**Sulfur Reduction in Gasoline and Diesel Fuels by Extraction/Adsorption of
Refractory Dibenzothiophenes**

Final Report

September 1, 2000 – March 31, 2003

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ABSTRACT

Refractory 4,6-dimethyldibenzothiophene, which is difficult to remove from petroleum feedstocks, binds to the Ru in $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ by displacing the H_2O ligand. Thiophene, benzothiophene and dibenzothiophene (DBT) also react with $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ similarly. This binding ability of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ has been used to remove over 50% of the DBT in simulated petroleum feedstocks by a biphasic extraction process. The extraction phase is readily regenerated by air-oxidation thereby completing a cyclic process that removes DBT from petroleum feedstocks.

Solid phase extractants consisting of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$, $\text{CpRu}(\text{CO})_2(\text{BF}_4)$, $\text{CpFe}(\text{CO})_2(\text{C}_4\text{H}_8)^+$ and AgX (where $\text{X} = \text{BF}_4^-$, PF_6^- or NO_3^-) adsorbed on silica have also been used to remove DBT and 4,6-Me₂DBT from simulated petroleum feedstocks. The AgX/silica adsorbents remove 90% of the DBT and 4,6-Me₂DBT and can be regenerated

and re-used for multiple extractions, which makes these adsorbents of potential industrial use for the removal of refractory dibenzothiophenes from petroleum feedstocks.

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EXECUTIVE SUMMARY

The removal of sulfur from gasoline and diesel fuels is an important aspect of this nation's effort to reduce pollution of the atmosphere by sulfur oxides. The current EPA-mandated 0.04% by weight limit on sulfur in gasoline will be reduced to 0.0025% by weight in 2006. This reduction will require the development of new technologies. Such reductions in sulfur content must focus on the unreactive dibenzothiophene (DBT) derivatives that contain alkyl groups near the sulfur; these compounds constitute the bulk of the remaining sulfur compounds in hydrotreated petroleum feedstocks.

The present investigation focuses on metal complexes that are capable of binding DBT and its derivatives. We have observed that $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ binds to DBT as well as its hindered 4,6-dimethyldibenzothiophene (4,6-Me₂DBT) analog. It also reacts with thiophene and benzothiophene in acetone at 25° C. By employing a solution of dimethylformamide and water (70:30) containing $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$, we have extracted 50% of the DBT present in a simulated petroleum feedstock. We have also demonstrated oxidative release of DBT from the resulting $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ complex. The oxidized ruthenium can be reduced back to $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ for further use. A reactor design has been proposed to make use of this DBT extraction process.

We have taken the logical next step in the use of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ by adsorbing it to silica, to heterogeneously remove DBT from petroleum. After finding that this does indeed work, we followed this same procedure for the adsorption of ruthenium blue (RuCl_2), $\text{CpRu}(\text{CO})_2(\text{BF}_4)$, $\text{CpFe}(\text{CO})_2(\text{C}_4\text{H}_8)^+$ and AgX (where $\text{X} = \text{BF}_4^-$, PF_6^- or NO_3^-)

onto mesoporous silica. In each case we found that DBT is adsorbed from the petroleum feedstock onto the surface, forming new bonds between the metal and sulfur atoms. The ruthenium and iron based extractants have a number of drawbacks, chief among them their material high cost and the difficulty involved in their regeneration. The Ag^+ -based extractant is readily regenerated and has relatively low material cost. These factors may make it a practical solid phase extractant for the industrial removal of DBT from petroleum.

INTRODUCTION

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 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 extent of petroleum feedstock desulfurization 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 dibenzothiophenes (R = H) (Th* denotes a generic thiophene, Chart 1). It is the hindered dibenzothiophene (R₂DBT), particularly those with alkyl groups in the 4 and 6

Chart 1. Structures of thiophenes.

positions that are the slowest to undergo hydrodesulfurization. These R₂DBT'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 proposed⁴ that dibenzothiophene (DBT) adsorbs through its sulfur to an exposed Mo atom on the supported MoS₂ 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-Me₂DBT) complex,⁵ (η^5 -C₅Me₅)Ru(CO)₂(4,6-Me₂DBT)⁺, and the 4,6-Me₂DBT ligand in this complex binds much less strongly than DBT. Another sulfur-coordinated (η^1 -S) 4,6-Me₂DBT complex ([Cp^{*}Rh(PMe₃)(4,6-Me₂DBT)]) was reported,⁶ but it was too unstable to be fully characterized. On the other hand, numerous DBT complexes are described in the literature.^{7, 8}

These results suggest it is the bulkiness of the R groups in 4,6-R₂DBT 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-R₂DBT molecules from petroleum. Recent investigations include deep desulfurization by selective adsorption of R₂DBT⁹, deep desulfurization by precipitation of an insoluble DBT-sulfimide (by reaction with sodium N-chlorotoluene-*p*-sulfonamide)¹⁰, extraction of DBT by ionic liquids¹¹, and the oxidation of DBT and 4,6-Me₂DBT to the corresponding sulfones in a liquid biphasic system.¹²

We have developed, and report here, several different approaches to the removal of hindered dibenzothiophenes (R_2DBT) from petroleum. The first such approach uses the reaction of the coordination compound $Ru(NH_3)_5(H_2O)^{2+}$ with dibenzothiophene and the use of this complex in aqueous solution to selectively bind and extract 4,6- R_2DBT 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.

The second approach uses organometallic and inorganic complexes on a surface. We chose complexes that have been previously shown to coordinate DBT in solution. Therefore, $[CpRu(CO)_2][BF_4]$, $[CpFe(CO)_2(THF)][PF_6]$, $[Ru(NH_3)(H_2O)][PF_6]_2$ and ruthenium blue (which unlike the others has no affinity for DBT in solution) were adsorbed on mesoporous silica. We found that all of these adsorbed complexes extracted both DBT and 4,6- Me_2DBT from a simulated petroleum feedstock to form the corresponding metal-DBT complexes on the surface. In order to characterize the complexes on the surface, the novel R_2DBT complexes $CpRu(CO)_2(DBT)^+$ and $CpFe(CO)_2(4,6-Me_2DBT)^+$ (where Cp = the cyclopentadienyl ligand) were synthesized and their structures established by X-ray diffraction studies. This represents only the second-ever reported crystal structure containing the important 4,6- Me_2DBT ligand, and is the first such complex reported with iron.

The third method for the removal of DBT from petroleum that we have developed, is the use of AgX (where $X = BF_4^-$, PF_6^- or NO_3^-) on a surface. We adsorbed AgX onto mesoporous silica, and found that it behaves unlike any other $M-R_2DBT$ complexes found in the literature because it has slightly *greater* affinity for 4,6- Me_2DBT

than DBT. We believe the small size and absence of a formal ligand environment around the Ag^+ is responsible for this behavior. The Ag^+ based extractant has the added benefit that it may be regenerated after each use, making practical its use for the industrial removal of DBT from petroleum feedstocks. Because of the uniqueness of the Ag^+ -DBT chemistry, its chemistry is reported in a separate section from the other solid phase extractants near the end of this report.

