# The Organometallic *fac*-[(CO)₃Mn(H₂O)₃]⁺ Aquaion: Base-Hydrolysis and Kinetics of H₂O-Substitution

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The novel organometallic aqua complex [(CO)₃Mn(H₂O)₃]⁺ (**1⁺**) was obtained through hydrolysis of the analogous acetone complex. IR [$\nu_{CO}$ = 2051, 1944 cm⁻¹] and ¹⁷O NMR spectroscopy revealed the presence of a *fac* tricarbonyl unit. Potentiometric titrations established that the trimer [(CO)₃Mn₃(OH)₄]⁻ was the principal condensation product in the pH range >6 prior to slow formation of the tetramer [{(CO)₃Mn}(OH)]₄. Water exchange in **1⁺**, determined by NMR line broadening as $k_{ex}$ = 19 ± 4 s⁻¹ at 298 K, is four orders faster than with the analogous Re complex. The activation volume $\Delta V^{\ddagger}$ = −4.5 ± 0.4 cm³ mol⁻¹ is indicative of an associatively activated (I$_a$) process.

## Introduction

The chemistry of organometallic aqua ions, transition metal complexes featuring a $\pi$-cyclic ligand such as an $\eta^6$-arene or $\eta^5$-cp, olefin, or carbonyl with only water as the coligands, was hitherto mainly restricted to second and third row transition metals.[1−4] In search of a first row example, we sought to extend the series of group VII carbonyl aqua ions [(CO)₃M(H₂O)₃]⁺, M = Re, Tc,[2−4] to the first row congener Mn. Various (CO)$_n$Mn$^I$X(solvent) species have been reported in the literature.[5−7] Bamford and Coldbeck studied the

hydrolysis of Mn(CO)₅Cl in benzene/water and postulated that the [(CO)₃Mn(H₂O)₃]⁺ cation **1⁺** was present in neutral solution.[8] The stoichiometry of the Mn carbonyl aqua complex was derived mainly from the amount of CO liberated on hydrolysis of the pentacarbonyl complex, and there was no direct spectroscopic evidence for the tricarbonyl species. Moreover, the authors interpreted their results from potentiometric titrations as a sequence of deprotonations leading successively to neutral and anionic species [(CO)₃Mn-(H₂O)₂(OH)], [(CO)₃Mn(H₂O)(OH)₂]⁻, etc. Detailed investigation of the very stable analogous Re compound, *fac*-[(CO)₃Re(H₂O)₃]⁺, in neutral and alkaline solution has established the importance of condensation reactions in the course of deprotonation.[9] Similar polynuclear Mn$_x$(CO)$_y$(OH)$_z$ clusters were reported by Zaworotko for Mn.[10] The neutral, water insoluble monodeprotonated species, first prepared by

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Hieber and Stanner[11] and assigned the formula $[(CO)_3Mn(H_2O)_2(OH)]$ by them, is in fact most probably $[(CO)_3Mn(OH)]_4$.[12]

A more detailed characterization of the purported aqua ion ($1^+$) appeared highly desirable. Since $1^+$ is the first example of a 3d metal of these carbonyl aqua ions, such results would provide the first direct comparison of structurally analogous 3d, 4d, and 5d organometallic aqua complexes.

## Experimental Section

**General.** Infrared spectra were recorded on a Perkin-Elmer 1722x FT spectrometer using 0.1 mm $CaF_2$ windows for aqueous solutions. UV−vis spectra were recorded on a Polytech J&M diode array UV−vis spectrometer. $^{17}O$ NMR spectra were measured at 67.7 MHz on a Varian Unity 500 and at 54.2 MHz on a Bruker AM-400 spectrometer in 5 mm tubes. NMR measurements at high pressure were performed as described previously.[13]

**Solutions of $[(CO)_3Mn(H_2O)_3]^+$ ($1^+$).** The acetone complex $[(CO)_3Mn(acetone)_3]CF_3SO_3$ (2 mmol), prepared analogously to the perchlorate salt,[7] was dissolved in 100 mL of 0.01 M aqueous $CF_3SO_3H$, and the liberated acetone was removed under vacuum. The resulting aqueous solutions were handled and stored in the dark under nitrogen. To obtain solutions free from $Mn^{2+}$, a Dowex 50 W X2 column was charged with 100 mL of the above solution and eluted with 0.05 M triflic acid (600 mL). The concentration of $1^+$ in the resulting solution was determined by AAS ($3.26 \times 10^{-3}$ M). For NMR measurements, the ionic strength was adjusted to 0.1 M with $CF_3SO_3H$.

