Arene Binding Affinities in [CpRu(η^6-arene)]$^+$ Complexes: Models for the Adsorption of Arenes on Hydrodesulfurization Catalysts

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Product/reactant ratios (*Y*) were determined for the reactions CpRu(η^6-DBT)$^+$ + L ⇌ CpRu(η^6-L)$^+$ + DBT (where DBT is dibenzothiophene and L is a homo- or heterocyclic arene), which were conducted under UV photolysis conditions. In the photostationary state, the *Y* values for the different arenes decrease in the following order: mesitylene (17) > toluene (13) > indole (9.1) > carbazole (6.7) > benzene (5.9) > fluorene (5.1) > biphenyl (3.9) > DBT (1.0) > phenanthrene (0.65) > naphthalene (0.35). In general, alkyl-substituted arenes have a higher binding affinity than the parent arene, except for *tert*-butyl groups, which decrease the *Y* values. These trends in η^6-arene binding to CpRu$^+$ provide a basis for understanding competitive adsorption of arenes on metal sites of hydrotreating catalysts. Such arene components in petroleum feedstocks reduce the rates of hydrodesulfurization of dibenzothiophenes.

Introduction

The removal of sulfur from petroleum fractions has become increasingly important, as the sulfur content in transportation fuels has been limited by ever-tightening environmental regulations.[1] Currently the U.S. Environmental Protection Agency and European Commission regulations require sulfur levels of 10 to 15 ppmw in on-road diesel fuel. Similar regulations for off-road diesel fuel are expected in the near future. The sulfur and nitrogen atoms in heterocyclic aromatic compounds are removed by the industrial hydrotreating process.[2] Conventional catalytic hydrodesulfurization (HDS), the process by which sulfur is removed from transportation fuels by treatment with hydrogen over a sulfided Mo-Co/Al_2O_3 (or Mo-Ni/Al_2O_3) catalyst, removes most of the sulfur but leaves the alkyldibenzothiophenes with one or two alkyl groups in the 4- and/or 6-positions untreated.[3] A recent study shows that RuS_2 is far more active than commercial MoS_2-based catalysts for the HDS of these refractory dibenzothiophenes. This was observed in tests with a difficult-to-desulfurize petroleum distillate at hydrogen pressures as low as 0.79 MPa.[4] The basis for this extraordinarily high activity of RuS_2 is poorly understood.

Petroleum feedstocks also contain organic nitrogen compounds and homocyclic aromatics. A vitally important inhibiting effect in industrial HDS arises from competitive adsorption of such indigenous nitrogen and aromatic compounds on the catalyst surface.[2] Aromatic nitrogen compounds are more difficult to denitrogenate than sulfur compounds and require more severe hydrotreating conditions.[2] It has been found that the presence of Cr in metal sulfide hydrotreating catalysts can significantly improve the hydrodenitrogenation (HDN) rate.[5] Most of the nitrogen in refractory petroleum fractions is present as heterocyclic arenes, such as quinolines, acridines, indoles, carbazoles, and benzocarbazoles.[6] These compounds have been shown to inhibit the HDS of dibenzothiophenes.[7] Other studies show that arenes such as anthracene, phenanthrene, fluorene, and carbazole (Figure 1) inhibit the deep HDS of 4,6-dimethyldibenzothiophene.[8] Computational studies of the adsorption of benzene suggest that adsorbed benzene blocks metal sites on the catalyst surface.[9] Investigations of the poisoning effects of nitrogen compounds on the HDS of 4,6-diethyldibenzothiophene, one of the most refractory organosulfur compounds, show that a trace amount of 3-ethylcarbazole can severely retard the HDS rate.[10a,b] It has also been found that

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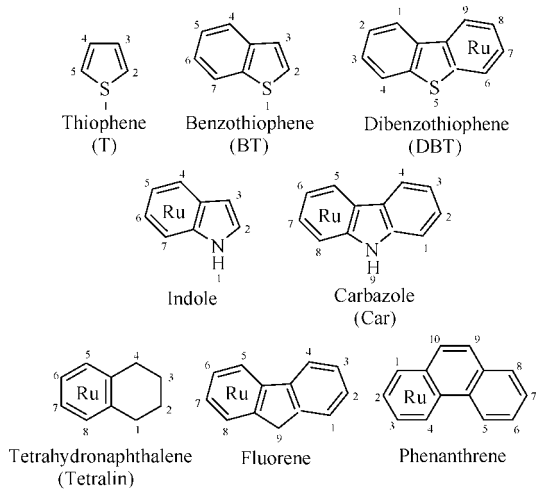

Figure 1. Structures and numbering schemes for arenes. The position of the η^6-coordinated Ru in the complexes is indicated by Ru.

tetrahydroquinoline is a stronger poison than quinoline in the HDS of both DBT and 4,6-dimethyldibenzothiophene.[10c]

Another significant factor that affects the effectiveness of HDS catalysts is coke formation, which limits the catalyst lifetime. Strong binding of some nitrogen and polynuclear homoaromatic compounds on the catalyst surface may eventually lead to coke formation through oligomerization/polymerization, thereby deactivating the catalyst.[11] Coke formation is ubiquitous in catalytic hydrotreating.

Recently, new approaches to desulfurization and denitrogenation have been developed using adsorbents or solid phase extractants to selectively bind and remove heterocyclic aromatic compounds such as 4-substituted and 4,6-disubstituted dibenzothiophenes and carbazole derivatives, whose heteroatoms are difficult to remove by the conventional hydrotreating process.[12] Another emerging technology for the desulfurization of hydrocarbon fuels is oxidation of refractory dibenzothiophenes to the corresponding sulfones or sulfoxides, which can then be removed by extraction or adsorption.[13] Currently, the most cost-effective method of removing sulfur and nitrogen heteroatoms remains the conventional hydrotreating process.

