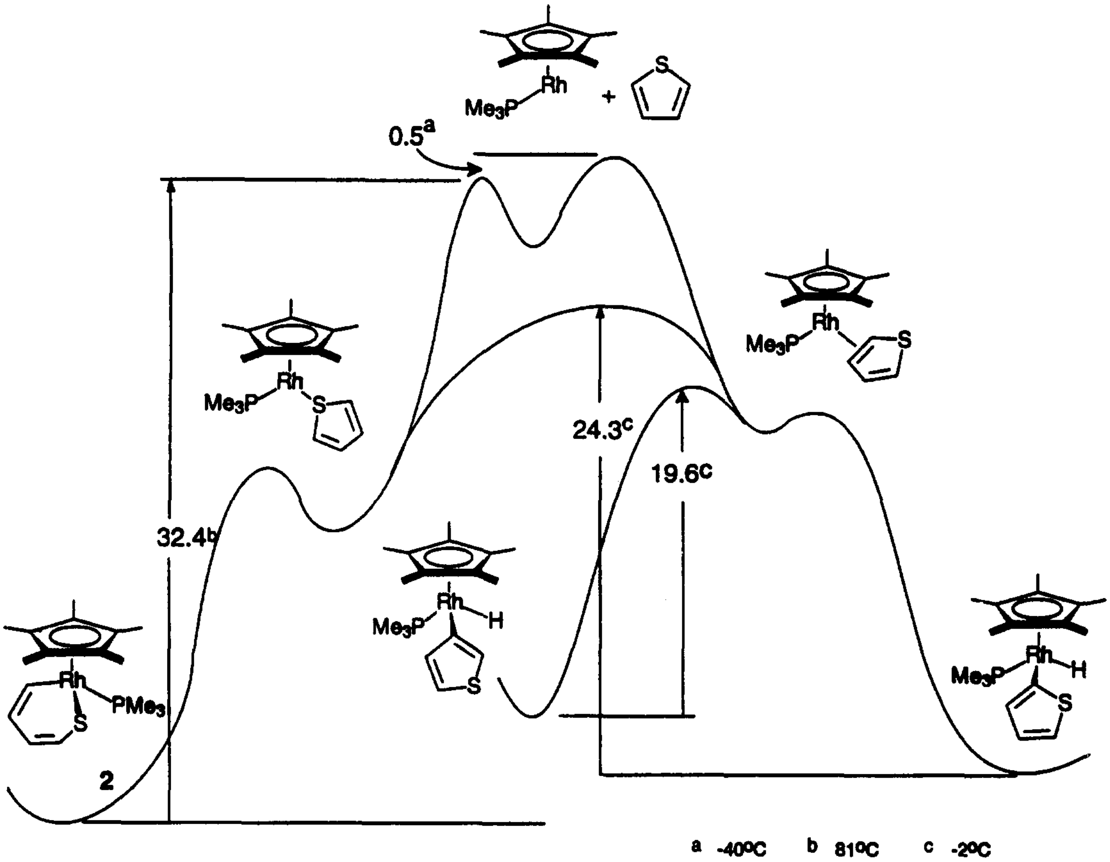


Fig. 3. Free energy diagram for the interaction of the fragment $(C_5Me_5)Rh(PMe_3)$ with thiophene.

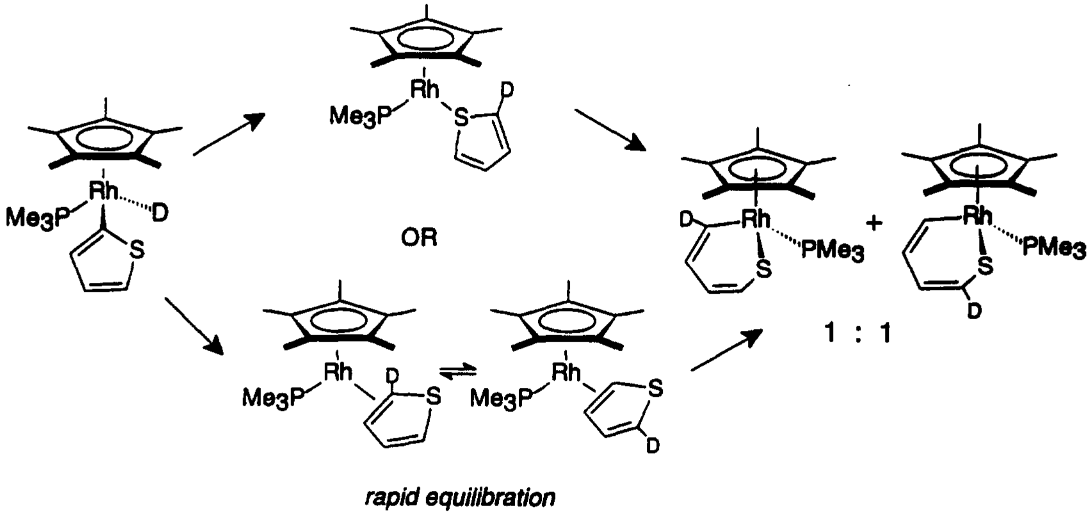
by *sec*-butylborodeuteride. Rearrangement to the C—S insertion complex takes place in a nonregiospecific fashion, producing a 1:1 mixture of the two deuterated isomers. This observation could be interpreted in terms of occurring either through a symmetrical S-bound intermediate or by way of an η^2-thiophene complex that rapidly equilibrates between the double bonds of the thiophene (Scheme III).

