stretching vibration.[22] However the possibility of this being the bending vibration δ(Os–NN) is not excluded. The low-frequency absorptions may be assignable to either the ν(Os–N), ν(Os–C), or ν(Os–P) stretching vibrations, all of which should occur in the region between 500 and 300 cm^{-1}. Therefore, it is rather difficult to gain useful information from a study of the far-infrared spectra of these type complexes. A similar conclusion was reached by Chatt and coworkers[13] for the Nujol mull spectra of several dinitrogen–osmium complexes observed in the far-infrared region.

Conclusions

Data from infrared intensity measurements, as contrast with relative infrared frequency shifts of ν_{N_2} and ν_{CO} in metal dinitrogen and analogous metal carbonyl complexes, correlate exceeding well with other observations, such as Mössbauer studies, stability and reactivity studies, and molecular orbital calculations. All of these studies indicate the metal–N_2 bond to be less stable than the metal–CO bond in analogous complexes. However, the decrease in ν_{N_2} or μ'_{OsN_2} in a series of dinitrogen complexes can be attributed to differences in the stabilities of the Os–N_2 bonds.

Acknowledgments.—The author is most grateful to Professor Fred Basolo for making his article available prior to publication and for the gift of several dinitrogen complexes. He also thanks the Petroleum Research Fund administered by the American Chemical Society for Grant 1705-G3 which supported this research.

[22] A. D. Allen and J. R. Stevens, *Chem. Commun.*, 1147 (1967).

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The Ion Dihydridobis(ethylenediamine)osmium(IV)

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Reduction by zinc amalgam of an acidic solution containing $[OsO_2(en)_2]Cl_2$ leads to the formation in high yield of a salt having the composition $[OsH_2(en)_2]ZnCl_4$. Investigation of solutions by nmr shows two hydride hydrogens to be present for each osmium, and the structure of the part of the nmr spectrum attributable to the methylene protons of the coordinated amines suggests that the hydrides occupy cis positions. The hydrides are readily exchangeable for deuterium in an acidic solution in D_2O. In strongly basic solution, there is a shift in the nmr absorption but no change in the number of hydridic protons. The most likely explanation of the shift is that coordinated NH_2 is partly converted to NH^- by strong base. Three equivalents of iodine is consumed per mole of $OsH_2(en)_2^{2+}$ producing Os in the oxidation state 3+. The hydride does not produce Os(II) from Os(III) when mixed with it in equivalent amount.

Introduction

The reduction of $Os(NH_3)_6^{3+}$ to the dipositive state is known to be difficult.[2] The production of Os(II) in an environment of saturated ligands was of particular interest to us in our studies of the chemistry of N_2 as a ligand. Relying on experience with Ru,[3] which showed that the aquo ion is more easily reduced than the ammine, we turned to the reduction of the ion $OsO_2(en)_2^{2+}$ which is expected to form $Os(OH_2)_2(en)_2^{2+}$ when it is reduced to the 2+ state. Reduction of $OsO_2(en)_2^{2+}$ does take place, but instead of Os(II) being formed, the new species $OsH_2(en)_2^{2+}$ was encountered, where the protons shown are to be regarded as hydridic. Though in terms of its general composition the new ion is bracketed by $RhH_2(en)_2^{+}$ [4] on the one hand (metal in lower oxidation state) and ReH_7^{2-} and TeH_9^{2-} [5] on the other (metal in higher oxidation state and hydrogen: metal ratio higher), metal hydrides having only saturated amine ligands are rare enough to justify the description of the preparation and properties of this new ion being offered in this paper. In particular, it should be noted that all osmium hydrides thus far reported[6a] contain some unsaturated ligands.[6b]

Experimental Section

Only preparations of solid compounds will be dealt with in this section. The methods used for characterization of the ion were standard ones, and do not require discussion apart from that which is appropriate to the presentation of results in the next section.

