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Huckett, Sara C., Ph.D.

Iowa State University, 1987

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Ruthenium, Rhodium, and Iridium complexes of thiophene and benzo[b]thiophenes: Models for catalytic hydrodesulfurization

by

Sara C. Huckett

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Iowa State University
Ames, Iowa

1987

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DEDICATION

To Steve, Jenny, and Ben

PREFACE

Although numerous attempts to elucidate the mechanism of thiophene and benzo[b]thiophene catalytic hydrodesulfurization by means of heterogeneous reactor studies have been reported, important questions concerning this process remain unanswered. Therefore, a different method of approaching the problem would seem to be indicated. The synthesis of model complexes of thiophene and benzo[b]thiophene bound to transition metals would provide an opportunity to investigate the preferred coordination modes of these organosulfur compounds. These complexes would also provide an opportunity to study the reactivity of the thiophenic ligands, focusing on reactions which are analogous to those believed to occur over HDS catalyst surfaces. The research presented in this thesis consists of the synthesis of Ru, Rh, and Ir model complexes of thiophene and benzo[b]thiophene. Subsequent studies of the reactivity of the coordinated thiophene and benzo[b]thiophene ligands are also described.

This thesis consists of four sections. The first section is an introduction to catalytic benzo[b]thiophene hydrodesulfurization and the following sections represent the research as it was submitted for journal publication. Literature citations, tables, and figures pertain only to the section in which they are included.

SECTION I. THE HYDRODESULFURIZATION OF BENZO[b]THIOPHENE

INTRODUCTION

Hydrodesulfurization (HDS) is probably the most important chemical reaction currently performed.[1] This process involves the removal of sulfur from sulfur-containing hydrocarbons and is usually accomplished by the catalytic reaction of hydrogen with the sulfur compound to produce H_2S and hydrocarbons.

The principal application of this process is in the petroleum refining industry where it is performed for several reasons. The first concerns air pollution. Because the combustion of sulfur-containing fuel oils produces sulfur dioxide, current standards require the removal of up to 80% of the sulfur present. In addition, the sulfur content of gas oil fed to catalytic crackers must be reduced in order to prevent emission of sulfur dioxide during regeneration of the catalyst. Another important reason for reducing the sulfur content of petroleum feeds is that many of the catalysts used to process them are poisoned by sulfur. Bimetallic reforming catalysts are quite sensitive and the sulfur content of the feed must be limited to 1 ppm or less. Hydrocracking catalysts are also sensitive to sulfur poisoning. Finally, decreasing the amount of sulfur helps reduce corrosion during the refining and handling of the product as well as improving its odor.[2]

The identification of sulfur-containing compounds in feedstocks ranging from light petroleum fractions to petroleum residua and coal-derived oils has been an area of ongoing research.[3] Although the sulfur content of petroleum can vary from 0.01 to 10 wt. %, attention has primarily been focused on the highly sulfurous petroleums and the high boiling distillates where the bulk of the organosulfur compounds are concentrated.[3a] The classes of compounds encountered are illustrated in Figure 1.1 in approximate order of decreasing HDS reactivity.[4] The most important class is the thiophenic compounds which constitute up to 84% of the sulfur compounds found in middle and high boiling fractions.[5] In alternative fossil fuel sources such as coal, oil shale, and tar sands the sulfur compounds are also predominantly thiophenic.[6] A survey of structural group compositions of the thiophenic class shows that benzo[b]thiophene derivatives usually comprise the greatest fraction although dibenzothiophenes constitute a significant proportion.[3]

The most important industrial HDS catalysts are Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3 which are used in their sulfided forms.[7] The Ni-W/Al_2O_3 catalysts are also quite active but are more expensive and less widely used.[8] Extensive research has been directed at learning more about the active sites, promotional effects of Co and Ni, and role played by the support in these catalysts. Recent reviews have summarized the results of these studies.[7,9]

The mechanism of the desulfurization process for organosulfur compounds has also been the subject of numerous investigations but it is still not well understood. Spectroscopic and heterogeneous reactor studies have been used in attempts to elucidate adsorption modes of the sulfur compound on the catalyst surface and the subsequent reactions which it undergoes. Model sulfur-containing compounds which are representative of those found in crude oils and coal liquids are often used in these studies. Thiophene is the compound most frequently employed because of

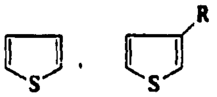
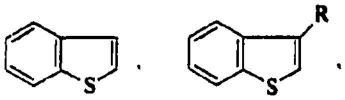
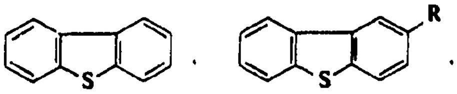
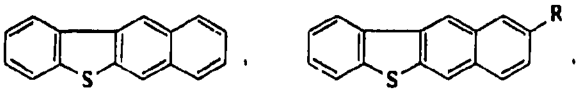
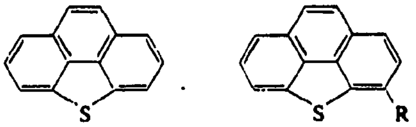
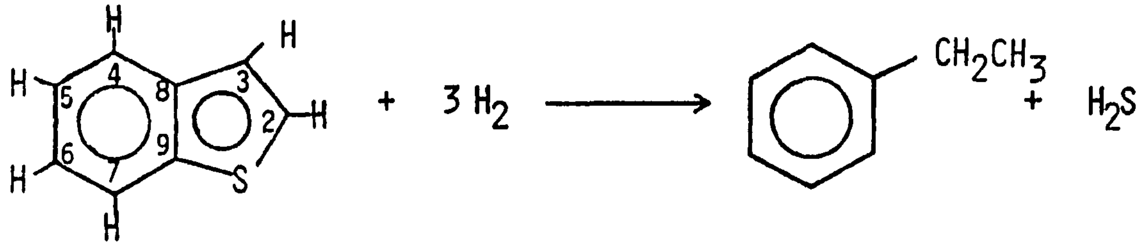
Compound class	Structure
Thiols (mercaptans)	RSH
Disulfides	RSSR′
Sulfides	RSR′
Thiophenes	, etc.
Benzothiophenes	, etc.
Dibenzothiophenes	, etc.
Benzonaphthothiophenes	, etc.
Benzo[*def*]dibenzothiophenes	, etc.

Figure 1.1. Sulfur compounds found in petroleum

the large proportion of thiophenic compounds present in HDS feeds and its low reactivity as compared to thiols, disulfides, and sulfides.[10] However, since benzo[b]thiophene and its derivatives are actually present in significantly greater quantities than thiophene it should provide a better model for studying the HDS process. The next five sections consist of an exhaustive review of the catalytic HDS of benzo[b]thiophenes.

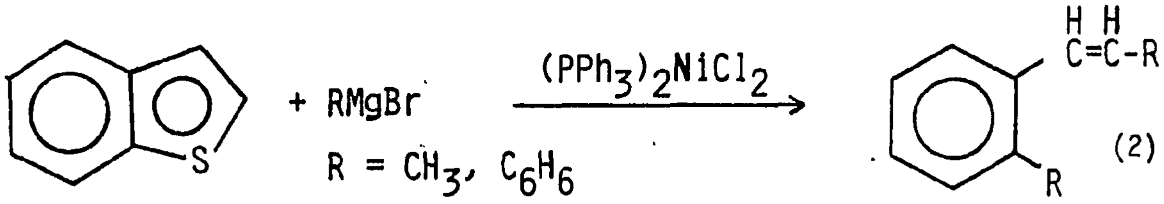
PROPOSED MECHANISMS

The HDS reaction for benzo[b]thiophene (BT), shown in eq. 1, produces H_2S and ethylbenzene (EB).



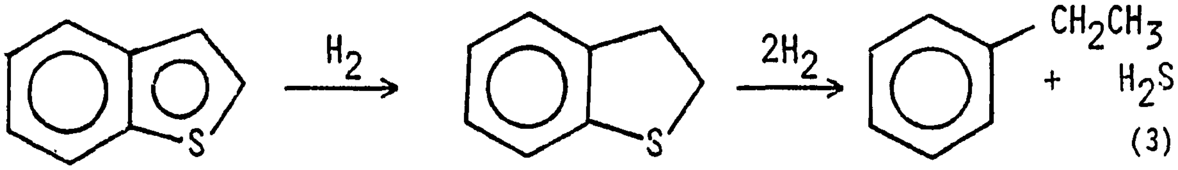
(1)

This reaction is catalyzed industrially by promoted Mo/Al_2O_3 catalysts[7] but Raney Nickel or a heated palladium catalyst can also be used.[11] Grignard reagents and a nickel catalyst have been used to desulfurize BT.[12] However, the ultimate goal of mechanistic studies of BT HDS is usually to provide information which will facilitate improvement of the commercial process. Therefore, most of the research in this area is done with catalysts which are actually used or are similar to those used industrially.



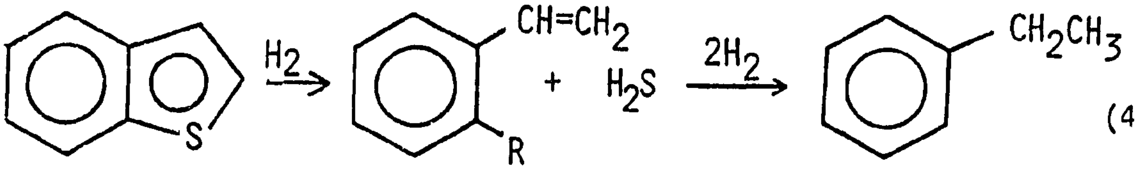
(2)

The mechanism of BT HDS has been much less widely studied than that of thiophene (T)[13] but between 1951 and 1987 approximately 50 publications on this subject appeared. In spite of this effort key aspects of the mechanism are still disputed. An important point of contention is whether or not it is necessary to hydrogenate the C2-C3 double bond before the desulfurization occurs, eq. 3. The alternative is hydrogenolysis, eq. 4,



(3)

in which hydrogenation and desulfurization occur simultaneously. There is also disagreement as to how BT binds to the catalyst surface. For this

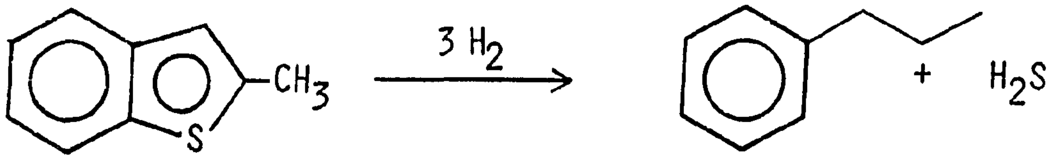


(4)

type of compound both coordination via sulfur or the π-electrons seem reasonable and both have been suggested. In the next section the results of mechanistic investigations which led to these proposals will be discussed.

Hydrogenation Givens and Venuto[14] studied the HDS of BT and its derivatives (BTs) over cobalt molybdena and noble metal (Pt, Rh, Pd) catalysts which were supported on alumina. The results discussed here pertain only to the cobalt molybdena catalysts. A continuous flow reactor system was used at 400°C and 1 atm pressure. A variety of BTs ranging from mono-, di-, and tri-methylated BTs (MeBTs, Me_2BTs, Me_3BTs) to dihydroBTs (DHBTs) were examined.

Their results indicated that the principal hydrocarbon products resulting from the HDS reactions were those that would arise from a simple direct sulfur extrusion reaction. For example, 2-MeBT gave n-propylbenzene as the major product. However, side reactions such as



(5)

alkyl migration and dealkylation were also observed, as shown in equations 6 and 7, respectively. Hydrocarbon products resulting from HDS of the rearranged BTs were detected in small amounts.

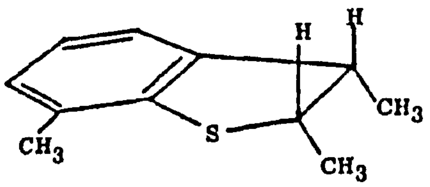
(6)

(7)

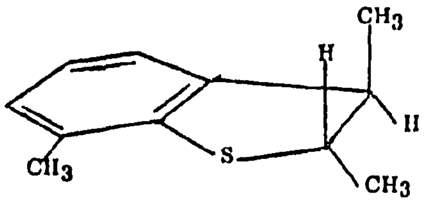
Their results also showed that an increase in the number of methyl groups present generally decreased both conversion and HDS selectivity. Conversion is the percentage of reactant converted to either organic or other organosulfur compounds and selectivity is the (percent desulfurization/percent conversion) X 100%. For example, the conversions of BT, 2-MeBT and 2,3-Me_2BT are 99%, 74%, and 39%, respectively. The selectivities of these compounds are 100%, 89% and 38%. An exception to this trend is 2,3,7-Me_3BT which undergoes a 47% conversion. However, this compound did have one of the lowest selectivities of those studied, 34%. In terms of selectivity the position of the methyl substituent seems to be important. The 3-MeBT shows a noticeably lower selectivity (75%) than 2-MeBT, but 7-MeBT has a 95% selectivity. It appears that a substituent on the benzene ring has a less pronounced effect on the reactivity of the sulfur containing compound.

The researchers were interested in learning more about possible intermediates in the HDS process. With this in mind, they performed experiments at both low temperatures and very high flow rates. In these cases, DHBT was observed in the reaction products. In fact, at 300°C equal amounts of DHBT and EB were produced. Hydrogenated products were also observed for runs performed using 2,3,7-Me_3BT and 2,3-Me_2BT. The desulfurized products resulting from these reactions were 3-sec-butyltoluene and sec-butylbenzene, respectively.

The hydrogenated compounds were present as the erythro and threo isomers, shown below for DH(2,3,7-Me_3)BT.



erythro



threo

These results suggested the intermediacy of DHBTs in the HDS process. Therefore, reactor studies using DHBT as a feed were undertaken. The DHBT HDS produces EB at a rate comparable to that observed for BT. However, DHBT is also in rapid equilibrium with BT and, therefore, on the basis of these experiments it was not possible to determine the source of the desulfurized product.

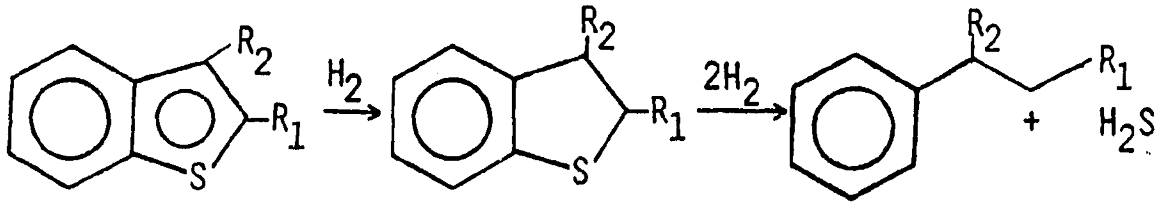
Other possible reaction pathways which might involve intermediate thiophenols, C-C bond cleavage steps, or partial hydrogenation of the benzene ring were also investigated but evidence for occurrence of these alternate mechanisms was not obtained.

On the basis of the results for all of the compounds investigated Givens and Venuto concluded that DHBTs "appear to be" intermediates in the HDS of BT. As stated earlier this conclusion must be taken somewhat cautiously in view of the indeterminate nature of the DHBT reactor studies. However, they feel that the detection of DHBTs under relatively mild reaction conditions and their behavior over HDS catalysts supports this conclusion.

Givens and Venuto's conclusions concerning the intermediacy of partially hydrogenated BTs are supported by the results of studies done to examine the HDS and hydrogenation properties of Co and Ni promoted MoS_2 and WS_2 catalysts (supported on γ-Al_2O_3). These experiments were performed under continuous flow conditions at medium pressure (100 atm) and slightly lower temperature conditions (250°C).[15] It was noted that as HDS activity of the catalysts decreased as a function of run time the concentration of DHBT in the reaction products increased significantly faster than that of BT. No benzene ring saturation was observed. This increase in percentage of hydrogenated reaction products with decreasing HDS activity was not observed for thiophene (T). This was interpreted to indicate that there is a contrast in the mechanism of HDS of BT and T; in the latter case desulfurization does not require partial hydrogenation of the substrate. No further experiments which would better support the proposed DHBT intermediate were reported.

Geneste[16] and coworkers have studied the HDS of dibenzothiophene (DBT) and BTs as well as their sulfoxides and sulfones. They used a sulfided CoO-MoO_3-Al_2O_3 catalyst under stirred batch reactor conditions. Pressures ranged from 30-70 atm and temperatures from 200-300°C.

The only products obtained from the BT runs were DHBT and EB. The 2-MeBT, 3-MeBT and 2,3-Me_2BT derivatives were also used and gave products as shown in the following equation. In agreement with Givens and Venuto



(8)

$R_1 = R_2 = H$ (BT)
$R_1 = CH_3$, $R_2 = H$ (2-MeBT)
$R_1 = H$, $R_2 = CH_3$ (3-MeBT)
$R_1 = R_2 = CH_3$ (2,3-diMeBT)

they felt that for BT and its derivatives the C1-C2 double bond is hydrogenated before C-S bond cleavage occurs. The rate constants and apparent activation energies for the hydrogenation step were determined and are presented in Table 1.1. The rates for the hydrogenation of the BTs decrease in the order,

$$BT > 2\text{-}MeBT > 3\text{-}MeBT > 2,3\text{-}Me_2BT$$

which is the same order of conversion and selectivity towards HDS found by Givens and Venuto.[14] However, in contrast to the results presented by these authors Geneste et al. did not observe either dealkylation or methyl migration reactions. Additionally, when DHBT was used as a feed under these conditions there was no dehydrogenation to BT. These inconsistencies with the earlier work were attributed to differences in operating conditions such as temperature, pressure, catalyst preparation and concentration of the organosulfur reactant.

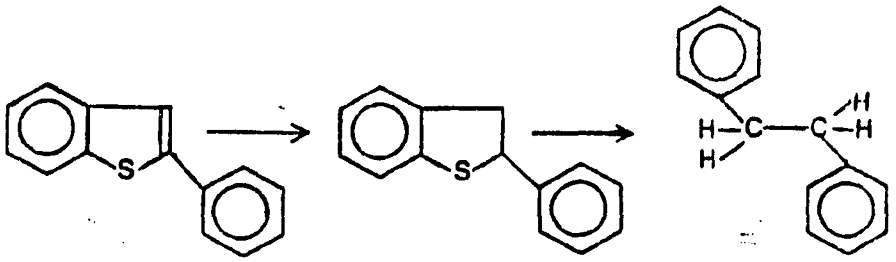
Geneste felt that an electronic effect (as opposed to steric) was responsible for the differences in the rates of hydrogenation of the BTs. To support this hypothesis he found that a plot of log k ("of the first step of HDS", hydrogenation) versus the vertical ionization potential for each of the compounds studied was linear. This correlation was interpreted as representing the relationship between the reactivity of the BTs and their HOMOs.

The reactivity of the BTs was contrasted to that of DBT for which HDS was proposed to occur without initial hydrogenation of the compound. The primary products found in this case were biphenyl (BP) and phenylcyclohexane (PCH).

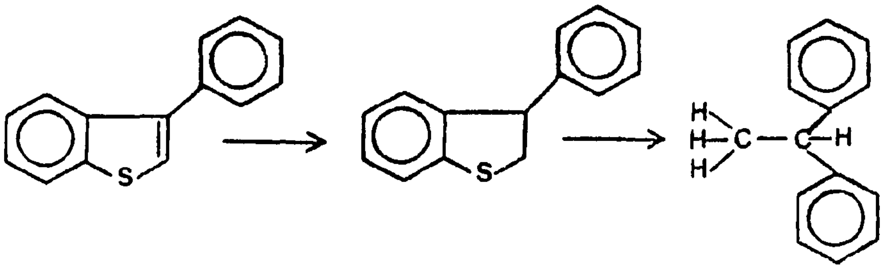
Table 1.1. Kinetic data for the hydrogenation of BTs at P_{H2} = 50 atm

Compound	T (°C)	10^4k (min^{-1})	Activation energy (kcal mol^{-1})
BT	200	4.1	25
	230	28	
	250	84	
	280	240	
	300	470	
2-MeBT	250	31	
3-MeBT	200	0.6	32
	230	6	
	250	15	
	280	82	
	300	220	
2,3-Me_2BT	200	0.1	37
	230	2.1	
	250	9	
	280	37	
	300	100	

Geneste has also studied the HDS of 2-phenylBT (2-PhBT) and 3-phenylBT (3-PhBT) over a sulfided Ni-Mo/γ-Al_2O_3 catalyst (autoclave reactor, 250°C, 40 atm).[17] The products of 2-PhBT and 3-PhBT HDS are shown in equations 9 and 10. As depicted in the equations desulfurization was again believed to occur after initial hydrogenation of the BT. The extended reactivity order for hydrogenation of these BTs is BT > 2-PhBT > 3-PhBT > 2-MeBT > 3-MeBT. In contrast to the explanation previously offered, the decrease in rate for the methylated derivatives is suggested to be due to steric effects.



(9)



(10)

Studies by Pokorny and Zdrazil[18] indicate that the mechanism of HDS of all aromatic sulfur-containing heterocyclic compounds is similar. The cleavage of a C-S bond is preceded by at least partial cancellation of the aromaticity by hydrogenation. Their experiments were performed over sulfided Co-Mo-Al_2O_3 and MoS_2 catalysts in a tubular flow reactor between 270 and 350°C and at 20 atm.

As in earlier investigations, significant amounts of DHBT were produced from the BT runs. A simplified reaction mechanism, Figure 1.2, was presented and discussed with respect to these results and the known properties of BT. It was suggested that either o-vinylthiophenol, o-ethylthiophenol or styrene, which are all very unstable under HDS conditions, could be the unidentified intermediate. Since Pokorny and Zdrazil were interested in exploring the possible intermediacy of DHBT neither the origins nor the identities of these possible intermediates were pursued. Step a is supported by the experimental work but the inability to draw conclusions from the kinetic data as to whether step b is operative as opposed to c, or whether both occur in parallel was acknowledged. However, it was noted that reactions involving cleavage of C-S bonds with double bond character are not typical of the chemistry of sulfur containing heterocyclic compounds. Pathways proposed for the hydrogenation of aromatic hydrocarbons are discussed and compared to those proposed for BT HDS. They felt this was a valid comparison since the electronic structures of thiophenic compounds are analogous to those of aromatic hydrocarbons. Because aromatic hydrocarbons have been proposed to form π-complexes on sulfided Co-Mo-Al_2O_3 catalysts and then undergo hydrogenation, it was suggested that similar behavior would be exhibited by the thiophenic compounds under these conditions. The instability of these intermediates under reactor conditions prevents their detection under most conditions. In contrast to most others who propose DHBT as an intermediate in the HDS process Pokorny and Zdrazil went one step further to suggest that partial saturation of the benzene ring is also

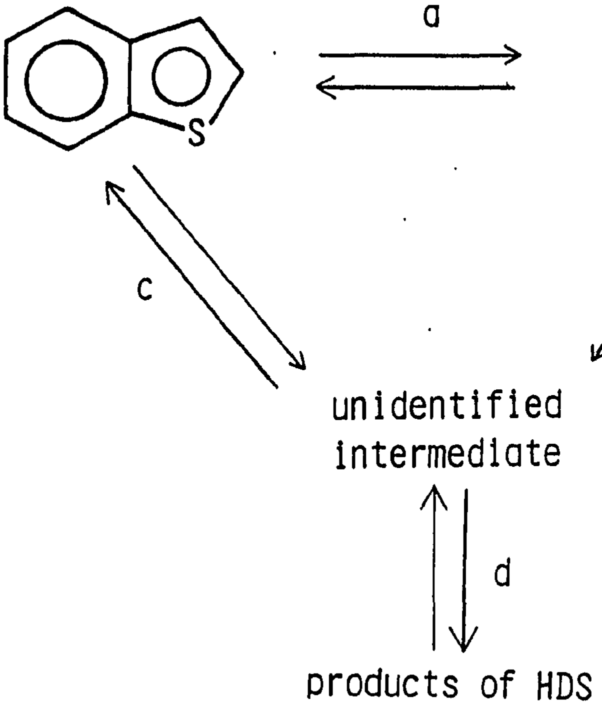
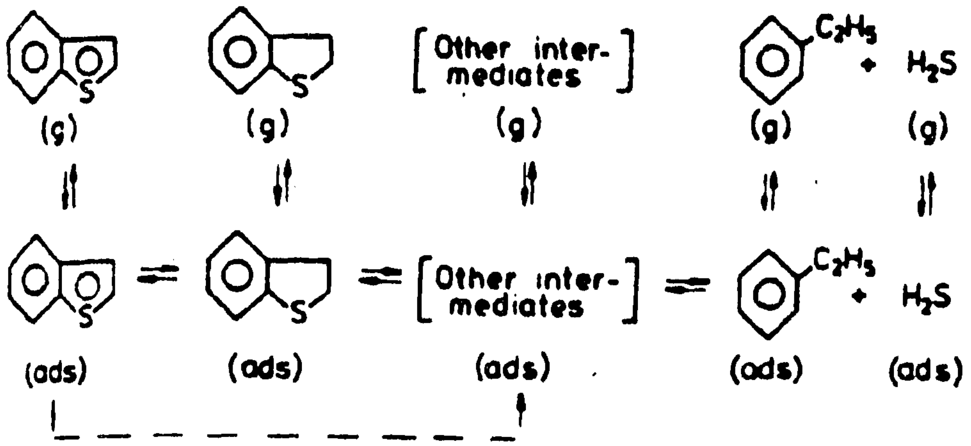


Figure 1.2. Simplified reaction mechanism presented by Pokorny and Zdrazil[18]

required. However, these types of intermediates were neither included in their proposed reaction mechanism nor further identified. The saturation of the benzene ring is said to be necessary because there is still interaction of the S with the benzene ring aromatic system in DHBT giving rise to a C9-S bond order of greater than one. As support for this suggestion he cited the hydrogenative cleavage of phenols over sulfide catalysts. These reactions are generally assumed to occur via cyclohexanol to give cyclohexene. Even under hydrogenation conditions benzene can be the final product of this reaction.

Lopez et al. have reported further studies with sulfided Mo/Al_2O_3, Co-Mo/Al_2O_3, and Ni-Mo/Al_2O_3 catalysts.[19] In this case a similar but more complex reaction network for BT HDS was presented, Figure 1.3. The dotted line presumably represents the disfavored but not disproven hydrogenolysis mechanism. The conversion of BT to DHBT was determined for each of the catalysts studied. The results showed that addition of Ni to a Mo/Al_2O_3 catalyst resulted in lower selectivity to DHBT. Previous results had shown that addition of Co to a Mo/carbon catalyst decreased selectivity to tetrahydrothiophene (THT) in T HDS. Therefore, the conclusion was that one of the roles of the promoter is to decrease the stability of the hydrogenated intermediate.

The importance of partially hydrogenated intermediates has also been suggested by Odebunmi and Ollis.[20] Their work was performed at 400°C and 69 atm of H_2 pressure. Although the major product of BT HDS was EB trace amounts of DHBT and phenylethanethiol were also formed.



(g)—gas phase, (ads)—adsorbed

Figure 1.3. Reaction network for BT HDS proposed by Lopez et al.[19]

Mercaptans have been reported by Landa and Mrnkova as products of BT reacting over MoS_2 in an autoclave at 1 atm and 320°C.[21] They considered these mercaptans to be the first intermediates in the HDS process. The thiols were produced in small amounts relative to EB but this was explained in terms of the high reactivity of these species under HDS conditions. In an interesting contrast to other investigations, ethylcyclohexane (EC) was also observed in the products in significant quantities. This lends support to Pokorny and Zdrazil's proposal that the benzene ring of BT must also undergo at least partial hydrogenation in the HDS process.

Hydrogenolysis Bartsch and Tanielian used a fixed bed microreactor at 300-400°C and 1 atm pressure to study the HDS of BT over a sulfided Co-Mo/Al_2O_3 catalyst.[22] The only product reported was EB. DBT was also studied and gave only BP. PCH showed no evidence of dehydrogenating to BP over the catalyst, therefore, it was proposed that hydrogenation of the aromatic compound was not necessary in order to obtain easier opening and subsequent sulfur removal.

Furimsky and Amberg[23] became interested in learning more about the role of DHBT in BT HDS as a result of the conflicting reports of Givens and Venuto[14] and Bartsch and Tanielian.[22] They examined HDS of BT and DHBT from 250-400°C at 1 atm pressure in a flow microreactor. Two catalysts were used. Over a Co-Mo/Al_2O_3 catalyst the reaction BT produced only EB. DHBT produced both BT and EB as products showing that dehydrogenation as well as desulfurization took place under these conditions.

An unsupported Co-promoted MoS_2 catalyst was also used. Over this catalyst styrene (STY) was produced in both the BT and DHBT reactions. If the amount of catalyst was increased the relative yield of STY decreased, presumably due to longer residence of STY in the catalyst bed which would result in increased hydrogenation. This suggested that STY could have also been a product for the supported catalyst runs but was too rapidly hydrogenated to be detected. A separate experiment showed that STY pulsed into a reactor containing the supported catalyst was completely converted to EB.

The observation of STY in the HDS products of both BT and DHBT was cited as support for the mechanism which involves direct C-S bond cleavage without intermediate hydrogenation of the thiophene ring. The fact that DHBT is extensively dehydrogenated under these conditions is suggested to imply that BT could be the intermediate source of desulfurization products for DHBT HDS. A scheme for the HDS of BT which explains the formation of STY but includes all possible pathways was proposed, Figure 1.4. The formation of DHBT was considered improbable under the conditions studied due to the extensive dehydrogenation of DHBT which was observed. In spite of this, steps c' and c" were included for completeness since runs using DHBT produced both EB and STY when He was used as a carrier gas instead of H_2. Step a was supported by Givens' and Venuto's observation that 3-MeBT which lacks a β-hydrogen was desulfurized more slowly than BT. Therefore, although the conclusion was that C-S bond cleavage is the first step in BT HDS a sincere attempt was made to explore other possible pathways.

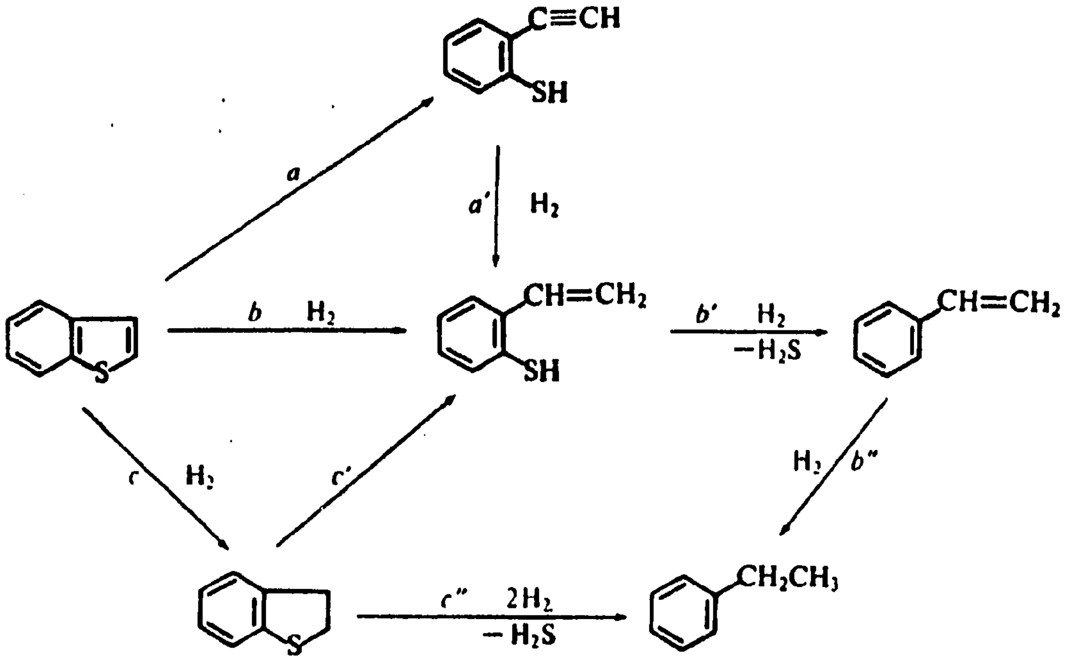


Figure 1.4. Possible pathways for BT HDS reported by Furmisky and Amberg[23]

Although iron had been described, in terms of its ability to act as a desulfurizing agent for petroleum fractions, in the patent literature, few studies of its activity have been reported. Bartsch and Tanielian were the first to investigate its activity towards BT HDS.[24] They used an Fe_2O_3/Al_2O_3 catalyst at 1 atm pressure and 300-400°C. The catalyst appeared to be less active than the Co-Mo/Al_2O_3 catalysts. DHBT was not observed as a product from BT but STY was observed at 300°C during activation phase of the catalyst runs. This was viewed as supporting the initial step as C-S bond cleavage as opposed to hydrogenation.

Rollman has investigated the heteroatom removal from N, O and S heterocycles.[25] Sulfided CoMo and SiO_2-stabilized CoMo catalysts were used at 20-102 atm and 300-450°C in a down-flow stainless steel reactor. BT, DBT, indole, benzofuran and other heterocycles were used as feeds. BT produced only EB and had one of the fastest rates of reaction. This was interpreted as an example of facile heteroatom removal which did not involve significant hydrogenation of the aromatic ring system. For the oxygen and nitrogen systems prior saturation of the aromatic ring was required.

Low pressure reactivity studies of thiophenic compounds over a sulfided $CoO\text{-}MoO_3/\gamma\text{-}Al_2O_3$ catalyst have also been undertaken by Kilanowski et al.[26] They used a pulse microreactor (1 atm, 350-450°C) and BT, methylated BTs and DHBT feeds in these experiments. The fractional conversions of these reactants at 450°C are given in Table 1.2. The products, except for the BT and DHBT runs, were the alkylbenzenes which would be expected for direct sulfur extrusion reactions. In both of these

Table 1.2. Fractional conversion of organosulfur compounds reported by Kilanowski et al.[26]

Reactant	Fractional Conversion
BT	0.14
2-MeBT	0.10
3-MeBT	0.093
7-MeBt	0.10
$3,7\text{-}Me_2BT$	0.033
DHBT	0.97

cases STY was observed as a major product in addition to EB. Dehydrogenation of DHBT was also observed in a significant amount (28%). This result and the lack of any observed dealkylation or alkyl migration reactions contrasts the results previously reported by Givens and Venuto[14] but is in agreement with those of Bartsch and Tanielian[22] as well as Furimsky and Amberg.[23] Differences in reaction temperature or catalyst structures were cited as possible explanations for this discrepancy. The temperature difference (400°C for Givens and Venuto, 450°C for Kilanowski) would seem too small to have such a significant effect on the product distributions. However, the CoMo/γ-Al_2O_3 used by Givens and Venuto was not sulfided before use and, therefore, the possibility of different catalyst structures for the two experiments seems reasonable.

The lack of observation of saturated or partially saturated intermediates (such as sulfides, mercaptans or DHBT) is again used to suggest that hydrogenation is not a prerequisite to C-S bond scission. The production of STY is taken as further support for this conclusion.

Ramachandran and Massoth[27] have examined the effects of pyridine and coke poisoning on BT HDS and hexene hydrogenation over a commercial sulfided CoMo/Al_2O_3 catalyst at 0.85 atm and 350°C. Their results suggest that the three reactions of HDS, hydrogenation, and cracking take place on different sites. Additional studies showed that the HDS reaction was strongly inhibited by H_2S but only slightly by H_2. In contrast the hydrogenation of hexene was inhibited by H_2. This provides support for HDS via nonhydrogenated intermediates which is not based only on observed product distributions or conversions.

Dual Pathways Although the previously discussed efforts have attempted to put forth either hydrogenation or hydrogenolysis as the first step in the process of BT HDS, a number of researchers have come to the conclusion that the two pathways are both operative. The reaction network proposed by Daly, Figure 1.5, incorporates both DHBT and STY as intermediates.[13] The conversion of BT was studied in a bomb reactor at 85 atm between 200-400°C over a sulfided $CoO-MoO_3/Al_2O_3$ catalyst. In addition to EB formation DHBT, STY, 1-phenylethanethiol and 2-phenylethanethiol were also observed as products. The thiols were suggested to result from reaction of STY with H_2S. The reaction of H_2S and alkenes, catalyzed by elemental sulfur, has previously been reported.[28] When Daly added sulfur to the reactor the rate of formation of the thiols increased, presumably due to a sulfur-catalyzed back reaction of H_2S and styrene. Therefore, in this case the production of thiols from STY is competing with the HDS process. This contrasts the proposals by Lopez et al.[19] and Landa and Mrnkova[21] in which the thiols are present only as intermediates of HDS.

