Inorg. Chem. **1998,** *37,* 5915−5924

Mechanism of Complex Formation of Ruthenium(II) Aquacomplexes with $H_2C{=}CH_2$, MeCN, Me_2SO, and CO: Metal−Water Bond Rupture as Rate-Determining Step

Nicolas Aebischer, Raphaël Churlaud, Lilian Dolci, Urban Frey, and André E. Merbach*

Institut de Chimie Minérale et Analytique, Université de Lausanne, BCH-Dorigny, CH-1015 Lausanne

Received June 5, 1998

The reaction $[Ru(H_2O)_6]^{2+} + L \xrightarrow{k_f} [Ru(H_2O)_5L]^{2+} + H_2O$ was followed as a function of temperature and ethylene concentration (up to 40 MPa) using a homemade high gas pressure NMR microreactor. The reaction was first order in $H_2C{=}CH_2$ with $10^3k_f^{298}$/kg mol^{-1} s^{-1} = 1.22 ± 0.06, $\Delta H_f^{\ddagger}$/kJ mol^{-1} = 76.9 ± 2, and $\Delta S_f^{\ddagger}$/J K^{-1} mol^{-1} = −42.9 ± 8. These results confirm previous works on mono-complex formation reactions where an I_d mechanism was proposed. The reaction $[Ru(H_2O)_5L]^{2+} + {*L} \overset{k_L}{\rightleftarrows} [Ru(H_2O)_5{*L}]^{2+} + L$ of exchange of L on the mono-complex was followed for L = $H_2C{=}CH_2$ (10^3k_L/kg mol^{-1} s^{-1} = 10.8 at 298.2 K), Me_2SO (0.35 at 278.5 K), and CO (0.052 at 298.3 K); the rate-determining step is the rupture of the $Ru{-}H_2O_{ax}$ bond with *trans*-$[Ru(H_2O)_4L_2]^{2+}$ as reaction intermediate. Due to the trans effect exercised by these strong π-accepting ligands, the ligand exchange reaction is faster than the mono-complex formation reactions. The *cis*-bis-complex formation reaction, $[Ru(H_2O)_5L]^{2+} + L \xrightarrow{k_{cis}}$ *cis*-$[Ru(H_2O)_4L_2]^{2+} + H_2O$, was also investigated for L = MeCN (10^3k_{cis}/kg mol^{-1} s^{-1} = 0.111 at 298.1 K), Me_2SO (0.019 at 321.6 K), and $H_2C{=}CH_2$ (0.007 at 298.1 K, $\Delta H_{cis}^{\ddagger}$/kJ mol^{-1} = 129.9 ± 4, and $\Delta S_{cis}^{\ddagger}$/J K^{-1} mol^{-1} = +92.0 ± 11); here, too, the $Ru{-}H_2O_{eq}$ bond breaking is rate determining, but due to the decrease of the lability of water molecules cis to π-accepting ligands, these reactions are much slower. In the case of MeCN, the reaction scheme includes the formation of the *trans*-bis-complex and of the *mer*-triscomplex. As a general rule, the rate of these complex formation reactions, of dissociative nature, can be predicted from the oxygen-17 determined water exchange rates.

Introduction

Shortly after the publication of the first facile synthesis of $[Ru(H_2O)_6](tos)_2$,[1] a very interesting and promising chemistry has started on the organometallic chemistry of Ru(II) in water. For example, $[Ru(H_2O)_6](tos)_2$,[1] was shown to be an ideal starting material for a series of new aquacomplexes with ligands such as N-heterocycles,[2] phosphines, THF,[3] arenes,[4] and olefins[5,6] and for the straightforward syntheses of $[Ru(H_2O)_5L]^{2+}$ (L = N_2,[7] CO,[8] $H_2C{=}CH_2$[9]). Ru(II) complexes have also promising potential applications, in particular as antitumor agents[10] or as catalysts for the polymerization of cyclic (ring opening metathesis polymerization, ROMP)[11] or acyclic olefins.[12]

To better understand the mechanism of substitution reactions on ruthenium(II) aquacomplexes, a mechanistic study on the mono-complex formation reactions between $[Ru(H_2O)_6]^{2+}$ and ligands with various nucleophilicity has already been reported.[13] The key conclusion was that the rate of the reaction was independent of the nature of the incoming ligand, and an interchange dissociative mechanism was thus assigned. The effect of the coordinating ligand on the reactivity of the water molecules of the first coordination sphere has also been investigated.[14]

In the present study, we propose to use the data on the reactivity of the water molecules in the first coordination sphere as well as simple physicochemical parameters like the redox potentials to understand and predict the conditions for the formation of new bis- and tris-complexes of ruthenium(II). Taking into account statistical factors, a detailed procedure is proposed to compare water exchange and complex formation rates in the frame of a dissociatively activated mechanism.

Experimental Section

Chemicals and Solutions. Dimethyl sulfoxide (Me_2SO, Fluka, p.a.), deuterated dimethyl sulfoxide (Armar, 99.8 atom % D), acetonitrile (MeCN, Fluka, p.a.), carbon monoxide (Carbagas, 99.97%), carbon-

---

(1) Bernhard, P.; Bürgi, H.-B.; Hauser, J.; Lehmann, H.; Ludi, A. *Inorg. Chem.* **1982**, *21*, 3936.

(2) Bernhard, P.; Lehmann, H.; Ludi, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1216.

(3) Bailey, O. H.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 2582.

(4) Röthlisberger-Stebler, M.; Hummel, W.; Pittet, P.-A.; Bürgi, H. B.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1358.

(5) Kölle, U.; Flunkert, G.; Görissen, R.; Schmidt, M. U.; Englert, U. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 440.

(6) McGrath, D. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3611.

(7) Laurenczy, G.; Helm, L.; Ludi, A.; Merbach, A. E. *Inorg. Chim. Acta* **1991**, *189*, 131.

(8) Laurenczy, G.; Helm, L.; Ludi, A.; Merbach, A. E. *Helv. Chim. Acta* **1991**, *74*, 1236.

(9) Laurenczy, G.; Merbach, A. E. *J. Chem. Soc., Chem. Commun.* **1993**, 187.

(10) *Metal Complexes in Cancer Chemotherapy*; Keppler, B. K., Ed.; VCH: Weinheim, Germany, 1993; pp 129−220.

(11) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542.

(12) France, M. B.; Grubbs, R. H.; McGrath, D. V.; Paciello, R. A. *Macromolecules* **1993**, *26*, 4739.

(13) Aebischer, N.; Laurenczy, G.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1993**, *32*, 2810.

(14) Aebischer, N.; Sidorenkova, E.; Ravera, M.; Laurenczy, G.; Osella, D.; Weber, J.; Merbach, A. E. *Inorg. Chem.* **1997**, *36*, 6009.

10.1021/ic980628z CCC: $15.00

13 enriched carbon monoxide (Cambridge Isotope Laboratories, 99%), ethylene (Carbagas, 99.95%), deuterated ethylene ($D_2C{=}CD_2$, Cambridge Isotope Laboratories, 98% D), and *p*-toluenesulfonic acid (Htos, Fluka, puriss.) were used during syntheses and reactions of the Ru(II) complexes without further purification. $[Ru(H_2O)_6](tos)_2$ ($tos^- =$ *p*-toluenesulfonate or tosylate anion) was prepared using the method described by Bernhard et al.[15] The product was recrystallized from an aqueous solution of *p*-toluenesulfonic acid 1.2 mol kg^{-1}. $[Ru(H_2O)_5(H_2C{=}CH_2)](tos)_2$[9] and $[Ru(H_2O)_5(Me_2SO)](tos)_2$[14] were prepared following published procedures. The complex $[Ru(H_2O)_5{}^{13}CO](tos)_2$ was synthesized in a 10 mm NMR sapphire tube[16] by dissolving $[Ru(H_2O)_6](tos)_2$ (0.1 mol kg^{-1}) in 3 g of a 0.1 mol kg^{-1} tosylic acid solution and applying a pressure of 1.3 MPa of ^{13}CO to the solution further pressurized to 5.5 MPa with nonenriched carbon monoxide. When the reaction was completed, the solvent was removed under vacuum. All solutions used for the syntheses and the kinetic measurements were prepared at ambient temperature in a glovebox (oxygen content <2 ppm). Water (solvent) was deoxygenated using an argon stream before use and all the kinetic runs were performed in the absence of O_2. The ^1H, ^{13}C, and ^{17}O NMR chemical shifts are referenced to TMS (proton and carbon) and bulk water respectively, and measured with respect to the methyl protons ($\delta = 2.38$ ppm), methyl carbon ($\delta = 22.9$ ppm) of the tosylate anion and bulk water ($\delta = 0$ ppm), respectively. For the ^{17}O NMR measurements, doubly distilled water and 7−10% oxygen-17 enriched water (Yeda) were used. The solvent for the kinetic measurements was 99.95% deuterated water or doubly distilled water.

