Ring Shift Isomerization Reaction of Monocyclopentadienylruthenium(II) Complexes of Rubrene. Kinetic and Thermodynamic Studies of Metal-Arene Binding Selectivity

Robert S. Koefod and Kent R. Mann*

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received February 26, 1990*

Abstract: The synthesis and characterization of two isomeric complexes containing a $CpRu^+$ ($Cp = \eta^5$-C_5H_5) moiety bound to rubrene (5,6,11,12-tetraphenylnaphthacene) are reported. Reaction of rubrene with 1 equiv of $CpRu(CH_3CN)_3^+$ at room temperature yields the isomer with one $CpRu^+$ moiety bound to an end naphthacene ring, while the analogous reaction at elevated temperatures yields the isomer with the $CpRu^+$ group bound to a substituent phenyl group on the naphthacene core. The naphthacene-bound isomer undergoes slow conversion to the phenyl-bound isomer in acetone solution. Kinetic studies of arene complexation by $CpRu^+$ (arene = anthracene, benzene) in acetone solution are reported and used to explain the selectivity exhibited by $CpRu(CH_3CN)_3^+$ toward different arene rings in rubrene. The rate constant for the complexation of anthracene in acetone solution is $\sim$4.9 (7) $\times 10^3$ times greater than that for the corresponding complexation of benzene. This result is consistent with the ground-state destabilization of anthracene because of its lower resonance energy and with a proposed transition state that involves the partial disruption of the arene's aromaticity by the metal. Plots of k_{obsvd} vs $[CH_3CN]$ are consistent with mechanisms in which preequilibria result in the loss of two or three acetonitriles before the transition state in the formation of the $CpRu(\eta^6\text{-arene})^+$ complex. For benzene the overall equilibrium greatly favors the arene complex ($K_{eq} > 4 \times 10^3$ M^2) but for anthracene the equilibrium is much less favorable ($K_{eq} \sim 5.7(9)$ M^2). The interplay of kinetic and thermodynamic factors permits arenes with higher degrees of aromaticity (such as biphenyl) to replace kinetically favored arenes (such as anthracene) to yield the thermodynamic product.

Introduction

For the past several years our group has been interested in the thermal and photochemical behavior of the iron triad transition-metal-arene complexes. Efforts in this area have involved the synthesis and characterization of a wide variety of $CpRu(arene)^+$ and $Cp^*Ru(arene)^+$ ($Cp = \eta^5$-C_5H_5, $Cp^* = \eta^5$-$C_5(CH_3)_5$; arene = η^6-arene) compounds, including complexes of substituted benzenes,[1-3] polyaromatic hydrocarbons,[4] azulene derivatives,[5] and most recently highly fluorescent arenes such as the 7-aminocoumarin laser dyes.[6] Complexes of this type can be prepared by taking advantage of the reaction between $[CpRu(CH_3CN)_3]^+$ or $[Cp^*Ru(CH_3CN)_3]^+$ and arenes in which the relatively labile acetonitrile ligands are readily substituted by a 6π-electron donor (reaction 1). For some arenes this reaction is reversible. Our

$$[CpRu(CH_3CN)_3]^+ + \text{arene} \rightarrow [CpRu(\eta^6\text{-arene})]^+ + 3CH_3CN \quad (1)$$

group has previously reported kinetic measurements on the thermal displacement of arene by acetonitrile (reaction 2) for a series of $CpRu(arene)^+$ complexes and discussed the possible mechanisms of the reaction, but at this time no mechanistic study of the corresponding complexation reaction (reaction 1) has appeared.

$$[CpRu(\eta^6\text{-arene})]^+ + 3CH_3CN \rightarrow [CpRu(CH_3CN)_3]^+ + \text{arene} \quad (2)$$

We noted with interest Fagan and co-workers' recent report of the unusual products produced from reaction of $Cp^*Ru(CH_3CN)_3^+$ with the highly emissive, aromatic hydrocarbon rubrene (5,6,11,12-tetraphenylnaphthacene).[7] Reaction of rubrene with 1 equiv of $Cp^*Ru(CH_3CN)_3^+$ yielded a compound in which the rubrene's end naphthacene ring was complexed by a Cp^*Ru^+ group while reaction of the arene with >4 equiv of the ruthenium starting material yielded an emissive product in which the rubrene's four substituent phenyl rings were complexed by the Cp^*Ru^+ moiety. We became interested in understanding the factors that control the ring selectivity in these reactions as well as the photochemical/photophysical mechanisms that operate in these compounds.

To this end we have synthesized, isolated, and characterized five new complexes of rubrene substituted with from 1 to 4 $CpRu^+$ groups. The two isomeric compounds with a single $CpRu^+$ group will be the subject of this report while the more highly substituted complexes and their photochemical properties will be reported elsewhere.[8] Kinetic studies of reaction 1 were undertaken to elucidate the differences in reactivity observed toward complexation of the different aromatic rings of rubrene. Model arenes were chosen to emulate the different types of arene rings present in rubrene. Anthracene was chosen to model the behavior of the naphthacene moiety and biphenyl and benzene were used to model the reactivity of rubrene's substituent phenyl groups. On the basis of these measurements, we propose a mechanism for the complexation of arenes by $CpRu^+$ that explains the high selectivity $CpRu^+$ exhibits toward the different types of arene rings in rubrene on the basis of kinetic and thermodynamic effects.

Experimental Section

Dichloromethane and acetonitrile were of spectroscopic grade and were used without further purification. Rubrene was purchased from Aldrich Chemical Co. and used without further purification. Room temperature UV-vis spectra of the compounds were obtained with a Cary 17D spectrometer. Standard 1-D, ^1H NMR spectra were obtained on an IBM Bruker 200-MHz spectrometer and 2-D, COSY ^1H spectra were obtained on an IBM Bruker 300-MHz spectrometer.

Synthesis of Compounds. The starting materials $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and $[CpRu(CH_3CN)_3]PF_6$ were prepared by literature procedures.[4,5]

[CpRu(biphenyl)]PF_6. To a degassed flask containing 78.2 mg (0.180 mmol) of $[CpRu(CH_3CN)_3]PF_6$ and 29.1 mg (0.189 mmol) of biphenyl, 30 mL of N_2-degassed 1,2-dichloroethane was added. The resulting

* Author to whom correspondence should be addressed.

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yellow solution was refluxed under a slow N_2 purge for 8 h during which time the solution gradually paled in color. The solvent was evaporated with a stream of N_2 to yield a solid that was dissolved in acetone and eluted down a short alumina column. Concentration of the eluant followed by addition of diethyl ether and washing the resulting precipitate with ether yielded 59 mg (0.127 mmol) of off white [CpRu(biphenyl)]-PF_6 (71% yield). ^1H NMR (acetone-d_6): δ 7.78 (m, 2 H, unbound ring), 7.51 (m, 3 H, unbound ring), 6.81 (d, 2 H, bound ring, $H_{1,5}$, J = 5.9 Hz), 6.53 (d, 2 H, bound ring, $H_{3,5}$, J = 6.1 Hz), 6.42 (t, 1 H, bound ring, H_4, J = 5.7 Hz), 5.52 (s, 5 H, Cp). Anal. Calcd for $C_{17}H_{15}RuPF_6$: C, 43.88; H, 3.25. Found: C, 44.00; H, 3.33.