**Potentiometry and Evaluation of Equilibrium Constants.** Potentiometric titrations were carried out in a darkroom in a batchwise manner at 25.0 °C under nitrogen as described previously,[14] using a Metrohm 665 piston buret for the addition of base (0.1 M KOH). The pH ($-\log[H^+]$) as a function of time was registered on a PC using a Metrohm 713 pH/mV-meter and a combined glass electrode (Metrohm) with an internal Ag/AgCl reference. The electrode was calibrated by titrating $2 \times 10^{-3}$ M $HNO_3$ solutions with 0.1 M KOH ($pK_w = 13.79$). The ionic strength of all sample solutions was 0.1 M ($CF_3SO_3K$ or $KNO_3$). All equilibrium constants were calculated as concentration quotients using computer programs SUPERQUAD[15] and BEST.[16]

## Results

**Preparation and Characterization of $[(CO)_3Mn(H_2O)_3]^+$ ($1^+$).** The acetone complex $[(CO)_3Mn(acetone)_3]X$, X = $BF_4$, $ClO_4$, or $CF_3SO_3$, is a convenient starting material for the preparation of salts $[1]X$.[6] The protocol developed for the preparation of the aqua complex with $X^- = CF_3SO_3^-$ involves dehalogenation of $Mn(CO)_5Cl$ in $CH_2Cl_2$ using $AgCF_3SO_3$, separation of AgCl, and reflux of the residue in

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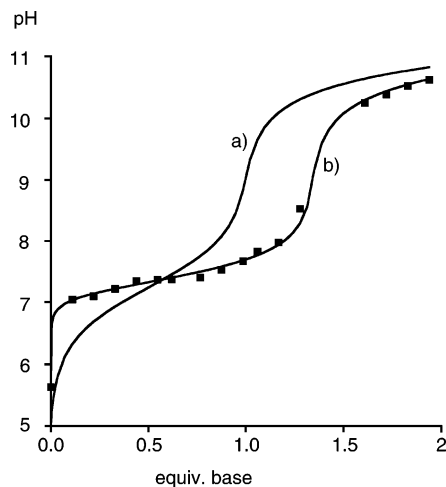(16) Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.* **1982**, *60*, 2403.

acetone overnight to effect decarbonylation. After evaporation of the solvent, $[(CO)_3Mn(acetone)_3]CF_3SO_3$ remains as a yellow oil that can be stored under nitrogen at low temperature for long periods of time without obvious decomposition. Dissolution of the oil in dilute aqueous $CF_3SO_3H$ (pH 2) gives a yellow ($\lambda_{max} = 387$ nm), light sensitive solution of $1^+$.[8] The IR spectrum of this solution has bands in the $\nu_{CO}$ region at 2051 (A1) and 1944 (E) $cm^{-1}$ consistent with a *fac*-tricarbonyl coordination. Cyclic voltammograms in $H_2O$/DMF 10:90 at a glassy carbon electrode exhibit an irreversible oxidation wave at 1.23 V versus SCE. The complex decomposes at pH 2 in daylight within some hours with evolution of CO (and $H_2$) to give clear colorless $Mn^{2+}$ solutions.

**Deprotonation and Hydrolytic Condensation.** Samples prepared by the above procedure contain up to 15% $Mn^{2+}$ as shown by the broadened water signal in the $^{17}O$ NMR spectrum. For titration experiments, solutions were passed through a cation exchange column, and $1^+$ was eluted with 0.05 M $CF_3SO_3H$ to separate it from $Mn^{2+}$. Bamford had already noted a change of the UV−vis characteristics of such solutions at elevated pH.[8] Formation of the corresponding species could conveniently be followed by IR spectroscopy. A tricarbonyl complex with $\nu_{CO}$ at 2008 and 1915 $cm^{-1}$ appeared as an intermediate above pH 6 after addition of base. This complex appeared to carry a negative charge as evidenced by its rapid precipitation as a $AsPh_4$-salt upon addition of $AsPh_4Cl$. The final product above pH 5 is the neutral heterocubane $[(CO)_3Mn(OH)]_4$,[10] which was identified by $\nu_{CO}$ bands at 2020 and 1921 $cm^{-1}$. The tetramer precipitated as a colorless solid after a few hours from solutions around pH 7.