The present study seeks to gain an understanding of the inhibiting effects of various sulfur and nitrogen heterocycles and aromatics on the HDS of dibenzothiophenes by investigating their binding to the $CpRu^+$ fragment as a model for their adsorption through six carbon atoms (η^6) to a metal site on the catalyst surface. In the CpRu(η^6-arene)$^+$ complexes, it is known that the aromatic ligands are η^6-coordinated, and it is assumed that they are coordinated in a similar way on the catalyst. As a model for competitive binding of aromatics in petroleum feedstocks, we have sought to determine the binding affinities of a series of arenes (L) in the [CpRu(η^6-arene)]$^+$ complexes by studying the reaction in eq 1.

$$[\mathrm{CpRu}(\eta^6\text{-DBT})]\mathrm{PF_6} + \mathrm{L} \underset{25\ ^\circ\mathrm{C},\ h\nu}{\overset{d_6\text{-acetone}}{\rightleftharpoons}} [\mathrm{CpRu}(\eta^6\text{-L})]\mathrm{PF_6} + \mathrm{DBT} \quad \mathrm{L} = \text{arene} \quad (1)$$

These arene exchange reactions are thermally *very* slow at 25° and even at 50 °C. It was therefore not possible to measure equilibrium constants for these reactions. However, the reaction in eq 1 does occur under ultraviolet photolysis and reaches a photostationary state[14] where the ratio (Y in eq 2) of products

$$Y = \frac{[\mathrm{CpRu}(\eta^6\text{-L})^+][\mathrm{DBT}]}{[\mathrm{CpRu}(\eta^6\text{-DBT})^+][\mathrm{L}]} \quad (2)$$

to reactants does not change with further photolysis. In the photostationary state, the value of Y is determined by the quantum yields of the forward and reverse reactions. A previous study by Mann and co-workers[15] shows that quantum yields (Φ) for the photolytic substitution of various arenes in CpRu(η^6-arene)$^+$ by acetonitrile (eq 3) decrease with the arene in the following order: benzene (0.61) >

$$\mathrm{CpRu}(\eta^6\text{-arene})^+ + 3\ \mathrm{MeCN} \rightarrow \mathrm{CpRu(NCMe)_3^+} + \text{arene} \quad (3)$$

toluene (0.17) > mesitylene (0.085) > C_6Me_6 (0.014). Although these Φ values are affected by a variety of factors,[15] the trend suggests that photolytic substitution of arenes becomes less favorable as the number of electron-donating methyl groups in the arene increases. This is the same trend that is observed in several thermodynamic studies[16] of arene binding in transition metal complexes (also see Results and Discussion section), which suggests that the quantum yields for reaction 3 reflect the relative binding abilities of different arenes in CpRu(η^6-arene)$^+$ complexes. In the present studies of reaction 1, where CpRu(η^6-DBT)$^+$ and CpRu(η^6-L)$^+$ are interconverted photolytically, the product ratio Y is likely to reflect the relative binding affinities of the η^6-DBT and η^6-L ligands. Thus, a series of arenes that are present in petroleum feedstocks were investigated in reaction 1 with the goal of gaining some understanding of their relative binding affinities in the CpRu(η^6-arene)$^+$ complexes. The results of these studies are compared with those obtained from previous η^6-arene binding studies in Mo and Cr organometallic complexes. Also, the results are compared with equilibrium investigations for $\eta^1(S)$-coordinated substituted dibenzothiophenes. The present results are discussed in the context of understanding the inhibiting effects of nitrogen heterocycles and aromatics on the HDS of refractory dibenzothiophenes. In addition to the binding affinity studies, the structures of two of the complexes, [CpRu(η^6-Carbazole)](PF_6) (**1**) and [CpRu(η^6-Tetralin)])PF_6) (**2**), containing

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η^6-arene ligands were determined by X-ray diffraction crystallography.

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 toluene were purified on alumina using a Solv-Tek solvent purification system, similar to that described by Grubbs and co-workers.[17] Acetone was stirred with anhydrous potassium carbonate overnight, distilled, and stored under argon and 4 Å molecular sieves. CH_3CN was distilled from CaH_2, and 1,2-dichloroethane (DCE) was distilled from P_2O_5 under argon. CD_3COCD_3 was dried with 4 Å molecular sieves and stored under argon in a glovebox. Dibenzothiophene (DBT), carbazole (Car), 3,6-dibromocarbazole (3,6-Br_2Car), indole, 3-methylindole (3-MeIndole), biphenyl, fluorene, naphthalene (Nap), 1-methylnaphthalene (1-MeNap), 2-methylnaphthalene (2-MeNap), 1,2,3,4-tetrahydronaphthalene (Tetralin), and phenanthrene were purchased from Aldrich. 4,6-Diethyldibenzothiophene (4,6-Et_2DBT) and 3-ethylcarbazole (3-EtCar) were purchased from Bal Pharma Ltd., Bangalore, India. 3,6-Di(*tert*-butyl)carbazole (3,6-(*t*-Bu)$_2$Car) was purchased from Eburon Organics. Dibenzothiophene and indole were sublimed prior to use. Carbazole was recrystallized from acetone/EtOH solution. All other compounds were used without further purification. Complexes [CpRu(η^6-C_6H_6)](PF_6)[18] and [CpRu(η^6-DBT)](PF_6)[19] were prepared as described previously.

Solution NMR spectra were recorded on a Bruker DRX-400 spectrometer using CD_3COCD_3 as the solvent, internal lock, and reference. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer. UV photolyses were performed using a 450-W Hanovia low-pressure immersion lamp.

General Procedure for the Preparation of the [CpRu(η^6-L)](PF_6) Complexes. The [CpRu(η^6-L)](PF_6) complexes were synthesized by a method similar to that used for [CpRu(η^6-DBT)](PF_6).[19] As described by Mann et al.,[18] [CpRu(η^6-C_6H_6)](PF_6) (0.20 g, 0.51 mmol) was photolyzed in 30 mL of CH_3CN for 12 h to give [CpRu(CH_3CN)$_3$](PF_6). After evaporation of the solution to dryness under vacuum, the resulting brown solid was dissolved in 30 mL of DCE. The DCE solution of [CpRu(CH_3CN)$_3$](PF_6) and 1.0 mmol of the desired arene ligand (L) was refluxed under argon for 12 h and then evaporated to dryness in vacuo. After the residue was washed with Et_2O, the product was obtained by recrystallization from acetone/Et_2O. Isolated yields were typically 65–80%.

