Dihydrogen as a Coligand in Substitution and Cis/Trans Isomerization Reactions

Zai-Wei Li and Henry Taube*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305

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Abstract: This study is devoted to understanding the nature of the substitution and geometrical isomerization reactions for species of the series *trans*-$[Os^{II}(en)_2(\eta^2\text{-}H_2)L]$, where L is a variable ligand. In aqueous solution, when the counterion is $CF_3SO_3^-$, the complex assumes the composition *trans*-$[Os(en)_2(\eta^2\text{-}H_2)H_2O]^{2+}$, **1**. Formation constants, K_f, vary from values in excess of 10^5 for certain S and N donors to $<10^{-3}$ for $CF_3SO_3^-$. Evidence is adduced for the conclusion that substitution takes place by loss of a ligand, H_2O in the case of **1**. Considerable activation is required for the entry of a nucleophile into the coordination sphere of the resulting intermediate. This is evidenced by the fact that relative rates of entry of neutral ligands cover a range of 700. We infer that the intermediate is stabilized by rearrangement to $[Os(en)_2(H)_2]^{2+}$, a dihydride of Os(IV). The foregoing reactions take place without isomerization to the cis form. The experimental results indicate that, in contrast to substitution, isomerization takes place by intramolecular rearrangement. In view of the known low-energy barrier for the conversion of an $\eta^2\text{-}H_2$ complex to a dihydride, it is reasonable to assume that this provides a path for isomerization. The ^1H NMR data ($\eta^2\text{-}H_2$) accumulated in the course of these studies are reported, enabling a comparison of δ, J_{HD}, and T_1 for cis and trans isomers. With the exception of those for the I^- derivative, the values of these parameters differ little for the isomeric forms.

Introduction

The sensitivity of J_{HD} in the dihydrogen complexes of the tetraamine series $[Os^{II}(en)_2(\eta^2\text{-}H_2)L]$ and $[Os^{II}(NH_3)_4(\eta^2\text{-}H_2)L]$ to the identity of a variable ligand L has been reported.[1] Whether the H–H distance is also sensitive to the choice of L is not yet known, though the chemical behavior suggests that this is the case. The H–H distance has been determined[2] only for a single compound, *trans*-$[Os(en)_2(H_2)CH_3CO_2]^+$ ($d_{H\text{-}H}$ = 1.34 Å, $J_{H\text{-}D}$ = 9.0 Hz). We have been particularly interested in the reactivity of these complexes; thus reports on their use in the preparation of novel metallocyclics have appeared.[3-5] Reference[6] has also been made to two other basic reaction types: substitution, where the identity of L is changed while preserving the composition of the remainder of the molecule; and isomerization, trans to cis where the composition remains unchanged. We have now investigated these two reaction types further to determine equilibrium constants and reaction rates and have performed experiments to provide insight into the reaction mechanisms. In this work, we have dealt with a wide choice of the variable ligand, and thus this report is in the nature of a survey. Most of the work has been done with salts of the bis-ethylenediamine complex because of its superior stability in storage as compared to the tetraammine.

Experimental Section

Instrumentation. ^1H NMR spectra were recorded on a Varian XL-400 or a Gemini-200 spectrometer, infrared spectra on a Perkin-Elmer 1600 FTIR spectrometer, and UV–vis spectra on a Hewlett-Packard 8542A spectrophotometer.

Measurement of Equilibrium Constants. For both reaction types this was done by the use of ^1H NMR as described in an earlier publication.[6] The method is straightforward because, with one exception, in each reaction type reactant and product complexes yield discrete ^1H NMR signals for $\eta^2\text{-}H_2$. Only in the case of conversion of coordinated water to OH^- do the signals coalesce.

Measurement of Reaction Rates. For most of the reactions which are sufficiently slow, ^1H NMR was used. For the more rapid reactions, it was necessary to resort to a method having a more rapid response. The kinetic data reported here were obtained by manual mixing.

Preparations. The dihydrogen complexes are sensitive to air. All manipulations involving them were done in the absence of O_2.

$[Os(NH_3)_4(H_2)](BPh_4)_2$. This compound has been reported previously.[1]

$[Os(en)_2(O)_2](CF_3SO_3)_2$. $[Os(en)_2(O)_2]Cl_2$[7] was dissolved in water, and 2.0 equiv of $AgCF_3SO_3$ was added slowly to the solution. After filtration, a golden yellow solution was obtained and then dried by rotary evaporation. Golden crystals were collected. Yield: 96%. Anal. Calcd: C, 11.25; H, 2.50; N, 8.75. Found: C, 11.20; H, 2.62; N, 8.43.

***trans*-$[Os(en)_2(H_2)](BPh_4)_2$.** $[Os(en)_2(O)_2](CF_3SO_3)_2$ (500 mg) was dissolved in 10 mL of H_2O and 1 M CF_3SO_3H, and 2 g of granular Zn/Hg was added. The mixture was stirred for ca. 3 h, the color turning from yellow to dark purple and then to yellow again. After filtration the solution was treated dropwise with 10 mL of an aqueous solution of $NaBPh_4$ (0.2 M). The resulting precipitate was filtered and dried by vacuum. Yield: 92%. Anal. Calcd for $Os(en)_2(H_2)[B(C_6H_5)_4]_2(2H_2O)$: C, 63.24; H, 6.28; N, 5.68. Found: C, 62.88; H, 6.11; N, 5.21. ^1H NMR (acetone-d_6, ppm): 7.40–6.70 (m, 40H, C_6H_5), 5.41 (s, br, 4H, NH_2), 3.66 (s, br, 4H, NH_2), 2.50 (m, 4H, CH_2), 2.10 (M, 4H, CH_2), −13.38 (s, 2H, Os-H_2).

***trans*-$[Os(en)_2(H_2)](CF_3SO_3)_2$.** $[Os(en)_2(H_2)](BPh_4)_2$ (200 mg) was dissolved in 5 mL of acetone, and a solution of 100 mg of $TlCF_3SO_3$ in 5 mL of acetone was added slowly. A white precipitate formed immediately. This was removed by filtration, and the solution was evaporated to 3 mL and treated with 50 mL of ether. The resulting solid was collected and dried by vacuum. Yield: 81%. Anal. Calcd for $Os(en)_2(H_2)(CF_3SO_3)_2$: C, 11.80; H, 2.95; N, 9.18. Found: C, 11.86; H, 3.12; N, 8.83. ^1H NMR (D_2O, ppm): 5.37 (s, br, 4H, NH_2), 3.86 (s, br, 4H, NH_2), 2.34 (m, 4H, CH_2), 2.02 (m, 4H, CH_2) −13.44 (s, 2H, Os-H_2). IR (KBr): 2155 cm^{-1}.

***trans*-$[Os(en)_2(H_2)](PF_6)_2$.** $[Os(en)_2(H_2)](BPh_4)_2$ (200 mg) was dissolved in 5 mL of acetone, and a solution of 100 mg of $TlPF_6$ in 5 mL of acetone was added. A white precipitate formed immediately and was removed by filtration. The resulting solution was evaporated to 3 mL and treated with 50 mL of ether. The resulting solid was collected and dried by vacuum. Yield: 82%. Anal. Calcd for $Os(en)_2(H_2)(PF_6)_2$: C,

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7.97; H, 2.99; N, 9.30. Found: C, 8.11; H, 2.87; N, 9.70. ^{1}H NMR (acetone-d_6, ppm): 5.75 (s, br, 4H, NH_2), 4.34 (s, br, 4H, NH_2), 2.75 (m, 4H, CH_2), 2.36 (m, 4H, CH_2), −13.19 (s, 2H, Os-H_2). IR (KBr): 2155 cm^{-1}.

Note. Although the anions $CF_3SO_3^-$, BPh_4^-, and PF_6^- are weakly nucleophilic, anhydrous solids can be prepared by prolonged drying (24 h) under vacuum at room temperature. While the absence of water is difficult to establish by analysis, this is readily done by ^{1}H NMR. No significant increase in the proton content of CD_3OD as revealed by the ^{1}H NMR signal at $\delta = -4.75$ ppm is observed on dissolving salts treated as above. Water equivalent to the Os(II) introduced would easily be observed.

