Determination of the Structure of $[Os(\eta^2\text{-}H_2)en_2CH_3CO_2]PF_6$ by X-ray and Neutron Diffraction[1]

Tai Hasegawa,*[,2a] Zaiwei Li,[2a] Sean Parkin,[2b] Håkon Hope,[2b] Richard K. McMullan,[2c] Thomas F. Koetzle,[2c] and Henry Taube*[,2a]

Contribution from the Departments of Chemistry, Stanford University,
Stanford, California 94305, University of California at Davis, Davis, California 95616,
and Brookhaven National Laboratory, Upton, New York 11973

Received August 9, 1993®

Abstract: The structure of $[Os(\eta^2\text{-}H_2)en_2CH_3CO_2]PF_6$ (**1**) has been studied by X-ray diffraction at 120 K and neutron diffraction at 165 K. Compound **1** belongs to a series of dihydrogen complexes of osmium(II) amines, exhibiting an extensive range in the strength of the H–H interaction as judged by the wide variation in observed J_{H-D} coupling constants. The ethylenediamine ligands in **1** have a trans arrangement. The H_2 and the acetate ligands occupy positions on opposite sides of the OsN_4 plane, giving overall approximately octahedral coordination. Consistent with the relatively low J_{H-D} value (9.0 Hz), the H–H distance in **1**, 1.34(2) Å as determined by neutron diffraction, is unusually long and approaches that of 1.357(7) Å found in the polyhydride $ReH_7\{P(p\text{-tolyl})_3\}_2$. It is presumed that **1** may represent an intermediate stage in the oxidative addition of dihydrogen at transition-metal centers. The Os–H distances in **1**, 1.59(1) Å and 1.60(2) Å, are shorter than those in the classical osmium polyhydride $OsH_4(PMe_2Ph)_3$ (mean Os–H 1.659(3) Å) lending support to the assertion that the $Os(\eta^2\text{-}H_2)$ interaction is relatively strong. Crystal data: $C_6H_{19}F_6N_4O_2OsP$, fw 514.4, monoclinic, $P2_1/n$, $Z = 4$, $a = 11.671(2)$ Å, $b = 10.639(2)$ Å, $c = 11.775(2)$ Å, $\beta = 96.02(1)°$ at 165 K, $d_{calc} = 2.706$ g cm^{-1}. Structure analysis: (X-ray) $R(F) = 0.041$ for 1603 reflections ($F > 4\sigma(F)$); (neutron) $R(F) = 0.088$ for 1897 reflections ($F^2 > \sigma(F^2)$).

Since Kubas reported the first isolable dihydrogen compounds,[3–5] a number of other compounds of this type have been described.[6–9] Neutron diffraction values of H–H distances reported to date are the following: 0.82(1) Å in $WH_2(CO)_3\{P(i\text{-}Pr)_3\}_2$[10] ($J_{H-D} = 34$ Hz), 0.816(16) Å in *trans*-$[Fe(H_2)(H)(dppe)_2]BF_4$[11] ($J_{H-D} = 32$ Hz), 0.821(10) Å in *cis,mer*-$Fe(H_2)(H)_2(PEtPh_2)_3$[12] (J_{H-D} is not reported), 0.736(10) Å in $Mo(H_2)(CO)(dppe)_2\cdot 4.5C_6D_6$[13] ($J_{H-D} = 34$ Hz), and more recently 1.11(3) Å in $Ir(H_2)(H)Cl_2\{P(i\text{-}Pr)_3\}_2$[14] ($J_{H-D} = 12$ Hz). Although the H–H distance of 1.357(7) Å is reported in $ReH_7\{P(p\text{-tolyl})_3\}_2$,[15] the measurement of J_{H-D} for this complex was not found to be feasible. It has been suggested that this intermediate H–H distance is attributable to the crowded nature of a highly coordinated polyhydride complex.[16]

The dihydrogen complexes of osmium(II) amines recently reported provide a unique opportunity to modify the H–H interaction, as reflected in the values of J_{H-D}, by substitution at a single site, the composition otherwise remaining unaltered.[17,18] Detailed study of examples over a range of J_{H-D} values can provide correlations of properties such as J_{H-D}, relaxation times, and reactivity with H–H distances, as determined by neutron diffraction or, in favorable cases, by X-ray diffraction from crystals. In this paper we present structural results for $[Os(\eta^2\text{-}H_2)en_2CH_3CO_2]PF_6$ (**1**) containing a cation selected as having a relatively low value of J_{H-D} (9.0 Hz, vide infra).

Experimental Section

Materials. Compound **1** was prepared by simple substitution on a salt (PF_6^- or $CF_3SO_3^-$) of *trans*-$[Os(\eta^2\text{-}H_2)en_2]^{2+}$ (**2**)[19] dissolved in CH_3OH. Lithium acetate (100 mg) was added to a solution of **2** in CH_3OH (100 mg, 5 mL) and after 0.5 h ether was added. The precipitate was collected and washed with ether. Yield, 91%. Anal. Calcd for $[Os(\eta^2\text{-}H_2)en_2CH_3CO_2]PF_6$: C, 13.95; H, 4.06; N, 10.84. Found: C, 14.25; H, 3.98; N, 11.12. Crystals suitable for structure determination were obtained by slow diffusion of ether into a solution of **1** in methanol.