For the ^{1}H NMR assignments in the following [CpRu(η^6-L)](PF_6) compounds, the proton labels and the site of Ru coordination are indicated in Figure 1.

Characterization of [CpRu(η^6-Car)](PF_6) (1). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 10.42 (br s, 9-H, 1H), 8.23 (d, J = 7.6 Hz, 4-H, 1H), 7.63 (pseudo t, J = 7.2 Hz, 2-H, 1H), 7.56 (d, J = 8.4 Hz, 5-H, 1H), 7.44 (d, J = 5.6 Hz, 1-H, 1H), 7.33(pseudo t, J = 8.4 Hz, 3-H, 1H), 7.15 (d, J = 6.0 Hz, 8-H, 1H), 6.21(pseudo t, J = 5.6 Hz, 7-H, 1H), 6.13(pseudo t, J = 5.6 Hz, 6-H, 1H), carbazole; 5.04 (s, 5H), Cp. Anal. Calcd for $C_{17}H_{14}NF_6PRu$: C, 42.69; H, 2.95; N, 2.93. Found: C, 42.63; H, 2.70; N, 2.99.

Characterization of [CpRu(η^6-tetralin)](PF_6) (2). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 6.24−6.16 (m, 5-H−8-H, 4H), 2.84 (m, 1-H, 4-H, 4H), 1.82 (m, 2-H, 3-H, 4H), Tetralin; 5.46 (s, 5H), Cp. Anal. Calcd for $C_{15}H_{17}F_6PRu$: C, 40.64; H, 3.86. Found: C, 40.32; H, 3.99.

Characterization of [CpRu(η^6-3,6-Br_2Car)](PF_6). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 10.63 (br s, 9-H, 1H), 8.50 (d, J = 2.0 Hz, 2-H, 1H), 8.00 (br. s, 4-H, 1H), 7.77 (d of d, J = 8.4 Hz, J = 2.0 Hz, 1-H, 1H), 7.55 (d, J = 8.8 Hz,7-H, 1H), 7.26 (d, J = 6.4 Hz, 5-H, 1H), 6.70 (d of d, J = 6.4 Hz, J = 1.2 Hz, 8-H, 1H), 3,6-Br_2Carbazole; 5.20 (s, 5H), Cp. Anal. Calcd for $C_{17}H_{12}Br_2NF_6PRu$: C, 32.10; H, 1.90; N, 2.20. Found: C, 32.32; H, 2.03; N, 2.21.

Characterization of [CpRu(η^6-4,6-Et_2DBT)](PF_6). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.23 (m, 1-H, 1H), 7.60 (m, 2-H, 9-H, 2H), 7.48 (d, J = 5.6 Hz, 3-H,1H), 6.51 (d, J = 5.6 Hz, 7-H, 1H), 6.39 (pseudo t, J = 5.6 Hz, 8-H, 1H), 3.13 (q, J = 7.6 Hz, 4-CH_2, 2H), 2.88 (q, J = 7.6 Hz, 6-CH_2, 2H), 1.51 (t, J = 7.6 Hz, 4-CH_3, 3H), 1.35 (t, J = 7.6 Hz, 6-CH_3, 3H), 4,6-Et_2DBT; 5.16 (s, 5H), Cp. Anal. Calcd for $C_{21}H_{21}F_6PRuS$: C, 45.74; H, 3.84. Found: C, 45.49; H, 3.99.

Characterization of [CpRu(η^6-3-MeIndole)](PF_6). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 10.22 (br s, 1-H, 1H), 7.61 (s, 2-H, 1H), 7.11 (d, J = 6.4 Hz, 4-H,1H), 6.94 (d, J = 5.6 Hz, 7-H, 1H), 6.01 (pseudo t, J = 6.4 Hz, 6-H, 1H), 5.93 (pseudo t, J = 5.6 Hz, 5-H, 1H), 2.29 (s, Me, 3H), 3-MeIndole; 5.02 (s, 5H), Cp.

Characterization of [CpRu(η^6-2-MeNap)](PF_6). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.83−7.66 (m, 5-H−8-H, 4H), 7.22 (s, 1-H, 1H), 7.17 (d, J = 6.0 Hz, 4-H, 1H), 6.46 (d, J = 6.0 Hz, 3-H, 1H), 2.52 (s, Me, 3H), 2-MeNaphthalene; 5.10 (s, 5H), Cp. Anal. Calcd for $C_{16}H_{15}F_6PRu$: C, 42.39; H, 3.34. Found: C, 41.78; H, 3.36.

Characterization of [CpRu(η^6-fluorene)](PF_6). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.96 (d, J = 6.4 Hz, 4-H, 1H), 7.60 (d, J = 6.4 Hz, 1-H, 1H), 7.48 (m, 2-H, 5-H, 2H), 7.20 (t, J = 6.0 Hz, 3-H, 1H), 6.97 (d, J = 6.0 Hz, 8-H, 1H), 6.35 (pseudo t, J = 5.6 Hz, 7-H, 1H), 6.30 (pseudo t, J = 5.6 Hz, 6-H, 1H), 4.11 (s, 9-H, 2H), fluorene; 5.23 (s, 5H), Cp. Anal. Calcd for $C_{18}H_{15}F_6PRu$: C, 45.29; H, 3.17. Found: C, 45.15; H, 3.25.

X-ray Structural Determinations of [CpRu(η^6-Car)](PF_6) (1) and [CpRu(η^6-tetralin)](PF_6) (2). Single crystals of **1** and **2** for the X-ray diffraction studies were obtained by vapor diffusion of Et_2O into an acetone solution of the compound 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 Apex diffractometer with Mo Kα (λ = 0.71073 Å) radiation and a collector-to-crystal distance of 5.99 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 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.[20] Positions of the heavy atoms were located by the direct 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 the full-matrix anisotropic approximation. All hydrogen atoms were placed in the structure factor calculations at idealized positions and refined using a riding model. Complete data collection and reduction information for the compounds are given in Table 1.

