

Monohydrido Complexes of Os(IV) Amines of Coordination Number 7

Zai-Wei Li, Andrew Yeh, and Henry Taube*

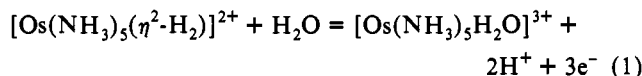
Department of Chemistry
Stanford University
Stanford, California 94305-5080

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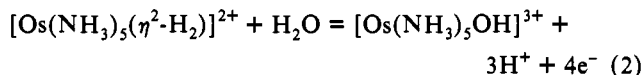
Herein we introduce evidence bearing on the conclusion that the chemical oxidation¹ of η^2 -H₂ complexes of osmium(II) amines leads to monohydrido complexes of Os(IV) and, moreover, that in addition to H⁻, the metal can carry six other ligands. Alternatively, the product can be considered to be a protonated Os(II) species; the Os(IV)-H⁻ designation is selected arbitrarily. Preliminary studies show promise of a rich chemistry for these novel species. Because the lines of evidence obtained from them to some extent are complementary, the results obtained in the oxidation of two complexes, closely related in composition, are dealt with.

The oxidation in methanol of [Os(NH₃)₅(η^2 -H₂)]²⁺ (**1**) by FeCp₂(CF₃SO₃) was found to proceed rapidly. Gas is not evolved,³ and two moles of the oxidizing agent are consumed per mole of **1**. A solid conforming to the composition Os(NH₃)₅(H)(CH₃-OH)·3CF₃SO₃ (**2**) was recovered from the solution in 80% yield.⁴ We conclude from these observations that neither H₂ nor NH₃ is released in the course of the oxidation. The same reaction was carried out in water and was found to proceed rapidly, again without gas evolution, precisely two moles FeCp₂⁺ being consumed per mole of **1**. Measurement of the pH of the final solution leads to a value within 0.1 unit of that of a strong acid at the same concentration as the metal complex, 0.020 M.

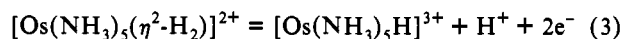
These observations cannot be accounted for by the formation of Os(III)—this would lead to the stoichiometry shown in eq 1:



Nor can these observations be accounted for by the formation of an orthodox Os(IV) species, that is, one stabilized by NH₃, H₂O, or ions derived therefrom—this would lead to the stoichiometry shown in eq 2:



Os(IV) is strongly electron-withdrawing, and the release of three protons as shown in eq 2 is a minimum number to be expected. The observations are fully accounted for by the incorporation of H⁻ into the formula of the product of oxidation, thus resulting in the stoichiometry shown in eq 3:



Hydride is strongly electron-releasing and stabilizes Os(IV), thus greatly reducing the acidity of the coligands.

The IR spectrum of **2** shows an absorption band at 1358 cm⁻¹, which disappears on deuteration, while a new band appears at 966 cm⁻¹. The shift by a factor of 1.41 shows that the atom to which H is attached does not participate materially in the vibration. While it is tempting to ascribe this to an Os-H stretch, because the frequency is several hundred units lower than any previously recorded values for metal hydride stretching frequencies, alternative assignments must be considered. During the 24-h exposure of **2** to weakly acidified D₂O, ammine protons also exchange. The isotopic shift is too great to be ascribed to a symmetric deformation of bound NH₃, which often appears in the 1300 cm⁻¹ frequency range,⁵ but other possibilities involving NH stretches remain, among them an agostic interaction.⁶ Efforts to answer the question by structure determination on a solid continue.

By following the procedure described⁴ for the preparation of **2**, but now with [Os(η²-H₂)]²⁺ (**3**)⁷ as the reducing agent, a solid of composition Os(η²-H)(CH₃OH)·3CF₃SO₃ (**4**) was prepared.⁸ In this case, clear observation of an Os-H stretch is precluded by interference, but on deuteration of a new band appears at 957 cm⁻¹. As in the case of **1**, oxidation by FeCp₂⁺ in aqueous solution takes place without gas evolution, and one mole of H⁺ is produced per mole of **3** consumed.

Substituted derivatives of **1** and **3** are oxidized rapidly by O₂, and if contact with O₂ is not prolonged, the formation of the respective Os(IV)-H⁻ species is quantitative. Further oxidation does take place on continued exposure to O₂ to yield an *osmium(III)* species. This reaction has been used⁹ to convert **3** to *trans*-Os(III)Cl₂⁺ in good yield (reaction time 12 h, 3 M HCl), and the oxidation with O₂ eventually leading to Os(III) has been confirmed by us. The eventual production of Os(III) shows that a reducing ligand remains bound when **3** is oxidized by a 2e⁻ change. In the second slower oxidation, Os(IV) and an external oxidant cooperate in oxidizing ligand H⁻ to H⁺:



Observations now to be outlined show that the cations in question can bear six ligands in addition to H⁻. When **2** is dissolved in (CD₃)₂CO, only trace amounts of free methanol are seen. On addition of pyridine (0.25 M), the ¹H NMR signal for free CH₃-OH increases slowly, with a half-life of ca. 5 min at 25 °C. The slowness of the formation of the pyridine species is incompatible with loosely bound, e.g., hydrogen-bonded, CH₃OH, and the only reasonable interpretation is that CH₃OH in the coordination sphere is being replaced by pyridine. We conclude that the coordination number of the metal in the solid is 7.

