

Mechanism for Solvent Exchange on *trans*-[Os(en)₂(η²-H₂)S]²⁺Urban Frey,^{*,1} Zai-Wei Li,² and Anne Matras¹

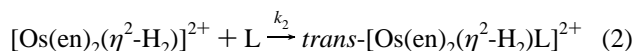
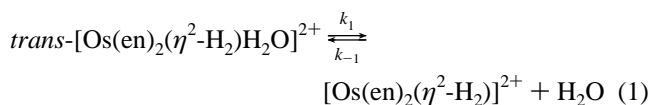
Institut de Chimie Minérale et Analytique, Université de Lausanne, BCH, CH-1015 Lausanne, Switzerland, and Department of Chemistry, Stanford University, Stanford, California 94305

Received August 18, 1995[⊗]

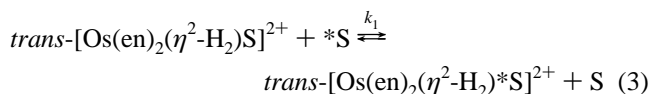
Solvent exchange on *trans*-[Os(en)₂(η²-H₂)S]²⁺ (S = H₂O, CH₃CN) has been studied in neat solvent as a function of temperature and pressure by ¹⁷O NMR line-broadening and isotopic labeling experiments (S = H₂O) and by ¹H NMR isotopic labeling experiments (S = CH₃CN). Rate constants and activation parameters are as follows for S = H₂O and CH₃CN, respectively: $k_{\text{ex}}^{298} = 1.59 \pm 0.04$ and $(2.74 \pm 0.03) \times 10^{-4} \text{ s}^{-1}$; $\Delta H^\ddagger = 72.4 \pm 0.5$ and $98.0 \pm 1.4 \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = +1.7 \pm 1.8$ and $+15.6 \pm 4.9 \text{ J mol}^{-1} \text{ K}^{-1}$; $\Delta V^\ddagger = -1.5 \pm 1.0$ and $-0.5 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$. The present investigation of solvent exchange when compared with a previous study on substitution reactions on the same complexes leads to the conclusion that substitution reactions on these compounds undergo an interchange dissociative, I_d, or dissociative, D, reaction mechanism, where solvent dissociation is the rate-limiting step.

Introduction

The chemistry of dihydrogen complexes has attracted much attention³ since their initial discovery by Kubas and co-workers.⁴ Taube and co-workers⁵ recently reported a series of tetraamine osmium dihydrogen complexes of the form [Os^{II}N₄(η²-H₂)S] (N₄ = (NH₃)₄ or (en)₂ (en = ethylenediamine) and S = variable ligand) in which H₂ release is observed only in the case where the variable ligand is a strong π acid. Substitution reactions, as well as the *trans*–*cis* isomerization reaction exhibited by these complexes, were reported recently.⁶ Evidence was obtained to support the conclusion that substitution may take place through a dissociative, D, mechanism by loss of a ligand, H₂O, in the case of *trans*-[Os^{II}N₄(η²-H₂)H₂O]²⁺ as shown in eqs 1 and 2. However, for the fundamental reaction of solvent



exchange, kinetic data such as rate constants and activation parameters were missing. Therefore, to address this concern, we have investigated the exchange reaction (eq 3) where S =



H₂O and CH₃CN. This study was undertaken to obtain a better understanding of the reaction mechanism for solvent exchange

as well as for ligand substitution reactions. The reaction rates as a function of temperature and pressure were followed, and the kinetic parameters were determined and then compared to those obtained for other substitution reactions. A reaction pathway for solvent exchange of these dihydrogen complexes was then inferred.

