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Synthesis and Characterization of *trans*-$[Os(en)_2py(H)]^{2+}$ and Related Studies

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trans-$[Os(en)_2pyH](Otf)_2$, **2**, is recovered from an acidic solution of *trans*-$[Os(en)_2py(H_2)](OTf)_2$, **1**, which has been subjected to one electron oxidation. The structures of both **1** and **2** have been determined by single crystal X-ray analysis. In cyclic voltammetry, **2** shows a one electron oxidation wave at 0.95 V and a one electron reduction wave at –1.2 V, neither accompanied by a signal for the reverse process. Reduction of **2** by Zn/Hg in methanol solution leads to quantitative formation of $[Os(en)_2(py)H_2)]^{2+}$, predominantly in the *trans*-form. In aqueous solution, species **2** reacts rapidly with *N*-methylacridium ion, $[MAH]^+$, by hydride transfer. One electron chemical oxidation of **2** to the corresponding Os(IV) is slower than that of **1** to **2** owing to the increase in coordination number when Os(IV) is produced. Treatment of **1**, or the *cis*-form, **1′**, in DMSO by sodium *t*-butoxide produces mainly the corresponding isomers of the monohydrides of Os^{II}, that derived from **1′** is deep red in color while the *trans*-monohydride is colorless. Both react with $[MAH]^+$ to form $[MAH]_2$, and both disappear rapidly in acetone or acetonitrile, presumably by reducing the solvents. Reaction of *trans*-$[Os(NH_3)_4(H_2)H_2O](BPh_4)_2$, **4**, in acetone-$d_6$ as solvent with either CH_3CHO or styrene leads to hydrogenation of the substrate. Reactions which compete with *trans*-$[Os(en)_2(\eta^2\text{-}H_2)(CF_3SO)_3]CF_3SO_3$ release of substrate from the *trans*-complex before isomerization to the *cis*-form, required for hydrogenation to occur, result in the *trans*-derivative of the added solute. When $H_2C{=}CH{-}CH_2{-}SCH_3$ is the substrate, binding takes place at sulfur. Complete conversion to the *cis*-substrate isomer is observed, without hydrogenation occurring even though contact between dihydrogen and the double bond is possible.

Introduction

Numerous examples of dihydrogen complexes are described in the literature, the deprotonation of which is favored by electron withdrawing co-ligands or an increase in the oxidation state of the metal. An example[1] of the latter, closely related to the present study, is the one electron oxidation of $[Os(NH_3)_5H_2]^{2+}$, in which the dihydrogen is very difficult to deprotonate, to yield $[Os(NH_3)_5(H_2)]^{3+}$ which in water as a solvent is moderately acidic. Oxidation in this example was achieved by cyclic voltammetry, and no effort was made to isolate the oxidized product. Later work in this laboratory focused on the two electron oxidation of dihydrogen complexes of osmiumamines to form monohydrides of Os^{IV},[2,3] all of which have a very low affinity for protons. In one study, the complex of $[Os(en)_2(H_2)]^{2+}$ with $[Fe(CN)_6]^{4-}$ in aqueous solution was titrated with an oxidant, and the optical density was measured at stages in the overall two electron oxidation.[3] It was found to be accounted for quantitatively by the oxidant having been consumed to form the equivalent amount of the final product which is the complex of $[Fe(CN)_6]^{4-}$ with the monohydride of Os^{IV}. No evidence for the formation of an intermediate dihydrogen or monohydrido complex of Os^{III} having been observed, and no other evidence for the stability of this intermediate in other oxidations having been encountered, the view developed that monohydrido complexes of Os^{III} with amines as co-ligands were fugitive in nature. This was bolstered by fact that at this time only two cases of one electron oxidation of dihydrogen complexes were known, that introduced above, and that reported earlier[4] as the net one electron oxidation of $[Re(PMePh_2)_4(H_2)Cl]$. The present work rectifies the misapprehension about the stability of the products resulting from the one electron oxidation of dihydrogen complexes of Os^{II} amines.

Experimental Section

General Procedures. *N*-Methylacridinium iodide, [MAH]I, was synthesized according to a published procedure.[7] Acetone, aceto-

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(1) Harman, D. W.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261.
(2) Li, Z. W.; Yeh, A.; Taube, H. *J. Am. Chem. Soc.* **1993**, *115*, 10384.
(3) Li, Z. W.; Taube, H. *Inorg. Chem.* **1994**, *33*, 2874.
(4) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 2181.

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nitrile, and DMSO were purified by vacuum distillation from CaH_2, diethyl ether by distillation from sodium/benzophenone ketyl, and MeOH by distillation under nitrogen from Mg turnings. Water was degassed by sparging with argon prior to use. All reactions were carried out under an inert atmosphere using either a nitrogen filled glovebox or standard Schlenk techniques.

Infrared spectra were recorded on a Mattson Infinity 60AR FTIR spectrometer. ^1H NMR spectra were recorded on a Varian XL-400 spectrometer. Electrochemical measurements were performed using a BAS-50 potentiostat and a platinum working electrode, a platinum counter electrode, and a silver wire reference electrode. Unless otherwise noted, electrochemical experiments were conducted with a scan rate of 200 mV/s. All measured potentials are referenced to the ferrocene/ferricenium couple. UV−vis spectra were recorded on a Hewlett-Packard 8452A or 8453 diode array spectrophotometer using 1 cm cells. Magnetic susceptibility measurements were made by the Evans method[8] using a 400 MHz instrument and a 5 mm NMR tube microcell assembly purchased from Wilmad Glass Company. The general procedure was to dissolve the solute in a d_4-MeOH solution containing CH_2Cl_2 as the reference. The reference solution was placed in a spherical capillary bulb attached to a Teflon sleeve and lowered into a 5 mm NMR tube containing the d_4-MeOH/d_2-CH_2Cl_2 solution. Measurements were carried out at temperatures between 190 and 310 K.

