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Deep desulfurization of petroleum feedstocks by selective adsorption and extraction

Scott Groh McKinley
Iowa State University

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Deep desulfurization of petroleum feedstocks by selective adsorption and extraction

by

Scott Groh McKinley

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Robert Angelici, Major Professor
James Espenson
John Verkade
Valerie Sheares Ashby
Victor Lin

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Scott Groh McKinley

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Major Professor

Signature was redacted for privacy.

For the Major Program

For the people in my life who mean the most to me:

My wife Molly, my parents Scott and Nora and my sister Anne

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ABSTRACT

In an effort to demonstrate that $Ru(NH_3)_5(H_2O)^{2+}$ can be used to remove dibenzothiophene from hydrotreated petroleum feedstocks, this metal complex was reacted with a variety of thiophenes (Th*), including dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-Me_2DBT) to give complexes of the type $Ru(NH_3)_5(Th^*)^{2+}$. This ability of $Ru(NH_3)_5(H_2O)^{2+}$ to bind to thiophenes has been used in an extraction process in which a solution of $Ru(NH_3)_5(H_2O)^{2+}$ in 70% DMF and 30% H_2O is contacted with a simulated petroleum feedstock (45% toluene / 55% hexanes) containing 400 ppm of DBT. One extraction removes 50% of the DBT from the feedstock phase as $Ru(NH_3)_5(DBT)^{2+}$, which is present in the DMF/H_2O phase. Five successive extractions reduce the amount of DBT in the simulated feedstock from 400 ppm to 25 ppm. The $Ru(NH_3)_5(H_2O)^{2+}$ extractant can be regenerated from the $Ru(NH_3)_5(DBT)^{2+}$ either by air-oxidation followed by H_2-reduction or by displacement of the DBT by adding H_2O to the DMF/H_2O phase. Extraction of 4,6-Me_2DBT from the simulated feedstock using $Ru(NH_3)_5(H_2O)^{2+}$ in 70% N,N-dimethylacetamide and 30% H_2O was less successful as the 4,6-Me_2DBT concentration was only reduced from 400 ppm to 340 ppm.

Complexes $CpRu(CO)_2(BF_4)$ and $CpFe(CO)_2(THF)^{2+}$ were adsorbed onto a mesoporous silica substrate. These complexes were shown by CP MAS ^{29}Si and DRIFT-IR spectroscopies to interact with the silica surface via hydrogen bonding to surface silanols. When these modified silica surfaces are stirred with a simulated gasoline feedstock containing 400 ppm(S) DBT, they form $CpRu(CO)_2(DBT)^+$ and $CpFe(CO)_2(DBT)^+$ on the silica surface and lower DBT levels by 98% and 70% respectively, as determined by GC.

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These metal-complex modified surfaces behave as solid phase extractants (SPEs) towards sulfur impurities in gasoline and diesel fuels. The surface metal-DBT complexes, have been characterized by CP MAS ^{13}C NMR and XPS. Through their independent synthesis, the X-ray structures of CpRu(CO)$_2$(DBT)$^+$ and CpFe(CO)$_2$(DBT)$^+$ were solved.

Finally, we report the use of solid phase extractants (SPE) consisting of Ag$^+$ salts (SPE-Ag) adsorbed on mesoporus SBA-15 or amorphous silica for the removal of DBT and 4,6-Me$_2$DBT from a simulated diesel feedstocks. In these extractions SPE-Ag was stirred with DBT in decanes. It was observed that within 1 min, the DBT level was reduced from 400 ppm to 72 ($\pm$ 9) ppm, while 4,6-Me$_2$DBT was reduced to 75 ($\pm$ 6) ppm. These studies show that the concentration of DBT and 4,6-Me$_2$DBT in decanes can be reduced even further from 400 ppm to approximately 8 ppm by doubling the amount of SPE-Ag used and by extracting not by stirring, but DBT by column chromatography. The active SPE-Ag may be regenerated by washing with diethylether, thereby separating the DBT from the petroleum feedstocks. The easy regeneration of these adsorbents makes them attractive for the deep desulfurization of petroleum feedstocks.

CHAPTER ONE: GENERAL INTRODUCTION

Dissertation Organization

This dissertation contains three papers in the format required for journal publication, describing the research I performed at Iowa State University. Preceding these papers is a literature review of the problems associated with deeply desulfurizing petroleum feedstocks. In the literature review as well as the papers, the literature citations, schemes, tables and figures pertain only to the chapters in which they appear. After the final paper is a general summary.

Literature Review

The removal of sulfur from transportation fuels is an important aspect of this nation's effort to reduce pollution of the atmosphere by sulfur oxides.[1] The problem of desulfurizing fuels has become more serious because sulfur levels in raw crude has been steadily rising in the past decades.[2] Currently, sulfur content in diesel is limited to 500 ppm (0.05% by weight), but the EPA has recently introduced new restrictions that will reduce this level gradually to 15 ppm (0.0015% by weight) by 2006.[3] The sulfur content in gasoline must also undergo similar reductions. Since sulfur has been shown to poison catalytic converters, these lower sulfur levels will have the additional benefits of increasing the converters lifetime and reducing the amount of NO_x released into the atmosphere.

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Petroleum distillate fuels (gasoline, jet fuel and diesel fuel) are mixtures of organic molecules that fall into specific boiling point ranges. Gasoline has the lowest boiling point range, followed by jet fuel with a median boiling point range and diesel fuel with the highest boiling point range. The identity of the sulfur impurities present in petroleum feedstocks reflect the differences in boiling points of the specific fraction (boiling point range). The sulfur impurities in gasoline are mainly lower boiling point (typically ~50° C) thiophene and its alkyl derivatives. Jet fuel's sulfur impurities are mainly benzothiophene derivatives which melt at room temperature. Diesel fuel, having the highest boiling point, has the heaviest of the sulfur impurities, dibenzothiophene and alkyl substituted dibenzothiophenes, both solids at room temperature; some of which sublime at temperatures over 200° C.[4]

Diesel fuel is of particular interest, because diesel engines are more efficient than gasoline engines. Currently 2.2 million barrels of diesel fuel is consumed everyday[5] in the US road transportation market, this is expected to increase significantly in the early part of the 21ˢᵗ century.[6] For these reasons, the removal of R_2DBT from diesel feedstocks is of great importance.

Currently the desulfurization of petroleum feedstocks depends on the catalytic hydrodesulfurization (HDS) process.[7] In the HDS process, an organosulfur compound is converted to a hydrocarbon and H_2S, eq (1). The HDS reaction requires the catalysts Ni/Mo

$$C_aH_bS + H_2 \rightarrow H_2S + C_aH_d \qquad (1)$$

and Co/Mo sulfides (supported on alumina), high temperatures (350° C) and high partial pressure H_2 (50 atm) for the reaction to occur. The most easily desulfurized components of

the feedstock are the thiols (RSH) and thioethers (R'SR''). Improvements in past decades have yielded catalysts that are also capable of desulfurizing the thiophenes, benzothiophenes and dibenzothiophene (R = H).[1] It is the hindered dibenzothiophenes (R_2DBT, where R = Me or Et), particularly those with alkyl groups in the 4 and 6 positions that are the slowest to undergo HDS.[8]
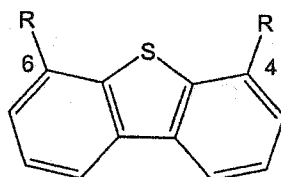
Dibenzothiophene

For a number of reasons, new technologies must be developed in order to meet the EPA's mandated 98% reduction in sulfur content in fuels. The target levels of sulfur can be met by traditional HDS, but this requires increasing the volume of the HDS reactor by a factor of 3.5. Unfortunately, this is prohibitively expensive. HDS reactors operate at both high temperature and pressure, and are very expensive to build and operate. The target levels of sulfur could also be met if the activity of HDS catalysts could be improved by a factor of 3.5. This is however a lofty goal unlikely to be reached. HDS catalysts have been exhaustively studied for decades with only incremental advances over time. It is unlikely that a breakthrough of the magnitude needed will occur. Therefore, to solve this problem, a different approach is required.

The problem with HDS, particularly when dealing with diesel fuel, is the rate at which R_2DBT is desulfurized. It has been proposed in the HDS process that DBT adsorbs through its sulfur to an exposed Mo atom on the supported MoS_2 catalyst; subsequently the

DBT is desulfurized by reaction with hydrogen. When methyl groups occupy the 4,6-positions in DBT, the bulkiness of these groups interferes with DBT sulfur binding to a Mo site. Even in coordination compounds, where 4,6-methyl groups should be much less of a concern than on a catalytic surface, there is only one reported example of a fully characterized 4,6-dimethyldibenzothiophene (4,6-Me$_2$DBT) complex[9], (η^5-C$_5$Me$_5$)Ru(CO)$_2$(4,6-Me$_2$DBT)$^+$, and the 4,6-Me$_2$DBT ligand in this complex binds much less strongly than DBT. Another sulfur-coordinated 4,6-Me$_2$DBT complex (η^5-C$_5$Me$_5$)Rh(PMe$_3$)(4,6-Me$_2$DBT) was reported,[10] but it was too unstable to be isolated and fully characterized.

Contrary to the very small number of 4,6-Me$_2$DBT complexes in the literature, there are numerous DBT complexes.[11, 12] Dibenzothiophene complexes have been shown to coordinate to single metal compounds through the sulfur (η^1(S)), through two carbon atoms (η^2), through four carbon atoms of a benzo ring(η^4), or through all six carbon atoms of a benzo ring (η^6).[12] Metals will often insert themselves into R$_2$DBT complexes resulting in C-S bond cleavage. This occurs in the case of a Pt phosphine complex promotes metal insertion reactions into the C-S bond of 4,6-Me$_2$DBT to form a stable metallocyclic complex.[13]

Substantial efforts have been devoted to finding new methods for the removal of 4,6-R$_2$DBT molecules from petroleum. Recent investigations have found a variety of methods to achieve this goal. One such method is the selective adsorption of R$_2$DBT, which at this point, the authors wish to keep the specifics secret for intellectual property reasons.[14] Another method is the removal of DBT by its precipitation as an insoluble DBT-sulfimide (by

reaction with sodium N-chlorotoluene-*p*-sulfonamide), eq (2).[15] Microbial desulfurization

can be accomplished by a several different strains of bacteria, *Rhodococcus erythropolis*

$$TsN(H)(Cl) + DBT \quad HCl + DBT(S)=N\text{-}Ts \qquad (2)$$

degrades DBT by oxidizing DBT to its corresponding sulfone.[16] This ability has even been

transferred to *Escherivhia coli* by cloning the *Taq*I fragment that contains these genes from

Rhodococcus erythropolis.[17] Extraction of DBT by ionic liquids has also been reported. 1-*n*-

butyl-3-methylimidazolium chloride in a 1:2 ratio with $AlCl_3$, which melts at room

temperature, extracts DBT from *n*-dodecane.[18] Additionally, DBT and 4,6-Me_2DBT may be

oxidized to their corresponding sulfones in a liquid biphasic system by the action of 12-

tungstophosphoric acid and hydrogen peroxide.[19] The R_2DBT sulfones are insoluble in

petroleum and are removed by filtration.

If selective adsorption of R_2DBT could be carried out by a solid phase extractant

(SPE), it would be an appealing alternative to HDS. SPEs are attractive for this use, because

unlike the hydrotreating conditions in HDS, they only have an effect on the target molecule

or group of molecules (in this case thiophenes). The ideal method for the removal of

R_2DBT's would be an SPE, which would bind R_2DBT, be tolerant of the aromatic

constituents of petroleum, and release the R_2DBT under appropriate conditions in order to

regenerate the SPE.

The holy grail of desulfurization of petroleum feestocks is to deeply desulfurize them,

which means to reduce S levels to less than 0.1 ppm. The near absence of sulfur in the fuel

would allow new technologies to develop. One of these is the application of noble metals for

the deep dearomatization of fuels. The deep dearomatization of fuels would cut CO and hydrocarbon emissions from exhaust, eliminating some of the environmental problems associated with internal combustion engines. Thermodynamically, hydrogenation is best at lower temperatures, since it is an exothermic process. However for hydrogenation to occur at low temperatures, noble metals must be used, which are poisoned by sulfur because they readily form metal sulfides. Obviously, this means that petroleum needs to be deeply desulfurized before being dearomatized.

Ideally the world would prefer to move beyond the internal combustion engines as a power source for automobiles and switch to fuel cells. Fuel cells electrochemically oxidize a fuel on noble metal electrodes (often Pt) to make electricity. This is in contrast to internal combustion engines which chemically oxidize (burn) a fuel to make mechanical energy. Because of this difference, fuel cells are much more thermodynamically efficient, 80-90% efficient versus 10-14% of that of a typical internal combustion engine. Currently commercial fuel cells available use H_2 gas as a fuel by oxidizing H_2 into H_2O. However, H_2 has several limitations, it is an explosive gas, it has a high cost, and it lacks the infrastructure to deliver it to the consumer. If a fuel cell can be designed to utilize petroleum as a fuel, these limitations disappear. Imagine, filling your gas tank with 20 gallons of gasoline and traveling to California without stopping to refuel.

Part of the challenge is creating a fuel cell to burn hydrocarbon fuels. The other barrier for this technology is low cost, highly desulfurized petroleum for the fuel cell to use. To be practical, petroleum needs to be very deeply desulfurized. It is thought that levels of

<0.1 ppm sulfur by weight would be required for the fuel cell technology to be compatible with petroleum distalates.[4]

As outlined, there are several economic and environmental reasons to pursue new means for the desulfurization of petroleum feedstocks. As I will discuss in detail in the rest of my dissertation, we believe that we have made significant progress in the goal of finding a practical method to deeply desulfurize petroleum feedstocks.