$[OsO_2(en)_2]Cl_2$.—This compound has not heretofore been described. It was obtained by analogy with Gibbs' synthesis of $[OsO_2(NH_3)_4]Cl_2$.[7] In a typical preparation, a solution of 2.07 g of $K_2[OsO_2(OH)_4]$ dissolved in the minimum amount of water was added dropwise to a minimum volume aqueous solution containing 4 g of en·2HCl. The sparingly soluble product precipitated during this process. After filtration, a first crop (1.97 g) of crude $[OsO_2(en)_2]Cl_2$ was obtained, which was a dull yellow-orange product. By addition of sodium salts of Br^-, I^-, ClO_4^-, or tosylate, the osmyl salts of those anions were easily prepared from solutions of the chloride salt. *Anal.* Calcd for $[OsO_2(en)_2]Cl_2$: N, 13.61; H, 3.87; Cl, 17.2. Found: N, 13.4; H, 3.90; Cl, 17.3. Calcd for $[OsO_2(en)_2](ClO_4)_2$: C, 8.88; N, 10.4; H, 2.98; Cl, 13.1. Found: C, 8.76; N, 10.5; H, 2.82; Cl, 12.9. Potassium osmate, $K_2[OsO_2(OH)_4]$, was prepared by

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[1] National Academy of Sciences Overseas Research Fellow, University of São Paulo, Sao Paulo, Brazil, 1970–1972.

[2] W. P. Griffith, "The Chemistry of the Rarer Platinum Metals," Interscience, New York, N. Y., 1967, p 88.

[3] (a) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968); (b) R. E. Mercer and R. E. Buckley, *ibid.*, **4**, 1093 (1965).

[4] J. A. Osborne, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 3168 (1964); R. D. Gillard and G. Wilkinson, *ibid.*, 3594 (1963).

[5] A. P. Ginsberg and C. R. Sprinkle, *Inorg. Chem.*, **8**, 2212 (1969); A. P. Ginsberg, *ibid.*, **3**, 567 (1964).

[6] (a) See, for example, J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 6017 (1963); L. Vaska, *Inorg. Nucl. Chem. Lett.*, **1**, 89 (1965); W. P. Griffith, "The Chemistry of the Rarer Platinum Metals," Interscience, New York, N. Y., 1967, Chapter 3. (b) Phosphines are included among unsaturated ligands because they have the capacity to function as π acids, but we take no position on the question of the extent to which they function in this role in the combinations under consideration.

[7] L. Gibbs, *Amer. J. Chem.*, **3**, 233 (1881); L. Wintrebert, *Ann. Chim. Phys.*, **28**, 15 (1903).

Fremy's method.[8] All operations involving air-sensitive reagents were performed using argon or nitrogen as the blanketing gas. No effect on the experiments could be detected on substituting Ar for N_2.

The solid tetrachlorozincate salt of the hydrido species was prepared in the following way. A sample of $[OsO_2(en)_2]Cl_2$ (0.22 g) was reduced in 6 ml of 1 *M* HCl with approximately 4 g of mossy zinc amalgam while bubbling with argon. After several hours the yellow product solution was evaporated under vacuum to about 2 ml causing a bright yellow precipitate to form. This was collected on a fritted-glass filter in an inert atmosphere and, after washing with deaerated ethanol, was dried under vacuum. The dry salt could be exposed to dry air for several hours before discoloration, signifying that oxidation of the compound took place; yield 0.196 g. *Anal.* Calcd for $[OsH_2(en)_2]ZnCl_4$: C, 9.25; N, 10.8; H, 3.49; Cl, 27.3. Found: C, 9.25; N, 10.8; H, 3.42; Cl, 27.2. Zinc (calcd 12.6%) was determined as 12 ± 1% by precipitation of zinc pyrophosphate.

Preparation of $[OsH_2(en)_2]Cl_2$ was attempted by evaporating an acidic solution of the hydride obtained from a cation-exchange column after Zn^{2+} was eluted. The solid was hygroscopic and sensitive to oxygen. *Anal.* Calcd for $[OsH_2(en)_2]Cl_2 \cdot H_2O$: C, 12.0; N, 14.0; H, 5.0; Cl, 17.7. Found: C, 11.8; N, 13.8; H, 4.8; Cl, 17.3.

Results

The most definite evidence on the nature of the species produced when $OsO_2(en)_2^{2+}$ is reduced in acidic solution by Zn amalgam was provided by nmr measurements.

In Figure 1 is shown the upfield region of a 60-MHz nmr spectrum (recorded using a Varian Associates, Inc., T-60 instrument) of a solution 0.091 *M* in reduced $OsO_2(en)_2^{2+}$. At δ 15.4 ppm, upfield of the internal *tert*-butyl alcohol standard (methyl proton signal), the single symmetrical peak characteristic of the metal hydride is seen. Using the known concentration (0.112 *M*) of *tert*-butyl alcohol and the relative areas of the *tert*-butyl alcohol and osmium hydrido peaks (5.63 methyl protons per hydridic proton) the number of hydridic protons per osmium was calculated as 1.96 ± 0.1 The solution, in a sealed tube, gave the same relative peak areas after several days.

