**Coordination of dibenzothiophenes and corannulenes to organometallic
ruthenium(II) fragments**

by

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ABSTRACT

Structural, equilibrium and kinetic studies of several $[\text{Cp}'\text{Ru}(\text{CO})_2(\eta^1(S)\text{-DBTh})]^+$ complexes, where $\text{Cp}' = \text{Cp}$ ($\eta^5\text{-C}_5\text{H}_5$) or Cp^* ($\eta^5\text{-C}_5\text{Me}_5$) and $\text{DBTh} = \text{DBT}$, 4-MeDBT, 4,6-Me₂DBT or 2,8-Me₂DBT, were undertaken to determine how methyl groups in the 4- and 6-

Dibenzothiophene (DBTh)

positions of DBTh influence its sulfur-binding ability. Only in the complex $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-4,6-Me}_2\text{DBT})]^+$ is there structural evidence for steric crowding between the Cp' and DBTh ligands. Relative equilibrium constants (K') for the binding of the DBTh ligands in both the Cp and Cp^* complexes increase in the order, 4,6-Me₂DBT < 4-MeDBT < DBT < 2,8-Me₂DBT, and show that methyl groups in the 4,6-positions of DBTh substantially reduce the thermodynamic strength of the Ru-S bond. Kinetic studies of the substitution of the DBTh ligand in both the Cp and Cp^* complexes by phosphorus donor ligands established the following order of DBTh lability, 4,6-Me₂DBT < DBT < 2,8-Me₂DBT, which is the same as the trend in K' values. The most labile DBTh ligand in both series of complexes is 4,6-Me₂DBT in $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-4,6-Me}_2\text{DBT})]^+$, where both steric crowding and electron-donation by the Cp^* ligand increases the rate of dissociation.

A $\mu_2\text{-}\eta^1(S), \eta^6$ bridging mode for dibenzothiophenes is demonstrated by synthesis of the $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(S), \eta^6\text{-DBT})\text{RuCp}]^{2+}$ complexes. An X-ray crystallographic study of $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(S), \eta^6\text{-DBT})\text{RuCp}^*][\text{PF}_6]_2$ shows that the $\{\text{CpRu}(\text{CO})_2\}^+$ and $\{\text{Cp}^*\text{Ru}\}^+$

groups bind through the sulfur and an arene ring (η^6), respectively, on opposite sides of a planar DBT ligand. A kinetic investigation of $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(\text{S}),\eta^6\text{-DBT})\text{RuCp}^*]^{2+}$ shows that the η^6 -coordinated $\{\text{Cp}^*\text{Ru}\}^+$ group dramatically increases the lability of the Ru-S bond as compared to that in $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})]^+$, much more than alkyl groups in the 4,6-positions of dibenzothiophene.

The reaction of $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ with Ag^+ and the curved-surface buckybowl corannulene ($\text{C}_{20}\text{H}_{10}$) in CD_3NO_2 solvent affords both $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})]^+$ and $[\text{Cp}^*\text{Ru}(\mu_2\text{-}\eta^6,\eta^6\text{-C}_{20}\text{H}_{10})]^{2+}$ depending on the stoichiometry of the reaction. An X-ray crystallographic investigation of $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]$ shows an $\eta^6\text{-}\{\text{Cp}^*\text{Ru}\}^+$ unit that is attached to the convex side of corannulene, and the corannulene unit is flattened where the $\{\text{Cp}^*\text{Ru}\}^+$ group is attached to it. The corannulene unit is flattened even more in the structure of $[\text{Cp}^*\text{Ru}(\mu_2\text{-}\eta^6,\eta^6\text{-C}_{20}\text{H}_{10})][\text{PF}_6]_2$, where two $\eta^6\text{-}\{\text{Cp}^*\text{Ru}\}^+$ groups are coordinated to non-adjacent arene rings on opposite sides of corannulene. The X-ray determined structure of the analogous SbF_6^- salt, $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6\text{-}\eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]_2$ shows that the corannulene bowl is almost completely flat. Low temperature NMR studies of the analogous 1,2,5,6-tetramethylcorannulene complex $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6\text{-}\eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)]^{2+}$ show that there is a very low barrier to inversion of the bowl even at -90°C .

Corannulene ($\text{C}_{20}\text{H}_{10}$)

CHAPTER 1: GENERAL INTRODUCTION

Thesis Organization

This dissertation contains five papers in the format required for journal publication which describe (in part) my research accomplishments as a graduate student at Iowa State University. This work can be broadly categorized as the binding of weakly-coordinating ligands to cationic organometallic ruthenium fragments, and consists of two main areas of study. Chapters 2-4 are investigations into factors that influence the binding of dibenzothiophenes to $\{\text{Cp}^*\text{Ru}(\text{CO})_2\}^+$ fragments, where $\text{Cp}^* = \eta^5\text{-C}_5\text{H}_5$ (Cp) and $\eta^5\text{-C}_5\text{Me}_5$ (Cp^*). Chapters 5 and 6 present the synthesis and structural characterization of complexes containing corannulene buckybowls that are η^6 -coordinated to $\{\text{Cp}^*\text{Ru}\}^+$ fragments. The first chapter contains a brief description of the difficulty in lowering sulfur levels in diesel fuel along with a review of corannulene derivatives and their metal complexes. After the final paper is a short summary of the work herein (Chapter 7). Each chapter is independent, and all equations, schemes, figures, tables, references, and appendices in this dissertation pertain only to the chapter in which they appear.

Literature Review

Importance of the Removal of Hindered Dibenzothiophenes

The combustion of organosulfur compounds in transportation fuels (gasoline, jet and diesel fuels) contributes to atmospheric pollution by sulfur oxides,¹ which can form acid rain that causes damage to both the environment and infrastructure (buildings, bridges, etc.). Sulfur compounds in these fuels also poison catalytic converters, impairing the vehicle

emission control systems necessary to reduce levels of nitrogen oxides released into the atmosphere during fuel combustion.^{1a} These important environmental and economic issues have led to considerable effort being devoted to the removal of sulfur compounds from transportation fuels prior to combustion.

Sulfur is currently removed from transportation fuels using a catalytic process known as hydrodesulfurization (HDS). The most difficult of the sulfur-containing compounds to be removed using HDS are the hindered dibenzothiophenes, which contain alkyl groups near the sulfur in either the 4- and/or 6-positions and are found in diesel fuel.^{1a,2} Sulfur levels in U.S. diesel fuel must undergo a 97% reduction from the current average of 500 ppm to a maximum of 15 ppm by 2006,³ which necessitates the removal of these dibenzothiophenes derivatives. Although it is unclear exactly how dibenzothiophenes interact with the catalyst surface during HDS, it has been proposed that an initial step is binding of the substrate through the sulfur atom to active metal sites.⁴ The slow rates for the HDS of 4-methyldibenzothiophene (4-MeDBT) and 4,6-dimethyldibenzothiophene (4,6-Me₂DBT) may be due to steric hindrance by alkyl groups in the 4,6-positions that interfere with their binding to such sites.

Dibenzothiophene (DBT)

Improvements in the HDS process have not adequately addressed the difficulties of desulfurizing hindered dibenzothiophenes, and focus has shifted towards developing new technologies for desulfurization.^{2,5} One promising new method is the use of adsorbents or

solid phase extractants (SPEs) to selectively bind and remove sulfur compounds such as the hindered dibenzothiophenes.^{2,5,6} Adsorbent technologies have the potential advantage of being relatively simple to incorporate into the existing infrastructure as either a pre- or post-HDS treatment. Another emerging technology for desulfurization of hydrocarbon fuels is catalytic oxidation of hindered dibenzothiophenes to the sulfones or sulfoxides, followed by extraction or adsorption.⁷ In both of these new desulfurization approaches, an important step involves binding of the dibenzothiophene to either the adsorbent or catalyst.

Several experimental and theoretical studies on the sulfur-coordination of thiophenes, benzothiophenes, and dibenzothiophenes to transition metal complexes have been reported.⁸ However, prior to the work in this dissertation, there were no examples of hindered dibenzothiophenes that are $\eta^1(S)$ -coordinated in metal complexes, presumably a result of the instability of such complexes. Our goal was to prepare metal complexes of the hindered dibenzothiophenes 4-MeDBT and 4,6-Me₂DBT and investigate how steric and electronic factors affect sulfur coordination. An understanding of the relative bond strengths and kinetic labilities of hindered dibenzothiophenes in metal complexes may be useful in the development and optimization of new methods for sulfur removal from diesel fuel.

Corannulene Derivatives and Their Metal Complexes

The compound dibenzo[ghi,mno]fluoranthene (C₂₀H₁₀), commonly referred to as corannulene, is a polycyclic aromatic hydrocarbon (PAH) that is curved due to the fusion of five six-membered rings around a five carbon atom core. It was first synthesized in 1966 by Barth and Lawton,⁹ and its structure was confirmed shortly thereafter by an X-ray diffraction study.¹⁰ The deviation of the carbon atoms in corannulene from their preferred trigonal planar

arrangement offers an interesting opportunity to investigate how strain affects aromaticity and reactivity in PAH systems. However, the difficulty in obtaining corannulene in large enough amounts for research hindered investigation into its reactivity for over two decades after the initial synthetic report.

The synthesis and isolation of buckminsterfullerene C_{60} ,¹¹ a highly symmetrical {three-dimensional} carbon cage that is commonly referred to as “buckyball”, led to renewed interest in curved PAH compounds. Buckminsterfullerene consists of 12 nonadjacent five-membered and 20 six-membered rings that are fused together to form a truncated icosahedral structure.¹² The curved, or bowl-shaped, PAHs with carbon atom frameworks represented on the surface of C_{60} were eventually termed “buckybowls”.¹³ Buckybowls have both a convex and a concave surface where chemistry may occur. They are potential synthetic intermediates for the preparation of carbon cage compounds like fullerenes and carbon nanotubes, which may provide a means to encapsulate molecules within closed carbon frameworks. Corannulene is the smallest of these buckybowl compounds, and may be described as the cap of buckminsterfullerene.

Buckminsterfullerene (C_{60})

The initial synthesis of corannulene reported by Barth and Lawton was lengthy and difficult, involving a 16 or 17-step reaction sequence that yielded low overall yields (3-6%) of product.^{9b} Initial improvements in the synthesis of corannulene came from the observation that the curved surfaces of C_{60} and other fullerenes are formed under high energy conditions in the gas-phase.¹⁴ Scott and coworkers were the first to report new syntheses of corannulene by using flash vacuum pyrolysis (FVP) of carefully constructed precursor molecules to obtain yields of corannulene as high as 30-40%.¹⁵ Eventually, a three-step synthetic procedure for corannulene was developed by Scott's group that utilized commercially available heptane-2,4,6-trione starting material and FVP to obtain corannulene in overall yields of 20-25%.^{15c} More recently, solution based methods for the synthesis of corannulene in good yields have been reported in both Siegel's¹⁶ and Rabideau's¹⁷ groups and make it possible to prepare corannulene derivatives and larger buckybowl compounds that are difficult to obtain by FVP methods. These new synthetic procedures for corannulene, which readily yield gram quantities of product, have stimulated new research into its properties and reactivity.

The curvature in corannulene can be described by a π -orbital axis vector (POAV) analysis and by a bowl depth determination. POAV analysis is a method of describing the

curvature of carbon atoms in non-planar ring systems.¹⁸ In planar PAH systems like graphite, the POAV value is 0°, and the larger the POAV value, the more curvature there is at the carbon atom of interest. The values for the non-hydrogen containing carbon atoms in corannulene are 8.4° for the internal, or “core” carbons and 3.8° for the external rim quaternary carbon atoms. For comparison, there is only one POAV value for all the equivalent carbon atoms in C₆₀, 11.6°. Bowl depth can be used to describe the overall curvature in buckybowl compounds and is the distance between the centroid of the five core carbon atoms and the centroid of the ten tertiary rim carbons. The bowl depth in corannulene is 0.87 Å. A similar calculation performed on the cap of C₆₀ gives a value of 1.49 Å.^{12c} Corannulene is less curved than buckminsterfullerene as evidenced by its smaller POAV values and its bowl depth.

Corannulene is a highly flexible molecule, undergoing rapid bowl-to-bowl inversion in solution at room temperature.¹⁹ Inversion barriers ($\Delta G^\ddagger$) of corannulene derivatives that are mono-functionalized on the rim with dimethylcarbinol, isopropyl, and benzyl groups, which presumably do not alter the structure of the corannulene unit significantly, are determined to be 10.2 kcal/mol at 209 K,¹⁹ 11.3 kcal/mol at 242 K,²⁰ and 11.2 kcal/mol at 234 K,²⁰ respectively. In another study, the inversion barrier for free corannulene was estimated to be 11.5 kcal/mol based on the experimentally determined inversion barriers of two bis(bromomethyl)corannulene derivatives (10.4-10.5 kcal/mol) and bromomethylcorannulene (11.0 kcal/mol).²¹ These results suggest that the inversion of free corannulene is between 10-12 kcal/mol. Experimental and theoretical studies indicate that inversion barriers in corannulene and its derivatives are highly dependent on their curvatures and bowl depths.^{21,22} Those substituents and interactions that lead to a decrease in the

curvature and flattening of the bowl result in structures with lower barriers to inversion, whereas those substitutions that cause an increase in the curvature and bowl depth give structures with larger barriers to inversion.

Within a year after the reported synthesis and isolation of buckminsterfullerene, metal complexes of C_{60} began to appear in the literature. In the numerous transition metal complexes of C_{60} , the metal is always bonded η^2 to two carbon atoms at the juncture of two six-membered rings. No complexes of greater hapticity for C_{60} have been reported, presumably due to the poor orbital overlap between the splayed out p-orbitals on the surface of C_{60} and the orbitals of the metal fragments involved in binding. In contrast, metal complexes of corannulene are rare and did not appear until after 30 years following the initial report by Barth and Lawton.

The first transition metal complex of corannulene, $[Cp^*Ru(\eta^6-C_{20}H_{10})][O_3SCF_3]$ (Figure 1),²³ was reported by Siegel and coworkers in 1997. This compound was prepared by combining $[Cp^*Ru(NCMe)_3][O_3SCF_3]$, the source of the $\{Cp^*Ru\}^+$ fragment, with corannulene in CD_2Cl_2 solvent. In order for the reaction to proceed to completion, it was necessary to remove the CD_2Cl_2 solvent and the displaced MeCN ligands under vacuum and add fresh CD_2Cl_2 . Apparently, the presence of acetonitrile in solution prevented complete conversion to $[Cp^*Ru(\eta^6-C_{20}H_{10})][O_3SCF_3]$. (It is interesting to note that the reaction of $[Cp^*Ru(NCMe)_3][O_3SCF_3]$ with C_{60} forms an η^2 complex in which two molecules of acetonitrile are still bound to the ruthenium.^{12c}) It was not until six years later in 2003 that a second transition metal complex of corannulene was reported. Alvarez in this group prepared the η^6 complex $[Cp^*Ir(\eta^6-C_{20}H_{10})][BF_4]_2$ ²⁴ (Figure 1) by combining $[Cp^*Ir(acetone)_3][BF_4]_2$

with corannulene in nitromethane solvent. The complex did not form when $[\text{Cp}^*\text{Ir}(\text{acetone})_3][\text{BF}_4]_2$ was reacted corannulene in acetone solvent.

The η^6 -corannulene ligand in $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{O}_3\text{SCF}_3]$ and $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{BF}_4]_2$ is very weakly coordinated. As mentioned above, even weakly coordinating molecules such as acetonitrile and acetone solvent interfere with their preparation. Once formed, addition of excess acetonitrile or benzene to CD_2Cl_2 solutions of $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{O}_3\text{SCF}_3]$ yields free corannulene and either $[\text{Cp}^*\text{Ru}(\text{NCMe})_3][\text{O}_3\text{SCF}_3]$ or $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_6\text{H}_6)][\text{O}_3\text{SCF}_3]$, respectively.²³ Similarly, addition of ~10 equivalents acetone or benzene to CD_3NO_2 solutions of $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{BF}_4]_2$ yields $[\text{Cp}^*\text{Ir}(\text{acetone})_3][\text{BF}_4]_2$ or $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_6)][\text{BF}_4]_2$, respectively, within 4-6 hours.²⁴

The complexes $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{O}_3\text{SCF}_3]$ and $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{BF}_4]_2$ were characterized by their mass spectra and also by NMR spectroscopy, which confirmed η^6 -coordination of the metal fragments. The ^1H NMR spectra of both compounds showed that the one signal for free corannulene (~7.9 ppm) was split into four doublets and a singlet upon coordination to the metal fragments, which indicates a plane of symmetry through the corannulene in both complexes. Also, only one peak corresponding to the methyl groups of the Cp^* ligands was observed in the ^1H NMR spectra of both complexes. Theoretically, the metal fragments can bind to either the outside (convex) surface or to the inside (concave) surface of corannulene, and each of the two possible isomers should have different chemical shifts for the Cp^* ligands due to different shielding on each side of the bowl. Since only one signal for the Cp^* methyl groups was observed in the ^1H NMR spectrum of both $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{O}_3\text{SCF}_3]$ and $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{BF}_4]_2$, it must mean that either one isomer is

strongly preferred over the other, or that the corannulene unit undergoes rapid bowl-to-bowl inversion, as was described above for the free corannulene derivatives. Unfortunately, molecular structures of $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{O}_3\text{SCF}_3]$ or $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{BF}_4]_2$ were not reported, presumably because suitable crystals for X-ray crystallographic studies could not be obtained.

Siegel and coworkers searched for fluxional processes in $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{O}_3\text{SCF}_3]$ by performing variable temperature ^1H NMR experiments.²³ A low temperature study of the complex in CD_2Cl_2 showed no change in the ^1H NMR spectrum even at $-90\text{ }^\circ\text{C}$. If the single Cp^* peak at this low temperature arises from a fluxional bowl inversion process, it suggests that η^6 -coordination of $\{\text{Cp}^*\text{Ru}\}^+$ lowers the barrier to inversion for corannulene, perhaps by flattening of the bowl. A high temperature study of $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{O}_3\text{SCF}_3]$ in $\text{C}_2\text{D}_2\text{Cl}_4$ showed no change in the ^1H NMR spectrum up to $150\text{ }^\circ\text{C}$ at which point irreversible decomposition occurred, which indicates that intramolecular $\{\text{Cp}^*\text{Ru}\}^+$ migration from one arene ring to another (which would cause the hydrogen signals for the corannulene ligand to become equivalent), if possible, is slow on the NMR timescale even at $150\text{ }^\circ\text{C}$.

As mentioned above, a question that arises in the coordination chemistry of corannulene and other buckybowls is to which side of the bowl the metal fragments prefer to bind, i.e., the convex or the concave side. Siegel *et. al.* attempted to answer this question by performing a theoretical investigation on $[\text{CpRu}(\eta^6\text{-C}_{20}\text{H}_{10})]^+$,²³ a complex in which the Cp^* ligand of $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})]^+$ was replaced with Cp ($\eta^5\text{-C}_5\text{H}_5$) in order to save computation time. Their results predicted that the isomer in which the $\{\text{CpRu}\}^+$ group is bound to the

convex side of corannulene to be ~ 6 kcal/mol more stable than the isomer in which it is bound to the concave side. This study also indicated that the methyl groups on the Cp* ligand of $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})]^+$ would come into contact with the underside of the corannulene ligand if $\{\text{Cp}^*\text{Ru}\}^+$ was bound to the concave face. However, there were no experimental data to support these conclusions.

There are two other metal complexes of η^6 -coordinated buckybawls in the literature. Reaction of $[\text{Cp}^*\text{Ir}(\text{acetone})_3][\text{BF}_4]_2$ with the corannulene derivative 1,2,5,6-tetramethylcorannulene in CD_3NO_2 solvent affords the complex $[\text{Cp}^*\text{Ir}(\eta^6\text{-Me}_4\text{C}_{20}\text{H}_6)][\text{BF}_4]_2$ ²⁴ which initially exists as a mixture of three isomers that correspond to the three different types of arene rings in the buckybowl ligand (Figure 2): isomer **A** in which the $\{\text{Cp}^*\text{Ir}\}^{2+}$ group is bound to a methylated ring, isomer **B** in which the $\{\text{Cp}^*\text{Ir}\}^{2+}$ group is bound to one of the two non-methylated rings between the two methylated rings, and isomer **C** in which the $\{\text{Cp}^*\text{Ir}\}^{2+}$ group is bound to the single non-methylated ring between the two methylated rings. After three minutes of reaction, the ^1H NMR spectrum showed the ratio of **A**:**B**:**C** to be 23:61:16. However, after six hours, isomer **B** was no longer observed and only isomers **A** and **C** remained in a 9:1 ratio. It was not clear whether isomerization occurred by ring-to-ring migration on the surface of 1,2,5,6-tetramethylcorannulene or by complete dissociation of the $\{\text{Cp}^*\text{Ir}\}^{2+}$ fragment. Either process may be facilitated by the residual acetone that remains in solution from the synthesis reaction.

The other example of an η^6 -buckybowl complex is prepared by the reaction of $[\text{Cp}^*\text{Ru}(\text{NCMe})_3][\text{O}_3\text{SCF}_3]$ with acecorannulene in CD_2Cl_2 solvent.²⁵ Acecorannulene (Figure 3) is a non-fluxional buckybowl at room temperature that has three differently curved arene rings (**X**, **Y**, **Z**) with average POAV values of 8.1° , 5.3° , and 5.1° , respectively. When

the reaction was performed at -80 °C only the $[\text{Cp}^*\text{Ru}(\text{NCMe})_3][\text{O}_3\text{SCF}_3]$ starting material and the isomer in which the $\{\text{Cp}^*\text{Ru}\}^+$ fragment is bound to ring **Y** was observed in a 3:1 ratio. Upon warming to room temperature, a 6:2:1 ratio of starting material to the isomers in which the $\{\text{Cp}^*\text{Ru}\}^+$ fragment is bound to rings **Y** and **Z**, respectively, is observed (note that the presence of residual acetonitrile in this reaction prevents complete conversion to products as was observed in the analogous reaction with corannulene). The authors suggest that migration of the $\{\text{Cp}^*\text{Ru}\}^+$ unit from ring **Y** to ring **Z** may be catalyzed by residual acetonitrile in solution; the 2:1 ratio between coordinated **Y** and **Z** is most likely due to the ratio of these similarly curved rings in the acecorannulene buckybowl. The isomer in which the $\{\text{Cp}^*\text{Ru}\}^+$ fragment is coordinated to the most curved arene ring (**X**) was never observed and is presumably due to the preference of $\{\text{Cp}^*\text{Ru}\}^+$ for η^6 -coordination to more planar arene rings where there is better p-orbital overlap.

Aside from $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{O}_3\text{SCF}_3]$ and $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{BF}_4]_2$, the only other metal complexes of corannulene are the η^2 complexes $[[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]_m \cdot (\text{C}_{20}\text{H}_{10})_n]$ ($m:n = 1:1$ and $3:2$). These complexes are prepared by using a solvent-free, gas-phase deposition method that has been used previously for the synthesis of η^2 complexes of planar PAHs.²⁶ X-ray structural investigations of both complexes, the first examples of molecular structure determinations for metal complexes of corannulene, show that the dirhodium units are coordinated η^2 to the rim bonds of corannulene on both the convex and the concave sides. The complex $[[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]_1 \cdot (\text{C}_{20}\text{H}_{10})_1]$ consists of a one-dimensional array of alternating dirhodium units and corannulene molecules; one rhodium of the dirhodium unit is coordinated to the convex side of one corannulene molecule and the other is coordinated to the concave side of a second corannulene molecule. Complex $[[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]_3 \cdot (\text{C}_{20}\text{H}_{10})_2]$

forms a two dimensional array of dirhodium units and corannulene molecule. Three dirhodium units coordinate to each corannulene molecule through one of the rhodium atoms; two are bound on the convex side of corannulene to non-adjacent rings while the third is bound on the concave side to the ring between the other two dirhodium units. Unlike the structure of the $m:n = 1:1$ complex where each dirhodium unit binds to both a convex and concave surface, each dirhodium unit in the structure of $[[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]_3 \cdot (\text{C}_{20}\text{H}_{10})_2]$ binds exclusively to one side (either convex or concave) of both independent corannulene molecules. In both complexes, no significant structural changes were observed in the corannulene unit by X-ray crystallography when compared to the structure of free corannulene. Also, complete dissociation of corannulene was observed in both $[[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]_m \cdot (\text{C}_{20}\text{H}_{10})_n]$ ($m:n = 1:1$ and $3:2$) when the compounds were dissolved in acetone, indicating that the corannulene is weakly bound in these η^2 complexes as was observed in the η^6 complexes of corannulene.

The research in Chapters 5 and 6 of this dissertation began when I found in the literature that $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ had been used in the preparation of $[\text{Cp}^*\text{Ru}(\eta^6\text{-arene})]^+$ complexes and realized that it should provide a better source of $\{\text{Cp}^*\text{Ru}\}^+$ for corannulene than $[\text{Cp}^*\text{Ru}(\text{NCMe})_3]^+$ since it eliminated the competing acetonitrile ligands from the synthesis. Nitromethane- d_3 was chosen for the reaction solvent since it is very weakly-coordinating and able to solubilize complexes with multiple cationic charges. This methodology led to the preparation of a new (bridging) corannulene complex with two η^6 - $\{\text{Cp}^*\text{Ru}\}^+$ fragments and should be useful in the synthesis and investigation of other buckybowl derivatives that are coordinated to one or more η^6 - $\{\text{Cp}^*\text{Ru}\}^+$ fragments. The first

X-ray structure investigations of an η^6 -coordinated buckybowl (corannulene) are also presented and discussed in Chapters 5 and 6.

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Figure 1. The η^6 -corannulene complexes $[\text{Cp}^*\text{Ru}(\text{C}_{20}\text{H}_{10})][\text{O}_3\text{SCF}_3]$ and $[\text{Cp}^*\text{Ir}(\text{C}_{20}\text{H}_{10})][\text{BF}_4]_2$.

Figure 2. The bucky bowl 1,2,5,6-tetramethylcorannulene ($C_{20}Me_4H_6$, top left) and isomers **A**, **B**, and **C** of the η^6 -complex $[Cp^*Ir(C_{20}Me_4H_6)]^{2+}$.

Figure 3. The buckybowl acecorannulene. Average POAV values for the differently-curved rings **X**, **Y**, and **Z** are 8.1° , 5.3° , and 5.0° , respectively.

