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Electronic Effects on the Rates of Coupled Two-Electron/Halide Self-Exchange Reactions of Substituted Ruthenocenes

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The complexes $(\mathrm{Me}_m\mathrm{Cp})(\mathrm{Me}_n\mathrm{Cp})\mathrm{Ru}$ ($m,n = 1,1; 0,4; 0,5; 1,5$) have been synthesized along with the corresponding halometalloceniums $[(\mathrm{Me}_m\mathrm{Cp})(\mathrm{Me}_n\mathrm{Cp})\mathrm{RuX}]^+$ (X = Cl, Br, I). The two-electron/halide transfer self-exchange kinetics have been determined and compared to those of the $\mathrm{Cp_2Ru}/[\mathrm{Cp_2RuX}]^+$ parent system. Methylation decreases the rate of exchange monotonically, and plots of $\ln(k_{\mathrm{ex}})$ vs number of methyl groups are linear for constant X. It is concluded that steric effects do not contribute significantly to the observed kinetics. Thermodynamic studies of halide substitution equilibria support the conclusion that the electronic effects of methylation are essentially additive.

Introduction

The characterization of multielectron/group transfer reactions, often termed "atom-transfer reactions",[1] is of considerable recent interest.[2] The self-exchange reactions of ruthenocene and osmocene derivatives given in eq 1 have provided a synthetically accessible series of complexes for the study of fundamental aspects of these reactions.[3−6]

$$[\mathrm{Cp_2MX}]^+ + \mathrm{Cp_2M} \rightarrow \mathrm{Cp_2M} + [\mathrm{Cp_2MX}]^+ \qquad (1)$$

$$(\mathrm{M = Ru, Os;\ X = Cl, Br, I})$$

Previous studies[3−6] have focused on the effects of varying the transferred atom, the counterions, and the solvent on the observed self-exchange kinetics and have resulted in mechanistic proposals that invoke a halogen-bridged transition state. Thermodynamic and structural studies[6] have also led to the conclusion that electronic factors are responsible for the large halide dependence of the rates.

Another approach to modifying the electronic properties of the complexes is to add substituents to the cyclopentadienyl rings. For methyl substituents, it has been shown,[3] for example, that the self-exchange rates for the $[\mathrm{Cp^*_2RuX}]^+/\mathrm{Cp^*_2Ru}$ couples (Cp* = pentamethylcyclopentadienyl) were too slow for detection by dynamic NMR techniques. This is in contrast to the observed *increase* in the rate of one-electron outer-sphere transfer for decamethylferrocenium/decamethylferrocene relative to the corresponding ferrocenium/ferrocene rate.[7a] The results for the ferrocene-based systems have been rationalized in terms of increased delocalization of charge with increasing methylation and/or decreased solvent contribution to the reorganizational energy.[7] The origin of the dramatic *decrease* in rate for the ruthenocenium/ruthenocene system, however, has not been established. In particular, the relative importance of electronic effects on the magnitude of the electronic coupling in the transition state and the steric effects that might be expected to inhibit the formation of a halogen-bridged transition state has not been defined.

We have synthesized a series of methyl-substituted ruthenocenes and their haloruthenocenium derivatives and have determined their two-electron/halide transfer self-exchange rate constants. The results lead to the conclusion that relative self-exchange rates are governed by electronic effects, not steric effects, for complexes with up to six methyl substituents. In addition, the relative energetics of the reaction coordinates have been defined from the activation parameters and the relative reactant state free energies.