Solubility Measurements. The solubility of ethylene in a solution containing 0.1 mol kg^{-1} Htos in D_2O, was measured by ^1H NMR at 304 and 308 K and at pressures between 2 and 40 MPa. The measurements were performed on a Bruker ARX-400 spectrometer with a high gas pressure probe equipped with a gas−liquid mixing unit.[17] This probe was designed to fit in a narrow bore (50 mm ∅) cryomagnet and to safely support gas pressures up to ca. 100 MPa. The concentration of ethylene was obtained by calculating the ratio of the integrals of the protons of dissolved ethylene to the integral of the CH_3 group in Htos. The calculated concentrations are collected in Figures S1a−g of the Supporting Information. These data were combined to the data reported in a previous paper[18] and a global pressure−temperature empirical smoothing equation (eq 1)[19] describing the natural

$$\ln(x_{\text{ethylene}}) = -114.47 + 5439.2/T + 15.8307\ln(T) + 0.20135\ln(P) - 1.4911/P \quad (1)$$

logarithm of the molar fraction of dissolved ethylene, x_{ethylene}, as a function of the temperature and the pressure was derived. The standard deviation in x_{ethylene} is 7% for a temperature range between 300 and 380 K and a pressure range between 2 and 40 MPa.

The solubility of CO gas at 5.4 MPa in a solution of Htos (0.1 mol kg^{-1}) in D_2O was measured by ^{13}C NMR at 298.2 K. The concentration of dissolved CO was determined by calculating the ratio of the integral of the ^{13}C NMR signal of free CO to the average of the integrals of the aromatic carbons of the tosylate anion (as described below), times the concentration of the tosylate. To prevent any error resulting from the different longitudinal relaxation times of the signals, we have first measured all the longitudinal relaxation times, T_1, using the inversion−recovery pulse sequence. The following relaxation times were obtained: 1.5 s (signal of free CO at 187 ppm), 6.1 s (tos^-, 145 ppm), 10.6 s (tos^-, 142 ppm), 4.2 s (tos^-, 132 ppm), and 4.2 s (tos^-, 128 ppm). A relaxation delay of 20 s then was applied during the measurements. Consequently, only the two signals at 132 and 128 ppm, which have short enough T_1, were used to calculate the concentration. A CO concentration of 0.053 mol kg^{-1} was obtained with this method. In a previous work, the solubility of the gas was measured at different CO pressures.[20] The reported concentrations were 0.0161, 0.0317, and 0.048 M for pressures of 2.0, 4.0, and 6.0 MPa, respectively. Our value is slightly higher than these published results. Nevertheless, the authors mentioned that the concentration could increase in the presence of salt like acetic acid or propionic acid. Our higher concentration value may result from the presence of tosylic acid in the solution.

Kinetic Studies. The complex formation reactions between $[Ru(H_2O)_6]^{2+}$ and ethylene was followed at different ethylene pressures by ^1H NMR using the high gas pressure probe described above. The initial metal concentrations were between 0.09 and 0.11 mol kg^{-1} and the ethylene concentrations were between 0.033 and 0.238 mol kg^{-1}, which correspond to gas pressures between 1.1 and 39.8 MPa. The ionic strengths were 0.30 mol kg^{-1}. In a typical run, a solution of aquacomplex of Ru(II) in D_2O was prepared in a 5 mm NMR tube and transferred into the homemade high gas pressure probe. Upon application of the ethylene pressure, the solution and the gas were mixed using a mixing unit fitting inside the probe.[17] The mixer was stopped during acquisition of a spectrum and was working between two acquisitions. This ensured a constant gas concentration in the solution and consequently the kinetics were zero order in ethylene. The ^1H NMR spectra were obtained using a 90° pulse length of 20 μs in the quadrature detection mode, with 16K data points resulting from 4 scans accumulated over a total spectral width of 3.8 kHz.

The ethylene exchange on $[Ru(H_2O)_5(H_2C{=}CH_2)]^{2+}$ was studied as follows: $[Ru(H_2O)_5(\mathit{H}_2C{=}C\mathit{H}_2)](tos)_2$ was first dissolved in degassed D_2O containing Htos 0.1 mol kg^{-1} in a sapphire tube. After having applied to the solution a pressure of 2.1 MPa of $\mathit{D}_2C{=}C\mathit{D}_2$ the tube was shaken for 2 min to saturate the water with ethylene and immediately transferred into the NMR probe at 298.2 K. The time between the mixing of the reactants and the beginning of the acquisitions was about 3 min. The time of the beginning of the reaction, *t*(0), was treated as an adjustable parameter. The reaction was followed by ^1H NMR on a Bruker ARX-400 spectrometer and the same NMR parameters as for the complex formation were used (vide supra).

The exchange of Me_2SO on $[Ru(H_2O)_5Me_2SO]^{2+}$ was studied by ^1H NMR on a Bruker AC-200 spectrometer. The complex $[Ru(H_2O)_5(Me_2SO\text{-}\eta_6)]^{2+}$ was first prepared in a 5 mm NMR tube by dissolving $[Ru(H_2O)_6]^{2+}$ (0.1108 mol kg^{-1}), $Me_2SO\text{-}\eta_6$ (0.1109 mol kg^{-1}), and Htos (0.107 mol kg^{-1}) in 0.7002 g of D_2O. The solution was kept 2 h at 321.6 K to allow the mono-complex to form and then cooled to room temperature. Then 0.0584 g (0.9913 mol kg^{-1}) of $Me_2SO\text{-}d_6$ was added to the solution. After homogenization of the solution, the tube was transferred into the NMR probe and the exchange reaction was followed at 278.5 K using the following parameters: 1.5 μs pulse length in the quadrature detection mode, 16 scans accumulated over a spectral width of 1500 Hz with 16K data points.

The formation of the bis-complex $[Ru(H_2O)_4(Me_2SO)_2]^{2+}$ was followed using the same solution and by setting the NMR probe at 321.6 K. The same NMR parameters were used as for the exchange of Me_2SO. When the formation of $[Ru(H_2O)_4(Me_2SO)_2]^{2+}$ was completed, we have added a few drops of ^{17}O enriched water (10 atom %) to obtain a final solution about 1 atom % in ^{17}O, kept the solution 50 h at 321.6 K, until no more significant change could be observed in the ^{17}O NMR spectra and finally checked the nature of the product by ^{17}O NMR.

To study the exchange of CO, we first dissolved the enriched complex, $[Ru(H_2O)_5{}^{13}CO](tos)_2$, in water ([Ru(II) $= 0.01$ mol kg^{-1}, Htos $= 0.1$ mol kg^{-1}), and 5.4 MPa of ^{12}CO was then applied. The NMR tube was kept at 298.2 K in a water bath during the reaction and transferred regularly into the NMR probe to record the ^{13}C NMR spectra. Several times a day, the solution was shaken to ensure the isotopic equilibrium between liquid and gas phases. The measurements were performed on a Bruker AM-360 spectrometer with the following parameters: 5.0 μs (90° $= 21$ μs) pulse length in the quadrature

---

(15) Bernhard, P.; Biner, M.; Ludi, A. *Polyhedron* **1990**, *9*, 1095.

(16) Cusanelli, T.; Frey, U.; Richens, D. T.; Merbach, A. E. *J. Am. Chem. Soc.* **1996**, *118*, 5265.

(17) Cusanelli, T.; Frey, U.; Marek, D.; Merbach, A. E. *Spectrosc. Eur.* **1997**, *9/3*, 22.

(18) Bradbury, E. J.; McNulty, D.; Savage, R. L.; McSweeney, E. E. *Ind. Eng. Chem.* **1951**, *44*, 211.

(19) Fogg, P. G. T.; Gerrard, W. *Solubility of Gases in Liquids*; John Wiley & Sons: Chichester, U.K., 1991; p 282.

(20) Dake, S. B.; Chaudhari, R. V. *J. Chem. Eng. Data* **1985**, *30*, 400.

detection mode, 2000 scans accumulated over a spectral width of 25 kHz with 16K data points. A relaxation delay of 10 s was set between each pulse.

The reaction between $[Ru(H_2O)_6]^{2+}$ (0.098 mol kg^{-1}) and an excess of acetonitrile (0.393 mol kg^{-1}) was followed by ^{1}H NMR at 297.8 K in a solution of tosylic acid (0.099 mol kg^{-1}) in D_2O. The same spectrometer and the same parameters as for the Me_2SO exchange were used (vide supra).

For all the kinetics performed at ambient pressure, the temperature was measured by a substitution technique using a 100-Ω Pt resistor.[21] The kinetic analysis were accomplished by a nonlinear least-squares fitting program. When differential equations were used, the mole fractions were calculated by integrating numerically the equations using the fourth-order Runge−Kutta method. The typical estimated precision of the individual rate constants is 1−2% for the NMR measurements.