Crystal Structure Determinations for *trans*-[Os(en)$_2$py(H$_2$)](OTf)$_2$ (1) and *trans*-[Os(en)$_2$py(H)](OTf)$_2$ (2). Single crystals for the [OTf]$^-$ salt of *trans*-[Os(en)$_2$py(H$_2$)]$^{2+}$ are, at -104 ± 2 °C, triclinic, space group $P\bar{1}$ (No. 2) with $a = 10.0245(3)$ Å, $b = 10.3111(3)$ Å, $c = 12.4820(3)$ Å, $\alpha = 94.670(1)°$, $\beta = 111.545(2)°$, $\gamma = 111.446(2)°$, $V = 1081(1)$ Å^3, and $Z = 2$ $\{d_{calcd} = 2.117$ g·cm^{-1}; μ_a(Mo Kα) = 6.18 mm$^{-1}\}$. Single crystals for the [OTf]$^-$ salt of *trans*-[Os(en)$_2$py(H)]$^{2+}$ are, at -90 ± 1 °C, triclinic, space group $P\bar{1}$ (No. 2) with $a = 10.021(2)$ Å, $b = 10.330(2)$ Å, $c = 12.470(2)$ Å, $\alpha = 94.81(3)°$, $\beta = 111.03(3)°$, $\gamma = 111.25(3)°$, $V = 1088(2)$ Å^3, and $Z = 2$ $\{d_{calcd} = 2.101$ g·cm^{-1}; μ_a(Mo Kα) = 6.14 mm$^{-1}\}$. Totals of 5918(3676) (**1**) and 5970(3721) (**2**) independent (unique) reflections having 2θ (Mo Kα) < 52.0° (**1**) or 51.9° (**2**) [the equivalent of 0.60 (**1**) and 1.00 (**2**) limiting Cu Kα spheres] were collected on a Siemens SMART-CCD diffractometer and absorption corrected using the Siemens SADABS program. Both structures were solved using "heavy-atom" Patterson techniques with the Siemens SHELXTL-PC software package. The resulting structural parameters have been refined to convergence {R (based on F^2) = 0.0644 (**1**) and 0.0686 (**2**) for 3632 (**1**) and 3652 (**2**) independent absorption-corrected reflections having 2θ(Mo Kα) < 52.0 (**1**) or 51.9 (**2**) and $I > 0$}, {R1 (unweighted, based on F) = 0.0253 (**1**) and 0.0279 (**2**) for 3502 (**1**) and 3412 (**2**) independent absorption-corrected reflections having 2θ(Mo Kα) < 52.0 (**1**) or 51.9 (**2**) and $I > 4\sigma(I)$} using counter-weighted full-matrix least-squares techniques and structural models which incorporated anisotropic thermal parameters for all full-occupancy non-hydrogen atoms.

With the exception of the hydrogen atom(s) of the dihydrogen (**1**) and the hydride (**2**), all hydrogen atoms were included in the final refinement cycles at idealized positions with the isotropic thermal parameter fixed at 1.2 times the equivalent isotropic thermal parameter of the atom to which it is bonded. The dihydrogen ligand in **1** (H_1 and H_2) and the hydride ligand in **2** (H_1) were included in the model as unrestrained isotropic atoms and refined to convergence.

***trans*-[Os(en)$_2$py(H$_2$)](OTf)$_2$, 1.** The synthesis of this compound has been reported.[5] In the present work, pyridine (60 drops) was added to a solution of [Os(en)$_2$H$_2$O(H$_2$)](OTf)$_2$ (1.50 g) in acetone (40 mL) and the mixture kept at room temperature while being stirred. The yellow powder that formed was collected, washed with acetone and ether, and dried. Yield = 1.20 g (70%). ^{1}HMR (d_6-DMSO) δ −9.25 (s, 2H), 1.73 (s, 2H), 1.91 (s, 2H), 4.05 (s, 2H), 5.68 (s, 2H), 7.65 (t, J = 6.3 Hz, 2H), 8.05 (t, J = 7.5 Hz, 1H), 8.84 (d,J = 5.7 Hz, 2H). No major peaks in the NMR spectrum were unaccounted for. UV−vis, 3.30×10^{-4} M in H_2O, 1.00×10^{-2} M HOTf (λ_{max}, nm; (ϵ, M^{-1} cm^{-1})): 202 (6.4×10^3); 242 (5.3×10^3); 340 (3.7×10^3).

There was no precedent in the literature for obtaining crystals of **1** suitable for structure determination by X-ray diffraction. A difficulty encountered is the isomerization[5] of **1** to the *cis*-form, **1′**, which we circumvented by using methanol as a solvent and reducing the temperature. The methanol solution of **1** (0.04 M) was kept at −10 °C, and diethyl ether was allowed to diffuse into the mother liquor from the vapor phase. After 5 days, well formed crystals appeared. IR (KBr) = 2020 cm^{-1}.

***trans*-[Os(en)$_2$py(H)](OTf)$_2$, 2. Method 1.** Ferricenium triflate, [Fc]OTf (1.2 mL of 0.14 M solution), was added dropwise to a methanol solution of **1** (90 mg, 0.13 mmol). The blue color of Fc$^+$ immediately dissipates resulting in a yellow solution. Following addition of 1.2 mL of a 0.14 M methanolic solution of Na(O*t*-Bu), the resulting solution was concentrated to 3 mL, and ether was added to precipitate a yellow powder. This was removed by filtration, washed with ether, and dried in vacuo. Yield = 81 mg (90%).