Product/Reactant Ratios (*Y*) in the Photostationary State. Solutions used in the photolysis studies (eq 1) were prepared by placing 0.020 mmol of [CpRu(η^6-DBT)](PF_6) and an equimolar amount of an arene ligand (L) in a 5 mm NMR tube in the glovebox. Approximately 0.6 mL of CD_3COCD_3 was added to dissolve the reactants. After capping the tube with a septum and removing it from the drybox, the reaction solution was frozen in liquid nitrogen. The solution was subjected to a freeze–pump–thaw cycle, and the tube was flamed-sealed under vacuum at −173 °C. The tube was slowly warmed to room temperature

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Table 1. Crystal Data and Structure Refinement for [CpRu(η^6-Car)](PF$_6$) (1) and [CpRu(η^6-tetralin)](PF$_6$) (2)

	[CpRu(η^6-Car)]PF$_6$ (**1**)	[CpRu(η^6-tetralin)]PF$_6$ (**2**)
empirical formula	$C_{17}H_{14}F_6NPRu$	$C_{15}H_{17}F_6PRu$
fw	478.33	443.33
temperature	293(2) K	293(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	monoclinic	monoclinic
space group	*P*2(1)/*c*	*P*2(1)/*c*
unit cell dimens	a = 9.7862(5) Å	a = 7.6786(6) Å
	b = 16.7367(8) Å	b = 15.0610(11) Å
	c = 11.0019(5) Å	c = 14.3333(10) Å
	β = 112.949(1)°	β = 103.292(1)°
volume	1659.36(14) Å^3	1613.2(2) Å^3
Z	4	4
cryst color, habit	yellow prism	yellow prism
density(calcd)	1.915 Mg/m^3	1.825 Mg/m^3
abs coeff	1.105 mm^{-1}	1.126 mm^{-1}
F(000)	944	880
cryst size	0.24 × 0.14 × 0.11 mm	0.28 × 0.28 × 0.42 mm
θ range for data collection	2.26 to 28.30°	2.70 to 28.37°
index ranges	$-12 \le h \le -12$	$-10 \le h \le 9$
	$-22 \le k \le -22$	$-19 \le k \le -19$
	$-14 \le l \le 14$	$-18 \le l \le 18$
no. of reflns collected	14 058	13 927
no. of indep reflns	3897[R(int) = 0.0168]	3802[R(int) = 0.0205]
completedness to θ = 25	100%	100%
abs corr	empirical with SAD	empirical with SAD
max. and min. transmn	1.00 and 0.87	1.00 and 0.89
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	3897/0/239	3802/0/208
goodness-of-fit on F^2	1.070	1.046
final R^a indices [$I > 2\sigma(I)$]	R1 = 0.0549, wR2 = 0.1659	R1 = 0.0494, wR2 = 0.1461
R^a indices (all data)	R1 = 0.0581, wR2 = 0.1689	R1 = 0.0548, wR2 = 0.152
largest diff peak and hole	1.366 and −0.880 e Å^{-3}	0.826 and −0.652 e Å^{-3}

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

and placed in a glass circulating bath thermostated at 25.0 ± 0.2 °C. The reaction tube was irradiated with a Hanovia low-pressure UV lamp. The reaction progress was monitored periodically by ^{1}H NMR spectroscopy using CD_3COCD_3 as the internal lock and reference (δ = 2.03) with a 60 s pulse delay between scans to ensure complete relaxation of the Cp protons. Values of Y were calculated from the ^{1}H NMR spectra when the reaction reached the photostationary state, as indicated by the lack of change in the reactant and product concentrations, using the equation $Y = (\mathrm{Int}_{Cp'})^2/(\mathrm{Int}_{Cp})^2$, where $\mathrm{Int}_{Cp'}$ and Int_{Cp} are the Cp peak integrals for CpRu(η^6-L)$^+$ and CpRu(η^6-DBT)$^+$, respectively. Values of Y determined for the reaction of [CpRu(η^6-DBT)]$^+$ with carbazole and the reaction of [CpRu(η^6-Car)]$^+$ with DBT were the same within experimental error. The results (Table 2) are the average of two independent experiments for each reaction. All values in Table 2 are reproducible within 15%. All reactions reached the photostationary state within 4 days or less.

Table 2. Product/Reactant Ratios (Y) for Reactions (eq 1) of [CpRu(η^6-DBT)]$^+$ with L in (CD$_3$)$_2$CO Solvent at 25 °C under UV Photolysis

η^6-L	Y
mesitylene	17
toluene	13
3-Meindole	10
tetralin	10
indole	9.1
Car	6.7
3-EtCar	6.5
benzene	5.9
fluorene	5.1
3,6-(*t*-Bu)$_2$Car	4.9
biphenyl	3.9
4,6-Et$_2$DBT	1.1
DBT	1.0
phenanthrene	0.65
2-MeNap	0.56
1-MeNap	0.43
Nap	0.35
3,6-Br$_2$Car	0.1

Results and Discussion

Syntheses of the [CpRu(η^6-L)](PF$_6$) Complexes. The η^6-arene complexes [CpRu(η^6-L)](PF$_6$), where L = DBT, Car, 3,6-Br$_2$Car, 4,6-Et$_2$DBT, 3-MeIndole, 1-MeNap, 2-MeNap, tetralin, and fluorene, were prepared in 65–80% yield by reaction of [CpRu(NCCH$_3$)$_3$](PF$_6$) with the arene ligand (L) in refluxing DCE (eq 4). Complexes were isolated as air-stable, pale yellow solids that are insoluble in

$$[\mathrm{CpRu(NCCH_3)_3}](\mathrm{PF_6}) + \mathrm{L} \xrightarrow[-3\ \mathrm{CH_3CN}]{\mathrm{DCE}} [\mathrm{CpRu}(\eta^6\text{-L})](\mathrm{PF_6}) \quad (4)$$