**CHAPTER 2: SYNTHETIC, STRUCTURAL AND BINDING STUDIES
OF THE 4,6-DIMETHYLDIBENZOTHIOPHENE COMPLEX $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-4,6-Me}_2\text{DBT})]\text{BF}_4$: TOWARD AN
UNDERSTANDING OF DEEP HYDRODESULFURIZATION**

A Communication published in the Journal of the American Chemical Society*

Paul A. Vecchi, Arkady Ellern, Robert J. Angelici

Abstract

The synthesis of the first completely characterized transition metal complex containing a sulfur-bound 4,6-dimethyldibenzothiophene (4,6-Me₂DBT) ligand, $[\text{Cp}^\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-4,6-Me}_2\text{DBT})]\text{BF}_4$ (1) ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), is reported. X-ray studies of 1 and its 4-methyldibenzothiophene and dibenzothiophene analogues, $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-4-MeDBT})]\text{BF}_4$ (2) and $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})]\text{BF}_4$ (3), show that the Ru-S bond distances increase in the order, $3 < 2 < 1$. Equilibrium studies on the series of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ compounds, where DBTh = DBT, 4-MeDBT, 4,6-Me₂DBT, and 2,8-Me₂DBT, show that the relative binding strengths of the dibenzothiophene ligands increase in the order 4,6-Me₂DBT (1) < 4-MeDBT (20.2(1)) < DBT (62.7(6)) < 2,8-Me₂DBT (223(3)). These results*

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are the first to quantify the steric effect of 4-and 6-methyl groups on the sulfur-coordinating ability of dibenzothiophenes to transition metal centers. They are also consistent with the proposal that 4-and 6-methyl groups reduce the coordination of dibenzothiophenes to active metal sites on hydrodesulfurization (HDS) catalysts, which could account for the slow rates of 4-MeDBT and 4,6-Me₂DBT hydrodesulfurization in petroleum feedstocks.

The removal of organosulfur compounds from automotive and diesel fuels is important for the reduction of atmospheric pollution by sulfur oxides that form acid rain in the atmosphere.¹ Sulfur compounds in these fuels also impair new vehicle emission control systems that lower the levels of nitrogen oxides (NO_x) and particulate matter released into the atmosphere during fuel combustion.² The EPA has mandated that sulfur in gasoline be reduced from the current average of 270 ppm to an average of 30 ppm by 2005,^{2a} and that sulfur in diesel fuel be reduced from the current limit of 500 ppm to 15 ppm by 2006.^{2b} Sulfur is currently removed from gasoline and diesel fuels utilizing the industrial catalytic process known as hydrodesulfurization (HDS). The most difficult of the sulfur-containing compounds to be removed are the hindered dibenzothiophene derivatives (DBTh) that contain alkyl groups near the sulfur in the 4- and 6-positions.^{1b,3-5} It is these hindered compounds that must be removed in order to meet the upcoming EPA requirements, and the process for removing these remaining sulfur compounds to obtain sulfur levels below 50 ppm has been termed "deep desulfurization".⁶ Numerous studies⁷ of the HDS of DBT and its 4- and 4,6-methyl substituted derivatives indicate that the rates of HDS decrease in the order: DBT > 4-MeDBT > 4,6-Me₂DBT. It has been proposed that the slow rates of 4-MeDBT and 4,6-Me₂DBT hydrodesulfurization are due to their weak coordination to metal sites on the

catalyst surface because of steric repulsion by the 4- and 6- methyl groups. Indeed, there is only one report⁸ of a sulfur-coordinated 4,6-Me₂DBT complex, Cp*Rh(PMe₃)(4,6-Me₂DBT), which was characterized only by its ¹H-NMR spectrum due to its instability. The purpose of the present work was to prepare stable complexes of 4-MeDBT and 4,6-Me₂DBT and determine the effect of the 4- and 6-methyl groups on the coordinating abilities of these dibenzothiophenes to metal centers, and to relate their coordinating abilities to their rates of catalytic HDS.

The complexes [Cp*Ru(CO)₂(η^1 (S)-DBTh)]BF₄, where Cp* = η^5 -C₅Me₅ and DBTh = 4,6-Me₂DBT (1), 4-MeDBT (2), DBT (3), and 2,8-Me₂DBT (4), were prepared by reacting 0.30 mmol of Cp*Ru(CO)₂Cl with 0.35 mmol of DBTh and 0.35 mmol of AgBF₄ in 15 mL of CH₂Cl₂ for 30 min. according to eq 1. After filtration of the reaction

mixture and precipitation with cold Et₂O, the solid products [Cp*Ru(CO)₂(η^1 (S)-DBTh)]BF₄ were isolated in 80-90% yields and characterized by their elemental analyses, infrared, ¹H and ¹³C-NMR spectra.⁹ The pale-yellow powders are air and moisture stable and can easily be handled in the atmosphere. However, [Cp*Ru(CO)₂(η^1 (S)-4,6-Me₂DBT)]⁺ must be handled below 0 °C for spectroscopic characterization, as it immediately begins to decompose at room temperature in solution (CD₂Cl₂, CD₃NO₂).

Crystals of both 1 and 3 for X-ray diffraction studies were obtained by layering a methylene chloride solution of each compound with diethyl ether and storing at -25 °C for one week.^{10a,c} Crystals of 2 were obtained by slow diffusion of hexanes into an acetone solution of the compound and storing at -25 °C for one week.^{10b} In all three structures

(Figure 1), the DBTh ligands are oriented exo with respect to the Cp* ligand, as was previously observed in the related $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})]^+$.¹¹ Selected distances and angles for compounds **1**, **2** and **3** are listed in Table 1. The X-ray structures show that the Ru-S distance increases with the number of 4- and 6-methyl groups in the DBTh ligand: **3** (2.3936(5) Å) < **2** (2.4013(9) Å)¹² < **1** (2.4186(7) Å). To illustrate further the steric effects of the 4- and 6-methyl groups, one can examine the orientation of the DBTh ligand around the Ru-S bond by considering the dihedral angle defined by the Cp* centroid-Ru-S-midpoint between C(10) and C(11). For a symmetrical orientation of the DBTh ligand, this angle would be 180°; we define deviations from 180° as the twist angle. In **1**, the twist angle is only 0.4° because the 4,6-Me₂DBT ligand is prevented from rotating around the Ru-S bond by the close approach (3.076 Å, 3.111 Å) of the methyl carbon atoms, C(14) and C(16), to a plane defined by the Cp* methyl carbon atoms. In **2**, the twist angle is 11.8° with the methyl carbon in the 4-MeDBT ligand at a distance (3.463 Å) that is longer than that in **1**. In **3**, the twist angle (20.2°) is even larger, which indicates that there is even greater freedom of rotation around the Ru-S bond; the distance of closest approach of the DBT carbon atom C(6) to the Cp* methyl plane is 3.416 Å. This distance, as well as the distance of closest approach (3.463 Å) in **2**, are similar, which suggests that a distance of 3.42-3.51 Å between a DBTh carbon and the Cp* methyl carbon plane is sterically non-crowding. This means that the shorter distances (3.076 Å, 3.111 Å) in **1** indicate crowding of the 4,6-Me₂DBT methyl groups and the Cp* ligand.

In order to quantify the effect of hindering methyl groups on the coordinating abilities of the dibenzothiophenes, equilibrium constants (*K*) for the displacement of one dibenzothiophene by another (eq (2)) were determined at 25.0 °C in CD₂Cl₂.¹²

The relative equilibrium constants, K' (given in parentheses), for the displacement of DBT from $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-DBT})]^+$ by 4-MeDBT, 4,6-Me₂DBT, and 2,8-Me₂DBT increase in the order: 4,6-Me₂DBT (1.00) < 4-MeDBT (20.2(1)) < DBT (62.7(6)) < 2,8-Me₂DBT (223(3)). The K' value for 2,8-Me₂DBT (223) indicates that the electron-donating methyl groups increase the binding ability of DBT by a factor of 3.6. On the other hand, when the methyl groups are in the sterically hindering 4,6-positions, the 4,6-Me₂DBT ligand is 62.7 times *less* strongly binding than DBT. Thus, the steric effect of the 4,6-methyl groups substantially reduces the binding ability of 4,6-Me₂DBT. The K' value (20.2(1)) for 4-MeDBT is only 3.1 times less than that for DBT, which shows that the steric effect of one hindering methyl group is much less than that of two.

In summary, we have shown that the highly hindered 4,6-Me₂DBT forms the air stable $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-4,6-Me}_2\text{DBT})]^+$ complex, the first fully characterized complex containing a sulfur bound 4,6-Me₂DBT ligand. Equilibrium studies show that 4,6-Me₂DBT is the most weakly coordinated dibenzothiophene in the series of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-DBTh})]^+$ complexes, whose relative binding constants K' increase in the same order (4,6-Me₂DBT < 4-MeDBT < DBT < 2,8-Me₂DBT) as their rates of hydrodesulfurization on a variety of transition metal sulfide catalysts.⁷ This trend in HDS activity is consistent with a mechanism in which equilibrium coordination of the DBTh to an active metal site on the catalyst surface precedes hydrogenation that leads to desulfurization.

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- (9) Characterization of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-4,6-Me}_2\text{DBT})]\text{BF}_4$ (1): ^1H NMR (δ , ppm in CD_2Cl_2) 8.03 (d, $J = 7.6$ Hz, 2H), 7.63 (t, $J = 7.6$ Hz, 2H), 7.44 (d, $J = 7.6$ Hz, 2H), 2.52 (s, 6H, CH_3), 2.00 (s, 15H, CH_3). ^{13}C NMR (δ , ppm in CD_2Cl_2) 195.92 (CO); 139.61, 137.90, 134.55, 130.75, 130.64, 121.77, 21.63 (4,6-Me₂DBT); 103.63, 10.57 (Cp*). IR (CH_2Cl_2 , $\nu(\text{CO})$ cm^{-1}) 2057(s), 2014(s). Anal. Calcd for $\text{C}_{26}\text{H}_{27}\text{BF}_4\text{O}_2\text{RuS}$: C, 52.80; H, 4.60; S, 5.42. Found: C, 52.49; H, 4.89; S, 5.13. Characterization of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-4-MeDBT})]\text{BF}_4$ (2): ^1H NMR (δ , ppm in CD_2Cl_2) 8.18-8.16 (m, 1H), 8.09 (d, $J = 7.6$ Hz, 1H), 7.76-7.65 (m, 4H), 7.46 (d, $J = 7.6$ Hz, 1H), 2.51 (s, 3H, CH_3), 1.92 (s, 15H, CH_3). ^{13}C NMR (δ , ppm in CD_2Cl_2) 196.11 (CO); 140.67, 138.33, 137.55, 136.61, 135.03, 130.89, 130.87, 130.27, 130.19, 124.16, 123.83, 121.82, 21.07 (4-MeDBT); 103.83, 10.31 (Cp*). IR (CH_2Cl_2 , $\nu(\text{CO})$ cm^{-1}) 2057(s), 2013(s). Anal. Calcd for $\text{C}_{25}\text{H}_{25}\text{BF}_4\text{O}_2\text{RuS}$: C, 52.00; H, 4.36; S, 5.55. Found: C, 51.69; H, 4.10; S, 5.35. Characterization of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-DBT})]\text{BF}_4$ (3): ^1H NMR (δ , ppm in CD_2Cl_2) 8.22-8.20 (m, 2H), 7.76-7.68 (m, 6H), 1.92 (s, 15H, CH_3). ^{13}C NMR (δ , ppm in CD_2Cl_2) 196.11 (CO); 138.65, 137.94, 130.40, 130.09, 124.72, 123.92 (DBT); 104.02, 10.29 (Cp*). IR (CH_2Cl_2 , $\nu(\text{CO})$ cm^{-1}) 2058(s), 2014(s). Anal. Calcd for $\text{C}_{24}\text{H}_{23}\text{BF}_4\text{O}_2\text{RuS}$: C, 51.17; H, 4.11; S, 5.69. Found: C, 50.81; H, 4.49; S, 5.64. Characterization of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-2,8-Me}_2\text{DBT})]\text{BF}_4$ (4): ^1H NMR (δ , ppm in CD_2Cl_2) 7.97 (s, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 2.57 (s, 6H, CH_3), 1.91 (s, 15H, CH_3). ^{13}C NMR (δ , ppm in CD_2Cl_2) 196.28 (CO); 141.23, 138.13, 135.66, 131.12, 124.37, 124.14, 21.93 (2,8-Me₂DBT); 103.91, 10.27 (Cp*).

IR (CH₂Cl₂, $\nu(\text{CO})$ cm⁻¹) 2057(s), 2012(s). Anal. Calcd for C₂₆H₂₇BF₄O₂RuS: C, 52.80; H, 4.60; S, 5.42. Found: C, 52.80; H, 4.82; S, 5.87.

- (10) Crystal data for the following: (a) [Cp*Ru(CO)₂(η^1 (S)-4,6-Me₂DBT)]BF₄·1CH₂Cl₂ (1), yellow crystal, C₂₆H₂₇BF₄O₂RuS·1CH₂Cl₂, $M = 676.34$, monoclinic, space group $P2(1)/c$, $a = 15.467(3)$ Å, $b = 11.661(2)$ Å, $c = 17.591(3)$ Å, $\alpha = 90^\circ$, $\beta = 115.373(3)^\circ$, $\gamma = 90^\circ$, $V = 2866.5(9)$ Å³, $Z = 4$, $D_c = 1.567$ g cm⁻³, $\lambda = 0.71073$ Å, $\mu(\text{Mo K}\alpha) 0.856$ mm⁻¹. $R1 = 0.0318$, $wR2 = 0.0859$ for $I > 2\sigma(I)$. (b) [Cp*Ru(CO)₂(η^1 (S)-4-MeDBT)]BF₄ (2), yellow crystal, C₂₅H₂₅BF₄O₂RuS, $M = 577.39$, monoclinic, space group $P2(1)/c$, $a = 28.147(5)$ Å, $b = 10.726(2)$ Å, $c = 16.723(3)$ Å, $\alpha = 90^\circ$, $\beta = 106.583(4)^\circ$, $\gamma = 90^\circ$, $V = 4838.7(16)$ Å³, $Z = 8$, $D_c = 1.585$ g cm⁻³, $\lambda = 0.71073$ Å, $\mu(\text{Mo K}\alpha) 0.786$ mm⁻¹. $R1 = 0.0348$, $wR2 = 0.0794$ for $I > 2\sigma(I)$. (c) [Cp*Ru(CO)₂(η^1 (S)-DBT)]BF₄ (3), yellow crystal, C₂₄H₂₃BF₄O₂RuS, $M = 563.36$, monoclinic, space group $P2(1)/n$, $a = 10.8541(14)$ Å, $b = 11.6452(15)$ Å, $c = 19.156(3)$ Å, $\alpha = 90^\circ$, $\beta = 105.468(2)^\circ$, $\gamma = 90^\circ$, $V = 2333.6(5)$ Å³, $Z = 4$, $D_c = 1.603$ g cm⁻³, $\lambda = 0.71073$ Å, $\mu(\text{Mo K}\alpha) 0.812$ mm⁻¹. $R1 = 0.0261$, $wR2 = 0.0665$ for $I > 2\sigma(I)$. For all x-ray data, $R1 = \Sigma||F_o| - ||F_c|| / |F_o|$ and $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w\{F_o^2\}^2]\}^{1/2}$.
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- (12) The X-ray data show that [Cp*Ru(CO)₂(η^1 (S)-4-MeDBT)]BF₄, (2), contains two structurally independent molecules (enantiomers of each other) in the asymmetric unit cell. Distances discussed within the text are averages of the parameters for the enantiomers.
- (13) Exactly 0.020 mmol of each reactant, along with triphenylmethane as an internal standard, was introduced into an NMR tube and dissolved in 0.8 mL of CD₂Cl₂. After

three freeze-pump-thaw cycles, the tube was flame-sealed under argon and thermostatted in a bath at 25.0 °C. Relative concentrations of reactants and products were determined by integration of the DBTh and DBTh' proton signals in the ^1H NMR spectra. Equilibria for all reactions were established within 48 hours and were unchanged after 96 hours. Experimentally-determined equilibrium constants for reaction 2 expressed as $K[\text{DBTh}; \text{DBTh}']$ follow: 0.0159(2)[DBT; 4,6-Me₂DBT], 0.329(10)[DBT, 4-MeDBT], 3.55(2)[DBT; 2,8-Me₂DBT], 0.0496(2)[4-MeDBT; 4,6-Me₂DBT], where each K value is the K for the forward reaction and $1/K$ of the reverse reaction; the deviation from this average is given in parentheses.

Figure 1. Thermal ellipsoid drawings of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-4,6-Me}_2\text{DBT})]\text{BF}_4$ (**1**), $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-4-MeDBT})]\text{BF}_4$ (**2**), and $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-DBT})]\text{BF}_4$ (**3**). Ellipsoids are shown at the 30% probability level; hydrogen atoms are omitted for clarity.

Table 1. Selected Distances (Å) and Twist Angles (°) for Compounds **1**, **2**, and **3**.

Ligand	Ru-S (Å)	<i>d</i> C ₅ Me ₅ Plane (Å)				Twist Angle (°)
		C(4)	C(6)	C(14)	C(16)	
4,6-Me ₂ DBT (1)	2.4186(7)	4.436	4.477	3.076	3.111	0.4
4-MeDBT (2) ^a	2.3987(9)	4.694	3.793	3.417		11.3
	2.4038(9)	3.795	4.767		3.508	12.3
DBT (3)	2.3936(5)	4.946	3.416			20.2

^a Values for the two enantiomers.

CHAPTER 3: STERIC EFFECTS IN THE BINDING OF HINDERED DIBENZOTHIOPHENE LIGANDS IN $[\text{Cp}'\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ COMPLEXES

A Paper submitted to Organometallics*

Paul A. Vecchi, Arkady Ellern, Robert J. Angelici

Abstract

Structural studies of several complexes of the type $[\text{Cp}'\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$, where $\text{Cp}' = \text{Cp}$ or Cp^ and $\text{DBTh} = \text{DBT}$, 4-MeDBT, 4,6-Me₂DBT, or 2,8-Me₂DBT, show that only in $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-4,6-Me}_2\text{DBT})]^+$ is there evidence for steric crowding between the Cp' and DBTh ligands. However, relative equilibrium constants (K') for the binding of the DBTh ligands in both the Cp and Cp^* complexes show evidence of steric effects in those that contain 4-MeDBT and 4,6-Me₂DBT as the K' values increase in the order: 4,6-Me₂DBT < 4-MeDBT < DBT < 2,8-Me₂DBT. Kinetics studies of the substitution of the DBTh in $[\text{Cp}\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ by phosphorus donor ligands established the following order of DBTh lability, 4,6-Me₂DBT > 4-MeDBT > DBT > 2,8-Me₂DBT, which is consistent with the trend in K' values. The most labile DBTh ligand in both series of*

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*complexes is 4,6-Me₂DBT in [Cp*Ru(CO)₂(η¹(S)-4,6-Me₂DBTh)]⁺, where both steric crowding and electron-donation by the Cp* accelerate the rate of 4,6-Me₂DBT dissociation.*

Introduction

The removal of organosulfur compounds from petroleum feedstocks is important for the reduction of atmospheric pollution caused by sulfur oxides.¹ Sulfur compounds in these fuels also poison catalytic converters, impairing the vehicle emission control systems necessary to reduce levels of nitrogen oxides released into the atmosphere during fuel combustion. In addressing these issues, the United States government through the Environmental Protection Agency (EPA) has established lower sulfur limits in transportation fuels.²

Sulfur is currently removed from gasoline and diesel fuels using a catalytic process known as hydrodesulfurization (HDS). The most difficult of the sulfur-containing compounds to be removed using HDS are the dibenzothiophenes derivatives (DBTh) that contain alkyl groups near the sulfur in the 4- and 6-positions (Figure 1).³ These 'hindered' dibenzothiophenes are found in diesel fuel and must be removed in order to lower its sulfur content. Although it is unclear exactly how dibenzothiophenes interact with the catalyst surface during HDS, it has been proposed that an initial step is binding of the substrate through the sulfur atom to active metal sites.⁴ The slow rates for the HDS of 4-methyldibenzothiophene (4-MeDBT) and 4,6-dimethyldibenzothiophene (4,6-Me₂DBT) have been attributed to steric hindrance by alkyl groups in the 4,6-positions that interfere with their binding to such sites. Alkyl groups in these positions have also been proposed to

sterically hinder C-S bond cleavage during HDS.⁵ Improvements in the HDS process have not adequately addressed the difficulties of desulfurizing hindered dibenzothiophenes.

Recently, the focus has shifted away from improving current HDS processes towards developing new technologies for desulfurization.^{3,6} One promising new method is the use of adsorbents or solid phase extractants (SPEs) to selectively bind and remove sulfur compounds such as the hindered dibenzothiophenes.^{3,6-8} Adsorbent technologies have the potential advantage of being relatively simple to incorporate into the existing infrastructure as either a pre- or post-HDS treatment. Such treatments may also be designed to operate under relatively mild conditions, unlike HDS which currently involves the use of moderately high temperatures (350-500 °C) and pressures (50-150 psi) of hydrogen. Another emerging technology for desulfurization of hydrocarbon fuels is catalytic oxidation of hindered dibenzothiophenes to the sulfones or sulfoxides, followed by their removal via extraction or adsorption.⁹ In both of these new desulfurization approaches, an important step involves binding of the dibenzothiophene to either the adsorbent or catalyst.

Several experimental and theoretical studies on the binding of thiophenes, benzothiophenes, and dibenzothiophenes to transition metal complexes have been reported.¹⁰ However, there are comparatively few experimental studies of hindered dibenzothiophenes that are $\eta^1(S)$ -coordinated in metal complexes,¹¹ presumably a result of the instability of such complexes. An understanding of the relative bond strengths and kinetic labilities of hindered dibenzothiophenes in metal complexes should be useful for developing new approaches to petroleum feedstock desulfurization. We recently reported the synthesis and structural characterization of the first transition metal complexes of $\eta^1(S)$ -bound 4-MeDBT and 4,6-Me₂DBT, $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-4-MeDBT})]^+$ and $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-4,6-Me}_2\text{DBT})]^+$, where

$\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$.¹¹ Equilibrium studies of the displacement of 4,6-Me₂DBT in $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-4,6-Me}_2\text{DBT})]^+$ by the dibenzothiophenes DBT, 4-MeDBT, and 2,8-Me₂DBT (eq 1) showed that their binding abilities increase in following order: 4,6-Me₂DBT (1.00) < 4-MeDBT (20.2(1)) < DBT (62.7(6)) < 2,8-Me₂DBT (223(3)). In this

report, we continue our investigations of sulfur-bound dibenzothiophenes, with special attention directed toward understanding the role of steric and electronic effects in both the $[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-DBTh})]^+$ and $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-DBTh})]^+$ series of complexes (where $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, and $\text{DBTh} = \text{DBT}, 4\text{-MeDBT}, 4,6\text{-Me}_2\text{DBT}$ and $2,8\text{-Me}_2\text{DBT}$). Equilibrium binding constants and rates of DBTh substitution for these complexes provide insight into factors that influence the thermodynamic and kinetic binding of 4- and 4,6- methyl substituted dibenzothiophenes to $\{\text{Cp}'\text{Ru}(\text{CO})_2\}^+$, where $\text{Cp}' = \text{Cp}$ and Cp^* .

Experimental Section

General Considerations. All reactions were performed under an atmosphere of dry argon using standard Schlenk techniques. Methylene chloride (CH_2Cl_2), diethyl ether (Et_2O), and hexanes were purified on alumina using a Solv-Tek solvent purification system, similar to that described by Grubbs and co-workers.¹² Nitromethane (CH_3NO_2 , 96+%) was purchased from Aldrich and subjected to 3 freeze-pump-thaw cycles before use. Acetone was stirred with calcium chloride overnight, distilled, subjected to three freeze-pump-thaw cycles and stored under argon until use. Methylene chloride-*d*₂ (CD_2Cl_2) was refluxed overnight

with calcium hydride, distilled, subjected to three freeze-pump-thaw cycles and stored under argon until use. Nitromethane- d_3 (CD_3NO_2) was purchased from Aldrich, subjected to three freeze-pump-thaw cycles and stored under argon before use. Solid DBT and 4-MeDBT were purchased from Aldrich and sublimed prior to use. Solid 4,6-Me₂DBT and 2,8-Me₂DBT were purchased from Acros and TCI, respectively, and used without further purification. Compounds $AgBF_4$ (99.99+%), $P(OPh)_3$, PPh_3 , and PPh_2Me were purchased from Aldrich and used without further purification. Complexes $CpRu(CO)_2Cl$,¹³ $[CpRu(CO)_2(\eta^1-(S)\text{-DBT})]BF_4$ (1),¹⁴ and $[Cp^*Ru(CO)_2(\eta^1-(S)\text{-DBTh})]^+$ (DBTh = DBT (5), 4-MeDBT (6), 4,6-Me₂DBT (7), 2,8-Me₂DBT (8))¹¹ were prepared as described previously.

Filtrations were performed with Celite on filter paper. Solution NMR spectra were recorded on either a Bruker DRX-400 spectrometer or a modified 400 MHz Varian VXR-300 spectrometer using either CD_2Cl_2 ($\delta = 5.32$ (1H), 54.0 (^{13}C)) or CD_3NO_2 ($\delta = 4.33$ (1H), 62.8 (^{13}C)) as the solvent, internal lock, and reference. 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. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer.

General Procedure for Preparation of the $[CpRu(CO)_2(\eta^1(S)\text{-DBTh})]BF_4$ Complexes (2-4). To a solution of $CpRu(CO)_2Cl$ (75 mg, 0.291 mmol) and 0.320 mmol of DBTh (DBTh = 4-MeDBT, 4,6-Me₂DBT, 2,8-Me₂DBT) in 10 mL of CH_2Cl_2 was added solid $AgBF_4$ (58.4 mg, 0.300 mmol), and the solution was stirred at room temperature under argon for 30 minutes. A solid precipitate formed and the yellow solution color gradually lightened during the reaction. The reaction solution was then filtered and transferred by cannula into a flask containing 40 mL of diethyl ether in an ice water bath, which resulted in

precipitation of the product. The remaining solid in the reaction flask was washed with a 1 mL portion of CH_3NO_2 , and the solution was also transferred by cannula into the diethyl ether to insure complete transfer of the product. The light yellow solid products were isolated by filtration and washed with three 5 mL portions of diethyl ether to remove excess DBTh. Isolated yields were typically 70-85%. Due to the low solubility of the products in methylene chloride, ^1H NMR and ^{13}C NMR spectra were acquired in CD_3NO_2 . Spectroscopic data for compound **1** were reported previously.¹⁴

Characterization of compounds 2-4. $[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-4-MeDBT})][\text{BF}_4]$ (**2**). ^1H NMR (400 MHz, CD_3NO_2): δ 8.29-8.26 (m, 1H), 8.18 (d, $J = 7.6$ Hz, 1H), 8.05-8.03 (m, 1H), 7.76-7.69 (m, 3H), 7.51 (d, $J = 7.6$ Hz, 1H), 2.64 (s, 3H, CH_3), 4-MeDBT; 5.79 (s, 5H), Cp. ^{13}C NMR (100.6 MHz, CD_3NO_2): δ 194.53 (CO); 142.98, 140.22, 138.79, 138.31, 136.44, 131.85, 131.69, 131.13, 131.06, 126.67, 124.80, 122.62, 21.42 (4-MeDBT); 91.37 (Cp). IR (CH_2Cl_2): $\nu(\text{CO})$ (cm^{-1}) 2076(s), 2033(s). Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{BF}_4\text{O}_2\text{RuS}$: C, 47.35; H, 2.98; S, 6.32. Found: C, 47.16; H, 2.95; S, 6.28.

