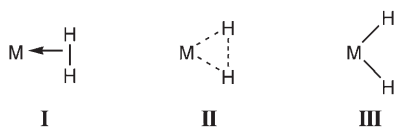


A Neutron Diffraction Study of $[\text{OsClH}_3(\text{PPh}_3)_3]$: A Complex Containing a Highly “Stretched” Dihydrogen Ligand**

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Oxidative addition of dihydrogen to a transition metal is one of the most important steps in many catalytic processes.^[1] Some years ago, Kubas and co-workers^[2] used neutron diffraction to show for the first time that H_2 could bind to a metal in a sideways fashion as $\eta^2\text{-H}_2$, now called the non-classical dihydrogen ligand (**I**). Further insertion of the metal into the dihydrogen ligand, upon continuation of the oxidative addition process, weakens the H–H bond causing it to lengthen (**II**) and finally cleave to form two terminal hydride ligands (**III**). The weakening of the H–H bond (**II**) is considered to be an intermediate step along the pathway, and it is this step that has garnered a considerable amount of interest.^[3–5]



Structural studies^[5] in this area have thus far provided significant information regarding the metal–dihydrogen interaction along the reaction pathway. The side-on, or non-classical dihydrogen complexes **I**, have an H–H bond length of the order of 0.8–1.0 Å (not much longer than the H–H distance of 0.74 Å in H_2 itself^[6]) while classical dihydride complexes **III** (with essentially no H···H interactions) generally have H···H distances greater than 1.7 Å. The inter-

mediate, or stretched dihydrogen complexes **II** (also called “compressed dihydride” complexes^[3a,f,g]) have H–H distances in the range 1.1–1.5 Å.^[4] Although a moderate number of stretched dihydrogen complexes have been reported, the H–H distances in these complexes have mainly been obtained from NMR spectroscopic data (T_1 and $J_{\text{H,D}}$ measurements) or from X-ray data, which are not very sensitive to H positions.^[3]

The most reliable technique to determine H–H distances in hydride complexes is neutron diffraction. However, only a few examples of molecules exhibiting the intermediate stage **II** have been structurally characterized by this technique.^[4,5] Intramolecular “reaction trajectories” have been mapped out before in a classical series of studies of organic molecules by Bürgi and Dunitz using X-ray crystallography.^[7a] In addition, Crabtree et al.^[7b] have used a series of X-ray and some neutron structures to map the lengthening of a C–H bond during metal insertion, although the variation in those C–H distances (± 0.1 Å) is much less pronounced than the large distributions of H···H distances we will discuss later in Table 1. Several authors have pointed out^[3a,h,i] that the energy barrier for moving the H···H distance from 1.00 to 1.60 Å is only about 4 kcal mol^{−1}, which suggests that the ligand environment around the metal atom should have a significant effect.^[3c] Clearly, a more complete set of stretched dihydrogen ligands is needed to obtain a clearer understanding of this intriguing interaction. In this regard, we report herein a new example of the stretched dihydrogen phenomenon in the complex $[\text{OsClH}_3(\text{PPh}_3)_3]$ (**1**).

The title complex was prepared by the reaction of $[\text{OsCl}_2(\text{PPh}_3)_3]$ ^[8a] with H_2 in the presence of NEt_3 , as described by Caulton and co-workers.^[8b] The compound **1** was first made about 30 years ago, but was wrongly formulated as $[\text{OsClH}(\text{PPh}_3)_3]$.^[8c] However, a careful analysis of the ^1H NMR spectroscopic data by Caulton et al. showed that the complex **1** was actually $[\text{OsClH}_3(\text{PPh}_3)_3]$ with a nonclassical dihydrogen ligand, as suggested by the short relaxation time ($T_1 = 26$ ms) of the hydride at -40°C and 300 MHz. However, a minimum T_1 value could not be determined due to the low solubility of the Os complex at low temperatures, nor was it possible to conclude from the NMR study if the suspected dihydrogen ligand was *trans* to a chloride or a phosphane ligand.^[8b] It was also difficult to determine the $J_{\text{H,D}}$ coupling constant for the isotopolog $[\text{OsClHD}_2(\text{PPh}_3)_3]$ due to the broadness of the hydride signal. Thus, it was impossible to estimate the H–D distance in the complex. In the present study, the structure has been unequivocally determined by a single-crystal neutron diffraction analysis.