EXPERIMENTAL

General Considerations. All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Diethyl ether (Et₂O), hexanes and toluene were all purified on alumina using a Solv-Tech solvent purification system, as described by Grubbs and co-workers.¹³ 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.

Solution infrared spectra of the compounds in CH₂Cl₂ were recorded on a Nicolet-560 spectrometer using NaCl cells with 0.1 mm spacers. In situ diffuse reflectance infrared (DRIFT) spectra were collected on a Nicolet MAGNA-IR AEM infrared spectrophotometer operating between 400 and 4000 cm⁻¹. The DRIFT chamber was connected to an air purification system to keep the stage dry. Oven dried KBr was used as a background and the amount of silica (weight %) was kept constant in each sample (by varying the amount of KBr) to allow direct comparison of the intensity of the Si-OH peaks. All spectra were recorded at 4 cm⁻¹ resolution with 1000 scans.

NMR spectra were obtained on a modified 400 MHz Varian VXR-400 spectrometer using acetone-d₆ 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 equipped with a HP-5 column. The GC conditions are as follows: DBT and 4,6-Me₂DBT (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. Solid state CP MAS ^{13}C NMR were performed on a Bruker MSL 300 at a spin rate of 2.8 KHz. XPS were performed on a Physical Electronics 5500 Multi-technique system using the standard Al source.

Synthesis of $[\text{Ru}(\text{NH}_3)_5(4,6\text{-Me}_2\text{DBT})][\text{PF}_6]_2$ (1**).** To a 50 mL flask containing 15 mL of acetone (or dimethylformamide {DMF}), freshly prepared $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{PF}_6]_2$ (50.0 mg, 0.102 mmol),¹⁴ 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, $J_{\text{H-H}} = 9.1$ Hz, 2 H, DBT-*H*), 7.44 (t, $J_{\text{H-H}} = 9.2$ Hz, 2 H, DBT-*H*), 7.36 (d, $J_{\text{H-H}} = 9.0$ Hz, 2 H, DBT-*H*), 2.62 (s, 6H, DBT-CH₃), 2.70 (s, br, 12 H, NH₃), 2.52 (s, br, 3 H, NH₃) ppm. ^{13}C 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 $[\text{Ru}(\text{NH}_3)_5(\text{DBT})][\text{PF}_6]_2$ (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, NH₃), 2.53 (s, br, 3 H, NH₃) ppm. ¹³C NMR (400 MHz, CD₃COCD₃): δ 143.12, 138.62, 127.95, 125.10, 123.11, 121.95 ppm.

Synthesis of $[\text{Ru}(\text{NH}_3)_5(\text{BT})][\text{PF}_6]_2$ (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-Me₂DBT. ¹H NMR (400 MHz, CD₃COCD₃): 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, NH₃), 2.56 (s, br, 3 H, NH₃) ppm. ¹³C NMR (400 MHz, CD₃COCD₃): δ 128.12, 127.72, 125.98, 124.68, 123.85, 122.56, 35.32, 34.96 ppm.

Synthesis of $[\text{Ru}(\text{NH}_3)_5(\text{T})][\text{PF}_6]_2$ (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-Me₂DBT. ¹H NMR (400 MHz, CD₃COCD₃): δ 7.49(m, 2H, T-*H*), 7.13 (m, 2H, T-*H*), 2.71 (s, br, 12 H, NH₃), 2.48 (s, br, 3 H, NH₃) ppm. ¹³C NMR (400 MHz, CD₃COCD₃): δ 127.08, 125.34 ppm.

Extraction of DBT and 4,6-Me₂DBT 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-Me₂DBT (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 H₂O, 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(NH₃)₅(H₂O)][PF₆]₂ relative to the 4,6-R₂DBT amounts were added. After two freeze/pump/thaw cycles, the mixture was warmed to room temperature, and H₂ 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/H₂O mixture containing [Ru(NH₃)₅(H₂O)][PF₆]₂ under argon followed by one freeze/pump/thaw cycle. The mixture was sonicated (or stirred), and 0.4 mL aliquots of the top hydrocarbon phase 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 CD₃COCD₃. 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.

Calculation of Equilibrium Constants. The data needed to calculate K₁ and K₂ (as discussed later in this paper) was collected in the following manner. First, 10 mL of the simulated gasoline mixture, containing 400 ppm of the generic thiophene (Th*), was added to 10 mL of the 70% DMF/30% H₂O mixture. The content of the hydrocarbon phase was measured versus an internal standard (previously shown not to extract into the

aqueous mixture). After equilibrium was established (1 h), the decrease in Th* from the organic phase was determined by GC, which permitted the amount of thiophenes present

in each phase and K_1 to be calculated. When the extraction was repeated with $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ present in the aqueous phase, the values needed to calculate K_2 were

$$K_1 = \frac{\text{Th}^*_{(\text{organic})}}{\text{Th}^*_{(\text{aqueous})}} \quad K_2 = \frac{[\text{Th}^*_{(\text{aqueous})}] [\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}]}{[\text{Ru}(\text{NH}_3)_5(\text{Th}^*)^{2+}] [\text{H}_2\text{O}]}$$

determined. The decrease in the amount of Th* in the organic phase beyond that determined in the absence of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ was used to calculate K_2 (eq 2). The K_2 values calculated for T, BT and DBT are stated in Table 2. The values are the averages of three runs; the errors are given as average deviations.

Synthesis of $[\text{CpRu}(\text{CO})_2(\text{DBT})][\text{BF}_4]$ (5). This was performed according to the procedure of Benson and Angelici.¹⁵

Synthesis of $[\text{CpFe}(\text{CO})_2(4,6\text{-Me}_2\text{DBT})][\text{BF}_4]$ (6). This was performed according to the procedure of Goodrich *et al*, except 4,6-Me₂DBT was used in place of DBT.¹⁶ ¹H-NMR (δ , ppm in CD₃NO₂) 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, CH₃). ¹³C-NMR (δ , ppm in CD₃NO₂) δ = 208.71 (CO); 140.61, 139.37, 136.56, 132.06, 131.64, 122.91, 21.78 (4,6-Me₂DBT); 89.03 (Cp). IR (CH₂Cl₂, ν_{CO} cm⁻¹) 2069(s), 2030(s). Anal. Calcd for C₂₁H₁₇BF₄O₂FeS: C, 52.98; H, 3.60; S, 6.74. Found: C, 52.53; H, 3.63; S, 6.75.

X-ray Crystal Structure Determinations of Complexes 5 and 6. Single crystals of complexes **5** and **6** suitable for X-ray diffraction study were obtained by recrystallization from CH₂Cl₂ (**5**) or slow diffusion of hexanes into a saturated CH₂Cl₂ solution (**6**). 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.

The structures of **1** and **2** were solved by direct methods. Data collection for **6** was performed at 293K as all attempts to collect data at low temperature failed due to breaking of the sample around 270K. The high thermal amplitudes of atoms in the BF₄⁻ anion led to comparatively high values of the R-factor.