$[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-4,6-Me}_2\text{DBT})][\text{BF}_4]$ (**3**). ^1H NMR (400 MHz, CD_3NO_2): δ 8.12 (d, $J = 7.6$ Hz, 2H), 7.69 (t, $J = 7.6$ Hz, 2H), 7.50 (d, $J = 7.6$ Hz, 2H), 2.62 (s, 6H, CH_3), 4,6-Me₂DBT; 6.02 (s, 5H), Cp. ^{13}C NMR (100.6 MHz, CD_3NO_2): δ 194.15 (CO); 141.23, 138.87, 135.94, 131.89, 131.49, 122.66, 21.39 (4,6-Me₂DBT); 91.28 (Cp). IR (CH_2Cl_2): $\nu(\text{CO})$ (cm^{-1}) 2076(s), 2033(s). Anal. Calcd for $\text{C}_{21}\text{H}_{17}\text{BF}_4\text{O}_2\text{RuS}$: C, 48.38; H, 3.29; S, 6.15. Found: C, 47.98; H, 3.43; S, 6.04.

$[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-2,8-Me}_2\text{DBT})][\text{BF}_4]$ (**4**). ^1H NMR (400 MHz, CD_3NO_2): δ 8.08 (s, 2H), 7.85 (d, $J = 8.4$ Hz, 2H), 7.52 (d, $J = 8.4$ Hz, 2H), 2.56 (s, 6H, CH_3), 2,8-Me₂DBT; 5.82 (s, 5H), Cp. ^{13}C NMR (100.6 MHz, CD_3NO_2): δ 194.63 (CO); 142.17, 139.02, 138.48,

131.74, 126.40, 124.91, 21.65 (2,8-Me₂DBT); 91.16 (Cp). IR (CH₂Cl₂): ν (CO) (cm⁻¹) 2076(s), 2032(s). Anal. Calcd for C₂₁H₁₇BF₄O₂RuS: C, 48.38; H, 3.29; S, 6.15. Found: C, 47.99; H, 3.46; S, 6.04.

X-ray Structural Determinations of [CpRu(CO)₂(η^1 (S)-4-MeDBT)][BF₄] (2), [CpRu(CO)₂(η^1 (S)-4,6-Me₂DBT)][BF₄] (3) and [CpRu(CO)₂(η^1 (S)-2,8-Me₂DBT)][BF₄] (4). A yellow single crystal of **2** suitable for an X-ray diffraction study was obtained by slow cooling of a saturated CH₂Cl₂ solution of the complex at -25 °C for 1 week. A yellow single crystal of **3** suitable for an X-ray diffraction study was obtained by layering a saturated CH₂Cl₂ solution of the complex with Et₂O under argon and storing at -25 °C for 1 week. Crystals of **4**, also yellow, were obtained by preparing an acetone solution of the complex, filtering it through Celite and allowing it to slowly evaporate in air at room temperature.

The crystals were selected under ambient conditions, coated in epoxy, and mounted on the end of a glass fiber. Crystal data collection was performed on a Bruker CCD-1000 diffractometer with Mo K α (λ = 0.71073 Å) radiation and a collector-to-crystal distance of 5.03 cm. Cell constants were determined from a list of reflections found by an automated search routine. Data were collected using the full sphere routine and were corrected for Lorentz and polarization effects. The absorption corrections were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements using SADABS software.¹⁵ Positions of the heavy atoms were found by the Patterson method. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in full-matrix anisotropic approximation. All hydrogen atoms were placed in the structure factor calculation at idealized positions and

refined using a riding model. Complete data collection and reduction information for each compound are given in Table 1.

Equilibrium Studies. Solutions for the equilibrium studies (eq 2) were prepared by placing 0.020 mmol of $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})][\text{BF}_4]$ (DBTh = DBT, 4-MeDBT, 4,6-Me₂DBT, 2,8-Me₂DBT) and an equimolar amount of a different dibenzothiophene (DBTh')

in an NMR tube. Approximately 0.7 mL of CD₃NO₂ was added to dissolve the reactants, and the reaction solution was frozen in liquid nitrogen. After degassing, the solution was thawed and flame-sealed under argon at room temperature. The tube was then placed in a circulating bath thermostatted at 25.0 ± 0.1 °C, and the reaction progress was monitored periodically by ¹H NMR spectroscopy using CD₃NO₂ as internal lock and reference (δ = 4.33) with a 10 second pulse delay between scans to insure complete relaxation of proton signals. Equilibrium constants (K) were calculated from the ¹H NMR spectra using eq 3 where I_{Cp'} and I_{Cp} are the Cp peak integrals of $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh}')^+]$ and $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$, respectively. All equilibria were established from

$$K = \frac{(I_{\text{Cp}'}/5)^2}{(I_{\text{Cp}}/5)^2} = \frac{[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh}')^+][\text{DBTh}]}{[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+[\text{DBTh}]} \quad (3)$$

both reaction directions by separate experiments, and the results (Table 3) are the average of the forward and reverse reactions with the average deviation given in parentheses. All equilibria were established within 10 days and no changes in the ¹H NMR spectra were observed when examined after 14 days. Equilibrium constants for analogous reactions of the

$[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-DBTh})][\text{BF}_4]$ complexes (DBTh = DBT, 4-MeDBT, 4,6-Me₂DBT, 2,8-Me₂DBT) were reported previously.¹¹

Kinetic Studies. Solutions of $[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-DBTh})][\text{BF}_4]$ (DBTh = DBT, 4-MeDBT, 4,6-Me₂DBT, 2,8-Me₂DBT) for kinetic studies were prepared according to the following procedure: A 0.010 mmol sample of the complex was added to an NMR tube, and the tube was evacuated and flushed with argon. Then CD_3NO_2 was added, followed by a measured excess of $\text{P}(\text{OPh})_3$ so that the total volume of the reaction mixture was 0.50 mL. The tube was capped with a septum, shaken to dissolve the reactants and placed in a circulating bath thermostatted at 25.0 ± 0.1 °C. At periodic intervals, the reaction tube was removed and monitored by ^1H NMR spectroscopy using CD_3NO_2 as the internal lock and reference with a 10 second pulse delay between scans. The products formed during the course of the kinetic reactions were $[\text{CpRu}(\text{CO})_2(\text{P}(\text{OPh})_3)]^{+16}$ and the free dibenzothiophenes (eq 4), which were identified by their NMR spectra. Relative concentrations of reactants and products were determined

$\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$; $\text{PR}_3 = \text{P}(\text{OPh})_3, \text{PPh}_3$

$\eta^5\text{-C}_5\text{Me}_5$; $\text{PR}_3 = \text{PPh}_3, \text{PPh}_2\text{Me}$

by integration of the ^1H NMR signals for the Cp ligands. Rate constants, k_{obs} , were obtained from the least square slopes of plots of $\ln(1 + F)$ (where $F = [\text{product}] / [\text{reactant}]$) vs. time, and the correlation coefficients of these plots were always greater than 0.995.

Solutions of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-DBTh})][\text{BF}_4]$ (DBTh = DBT, 4-MeDBT, 4,6-Me₂DBT, 2,8-Me₂DBT) for the kinetic studies were prepared in a slightly different manner. A 0.010 mmol sample of the complex was added to a 5 mm NMR tube with an excess,

weighed amount of PPh_3 . The tube was then evacuated and flushed with argon. A 0.50 mL aliquot of CD_2Cl_2 was added and the tube was capped with a septum and shaken to dissolve the reactants. The tube was immediately placed into the probe of a Bruker DRX-400 spectrometer thermostatted at 25.0 ± 0.1 °C. The spectrometer was preprogrammed to acquire ^1H NMR spectra at specific time intervals using CD_2Cl_2 as the internal lock and reference ($\delta = 5.32$); the acquisition time to take each spectrum was 60 s (16 scans at 3.744 s/scan). Typically 8-12 data points were collected over 2-3 half-lives for each reaction. The products formed during the course of these kinetic reactions were $[\text{Cp}^*\text{Ru}(\text{CO})_2(\text{PPh}_3)]^+$,¹⁷ and the free dibenzothiophenes, which were identified by their NMR spectra. Relative concentrations of reactants and products were determined by integration of methyl groups on the Cp^* and/or DBTh ligands. Rate constants, k_{obs} , were obtained as described above, and the correlation coefficients of these plots were always greater than 0.995. Reactions with the liquid phosphine PPh_2Me were undertaken in the same manner, except that the phosphine was injected by syringe immediately after the deuterated solvent had been added. The ruthenium product, $[\text{Cp}^*\text{Ru}(\text{CO})_2(\text{PPh}_2\text{Me})]^+$, gave an ^1H NMR spectrum (for PPh_2Me , $\delta = 2.27$, d, $^3J(\text{P},\text{H}) = 9.3$ Hz, 3H; for Cp^* , $\delta = 1.87$, d, $J(\text{P},\text{H}) = 2.0$ Hz, 15H) which is similar to that of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\text{PPh}_3)]^+$. The amount of deuterated solvent in each reaction was calibrated to insure that the total volume of each reaction solution was 0.50 mL.

Results and Discussion

Synthesis of the $[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-DBTh})][\text{BF}_4]$ Complexes. The complexes $[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-DBTh})][\text{BF}_4]$, where DBTh = DBT (1), 4-MeDBT (2), 4,6-Me₂DBT (3), and 2,8-Me₂DBT (4), are prepared by Cl^- abstraction from $\text{CpRu}(\text{CO})_2\text{Cl}$ with AgBF_4 in the

presence of excess dibenzothiophene ligand in CH_2Cl_2 (eq 5). Complexes **1-4** are

isolated as air-stable, pale-yellow powders that are insoluble in diethyl ether and hexanes, minimally soluble in CH_2Cl_2 and acetone, and soluble in CH_3NO_2 . ^1H NMR data show that the signals of the DBTh ligands in these complexes are shifted slightly downfield of the free ligand signals, as is observed in other $\eta^1(\text{S})$ complexes of dibenzothiophene.^{8,11,18} If the DBTh ligand were bound η^2 through a $\text{C}=\text{C}$ bond or η^6 to one of the arene rings, one would expect to see significant upfield ^1H and ^{13}C NMR shifts for signals of the coordinated groups, as is observed for η^2 -olefin¹⁹ and η^6 -arene complexes of ruthenium.²⁰ The IR spectra of these complexes in CH_2Cl_2 exhibit two $\nu(\text{CO})$ signals (2076, 2033 cm^{-1}) that are essentially the same for all four compounds and are on average 25 cm^{-1} higher than those ($\nu(\text{CO}) = 2056$, 2004 cm^{-1} in CH_2Cl_2) of the $\text{CpRu(CO)}_2\text{Cl}$ starting material. The ^{13}C NMR spectrum for $[\text{CpRu(CO)}_2\eta^1(\text{S})\text{-4-MeDBT}]^+$ (**2**) has only one signal for the two diastereotopic carbonyl ligands at room temperature, indicating that there is a dynamic process at room temperature that makes the CO groups equivalent on the ^{13}C NMR timescale. This process is likely to involve rapid inversion at the sulfur atom. Due to the poor solubility of **2** in CD_2Cl_2 , $\text{THF-}d_6$ and $(\text{CD}_3)_2\text{O}$, NMR studies of the complex were limited to temperatures above the freezing point of CD_3NO_2 (244 K) where inversion remained rapid. In previous studies of related complexes, the $\Delta G^\ddagger$ barriers to inversion were determined for $[\text{CpRu(CO)}_2(\eta^1(\text{S})\text{-BT})]^+$ (43

kJ/mol at 205 K; BT = benzothiophene),¹⁴ $[\text{CpRu}(\text{CO})(\text{PPh}_3)(\eta^1(\text{S})\text{-Th})]^+$ (40 kJ/mol at 213 K; Th = 2,5-Me₂T and Me₄T),^{18a} and $[\text{CpFe}(\text{CO})_2(\eta^1(\text{S})\text{-BT})]^+$ (39 kJ/mol at 190 K).^{18b}

Structures of Compounds 2, 3 and 4. In all of the structures (Fig. 2) of the $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})][\text{BF}_4]$ (2-4) complexes, the DBTh ligands are η^1 -coordinated through a pyramidal sulfur atom and the DBTh ligand is oriented away from the Cp ligand, as has been observed in other cationic complexes containing $\eta^1(\text{S})$ -bound dibenzothiophene ligands: $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})][\text{BF}_4]$,⁸ $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})][\text{BF}_4]$ (where DBTh = DBT, 4-MeDBT, 4,6-Me₂DBT),¹¹ and $[\text{CpFe}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})][\text{BF}_4]$.^{18b} The Ru-S distances (Table 2) for complexes 1,⁸ 2, 3 and 4 are 2.398(2), 2.377(2), 2.405(1) and 2.400(2) Å, respectively. All of these values are very similar to each other except in complex 2, which has a shorter Ru-S bond than the other complexes. The orientation of the DBTh ligand around the M-S bond may be defined by 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 compounds 1, 2, 3, and 4, this angle is 22.8°, 8.6°, 8.9°, and 25.0°, respectively (Table 2). These angles indicate that there is some degree of rotational freedom around the Ru-S bond in all of the complexes, even in the 4,6-Me₂DBT complex (3).

Thus, there is no structural evidence for steric crowding caused by the 4,6-methyl groups in the $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ complexes 1-4. This is in contrast to a previous structural investigation of the series of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ complexes,¹¹ where DBTh = DBT, 4-MeDBT and 4,6-Me₂DBT, in which methyl groups in both the 4- and 4,6-positions affect significantly the structures of these complexes. In that study, the Ru-S

distance (Table 2) increased with the number of 4,6-methyl groups as follows: DBT (2.394(1)) $\leq$ 4-MeDBT (2.399(1), 2.404(1))²¹ < 4,6-Me₂DBT (2.419(1)). The lengthening of the Ru-S bond, especially for the 4,6-Me₂DBT complex, was attributed to steric repulsions between methyl groups on the DBTh ligand and Cp* methyl groups. The twist angles for the [Cp*Ru(CO)₂(η^1 (S)-DBTh)]⁺ complexes (Table 2) decrease with an increasing number of 4,6-methyl groups: DBT (20.2°) > 4-MeDBT (11.3°, 12.3°) > 4,6-Me₂DBT (0.4°). Especially in [Cp*Ru(CO)₂(η^1 (S)-4,6-Me₂DBT)]⁺, rotation around the Ru-S bond is prevented by the close approach (3.076 Å, 3.111 Å) of the 4,6 methyl groups to a plane defined by the Cp* methyl carbon atoms, which restricts the twist angle to only 0.4°. In [Cp*Ru(CO)₂(η^1 (S)-4-MeDBT)]⁺, the twist angle is larger (11.3°, 12.3°) and the 4-MeDBT ligand is oriented along the Ru-S bond such that the 4-methyl group is twisted away from the Cp* ligand, reducing the steric interaction between the 4-methyl group and the Cp* methyl groups; distances between the 4-methyl carbon atoms and the Cp* planes are 3.417 Å and 3.508 Å. An even larger twist angle (22.3°) was observed in [Cp*Ru(CO)₂(η^1 (S)-DBT)]⁺ where the distance of closest approach was 3.463 Å; the large twist angle in this complex is presumably controlled by crystal packing forces. The similar values for the distances of closest approach of DBTh carbon atoms in [Cp*Ru(CO)₂(η^1 (S)-4-MeDBT)]⁺ and [Cp*Ru(CO)₂(η^1 (S)-DBT)]⁺ to the Cp* planes (3.42-3.51 Å) suggest that those distances are sterically non-crowding. The significantly shorter values in [Cp*Ru(CO)₂(η^1 (S)-4,6-Me₂DBT)]⁺ (3.076 Å and 3.111 Å) indicates crowding of the 4,6-Me₂DBT methyl groups and the Cp* ligand. Thus, these structural studies show that [Cp*Ru(CO)₂(η^1 (S)-4,6-Me₂DBT)]⁺ (7) is the only complex in the series of either Cp or Cp* [Cp*Ru(CO)₂(η^1 (S)-

DBTh)]⁺ complexes for which there is clear evidence of steric crowding between the 4- or 6-methyl groups on the DBTh and the Cp' ligands.

Equilibrium Studies. Equilibrium constants (K) for the exchange of one dibenzothiophene by another in $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ were calculated using eq 2, and the values obtained are listed in Table 3. Relative equilibrium constants, K' (given in parentheses), for the displacement of 4,6-Me₂DBT from $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-4,6-Me}_2\text{DBT})]^+$ by 4-MeDBT, DBT and 2,8-Me₂DBT are calculated from the experimental K values and are listed in Table 4. The K' values increase in the order: 4,6-Me₂DBT (1.00) < 4-MeDBT (2.79 (7)) < DBT (9.71(9)) < 2,8-Me₂DBT (36.5(3)). The larger K' value for 2,8-Me₂DBT (36.5) demonstrates that electron-donating methyl groups in the non-hindering 2,8-positions increase the binding ability of DBT by a factor of 3.8, presumably by making the sulfur atom on DBT a better donor to ruthenium. On the other hand, the 4-MeDBT and 4,6-Me₂DBT ligands are only 0.29 and 0.10 times as strongly binding, respectively, as DBT. The first methyl group in the 4-position decreases binding by a factor of 0.29, while a second methyl group in the 6-position reduces the binding even further by a factor of 0.36. Although there is no direct evidence for steric crowding by the 4,6-methyl groups in structural studies of the $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ complexes, there is clearly an effect on the equilibrium constants. These constants show that the steric effect of the 4,6-methyl groups overrides their increased electron-donating ability.

The relative trend in K' values for the DBTh ligands in the $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ complexes is the same as that reported previously for the $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ complexes that contain the bulkier $\eta^5\text{-C}_5\text{Me}_5$ ligand (Table 4).¹¹ As mentioned in

the paragraph above, K' values for the 2,8-Me₂DBT and 4-MeDBT ligands are factors of 3.8 times and 0.29 times, respectively, of that for DBT in the $[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-DBTh})]^+$ complexes. These values are very similar to factors of 3.6 times and 0.32 times for 2,8-Me₂DBT and 4-MeDBT, respectively, as compared with DBT in the $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-DBTh})]^+$ complexes. The major difference between K' values for the Cp and Cp* series of complexes is that between 4,6-Me₂DBT and 4-MeDBT. For the Cp complexes (2 and 3), 4-MeDBT is 2.8 times more strongly binding than 4,6-Me₂DBT. On the other hand, for the Cp* complexes (6 and 7), 4-Me₂DBT binds *20 times* more strongly than 4,6-Me₂DBT. This much larger decrease in the binding ability of 4,6-Me₂DBT as compared with 4-MeDBT in the Cp* complexes undoubtedly reflects the substantial steric crowding between the 4,6-Me₂DBT methyl groups and the Cp* ligand that was evident in the structural studies.

Previous work showed that in the series of $[\text{CpRu}(\text{CO})(\text{PPh}_3)(\eta^1(S)\text{-Th})]^+$ complexes, where Th denotes the thiophene (T), benzothiophene (BT), or dibenzothiophene ligands, relative equilibrium constants (K') follow the order: T (1.00) < BT (29.9) < DBT (74.1) < 2,8-Me₂DBT (358).²² A similar study for the $[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-Th})]^+$ complexes revealed the same relative trend for T (1.00) and BT (47.6), but DBT was not examined due to its poor solubility in the chosen CH₂Cl₂ solvent system.¹⁴ In order to directly compare our results to the previous study undertaken in methylene chloride, three independent reactions of $[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-BT})]^+$ and DBT were performed in CD₃NO₂; the K was determined to be 0.0597(9). This K value allows for the calculation of the relative equilibrium constants listed in Table 5. The weakest ligand in this series is thiophene and the strongest is tetrahydrothiophene (THT). It is clear that although methyl groups in the 4- and 6-positions reduce binding of DBT to $\{\text{CpRu}(\text{CO})_2\}^+$, 4,6-Me₂DBT is still a better ligand than

benzothiophene in this series. This suggests that it should be possible to use metal complexes to remove hindered dibenzothiophenes from diesel fuels by solution-phase or solid extraction.

The DBTh binding studies discussed above were the basis for the use of $\{\text{CpRu}(\text{CO})_2\text{BF}_4\}$ adsorbed on silica-based supports for the removal of dibenzothiophenes from a simulated gasoline/diesel fuel.⁸ The adsorbent was created by reacting $\text{CpRu}(\text{CO})_2\text{Cl}$ with AgBF_4 in CH_2Cl_2 , filtering the solution onto a solid silica-based support and evaporating the solution to dryness. Simulated petroleum solutions of DBT and of 4,6- Me_2DBT were then stirred with the solid phase adsorbent. Within 30 minutes, the sulfur levels were reduced from 400 ppm to 4 ppm for a DBT solution and from 400 ppm to 113 ppm for a 4,6- Me_2DBT solution, corresponding to decreases in the sulfur levels of 96% and 72%, respectively. The less-efficient removal of 4,6- Me_2DBT is a direct consequence of methyl groups in the 4,6-positions sterically hindering sulfur coordination to the adsorbent. These results indicate that solution binding studies can be useful in developing new strategies for sulfur removal.

Kinetic Studies of Substitution Reactions of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$. Kinetic studies of the reactions of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ with either $\text{P}(\text{OPh})_3$, PPh_3 , or PPh_2Me according to eq 4 were performed under pseudo-first order conditions with a minimum of 10-fold excess of PR_3 . The pseudo-first order rate constants, k_{obs} , are listed in Table 6. Plots of k_{obs} vs. $[\text{PR}_3]$ for the reactions of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ are independent of the PR_3 concentration so that $k_{\text{obs}} = k_1$. However, for the $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ complexes, k_{obs} depends partially on the concentration of the phosphine such that $k_{\text{obs}} = k_1 + k_2[\text{PR}_3]$. The k_1 values for both series of complexes are given in Table 7.

The first-order rate law indicates that the reaction of $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ with $\text{P}(\text{OPh})_3$ proceeds by a mechanism involving slow dissociation of the DBTh ligand followed by rapid reaction of the unsaturated intermediate with $\text{P}(\text{OPh})_3$ to give the final product. The k_1 values for these reactions, listed in Table 7, decrease with the DBTh ligand in the following order: 4,6-Me₂DBT ($5.18(5) \times 10^{-6} \text{ s}^{-1}$) > 4-MeDBT ($4.50(10) \times 10^{-6} \text{ s}^{-1}$) > DBT ($4.01(3) \times 10^{-6} \text{ s}^{-1}$) > 2,8-Me₂DBT ($1.33(5) \times 10^{-6} \text{ s}^{-1}$). This trend parallels the trend observed in the equilibrium studies (Table 4), which shows that the more strongly binding the DBT ligand thermodynamically, the slower its rate of dissociation from $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$. The rate of dissociation of the 2,8-Me₂DBT ligand is a factor of 0.33 as fast as that of DBT. Thus, electron-donating methyl groups located away from the sulfur atom in 2,8-Me₂DBT not only increase the thermodynamic stability of the Ru-S bond, as the equilibrium studies indicate, but also decrease the kinetic lability of the Ru-S bond. On the other hand, the rates of dissociation of the 4-MeDBT and 4,6-Me₂DBT ligands are 1.13 and 1.30 times faster, respectively, than that of DBT. The steric effects of methyl groups in the 4,6-positions of DBT outweigh their electron-donating effects, which results in lower thermodynamic stabilities and greater kinetic labilities of the Ru-S bond in the 4-MeDBT and 4,6-Me₂DBT complexes.

When PPh_3 was used as the incoming ligand (eq 4), $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-4,6-Me}_2\text{DBT})]^+$ reacted cleanly to give $[\text{CpRu}(\text{CO})_2(\text{PPh}_3)]^+$, whose ^1H NMR spectrum was nearly identical to that reported previously for this compound.²³ Due to the relative insolubility of PPh_3 in CD_3NO_2 , reaction solutions containing only 10, 15 and 20-fold excess of PPh_3 were possible. The rates of these reactions were independent of the PPh_3 concentration (Table 6), and the k_1 rate constant was the same within experimental error as

that with P(OPh)_3 (Table 7). However, reactions of the DBT (1) and 4-MeDBT (2) complexes with PPh_3 resulted in the formation of two phosphine products within 12 hours: $[\text{CpRu}(\text{CO})_2(\text{PPh}_3)]^{+23}$ and a product whose ^1H NMR spectrum was similar to that reported for $[\text{CpRu}(\text{CO})(\text{PPh}_3)_2]^+.$ ²⁴ Qualitatively, this reaction occurred more rapidly and more of the second phosphine product was formed in the reactions of the DBT compound (1) than the 4-MeDBT compound (2). Because these reactions yielded two products, their kinetics were not investigated further.

The k_{obs} rate constants for reactions of the $[\text{Cp}^*\text{Ru}(\text{CO})_2\eta^1(\text{S})\text{-DBTh}]^+$ complexes with PPh_3 and PPh_2Me show (Table 6) a small but discernible contribution from a second order (k_2) pathway in addition to the k_1 pathway. The k_1 values for the reactions of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ with PPh_3 decrease in the following order: 4,6-Me₂DBT ($(451 \pm 8) \times 10^{-6} \text{ s}^{-1}$) > DBT ($(115 \pm 2) \times 10^{-6} \text{ s}^{-1}$) > 4-MeDBT ($(63.9 \pm 0.3) \times 10^{-6} \text{ s}^{-1}$) > 2,8-Me₂DBT ($(26.8 \pm 1.5) \times 10^{-6} \text{ s}^{-1}$). The reactions of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})]^+$ and $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-4-MeDBT})]^+$ with PPh_2Me yielded k_1 values ($(62.7 \pm 2.1) \times 10^{-6} \text{ s}^{-1}$ for DBT and $(120 \pm 2) \times 10^{-6} \text{ s}^{-1}$ for 4-MeDBT) that were the same within experimental error as those determined using PPh_3 . The rate-determining step for the k_1 pathway in the reactions of the $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ complexes with both PPh_3 and PPh_2Me is likely dissociation of the DBTh ligand. As for the $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ complexes, the rates for three of the four $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ complexes decrease as follows: 4,6-Me₂DBT > DBT > 2,8-Me₂DBT. Steric and electronic factors account for this trend, as discussed above. On the other hand, the 4-MeDBT ligand in $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-4-MeDBT})]^+$ (6) dissociates *more slowly* than DBT from $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})]^+$, which is

different than the trend in rates for the $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ complexes and different than the trend in equilibrium binding constants (Table 4) for both series of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ complexes. In order to explain the anomalously slow rates of 4-MeDBT dissociation from **6**, one can propose that the low energy pathway for 4-MeDBT dissociation is one in which the DBTh ligand is oriented so that the complex has a plane of symmetry; that is, the complex has a 0° twist angle. The 4,6-Me₂DBT complex is forced by steric factors to have this orientation, and the DBT and 2,8-Me₂DBT ligands can easily achieve this orientation by rotation around the Ru-S bond. However, there will be a barrier to achieving this orientation with the 4-MeDBT ligand because of steric repulsion between the 4-methyl group and the Cp* methyl groups. This barrier to achieving a symmetrical structure may account for the unusually slow rate of 4-MeDBT dissociation from **6**.

