ไฮโดรดีซัลเฟอไรเซชันของสารประกอบอะโรมาติกซัลเฟอร์ที่เร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนรูทีเนียมไฮไดรด์

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สาขาวิชาเคมี ภาควิชาเคมี

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

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HYDRODESULFURIZATION OF AROMATIC SULFUR COMPOUNDS CATALYZED BY RUTHENIUM HYDRIDE COMPLEXES

Mr. Somsak Angdonka

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By	Mr.Somsak Angdonka
Field of Study	Chemistry
Thesis Advisor	Oravan Sanguanruang, Ph.D
Thesis Co-Advisor	Associate Professor Wimonrat Trakarnpruk, Ph.D

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……………………………………Deputy Dean for Administrative Affairs,
Acting Dean, Faculty of Science
(Associate Professor Pipat Karntiang, Ph.D.)

Thesis Committee

………………………………………… Chairman
(Professor Udom Kokpol, Ph.D.)

…………………………………………. Thesis Advisor
(Oravan Sanguanruang, Ph.D.)

……………………………………… …Thesis Co-advisor
(Associate Professor Wimonrat Trakarnpruk, Ph.D)

………………………………………… Member
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

………………………………………… Member
(Aticha Chaisuwan, Ph.D.)

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สารเชิงซ้อนรูทีเนียมไฮไดรด์ $[C_5Me_5RuH_2]_2$ ถูกเตรียมขึ้นจากปฏิกิริยาของ $[(C_5Me_5)RuCl_2]_2$ กับลิเทียมอะลูมิเนียมไฮไดรด์ ($LiAlH_4$) จากข้อมูลผลการทดลองสามารถสรุปได้ว่าภาวะที่เหมาะสมในปฏิกิริยาไฮโดรดีซัลเฟอไรเซชันของเบนโซไทโอฟีนคือ เวลาของปฏิกิริยา 24 ชั่วโมง อัตราส่วนโมลของเบนโซไทโอฟีนต่อรูทีเนียมเท่ากับ 10 และอุณหภูมิ 110 องศาเซลเซียส ผลิตภัณฑ์จากปฏิกิริยาพิสูจน์เอกลักษณ์ด้วยเทคนิค NMR และ IR สเปกโทรสโกปีข้อมูลนี้สรุปว่าเกิดการกระตุ้นร่วมกันของโลหะในอินเทอร์มีเดียตเร่งปฏิกิริยา นอกจากนั้นผลที่ได้แสดงให้เห็นว่าปฏิกิริยา *in-situ* ให้ผล % การเปลี่ยนรูปของเบนโซไทโอฟีนสูงกว่าวิธีแรก และกรณีของปฏิกิริยาที่มีการเติมแก๊สไฮโดรเจน % การเปลี่ยนรูปของเบนโซไทโอฟีนเพิ่มขึ้น ผลิตภัณฑ์ไฮโดรดีซัลเฟอไรเซชันที่สมบูรณ์คือเอทิลเบนซีนซึ่งพิสูจน์ได้จาก GC-MS

การศึกษาทางจลนศาสตร์และกลไกการเกิดปฏิกิริยาไฮโดรดีซัลเฟอไรเซชันของเบนโซไทโอฟีนโดยใช้ $(PPh_3)_3RuCl_2$ เป็นตัวเร่งปฏิกิริยาในตัวทำละลายทอลูอีน ที่อุณหภูมิ 150 องศาเซลเซียส ทำการทดลองทางจลนศาสตร์โดยการแปรเปลี่ยนความเข้มข้นของคะตาลิสต์ เบนโซไทโอฟีน แก๊ซไฮโดรเจนและที่อุณหภูมิต่างกัน ปฏิกิริยาดำเนินไปตามกฎอัตราเร็ว $r = k_{cat}[Ru][H_2]$ ค่า $\square S^{\square}$ เป็นลบมากซึ่งแสดงถึงการเกิดพันธะที่มากที่สถานะทรานสิชัน ข้อมูลการทดลองสอดคล้องกับกลไกปฏิกิริยาที่อัตราการเกิดการเคลื่อนย้ายของไฮไดรด์ไปบนโคออร์ดิเนทเบนโซไทโอฟีน $[M(H)(Cl)\eta^2\text{-}(C{=}C)\text{-}BT]\text{-}(PPh_3)_2]$ เป็นขั้นกำหนดอัตราเร็ว ไดเบนโซไทโอฟีนและเอทิลเบนซีนเป็นผลิตภัณฑ์จากปฏิกิริยาคะตาไลสิสโดย $(PPh_3)_3RuCl_2$ ที่ 200-250 องศาเซลเซียส และความดันไฮโดรเจน 30 บาร์

สาขาวิชา เคมี ลายมือชื่อนิสิต...

หลักสูตร เคมี ลายมือชื่ออาจารย์ที่ปรึกษา..

ปีการศึกษา 2001 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม..................................

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SOMSAK ANGDONKA: (HYDRODESULFURIZATION OF AROMATIC SULFUR COMPOUNDS CATALYZED BY RUTHENIUM HYDRIDE COMPLEXES. THESIS ADVISOR: ORAVAN SANGUANRUANG, Ph.D., THESIS CO-ADVISOR: ASSOC. PROF. WIMONRAT TRAKARNPRUK, Ph. D., 106 pp. ISBN 947-03-1706-5.

Ruthenium hydride complex ($[C_5Me_5RuH_2]_2$) is prepared by the reaction of $[C_5Me_5RuCl_2]_2$ with $LiAlH_4$. From the experimental data, it can be concluded that the optimum conditions in hydrodesulfurization reaction of benzothiophene was 24 hours reaction time, benzothiophene/Ru mole ratio = 10, temperature at 110 ºC. The reaction product was characterized by NMR and FT-IR spectroscopies. These data show that this reaction may be promoted by the cooperation of metal atom in the catalytic intermediates. Moreover, the result indicated *in-situ* procedure gives higher % conversion of benzothiophene. In the case of the reaction with the addition of hydrogen gas, % conversion of benzothiophene increases. The complete hydrodesulfurization product is ethyl benzene, confirmed by GC-MS.

Kinetic and mechanistic studies of benzothiophene hydrodesulfurization was carried out by using $(PPh_3)_3RuCl_2$ as catalyst in toluene as solvent at 150 ºC. The kinetic runs were carried out at different concentrations of catalyst, benzothiophene, and hydrogen and at different temperatures. The reaction proceeds according to the rate law is $r = k_{cat}[cat][H_2]$. Large negative value of $\Delta S^{\#}$ indicates high degree of bond formation at the transition state. The experimental data are consistent with a mechanism in which the transfer of hydride to coordinated benzothiophene in $[M(H)(Cl)\eta^2\text{-}(C{=}C)\text{-}BT]\text{-}(PPh_3)_2]$ is the rate determining step of the catalytic cycle. Dihydrobenzothiophene and ethylbenzene were obtained as end products of the $(PPh_3)_2RuCl_2$ catalytic reaction at 200-250 °C and hydrogen pressure of 30 bar.

Department Chemistry Student's signature.................................
Field of study Chemistry Advisor's signature.................................
Academic year 2001 Co-Advisor's signature...........................

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LIST OF ABBREVIATIONS

THF	tetrahydrofuran
FID	flame ionization detector
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
s	singlet
d	doublet
t	triplet
m	multiplet
br	broad
FT-IR	Fourier transform infrared spectroscopy
cm^{-1}	unit of wave number
st.	stretching
ml	milliliter (s)
ºC	degree Celcius
δ	chemical shift
$CDCl_3$	deuterochloroform
C_6D_6	benzene-d_6
m/z	mass per charge
^{1}H-NMR	proton nuclear magnetic resonance
^{13}C-NMR	carbon nuclear magnetic resonance
Hz	Hertz
ppm	parts per million

CHAPTER I

INTRODUCTION

1.1 Sulfur compounds in crude oil

The chemical compositions of crude oil are surprisingly uniform even though their physical characteristics vary widely.[1] The elementary composition of crude oil usually falls within the following ranges in Table 1.1.

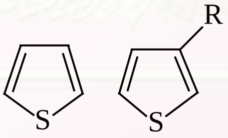
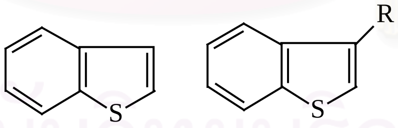
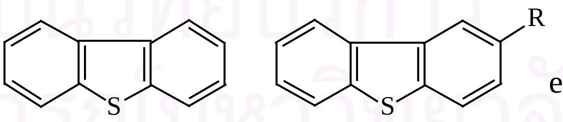
Table 1.1 Elementary composition of crude oil

Element	% By weight
Carbon	84-87
Hydrogen	11-14
Sulfur	0-3
Nitrogen	0-0.6

Sulfur content and API gravity are two properties, which have had the greatest influence on the value of crude oil, although nitrogen and metal contents are increasing in importance. The sulfur content is expressed as percent sulfur by weight and varies from less than 0.1% to greater than 5%. Sulfur is the heteroatom frequently found in crude oil. Sulfur concentration can range from 0.1% to greater than 8% by weight; moreover, this content is correlated with the gravity of the crude oil and, therefore, its quality (light or heavy oil).

The sulfur compounds found in petroleum or synthetic oils are generally classified into one of two types: heterocycles and nonheterocycles. The latter comprises thiols, sulfides and disulfides. Heterocycles are mainly composed of thiophenes with one to several rings and their alkyl or aryl substituents. Examples of sulfur compounds are shown in Table 1.2; only heterocycles are found in coal-derived liquids. The compound classes are listed apporoximately in order of decreasing reactivity in hydrodesulfurization: thiols are very reactive, and compounds in the class of thiophenes are much less reactive.

Table 1.2 Examples of the sulfur compounds found in petroleum

Compound class	Structure
Thiols (mercaptane)	RSH
Disulfides	RSSR'
Sulfides	RSR'
Thiophene	 etc.
Benzothiophene	 etc.
Dibenzothiophene	 etc.

International regulations on emission control will soon require reducing the sulfur content in fuels and distillates to less than 300 ppm.[2] Under this incentive, intense research efforts are currently being directed to the development of more efficient or alternative routes to improve gasoline quality by reducing the content of sulfur without making significant changes in octane rating. Major source of aromatic sulfur compounds in gasoline are coking and cracking naphtha. In the latter, the content of sulfur may be as high as 1300 ppm with a 2:1 predominance of benzothiophenes over thiophene. This characteristic of fuels such as these increases the difficulty of their purification, as benzothiophenes are more refractory to hydrodesulfurization than thiophenes, and motivates the increasing interest in the chemistry of benzothiophene.

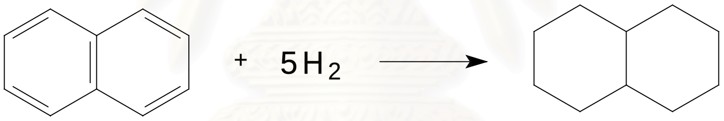
Hydrodesulfurization is catalytic hydrogenation process which removes sulfur in petroleum and primarily constitute hydroprocessing or hydrotreating. In the 1960’s, the process of hydrodesulfurization was developed remarkably to remove high concentration of sulfur in fuels. In recent years, the air pollution by particulate matters included in diesel exhaust gas in large city area has become a serious problem. It is important to reduce the sulfur content in light gas oil. The problem has been caused by the rapid increase in petroleum product demand throughout the world, especially the Asia-Pacific area. The demand for petroleum in this area up to the early part of the 21st century is increasing approximately parallel to the increase in the demand worldwide. Although demand for fuel oil will hardly change early in the 21st century. The sulfur content of distillate in Japan was also regulated to 0.05 wt% in 1997. In 0.05 wt% of sulfur content most products must be hydrotreated, thus the hydrotreating process plays a very important role under such regulations.

The sulfur compounds that occur in light petroleum distillate are usually degradation products formed from higher molecular weight materials during distillation or cracking. The removal of these various classes of sulfur compounds presents a series of individual problem. The elementary sulfur in light distillate may be a product of oxidation (air) or treating of hydrogen disulfide. If the distillate is heated, most of the sulfur appears as hydrogen sulfide and is removed in the stabilizing tower of the fractioning system. The remaining traces are easily removed by washing with aqueous alkali. The sulfur compounds and elemental sulfur in petroleum oils, as well as their thermal decomposition products, are probably responsible for heavy corrosion losses in refinery equipment.

1.2 Hydrodesulfurization reaction

Two reactions which occurred in hydrodesulfurization process are:

(I) hydrogenation of unsaturated compounds that occurs during hydrodesulfurization, and the reaction rates are significant compared with those of hydrodesulfurization ;



(II) hydrogenolysis which results in cleavage of a C-S bond;

$$R\text{-}SH + H_2 \longrightarrow RH + H_2S \qquad (1)$$

Under industrial reaction conditions, hydrogenolysis reaction resulting in breaking of C-C bonds also occurs, e.g., the hydrocracking reaction.

The hydrodesulfurization reactions are virtually irreversible at temperatures and pressures ordinarily applied, roughly 300 to 450^{o}C and up to 200 atm. The reactions are exothermic with heats of reaction of the order of 10 to 20 kcal/mol of hydrogen consumed.

Coking reactions occur as well in hydrodesulfurization. Coke not only poisons catalyst surfaces but also contributes to blocking of catalyst pores and fixed-bed interstices.

1.2.1 Hydrogenation reaction

The development of efficient catalysts for the plain hydrogenation of thiophenes remains an important goal in hydrodesulfurization chemistry.[3-4] A real example of catalytic hydrogenation of thiophene to tetrahydrothiophene has not been reported.[5] However, a case is known in which there is catalytic product of tetrahydrothiophene. The starting complex used in the hydrogenation of thiophene is the Ir^{III} dihydride $[IrH_2(\sigma\text{-}SC_4H_4)_2(PPh_3)_2$, readily obtainable by treatment of $[IrH_2(cod)(PPh_3)_2]PF_6$ with H_2 in the presence of excess thiophene. The dihydride complex reacts with thiophene under stream of H_2 converting to the bis(tetrahydrothiophene) dihydride complex.

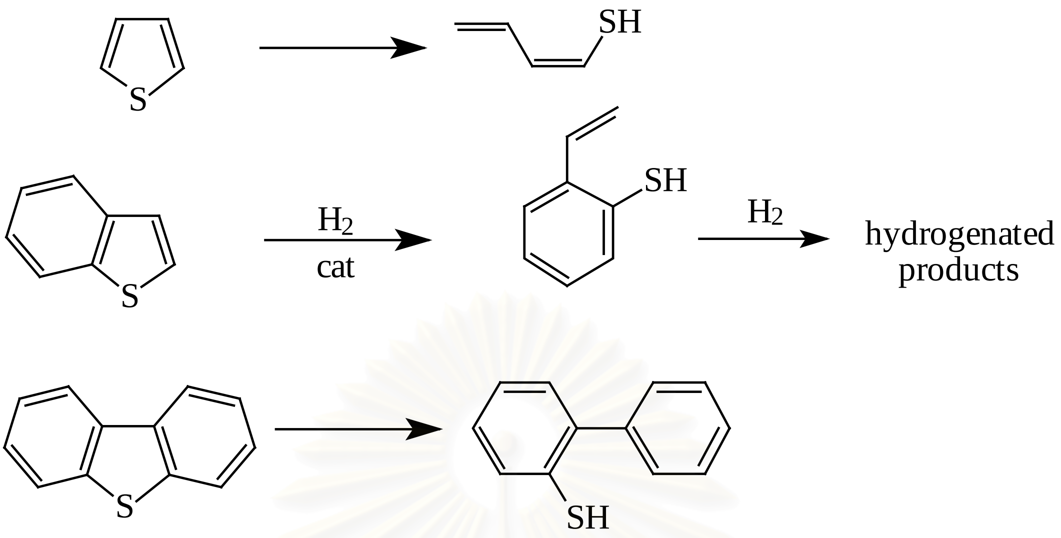
Benzothiophene is a particularly interesting substrate since it represents one of the most abundant and refractory compounds in heavy oils. It is believed that hydrodesulfurization of benzothiophene over solid catalysts involves the selective hydrogenation to 2,3-dihydrobenzothiophene prior to desulfurization to give ethyl benzene. Indeed, some studies of homogeneous hydrogenation of benzothiophene to 2,3-dihydrobenzothiophene have recently been reported. The regioselective hydrogenation of benzo[b]thiophene to dihydrobenzothiophene in homogeneous phase has primarily been reported by Fish et al. in 1984.[6] Since then a variety of soluble transition metal complexes has been described to catalyse this reaction[7], these include $[RhCl(PPh_3)_3]$, $[(Rh(cod)(PPh_3)_2]PF_6$ (cod = cycloocta-1,5-diene), $[(Ir(cod)(PPh_3)_2]PF_6[$, $[OsH(Cl)(CO)(PPh_3)_3]$, $[Rh(Cp^*)(MeCN)_3][BF_4]_2$ (Cp* = pentamethyl-cyclopentadienyl).

Frediani et al.[8] studied the activity of mononuclear and polynuclear ruthenium complexes in the hydrodesulfurization of benzothiophene. The best performance was provided by $H_4Ru_4(CO)_8(PPh_3)_4$ when working at 170 ^oC. Under these conditions benzothiophene is hydrogenated to 2,3-dihydrobenzothiophene with a conversion of 38.2% after 96 h or 81.2% after 384 h. Ethyl benzene (conversion 4.9%) is also formed confirming that a complete hydrodesulfurization of the substrate may be obtained.

Bianchini et al.[9] showed that ruthenium (II) tris-acetonitrile complex [(triphos) $Ru(MeCN)_3]BPh_4$ is an extremely efficient catalyst precursor for the regioselective hydrogenation of benzothiophene to 2,3-dihydrobenzothiophene in homogeneous phase under mild reaction (THF, 40-100 ^oC, 1-30 bar H_2) [triphos = $MeC(CH_2PPh_2)_3$].

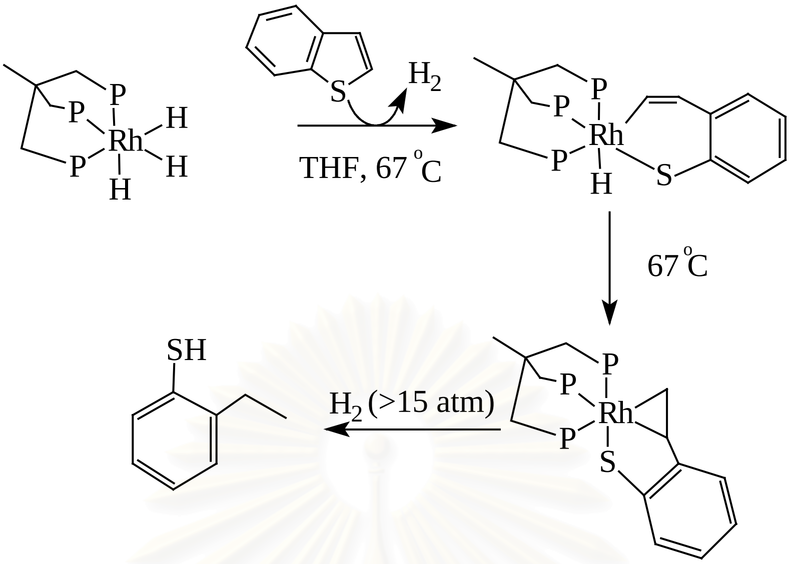
1.2.2 Hydrogenolysis reaction

For hydrogenolysis reactions, it means those metal-mediated transformation of thiophenic molecules that result in the opening ring and hydrogenation of the substrates to give the corresponding unsaturated thiols (Scheme 1.1).[10]



Scheme 1.1 Hydrogenolysis of thiophenic molecules.

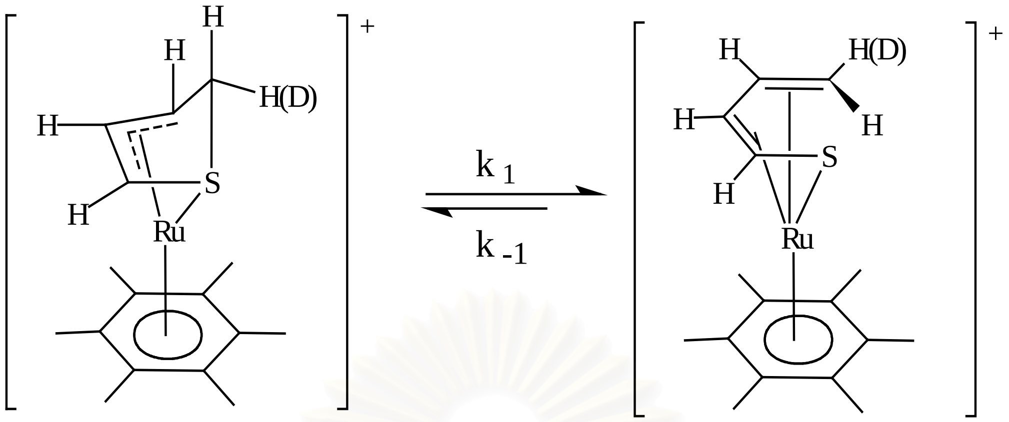
Bianchini et al.[11] used the 16-electron fragment [RhH(triphos)], generated *in situ* by thermolysis of the trihydride [RhH_3(triphos)] in refluxing THF, to react with benzothiophene which gave the 2-vinylthiophenolate complex (Scheme 1.2). The latter 2-ethylthiophenolate complex reacted with H_2 > 15 atm to give 2-ethylthiophenol as product.



Scheme 1.2 Hydrogenolysis of benzothiophene by using [RhH$_3$(triphos)] as catalyst.

The result obtained from homogeneous [Ru(triphos)] system unambiguously shows that the hydrogenolysis of benzothiophene to 2-ethylthiophenol occurs only after the substrate has been C-S inserted, prior to the desulfurization step.

In 1993, Rauchfuss et al.[12] examined that (C$_6$Me$_6$)Ru(η^4-C$_4$H$_4$S) undergoes protonation by weak acid (e.g., NH$_4^+$) to give (C$_6$Me$_6$)Ru(η^4-2-H-C$_4$H$_4$S)$^+$. This process defines a new pathway by which hydrogen can be transferred to the heterocycle. They found that (C$_6$Me$_6$)Ru(η^4-2-H-C$_4$H$_4$S)$^+$ undergoes spontaneous C-S bond cleavage (acetone solution, 55 °C, $t_{1/2}$ = 2.58 h) to give the ring-opened product, which is shown in Scheme 1.3.



Scheme 1.3 Ring opening of benzothiophene by hydrogen transfer.

1.3 Hydrodesulfurization catalysts

Most the catalytic reactions can be classified as homogeneous and heterogeneous reactions. Both of these classes have different conditions and end effect. Catalytic reactions involve catalyst and reactants to produce products and unchanged in the ideal sense. In homogeneous catalyst, catalyst, components reactants and products are in the same physical state and remain only in one phase. In the cae of heterogeneous catalyst, catalyst, components of reactants and products are in different physical states, it have different phase peparated by a phase boundary. The differences of two types of catalysts, heterogeneous catalysts are most important in petroleum process, such as hydrocracking, reforming, hydrotreating. It is essential to develop highly active in hydrotreating catalyst, including elucidation of the reaction mechanism. A number of attempts have been made to elucidate mechanism of hydrodesulfurization by studying the kinetics. There are few examples clarifying the behavior of heteroatom on the hydrotreating catalyst. In order to develop new catalysts on a continuous basis, it is essential to understand these mechanisms, which will be the foundation for marking rapid progress in the development of the necessary catalysts.

1.3.1 Heterogeneous catalysts

In industry, the catalysts applied in hydrodesulfurization have evolved from those developed in prewar Germany for hydrogenation of coal-derived liquids[22]. They are formed from alumina-supported oxides of Co and Mo, and the surfaces are usually sulfided in operation. Catalysts of this type are often referred to as cobalt molybdate. Industrial catalysts may contain as much as 10 to 20 percent of Co and Mo. A number of metal with related compositions have been applied, including, for example, Ni and W have been used to replace Co and Mo. Molybdenum or tungsten appears to be a necessary constituent of a hydrodesulfurization catalyst. Combinations of Co (or Ni) and Mo (or W) are more active than Mo or W alone, and Co and Ni are therefore generally described as promoters.[13] Hydrodesulfurization catalysts are used as porous particles, typically having dimensions of 1.5 to 3 mm. The particle sizes and pore geometry significantly influence catalyst performance, especially for the heaviest feeds, since intraparticle mass transport has a significant influence on reaction rate.

Alumina-supported Co-Mo and Ni-Mo[14-16] have been conventional catalysts of petroleum hydrotreatment for a long time. However, the development of novel catalysts with high catalytic activity is needed in order to achieve clean fuel production. Molybdenum is a major active element for hydrotreatment, cobalt and nickel are the most important promoters. Hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene have been studied by Farag et al. The reaction with Co-Mo-based carbon as catalysts has been done by using an autoclave reactor operating at 2.9

mPa hydrogen pressure. The activity results were compared with that of the conventional commercial Co-Mo/Al_2O_3 catalyst. Co-Mo/C catalysts had about twice the activity of the commercial catalyst. It was found that the activity of hydrodesulfurization depends on the metal loading as well as the order of metal addition during preparation. The highest synergetic effect between on Co and Mo for hydrodesulfurization activity was observed at a Co/Mo atomic ratio of 0.325.

In 1996 Isoda et al.[17] studied the hydrodesulfurization of 4,6-dimethyldibenzothiophene(4,6-DMDBT). The reaction was done over a zeolite-Y containing Co-Mo/Al_2O_3, conventional Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3. Isomerization and considerable transalkylation of 4,6-DMDBT into 3,6-DMDBT and into tri- or tetramethyldibenzothiophenes, respectively, were observed characteristically over Co-Mo/Al_2O_3-zeolite catalyst. Migration of methyl groups enhances the hydrodesulfurization reactivity of the sulfur species by diminishing the steric hindrance. From the result, they found that Co-Mo/Al_2O_3-zeolite exhibited the best activity for hydrodesulfurization of the sulfur species through the effective desulfurization of refractory alkyldibenzothiophene.

1.3.2 Homogeneous catalyst

For the most common organosulfur compound was thiophenic molecule, which was generally used as sulfur model compound to study hydrodesulfurization reaction. A great deal of fundamental research has been carried out in trying to understand the salient features of hydrodesulfurization process of benzothiophenes. Insights into the mechanism primarily obtained from the study of the coordination are reactivity of benzothiophene with soluble metal complexes as well as in surface science studies of benzothiophene on single crystals. Despite the numerous studies devoted to the homogeneous metal-assisted activation of benzothiophene[18-21], there are no reports with detail of catalytic opening and hydrogenation of benzothiophene assisted by transition metal complexes. Thus, most of the elementary steps involved in hydrodesulfurization of benzothiophene are still the result of indirect evidence.

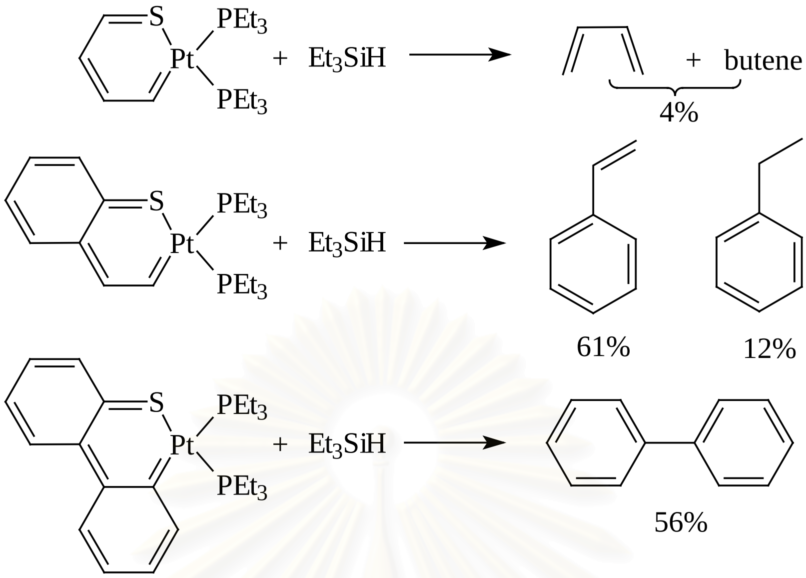
In general, a few examples of hydrodeulfurization reaction of aromatic sulfur compounds have been observed by using mononuclear metal system complexes. In the case of polynuclear metal system have been studied very much. From the literature[22], it was suggested that polynuclear metal system might be required for cleavage of both C-S bonds.