Instruments. ^{1}H NMR spectra were obtained on Varian XL-400 (400 MHz) or Gemini (200 MHz) spectrometers. Relaxation rate (T_1) experiments employed the saturation recovery method. X-ray diffraction data were collected on a Siemens P4RA diffractometer equipped with a locally modified LT-2 low-temperature device.

X-ray Diffraction Analysis. Crystals of **1** in their mother liquor were covered with paratone N (Exxon) oil and examined under a polarizing microscope. A suitable specimen of dimensions 0.16 × 0.16 × 0.08 mm (0.002 mm^3) was mounted on a Siemens P4RA diffractometer and flash cooled to 120 K in a cold N_2 stream. Data were collected using nickel

---

® Abstract published in *Advance ACS Abstracts,* April 15, 1994.

[1] Presented in part at the International Conference on Coordination Chemistry, Lausanne, July 1992. Hasegawa, T.; Li, Z.; Parkin, S.; McMullan, R.; Taube, H. *Proc. ICCC* **1992,** *29,* 150.

[2] (a) Stanford University. (b) University of California, Davis. (c) Brookhaven National Laboratory.

[3] Kubas, G. J.; Ryan, R. R.; Swanson, B. J.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984,** *106,* 451.

[4] Kubas, G. J.; Unkefer, C. J.; Swanson, B. J.; Fukushima, E. *J. Am. Chem. Soc.* **1986,** *108,* 7000.

[5] Kubas, G. J.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986,** *108,* 1339.

[6] Kubas, G. J. *Acc. Chem. Res.* **1988,** *21,* 120.

[7] Crabtree, R. H. *Acc. Chem. Res.* **1990,** *23,* 95.

[8] Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992,** *121,* 155.

[9] Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993,** *93,* 913.

[10] Vergamini, P. J.; Wasserman, H. J.; Koetzle, T. F.; Kubas, G. J., unpublished work cited in footnote 9 of ref 4.

[11] Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989,** *111,* 8823.

[12] Van Der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hull, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990,** *112,* 4831.

[13] Kubas, G. J.; Burns, C. J., Eckert, J.; Johnson, S. W.; Larson, A. C.; Vergamini, P. J.; Unkefer, C. J.; Khalsa, G. R. K.; Jackson, S. A.; Eisenstein, O. *J. Am. Chem. Soc.* **1993,** *115,* 569.

[14] Albinati, A.; Bakhmutov, V. I.; Caulton, K. G.; Clot, E.; Eckert, J.; Eisenstein, O.; Gusev, D. G.; Grushin, V. V.; Hauger, B. E.; Klooster, W. T.; Koetzle, T. F.; McMullan, R. K.; O'Loughlin, T. J.; Pélissier, M.; Ricci, J. S.; Sigalas, M. P.; Vymenits, A. B. *J. Am. Chem. Soc.* **1993,** *115,* 7300.

[15] Brammer, L.; Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L.; Stringer, A. M. *J. Chem. Soc., Chem. Commun.* **1991,** 241.

[16] Craw, J. S.; Bacskay, G. B.; Hush, N. S. *Inorg. Chem.* **1993,** *32,* 2230.

[17] Li, Z. W.; Taube, H. *J. Am. Chem. Soc.* **1991,** *113,* 8946.

[18] Li, Z. W.; Taube, H. *Science* **1992,** *256,* 210.

[19] Paper in preparation. In a methanol solution, this cation is formulated as *trans*-$[Os(\eta^2\text{-}H_2)en_2CH_3OH]^{2+}$. In the solid, it may be *trans*-$[Os(\eta^2\text{-}H_2)en_2PF_6]^+$ or the corresponding $CF_3SO_3^-$ salt.

0002-7863/94/1516-4352$04.50/0 © 1994 American Chemical Society

filtered Cu Kα radiation. Initial cell constants at 120 K were determined from 24 reflections (2θ range 45–55°) distributed among all octants of reciprocal space. The indexing suggested triclinic lattice symmetry with tentative cell constants $a = 11.653(4)$ Å, $b = 10.573(4)$ Å, $c = 11.790(4)$ Å, $\alpha = 90.65(3)°$, $\beta = 95.78(3)°$, and $\gamma = 90.84(3)°$. Similar cell constants were obtained at temperatures between 120 and 190 K. The α and γ angles, however, were observed to slowly change to 90°, and estimated standard deviations for all cell constants decreased somewhat. After about 36 h at 120 K, the cell dimensions were $a = 11.686(2)$ Å, $b = 10.573(2)$ Å, $c = 11.796(2)$ Å, and $\beta = 95.57(1)°$. Subsequent small searches through reciprocal space confirmed the monoclinic setting, and systematic absences suggested the space group $P2_1/n$. Data were collected at 120 K using the θ–2θ scan technique.