***cis*-[Os(NH$_3$)$_4$(η^2-H$_2$)I](PF$_6$).** [Os(NH$_3$)$_4$(H$_2$)](PF$_6$)$_2$ (100 mg) was dissolved in 5 mL of acetone, and NaI (50 mg) was added. After 3 days, the orange solution was treated with ether, and a yellow precipitate appeared, which was separated, washed with ether, and dried. Yield: 40%. ^{1}H NMR (in acetone-d_6, ppm): 4.59 (s, br, 3H, NH_3), 4.18 (s, br, 3H, NH_3), 3.71 (s, br, 6H, 2NH_3), −8.21 (s, 2H, Os-H_2). J(HD) = 17.0 Hz, T_1(H$_2$) = 130 ms (20 °C, 200 MHz), $T_1(H_2)_{min}$ = 87 ms (−70 °C, 400 M Hz).

***trans*-Os(en)$_2$[(η^2-H$_2$)CH$_3$CN](CF$_3$SO$_3$)$_2$.** Os(en)$_2$(H$_2$)(CF$_3$SO$_3$)$_2$ (200 mg) was dissolved in CH_3CN (3 mL). After 0.5 h ether (500 mL) was added to the solution. The colorless precipitate which formed was collected, washed with ether, and dried by vacuum. Yield: 84%. Anal. Calcd for Os(en)$_2$(H$_2$)(CH$_3$CN)(CF$_3$SO$_3$)$_2$: C, 14.74; H, 3.22; N, 10.75. Found: C, 14.99; H, 3.20; N, 10.44. ^{1}H NMR (acetone-d_6, ppm): 5.36 (s, br, 4H, NH_2), 4.66 (s, br, 4H, NH_2), 2.76 (s, 3H, CH_3CN), 2.67 (m, 4H, CH_2), 2.34 (m, 4N, CH_2), −9.13 (s, 2H, Os-H_2). J(HD) = 17.7 Hz, T_1(H$_2$) = 79 ms (20 °C, 200 MHz), $T_1(H_2)_{min}$ = 32 ms (−71 °C, 400 MHz). IR (KBr): 2176 cm^{-1}.

***trans*-[Os(en)$_2$(η^2-H$_2$)Py](CF$_3$SO$_3$)$_2$.** Os(en)$_2$(H$_2$)(CF$_3$SO$_3$)$_2$ (200 mg) was dissolved in 3 mL of acetone, and pyridine (20 mg) was added, whereupon an orange color developed. After the solution was kept at 0 °C for 0.5 h, ether was added. The precipitate (orange) was recovered by filtration. Yield: 81%. Anal. Calcd for [Os(en)$_2$(H$_2$)py](CF$_3$SO$_3$)$_2$: C, 19.15; H, 3.34; N, 10.16. Found: C, 19.23; H, 3.39; N, 9.99. ^{1}H NMR (acetone-d_6, ppm): 9.19 (d, 2H, py), 8.18 (t, 1H, py), 7.79 (d, 2H, py), 5.81 (d, br, 4H, NH_2), 4.18 (d, br, 4H, NH_2), 2.30 (m, 8H, CH_2), −8.42 (s, 2H, Os-H_2), J(HD) = 19.0 Hz, T_1(H$_2$) = 74 ms (20 °C, 200 MHz), $T_1(H_2)_{min}$ = 32 ms (−61 °C, 400 MHz). IR (KBr): 2285 cm^{-1}.

***cis*-[Os(en)$_2$(η^2-H$_2$)py](CF$_3$SO$_3$)$_2$.** *trans*-[Os(en)$_2$(η^2-H$_2$)py](CF$_3$SO$_3$)$_2$ (100 mg) was dissolved in acetone and was stored for 1 week. The solution was then treated with ether to precipitate the product. Yield: 90%. Anal. Calcd for Os(en)$_2$(H$_2$)(C$_5$H$_5$N)(CF$_3$SO$_3$)$_2$: C, 19.15; H, 3.34; N, 10.16. Found: C, 18.81; H, 3.26; N, 10.04. ^{1}H NMR (acetone-d_6, ppm): 8.76 (d, 2H, py), 7.74 (t, 1H, py), 7.25 (d, 2H, py), 6.51 (d, br, 1H, NH), 6.14 (d, br, 1H, NH), 5.80 (d, br, 1H, NH), 5.38 (d, br, 1H, NH), 5.13 (m, br, 3H, NH), 4.17 (d, br, 1H, NH), 3.14 (m, 2H, CH_2), 3.00 (m, 1H, CH_2), 2.62 (m, 5H, CH_2), −7.44 (s, 2H, Os-H_2), T_1(H$_2$) = 73 ms (20 °C, 200 MHz), $T_1(H_2)_{min}$ = 27 ms (−58 °C, 400 MHz). IR (KBr): 2350 cm^{-1}.

Results

Substitution. Equilibrium Constants, K_f, for Complex Formation. Some values for the affinities in D_2O of ligands for *trans*-[Os(en)$_2$H$_2$(H$_2$O)]$^{2+}$, **1**, have been reported.[6] This list has now been extended and is no longer limited to nucleophilic centers of biomolecules. As before, ^{1}H NMR spectroscopy has been used to determine the ratio of the concentration of the complex to that of **1** at equilibrium. For some ligands, the affinities are so high that this ratio cannot be determined, and in these cases, only a lower limit on the equilibrium constant for complex formation can be set. The contrary case arises with $CF_3SO_3^-$ as nucleophile, where no signal for the complex appears even at high concentration of the anion and only an upper limit on K_f can be set. With certain other anions, the affinity is so low that a high concentration must be used to bring up the signal for the complex. In these cases the values of K_f can vary significantly with ionic strength. No effort was made to maintain constant ionic strength throughout the anion series, but the concentration of the anion salt applicable in each case is specified in Table 1, where the data are summarized.

In two cases, the product isomerized essentially completely to the cis form before the ^{1}H NMR measurements were made. As it happens, in these cases the affinities are so high that the data yield only a lower limit for the equilibrium quotient, which now is of the form

$$[cis\text{-}[Os(en)_2(H_2)L]^{2+}]/[trans\text{-}[Os(en)_2(H_2)(H_2O)^{2+}][L]$$

The system with I^- as ligand has both the cis and trans forms of the complex in equilibrium with **1**, and consequently the ratio of the formation constants is the equilibrium constant for the trans to cis conversion ($K_{c/t}$ = 1.5).

Even though the equilibrium constant for replacement of H_2O in the aquo ion by OH^- is high, it was possible to obtain a reasonably good value by measuring pK_a for the reaction:

$$trans\text{-}[Os(en)_2(H_2)D_2O]^{2+} = trans\text{-}[Os(en)_2(H_2)(OD)]^{+} + D^{+}$$

A solution of $[Os(en)_2(H_2)O_3SCF_3]O_3SCF_3$, 3.0×10^{-3} M in D_2O, was titrated with a solution (0.100 M) of LiOD in D_2O. On addition of LiOD, δ(H$_2$) shifts from −13.44 ppm to −12.05 ppm as the limiting value. At the midpoint in the change, the pD is 9.2. Conversion of pD to pH is commonly done[8] by subtracting 0.5, in which case, when the resulting value is combined with the dissociation constant for H_2O, the association quotient for OH^- shown in the table results. Though base does catalyze (η^2-H$_2$)/D_2O exchange, the rate is very sensitive to the nature of L. In the present system, this rate is extremely slow.