Results

Reactivity of $[Ru(H_2O)_6]^{2+}$ with $H_2C{=}CH_2$ in Water. For the first time, we report here a complete mechanistic study followed by NMR of a reaction between an aquacomplex and a dissolved gas under pressure. The reaction between the hexaaquacomplex of ruthenium(II) and ethylene is of particular interest since $[Ru(H_2O)_6]^{2+}$ is involved in numerous processes leading to the polymerization or isomerization of olefins.[9,22,23] In the present study, we have followed by ^{1}H NMR the reaction of $[Ru(H_2O)_6]^{2+}$ with ethylene at temperatures between 296 and 325 K, and ethylene pressures between 1 and 40 MPa. To ensure a constant ethylene concentration, the solution and the pressurized gas were vigorously mixed during the reaction. The mono-complex, $[Ru(H_2O)_5(C_2H_4)]^{2+}$, and the bis-complex, *cis*-$[Ru(H_2O)_4(C_2H_4)_2]^{2+}$, were characterized by ^{1}H, ^{13}C, and ^{17}O NMR in an earlier paper.[9]

For gas pressures lower than 4 MPa, the reaction was slow compared to the time needed to acquire a spectrum. In this case the concentration of ethylene was directly measured on the ^{1}H NMR spectra by integrating the signal of free ethylene at 5.04 ppm, and comparing this value to the integral of the methyl of the tosylate anion, whose concentration was known by weighing. For gas pressures higher than 4 MPa, the reaction between Ru^{II}(aq) and ethylene is too fast to allow the accurate measurement of the gas concentration in the solution from the integral of the NMR signals. Therefore, the concentration of dissolved ethylene was calculated using eq 1.

The first step of the reaction between $[Ru(H_2O)_6]^{2+}$ and ethylene is represented by eq 2.

$$[Ru(H_2O)_6]^{2+} + C_2H_4 \xrightarrow{k_f} [Ru(H_2O)_5(C_2H_4)]^{2+} + H_2O \qquad (2)$$

As the bis-complex formation is slow compared to the mono-complex formation the second step was neglected in the analysis. Under pseudo-first-order conditions, and with 0 as initial concentration of the mono-complex, the variation of the integral of the ^{1}H NMR signal of bound ethylene in $[Ru(H_2O)_5(C_2H_4)]^{2+}$ as a function of time, I(RuL), can be expressed by eq 3

$$I(\mathrm{RuL}) = I(\mathrm{RuL})_\infty(1 - \exp(k_{\mathrm{obs,f}}t)) \qquad (3)$$

where $I(\mathrm{RuL})_\infty$ is the integral at the end of the reaction and $k_{\mathrm{obs,f}}$ the observed pseudo-first-order rate constant.

$k_{\mathrm{obs,f}}$ was obtained by a nonlinear least-squares fitting program using eq 3 with $I(\mathrm{RuL})_\infty$ and $k_{\mathrm{obs,f}}$ as adjustable parameters. An example fit is shown in Figure 1a. $k_{\mathrm{obs,f}}$ is a linear function of ethylene concentration (Figure 1b). Values of the second-order rate constant for the mono-complex formation, $k_f = k_{\mathrm{obs,f}}/[C_2H_4]$ are reported in Table S1 of the Supporting Information. $\Delta H_f^‡$ and $\Delta S_f^‡$ (Table 1) were obtained by fitting k_f to the Eyring equation.

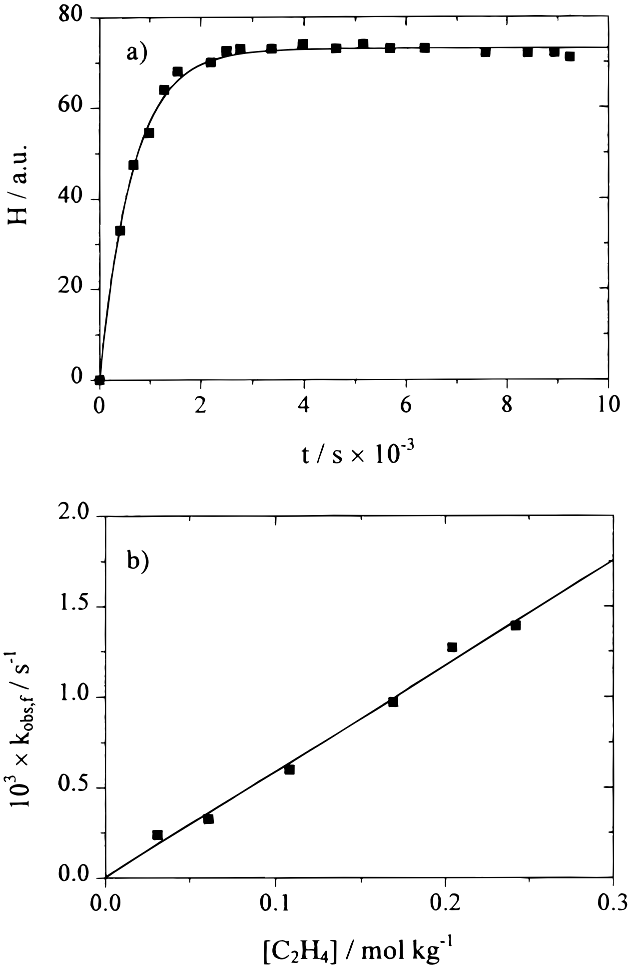


Figure 1. (a) Mono-complex formation reaction between $[Ru(H_2O)_6]^{2+}$ and $H_2C{=}CH_2$ in water: evolution as a function of time, at 319 K, of the height of the ^{1}H NMR signal of bound $H_2C{=}CH_2$ in $[Ru(H_2O)_5(H_2C{=}CH_2)]^{2+}$ after mixing a solution of $[Ru(H_2O)_6]^{2+}$ 0.10 mol kg^{-1} with $H_2C{=}CH_2$ at 10 MPa (corresponding to a concentration of 0.16 mol kg^{-1} of free dissolved ethylene). (b) Dependence of the observed first-order mono-complex rate constant, $k_{\mathrm{obs,f}}$, as a function of the concentration of free dissolved ethylene at 317 K. The different $H_2C{=}CH_2$ concentrations correspond to gas pressures from 1.1 to 39.8 MPa; $[Ru(H_2O)_6]^{2+}$ = 0.1 mol kg^{-1}, [Htos] = 0.1 mol kg^{-1}.

The bis-complex formation reaction between $[Ru(H_2O)_5(C_2H_4)]^{2+}$ and ethylene was also followed by ^{1}H NMR (eq 4).

$$[Ru(H_2O)_5(C_2H_4)]^{2+} + C_2H_4 \xrightarrow{k_{\mathrm{cis}}} cis\text{-}[Ru(H_2O)_4(C_2H_4)_2]^{2+} + H_2O \qquad (4)$$

The variation of the integral of the ^{1}H NMR signal of bound ethylene in *cis*-$[Ru(H_2O)_4(C_2H_4)_2]^{2+}$ as a function of time, $I(\mathrm{RuL_2})$, can be expressed by eq 5

$$I(\mathrm{RuL_2}) = I(\mathrm{RuL_2})_\infty\left(1 - \frac{k_{\mathrm{obs,cis}}\exp(-k_{\mathrm{obs,f}}t) - k_{\mathrm{obs,f}}\exp(-k_{\mathrm{obs,cis}}t)}{k_{\mathrm{obs,cis}} - k_{\mathrm{obs,f}}}\right) \qquad (5)$$

---

[21] Ammann, C.; Meier, P. F.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319.

[22] Karlen, T.; Ludi, A. *Helv. Chim. Acta* **1992**, *75*, 1604.

[23] McGrath, D. V.; Grubbs, R. H. *Organometallics* **1994**, *13*, 224.

Table 1. Reaction of $[Ru(H_2O)_6]^{2+}$ with Ethylene: Second-Order Rate Constants, k_f and k_{cis}, and Activation Parameters for the Reactions of Formation of $[Ru(H_2O)_5(H_2C{=}CH_2)]^{2+}$ and *cis*-$[Ru(H_2O)_4(H_2C{=}CH_2)_2]^{2+}$

$[Ru(H_2O)_5(H_2C{=}CH_2)]^{2+\ a}$		*cis*-$[Ru(H_2O)_4(H_2C{=}CH_2)_2]^{2+\ b}$	
k_f^{298}/kg mol^{-1} s^{-1}	$(1.22 \pm 0.06) \times 10^{-3}$	k_{cis}^{298}/kg mol^{-1} s^{-1}	$(6.9 \pm 1.0) \times 10^{-6}$
$\Delta H_f^{\ddagger}$/kJ mol^{-1}	76.9 ± 2	$\Delta H_{cis}^{\ddagger}$/kJ mol^{-1}	129.9 ± 4
$\Delta S_f^{\ddagger}$/J K^{-1} mol^{-1}	-42.9 ± 8	$\Delta S_{cis}^{\ddagger}$/J K^{-1} mol^{-1}	$+92.0 \pm 11$

where $I(RuL_2)_\infty$ is the integral at the end of the reaction and $k_{obs,cis}$ the observed pseudo-first-order rate constant for the second step. $k_{obs,cis}$ was calculated using eq 5 with $I(RuL_2)_\infty$ and $k_{obs,cis}$ as adjustable parameters; $k_{obs,f}$ was fixed using the activation parameters obtained above. The values of $k_{obs,cis}$ obtained at different temperatures, and the corresponding k_{cis} values, $k_{cis} = k_{obs,cis}/[C_2H_4]$, are reported in the Supporting Information. $\Delta H_{cis}^{\ddagger}$ and $\Delta S_{cis}^{\ddagger}$ (Table 1) were obtained by fitting k_{cis} to the Eyring equation.