Et$_2$O and hexanes, but soluble in acetone and CH$_2$Cl$_2$. Peaks in the ^{1}H NMR spectrum of [CpRu(η^6-Car)](PF$_6$) (**1**) were assigned by comparison to those of free carbazole, whose ^{1}H NMR spectrum has been assigned in the literature.[21] Chemical shifts of the coordinated ring H5−H8 resonances in **1** are 0.5–1.3 ppm upfield of those of free carbazole. However, the shifts of the uncoordinated ring are very similar to those of free carbazole or slightly downfield (0.1–0.3 ppm). ^{1}H NMR data for the other complexes show similar upfield shifts for ^{1}H signals of the coordinated arene group as compared with shifts of the free arene and of the uncoordinated ring of the arene ligand in

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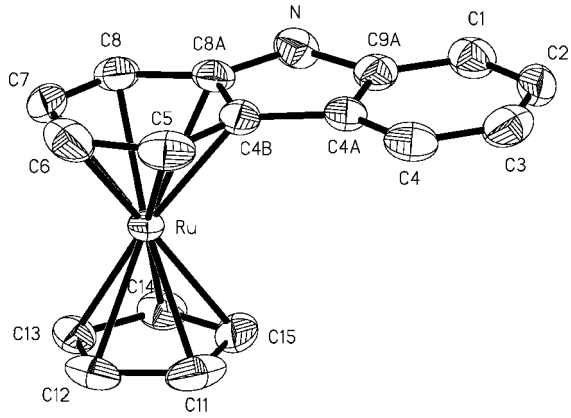

Figure 2. Thermal ellipsoid drawing of the [CpRu(η^6-Car)]$^+$ cation in **1**. Ellipsoids are shown at the 30% probability level; hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ru–C(4B) 2.246(4), Ru–C(5) 2.202(5), Ru–C(6) 2.200(6), Ru–C(7) 2.197(5), Ru–C(8) 2.226(5), Ru–C(8A) 2.281(5), C(1)–C(2) 1.359(9), C(1)–C(9A) 1.374(8), C(2)–C(3) 1.384(10), C(3)–C(4) 1.381(10), C(4)–C(4A) 1.373(9), C(4A)–C(4B) 1.466(7), C(4A)–C(9A) 1.362(8), C(4B)–C(5) 1.412 (9), C(4B)–C(8A) 1.438(8), C(5)–C(6) 1.417(11), C(6)–C(7) 1.379(14), C(7)–C(8) 1.378(10), C(8)–C(8A) 1.401(8), N–C(8A) 1.372(8), N–C(9A) 1.399(7).

the CpRu(η^6-L)$^+$ complexes. Such upfield shifts have been reported for CpRu(η^6-Nap)$^{+22}$ and other η^6-arene complexes of ruthenium.[18,23] The compounds where η^6-L is indole, benzene, toluene, mesitylene, biphenyl, naphthalene, and phenanthrene were reported previously in the literature and identified by comparison with their ^{1}H NMR spectra.[24]

Structures of [CpRu(η^6-Car)](PF$_6$) (1) and [CpRu(η^6-tetralin)](PF$_6$) (2). Structures of these compounds, determined by X-ray crystallography, are shown in Figures 2 and 3. In complex **1**, the η^6-carbazole ligand is essentially planar, with individual atoms showing small deviations (0.015 Å) from the average carbazole plane. The planes of the Cp and arene rings in **1** are essentially parallel (dihedral angle = 0.4°). The N−C(8A) (1.372(8) Å) bond distance is slightly shorter than the N−C(9A) (1.399(7) Å) distance on the noncoordinated side of the carbazole, which is similar to that observed for the coordinated side C−N (1.373(2) Å) and uncoordinated side C−N (1.392(2) Å) bond distances in the (η^6-*N*-ethylcarbazole)-Cr(CO)$_3$ complex.[25] The N−C(8A) (1.372(8) Å) distance of the coordinated arene side is also slightly shorter than those of free carbazole (1.394(6) Å)[26a,b] and *N*-vinylcarbazole (1.393(11) Å),[26c] while the uncoordinated side N−C(9A) (1.399(7) Å) distance in **1** is similar to those of free carbazole and *N*-vinylcarbazole. The average C−C distance (1.40(1) Å) of the coordinated arene ring in **1** is 0.03 Å longer than that (1.37(1) Å) of the uncoordinated ring. A similar C−C bond lengthening

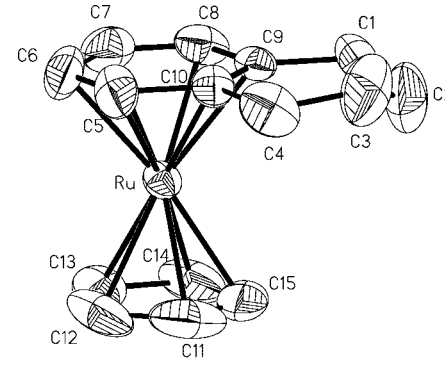

Figure 3. Thermal ellipsoid drawing of the [CpRu(η^6-tetralin)]$^+$ cation in **2**. Ellipsoids are shown at the 30% probability level; hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ru−C(5) 2.181(5), Ru−C(6) 2.178(6), Ru−C(7) 2.188(6), Ru−C(8) 2.192(5), Ru−C(9) 2.210(4), Ru−C(10) 2.222(4), C(1)−C(2) 1.441(10), C(1)−C(9) 1.487(6), C(2)−C(3) 1.398(12), C(3)−C(4) 1.454(11), C(4)−C(10) 1.517(7), C(5)−C(6) 1.395(10), C(5)−C(10) 1.417(7), C(6)−C(7) 1.416(11), C(7)−C(8) 1.376(11), C(8)−C(9) 1.413(7), C(9)−C(10) 1.401(7).

is observed in other η^6-arene complexes.[16,27] The average C−C distances in the coordinated ring (1.406(3), 1.408(6) Å) are also slightly longer than those in the uncoordinated arene ring (1.388(3), 1.393(6) Å) in (η^6-*N*-ethylcarbazole)Cr(CO)$_3$ and (η^6-*N*-ethylcarbazole)Cr(CO)$_2$(PPh$_3$), respectively.[25]

The Ru in **1** is not equally bonded to all six arene carbon atoms but is slipped away from C(4B) and C(8A). The difference between the average Ru−C(6) and Ru−C(7) distance (2.198(6) Å) and the average Ru−C(4B) and Ru−C(8A) distance (2.263(5) Å) is the same (0.07 Å) as that in [CpRu(η^6-BT)](PF$_6$).[28] In other transition-metal complexes containing fused arene ring ligands (naphthalene, phenanthrene, anthracene, octamethylnaphthalene), a similar slippage away from bridgehead carbons has been observed, and the slipped distances range from 0.03 to 0.12 Å.[16,27] This slippage may be favored because the uncoordinated ring is able to retain more of its aromatic character, and the bridgehead carbons cannot interact as effectively with the metal because they are already π-bonded to three other atoms.