A second labeling experiment proceeded similarly using 3-thienyllithium followed by *sec*-butylborodeuteride to generate the 3-thienyl deuteride complex. Rearrangement of the 3-thienyl deuteride complex to the 2-thienyl hydride complex proceeds regiospecifically, i.e. only the 3-deutero-2-thienyl product is formed (Scheme IV). A second, slower rearrangement to the C—S insertion product then proceeds nonregiospecifically, as observed in the previous experiment. The η^2-thiophene intermediate shown in Scheme IV explains the regiospecificity, since the metal remains on a single double bond in the thiophene molecule. Only by proceeding on to the S-bound complex does the molecule become symmetric and then the C—S bond is broken.

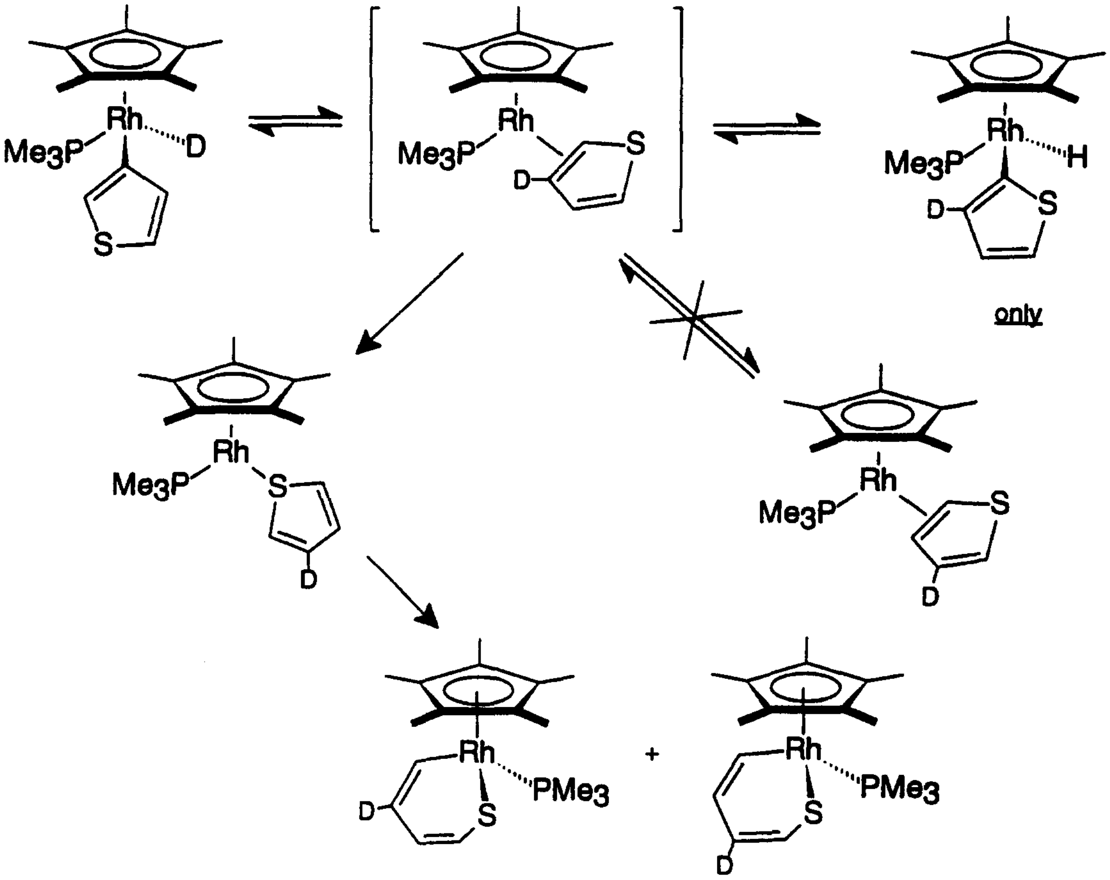
These reactions are summarized in the free energy diagram shown in Fig. 3. Note that the figure shows the preferred kinetic selectivity for C—S bond cleavage over C—H bond activation and that the C—S insertion product is more stable than the C—H insertion product. The presence of the η^2-thiophene and S-thiophene intermediates and their connections with the observed species are also made clear. Support for this reaction sequence is found from *ab initio* calculations done by Sargent, which indicates the presence of a low energy pathway from the S-thiophene complex to the C—S insertion complex [21].

Only one thiophene examined did not undergo C—S cleavage, tetramethylthiophene. Reaction with $(C_5Me_5)Rh(PMe_3)PhH$ leads to the formation of the S-bound thiophene complex $(C_5Me_5)Rh(PMe_3)(S\text{-}C_4Me_4S)$. The reason for this lack of reactivity has not been determined, but possibilities include a "buttressing effect" that increases the steric interactions of the methyl groups in the six-membered ring or a combined electronic effect of the four methyl groups that changes the energetics of the interaction. A simple steric effect of a methyl group on the carbon attached to sulfur can be ruled out, since 2,5-dimethylthiophene is readily cleaved.

Benzothiophene was also found to undergo cleavage upon reaction with $(C_5Me_5)Rh(PMe_3)PhH$. The product formed arises from insertion of rhodium into the sulfur–vinyl bond only. An X-ray structure of this product shows puckering of the metallacycle ring and bond length alternation consistent with localized bonding [13].