Preparation of Ruthenium Blue Modified Pd/SBA-15. To a flask containing Pd/SBA-15 (250 mg) and RuCl₃*3H₂O (133 mg, 0.508 mmol), 10 mL of acetone was added. The solution was cycled through three freeze/pump/thaw cycles and warmed to room temperature. Consistent with literature methods, H₂ was bubbled through the mixture for 25 min, which first turns green, then blue when the reduction is complete, forming ruthenium blue.¹⁷ The mixture of ruthenium blue and Pd/SBA-15 was stirred for 30 additional minutes. The acetone was then removed under vacuum, yielding the blue/black SPE-1.

Preparation of [Ru(NH₃)₅(H₂O)][PF₆]₂ Modified Pd/SBA-15. The synthesis was the same as ruthenium blue modified Pd/SBA-15 with the exception that 250 mg (0.508 mmol) of [Ru(NH₃)₅(H₂O)][PF₆]₂ was used in place of RuCl₃*3H₂O.¹⁸

Preparation of [CpRu(CO)₂][BF₄] Modified SBA-15. To a flask containing CpRu(CO)₂Cl (131 mg, 0.508 mmol), 10 mL of CH₂Cl₂ and AgBF₄ (193 mg, 0.763

mmol) were added. The solution was cycled through one freeze/pump/thaw cycle, warmed to room temperature and allowed to stir for 1 hour. The IR spectrum was then checked to ensure complete reaction. When complete, the solution was filtered into a separate flask containing 250 mg of SBA-15 (the mesoporous silica SBA-15 was synthesized and aged at 100° C as described by Zhao and coworkers)¹⁹ and stirred for 30 min. The mixture was then dried under vacuum to yield a tan solid.

Preparation of [CpFe(CO)₂(THF)][PF₆] Modified SBA-15. [CpFe(CO)₂(THF)][PF₆] was synthesized according to the procedure of Forschner and Cutter.²⁰ To a flask containing [CpFe(CO)₂(THF)][PF₆] (194.6 mg, 0.508 mmol), 10 mL of CH₂Cl₂ was added and cycled through one freeze/pump/thaw cycle, 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 then dried under vacuum to yield a red solid.

Preparation of AgX (Where X = BF₄⁻, PF₆⁻ or NO₃⁻) Modified SBA-15. To a flask containing 250 mg SBA-15, of AgBF₄ (99 mg, 0.51 mmol) (other salts of the form AgX may be used) and 10 ml EtOH was added. The mixture was stirred for 10 min, then dried under vacuum to yield a white solid.

Extraction of R₂DBT by Metal Complex Modified SBA-15. For the hydrocarbon phase we use either a 55% hexanes and 45% toluene mixture to simulate gasoline or decane to simulate diesel.²¹ Into 10 mL of this liquid, DBT (17.6 mg, 0.096 mmol, 0.04% by weight) and decahydronaphthalene (15 µL) (internal standard) were dissolved. After one freeze/pump/thaw cycle, the mixture was warmed to room temperature and an aliquot (0.4 mL) removed. In a separate flask metal modified SBA-15 (the SPE contained 0.51 mmol of metal complex) was added and degassed under vacuum for 5 min. The solution

of DBT in hydrocarbon solvent was added to the SPE, put through one freeze/pump/thaw cycle, warmed to room temperature and stirred. Aliquots were removed to check the extent of DBT adsorption. The ratio of DBT relative to decahydronaphthalene was determined by GC to establish the amount of DBT that was removed for GC analysis from the simulated fuel mixture.

CP MAS ^{13}C -NMR of R_2DBT Extracted by $\text{CpRu}(\text{CO})_2(\text{BF}_4)/\text{SBA-15}$. A sample of a metal complex modified SBA-15 (containing 0.51 mmol of metal complex) was allowed to extract R_2DBT from a simulated gasoline as described in the extraction scheme above. After stirring for 1 hr, the solid was removed by filtration. The solid was washed by adding fresh, degassed hexane (20 mL), the mixture was allowed to stir for 5 min and then filtered. This was repeated twice, to insure that all of the R_2DBT not bound to the SPE's surface would be removed from the sample. The sample was then dried under vacuum, and loaded into a CP MAS NMR sample tube under Ar. Selected chemical shifts are given in Table 3.

DRIFT-IR Spectra of Metal Complex Modified SBA-15. In situ diffuse reflectance infrared (DRIFT) spectra were collected on a Nicolet MAGNA-IR AEM infrared spectrophotometer operating between 400 and 4000 cm^{-1} . The DRIFT chamber was connected to an air purification system to keep the stage dry. Oven dried KBr was used as a background and the amount of silica (wgt %) was kept constant in each sample by varying the amount of KBr. All spectra were recorded at 4 cm^{-1} resolution with 1000 scans. Spectra of SBA-15, metal complex modified SBA-15 or DBT reacted with metal complex modified SBA-15 are discussed in the body of this report and shown in Figure 6.

RESULTS AND DISCUSSION

Syntheses and Structures of [Ru(NH₃)₅(Thiophenes)][PF₆]₂. There are several reasons for choosing Ru(NH₃)₅(H₂O)²⁺ as the extracting agent in our studies. The Ru(II) in this complex has a d⁶ electron configuration, which is typical of metal complexes that bind to thiophene.⁸ The complex Ru(NH₃)₅(H₂O)²⁺ has been previously reported²² to react with thiophene (T) to give Ru(NH₃)₅(T)²⁺, which was too unstable to be characterized by elemental analysis as we also observed. Another Ru(II) complex CpRu(CO)(PPh₃)(T)⁺²³, where Cp = η⁵-C₅H₅, was stable enough to be fully characterized. The equilibrium

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(NH₃)₅(DBT)²⁺ to be more stable than Ru(NH₃)₅(T)²⁺. Another advantage for Ru(NH₃)₅(DBT)²⁺ is that the NH₃ ligands are small and should not pose a steric barrier to the coordination of 4,6-Me₂DBT, according to molecular models. In addition, the H₂O ligand in Ru(NH₃)₅(H₂O)²⁺ is known²⁴ to be labile and rapidly substituted by a variety of ligands.

In the present studies, we find that 4,6-Me₂DBT in acetone or DMF does indeed react with Ru(NH₃)₅(H₂O)²⁺ within 1 h at room temperature to give Ru(NH₃)₅(4,6-Me₂DBT)²⁺ in 86% yield (Scheme 1). Reactions of DBT, BT and T with Ru(NH₃)₅(H₂O)²⁺ give the 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 ¹³C NMR spectra as discussed below.

The ^1H and ^{13}C NMR spectra (Table 1) of $\text{Ru}(\text{NH}_3)_5(4,6\text{-Me}_2\text{DBT})^{2+}$ (**1**) show that the arene protons are slightly downfield (δ 8.15, 8.74, 7.36) of those in free 4,6-Me₂DBT (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 (δ 15.01) in **1** as compared with that of free 4,6-Me₂DBT (δ 19.82). Small shifts in ligand ^1H and ^{13}C NMR signals are also observed upon coordination of DBT and T in $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ (**2**) and $\text{Ru}(\text{NH}_3)_5(\text{T})^{2+}$ (**4**) (Table 1). Such small shifts are characteristic of S-coordinated thiophene ligands as has been observed in $\text{CpRu}(\text{CO})_2(\text{Th}^*)^{+}$,²⁵ and $\text{CpRe}(\text{CO})_2(\text{Th}^*)$.²⁶ On the other hand, the proton signals (δ 6.51, 5.98) for H(2) and H(3) in the BT ligand of $\text{Ru}(\text{NH}_3)_5(\text{BT})^{2+}$ (**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

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C(2) and C(3) in the ^{13}C NMR spectrum of the compound. These large and 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 $\text{CpRe}(\text{CO})_2(\eta^2\text{-BT})$.²⁶

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.