The above-mentioned reactions with an anionic intermediate and the uncharged tetramer as the final product must obviously be interpreted in terms of an initial deprotonation of the aqua complex $1^+$, followed by condensation. A series of potentiometric titration experiments was performed to elucidate the course of these processes. In a conventional titration experiment, small increments of KOH were added slowly (1.5 h waiting time per point) to an acidified solution of $1^+$. However, the subsequent titration with $HNO_3$ showed a large hysteresis with the curve of the back-titration displaced toward lower pH. Moreover, the titration was complicated by slow precipitation of the tetramer around pH 6.5 after about 1 h. These observations are clear indications that the entire system was not in equilibrium. A batch procedure proved helpful to circumvent some of these problems. For this purpose, fresh sample solutions were used for each point of the titration curve. The required amount of base was added in one portion, and the pH was then registered as a function of time. Inspection of the pH versus time curves exhibited a strongly biphasic behavior with a rapid increase of pH at the beginning and a subsequent small but steady drift covering a period up to several hours.

It should be noted that an interpretation of such nonequilibrium conditions by means of thermodynamic formation constants is in general highly problematic. However, since the entire reaction pathway can be divided into two well

**Figure 1.** Titration curve of **1**⁺ constructed from the extrapolated data of the batch procedure. Curves represent the best fit (weighted least squares) for the two different models: (a) formation of the mononuclear $[(CO)_3Mn(H_2O)_2(OH)]$, and (b) formation of the trinuclear $[(CO)_9Mn_3(OH)_4]^-$.
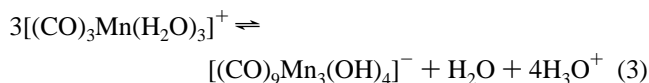
separated steps, the system can be analyzed in terms of a rapid pre-equilibrium, followed by a very slow consecutive step where only the forward reaction is significant. Although the pH versus time curve could not be described by an explicit rate law, the amount of base which was consumed by the latter reaction could be estimated by linear extrapolation, $pH_{(t=0)} = pH_{(\Delta t)} - \partial pH/\partial t_{(\Delta t)} \times \Delta t$. This procedure was used to calculate the hypothetical pH for a system, where equilibration of the first step is completed but consumption of base for the second step is negligible. The corresponding titration curve is shown in Figure 1. It exhibits a pH-jump at the addition of 1.33 equiv of base and a significantly flattened buffer region around pH 7−8. Both observations are clear indications for the formation of polynuclear species. In agreement with the IR data and the observation of an anionic intermediate, we interpret the first step as a rapid formation of the trinuclear $[(CO)_9Mn_3(OH)_4]^-$ (eq 1):

$$3[(CO)_3Mn(H_2O)_3]^+ + 4OH^- \rightleftharpoons$$
$$[(CO)_9Mn_3(OH)_4]^- + 9H_2O \quad (1)$$
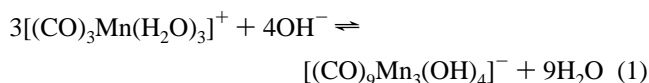
The second step corresponds obviously to the formation of the tetramer (eq 2):

$$[(CO)_9Mn_3(OH)_4]^- + [(CO)_3Mn(H_2O)_3]^+ \rightleftharpoons$$
$$[(CO)_3Mn(OH)]_4 + 3H_2O \quad (2)$$
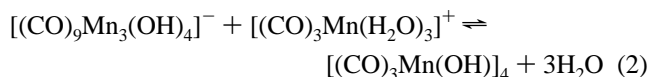
The experimental points of Figure 1 could be fitted satisfactorily by the two-component model of reaction 1. The overall formation constant $\beta_{3,-4} = [[(CO)_9Mn_3(OH)_4]^-] \times [\mathbf{1}^+]^{-3} \times [H^+]^4$ according to eq 3 was evaluated as log $\beta_{3,-4} = -23.7 \pm 0.1$.