Method 2. A solution of Ag(OTf) in MeOH (2 mL, 0.871 mmol) was added to a solution of *trans*-[Os(en)$_2$py(H$_2$)](OTf)$_2$ in MeOH (30 mL, 0.870 mmol), and the mixture was stirred for 3 h in darkness. The precipitate, Ag metal, was collected by filtration, washed with MeOH, and then dried in a vacuum (yield 92.7 mg, 98.6%). Sodium *tert*-butoxide (84.5 mg, 0.879 mmol) was added to the filtrate, and the liquid was evaporated to a volume of ∼5 mL. Ether (∼50 mL) was added causing precipitation of a yellow powder which was collected, washed with ether, and then dried in vacuo. Yield 425 mg (71%). Anal. Calcd for ($C_{11}H_{22}N_5S_2F_6O_6$-Os): C, 19.2; H, 3.2; N, 10.2. Found: C, 19.2, H, 3.1, N, 10.0. IR (KBr) ν_{OsH} = 2020 cm^{-1}. $\mu_{eff} = 1.8\ \mu_B$. Crystals of **2** were grown following the procedure used for **1**.

***trans*-[Os(en)$_2$py(H)](OTf), 3.** Sodium *tert*-butoxide (1.2 equiv) was added to a d_6-DMSO solution of **1** causing the solution to turn faint pink. ^{1}H NMR (d_6-DMSO): 8.55 (d, 2H, J = 4 Hz), 7.77 (t, 1 H, J = 6 Hz), 7.65 (t, 2H, J = 7 Hz), 2.0−2.6 (m, 16 H), −3.64 (s, 1H). Resonances for t-BuOH are seen at 1.20 and 2.60 ppm. Despite its pink hue, no band maxima were observed in the visible range. The pink color may is attributable to a trace of the *cis*-isomer, which is the more stable form.

***cis*-[Os(en)$_2$py(H)](OTf), 3′.** The same procedure was followed as for **3** but with the *cis*-form of the dihydrogen complex, prepared as previously described.[5] The resultant solution is deep red. ^{1}H NMR (d_6-DMSO): 8.92 (d, 2 H, J = 6 Hz), 7.47 (t, 1 H, J = 7 Hz), 6.94 (t, 2 H, J = 6 Hz), 2.3−2.6 (m, 8 H), −4.02 (s, 1 H). Resonances for t-BuOH are seen at 1.20 and 2.60 ppm. UV−vis (DMSO): 408 nm, ϵ = 3800 M^{-1} cm^{-1}; 501 nm, ϵ = 3943 M^{-1} cm^{-1}.

***trans*-[Os(NH$_3$)$_4$(H$_2$O)(H$_2$)] (BPh$_4$)$_2$, 4.** This compound was prepared as previously reported.[6]

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(5) Li, Z. W.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 9506.
(6) Li, Z. W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946.
(7) (a) Hembre, R. T.; McQueen, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 2141. (b) Hembre, R. T.; McQueen, J. S. *Angew. Chem.* **1997**, *36*, 65.
(8) As described by: Crawford, T. H.; Swanson, J. *J. Chem. Educ.* **1971**, *48*, 382.

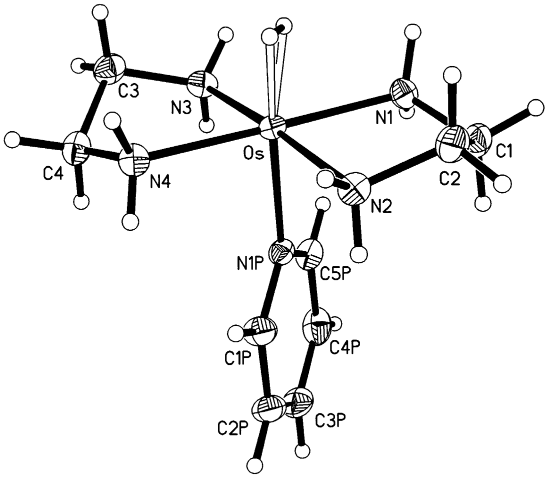

Figure 1. Perspective drawing of the *trans*-[Os(en)$_2$py(H$_2$)]$^{2+}$ cation present in crystalline *trans*-[Os(en)$_2$py(H$_2$)](OTf)$_2$ (**1**). All non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density; hydrogen atoms are represented by small spheres.

Oxidative Titration of 1. An aqueous solution of **1** (4.0×10^{-3} M) was titrated with a solution of ferricenium triflate of the same concentration. The ensuing reaction is rapid, and the end point was indicated by the persistence of absorbance maxima at 251 nm, attributable to ferricenium ion.

Reduction of [MAH]I with *trans*-[Os(en)$_2$py(H)](OTf)$_2$. An aqueous solution (0.5 mL, 0.03 M) of **2** was added to an equimolar solution of [MAH]I and the resulting solution stirred for 1 h in the dark. A white solid was removed from the resulting yellow solution by filtration which was washed with H_2O and dried in vacuo. NMR analysis of the solid in $CDCl_3$ confirms it as being MAH$_2$. ^{1}H NMR: δ 7.19 (t), 7.15 (d), 6.91 (t), 6.87 (t), 3.86 (s, 3H). UV−vis (CH_3CN): 349, 395, 411.

