Inorg. Chem. **2003**, *42*, 3516–3526

Inorganic Chemistry

Article

Reactivity of the Organometallic *fac*-$[(CO)_3Re^I(H_2O)_3]^+$ Aquaion. Kinetic and Thermodynamic Properties of H_2O Substitution

Bernadette Salignac, Pascal V. Grundler, Sonia Cayemittes, Urban Frey, Rosario Scopelliti, and André E. Merbach*

Ecole Polytechnique Fédérale de Lausanne, Institut de Chimie Moléculaire et Biologique, BCH,
CH-1015 Lausanne, Switzerland

Roman Hedinger and Kaspar Hegetschweiler*

Anorganische Chemie, Universität des Saarlandes, Postfach 15 11 50,
D-66041 Saarbrücken, Germany

Roger Alberto*

Universität Zürich, Anorganisch-Chemisches Institut, Winterthurerstr. 190,
8057 Zürich, Switzerland

Ulrich Prinz, Gerhard Raabe, and Ulrich Kölle*

Institut für Anorganische Chemie, RWTH-Aachen, D-52056 Aachen, Germany

Syd Hall

Department of Crystallography, University of Western Australia, Nedlands WA 6907, Australia

Received February 17, 2003

The water exchange process on $[(CO)_3Re(H_2O)_3]^+$ (**1**) was kinetically investigated by ^{17}O NMR. The acidity dependence of the observed rate constant k_{obs} was analyzed with a two pathways model in which k_{ex} ($k_{ex}^{298} = (6.3 \pm 0.1) \times 10^{-3}\ s^{-1}$) and k_{OH} ($k_{OH}^{298} = 27 \pm 1\ s^{-1}$) denote the water exchange rate constants on **1** and on the monohydroxo species $[(CO)_3Re^I(H_2O)_2(OH)]$, respectively. The kinetic contribution of the basic form was proved to be significant only at $[H^+] < 3 \times 10^{-3}$ M. Above this limiting $[H^+]$ concentration, kinetic investigations can be unambiguously conducted on the triaqua cation (**1**). The variable temperature study has led to the determination of the activation parameters $\Delta H^\ddagger_{ex} = 90 \pm 3$ kJ mol^{-1}, $\Delta S^\ddagger_{ex} = +14 \pm 10$ J K^{-1} mol^{-1}, the latter being indicative of a dissociative activation mode for the water exchange process. To support this assumption, water substitution reaction on **1** has been followed by $^{17}O/^1H/^{13}C/^{19}F$ NMR with ligands of various nucleophilicities (TFA, Br^-, CH_3CN, $Hbipy^+$, $Hphen^+$, DMS, TU). With unidentate ligands, except Br^-, the mono-, bi-, and tricomplexes were formed by water substitution. With bidentate ligands, bipy and phen, the chelate complexes $[(CO)_3Re(H_2O)(bipy)]CF_3SO_3$ (**2**) and $[(CO)_3Re(H_2O)(phen)](NO_3)_{0.5}(CF_3SO_3)_{0.5}\cdot H_2O$ (**3**) were isolated and X-ray characterized. For each ligand, the calculated interchange rate constants k'_i (2.9×10^{-3} (TFA) < k'_I < 41.5×10^{-3} (TU) s^{-1}) were found in the same order as the water exchange rate constant k_{ex}, the S-donor ligands being slightly more reactive. This result is indicative of I_d mechanism for water exchange and complex formation, since larger variations of k'_i are expected for an associatively activated mechanism.

Introduction

Although water is an ubiquitous solvent, of environmentally benign nature,[1,2] its role in organometallic chemistry received little attention for a long time. However, the last two decades have seen the emergence of a rich, new chemistry of organometallic complexes in water.[3] The growing interest in this area of chemistry has spurred the intensive development of new fields of research, such as bioorganometallic chemistry[4] and water soluble organometallics as

---

* To whom correspondence should be addressed. E-mail: Andre.Merbach@epfl.ch (A.E.M.); hegetschweiler@mx.uni-saarland.de (K.G.); Ariel@aci.unizh.ch (R.A.); U.koelle@ac.rwth-aachen.de (U.K.).

10.1021/ic0341744 CCC: $25.00

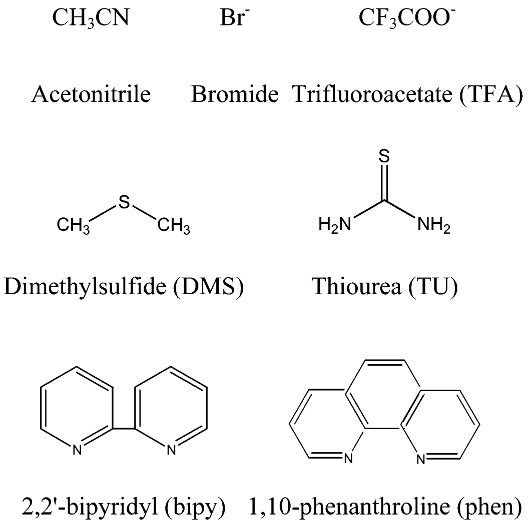
© 2003 American Chemical Society
Published on Web 05/02/2003

homogeneous catalysts.[5] In this context, organometallic aqua ions of composition $[L_qM(H_2O)_p]^{n+}$, where L denotes a C-bonded ligand, such as CO, olefins, η^5-$C_5R_5^-$, η^6-C_6R_6, or an alkyl group, represent a class of key compounds.

In contrast to a simple, hydrated metal ion ($M(H_2O)_x{}^{m+}$), the properties of organometallic aqua ions $[L_qM(H_2O)_p]^{n+}$ depend on the steric and electronic demands of the coligands L, as well as the nature of the metal center. When L is significantly more stable than the coordinated water molecules, the aquaions $[L_qM(H_2O)_p]^{n+}$ could be described as inert $[L_qM]^{n+}$ moieties bearing *p* labile water molecules; however, the lability of coordinated water is strongly affected by the nature of the coligands L. In the so-called half-sandwich $[Cp^*M(H_2O)_3]^{2+}$ ($M = Rh^{III}, Ir^{III}$) and $[(C_6H_6)Ru(H_2O)_3]^{2+}$ complexes, it has already been shown that the water exchange rate increases by 14 orders of magnitude for Rh^{III} and Ir^{III} and by 3 for Ru^{II},[6] compared to the corresponding $[M(H_2O)_6]^{m+}$ aquaions.[7] These results are not indicative of a general trend for water exchange on half-sandwich complexes, as aqua-carbonyl Ru^{II} complexes exhibit more complex behavior,[8] with the water exchange rate on $[(CO)_3Ru(H_2O)_3]^{2+}$ being estimated between 1 and 2 orders of magnitude lower than on the hexaaquaion $[Ru(H_2O)_6]^{2+}$.[8b] Further, Re^I has been shown to form $[(CO)_5Re(H_2O)]^+$ and $[(CO)_4Re(H_2O)_2]^+$ aquaions, with the latter being labile and slowly converting to the pentacarbonyl aquaion,[9] whereas the half-sandwich *fac*-$[(CO)_3Re(H_2O)_3]^+$ (**1**) is remarkably stable in water.[10]

Rhenium and technetium complexes, bearing the $M(CO)_3$ entity ($M = Tc(I), Re(I)$), have received much attention over the last years, due to their potential use as in vivo radiotracers, in diagnostic and therapeutic medicine. The reactivity of these complexes must be fully characterized to enable the development of a method by which radionuclides ^{99m}Tc and ^{188}Re can be incorporated into the appropriate biomolecules. The thermodynamic and kinetic properties of H_2O substitution on **1** are of particular interest, and one of the key properties is the mean residence time of a coordinated water molecule. The water exchange reaction represents a process with $\Delta G = 0$ and, therefore, is a convenient measure for the intrinsic lability of the metal ion. In addition, to probe the mechanism of the water exchange on **1**, we have extended the kinetic investigation to the substitution of coordinated water molecules by charged and uncharged ligands (Scheme 1) with various nucleophilicities. In this paper, we present the first thermodynamic and kinetic data obtained for water exchange on *fac*-$[(CO)_3Re(H_2O)_3]^+$ (**1**), as well as the results of ^{17}O, ^{13}C, ^{19}F, and ^1H NMR studies of the water substitution on **1**, carried out with the ligands CH_3CN, Br^-, DMS, TFA, TU, bipy, and phen at 298 K and ambient pressure.

Scheme 1



Experimental Section

Materials. ^{17}O atom enriched water (10%) was obtained from Yeda R&D, Rehovot, Israel. Enriched TU, 99% ^{13}C labeled, was purchased at ISOTEC. Deuterated solvents were purchased from Aldrich and CIL. The buffers PIPBS (piperazine-*N*,*N*′-bis(4-butanesulfonic acid)) and PIPES (1,4-bis(2-sulfoethyl)piperazine) were purchased from GFS Chemicals (Columbus, Ohio). Solutions of commercial $NaCF_3SO_3$ (Aldrich) were found to be basic, probably due to alkaline traces. Therefore, the $NaCF_3SO_3$ salt was neutralized by addition of CF_3SO_3H. All other chemicals were the commercially available products of highest possible quality (Fluka, Merck, Riedel de Haen) and were used without further purification.

$[(CO)_3Re(H_2O)_3]^+$ (1). Complex **1** was synthesized in aqueous solution according to the published method, using $(NEt_4)_2[(CO)_3ReBr_3]$ as precursor.[11] The addition of 3 equiv of AgX ($X = CF_3SO_3^-$; ClO_4^-) to a 0.1 M HX acidic ($X = CF_3SO_3^-$; ClO_4^-) solution of $(NEt_4)_2[(CO)_3ReBr_3]$ provides a solution of **1**, after AgBr removal by filtration. **Caution! The perchlorate salts are potentially explosive and must be handled with care.**

---

(1) Stumm, W.; Morgan, J. J. *Aquatic Chemistry*; Wiley: New York, 1981.