Production of 1-phenylethanethiol was also observed by Guin et al. for the reaction of BT over pyrite (bomb reactor, 410°C, 85 atm).[29] DHBT was the major product and small amounts of EB were formed. STY was not observed. Thus, the pyrite catalyst efficiently catalyzed the hydrogenation of BT but was not as effective as $Co-Mo/Al_2O_3$ catalysts in the desulfurization step. The 1-phenylethanethiol was assumed to be a product of H_2S reaction with STY as was proposed by Daly.[13] The reaction network is similar to that presented by Daly except that the C-S bond

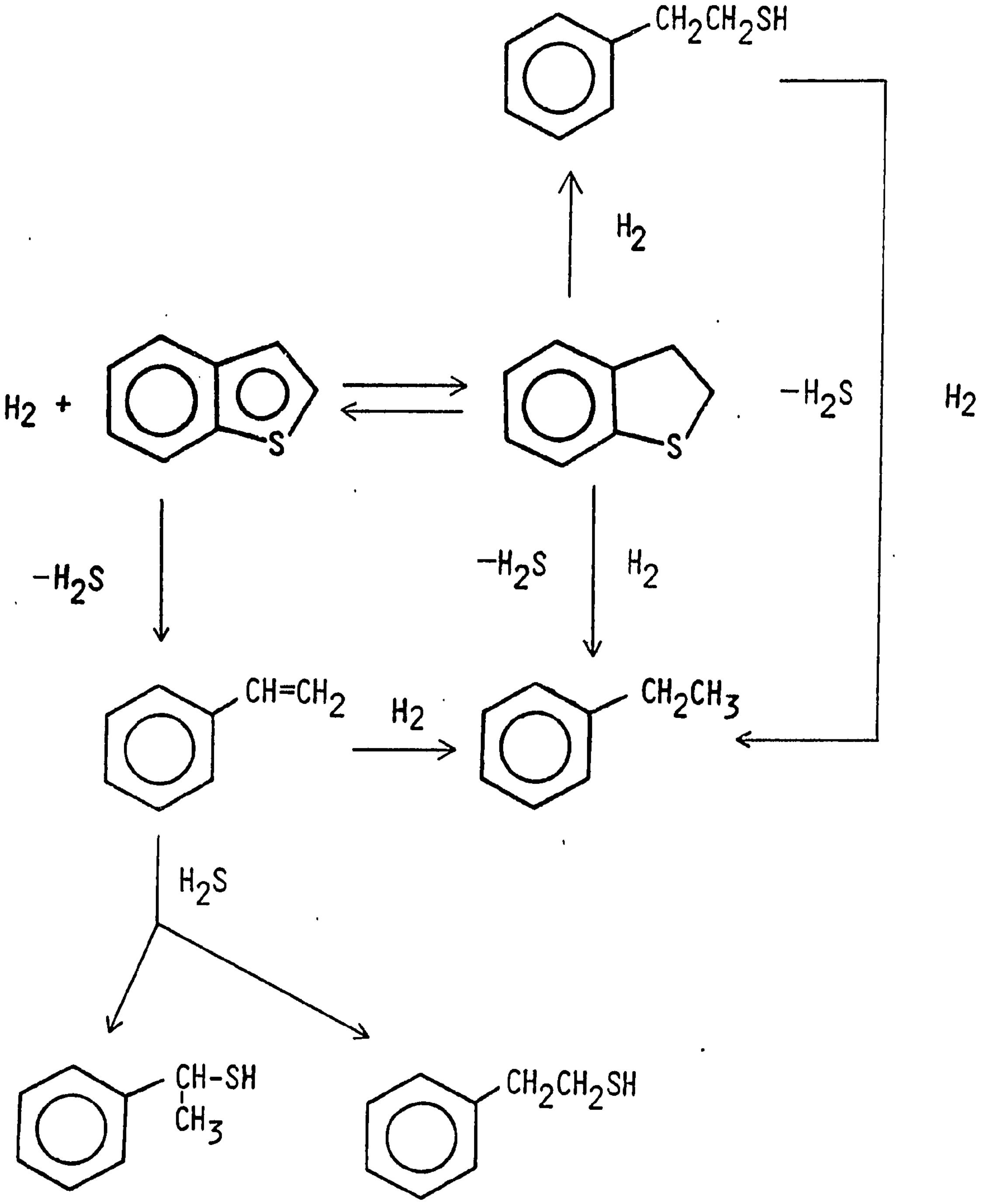


Figure 1.5. BT HDS mechanism proposed by Daly[13]

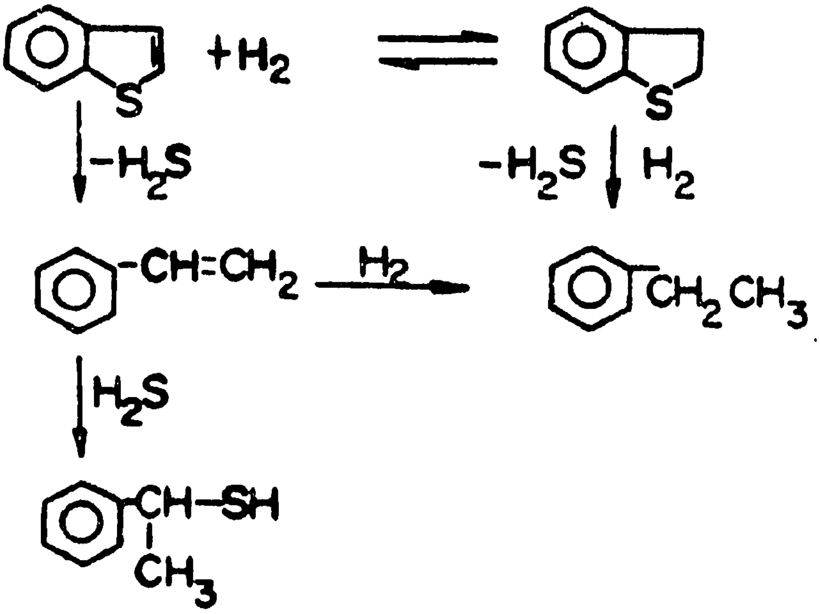


Figure 1.6. Mechanism for BT HDS proposed by Guin et al.[29]

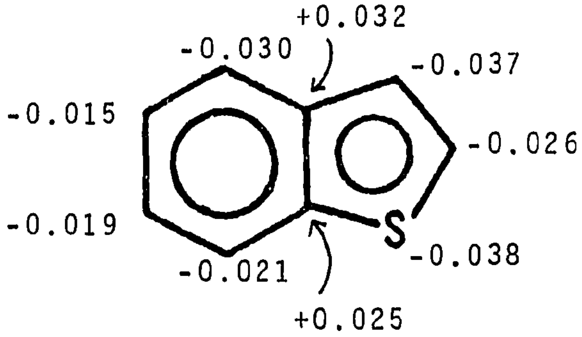
cleavage reaction of DHBT to give 2-phenylethanethiol, which was not observed in the product stream, was not included. Because pyrite is readily reduced by H_2 at 400°C, as shown in eq. 11, H_2S is liberated from the catalyst during the course of the reaction to form pyrrhotite. According to the proposed mechanism H_2S should inhibit the reactions of

$$FeS_2 + x\,H_2 \longrightarrow FeS_{2-x} + x\,H_2S \qquad (11)$$
$$0.86 < x < 1$$

DHBT and BT to form EB and increase the relative amount of thiol produced. The identification of 1-phenylethanthiol as well as the low yields of EB are consistent with this interpretation. The high yields of DHBT were attributed to the relatively high H_2 pressures used in this study. Large amounts of DHBT were also produced from BT in Daly's work which was performed at 85 atm.[13]

The dual pathway mechanism has been suggested by Lopez based on the results of his work with unpromoted and Ni-promoted Mo/Al_2O_3 catalysts.[30] His studies were performed with the sulfided catalysts between 280-400°C and 20 atm. His data were consistent with the proposal that two types of active sites are present, one for hydrogenation, the other for hydrogenolysis. The relative importance of the hydrogenation step was found to decrease upon addition of the Ni promoter.

A theoretical approach to the problem of hydrogenation versus hydrogenolysis has been reported by Geneste et al.[31] CNDO molecular orbital calculations for a series of thiophenic compounds (BTs, DBT, and napthobenzothiophene (NBT)) were performed. The localized charges for each of the carbon and sulfur atoms of these compounds were reported. The results for BT are shown below. The localized charges give rise to zones

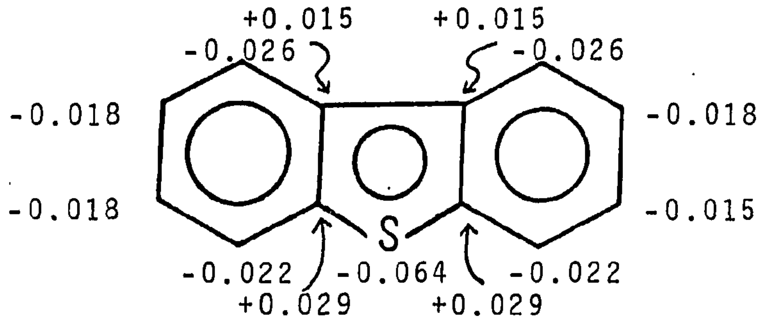


of negative and positive charge. The fact that the localized negative charge is approximately equal for S, C2 and C3 is suggested to orient the molecule so that these atoms interact most strongly with the catalyst surface. The subsequent expectation then is that a competition between hydrogenolysis and hydrogenation reactions will result. The order of HDS reactivity for a series of BT derivatives[17] was correlated with the

BT	>	2-PhBT	>	3-PhBT	>	2-MeBT	>	3-MeBT
-0.101		-0.090		-0.080		-0.067		-0.062

magnitude of the charge in the zone of negative charge. These numbers are shown below each compound and are the sum of the localized charges for S, C2 and C3.

In contrast to these results, those obtained for DBT are shown on the following page. In this case the negative charge is localized on the sulfur and, therefore, hydrogenolysis as opposed to hydrogenation would be expected to occur for this compound.



Since dual hydrogenolysis and hydrogenation pathways have been proposed for BT[13,27,28] and a hydrogenolysis only pathway for DBT HDS[32] the authors concluded that these types of calculations are useful for elucidating favored reaction pathways of thiophenic compounds over HDS catalysts. However, others have proposed that BT HDS occurs via either hydrogenolysis[22-27] or hydrogenation[15-21] only as well as that DBT undergoes HDS via a dual pathway mechanism.[25,33] These pathways are not consistent with those predicted by the localized charge calculations but this point was not addressed by the authors.

BT desulfurization via H_2 supplied by the water gas shift reaction has recently been accomplished.[34] A sulfided Ni-Mo/Al_2O_3 catalyst at 68 atm from 310-370°C was employed in these experiments; CO_2, H_2O and CO were also present in the reactor. This system was found to be very effective in the HDS of BT and it was also suggested that the water present may have inhibited the rate of coking of the catalyst. EB was the major product, only traces of DHBT were detected. These observations led to the conclusion that the HDS reaction could have taken place through two different reaction pathways, hydrogenation and hydrogenolysis.

Van Parijs et al. have studied the HDS of BT over a Co-Mo/γ-Al_2O_3 catalyst in a tubular reactor.[35] The temperature range was 240-300°C and the pressure 5-30 atm. A kinetic model for both the hydrogenolysis of BT to EB and hydrogenation to DHBT with subsequent production of EB was determined. On the basis of this model the rate-determining step was proposed to be the concerted surface reaction between BT or DHBT and two adsorbed hydrogen atoms.

Summary The mechanism of BT HDS has been studied over a variety of catalysts, temperatures and pressures. Mechanistic pathways are generally proposed on the basis of the observed products as well as the observed reactivities of these products under the given conditions. The diversity of reported results prevents a determination of the important reaction pathway (or pathways) under industrial conditions even though this is in fact the reason that many of these investigations were undertaken. When considering the complex nature of heterogeneous catalysts it seems reasonable that a multipath reaction network might exist but on the basis of the available data no definite conclusions can be drawn.

HYDRODESULFURIZATION REACTIVITY OF BENZO[b]THIOPHENE

The HDS reactivity of BT relative to that of other thiophenic compounds is as much disputed as the HDS mechanism. An excellent example of the conflicting nature of the reports in this area is found in the first two sentences of a paragraph discussing BT and DBT HDS mechanisms.[36] "Benzothiophene and dibenzothiophene are as readily desulfurized as thiophene. The order of desulfurization reactivity is: thiophene > benzothiophene > dibenzothiophene."

Early work addressing this problem was reported by Obolentsev and Mashkina.[37] They studied the kinetics of the hydrogenolysis of sulphides and thiophenic compounds over an aluminum-cobalt-molybdenum catalyst (P_{H_2} = 33 atm, T = 375°C). The following reactivity order was established.

$$\mathrm{DBT} < 2,5\text{-}\mathrm{Et_2T} < 2\text{-octyl T},\ 2,5\text{-}\mathrm{Bu_2T} < \mathrm{BT}$$

Experiments performed by Yamada[38] using MoS_3 in an autoclave reactor (300-450°C, 20-40 atm) showed that BT was more difficult to hydrogenate than T. In contrast to these results are those reported for a cobalt molydate catalyst (400°C, 1 atm) which was used to hydrogenate T, BT and DBT.[39] The respective conversions were 87, 91 and 73% for separate experiments which were performed under the same conditions. This suggests that there is relatively little difference in the reactivity towards hydrogenation for BT and T. The lower reactivity of DBT relative to BT has also been observed for the HDS reaction.[20,40]

Frye and Mosby[41] have investigated the desulfurization rate of two Me_3-BTs and DBT. A sulfided CoMo/Al_2O_3 catalyst was used at 15 atm and 290°C. The feeds were commercial catalytic cycle oils containing 0.4 to 2.0 wt % sulfur. The specific identities of the Me_3-BT isomers (A and B) were not reported but it was determined that B was desulfurized at a rate approximately 1.6 times that of A. Isomer A was desulfurized about 3.8 times faster than DBT.

In a separate study the activation energies of the HDS of BT and DBT were reported for reaction over a sulfided CoMo/Al_2O_3 catalyst.[22] The values were 4.9 kcal/ mol for BT and 5.3 kcal/mol for DBT. Thus, to desulfurize DBT to the same extent as BT approximately three times as much catalyst was required.

Similar rates of desulfurization for BT and DBT were observed by Rollman (sulfided CoMo catalysts, 300-450°C, 20-102 atm).[25] He suggested that diffusion effects might have been responsible for the previously proposed[22,41] higher reactivity of BT. The similar reactivities of BT and DBT were also proposed by Kilanowski based on fractional conversions over a sulfided CoMo/γ-Al_2O_3 catalyst (1 atm, 450°C).[26a] Surprisingly, both compounds were approximately twice as reactive as T under these conditions. This lower reactivity of T as compared to BT and DBT was suggested to be due to the low pressure conditions. This would result in a lower surface concentration of T and, therefore, a lower conversion.

Nag et al. have performed high pressure studies which indicate that under these conditions T is the most reactive of the thiophene compounds investigated.[42] A sulfided Co-Mo/γ-Al_2O_3 catalyst at 300°C and 71 atm was used in this work. The compounds studied were T, BT, DBT and BNT. The pseudo first order rate constants determined for the disappearance of the reactant are given in Table 1.3. These results show that although the reactivity tends to decrease sharply as the number of rings in the reactant increase, the reactivity is not governed solely by the size of the molecule as indicated by the increase in rate constant for BNT relative to DBT. On the basis of these results DBT appears to be the least reactive aromatic heterocycle.

The change in relative reactivities of BT and T with their changing pressures has also been addressed by Morooka and Hamrin.[43] In this case two different catalysts were used: mineral matter from Kentucky No. 11 coal as well as a CoMo/Al_2O_3 catalyst. Both were sulfided prior to use. Temperatures ranged from 350-440°C and the total pressure in the reactor was 1 atm. They found that at very low partial pressures of the sulfur compound the BT desulfurization rate is up to 2.8 times as fast as that of T. However, for partial pressures above 0.1 atm the rate of T HDS was always greater than that of BT.

Further support for the pressure reactivity relationship has been reported by Kilanowski and Gates.[44] At low partial pressures (0.015-0.23 atm) over a sulfided CoMo/Al_2O_3 catalyst at 252-332°C BT was approximately half as reactive as T (as determined by the rates of conversion of BT or T). Pokorny and Zdrazil[18] have also performed relative reactivity studies of BT and T at low partial pressures of sulfur compound. They used both MoS_2 and sulfided Co-Mo/Al_2O_3 catalysts at temperatures from 270-350°C and

Table 1.3. Reactivities of thiophenic compounds as determined by Nag et al.[42]

Reactant	k (cm^3/g catalyst, h)
T	4980
BT	2920
DBT	220
BNT	580

a total pressure of 20 atm. For partial pressures of BT and T ranging from 0.05-0.14 atm BT is more reactive than T (as determined by conversion).

The proposed approximate reactivity order of thiophenic compounds,[4] T > BT > DBT, under industrial conditions is supported by these investigations. The reverse order for BT and T noted for studies performed under low partial pressures[18,26a,39,42,44] of sulfur compound are presumably due to decreased surface concentrations of T relative to BT and would generally not apply to the high pressure industrial process. The effect of alkyl substituents on the HDS rate can be complex; depending on the number and positions of the groups the reactivity can either increase or decrease.[2,14,45] Extended reactivity studies addressing the relative order for the HDS of T, BT, and DBT derivatives have not been reported.

MODES OF ADSORPTION

Three types of adsorption modes for T binding to catalyst surfaces have been proposed. These include a one-point adsorption in which T is bound to the catalyst surface only through the lone pair of the sulfur atom,[46] a two point adsorption via the C2-C3 double bond[47] and a flat π-bound coordination mode.[36,48] These types of bonding modes have also been proposed for BT.

Kilanowski et al. have proposed that one-point adsorption of BT on a single anion vacancy should be the dominate coordination mode at low hydrogen partial pressures.[26] They suggested that sulfur only coordination favors a hydrogenolysis as opposed to a hydrogenation mechanism for HDS. These single anion vacancy sites have also been proposed to be responsible for the high reactivity of DHBT which lacks the π electrons which would be required for flat adsorption. The electrons available from the benzene ring are evidently not considered in this interpretation. At higher H_2 pressures the flat π-bound adsorption mode is proposed to play a more important role, presumably facilitating hydrogenation reactions.

A two point adsorption mode for coordination of BT to HDS catalysts has been proposed by Kwart et al.[47] In this case the C2-C3 bond would be coordinated at an anion vacancy of the catalyst. This interpretation was proposed to help account for the lower reactivity of 3-MeBT compared to 2-MeBT.[14] If the coordination occurred via sulfur only, steric effects might be expected to decrease the relative reactivity of 2-MeBT. Benzene is proposed to coordinate parallel to the catalyst surface, however, it has been suggested that the type of anion vacancy used in this case could be too small to accommodate larger aromatic molecules, such as BT.[49] Therefore, edge adsorption via C2-C3 could become important.

The flat π-bound coordination of BT to catalyst surfaces has been proposed by Pokorny and Zdrazil.[18,48b] The hydrogenation of aromatic hydrocarbons such as benzene sulfided over CoMo/Al_2O_3 catalysts has been proposed to occur via a π-complex of the reactant on the catalyst surface. Due to the aromaticity of T and BT it seems reasonable that they would also favor parallel adsorption to the catalyst surface allowing for maximal interaction of the π-system. This view has also been supported by Nag et al.[42]

Cowley[36] has proposed that BT coordinates to the HDS catalyst in a flat π-fashion through the thiophene ring to account for the results of his deuterium exchange experiments. Deuterium incorporation into the 2- and 3-positions of BT was postulated to occur through a series a π- and σ-complexes as shown in Figure 1.7 for exchange of H2. He felt that a one-point sulfur coordination mode would give rise to exchange of the 2- and 7-positions. For DBT[33b] and BNT[32] π-bonding to the catalyst surface via a benzene ring has also been suggested.

Both the one-point and multipoint adsorption modes can be considered consistent with the available data. The π-bound mode may seem more reasonable in terms of the aromatic nature of BT. Spectroscopic data supporting π-adsorption of T to catalyst surfaces have been reported[50] but no such studies have been performed for BT.

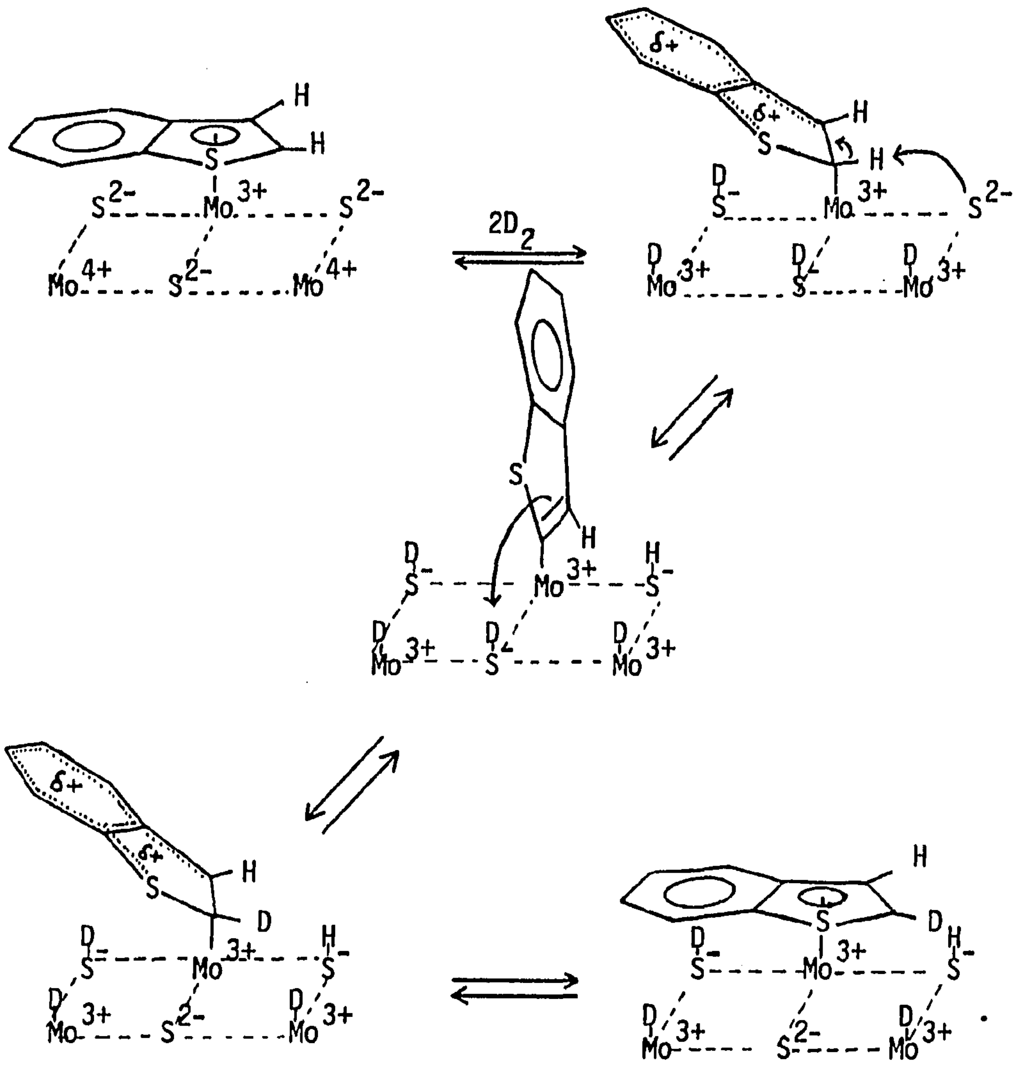


Figure 1.7. The Cowley mechanism for BT exchange[36]

NONMECHANISTIC STUDIES OF BENZO[b]THIOPHENE HYDRODESULFURIZATION

In addition to serving as a representative sulfur-containing compound for HDS mechanistic studies, BT has been used as a model in other investigations. These include the testing of new HDS catalysts, optimization of sulfiding conditions and determination of the number of anion vacancies.

Graphite supported MK (or Na) catalysts (M = FeS, NiS, CoS, MoS, $FeCl_3$, $OsCl_3$, $MoCl_3$, WCl_6, CrO_3) were shown to desulfurize BT.[51] HDS of BT by vanadyltetraphenylporphyrin has also been reported.[52]

Gissy et al. have carried out the HDS of BT over a commercial $CoMo/Al_2O_3$ catalyst at 1 atm and 250-350°C.[53] The effects of pretreating conditions on catalytic activity were investigated by following the conversion of BT as a function of run time. It was found that presulfiding at 250°C, as opposed to higher temperatures, led to the most active catalyst. The effect of feed components on the catalyst activation procedure was also studied.[54] Presulfiding with H_2S was found to give better BT HDS activity than presulfiding with T. The hydrogenolysis of T was proposed to result in the formation of a coke precurser which would decrease the activity of the catalyst. The H_2S was thought to help protect the catalyst during the initial stages of feed supply by quickly forming sulfided sites.

The effect of cobalt on the HDS activities of $CoMo/Al_2O_3$ catalysts in sulfided and unsulfided forms was probed by considering the percent conversion of BT (300°C, 1 atm).[55] It was found that Co actually has an inhibitory effect on the HDS activity of the unsulfided form. The HDS promotional effect of cobalt appeared only in the sulfided form.

Hillerova et al.[56] have found that cobalt-promoted Mo/Al_2O_3 catalysts show greater increases in HDS activity for BT than the nonpromoted catalysts. Their results were interpreted as evidence that cobalt plays a complex role in the transformation of the oxidic precurser into the sulfidic state as well as being directly involved in the active surface.

Pyridine poisoning experiments have been used to determine the active site vacancy concentration of a sulfided Mo/Al_2O_3 catalyst.[57] The effects of pyridine on the BT conversion and catalyst weight change were noted (347°C, P_{BT} = 0.0032 atm). The major product was EB but minor amounts of STY, DHBT, benzene and toluene were also observed. The presence of the latter two products was not discussed. Pyridine was found to adsorb on active desulfurization sites, with 0.24 molecules of pyridine adsorbing per molybdenum atom. The value is reported to be in good agreement with values for anion vacancies previously determined by kinetic and adsorption measurements for T reaction over a Mo/Al_2O_3 catalyst.

The effect of the volatile liquid phase on BT HDS in a trickle bed reactor system has been investigated.[58] The results show that the choice of solvent can significantly affect the rate of reaction. A solvent which is more volatile than BT will concentrate the sulfur compound in the liquid phase and increase BT conversion. If a less volatile solvent is used the opposite effect is noted.

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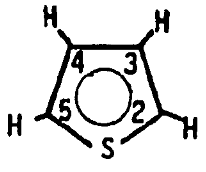
SECTION II. Ru, Rh, AND Ir COMPLEXES OF π-BOUND THIOPHENE AND BENZO[b]THIOPHENES: MODELS FOR THIOPHENE BINDING TO HDS CATALYSTS[1]

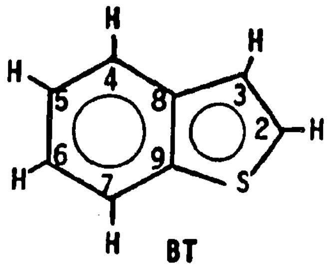
INTRODUCTION

The process of catalytic hydrodesulfurization (HDS) is performed industrially on a very large scale in order to remove sulfur from crude oils.[2] Typically, sulfided-cobalt-promoted molybdenum catalysts are used.[3] The mechanism of desulfurization has been investigated intensively but in spite of this effort key aspects of HDS such as binding of sulfur-containing hydrocarbons to the catalyst surface as well as important steps in the HDS process are not well understood.[4]

Thiophene (T) has frequently been used as a representative sulfur-containing compound in mechanistic investigations involving heterogeneous reactor studies.[5] It serves as a good model because it is difficult to desulfurize, presumably as a result of the aromatic stabilization provided by the delocalized π-system.[6] However, studies of other aromatic compounds, such as benzo[b]thiophenes (BTs: benzo[b]thiophene, BT; 3-methylbenzo[b]thiophene, 3-MeBT; 2,3-dimethylbenzo[b]thiophene, 2,3-Me_2BT), have also been reported.[6,7] For both T and BTs, π-bonding of the aromatic system to a metal site on the surface of the catalyst, as opposed to the frequently proposed S-coordination, has been suggested.[8] The π-bonded proposal is supported by heterogeneous reactor studies.[2b,8d,9] In the case of T, results of recent spectroscopic[10] and



T



BT

discrete transition metal model complex[11] studies also support the π-bound adsorption mode.

Therefore, in order to learn more about the process of HDS our group has chosen to explore the reactivity of π-bound T and BTs in model complexes. BTs are of particular interest because they are present in crude oils in significantly greater quantities than T[7d,12] and have been reported to be more difficult to desulfurize.[13] Since BTs are made up of two fused aromatic rings, they offer the possibility of forming π-complexes with transition metals by coordination of either one or both of these rings.

The syntheses of a number of π-thiophene complexes have been reported,[14] but only two of BT are known. In $Cr(CO)_3(\eta^6\text{-}BT)$[15] the BT was proposed, on the basis of ^1H NMR data, to be coordinated through the benzene ring. King and Stone[15b] reported the preparation of $Fe_2(CO)_5(BT)$ in 1960. They proposed that $Fe(CO)_2$ and $Fe(CO)_3$ groups are coordinated to both rings of the BT ligand.

Sulfur-coordinated complexes of T[16] and very recently BT[16c] have also been reported. However, the S-bound T and BT ligands are easily displaced by coordinating solvents or CO and have not been reported to undergo any reactions.

In this publication we describe the synthesis and characterization of Ru, Rh, and Ir complexes containing π-bound T and BTs. The $[Cp^*ML](A)_2$ (M

= Rh, Ir; L = T, BTs; Cp* = η-C_5Me_5; A = PF_6,BF_4) complexes are the first dicationic of either T or BTs. Previously reported attempts to prepare Rh and Ir compounds of unsubstituted T were unsuccessful.[14d] The first X-ray structure determination of a BT complex is also discussed.

EXPERIMENTAL SECTION

General Procedures All reactions were performed under N_2 in reagent grade solvents. Methylene chloride (CH_2Cl_2) was dried over CaH_2 and distilled. Diethyl ether (Et_2O) was distilled from Na/benzophenone, and dichloroethane (DCE) was distilled from P_2O_5. The solvents were stored over 4-Å molecular sieves, except for acetone which was stored over $MgSO_4$, and purged with N_2 prior to use. Commercial T and 3-MeBT were stirred with $AgNO_3$ (0.01 g/mL) for 24 h, decanted, and then distilled. Commercial BT was sublimed prior to use. The 2,3-Me_2BT,[17] $[Cp^*IrCl_2]_2$(Cp^*=η-C_5Me_5),[18] $[Cp^*RhCl_2]_2$,[18] $CpRu(PPh_3)_2Cl$(Cp=η-C_5H_5),[19] and $[CpRu(NCCH_3)_3]PF_6$[20] can be prepared by literature methods. The products were all characterized by elemental analysis (Table 2.4), ^1H, and ^{13}C NMR (Tables 2.5 and 2.6). ^1H, ^{13}C, and ^1H-^{13}C 2D NMR spectra were obtained on a Nicolet NT-300 spectrometer using deuterated solvents as internal locks and referenced to $Si(CH_3)_4$. Conductivity data were obtained using a Markson Electromark analyzer and calibrated with a standard potassium chloride solution. Fast Atom Bombardment (FAB) spectra were run on a Kratos MS-50 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc.

[CpRu(BT)]A(A=PF_6 or BF_4), 1 This complex was prepared by using either $CpRu(PPh_3)_2Cl$ or $[CpRu(NCCH_3)_3]PF_6$ as described in Methods A and B respectively. Method A: To a solution of $CpRu(PPh_3)_2Cl$ (0.52 g, 0.71 mmol) in CH_3OH (2 mL) was added BT (1.9 g, 14 mmol), and $AgBF_4$ (0.21 g, 1.1 mmol). The mixture was refluxed for 39 h. The solution was filtered and then evaporated to dryness. The residue was extracted with CH_2Cl_2 and the product precipitated by addition of Et_2O. Numerous recrystallizations from CH_2Cl_2/Et_2O were required to remove impurities resulting in a low yield (<15%) of the ivory colored product, 1 (A=BF_4). FAB (glycerol), m/e 301(M^+). Method B: BT (1.89 g, 14.1 mmol) was added to a solution of $[CpRu(NCCH_3)_3]PF_6$ (0.400 g, 0.921 mmol) in DCE (20 mL). The solution was refluxed under N_2 for 21.5 h and then evaporated to dryness in vacuo. The brown residue was extracted with acetone. Addition of Et_2O resulted in precipitation of the tan-colored product: yield, 0.318 g (77.5%). The product was purified by stirring in 10 mL of a 0.95 M solution of KOH in CH_3OH for 12 h. A stream of CO_2 was passed through the solution for 1.5 h and the resulting suspension evaporated to dryness in vacuo. The residue was extracted with acetone (4 x 10 mL) and filtered. The volume of the filtrate was reduced to approximately 5 mL followed by addition of Et_2O to precipitate the ivory colored product, 1 (A=PF_6). The purification step generally decreases the yield by approximately 15-20%.

$[CpRu(3\text{-}MeBT)]PF_6$, 2 This complex was prepared analogously to 1 using Method B. The 3-MeBT (2.74 g, 18.5 mmol) was added to $[CpRu(NCCH_3)_3]PF_6$ (0.532 g, 1.22 mmol) in DCE (30 mL) and refluxed for 24 h. The solution was evaporated to dryness in vacuo and extracted with acetone (2 x 10 mL). The resulting solution was filtered, the volume reduced in vacuo, and the tan product was precipitated by addition of Et_2O: yield, 0.501 g (89.4%). The purified pale yellow product was isolated after stirring in KOH/CH_3OH as for 1.

$[Cp^*Rh(T)](PF_6)_2$, 3 To a stirred solution of $[Cp^*RhCl_2]_2$ (70.4 mg, 0.114 mmol) in acetone (4 mL) was added $AgPF_6$ (121 mg, 0.480 mmol). The solution was stirred 5 min and filtered through Celite into a flask containing T (3.0 mL, 3.2 g, 38 mmol). The volume of the solution was reduced to 4 mL in vacuo. After stirring for 2 min, CH_2Cl_2 (20 mL) was added, and the resulting cream-colored solid was filtered, washed with additional CH_2Cl_2, and dried in vacuo: yield, 79.3 mg (56.8%).

$[Cp^*Rh(BT)](PF_6)_2$, 4 This complex was synthesized in the same manner as **3** using $[Cp^*RhCl_2]_2$ (0.15 g, 0.24 mmol), $AgPF_6$ (0.24 g, 0.96 mmol) and BT (0.33 g, 2.4 mmol). The product, **4**, was isolated as a pale yellow solid: yield, 0.21 g (65%).

$[Cp^*Ir(T)](BF_4)_2$, 5 To a solution of $[Cp^*IrCl_2]_2$ (0.440 g, 0.552 mmol) in acetone (5 mL) was added $AgBF_4$ (0.430 g, 2.21 mmol), and the resulting mixture was filtered through Celite. The volume of the filtrate was reduced to 3 mL and T (1.6 mL, 1.7 g, 20 mmol) was added. The solution was refluxed for 5 min and then cooled to room temperature. A slightly gray solid was produced by addition of CH_2Cl_2. The gray solid was filtered from the solution and then dissolved in CH_3NO_2. The CH_3NO_2 solution was filtered to remove a black insoluble impurity. Addition of CH_2Cl_2 to the filtrate gave the product, **5**, as a white solid which was separated by filtration and dried in vacuo: yield, 0.453 g (70.1%). This complex is slightly moisture sensitive and should be stored in a sealed container in a desiccator. Λ_m (mho cm^2 mol^{-1}, 1.02×10^{-3} M in CH_3NO_2): 165.

$[Cp^*Ir(BT)](BF_4)_2$, 6 This complex was prepared in the same manner as 5. A solution of $[Cp^*IrCl_2]_2$ (0.452 g, 0.568 mmol) in acetone (15 mL) was treated with $AgBF_4$ (0.446 g, 2.29 mmol), filtered, and refluxed with BT (3.09 g, 23.0 mmol) for 10 min. The white product, 6, was isolated from the reaction mixture by addition of CH_2Cl_2: yield, 0.591 g (81.9%). This reaction was also performed using $AgPF_6$ and without refluxing but the yields are lower (~50%). Λ_m (mho cm^2 mol^{-1}, 1.01 x 10^{-3} M in CH_3NO_2): 179.

$[Cp^*Ir(3\text{-}MeBT)](BF_4)_2$, 7 The synthesis proceeds as for 5 using $[Cp^*IrCl_2]_2$ (0.300 g, 0.377 mmol), $AgBF_4$ (0.294 g, 1.51 mmol), and 3-MeBT (1.47 g, 9.96 mmol). A pale yellow product, 7, was isolated: yield, 0.394 g (80.6%). Λ_m (mho cm^2 mol^{-1}, 1.05 x 10^{-3} M in CH_3NO_2): 182.

$[Cp^*Ir(2,3\text{-}Me_2BT)](BF_4)_2$, 8 This complex was prepared analogously to 5 from $[Cp^*IrCl_2]_2$ (0.202 g, 0.254 mmol), $AgBF_4$ (0.198 g, 1.02 mmol), and 2,3-Me_2BT (1.01 g, 6.22 mmol) to give a pale yellow product: yield, 0.229 g (68.0%).

X-ray Structure Determination of $[CpRu(BT)]BF_4$, 1 Gold-colored crystals of 1 were grown from CH_2Cl_2/Et_2O. A crystal of approximate dimensions 0.45 x 0.05 x 0.05 mm was mounted on the end of a glass fiber using Duco cement and attached to a standard goniometer head. The crystal was aligned on a four-circle Datex X-ray diffractometer from which four preliminary ω-oscillation photographs were taken at various ϕ settings. The approximate positions of 20 reflections were selected from these photographs and used as input into an automatic indexing program.[21] The resulting reduced cell and reduced cell scalars indicated a monoclinic lattice. Observed layer spacings from three axial ω-oscillation photographs were within experimental error of those predicted for this cell.

Accurate unit cell parameters were obtained by a least squares fit to ± 2θ values of 25 independent high angle reflections on a previously aligned four-circle diffractometer at room temperature using graphite-monochromated MoKα radiation. The data were collected using a four-circle fully automated Datex diffractometer which was interfaced to a VAX 730 computer in a real time mode. An empirical absorption correction was made[22] ($\mu = 12.80\ \text{cm}^{-1}$) where the maximum and minimum trans mission factors were 0.995 and 0.886, respectively. Further details concerning the data collection are given in Table 2.1.

The position of the Ru atom in 1 was obtained from an analysis of a standard sharpened three-dimensional Patterson map. The positions of the remaining nonhydrogen atoms were determined by successive structure factor[23] and electron density map calculations.[24] The positional and anisotropic thermal parameters for the nonhydrogen atoms were refined initially by block-matrix and finally by full-matrix least-squares procedures,[23] minimizing the function $\sum \omega\ (|F_o|-|F_c|)^2$ to a conventional residual index of $R = \sum ||F_o|-|F_c||/\sum|F_o| = 0.048$ and a weighted residual index of $R_w = [\sum \omega(|F_o|-|F_c|)^2/\sum \omega|Fo|^2]^{1/2} = 0.062$, $\omega = 1/\sigma_F{}^2$. The hydrogen positions were calculated and not refined. The final positional and thermal parameters for 1 are listed in Table 2.2. The bond lengths

Table 2.1. Crystal parameters for the X-ray diffraction study of $[CpRuBT]BF_4$, 1

formula	$BC_{13}F_4H_{11}RuS$
mol wt, g mol^{-1}	387.17
crystal system	monoclinic
space group	$P2_1/c$
a, Å	8.882(2)
b, Å	11.034(1)
c, Å	13.936(2)
β, deg	94.60(1)
V, $Å^3$	1361.5
Z	4
D(calcd), g cm^{-3}	1.85
μ (MoKα), cm^{-1}	12.80 (correction applied)
T_{min}/T_{max}	0.886/0.995
temperature, °C	20
Radiation (graphite monochromated)	MoKα (λ = 0.71032)
Reflection Measured	hkl, $\overline{hk}l$, $\overline{h}k\overline{l}$, $h\overline{kl}$ (4 octants)
Scan Type	ω-stepscan
Max 2θ, deg	50
Standard reflections	1, measured every 50 reflections (no observed decay)
Reflections collected	4764
Reflections observed ($I \geq 3\sigma(I)$)	3897
Reflections after averaging	1748
R (ave)	0.028
R (conventional)	0.048
R (weighted)	0.062

Table 2.2. Positional (X 10^4) and thermal parameters (Å^2, X 10^3) for [CpRu(BT)]BF_4, 1

Atom	x	y	z	B(ave)[a]
Ru	2282.0(6)	2208.4(5)	395.0(4)	49
S	3119(3)	5153(2)	-595(2)	84
C2	1794(16)	4767(11)	-1516(6)	103
C3	777(6)	4097(5)	-1400(4)	38
C4	-57(7)	2915(7)	157(6)	60
C5	306(9)	2711(7)	1153(6)	70
C6	1606(11)	3208(8)	1634(5)	71
C7	2572(9)	3955(7)	1168(6)	65
C8	891(7)	3707(6)	-315(4)	48
C9	2190(7)	4239(6)	175(5)	54
C10	3742(11)	1417(8)	-601(6)	80
C11	4549(9)	1495(8)	274(7)	79
C12	3825(11)	796(8)	950(7)	82
C13	2565(13)	265(7)	436(8)	92
C14	2505(11)	634(8)	-519(7)	81
B	6812(13)	2311(8)	2788(7)	72
F1	7342(8)	1510(7)	2168(5)	124
F2	5815(7)	3123(6)	2378(5)	107
F3	8076(10)	2972(6)	3145(6)	124
F4	6249(17)	1751(10)	3511(9)	229

[a] Given in the form of the isotropic displacement equivalent displacement parameter defined as $4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma B_{12}) + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

and the bond angles are listed in Table 2.3. An ORTEP[25] drawing of the molecule is given in Figure 2.1.

Residual electron density near C3 indicated a possible structural disorder. Attempts to model the disorder by introducing disorder partners of C2, C3, and S, constrained to either a 2-fold axis or a mirror plane perpendicular to the C8-C9 bond, converged to an occupancy ratio of 80:20. However, the residual indices, the C2-C3 bond distance, and the C2 thermal ellipsoid did not improve. In an independent study[26] the occupancies of these three atoms and their disorder partners were allowed to refine without constraints. However, the pairs of atoms converged to their mean positions.

The data were, therefore, reweighted based on $\sin(\theta)/\pi$ such that $\overline{\omega\Delta^2}$, $\Delta = |F_o| - |F_c|$, was approximately constant and further refined. The parameters listed in Tables 2.1, 2.2, and 2.3 are for the structure refined without consideration of the disordering.