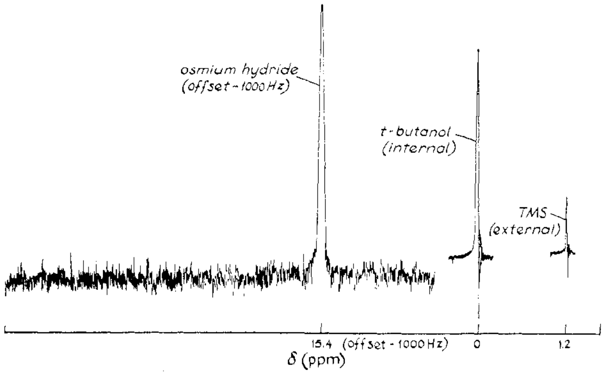

Figure 1.—Nmr spectrum of the $OsH_2(en)_2^{2+}$ (0.091 *M*) upfield region.

To determine if the osmium hydride persists through a precipitation cycle, $[OsH_2(en)_2]ZnCl_4$ (0.0327 g) was dissolved in 0.80 ml of a solution 1 *M* in HCl and 0.094 *M* in *tert*-butyl alcohol. The measured ratio of the proton peak areas was 5.56 methyl protons per osmium hydrido proton signifying 1.9 ± 0.1 hydrides per osmium.

The downfield region of a 60-MHz nmr spectrum of a solution of 0.118 g of $[OsH_2(en)_2]ZnCl_4$ dissolved in 2 ml of D_2O ($[D^+]$ = 0.1 *M*) showed peaks at δ −4.1 (with respect to internal *tert*-butyl alcohol) and δ −2.75 ppm which are attributed to hydrogen bound to nitrogen in ethylenediamine. A complex, symmetrical grouping at δ −1.11 ppm due to the ethylene hydrogens was also registered. Figure 2 shows the 100-MHz spectrum (Varian HA 100) of the same solution in which the fine structure at δ −1.11 ppm resolved into two groups. The integrated intensities of the peaks were measured in D_2O solution. In a separate experiment in H_2O solution, the integrated intensity of the hydrido peak was compared with that of the ethylene peak. The combined results of the two experiments yielded the overall ratio hydride:ethylene protons:amine protons of 2:9.1:8.1, respectively. Within experimental error the results are consistent with a formulation containing 2 ethylenediamines and 2 hydrides per osmium.

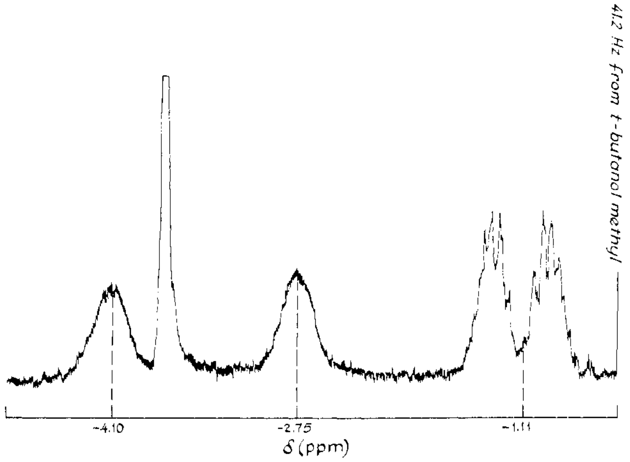

Figure 2.—The nmr spectrum (100-MHz) of $[OsH_2(en)_2]ZnCl_4$ in D_2O, showing resolution of the ethylene proton peaks.

If the $OsH_2(en)_2^{2+}$ ion is six-coordinate based on the octahedron, the nmr data indicate that the configuration is cis. A trans compound of this formulation would have only one signal arising from the protons bound to nitrogen. Also, although conformational differences might contribute to the fine structure observed for ethylene protons, the large number of lines in the spectrum is consistent with a cis rather than a trans formulation.

Dissolution of 0.0271 g of $[OsH_2(en)_2]ZnCl_4$ in 0.80 ml of D_2O, acidified approximately 0.1 *M* with HCl, yielded no detectable hydride signal. However, addition of 0.4 ml of H_2O caused the hydride signal to appear. At its final intensity the hydrido peak corresponded to $[OsH_2(en)_2^{2+}]$ = 0.016 ± 0.002 *M*. The predicted concentration was 0.015 *M*. The experiments show that exchange of hydride for protons in the bulk solvent is fairly rapid.

