The Kubas Complex Revisited. A Theoretical Study of Dihydrogen Addition and Structure of the Dihydride Form

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The dihydrogen (**DiH$_2$**) and the dihydride forms of the $W(CO)_3(PH_3)_2(H_2)$ complex are studied by means of DFT (B3LYP) and ab initio (MP2, MP4(SDTQ), and CCSD(T)) calculations. The oxidative-addition process involving simple H−H breaking (**DiH$_2$** → **PB1**) is found to be a very low energy process ($\Delta H^\ddagger = 2.50$ kcal/mol at the CCSD(T) level). An essentially zero energy barrier for the reverse reaction explains why this structure with both the hydride and phosphorus ligands equivalent is not that observed in low-temperature NMR experiments. A new structure is proposed for the dihydride form, **PB2**, which accounts for both the spectroscopic and thermodynamic experimental data. It can be described as a pentagonal-bipyramidal structure, with two axial carbonyl ligands and two equatorial hydrides separated by a phosphine ligand. The enthalpy difference between **DiH$_2$** and **PB2** is computed to be equal to 1.29 kcal/mol (in favor of **DiH$_2$**) at the CCSD(T) level, in good agreement with the experimental data on related complexes (1.2−1.5 kcal/mol).

Introduction

The discovery by Kubas, in 1984, that a dihydrogen molecule can coordinate a transition-metal complex without breaking of the H−H bond has been considered as one of the most significant recent developments in inorganic chemistry.[1] It has given rise to a burst of scientific activity and has reshaped the view on the way σ bonds interact with metal atoms.[2]

The first structural evidence of η^2-H_2 coordination was provided by single-crystal neutron diffraction studies of the $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}H_2)$ complex.[3] After this initial characterization, the so-called Kubas complexes $W(CO)_3(PR_3)_2(H_2)$ were extensively studied, and it was shown by both NMR and IR spectroscopy that a dihydrogen−dihydride dynamic equilibrium takes place in solution.[4] Later, such an equilibrium was found to be a relatively common process in polyhydride complexes, demonstrating that dihydrogen complexes can be intermediates in the oxidative addition of H_2 to metal centers.[1,5]

In Kubas complexes, the thermodynamic parameters associated with the dihydride → dihydrogen reaction were obtained from $^1H\{^{31}P\}$ NMR studies:[6] $\Delta H° = -1.2 \pm 0.6$ kcal/mol, $\Delta S° = -1.2 \pm 2.6$ eu, and $\Delta G° = -0.80 \pm 0.12$ kcal/mol (298 K) for R = *i*-Pr and $\Delta H° = -1.5 \pm 0.4$ kcal/mol, $\Delta S° = -2.4 \pm 1.4$ eu, and $\Delta G° = -0.75 \pm 0.12$ kcal/mol (298 K) for R = Cyp (Cyp = cyclopentyl). The very low enthalpy difference (of about 1 kcal/mol) between the dihydrogen and the dihydride complexes is thus responsible for the equilibrium between these two forms in solution. The structure of the dihydride complex is, however, essentially unknown. It was found to be stereochemically nonrigid, as is commonly found for seven-coordinate species. However, low-temperature NMR studies showed that both the hydride and phosphorus ligands are chemically inequivalent in the fluxional dihydride species:[4b] a $\Delta G^\ddagger$ value of 11 kcal/mol (253 K) was derived from NMR coalescence data for the exchange between inequivalent hydrides. Last but not least, the bulky phosphines are sterically constrained to be essentially *trans*. With all these requirements in mind, a capped-octahedron structure with one of the hydrides or a CO in the capping position has been suggested by Kubas and co-workers,[4b] *i.e.* a structure similar to that found in the related seven-coordinate $MoCl_2(CO)_3(PEt_3)_2$ complex[7] (CO-capped octahedral geometry). Whatever the actual structure of the dihydride, it cannot result from a simple H−H

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(1) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Kubas, G. J. *Comments Inorg. Chem.* **1988**, *7*, 17. (c) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (d) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (e) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.

(2) (a) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (b) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.

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

(4) (a) Kubas, G. J.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339. (b) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000.

(5) (a) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (c) Luo, X.-L.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1990,** 189. (d) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912. (e) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. (f) Luo, X.-L.; Michos, D.; Crabtree, R. H. *Organometallics* **1992**, *11*, 237.

(6) Khalsa, G. R. K.; Kubas, G. J.; Unkefer, C. J.; Van Der Sluys, L. S.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1990**, *112*, 3855.

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breaking in the dihydrogen complex: both the hydride and the phosphorus ligands would be equivalent. Some further reorganization has to occur in order to make the structure agree with the experimental data recalled above.