During the formation of the mono and bis ethylene complexes, no other ruthenium species could be detected in the ^{1}H, ^{17}O, and ^{13}C NMR spectra. Nevertheless, when a pressure of deuterated ethylene ($D_2C{=}CD_2$) was applied to an aqueous solution of $[Ru(H_2O)_5(H_2C{=}CH_2)]^{2+}$, the signal of coordinated ethylene was progressively decreasing, and the signal of the free gas was simultaneously increasing. As no other species could be detected in the spectra during this process, we have attributed these changes to an exchange between coordinated and free ethylene (eq 6).

$$[Ru(H_2O)_5(H_2C{=}CH_2)]^{2+} + D_2C{=}CD_2 \overset{k_L}{\rightleftarrows} [Ru(H_2O)_5(D_2C{=}CD_2)]^{2+} + H_2C{=}CH_2 \quad (6)$$

This exchange was much faster than the formation of the *cis*-bis-complex. Consequently, this latter reaction was not considered in the mathematical treatment of the exchange (vide infra). The rate law corresponding to eq 6 is expressed by eq 7,

$$\frac{d[RuL]}{dt} = -k_L[RuL][{*}L] + k_L[Ru{*}L][L] \quad (7)$$

where L and *L represent ethylene containing four protons and four deuteriums, respectively. Experiments have shown that in the absence of agitation the diffusion of gas between the two phases is slower than the time scale of the ligand exchange. Consequently, in the mathematical treatment of eq 7, we have neglected any exchange between the liquid and the gaseous phases (see Figure S2 of the Supporting Information). With this approximation, the total concentrations of metal, C_{Ru}, and ligand, C_L, in the solution are constant and can be introduced in eq 7 leading to eq 8.

$$\frac{d[RuL]}{dt} = k_L(C_{Ru}[L] - C_L[RuL]) \quad (8)$$

If we divide both sides by the total concentration of protonated ethylene in solution ([L] + [RuL]), we obtain an expression for the mole fraction of coordinated protonated ethylene, x_c (eq 9), that can be easily integrated (eq 10).

$$\frac{dx_c}{dt} = k_L(C_{Ru} - x_c(C_{Ru} + C_L)) \quad (9)$$

$$x_c = \frac{1}{C_{Ru} + C_L}\{C_{Ru} - (C_{Ru} - (C_{Ru} + C_L)x_c(0)) \times \exp[-k_L t(C_{Ru} + C_L)]\} \quad (10)$$

This analytical expression was fitted to the experimental mole fractions calculated from the integrals of the ^{1}H NMR signals of free and coordinated ethylene. During the fit $x_c(0)$, the mole fraction of coordinated ethylene at $t = 0$, k_L and C_L were treated as adjustable parameters (Figure S2). The following results were obtained: $k_L^{298.2} = (1.08 \pm 0.02) \times 10^{-2}$ kg mol^{-1} s^{-1} and $C_L = 0.0955 \pm 0.0008$ mol kg^{-1}.

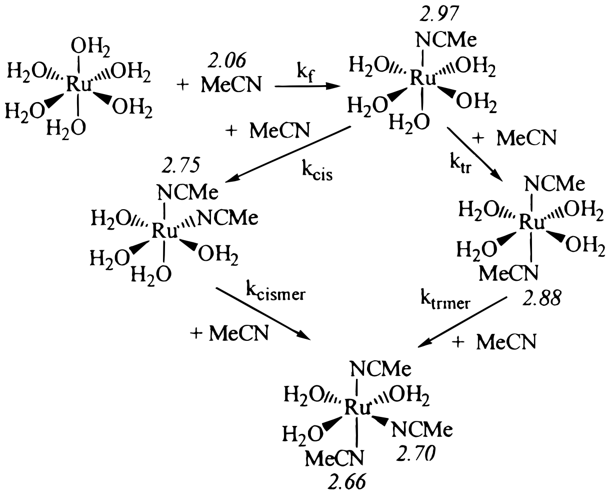
Reactivity of $[Ru(H_2O)_5Me_2SO]^{2+}$ with Me_2SO. The mono-complex formation reaction between $[Ru(H_2O)_6]^{2+}$ and Me_2SO has already been reported[13] but not the ligand exchange or the bis-complex formation. By mixing aqueous $[Ru(H_2O)_5(Me_2SO\text{-}\eta_6)]^2$ and $Me_2SO\text{-}d_6$ at 278.5 K, we first observed in the ^{1}H NMR spectra a decrease of the signal of bound $Me_2SO\text{-}\eta_6$ (at 3.55 ppm) and a simultaneous increase of the signal of free $Me_2SO\text{-}\eta_6$ (2.70 ppm) which showed that a chemical exchange between the two sites took place. No other signal appeared during the exchange reaction and the sum of the integrals of these two signals remained constant throughout the experiment, indicating that no other reaction took place during the exchange process. The experimental mole fractions of coordinated $Me_2SO\text{-}\eta_6$ were fitted by eq 10 with k_L and $x_c(0)$ as adjustable parameters (Figure S3, Supporting Information). The following rate constant was obtained: $k_L^{278.5} = (3.45 \pm 0.02) \times 10^{-4}$ kg mol^{-1} s^{-1}.

The same solution was then heated at 321.6 K, and a new signal assigned to the *cis*-bis-complex (vide infra) appeared at 3.36 ppm in the spectra with the concomitant decrease of the signals at 3.55 and 2.70 ppm (eq 11). The variation as a function of time of the mole fractions of these three species was analyzed kinetically giving $k_{cis}^{321.6} = (1.85 \pm 0.02) \times 10^{-5}$ kg mol^{-1} s^{-1}. The mathematical treatment and the fit is shown in the Supporting Information (Figure S4). This rate constant measured at 321.6 K is 30 times smaller than the rate constant for the exchange of Me_2SO measured at 278.5 K. At the same temperature, the two rate constants would probably differ by at least 2 orders of magnitude, which confirms the approximation made above, i.e., the formation of the bis-complex was not significant during the ligand exchange process and could be neglected.

$$[Ru(H_2O)_5Me_2SO]^{2+} + Me_2SO \xrightarrow{k_{cis}} cis\text{-}[Ru(H_2O)_4(Me_2SO)_2]^{2+} + H_2O \quad (11)$$

To check the nature of the complex formed at 3.36 ppm, we added water enriched in oxygen-17 to the solution and waited until no more changes could be observed in the ^{17}O NMR spectra. Immediately upon the addition of enriched water, a peak at −66 ppm appeared followed by the slow appearance of a second peak at −150 ppm. These two peaks were the only ones present beside the huge solvent peak. After 2 days at 321.6 K, the signal at −150 ppm stopped growing. During this period, no change could be observed in the ^{1}H NMR spectra. At equilibrium, the ratio of the integrals of the peaks at −150 and −66 ppm was one within experimental errors as expected for the *cis*-$[Ru(H_2O)_4(Me_2SO)_2]^{2+}$ complex (only one peak would have been expected for the trans complex).

Scheme 1. Complexes Formed During the Reaction of $[Ru(H_2O)_6]^{2+}$ with an Excess Acetonitrile (Ratio 1:4)[a]



[a] The numbers are the ^{1}H NMR chemical shifts of the corresponding acetonitrile.

Exchange of CO on $[Ru(H_2O)_5CO]^{2+}$. When a pressure of 5.4 MPa of ^{12}CO is applied to a solution of $[Ru(H_2O)_5{}^{13}CO]^{2+}$ 0.01 mol kg^{-1} in D_2O, we observe a very slow decrease of the ^{13}C NMR signal of bound CO at 205.5 ppm. The half-life of the reaction was more than 1 day. In this case, the ^{13}CO diffusion between the liquid and gaseous phases could not be neglected, and the total concentration of ^{13}CO (free and bound) in solution is no longer constant throughout the reaction. Nevertheless, taking into account the diffusion processes, we assumed in our case (5.4 MPa pressure of ^{12}CO), that the concentration of free ^{13}CO in solution is always negligible compared to the concentration of free ^{12}CO. This hypothesis is perfectly valid even after several half-lives. Thus, eq 8 (where RuL represents the enriched complex $Ru^{13}CO$, which is the NMR active species) can be simplified (eq 12)

$$\frac{d[RuL]}{dt} = -k_L[RuL]C_L \qquad (12)$$

and easily integrated (eq 13),

$$[RuL] = fH_{RuL}(t) = [RuL]_0 \exp(-k_L C_L t) = fH_{RuL}(0) \exp(-k_L C_L t) \qquad (13)$$

where $H_{RuL}(0)$ and H_{RuL} are the heights of the ^{13}C NMR signal of bound CO at $t = 0$ and at sampling time respectively, and f the proportionality factor between the height and the concentration. Equation 13 was fitted to the experimental heights with k_L and $H_{RuL}(0)$ as adjustable parameters and using a value of 0.053 mol kg^{-1} for C_L (Figure S5 of the Supporting Information). The following rate constant was obtained: $k_L^{298.3} = (5.2 \pm 0.2) \times 10^{-5}$ kg mol^{-1} s^{-1}.