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CHAPTER TWO: EXTRACTION OF DIBENZOTHIOPHENES FROM PETROLEUM FEEDSTOCKS USING A RUTHENIUM COMPLEX IN AQUEOUS SOLUTION

A paper published in the journal *Energy & Fuels*

Scott G. McKinley and Robert J. Angelici

Abstract

In an effort to demonstrate that $Ru(NH_3)_5(H_2O)^{2+}$ can be used to remove dibenzothiophene from hydrotreated petroleum feedstocks, this metal complex was reacted with a variety of thiophenes (Th*), including dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-Me$_2$DBT) to give complexes of the type $Ru(NH_3)_5(Th^*)^{2+}$. This ability of $Ru(NH_3)_5(H_2O)^{2+}$ to bind to thiophenes has been used in an extraction process in which a solution of $Ru(NH_3)_5(H_2O)^{2+}$ in 70% DMF and 30% H_2O is contacted with a simulated petroleum feedstock (45% toluene / 55% hexanes) containing 400 ppm of DBT. One extraction removes 50% of the DBT from the feedstock phase as $Ru(NH_3)_5(DBT)^{2+}$, which is present in the DMF/H_2O phase. Five successive extractions reduce the amount of DBT in the simulated feedstock from 400 ppm to 25 ppm. The $Ru(NH_3)_5(H_2O)^{2+}$ extractant can be regenerated from the $Ru(NH_3)_5(DBT)^{2+}$ either by air-oxidation followed by H_2-reduction or by displacement of the DBT by adding H_2O to the DMF/H_2O phase. Extraction

of 4,6-Me$_2$DBT from the simulated feedstock using Ru(NH$_3$)$_5$(H$_2$O)$^{2+}$ in 70% N,N-dimethylacetamide and 30% H$_2$O was less successful as the 4,6-Me$_2$DBT concentration was only reduced from 400 ppm to 340 ppm.

Introduction

The removal of sulfur from transportation fuels is an important aspect of the effort to reduce pollution of the atmosphere by sulfur oxides.[1] Currently, sulfur content in gasoline is limited to 400 ppm (0.04% by weight), but the EPA has recently introduced new restrictions that will reduce this level gradually to 25 ppm (0.0025% by weight) by 2006.[2] This ambitious agenda will require the rapid development of new technologies in order to achieve such a large reduction in sulfur content in a short period of time.

Currently the desulfurization of petroleum feedstock depends on the catalytic hydrodesulfurization (HDS) process.[3] The most easily desulfurized components of the feedstock are the thiols (RSH) and thioethers (R'SR''). Recent improvements have yielded catalysts that are also capable of desulfurizing the thiophenes, benzothiophenes and dibenzothiophene (R = H) (Chart 1). It is the hindered dibenzothiophenes (R$_2$DBT), particularly those with alkyl groups in the 4 and 6 positions that are the slowest to undergo HDS. These 4,6-R$_2$DBT's constitute the bulk of the remaining sulfur compounds and must be removed in order to meet the EPA requirements.[4]

In the HDS process, it has been proposed[4] that dibenzothiophene (DBT) adsorbs through its sulfur to an exposed Mo atom on the supported MoS$_2$ catalyst; subsequently the DBT is desulfurized by reaction with hydrogen. When methyl groups occupy the 4,6-

positions in DBT, the bulkiness of these groups interferes with DBT sulfur binding to a Mo site. Even in coordination compounds, where 4,6-methyl groups should be much less of a concern than on a catalytic surface, there is only one reported example of a fully characterized 4,6-dimethyldibenzothiophene (4,6-Me$_2$DBT) complex[5], (η^5-C$_5$Me$_5$)Ru(CO)$_2$(4,6-Me$_2$DBT)$^+$, and the 4,6-Me$_2$DBT ligand in this complex binds much less strongly than DBT. Another sulfur-coordinated 4,6-Me$_2$DBT complex (η^5-C$_5$Me$_5$)Rh(PMe$_3$)(4,6-Me$_2$DBT) was reported,[6] but it was too unstable to be isolated and fully characterized. On the other hand, numerous DBT complexes are described in the literature.[7, 8]

These results suggest that it is the bulkiness of the R groups in the 4,6-R$_2$DBT molecules that are responsible for their slow rates of desulfurization under HDS conditions. Substantial efforts have been devoted to finding new methods for the removal of 4,6-R$_2$DBT molecules from petroleum. Recent investigations include deep desulfurization by selective adsorption of R$_2$DBT,[9] by precipitation of an insoluble DBT-sulfimide (by reaction with sodium N-chlorotoluene-p-sulfonamide),[10] extraction of DBT by ionic liquids,[11] oxidation of DBT and 4,6-Me$_2$DBT to the corresponding sulfones in a liquid biphasic system,[12] and several other processes.[13]

We have developed a completely different approach to the removal of hindered dibenzothiophenes (4,6-R$_2$DBT) from petroleum, which makes use of the ability of certain Ru(II) complexes to bind to dibenzothiophene. In this report, we describe the reaction of the coordination compound Ru(NH$_3$)$_5$(H$_2$O)$^{2+}$ with dibenzothiophene and the use of this complex in aqueous solution to selectively bind and extract 4,6-R$_2$DBT molecules from the

hydrocarbon phase of simulated petroleum feedstocks. We also demonstrate that the 4,6-R_2DBT ligands can be released from the Ru(II) thereby allowing $Ru(NH_3)_5(H_2O)^{2+}$ to be regenerated and re-used in additional 4,6-R_2DBT extractions.

Experimental

General Considerations. All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Diethyl ether (Et_2O), hexanes and toluene were all purified on alumina using a Solv-Tech solvent purification system, as described by Grubbs and co-workers.[14] Acetone was purchased from Aldrich and dried over type 4A molecular sieves and stored under argon. All other chemicals were used without further purification as purchased from Aldrich. Filtrations were performed with Celite on filter paper. Sonication was conducted in a Fisher Scientific FS30 sonicator.

NMR spectra were obtained on a modified 400 MHz Varian VXR-400 spectrometer using acetone-d_6 as internal lock and reference. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer. Gas chromatography was performed on a Hewlett Packard 6890 series instrument with a HP-5 column. The GC conditions are as follows: DBT (190° C, decahydronaphthalene internal standard), BT (150° C, decahydronaphthalene internal standard) or T (40° C, p-xylene internal standard). UV-Vis spectra were obtained on a Hewlett Packard 8452A Diode Array Spectrophotometer with a deuterium lamp, using quartz cuvettes.

Synthesis of [Ru(NH₃)₅(4,6-Me₂DBT)][PF₆]₂ (1). To a 50 mL flask containing 15 mL of acetone (or dimethylformamide {DMF}), freshly prepared [Ru(NH₃)₅(H₂O)][PF₆]₂ (50.0 mg, 0.102 mmol),[15] 4,6-Me₂DBT (43.1 mg, 0.203 mmol), and 10 mg of Pd/C (10% by weight, Pd on activated carbon) were added. The solution was cycled through three freeze/pump/thaw sequences to remove oxygen from the system in order to prevent oxidation of the Ru(II) complex. The flask was warmed to room temperature and H₂(g) was bubbled through the solution for 15 min. The resulting yellow solution was stirred under H₂ for 45 min. The product, containing Pd/C, was precipitated with 35 mL of degassed Et₂O, and the solution was filtered by cannula. The precipitate was treated with 10 mL of acetone, which had been cycled through two freeze/pump/thaw sequences. Then, H₂ was bubbled through the solution for 5 min. The solution was then filtered (to remove Pd/C) into another flask containing 35 mL of degassed Et₂O, which gave the product as a precipitate. The Et₂O was removed by filtration and the product was dried under vacuum for 15 min to give an 86% yield of the very air-sensitive **1**. ¹H NMR (400 MHz, CD₃COCD₃): δ 8.15 (d, J_{H-H} = 9.1 Hz, 2 H, DBT-*H*), 7.44 (t, J_{H-H} = 9.2 Hz, 2 H, DBT-*H*), 7.36 (d, J_{H-H} = 9.0 Hz, 2 H, DBT-*H*), 2.62 (s, 6H, DBT-C*H₃*), 2.70 (s, br, 12 H, N*H₃*), 2.52 (s, br, 3 H, N*H₃*) ppm. ¹³C NMR (400 MHz, CD₃COCD₃): δ 139.24, 136.39, 132.37, 127.50, 125.32, 119.82, 15.01 ppm. Compound **1**, as well as **2-4**, was too unstable to give satisfactory elemental analyses.

Synthesis of [Ru(NH₃)₅(DBT)][PF₆]₂ (2). The procedure for the synthesis of **1** was followed with the exception that DBT (37.4 mg, 0.203 mmol) was used in place of 4,6-Me₂DBT. ¹H NMR (400 MHz, CD₃COCD₃): δ 8.38 (d, 2H, J_{H-H} = 7.6 Hz, DBT-*H*), 8.05 (d, 2H, J_{H-H} = 7.5 Hz, DBT-*H*), 7.68 (t, 2H, J_{H-H} = 7.6 Hz, DBT-*H*), 7.54 (t, 2H, J_{H-H} = 7.6 Hz, DBT-*H*), 2.69

(s, br, 12 H, NH_3), 2.53 (s, br, 3 H, NH_3) ppm. ^{13}C NMR (400 MHz, CD$_3$COCD$_3$): δ 143.12, 138.62, 127.95, 125.10, 123.11, 121.95 ppm.

Synthesis of [Ru(NH$_3$)$_5$(BT)][PF$_6$]$_2$ (3). The procedure for the synthesis of 1 was followed with the exception that BT (27.2 mg, 0.203 mmol) was used in place of 4,6-Me$_2$DBT. ^{1}H NMR (400 MHz, CD$_3$COCD$_3$): δ 8.15-7.42 (m, 4H, BT-H), 6.51 (d, 1H, J_{H-H} = 6.3 Hz, BT-H), 5.98 (d, 1H, J_{H-H} = 6.3 Hz, BT-H), 2.72 (s, br, 12 H, NH_3), 2.56 (s, br, 3 H, NH_3) ppm. ^{13}C NMR (400 MHz, CD$_3$COCD$_3$): δ 128.12, 127.72, 125.98, 124.68, 123.85, 122.56, 35.32, 34.96 ppm.

Synthesis of [Ru(NH$_3$)$_5$(T)][PF$_6$]$_2$ (4). The procedure for the synthesis of 1 was followed with the exception that T (16.3 μL, 0.203 mmol) was used in place of 4,6-Me$_2$DBT. ^{1}H NMR (400 MHz, CD$_3$COCD$_3$): δ 7.49(m, 2H, T-H), 7.13 (m, 2H, T-H), 2.71 (s, br, 12 H, NH_3), 2.48 (s, br, 3 H, NH_3) ppm. ^{13}C NMR (400 MHz, CD$_3$COCD$_3$): δ 127.08, 125.34 ppm.

Extraction of DBT and 4,6-Me$_2$DBT from Simulated Petroleum Fuel. A mixture of toluene and hexanes (45% and 55% by volume, respectively) was prepared in order to simulate the composition of a hydrotreated gasoline feedstock.[4a] Into 10 mL of this hydrocarbon solution, DBT or 4,6-Me$_2$DBT (17.6 mg, 0.095 mmol, or 19.9 mg, 0.095 mmol, respectively) and triphenylmethane (15.0 mg, 0.061 mmol as internal standard) were dissolved. After two freeze/pump/thaw cycles, the mixture was warmed to room temperature. Into a separate flask, 7.0 mL of DMF, 3.0 mL of H$_2$O, 10 mg of Pd/C (10% Pd by weight on activated carbon), and either five equivalents (235 mg, 0.477 mmol) or ten equivalents (470

mg, 0.954 mmol) of $[Ru(NH_3)_5(H_2O)][PF_6]_2$ relative to the 4,6-R_2DBT amounts were added.

After two freeze/pump/thaw cycles, the mixture was warmed to room temperature, and H_2

was bubbled through the solution for 5 min. A 0.4 mL aliquot of the hydrocarbon solution

was taken for NMR analysis; then the remainder of the solution was added to the DMF/H_2O

mixture containing $[Ru(NH_3)_5(H_2O)][PF_6]_2$ under argon followed by one freeze/pump/thaw

cycle. The mixture was sonicated (or stirred), and 0.4 mL aliquots of the hydrocarbon phase

(the upper layer) were removed after 0.25, 0.50, 0.75, 1.00, 2.00, and 4.00 h of extraction

time. The organic solvents were removed from these aliquots by evaporation under an Ar

stream in an NMR tube; the resulting residues were dissolved in 2 mL of CD_3COCD_3. The

ratio of DBT (δ 8.33 ppm) to triphenylmethane (δ 5.63 ppm) was determined by integration

of their ^1H NMR bands to establish the amount of DBT that was removed from the simulated

hydrocarbon fuel phase. The same results were obtained when the amount of DBT in the

hydrocarbon phase was determined by GC using internal standards and the conditions

described in the General Considerations section.

Calculation of Equilibrium Constants. The data needed to calculate K_1 and K_2 were

collected in the following manner. For K_1 (eq 1), 10 mL of the feedstock mixture, containing

400 ppm of the thiophene (Th* = T, BT, or 4,6-R_2DBT), was added to 10 mL

$$Th^*{}_{[hc]} \rightleftharpoons Th^*{}_{[DMF/H2O]} \tag{1}$$

$$K_1 = \frac{Th^*{}_{[hc]}}{Th^*{}_{[DMF/H2O]}}$$

of the 70% DMF / 30% H_2O phase. The mixture was vigorously stirred or sonicated. After equilibrium was established ($\sim$ 1 h), the decrease in the amount of Th* from the hydrocarbon (hc) phase was determined by GC (as described in General Considerations) using the internal standards decahydronapthalene or *p*-xylene (both shown not to extract into the aqueous mixture). From this measurement the concentration of Th* present in each phase was calculated, which gives K_1 (Table 2) according to eq (1). When the extraction was repeated with $Ru(NH_3)_5(H_2O)^{2+}$ present in the aqueous phase, K_2 values (eq 2) were calculated from the additional amount of Th* that was removed

$$Ru(NH_3)_5(H_2O)^{2+}{}_{[DMF/H2O]} + Th^*{}_{[DMF/H2O]} \rightleftharpoons Ru(NH_3)_5(Th^*)^{2+}{}_{[DMF/H2O]} + H_2O{}_{[DMF/H2O]} \quad (2)$$

$$K_2 = \frac{[Ru(NH_3)_5(Th^*)^{2+}{}_{[DMF/H2O]}]\,[H_2O_{[DMF/H2O]}]}{[Th^*{}_{[DMF/H2O]}]\,[Ru(NH_3)_5(H_2O)^{2+}{}_{[DMF/H2O]}]}$$

from the hydrocarbon phase as a result of Th* binding to $Ru(NH_3)_5(H_2O)^{2+}$ to form $Ru(NH_3)_5(Th^*)^{2+}$. The resulting K_2 values for T, BT, and DBT are given in Table 2. The values are averages of three runs with errors calculated as average deviations.