Reduction of [MAH]I with *trans*-[Os(en)$_2$py(H)]OTf. A solution of [MAH]I (5.8 mg, 0.018 mmol) was added to an NMR tube containing 0.50 mL of 3.6×10^{-2} M in d_6-DMSO. The solution darkened, and the white solid which forms was filtered off, washed with H_2O, and dried in vacuo. The ^{1}H NMR spectrum of the white solid dissolved in $CDCl_3$ confirms the formation of (MAH)$_2$. ^{1}H NMR: δ 7.12 (t), 6.71 (t), 6.48 (d), 3.92 (s, 2H), 2.99 (s, 6H).

Reduction of 2 in MeOH or H$_2$O. Zn/Hg amalgam (~300 mg) was added to an aqueous solution of **2**, and the mixture was stirred for 12 h in darkness. The solvent was removed in vacuo and the residue extracted with d_4-MeOH. ^{1}H NMR analysis yielded a 9/1 mixture of **1** and the *cis*-isomer, **1′**. Reformation of the dihydrogen complexes of Os(II) was quantitative as demonstrated by conducting the reduction of **2** in d_4-MeOH containing an internal standard. The reduction of **2** is slow enough so that the *trans*-isomer, if formed as the initial product, can isomerize to the *cis*.[5]

Reduction of 2 in MeCN. The procedure already described was followed, but in this case, the residue was extracted with CD_3CN. Analysis by ^{1}H NMR shows that three products, *trans*-[Os(en)$_2$MeCN(H$_2$)]$^{2+}$/**1′**/**1**, are formed in a 90:8:2 ratio, characterized by dihydrogen resonances at δ −9.31, −7.76, and −8.78 for the three products, respectively.

Results and Discussion

The molecular structure of **1** as determined by X-ray diffraction is shown in Figure 1. The H−H axis lies between the N atoms of the two chelate rings in an orientation observed also for *trans*-[Os(en)$_2$OAc(H$_2$)]$^{2+}$ and [Os(dppe)-Cl(H$_2$)]$^+$.[9,10]

The Os−H bond lengths found for **1**, 1.61(6) and 1.48(7) Å, are close to those observed for [Os(en$_2$)OAc(H$_2$)]$^+$ (1.59(1) and 1.60(1) Å), but the H−H distances differ markedly. For the acetato complex, a distance of 1.34(1) Å has been measured by neutron diffraction,[9] that observed for **1** is 0.85(8) Å by X-ray diffraction, and that suggested by the empirical correlation of J_{H-D} with H−H distance is 1.15 Å. As expected, replacement of a σ-donor ligand by one that is also a π-acceptor leads to a contraction of the H−H distances. This culminates in instability of the metal−dihydrogen bond as illustrated by the release of dihydrogen when a co-ligand is a strong π-acid, e.g., CO, HCN, isonitriles, or pyrazimium ion.[11]

The four amine nitrogens attached to the metal center are coplanar with a maximum atomic displacement of 0.066(2) Å from the least-squares mean plane through the five atoms. As expected, the pyridine ring is nearly perpendicular (87.9(1)°) to the equatorial plane already described. The Os−N average[12a] distance, 2.142(4,5,7,4) Å, is close to that found in *trans*-[Os(en)$_2$(OAc)(H$_2$)]$^+$ which is reported[9] as 2.13(5) Å. The out-of-plane bending of the ethylene carbon backbone is evidenced by the N−C−C−N dihedral angles in both ligands of 54°, similar to that observed for *trans*-[Os(en)$_2$-(OAc)(H$_2$)]$^+$.

Although the preparation of **1** has been described in the literature,[5] the absorption spectrum has not been reported. We observe an intense absorption band at 340 nm and assign it to a $\pi d \rightarrow \pi^*$ (pyridine) transition. This is shifted to higher energy as compared to that in [Ru(NH$_3$)$_5$(py)]$^{2+}$, a result of the replacement of an NH$_3$ ligand by the electron withdrawing ligand η_2-H$_2$. The absorbance at 242 nm is the $\pi \rightarrow \pi^*$ transition for pyridine, and that at 202 nm we attribute to a $\pi d \rightarrow \sigma^*$ (H$_2$) transition. Many of the dihydrogen complexes of the Os^{II} amine series show a well defined absorption band of high intensity in this energy region, not attributable to absorption by co-ligands.[13]

Synthesis and Properties of [Os(en)$_2$py(H)](OTf)$_2$, 2. The titration of **1** in methanol with either [Fc]OTf or AgOTf shows that one proton is released for each equivalent of oxidant consumed; no gas evolution is observed. No ^{1}H NMR signals are observed for **2** in solution except for two broad signals at 20 and 25 ppm. An IR band at 2020^{-1} cm is attributed to the Os−H stretch which replaces the dihydrogen signal of **1** at 2292 cm^{-1}. All other bands are almost identical to those observed for **1**. This suggests that the electron

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(10) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T.; Srivastava, R. C. *J. Am. Chem. Soc.*. **1996**, *118*, 5396.

(11) Li, Z. W. Ph.D. Thesis, Stanford University, 1993, pp 61−62

(12) The first number in parentheses following an average value of a bond length is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the average value, respectively. The fourth number represents the number of individual measurements which are included in the average.

(13) Reference 11, p 147 and pp 136−139.

densities on the metal atoms in $[Os(en)_2py(H_2)]^{2+}$ and $[Os(en)_2py(H)]^{2+}$ are almost the same, an accidental result of dihydrogen acting as an electron withdrawing ligand on Os^{II}, compensating for the electron donating capacity of the hydride anion (H−) when the metal is in the higher oxidation state.