Reactivity of $[Ru(H_2O)_6]^{2+}$ with Acetonitrile. The reactivity of $[Ru(H_2O)_6]^{2+}$ with an excess of acetonitrile is different from the previous cases of this study. Concomitant with the decrease of the signal of free acetonitrile (Scheme 1), we observed first in the ^{1}H NMR spectra the increase of the signal at 2.97 ppm attributed to $[Ru(H_2O)_5MeCN]^{2+}$,[13] followed by the appearance of two new signals at 2.88 and 2.75 ppm. As the trans water molecule was shown to be more labile than the cis water in $[Ru(H_2O)_5MeCN]^{2+}$,[14] we attributed the signal at 2.88 ppm which appeared first to the *trans*- and the one at 2.75 ppm to the *cis*-$[Ru(H_2O)_4(MeCN)_2]^{2+}$. Finally, two other signals appeared in the spectra at 2.70 and 2.66 ppm. The ratio of the integrals of these two peaks was always equal to two throughout the reaction and within experimental errors. Consequently, we attributed these two latter signals to the complex *mer*-$[Ru(H_2O)_3(MeCN)_3]^{2+}$, where two trans acetonitrile molecules are equivalent and the third one is different. It appears that the chemical shift decreases with the number of acetonitrile coordinated to the metal. By comparison, the chemical shift of $[Ru(MeCN)_6]^{2+}$ in acetonitrile was found at 2.59 ppm.[24] An example of a spectrum is given in Figure S6 of the Supporting Information.

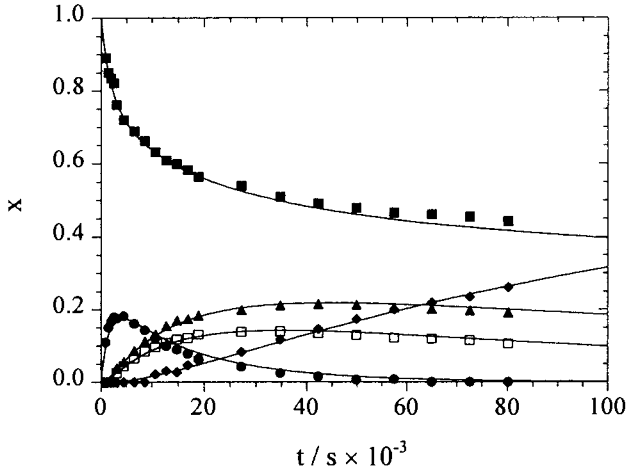


Figure 2. Reaction of $[Ru(H_2O)_6]^{2+}$ with an excess acetonitrile in D_2O at 297.8 K: evolution as a function of time of the mole fractions of free acetonitrile (■), $[Ru(H_2O)_5MeCN]^{2+}$ (●), *trans*-$[Ru(H_2O)_4(MeCN)_2]^{2+}$ (▲), *cis*-$[Ru(H_2O)_4(MeCN)_2]^{2+}$ (□), and *mer*-$[Ru(H_2O)_3(MeCN)_3]^{2+}$ (◆) in a solution containing initially Htos (0.099 mol kg^{-1}), Ru(II) (0.098 mol kg^{-1}), and MeCN (0.393 mol kg^{-1}).

These pathways are supported by the fact that the sum of the integrals of the signals of the different acetonitrile species in Scheme 1 is constant to within 5%, indicating that no other species has a significant concentration during the reaction. This statement was translated mathematically (eqs 14 and 15),

$$C_L = [L] + [ML] + 2[trans\text{-}ML_2] + 2[cis\text{-}ML_2] + 3[mer\text{-}ML_3] \qquad (14)$$

$$C_M = [M] + [ML] + [trans\text{-}ML_2] + [cis\text{-}ML_2] + [mer\text{-}ML_3] \qquad (15)$$

where C_L and C_M are the initial concentrations of ligand and metal, respectively. The resulting rate laws describing the variation of the different species shown in Scheme 1 are listed in eqs 16−20.

$$d[L]/dt = -k_f[L][M] - k_{tr}[L][ML] - k_{cis}[L][ML] - k_{trmer}[L][trans\text{-}ML_2] - k_{cismer}[L][cis\text{-}ML_2] \qquad (16)$$

$$d[ML]/dt = k_f[L][M] - (k_{tr} + k_{cis})[L][ML] \qquad (17)$$

$$d[trans\text{-}ML_2]/dt = k_{tr}[L][ML] - k_{trmer}[L][trans\text{-}ML_2] \qquad (18)$$

$$d[cis\text{-}ML_2]/dt = k_{cis}[L][ML] - k_{cismer}[L][cis\text{-}ML_2] \qquad (19)$$

$$d[mer\text{-}ML_3]/dt = k_{trmer}[L][trans\text{-}ML_2] + k_{cismer}[L][cis\text{-}ML_2] \qquad (20)$$

---

(24) Rapaport, I.; Helm, L.; Merbach, A. E.; Bernhard, P.; Ludi, A. *Inorg. Chem.* **1988**, *27*, 873.

Table 2. Second-Order Rate Constants (in kg mol^{-1} s^{-1}) for the Formation of the Complexes with the General Formula $[Ru(H_2O)_{6-n}(MeCN)_n]^{2+}$ (n = 1, 2, 3), Produced at 297.8 K, in D_2O, by the Reaction between $[Ru(H_2O)_6]^{2+}$ and an Excess of Acetonitrile (1:4)

k_f	$(1.63 \pm 0.06) \times 10^{-3}$
k_{tr}	$(1.50 \pm 0.04) \times 10^{-4}$
k_{cis}	$(1.11 \pm 0.04) \times 10^{-4}$
k_{trmer}	$(2.85 \pm 0.3) \times 10^{-5}$
k_{cismer}	$(5.09 \pm 0.4) \times 10^{-5}$

We can divide all these expressions by C_L to obtain the variation of the mole fractions as a function of time. Combining thereafter eqs 14–20 yields eqs 21–25.

$$\frac{dx_L}{dt} = -C_L x_L \left\{ k_f \left(\frac{C_M}{C_L} - x_{ML} - \frac{x_{trans-ML_2} + x_{cis-ML_2}}{2} - \frac{x_{mer-ML_3}}{3} \right) + (k_{tr} + k_{cis}) x_{ML} + k_{trmer} \frac{x_{trans-ML_2}}{2} + k_{cismer} \frac{x_{cis-ML_2}}{2} \right\} \quad (21)$$

$$\frac{dx_{ML}}{dt} = C_L x_L \left\{ k_f \left(\frac{C_M}{C_L} - x_{ML} - \frac{x_{trans-ML_2} + x_{cis-ML_2}}{2} - \frac{x_{mer-ML_3}}{3} \right) - (k_{tr} + k_{cis}) x_{ML} \right\} \quad (22)$$

$$\frac{dx_{trans-ML_2}}{dt} = C_L x_L \{ 2k_{tr} x_{ML} - k_{trmer} x_{trans-ML_2} \} \quad (23)$$

$$\frac{dx_{cis-ML_2}}{dt} = C_L x_L \{ 2k_{cis} x_{ML} - k_{cismer} x_{cis-ML_2} \} \quad (24)$$

$$\frac{dx_{mer-ML_3}}{dt} = {}^3/_2 C_L x_L \{ k_{trmer} x_{trans-ML_2} + k_{cismer} x_{cis-ML_2} \} \quad (25)$$

These analytical expressions were fitted to the experimental mole fractions (Figure 2) and the obtained rate constants are reported in Table 2. All the experimental mole fractions used for the fit and the corresponding calculated mole fractions are reported in Table S2 of the Supporting Information.

Discussion

Procedure To Compare Water Exchange with Complex Formation Rates in the Case of an I_d Mechanism. In previous mechanistic or kinetic studies on ruthenium(II) aqua-complexes, the dissociative character of the substitution reactions was demonstrated. For example, the rates of mono-complex formation reactions between $[Ru(H_2O)_6]^{2+}$ and various ligands were independent of the nature of the incoming ligand (Table 3).[13] More recently, the exchange rates of both types of water molecules in $[Ru(H_2O)_5(H_2C{=}CH_2)]^{2+}$ were determined.[14] It was shown that ethylene greatly labilized the axial water molecule ($k_{ax}^{298} = 2.9$ s^{-1}) and greatly decreased the reactivity of the four equatorial water molecules ($k_{eq}^{298} = 2.8 \times 10^{-4}$ s^{-1}) compared to the exchange on the hexa-aquacomplex ($k_{ex}^{298} = 1.8 \times 10^{-2}$ s^{-1}). Despite this large difference of reactivity, similar and positive activation volumes for the exchange of both types of water molecules ($\Delta V_{ex}^{\ddagger}$/cm^{3}mol^{-1} = +6.1 and +6.5 for the equatorial and axial positions, respectively) were obtained.