1.3.3 Catalyst systems

1.3.3.1 Mononuclear metal system

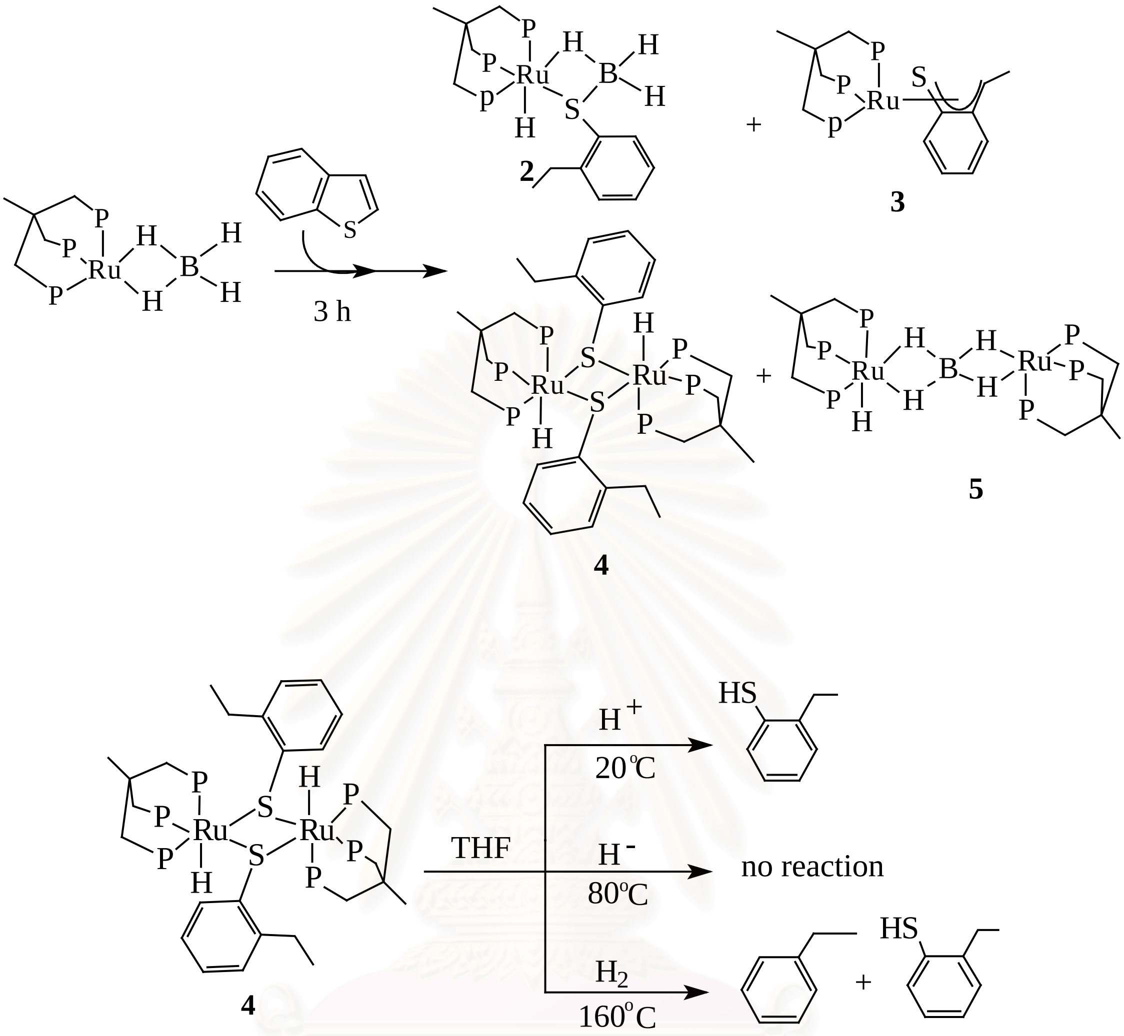
Hydrodesulfurization reactions of thiophenes have been observed by using mononuclear metal species. In general, an external source of hydrogen atom is required to bring about the hydrodesulfurization step.

The thiaplatinacycles, $[Pt(SC_4H_4)(PEt_3)_2]$, $[Pt(SC_8H_6)(PEt_3)_2]$ and $[Pt(SC_{12}H_8)(PEt_3)_2]$ (Scheme 1.4), obtained from reactions of $[Pt(PEt_3)]$ with the appropriate thiophenes, are hydrodesulfurized by hydride releasing agents (Et_3SiH, $NaBH_4$ or $LiAlH_4$) in refluxing toluene to give butadiene and butene, styrene and ethyl benzene or biphenyl, respectively.[23] The formation of the platinum thiol $[PtH(PEt_3)_2(SH)]$ invariably accompanies all of these hydrodesulfurization processes.



Scheme 1.4 Hydrodesulfurization of aromatic complexes by hydride releasing agent.

Bianchini et al.[24] investigated the hydrodesulfurization of benzothiophene. They found that [(triphos)RuH(BH_4)] reacted with benzothiophene to give four different complexes (Scheme 1.5). The μ-thiolate complex **4** reacts with hydrogen gas ($\geq 160^{o}C$, 30 bar H_2) or with $HBF_4.OEt_2$ ($20^{o}C$) yielding ethyl benzene and 2-ethylthiophenol, respectively. No reaction occurs with $LiHBEt_3$.



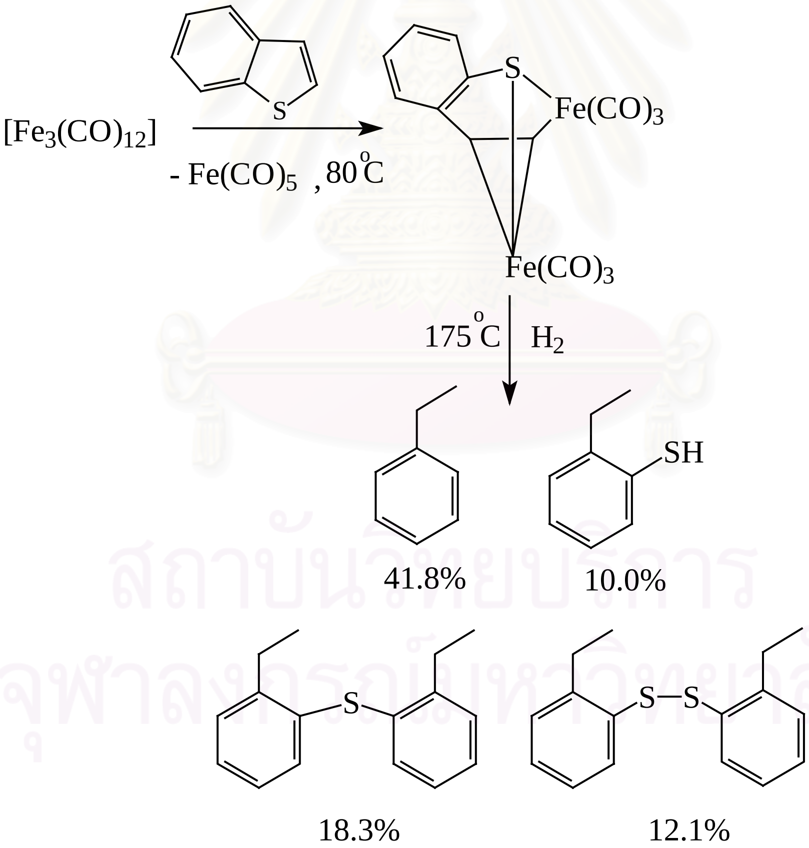
Scheme 1.5 Hydrodesulfurization of benzothiophene using [(triphos)RuH (BH_4)] as catalyst.

1.3.3.2 Polynuclear metal system

As for actual hydrodesulfurization of thiophenic molecules, multimetallic homogeneous systems, especially when both component and promoter metals are present, are much more effective than are monometallic systems. As an example, in

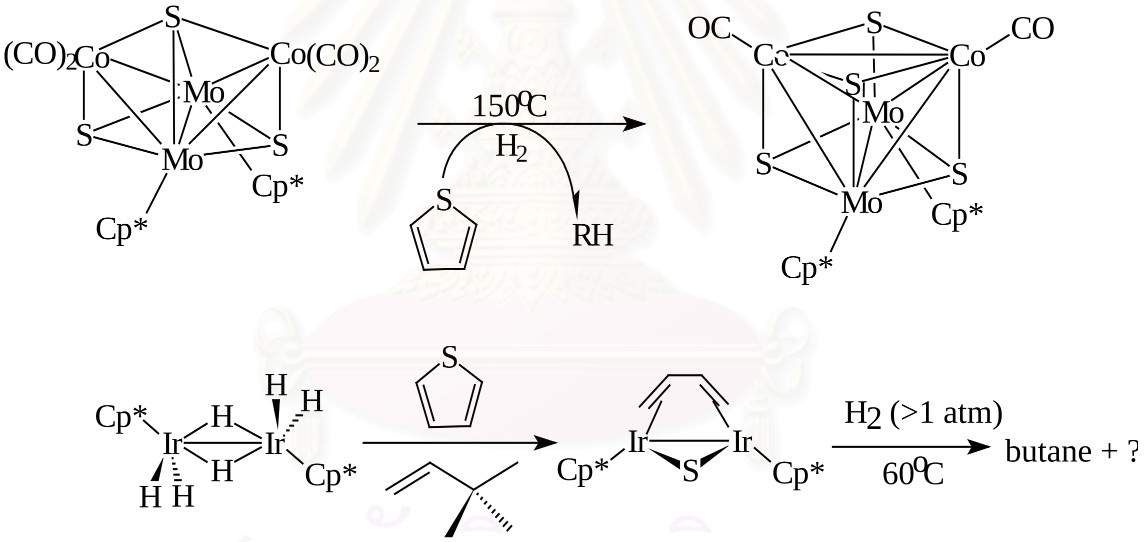
1996, Bianchini et al.[25] studied the effect of C-S insertion in benzo[b]thiophene which occurred at a promoter metal(Rh). But desulfurization required the addition of a component metal (W), which reacted to give a bimetallic intermediate from which sulfur was eliminated as WS_2.

The first example of metal-assisted opening and hydrogenation of benzo[b] thiophene was described by Rauchfuss et al.[26-28] He treated benzo[b]thiophene with $[Fe_3[CO)_{12}]$ to obtain the benzothiaferrole $[Fe_2(C_8H_6S)(CO)_6]$, which was hydrogenated to give ethyl benzene together with some 2-ethyl benzenethiol, bis(2-ethylphenyl)sulfide, and bis(2-ethylphenyl)disulfide as shown in Scheme 1.6.]



Scheme 1.6 Hydrodesulfurization of benzothiophene catalyzed by $[Fe_3[CO)_{12}]$ as catalyst.

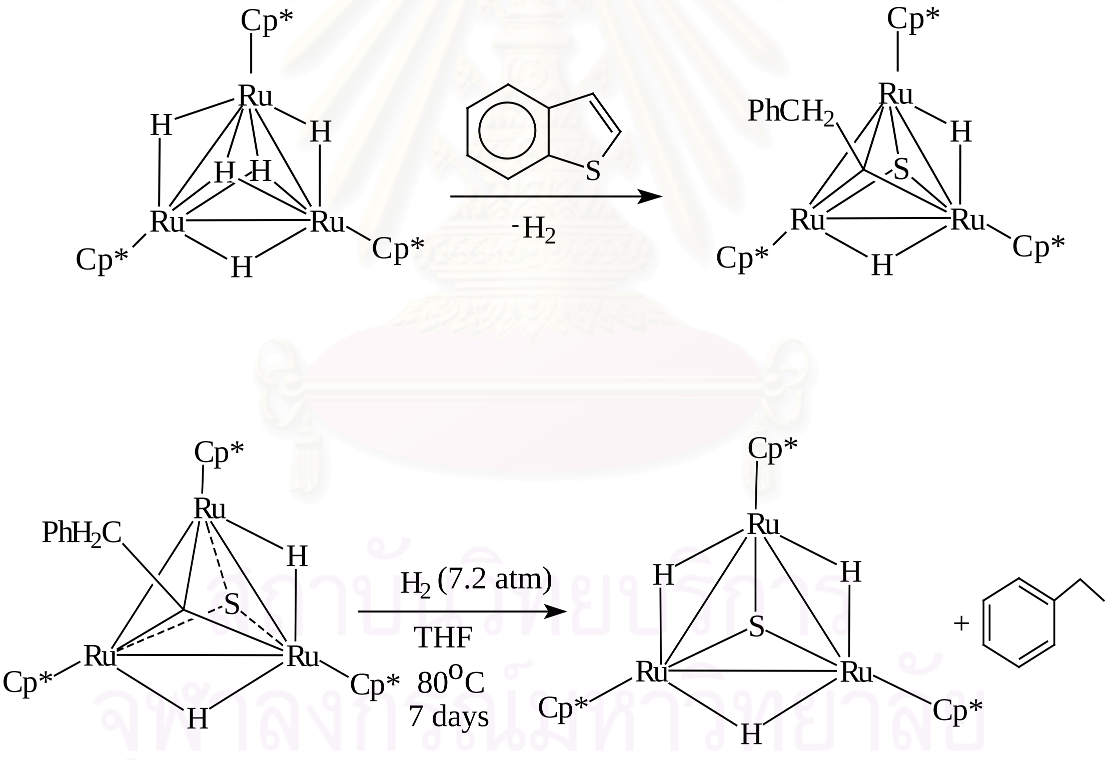
In 1997, Curtis et al.[29] used the Mo_2Co_2 sulfido clusters as catalyst in hydrodesulfurization reaction. The species $Cp^*_2Mo_2Co_2S_3(CO)_4$ can react with thiophene in the presence of H_2 at 150°C to give the cluster $Cp^*_2Mo_2Co_2S_4(CO)_4$ and a mixture of C_2-C_4 hydrocarbon (Scheme 1.7). Adams et al.[30-31] used osmium carbonyl clusters to cleave C-S bond in thietanes. Jones et al.[32] studied the reaction of iridium dimer $[Cp^*IrH_3]_2$ with thiophene in the presence of a hydrogen acceptor to give a product in which both C-S bonds have been cleaved (Scheme 1.7).



Scheme 1.7 Hydrogenolysis of thiophene by Mo_2Co_2 sulfido clusters and $[Cp^*IrH_3]_2$ as catalysts.

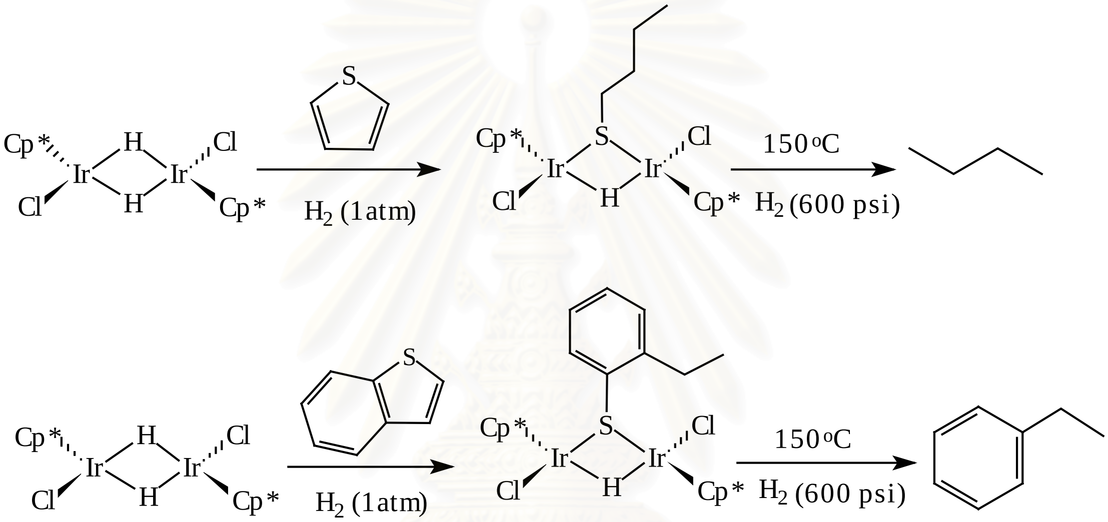
Arce et al.[33] investigated the reaction of $[Ru_3(CO)_{12}]$ with thiophene and 2-methylthiophene. This reaction was carried out in THF at reflux temperature which gives two metallocyclopentadiene complexes, $[Ru_2(\mu\text{-}C_4H_3R)(CO)_6]$ and $[Ru_4(\mu_3\text{-}S)(\mu\text{-}C_4H_3R)(CO)_{11}]$ (R = H or Me), by C-S bond cleavage. In the latter compound, the inorganic (S) and the organic fragment (C_4H_3R) remain co-ordinated within the same organometallic framework.

Recently, Matsubara et al.[34] used a trinuclear ruthenium cluster $[\eta^5\text{-}C_5Me_5)Ru]_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ to react with benzothiophene. They demonstrated that the trimetallic metal hydride cluster can effectively activate benzothiophene under relatively mild conditions to cleave their C-S bond selectively due to the cooperative action of the metal centers (Scheme 1.8).



Scheme 1.8 Hydrodesulfurization of benzothiophene by trinuclear ruthenium cluster.

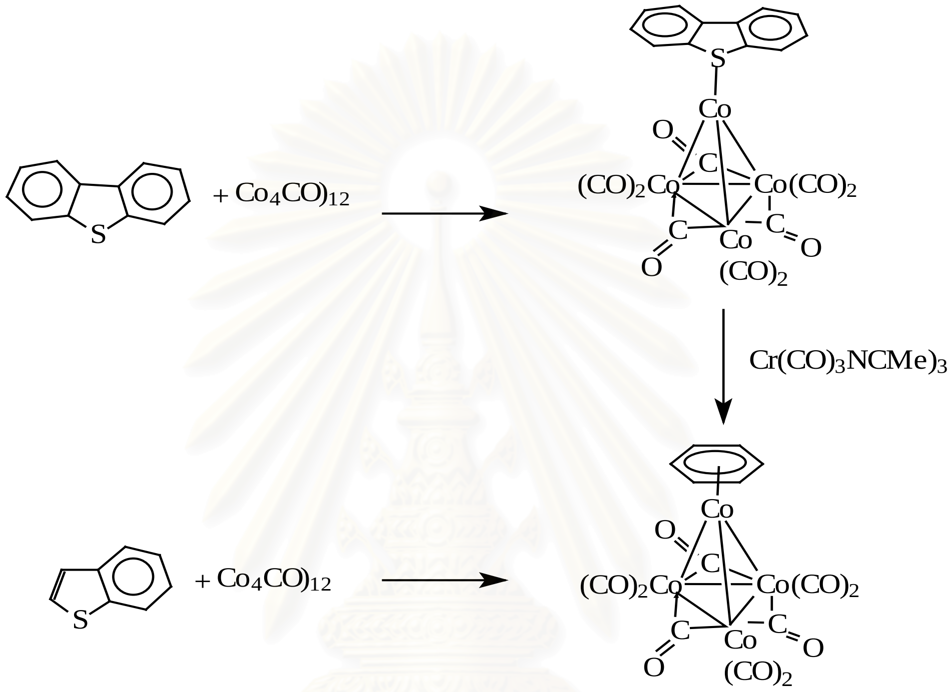
Jones et al.[35] investigated the reaction of $[Cp^*IrHCl]_2$ with thiophene and benzothiophene. The reactions were carried out in the pressure of H_2 and gave the products $[Cp^*IrCl]_2(\mu\text{-}H)(\mu\text{-}SC_4H_9)$ and $[Cp^*IrCl]_2[(\mu\text{-}H)(\mu\text{-}SC_6H_4)CH_2CH_3]$. Furthermore, they found that the less reactive chloro dimer $[Cp^*IrH(\mu\text{-}Cl)]_2$ cleaves not only one bond in thiophene and benzothiophene, but also hydrogenates the hydrocarbon portion of the fragment (Scheme 1.9).



Scheme 1.9 Hydrodesulfurization of thiophene and benzothiophene by binuclear Iridium complex.

Reactions of cobalt cluster with dibenzothiophene and benzothiophene have been studied by Angelici et al.[36] They found that $Co_4(CO)_{12}$ reacted with dibenzothiophene(DBT) to give $(\eta^6\text{-DBT})Co_4(CO)_9$, in which one arene ring of DBT is η^6-coordinated to a Co atom. This cluster reacts with $Cr(CO)_3(NCMe)_3$ to give the desulfurized complex $(\eta^6\text{-benzene})Co_4(CO)_9$. It was surprising to obtain $(\eta^6\text{-benzene})$

$Co_4(CO)_9$ as the only isolated metal complex from the reaction of $Co_4(CO)_{12}$ with benzothiophene (Scheme 1.10).



Scheme 1.10 Hydrodesulfurization of dibenzothiophene and benzothiophene by cobalt cluster complex.

1.4. Kinetic studies

A number of hydrodesulfurization processes have been studied. For heterogeneous catalyst, it has been believed that sulfur anion vacancies are the active sites for hydrodesulfurization because the coordinatively unsaturated sites are needed for the adsorption of thiophene to occur. There are two adsorption modes of thiophene: one-point (end-on) mode with sulfur atom and multiple points (side-on) mode. The latter may involve the adsorption with all or some member of the thiophene ring. It was proposed that hydrodesulfurization proceeds through the adsorption of thiophenes on anion vacancies, including hydrogenolysis and hydrogenation reactions with metal hydride or SH species, and the regeneration of anion vacancies.

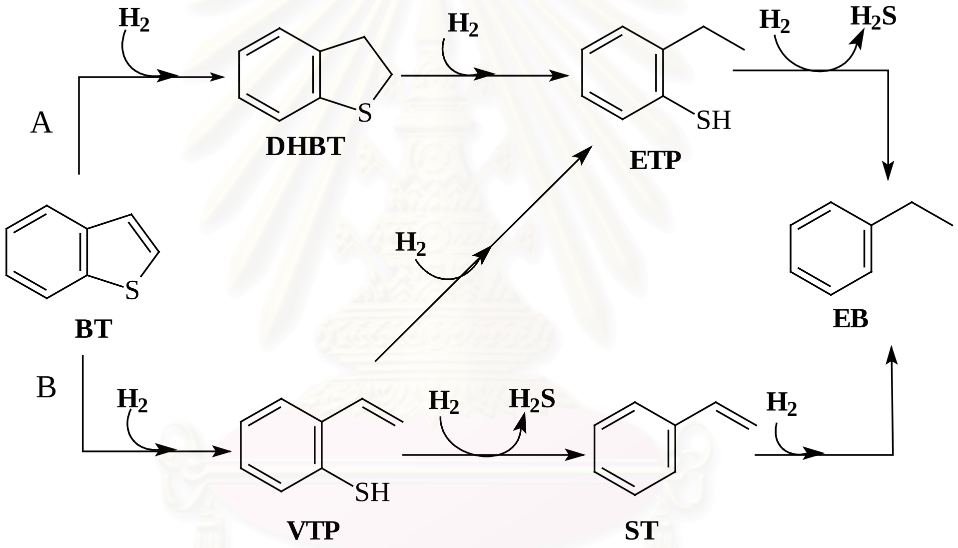
To understand the mechanism of thiophene hydrodesulfurization, the structure and the reactivity of thiophene on organometallic complexes have been investigated.[37] Organometallic chemistry provides not only visual pictures of the coordination and reaction of thiophene derivertives but also the possibility that such similar reactions as seen in those pictures may occur actually on a catalysts surface. It is difficult to cleave the C-S bond compared with thiols or sulfides because the thiophene ring has aromatic character. However, the C-S bonds in thiophenes can easily be cleaved on organometallic complexes.

Organometallic compounds can provide well-defined structural models whose spectral properties may be used to interpret the spectra of the complex catalyst. Similarly, the types of reactions exhibited by organometallic compounds in solution are often found to occur also on the surface of heterogeneous catalysts. The mechanism understanding obtained in solution can often be applied to the surface counterparts.[38-39]

The hydrodesulfurization reaction is of prime importance in the petroleum and coal industries. An intense effort has been devoted over the years to the fundamental understanding of the mechanisms, which are operative in such processes over heterogeneous catalysts. A mechanistic approach which continues to attract considerable attention is the development of the coordination chemistry of thiophene and benzothiophene. A particularly interesting mode of activation in relation to hydrodesulfurization mechanisms is the one involving C-S bond scission to produce thaimetallacyclic species. However, the reactivity of such ring-opened C_4H_4S and

C_8H_6S fragments,[40] which is key to the understanding of the pathways leading to sulfur extrusion, has not been studied in much detail.

In heterogeneous catalyst, it was found that the most widely accepted mechanisms proposed for hydrodesulfurization of benzothiophene[41] over solid catalysts are shown in Scheme 1.11. Path (A) begins with the selective hydrogenation to dihydrobenzothiophene (DHBT) prior to desulfurization to give ethyl benzene (ET). Path (B) involves initial C-S bond scission to give vinyl thiophenol (VTP), followed by hydrogenation of the cleaved benzothiophene molecule.



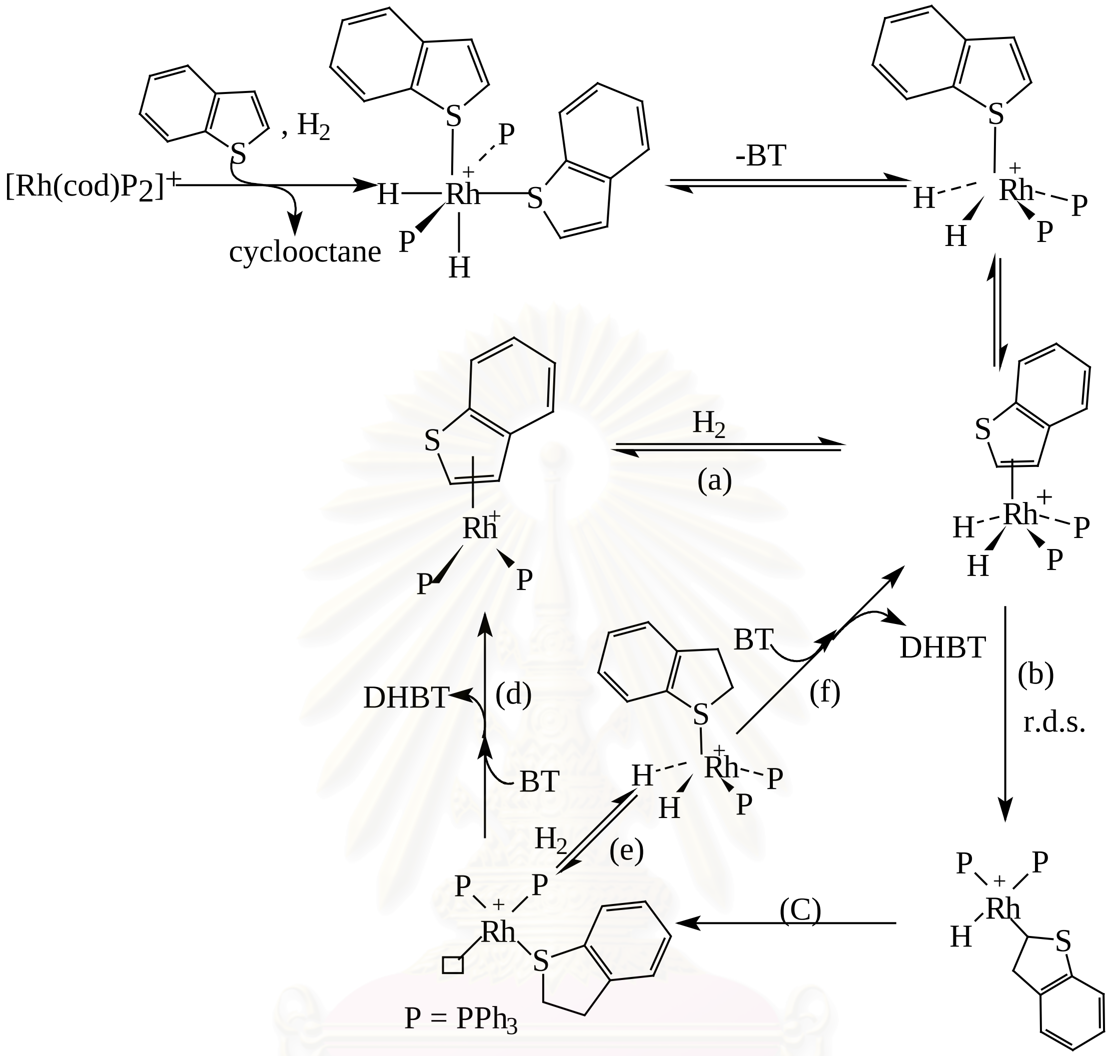
Scheme 1.11 The proposed mechanisms for hydrodesulfurization of benzothiophene over solid catalysts.