Scheme 1. Reaction of 4,6-dimethyldibenzothiophene with $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$.

Table 1. ^1H and ^{13}C NMR Data (ppm, in acetone- d_6) for thiophene (T), benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6- Me_2DBT), unbound and bound in $\text{Ru}(\text{NH}_3)_5(\text{Thiophene})^{2+}$.

Ligand	^1H NMR Unbound	^1H 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_2DBT	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

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 $\text{Ru}(\text{III}$ and $\text{IV})$ products are reduced back to $\text{Ru}(\text{II})$ by reaction with H_2 when catalyzed by Pd/C .²⁷ 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 $\text{Ru}(\text{NH}_3)_5(\text{thiophenes})^{2+}$ for 15 min to keep them in the reduced $\text{Ru}(\text{II})$ form. Additional H_2 may be added periodically when the bright yellow solution

begins to darken indicating the formation of the red $\text{Ru}^{3+/4+}$ cluster, which is discussed later in this report.

While many $\eta^1(\text{S})$ -coordinated DBT metal complexes are known⁸, $\text{Ru}(\text{NH}_3)_5(4,6\text{-Me}_2\text{DBT})^{2+}$ is a rare example of a 4,6- Me_2DBT complex.⁵ As for $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{CO})_2(4,6\text{-Me}_2\text{DBT})^+$, the 4,6- Me_2DBT in **1** binds less strongly than the DBT ligand in **2**. This was established by the reaction of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ with a 10-fold excess of both DBT and 4,6- Me_2DBT , which yielded $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ 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- Me_2DBT to the metal. In earlier studies $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{CO})_2(\text{dibenzothiophene})^+$,⁵ and $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2(\text{dibenzothiophene})^{+23}$ it was established that methyl groups in the non-hindering 2,8-positions enhance the binding of 2,8- Me_2DBT as compared with DBT.

Removal of DBT from $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ by Oxidation. If $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ is to be used to remove DBT from hydrotreated feedstocks, it is necessary to remove DBT from its $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ extracted form, and convert it back to $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$. We first considered displacing DBT by the addition of a gas. Dinitrogen (N_2) is reported²² to displace T from $\text{Ru}(\text{NH}_3)_5(\text{T})^{2+}$ with an equilibrium constant of approximately ~ 3300 , which suggested that it would also displace DBT from **2**. However, stirring $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ 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 $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ within 30 minutes at room temperature in acetone to give $\text{Ru}(\text{NH}_3)_5(\text{CO})^{2+}$, which was identified by its characteristic ν_{CO} adsorption at 1948 cm^{-1} .²⁸ However it is not possible to remove the CO ligand under vacuum (room temperature)

from solid $\text{Ru}(\text{NH}_3)_5(\text{CO})^{2+}$ to reform $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$. These observations suggested that we should attempt other means to displace DBT from Ru.

Another possible approach to the removal of DBT from $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ is the oxidation of the complex to $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{3+}$, which we assume will bind DBT much less strongly. This assumption is based on the fact²⁴ that the equilibrium constant (~ 10) for the reaction of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ with T is favorable, while the equilibrium constant (2.5×10^{-8}) for the reaction of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ with T is highly unfavorable. Unfortunately, we were unable to find an oxidant that would simply oxidize $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ to $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{3+}$. Ferrocenium ion (Cp_2Fe^+) does not react with either $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ or $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ in acetone solution, as investigated by UV-Vis spectroscopy over a period of 1 h.

Air was then bubbled through a DMF/ H_2O solution of $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$; however, $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ is not formed. Rather, $[(\text{NH}_3)_5\text{RuORu}(\text{NH}_3)_5]^{4+}$ (λ_{max} 503, 386 nm) is formed and 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).²⁹ It should be noted that air oxidation of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ was previously reported to give the same products.³⁰ However, the oxidation does remove DBT from the Ru. When air is bubbled for 30 min through a solution of $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ in 10 mL of DMF/ H_2O with 10 mL of hexanes layered over it, DBT is released into the hexanes phase (observed via ^1H NMR). This release of DBT coincides with the formation of the oxidized ruthenium clusters (Scheme 2).

Scheme 2. Oxidation of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ or $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ to ruthenium red.

When the DMF/ H_2O solution of $[(\text{NH}_3)_5\text{RuORu}(\text{NH}_3)_5]^{4+}$ was treated with bubbling H_2 in the presence of Pd/C, $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ was formed in $\sim 90\%$ yield. This yield was estimated by using this recycled $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ solution in a second extraction of DBT from toluene/hexanes (under the original conditions); a $\sim 10\%$ 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. Perhaps one of the side products responsible for the 10% loss in activity is ruthenium red. One can envisage the reduction of $[(\text{NH}_3)_5\text{RuORu}(\text{NH}_3)_5]^{4+}$ to $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$, but ruthenium red has an interior $[\text{Ru}(\text{NH}_3)_4]$ fragment which requires an additional NH_3 group in order to reform $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$; thus ruthenium red may be responsible for the decrease in extraction ability.

Removal of DBT from $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ by Displacement with H_2O . Because of the reduction in extraction activity using the oxidation-reduction recycling method, we sought a simpler method of removing DBT from $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$. On the basis of the extraction studies (see below), it is likely that the DBT could be displaced by H_2O if the concentration of water in the DMF/ H_2O phase were increased. Following a typical extraction of DBT from 45% toluene / 55% hexanes with $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ in 70% DMF / 30% H_2O , the DMF/ H_2O phase containing $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ 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

Figure 1. Extraction of DBT into a 45% toluene / 55% hexanes phase from $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}/\text{DMF}/\text{H}_2\text{O}$ by the addition of H_2O .

present in the $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}/\text{DMF}/\text{H}_2\text{O}$ phase (Figure 1). When water was added to the $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}/\text{DMF}/\text{H}_2\text{O}$ phase to give a 60% DMF / 40% H_2O 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 $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}/\text{DMF}/\text{H}_2\text{O}$ phase. Thus, the majority of the $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ in the DMF/ H_2O can be converted back to $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ by extracting DBT with a toluene/hexanes phase while adding water to the $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}/\text{DMF}/\text{H}_2\text{O}$ phase. This method of regenerating $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ from $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ avoids the complications of the oxidation-reduction method described earlier.