A question that arises is whether **2** is stable. As a solid, **2** is robust and can be stored for extended periods of time without change. When it is dissolved, the question arises as to whether it is stable with respect to disproportionation to **1** and a monohydride of Os^{IV} in the thermodynamic sense, or whether it is only kinetically stable and appears in the present system because the one electron oxidation of **1** is much more rapid than that of **2**. The equilibrium issue cannot be answered on the basis of the present information. What is known is that, at moderate acidities (1×10^{-3} to 1 M), **1** and the Os^{IV} monohydride coexist for long periods of time without evidence of reaction. This is not surprising in view of the fact that one electron oxidation of **2**, unless the driving force is very great, is expected to be slow because an increase in coordination number accompanies the oxidation.[2,3] On this account, regardless of the state of the equilibrium, the disproportionation of **2** is expected to be slow. The oxidation of **2** to the corresponding monohydride of Os^{IV} is found to be much slower than is oxidation of **1** to **2**, in keeping with the aforementioned deep seated structural change accompanying the former. The product of the second stage has a magnetic moment of 2.6 μ_B, close to the values observed for other $Os^{IV}(en)_2$ monohydrides which have been encountered.[2] The quantitative formation of **2** by the use of one electron oxidants raises the question of why the oxidation of $[Os^{II}(en)_2(H_2)(Fe(CN)_6)]^{2-}$, as mentioned in the Introduction, takes such a different course from that of **1**. The reaction of O_2 with $[Os^{II}(en)_2(H_2)(Fe(CN)_6)]^{2-}$ has been observed to be 500 times faster than it is with the corresponding complex with $[Ru(CN)_6]^{4-}$ replacing $[Fe(CN)_6]^{4-}$.[14] The major difference between the two anions is that $[Fe(CN)_6]^{4-}$ is oxidized at a much lower potential than $[Ru(CN)_6]^{4-}$ so that $[Fe(CN)_6]^{4-}$ can mediate in the redox reactions at issue. Thus, it is an atypical ligand, and it can be expected that stable (at least kinetically stable) Os^{III} monohydride complexes of the present series will be found with a wide range of co-ligands.

Electrochemical Studies. Cyclic voltammetry of **1** in dry acetonitrile solution yields an irreversible one electron oxidation wave at +0.65 V (vs Fc^+/Fc couple) when a switching potential of 1.0 V is maintained. When repeated scans from 1.0 to −1.5 V are taken, a small reduction wave is observed at −1.1 V. In cyclic voltammetry, **2** undergoes one electron oxidation at +0.95 V and one electron reduction at −1.2 V, the complementary waves being absent. While the latter potential is close to that observed for **1** on repeated scans, it is probably not ascribable to an accumulation of **2**. When multiple scans are taken with **2**, nearly reversible waves are seen at −0.34 and −0.77 V.

In a following section, **2** is shown to be an active H^- transfer agent, as is the case also for $[Os(NH_3)_5(H)]^{2+}$.[1] Loss of H^- leaves a vacant site on the metal, which can be filled by the solvent so that the signal at −0.34 V can reasonably be assigned to the $[Os(en)_2(py)CH_3CN]^{3+/2+}$ couple. An alternative reaction mode analogous to that of $[Os(NH_3)_5(H)]^{2+}$ with acetone, to yield the isopropyl alcohol complex of $[Os(NH)_5]^{3+}$, is that the product of the addition of H^- to CH_3CN remains attached to the metal.

When methanol is the solvent for **2**, no subsidiary waves appear even on repeated scans, which is behavior consistent with the attribution made for such waves in the reducible solvent, CH_3CN. An oxidation wave is observed at 0.74 V and a reduction wave at −0.82 V, neither accompanied by a signal for the complementary processes. When the medium is acidified (0.10 M HOTf), there is no change in the cathodic wave, and no hint of the appearance of complementary oxidation wave. Acidification does shift the anodic wave to 0.64 V, but again, there is no hint of a complementary process. It is difficult to see how protons could affect the oxidation of **2** to the corresponding Os^{IV} species, and it is likely that what is being observed is an effect of the anion: it, rather than H_2O, is acting as the seventh ligand.

When cyclic voltammetry is performed on $[Os(NH_3)_5(H_2)]^{2+}$ in water, a one electron anodic signal is observed at −0.12 V, without a signal in this potential range for the complementary reduction. However, in 1 M H^+, a fully reversible signal for the $[Os(NH_3)_5(H_2)]^{3+/2+}$ couple is observed, ($E_{1/2} = -0.14$ V) showing that $[Os(NH_3)_5(H_2)]^{3+}$ is not a strong acid. Because on the addition of acid with **2** as the subject of study, there is no hint of reduction to $[Os(en)_2py(H_2)]^{3+}$, we can conclude that at the prevailing concentration, it is almost completely deprotonated in water, the latter is a much stronger acid than $[Os(NH_3)_5(H_2)]^{3+}$, a result which is in harmony with the much reduced basicity of the co-ligand pyridine compared to ammonia or an amine.

There is an interesting difference between the behavior of $[Os(NH_3)_5H]^{2+}$ which is formed on one electron oxidation of $[Os(NH_3)_5(H_2)]^{2+}$ in unacidified water and that of species **2**. After $[Os(NH_3)_5(H)]^{2+}$ is formed, it undergoes a two electron irreversible oxidation at 0.33 V which leads to $[Os(NH_3)_5H_2O]^{3+}$ and H^+, corresponding to the oxidation of H^-. In sharp contrast, *trans*-$[Os(en)_2py(H)]^{2+}$ undergoes one electron oxidation to a monohydride of Os^{IV}; i.e., the hydride remains intact. The difference is less ascribable to the difference in four NH_3 compared to two en species as co-ligands, than to that between py and NH_3. Because of the electron withdrawing power of py, more electron density is withdrawn from the hydride ligand in the case of **2**, making it less susceptible to oxidation.