The kinetic studies of benzothiophene hydrodesulfurization over wide range of temperature was reported by Kilanowski and Gates. They performed the reaction of benzothiophene with hydrogen at temperature 525, 575 and 605 K, the pressure is below 2 atm on Co-Mo/Al_2O_3. They discovered that hydrogen and hydrogen sulfides were competitively adsorbed at the same adsorption sites. The activation energy was 20±3 kcal/mol.

For homogeneous catalyst, Sanchez-delgaldo et al.[42] studied the kinetics and mechanism of the homogeneous hydrogenation of benzothiophene to 2, 3-dihydrobenzothiophene by using $[Rh(cod)(PPh_3)_2]PF_6$ as catalyst, in 2-methoxyethanol as solution. In particular, the experimental rate law can be written as:

$$d[C_8H_8]/dt = k_{cat}[Rh][H_2]$$

The value for the catalytic rate constant at 25 ^{o}C : k_{cat} is 1.24×10^{-4} $dm^3mol^{-1}s^{-1}$. The activation parameters are E_a = 20.7 $kcalmol^{-1}$ and $\Delta S^{\neq}$ = -11.1 e.u. The catalytic mechanism is illustrated in Scheme 1.12.



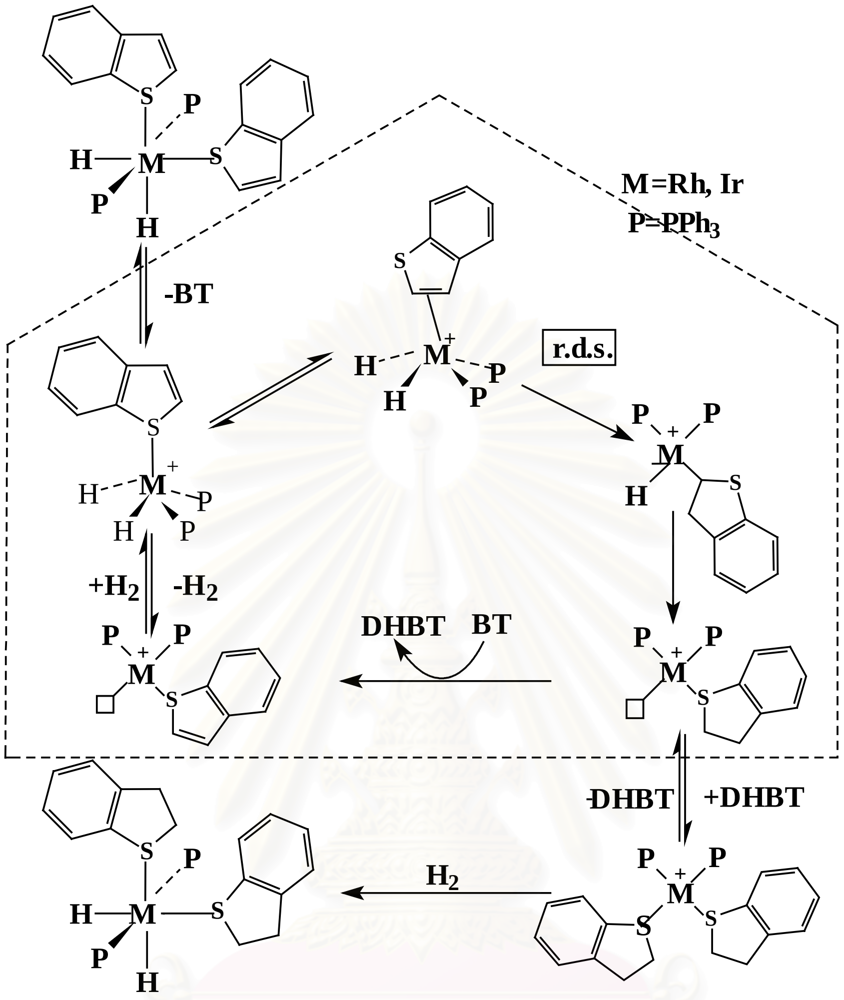
Scheme 1.12 Proposed mechanism for the hydrogenation of benzothiophene by use of $[Rh(cod)(PPh_3)_2]PF_6$ as catalyst.

An active species the $[Rh(\eta^5\text{-}C_8H_6S)(PPh_3)_2]^+$, is in equilibrium with the product resulting from the oxidative addition of H_2, (step a). The migration of one of the terminal hydrides from the metal to the C^2 carbon atom of the dihapto-bond benzothiophene ligand gives the (2-benzothienyl) hydride intermediate as the rate-determining step of catalytic reaction (step b). The reductive coupling between the remaining hydride and the thienyl ligand then gives a σ-SC_8H_8 unsaturated complex. This complex either reacts with benzothiophene to give the η^5-C_8H_6S complex (step d) or adds H_2 to give hydride complex (step e). Then it reacts with benzothiophene to yield dihydrobenzothiophene product.

Herrera et al.[43] have studied the kinetics and mechanism of homogeneous hydrogenation of benzothiophene using rhodium and iridium complex $[M(cod)(PPh_3)_2]PF_6$(M = Rh, Ir) as the catalyst. Kinetic and mechanistic studies of benzothiophene hydrogenation were monitored by using both complexes as catalyst precursors in 1, 2-dichloroethane solution at 40 °C. For both complexes, the reaction proceeds according to the rate law:

$$d[DHBT]/dt = k_{cat}[M][H_2]$$

The reaction mechanism was shown in Scheme 1.13. In general mechanism in which the transfer of the hydrides to coordinated benzothiophene in $[M(H)_2(\eta^2(C{=}C)\text{-}BT)\text{-}(PPh_3)_2]PF_6$ is the rate-determining step of the catalytic cycle.

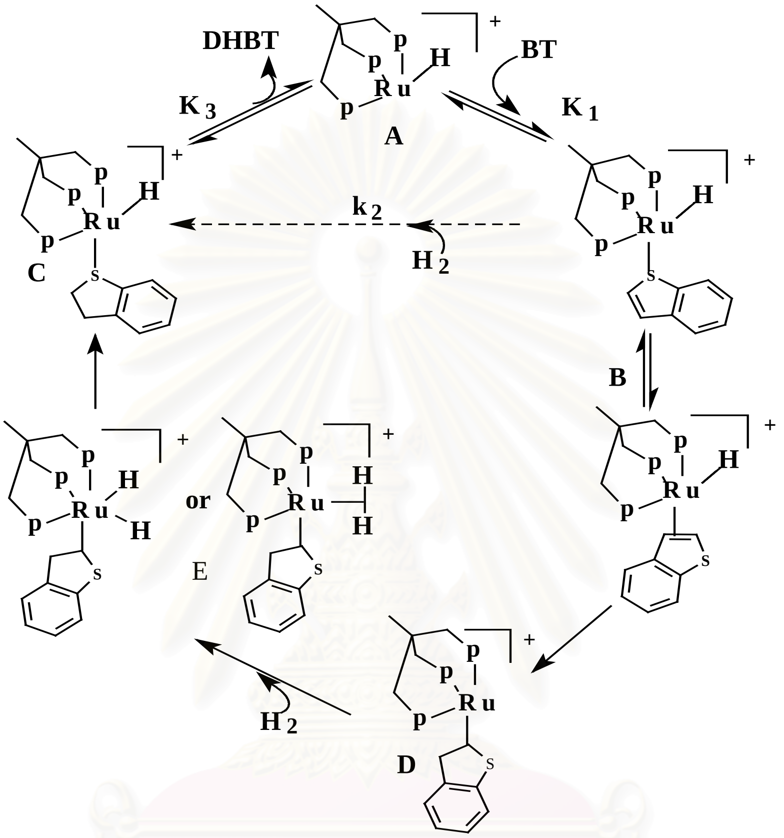


Scheme 1.13 Proposed mechanism for the hydrogenation of benzothiophene using of $[M(cod)(PPh_3)_2]PF_6$(M = Rh, Ir) as catalyst precursors.

Biachini et al.[44] have studied the homogeneous hydrogenation of benzothiophene to 2-ethylthiophenol catalyzed by $K[(triphos)RuH_3]$. In kinetic measurement, the catalytic runs were studied in situ by HPNMR spectroscopy by gas adsorption technique at different catalyst, substrate and dihydrogen concentration and at different temperature. In particular, the experimental rate law can be written as:

$$d[DHBT]/dt = k_{cat}[Ru][BT][H_2]$$

k_{cat} = 1.01 x 10^3 $M^{-1}s^{-1}$. The catalytic mechanism for hydrogenation of benzothiophene is illustrated in Scheme 1.14.



Scheme 1.14 Proposed mechanism for the hydrogenation of benzothiophene by using K[(triphos)RuH_3] as catalyst.

In catalytic cycle, benzothiophene is coordinated with $[(tripos)RuH]^+$ and reversible to form [(triphos)RuH(BT)]. The migration of one of hydride from the metal to give complex D. Oxidative addition of H_2 to a Ru(II) species gives hydride complex via η^2-H_2-Ru as the intermediate. Dihydrobenzothiophene is released from complex C and returns to complex A as active species.

1.5 Objectives and scope of this research

The main goals of this research are synthesis, characterization and hydrodesulfurization of ruthenium hydride complex and study of the kinetics and mechanism of hydrodesulfurization of benzothiophene using $(PPh_3)_3RuCl_2$ complex (structures of both complexes shown in Figure 1.1).

Part I

Ruthenium hydride is a bimetallic complex with four hydride atoms that served for hydrodesulfurization with benzothiophene *via* hydrogenolysis or hydrogenation. The resulting complex organic is characterized by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR). The product of hydrodesulfurization was investigated by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). In addition, the effect of reaction parameters: time, temperature, kinds of reducing agent on hydrodesulfurization reaction of benzothiophene were examined.

Part II

Ruthenium triphosphine complex is used for kinetic study of benzothiophene hydrodesulfurization. Rate law and activation parameters are determined to clarify the mechanism of this reaction.

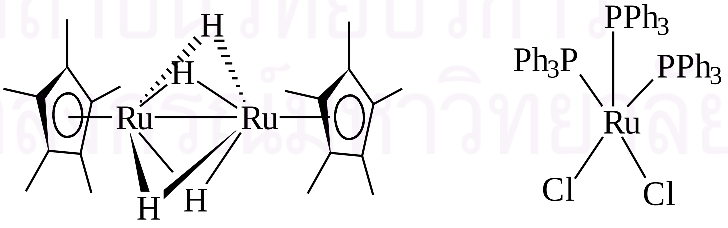


Figure 1.1 Structures of ruthenium hydride and $(PPh_3)_3RuCl_2$ complex.

CHAPTER II

EXPERIMENTAL

2.1. Operation and Apparatus

The preparations of ruthenium hydride complexes were done in an inert gas atmosphere (prepurified nitrogen) and used Schlenk line.[45-46]

2.1.1 Schlenk line

Schlenk line consists of nitrogen and vacuum lines. The vacuum line was equipped with a solvent trap and a vacuum pump, respectively. The nitrogen line was connected to the moisture trap and the oil bubbler that contained enough oil to provide a seal from the atmosphere. The Schlenk line is shown in Figure 2.1.

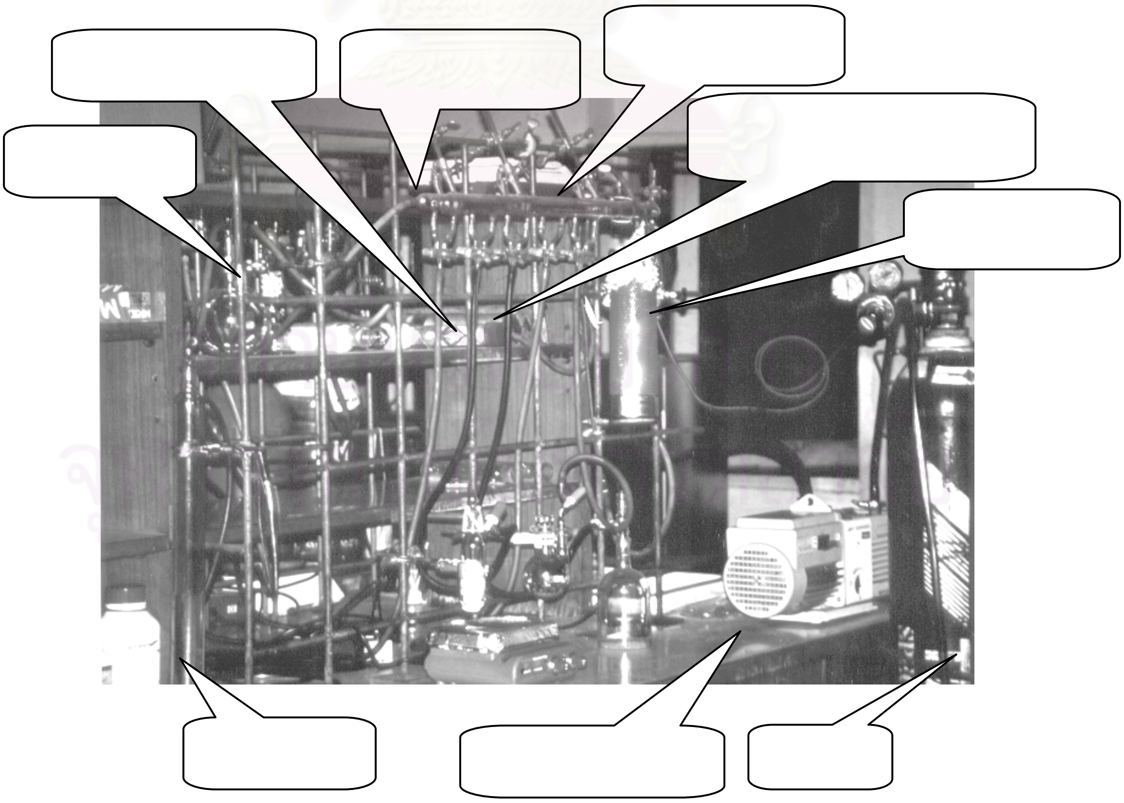


Figure 2.1 Schlenk line

2.1.2 Schlenk flask

A Schlenk flask has a side-arm to connect to the Schlenk line. Some typical models are shown in Figure 2.2.

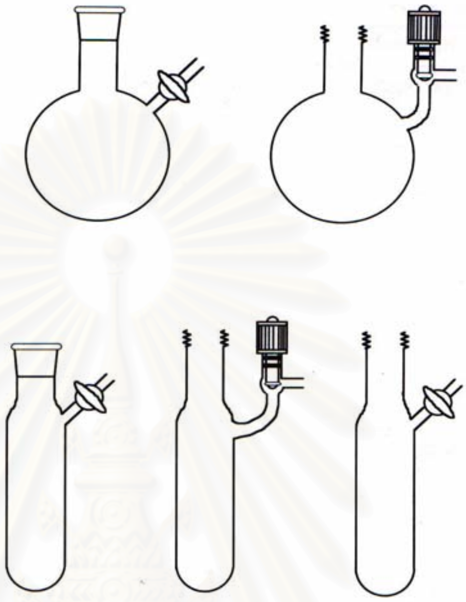


Figure 2.2 Round-bottomed and tube designed for Schlenk flasks

2.1.3 Vacuum pump

A pressure of $10^{-3} – 10^{-1}$ mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line.

2.1.4 Heating bath

The heating bath with thermometer was used to hold the high temperature of reaction.

2.1.5 Inert gas supply

Nitrogen gas was purified by passing 4 A° molecular sieve, NaOH and P_2O_5 respectively. The high purity nitrogen gas was passed through drying columns. The inert gas was used to feed in the nitrogen line of Schlenk line.

2.1.6 Glove bag

Glove bag is a moderate-volume gas-tight container which air or moisture is excluded. The glove bag has a way to connect to Schlenk line, which can be evacuated and filled with nitrogen gas.

2.2 Reagents and Solvents

All chemicals in analytical grade were obtained as follows:

Chemicals	Suppliers
High purity hydrogen gas (99.99%)	Thai Industry Gas Co.,Ltd.,Thailand
High purity nitrogen gas (99.99%)	Thai Industry Gas Co.,Ltd.,Thailand
Toluene	Lab scans Co., Ltd., Ireland
Benzothiophene	Fluka Chemie A.G., Switzerland
Ruthenium trichloride hydrate	Aldrich Chemical Company, Inc., USA.
Tris-triphenylphosphine ruthenium (II) chloride	Fluka Chemie A.G., Switzerland
Ethanol	Lab scans Co., Ltd., Ireland
Cyclohexanol	Lab scans Co., Ltd., Ireland
Tetrahydrofuran	Fluka Chemie A.G., Switzerland
Haxane	Lab scans Co., Ltd., Ireland
Lithium aluminium hydride	Aldrich Chemical Company, Inc., USA.
Potassium tertiary butyl borohydride	Fluka Chemie A.G., Switzerland

Solvents were dried before used. Anhydrous diethyl ether was dried in 4 A^{o} molecular sieves. Tetrahydrofuran, hexane and toluene were dried with sodium and benzophenone.[47] Freshly cut sodium (1 g) was added into the solvent (650 ml) and benzophenone (4g) was added. After swirling to dissolve benzophenone, a blue color should form at the metal surface. This localized color will initially disappear but, on refluxing, the bulk of the solvent should gradually turned green and then blue as all of water and oxidizing impurities were removed.

Ethanol was dried with magnesium ethoxide, prepared by placing 5g of clean dry magnesium turnings and 0.5g of iodine in a 2L flask, followed by 50-75 ml of absolute ethanol, and warmed the mixture until a vigorous reaction occurs. When this subsides, heating was continued until all the magnesium was converted to magnesium ethoxide. Up to 1L of ethanol was added and, after an hour’s reflux, it is distilled off.

2.3 Physical and Analytical Measurements

2.3.1 Nuclear magnetic resonance

^{1}H NMR spectra were obtained on a Bruker ACF 200 MHz at Chemistry Department, Chulalongkorn University. The spectra were referenced to the residual proton peaks in the deuterated solvent: deuterochloroform (7.24 ppm) and deuterobenzene-d_6 (7.15 ppm). Chemical shifts were given in parts per million (ppm) and coupling constant (J) in hertz (Hz).

2.3.2 Fourier transform infrared spectrometry

Fourier transform infrared spectra were recorded on Nicolet FT-IR Impact 410 Spectrophotometer at Department of Chemistry, Chulalongkorn University. The samples were made into a KBr pellet. Infrared spectra were recorded between 400 cm^{-1} to 4000 cm^{-1} in transmittance mode.

2.3.4 Gas chromatography

Capillary column gas chromatograph GC16A, Shimadzu was used for the determination of % conversion of substrate. The conditions are as follows:

Column: DB wax

Programmed Temp: 90 ^{o}C for 1 min, increased at 15 ^{o}C /min to 220 ^{o}C

Detector: Frame ionization (FID)

Detector Temp: 240 ^{o}C

Injection Temp: 220 ^{o}C

Carrier gas: N_2

Flow rate: 50 ml/min

2.3.5 GC-Mass spetrometry

Gas chromatography was carried out on Varian, Star 3400CX and mass spectrometry was carried out on Varian, Saturn 4D, Chemistry Department, Chulalongkorn University.

2.3.6 Column chromatography

Column chromatography was used to separate the product of hydrodesulfurization. The column was glass tube, 1 cm diameter and 25 cm length. Stationary phase was 70-230 mesh of silica.

2.3.7 Reactor

A Parr 4042, 600 ml of Parr reactor, stainless-steel pressure reactor was used for kinetic studies on hydrodesulfurization and is shown in Figure 2.3. The reactor is contained with a pressure gauge, safety rupture disc, valves for admitting, valve for releasing gas and valve for removing liquid, a thermocouple and a gas-tight stirrer.

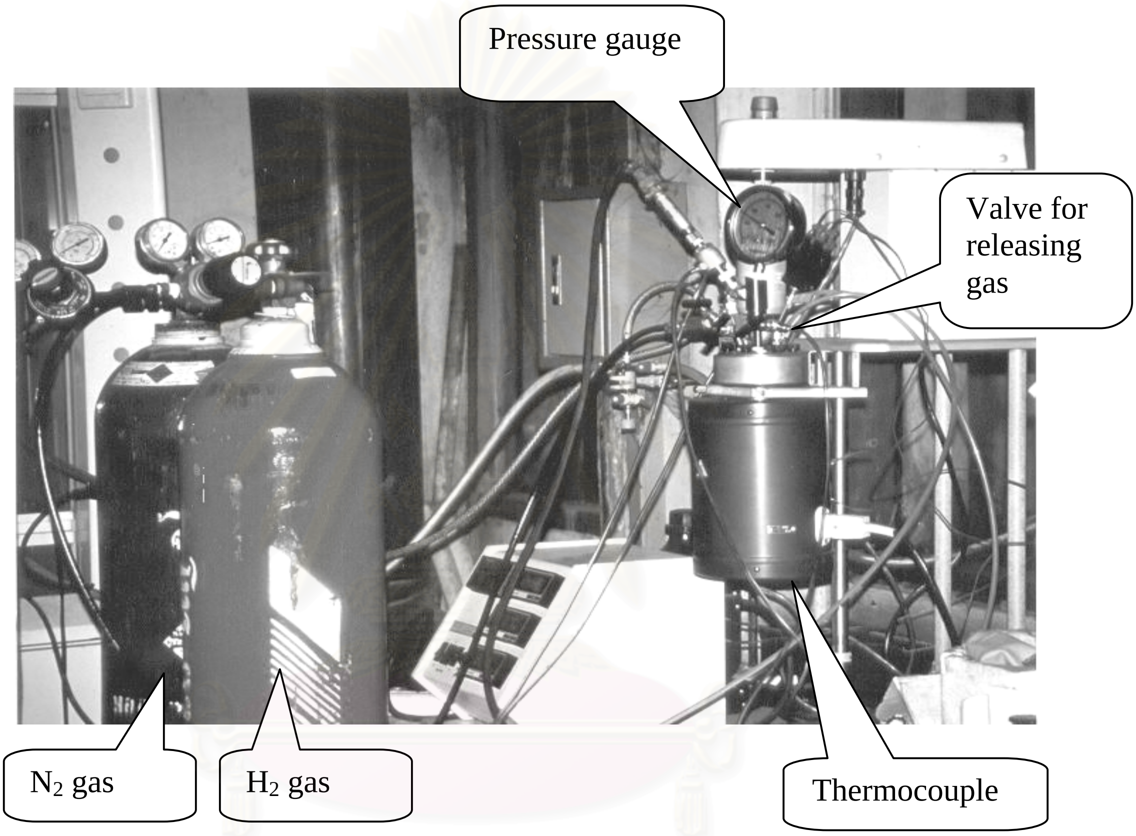


Figure 2.3 Equipment for kinetic study of hydrodesulfurization.

2.4 Preparation of Ruthenium Complexes

2.4.1 Preparation of pentamethyl cyclopentadienyl ruthenium chloride

$[C_5Me_5RuCl_2]_2$

Pentamethyl cyclopentadienyl ruthenium chloride[48] was prepared by the reaction of trichloro ruthenium hydrate 1.17 g (5.21 mmol) with pentamethylcyclopentadiene 1.85 ml (18.28 mmol) in 20 ml of ethanol. The mixture was refluxed at 75 ^oC for 3 hours. The product precipitation was collected on a fine frit and was successively washed with two portions of 5 ml of ethanol and two portions of 7 ml of dry diethyl ether. Drying under reduced pressure gave the complex in 0.97 g (61 % yield)

$[(C_5Me_5)RuCl_2]_2$	dark brown solid
FTIR (KBr): ν (cm^{-1})	2983, 2906, 1478, 1375, 1023, 440
^{1}H-NMR (C_6D_6): δ (ppm)	4.90 (s, 30H)
^{13}C-NMR (C_6D_6): δ (ppm)	57 (s), 18 (s)

2.4.2 Preparation of ruthenium hydride

$[C_5Me_5RuH_2]_2$

There are two methods for the preparation of $[C_5Me_5RuH_2]_2$ in which different hydride regent is used.

Method I

The suspension of $[C_5Me_5RuCl_2]_2$ (0.83 g, 1.36 mmol) was stirred with lithium aluminum hydride[49] (0.40 g, 0.0101 mol)(1:7.5 ratio) in diethyl ether (25 ml) for 24 h at room temperature. The mixture was pump off solvent and stirred with 25 ml ethanol at -78°C for 2 hours. The solvent was removed under reduced pressure.

Extraction of the crude product with diethyl ether followed by recrystallization from toluene gave the ruthenium hydride ($[C_5Me_5RuH_2]_2$) in 42 % yield.

Method II

The same procedure as the method I was done except that KBu_3BH was used in place of $LiAlH_4$. This method gives 23 % yield.

$[C_5Me_5RuH_2]_2$	Red plates
FTIR (KBr): ν (cm^{-1})	2958, 2899, 1794, 1652, 1421, 1376, 1261, 1078, 1026, 582, 453
^{1}H-NMR (C_6D_6): δ (ppm)	1.86 (s, 30H), -13.97 (s, 4H)
^{13}C-NMR (C_6D_6): δ (ppm)	87.65 (s), 11.98 (s)

2.5 Reaction of Ruthenium Hydride Complex with Benzothiophene

2.5.1 Procedure for hydrodesulfurization

The hydrodesulfurization was performed under nitrogen atmosphere. A prescribed amount of catalyst $[C_5Me_5RuH_2]_2$ and benzothiophene were dissolved in 20 ml toluene. The reaction mixture was stirred at the desired time and temperature. Samples of the solution were collected after 1 min, 1, 3, 6, 9, 12, 24, 48, 72 hours of the reaction time. This sampling liquid 0.5 ml was passed through an alumina column to eliminate solid. The obtained solution was added with cyclohexanol (internal standard) 1.0 ml and toluene to make volume equal 10.0 ml. The solution was analyzed to determine dihydrobenzothiophene produced by GC. GC-MS data were collected to confirm the identity of the product. After the residues in flask was removed under reduced pressure. The residue was recrystallized from a mixture of toluene and hexane (7 : 5 ml) at 30 °C to give the product which was characterized by NMR and FT-IR spectroscopies.

FT-IR (KBr): ν (cm^{-1})	2962, 2857, 2352, 1839, 1728, 1631, 1488, 1430, 1384, 1261, 1099, 802, 528
^{1}H-NMR (C_6D_6): δ (ppm)	7.70, 7.00 (m, 8H), 3.35 (q, 4H), 1.80, 1.50 (m, 30H), 0.99 (t, 6H)
^{13}C-NMR (C_6D_6): δ (ppm)	67.72, 38.89, 30.51, 29.90, 28.99, 23.04, 13.96, 10.86, 1.10
GC-MS (m/z)	106

The various effects on the hydrodesulfurization of ruthenium hydride with benzothiophene and optimized conditions were investigated.

2.5.2 The effect of time

The effect of time in hydrodesulfurization was investigated by varying time from 1 to 72 hours. The reaction conditions were set at room temperature, 0.107 mmol of catalyst and 10 mole ratio of benzothiophene. The procedure is described in Section 2.5.1.

2.5.3 The effect of benzothiophene/Ru mole ratio

The effect of benzothiophene/Ru was studied by varying benzothiopene/Ru ratio: 5.0, 7.5, 10.0, 12.5, and 15.0. The other parameters were set at room temperature, 0.107 mmol of catalyst and reaction time 48 hours. The procedure is described in Section 2.5.1.

2.5.4 The effect of temperature

The effect of temperature was studied by varying the hydrodesulfurization temperature : room temperature, 75 °C and 110 °C. The other parameters were fixed at 0.107 mmol of catalyst, 10 mole ratio of benzothiophene/Ru and reaction time 48 hours. The procedure is described in Section 2.5.1.

2.5.5 The effect of hydrogen gas

The hydrodesulfurization with hydrogen gas was studied by passing hydrogen gas(1 atm) into the reaction. The other parameters were fixed: room temperature, 0.107 mmol of catalyst, 10 mole ratio of benzothiophene/Ru and reaction time 24 hours. The procedure is described in Section 2.5.1.