Neutron Diffraction Analysis. The crystal selected for neutron diffraction study exhibited prominent forms {010}, {101}, {–101} and had dimensions 5.5 × 1.5 × 0.2 mm (1.7 mm³) where the longest dimension is coincident with the *b* axis. The data were collected on the four-circle diffractometer at port H6S of the Brookhaven high flux beam reactor. The neutron beam, monochromated by Ge(220) planes in transmission geometry, was of wavelength 1.1584(1) Å as calibrated against a KBr crystal ($a_0 = 6.6000$ Å at 295 K).[20] The sample crystal was covered in a protective film of halocarbon grease, mounted on its (010) face to an aluminum pin, and sealed inside an aluminum canister under helium gas. Sample cooling at ~2° min^{-1} was effected using a helium refrigerator[21] while monitoring strong reflections 1,–2,0 and –1,–2,0 by means of ω scans. Between 160 and 150 K the scan profiles broadened markedly and at lower temperatures separated into poorly resolved peaks. The indicated phase transformation was reversible: warming above 160 K produced sharpening of the profiles. The intended measurement temperature of 15 K was thus unattainable without loss of crystal integrity. The data were collected within a three-week period at 165 ± 0.1 K. The lattice parameters were determined by a least-squares fit of $\sin^2\theta$ values for 32 reflections within the range $34° < 2\theta < 56°$. Intensity data in two quadrants, $[h,-k,\pm l;\ h \le 16,\ |k| \le 15,\ |l| \le 16;\ \sin\theta/\lambda < 0.69\ \text{Å}^{-1}]$ and $[-h,-k,\pm l;\ |h| \le 16,\ |k| \le 15,\ |l| \le 16;\ 0.55\ \text{Å}^{-1} < \sin\theta/\lambda < 0.62\ \text{Å}^{-1}]$, were measured by the $\theta/2\theta$ step–scan method using scan widths of $\Delta 2\theta = 2.6°$ for $\sin\theta/\lambda \le 0.36\ \text{Å}^{-1}$ and $\Delta 2\theta = (1.143 + 2.807 \tan\theta)°$ for $\sin\theta/\lambda > 0.36\ \text{Å}^{-1}$. The intensities of two reflections, [5,–1,6; 2,–8,2] monitored at regular intervals showed no systematic variations. Integrated intensities I_0 and variances $\sigma^2(I_0)$ were derived from the scan profiles as described previously.[22]

Results

Structure of 1 by X-ray Diffraction. The crystal and related data are shown in Table 1: $C_6H_{19}F_6N_4O_2OsP$, fw = 514.4, monoclinic, $P2_1/n$, $Z = 4$, $V = 1447.6(4)$ Å³, $\rho_{calc} = 2.360$ g cm^{-3}, μ(Cu Kα) = 184.56 cm^{-1}. Index ranges: $-12 \le h \le 12$, $0 \le k \le 11$, $0 \le l \le 12$. Reflections measured: 3554. Independent reflections: 1777 ($R_{int} = 3.4\%$). Reflections used with $F > 4.0\sigma(F)$: 1603. Absorption was corrected with the XABS program.[23] The structure was solved by direct methods and refined by full-matrix weighted least-squares techniques.[24,25] Final fit indices (obs data): $R = 0.041$, $R_w = 0.047$.[26] Goodness-of-fit, $S = 1.21$.[27]

The structure suffers from disorder,[28] which has been observed also in other compounds of this type,[29] of the carbon atoms in one of the ethylenediamine groups. The disordered ethylenediamine was refined with a restrained model with all equivalent bond lengths and angles tied to the same value. The four carbon atoms exhibiting fractional occupany (C1, C1′, C2, C2′) were refined isotropically with the two pairs C1 and C1′, and C2 and C2′ having the tied parameters. All the other ordered non-hydrogen atoms were refined anisotropically. The populations of the two disordered conformations were also refined to be so close to 50:50 that we fixed them at half occupancy. The *U*'s for all the hydrogen atoms were fixed and isotropic. The bond distances and angles are in good agreement with other data.[30]

Table 1. Crystal Data and Details of the Intensity Measurements and Structure Refinements for *trans*-$[Os(\eta^2\text{-}H_2)en_2CH_3CO_2]PF_6$