[CpRu(rubrene)]PF_6 (Naphthacene-Bound Isomer). To a degassed flask containing 50.2 mg (0.116 mmol) of [CpRu$(CH_3CN)_3$]PF_6 and 61.8 (0.116 mmol) of rubrene, 20 mL of N_2-degassed 1,2-dichloroethane was added. The solution was stirred for 3 h, and then the solvent was removed by rotary evaporation to yield a dark blue green solid. The solid was redissolved in dichloromethane and eluted down a short diatomaceous earth column to remove a dark brown impurity. This procedure was repeated a second time. Concentration of the eluant followed by addition of diethyl ether and washing the resulting precipitate with ether to remove the excess rubrene yielded 81 mg (0.096 mmol) of dark blue green [CpRu(rubrene)]PF_6 (naphthacene-bound isomer) (83% yield). ^1H NMR (acetone-d_6): δ 7.2 (m, 19 H, unbound rings), 6.90 (m, 5 H, unbound rings), 6.77 (m, 2 H, bound naphthacene ring, $H_{1,4}$), 6.47 (m, 2 H, bound naphthacene ring, $H_{2,3}$), 5.21 (s, 5 H, Cp). UV-vis data (dichloromethane solution): λ_{max} = 660 nm (ϵ_{max} = 7000 M^{-1} cm^{-1}). Anal. Calcd for $C_{47}H_{35}ORuPF_6$ ([CpRu(rubrene)]PF_6·1H_2O): C, 65.50; H, 4.09. Found: C, 65.06; H, 4.15.

[CpRu(rubrene)]PF_6 (Phenyl-Bound Isomer). To a degassed flask containing 76.8 mg (0.177 mmol) of [CpRu$(CH_3CN)_3$]PF_6 and 94.2 mg (0.177 mmol) of rubrene, 60 mL of N_2-degassed acetone was added. While the solution was refluxed for 65 h its color gradually changed from dark blue green to dark purple. The solvent was removed with a stream of N_2 to yield a dark purple solid. The solid was redissolved in acetonitrile and eluted down to a short diatomaceous earth column, which removed insoluble, excess rubrene from the product. Repetition of this procedure followed by recrystallization of the product from acetone–ether yielded 60 mg (0.071 mmol) of bright purple [CpRu(rubrene)]PF_6 (phenyl-bound isomer) (40% yield). ^1H NMR (acetone-d_6): δ 8.97 (d, 1 H, unbound naphthacene ring adjacent to the metal bearing phenyl group, H_1, J = 9.15 Hz), 7.64 (m, 2 H, $H_{2,3}$), 7.30 (m, 9 H, H_4 and unbound phenyl rings), 7.15 (m, 8 H, unbound phenyl rings), 6.86 (m, 4 H, unbound naphthacene ring opposite the metal bearing phenyl group, $H_{5,6,7,8}$), 6.27 (m, 5 H, bound phenyl group), 5.40 (s, 5 H, Cp). UV-vis data (acetonitrile solution): λ_{max} = 523 nm (ϵ_{max} = 8300 M^{-1} cm^{-1}), λ_{max} = 553 nm (ϵ_{max} = 8400 M^{-1} cm^{-1}). Anal. Calcd for $C_{47}H_{35}ORuPF_6$ ([CpRu(rubrene)]PF_6·1H_2O): C, 65.50; H, 4.09. Found: C, 65.73; H, 4.09.

Competitive Reaction of [CpRu$(CH_3CN)_3$]PF_6 with Biphenyl and Anthracene. A sample of 4.0 mg (0.022 mmol) of anthracene, 3.6 mg (0.023 mmol) of biphenyl, and 10.0 mg (0.023 mmol) of [CpRu$(CH_3CN)_3$]PF_6 was placed in an NMR tube, and 0.5 mL of acetone-d_6 was added. A ^1H NMR spectrum of the sample obtained after 30 min of reaction time indicated that 80% of the [CpRu$(CH_3CN)_3$]$^+$ had been converted to [CpRu(anthracene)]$^+$ and 5% had been converted to [CpRu(biphenyl)]$^+$. A ^1H NMR spectrum of the same sample after 13 h indicated the composition of the solution had changed to 61% [CpRu(anthracene)]$^+$ and 39% [CpRu(biphenyl)]$^+$. A ^1H NMR spectrum of the same sample run after 2 weeks indicated the composition of the solution had changed to 0.5% [CpRu(anthracene)]$^+$ and 99.5% [CpRu(biphenyl)]$^+$.

Estimation of K_{eq} for the Formation of [CpRu(η^6-benzene)]$^+$ from Benzene and [CpRu$(CH_3CN)_3$]$^+$ by ^1H NMR. A solution of 0.0200 M [CpRu(η^6-benzene)]$^+$ and 0.175 M CH_3CN in acetone-d_6 was prepared in an NMR tube. The solution was degassed (3 freeze–pump–thaw cycles) and then the tube was sealed under vacuum. The solution was photolyzed for 90 min (λ > 250 nm) and then ^1H NMR spectra were run at intervals over several weeks. The spectrum obtained immediately after photolysis indicated that 9.4% of the [CpRu(η^6-benzene)]$^+$ had been converted to [CpRu$(CH_3CN)_3$]$^+$ and free benzene. Spectra recorded at later times indicated that the reaction of benzene and [CpRu-$(CH_3CN)_3$]$^+$ very gradually occurred to regenerate [CpRu(η^6-benzene)]$^+$ until, after 4 weeks, the resonances due to the photoproducts were just barely detectable. By integrating the peaks of this spectrum it was possible to calculate a lower limit for the equilibrium concentrations of benzene, [CpRu$(CH_3CN)_3$]$^+$, and [CpRu(η^6-benzene)]$^+$ and to estimate a lower limit for the equilibrium constant for the complexation of benzene by [CpRu$(CH_3CN)_3$]$^+$. These measurements yielded $K_{eq} > 4 \times 10^3$ M^2.