Experimental Section

Materials and Solutions. The complexes [Os(en)₂(η²-H₂)](trif)₂ (trif = triflate; en = ethylenediamine) and *trans*-[Os(en)₂(η²-H₂)CH₃CN](trif)₂ were prepared according to literature methods.⁶ ¹⁷O-enriched water (Yeda) and CH₃CN were degassed under argon prior to use. The solutions used for the NMR measurements were freshly prepared in a nitrogen-filled glovebox. All samples were prepared by weight by adding the solvent directly to the reagent. Consequently, concentrations are given in terms of molality, *m*, in moles per kilogram of solvent. As the dihydrogen complexes are sensitive to air, all the manipulations were done in the absence of O₂ (<1 ppm) and, in the case of the acetonitrile complex, in the absence of H₂O (<2 ppm) as well. The aqua-substituted complex *trans*-[Os(en)₂(η²-H₂)H₂O]²⁺ (**1**) was obtained by dissolving [Os(en)₂(η²-H₂)](trif)₂ in water. The concentrations of the solutions were 0.3 *m* in complex and 10 atom % H₂¹⁷O for the variable-temperature and -pressure study and 0.3 *m* in complex and 6 atom % H₂¹⁷O for the fast-injection experiments. The concentrations of the solutions containing *trans*-[Os(en)₂(η²-H₂)CH₃CN]²⁺ (**2**) were 0.05 *m* in complex.

Measurements. The ¹⁷O NMR spectra were recorded by using a Bruker AM-400 spectrometer equipped with a 9.4 T wide-bore cryomagnet working at 54.2 MHz, and the ¹H NMR spectra were recorded by using a Bruker ARX-400 spectrometer equipped with a 9.4 T narrow-bore cryomagnet working at 400.18 MHz. The ambient-pressure measurements were followed in a commercial thermostated probe, and the temperature was found to be constant within ±0.2 K as measured by a substitution technique.⁷ Variable-pressure measurements were made up to 200 MPa by using a high-pressure probe.⁸ The fast-injection measurements were made with use of equipment described in a previous publication.⁹

The variable-temperature (variable-pressure) ¹⁷O NMR spectra were obtained using a 90° pulse length of 14 μs (12 μs) in the quadrature detection mode, with 4K data points resulting from 7000–10000 scans

[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1996.

- (1) University of Lausanne.
- (2) Stanford University.
- (3) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (c) Morris, J. H.; Jessop, P. G. *Coord. Chem. Rev.* **1992**, *121*, 155. (d) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.
- (4) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.
- (5) (a) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946. (b) Li, Z.-W.; Taube, H. *Science* **1992**, *256*, 210. (c) Li, Z.-W.; Yeh, A.; Taube, H. *J. Am. Chem. Soc.* **1993**, *115*, 10384.
- (6) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 9506.

(7) Amman, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319.

(8) Frey, U.; Helm, L.; Merbach, A. E. *High Pressure Res.* **1990**, *2*, 237.

(9) Bernhard, P.; Helm, L.; Ludi, A.; Merbach, A. E. *J. Am. Chem. Soc.* **1985**, *107*, 312.

accumulated over a total spectral width of 15 kHz. Bulk water signal suppression and maximum excitation of the bound water signal was obtained by use of the “1, -3, 3, -1” pulse sequence,¹⁰ i.e., 11.25°-D2-(-33.75°)-D2-(33.75°)-D2-(-11.27°)-acquisition, with D2 = 1/(2Δω) where Δω is the chemical shift difference between the bulk and the bound water signals in Hertz. A line broadening (LB) of 5–10% of the line width at half-height, Δν_{1/2}, of the coordinated water signal was applied. The NMR signal was fitted to a Lorentzian curve, and the transverse relaxation rate, 1/T₂^b, was obtained from Δν_{1/2} corrected for the LB by using the relation 1/T₂^b = π(Δν_{1/2} - LB). The spectra from the fast-injection experiments were obtained under the same conditions as for the variable-temperature measurements. However, only 200 scans with 1K data points were accumulated. The ¹⁷O NMR spectra were referenced to the bulk water signal.

The variable-temperature (variable-pressure) ¹H NMR spectra were obtained using a 90° pulse length of 6 μs (10 μs) in the quadrature detection mode, with 16K data points resulting from 16 scans accumulated over a total spectral width of 2760 Hz. ¹H NMR chemical shifts are referred to tetramethylsilane (TMS) and measured with respect to the nondeuterated solvent CH₃CN at 2.10 ppm.