(2) Richens, D. T. *The Chemistry of Aqua Ions*; Wiley: Chichester, U.K., 1997.

(3) (a) Süss-Fink, G.; Meister, G.; Haak, S.; Rheinwald, G.; Stoeckli-Evans, H. *New J. Chem.* **1997**, *21*, 785. (b) Roundhill, D. M. *Adv. Organomet. Chem.* **1995**, *39*, 155. (c) Koelle, U. *Coord. Chem. Rev.* **1994**, *145/136*, 623. (d) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405. (e) Ogo, S.; Chen, H.; Olmstead, M. M.; Fish, R. H. *Organometallics* **1996**, *15*, 2009.

(4) Severin, K.; Bergs, R.; Beck, W. *Angew. Chem., Int. Ed.* **1998**, *37*, 1634.

(5) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem.* **1993**, *105*, 1588.

(6) (a) Stebler-Röthlisberger, M.; Hummel, W.; Pittet, P.-A.; Bürgi, H.-B.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1358. (b) Dadci, L.; Elias, H.; Frey, U.; Höring, A.; Koelle, U.; Merbach, A. E.; Paulus, H.; Schneider, J. S. *Inorg. Chem.* **1995**, *34*, 306. (c) Cayemittes, S.; Poth, T.; Fernandez, M. J.; Lye, P. G.; Becker, M.; Elias, H.; Merbach, A. E. *Inorg. Chem.* **1999**, *38*, 4309.

(7) (a) Rapaport, I.; Helm, L.; Merbach, A. E.; Bernhard, P.; Ludi, A. *Inorg. Chem.* **1988**, *27*, 873. (b) Laurenczy, G.; Rapaport, I.; Zbinden, D.; Merbach, A. E. *Magn. Res. Chem.* **1991**, *29*, 845. (c) Cusanelli, A.; Frey, U.; Richens, D. T.; Merbach, A. E. *J. Am. Chem. Soc.* **1996**, *118*, 5265. (d) Aebisher, N.; Laurenczy, G.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1993**, *32*, 2810. (e) De Vito, D.; Sidorenkova, E.; Rotzinger, F. P.; Weber, J.; Merbach, A. E. *Inorg. Chem.* **2000**, *39*, 5547.

(8) (a) Aebischer, N.; Sidorenkova, E.; Ravera, M.; Laurenczy, G.; Osella, D.; Weber, J.; Merbach, A. E. *Inorg. Chem.* **1997**, *36*, 6009. (b) Meier, U. C.; Scopelliti, R.; Solari, E.; Merbach, A. E. *Inorg. Chem.* **2000**, *39*, 3816. (c) Grundler, P. V.; Laurenczy, G.; Merbach, A. E. *Helv. Chim. Acta* **2001**, *84*, 2854.

(9) (a) Raab, K.; Beck, W. *Chem. Ber.* **1985**, *118*, 3830. (b) Lippmann, E.; Krämer, R.; Beck, W. *J. Organomet. Chem.* **1994**, *466*, 167.

(10) Egli, A.; Hegetschweiler, K.; Alberto, R.; Abram, U.; Schibli, R.; Hedinger, R.; Gramlich, V.; Kissner, R.; Schubiger, P. A. *Organometallics* **1997**, *16*, 1833.

(11) Alberto, R.; Egli, A.; Abram, U.; Hegetschweiler, K.; Gramlich, V.; Schubiger, P. A. *J. Chem. Soc., Dalton Trans.* **1994**, 2815.

$[(CO)_3Re(H_2O)(bipy)]CF_3SO_3$ (2). $(NEt_4)_2[(CO)_3ReBr_3]$ (0.46 g; 0.6 mmol) was dissolved under stirring in 10 mL of a 0.04 M CF_3SO_3H aqueous solution. $AgCF_3SO_3$ (0.46 g; 1.8 mmol) was then added, leading to the immediate precipitation of AgBr. The solution was incubated at 50 °C with stirring for 15 min before filtration under vacuum. The precipitate was then washed with water. 2,2′-Bipyridyl (1 equiv, 94 mg; 0.6 mmol) was added to the resulting $[(CO)_3Re(H_2O)_3]^+$ (**1**) solution, and the stirring and heating continued to accelerate the complex formation. Within 20 min, a bright yellow solution, typical of $[(CO)_3Re(H_2O)(bipy)]^+$, was formed and the volume adjusted to 20 mL with water before standing at room temperature for 5 days. Yellow monocrystals of **2** were collected and used for X-ray diffraction analysis. ^1H NMR (D_2O): 8.99 (d, 2 H, $J = 5.5$ Hz), 8.36 (d, 2 H, $J = 8.2$ Hz), 8.15 (observed as a t, 2 H, $J_{app} = 7.9$ Hz), 7.58 (observed as a t, 2 H, $J_{app} = 6.6$ Hz). $^{13}C\{^1H\}$ NMR (D_2O): 154.5, 152.2, 139.5, 126.3, 122.5.

$[(CO)_3Re(H_2O)(phen)](NO_3)_{0.5}(CF_3SO_3)_{0.5}\cdot H_2O$ (3). The $[(CO)_3Re(H_2O)_3]^+$ (**1**) solution was obtained as described. 1,10-Phenanthroline (1 equiv, 0.11 g; 0.6 mmol) was added to this solution, which was then incubated at 50 °C with stirring for 20 min. $NaNO_3$ (0.35 g; 4.1 mmol) was added to the resulting yellow solution, which was then adjusted to 20 mL with water before standing at room temperature for one week. Yellow monocrystals of **3** were collected and used for X-ray diffraction analysis. ^1H NMR (D_2O): 9.52 (d, 2 H, $J = 5.2$ Hz), 8.85 (d, 2 H, $J = 8.4$ Hz), 8.19 (s, 2 H), 8.03 (dd, 2 H, $J = 8.3-5.2$).

Crystal Structure Determination. Diffraction data for **2** were collected at ambient temperature on a Bruker Smart CCD diffractometer using monochromated Mo Kα radiation. Cell parameters have been determined from 7881 reflections with Bruker standard software. SADABS[12] was used for absorption correction. The structure was solved by means of direct methods as implemented in the XTAL3.7 set of crystallographic routines employing GENSIN[13] to generate structure-invariant relationships and GENTAN for the general tangent phasing procedure. CRYSLQ has been used for the final full-matrix least-squares refinement of 248 parameters on F^2 involving 3495 observed reflections. Two peaks of the electron density close to oxygen O4 were assigned to the hydrogen of the water molecule. All other H atoms were calculated in idealized positions, and no hydrogen parameters have been refined. Hydrogen U_{eq} values have been fixed at $1.5U_{eq}$ of the relevant heavy atom prior to the final refinement. The severe disorder of the $CF_3SO_3^-$ anion was treated with two split positions, assuming equal occupation and allowing for isotropic refinement of O and F atoms.

The data for **3** were collected using a marresearch mar345 imaging plate detector system. Cell refinement and data reduction were carried out on both compounds with CrysAlis RED,[14] release 1.6.9 β. The data were corrected for absorption using the DELABS algorithm.[15] Structure solutions, structure refinements, molecular graphics, and geometrical calculations were performed with the SHELXTL software package.[16] The structures were refined using the full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. All H atoms were included in idealized positions except those belonging to water molecules. Crystallographic data are in CIF format. Data have been deposited at the CCDC.

NMR Measurements. NMR spectra were measured on Bruker ARX-400 and DPX-400 spectrometers with resonance frequencies at 400.13 MHz for ^1H, 100.63 MHz for ^{13}C, 54.25 MHz for ^{17}O, and 376.50 MHz for ^{19}F. ^1H and ^{13}C chemical shifts are referenced to TMS and measured with respect to the methyl group of NEt_4^+ ($\delta_{1H} = 1.25$ ppm, methyl group; $\delta_{13C} = 54.4$ ppm, methylene group). ^{17}O and ^{19}F chemical shifts are referenced to bulk water ($\delta = 0.0$ ppm) and $CFCl_3$, respectively, as external standards in a coaxial capillary tube.

Kinetic Data Treatment. Kinetic experiments were conducted by following the evolution of NMR signals with time. The NMR integrals were obtained by fitting the signals to a Lorentzian function with the program NMRICMA 2.8 for MATLAB.[17] The time dependent concentrations were extracted from the integrals, and the experimental data were fitted using the programs VISUALISEUR 2.3.0 and OPTIMISEUR 2.3.0 for MATLAB[18] and the SCIENTIST[19] program.

Results

Characterization and Properties of $[(CO)_3Re(H_2O)_3]^+$ (1). Alberto et al. have reported a quantitative and straightforward synthesis for $[(CO)_3Re(H_2O)_3]^+$ (**1**), based on the quantitative dissociation of $[(CO)_3ReBr_3]^{2-}$ in aqueous solution.[11] Addition of the appropriate silver salt produces concentrated (0.1 M) and bromide free solutions of (**1**), suitable for kinetic experiments. Compound **1** tends to polymerize by hydrolysis (p$K_a = 7.5$);[10] therefore, the synthesis was performed in acidic aqueous medium ($[H^+] = 0.1$ M) using perchloric or triflic acids, due to their weakly coordinating anions ClO_4^- and $CF_3SO_3^-$. It is well-known that low valent metal cations can be oxidized by $HClO_4$,[20] and decomposition of **1** at high $HClO_4$ concentrations (>1 M) was observed, but in aqueous 0.1 M $HClO_4$, the rate of decomposition was very slow and did not interfere with the kinetic and thermodynamic measurements. ^{17}O NMR allows convenient monitoring of the $[(OC)_3Re(OH_2)_3]^+$ (**1**) complex in solution, which was characterized by a two signal pattern; the sharp signal at 334 ppm was assigned to the CO groups of **1**, according to the usual 300−400 ppm range for terminal carbonyl groups (e.g., 335.4 ppm[21] for the equatorial CO in $(CO)_5ReBr$), and the signal at −40 ppm was assigned to the three equivalent coordinated water molecules.