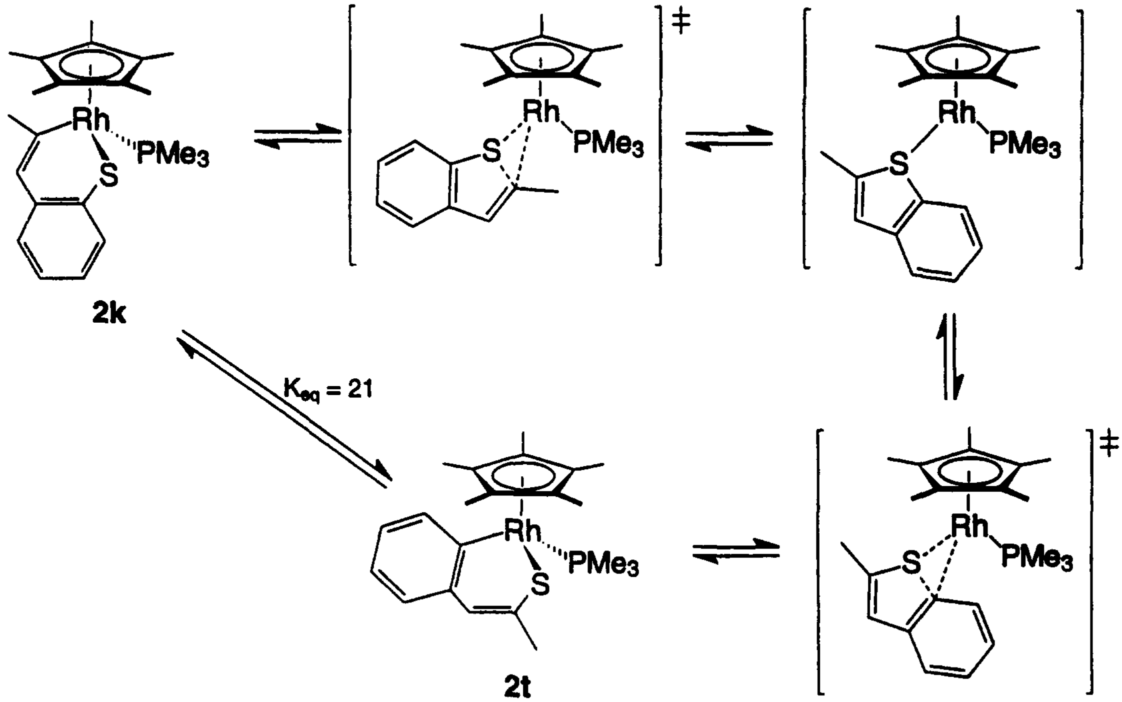


Scheme III.



Scheme IV.

Reaction of $(C_5Me_5)Rh(PMe_3)PhH$ with 2-methylbenzothiophene results in a similar product with cleavage of the sulfur–vinyl bond. In this case, however, continued heating of the sample leads to the rearrangement to a more stable product in which the metal has inserted into the sulfur-aryl bond (Scheme V). Apparently, the methyl group destabilizes the kinetic product sufficiently to allow it to rearrange to the thermodynamically preferred product. The origin of this preference can be attributed to the greater bond strength of a rhodium–aryl bond compared with a rhodium–vinyl bond. X-ray examination of both of



Scheme V.

these adducts show puckered, localized bonding structures. The rearrangement of the kinetic product to the thermodynamic product is intramolecular, as addition of 10 equiv. of thiophene during the rearrangement does not result in the formation of any of the thiophene C—S insertion product. The selectivities and interconversion can be accounted for in terms of the choices available to the S-bound complex, which is formed reversibly. At equilibrium, there is a 21 : 1 ratio of thermodynamic to kinetic product [12].

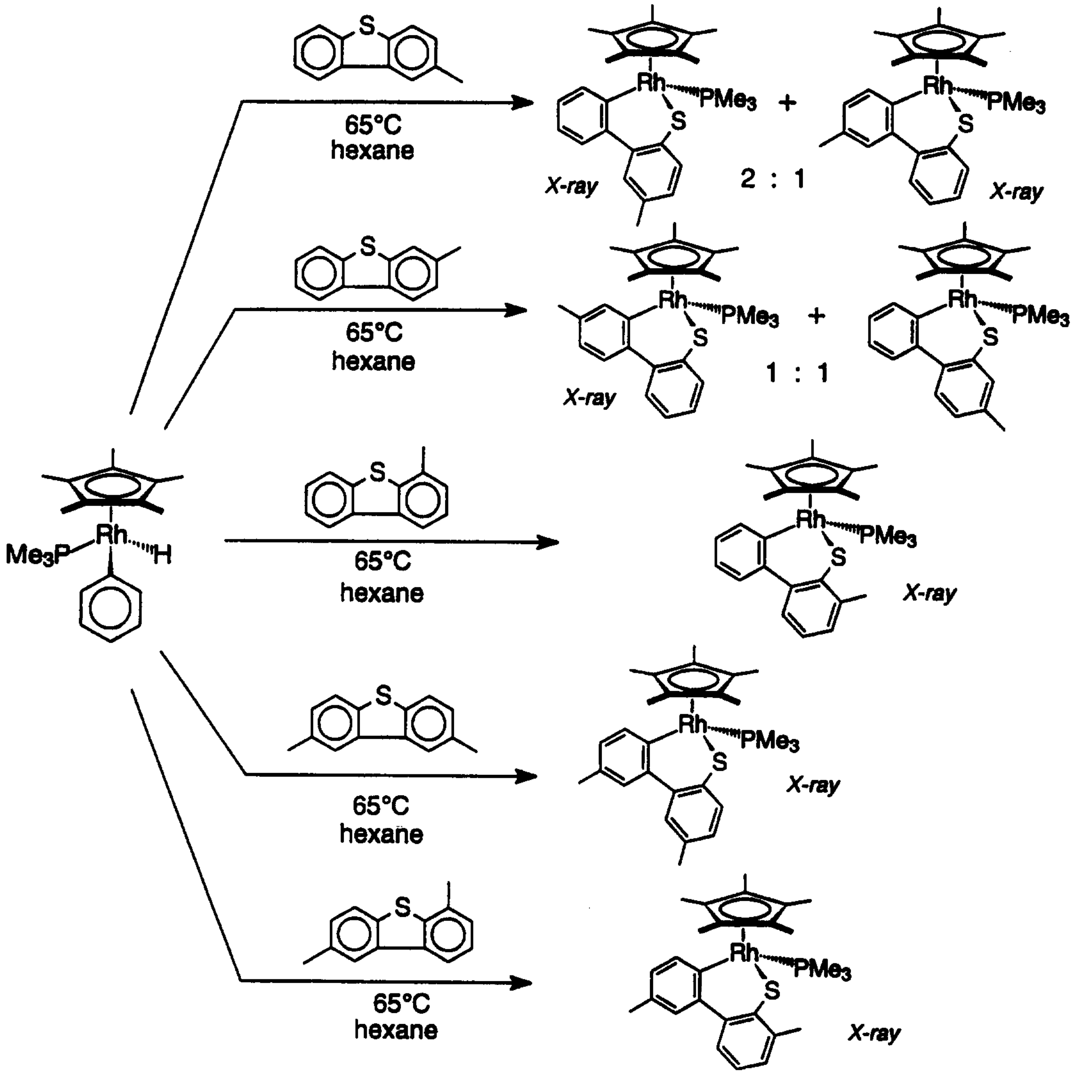
Dibenzothiophene also reacts with $(C_5Me_5)Rh(PMe_3)PhH$ to give a C—S insertion product. Examination of the structure shows a strongly puckered metallathiabenzene ring and a twisting along the biphenyl axis [13]. Similar insertion reactions are seen with a variety of substituted dibenzothiophenes. In an effort to determine the effects of methyl substitution, reactions of 2-methyldibenzothiophene, 3-methyldibenzothiophene and 4-methyldibenzothiophene with $(C_5Me_5)Rh(PMe_3)PhH$ were examined. While the former two substrates showed little preference for cleavage of one C—S bond *versus* the other, the latter substrate showed exclusive cleavage of the C—S bond away from the adjacent methyl substituent. A similar observation was made with disubstituted 2,6-dimethyldibenzothiophene (Scheme VI) [22].

