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Mechanistic Investigation on the Water Substitution in the η^5-Organometallic Complexes $Cp^*Ir(H_2O)_3{}^{2+}$ and $Cp^*Rh(H_2O)_3{}^{2+}$

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The substitution of water in the half-sandwich complexes $Cp^*Rh(H_2O)_3{}^{2+}$ and $Cp^*Ir(H_2O)_3{}^{2+}$ (Cp^* = η^5-pentamethylcyclopentadienyl anion) by Cl^-, Br^-, I^-, SCN^-, py-CN (4-cyanopyridine), py-nia (nicotinamide), py (pyridine), TU (thiourea), and DMS (dimethylsulfide) was studied by stopped-flow spectroscopy at variable concentration, temperature, and pressure. The proton dissociation constants of the triaqua complexes, $pK_a = 6.47$ (for rhodium) and $pK_a = 3.86$ (for iridium), as well as the equilibrium constants for the formation of the dinuclear species $(Cp^*M)_2(\mu\text{-OH})_3{}^+$ were obtained by spectrophotometric titrations. The equilibrium constants K_1 for the formation of the monosubstituted complexes $Cp^*M(H_2O)_2L^{+/2+}$, as determined for anionic and neutral ligands L, lie in the range 10^2−10^5 M^{-1} and follow the sequences $K(Cl^-) < K(Br^-) < K(I^-)$ and $K(\text{py-CN}) < K(\text{py-nia}) < K(\text{py}) < K(\text{TU,DMS})$. Assuming the Eigen−Wilkins mechanism for the formation of the monosubstituted complexes, second-order rate constants $k_{f,1}$ were corrected for outer sphere complex formation and for statistical factors to obtain rate constant k_i' for the interchange step. The interchange rates k_i' are nearly independent of the nature of L and very close to the rate of water exchange ($k_{ex}(Rh) = (1.6 \pm 0.3) \times 10^5$ s^{-1} and $k_{ex}(Ir) = (2.5 \pm 0.08) \times 10^4$ s^{-1}). In all cases, i.e., for M = Rh and Ir and for L = anionic or neutral, the volume of the transition state is larger than that of the triaqua species. These findings support the operation of an I_d mechanism without excluding a D mechanism. For a given ligand L, the substitution of another water molecule in the complexes $Cp^*M(H_2O)_2L^{+/2+}$ is by 1 order of magnitude slower than the substitution of the first water molecule in the triaqua species $Cp^*M(H_2O)_3{}^{2+}$, as verified, for example, by $k_{f,1} = 2.61 \times 10^3$ and $k_{f,2} = 3.09 \times 10^2$ M^{-1} s^{-1} for M = Ir and L = py.

Introduction

Although water-soluble organometallic complexes and catalysis in water have been known for quite a while,[1,2] complexes that combine organic carbocyclic ligands, such as π-Cp*, with water at the same metal center are relatively rare species.[3] In recent years work on complexes of the type $Cp^*Rh(S/L)_3{}^{2+}$ and $Cp^*Ir(S/L)_3{}^{2+}$ (S = solvent, L = ligand) have shown to be of great interest.[4,5] The corresponding aqua species $Cp^*Rh(H_2O)_3{}^{2+}$ and $Cp^*Ir(H_2O)_3{}^{2+}$ show a rich chemistry and are particularly effective as catalysts and in the coordination of biologically important molecules.[6,7,8] Therefore information about the reactivity and the mechanism of water/solvent substitution in these species is of fundamental importance.

In general, for metal−solvento species $MS_n{}^{q+}$, complex formation according to eq 1 is strongly related to the reactivity

$$[MS_n]^{q+} + L \rightleftarrows [MS_{n-1}L]^{q+} + S \qquad (1)$$

of the coordinated solvent molecules. The reactivity or rate of solvent exchange according to eq 2, characterized by rate

$$[MS_n]^{q+} + nS^* \xrightleftharpoons{k_{ex}} [MS^*_n]^{q+} + nS \qquad (2)$$

constant k_{ex}, is a good measure for the lability of the solvated metal ion $MS_n{}^{q+}$. Considerable effort has been made over the past two decades to determine k_{ex} and the mechanism of solvent exchange for a wide variety of solvents and metals.[9−11] Kinetic studies on the hexaaqua complexes of iridium(III) and rhodium(III) have shown extremely slow water exchange rate constants of 1.1×10^{-10} and 2.2×10^{-9} s^{-1}, respectively.[12] For both metals the activation parameters obtained support an associative interchange I_a mechanism for the solvent exchange.

It is known that, for a given solvated metal ion, the rate and mechanism of solvent exchange depends on the nature of the solvent S and on changes in the solvent shell of the metal ion

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[†] Université de Lausanne.
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(1) Barton, M.; Atwood, J. D. *J. Coord. Chem.* **1991**, *24*, 43.
(2) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524.
(3) Koelle, U. *Coord. Chem. Rev.* **1994**, *135/136*, 623.
(4) Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2335.
(5) Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2339.
(6) Krämer, R.; Polborn, K.; Robl, C.; Beck, W. *Inorg. Chim. Acta* **1992**, *198−200*, 415.
(7) Severin, K.; Bergs, R.; Beck, W. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1086.
(8) Fish, R. H.; Kim, H.-S.; Babin, J. E.; Adams, R. D. *Organometallics* **1988**, *7*, 2250.
(9) Merbach, A. E. *Pure Appl. Chem.* **1987**, *59*, 161.
(10) Merbach, A. E.; Akitt, J. W. *NMR: Basic Princ. Prog.* **1990**, *24*, 189.
(11) Lincoln, S. F.; Merbach, A. E. *Advances in Inorganic Chemistry*; Academic Press: London, 1994; Vol. 42, pp 1−87.
(12) Cusanelli, A.; Frey, U.; Richens, D. T.; Merbach, A. E. *J. Am. Chem. Soc.* **1996**, *118*, 5265.

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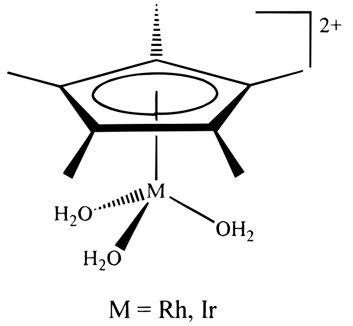
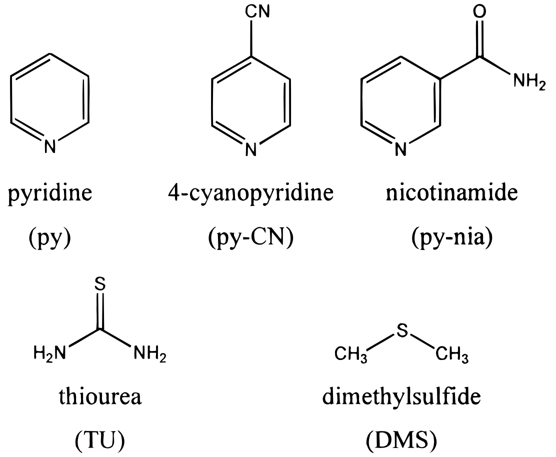
Scheme 1



Scheme 2



M^{q+}. Substitution of three water molecules by the Cp* ligand (Cp* = η^5-pentamethylcyclopentadienyl anion) in the case of iridium(III) and rhodium(III) leads to a dramatic increase of 14 orders of magnitude in the respective rate constants k_{ex} for water exchange and a changeover in the exchange mechanism from an associative interchange I_a mechanism[12] to a dissociative interchange I_d (in water)[13,14] or dissociative D mechanism (in organic solvents).[15] The kinetic data so far reported for these half-sandwich complexes (Scheme 1) are not sufficient to assign the mechanism conclusively.