^{13}C NMR of ^{13}C enriched complex **1**, prepared under 30 bar of 99% enriched ^{13}CO, exhibits one signal at 182.7 ppm, assigned to the carbonyl groups. In the ^{17}O NMR spectrum of $[(^{13}CO)_3Re(H_2O)_3]^+$, $^{17}O-^{13}C$ coupling was observed with a coupling constant ($J^1 = 19$ Hz) close to that reported for CO dissolved in $CDCl_3$.[22]

---

(12) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 1996.

(13) Hall, S. R.; Du Boulay, D. J.; Olthof-Hazekamp, R. *XTAL3.7 System*; University of Western Australia: Nedlands WA, Australia, 2000.

(14) *CrysAlis RED*; Oxford Diffraction Ltd.: Abingdon, Oxfordshire, U.K., 2001.

(15) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166.

(16) Sheldrick, G. M. *SHELXTL*; University of Göttingen: Göttingen, Germany, 1997; Bruker AXS Inc.: Madison, WI, 1997.

(17) Helm, L.; Borel, A. *NMRICMA 2.8 for MATLAB*; Institut de Chimie Moléculaire et Biologique, Ecole Polytechnique Fédérale de Lausanne: Switzerland.

(18) Yerly, F. *VISUALISEUR 2.3.0 and OPTIMISEUR 2.3.0 for MATLAB*; Institut de Chimie Moléculaire et Biologique, Ecole Polytechnique Fédérale de Lausanne: Switzerland, 1999−2001.

(19) *Scientist*, version 2.0; Micromath, Inc.: Salt Lake City, UT, 1995.

(20) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988, p 568.

(21) Hickey, J. P.; Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* **1979**, *179*, 159−68.

(22) Wasylishen, R. E.; Friedrich, J. O.; Mooibroek, S.; Macdonald, J. B. *J. Chem. Phys.* **1985**, *83*, 548−51.

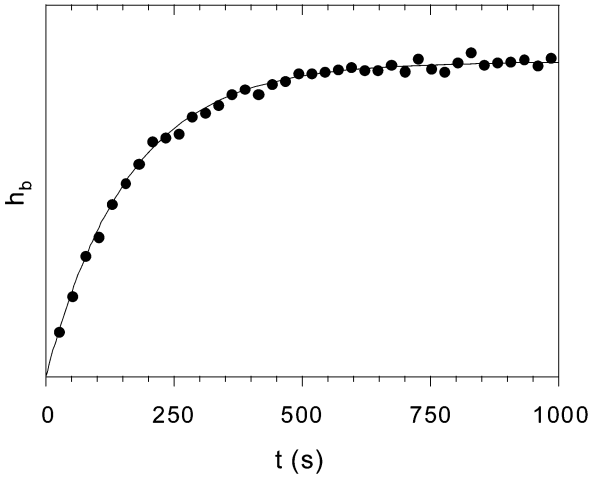


Figure 1. Increase as a function of time of ^{17}O NMR signal height h_b (arbitrary units) of bound water in $[(CO)_3Re(H_2O)_3]^+$ (**1**) (0.1 M CF_3SO_3H; $I = 1$ M), at $T = 298$ K; experimental values are represented as closed circles (●), and the fit according to eq 2 is shown as a solid line (—).

Water Exchange on $[(CO)_3Re(H_2O)_3]^+$ (1). The water substitution (eq 1) was followed at 298 K by ^{17}O NMR using a fast injection device.[23]

$$[(CO)_3Re(OH_2)_3]^+ + 3H_2{*}O \rightleftarrows [(CO)_3Re(H_2{*}O)_3]^+ + 3H_2O \quad (1)$$

Samples were prepared by injection of ^{17}O-enriched water to a solution of **1**. The signal of the bulk water was suppressed using the 1 −3 3 −1 pulse sequence.[24] For each experiment, the concentration and ionic strength of the samples correspond to the initial values after mixing the components. Due to the ^{17}O-enriching exchange process, the signal intensity of coordinated water molecules increased with time, and the experimental signal heights have been least-squares fitted to eq 2, where h_b and $h_{b,\infty}$ denote the heights of the metal bound $H_2{}^{17}O$ peak at times t and t_∞, respectively, and x_∞ is the mole fraction of coordinated $H_2{}^{17}O$ at t_∞ (Figure 1).[25]

$$h_b = h_{b\infty}\left(1 - \exp\left(\frac{k_{obs}t}{1 - x_\infty}\right)\right) \quad (2)$$

The effects of both acidity and temperature on the water exchange rate were separately investigated using this procedure.

The variable acidity experiment was performed on solutions of **1** ([**1**] = 0.05 M; 3.2% ^{17}O enrichment; $I = 1$ M adjusted with $NaCF_3SO_3$) with $[H^+]$ concentrations ranging from 1 M to 1×10^{-4} M. The highest acidities were adjusted with CF_3SO_3H, whereas weakly coordinating buffers[26] were used for the lower $[H^+]$ concentrations (concentrations and not activities are used throughout the text). The kinetic measurements show that the observed rate constant increases as the acidity decreases (Figure 2). This observation can be explained assuming the reaction takes place according to eq 3, where both the triaqua and the monohydroxo species contribute to the exchange process, in a proportion determined by the acid dissociation constant K_a.

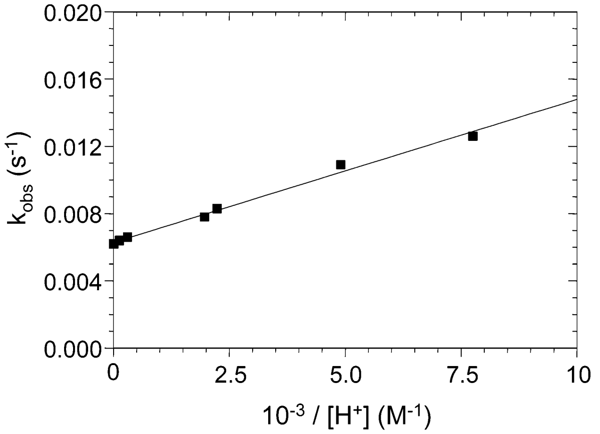


Figure 2. Acidity dependence of the water exchange rate on $[(CO)_3Re(H_2O)_3]^+$ (**1**), at 298 K, rate constant k_{obs} (■) and best fit (—) corresponding to eq 4.

$$\left\{\begin{matrix} [(CO)_3Re(H_2O)_3]^+ + 3H_2{*}O \\ \upharpoonleft\downharpoonright k_{ex} \\ [(CO)_3Re(H_2{*}O)_3]^+ + 3H_2O \end{matrix}\right\} \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} \left\{\begin{matrix} [(CO)_3Re(OH)(H_2O)_2] + 3H_2{*}O \\ \upharpoonleft\downharpoonright k_{OH} \\ [(CO)_3Re({*}OH)(H_2{*}O)_2] + 3H_2O \end{matrix}\right\} \quad (3)$$

This kind of behavior is well documented for the hexaaqua Fe^{III} ion,[27] and therefore, a similar kinetic model was used here to give eq 4.

$$k_{obs} = k_{ex} + \frac{k_{OH}K_a}{[H^+]} \quad (4)$$

Using a linear regression of k_{obs} (see Table S1) vs $1/[H^+]$ (Figure 2) and the literature value of $K_a{}^{298}$ ($10^{-7.5}$),[10] $k_{ex}{}^{298}$ and $k_{OH}{}^{298}$ were determined as $(6.3 \pm 0.1) \times 10^{-3}$ s^{-1} and 27 ± 1 s^{-1}, respectively. These results show that the water exchange rate is only influenced by the monohydrolyzed species below $[H^+] = 3 \times 10^{-3}$ M. Indeed, between $[H^+] = 3 \times 10^{-3}$ M and $[H^+] = 2 \times 10^{-4}$ M, the exchange rate increased by 75%.

Varying the temperature from 276 to 304 K ([**1**] = 0.05 M; 2% ^{17}O enrichment; 0.1 M $HClO_4$; $I = 0.25$ M with $NaClO_4$; see Table S2) and fitting the water exchange rate constants to the Eyring equation (eq 5) gave $k_{ex}{}^{298}$ as $(5.5 \pm 0.3) \times 10^{-3}$ s^{-1}, $\Delta H^\ddagger_{ex}$ as 90 ± 3 kJ mol^{-1}, and $\Delta S^\ddagger_{ex}$ as $+14 \pm 10$ J K^{-1} mol^{-1}.

$$\ln\frac{k_{ex}}{T} = \ln\frac{k_B}{h} + \frac{\Delta S_{ex}{}^\ddagger}{R} - \frac{\Delta H_{ex}{}^\ddagger}{RT} \quad (5)$$

Although acidity and temperature studies have been conducted under different experimental conditions ($CF_3SO_3{}^-$/$ClO_4{}^-$; ionic strengths 1 M/0.25 M), both calculated values

---

[23] Bernhard, P.; Helm, L.; Ludi, A.; Merbach, A. E. *J. Am. Chem. Soc.* **1985**, *107*, 312.

[24] Hore, P. J. *J. Magn. Reson.* **1983**, *54*, 539.

[25] McKay, H. *J. Am. Chem. Soc.* **1943**, *65*, 702.

[26] Kandegedara, A.; Rorabacher, D. B. *Anal. Chem.* **1999**, *71*, 3140.

[27] (a) Grant, M.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 55. (b) Swaddle, T. W.; Merbach, A. E. *Inorg. Chem.* **1981**, *20*, 4212.