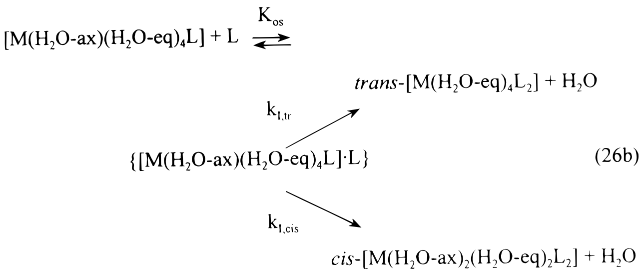
Table 3. Reaction between $[Ru(H_2O)_6]^{2+}$ and Neutral Monodentate Ligands: Second-Order Mono-Complex Formation Rate Constants, k_f, and First-Order Rate Constants, k_I', Obtained Using Eq 28 with the Values K_{os} = 0.16 mol kg^{-1}, n_c = 6, and f = 12

ligand	$10^3 \times k_f^{298\ a}$ (kg mol^{-1} s^{-1})	$10^3 \times k_I'^{,298}$ (s^{-1})
H_2O	–	18[b]
MeCN	2.07	26
Me_2SO	1.31	16
1,4-thioxane	2.2	28
tetrahydrothiophene	2.4	30
maleic acid	2.18	27
fumaric acid	1.72	22
2,5-dihydrofuran	1.06	13
$H_2C{=}CH_2$	1.22[c]	15

[a] Reference 13 and refs therein. [b] Rate constant for the exchange of a particular water molecule (ref 24). [c] This work.

In the following discussion, and based on the previous studies mentioned above, we will assume that an I_d mechanism operates. In this case, the second order complex formation rate constant, k, cannot be directly compared to the first-order water exchange rate, k_{ex}. To get comparable values, we need to use the Eigen–Wilkins model[25] which describes the substitution mechanism on octahedral complexes. This model is shown in eqs 26a and 26b for the substitution on a homoleptic hexa-aquacomplex and on a mono-complex, respectively. It is worth mentioning that, in the latter case, the substitution can take place on two distinct sites, leading to two different products, the *cis*- and *trans*-complexes. According to the Eigen–Wilkins model, the complex formation is divided into two consecutive steps. The first one is the of formation of an outer-sphere complex where the ligand, L, occupies one of the available sites in the second coordination sphere and is quantified by the equilibrium constant K_{os}. The second step, rate determining, is the exchange of ligands between the first and the second coordination spheres and is described by the first-order rate constant, k_I. For dilute solutions of L eq 27 applies.

$$[M(H_2O)_6] + L \overset{K_{os}}{\rightleftharpoons} \{[M(H_2O)_6]\cdot L\} \xrightarrow{k_{I,f}} [M(H_2O)_5L]^1 + H_2O \quad (26a)$$



(26b)

$$k_I = k/K_{os} \quad (27)$$

k_I, as obtained from eq 27, cannot be directly compared to the water exchange rate constant, k_{ex}, for two distinct reasons. First, because there is a fundamental difference in the definition of these two constants. k_I is the rate of replacement by L of any of the n_c water molecules coordinated in a distinct coordination site, but k_{ex} defines the rate of replacement of one particular water molecule. This difference, resulting purely from the definition of the two rate constants, has been extensively

---

(25) Eigen, M.; Tamm, K. *Z. Elektrochem.* **1962**, *66*, 93.

discussed in a recent review.[26] To compensate for the different definitions of the two constants, we must multiply k_{ex} by the number of coordinated water, n_c. For example, for the reactions on a mono-complex, n_c is equal to 4 for the substitution of an equatorial water molecule, and equal to 1, for the substitution of an axial water.

The second reason for the difference between the two constants is purely statistical. In the Eigen−Wilkins mechanism, it is considered that the molecule leaving the first coordination sphere is replaced by a molecule of the second coordination sphere. If the solvent is the only species present in the second shell, the probability that the leaving molecule is replaced by a molecule of solvent is one. This is the situation when the water exchange reactions are studied in the absence of other coordinating ligand present in the solution. During the complex formation reaction between a metal center and L, the situation is different. If there are f molecules in the second coordination sphere, L occupies one and only one of these f sites according to the Eigen−Wilkins model. For a dissociative interchange mechanism there is no discrimination between incoming ligands, the probability that the leaving molecule is replaced by L is therefore $1/f$. Consequently, to compare the exchange reaction with the complex formation, k_I must be multiplied by f.

Several models were suggested to estimate the value of f. In a first approach the second shell was viewed as a compact arrangement around the ligands of the first shell. In this model presented for the first time by Taube and co-workers,[27] eight molecules occupy the eight faces of an octahedron and are in the position of closest approach of the metal center. This is the location where the electrostatic field produced by the metal beyond the first coordination sphere is the most intense.

This picture of a second coordination sphere made of eight water molecules located at the eight faces of the octahedron has been questioned since by several authors. Several experimental studies have shown that the second shell of some trivalent metal cations such as $[Al(H_2O)_6]^{3+}$ [28] and $[Cr(H_2O)_6]^{3+}$ [29] consisted of twelve water molecules. A value of 13 ± 1 was also reported for $[Rh(H_2O)_6]^{3+}$.[30] More recently, molecular dynamics calculations on the $[Cr(H_2O)_6]^{3+}$ system have evidenced strong hydrogen binding resulting from polarization of first coordination sphere water molecules which led to a mean coordination number of 12.9 waters in the second shell.[31]

These studies have shown that the residence time of a water molecule in the second coordination sphere was very short ($<5 \times 10^9\ s^{-1}$).[31] This time is probably even shorter in the case of divalent cations. In this case, the structure of the second coordination sphere does not seem so well defined as shown by a review of the different results obtained by X-ray diffraction.[32] This difficulty to define accurately the second coordination sphere structure resulted probably from the weaker polarization of the water molecule in the first shell which leads to a less ordered second coordination sphere. Nevertheless, despite this difference between di- and trivalent cations, it seems reasonable to consider a second coordination sphere made of twelve water molecules, even in the case of divalent cations. Based on this hypothesis, the probability factor, $1/f$ (vide supra), for a water molecule leaving the first shell to be replaced by L is 1/12. Consequently, taking into account the Eigen−Wilkins model, the different definitions of the rate constants and the probability factor discussed above, eq 28

$$k_I' = \frac{k}{K_{os}} f \frac{1}{n_c} = k_I f \frac{1}{n_c} = k_I\, 12\, \frac{1}{n_c} \qquad (28)$$

must be applied to transform the rate constant of complex formation, k, into the first-order rate constant, k_I', which can be directly compared to the water exchange rate constant, k_{ex}.

It is important to mention that when the exchange takes place on an hexa-aquaion like $[Ru(H_2O)_6]^{2+}$, n_c is equal to 6. The ratio f/n_c is thus equal to 2 considering twelve water molecules in the second shell, or equal to $^4/_3$ if the previous model assuming eight water molecules in the second coordination sphere is taken into account.[33] This latter correction factor is smaller than the error on the calculated K_{os} values and was thus very often neglected.[34] But when we want to compare the exchange rate of the trans water molecule in $[Ru(H_2O)_5L]^{2+}$, with the rate of formation of the *trans*-$[Ru(H_2O)_4L_2]^{2+}$ complex, n_c is equal to 1 and the ratio f/n_c is 12 using our model. This is a 1 order of magnitude correction that cannot be neglected anymore.

Reactivity of $[Ru(H_2O)_6]^{2+}$ with Neutral Monodentate Ligands. The second-order rate constants, k_f, obtained for the mono-complex formation reaction between $[Ru(H_2O)_6]^{2+}$ and neutral monodentate ligands are reported in Table 3. Equation 28 was applied to these data to obtain the corresponding k_I' values. For the calculation of k_I', we have taken the K_{os} values calculated using the Fuoss equation[35] for complex formation reactions of $[Ni(H_2O)_6]^{2+}$.[36] As Ni(II) and Ru(II) have similar ionic radii and identical charges, the K_{os} should not differ too widely for the two cations. The rate constant calculated for the reaction with ethylene ($k_f^{298} = 1.22 \times 10^{-3}$ kg s^{-1} mol^{-1}) is also reported. We can see in Table 3, that all the k_I' values are very similar. They are all equal to the water exchange rate constant, within experimental errors. The large difference of nucleophilicity among the ligands used for this comparison is to be emphasized. On one side, ethylene is a soft base whose bond to ruthenium is constituted of a σ-donation and a π-backbonding component,[14] and on the other side, water, is a hard base, whose bond has only a σ component. Despite this large difference of nucleophilicity and binding mode, the mono-complex formation reactions take place at the same rate for both ligands. This confirms thus the mechanistic assignment, i.e., an interchange dissociative, I_d, mechanism where the rate-determining step is the dissociation of the Ru−OH$_2$ bond.