Computational Methods. The analysis of the experimental data was accomplished by a nonlinear least-squares program fitting the values of the desired parameters. Reported errors are one standard deviation.

Results

Water Exchange on *trans*-[Os(en)₂(η²-H₂)H₂O]²⁺ (1). The water exchange on **1** (eq 3) was followed by ¹⁷O NMR line-broadening and isotopic labeling experiments. The ¹⁷O NMR spectrum of a dilute aqueous solution of **1** shows two resonances: an intense peak due to the bulk water and a small peak at -47 ppm due to the coordinated water. This small peak is difficult to detect and to analyze by line shape methods. To compensate, a solvent suppression pulse sequence was used, resulting in a ~1000-fold depression of the bulk water signal, and thus allowing the accurate detection and analysis of the bound-water signal. In the slow-exchange limit, the transverse relaxation rate of the ¹⁷O NMR signal of water bound to a diamagnetic metal center is given by eq 4, where T_{2Q}^b is the

$$1/T_2^b = 1/T_{2Q}^b + 1/\tau \quad (4)$$

quadrupolar relaxation time and τ is the mean lifetime of water in the first coordination sphere. The temperature dependence of 1/τ and its relation to the pseudo-first-order exchange rate constant, *k*, can be expressed by eq 5, where Δ*S*[‡] and Δ*H*[‡] are

$$1/\tau = k = k_b T/h \exp\left(\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}\right) \quad (5)$$

the entropy and enthalpy of activation, respectively. An Arrhenius temperature dependence can be assumed for the quadrupolar relaxation rate (eq 6) where (1/T_{2Q}^b)²⁹⁸ is the contribution at 298.15 K and E_Q^b is the corresponding activation energy.

$$1/T_{2Q}^b = (1/T_{2Q}^b)^{298} \exp[E_Q^b/R(1/T - 1/298.15)] \quad (6)$$

For the coordinated water in **1**, 1/T₂^b is dominated by the quadrupolar relaxation term over most of the temperature domain under investigation. To obtain accurate activation parameters, we performed two isotopic labeling experiments at low temperature. The water exchange was followed by monitoring the enrichment of the aqua complex in ¹⁷O after fast-injection of oxygen-17-enriched water into a solution of

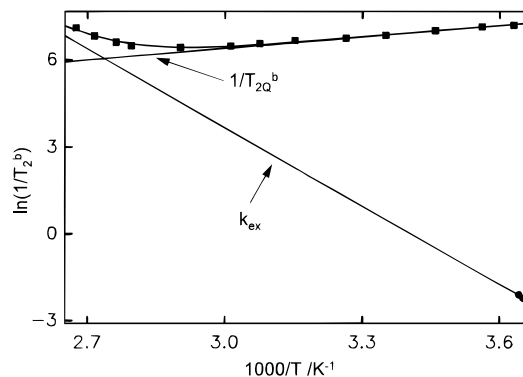


Figure 1. Temperature dependence of 1/T₂^b (■) from the bound water ¹⁷O NMR signal of *trans*-[Os(en)₂(η²-H₂)H₂O](trif)₂ in aqueous solutions. (●) *k* obtained from fast-injection experiments. Concentrations are given in the Experimental Section.

Table 1. Derived NMR and Kinetic Parameters for the Variable-Temperature and -Pressure Studies of Solvent Exchange on *trans*-[Os(en)₂(η²-H₂)S]²⁺