Extraction of DBT from Simulated Fuel by $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{PF}_6]_2$. The ability of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ to react with 4,6-Me₂DBT and DBT to give complexes **1** and **2** suggested that $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ could be used to extract these dibenzothiophenes from petroleum feedstocks. The approach described herein involves using $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ 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 $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ (with respect to the number of moles of DBT in the hydrocarbon {hc} phase) in a 70% DMF / 30% H₂O phase are sonicated or stirred with the DBT/hc phase, the amount of DBT in the hc phase is reduced from 400 ppm to only 270 ppm sulfur (middle dashed line Figure 2). When the amount of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ 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 H₂ atmosphere in the presence of suspended Pd/C to keep the ruthenium complexes in the 2+ oxidation state. This extraction of DBT into the $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ /DMF/H₂O phase is primarily due to $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ because extraction of the DBT/hc phase with only 70% DMF/ 30% H₂O in the absence of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ reduced the DBT content in the hc phase to only 350 ppm. This reduction indicates that DBT has a small but measurable solubility in 70% DMF / 30% H₂O (eq 2). 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.

Figure 2. Extraction of DBT from simulated petroleum fuel with $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{PF}_6]_2$ in 70% DMF / 30% H_2O .

These experiments indicate that the extraction of DBT into the $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}/\text{DMF}/\text{H}_2\text{O}$ phase involves two equilibria. The first is a distribution equilibrium of DBT between the DMF/ H_2O and hc phases, (eq 1). The second is that for the reaction of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ 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 2. The control experiment yields the value for K_1 and the value for K_2 are calculated from the $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}/\text{DMF}/\text{H}_2\text{O}$ data as described in the Experimental section. Equilibrium constants K_1 and K_2 for DBT, BT and T were collected by similar means by GC and are presented in Table 2.

Table 2. Equilibrium constants, K_1 and K_2 , for reaction (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

The trend in K_1 values (DBT < BT < T) shows that T is the most soluble in the DMF/H₂O phase. The K_2 values for the binding of the thiophene by $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ increases in the order 56 (T) < 339 (BT) < 559 (DBT). This is the same trend that was previously observed for their coordination to $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{PPh}_3)^+$.²³

Extraction of 4,6 Me₂DBT from Simulated Fuel by $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{PF}_6]_2$. Although the extraction process removes DBT from a simulated petroleum feedstock, 4,6-Me₂DBT is not removed in appreciable amounts by the same system. Under the same conditions for which DBT was extracted to 200 ppm levels, no 4,6-Me₂DBT was removed from the hc phase. Part of the reason for this behavior is the low value of K_1 for 4,6-Me₂DBT. In the measurement of K_1 for DBT, ~12% of the DBT was extracted into the DMF/H₂O phase. When the same extraction was performed with 4,6-Me₂DBT, no observable amount of 4,6-Me₂DBT was extracted into the DMF/H₂O phase. The two methyl groups probably make 4,6-Me₂DBT more hydrophobic than DBT and therefore insoluble in the polar DMF/H₂O phase. Also contributing to the inability of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ /DMF/H₂O to extract 4,6-Me₂DBT from the hc phase is a smaller value of K_2 , as demonstrated by the DBT/4,6-Me₂DBT competition experiments described above as well as the binding constants of the molecules in $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{CO})_2(\text{R}_2\text{DBT})^+$.⁵

Figure 3. Extraction of 4,6-Me₂DBT from simulated petroleum fuel by [Ru(NH₃)₅(H₂O)][PF₆]₂ in 70% DMAC / 30% H₂O.

In an attempt to increase the value of K_1 , the DMF content was increased to 80% DMF / 20% H₂O; however, this did not improve the 4,6-Me₂DBT extraction. Using the less polar DMAC (N,N-dimethylacetamide) in place of DMF in the aqueous phase did improve the solubility of 4,6-Me₂DBT (Figure 3) in the polar phase (70% DMAC / 30% H₂O) and also reduced the 4,6-Me₂DBT in the hc phase from 400 to 340 ppm. 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 3) for the extraction of DBT from simulated hydrotreated fuel using a polar Ru(NH₃)₅(H₂O)²⁺/DMF/H₂O phase. The 70% DMF / 30% H₂O extraction solvent was chosen because both [Ru(NH₃)₅(H₂O)²⁺][PF₆]₂ and DBT are soluble in it. Also, the H₂O 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/H₂O phase, as determined by GC analyses.

The overall process (Scheme 3) 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(NH₃)₅(H₂O)²⁺/DMF/H₂O phase to remove DBT as Ru(NH₃)₅(DBT)²⁺. The DMF/H₂O phase containing Ru(NH₃)₅(DBT)²⁺ is then separated from the desulfurized hydrocarbon phase. The extractant phase is then regenerated by

Scheme 3. Cyclic process for the extraction of DBT from simulated petroleum fuel using a Ru(NH₃)₅(H₂O)²⁺ / DMF / H₂O extractant.

treating the Ru(NH₃)₅(DBT)²⁺/DMF/H₂O solution with air (O₂) which would release the DBT and form [(NH₃)₅RuORu(NH₃)₅]⁴⁺ and a small amount of [(NH₃)₅RuORu(NH₃)₄ORu(NH₃)₅]⁴⁺. The released DBT is extracted into a pure hydrocarbon phase such as hexanes. Finally, the ruthenium cluster in DMF/H₂O is reduced by treatment with H₂ and Pd/C to regenerate Ru(NH₃)₅(H₂O)²⁺ in the DMF / H₂O phase, which is used for another extraction. Alternately, after the Ru(NH₃)₅(DBT)²⁺ is separated from the feedstock, the H₂O content of the DMF/H₂O phase could be increased

Figure 4. Stepwise extraction of DBT from simulated petroleum fuel by $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{PF}_6]_2$ in 70% DMF / 30% H_2O .

to 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.

In an attempt to determine whether multiple extractions of DBT from a simulated fuel could reduce the DBT to target levels, the fuel was treated with $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ (10 equivalents) / DMF / H_2O in five successive extractions. As shown in Figure 5, 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.

Synthesis and Structures of $\text{CpM}(\text{CO})_2(\text{R}_2\text{DBT})^+$ Complexes. Before attempting a heterogeneous extraction of DBT by $\text{CpM}(\text{CO})_2(\text{X})^+$, we independently synthesized the complexes and solved their X-ray structures. The complex $\text{CpRu}(\text{CO})_2(\text{DBT})^+$ (**5**) was prepared by reacting $\text{CpRu}(\text{CO})_2\text{Cl}$ with AgBF_4 , in the presence of DBT, in CH_2Cl_2 solution. The Ag^+ abstracts the Cl^- ligand from the $\text{CpRu}(\text{CO})_2\text{Cl}$ forming the insoluble

AgCl and the metal cation $\text{CpRu}(\text{CO})_2(\text{solvent})^+$, which quickly reacts with the DBT to form the product $\text{CpRu}(\text{CO})_2(\text{DBT})^+$.

