Synthesis and Spectroscopic and Theoretical Characterization of the Elongated Dihydrogen Complex $OsCl_2(\eta^2\text{-}H_2)(NH{=}CPh_2)(P^iPr_3)_2$

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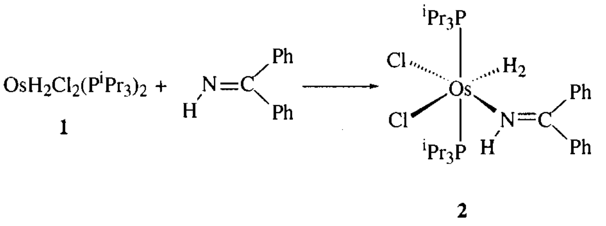
Introduction

Nowadays the existence of two classes of compounds with two hydrogen atoms in the coordination sphere of a transition metal is well-established: dihydridos, with hydrogen−hydrogen separations longer than 1.6 Å and without H−H bonds, and dihydrogen complexes in which the hydrogen molecule is coordinated to the metal, the separation between the hydrogen atoms lying between 0.8 and 1.0 Å.[1] However, there is an increasing number of complexes more difficult to classify because the hydrogen−hydrogen distances range between 1.0 and 1.5 Å. A useful indicator of this bonding behavior (elongated dihydrogen, also referred as to "stretched") is the J(HD) value in the M(HD) isotopomer. It has been proposed that when this coupling falls between 5 and 25 Hz, an elongated dihydrogen ligand is present.[2]

Although these complexes are often seen as frozen structures at various points on the reaction path for the oxidative addition−reductive elimination of molecular hydrogen at the metallic center, their nature is still an open question. In this paper the synthesis and characterization of a new complex of this type is reported, with a hydrogen−hydrogen distance which precisely lies at the center of the reported range. Furthermore, high-level ab initio calculations were performed on this complex leading to a new perspective for the understanding of this fascinating class of compounds. Instead of species where the oxidative addition−reductive elimination is arrested at some intermediate stage, the picture that emerges from our results is that they actually can be considered as involving two delocalized hydrogen atoms.

Results and Discussion

Treatment under reflux of a pentane suspension of the six-coordinate complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) with 1 equiv of benzophenone imine produces after 6 h the derivative $OsCl_2(\eta^2\text{-}H_2)(NH{=}CPh_2)(P^iPr_3)_2$ (**2**), which was isolated as an orange solid in 85% yield (eq 1). This is in agreement with the tendency of **1** to afford dihydrogen compounds by addition of nucleophilic reagents.[3]



(1)

The most noticeable spectroscopic feature of **2** is the dihydrogen signal in the ^1H NMR spectrum, which appears at −7.77 ppm as a triplet with a P−H coupling constant of 9.5 Hz. A variable-temperature 300 MHz T_1 study of this peak shows a slight broadening of the signal, as a result of the decrease of T_2 with decreasing temperature,[4] and gives a T_1(min) of 32 ms at 233 K. This T_1(min) value corresponds to a hydrogen−hydrogen distance of 1.00 (fast spinning) or 1.27 Å (slow spinning).[1c] The reaction of $Os(H)(D)Cl_2(P^iPr_3)_2$ (**1**-d_1) with benzophenone imine yields the partially deuterated dihydrogen derivative $OsCl_2(\eta^2\text{-}HD)(NH{=}CPh_2)(P^iPr_3)_2$ (**2**-d_1), which has a H−D coupling constant of 10.5 Hz. Using the standard equation,[5] this value leads to a separation between the hydrogen atoms of the dihydrogen ligand of **2** equal to 1.24 Å.

High-level ab initio calculations have proven to be very efficient to determine structural and bonding properties of transition metal dihydrogen complexes.[6] With this aim the structure of the model complex $OsCl_2(\eta^2\text{-}H_2)(NH{=}CH_2)(PH_3)_2$ (**2t**) was optimized at the B3LYP level[7−10] (Figure 1). The

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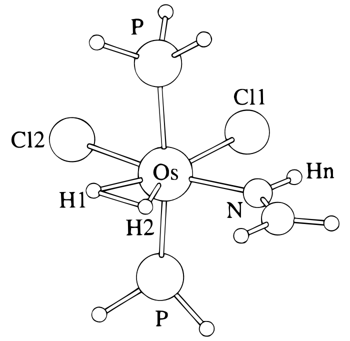

Figure 1. B3LYP-optimized structure of **2t**. Selected distances (Å) and angles (deg): Os−Cl(1), 2.527; Os−Cl(2), 2.492; Os−H(1), 1.611; Os−H(2), 1.617; Os−N, 2.067; Os−P, 2.356; H(1)−H(2), 1.294; N−Hn, 1.029; Cl(1)···Hn, 2.381; Cl(1)−Os−Cl(2), 86.4; Cl(2)−Os−H(1), 71.2; H(1)−Os−H(2), 47.3; H(2)−Os−N, 76.1; N−Os−Cl(1), 78.5; P−Os−P, 169.5; Os−N−Hn, 106.7.