Experimental Section

Materials. Ruthenocene and decamethylruthenocene were obtained from Strem Chemicals, Inc. and were sublimed prior to use. Cyclopentadiene dimer and methylcyclopentadiene dimer were obtained from Aldrich Chemical Co. and were cracked by distillation immediately prior to use. Tetramethylcyclopentadiene and $\mathrm{RuCl_3{\cdot}}x\mathrm{H_2O}$ were purchased from Strem Chemicals, Inc. and were used as received. Other materials were obtained commercially and were used as received. Published procedures were used for syntheses of $[\mathrm{Cp_2RuX}]\mathrm{PF_6}$ (X = Cl, Br, I),[4,6] $[\mathrm{Cp^*RuCl_2}]_x$,[8] $(\mathrm{MeCp})_2\mathrm{Ru}$,[9] Cp*CpRu,[8] $(\mathrm{Me_5Cp})(\mathrm{MeCp})$-

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Ru[10] (Cp* = pentamethylcyclopentadienyl anion; MeCp = methylcyclopentadienyl anion), $(R_4N)X_2Y$, and $(R_4N)X_3$[11,12] (R = Me, Et, *n*-Bu; X, Y = Cl, Br, I).

CD_3CN for kinetic measurements was obtained from Cambridge Isotopes in sealed glass ampules and contained <1% water as determined by NMR. For other NMR experiments, CD_3CN from Aldrich or Cambridge Isotopes was distilled over CaH_2 prior to use. Reported chemical shifts are referenced to the solvent peak (C*H*D_2CN at 1.93 ppm). A Hewlett-Packard 8451A diode array UV−vis spectrophotometer was used for optical absorbance measurements.

$(Me_4Cp)CpRu$ (Me_4Cp = 1,2,3,4-Tetramethylcyclopentadienyl Anion). Tetramethylruthenocene has not been previously reported but can be approached by modification of published routes to pentadienyl complexes.[13] $RuCl_3 \cdot xH_2O$ (5.00 g, 24 mmol) was added under N_2 to 100 mL of degassed (three freeze−thaw cycles) EtOH and was stirred until complete dissolution had occurred to yield a green-brown solution (2−3 h). Exactly 1.59 mL of cyclopentadiene (23.7 mmol) was added followed by 8.00 g (65.5 mmol) of tetramethylcyclopentadiene. It is critical that a 1:1 ratio of $RuCl_3$ to HCp is used. If an excess of cyclopentadiene is present, then a significant increase in the yield of ruthenocene is observed. If there is too little, octamethylruthenocene becomes the major product of the reaction. An amount of 15.8 g of Zn dust was added slowly, and the solution was heated at reflux for 6 h. The solvent and other volatiles were removed under vacuum. The solid residue was extracted with hot hexanes, and the extracts were filtered through a Celite pad. The filtrate was then loaded onto a short, basic Al_2O_3 column and eluted with hexanes. The solvent was removed from the combined metallocene-containing fractions by rotary evaporation to give an oil containing $(Me_4Cp)CpRu$ (46.7%), Cp_2Ru (21.4%), and $(Me_4Cp)_2Ru$ (31.9%). Separation of the metallocenes proved to be difficult, and the mixture was used for subsequent experiments requiring tetramethylruthenocene and its derivatives. ^1H NMR (CD_3CN, ppm) of $(Me_4Cp)CpRu$: 4.39 (s, 1H), 4.24 (s, 5H), 1.93 (s, 6H), 1.88 (s, 6H).

Oxidation of Metallocenes. Two general pathways were employed for metallocene oxidation. For chloro- or bromometalloceniums, the metallocene may be oxidized by Fe(III) in the presence of the halide.[3] In a typical preparation, a solution of ∼1.6 mmol metallocene in 30 mL of benzene was added to a solution containing an excess of Fe(III) in 15 mL of dilute (∼4M) aqueous HX (X = Cl, Br). After the solution was vigorously stirred for several hours, the aqueous phase was separated and washed with benzene and ether. An excess of NH_4PF_6 dissolved in a small amount of water was added, and the solution was allowed to stand overnight. The product was collected as a powder by filtration, washed with benzene and ether, and recrystallized from CH_3CN/Et_2O.