Results and Discussion

Syntheses and Structures of [Ru(NH$_3$)$_5$(Th*)][PF$_6$]$_2$. There are several reasons for choosing $Ru(NH_3)_5(H_2O)^{2+}$ as the extracting agent in our studies. The Ru(II) in this complex has a d^6 electron configuration, which is typical of metal complexes that bind to thiophene.[8] The complex $Ru(NH_3)_5(H_2O)^{2+}$ has been previously reported[16] to react with thiophene (T) to

give $Ru(NH_3)_5(T)^{2+}$, which was too unstable to be characterized by elemental analysis as we also observe. Another Ru(II) complex $CpRu(CO)(PPh_3)(T)^{+}$,[17] where $Cp = \eta^5-C_5H_5$, was stable enough to be fully characterized. The equilibrium

$$CpRu(CO)(PPh_3)(T)^+ + DBT \rightleftharpoons CpRu(CO)(PPh_3)(DBT)^+ + T \qquad (3)$$
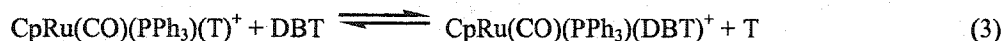
constant for its reaction (eq 3) with DBT is 76.1, which indicates that DBT binds substantially more strongly than T. We therefore expected $Ru(NH_3)_5(DBT)^{2+}$ to be more stable than $Ru(NH_3)_5(T)^{2+}$. Another advantage for $Ru(NH_3)_5(DBT)^{2+}$ is that the NH_3 ligands are small and may not pose a steric barrier to the coordination of 4,6-Me_2DBT, according to molecular models. In addition, the H_2O ligand in $Ru(NH_3)_5(H_2O)^{2+}$ is known[18] to be labile and rapidly substituted by a variety of ligands such as pyridine ($k_{pyridine} = 9.32 \pm 0.12 \times 10^2$ $M^{-1} s^{-1}$).

In the present studies, we find that 4,6-Me_2DBT in acetone or DMF does indeed react with $Ru(NH_3)_5(H_2O)^{2+}$ within 1 h at room temperature to give $Ru(NH_3)_5(4,6-Me_2DBT)^{2+}$ in 86% yield (eq 4). Reactions of DBT, BT and T with $Ru(NH_3)_5(H_2O)^{2+}$
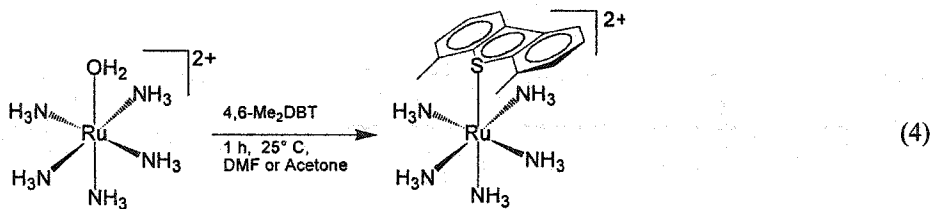
give analogous complexes of these ligands. Due to their sensitivity to oxidation by air we were unable to obtain satisfactory elemental analyses of the isolated complexes, even when they were handled under an argon atmosphere. However, the complexes were characterized by their ^1H and ^{13}C NMR spectra as discussed below.

The ^1H and ^{13}C NMR spectra (Table 1) of Ru(NH$_3$)$_5$(4,6-Me$_2$DBT)$^{2+}$ (**1**) show that the arene protons are slightly downfield (δ 8.15, 7.44, 7.36) of those in free 4,6-Me$_2$DBT (δ 8.12, 7.43, 7.35). Similar small shifts in the ^{13}C NMR spectrum are observed for the aromatic carbons; a larger shift is observed for the methyl groups (δ15.01) in **1** as compared with that of free 4,6-Me$_2$DBT (δ 19.82). Small shifts in ligand ^1H and ^{13}C NMR signals are also observed upon coordination of DBT and T in Ru(NH$_3$)$_5$(DBT)$^{2+}$ (**2**) and Ru(NH$_3$)$_5$(T)$^{2+}$ (**4**) (Table 1). Such small shifts are characteristic of S-coordinated thiophene ligands as has been observed in CpRe(CO)$_2$(Th*)[19,20]. On the other hand, the proton signals (δ 6.51, 5.98) for H(2) and H(3) in the BT ligand of Ru(NH$_3$)$_5$(BT)$^{2+}$ (**3**), are a full 0.92 and 1.38 ppm upfield compared to that of the free ligand (δ 7.43, 7.36). A large upfield shift of over nearly 90 ppm is also observed for C(2) and C(3) in the ^{13}C
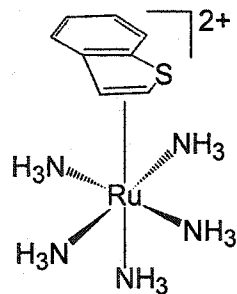
3

NMR spectrum of the compound. These large, upfield shifts for H(2), H(3), C(2) and C(3) are typical for M-BT complexes in which the BT is coordinated through the olefin group at C(2)=C(3), as has been reported for CpRe(CO)$_2$(η^2-BT).[20]

All of these Ru(II) complexes are very sensitive to air oxidation. When acetone solutions of *1-4* are exposed to air, they are oxidized with a half-life of about 30 min. They

are even slowly oxidized by trace amounts of O_2 present in flasks that have been treated with multiple freeze/pump/thaw cycles. Fortunately, the Ru(III and IV) products are reduced back to Ru(II) by reaction with H_2 when catalyzed by Pd/C.[21] For this reason, 10 mg of Pd/C (10% Pd by weight on activated carbon) was added and H_2 was bubbled through solutions of $Ru(NH_3)_5(Th^*)^{2+}$ for 15 min to keep them in the reduced Ru(II) form. Additional H_2 may be added periodically when the bright yellow solution begins to darken indicating the formation of the red $Ru^{3+/4+}$ cluster, which is discussed in the next section.

While many $\eta^1(S)$-coordinated DBT metal complexes are known[8], $Ru(NH_3)_5(4,6\text{-}Me_2DBT)^{2+}$ is a rare example of a $4,6\text{-}Me_2DBT$ complex.[5] As for $(\eta^5\text{-}C_5Me_5)Ru(CO)_2(4,6\text{-}Me_2DBT)^{+}$,[5] the $4,6\text{-}Me_2DBT$ in **1** binds less strongly than the DBT ligand in **2**. This was established by the reaction of $Ru(NH_3)_5(H_2O)^{2+}$ with a 10-fold excess of both DBT and $4,6\text{-}Me_2DBT$, which yielded $Ru(NH_3)_5(DBT)^{2+}$ as the only product, as determined by an ^1H NMR spectrum of the solution. Presumably, the methyl groups in the 4,6-positions sterically hinder the coordination of the sulfur in $4,6\text{-}Me_2DBT$ to the metal. In earlier studies of $(\eta^5\text{-}C_5Me_5)Ru(CO)_2(\text{dibenzothiophene})^{+}$,[5] and $(\eta^5\text{-}C_5H_5)Ru(CO)_2(\text{dibenzothiophene})^{+}$,[17] it was established that methyl groups in the non-hindering 2,8-positions enhance the binding of $2,8\text{-}Me_2DBT$ as compared with DBT.

Removal of DBT from $Ru(NH_3)_5(DBT)^{2+}$ by Oxidation. If $Ru(NH_3)_5(H_2O)^{2+}$ is to be used to remove DBT from hydrotreated feedstocks, it is necessary to remove DBT from its $Ru(NH_3)_5(DBT)^{2+}$ form and convert it back to $Ru(NH_3)_5(H_2O)^{2+}$. We first considered displacing DBT by the addition of a gas. Dinitrogen (N_2) is reported[16] to displace T from

$Ru(NH_3)_5(T)^{2+}$ with an equilibrium constant of approximately ~3300, which suggested that it would also displace DBT from **2**. However, stirring $Ru(NH_3)_5(DBT)^{2+}$ in acetone at room temperature under N_2 (1 atm) for 3 days did not displace the DBT in favor of N_2. On the other hand, CO (1 atm) completely displaces DBT from $Ru(NH_3)_5(DBT)^{2+}$ within 30 minutes at room temperature in acetone to give $Ru(NH_3)_5(CO)^{2+}$, which was identified by its characteristic v_{CO} adsorption at 1948 cm^{-1}.[22] However we were not successful in removing CO from $Ru(NH_3)_5(CO)^{2+}$ to reform $Ru(NH_3)_5(H_2O)^{2+}$.

So, we investigated the removal of DBT from $Ru(NH_3)_5(DBT)^{2+}$ by oxidation to $Ru(NH_3)_5(DBT)^{3+}$, which we assume will bind DBT much less strongly. This assumption is based on the fact[18] that the equilibrium constant (~10) for the reaction of $Ru(NH_3)_5(H_2O)^{2+}$ with T is favorable, while the equilibrium constant (2.5×10^{-8}) for the reaction of $Ru(NH_3)_5(H_2O)^{3+}$ with T is highly unfavorable. Unfortunately, we were unable to find an oxidant that would simply oxidize $Ru(NH_3)_5(DBT)^{2+}$ to $Ru(NH_3)_5(DBT)^{3+}$. Ferrocenium ion (Cp_2Fe^+) does not react with either $Ru(NH_3)_5(DBT)^{2+}$ or $Ru(NH_3)_5(H_2O)^{2+}$ in acetone solution as determined by UV-vis spectroscopy over a period of 1 h.

Air was then bubbled through a DMF/H_2O solution of $Ru(NH_3)_5(DBT)^{2+}$; however, $Ru(NH_3)_5(H_2O)^{3+}$ is not formed. Rather, $[(NH_3)_5RuORu(NH_3)_5]^{4+}$ (λ_{max} 503, 386 nm) is formed which reacts further to form a tri-ruthenium cluster commonly called ruthenium red (λ_{max} 532 nm) because of its color; its formation was established by a UV-vis spectrum of the solution (Scheme 1).[23] It should be noted that air oxidation of $Ru(NH_3)_5(H_2O)^{2+}$ was previously reported to give the same products.[24] When air is bubbled for 30 min through a solution of $Ru(NH_3)_5(DBT)^{2+}$ in 10 mL of DMF/H_2O with 10 mL of hexanes layered over it,

DBT is released into the hexanes phase (observed via ^{1}H NMR). This release of DBT coincides with the formation of the oxidized ruthenium clusters (Scheme 1). When the DMF/H$_2$O solution of [(NH$_3$)$_5$RuORu(NH$_3$)$_5$]$^{4+}$ was treated with bubbling H$_2$ in the presence of Pd/C, Ru(NH$_3$)$_5$(H$_2$O)$^{2+}$ was formed in ~ 90% yield. This yield was estimated by using this recycled Ru(NH$_3$)$_5$(H$_2$O)$^{2+}$ solution in a second extraction (see below) of DBT from toluene/hexanes (under the original conditions); a ~10% decrease in the amount of DBT extracted was observed. We attribute this loss in activity to the formation of small amounts of unknown side products in the oxidation of Ru(NH$_3$)$_5$(DBT)$^{2+}$. Perhaps the side products responsible for the 10% loss in activity are due to the formation of ruthenium red because it contains a [Ru(NH$_3$)$_4$] unit that may not be capable of reforming Ru(NH$_3$)$_5$(H$_2$O)$^{2+}$.

Removal of DBT from Ru(NH$_3$)$_5$(DBT)$^{2+}$ by Displacement with H$_2$O. Because of the loss of some extraction ability during the oxidation-reduction recycling, we sought a simpler method of removing DBT from Ru(NH$_3$)$_5$(DBT)$^{2+}$. On the basis of the extraction studies (see below), it is likely that the DBT could be displaced by H$_2$O if the concentration of water in the DMF/H$_2$O solution were increased. Following a typical extraction of DBT from 45% toluene / 55% hexanes with Ru(NH$_3$)$_5$(H$_2$O)$^{2+}$ in 70% DMF / 30% H$_2$O, the DMF/H$_2$O phase containing Ru(NH$_3$)$_5$(DBT)$^{2+}$ was separated and layered with 45% toluene / 55% hexanes. After sonication of this mixture for 1 h, the 45% toluene / 55% hexanes layer was observed to contain 60% of the DBT that was originally present in the Ru(NH$_3$)$_5$(DBT)$^{2+}$/DMF/H$_2$O phase. When water was added to the Ru(NH$_3$)$_5$(DBT)$^{2+}$/DMF/H$_2$O phase to give a 60% DMF / 40% H$_2$O composition, even more DBT (74%) was extracted into the hydrocarbon phase.

When the water content was increased to 40% DMF / 60% H_2O, 83% of the DBT was extracted from the $Ru(NH_3)_5(DBT)^{2+}$/DMF/H_2O phase. Thus, the majority of the $Ru(NH_3)_5(DBT)^{2+}$ in the DMF/H_2O can be converted back to $Ru(NH_3)_5(H_2O)^{2+}$ by extracting DBT with a toluene/hexanes phase while adding water to the $Ru(NH_3)_5(DBT)^{2+}$/DMF/H_2O phase. This method of regenerating $Ru(NH_3)_5(H_2O)^{2+}$ from $Ru(NH_3)_5(DBT)^{2+}$ avoids the complications of the oxidation-reduction method described above.