2.5.6 The effect of high pressure and high temperature

Benzothiophene (0.15 ml, 1.33 mmol) was dissolved in 50 ml of toluene and $[C_5Me_5RuH_2]_2$ (0.050 mg, 0.104 mmol) was added. The mixture was introduced into the Parr reactor under nitrogen atmosphere. The reaction was carried out at a hydrogen pressure of 10, 20 bars at 150 ^{o}C and stir rate of 400 rpm. Samples of the solution were collected after 1, 6, 9, 12, 24 and 48 hours of the reaction time. This sampling liquid 2.0 ml was passed through an alumina column to eliminate solid. The obtained solution was added with cyclohexanol (internal standard) 1.0 ml and toluene to make volume equal to 10.0 ml. The compound analyzed is dihydrobenzothiophene by GC. GC-MS data confirms the identity of the product.

2.5.7 The effect of hydride reagents

The suspension of $[C_5Me_5RuCl_2]_2$ (0.31 g, 0.51 mmol) was stirred with lithium aluminum hydride, sodium borohydride or potassium tertiary butyl borohydride (1:7.5 ratio) in diethyl ether (25 ml) for 24 h at room temperature. The mixture was pumped off solvent and stirred with 25 ml ethanol at -78°C for 2 hours. The solvent was removed under reduced pressure. Ruthenium hydride and benzothiophene were dissolved in 20 ml toluene. The procedure is described in Section 2.5.1.

2.6 Kinetic Measurements of Benzothiophene Hydrodesulfurization

All manipulations and reactions were conducted under a nitrogen atmosphere by use of standard Schlenk line techniques or by use of glove bag. A stainless steel Parr High Pressure Reactor was used for all reactions. The reaction rate as a function of change in the reaction conditions: concentrations of $[(PPh_3)_3RuCl_2]$ catalyst, benzothiophene, hydrogen gas and reaction temperatures were studied at a very early stage of the reaction. The reaction was followed by monitoring the appearance of dihydrobenzothiophene product as a function of time. The initial rates method was used for kinetic data analysis. It is reported that in the absence of added triphenylphosphine this catalyst forms dimers which complicate the nature of reaction mechanism. Therefore, all the experiments were carried out in the presence of triphenylphosphine.

2.6.1 General procedure

$(PPh_3)_3RuCl_2$ 0.7701 g (0.20 mmol) dissolved in 20.0 ml of toluene and benzothiophene 7.00 ml in toluene 30.0 ml were prepared as stock solutions. In a typical reaction, the appropriate amounts of $(PPh_3)_3RuCl_2$, benzothiophene and triphenylphosphine 1.00 mg were placed in a two-necked 250 ml flask with one neck connected to a gas line, which in turn was connected to a vacuum line. Toluene was added in the flask and the reaction volume was kept constant at 50.0 ml for every batch. The flask was closed by a stopcock and the system was evacuated and filled with nitrogen gas. The mixture was then placed in a stainless steal autoclave in which a nitrogen atmosphere was present. The autoclave was sealed and the system was evacuated and filled with hydrogen gas 3 times and pressurized with hydrogen up to 30 bar at room temperature. The reaction was heated to the required temperature by circulating a thermostatted liquid through a jacket around the reactor and stirred at 400 rpm. Samples of the solution were collected after 1 min, 1, 3, 6, and 9 hours of the reaction time. This 2.0 ml sampling liquid was passed through an alumina column to eliminate solid. The obtained solution was added with 2.0 ml cyclohexanol (internal standard) and toluene to make volume equal 10.0 ml. The solution was analyzed to determine dihydrobenzothiophene product by using GC. GC-MS data were collected to confirm the identity of the product.

2.6.2 The effect of the concentration of $(PPh_3)_3RuCl_2$ catalyst

The experiments were carried out by varying the concentration of catalyst from 8.00×10^{-4} M to 13.50×10^{-4}M (1.00-1.68 ml) at 150 °C. The concentration of benzothiophene was 8.00×10^{-2} M (2.00 ml) and hydrogen pressure was 30 bar. The procedure is described in Section 2.6.1. The concentration of product versus time was then plotted.

2.6.3 The effect of the concentration of benzothiophene

The experiments were carried out by using the concentration of catalyst at 8.00×10^{-4} M (1.00 ml) and varying the concentration of benzothiophene from 8.00×10^{-2} M to 1.20×10^{-2} M (2.00-3.00 ml) at 150 C and hydrogen pressure 30 bar. The procedure is described in Section 2.6.1. The concentration of product versus time was then plotted.

2.6.4 The effect of concentration of hydrogen gas

The concentration of catalyst and benzothiophene were fixed at 8.00×10^{-4} M (1.00 ml) and 8.00×10^{-2} M (2.00 ml), respectively. The pressure hydrogen gas was varied from 15 to 30 bars. The operation is mentioned in Section 2.6.1. The concentration of product versus time was then plotted.

2.6.5 The effect of hydrodesulfurization temperature

The hydrodesulfurization temperature was investigated by fixing the concentration of catalyst and benzothiophene at 8.00×10^{-4} M (1.00 ml) 8.00×10^{-2} M (2.00 ml), respectively. The reaction temperature was varied from 120 to 160 ± 1 ^{o}C and the operation is described in Section 2.6.1. The concentration of product versus time was then plotted.

2.6.6 The effect of hydrodesulfurization temperature ≥ 200 ^{o}C

The concentration of catalyst and benzothiophene were fixed at 8.00×10^{-4} M (1.00 ml) of $(PPh_3)_3RuCl_2$ and 8.00×10^{-2} M (2.00 ml). The reaction was carried out at hydrogen pressure of 30 bars, reaction temperature at 200, 220 and 250 ± 1 ^{o}C and reaction time 72 hours. The operation is the same as mentioned in Section 2.6.1

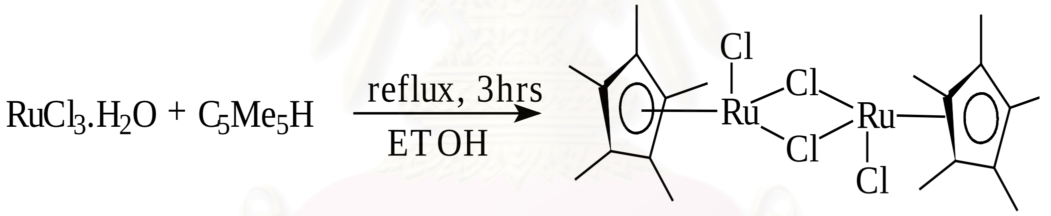
CHAPTER III

RESULTS AND DISCUSSION

3.1 Preparation of Ruthenium Complexes

3.1.1 Pentamethyl cyclopentadienyl ruthenium chloride $[C_5Me_5RuCl_2]_2$

Pentamethyl cyclopentadienyl ruthenium chloride was prepared by the reaction of trichloro ruthenium hydrate with pentamethylcyclopentadiene in refluxing ethanol as shown in equation 3.1.



(3.1)

Trichloro ruthenium hydrate was reacted with pentamethylcyclopentadiene (1 : 3.5 mole ratio) to produce dark brown solution from which $[C_5Me_5RuCl_2]_2$ was isolated in 61 % yield. ^{1}H, ^{13}C- NMR spectra and the data of complex were shown in Figures 3.1, 3.2, Tables 3.1, 3.2, respectively. ^{1}H-NMR spectrum showed a broad signal for methyl proton at 4.3 ppm while ^{13}C-NMR showed a CH_3 group of pentamethylcyclopentadienyl ring at 18.0 ppm and $\underline{C}(CH_3)_3$ at 57.5 ppm.

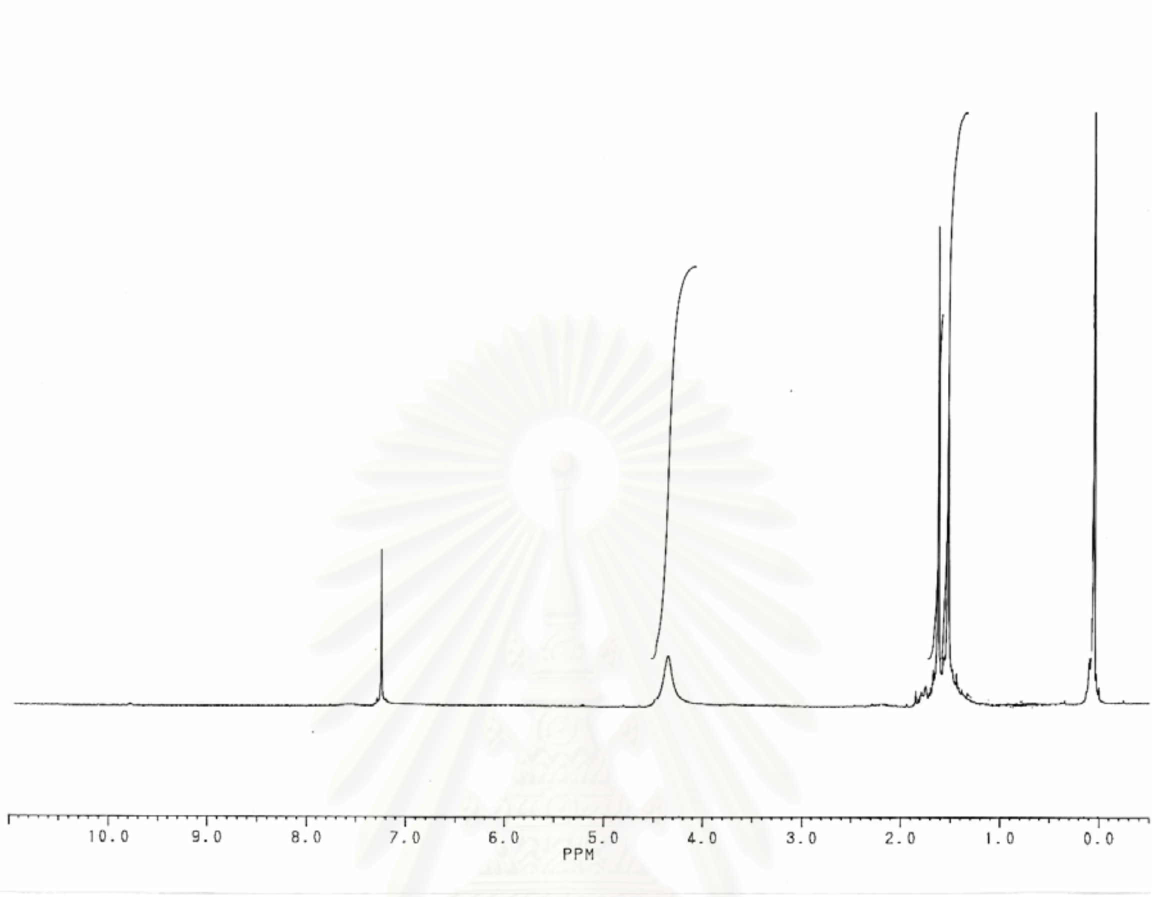


Figure 3.1 ^{1}H-NMR spectrum of pentamethyl cyclopentadienyl ruthenium chloride.

Table 3.1 ^{1}H-NMR data of pentamethyl cyclopentadienyl ruthenium chloride

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
4.35	Singlet	30	CH_3

Reference[48]: ^{1}H-NMR ($CDCl_3$) δ 4.90 ppm.

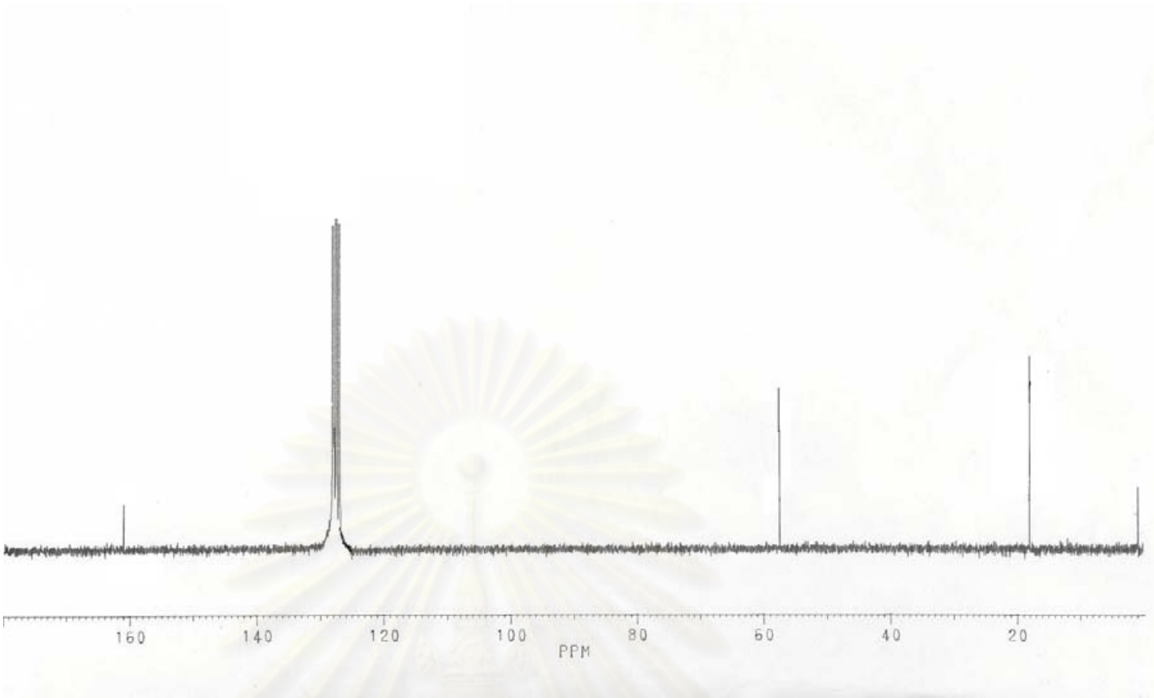


Figure 3.2 $^{13}C\{^1H\}$-NMR spectrum of pentamethyl cyclopentadienyl ruthenium chloride.

Table 3.2 $^{13}C\{^1H\}$-NMR data of pentamethyl cyclopentadienyl ruthenium chloride

Chemical shift (ppm)	Multiplicity	Assignment
57.5	Singlet	$\underline{C}(CH_3)$
18.0	Singlet	$\underline{C}H_3$

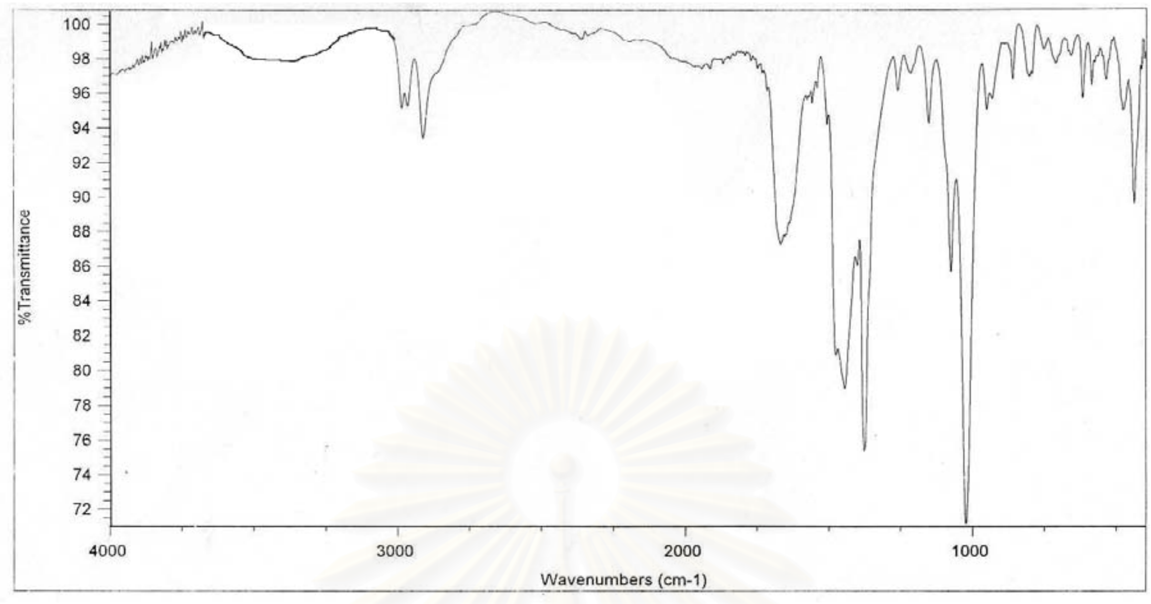


Figure 3.3 FT-IR spectrum of pentamethyl cyclopentadienyl ruthenium chloride.

FT-IR spectrum and data of $[(C_5Me_5)RuCl_2]_2$ were shown in Figure 3.3 and Table 3.3. The spectrum showed $-CH_3$ stretching at 2910-2985 cm^{-1}, Ru-Cl stretching vibration at 436 cm^{-1}.

Table 3.3 FT-IR data of pentamethyl cyclopentadienyl ruthenium chloride

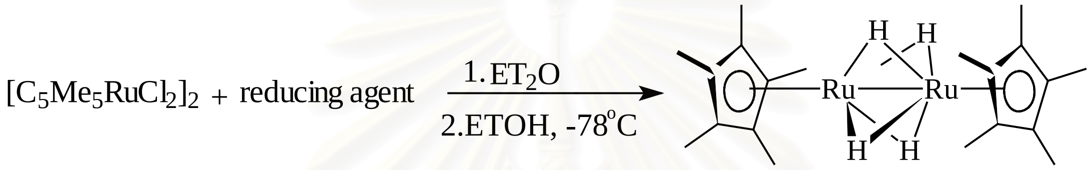
Wavenumber (cm^{-1})	Assignment
2910, 2985	$-C-H_3$ stretching
1668	C=C stretching
1477	$-CH_2$ stretching
1024, 1375	$-CH_3$ stretching
436	Ru-Cl stretching

Reference[48]: IR (KBr) 2983, 2906, 1670, 1478, 1375, 1023 and 440 cm^{-1}.

3.1.2 Ruthenium hydride complex

$[C_5Me_5RuH_2]_2$

The ruthenium hydride $[C_5Me_5RuH_2]_2$ was prepared as a red crystalline solid by the reaction of $[C_5Me_5RuCl_2]_2$ with $LiAlH_4$ (1 : 7.5 mole ratio) as described in the literature[49] and shown in equation 3.2. In addition, this complex can also be prepared using K^tBu_4BH.



(3.2)

reducing agent = $LiAlH_4$, K^tBu_4BH

The structure of $[(C_5Me_5)_2RuH_2]_2$ was revealed by spectroscopic techniques. ^{1}H-NMR spectrum (Figure 3.4) and data (Table 3.4) showed C_5Me_5 resonance at 1.87 ppm and hydride at –13.98 ppm. ^{13}C-NMR spectrum (Figure 3.5) and data (Table 3.5) showed $\underline{C}H_3$ group on pentamethylcyclopentadienyl ring at 12.5 ppm and $\underline{C}(CH_3)_3$ at 88.0 ppm.

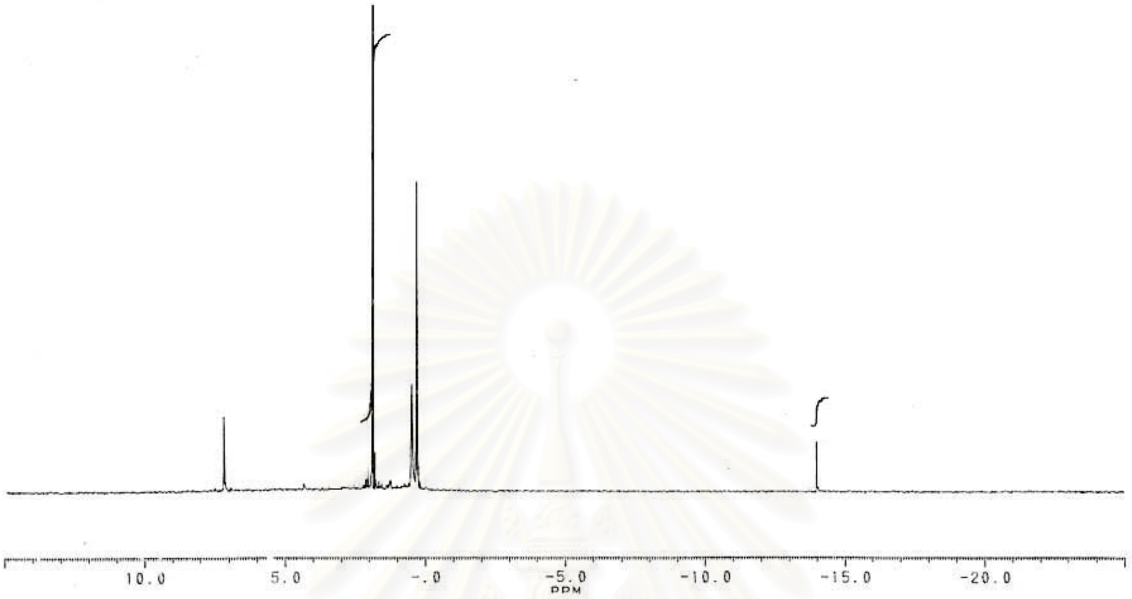


Figure 3.4 ^{1}H-NMR spectrum of ruthenium hydride complex.

Table 3.4 ^{1}H-NMR data of ruthenium hydride complex

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
1.87	singlet	30	$C_5(C\underline{H}_3)_5$
-13.98	singlet	4	H-bridge

Reference[49]: ^{1}H-NMR (C_6D_6) δ 1.87 (s, 30H), -13.99 (s, 4H)

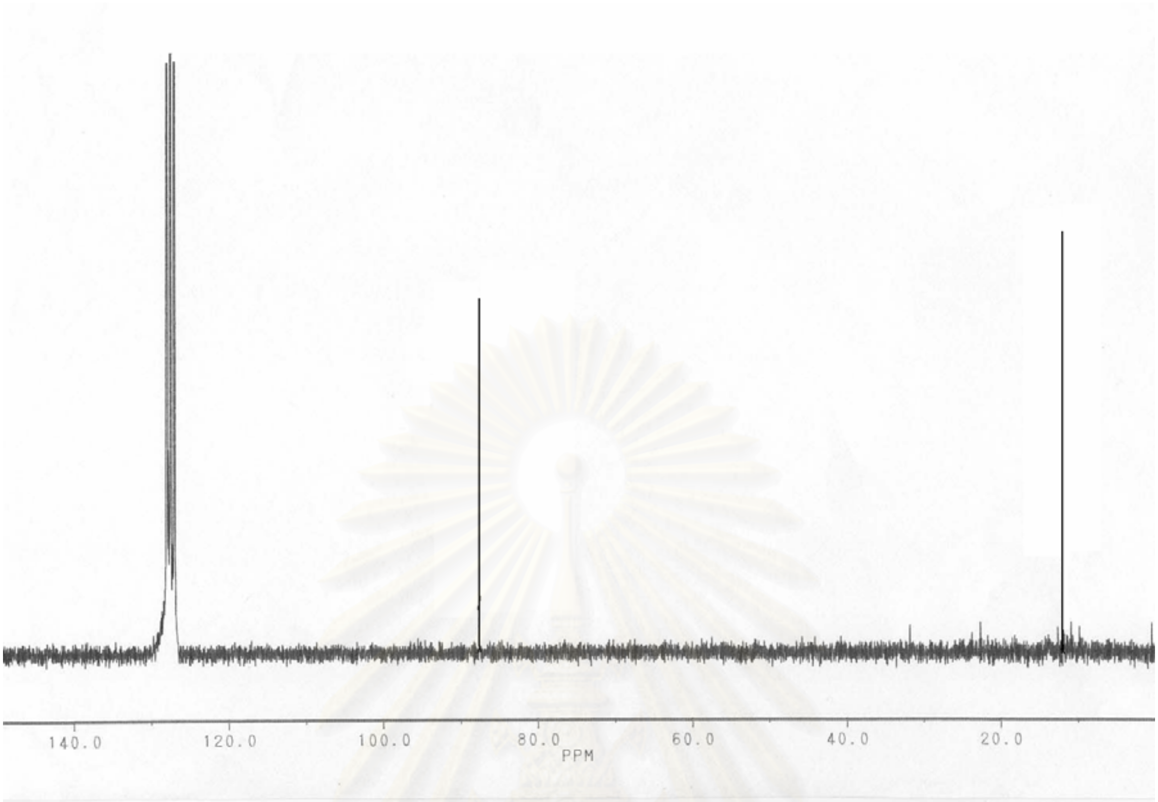


Figure 3.5 $^{13}C\{^{1}H\}$-NMR spectrum of ruthenium hydride complex.

Table 3.5 $^{13}C\{^{1}H\}$-NMR data of ruthenium hydride complex

Chemical shift (ppm)	Assignment
88.0	$\underline{C}_5(CH_3)_5$
12.5	$C_5(\underline{C}H_3)_5$

Reference[49]: ^{13}C-NMR (C_6D_6) δ 88.2 (s, C_5Me_5), 12.5 (s, C_5Me_5)

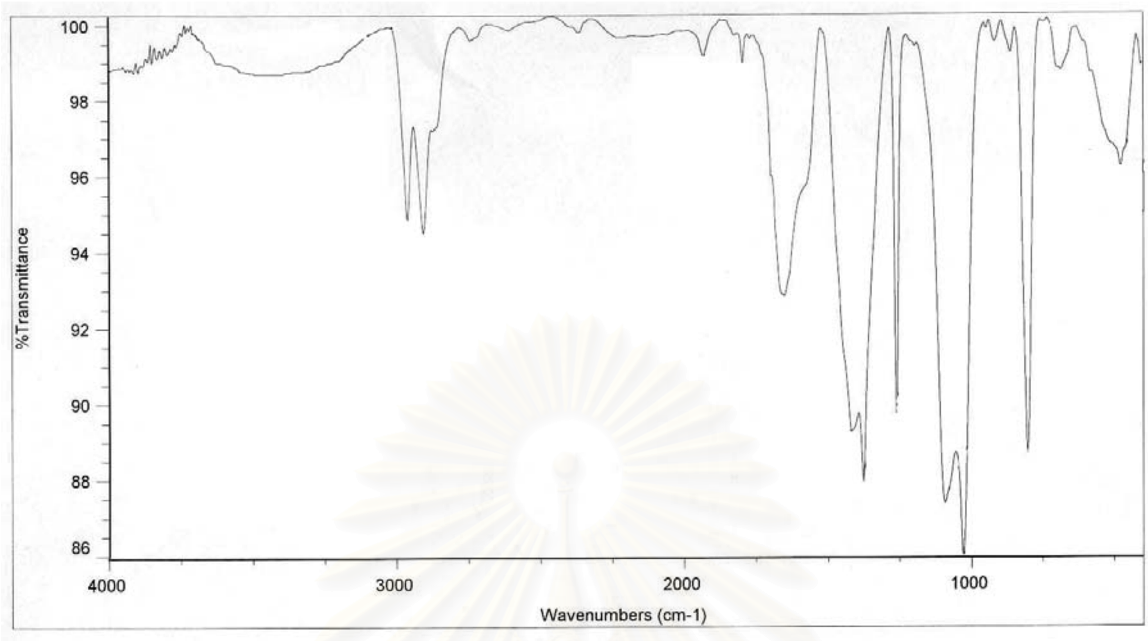


Figure 3.6 FTIR spectrum of ruthenium hydride complex.

FT-IR spectrum is shown in Figure 3.6. In Table 3.6, -CH_3 stretching appears at 1794 cm^{-1}, -C=C- appears at 1652 cm^{-1}. The absence of the characteristic Ru-H absorption in the spectrum suggests that four hydride ligands are positioned on the mirror plane laid between two (η^5-C_5Me_5)Ru units, resulting in no change in dipole moment.