A second pathway for metallocene oxidation involved oxidation by $[Cp_2RuX]PF_6$ (X = Cl, Br, I). It has been established from potentiometric studies that for the complexes reported herein the oxidizing ability of haloruthenocenium cations decreases with increasing number of methyl groups.[14] A substoichiometric amount of $[Cp_2RuX]PF_6$ was added to a solution of the metallocene in CH_2Cl_2. The mixture was stirred for 0.5 h, then the solvent was removed by rotary evaporation and the reduced metallocenes were extracted from the powder using hexanes. The oxidized product in the residue was then recrystallized from CH_3CN/Et_2O.

The atom-transfer oxidation method has advantages over the more direct approaches when selective oxidation of a mixture of metallocenes is required. For example, samples of tetramethylruthenocene were invariably contaminated with ruthenocene and octamethylruthenocene. Addition of a substoichiometric amount of $[Cp_2RuX]^+$ preferentially oxidizes the octamethylruthenocene present in the sample. Once the octamethylruthenocene has been quantitatively converted to halooctamethylruthenocenium, additional $[Cp_2RuX]^+$ oxidizes tetramethylruthenocene only. Similarly, hexamethylruthenocene can be selectively oxidized in the presence of pentamethylruthenocene contamination.

Detailed preparative procedures and analytical data for all the new complexes are available elsewhere.[15] ^1H NMR and optical absorbance spectral data for all oxidized metallocenes are available in the Supporting Information.

NMR Kinetics. All NMR data were collected on a Varian Gemini 300 MHz spectrometer. Integrations of 1D and 2D data were performed using routines supplied by Varian.

For exchange rates greater than about $10^4\ M^{-1}\ s^{-1}$, standard line broadening techniques[16] based on a temperature-dependent line width analysis in a near-fast exchange limit were employed. For slower rates, 2D exchange spectroscopy (EXSY)[17] was used to measure the rates. To obtain kinetic data, appropriate amounts of a haloruthenocenium salt and its corresponding reduced form were weighed into an NMR tube and CD_3CN was added to give final concentrations of the two species near 5 mM. For tetramethylruthenocene and hexamethylruthenocene, however, purified samples were not available and the oxidations were performed in situ. In these cases, the mixture of reduced metallocenes was placed in an NMR tube with CD_3CN, and $[Cp_2RuX]^+$ was added until there were approximately equal amounts of the oxidized and reduced forms of the compound of interest. The relative concentrations of the exchanging species were determined from a 1D NMR spectrum of the solution. The absolute concentrations were determined after the kinetic data were obtained from optical absorbance data and the molar absorptivities of the haloruthenoceniums.

A standard EXSY pulse sequence was used to acquire two-dimensional exchange data.[17] For each experiment, 256 1024W free induction decays of eight scans each over a sweep width of 1800−2000 Hz with a recycle delay of 0.5−20.0s were collected in phase-sensitive mode. The integrated EXSY peak intensities were used to determine the exchange rate constants and variances as described elsewhere.[6,17] After each EXSY experiment, the 1D spectrum was reacquired to ensure that no decomposition had occurred. A tabulation of the 2D integrals is given in the Supporting Information.

Halide Substitution Equilibria. Equilibrium constants for the halide substitution of haloruthenoceniums were obtained using procedures described previously.[6] CD_3CN solutions of the haloruthenoceniums were mixed with substoichiometric amounts (∼0.1 molar ratio) of $(R_4N)XY_2$ or $(R_4N)X_3$ (R = Me, Et, *n*-Bu; X,Y = Cl, Br, I) at 298 K. The NMR spectrum and optical absorption of the mixture were monitored periodically until no further change was detected (6−12 h, depending on X and Y). The UV−vis absorption spectrum of the equilbrium mixture was fit to a sum of reference spectra of the absorbing species using a nonlinear least-squares fitting program[18] to obtain the equilibrium concentrations of each species. Errors in calculated concentrations range from 1% to 5% for reactions involving iodo and bromo species and from 5% to 10% for reactions involving chloro species.[19] The UV−vis fits and equilibrium concentrations are provided in the Supporting Information.