Table 1. Rate and Equilibrium Constants of Complex Formation of $[(CO)_3Re(H_2O)_3]^+$ (**1**) with Various Ligands L, at $I = 1$ M, $T = 298$ K

L	TFA	Br^-	CH_3CN	$HBipy^+$	$HPhen^+$	DMS	TU
$10^3\ k_{f,1}/M^{-1}\ s^{-1}$	0.81 ± 0.01	1.6 ± 0.3	0.76 ± 0.04	0.42 ± 0.03	0.34 ± 0.01	1.51 ± 0.23	2.49 ± 0.09
$10^5\ k_{r,1}/s^{-1}$	99 ± 2	230 ± 100	16 ± 2			3.9 ± 1.7	1.6 ± 0.2
$10^3\ k_{f,2}/M^{-1}\ s^{-1}$						0.53 ± 0.01	4.7 ± 1.7
$10^5\ k_{r,2}/s^{-1}$						0.98 ± 0.02	
$10^3\ k_{f,3}/M^{-1}\ s^{-1}$						0.10 ± 0.01	5.7 ± 1.2
$10^5\ k_{r,3}/s^{-1}$						0.02 ± 0.01	
K_1	0.82 ± 0.02	0.7 ± 0.3	4.8 ± 0.5			38 ± 18	160 ± 8
K_2						54 ± 1	
K_3						511 ± 320	

for k_{ex}^{298} are close. The water exchange has also been studied in d_8-THF at 278 K by ^{17}O NMR with a solution containing **1** (0.474 M) and 3 equiv excess of 15% enriched water. The water exchange rate constant k_{ex}^{278} was determined as $(2.37 \pm 0.14) \times 10^{-4}\ s^{-1}$, close to that found in water $(k_{ex}^{276} = (2.58 \pm 0.09) \times 10^{-4}\ s^{-1})$, indicating that the solvent does not have a major influence on the exchange rate. The activation volume of the water exchange on **1** could not be determined since the fast injection device does not allow for work under pressure.

Water Substitution on $[(CO)_3Re(H_2O)_3]^+$ (1) by Unidentate Ligands. The kinetic and thermodynamic properties for complex formation between **1** and a series of L ligands of various nucleophilicities (Scheme 1) have been investigated. For each experiment, the concentration and ionic strength correspond to the initial values after mixing the components.

The reaction of **1** with CH_3CN led to the formation of the mono-, bi-, and triacetonitrile complexes,[28] each characterized by a single ^1H NMR signal due to bound CH_3CN at 2.454, 2.459, and 2.450 ppm, respectively (eq 6a,b,c).

$$[(CO)_3Re(H_2O)_3]^+ + L \rightleftarrows [(CO)_3Re(L)(H_2O)_2]^+ + H_2O \quad k_{f,1}, k_{r,1} \tag{6a}$$

$$[(CO)_3Re(L)(H_2O)_2]^+ + L \rightleftarrows [(CO)_3Re(L)_2(H_2O)]^+ + H_2O \quad k_{f,2}, k_{r,2} \tag{6b}$$

$$[(CO)_3Re(L)_2(H_2O)]^+ + L \rightleftarrows [(CO)_3Re(L)_3]^+ + H_2O \quad k_{f,3}, k_{r,3} \tag{6c}$$

Unfortunately, the three signals of bound CH_3CN were too close to allow proper integration. In order to follow the first step only, **1** was used in excess, to avoid the formation of the bi- and triacetonitrile complexes. Complex formation between **1** (50 mM) and acetonitrile was followed with time at 298 K for three initial CH_3CN concentrations (11, 23, and 33 mM) in CF_3SO_3H (0.1 M) ($I = 1$ M adjusted with $NaCF_3SO_3$). Equation 7a,b, derived from eq 6a, was fitted to the experimental data, assuming second order kinetics, and the results are given in Table S3 and summarized in Table 1.

$$\frac{d[L]}{dt} = -k_{f,1}[Re][L] + k_{r,1}[ReL] \tag{7a}$$

$$\frac{d[ReL]}{dt} = k_{f,1}[Re][L] - k_{r,1}[ReL] \tag{7b}$$

The complex formation with CH_3CN can also be followed by ^{17}O NMR. Using this technique, the mono and bi complexes, $[(CO)_3Re(H_2O)_2(CH_3CN)]^+$ and $[(CO)_3Re(H_2O)(CH_3CN)_2]^+$, were well characterized by the signals of the bound water molecule(s), at −49 and −65 ppm, respectively, while the water signal of **1** appeared at −40 ppm.

With halide anions, complexes of the type $[(CO)_3ReX_3]^{2-}$ (X = Cl, Br, I) are well-known,[11,29] e.g., $[(CO)_3ReBr_3]^{2-}$, the precursor of the aquaion **1**. Their complex formation has thus been investigated at 298 K using the ^{17}O NMR signals of the residual bound water molecule(s). In order to achieve partial complexation, a large excess of NaX salt (15 equiv) had to be added to solutions of **1** (0.1 M) in 0.1 M $HClO_4$. With Cl^-, a weak shoulder was observed at −41 ppm, attributed to the mono complex $[(CO)_3Re(H_2O)_2Cl]$. However, this signal was too close to that of **1** (−40 ppm) to allow quantitative investigations. Addition of NaI resulted in the formation of the triply substituted iodo complex $[(CO)_3ReI_3]^{2-}$, which precipitated as a NEt_4^+ salt.[29] The signals of $[(CO)_3Re(H_2O)_2I]$ and $[(CO)_3Re(H_2O)I_2]^-$ were observed at −52 and −71 ppm, respectively, at lower iodide concentrations (0.2 M). A quantitative evaluation of the successive equilibria was not further pursued at that point. More conveniently, the reaction of **1** with Br^- leads only to the formation of $[(CO)_3Re(H_2O)_2Br]$, which appeared as a readily observable shoulder at −44 ppm. Therefore, the reaction between **1** (0.075 M) and Br^- (1.3 M) was followed with time at 298 K by ^{17}O NMR in $HClO_4$ (0.06 M) (3.2% ^{17}O-enriched solution). Due to the high bromide concentration, complex formation was faster than in the case of the acetonitrile ligand and, thus, required the use of the fast injection device. The NMR integrals were obtained by fitting the decreasing signal of **1** at −40 ppm and the increasing signal of $[(CO)_3Re(H_2O)_2Br]$ at −44 ppm with two Lorentzian functions. As for the CH_3CN experiments, eq 7a,b were applied for the fit. The obtained rate and equilibrium constants are collected in Table 1.

The reaction between **1** (0.05 M) and CF_3COO^- (0.25 M) was followed with time at 298 K by ^{19}F NMR in CF_3SO_3H (0.1 M) ($I = 1$ M adjusted with $NaCF_3SO_3$). Under these experimental conditions, it was necessary to use the fast

---

(28) (a) Reimann, R. H.; Singelton, E. *J. Organomet. Chem.* **1973**, *59*, C24. (b) Chan, E. E.; Isaac, L. Y. Y.; Graham, W. A. G. *Can. J. Chem.* **1977**, *55*, 111. (c) Edwards, D. A.; Marshalsea, J. *J. Organomet. Chem.* **1977**, *131*, 73. (d) Christopher, R. E.; Venanzi, L. M. *Inorg. Chim. Acta* **1973**, *7*, 489.

(29) (a) Abel, E. W.; Butler, I. S.; Ganorkar, M. C.; Jenkins, C. R.; Stiddard, M. H. B. *Inorg. Chem.* **1966**, *5*, 25. (b) Hawkes, M. J.; Ginsberg, A. P. *Inorg. Chem.* **1969**, *8*, 2189.

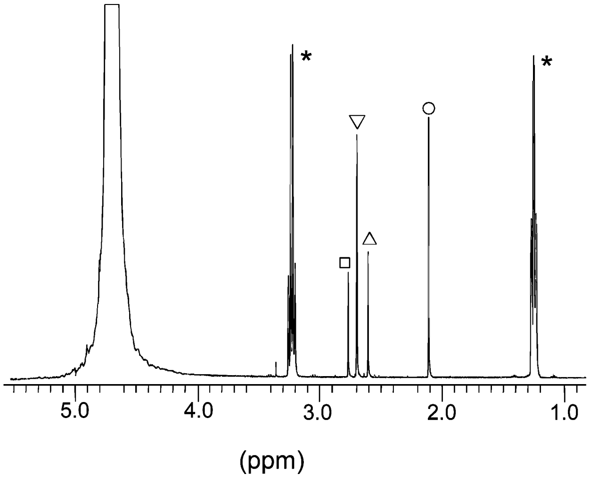


Figure 3. ^1H NMR spectrum at $T = 298$ K of a solution containing initially $[(CO)_3Re(H_2O)_3]^+$ (**1**) 0.05 M and DMS 0.09 M, in 0.1 M CF_3SO_3H, 32 h after addition of DMS. Free DMS (○), $Re(DMS)^+$ (△), $Re(DMS)_2{}^+$ (▽), $Re(DMS)_3{}^+$ (□), NEt_4 (∗).

injection technique to follow the kinetics of the reaction. The CF_3COO^- anion is mostly unprotonated at $[H^+] = 0.1$ M due to its low pK_a (0.52). Spectra show the signal of free CF_3COO^- at -75.78 ppm, the intensity of which decreased with time. Conversely, two other signals of increasing intensity appeared successively at -75.06 ppm and then at -75.09 ppm, assigned to coordinated CF_3COO^- in the mono and in the bi complexes, respectively. However, the latter signal was ignored in the analysis due to its very low intensity. The tristrifluoroacetate complex, which has been isolated and X-ray characterized as $(NEt_4)_2[(CO)_3Re(O_2CCF_3)_3]$,[10] was not observed in this experiment. Using eq 7a,b, rate and equilibrium constants were obtained, as given in Table 1.

The reaction between **1** (0.05 M) and DMS (0.09 M), in CF_3SO_3H (0.1 M) ($I = 1$ M adjusted with $NaCF_3SO_3$), was followed with time at 298 K by ^1H NMR. Due to the high volatility of DMS, all measurements were performed in sealed tubes. Free DMS was initially observed at 2.27 ppm. In the course of several hours, three new signals of increasing intensities successively emerged, assigned to the mono (2.65 ppm), bi (2.74 ppm), and tri (2.81 ppm) complexes, according to their order of appearance (Figures 3 and 4). Rate and equilibrium constants were determined from the NMR integrals for the three steps (eqs S1−S5) and are reported in Table 1.