In only one case, that in which **1** is converted to the hydroxo complex, do we find the ^{1}H NMR signals for **1** and the product of substitution averaged at room temperature. The reaction, in this case only, takes place without disruption of the metal to oxygen bond. To investigate the ^{1}H NMR behavior at higher temperatures in at least one case we chose as nucleophile Br^-, which has a low affinity for [Os(en)$_2$(H$_2$)]$^{2+}$. The ^{1}H NMR traces obtained in this experiment are shown in Figure 1. While considerable broadening of the peaks for η^2-H$_2$ in the two complexes is observed at 93 °C, even at this temperature they remain distinct. The relative intensity of the peaks [Os^{II}–Br$^-$]/[**1**] = 3.4 at 20 °C and does not change by more than 10% over the 70-deg temperature range, indicating that ΔH for the particular reaction is small.

Table 1. Equilibrium Constants, K_f,[a] for Complex Formation[b] in D_2O. Summary of ^{1}H NMR Data

L	K_f (M)	concn of salt
D_2O		
$CF_3SO_3^-$	$<10^{-3}$	2.00
Cl^-	7.2	1.00
Br^-	3.0	1.00
I^-	1.67	1.00
I^- [e]	2.4	1.00
$CH_3CO_2^-$	2.0×10^2	0.0100
SO_4^{2-}	1.0	2.00
NO_3^-	0.5	2.00
$H_2PO_4^-$	1.7×10	0.0100
HPO_4^{2-}	8.9×10^2	
N_3^-	6.6×10^2	0.0100
NCS^-	1×10^5	0.040
OD^- [c]	$\sim 6.3 \times 10^4$	
Im[d]	1.0×10^2	
AN[d]	4.0×10^2	
Py[d]	$>10^5$	
$(CH_3)_2S$[d,e]	$>10^5$	
$(NH_2)_2CS$[d,e]	$>10^5$	

[a] K_f = [Os^{II}(en)$_2$(H$_2$)L]/[Os^{II}(en)$_2$(H$_2$)D$_2$O] [L]. [L] is the concentration of free ligand; concentrations in moles/liter. [b] Concentration of *trans*-[Os(en)$_2$(H$_2$)D$_2$O]$^{2+}$, 1.00×10^{-2} M. Temperature, 20 °C. [c] K_f determined by acid–base titration. See text. [d] Nucleophile concentration, 1.00×10^{-2} M. [e] Complex in the cis configuration.

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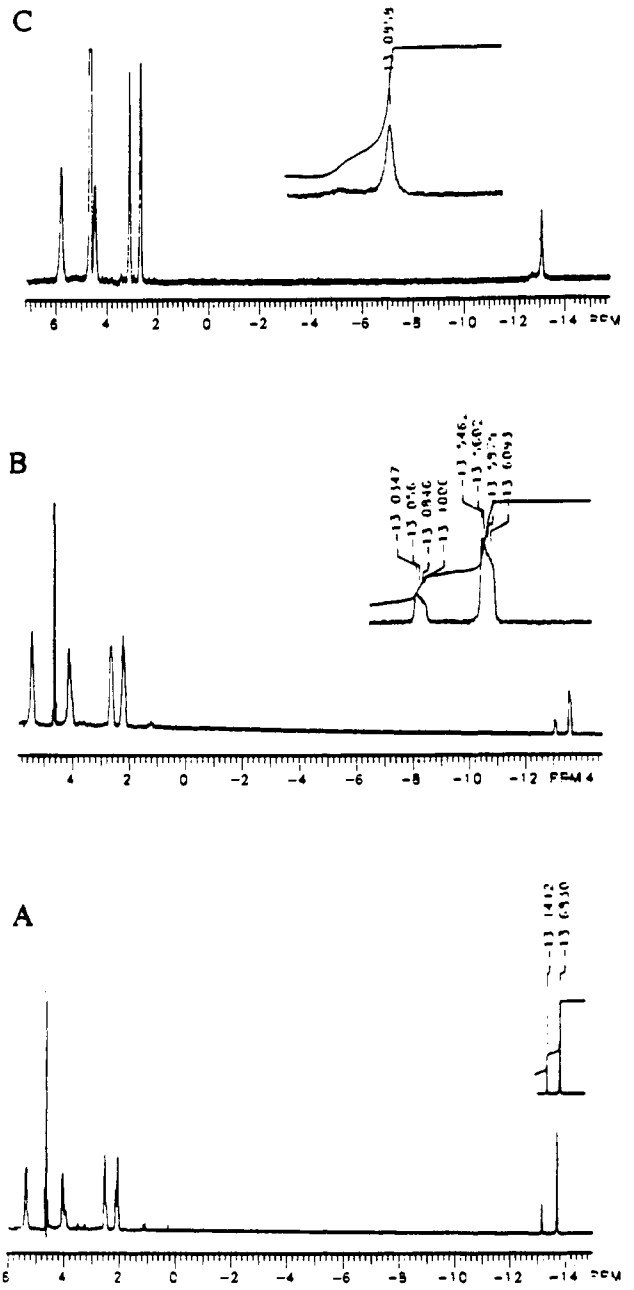

Figure 1. ^{1}H NMR spectra (400 M Hz) of $[Os(en)_2(\eta^2\text{-}H_2)D_2O]^{2+}$ (3.9×10^{-3} M) in 2.1 M LiBr aqueous (D_2O) solution: A, 20 °C; B, 41 °C; C, 93 °C.

Speciation of $[Os^{II}(en)_2(H_2)]$ Salts of Weakly Nucleophilic Anions in Some Oxygen Donor Solvents. The salt $[Os(en)_2(H_2)O_3SCF_3]O_3SCF_3$ dissolves in water to give the aquo ion, but in weakly nucleophilic solvents, the possibility that $CF_3SO_3^-$ remains in the coordination sphere must be considered. In particular, solvents which are oxygen donors require special attention in this connection; in general, oxygen donors enter into relatively weak and labile interactions with $[Os(en)_2(H_2)]^{2+}$. Three commonly used oxygen donor solvents are dealt with below. The experiments to be described were done with preparations of salts with a very low content of water, as shown by the ^{1}H NMR response when dissolved in CD_3OD (see Experimental Section). The concentration of the salts was in every case 1.00×10^{-2} M.

The salts of $[Os(en)_2(\eta^2\text{-}H_2)]^{2+}$ with PF_6^- and BPh_4^- as counterions when dissolved in CD_3OD give almost identical ^{1}H NMR (H_2) shifts, $\delta = -13.44$ and -13.42 ppm, while, for the $CF_3SO_3^-$ salt, $\delta = -13.64$ ppm. Because PF_6^- and BPh_4^- are weaker nucleophiles than $CF_3SO_3^-$ and because the shifts are, within experimental error, identical for the two cases, we infer that their salts dissolve to yield the solvento species, while the $CF_3SO_3^-$ salt, which gives rise to a different shift, remains as the anion complex. It is of some interest that the values of δ for the amine protons in the three cases are distinguishable. They are 5.68 and 3.92, 5.18 and 3.46, and 5.81 and 4.10 ppm for PF_6^-, BPh_4^-, and $CF_3SO_3^-$, respectively. We ascribe the differences to direct association of the anions with the amine protons, except possibly in the case of BPh_4^-.

In acetone ($(CD_3)_2CO$) as solvent, the values of δ (η-H_2, ppm) for the $CF_3SO_3^-$, PF_6^-, and BPh_4^- salts of *trans*-$[Os(en)_2(H_2)]^{2+}$, each at 1.0×10^{-2} M, are -13.15, -13.08, and 13.15 ppm, respectively. On the addition of $NaCF_3SO_3$ (1.25 M) to the solution of the $CF_3SO_3^-$ salt, a new peak in ^{1}H NMR spectrum appears at -12.67 ppm, which we attribute to $CF_3SO_3^-$ as the coordinated species. (K_f for the formation of the $CF_3SO_3^-$ complex is ca. 0.1 M^{-1}.) Because both BPh_4^- and PF_6^- are weaker nucleophiles than $CF_3SO_3^-$, we infer that each of the three salts, at the prevailing concentration level, dissolves in $(CD_3)_2CO$ to yield the solvento species and that the anions, as in the case of $CF_3SO_3^-$, would only enter the coordination spheres at higher concentrations. The shifts (δ, ppm) of the NH_2 protons for the $CF_3SO_3^-$, PF_6^-, and BPh_4^- salts respectively are 5.80 and 4.44, 5.83 and 4.40, and 5.41 and 3.66. As in the case of CD_3OD as solvent, the differences are attributable to differences in the extent of hydrogen bonding with the anions.