The k_1 values for the $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ complexes are all significantly greater than those determined for the $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBTh})]^+$ complexes. For example, the rate of dissociation of DBT is 29 times faster in the Cp* complex ($115 \times 10^{-6} \text{ s}^{-1}$) as compared with that in the Cp complex ($4.01 \times 10^{-6} \text{ s}^{-1}$). Since there is little steric influence in both the Cp and Cp* complexes of DBT, the faster rate for the Cp* complex presumably is a result of the more electron-donating ability of the Cp* ligand. The added electron density reduces the Lewis acidity of the Ru atom, which weakens the Ru-S bond and makes the DBT ligand more labile in $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})]^+$ (**5**) as compared to the Cp complex **1**. The dissociation rate of 4-MeDBT from $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-4-MeDBT})]^+$ is 14 times faster than that from its Cp analogue, and the rate for 2,8-Me₂DBT dissociation from $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-2,8-Me}_2\text{DBT})]^+$ is 20 times faster than that from its Cp analogue. The

increases in the kinetic labilities of the 4-MeDBT and 2,8-Me₂DBT ligands in the Cp* complexes as compared with the Cp complexes are also likely a result of the greater electron-donating ability of the Cp* ligand as described for DBT above. On the other hand, the dissociation rate of 4,6-Me₂DBT from [Cp*Ru(CO)₂(η^1 (S)-4,6-Me₂DBT)]⁺ (7) is *86 times* its rate of dissociation from [CpRu(CO)₂(η^1 (S)-4,6-Me₂DBT)]⁺. This much larger rate of dissociation of 4,6-Me₂DBT in the Cp* complex than in its Cp analogue (3) is due not only to the higher electron-donating ability of Cp*, but also to the steric effect of the more bulky Cp* ligand. On the basis of the above comparisons, the electronic effect of the Cp* ligand increases the rate of 4,6-Me₂DBT dissociation from 7 by a factor of approximately 20, which means that the steric enhancement is a factor of approximately 4.

The k_2 values obtained from the plots of k_{obs} versus phosphine concentration for the reactions of the [Cp*Ru(CO)₂(η^1 (S)-DBTh)]⁺ complexes with PPh₃ and PPh₂Me are listed in Table 7. The k_2 values for the reaction with PPh₃ decrease in the same order as the k_1 values; 4,6-Me₂DBT ((152±13) × 10⁻⁶ s⁻¹) > DBT ((86.5±2.8) × 10⁻⁶ s⁻¹) > 4-MeDBT ((34.2±0.4) × 10⁻⁶ s⁻¹) > 2,8-Me₂DBT ((18.6±2.2) × 10⁻⁶ s⁻¹). The similarity of the trends in k_1 and k_2 values suggests that Ru-S bond breaking primarily determines the overall rate of the second order reaction. That bond-making with the incoming PR₃ ligand is less important is indicated by the fact that the k_2 values for PPh₃ and PPh₂Me in their reactions with 5 and 6 are nearly the same (Table 7). If the mechanism were to involve nucleophilic attack of the phosphine on the Ru, one would expect a much larger difference in their rates.²⁵ Thus, the mechanism for the k_2 pathway is best described as a dissociative interchange (I_d) where the nature of the [Cp*Ru(CO)₂(DBTh)][BF₄].PR₃ intermediate is not clear. It should be noted that this I_d pathway contributes to the total rate only at relatively high concentrations of the phosphine.

Conclusions

Investigations of the two series of dibenzothiophene complexes $[\text{Cp}'\text{Ru}(\text{CO})_2(\eta^1(S)\text{-DBTh})]^+$, where $\text{Cp}' = \text{Cp}$ or Cp^* , show that only in the structure of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-4,6-Me}_2\text{DBT})]^+$ is there evidence for steric crowding between methyl groups in the 4,6-Me₂DBT and Cp* ligands. This effect is also evident in the equilibrium binding constants (K') for the coordination of 4,6-Me₂DBT to $\{\text{Cp}^*\text{Ru}(\text{CO})_2\}^+$ which are much smaller than those for 4-MeDBT. In both series of complexes, both steric and electronic factors affect the K' values which increase in the order: 4,6-Me₂DBT < 4-MeDBT < DBT < 2,8-Me₂DBT. The rates of DBTh substitution by PR₃, following a dissociative mechanism, are especially fast for the sterically-crowded $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-4,6-Me}_2\text{DBT})]^+$, but steric and electronic effects also contribute to the rates of substitution of the other DBTh ligands.

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Figure 1. Numbering schemes for the aromatic thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT) compounds found in petroleum feedstocks.

Figure 2. Thermal ellipsoid drawings of $[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-4-MeDBT})]\text{BF}_4$ (**2**), $[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-4,6-Me}_2\text{DBT})]\text{BF}_4$ (**3**), and $[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-2,8-Me}_2\text{DBT})]\text{BF}_4$ (**4**). Ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted for clarity.

Table 1. Crystal Data and Structure Refinement for **2**, **3** and **4**.

COMPOUND	[CpRu(CO) ₂ (η^1 (S)-4-MeDBT)]BF ₄ (2)	[CpRu(CO) ₂ (η^1 (S)-4,6-Me ₂ DBTh)]BF ₄ (3)	[CpRu(CO) ₂ (η^1 (S)-2,8-Me ₂ DBTh)]BF ₄ (4)
Empirical formula	C ₂₀ H ₁₅ BF ₄ O ₂ RuS	C ₂₁ H ₁₇ BF ₄ O ₂ RuS	C ₂₁ H ₁₇ BF ₄ O ₂ RuS
Formula weight	507.26	521.29	521.29
Temperature	173(2) K	293(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>n</i>
Unit cell dimensions	<i>a</i> = 11.699(4) Å	<i>a</i> = 9.3637(8) Å	<i>a</i> = 9.394(4) Å
	<i>b</i> = 12.520(5) Å	<i>b</i> = 10.4141(9) Å	<i>b</i> = 11.003(5) Å
	<i>c</i> = 13.149(5) Å	<i>c</i> = 11.7381(9) Å	<i>c</i> = 19.963(9) Å
	α = 90.0°	α = 73.448(1)°	α = 90.000°
	β = 94.534(6)°	β = 69.504(1)°	β = 98.660(8)°
	γ = 90.0°	γ = 88.382(2)°	γ = 90.000°
Volume	1920.0(12) Å ³	1024.48(15) Å ³	2039.7(16) Å ³
<i>Z</i>	4	2	4
Cryst. color, habit	yellow, plate	yellow, prism	yellow, prism
Density (calcd.)	1.755 Mg/m ³	1.690 Mg/m ³	1.698 Mg/m ³
Abs. coeff.	0.977 mm ⁻¹	0.918 mm ⁻¹	0.922 mm ⁻¹
<i>F</i> (000)	1008	520	1040
Cryst. size	0.20 x 0.20 x 0.10 mm ³	0.30 x 0.28 x 0.21 mm ³	0.30 x 0.30 x 0.23 mm ³

Table 1. (continued)

θ range for data collection	1.75 to 25.00°	1.94 to 26.37°	2.06 to 28.29°
Index ranges	-13 ≤ h ≤ 13 -13 ≤ k ≤ 14 -15 ≤ l ≤ 14	-11 ≤ h ≤ 11 -13 ≤ k ≤ 8 -14 ≤ l ≤ 14	-11 ≤ h ≤ 12 -14 ≤ k ≤ 14 -26 ≤ l ≤ 26
No. of reflns collected	13529	6757	19275
No. of ind reflns	3341 [$R(\text{int}) = 0.0422$]	4112 [$R(\text{int}) = 0.0183$]	4706 [$R(\text{int}) = 0.0394$]
Completeness to $\theta =$	25.00° = 98.8%	26.37° = 98.1%	28.29° = 99.0%
abs corr	Semi-empirical with equivalents	empirical with SADABS	Semi-empirical from equivalents
Max. and min. transmn	0.44 and 0.31	0.86 and 0.76	1.00 and 0.88
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
No. of data / restraints / params	3341 / 0 / 262	4112 / 0 / 271	4706 / 0 / 271
Goodness-of-fit on F^2	1.100	1.013	1.221
Final R^a indices [$I > 2\sigma(I)$]	$R1 = 0.0677$ $wR2 = 0.2007$	$R1 = 0.0311$ $wR2 = 0.0777$	$R1 = 0.0787$ $wR2 = 0.1936$
R^a indices (all data)	$R1 = 0.0744$ $wR2 = 0.2085$	$R1 = 0.0380$ $wR2 = 0.0805$	$R1 = 0.0833$ $wR2 = 0.1956$
largest diff peak and hole	4.094 and -0.874 e Å ⁻³	0.785 and -0.782 e Å ⁻³	2.792 and -1.822 e Å ⁻³

^a $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $wR2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$

Table 2. Ru-S Bond Distances (Å) and Twist Angles (°) for [CpRu(CO)₂(η^1 (S)-DBTh)][BF₄] Complexes **1-4** and for the [Cp*Ru(CO)₂(η^1 (S)-DBTh)][BF₄] Complexes **5-7**.

Complex	Ru-S distance (Å)	Twist Angle (°)
[CpRu(CO) ₂ (η^1 (S)-DBT)] ^{+,a} (1)	2.398(2)	22.8
[CpRu(CO) ₂ (η^1 (S)-4-MeDBT)] ^{+,b} (2)	2.377(2)	8.6
[CpRu(CO) ₂ (η^1 (S)-4,6-Me ₂ DBT)] ^{+,b} (3)	2.405(1)	8.9
[CpRu(CO) ₂ (η^1 (S)-2,8-Me ₂ DBT)] ^{+,b} (4)	2.400(1)	25.0
[Cp*Ru(CO) ₂ (η^1 (S)-DBT)] ^{+,c} (5)	2.394(1)	20.2
[Cp*Ru(CO) ₂ (η^1 (S)-4-MeDBT)] ^{+,c} (6)	2.399(1), 2.404(1)	11.3, 12.3
[Cp*Ru(CO) ₂ (η^1 (S)-4,6-Me ₂ DBT)] ^{+,c} (7)	2.419(1)	0.4

^a Reference 8.

^b This study.

^c Reference 11.

Table 3. Equilibrium Constants, K , for Reactions (eq 2) of $[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-DBTh})]^+$ with DBTh' at 25.0 °C in CD_3NO_2 .

DBTh	DBTh'	K
DBT	4-MeDBT	0.358(8)
DBT	4,6-Me ₂ DBT	0.103(2)
DBT	2,8-Me ₂ DBT	3.77(3)
4-MeDBT	4,6-Me ₂ DBT	0.344(15)

Table 4. Relative Equilibrium Constants, K' , for Reactions of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-4,6-Me}_2\text{DBT})]^+$ with DBTh in CD_3NO_2 or CD_2Cl_2 at 25.0 °C.

DBTh	$[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-DBTh})]^+,^a$	$[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-DBTh})]^+,^b$
4,6-Me ₂ DBT	1.00	1.00
4-MeDBT	2.79(7)	20.2(1)
DBT	9.71(9)	62.7(6)
2,8-Me ₂ DBT	36.5(3)	223(3)

^a This study. CD_3NO_2 solvent.

^b Reference 11. CD_2Cl_2 solvent.

Table 5. Relative Equilibrium Constants (K') for the Reactions of $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-T})]^+$ with Th at 25.0 °C.

Th	K'
T^{a}	1.00
2-MeT ^a	3.30
3-MeT ^a	4.76
2,5-Me ₂ T ^a	20.7
BT ^{a,b}	47.6
4,6-Me ₂ DBT ^b	80.9
4-MeDBT ^b	233
DBT ^b	800
Me ₄ T ^a	887
2,8-Me ₂ DBT ^b	3016
THT ^a	$>10^5$

^a Reference 14. CD_2Cl_2 solvent.

^b This study. CD_3NO_2 solvent.

Table 6. Rate Constants, k_{obs} (s^{-1}), for Reactions (eq 4) of 0.020 M $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-DBTh})]^+$ with PR_3 25.0 °C.

DBTh	PR ₃	[PR ₃], (M)	10 ⁶ k _{obs} , s ⁻¹
[CpRu(CO) ₂ (η ¹ (S)-DBTh)] ^{+,a}			
4,6-Me ₂ DBT	PPh ₃	0.10	5.21
		0.20	5.30
		0.30	5.28
		0.40	5.25
		P(OPh) ₃	0.20
0.60	5.07		
1.00	5.25		
4-MeDBT	P(OPh) ₃		0.20
		0.60	4.54
DBT	P(OPh) ₃	0.20	3.97
		0.20	4.03
		0.60	4.02
2,8-Me ₂ DBT	P(OPh) ₃	0.20	1.32
		0.20	1.28
		1.00	1.38
[Cp*Ru(CO) ₂ (η ¹ (S)-DBTh)] ^{+,b}			
4,6-Me ₂ DBT	PPh ₃	0.20	475
		0.40	517
		0.60	548
		1.00	600
DBT	PPh ₃	0.20	131
		0.40	150
		0.60	169
		0.80	183
	PPh ₂ Me	1.00	201
		0.20	139
		0.60	175
		0.80	194
		1.00	214

^a CD₃NO₂ solvent.

^b CD₂Cl₂ solvent.

Table 6. (continued)

4-MeDBT	PPh ₃	0.20	71.0(5)
		0.40	77.4
		0.60	84.1
		0.80	91.4
		1.00	98.2
	PPh ₂ Me	0.20	71.1
		0.40	78.0
		0.60	85.9
		0.80	97.8
		1.00	101
2,8-Me ₂ DBT	PPh ₃	0.20	29.2
		0.40	35.1
		0.60	38.9
		0.80	42.5
		1.00	44.0

Table 7. First and Second-Order Rate Constants, k_1 and k_2 , for the Substitution of DBTh in $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(S)\text{-DBTh})]^+$ by PR_3 at 25.0 °C according to eq 4.

DBTh	$[\text{CpRu}(\text{CO})_2(\text{DBTh})]^+,^a$	$[\text{Cp}^*\text{Ru}(\text{CO})_2(\text{DBTh})]^+,^b$	
	$10^6 k_1, \text{s}^{-1}$	$10^6 k_1, \text{s}^{-1}$	$10^6 k_2, \text{M}^{-1}\text{s}^{-1}$
4,6-Me ₂ DBT	5.18(10) ^c , {5.26(4)} ^d	451 ^d	152 ^d
4-MeDBT	4.50(3) ^c	63.9 ^d , {62.7} ^e	34.2, ^d {40.2} ^e
DBT	4.01(3) ^c	115 ^d , {120} ^e	86.5, ^d {93.0} ^e
2,8-Me ₂ DBT	1.33(5) ^c	26.8 ^d	18.5 ^d

^a In CD_3NO_2 .

^b In CD_2Cl_2 .

^c For $\text{PR}_3 = \text{P}(\text{OPh})_3$.

^d For $\text{PR}_3 = \text{PPh}_3$.

^e For $\text{PR}_3 = \text{PPh}_2\text{Me}$.

CHAPTER 4: SYNTHETIC, STRUCTURAL AND KINETIC STUDIES
OF [CpRu(CO)₂(μ₂-η¹(S),η⁶-DBT)RuCp*][PF₆]₂: A
DIBENZOTHIOPHENE BRIDGE BETWEEN TWO RUTHENIUM
FRAGMENTS

A Paper in the format required for *Organometallics*

Paul A. Vecchi, Arkady Ellern, and Robert J. Angelici

Abstract

*The [CpRu(CO)₂(μ₂-η¹(S),η⁶-DBT)RuCp']²⁺ (Cp' = η⁵-C₅H₅ (3), η⁵-C₅Me₅ (4)) complexes were synthesized and shown by X-ray crystallography to contain a bridging dibenzothiophene ligand that is coordinated to {CpRu(CO)₂}⁺ through the sulfur atom and to {Cp'Ru}⁺ through an arene ring (η⁶). Kinetic studies of the displacement of the [Cp*Ru(η⁶-DBT)]⁺ ligand in 4 by P(OPh)₃ show that the η⁶-coordinated {Cp*Ru}⁺ group on DBT weakens the Ru-S bond, as compared to that in [CpRu(CO)₂(η¹(S)-DBT)]⁺, and greatly increases the rate of DBT dissociation.*

Introduction

The removal of sulfur compounds from transportation fuels is important for the elimination of NO_x and SO_x atmospheric pollution.¹ The main process by which sulfur is currently removed from petroleum feedstocks is through an industrial catalytic process

known as hydrodesulfurization (HDS).² One of the more difficult classes of sulfur compounds to process using HDS is the dibenzothiophenes (Figure 1) which are found mainly in diesel fuel. In order to reduce the amount of pollution from diesel fuel combustion, the United States has mandated a reduction in sulfur levels from a current average of 500 ppm to 15 ppm starting in 2006.^{1a,3} Europe has a similar plan in place with a goal of 2008.^{3a,4} The removal of dibenzothiophenes from diesel fuels is necessary in order to meet these low sulfur requirements.

Various new approaches to the removal of dibenzothiophenes (DBTh) from diesel take advantage of the ability of DBTh to bind to transition metals in their complexes.⁵ The two most common binding modes of dibenzothiophenes in transition metal compounds are $\eta^1(S)$, where coordination occurs through the sulfur atom, and η^6 , where binding occurs to one (or both) of the dibenzothiophene rings. We have previously demonstrated that methyl groups in the 4,6-positions of DBTh sterically hinder the $\eta^1(S)$ -coordination of dibenzothiophenes to cationic $\{Cp'Ru(CO)_2\}^+$ fragments ($Cp' = \eta^5-C_5H_5$ and $\eta^5-C_5Me_5$).⁶ Sweigart and co-workers have shown that η^6 -coordination of dibenzothiophene to a cationic $\{Mn(CO)_3\}^+$ fragment can be used to activate C-S bond to cleavage by $Pt(PPh_3)_2$,⁷ a process that is proposed to occur after formation of a short-lived $\eta^1(S)$ intermediate.^{7a,b} An earlier study in this group showed that η^6 -coordination of benzothiophene (Figure 1) to a neutral $\{Cr(CO)_3\}$ fragment causes the benzothiophene to favor η^2 -olefin binding to $\{CpRe(CO)_2\}$ over $\eta^1(S)$ -coordination.⁸ This was attributed to a decrease in the electron-donating ability of the sulfur atom caused by the electron-withdrawing $Cr(CO)_3$ fragment; without the η^6 - $\{Cr(CO)_3\}$ group, the $CpRe(CO)_2BT$ complex exists as an equilibrium mixture of η^2 and

$\eta^1(S)$ complexes. In the present study, we examine the ability of an η^6 -coordinated $\{Cp^*Ru\}^+$ group on DBT to influence the binding through its sulfur to $\{CpRu(CO)_2\}^+$. As part of this investigation, we characterize complexes in which DBT is both η^6 - and $\eta^1(S)$ -coordinated to cyclopentadienyl ruthenium units. Kinetic studies of the cleavage of the Ru-S bond in $[CpRu(CO)_2(\mu_2-\eta^1(S), \eta^6-DBT)RuCp^*][PF_6]_2$ show that the η^6 -coordinated $\{Cp^*Ru\}^+$ unit weakens this Ru-S bond.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of dry argon in reagent grade solvents using standard Schlenk techniques. Hexanes, methylene chloride (CH_2Cl_2) and diethyl ether (Et_2O) were purified on alumina using a Solv-Tek solvent purification system similar to that described by Grubbs and co-workers.⁹ Nitromethane (CH_3NO_2 , 96+%) and deuterated nitromethane (CD_3NO_2), both purchased from Aldrich, were deoxygenated by three freeze-pump-thaw cycles and stored under argon until use. Acetone was stirred with calcium chloride overnight, distilled, subjected to three freeze-pump-thaw cycles and stored under argon, while 1,2-dichloroethane (DCE) was stirred overnight with P_2O_5 before being distilled, deoxygenated and stored under argon. Neutral alumina (Brockman, activity I) was deoxygenated under vacuum for 24 hours, deactivated with 7.5% w/w argon-saturated water (Ultrapure) and stored under argon until use. Dibenzothiophene (DBT) was purchased from Aldrich and sublimed before use. Solid $AgPF_6$ (99.99+%) and $AgBF_4$ (99.99+%) were purchased from Aldrich and used without further purification. The complexes $[CpRu(NCMe)_3][PF_6]$,¹⁰ $CpRu(CO)_2Cl$,¹¹ $[CpRu(CO)_2(\eta^1(S)-DBT)][BF_4]$,¹² $[Cp^*Ru(NCMe)_3][PF_6]$,¹³ and $[Cp^*Ru(\mu_3-Cl)]_4$ ¹⁴ were all

prepared according to published literature methods. Filtrations were performed through a plug of filter paper, Celite and cotton that was prepared from a cut 1 mL syringe, and the solutions were transferred via thin-wall Teflon tubing (Alpha Wire Corporation).

Solution ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer using CD_3NO_2 as the solvent, internal lock, and reference ($\delta = 4.33$ (^1H), 62.8 (^{13}C)). Solution infrared spectra of the compounds in CH_3NO_2 were recorded on a Nicolet-560 spectrometer using NaCl cells with 0.1 mm spacers. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer.

Synthesis of $[\text{CpRu}(\eta^6\text{-DBT})][\text{PF}_6]$ (1). This complex was prepared in a manner similar to that reported previously.¹⁵ To solid $[\text{CpRu}(\text{NCMe})_3][\text{PF}_6]$ (100 mg, 0.230 mmol) and DBT (63.6 mg, 0.345 mmol) was added 20 mL of DCE, and the solution was gently refluxed for 15 h. The solution was cooled to room temperature and filtered into diethyl ether to precipitate the product. The tan-colored solid was isolated by filtration and washed with both diethyl ether and hexanes to remove any excess DBT. Reaction yields were greater than 95% before workup as described next. The crude solid product was dissolved in acetone (~5 mL) and filtered onto a short column of alumina packed in hexanes. The product was eluted with a 1:1 acetone- CH_2Cl_2 solution, leaving an unidentified tan impurity on the column. The solvents were removed under vacuum, the remaining solid was redissolved in CH_2Cl_2 , and the resulting solution was filtered into cold diethyl ether to precipitate the pure product. Removal of the solvent by filtration yielded 89.0 mg (0.180 mmol) of **1** as a white solid in 78% overall yield. This method of purification was superior to recrystallization from benzene as was described previously.¹⁵ ^1H NMR (400 MHz, CD_3NO_2): δ 8.27 (d, $^3J(\text{H,H}) = 7.6$ Hz, 1H), 7.93 (d, $^3J(\text{H,H}) = 7.6$ Hz, 1H), 7.71 (t, $^3J(\text{H,H}) = 7.6$ Hz, 1H), 7.62 (t, $^3J(\text{H,H}) = 7.6$ Hz,

1H), 7.33 (d, $^3J(\text{H,H}) = 5.6$ Hz, 1H), 7.21 (d, $^3J(\text{H,H}) = 5.6$ Hz, 1H), 6.38-6.27 (d-of-t, $^3J(\text{H,H}) = 5.6$ Hz, 2H), DBT; 5.12 (s, 5H), Cp. ^{13}C NMR (100.6 MHz, CD_3NO_2): δ 142.01, 133.38, 131.83, 127.53, 124.93, 124.90, 111.19, 101.46, 85.07, 84.65, 81.82, 79.67 (DBT); 82.73 (Cp).

Synthesis of $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})][\text{PF}_6]$ (2). **Method A:** To solid $[\text{Cp}^*\text{Ru}(\text{NCMe})_3][\text{PF}_6]$ (200 mg, 0.396 mmol) and DBT (110 mg, 0.597 mmol) was added 25 mL of DCE, and the solution was gently refluxed for 15 h. Evaporation of the solvent yielded a tan residue, which was washed with both diethyl ether and hexanes to remove any excess DBT. Reaction yields were nearly quantitative before workup, which was performed in the manner described above for 1. After isolation, 178 mg (0.315 mmol) of $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})][\text{PF}_6]$ (2) was obtained as a white, air-stable solid (80% yield). ^1H NMR (400 MHz, CD_3NO_2): δ 8.15 (d, $^3J(\text{H,H}) = 7.6$ Hz, 1H), 7.96 (d, $^3J(\text{H,H}) = 7.6$ Hz, 1H), 7.71-7.61 (m, 2H), 6.79 (d, $^3J(\text{H,H}) = 5.2$ Hz, 1H), 6.64 (d, $^3J(\text{H,H}) = 5.2$ Hz, 1H), 6.05-5.99 (m, 2H), DBT; 1.61 (s, 15H), Cp*. ^{13}C NMR (100.6 MHz, CD_3NO_2): δ 141.60, 132.51, 131.34, 127.60, 124.89, 124.78, 109.78, 100.32, 87.49, 87.28, 83.38, 81.19 (DBT); 96.92, 9.45 (Cp*). Anal. Calcd for $\text{C}_{22}\text{H}_{23}\text{F}_6\text{PRuS}$: C, 46.72; H, 4.10. Found: C, 46.66; H, 4.31.

Method B: To a 50 mL Schlenk flask containing freshly prepared $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ (180 mg, 0.166 mmol), DBT (183 mg, 0.993 mmol) and AgPF_6 (172 mg, 0.680 mmol) was added 25 mL of CH_2Cl_2 . The reaction solution was allowed to stir at room temperature for 2 h, during which time the solution color changed from a dark orange to light yellow with formation of a AgCl precipitate. The reaction solution was then filtered into cold diethyl ether to give a pale-yellow solid which was isolated and purified as described above. Using

this method 325 mg (0.575 mmol) of white $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]\text{PF}_6$ (**2**) was obtained (87% yield).