In an effort to clarify the mechanism governing the water exchange on these half-sandwich complexes, we have therefore extended the kinetic investigation to the substitution of coordinated water molecules by charged and uncharged ligands. In this paper we report the results of stopped-flow UV/vis spectrophotometric studies on the substitution of water in the cations $Cp^*M(H_2O)_3^{2+}$ (M = Rh, Ir; Cp* = η^5-pentamethylcyclopentadienyl anion), carried out with the ligands Cl^-, Br^-, I^-, SCN^-, py, py-CN, py-nia, DMS, and TU (Scheme 2) at variable ligand concentration, temperature, and pressure.

Experimental Section

Unless stated otherwise, the metal salts, organic solvents, and ligands (reagent grade) are commercially available and were used without further purification. CF_3SO_3H was obtained from Janssen Chimica, $NaCF_3SO_3$, $AgCF_3SO_3$, 4-cyanopyridine from Aldrich, and NaCl, NaBr, thiourea, dimethyl sulfide, nicotinamide, and pyridine from Fluka. $[Cp^*RhCl_2]_2$ is commercially available from Aldrich $[Cp^*IrCl_2]_2$ has been synthesized according to published procedures.[16] $NaClO_4$ and $HClO_4$ (70%) have been purchased from Merck. The deionized water was doubly distilled in a quartz apparatus before use.

Preparation of $[Cp^*Ir(H_2O)_3](OTf)_2$ and $[Cp^*Rh(H_2O)_3](OTf)_2$ (Similar to the Procedure Described by Eisen et al.).[17] A solution of $[Cp^*IrCl_2]_2$ (and similarly $[Cp^*RhCl_2]_2$) (200 mg, 0.251 mmol) and AgOTf (258.14 mg, 1.005 mmol) in anhydrous CH_2Cl_2 (12 mL) was stirred at ambient temperature for 3 h, and then it was filtered. The filtrate was carefully layered with H_2O (27.126 μL, 1.51 mmol). The layered filtrate was allowed to stand at ambient temperature for 12 h to give an amber crystalline product for the rhodium complex and a powder for the iridium complex in quantitative yield (167.40 mg, 49.11%). Elemental analysis for $C_{12}H_{21}F_6O_9IrS_2$: Calcd: C, 21.21; H, 3.09; F, 16.19; S, 9.42. Found: C, 21.08; H, 3.01; F, 16.50; S, 9.61. Elemental analysis for $C_{12}H_{21}F_6O_9RhS_2$: Calcd: C, 24.41; H, 3.56; F, 19.32; S, 10.87. Found: C, 24.17; H, 3.42; F, 19.10; S, 11.01.

Instrumentation. Kinetic measurements were made at ambient pressure, with either an Applied Photophysics SX 18 MV stopped-flow instrument (charged ligands) or with a J&M fast diode array (combined deuterium/tungsten light source) in combination with a thermostated manual syringe block (neutral ligands). pH measurements were made with a glass electrode (Metrohm) in combination with an automatic titration apparatus (Titrino 716 DMS), calibrated at $I = 0.2$ M and 25 °C from the titration of a strong acid ($[H^+] = 0.1$ M) with a strong base (0.1 M NaOH). Variable-pressure measurements were made by use of high-pressure stopped-flow equipment designed and built in the house,[18] and spectrophotometric titrations were performed by use of a J&M fast diode array (combined deuterium/tungsten light source) in combination with a Titrino.

Spectrophotometric Titrations. Spectrophotometric titrations were performed by use of a J&M diode array coupled to an Hellma optical cell (10 mm path length) at 298 K. Stability constants and limiting spectra were obtained using the Global Analysis[19] software Specfit.[20] The titrations were carried out at variable ligand concentration to determine the stability constants K_1 for the various ligands studied and at variable proton concentration to determine the acid dissociation constants K_a of the complex cations $Cp^*M(H_2O)_3^{2+}$ and the equilibrium constants β_{din} for the formation of the dinuclear species $(Cp^*M)_2(\mu\text{-}OH)_3^+$.

Kinetic Measurements. The water substitution reactions were followed by stopped-flow spectrophotometry under pseudo-first-order conditions (pH = 1−2; $I = 0.2$ M). Pseudo-first-order conditions were achieved by having the ligand in at least 10-fold excess. For the pyridine ligands the situation was special in the sense that, at pH 1−2, these ligands are protonated to a large extent and the fraction of the nonprotonated pyridine ligand is therefore small, but constant. Rate constants were obtained by computer fitting of the absorbance/time data to exponential functions with the Global Analysis[19] software Specfit.[20] Reported errors are 1 standard deviation.

Results

Spectrophotometric Titrations. The chemical state of the aqua complexes $Cp^*M(H_2O)_3^{2+}$ (M = Rh, Ir) is strongly pH-dependent.[17] At higher pH, hydroxo species are formed and subsequent condensation reactions lead to the formation of dinuclear complexes. It was necessary therefore to study the pH behavior of the triaqua complexes in aqueous solution. For the complex cation $Cp^*Rh(H_2O)_3^{2+}$, some information can be

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[13] Dadci, L.; Elias, H.; Frey, U.; Hörnig, A.; Koelle, U.; Merbach, A. E.; Paulus, H.; Schneider, J. S. *Inorg. Chem.* **1995**, *34*, 306.

[14] Cusanelli, A.; Nicula-Dadci, L.; Frey, U.; Merbach, A. E. *Chimia* **1996**, *50*, 618.

[15] Cusanelli, A.; Nicula-Dadci, L.; Frey, U.; Merbach, A. E. *Inorg. Chem.* **1997**, *36*, 2211−2217.

[16] White, C.; Yates, A.; Maitlis, P. M. *Inorganic Synthesis*; Grimes, R. N., Ed.; John Wiley & Sons: New York, 1992; Vol. 29, pp 228−234.

[17] Eisen, M. S.; Haskel, A.; Chen, H.; Olmstead, M. M.; Smith, D. P.; Maestre, M. F.; Fish, R. H. *Organometallics* **1995**, *14*, 2806.

[18] Bugnon, P.; Laurenczy, G.; Ducommun, Y.; Sauvageat, P. Y.; Merbach, A. E.; Ith, R.; Tschanz, R.; Doludda, M.; Berghauer, R.; Grell, E. *Anal. Chem.* **1996**, *68*, 3045.

[19] Gampp, H.; Maeder, M.; Meyer, C. J.; Zuberbühler, A. D. *Talanta* **1986**, *33*, 943.