	X-ray	neutron
empirical formula	$C_6H_{19}F_6N_4O_2OsP$	$C_6H_{19}F_6N_4O_2OsP$
fw	514.4	514.4
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
cell dimensions		
a, Å	11.686(2)	11.671(2)
b, Å	10.573(2)	10.639(2)
c, Å	11.796(2)	11.775(2)
β, °	95.57(1)	96.02(1)
V, Å³	1447.6(4)	1454.0(4)
T, K	120	165
Z	4	4
d_{calc}, g cm^{-1}	2.360	2.370
μ, cm^{-1}	184.56 [Cu Kα]	2.706
radiation	Cu Kα rotating anode	neutrons, λ = 1.1584(1) Å
2θ range	0.0 to 108.5°	0.0 to 106.0°
scan type	2θ–θ	2θ–θ
scan speed	constant (60.00° min^{-1} in 2θ)	variable step scans
crystal size, mm	0.16 × 0.16 × 0.08	5.5 × 1.5 × 0.2
no. of reflns measd	3554	6287
no. of reflns used	1603 ($F > 4.0\sigma(F)$)	1897 ($F^2 > 1.0\sigma(F^2)$)
R(*F*)	0.0407	0.0881
$R_w(F)$	0.0468	
goodness-of-fit	1.21	1.097

The ethylenediamines have a trans arrangement, as already suggested by ¹H NMR data.[16] The H_2 and the acetate ligands occupy positions on opposite sides of the OsN_4 plane, giving overall approximately octahedral coordination.

In the final electron density difference map, there were many small ripples about the Os center. Two of these, with peak heights of about 0.5–0.6 e Å^{-3}, were 1.25 Å apart and were in positions which could be consistent with dihydrogen attached to the osmium. The angle formed by the vector from the midpoint of these two "atoms" to the osmium with the plane of Os–N3–N4, however, was 81.9°. For the true hydrogen positions, this angle ought to be near 90°, with the vector bisecting the angle between Os–N1–N2 and Os–N3–N4. To resolve the uncertainty in the H_2 position, we concluded that further investigation by neutron diffraction would be desirable.

Structure of 1 by Neutron Diffraction. The crystal and related data are shown in Table 1. Of the 6287 recorded reflections, only 3122 had $I_0 > \sigma(I_0)$, the large number of weak reflections being attributed to the relatively small crystal size. Absorption corrections[31,32] were applied using $\mu_n = 2.706$ cm^{-1} evaluated from $\mu/\rho = 2.641$ cm² g^{-1} for hydrogen[33] and μ/ρ values for non-hydrogen atoms given in the *International Tables for X-ray Crystallography*.[34] Minimum and maximum calculated transmission factors were 0.468 and 0.947. Averaging $F_o^2 > \sigma(F_o^2)$

---

(20) Donnay, J. D. H., Ondik, H. M., Eds. *Crystal Data Determinative Tables*, 3rd ed.; U.S. Department of Commerce and Joint Committee on Powder Diffraction Standards: Washington, DC, 1973; Vol. 2, p C-164.

(21) *DISPLEX* Model CS-202. Air Products & Chemicals, Inc.

(22) McMullan, R. K.; Epstein, J.; Ruble, J. R.; Craven, B. M. *Acta Crystallogr*. **1979**, *B35*, 688.

(23) Program *XABS* provides an empirical correction based on F_o and F_c differences. Hope, H.; Moezzi, B. Chemistry Department, University of California, Davis.

(24) Sheldrick, G. M. *SHELXTL PLUS*, A Program For Crystal Structure Determination, Version 4.0, 1989, Siemens Analytical X-ray Instruments, Madison, WI.

(25) Scattering factors (neutral atoms) are from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(26) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}$. Weighting scheme: $w^{-1} = \sigma^2(F) + 0.0012F^2$.

(27) $S = [\sum(w||F_o| - |F_c||^2)/(n - p)]^{1/2}$ where *n* is the number of observed reflections and *p* is the number of parameters refined.

(28) Raymond, K. N.; Corfield, P. W. R.; Ibers, J. A. *Inorg, Chem.* **1968**, *7*, 1362.

(29) Hasegawa, T.; Parkin, S.; Li, Z.; Taube, H., paper in preparation.

(30) Davis, B. R.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 2768.

(31) Meulenaer, J. De; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014.

(32) Templeton, L. K.; Templeton, D. H. *Abstr. Am. Crystallogr. Assoc. Meet.*, Storrs, CT, 1973, 143.

(33) Koetzle, T. F.; McMullan, R. K. *HFBR Research Memorandum* 1980, C-4.

(34) *International Tables for X-ray Crystallography*; Kynoch Press: Birminham, 1962; Vol. 3, p 197.

for 455 symmetry-related pairs of reflections gave $R_{int} = 5.5\%$ and yielded 2265 independent observations. Of these, 1897 reflections with $F_o^2 > \sigma(F_o^2)$ were used in the structure refinement.

The refinement was initiated with an ordered model of non-hydrogen atoms derived from the 120 K X-ray analysis. The hydrogen positions were located in difference maps. Coherent neutron scattering lengths (fm) for H (–3.7409), C (6.6484), O (5.803), P (5.13), F (5.66), and Os (10.8) were taken from the tabulation of Koester.[35] The refinement was carried out by full-matrix least-squares methods using the program of Lundgren.[36] The residual $\sum w(F_o^2 - F_c^2)^2$ was minimized with weights $w = [\sigma^2(F_o^2) + (0.02F_o^2)^2]^{-1}$. The variable parameters were coordinates, anisotropic thermal factors, one scale factor, and the isotropic secondary extinction parameter for a type I crystal.[37] The data were marginally affected by extinction, the largest correction ($\times F_o^2$) being 1.05 for reflection 200. At convergence, difference maps revealed residual density attributable to disorder of the ethylenediamine group as also was found in the X-ray analysis. A common occupancy factor for the group of larger density, included as a variable parameter, refined to a value of 0.66(2) with the summed occupancy constrained to 1.0 for the two configurations.