Extraction of DBT from Simulated Fuel with $[Ru(NH_3)_5(H_2O)][PF_6]_2$. The ability of $Ru(NH_3)_5(H_2O)^{2+}$ to react with 4,6-Me_2DBT and DBT to give complexes 1 and 2 suggested that $Ru(NH_3)_5(H_2O)^{2+}$ could be used to extract these dibenzothiophenes from petroleum feedstocks. The approach described herein involves using $Ru(NH_3)_5(H_2O)^{2+}$ in a polar phase to extract DBT from a simulated hydrocarbon fuel phase. The simulated fuel feedstock consists of 45% toluene, 55% hexane, and 400 ppm DBT, which is the current EPA sulfur limit in gasoline. When five equivalents of $Ru(NH_3)_5(H_2O)^{2+}$ (with respect to the number of moles of DBT in the hydrocarbon {hc} phase) in a 70% DMF / 30% H_2O phase are sonicated or stirred with the DBT/hc phase, the amount of DBT in the hc phase is reduced from 400 ppm to 270 ppm sulfur (middle dashed line in Figure 1). When the amount of $Ru(NH_3)_5(H_2O)^{2+}$ is increased to ten equivalents (bottom solid line), the DBT content of the feedstock phase is reduced even further to 200 ppm. These extractions are performed under a H_2 atmosphere in the presence of suspended Pd/C to keep the ruthenium complexes in the 2+ oxidation state. This extraction of DBT into the $Ru(NH_3)_5(H_2O)^{2+}$/DMF/H_2O phase is primarily due to $Ru(NH_3)_5(H_2O)^{2+}$ because extraction of the DBT/hc phase with only 70% DMF / 30% H_2O reduced the DBT content in the hc phase to only 350 ppm (Figure 1). This

result indicates that DBT has a small but measurable solubility in 70% DMF / 30% H_2O (eq 1). In order to ensure that the small amount of DBT extracted was not due to reaction with the Pd/C, the same extraction was performed in the absence of Pd/C; it also reduced the DBT level to 350 ppm in the hc phase.

These experiments indicate that the extraction of DBT into the $Ru(NH_3)_5(H_2O)^{2+}$/DMF/H_2O phase involves two equlibria. The first distribution equilibrium represents a distribution of DBT between the DMF/H_2O and hc phases, (eq 1). The second is that for the reaction of $Ru(NH_3)_5(H_2O)^{2+}$ with DBT (eq 2) in the DMF/H_2O phase. These thiophene extractions reach equilibrium within one hour at room temperature. The equilibrium constants (K_1 for eq 1 and K_2 for eq 2) for DBT were calculated from the data in Figure 1. The control experiment yields the value for K_1 and the value for K_2 is calculated from the $Ru(NH_3)_5(H_2O)^{2+}$/DMF/H_2O experiments as described in the Experimental section. Equilibrium constants K_1 and K_2 for DBT, BT and T were collected similarly and are presented in Table 2.

The trend in K_1 values (DBT < BT < T) shows that T is the most soluble in the DMF/H_2O phase (eq 1). The K_2 values for the binding of the thiophene by $Ru(NH_3)_5(H_2O)^{2+}$ (eq 2) increases in the order: 56 (T) < 339 (BT) < 559 (DBT). This is the same trend that was previously observed for their coordination to $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)^+$.[17]

Extraction of 4,6 Me$_2$DBT from Simulated Fuel with [Ru(NH$_3$)$_5$(H$_2$O)][PF$_6$]$_2$. Although the extraction process removes a significant amount of the DBT in a simulated petroleum feedstock, 4,6-Me$_2$DBT is not removed in appreciable amounts by the same system. Under the same conditions in which 400 ppm of DBT was reduced to 200 ppm, no 4,6-Me$_2$DBT

was removed from the hc phase. Part of the reason for this behavior is the low value of K_1 for 4,6-Me$_2$DBT. In the measurement of K_1 for DBT, ~12% of the DBT was extracted into the DMF/H$_2$O phase. When the same extraction was performed with 4,6-Me$_2$DBT, no observable 4,6-Me$_2$DBT was extracted into the DMF/H$_2$O phase. The two methyl groups probably make 4,6-Me$_2$DBT more hydrophobic than DBT and therefore insoluble in the polar DMF/H$_2$O phase. Also contributing to the inability of Ru(NH$_3$)$_5$(H$_2$O)$^{2+}$/DMF/H$_2$O to extract 4,6-Me$_2$DBT from the hc phase is a much smaller value of K_2 for 4,6-Me$_2$DBT than for DBT, as demonstrated in the DBT/4,6-Me$_2$DBT competition experiments described above.

In an attempt to increase the value of K_1, the DMF content was increased to 80% DMF / 20% H$_2$O; however, this did not improve the 4,6-Me$_2$DBT extraction. Using the less polar DMAC (N,N-dimethylacetamide) in place of DMF in the aqueous phase did improve the solubility of 4,6-Me$_2$DBT (Figure 2) in the polar phase (70% DMAC / 30% H$_2$O) and also reduced the 4,6-Me$_2$DBT in the hc phase from 400 to 340 ppm in a Ru(NH$_3$)$_5$(H$_2$O)$^{2+}$/DMAC/H$_2$O extraction. However, this extraction was substantially less effective than those for DBT.

Overall System for the Extraction of DBT from Hydrotreated Fuels. On the basis of the above studies, one can propose a process (Scheme 2) for the extraction of DBT from simulated hydrotreated fuel using a polar Ru(NH$_3$)$_5$(H$_2$O)$^{2+}$/DMF/H$_2$O phase . The 70% DMF / 30% H$_2$O extraction solvent was chosen because both [Ru(NH$_3$)$_5$(H$_2$O)$^{2+}$][PF$_6$]$_2$ and DBT are soluble in it. Also, the H$_2$O causes this phase to separate from the DBT / 45% toluene / 55% hexanes phase. After an extraction, no DMF is detected in the hc phase, while

only 0.44% of the hexanes was observed in the DMF/H_2O phase, as determined by GC analyses.

The overall process (Scheme 2) for the extraction of DBT from a hydrotreated petroleum feedstock could be envisaged to occur as follows: the hydrotreated feedstock is first extracted with the $Ru(NH_3)_5(H_2O)^{2+}/DMF/H_2O$ phase to remove DBT as $Ru(NH_3)_5(DBT)^{2+}$. The DMF/H_2O phase containing $Ru(NH_3)_5(DBT)^{2+}$ is then separated from the desulfurized hydrocarbon phase. The extractant phase is then regenerated by treating the $Ru(NH_3)_5(DBT)^{2+}/DMF/H_2O$ solution with air (O_2) which would release the DBT and form $[(NH_3)_5RuORu(NH_3)_5]^{4+}$ and a small amount of $[(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5]^{4+}$. The released DBT is extracted into a pure hydrocarbon phase such as hexanes. Finally, the ruthenium cluster in DMF/H_2O is reduced by treatment with H_2 and Pd/C to regenerate $Ru(NH_3)_5(H_2O)^{2+}$ in the DMF / H_2O phase, which is used for another extraction. An alternative method for regenerating $Ru(NH_3)_5(H_2O)^{2+}$ from the $Ru(NH_3)_5(DBT)^{2+}/DMF/H_2O$ solution is to add H_2O until it reaches 60%, thereby driving the DBT into a pure hydrocarbon phase. The extra water added to the DMF/H_2O phase could be removed by distillation later.

In an attempt to determine whether multiple extractions of DBT from a simulated fuel could reduce the DBT to target levels, the same simulated fuel (400 ppm of DBT) was treated with $Ru(NH_3)_5(H_2O)^{2+}$ (10 equivalents) / DMF / H_2O in five successive extractions. As shown in Figure 3, these multiple extractions reduced the DBT level by approximately 50% in each step to give a final hydrocarbon phase containing only 25 ppm of DBT, which is the target for gasoline.

Conclusions

The synthesis of $Ru(NH_3)_5(4,6\text{-}Me_2DBT)^{2+}$, as well as the DBT, BT and T analogs, shows that $Ru(NH_3)_5(H_2O)^{2+}$ is capable of binding to these thiophenes. Using this binding ability, we have demonstrated that 50% of the DBT (400 ppm) in a simulated hydrotreated petroleum feedstock can be removed in a single extraction with a DMF/H_2O solution of $Ru(NH_3)_5(H_2O)^{2+}$. Five sequential extractions remove 94% of the DBT. The DBT can be removed from the resulting $Ru(NH_3)_5(DBT)^{2+}$ complex and converted back to $Ru(NH_3)_5(H_2O)^{2+}$ by either oxidation/reduction steps or the addition of water. The extraction of $4,6\text{-}Me_2DBT$ from a simulated feedstock is possible in $DMAC/H_2O$, but at only 25% of the level achieved with DBT.

Table 1. ^{1}H and ^{13}C NMR Data (ppm, in acetone-d$_6$) for Thiophene (T), Benzothiophene (BT), Dibenzothiophene (DBT) and 4,6-Dimethyldibenzothiophene (4,6-Me$_2$DBT), Unbound and Bound in Ru(NH$_3$)$_5$(Th*)$^{2+}$.

Ligand	^{1}H NMR Unbound	^{1}H NMR Bound	^{13}C NMR Unbound	^{13}C NMR Bound
T	7.47, 7.15	7.49, 7.13	127.12, 125.39	127.08, 125.34
BT	7.99-7.85 (m), 7.64, 7.43, 7.36	8.1-7.4 (m), 6.51, 5.98	140.08, 139.91, 126.81, 124.46, 124.39, 124.16, 123.82, 122.62	128.12, 127.72, 125.98, 124.68, 123.85, 122.56 35.32, 34.96
DBT	8.33, 7.98, 7.51 (m)	8.38, 8.05, 7.68, 7.54	139.38, 136.82, 127.23, 124.82, 123.05, 122.01	143.12, 138.62, 127.95, 125.10, 123.11, 121.95
4,6-Me$_2$DBT	8.12, 7.43, 7.35, 2.59	8.15, 7.44, 7.36, 2.62	139.04, 136.27, 127.27, 125.30, 132.31, 119.71, 19.82	139.24, 136.39 127.50, 125.32, 132.37, 119.82, 15.01

Table 2. Equilibrium Constants, K_1 and K_2, for Reactions (1) and (2) for T, BT and DBT.

Thiophene	K_1	K_2
DBT	0.139 ± 0.01	559 ± 83
BT	0.173 ± 0.002	339 ± 28
T	0.349 ± 0.002	56 ± 3

Scheme 1. Oxidation of $Ru(NH_3)_5(H_2O)^{2+}$ or $Ru(NH_3)_5(DBT)^{2+}$.

Ruthenium Red
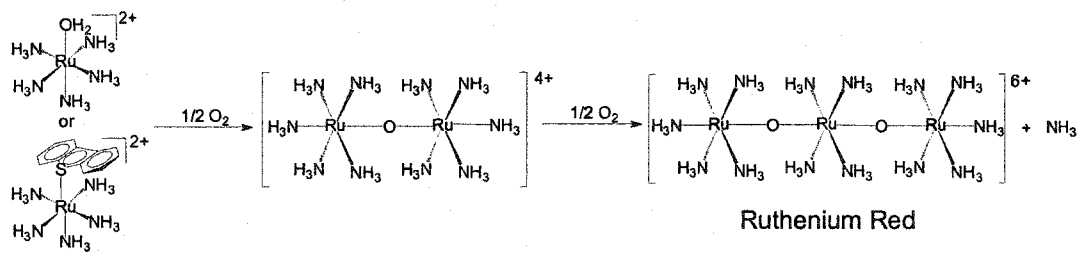
Scheme 2. Cyclic process for the extraction of DBT from simulated petroleum fuel using a Ru(NH$_3$)$_5$(H$_2$O)$^{2+}$/DMF/H$_2$O extractant.

32
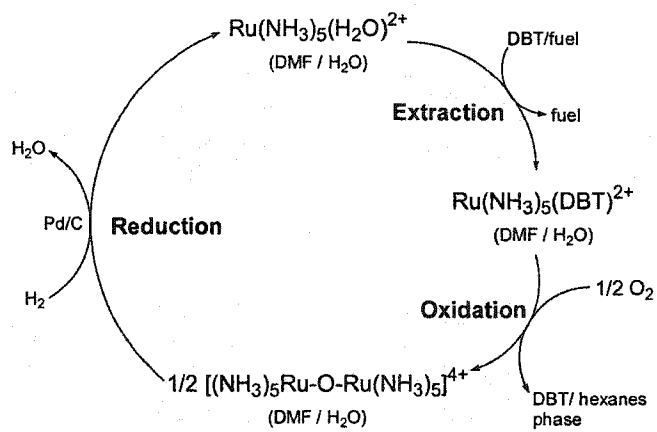
Chart 1. Structures of thiophenes.
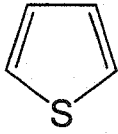
thiophene, T
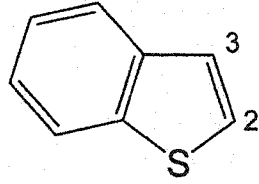
benzothiophene, BT
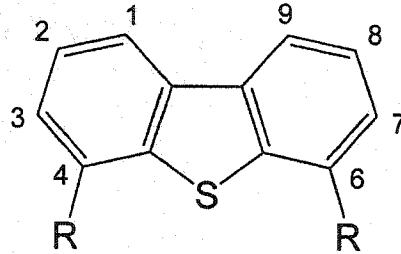
dibenzothiophenes, R_2DBT
where R= H, Me