[20] *SPECFIT 2.11 for MS-DOS*; Spectrum Software Associates: P.O. Box 4494, Chapel Hill, NC 27515. E-mail: SpecSoft@compuserve.com.

Scheme 3

$$Cp^*M(H_2O)_3^{2+} \overset{K_a}{\rightleftarrows} Cp^*M(H_2O)_2(OH)^+ + H^+$$

$$2\ Cp^*M(H_2O)_2(OH)^+ \overset{K_{din}}{\rightleftarrows} (Cp^*M)_2(\mu\text{-}OH)_3^+ + H^+ + 3H_2O$$

Table 1. Proton Dissociation Constant pK_a of $Cp^*M(H_2O)_3^{2+}$ and Equilibrium Constant $\log \beta_{din}$ for the Formation of $(Cp^*M)_2(\mu\text{-}OH)_3^+$ [a]

	M = Rh	M = Ir
pK_a	6.47 ± 0.03	3.86 ± 0.03
$\log \beta_{din}$	-8.90 ± 0.03	-1.59 ± 0.07

[a] $pK_a = -\log K_a$, $\log \beta_{din} = 2 \log K_a + \log K_{din}$ (for K_a and K_{din}, see Scheme 3).

found in the literature. On the basis of NMR pH titration, Fish and co-workers established an equilibrium between $Cp^*Rh(H_2O)_3^{2+}$ and $(Cp^*M)_2(\mu\text{-}OH)_3^+$ via the plausible intermediates $Cp^*M(OH)(H_2O)_2^+$ and $(Cp^*M)_2(\mu\text{-}OH)_2(H_2O)_2^{2+}$. They also performed potentiometric pH titrations and observed, surprisingly, only one pK_a value ($pK_a = 5.3$) upon titration of the species $Cp^*Rh(H_2O)_3^{2+}$.[17]

On the basis of the model described in Scheme 3 we determined the dissociation constant K_a as well as the equilibrium constant β_{din} for the formation of the dinuclear species $(Cp^*M)_2(\mu\text{-}OH)_3^+$ by spectrophotometric titration of the cations $Cp^*Ir(H_2O)_3^{2+}$ and $Cp^*Rh(H_2O)_3^{2+}$. The values obtained are given in Table 1. Our spectrophotometric titrations show that only one intermediate, $Cp^*M(H_2O)_2(OH)^+$, can be detected by going from the triaqua species $Cp^*M(H_2O)_3^{2+}$ to the dinuclear complex $(Cp^*M)_2(\mu\text{-}OH)_3^+$ at higher pH. The percentage of this intermediate is small. The spectral changes associated with the spectrophotometric titrations as well as the pH-dependent distribution of the species involved can be seen in Figure 1.

In addition to spectrophotometric titrations, potentiometric titrations as well as NMR pH titrations were undertaken. The NMR spectra are included in the Supporting Information. ^1H NMR and ^{13}C NMR pH titrations have already been reported for the cation $Cp^*Rh(H_2O)_3^{2+}$.[17] We focused our attention therefore on the corresponding iridium complex. The potentiometric titrations show that, for both the iridium complex and the rhodium complex, 1.5 protons per complex $Cp^*M(H_2O)_3^{2+}$ are consumed by going from pH 1 to pH 11. This is in agreement with the model shown in Scheme 3. The ^1H NMR spectra for the cation $Cp^*Ir(H_2O)_3^{2+}$ show two signals, one at 1.58 ppm for the triaqua species $Cp^*Ir(H_2O)_3]^{2+}$ and one at 1.56 ppm for the dinuclear species $(Cp^*Ir)_2(\mu\text{-}OH)_3^+$ at higher pH. Two signals were observed in the ^{13}C NMR spectrum, one at 87.64 ppm for the triaqua species and one at 82.96 ppm for the dinuclear species. These observations are in agreement with the spectrophotometric titrations and provide further support to the model shown in Scheme 3.

One would expect that the coordinated water molecules in the species $Cp^*M(H_2O)_3^{2+}$ are easily replaced by stronger nucleophiles. Before investigating the kinetics of substitution according to reaction 3, the stability of the complexes formed

$$Cp^*M(H_2O)_3^{2+} + L \overset{K_1}{\rightleftarrows} Cp^*M(H_2O)_2L^{2+} + H_2O \qquad (3)$$

was studied by spectrophotometric titration, leading to the corresponding equilibrium constants K_1 (see Tables 2 and 3). As an example, the spectrophotometric titration of $Cp^*Rh(H_2O)_3^{2+}$ with $L = Cl^-$ is shown in Figure S14 (see Supporting Information). The limiting spectra and the concentration profiles resulting from the computer fit of these data can be seen in Figures S15 and S16 (see Supporting Information). The characteristics of the absorption spectra for all the systems investigated are summarized in Table S1 (see Supporting Information).

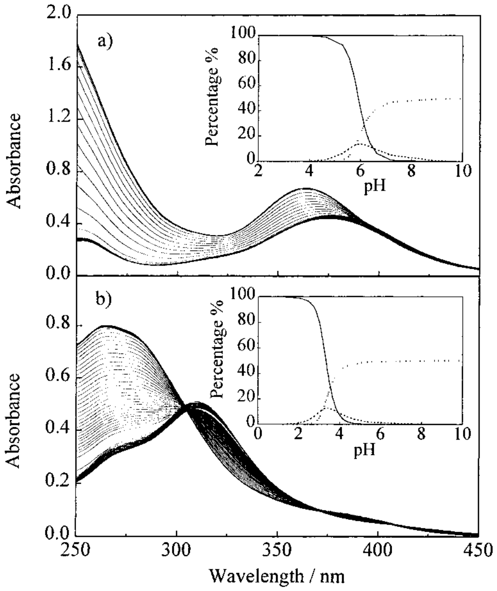

Figure 1. Spectrophotometric titration of $Cp^*Rh(H_2O)_3^{2+}$ (a) and $Cp^*Ir(H_2O)_3^{2+}$ (b) with NaOH at 298 K. Dilution effect was corrected. $[Cp^*M(H_2O)_3^{2+}] = 3.0 \times 10^{-4}$ M, [NaOH] = 0.1 and 1 M. $Cp^*M(H_2O)_3^{2+}$ (—); $Cp^*M(H_2O)_2(OH)^+$ (- - -); $(Cp^*M)_2(\mu\text{-}OH)_3^+$ (···).

Kinetics of Substitution with Anionic Ligands. Ligand substitution according to eq 3 with M = Ir, Rh was studied in acidic solution under pseudo-first-order conditions (excess of L). The change in absorbance with time could be well fitted with a monoexponential function, which shows that a single water molecule is substituted and that the rate of anation is first-order in complex concentration. The plots of $k_{obsd} = f([L])$ were found to be linear, with an intercept at $[L] = 0$ (see Figure 2).

The occurrence of an intercept points to a reversible reaction, as described by rate law 4.

$$\text{rate} = (k_f[L] + k_r)[\text{complex}] = k_{obsd}[\text{complex}] \qquad (4)$$

The plots of k_{obsd} vs [L] yield second-order rate constant k_f for the formation reaction (slope) and first-order rate constant k_r for the back reaction (intercept), with $k_f/k_r = K^{298}$. The data for K^{298} thus obtained kinetically are in good agreement with those obtained by spectrophotometric titration (see Table 2).