Measurement of Kinetic Parameters. The procedure for determining the rate constants involved monitoring the absorption changes that occurred during reaction 1 as a function of time. For the reaction of anthracene, the growth of the absorption band due to metal–arene complex was monitored at 470 nm, while for the benzene reaction the disappearance of the absorption band due to the [CpRu$(CH_3CN)_3$]$^+$ starting material at 370 nm was followed. Sampling was controlled through computer software designed for this purpose. Stock solutions of anthracene or benzene were prepared in acetone, which had been freshly distilled from B_2O_3, and which were either 0.191 or 0.0382 M in acetonitrile, respectively. Stock solutions that contained excess acetonitrile were necessary in order to observe pseudo-first-order behavior due to an inhibition effect caused by the release of small amounts of free acetonitrile from [CpRu$(CH_3CN)_3$]$^+$ as the reaction proceeds (vide infra). In order to measure the effect of [CH_3CN] on the rate, stock solutions of acetonitrile were prepared in freshly distilled acetone that were either 0.0116 M in anthracene or 0.484 M in benzene. Doses (4 mL) of the stock solutions were delivered via syringe into degassed quartz cells equipped with serum stoppers that contained 1.0 mg of [CpRu-$(CH_3CN)_3$]PF_6. Kinetic data were also obtained for the displacement of anthracene from CpRu(anthracene)$^+$ with the same procedure used to measure the rate constants for complexation of anthracene with the exception that 1.0 mg of [CpRu(anthracene)]PF_6 was used in place of [CpRu$(CH_3CN)_3$]PF_6. Samples were vigorously stirred throughout the reaction by a magnetic stir bar, and timing of the reaction was begun 5 s after the addition of the acetone solution to ensure adequate mixing. Cells and stock solutions were equilibrated in a circulating bath of ethylene glycol/water held at 25 °C (±0.5 °C) for at least 15 min before introduction to the cell holder. The temperature of the cells was controlled (±0.5 °C) by circulating the thermostated solvent mixture through a cell holder filled with 2-propanol.

The value of k_{obsvd} for each experiment was determined by least-squares evaluation of a plot of ln [($|A_t - A_f|$)/l] vs. time according to eq 3, where A_t = absorption at time t, A_f = absorption at infinity, l = path

$$\ln [(|A_f - A_t|)/l] = \ln [(|\epsilon_i - \epsilon_f|)C_0] \pm k_{obsvd}t \quad (3)$$

length of the cell, ϵ_i = extinction coefficient of reactants at the monitoring wavelength, and ϵ_f = extinction coefficient of products at the monitoring wavelength. The "+" sign in the equation applies for the benzene reaction, while the "−" sign applies for the anthracene reaction. All plots based on eq 3 were linear through at least 5 half-lives. The precision of the rate constants reported here is ±10%.

Results and Discussion

Synthesis, Characterization, and Chemical Reactivity of Compounds. The utility of the tris–acetonitrile adduct of $CpRu^+$ as a synthetic precursor to [CpRu(η^6-arene)]$^+$ complexes has been well-established and high-yield, facile syntheses of the $CpRu^+$ complexes of a wide variety of arenes and other π-donor ligands have been reported.[9] Many of the arenes used as ligands in these complexes offer two or more chemically distinct arene rings for metal binding. It is interesting to note that the reaction of [CpRu$(CH_3CN)_3$]$^+$ with these polyaromatic hydrocarbons is dominated by a single product. In anthracene, for instance, the two end rings are chemically equivalent and distinct from the center ring, providing two possible binding sites for the $CpRu^+$ moiety in the arene complexation reaction. On the basis of purely statistical considerations, one would expect the reaction of anthracene with [CpRu$(CH_3CN)_3$]$^+$ to yield a 2:1 mixture of end-ring bound to center-ring-bound structural isomers. In practice, however, the reaction yields exclusively the end-ring-bound isomer. The exclusive binding of the end ring of polycyclic arenes has also been observed in condensed arene complexes of $Cr(CO)_3$.[10] Furthermore, to our knowledge, no evidence for the existence of such "ring binding isomers" in any complexes of this type has been reported.

We have found that by making small changes in the reaction conditions, the reaction of [CpRu$(CH_3CN)_3$]$^+$ with rubrene (5,6,11,12-tetraphenylnaphthacene) can be tuned to yield two structurally and spectroscopically distinct "ring-binding isomers". Reaction of 1 equiv of [CpRu$(CH_3CN)_3$]$^+$ with rubrene in 1,2-dichloroethane at room temperature yields the end-naphthacene-ring-bound isomer, as is shown in Figure 1a. This product is chemically and spectroscopically analogous to the

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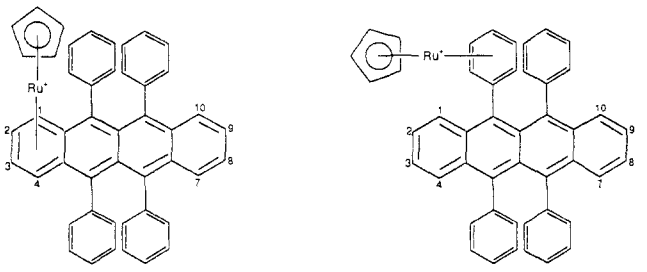

A B

Figure 1. (A) Proposed structure of the naphthacene-bound isomer of CpRu(rubrene)$^+$. (B) Proposed structure of the phenyl-bound isomer of CpRu(rubrene)$^+$.

corresponding anthracene product in which the metal is bound to the end-anthracene ring. Like [CpRu(anthracene)]$^+$, the end-bound [CpRu(rubrene)]$^+$ isomer is characterized by a ^{1}H NMR spectrum that exhibits two multiplets shifted upfield[11] from the other arene proton resonances that integrate as 4 hydrogens; additionally a 2-d COSY ^{1}H NMR spectrum reveals these two multiplets are coupled only to each other. The most reasonable assignment of these multiplets is to hydrogens 1, 2, 3, and 4 on the end naphthacene ring of rubrene.

The UV–vis absorption spectrum of the end-bound rubrene complex is also very similar to that exhibited by the "end-ring"-bound anthracene complex; both molecules exhibit a relatively weak, unstructured metal-to-ligand charge-transfer band. Solution spectra of the CpRu$^+$ complexes of the series benzene, naphthalene, and anthracene indicate that the position of this charge-transfer band shifts further to the red with each extension of the acene's conjugation.[4] In accord with this trend, the end-bound rubrene isomer, in which the conjugation is carried over four fused rings in the naphthacene core, exhibits a visible absorption maximum at 660 nm—the longest wavelength absorption observed in the series.

The chemical reactivity of the "end-ring"-bound rubrene isomer is also consistent with the trend observed in the complexes of the series benzene, naphthalene, and anthracene. The increase in the conjugation of the acene is associated with an increase in the thermal lability of the bound arene in acetonitrile solution, as has been confirmed by previous kinetic measurements.[4] On this basis the "end-ring"-bound complex of rubrene, which contains the longest conjugated acene π-system yet complexed by CpRu$^+$, is predicted to be very unstable with respect to displacement of the bound rubrene by acetonitrile to yield free rubrene and [CpRu-$(CH_3CN)_3$]$^+$. This result is indeed observed experimentally as the blue-green "end-ring"-bound rubrene isomer immediately decomposes in pure acetonitrile solution to give the fluorescent orange solution characteristic of the free dye.