Table 3.6 FTIR data of ruthenium hydride complex

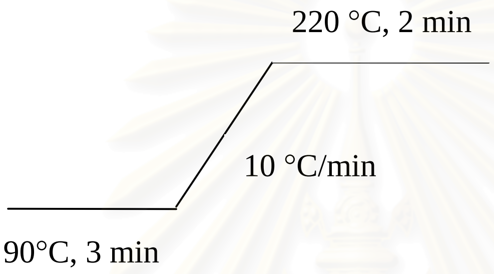
Wavenumber (cm^{-1})	Assignment
2899, 2958	-C-H stretching
1652	C=C stretching
1421	-CH_2 stretching
1026, 1376	-CH_3 stretching

Reference[49]: IR (KBr) 2978, 2954, 2900, 1425, 1376,1027 cm^{-1}

3.2 Determination of % Conversion of Benzothiophene and % Yield of Product

3.2.1 Condition for GC analysis

% Conversion of benzothiophene is detected by using internal standard. The measure data was corrected using effective carbon numbers (Appendix A). The condition of GC used is as follows:



3.2.2 % Conversion of benzothiophene

The data from chromatogram, effective carbon numbers and using cyclohexanol as internal standard was calculated amount of substrate using equation 3.3.

$$mol_x = \frac{C_{std}}{C_x} \times \frac{A_x}{A_{std}} \times mol_{std} \qquad (3.3)$$

where mol_x = mole of substrate

mol_{std} = mol of internal standard

C_x = Carbon effective number of substrate

C_{std} = Carbon effective number of internal standard

A_x = Peak area of substrate

A_{std} = Peak area of internal standard

% Conversion of benzothiophene was calculated from equation 3.4.

$$\%\ \text{Conversion} = \frac{\text{initial mole of benzothiophene - residual of benzothiophene}}{\text{initial mole of benzothiophene}} \times 100 \quad (3.4)$$

3.3 Hydrodesulfurization of Benzothiophene with Ruthenium Hydride as Catalyst

3.3.1 The effect of time

The effect of time in hydrodesulfurization was investigated by varying time: 1, 6, 12, 24, 48 and 72 hours. The reaction conditions were set at room temperature 33 °C, 0.107 mmol of catalyst, 10 mole ratio of benzothiophene/Ru and toluene as solvent. The experimental results and relationship between % conversion versus time are shown in Table 3.7 and Figure 3.7.

Table 3.7 % Conversion of benzothiophene at different time

Time (hour)	% Conversion of benzothiophene
1	7.3
6	25.2
12	39.8
24	49.2
48	57.3
72	61.2

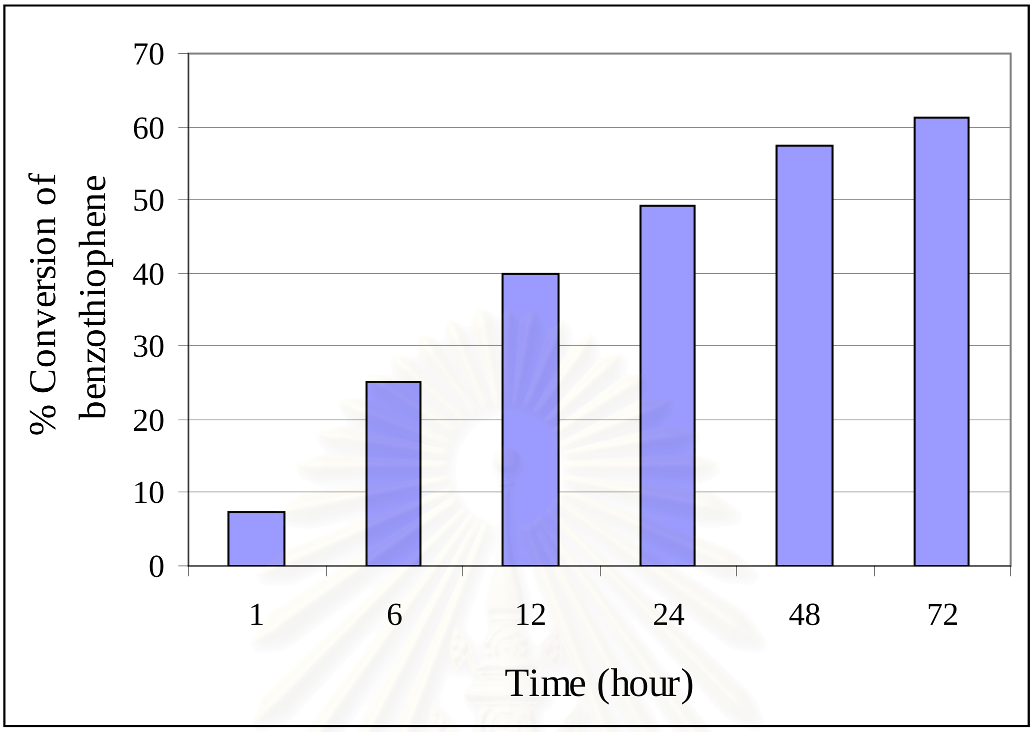


Figure 3.7 Graph plotted between time versus % conversion of benzothiophene.

The results demonstrated that % conversion of benzothiophene increased with time. Maximum % conversion is reached on 48 hrs and slowly increased with further increasing of time. The slowly increasing activity with time over 48 hours might be caused by the decline of active species since the catalyst was used in the reaction. Fourty-eight hours were chosen for further study of hydrodesulfurization of benzothiophene.

3.3.2 The effect of temperature

The hydrodesulfurization temperature was varied: 33, 75 and 110 °C. The other parameters were fixed at 0.107 mmol of catalyst, 10 mole ratio of benzothiophene/Ru and reaction time 48 hours. The experimental results and relationship between % conversions and temperature are shown in Table 3.8 and Figure3.8.

Table 3.8 % Conversion of benzothiophene at different temperature

Temperature (°C)	% Conversion of benzothiophene
33	57.3
75	63.1
110	71.8

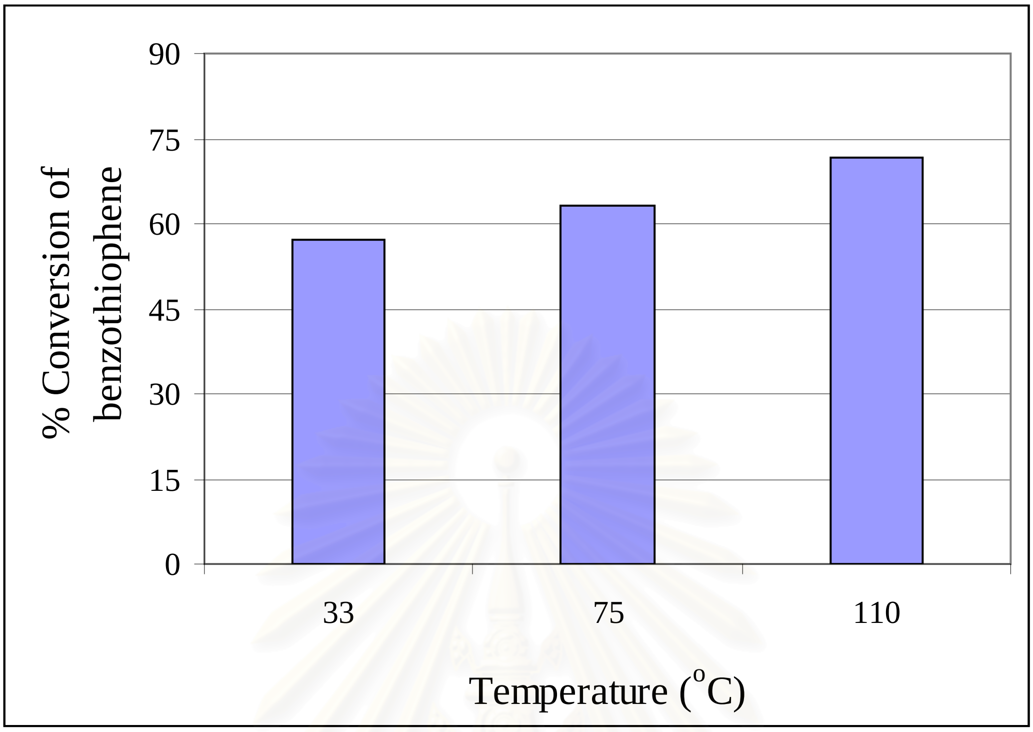


Figure 3.8 Graph plotted between temperature versus % conversion of benzothiophene

From the results, it can be indicated that % conversion of benzothiophene is enhanced with increasing temperature. This data obtained is corresponded with those in the literature.[50-51] Ruthenium carbonyl[8] ($H_4Ru(CO)_8(PPh_3)_4$) was reacted with benzothiophene at 150 ºC and 384 hrs, benzothiophene is converted into dihydrobenzothiophene (42.8 %) while at 170 ºC and 384 hrs the conversion is increased to 81.2 %.

3.3.3 The effect of benzothiophene/Ru mole ratio

The effect of benzothiophene/Ru mole ratio was studied: 5.0, 7.5, 10, 12.5 and 15.0. The reactions were conducted at room temperature, 0.107 mmol of catalyst and reaction time 48 hours. The results are summarized in Table 3.9. The % conversion of benzothiophene versus benzothiophene/Ru mole ratio was plotted in Figure 3.9.

Table 3.9 % Conversion of benzothiophene at different benzothiophene/Ru mole ratio

Benzothiophene/Ru mole ratio	% Conversion of benzothiophene
5.0	82.6
7.5	67.2
10.0	57.3
12.5	57.0
15.0	55.1

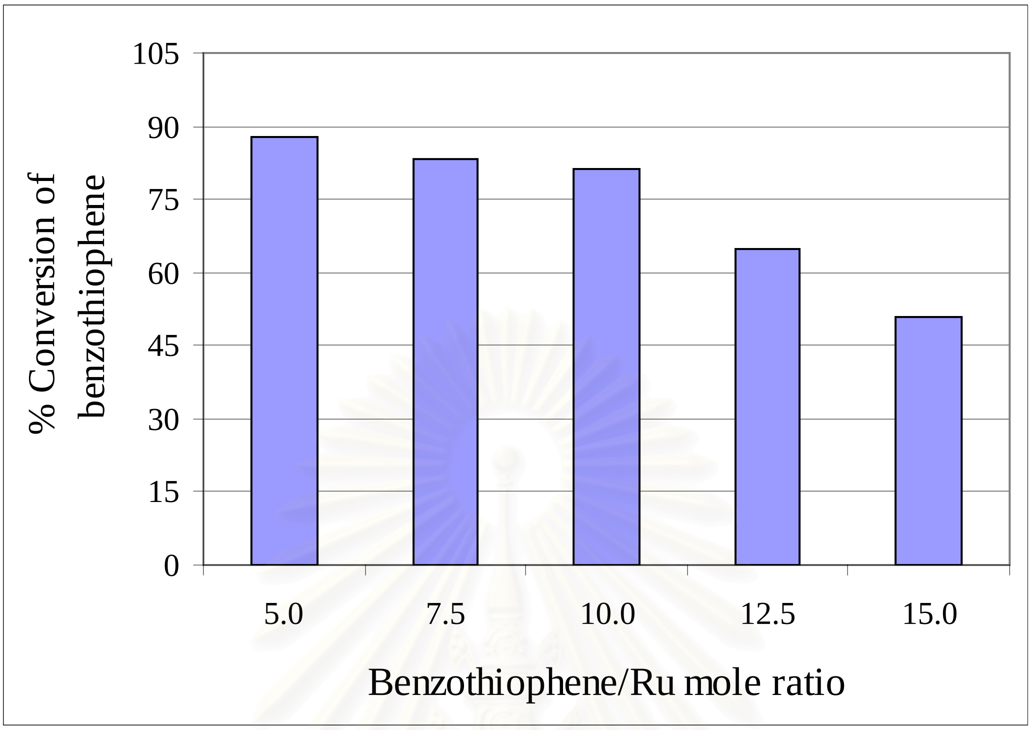


Figure 3.9 Graph plotted between benzothiophene/Ru mole ratio versus % conversion of benzothiophene.

From Figure 3.9, it can be concluded that the benzothiophene/Ru mole ratio affects in hydrodesulfurization. The % conversion shows a tendency to increase with the decrease of benzothiophene/Ru mole ratio. The decreasing % conversion of benzothiophene at benzothiophene/Ru mole ratio higher than 10 may be the steric effect of the bulky molecule of benzothiophene, preventing the approach to the active site of ruthenium hydride.

3.3.4 The effect of hydrogen gas pressure

The hydrodesulfurization was studied by varying hydrogen gas pressure: 1, 10, 20, 30 atm. The other parameters were set at 0.107 mmol of catalyst, 10 mole ratio of benzothiophene/Ru, room temperature and 24 hours. The results are summarized in Table 3.10. The % conversion of benzothiophene versus hydrogen gas pressure is shown in Figure 3.10.

Table 3.10 % Conversion of benzothiophene at different hydrogen gas pressure

Hydrogen gas pressure (atm)	% Conversion of benzothiophene	% Ethyl benzene
1	79.4	12.5
10	88.4	38.1
20	96.5	61.5
30	97.9	73.1

The % conversion of benzothiophene increases with increasing hydrogen gas pressure. In the case of ethyl benzene, it was found to increase with increasing hydrogen gas. From the data, it can be explained that in the hydrogenolysis of benzothiophene, ruthenium hydride causes C-S bond breaking.[52] Then thiolate ligand was hydrogenated with hydrogen gas to yield ethyl benzene.

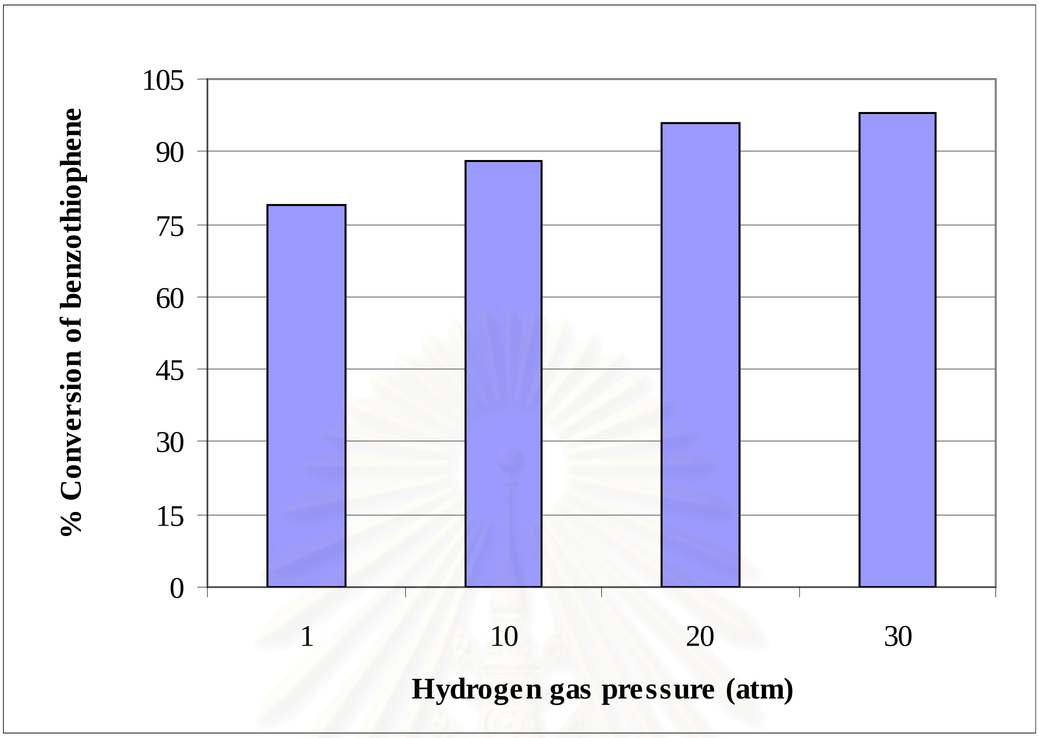


Figure 3.10 Graph plotted between hydrogen gas pressure versus % conversion of benzothiophene.

3.4 Reaction of Ruthenium Hydride Complex with Benzothiophene

$[(C_5Me_5)_2RuH_2]_2$ was reacted with benzothiophene (1:10 mole ratio) at room temperature for 48 hrs. A dark brown product was obtained at 45 % yield.

^{1}H-NMR spectrum and the data of complex are shown in Figure 3.11 and Table 3.11. ^{1}H-NMR spectrum shows ethyl proton on thiolate ligand at 0.99 ($H\text{-}CH_2C\underline{H}_3$), 3.35 ($H\text{-}C\underline{H}_2CH_3$) ppm and protons at two cyclopetadienyl ligands appear at 1.50 and 1.82 ppm.

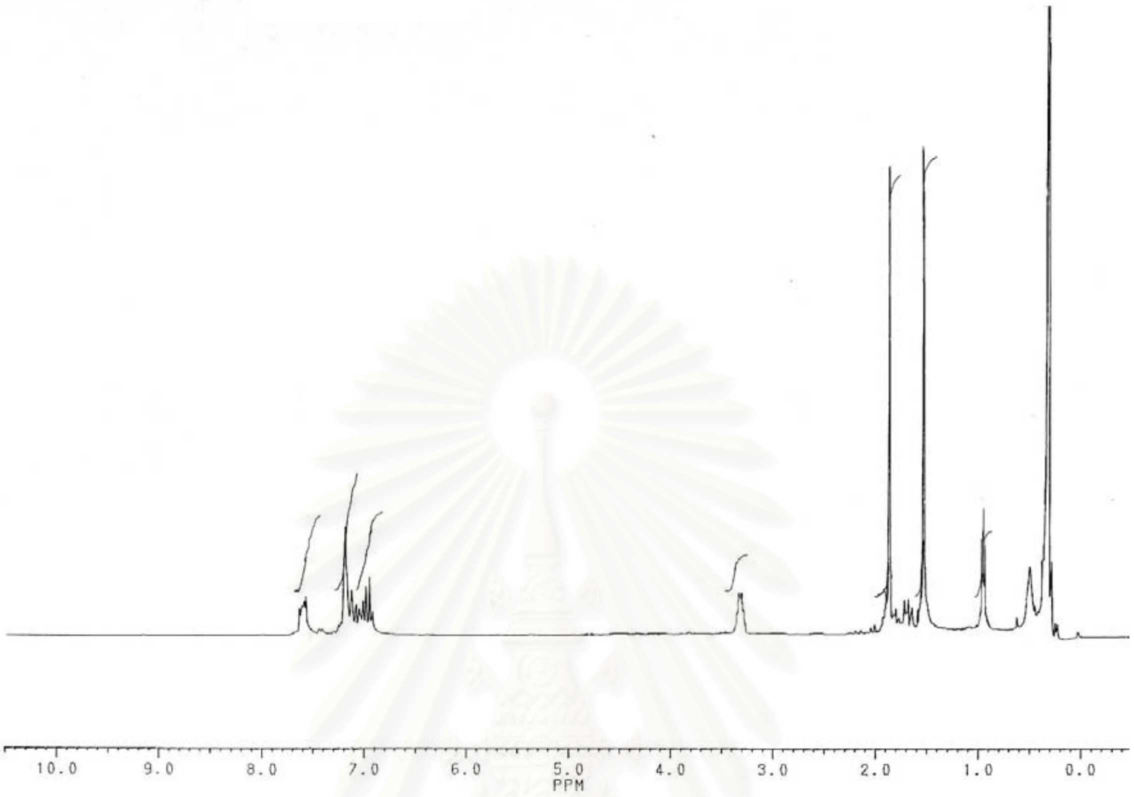


Figure 3.11 ^{1}H-NMR spectrum of the product from the reaction of ruthenium hydride complex with benzothiophene.

^{1}H-NMR spectrum is shown in Figure 3.11 and Table 3.11, protons of pentamethylcyclopentadienyl resonate at 1.50 ppm. Chemical shifts at 0.99 and 3.35 ppm. belong to the thiolate ligand protons. Aromatic ring protons appear around 7.00 ppm. From this peak assignment, it is therefore proposed the structure of the resulting complex as shown in Equation 3.5 . In addition, there appears an extra peak which could be assigned to be another pentamethylcyclopentadienyl ligand. That means that there is more than one complex occurred in this reaction.

Table 3.11 ^{1}H NMR data of the product from the reaction of ruthenium hydride complex with benzothiophene

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
0.99	triplet	3H	$\text{H-CH}_2\text{C}\underline{\text{H}}_3$
1.50	singlet	15H	$\text{H-C}_5(\text{CH}_3)_5$
1.82	singlet	15H	$\text{H-C}_5(\text{CH}_3)_5$
3.35	quartet	2H	$\text{H-C}\underline{\text{H}}_2\text{CH}_3$
7.00	multiplet	4H	H-phenyl
7.70	multiplet	4H	H-phenyl

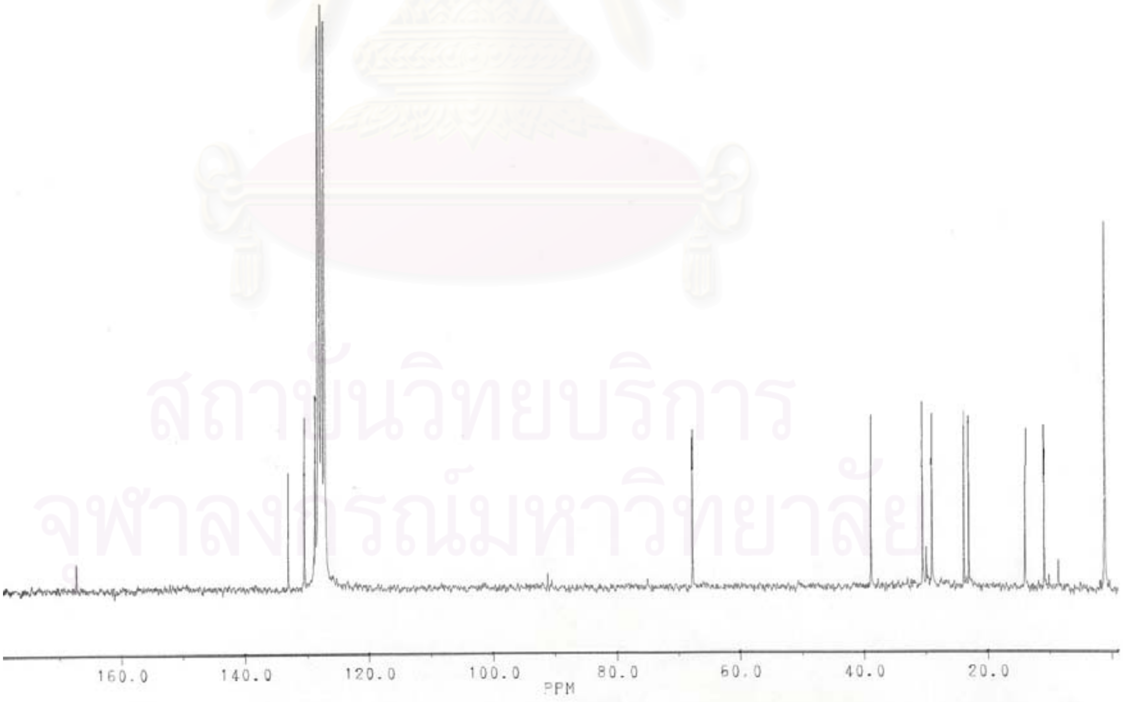


Figure 3.12 ^{13}C{^{1}H}-NMR spectrum of the product from the reaction of ruthenium hydride complex with benzothiophene.

^{13}C-NMR spectrum is shown in Figure 3.12 and Table 3.12, one set of resonances could be assigned to be belonged to the complex proposed in Equation 3.5. They are 10.8 and 67.0 ppm. (pentamethylcyclopentadienyl), 23.0 and 28.9 ppm. (C-$CH_2\underline{C}H_3$ and C-$\underline{C}H_2CH_3$ of the thiolate ligand. Carbon atoms at aromatic rings appear at 127-130 ppm.

In addition, from the spectrum it is appeared another set of peaks (namely, 13.9, and 23.8 ppm.) which revealed the existence of another thiolate ligand. However, the data is not sufficient to make any concrete conclusion unless other data is available. Therefore, it is only able to say that there are probably two complexes occurred from the reaction.

Table 3.12 $^{13}C\{^1H\}$-NMR data of the product from the reaction of ruthenium hydride complex with benzothiophene

Chemical shift (ppm)	Assignment
10.8	C-$C_5(\underline{C}H_3)_5$
13.9	C-$C_5(\underline{C}H_3)_5$
23.0	C-$CH_2\underline{C}H_3$
28.9	C-$\underline{C}H_2CH_3$
67.0	C-$\underline{C}_5(CH_3)_5$
127.1-130.3	C-thiolate

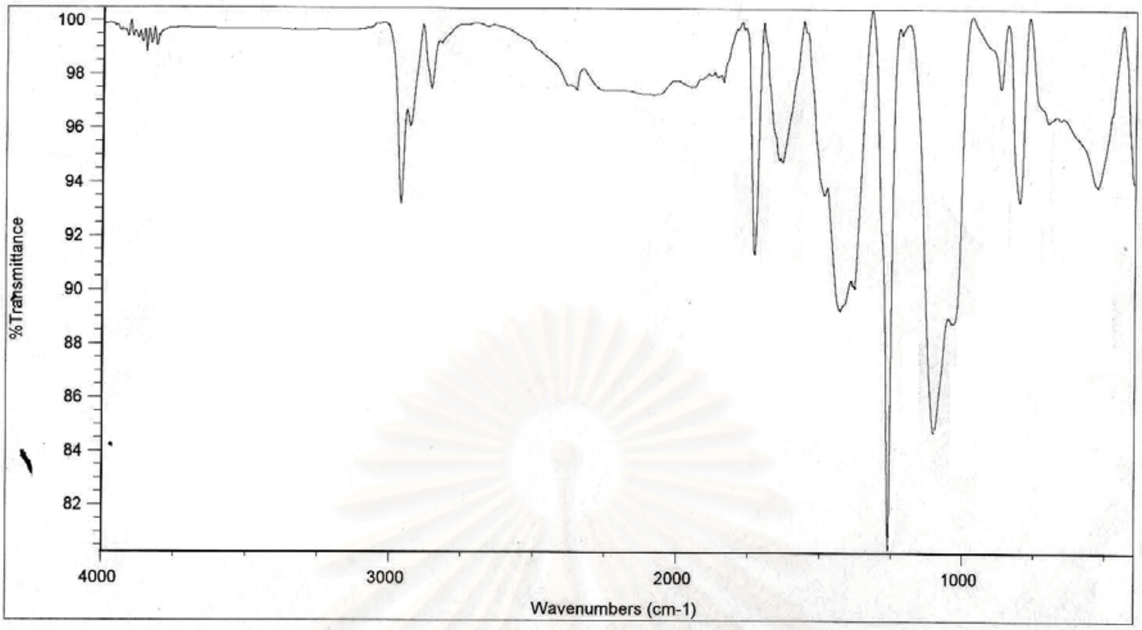


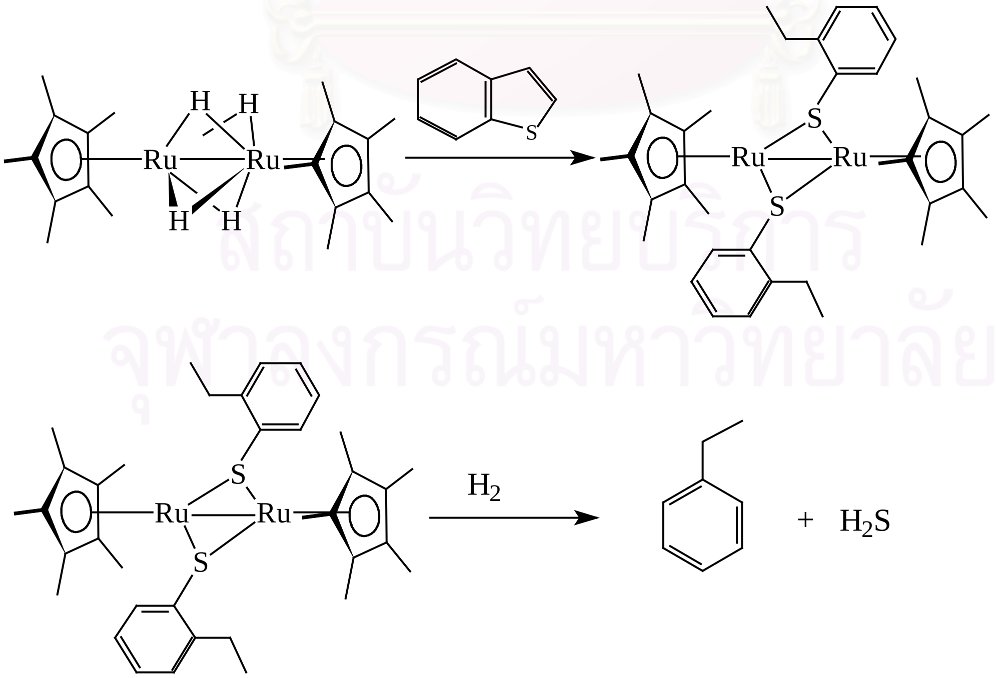
Figure 3.13 FTIR spectrum of the product from the reaction of ruthenium hydride complex with benzothiophene.