Thiourea, the thio analogue of urea, generally coordinates to soft and borderline metal centers via sulfur and has found widespread use as a nonionic substituent in coordination chemistry. Complex formation of thiourea with $[(CO)_3Re(H_2O)_3]^+$ (**1**) was studied using ^{13}C NMR. In order to obtain quantitative data, ^{13}C NMR measurements were recorded taking into account free and bound thiourea relaxation delays, $T_1 = 10$ and 8 s, respectively. Spectra of a solution containing $[(CO)_3Re(H_2O)_3]^+$ (**1**) (5.0×10^{-3} M) and TU (0.1 M) in 0.01 M CF_3SO_3H ($I = 1$ M adjusted with $NaCF_3SO_3$) were recorded as a function of time at 298 K. The chemical shift of the free thiourea was 182.02 ppm, according to previously published data.[30] Three new peaks of increasing intensities with time appeared successively at 178.81, 178.20, and 178.65 ppm and were assigned to the mono, bi, and tri complexes, respectively. The latter compound $[(CO)_3Re(TU)_3](NO_3)$ was previously isolated and characterized by X-ray diffraction and IR spectroscopy.[31] In the solid state, the rhenium atom was shown to adopt an octahedral arrangement, composed of three facial carbonyl and three monodentate thiourea ligands, coordinated via the sulfur atom. The rate and equilibrium constants were determined from the NMR integrals for the three substitution steps (eqs S1−S5) and are shown in Table 1.

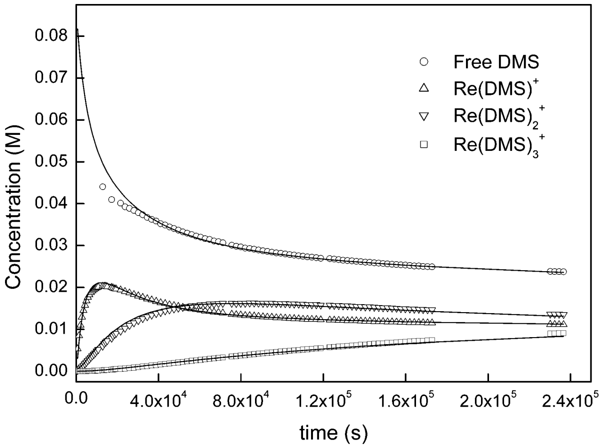


Figure 4. Plot of the concentrations of free DMS and of the mono, bi, and tri complexes as a function of time. Initial composition $[(CO)_3Re(OH_2)_3]^+$ (**1**) 0.05 M and DMS 0.09 M in 0.1 M CF_3SO_3H, $T = 298$ K.

Substitution of the water molecules on **1** (0.1 M) by the neutral ligands DMSO, DMF, and MeOH was not observed in aqueous solution, at ligand concentrations of up to15 equiv.

Water Substitution on $[(CO)_3Re(H_2O)_3]^+$ (1) by Bidentate Ligands. Replacement of water on **1** has been studied with the bidentate ligands (jointly abbreviated as N∧N) 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen). The cation $[(CO)_3Re(H_2O)(bipy)]^+$ has previously been prepared by Horn and Snow[32] as $AsF_6{}^-$ and $BF_4{}^-$ salts, and by Lehn[33] and co-workers as the $BF_4{}^-$ salt. Due to the role of Re(I) polypyridine complexes as photocatalysts, many $[(CO)_3Re(bipy)L]$ and $[(CO)_3Re(phen)L']$ complexes have been reported in nonaqueous media with various organic and inorganic ligands.[34,35] Addition of the N∧N ligands to $[(CO)_3Re(H_2O)_3]^+$ (**1**) leads to substitution of two water molecules to produce $[(CO)_3Re(H_2O)(N{\wedge}N)]^+$. Single crystal

---

(30) Olah, G. A.; Burrichter, A.; Rasul, G.; Christe, K. O.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1997**, *119*, 4345−4352.

(31) Abram, U.; Abram, S.; Alberto, R.; Schibli, R. *Inorg. Chim. Acta* **1996**, *248*, 193−202.

(32) Horn, E.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 1375.

(33) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990.

(34) (a) Rajendran, T.; Manimaran, B.; Lee, F. Y.; Lee, G. H.; Peng, S. M.; Wang, C. M.; Lu, K. L. *Inorg. Chem.* **2000**, *39*, 2016. (b) Czerwieniec, R.; Kapturkiewicz, A.; Anulewicz-Ostrowska, R.; Nowacki, J. *J. Chem. Soc., Dalton Trans.* **2002**, 3434. (c) Hori, H.; Koike, K.; Ishizuka, M.; Takeushi, K.; Ibusuki, T.; Ishitani, O. *J. Org. Chem.* **1997**, *530*, 169. (d) Scheiring, T.; Kaim, W.; Fiedler, J. *J. Org. Chem.* **2000**, *598*, 136. (e) Horn, E.; Snow, M. R. *Aust. J. Chem.* **1980**, *33*, 2369. (f) Hevia, E.; Pérez, J.; Riera, V.; Miguel, D. *Chem. Commun.* **2002**, 1914.

(35) Calabrese, J. C.; Tam, W. *Chem. Phys. Lett.* **1987**, *133*, 244.

Table 2. Summary of Crystal, Intensity, Collection, and Refinement Data for Complexes $[(CO)_3Re(bipy)(H_2O)](CF_3SO_3)$ (**2**) and $[(CO)_3Re(phen)(H_2O)](NO_3)_{0.5}(CF_3SO_3)_{0.5}\cdot H_2O$ (**3**)

	2	**3**
empirical formula	$C_{14}H_{10}F_3N_2O_7SRe$	$C_{15.5}H_{12}F_{1.5}N_{2.5}O_8S_{0.5}Re$
fw	593.5	592.01
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a (Å)	10.834(1)	13.413(3)
b (Å)	9.839(1)	22.156(3)
c (Å)	17.719(2)	12.503(2)
β (deg)	92.316(2)	100.764(13)
V (Å^3)	1887.4(4)	3650.3(9)
Z	4	8
T (K)	293	140(2)
D_{calcd} (Mg/m^3)	2.089	2.154
F(000)	1128	2264
λ(Mo Kα) (Å)	0.71070	0.71070
cryst size (mm^3)	0.64 × 0.51 × 0.35	0.32 × 0.26 × 0.21
μ (mm^{-1})	6.617	6.78
GOF on F^2	1.077	1.079
R1^a (wR2) [$I > 2\sigma(I)$]	0.044 (0.083)	0.0395 (0.1001)
R1 (wR2) (all data)	0.062 (0.09)	0.0525 (0.1133)

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

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complexes **2** and **3**

	2	**3**
Re(1)−C(1)	1.882(10)	1.898(7)
Re(1)−C(2)	1.901(9)	1.938(7)
Re(1)−C(3)	1.914(10)	1.931(7)
Re(1)−N(1)	2.161(6)	2.161(5)
Re(1)−N(2)	2.165(6)	2.183(5)
Re(1)−O(4)	2.190(5)	2.181(5)
C(1)−O(1)	1.147(13)	1.146(8)
C(2)−O(2)	1.139(12)	1.133(8)
C(3)−O(3)	1.148(12)	1.132(8)
C(1)−Re(1)−C(2)	89.1(4)	90.4(3)
C(1)−Re(1)−C(3)	86.6(4)	86.7(3)
C(2)−Re(1)−C(3)	87.3(4)	90.2(3)
C(1)−Re(1)−N(1)	96.0(3)	93.2(2)
C(2)−Re(1)−N(1)	172.8(3)	172.0(2)
C(3)−Re(1)−N(1)	98.0(3)	97.1(2)
C(1)−Re(1)−N(2)	94.2(3)	94.8(2)
C(2)−Re(1)−N(2)	99.7(3)	96.9(2)
C(3)−Re(1)−N(2)	172.9(3)	172.8(2)
C(1)−Re(1)−O(4)	174.6(3)	174.3(2)
C(2)−Re(1)−O(4)	94.1(3)	94.4(2)
C(3)−Re(1)−O(4)	97.8(3)	96.4(3)
N(1)−Re(1)−O(4)	80.5(2)	81.7(2)
N(1)−Re(1)−N(2)	75.0(2)	75.7(2)
N(2)−Re(1)−O(4)	81.0(2)	81.55(19)

structure determinations of $[(CO)_3Re(H_2O)(bipy)]CF_3SO_3$ (**2**) and $[(CO)_3Re(H_2O)(phen)](NO_3)_{0.5}(CF_3SO_3)_{0.5}\cdot H_2O$ (**3**) have confirmed the binding of the chelating N∧N ligand and one water molecule to the *fac*-{Re(CO)$_3$} moiety. The crystallographic and refinement data are shown in Table 2.

The molecular structures of **2** and **3** are shown in Figure 5a,b, respectively, with the corresponding atom numbering schemes. Relevant bond lengths and angles are presented in Table 3. In **3**, the asymmetric unit was found to contain two $[(CO)_3Re(H_2O)(phen)]^+$ cations, labeled A and B, whose molecular structures were very similar, and therefore, the distances and angles (Table 3) presented are only for cation A in Figure 5b. In **2** and **3**, the coordination geometry around the Re atom is a distorted octahedron with three facial carbonyl ligands and a water molecule. Completing the six-environment, Re is coordinated to nitrogen atoms of the chelating N∧N ligand, to form a five-membered ring. The Re−N bond lengths ((**2**) 2.161(6)−2.165(6) Å; (**3**) 2.161(5)−2.183(5) Å) are consistent with those observed in similar complexes.[34] The *trans* angles at the Re(I) sites were in the ranges 172.8(3)−174.6(3)° in **2** and 172.0(2)−174.3(2)° in **3**, showing a slight deviation from an ideal octahedral arrangement. In addition, the N(1)−Re(1)−N(2) angles of 75.0(2)° in **2** and 75.7(2)° in **3** were significantly smaller than 90°, as a result of the small bite angle between the pyridyl rings.