The sample was initially characterized by X-ray diffraction^[9] in order to determine the atomic coordinates used for neutron diffraction data analysis. The neutron data analysis was carried out both at room temperature and at 5 K on a crystal measuring $1.2 \times 0.8 \times 0.3$ mm³ using the VIVALDI diffractometer at the Institut Laue–Langevin in Grenoble.^[10] Full-matrix least-squares refinement of atomic positions yielded the following agreement factors for the low-temperature data set: $R(F) = 0.0831$ for 3560 independent reflections ($I > 2\sigma(I)$).^[11]

Figure 1 shows the molecular structure of **1** and its core at 5 K. Our results reveal the presence of a dihydrogen ligand

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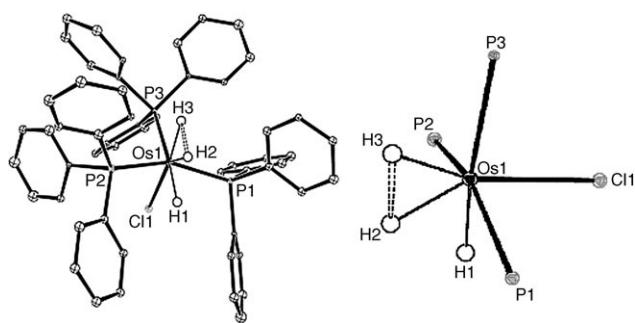


Figure 1. Molecular structure of $[\text{OsClH}_3(\text{PPh}_3)_3]$ (**1**, left) and its core (right). The H2–H3 distance is 1.48(2) Å and the H1...H2 distance is 1.67(2) Å, as determined from this neutron study. Other notable bond distances include: Os–H2 = 1.59(2) and Os–H3 1.61(1) Å.

(H2...H3), although not of the nonclassical type originally envisioned,^[8b] but of the “stretched” variety (**II**), with an H...H bond distance of 1.48(2) Å. In addition, one terminal hydride ligand (H1) was located, plus one chloride and three phosphane ligands. The Os–H1 distance to the terminal hydride ligand (1.62(2) Å) is similar to other Os–H distances reported in literature,^[12] and this terminal hydride ligand H1 is positioned 1.67(2) Å from the H2 atom of the dihydrogen ligand, a distance which is in the range of slightly nonbonding interactions.^[5] It should be noted that, within experimental error, we found a barely significant increase in geometry between the neutron structures refined at 5 K and at 295 K,^[13a] which is somewhat consistent with a theoretical study which suggests that the H...H distance in a stretched dihydrogen ligand could be temperature dependent.^[13b]

The molecule is substantially distorted from an ideal octahedral geometry. The terminal hydride is located *trans* to

a phosphane ligand (H1–Os1–P3 172.5(6)°) while the dihydrogen ligand sits essentially *trans* to the chloride ligand (X–Os1–Cl1 171.4(3)°, where X represents the center of the dihydrogen ligand). The dihydrogen, hydride, and chloride ligands lie in the same plane (Figure 1), which is similar to the atomic arrangement in $[\text{IrCl}_2\text{H}(\text{H}\cdots\text{H})(\text{PiPr}_3)_2]$.^[4e] Two other stretched dihydrogen moieties previously studied by neutron diffraction, in which the dihydrogen ligands were also located *trans* to negatively charged ligands, were also found in six-coordinate osmium complexes.^[4b,c]

Speculation can be made as to the role of the chloride ligand in influencing the geometry of complex **1**. Some years ago we reported the results of a neutron diffraction analysis of $[\text{OsH}_4(\text{PMe}_2\text{Ph})_3]$, which contains four terminal hydrides with an average Os–H bond distance of 1.659(3) Å.^[12a] The only apparent difference between that complex and the present complex **1** (besides the difference in phosphane ligands) is the substitution of a chloride ligand for a hydride ligand. Perhaps the presence of the *trans* chloride ligand, which is more electronegative than hydride, promotes closer H...H interactions,^[3b] and this could be the driving force for formation of the stretched dihydrogen ligand.

The main point of our communication is shown in Table 1, which summarizes experimental data, from which a crude approximation of a “reaction profile” can be derived, for the specific process of oxidative addition of a metal atom into an H–H bond. In this table, we have included all neutron diffraction data on H–H complexes that were available to us, with the exception of the last category at the bottom of the table (“classical” hydride complexes, in which there are no H...H bonding interactions), for which neutron results are too numerous to be listed in full.

Table 1: A selection of H...H distances [Å] and H–M–H angles [°] determined by neutron diffraction.^[a]