In [CpRu(η^6-tetralin)](PF$_6$) (**2**), the arene ring of tetralin is flat within 0.004 Å, and the cyclohexene ring adopts a half-chair conformation as in (η^6-2-aminotetralin)Cr(CO)$_3$.[29] The Cp and arene rings in **2** are essentially coplanar (dihedral angle = 1.7°). The Cp ring carbons are symmetrically bonded to the Ru atom. However, the Ru atom is not symmetrically bonded to all six arene carbons but is slipped away from the bridgehead carbon atoms toward C(6) and C(7), as indicated by the slightly shorter average Ru−C(6) and Ru−C(7) distance (2.183(6) Å) as compared with the average Ru−C(9) and Ru−C(10) distance (2.2163(6) Å). The C(5)−C(6) (1.395(10) Å) and C(7)−C(8) (1.376(11) Å) bonds are somewhat shorter than the other C−C bonds (1.401(7), 1.413(7), 1.416(11), 1.417(7) Å) of the arene ring, suggesting a delocalized 1,3-diene type of unit for C(5)═C(6)−C(7)═C(8).

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Product/Reactant Ratios (*Y*) in the Photostationary State of Reactions of CpRu(η^6-DBT)$^+$ with Arenes According to Eq 1. When solutions of [CpRu(η^6-DBT)]$^+$ and carbazole in d_6-acetone were heated at 50 °C, no reaction occurred over a period of 7 days. However, UV irradiation facilitates reactions of CpRu(η^6-DBT)$^+$ with arene ligands at 25 °C according to eq 1. In the photolytic reactions of [CpRu(η^6-DBT)](PF$_6$) with unsymmetrically alkyl-substituted arene ligands, such as 1-MeNap, 2-MeNap, and 3-EtCar, two new Cp resonances in the ^{1}H NMR spectrum appeared, which indicates that two isomers are produced in approximately a 1:1 ratio; these are isomers resulting from CpRu$^+$ coordination to either the alkyl-substituted arene ring or the nonsubstituted arene ring. In the photostationary state, values of *Y* for the reaction (eq 1) involving exchange of dibenzothiophene in [CpRu(η^6-DBT)]$^+$ with other arenes were calculated and are listed in Table 2. The *Y* values decrease in the order mesitylene (17) > toluene (13) > 3-MeIndole (10) ∼ tetralin (10) ∼ indole (9.1) > carbazole (6.7) ∼ 3-EtCar (6.5) > benzene (5.9) > fluorene (5.1) ∼ 3,6-(*t*-Bu)$_2$Car (4.9) > biphenyl (3.9) > 4,6-Et$_2$DBT (1.1) ∼ DBT (1.0) > phenanthrene (0.65) > 2-MeNap (0.56) ∼ 1-MeNap (0.43) ∼ naphthalene (0.35) > 3,6-Br$_2$Car (0.1).

Product/Reactant Ratios (*Y*) in Reactions of CpRu(η^6-DBT)$^+$ with Unsubstituted Arenes. A comparison of the different types of unsubstituted arenes shows that the *Y* values decrease in the order indole (9.1) > carbazole (6.7) > benzene (5.9) > fluorene (5.1) > DBT (1.0) > phenanthrene (0.65) > naphthalene (0.35). This trend indicates that the nitrogen-containing arenes, indole and carbazole, have higher binding affinities than the sulfur-containing arene, dibenzothiophene. The non-heteroatom-containing arenes, benzene and fluorene, bind less strongly than the nitrogen-containing arenes but more strongly than DBT. Among the unsubstituted arenes, the *Y* values decrease in the order benzene (5.9) > fluorene (5.1) > phenanthrene (0.65) > naphthalene (0.35).

Qualitative equilibrium studies[30] of the exchange of the η^6-arene in (1–5-η^5-cyclooctadienyl)Ru(η^6-arene)$^+$ show that arene binding decreases in the following order: benzene ∼ triphenylene > phenanthrene > naphthalene > perylene ∼ pyrene > anthracene. This trend was correlated with the loss of aromaticity in the uncoordinated part of the arene ligand. For the common ligands (benzene > phenanthrene > naphthalene) in the CpRu(η^6-arene)$^+$ and (1–5-η^5-cyclooctadienyl)Ru(η^6-arene)$^+$ series of complexes, the trend in binding is the same.

Product/Reactant Ratios (*Y*) in Reactions of CpRu(η^6-DBT)$^+$ with Substituted Arenes. Substituents on the arene rings have a significant effect on the *Y* values. As discussed in the Introduction, quantum yields for reaction 3 suggest that electron-donating methyl groups increase the binding affinity of arenes. Indeed, the trend in decreasing *Y* values for mesitylene (17) > toluene (13) > tetralin (10) > benzene (5.9) demonstrate that electron-donating alkyl groups on the benzene do increase the binding ability of the arenes. On the other hand, fluorene (5.1) and biphenyl (3.9) are less strongly binding than benzene presumably because of electron delocalization into the adjacent aryl rings. For the naphthalene ligands, an electron-donating methyl group also increases binding, as reflected in the following decrease in *Y* values: 2-MeNap (0.56) > 1-MeNap (0.43) > Nap (0.35). However, the differences in these *Y* values are small, which is also true for the *Y* values for 4,6-Et$_2$DBT (1.1) and DBT (1.0). The electron-donating effect of the methyl group in 3-MeIndole (10) as compared to indole (9.1) is also small. The effect of the ethyl group in 3-EtCar (6.5) is negligible as compared with Car (6.7). On the other hand, the effect of the electron-withdrawing Br atoms in 3,6-Br$_2$Car on *Y* values for 3,6-Br$_2$Car (0.1), as compared with the Car (6.7) ligand, is large. The smaller *Y* value for 3,6-Br$_2$Car (0.1) may reflect not only the electron-withdrawing effect of the Br groups but also a steric effect. Such a steric effect may also be a factor in the smaller *Y* value for 3,6-(*t*-Bu)$_2$Car (4.9) than Car (6.7). These latter constants suggest that the steric effect of the 4,6-(*t*-Bu)$_2$ groups overrides their electron-donating ability. It should also be noted that a large steric effect by *t*-Bu groups was detected in the much lower quantum yield for the reaction (eq 3) of CpRu(η^6-1,3,5-(*t*-Bu)$_3$C$_6$H$_3$)$^+$ (0.0031) as compared with CpRu(η^6-C$_6$H$_6$)$^+$ (0.34).[15]