The kinetics of the interconversion between the dihydrogen and the dihydride ($R = i$-Pr) was also studied using spin saturation transfer techniques.[6] The activation parameters (dihydrogen → dihydride) were found to be $\Delta H^{\ddagger} = 10.1 \pm 1.8$ kcal/mol, $\Delta S^{\ddagger} = -19.9 \pm 6.0$ eu, and $\Delta G^{\ddagger} = 16.0 \pm 0.2$ kcal/mol at 298 K. A $\Delta H^{\ddagger}$ value of 14.4 ± 0.5 kcal/mol was derived by Hoff and coworkers for the reductive elimination of H_2 from the dihydride in the PCy_3 analogue (stopped-flow kinetic techniques).[8] The general picture which emerges from these experimental data is that of nearly isoenergetic dihydrogen and dihydride forms, separated by a barrier of 10−15 kcal/mol. Note that this activation energy is associated with the overall interconversion process, which is likely to involve both the oxidative addition of H_2 and a structural reorganization in the seven-coordinate dihydride species.

Theoretical studies have played an important role in the understanding of the structure, the bonding,[9,10] and the dynamic processes[11] at work in dihydrogen and polyhydride complexes. In particular, the Kubas complexes have been the target of several studies.[12] While the geometrical parameters associated with the dihydrogen complex are satisfactorily reproduced,[12c,e,f] the computed energy differences between the dihydrogen and the dihydride forms were consistently in strong disagreement with the experimental values: at the Hartree−Fock level,[12b] the dihydride was found to be 10 kcal/mol higher in energy than the dihydrogen species. An even worse result (17 kcal/mol) was reported later on the basis of MP2 calculations,[12d] while more recent DFT calculations gave an energy difference of 10.1 kcal/mol.[12f] None of these values are consistent with the experimentally observed dihydrogen−dihydride equilibrium, which implies an energy difference of only *ca.* 1 kcal/mol in favor of the dihydrogen complex.[6] Although various arguments could be given to explain such a discrepancy, let us note that the dihydride structure computed in all these previous theoretical studies cannot be the experimental one! As a matter of fact, it was that structure obtained by simple breaking of the H−H bond which leads to a pentagonal-bipyramidal structure with both the hydride and phosphorus ligands equivalent, i.e. in full contradiction with the low-temperature NMR data.

The purpose of this work is to get a deeper insight into the thermodynamics, the kinetics, and the structural aspects of the dihydrogen−dihydride interconversion in the Kubas complexes. In order to clarify why the dihydride formed by simple H−H breaking is not that observed experimentally, the energy profile associated with this oxidative-addition process is calculated. On the other hand, 18 7-coordinate structures which fit the spectroscopic data for the $WH_2(CO)_3(PR_3)_2$ complex are explored. These calculations lead us to propose a new structure for this dihydride, consistent with both the spectroscopic and the thermodynamic experimental data.

Method of Calculation

Calculations were performed with the GAUSSIAN 94 series of programs.[13] Geometry optimizations were carried out using the density functional theory (DFT)[14] with the B3LYP functional,[15] which has already been used with success to study several dihydrogen and polyhydride systems.[11d,12e,16] An effective core potential operator was used to represent the 60 innermost electrons of the tungsten atom.[17] The basis set for the metal atom was that associated with the pseudopotential,[17] with a standard valence double-ζ LANL2DZ contraction.[13] The basis set for the hydrogen atoms directly attached to the metal was a double-ζ supplemented with a polarization p shell.[18ab] A 6-31G basis set was used for the other H atoms, as well as for carbon and oxygen atoms.[18a] The phosphorus atoms were described with the 6-31G* basis set.[18c] In order to check the basis set dependence of the results, single-point B3LYP calculations were carried out at the previously optimized geometries with an enhanced basis set including an f shell on the W atom[18d] and d basis functions on oxygen and carbon atoms (B3LYP*//B3LYP).[18a,b,c] Stationary points on the B3LYP potential energy surface were characterized by diagonalization of the numerically calculated Cartesian Hessian matrices. Vibrational frequencies were obtained, and $\Delta H°$, $\Delta S°$, and $\Delta G°$ values (1 atm, 298.15 K), including the zero-point energy correction, were calculated to get results more readily comparable with experimental data. For comparative purposes, single-point MP2 and MP4(SDTQ) calculations[19] using the B3LYP optimized geometries (MP2//B3LYP and MP4//B3LYP,

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(7) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1977**, 194.

(8) Zhang, K.; Gonzalez, A. A.; Hoff, C. D. *J. Am. Chem. Soc.* **1989**, *111*, 3627.

(9) (a) Dedieu, A., Ed. *Transition Metal Hydrides*; VCH: Weinheim, Germany, 1991. (b) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1994**, *135/136*, 845.