The investigation of reactions 3 at variable temperature led to the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, according to eq 5.

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \qquad (5)$$

Figure 2 shows the results for the reaction of $Cp^*Rh(H_2O)_3^{2+}$ with chloride ions at variable temperature.

Similarly, the pressure dependence of the anation rates, as described by eq 6, led to the volume of activation, $\Delta V^{\ddagger}$.

$$\ln k = \ln k_o - P\frac{\Delta V^{\ddagger}}{RT} \qquad (6)$$

As an example, the results of the pressure dependence for the reaction of the cation $Cp^*Rh(H_2O)_3^{2+}$ with Cl^- are shown in Figure S17 (Supporting Information). The detailed results

Table 2. Thermodynamic and Kinetic Parameters for the Reactions of $Cp^*M(H_2O)_3^{2+}$ with Cl^- and Br^- [a]

	M = Rh[b]		M = Ir[b]	
	L = Cl^-	L = Br^-	L = Cl^-	L = Br^-
$k_f^{298} \times 10^{-4}/M^{-1}\,s^{-1}$	1.11 ± 0.06	2.68 ± 0.06	0.52 ± 0.01	1.34 ± 0.03
k_r^{298}/s^{-1}	88 ± 5	48 ± 5	11 ± 1	4.6 ± 1.7
$\log(K_1^{298}/M^{-1})$	2.1 ± 0.1 $(2.3 \pm 0.1)^c$	2.8 ± 0.1 $(3.1 \pm 0.1)^c$	2.7 ± 0.1 $(2.8 \pm 0.1)^c$	3.5 ± 0.4 $(3.5 \pm 0.1)^c$
$\Delta H_f^\ddagger/kJ\,mol^{-1}$	42.5 ± 4	45.2 ± 2	62.3 ± 2	54.9 ± 1
$\Delta H_r^\ddagger/kJ\,mol^{-1}$	62.3 ± 4	76.4 ± 7	51.4 ± 7	68.6 ± 23
$\Delta H^\circ/kJ\,mol^{-1}$	-19.8 ± 9	-31.2 ± 9	11.0 ± 8	-13.7 ± 24
$\Delta S_f^\ddagger/J\,K^{-1}\,mol^{-1}$	-25.0 ± 15	-8.5 ± 5	$+35.2 \pm 6$	$+18.3 \pm 4$
$\Delta S_r^\ddagger/J\,K^{-1}\,mol^{-1}$	$+1.1 \pm 14$	$+43.4 \pm 24$	-52.7 ± 22	$(-2.1 \pm 76)^d$
$\Delta S^\circ/J\,K^{-1}\,mol^{-1}$	-26.1 ± 28	-51.9 ± 28	$+87.9 \pm 27$	$(+20.4 \pm 80)^d$
$\Delta V_f^{\ddagger\,e}/cm^3\,mol^{-1}$	$+1.1 \pm 0.7$	$+0.8 \pm 0.5$	$+4.7 \pm 0.4$	$+3.9 \pm 0.3$
$\Delta V_r^{\ddagger\,e}/cm^3\,mol^{-1}$	-2.4 ± 0.7	-4.8 ± 2.1	-2.3 ± 1.4	$(-10.1 \pm 19)^d$
$\Delta V^{\circ\,e}/cm^3\,mol^{-1}$	$+3.5 \pm 1.4$	$+5.6 \pm 2.6$	$+7.0 \pm 1.8$	$(+14.0 \pm 19)^d$

[a] $I = 0.2$ M ($NaCF_3SO_3$), $[H^+] = 0.1$ M (HCF_3SO_3). [b] Variable temperature measurements, $T = 278-308$ K, $[Cp^*M(H_2O)_3^{2+}] = (2.0-2.5) \times 10^{-4}$ M, and [ligand] $= (2.6-12.5) \times 10^{-3}$ M. [c] Determined by spectrophotometric titrations at pH 1. [d] The errors on these values are quite large due to the small value of the rate for the back reaction; they are therefore of little significance. [e] Variable pressure measurements, $P = 2-200$ MPa, $T = 298$ K.

Table 3. Thermodynamic and Kinetic Parameters for the Reactions of $Cp^*M(H_2O)_3^{2+}$ with py-CN and py-nia[a]

	M = Rh[b]		M = Ir[b]	
	L = py-CN	L = py-nia	L = py-CN	L = py-nia
$k_{f,1}^{298} \times 10^{-3}/M^{-1}\,s^{-1}$	1.29 ± 0.02	1.17 ± 0.03	1.23 ± 0.02	1.77 ± 0.02
$k_{r,1}^{298}/s^{-1}$	0.81 ± 0.04	0.27 ± 0.02		
$k_{f,2}^{298}/M^{-1}\,s^{-1}$			141 ± 5	137 ± 5
$k_{r,2}^{298}/s^{-1}$			0.17 ± 0.03	$(73.0 \pm 3.6) \times 10^{-3}$
$\log(K_1^{298}/M^{-1})$	3.2 ± 0.1 $(3.5 \pm 0.1)^c$	3.6 ± 0.1 $(3.6 \pm 0.1)^c$		
$\log(K_2^{298}/M^{-1})$			2.9 ± 0.1	3.3 ± 0.1
$\Delta V_{f,1}^{\ddagger\,d}/cm^3\,mol^{-1}$	$+2.3 \pm 0.6$	$+4.6 \pm 0.4$	$+4.4 \pm 0.4$	$+5.4 \pm 0.4$
$\Delta V_{r,1}^{\ddagger\,d}/cm^3\,mol^{-1}$	$+8.1 \pm 2$	$+3.5 \pm 0.7$		
$\Delta V_1^{\circ\,d}/cm^3\,mol^{-1}$	-5.8 ± 3	$+1.1 \pm 1$		
$\Delta V_{f,2}^{\ddagger\,d}/cm^3\,mol^{-1}$			$+3.9 \pm 1.0$	$+6.5 \pm 1.6$
$\Delta V_{r,2}^{\ddagger\,d}/cm^3\,mol^{-1}$			$+8.1 \pm 4$	$+6.9 \pm 1.6$
$\Delta V_2^{\circ\,d}/cm^3\,mol^{-1}$			-4.2 ± 5	-0.4 ± 3

[a] $I = 0.2$ M ($NaClO_4$), $[H^+] = 0.01$ M ($HClO_4$). [b] $[Cp^*M(H_2O)_3^{2+}] = (1.5-15.0) \times 10^{-5}$ M, [ligand] $= (3.8-95.0) \times 10^{-3}$ M. [c] Determined by spectrophotometric titrations at pH 2. [d] Variable pressure measurements, $P = 2-200$ MPa, $T = 298$ K.