FTIR spectrum of the product from the reaction of ruthenium hydride complex with benzothiophene is shown in Figure 3.13 and Table 3.13. The spectrum shows a CH_3 stretching vibration at 2957-2862 cm^{-1}, -C=C- in cyclopentadienyl ring appears at 1631 cm^{-1}.

Table 3.13 FTIR data of the product from the reaction of ruthenium hydride complex with benzothiophene

Wavenumber (cm^{-1})	Assignment
2857, 2962	C-H streching
1631	C=C stretching
1348, 1430, 1488	$-CH_2$ stretching
1033, 1261	$-CH_3$ stretching
802	C-S steching

From the NMR and FT-IR spectra and data, it can be concluded that the product from the reaction of ruthenium hydride with benzothiophene is $[(C_5Me_5)Ru(\mu\text{-}S(C_6H_4CH_2CH_3)]_2$. Furthermore, the product from complete hydrodesulfurization gives ethyl benzene as a final product. The anticipated reaction is shown in equation 3.5.



(3.5)

3.5 Hydrodesulfurization of Benzothiophene by *In-situ*

The hydrodesulfurization was studied by reducing $[C_5Me_5RuCl_2]_2$ with reducing agent: $LiAlH_4$, $NaBH_4$ or KBu_3BH. The other parameters were set at room temperature, 0.107 mmol of catalyst, 10 mole ratio of benzothiophene/Ru and reaction time 48 hours. The result is summarized in Table 3.14. The % conversion of benzothiophene versus benzothiophene/Ru mole ratio is plotted in Figure 3.14.

Table 3.14 % Conversion of benzothiophene using different reducing agent

Reducing agent	% Conversion of benzothiophene
$LiAlH_4$	79.3
$NaBH_4$	63.1
KBu_3BH	55.7

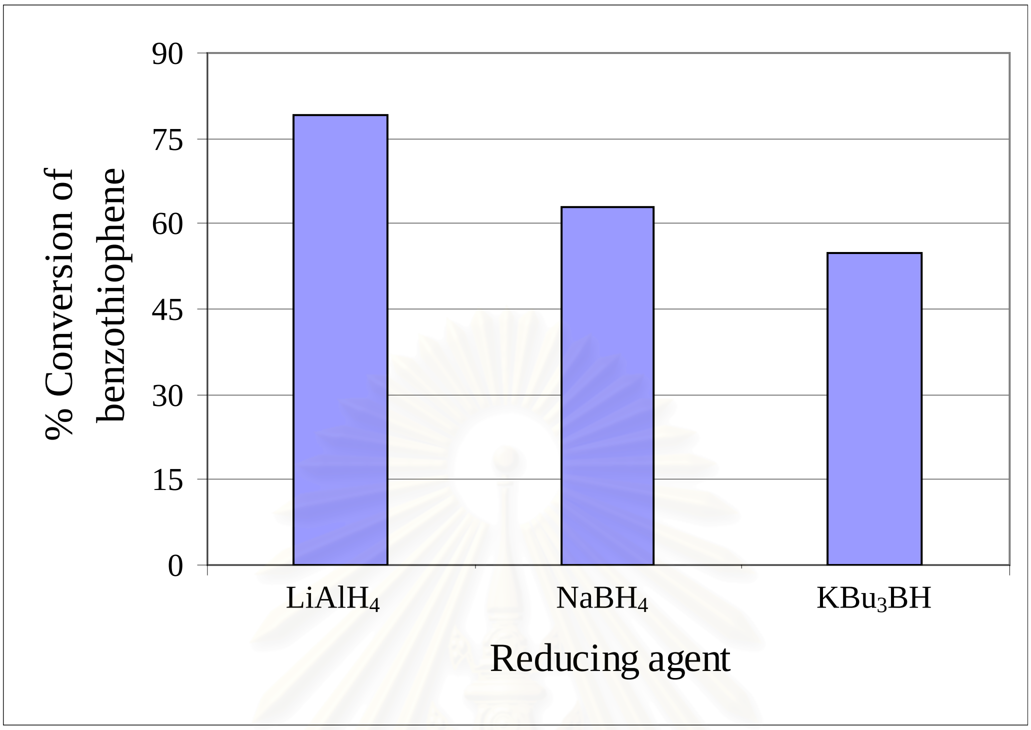


Figure 3.14 Graph plotted between reducing agent versus % conversion of benzothiophene.

From Figure 3.14, it was found that % conversion of benzothiophene depends on type of reducing agent. $LiAlH_4$ is the best reducing agent while KBu_3BH is the poorest. The activity sequence of reducing agent was $LiAlH_4$ > $NaBH_4$ > KBu_3BH. The difference of activity may due to the amount of hydride atom in reducing agent $LiAlH_4$ > $NaBH_4$ > KBu_3BH stabilizes the intermediated in the reaction.

When comparing between the reaction using reducing agent (*in-situ*) and the reaction using ruthenium hydride, it was found that the reaction by *in-situ* gives 79.3% conversion of benzothiophene, while the latter gives 57.3% conversion of benzothiophene. This can be explained that reducing agent may stabilize the reaction intermediate.

3.6 Characterization of Product

3.6.1 Gas chromatography-mass spectrometry

The hydrodesulfurization product is ethyl benzene, which was revealed by GC-MS spectrum(Figure 3.15). It showed peak at m/z = 106.

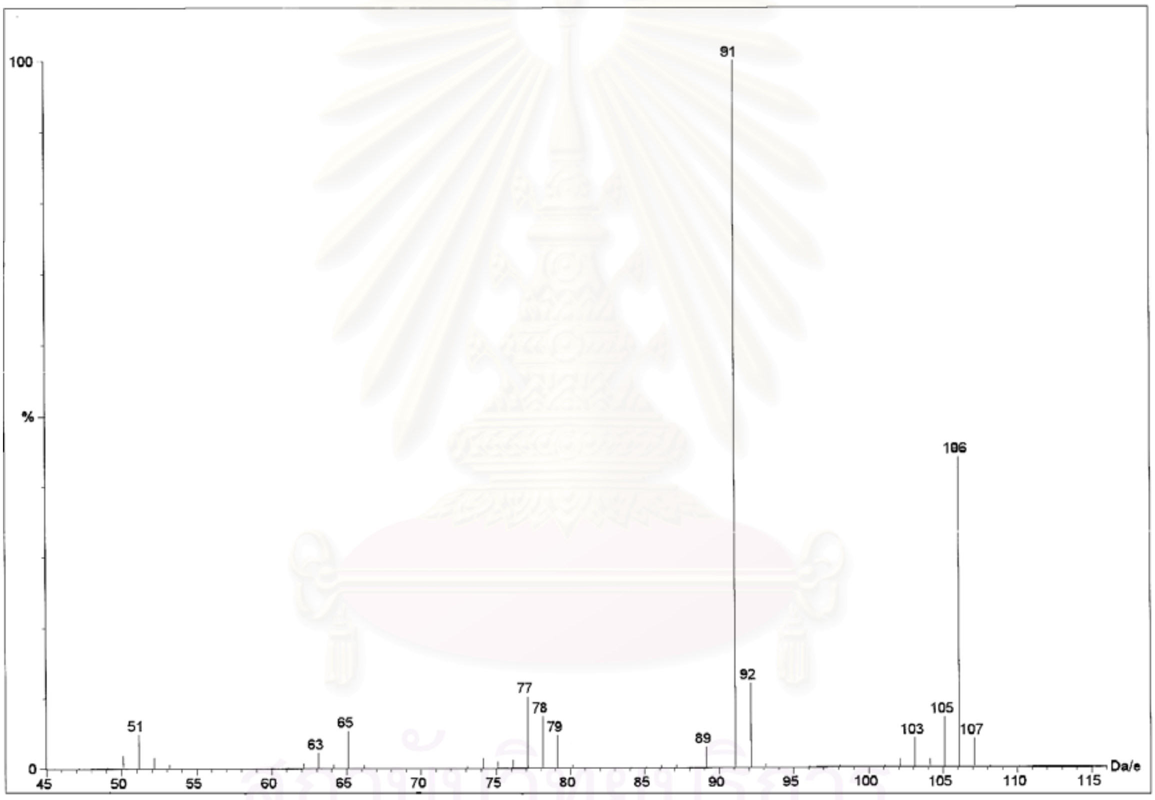


Figure 3.15 Mass spectrum showing ethyl benzene formation

3.6.2 Nuclear magnetic resonance

^{1}H-NMR spectrum (Figure 3.16) and data (Table 3.15) of ethyl benzene showed ethyl proton at 1.08 (H-$CH_2C\underline{H}_3$), 2.42 (H-$C\underline{H}_2CH_3$) ppm and protons at benzene ring appear at 7.01-7.23 ppm.

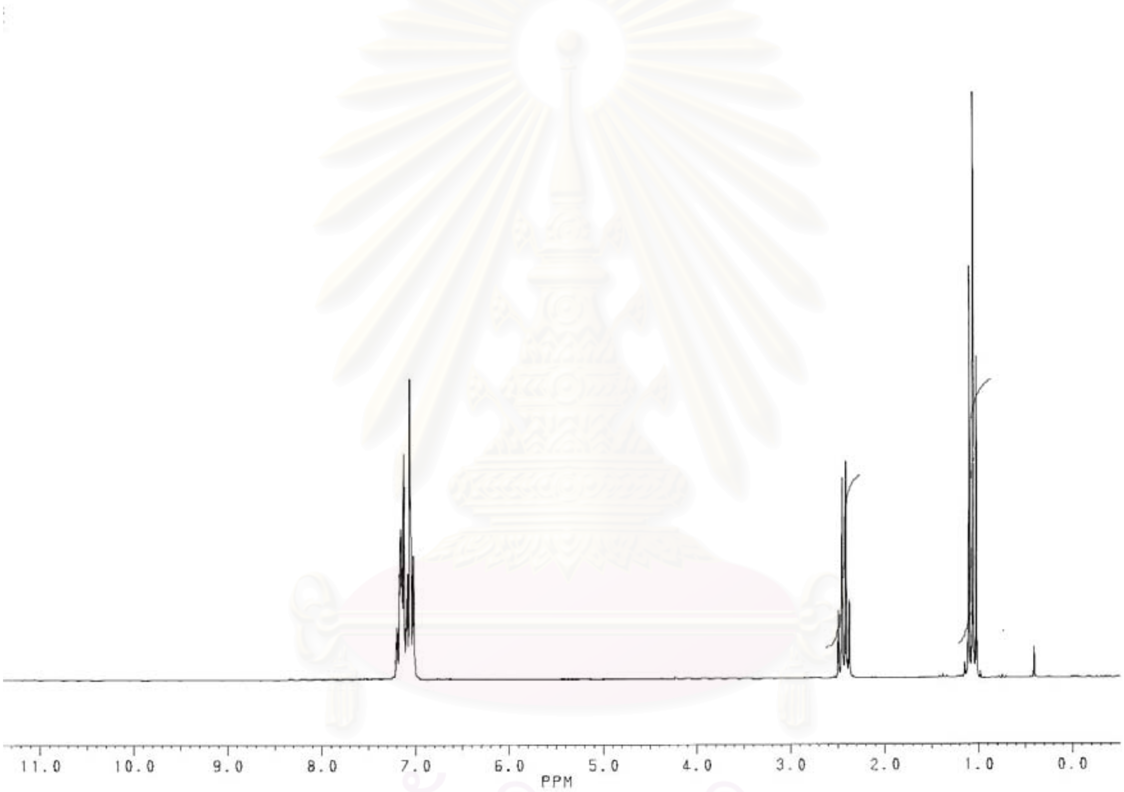


Figure 3.16 ^{1}H-NMR spectrum of ethyl benzene.

Table 3.15 ^{1}H-NMR data of ethyl benzene

Chemical shift (ppm)	Multiplicity	Assignment
1.08	triplet	$H\text{-}CH_2C\underline{H}_3$
2.42	quartet	$H\text{-}C\underline{H}_2CH_3$
7.01-7.23	multiplet	H-phenyl

3.7 Kinetic Studies

The kinetics of the hydrodesulfurization of benzothiophene to dihydrobenzothiophene was studied by using $(PPh_3)_3RuCl_2$ as catalyst. The kinetic runs were carried out at various concentration of catalyst, benzothiophene, hydrogen and at different temperatures. The measured value of DHBT is converted to molar concentration and the data were plotted as molar concentrations of DHBT as a function of time, yielding straight lines. Initial rates were then obtained from the corresponding slope. Example of a plot of concentration of DHBT *versus* time is shown in Figure 3.17 and all plots are shown in Appendix B.

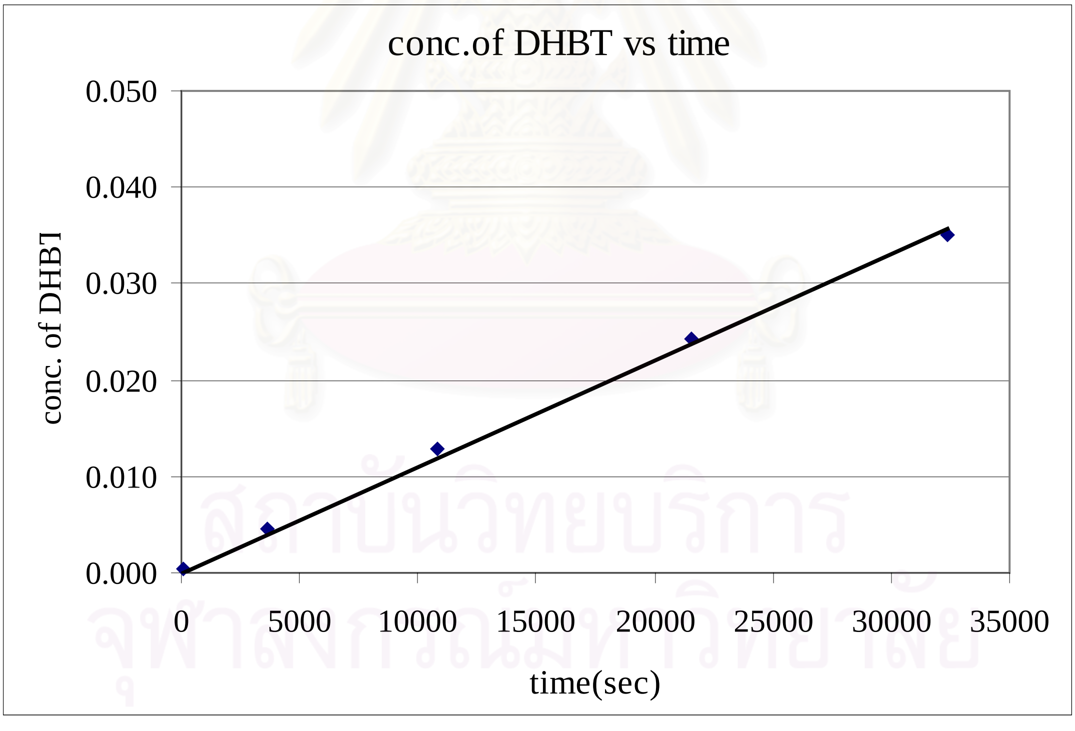


Figure 3.17 A plot of concentration of DHBT versus time.

3.7.1 The effect of the concentration of $(PPh_3)_3RuCl_2$ catalyst

The effect of the concentration of catalyst on the initial rate was investigated in the range of 8.00 x 10^{-4}-13.50 x 10^{-4} M, 8.00 x 10^{-2} M of benzothiophene, 4.05 x 10^{-3} M (30 bar) of hydrogen gas and at 150 ºC. The kinetic data are shown in Table 3.16.

Table 3.16 Kinetic data for the hydrodesulfurization of benzothiophene with $(PPh_3)_3RuCl_2$ as the catalyst at difference concentrations of catalyst, at 150 ºC and hydrogen pressure 30 bar (4.05 x 10^{-3} M)

Entry	10^4[Ru] M	10^2[BT] M	10^3[H_2] M	10^6[ri], Ms^{-1}
1	8.00	8.00	4.05	1.10
2	9.50	8.00	4.05	1.33
3	11.00	8.00	4.05	1.51
4	12.00	8.00	4.05	1.67
5	13.50	8.00	4.05	1.90

The initial rate of hydrodesulfurization of benzothiophene was found to be first-order dependence with respect to catalyst concentration, as confirmed by the plot of log r_i versus log [cat] which yielded straight line with slope of 1.1 and as shown in Figure 3.18.

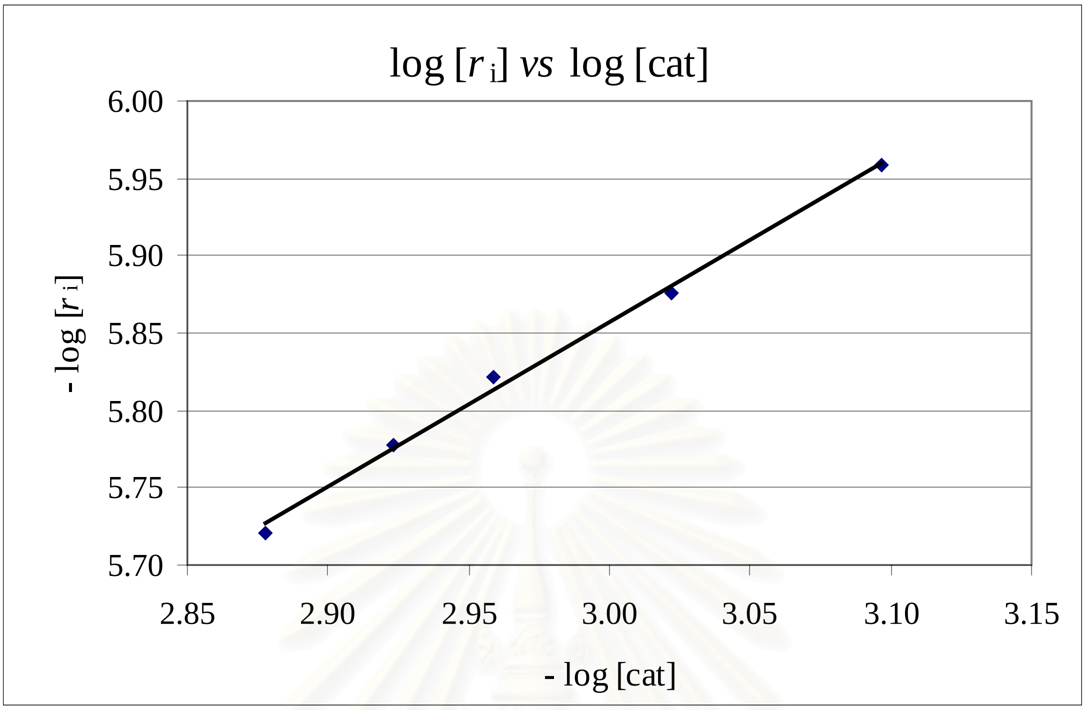


Figure 3.18 Plot of log r_i *versus* log [cat].

3.7.2 The effect of concentration of benzothiophene

The effect of concentration of benzothiophene on initial rate was studied in the range of 6.00 x 10^{-2}-12.00 x 10^{-2} M, 8.00 x 10^{-4} M of catalyst, 4.05 x 10^{-3} M of hydrogen gas and at 150 ºC. The kinetic data are shown in Table 3.17.

Table 3.17 Kinetic data for the hydrodesulfurization of benzothiophene with $(PPh_3)_3RuCl_2$ as the catalyst at different concentration of benzothiophene at 150 ºC and hydrogen pressure 30 bar (4.05×10^{-3} M)

Entry	10^4[Ru]] M	10^2[BT] M	$10^3[H_2]$ M	$10^6[r\mathrm{i}]$, Ms^{-1}
1	8.00	6.00	4.05	1.09
2	8.00	8.00	4.05	1.10
3	8.00	10.00	4.05	1.10
4	8.00	12.00	4.05	1.11

No effect on the rate was detected on varying the benzothiophene concentration by the plot of log r_i *versus* log [benzothiophene](Figure 3.19). The result indicates that the hydrodesulfurization rate is zero order in benzothiophene concentration.

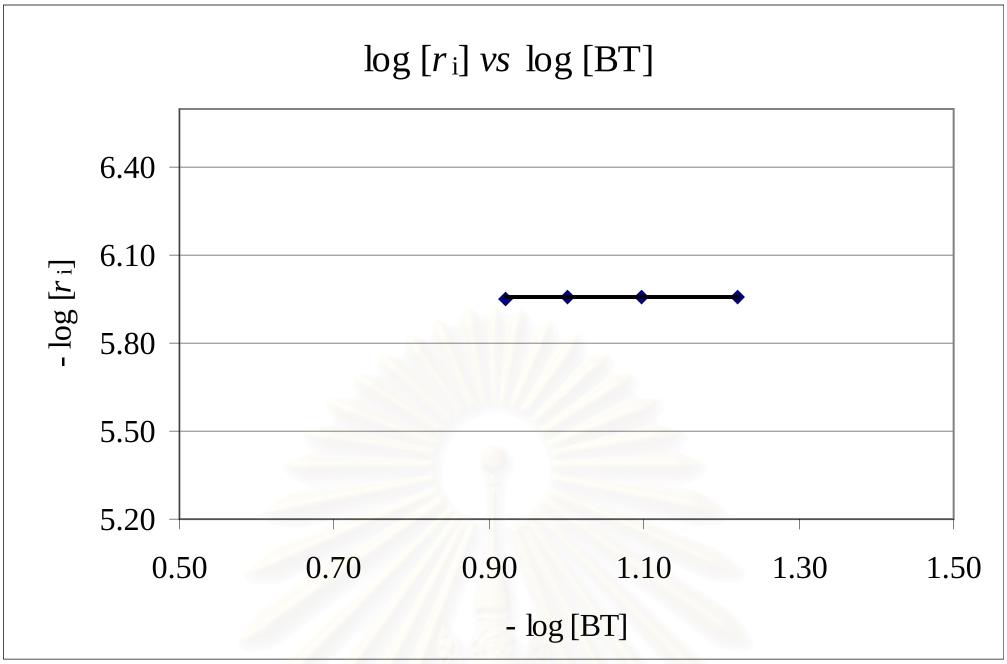


Figure 3.19 Plot of log r_i *versus* log [benzothiophene].

3.7.3 The effect of concentration of hydrogen gas

The effect of concentration of hydrogen gas on the initial rate was investigated in the range of 3.41×10^{-3} - 4.05×10^{-3} M, 8.00×10^{-4} M of catalyst, 8.00×10^{-2} M of benzothiophene and at 150 °C. The kinetic results are shown in Table 3.18.

Table 3.18 Kinetic data for the hydrodesulfurization of benzothiophene with $(PPh_3)_3RuCl_2$ as the catalyst at different concentration of hydrogen gas at 150 °C

Entry	10^4[Ru] M	10^2[BT] M	$10^3[H_2]$ M	$10^6 r$i, Ms^{-1}
1	8.00	8.00	3.41	0.94
2	8.00	8.00	3.60	0.97
3	8.00	8.00	3.82	1.05
4	8.00	8.00	4.05	1.10

The variation of initial rates with hydrogen concentration indicates a first-order dependence with respect to hydrogen concentration as determined by the plot of log r_i *versus* log $[H_2]$, which yielded straight line with slope 1.0, (Figure 3.20).

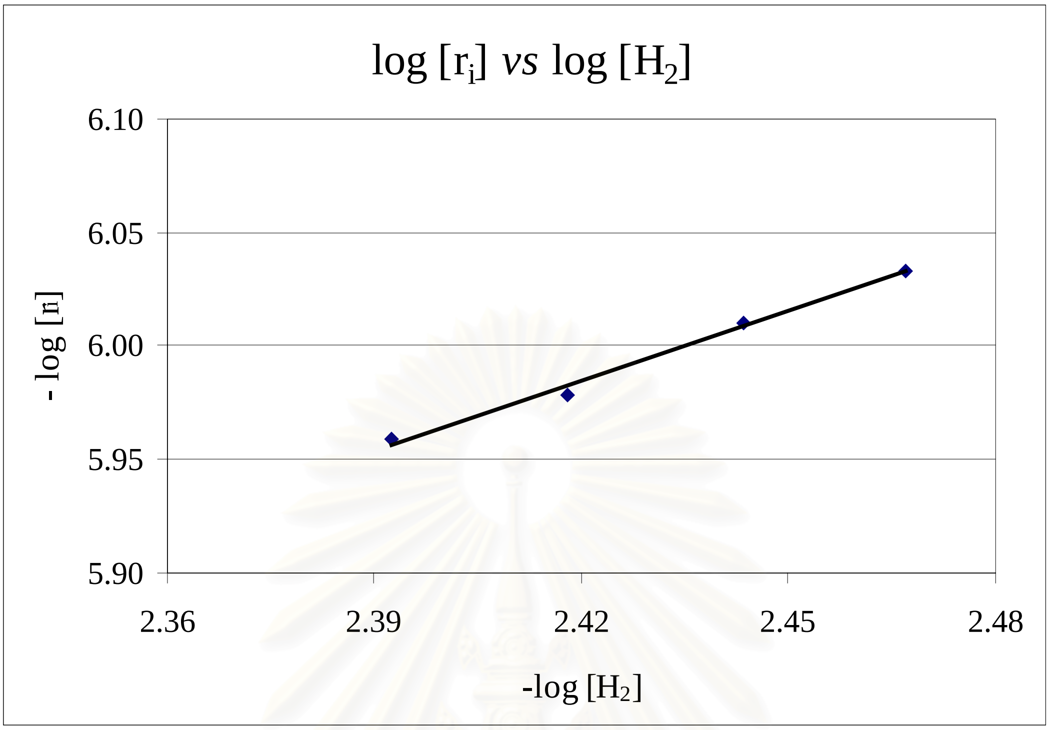


Figure3.20 Plot of log r_i *versus* log [H_2].

The complete data are listed in Table 3.19. It is concluded that the initial rate of hydrodesulfurization of benzothiophene is first order with respect to catalyst and hydrogen concentration and zero order with respect to benzothiophene concentration.

Table 3.19 Kinetic data for the hydrodesulfurization of benzothiophene with $(PPh_3)_3RuCl_2$ as the catalyst at 150 ^{o}C

Entry	10^4[Ru]	10^2[BT]	$10^3[H_2]$	$10^6 r$i, Ms^{-1}	k_{cat}, $M^{-1}s^{-1}$
1	8.00	8.00	4.05	1.10	0.340
2	9.50	8.00	4.05	1.33	0.345
3	11.00	8.00	4.05	1.51	0.339
4	12.00	8.00	4.05	1.67	0.344
5	13.50	8.00	4.05	1.90	0.348
6	8.00	6.00	4.05	1.10	0.341
7	8.00	10.00	4.05	1.10	0.340
8	8.00	12.00	4.05	1.11	0.342
9	8.00	8.00	3.41	0.94	0.344
10	8.00	8.00	3.60	0.97	0.339
11	8.00	8.00	3.82	1.05	0.343

Consequently, the experimental rate law can be written as the following:

$$d[DHBT]/dt = k_{cat}[cat][H_2] \quad (3.4)$$

The average value for the catalytic rate constant at 423 K was calculated from eq. 3.4: $k_{cat} = 0.34 \pm 0.01\ M^{-1}s^{-1}$. The experimental rate law found for ruthenium complex in toluene (eq 3.4) is identical to $[Rh(COD)(PPh_3)_3]PF_6$ in 2-methoxyethanol as solvent[42] (rate law = $d[DHBT]/dt = k_{cat}[Rh][H_2]$). The activity of the ruthenium complex in this experiment is higher than that observed for Rh complex in 2-methoxyethanol as solvent ($k_{cat} = 1.24 \times 10^{-4}\ M^{-2}s^{-1}$). On the contrary, rate constant for this ruthenium complex is lower than that for $[Rh(COD)(PPh_3)_3]PF_6$ in 1, 2-dichloroethane (k_{cat} = 131 $M^{-1}s^{-1}$). It can be explained that coordinating solvent such as 2-methoxyethanol can compete with the benzothiophene substrate for the vacant coordination site. The efficient competition can slow down the reaction. On the other hand toluene and 1, 2-dichloroethane coordinate poorly to the metal and thus favor higher concentration of unsaturated complexes. These complexes may then bind benzothiophene effectively, resulting in the higher catalytic rates observed in these two solvents.