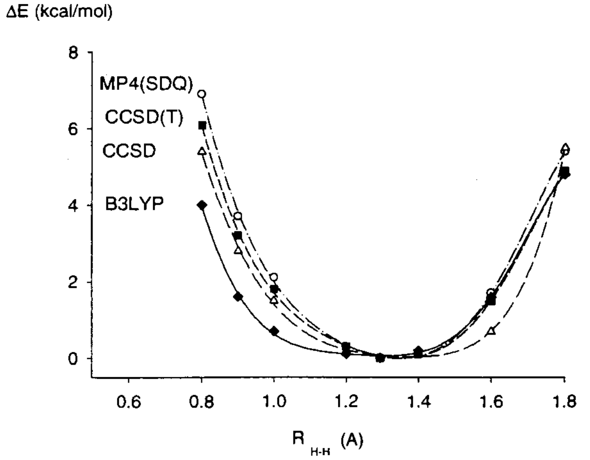

Figure 2. Energy profiles associated with the H−H stretch in **2t** at different calculational levels.

results agree well with the spectroscopic characterization of **2**. The H(1)−H(2) distance is 1.294 Å, a value very close to that obtained from the *J*(HD) coupling. Other interesting features are the values of the N−Os−Cl(1) (78.5°) and Os−N−Hn (106.7°) bond angles, due to the presence of a hydrogen bond between Cl(1) and the imine proton Hn. The lengthening of the N−Hn distance caused by this interaction accounts for the low N−H stretching frequency found in the IR spectrum (3200 cm^{-1}).[11]

In order to know the energy required to achieve the oxidative addition of the coordinated dihydrogen molecule in **2**, the potential energy curve for the H−H stretch in **2t** was calculated by varying the H(1)−H(2) distance ($R_{\mathrm{H-H}}$) from 0.80 to 1.80 Å. All of the geometrical parameters were optimized for each fixed $R_{\mathrm{H-H}}$ distance (Figure 2). B3LYP calculations indicate that the H−H stretch is practically free in **2t**: it costs only 1.5 kcal mol^{-1} to elongate the H−H distance from 0.90 to 1.60 Å. To assure that this result is not dependent on the B3LYP methodology, the potential energy profile for the whole range of H−H distances was recalculated at the MP4(SDQ),[12] CCSD, and CCSD(T)[13] levels of theory, using the optimized B3LYP geometries. Whatever the methodology employed, the energy cost to move the two hydrogen atoms between 1.0 and 1.60 Å is lower than 2 kcal mol^{-1}. In other words, in this system the H_2 molecule is coordinated to the metal in such a way that the oxidative addition of dihydrogen and its reverse, reductive elimination, can occur with essentially no activation barrier.

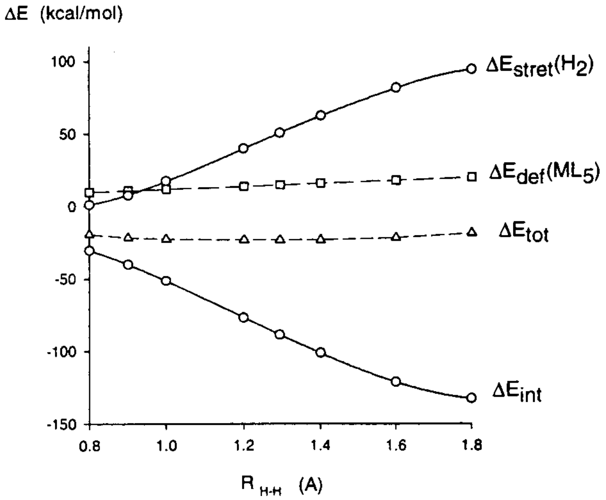

Figure 3. Variation of the different energetic terms as a function of the H−H distance in **2t**.