Synthesis of $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(\text{S}),\eta^6\text{-DBT})\text{RuCp}][\text{PF}_6]_2$ (3**).** A flask containing solid $\text{CpRu}(\text{CO})_2\text{Cl}$, (50.0 mg, 0.194 mmol), $[\text{CpRu}(\eta^6\text{-DBT})][\text{PF}_6]$ (95.0 mg, 0.192 mmol), and AgPF_6 (52.0 mg, 0.206 mmol) was placed in an ice bath, and 5 mL of cold CH_2Cl_2 was added. The solution was allowed to stir at 0 °C for 1 h, during which time the yellow solution color lightened and a light colored precipitate formed. The reaction mixture was allowed to settle for a few minutes before the solution was removed by filtration. The remaining solid was extracted with ~1 mL of CH_3NO_2 and filtered into cold diethyl ether, precipitating the pale yellow product. This solid was isolated by filtration, washed with a small amount of cold CH_2Cl_2 (< 1 mL) and dried under vacuum to obtain 103 mg (0.119 mmol) of $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(\text{S}),\eta^6\text{-DBT})\text{RuCp}][\text{PF}_6]_2$ (**3**) as a moderately air-stable powder (62 % yield). Compound **3** is insoluble in diethyl ether and hexanes and minimally soluble in CH_2Cl_2 . Although it is soluble in CH_3NO_2 and acetone, compound **3** undergoes some decomposition in solution at room temperature and must be kept cold for NMR characterization. ^1H NMR (400 MHz, CD_3NO_2 , 273 K): δ 8.29 (d, $^3J(\text{H},\text{H}) = 7.6$ Hz, 1H), 8.00 (d, $^3J(\text{H},\text{H}) = 7.6$ Hz, 1H), 7.90-7.80 (m, 2H), 7.45-7.42 (m, 1H), 7.25-7.22 (m, 1H), 6.55-6.53 (m, 2H), DBT; 5.90 (s, 5H), 5.35 (s, 5H) Cp. ^{13}C NMR (100.6 MHz, CD_3NO_2 , 273 K): δ 194.14, 193.80 (CO); 141.60, 134.11, 133.81, 131.93, 127.47, 126.24, 110.07, 101.82, 86.89, 86.65, 84.31, 81.50 (DBT); 91.35, 84.81 (Cp). IR (CH_3NO_2): $\nu(\text{CO})$ (cm^{-1}) 2082(s), 2039(s). Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{F}_{12}\text{O}_2\text{P}_2\text{Ru}_2\text{S}$: C, 33.42; H, 2.10; S, 3.72. Found: C, 33.13; H, 1.64; S, 3.88.

Synthesis of $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(S),\eta^6\text{-DBT})\text{RuCp}^*][\text{X}]_2$ ($\text{X} = \text{PF}_6^-$ (4a), BF_4^- (4b)).

Method A: A flask containing solid $\text{CpRu}(\text{CO})_2\text{Cl}$, (150 mg, 0.582 mmol), $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]\text{PF}_6$ (326 mg, 0.576 mmol), and AgPF_6 (150 mg, 0.593 mmol) was placed in an ice bath, and 15 mL of cold CH_2Cl_2 was added. The solution was stirred at 0 °C for 1 h, during which time the solution color lightened and a precipitate formed. The solution was then filtered into cold diethyl ether resulting in precipitation of a pale yellow product. The remaining solid in the reaction vessel was extracted with ~ 2 mL of CH_3NO_2 , and this solution was also filtered into the cold diethyl ether to precipitate the rest of the product. The pale yellow solid was isolated by filtration followed by drying under vacuum to give 441 mg (0.473 mmol) of $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(S),\eta^6\text{-DBT})\text{RuCp}^*][\text{PF}_6]_2$ (4a) as a moderately air-stable solid (82% yield). If impurities are present, they can be removed by washing with a small amount (< 1 mL) of cold CH_2Cl_2 . ^1H NMR (400 MHz, CD_3NO_2 , 273 K): δ 8.25-8.22 (m, 1H), 8.08-8.05 (m, 1H), 7.89-7.86 (m, 2H), 6.97 (d, $^3J(\text{H,H}) = 5.6$ Hz, 1H), 6.83 (d, $^3J(\text{H,H}) = 5.6$ Hz, 1H), 6.32-6.26 (m, 2H), DBT; 5.88 (s, 5H), Cp; 1.68 (s, 15H), Cp^* . ^{13}C NMR (100.6 MHz, CD_3NO_2 , 273 K): δ 194.15, 193.77 (CO); 141.23, 133.43, 133.21, 132.26, 127.55, 126.06, 108.41, 100.09, 89.04, 88.75, 85.08, 83.03 (DBT); 91.34 (Cp); 99.66, 9.60 (Cp^*). IR (CH_3NO_2): $\nu(\text{CO})$ (cm^{-1}) 2081(s), 2038(s). Anal. Calcd for $\text{C}_{29}\text{H}_{28}\text{F}_{12}\text{O}_2\text{P}_2\text{Ru}_2\text{S}$: C, 37.35; H, 3.03; S, 3.44. Found: C, 36.89; H, 2.89; S, 3.31.

Method B: A reaction vessel containing solid $[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-DBT})][\text{BF}_4]$ (50.0 mg, 0.101 mmol), freshly prepared $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ (27.5 mg, 0.0253 mmol), and AgBF_4 (20.0 mg, 0.103 mmol) was placed in an ice bath, and ~ 2 mL of cold CH_3NO_2 was added. The mixture was stirred for 1 h during which time the dark orange solution changed to

yellow, and a precipitate was observed. The solution was then filtered into another flask containing cold diethyl to precipitate the product. The solid was isolated by filtration, washed with ~1 mL of cold CH₂Cl₂ and dried under vacuum to yield 52.0 mg (0.0637 mmol) of [CpRu(CO)₂(μ₂-η¹(S),η⁶-DBT)RuCp*][BF₄]₂ (**4b**) as a light yellow powder (63% yield). The solution ¹H and ¹³C NMR spectra in CD₃NO₂ were nearly identical to that reported above for **4a**.

X-ray Structural Determination of [CpRu(CO)₂(μ₂-η¹(S),η⁶-DBT)RuCp*][PF₆]₂ (4a**).** A yellow single crystal of **4a** suitable for an X-ray diffraction study was obtained by layering a cold acetone solution of the complex with Et₂O under argon and storing at -25 °C for 1 week. The crystal was selected from the mother liquor under ambient conditions and quickly coated in premixed epoxy glue. The covered crystal was mounted onto the end of a glass fiber, placed in a stream of cold nitrogen and centered in the X-ray beam using a video camera. Crystal evaluation and data collection were performed at 173 K on a Bruker CCD-1000 diffractometer with Mo Kα (λ = 0.71073 Å) radiation and a collector-to-crystal distance of 5.03 cm. Cell constants were determined from a list of reflections found by an automated search routine. Data were collected using the full sphere routine and were 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 using SADABS software.¹⁶ Positions of the heavy atoms were found by the Patterson method. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined using a full-matrix anisotropic approximation. Hydrogen atoms were placed in the structure factor calculation at

idealized positions and refined using a riding model. Other crystallographic data are given in Table 1.

Kinetic Studies. Solutions of $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(\text{S}),\eta^6\text{-DBT})\text{RuCp}^*][\text{PF}_6]_2$ and liquid $\text{P}(\text{OPh})_3$ were prepared for kinetic studies according to the following procedure: A 0.010 mmol sample of the complex was added to an NMR tube, and the tube was evacuated and flushed with argon. To the NMR tube was first added CD_3NO_2 followed immediately by the $\text{P}(\text{OPh})_3$ such that the total volume of the reaction solution was always 0.50 mL. The tube was capped tightly with a septum, shaken and immediately placed into the probe of a Bruker DRX-400 NMR spectrometer thermostatted at 25.0 ± 0.1 °C. The spectrometer was preprogrammed to acquire spectra at specific time intervals. Three independent experiments were carried out for 5 different concentrations of $\text{P}(\text{OPh})_3$. The products formed during the course of the reactions were $[\text{CpRu}(\text{CO})_2(\text{P}(\text{OPh})_3)]^{+17}$ and $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]^+$, which were identified by their NMR spectra. Concentrations of reactants and products were determined by integration of the Cp and Cp* signals in the ^1H NMR spectrum.

Results and Discussion

Synthesis and characterization of $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(\text{S}),\eta^6\text{-DBT})\text{RuCp}'][\text{PF}_6]_2$ (Cp' = Cp (3), Cp* (4a)). The precursor complexes $[\text{Cp}'\text{Ru}(\eta^6\text{-DBT})][\text{PF}_6]$ (Cp' = Cp (1), Cp* (2)) are prepared in high yields by reactions of $[\text{Cp}'\text{Ru}(\text{NCMe})_3][\text{PF}_6]$ with DBT in DCE in a manner similar to that described previously for $[\text{CpRu}(\eta^6\text{-DBT})][\text{PF}_6]$.¹⁵ Both 1 and 2 are soluble in acetone, methylene chloride and nitromethane, and insoluble in hexanes and diethyl ether. Compound 2 may also be prepared by the reaction of freshly prepared

$[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ with AgPF_6 and DBT in CH_2Cl_2 at room temperature. This method is preferred because the starting material $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ is more readily prepared than $[\text{Cp}^*\text{Ru}(\text{NCMe})_3][\text{PF}_6]$, and the reaction to form $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})][\text{PF}_6]$ is complete within 2 hours at room temperature as opposed to refluxing in DCE for longer periods of time. It also allows for direct incorporation of different anions into **2** by appropriate choice of the silver salt. The solution NMR spectra of **1** and **2** exhibit ^1H and ^{13}C signals for the uncoordinated ring of DBT with chemical shifts that are similar to those of free DBT [^1H NMR (400 MHz, CD_3NO_2): δ 8.27-8.24 (m, 2H), 7.95-7.94 (m, 2H), 7.55-7.50 (m, 4H). ^{13}C NMR (100.6 MHz, CD_3NO_2): δ 140.65, 136.85, 128.36, 125.99, 124.15, 123.04]. There are also signals that are upfield by 0.9-1.5 and 28-45 ppm in the ^1H and ^{13}C NMR spectra, respectively, for the ring that is η^6 -coordinated to the $\{\text{Cp}^*\text{Ru}\}^+$ fragment as reported previously for $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})][\text{PF}_6]$.¹⁵

The compounds $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(S),\eta^6\text{-DBT})\text{RuCp}'][\text{PF}_6]_2$ ($\text{Cp}' = \text{Cp}$ (**3**), Cp^* (**4a**)), with $\mu_2\text{-}\eta^1(S),\eta^6$ bridging DBT ligands, are prepared by reactions of $\text{CpRu}(\text{CO})_2\text{Cl}$ with AgPF_6 and the appropriate $[\text{Cp}'\text{Ru}(\eta^6\text{-DBT})][\text{PF}_6]$ in cold CH_2Cl_2 as shown in eq 1.

Alternatively, $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(S),\eta^6\text{-DBT})\text{RuCp}^*][\text{BF}_4]_2$ (**4b**) was prepared by reaction of $[\text{CpRu}(\text{CO})_2(\eta^1(S)\text{-DBT})][\text{BF}_4]$ with $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ and AgBF_4 in cold CH_2Cl_2 .

Compounds **3** and **4** are moderately stable as solids but undergo some decomposition in solution by dissociation of the $[\text{CpRu}(\eta^6\text{-DBT})]^+$ unit at room temperature. Therefore, their NMR spectra in CD_3NO_2 solvent were recorded at 273 K at which temperature both complexes were stable indefinitely. The chemical shifts of the DBT protons in **3** and **4** are shifted slightly (0.02 - 0.27 ppm) downfield as compared to those of the free $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]^+$ ligands. Similar small downfield shifts in the proton NMR signals of $\eta^1(\text{S})$ -coordinated DBT have been observed in $[\text{CpFe}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})]^+$,¹⁸ and $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})]^+$.¹² Shifts for the hydrogen and carbon atoms of the η^6 -coordinated DBT ring in compounds **3** and **4** remain significantly upfield of those in free DBT.

The ^{13}C NMR spectra for both **3** and **4a** at 273 K show two distinct chemical resonances for each of the two diastereotopic CO ligands. On the other hand, the benzothiophene complexes $[\text{CpFe}(\text{CO})_2(\eta^1(\text{S})\text{-BT})]^+$,¹⁸ and $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-BT})]^+$,¹² contain only one carbonyl resonance at room temperature. The occurrence of only one CO signal in these compounds was attributed to a dynamic process in which there is inversion at the sulfur atom coupled with rapid rotation around the M-S bond. Only upon cooling CD_2Cl_2 solutions of $[\text{CpFe}(\text{CO})_2(\eta^1(\text{S})\text{-BT})]^+$ and $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-BT})]^+$ to 170 K and 198 K, respectively, was it possible to observe both diastereotopic carbonyl signals by NMR and to calculate the free energies of activation ($\Delta G^\ddagger$) for sulfur inversion: $\Delta G^\ddagger = 39$ kJ/mol at 190 K (T_c) for $[\text{CpFe}(\text{CO})_2(\eta^1(\text{S})\text{-BT})]^+$,¹⁸ and $\Delta G^\ddagger = 43$ kJ/mol at 205 K (T_c) for $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-BT})]^+$.¹² The observation of two CO signals for **3** and **4a** indicates that the inversion at the sulfur must be much slower than in $[\text{CpFe}(\text{CO})_2(\eta^1(\text{S})\text{-BT})]^+$ and $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-BT})]^+$ due to a higher inversion barrier. Because of the instabilities of **3**

and **4a**, it was not possible to heat their solutions for the purpose of observing coalescence of the carbonyl signals.

Infrared spectra of **3** and **4a** in CH₃NO₂ show $\nu(\text{CO})$ absorptions (2082, 2038 and 2081, 2038 cm⁻¹, respectively) that are 28-39 cm⁻¹ higher in energy than those observed for the neutral starting material CpRu(CO)₂Cl (2053, 1999 cm⁻¹ in CH₃NO₂). These values are 4-5 cm⁻¹ higher than those for [CpRu(CO)₂($\eta^1(\text{S})$ -DBT)][BF₄] in CH₃NO₂ (2077, 2033 cm⁻¹), which indicates that the η^6 -coordinated {Cp^{*}Ru}⁺ group reduces the electron-donor ability of the DBT ligand to the {CpRu(CO)₂}⁺ unit.

The molecular structure (Figure 2) of the cation in [CpRu(CO)₂(μ_2 - $\eta^1(\text{S})$, η^6 -DBT)RuCp^{*}][PF₆]₂ (**4a**), as determined by an X-ray diffraction study, confirms the μ_2 - $\eta^1(\text{S})$, η^6 binding mode for the DBT ligand. Compound **4a** contains a planar DBT ligand that is bound to {CpRu(CO)₂}⁺ through a pyramidal sulfur atom, which is typical of $\eta^1(\text{S})$ -bonded thiophenes.⁵ The [Cp^{*}Ru(η^6 -DBT)]⁺ ligand is oriented away from the Cp ligand, and the {Cp^{*}Ru}⁺ fragment is on the opposite side of the DBT plane from the {CpRu(CO)₂}⁺. The structure of **4a** provides a reasonable explanation for the observation of separate signals for the CO ligands in the ¹³C NMR spectrum (see above). If inversion of the sulfur were to occur, as described above for [CpRu(CO)₂($\eta^1(\text{S})$ -BT)]⁺, the {Cp^{*}Ru}⁺ and {CpRu(CO)₂}⁺ units in **4a** would be sterically-crowded, which would reduce the rate of inversion at the sulfur. This slower rate of inversion would account for the fact that the two CO ligands in the {CpRu(CO)₂}⁺ unit remain inequivalent on the ¹³C NMR timescale. The Ru-S distance in **4a** (2.392(1) Å) is essentially the same as the corresponding distances in [CpRu(CO)₂($\eta^1(\text{S})$ -DBT)]⁺ (2.398(2) Å)¹⁹ and [Cp^{*}Ru(CO)₂($\eta^1(\text{S})$ -DBT)]⁺ (2.394(1) Å).^{6a} The tilt angle in **4a**,

which is the angle defined by Ru-S-Midpt (where Midpt is the midpoint between the C10 and C11 bond) is 114.5° , which is smaller than the values found for $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})]^+$ (119.3°),¹⁹ $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})]^+$ (121.0°)^{6a} and $[\text{CpFe}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})]^+$ (119.4°).¹⁸ These angles are probably determined by crystal packing energies.

Kinetic studies of $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]^+$ substitution by $\text{P}(\text{OPh})_3$ in **4a.** In order to determine the effect of the $\eta^6\text{-}\{\text{Cp}^*\text{Ru}\}^+$ fragment on the lability of the Ru-S bond, the substitution (eq 2) of the $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]^+$ ligand in **4a** by $\text{P}(\text{OPh})_3$ was investigated.

These studies were performed under pseudo-first order conditions with at least a 10-fold excess of the phosphite ligand. First-order plots of the disappearance of **4a** gave rate constants (k_{obs} , Table 2) that follow a two-term rate law (eq 3). Values of k_1 ($0.88 \pm 0.03 \times 10^{-4} \text{ s}^{-1}$) and k_2 ($0.34 \pm 0.04 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$) were determined from a graph (Figure 3) of k_{obs} vs. $\text{P}(\text{OPh})_3$ concentration according to equation 3. The k_1 term presumably corresponds to a

$$k_{\text{obs}} = k_1 + k_2[\text{P}(\text{OPh})_3] \quad (3)$$

pathway in which rate-determining dissociation of the $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]^+$ from **4a** is followed by rapid addition of $\text{P}(\text{OPh})_3$ to give the $[\text{CpRu}(\text{CO})_2(\text{P}(\text{OPh})_3)]^+$ product. The k_2 term in the rate law most likely corresponds to a dissociative interchange (I_d) mechanism (where the nature of the $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(\text{S}), \eta^6\text{-DBT})\text{RuCp}^*][\text{PF}_6] \cdot \text{P}(\text{OPh})_3$ intermediate is not clear) as was previously described in the kinetic reactions of $[\text{Cp}^*\text{Ru}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})]^+$.

DBTh][BF₄] with PPh₃ and PPh₂Me, where DBTh = DBT, 4-MeDBT, 4,6-Me₂DBT or 2,8-Me₂DBT.^{6b} However, an associative or nucleophilic pathway for k_2 cannot be ruled out, since reactions of **4a** with a 10-fold excess of the more nucleophilic PPh₂Me under the same conditions (CD₃NO₂ solvent, 25.0 °C) were complete before the first ¹H NMR spectrum could be taken (~5 min.), forming two different products with separate Cp and PPh₂Me ¹H NMR signals. These products are presumably [CpRu(CO)₂(PPh₂Me)]⁺ (for Cp, δ = 5.73, 5H; for PPh₂Me, δ = 2.49, d, ³J(P,H) = 10.5 Hz, 3H) and [CpRu(CO)(PPh₂Me)₂]⁺ (for Cp, δ = 5.34, 5H; for PPh₂Me, δ = 2.01, d, ³J(P,H) = 13.3 Hz, 6H) based on comparisons with ¹H NMR data for [CpRu(CO)₂(PPh₃)]⁺,²⁰ [CpRu(CO)(PPh₃)₂]⁺,²¹ [CpRu(CO)₂(PPh₂Me)]⁺,¹² [(CpRu(CO)(PPh₃)(PPh₂Me)]⁺,¹² and [(CpRu(CO)(PPh₂Me)₂]⁺,²² that have been previously reported.

In a previous kinetic study^{6b} of the reactions (eq 4) of [CpRu(CO)₂(η^1 (S)-DBTh)]⁺ complexes (where DBTh = DBT, 4-MeDBT, 4,6-Me₂DBT, and 2,8-Me₂DBT) with P(OPh)₃

under the same reaction conditions (CD₃NO₂, 25.0°C), the k_1 values decreased in the following order: 4,6-Me₂DBT (5.18(5) x 10⁻⁶ s⁻¹) > 4-MeDBT (4.50(10) x 10⁻⁶ s⁻¹) > DBT (4.01(3) x 10⁻⁶ s⁻¹) > 2,8-Me₂DBT (1.33(5) x 10⁻⁶ s⁻¹).^{6b} In that study, methyl groups in the sterically-hindering 4- and 6-positions of DBT were found to increase the kinetic lability of DBT by factors of 1.13 and 1.31, respectively, for 4-MeDBT and 4,6-Me₂DBT. On the other hand, electron-donating methyl groups in the non-hindering 2,8-positions of DBT reduced the rate by a factor of 0.23. The k_1 value (0.88 x 10⁻⁴ s⁻¹) determined in the present study for the dissociation of [Cp*Ru(η^6 -DBT)]⁺ from **4a** shows that η^6 -coordination of a {Cp*Ru}⁺

fragment to the DBT increases the kinetic lability of the DBT ligand by a factor of 22 times as compared to the DBT ligand itself. Thus, the $\{\text{Cp}^*\text{Ru}\}^+$ fragment labilizes the Ru-S bond much more than placing methyl groups in the 4- and 6-positions. The labilizing effect of the $\{\text{Cp}^*\text{Ru}\}^+$ group is presumably due to the electron-withdrawing ability of the $\{\text{Cp}^*\text{Ru}\}^+$ cationic group, which reduces the electron-donating ability of the DBT sulfur atom.

In order to determine the relative thermodynamic binding abilities of DBT and $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]^+$, 0.020 mmol of **4a** was reacted (eq 5) with 0.020 mmol of DBT in 1.0 mL of CD_3NO_2 at 25.0 °C. This resulted in complete displacement of the $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]^+$

ligand by DBT within 8 hours to form only $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})]^+$ and $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]^+$. When the products in eq 5, 0.020 mmol $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]^+$ and 0.20 mmol $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]^+$, were reacted in 1.0 mL of CD_3NO_2 at 25.0 °C, there was no reaction after 1 day. Thus, the η^6 -coordination of $\{\text{Cp}^*\text{Ru}\}^+$ to DBT also substantially reduces the thermodynamic binding ability of DBT to $\{\text{CpRu}(\text{CO})_2\}^+$.

Conclusions

Dibenzothiophene forms a new type of dinuclear complex in which the DBT is $\eta^1(\text{S})$ -coordinated to a $\{\text{CpRu}(\text{CO})_2\}^+$ group and η^6 -coordinated to $\{\text{Cp}^*\text{Ru}\}^+$. An X-ray study of $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(\text{S}),\eta^6\text{-DBT})\text{RuCp}^*][\text{PF}_6]_2$ (**4a**) shows that the two ruthenium moieties are on opposite sides of the planar DBT ligand. Infrared studies suggest that the Ru-S bond in

the $\{\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})\}^+$ portion of **4a** is weakened by attachment of the $\eta^6\text{-}\{\text{Cp}^*\text{Ru}\}^+$ group to the DBT. This weakening is reflected in a much faster rate of dissociation of $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]^+$ than DBT from $[\text{CpRu}(\text{CO})_2(\eta^1(\text{S})\text{-L})]^+$, where $\text{L} = \text{DBT}$ or $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]^+$. Equilibrium studies also show that $[\text{Cp}^*\text{Ru}(\eta^6\text{-DBT})]^+$ is much less strongly coordinated than DBT to $\{\text{CpRu}(\text{CO})_2\}^+$.

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Figure 1. Numbering schemes for dibenzothiophene (DBT) and benzothiophene (BT).

Figure 2. Thermal ellipsoid drawing (ORTEP) of $[\text{CpRu}(\text{CO})_2(\mu_2-\eta^1(\text{S}), \eta^6\text{-DBT})\text{RuCp}^*][\text{PF}_6]_2 \cdot 2(\text{CH}_3)_2\text{CO}$ (**4a**•2(CH₃)₂CO). Ellipsoids are shown at the 50% probability level; hydrogen, anion and solvent atoms are omitted for clarity. The Ru-S bond distance is 2.392(1) Å and the angle defined by Ru-S-Midpt is 114.5°.

Figure 3: Plot of k_{obs} vs P(OPh)_3 concentration (eq 3) for reactions with $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(\text{S}),\eta^6\text{-DBT})\text{Cp}^*\text{Ru}][\text{PF}_6]_2$ at 25.0 °C in CD_3NO_2 .

Table 1. Crystal Data and Structure Refinement for $[\text{CpRu}(\text{CO})_2\{\mu_2-\eta^1(\text{S}),\eta^6\text{-DBT}\}\text{RuCp}^*][\text{PF}_6]_2$ (**4a**).

COMPOUND	$[\text{CpRu}(\text{CO})_2\{\mu_2-\eta^1(\text{S}),\eta^6\text{-DBT}\}\text{RuCp}^*](\text{PF}_6)_2 \cdot 2(\text{CH}_3)_2\text{CO}$ (4a)
Empirical formula	$\text{C}_{29}\text{H}_{28}\text{F}_{12}\text{O}_2\text{P}_2\text{Ru}_2\text{S} \cdot 2 \text{C}_3\text{H}_6\text{O}$
Formula weight	1048.81
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	$a = 14.475(3)$ Å $b = 13.038(2)$ Å $c = 21.687(3)$ Å $\alpha = 90.000^\circ$ $\beta = 95.772(5)^\circ$ $\gamma = 90.000^\circ$
Volume	4072.0(12) Å ³
Z	4
Density (calculated)	1.711 Mg/m ³
Absorption coefficient	0.963 mm ⁻¹
$F(000)$	2096
Crystal size	0.30 x 0.30 x 0.23 mm ³
θ range for data collection	1.82 to 28.19°
Index ranges	$-18 \leq h \leq 13$, $-15 \leq k \leq 15$, $-28 \leq l \leq 8$
No. of reflns collected	13059
No. of ind reflns	6448 [$R(\text{int}) = 0.0358$]
Completeness to $\theta =$	22.00° = 96.5%
Absorption correction	Semi-empirical from equivalents
Max. and Min. transmn.	1.00 and 0.71
Refinement method	full-matrix least-squares on F^2
Data / restraints / params.	6448 / 0 / 505
Goodness-of-fit on F^2	1.042
Linear R^a indices [$I > 2\sigma(I)$]	$R1 = 0.0325$, $wR2 = 0.0869$
R^a indices (all data)	$R1 = 0.0376$, $wR2 = 0.0900$
Largest diff peak and hole	0.698 and -0.450 e Å^{-3}

^a $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $wR2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$

Table 2. Rate constants, k_{obs} (s^{-1}), for reactions (eq 2) of 0.020 M $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(\text{S}),\eta^6\text{-DBT})\text{RuCp}^*][\text{PF}_6]_2$ with $\text{P}(\text{OPh})_3$ at 25.0 °C in CD_3NO_2 .