$$3[(CO)_3Mn(H_2O)_3]^+ \rightleftharpoons$$
$$[(CO)_9Mn_3(OH)_4]^- + H_2O + 4H_3O^+ \quad (3)$$

It should be kept in mind that eqs 1−3 refer to stoichiometric overall processes, and that the experimental data do not provide any information about the mechanism of the
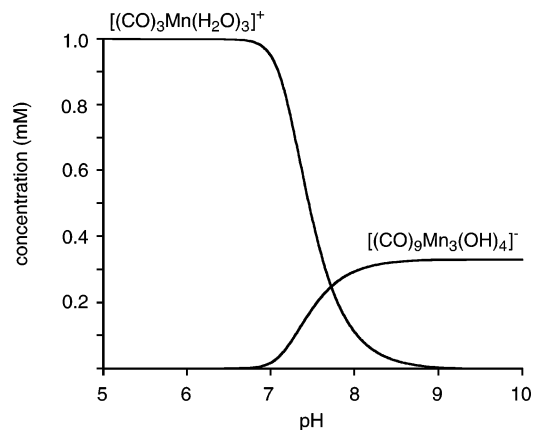


**Figure 2.** pH dependent distribution of principal species derived from the titration curve (Figure 1) using log $\beta_{3,-4} = -23.7$ for the formation of the trinuclear $[(CO)_9Mn_3(OH)_4]^-$ (total Mn concentration = 1.0 mM).

condensation reactions. It is obvious that further intermediates such as the mononuclear deprotonation product $[(CO)_3Mn(H_2O)_2(OH)]$, and possibly a dinuclear species such as $[(CO)_6Mn_2(H_2O)_2(OH)_2]$,[12] must be present prior to the formation of the trinuclear or tetranuclear complexes. In contrast to the Re-system, formation and subsequent decay of such early intermediates is too fast to be followed by potentiometric methods. Further aggregation occurs, and mono- or dinuclear hydroxo complexes do not participate to a significant extent in the pre-equilibrium (reaction 1) established after a few minutes (Figure 2).

**¹⁷O NMR Spectra and Water Exchange Kinetics.** ¹⁷O NMR spectra of aqueous solutions of **1**⁺, to which a few drops of ¹⁷O enriched water have been added, show two relatively sharp signals at ambient temperature at −65 and 389 ppm referred to (external) water. The signal of the bulk water is broadened by the presence of $Mn^{2+}$, arising from the synthesis (see above), and is not visible in the spectrum. The high field signal with line width 185 Hz at 30 °C is assigned to the coordinated water of **1**⁺ in accord with chemical shifts of water coordinated to numerous diamagnetic transition metal ions.[17] The much sharper low field signal is attributed to the carbonyl oxygen. Its chemical shift is at rather low field which is typical for Mn carbonyls. This signal gained in intensity slowly due to ¹⁷O exchange indicating a water gas shift related chemistry, eq 4, occurring at the carbonyl groups of **1**⁺.
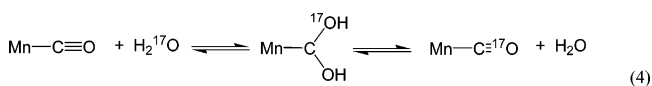


This type of carbonyl oxygen exchange was not found for the Re-congener. It has, however, been observed in $[Ru(CO)_3(H_2O)_3]^{2+}$ and in a number of related carbonyl aqua ions of $Ru^{II}$.[18]

The signal for water coordinated to **1**⁺ broadens with increasing temperature, allowing the determination of the water exchange rate by the usual line broadening technique.