(10) Some theoretical studies: (a) Maseras, F.; Duran, M.; Lledós, A.; Bertrán, J. *J. Am. Chem. Soc.* **1991**, *113*, 2879. (b) Maseras, F.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1993,** *115*, 8313. (c) Craw, J. S.; Backslay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **1994**, *116*, 5937. (d) Dapprich, S.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 354. (e) Li, J.; Dickson, R. M.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 11482.

(11) (a) Maseras, F.; Duran, M.; Lledós, A.; Bertrán, J. *J. Am. Chem. Soc.* **1992**, *114*, 2922. (b) Jarid, A.; Moreno, M.; Lledós, A.; Lluch, J. M.; Bertrán, J. *J. Am. Chem. Soc.* **1995**, *117*, 1069. (c) Clot, E.; Leforestier, C.; Eisenstein, O.; Pélissier, M. *J. Am. Chem. Soc.* **1995**, *117*, 1797. (d) Camanyes, S.; Maseras, F.; Moreno, M.; Lledós, A.; Lluch, J. M.; Bertrán, J. *J. Am. Chem. Soc.* **1996**, *118*, 4617. (e) Demachy, I.; Esteruelas, M. A.; Jean, Y.; Lledós, A.; Maseras, F.; Oro, L. A.; Valero, C.; Volatron, F. J. *J. Am. Chem. Soc.* **1996**, *118*, 8388.

(12) (a) Jean, Y.; Eisenstein, O.; Volatron, F.; Maouche, B.; Sefta, F. *J. Am. Chem. Soc.* **1986**, *108*, 6587. (b) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705. (c) Eckert. J.; Kubas, G. J.; Hall, J. H.; Hay, P. J.; Boyle, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 2324. (d) Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 6102. (e) Maseras, F.; Lledós, A.; Costas, M.; Poblet, J. M. *Organometallics* **1996**, *15*, 2947. (f) Li, J.; Ziegler, T. *Organometallics* **1996**, *15*, 3844.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94; Gaussian Inc.: Pittsburgh, PA, 1995.

(14) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U.K., 1989.

(15) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(16) (a) Bytheway, I.; Backsay, G. B.; Hush, N. S. *J. Phys. Chem.* **1996**, *100*, 6023. (b) Jarid, A.; Lledós, A.; Lauvergnat, D.; Jean, Y. *New. J. Chem.* **1997**, *21*, 953.

(17) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(18) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (c) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. (d) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.: Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.: Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111.

Table 1. Optimized Geometrical Parameters Associated with the DiH_2, PB1, and PB2 Structures[a]

	DiH_2	exptl[b]	**PB1**	**PB2**
H2−H3	0.832	0.82(1)	1.565	3.351
W−H2	1.918	1.89(1)	1.743	1.788
W−H3	1.918	1.89(1)	1.743	1.753
W−P4	2.470	2.487	2.483	2.472
W−P5	2.470	2.503	2.483	2.489
W−C6	1.980	1.977	2.056	2.031
W−C7	2.026	2.036	2.022	2.021
W−C8	2.026	2.025	2.022	2.021
H2−W−H3	25.0		53.4	142.3
H2−W−P4	78.4		68.6	69.5
H3−W−P5	78.4		68.6	72.4
H2−W−P5	103.4		122.0	69.9
H3−W−C6	167.5		153.3	62.7
C6−W−P4	89.1	89.3	84.7	85.5
C7−W−C8	177.1	175.9	168.8	174.8
P4−W−C7	90.0	90.1	90.5	88.2
P4−W−C8	90.0	90.9	90.5	88.2
P5−W−C7	90.0	91.6	90.5	90.1
P5−W−C8	90.0	90.3	90.5	90.1
P4−W−C6	89.1	89.3	84.7	135.1
P5−W−C6	89.1	89.3	84.7	85.5
P4−W−P5	181.8	181.7	169.4	136.6

[a] For the atom numbering, see Figures 1 and 3. Distances are given in Å and angles in deg. [b] The experimental values are those reported for the $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ complex.[3,22] Missing data are not available.