The refinement converged ($\Delta p_i/\sigma(p_i) < 0.01$) with fit indices $R(F^2) = 0.121$, $wR(F^2) = 0.113$, and $S = 1.097$.[38] The conventional R value on F is 0.088. In the final ΔF map, the largest $|\Delta\rho|$ errors were ~3.0% of the peak maximum for nitrogen in the ρ_0 map; the residuals occurred near the disordered ethylenediamine group and are attributed to details that are unresolved by the present data.

Nuclear coordinates and equivalent isotropic displacement parameters for **1** are listed in Table 2. Two approximately orthogonal views of the structure of **1** are shown in Figures 1 and 2.[39] The H–H distance determined by neutron diffraction is 1.34(2) Å. The two Os–H distances are 1.59(1) and 1.60(1) Å. The H–Os–H plane is tilted 20° from the acetate C_2O_2 plane and 47° from the N2–Os–N4 plane. This conformation and alignment of the H–H bond differ from that expected on the basis of structures of other octahedral H_2 complexes[10,11] where H–H lines up with one of the vectors connecting a pair of trans ligands.

Discussion

At this writing, **1** has the lowest J_{H-D} value observed for a system with a structure confirmed by neutron diffraction and for which the one-bond coupling in the dihydrogen could be measured. The long H–H distance of 1.34(2) Å found in **1** is consistent with the relatively small J_{H-D} value of 9.0 Hz. Only one polyhydride complex, $ReH_7\{P(p\text{-tolyl})_3\}_2$ mentioned above, has been described in which the H–H distance is near to that which we report here, and unfortunately, the measurement of J_{H-D} for this complex was not possible; furthermore, the rhenium compound may be a classical polyhydride.[14] It is presumed that **1** may represent an intermediate stage in the oxidative addition of dihydrogen at transition-metal centers, which in this case in the limit would lead to a dihydride of Os(IV) of coordination number 7.

Table 2. Nuclear Coordinates (×10⁴) and Displacement Parameters (Å² × 10³) $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$

atom	x	y	z	U_{eq}
Os	1802(2)	1122(2)	757(2)	19(1)
N1	803(4)	1715(3)	2079(3)	32(1)
N2	1371(3)	–657(3)	1436(3)	26(1)
N3	3056(3)	504(4)	–327(3)	35(1)
N4	2501(4)	2870(3)	337(3)	37(1)
C1	120(8)	727(8)	2407(8)	33(3)
C2	861(12)	–474(14)	2477(15)	34(4)
C3	3881(6)	1547(6)	–467(6)	50(2)
C4	3203(6)	2757(6)	–606(5)	51(2)
C5	3844(4)	446(4)	2570(4)	31(1)
C6	4833(5)	914(6)	3419(5)	39(2)
O1	3209(5)	1284(5)	2070(5)	28(1)
O2	3686(7)	–688(6)	2459(9)	85(3)
P1	2834(6)	6752(6)	–833(6)	35(2)
F1	2299(7)	5638(7)	–131(7)	62(3)
F2	1612(9)	7360(10)	–1052(11)	96(4)
F3	3342(10)	7841(9)	–1516(8)	83(4)
F4	4065(7)	6140(10)	–558(8)	73(3)
F5	2644(10)	5942(9)	–1955(7)	84(4)
F6	3059(9)	7563(7)	311(6)	64(3)
HOs1	721(11)	1709(11)	7(10)	62(4)
HOs2	966(10)	525(11)	–261(9)	60(4)
HN1A	210(17)	2300(23)	1877(14)	126(9)
HN1B	1254(15)	2169(16)	2663(13)	87(6)
HN2A	2129(10)	–1085(10)	1687(11)	56(4)
HN2B	912(14)	–1188(13)	852(10)	75(5)
HN3A	3482(12)	–265(11)	48(13)	68(5)
HN3B	2668(11)	245(11)	–1108(10)	59(4)
HN4A	1923(13)	3604(11)	188(12)	71(5)
HN4B	3016(14)	3126(13)	1039(12)	75(5)
HC1A	–104(14)	851(14)	3354(14)	88(3)
HC1B	–593(16)	615(19)	1786(17)	60(3)
HC2A	426(7)	–1311(7)	2753(6)	68(3)
HC2B	1593(9)	–290(10)	3183(8)	63(4)
HC3A	4366(12)	1361(18)	–1208(12)	88(6)
HC3B	4487(11)	1626(13)	302(12)	70(5)
HC4A	2612(16)	2737(15)	–1406(10)	83(6)
HC4B	3785(13)	3603(13)	–627(15)	87(6)
HC6A	5363(16)	251(16)	3706(18)	113(8)
HC6B	4563(16)	1337(21)	4069(16)	108(8)
HC6C	5294(14)	1609(20)	3051(14)	110(8)
C1′ [a]	754(8)	10563(7)	2944(7)	26(3)
C2′ [a]	472(10)	–647(17)	2306(16)	37(4)
HC1′B[a]	1578(20)	613(20)	3350(15)	61(7)
HC2′B[a]	–372(10)	–563(17)	1835(11)	42(5)