In 1 *M* NaOH the hydrido nmr peak is shifted to δ 13.1 ppm (upfield of internal *tert*-butyl alcohol). However, the intensity of the peak is not measurably decreased from 2 hydrides per osmium. Increasing the concentration of OH^- to 2 *M* does not alter the resonance frequency or the intensity of the hydride absorption any further. Reacidification of the solution moves the peak back to its original position. The result that

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(8) E. Fremy, *J. Prakt. Chem.*, **33**, 412 (1844).

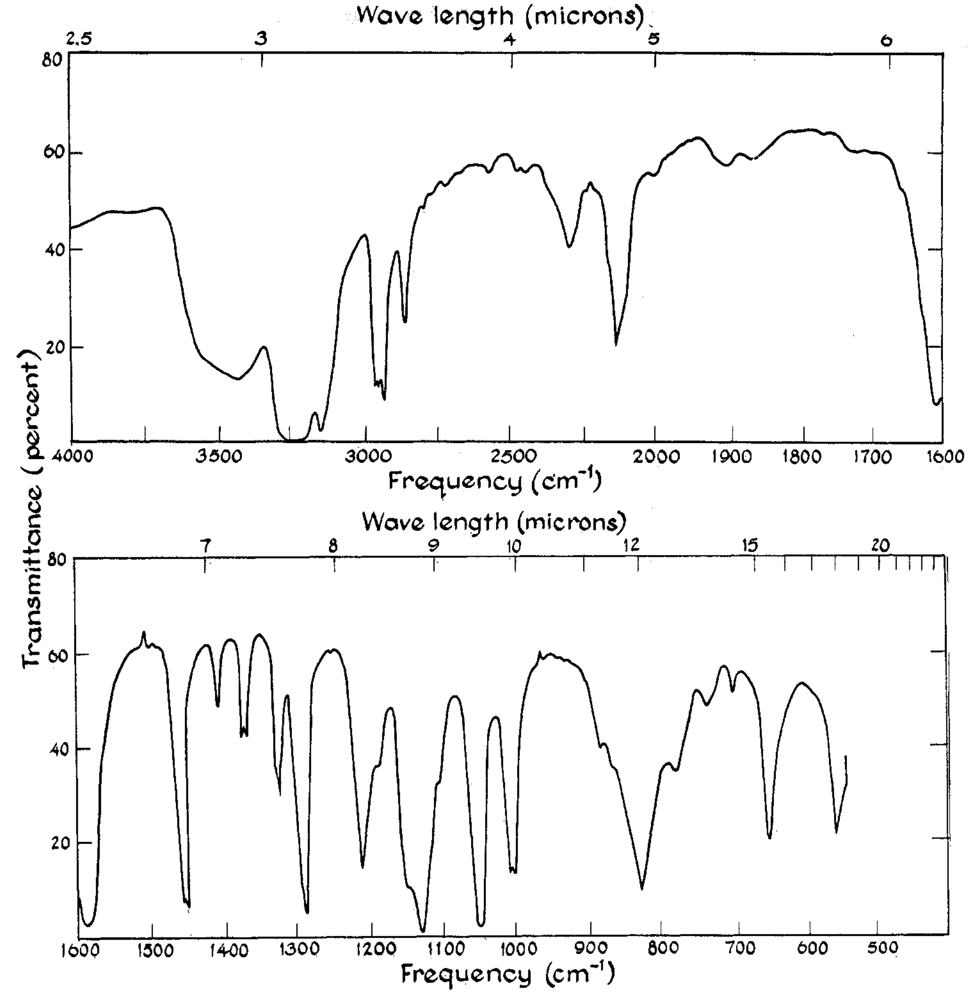

Figure 3.—The infrared spectrum of $[OsH_2(en)_2]ZnCl_4$ in KBr pellet.

the peak size is undiminished in basic solution shows that at concentrations up to 2 *M* OH^- the compound resists deprotonation at the hydride sites. The shift in the peak could result from a rapid exchange between a small amount of monodeprotonated hydride and the hydride itself, but this seems unlikely since the effect is not augmented by the twofold increase in $[OH^-]$. It is more likely that the shift is caused by deprotonation of the amines or by substitution of hydroxide in the inner coordination sphere. The former has precedent in Os(IV) compounds.[9,10]