$[\text{P}(\text{OPh})_3]$ (M)	$10^4 k_{\text{obs}}, \text{s}^{-1}$
0.20	0.934
	0.946
	0.965
0.40	0.996
	1.00
	1.01
0.60	1.10
	1.11
	1.12
0.80	1.12
	1.14
	1.15
1.00	1.21
	1.22
	1.27

CHAPTER 5: SYNTHESIS AND STRUCTURE OF A DIMETALLATED BUCKYBOWL: COORDINATION OF ONE $\{\text{Cp}^*\text{Ru}\}^+$ UNIT TO EACH SIDE OF CORANNULENE

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Abstract

Reaction of $[\text{Cp}^\text{Ru}(\mu_3\text{-Cl})]_4$ with Ag^+ and the curved-surface bucky bowl corannulene ($\text{C}_{20}\text{H}_{10}$, **1**) in CD_3NO_2 solvent affords the dimetallated corannulene complex $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})]^{2+}$ (**2**). An X-ray structure analysis of $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{PF}_6]_2$ (**2b**) shows a $\{\text{Cp}^*\text{Ru}\}^+$ moiety η^6 -coordinated to each side of a significantly flattened corannulene.*

In the numerous transition metal complexes of buckminsterfullerene (C_{60}),^[1] the metal is bonded to two carbon atoms (η^2) shared by two six-membered rings. On the other hand, curved-surface fragments of C_{60} , called buckybowls, are difficult to prepare and few transition metal complexes of them have been reported.^[2-4] Improved procedures for the

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synthesis of corannulene^[5,6] ($C_{20}H_{10}$, **1**) have led to the preparation of the η^6 complexes $[Cp^*Ru(\eta^6-C_{20}H_{10})](O_3SCF_3)^{[3]}$ and $[Cp^*Ir(\eta^6-C_{20}H_{10})](BF_4)_2^{[14]}$ where $Cp^* = \eta^5-C_5Me_5$. Although these complexes have been well-characterized by their NMR spectra, neither has been isolated as the analytically pure solid. Recently, the (solventless) gas-phase deposition synthesis of $[[Rh_2(O_2CCF_3)_4]_m \cdot (C_{20}H_{10})_n]$ ($m:n = 1:1$ and $3:2$), were reported.^[12a] Their structures, as determined by X-ray diffraction studies, contain 1- and 2-dimensional networks of $Rh_2(O_2CCF_3)_4$ and corannulene units in which the Rh_2 groups are η^2 -coordinated to both the convex and concave sides of the corannulene. These are the only crystal structures of transition metal complexes of corannulene. In the present work, we report the first X-ray structural characterization of a corannulene containing η^6 -coordinated metal fragments. Of particular interest are the observations that the two $\{Cp^*Ru\}^+$ fragments are on opposite sides of the corannulene bowl, which is significantly flattened as compared to free corannulene.

The reaction of $[Cp^*Ru(\mu_3-Cl)]_4^{[7]}$ (0.020 mmol) with $AgBF_4$ (for **2a**) or $AgPF_6$ (**2b**) (0.081 mmol) and **1** (0.040 mmol) in a 2:1 ratio of $\{Cp^*Ru\}^+$ to $C_{20}H_{10}$ in CD_3NO_2 under an Ar atmosphere at room temperature gave the dimetallated complex $[(Cp^*Ru)_2(\mu_2-\eta^6, \eta^6-C_{20}H_{10})]X_2$ ($X = BF_4^-$ (**2a**), PF_6^- (**2b**)) (Figure 1). Both **2a** and **2b** are stable in CD_3NO_2 and CH_2Cl_2 , very soluble in CD_3NO_2 , and moderately soluble in CH_2Cl_2 at room temperature. They are insoluble in diethyl ether and hexanes, and the $\{Cp^*Ru\}^+$ units are displaced from the corannulene when the complex is dissolved in acetone. In the solid state, **2a** and **2b** are stable under atmospheric conditions for weeks. After 1 week, a solution of **2b** in CD_3NO_2 exposed to air decomposed ~50% to $[Cp^*Ru(\eta^6-C_{20}H_{10})]^+$ with no evidence for free

corannulene in the ^1H NMR spectrum. Shaking a CD_3NO_2 solution of **2b** with water results in fast decomposition with the liberation of free corannulene. While the existence of $[(\text{Cp}^*\text{Ru})_2(\mu_2-\eta^6, \eta^6-\text{C}_{20}\text{H}_{10})]^{2+}$ was previously proposed on the basis of unspecified NMR data,^[3] it was not further characterized.

The ^1H NMR spectrum of **2a** in the corannulene region (Figure 2) has signals in the narrow range (6.87-6.74) that are shifted upfield with respect to the signal of free corannulene (e.g., $\delta = 7.92$ ppm for **1** in CD_3NO_2). These protons (H1, H2, H5, H6), which are doublets with J_{HH} values of 6 Hz, are assigned to the 6-membered rings that are η^6 -coordinated to the $\{\text{Cp}^*\text{Ru}\}^+$ units. Such upfield shifts are typical of other $[\text{Cp}^*\text{Ru}(\eta^6\text{-arene})]^+$ compounds.^[7,8] The chemical shifts of the protons on the carbons not bonded to Ru are downfield of free corannulene, as is observed in $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})]^{+[3]}$ and $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_{20}\text{H}_{10})]^{2+}$.^[4] These six protons appear as two doublets ($J_{\text{HH}} = 9$ Hz) and a singlet. Only one methyl peak is observed in the ^1H NMR spectrum, and it integrates to 30 H. A COSY NMR experiment was carried out on complex **2a**, and used to aid in the assignment of the proton chemical shifts. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2a** shows six carbon signals between 98.7 and 81.1 ppm, which were assigned to the carbons bonded directly to the two Ru atoms. These signals are substantially upfield with respect to the uncoordinated carbon atoms (140.2 – 126.7 ppm) and free corannulene (136.3, 132.0 and 128.2 ppm for **1** in CD_3NO_2), a trend that is also observed in other $[\text{Cp}^*\text{Ru}(\eta^6\text{-arene})]^+$ complexes.^[7,8] The NMR data clearly show that the ruthenium atoms are η^6 coordinated to two of the six-membered rings of corannulene.

Orange crystals of $[(\text{Cp}^*\text{Ru})_2(\mu_2-\eta^6, \eta^6-\text{C}_{20}\text{H}_{10})][\text{PF}_6]_2$ (**2b**) suitable for an X-ray structure investigation were grown by inverse diffusion of a saturated methylene chloride solution of the complex surrounded by hexanes at $-25\text{ }^\circ\text{C}$ over a period of one week.^[9] The crystals, which contained 4 molecules of CH_2Cl_2 per unit cell, quickly deteriorated when removed from the methylene chloride solution. The structure reveals that the $\{\text{Cp}^*\text{Ru}\}^+$ units bind to both the convex and concave sides of the $\text{C}_{20}\text{H}_{10}$ bowl (Figure 3). Coordination of the two $\{\text{Cp}^*\text{Ru}\}^+$ cations to the corannulene causes significant structural changes in the shape of the bowl. Differences in bond lengths are observed in the 6-membered rings to which the $\{\text{Cp}^*\text{Ru}\}^+$ groups are coordinated; in these rings, the $\text{HC}=\text{CH}$ rim bonds are elongated to an average of $1.454(11)\text{ \AA}$ from $1.402(5)\text{ \AA}$ in free corannulene.^[10] This elongation releases some strain in the corannulene subunit of **2b** causing a notable flattening of the bowl as compared to **1**. The diminished curvature of the coordinated bowl is clearly demonstrated by a π -orbital axis vector (POAV) analysis.^[11] (Figure 4). The pyramidalization angles of the five central carbon atoms and those that are attached to them are on average 4.2° and 1.3° in **2b**, respectively, while the analogous values for corannulene and its derivatives are 8.4° and 3.8° , respectively.^[11,12] Thus, the curvature of the corannulene bowl in **2b** is reduced to approximately half of the curvature of corannulene. A closer view of the POAV values shows that they are smaller for the carbon atoms bonded to the convex $\{\text{Cp}^*\text{Ru}\}^+$ unit ($0.8, 3.5, 3.7, 0.5^\circ$) than for those bonded to the concave $\{\text{Cp}^*\text{Ru}\}^+$ unit ($2.1, 4.3, 4.4, 1.2^\circ$). This flattening of the bowl might be expected to reduce the barrier to inversion of the $\text{C}_{20}\text{H}_{10}$ bowl, which is known to have a barrier of 10-11 kcal/mol in corannulenes functionalized by organic groups on the rim carbons.^[13] A previous investigation of corannulene derivatives showed that a flattening of the bowl leads to a decrease in the bowl inversion barrier.^[13b] The

methyl carbons of the two Cp* ligands occur as a singlet in the room temperature ^{13}C NMR spectrum of **2b** in CD_2Cl_2 indicating rapid inversion of the bowl. Due to the insolubility of **2b** in CD_2Cl_2 at low temperatures, separate resonances for the convex and concave $\{\text{Cp}^*\text{Ru}\}^+$ groups have not been observed.

Besides the different effects that the concave and convex $\{\text{Cp}^*\text{Ru}\}^+$ units have on the flattening of the bowl, they also appear to interact with the six ring carbons differently. The Ru2-C distances for the concave $\{\text{Cp}^*\text{Ru}\}^+$ unit are significantly shorter to the rim carbons (C5, C6) (2.170(8) Å) than to the other four carbons (C14, C20, C19, C13) (2.264(7) Å). However, the Ru1-C distances for the convex $\{\text{Cp}^*\text{Ru}\}^+$ group are significantly longer to carbons C11 and C12 (2.345(7) Å) than to the other four carbons (C1, C2, C18, C17) (2.213(7) Å). Although these results await a theoretical interpretation, it is obvious that the binding of $\{\text{Cp}^*\text{Ru}\}^+$ is different to the two sides of the bowl. It should be noted that a study of $[\text{Cp}^*\text{Ru}(\eta^6\text{-fluoradene})]^+$,^[8] where fluoradene ($\text{C}_{19}\text{H}_{12}$) is another type of curved surface hydrocarbon, showed that $\{\text{Cp}^*\text{Ru}\}^+$ binds more strongly to the concave side than to the convex side.

In conclusion, complex **2b** is the first structurally characterized compound in which a buckybowl is η^6 -coordinated. The $\{\text{Cp}^*\text{Ru}\}^+$ moieties bind to non-adjacent arene rings on opposite sides of corannulene, and ^{13}C NMR evidence shows that the bowl undergoes rapid inversion at room temperature. Coordination of the $\{\text{Cp}^*\text{Ru}\}^+$ fragments significantly reduces the overall curvature of the buckybowl, with the convex $\{\text{Cp}^*\text{Ru}\}^+$ group causing a greater flattening than the concave $\{\text{Cp}^*\text{Ru}\}^+$ unit. These substantial structural effects of the $\{\text{Cp}^*\text{Ru}\}^+$ units, which contrast with the absence of significant structural changes upon η^2 -coordination to $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$.^[2a]

Experimental Section

Synthesis and Characterization of $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})](\text{X})_2$ ($\text{X} = \text{BF}_4^-$ (2a**), PF_6^- (**2b**)).** To a solution of 0.022 g (0.020 mmol) of $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ and 0.010 g (0.040 mmol) of corannulene (**1**) in 1 mL of CD_3NO_2 was added 0.081 mmol of AgBF_4 or AgPF_6 . The solution was stirred at room temperature for 1 h, and the AgCl precipitate was removed by filtration. The resulting dark orange solution was evaporated to dryness under vacuum to give an oily residue of **2a** or **2b**. These reactions are nearly quantitative by NMR spectroscopy. The residue was washed with diethyl ether (2×3 mL) and dried under vacuum. After dissolving **2a** or **2b** in 1-2 mL of CH_2Cl_2 , the resulting solution was added to ~5 mL of hexanes via cannula to give orange powders (0.034 g, 85% yield, for **2b**). ^1H NMR (400.13 MHz, CD_3NO_2 , RT, **2a**): δ = 8.51 (d, $^3J(\text{H},\text{H})$ = 9 Hz, 2H, H8,9), 8.20 (s, 2H, H3,4), 8.17 (d, $^3J(\text{H},\text{H})$ = 9 Hz, 2H, H7,10), 6.87 (d, $^3J(\text{H},\text{H})$ = 6 Hz, 2H, H1,6), 6.80 (d, $^3J(\text{H},\text{H})$ = 6 Hz, 2H, H2,5), 1.27 (s, Cp^* , 30H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CD_3NO_2 , RT, **2a**): δ = 135.1 (C8,9), 132.2 (C3,4), 128.8 (C7,10), 98.7 (C-Ru), 98.5 (C-Ru), 96.9 (C-Ru), 96.8 (C_5Me_5), 95.6 (C-Ru), 86.9 (C2,5), 85.8 (C1,6), 9.0 (C_5Me_5), 135.6, 132.7 (C15, C16). MS m/z 362 ($[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})]^{2+}$), electrospray in CD_3NO_2 . Anal. Calcd for $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})](\text{PF}_6)_2 \cdot 1\text{CH}_2\text{Cl}_2$: C, 44.86; H, 3.86. Found: C, 45.32; H, 3.99. The presence of CH_2Cl_2 in the sample was confirmed by an ^1H NMR spectrum of the compound in CD_3NO_2 .

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solution of the complex surrounded by hexanes at -25 °C over a period of one week. The crystals decomposed within seconds if contacted with air, and were therefore covered with premixed epoxy glue under the layer of solvent. The sample was immediately mounted under a stream of cold nitrogen and centered in the X-ray beam using a video camera for data collection. $\text{C}_{40}\text{H}_{40}\text{F}_{12}\text{P}_2\text{Ru}_2 \cdot 4\text{CH}_2\text{Cl}_2$, $M = 1352.50$, triclinic, space group $P\bar{1}$, $a = 11.351(4)$ Å, $b = 12.414(4)$ Å, $c = 19.508(7)$ Å, $\alpha = 89.068(6)^\circ$, $\beta = 74.322(6)^\circ$, $\gamma = 82.114(6)^\circ$, $V = 2620.9(16)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.714$ g cm⁻³; crystal dimensions 0.30 x 0.20 x 0.20 mm. A total of 23448 reflections (11787 unique, $R_{\text{int}} = 0.0398$) were collected using a full-sphere ω -scan routine ($2\theta_{\text{max}} = 56.64^\circ$) with Bruker SMART APEX CCD diffractometer, $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) at $T = 193(2)$ K. Data were corrected for absorption effects by empirical methods using SADABS software (min/max. transmission 0.67). The structure was solved by direct methods and refined against using the SHELXTL (version 5.1) software package in full-matrix anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms were placed at idealized positions and refined using the "riding model". The refinement converged to $R1 = 0.0760$, $wR2 = 0.2048$ for $I > 2\sigma(I)$, and $R1 = 0.1076$, $wR2 = 0.2357$ for all data, and a goodness-of-fit of 1.048. All significant electron density residuals were found approximately 1 Å from Ru atoms. CCDC-236736 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Figure 1. Atom labeling scheme for compound **2**.

Figure 2. ^1H NMR spectrum of the corannulene region of **2a** in CD_3NO_2 .

Figure 3. Thermal ellipsoid drawing of $[(\text{Cp}^*\text{Ru})_2(\mu_2-\eta^6, \eta^6-\text{C}_{20}\text{H}_{10})][\text{PF}_6]_2$ (**2b**). Ellipsoids are shown at the 30% probability level; hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ru1-C1, 2.219(7); Ru1-C2, 2.214(6); Ru1-C12, 2.346(6); Ru1-C18, 2.209(6); Ru1-C17, 2.209(6); Ru1-C11, 2.343(7); Ru2-C5, 2.171(8); Ru2-C6, 2.169(7); Ru2-C14, 2.266(7); Ru2-C20, 2.276(7); Ru2-C19, 2.264(7); Ru2-C13, 2.263(7).

Figure 4. POAV pyramidalization angles and C-C bond lengths (Å) as found in corannulene (**1**) and $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})](\text{PF}_6)_2 \cdot 4\text{CH}_2\text{Cl}_2$ (**2b**). Only the carbon atoms of the corannulene are shown for clarity.

Appendix

General Considerations. All manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. Diethyl ether and methylene chloride were purified on alumina using a Solv-Tech solvent purification system, as described by Grubbs and co-workers.^a Deuterated nitromethane was purchased from Aldrich and subjected to three freeze-pump-thaw cycles before use. Corannulene^b and $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})_4]^{\text{c}}$ were synthesized following published methods. All other chemicals (AgBF_4 , AgPF_6 , 99.99+%) were used without further purification as purchased from Aldrich. Filtrations were performed with Celite on filter paper. NMR spectra were obtained on a Bruker DRX-400 spectrometer using CD_3NO_2 as solvent, internal lock, and internal reference ($\delta = 4.33$). Electrospray ionization mass spectra were obtained on a Finnigan TSQ700 triple quadrupole mass spectrometer Finnigan MAT, San Jose, CA, fitted with a Finnigan ESI interface (Finnigan MAT, San Jose, CA). Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer.

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Figure A1. ^1H NMR spectrum (top) and ^{13}C NMR spectrum (middle) of free corannulene (**1**, bottom) in CD_3NO_2 .

Figure A2. ^1H NMR spectrum of **2a** in CD_3NO_2 .

Figure A3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the corannulene region of **2a** in CD_3NO_2 .

Figure A4. COSY NMR spectrum of the corannulene region of **2a** in CD_3NO_2 .

Figure A5. HETCOR NMR spectrum of the corannulene region of **2a** in CD_3NO_2 .

CHAPTER 6: FLATTENING OF A CURVED-SURFACE BUCKBOWL BY η^6 -COORDINATION TO $\{\text{Cp}^*\text{Ru}\}^+$

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Abstract

The corannulene complex $[\text{Cp}^\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})]^+$ (3^+), where $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, prepared by the reaction of $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ with Ag^+ and the curved-surface buckybowl corannulene ($\text{C}_{20}\text{H}_{10}$, **1**), has a structure in which the bowl is flattened in the region where the $\eta^6\text{-}\{\text{Cp}^*\text{Ru}\}^+$ unit is attached to it. The corannulene group in $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{PF}_6]_2$ (**4** [PF_6]₂), containing two $\eta^6\text{-}\{\text{Cp}^*\text{Ru}\}^+$ units coordinated on opposite sides of the corannulene, is flattened substantially more. The X-ray-determined structure of the analogous SbF_6^- salt, $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6\text{-}\eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]_2$ (**4** [SbF_6]₂) shows that the corannulene bowl is almost completely flat. Low temperature NMR studies of the analogous 1,2,5,6-tetramethylcorannulene complex $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6\text{-}\eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)]^{2+}$ (**6**²⁺) show that there is a very low barrier to inversion of the bowl even at -90°C .*

Introduction

The discovery of buckminsterfullerene (C_{60}),¹ commonly known as "buckyball", in the 1980's has led to a renewed interest in the chemistry of curved carbon surfaces. Those compounds that have carbon atom frameworks that can be identified on the surface of C_{60} have been termed "buckybowls".² Buckybowl compounds differ from traditional polyaromatic hydrocarbons in that they are strained (curved) and contain both concave and convex surfaces. The smallest buckybowl compound is corannulene ($C_{20}H_{10}$, **1**), which may be described as the cap of C_{60} (Fig. 1). It was first prepared in 1966 by a multi-step reaction sequence.³ Its molecular structure was determined by Hanson in 1976,⁴ confirming the curved nature of corannulene that results from the fusion of five six-membered rings around a five carbon atom core. The low overall yields obtained using the early procedures made it difficult to obtain quantities of corannulene suitable for extensive investigation. Recently, improved syntheses of corannulene⁵ have enabled new research into its chemistry and reactivity.

Although both C_{60} and corannulene are curved carbon surfaces, they exhibit very different reactivities from one another. In transition metal complexes of C_{60} ,⁶ the metal is always bonded η^2 to two carbon atoms, and although C_{60} contains 20 six-membered rings, there are no reported examples of a complex in which C_{60} is η^6 -coordinated to a transition metal. In the first reported transition metal complexes of corannulene, the metal fragments are bound η^6 to the carbon atoms of a six-membered ring.⁷⁻⁹ More recently, the η^2 corannulene complexes $[[Rh_2(O_2CCF_3)_4]_m \cdot (C_{20}H_{10})_n]$ ($m:n = 1:1$ and $3:2$) were prepared by a gas-phase deposition method.¹⁰ An X-ray structural investigation of these compounds showed that the Rh_2 units are η^2 coordinated to both the convex and concave sides of the

corannulene in 1- and 2-dimensional arrays. The structures of the corannulene units in the η^2 complexes were not significantly different than that of free corannulene.⁴

We recently communicated the synthesis and X-ray structural characterization of $[(\text{Cp}^*\text{Ru})_2(\mu_2-\eta^6, \eta^6-\text{C}_{20}\text{H}_{10})][\text{PF}_6]_2$ (**4** $[\text{PF}_6]_2$) where $(\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5)$.⁹ The structural results showed that the two $\{\text{Cp}^*\text{Ru}\}^+$ fragments are η^6 bound to non-adjacent rings on opposite sides of the corannulene. Significant flattening of the corannulene ligand upon coordination of the $\{\text{Cp}^*\text{Ru}\}^+$ units was observed; the convex $\{\text{Cp}^*\text{Ru}\}^+$ group caused a greater flattening than the concave $\{\text{Cp}^*\text{Ru}\}^+$ unit. Solution NMR studies indicated that the corannulene unit undergoes rapid inversion at room temperature. In this report, we describe the dramatic effect of one and two $\eta^6\text{-}\{\text{Cp}^*\text{Ru}\}^+$ groups on the shape of the corannulene ligand in $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]$ (**3** $[\text{SbF}_6]$) and $[(\text{Cp}^*\text{Ru})_2(\mu_2-\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]_2$ (**4** $[\text{SbF}_6]_2$) (Fig. 2).

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Methylene chloride (CH_2Cl_2), diethyl ether (Et_2O), and hexanes were purified on alumina using a Solv-Tek solvent purification system, similar to that reported by Grubbs and co-workers.¹¹ Methylene chloride- d_2 (CD_2Cl_2) was refluxed overnight with calcium hydride, distilled, and subjected to three freeze-pump-thaw cycles before use. Nitromethane- d_3 (CD_3NO_2) was purchased from Aldrich and subjected to three freeze-pump-thaw cycles before use. Corannulene (**1**),^{5a} 1,2,5,6-tetramethylcorannulene (**2**, Fig. 2),^{5a} and $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ ¹² were synthesized following published methods. The complexes $[(\text{Cp}^*\text{Ru})_2(\mu_2-\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{X}]_2$, where $\text{X} = \text{BF}_4^-$ and PF_6^- , were synthesized as

reported previously.⁹ All other chemicals (AgBF₄, AgPF₆, AgSbF₆, 99.99+%) were used without further purification as purchased from Aldrich. Filtrations were performed through a plug of filter paper, Celite, and cotton that was prepared from a cut 1 mL syringe, and the solutions were transferred via thin-wall Teflon tubing (Alpha Wire Corporation). All of the {Cp*Ru}⁺ complexes of **1** and **2** are sensitive to moisture. They are stable for hours exposed to dry air in both the solid state and in CD₃NO₂ solution.

Solution NMR spectra were obtained on a Bruker DRX-400 spectrometer using either CD₃NO₂ or CD₂Cl₂ as the solvent, internal lock, and internal reference (δ = 4.33 (¹H), 62.8 (¹³C) and 5.32 (¹H), 54.0 (¹³C) respectively). Electrospray ionization mass spectra were obtained on a Finnigan TSQ700 triple quadrupole mass spectrometer (Finnigan MAT, San Jose, CA) fitted with a Finnigan ESI interface. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer.

Synthesis of [Cp*Ru(η^6 -C₂₀H₁₀)][X]**, **3**[BF₄], **3**[PF₆], **3**[SbF₆].** To a flask containing freshly prepared [Cp*Ru(μ_3 -Cl)]₄ (11.0 mg, 0.0101 mmol), corannulene (**1**, 10.2 mg, 0.0407 mmol) and either AgBF₄, AgPF₆ or AgSbF₆ (0.0420 mmol) was added 1 mL of CD₃NO₂. The solution was stirred at room temperature for 15 min, and the AgCl precipitate was removed by filtration. The resulting orange solution was evaporated to dryness under vacuum to give an oily residue of **3**[X]. These reactions are nearly quantitative as indicated by NMR spectroscopy. The dark orange residue was then washed with diethyl ether (2 $\times$ 3 mL) and dried under vacuum. After dissolving **3**[X] in 1-2 mL of CH₂Cl₂, the resulting solution was then filtered into 5 mL of hexanes to give orange powders of [Cp*Ru(η^6 -C₂₀H₁₀)]**[X]** (23.2 mg, 91% yield, for **3**[PF₆]; yields of the BF₄⁻ and SbF₆⁻ salts were similarly high). Anal. Calcd for **3**[SbF₆] $\cdot$ 2H₂O: C, 47.51; H, 3.85. Found: C, 47.01; H, 3.71. The solution NMR

spectrum of $3[\text{PF}_6]$ is very similar to that of $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{O}_3\text{SCF}_3]$ that was prepared via a different route and reported previously.⁷

Synthesis and Characterization of $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]_2$, $4[\text{SbF}_6]$.