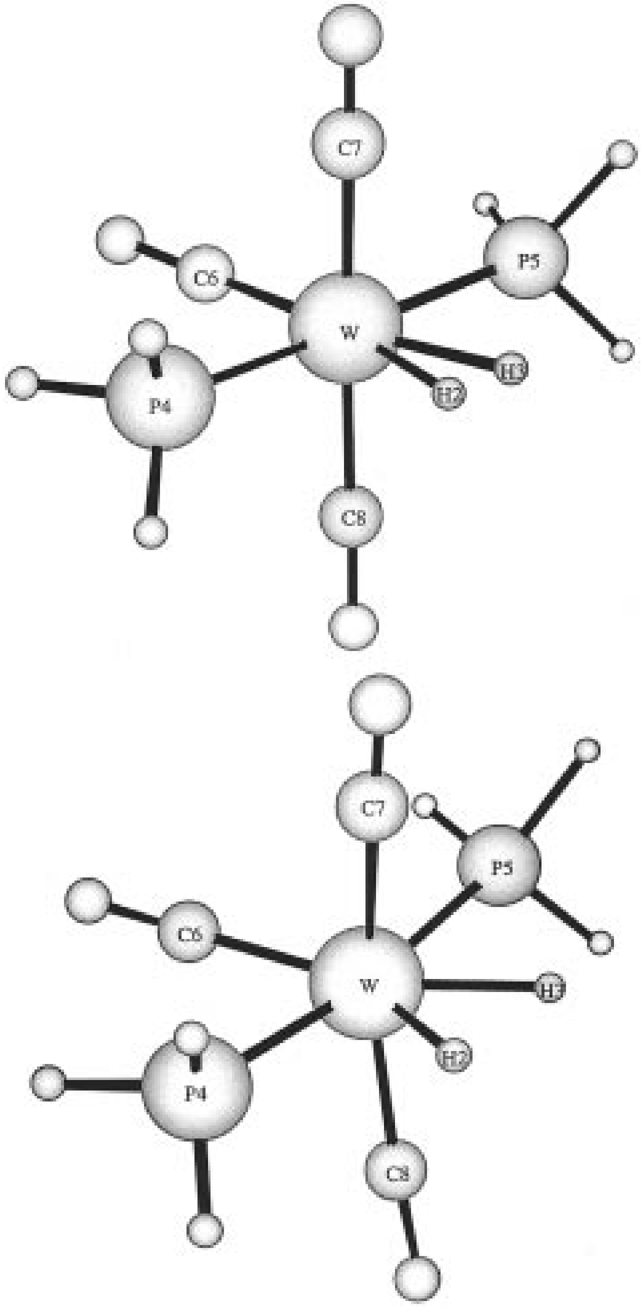

Figure 1. Structure of the (a, top) dihydrogen (**DiH_2**) and (b, bottom) dihydride (**PB1**) forms of the $W(CO)_3(PH_3)_2(H_2)$ complex. For detailed geometrical parameters, see Table 1.

respectively) were also performed. To obtain accurate estimations for the relative energies of the stationary points, as well as for the oxidative-addition energy profile, the energies were recalculated at the B3LYP geometries using coupled-cluster theory with single, double, and noniterative estimation of triple excitations (CCSD(T)//B3LYP).[20] This calculational scheme, based on geometry optimization at the B3LYP level of theory and energy calculation using the coupled-cluster methods, has been proposed to obtain accurate energy values.[21] It has recently been proved in several transition-metal dihydrogen complexes that a similar approach, based on single-point CCSD(T) calculations on MP2 optimized geometries, gives energetic results in excellent agreement with the experimental data.[10d,22]

The Dihydrogen Complex

In these calculations, the dihydrogen complex $W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$ (**DiH_2**) was taken as a model for the Kubas complexes. Maseras et al.[12e] have already shown that the B3LYP optimization leads to geometrical parameters in very good agreement with the experimental values[3,23] (see Table 1 and Figure 1a for the atom numbering).

The **DiH_2** structure was characterized as a minimum on the B3LYP potential energy surface. The vibrational frequencies associated with the two symmetric M−H and H−H stretching modes are 943 and 3022 cm^{-1}, respectively. These values are in the range of that found in a previous ab initio SCF study (963 and 3181 cm^{-1}).[12c] In comparison to the experimental values,[4b] the former is satisfactorily reproduced (953 cm^{-1} for both R = *i*-Pr and Cy), but the H−H stretching frequency is significantly overestimated (experimental values 2695 and 2690 cm^{-1} for R = *i*-Pr, Cy, respectively). Similar overestimation was found for the $M(CO)_5(\eta^2\text{-}H_2)$ (M = Cr, Mo, W) complexes, and it was suggested that it comes from the harmonic approximation used in the calculations.[10d] This suggestion is supported by a very recent normal-coordinate analysis on the $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$ complex, where an extensive mixing between the H−H stretch and the $W{-}H_2$ stretch has been found.[24]

The H_2 dissociation energy was calculated as the energy difference between the optimized structures of

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(19) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(20) (a) Bartlett, R. J. *J. Phys. Chem.* **1989**, *93*, 1697. (b) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *165*, 513.

(21) (a) Bauschlicher, C. W., Jr.; Partridge, H. *J. Chem. Phys.* **1995**, *103*, 1788. (b) Mebel, A. M.; Morokuma, K.; Lin, M. C. *J. Chem. Phys.* **1995**, *103*, 7414.

(22) Dapprich, S.; Frenking, G. *Organometallics* **1996**, *15*, 4547.