This rate law differs from the one deduced for the catalytic hydrogenation of benzothiophene by $K[(triphos)RuH]^+$. It is reported that rate = $k_{cat}[Ru][HT][H_2]$ and k_{cat} = 1.01×10^3 $M^{-2}s^{-1}$ at 46 °C and low hydrogen pressure. The steric crowding of coordinating ligand (triphos) at the metal center provides an explanation for higher activity of $K[(triphos)RuH]^+$ complex as compared with $(PPh_3)_3RuCl_2$ catalyst.

3.7.4 The effect of hydrodesulfurization temperature

The effect of temperature on the rate constant was studied in the range of 393-433 K (120-160 ^oC) for the concentration of catalyst at 8.00×10^{-4} M, benzothiophene at 8.00×10^{-2} M and dissolved hydrogen at 4.05×10^{-3} M. The result is shown in Table 3.20.

Table 3.20 Kinetic data for the hydrodesulfurization of benzothiophene with $(PPh_3)_3RuCl_2$ as the catalyst at different temperatures

Entry	10^4[Ru] M	10^2[BT] M	$10^3[H_2]$ M	T, ^oC	$10^6 ri$, Ms^{-1}	k_{cat}, $M^{-1}s^{-1}$
1	8.00	8.00	4.05	120	0.96	0.140
2	8.00	8.00	4.05	130	1.00	0.202
3	8.00	8.00	4.05	140	1.05	0.278
4	8.00	8.00	4.05	150	1.10	0.340
5	8.00	8.00	4.05	160	1.30	0.431

The rate of reaction is affected by temperature, the most common behavior is that observed by Arrhenius.[53] The empirical expression is shown in equation 3.5.

$$k = A \exp(-Ea/RT) \qquad (3.5)$$

Thus a plot of ln k_{cat} *versus* $1/T$ allowed us to calculate the activation energy E_a (slope = $-E_a/R$)(Figure 3.21).

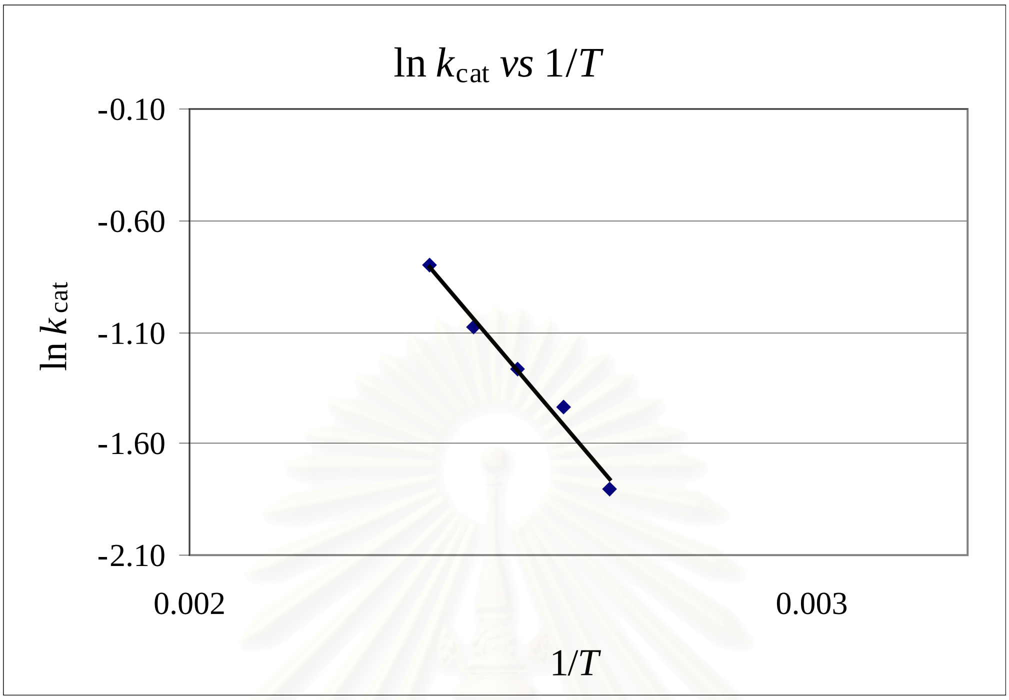


Figure 3.21 Plot of ln (k_{cat}) *versus* 1/*T*

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The values of enthalpy, entropy and free energy of activation were calculated from Eyring plot.[54] The related parameter are shown in eqs. 3.6 and 3.7.

$$\ln (k/T) = \ln (k_b/h) + \Delta S^{\neq}/R - \Delta H^{\neq}/RT \quad (3.6)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (3.7)$$

A plot of ln (k_{cat}/T) *versus* 1/*T* (Figure3.22) allowed us to calculate $\Delta H^{\neq}$ (slope = $\Delta H^{\neq}/R$), and intercept ($\ln k_b/h + \Delta S^{\neq}/R$) = ($23.8 + \Delta S^{\neq}/R$). Activation parameters for the hydrodesulfurization of benzothiophene with $(PPh_3)_3RuCl_2$ as the catalyst are listed in Table 3.21.

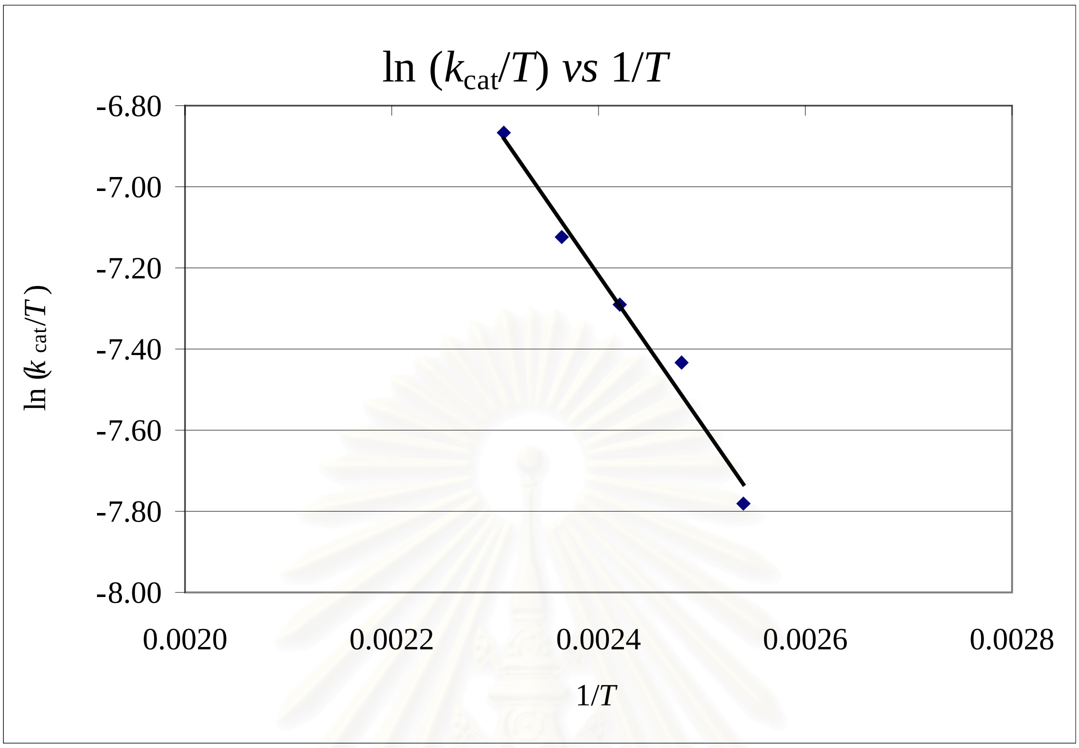


Figure 3.22 Plot of ln (k_{cat}/T) *versus* 1/T.

Table 3.21 Activation parameters for the hydrodesulfurization of benzothiophene with $(PPh_3)_3RuCl_2$ as the catalyst

Activation parameters	
Ea (k_{cal}/mol)	8.166 ± 0.001
k_{cat} (150 °C)($M^{-2}s^{-1}$)	0.34 ± 0.01
$\Delta H^{\neq}$ (k_{cal}/mol)	7.33 ± 0.02
$\Delta S^{\neq}$ (eu)	-44 ± 1
$\Delta G^{\neq}$ (k_{cal}/mol)	25.9 ± 0.1

Activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ can provide information on the structure of the trasition state complex. The value of $\Delta H^{\neq}$ and negative $\Delta S^{\neq}$ indicate that the transition state is formed early in the reaction. Large negative $\Delta S^{\neq}$ for the reaction implies a high degree of bond formation with little bond breakage.

3.8 Characterization of Product

3.8.1 Gas chromatography-mass spectroscopy

Dihydrobezothiophene is one of the products from hydrodesulfurization catalyzed by $(PPh_3)_3RuCl_2$. GC-MS spectrum (Figure 3.23) showed m/z = 136, which is the molecular mass of dihydrobenzothiophene. Moreover, the other product identified by GC is ethyl benzene.

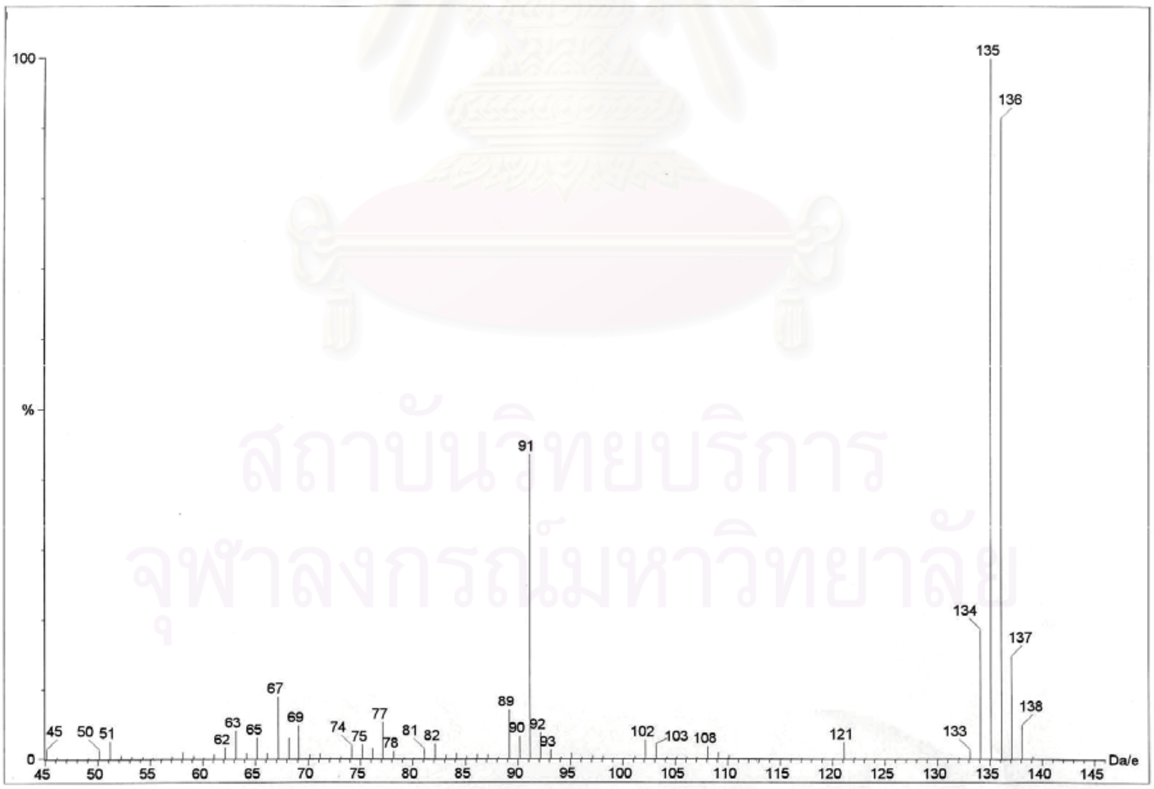
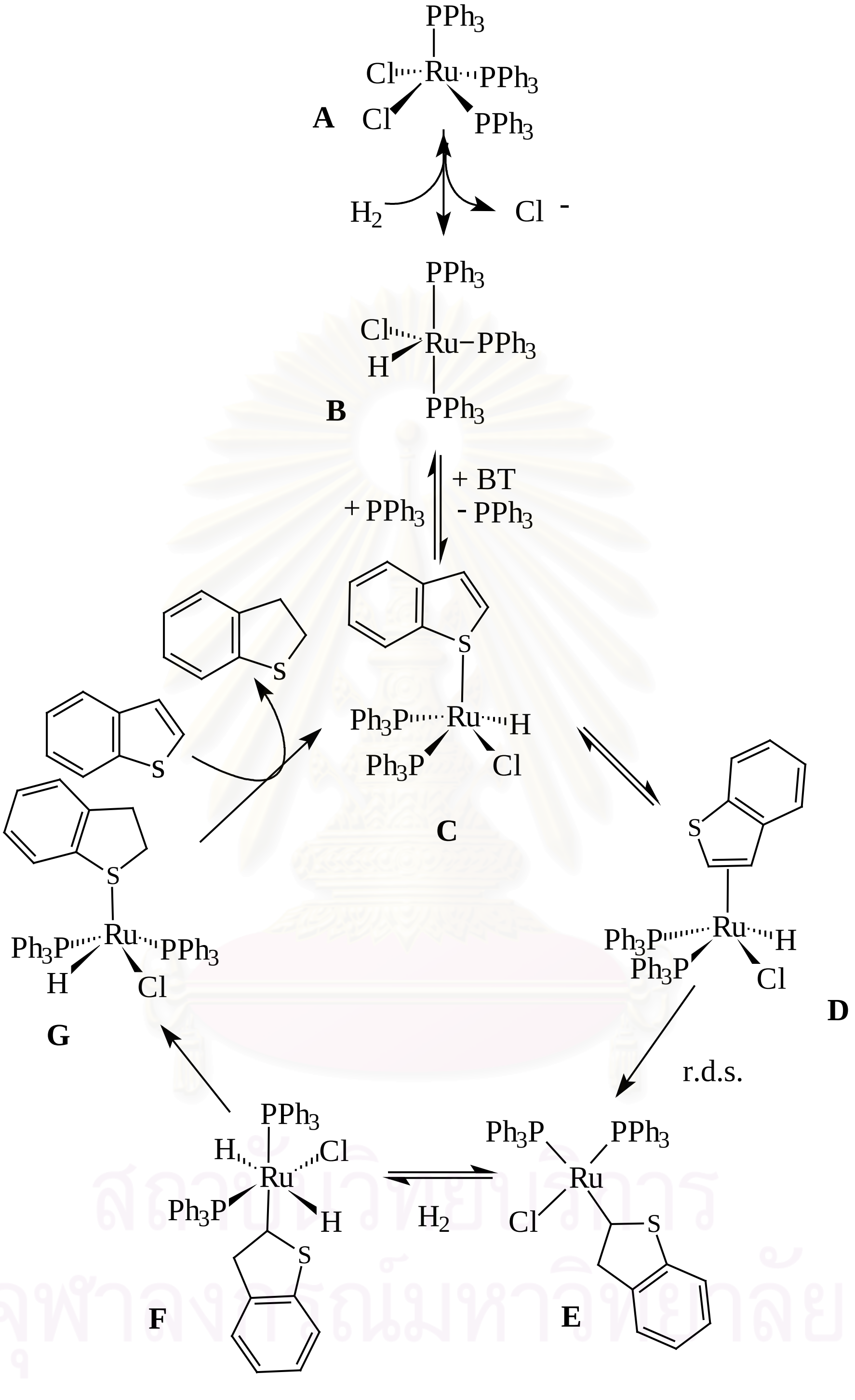


Figure 3.23 Mass spectrum of dihydrobenzothiophene.

3.9 The Mechanism of Benzothiophene Hydrodesulfurization

From rate law d[DHBT]/dt = k_{cat}[Ru][H_2], it means that the reaction rate is first order with respect to both of the catalyst and hydrogen gas concentrations. The rate law found in this experiment is identical to the one determined for the rhodium system in 2-methoxyethanol. It is suggested that the mechanisms for both catalysts are closely related. The mechanism is proposed in Scheme 3.1. $(PPh_3)_3RuCl_2$ catalyst is rapidly transformed into complex **B** by dissociation of chrolide ion and addition of H_2. The benzothiophene may approach the metal using either the sulfur atom or the C2-C3 double bond or equilibrium between these two bonding modes.[55-57] The η^2-benzothiophene coordination mode is generally accepted to be the crucial one for the hydrogenation of the thiophenic ring.[58] Hydride migration has previously been proposed to take place onto C_2 or C_3 to produce a 3- or 2-hydridobezothienyl complex, respectively. On the basis of theoretical studies including recent ab initio calculation, it indicates that the C_2 atom of free benzothiophene has a greater negative charge than the C_3 atom, a 2-hydridobenzothienyl intermediate (**E**) is most likely. Oxidative addition of H_2 to complex **E** is a well-known process, eventually occurring complex **F**. Transfer of the hydride to coordinated complex hydrobenzothiophene generates complex **G**. This complex reacts with benzothiophene and dissociates dihydrobenzothiophene to regenerate **C.**



Scheme 3.1 Proposed mechanism of hydrodesulfurization of benzothiophene catalyzed by $(PPh_3)_3RuHCl$.

In addition to dihydrobenzothiophene, a small amount of ethyl benzene is also obtained as product. It is suggested that hydrodesulfurization of benzothiophene proceeds through hydrogenation of benzothiophene and then hydrogenolysis to give ethyl benzene.

3.10 The Effect of Hydrodesulfurization Temperature ≥ 200 °C

Hydrodesulfurization of benzothiophene catalyzed by $(PPh_3)_3RuCl_2$ was carried out at 200-250 °C and hydrogen pressure 30 bar. The other parameters were 8 x 10^{-4} M of catalyst, 8 x 10^{-2} M of benzothiophene and reaction time 24 hours. The results were summarized in Table 3.22. The % conversion of benzothiophene versus temperture is shown in Figure 3.24.

Table 3.22 Hydrodesulfurization of benzothiophene catalyzed by $(PPh_3)_3RuCl_2$ as catalyst

Temperature (ºC)	% conversion of benzothiophene	% DHBT	% ethyl benzene
200	70.1	51.1	7.8
220	79.6	54.4	11.6
250	89.4	58.3	21.3

From the experimental data, it reveals that % conversion of benzothiophene increases with increasing temperature. The amount of dihydrobenzothiophene and ethyl benzene also increase with increasing temperature. This result is similar to that obtained from using $[C_5Me_5RuH_2]_2$ catalyst. However, the mechanisms of the two catalyzed reactions are different. Hydrodesulfurization of benzothiophene catalyzed by (PPh_3)

$_3RuCl_2$ is hydrogenation prior to hydrgenolysis reaction. In the case of ruthenium hydride complex, the reaction is hydrogenolysis prior to hydrogenation.

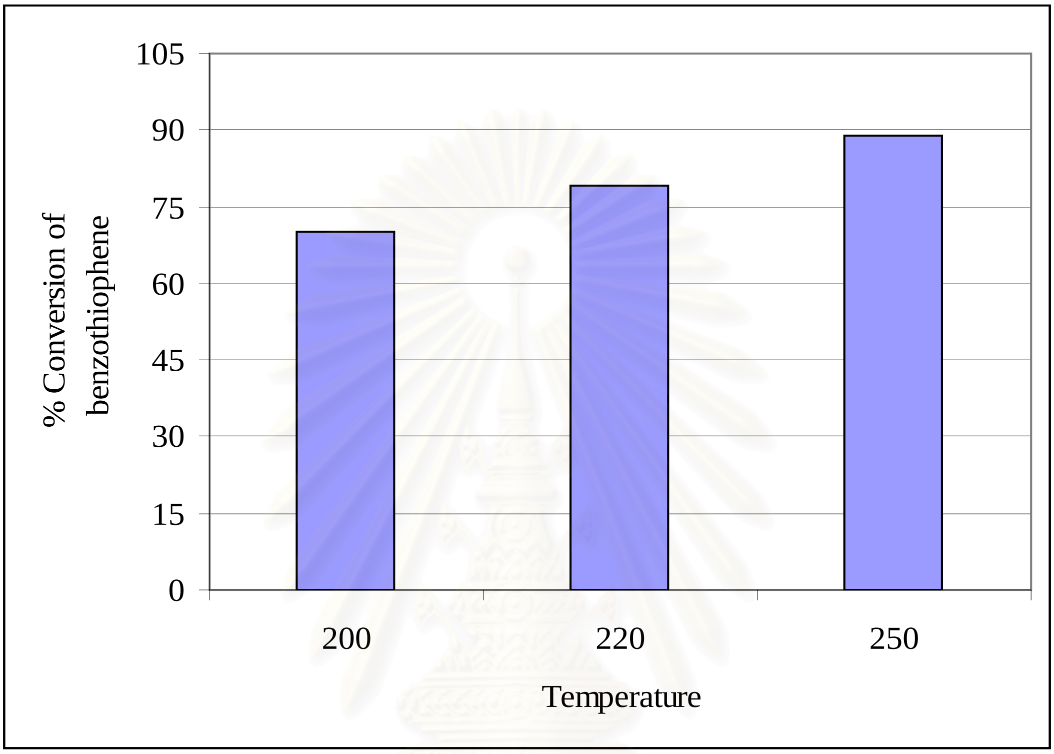


Figure 3.24 Plot of % conversion of benzothiophene versus temperature.

CHAPTER IV

CONCLUSIONS

4.1 Conclusions

The preparation of ruthenium hydride has two steps. (I) Pentamethyl cyclopentadienyl ruthenium chloride $[C_5Me_5RuCl_2]_2$ which was prepared from $RuCl_3.H_2O$ and $(CH_3)_5C_5$ (1 : 3.5 mole ratio) in the reflux ethanol. The product obtained is 61 % yield. (II) Ruthenium hydride $[C_5Me_5RuH_2]_2$ was prepared by the reaction of $[C_5Me_5RuCl_2]_2$ with $LiAlH_4$ (1 : 10 mole ratio)(42 %yields), this complex can also be prepared using KBu_3BH (23 % yields). Factor affecting the hydrodesulfurization reaction of benzothiophene in toluene as solvent were studied: time, benzothiophene/Ru mole ratio, temperature and hydrogen gas pressure. From the experimental data, the optimum conditions of hydrodesulfurization of benzothiophene are reaction time 48 hours, 10 mole ratio of benzothiophene/Ru and temperature at 110 ^{o} C. At the best condition % conversion of benzothiophene was 75 %. The addition of hydrogen gas 30 bars into the reaction, % conversion is increased to 98 % and gives ethyl benzene as one final product. In addition, the reaction by *in-situ* gives % conversion of benzothiophene 79.3 % which higher than that using ruthenium hydride. The reaction complex was characterized by NMR and FTIR spectroscopies. From all the experimental data, it was found that $[C_5Me_5RuH_2]_2$, in the presence of H_2, was able to completely hydrodesulfurize benzothiophene to ethyl benzene. Hydrodesulfurization reactions proceed via organometallic intermediates containing bridging thiolate ligand. The further evidence supportes that cleavage of both carbon-sulfur bonds may require the one metal center with the capability to form to form a bridging thiolate intermediate.[32, 34-35]

Kinetic measurement of benzothiophene hydrodesulfurization using $(PPh_3)_3RuCl_2$ catalyst was investigated. The reaction was carried out in Parr Reactor and toluene as solvent. The kinetic runs were done at different concentrations of catalyst, benzothiophene, hydrogen and at difference temperatures. From experimental data, it is concluded that the initial rate of hydrodesulfurization of benzothiophene is first-order with respect to catalyst and hydrogen gas concentration. No effect on the hydrodesulfurization rates was observed on varying concentration of benzothiophene. The reaction rate law can be written as $d/[DHBT]/dt = k_{cat}[M][H_2]$ and k_{cat} at 150 ºC = $0.34 \pm 0.01\ M^{-1}s^{-1}$. The activation parameters are $\Delta H^{\neq} = 7.33 \pm 0.02\ k_{cal}/mol$, $\Delta S^{\neq} = -44 \pm 1$ eu and $\Delta G^{\neq} = 25.9 \pm 0.1\ k_{cal}/mol$. The catalytic mechanism is similar to the one that published elsewhere.[42-44] In catalytic cycle, the transfer of hydrides to coordinated benzothiophene in $[M(H)(Cl)\eta^2\text{-}(C{=}C)\text{-}BT]\text{-}(PPh_3)_2]$ is the rate determining step. Dihydrobenzothiophene is the major product of the hydrodesulfurization process at 150 °C. This catalytic reaction is presumed to go through hydrogenation and then hydrogenolysis to give ethyl benzene product. With the use of $(PPh_3)_3RuCl_2$ catalyst, the benzothiophene hydrodesulfurization gives 21.3 % of ethyl benzene at temperature 250 °C and 30 bar of hydrogen pressure.

4.2 Suggestions

From all aforementioned results and discussion, the future work should be focused on the following:

1. The catalyst might be developed by changing kinds of metal and ligand.
2. The hydrodesulfurization reaction with base as cocatalyst; such as KBu_4OH should be studied.
3. Hydrodesulfurization reaction by supporting metal on molecular sieve or other supports should be tried.

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APPENDICES

Appendix A

Table A1 Contributions to effective carbon number[59]

Atom	Type	Effective carbon number contribution
C	aliphatic	1.0
C	aromatic	1.0
C	olefinic	0.95
O	primary alcohol	-0.6
O	secondary alcohol	-0.75

Appendix B

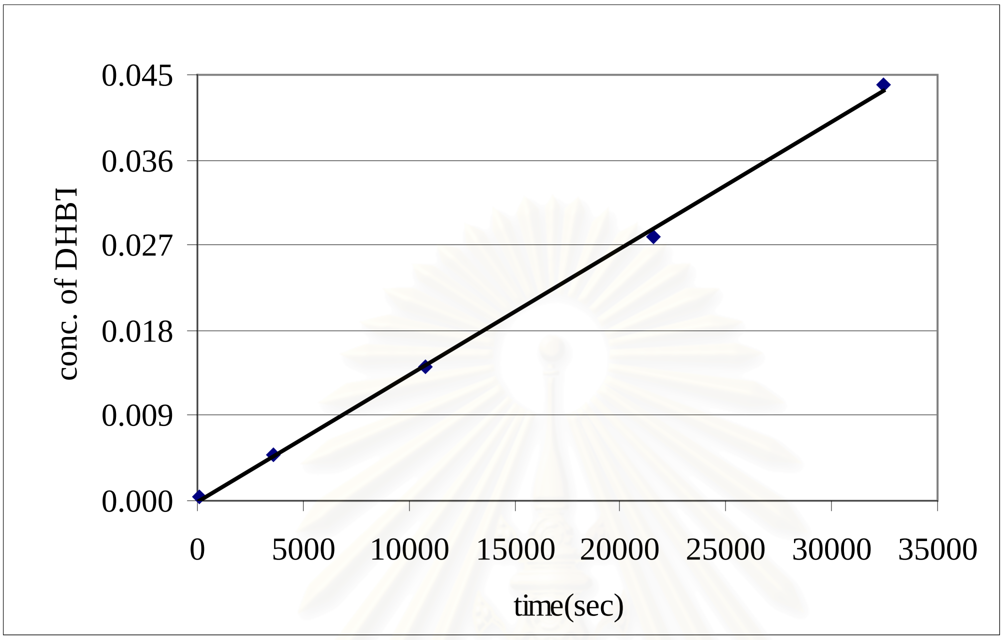

Figure B1 A plot of concentration. of DHBT versus time at 150 ºC $[(PPh_3)_3RuCl_2] = 9.50 \times 10^{-4}$ M, $[BT] = 8.00 \times 10^{-2}$, $[H_2] = 4.05 \times 10^{-3}$ M.