Heteroatom substituents on dibenzothiophene were found to have only modest effects on the insertion selectivity. Reactions of $(C_5Me_5)Rh(PMe_3)PhH$ with 2-methoxy-, 2-fluoro-, 2-bromo-, 2-cyano and 2-trifluoromethyldibenzothiophene were found to give mixtures of both insertion products, indicative of only slight electronic directing effect in the cleavage reaction (Scheme VII). Two benzonapthothiophenes were examined. Reaction with one isomer gave only a single C—S insertion product that was characterized by X-ray crystallography as resulting from insertion away from the bulky naphthalene ring (Scheme VIII). Reaction with a second isomer gave a 2 : 1 ratio of products, since steric interference of the naphthalene ring was not problematic [22].

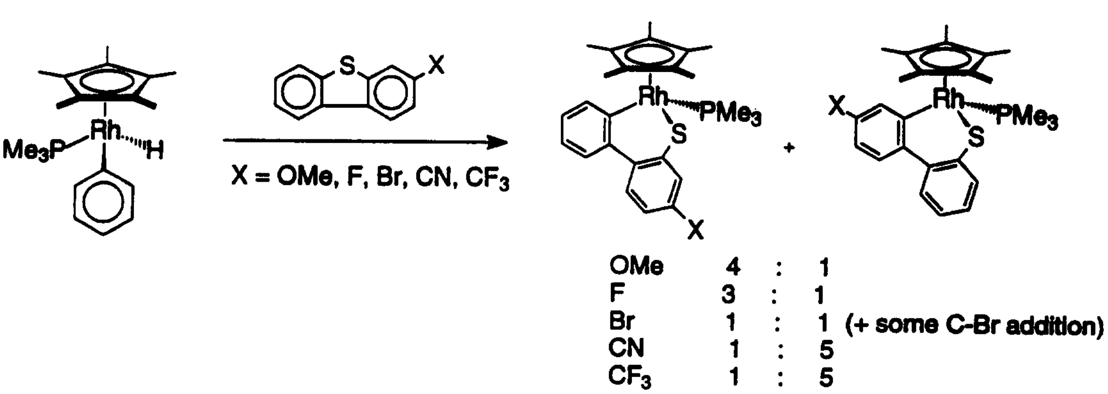
Most of the above dibenzothiophene products were characterized by X-ray crystallography, since this proved to be the only reliable method for determining the direction of insertion. In all cases except thiophene, puckering of the six-membered ring was observed. For the dibenzothiophenes, a twisting along the biphenyl linkage was also observed. Table 1 summarizes these structural features for the complexes.

Only one dibenzothiophene complex did not undergo C—S cleavage upon reaction with $(C_5Me_5)Rh(PMe_3)PhH$. 4,6-Dimethyldibenzothiophene reacts to give an S-bound complex, which is labile, reacting with PMe_3 to give $(C_5Me_5)Rh(PMe_3)_2$ plus free thiophene ($\Delta G^{\ddagger} = 24.5$ kcal mol^{-1}, 25°C). A similar S-bound complex is formed with 4,6-diethyldibenzothiophene.