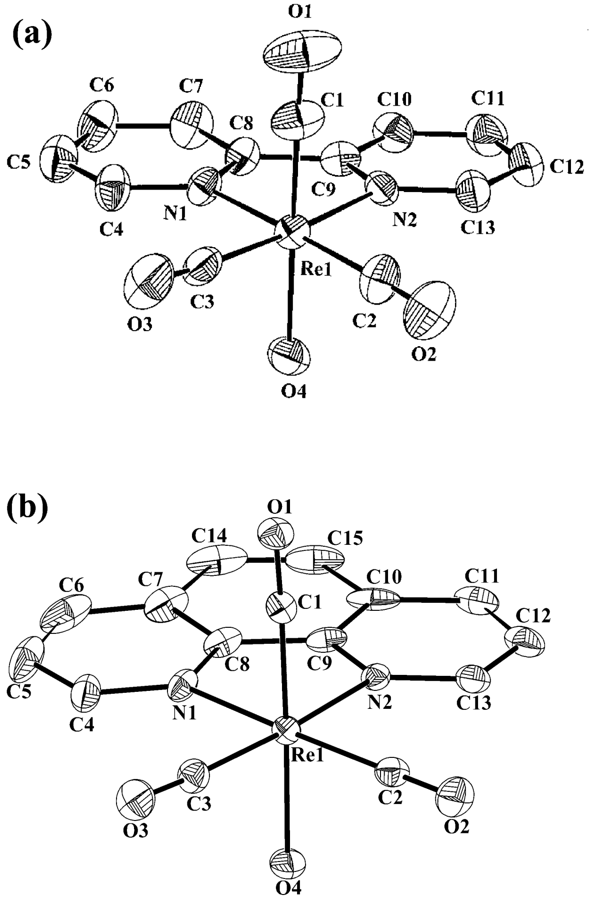


Figure 5. ORTEP views (30% ellipsoids) and atom numbering schemes of $[(CO)_3Re(H_2O)(N{\wedge}N)]^+$ complexes: (a) N∧N = 2,2-bipyridyl (**2**), (b) N∧N = 1,10-phenanthroline (**3**).

Complex formation with bipy and phen was followed at 298 K by ^{1}H NMR. The spectra of solutions containing **1** (0.02 M) and N∧N (0.006 M) in 0.025 M CF_3SO_3H ($I = 1$ M adjusted with $NaCF_3SO_3$) were recorded with time. In view of the similarity of ^{1}H NMR experiments with bipy and phen, a common qualitative description of both was adopted for conciseness. Selected spectra for the experiment with bipy are shown in Figure 6. Quantitative data, ^{1}H chemical shifts and multiplicities of signals, are summarized in Table 4 for the free N∧N ligands and $[(CO)_3Re(H_2O)(N{\wedge}N)]^+$ chelate complexes **2** and **3**.

Upon addition of $[(CO)_3Re(H_2O)_3]^+$ (**1**) to bipy and phen, the four multiplets of the free ligand shift upfield to varying extent. Complete peak assignment was made according to

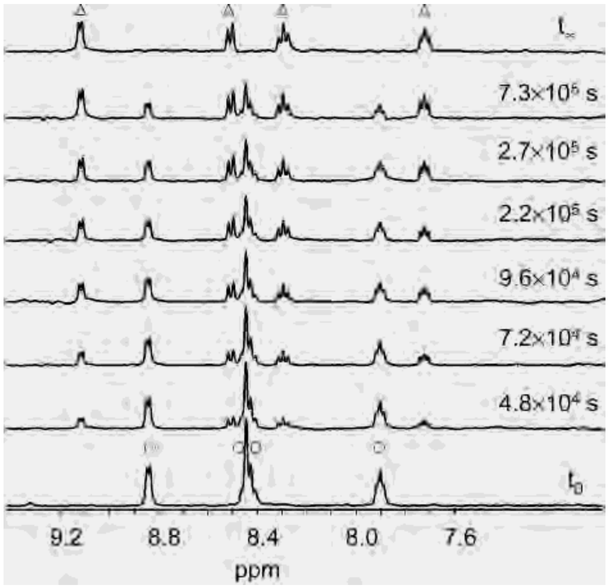
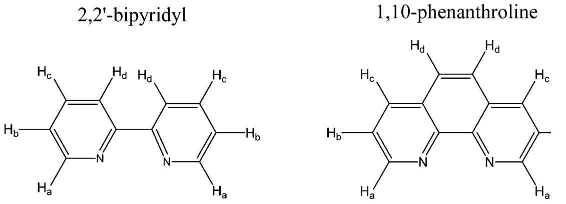


Figure 6. ^{1}H NMR spectra of a solution containing initially $[(CO)_3Re(OH_2)_3]^+$ (**1**) 0.02 M and bipy 0.006 M in 0.025 M CF_3SO_3H ($T = 298$ K). Free bipy (○), bound bipy (△).

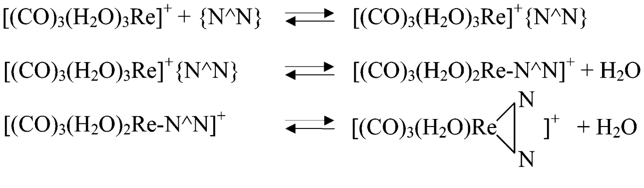
Table 4. ^{1}H NMR Chemical Shifts and Peak Assignments for the Free and Bound N∧N Ligands (N∧N = 2,2′-Bipyridyl; 1,10-Phenanthroline)



	free	bound in **2**	free	bound in **3**
H_a	8.841 (d, 2H)	9.114 (d, 2H)	9.173 (d, 2H)	9.478 (d, 2H)
H_b	7.902 (t, 2H)	7.723 (t, 2H)	8.124 (dd, 2H)	8.031 (dd, 2H)
H_c	8.426 (t, 2H)	8.295 (t, 2H)	8.891 (d, 2H)	8.820 (d, 2H)
H_d	8.445 (d, 2H)	8.496 (d, 2H)	8.175 (s, 1H)	8.148 (s, 1H)

the literature.[36,37] The signal pattern, showing the same multiplicity as in the free ligand(s), also ascertains the bidentate binding mode of these ligands throughout the reaction. This conclusion has been confirmed for the solid state by X-ray diffraction analysis.

Kinetics of Substitution on [(CO)$_3$Re(H$_2$O)$_3$]$^+$ (1) by Bidentate Ligands. Extension of the Eigen mechanism to chelate formation leads to a three step mechanism: the first step is comparatively rapid and provides the outer sphere complex (eq 8a), the second step leads to the formation of the inner sphere complex (eq 8b) with the ligand monodentate, and the final step is ring closure (eq 8c).



However, for both N∧N ligands, the [Re−N∧N] complex was not observed by ^{1}H NMR, indicating that ring-closure was much faster than the [Re−N∧N] formation step. Consequently, the overall rate of rhenium chelate formation was determined from the rate of formation of the [Re−N∧N] complex, which is assumed to be controlled by the same factors as those controlling the formation of monodentate ligand complexes. This mechanism has been termed *normal substitution* and contrasts to *sterically controlled substitution*[38] where the rate-determining step is ring-closure. Another important feature of the chelate formation reactions is their irreversiblity, as all of the free N∧N ligand is consumed at the end of the reaction.

The mechanism of complex formation cannot be properly established without considering the protonation of the N∧N ligands. The pK_a values for the two successive deprotonation steps of $HN\wedge NH^{2+}$ are given in the literature as 1.5−4.65 for bipy and 1.5−5.17 for phen.[39] Thus, under the experimental conditions used, $HN\wedge NH^{2+}$ and $HN\wedge N^+$ were the only species present, and the NMR signals of the free ligand represented a rapidly interchanging mixture of these two. On the basis of the intensities, time dependent concentrations of free and bound bipy and phen and unreacted $[(CO)_3Re(H_2O)_3]^+$ (**1**) were calculated for each spectrum, and using the pK_a values, concentrations of $HN\wedge NH^{2+}$, $HN\wedge N^+$, and H^+ were deduced. Under the experimental conditions, it can be assumed that the only ligand form that binds to the metal atom was the monoprotonated $HN\wedge N^+$. Thus, the kinetic data obtained with bipy and phen were analyzed using eq 9a,b.

$$[(CO)_3Re(H_2O)_3]^+ + HN\wedge N^+ \rightarrow [(CO)_3Re(H_2O)(N\wedge N)]^+ + H^+ + 2H_2O \quad k_f \quad (9a)$$

$$\frac{d[Re(N\wedge N)]}{dt} = -\frac{d[Re]}{dt} = -\frac{d[HN\wedge N]}{dt} = k_f\,[(CO)_3Re(H_2O)_3][HN\wedge N] \quad (9b)$$

Experimental and fitted concentrations of **1** and total free and bound phen were ploted as a function of time as shown in Figure 7. The optimized values of the formation rate constants are collected in Table 1 for each kinetic experiment, together with the values obtained for unidentate ligands.

Discussion

Water Exchange on [(CO)$_3$Re(H$_2$O)$_3$]$^+$ (1). We report the first kinetic study of water exchange on Re(I) and one of the rare water exchange reactions at a 5d metal center. Water exchange has been studied on the d^6 hexaaqua ions of Ru^{II}, Rh^{III}, and Ir^{III} and on the half-sandwich organometallic aqua derivatives $[LM(H_2O)_3]^{n+}$ (M = Rh^{III}, Ir^{III}, Ru^{II},

---

(36) Castellano, S. *J. Phys. Chem.* **1965**, *69*, 4166.

(37) Itokazu, M. K.; Polo, A. S.; de Faria, D. L. A.; Bignozzi, C. A.; Iha, N. Y. M. *Inorg. Chim. Acta* **2001**, *313*, 149−155.