Other work^{7,10} has shown that **3** readily undergoes substitution by a wide range of nucleophiles. When Fe(CN)₆⁴⁻ is added to a solution of **3** in dilute (1.0 × 10⁻³ M) HCF₃SO₃, a stable colorless 1:1 complex is formed. Oxidation by FeCp₂⁺ (or S₂O₈²⁻) leads to the development of a blue color (broad absorption with λ_{max} at 660 nm), which reaches a limiting extinction coefficient (ε ~ 2.1 × 10³ M⁻¹ cm⁻¹) when 2 equiv of oxidant is added per mole

* Author to whom correspondence should be addressed. Present address: Chung-Yuan Christian University, Department of Chemistry, Chung Li, Taiwan 32023, Republic of China.

(1) As contrasted with electrochemical oxidation² (by cyclic voltammetry), which leads to unstable [Os(NH₃)₅H₂]³⁺ as an intermediate and to [Os(NH₃)₅(solvent)]³⁺ as final product.

(2) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261.

(3) The addition of a strong π acid such as an isonitrile to a solution of a dihydrogen complex of the present series leads to replacement of η²-H₂ by the isonitrile, as evidenced by vigorous bubbling. The concentration level which was used in these experiments is the same as it is in the present study.

(4) A solution (0.170 M) of Fe(Cp)₂(CF₃SO₃) in methanol was added to 2 mL of a methanol solution (0.085 M) of [Os(NH₃)₅(η²-H₂)](CF₃SO₃)₂. The blue color of the oxidizing solution is discharged on addition until an equal volume has been added. Addition of ether to the bright orange product solution caused precipitation of an off-white solid. This was collected, washed with ether, and dried. Anal. Calcd: C, 6.36; H, 2.65; N, 9.27. Found: C, 6.20; H, 2.46; N, 8.74.

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(6) Blake, A. J.; Holder, R. J.; Roberts, Y. U.; Schroder, M. *Chem. Commun.* **1993**, 260. We are grateful to the editor (J.N.) for drawing our attention to this and related recent work.

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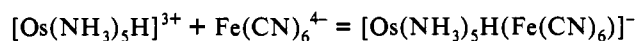
(8) Anal. Calcd for Os(η²-H)CH₃OH·3CF₃SO₃: C, 12.15; H, 2.66; N, 7.09. Found: C, 12.55; H, 2.75; N, 6.92. Yield, 95%.

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of **3**. Neither $\text{Fe}(\text{CN})_6^{4-}$ nor $[\text{Os}(\eta^2\text{H}_2)]^{3+}$ has significant absorption in this region of the spectrum. (Detailed studies¹¹ with $\text{Fe}(\text{CN})_6^{4-}$ and related species $\text{Os}(\text{CN})_6^{4-}$, $\text{Ru}(\text{CN})_6^{4-}$, $\text{Co}(\text{CN})_6^{3-}$, and $\text{Mo}(\text{CN})_6^{4-}$ as nucleophiles lead to the conclusion that the band in question arises from $\text{Fe}(\text{CN})_6^{4-}$ to $\text{Os}(\text{IV})$ charge transfer.) On the addition of more $\text{Fe}(\text{CN})_6^{4-}$ to the solution, the extinction coefficient rises slowly as described in footnote 12, after 5 days reaching $4.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ($\lambda_{\text{max}} = 670 \text{ nm}$). The doubling indicates that a second $\text{Fe}(\text{CN})_6^{4-}$ enters the coordination sphere. The detail on pH measurements given in footnote 12 shows that the ligation of additional $\text{Fe}(\text{CN})_6^{4-}$ does not open a chelate ring, and we conclude that the coordination number of Os in the final product is 7. With the nucleophiles Cl^- and SO_4^{2-} , small, slow shifts in wavelength are observed but without loss of integrated intensity. We conclude that these nucleophiles also enter the coordination sphere without displacing $\text{Fe}(\text{CN})_6^{4-}$. Presumably the addition reactions involve displacement of water from the coordination sphere of osmium, but since the number of water molecules ligated to the metal has not been established, solvent is omitted from the formulas.