Complex $\text{CpFe}(\text{CO})_2(4,6\text{-Me}_2\text{DBT})^+$ (**6**) must be made via a different route, since the reaction of $\text{CpFe}(\text{CO})_2\text{Cl}$ with Ag^+ yields a series of bridged Cl compounds and not $[\text{CpFe}(\text{CO})_2(\text{solvent})^+]$. Complex **6** was prepared by the reaction of $\text{CpFe}(\text{CO})_2(\text{C}_4\text{H}_8)^+$ with 4,6-Me₂DBT. This iron complex represents only the second, fully characterized metal 4,6-Me₂DBT complex, and is the first such complex with iron.

The crystal structure of **6**, Figure 5, differs from **5** in several respects. The structure of **5** shows a significant twist of the DBT ligand as defined by the dihedral angle $\angle \text{Cp}(\text{centroid})\text{-Ru-S-(C11-C12 centroid)}$ of 157.2° (a measurement of 180° corresponds to no observed twist). This is surprising because one would assume that any amount of twist would bring the DBT ligand closer to the Cp plane causing possible steric interactions. The twist angle in **2**, as defined by $\angle \text{Cp}(\text{centroid})\text{-Fe-S-(C11-C12 centroid)}$, is 176.6° , which when compared to the Ru-DBT complex, is much more symmetrical. The tilt angle (as defined by $\angle \text{M-S-}\{\text{C11-C12 centroid}\}$) are 121.44° and 115.8° for **5** and **6** respectively. This is consistent with the notion that the methyl groups occupying the 4,6 positions in complex **6** push the 4,6-Me₂DBT ligand so as to minimize the steric interaction between the methyl groups and the Cp ring. Complex **5**, of course does not have methyl groups in the 4,6 positions and can have a larger tilt.

The uniqueness of 4,6-Me₂DBT complexes such as (**6**) are due twofold. First, although many DBT complexes are known,⁸ the ligand itself is a weak donor and is

Figure 5. Thermal ellipsoid drawing of $[\text{CpRu}(\text{CO})_2(\text{DBT})][\text{BF}_4]$ (**5**) and $[\text{CpFe}(\text{CO})_2(4,6\text{-Me}_2\text{DBT})][\text{BF}_4]$ (**6**). Ellipsoid is shown at the 30% probability level; hydrogens are omitted for clarity. Selected bond distances (Å) and angles (deg) for **5** are as follows: Ru-S = 2.398(2) Å; Tilt Angle: Ru-DBT: 121.44°; Twist Angle: Ru-DBT: 157.2°. Selected bond distances (Å) and angles (deg) for **6** are as follows: Fe-S = 2.310(2) Å; Tilt Angle: Fe-4,6-Me₂DBT: 115.8°; Twist Angle: Fe-4,6-Me₂DBT 176.6°.

difficult to coordinate to a metal center. Second, and more importantly, the methyl groups in the 4,6 positions pose a significant steric problem in the coordination of the 4,6-Me₂DBT ligand. Only two complexes of this type have ever been reported, and the only crystal structure (prior to this report) has just been recently published by our research group.⁵

Synthesis and Characterization of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{PF}_6]_2/\text{SBA-15}$, Ruthenium Blue/SBA-15, $[\text{CpRu}(\text{CO})_2][\text{BF}_4]/\text{SBA-15}$ and $[\text{CpFe}(\text{CO})_2(\text{THF})][\text{PF}_6]/\text{SBA-15}$.

Having made the new metal-DBT complexes in solution we adsorbed the precursors of such complexes onto silica to make solid phase extractants. Rather than using tethers^{31,32} to attach the metal complexes to the silica, we simply evaporated a solution of the metal complex onto the silica. This method has been used before as a means to make

homogeneous catalysts into heterogeneous catalysts.³³ Specifically, the SPE's were made by evaporating solutions of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{PF}_6]_2$, ruthenium blue,²⁷ $[\text{CpRu}(\text{CO})_2][\text{BF}_4]$, or $[\text{CpFe}(\text{CO})_2(\text{THF})][\text{BF}_4]$ onto SBA-15, a mesoporous silica. The resulting SPE's were characterized by their CP MAS ^{29}Si -NMR and DRIFT spectra.

The CP MAS ^{29}Si NMR spectra are particularly useful for characterizing the interaction between the metal complexes and the adsorbent (SBA-15). In a sample of unmodified SBA-15, three ^{29}Si peaks are observed in the solid state (94.10, 102.05 and 112.50 ppm), reflecting silicon atoms with zero ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$), one ($\equiv\text{Si}-\text{OH}$) or two ($=\text{Si}-(\text{OH})_2$) hydroxyl groups. The CP MAS ^{29}Si -NMR data for all the metal modified SBA-15 (SPEs) showed no new silicon signals. If the silicon or an attached $-\text{OH}$ were bonded directly to the adsorbed complex, the chemical environment around the Si would change and would be reflected by new peaks in the ^{29}Si NMR. The absence of new peaks, indicates that no covalent bonds to adsorbed metal complexes were formed.

This conclusion is further confirmed by the silanol stretching frequency observed in the surface IR data. The $\text{Si}-\text{OH}$ band has been used previously to confirm hydrogen bonding of complexes to silica surfaces.³² A decrease in the $\text{Si}-\text{OH}$ stretching frequency (3742 cm^{-1}) as compared with unmodified SBA-15 suggests hydrogen bonding between the surface and the metal complexes. The results of the ^{29}Si NMR and DRIFT IR spectroscopies suggest that both metal complexes are hydrogen bonded to terminal $\text{Si}-\text{OH}$ groups on the silica surface. The surface likely consists of BF_4^- anions randomly hydrogen-bonded to the mesoporous silica surface with the metallic cations immobilized nearby by an electrostatic attraction to the BF_4^- . The ruthenium blue complex, though non-ionic, showed the same results in the ^{29}Si NMR and DRIFT IR spectroscopies.

The Surface Reaction Between DBT and the SPE's. The reaction between DBT and the SPE occurs in much the same way that complexes react with DBT in solution as determined by DRIFT IR. This reaction can be followed most easily for $[\text{CpRu}(\text{CO})_2][\text{BF}_4]/\text{SBA-15}$. The upper trace (**A**) in Figure 6 is $[\text{CpRu}(\text{CO})_2][\text{BF}_4]/\text{SBA-15}$ that has been allowed to stir with 1 eq of DBT for 1.5 hours, the middle trace (**B**) is SBA-15 with $[\text{CpRu}(\text{CO})_2][\text{BF}_4]$ adsorbed onto the surface, and the bottom trace (**C**) is unmodified SBA-15. The $[\text{CpRu}(\text{CO})_2][\text{BF}_4]$ in $[\text{CpRu}(\text{CO})_2][\text{BF}_4]/\text{SBA-15}$ has ν_{CO} bands at 2075 and 2025 cm^{-1} . After stirring with DBT the ν_{CO} bands shift 2078 and 2034 cm^{-1} , indicating that a reaction has taken place; i.e. $[\text{CpRu}(\text{CO})_2][\text{BF}_4]$ has reacted on the silica surface with DBT to form $\text{CpRu}(\text{CO})_2(\text{DBT})^+$. Indeed, there is good agreement between the surface ν_{CO} pattern and those observed in solution $[(\text{CpRu}(\text{CO})_2(\text{DBT}))^+ \{\text{CH}_2\text{Cl}_2\}]$ 2079, 2036 cm^{-1} . The small shift observed between the solution IR and the DRIFT IR of the surface $\text{CpRu}(\text{CO})_2(\text{DBT})^+$ is due to the fact that the surface is actually a mixture of 75% $\text{CpRu}(\text{CO})_2(\text{DBT})^+$ and 25% $[\text{CpRu}(\text{CO})_2][\text{BF}_4]$. The electronic interaction of the DBT with $[\text{CpRu}(\text{CO})_2][\text{BF}_4]$ on the surface, as judged by the ν_{CO} , is nearly identical to that in solution.