	S = H ₂ O	S = CH ₃ CN
<i>k</i> ²⁹⁸ /s ⁻¹	1.59 ± 0.04	(2.74 ± 0.03) × 10 ⁻⁴
Δ <i>H</i> [‡] /kJ mol ⁻¹	72.37 ± 0.5	97.98 ± 1.4
Δ <i>S</i> [‡] /J mol ⁻¹ K ⁻¹	+1.7 ± 1.8	+15.6 ± 4.9
Δ <i>V</i> [‡] /cm ³ mol ⁻¹	-1.5 ± 0.5	-0.5 ± 0.2
(1/T _{2Q} ^b) ²⁹⁸ /s ⁻¹	945 ± 14	
E _Q /kJ mol ⁻¹	10.9 ± 0.5	
Δ <i>V</i> _Q [‡] /cm ³ mol ⁻¹	+0.4 ± 0.3	

the complex. The data were fitted according to eq 7, where

$$h_b = h_{b\infty}[1 - \exp(-kt/(1 - P_m))] \quad (7)$$

*h*_{b∞} is the height of the bound water peak at *t* = ∞ and *P*_m is the mole fraction of coordinated water calculated from the concentrations. The adjustable parameters are *h*_{b∞} and *k*. The experiments (Supporting Information, Figures S1 and S2) were performed at 273.9 K (*k* = 0.109 ± 0.006 s⁻¹) and at 274.6 K (*k* = 0.122 ± 0.014 s⁻¹). These low-temperature *k* values were added to the 1/T₂^b data (Table S1) and eqs 4–6 were fitted to the global data set. The resulting quadrupolar relaxation and exchange parameters are listed in Table 1, and the experimental data are represented in Figure 1.

The pressure dependence of ln *k* can be described by the linear equation (8), since we can assume that the corresponding

$$\ln k = \ln k_0 - P\Delta V^\ddagger/RT \quad (8)$$

volumes of activation, Δ*V*[‡], are pressure independent as is usual for simple solvent exchange reactions; *k*₀ is the exchange rate at zero pressure. A similar equation (9) describes the pressure

$$\ln(1/T_{2Q}^b) = \ln(1/T_{2Q}^b)_0 - P\Delta V_Q^\ddagger/RT \quad (9)$$

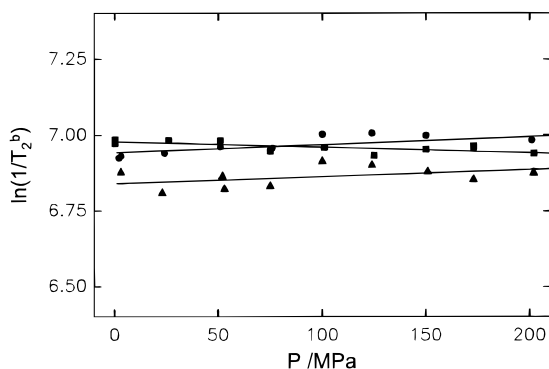
dependence of the quadrupolar relaxation rate as a function of the quadrupolar activation volume Δ*V*_Q[‡] and the contribution at zero pressure (1/T_{2Q}^b)₀. The transverse relaxation rates were determined at pressures up to 200 MPa and at three temperatures to define the quadrupolar (one low-temperature) and kinetic (two high-temperatures) pressure dependence. The data (Table S2) was fitted simultaneously to eqs 4, 8, and 9. In theory, *k*₀ and (1/T_{2Q}^b)₀ at each temperature could be fixed at the values obtained from the variable-temperature analysis. In practice, small differences in temperature calibration between the variable-temperature and variable-pressure experiments could cause nonrandom errors in the 1/T₂^b measurements. Thus, those parameters that contributed to the smaller part of Δ*V*[‡] values were

(10) Hore, P. J. *J. Magn. Reson.* **1983**, *55*, 283.

Table 2. Derived NMR and Kinetic Parameters for the Variable-Pressure Studies of Water Exchange on $trans\text{-}[\text{Os}(\text{en})_2(\eta^2\text{-H}_2)\text{H}_2\text{O}]^{2+}$ ^a

<i>T</i> /K	<i>k</i> ₀ /s ⁻¹	% <i>k</i> ₀ ^b	(1/ <i>T</i> _{2Q} ^b) ₀ /s ⁻¹	% (1/ <i>T</i> _{2Q} ^b) ₀ ^b	1/ <i>T</i> ₂ ^b /s ⁻¹	1/ <i>T</i> ₂ ^b /s ^{-1c}
284.2	(0.4)	0.1	1072 ± 14	99.9	1072	1176
369.3	529 ± 10	56.7	(406)	43.4	935	943
371.0	635 ± 11	61.3	(400)	38.7	1035	1011

^a The values within parentheses were fixed to the values obtained from the variable-temperature study during the fitting procedure. ^b Each contribution is expressed as a percentage of the value of 1/*T*₂^b. ^c 1/*T*₂^b values as obtained from the variable-temperature study.