The infrared spectrum of $[OsH_2(en)_2]ZnCl_4$ in a KBr pellet is shown in Figure 3. The peak at 2150 cm^{-1} is assigned to metal–hydride stretching vibrations. When the hydride was prepared in D_2O solution and the spectrum was recorded using a pellet slightly damp with D_2O, the 2150-cm^{-1} peak was diminished, and there appeared a new peak at 1537 cm^{-1}. The observed shift of 613 cm^{-1} is in good agreement with the shift of 628 cm^{-1} predicted for the 2150-cm^{-1} peak on deuteration and indicates that the parent peak corresponds to an osmium–hydride stretching vibration. The effect of deuterium substitution on the smaller 2300-cm^{-1} peak could not be determined because of interference with other peaks. The two peaks at 2150 and 2300 cm^{-1} almost certainly do not constitute the expected doublet for a cis dihydride, since the magnitude of the splitting is much greater than is observed for a heavy metal cis dihydride.[11] A possible explanation is that the 2300-cm^{-1} peak[12] is an overtone and the doublet is contained within the rather asymmetrical 2150-cm^{-1} peak.[13]

The uv spectrum of the yellow osmium dihydride in acidic aqueous solution consists of a smooth end absorption. The extinction coefficients at 210, 250, 300, and 350 nm are, respectively (in M^{-1} cm^{-1}), 2.1×10^3, 8.7×10^2, 2.5×10^2, and 96.

The magnetic susceptibility of solid $[OsH_2(en)_2]ZnCl_4$ was measured by the Gouy method at two temperatures, using water at 25° to calibrate the Gouy tube. At 25 and $-90°$, the molar susceptibilities ($\times 10^6$) of the compound were found to be, respectively, -182 and -195 cgs. After subtraction of individual atomic diamagnetic corrections, the magnetic moment of osmium was calculated to be 0.22 and 0.10 BM at 25 and at $-90°$, respectively. Osmium in the compound is therefore diamagnetic or, at most, slightly paramagnetic, depending on the size of the diamagnetic corrections used

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[9] F. P. Dwyer and J. W. Hogarth, *J. Amer. Chem. Soc.*, **77**, 6152 (1955).

[10] G. W. Watt, J. T. Summers, E. M. Potrafke, and E. R. Birnbaum, *Inorg. Chem.*, **5**, 857 (1966).

[11] J. A. Osborn, F. A. Jardim, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

[12] A referee has suggested that the 2300-cm^{-1} peak is caused by carbon dioxide. We consider our explanation to be more likely because a broad, weak band slightly displaced from 2300 cm^{-1} is seen in the spectrum of $OsO_2(en)_2Cl_2$.

[13] In the solid precipitation with HBr, the hydride region was shifted and slightly split, giving ν_{M-H} 2110 and 2130 cm^{-1}.

in calculating the magnetic moment. The ease with which the hydride, ethylene, and amine protons were detected in solution by nmr technique is inconsistent with paramagnetic broadening.

To determine the reducing power of the new species, solutions of air-free triiodide ion were titrated with solutions of $[OsO_2(en)_2]Cl_2$ which had been reduced by zinc amalgam in acidic aqueous media ($[H^+] \geq 0.1$ *M*). In 0.1 *M* $[I^-]$ a 9.0-ml sample of a solution 5.67×10^{-4} *M* in total iodine concentration required 8.79 ml of 3.85×10^{-4} *M* osmium solution, showing that 3.0 equiv of iodine is consumed per mole of osmium. (Triiodide solutions were standardized spectrophotometrically using the extinction coefficients and equilibrium data of Awtrey and Connick.[14]) Three other experiments of this type gave values of 3.0 equiv of reducing power (*vs.* I_3^-) per mole of osmium. That the product of oxidation of the complex contains osmium in the 3+ oxidation state is indicated by the following observations. First, we find that iodine does not oxidize pentaammineaquoosmium(III) in aqueous solution at low pH; similar behavior might be expected of a bis(ethylenediamine)-substituted Os(III) ion. Second, reaction between gaseous nitric oxide and the oxidation product yields a compound which is characterized by its strong ir absorption band at 1853 cm^{-1} as being an osmium–nitrosyl complex. Osmium nitrosyls have been shown to be formed from osmium(III) ammines and NO.[15] The corresponding reaction with compounds of higher oxidation states of osmium is not known and is not to be expected. Thus we write the reaction of $OsH_2(en_2)^+$ with I_3^- as follows (the form of Os(III) is assumed but not known to be $Os(H_2O)_2(en)_2^{3+}$)

$$OsH_2(en)_2^{2+} + {}^3/_2I_3^- + 2H_2O = Os(H_2O)_2(en)_2^{3+} + 2H^+ + {}^9/_2I^-$$