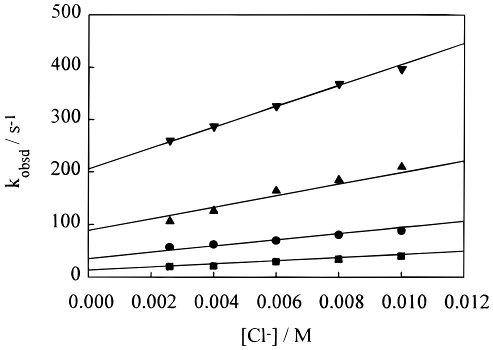

Figure 2. Values of k_{obsd} for the reaction of $Cp^*Rh(H_2O)_3^{2+}$ with Cl^- at variable temperature. $[Cp^*Rh(H_2O)_3^{2+}] = 2 \times 10^{-4}$ M, $I = 0.2$ M ($NaCF_3SO_3$), $[H^+] = 0.1$ M (HCF_3SO_3). $T = 278$ (■), 288 (●), 298 (▲), and 308 K (▼).

for the anation reactions of both metal complexes by Cl^- and Br^- are summarized in Table 2. Rate constants for the anation reactions with SCN^- and I^- at 298 K are reported in Table 4. The pressure dependence for the anation of $Cp^*Ir(H_2O)_3^{2+}$ by SCN^- was also measured and found to be $\Delta V_{f,1}^\ddagger = +3.4 \pm 0.6$ $cm^3\,mol^{-1}$ ($k_{r,1}$ was close to 0, and therefore $\Delta V_{r,1}^\ddagger$ was not determined). The measurements were performed under the same conditions as in the case of the other ligands (see Supporting Information).

Kinetics of Substitution with Neutral Ligands. The neutral ligands (see Scheme 2) were selected to cover a wide range of both basicity (py-CN, py-nia, py; see pK_a values[21,22]) and nucleophilicity (py, DMS, TU; see n_{Pt}° values[23]). The substitution reactions of the complexes $Cp^*M(H_2O)_3^{2+}$ with neutral ligands were studied at pH 2. This means that, depending on their pK_a, the pyridine ligands were more or less protonated. Experiments at different pH values confirmed that the pyridinium cations formed are not reactive; i.e., they are not coordinated. The concentration of the reactive, nonprotonated pyridine, as calculated according to eq 7, was introduced in eq 4 to obtain rate constants referring to the anation reactions with nonprotonated pyridine ligands. pH titrations showed that, at

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(21) Martell, A. E.; Smith, R. M. *Critical Stability Constants;* Plenum Press: New York, 1974.

(22) Castro, E. A.; Ureta, C. *J. Chem. Soc.*, *Perkin Trans.* **1991**, 64.

(23) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley & Sons: New York, 1967; p 399.

Table 4. Kinetic Parameters for the Reaction of $Cp^*M(H_2O)_3^{2+}$ with py,[a] DMS,[a] TU,[a] SCN^-,[b] and I^- [b]

	L = py[c]	L = DMS[c]	L = TU[c]	$L = SCN^-$ [d]	$L = I^-$ [c]
		M = Rh			
$k_{f,1}^{298} \times 10^{-3}/M^{-1}\,s^{-1}$	1.17 ± 0.08	11.7 ± 0.3	15.4 ± 0.3	79 ± 3	
$k_{r,1}^{298}/s^{-1}$	0.029 ± 0.001	4.2 ± 0.6		0.7 ± 0.4	
$\log(k_1^{298}/M^{-1})$	4.6 ± 0.1	3.4 ± 0.2	> 6	5.1 ± 0.1	
		M = Ir			
$k_{f,1}^{298} \times 10^{-3}/M^{-1}\,s^{-1}$	2.61 ± 0.04	3.99 ± 0.02	8.66 ± 0.03	88 ± 4	25 ± 1
$k_{f,2}^{298}/M^{-1}\,s^{-1}$	309 ± 12	468 ± 20	1433 ± 140		
$k_{r,2}^{298} \times 10^3/s^{-1}$	4.0 ± 0.2				
$\log(K_2^{298}/M^{-1})$	4.9 ± 0.1	> 6	> 6		

[a] $I = 0.2$ M ($NaClO_4$), $[H^+] = 0.01$ M ($HClO_4$). [b] $I = 0.2$ M ($NaCF_3SO_3$), $[H^+] = 0.1$ M (HCF_3SO_3). [c] $[Cp^*M(H_2O)_3^{2+}] = (5.0-10.0) \times 10^{-5}$ M, [ligand] $= (0.25-50.0) \times 10^{-3}$ M. [d] $[Cp^*M(H_2O)_3^{2+}] = (4.0-20.0) \times 10^{-5}$ M, [ligand] $= 4.0 \times 10^{-6}$ M.

$$[L] = [py]_{tot}\{K_a/(K_a + [H^+])\} \qquad (7)$$

pH 2, ca. 0.01% of the iridium triaqua species has undergone condensation and 1.3% of the monohydroxo species $Cp^*M(H_2O)_2(OH)^+$ is present (Figure 1b). Kinetic runs with DMS and $Cp^*Ir(H_2O)_3^{2+}$ at pH 1 and pH 2 yielded identical rate constants, proving that the kinetic effect of the deprotonation and condensation reactions is negligible at this pH level.

As in the case of anionic ligands, the absorbance/time data obtained for the reaction of the complex $Cp^*Rh(H_2O)_3^{2+}$ with neutral ligands L can be fitted satisfyingly with a single exponential function, which confirms the substitution of only one water molecule. The plots of k_{obsd} vs [L] were linear, and an intercept was observed for the reaction of the pyridine ligands and for DMS. The intercept was missing however in the case of L = TU, which is obviously due to the high stabiliy of the species $Cp^*Rh(H_2O)_2(TU)^{2+}$ ($\log K_1^{298} > 6$; see Table 4). This means that for L = TU reaction 3 goes to completion and appears to be irreversible ($k_r \approx 0$).

The reaction of the complex $Cp^*Ir(H_2O)_3^{2+}$ with neutral ligands L was found to be biphasic. Fitting of the absorbance/time data to the sum of two exponentials led to first-order rate constants $k_{obsd,1}$ (fast step) and $k_{obsd,2}$ (slow step). For the concentration range studied the dependency $k_{obsd} = f\,[L]$ was found to be linear for both $k_{obsd,1}$ and $k_{obsd,2}$. In contrast to the rhodium species, an intercept for the fast reaction step was not observed. An intercept was found however for the plots of $k_{obsd,2}$ vs [L] for L = pyridine ligands. This intercept could not be detected for L = DMS and TU.

The observed biphasic kinetics can be explained by assuming two succesive substitution reactions according to eqs 8 and 9.

$$[Cp^*M(H_2O)_3]^{2+} + L \underset{k_{r,1}}{\overset{k_{f,1}}{\rightleftharpoons}} [Cp^*M(H_2O)_2L]^{2+} + H_2O \qquad (8)$$

$$[Cp^*M(H_2O)_2L]^{2+} + L \underset{k_{r,2}}{\overset{k_{f,2}}{\rightleftharpoons}} [Cp^*M(H_2O)L_2]^{2+} + H_2O \qquad (9)$$

The fast reaction step is assigned to the substitution of a first water molecule, occurring with rate constant $k_{f,1}$. Under the conditions employed, the reaction (eq 8) goes to completion for all of the ligands L and therefore $k_{r,1}$ is close to 0. The slow reaction step describes the substitution of a second water molecule according to eq 9. Since the plots of $k_{obsd,2}$ vs [pyridines] show a clear intercept, these reactions are obviously reversible. Due to the high stability of the complexes formed, the reaction (eq 9) is found to be irreversible for L = DMS and TU ($k_{r,2} \approx 0$).