Table 2.3. Bond distances and angles for [CpRu(BT)]BF_4, 1

Bond Distances (Å)

Ru-C4	2.219(7)	C4-C5	1.418(11)
Ru-C5	2.191(8)	C5-C6	1.400(12)
Ru-C6	2.174(8)	C6-C7	1.389(12)
Ru-C7	2.213(8)	C7-C9	1.432(10)
Ru-C8	2.246(6)	C8-C9	1.420(9)
Ru-C9	2.262(7)	C10-C11	1.367(13)
Ru-C10	2.159(9)	C10-C14	1.410(13)
Ru-C11	2.182(8)	C11-C12	1.412(13)
Ru-C12	2.176(9)	C12-C13	1.407(14)
Ru-C13	2.159(8)	C12-C14	1.388(15)
Ru-C14	2.172(9)		
S-C2	1.724(11)		
S-C9	1.730(7)		
C2-C3	1.188(14)		
C3-C8	1.568(8)		
C4-C8	1.412(9)		

Bond Angles (°)

S-C2-C3	122.3(7)	C7-C9-S	129.7(5)
C2-C3-C8	108.1(6)	C3-C8-C4	128.6(6)
C3-C8-C9	109.7(5)	C10-C11-C12	109.1(8)
C8-C9-S	110.6(5)	C11-C12-C13	105.9(9)
C9-S-C2	89.2(4)	C12-C13-C14	109.5(9)
C4-C5-C6	121.4(7)	C13-C14-C15	106.7(9)
C5-C6-C7	121.7(7)	C14-C15-C10	108.8(8)
C6-C7-C9	118.3(7)		
C7-C9-C8	119.6(6)		
C9-C8-C4	121.6(6)		
C8-C4-C5	117.2(6)		

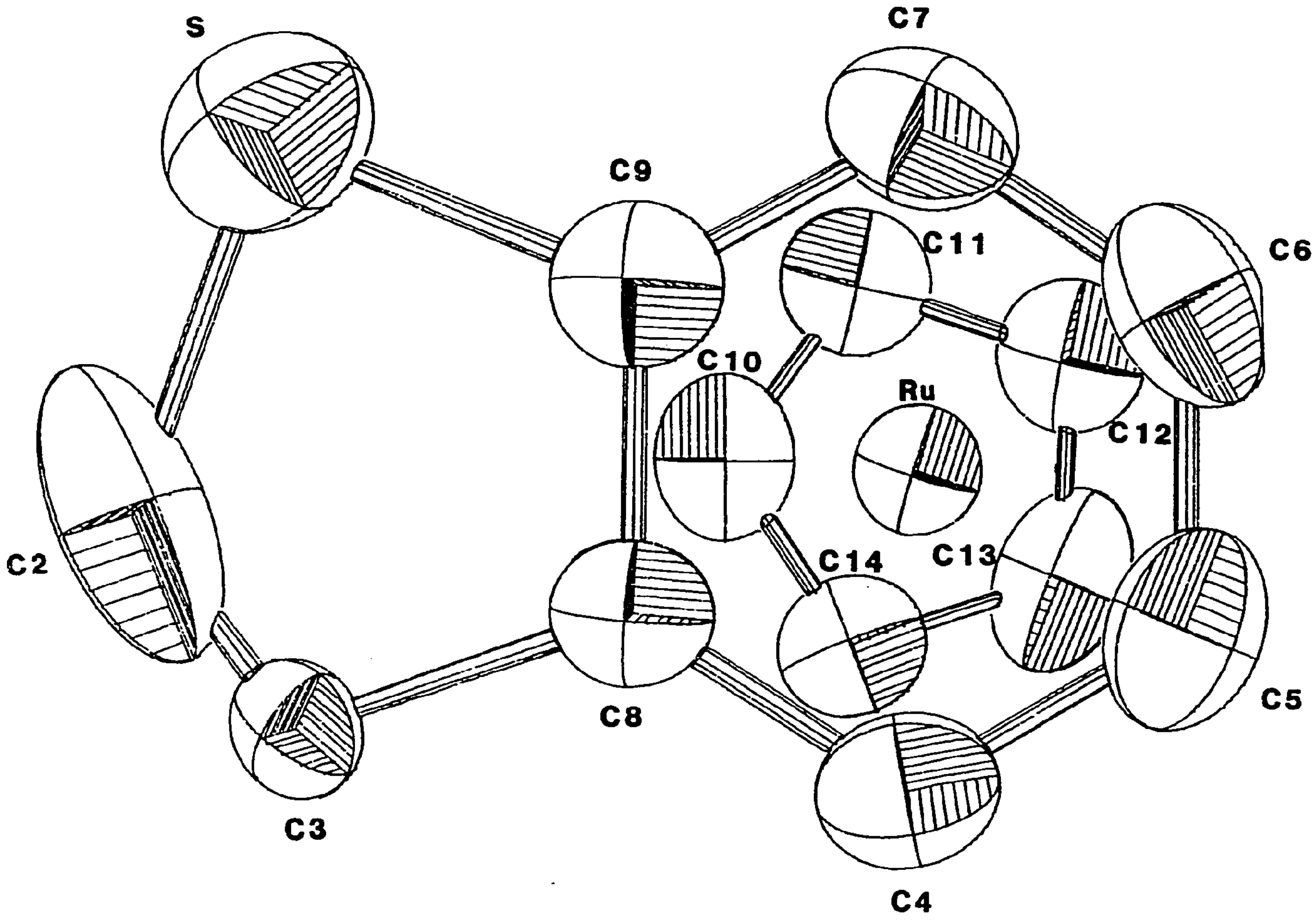
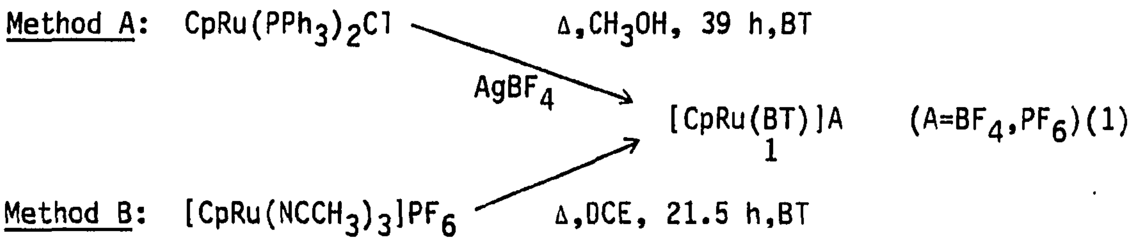


Figure 2.1. An ORTEP drawing of [CpRu(BT)]BF_4, 1

RESULTS AND DISCUSSION

[CpRu(BT)]A (A=BF_4,PF_6) and [CpRu(3-MeBT)]PF_6, 1 and 2 The reaction of either CpRu$(PPh_3)_2$Cl or [CpRu$(NCCH_3)_3$]PF_6 with BT results in the formation of $[CpRu(BT)]^+$ as shown in eq. 1.



The 3-MeBT complex, **2**, is synthesized analogously using Method B. Method B is preferred due to the higher yield and purer product which results. Gill and Mann[20] have used this method to synthesize a variety of other CpRu(η^6-arene)$^+$ complexes. The complexes **1** and **2** are air stable in the solid state. The BT and 3-MeBT ligands are not displaced by coordinating solvents such as acetone, methanol or water at room temperature over 24 h.

Complex **1** was identified by its elemental analysis, ^1H and ^{13}C NMR spectra (Tables 2.4, 2.5, and 2.6). The ^1H NMR spectrum was assigned using the results of selective decoupling, ^1H-^{13}C 2D, and gated-decoupled ^{13}C NMR experiments. The initial step in assigning the ^1H NMR spectrum was obtaining the gated-decoupled ^{13}C NMR spectrum (d_6-acetone) which showed only one resonance as a simple doublet of doublets. This could clearly be only the C2 peak because it is split only by H2 ($^1J_{C2-H2}$=189 Hz) and H3 ($^3J_{C2-H3}$= 7 Hz). From the ^1H-^{13}C 2D NMR spectrum the H2 peak could then be assigned. The H3 resonance was identified by selectively decoupling H2. The H7 peak was assigned by observation of long range

Table 2.4. Elemental analyses of the complexes

	% C (calc)	% H (calc)
$[CpRu(BT)]BF_4$, 1	40.44 (40.33)	2.86 (2.86)
$[CpRu(3\text{-}MeBT)]PF_6$, 2	36.62 (36.61)	2.84 (2.85)
$[Cp^*Rh(T)](PF_6)_2$, 3	27.51 (27.41)	3.34 (3.13)
$[Cp^*Rh(BT)](PF_6)_2$, 4	32.72 (32.64)	3.51 (3.20)
$[Cp^*Ir(T)](BF_4)_2$, 5	28.47 (28.74)	3.22 (3.27)
$[Cp^*Ir(BT)](PF_6)_2$, 6	28.54 (28.77)	2.53 (2.82)
$[Cp^*Ir(3\text{-}MeBT)](BF_4)_2$, 7	34.82 (35.15)	3.57 (3.57)
$[Cp^*Ir(2,3\text{-}Me_2BT)](BF_4)_2$, 8	36.27 (36.22)	4.04 (3.80)

Table 2.5. ^{1}H NMR data for the complexes

Compound	H2	H3	H4	H5
1[a]	8.16 d[b]	7.46 d[b]	7.26 d	6.32 t
2[a]	7.75 q[c]		7.08 d	6.29 t
3[e]	7.51 m	7.65 m	7.65 m	7.51 m
4[e]	8.88 d[f]	7.71 d[f]	7.96 m	7.35 m
5[e]	7.55 m	7.60 m	7.60 m	7.55 m
6[e]	8.83 d[g]	7.61 d[g]	8.01 m	7.37 m
7[e]	8.41 q[h]		7.94 m	7.37 m
8[e]			7.82 d	7.28 m
T[e]	7.43 m	7.15 m	7.15 m	7.43 m
BT[a,j]	7.61 d	7.41 d	7.87 m	7.37 m
3-MeBT[e]	7.19 q		7.78 dd	7.38 td
2,3-Me_2BT[e]			7.63 d	7.29 m

[a] d_6-acetone.

[b] $^3J_{H2H3}$ = 5.8 Hz.

[c] $^4J_{H2-CH_3}$=0.8 Hz.

[d] $C3-C\underline{H}_3$.

[e] CD_3NO_2.

[f] $^3J_{H2H3}$ = 5.6 Hz.

[g] J_{H2H3} = 5.7 Hz.

[h] J_{H2-CH_3} = 1.0 Hz.

[i] $C2-C\underline{H}_3$.

[j] Reference 27.

H6	H	Cp	Cp*	Other
6.37 t	7.55 d	5.22 s		
6.36 t	7.49 d	5.22 s		2.48 d[c,d]
			2.35 s	
7.35 m	8.14 m		2.03 s	
			2.50 s	
7.37 m	8.19 m		2.12 s	
7.37 m	8.16 m		2.12 s	2.58 d[h,d]
7.28 m	8.04 d		2.17 s	2.88 s[i], 2.47 s[d]
7.35 m	7.95 m			
7.45 td	7.90 dd			2.45 d
7.37 m	7.78 m			2.48 s, 2.30 s

Table 2.6. $^{13}C\ \{^1H\}$ NMR data for the complexes

Compound	C2	C3	C4	C5	C6
1[a]	137.7	123.7	81.6	84.4	83.9
2[a]	132.3	131.4	81.6	84.1	83.8
3[c]	107.1 d[d]	110.3 d[e]	110.3 d[e]	107.1 d[d]	
4[c]	147.7	122.4	103.3	103.6 d[g]	102.4 d[h]
5[c]	95.0	101.3	101.3	95.0	
6[c]	148.6	121.8	93.8	95.9	94.7
7[c]	141.8	131.6	94.0	95.5	94.6
8[c]	157.9	125.9	93.1	95.2	93.8
T[a,k]	125.6	127.3	127.3	125.6	
BT[l,m]	126.2	123.8	123.6	124.1	124.2
3-MeBT[l,m]	121.4	132.0	121.6	123.7	124.0
2,3-Me_2BT[l,m]	133.6	127.9	121.0	123.7	123.3

[a] d_6-acetone.

[b] C3-$\underset{\sim}{C}H_3$.

[c] CD_3NO_2.

[d] J_{Rh-C} = 4.0 Hz.

[e] J_{Rh-C} = 2.7 Hz.

[f] J_{Rh-C} = 9.1 Hz.

[g] J_{Rh-C} = 3.6 Hz.

[h] J_{Rh-C} = 3.1 Hz.

[i] J_{Rh-C} = 8.4 Hz.

[j] C2-$\underset{\sim}{C}H_3$.

[k] Reference 28.

[l] $CDCl_3$.

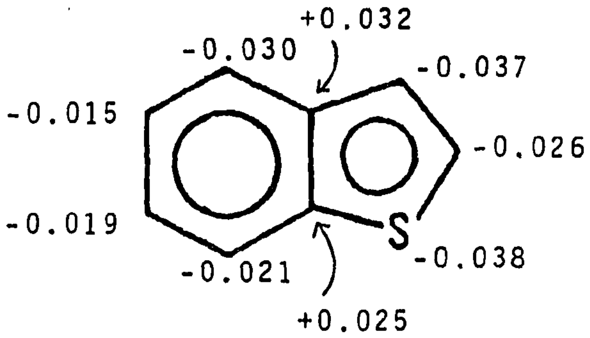
[m] Reference 29.

C7	C8	C9	$\underset{\sim}{C}_5H_5$	$\underset{\sim}{C}_5(CH_3)_5$	$C_5(\underset{\sim}{C}H_3)_5$	Other
81.3	106.2	110.2	81.6			
79.9	105.8	110.9	81.3			13.3[b]
				114.3 d[f]	11.3	
102.6	122.4	126.4		112.1 d[i]	9.7	
				107.7	10.7	
93.4	117.3	121.2		105.7	9.2	
91.8	116.7	121.3		105.4	9.3	13.7[b]
90.8	118.9	125.9		105.2	9.3	15.6[j],11.5[b]
122.4	139.6	139.7				
122.6	139.6	140.2				13.8
121.9	140.0	138.0				13.6, 11.2

H_3-H_7 ($^5J_{H_3H_7}$ = 0.7 Hz) coupling[30] in a dilute solution (~1 mg/0.30 mL) of **1** in d_6-acetone. The use of a dilute solution resulted in enhanced resolution in the ^{1}H NMR spectrum; this H_3-H_7 coupling was not usually observed. The H_4, H_3, and H_6 resonances were then assigned on the basis of further selective decoupling experiments.

For BT two coordination modes are possible; coordination of either the benzene or thiophene ring would result in 6 e^- donation to Ru. A comparison of the ^{1}H NMR shifts for **1** with those for uncoordinated BT suggests that it is bound in an η^6 fashion through the benzene ring as proposed for $Cr(CO)_3(BT)$.[15] The H2 and H3 resonances for $Cr(CO)_3BT$ shift downfield with respect to the free ligand while those of H4, H5, H6, and H7 shift upfield. This was also observed for **1**. In general, upfield shifts are observed upon coordination of arenes to neutral or cationic transition metal centers.[18] However, to clearly identify the coordination mode, in addition to learning more about the structural effects of coordination on the BT ligand, an X-ray diffraction study of **1** was undertaken.

The crystal structure of **1** (Figure 2.1) shows that the benzo portion of the ligand is coordinated to the metal. The Ru-C_8C_9, Ru-C_4C_7, and Ru-C_5C_6 distances show evidence of ring slippage which has been observed in other transition metal complexes containing fused arene ring ligands (napthalene, phenanthrene, anthracene, octamethylnapthalene).[31] The slipped distance (the average Ru-C_8C_9 distance minus the average Ru-C_5C_6 distance) for 1 is 0.07 Å; in other complexes slippage from 0.03 to 0.12 Å has been observed. One explanation offered for this phenomenon is that slippage allows the uncoordinated ring to retain more of its aromatic character, but it has also been suggested that the junction carbons cannot interact as effectively with the metal because they are already π-bonded to three other atoms.[31a] CNDO molecular orbital calculations of the localized charges for each of the carbon atoms and sulfur have been reported. These results, shown below, suggest that there is less electron density available at C8 and C9 for bonding to Ru.[32] The BT and Cp rings are, within experimental error, parallel (Table 2.7). The atoms in the BT ligand show slight deviations ($\leq$ 0.034Å) from planarity.



Comparison of the ^{1}H NMR shifts of the 3-MeBT ligand of **2** to those for uncoordinated 3-MeBT and 1 (Table 2.5) suggests that the ligand is bound via the benzene ring. Thus, the H2 and C3-CH_3 resonances move downfield relative to free 3-MeBT while those for H4-H7 move upfield.

Preparation of $[Cp^*Rh(T)](PF_6)_2$, 3, and $[Cp^*Rh(BT)](PF_6)_2$, 4

Complex **3** was prepared in 56.8% yield from $[Cp^*RhCl_2]_2$, $AgPF_6$, and T as shown in eq. 2.

Table 2.7. Interplanar angles for [CpRu(BT)]BF_4, 1[a]

Rings	Interplanar Angles (deg)
1, 2	178.38
1, 3	179.47
1, 4	178.86
2, 3	1.47
2, 4	0.60
3, 4	0.88

[a] Ring 1: C10, C11, C12, C13, C14; Ring 2: C4, C5, C6, C7, C8, C9; Ring 3: S, C2, C3, C8, C9; Ring 4: Ring 2 + Ring 3.

$$[Cp^*RhCl_2]_2 + 4\ AgPF_6 \xrightarrow[\text{xs T}]{\text{acetone}} 2[Cp^*Rh(T)](PF_6)_2 + 4\ AgCl \qquad (2)$$

$$\underset{}{3}$$

The $[Cp^*RhCl_2]_2$ and $AgPF_6$ react to form $[Cp^*Rh(acetone)_3](PF_6)_2$ which was previously reported by White et al. and has been used to synthesize other Cp*Rh (arene) dications.[33] The Rh complexes are air stable as solids. However, the T and BT ligands are easily displaced by acetone (both in less than 15 min). They are relatively stable in nitromethane (**3**, at least 1 h; **4**, 12 h).

The ^1H NMR of **3** shows a downfield shift of the thiophene protons relative to free T (Table 2.8) as has been observed for other dicationic arene complexes.[33] The BT protons of **4** also shift downfield relative to the free ligand. However, the H2 and H3 resonances show large downfield shifts, H4 and H7 shift to slightly lower field, and H5 and H6 show little change relative to uncoordinated BT.

Cp^*IrL^{2+} (L = T,BT,3-MeBt and 2,3-Me_2BT), 5-8 The preparation of **5** from $[Cp^*Ir(acetone)_3](BF_4)_2$ proceeds analogously to that of **3** shown in eq. 2. This method has been used by White et al. to synthesize other Ir arene dications.[33] For the Rh complexes refluxing had little effect on the yield, but for Ir the yield is increased approximately two-fold when the reactions are refluxed. The complexes **6-8** are synthesized in a similar manner.

The compounds **5-8** have all been characterized by ^1H and ^{13}C NMR as well as elemental analysis (Tables 2.4, 2.5, and 2.6). The solids are all

Table 2.8. A comparison of ^1H NMR shifts for uncoordinated and π-bound T (ppm)

Compound	$H_{2,5}$	$H_{3,4}$
$Cr(CO)_3(T)^{a,b}$	5.37	5.59
$CpRu(T)^{+,c,d}$	6.50	6.57
T^e	7.43	7.15
$Cp^*Rh(T)^{2+,e}$	7.51	7.65
$Cp^*Ir(T)^{2+,e}$	7.55	7.60

[a] Reference 14g.

[b] $CDCl_3$.

[c] d_6-acetone.

[d] Reference 11b.

[e] CD_3NO_2.

air stable, but **5** is extremely moisture sensitive. The Ir complexes are much more stable than the Rh analogs towards ligand displacement. Acetone displaces T from **5** in approximately 2 h at room temperature while **6** will not lose BT even after 12 h in acetone.

The ^{1}H NMR spectra of **6-8** suggest that coordination occurs through the benzene ring of BT, 3-MeBT and 2,3-Me_2BT. Thus, the H2, H3, C2-CH_3 and C3-CH_3, resonances move further downfield relative to the free ligand upon coordination to Ir, than those of H4-H7 (Table 2.5).

CONCLUSION

In all of the Ru, Rh, and Ir complexes the BTs coordinate through the π-system of the benzene ring as in $Cr(CO)_3(BT)$.[15] Even in the case of 2,3-Me_2BT, where the presence of two electron donating methyl groups might be expected to promote thiophene coordination, the benzene ring was bound.

All of the metals used in these complexes are active HDS catalysts.[34] We are exploring the reactivities of these complexes as possible models for reactions of π-bound T and BTs on catalysts in the HDS process.

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SUPPLEMENTARY MATERIAL

Table 2.9. The least squares planes for [CpRu(BT)]BF_4, 1[a]

Ring	Plane
1	0.57652 x - 0.78459 y - 0.22165 z = 0.92045
2	-0.56187 x + 0.78991 y + 0.24563 z = 2.65516
3	-0.57974 x + 0.78195 y + 0.22903 z = 2.60708
4	-0.56999 x + 0.78571 y + 0.24035 z = 2.62569

Table 2.9. Continued

Ring	Origin (x,y,z)	s^2(x,y,z)
1	3.0410, 1.0167, 0.1498	0.0003
2	1.0376, 3.8134, 0.9196	0.0017
3	1.6399, 4.8470, -1.0142	0.0003
4	1.2969, 4.2609, 0.0712	0.0036

[a] s^2 = (sum of atomic deviations from the plane)^2.

Table 2.10. Bond distances and angles for the BF_4^- anion in $[CpRu(BT)]BF_4$, 1

Bond Distances (Å)		Bond Angles (°)	
B-F1	1.347(12)	F1-B-F2	114.5(8)
B-F2	1.354(12)	F1-B-F3	105.1(9)
B-F3	1.397(14)	F1-B-F4	111.0(9)
B-F4	1.315(16)	F2-B-F3	106.5(8)
	F2-B-F4	111.0(10)	
	F3-B-F4	108.4(9)	

Table 2.11. Structure factor table for [CpRu(BT)]BF_4, **1.** The k index serves as column headings. Its maximum value is 13 and its minimum value is 0. The number of pieces of data = 1748 and the multiplicative scale factor for FO and FC = 10.000; FO will be signed. There are sixteen columns across the table

K = 0

H	L	FO	FC
0	2	1749	1962
0	4	831	886
0	6	180	126
0	8	324	-372
0	10	679	-669
0	12	503	-473
0	14	270	-250
0	16	129	-146
1	-16	199	-189
1	-14	82	-82
1	-12	173	166
1	-10	424	403
1	-8	869	867
1	-6	1213	1178
1	-4	440	427
1	-2	1249	1137
1	0	105	-27
1	2	464	-566
1	4	842	-717
1	6	172	-173
1	8	614	-667
1	10	419	-406
1	12	295	-298
1	16	108	112
2	-16	64	51
2	-14	147	164
2	-12	404	404
2	-10	434	463
2	-8	665	674
2	-6	704	723
2	-4	216	-187
2	-2	1103	-1063
2	0	2225	-2225
2	2	1132	-1226
2	4	960	-970
2	6	596	-579
2	8	432	471
2	10	485	475
2	12	391	368
2	14	254	252
2	16	144	160
3	-16	210	187
3	-14	223	202
3	-10	265	-254
3	-8	630	-629
3	-6	1201	-1247
3	-4	1269	-1192
3	-2	671	-552
3	0	50	-17
3	2	517	489
3	4	480	482
3	6	325	346
3	8	746	724
3	10	523	506
3	12	134	139
4	-14	154	-179
4	-12	370	-397
4	-10	304	-310
4	-8	659	-680
4	-6	680	-662
4	-4	69	34
4	-2	418	369
4	0	1143	1112
4	2	1497	1546
4	4	1118	1115
4	6	711	717
4	8	295	315
4	10	128	-116
4	12	247	-233
4	14	209	-203
5	-8	406	422
5	-6	678	721
5	-4	1072	1086
5	-2	688	630
5	0	629	609
5	4	408	-428
5	6	299	-282
5	8	388	-384
5	10	228	-247
5	12	123	-146
6	-14	83	97
6	-12	251	283
6	-10	357	375
6	-8	321	338
6	-6	422	413
6	-4	156	137
6	0	563	-549
6	2	703	-685
6	4	660	-638
6	6	393	-381
6	8	240	-234
6	12	135	127
7	-12	209	197
7	-10	177	179
7	-8	131	-116
7	-6	296	-313
7	-4	533	-515
7	-2	612	-589
7	0	413	-381
7	2	278	-251
7	4	203	200
7	6	93	82
7	8	236	223
7	10	199	196
8	-10	190	-190
8	-8	259	-262
8	-6	359	-361
8	-4	204	-185
8	0	116	125
8	2	299	290
8	4	326	321
8	6	326	321
8	8	183	159
9	-6	130	135
9	-4	417	402
9	-2	515	501
9	0	348	342
9	2	190	184
9	6	55	-21
10	-6	184	188
10	-4	166	171
10	-2	118	120
10	2	84	-107
10	4	114	-122

K = 1

H	L	FO	FC
0	1	246	-136
0	2	736	-765
0	3	554	518
0	4	1220	-1237
0	5	55	56
0	6	1050	-1015
0	7	385	-330
0	8	613	-624
0	10	459	-474
0	12	132	-127
0	13	92	-103
0	16	156	149
1	-16	104	92
1	-14	291	271
1	-12	406	400
1	-11	62	-54
1	-10	575	531
1	-9	69	53
1	-8	380	382
1	-7	101	115
1	-6	174	-185
1	-5	381	405
1	-4	291	-257
1	-3	592	567
1	-2	1920	-1877
1	-1	276	-252
1	0	1372	-1351
1	1	642	-643
1	2	2199	-2366
1	3	502	-548
1	4	497	-515
1	5	325	-375
1	6	63	-60
1	7	469	-479
1	8	163	146
1	9	103	-133
1	10	468	477
1	11	65	69
1	12	353	343
1	14	296	272
1	16	148	143
2	-16	176	184
2	-14	153	157
2	-12	61	73
2	-11	136	128
2	-10	66	-84
2	-9	169	163
2	-8	742	-756
2	-7	226	227
2	-6	1033	-1000
2	-5	520	-555
2	-4	1072	-1049
2	-3	175	-217
2	-2	421	-404
2	-1	58	46
2	0	1014	-892
2	1	230	-149
2	2	605	571
2	4	614	613
2	5	76	56
2	6	771	781
2	8	494	532
2	9	59	-56
2	10	481	485
2	12	131	125
2	13	75	84
3	-14	235	-222
3	-13	83	88
3	-12	247	-244
3	-11	124	137
3	-10	530	-519
3	-9	123	126
3	-8	529	-486
3	-7	92	-98
3	-6	317	-325
3	-5	68	-73
3	-4	298	241
3	-3	406	-424
3	-2	706	654
3	-1	89	-111
3	0	875	864
3	1	518	-563
3	2	1047	988
3	3	115	-92
3	4	994	967
3	5	121	129
3	6	250	289
3	7	324	353
3	8	116	120
3	10	210	-223
3	12	317	-290
3	14	217	-199
4	-14	160	-173
4	-12	81	-94
4	-11	184	-190
4	-10	177	190
4	-9	169	-174
4	-8	372	384
4	-6	811	795
4	-5	281	289
4	-4	1085	1071
4	-3	344	340
4	-2	1389	1292
4	-1	141	164
4	0	473	456
4	1	195	200
4	3	183	-196

Table 2.11. Continued

4	4	431	-403
4	5	98	84
4	6	555	-592
4	7	68	-94
4	8	546	-572
4	9	102	-106
4	10	445	-446
4	11	74	-57
4	12	194	-191
5	-11	79	-84
5	-10	485	518
5	-8	396	393
5	-6	333	337
5	-5	94	-97
5	-4	274	252
5	-3	206	182
5	-2	493	-478
5	-1	311	293
5	0	737	-701
5	1	366	381
5	2	985	-975
5	3	80	118
5	4	643	-659
5	5	123	-131
5	6	402	-410
5	7	171	-196
5	8	171	-171
5	9	179	-184
5	11	66	-64
5	12	198	197
6	-14	160	177
6	-12	178	205
6	-11	79	84
6	-9	118	126
6	-7	62	89
6	-6	337	-318
6	-5	112	-106
6	-4	505	-496
6	-3	217	-218
6	-2	624	-606
6	-1	135	-163
6	0	559	-544
6	2	217	-204
6	6	376	376
6	7	112	122
6	8	194	187
6	9	88	66
6	10	275	261
6	12	158	156
7	-12	178	-178
7	-10	261	-254
7	-8	380	-355
7	-7	112	106
7	-6	343	-324
7	-5	87	89
7	-4	162	-165
7	-2	223	220
7	0	359	335
7	1	110	-122
7	2	386	391
7	3	122	-119
7	4	440	440
7	6	279	272
7	8	93	94
7	9	64	71
8	-9	134	-137
8	-7	144	-147
8	-6	227	203
8	-5	65	-69
8	-4	416	397
8	-2	474	472
8	-1	118	108
8	0	420	416
8	1	180	180
8	2	201	206
8	3	89	95
8	4	145	140
8	8	157	-154
9	-8	265	272
9	-6	312	302
9	-4	235	232
9	0	121	-134
9	1	65	70
9	2	185	-184
9	4	251	-259
9	6	184	-188
10	-6	69	-55
10	-4	136	-136
10	-2	217	-226
10	0	187	-178
10	1	78	-69
10	2	132	-136
10	4	65	-66

K = 2

H	L	FO	FC
0	0	1532	-1422
0	1	229	-165
0	2	201	-158
0	3	259	-236
0	4	857	-848
0	5	201	-189
0	6	288	-298
0	7	346	-352
0	8	73	89
0	9	261	-249
0	10	259	249
0	11	119	-117
0	12	374	345
0	14	279	271
0	16	123	122
1	-16	151	133
1	-14	171	156
1	-12	92	97
1	-11	115	125
1	-10	276	-248
1	-9	410	370
1	-8	651	-655
1	-7	204	197
1	-6	1031	-1039
1	-5	356	415
1	-4	855	-840
1	-3	742	-744
1	-2	1823	-1801
1	-1	480	-495
1	0	303	-396
1	1	513	-535
1	2	669	697
1	3	726	-705
1	4	833	915
1	6	877	943
1	7	250	243
1	8	842	837
1	9	124	134
1	10	230	201
1	11	214	197
1	13	145	144
1	16	124	-116
2	-16	80	-89
2	-14	215	-220
2	-13	61	77
2	-12	379	-364
2	-10	375	-363
2	-9	172	-161
2	-8	455	-445
2	-6	94	99
2	-5	407	-379
2	-4	554	530
2	-3	79	-89
2	-2	180	-120
2	-1	826	689
2	0	349	348
2	1	706	706
2	2	593	526
2	3	533	-511
2	4	252	238
2	5	452	453
2	6	301	289
2	7	144	136
2	8	108	-125
2	9	70	70
2	10	225	-199
2	12	281	-267
2	14	201	-192
3	-16	137	-141
3	-14	172	-176
3	-13	82	-87
3	-12	100	-106
3	-11	213	-214
3	-9	350	-332
3	-8	99	87
3	-7	77	-89
3	-6	744	762
3	-5	418	-375
3	-4	1103	1065
3	-3	136	129
3	-2	1006	1009
3	-1	421	390
3	0	467	535
3	1	53	29
3	2	68	-57
3	3	678	708
3	4	486	-541
3	5	304	316
3	6	867	-867
3	7	200	177
3	8	736	-736
3	9	136	-116
3	10	391	-365
3	11	145	-132
3	12	91	-104
3	13	109	-100
4	-14	167	181
4	-13	101	-124
4	-12	342	343
4	-11	130	-140
4	-10	303	295
4	-8	479	504
4	-7	214	199
4	-6	206	189
4	-5	408	438
4	-4	316	-307
4	-2	591	-595
4	-1	425	399
4	0	781	-747
4	1	220	186
4	2	714	-728
4	3	253	260
4	4	330	-327
4	5	265	-292
4	6	329	-315
4	7	163	-160
4	8	147	-154
4	9	59	-50
4	10	143	132
4	11	82	-95
4	12	110	132
4	14	132	147
5	-12	97	112
5	-9	143	141
5	-8	116	-115
5	-7	92	88
5	-6	306	-315
5	-5	99	-90
5	-4	755	-754
5	-3	73	-32
5	-2	773	-734
5	-1	242	-229
5	0	771	-808
5	2	305	-296
5	3	383	-384
5	4	205	229
5	5	200	-191
5	6	314	313
5	8	437	443
5	9	142	135

Table 2.11. Continued

5	10	334	328
5	12	168	166
6	-12	169	-194
6	-10	369	-387
6	-8	432	-459
6	-7	134	-125
6	-6	288	-295
6	-5	89	-116
6	-3	206	-196
6	-1	255	-259
6	0	369	388
6	2	493	486
6	3	59	61
6	4	384	363
6	5	97	94
6	6	157	145
6	7	246	236
6	9	118	126
6	10	69	-56
6	12	83	-80
7	-12	139	-138
7	-10	97	-111
7	-9	208	-203
7	-7	118	-126
7	-6	125	138
7	-5	114	-117
7	-4	336	302
7	-3	119	-128
7	-2	343	338
7	0	316	327
7	1	121	116
7	2	377	358
7	3	134	132
7	5	97	100
7	6	132	-139
7	8	295	-297
7	10	218	-205
8	-10	235	232
8	-8	314	303
8	-6	300	296
8	-5	65	60
8	-4	189	172
8	-2	82	-92
8	-1	103	102
8	0	249	-241
8	1	80	76
8	2	374	-382
8	4	297	-295
8	6	247	-245
8	8	78	-104
9	-9	82	87
9	-5	68	78
9	-4	185	-195
9	-2	236	-230
9	0	249	-260
9	1	78	-83
9	2	191	-209
9	3	91	-101
9	4	76	-84
9	5	82	-101
10	-6	202	-203
10	-4	208	-194
10	-2	84	-76
10	-1	78	-85
10	2	147	150

K = 3

H	L	FO	FC
0	1	808	-842
0	2	542	488
0	3	582	-583
0	4	809	794
0	5	210	-223
0	6	722	733
0	7	384	407
0	8	728	728
0	9	337	331
0	10	273	277
0	11	222	220
0	13	149	150
0	14	84	-83
0	16	90	-92
1	-16	74	-83
1	-15	71	77
1	-14	216	-211
1	-12	309	-291
1	-11	181	-173
1	-10	517	-498
1	-9	286	-280
1	-8	462	-448
1	-7	333	-320
1	-5	503	-428
1	-4	430	375
1	-3	443	467
1	-2	95	180
1	-1	918	824
1	0	71	146
1	2	1258	1281
1	3	405	383
1	4	851	838
1	5	392	366
1	6	100	-57
1	7	369	345
1	8	133	-138
1	9	205	211
1	10	236	-236
1	11	199	201
1	12	267	-257
1	13	61	51
1	14	199	-197
2	-16	131	-135
2	-14	131	-144
2	-11	241	-247
2	-10	70	90
2	-9	166	-189
2	-8	471	513
2	-7	486	-502
2	-6	532	519
2	-4	857	856
2	-3	332	-323
2	-2	112	79
2	-1	656	674
2	0	274	239
2	1	941	950
2	2	144	113
2	3	730	736
2	4	671	-695
2	5	651	637
2	6	886	-865
2	7	76	91
2	8	531	-505
2	9	175	-184
2	10	115	-124
2	11	144	-143
2	12	69	-75
2	13	186	-166
2	15	94	-89
3	-15	102	-106
3	-14	136	140
3	-13	88	-83
3	-12	217	225
3	-10	454	448
3	-9	188	194
3	-8	302	287
3	-7	556	543
3	-6	234	267
3	-5	254	249
3	-4	179	-179
3	-3	458	459
3	-2	467	-416
3	0	921	-912
3	1	371	342
3	2	823	-838
3	3	324	-357
3	4	656	-681
3	5	123	136
3	6	216	-225
3	7	169	-182
3	10	259	260
3	11	94	-95
3	12	279	266
3	13	64	-63
3	14	157	140
4	-14	131	132
4	-12	94	101
4	-11	183	204
4	-9	173	190
4	-8	242	-252
4	-7	193	198
4	-6	514	-565
4	-5	301	322
4	-4	688	-725
4	-3	192	196
4	-2	597	-614
4	0	343	-304
4	1	612	-615
4	3	318	-324
4	4	470	430
4	5	671	-682
4	6	411	407
4	7	99	-111
4	8	314	318
4	10	269	280
4	11	96	97
4	12	172	174
4	13	106	104
5	-14	84	-82
5	-13	94	105
5	-12	170	-189
5	-11	113	128
5	-10	272	-296
5	-9	113	-113
5	-8	291	-299
5	-7	309	-325
5	-6	380	-386
5	-5	366	-380
5	-4	115	-118
5	-3	488	-476
5	-2	155	159
5	-1	289	-271
5	0	378	400
5	2	466	471
5	3	172	168
5	4	493	502
5	5	184	201
5	6	288	287
5	7	190	191
5	9	217	217
5	12	137	-127
5	13	82	90
6	-12	185	-199
6	-8	157	173
6	-7	167	-175
6	-6	368	352
6	-5	184	-178
6	-4	460	443
6	-3	81	-94
6	-2	486	476
6	0	286	285
6	1	189	180
6	2	60	49
6	3	234	250
6	4	75	-90
6	5	306	302
6	6	315	-312
6	7	222	215
6	8	257	-260
6	10	218	-216
6	12	94	-96
7	-11	97	-84
7	-10	212	222
7	-8	294	289
7	-7	99	94
7	-6	229	219
7	-5	235	233
7	-4	77	91

Table 2.11. Continued

7	-3	323	302
7	-2	65	56
7	-1	258	261
7	0	135	-141
7	1	107	124
7	2	283	-285
7	4	419	-418
7	6	243	-238
7	7	89	-79
7	8	107	-105
7	9	104	-108
8	-11	70	76
8	-10	67	69
8	-9	98	115
8	-7	206	208
8	-6	241	-221
8	-5	153	150
8	-4	324	-319
8	-3	194	186
8	-2	286	-292
8	-1	104	116
8	0	198	-203
8	2	129	-145
8	3	129	-146
8	5	152	-160
8	6	188	198
8	7	161	-163
8	8	167	169
8	9	87	-83
9	-9	77	79
9	-8	134	-128
9	-6	163	-163
9	-5	67	-82
9	-4	139	-151
9	-3	168	-161
9	-1	143	-150
9	0	106	116
9	1	159	-162
9	2	136	146
9	4	188	204
9	6	157	178
10	-4	83	80
10	-2	187	189
10	0	200	203
10	2	132	125
K =	4		
H	L	FO	FC
0	0	941	968
0	1	127	-133
0	2	892	911
0	3	710	716
0	4	387	369
0	5	810	775
0	7	589	589
0	8	315	-330
0	9	301	296
0	10	316	-310
0	11	197	187
0	12	265	-246
0	14	151	-143
0	15	90	-82
1	-15	78	-74
1	-14	78	-89
1	-13	198	-178
1	-11	295	-288
1	-10	331	318
1	-9	63	-73
1	-8	394	391
1	-7	272	247
1	-6	759	802
1	-5	230	-237
1	-4	510	451
1	-3	710	711
1	-2	371	338
1	-1	778	745
1	0	277	260
1	1	466	449
1	2	142	-138
1	3	461	464
1	4	446	-427
1	5	441	456
1	6	689	-680
1	7	65	58
1	8	365	-342
1	9	94	-104
1	10	263	-252
1	11	287	-270
1	13	138	-146
1	15	123	-124
2	-15	68	-75
2	-14	112	117
2	-12	284	291
2	-11	73	89
2	-10	442	451
2	-9	267	275
2	-8	536	568
2	-7	347	360
2	-6	113	138
2	-5	639	654
2	-4	99	-102
2	-3	1009	965
2	-2	591	-605
2	-1	635	607
2	0	1077	-1083
2	1	159	-174
2	2	1175	-1209
2	3	196	-195
2	4	667	-721
2	5	778	-827
2	6	314	-278
2	7	357	-344
2	8	170	166
2	9	433	-400
2	10	304	296
2	11	217	-215
2	12	218	195
2	14	169	151
3	-15	88	86
3	-14	78	74
3	-13	212	208
3	-11	255	257
3	-10	71	-61
3	-9	245	239
3	-8	253	-259
3	-7	107	117
3	-6	711	-738
3	-5	377	364
3	-4	371	-344
3	-3	241	-260
3	-2	122	-104
3	-1	564	-620
3	1	219	-199
3	2	192	214
3	3	803	-780
3	4	261	247
3	5	389	-350
3	6	495	461
3	7	122	-117
3	8	263	269
3	10	204	206
3	12	81	92
3	13	122	140
4	-14	88	-84
4	-13	117	125
4	-12	168	-198
4	-10	211	-225
4	-8	290	-320
4	-7	224	-232
4	-6	205	-220
4	-5	481	-575
4	-4	124	-162
4	-3	772	-806
4	-2	665	602
4	-1	758	-729
4	0	736	727
4	1	100	-122
4	2	641	701
4	3	125	-108
4	4	583	607
4	5	297	304
4	6	298	305
4	7	377	356
4	9	261	257
4	10	239	-237
4	11	171	169
4	12	145	-142
5	-14	98	-133
5	-12	125	-132
5	-11	135	-157
5	-9	307	-304
5	-8	330	328
5	-7	242	-242
5	-6	492	496
5	-4	464	472
5	-2	486	451
5	-1	468	473
5	0	244	234
5	1	255	282
5	2	62	-82
5	3	429	433
5	4	179	-188
5	5	217	221
5	6	152	-161
5	7	173	186
5	8	214	-223
5	9	62	70
5	10	154	-179
5	12	76	-100
5	13	96	-99
6	-12	78	104
6	-11	60	-85
6	-10	188	191
6	-9	71	-62
6	-8	285	300
6	-7	214	203
6	-5	299	285
6	-4	209	199
6	-3	438	441
6	-1	389	389
6	1	293	280
6	2	429	-410
6	3	98	100
6	4	452	-434
6	6	271	-259
6	7	250	-231
6	8	65	-60
6	9	182	-173
6	11	181	-173
7	-12	133	112
7	-11	133	133
7	-9	272	262
7	-8	175	-171
7	-7	267	260
7	-6	382	-359
7	-5	277	264
7	-4	442	-424
7	-3	90	94
7	-2	320	-299
7	-1	87	-88
7	0	159	-164
7	1	224	-228
7	3	191	-184
7	4	126	141
7	5	257	-274
7	6	247	243
7	7	166	-178
7	8	232	227
7	10	98	108
8	-10	123	-127
8	-8	159	-165
8	-6	115	-110
8	-5	101	-99
8	-4	104	-95
8	-3	156	-175
8	-1	330	-322