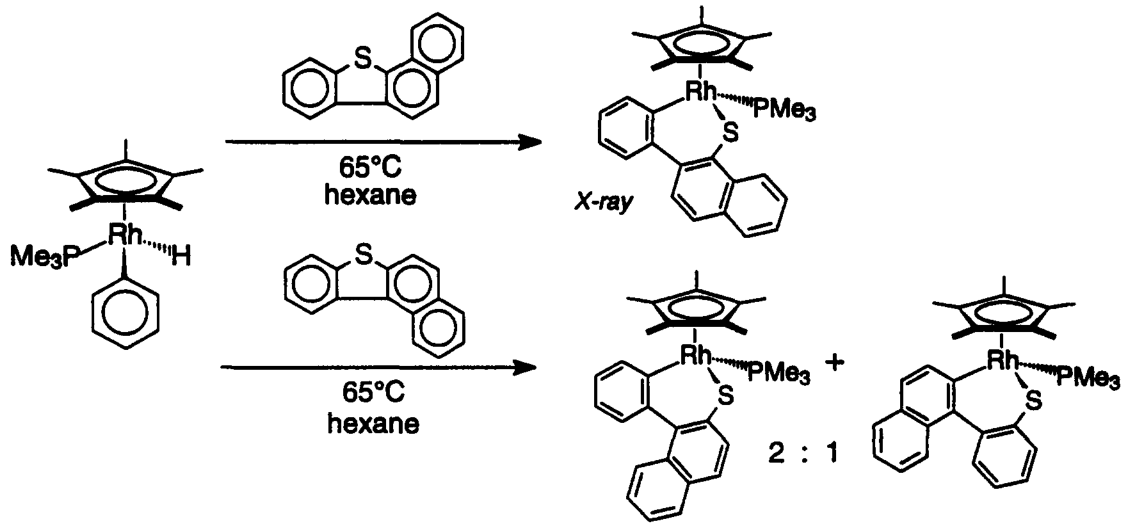
The above reactivity patterns of substituted dibenzothiophenes are remarkably similar to that observed with the commercial Mo/Co industrial catalysts [1,2]. There is difficulty associated with cleavage of a dibenzothiophene C—S linkage when the adjacent carbon bears an alkyl substituent. No such steric barriers exist for substituted thiophenes or benzothiophenes, which are readily desulfurized and also react readily with $(C_5Me_5)Rh(PMe_3)PhH$. The simi-



Scheme VI.



Scheme VII.



Scheme VIII.

larity of reactivity suggests that a similar mechanism may be operative in the homogeneous and heterogeneous cases, i.e. it is the S-bound complex that is the immediate precursor of C—S bond cleavage. The similarity ends here, however, in that the $(C_5Me_5)Rh(PMe_3)$ fragment can only cleave one C—S bond and then becomes unreactive towards further cleavages or reaction with hydrogen.

The lack of further reactivity of the rhodium C—S insertion products can be attributed to the fact that the products are nonlabile, coordinatively saturated Rh^{III} complexes. In an attempt to produce a product with enhanced reactivity, the reactions of $(C_5Me_5)Co(C_2H_4)_2$ with thiophene [6], benzothiophene [23] and dibenzothiophene were examined [10]. In all three cases, a similar product was observed upon heating the cobalt complex (70°C) in the presence of the substrate. The product can be described as a C—S cleavage adduct similar to those found with $(C_5Me_5)Rh(PMe_3)$, except that the coordination site occupied by PMe_3 is replaced by a bridging $(C_5Me_5)Co$ fragment (Scheme IX). Similar structures were observed in the reaction of benzothiophene with $Fe_3(CO)_{12}$ [24] and of $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$ [20].

These molecules display an interesting fluxional process that equilibrates the two inequivalent C_5Me_5 rings. These two rings differ only due to the bonding of the C_β carbon, since the sulfur and C_α both bridge the two cobalt centers. The migration of C_β from one metal to the other equilibrates the two C_5Me_5 rings. This process occurs most readily for the dibenzothiophene complex, and less easily for the thiophene complex, since η^2-coordination of the olefinic portion of the molecule disrupts the aromaticity in the dibenzothiophene.

Since the rhodium complex was only capable of breaking one C—S bond, and the cobalt complex showed a tendancy to form a dinuclear complex, a binuclear iridium complex was next examined for reactivity with thiophene. The complex $[(C_5Me_5)IrH_3]_2$ was found to react with thiophene in the presence of a hydrogen acceptor to give a product in which both C—S bonds had been cleaved to give a butadiene ligand and the sulfur remained as a μ-sulfido ligand [5]. Two intermediates are seen in the course this reaction, each of which grows in and then goes away. Scheme X shows the proposed mechanism for the formation of the butadiene containing product [7]. The role of the *tert*-butylethylene is believed to be to produce the coordinatively unsaturated and reactive iridium complex, $[(C_5Me_5)IrH]_2$. Heating $[(C_5Me_5)IrH_3]_2$ alone under vacuum produces $[(C_5Me_5)IrH_2]_2$, which can also be used to desulfurize thiophene, but the reaction is still slow without added *tert*-butylethylene. Coordination of sulfur followed by insertion of Ir^I into the C—S bond gives intermediate A, a structure similar to that observed with cobalt but now with hydride ligands present. Reductive elimination of the vinyl hydride gives a butadienethiolate ligand, which can then coordinate to the coordinatively unsaturated iridium center to give intermediate B, also seen by ^1H NMR spectroscopy. From here, insertion of the internal olefin into the remaining Ir—H bond followed by β-elimination of the sulfur would lead directly to the butadiene μ-sulfido product with the correct regiochemistry for the butadiene, i.e. with the *endo* hydrogens above the sulfido ligand.