The temperature and pressure dependence of reaction rates involving neutral ligands was analyzed as described above. The results are summarized in Table 3. The results obtained for the concentration dependence are compiled in Table 4. As an example, the spectral changes associated with the reaction of the complex $Cp^*Ir(H_2O)_3^{2+}$ with DMS are shown in Figure S18 (Supporting Information).

Discussion

pH Effects on the Stability of the Species $Cp^*M(H_2O)_3^{2+}$ (M = Rh, Ir). The availability of reliable data on the stability of the complex cations $Cp^*M(H_2O)_3^{2+}$ (M = Rh, Ir) at variable pH is an important condition for the kinetic investigation of the substitution reactions according to eq 3. The acid/base properties of both complexes were therefore studied in detail.

The pH-spectrophotometric titrations, confirmed by ^1H and ^{13}C NMR pH titrations, show that the water molecules in the iridium complex are more acidic than those in the rhodium complex ($pK_a(Ir) = 3.86$ and $pK_a(Rh) = 6.47$), and as a direct consequence, the iridium complex $Cp^*Ir(H_2O)_3^{2+}$ undergoes condensation at a lower pH than the rhodium triaqua complex ($\log \beta_{din}(Ir) = -1.59$ and $\log \beta_{din}(Rh) = -8.90$; see also Figure 1). This increase in the acidity of water coordinated to iridium was previously also reported for the complexes $Cp^*M(bpy)(H_2O)^{2+}$ ($pK_a(Ir) = 7.5$ and $pK_a(Rh) = 8.2$).[13]

Under the experimental conditions of the kinetic experiments, the triaqua species $Cp^*Ir(H_2O)_3^{2+}$ and $Cp^*Rh(H_2O)_3^{2+}$ were the only reacting species and therefore any kinetic effects stemming from complex formation with the monohydroxo species $Cp^*M(H_2O)_2(OH)^+$ or with the dinuclear species $(Cp^*M)_2(\mu\text{-}OH)_3^+$ could be neglected.

Stability Constants of the Complexes $[Cp^*M(L^{-n})_m(H_2O)_{3-m}]^{(2-mn)+}$ (M = Rh, Ir; n = 0, 1; m = 1, 2). It follows from the results obtained for complex formation of the complex cations $Cp^*M(H_2O)_3^{2+}$ with a wide range of charged and neutral ligands L that, in the case of M = Rh, monosubstituted complexes $Cp^*Rh(H_2O)_2L^{2+/+}$ are formed only under kinetic conditions (see Tables 2, 3, and 5). In the case of M = Ir, however, both mono- and bisubstituted complexes, $Cp^*Ir(H_2O)_2L^{2+}$ and $Cp^*Ir(H_2O)L_2^{2+}$, are formed when L is a neutral ligand. In all cases the iridium complexes formed are more stable than the corresponding rhodium complexes. Furthermore, for L = anionic ligand, the stability increases upon going from chloride to bromide and to iodide. The complexes formed with neutral ligands L are more stable than those formed with charged ligands L. For the pyridine ligands an increase in stability is observed upon going from $Cp^*M(py\text{-}CN)_m(H_2O)_{3-m}^{2+}$ to $Cp^*M(py)_m(H_2O)_{3-m}^{2+}$, which goes hand in hand with the increasing basicity of the pyridine ligand. The highest stability constants are found for the sulfur-containing ligands DMS and

Table 5. Interchange Rate Constants k_i' for the Substitution of Water in the $Cp^*M(H_2O)_3^{2+}$ Complexes[a]

	M = Rh		M = Ir	
L	$k_{f,1}^{298} \times 10^{-4}$/M^{-1} s^{1}	$k_i' \times 10^{-4}$/s^{-1}	$k_{f,1}^{298} \times 10^{-4}$/M^{-1} s^{1}	$k_i' \times 10^{-4}$/s^{-1}
H_2O[b]		16 ± 3		2.53 ± 0.08
Cl^-	1.11 ± 0.06	4.04	0.52 ± 0.012	1.88
Br^-	2.68 ± 0.06	9.76	1.34 ± 0.03	4.88
I^-			2.47 ± 0.03	9.28
SCN^-	7.90 ± 0.34	28.72	8.77 ± 0.38	31.88
py-CN	0.129 ± 0.002	2.16	0.123 ± 0.003	2.04
py-nia	0.117 ± 0.003	1.96	0.177 ± 0.003	2.96
py	0.117 ± 0.008	1.96	0.261 ± 0.004	4.36
DMS	1.17 ± 0.03	19.52	0.399 ± 0.002	6.64
TU	1.54 ± 0.03	25.68	0.866 ± 0.003	14.44

[a] $k_i' = (k_{f,1}f)/(K_{OS}n_c)$ with $1/f$ = probability factor = 1/12, n_c = coordination number = 3, $K_{OS} = 1.10$ M^{-1} for charged ligands, and $K_{OS} = 0.24$ M^{-1} for neutral ligands. [b] k_{ex} = rate constants[13] for the exchange of a particular water molecule.[9] $\Delta V^{\ddagger}_{ex} = +0.6 \pm 0.6$ and $\Delta V^{\ddagger}_{ex} = +2.4 \pm 0.5$ cm^3 mol^{-1} for the exchange of water on $Cp^*Rh(H_2O)_3^{2+}$ and $Cp^*Ir(H_2O)_3^{2+}$ respectively were then reported.[13]

TU, which is most probably due to the high nucleophilicity of these ligands L.

It follows from the visible absorption data (Table S1, Supporting Information) that there is a red shift of the absorption bands when coordinated water is replaced by Cl^- or Br^- (Figure S15, Supporting Information) and a blue shift when the water is replaced by the pyridines and sulfur-containing ligands. These shifts reflect a decrease and increase, respectively, of the ligand field strength.

Kinetics. Compared to the extremely inert hexaaqua species $Rh(H_2O)_6^{3+}$ and $Ir(H_2O)_6^{3+}$, the results obtained for complex formation of the species $Cp^*M(H_2O)_3^{2+}$ (M = Rh, Ir) demonstrate once more the extreme labilization of the residual water upon coordination of the Cp* ligand.

With all ligands L $Cp^*Rh(H_2O)_3^{2+}$ only forms the monosubstituted species $Cp^*Rh(H_2O)_2L^{+/2+}$. The anation of the iridium species $Cp^*Ir(H_2O)_3^{2+}$ is quite similar to that of the rhodium. The kinetic behavior of the iridium species upon water substitution by neutral ligands is however rather different. For all neutral ligands L, a second reversible substitution step is clearly observed. The second ligand enters at a rate which is roughly by 1 order of magnitude lower than the rate of the entry of the first ligand ($k_{f,1} = 2.61 \times 10^3$ and $k_{f,2} = 3.09 \times 10^2$ M^{-1} s^{-1} for the substitution of water by pyridine). Although statistical factors have to be considered, they cannot solely account for this effect. Under the conditions employed a third substitution step was not observed. The rate for the substitution of the third water molecule can be approximated, however, by the kinetic data obtained for the monoaqua complex $Cp^*Ir(bpy)(H_2O)^{2+}$, in which 2,2′-bipyridine can be regarded as being equivalent to two coordinated pyridine molecules. Since the substitution rate for this complex is further reduced by ca. 1 order of magnitude ($k_{f,3} = 1.05 \times 10^1$ M^{-1} s^{-1}),[24] it can be concluded that consecutive substitution of water molecules by neutral monodentate ligands markedly reduces the lability of the residual water.