Table 2.11. Continued

8	0	65	76
8	1	214	-221
8	2	230	250
8	3	134	-137
8	4	236	244
8	6	218	229
8	8	124	129
9	-7	164	-169
9	-6	85	91
9	-5	150	-150
9	-4	212	205
9	-3	89	-90
9	-2	235	218
9	0	214	222
9	1	87	98
9	3	171	184
9	5	134	150
9	6	84	-82
10	-3	116	127
10	-1	138	142

K = 5

H	L	FO	FC
0	1	654	573
0	2	443	-439
0	3	518	500
0	4	812	-846
0	5	342	368
0	6	532	-498
0	7	70	69
0	8	392	-385
0	9	226	-213
0	10	138	-140
0	11	256	-246
0	12	76	-86
0	13	309	-287
0	14	67	63
0	15	119	-105
1	-15	107	-111
1	-14	104	131
1	-13	71	-63
1	-12	257	256
1	-10	327	326
1	-9	243	254
1	-8	104	101
1	-7	530	531
1	-5	916	922
1	-4	234	-252
1	-3	666	690
1	-2	527	-507
1	-1	733	724
1	0	781	-813
1	1	117	-125
1	2	339	-367
1	3	696	-707
1	4	465	-451
1	5	877	-876
1	6	152	-165
1	7	697	-699
1	9	363	-366
1	10	62	61
1	11	191	-203
1	12	107	113
1	14	111	116
1	15	89	87
2	-15	109	119
2	-13	273	273
2	-11	289	283
2	-9	127	135
2	-8	308	-323
2	-7	122	109
2	-6	408	-394
2	-5	304	-301
2	-4	694	-705
2	-3	469	-466
2	-2	399	-389
2	-1	805	-791
2	0	161	-171
2	1	675	-709
2	2	135	-117
2	3	584	-566
2	4	566	555
2	5	332	-317
2	6	465	455
2	7	100	-118
2	8	433	416
2	9	72	65
2	10	183	183
2	11	66	77
2	12	98	103
2	13	215	203
3	-14	114	-117
3	-13	130	142
3	-12	248	-242
3	-10	301	-298
3	-9	273	-277
3	-8	175	-164
3	-7	340	-363
3	-6	112	-97
3	-5	551	-566
3	-4	553	532
3	-3	1254	-1160
3	-2	941	860
3	-1	1090	-1017
3	0	692	660
3	1	289	-321
3	2	487	502
3	3	416	407
3	4	453	444
3	5	292	293
3	6	193	202
3	7	570	580
3	8	150	-149
3	9	381	387
3	10	62	-71
3	11	205	206
3	12	135	-149
3	14	101	-120
4	-3	184	201
4	-2	332	355
4	-1	277	306
4	0	288	308
4	1	795	793
4	2	91	99
4	3	274	258
4	4	70	-61
4	5	204	211
4	6	231	-230
4	7	107	112
4	8	309	-300
4	9	69	76
4	10	195	-199
4	12	83	-87
4	13	121	-134
5	-13	76	-98
5	-10	254	250
5	-8	226	216
5	-7	64	63
5	-6	181	183
5	-5	434	411
5	-4	117	-110
5	-3	547	516
5	-2	149	-151
5	-1	496	487
5	0	460	-447
5	1	197	196
5	2	375	-386
5	3	90	103
5	4	268	-275
5	5	181	-186
5	6	83	-93
5	7	303	-331
5	9	298	-316
5	11	150	-157
5	12	69	89
6	-9	274	311
6	-7	309	301
6	-6	240	-233
6	-5	186	174
6	-4	288	-274
6	-3	72	-79
6	-2	340	-334
6	-1	417	-414
6	0	302	-297
6	1	499	-488
6	2	155	-147
6	3	301	-302
6	5	247	-248
6	6	169	179
6	7	285	-281
6	8	184	182
6	10	127	127
6	11	62	55
7	-10	199	-181
7	-8	228	-213
7	-6	195	-181
7	-5	239	-229
7	-3	342	-301
7	-2	75	78
7	-1	456	-436
7	0	301	301
7	1	364	-378
7	2	260	265
7	3	186	-193
7	4	279	274
7	6	152	153
7	9	165	160
8	-9	190	-175
8	-7	287	-275
8	-6	123	128
8	-5	218	-206
8	-4	175	165
8	-3	104	-109
8	-2	215	214
8	-1	73	66
8	0	117	117
8	1	158	159
8	2	75	72
8	3	226	231
8	5	162	168
8	7	98	105
9	-6	134	132
9	-3	166	168
9	-1	169	184
9	0	120	-124
9	1	151	164
9	2	150	-149
9	4	121	-132

K = 6

H	L	FO	FC
0	0	166	-161
0	1	71	55
0	2	437	-441
0	3	572	-564
0	5	446	-426
0	7	405	-371
0	8	82	-81
0	9	293	-277
0	11	85	-91
0	12	158	161
0	14	91	88
1	-13	219	224
1	-11	351	348
1	-10	76	-72
1	-9	232	224
1	-8	138	-137
1	-7	223	246
1	-6	404	-428
1	-4	469	-477
1	-3	769	-761
1	-2	449	-445
1	-1	987	-983
1	0	349	-335
1	1	875	-973
1	2	235	266

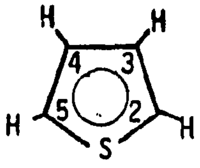
SECTION III. REACTIVITY OF HDS MODEL COMPLEXES: NUCLEOPHILIC ADDITION TO π-COORDINATED THIOPHENE AND BENZO[b]THIOPHENES[1]

INTRODUCTION

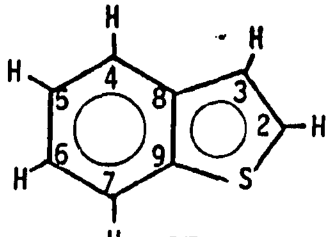
The process of catalytic hydrodesulfurization (HDS) is employed extensively in industry to remove sulfur, in the form of H_2S, from sulfur-containing hydrocarbons present in crude oils and coal liquids.[2] The desulfurization of these feeds is necessary because many of the catalysts used to process petroleum are poisoned by sulfur. In addition, the combustion of sulfur-containing fuels produces the air pollutant sulfur dioxide.[3]

Despite numerous investigations, the mechanism of HDS is not understood; therefore, elucidation of important reaction pathways on catalyst surfaces continues to be an active area of research. Mechanistic studies generally involve reaction of a representative sulfur-containing compound over an HDS catalyst; the compound most often used as a model is thiophene (T). The thiophenic compounds represent the largest class of organosulfur compounds found in crude oils and coal liquids[4] and are also the most difficult to desulfurize.[5] However, within this class, benzo[b]thiophene (BT) and its derivatives (BTs) are present in significantly greater quantities[6] and are less reactive under HDS conditions than Ts.[5,7] This suggests that BTs are also important compounds for the study of HDS.

Because heterogeneous reactor studies have yielded few details of the HDS mechanism of thiophenes,[8] our group has been investigating transition metal complexes of thiophenes in order to learn more about the reactivity of coordinated sulfur-containing compounds. These model complexes incorporate π-bound thiophenic ligands; π-bonding of the aromatic system



T



BT

of thiophenes to the catalyst surface has been proposed to be an important mode of adsorption[7a,b,9] and for T is supported by spectroscopic data.[10] In the case of $[(CO)_3Mn(T)]^+$ and $[CpRu(T)]^+$, this approach has provided useful insights into reactions such as hydride addition, deuterium exchange, and carbon-sulfur bond cleavage, which occur also over HDS catalysts.[11] An important extension of this work would include studying the reactivity of π-bound BTs in transition metal complexes.

This paper describes the reactivity of π-bound T and BTs in cationic cyclopentadienyl Ru, Rh, and Ir complexes with respect to addition of a variety of nucleophiles (H^-, MeO^-, $(MeO_2C)_2CH^-$, EtS^-, and phosphines); nucleophilic species such as hydrides and sulfides have been proposed to be present on HDS catalyst surfaces.[12] The complexes are the first isolable transition metal cyclohexadienyl complexes derived from fused-ring aromatic ligands.[13] The X-ray structure determination of one of the complexes, CpRu(BT•H), **6**, is also reported.

EXPERIMENTAL SECTION

General Procedures All reactions were performed under N_2 in reagent grade solvents. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from Na/benzophenone, CH_2Cl_2 and hexanes from CaH_2, MeOH from NaOMe and benzene was distilled from $LiAlH_4$. The solvents were stored over 4 Å molecular sieves, except for acetone which was stored over $MgSO_4$, and purged with N_2 prior to use. Commercial benzo[b]thiophene, BT, was sublimed at room temperature onto a water-cooled probe prior to use. The 2-MeBT,[14] $[Cp^*IrCl_2]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$),[15] $[Cp^*Ir(L)](BF_4)_2$ (L = BT, 3-MeBT,2,3-Me_2BT,T),[16] $[CpRu(BT)]PF_6$ ($Cp = \eta\text{-}C_5H_5$),[16] PPN$[HFe(CO)_4]$,[17] NaSEt,[18] and $NaCH(CO_2Me)_2$[19] were prepared according to literature methods. However, the $NaCH(CO_2Me)_2$[19] was not used in situ but was precipitated by addition of CH_2Cl_2 and then hexanes; the white solid was filtered, washed with additional CH_2Cl_2, and then dried in vacuo. The NaSEt was stored in a desiccator and the $NaCH(CO_2Me)_2$ was stored under N_2. Both compounds were weighed in a glove bag under a N_2 atmosphere.

The products **1-12** were characterized by elemental analysis (Galbraith Laboratories, Inc., Table 3.3) and their ^1H NMR spectra (Table 3.4). The ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Nicolet NT-300 spectrometer using deuterated solvents as internal locks and referenced to $SiMe_4$. Fast atom bombardment (FAB) spectra were run on a Kratos MS-50 mass spectrometer. Electron-ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Conductivity data were obtained on a Markson Electro Mark analyzer and calibrated with a standard KCl solution.

The electrochemical measurements were made using a Bioanalytical Systems CV-1B Cyclic Voltammograph under an Ar atmosphere at RT. A three-electrode cell was used with a Ag/AgCl (NaCl, 3.0 M) reference electrode, a Pt wire counter electrode, and a stationary Pt disc working electrode (area = 3.1 mm^2). The supporting electrolyte, Bu_4NPF_6, was prepared according to a literature method[20] and dried at 100 °C under vacuum for 30 h. A 0.1 M concentration of Bu_4NPF_6 was used for the cyclic voltammetric experiments. Analyte concentrations in the solvent, CH_3NO_2, varied from 1.1 to 0.73 mM.

[Cp*Ir(2-MeBT)](BF$_4$)$_2$, 1 To a stirred solution of $[Cp^*IrCl_2]_2$ (0.236 g, 0.296 mmol) in 5 mL of acetone was added $AgBF_4$ (0.230 g, 0.118 mmol). The solution was stirred 5 min and filtered through Celite which was rinsed with additional acetone (~4 mL). The volume of the filtrate was reduced to ~4 mL in vacuo, and then 2-MeBT (0.701 g, 0.473 mmol) was added. The reaction mixture was refluxed for 2 min and then cooled to RT. Approximately 20 mL of CH_2Cl_2 was added to precipitate the product which was filtered, dried in vacuo, and then recrystallized from CH_3NO_2/CH_2Cl_2 to give a white solid: yield, 0.260 g (67.8%); ^1H NMR (CD_3NO_2) δ 8.07 (m,H7), 7.86 (m,H4), 7.28 (m, H3,H5,H6), 2.98 (d,$J_{H3-C2C\underset{\sim}{H}_3}$ = 1.1 Hz, $C_2C\underset{\sim}{H}_3$), 2.11 (s, $C_5(C\underset{\sim}{H}_3)_5$; $^{13}C\{^1H\}$NMR(CD_3NO_2) δ 165.9 (C2), 120.3 (C9), 118.9 (C8), 118.3 (C3), 105.2 ($\underset{\sim}{C}_5(CH_3)_5$), 95.6 (C5), 93.8 (C6), 93.0 (C4), 92.0 (C7), 17.7 ($C2\underset{\sim}{C}H_3$), 9.1 ($C_5(\underset{\sim}{C}H_3)_5$).

[Cp*Ir(BT•H)]BF$_4$, 2 Approximately 5 mL of H_2O and 5 mL of CH_2Cl_2 were purged with N_2 for 5 min. To this stirred solution was added

[Cp*Ir(BT)]$(BF_4)_2$ (43.0 mg, 0.0677 mmol) and then $NaBH_4$ (5.1 mg, 0.13 mmol). After 5 min the layers were separated, and the water layer was extracted with CH_2Cl_2 (3 x 5 mL). The CH_2Cl_2 extracts were combined, dried for ~30 min over Na_2SO_4, and filtered. The yellow product was precipitated from the filtrate by addition of Et_2O: yield, 29 mg (78%); FAB(2-nitrophenyloctylether-CH_2Cl_2), m/e 463 (M^+); Λ_M (0.98 x 10^{-3} M in CH_3NO_2): 79 mho cm^2 mol^{-1}.

[Cp*Ir(3-MeBT•H)]BF_4, 3 To a stirred solution of [Cp*Ir(3-MeBT)]$(BF_4)_2$ (40.0 mg, 0.0616 mmol) in 3 mL of H_2O and 3 mL of CH_2Cl_2 was added $NaBH_4$ (4.7 mg, 0.12 mmol). The layers were separated after 3 min, and the H_2O layer was extracted with additional CH_2Cl_2. The yellow CH_2Cl_2 solution was treated as for **2** resulting in the isolation of a pale yellow solid: yield, 27 mg (79%); Λ_M (1.0 x 10^{-3} M in CH_3NO_2): 81 mho cm^2 mol^{-1}.

[Cp*Ir(2-MeBT•H)]BF_4, 4 This complex was prepared analogously to **2** from **1** (52.0 mg, 0.0801 mmol) and $NaBH_4$ (6.1 mg, 0.16 mmol). The product was isolated as a bright yellow solid: yield, 35 mg (78%).

Cp*Ir(2,3-Me_2BT•H)]BF_4, 5 This preparation was performed as for **2** from [Cp*Ir(2,3-Me_2BT)]$(BF_4)_2$ (55.0 mg, 0.0829 mmol) and $NaBH_4$ (6.3 mg, 0.17 mmol). A bright yellow solid was obtained: yield, 32.8 mg (68.5%).

CpRu(BT•H), 6 To a stirred solution of [CpRu(BT)]PF_6 (0.103 g, 0.231 mmol) in CH_2Cl_2 (5 mL) was added $NaBEt_3H$ (0.23 mL of a 1 M solution in THF, 0.23 mmol). The solution was stirred 5 min and evaporated to a yellow oil in vacuo. The oil was extracted with Et_2O, the Et_2O extract filtered, and the yellow filtrate passed through a short column (~4 cm) of alumina. The yellow Et_2O solution was then evaporated to dryness and the residue sublimed at room temperature onto a water cooled probe in vacuo to give a bright yellow solid: yield, 49.5 mg (71.2%); EIMS (18 eV), m/e 302 (base peak, M^+-H), 167 (M^+-BT•H), 134 (BT^+).

[Cp*Ir(BT•OMe)]BF_4, 7 To freshly distilled MeOH (5 mL) was added Na (1.8 mg, 0.078 mmol). The solution was stirred until all of the Na had dissolved. Then $[Cp^*Ir(BT)](BF_4)_2$ (51.3 mg, 0.0808 mmol) was added, and the mixture was stirred until none of the solid $[Cp^*Ir(BT)](BF_4)_2$ remained (~5 min). The yellow solution was evaporated to dryness, the residue extracted with CH_2Cl_2 (15 mL) and then the CH_2Cl_2 solution filtered. The volume of the yellow filtrate was reduced to 2 mL, and Et_2O (4 mL) was added to precipitate the product as a yellow solid which was then filtered, washed with Et_2O, and dried in vacuo: yield, 42.5 mg (93.7%); Λ_M (mho cm^2 mol^{-1}, 0.90 x 10^{-3} M in CH_3NO_2): 76.

[Cp*Ir(3-MeBT•OMe)]BF_4, 8 The preparation of this complex from Na (1.8 mg, 0.078 mmol) and $[Cp^*Ir(3\text{-}MeBT)](BF_4)_2$ (51.9 mg, 0.0799 mmol) in freshly distilled MeOH proceeded analogously to that for **6**. A pale yellow product was isolated: yield, 36.7 mg (77.4%). Λ_M (1.0 x 10^{-3} in CH_3NO_2): 75 mho cm^2 mol^{-1}.

[Cp*Ir(BT•CH($CO_2Me)_2$)]BF_4, 9 Under N_2, $NaCH(CO_2Me)_2$ (12.9 mg, 0.083 mmol) was weighed into a Schlenk flask. Acetone (4 mL) was vacuum distilled into the flask (cooled to -78 °C) which was stirred as it warmed to room temperature. Then, [Cp*Ir(BT)]$(BF_4)_2$ (53.6 mg, 0.0844 mmol) was added, the solution stirred for 2 min and then evaporated to dryness. The residue was extracted with CH_2Cl_2, and the yellow solution was filtered through a short alumina column (4 cm). The volume of the filtrate was reduced to ~0.5 mL in vacuo and 25 mL of Et_2O was added. The mixture was frozen in $N_2(\ell)$ and then slowly warmed to RT. This freezing process was repeated and the resulting yellow solid was filtered from the solution while it was still cold and then washed with cold Et_2O and dried in vacuo: yield, 22.6 mg (40.0%); Λ_M (1.0×10^{-3} M in CH_3NO_2): 75 mho cm^2 mol^{-1}.

[Cp*Ir(3-MeBT•CH$(CO_2Me)_2$)]BF_4, 10 This preparation was performed analogously to that for **8**, from NaCH$(CO_2Me)_2$ (12.0 mg, 0.0774 mmol) and [Cp*Ir(3-MeBT)]$(BF_4)_2$ (50.8 mg, 0.0782 mmol). The bright yellow oily product was crystallized by dissolving in CH_2Cl_2 (0.5 mL), adding Et_2O (80 mL) and storing at -20 °C for 58 h: yield, 31.9 mg (58.8%); Λ_M (1.2×10^{-3} M in CH_3NO_2): 65 mho cm^2 mol^{-1}.

[Cp*Ir(BT•SEt)]BF_4, 11 Under N_2, NaSEt (8.2 mg, 0.098 mmol) was weighed into a Schlenk flask. Then HSEt (1 mL) was added followed by acetone (5 mL, vacuum distilled into flask cooled to -78 °C). After the solution had warmed to 25°C additional HSEt (1 mL) was added, followed by [Cp*Ir(BT)]$(BF_4)_2$ (62.5 mg, 0.0984 mmol). The reaction mixture was stirred for 2 min and then evaporated to dryness in vacuo. The residue was extracted with CH_2Cl_2 and the solution was chromatographed on an alumina column (4 cm). The yellow product was eluted with acetone, and this solution was evaporated to a yellow oil in vacuo. The product was crystallized by dissolving in CH_2Cl_2 (0.5 mL), adding Et_2O (30 mL) and storing at -20 °C for 48 h. The green-yellow solid was filtered from the CH_2Cl_2/Et_2O solution and dried in vacuo: yield, 37.5 mg (62.5%).

[Cp*Ir(3-MeBT•SEt)]BF$_4$, 12 This compound was prepared from NaSEt (8.0 mg, 0.095 mmol) and [Cp*Ir(3-MeBT)]$(BF_4)_2$ (64.9 mg, 0.100 mmol) using a method analogous to that for **10** to give a green solid: yield, 22.1 mg (37.2%).

[Cp*Ir(BT•PMe$_3$)](BF$_4$)$_2$, 13 To an NMR tube containing CD_3NO_2 (0.25 mL) was added first [Cp*Ir(BT)]$(BF_4)_2$ (45.1 mg, 0.0710 mmol) and then PMe_3 (11 μL, 0.11 mmol). The clear solution turned bright yellow upon addition of the PMe_3; none of the [Cp*Ir(BT)]$(BF_4)_2$ was observed by ^{1}H NMR. The solution was evaporated to a yellow oil in vacuo. FAB (dithioerythritol/dithiothreitol), m/e 481 (base peak, $M^{2+}-PMe_3 + F^-$).

[Cp*Ir(d$_2$-BT)](BF$_4$)$_2$ To a solution of KOH (2.1 g, 37 mmol) in MeOD (40 mL) was added [CpRu(BT)]PF_6 (1.776 g, 3.988 mmol); the mixture was stirred at room temperature for 19 h.[11g] Then, CO_2 was bubbled through the solution for 1.75 h. After evaporation of the reaction mixture to dryness in vacuo, the residue was extracted with CH_2Cl_2 and then acetone. The extracts were filtered, and Et_2O was added to precipitate out [CpRu(d$_2$-BT)]PF_6 which was dried in vacuo: yield, 1.354 g (76.24%). The compound was dissolved in CH_3CN (250 mL) and photolyzed (450 W Canrad-Hanovia medium-pressure, quartz, mercury-vapor lamp) for 7 days to give $CpRu(NCMe_3)_3^+$ and d$_2$-BT. The solvent was removed from the resulting orange solution by rotoevaporation giving a brownish oil which was extracted with pentane (100 mL). The bulk of the pentane was removed by rotoevaporation and then the last 0.5 mL was removed in vacuo. The d_2-BT remaining was purified by sublimation in vacuo at 25°C onto a water-cooled probe: yield 0.325 g (79.7% from [CpRu(BT)]PF_6). The d_2-BT, with deuterium at the 2- and 7-positions (as determined by ^{1}H NMR), was then used in the preparation of [Cp*Ir(d_2-BT)]$(BF_4)_2$ from [Cp*IrCl_2]$_2$ by the method which has been previously described.[16]

X-ray Structure Determination of CpRu(BT•H), 6 Gold-colored crystals of **6** were grown by slow evaporation of a concentrated hexanes solution at -1 °C. The crystal,[21] of approximate dimensions 0.3 x 0.3 x 0.5 mm was mounted on the end of a glass fiber and coated with a thin layer of epoxy cement. A least-squares fit of 25 reflections found in the range $20° < 2\theta < 30°$ by an automated search routine indicated a monoclinic crystal system. The intensities from ϕ-scans of eight reflections were used to apply an empirical absorption correction to the data. Lorentz and polarization corrections were applied to the data, and the intensities of equivalent reflections were averaged.

The position of the Ru atom was determined by direct methods. The remaining non-hydrogen atoms were then located from a difference Fourier synthesis. Following full-matrix refinement[22] of all parameters for the non-hydrogen atoms, a difference Fourier map revealed peaks corresponding to all of the hydrogen atoms. Attempted full-matrix refinement using isotropic hydrogen atoms was unsuccessful. Therefore, only the hydrogen atoms on the cyclopentadienyl ring were refined. The positions of the hydrogen atoms in the BT•H ligand were calculated (C-H bond length = 0.95 Å, isotropic temperature factor = 1.3 B_{eqv} for the attached carbon atom) and used in the structure factor calculations. Final refinement resulted in convergence to R = 0.029 and R_w = 0.043.

The crystal and data collection parameters for **6** are given in Table 3.1. The final positional and thermal parameters are listed in Table 3.2. Bond lengths and angles are presented in **Table 3.6**, and an ORTEP[23] drawing of **6** is given in Figure 3.3.

Table 3.1. Crystal and data collection parameters for the X-ray diffraction study of CpRu(BT•H), **6**, isomer A

Formula	$RuSC_{13}H_{12}$
Formula weight	301.37
Space group	$P2_1/n$
a, Å	5.914(2)
b, Å	14.234(2)
c, Å	12.800(2)
β, deg	91.36(2)
V, $Å^3$	1077.2
Z	4
d_{calc}, g/cm^3	1.86
Crystal size, mm^3	0.3 x 0.3 x 0.5
$\mu(MoK_\alpha)$, cm^{-1}	15.7
Diffractometer	Enraf-Nonius CAD4
Radiation (monochromated in incident beam)	$MoK_\alpha(\lambda_2 = 0.71073$ Å)
Temperature, °C	21
Scan method	ω-2θ
Max 2θ, deg	55.0
Standard reflections	3, measured every hour of exposure (no observed decay)
Total unique reflections	2469
Unique reflections observed ($F_o^2 > 3\sigma(F_o^2)$)	2198
Number of parameters refined	156
T_{min}/T_{max}	0.996, 0.793

Table 3.1. Continued

R^a	0.029
R_w^b	0.043
Quality of fit indicator[c]	1.47
Largest shift/esd, final cycle	0.01
Largest peak, e/Å^3	0.73

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[b] $R_w = [\sum \omega(|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2}$; $\omega = 1/\sigma^2(|F_o|)$.

[c] Quality of fit $= [\sum \omega(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$.

Table 3.2. Positional and Thermal Parameters for CpRu(BT•H), **6**

Atom	x	y	z	B(ave, Å^2)[a]
Ru	0.07475(3)	0.68578(1)	0.19505(1)	1.909(4)
S	0.0256(1)	0.92682(5)	0.11371(7)	3.26(1)
C2	0.2929(6)	0.9116(2)	0.0658(3)	3.59(6)
C3	0.4243(5)	0.8499(2)	0.1181(2)	2.79(5)
C4	0.3738(5)	0.7379(2)	0.2788(3)	3.06(5)
C5	0.2130(6)	0.7052(2)	0.3509(2)	3.08(5)
C6	-0.0472(5)	0.7427(2)	0.3487(2)	2.83(5)
C7	-0.0472(5)	0.8425(2)	0.3127(2)	2.74(5)
C8	0.3007(5)	0.8087(2)	0.2067(2)	2.32(5)
C9	0.0738(4)	0.8415(2)	0.2117(2)	2.22(4)
C10	-0.1885(5)	0.6390(2)	0.0831(3)	3.67(6)
C11	0.1714(6)	0.5742(2)	0.1636(3)	3.95(7)
C12	0.0481(7)	0.5347(2)	0.1648(3)	4.01(7)
C13	0.1657(6)	0.5762(2)	0.0815(3)	3.72(6)
C14	0.0207(6)	0.6407(3)	0.0322(2)	3.71(6)
H10	-0.311(6)	0.676(2)	0.060(3)	1.7(8)
H11	-0.262(7)	0.566(3)	0.196(4)	3(1)
H12	0.096(6)	0.496(4)	0.205(3)	4(1)
H13	0.288(7)	0.561(3)	0.054(4)	3(1)
H14	0.071(6)	0.674(2)	-0.029(3)	1.9(8)

[a] Given in the form of the isotropic equivalent displacement parameter defined as $4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

RESULTS AND DISCUSSION

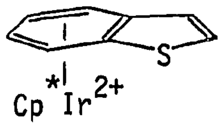
Preparation of $[Cp^*Ir(2\text{-}MeBT)](BF_4)_2$, 1 The reaction of $[Cp^*IrCl_2]_2$, $AgBF_4$, and 2-MeBT produces 1, as shown in eq. 1.

$$[Cp^*IrCl_2]_2 + 4\ AgBF_4 \xrightarrow[\text{xs 2-MeBT}]{\text{acetone}} \underset{\mathbf{1}}{2[Cp^*Ir(2\text{-}MeBT)](BF_4)_2} + 4\ AgCl \qquad (1)$$

This method has previously been used to synthesize other iridium T and BT compounds.[16] Complex 1 is air stable in the solid state.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of 1 were assigned by comparison with spectra for the analogous complexes, $[Cp^*IrL]^{2+}$ (L = BT, 3-MeBT, 2,3-Me_2BT),[14] as well as by comparison with spectra for uncoordinated 2-MeBT.[24] The H3, H4, H7, and C2-CH_3 ^1H NMR resonances in 1 are downfield of those for free 2-MeBT, while the chemical shifts for H5 and H6 show very little change. The larger downfield shifts in 1 for H2 and C2-CH_3 relative to those for H4 and H7 suggest that the ligand is bound through the benzene ring. A similar trend was observed for the π-benzene-bound BT and 3-MeBT in $[CpRuL]^+$ (L = BT, 3-MeBT). The ruthenium BT complex was structurally characterized by X-ray crystallography.[16]

Reactions of $[Cp^*Ir(BTs)]^{2+}$ and $[CpRu(BT)]^+$ with Hydrides Complex 2 was prepared by reaction of $NaBH_4$ and $[Cp^*Ir(BT)](BF_4)_2$ in CH_2Cl_2/H_2O as shown in eq.2.



$$+ NaBH_4 \xrightarrow[\text{5 min}]{CH_2Cl_2/H_2O} \underset{\mathbf{2}}{[Cp^*Ir(BT\cdot H)]BF_4} + NaBF_4 \qquad (2)$$

The bright yellow solid, **2**, is air stable and was characterized by its elemental analyses (Table 3.3), FAB mass spectrum, molar conductivity, and ^1H NMR spectrum (Table 3.4).[24]

The ^1H NMR spectrum (a portion of which is shown in Figure 3.1) is much more complex than that which might be expected from a single compound. The complexity arises from the presence of four isomers of 2 which are shown in Figure 3.2. The ^1H NMR resonances corresponding to these isomers were assigned by selective decoupling experiments and by the use of $[Cp^*Ir(d_2\text{-}BT)]^{2+}$ to synthesize $[Cp^*Ir(d_2\text{-}BT{\bullet}H)]^+$. The $[Cp^*Ir(d_2\text{-}BT)]^{2+}$ had deuterium substituted for hydrogen at the 2- (93%) and 7- (75%) positions.[11g] For isomer **A** of **2**, the resonance corresponding to H2 was no longer present, and the doublet for H3 ($J_{H2\text{-}H3}$ = 5.4 Hz) had collapsed to a singlet ($J_{H\text{-}H}/J_{H\text{-}D} \cong 6.51$).[25] The H4 (d,$J_{H4\text{-}H5}$ = 4.9 Hz) and H5 (virtual t, $J_{H5\text{-}H6} \cong 5.8$ Hz) resonances were unchanged. Due to the presence of deuterium at the 7-position the virtual triplet corresponding to H6 ($J_{H6\text{-}H7}$ = 6.3 Hz) collapsed to a doublet and the H_{exo} resonance collapsed to a singlet ($J_{H7\text{-}H_{exo}}$ = 13.0 Hz).

The magnitude of the coupling constant between H7 (the endo hydrogen at C7) and H6 is expected to be greater than that between H6 and H_{exo} based on the Karplus relationship.[26] This trend in coupling constants has been observed in analogous organometallic systems.[27] A resonance for H7, which should be a doublet of doublets due to H6 and H_{exo} coupling, was not observed. Using undeuterated **2**, the approximate position of the H7 resonance was assigned by observing that H6, a virtual triplet, collapsed to a doublet upon irradiation of the multiplet in the 4.00-3.93 ppm

Table 3.3 Analytical data for the complexes

Compound	%C Found (calc)	%H Found (calc)
$[Cp^*Ir(2\text{-}MeBT)](BF_4)_2$, 1	34.98 (35.15)	3.69 (3.57)
$[Cp^*Ir(BT{\bullet}H)]BF_4$, 2	39.26 (39.35)	4.43 (4.04)
$[Cp^*Ir(3\text{-}MeBT{\bullet}H)]BF_4$, 3	40.26 (40.50)	4.20 (4.29)
$[Cp^*Ir(2\text{-}MeBT{\bullet}H)]BF_4$, 4	40.23 (40.50)	4.41 (4.29)
$[Cp^*Ir(2,3\text{-}Me_2BT{\bullet}H)]BF_4$, 5	41.45 (41.60)	4.93 (4.54)
$CpRu(BT{\bullet}H)$, 6	51.32 (51.81)	4.39 (4.01)
$[Cp^*Ir(BT{\bullet}OMe)]BF_4$, 7	39.10 (39.38)	4.24 (4.17)
$[Cp^*Ir(3\text{-}MeBT{\bullet}OMe)]BF_4$, 8	40.23 (40.48)	4.43 (4.42)
$[Cp^*Ir(BT{\bullet}CH(CO_2Me)_2)]BF_4$, 9	40.89 (40.65)	4.03 (4.15)
$[Cp^*Ir(3\text{-}MeBT{\bullet}CH(CO_2Me)_2]BF_4$, 10	41.41 (41.56)	4.31 (4.36)
$[Cp^*Ir(BT{\bullet}SEt)]BF_4$, 11	39.14 (39.41)	4.35 (4.30)
$[Cp^*Ir(3\text{-}MeBT{\bullet}SEt)]BF_4$, 12	40.13 (40.45)	4.29 (4.53)

Table 3.4. ^{1}H NMR Data for Isomers of Complexes **2-13**^{a}

Compound	H2	H3	H4	H5	H6
[Cp*Ir(BT•H)]BF$_4$, **2**					
A^b	7.76d	7.09 d	7.23 d	5.58 t	4.07 t
B^b	8.00 d	6.64 d	4.00-3.93^c	3.86 t	5.60 t
C^b	8.26 d	7.28 d	6.09 d	4.11-3.92^c	3.23 p
D^b	8.17 d	6.87 d	4.11-3.93^c	3.14 p	4.11-3.39^c
[Cp*Ir(3-MeBT•H)]BF$_4$, **3**					
A^b	7.36 q		7.13 d	5.58 t	4.08 t
B^b	7.59 q		3.85-3.95^c	3.87 t	5.61 t
C^b	7.85 q		6.02 d	4.00-3.93^c	3.23 p

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[a] d = doublet, t = virtual triplet, q = quartet, p = virtual pentet, br = broad.

[b] d_6-acetone.

[c] Exact position of peak within the complex multiplet not determined.

[d] Peak either not observed or could not be definitively assigned.

H7	C_2-CH_3	C_3-CH_3	C_5H_5	$C_5(CH_3)_5$	Nucleophile	Selected coupling constants (Hz)
4.00–3.93^c				1.87 s	5.03 d(H_{exo})	$J_{H7-H_{exo}}$ = 13.0
7.44 d				1.91 s	5.23 d(H_{exo})	$J_{H4-H_{exo}}$ = 13.4
4.28 d				d	4.30 d(H_{exo})	$J_{H6-H_{exo}}$ = 12.7
6.28 d				d	4.19 d (H_{exo})	$J_{H5-H_{exo}}$ = 12.3
3.95–3.91^c		2.19 d		1.88 s	5.02 d(H_{exo})	$J_{H7-H_{exo}}$ = 13.1 $J_{H2-C3-CH_3}$ = 1.2
7.40 d		2.27 d		d	5.15 d(H_{exo})	$J_{H4-H_{exo}}$ = 12.6 $J_{H2-C3-CH_3}$ = 1.1
4.25 d		2.40 d		d	4.28 d(H_{exo})	$J_{H6-H_{exo}}$ = 13.5 $J_{H2-C3-CH_3}$ = 1.2

Table 3.4. Continued

Compound	H2	H3	H4	H5	H6
D^b	7.78 q		3.87-3.83^c	3.16 p	3.80-3.95^c
[Cp*Ir(2-MeBT•H)]BF$_4$, 4					
A^b		6.79 br,s	7.10 d	5.52 t	4.03 t
B^b		6.34 br,s	3.95-3.75^c	4.10-3.75^c	5.34 t
C^b		7.00 br,s	5.97 d	4.05-3.76^c	3.18 p
D^b		6.59 br,s	4.05-3.76^c	3.10 p	4.05-3.76^c
[Cp*Ir(2,3-Me$_2$BT•H)]BF$_4$, 5					
A^b			7.06 d	5.53 t	4.04 t
B^b			3.95-3.75^c	3.78 t	5.55 t
C^b			5.96 d	4.10-3.95^c	3.19 p
D^b			4.10-3.75^c	3.12 p	4.10-3.75^c

H7	C_2-CH_3	C_3-CH_3	C_5H_5	$C_5(CH_3)_5$	Nucleophile	Selected coupling constants (Hz)
6.24 d		2.08 d		d	4.20 d(H_{exo})	$J_{H5-H_{exo}}$ = 13.2 $J_{H2-C3-CH_3}$ = 1.2
3.95- 3.75[c]	2.60 br,s			1.92 s	4.94 d(H_{exo})	$J_{H7-H_{exo}}$ = 12.9
7.33 d	2.39 br,s			1.90 s	5.19 d(H_{exo})	$J_{H4-H_{exo}}$ = 13.2
4.20 d	2.73 br,s			1.95 s	4.28 d(H_{exo})	$J_{H6-H_{exo}}$ = 12.7
6.19 d	2.71 br,s			1.94 s	4.21 d(H_{exo})	$J_{H5-H_{exo}}$ = 12.6
3.95- 3.75[c]	2.50 d	2.11 br,s		1.90 s	4.90 d(H_{exo})	$J_{H7-H_{exo}}$ = 12.8
7.30 d	2.30 br,s	2.17 d		1.89 s	5.13 d(H_{exo})	$J_{H4-H_{exo}}$ = 13.4
4.17 d	2.60 d	2.07 d		1.94 s	4.26 d(H_{exo})	$J_{H6-H_{exo}}$ = 12.7
6.15 d	2.63 d	2.31 d		1.93 s	4.19 d(H_{exo})	$J_{H5-H_{exo}}$ = 12.2

Table 3.4. Continued

Compound	H2	H3	H4	H5	H6
CpRu(BT•H), 6					
A[e]	6.44 d	6.34 d	6.13 d	4.27 t	2.96 t
B[e]	6.37 d	6.27 d	3.26 dd	2.69 t	4.33 t
C[e]	6.77 d	6.86 d	5.20 d	2.48-2.55[c]	2.73-2.54[c]
D[c]	6.72 d	6.35 d	2.73-2.54[c]	2.73-2.54[c]	2.48-2.55[c]
$[Cp^*Ir(BT\cdot OMe)]BF_4$, 7					
A[b]	7.94 d	7.10 d	7.15 d	5.69 t	4.71 t
B[b]	7.95 d	6.92 d	4.76 d	4.62 t	5.34 t
C[b]	8.26 d	7.24 d	6.27 d	4.60-4.80[c]	4.12 t
D[b]	8.22 d	6.97 d	d	4.06 t	d
$[Cp^*Ir(3\text{-}MeBT\cdot OMe)]BF_4$, 8					
A[b]	7.56 q		7.05 d	5.70 d	4.71 t
B[b]	7.52 q		4.77-4.65[c]	4.77-4.65[c]	5.60-5.68[c]
C[b]	7.86 q		d	d	d
D[b]	7.83 q		d	d	d

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[e] d_6-benzene.