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Table 1: Self-Exchange Rates and Free Energies of Activation for $(Me_mCp)(Me_nCp)Ru/[(Me_mCp)(Me_nCp)RuX]^+$ Couples in CD_3CN at 298 K

m,*n*	X	k_{ex} ($M^{-1}\,s^{-1}$)	$\Delta G^{\ddagger}$ ($kJ\,mol^{-1}$)[a]
0,0	Cl	16.5 ± 0.1	66.1 ± 0.2
0,0	Br	1950 ± 87	54.2 ± 0.9
0,0	I	$(2.1 \pm 0.2) \times 10^6$ [b,c]	36.9 ± 0.2 [d]
1,1	Cl	0.42 ± 0.02	75.1 ± 0.1
1,1	Br	166.1 ± 3.6	60.3 ± 0.1
1,1	I	$(3.3 \pm 0.7) \times 10^4$ [b]	47.1 ± 0.3 [d,e]
0,4	Cl	<0.01[f]	
0,4	Br	10 ± 4	67.2 ± 0.8
0,5	Cl	<0.01[f]	
0,5	Br	6.55 ± 0.32	68.3 ± 0.1
0,5	I	841 ± 18	56.3 ± 0.1
1,5	Cl	<0.01[f]	
1,5	Br	4.37 ± 0.28	69.3 ± 0.2
1,5	I	550 ± 50	57.3 ± 0.2

[a] Estimated using the Eyring equation except as noted. [b] Determined by NMR line broadening. [c] From ref 4b. [d] Estimated from the enthalpy and entropy of activation. [e] $\Delta H^{\ddagger} = 30.5 \pm 0.5$ kJ mol^{-1}; $\Delta S^{\ddagger} = -48 \pm 7$ kJ mol^{-1} K^{-1}. [f] Too slow for EXSY.

Results

Self-Exchange Rates. Self-exchange rates determined either by line broadening or EXSY techniques for the series of compounds are presented in Table 1. In the EXSY spectra, cross-peaks between the resonances of the reduced and oxidized forms provided evidence for the exchange reaction. For species containing multiple proton resonance frequencies (e.g., hexamethylruthenocene), identical rate constants were obtained regardless of which pairs of exchanging resonances were analyzed.

Although analytically pure samples of tetramethylruthenocene and hexamethylruthenocene were not obtained, the self-exchange rate constants could still be determined via the EXSY technique. For example, a solution containing roughly equal concentrations of $(Me_4Cp)CpRu$ and $[(Me_4Cp)CpRuBr]^+$ was obtained by titrating $[Cp_2RuBr]^+$ into a mixture of tetramethylruthenocene, octamethylruthenocene, and ruthenocene. The EXSY spectrum of this mixture, obtained at a mixing time of 3.0 s, showed cross-peaks between the tetramethyl resonances only. Any peaks due to cross-reactions with the other ruthenocene species present were indistinguishable from the spectral noise, and the rate constants reported in Table 1 are based on an analysis that included only the tetramethylruthenocene/tetramethylruthenocenium-based diagonal and cross-peaks. An analysis was also performed that included diagonals for all metallocene species present and that used the spectral noise level as an upper limit for the unobserved cross-peak intensities. For both analyses, the calculated self-exchange rate constants for the species of interest were identical within the error of the experiment.