The dependence of substitution rates on the chemical nature of the entering ligand has always been a classical criterion for the type of mechanism operating. According to the Eigen–Wilkins model a substitution reaction can be divided into two steps, an outer-sphere complex formation according to eq 10 followed by a ligand interchange according to eq 11.

$$[Cp^*M(H_2O)_3]^{2+} + L^{-n} \overset{K_{OS}}{\rightleftharpoons} \{[Cp^*M(H_2O)_3]^{2+}, L^{-n}\} \quad (10)$$

$$\{[Cp^*M(H_2O)_3]^{2+} + L^{-n}\} \xrightarrow{k_i} [Cp^*M(H_2O)_2L]^{(2-n)+} + H_2O \quad (11)$$

For dilute solutions, the rate of substitution is given by eq 12, where k_i is the interchange rate and K_{OS} is the equilibrium

$$k_f = k_i K_{OS} \quad (12)$$

constant for the formation of the outer-sphere complex.

To allow a comparison with k_{ex} (=rate constant for water exchange), rate constant k_i needs to be corrected for statistical reasons. One must indeed take into account the probability for a water molecule to be replaced by a ligand. This probability depends on f (number of water molecules in the second shell) as well as on n_c (number of water molecules in the first shell). The corrected rate of interchange k_i' is then given by eq 13,

$$k_i' = k_i(f/n_c) \quad (13)$$

which is described in detail by Aebischer et al.[25] The corrected interchange rate k_i' was calculated for all of the systems studied (see Table 5).

As described above, nucleophilicity as well as basicity seems to influence the processes under study. To quantify these results for the complexes $Cp^*M(H_2O)_3^{2+}$ (M = Rh, Ir), we choose the $n_{Pt}°$ values as a measure for nucleophilicity (see Figure 3). Plots of log k_i' vs pK_a and $n_{Pt}°$ yield linear dependencies. In the case of the complex $Cp^*Ir(H_2O)_3^{2+}$ the basicity of the pyridine ligand has a moderate effect on the size of k_i'. This effect is however absent in the case of $Cp^*Rh(H_2O)_3^{2+}$. Since for the iridium species the neutral ligands studied can be considered to be better nucleophiles than for the rhodium (higher stability constants), one would also expect a greater reactivity in the case of an associative activation. This is not the case, since the iridium complex is roughly by 1 order of magnitude less labile than the rhodium complex (Figure 3). Furthermore, in the case of both $Cp^*Rh(H_2O)_3^{2+}$ and $Cp^*Ir(H_2O)_3^{2+}$ the influence of nucleophilicity is larger for the anionic ligands than for the neutral ones.

Due to the enhanced polarizability and σ-donating ability of the sulfur ligand, one cannot totally discount an associative mechanism that encompasses the ability of the Cp* ligand undergoing a ring slip ($\eta^5 \rightarrow \eta^3$) to accommodate the incoming nucleophile/ligand, with expulsion of the H_2O ligand on reversion of the Cp* ligand from $\eta^3 \rightarrow \eta^5$. This mechanism has been suggested by Fish and co-workers for the regioselective Cp*RhH hydride transfer reaction to 3-substituted pyridinium

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(24) Poth, T. Dr.-Ing. Dissertation, 1999, to be submitted to the Technische Universität Darmstadt, D17.

(25) Aebischer, N.; Churlaud, R.; Dolci, L.; Frey, U.; Merbach, A. E. *Inorg. Chem.* **1998**, *37*, 5915–5924.

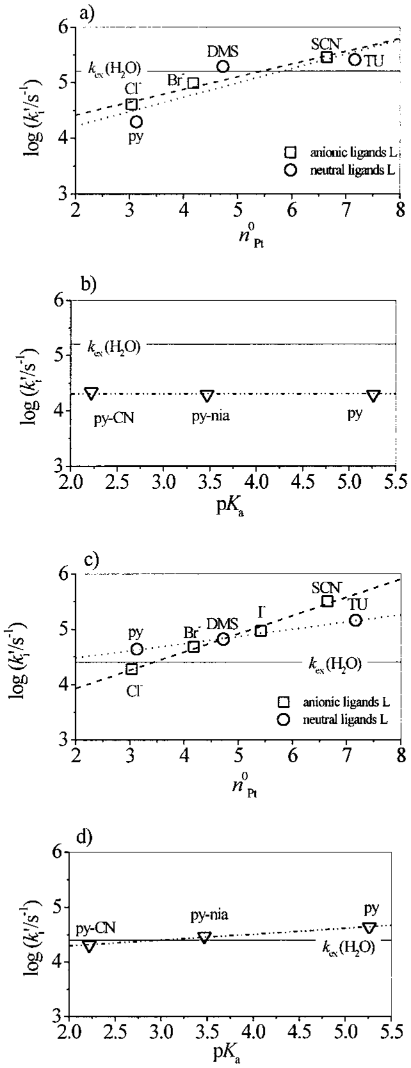

Figure 3. Dependence of the rate constant k_i' on the nucleophilicity of the charged ligands (□, - - -), on the nucleophilicity of the neutral ligands (○, •••), and on the basicity of the pyridine ligands (▽, — •• —) for substitution in $Cp^*Rh(H_2O)_3^{2+}$ (a, b) and $Cp^*Ir(H_2O)_3^{2+}$ (c, d). $k_{ex} = (1.6 \pm 0.3) \times 10^5$ s^{-1} for rhodium and $k_{ex} = (2.5 \pm 0.08) \times 10^4$ s^{-1} for iridium. $k_i' = (k_{f,1}f)/(K_{OS}n_c)$ with $K_{OS} = 1.10$ M^{-1} for charged ligands and $K_{OS} = 0.24$ M^{-1} for neutral ligands.

salts; i.e., binding to the Cp*Rh metal center was a prerequisite for hydride transfer reaction to substrate and the 3-sulfur substituent was 1.3 times more reactive than the oxygen analogue.[26]

The effect of nucleophilicity on the rate constants could lead us to think that entering of the ligand (with or without ring slip of the Cp*) is the rate-determining step, supporting therefore an associative mechanism. However, this effect is quite small compared to systems in which the substitution reactions follow an associative mode of activation. Indeed the nucleophilic discrimination factor *S*, described by eq 14, varies from 0.6 to

$$\log k = S n_{Pt}^{\circ} + c \qquad (14)$$

1.4 for typical associative substitutions on Pt(II) complexes.[27] In the present study, however, only $S \leq 0.3$ is found (Figure 3). Therefore, we can exclude an associative mechanism.