Parallel observations on substitution are made with **1**. An aqueous solution ($1.9 \times 10^{-3} \text{ M}$) of $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-H}_2)]^{2+}$ was oxidized by 2 equiv of FeCp_2^+ , and the solution was filtered. A 9-fold excess of $\text{Fe}(\text{CN})_6^{4-}$ was added, whereupon a slow development of color set in. The pH of the solution at this stage was 4.1. After 3 days, the absorption spectrum was recorded ($\lambda_{\text{max}} 626 \text{ nm}$; $\epsilon = 1.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). The pH taken on an aliquot was found to be unchanged, but on addition of $1.9 \times 10^{-3} \text{ M NH}_3$, the pH rose to 8.5. No further increase in absorptivity was noted even after 2 weeks. This experiment proves that $\text{Fe}(\text{CN})_6^{4-}$ enters the coordination sphere without displacing NH_3 , and we conclude that the metal center attains a coordination number of 7 in the product



That a πd^4 metal center can have a coordination number of 7 is not surprising because this leads to an $18e^-$ valence shell, and hydrides of coordination number 7 are well known.¹³ Less easy to adjust to is the finding that both **2** and **4** are paramagnetic. The magnetic moment determined on a sample of **4** dissolved in $(\text{CD}_3)_2\text{CO}$ by a modification of the Evans method¹⁴ was found to be $2.37 \pm 0.05 \mu_B$ (temperature range -90°C to 25°C). A recent paper provides precedent for this kind of behavior in an $18e^-$ system for two metal centers in low oxidation states ($\text{Cr}(0)$ and $\text{Mn}(1)$).¹⁵ While all $\text{Os}(\text{IV})$ complexes heretofore reported show apparent magnetic moments of $1.5 \pm 0.2 \mu_B$ (at 25°C), this

(11) Li, Z.-W.; Yeh, A.; Taube, H., Manuscript in preparation.

(12) A slight excess of $\text{Fe}(\text{CN})_6^{4-}$ was added to an aqueous solution of $[\text{Os}(\eta^2\text{-H}_2)](\text{CF}_3\text{SO}_3)_2$ ($1.7 \times 10^{-3} \text{ M}$) followed by 2 equiv of FeCp_2^+ . After filtration to separate FeCp_2 , the absorption spectrum was recorded (λ_{max} at 660 nm ; $\epsilon = 2.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). The pH after addition of $6.8 \times 10^{-3} \text{ M Fe}(\text{CN})_6^{4-}$ was 3.7. After 5 days, the pH was measured as 3.8; on addition of $1.7 \times 10^{-3} \text{ M NH}_3$ it rose to 8.4, thus showing that there is at most weak buffer action in the solution.

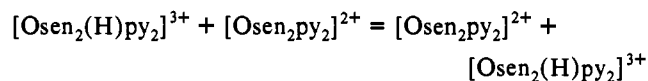
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(14) Lölliger, J.; Scheffold, R. *J. Chem. Educ.* **1972**, *49*, 646.

magnetization is temperature independent.^{16,17} Moreover, many known $\text{Os}(\text{IV})$ complexes give good $^1\text{H NMR}$ spectra.¹⁷⁻¹⁹ In contrast, the $^1\text{H NMR}$ spectrum of a solution prepared by the $2e^-$ oxidation of **3** in D_2O yields only very broad signals, shifted strongly upfield and downfield.

The experiment now to be described shows that deprotonation of an $[\text{Os}^{\text{IV}}\text{-H}]^-$ complex leads to an $\text{Os}(\text{II})$ product. A sample of $[\text{Os}(\eta^2\text{H}_2)(\text{CH}_3\text{OH})\cdot 3\text{CF}_3\text{SO}_3]$ was dissolved in pyridine, and after 2 h ether was added to the solution, yielding a precipitate which was collected, washed with ether, and dried. The analytical results on the solid show that each Os is accompanied by 2en, $2\text{C}_6\text{H}_5\text{N}$, and $2.5\text{CF}_3\text{SO}_3$. When the solid is dissolved in $(\text{CD}_3)_2\text{CO}$, no $^1\text{H NMR}$ signal ascribable to solute is observed. However, when the solution is treated with $\text{NaOC}(\text{CH}_3)_3$, clean signals identical to those of authentic *cis*- $[\text{Os}(\eta^2\text{py}_2)]^{2+}$ are observed in $^1\text{H NMR}$.

We infer that when the hydrido species is dissolved in pyridine, substitution by the solvent occurs, as well as partial conversion to $[\text{Os}(\eta^2\text{py}_2)]^{2+}$ by deprotonation. The disappearance of the $^1\text{H NMR}$ signal for the $\text{Os}(\text{II})$ species can be accounted for by H^+ exchange with the paramagnetic hydrido complex:



On addition of a strong base to the mixture dissolved in acetone, deprotonation is completed, and thus the $^1\text{H NMR}$ signal for the $\text{Os}(\text{II})$ product now appears.

When $[\text{Os}(\eta^2\text{py}_2)](\text{CF}_3\text{SO}_3)_2$ is dissolved in D_2O , on addition of D_2SO_4 (1 M in the final solution) in 15 min a color change from dark red to yellow is complete, and the resulting solution shows only broad $^1\text{H NMR}$ peaks, which are strongly shifted upfield. We conclude that $[\text{Os}(\eta^2\text{py}_2)]^{2+}$ is readily protonated. Both protonation and deprotonation are measurably slow reactions.

Meyer and co-workers²⁰ report on the reversible protonation in solution of the molecules of the type $[\text{Os}(2,2'\text{-bipyridine})\text{-}(\text{PPh}_3)_2(\text{CO})\text{H}]^+$, protonation leading to a species of coordination number 7. From the fact that the protonated form yields good $^1\text{H NMR}$ signals, we infer that its paramagnetism is of the temperature-independent kind.

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