(38) Kustin, K.; Pasternack, R. F.; Weinstock, E. M. *J. Am. Chem. Soc.* **1966**, *88*, 4610−15.

(39) Smith, R. M.; Martell, A. E.; Motekaitis, R. J. *Critically Selected Stability Constants of Metal Complexes*; NIST Standard Reference Database 46, Version 3.0; NIST Standard Reference Data: Gaithersburg, MD, 1997.

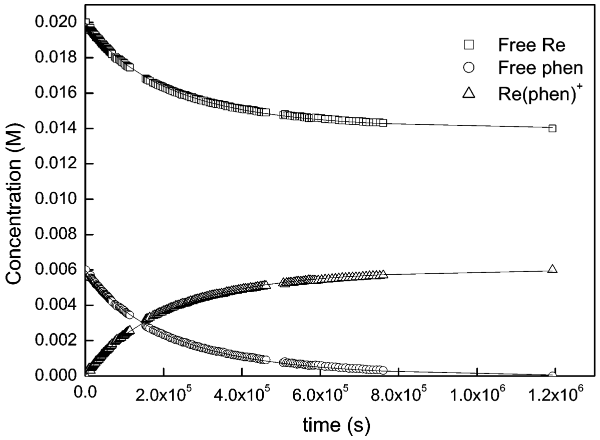


Figure 7. Plot, as a function of time, of the concentrations of $[(CO)_3Re(H_2O)_3]^+$ (**1**) and free and bound phen. Initial composition $[(CO)_3Re(H_2O)_3]^+$ (**1**) 0.02 M and phen 0.006 M in 0.025 M CF_3SO_3H (T = 298 K).

Os^{II}; L = η^5-Cp*, η^6-C_6H_6)[6] (Table 5).[7] The coordination of an aromatic moiety on these hexaaqua ions leads to an increase in the water exchange rate constant k_{ex} by several orders of magnitude. The *trans* effect of these organic ligands on the water ligands also alters the exchange mechanism, which changes toward a more dissociative activated process. In the $[(CO)_3Re(H_2O)_3]^+$ (**1**) complex, the three inert and facially arranged carbonyl groups adopt a configuration similar to that of the half-sandwich complexes, allowing us to compare their water exchange properties. The water exchange rate on **1** is the slowest found for a d^6 organometallic-aqua complex (except the estimated value for $[(CO)_3Ru(H_2O)_3]^{2+}$). For the three 5d^6 isoelectronic complexes $[(CO)_3Re(H_2O)_3]^+$ (**1**), $[(\eta^6\text{-}C_6H_6)Os(H_2O)_3]^{2+}$, and $[(\eta^5\text{-}Cp^*)Ir(H_2O)_3]^{2+}$, the water exchange rate increases from Re^I to Os^{II} and from Os^{II} to Ir^{III} by approximately 3 orders of magnitude. However, trends cannot be deduced from these observations, since both metal and the coligands change. Since a Re(I) hexaaquaion has not yet been prepared, a quantification of the CO effect in **1** is not possible, whereas in $[Ru(H_2O)_6]^{2+}$ the coordination of one single CO leads to less than a 2-fold increase in the rate of the *trans* water exchange but a four orders of magnitude decrease in that of the *cis* H_2O.[8] Subsequent water substitution produces $[(CO)_2Ru(H_2O)_4]^{2+}$, resulting in a large decrease in both *trans* and *cis* water exchange rates. Further kinetic studies on the tricarbonyl $[(CO)_3Ru(H_2O)_3]^{2+}$ complex (pK_a = −0.14) are obscured by the high reactivity of the monohydroxo species $[(CO)_3Ru(H_2O)_2(OH)]^+$ (k_{OH} = 0.053 s^{-1} at 262 K), which is present even in strongly acidic conditions. However, the water exchange rate on $[(CO)_3Ru(H_2O)_3]^{2+}$ could only be estimated and is roughly 2 orders of magnitude slower than $[Ru(H_2O)_6]^{2+}$ (Table 5). On the basis of these results with the Ru complexes, we deemed it necessary to explore the water exchange on **1** as a function of [H$^+$]. The pK_a of **1** has been reported as 7.5, with the conclusion that rhenium atom in **1** seemed to behave rather like a M^{2+} than a M$^+$ center.[10] The measured k_{ex} (6.3 × 10^{-3} s^{-1}; 298 K) and k_{OH} (27 ± 5 s^{-1}; 298 K) showed an enhanced exchange reactivity for the hydroxo complex. In contrast to ruthenium analogues, the kinetic contribution of the monohydroxo species $[(CO)_3Re(H_2O)_2(OH)]$ could be avoided in acidic media ([H$^+$] > 3 × 10^{-3} M), allowing further kinetic investigations (complex formation) exclusively on **1**.

Electronic information for these carbonyl complexes can be deduced from the IR vibration frequencies ν(CO): those given in the literature[8] for $[(CO)_3Ru(H_2O)_3]^{2+}$ are significantly higher (2156, 2089 cm^{-1})[8] than those of $[(CO)_3Re(H_2O)_3]^+$ (**1**) (2037, 1916 cm^{-1}), which indicates a greater back-donation by the Re^I center in **1**. Similarly, ^{17}O NMR shifts show the water molecules in **1** less shielded (−40 ppm) than the ones in $[(CO)_3Ru(H_2O)_3]^{2+}$ (−71 ppm),[8] probably due to the more reduced electron density at the Re^I atom. Examining the water exchange mechanism on **1**, one can conclude that the positive activation entropy for the water exchange ($\Delta S^\ddagger_{ex}$ = +14 ± 10 J K^{-1} mol^{-1}) seems to support a dissociative interchange (I$_d$) mechanism, in agreement with all the half-sandwich complexes in Table 5. However, this entropy value, due to its inherent error, is not sufficient to conclusively assign a mechanism.

Water Substitution on $[(CO)_3Re(H_2O)_3]^+$ (1) by Unidentate and Bidentate Ligands. In this current investigation, all three H_2O ligands of **1** have been shown to be readily substituted by the unidentate ligands TFA, CH_3CN, DMS, TU, and I$^-$ in aqueous solution. However, only partial substitution occurs with Br$^-$ and Cl$^-$, and interactions with hard nucleophiles, such as DMSO, DMF, and MeOH, were not observed. For the substitution of water with bidentate bipy and phen ligands, the persistence of the $[(CO)_3Re]^+$ moiety in the chelate complexes has been proven with molecular structures of **2** and **3**, respectively. Within the whole series of unidentate ligands L, the monosubstituted complexes $[(CO)_3ReL(H_2O)_2]^+$ show the highest stability constants with the sulfur-containing ligands DMS and TU (Table 1). With DMS, the three successive reversible steps of water substitution in **1** have been identified kinetically and thermodynamically. The formation rate of the mono-, bi-, and tri-DMS complexes decreases as the degree of substitution increases ($k_{f,1}$ = 1.51 × 10^{-3}, $k_{f,2}$ = 0.53 × 10^{-3}, and $k_{f,3}$ = 0.10 × 10^{-3} M^{-1} s^{-1}). Although statistical factors have to be considered, they cannot solely account for this rate decrease, which has previously been noted with the Ru^{II}, Rh^{III}, and Ir^{III} half-sandwich complexes.[6] In $[(\eta^6\text{-}C_6H_6)Ru(bipy)(H_2O)]^{2+}$, $[Cp^*Rh(bipy)(H_2O)]^{2+}$, and $[Cp^*Ir(bipy)(H_2O)]^{2+}$ (Table 5), the water exchange rate is dramatically slower, by 2 or 3 orders of magnitude, than that on the analogue triaqua complexes. In contrast, with the other S-donor ligand studied, TU, the three water substitution steps, where only the first is reversible, exhibit a slight increase in k_f for each successive substitution.

The dependence of substitution rates on the chemical nature of the entering ligand has been the classical criterion for the assignment of the activation mode of the reaction. According to the Eigen−Wilkins model, a substitution reaction can be divided into two steps: an outer sphere complex formation, followed by the rate determining ligand interchange (eq 10a,b).

Table 5. Collection of Reported Kinetic Data and Mechanisms of Water Exchange for Half-Sandwich Complexes of Rh^{III}, Ir^{III}, Ru^{II}, Os^{II}, and Re^I at 298 K