Bis-Complex Formation between $[Ru(H_2O)_5L]^{2+}$ Type Complexes and L. The rate constants for the formation of trans-, k_{tr}, and *cis*-bis-complex, k_{cis}, are reported in Table 4, as well as the corresponding k_I' values obtained using eq 28. For the outer-sphere equilibrium constant, K_{os}, and the number of water molecules in the second coordination sphere, f, we have taken the same values as for the mono-complex formation reactions, i.e., 0.16 mol kg^{-1} and 12, respectively. For the formation of the *trans*-bis-complex, n_c is of course equal to 1 and for the formation of the *cis*-bis-complex, n_c is equal to 4 (eq 26b). The comparison between the k_{ex} and the k_I' values

---

(26) Lincoln, S. F.; Merbach, A. E. *Adv. Inorg. Chem.* **1995**, *42*, 1.

(27) Olson, M.; Kanazawa, Y.; Taube, H. *J. Chem. Phys.* **1969**, *51*, 289.

(28) Akitt, J. *J. Chem. Soc., Dalton Trans.* **1973**, 1177.

(29) Caminiti, R.; Licheri, G.; Piccaluga, G.; Pinna, G. *J. Chem. Phys.* **1976**, *65*, 3134.

(30) Read, M. C.; Sandstrom, M. *Acta Chem. Scand.* **1992**, *46*, 1177.

(31) Bleuzen, A.; Foglia, F.; Furet, E.; Helm, L.; Merbach, A. E.; Weber, J. *J. Am. Chem. Soc.* **1996**, *118*, 12777.

(32) Ohtaki, H.; Radnai, T. *Chem. Rev.* **1993**, *93*, 1157.

(33) Neely, J.; Connick, R. *J. Am. Chem. Soc.* **1970**, *92*, 3476.

(34) Burgess, J. *Ions in Solution*; Ellis Horwood Limited: Chichester, U.K., 1988; Chapter 10.

(35) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

(36) Burgess, J. *Metal Ions in Solution*; Ellis Horwood Limited: Chichester, U.K., 1978; Chapter 12 and references therein.

Table 4. Comparison between the Water Exchange Rate Constants, k_{ex}, the Ligand Exchange Rate Constants, k_L, and the Bis-Complex Formation Rate Constants, k, Determined on $[Ru(H_2O)_5L]^{2+}$ Type Complexes; k_I' Values Were Calculated from the k or k_L Values Using Eq 28 with $K_{os} = 0.16$, $f = 12$, and $n_c = 4$ or 1 for the Substitution on Equatorial or Axial Positions, Respectively

ligand	$H_2C{=}CH_2$		MeCN		Me_2SO		CO
site	axial	equat	axial	equat	axial	equat	axial
T/K	298.2	298.1	298.1	298.1	278.5	321.6	298.3
$10^3 \times k$/kg mol^{-1} s^{-1} [a]	–	0.007	0.15	0.11	–	0.019	–
$10^3 \times k_L$/kg mol^{-1} s^{-1}	10.8	–	–	–	0.35	–	0.052
$10^3 \times k_I'$/s^{-1}	1600	0.13	11	2.1	53	0.36	7.5
$10^3 \times k_{ex}$/s^{-1} [b]	2900	0.28	7.2	1.5	68	0.56	3.8[c]
k_I'/k_{ex}	0.6	0.5	1.5	1.4	0.8	0.6	–

[a] $k = k_{cis}$ or k_{tr} for the formation of *cis*- or *trans*-bis-complex, respectively. [b] $k_{ex} = k_{ax}$ or k_{eq} depending on the coordination site (ref 14). [c] 279.4 K.

will be discussed later, but in order to include the ligand exchange reaction (eq 29), we need first to discuss this pathway.

$$[Ru(H_2O)_5L]^{2+} + {}^*L \overset{k_L}{\rightleftharpoons} [Ru(H_2O)_5{}^*L]^{2+} + L \qquad (29)$$

The $[Ru(H_2O)_5(H_2C{=}CH_2)]^{2+}$ and $[Ru(H_2O)_5CO]^{2+}$ complexes were found to be stable in solution for several weeks at ambient pressure.[8,9] Moreover, functional density calculations performed on these two complexes have shown that the Ru–L bond was more stable than the cis and trans Ru–H_2O bonds of the complex.[14] Consequently, a ligand exchange reaction pathway where the first step is the dissociation of the Ru–L bond is to be ruled out. This is confirmed by the fact that no departure of L is observed in the ^{1}H, ^{17}O, and ^{13}C NMR spectra upon dissolution of the mono-complexes in water. If a dissociation of the Ru-L bond occurred, the liberated gas (CO or $H_2C{=}CH_2$) would diffuse out of the solution and substantial amount of $[Ru(H_2O)_6]^{2+}$ complex would form and be detected in the ^{17}O NMR spectra. Moreover, as the exchange of L (eq 29) is much faster than the exchange of the equatorial water molecules, we can also admit that these water molecules are not involved in the mechanism.

The other possibility is a pathway where the first step is the dissociation of the Ru–H_2O_{ax} bond (I_d or D). The leaving water molecule can be substituted by *L which leads to the formation of a *trans*-$[Ru(H_2O)_4L{}^*L]^{2+}$ intermediate (eq 30). The latter can either loose L* to give back the initial reactant, or loose L to give the product where L is replaced by *L. In other words, the rate of formation of the final product $[Ru(H_2O)_5{}^*L]^{2+}$, described by the rate constant k_L, is twice slower than the rate of formation of the *trans*-bis-complex intermediate. Consequently, we must multiply k_L by two to obtain the rate constant for the formation of the trans bis-complex intermediate, k_{tr}. Then, by introducing $k_{tr} = 2k_L$ into eq 28, the corresponding k_I' are obtained (Table 4). These values can now be directly compared to the rate constants for the exchange of the axial water molecule in the corresponding complex.

$$\begin{tikzcd}
& \textit{trans}\text{-}[Ru(H_2O)_4L{}^*L] + H_2O \arrow[dl, shift left] \arrow[dr, shift left, "k_{tr}"] & \\
{[Ru(H_2O\text{-}\mathit{eq})_4(H_2O\text{-}\mathit{ax})L] + {}^*L} \arrow[ur, shift left, "k_{tr}"] & & {[Ru(H_2O\text{-}\mathit{eq})_4(H_2O\text{-}\mathit{ax}){}^*L] + L} \arrow[ul, shift left]
\end{tikzcd} \qquad (30)$$

We can see in Table 4, that the k_I' values calculated from the ligand exchange rate constants, k_L, or from the bis-complex formation rate constants, k_{cis} and k_{tr}, are all equal to the rate constants for the exchange of the water molecule in the corresponding coordination site. In every case, the ratio k_I'/k_{ex} remains close to unity. The difference between k_I' and k_{ex} is smaller than the errors associated with the different constants used for the calculation of the k_I' values. For example, the K_{os} values are usually considered to be known within a factor of 2–4.[37] In the case of the reactivity of the axial site in $[Ru(H_2O)_5CO]^{2+}$, the comparison is slightly more difficult to make as the two rate constants have been measured at different temperatures due to experimental limitations. Nevertheless, if we apply the very rough approximation that the rate constant could increase by a factor of 2 if the temperature is raised by 10 degrees, we can see that the k_I' and k_{ax} are of comparable magnitude. Consequently, the comparison between the different rate constants confirms the I_d mechanistic hypotheses made above which can be summarized as follows: the rate determining step for all the substitution reactions on $[Ru(H_2O)_6]^{2+}$ or $[Ru(H_2O)_5L]^{2+}$ type complexes is the dissociation of a Ru–H_2O bond.

The reaction between a ruthenium(II) mono-complex and a ligand is always kinetically controlled by the dissociation of a water molecule but the complex formed is not always thermodynamically stable enough to be observed on the spectra. In this latter case, the new formed bis-complex loses immediately one of the two ligands, which results in an observed exchange of L. This situation was observed for the intermediate *trans*-$[Ru(H_2O)_4L_2]^{2+}$, with L = $H_2C{=}CH_2$, CO, and Me_2SO. The energy profile for the different possible substitution reactions on $[Ru(H_2O)_5L]^{2+}$, where L = $H_2C{=}CH_2$, CO, and Me_2SO is thus summarized in Figure 3.