[a] Occupancy factors of C1′, C2′, HC1′B, and HC2′B of the disordered en group are 0.34(2). Occupancy factors of the corresponding unprimed atoms are 0.66(2).

Notwithstanding the lack of a value for J_{H-D}, the structural results for $ReH_7\{P(p\text{-tolyl})_3\}_2$ nevertheless provide a useful perspective on those we have obtained for **1**. The heptahydridorhenium complex shows one H–H separation of 1.357(7) Å with all others exceeding 1.74 Å. The Re–H distances lie between 1.67 and 1.70 Å. The Os–H distances in **1**, 1.59(1) and 1.60(1) Å, are much shorter than the W–H distance of 1.89(1) Å found in $WH_2(CO)_3\{P(i\text{-Pr})_3\}_2$. Among the hydride complexes of third-row transition metals, the M–H distances most nearly comparable to those in **1** occur in $[Ir(\eta\text{-}C_5H_5)PMe_3H_3]BF_4$, for which the mean Ir–H distance is 1.587 Å,[40] the H–H distances being 1.67(1), 1.70(12), and 2.66(1) Å. In $OsH_4(PMe_2Ph)_3$,[41] a classical hydride complex, the mean Os–H distance is 1.659(3) Å, which is again slightly longer than that in **1**.

By contrast, in both *trans*-$[Fe(H_2)(H)(dppe)_2][BF_4]$[11] and *cis,mer*-$Fe(H_2)(H)_2(PEtPh_2)_3$,[12] the Fe–H distance to dihydrogen is 0.07–0.08 Å longer than the Fe–H distance to the hydride ligand(s). The relatively short Os–H distances in **1**, then, are consistent with comparatively strong Os–H bonding, as might be expected to accompany a low J_{H-D} value and long H–H distance.

The ^1H NMR spectrum of **1** dissolved in CD_3OD is shown in Figure 3a. Two hydridic protons show a single sharp peak at –12.8 ppm while the protons in en appear (ppm) at 5.5 and 4.6 (8 H, NH_2) and 2.4 and 2.1 (8 H, CH_2) and those in the acetate

---

(35) Koester, L. In Neutron Physics. *Springer Tracts in Modern Physics*; Hoehler, G., Ed.; Springer: Berlin, 1978; Vol. 80, p 35.

(36) Lundgren, J.-O. *UPALS*; A Full-Matrix Least-Squares Refinement Program. Report UUIC-B13-4-05, Institute of Chemistry, University of Uppsala: Uppsala, Sweden, 1982.

(37) Becker, P. J.; Coppens, P. *Acta Crystallogr.* **1974**, *A30*, 129–147.

(38) $R(F^2) = \sum\Delta/\sum F_o^2$; $wR(F^2) = [\sum w\Delta^2/\sum(wF_o^2)^2]^{1/2}$; $S = [\sum w\Delta^2/(n-p)]^{1/2}$, where $\Delta = |F_o^2 - F_c^2|$, and n and p are the numbers of observations and parameters, respectively.

(39) Johnson, C. K. *ORTEPII*, Report ORNL-5138, Oak Ridge National Laboratory, TN, 1976.

(40) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909.

(41) Hart, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 7557.

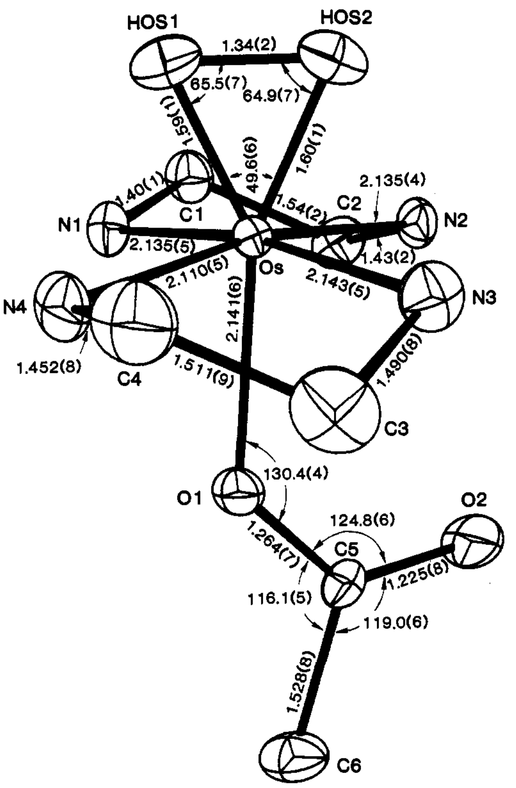

Figure 1. Structure of **1**, as determined by neutron diffraction, viewed approximately normal to the $Os(H_2)$ plane. The PF_6^- counterion is omitted and only one of the two conformations of the disordered en ligand is shown for clarity.

