Elongated H-H in *trans*-[Os(η^2-H_2)en_2Cl]Cl

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The structure of *trans*-[Os(η^2-H_2)en_2Cl]Cl has been determined by X-ray analysis of a crystal at 118(2) K. A study of the two independent crystals confirms the trans arrangement. In both crystals the H-H bonds orientate along the N-Os axis and the H-H distances are in the mid-range between those of dihydride compounds and of dihydrogen.

Dihydrogen complexes provide an opportunity to understand the intermediate stages in the oxidative addition of dihydrogen to transition metal centers.[1,2] Although dihydrogen complexes with elongated H-H bonds (Figure 1) constitute an intermediate stage of oxidative addition, well documented examples are rare. Even rarer are compositions in which the co-ligands are simple enough to provide the basic for insights provided by ab initio theoretical treatment.[3]

We have been working on dihydrogen complexes of Os(II) with the simple N donors, NH_3 or en, comprising most of the co-ligands,[4,5,6,7] and for the purposes of this paper were interested in the structure of *trans*-[Os(η^2-H_2)en_2Cl]Cl, **1**, partly because it was originally reported as being a *cis*-dihydride[8], and partly because the value of $J_{H\text{-}D}$ as measured in $(CD_3)_2CO$ suggested that the H-H distance is in the unusual elongated range. Hush et al. calculated the H-H distance for a series of *trans*-[Os(η^2-H_2)$(NH_3)_4$L] complexes using MP2, MP3, and ACPF programs. They calculated the H-H distance for *trans*-[Os(η^2-H_2)$(NH_3)_4$Cl]$^+$ complex as 1.4 Å.[9] Our study provides support for their evaluation.

The compound, **1**, was synthesized by the reaction of *trans*-[Os(H_2)en_2]$(BPh_4)_2$ with LiCl.[10] The diffraction data were collected, after flash cooling the crystal to 118(2) K, using a rotating anode source. A newly developed accurate absorption correction was applied.[11]

Even though refinement of the hydrogen atoms appeared to be successful, the general difficulty of locating hydrogen atoms in the vicinity of Os led us to repeat the experiment on a separate crystal. The positions assigned as dihydrogen in both refinements of **1** were in fair agreement.

Figure 2 shows the structure of the cation of **1**.[12] The first crystal of **1** has the following characteristics: the H-H distance is 1.35(12) Å with Os-H distances of 1.41(7) Å and 1.38(6) Å. In the second crystal of **1**, the H-H distance is 1.40(11) Å and the Os-H distances are 1.52(6) Å and 1.51(6) Å. In both crystals the H-H distances are in the mid-range between those of dihydride compounds and of dihydrogen. The observed H-H distances are close to the value of 1.40 Å calculated by Hush et. al. using the MP2 program.

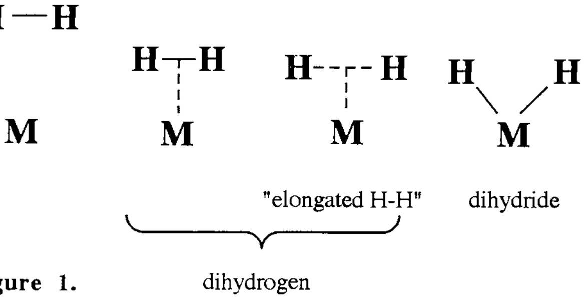


Figure 1.

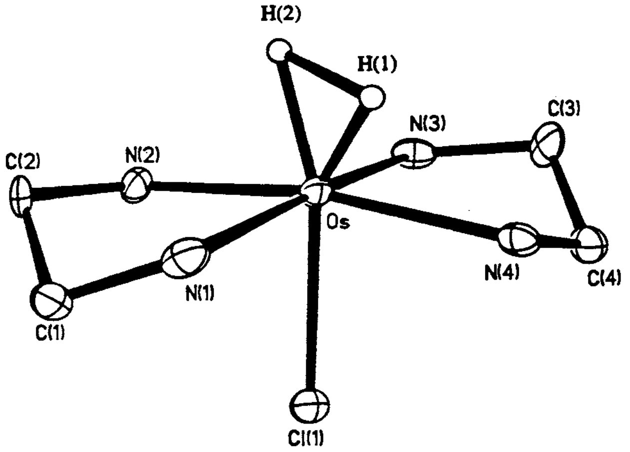
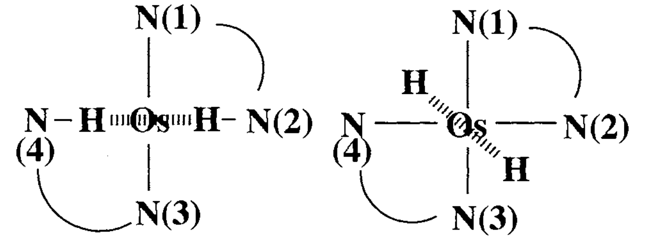