In contrast to the reaction of equimolar quantities of rubrene and [CpRu$(CH_3CN)_3$]$^+$ in dichloroethane which yields the blue-green, end-bound isomer, carrying out the reaction in refluxing acetone yields a very different, bright purple product with an identical elemental analysis. The ^{1}H NMR spectrum of this purple product exhibits a single singlet in the Cp region that integrates as 5 hydrogens and is shifted 0.19 ppm downfield from the position of the Cp resonance in the end-ring-bound isomer. Furthermore, the rubrene protons resonate very differently in this purple product than they do in the blue-green product. This indicates that the purple product is an isomeric monometalated rubrene complex that is structurally distinct from the blue-green "end-ring"-bound isomer.

The ^{1}H NMR spectrum of this purple product suffices to determine its structure. The downfield shift of the Cp resonance is characteristic of binding a CpRu$^+$ group to an arene ring with a large amount of aromaticity; the greater π acceptor ability of such an arene results in deshielding of the Cp$^-$ H atoms. Greater accepting ability, in turn, is associated with arene rings with greater aromatic character, i.e. are more benzene-like, with resonance structures that share the ring's σ-bonded 6 π electrons with as few other rings as possible (vide infra). This consideration implicates the binding of the CpRu$^+$ group to one of the substituent phenyl groups as is depicted in Figure 1b. Because conjugation of the substituent phenyl groups to the naphthacene core is relatively weak, their aromatic character is undiminished and quite high.

The rubrene proton resonances are also consistent with the assignment of the purple product's structure to an isomer in which the metal is bound to one of the pendant phenyl groups. The increased number of arene proton resonances in the purple isomer indicates that it has lower overall symmetry than the "end-ring"-bound isomer. An isomer with the CpRu$^+$ group bound to one of the center naphthacene rings would not have decreased molecular symmetry with respect to the "end-ring"-bound isomer, but binding the metal moiety to a phenyl group would lower the symmetry. The furthest upfield arene resonance in the purple isomer, which in related compounds is almost always due to the protons on the ruthenium-bound arene ring, is a multiplet that integrates as 5 hydrogens, which is also consistent with structure B, Figure 1. Furthermore, the purple isomer exhibits a conspicuous doublet that integrates as 1 hydrogen and is shifted unusually far downfield. The only structure with the correct symmetry to permit a single proton to be chemically inequivalent to all the other protons on rubrene is the one shown in structure B, Figure 1; the downfield doublet is readily assigned to the "bay" proton,[12] H_1. The extraordinary downfield shift is characteristic of the proximal binding of the CpRu(η^6-phenyl)$^+$ substituent and may result from a through-space inductive or a ring current effect. The UV–visible spectrum of the purple isomer is also consistent with an isomeric structure in which the metal is not bound to the naphthacene core. Instead of the relatively weak, unstructured absorption band that usually results from direct binding of a CpRu$^+$ to an acene, the purple rubrene isomer exhibits an intense, structured absorption band (λ_{max} = 523 nm; ϵ = 8300 M^{-1} cm^{-1}). This band is likely due to the rubrene's intense π–π^* transitions which are centered in the naphthacene core and are only slightly perturbed by the metal binding to a substituent phenyl group. We have previously observed this behavior in our studies of the complexes of 7-aminocoumarin laser dyes. Binding CpRu$^+$ to the arene ring of the coumarin chromophore yields a complex in which the dye's extremely intense absorption band is replaced by relatively weak metal-to-ligand charge-transfer bands. Conversely, binding the metal to an aromatic ring that is removed from the main coumarin chromophore yields a complex with a UV–visible spectrum dominated by an extremely intense, slightly perturbed dye band.[6]

Finally, the reactivity of the purple isomer is also consistent with its structure assignment as B, Figure 1. As previously mentioned, the thermodynamic stability of [CpRu(arene)]$^+$ complexes in acetonitrile decreases with an increase in the conjugation of the bound arene ring. Thus, we expect the phenyl-bound rubrene complex to be much more stable toward substitution of the bound arene by acetonitrile than the naphthacene-bound isomer. This is born out experimentally, as the purple isomer is indefinitely stable in acetonitrile, while the naphthacene-bound isomer decomplexes immediately upon dissolution in acetonitrile.

Our successful synthesis synthesis of two distinct "ring-binding isomers" of the monometalated rubrene complex by changing the solvent and the reaction temperature suggested that interconversion of the two isomers might be observable under appropriate conditions. ^{1}H NMR experiments were carried out to investigate this possibility. ^{1}H NMR spectra recorded periodically over 2 weeks indicated that the naphthacene-bound isomer is indefinitely stable in dichloromethane-d_2. However, the ^{1}H NMR spectra of an

(11) The upfield shift in aromatic ring proton resonances incurred upon binding a CpRu$^+$ group to the ring has been well-established experimentally[9] as well as on theoretical grounds for related compounds.[13]

(12) Clar refers to the sterically hindered protons that lie in the "bays" formed by substituent arene rings in polycyclic hydrocarbons as the "bay protons".[14] Thus, in rubrene there are 4 bay protons: H_1, H_4, H_7, and H_{10}.

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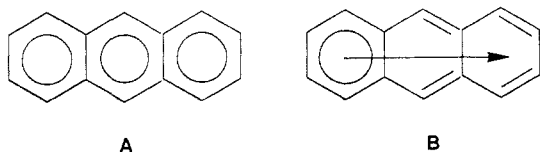
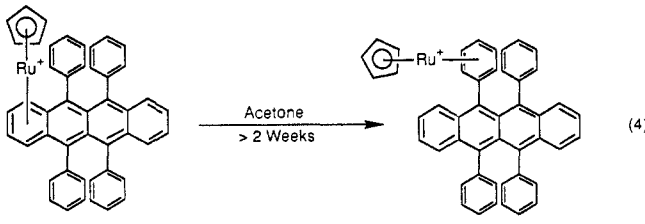


Figure 2. (A) An inaccurate representation of anthracene that implies each of the three rings possesses a highly stable, 6-electron aromatic π-system. (B) A more accurate representation of anthracene showing a single, fully aromatic π-system that is diluted through conjugation with two other rings.[12]

acetone-d_6 solution of the naphthacene-bound isomer taken over a 2-week period indicated a very gradual decrease of the resonances due to the naphthacene-bound isomer and a concomitant appearance and growth of resonances characteristic of the phenyl-bound isomer (reaction 4). This experiment demonstrates



(4)

that the naphthacene-bound isomer interconverts thermally to the more stable phenyl bound isomer as is depicted in Figure 1. In control experiments, we have not observed any evidence that the interconversion of the phenyl-bound isomer to the naphthacene-bound isomer occurs. This facile interconversion of the naphthacene-bound to the phenyl-bound isomer has prompted us to investigate this interesting reactivity pattern further.