Compound		1 H–H	2 H–M–H	3 Av. M–H	4 “Adjusted” av. M–H ^[b]	5 M–X ^[c]	6 “Adjusted” M–X ^[b,c]
Nonclassical Complexes (with “almost unstretched” H...H distances)	$[\text{Mo}(\text{CO})(\eta^2\text{-H}_2)(\text{dppe})_2]$	0.80–0.85 ^[14e]	24.0–25.6	1.922(15)	1.79	1.886(15)	1.76
	$[\text{Fe}(\text{H})(\eta^2\text{-H}_2)(\text{dppe})_2]^+$	0.816(16) ^[14a]	29.3(5)	1.616(10)	1.62	1.616(10)	1.62
	$[\text{W}(\text{CO})_3(\eta^2\text{-H}_2)(\text{PiPr}_3)_2]$	0.82(1) ^[14b]	25.1	1.89(1)	1.76	1.89(1)	1.76
	$[\text{FeH}_2(\eta^2\text{-H}_2)(\text{PPh}_2\text{Et})_3]$	0.821(10) ^[14d]	29.9(4)	1.592(8)	1.59	1.538(8)	1.54
	$[\text{Ir}(\text{H})_2(\text{I})(\eta^2\text{-H}_2)(\text{PiPr}_3)_2]$	0.856(9) ^[14c]	28.2(3)	1.756(7)	1.66	1.703(7)	1.60
Slightly Stretched H...H distances	$[(\text{C}_5\text{Me}_5)\text{OsH}_2(\eta^2\text{-H}_2)(\text{PPh}_3)]^+$	1.014(11) ^[4g]	35.4(4)	1.669(9)	1.58	1.589(9)	1.50
	$[(\text{C}_5\text{Me}_5)\text{Ru}(\eta^2\text{-H}_2)(\text{dppm})]^+$	1.10(2) ^[4d]	38(1)	1.67(2)	1.59	1.58(2)	1.50
	$[\text{IrCl}_2\text{H}(\eta^2\text{-H}_2)(\text{PiPr}_3)_2]$	1.11(3) ^[4e]	42.3(9)	1.444(18)	1.34	1.347(18)	1.25
Significantly Stretched H...H distances	$[\text{OsCl}(\eta^2\text{-H}_2)(\text{dppe})_2]^+$	1.22(3) ^[4c]	42.6(12)	1.58(2)	1.49	1.47(2)	1.38
	$[\text{Os}(\text{CH}_3\text{CO}_2)(\eta^2\text{-H}_2)(\text{en})_2]^+$	1.34(2) ^[4b]	49.6(6)	1.60(1)	1.51	1.45(1)	1.36
	$[\text{ReH}_7[\text{P}(p\text{-tolyl})_3]_2]$	1.357(7) ^[4a]	47.6(2)	1.681(4)	1.57	1.538(4)	1.43
	$[\text{OsClH}_3(\text{PPh}_3)_3]$	1.48(2) ^[d]	55.1(8)	1.60(2)	1.51	1.42(2)	1.33
	$[\text{OsH}_5(\text{PMe}_2\text{Ph})_3]^+$	1.49(4) ^[4f]	54.1(1)	1.64(2)	1.55	1.46(2)	1.37
Classical Complexes (no H...H bonding)	$[\text{OsH}_4(\text{PMe}_2\text{Ph})_3]$	1.840(6) ^[12a]	67.9(2)	1.646(3)	1.56	— ^[e]	— ^[e]
	$[\text{ReH}_5(\text{PMePh}_2)_3]$	1.845(7) ^[15a]	66.8(3)	1.677(5)	1.57	— ^[e]	— ^[e]
	$[\text{FeH}_2(\text{CO})_2[\text{P}(\text{OPh})_3]_2]$	2.011(3) ^[15b]	82.5(1)	1.525(2)	1.53	— ^[e]	— ^[e]

[a] Abbreviations: dppe = 1,2-bis(diphenylphosphanyl)ethane; dppm = 1,2-bis(diphenylphosphanyl)methane; en = ethylenediamine. [b] The “adjusted” M–H and M–X distances were corrected for the differences in the atomic radii of the metal atoms; the correction term for Fe was arbitrarily set to be zero. Atomic radii data from Ref. [16]. [c] M–X distances involved with the H₂ ligand; X is the center of the H...H bond. [d] Present work. [e] The position of “X” (the mid-point of the H...H bond) is not meaningful for classical hydrides, in which there are no H...H interactions.

Columns 1, 2, and 3 list the experimental H–H distances, H–M–H angles, and M–H distances, respectively, sorted in the order of increasing H–H distance. One can discern a very crude general trend of longer H–H distances coupled with shorter M–H distances. However, one has to account for differences in atomic radii of the metal atoms, and so in column 4 we list “adjusted” M–H distances in which the differences in atomic radii are used as “correction factors”, with the atomic radius of iron selected arbitrarily as a “standard”. One can see that column 4 is somewhat “smoother” than column 3. Finally, recognizing that one should rather consider metal–ligand distances instead of metal–hydrogen distances, we have provided two extra columns in which M–X distances are tabulated (X is the midpoint of the H–H bond). Once again, we give “unadjusted” and “adjusted” values (columns 5 and 6, respectively), in which column 6 contains the values “corrected” for differences in atomic radii. The differences between M–H distances (column 3) and metal–ligand distances (column 5) are not large for true nonclassical H₂ complexes (top portion of Table 1), but the differences become more apparent where “slightly stretched” and “significantly stretched” dihydrogen complexes are concerned (middle portion of Table 1).

Perhaps the most meaningful comparison is between column 1 (or column 2) and column 6. Although there is obviously some scatter in the data, one can discern a definite trend in which an increasing H–H distance appears to be correlated with a decreasing metal–ligand distance. In other words, this is experimental evidence for the reaction pathway **I**→**II**→**III**. A somewhat similar conclusion for metal insertion into a C–H bond has appeared earlier,^[7b] but in that case only a small spread of C–H distances was observed, much more subtle than the large spread in H–H distances listed in Table 1. One can conclude from this comparison that the process of oxidative addition into an H–H bond is intrinsically different to oxidative addition into a C–H bond.

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