Figure 1. Extraction of DBT from simulated petroleum fuel with $[Ru(NH_3)_5(H_2O)][PF_6]_2$ in 70% DMF / 30% H_2O.
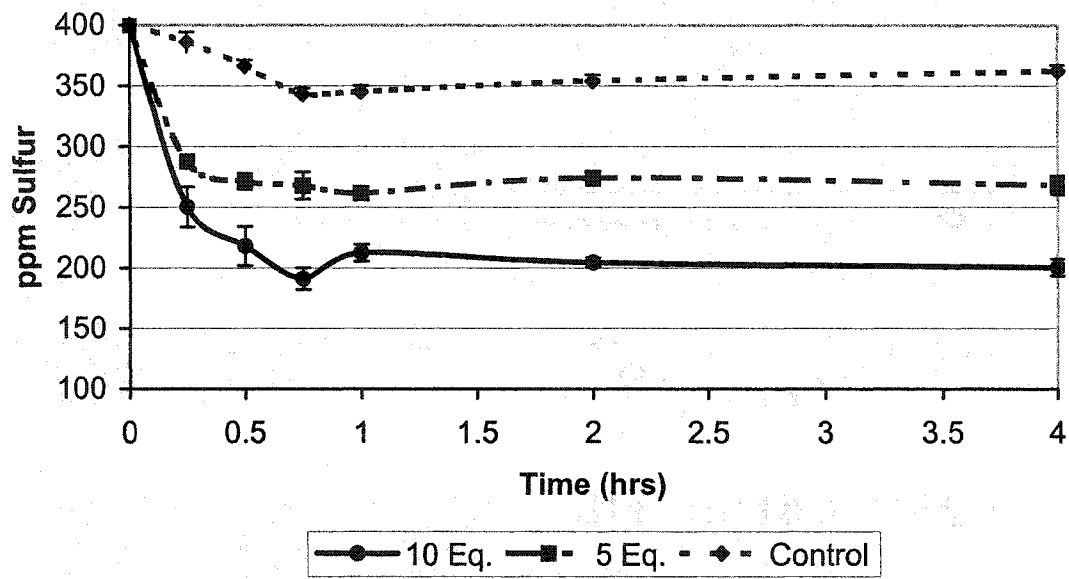
Figure 2. Extraction of 4,6-Me$_2$DBT from simulated petroleum fuel by [Ru(NH$_3$)$_5$(H$_2$O)][PF$_6$]$_2$ in 70% DMAC / 30% H$_2$O.
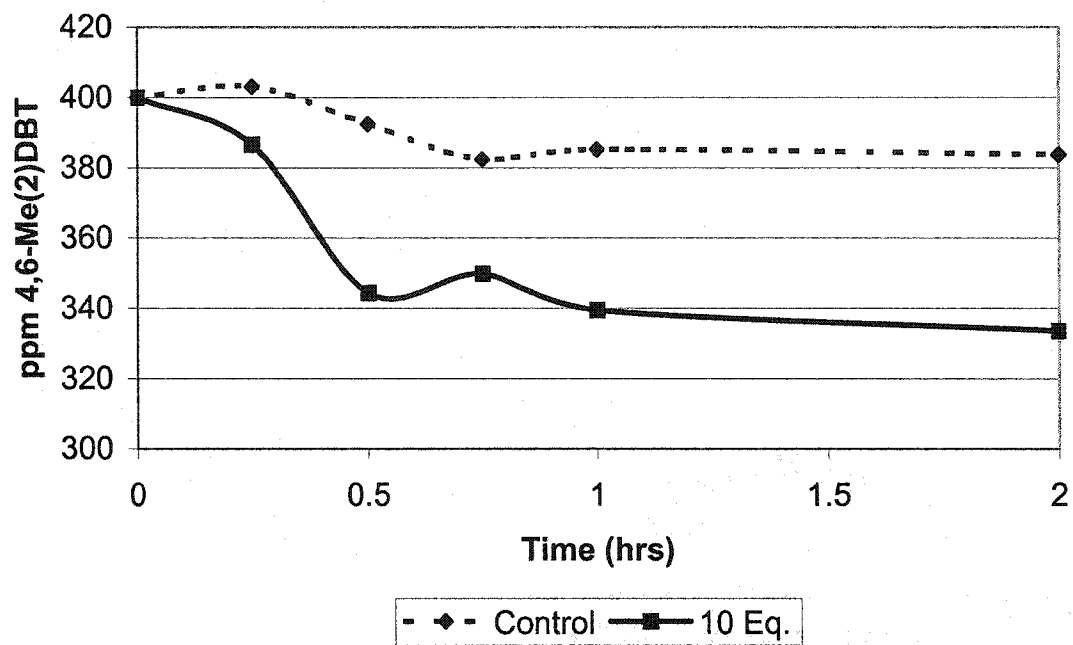
Figure 3. Stepwise extraction of DBT from simulated petroleum fuel by [Ru(NH$_3$)$_5$(H$_2$O)][PF$_6$]$_2$ in 70% DMF / 30% H$_2$O.

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CHAPTER THREE: MODELING OF AN ACTIVE ADSORPTION SITE FOR THE REMOVAL OF DIBENZOTHIOPHENE FROM SIMULATED PETROLEUM: THE USE OF CpRu(CO)$_2$(BF$_4$) AND [CpFe(CO)$_2$(THF)]$^+$ AS SOLID PHASE EXTRACTANTS TO INVESTIGATE THE DESULFURIZATION PROCESS

Scott G. McKinley, Paul A. Vecchi, Arkady Ellern and Robert J. Angelici

Department of Chemistry, Iowa State University, Ames, IA 50011

Abstract

The complexes, CpRu(CO)$_2$(BF$_4$) and [CpFe(CO)$_2$(isobutene)][BF$_4$], react with dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-Me$_2$DBT) to give [CpRu(CO)$_2$(DBT)][BF$_4$] and [CpFe(CO)$_2$(4,6-Me$_2$DBT)][BF$_4$], whose structures were established by X-ray diffraction studies. The same types of products are obtained when dibenzothiophenes react with CpRu(CO)$_2$(BF$_4$) and [CpFe(CO)$_2$(THF)][BF$_4$] that are adsorbed on the mesoporous silica SBA-15. DRIFT, CP MAS ^{29}Si NMR, and XPS studies indicate that CpRu(CO)$_2$(BF$_4$) and [CpRu(CO)$_2$(DBT)][BF$_4$] are adsorbed on the SBA-15 by

hydrogen-bonding of the BF₄⁻ anions to surface Si-O-H groups. CpRu(CO)₂(BF₄)/SBA-15

removes 99% of the DBT (400 ppm) from a 45% toluene/55% hexanes simulated petroleum

feedstock. This solid phase extractant is less successful for sterically-hindered 4,6-Me₂DBT,

as only 72% of it is removed. The results suggest that selected organometallic complexes on

solid supports are capable of reducing substantially the amounts of sulfur in petroleum

feedstocks by removing dibenzothiophenes.

Introduction

The removal of sulfur from transportation fuels is necessary for the reduction of

atmospheric pollution by sulfur oxides.[1] Sulfur content in gasoline is currently limited to 400

ppm (0.04% by weight), but the EPA has introduced new regulations that will reduce this

level gradually to 30 ppm (0.003% by weight) by 2006.[2] The sulfur content in diesel fuel

must undergo similar reductions. Since sulfur has been shown to poison catalytic converters,

these lower sulfur levels will have the additional benefits of increasing catalyst lifetimes and

reducing the amount of NO_x released into the atmosphere. The new sulfur mandates will

require significant improvements in current desulfurization methods or the development of

new technologies.

Sulfur is now removed from petroleum feedstocks using a catalytic process called

hydrodesulfurization (HDS).[3] The most easily desulfurized components of the feedstocks are

the thiols (RSH) and thioethers (R'SR''). Catalytic systems have been developed that are also

capable of desulfurizing the thiophenes, benzothiophenes and unhindered dibenzothiophenes.

It is the hindered dibenzothiophenes, those with alkyl groups in the 4 and 6 positions that are

the slowest to undergo HDS. These 4,6-R_2DBT compounds constitute the bulk of the remaining sulfur compounds in petroleum fuels and must be removed in order to meet the EPA requirements.[4]

It has been proposed[4] that during the HDS process, dibenzothiophenes initially adsorb through their sulfur to an active site on the supported catalyst surface. They are subsequently
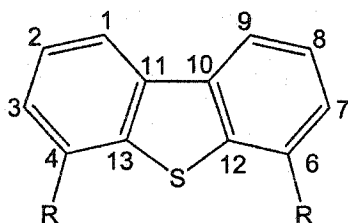
Dibenzothiophenes, 4,6-R_2DBT
where R= H, Me

desulfurized by reaction with hydrogen (usually >50 atm) to produce H_2S and hydrocarbons, as shown in eq (1). The slow rate of hindered dibenzothiophene HDS is often attributed to

$$C_aH_bS + cH_2 \quad C_aH_d + H_2S \tag{1}$$

steric hindrance by methyl groups in the 4 and 6 positions which interfere with sulfur binding to an adsorption site on the catalyst surface. Indeed, there is only one reported example of a fully characterized sulfur-bound 4,6-dimethyldibenzothiophene (4,6-Me_2DBT) complex[5], $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2(4,6\text{-}Me_2DBT)]^+$, and the equilibrium constant for 4,6-Me_2DBT binding in this complex is 62.7 times lower than that for DBT. Despite the rarity of sulfur-coordinated 4,6-Me_2DBT transition metal complexes, numerous sulfur-bound DBT complexes are described in the literature.[6,7] These results suggest that it is the bulkiness of

the R groups in the 4,6-R_2DBT molecules that hinder the initial adsorption and thereby reduce the overall rates of desulfurization under HDS conditions.

Research on the HDS process has not yielded an economically viable method for the deep desulfurization of petroleum feedstocks. Therefore substantial efforts have been devoted to finding new ways to remove 4,6-R_2DBT molecules from petroleum. Recent methods include deep desulfurization by selective adsorption of R_2DBT,[8] precipitation of an insoluble DBT-sulfimide (by reaction with sodium N-chlorotoluene-p-sulfonamide),[9] extraction of DBT by ionic liquids[10] and the oxidation of DBT and 4,6-Me_2DBT to the corresponding sulfones and sulfoxides.[11]

The adsorptive removal of dibenzothiophene from petroleum feedstocks using solid phase extractants (SPEs) is currently an active field of research.[8] A preliminary study using activated carbon has been reported.[12] The focus of this report is on the use of organometallic complexes that are known to bind DBT and hindered DBT, as components in solid phase extractants that can remove dibenzothiophenes from simulated petroleum feedstocks. The organometallic complexes used in these studies are based on $Cp^*Ru(CO)_2(BF_4)$ and $[CpFe(CO)_2(isobutene)]^+$ which react in solution with 4,6-R_2DBT (R = H, Me) to give $[Cp^*Ru(CO)_2(4,6\text{-}Me_2DBT)][BF_4]^5$ and $[CpFe(CO)_2(DBT)]^{+,13}$ (Cp = η^5-C_5H_5). The precursor complexes, $CpRu(CO)_2(BF_4)$ and $[CpFe(CO)_2(THF)]^+$, have been adsorbed onto mesoporus silica (SBA-15) to form SPE's that remove 4,6-R_2DBT compounds from simulated petroleum feedstocks. These SPE's are characterized before and after 4,6-R_2DBT adsorption by CP MAS ^{13}C and ^{29}Si NMR, IR (DRIFT), and XPS spectroscopic studies.

Experimental

General Considerations. All reactions and metal complex treatments were carried out under an atmosphere of dry argon using standard Schlenk techniques. Diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), hexanes and toluene were all purified on alumina using a Solv-Tech solvent purification system, as described by Grubbs and co-workers.[14] $RuCl_3 \cdot 3H_2O$ was purchased from Pressure Chemical, and 4,6-Me_2DBT was purchased from Acros Organics. [CpFe(CO)$_2$(isobutene)][BF$_4$],[15] [CpFe(CO)$_2$(THF)][BF$_4$],[16] CpRu(CO)$_2$Cl[17] and [CpRu(CO)$_2$(DBT)][BF$_4$][18] (1) were synthesized according to published literature methods. All other chemicals were used without further purification as purchased from Aldrich. Filtrations were performed with Celite on filter paper.

Solution infrared spectra of the compounds in CH_2Cl_2 were recorded on a Nicolet-560 spectrometer using NaCl cells with 0.1 mm spacers. Solution NMR spectra were obtained on a modified 400 MHz Varian VXR-400 spectrometer using CD_3NO_2 or CD_2Cl_2 as the internal lock and reference. Solid state CP MAS ^{29}Si and ^{13}C NMR studies were performed on a Bruker MSL 300 instrument at a spin rate of 2.8 KHz. XPS were obtained on a Physical Electronics 5500 Multi-technique system using a standard Al source. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer. Gas chromatographic determinations were performed on a Hewlett Packard 6890 series instrument with a HP-5 column at 180° C, using decahydronaphthalene as an internal standard

Synthesis of [CpFe(CO)$_2$(4,6-Me$_2$DBT)][BF$_4$] (2). Compound **2** was synthesized following

a similar procedure[13] for [CpFe(CO)$_2$(DBT)][BF$_4$], except 4,6-Me$_2$DBT was used in place of

DBT. A solution of [CpFe(CO)$_2$(isobutene)][BF$_4$] (200 mg, 0.625 mmol) and 4,6-Me$_2$DBT

(150 mg, 0.708 mmol) in ClCH$_2$CH$_2$Cl (25 mL) was refluxed for 8 h. The reaction was

checked by IR to ensure completion, and volatiles were removed under vacuum. The solid

residue was dissolved in 20 mL of CH$_2$Cl$_2$, and the solution was filtered through Celite via

canula into cold diethyl ether, precipitating the product. This solid was isolated by filtration

and washing with diethyl ether). ^{1}H-NMR (δ, ppm in CD$_3$NO$_2$) δ = 8.10 (d, J = 7.6 Hz, 2H),

7.70 (t, J = 7.6 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 5.76 (s, 5H), 2.73 (s, 6H, CH$_3$). ^{13}C-NMR

(δ, ppm in CD$_3$NO$_2$) δ = 208.71 (CO); 140.61, 139.37, 136.56, 132.06, 131.64, 122.91, 21.78

(4,6-Me$_2$DBT); 89.03 (Cp). IR (CH$_2$Cl$_2$, υ_{CO} cm^{-1}) 2069(s), 2030(s). Anal. Calcd for

C$_{21}$H$_{17}$BF$_4$O$_2$FeS: C, 52.98; H, 3.60; S, 6.74. Found: C, 52.53; H, 3.63; S, 6.75. to yield

[CpFe(CO)$_2$(4,6-Me$_2$DBT)]BF$_4$ as a bright orange solid (254 mg, 85% yield

X-ray Crystal Structure Determinations of Complexes 1 and 2. Single crystals of

complexes **1** and **2** suitable for X-ray diffraction studies were obtained by recrystallization at

room temperature (**1**) or slow diffusion of hexanes into a saturated CH$_2$Cl$_2$ solution at -20° C

(**2**). The single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray

diffraction intensity data for both compounds were collected on a Bruker CCD-1000

diffractometer. Data collection for **2** was performed at 293 K as all attempts to collect data at

low temperature failed due to fracture of the crystal around 270 K. The high thermal

amplitudes of atoms in the BF$_4$$^-$ anion led to comparatively high values of the R-factor. The

reflections were successfully indexed by an automated indexing routine in the SMART

program. This dataset was corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements[19] using SADABS[20] software.