(23) Vergamini, P. J.; Wasserman, H. J.; Koetzle, T. F.; Kubas, G. J. Unpublished work cited in footnote 9 of ref 4b.

(24) Bender, B. R.; Kubas, G. J.; Jones, L. H.; Swanson, B. I.; Eckert, J.; Capps, K. B.; Hoff, C. D. *J. Am. Chem. Soc.* **1997**, *119*, 9179.

both **DiH$_2$** and the W(CO)$_3$(PH$_3$)$_2$ and H$_2$ fragments. A value of 21.3 kcal/mol was found at the CCSD(T)//B3LYP level. This binding energy compares well with the 20.9 kcal/mol recently reported by Li and Ziegler (DFT calculations)[12f] but is significantly higher than that provided by previous HF calculations (15 kcal/mol).[12c] The experimental H$_2$ binding enthalpy in the W(CO)$_3$(PCy$_3$)$_2$(H$_2$) complex is only 10.0 ± 1 kcal/mol.[25] However, an agostic interaction is at work in the W(CO)$_3$(PCy$_3$)$_2$ fragment,[26] which has to be destroyed upon H$_2$ binding. The enthalpy associated with this agostic interaction has been estimated to be 10–15 kcal/mol.[25,27] Accordingly, the "intrinsic" H$_2$ binding energy would be lying between 20–25 kcal/mol, in the range of our calculated value (21.3 kcal/mol).

Finally, the rotational barrier of the dihydrogen ligand was computed to be 0.99 kcal/mol at the CCSD(T)//B3LYP level (experimental values 2.2–2.4 kcal/mol).[28] Previous theoretical studies have traced this barrier to the decrease of the back-donation toward the $\sigma^*_{H_2}$ orbital when the H–H ligand becomes coplanar with the adjacent metal–carbonyl bonds.[12a–c,f] The evolution of the W–H$_2$ geometrical parameters in going from the minimum **DiH$_2$** to the optimized transition state structure supports this analysis: the H–H distance decreases from 0.832 to 0.805 Å and at the same time the W–H distances increase from 1.918 to 1.965 Å.

The Oxidative-Addition Process

The energy profile associated with the oxidative-addition process was studied by varying the H–H distance from its value in **DiH$_2$** (0.832 Å) to 2.0 Å (by steps of 0.2 Å between 1.0 and 2.0 Å). All the geometrical parameters were optimized at each fixed H–H distance.

The addition was found to proceed without any H$_2$ rotation, leading to a pentagonal-bipyramidal type structure with the two hydrides lying in the equatorial plane *cis* to each other. The energy curves associated with the H–H cleavage are reported in Figure 2 at the different levels of calculation.

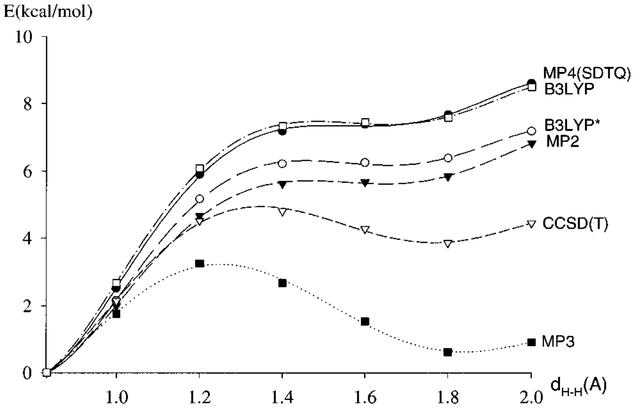

Figure 2. Energy profiles associated with the H–H bond breaking in **DiH$_2$** at the various levels of calculation. Energies relative to the **DiH$_2$** complex are in kcal/mol, H–H distance in angstroms.

Table 2. Energetic Results (kcal/mol) for the DiH$_2$, PB1, and PB2 Structures at Various Levels of Calculation

	DiH$_2$	**PB1**	**PB2**	exptl[b]
B3LYP	0.00	7.37	6.76	
B3LYP*	0.00	6.24	5.23	
MP2	0.00	5.66	4.87	
MP3	0.00	1.53	-0.59	
MP4(SDTQ)	0.00	7.46	5.99	
CCSD(T)	0.00	4.31	2.34	
Δ(E + ZPE)[a]	0.00	3.18	1.46	
Δ*H*(298.3 K)[a]	0.00	2.50	1.29	1.2, 1.5
Δ*G*(298.3 K)[a]	0.00	4.80	1.87	0.80, 0.75

[a] The relative energies are calculated at the CCSD(T) level, and ZPE and thermal corrections are computed using the characterization of stationary points at the B3LYP level. [b] The experimental values are given for the W(CO)$_3$(PR$_3$)$_2$(H$_2$) complexes, with R = *i*-Pr, Cyp, respectively.