This model for thiophene C—S cleavage would require two adjacent metal centers, a situation that could readily be accomodated at the edge of a MoS_2 crystallite in the commercial catalyst, either on the $\bar{1}010$ or $10\bar{1}0$ edge. Figure 4 illustrates some of the different types of coordinatively unsaturated sites that are possible at the edge of a MoS_2 crystallite [1]. One can imagine a thiophene molecule undergoing C—S cleavage at one of these exposed metal centers and forming a μ-sulfido bridge as in the dinuclear cobalt complexes. Further reaction, as seen with the diirid-

Table 1. Summary of X-ray structural data for thiophene insertion compounds

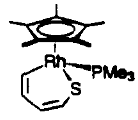
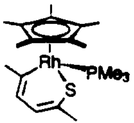
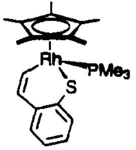
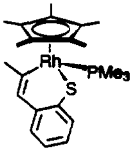
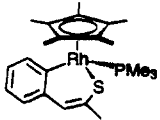
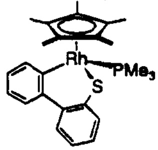
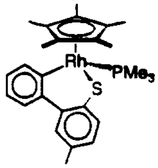
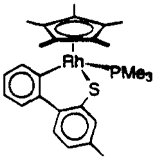
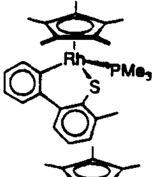
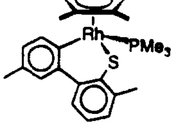
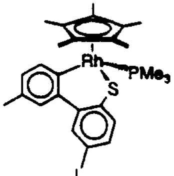
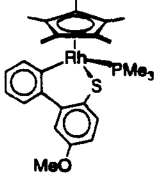
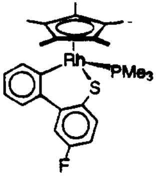
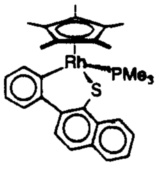
Compound	d_{Rh-S} (Å)	d_{Rh-C_α} (Å)	$d_{C_\alpha-C_\beta}$ (Å)	$d_{C_\beta-C_\gamma}$ (Å)	$d_{C_\gamma-C_\delta}$ (Å)	d_{S-C_δ} (Å)	Fold angle  (biphenyl twist)	Space group
	2.346(3)	2.013(13)	1.34(2)	1.451(11)	1.308(12)	1.748(9)	4.1	$Pca2_1$
	2.336(3)	2.067(8)	1.35(1)	1.44(1)	1.34(1)	1.741(8)	26	$P\bar{1}$
	2.325(2)	2.032(6)	1.263(9)	1.467(9)	1.410(9)	1.761(7)	14.4	$P2_1/n$
	2.343(1)	2.048(5)	1.338(7)	1.465(8)	1.416(7)	1.748(6)	42.5	$P2_12_12_1$
	2.367(6)	2.03(2)	1.44(3)	1.45(3)	1.36(3)	1.74(2)	24.6	$P\bar{1}$
	2.318(6)	2.01(2)	1.44(2)	1.47(2)	1.43(2)	1.77(2)	41.5 (32.0)	$Pca2_1$
	2.35(1)	2.14(6)	1.23(6)	1.54(5)	1.50(5)	1.74(3)	48.9 (42.4)	$Pbca$
	2.336(9)	2.02(1)	1.41(1)	1.50(2)	1.38(2)	1.77(1)	47.7 (40)	$P2_1/c$
	2.340(1)	2.034(5)	1.417(7)	1.480(7)	1.410(8)	1.757(6)	47.3 (37.0)	$P2_1$
	2.356(2)	2.038(6)	1.407(9)	1.498(8)	1.422(8)	1.764(6)	53.2 (42.5)	$P2_1/n$

Table 1. (*Continued*)

Compound	d_{Rh-S} (Å)	d_{Rh-C_α} (Å)	$d_{C_\alpha-C_\beta}$ (Å)	$d_{C_\beta-C_\gamma}$ (Å)	$d_{C_\gamma-C_\delta}$ (Å)	d_{S-C_δ} (Å)	Fold angle  (biphenyl twist)	Space group
	2.335(2)	2.047(6)	1.414(9)	1.493(9)	1.42(1)	1.754(7)	46.4 (32.7)	$P2_1/n$
	2.332(3)	2.037(8)	1.39(1)	1.48(1)	1.43(1)	1.74(1)	52.5 (38.2)	$P2_1/n$
	2.333(2)	2.037(5)	1.411(7)	1.492(8)	1.406(8)	1.740(6)	45.4 (30.8)	$P2_1/n$
	2.327(1)	2.031(5)	1.397(7)	1.483(7)	1.399(7)	1.748(5)	58.7 (36.6)	$P2_12_12_1$