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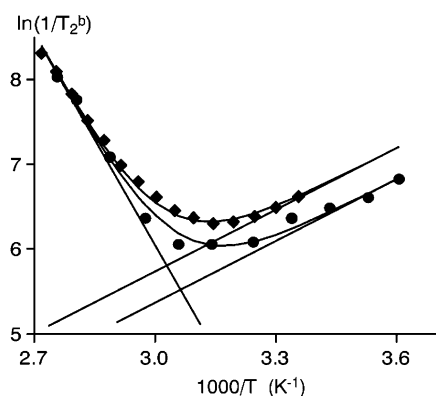
**Figure 3.** Temperature dependence of the logarithm of the transverse relaxation rate $1/T_2^b$ obtained from the $^{17}$O NMR signal of the bound water in $\mathbf{1}^+$ measured at 67.74 MHz in D$_2$O ($\blacklozenge$) and 54.25 MHz in H$_2$O ($\bullet$): $\mathbf{1}^+$ 0.02 M, CF$_3$SO$_3$H 0.1 M; $^{17}$O 12% enriched (D$_2$O) or 6% (H$_2$O). The lines represent a simultaneous nonlinear least-squares fit to all data points displayed.

In the slow exchange limit, the transverse relaxation rate ($\pi \times$ line width at half-height in Hz) of bound water in $[(CO)_3Mn(H_2O)_3]^+$ is given by eq 5, where $\tau$ is the mean lifetime of H$_2$O in the first coordination sphere, and T$_{2Q}^b$ is the quadrupolar relaxation time.

$$1/T_2^{\,b} = 1/\tau + 1/T_{2Q}^{\,b} \qquad (5)$$

From transition state theory, the temperature dependence of $\tau$ and its relation to $k_{ex}$, the pseudo-first-order rate constant for the exchange of a particular H$_2$O molecule are described by eq 6, where $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are the entropy and enthalpy of activation, respectively, and the other symbols have their usual meanings.

$$\frac{1}{\tau} = k_{ex} = \frac{k_b T}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}\right) = \frac{k_{ex}^{298} T}{298.15} \exp\left[\frac{\Delta H^{\ddagger}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \quad (6)$$

An Arrhenius temperature dependence can be assumed for the quadrupolar relaxation rate (eq 7) where $(T_{2Q}^b)^{298}$ is the contribution at 298.15 K and $E_Q^b$ is the corresponding activation energy.

$$\frac{1}{T_{2Q}^{\,b}} = \left(\frac{1}{T_{2Q}^{\,b}}\right)^{298} \exp\left[\frac{E_Q^{\,b}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \qquad (7)$$

At low temperatures, slightly different line widths were found in D$_2$O and H$_2$O due to the greater viscosity of D$_2$O, which in turn affects the quadrupolar relaxation. The temperature dependent line widths in both solvents were fitted simultaneously and are depicted in Figure 3. The fitting procedure gives the following kinetic parameters: $k_{ex} = 19 \pm 4$ s$^{-1}$ at 298 K, $\Delta H^{\ddagger} = 68.0 \pm 3$ kJ mol$^{-1}$, $\Delta S^{\ddagger} = 7.7 \pm 9$ J mol$^{-1}$ K$^{-1}$. Quadrupolar relaxation parameters were evaluated as $1/T_{2Q}(H_2O)^{298} = 509 \pm 19$ s$^{-1}$, $1/T_{2Q}(D_2O)^{298} = 734 \pm 26$ s$^{-1}$, $E_Q = 19.9 \pm 2$ kJ/mol.

In order to determine the activation volume $\Delta V^{\ddagger}$, a pressure study was undertaken, recording the line width and respective
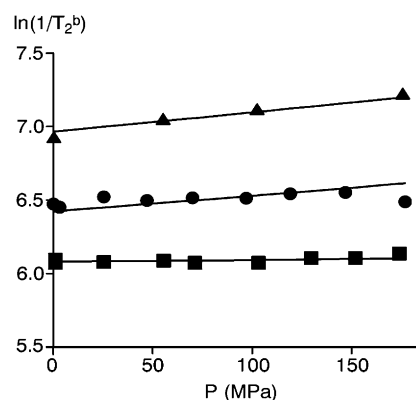
**Figure 4.** Pressure dependence of the logarithm of the transverse relaxation rate $1/T_2^b$ from the $^{17}$O NMR signal of $\mathbf{1}^+$ at 309.4 K ($\blacksquare$), 334.6 K ($\bullet$), and 343.3 K ($\blacktriangle$). The lines represent a simultaneous nonlinear least-squares fit to all data points displayed.