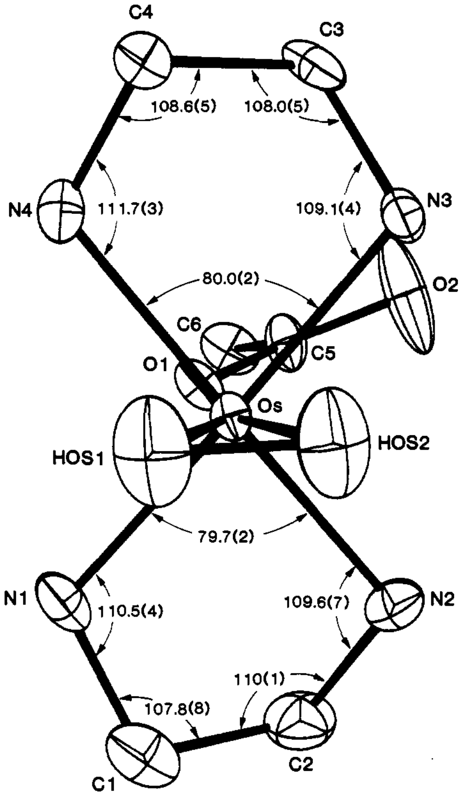

Figure 2. Structure of **1**, similar to Figure 1, viewed approximately normal to the $Os(en)_2$ plane.

appear at 2.1 (3 H, CH_3). On treatment with a trace of CF_3SO_3H in D_2O, a clear triplet (1:1:1, see Figure 3b) emerges, showing an isotopic shift of 16.3 Hz. The value of $J_{H\text{-}D}$ calculated from the splitting is 9.0 Hz.

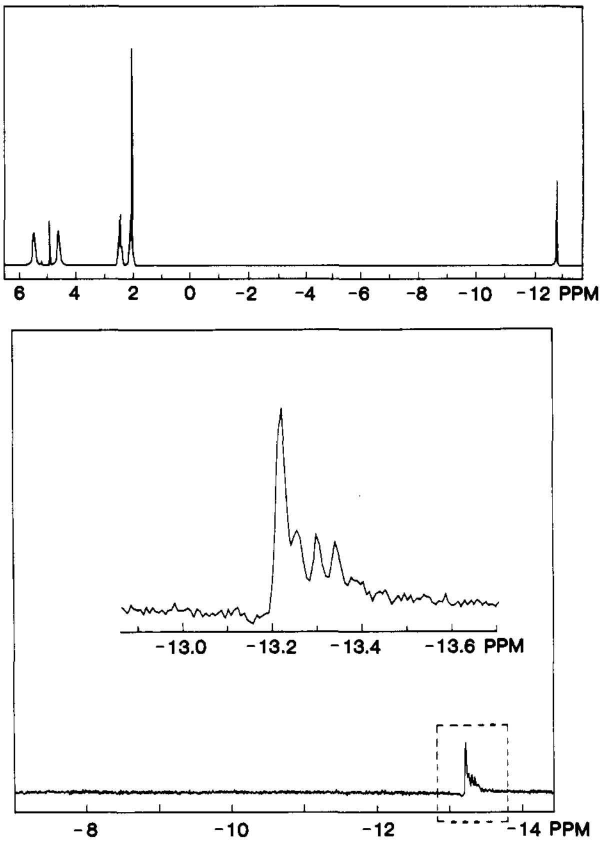

Figure 3. (a, top) The ^1H NMR spectrum of **1** in CD_3OD. (b, bottom) The ^1H NMR spectrum of **1** after treatment with a trace of CF_3SO_3H in D_2O.