When a sample of the $CF_3SO_3^-$ salt of $[Os(en)_2(\eta^2\text{-}H_2)]^{2+}$ containing a small amount of H_2O is dissolved in $(CD_3)_2CO$, in addition to the peak at $\delta = -13.15$ attributable to $[Os(en)_2(\eta^2\text{-}H_2)(CD_3)_2CO]$ another is observed at -13.27 ppm. On the addition of D_2O, the latter peak grows at the expense of the former and is therefore assignable to $[Os(en)_2(\eta^2\text{-}H_2)H_2O]^{2+}$. From the relative peak heights and the content of free water (mainly D_2O) the equilibrium constant for the reaction

$$\{Os(en)_2(\eta^2\text{-}H_2)((CD_3)_2CO)]^{2+} + H_2O = [Os(en)_2(\eta^2\text{-}H_2)H_2O]^{2+} + (CD_3)_2CO$$

was calculated at 62 M^{-1}. The existence of two forms of the (η^2-H_2) complex in wet $(CD_3)_2CO$ is revealed also by the ^{1}H NMR signals for N–H, but the peaks are not clearly resolved.

Dimethylformamide (DMF) is recognized as being a rather good donor molecule, and the evidence suggests that also $CF_3SO_3^-$ is displaced from the η^2-H_2 complex by solvent in this case. The main item of evidence depends on a comparison of the rates of conversion of $[Os(en)_2(\eta^2\text{-}H_2)(O_3SCF_3)]O_3SCF_3$ to $[Os(en)_2(\eta^2\text{-}H_2)\text{pyridine}]^{2+}$ when the solute is dissolved in DMF, and a small amount of this solution is added to pyridine, compared to the rate when the solid is added to neat pyridine (vide infra). The ^{1}H NMR properties are consistent with this conclusion: for example, the values of $\delta(H_2)$ for the BPh_4^- and $CF_3SO_3^-$ salts dissolved in DMF as -13.42 and -13.50 ppm, respectively, are the same within experimental error, but add little weight to the proof because pairs of oxygen donors can yield very similar values of ^{1}H NMR properties. In contrast to what is observed in CD_3OD and $(CD_3)_2CO$ solutions, the shifts observed for the amine protons are virtually identical (5.96, 4.66; 5.95, 4.65 ppm) for the $CF_3SO_3^-$ and BPh_4^- salts, respectively. This speaks to the superior nucleophilic power of DMF as compared to methanol or acetone, the anions being displaced from the amine protons by solvent molecules.

Kinetics of Substitution. Data on rates of substitution in water, mainly for neutral nucleophiles, but including also three anions, are summarized in Table 2. In each case the concentrations of the nucleophiles were high enough so as to ensure that pseudo-first-order conditions obtained and that the reverse reaction was negligible.

Included are data determined at a temperature other than 20 °C, to provide at least an approximate measure of the activation

Table 2. Rates[a-c] of Substitution by L in *trans*-$[Os(en)_2(H_2)H_2O]^{2+}$

L	k_{bi}, M^{-1} s^{-1} at 20.0 °C	k_{bi}, M^{-1} s^{-1} at *T* specified
thiourea	5.6×10^{-2}	
acetonitrile	3.9×10^{-2}	
imidazole	1.9×10^{-3}	
methionine	2.1×10^{-4}	
pyridine	1.9×10^{-4}	1.0×10^{2} (67 °C)
dimethyl sulfide	8.0×10^{-5}	4.2×10^{-3} (68 °C)
trimethyl phosphite[c]	7.5×10^{-5}	
$CH_3CO_2^-$	0.26	
N_3^-	1.6	0.45 (0.0 °C)
$Co(CN)_6^{3-}$	4.5×10	

[a] $[Os(en)_2(H_2)H_2O](O_3SCF_3)_2]$, 1.00×10^{-2} M except in the case of the anions, where it was 1.0×10^{-3} M. [b] For neutral ligands, the concentrations were in the range 0.033–0.15 M and the rates were measured in D_2O by ^1H NMR (H_2). For N_3^- and $CH_3CO_2^-$, the concentrations of the sodium salts were 0.024 and 0.050 M, respectively, and the rates were measured in H_2O, spectrophotometrically. [c] In all but one case, the product is *trans*-$[Os^{II}(en)_2(H_2)L]$. For $L = P(OCH_3)_3$, the product is *trans*-$[Os(en)_2(P(OCH_3)_3)_2]^{2+}$ (H_2 gas is liberated).

Table 3. Kinetic Studies on Solvent Exchange and Substitution (by NCS^-) for *trans*-$[Os(en)_2(H_2)CH_3CN](O_3SCF_3)_2$[a] in CD_3CN at 20 °C

[NaNCS] (M)	k_{obs}[b] (s^{-1}) $\times 10^4$ complex formation	k'_{obs}[b] (s^{-1}) $\times 10^4$ CH_3CN release
0		2.2
0.10	2.3	2.3
0.50	1.6	1.8
1.00	1.5	1.7

[a] Concentration = 1.00×10^{-2} M. [b] Limits of error, ±0.2.

parameters. The values of $\Delta H^{\ddagger}$ (kcal/mol) and $\Delta S^{\ddagger}$ (cal/(mol K)) for the pyridine, methyl disulfide, and azide reactions respectively are 16.1 and −21, 15.5 and −24, and 9.5 and −25, 20 °C.

A single comparison was made of the rates of substitution in trans and cis isomers. The $CF_3SO_3^-$ salts of *cis*- and *trans*-$[Os(en)_2(\eta^2\text{-}H_2)CH_3CN]^{2+}$ were dissolved in separate samples of pyridine-d_5 (concentrations 0.015 and 0.010 M, respectively), and the progress of reaction was followed by ^1H NMR. The specific rate for the trans species at 20 °C was measured as 7.8×10^{-3} s^{-1}; that for the cis was found to be lower by a factor of $>1.3 \times 10^3$. The value of $K_{c/t}$ is recorded as 16 (vide infra).

The wide range in the values of k_{bi}, approaching a factor of 10^3 for the neutral ligands, on the face of it suggests considerable S_N2 character in the substitution process, and we undertook to determine the mechanism of substitution. While the issue of the extent of bond-making by the entering group in the activated complex for substitution is in general difficult to settle, in the event that a rather stable intermediate of lower coordination number is involved, a definite conclusion can be reached by a study of the kinetics. We measured the rate at which CH_3CN in *trans*-$[Os(en)_2H_2(CH_3CN)]^{2+}$ enters the solvent CD_3CN at various concentrations of the entering nucleophile, in our case NCS^-, comparing this to the rate of complex formation in the same solutions. The half-life for the release of CH_3CN was followed by the ^1H NMR signals for CH_3CN, and that for complex formation by the growth of the H_2 signal in *trans*-$[Os(en)_2(H_2)NCS]^+$. The results of the measurements are summarized in Table 3.

The agreements of k_{obs} and k'_{obs} for solutions containing the entering nucleophile show that the nucleophile at high enough concentrations completely blocks exchange, the release of CH_3CN being accounted for by its replacement by NCS^-. It follows that the two reactions proceed by a common intermediate and the results leave no room for a significant contribution, under these conditions, of an S_N2 path. It is remarkable that NCS^- even at 0.10 M ($NCS^-/CH_3CN = 0.005$) is abundant enough to block exchange, but this circumstance may be the result of ion pair formation in this nonprotic solvent, which in effect would provide a high local concentration of the entering group.