transverse relaxation rate of the coordinated water signal at three different temperatures, 309.4, 334.6, and 343.3 K, and at pressures between 0.1 and 177 MPa (Figure 4). The pressure dependence of the line width increases with increasing temperature due to the fact that an increasing proportion of the line width is affected by exchange broadening. At higher temperature, however, the line width is such that a vast number of transients had to be accumulated to obtain a reasonable spectrum.

The variable pressure dependence of $k_{ex}$ can be described by eq 8, since we can assume that the corresponding volume of activation $\Delta V_{ex}^{\ddagger}$ is pressure independent, as is usual for simple solvent-exchange reactions. $k_{ex,0}$ is the exchange rate at zero pressure.

$$k_{ex,p} = k_{ex,0} \exp(-P\Delta V_{ex}^{\ddagger}/RT) \qquad (8)$$

A similar equation, eq 9, describes the pressure dependence of the quadrupolar relaxation rate as a function of the quadrupolar activation volume $\Delta V_Q^{\ddagger}$ and the contribution at zero pressure $(1/T_{2Q}^b)_0$.

$$(1/T_{2Q}^{\,b})_p = (1/T_{2Q}^{\,b})_0 \exp(-P\Delta V_Q^{\ddagger}/RT) \qquad (9)$$

At low temperature (309.4 K), the contribution of $k_{ex,0}$ to $1/T_{2,0}^b$ is 12%, and its value was fixed from the VT experiments in the fitting procedure. On the contrary, at higher temperatures (334.6 and 343.3 K), the contributions of $1/T_{2Q}^b,_0$ to $1/T_{2Q}$ were small, 34% and 17%, respectively, and fixed. The activation volumes found for water exchange and for quadrupolar relaxation of bound water in $\mathbf{1}^+$ were $\Delta V_{ex}^{\ddagger} = -4.5 \pm 0.4$ cm$^3$ mol$^{-1}$ and $\Delta V_Q^{\ddagger} = 0.3 \pm 0.6$ cm$^3$ mol$^{-1}$, respectively.

**Discussion**

The Mn carbonyl aqua ion together with its Tc and Re congener is one of the rare cases, where the complete set of 1st, 2nd, and 3rd row transition metal aqua ions with an identical coordination environment can be compared. The +I oxidation state is rather uncommon for aqueous chemistry in general, and specifically for $\sigma$-ligand coordination compounds of Mn, Tc, and Re. Complexes $[(Mn, Tc, Re)(L_\sigma)_n]^+$

would be strongly reducing. It is the CO groups that, in stabilizing the $t_{2g}$ orbitals by back-bonding, effect a low spin configuration and, by shifting the oxidation potential $M^{2+/+}$ to a more positive value, stabilize the monovalent species.

The $pK_a$ of $[(CO)_3Re(H_2O)_3]^+$ (7.6) is unusually low for a $M^+$ aqua ion.[14] Although the determination of $pK_a$ for $1^+$ is not possible due to rapid condensation in the course of the first deprotonation, a $pK_a$ of 9–10 may be envisaged for the Mn complex. This is higher than for the Re congener. The estimate follows from the observation that the trinuclear anions as the main condensation products form around pH 5–6 (Re) and pH 7–8 (Mn). Intriguingly, the $pK_a$ values for these monopositive triaqua ions are of the same order as those quoted for the dipositive hexaaqua transition metals.[17]

No dimer of the form $[(CO)_3Mn(\mu_2\text{-OH})_3Mn(CO)_3]^-$ was observed. This is in contrast to the Re system, where a corresponding dinuclear complex has been isolated and characterized.[9c] Since the OH⁻/M ratio in such a dimer is 3:2, its predominant formation is at higher pH than that of the trimer. In the Re system, the dimer is predominantly formed in strongly alkaline solution. Since deprotonation and subsequent condensation reactions appear to take place at a higher pH in the Mn system, the dimer may not form substantially in the pH range that was investigated.