Relation of Aromaticity to Ring Selectivity and Thermodynamic Stability. It has long been recognized that the different rings of fused polycyclic aromatic hydrocarbons have different degrees of relative aromaticity. Clar[12] pointed out almost 20 years ago that it was inappropriate to draw the structure of anthracene, for instance, with the common circle aromaticity symbol in each ring as is shown in Figure 2A. Such a representation implies that each ring possesses an equal degree of benzene-like, aromatic stability and that the molecule contains $3 \times 6 = 18$ π electrons—all untrue. A much more accurate portrayal of anthracene is depicted in Figure 2B. According to Clar's highly useful "sextet rule", anthracene is best represented as a single aromatic sextet (represented by the circle aromaticity symbol) that is shared among and "diluted" by the two other rings through aromatic conjugation. The greater the number of rings the sextet is shared among, the greater the loss of benzenoid character. Thus, the aromaticity (and hence the resonance energy) of the end ring in the acene series decreases in the order benzene > naphthalene > anthracene > naphthacene. Since Clar's postulation of the sextet rule, a number of different methods have been proposed to estimate the relative aromaticity of different aromatic rings including the graph theoretical method,[15] semiempirical quantum theory,[16] MNDO calculations,[17] the Kekulē index,[18] the sextet polynomial,[19] resonance energy per atom,[20] and the method of conjugated circuits,[21] among others.

Consideration of the relative aromaticity of the aromatic ring that reacts with $[CpRu(CH_3CN)_3]^+$ provides a useful criterion with which to understand the selectivity $CpRu^+$ exhibits in complexing arene rings. Previous kinetic studies of the decomplexation of arene from $[CpRu(arene)]^+$ complexes in acetonitrile (reaction 2) are consistent with a transition state in which the arene is only partially bound to the metal, e.g. in an η^4-fashion, with the extra coordination site occupied by a nucleophilic acetonitrile ligand.[4] Microscopic reversibility requires that the same transition state must lie along this reaction coordinate for the complexation of arenes by $[CpRu(CH_3CN)_3]^+$. Consequently, a significant energy barrier to form the transition state for the complexation of arenes by $CpRu^+$ will be provided by the disruption of the aromatic stabilization of the arene ring. This is consistent with the "ring slip" mechanism that has been proposed for the arene exchange reactions of a number of other transition-metal–arene complexes[22-26] in which the η^6-bound arene undergoes a reduction in its hapticity as the reaction coordinate is traversed. Theoretical calculations[27] as well as the experimental data indicate that the transition state in which the arene is bound to the metal in less than full η^6-fashion will be a relatively high energy species. This representation of the transition state predicts a rate enhancement for the complexation of arenes with "diluted" benzenoid character, such as anthracene, over and above more benzene-like arenes, such as biphenyl.

In addition to the isomeric rearrangement discussed above, we have demonstrated this phenomenon by following the competitive reaction of $[CpRu(CH_3CN)_3]^+$ in acetone with equimolar quantities of anthracene and biphenyl by ^1H NMR. As predicted, the reaction mixture rapidly forms an almost quantitative yield of the anthracene complex. However, as time passes, a very gradual conversion of [CpRu(anthracene)]$^+$ into [CpRu(biphenyl)]$^+$ is observed until, after about 2 weeks, the conversion to the biphenyl complex is nearly quantitative. This is clear evidence that kinetic and thermodynamic factors influence the selectivity exhibited by $CpRu^+$ toward complexation of arene rings. We suggest that the kinetically favored complexation reaction is the one in which the $CpRu^+$ binds the arene ring with the lesser degree of benzenoid character because such an arene ring provides a minimal energy transition state as the incoming metal interrupts the arene's aromatic stabilization. The thermodynamically favored product, on the other hand, is the one in which the metal binds the ring with the greatest degree of aromatic stabilization. Tentative explanations for the increased stability of these products are either relatively stronger Ru–arene bonds are present in the more aromatic arenes or enhanced aromatic stabilization increases the transition-state energy for Ru–arene bond cleavage.

Kinetic Measurements of Arene Complexation by $CpRu^+$. We quantified our qualitative observations with kinetic studies. It was convenient to follow the reaction of $[CpRu(CH_3CN)_3]^+$ with arene (arene = benzene, anthracene) by monitoring the changes at an appropriate wavelength in the UV–vis spectrum. Initial studies with both arenes and no added acetonitrile were carried out in both dichloromethane and acetone, but these rate data failed to exhibit either simple first- or second order behavior. Plots of $\ln [(|A_t - A_f|)/I]$ vs time exhibited concave curvature, indicating the rate fell off faster than would be predicted by simple pseudo-first-order kinetics. The generation of free acetonitrile required by the reaction stoichiometry suggested that acetonitrile might be the source of the rate inhibition at late reaction times. This suggestion was proven correct because kinetic runs in the presence of excess acetonitrile as well as excess arene, which ensured pseudo-first-order conditions in both reagents, resulted in linear $\ln [(|A_t - A_f|)/I]$ vs time plots. Under these conditions, the reaction

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(28) When CD_3CN is added to a solution of $CpRu(CH_3CN)_3^+$ in acetone-d_6 the peak at δ 4.22 disappears completely. With the initial [$CpRu(CH_3CN)_3^+$] of 0.01 M, the [CD_3CN] of 0.04 M, and a detection limit of 1% for $CpRu(CH_3CN)_2(acetone)^+$ an upper limit for K_1 for reaction 10 of 4.0×10^{-4} M is calculated.

Table I. Concentration Study of the Kinetics of Reaction of $[CpRu(CH_3CN)_3]PF_6$[a] with Benzene in Acetone in the Presence of CH_3CN

$[CH_3CN]$, M	[benzene], M	k_{obsvd}, s^{-1}	k_{calc}, s^{-1}
0.0383	0.0438	1.5×10^{-3}	1.3×10^{-3}
0.0386	0.0900	3.0×10^{-3}	2.6×10^{-3}
0.0374	0.131	4.1×10^{-3}	4.2×10^{-3}
0.0388	0.222	6.7×10^{-3}	6.4×10^{-3}
0.0380	0.484	1.5×10^{-2}	1.5×10^{-2}
0.0460	0.484	8.6×10^{-3}	8.9×10^{-3}
0.0578	0.485	4.9×10^{-3}	5.0×10^{-3}
0.0757	0.484	2.6×10^{-3}	2.5×10^{-3}
0.113	0.484	9.1×10^{-4}	9.4×10^{-4}
0.153	0.485	4.9×10^{-4}	4.6×10^{-4}
0.191	0.485	2.7×10^{-4}	2.8×10^{-4}

[a] The initial $[CpRu(CH_3CN)_3PF_6]$ was maintained at approximately 5.8×10^{-4} M for all runs.

Table II. Concentration Study of the Kinetics of Reaction of $[CpRu(CH_3CN)_3]PF_6$[a] with Anthracene in Acetone in the Presence of CH_3CN

$[CH_3CN]$, M	[anthracene], M	k_{obsvd}, s^{-1}	k_{calc}, s^{-1}
0.133	0.0115	0.049	0.050
0.152	0.0117	0.039	0.039
0.191	0.0116	0.023	0.026
0.279	0.0116	0.015	0.015
0.382	0.0116	0.011	0.011
0.764	0.0117	0.010	0.011
0.192	0.00588	0.012	0.014
0.191	0.0116	0.023	0.026
0.190	0.0230	0.049	0.050
0.192	0.0346	0.071	0.072

[a] The initial $[CpRu(CH_3CN)_3PF_6]$ was maintained at approximately 5.8×10^{-4} M for all runs.

rates for arene complexation in dichloromethane/acetonitrile are inconveniently slow so the kinetic measurements for arene complexation were ultimately made in acetone/acetonitrile solutions. Under otherwise identical conditions, the rates of arene complexation measured for acetone solutions are roughly 1000 times faster than those measured for dichloromethane solutions. This observation has mechanistic implications and will be discussed further below.