Halide Substitution Thermodynamics. As has been shown previously for the parent $[Cp_2RuX]^+$ species,[6] the relative reaction coordinate energetics for the self-exchange reactions can be constructed from the free energies of activation and the equilibrium constants for the generalized halide substitution reaction

$$[(Me_mCp)(Me_nCp)RuX]^+ + Y^- \rightarrow [(Me_mCp)(Me_nCp)RuY]^+ + X^- \quad (2)$$

The halometalloceniums are relatively good oxidants, however, and the direct reaction of halometalloceniums with halides gives ruthenocene and mixed trihalide anions.[6] Thus, the equilibrium constant for eq 2 must be obtained from a thermodynamic cycle as given in the scheme below.

$$\begin{tikzcd}
3\,[Cp_2RuX]^+ + 3\,Y^- \arrow[r, shift left, harpoon, "3\Delta G^\circ_{[Cp_2MX]^+,Y^-}"] \arrow[d, shift left, harpoon, "\Delta G^\circ_{Y^-,Y_3^-}"] & 3\,[Cp_2RuY]^+ + 3\,X^- \arrow[l, shift left, harpoon] \arrow[d, shift left, harpoon, "-2\,e^-"] & (3a) \\
3\,[Cp_2RuX]^+ + Y_3^- \arrow[u, shift left, harpoon, "+2\,e^-"] \arrow[r, shift left, harpoon] & 3\,[Cp_2RuY]^+ + X_3^- \arrow[l, shift left, harpoon, "\Delta G^\circ_{[Cp_2MX]^+,Y_3^-}"] \arrow[u, shift left, harpoon, "\Delta G^\circ_{X_3^-,X^-}"] & (3b)
\end{tikzcd}$$

As described previously,[6] from the spectrophotometrically estimated equilibrium constants for reaction 3b and the known trihalide reduction potentials,[12,20] the equilibrium constants for reaction 2 can be determined. The results are given in Table 2.

Discussion

For all the ruthenocenes, the self-exchange rates exhibit a strong dependence on the nature of the transferred group. As shown in Table 1, for fixed $(m + n)$, the rate constants decrease in the order I > Br > Cl. This ordering is well established for the parent ruthenocene and osmocene systems[3−6] where it has been interpreted as reflecting the influence of both the differences in M−X bond strengths and the magnitude of halide-mediated electronic coupling between the metals in the transition state.[6]

From Table 1 it is also clear that the self-exchange rates for constant X decrease monotonically with increasing $(m + n)$. The trend is due to the electronic effects of methylation on the reaction coordinate energetics and/or the steric effects of methylation on the formation of the bridged transition-state structure. The steric effects may, in turn, arise in two distinct ways. Large substituents on the Cp rings might inhibit formation of the halide-bridged intermediate. Such intermolecular steric effects would raise the activation barrier and lead to a slower rate of exchange, as is observed. At lower levels of methylation, it would be possible to minimize these effects by arranging the substitutents away from the intermolecular space as the transition state forms. For high levels of methylation (e.g., decamethylruthenocene) no alternative conformations are possible and direct steric effects might become important. Alternatively, steric interactions between the two Cp rings in the bent oxidized metallocenium may influence the exchange rate. At higher degrees of methylation, steric crowding may inhibit the reorganization of the metallocene to the bent metallocenium structure. This additional intramolecular steric contribution to the activation energy would decrease the exchange rate.

Figure 1 presents a plot of $\ln(k_{ex})$ vs $(m + n)$ for the data in Table 1. The plots are essentially linear over the limited range of data available. If steric effects were dominating the differences in exchange rates, it would be expected that the plots would show marked deviations from linearity and that the rates would decrease more quickly than linearly, particularly at higher values of $(m + n)$. The data in Figure 1 suggest, however, that steric effects are not important contributors to the differences in exchange kinetics, at least up to six methyl groups.