At the B3LYP level, a stationary point was found for H–H = 1.565 Å, a value close to that reported recently by Li and Ziegler (1.554 Å) in their DFT calculations[12f] for the same dihydride (the other geometrical parameters are also very similar). This structure (**PB1**) is pictured in Figure 1b, and its main geometrical parameters are listed in Table 1. Diagonalization of the numerically calculated Cartesian Hessian matrix for **PB1** gives, however, one negative eigenvalue, with a very low imaginary frequency of $-29.3i$ cm^{-1}, associated with the H–H stretching mode. Although two stationary points might have been expected, one minimum and one transition state, we did not succeed in finding a second stationary point for the dihydride form and we believe this is due to the extreme flatness of the B3LYP curve for H–H distances between 1.4 and 1.8 Å (Figure 2). The extension of the basis set (B3LYP*//B3LYP calculations) leaves the energy profile almost unchanged: the energy values were found to differ at most by 1.5 kcal/mol from those obtained with the former basis set. At our highest level of calculation (CCSD(T)//B3LYP), the potential energy curve still exhibits essentially the same pattern, although a very shallow minimum appears for the dihydride structure with H–H ≈ 1.8 Å (Figure 2). It must be stressed that enlarging the MP series from MP2 to MP4(SDTQ) does not give energy values closer to the CCSD(T) values. Therefore, it seems that, in this case, the MP energy convergence has not been achieved at the MP4 level.

The energetic results for **DiH$_2$** and **PB1** structures are summarized in Table 2. The B3LYP relative energy of **PB1** (7.4 kcal/mol) is not much different from the value previously obtained by DFT calculations (10.1 kcal/mol).[12f] In contrast, the MP2 value (5.7 kcal/mol) is much lower than the value reported by Lin and Hall (17.0 kcal/mol).[12d] One reason for such a discrepancy is that the dihydride calculated in this previous study is that obtained by oxidative addition with H–H parallel to the C–W–C axis (see structures **29** and **30** in ref 12d). This reaction path is known to be less favorable than that involving an addition of H$_2$ parallel to the P–W–P axis.[12a,b,29]

At the CCSD(T)//B3LYP level, the energy difference between **DiH$_2$** and **PB1** is 4.3 kcal/mol, and adding the

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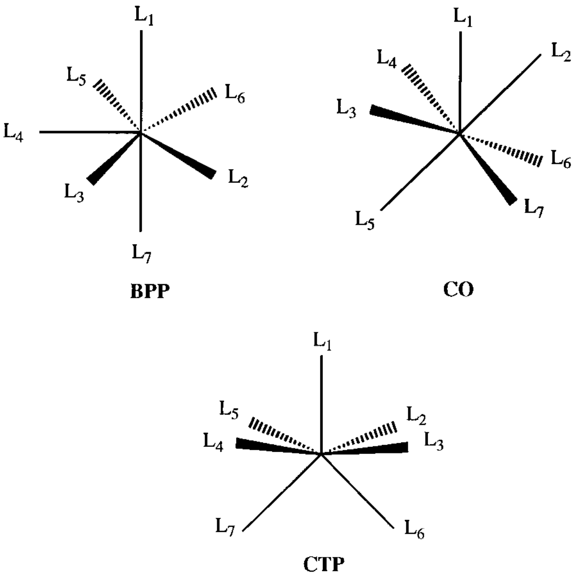
(25) (a) Gonzalez, A. A.; Zhang, K.; Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, *7*, 2429. (b) Gonzalez, A. A.; Hoff, C. D. *Inorg. Chem.* **1989**, *28*, 4295.

(26) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294.

(27) Morse, J. M.; Parker, G. H.; Burkey, T. J. *Organometallics* **1989**, *8*, 2471.

(28) (a) Eckert, J.; Kubas, G. J.; Dianoux, A. J. *J. Chem. Phys.* **1988**, *88*, 466. (b) Eckert, J.; Kubas, G. J. *J. Phys. Chem.* **1993**, *97*, 2378.

Chart 1



BPP **CO**

CTP

zero-point energy and the thermal corrections leads to an enthalpy difference of only 2.5 kcal/mol.

Two main conclusions can be drawn from these results.

(i) The potential energy curves reported in Figure 2 explain why the experimentally observed dihydride is not that obtained by simple breaking of the H−H bond (**PB1**), in which both the hydride and the phosphine ligands are equivalent. As a matter of fact, the energy barrier for the reverse reaction (**PB1** → **DiH$_2$**) is essentially equal to zero.