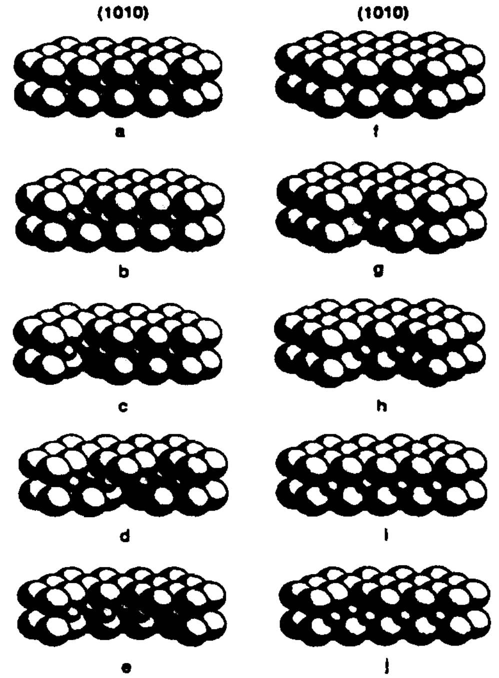
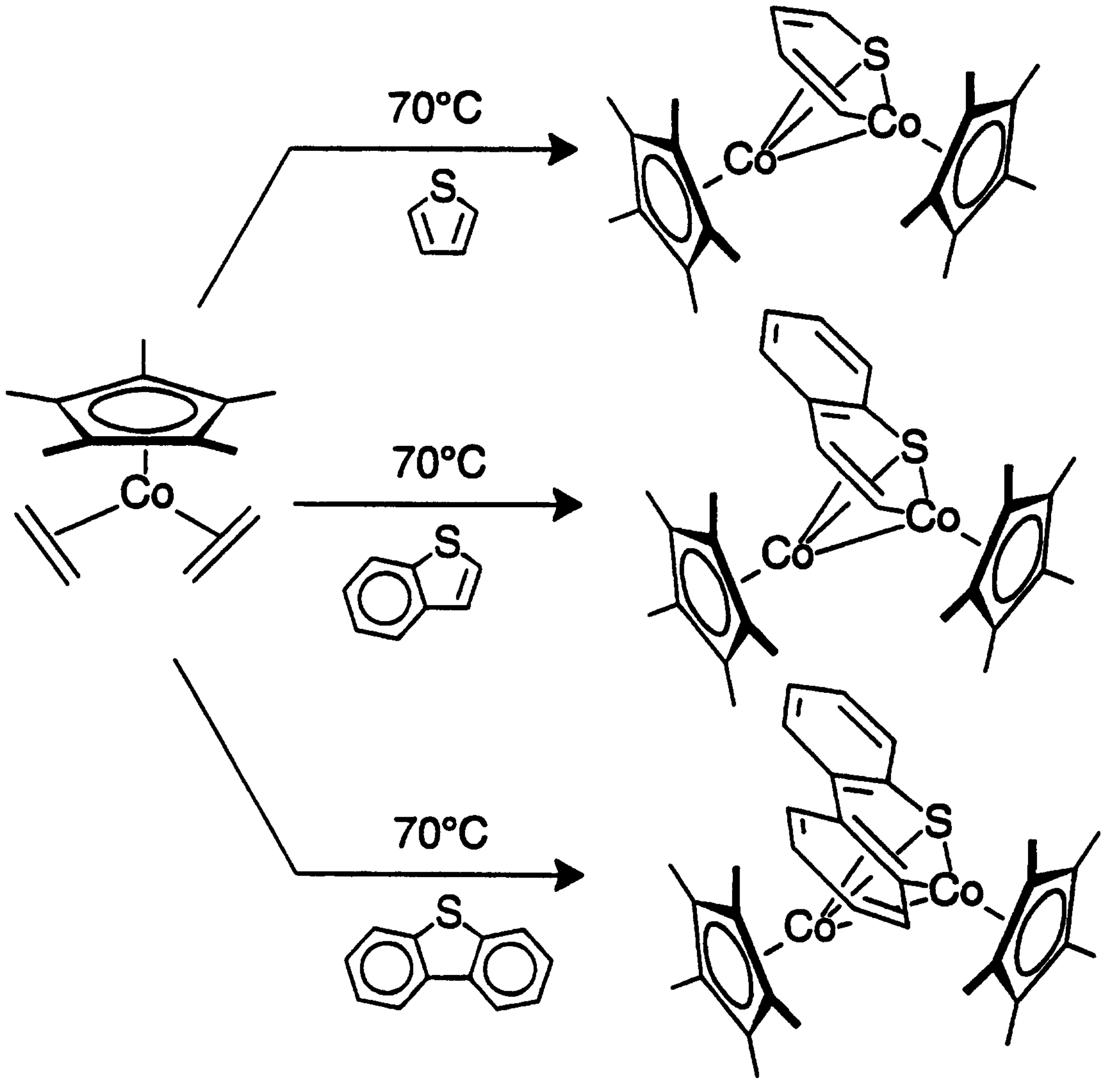


Fig. 4. Illustration of some of the different types of coordinatively unsaturated sites which are possible at the $\bar{1}010$ (a)–(e) and $10\bar{1}0$ (f)–(j) edges of MoS_2 (reproduced with permission from [1]).

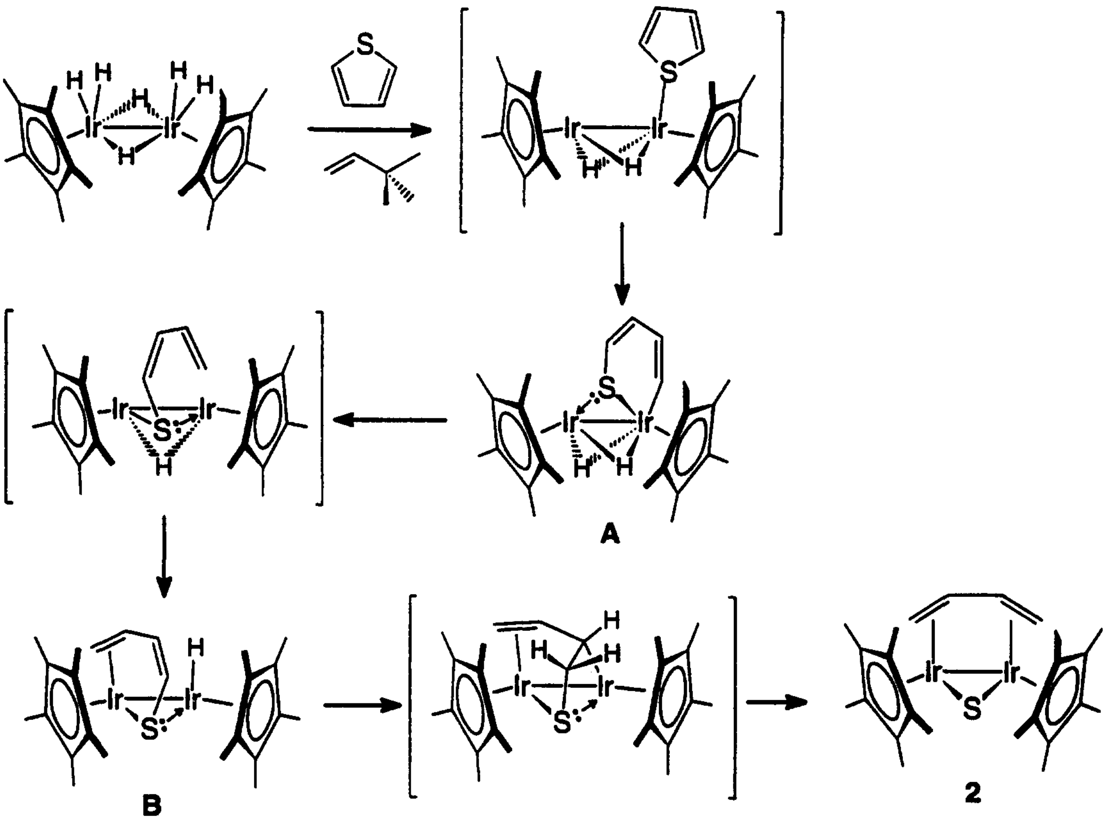
ium system, would then lead to desulfurization and the generation of the organic product plus a sulfur filled coordination site. Regeneration of the vacant site would occur under the reducing conditions of high temperature and high hydrogen pressure. Future studies and future catalysts will have to be able to also cleave C—S bonds of the hindered dibenzothiophenes and it is hoped that studies such as these will lead to the next generation of catalysts.