To a flask containing freshly prepared $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ (22.0 mg, 0.0202 mmol), corannulene (**1**, 10.0 mg, 0.0400 mmol), and AgSbF_6 (28.5 mg, 0.0830 mmol) was added 1 mL of CD_3NO_2 . The solution was stirred at room temperature for 1 h, and the AgCl precipitate was removed by filtration. The resulting dark orange solution was evaporated to dryness under vacuum to give a residue of $4[\text{SbF}_6]$. These reactions are nearly quantitative as indicated by NMR spectroscopy. The dark-orange residue was dissolved in 5 mL of CH_2Cl_2 and filtered into 10 mL of hexanes to give $4[\text{SbF}_6]$ (39.1 mg, 82% yield) as an orange solid. The ^1H NMR spectrum of the compound was nearly identical to that reported previously for $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{BF}_4]_2$.⁹

Synthesis and Characterization of $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)][\text{X}]$, $5[\text{BF}_4]$, $5[\text{PF}_6]$, $5[\text{SbF}_6]$. To a flask containing freshly prepared $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ (11.0 mg, 0.0101 mmol), 1,2,5,6-tetramethylcorannulene (**2**, 12.5 mg, 0.0408 mmol) and either AgBF_4 , AgPF_6 or AgSbF_6 (0.0420 mmol) was added 1 mL of CD_3NO_2 . The solution was stirred at room temperature for 15 min, and the AgCl precipitate was removed by filtration. The resulting dark orange solution was evaporated to dryness under vacuum. The residue was washed with diethyl ether (2×3 mL) and dried under vacuum to give $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)][\text{X}]$ (25.0 mg, 90% yield for $5[\text{PF}_6]$) as an orange solid consisting of two isomers, 5A^+ and 5B^+ (see Figure 3 for labeling scheme) in a 2:1 ratio, respectively.. Sometimes the dark orange residue was oily, and solid samples could often be obtained by dissolving it in 1-2 mL of CH_2Cl_2 and

filtering into 5 mL of hexanes to give orange powders. Slow cooling of a CH_2Cl_2 solution (or slow diffusion of diethyl ether into a CH_2Cl_2 solution) at $-25\text{ }^\circ\text{C}$ with careful exclusion of H_2O also yielded solid products, although the $5\text{A}^+ : 5\text{B}^+$ isomer ratio in the solid was different each time. Recrystallization as described above often resulted in the enrichment of one isomer over the other, which aided in the chemical shift assignments of the two isomers. ^1H NMR (400.13 MHz, CD_3NO_2 , RT, $5[\text{SbF}_6]$): For $5\text{A}[\text{SbF}_6]$, δ 8.23 (d, $^3J(\text{H,H}) = 9.2\text{ Hz}$, 1H, H9), 8.07 (d, $^3J(\text{H,H}) = 8.8\text{ Hz}$, 1H, H6), 7.94 (d, $^3J(\text{H,H}) = 8.8\text{ Hz}$, 1H, H5), 7.62 (d, $^3J(\text{H,H}) = 9.2\text{ Hz}$, 1H, H10), 6.46-6.42 (AB quartet, $^3J(\text{AB}) = 5.8\text{ Hz}$, 2H, H1 and H2), 2.83 (d, $^5J(\text{H,H}) = 0.8\text{ Hz}$, 3H, Me), 2.75 (s, 3H, Me), 2.73 (s, 3H, Me), 2.62 (q, $^5J(\text{H,H}) = 0.8\text{ Hz}$, 3H, Me), 1.25 (s, 15H, Cp*) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CD_3NO_2 , RT, $5\text{A}[\text{SbF}_6]$), δ 84.47 and 98.55 (C1 and C2); 82.10, 94.90, 97.00, 101.59 (Ru-C); 125.55, 127.74, 128.66, 133.16 (C5, C6, C9, C10); 140.86, 137.97, 137.03, 136.49, 134.94, 134.74, 134.06, 133.70, 133.28, 130.64 (non-hydrogen containing C not bonded to Ru, $\text{C}_{20}\text{H}_6\text{Me}_4$); 15.94, 15.90, 15.68, 15.41 ($\text{C}_{20}\text{H}_6\text{Me}_4$); 94.55, 9.60 (C_5Me_5). For $5\text{B}[\text{SbF}_6]$, δ 8.05 (d, $^3J(\text{H,H}) = 8.8\text{ Hz}$, 2H, H6,7), 7.98 (d, $^3J(\text{H,H}) = 8.8\text{ Hz}$, 2H, H5,8), 6.45 (s, 2H, H1,2), 2.83 (d, $^5J(\text{H,H}) = 0.8\text{ Hz}$, 6H, Me), 2.61 (d, $^5J(\text{H,H}) = 0.8\text{ Hz}$, 6H, Me), 1.37 (s, 15H, Cp*) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CD_3NO_2 , RT, $5\text{B}[\text{SbF}_6]$): δ 15.97, 15.78 ($\text{C}_{20}\text{H}_6\text{Me}_4$), 94.82, 9.95 (C_5Me_5). The carbons of the corannulene ligand in $5\text{B}[\text{SbF}_6]$ could not be fully assigned because its weak peaks were obscured by those of $5\text{A}[\text{SbF}_6]$. For comparison, the ^1H and ^{13}C NMR spectra of **2**: ^1H NMR (400.13 MHz, CD_3NO_2 , RT): δ 8.00 (s, 2H), 7.97 (d, $^3J(\text{H,H}) = 8.8\text{ Hz}$, 2H), 7.86 (d, $^3J(\text{H,H}) = 8.8\text{ Hz}$, 2H) 2.746, 2.742 (2 s, 12 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CD_3NO_2 , RT): 136.32, 134.87, 134.50, 134.37, 134.05, 132.96, 132.14, 130.71, 128.11, 126.21, 125.99, 15.15, 15.12.

Synthesis and Characterization of $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)][\text{X}]_2$, $6[\text{BF}_4]_2$, $6[\text{PF}_6]_2$, $6[\text{SbF}_6]_2$. To a flask containing freshly prepared $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ (25.0 mg, 0.0230 mmol), 1,2,5,6-tetramethylcorannulene (**2**, 13.5 mg, 0.0441 mmol) and either AgBF_4 , AgPF_6 , or AgSbF_6 (0.0950 mmol) was added 1 mL of CD_3NO_2 . The solution was stirred for 1 hour at room temperature, and the AgCl precipitate was removed by filtration. The dark orange solution was evaporated to dryness under vacuum. The residue was washed with diethyl ether and dried under vacuum to give $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)][\text{X}]_2$, $6[\text{X}]_2$, as a dark orange oil or solid (40.0 mg, 85% yield for $6[\text{PF}_6]_2$). ^1H NMR (400.13 MHz, CD_3NO_2 , RT, $6[\text{PF}_6]_2$): δ 8.56 (d, $^3J(\text{H,H}) = 9.2$ Hz, 1H, H9), 8.14 (d, $^3J(\text{H,H}) = 9.2$ Hz, 1H, H10), 6.82 (d, $^3J(\text{H,H}) = 6.0$ Hz, 1H, H6), 6.81 (d, $^3J(\text{H,H}) = 6.0$ Hz, 1H, H1), 6.75 (d, $^3J(\text{H,H}) = 6.0$ Hz, 1H, H5), 6.73 (d, $^3J(\text{H,H}) = 6.0$ Hz, 1H, H2), 3.02 (q, $^5J(\text{H,H}) = 1.2$ Hz, $\text{C}_{20}\text{H}_6\text{Me}_4$, 3H), 2.86 (s, br, $\text{C}_{20}\text{H}_6\text{Me}_4$, 6H), 2.77 (q, $^5J(\text{H,H}) = 1.2$ Hz, $\text{C}_{20}\text{H}_6\text{Me}_4$, 3H), 1.23 (s, 15H, Cp^*), 1.20 (s, 15H Cp^*) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CD_3NO_2 , RT, $6[\text{PF}_6]_2$): δ 133.8 (C9), 129.0 (C10), 99.4 (C-Ru), 98.9 (C-Ru), 98.5 (C-Ru), 98.0 (C-Ru), 96.7 (C_5Me_5), 96.5 (C_5Me_5), 96.5 (C-Ru), 96.2 (C-Ru), 95.8 (C-Ru), 93.9 (C-Ru), 85.9 (C1), 85.3 (C2), 85.2 (C5), 84.1 (C6), 17.0 (Me), 16.9 (2 Me), 16.4 (Me), 9.24 (C_5Me_5), 9.07 (C_5Me_5), 142.7, 137.7, 137.4, 135.4, 134.9, 133.78 (unassigned) ppm. MS m/z 390 ($[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)]^{2+}$) electrospray in CD_3NO_2 . Due to the extreme moisture sensitivity of $6[\text{X}]_2$ it was not possible to obtain satisfactory elemental analyses.

Competition Experiments. A 5-mL flask was charged with corannulene (5.0 mg, 0.020 mmol), 1,2,5,6-tetramethylcorannulene (6.1 mg, 0.020 mmol), AgPF_6 (5.3 mg, 0.021 mmol), and only enough $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ (5.4 mg, 0.0050 mmol) to provide 0.020 mmol of

$\{\text{Cp}^*\text{Ru}\}^+$. To the flask was added 1.0 mL of CD_3NO_2 , and the solution was stirred for two hours. The reaction mixture was filtered into an NMR tube and flamed-sealed under argon. Relative concentrations of $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})]^+$ (3^+) and $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)]^+$ (5A^+ and 5B^+) were determined by integration of ^1H NMR signals of the C-H protons in **1** and **2** that are coordinated to the $\{\text{Cp}^*\text{Ru}\}^+$ fragments. Two independent experiments were performed and monitored periodically during three weeks at 25.0 °C.

Variable Temperature NMR Studies. Low temperature solution NMR studies were performed in CD_2Cl_2 solvent on a Bruker AC-200 spectrometer equipped with a Bruker BVT-1000 variable temperature unit. High temperature solution NMR studies were undertaken in CD_3NO_2 solvent on a DRX-400 spectrometer, also equipped with a Bruker BVT-1000 variable temperature unit.

Molecular Structure Determinations of Complexes $3[\text{SbF}_6]\cdot\text{Et}_2\text{O}$ and $4[\text{SbF}_6]_2\cdot 2\text{CH}_2\text{Cl}_2$. Orange crystals of $3[\text{SbF}_6]\cdot\text{Et}_2\text{O}$ suitable for an X-ray diffraction study were obtained by layering a methylene chloride solution of the complex with diethyl ether in an 8 mm wide Schlenk tube and storing at -25 °C overnight. Orange crystals of $4[\text{SbF}_6]_2\cdot 2\text{CH}_2\text{Cl}_2$ suitable for an X-ray diffraction study were grown by recrystallization from a saturated CH_2Cl_2 solution of the complex that was surrounded by hexanes and stored at -25 °C for two weeks.

The crystals of both complexes decomposed within seconds if they were removed from the crystallization solvents. Therefore, they were surrounded by premixed epoxy glue under a layer of the mother liquor. The covered crystals were then quickly mounted on a goniometer head under a stream of cold nitrogen and centered in the X-ray beam using a video camera. Crystal evaluation and data collection were performed at 193 K on a Bruker

CCD-1000 diffractometer with Mo K_{α} ($\lambda = 0.71073$) radiation and a detector-to-crystal distance of 5.03 cm. The data were collected using the full sphere routine and were corrected for Lorentz and polarization effects. Absorption corrections were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements¹³ using SADABS software.¹⁴ The structure solutions were accomplished by direct methods. All non-hydrogen atoms were refined by using a full-matrix anisotropic approximation. Hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Other crystallographic data are given in Table 1.

In $3[\text{SbF}_6] \cdot \text{Et}_2\text{O}$, one 3^+ cation, one SbF_6^- anion (distributed in three non-equivalent ordered special positions with occupancy factors 1/6, 2/6, and 1/2, giving three crystallographically nonequivalent positions for Sb and seven for F atoms), and one Et_2O solvent molecule were found in an asymmetric unit of the rhombohedral cell. The symmetry and space group determinations for $4[\text{SbF}_6]_2 \cdot 2\text{CH}_2\text{Cl}_2$ lead to the very common $C2/c$ space group. No unusual obstacles were found in the data reduction, the direct methods solution, or the full-matrix refinement. One half of a positively charged 4^{2+} cation (in a special position on a two-fold axis), an isolated SbF_6^- counteranion in a general position, and one CH_2Cl_2 solvent molecule were found in an asymmetric unit of the C-centered monoclinic cell. All geometrical parameters, thermal displacement coefficients, and refinement results were found to be reasonable.

Results and Discussion

Synthesis and Structural Characterization of $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})]^+$ (3^+). The first characterization (by NMR spectroscopy) of an η^6 -coordinated corannulene complex,

$[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{O}_3\text{SCF}_3]$, was reported by Siegel, O'Connor, and co-workers.⁷ Their synthetic procedure involved combining $[\text{Cp}^*\text{Ru}(\text{NCMe})_3][\text{O}_3\text{SCF}_3]$, the source of the $\{\text{Cp}^*\text{Ru}\}^+$ fragment, with corannulene in CD_2Cl_2 solvent. In order for the reaction to proceed to completion, it was necessary to remove the CD_2Cl_2 solvent and the displaced MeCN ligands under vacuum and re-dissolve the solid in CD_2Cl_2 . The presence of acetonitrile in solution prevented complete conversion to $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})]^+$. The η^6 complexes $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{BF}_4]_2$ and $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)][\text{BF}_4]_2$ were prepared similarly by combining $[\text{Cp}^*\text{Ir}(\text{acetone})_3][\text{BF}_4]_2$ with **1** or **2** in nitromethane solvent.⁸ On the other hand, the corannulene complexes did not form when $[\text{Cp}^*\text{Ir}(\text{acetone})_3]^{2+}$ was reacted with **1** or **2** in acetone solvent. From these results, it is apparent that the acetonitrile and acetone solvents, although weakly-coordinating, compete with corannulene for coordination to the metal fragments.

Our solution to the problem of competing ligands was to use a more reactive source of the $\{\text{Cp}^*\text{Ru}\}^+$ fragment, one without acetonitrile ligands, and a more weakly coordinating solvent. The complex $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ was used as the $\{\text{Cp}^*\text{Ru}\}^+$ source¹² and CD_3NO_2 as the solvent. When $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ reacts with four equivalents of Ag^+ and one equivalent of corannulene in CD_3NO_2 solvent under an argon atmosphere at room temperature, $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})]^+$ (**3**⁺) is formed in nearly quantitative yield within 15 minutes. Although the $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{X}]$ complexes ($\text{X} = \text{BF}_4^-$, PF_6^- , or SbF_6^-) were isolated, they are very sensitive to moisture. The previously reported $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{O}_3\text{SCF}_3]$ was assigned a structure in which the $\{\text{Cp}^*\text{Ru}\}^+$ unit is η^6 -coordinated to corannulene based on solution ^1H and ^{13}C NMR studies.⁷ In the same study, a theoretical investigation suggested that the

$\{\text{Cp}^*\text{Ru}\}^+$ group was bound on the convex side of the corannulene, although there was no experimental data to support that conclusion.

After numerous attempts, we were successful in obtaining X-ray quality crystals of $3[\text{SbF}_6] \cdot 2\text{Et}_2\text{O}$. The molecular structure (Fig. 4) of the cation in $3[\text{SbF}_6] \cdot 2\text{Et}_2\text{O}$ shows that the $\{\text{Cp}^*\text{Ru}\}^+$ unit is η^6 -coordinated to the convex side of corannulene, as the previous theoretical studies predicted. Of special interest is the partial flattening of the corannulene bowl where it is bound to the $\{\text{Cp}^*\text{Ru}\}^+$ unit. This distortion of the corannulene curvature is most evident in the π -orbital axis vector (POAV) analysis,¹⁵ which is a method of quantifying the curvature of a carbon atom framework in non-planar ring systems. In free corannulene, the five core carbon atoms are the most pyramidalized having POAV values of 8.4° (Fig. 5). The five rim quaternary carbon atoms are less pyramidalized and have POAV values of 3.8° . In 3^+ , the two core carbons bonded to Ru have POAV values that are slightly reduced to 6.6° and 6.8° , as compared with the other three core carbons that have POAV values (8.4° , 7.8° , 8.3°) that are similar to those of free corannulene. The two rim quaternary carbon atoms that are coordinated to $\{\text{Cp}^*\text{Ru}\}^+$ also have smaller POAV values (2.0° , 1.5°) than in free **1** (3.8°), while those that are not attached to the $\{\text{Cp}^*\text{Ru}\}^+$ unit have POAV values (4.1° , 4.4° , 3.4°) that are similar to those in free **1**. These results show that the $\{\text{Cp}^*\text{Ru}\}^+$ unit causes a flattening of the corannulene unit where it is coordinated.

In the previously reported structure of $[(\text{Cp}^*\text{Ru})_2(\mu_2-\eta^6, \eta^6-\text{C}_{20}\text{H}_{10})][\text{PF}_6]_2$ (**4** $[\text{PF}_6]_2$),⁹ it was found that coordination of η^6 - $\{\text{Cp}^*\text{Ru}\}^+$ fragments to both the convex and concave sides of the bowl reduced the curvature of the corannulene ligand to a much greater extent. The flattening of the carbon atoms coordinated to the convex $\{\text{Cp}^*\text{Ru}\}^+$ unit in **4** $[\text{PF}_6]_2$ was

greater than in $3[\text{SbF}_6]$ as indicated by POAV values (Fig. 5) for the core carbons (3.5° , 3.7°) and the rim quaternary carbon atoms (0.8° , 0.5°). For the carbon atoms bound to the concave $\{\text{Cp}^*\text{Ru}\}^+$ unit, the POAV values for both the core (4.4° and 4.3°) and the rim quaternary carbons (2.1° and 1.2°) are slightly larger than those for the convex $\{\text{Cp}^*\text{Ru}\}^+$ unit. Even the core and rim quaternary carbon atoms that are not coordinated to a $\{\text{Cp}^*\text{Ru}\}^+$ group with POAV values of 5.1° and 1.8° , respectively, were flattened in $4[\text{PF}_6]_2$ as compared to free corannulene. The significant changes in the POAV angles of corannulene upon η^6 -coordination to $\{\text{Cp}^*\text{Ru}\}^+$ in both $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]$ ($3[\text{SbF}_6]$) and $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{PF}_6]_2$ ($4[\text{PF}_6]_2$) contrasts with the structures of the η^2 corannulene complexes $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]_m \cdot (\text{C}_{20}\text{H}_{10})_n$ ($m:n = 1:1$ and $3:2$) where no changes in the structure of the corannulene was observed.¹⁰

A parameter that is used to describe the overall curvature of a buckybowl is the bowl depth, which is the distance between the centroid of the five core carbon atoms and the centroid of the ten tertiary rim carbons. In free corannulene, the bowl depth is $0.87 \text{ \AA}$, while it is $0.78 \text{ \AA}$ in $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]$, $3[\text{SbF}_6]$. The even greater flattening of corannulene in $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{PF}_6]_2$, $4[\text{PF}_6]_2$, is evident in its bowl depth of only $0.42 \text{ \AA}$.

The flattening of corannulene must be accompanied by structural changes that relieve the strain in the bowl. There are several changes in C–C bond distances (Fig. 5) in $3[\text{SbF}_6]$ as compared with those in **1** that illustrate the effect of $\{\text{Cp}^*\text{Ru}\}^+$ coordination on the bowl shape. Although the C17–C18 distance (Fig. 4) in the five-carbon core is essentially the same in $3[\text{SbF}_6]$ ($1.42(2) \text{ \AA}$) as it is in **1** ($1.413(3) \text{ \AA}$), the C1–C2 distance on the rim of $3[\text{SbF}_6]$ is

1.44(1) Å as compared with 1.402(5) Å in 1. This lengthening of C1–C2 caused by $\{\text{Cp}^*\text{Ru}\}^+$ coordination relieves strain in the curved bowl and allows the carbon atoms bonded to Ru to become more planar. A similar lengthening (1.45(1) Å) of C–C distances for the carbon atoms bonded to the convex and concave $\{\text{Cp}^*\text{Ru}\}^+$ was also observed in $4[\text{PF}_6]_2$ (Fig. 5).⁹ Such C–C bond length increases have been reported for many other η^6 -arene metal complexes and are explained by a charge-transfer between the arene and metal complex that results in a net reduction in C–C bond orders.¹⁶

In contrast to the lengthening of Ru-coordinated rim C–C bond distances, the non-coordinated rim C–C units in $3[\text{SbF}_6]$ have shorter C–C distances (1.35(2), 1.34(2), 1.36(2), 1.38(2) Å) than that in free corannulene (1.402(5) Å). This trend is also observed in the previously reported structure of $4[\text{PF}_6]_2$ where the uncoordinated C–C bond lengths are 1.38(1), 1.37(1), and 1.38(1). This decrease in the C–C bond lengths can be rationalized by assuming that six π electrons are localized in the six-membered rings coordinated to $\{\text{Cp}^*\text{Ru}\}^+$. The remaining π -electrons in the corannulene ligand may then be localized in alternate single and double C–C bonds as shown in Fig. 5. Such localization of electron density in non-coordinated portions of polyaromatic hydrocarbons that are η^6 -coordinated to a transition metal fragment have been observed in several other complexes.¹⁶

Another interesting feature of the carbon framework in $3[\text{SbF}_6]$ is the folding of the six-membered ring to which the $\{\text{Cp}^*\text{Ru}\}^+$ unit is coordinated. The fold occurs along the C11–C12 vector (Fig. 4) in a way that moves C1 and C2 up toward the Ru and gives a 12° angle between the planes defined by C1, C2, C12, C11 and C12, C18, C17, C11. All of the non-coordinated six-membered rings in $3[\text{SbF}_6]$ are folded similarly with fold angles in the

range 8.2-12.6°. Moreover, the six-membered rings in free corannulene are folded in a similar manner with fold angles of 8.8-11.2°.⁴ In 4[PF₆]₂, the fold angle of the six-membered ring coordinated to the convex {Cp*Ru}⁺ unit is 7.8°, while the fold angle for the ring coordinated to the concave {Cp*Ru}⁺ is 5.6°. The fold angles (6.4-8.1°) of the non-coordinated six-membered rings in 4[PF₆]₂ are also smaller than those in either 1 or 3[SbF₆]. These smaller fold angles in 4[PF₆]₂ reflect the smaller POAV angles described above.

In 3[SbF₆] (Fig. 4), the Ru-C distances are shortest to C1 (2.221(7) Å), C2 (2.211(7) Å), C17 (2.231(8) Å), and C18 (2.222(8) Å) and significantly longer to C11 (2.382(7) Å) and C12 (2.361(8) Å), which reflects folding of the ring along the C11-C12 vector as described above. This same pattern of Ru-C distances is observed in 4[PF₆]₂ for the {Cp*Ru}⁺ unit bonded to the convex face,⁹ where the Ru-C distances are also shortest to C1 (2.219(7)), C2 (2.214(6)), C17 (2.209(6)), and C18 (2.209(6)), and the C11 (2.343(7)) and C12 (2.346(6)) distances are longer. The bonding pattern for {Cp*Ru}⁺ on the convex side of corannulene is significantly different than that for the concave {Cp*Ru}⁺ in 4[PF₆]₂ which has short Ru-C distances (2.176(7) and 2.169(7) Å) to the two rim carbons (C5 and C6 in Fig. 4) but longer Ru-C bonds (2.263(7), 2.266(7), 2.264(7), and 2.276(7) Å) to the other four carbon atoms C13, C14, C19, and C20. The different Ru-C bond lengths to the coordinated arene rings of 3[SbF₆] and 4[PF₆]₂ are in contrast to those reported for other [Cp*Ru(η⁶-arene)]⁺ complexes such as [Cp*Ru(η⁶-C₆(CH₃)₆)]⁺ in which all the Ru-C bond distances are very similar in the range 2.18-2.22 Å.¹²

The extended structure (Fig. 6) of [Cp*Ru(η⁶-C₂₀H₁₀)]₂[SbF₆]₂, 3[SbF₆], shows that two [Cp*Ru(η⁶-C₂₀H₁₀)]⁺ complexes arrange themselves in such a way that the concave

faces of the corannulene ligands face each other, which leaves a vacant pocket between them. Although diethyl ether molecules are present elsewhere in the crystal lattice, none were observed inside the cavity. The shortest carbon-to-carbon distance between carbon atoms on the two $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})]^+$ units is 3.4 Å, which is sufficiently long to indicate that there is no bonding between the corannulene groups.

Synthesis and Characterization of $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)]^+$ (5^+). When $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ reacts with four equivalents of 1,2,5,6-tetramethylcorannulene (**2**) and four equivalents of a AgX salt ($\text{X} = \text{BF}_4^-, \text{PF}_6^-, \text{SbF}_6^-$) at room temperature in CD_3NO_2 solvent, the $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)]^+$ complex (5^+) is formed within five minutes. Two isomers of the product were observed by solution ^1H NMR in a 2:1 ratio for $5\text{A}^+ : 5\text{B}^+$ (Fig. 3). Crystallization of the mixture of 5A^+ and 5B^+ often resulted in the enrichment of one isomer over the other, which aided in the spectroscopic assignments; however, attempts to obtain X-ray quality crystals were unsuccessful. The ^1H NMR signals of a sample enriched in 5B^+ are all ~0.1 ppm downfield of those in the initial 2:1 mixture; the cause of this shift is not clear. ^1H - ^1H COSY, ^1H - ^{13}C HETCOR, and ^1H - ^1H NOESY experiments, along with relative shifts in ^1H NMR signals, were used to make tentative proton and carbon assignments in the spectra of the mixtures of the 5A^+ and 5B^+ isomers. The hydrogen signals for H5, H6, H9, and H10 of the major isomer (5A^+) occur as doublets at 8.23, 8.07, 7.94, and 7.62 ppm. There are upfield signals between 6.46-6.42 that arise from second order AB coupling and are assigned to H1 and H2. The four methyl groups in $\text{C}_{20}\text{H}_6\text{Me}_4$ of 5A^+ are observed as four signals between 2.9 – 2.6 ppm. The middle two methyl signals are singlets and are located in the same region (although better resolved) as those for the methyl signals of the free **2** (2.746, 2.742 ppm). The other two methyl group signals are unresolved quartets ($J(\text{H},\text{H}) = 0.8$ Hz);

one is shifted ~ 0.1 ppm upfield and the other ~ 0.1 ppm downfield from those of the free **2**. The more symmetrical minor isomer, **5B**⁺, has a much simpler ¹H NMR spectrum. Doublets at 8.05 and 7.98 ppm may be assigned to H6, H7, and H5, H8, while a singlet at 6.45 ppm may be assigned to H1 and H2. There are two methyl signals; one is shifted $\sim 0.1 - 0.2$ ppm upfield while the other is shifted ~ 0.1 ppm downfield of those in free **2**. These methyl group signals both appear as unresolved quartets with $J(\text{H,H}) = 0.8$ Hz. In both **5A**⁺ and **5B**⁺, only one peak is observed for the Cp* methyl groups.

The significant upfield shifts (1.3-1.5 ppm) of the signals assigned to the coordinated C-H groups in **5A**⁺ and **5B**⁺ are similar in magnitude to those observed in the ¹H NMR spectra of both [Cp*Ru(η^6 -C₂₀H₁₀)]([O₃SCF₃)]⁷ and [(Cp*Ru)₂(μ_2 - η^6 , η^6 -C₂₀H₁₀)](PF₆)₂(4[PF₆])₂,⁹ and are typical of other [Cp*Ru(η^6 -arene)]⁺ compounds.^{12,17} These large upfield shifts and the simplicity of the ¹H NMR spectrum of the minor isomer **5B**⁺ (containing symmetrical corannulene unit) suggests that {Cp*Ru}⁺ is η^6 -bound to non-methylated rings of **2** in both **5A**⁺ and **5B**⁺ (Fig 3). It should also be noted that in free **2**, there are two types of non-methylated arene rings in a 2:1 ratio: a single ring located between the two methylated rings and two equivalent, adjacent rings (Fig. 1). It seems plausible that the 2:1 ratio of ring types leads to the 2:1 ratio for **5A**⁺:**5B**⁺. It is interesting that the methyl signals of **5A**⁺ and **5B**⁺ appear as quartets, with small coupling constants (0.8 Hz), presumably the result of ⁵ $J(\text{H,H})$ homoallylic coupling¹⁸ between methyl groups. The pattern of singlets and unresolved quartets in **5A**⁺ suggests that this coupling is only observed for those methyl groups that are located on the rings directly next to those containing a coordinated η^6 -{Cp*Ru}⁺ group.