A noticeable difference of behavior is observed between ethylene, CO and Me_2SO on one side and acetonitrile on the other side. For the three former ligands, no *trans*-$[Ru(H_2O)_4L_2]^{2+}$ could be observed, while with acetonitrile, the formation of a *trans*-bis-complex could be observed in the ^{1}H NMR spectra because of its higher stability. The nature of this complex was confirmed by the similarity between the rate of exchange of the trans and cis water molecules in $[Ru(H_2O)_5MeCN]^{2+}$ with the rate of formation of the *trans*- and *cis*-bis-complexes (Table 3). A close analysis of the redox potentials of the $[Ru(H_2O)_5L]^{2+}$ complexes, with L = H_2O, MeCN, $H_2C{=}CH_2$, CO, and Me_2SO[14] reveals that for the two former ligands, the $E°'$ value is much less positive (by at least 350 mV) than for the three latter ones. The high $E°'$ values were interpreted as resulting from a strong π-back-donation from the metal to the ligand leading to a strong polarization of the d_{xz} or d_{yz} orbitals of the metal. The metal is thus unable to share the d_{xz} and d_{yz} orbitals with two π-accepting ligands trans to each other. For L = MeCN the polarization is weaker as reflected by the low $E°'$ value, the metal can share the π orbitals with two ligands trans to each other and the *trans*-bis-complex is thus stable under the experimental conditions. It is worth mentioning that strong π-accepting ligands can bind to Ru(II) in a trans configuration only under drastic conditions as

---

(37) Wilkins, R. G. *Acc. Chem. Res.* **1970**, *3*, 408.

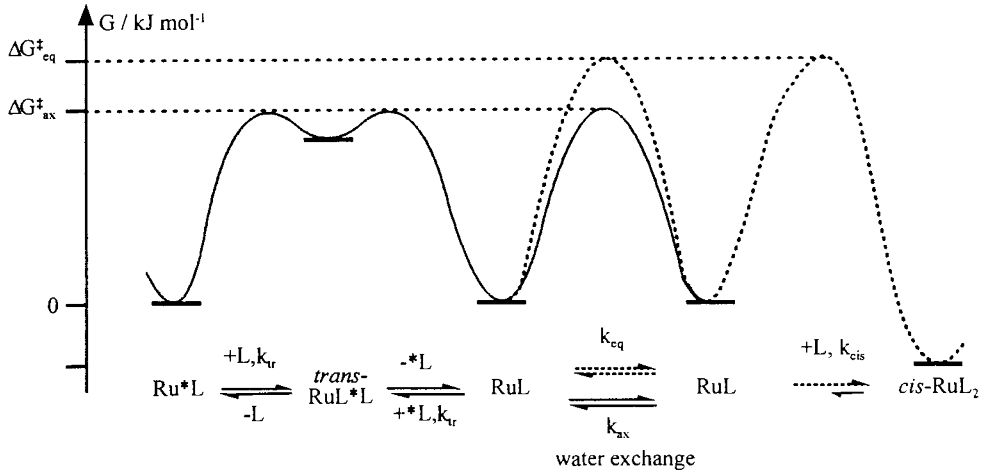


Figure 3. Energy profiles for the complex formation reactions and for the water exchange reactions on $[Ru(H_2O)_5L]^{2+}$ type complexes based on the hypothesis that the rate determining step for all the substitutions is the dissociation of a Ru−H$_2$O bond.

exemplified by the synthesis of $[Ru(CO)_6](Sb_2F_{11})_2$ in the superacid solvent SbF_5.[38]

Prediction of the Rate of Formation of Bis- or Tris-Complexes. It has been reported that the exchange of the axial water in $[Ru(H_2O)_5Me_2SO]^{2+}$ was much faster than the exchange of the equatorial ones. This was interpreted as a trans effect of the dimethyl sulfoxide ligand.[14] The same type of behavior was observed for the bis-complex *cis*-$[Ru(H_2O)_4(Me_2SO)_2]^{2+}$. When $H_2{}^{17}O$ was added to a solution of this bis-complex, a first signal appeared immediately at −66 ppm in the ^{17}O NMR spectra and a second signal appeared very slowly at −150 ppm. By comparison with the lability of the water molecules in the mono-complex, we can attribute the former signal to the two water molecules trans to Me_2SO and the latter one to the two *cis* waters. This attribution of the ^{17}O NMR signals is confirmed by the values of the chemical shifts, as it was shown in the case of the $[Ru(H_2O)_5L]^{2+}$ complexes, that the ^{17}O NMR signal of the equatorial water molecules appeared always at a more negative chemical shift than the signal of the axial water molecules. We have already mentioned that the bis-complex with two Me_2SO trans to each other is thermodynamically unstable in water. Nevertheless, *fac*-$[Ru(H_2O)_3(Me_2SO)_3]^{2+}$ has been obtained as the final product of the aquation of $[Ru(Me_2SO)_n(X)_{6-n}]^{2+}$ (n = 3−6, X = Cl$^-$, Br) type complexes.[39,40] Using eq 28, we can roughly predict the time for the formation of the *fac*-$[Ru(H_2O)_3(Me_2SO)_3]^{2+}$ complex by reacting Me_2SO with the *cis*-bis-complex. As mentioned above, the signal at −150 ppm was not growing anymore after 2 days at 321.6 K. We can therefore estimate that the half-time for the exchange of the cis water molecules is approximately half a day or 4×10^3 s. If we apply eq 28, we obtain an approximate k_f value of 5×10^{-7} mol^{-1} kg s^{-1} for the formation of the *fac*-triscomplex. Consequently, if we prepare an equimolar solution of $[Ru(H_2O)_4(Me_2SO)_2]^{2+}$ and Me_2SO, both 0.1 mol kg^{-1}, half of the triscomplex product should be formed after 243 days or 10% after 35 days at 321.6 K.

The same type of calculation can be applied to calculate the time needed to prepare the *cis*-$[Ru(H_2O)_4(CO)_2]^{2+}$ complex by reacting the mono-complex with CO. The rate constant for the exchange of the cis water molecules on $[Ru(H_2O)_5CO]^{2+}$ is 2.9×10^{-6} s^{-1}.[14] We can apply eq 28 and obtain a k_{cis} of 1.5×10^{-7} s^{-1} mol^{-1} kg for the formation of the *cis*-$[Ru(H_2O)_4(CO)_2]^{2+}$. To observe the formation of 10% (50%) of *cis*-bis-complex when a pressure of 5.4 MPa of CO is applied to a solution of $[Ru(H_2O)_5CO]^{2+}$ 0.1 mol kg^{-1}, we should wait 83 days (625 days).

Conclusion

Successive steps of complex formation reaction of $[Ru(H_2O)_6]^{2+}$ occur with metal−water bond rupture activation. Powerful π-accepting ligands increase the lability of the *trans*-water molecule, but decrease drastically the reactivity of the *cis*-water molecules where substitution is taking place to form the thermodynamically stable new *cis*-metal−ligand bond. It follows that the rates of *cis*-bis-complex formation, and further the rates of *fac*-triscomplexes formation are strongly slowed-down compared to the rates of mono-complex formation. These rates can be tuned by changing the donor/acceptor properties of the ligand as reflected by the redox potential of the complexes. By using acetonitrile for example, it was possible to stabilize the Ru(II) metal center toward oxidation without decreasing too much the reactivity. This way, it was possible to prepare rapidly and quantitatively *cis*- and *trans*-bis-complexes. The effect of numerous ligands on the redox behavior of a ruthenium(II) metal center have been reported.[41] Using these data, it may be possible to design new efficient Ru(II) catalysts or anticancer drugs.

Acknowledgment. The authors thank the Swiss National Science Foundation for financial support (Grant 2000-052630.97/1).

Supporting Information Available: Plots of dissolved ethylene concentration as a function of ethylene pressure and temperature fitted with eq 1 (Figure S1a−g); evolution as a function of time of the mole fractions of free and bound L (L = $H_2C{=}CH_2$, CO, Me_2SO) during the exchange of L in $[Ru(H_2O)_5L]^{2+}$ (Figures S2, S3, and S5, respectively); temperature dependence of the observed first-order rate constants, $k_{obs,f}$ and $k_{obs,cis}$, for the reactions of formation of $[Ru(H_2O)_5(H_2C{=}CH_2)]^{2+}$ and *cis*-$[Ru(H_2O)_4(H_2C{=}CH_2)_2]^{2+}$ (Table S1); bis-complex formation reaction between $[Ru(H_2O)_5Me_2SO]^{2+}$ and Me_2SO,

---

(38) Wang, C.; Bley, B.; Balzer-Jöllenbeck, G.; Lewis, A. R.; Siu, S. C.; Willner, H.; Aubke, F. *J. Chem. Soc., Chem. Commun.* **1995**, 2071.
(39) Alessio, E.; Mestroni, G.; Nardin, G.; Attia, W. M.; Calligaris, M.; Sava, G.; Zorzet, S. *Inorg. Chem.* **1988**, *27*, 4099.
(40) Barnes, J. R.; Goodfellow, R. J. *J. Chem. Research (S)* **1979**, 350.
(41) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.

with mathematical treatment of the kinetics (eqs S1−S6) and evolution as a function of time of the mole fractions of Me_2SO in the different coordination sites (Figure S4); reaction between $[Ru(H_2O)_6]^{2+}$ and an excess of MeCN, with example of a ^1H NMR spectrum (Figure S6); and measured and calculated mole fractions of MeCN in the different chemical sites used for plotting Figure S5 (Table S2) (12 pages). Ordering information is given on any current masthead page.

IC980628Z