H7	C_2-$C\underset{\sim}{H}_3$	C_3-$C\underset{\sim}{H}_3$	$C_5\underset{\sim}{H}_5$	$C_5(C\underset{\sim}{H}_3)_5$	Nucleophile	Selected coupling constants (Hz)
3.44 dd			4.31 s		3.19 d(H_{exo})	$J_{H7-H_{exo}}$ = 11.6
6.38-6.33^c			4.29 s		3.15 d(H_{exo})	$J_{H4-H_{exo}}$ = 11.3
2.73-2.54^c			d		2.73-2.54^c (H_{exo})	
5.50 d			d		2.73-2.54^c (H_{exo})	
4.83 d				1.90 s	3.02 s($OC\underset{\sim}{H}_3$)	
7.35 d				1.91 s	2.95 s($OC\underset{\sim}{H}_3$)	
5.24 d				d	2.98 s($OC\underset{\sim}{H}_3$)	
6.46 d				d	2.97 s($OC\underset{\sim}{H}_3$)	
4.78 d		2.24 d		1.92 s	3.03 s($OC\underset{\sim}{H}_3$)	
7.00-7.05^c		2.25 d		d	3.02 s($OC\underset{\sim}{H}_3$)	
d		2.39 d		d	d	
d		2.33 d		d	d	

Table 3.4. Continued

Compound	H2	H3	H4	H5	H6
[(Cp*Ir(BT•CH(CO$_2$Me)$_2$]BF$_4$, 9					
A^b	7.79 d	7.09 d	7.28 d	5.53 t	4.27 t
B^b	7.89 d	6.59 d	4.45 dd	4.15 t	5.68 t
C^b	8.28 d	d	6.14 d	d	d
D^b	8.22 d	6.89 d	d	d	d
[Cp*Ir(3-MeBT•CH(CO$_2$Me)$_2$]BF$_4$, 10					
A^b	7.40 q		7.19 d	5.56 t	4.27 t
B^b	7.51 q		4.45- 4.20^c	4.40- 4.20^c	5.58 t
C^b	7.88 q		6.06 d	d	d
D^b	7.84 q		d	d	d
[Cp*Ir(BT•SEt)]BF$_4$, 11					
A^b	7.88 d	7.07 d	7.23 d	5.67 t	4.54 t

H7	$C_2\text{-}C\underset{\sim}{H}_3$	$C_3\text{-}C\underset{\sim}{H}_3$	$C_5\underset{\sim}{H}_5$	$C_5(C\underset{\sim}{H}_3)_5$	Nucleophile	Selected coupling constants (Hz)
4.54 dd				1.89 s	2.87 d($C\underset{\sim}{H}$) 3.52 s($C\underset{\sim}{H}_3$) 3.61 s($C\underset{\sim}{H}_3$)	$J_{H7\text{-}CH}$ = 8.2
7.48 d				1.90 s	2.81 d($C\underset{\sim}{H}$) 3.48 s($C\underset{\sim}{H}_3$) 3.61 s($C\underset{\sim}{H}_3$)	$J_{H4\text{-}CH}$ = 8.4
4.63 d				d	d	
6.34 d				d	d	
4.50 dd		2.21 d		1.90 s	2.87 d($C\underset{\sim}{H}$) 3.53 s($C\underset{\sim}{H}_3$) 3.61 s($C\underset{\sim}{H}_3$)	$J_{H7\text{-}CH}$ = 8.4
7.46 d		2.23 d		d	2.82 d($C\underset{\sim}{H}$) 3.46 s($C\underset{\sim}{H}_3$) 3.61 s($C\underset{\sim}{H}_3$)	$J_{H4\text{-}CH}$ = 8.4
4.58 d		2.39 d		d	d	
6.29 d		2.10 d		d	d	
5.25 d				1.90 s	1.06 m($C\underset{\sim}{H}_3$) 2.36 m($C\underset{\sim}{H}_2$)	

Table 3.4. Continued

Compound	H2	H3	H4	H5	H6
B^b	8.01 d	6.83 d	5.17 d	4.42 t	5.73 t
C^b	8.31 d	7.28 d	d	d	d
D^b	8.24 d	d	d	d	d
[Cp*Ir(3-MeBT•SEt)]BF$_4$, 12					
A^b	7.48 q		7.14 d	5.67 t	4.54 t
B^b	7.51 q		e	4.68 t	d
C^b	7.64 q		6.17 d	d	d
D^b	7.56 q		d	d	d
[Cp*Ir(BT•PMe$_3$)](BF$_4$)$_2$, 13					
A^f	7.81 d	7.15 d	7.28 d	5.71 t	4.28 t
B^f	8.07 d	6.79 d	5.47- 5.40^c	4.19 t	5.75- 5.65^c
C^f	8.25 d	7.24 d	6.17 d	d	d
D^f	8.20 d	6.90 d	d	d	d

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[f] CD$_3$NO$_2$.

H7	C_2-CH_3	C_3-CH_3	C_5H_5	$C_5(CH_3)_5$	Nucleophile	Selected coupling constants (Hz)
7.44 d				d	d	
d				d	d	
d				d	d	
5.19 d		2.22 d		1.90 s	1.10 m(CH_3)	
					2.37 m(CH_2)	
7.03 d		2.34 d		1.91 s	d	
d		2.16 d		d	d	
d		2.63 d		d	d	
5.42 dd				1.89 s	1.61 d(PMe_3)	J_{H7-P} = 3.3
						J_{P-CH_3} = 13.4
7.42 d				d	1.42 d(PMe_3)	J_{P-CH_3} = 12.8
d				d	d	
6.29 d				d	d	

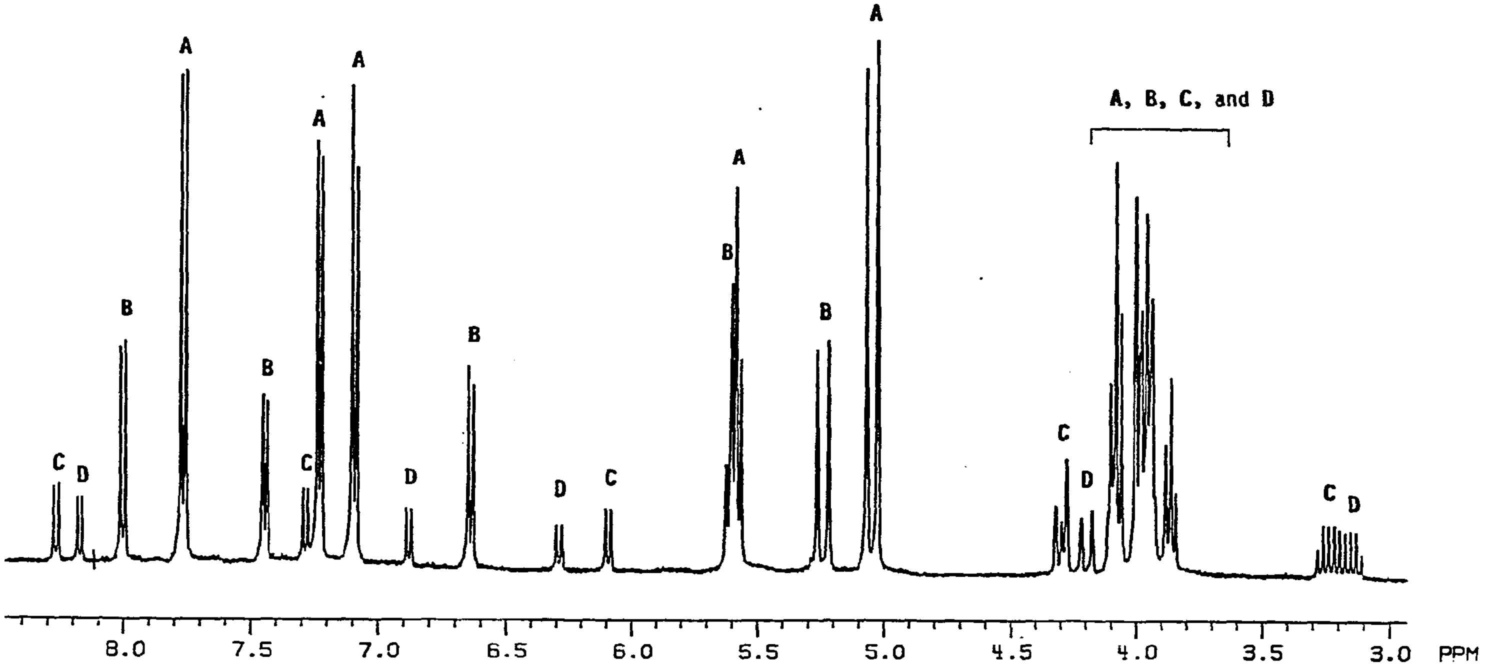
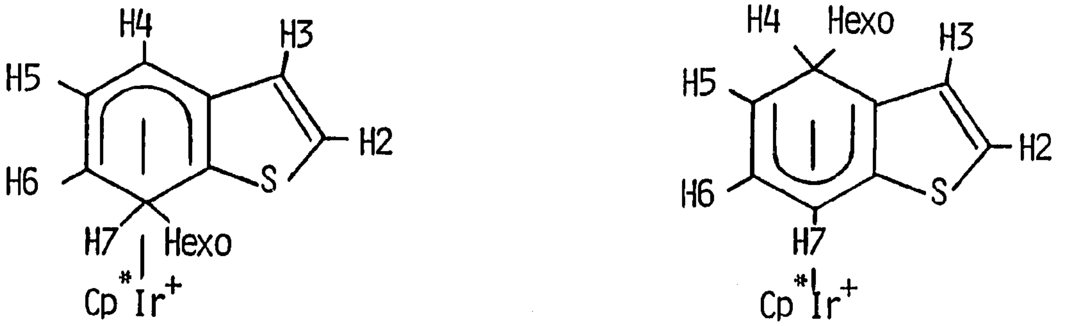
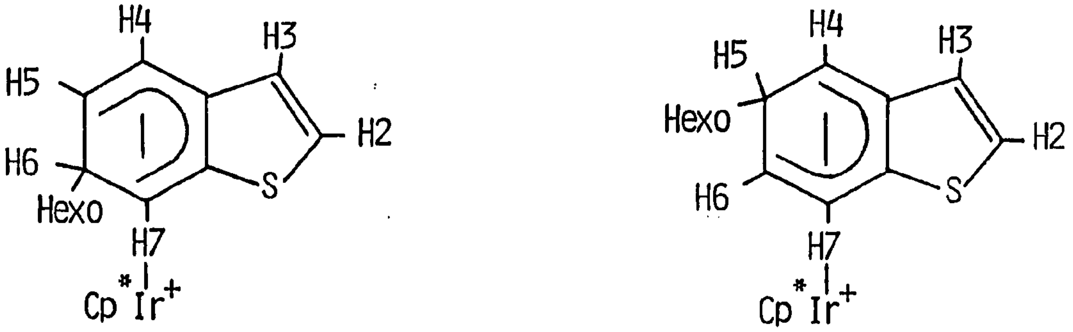


Figure 3.1. ^{1}H NMR Spectrum of [Cp*Ir(BT•H)]$^+$, 2, in d_6-acetone



Isomer A

Isomer B



Isomer C

Isomer D

Figure 3.2. Isomers A-D of $[Cp^*Ir(BT\bullet H)]^+$, 2

region. The downfield shift of the H_{exo} resonance relative to that for the endo proton, H7, is unusual[28] but has previously been observed for $[Cp^*Ir(C_6H_6{\bullet}H)]^+$.[29] A reaction performed using $NaBD_4$ and $[Cp^*Ir(BT)]^{2+}$ showed that D^- addition occurs only at the exo face of the BT ligand. The integral of the H_{exo} doublet was small (but was observed, due to $NaBH_4$ impurities in the $NaBD_4$) relative to the other resonances for **A** and the singlet at this position which would have resulted from an endo D was not observed.

The chemical shifts for isomers **B**, **C**, and **D** were assigned analogously to those for **A**. The virtual pentets corresponding to H6 in isomer **C** and H5 in isomer **D** result from coupling to H_{exo} and further splitting of the resonances by the two vicinal protons (C: J_{H6-H5} = 6.3 Hz, J_{H6-H7} = 6.0 Hz; D: $J_{H5-H4} \cong J_{H5-H6} \cong 6.6$ Hz). The Cp* resonances of isomers **C** and **D** were not resolved from the peaks for **A** and **B**. The $^{13}C\{^1H\}$ NMR spectrum of **2** was obtained but assignments of the numerous resonances were not made.

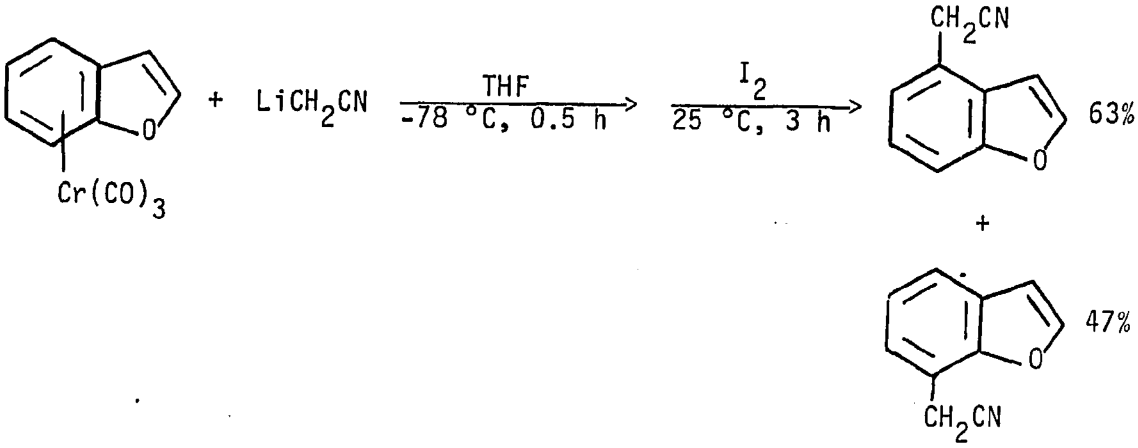
The percentages of the isomers **A-D** present were determined by integration of the respective ^1H NMR signals and are given in Table 3.5. During 3 days at 25°C in d_6-acetone these percentages remained unchanged. The relative amounts of **A-D** were also the same when **2** was dissolved in $CDCl_3$ and CD_3NO_2 at 25°C. Therefore, there is no isomer interconversion under these conditions. The distribution of isomers does change slightly with different preparations. As compared to the percentages given in Table 3.5, the amounts of **A**, **B**, **C**, and **D** formed in three other preparations of **2**, performed analogously to that described in the Experimental Section, were (56, 23, 11, 10%), (60, 25, 8, 7%), and

Table 3.5. Percentages of Isomers A-D of Complexes **2-13**

Compound	% Isomer A	B	C	D
$[\mathrm{Cp^*Ir(BT{\bullet}H)]BF_4}$, **2**	61	25	8	6
$[\mathrm{Cp^*Ir(3\text{-}MeBT{\bullet}H)]BF_4}$, **3**	58	27	8	7
$[\mathrm{Cp^*Ir(2\text{-}MeBT{\bullet}H)]BF_4}$, **4**	60	23	9	8
$[\mathrm{Cp^*Ir(2,3\text{-}Me_2BT{\bullet}H)]BF_4}$, **5**	60	25	8	7
$\mathrm{CpRu(BT{\bullet}H)}$, **6**	78	15	5	2
$[\mathrm{Cp^*Ir(BT{\bullet}OMe)]BF_4}$, **7**	70	18	10	2
$[\mathrm{Cp^*Ir(3\text{-}MeBT{\bullet}OMe)]BF_4}$, **8**	80	15	3	2
$[\mathrm{Cp^*Ir(BT{\bullet}CH(CO_2Me)_2)]BF_4}$, **9**	61	26	8	5
$[\mathrm{Cp^*Ir(3\text{-}MeBT{\bullet}CH(CO_2Me)_2]BF_4}$, **10**	53	25	11	11
$[\mathrm{Cp^*Ir(BT{\bullet}SEt)]BF_4}$, **11**	87	9	3	1
$[\mathrm{Cp^*Ir(3\text{-}MeBT{\bullet}SEt)]BF_4}$, **12**	70	23	4	3
$[\mathrm{Cp^*Ir(BT{\bullet}PMe_3)](BF_4)_2}$, **13**	75	14	8	3

(63, 24, 7, 6%). When PPN[HFe(CO)$_4$] was used as a H$^-$ source the relative amounts of **A** and **B** in **2** were 77 and 23 respectively. The amounts of **C** and **D** were not determined due to the relatively poor quality of the spectrum. The relative amounts of **A** and **B** in the NaBH$_4$ reaction were 71 and 29. Therefore, the H$^-$ source has little effect on the isomeric distribution in **2**. The isomers could not be separated by either chromatography or fractional crystallization.

The only other reports of nucleophilic attack on transition-metal-bound fused ring aromatic ligands are for Cr(CO)$_3$L (L = naphthalene,[30] benzofuran,[13b] and indole[13b,31]). The reaction of carbon nucleophiles with the chromium complexes to generate anionic cyclohexadienyl intermediates was followed by oxidation to produce the uncoordinated substituted ligand as shown in eq. 3 for benzofuran.[30a, 13b]



(3)

The nucleophilic addition reactions occurred preferentially at C4 except for 3 of the 17 reactions studied (in these cases, C7 addition was preferred).[13b] Attack at C6 was reported to give rise to a minor product in only a few of the reactions. Semmelhack et al.[13b,30a] performed molecular orbital analyses for naphthalene and indole and found that the selectivity correlated with the magnitude of the LUMO coefficients for the free ligands.

The preference for H^- attack at C7 in $[Cp^*Ir(BT)]^{2+}$ and the significant amounts of isomers resulting from attack at C5 and C6 contrasts with the results reported for the chromium complexes. At this time the LUMO coefficients for BT (either coordinated to a transition metal or unbound) have not been reported and, therefore, conclusions regarding the controlling factors in this reaction cannot be drawn.

The preparations of **3**, **4**, and **5** proceed analogously to that of 2 and result in the isolation of yellow air-stable solids. These complexes were characterized by their elemental analyses (Table 3.3) and ^1H NMR spectra (Table 3.4). The ^1H NMR spectra of **4** and **5** showed weak peaks due to **3**, which was formed from $[Cp^*Ir(2\text{-}MeBT)]^{2+}$ impurities in $[Cp^*Ir(3\text{-}MeBT)]^{2+}$ and $[Cp^*Ir(2,3\text{-}Me_2BT)]^{2+}$ starting materials. The 2-MeBT impurities were present in the commercial 3-MeBT which was used to synthesize 2,3-Me_2BT and the iridium complexes. The ^1H NMR spectra were assigned by analogy with **2**. As shown in Table 3.5, the distribution of isomers was not significantly affected by the presence or position of the methyl substituents.

Complex **6** is prepared from $NaBEt_3H$ and $[CpRu(BT)]PF_6$ as shown in eq. 4.

$$[CpRu(BT)]PF_6 + NaBEt_3H \xrightarrow[5\ min]{CH_2Cl_2} \underset{\mathbf{6}}{CpRu(BT{\cdot}H)} + NaPF_6 + BEt_3 \qquad (4)$$

The resulting air-sensitive yellow solid was identified by its elemental analyses (Table 3.3), EIMS, and ^1H NMR spectrum (Table 3.4). As for compounds **2-5**, four isomers of **6** are produced. The ^1H NMR resonances for these isomers were assigned by selective decoupling experiments and by analogy with the assignments for **2**. The assignments were confirmed by synthesis of CpRu(d_2-BT•H) and comparison of its ^1H NMR spectrum with the spectrum for **6**. The intensities and splittings of the resonances in the spectrum of CpRu(d_2-BT•H) also established that H^- addition occurs in an exo fashion.

Integration of the resonances in the ^1H NMR spectrum provided the isomeric distribution given in Table 3.5. In contrast to 2 the isomeric distribution of **6** changes significantly with different preparations. When a slight excess of $NaBEt_3H$ was used, the percentages of A-D in **6** were 51, 26, 14, and 9%, respectively, as compared to 78, 15, 5, and 2% given in Table 3.5. There is no interconversion of isomers in d_6-benzene after 24 h at 25°C.

Structural Characterization of CpRu(BT•H), 6 Complexes **2-12** represent the first isolable cyclohexadienyl complexes derived from fused-ring aromatic systems. The $[Cr(CO)_3(\eta^5\text{-naphthalene}\bullet H)]^-$ resulting from protonation of $[Cr(CO)_3(\text{naphthalene})]^{2-}$ has only been observed spectroscopically.[13a,32] We were, therefore, interested in elucidating the structural characteristics of this type of complex by an X-ray diffraction study of **6**.

The crystal structure of **6** (which turned out to be the major isomer, A), Figure 3.3, clearly shows the cyclohexadienyl nature of the BT•H

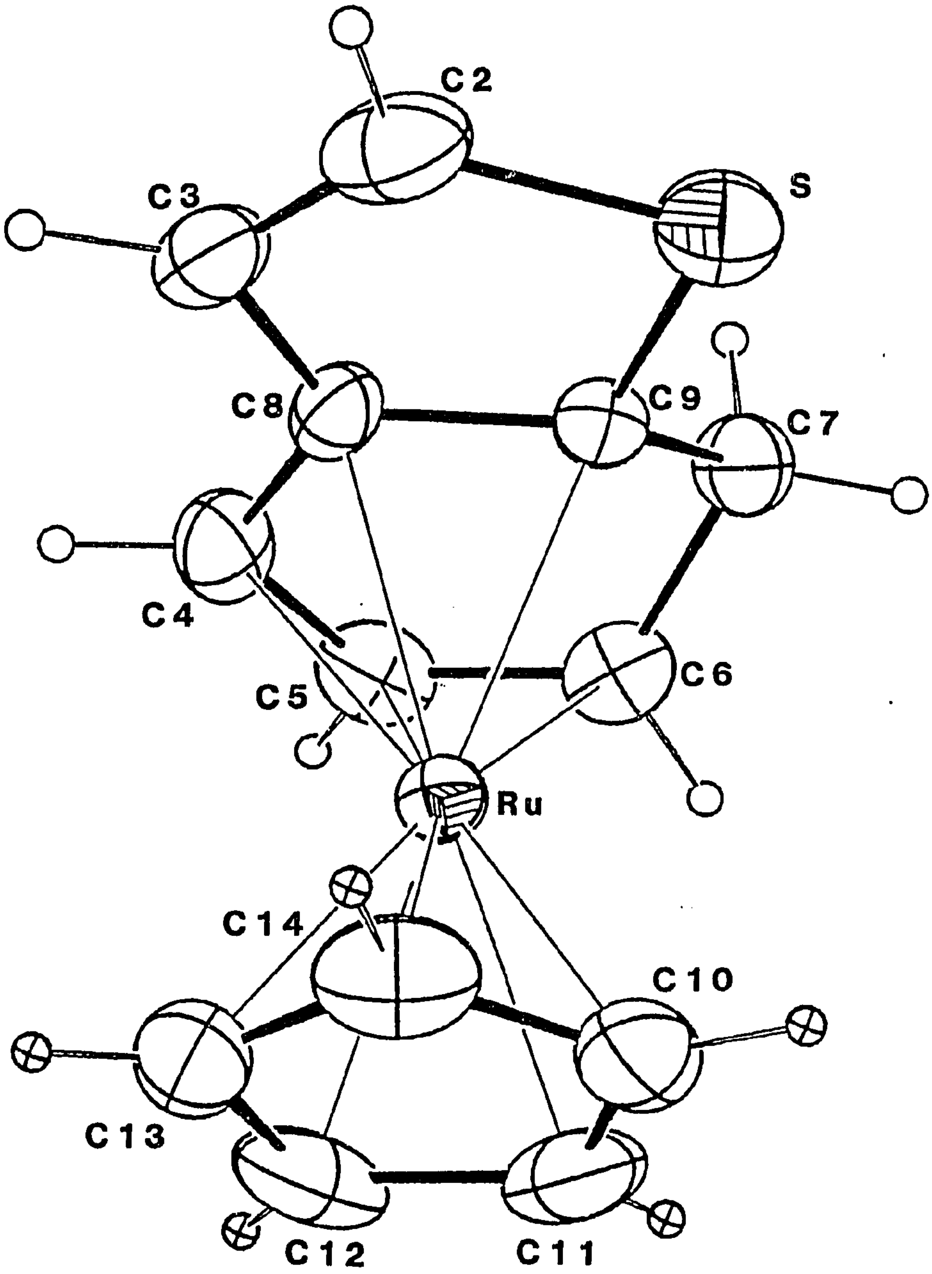


Figure 3.3. Ortep Drawing of CpRu(BT•H), 6, Isomer A

ligand. The C7 atom is displaced 0.645(3) Å from the least-squares plane defined by C4, C5, C6, C8, and C9 (Table 3.8, Supplementary Material). None of these five atoms deviates from the least-squares plane by more than 0.001(3) Å. The C6-C7 and C9-C7 bond lengths (Table 3.6), 1.509(4) and 1.493(4) Å, respectively, are slightly shorter than expected for a C(sp^3)-C(sp^2) bond (1.51 Å)[33] but are within the range observed for other η^5-cyclohexadienyl complexes (1.49-1.55 Å).[33-34] The C6-C7-C9 angle, 100.6(2), is smaller than the ideal tetrahedral value of 109.46° but again near the range reported for analogous compounds (101-104°).[33,34b,35] The C-C bond lengths in the cyclohexadienyl ring (excluding C6-C7 and C9-C7) have an average value of 1.42 Å. This value is only slightly longer than the average C-C bond length of 1.41 Å in the benzene ring of [CpRu(BT)]BF_4[16] and within the range of analogous bond distances in other cyclohexadienyl complexes (1.40-1.44 Å).[33,34]

The average Ru-C distance for C4, C5, C6, C8, and C9 is 2.19 Å. The average value for the six carbons of the benzene ring bonded to Ru in [CpRu(BT)]BF_4 is 2.22 Å.[16] The BT ligand in [CpRu(BT)]BF_4 showed evidence of ring slippage[36] (the average Ru-C_5C_6 distance minus the average Ru-C8C9 distance = 0.07 Å). This slippage is also apparent in **6** but is of a much smaller magnitude (= 0.04 Å). The planes of the cyclohexadienyl and Cp rings are essentially parallel (dihedral angle = 2.8° ± 1.9 °).

H^- Abstraction from [Cp*Ir(BT•H)]$^+$, 2 and CpRu(BT•H), 6 To an NMR tube containing **2** (8.0 mg, 0.014 mmol) was added d_6-acetone (0.3 mL) and cyclohexane (0.1 μL). The ^1H NMR spectrum was obtained and then HBF_4•Et_2O (20 μL, 0.14 mmol) was added. The reaction, eq. 5, was monitored by ^1H

Table 3.6. Bond distances and angles for CpRu(BT•H), 6

Bond Distances (Å)			
Ru-C4	2.176(3)	C3-C8	1.485(4)
Ru-C5	2.155(3)	C4-C8	1.427(4)
Ru-C6	2.195(3)	C4-C5	1.419(4)
Ru-C8	2.204(3)	C5-C6	1.416(4)
Ru-C9	2.227(3)	C6-C7	1.509(4)
Ru-C10	2.194(3)	C7-C9	1.493(4)
Ru-C11	2.185(3)	C8-C9	1.424(4)
Ru-C12	2.191(3)	C10-C11	1.385(5)
Ru-C13	2.207(3)	C11-C12	1.415(5)
Ru-C14	2.198(3)	C12-C13	1.415(5)
S-C2	1.723(4)	C13-C14	1.397(5)
S-C9	1.764(3)	C14-C10	1.412(5)
C2-C3	1.341(4)		

Bond Angles (°)			
S-C2-C3	115.5(3)	C7-C9-C8	120.9(2)
C2-C3-C8	110.5(3)	C9-C8-C4	118.3(3)
C3-C8-C9	112.7(2)	C8-C4-C5	117.0(3)
C8-C9-S	109.3(2)	C10-C11-C12	108.9(3)
C9-S-C2	91.9(1)	C11-C12-C13	107.0(3)
C4-C5-C6	119.9(3)	C12-C13-C14	107.9(3)
C5-C6-C7	119.6(3)	C13-C14-C10	108.4(3)
C6-C7-C9	100.6(2)	C14-C10-C11	107.8(3)

NMR over 43 h until all of **2** had reacted to form $[Cp^{*}Ir(BT)](BF_4)_2$.

$$\underset{\mathbf{2}}{[Cp^{*}Ir(BT{\cdot}H)]BF_4} + HBF_4{\cdot}Et_2O \xrightarrow[43\ h]{d_6\text{-acetone}} [Cp^{*}Ir(BT)](BF_4)_2 + H_2 \qquad (5)$$

The integrals corresponding to the relative amounts of isomers **A**-**D** of **2** and $[Cp^{*}Ir(BT)]^{2+}$, relative to an internal integration standard (cyclohexane), were determined from the ^1H NMR spectra obtained during the reaction. The percentages of **A**-**D** in **2** before addition of $HBF_4{\cdot}Et_2O$ were 63, 24, 7, and 6%. After 5.5 h isomer **D** was no longer observed and the percentages of **A**-**C** were 82, 14, and 4%. After 20 h only **A** and **B** were present (92 and 8%, respectively) and peaks due to uncoordinated BT were present in the spectrum. This is a result of acetone displacement of BT from $[Cp^{*}Ir(BT)]^{2+}$. After 24 h only **A**, $[Cp^{*}Ir(BT)]^{2+}$ and BT were present in the solution. By comparing integrals for **A**-**D** and $[Cp^{*}Ir(BT)]^{2+}$ it is clear that isomerization of **B**-**D** to **A** is not occurring under these conditions and that this reaction occurs by preferential H^- abstraction from isomers **B**-**D** relative to **A**. Reports of other selective H^- abstraction reactions have not been published, and it is not clear what factors determine the observed selectivity. Complex **2** does not react with $(Ph_3C)BF_4$.

The reaction of **6** with $(Ph_3C)BF_4$ is shown in eq. 6.

$$\underset{\mathbf{6}}{CpRu(BT{\cdot}H)} + (CPh_3)BF_4 \xrightarrow{CH_2Cl_2} [CpRu(BT)]BF_4 + HCPh_3 \qquad (6)$$

This reaction was also monitored by ^1H NMR. The spectrum of a solution of

6 (4 mg, 0.01 mmol) in CD_2Cl_2 (0.3 mL) was obtained and then $(Ph_3C)BF_4$ (6.1 mg, 0.018 mmol) was added. A spectrum obtained after 1 h showed that all of **6** had reacted and that $[CpRu(BT)]^+$ was the only BT-containing product. When approximately half of **6** had reacted, the relative amounts of **A** and **B** were 85 and 15% (only trace amounts of **C** and **D** were observed at this time) compared to 66 and 34% of **A** and **B** in **6** before addition of $(CPh_3)BF_4$. Thus, this reaction also occurs selectively as observed for the reaction of **2** with $HBF_4 \cdot Et_2O$.

Preparation of $[Cp^*Ir(BT \cdot Nuc)]^+$ and $[Cp^*Ir(3\text{-}MeBT \cdot Nuc)]^+$ (Nuc = OMe, $CH(CO_2Me)_2$ and SEt), 7-12 These air-stable compounds were prepared by reaction of $[Cp^*Ir(BT)]^{2+}$ or $[Cp^*Ir(3\text{-}MeBT)]^{2+}$ with the nucleophiles as described in eq. 2 and characterized by their elemental analyses (Table 3.3), ^1H NMR spectra (Table 3.4) and in some cases by their molar conductivities. The ^1H NMR spectra were assigned by analogy to **2** and **3**. Selective decoupling experiments were used to confirm the assignments for **9** and **10**. The ^1H NMR spectra show that addition of MeO^-, $(MeO_2C)_2HC^-$ and EtS^- to either $[Cp^*Ir(BT)]^{2+}$ or $[Cp^*Ir(3\text{-}MeBT)]^{2+}$ results in the production of four isomers as was observed for the H^- addition reactions. The percentages of these isomers, **A-D**, were determined by integration of the ^1H NMR spectra of the compounds and are presented in Table 3.5. The methoxide and thioethoxide nucleophiles show a stronger preference for attack at C7 than H^-. The malonate anion shows approximately the same selectivity as H^-. The 3-Me group does not appear to cause major changes in the distributions of isomers.

The addition of an excess of $(Ph_3C)BF_4$ to an NMR tube solution of 7 in d_6-acetone results in immediate reaction to regenerate the iridium BT dication as shown in eq. 7.

$$\underset{\textbf{7}}{[Cp^*Ir(BT{\cdot}OMe)]^+} + Ph_3C^+ \xrightarrow[10\ min]{d_6\text{-acetone}} [Cp^*Ir(BT)]^{2+} + Ph_3COMe \qquad (7)$$

The only BT containing product observed in the ^1H NMR spectrum was the iridium dicationic complex.

The malonate adduct, **9**, also undergoes an abstraction reaction, eq. 8. A solution of **9** (21 mg, 0.031 mmol) in d_6-acetone (0.3 mL) was

$$\underset{\textbf{9}}{[Cp^*Ir(BT{\cdot}CH(CO_2Me)_2)]^+} + HBF_4{\cdot}Et_2O \xrightarrow[5.5\ h]{d_6\text{-acetone}} [Cp^*Ir(BT)]^{2+} + H_2C(CO_2Me)_2 \qquad (8)$$

prepared in an NMR tube. After obtaining the ^1H NMR spectrum, $HBF_4{\cdot}Et_2O$ (20 μL, 0.14 mmol) was added and the NMR spectrum was obtained periodically for 5.5 h at which time all of **9** had reacted. The BT iridium dication was the only BT-containing product. Cleavage of the C-C bond in **9** might seem surprising, however, abstractions of exo carbon groups by electrophiles have been reported. Semmelhack et al. found that $[Cr(CO)_3(\eta^5\text{-}C_6H_6{\cdot}R)]^-$ complexes (R = CN, CH_2CH, $C(CH_3)_2CN$, $CH(CO_2Et)_2$, and CH_2Ph for example) react with electrophiles (CH_3I, benzophenone, Ph_3C^+, Et_3B, acetic acid, CF_3CO_2H, H_2O) to produce $Cr(CO)_3(\eta\text{-}C_6H_6)$ and the reacted carbanion.[34a,37]

Reactions of $[Cp^*Ir(BT)]^{2+}$ with Phosphines The reaction of PMe_3 with a CD_3NO_2 solution of $[Cp^*Ir(BT)]^{2+}$ was monitored by ^1H NMR. The resonances in the spectrum of the quantitatively-produced yellow $[Cp^*Ir(BT{\bullet}PMe_3)]^{2+}$, **13** were assigned by analogy to **2**. The assignments were verified by selective decoupling experiments and also by synthesis of $[Cp^*Ir(d_2\text{-}BT{\bullet}PMe_3)]^{2+}$. The ^1H NMR spectrum of the deuterated product exhibited changes in the splitting patterns and peak intensities expected for a compound with deuterium at the 2- and 7-positions. The four isomers, **A-D**, were produced in the relative amounts given in Table 3.5. The stronger preference for C7 addition in this reaction (relative to H^- and $(MeO_2C)_2HC^-$) is similar to that observed for the MeO^- and EtS^- addition reactions. Complex **13** can be isolated as a yellow oil by addition of Et_2O to the reaction mixture.

If only half an equivalent of PMe_3 is added, the relative amounts of **A** and **B** in **13** are the same as those observed when an excess of PMe_3 is added. Compound **13** does not undergo further addition of PMe_3 to form a bis phosphine complex even when a three-fold excess of the phosphine is added to **13**. There is no reaction between PMe_3 and $[CpRu(BT)]^+$.

Nucleophilic addition of PPh_2Me to $[Cp^*Ir(BT)]^{2+}$ also occurs. The broadness of the peaks in the ^1H NMR spectrum of $[Cp^*Ir(BT{\bullet}PPh_2Me)]^{2+}$ precluded the determination of the chemical shifts for the minor isomers and the percentages of isomers present. However, the positions of the resonances for the major isomers were quite similar to those observed for **13A** suggesting that an analogous complex had resulted from the reaction. In contrast to **13**, $[Cp^*Ir(BT{\bullet}PPh_2Me)]^{2+}$ could not be isolated. Addition of Et_2O to a CD_3NO_2 solution of the PPh_2Me adduct precipitates $[Cp^*Ir(BT)]^{2+}$ suggesting that PPh_2Me is bound less strongly than PMe_3 in **13**. The $[Cp^*Ir(BT)]^{2+}$ complex (1.7 mg, 2.3 μmol) does not react with PPh_3 (0.6 mg, 2.3 μmol) in CD_3NO_2 (0.25 mL).

Double Nucleophilic Addition Reactions of $[Cp^*Ir(BT)]^{2+}$ and $[Cp^*Ir(3\text{-}MeBT)]^{2+}$ A compound tentatively identified as $Cp^*Ir(BT{\bullet}H_2)$ was produced by reaction of $[NaAlH_2(OCH_2CH_2OMe)_2]$ (0.20 mL of a 0.058 M solution in benzene, 0.012 mmol) and **2** (8.5 mg, 0.016 mmol) in benzene (3 mL) at 25°C. Filtration of the reaction mixture followed by evaporation of the filtrate in vacuo produced an orange-yellow oil. The ^1H NMR spectrum of the complex ($CDCl_3$) was quite complex and definitive assignments of the resonances were not made. However, the number and different intensities of the resonances suggested that more than one isomer of the product was present, which would seem reasonable for H^- addition to the four isomers of **2**. Peaks at m/e 464, 462, and 360 corresponding to M^+, $M^+\text{-}H_2$, and $M^+\text{-}C_8H_8$, respectively, were observed in the mass spectrum (EIMS) of the oil.

The addition of H^- to **4** (6.2 mg, 0.011 mmol) by reacting an excess of $Na[AlH_2(OCH_2CH_2OMe)_2]$ (0.1 mL of a 3.4 M solution in toluene, 0.34 mmol) in Et_2O produced a yellow solution. Filtration of the reaction mixture and evaporation of the solvent from the filtrate in vacuo yielded a tan oil. The ^1H NMR spectrum ($CDCl_3$) of the oil was complex and the resonances were not assigned, but the pattern and intensities of the peaks imply that more than one isomer of the product was produced in this reaction. The proposed product, Cp*Ir(3-MeBT•H_2) was characterized by its mass spectrum (EIMS; m/e, 478 (M^+), 476 (M^+-H_2), 360 (M^+-C_9H_{10})).

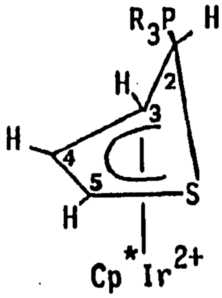
The complex Cp*Ir(BT•$(OMe)_2$) was synthesized from NaOMe (from 2 mg Na, 0.07 mmol) and 7 (9.8 mg, 0.017 mmol) stirring in MeOH (6 mL) at RT for 19 h. The solution was evaporated to dryness in vacuo and the resulting residue extracted with Et_2O. The Et_2O extract was filtered and the filtrate evaporated in vacuo to give a tan oil. The product was identified by its mass spectrum (EIMS; m/e, 524 (M^+), 492 (M^+-OCH_3), 462 (M^+-2 OCH_3)).

These three complexes, Cp*Ir(BT•H_2), Cp*Ir(3-MeBT•H_2) and Cp*Ir(BT•$(OMe)_2$) are very unstable; the initially yellow compounds slowly decompose under N_2 (within ~1-10 h). An η^4-coordination mode of the BT•H_2 (or BT•$(OMe)_2$) ligand would be the most reasonable for these neutral complexes. The analogous Cp*Ir(η^4-C_6H_6•H_2)[29] was characterized by mass spectrometry, and ^1H and ^{13}C NMR spectra, but it was too unstable for elemental analysis.