complex		k_{ex}/s^{-1}	$\Delta H_{ex}^‡/kJ \cdot mol^{-1}$	$\Delta S_{ex}^‡/J \cdot K^{-1} \cdot mol^{-1}$	$\Delta V_{ex}^‡/cm^3 \cdot mol^{-1}$	mechanism	ref
			Rh^{III}				
$[Rh(H_2O)_6]^{3+}$		2.2×10^{-9}	131 ± 23	29 ± 69	-4.2	I_a	7b,e
$[Cp^*Rh(H_2O)_3]^{2+}$		$(1.6 \pm 0.3) \times 10^5$	65.6 ± 7	75.3 ± 24	+0.6	I_d	6b
$[Cp^*Rh(bipy)(H_2O)]^{2+}$		1590 ± 760[a]	48.5 ± 3[b]	-20 ± 10[b]			6b
			Ir^{III}				
$[Ir(H_2O)_6]^{3+}$		$(1.1 \pm 0.1) \times 10^{-10}$	130.5 ± 0.6	2.1 ± 1.7	−5.7	I_a	7c
$[Cp^*Ir(H_2O)_3]^{2+}$		$(2.53 \pm 0.8) \times 10^4$	54.9 ± 3	23.6 ± 8	+2.4	I_d	6b
$[Cp^*Ir(bipy)(H_2O)]^{2+}$		219 ± 85[a]	60 ± 4[b]	3 ± 9[b]			6b
			Ru^{II}				
$[Ru(H_2O)_6]^{2+}$		$(1.8 \pm 0.2) \times 10^{-2}$	87.8 ± 4	16.1 ± 15	-0.4	I_d	7a,e
$[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$		11.5 ± 3.1	75.9 ± 3.8	29.9 ± 10.6	+1.5	I_d	6a
$[(\eta^6\text{-}C_6H_6)Ru(bipy)(H_2O)]^{2+}$		$(6.80 \pm 3.8) \times 10^{-2}$ [a]	69 ± 4	-27 ± 9			6b
$[(CO)Ru(H_2O)_5]^{2+}$	*trans*	$(3.54 \pm 0.02) \times 10^{-2}$	81			I_d	8b
	cis	$(2.54 \pm 0.05) \times 10^{-6}$	116 ± 0.4	22.4 ± 1		I_d	8b
$[(CO)_2Ru(H_2O)_4]^{2+}$	*trans*	$(4.53 \pm 0.08) \times 10^{-4}$	97.9 ± 1	19.3 ± 3		I_d	8b
	cis	$(1.58 \pm 0.54) \times 10^{-7}$	120 ± 2	28.4 ± 4		I_d	8b
$[(CO)_3Ru(H_2O)_3]^{2+}$		$10^{-4} < k_{ex} < 10^{-3}$					8b
$[(CO)_3Ru(H_2O)_2(OH)]^+$		0.053 ± 0.006[c]					8b
			Os^{II}				
$[(\eta^6\text{-}C_6H_6)Os(H_2O)_3]^{2+}$		11.8 ± 2.0	65.5 ± 2.2	-4.8 ± 6.1	+2.9	I_d	6a
			Re^I				
$[(CO)_3Re(H_2O)_3]^{+}$[d]		$(5.5 \pm 0.3) \times 10^{-3}$	90 ± 3	14 ± 10		I_d	this work
$[(CO)_3Re(H_2O)_2(OH)]$[e]		27 ± 5					this work

[a] As obtained on the basis of the approximation $k_{ex} \approx k_i$ (average) from anation studies at 293 K and extrapolated at 298 K using $\Delta H_{ex}^‡$ (see ref 6b, Table 9). [b] See ref 6b, Table 10. [c] k_{OH} at 262 K. [d] $I = 0.25$ M, adjusted with $NaClO_4$. [e] k_{OH} at $I = 1$ M, adjusted with $NaCF_3SO_3$.

Table 6. Interchange Rate Constants k_i' for the Water Substitution on $[(CO)_3Re(H_2O)_3]^+$ (**1**) at 298 K ($I = 1$ M adjusted with $NaCF_3SO_3$)[a]

L	$10^3\ k_{f,1}^{298}/M^{-1}\ s^{-1}$	$10^3\ k_i'/s^{-1}$
H_2O[b]	6.3	6.3
TFA	0.81	2.9
Br^-	1.6	5.8
CH_3CN	0.76	12.7
$Hbipy^+$	0.42	1.5
$Hphen^+$	0.35	1.3
DMS	1.52	25.3
TU	2.49	41.5

[a] $k'_i = (k_{f,1}f)/(K_{os}n_c)$ with $1/f$ = probability factor = 1/12, n_c = coordination number = 3, $K_{OS} = 1.1\ M^{-1}$ for charged ligands, and $K_{OS} = 0.24\ M^{-1}$ for neutral ligands. [b] k_{ex} = rate constant for the exchange of a particular water molecule.

$$[(CO)_3Re(H_2O)_3]^+ + L^{n-} \rightleftarrows \{[(CO)_3Re(H_2O)_3]^+ + L^{n-}\} \quad K_{os} \quad (10a)$$

$$\{[(CO)_3Re(H_2O)_3]^+ + L^{n-}\} \rightarrow [(CO)_3Re(H_2O)_2L]^{(1-n)+} + H_2O \quad k_i \quad (10b)$$

For dilute solutions, the rate of substitution is then given by eq 11, where k_i is the interchange rate constant and K_{os} is the equilibrium constant for the formation of the outer sphere complex.

$$k_f = k_i K_{os} \qquad (11)$$

Since K_{os} can be estimated on the basis of the Fuoss–Eigen electrostatic model, the rate constant k_i can be determined.[40] However, to allow comparison with the water exchange rate constant k_{ex}, k_i needs to be corrected for statistical differences, and the probability of a water molecule to be replaced by a ligand has to be considered. This probability depends on n_c and f, which are the number of water molecules in the first and second shells, respectively. The corrected rate of interchange k'_i can be given by eq 12, as described in detail by Aebischer et al.[41]

$$k'_i = k_i(f/n_c) \qquad (12)$$

The interchange rate constant k'_i was calculated for all of the systems studied (Table 6). The interchange rate constants k'_i may or may not depend on the nature of the entering ligand. The interchange k'_i constant slightly increases from the harder O-donor ligand TFA to the softer S-donor TU, as defined in Pearson HSAB classification. Accordingly, we observe the facile formation of the TU-substituted complex $[(CO)_3Re(TU)_3]^+$, but as mentioned, no significant interaction with the O-donors CH_3OH, DMF, and DMSO was observed. The affinity for the heavier halides was generally low, and with the exception of I^-, significant complex formation was only observed at high ligand concentrations (>0.1 mol·L^{-1}). In order to place the $[(CO)_3Re]^+$ moiety in Pearsons HSAB scheme,[42] its recent modification by R. B. Martin was employed,[43] which suggested the use of the difference in stability constants of two ligands of different hardness/softness toward a metal center as a measure for the metal center hardness. Taking $\log(\beta(Br^-)) = -0.15$ (Table 1) and $\log(\beta(OH^-)) = 6.5$ from the pK_a (7.5) of the triaqua ion gives $\Delta\beta = 6.65$. A comparison of $\Delta\beta$ values calculated from stability constants for a range of metal ions with the same two ligands[43] places the $[(CO)_3Re]^+$ moiety close to Cu^{2+} ($\Delta\beta = 6.56$) and slightly harder than Pb^{2+} ($\Delta\beta = 5.19$) and

---

(40) Fuoss, R. M. *J. Am. Chem. Soc.* **1968**, *80*, 5059.

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

(42) Pearson, R. G. *Chemical Hardness*; WILEY-VCH: Weinheim, 1997.

(43) Martin, R. B. *Inorg. Chim. Acta* **2002**, *339*, 27–33.

Co^{2+} and Ni^{2+} ($\Delta\beta \approx 4.6$), the latter being usually considered as "intermediate" or "borderline" metal ions. This placement is somewhat surprising since a monovalent third row transition element cation, such as Re^{I}, would be expected to be very soft. Clearly, the three carbonyl ligands, which remove electron density from the metal center by π-backbonding, must make the cation harder.

With bidentate ligands $Hbipy^+$ and $Hphen^+$, the k'_i constants were calculated as 1.5×10^{-3} and 1.3×10^{-3} s^{-1}, respectively, which is significantly slower than with the N-donor, monodentate CH_3CN ligand ($k'_i = 12.7 \times 10^{-3}$ s^{-1}). This appears at first sight to be unusual because for Ni^{2+} no significant difference has been found for water substitution by bipy or by its monodentate analogue pyridine.[44] Obviously, the simple "hard and soft" considerations are not sufficient to explain this phenomenon, and one must take into account the fact that the coordination of a bidentate ligand is a multistep process with a transient monocoordinated species. The data show that the rate-determining step is the coordination of the first N atom of the ligand, and therefore, if this first step is assumed to be governed by the same factors as with CH_3CN, the k'_i decrease suggests that steric hindrance inhibits the coordination of the larger bipy and phen ligands.

The nucleophilic dependence of complex formation can be used to prove an associative mechanism. Taking the $n_{Pt}°$ values as a measure of nucleophilicity for the two ligands with the extreme rate constant values, Br^- ($n_{Pt}° = 4.18$) and TU ($n_{Pt}° = 7.17$), the nucleophilic discrimination factor S (eq 13) can be estimated as 0.3.

$$\log k = Sn°_{Pt} + c \tag{13}$$

For typical associative substitution mechanisms, as on Pt^{II} complexes, S varies between 0.6 and 1.4;[45] hence, an associative mechanism would be expected to give a much stronger dependence of the reaction rate on the nature of the incoming ligand. Moreover, although similar k'_i variations to the Pt^{II} complexes have been observed with $[Cp^*Rh(H_2O)_3]^{2+}$ and $[Cp^*Ir(H_2O)_3]^{2+}$ complexes, an I_d mechanism was found for the water exchange using variable pressure experiments. Although a mechanism cannot be definitively assigned at this point of the investigations, there is growing evidence to support a dissociatively activated interchange I_d mechanism for the water exchange and complex formation on **1**: the slightly positive $\Delta S_{ex}^{\ddagger}$ value, the observation that the water exchange process on **1** showed about the same rate in H_2O and in THF, and the reasonable agreement of the k'_i rate constants with k_{ex}. However, with the more reactive S-donor ligands, it is possible that a slight deviation in the complex formation mechanism occurs toward a more associative activation. A detailed insight into the complex formation mechanism could be obtained using high-pressure kinetic studies, as with the half-sandwich complexes of Rh^{III} and Ir^{III}, which would allow the conclusive determination of the water substitution mechanism on **1**.

Acknowledgment. We thank Dr. P. Osvath (Melbourne, Australia) for helpful advice and suggestions. Financial support by the Fonds der Chemischen Industrie, Frankfurt/M (to U.K. and K.H.), and by the Swiss National Science Foundation (R.H. and A.E.M.) is gratefully acknowledged. R.H. thanks Prof. W. Koppenol (ETH Zürich, Switzerland) for his kind hospitality.

Supporting Information Available: Additional equations, tables, and figures. X-ray crystallographic files including the structural data for $[(CO)_3Re(H_2O)(bipy)]CF_3SO_3$ (**2**) and $[(CO)_3Re(H_2O)(phen)](NO_3)_{0.5}(CF_3SO_3)_{0.5}\cdot H_2O$ (**3**), in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0341744

---

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

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