In the simplest case all the specific rates at rate saturation would be the same. While k_{obs} at 0.10 M NCS^- is, within experimental error, identical to k'_{obs} in the absence of the nucleophile, higher concentrations of the nucleophile do lead to a diminution of the values of k_{obs} and k'_{obs}. In the course of the measurement of the rate of solvent exchange it was noted that water, even at low concentration, decreases the rate of reaction. Thus, when H_2O is present at ca. 2.0×10^{-2} M (concentration determined by the ^1H NMR signal in CD_3CN), k'_{obs} was observed to be 0.96×10^{-4} s^{-1} as compared to 2.2×10^{-4} s^{-1} in "dry" solvent. All the data entered in Table 3 were obtained with the same sample of CD_3CN, in which the concentration of H_2O was low.

"Saturation" kinetics are not observed for substitution by pyridine in DMF as solvent. On the contrary, the values of the second-order specific rates remain constant up to quite high concentrations of pyridine. For this solute at 0.100, 1.00, 3.00, 6.2, and 9.2 M, the values at 20 °C of the second-order specific rates ($k_{bi} \times 10^4$, M^{-1} s^{-1}) as measured spectrophotometrically are 2.3, 2.7, 2.2, 2.3, and 4.6, respectively. In the last solution, the mole fraction of pyridine greatly exceeds that of DMF, and it is not surprising that the specific rate is different from that in the other cases. The solutions were prepared by dissolving the dihydrogen compound in DMF and then adding pyridine. This procedure is obviously impossible for pure pyridine, where the solution was prepared by dissolving $[Os(en)_2(H_2)O_3SCF_3]O_3SCF_3$ in the solvent. The half-time for the formation of the pyridine complex in pure pyridine is 51 times shorter than it is for 9.2 M pyridine in DMF, a composition which approaches that of pure pyridine (12.5 M). This enormous increase in rate is reasonably ascribable to the reaction now being replacement of $CF_3SO_3^-$ rather than, as in the other cases, of DMF; i.e., when the solute is dissolved in DMF, $[Os(en)_2(\eta^2\text{-}H_2)DMF]^{2+}$ is formed.

The simple strategy adopted for the study of the mechanism of substitution in CD_3CN is not readily applicable in water: H/D exchange usually does not measure the rate of water replacement at a metal ion center, and following the reaction by use of either ^{18}O or ^{17}O is difficult. A strategy based on rate comparisons, though not as definitive as that applied above, nevertheless can provide a basis for a conclusion.

In the absence of complications from labile association between the reactants, the onset of a saturation effect, i.e., the pseudo-first-order rate constant, k_{obs}, becoming independent of the concentration of the nucleophile, is indicative of an S_N1 process. This approach is applicable only when the nucleophile competes effectively against the solvent for reaction with the intermediate. An examination of the data of Table 2 shows that the only promising candidates are anions. However, their use does introduce the complication that labile association of the anion with the cation will also lead to saturation kinetics, irrespective of the reaction mechanism. Even with this complication, when the same saturation value of k_{obs} is obtained with a variety of anions, we can be certain that a common intermediate accounts for the substitution.

Unfortunately, we are extremely limited in the choice of anion. For many the affinity is so small that very high concentrations would be needed. Many good nucleophiles such as RS^- are disqualified because they are basic and result in deprotonation of the coordinated water. Cyanide ion fails because it leads to liberation of hydrogen; $S_2O_3^{2-}$, HSO_3^-, and even NCS^- (in water) react in still undetermined ways. The results obtained for three nucleophiles, N_3^-, $Co(CN)_6^{3-}$, and $CH_3CO_2^-$ for which the chemistry is simple, are plotted in Figure 2.

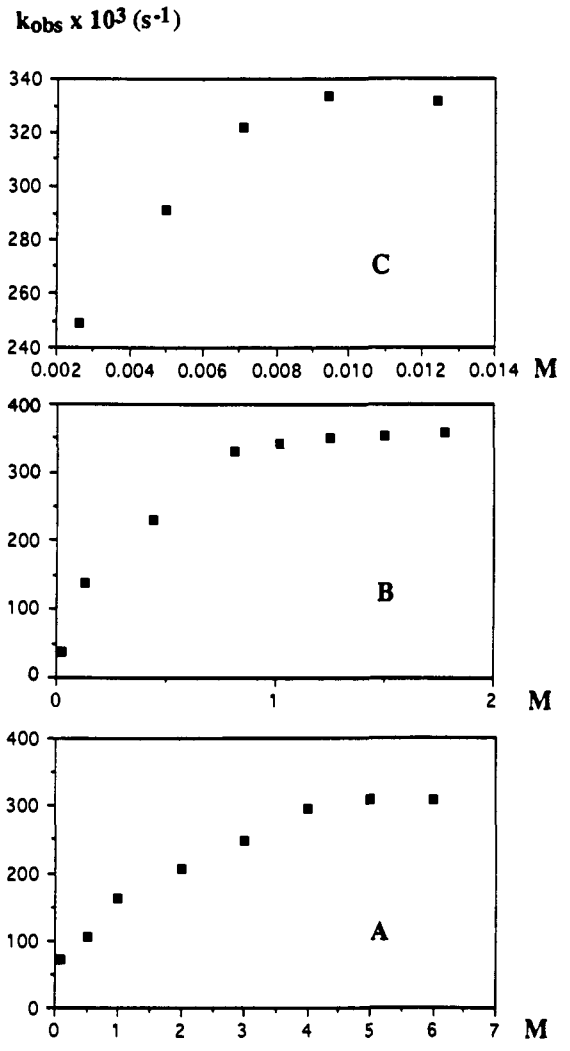

Figure 2. Plots of k_{obs} (s^{-1}) vs [L] for substitution on $[Os(en)_2(\eta^2\text{-}H_2)H_2O]^{2+}$ in H_2O; 20 °C: A, L = $CH_3CO_2^-$; B, L = N_3^-; C, L = $Co(CN)_6^{3-}$.

The mechanism for substitution at the S_N1 limit is shown below:

$$[Os(en)_2(H_2)S]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [Os(en)_2(H_2)]^{2+} + S \qquad (1)$$

$$[Os(en)_2(H_2)]^{2+} + L \xrightarrow{k_2} [Os(en)_2(H_2)L]^{2+} \qquad (2)$$

$$k_{obs} = -d \ln [[Os(en)_2(H_2)S]^{2+}]/dt = \frac{k_1 k_2 [L]}{k_{-1} + k_2 [L]}$$

At sufficiently high [L] k_{obs} is expected to become independent of [L]. Each of the nucleophiles, N_3^-, $CH_3CO_2^-$, and $Co(CN)_6^{3-}$, leads to a leveling off of the values of k_{obs} at high concentration, reaching the limits of ca. 0.36, 0.31, and 0.33, respectively. Particularly in the case of N_3^-, the concentration range in which the effect is prominent is too low to be ascribed to ion association, and we infer that ~0.36 s^{-1} measures the rate at which H_2O is lost from **1** to form an intermediate. The conclusion is bolstered by the observations made in the other cases. Certainly $Co(CN)_6^{3-}$ has a character quite different from that of the other nucleophiles, yet k_{obs} in the limit is close to that observed with the other two. We believe that, for each system, the reaction rate at the limit is governed by the rate at which solvent is lost from **1**. The fact that the limiting values are not identical does not negate this conclusion. In the case of substitution in CH_3CN, we noted quite pronounced effects on rates of solvent exchange brought about by small amounts of water. Because the rates actually decrease rather than increase on the addition of water, the effect cannot be ascribed to an S_N2 contribution. There is no a priori reason to suppose that the rate of loss of a ligand from the coordination sphere will be insensitive to medium effects.

Table 4. Equilibrium Constants of $K_{c/t}$ for Isomerization[a]

L	$K_{c/t}$
nitrogen donors	
NH_3	3
CH_3CN	16
$Fe(CN)_6^{4-}$	0.3[b]
imidazole	7
pyridine	89
pyrazine	1
pyridazine	1
phenanthridine	>300
phenanthroline	>300
sulfur donors	
$CH_3CH_2S^-$	2
$(CH_3)_2S$	>1000
$(NH_2)_2CS$	>1000
halides	
I^-	1.5[b]

[a] In acetone-d_6, $K_{c/t}$ = [cis form]/[trans form], all at 25 °C. [b] In D_2O.