Reactions of $[Cp^*Ir(T)]^{2+}$ with Phosphines and $NaBEt_3H$ The thiophene ring in $[Cp^*Ir(T)](BF_4)_2$ is even more reactive towards nucleophilic attack than the BT ligand in $[Cp^*Ir(BT)]^{2+}$. The reactions of $[Cp^*Ir(T)]^{2+}$ and phosphines were studied by NMR experiments. When PMe_3, PPh_2Me, and PPh_3 were added to solutions of $[Cp^*Ir(T)]^{2+}$ in CD_3NO_2, the ^1H NMR spectra of the resulting NMR tube solutions showed signals[38] corresponding to an η^4-T complex, as shown in eq. 10, as the only product. The analogous $[Cp^*Rh(T)]^{2+}$ also reacted with PMe_3 to give

$$[Cp^*Ir(T)]^{2+} + PR_3 \xrightarrow{CD_3NO_2}$$

$$PR_3 = PMe_3, PPh_2Me, PPh_3$$



(10)

an η^4-complex as the only product (in a CD_3NO_2 solution monitored by ^1H NMR).[39] Reaction of $P(OMe)_3$ with $[Cp^*Ir(T)]^{2+}$ in CD_3NO_2 resulted in the formation of $[Cp^*Ir(T\cdot P(O)(OMe)_2)]^+$ which was identified by its ^1H NMR spectrum (the $P(O)(O\underline{Me})_2$ resonance integrated to 6H as opposed to 9H which would have been expected for the $P(OMe)_3$ adduct).[40] This reaction probably proceeds by initial addition of $P(OMe)_3$ to the T ring of $[Cp^*Ir(T)]^{2+}$ followed by a Michaelis-Arbuzov type rearrangement, as shown in eq. 11. The proposed phosphonium intermediate was not observed in the

$$[Cp^*Ir(T)]^{2+} + P(OMe)_3 \xrightarrow{CD_3NO_2} \left[Cp^*Ir(T\cdot P(OMe)_3)\right]^{2+}$$

$$\xrightarrow{H_2O} [Cp^*Ir(T\cdot P(O)(OMe)_2)]^+ + MeOH + H^+ \qquad (11)$$

^1H NMR spectrum of the reaction mixture but an H_2O peak was. The reactions of $[(\eta\text{-}C_6H_6)_2Ru]^{2+}$,[41] and $[(\eta\text{-}C_5Me_4Et)Rh(\eta\text{-}C_6H_6)]^{2+}$,[42] with $P(OMe)_3$ also result in the formation of a phosphonate product. The $[Cp^*Ir(T)]^{2+}$ complex does not react with $P(OPh)_3$ in CD_3NO_2 at 25°C.

The reaction of $[Cp^*Ir(T)]^{2+}$ (14 mg, 0.024 mmol) and $NaBEt_3H$ (40 µL of a 1 M solution in THF, 0.040 mmol) in benzene (5 mL) produced a gold-colored solution after 5 min at RT. The solution was filtered and the solvent removed from the filtrate in vacuo which gave an orange residue. The ^1H NMR spectrum ($CDCl_3$) of the product showed signals at 4.78 (m, 2H), 4.31 (m, 2H), and 1.99 ppm (s, 15H). The splitting patterns of the 4.78 and 4.31 ppm resonances are similar to those observed for T but the chemical shifts occur at much higher field than those of T ($CDCl_3$: 7.35 (m; H2, H5), 7.14 (m; H3, H4)).[43] The ^1H NMR spectrum suggests that the reaction which occurred was not H^- addition to the T ligand but rather a $2e^-$ reduction of the iridium complex as shown in eq. 12. Other reductions

$$[Cp^*Ir(T)](BF_4)_2 + 2\ NaBEt_3H \xrightarrow[5\ min]{benzene} Cp^*Ir(\eta^4\text{-}T) + 2\ NaBF_4 + 2\ BEt_3 + H_2 \qquad (12)$$

of transition metal complexes by $NaBEt_3H$ have been reported.[44] The proposed identity of the product is supported by its mass spectrum (EIMS; m/e, 412 (M^+), 360 ($M^+-C_4H_4$), 84 (T^+)) and also by its preparation from $[Cp^*Ir(T)]^{2+}$ and an excess of Cp_2Co[45,46] in CH_2Cl_2 at 25°C, eq. 13. The

$$[Cp^*Ir(T)]^{2+} + 2\ Cp_2Co \xrightarrow[5\ min]{CH_2Cl_2} Cp^*Ir(\eta^4\text{-}T) + 2\ Cp_2Co^+ \qquad (13)$$

η^4-T complex is relatively unstable and has not been characterized by elemental analysis.

The η^4-bonding mode is proposed on the basis of the ^1H NMR chemical shifts for the T ligand and by analogy to the $Cp^*Ir(\eta^4\text{-}C_6Me_6)$ complex.[47] The T resonances in the ^1H NMR spectrum ($CDCl_3$) of $Cr(CO)_3(\eta\text{-}T)$ occur at 5.59 (m; H3, H4) and 5.37 ppm (m; H2, H5).[43] An η^4-coordination of T would make the ligand more diene-like and consequently shift the ^1H resonances to higher field. The Cp*Ir(η^4-C_6Me_6) complex can be synthesized by electrochemical or chemical reduction of [Cp*Ir(η^4-C_6Me_6)]$^{2+}$ and the η^4-bonding of C_6Me_6 is clearly established by its ^1H NMR spectrum (2.19 (s, 6H), 1.74 (s, 6H), 1.66 (s, 6H), and 1.91 ppm (s, 15H)) but neither mass spectral nor microanalytical data were reported for this compound. η^4-Arene bonding to transition metals has been reported for other complexes[32,36,48] but Cp*Ir(η^4-T) represents a novel coordination mode for the T ligand.[49]

A cyclic voltammogram of [Cp*Ir(T)]$^{2+}$ shows irreversible cathodic peaks at -0.33 and -0.53 V (Table 3.7) possibly due to production of Cp*Ir(T). The [Cp*Rh(T)]$^{2+}$ complex also has two irreversible cathodic peaks in its cyclic voltammogram. The cyclic voltammogram of [Cp*Rh(BT)]$^{2+}$ was similar to that observed for [Cp*Rh(T)]$^{2+}$; however, the electrochemical reduction of [Cp*Ir(BT)]$^{2+}$ was quasi-reversible. The chemically reversible reduction of [Cp*Ir(C_6Me_6)]$^{2+}$ to [Cp*Ir(η^4-C_6Me_6)][41] suggests that η^4-C_6Me_6 bonding might be more stable than η^4-thiophene bonding in Cp*Ir(T).

Table 3.7. Cyclic voltammetic data[a]

Complex	Cathodic Peak Potential(s)[b,c] (V)
$[Cp^*Rh(T)](PF_6)_2$	-0.56, -0.77, i
$[Cp^*Rh(BT)](PF_6)_2$	-0.43, -0.79, i
$[Cp^*Ir(T)](BF_4)_2$	-0.33, -0.53, i
$[Cp^*Ir(BT)](BF_4)_2$	-0.54, q

[a] All measurements made in CH_3NO_2, scan rate = 500 mV/sec, with 0.1 M Bu_4NPF_6 as the supporting electrolyte.

[b] Referenced to Ag/AgCl (3.0 M NaCl).

[c] i = irreversible, q = quasi-reversible.

CONCLUSIONS

Reactions of transition metal model complexes of π-bound T with nucleophilic species such as hydride and sulfide, that are likely to be on HDS catalyst surfaces, have provided a basis for understanding the reactivity of T adsorbed on HDS catalysts.[11] Hydride addition to $[CpRu(T)]^+$ resulted in C-S bond cleavage[11c,d] and to $[Mn(CO)_3(T)]^+$ produced $Mn(CO)_3(T{\bullet}H)$[11a] which could be protonated to give a 2,3-dihydrothiophene (2,3-DHT) complex. The intermediacy of 2,3-DHT in the HDS of T has been proposed[50] and cleavage of the C-S bond of T is certainly an important step in the HDS process. Other types of reactions which occur over HDS catalysts, such as deuterium exchange, have been accounted for by studies of $[CpRu(\eta\text{-}T)]^+$ compounds. Thus, π-thiophene complexes serve as very useful models for reactions of T that might occur on HDS catalysts.

In attempts to model reactions of benzo[b]thiophene on HDS catalysts, we find that BT prefers to π-coordinate via the benzene, rather than the thiophene ring, in $[CpRu(BT)]^+$, $[Cp^*Ir(BT)]^{2+}$ and $[Cp^*Rh(BT)]^{2+}$ complexes. This type of coordination activates C4-C7 towards reactions with H^- and other nucleophiles giving primarily C7 adducts. Products which might lead to or are similar to proposed intermediates in the HDS of BT, such as 2,3-dihydrobenzothiophene[51] or thiophenols,[7a,52] were not observed. Thus, the π-arene-bonded complexes do not seem to account for the HDS reactivity of BT. Better model complexes might involve coordination of all or part of the thiophene ring of BT to the transition metal center.

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(39) The spectrum was obtained in CD_3NO_2 and assigned by analogy to $[Mn(CO)_3(T \cdot PBu_3)]^+$.[10a] δ 6.66 (m, H5), 6.20 (m, H4), 5.64 (d, H2, J = 2.42 Hz), 4.49 (m, H3), 2.08 (s, Cp*), 1.82 (d, PMe_3, J_{H-P} = 14.2 Hz).

(40) (CD_3NO_2): δ 6.34 (br s, H5), 6.23 (m, H4), 5.40 (m, H2), 4.25 (m, H3), 3.74 (d, $PO(OMe)_2$, J_{H-P} = 12.1 Hz), 2.18 (s, Cp*).

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SUPPLEMENTARY MATERIAL

Table 3.8. Least-squares planes for CpRu(BT•H), 6

1(-0.2763 x - 0.7076 y - 0.6503 z = 10.3401)	C9(0.3719, 11.9780, 2.7094)	0.000(3)
	C8(1.7152, 11.5109, 2.6463)	-0.001(3)
	C4(2.1256, 10.5026, 3.5677)	0.001(3)
	C5(1.1528, 10.0378, 4.4898)	-0.001(3)
	C6(-0.1586, 10.5716, 4.4623)	0.001(3)
2(-0.3114 x - 0.7207 y - 0.6194 z = 6.8587)	C10(-1.1401, 9.0954, 1.0635)	-0.003(3)
	C11(-1.0634, 8.1732, 2.0935)	0.000
	C12(0.2344, 7.6104, 2.1084)	0.003(3)
	C13(0.9551, 8.2010, 1.0432)	-0.005(3)
	C14(0.1124, 9.1191, 0.4118)	0.005(3)
3(-0.3148 x - 0.7285 y - 0.6084 z = 10.5154)	S(0.1167, 13.1923, 1.4551)	-0.018(1)
	C2(1.7125, 12.9757, 0.8420)	0.011(3)
	C3(2.4733, 12.0975, 1.5117)	0.004(3)
	C8(1.7152, 11.5109, 2.6453)	-0.020(3)
	C9(0.3719, 11.9780, 2.7094)	0.023(3)

Table 3.9. Structure factor table for CpRu(BT•H), **6**

H	K	L	Fobs	Fcalc	SigF
0	0	2	1575	1607	16
0	0	4	522	523	2
0	0	6	509	537	5
0	0	8	844	856	24
0	0	10	798	802	42
0	0	12	422	425	32
0	0	14	57	43	5
0	0	16	196	195	26
0	1	1	164	172	5
0	1	2	1364	1366	13
0	1	3	439	434	3
0	1	4	681	687	5
0	1	5	863	890	7
0	1	6	966	974	6
0	1	7	290	293	2
0	1	8	558	556	6
0	1	9	344	337	4
0	1	10	135	128	9
0	1	11	250	255	9
0	1	12	561	570	36
0	1	13	72	83	4
0	1	14	474	476	42
0	1	15	92	88	8
0	1	16	202	197	21
0	2	0	1330	1329	4
0	2	1	671	657	6
0	2	2	1303	1308	10
0	2	3	436	442	2
0	2	4	486	492	2
0	2	6	498	498	2
0	2	7	810	818	8
0	2	8	626	618	3
0	2	9	481	472	8
0	2	10	418	410	8
0	2	11	102	99	3
0	2	12	256	260	8
0	2	14	80	82	4
0	2	16	106	101	14
0	3	1	458	472	1
0	3	2	1161	1149	14
0	3	3	495	523	2
0	3	4	589	583	8
0	3	5	975	976	5
0	3	6	573	583	3
0	3	7	607	604	3
0	3	8	83	80	4
0	3	9	70	54	6
0	3	10	141	150	3
0	3	11	440	431	7
0	3	12	191	189	4
0	3	13	511	517	16
0	3	14	188	191	5
0	3	15	281	286	19
0	3	16	128	120	8
0	4	0	588	590	2
0	4	1	1124	1145	5
0	4	2	404	389	2
0	4	3	111	111	2
0	4	4	106	94	4
0	4	5	165	178	3
0	4	6	230	219	3
0	4	7	389	389	3
0	4	8	118	101	3
0	4	9	589	570	3
0	4	10	187	179	4
0	4	11	535	529	6
0	4	12	85	81	3
0	4	13	109	109	6
0	4	14	79	80	7
0	4	15	219	213	8
0	4	16	46	54	7
0	5	1	388	399	3
0	5	2	204	178	2
0	5	3	735	759	6
0	5	4	455	468	6
0	5	5	672	668	8
0	5	6	605	596	5
0	5	7	502	500	4
0	5	8	153	150	3
0	5	9	96	91	3
0	5	10	41	41	7
0	5	11	390	387	4
0	5	12	74	74	4
0	5	13	510	514	4
0	5	14	129	129	3
0	5	15	264	271	5
0	6	0	630	624	2
0	6	1	1003	997	3
0	6	2	847	833	5
0	6	3	497	493	2
0	6	4	521	524	7
0	6	5	350	345	3
0	6	6	492	489	3
0	6	7	515	517	4
0	6	8	702	693	3
0	6	9	462	448	4
0	6	10	507	502	6
0	6	11	173	166	3
0	6	12	260	259	7
0	6	13	56	57	5
0	6	15	70	73	5
0	7	1	286	291	2
0	7	2	790	778	4
0	7	3	153	142	3
0	7	4	1213	1213	9
0	7	5	385	390	5
0	7	6	755	769	8
0	7	7	169	183	3
0	7	8	277	268	6
0	7	9	85	90	3
0	7	10	78	83	6
0	7	11	146	147	3
0	7	12	331	332	6
0	7	13	63	59	4
0	7	14	333	342	4
0	7	15	105	103	3
0	8	0	1337	1335	8
0	8	1	93	75	2
0	8	2	787	787	5
0	8	3	222	213	5
0	8	4	71	77	2
0	8	5	104	105	2
0	8	6	368	359	6
0	8	8	577	566	3
0	8	9	41	45	6
0	8	10	634	624	4
0	8	11	43	40	6
0	8	12	284	290	4
0	8	13	47	50	6
0	8	14	71	65	4
0	9	1	145	139	3
0	9	2	726	736	5
0	9	3	373	366	3
0	9	4	743	739	3
0	9	5	518	512	3
0	9	6	538	526	3
0	9	7	247	233	3
0	9	8	363	358	3
0	9	9	160	160	6
0	9	10	133	130	3
0	9	11	182	178	13
0	9	12	324	322	4
0	9	13	88	86	3
0	9	14	331	331	4
0	10	0	238	245	3
0	10	1	279	279	3
0	10	2	325	331	5
0	10	3	468	460	3
0	10	4	133	130	3
0	10	6	175	165	7
0	10	7	455	451	4
0	10	8	374	372	3
0	10	9	434	432	5
0	10	10	247	247	4
0	10	11	151	150	5
0	10	12	93	94	7
0	11	1	102	107	4
0	11	2	142	141	7
0	11	3	596	600	3
0	11	4	321	324	3
0	11	5	655	659	7
0	11	6	326	335	3
0	11	7	297	307	4
0	11	10	139	145	3
0	11	11	201	199	4
0	11	12	36	50	19
0	11	13	265	270	9
0	12	0	335	348	3
0	12	1	646	672	3
0	12	2	82	80	3
0	12	3	267	263	3
0	12	4	71	74	3
0	12	5	224	237	6
0	12	6	67	66	5
0	12	7	279	284	8
0	12	8	44	43	5
0	12	9	401	408	9
0	12	10	126	122	3
0	12	11	362	368	12
0	12	12	56	64	5
0	13	1	280	287	3
0	13	2	109	116	2
0	13	3	523	538	7
0	13	4	301	307	3
0	13	5	303	318	4
0	13	6	271	272	9
0	13	7	215	223	4
0	13	8	79	74	3
0	13	9	146	139	5
0	13	10	100	104	3
0	13	11	137	139	10
0	14	0	200	213	4
0	14	1	345	358	7
0	14	2	409	426	7
0	14	3	80	89	3
0	14	4	222	236	4
0	14	5	49	53	5
0	14	6	254	270	6
0	14	7	176	185	3
0	14	8	361	379	4

Table 3.9. Continued

H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
0	14	9	249	254	7	1	1	-3	125	124	2	1	2	15	218	226	4	1	4	11	70	70	4
0	14	10	199	200	5	1	1	-2	495	482	2	1	2	16	226	234	4	1	4	12	449	450	4
0	15	2	143	152	3	1	1	-1	1363	1395	4	1	3	-16	269	253	5	1	4	14	469	493	4
0	15	4	509	535	9	1	1	0	650	590	4	1	3	-14	249	246	5	1	4	16	242	252	4
0	15	5	142	148	3	1	1	1	2026	1936	4	1	3	-12	91	91	3	1	5	-14	244	247	5
0	15	6	386	409	4	1	1	2	32	20	3	1	3	-11	136	135	2	1	5	-13	58	50	5
0	15	7	132	143	6	1	1	3	772	770	2	1	3	-10	416	409	3	1	5	-12	58	68	5
0	15	8	90	92	3	1	1	4	375	396	2	1	3	-9	200	187	4	1	5	-11	161	162	3
0	16	0	400	416	3	1	1	5	215	203	2	1	3	-8	520	511	3	1	5	-10	424	411	3
0	16	1	130	127	3	1	1	6	192	193	3	1	3	-7	425	426	3	1	5	-9	440	435	3
0	16	2	294	314	4	1	1	7	318	319	2	1	3	-6	580	583	2	1	5	-8	536	521	3
0	16	6	148	155	3	1	1	8	431	431	3	1	3	-5	400	384	2	1	5	-7	611	594	3
0	16	7	51	49	7	1	1	9	552	541	3	1	3	-4	347	355	2	1	5	-6	633	640	3
0	16	8	234	244	7	1	1	10	122	115	2	1	3	-3	214	218	2	1	5	-5	125	126	3
0	17	1	47	61	5	1	1	11	595	608	3	1	3	-2	515	517	2	1	5	-4	393	406	2
0	17	2	305	323	4	1	1	12	90	90	3	1	3	-1	140	132	2	1	5	-3	288	287	2
0	17	3	146	160	3	1	1	13	327	341	4	1	3	0	1204	1242	5	1	5	-2	458	477	2
0	17	4	241	255	15	1	1	14	80	76	3	1	3	1	352	358	2	1	5	-1	323	327	2
0	17	5	139	147	3	1	1	15	46	51	5	1	3	2	251	292	2	1	5	0	1193	1222	6
0	17	6	198	208	4	1	2	-16	99	107	4	1	3	3	628	668	2	1	5	1	202	215	2
0	18	0	312	328	4	1	2	-15	218	214	4	1	3	4	365	408	2	1	5	2	1031	1082	2
0	18	1	272	282	4	1	2	-14	226	215	4	1	3	5	225	239	2	1	5	3	1049	1085	2
0	18	2	114	117	3	1	2	-13	341	334	4	1	3	7	379	389	3	1	5	4	152	178	3
0	18	3	197	205	5	1	2	-12	354	354	4	1	3	8	453	439	3	1	5	5	874	851	2
1	0	-15	208	191	4	1	2	-11	392	390	4	1	3	9	221	216	3	1	5	6	123	120	2
1	0	-13	689	666	4	1	2	-10	437	436	3	1	3	10	601	594	3	1	5	7	382	392	3
1	0	-11	611	604	3	1	2	-9	186	178	4	1	3	11	80	74	3	1	5	8	327	335	3
1	0	-9	134	117	2	1	2	-8	193	179	3	1	3	12	510	519	3	1	5	9	344	328	3
1	0	-7	455	441	2	1	2	-7	360	358	3	1	3	13	166	169	3	1	5	10	678	668	3
1	0	-5	987	996	2	1	2	-6	561	590	2	1	3	14	100	100	3	1	5	11	201	204	3
1	0	-3	1303	1340	5	1	2	-5	793	778	2	1	3	16	140	138	3	1	5	12	463	464	4
1	0	-1	2222	2197	4	1	2	-4	946	958	2	1	4	-14	413	421	4	1	5	13	190	182	4
1	0	3	881	868	2	1	2	-3	726	718	2	1	4	-12	638	643	4	1	5	14	85	85	4
1	0	5	962	923	2	1	2	-2	1095	1080	5	1	4	-10	199	179	3	1	5	15	46	53	6
1	0	7	986	967	2	1	2	-1	538	546	1	1	4	-8	132	123	2	1	6	-15	177	172	4
1	0	9	576	601	3	1	2	0	48	44	2	1	4	-6	194	193	3	1	6	-14	202	196	4
1	0	11	39	35	5	1	2	1	899	896	5	1	4	-5	30	18	4	1	6	-13	190	191	3
1	0	13	336	358	3	1	2	2	409	390	2	1	4	-4	860	859	2	1	6	-12	233	226	4
1	0	15	245	256	4	1	2	3	440	417	2	1	4	-3	218	196	2	1	6	-11	348	356	4
1	1	-16	82	81	5	1	2	4	672	668	2	1	4	-2	1435	1476	6	1	6	-10	327	329	4
1	1	-15	329	314	5	1	2	5	1136	1121	2	1	4	-1	64	59	2	1	6	-9	351	351	3
1	1	-13	229	227	5	1	2	6	1116	1125	2	1	4	0	684	710	2	1	6	-7	94	95	3
1	1	-12	99	102	3	1	2	7	942	911	2	1	4	1	328	351	2	1	6	-6	510	505	3
1	1	-11	240	246	4	1	2	8	267	269	3	1	4	2	551	593	2	1	6	-5	655	660	2
1	1	-9	713	698	3	1	2	9	234	232	3	1	4	4	866	914	2	1	6	-4	693	695	2
1	1	-8	481	492	3	1	2	10	114	106	2	1	4	5	102	91	2	1	6	-3	779	789	2
1	1	-7	1151	1131	2	1	2	11	39	17	6	1	4	6	922	926	2	1	6	-2	413	430	2
1	1	-6	468	468	2	1	2	12	213	231	4	1	4	7	68	41	2	1	6	-1	407	405	2
1	1	-5	929	939	2	1	2	13	177	180	4	1	4	8	725	722	3	1	6	0	481	504	2
1	1	-4	126	123	2	1	2	14	267	277	4	1	4	10	176	174	3	1	6	1	325	337	2

Table 3.9. Continued

H	K	L	Fobs	Fcalc	SigF
1	6	2	52	48	2
1	6	3	49	47	3
1	6	4	878	889	2
1	6	5	1123	1157	2
1	6	6	651	668	3
1	6	7	636	653	3
1	6	8	364	362	3
1	6	10	81	77	3
1	6	12	174	174	3
1	6	13	127	124	3
1	6	14	174	179	4
1	6	15	262	256	5
1	7	-15	259	254	5
1	7	-14	47	39	6
1	7	-13	116	118	3
1	7	-12	140	153	3
1	7	-11	222	226	4
1	7	-9	705	696	3
1	7	-8	582	576	3
1	7	-7	824	812	3
1	7	-6	375	373	3
1	7	-5	614	616	3
1	7	-4	311	308	3
1	7	-3	96	86	2
1	7	-2	403	415	2
1	7	-1	790	812	2
1	7	0	49	41	3
1	7	1	1044	1091	2
1	7	2	474	481	2
1	7	3	1065	1101	2
1	7	4	223	243	3
1	7	5	424	433	3
1	7	6	189	182	3
1	7	7	281	285	3
1	7	8	279	283	3
1	7	9	498	498	3
1	7	10	152	144	3
1	7	11	491	482	4
1	7	12	61	68	5
1	7	13	271	274	4
1	7	14	142	144	3
1	8	-13	434	446	4
1	8	-12	129	133	3
1	8	-11	464	470	4
1	8	-9	226	221	4
1	8	-8	109	104	3
1	8	-7	88	86	3
1	8	-6	179	176	3
1	8	-5	445	444	3
1	8	-4	87	68	2
1	8	-3	1007	1024	2
1	8	-2	365	354	2
1	8	-1	977	998	2
1	8	2	336	333	2
1	8	3	831	848	2
1	8	5	534	535	3
1	8	6	73	69	3
1	8	7	489	481	3
1	8	9	422	424	3
1	8	11	102	97	3
1	8	12	130	125	3
1	8	13	314	314	4
1	8	14	78	70	4
1	9	-13	88	88	3
1	9	-11	245	249	4
1	9	-10	126	120	3
1	9	-9	511	504	3
1	9	-8	306	304	3
1	9	-7	498	491	3
1	9	-6	260	257	3
1	9	-5	378	378	3
1	9	-3	47	40	3
1	9	-2	138	129	3
1	9	-1	457	471	3
1	9	0	233	219	3
1	9	1	890	905	2
1	9	2	327	333	3
1	9	3	366	369	3
1	9	4	263	271	3
1	9	5	78	77	3
1	9	6	47	40	4
1	9	7	270	277	3
1	9	8	219	211	4
1	9	9	378	373	3
1	9	10	200	200	3
1	9	11	504	514	4
1	9	12	97	89	3
1	9	13	188	195	4
1	10	-13	230	242	5
1	10	-12	189	199	4
1	10	-11	238	243	4
1	10	-10	402	414	4
1	10	-9	215	218	4
1	10	-8	125	124	2
1	10	-6	463	469	3
1	10	-5	312	306	3
1	10	-4	612	606	3
1	10	-3	455	454	3
1	10	-2	268	260	3
1	10	-1	382	384	3
1	10	0	145	145	3
1	10	1	170	166	3
1	10	3	332	340	3
1	10	4	513	506	3
1	10	5	344	340	3
1	10	6	530	530	3
1	10	7	350	346	3
1	10	8	232	237	4
1	10	9	170	168	3
1	10	10	47	37	5
1	10	11	153	151	3
1	10	12	132	126	3
1	10	13	164	163	3
1	11	-11	55	50	5
1	11	-10	293	303	4
1	11	-9	58	67	5
1	11	-8	588	600	3
1	11	-7	228	236	4
1	11	-6	445	440	3
1	11	-5	134	124	2
1	11	-4	66	35	3
1	11	-3	130	143	3
1	11	-2	365	356	3
1	11	0	489	493	3
1	11	1	79	77	3
1	11	2	737	723	3
1	11	3	232	236	3
1	11	4	486	471	3
1	11	5	171	178	3
1	11	7	94	88	3
1	11	8	336	340	4
1	11	9	110	102	3
1	11	10	406	418	4
1	11	12	313	310	4
1	12	-12	284	301	4
1	12	-10	214	227	4
1	12	-9	63	61	4
1	12	-7	143	143	3
1	12	-6	194	196	3
1	12	-5	80	81	3
1	12	-4	526	532	3
1	12	-3	38	34	5
1	12	-2	619	631	3
1	12	-1	110	112	2
1	12	0	298	309	3
1	12	2	254	254	4
1	12	3	107	110	3
1	12	4	589	584	3
1	12	5	141	138	3
1	12	6	465	462	3
1	12	7	67	55	4
1	12	8	354	347	4
1	12	9	233	241	4
1	12	10	64	63	5
1	12	12	192	178	4
1	13	-10	322	329	4
1	13	-9	158	163	3
1	13	-8	347	350	4
1	13	-7	269	276	4
1	13	-6	319	333	4
1	13	-5	174	180	3
1	13	-4	198	211	4
1	13	-3	59	52	4
1	13	-2	227	235	4
1	13	-1	133	139	3
1	13	0	646	656	3
1	13	1	339	344	3
1	13	2	664	658	3
1	13	3	344	338	3
1	13	4	240	237	4
1	13	5	60	49	4
1	13	7	91	90	3
1	13	8	224	241	4
1	13	9	267	256	4
1	13	10	422	406	4
1	13	11	155	153	3
1	14	-10	76	83	4
1	14	-9	201	211	4
1	14	-7	66	66	4
1	14	-6	146	145	3
1	14	-5	407	427	4
1	14	-4	221	232	4
1	14	-3	419	432	3
1	14	-2	242	248	4
1	14	-1	198	197	4
1	14	0	150	154	3
1	14	1	197	200	3
1	14	2	115	108	3
1	14	3	137	139	3
1	14	4	279	274	4
1	14	5	466	459	4
1	14	6	284	288	4
1	14	7	398	380	4
1	14	8	195	185	4
1	14	9	120	118	3
1	15	-9	243	236	4
1	15	-8	181	187	4
1	15	-7	338	340	4
1	15	-6	108	110	3
1	15	-5	300	313	4

Table 3.9. Continued

H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
1	15	-4	139	132	2	2	0	2	1523	1402	6	2	2	-1	231	224	2	2	4	-9	513	490	3
1	15	-2	117	126	2	2	0	4	925	909	2	2	2	0	448	418	2	2	4	-8	87	68	3
1	15	-1	260	269	4	2	0	6	423	415	2	2	2	1	377	359	2	2	4	-7	528	507	3
1	15	0	48	57	5	2	0	8	164	153	3	2	2	2	684	668	2	2	4	-6	106	89	2
1	15	1	355	366	3	2	0	10	527	539	3	2	2	3	962	965	2	2	4	-5	860	888	2
1	15	2	75	83	3	2	0	12	640	667	3	2	2	4	950	969	2	2	4	-3	632	666	2
1	15	3	425	425	4	2	0	14	135	149	3	2	2	5	725	726	2	2	4	-2	115	107	2
1	15	4	167	169	3	2	1	-16	80	78	5	2	2	6	413	399	2	2	4	-1	435	456	2
1	15	5	129	129	3	2	1	-14	201	194	4	2	2	7	200	192	3	2	4	0	76	75	2
1	15	7	178	182	3	2	1	-13	73	75	4	2	2	8	214	219	3	2	4	1	1039	1068	6
1	15	8	115	109	3	2	1	-12	511	501	4	2	2	9	260	250	3	2	4	2	91	78	2
1	15	9	273	264	5	2	1	-11	181	182	4	2	2	10	287	279	3	2	4	3	982	1006	2
1	16	-8	42	38	6	2	1	-10	377	374	3	2	2	11	293	293	4	2	4	4	138	138	3
1	16	-7	73	72	4	2	1	-9	506	503	3	2	2	12	275	277	4	2	4	5	625	635	2
1	16	-5	230	239	4	2	1	-8	355	350	3	2	2	13	307	317	4	2	4	6	65	60	2
1	16	-4	65	67	4	2	1	-7	95	86	2	2	2	14	208	216	4	2	4	7	192	195	3
1	16	-3	419	446	4	2	1	-6	92	87	2	2	2	15	155	162	3	2	4	9	276	273	3
1	16	-2	124	129	3	2	1	-5	631	636	2	2	3	-13	362	374	4	2	4	10	108	106	3
1	16	-1	329	341	4	2	1	-4	641	636	2	2	3	-11	556	565	4	2	4	11	673	661	3
1	16	0	89	93	3	2	1	-3	186	197	2	2	3	-10	344	338	4	2	4	12	171	170	3
1	16	2	53	53	4	2	1	-2	1067	1024	6	2	3	-9	529	501	3	2	4	13	440	448	4
1	16	3	201	200	4	2	1	-1	372	324	2	2	3	-8	261	265	3	2	4	15	95	98	3
1	16	4	62	65	4	2	1	0	775	745	2	2	3	-7	228	220	3	2	5	-14	77	82	4
1	16	5	298	287	4	2	1	1	551	497	2	2	3	-6	146	163	3	2	5	-13	307	322	4
1	16	7	308	293	4	2	1	2	109	101	2	2	3	-5	453	449	2	2	5	-12	116	110	3
1	17	-6	135	131	3	2	1	3	91	88	2	2	3	-4	166	176	3	2	5	-11	552	544	4
1	17	-5	187	195	4	2	1	4	382	373	2	2	3	-3	920	961	2	2	5	-10	191	179	4
1	17	-3	99	99	3	2	1	5	619	617	2	2	3	-2	56	62	2	2	5	-9	342	326	4
1	17	-2	58	53	4	2	1	6	673	670	2	2	3	-1	1224	1253	6	2	5	-8	327	312	3
1	17	-1	240	246	4	2	1	7	433	437	3	2	3	0	172	177	2	2	5	-7	243	223	3
1	17	0	133	134	3	2	1	8	678	664	3	2	3	1	594	581	2	2	5	-6	144	140	3
1	17	1	345	348	4	2	1	10	471	476	3	2	3	2	240	253	2	2	5	-5	140	131	2
1	17	2	248	260	4	2	1	11	50	43	4	2	3	3	162	158	2	2	5	-4	560	559	2
1	17	3	113	113	2	2	1	12	90	88	3	2	3	4	129	129	2	2	5	-3	1162	1203	2
1	17	4	115	120	3	2	1	14	264	277	4	2	3	5	873	873	2	2	5	-2	490	479	2
1	17	5	47	40	5	2	1	15	121	128	3	2	3	6	612	616	2	2	5	-1	1269	1298	7
1	18	-3	183	183	3	2	2	-16	205	196	4	2	3	7	783	777	3	2	5	0	280	295	2
1	18	-2	143	148	3	2	2	-15	213	215	4	2	3	8	273	272	3	2	5	1	457	459	2
1	18	-1	210	206	4	2	2	-14	189	194	3	2	3	9	496	489	3	2	5	2	343	371	2
1	18	0	113	119	3	2	2	-13	176	183	4	2	3	10	126	123	2	2	5	3	369	388	2
1	18	3	104	108	3	2	2	-12	168	156	3	2	3	11	213	208	4	2	5	4	145	130	2
2	0	-16	305	311	5	2	2	-11	96	91	3	2	3	13	225	221	4	2	5	5	669	676	2
2	0	-14	497	499	4	2	2	-10	68	56	4	2	3	14	51	70	6	2	5	6	502	533	3
2	0	-12	102	95	3	2	2	-9	283	266	4	2	3	15	313	334	4	2	5	7	646	655	3
2	0	-10	364	373	3	2	2	-8	618	591	3	2	4	-15	354	362	5	2	5	8	231	224	3
2	0	-8	577	556	3	2	2	-7	937	908	3	2	4	-14	108	103	4	2	5	9	549	552	3
2	0	-6	1230	1211	2	2	2	-6	872	854	3	2	4	-13	368	381	4	2	5	10	138	131	2
2	0	-4	1206	1187	7	2	2	-5	306	328	2	2	4	-12	53	64	6	2	5	11	124	122	3
2	0	-2	67	68	2	2	2	-4	460	464	2	2	4	-11	191	187	3	2	5	12	103	101	3
2	0	0	1357	1240	5	2	2	-3	185	161	2	2	4	-10	102	104	3	2	5	13	199	192	4

Table 3.9. Continued

H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
2	5	15	255	260	5	2	7	8	475	486	3	2	9	10	304	316	4	2	12	-9	286	296	4
2	6	-15	199	202	4	2	7	9	132	143	3	2	9	11	42	26	6	2	12	-8	53	50	5
2	6	-14	211	208	4	2	7	10	261	253	4	2	9	12	54	47	5	2	12	-7	405	413	4
2	6	-13	144	150	3	2	7	12	51	48	5	2	9	13	67	59	4	2	12	-6	78	82	4
2	6	-12	162	152	4	2	7	13	94	85	3	2	10	-13	101	106	3	2	12	-5	569	564	3
2	6	-11	50	55	6	2	7	14	166	154	3	2	10	-12	157	166	3	2	12	-4	187	180	3
2	6	-9	396	383	4	2	8	-14	368	367	4	2	10	-11	98	104	3	2	12	-3	359	355	4
2	6	-8	565	544	3	2	8	-13	107	107	3	2	10	-10	96	96	3	2	12	-1	304	300	3
2	6	-7	650	641	3	2	8	-12	154	160	3	2	10	-9	246	240	4	2	12	0	194	195	3
2	6	-6	811	795	3	2	8	-10	258	251	4	2	10	-8	250	253	4	2	12	1	713	716	3
2	6	-5	611	602	3	2	8	-9	65	55	4	2	10	-7	550	562	3	2	12	2	188	196	3
2	6	-4	358	354	3	2	8	-8	459	448	4	2	10	-6	182	177	3	2	12	3	567	564	3
2	6	-3	155	151	2	2	8	-7	188	183	3	2	10	-5	288	276	4	2	12	4	42	33	5
2	6	-2	53	55	3	2	8	-6	456	443	3	2	10	-4	106	105	3	2	12	5	360	360	3
2	6	-1	247	247	2	2	8	-5	69	59	3	2	10	-3	52	47	4	2	12	6	82	77	3
2	6	0	406	416	2	2	8	-4	520	528	3	2	10	-2	57	51	4	2	12	7	154	154	3
2	6	1	621	624	2	2	8	-3	174	160	3	2	10	1	245	242	3	2	12	8	188	181	3
2	6	2	588	633	2	2	8	-2	164	163	3	2	10	2	311	306	3	2	12	9	339	339	4
2	6	3	771	815	2	2	8	-1	40	32	4	2	10	3	577	577	3	2	12	10	58	64	5
2	6	4	959	1011	2	2	8	0	485	501	3	2	10	4	313	315	3	2	12	11	424	422	4
2	6	5	462	499	2	2	8	1	75	72	2	2	10	5	417	421	3	2	13	-11	289	286	5
2	6	6	308	303	3	2	8	2	809	833	2	2	10	6	169	170	3	2	13	-10	209	214	4
2	6	7	132	127	2	2	8	4	416	418	3	2	10	8	107	106	3	2	13	-9	155	163	4
2	6	8	412	422	3	2	8	5	144	148	3	2	10	9	282	289	4	2	13	-8	63	59	4
2	6	9	332	333	3	2	8	6	289	304	3	2	10	10	301	302	4	2	13	-7	121	128	3
2	6	10	348	364	4	2	8	7	172	167	3	2	10	11	262	262	4	2	13	-6	62	76	4
2	6	11	332	328	4	2	8	9	56	59	4	2	10	12	198	207	4	2	13	-5	83	80	3
2	6	12	308	308	4	2	8	10	525	532	3	2	10	13	261	248	5	2	13	-4	193	189	4
2	6	13	220	221	4	2	8	12	482	484	4	2	11	-11	319	336	4	2	13	-3	644	650	3
2	6	14	224	218	4	2	8	14	199	189	4	2	11	-10	195	198	4	2	13	-2	184	177	4
2	6	15	123	113	3	2	9	-13	78	89	4	2	11	-9	402	415	4	2	13	-1	721	713	3
2	7	-14	159	162	4	2	9	-12	346	357	4	2	11	-8	233	236	4	2	13	0	230	221	4
2	7	-12	284	286	4	2	9	-11	253	261	4	2	11	-7	79	66	3	2	13	1	220	217	4
2	7	-11	50	46	5	2	9	-10	404	400	4	2	11	-5	366	360	4	2	13	2	169	161	3
2	7	-10	471	468	4	2	9	-9	311	312	4	2	11	-4	200	198	4	2	13	3	185	180	3
2	7	-9	297	305	4	2	9	-8	162	158	3	2	11	-3	614	592	3	2	13	4	100	100	3
2	7	-8	434	414	4	2	9	-6	49	56	5	2	11	-2	160	159	3	2	13	5	241	236	4
2	7	-5	390	372	3	2	9	-5	283	281	3	2	11	-1	630	624	3	2	13	6	235	229	4
2	7	-4	637	642	3	2	9	-4	361	359	3	2	11	0	167	160	3	2	13	7	355	354	4
2	7	-3	197	178	3	2	9	-3	281	285	3	2	11	1	420	417	3	2	13	8	300	294	4
2	7	-2	1077	1100	2	2	9	-2	757	765	3	2	11	2	129	128	2	2	13	9	352	347	4
2	7	-1	43	32	3	2	9	-1	263	250	3	2	11	3	45	38	5	2	13	10	97	102	3
2	7	0	818	851	2	2	9	0	682	691	3	2	11	4	180	180	3	2	14	-9	202	196	4
2	7	1	260	277	2	2	9	1	314	318	3	2	11	5	331	322	3	2	14	-8	288	294	4
2	7	2	124	128	2	2	9	4	355	357	3	2	11	6	312	310	3	2	14	-7	244	248	4
2	7	3	42	44	3	2	9	5	367	361	3	2	11	7	560	568	3	2	14	-6	387	396	4
2	7	4	349	363	3	2	9	6	173	167	3	2	11	9	406	421	4	2	14	-5	257	276	4
2	7	5	160	163	3	2	9	7	289	296	3	2	11	10	162	160	3	2	14	-4	260	258	4
2	7	6	532	553	3	2	9	8	466	464	3	2	11	11	95	86	3	2	14	-3	88	94	3
2	7	7	326	335	3	2	9	9	136	130	3	2	12	-10	112	110	3	2	14	-1	158	157	3