In the context of this, it is of interest to note that the one electron oxidation of a coordinated hydride by an external reagent has also been encountered.[2] The action of a one electron oxidant on the monohydride of Os^{IV} yields Os^{III}:

$$[Os(en)_2H]^{3+} = [Os(en)_2]^{3+} + H^+ + e^-$$

Os^{IV} and the external oxidant cooperate in converting H^- to H^+.

Magnetic Susceptibility Measurements on 2. The NMR samples were prepared as outlined in the subsection General

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(14) Reference 11, p 147.

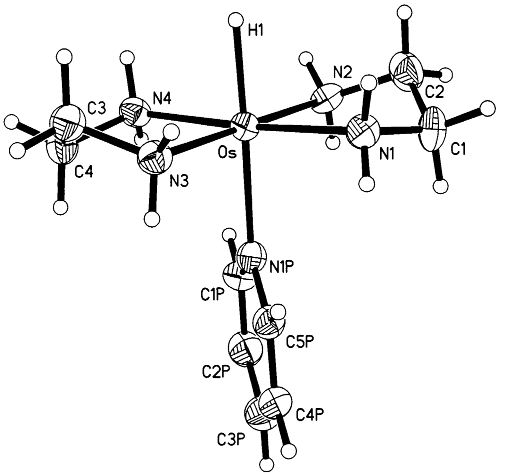

Figure 2. Perspective drawing of the *trans*-[Os(en)$_2$py(H)]$^{2+}$ cation present in crystalline *trans*-[Os(en)$_2$py(H)](OTf)$_2$ (**2**). All non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density; hydrogen atoms are represented by small spheres.

Procedures, with CH_2Cl_2 being used as an internal reference. The data were treated as described in ref 8, resulting in a value of 1.8 μ_B at 300 K, as expected for one unpaired electron.

Structure of 2 in the Solid State. Analysis of the results of the X-ray diffraction study shows the amine ligands to be in a plane with hydride and pyridine occupying the remaining positions (Figure 2). The pyridine N−Os bond length in **2** is 2.183(4) Å compared to 2.135(4) Å in **1** while the amine N−Os average[12] bond lengths compare as 2.118(4,6,11,4) and 2.142(4,5,7,4) Å, respectively. The contraction of the pyridine N−Os bond length for the metal in the lower oxidation state is ascribable to a greater contribution by backbonding to the interaction for Os^{II} compared to Os^{III}, with this extra component more than compensating for the greater radius of Os^{II}.[15] In contrast, with the amines acting as simple σ-donors, the bond distances in the two oxidation states show the more usual relationship. The Os−H bond length in **2** is 1.69(5) Å to be compared with the average[12] of Os−H bond lengths in **1** as 1.55(7,7,7,2) Å. Apparently, the shrinkage of the electron cloud of H^- occasioned by the addition of a proton more than compensates for the increased radius of the metal ion. In this context, comparisons of these distances when pyridine is replaced by a simple σ-donor ligand, which results in a much weaker H−H bond, would be of interest. The remaining distances and angles for **1** and **2** are very similar.

Reduction of 2. When a solution of **2** in acetonitrile is stirred over Zn/Hg for 12 h in the dark, *trans*-[Os(en)$_2$(CH$_3$CN)(H$_2$)]$^{2+}$ is formed in 90% yield. Along with this product, free pyridine appears as does a small amount of *cis*-[Os(en)$_2$py(H$_2$)]$^{2+}$. The reduction of **2** in acetonitrile is expected to be slow, because H^+ must be gathered from proton-labile impurities to convert H^- to H_2, affording time for partial conversion of **2** to the *cis*-isomer, **2′**. We attribute the replacement of pyridine to the labilizing effect of the *trans*-hydride. In the *cis*-isomer, such labilizing effects commonly are less pronounced in line with the behavior we observe. When the reaction is conducted in H_2O or methanol, *cis*-[Os(en)$_2$py(H$_2$)]$^{2+}$ is produced in 90% yield. The important difference likely is that, in solvents where disassociable protons are abundant, reduction is rapid, and the isomerization occurs after reduction.

Use of 2 as a Reducing Agent. The reducing capabilities of **2** were investigated using the organic oxidant *N*-methylacridinium ion (MAH$^+$). This substrate is readily reduced by either electron transfer or hydride transfer, the products [MAH]$_2$ and MAH$_2$, respectively, being easily identified. When an aqueous solution of **2** is added to an equimolar solution of MAH$^+$, the hydride transfer product MAH$_2$ is formed nearly quantitatively, a small amount (3%) of the electron transfer product being formed. When the same reaction is run in acetonitrile, formation of MAH$_2$ is quantitative. The facile hydride transfer by a monohydride of Os^{III} has precedent in the quantitative reduction of acetone to 2-propanol by $[Os(NH_3)_5(H_2)]^{3+}$ ($\equiv[Os(NH_3)_5H]^{2+} + H^+$).

In principle, [Os(en)$_2$py(H)]$^{2+}$ can react with [Os(en)$_2$py(H$_2$)]$^{2+}$ by transfer of a H atom (equivalent to a proton and electron) from the latter to the former. If rapid enough, its occurrence could be observed by line broadening of the ^{1}H NMR signals observed for **1**. With the concentrations of the reactants at the millimolar level, no line broadening was observed in an experiment performed to look for this effect. A methanolic solution of **1** and MAH$^+$, at millimolar concentrations and kept overnight, shows no evidence of reduction of MAH$^+$, but almost complete conversion to the *cis*-isomer does occur.