There was no NMR evidence for the formation of other isomers in the reactions of **2** with $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})_4]$ and AgX . Even after the initial CD_3NO_2 solution of the isomers was heated to 101 °C for 24 hours, the ratio of $5\text{A}^+ : 5\text{B}^+$ remained 2:1. In attempts to determine whether 5A^+ and 5B^+ could be interconverted, a CD_3NO_2 solution containing them was allowed to stand for two weeks at room temperature, and no change was observed in the $5\text{A}^+ : 5\text{B}^+$ ratio. The $5\text{A}^+ : 5\text{B}^+$ isomer ratio also remained unchanged (2:1) when the mixture of isomers in CD_3NO_2 was heated at 50 °C for two days followed by recording the ^1H NMR spectrum at 50 °C. Only by recrystallization of the mixture of isomers $5\text{A}[\text{SbF}_6]$ and $5\text{B}[\text{SbF}_6]$ was the ratio changed from 2:1. All of the studies show that 5A^+ and 5B^+ do not interconvert under the above conditions. This inability of the $\{\text{Cp}^*\text{Ru}\}^+$ group to migrate from one six-membered ring of **2** to another may account for the fact that an isomer in which the $\{\text{Cp}^*\text{Ru}\}^+$ unit is on a methylated ring is not observed. Ring migration of the $\eta^6\text{-}\{\text{Cp}^*\text{Ru}\}^+$ group is reported in the reaction of $[\text{Cp}^*\text{Ru}(\text{NCMe})_3][\text{O}_3\text{SCF}_3]$ with acecorannulene,¹⁹ a corannulene derivative that is non-fluxional at room temperature and has three differently-curved six-membered rings, in CD_2Cl_2 . The migration of the $\{\text{Cp}^*\text{Ru}\}^+$ group across acecorannulene was thought to be catalyzed by residual acetonitrile that remains in the reaction mixture. {It is interesting to note that the $\{\text{Cp}^*\text{Ru}\}^+$ groups coordinate η^6 to the least curved rings of acecorannulene (average POAV values of 5.0° and 5.3° for the free ligand) and were never observed to bind to the most curved ring (average POAV value of 8.4° in the free ligand).} In the reaction of $[\text{Cp}^*\text{Ir}(\text{acetone})_3]^{2+}$ with **2**,⁸ the major isomer of $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)]^{2+}$ that forms initially is that in which the $\{\text{Cp}^*\text{Ir}\}^{2+}$ unit binds to one of the equivalent, adjacent non-methylated rings. However, within six hours, this isomer completely rearranges to the isomer in which $\{\text{Cp}^*\text{Ir}\}^{2+}$ is coordinated to a methylated ring.

The total absence of such an isomer of 5^+ is possibly due to the fact that migration of the $\{\text{Cp}^*\text{Ru}\}^+$ unit in this system, in which there are no residual acetonitrile or acetone molecules to help facilitate isomerization, is very slow. It is also possible that this isomer is thermodynamically unstable with respect to 5A^+ and 5B^+ .

In an attempt to determine whether **1** or **2** binds more strongly to $\{\text{Cp}^*\text{Ru}\}^+$, a competition experiment in which one equivalent of **1**, one equivalent of **2**, and one equivalent of $\{\text{Cp}^*\text{Ru}\}^+$ were reacted. The reaction was initiated by adding CD_3NO_2 solvent to the following mixture of solids, **1**, **2**, $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$, and AgPF_6 , in a 1:1:1/4:1 molar ratio. The reaction was stirred at room temperature for two hours before being filtered into an NMR tube and sealed. The tube at room temperature was monitored periodically over a period of three weeks. The relative concentrations of the mono-metallated products 3^+ , 5A^+ , and 5B^+ were determined by integration of the signals in the ^1H NMR spectra between 6.5-6.3 ppm corresponding to the hydrogens on those rings to which the $\{\text{Cp}^*\text{Ru}\}^+$ fragments are bound. No products with two $\{\text{Cp}^*\text{Ru}\}^+$ units coordinated to **1** or **2** were observed. Results of two independent runs showed that the ratio $3^+:(5\text{A}^+ + 5\text{B}^+)$ was 1:2.77 and 1:3.00 for the two runs and that this ratio remained unchanged after the first measurement immediately following the reaction. Because there was no change in this ratio with time and because studies of the isomerization of 5A^+ and 5B^+ showed that the $\{\text{Cp}^*\text{Ru}\}^+$ groups are not labile, it seems likely that the observed 1:2.9 ratio of $3^+:5^+$ indicates that $\{\text{Cp}^*\text{Ru}\}^+$ reacts kinetically more rapidly with **2** than with **1** under the conditions of this study. However, the ratio does not establish the relative thermodynamic stabilities of 3^+ and 5^+ .

Synthesis and Characterization of $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]_2$ ($4[\text{SbF}_6]_2$) and $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)]^{2+}$ (6^{2+}). The compound $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]_2$ ($4[\text{SbF}_6]_2$)

$C_{20}H_{10})][SbF_6]_2$ ($4[SbF_6]_2$) was synthesized in a manner identical to that previously reported for the BF_4^- and PF_6^- salts, $4[BF_4]_2$ and $4[PF_6]_2$,⁹ except that $AgSbF_6$ was used as the AgX reagent. Unlike the previously reported structure of $4[PF_6]_2 \cdot 4CH_2Cl_2$, the structure of $4[SbF_6]_2 \cdot 2CH_2Cl_2$ (Fig. 8) contains $\{Cp^*Ru\}^+$ fragments that are crystallographically equivalent and related by a C_2 axis of symmetry. The relatively large R -factor (8.9%) for $4[SbF_6]_2 \cdot 2CH_2Cl_2$ seems to be related to significant thermal motion in the core five-membered ring of the corannulene unit as two other independently prepared crystal samples, obtained under the same crystallization conditions, had similarly large R -factors, but also the same symmetry and solvent-to-complex ratios. The structure reveals a corannulene subunit that no longer has a bowl shape; it is more like a "plate." The C_{20} unit is very nearly flat as the RMS deviation from the "best" plane is only 0.013 Å. There are, however, small distortions from planarity as indicated by the POAV values (0.6° and 0.2° in Fig. 8) for the core carbon atoms of $4[SbF_6]_2$ that are attached to $\{Cp^*Ru\}^+$. These numbers are significantly smaller than those in $4[PF_6]_2 \cdot 4CH_2Cl_2$, which had values of 3.5° and 3.7° for the core carbon atoms attached to the convex $\{Cp^*Ru\}^+$ fragment and 4.3° and 4.4° for the core carbons attached to the concave $\{Cp^*Ru\}^+$ fragment. The POAV values for the rim quaternary carbon atoms attached to the $\{Cp^*Ru\}^+$ unit in $4[SbF_6]_2 \cdot 2CH_2Cl_2$ (0.4° and 0.9°) are the same as those in the corannulene ring bound to the convex $\{Cp^*Ru\}^+$ fragment in $4[PF_6]_2$ (0.8° and 0.5°) but smaller than those for the ring bound to the concave $\{Cp^*Ru\}^+$ fragment (2.1° and 1.2°) (Fig. 5). The smaller pyramidalization values of the core carbon atoms in $4[SbF_6]_2$ illustrates a more flattened corannulene unit than observed in $4[PF_6]_2$. However, the corannulene is not completely flat, as indicated by the longer Ru-C distances to C1 (2.33(2) Å) and C8 (2.30(2) Å) than to C6 (2.23(2) Å), C7 (2.22(1) Å), C10 (2.19(2)

Å), and C11 (2.19(2) Å). Thus, the ring is folded along the C1-C8 vector, as was observed in free corannulene and in the corannulene rings that are coordinated to convex $\{\text{Cp}^*\text{Ru}\}^+$ units in $3[\text{SbF}_6]$ and $4[\text{PF}_6]_2$. The fold angle, defined as the dihedral angle between the C1, C6, C7, C8 and C8, C10, C11, C1 planes in Fig. 8, in each of these structures decreases in the series: 12° for $3[\text{SbF}_6]$, 7.8° for $4[\text{PF}_6]_2$, and 1.2° for $4[\text{SbF}_6]_2$. The observation that the corannulene is much flatter in $4[\text{SbF}_6]_2 \cdot 2\text{CH}_2\text{Cl}_2$ than in $4[\text{PF}_6]_2 \cdot 4\text{CH}_2\text{Cl}_2$ shows that the corannulene ligand in 4^{2+} is sufficiently flexible that its shape depends upon the lattice energy of the crystals, which is influenced by the anion (PF_6^- vs. SbF_6^-) and the number of CH_2Cl_2 molecules (4 vs. 2) in the lattice.

Like 1, 2 also reacts with $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})_4]$ in a 2:1 ratio of 2 to $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})_4]$ and four equivalents of Ag^+ to give only one isomer of $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_6\text{Me}_4)]^{2+}$ (6^{2+}) in which two $\{\text{Cp}^*\text{Ru}\}^+$ units are η^6 -coordinated to the corannulene framework. Complex 6^{2+} was characterized by its NMR and mass spectra and shown to have the structure in Fig. 3. The ^1H NMR spectrum (Fig. 7) of the $\text{C}_{20}\text{H}_6\text{Me}_4$ ligand in $6[\text{PF}_6]_2$ shows doublets at 8.56 and 8.14 ppm that are coupled together in the COSY NMR spectrum and may be assigned to H9 and H10. There are also four upfield doublets at 6.9 – 6.7 ppm which are correlated in the COSY spectrum and may be assigned to H1, H2, H5 and H6. A NOESY NMR study of $6[\text{BF}_4]_2$ revealed a correlation between H1 and H10, which is further support for the conclusion that the $\{\text{Cp}^*\text{Ru}\}^+$ units coordinate to the non-methylated rings of 2. There are three methyl signals for $6[\text{PF}_6]_2$ between 3.1 and 2.7 ppm in the ^1H NMR spectrum (Fig 7, bottom). Two of these signals are unresolved quartets that each integrate to three hydrogens. The third signal is a broad singlet between them corresponding to six hydrogen atoms; all three signals are shifted only slightly downfield (0 - 0.3 ppm) from that of the methyl groups

in free **2**. There are also two separate signals for the methyl groups of the Cp* ligands that each integrate to 15 hydrogen atoms. The ^1H NMR data indicate that the only isomer formed is that in which both $\{\text{Cp}^*\text{Ru}\}^+$ units are η^6 -coordinated to non-methylated, non-adjacent six-membered rings (Fig 3). Presumably, the $\{\text{Cp}^*\text{Ru}\}^+$ units are on opposite sides of the buckybowl ligand as was observed in the structures of $4[\text{PF}_6]_2$ and $4[\text{SbF}_6]_2$. However, numerous attempts to obtain X-ray quality crystals of 6^{2+} using various anions and crystallization methods were unsuccessful.

Corannulene undergoes rapid bowl-to-bowl inversion in solution at room temperature.²⁰ The inversion barrier ($\Delta G^\ddagger$) for corannulene derivatives that are monofunctionalized on the rim by dimethylcarbinol, isopropyl, and benzyl groups, which presumably do not alter the structure of the corannulene unit significantly, are determined to be 10.2 kcal/mol at 209 K,²⁰ 11.3 kcal/mol at 242 K,²¹ and 11.2 kcal/mol at 234 K,²¹ respectively. The inversion barriers for corannulene functionalized with two (10.4-10.5 kcal/mol) or one (11.0 kcal/mol) bromomethyl groups on the rim have been used to estimate the inversion barrier in free corannulene (**1**) at 11.5 kcal/mol.²² Experimental and theoretical studies indicate that inversion barriers in corannulene and its derivatives are highly dependent (directly proportional to) on their curvatures and bowl depths.²¹⁻²³ Those substituents and interactions that lead to a decrease in the curvature and flattening of the buckybowl result in structures with lower barriers to inversion, whereas those substitutions that cause an increase in the curvature and bowl depth give structures with larger barriers to inversion. The previously reported solution NMR spectrum for $[(\text{Cp}^*\text{Ru})_2(\mu_2-\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{PF}_6]_2$ (**4** $[\text{PF}_6]_2$) contained only one signal for the methyl groups of the Cp* ligands at room temperature. If the inversion was slow on the NMR timescale, one would expect

separate signals for the $\{\text{Cp}^*\text{Ru}\}^+$ units that are on the convex and concave sides of the corannulene. The observation of only one Cp^* signal indicates that the inversion is fast. Attempts to determine the spectrum of $4[\text{PF}_6]_2$ at low temperature were not possible because of its low solubility in CD_2Cl_2 . Complex 6^{2+} is much more soluble in CD_2Cl_2 than 4^{2+} , and low temperature NMR studies were undertaken with it in an attempt to determine the inversion barrier of these dimetallated corannulene complexes. The ^1H and ^{13}C NMR spectra of $6[\text{PF}_6]_2$ in CD_2Cl_2 showed only two signals for the methyl groups on the Cp^* ligands down to 183 K, suggesting that either a fast inversion process occurs even at this low temperature, or one of the isomers is strongly favored, which seems unlikely. The flattened geometries of the corannulene ligand in the structures of $4[\text{PF}_6]_2$ and $4[\text{SbF}_6]_2$ is consistent with a lower barrier of inversion than the uncoordinated corannulene derivatives. The fact that the corannulene ligand in $4[\text{PF}_6]_2 \cdot 4\text{CH}_2\text{Cl}_2$ retains some curvature but is almost flat in $4[\text{SbF}_6]_2 \cdot 2\text{CH}_2\text{Cl}_2$ indicates that the energy required to change the shape of the corannulene from curved to flat is less than the difference in crystal packing energies in the two solids.

Conclusions

A new synthetic procedure has been developed for the attachment of one and two η^6 - $\{\text{Cp}^*\text{Ru}\}^+$ fragments to corannulenes in high yields, based on the use of $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$ as the source of $\{\text{Cp}^*\text{Ru}\}^+$ and CD_3NO_2 as the solvent. X-ray structural investigations show that the $\{\text{Cp}^*\text{Ru}\}^+$ fragment is attached (η^6) to the convex side of corannulene in $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]$ ($3[\text{SbF}_6]$) and that the $\{\text{Cp}^*\text{Ru}\}^+$ units in $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{PF}_6]_2$ ⁹ ($4[\text{PF}_6]_2$) and $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]_2$ ($4[\text{SbF}_6]_2$) are η^6 -coordinated to non-adjacent arene rings on opposite sides of corannulene. Coordination of the $\{\text{Cp}^*\text{Ru}\}^+$

fragments results in significant flattening of the corannulene, particularly at the point of attachment, which is the likely reason for the low barrier to corannulene inversion in $[(\text{Cp}^*\text{Ru})_2(\mu_2-\eta^6, \eta^6-\text{C}_{20}\text{H}_6\text{Me}_4)][\text{PF}_6]_2$ ($6[\text{PF}_6]_2$). This flattening of the corannulene unit upon η^6 -coordination of $\{\text{Cp}^*\text{Ru}\}^+$ may account for the absence of η^6 complexes of fullerene C_{60} , in which the rigid carbon cage prevents flattening that would cause severe strains in the C-C bonds adjacent to that area.

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Figure 1. The curved surface buckybowls corannulene (1) and 1,2,5,6-tetramethylcorannulene (2).

Figure 2. Atom labeling schemes for the corannulene ligand in $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})]^+$ (3^+) and $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6,\eta^6\text{-C}_{20}\text{H}_{10})]^{2+}$ (4^{2+}).

Figure 3. Labeling schemes for $5A^+$, $5B^+$ and 6^{2+} .

Figure 4. Thermal ellipsoid drawing of the 3^+ cation in $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]$ ($3[\text{SbF}_6]$). Ellipsoids are shown at the 30% probability level; hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ru1-C1, 2.221(7); Ru1-C2, 2.211(7); Ru1-C12, 2.361(8); Ru1-C18, 2.222(8); Ru1-C17, 2.231(8); Ru1-C11, 2.382(7).

Figure 5. POAV pyramidalization angles ($^{\circ}$) and C–C bond lengths ($\text{\AA}$) in corannulene (**1**),⁴ $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6] \cdot (\text{C}_2\text{H}_5)_2\text{O}$ (**3** $[\text{SbF}_6]$), and $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{PF}_6]_2 \cdot 4\text{CH}_2\text{Cl}_2$ (**4** $[\text{PF}_6]_2$).¹⁰ Only the carbon atoms of corannulene are shown.

Figure 6. Thermal ellipsoid diagram of the packing arrangement between two $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})]^{2+}$ units of $3[\text{SbF}_6]$. Ellipsoids are drawn at the 30% probability level; hydrogen atoms, anions and solvent molecules are not shown.

Figure 7. ^1H NMR spectrum of the $\text{C}_{20}\text{H}_6\text{Me}_4$ ligand (C–H region, top; C–CH₃ region, bottom) in $[(\text{Cp}^*\text{Ru})_2(\mu_2-\eta^6, \eta^6-\text{C}_{20}\text{H}_6\text{Me}_4)][\text{PF}_6]_2$ (**6** $[\text{PF}_6]_2$) in CD_3NO_2 .

Figure 8. Thermal ellipsoid drawings (top) of $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]_2$ ($4[\text{SbF}_6]_2$). Ellipsoids are shown at the 30% probability level; hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ru-C10, 2.189(15); Ru-C11, 2.189(15); Ru-C6, 2.228(15); Ru-C7, 2.220(13); Ru-C1, 2.331(15); Ru-C8, 2.304(15). POAV pyramidalization angles (bold, °) and C-C bond lengths (Å) (bottom). Ellipsoids are shown at the 30% probability level; hydrogen atoms are omitted for clarity.

Table 1. Crystal Data and Structure Refinement for $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]$ (**3** $[\text{SbF}_6]$) and $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]_2$ (**4** $[\text{SbF}_6]_2$).

COMPOUND	3 $[\text{SbF}_6]$	4 $[\text{SbF}_6]_2$
Empirical formula	$\text{C}_{30}\text{H}_{25}\text{F}_6\text{RuSb}\cdot(\text{C}_2\text{H}_5)_2\text{O}$	$\text{C}_{40}\text{H}_{40}\text{F}_{12}\text{Ru}_2\text{Sb}_2\cdot 2\text{CH}_2\text{Cl}_2$
Formula weight	796.44	1364.21
Temperature	193(2) K	193(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	rhombohedral	monoclinic
Space group	$R\bar{3}c$	$C2/c$
Unit cell dimensions	$a = 22.764(4)$ Å $b = 22.764(4)$ Å $c = 60.76(2)$ Å $\alpha = 90.00^\circ$ $\beta = 90.00^\circ$ $\gamma = 120.00^\circ$	$a = 17.091(3)$ Å $b = 18.695(3)$ Å $c = 14.903(2)$ Å $\alpha = 90.00^\circ$ $\beta = 94.067(4)^\circ$ $\gamma = 90.00^\circ$
Volume	$27269(11)$ Å ³	$4749.8(13)$ Å ³
<i>Z</i>	36	4
Density (calcd)	1.746 Mg/m ³	1.908 Mg/m ³
Absorption coefficient	1.454 mm ⁻¹	2.052 mm ⁻¹
<i>F</i> (000)	14256	2648
Crystal size	$0.30 \times 0.30 \times 0.20$ mm ³	$0.30 \times 0.20 \times 0.11$ mm ³
θ range for data collection	1.69 to 25.37°	1.62 to 24.72°
Index ranges	$-27 \leq h \leq 26$ $-27 \leq k \leq 27$ $-71 \leq l \leq 73$	$-20 \leq h \leq 19$ $-21 \leq k \leq 21$ $-16 \leq l \leq 17$
No. of reflns. collected	53816	15747
No. of independent reflns.	5545 [$R(\text{int}) = 0.0439$]	4048 [$R(\text{int}) = 0.0377$]
Completeness to $\theta =$	$25.37^\circ = 99.3\%$	$24.72^\circ = 99.8\%$
Absorption correction	Semi-empirical	Semi-empirical
Max. and Min. Transmn.	1.00 and 0.81	1.00 and 0.65
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
No. of data / restraints / params	5545 / 5 / 395	4048 / 0 / 286
Goodness-of-fit on F^2	1.050	1.224
Final R^a indices [$I > 2\sigma(I)$]	$R1 = 0.0578$, $wR2 = 0.1495$	$R1 = 0.0887$, $wR2 = 0.1909$
R^a indices (all data)	$R1 = 0.0840$, $wR2 = 0.1775$	$R1 = 0.1028$, $wR2 = 0.1967$
Largest diff peak and hole	2.341 and -2.099 e Å ⁻³	1.368 and -0.975 e Å ⁻³

^a $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $wR2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$

Appendix

Figure A1. ^1H NMR spectrum (top) and ^{13}C NMR spectrum (middle) of free corannulene (**1**, bottom) in CD_3NO_2 .

Figure A2. ^1H NMR spectrum (top) and ^{13}C NMR spectrum (middle) of free 1,2,5,6-tetramethylcorannulene (**2**, bottom) in CD_3NO_2 .

Figure A3. ^1H NMR spectrum of the mixture of **5A**[BF₄], **5B**[BF₄] and **6**[BF₄] in CD₃NO₂.

The A, B and Ru2 peak assignments refer to compounds **5A**[BF₄], **5B**[BF₄] and **6**[BF₄], respectively.

Figure A4. COSY NMR spectrum of the mixture of **5A**[BF₄], **5B**[BF₄] and **6**[BF₄] in CD₃NO₂.

Figure A5. ^1H NMR spectrum of $5\text{A}[\text{SbF}_6]$ enriched sample in CD_3NO_2 .

Figure A6. ^1H NMR spectrum of **5B**[SbF₆] enriched sample in CD_3NO_2 .

Figure A7. ^1H NMR spectrum of $6[\text{BF}_4]_2$ in CD_3NO_2 .

Figure A8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $6[\text{BF}_4]_2$ in CD_3NO_2 .

Figure A9. COSY NMR spectrum of $6[\text{BF}_4]_2$ in CD_3NO_2 .

Figure A10. NOESY NMR spectrum of $6[\text{BF}_4]_2$ in CD_3NO_2 .

CHAPTER 7: GENERAL CONCLUSIONS

This thesis discusses my accomplishments at Iowa State University in two separate areas of research involving organometallic Ru(II) complexes; studies of the structural and electronic factors that influence the sulfur-binding ability of dibenzothiophenes, with particular emphasize on the difficult to desulfurize 4-MeDBT and 4,6-Me₂DBT, and investigations into the η^6 -coordination of the bucky bowl corannulene.

In Chapters 2 and 3, the synthesis and full characterization of the first transition metal complexes containing sulfur-bound 4-MeDBT and 4,6-Me₂DBT were presented, $[\text{Cp}'\text{Ru}(\text{CO})_2\eta^1(\text{S})\text{-4-MeDBT}]^+$ and $[\text{Cp}'\text{Ru}(\text{CO})_2\eta^1(\text{S})\text{-4,6-Me}_2\text{DBT}]^+$, where $\text{Cp}' = \text{Cp}$ and Cp^* . These compounds allow for binding studies which demonstrate that alkyl groups in the 4,6- positions near the sulfur atom sterically-hinder the sulfur-coordination of dibenzothiophenes in transition metal complexes. A new solid phase extractant was developed based on these metal complexes and was shown to remove dibenzothiophenes from simulated petroleum. In Chapter 4, the synthesis of a dinuclear complex in which dibenzothiophene is $\eta^1(\text{S})$ -coordinated to a $\{\text{CpRu}(\text{CO})_2\}^+$ group and η^6 -coordinated to $\{\text{Cp}'\text{Ru}\}^+$ confirms an new $\mu_2\text{-}\eta^1(\text{S}),\eta^6$ bridging mode for dibenzothiophenes. An X-ray structural investigation of the complex $[\text{CpRu}(\text{CO})_2(\mu_2\text{-}\eta^1(\text{S}),\eta^6\text{-DBT})\text{RuCp}^*][\text{PF}_6]_2$ shows that the two ruthenium moieties are on opposite sides of the planar DBT ligand. Infrared studies show that (pre-) coordination of $\eta^6\text{-}\{\text{Cp}'\text{Ru}\}^+$ to dibenzothiophene reduces the electron donating ability of the sulfur atom. Kinetic investigations reveal that η^6 -precoordination by a $\{\text{Cp}^*\text{Ru}\}^+$ fragment increases the rates of DBT dissociation significantly, even more than methyl groups in the 4- and 6-positions, and illustrates the

importance of electronic factors in sulfur-coordination to transition metal complexes. It is hoped that these binding studies will be useful in the development and optimization of methods for sulfur compound removal from fossil fuels.

Chapters 5 and 6 describe a new synthetic method that was developed for the direct attachment of one and two $\eta^6\text{-}\{\text{Cp}^*\text{Ru}\}^+$ fragments to corannulenes in high yields, and should be useful in the attachment of one and more $\eta^6\text{-}\{\text{Cp}^*\text{Ru}\}^+$ fragments to other bucky bowl compounds. The first X-ray structural characterizations of η^6 -corannulene complexes are obtained using this procedure. The structure of the monometallated complex $[\text{Cp}^*\text{Ru}(\eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]$, shows that the $\eta^6\text{-}\{\text{Cp}^*\text{Ru}\}^+$ unit is attached to the convex side of the corannulene unit. In the structures of the dimetallated complexes $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{PF}_6]_2$ and $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-}\eta^6, \eta^6\text{-C}_{20}\text{H}_{10})][\text{SbF}_6]_2$, the $\eta^6\text{-}\{\text{Cp}^*\text{Ru}\}^+$ units are η^6 -coordinated to non-adjacent arene rings on opposite sides of corannulene. Coordination of the $\{\text{Cp}^*\text{Ru}\}^+$ fragments results in significant flattening of the corannulene bowl, particularly at the point of attachment, which is the likely reason for the lower barrier to corannulene inversion in the dimetallated complexes as compared to that in free corannulene. The C-C bond distances in the corannulene units indicates localization of electron density upon η^6 -coordination of $\{\text{Cp}^*\text{Ru}\}^+$. The η^6 -coordination of arenes to transition metals has often been used as a way of activating arenes towards reactions that are not possible for the free ligands, and investigations into the reactivity of η^6 -coordinated buckybowl complexes like those in Chapters 5 and 6 may offer routes to new buckybowl complexes that are either difficult to prepare or inaccessible using current methodologies.

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