(ii) Although the Kubas complex is a prototype of the family of "true" dihydrogen complexes, with a short H−H distance, the enthalpy required for the H−H bond breaking is very low (2.5 kcal/mol at the CCSD(T) level). It means that only one-fourth of the experimental activation enthalpy (10.1 kcal/mol) for the dihydrogen → dihydride conversion is used for the oxidative-addition process itself. The remaining part is likely to be involved in the reorganization of **PB1** toward a new structure of the heptacoordinated dihydride in which both the hydride and phosphine ligands are inequivalent and which cannot convert too easily to the dihydrogen complex **DiH$_2$**.

Possible Structures for the Dihydride Complex

In seven-coordinate complexes, there are three basic geometries: the pentagonal bipyramid (PB), the capped octahedron (CO), and the capped trigonal prism (CTP).[30] In hypothetical idealized complexes with seven identical ligands, these structures are of D_{5h}, C_{3v}, and C_{2v} symmetry, respectively (Chart 1). The actual low-temperature structure of the $WH_2(CO)_3(PR_3)_2$ dihydride should belong to one of these families or be close to one of them. As a matter of fact, a capped-octahedral structure, with one carbonyl or one of the hydrides in the capping position, has been proposed for this dihydride.[4b] Due to the different nature of the ligands, there is actually a very large number of possible structures, but the problem can be greatly simplified by taking into account the experimental data: (i) both the phosphine and hydride ligands are inequivalent; (ii) the P−W−P angle must be large enough to accommodate the phosphine substituents (*i*-Pr or Cyp). According to the Tolman cone angles (160 and 170°, respectively),[31a] the two phosphines should be essentially *trans* to each other. However, smaller values (137 and 149°, respectively) have also been proposed for these ligands.[31b,c] In practice, we limited our study to the structures in which the P−W−P angle is larger than 120°.

Table 3. Relative Energies (*E*, in kcal/mol) Computed for the PB2 and PB3, CO1−CO8, and CTP1−CTP8 Structures of the $WH_2(CO)_3(PH_3)_2$ Dihydride Complex[a]

	L_1	L_2	L_3	L_4	L_5	L_6	L_7	E	→ ?
PB2	CO	H	P	H	CO	P	CO	0.0	**PB2**
PB3	CO	CO	P	H	CO	P	H	27.8	
CO1	CO	CO	P	H	H	P	CO	27.3	
CO2	CO	CO	P	H	CO	P	H	21.4	
CO3	H	CO	P	CO	CO	P	H	12.8	**PB2**
CO4	H	CO	P	H	CO	P	CO	16.6	**DiH$_2$**
CO5	P	CO	H	CO	CO	P	H	27.7	
CO6	P	CO	H	H	CO	P	CO	26.2	
CO7	P	CO	H	CO	CO	H	P	22.3	
CO8	P	CO	H	CO	P	CO	H	28.2	
CTP1	CO	CO	P	H	P	CO	H	26.2	
CTP2	CO	P	H	P	CO	CO	H	20.3	
CTP3	H	P	H	P	CO	CO	CO	18.8	
CTP4	H	P	CO	P	CO	CO	H	9.5	**PB2**
CTP5	P	CO	H	CO	H	CO	P	22.5	
CTP6	P	H	CO	CO	H	CO	P	28.2	
CTP7	P	CO	H	CO	CO	H	P	21.1	
CTP8	P	CO	CO	H	CO	H	P	14.8	**PB2**

[a] See Chart 1 for the ligand numbering. In the last column (→ ?) is given the result of a full geometry optimization on the five lowest energy structures.

Under these conditions, 18 structures were found to be possible candidates for the dihydride form: two PB, eight CO, and eight CTP. They are listed in Table 3 (**PB2** and **PB3, CO1−CO8**, and **CTP1−CTP8**), the ligand numbering being that defined in Chart 1. Partial geometry optimizations were performed at the B3LYP level on these 18 structures. P−H bond lengths and H−P−W angles were fixed to 1.42 Å and 120°, respectively. All the other bond lengths were optimized. Some angular constraints were also imposed in order to avoid interconversions between different structures (Chart 1). In the PB complexes, the equatorial bond angles were optimized by keeping the five ligands coplanar and the axial bonds perpendicular to that plane (pseudo D_{5h} structures). In the CO complexes, a pseudo C_{3v} structure was retained by making $\theta_2 = \theta_3 = \theta_4$ and $\theta_5 = \theta_6 = \theta_7$ ($\theta_i = L_1{-}W{-}L_i$). Finally, in the CTP complexes, pseudo C_{2v} optimizations were performed by fixing $\theta_2 = \theta_3 = \theta_4 = \theta_5$, and $\theta_6 = \theta_7$ and by optimizing a single dihedral angle for the four ligands belonging to the capped face ($\phi_2 = -\phi_3 = 180 + \phi_4 = 180 - \phi_5$).