**Figure 2.** Pressure dependence of the transverse relaxation rate, 1/*T*₂^b, for $trans\text{-}[\text{Os}(\text{en})_2(\eta^2\text{-H}_2)\text{H}_2\text{O}](\text{trif})_2$ aqueous solutions: (■) *T* = 284.2 K; (▲) *T* = 369.3 K; (●) *T* = 371.0 K. Concentrations are given in the Experimental Section.**Table 3.** Rate Constants, *k*, of Acetonitrile Exchange on $trans\text{-}[\text{Os}(\text{en})_2(\eta^2\text{-H}_2)\text{CH}_3\text{CN}]^{2+}$ (5×10^{-2} m) in Deuterated Acetonitrile at Variable-Temperature

<i>T</i> /K	<i>k</i> /s ⁻¹	<i>T</i> /K	<i>k</i> /s ⁻¹
278.7	(1.62 ± 0.01) × 10 ⁻⁵	300.1	(3.49 ± 0.01) × 10 ⁻⁴
279.6	(1.86 ± 0.01) × 10 ⁻⁵	305.6	(6.86 ± 0.04) × 10 ⁻⁴
288.5	(7.42 ± 0.09) × 10 ⁻⁵	312.1	(1.78 ± 0.08) × 10 ⁻³
293.7	(1.27 ± 0.01) × 10 ⁻⁴		

Table 4. Rate Constants, *k*, of Acetonitrile Exchange on $trans\text{-}[\text{Os}(\text{en})_2(\eta^2\text{-H}_2)\text{CH}_3\text{CN}]^{2+}$ (5×10^{-2} m) in Deuterated Acetonitrile at 298.4 K and at Different Pressures

<i>P</i> /MPa	<i>k</i> /s ⁻¹	<i>P</i> /MPa	<i>k</i> /s ⁻¹
0	(2.72 ± 0.06) × 10 ⁻⁴	160	(2.78 ± 0.03) × 10 ⁻⁴
84	(2.81 ± 0.08) × 10 ⁻⁴	200	(2.85 ± 0.05) × 10 ⁻⁴

fixed at their atmospheric pressure values. The *k*₀ and (1/*T*_{2Q}^b)₀ values, fixed and fitted, are reported in Table 2, the corresponding activation volumes are given in Table 1, and the experimental data are shown in Figure 2.

Acetonitrile Exchange on $trans\text{-}[\text{Os}(\text{en})_2(\eta^2\text{-H}_2)\text{CH}_3\text{CN}]^{2+}$ (2). The exchange (eq 3) was followed by monitoring the decrease of the bound acetonitrile ¹H NMR signal (2.75 ppm) after dissolution of 2 in deuterated acetonitrile. The time dependence of the signal height, *h*_b, which is proportional to the mole fraction, *x*, was fitted to eq 10. With *h*_{b0} = *h*_b at *t* =

$$h_b = h_{b\infty} + (h_{b0} - h_{b\infty}) \left[\exp\left(-\frac{kt}{1 - P_m}\right) \right] \quad (10)$$

0; *P*_m was calculated from the concentrations. The adjustable parameters were *h*_{b∞}, *h*_{b0}, and *k*. The increase in intensity of the proton NMR signal of free CH₃CN (2.100 ppm) was not monitored due to its overlap with the CD₂H₂CN signal. The variable-temperature and variable-pressure rate constants (Tables 3 and 4) were fitted to eqs 5 and 8, respectively, leading to the kinetic parameters given in Table 1.