Steric effects do, however, appear to be important for more highly methylated species. Extrapolation of the data in the figure predicts that the rate of the $[Cp^*_2RuI]^+/Cp^*_2Ru$ self-exchange should be approximately 1 $M^{-1}\,s^{-1}$, a rate easily accessible by EXSY. No evidence for cross-peaks could be obtained from

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Table 2. Equilibrium Constants for Eq 3b and Calculated Differences in Free Energies of Formation for Haloruthenoceniums at 298 K

m,n [a]	X,Y	$K_{([(\mathrm{Me}_m\mathrm{Cp})(\mathrm{Me}_n\mathrm{Cp})\mathrm{RuX}]^+/\mathrm{I}_3^-)}$	$\Delta G_{[(\mathrm{Me}_m\mathrm{Cp})(\mathrm{Me}_n\mathrm{Cp})\mathrm{RuX}]^+,\mathrm{I}^-}$ (kJ mol^{-1})[b]	$\Delta\Delta G°_{(\mathrm{X,I})}$ (kJ mol^{-1})[c]
0,0	Br,I	18 ± 6	25 ± 5	−63 ± 8
0,0	Cl,I	8 ± 10	49 ± 6	−103 ± 8
1,1	Br,I	3.0 ± 0.4	27 ± 4	−65 ± 4
1,1	Cl,I	12 ± 10	55 ± 7	−109 ± 7
0,5	Br,I	0.05 ± 0.01	30 ± 5	−68 ± 6
0,5	Cl,I	925 ± 5	46 ± 9	−100 ± 9
5,5	Br,I	0.09 ± 0.02	30 ± 7	−68 ± 8
5,5	Cl,I	13 ± 1	54 ± 7	−108 ± 8

[a] For the formulation $[(\mathrm{Me}_m\mathrm{Cp})(\mathrm{Me}_n\mathrm{Cp})\mathrm{RuX}]^+$. [b] Calculated ΔG for eq 2. [c] Calculated $\Delta G_{\mathrm{formation}}$ of $[\mathrm{Cp}_2\mathrm{RuX}]^+$ relative to that of $[\mathrm{Cp}_2\mathrm{RuI}]^+$.

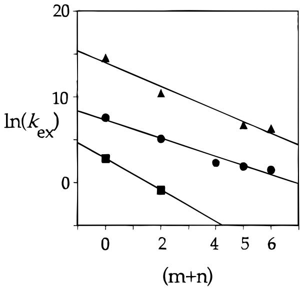

Figure 1. Plot of ln(k_{ex}) vs total number of methyl groups ($m + n$) for self-exchange reactions in Table 1: X = Cl (■), Br (●), I (▲). The lines represent linear least-squares fits of the data to ln(k_{ex}) = $M(m + n) + B$. The best fit values of M and B are the following: (X = Cl) −1.46 ± 0.22, 2.53 ± 0.81; (X = Br) −1.01 ± 0.11, 7.39 ± 0.46; (X = I) −1.37 ± 0.18, 13.97 ± 0.72.

the EXSY spectra of the system, however, even for mixing times as long as 20 s. Thus, at higher levels of methylation, the rates must decrease more quickly than extrapolation of the data in the figure would imply. The most likely source of such a deviation is the onset of significant steric effects inhibiting the formation of the halide-bridged species in the decamethyl systems.

Intramolecular steric effects are not likely to be important for these reactions, however. If significant intramolecular Cp*−Cp* steric interactions are present, there should be significant differences in the energies of the eclipsed and staggered conformations of $[\mathrm{Cp}_2{}^*\mathrm{RuX}]^+$ with staggered being favored. This would also imply a significant barrier to Cp* rotation and the inequivalence of the methyl groups on the NMR time scale. For all complexes at all temperatures, we have observed NMR spectroscopic features consistent with free rotation of each Cp* group about the Cp*−M axis and no NMR inequivalencies are evident. Thus, even if there are energetically preferred conformations, interconversion is very fast on the time scale of the atom-transfer reaction and cannot play a significant role in the observed kinetics. It is also of interest to note that X-ray crystallographic data indicate that the Cp(centroid)−Ru−Cp(centroid) angle in the $[\mathrm{Cp}_2\mathrm{RuBr}]^+$ cation is 36.7°.[21] The corresponding angle in $[\mathrm{Cp}^*{}_2\mathrm{RuBr}]^+$ is 30.7°, and the closest approach of two methyl hydrogen atoms on different Cp* rings is 2.76 Å.[22] The significantly *smaller* angle in the decamethylruthenocenium is unexpected if intramolecular steric crowding were important.