CONCLUSIONS

A variety of C—S insertion reactions into thiophenes, benzothiophenes and dibenzothiophenes are observed with rhodium, cobalt and iridium fragments in the +1 oxidation state. The rhodium system provides evidence for the coordination of thiophene through sulfur as the immediate precursor to C—S bond cleavage. The inability to cleave certain substituted dibenzothiophenes is attributable to a steric effect on the accessibility to the C—S bond, rather than to an electronic deactivation of the C—S bond towards cleavage. Two metal centers in a bimetallic complex are found to be capable of activating both C—S bonds in thiophene and the presence of the μ-



Scheme IX.



Scheme X.

sulfido bridge may be important in this second bond cleavage.

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REFERENCES

1. Topsøe, H., Clausen, B. S., and Massoth, F. E., *Hydrotreating Catalysis*. Springer-Verlag, Berlin, 1996.
2. Kabe, T., Ishihara, A. and Tajima, H., *Ind. Eng. Chem. Res.* 1992, **31,** 1577.
3. Jones, W. D. and Dong, L., *J. Am. Chem. Soc.* 1991, **113,** 559.
4. Dong, L., Duckett, S. B., Ohman, K. F. and Jones, W. D., *J. Am. Chem. Soc.* 1992, **114,** 151.
5. Chin, R. M. and Jones, W. D., *Angew. Chem. Int. Ed. Engl.* 1992, **31,** 357.
6. Chin, R. M. and Jones, W. D., *Organometallics*, 1992, **11,** 2698.
7. Jones, W. D. and Chin, R. M., *J. Am. Chem. Soc.* 1992, **114,** 9851.
8. Rosini, G. P. and Jones, W. D., *J. Am. Chem. Soc.* 1992, **114,** 10767.
9. Jones, W. D. and Chin, R. M., *J. Am. Chem. Soc.* 1994, **116,** 198.
10. Jones, W. D. and Chin, R. M., *J. Organomet. Chem.* 1994, **472,** 311.
11. Jones, W. D., Chin, R. M., Crane, T. W. and Baruch, D. M., *Organometallics*, 1994, **13,** 4448.
12. Myers, A. W., Jones, W. D. and McClements, S. M., *J. Am. Chem. Soc.* 1995, **117,** 11704.
13. Blonski, C., Myers, A. W., Palmer, M., Harris, S. and Jones, W. D., *J. Am. Chem. Soc.*, submitted.
14. Chen, J., Daniels, L. M. and Angelici, R. J., *J. Am. Chem. Soc.* 1990, **112,** 199.
15. Chen, J., Daniels, L. M. and Angelici, R. J., *Polyhedron*, 1990, **9,** 1883.
16. Selnau, H. E. and Merola, J. S., *Organometallics*, 1993, **12,** 1583.
17. Bianchini, C., Meli, A., Peruzzini, M., Vizza, F., Frediani, P., Herrera, V. and Sanchez-Delgado, R. A., *J. Am. Chem. Soc.* 1993, **115,** 7505.
18. Buys, I. E., Field, L. D., Hambley, R. W., and McQueen, A. E. D., *J. Chem. Soc., Chem. Commun.* 1994, 557.
19. Garcia, J. J., Mann, B. E., Adams, H., Bailey, N. A. and Maitlis, P. M., *J. Am. Chem. Soc.* 1995, **117,** 2179.
20. Luo, S., Skaugset, A. E., Rauchfuss, T. B. and Wilson, S. R., *J. Am. Chem. Soc.* 1992, **114,** 1732.
21. Sargent, A. L., *Thiophene Hydrodesulfurization: an Ab Initio Analysis of C—S Bond Activation*

INOR 542, 211th American Chemical Society National Meeting, New Orleans, LA, March 1996.

22. Myers, A. W. and Jones, W. D., *Organometallics*, 1996, **15**, 2905.
23. Jones, W. D. and Roache, J. H., unpublished results.
24. Ogilvy, A. E., Draganjac, M., Rauchfuss, T. B. and Wilson, S. R., *Organometallics*, 1988, **7**, 1171.