Table 3.9. Continued

H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
2	14	0	175	178	4	3	0	-1	1555	1419	7	3	2	-2	251	255	2	3	4	-6	450	436	3
2	14	1	282	287	4	3	0	1	964	983	2	3	2	-1	481	475	2	3	4	-4	167	152	3
2	14	2	436	436	4	3	0	3	357	326	2	3	2	0	694	697	2	3	4	-3	111	111	2
2	14	3	349	347	4	3	0	5	229	210	3	3	2	1	676	644	2	3	4	-2	1139	1181	2
2	14	4	413	408	4	3	0	7	431	416	3	3	2	2	805	777	2	3	4	-1	149	148	3
2	14	5	264	252	4	3	0	9	739	742	3	3	2	3	459	442	2	3	4	0	934	980	2
2	14	6	97	85	3	3	0	11	526	534	3	3	2	4	63	52	2	3	4	1	52	36	2
2	14	8	188	179	3	3	0	13	111	114	3	3	2	5	105	109	2	3	4	2	265	249	2
2	14	9	164	149	3	3	0	15	190	202	4	3	2	6	520	523	3	3	4	3	74	77	2
2	15	-8	196	199	4	3	1	-15	270	289	5	3	2	7	474	464	3	3	4	4	161	167	3
2	15	-6	83	82	3	3	1	-14	87	91	4	3	2	8	460	444	3	3	4	5	81	76	2
2	15	-5	182	182	4	3	1	-13	359	372	4	3	2	9	402	398	3	3	4	6	225	217	3
2	15	-4	251	259	4	3	1	-11	142	134	3	3	2	10	339	342	4	3	4	7	78	63	3
2	15	-3	106	104	3	3	1	-10	215	230	4	3	2	11	238	236	4	3	4	8	615	618	3
2	15	-2	342	337	4	3	1	-9	133	138	3	3	2	12	74	81	4	3	4	10	612	611	3
2	15	0	338	337	4	3	1	-8	96	86	3	3	2	13	58	53	5	3	4	11	144	143	2
2	15	1	125	123	3	3	1	-7	480	481	3	3	2	14	60	64	4	3	4	12	157	156	3
2	15	2	159	156	3	3	1	-6	546	557	3	3	2	15	148	146	3	3	4	14	164	157	3
2	15	3	96	98	3	3	1	-5	757	762	3	3	3	-14	351	351	5	3	5	-14	342	339	5
2	15	4	195	184	4	3	1	-3	860	851	2	3	3	-13	56	61	6	3	5	-13	193	200	4
2	15	5	110	110	3	3	1	-2	130	117	2	3	3	-12	271	267	4	3	5	-12	351	348	4
2	15	6	422	404	4	3	1	-1	145	148	3	3	3	-11	229	213	4	3	5	-11	107	106	4
2	15	7	81	80	4	3	1	0	461	435	2	3	3	-10	118	126	3	3	5	-9	138	140	3
2	15	8	319	299	4	3	1	1	989	937	2	3	3	-9	58	60	5	3	5	-8	277	266	4
2	16	-6	242	254	4	3	1	2	298	277	2	3	3	-8	200	181	3	3	5	-7	546	550	3
2	16	-5	134	136	3	3	1	3	1172	1098	7	3	3	-7	348	334	3	3	5	-6	426	414	3
2	16	-4	226	233	4	3	1	4	647	651	2	3	3	-6	663	648	3	3	5	-5	352	352	3
2	16	-3	161	161	3	3	1	5	726	729	2	3	3	-5	316	298	3	3	5	-4	964	975	3
2	16	-2	77	78	4	3	1	6	210	202	3	3	3	-4	662	675	3	3	5	-3	181	158	3
2	16	-1	84	81	4	3	1	7	247	246	3	3	3	-3	106	97	2	3	5	-2	619	624	2
2	16	0	213	215	4	3	1	8	82	82	3	3	3	-2	556	557	2	3	5	-1	276	282	3
2	16	1	179	165	3	3	1	9	51	43	5	3	3	-1	76	60	2	3	5	0	375	389	2
2	16	2	323	316	4	3	1	10	102	93	3	3	3	0	50	51	2	3	5	1	106	117	2
2	16	4	231	222	4	3	1	11	463	463	3	3	3	1	94	81	2	3	5	2	598	610	2
2	16	5	48	39	5	3	1	12	97	104	3	3	3	2	505	506	2	3	5	3	484	496	2
2	16	6	121	114	3	3	1	13	422	438	4	3	3	3	385	386	2	3	5	4	605	617	2
2	17	-4	125	128	3	3	1	14	94	95	3	3	3	4	736	748	2	3	5	5	493	514	3
2	17	-3	146	152	3	3	1	15	223	229	4	3	3	5	350	350	2	3	5	6	522	537	3
2	17	-2	282	275	4	3	2	-15	49	48	7	3	3	6	562	561	3	3	5	7	124	122	2
2	17	-1	119	113	3	3	2	-13	116	106	3	3	3	8	209	195	3	3	5	8	155	151	3
2	17	0	244	231	5	3	2	-12	150	151	3	3	3	9	228	227	4	3	5	10	222	223	4
2	17	1	110	100	3	3	2	-11	335	332	4	3	3	10	219	222	4	3	5	11	126	120	3
2	17	4	125	112	3	3	2	-10	347	363	4	3	3	12	407	406	4	3	5	12	343	336	4
3	0	-15	111	112	4	3	2	-9	516	517	3	3	3	13	101	106	3	3	5	13	156	151	3
3	0	-13	287	290	4	3	2	-8	807	809	3	3	3	14	247	252	5	3	5	14	273	264	4
3	0	-11	519	537	4	3	2	-7	263	252	3	3	4	-12	384	385	4	3	6	-12	160	154	3
3	0	-9	398	421	3	3	2	-6	133	137	3	3	4	-10	618	613	4	3	6	-11	228	220	4
3	0	-7	324	332	3	3	2	-5	267	284	3	3	4	-9	55	60	5	3	6	-10	465	453	4
3	0	-5	117	122	2	3	2	-4	527	519	3	3	4	-8	549	534	3	3	6	-9	536	516	4
3	0	-3	542	541	2	3	2	-3	401	402	2	3	4	-7	39	36	6	3	6	-8	400	396	4

Table 3.9. Continued

H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
3	6	-7	360	340	4	3	8	-9	357	348	4	3	10	-6	86	84	4	3	12	6	172	169	3
3	6	-6	164	160	3	3	8	-7	342	332	4	3	10	-4	261	255	4	3	12	8	388	391	4
3	6	-5	283	290	3	3	8	-6	90	88	3	3	10	-3	364	372	3	3	12	9	115	111	3
3	6	-4	209	194	3	3	8	-5	142	143	2	3	10	-2	216	209	3	3	12	10	345	337	4
3	6	-3	410	405	3	3	8	-4	68	64	3	3	10	-1	322	332	3	3	13	-10	66	55	6
3	6	-2	490	506	3	3	8	-3	576	587	3	3	10	0	409	410	3	3	13	-9	53	59	6
3	6	-1	525	535	2	3	8	-2	236	239	3	3	10	1	176	170	3	3	13	-8	227	211	4
3	6	0	562	573	2	3	8	-1	820	846	3	3	10	2	515	521	3	3	13	-7	185	182	4
3	6	1	563	587	2	3	8	0	70	73	3	3	10	3	52	51	4	3	13	-6	300	290	4
3	6	2	490	511	2	3	8	1	469	476	3	3	10	5	138	135	3	3	13	-5	283	278	4
3	6	3	191	198	3	3	8	2	178	179	3	3	10	6	355	364	3	3	13	-4	584	591	4
3	6	4	88	98	2	3	8	3	53	47	4	3	10	7	348	354	3	3	13	-3	200	194	4
3	6	5	333	341	3	3	8	4	59	63	3	3	10	8	391	404	4	3	13	-2	393	388	4
3	6	6	257	259	3	3	8	5	194	188	3	3	10	9	280	286	4	3	13	-1	50	44	5
3	6	7	447	455	3	3	8	6	106	109	2	3	10	10	225	232	4	3	13	0	192	199	4
3	6	8	371	382	3	3	8	7	419	429	3	3	10	11	113	114	3	3	13	1	128	128	3
3	6	9	300	301	3	3	8	8	56	56	4	3	10	12	136	127	3	3	13	2	425	422	4
3	6	10	225	236	4	3	8	9	566	586	3	3	11	-11	110	103	3	3	13	3	219	221	4
3	6	11	241	247	4	3	8	11	327	331	4	3	11	-8	245	232	4	3	13	4	363	363	4
3	6	12	163	169	3	3	8	12	67	67	4	3	11	-7	144	140	3	3	13	5	236	240	4
3	6	13	139	138	3	3	9	-13	250	233	4	3	11	-6	508	494	4	3	13	6	319	315	4
3	7	-14	85	81	5	3	9	-12	126	129	3	3	11	-5	96	87	3	3	13	7	103	103	3
3	7	-13	312	303	5	3	9	-10	127	123	3	3	11	-4	513	505	4	3	13	8	123	119	3
3	7	-12	106	103	4	3	9	-9	199	184	4	3	11	-2	307	306	4	3	13	9	66	66	4
3	7	-11	138	140	3	3	9	-8	140	131	3	3	11	-1	49	49	4	3	14	-8	161	157	3
3	7	-10	77	79	4	3	9	-7	151	144	3	3	11	0	74	75	3	3	14	-7	188	181	4
3	7	-9	157	152	3	3	9	-6	275	278	4	3	11	1	65	72	4	3	14	-6	60	59	5
3	7	-8	204	182	4	3	9	-5	452	438	3	3	11	2	412	417	3	3	14	-5	74	67	4
3	7	-7	536	532	4	3	9	-4	171	171	3	3	11	3	149	146	3	3	14	-4	55	58	5
3	7	-6	325	321	3	3	9	-3	540	556	3	3	11	4	564	573	3	3	14	-3	269	263	4
3	7	-5	717	719	3	3	9	-2	97	100	3	3	11	5	205	213	4	3	14	-2	267	272	4
3	7	-4	121	131	3	3	9	-1	82	77	3	3	11	6	437	433	3	3	14	-1	277	285	4
3	7	-3	587	588	3	3	9	0	96	103	2	3	11	7	44	41	5	3	14	0	276	271	4
3	7	-2	88	81	2	3	9	1	249	252	3	3	11	8	138	139	2	3	14	1	340	337	4
3	7	-1	197	209	3	3	9	2	71	65	3	3	11	9	180	176	4	3	14	2	153	146	2
3	7	0	275	283	3	3	9	3	437	449	3	3	11	10	155	157	3	3	14	3	214	210	3
3	7	1	412	424	3	3	9	4	333	335	3	3	12	-10	381	356	5	3	14	5	147	147	3
3	7	2	302	305	3	3	9	5	495	505	3	3	12	-9	62	57	5	3	14	6	115	110	3
3	7	3	795	824	3	3	9	6	241	242	3	3	12	-8	285	281	5	3	14	7	363	362	4
3	7	4	508	533	3	3	9	7	351	362	3	3	12	-7	67	65	5	3	14	8	176	165	4
3	7	5	679	701	3	3	9	9	100	103	3	3	12	-6	269	260	4	3	15	-7	287	268	5
3	7	6	188	204	3	3	9	10	69	70	4	3	12	-5	139	133	3	3	15	-6	163	153	3
3	7	7	277	284	3	3	9	11	327	330	4	3	12	-4	112	104	3	3	15	-5	374	361	4
3	7	8	102	92	2	3	9	12	120	114	3	3	12	-2	617	610	3	3	15	-4	41	14	6
3	7	9	116	121	2	3	10	-12	90	98	4	3	12	-1	139	134	3	3	15	-3	192	189	3
3	7	10	87	84	3	3	10	-11	186	179	3	3	12	0	626	626	3	3	15	-2	73	71	4
3	7	11	307	301	4	3	10	-10	316	309	5	3	12	1	122	120	2	3	15	0	151	136	3
3	7	13	316	304	4	3	10	-9	315	300	4	3	12	2	230	237	4	3	15	1	159	152	3
3	8	-13	140	139	3	3	10	-8	433	423	4	3	12	3	108	110	3	3	15	3	322	306	4
3	8	-11	344	332	4	3	10	-7	202	193	4	3	12	5	79	83	3	3	15	4	228	225	4

Table 3.9. Continued

H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
3	15	5	324	316	4	4	2	-14	152	161	3	4	3	11	400	406	4	4	5	12	140	136	3
3	15	6	118	117	3	4	2	-13	198	220	5	4	3	12	145	142	3	4	5	13	104	99	3
3	15	7	143	133	3	4	2	-12	289	306	4	4	3	13	79	73	4	4	6	-13	180	176	3
3	16	-4	80	75	4	4	2	-11	253	271	4	4	4	-13	352	361	5	4	6	-12	305	300	5
3	16	-3	220	211	4	4	2	-10	277	287	4	4	4	-11	285	296	5	4	6	-11	283	289	5
3	16	-2	151	149	3	4	2	-9	222	233	4	4	4	-9	122	120	3	4	6	-10	247	252	5
3	16	-1	331	325	4	4	2	-8	124	120	3	4	4	-8	47	56	6	4	6	-9	176	181	4
3	16	0	112	108	3	4	2	-7	120	116	3	4	4	-7	68	62	4	4	6	-8	177	175	4
3	16	1	295	279	4	4	2	-6	567	558	3	4	4	-6	56	49	4	4	6	-7	168	159	3
3	16	3	91	92	3	4	2	-5	387	390	3	4	4	-5	378	369	3	4	6	-6	538	542	3
3	16	5	83	81	4	4	2	-4	590	592	3	4	4	-4	83	65	3	4	6	-5	464	476	3
3	17	0	67	66	5	4	2	-3	409	393	3	4	4	-3	871	881	3	4	6	-4	399	416	3
4	0	-14	322	354	5	4	2	-2	459	441	3	4	4	-2	92	94	2	4	6	-3	403	420	3
4	0	-12	336	366	4	4	2	-1	446	427	2	4	4	-1	472	486	3	4	6	-2	308	317	3
4	0	-10	273	296	4	4	2	0	235	237	3	4	4	0	48	43	3	4	6	-1	271	279	3
4	0	-6	609	613	3	4	2	1	129	124	2	4	4	1	317	308	3	4	6	0	246	266	3
4	0	-4	1161	1156	3	4	2	2	180	161	3	4	4	2	66	53	3	4	6	1	107	97	2
4	0	-2	1214	1137	3	4	2	3	438	409	2	4	4	3	228	214	3	4	6	2	169	168	3
4	0	2	594	597	2	4	2	4	528	515	2	4	4	4	65	65	3	4	6	3	385	382	3
4	0	4	641	619	2	4	2	5	488	507	3	4	4	5	330	328	3	4	6	4	688	699	3
4	0	6	678	673	3	4	2	6	439	445	3	4	4	6	177	175	3	4	6	5	430	447	3
4	0	8	466	458	3	4	2	7	170	163	3	4	4	7	530	545	3	4	6	6	564	596	3
4	0	10	45	23	6	4	2	8	231	232	4	4	4	8	95	86	3	4	6	7	188	200	4
4	0	12	290	284	4	4	2	9	109	102	3	4	4	9	261	263	4	4	6	8	199	206	4
4	1	-14	67	72	5	4	2	10	68	63	4	4	4	10	54	57	5	4	6	12	148	143	3
4	1	-13	81	80	4	4	2	11	71	68	4	4	4	11	164	165	3	4	7	-12	94	96	4
4	1	-12	177	179	3	4	2	12	97	95	3	4	4	12	80	80	3	4	7	-10	360	357	4
4	1	-10	332	353	4	4	2	13	175	175	3	4	4	13	298	291	5	4	7	-9	174	161	3
4	1	-9	226	238	4	4	3	-13	52	41	6	4	5	-11	223	224	4	4	7	-8	539	537	4
4	1	-8	465	488	3	4	3	-12	52	14	6	4	5	-10	226	222	4	4	7	-7	216	213	4
4	1	-7	336	340	4	4	3	-11	245	250	5	4	5	-9	405	398	4	4	7	-6	453	450	4
4	1	-6	335	338	3	4	3	-10	225	225	4	4	5	-8	442	431	4	4	7	-5	50	49	5
4	1	-5	43	35	5	4	3	-9	409	426	4	4	5	-7	372	368	4	4	7	-3	155	153	3
4	1	-4	91	83	3	4	3	-8	204	211	4	4	5	-6	96	91	3	4	7	-2	406	424	3
4	1	-3	80	70	3	4	3	-7	454	455	3	4	5	-5	328	336	3	4	7	-1	191	202	3
4	1	-2	445	429	3	4	3	-5	321	322	3	4	5	-4	115	110	2	4	7	0	601	630	3
4	1	-1	91	91	2	4	3	-4	195	197	3	4	5	-3	56	41	4	4	7	1	264	268	3
4	1	0	896	892	2	4	3	-3	35	20	5	4	5	-2	49	47	4	4	7	2	635	659	3
4	1	1	422	422	2	4	3	-1	638	631	2	4	5	-1	602	610	3	4	7	3	454	473	3
4	1	2	770	734	2	4	3	0	48	37	3	4	5	0	229	233	3	4	7	4	328	337	3
4	1	3	401	393	2	4	3	1	661	647	2	4	5	1	567	575	3	4	7	5	69	77	3
4	1	4	493	472	2	4	3	2	488	477	2	4	5	2	384	374	3	4	7	6	92	89	3
4	1	5	175	175	3	4	3	3	402	387	2	4	5	3	350	336	3	4	7	7	218	233	4
4	1	6	110	110	2	4	3	4	233	221	3	4	5	4	300	305	3	4	7	8	313	322	3
4	1	7	247	253	3	4	3	5	113	112	2	4	5	5	189	191	3	4	7	9	83	82	3
4	1	8	565	557	3	4	3	6	177	185	3	4	5	7	235	239	3	4	7	10	381	381	4
4	1	9	119	114	3	4	3	7	237	245	3	4	5	8	112	106	2	4	7	11	61	67	4
4	1	10	612	607	3	4	3	8	268	267	3	4	5	9	480	499	3	4	7	12	269	269	4
4	1	11	113	114	3	4	3	9	507	508	3	4	5	10	143	140	3	4	8	-12	289	275	5
4	1	12	279	282	4	4	3	10	171	172	3	4	5	11	323	328	4	4	8	-10	115	114	4

Table 3.9. Continued

H	K	L	Fobs	Fcalc	SigF
4	8	-7	49	34	6
4	8	-6	243	247	4
4	8	-5	170	176	3
4	8	-4	711	733	3
4	8	-3	91	81	3
4	8	-2	589	607	3
4	8	-1	83	77	3
4	8	0	78	82	3
4	8	1	178	177	3
4	8	2	351	364	3
4	8	3	78	81	3
4	8	4	541	558	3
4	8	5	61	50	4
4	8	6	529	552	3
4	8	7	100	104	3
4	8	8	344	362	4
4	8	11	71	70	4
4	8	12	270	265	5
4	9	-10	296	290	5
4	9	-9	236	231	4
4	9	-8	313	309	4
4	9	-7	266	267	4
4	9	-6	415	414	4
4	9	-5	80	93	4
4	9	-4	139	139	3
4	9	-2	407	433	3
4	9	-1	168	169	3
4	9	0	561	589	3
4	9	1	304	312	3
4	9	2	406	414	3
4	9	3	227	229	3
4	9	4	195	192	4
4	9	5	43	45	5
4	9	7	150	148	3
4	9	8	289	297	4
4	9	9	100	107	3
4	9	10	377	393	4
4	9	11	101	95	3
4	10	-11	235	213	5
4	10	-10	91	82	4
4	10	-9	136	130	3
4	10	-7	141	132	3
4	10	-6	122	116	3
4	10	-5	346	342	4
4	10	-4	269	264	4
4	10	-3	192	186	3
4	10	-2	241	248	4
4	10	-1	225	232	4
4	10	0	90	92	3
4	10	1	235	237	3
4	10	2	179	178	3
4	10	3	332	346	3
4	10	4	277	286	4
4	10	5	481	496	3
4	10	6	268	266	4
4	10	7	212	207	3
4	10	8	145	158	2
4	11	-10	147	143	3
4	11	-9	336	323	5
4	11	-8	200	188	4
4	11	-7	433	426	4
4	11	-5	233	227	4
4	11	-4	81	82	4
4	11	-3	183	183	4
4	11	-1	238	229	4
4	11	0	99	100	3
4	11	1	465	468	3
4	11	2	181	177	3
4	11	3	430	443	3
4	11	6	93	91	3
4	11	7	168	166	3
4	11	8	87	90	3
4	11	9	239	238	4
4	12	-9	55	58	6
4	12	-7	87	84	4
4	12	-5	395	401	4
4	12	-4	170	161	3
4	12	-3	489	497	4
4	12	-2	123	123	3
4	12	-1	217	218	4
4	12	1	69	65	4
4	12	3	308	311	4
4	12	5	371	380	4
4	12	6	81	72	3
4	12	7	338	333	4
4	12	8	98	97	3
4	13	-8	175	160	3
4	13	-7	260	251	5
4	13	-6	120	117	3
4	13	-5	239	227	5
4	13	-3	51	58	6
4	13	-2	114	115	3
4	13	-1	349	358	4
4	13	0	203	202	4
4	13	1	305	305	4
4	13	2	231	228	4
4	13	3	185	191	4
4	13	4	84	86	4
4	13	5	167	160	3
4	13	6	61	51	4
4	13	7	75	79	4
4	14	-6	263	245	5
4	14	-5	174	167	3
4	14	-4	289	283	5
4	14	-3	234	238	5
4	14	-2	200	196	3
4	14	-1	169	166	4
4	14	0	158	154	3
4	14	1	57	63	4
4	14	2	91	94	3
4	14	3	146	145	3
4	14	4	306	293	4
4	14	5	238	238	4
4	14	6	264	249	5
4	15	-2	171	168	3
4	15	-1	46	20	6
4	15	0	315	311	4
4	15	1	90	83	3
4	15	2	368	357	4
4	15	3	132	126	3
4	15	4	138	131	3
5	0	-11	173	170	3
5	0	-9	172	191	3
5	0	-7	504	524	4
5	0	-5	780	783	3
5	0	-3	361	341	3
5	0	-1	488	479	3
5	0	1	568	619	3
5	0	3	518	535	3
5	0	5	478	477	3
5	0	7	79	74	3
5	0	9	309	299	4
5	0	11	359	342	4
5	1	-12	115	127	3
5	1	-11	318	353	4
5	1	-10	217	235	4
5	1	-9	289	308	4
5	1	-8	50	53	6
5	1	-7	62	55	5
5	1	-6	145	144	3
5	1	-5	474	457	3
5	1	-4	144	146	3
5	1	-3	869	823	3
5	1	-2	125	113	3
5	1	-1	569	563	3
5	1	0	170	164	3
5	1	1	53	54	3
5	1	2	139	138	3
5	1	3	123	117	3
5	1	4	265	269	3
5	1	5	389	393	3
5	1	6	252	260	3
5	1	7	552	556	3
5	1	8	40	20	6
5	1	9	439	430	4
5	1	10	57	55	5
5	1	11	98	89	3
5	2	-12	145	148	3
5	2	-10	145	152	3
5	2	-9	273	287	4
5	2	-8	383	407	4
5	2	-7	339	345	4
5	2	-6	295	312	4
5	2	-5	286	291	4
5	2	-4	150	143	3
5	2	-3	280	257	3
5	2	-2	60	53	4
5	2	0	251	255	3
5	2	1	388	407	3
5	2	2	484	488	3
5	2	3	593	581	3
5	2	4	442	435	3
5	2	5	302	301	3
5	2	6	155	164	3
5	2	7	52	43	4
5	2	8	230	233	4
5	2	9	184	171	3
5	2	10	163	152	3
5	2	11	205	198	4
5	2	12	217	201	4
5	3	-12	246	253	4
5	3	-11	212	224	4
5	3	-10	276	302	5
5	3	-9	156	161	3
5	3	-8	141	136	3
5	3	-7	154	150	3
5	3	-6	117	119	3
5	3	-5	154	157	3
5	3	-4	321	323	3
5	3	-2	494	476	3
5	3	-1	164	153	3
5	3	0	287	277	3
5	3	1	243	237	3
5	3	2	78	70	3
5	3	3	83	84	2
5	3	4	228	228	3
5	3	5	254	247	3
5	3	6	455	469	3
5	3	7	165	165	3
5	3	8	374	379	3

Table 3.9. Continued

H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
5	3	9	125	130	3	5	6	-5	224	229	4	5	9	-6	59	53	5	5	12	0	333	339	4
5	3	10	164	168	3	5	6	-4	160	166	3	5	9	-5	218	225	4	5	12	1	41	32	6
5	3	11	106	102	3	5	6	-3	120	119	3	5	9	-4	82	84	4	5	12	2	329	332	4
5	3	12	95	89	4	5	6	-1	151	151	3	5	9	-3	407	419	4	5	12	4	222	225	4
5	4	-10	132	142	3	5	6	0	236	249	3	5	9	-2	123	124	3	5	12	5	70	67	4
5	4	-9	44	43	7	5	6	1	400	404	3	5	9	-1	382	400	4	5	12	6	160	152	3
5	4	-8	296	307	4	5	6	2	478	482	3	5	9	0	215	229	4	5	13	-4	303	285	5
5	4	-6	421	429	4	5	6	3	524	526	3	5	9	1	207	217	4	5	13	-3	146	135	3
5	4	-5	56	45	4	5	6	4	250	244	3	5	9	2	99	98	3	5	13	-2	395	399	4
5	4	-4	384	392	3	5	6	5	269	285	3	5	9	3	51	66	5	5	13	-1	187	180	3
5	4	-3	52	41	4	5	6	8	146	157	3	5	9	4	166	171	3	5	13	0	201	194	3
5	4	-2	54	46	4	5	6	9	146	147	3	5	9	5	167	179	3	5	13	1	120	123	3
5	4	-1	181	176	3	5	6	10	180	184	3	5	9	6	171	177	4	5	13	2	79	77	4
5	4	0	554	551	3	5	6	11	249	251	5	5	9	7	330	341	4	5	13	3	113	111	3
5	4	2	495	487	3	5	7	-11	355	341	5	5	9	8	47	52	5	5	13	4	115	113	3
5	4	3	62	63	3	5	7	-10	174	164	4	5	9	9	268	266	4	5	14	0	191	197	4
5	4	4	370	365	3	5	7	-9	279	276	5	5	10	-9	185	176	4	6	0	-10	291	331	5
5	4	5	98	101	2	5	7	-6	176	179	4	5	10	-8	316	304	5	6	0	-8	293	315	4
5	4	6	183	187	4	5	7	-5	281	293	4	5	10	-7	264	261	4	6	0	-6	167	174	3
5	4	7	79	83	3	5	7	-4	241	249	4	5	10	-6	277	273	5	6	0	-4	330	318	4
5	4	8	243	244	4	5	7	-3	560	576	3	5	10	-5	169	167	3	6	0	-2	582	570	3
5	4	10	430	438	4	5	7	-2	61	53	4	5	10	-4	46	48	6	6	0	0	359	377	3
5	4	11	74	84	4	5	7	-1	553	579	3	5	10	-2	60	63	5	6	0	2	249	278	3
5	5	-12	240	235	4	5	7	0	136	129	2	5	10	-1	61	56	4	6	0	6	263	265	4
5	5	-11	192	196	4	5	7	1	288	295	3	5	10	0	144	143	3	6	0	8	363	347	4
5	5	-10	226	228	4	5	7	3	111	110	2	5	10	1	295	304	4	6	0	10	303	279	5
5	5	-9	126	125	3	5	7	4	237	245	3	5	10	2	394	405	4	6	1	-9	92	103	4
5	5	-8	160	157	3	5	7	5	384	398	3	5	10	3	279	287	4	6	1	-8	135	146	3
5	5	-7	83	80	4	5	7	6	160	167	3	5	10	4	281	285	4	6	1	-7	210	210	4
5	5	-6	113	108	3	5	7	7	380	412	3	5	10	5	91	94	3	6	1	-6	356	362	4
5	5	-5	136	133	3	5	7	8	72	78	4	5	10	8	114	115	3	6	1	-5	119	122	3
5	5	-4	402	405	3	5	7	9	257	253	4	5	11	-8	101	103	4	6	1	-4	447	445	4
5	5	-3	238	239	4	5	7	10	87	82	3	5	11	-7	48	53	7	6	1	-3	61	62	4
5	5	-2	510	513	3	5	8	-9	226	218	4	5	11	-6	101	94	4	6	1	-2	164	161	4
5	5	-1	322	343	3	5	8	-7	416	437	4	5	11	-4	330	329	4	6	1	0	166	166	3
5	5	0	288	287	3	5	8	-5	480	496	4	5	11	-3	72	65	4	6	1	1	90	92	2
5	5	1	224	238	3	5	8	-3	99	97	3	5	11	-2	332	331	4	6	1	2	346	382	3
5	5	2	100	98	2	5	8	-1	324	337	4	5	11	-1	94	87	3	6	1	3	246	263	3
5	5	4	205	204	4	5	8	0	111	110	3	5	11	0	273	285	4	6	1	4	472	483	3
5	5	5	280	289	3	5	8	1	504	530	3	5	11	1	195	198	4	6	1	5	158	158	3
5	5	6	368	382	3	5	8	2	41	19	5	5	11	2	68	66	4	6	1	6	272	268	3
5	5	7	221	234	4	5	8	3	414	419	3	5	11	4	231	234	4	6	1	7	48	63	5
5	5	8	451	466	3	5	8	5	255	261	4	5	11	5	102	103	3	6	1	8	78	72	3
5	5	9	109	114	3	5	8	7	51	51	5	5	11	6	291	299	4	6	1	10	139	132	3
5	5	10	132	132	2	5	8	8	48	46	5	5	11	7	56	49	4	6	2	-10	308	323	5
5	6	-10	95	88	4	5	8	9	240	245	4	5	12	-6	330	309	5	6	2	-9	249	267	5
5	6	-9	292	292	5	5	8	10	65	59	4	5	12	-5	83	82	4	6	2	-8	222	230	4
5	6	-8	244	235	4	5	9	-9	190	195	4	5	12	-4	228	219	4	6	2	-7	95	91	4
5	6	-7	356	361	4	5	9	-8	80	87	4	5	12	-2	104	109	3	6	2	-5	77	78	4
5	6	-6	313	319	4	5	9	-7	96	97	4	5	12	-1	43	41	6	6	2	-4	84	87	4

Table 3.9. Continued

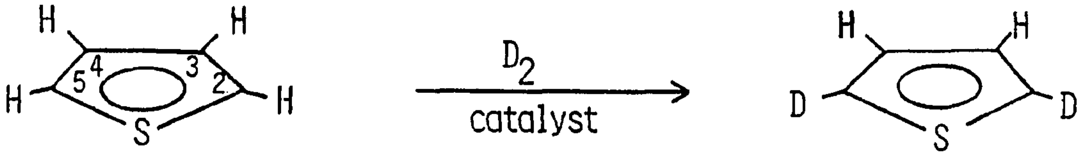
H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF	H	K	L	Fobs	Fcalc	SigF
6	2	-3	182	192	4	6	5	-8	185	186	4	6	8	-4	201	204	4	7	2	-3	191	192	4
6	2	-2	224	227	4	6	5	-7	277	278	5	6	8	-3	69	66	4	7	2	-2	263	254	4
6	2	-1	257	258	4	6	5	-6	139	137	3	6	8	-2	401	410	4	7	2	-1	194	193	4
6	2	0	375	384	3	6	5	-5	463	465	4	6	8	0	330	339	4	7	2	0	90	95	3
6	2	1	280	289	3	6	5	-4	111	110	3	6	8	2	175	168	4	7	2	2	182	192	3
6	2	2	250	264	3	6	5	-3	278	281	4	6	8	6	226	231	4	7	2	3	211	226	4
6	2	3	159	162	3	6	5	-2	194	194	3	6	9	-6	329	329	5	7	2	4	277	277	4
6	2	4	54	36	4	6	5	-1	108	100	3	6	9	-5	151	153	3	7	2	5	212	208	3
6	2	5	242	239	3	6	5	0	67	75	4	6	9	-4	353	349	4	7	2	6	156	153	3
6	2	6	204	200	4	6	5	1	373	382	3	6	9	-3	77	79	4	7	3	-6	217	211	4
6	2	7	255	255	4	6	5	2	191	179	3	6	9	-2	59	51	4	7	3	-4	62	44	5
6	2	8	199	202	3	6	5	3	384	384	3	6	9	0	123	123	3	7	3	-2	212	206	4
6	2	9	191	185	4	6	5	4	259	260	4	6	9	1	77	73	3	7	3	-1	105	100	3
6	3	-10	53	56	6	6	5	5	302	303	4	6	9	2	155	155	3	7	3	0	363	371	4
6	3	-9	81	81	4	6	5	6	62	65	4	6	9	3	174	167	4	7	3	1	217	209	4
6	3	-8	145	152	3	6	5	7	174	175	3	6	9	4	189	192	4	7	3	2	311	318	4
6	3	-7	337	345	4	6	5	9	117	118	3	6	9	5	114	110	3	7	3	3	47	40	5
6	3	-6	88	89	4	6	6	-9	216	205	4	6	9	6	248	249	5	7	3	4	105	98	3
6	3	-5	446	458	4	6	6	-8	195	189	4	6	10	-5	69	62	5	7	3	5	57	57	4
6	3	-4	45	37	6	6	6	-7	50	52	6	6	10	-3	142	148	3	7	4	-6	285	279	5
6	3	-3	260	260	4	6	6	-6	71	65	5	6	10	-2	118	124	3	7	4	-5	49	38	7
6	3	-2	173	167	3	6	6	-5	89	93	4	6	10	-1	248	252	4	7	4	-4	446	432	4
6	3	-1	114	114	2	6	6	-4	98	94	3	6	10	0	200	191	4	7	4	-2	270	263	4
6	3	1	295	303	3	6	6	-3	204	212	4	6	10	1	252	257	4	7	4	0	43	7	5
6	3	2	277	283	3	6	6	-2	282	289	4	6	10	2	143	139	2	7	4	2	156	169	3
6	3	3	424	433	3	6	6	-1	319	321	4	6	10	3	62	54	4	7	4	4	283	280	4
6	3	4	210	207	4	6	6	0	472	482	3	6	11	-3	224	207	4	7	4	5	76	66	4
6	3	5	367	372	3	6	6	1	292	285	4	6	11	-2	58	53	5	7	5	-2	294	281	4
6	3	6	62	59	4	6	6	2	260	265	4	6	11	-1	52	42	6	7	5	-1	124	120	3
6	3	7	118	114	3	6	6	4	162	161	3	6	11	1	220	208	4	7	5	0	327	329	4
6	3	8	39	38	6	6	6	5	161	157	3	6	11	2	98	91	3	7	5	1	254	237	4
6	3	9	105	110	3	6	6	6	305	303	4	7	0	-7	96	90	4	7	5	2	271	266	4
6	4	-9	243	249	4	6	6	7	246	249	4	7	0	-5	359	367	4	7	5	3	111	112	3
6	4	-8	43	39	7	6	6	8	213	214	4	7	0	-3	397	384	4	7	5	4	133	127	3
6	4	-7	271	273	5	6	7	-8	244	229	4	7	0	-1	102	99	3	7	6	-4	234	224	4
6	4	-5	47	24	6	6	7	-7	126	132	3	7	0	3	171	191	3	7	6	-3	152	149	3
6	4	-4	61	47	5	6	7	-6	376	370	4	7	0	5	363	361	4	7	6	-2	190	179	3
6	4	-3	409	410	4	6	7	-4	342	350	4	7	1	-7	239	240	4	7	6	-1	168	169	3
6	4	-2	94	89	3	6	7	-3	66	61	4	7	1	-5	68	56	4	7	6	0	74	65	4
6	4	-1	463	474	3	6	7	-2	181	190	4	7	1	-4	67	55	4	7	6	1	54	40	5
6	4	0	41	39	5	6	7	-1	77	71	4	7	1	-3	249	241	5	7	6	2	84	87	4
6	4	1	302	296	3	6	7	0	110	105	3	7	1	-1	362	354	4	7	6	3	280	260	4
6	4	2	57	57	4	6	7	1	136	140	2	7	1	0	196	191	3	7	7	-3	134	119	3
6	4	3	119	115	2	6	7	2	295	304	4	7	1	1	300	313	4	7	7	-2	62	58	5
6	4	4	45	48	5	6	7	3	212	224	4	7	1	2	169	183	3	7	7	-1	278	275	5
6	4	5	133	126	2	6	7	4	320	320	4	7	1	3	216	229	4	7	7	0	175	157	3
6	4	6	85	84	3	6	7	5	126	116	2	7	1	6	72	66	4	7	7	1	322	314	4
6	4	7	388	392	4	6	7	6	216	226	4	7	2	-6	183	178	3	7	7	2	174	159	4
6	4	9	413	416	4	6	8	-7	118	108	3	7	2	-5	170	180	4						
6	5	-9	75	73	5	6	8	-6	160	144	3	7	2	-4	195	193	3						

SECTION IV. DEUTERIUM EXCHANGE OF BENZO[b]THIOPHENE: MODEL COMPLEX AND HETEROGENEOUS REACTOR STUDIES[1]

INTRODUCTION

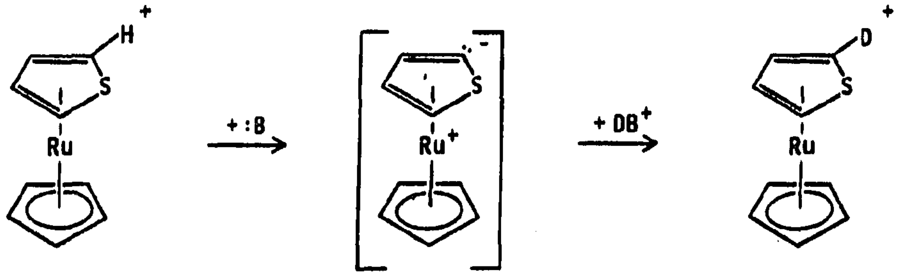
The industrial importance of the process of catalytic hydrodesulfurization (HDS), generally accomplished using a cobalt-promoted molybdenum catalyst and resulting in the removal of sulfur from organosulfur compounds found in crude oils and coal liquids,[2] is widely recognized.[3] Because of the extensive application of HDS, numerous investigations aimed at obtaining a better understanding of the process have been undertaken.[4] However, the mode of coordination of the sulfur compounds to the catalyst surface as well as key steps of the desulfurization are still not well understood.

Since the study of deuterium exchange reactions provides an opportunity for learning about the nature and reactivity of adsorbed intermediates on catalyst surfaces,[5] several deuterium exchange investigations of representative sulfur-containing compounds over HDS catalysts have been reported.[6] The compound usually chosen is thiophene (T)[6,7] which is the simplest member of the largest class of organosulfur compounds found in crude oils.[8] The exchange occurs most readily in the 2 and 5 positions, as shown in eq. 1, with lesser amounts of exchange



(1)

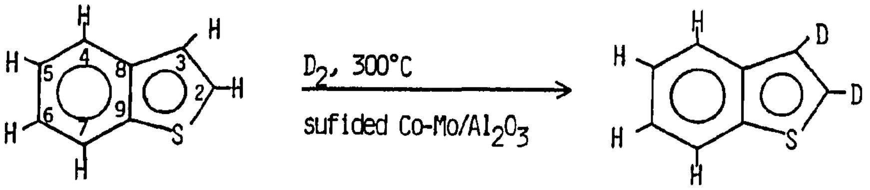
occurring in the 3 and 4 positions. The exchange of methyl derivatives of T has also been investigated.[7b,e] The results of these studies have been interpreted as supporting various adsorption modes, reaction pathways and types of catalytic sites present on the surface. Recently, the rates of deuterium exchange in the π-thiophene ligands of $[CpRuL]^+$ (L = T, 2-MeT, 3-MeT, 2,3-Me_2T), as models of π-adsorbed thiophenes on HDS catalysts, have been reported.[9] The rate-determining step of the exchange reaction, shown for the T complex in eq. 2, was proposed to be H^+ abstraction from T



(2)

by OH^-. The deuterated compound is then produced by D^+ transfer from the CD_3OD solvent.[9a] The rates of exchange for the different hydrogens in the complexes ($H_{2,5} > H_{3,4} > CH_3$) follows the same order as the relative amounts of deuterium exchanged into these positions over HDS catalysts. These results provide strong support for the proposal that π-adsorbed thiophenes (Ts) are intermediates in the deuterium exchange of Ts on catalyst surfaces.