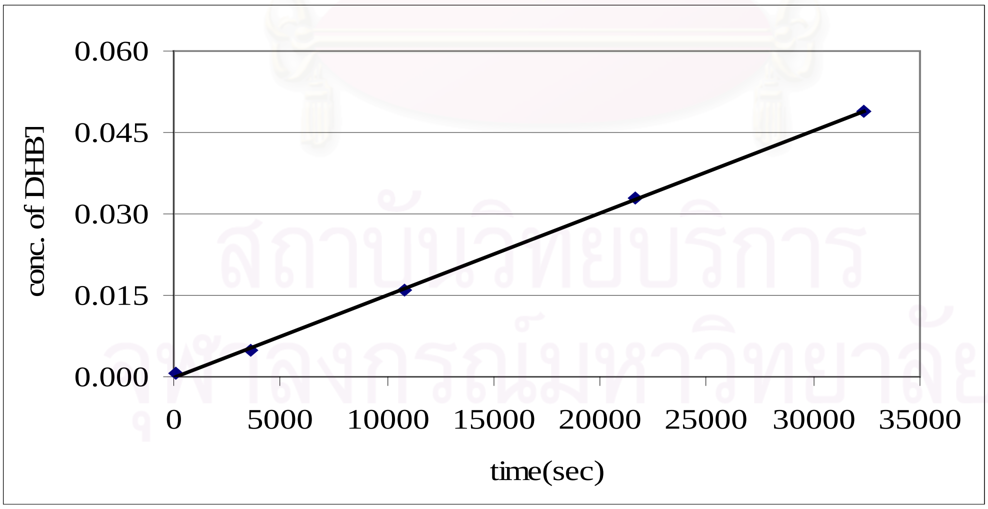

Figure B2 A plot of concentration. of DHBT versus time at 150 ºC $[(PPh_3)_3RuCl_2] = 1.10 \times 10^{-3}$ M, $[BT] = 8.00 \times 10^{-2}$, $[H_2] = 4.05 \times 10^{-3}$ M.

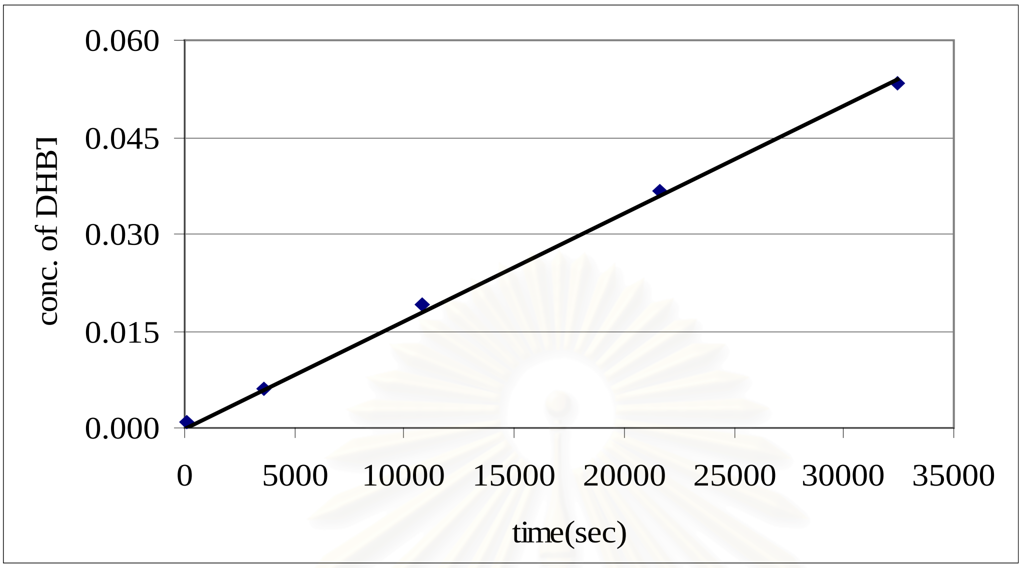

Figure B3 A plot of concentration. of DHBT versus time at 150 ºC $[(PPh_3)_3RuCl_2] = 1.20 \times 10^{-3}$ M, $[BT] = 8.00 \times 10^{-2}$, $[H_2] = 4.05 \times 10^{-3}$ M.

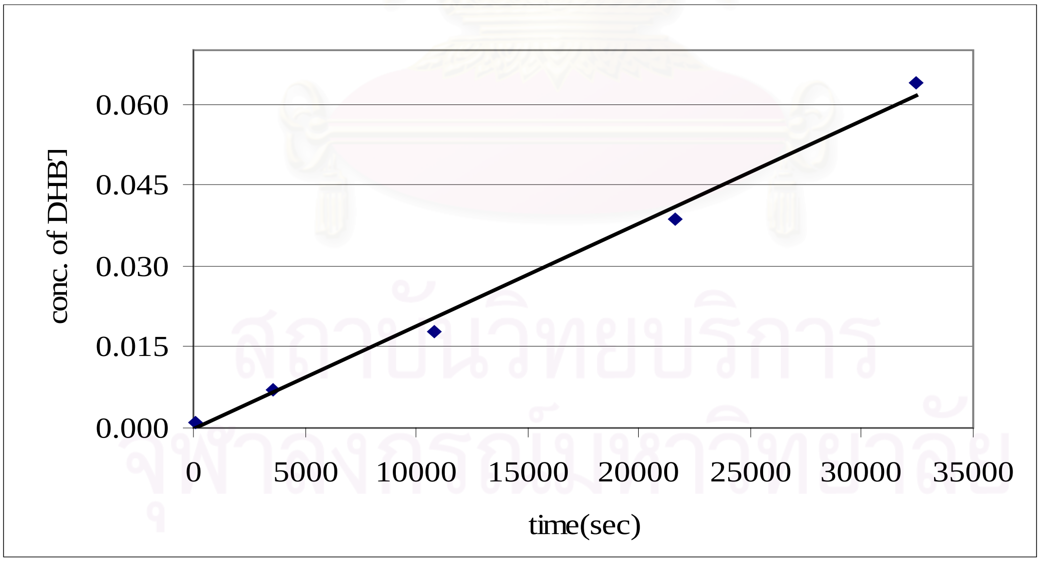

Figure B4 A plot of concentration. of DHBT versus time at 150 ºC $[(PPh_3)_3RuCl_2] = 1.35 \times 10^{-3}$ M, $[BT] = 8.00 \times 10^{-2}$, $[H_2] = 4.05 \times 10^{-3}$ M.

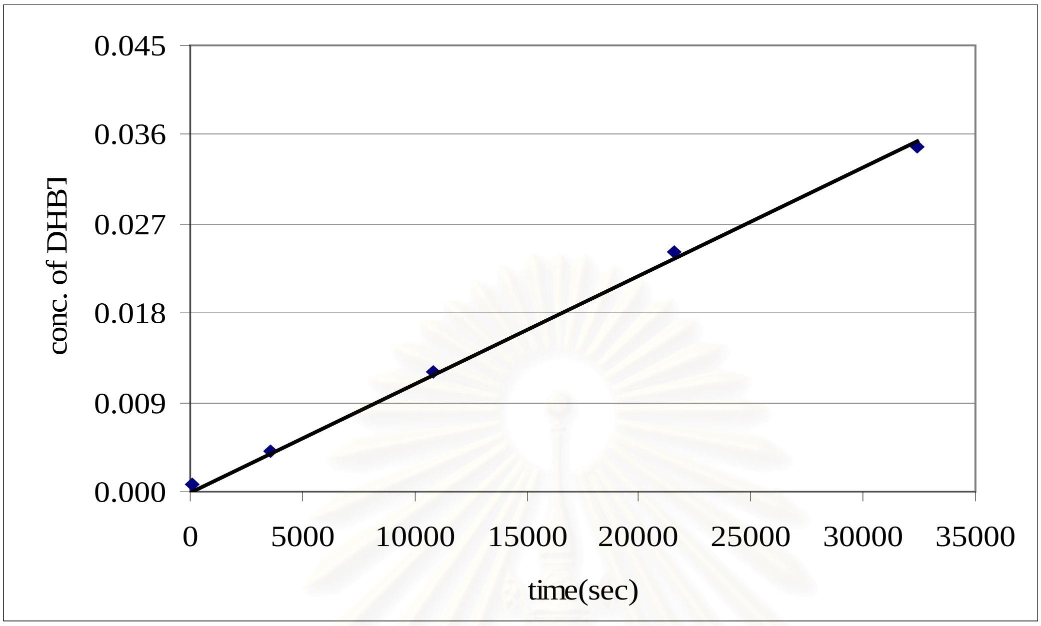

Figure B5 A plot of concentration. of DHBT versus time at 150 ºC $[(PPh_3)_3RuCl_2]$ = 8.00 x 10^{-4} M, [BT] = 6.00 x 10^{-2}, $[H_2]$ = 4.05 x 10^{-3} M.

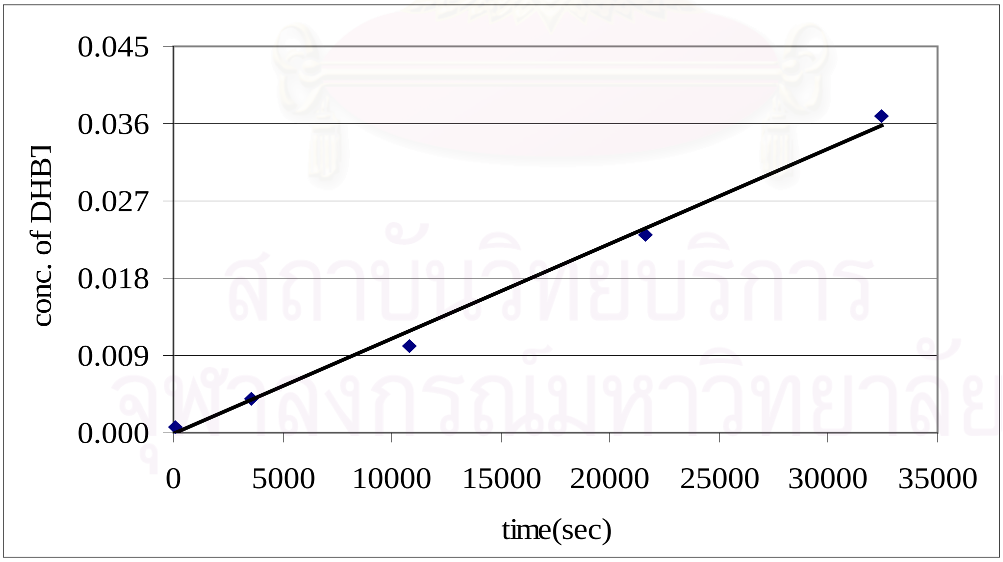

Figure B6 A plot of concentration. of DHBT versus time at 150 ºC $[(PPh_3)_3RuCl_2]$ = 8.00 x 10^{-4} M, [BT] = 1.00 x 10^{-1}, $[H_2]$ = 4.05 x 10^{-3} M.

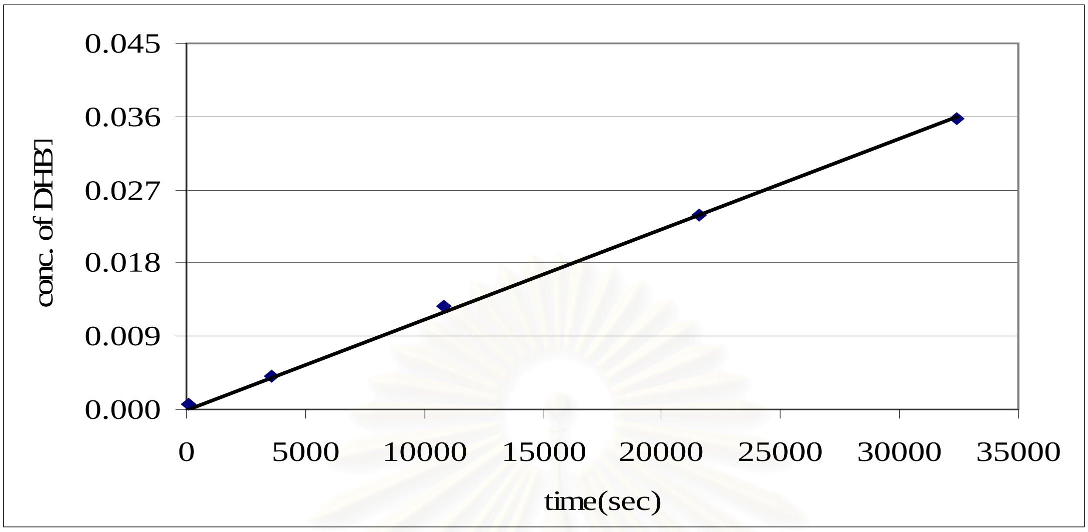

Figure B7 A plot of concentration. of DHBT versus time at 150 ºC $[(PPh_3)_3RuCl_2]$ = 8.00 x 10^{-4} M, [BT] = 1.20 x 10^{-1}, $[H_2]$ = 4.05 x 10^{-3} M.

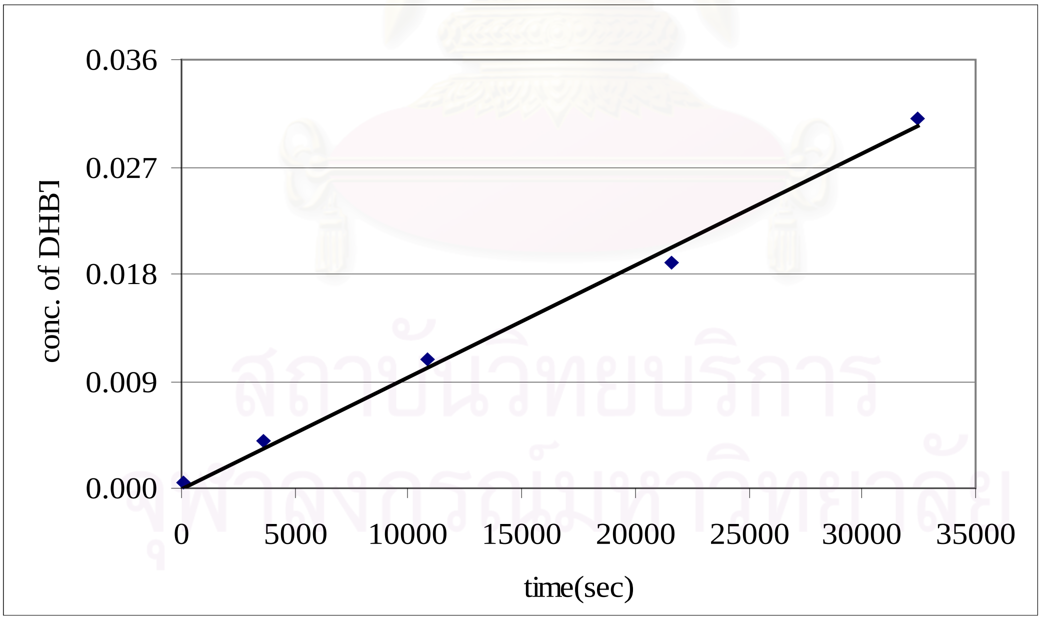

Figure B8 A plot of concentration. of DHBT versus time at 150 ºC $[(PPh_3)_3RuCl_2]$ = 8.00 x 10^{-4} M, [BT] = 8.00 x 10^{-2}, $[H_2]$ = 3.41 x 10^{-3} M.

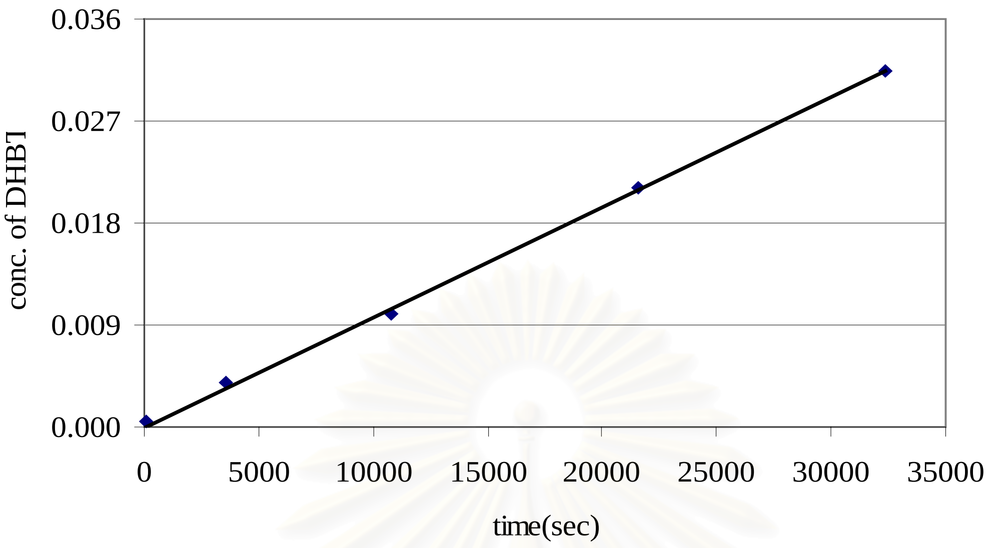

Figure B9 A plot of concentration. of DHBT versus time at 150 ºC $[(PPh_3)_3RuCl_2] = 8.00 \times 10^{-4}$ M, [BT] = 8.00×10^{-2}, $[H_2] = 3.60 \times 10^{-3}$ M.

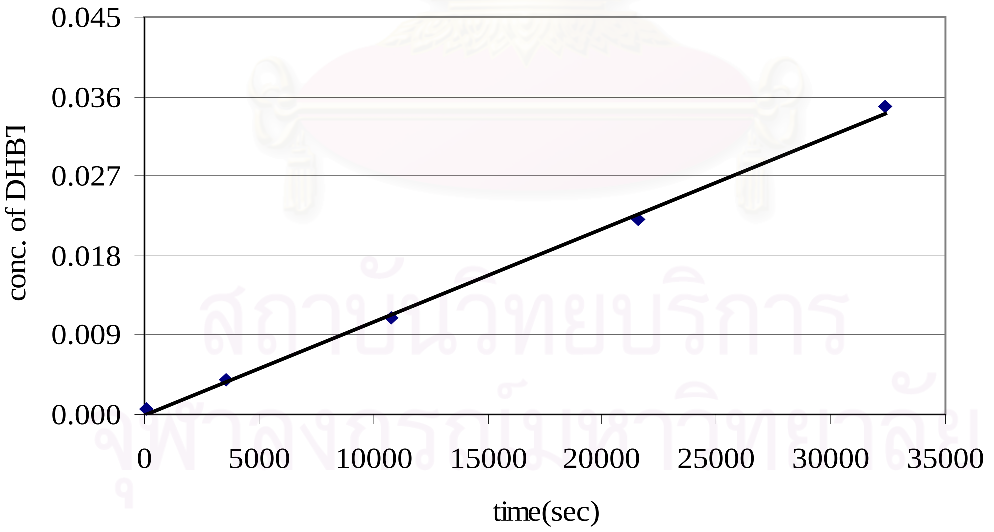

Figure B10 A plot of concentration. of DHBT versus time at 150 ºC $[(PPh_3)_3RuCl_2] = 8.00 \times 10^{-4}$ M, [BT] = 8.00×10^{-2}, $[H_2] = 3.82 \times 10^{-3}$ M.

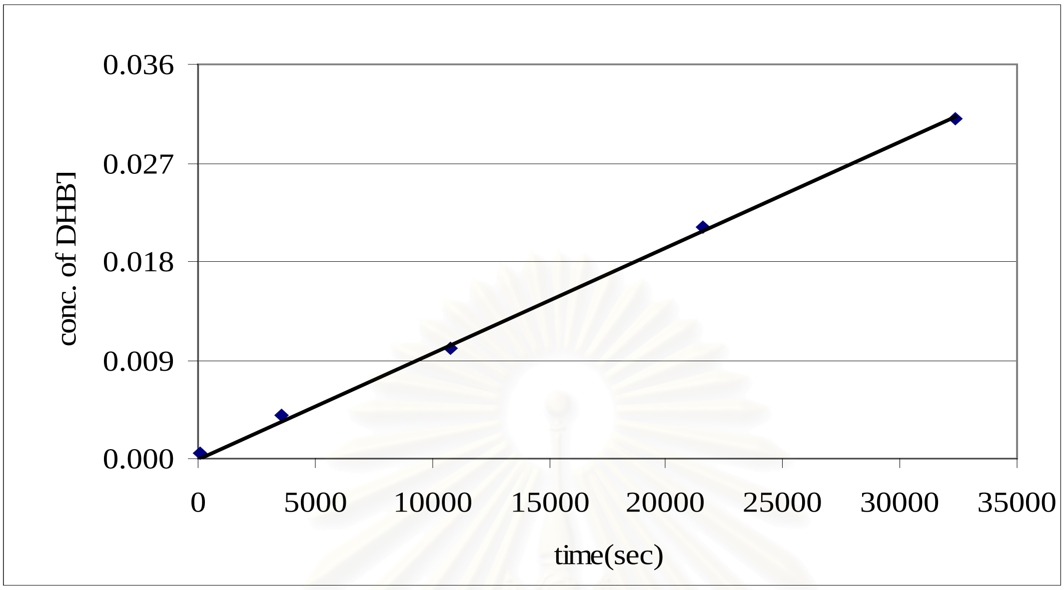

Figure B11 A plot of concentration. of DHBT versus time at 120 ºC $[(PPh_3)_3RuCl_2]$ = 8.00 x 10^{-4} M, [BT] = 8.00 x 10^{-2}, $[H_2]$ = 4.05 x 10^{-3} M.

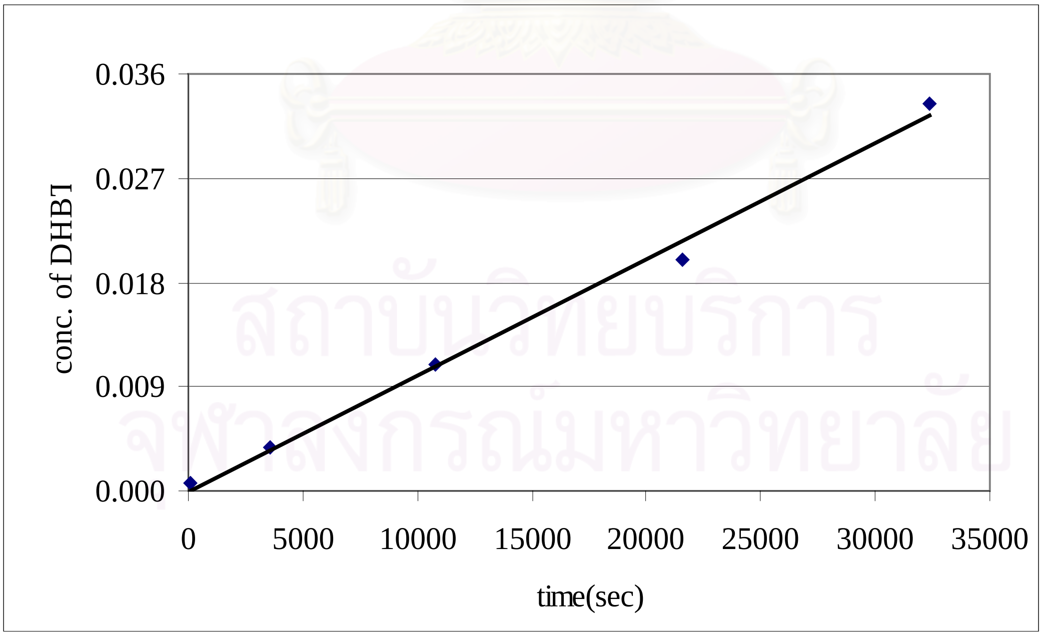

Figure B12 A plot of concentration. of DHBT versus time at 130 ºC $[(PPh_3)_3RuCl_2]$ = 8.00 x 10^{-4} M, [BT] = 8.00 x 10^{-2}, $[H_2]$ = 4.05 x 10^{-3} M.

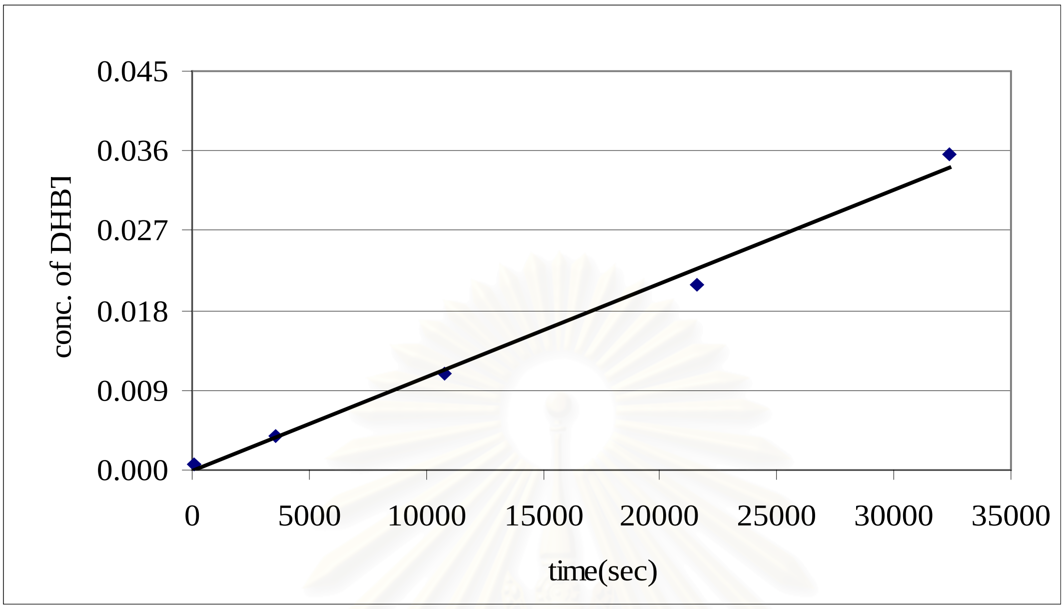

Figure B13 A plot of concentration. of DHBT versus time at 140 ºC [(PPh$_3$)$_3$RuCl$_2$] = 8.00 x 10^{-4} M, [BT] = 8.00 x 10^{-2}, [H$_2$] = 4.05 x 10^{-3} M.

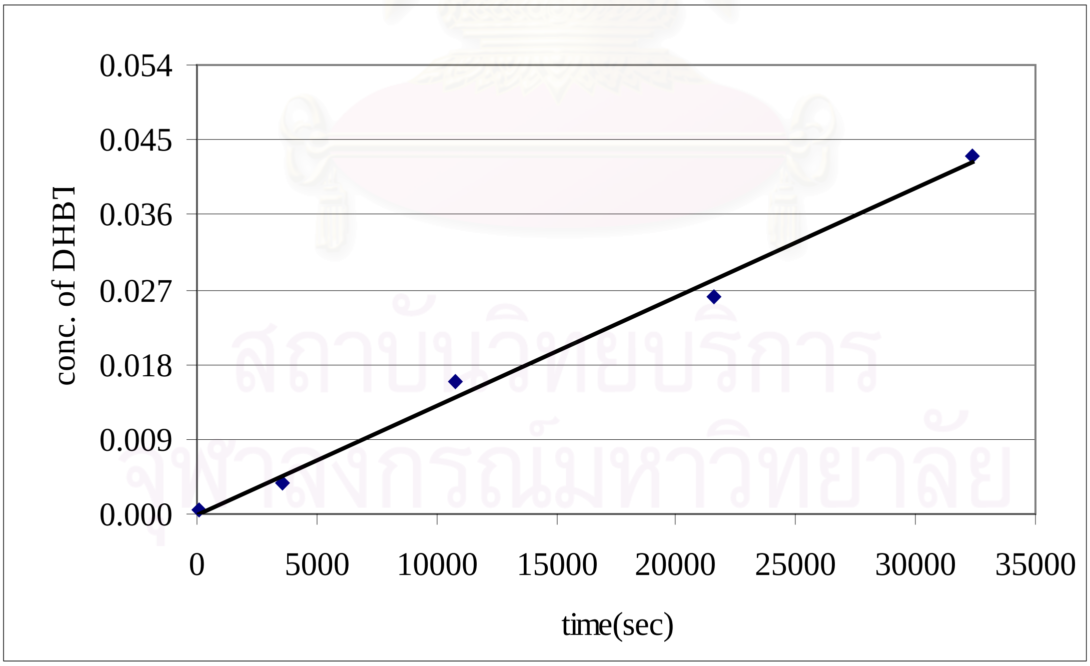

Figure B14 A plot of concentration. of DHBT versus time at 160 ºC [(PPh$_3$)$_3$RuCl$_2$] = 8.00 x 10^{-4} M, [BT] = 8.00 x 10^{-2}, [H$_2$] = 4.05 x 10^{-3} M.

VITA

Mr. Somsak Angdonka was born on December 10, 1976 in Nakornsawan, Thailand. He graduated with Bachelor’s Degree of Science in Chemistry from Naresuan University in 1998. He then pursued his Master’s degree in Chemistry at Chulalongkorn University and finished his study in 2002.