Since we plan to do structural studies on complexes of this series covering a range of values of $J_{H\text{-}D}$, it seems appropriate to comment on the possibilities open to us. To cover the wide range of such values, attempts to grow crystals of a salt containing *trans*-$[Os(\eta^2\text{-}H_2)en_2pyridine]^{2+}$ ($J_{H\text{-}D}$ = 19.0 Hz), *cis*-$[Os(\eta^2\text{-}H_2)en_2pyridine]^{2+}$ ($J_{H\text{-}D}$ = 18.0 Hz), *trans*-$[Os(\eta^2\text{-}H_2)en_2CH_3CN]^{2+}$ ($J_{H\text{-}D}$ = 17.7 Hz), and *cis*-$[Os(\eta^2\text{-}H_2)en_2CH_3CN]^{2+}$ ($J_{H\text{-}D}$ = 18.5 Hz) suitable for X-ray and neutron diffraction studies are underway. Structural studies by X-ray diffraction at low temperatures have been made but did not allow the H_2 to be located. A value of $J_{H\text{-}D} < 2.5$ Hz has been reported[16] for $[Os(NH_3)_4(\eta^2\text{-}H_2)Br]^+$ but this result is in error.[42] A reexamination of this sytem shows that $J_{H\text{-}D}$ is 11.8 Hz, which is in harmony with the values for Cl^- and I^-, 10.2 and 12.5 Hz, respectively. The lowest value of $J_{H\text{-}D}$ in the tetraammine series thus far observed and confirmed, <4.0 Hz, applies to the acetone derivative in $(CD_3)_2CO$ with $B(C_6H_5)_4^-$ as counterion. For the chloro and bromo complexes, $J_{H\text{-}D}$ for the ethylenediamine form is observed to be ca. 2–3 Hz less than it is for the tetraammine derivative.[43] A determination of $J_{H\text{-}D}$ for *trans*-$[Os(\eta^2\text{-}H_2)en_2acetone]^{2+}$ in $(CD_3)_2CO$ with $B(C_6H_5)_4^-$ as counterion shows it to be 3.3 Hz. Of all the nucleophilic solvents thus far investigated acetone is among the weakest. With either $B(C_6H_5)_4^-$ or PF_6^-, it has been found that acetone remains bound in solution, but whether this ligation survives the preparation of crystals suitable for diffraction studies remains to be seen.

With the revision of the value of $J_{H\text{-}D}$ for the bromo complex, the relation between these values and the nature of the variable ligand becomes clearer. At one extreme lie π acid ligands, which tend to give high values of $J_{H\text{-}D}$ and presumably draw the hydrogen atoms together. When the competition for π d electron density

---

[42] Rates of exchange are sensitive to the nature of the variable substituent, and the earlier failure to observe isotopic splitting is probably attributable to an unanticipated slow rate of exchange.

[43] Hasegawa, T.; Li, Z.; Parkin, S.; Hope, H. Submitted for publication.

is severe, as is the case for isonitriles, dihydrogen is evolved.[17] At another extreme lie ligands such as acetone, which are weak nucleophiles and, as against good π acids, do not compete effectively for π electron density. A weak nucleophile such as acetone approaches the limit of no nucleophile, in which limit the H–H bond may break completely yieldng a dihydride of coordination number 6. As a 16 e^- system such a complex can in principle adopt an additional ligand, but whether a genuine dihydride of coordination number 7 exists in our series remains to be seen.

There appears to be no simple relation between J_{H-D} and T_1. For *trans*-$[Os(\eta^2\text{-}H_2)en_2CH_3CO_2]^+$, where J_{H-D} is 9.0 Hz, T_1 at the temperature of the minimum (–40 °C) is 61 ms (CD_3OD, 400 MHz). For the molecule *trans*-$[Os(\eta^2\text{-}H_2)en_2CH_3CN]^{2+}$ (J_{H-D} = 17.7 Hz), which is rather similar in structure to the acetate complex, T_1 at the temperature of the minimum (–40 °C) is 54 ms, in the same solvent. Other values of T_1(min) are 38, 63, and 77 ms for pyridine, imidazole, and H_2O, respectively, as substituents in *trans*-$[Os^{II}(\eta^2\text{-}H_2)(NH_3)_4L]^{2+}$. The corresponding values of J_{H-D} are 19.6, 17.1, and 8.1 Hz. We have been investigating the reactivity of compounds of this type.[44–46]

A possible explanation of the phase transformation behavior observed in the X-ray diffraction studies follows. In the measurements, initial cooling to 120 K was rapid, and this could have "frozen in" a high-temperature form, which only slowly transformed to the low-temperature monoclinic form. For the neutron study, cooling was at 2° min^{-1}, which is comparatively very slow, and this could account for the differences observed.

Acknowledgment. The Stanford group gratefully acknowledges the National Institutes of Health for financial support (GM-13638-25). The neutron diffraction study and structure refinement were carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences. We thank Curt Koehler for technical assistance during the neutron measurements.

Supplementary Material Available: A listing of the structure determination summary and tables of atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, anisotropic displacement coefficients, hydrogen atom coordinates, and isotropic displacement coefficients from the X-ray analysis of **1** and tables listing the final atomic coordinates and anisotropic displacement parameters, bond lengths, and bond angles from the results of the neutron study (32 pages); tables of observed and calculated structure factors (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(44) Lin, P.; Hasegawa, T.; Parkin, S.; Taube, H. *J. Am. Chem. Soc.* **1992**, *114*, 2712.

(45) Lin, P.; Hasegawa, T.; Parkin, S.; Taube, H. *J. Am. Chem. Soc.* **1992**, *114*, 7609.

(46) Lin, P.; Hasegawa, T.; Parkin, S.; Taube, H. *J. Am. Chem. Soc.* **1993**, *115*, 2545.