Thermodynamic Studies of Mo(CO)$_3$(η^6-arene) Complexes. Trends in *Y* values observed for the reaction in eq 1 have been observed in thermodynamic studies of other η^6-arene complexes. For example, equilibrium constants (*K*) for the reaction Mo(CO)$_3$(η^6-toluene) + arene ⇌ Mo(CO)$_3$(η^6-arene) + toluene, at 22 °C in CD$_2$Cl$_2$ solvent, are largest for arenes containing the most methyl groups;[31] these equilibrium constants decrease in the order mesitylene (36) > *p*-xylene (3.2) > toluene (1.0) > benzene (0.32). This trend is the same as for the *Y* values of the CpRu(η^6-arene)$^+$ reactions. Calorimetric ΔH values for the reaction Mo(CO)$_3$(η^6-C$_6$H$_6$) + arene → Mo(CO)$_3$(η^6-arene) + C$_6$H$_6$ also show that *p*-xylene (−2.3 kcal/mol) coordinates more strongly than benzene (0.0 kcal/mol).[32]

Thermodynamic Studies of Cr(CO)$_3$(η^6-arene) Complexes. Calorimetric studies of the reaction Cr(CO)$_3$(η^6-C$_6$H$_6$) + arene → Cr(CO)$_3$(η^6-arene) + C$_6$H$_6$ give ΔH values (kcal/mol) that become less favorable with the arene in the following order: benzene (0.0) > phenanthrene (+3.7) > naphthalene (+4.9).[33] This is the same order for these arenes as in the CpRu(η^6-arene)$^+$ system. Thus, trends in equilibrium constants (*K*) and ΔH values for the Mo(CO)$_3$ and Cr(CO)$_3$ systems and the *Y* values in the CpRu$^+$ complexes are the same.

Equilibrium Studies of CpRu(η^5-thiophene)$^+$ with Alkylthiophenes. Earlier, we reported equilibrium constants for the displacement of η^5-thiophene (T) by methyl-substituted thiophenes (Th) according to the following equation: CpRu(η^5-T)$^+$ + Th ⇌ CpRu(η^5-Th)$^+$ + T in acetone at 50 °C. Equilibrium constants (*K*) for these reactions decreased as the number of methyl groups decreased: Me$_4$T (1300) > 2,3,5-Me$_3$T (300) > 2,5-Me$_2$T (35) > 2-MeT (6) > T (1.0).[34] This trend is similar to that of Y values for the exchange of methyl-substituted arenes in CpRu(η^6-arene)$^+$ in eq 1.

Equilibrium Studies of CpRu′(CO)$_2$(η^1(*S*)-DBT)$^+$ with Substituted Dibenzothiophenes and Thiophenes. While the effect of methyl groups on the binding ability of η^5-thiophenes and η^6-arenes is to increase the strength of the thiophene or arene coordination, the effect of methyl groups on the η^1(*S*)-coordination of substituted dibenzothiophenes (DBTh) can be very different, especially when the methyl groups are in the hindering 4- and/or 6-positions of the dibenzothiophene. Equi-

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librium constants[35] for the displacement of 4,6-Me_2DBT in $Cp'Ru(CO)_2(\eta^1(S)$-4,6-Me_2DBT)$^+$ by other dibenzothiophenes (eq 5) have been determined in CD_2Cl_2 or CD_3NO_2 at 25 °C. For the $CpRu(CO)_2(DBTh)^+$ complexes,

$$[Cp'Ru(CO)_2(\eta^1(S)\text{-}4,6\text{-}Me_2DBT)]^+ + DBTh \overset{K'}{\rightleftharpoons} [Cp'Ru(CO)_2(\eta^1(S)\text{-}DBTh)]^+ + 4,6\text{-}Me_2DBT \quad (5)$$

where Cp = η^5-C_5H_5, the K' values (eq 5) decrease in the order 2,8-Me_2DBT (36.5) > DBT (9.7) > 4-MeDBT (2.79) > 4,6-Me_2DBT (1.0).[35] The larger K' value for 2,8-Me_2DBT as compared to DBT demonstrates that electron-donating methyl groups in the nonhindering 2,8-positions increase the binding ability of DBT. On the other hand, the 4-MeDBT and 4,6-Me_2DBT ligands bind less strongly than DBT. This trend shows that the steric effect of the 4,6-methyl groups in the $\eta^1(S)$-DBTh coordination mode overrides their increased electron-donating ability. In the sterically more crowded Cp* series of complexes $Cp^*Ru(CO)_2(DBTh)^+$, where Cp* = η^5-C_5Me_5, the much larger decrease in the binding ability of 4,6-Me_2DBT as compared with 4-MeDBT reflects the substantial steric crowding between the 4,6-Me_2DBT methyl groups and the Cp* ligand: 2,8-Me_2DBT (223) > DBT (62.7) > 4-MeDBT (20.2) > 4,6-Me_2DBT (1.0).[35] In contrast to the substantial steric effects of 4,6-methyl groups in the binding of $\eta^1(S)$-coordinated dibenzothiophenes, steric effects of methyl groups in $\eta^1(S)$-coordinated thiophenes are relatively small. In an equilibrium study of $[Cp(CO)_2Ru(\eta^1(S)\text{-Th})]^+$, where Th denotes the thiophene (T), benzothiophene (BT), or DBT ligands, relative equilibrium constants decrease in the order 2,8-Me_2DBT (3016) > Me_4T (887) > DBT (800) > BT (47.6) > 2,5-Me_2T (20.7) > 3-MeT (4.76) > 2-MeT (3.30) > T (1.0).[36] These data show that the addition of methyl groups in thiophene *increases* the equilibrium constants, which reflects the electron-donating effects of these groups. Even methyl groups in the 2- and 5-positions increase $\eta^1(S)$-coordination to the Ru. It should be noted that there *is* a steric effect of the 2- and 5-methyl groups in $CpRu(CO)(PPh_3)(Th)^+$, where the bulky PPh_3 ligand poses a steric barrier to coordination by 2- and 5-methyl-substituted thiophenes.[36]