Isomerization. We find a wide variation in the equilibrium constants $K_{c/t}$ (≡[cis]/[trans]) in the series $[Os^{II}(en)_2(H_2)L]$ as a function of the nature of the variable ligand L. The data we have obtained in evaluating them are summarized in Table 4.

Absent from the table are entries for oxygen donors. For such molecules—those we have tried include oxyanions, H_2O, OH^-, acetone, and amides—in no case have we detected a signal (^1H NMR for H_2) assignable to a complex of cis configuration, even when **1** is exposed to donors of this class for many days. That this is the consequence of a very slow rate of isomerization is rendered unlikely because of the great substitution lability of complexes with oxygen donor ligands. Moreover, in the case of I^- as ligand, **1** is in equilibrium with both trans and cis forms of the iodo complex. In view of the observations made on substitution in *trans*-$[Os(en)_2(H_2)H_2O]^{2+}$, it is likely that substitution in the cis form also takes place without a change in configuration. This being so, I^- is expected to be a catalyst for the conversion of **1** to *cis*-$[Os(en)_2(H_2)H_2O]^{2+}$, but no hint of such a species appears in the system. When a dilute solution is prepared by dissolving *cis*-$[Os(en)_2(H_2)I]O_3SCF_3$ in D_2O, the only ^1H NMR (H_2) signal observed is that for **1**. It is likely that *cis*-$[Os(en)_2(H_2)H_2O]^{2+}$ is the product of the replacement of I^-, but isomerization is so rapid that the cis form is not observed. For none of the oxygen ligands does $K_{c/t}$ exceed 0.010. This limit applied also to Cl^-, Br^-, and N_3^-.

The ^1H NMR traces for the two forms of $[Os(en)_2(H_2)py]^{2+}$ are shown in Figure 3, as illustrating the difference between the ^1H NMR spectra of the isomeric forms. These observations provide a firm basis for the assignment of configuration. The most telling evidence is the appearance of two and only two signals, which are of equal intensity, in the range of δ characteristic of N–H, for the sample to which we assign the trans configuration. A much more complicated pattern is observed in the same region for the sample to which we assign a cis configuration.

A systematic study of the rates of isomerization for a wide choice of L has not been made. However, a few quantitative data have been obtained which are herewith summarized. For solutions of the trans forms in $(CD_3)_2CO$, 0.01 M in the respective $CF_3SO_3^-$ salts, and at 25 °C, the values of k_{iso} (s^{-1}) are 1.4×10^{-5}, 3.7×10^{-6}, and 1.2×10^{-2} for L = C_6H_5N, CH_3CN, and $(NH_2)_2CS$, respectively. In each case, they are much smaller than those for substitution. For L = py, the rates have been measured in different solvents. For conditions as above, the specific rates in D_2O, C_5D_5N, CD_3OD, and CD_3OD containing DO_3SCF_3 at 1 M, the values of k_{iso} (s^{-1}) are 1.3×10^{-4}, 2.4×10^{-5}, 5.2×10^{-5}, and 9.2×10^{-5}.

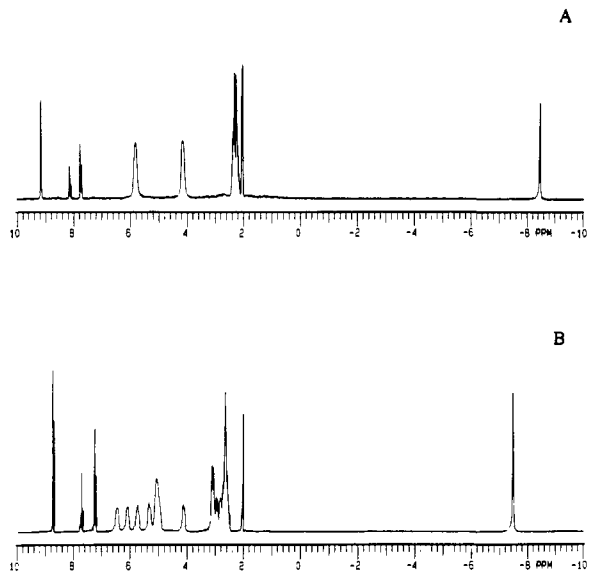

Figure 3. ^{1}H NMR spectra (in acetone-d_6; 200 M Hz, 20 °C): A, *trans*-$[Os(en)_2(\eta^2\text{-}H_2)Py](CF_3SO_3)_2$; B, *cis*-$[Os(en)_2(\eta^2\text{-}H_2)Py](CF_3SO_3)_2$. Concentration: 0.010 M.

The rates of isomerization of *trans*-$[Os(en)_2(H_2)py]^{2+}$ to the cis configuration were measured as a function of temperature, 25–72.0 °C, in D_2O as solvent. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ calculated from the data (four points) are 11.5 kcal/mol and −38 cal/(mol K). The value of k_{iso} at 25 °C is 1.3×10^{-4} s^{-1}.

In no case have we observed formation of a cis form of a complex concomitant with substitution on **1**. This is consistent with the conclusion that the two reactions proceed by independent mechanisms. The relative insensitivity of the isomerization rates to the influence of the medium indicates that the reaction proceeds intramolecularly. Particularly important in this connection is the experiment cited above on the isomerization of *trans*-$[Os(en)_2(H_2)py]^{2+}$ in CD_3OD as solvent which showed that acid even at high concentration does not interfere with isomerization. Were pyridine ejected from the coordination sphere, or were a chelate ring opened on the way to isomerization, the chemistry of the system would be altered. Neither protonated pyridine nor protonated NH_2 could compete with solvent for a site on the metal, particularly in 1 M HO_3SCF_3.

The results of other experiments also point to the conclusion that loss of ligand is not a requirement for isomerization. A solution (0.010 M) of *trans*-$[Os(en)_2(H_2)Py](O_3SCF_3)_2$ in pyridine-d_5 was prepared, and rates of exchange of C_5H_5N with C_5D_5N and of isomerization of trans to cis were monitored. After 42.5 h at 20 °C, isomerization was almost complete, but exchange of pyridine had proceeded to less than 5%. In contrast to most of the previous examples where the attachment of the variable ligand is rather labile, and the rate of substitution exceeds the rate of isomerization, in the present case, where the affinity of the variable ligand is very high, the reverse is true. The two reactions, exchange and isomerization, proceed as independent reactions.

In $(CD_3)_2CO$ as solvent, the isomerization of *trans*-$[Os(en)_2(H_2)CH_3CN]^{2+}$ (as $CF_3SO_3^-$ salt) proceeds cleanly, the specific rates in the presence of 0, 0.10, and 0.2 M CD_3CN and at 25 °C being 3.7×10^{-6}, 3.7×10^{-6}, and 3.9×10^{-6} s^{-1}, respectively. Clearly, CD_3CN does not inhibit isomerization as would be expected if the loss of CH_3CN from the coordination sphere were a prerequisite to isomerization. A similar experiment was done with *trans*-$[Os(NH_3)_4(H_2)py](BPh_4)_2$ dissolved in $(CD_3)_2CO$, to cover the eventuality that activation involves the opening of an end of a chelate ring, which closes after isomerization. Isomerization proceeds without a change in composition (i.e., $[Os(NH_3)_3(H_2)(py)_2]^{2+}$ is not formed) as would be expected were NH_3 ejected from the coordination sphere. Moreover, the specific rate of isomerization is unaffected by external py: k_{iso} in the absence of free py is 6.1×10^{-6} s^{-1} and 6.2×10^{-6} s^{-1} when 0.25 M py is present.

Rates of isomerization for $[Os^{II}(en)_2(H_2)L]$ and $[Os^{II}(NH_3)_4(H_2)L]$ are remarkably alike, despite the differences in geometry. In $(CD_3)_2CO$ as solvent the values of k_{iso} for the latter with L = C_6H_5N and CH_3CN are 6.1×10^{-6} and 3.6×10^{-6} s^{-1}, respectively, while the values for the former, already cited, are 1.4×10^{-5} and 3.7×10^{-6} s^{-1}.