The charge per osmium in aqueous solution was determined in the following way. In one experiment a solution 0.0914 *M* in reduced osmium was produced by zinc amalgam reduction of a known amount of $[OsO_2(en)_2]Cl_2$ in 1.00 *M* HCl solution. After complete reduction, the solution was exposed to air and the hydride oxidized. The concentration of hydrogen ion (0.220 *M*) was determined by titration, and the concentration of zinc ion (0.338 *M*) by precipitation of zinc pyrophosphate. The charge per osmium after air oxidation was calculated as 3.1 ± 0.5 from consideration of charge balance. In a second experiment, a solution containing Zn^{2+}, H^+, Cl^-, and the osmium hydride was eluted onto a cation-exchange column (Dowex 50-X2). Zinc ion was removed by washing the column with 5 volumes of 1 *M* HCl which moved the hydride species only slightly down the column. Afterward the osmium hydride was eluted with 3 *M* HCl, and the concentration of osmium hydride in the eluted solution was found by the nmr method to be 0.089 *M*. The chloride ion concentration, determined gravimetrically by silver chloride precipitation, was 2.49 *M* and the hydrogen ion concentration was 2.24 *M* after air oxidation. The charge per osmium after air oxidation was calculated as 2.8 ± 0.3, in agreement with the previous result. To infer the charge of the hydride itself, one may consider that oxidation of the dipositive dihydride by 3 equiv of oxygen would involve the consumption of 1 mol of hydrogen ion per mole of osmium. It must be admitted that the data are also consistent with four-electron oxidation by oxygen to yield an Os(IV) species, possibly aquo substituted, which would then be hydrolyzed to yield 1 mol of hydrogen ion according to the net reaction

$$H^+ + OsH_2(en)_2^{2+} + O_2 \longrightarrow Os(OH)(H_2O)(en)_2^{3+}$$

Either three- or four-electron oxidation of a dipositive dihydride is consistent with the results. The three-electron oxidation is more attractive in view of the results obtained in the triiodide titrations and upon considering the known resistance of osmium(III) ammines, *e.g.*, $OsOH_2(NH_3)_5^{3+}$, to air oxidation in acidic aqueous solution.

A partial explanation of why amine, ammine, and aquo complexes of Os(II) have not been found in aqueous media may reside in the remarkable stability of the hydrido ions. This stability is demonstrated by the following experiment. A sample of 0.0799 g of $[OsO_2(en)_2]Cl_2$ and 1.0 ml of 1 *M* HCl was deaerated with argon, and to it was added 4.0 ml of a solution 0.098 *M* in $OsH_2(en)_2^{2+}$. After 45 min at room temperature, the concentration of the dihydride was found to be 0.041 ± 0.004 *M*. Reduction of the osmyl compound to Os(III) by the hydride would have yielded 0.039 *M* $OsH_2(en)_2^{2+}$ at equilibrium. Formation of Os(II) would have consumed all the available hydride. Even after 18 hr, a strong hydride signal was observed. The experiment indicates that reduction of Os(III) to Os(II) by osmium hydride is either very slow or impossible thermodynamically.

The particular affinity of Os(IV) for the hydride ligand and the lack of strong paramagnetism compared to other Os(IV) compounds[16] is consistent with a greater degree of polarization than exists in the more reactive hydrides. Strong polarization in the asymmetical cis dihydride might lift the degeneracy of the t_{2g} orbitals sufficiently to give a d^4 low-spin compound. However, the possibility of a low-spin seven-coordinate compound with an ion occupying the seventh position has not been eliminated.

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[14] A. D. Awtrey and R. E. Connick, *J. Amer. Chem. Soc.*, **73**, 1842 (1951).

[15] J. N. Armor, H. Scheidegger, and H. Taube, *ibid.*, **90**, 5928 (1968).

[16] A. D. Westland and N. C. Bhiwandler, *Can. J. Chem.*, **39**, 1284 (1961); R. B. Johanneson and G. A. Candela, *Inorg. Chem.*, **2**, 67 (1963).