Values of k_{obsvd} for the complexation of benzene at constant $[CH_3CN]$ ($[CH_3CN]$ = 0.0382 M) and anthracene ($[CH_3CN]$ = 0.191 M) were measured at several different concentrations of arene and are tabulated in Tables I and II, respectively. Plots of k_{obsvd} vs [arene] for benzene and anthracene both yield straight lines that nearly pass through the origin (benzene: slope = 0.0306 (4) M^{-1} cm^{-1}, intercept = 0.0001 (2) s^{-1}; anthracene: slope = 2.07 (8) M^{-1} cm^{-1}, intercept = 0.000 (2) s^{-1}), indicating first-order dependencies of both reactions on arene concentration when a large excess of CH_3CN is present. A study of the effect of varying acetonitrile concentration on the rate of arene complexation was also carried out in order to determine the order of the reactions in acetonitrile. Values of k_{obsvd} for arene complexation in the presence of 0.484 M benzene or 0.0116 M anthracene are listed in Tables I and II, respectively. Plots of k_{obsvd} vs $[CH_3CN]$ for benzene (Figure 3) and anthracene (Figure 4) are *not* linear, indicating that there is a more complex dependence of the reaction rate on $[CH_3CN]$.

Taking account of the first-order dependence of the complexation reaction in $[CpRu(CH_3CN)_3]^+$, the rate law expressed in eq 5 allows a limited number of reasonable possibilities that can

$$\text{rate} = k_{obsvd}[\text{benzene}][CpRu(CH_3CN)_3^+] \qquad (5)$$

describe the effect of $[CH_3CN]$ on k_{obsvd} for the benzene reaction. The rate of arene complexation is inhibited by the acetonitrile released from $[CpRu(CH_3CN)_3]^+$, which suggests the rate dependence on acetonitrile concentration is inverse first, second, or third order, or some combination of these. All attempts to fit k_{obsvd} to a single term of inverse order (first, second, third, etc.) in $[CH_3CN]$ were unsuccessfull. The data are best fit by an expression for k_{obsvd} made up of two terms—one which is inverse second order in $[CH_3CN]$ and one which is inverse third order in $[CH_3CN]$ (eq 6). Other two-term expressions gave significantly

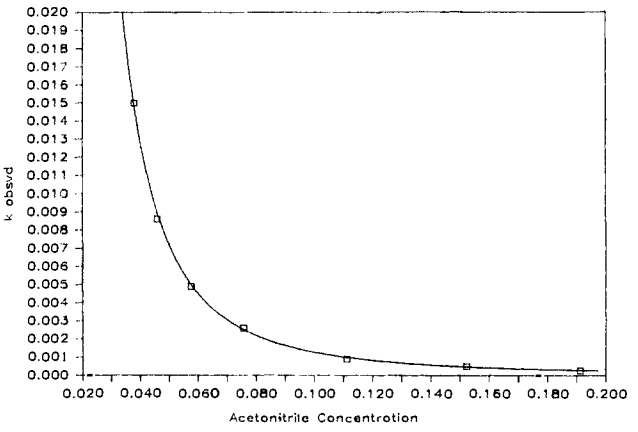


Figure 3. Plot of k_{obsvd} vs $[CH_3CN]$ for the reaction of $[CpRu(CH_3CN)_3]^+$ with benzene in acetone/acetonitrile. The k_{obsvd} values are those from Table I. The theoretical curve drawn through the experimental points was calculated from eq 6 with $k_1 = 1.1\ (1) \times 10^{-6}$ M^2 s^{-1} and $k_2 = 1.5\ (1) \times 10^{-5}$ M s^{-1}.

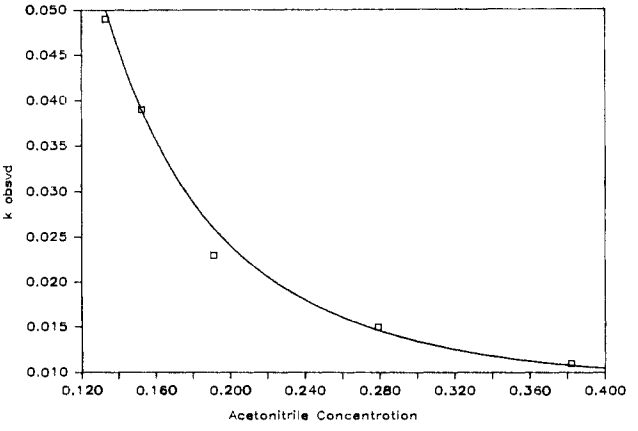


Figure 4. Plot of k_{obsvd} vs $[CH_3CN]$ for the reaction of $[CpRu(CH_3CN)_3]^+$ with anthracene in acetone/acetonitrile. The k_{obsvd} values are those from Table II. The theoretical curve drawn through the experimental points was calculated from eq 9 with $k_f = 0.074\ (6)$ M s^{-1} and $k_r = 0.013\ (1)$ M^{-1} s^{-1}.

$$k_{obsvd} = \frac{k_1}{[CH_3CN]^3} + \frac{k_2}{[CH_3CN]^2} \qquad (6)$$

poorer fits that in one case included a negative value for one of the rate constants. The substitution of the experimental values of k_{obsvd}, [benzene], and $[CH_3CN]$ into eq 3 and 4 allows the calculation of values for the rate parameters: ($k_1 = 1.1\ (1) \times 10^{-6}$ M^2 s^{-1} and $k_2 = 1.5\ (1) \times 10^{-5}$ M s^{-1}. The accuracy of the rate law was checked by calculating the value of k_{obsvd} as a function of $[CH_3CN]$ with the experimentally obtained values of k_1 and k_2 over the range of acetonitrile concentrations used in the kinetic measurements. This theoretical curve is plotted along with the experimental points in Figure 3 and can be seen to give an excellent fit. Theoretical values for k_{obsvd} for each individual kinetic run were also calculated with the rate law and are tabulated in Table I. Comparison of the calculated k_{calc} with the experimental k_{obsvd} also shows excellent agreement.