Table 5. Summary of ^{1}H NMR Data for Trans or Cis Dihydrogen Complexes $[Os(en)_2(\eta^2\text{-}H_2)L]$

	δ (ppm)		J_{HD} (Hz)		T_1 (ms)[b]		T_1(min) (ms)	
L	trans	cis[a]	trans	cis	trans	cis	trans	cis
Cl^- [c]	−12.51		7.2		254		61[d]	
Br^- [e]	−13.96		8.0		248		66[f]	
I^- [e]	−12.73	−8.48	9.1	15.2	213	114		
NH_3[c]	−10.25	−8.70	14.0	14.8	140	142		
CH_3CN[c]	−9.13	−7.45	17.7	18.5	79	54	54[g]	41[h]
SCN^- [e]	−10.15	−8.32	14.4		112	78		
$Fe(CN)_6^{4-}$ [e]	−10.24	−8.68	13.8		30	24		
N_3^- [e]	−11.82				178			
imidazole[e]	−9.26	−8.37	15.8		68	75		
pyridine[c]	−8.49	−7.44	19.0	18.0	74	73	32[i]	27[j]
pyridine[e]	−8.92	−7.90	19.2	18.1	66	71		
pyrazine[c]	−7.36	−7.06	21.1	18.6	45	71		
pyridazine[c]	−7.29	−6.80			50	68		
D_2O[e]	−13.44		8.8		218			
OD^- [e]	−12.02		9.0		184			
$(CH_3)_2CO$[c]	−13.15		<3.0		151		57[k]	
$CH_3CH_2S^-$ [c]	−11.31	−9.67	8.5	13.7				
$(CH_3)_2S$[c]	*l*	−8.00		17.8		73		
$(NH_2)_2CS$[e]	−9.20	−8.36				152		

[a] Where there is no entry in this column, the concentration of the cis form in equilibrium with the trans form is too low to be detected. [b] 20 °C, 200 MHz. [c] In acetone-d_6. [d] −74 °C, 400 MHz. [e] In D_2O. [f] −72 °C, 400 MHz. [g] −40 °C, 400 MHz. [h] −30 °C, 400 MHz. [i] −61 °C, 400 MHz. [j] −58 °C, 400 MHz. [k] −62 °C, 400 MHz. [l] Reaction to the cis form is very rapid; the trans form is not identified.

Comparison of ^{1}H NMR Data (η^2-H_2) for the Trans and Cis Isomers. In a number of cases in which trans forms of the dihydrogen complexes have been characterized, we have been able to obtain the ^{1}H NMR properties also of the cis form (δ, J_{H-D} and T_1). These are summarized in Table 5, which includes also data for a number of complexes in which the cis forms are too low in concentration to be detected.

Discussion

Some data on the affinity of $[Os(en)_2(\eta^2\text{-}H_2)]^{2+}$ for various nucleophiles in water solution have already been published,[6] but they feature only polar groups which are important in biological molecules. The extended list in Table 1 bears out the earlier evidence that oxygen donors show weak binding, but an important exception, OH^-, is now included, which shows an affinity 3×10^2 greater than that of the closest rival mononegative ion, $CH_3CO_2^-$. It is remarkable that despite the fact that the affinity of OD^- is, on a mole to mole basis, 3×10^6 greater than that of D_2O, the ^{1}H NMR properties of H_2 in the two complexes are much the same. Sulfur ligands appear to be a special category, showing as they do very strong binding to the dihydrogen complexes. In this connection the very high affinity of NCS^- relative to that of N_3 is noteworthy. For several cations, e.g., Co^{2+} and Ni^{2+}, the affinities are nearly alike, and our result therefore suggests binding to osmium(II) of S rather than N.

The formation of a 16e$^-$ intermediate as precursor to substitution is rather common for 18e$^-$ complexes. In traditional coordination complexes it is found that such intermediates are

stabilized by π donation from suitable coligands,[9] notably OH^- and NH_2^-, which in effect restores the 18e⁻ count. In the absence of such stabilization, as for example in the case of $Co(NH_3)_5^{2+}$, the S_N1 limit is approached only for very good leaving groups. In the compositions we have studied, the intermediate that results appears to be rather stable. This conclusion is suggested by the large differences in the value of k_{bi} even for neutral ligands where differences in encounter frequencies are expected to be small. Referring back the mechanism for S_N1 substitution which has been introduced, when $k_2[L] \ll k_{-1}$, second-order kinetics obtain and $k_{bi} = k_1k_2/k_{-1} = K_1k_2$ and $\Delta H^{\ddagger}_{bi} = \Delta H_1 + \Delta H_2^{\ddagger}$. For a given solvent system, K_1 is constant and variations in k_{bi} result from variations in k_2, so that a large range in k_2 values indicates a large range in $\Delta H_2^{\ddagger}$. It is suggested also by the low value of $\Delta H^{\ddagger}_{bi}$, namely, 9.6 kcal, for substitution by N_3^-. It is not unreasonable to suppose that $\Delta H_2^{\ddagger}$ be as large as 5 kcal—reaction 2 can hardly be extremely rapid if N_3^- at an abundance compared to H_2O as low as 0.02 can exclude the intermediate from reacting with water—and thus ΔH_1 may be as low as 5 kcal. Substitutions in CH_3OH or $(CH_3)_2CO$ when the leaving group is a solvent molecule (or $CF_3SO_3^-$) are much more rapid than in water. With the change in solvent, $\Delta H_2^{\ddagger}$ will change little, but $\Delta H^{\ddagger}_{bi}$ will decrese and the values of ΔH_1 will be correspondingly lower. It is likely therefore that $\Delta H^{\ddagger}_{bi}$ in these solvents is several kilocalories lower than it is in water. We infer that the 16e⁻ intermediate resulting from the loss of a ligand is stabilized by electronic rearrangement to $[Os(en)_2(H)_2]$, the dihydride of $[Os^{IV}(en)_2]$.

The supposition that the intermediate for substitution is a dihydride of Os(IV) is rendered likely also by a consideration of structural parameters. Although the H–H distance in **1** is not known, it has been determined for $[Os(en)_2(H_2)CH_3CO_2]PF_6$ as 1.34 Å.[3] Because the values of J_{HD} for the **1** and the acetato derivative are much the same, 8.8 and 9.1 Hz, respectively, the H–H distance in **1** is likely also large, indicating that it is well on the way to becoming a dihydride. The loss of a ligand, resulting as it does in a 16e⁻ system, is expected to make the conversion more favorable. The dihydrogen–dihydride equilibrium has been observed by Kubas and co-workers,[10] also for an 18e⁻ system.

The contrast between the present system, where the range of specific rates for a limited choice of neutral ligands is a factor of 800, and substitution in $[Ru(NH_3)_5H_2O]^{2+}$, where for a large number of neutral ligands, as disparate as NH_3, pyridine, acetonitrile, and N_2O, it is less than a factor of 3,[11] is striking. The small range just cited indicates that bond breaking is by far the dominant process in substitution on $[Ru(NH_3)_5H_2O]^{2+}$. In the limit this would lead to $Ru(NH_3)_5^{2+}$ as a 16e⁻ reaction intermediate. In contrast to $[Os(en)_2H_2]^{2+}$, where we can invoke stabilization by electron rearrangement, no similar mechanism exists for $Ru(NH_3)_5^{2+}$, and as a result, it is much more reactive in restoring an 18e⁻ system by adopting ligands from the environment, showing less discrimination between them.

The equilibrium constant for complex formation, K_f, is given by $k_1k_2/k_{-1}k_{-2}$ or k_{bi}/k_{-2}. Thus k_{-2} can be calculated from the relation $k_{-2} = k_{bi}/K_f$. For the nucleophiles for which both k_{bi} and K_f are known, the values of k_{-2} (s^{-1}) are as follows: CH_3CN, 0.97×10^{-4}; N_3^-, 2.4×10^{-3}; $CH_3CO_2^-$, 1.3×10^{-3}. The data are too sparse even to suggest whether a correlation between complex stability and rate of aquation exists, as it does for complexes of $Co(NH_3)_5^{3+}$.