The positions of the heavy atoms were found by the Patterson method. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All hydrogen atoms for 1 and 2 were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. Other crystallographic data are given in Table 1.

Synthesis of Solid Phase Extractant SPE-Ru, CpRu(CO)$_2$(BF$_4$)/SBA-15. To a flask containing CpRu(CO)$_2$Cl (131 mg, 0.508 mmol) in 10 mL of CH$_2$Cl$_2$ was added AgBF$_4$ (193 mg, 0.763 mmol). The reaction mixture was subjected to one freeze/pump/thaw cycle, warmed to room temperature and allowed to stir for 1 hour. The IR spectrum was checked to ensure complete reaction. The solution was then filtered into a separate flask containing 250 mg of SBA-15[21] and stirred for 30 min. The mixture was dried under vacuum to yield a tan solid, SPE-Ru.

Synthesis of Solid Phase Extractant SPE-Fe, [CpFe(CO)$_2$(THF)][BF$_4$]/SBA-15. A solution of [CpFe(CO)$_2$(THF)][BF$_4$] (194.6 mg, 0.508 mmol) in 10 mL of CH$_2$Cl$_2$ was subjected to one freeze/pump/thaw cycle and warmed to room temperature. The solution was then filtered into a separate flask containing 250 mg of SBA-15 and stirred for 30 min. The mixture was dried under vacuum to yield a pale red solid, SPE-Fe.

Preparation of Simulated Fuels. To simulate the petroleum feedstocks, a mixture of 55% hexanes and 45% toluene (by volume) was used for gasoline.[4a] Into 10 mL of this mixed solvent was added, DBT (17.6 mg, 0.096 mmol, 0.040% by weight) or 4,6-Me$_2$DBT (19.3 mg, 0.096 mmol, 0.040% by weight) and decahydronaphthalene (15 µL) (internal standard).

Extraction of R$_2$DBT by SPE-Ru and SPE-Fe. 10 mL of the simulated fuel was subjected to one freeze/pump/thaw cycle and then warmed to room temperature. A separate flask containing 381 mg of SPE-Ru (or 445 mg of SPE-Fe) was degassed under vacuum for 5 min. After adding 10 mL of the simulated fuel to the SPE, the mixture was treated to one freeze/pump/thaw cycle, warmed to room temperature and stirred. Then, 0.4 mL aliquots were removed periodically in order to determine the amount of DBT or 4,6-Me$_2$DBT that was removed from the simulated fuel phase. The ratio of the DBT to decahydronaphthalene GC peak areas established the amount of DBT that was removed from the simulated fuel. The errors given in the Results section are average deviations based on two duplicate runs. When only SBA-15, without the adsorbed Ru or Fe complex, was used in the extractions, no DBT or 4,6-Me$_2$DBT was removed from the simulated fuels.

CP MAS ^{13}C-NMR Spectra of SPE-Ru/DBT and SPE-Fe/DBT. A 381 mg sample of SPE-Ru or a 445 mg sample of SPE-Fe was used to extract R$_2$DBT from a simulated fuel as described in the previous section. After stirring for 1 h, the mixture was filtered. The tan solid was washed with hexane (3 x 20 mL). The sample was then dried under vacuum and loaded into a CP MAS NMR sample tube under Ar. SPE-Ru/DBT: CP MAS ^{13}C NMR δ = 137.07, 129.57, 126.16, 90.03 ppm. SPE-Ru/4,6-Me$_2$DBT: CP MAS ^{13}C NMR δ = 140.10,

137.16, 135.04, 135.06, 128.26, 119.56, 90.52, 21.12 ppm. SPE-Fe/DBT: CP MAS ^{13}C NMR

δ = 135-120 (br), 89.51 ppm. SPE-Fe/4,6-Me$_2$DBT: CP MAS ^{13}C NMR δ = 135-120 (br),

89.56, 20.83 ppm.

DRIFT-IR Spectra of SBA-15, SPE-Ru and SPE-Ru/DBT. Diffuse reflectance infrared

Fourier transform (DRIFT) spectra were collected in an Auxiliary Experiment Module on the

Nicolet 560 infrared spectrophotometer operating between 400 and 4000 cm^{-1}. The Harrick

DRIFT chamber was connected to an air purification system to keep the stage dry. Oven

dried KBr was used as the background, and the amount of SBA-15 (5% by weight) was kept

constant in each sample by varying the amount of KBr. All spectra were recorded at 4 cm^{-1}

resolution with 1000 scans.

Results and Discussion

Synthesis and Structures of [CpM(CO)$_2$(R$_2$DBT)]$^+$ Complexes. The complex

[CpRu(CO)$_2$(DBT)]$^+$ **(1)** was prepared according to a literature procedure[14] by reacting

CpRu(CO)$_2$Cl with AgBF$_4$ in the presence of DBT in CH$_2$Cl$_2$ solution. The complex

[CpFe(CO)$_2$(4,6-Me$_2$DBT)]$^+$ **(2)** must be made by a different route, because the reaction of

CpFe(CO)$_2$Cl with Ag$^+$ yields a series of Cl$^-$ bridged compounds and not

[CpFe(CO)$_2$(solvent)$^+$].[22] Therefore, [CpFe(CO)$_2$(isobutene)]$^+$ was refluxed in 1,2-

dichloroethane with 4,6-Me$_2$DBT to yield [CpFe(CO)$_2$(4,6-Me$_2$DBT)]$^+$ **(2)**, following a

procedure[13] previously used for the synthesis of CpFe(CO)$_2$(DBT)$^+$. This iron complex

represents only the second fully characterized sulfur-bound 4,6-Me_2DBT complex and is the first such complex with iron.

The molecular structures of compounds **1** and **2** are shown in Figure 1, and selected bond distances and angles are listed in Table 2. The Fe-S distance (2.3103(19) Å) in [CpFe(CO)$_2$(4,6-Me$_2$DBT)]$^+$ (**2**) is ~0.02 Å longer than that (2.289(1) Å)[13] in [CpFe(CO)$_2$(DBT)]$^+$. This lengthening of the Fe-S bond in the 4,6-Me_2DBT complex is attributed to steric repulsion between methyl groups in the 4,6- positions of DBT and the Cp ligand. The Ru-S distance (2.3980(18) Å) in CpRu(CO)$_2$(DBT)$^+$ (**1**) is longer than that in either of the iron complexes as expected, and is nearly identical to that in the recently reported [Cp*Ru(CO)$_2$(DBT)]$^+$ complex (Ru-S = 2.3936(5) Å).[5]

The orientation of the DBT ligand around the M-S bond was used previously[5] to illustrate steric effects of the 4- and 6- methyl groups: this orientation is defined as the dihedral angle Cp(centroid)-Ru-S-midpoint between C(10) and C(11). For a symmetrical orientation, this angle would be 180°, and the deviation from 180° is defined as the twist angle. In **2** the twist angle is only 3.4° because rotation around the Fe-S bond is restricted by the close approach (2.393 Å) of the methyl carbon atoms (C(14) and C(16)) in the 4,6-Me_2DBT ligand to a plane defined by the Cp carbon atoms. It is presumably the steric repulsions between the hydrogen atoms on C(14) and C(16) and the hydrogen atoms on the Cp ligand that give rise to the small twist angle. An even smaller twist angle (0.4°) was observed in Cp*Ru(CO)$_2$(4,6-Me$_2$DBT)$^{+}$,[5] where repulsions between the 4,6-methyl groups and the methyl groups on the Cp* ligand are even larger. In **1**, which does not contain alkyl groups in the 4,6- positions, the twist angle (22.8°) of the DBT ligand is much larger, indicating greater freedom of rotation around the Ru-S bond.

Synthesis and Characterization of CpRu(CO)$_2$(BF$_4$)/SBA-15 (SPE-Ru) and [CpFe(CO)$_2$(THF)][BF$_4$]/SBA-15 (SPE-Fe). The solid-phase extractants, SPE-Ru and SPE-Fe, used in these studies were prepared by evaporating the solvent from a CH$_2$Cl$_2$ solution of [CpRu(CO)$_2$][BF$_4$] or a THF solution of [CpFe(CO)$_2$(THF)][BF$_4$] that is stirred with SBA-15, a mesoporus silica is used for its high surface area (618 m^{2}g^{-1} surface area and 52.3 Å pore size).[21] The nature of the metal complex interaction with the silica surface in SPE-Ru and SPE-Fe was examined by CP MAS ^{29}Si-NMR and DRIFT spectroscopy. In the CP MAS ^{29}Si NMR spectrum of unmodified SBA-15, three ^{29}Si peaks are observed at 112.50, 102.05 and 94.10 ppm, which correspond to silicon atoms bound to zero (Si-O-Si), one (Si-OH) or two (=Si(OH)$_2$) hydroxyl groups respectively. These assignments are based on literature values for these types of Si(OH)$_n$ groups.[23] The CP MAS ^{29}Si NMR spectra of both SPE-Ru and SPE-Fe are the same as that of unmodified SBA-15, which indicates that no covalent bonds are formed between the Si or O atoms and the CpRu(CO)$_2^+$, CpFe(CO)$_2^+$ or BF$_4^-$ units. Previous studies show that covalent bond formation to either the Si or the O of the SiO$_2$ causes new peaks to arise in the CP MAS ^{29}Si NMR spectra.

The DRIFT spectrum of SBA-15 in the ν(SiO-H) region exhibits a strong band at 3742 cm^{-1} (Figure 2). In SPE-Ru, SPE-Ru/DBT, SPE-Fe or SPE-Fe/DBT this band is considerably reduced in intensity suggesting that there is hydrogen bonding between the Si-O-H groups and CpRu(CO)$_2$(BF$_4$) or [CpFe(CO)$_2$(THF)][BF$_4$]. The DRIFT spectra of SPE-Fe, SPE-Fe/DBT and SPE-Ru/DBT are not shown in Figure 2 because they are nearly identical to that of SPE-Ru in the ν(SiO-H) region. In order to determine whether the BF$_4^-$ ions in the ruthenium and iron compounds are interacting with the Si-O-H groups, [(*n*-Bu)$_4$N][BF$_4$] was adsorbed to SBA-15 in the same way and with the same loading (0.508

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mmol [(n-Bu)$_4$N][BF$_4$]) as SPE-Ru and SPE-Fe. The DRIFT spectrum (Figure 2) of [(n-Bu)$_4$N][BF$_4$]/SBA-15 also shows a considerable reduction in ν(SiO-H) absorption intensity, which suggests that the BF$_4^-$ anion is hydrogen-bonded to the silanol groups; a similar type of hydrogen bonding has been reported for sulfonate (RSO$_3^-$) anions on SiO$_2$.[24] Thus, the DRIFT studies suggest that the interaction of CpRu(CO)$_2$(BF$_4$) and [CpFe(CO)$_2$(THF)][BF$_4$] units with SBA-15 is through hydrogen bonding between the BF$_4^-$ group and the SiOH groups. The CpRu(CO)$_2^+$ cation appears not to interact directly with the SBA-15 surface as the ν(CO) bands for SPE-Ru (2083, 2018 cm^{-1}) are very similar to those (2075, 2026 cm^{-1}) of CpRu(CO)$_2$(BF$_4$) in CH$_2$Cl$_2$ solution. On the basis of these studies, we propose that CpRu(CO)$_2$(BF$_4$) is adsorbed to the SBA-15 as shown in Scheme 1.

Reactions of SPE-Ru and SPE-Fe with DBT. When SPE-Ru is stirred for 45 min with a 45:55 toluene/hexanes mixture containing an amount of DBT (0.508 mmol) equal to the CpRu(CO)$_2$(BF$_4$) in the SPE-Ru, a solid is obtained in which approximately 75% of the CpRu(CO)$_2$(BF$_4$) is converted to [CpRu(CO)$_2$(DBT)][BF$_4$] on the basis of extraction studies described below. The DRIFT spectrum (A in Figure 3) of this solid (SPE-Ru/DBT) shows ν(CO) bands at 2079 and 2036 cm^{-1} which are distinctly different than those (2083, 2018 cm^{-1}, B in Figure 3) of SPE-Ru, before the adsorption of DBT. Thus, the ν(CO) bands shift to higher wave numbers indicating that CpRu(CO)$_2$(BF$_4$) has reacted with DBT to form [CpRu(CO)$_2$(DBT)][BF$_4$] on the surface of SPE-Ru/DBT. This is supported by the fact that the ν(CO) bands (2079, 2036 cm^{-1}) for SPE-Ru/DBT are very similar to those for pure [CpRu(CO)$_2$(DBT)][BF$_4$] in CH$_2$Cl$_2$ solution (2078, 2034 cm^{-1}).

In addition to the two ν(CO) bands for the CpRu(CO)$_2{}^+$ unit in SPE-Ru and SPE-Ru/DBT, there is a strong band at 2136 cm^{-1}, which corresponds to CpRu(CO)$_3{}^+$. This is formed as a side product in the reaction of AgBF$_4$ with CpRu(CO)$_2$Cl in CH$_2$Cl$_2$. CpRu(CO)$_3{}^+$ has often been reported as a side product in similar chemistry in the literature.[25] As compared with the bands for CpRu(CO)$_2$(BF$_4$) in CH$_2$Cl$_2$ solution, the 2136 cm^{-1} band is only one-tenth the intensity. However, upon adsorption to SBA-15, the peak at 2136 cm^{-1} is nearly as large as the 2079 cm^{-1} peak for CpRu(CO)$_2$(BF$_4$) (Figure 3). When SPE-Ru is washed with CH$_2$Cl$_2$, the solution spectrum again shows a 2136 cm^{-1} band that is only one-tenth the intensity of the 2075 cm^{-1} band. The greater intensity of the 2136 cm^{-1} peak in the SPE-Ru spectrum may be due to inherent differences in the two types of IR spectroscopy. Solution IR measures solution absorbancies, while DRIFT measures surface absorbance reflections; the intensities of the same vibrational modes can differ substantially between the solution and the solid state.[26] Also, it has been shown, that certain absorption bands are favored over others in densely packed arrays on the surface. This is attributed to constraints placed on a system by physical crowding.[27] Thus, the amount of CpRu(CO)$_3{}^+$ present in SPE-Ru is likely to be much lower than is suggested by the strong 2136 cm^{-1} band.