Derivation of a rate law that fits all the data listed in Table II for the complexation of anthracene requires the consideration of a complicating factor that was not important in the analysis of the data obtained for the benzene reaction. While the formation reaction of the very stable $[CpRu(benzene)]^+$ complex always proceeds to essentially 100% completion under our experimental conditions ($K_{eq} > 4 \times 10^3$ M^2), the formation reaction of the considerably less stable $[CpRu(anthracene)]^+$ complex establishes an equilibrium that favors $[CpRu(CH_3CN)_3]^+$ and anthracene

Table III. Concentration Study of the Kinetics of Reaction of [CpRu(anthracene)]PF_6[a] with Anthracene in Acetone in the Presence of CH_3CN

$[CH_3CN]$, M	[anthracene], M	k_{obsvd}, s^{-1}	k_{calc}, s^{-1}
0.811	0.0230	0.013	0.012
0.811	0.0115	0.012	0.012
1.214	0.0115	0.017	0.016
1.593	0.0115	0.022	0.021

[a] The initial [CpRu(anthracene)PF_6] was maintained at approximately 5.1×10^{-4} M for all runs.

over the ruthenium–arene complex, at higher concentrations of acetonitrile. The equation appropriate for the analysis of a rate law with opposing first-order reactions contains an apparent first-order rate constant k_{obvsd}, which is the sum of the apparent forward first-order rate constant k_f^{app} and the reverse first-order rate constant k_r^{app}:

$$\text{rate} = k_{obvsd}[CpRu(CH_3CN)_3^+] \quad (7)$$

$$k_{obvsd} = k_f^{app} + k_r^{app} \quad (8)$$

Analysis of the kinetic data obtained under pseudo-first-order conditions of acetonitrile and anthracene concentrations yields the following expression for k_{obvsd}:

$$k_{obvsd} = \frac{k_f[\text{anthracene}]}{[CH_3CN]^2} + k_r[CH_3CN] \quad (9)$$

Substitution of the experimental concentration values into the equation yields the following values for the rate constants, k_f = 0.074 (6) M s^{-1} and k_r = 0.013 (1) M^{-1} s^{-1}. The quotient k_f/k_r gives the value for the equilibrium constant of reaction 1 for arene = anthracene of 5.7 (9) M^2. Additionally, these values for the rate constants allowed the calculation of k_{obvsd} values as a function of $[CH_3CN]$. The theoretical curve is drawn through the experimental points in Figure 4; an excellent fit is attained. Theoretical values for k_{obvsd} for each individual kinetics run were also calculated and are listed in Table II; comparison of the theoretical k_{calc} with the experimental k_{obvsd} also shows excellent agreement.

As a further check of the accuracy of the proposed reversible reaction mechanism for the formation of CpRu(anthracene)$^+$ additional kinetic measurements were made. The reversible mechanism in Scheme II (vide infra) requires that the kinetics of arene displacement from CpRu(anthracene)$^+$ must be governed by the same rate law that applies to the complexation of anthracene. In order to check this, the decomplexation kinetics of CpRu(anthracene)$^+$ in acetone/acetonitrile were studied. Pseudo-first-order plots of ln $[(A_t - A_f)/I]$ vs time were linear through six half-lives, and the resultant values of k_{obvsd} are reported in Table III along with the theoretical values of k_{calc} calculated from eq 9. Comparison of the theoretical predictions of k_{obvsd} for the decomplexation of anthracene, based on the rate law derived for the *complexation* of anthracene, with the actual experimental values shows excellent agreement.

Discussion of Proposed Mechanisms. The data collected for the reaction of benzene with $CpRu(CH_3CN)_3^+$ are consistent with the rate law expressed in eq 5 with k_{obvsd} given by eq 6. The dependence of the rate on the inverse squared and inverse cubed acetonitrile concentrations requires rapid preequilibria in the mechanism to generate reactive, acetone-complexed ruthenium intermediates that have dissociated acetonitrile ligands before the rate-determining steps. The exact nature and sequence of the dissociation steps relative to the introduction of the arene into the coordination sphere of the ruthenium cannot be determined from the kinetic measurements. It is clear, however, that in the case of the k_1 step, three acetonitriles are lost, while in the case of the k_2 step, two acetonitriles must be lost before the rate-determining step. We postulate that eq 10 is the first of the rapid preequi-

$$CpRu(CH_3CN)_3^+ \overset{K_1}{\rightleftharpoons} CpRu(CH_3CN)_2^+ + CH_3CN \quad (10)$$

librium steps. ^1H NMR spectra indicate that in acetone-d_6 a small peak at δ 4.22 is present.[28] We assign this peak as the Cp resonance of $[CpRu(CH_3CN)_2(acetone)]^+$. The equilibrium constant for this equilibrium and the additional equilibria required are small.

Scheme I. Proposed Rate-Determining Steps for the Complexation of Benzene by $[CpRu(CH_3CN)_3]^+$ in Acetone

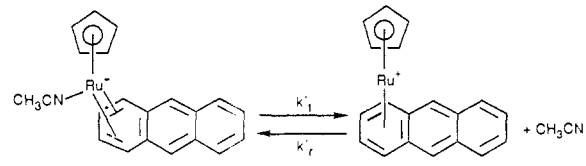
Pathway 1

$$CpRu(\eta^4\text{-benzene})(acetone)^+ \xrightarrow{k'_1} CpRu(\eta^6\text{-benzene})^+ + \text{acetone}$$

Pathway 2

$$CpRu(\eta^4\text{-benzene})(CH_3CN)^+ \xrightarrow{k'_2} CpRu(\eta^6\text{-benzene}) + CH_3CN$$

Scheme II. Proposed Reversible Rate-Determining Step for the Complexation of Anthracene by $[CpRu(CH_3CN)_3]^+$



The proposal that rapid dissociation preequilibria are required to produce the transition state is supported by our observation of much slower rates of arene complexation by $[CpRu(CH_3CN)_3]^+$ in dichloromethane solutions compared with acetone solutions. The less polar solvent and much poorer ligand dichloromethane is less able to stabilize "coordinatively unsaturated" intermediates generated by acetonitrile loss from $[CpRu(CH_3CN)_3]^+$ and other putative intermediates. Consequently, the preequilibria in dichloromethane solution favor larger concentrations of the relatively unreactive tris complex, resulting in the observed rate inhibition.

Substituting eq 6 into eq 5 yields the complete rate law for the complexation of benzene, as is shown in eq 11. This rate law is consistent with CH_3CN dissociation steps prior to the rate-de-

$$\text{rate} = \left(\frac{k_1[\text{benzene}]}{[CH_3CN]^3} + \frac{k_2[\text{benzene}]}{[CH_3CN]^2} \right) [CpRu(CH_3CN)_3^+] \quad (11)$$

termining steps and Scheme I, where k_1 and k_2 are composites that respectively contain the actual rate constants (k'_1 and k'_2) for the rate-determining steps, any necessary hapticity changes, and the equilibrium constants for the dissociation of respectively three and two acetonitrile ligands from Ru. It is interesting to note that if an $\eta^2 \rightarrow \eta^4$ hapticity change is required to attain the transition state, our data suggest that this hapticity change is not rate determining.