Properties of the *trans*- (3) and *cis*- (3′) Forms of [Os(en)$_2$py(H)]$^+$. Qualitative experiments[17] show that the conversion of η^2-H$_2$ to the deuterated form in [Os^{II}(en)$_2$L(η^2-H$_2$)] complexes in D$_2$O is accelerated when base is added to the medium, and that it takes place much more rapidly when the L is a π-acid such as pyridine than when it is a simple σ-donor (*trans*-[Os(en)$_2$OH(H$_2$)]$^+$ shows no exchange in 1.0 M OD$^-$ even after many hours). Though pyridine as coligand enhances the acidity of the coordinated η^2-H$_2$, **1** still is very weak acid, but it can be deprotonated by the action of a strong base in a nonprotic solvent. On the addition of Na[*t*-BuO] to a solution of **1** in d_6-DMSO, the ^{1}H NMR signal at −7.8 ppm disappears, and a new signal corresponding to a single proton appears at −3.6 ppm. We assign this peak to *trans*-[Os(en)$_2$H(py)]$^+$. The *cis*-isomer, **3′**, of the monohydride has also been produced by a similar procedure; it is characterized by a ^{1}H NMR signal at −4.0 ppm. No isomerization of either form is observed on the time scale of our observations, several hours.

Attempts to isolate solid forms of either isomer by the addition of ether to solutions in DMSO failed despite carrying out the operations in a controlled atmosphere box. When the solid, colorless when prepared from the *trans*-isomer and

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[15] Gress, M. E.; Creutz, C.; Quicksall, C. O. *Inorg. Chem.* **1981**, *20*, 1522.

[16] Luetkens, M. L.; Elcesser, W. L.; Huffman, J. C.; Settleberger, A. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1072.

[17] Li, Z. W. Unpublished results.

red when prepared from the *cis*-isomer, is dissolved in d_4-CH_3OH for ^1H NMR measurements, the hydride resonances disappear. Both hydrides decompose slowly in d_6-DMSO solution; the decomposition is obvious in the case of the *cis*-isomer because of its color. The changes were also followed by ^1H NMR spectroscopy. No new signals appear on decomposition indicating that the ligands remain attached to the metal, which has been oxidized to a paramagnetic state. Both **3** and **3′** are highly reactive reducing agents, as shown by the prompt disappearance of the hydride NMR signals when acetonitrile or acetone is added to the solution. Presumably, reaction with solvent also accounts for their disappearance in the DMSO. Species **3** reacts rapidly with MAH^+ to form $[MAH]_2$.

Much of the difference in behavior of the monohydrides of Os^{II} and Os^{III} as reducing agents can be understood without reference to the oxidant, on the basis of their properties alone. While the extent of covalency in the bond between the metal and hydride, which would be much less for the metal in the 2+ than in the 3+ state, would suggest that the former, being more like NaH, would be even more disposed to hydride transfer. This argument leaves out of consideration that the simple loss of an electron from **3** produces a stable product, the monohydride of Os^{III}, and because of its lower Franck–Condon barrier, a one electron change is favored over a two electron change. As to the monohydride of Os^{III} where hydride transfer is observed, again by considering its alternative, the loss of an electron, a low energy path is accessible only when it is accompanied by a change in coordination number, and it is thus inherently slow. The circumstances governing the choice of mechanism thus are rather specific to the present system and do not lend themselves to simple generalization.

The striking difference in the color of **3** and **3′**, and more particularly why **3** is colorless, merits consideration. The change from H_2 to H^- as co-ligand can hardly cause the πd $\rightarrow$ π^* transition, metal to pyridine, to disappear. Replacing η_2-H_2, which is electron withdrawing, by H^-, which is electron releasing, would raise the πd level relative to the π^* of pyridine, and if the resulting energy difference were small enough, the transition would appear in the NIR and be in a range which was not examined in our work. Another source of charge transfer absorption is interligand, which leads to a striking expected difference between the *cis*- and *trans*-forms. In the *cis*-geometry, direct overlap of the σ-orbital of H^- with a lobe of the π^* orbital of pyridine is possible and would account for one of the absorption bands, while in the *trans*-disposition, such overlap is nonexistent because of the σ-character of the filled orbital in hydride ion in relation to the π^*-orbital of pyridine. This interaction can explain the appearance of two absorption bands for the *cis*-isomer in the visible region. By raising the π^*-level sufficiently the πd–π^*absorption, suggested as appearing in the NIR region for the *trans*-form, now appears in the visible. It is to be noted that, in lacking π-character, H^- is unique among mononuclear anions.

The reactions with H_2O show unexpected complications in that conversion to the final products involves an intermediate stage suggesting that initial attack by a proton does not take place on the bound hydride. When DMSO solutions of **3** and **3′** are diluted with H_2O, yellow solutions result; the change is particularly striking in the case of **3′** where the red color is dissipated in less than a minute, being replaced by new bands at 362 and 431 nm, which, within 90 min themselves, are replaced by bands at 336 and 393 nm, these corresponding to the formation of *cis*-$[Os(en)_2py(H_2)]^{2+}$, the product expected upon protonation of **3′**. Two alternatives for the intermediate stage are the following: first, protonation of the π-cloud of the pyridine, made a possibility by the massive transfer of the πd-electrons of the metal to the π-acid, or direct protonation of the πd-electrons of the metal. Of the two, the former seems to be the more likely because of the depletion of the πd electron density by the π-acid.