Although the mechanism of T HDS has been intensively investigated, it has been suggested that benzo[b]thiophene (BT) and its derivatives would actually provide better models for studies of the HDS process.[10] In addition to their being more difficult to desulfurize than T they are usually the predominant type of thiophenic compound found in crude oils and coal liquids.[11,12] A number of reports of BT HDS reactor studies have appeared[4,8,12,13] but only one addresses the deuterium exchange reaction of BT.[7c] Cowley interpreted ^1H and ^2H NMR spectra as well as mass spectral fragmentation data of the deuterated BT to indicate that BT undergoes preferential exchange at the 2 and 3 positions of BT as shown in eq. 3. He concluded that this result supported π-coordination of the thiophene ring of BT to the catalyst surface because a one-point sulfur coordination mode would give rise to exchange at the 2 and 7 positions. Flat, π-coordination of BT to HDS catalysts has been proposed by others.[13a,14]



(3)

Our approach to the elucidation of BT adsorption modes and HDS reaction pathways includes studying the reactivity of π-bound BTs in transition metal model complexes.[15] In this publication, the base catalyzed deuterium exchange reaction of [CpRu(BT)]PF_6, 1, and [CpRu(3-MeBT)]PF_6, 2, are reported. Because Cowley's experiments were conducted using a 60 MHz NMR instrument, which was not capable of resolving either the H4 and H7 or the H2, H3, H5, and H6 resonances of BT, we also reexamined the exchange reactions of BT over HDS catalysts. By using a 300 MHz NMR instrument, all of the resonances of BT except H5 and H6 are resolved (Figure 4.1) and, therefore, the positions at which exchange

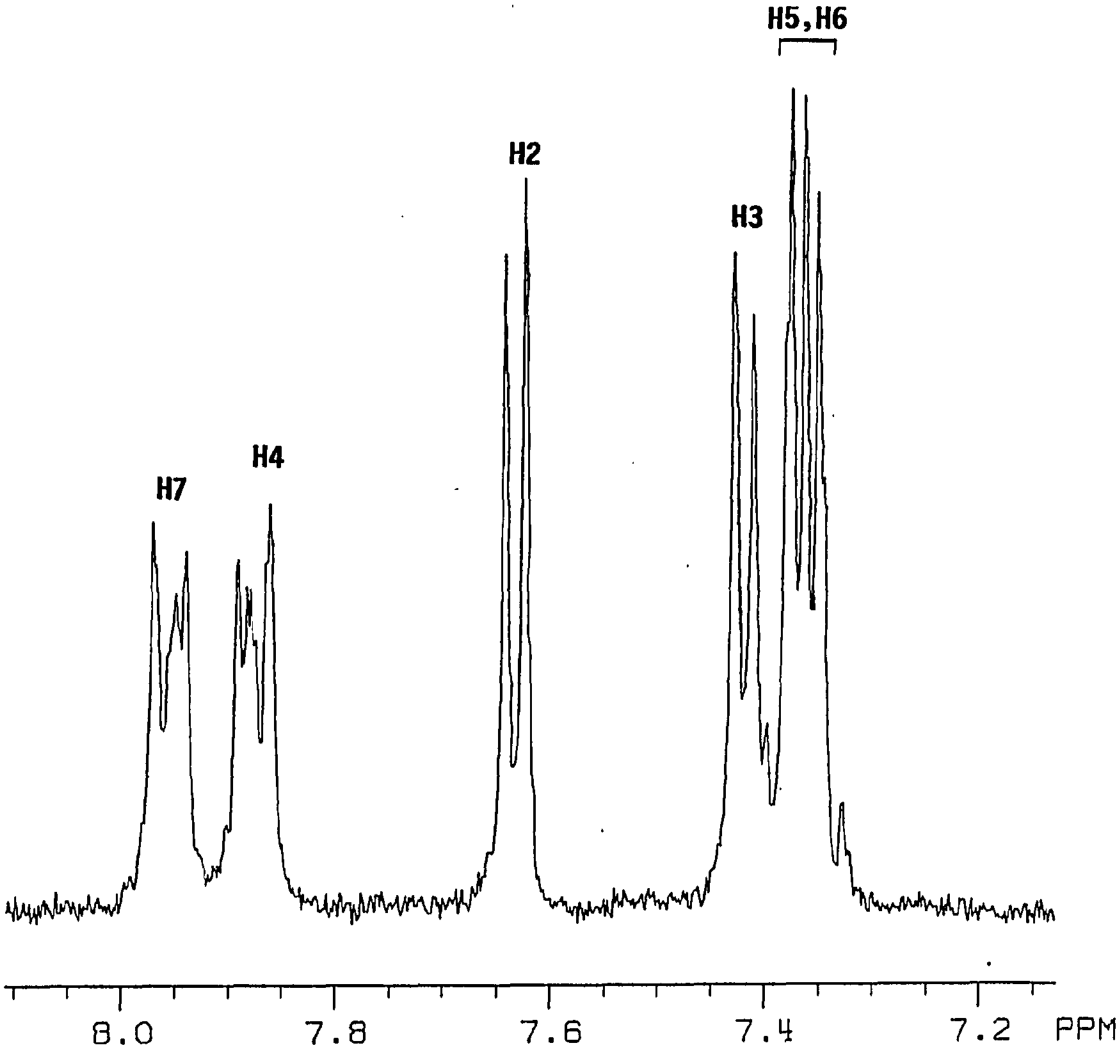


Figure 4.1. 300 MHz ^1H NMR spectrum of BT in d_6-acetone

occurs can be clearly established. The results of studies which employed a variety of catalysts ($PbMo_{6.2}S_8$, 1% Pt-10% Re/γ-Al_2O_3, $Co_{0.25}MoS$, and 5% Re/γ-Al_2O_3) as well as γ-Al_2O_3 are presented.

EXPERIMENTAL

General procedures The compounds [CpRu(BT)]PF_6[15], 1, [CpRu(3-MeBT)]PF_6[15], **2**, and [CpRu(η-C_6H_6)]PF_6[16] were prepared by literature methods. The CD_3OD (99.5%) was purchased from Cambridge Isotope Laboratories and stored over 4-Å molecular sieves under N_2. The BT and 0.5 N KOH/CH_3OH solution were purchased from Aldrich. The ^1H NMR spectra were obtained on a Nicolet NT-300 spectrometer using deuterated solvents as internal locks and the ^2H NMR spectra were obtained on a WM-300 spectrometer using acetone as an internal lock.

Preparation of samples, data collection, and analysis of the kinetic data The 0.10-1.1 M concentrations of KOH/CD_3OD solutions were obtained as follows. The required amount of the standard KOH/CH_3OH solution was measured using a 1.00 mL syringe and added to a 5 mm NMR tube which was then capped with a rubber septum. The CH_3OH solvent was removed in vacuo. Then, 0.30 mL of CD_3OD was added to the NMR tube which was recapped and shaken to dissolve the KOH. At this point either 1 (0.0046 g, 1.0×10^{-5} mol, 0.033 M) or 2 (0.0048 g, 1.0×10^{-5} mol, 0.033 M) was added to the NMR tube. The septum was then sealed with Parafilm.

The samples were thermostatted at 23.8°C in a constant temperature water bath. The exchange process was followed by removing the tubes from the bath at appropriate times, taking their ^1H NMR spectra, and returning the tubes to the bath. Peaks of the desired protons in the BT ligand were integrated against either the Cp, Me or H4 peaks, none of which underwent significant exchange under these conditions. This was verified by addition of 0.1 μL of an internal integration standard, t-BuOH, to the 0.20 M [KOH] runs with **1** and **2**. The data were collected until 55-70% exchange of the proton of interest had occurred. The timescale of these experiments ranged from 1 h (1.1 M [KOH]; **1**, H2) to 43 h (0.20 M [KOH]; 2, H7).

The 0.0 M [KOH] run for **1** was performed by adding **1** (0.0046 g, 1.0 x 10^{-5} mol, 0.033 M) to an NMR tube containing 0.30 mL of CD_3OD (0.30 mL). Without any KOH present, the polarity of the solution was too low to completely dissolve the compound. Integrals of H2 and H7 were monitored over a period of 143 h at 23.8°C. No exchange occurred. A similar experiment with **2** (0.0047 g, 1.0 x 10^{-5} mol, 0.033 M) showed that no exchange occurred over 90 h.

In order to determine whether uncoordinated BT undergoes base-catalyzed exchange under the conditions of these studies, the following experiment was performed. To 0.30 mL of a 1.1 M KOH/CD_3OD solution was added BT (approximately 0.005 g, 4 x 10^{-5} mole, 0.1 M), and the mixture was thermostatted at 23.8°C. The integrals of H2 and H7 were monitored for 88 h during which time no exchange occurred. The exchange reaction for $[CpRu(\eta\text{-}C_6H_6)]PF_6$ was also performed. To 0.30 mL of a 1.1 M KOH/CD_3OD solution was added $[CpRu(\eta\text{-}C_6H_6)]PF_6$ (0.0051 g, 1.3 x 10^{-5} mol, 0.044 M). The NMR tube was thermostatted at 23.8°C, and the integral of the benzene peak was monitored over a period of 116 h. No exchange occurred.

The observed rate constants, k_{obs}, were obtained from least squares analyses of plots of $\ln I_{HX}$ versus time (I_{HX} is the integral of proton X, X = 2 or 7; k_{obs} = -slope) and are presented in Table 4.1. The correlation coefficients for these plots averaged 0.98; the error in these values is primarily a result of the ±5% error in the integration of the H2 and H7 resonances in ^{1}H NMR spectra of the exchange reactions. The second order rate constants, k_{HX} (X = 2 or 7), in Figure 4.2, were obtained from least squares analyses of plots of $k_{obs,HX}$ versus [KOH]. The errors in the calculated values of k_{HX} are a result of errors in $k_{obs,HX}$ and in [KOH] due to small amounts of CH_3OH not being removed in vacuo from the standard KOH/CH_3OH solution.

Catalyst synthesis The lead Chevrel phase catalyst, $PbMo_{6.2}S_8$, was prepared from stoichiometric amounts of 200 mesh, powdered molybdenum metal (reduced at 1000°C in hydrogen for 18 h), lead sulfide, and powdered sulfur. The mixture was ground together thoroughly, pressed into 13 mm pellets, and then sealed in evacuated fused-silica tubes. The tubes were heated to 1200°C for 24 to 48 hours.

The unsupported $Co_{0.25}MoS$ catalyst was synthesized by preparing material with a molar cobalt to molybdenum ratio of 1:4, using the homogeneous precipitation technique,[17] followed by pretreatment at 450°C in 2% H_2S/H_2 for 4 h.

The supported rhenium catalyst was prepared by aqueous impregnation of Re_2O_7 into a calcined γ-Al_2O_3 support (Armak 03-331, 175 m^2/g) to give a 5% loading of Re by weight. The detailed procedure has been previously described.[18] The catalyst was sulfided in situ by flowing 2 mole % BT/H_2 at the reaction temperature for approximately 5 h.

The supported 1% Pt-10% Re/γ-Al_2O_3 catalyst was prepared by impregnation of a calcined γ-Al_2O_3 support (Armak 03-331) with an aqueous solution of Re_2O_7 to produce a 5 weight % loading of Re. A 10 weight % Re loading was achieved by consecutive drying and impregnation steps. The 1% Pt was added using an aqueous solution of chloroplatinic acid. After final drying, the catalyst was reduced by heating slowly in a stream of H_2 from room temperature to 500°C. Sulfiding was performed <u>in situ</u> in the same manner as for the 5% $Re/\gamma\text{-}Al_2O_3$ catalyst.

Catalyst characterization The purities of the $PbMo_{6.2}S_8$ and the $Co_{0.25}MoS$ catalysts were established by X-ray powder diffraction and laser Raman spectroscopy. A detailed description of the characterization methods and results has been previously given.[19] The catalysts were stable under the reaction conditions; no changes in purity or formation of other phases were noted.

The supported Re catalyst was characterized before and after pretreatment by laser Raman spectroscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, and thermogravimetric analysis.[18] Raman spectra showed that none of the Re_2O_7 starting material was present in the catalyst. Slow heating rates were required (2°C/min) during reduction of the catalyst to prevent the loss of Re. This catalyst was also shown to be very resistant to sulfiding treatments and remained stable under reaction conditions.

Apparatus and procedures The reactor for these studies consisted of a 1/4" stainless steel tube in which the catalyst was held in place with a stainless steel screen. Catalyst loadings were: $PbMo_{6.2}S_8$ (0.336 g), 1% Pt-10% $Re/\gamma\text{-}Al_2O_3$ (0.249 g), $Co_{0.25}MoS$ (0.164 g), 5% Re/γ-

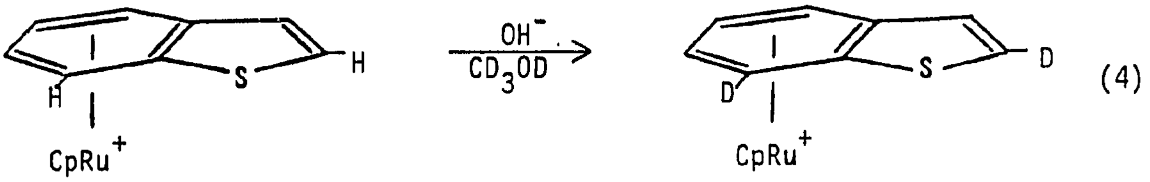
Al_2O_3 (0.199 g). Liquid BT (Aldrich, 97%) was fed to the system by a Sage 341 syringe pump from a 1 mL Hamilton "gas tight" syringe. BT is a solid at room temperature (m.p. 29-32°C), therefore, it was necessary to heat a small chamber surrounding the syringe to 40°C. The BT was pumped into a saturator, which was maintained at 230°C and packed with glass beads, where it was mixed with hydrogen or deuterium and vaporized. All lines downstream of the saturator were wrapped in heating tape and maintained at 235°C. Product analysis was performed using a 3% SP-2100 on a 100-120 mesh Suplecoport column in an Antek 310 gas chromatograph with a Hewlett Packard 3390A digital integrator. High purity helium (99.997%) was used as the carrier gas at 19 mL/min (STP).

The reactor was heated from room temperature to the reaction temperature in a flow of helium (1-2 h) for the $Co_{0.25}MoS$ and $PbMo_{6.2}S_8$ catalysts and in a flow of high-purity H_2 (99.997%) (12 h) for the supported Re catalyst. The He or H_2 was then replaced by a continuous flow of 2 mole % BT in research grade D_2 (99.99%) at 20 ml/min (STP). Reaction temperatures ranging from 250°-500°C were used as shown in Table 4.2. The system was allowed to stabilize at the reaction temperature (0.5-1 h), as evidenced by constant conversion of BT to other compounds (% conversion = 100-[percentage of d_0-d_6 BT in product stream]), before the BT collection began. Experiments were also performed using either the empty reactor or γ-Al_2O_3 (0.143 g) in the reactor. These experiments were undertaken to observe the ability, if any, of the alumina support in the Re and Pt-Re catalysts and of the stainless steel reactor to catalyze deuterium exchange in benzothiophene.

The exchanged BT was collected from the reactor stream in a 7 mm pyrex tube (cooled to 0°C) and was analyzed by mass spectrometry and ^{1}H and ^{2}H NMR. The error in integration of the ^{1}H NMR H2-H7 resonances (Table 4.3) is approximately ±10%.

RESULTS AND DISCUSSION

Base-catalyzed deuterium exchange of BT and 3-MeBT protons in [CpRu(BT)]PF_6, 1, and [CpRu(3-MeBT)]PF_6, 2 The 2 and 7 protons of the BT and 3-MeBT ligands in complexes **1** and **2**, respectively, undergo base-catalyzed exchange with deuterium as shown in eq. 4.



The kinetic data for this exchange reaction conform to the rate law,

$$-\frac{d[RuHX]}{dt} = k_{HX}\ [OH^-][RuHX] = k_{obs,HX}\ [RuHX]$$

where [RuHX] is the concentration of the unexchanged ruthenium complex **1** or **2**. The values calculated for k_{obs} are given in Table 4.1. From plots of $k_{obs,HX}$ versus $[OH^-]$ the second order rate constants, k_{HX}, are obtained. These results are presented in Figure 4.2. Only H2 and H7 are observed to exchange under the conditions of the studies.

The first order dependence of the exchange on $[OH^-]$ suggests that the slow step of the mechanism is proton abstraction from the Ru complex as has been proposed previously for deuterium exchange in T of $[CpRuT]^+$.[9] The mechanism for H2 exchange reaction may be depicted as in eq. 5. The H2 exchanges much more readily than H7 in **1**

Table 4.1. Rate constants, k_{obs}, for the KOH-catalyzed exchange of H2 and H7 in CD_3OD solvent at 23.8°C

[KOH] (M)	$10^5 k_{obs,H2}$ (s^{-1})	$10^5 k_{obs,H7}$ (s^{-1})
	[CpRu(BT)]PF_6, 1	
0.00	0.00	0.00
0.10	6.2	
0.20	6.8	0.61
0.50	11	1.3
0.70	16	1.7
1.1	20	2.2
1.5		3.3
	[CpRu(3-MeBT)]PF_6, 2	
0.00	0.00	0.00
0.20	1.2	0.58
0.50	1.6	0.76
0.70	2.4	1.3
0.90	2.8	1.3
1.1	3.7	1.4
1.3	4.3	1.8
1.5	5.0	2.2

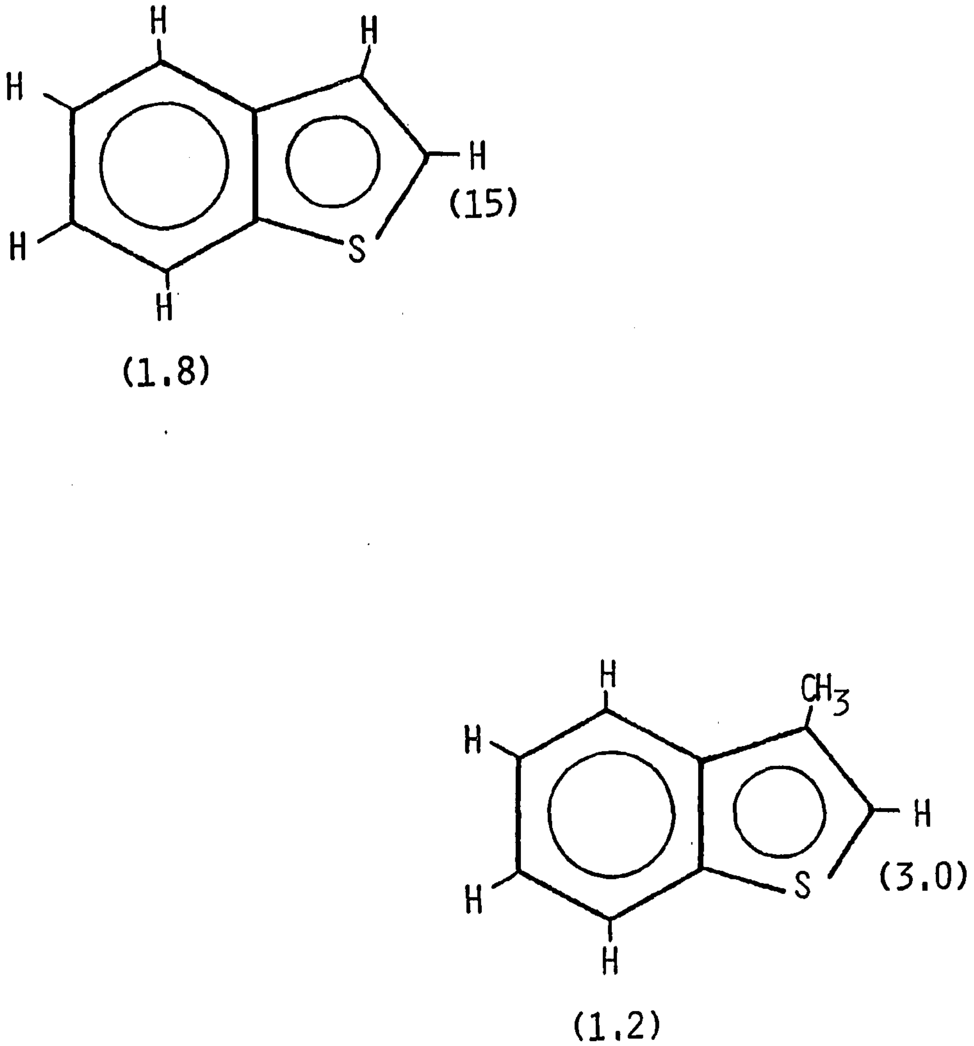
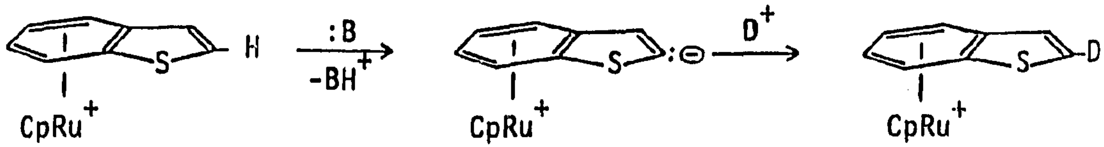


Figure 4.2. Second order rate constants, 10^5 k_{HX} ($M^{-1}s^{-1}$), for the deuterium exchange in the benzothiophene ligands of $[CpRu(BT)]^+$, 1, and $[CpRu(3\text{-}MeBT)]^+$, 2



(5)

(k_{H2} = 15 x 10^{-5} $M^{-1}s^{-1}$, k_{H7} = 1.8 x 10^{-5} $M^{-1}s^{-1}$) but k_{H2} decreases significantly upon substitution of a methyl group in the 3-position (for **2**, k_{H2} = 3.0 x 10^{-5} $M^{-1}s^{-1}$, k_{H7} = 1.2 x 10^{-5} $M^{-1}s^{-1}$). This decrease would be expected on the basis of the proposed mechanism since an electron donating 3-Me group would decrease the acidity of the H2 proton. A similar decrease is observed in the thiophene complexes, where the second order rate constant for H4 exchange in $[CpRu(T)]^+$ is approximately 7 times greater than k_{H4} for $[CpRu(3\text{-}MeT)]^+$.[9a] The H7 rate constant for 1 and 2 is not greatly affected by methyl substitution.

An alternative mechanism, which would proceed via initial attack of OH^- at C3, followed by D^+ addition at C2 and then stepwise loss of H^+ from C2 and OH^- from C3, cannot be ruled out on the basis of the kinetic data assuming that the addition of OH^- is the rate determining step and that all subsequent steps are rapid. However, nucleophilic addition (H^-) to **1** and to the related complex, $[(\eta\text{-}C_5(CH_3)_5)Ir(\eta^6\text{-}BT)](BF_4)_2$ (H^-, OCH_3^-, $SCH_2CH_3^-$, $CH(CO_2CH_3)_2^-$, and $P(CH_3)_3$), is known to occur preferentially at the 7-position[15] and there were no peaks in the ^1H NMR spectra of the exchange reactions which would suggest that OH^- adduct formation had occurred. Therefore, the alternative mechanism seems less reasonable than that presented in eq. 5.

The protons (H2 and H7) exchanged in **1** and **2** are at different positions than those exchanged in the base-catalyzed exchange reaction of uncoordinated BT, which has been reported to occur in the 2- and 3-positions.[20] Zatsepina and coworkers[20b] determined rate constants for deuterium exchange in BT in 0.57 N EtOK/EtOD between 50 and 150°C. The H2 ($k_{obs,\ 80°C} = 9.1 \times 10^{-5}\ s^{-1}$) exchanged faster than H3 ($k_{obs,\ 120°C} = 0.23 \times 10^{-5}\ s^{-1}$) but much slower than H2 in either **1** or **2**. Therefore, H7 and H2 of **1** and **2** are strongly activated to exchange by coordination of BT to Ru. However, H2 is not as strongly activated in **1** and **2** as it is in $[CpRu(T)]^+$ ($k_{H2} > 1.5\ M^{-1}\ s^{-1}$) where the T ring is directly coordinated to the transition metal center. The observed rate constant for H2 exchange in uncoordinated T ($3.3 \times 10^{-5}\ s^{-1}$ at 80°C) is less than that in BT.[20b] It is possible that H3 in **1** is also activated but still does not exchange at a measurable rate under these conditions. The presence of the sulfur atom and the coordination of the benzene ring of BT to $CpRu^+$ both clearly play an important role in activating both H7 and H2 to exchange. No exchange of the benzene ring protons in $[CpRu(\eta\text{-}C_6H_6)]^+$ was observed after 116 h in 1.1 M KOH at 23.8°C.

Deuterium exchange of BT protons over HDS catalysts

The results of the heterogeneous reactor studies are given in Table 4.2. The percent deuteration (±5%) of the BT for each of the runs in Table 4.2 was calculated from the mass spectrum of the product; corrections for the M+1 and M+2 peaks, due to the ^{13}C and ^{34}S isotopes, were made. For all the catalysts studied, the average number of deuterium atoms exchanged into BT, d_{ave}, generally increased with increasing temperature and percent

Table 4.2. Results of deuterium exchange of BT over heterogeneous HDS catalysts

Catalyst	Reactor Temperature (°C)	Conversion (%)
$PbMo_{6.2}S_8$	450	2
$PbMo_{6.2}S_8$	500	6
1% Pt-10% Re/γ-Al_2O_3	300	10
1% Pt-10% Re/γ-Al_2O_3	400	35
$Co_{0.25}MoS$	250	8
$Co_{0.25}MoS$	300	27
$Co_{0.25}MoS$	350	86
5% Re/γ-Al_2O_3	300	1
5% Re/γ-Al_2O_3	350	6
5% Re/γ-Al_2O_3	400	13
γ-Al_2O_3	250	0
γ-Al_2O_3	300	0
γ-Al_2O_3	350	0
none	400	0

[a] The values in parentheses represent the random exchange value calculated from the binomial expansion of $(H+D)^6$ where $D = d_{ave}/6$ and $H = (1-D)$.

% deuteration[a]							
d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_{ave}
21(23)	42(38)	27(27)	7(10)	2(2)	1(0)	0(0)	1.3
14(18)	40(36)	34(30)	9(13)	2(3)	1(0)	0(0)	1.5
0(3)	7(14)	44(28)	30(30)	11(18)	4(6)	4(1)	2.7
1(2)	7(9)	36(23)	28(31)	12(23)	8(10)	8(2)	3.0
3(3)	17(15)	41(29)	15(30)	9(17)	8(5)	7(1)	2.6
2(3)	13(14)	37(28)	25(30)	12(18)	8(6)	3(1)	2.7
3(3)	12(13)	36(28)	24(30)	13(19)	8(6)	4(1)	2.7
4(8)	13(24)	61(32)	17(24)	3(10)	1(2)	1(0)	2.1
1(1)	4(8)	31(22)	30(31)	21(25)	10(11)	3(2)	3.1
2(0)	2(1)	11(4)	11(14)	16(31)	26(34)	32(16)	4.4
43(37)	34(40)	16(18)	4(4)	2(1)	1(0)	0(0)	0.9
16(16)	32(33)	36(31)	10(15)	4(4)	2(1)	0(0)	1.6
5(3)	8(14)	30(28)	30(30)	18(19)	7(5)	2(1)	2.7
97(97)	3(3)	0(0)	0(0)	0(0)	0(0)	0(0)	0.03

conversion for a given catalyst. This was also true of the runs with γ-Al_2O_3. No significant exchange was observed for BT run through the empty reactor at 400°C. The 5% Re/γ-Al_2O_3 catalyst appears to be the most effective at catalyzing deuterium exchange. At 13% conversion (400°C) the d_{ave} = 4.4.

The random exchange values were calculated from the binomial expansion of $(H+D)^6$ where H and D represent the fraction of hydrogen, and deuterium, exchanged in each molecule of BT. Although the γ-Al_2O_3 runs resulted in significant exchange of BT (d_{ave} = 0.91 (250°C), 1.6 (300°C), 2.7 (350°C)) the distribution of d_0-d_6 BT species is clearly random. The ^1H NMR spectra of the BT from the γ-Al_2O_3 experiments show (Table 4.3) that the 2- and 3-positions are preferentially exchanged (the integrals for H4-H7 were all of approximately the same magnitude). The random distribution of d_0-d_6 for γ-Al_2O_3 suggests that this is not due to activation by γ-Al_2O_3 but is simply due to the higher intrinsic reactivity of BT at these positions. Essentially random distribution of the d_0-d_6 BT species is also found for $PbMo_{6.2}S_8$. However, in all of the other runs the d_0-d_6 distribution is non-random and in most cases the greatest deviation occurs in the percentage of d_2-BT found in the exchanged BT. This implies that two of the positions on the BT ring are activated towards exchange by the catalyst. Integrals of the resonances in the ^1H NMR spectra (d_6-acetone, Table 4.3) of the exchanged BT clearly show that these are the 2- and 3-positions for all runs.

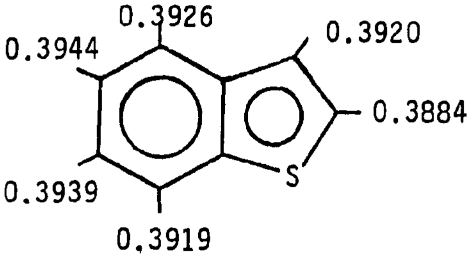
Cowley also reported deuterium exchange of H2 and H3 of BT for experiments performed with D_2 gas over a sulfided Co-Mo/Al_2O_3

Table 4.3. Integrals from ^{1}H NMR spectra of exchanged BT[a]

Catalyst	Temperature (°C)	H2	H3	H4	H5	H6	H7
$PbMo_{6.2}S$	400	58	102	101	187		100
$PbMo_{6.2}S$	450	62	106	100	189		100
$PbMo_{6.2}S$	500	38	91	102	183		100
1%Pt-10% Re/γ-Al_2O_3	300	5	8	88	165		100
$Co_{0.25}MoS$	250	5	28	101	165		100
$Co_{0.25}MoS$	300	10	20	87	198		100
$Co_{0.25}MoS$	350	5	34	112	199		100
5% Re/γ-Al_2O_3	300	10	30	99	183		100
5% Re/γ-Al_2O_3	350	5	14	99	193		100
5% Re/γ-Al_2O_3	400	1	24	102	250		100
γ-Al_2O_3	250	52	82	106	202		100
γ-Al_2O_3	300	31	31	93	184		100
γ-Al_2O_3	350	16	38	93	212		100
none	400	85	107	106	199		100

[a] Integrals are relative to that of the H7 resonance which was set to 100.

thiophene ring of BT on the surface of the catalyst as opposed to S-bound since he proposed that S-bound BT would give rise to H2 and H7 exchange. However, the results reported for the deuterium exchange of 1 and 2 do not support this argument since π-coordination of the benzene ring of BT was shown to result in H2 and H7 exchange. The results of ab initio molecular orbital calculations for BT[21] were cited to help account for the observed selectivity of the exchange reaction. The electron densities of the C-H bonds of BT determined by this calculation are shown below. However, it is interesting to note that although the C-H2 and C-H3 bonds have low electron densities which could result in facile bond cleavage, the C-H7 bond has an even lower electron density than C-H3.



The exchange of BT over the catalyst was proposed, by Cowley, to occur via σ-complex formation as shown in Figure 4.2 for H2 exchange.[7c] The first step of this sequence can be considered analogous to electrophilic attack at C2 by Mo^{3+}. However, BT undergoes electrophilic attack preferentially at C3; this is supported both experimentally[22] and by MO calculations (performed using the Pariser-Parr approach)[23] which give the π-electron densities at C2-C9 (shown below). Furthermore, because of the enhanced resolution available by using a 300 MHz NMR

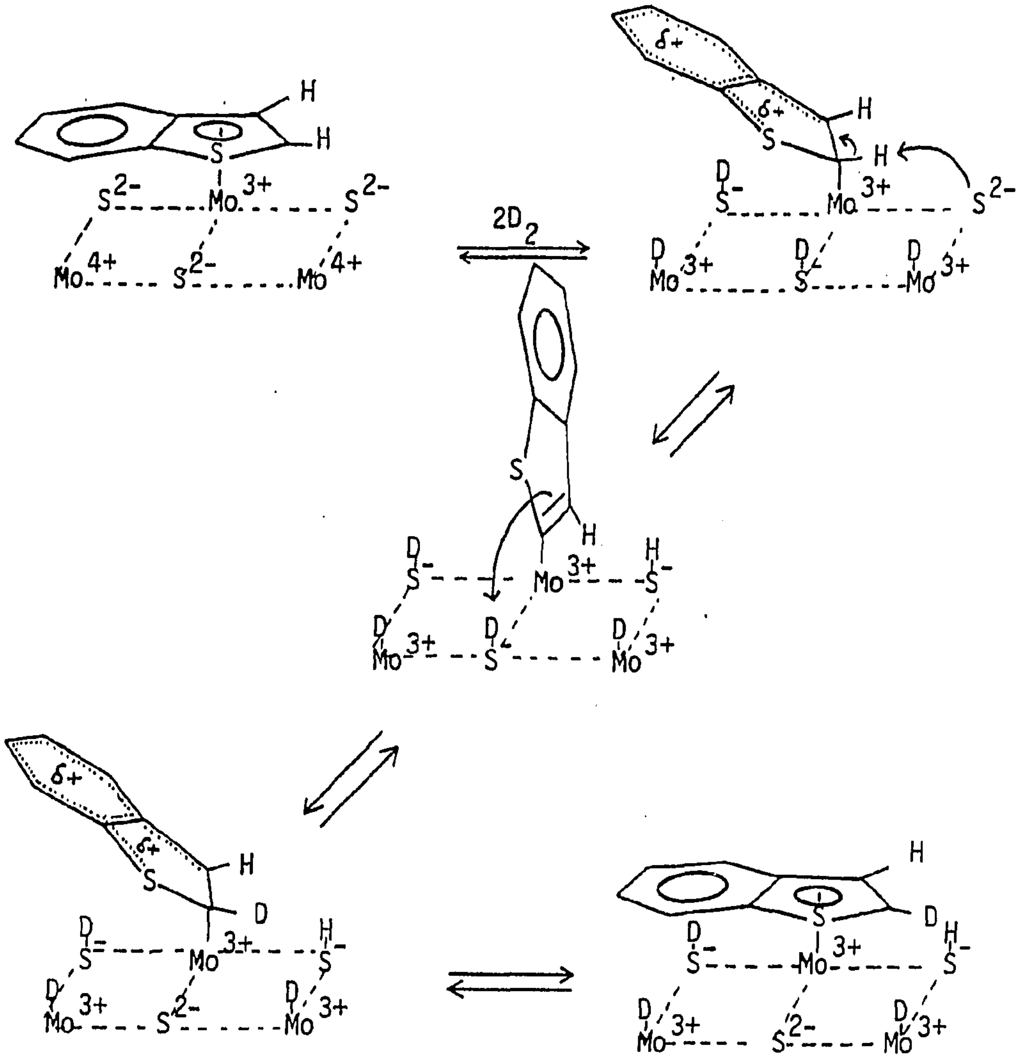
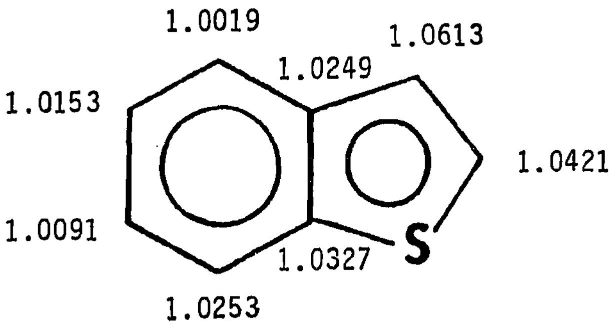


Figure 4.3. Cowley's proposed mechanism for deuterium exchange,[7c] shown for H2



might suggest that H3 would exchange faster than H2. However, it is now possible to show that H2 is more readily exchanged than H3 over HDS catalysts (Table 4.3). This implies that the C-H bond breaking step in the proposed mechanism, which would favor H2 exchange due to the lower electron density of the C-H2 bond, may also play an important role in determining the preferred site of exchange. Alternatively, the exchange could occur by deprotonation of π-coordinated BT, by a basic site such as S^{2-}, without σ-complex formation. The base-catalyzed exchange reactions of T and BT in $CpRu^+$ complexes provide precedent for direct deprotonation of π-bound thiophenic compounds.

In all of the samples, significant percentages of d_3-BT were also produced in addition to d_2-BT. It was of interest to determine if the third deuterium was preferentially exchanged into any of the positions on the benzene ring of BT, particularly in view of the relatively rapid exchange of H7 in $[CpRu(BT)]^+$. However, the resonances of H4-H7 in the deuterated BT integrated to approximately the same values for all of the runs. Therefore, the ^2H NMR spectrum of the deuterated BT from the $Co_{0.25}MoS$ (300°C) experiment was obtained. The integrals of the deuterium resonances were, D2(208), D3(202), D4(60), D5 and D6(100), and D7(40), which clearly illustrate the high degree of 2- and 3- exchange which had occurred as well as the lack of marked preference for exchange at any one of the 4-, 5-, 6- or 7-positions.

CONCLUSIONS

Coordination of either BT or 3-MeBT to $CpRu^+$ activates H2 and H7 towards deuterium exchange. However, over several HDS catalysts, BT is activated to exchange in the 2- and 3-positions and there is no activation of a particular position on the benzene ring to exchange. Thus, based on the different deuterium exchange patterns of BT in $[CpRu(BT)]^+$ and on the HDS catalysts, it is unlikely that BT adsorbs during deuterium exchange via its benzene ring despite the demonstrated preference of Ru, Ir, Rh and Cr to coordinate to the benzene rather than the thiophene ring.[15,24]

π-Coordination of BT through all or part of the thiophene ring cannot be ruled out on the basis of these studies. Since H2 and H3 were preferentially exchanged over the catalysts and H2 was strongly activated to exchange by π-coordination of the benzene ring to $CpRu^+$ in the model complexes, it seems reasonable that coordination of the thiophene ring of BT to the catalyst would activate H3 as well as H2 as occurred for exchange in $[CpRu(T)]^+$.[9a] However, coordination of the extended π-system, involving both the thiophene and benzene rings, is not supported by these results. In the benzene-bound model complexes, **1** and **2**, H7 was activated to exchange relative to H4, H5, and H6 but a similar trend was not observed over the HDS catalysts.

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SUMMARY

The synthesis of model complexes of T and BTs has provided an opportunity to study the preferred coordination modes and reactivities of these ligands. Both T and BTs favor π-coordination to transition metal centers; BTs coordinate in an η^6-fashion via the benzene ring. The T and BTs in these models are activated to nucleophilic addition and base catalyzed deuterium exchange reactions. Nucleophilic addition to η^6-BTs occurs only at the four tertiary carbons of the benzene ring. Because these reactions do not produce BT derivitives which are likely HDS intermediates, it was proposed that better models for BT coordination to catalyst surface would involve thiophene ring coordination to a transition metal center. This view was supported by the results of base catalyzed deuterium exchange experiments using $[CpRu(BT)]^+$ and $[CpRu(3\text{-}MeBT)]^+$ as well as by the results of deuterium exchange of BT over heterogeneous HDS catalysts. The latter results suggest that BT adsorption to catalyst surfaces does not occur through the extended aromatic system but through either a sulfur or π-interaction of the thiophene ring.

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