The CP MAS ^{13}C NMR spectrum of SPE-Ru/DBT and the solution (CD$_2$Cl$_2$) ^{13}C NMR spectrum of CpRu(CO)$_2$(DBT)$^+$ both have Cp absorptions at 90 ppm and DBT absorptions in the range from 135-120 ppm. These data support the conclusion that CpRu(CO)$_2$(DBT)$^+$ is present on the surface of SPE-Ru/DBT. The CP MAS ^{13}C NMR spectrum of SPE-Fe/DBT is much broader, probably because of the smaller amounts of DBT adsorbed and to the presence of small amounts of paramagnetic impurities. However, there is a Cp absorption at 89 ppm and a broad band (120-135 ppm) for DBT; the SPE-Fe/4,6-

Me$_2$DBT sample also exhibits an absorption (20.8 ppm) for the methyl groups of the 4,6-Me$_2$DBT ligand. The DRIFT spectrum also does not unequivocally identify CpFe(CO)$_2$(DBT)$^+$ in SPE-Fe/DBT because the IR spectra of SPE-Fe and SPE-Fe/DBT have ν(CO) bands (2070, 2029 cm^{-1}) that are very similar to one another.

XPS spectra of SPE-Ru/DBT and SPE-Fe/DBT contain a sulfur 2p peak at 164 eV, which may be attributed to DBT coordinated to the Ru or Fe; this peak is in the range for other organosulfur compounds from the literature.[28] The 164 eV peak is not due to DBT adsorbed directly on the SBA-15 because DBT and 4,6-Me$_2$DBT on SBA-15 sublime from the surface in the high vacuum conditions of the XPS instrument. Since the sulfur signal is observed, it must arise from the formation of a metal-DBT bond.

Extraction of DBT from Simulated Petroleum Feedstocks. Both SPE-Ru and SPE-Fe remove substantial amounts of DBT from simulated petroleum feedstocks. When 381 mg of SPE-Ru containing 0.508 mmol of CpRu(CO)$_2$(BF$_4$) was stirred with 0.096 mmol of DBT (400 ppm) in 10 mL of 45% toluene/55% hexanes, samples of the hydrocarbon phase showed that the DBT concentration decreased to 3.5 ($\pm$ 1) ppm over a period of 30 min and remained at that level for several hours. When the same experiment was performed with 400 ppm of 4,6-Me$_2$DBT in 45% toluene/55% hexanes, the 4,6-Me$_2$DBT level was reduced to 112 ($\pm$ 5) ppm.

These results indicate that 4,6-Me$_2$DBT binds less strongly than DBT to SPE-Ru. More quantitative measures of the different binding strengths of these ligands (DBTh) are the K_{eq} values for their adsorption reactions (eq 2). The K_{eq} values, calculated by dividing the

$$\text{SPE-Ru} + \text{DBTh} \rightleftharpoons \text{SPE-Ru-DBTh} \qquad (2)$$

number of moles of SPE-Ru/DBTh formed by the number of moles of unreacted $CpRu(CO)_2(BF_4)$ and the concentration (M) of DBTh in solution, gives K_{eq} values of 2630 and 40 for DBT and 4,6-Me$_2$DBT, respectively. The ratio of these K_{eq} values shows that DBT binds 66 times more strongly than 4,6-Me$_2$DBT.

We have previously reported[5] the equilibrium constant K_1 for the relative binding abilities of dibenzothiophenes in $Cp*Ru(CO)_2(DBTh)^+$ (where $Cp* = \eta^5$-Me$_5$C$_5$) in CD$_2$Cl$_2$ solution (eq 3) at 25° C. These K_1 values increase in the following order: 4,6-Me$_2$DBT (1.0)

$$[Cp*Ru(CO)_2(DBT)]^+ + DBTh \rightleftharpoons [Cp*Ru(CO)_2(DBTh)]^+ + DBT \qquad (3)$$
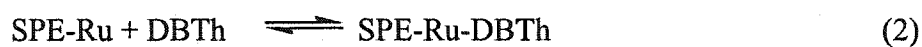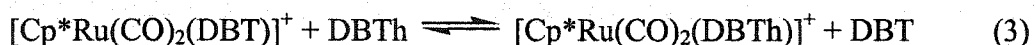
< 4- MeDBT (20.2) < DBT (62.7). Thus, in solution DBT binds 62.7 times more strongly than 4,6-Me$_2$DBT to $Cp*Ru(CO)_2^+$. Since the Cp* in $Cp*Ru(CO)_2^+$ is more sterically bulky than Cp in $CpRu(CO)_2^+$, one would expect DBT binding to be favored over 4,6-Me$_2$DBT binding more in $Cp*Ru(CO)_2^+$ than in $CpRu(CO)_2^+$. However the steric effect of the $CpRu(CO)_2^+$ unit in SPE-Ru is comparable to that of $Cp*Ru(CO)_2^+$ in solution. This suggests that the SBA-15 surface contributes to reducing the ability of SPE-Ru to bind to 4,6-Me$_2$DBT, as compared with DBT.

Although SPE-Ru is very effective for removing DBT from 45% toluene/55% hexanes, it has not been possible to regenerate SPE-Ru from SPE-Ru/DBT. Attempts at this regeneration have involved stirring SPE-Ru/DBT with solvents (CH$_2$Cl$_2$, THF, Et$_2$O and EtOH) both with and without heating. The DBT was not displaced from SPE-Ru/DBT at room temperature. Although DBT was liberated in refluxing CH$_2$Cl$_2$ or THF, decomposition of the Ru complex made the adsorbent inactive for additional extractions of DBT. Attempts to regenerate SPE-Fe from SPE-/DBT were similarly unsuccessful.

The use of 445 mg of SPE-Fe containing 0.508 mmol of [CpFe(CO)$_2$(THF)][BF$_4$] for the extraction of DBT (0.096 mmol, 400 ppm) from 10 mL of 45% toluene/55% hexanes resulted in a reduction in the DBT level from 400 ppm to 133 ppm. When the same extraction was performed on a solution of 4,6-Me$_2$DBT, the concentration of 4,6-Me$_2$DBT was reduced from 400 ppm to 189 ppm. Therefore, SPE-Fe was less effective than SPE-Ru for removing DBT and 4,6-Me$_2$DBT. Like SPE-Ru, SPE-Fe is more effective for removing DBT than 4,6-Me$_2$DBT.

Conclusion

The CpRu(CO)$_2$(BF$_4$) complex, which reacts with dibenzothiophenes (DBTh) to give [CpRu(CO)$_2$(DBTh)][BF$_4$], was adsorbed on mesoporus silica (SBA-15) and used to extract DBT and 4,6-Me$_2$DBT from 45% toluene/55% hexanes solution. DRIFTS, CP MAS ^{13}Si NMR and XPS studies indicate that the primary mode of CpRu(CO)$_2$(BF$_4$) and [CpRu(CO)$_2$(DBT)][BF$_4$] adsorption to the SBA-15 is through hydrogen bonds between surface Si-O-H groups and the BF$_4^-$ anions. The extraction of DBT from 45% toluene/55% hexanes solutions using the CpRu(CO)$_2$(BF$_4$)/SBA-15 adsorbent resulted in reducing the DBT concentration from 400 ppm (the current EPA sulfur limit for gasoline) to 3.5 ppm, which is less than the EPA target level of 30 ppm. The analogous extraction of 4,6-Me$_2$DBT is less effective, reducing the initial 400 ppm concentration to 112 ppm. Results of these investigations show that it is possible for organometallic complexes adsorbed on solid supports to remove dibenzothiophenes from simulated petroleum feedstocks.

Table 1. Crystal and Structure Refinement Data for 1 and 2.

Compound	[CpRu(CO)$_2$(η^1(S)-DBT)][BF$_4$] (1)	[CpFe(CO)$_2$(η^1(S)-4,6-Me$_2$DBT)][BF$_4$] (2)
Empirical formula	C$_{19}$H$_{13}$BF$_4$O$_2$RuS	C$_{21}$H$_{17}$BF$_4$O$_2$FeS
Formula weight	493.23	476.07
Temperature	173(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	triclinic	monoclinic
Space group	P-1	P2(1)/c
Unit cell dimensions	a = 9.2305(14) Å	a = 10.745(4) Å
	b = 10.3298(16) Å	b = 10.025(3) Å
	c = 10.9513(17) Å	c = 19.979(7) Å
	α = 103.680(3)°	α = 90.0°
	β = 111.307(2)°	β = 95.117(6)°
	γ = 93.487(3)°	γ = 90.0°
Volume	932.7(2) Å^3	2143.5(13) Å^3
Z	2	4
Density (calculated)	1.756 mg/m^3	1.475 mg/m^3
Absorption coefficient	1.003 mm^{-1}	0.849 mm^{-1}
F(000)	488	968
Crystal size	0.3 x 0.3 x 0.25 mm^3	0.50 x 0.20 x 0.08 mm^3
θ range for data collection	2.06 to 28.20°	1.90 to 23.11°
Index Ranges	-12 $\leq h \leq$ 11, -13 $\leq k \leq$ 12, -14 $\leq l \leq$ 14	-11 $\leq h \leq$ 11, -10 $\leq k \leq$ 11, -22 $\leq l \leq$ 22
Reflections collected	7007	19216
Observed reflections	4073 [R(int) = 0.0362]	3002 [R(int) = 0.0411]
Completeness to θ =	28.20° = 88.4%	23.11° = 99.5%
Absorption correction	empirical with SADABS	empirical with SADABS
Max. and min. transmission	0.82 and 0.70	0.93 and 0.82
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data / restraints / parameters	4073 / 0 / 254	3002 / 0 / 271
Goodness-of-fit on F^2	1.120	1.057
Final R^a indices [$I > 2\sigma(I)$]	$R1$ = 0.0642, w$R2$ = 0.1935	$R1$ = 0.0788, w$R2$ = 0.2068
R indices (all data)	$R1$ = 0.0669, w$R2$ = 0.1946	$R1$ = 0.0894, w$R2$ = 0.2160
Largest diff peak and hole	3.113 and –0.720 e Å^{-3}	1.139 and –0.700 e Å^{-3}
Extinction coefficient	0.0084(19)	-

[1] $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and w$R2 = \{\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$

Table 2. Selected bond distances (Å) and angles (deg) for compounds **1** and **2**.

Compound	M-S (Å)	d C_5H_5 Plane (Å)				Twist Angle
		C(4)	C(6)	C(14)	C(16)	
[CpRu(CO)$_2$(DBT)]$^+$ (**1**)	2.3980(18)	4.991	3.187			22.8
[CpFe(CO)$_2$(4,6-Me$_2$DBT)]$^+$ (**2**)	2.3101(19)	3.800	4.143	2.393	2.809	3.4