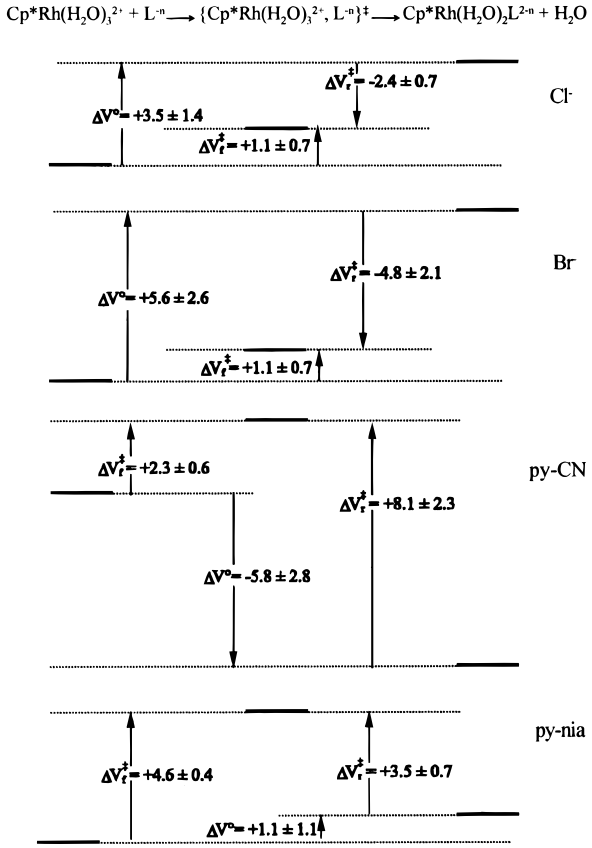

Figure 4. Volume profiles for the reaction of $Cp^*Rh(H_2O)_3^{2+}$ with Cl^-, Br^-, py-CN, and py-nia at 298 K, *V* (cm^3 mol^{-1}).

Furthermore, the effect observed could also be attributed to the difficulties of obtaining a good estimate for the outer-sphere equilibrium constant for the low-symmetry half-sandwich complexes under study. Taking into account these considerations, if one compares the interchange rates k_i' with the exchange rate of water, k_{ex} (see Figure 3 and Table 5), one can affirm that $k_i' \approx k_{ex}$. These observations suggest a dissociative interchange I_d, without excluding a limiting *D* mechanism.

In addition to the kinetics at ambient pressure and temperature, the high-pressure work gives more detailed insight into the mechanism (see Figure 4 and Tables 2 and 3). In all cases, Rh and Ir, charged and neutral ligands, the volume of the transition state is always larger than that of the triaqua species. This is also the case for the substitution of the second water molecule on the iridium complex ($\Delta V^{\ddagger}_{f,2} = +3.9$ cm^3 mol^{-1} for py-CN and $\Delta V^{\ddagger}_{f,2} = +6.5$ cm^3 mol^{-1} for py-nia), therefore supporting a mechanism with a more or less disssociative character rather than an associative character.

For a complete mechanistic assignment it is important to know the complete volume profile in order to compare the volume of the transition state with not only the volumes of the reaction partners, but also those of the products. Therefore, the reaction volumes ΔV° are also of interest. The reaction volumes ΔV° show a large difference between the charged and neutral ligands (see Tables 2 and 3). For the charged ligands the reaction volume is always positive, and the volume of the product of the anation reaction is larger than the triaqua species $Cp^*M(H_2O)_3^{2+}$ due to the loss of electrostriction. However, activation volumes for the aquation of the anionic ligands are all significantly negative due to significant charge creation during dissociation of the anionic ligands; i.e., an increase in electrostriction occurs that overules the volume increase due to bond breakage and results in an overall negative volume of activation.

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(26) Lo, H. C.; Buriez, O.; Kerr, J. B.; Fish, R. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1429.

(27) Tobe, M. L. *Inorganic Reactions Mechanisms: Studies in Modern Chemistry,* Nelson: London, 1972; p 52.

The volume of the transition state is always between the volumes of the reaction partners and products. The same situation can be found by looking at the entropies. Again, the entropy of the transition state is between the entropy of the triaqua species and the entropy of the products. Because of the larger errors on the activation entropies, the pressure dependence gives a more precise picture. Thus the variable pressure behavior is not very different from that observed for the water exchange on the complexes $Cp^*M(H_2O)_3^{2+}$, where volumes of $+0.6$ cm^3 mol^{-1} for iridium and $+2.4$ cm^3 mol^{-1} for rhodium have been observed.[13] Despite the small positive value of $\Delta V^\ddagger$, an I_d mechanism had been suggested with the explanation of a competition between a positive contribution, due to the loss of a water molecule, and a negative one, due to the contraction of the spectator water molecules around the small d^6 ion in the transition state. It should also be noted that the tremendous labilization induced by Cp* must cause a significant ground-state lengthening of the $M-OH_2$ bond. This means that the actual bond lengthening required to reach a dissociative transition state will be much smaller than for a process in which no ground-state labilization is present. Thus a volume of activation of only a few cm^3 mol^{-1} in the present systems could be perfectly in line with a limiting dissociative mechanism.

The situation is different for the neutral ligands. There is no general trend for the reaction volumes ΔV° because one exchanges a neutral water molecule by another neutral ligand. The reaction volumes are small, sometimes positive and sometimes negative (see Tables 2 and 3). Here the volume of the transition state is always larger than the volumes of the reaction partners and the products, which is a strong indication for a dissociative mechanism.

Although the activation volumes indicate a dissociative interchange mechanism I_d, a moderate dependency on the nucleophilicity of the entering ligand, and large k_i' values, especially for iridium and the sulfur-containing ligands, could in that case suggest an associative activation mode. However, the activation volume determined for the complex formation of $Cp^*Ir(H_2O)_3^{2+}$ with SCN^-, $\Delta V^\ddagger_{f,1} = +3.4$ cm^3 mol^{-1}, is clearly positive. These facts exclude once more the occurrence of an associative mechanism and further support the assignment of an I_d mechanism, or even a D mechanism.

Conclusion

The findings for the complex formation reactions on $Cp^*M(H_2O)_3^{2+}$ (M = Rh, Ir) are in agreement with previous kinetic studies on complex formation reactions on $Cp^*M(bpy)(H_2O)^{2+}$ analogues, where an I_d mechanism was suggested.[13] More recently a limiting D mechanism was assigned to the water exchange reactions on $Cp^*M(H_2O)_3^{2+}$ on the basis of the similarity of the behavior of these π-arene complexes in water and in nonaqueous solvents, acetonitrile, and dimethyl sulfoxide.[15]

Combining the different observations, we can assign a dissociative interchange mechanism I_d, without excluding a D mechanism for the complex formation reactions studied in this paper. A more definitive answer concerning the existence, or nonexistence, of an intermediate for these reactions must probably await ab initio calculations on these species.

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Supporting Information Available: Observed rate constants for water substitution at variable pressure and temperature, ^{1}H and ^{13}C NMR spectra, and spectrophotometric titration data. This material is available free of charge via the Internet at http://pubs.acs.org.

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