We rationalize this result by considering the energy of the transition states for the $\eta^2 \rightarrow \eta^4$ compared with the $\eta^4 \rightarrow \eta^6$ change. As discussed previously, it is reasonable to assume that the transition state for complexation of arenes by ruthenium(II) involves the interruption of the arene's aromatic stabilization by the metal center. Past molecular orbital calculations support this premise and predict that appreciable loss of aromaticity occurs upon complexation of arene rings in a number of different transition-metal sandwich and mixed-sandwich compounds.[13] As is shown in the qualitative energy diagram in Figure 5, the interaction of the different $CpRu(L)_n^+$ fragments with the arene should involve different energy expenditures. Anything less than η^6-binding of the metal to the arene π-system will localize the π-electrons. The amount of energy needed to localize the aromatic π-system should increase as the extent of the imposed localization increases. This localization energy contribution should be similar for η^2 and η^4 type intermediates. Because we observe no significant kinetic barrier for the $\eta^0 \rightarrow \eta^2 \rightarrow \eta^4$ steps, we believe that the relative strength of η^4 vs η^2 metal–arene binding actually controls the transition-state energy, and in this case the expected stronger η^4-arene–metal binding predominates.

Substitution of eq 9 into eq 7 yields the complete rate law for the reaction of $CpRu(CH_3CN)_3^+$ with anthracene (eq 12). As previously discussed, this rate law is consistent with a reversible

$$\text{rate} = \left(\frac{k_f[\text{anthracene}]}{[CH_3CN]^2} + k_f[CH_3CN] \right)[CpRu(CH_3CN)_3^+] \quad (12)$$

reaction mechanism, as is described in Scheme II, where the first term represents the mechanistic detail of the complexation reaction. According to this model, the predominant pathways for the complexation of anthracene and benzene both occur through the formation of η^4-arene transition states. For anthracene complexation, this route is so favorable at the concentrations of acetonitrile studied that it occurs to the exclusion of any observable product formation through the other η^4 pathway.

The rate laws expressed in eqs 11 and 12 permit direct comparison of the net rates of complexation of anthracene and benzene. The composite rate parameters k_2 and k_f both describe the rates of $\eta^4 \rightarrow \eta^6$ conversion of benzene and anthracene, respectively, along similar reaction coordinates through the intermediacy of the CpRu(η^4-arene)$(CH_3CN)^+$ species. Comparison of these two rate constants indicates that the net complexation of anthracene occurs 4900 times faster than the net complexation of benzene and results in a $\Delta(\Delta G^*)$ of 5.0 kcal/mol. This result is consistent with the qualitative energy diagram depicted in Figure 5 and with the model, outlined previously, that predicts that the rate of arene complexation varies inversely with the degree of the arene ring aromatic stabilization. Anthracene, in which the end-ring's π-system is already quite localized, provides a relatively lower energy barrier to form the η^6-anthracene complex. Benzene, on the other hand, has the highest degree of aromatic stabilization possible, and it provides a very high barrier toward the localization of its π-electrons.

These kinetic measurements are consistent with the unusual reaction chemistry we have observed for the complexation of rubrene by $CpRu^+$. The end naphthacene ring of rubrene is preferentially complexed in room temperature reactions by virtue of its highly compromised aromaticity. The benzenoid character of naphthacene is "diluted" through conjugation with three other arene rings, making it even less delocalized than anthracene. Consequently, the energy barrier for formation of the naphthacene ring-bound metal complex will be very low indeed, causing it to readily form as a kinetic product. The substituent phenyl groups on rubrene are only weakly conjugated to the naphthacene core, leaving their aromatic stabilization relatively undiluted and providing a high energy barrier for complexation, like that of benzene. Consequently, carrying out the rubrene complexation reaction at elevated temperatures or under conditions where decomplexation is also favorable will favor the phenyl-bound rubrene complex as the very stable thermodynamic product.

Conclusions

The ring that the $CpRu^+$ moiety binds upon reaction of $[CpRu(CH_3CN)_3]^+$ with rubrene can be varied by changing the reaction conditions. The source of this ring selectivity derives from competing kinetic and thermodynamic effects in the reaction of the $CpRu^+$ moiety with arenes. Kinetic measurements indicate that arene rings with partially localized aromatic π-systems, such as those in the naphthacene core of rubrene, complex $CpRu^+$ much more rapidly than more delocalized, highly aromatic rings, such as rubrene's substituent phenyl groups. This observation is consistent with a mechanism in which an incoming ruthenium center partially binds the arene ring in the transition state. This partial binding mode imposes localization of the ring's π-electrons and gives rise to an important component of the energy barrier in the reaction. After passing through the transition state, arene complexation is completed so that the metal binds the ring's total aromatic π-system symmetrically and delocalization of the arene is restored. The kinetic studies and the competition study between anthracene and biphenyl also demonstrate that the process by which the kinetic rubrene complex rearranges to the thermodynamic isomer does not involve an intramolecular "walk over" of the $CpRu^+$ group from one ring to another. Rather, the data are consistent with dissociation of the ruthenium fragment from the kinetically bound ring before complexation of the thermodynamically preferred ring can occur.

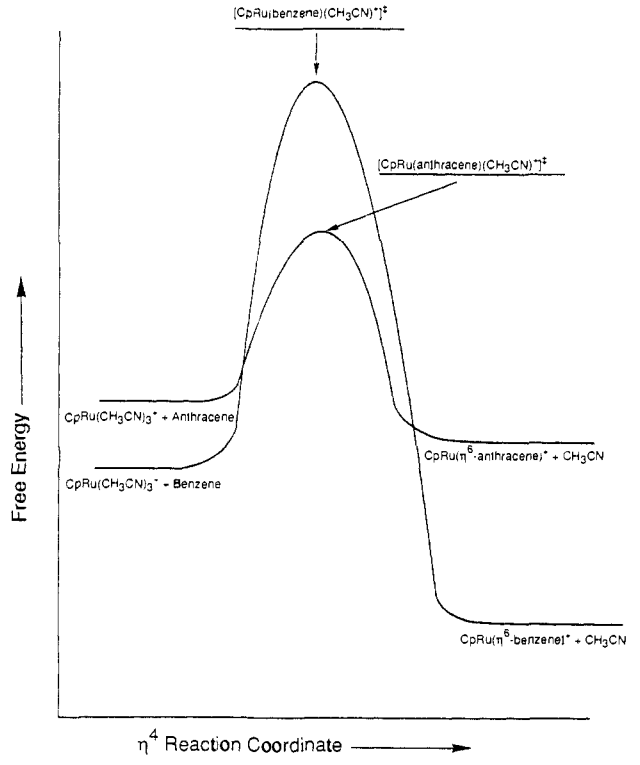


Figure 5. Qualitative energy diagram for the reaction of $[CpRu(CH_3CN)_3]^+$ with benzene and anthracene through the proposed η^4 transition state. Several shallow minima of undetermined position and energy that lie between the reactants and the transition state have been omitted from the diagram.

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Supplementary Material Available: Graphs of k_{obsd} vs [benzene] and k_{obsd} vs [anthracene] (2 pages). Ordering information is given on any current masthead page.