Several kinetic studies of rates of dissociation of substituted $\eta^1(S)$-Th and $\eta^1(S)$-DBTh ligands in $Cp(CO)(PPh_3)Ru(\eta^1(S)$-Th)$^+$,[36a] $Cp(CO)_2Re(\eta^1(S)$-Th),[37] and $[Cp(CO)_2Ru(\eta^1(S)$-DBTh)]$^+$[35] complexes follow the same trends that were observed in the equilibrium constants (K) discussed above. In general, alkyl groups on the Th or DBTh that increase the equilibrium constants decrease the rate of Th or DBTh dissociation.

Relevance to Hydrotreating. We now discuss the foregoing results in the context of commercial hydrotreating, a high-temperature, hydrogen-addition operation that is vastly different from the experiments of the present study. Yet, some of our results are consistent with those observed in hydrotreating. First, adsorption equilibrium constants obtained from kinetic studies of the inhibition of the HDS of 4,6-Me_2DBT on a sulfided $NiMo/Al_2O_3$ catalyst[8a] decrease in the order carbazole (10) > fluorene (3.75) > phenanthrene (0.14). This trend is the same as that of the Y values (Table 2) for the binding of these arenes in $CpRu(\eta^6\text{-arene})^+$. Second, partially hydrogenated arenes are known to be stronger HDS inhibitors than the parent arenes,[3c,10c,38] which is consistent with our observation that the Y value for tetralin (10) is higher than that for naphthalene (0.35). Third, the HDS of 4,6-Et_2DBT on $CoMo/Al_2O_3$-SiO_2 is inhibited more by 3-EtCar than by naphthalene,[10a,b] which is consistent with 3-EtCar adsorbing more strongly to a metal site than naphthalene, as found in the Y values for the $CpRu(\eta^6\text{-arene})^+$ complexes (Table 2). Fourth, the substituents in carbazoles are not a significant factor in the poisoning effects of the carbazoles[10a] in the HDS of 4,6-Et_2DBT. Specifically, the following electron-rich and electron-poor carbazoles have comparable poisoning effects: *N*-ethylcarbazole, 3-ethylcarbazole, 3-acetylcarbazole, and carbazole-9-carboxylic acid methyl ester.[10a] In the present study, the Y values (Table 2) for carbazole, 3-EtCar, and 3,6-(t-Bu)$_2$Car are also similar; the exception is 3,6-Br_2Car, which is not of interest in hydrotreating.

Studies indicate that the active sites on hydrotreating catalysts are sulfur vacancies associated with exposed Mo (or W) cations and SH^-/S^{2-} groups on the MoS_2 edge.[2] A heterocyclic arene, such as 4,6-Et_2DBT, may adsorb through its π-electrons (η^6) to a metal ion site that is adjacent to several sulfur vacancies. An alternative adsorption mode involves σ-bonding (e.g., $\eta^1(S)$ for dibenzothiophenes) on a smaller, single vacancy site. It is expected in hydrotreating that the adsorptivity of an arene (heterocyclic or homocyclic) is mainly governed by a balance between two factors.[39a] One is an acid–base interaction between the arene and a site on the catalyst surface.[39b] This interaction has been characterized by the proton affinity (PA) of the arene, which is correlated with its heat of adsorption on a $NiMo/Al_2O_3$ catalyst.[39b] The other factor is the size/mass of the adsorbing molecule. In a study of hydrotreatment over a $CoMo/Al_2O_3$ catalyst,[39c] it was found that equilibrium constants for the adsorption of 28 arenes and hydroarenes (benzene, naphthalene, phenanthrene, and their derivatives) were correlated with an increasing number of arene rings and the length of alkyl side chains. The data set did not, however, contain polynuclear aromatic compounds with five-membered rings (as in fluorenes) or their hydro derivatives.

In contrast to adsorption on a catalyst surface, there is no fundamental reason why the Y values for reaction 1 should reflect the effect of molecule size. Indeed, the Y values in Table 2 for benzene, naphthalene, and phenanthrene do not increase with the size of the arene. Moreover, the Y value for indole is larger than that for carbazole. It is relevant to point out that indole has a strong propensity to form coke on hydrotreating catalysts.[11a] In this context, it would be worthwhile to conduct studies that compare the adsorptivities of indole and carbazoles under deep HDS conditions.

Conclusions

For comparison with results of competitive adsorption studies in catalytic hydrotreating, binding affinities of a wide variety

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of homocyclic and heterocyclic arenes in the [CpRu(η^6-arene)]$^+$ series of complexes have been determined. The *Y* values for these reactions in the photostationary state follow systematic trends reflecting electronic as well as steric effects of the arene ligands. The results of this work, taken together with those of previous studies, indicate that trends in binding affinities of various homo- and heterocyclic arenes are very similar in the $CpRu^+$, (1–5-η^5-cyclooctadienyl)Ru^+, $Mo(CO)_3$, and $Cr(CO)_3$ systems. Moreover, the trends in *Y* values bear an important resemblance to those observed in hydrotreating catalysis and point to potentially fruitful directions for future fundamental studies of HDS.

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Supporting Information Available: Crystallographic files (CIF) for [CpRu(η^6-Car)](PF_6) (**1**) and [CpRu(η^6-tetralin)](PF_6) (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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