That substitution by NCS^- in *trans*-$[Os(en)_2(H_2)CH_3CN]^{2+}$ in CD_3CN is strictly zero order in $[NCS^-]$ even when its concentration is as low as 0.10 M is likely a result of strong ion pair formation in the solvent. Thus the first-order kinetics alone cannot be taken to prove S_N1 character; they only show that the activated complex has the same composition (leaving aside a conclusion about solvent content to which the kinetics are insensitive) as the activated complex. Also for an S_N2 reaction, because NCS^- is present in the dominant form of the metal complex in the reactant state as well as in the activated complex, k_{obs} would be expected to be independent of the concentration of NCS^-. As mentioned earlier, the proof of the S_N1 nature of the reactions rests on the observation that NCS^-, even at the lowest concentration, completely eliminates solvent exchange, diverting the intermediate from reaction with solvent to formation of the complex.

The sensitivity to the presence of water in CD_3CN as solvent in reducing the rate of solvent exchange is surprising. Stated in general terms, it means that H_2O stabilizes the reactant complex more than it does the activated complex. Without a systematic study it is difficult to go beyond this general statement to the particular, and the matter merits further study.

Proton NMR measurements of the kind performed for the $[Os(en)_2(H_2)H_2O]^{2+}$–Br^- system can yield valuable information about substitution rates, but only for systems which are labile enough. The single experiment of this kind we have done was undertaken mainly to learn the range of stability of the aquo ion, and the results are very encouraging in this respect. About 5 min was required to accumulate data at each temperature, and the total exposure to temperatures above 50 °C was about 20 min. On cooling the sample to 20 °C after the measurements at the highest temperature, 93 °C, were complete, we found no evidence of decomposition. In weakly nucleophilic solvents, e.g., CH_3OH and $(CD_3)_2CO$, substitution is much more rapid than in water, providing more scope for the application of ^1H NMR to study substitution lability.

The issue of the geometry of the postulated dihydride intermediate $[Os(en)_2(H)_2]^{2+}$, whether cis or trans, is left unanswered by our study. The former seems more reasonable as requiring less motion in accommodating the $(\eta^2\text{-}H_2) + 2e^- = 2H^-$ change. But if so, it is all the more remarkable that in no case have we observed isomerization accompanying substitution. This could arise from a different mode of attack on the intermediate than the reverse of its mode of formation. The principle of microscopic reversibility excludes such a path for the few cases we have studied. But it would be remarkable indeed if, for every choice of L, reaction were to proceed without isomerization. The possibility of isomerization within the 16e⁻ molecule $[Os(en)_2H_2]^{2+}$ also must be entertained. Isomerization from cis to trans by an intramolecular mechanism has been observed[12] for $[Os(NH_3)_4Cl_2]^{2+}$ and $[Os(NH_3)_4Br_2]^{2+}$. In these cases it is quite slow, but this does not exclude the possibility that it is more rapid when hydride replaces halogen.

A striking feature of the equilibrium data on isomerization is the high sensitivity of $K_{c/t}$ to the nature of a single variable ligand. It has already been mentioned that for no oxygen donor as L have we detected a cis form. The contrast between L = H_2O and L = NH_3 is particularly striking, both being considered to act mainly as σ donors, yet $K_{c/t}$ between the two cases differs by a factor of in excess of 3×10^3. Almost as striking is the comparison of $K_{c/t}$ for L = I^- on the one hand and Cl^- or Br^- on the other, where the difference factor is at least a factor of 200. π acceptor ligands all lead to a substantial proportion of the cis form at equilibrium. This correlation accounts qualitatively for the difference between L = $CH_3CH_2S^-$ and L = $(CH_3)_2S$ or $(NH_2)_2CS$. Because of the negative charge, $CH_3CH_2S^-$ is an indifferent π acid, but a good σ donor. The two neutral sulfur donors are much better π acids. Left out of the qualitative survey is the possible role of π donation from the ligand. In this respect, H_2O is superior to NH_3, and this may be a factor in accounting for the difference in $K_{c/t}$.

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(12) Buhr, J.; Winkler, J.; Taube, H. *Inorg. Chem.* **1980**, *19*, 2423. Both *cis*-$[Os(NH_3)_4Br_2]^+$ and *cis*-$[Os(NH_3)_4Cl_2]^+$ isomerize to trans in acidic solution. Loss of either halide or NH_3 as a prerequisite to isomerization would lead to a change in composition.

Nothing mentioned thus far accounts even qualitatively for the difference between pyridine and pyrazine.

Intramolecular isomerization is a very rare occurrence at least among traditional $18e^-$ coordination complexes. Dihydrogen as coligand does have the unique property of leading to an increase in coordination number by electron rearrangement. This favors an intramolecular path by the reduced symmetry of coordination number 7 which accommodates multiple closely spaced energy levels as the geometry changes.

In the single case in which we have measured the rate as a function of temperature, we note that the enthalpy barrier is low. This is in line with the idea that, for different configurations on the path from trans to cis, the energy differences are small. The unfavorable entropy of activation indicates that the reaction path involves a highly restricted succession of motions. Perhaps a detailed examination of possible reaction paths would provide an explanation of why the rates of isomerization of $[Os^{II}(en)_2(\eta^2\text{-}H_2)L]$ and $[Os^{II}(NH_3)_4(\eta^2\text{-}H_2)L]$ are so nearly alike.

The existence of a series of cis complexes which are thermodynamically stable with respect to the trans form opens up the study of effects associated with chirality. It will be of great interest to learn whether also in this kind of rearrangement the unique characteristic of dihydrogen as a ligand comes into play.

We find the difference between the behavior of the L = I^- system and the other halides altogether puzzling. The difference in $K_{c/t}$ for the iodide system as compared to the bromide has already been referred to. It can perhaps be correlated with the higher polarizability of the I^- as compared to Br^-, which would extend also to the comparison of S with O as a ligand. On the addition of I^- to a solution of $[Os(en)_2(\eta^2\text{-}H_2]^{2+}$, the ^1H NMR data show the immediate formation of a new peak in the $\eta^2\text{-}H_2$ region, and a reduction of the signal for $[Os(en)_2(\eta^2\text{-}H_2)H_2O]$, as well as two new peaks for the protons on the nitrogen. With the progress of time an additional signal appears in the $\eta^2\text{-}H_2$ region, and at least three additional well-resolved peaks in the N–*H* region, which shows that the species which appears slowly has lower symmetry than those present immediately on mixing.

We find little precedent in the literature for the comparison of the ^1H NMR properties of $\eta^2\text{-}H_2$ as a coligand in cis and trans isomers, such as our data provide. Observations have been reported[13] on the ^1H NMR properties of $[RuH(\eta^2\text{-}H_2)(diop)_2]^{2+}$ over the temperature range 83–303 K, where the appearance at low temperature of a broad singlet has been assigned to a cis form in equilibrium with the dominant trans form, the singlet arising from the coalescence of those for hydride and dihydrogen.

As to our own data, some consistent trends can be noted when the observations for I^- as the variable ligand are set aside. Though not all the data were obtained with a single solvent, whenever a comparison of ^1H NMR properties for cis and trans forms can be made, the solvent is the same. (We have in a single case, L = pyridine, obtained data in two solvents, D_2O and $(CD_3)_2CO$; the effect of the change is greatest for δ, and even here the shift is less than 0.50 ppm.) The values of δ for the cis forms are consistently less negative than those for the trans. The similarity of the values of T_1 is rather striking, considering that the environment of $\eta^2\text{-}H_2$ in the two forms can be considerably different; thus take the case of L = $Fe(CN)_6^{4-}$, where, in the trans isomer, four ligands cis to $\eta^2\text{-}H_2$ contain protons, whereas in the cis isomer only three do.

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