Figure 2. The cation of **1**, as determined by X-ray diffraction. All the en hydrogens are omitted for clarity. Selected bond distances (Å) and angles (deg) for the respective first and second crystals: Os-H(1) 1.41(7), 1.52(6); Os-H(2) 1.38(6), 1.51(6); H(1)-H(2) 1.35(12), 1.40(11); N(1)-Os-H(1) 91(3), 81(2); N(2)-Os-H(1) 110(3), 108(3); N(3)-Os-H(1) 95(3), 105(2); N(4)-Os-H(1) 82(3), 84(2); N(1)-Os-H(2) 114(3), 111(2); N(2)-Os-H(2) 64(3), 70(2); N(3)-Os-H(2) 68(3), 72(2); N(4)-Os-H(2) 123(3), 120(2); H(1)-Os-H(2) 58(4), 55(3).

The Os-H distances are shorter than the average W-H distance of 1.75 Å reported by Kubas et al. for W$(CO)_3$(P-i-Pr_3)$_2$(H_2)[13] which has an H-H distance of 0.84 Å. However, they are in reasonably good agreement with those of Os-H, 1.59(1) Å and 1.60(1) Å, observed in *trans*-[Os(η^2-H_2)$en_2$$CH_3COO$]$PF_6$[14,15] which has an H-H distance of 1.34 Å.

This structure provides the first example of an H-H bond oriented along the Os-N axis (N(2)-Os-N(4) in Figure 3) in the [Os(η^2-H_2)en_2L]$^{+/2+}$ series. This is in contrast with *trans*-[Os(η^2-H_2)$en_2$$CH_3COO$]$^+$, where the H-H vector is oriented nearly parallel to the C=O axis of the acetate ligand and nearly bisects the N(1)-Os-N(4) and N(2)-OS-N(3) angles (Figure 3).

Introduction of a π acid into the coordination sphere leads to larger values of $J_{H\text{-}D}$,[4b] and according to a published correlation,[16] to reduced values of the H-H bond distance. Replacement of an NH_3 by a strong π acid such as HCN, leads to the release of H_2.[17] The situation in the limit of a weak donor is complicated by the fact that losing an NH_3 so that H_2 has only 4 co-ligands would lead to a dihydride of Os(IV). There is evidence that this situation is realized in the substitution in aqueous solution of the bound water in [Osen_2(η^2-H_2)H_2O]$^{2+}$ by



trans-[Os(η^2-H_2)en_2Cl]$^+$ *trans*-[Os(η^2-H_2)en_2CH_3COO]$^+$

Figure 3. The orientations of the H-H bonds.

other ligands.[18]

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10 Anal. Found: C, 12.40; H, 4.67; N, 14.89; Cl, 18.20. Calcd for $C_8H_{18}N_4Cl_2Os$: C, 12.53; H, 4.70; N, 14.61; Cl, 18.53. ^1H NMR (CD_3OD, ppm): 5.57 (s, br, 4 H, NH_2), 4.14 (s, br, 4 H, NH_2), 2.64 (m, 4 H, CH_2), 2.08 (m, 4 H, CH_2), -12.85 (s, 2 H, Os-H_2). T_1: 254 ms (293 K; 200 MHz). T_1(min): 61 ms (199 K; 400 MHz in acetone-d_6). IR (KBr): 2155 cm^{-1} for ν(Os-H_2); this assignment is supported by an isotope exchange experiment. Single crystals were obtained by vapor diffusion of ether into a methanol solution of **1**.
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12 Single crystal diffraction data at 118(2) K were collected on a Siemens P3RA diffractometer using Cu $K\alpha$ radiation monochromated by Ni filter. Selected crystal and refinement data of **1**: monoclinic, $P2_1/c$. For the first crystal: a = 7.382(1) Å, b = 13.213(3) Å, c = 10.556(2) Å, β = 99.88(1) °, V = 1014.3(3) $Å^3$, Z = 4; 5032 reflections collected; 2344 unique reflections (R_{int} = 3.40%); R ($I>2\sigma(I)$) = 2.74%, R (all data) = 3.58%; Goodness of fit on F^2 = 1.049. For the second crystal: a = 7.378(1) Å, b = 13.195(3) Å, c = 10.567(3) Å, β = 99.86(2) °, V = 1013.5(4) $Å^3$, Z = 4; 9179 reflections collected; 2329 unique reflections (R_{int} = 3.50%); R ($I>2\sigma(I)$) = 2.69%, R (all data) = 2.94%; Goodness of fit on F^2 = 1.128.
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