Discussion

The obtained rate constants for water exchange on $trans\text{-}[\text{Os}(\text{en})_2(\eta^2\text{-H}_2)\text{H}_2\text{O}]^{2+}$ were compared to the rate constants for substitution reactions on the same complex obtained previously.⁶ The proposed D mechanism for these substitution reactions (eqs 1 and 2) leads to the rate law

$$k_{\text{obs}} = -d[\text{Os}(\text{en})_2(\text{H}_2)\text{S}^{2+}]/dt = \frac{k_1 k_2 [\text{L}]}{k_{-1} + k_2 [\text{L}]}$$

At sufficiently high [L] (where *k*₂[L] ≫ *k*₋₁), *k*_{obs} becomes independent of [L] and the value of *k*_{obs} reaches the limit of *k*₁. This behavior was observed at 293 K for the entering nucleophiles N₃⁻, CH₃CO₂⁻, and Co(CN)₆³⁻, and the limiting values of *k*_{obs} were 0.36, 0.31, and 0.33 s⁻¹, respectively.⁶ These rate constants are the rates at which water is released from 1 and, therefore, should be the same as the rate constant for water exchange. At 293 K, the rate constant for water exchange on 1 is 0.95 s⁻¹. This value is a factor 3 larger than the observed limiting rate constants for the substitution reactions. The difference can be attributed in part to the fact that the rate constants for the substitution reactions were obtained at relatively high concentrations of nucleophiles. Furthermore, when comparing substitution reactions with solvent exchange reactions, one should also take into account a statistical factor.¹¹ This factor describes the difference in probability of replacing the single water molecule in the first coordination sphere by a unique ligand in the second sphere for the substitution reaction, compared to the eight (or twelve) water molecules in the second coordination sphere for the water exchange reaction. Neglecting all steric or electronic influences, this statistical factor could be as small as 1/8 or 1/12 for eight or twelve molecules in the second coordination sphere, respectively. Therefore, the observed rate constant for substitution reactions must be smaller than the exchange rate constant. These observations support the proposed dissociative mode of activation for substitution reactions on $trans\text{-}[\text{Os}(\text{en})_2(\eta^2\text{-H}_2)\text{H}_2\text{O}]^{2+}$, where the water exchange reaction is the limiting step.

The acetonitrile exchange on $trans\text{-}[\text{Os}(\text{en})_2(\eta^2\text{-H}_2)\text{CH}_3\text{CN}]^{2+}$ is approximately 4 orders of magnitude slower than the water exchange (Table 1). The rate constant at 293 K (Table 3) is in satisfactory agreement with the preliminary value⁶ of 2.2 × 10⁻⁴ s⁻¹. The enormous difference in reactivity upon going from H₂O to CH₃CN can be explained by a higher thermodynamic stability for the softer acetonitrile ligand which is bound to the soft Os(II) center. An increase in the stability of the complex disfavors bond breaking for the leaving ligand, and therefore, in a dissociative reaction pathway, the rate constant for solvent exchange will decrease. The previously measured equilibrium constant for complex formation of the acetonitrile complex in deuterated water, *K*_{eq} = [2][D₂O]/[1][CH₃CN], is 2 × 10⁴. Thus, the increase in stability of the acetonitrile complex compared to the aqua complex, the decrease of the rate constant for solvent exchange by the same order of magnitude (×10⁴), and the observation that the complex formation reaction of 2 with NCS⁻ was found to be independent of the concentration of the entering nucleophile⁶ indicate that the exchange and substitution mechanisms for both complexes proceed *via* a dissociative mode of activation. Such a dissociative interchange, I_d, or dissociative, D, mechanism, may be expected to be favored by the electronic rearrangement of [Os^{II}(en)₂(H₂)²⁺ into the dihydride [Os^{IV}(en)₂(H)₂]²⁺. This would stabilize the transition state and/or the 16e⁻ intermediate. Such a dihydrogen-

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

dihydride equilibrium has been observed by Kubas and co-workers for similar $18e^-$ systems.¹²