The other ($\nu_{\text{CO}} = 2136 \text{ cm}^{-1}$) absorbance in the DRIFT spectrum is due to a small amount of $[\text{CpRu}(\text{CO})_3]^+$, which is formed as a side product in the reaction of AgBF_4 with $\text{CpRu}(\text{CO})_2\text{Cl}$. As judged by solution IR, $[\text{CpRu}(\text{CO})_3]^+$ is roughly 1/10 of the concentration of the $[\text{CpRu}(\text{CO})_2][\text{BF}_4]$ formed. Upon adsorption to SBA-15, the peak at 2136 cm^{-1} ($[\text{CpRu}(\text{CO})_3]^+$) grows and is nearly as large as the 2075 cm^{-1} peak ($[\text{CpRu}(\text{CO})_2][\text{BF}_4]$). Several factors contribute to the large differences between the solution IR and the surface DRIFT spectrum. First, the IR spectrum of a solution is very

different than a DRIFT spectrum of a species on a surface.³⁴ Also, it has been shown previously that certain absorption bands are favored over others in densely packed arrays on a surface, mainly due to physical crowding constraining such systems.³⁵ Thus, due to factors such as these, the impurity $[\text{CpRu}(\text{CO})_3]^+$ band at 2136 cm^{-1} in the DRIFT spectrum is much more intense than expected from its low concentration.

The DRIFT and CP MAS ^{13}C NMR results for $[\text{CpRu}(\text{CO})_2(\text{BF}_4)]/\text{SBA-15}$ and $[\text{CpFe}(\text{CO})_2(\text{THF})]/\text{SBA-15}$ are very similar to the analogous solution spectroscopy. This suggests that the chemical environments around the metals are approximately the same in solution as they are on the surface. In solution the steric differences between DBT and 4,6-Me₂DBT (already pointed out in the X-ray structures of **1** and **2**) result in differences between their reactivity as measured by equilibrium values (see below).

There are close similarities between the chemical shifts in the CP MAS ^{13}C NMR of $\text{CpRu}(\text{CO})_2(\text{DBT})^+/\text{SBA-15}$ and the solution ^{13}C NMR of $\text{CpRu}(\text{CO})_2(\text{DBT})^+$. $\text{CpRu}(\text{CO})_2(4,6\text{-Me}_2\text{DBT})^+/\text{SBA-15}$ is observed on the surface; indeed the resolution is good enough to compare and contrast the corresponding peaks observed in solution ^{13}C NMR spectra, as shown in Table 2. The CP MAS ^{13}C NMR of the iron complexes were less informative due to the smaller amounts of DBT adsorbed and to small amounts of paramagnetic impurities. For these reasons only broad resonances for the DBT and Cp carbons are visible, and direct comparisons with the peaks in solution ^{13}C NMR are impossible. We cannot observe the reaction of $\text{CpFe}(\text{CO})_2(\text{THF})^+$ on the surface with DBT by DRIFT, because the ν_{CO} of the starting material and the products are too similar to distinguish.

Table 3. Selected ^{13}C NMR data for compounds 1 and 2 in CD_2Cl_2 solution and on SBA-15 surface.

Compound	^{13}C NMR Signals (ppm)
[CpRu(CO)$_2$][BF$_4$]/SBA-15/ DBT	δ 137.07, 129.57, 126.16, 90.03
[CpRu(CO)$_2$(DBT)][BF$_4$]	(CD_2Cl_2): δ 140.6, 137.1, 130.3, 130.1, 125.8, 123.7, 90.1
[CpRu(CO)$_2$][BF$_4$]/SBA-15/ 4,6-Me$_2$DBT	δ 140.10, 137.16, 135.04, 135.06, 128.26, 119.56, 90.52, 21.12
[CpRu(CO)$_2$(4,6-Me$_2$DBT)][BF$_4$]	(CD_2Cl_2): δ 140.05, 137.94, 134.76, 131.31, 130.93, 122.00, 90.18, 21.56

Figure 6. Composite DRIFT IR of SBA-15/CpRu(CO) $_2$ (DBT) $^+$ (**A**) (ν_{CO} = 2079, 2036 cm^{-1} in CH_2Cl_2 solution; ν_{CO} = 2078, 2034 cm^{-1} on silica); SBA-15/CpRu(CO) $_2$ (DBT) $^+$ (**B**) (ν_{CO} = 2083, 2018 cm^{-1} in CH_2Cl_2 solution; ν_{CO} = 2075, 2026 cm^{-1} on silica); SBA-15 (**C**).

The reactions between DBT and the metal complexes on the surface is also confirmed by XPS. Sulfur is directly observed at 264 eV for all the SPEs studied.

Extraction of DBT from Simulated Petroleum by Surface Ru and Fe Complexes. In the previous sections, we have discussed the nature of the adsorption of metal complexes on mesoporous silica, and the interaction of R₂DBT with the adsorbed complexes. In this section, we discuss the bulk properties of these materials as SPE's toward DBT.

An isomolar amount (0.51 mmol) of each metal complex was adsorbed onto 250 mg of SBA-15 to test the effectiveness of each of the SPE's toward DBT. Stirring the SPE's with DBT results in maximum extraction of the DBT, within 45 minutes. The [CpRu(CO)₂][BF₄]/SBA-15 extractant lowered the DBT level from 400 ppm to 3.5 ppm and 4,6-Me₂DBT from 400 to 112 ppm. The iron complex CpFe(CO)₂(THF)⁺ lowered the DBT level from 400 ppm to 133 ppm and the Me₂DBT is reduced from 400 to 189 ppm. The Ru(NH₃)₅(H₂O)²⁺ based extractant reduced the DBT level from 400 ppm to 280 ppm and the Me₂DBT from 400 to 318 ppm. The ruthenium blue based extractant reduced the DBT level from 400 ppm to 200 ppm and the Me₂DBT from 400 to 325 ppm.

AgX as an SPE for the Removal of Sulfur from Petroleum Feedstocks. The previously described metal complexes all have multiple ligands and finely tuned environments to facilitate the binding of DBT. Here, we report the use of a silver based {Ag⁺/SBA-15} solid phase extractant for the removal of hindered dibenzothiophenes (R₂DBT) from petroleum. We propose that a lone pair of electrons on the sulfur of the R₂DBT binds to the Ag⁺ on the Ag⁺/SBA-15. Although no such reaction between Ag⁺ and R₂DBT has been reported on a surface or in solution, several solution silver-sulfur complexes have been reported in the literature in the form of silver thiolate³⁶ and thioether^{37,38} complexes.