Figure 1 is essentially a "Hammett-type" plot, and the similar slopes of the data for all three halides may be interpreted as reflecting similar mechanisms in each case, presumably coupled two-electron/halide transfer via a halide-bridged transition state. Furthermore, the negative slope of the plot suggests that the transition states exhibit a decrease in net bond order relative to the reactant state because as the number of methyl groups is increased, the ruthenocene becomes more nucleophilic. If bond formation were the dominant process, the increased nucleophilicity of the ruthenocene would lead to rate increases with increasing methylation. The decrease of rate with increasing nucleophilicity of the ruthenocene suggests that the new Ru−X bond is formed largely after the transition state and that the net Ru−X bond order in the transition state has decreased. This interpretation is supported by the thermodynamic studies discussed below.

The thermodynamic results in Table 2 show that for constant ($m + n$) the calculated relative free energy of formation of each metallocenium, $\Delta\Delta G°_{(\mathrm{X,I})}$, becomes more negative in the order I > Br > Cl. Furthermore, for constant X, the $\Delta\Delta G°_{(\mathrm{X,I})}$ values remain essentially constant within the error of the experiment and are thus independent of the number of methyl substituents. This result suggests a simple additive effect of each methyl group on the overall energetics. That is, addition of any number of methyl groups shifts the free energies of the X = Cl, Br, and I metalloceniums by approximately the same amount. This lack of change in $\Delta\Delta G°_{(\mathrm{X,I})}$ as the number of methyl groups is increased is consistent with the notion that methyl groups exert a relatively straightforward electronic effect on the energetics of the system.

These results may be interpreted in terms of a model in which methylation of the cyclopentadienyl rings essentially changes only the effective electronegativity of the ruthenium and thus the Ru−X bond strength. As the degree of methylation increases, the electronegativity of the metal decreases, the difference in electronegativity, $\chi_{\mathrm{X}} - \chi_{\mathrm{Ru}}$, increases, and the Ru−X bond strength increases. Since the kinetic results indicate that net Ru−X bond breaking is a feature of the transition state, this interpretation would predict that increasing methylation would decrease the exchange rate, which is consistent with the experimental observations.

From the data in Tables 1 and 2, it is possible to construct reaction coordinate diagrams for each self-exchange, as has been previously demonstrated for the $\mathrm{Cp}_2\mathrm{Ru}/[\mathrm{Cp}_2\mathrm{RuX}]^+$ and $\mathrm{Cp}_2\mathrm{Os}/[\mathrm{Cp}_2\mathrm{OsX}]^+$ systems.[6] Specific energetic parameters for the systems for which complete data are available can be calculated from the parameters in Tables 1 and 2 and are given in the Supporting Information. It is noteworthy that for a constant degree of methyl substitution, the relative energetics of the three halide transfer reactions are remarkably constant. In all cases, the transition states are closer in energy than the corresponding reactant states, providing further support for the conclusion that the transition state involves net bond breaking.

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Concluding Remarks

The thermodynamic and kinetic results given above indicate that in both the reactant states and the transition states, the effects of up to six methyl groups are electronic and quantitatively conform to a Hammett relationship. Steric effects play no significant role in the overall reaction. These results suggest that all the self-exchanges proceed by a similar mechanism, i.e., through a linear Ru−X−Ru bridged transition state.

Supporting Information Available: Tables of NMR and optical absorbance data for the new compounds, reaction coordinate parameters and diagram, integrated EXSY peak intensities, and a table and figures of the optical absorbance data for equilibrium mixtures corresponding to reaction 3b. This material is available free of charge via the Internet at http://pubs.acs.org.

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