The behavior of **3** is quite different in that the dihydrogen complex is not reconstituted on protonation. The yellow color which appears on reaction with water, attributable to an absorption band at 438 nm ($\epsilon \sim 1.04 \times 10^2$ M^{-1} cm^{-1}), reaches a maximum in 10 min and then slowly fades. The product of this change has not been identified. Protonation of the π-electron cloud of the pyridine is not useful for the conversion of H^- to H_2, but the resulting species could serve as an intermediate stage in reduction of pyridine with concomitant oxidation of the metal. Protonation with strong acid leads to the liberation of H_2, without reconstituting the dihydrogen complex.

Hydrogenation by Dihydrogen Complexes of Osmium-am(m)ines. In contrast to the action of the monohydrides of Os^{II} and Os^{III}, **2** and **3**, respectively, as described, under similar conditions, *trans*-$[Os(en_2)py(H_2)]^{2+}$, **1**, shows no evidence of reaction with $(MAH)^+$ even after many hours of exposure. This outcome is not surprising considering that the dihydrogen complex is not a good one electron reducing agent, nor is transfer of H^- from it to a substrate expected to be a kinetically facile process. The immediate product of such a reaction is $[Os(en)_2py(H)]^{3+}$, which can be regarded as a monohydride of Os^{IV}, but which requires an additional ligand to be stable.[2] As the experiments to be described show, with suitable modification of composition, the dihydrogen complexes Os^{II}am(m)ines can act as hydrogenation agents.

Most of the experiments were done[18] with a solid of composition *trans*-$[Os(NH_3)_4(H_2)(H_2O)](BPh_4)_2$, **4**, in acetone-$d_6$ as solvent. Hydrogenation activity depends on access by the substrate to a coordination site on the metal atom, a condition which is satisfied by the tetraammine dihydrogen residue in solution whether, H_2O, BPh_4^-, or d_6-acetone, each of which is readily replaceable occupies the sixth position, but not satisfied by pyridine.

Despite H_2 initially being *trans* to the accessible site, in a solution containing the dihydrogen complex at the 0.01 M level, with CH_3CHO at 0.46 M, after 2 h free CH_3CH_2OH is detected at a yield corresponding to the consumption of 48% of the dihydrogen complex. The reduction of aldehyde

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(18) See ref 11, pp 106–110.

is competitive with the formation of *trans*-[Os(NH$_3$)$_4$(η_2-CH$_3$CHO)L]$^{2+}$, where L is presumably d_6-acetone, in 41% yield. Ten minutes after the start of the reaction, a strong signal for η^2-H$_2$ is observed at −10.64 ppm, compared to that observed before the addition of aldehyde, −13.38 ppm. Taking account of the composition of the system, because the shift is in the region characteristic of oxygen donors, we attribute the signal to η^1-aldehyde, this intermediate then collapsing to *trans*-[Os(NH$_3$)$_4$(η^2-CH$_3$CHO)L]$^{2+}$ with release of H$_2$, or rearranging to the *cis*-form, following which, reduction of the aldehyde occurs. No signal for the osmium-containing product of the latter path is observed, and we infer that the Os^{II} species, which after hydrogenation loses the stabilizing action of η^2-H$_2$ as a π-acid, undergoes oxidative addition to a paramagnetic product by some component of the mixture. It should be mentioned that π-acids such as pyridine and CN$^-$ are known to favor isomerization of the *trans*- to the *cis*-form, and to facilitate the release of H$_2$, and thus, η^1-CH$_3$CHO is expected to act in a similar fashion.

When styrene was used as the substrate, present at the 0.020 M level, with the dihydrogen complex at 0.010 M, after 8 h, free ethylbenzene corresponding to 12% of the dihydrogen complex was detected. The only osmiumammine product observed, comprising 50% of that introduced, was *trans*-[Os(NH$_3$)$_4$(η^2-alkene)L]$^{2+}$. On starting with *trans*-[Os(en)$_2$(η^2-H$_2$)(CF$_3$SO$_3$)]CF$_3$SO$_3$, no hydrogenation was observed, and the only osmiumamine product detected was *cis*-[en$_2$(η^2-alkene)$_2$]$^{2+}$, in 70% yield. It is to be noted that rates of isomerization can be quite different for (en)$_2$ as compared to (NH$_3$)$_4$ as co-ligands.

The following experiments show that contact of (η^2-H$_2$) with an alkene function, though presumably a necessary condition for hydrogenation to occur, is not a sufficient condition. When H$_2$C═CH─CH$_2$─SCH$_3$ is used as a substrate in reaction with *trans*-[Os(en)$_2$(η^2-H$_2$)(CF$_3$SO$_3$)]CF$_3$SO$_3$, quantitative formation of the *cis*-dihydrogen complex with the substrate attached to the metal at the sulfur site is observed, and there is no subsequent reduction of the alkene function even though the *cis*-geometry is compatible with close contact between the dihydrogen and the alkene group. Thus, it is demonstrated that, for hydrogenation of an olefin to occur, both substrate and H$_2$ must be attached to the metal. With 2-vinyl pyridine, 2 h after the start of the reaction, free 2-ethylpyridine had appeared corresponding to 4% of the dihydrogen complex introduced; the bulk of the dihydrogen complex appeared in the *cis*-form, with substrate bound at N. With the passage of time, the amount of ethylpyridine did not increase. In this case, the preferential binding to the heteroatom compared to the alkene site is less favored than it is for the sulfur derivative, and hydrogenation takes place for a minor path in which alkene rather than N binds to the metal while H$_2$ is still attached.

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Supporting Information Available: Details pertaining to the X-ray crystallographic structural determination of **1** and **2** are available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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