We have previously shown that ionic compounds form hydrogen bonds to the surface Si-OH groups in silica, and we propose a similar interaction in AgX/SBA-15. The AgX/SBA-15 is added to 10 mL of decane containing 400 ppm S (as R₂DBT) along with an internal standard, and the mixture was stirred. The amount of R₂DBT extracted was determined by GC using the internal standard (decahydronaphthalene). In these extractions, DBT and 4,6-Me₂DBT levels were reduced from 400 ppm to 72 (±9) and 75 (±6) respectively. Since no R₂DBT was removed when only SBA-15 or NBu₄BF₄/SBA-15 was present, the removal of R₂DBT must be due to the presence of the Ag⁺ cation. We have found no difference between the activity of AgBF₄, AgPF₆ or AgNO₃ (suggesting the anions are merely spectator ions); thus we use each of these Ag⁺ salts interchangeably. The use of AgNO₃ is particularly attractive due to its low cost (it is 20X *less* expensive than AgPF₆) and availability from Aldrich pre-adsorbed onto a silica support. The extractions of R₂DBT from solution are complete within 1 min (the time it takes to completely mix the reactants and withdraw a sample for GC analysis).

A series of XPS were performed to confirm the presence of S on the surface of the DBT-Ag⁺/SBA-15. As can be seen in Figure 8, sulfur 2p emission bands are observed (at 264 eV) via XPS, confirming the presence of DBT on the surface since it is the only source of sulfur in this reaction. We observed ¹³C signals in the aromatic region of the CP MAS NMR, further confirming the presence of DBT on the surface. Since the only aromatic carbons anywhere in the reaction scheme belongs to DBT, their presence confirms that DBT is on the surface. Again, great care was used in preparing the samples for XPS and CP MAS ¹³C NMR analysis to ensure that only DBT bound to the surface was being observed. The DBT-Ag⁺/SBA-15 was washed several times with hexanes and

dried under vacuum, which would remove any DBT not bound chemically to Ag^+ . Interestingly, Ag^+ and DBT do not react in solution (as observed by ^1H NMR spectroscopically). The DBT- Ag^+ /SBA-15 interaction is likely a low energy bond, perhaps only a few kcal/mol, and only occurs in non-polar solvents. Polar solvents displace the DBT from DBT- Ag^+ /SBA-15.

In Figure 7, is shown the effect of increasing the weight % loading of AgBF_4 on the SBA-15 on the extent of extraction of DBT or 4,6- Me_2DBT . As the weight % of AgBF_4 increases, so does the extent of extraction of DBT and 4,6- Me_2DBT onto the surface. This trend ceases after the weight % of AgBF_4 increases beyond 30% by weight. At that point, the surface becomes saturated and supplementary AgBF_4 adsorbed to the surface has no additional benefit for extracting R_2DBT . There appears to be a small preference for the extraction of 4,6- Me_2DBT over DBT from the simulated diesel fuel.

The preference for 4,6- Me_2DBT over DBT is inconsistent with previous studies of the reactivity of 4,6- Me_2DBT and DBT. Previously, it was shown that in the case of $\text{CpRu}(\text{CO})_2(4,6\text{-R}_2\text{DBT})^+$ (where $\text{R} = \text{H}$ or Me), DBT binds 9.7 times more strongly than 4,6- Me_2DBT both in solution and on a surface.³⁹ For $\text{AgX}/\text{SBA-15}$, it appears that whatever negative steric effects the methyl groups in the 4,6-positions impart, they are cancelled out by the positive effect of the electron donating methyl groups. So, whereas the ligand environment around $\text{CpRu}(\text{CO})_2(4,6\text{-R}_2\text{DBT})^+$ forces steric considerations to prevail, the absence of a ligand environment causes Ag^+ to prefer 4,6- Me_2DBT over DBT.

Dibenzothiophene has not previously been observed to coordinate to a simple metal cation as silver (I). In fact, R₂DBT's (especially 4,6-Me₂DBT) are inherently difficult compounds to coordinate; the first crystal structure of 4,6-Me₂DBT has been solved only

Figure 7. DBT extraction after 1 min with various loadings of AgBF₄ on 250 mg SBA-15.

very recently and only 4 compounds are reported to exist in the literature.⁴⁰ In every previous complex, the 4,6-Me₂DBT coordinates in metal complexes that contain other ligands such as Cp, CO, and PR₃.^{1d} It appears that under the right conditions (in this case a metal ion dispersed on a solid support in a non-polar solvent) R₂DBT will, in fact, coordinate to simple metal ions.

Once the Ag⁺/SBA-15 is saturated by DBT, the DBT may be displaced from the DBT-Ag⁺/SBA-15 surface by polar solvents as a means to regenerate the active SPE. To streamline the process, we prepared a column with 867 mg of AgNO₃/SBA-15 (10% AgNO₃ by weight {0.51 mmol} on silica gel +200 mesh, Aldrich). When a 10 mL sample of decane containing 400 ppm DBT was passed through the column, the DBT level was

Figure 8. XPS of AgBF₄/SBA-15 after stirring with simulated diesel fuel with 400 ppm DBT.

Figure 9. Amounts of DBT in eluent from a AgNO₃/silica gel column after several treatments.

reduced to 57 (± 7) ppm, Figure 3. Nearly all of the DBT on the saturated column can be removed by eluting with diethyl ether. Then, this solvent-Ag⁺/SBA-15 column may be reused in further extractions with no observed loss of reactivity, Figure 9. These results show that DBT and 4,6-Me₂DBT may be selectively removed on a column, and the column may be regenerated and reused for additional extractions. These Ag⁺-based SPEs hold real promise for the removal of R₂DBT from petroleum feedstocks.

CONCLUSIONS

The synthesis of $\text{Ru}(\text{NH}_3)_5(4,6\text{-Me}_2\text{DBT})^{2+}$, as well as the DBT, BT and T analogs, shows that $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ 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 $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$. Five sequential extractions remove 94% of the DBT. The DBT can be removed from the resulting $\text{Ru}(\text{NH}_3)_5(\text{DBT})^{2+}$ and the $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ regenerated by either oxidation/reduction steps or the addition of water. The extraction of 4,6- Me_2DBT from a simulated feedstock is possible in DMAC/ H_2O , but at only 25% of the level achieved for DBT.

We have created several solid phase extractants by adsorbing $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$, ruthenium blue, $\text{CpRu}(\text{CO})_2(\text{BF}_4)$, $\text{CpFe}(\text{CO})_2(\text{THF})^+$ onto SBA-15. All of these SPEs are hydrogen bonded to the surface through Si-OH bonds. Each of these SPEs removes DBT and 4,6- Me_2DBT to varying degrees, and the reaction of $\text{CpRu}(\text{CO})_2(\text{BF}_4)/\text{SBA-15}$ with DBT has been characterized by DRIFT spectroscopy.

We have found that Ag^+ is the most attractive SPE, since it can bind or release R_2DBT , depending on the solvent. $\text{Ag}^+/\text{SBA-15}$ is potentially a practical extractant for DBT on the industrial scale.

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