According to general trends in transition metal groups, ligand exchange for the Mn complex is expected to be more rapid than for Tc and Re. The fast initial pH shift on titration resulting from reaction 1 is indicative of this. The batch titration curve of Figure 1 can be modeled satisfactorily with a two species model involving only $1^+$ and the trimer $[(CO)_9Mn_3(OH)_4]^-$ (Figure 2). This means that the rapid reactions comprise deprotonation and subsequent condensation to give the trimer. Such condensation reactions take more than 300 times longer for the analogous Re complexes. It has not proved possible to obtain salts of the trimer suitable for X-ray analysis, but we propose a structure similar to the Re congener, i.e., $[\{(CO)_3Mn(\mu_2\text{-OH})\}_3(\mu_3\text{-OH})]^-$.[9c]

The water exchange rate in $1^+$, characterized by $k_{ex}^{298} = 19 \pm 4$ s⁻¹, is almost 4 orders of magnitude larger than the value for the corresponding Re complex ($k_{ex}^{298} = 6.3 \times 10^{-3}$ s⁻¹).[3] For $[(CO)_3Tc(H_2O)_3]^+$, only a preliminary report on the water exchange kinetics has been published.[2] The half-life at 277 K has been estimated as 1 s to 1 min. The Mn complex is thus the most labile of the triad, and the exchange rate decreases in the order Mn > Tc > Re. Faster exchange of the Mn congener may be expected when comparing substitutional lability of 3d with the corresponding 4d/5d complexes. Examples for water exchange in such a series are, however, scarce because in most cases either the spin state or the coordination number is different. In fact, in the only complete triad of structurally identical transition aqua ions, Co³⁺ ($k_{ex}^{298} \approx 10^{-5}$–$10^{-6}$ s⁻¹), Rh³⁺ ($k_{ex}^{298} = 2.2 \times 10^{-9}$ s⁻¹), Ir³⁺ ($k_{ex}^{298} = 1.1 \times 10^{-10}$ s⁻¹), the value for [Co-$(H_2O)_6]^{3+}$ is uncertain due to the unavoidable presence of Co²⁺ and the very fast water exchange in the latter along

with rapid homogeneous Co³⁺/Co²⁺ electron transfer.[19] Moreover, it should be noted that this order can be reversed in organometallic aqua species. Thus, water exchange in $[Cp^*Co(bipy)(H_2O)]^{2+}$ was found to be more than three orders slower than in the corresponding Rh and Ir complexes.[20] In this particular case, the reversed order was attributed to the strong labilizing effect of the Cp* ($\eta^5$-C₅-Me₅) ligand (the effect of bipy on water exchange is rather small) which is much more pronounced for the heavier ($10^{12}$–$10^{13}$) as compared to the lighter metals. In contrast, it appears that the trend in the carbonyl aqua series $[(CO)_3M-(H_2O)_3]^+$ (M = Mn, Tc, Re) is the same as for the hexaaqua metal complexes.

The activation volume determined for water exchange in $1^+$ as $-4.5 \pm 0.4$ cm³ mol⁻¹ is indicative of an associative activation mode ($I_a$ or A mechanism).[17] For the Re cation, the exchange data were interpreted in terms of a dissociative interchange $I_d$ mechanism.[3] The change from $I_a$ to $I_d$ when going from the lighter to the heavier congener in the same group is remarkable. As shown in a recent investigation, the substitution behavior of $[(CO)_3Re(H_2O)_3]^+$ depends on the hardness of the entering ligand. A changeover of the reaction mechanism from $I_d$ with a hard donor to $I_a$ with a soft donor ligand was observed.[4] We do not yet know whether and how the mechanism of the substitution reaction of $1^+$ depends on the nature of the entering ligand.

The present investigation has provided the first detailed kinetic characterization of an organometallic 3d transition metal aqua complex. Such species not only are indispensable for a better understanding of bonding and ligand stability in transition metal coordination compounds but also may have implications for synthetic strategies. The relatively labile water ligands are readily substituted for a great variety of other σ-ligands under very smooth conditions, opening a vast array of mixed σ-/π-ligand coordination chemistry.

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