Interestingly, for both reactions investigated, the values obtained for the entropies of activation are close to zero and could therefore be taken as indicative of an interchange mechanism. However, the errors on these values are normally much greater than the reported standard deviation owing to the small temperature interval examined and the resulting extrapolation of the Eyring equation (eq 5) to obtain the activation entropy. So, the use of this parameter in the assignment of reaction mechanisms must be treated with care. Upon initial inspection, the near-zero values obtained for the activation volumes appear to be in contradiction with an I_d or D mechanism. However, if we consider that the substitution and exchange processes can be accompanied by an electronic rearrangement from dihydrogen–Os(II) to dihydride–Os(IV), the observed activation volume is the result of two contributions. One, positive, contribution comes from the dissociation of a solvent molecule. The second contribution, coming from the electronic rearrangement, is expected to be negative. This process can in part be compared to an oxidative addition reaction for which significant negative activation volumes have been reported.¹³ Therefore, the overall value of the activation volume for solvent exchange can be expected to be close to zero for a dissociative mode of activation.

It is also worthwhile to consider that, for the water exchange on another low-spin d^6 transition metal complex, $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$, an activation volume of $-0.4 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$ was obtained.¹⁴ Using the similarity of the interchange rate constant for complex formation as a criterion, the mechanism for these reactions was assigned as I_d .¹⁵ The overall zero value of the activation volume was explained to be due to the compensation of a positive contribution (dissociation of a water molecule) and a negative one (contraction of the bonds with the nonreactive ligands at the transition state). This demonstrates, once again, that only

an overall mechanistic picture, including all the available kinetic parameters, rate laws, and rate constants for exchange and complex formation reactions, may provide a clear understanding of the reaction mechanism.

To our knowledge, the only other exchange reaction studied for osmium(II) is the water exchange on triaqua(benzene)-osmium(II).¹⁶ The results obtained were $k_{\text{ex}}^{298} = 11.8 \pm 2.0 \text{ s}^{-1}$, $\Delta H^\ddagger = 65.5 \pm 2.2 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -5 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$, and $\Delta V^\ddagger = +2.9 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$, and it was inferred from these values that the mechanism of the reaction involved an interchange mechanism where the bond-breaking contribution has a larger weight than the bond-making one. Although this system is difficult to compare to the one presented in this paper, since in this case there is a π -bonding system *trans* to the exchanging water ligand whereas in our case a σ -bonded dihydrogen occupies this position, it is still worth noting that both examples show a dissociative mode of activation for solvent exchange. Due to the lack of studies of exchange reactions on the Os(II) center, the observed phenomenon of a dissociative mode of activation remains to be clarified.

In conclusion, it was observed that the water and acetonitrile exchange on *trans*- $[\text{Os}(\text{en})_2(\eta^2\text{-H}_2\text{S})]^{2+}$ undergoes a dissociative interchange, I_d , or dissociative, D, mechanism, and therefore, solvent dissociation is the rate-limiting step in complex formation reactions. Kinetic studies for solvent exchange reactions on such dihydrogen complexes are scarce, and to obtain a better understanding of how the electronic and/or steric effects influence the reactivity, further investigations on similar complexes would be of interest.

Acknowledgment. Support of this work by the Swiss National Science Foundation (Grant 21-40534.94) is gratefully acknowledged. The preparative work of Z.-W.L. was supported by NIH Grant GM 13638. We also thank Prof. Henry Taube and Prof. André Merbach for helpful discussions.

Supporting Information Available: Relaxation rates and chemical shifts of the bound water ^{17}O NMR signal as a function of temperature and pressure (Tables S1 and S2) and fast-injection experiments for water exchange (Figures S1 and S2) (2 pages). Ordering information is given on any current masthead page.

IC9510775

- (12) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000.
 (13) van Eldik, R. In *High Pressure Chemistry, Biochemistry and Material Science*; Winter, R., Jonas, J., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993; p 320.
 (14) Rapaport, I.; Helm, L.; Bernhard, P.; Ludi, A. *Inorg. Chem.* **1988**, *27*, 873.
 (15) Aebischer, N.; Laurency, G.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1993**, *32*, 2810.

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