Scheme 1. Proposed structures for SPE-Ru and SPE-Ru/DBT.
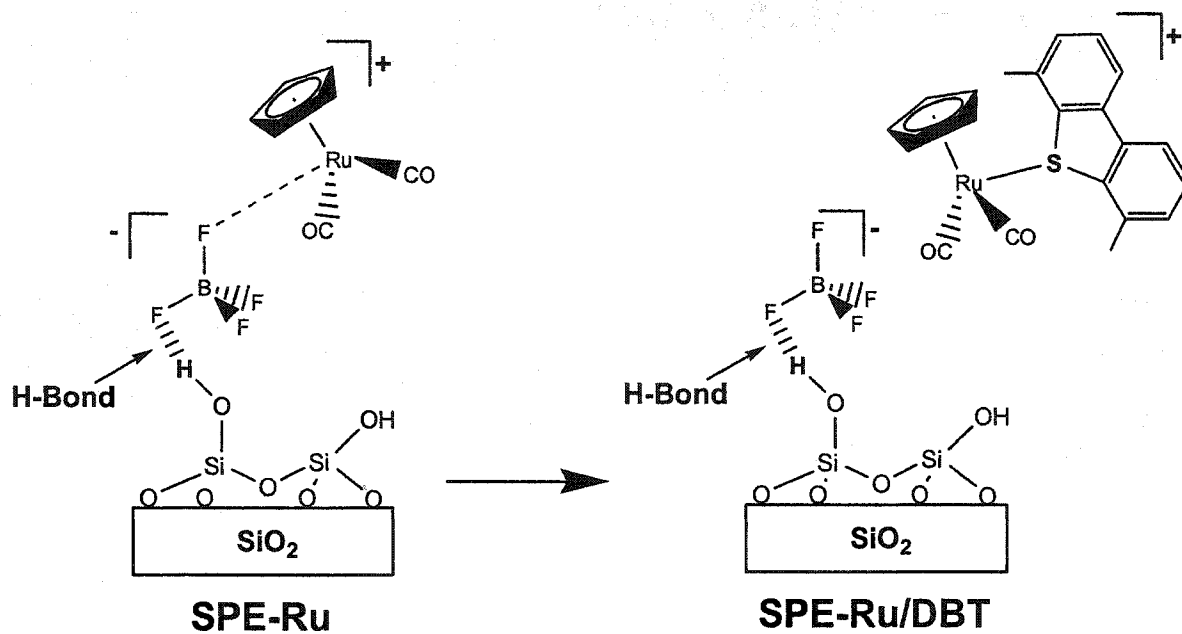
Figure 1. Thermal ellipsoid drawings of [CpRu(CO)₂(DBT)][BF₄] (**1**) and [CpFe(CO)₂(4,6-Me₂DBT)][BF₄] (**2**). Ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles are listed in Table 3.
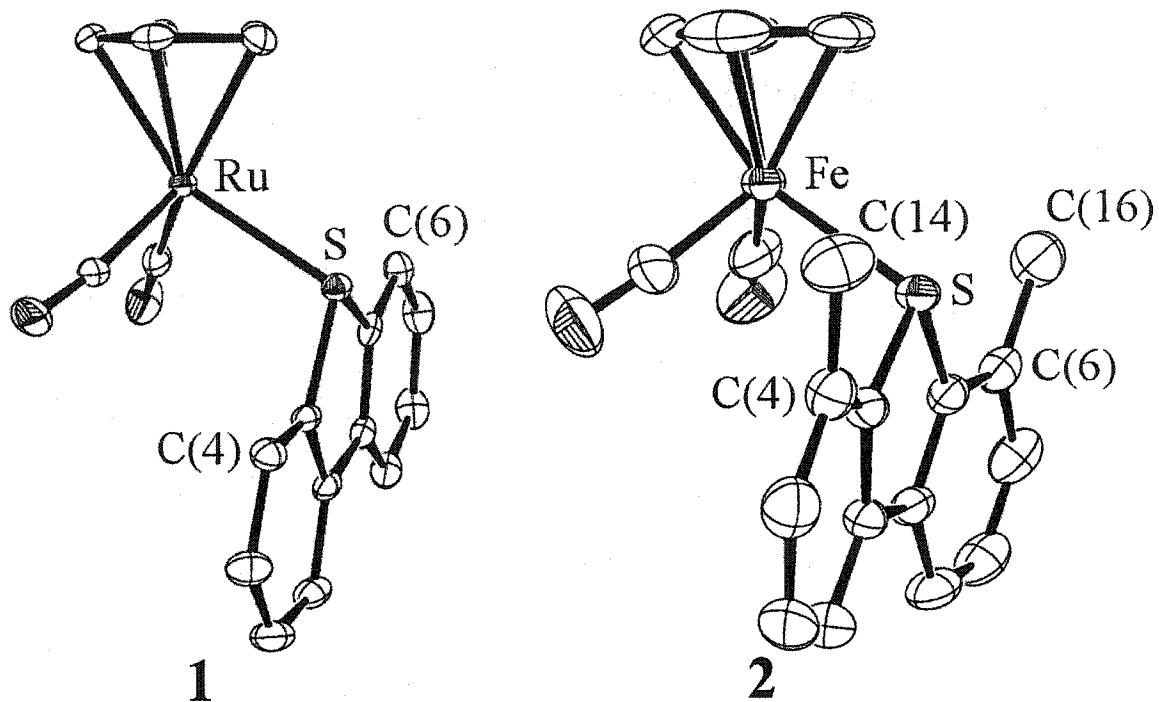
Figure 2. DRIFT spectra of the ν(SiO-H) region of SBA-15 (**A**), CpRu(CO)$_2$(DBT)$^+$/SBA-15 (**B**), [(n-Bu)$_4$N][BF$_4$]/SBA-15 (**C**).
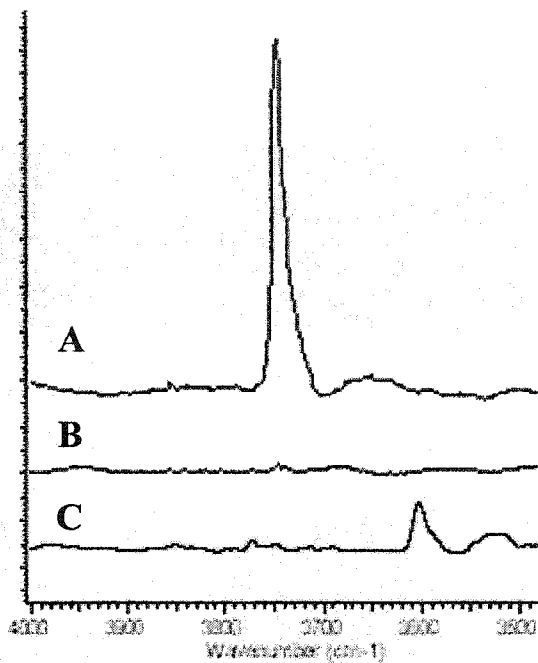
Figure 3. DRIFT spectra of ν(CO) region of $CpRu(CO)_2(DBT)^+$/SBA-15 (**A**), $CpRu(CO)_2(BF_4)$/SBA-15 (**B**), SBA-15 (**C**).

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CHAPTER FOUR: DEEP DESULFURIZATION BY SELECTIVE ADSORPTION OF DIBENZOTHIOPHENES ON Ag$^+$/SBA-15

Scott G. McKinley and Robert J. Angelici

The removal of sulfur from transportation fuels has been mandated by governments around the world in order to reduce atmospheric pollution by sulfur oxides.[1] Currently, sulfur content in diesel fuel is limited in the U.S. to 500 ppm (0.05% by weight) and 400 ppm (0.04 % by weight) is gasoline; but the EPA has recently introduced new restrictions that will reduce this level gradually to 15 ppm (0.0015% by weight) in diesel fuel by 2006.[2] While most of the sulfur is now removed from petroleum based feedstocks by hydrotreating, this process removes hindered dibenzothiophenes,[3] those with alkyl groups in the 4 and 6 positions are only removed if the hydrotreating environment is operated under extreme and costly conditions.[4] Since these 4,6-R$_2$DBT compounds constitute the bulk of the remaining sulfur compounds in diesel fuel, new approaches to deep desulfurization are required.
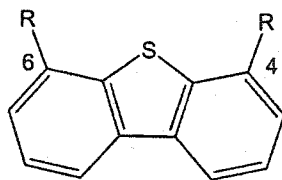
Dibenzothiophene

Recent reported methods include deep desulfurization by selective adsorption of R$_2$DBT,[5] precipitation of an insoluble DBT-sulfimide (by reaction with sodium N-

chlorotoluene-*p*-sulfonamide),[6] extraction of DBT with ionic liquids,[7] oxidation of DBT and 4,6-Me_2DBT to the corresponding sulfones in a liquid biphasic system,[8] and other processes.[9]

Herein, we report the use of solid phase extractants (SPEs) consisting of Ag^+ salts adsorbed on mesoporus SBA-15 or amorphous silica for the removal of DBT and 4,6-Me_2DBT from a simulated diesel feedstocks. In one series of experiments, the SPE was prepared by stirring 99 mg (0.51 mmol) of $AgBF_4$ dissolved in 5 mL of EtOH with 250 mg of SBA-15 for 20 min. SBA-15 is a mesoporus silica synthesized with a 618 m^2g^{-1} surface area and 52.3318 Å average pore size.[10] After the EtOH was evaporated under vacuum, the remaining solid, containing 9.0% by weight $AgBF_4$ was added to *n*-decane solution containing 400 ppm (0.096 mmol) of either DBT or 4,6-Me_2DBT. This mixture was stirred for 1 min at room temperature. Then, the amount of DBT or 4,6-Me_2DBT in the decalin phase was determined by GC on a HP-5 column. In these extractions, the DBT level was reduced from 400 ppm to 72 (± 9) ppm, while 4,6-Me_2DBT was reduced to 75 (± 6) ppm. The extractions reached equilibrium within 1 min, the required time to fully mix the reactants remove an aliquot for GC analysis.

Since no DBT or 4,6-Me_2DBT was extracted when only SBA-15 or [(*n*-Bu)$_4$N][BF_4]/SBA-15 was used, the Ag^+ is the active extracting ion. All three salts, $AgBF_4$, $AgPF_6$ and $AgNO_3$, were equally effective from the removal of DBT and 4,6-DBT.

The extent of DBT and 4,6-Me_2DBT (400 ppm) removal from 10 mL of decane increases (Figure 1) as the weight percent loading of $AgBF_4$ on 250 mg SBA-15 was increased from 9.0% to 28.4%. However, at high loadings of $AgBF_4$, no further DBT or 4,6-Me_2DBT is removed, probably because the excess $AgBF_4$ covers previously deposited $AgBF_4$ layers, and it is only the top layer that adsorbs DBT or 4,6-Me_2DBT.

Although it is obvious that many Ag$^+$ sites do not adsorb DBT or 4,6-Me$_2$DBT at high AgBF$_4$ loadings, even at 9.0% and 16.5% loadings the ratio of Ag$^+$ to DBT adsorbed are 5.4 and 6.7 respectively, which indicates that many Ag$^+$ ions do not act as DBT or 4,6-Me$_2$DBT adsorption sites. At low loadings, 4,6-Me$_2$DBT appears to adsorb slightly more strongly than DBT, which is surprising because it is well known[11] that 4,6-Me$_2$DBT binds much less strongly than DBT in their transition metal complexes. In these Ag$^+$/SBA-15 extractions, it appears that the 4,6-Me groups pose no steric hindrance to binding, and the electron-donating ability of the methyl groups may enhance adsorption.

In order to confirm by XPS and CP MAS ^{13}C NMR spectroscopy the presence of DBT on the 28.4% AgBF$_4$/SBA-15 solid after an extraction, the samples were washed several times with hexanes and dried in vacuo. The XPS spectrum of this sample shows a sulfur 2p band at 264 eV, which is characteristic of organosulfur compounds. The CP MAS ^{13}C NMR spectrum of the sample shows a broad resonance at 135-120 ppm which is characteristic of the aromatic carbons of DBT.

DBT and 4,6-Me$_2$DBT were also removed from decane using a column (2 cm X 5 cm) consisting of AgNO$_3$ (10% by weight) on 200-mesh silica gel. This 867 mg of AgNO$_3$/SiO$_2$ containing 0.51 mmol of AgNO$_3$ was prepared in decane. A 10 mL sample of decane containing 0.096 mmol of DBT (400 ppm) was passed through the column followed by a decane wash (5 mL). The amount of DBT in the 15 mL of eluted decane was only 0.014 mmol ($\pm$ 0.002) (57 $\pm$ 7 ppm), representing a 85.7% drop in DBT content. The DBT was removed from the column by eluting with 10 mL of Et$_2$O. The amount of DBT recovered in the ether elutent was 0.086 mmol ($\pm$ 0.015) (357 $\pm$ 35 ppm). The regenerated AgNO$_3$/SiO$_2$ column was used in a second extraction of DBT (400 ppm) in 10 mL of decane. This resulted

in the reduction of the DBT from 0.096 mmol (400 ppm) to 0.006 mmol (25 ppm) in the decane elutent.

When the total amount of $AgNO_3/SiO_2$ was doubled in the column (1.734 g, containing 1.02 mmol $AgNO_3$), and the same procedure followed, the amount of DBT in the decane eluted was reduced even further to 0.002 mmol (8 ± 6 ppm), a 98% drop from the initial DBT concentration.

These studies show that the concentration of DBT and 4,6-Me_2DBT in decanes can be reduced from 400 ppm to approximately 8 ppm. The easy regeneration of these adsorbents makes them attractive for the deep desulfurization of petroleum feedstocks.

Notes

All reactions were performed under argon and in the absence of light using standard Shlenck techniques. Decane and EtOH were distilled over CaH_2 and stored over molecular sieves. Hexanes and toluene were purified on alumina using a Solv-Tech solvent purification system, as described by Grubbs and co-workers.[12] Mesoporus silica SBA-15 was made according to the synthesis by Stucky and co-workers (BET/BJH analysis revealed a pore diameter of 52.3 Å and surface area of 618 m^2g^{-1}).[13] Ruthenium trichloride hydrate was purchased from Pressure Chemical. 4,6-Me_2DBT was bought from Acros. All other chemicals were used without further purification as purchased from Aldrich. Filtrations were performed with celite on filter paper. All the error in the text or figures are expressed as average errors.

Figure 1. Extractions of DBT and 4,6-Me$_2$DBT with various loading (weight %) of AgBF$_4$

on 250 mg of SBA-15.
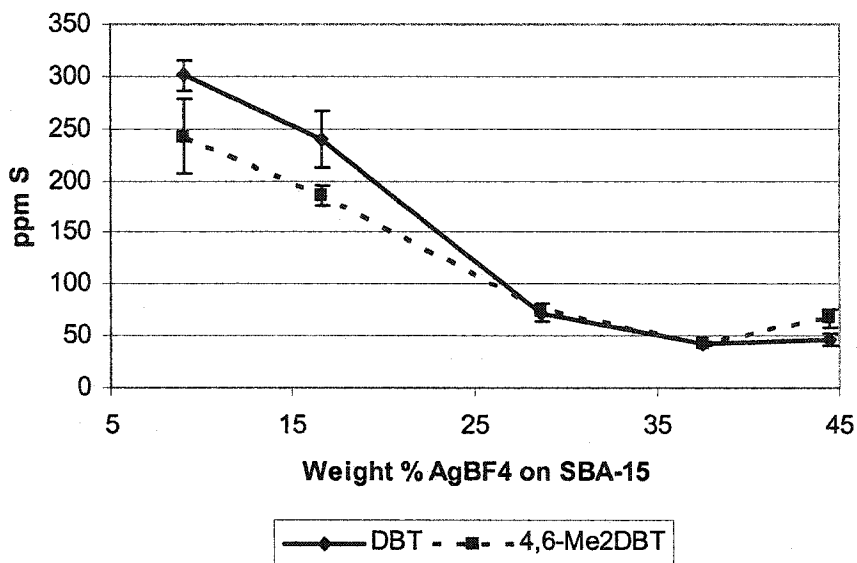
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CHAPTER FIVE: GENERAL CONCLUSIONS

As stated in the introduction of this dissertation, the deep desulfurization of petroleum fuels is an important goal. The impact of the discovery of a practical process to accomplish this would have positive ramifications as diverse as reducing atmospheric pollution to reducing this country's dependence on foreign oil. I have presented here three processes that represent advancements towards this goal.

First, is the liquid biphasic extraction using coordination compounds. This liquid extraction is the first such desulfurization technique discovered to use the ability of inorganic complexes to selectively bind thiophenes. The second process presented uses organometallic complexes, known to bind thiophenes, as solid phase extractants (SPEs) to remove R_2DBTs from petroleum feedstocks. The organometallic complexes on a surface allow the investigation of the initial event in HDS, the binding of R_2DBTs to the surface. We have found that this initial event changes little from the analogous solution reaction.

Finally, we have presented the use of a SPE based on Ag^+ salts. The previous two methods of removing DBT from petroleum both have the disadvantages of using the rather expensive metal ruthenium and suffer difficulties arising in their regeneration, if regeneration is possible. SPE-Ag has none of these problems. The $AgNO_3$ based SPE is cheap, reusable, has a fast reaction with DBT, and most importantly it is very active in the removal DBT from petroleum feedstocks.

Our hope as researchers is that this chemistry may someday find use in the future as an industrial desulfurization processes.

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