From the potential energy curve we have found for the stretch of the H−H unit in **2t**, a question arises: how is it possible that the H−H bond can be broken and formed without variation of the total energy of the system? To answer this question, the total energy was decomposed at each point on the energy profile in various components. At each value of the H−H distance ($R_{\mathrm{H-H}}$) between 0.80 and 1.80 Å, the complex $\mathrm{ML}_5(\eta^2\text{-}\mathrm{H}_2)$ can be viewed as built from two separate fragments (the H_2 molecule and the $\mathrm{OsCl_2(NH{=}CH_2)(PH_3)_2}$ fragment), each one being in its equilibrium geometry. Therefore, the process to obtain the whole system **2t** can be decomposed in three terms (eqs 2−4).

$$[\mathrm{H{-}H}](\mathrm{eq}) \rightarrow [\mathrm{H{-}H}](R_{\mathrm{H-H}});\quad \Delta E_{\mathrm{stret}}(\mathrm{H_2}) \tag{2}$$

$$[\mathrm{OsCl_2(NH{=}CH_2)(PH_3)_2}](\mathrm{eq}) \rightarrow [\mathrm{OsCl_2(NH{=}CH_2)(PH_3)_2}](R_{\mathrm{H-H}});\quad \Delta E_{\mathrm{def}}(\mathrm{ML_5}) \tag{3}$$

$$[\mathrm{OsCl_2(NH{=}CH_2)(PH_3)_2}](R_{\mathrm{H-H}}) + [\mathrm{H-H}](R_{\mathrm{H-H}}) \rightarrow [\mathrm{OsCl_2(H_2)(NH{=}CH_2)(PH_3)_2}](R_{\mathrm{H-H}});\quad \Delta E_{\mathrm{int}} \tag{4}$$

At each point the variation in the total energy (eq 5) can thus be obtained by adding the three contributions, two destabilizing [$\Delta E_{\mathrm{def}}(\mathrm{ML_5})$ and $\Delta E_{\mathrm{stret}}(\mathrm{H_2})$] and one stabilizing ($\Delta E_{\mathrm{int}}$).

$$\Delta E_{\mathrm{tot}} = \Delta E_{\mathrm{stret}}(\mathrm{H_2}) + \Delta E_{\mathrm{def}}(\mathrm{ML_5}) + \Delta E_{\mathrm{int}} \tag{5}$$

Figure 3 shows the variation of the four terms at the B3LYP level as a function of $R_{\mathrm{H-H}}$, and indicates that the very flat line for ΔE_{tot} results from the almost exact compensation of the stabilizing ΔE_{int} term and the destabilizing $\Delta E_{\mathrm{stret}}(\mathrm{H_2})$ term all along the reaction path.

In conclusion, the energy of complex **2** is practically independent of the hydrogen−hydrogen separation between 0.90 and 1.60 Å, so that it should be considered as a compound in which the oxidative addition and its reverse, the reductive

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(11) This value is even lower than those found in related compounds containing N−H···Cl hydrogen bonds. See: (a) García, M. P.; Esteruelas, M. A.; Martín, M.; Oro, L. A. *J. Organomet. Chem.* **1994**, *467*, 151. (b) Atencio, R.; Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1995**, 2171. (c) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Ruiz, N.; Sola, E.; Tolosa, J. I. *Inorg. Chem.* **1996**, *35*, 7811.

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elimination of H_2, occur in its coordination sphere without any activation barrier. In this way, the description of **2** as dihydrogen-like or dihydrido-like loses its significance, and it is more appropriate to describe it as a complex containing two hydrogen atoms moving freely in a wide region of the coordination sphere of the metal.

In light of these results, it is clear that further work is needed to fully understand the nature of the so-called elongated dihydrogen complexes, which cannot be described by simply interpolating the dihydrogen or dihydrido models.

Experimental Section

Preparation of $OsCl_2(\eta^2\text{-}H_2)(NH{=}CPh_2)(P^iPr_3)_2$ (2). A suspension of **1**[14] (200 mg, 0.35 mmol) in 10 mL of pentane was treated with 74.5 mg (0.42 mmol) of benzophenone imine. The mixture was heated under reflux for 6 h, and an orange precipitate was obtained: yield 139.2 mg (85%). IR (Nujol): ν (NH) 3200 cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 13.51 (br, 1 H, NH), 7.42 (m, 2 H, Ph), 7.33 (m, 2 H, Ph), 7.11 (br, 2 H, Ph), 7.09 (br, 2 H, Ph), 6.94 (br, 1 H, Ph), 6.93 (br, 1 H, Ph), 2.41 (m, 6 H, PCH), 1.26 [dvt, $N = 12.8$ Hz, $J(HH) = 6.7$ Hz, 18 H, $PCCH_3$], 1.15 [dvt, $N = 12.2$ Hz, $J(HH) = 6.3$ Hz, 18 H, $PCCH_3$], -7.77 [t, $J(PH) = 9.5$ Hz, 2 H, OsH_2]. $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ -4.4 (s). Anal. Calcd for $C_{31}H_{55}Cl_2NOsP_2$: C, 48.68; H, 7.24; N, 1.83. Found: C, 48.06; H, 6.97; N, 1.84. MS (FAB$^+$): m/e 763 ($M^+ - 2$ H). T_1 [ms, $Os(\eta^2\text{-}H_2)$, 300 MHz, C_7D_8]: 65 (293 K), 51 (273 K), 37 (253 K), 32 (233 K), 34 (213 K).

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