The energetic results of these geometry optimizations are reported in Table 3. The pentagonal-bipyramidal

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(29) To check this point, we have calculated a structure with axial phosphines (but with the equatorial hydrides not *cis* to each other). Its energy, 19.6 kcal/mol higher than that of **DiH$_2$**, is consistent with the previous MP2 result.

(30) (a) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748. (b) Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67. (c) Kepert, D. L. *Prog. Inorg. Chem.* **1979,** *25*, 41.

(31) (a) Tolman, C. A. *Chem. Rev.* **1977,** *77*, 313. (b) Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977,** *25*, 241. (c) White, D.; Coville, N. J. *Adv. Organomet. Chem.* **1994,** *36*, 95.

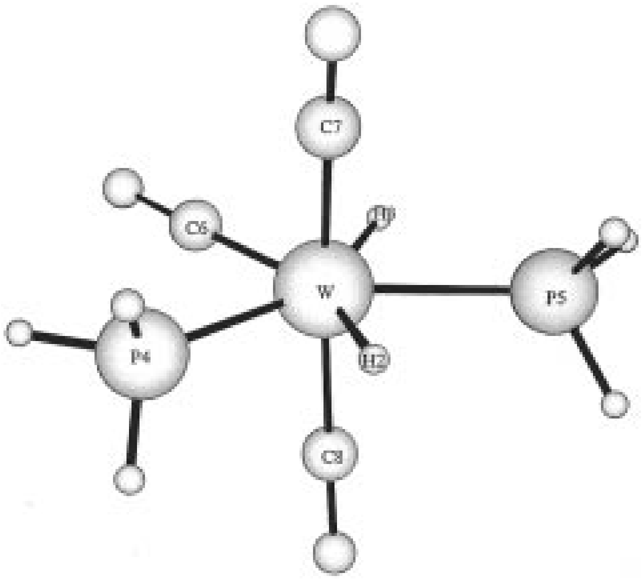

Figure 3. Structure of the $WH_2(CO)_3(PH_3)_2$ dihydride **PB2**. For detailed geometrical parameters, see Table 1.

PB2 was found to be much more stable than the other structures. Full geometry optimization (C_1) of **PB2** led to only slight geometrical changes, the coordination mode (PB) and the ligand site occupation being unchanged. This structure was characterized as a minimum on the potential energy surface, the main geometrical parameters being reported in Table 1. Four among the CO and CTP structures, **CO3, CO4, CTP4**, and **CTP8**, were found to be located between 9 and 17 kcal/mol above **PB2** (Table 3). Further geometry optimizations were performed on these structures to check whether relaxing the geometrical constraints might lead to other minima. However, they were found to collapse either to the **PB2** dihydride or to the molecular dihydrogen complex $\mathbf{DiH_2}$ (Table 3).

PB2: A Likely Candidate for the Dihydride Structure

The **PB2** structure is pictured in Figure 3. It can be described as a pentagonal-bipyramidal complex, with axial carbonyl ligands and the two hydrides lying in the equatorial plane and being separated by a phosphine ligand. This structure fits the experimental spectroscopic data, since both the hydrides and the phosphine ligands are inequivalent. Furthermore, in agreement with the results of $^1H-^{31}P$ coupling and selective decoupling experiments in the dihydride $WH_2(CO)_3(P\text{-}i\text{-}Pr_3)_2$,[4b] one hydride is positioned symmetrically with respect to the phosphine ligands while the other hydride is asymmetrically positioned. Finally, the P−W−P angle (136.6°) seems large enough to accommodate encumbered phosphines such as $P(i\text{-}Pr)_3$ and $P(Cyp)_3$.

The enthalpy difference between the dihydrogen complex $\mathbf{DiH_2}$ and the dihydride **PB2** was computed to be equal to 1.29 kcal/mol (Table 2) at our highest level of calculation (CCSD(T)), in nice agreement with the experimental values of 1.2(0.6) and 1.5(0.4) kcal/mol for R = *i*-Pr and R = Cyp, respectively. Taken together, these structural and energetic results make **PB2** a likely candidate for the structure of the dihydride at low temperature. Furthermore, its structure is similar to that characterized (X-ray) for the related Mo(II) dihydrides $MoH_2(CO)(Et_2PCH_2CH_2PEt_2)_2$ and $MoH_2(PMe_3)_5$.[32] Both adopt a BP geometry with an axial carbonyl group in the former and, in both complexes, two equatorial hydrides separated by a P ligand. The ligand site occupation in **PB2** also is consistent with the rules given by Hoffmann et al.[33] for the substituent site preference in d^4 pentagonal-bipyramidal complexes. As a matter of fact, two π-acceptor ligands (CO) are located at the axial sites and the two better σ-donor hydrides are equatorial.[34]

A reasonable assumption for the overall oxidative-addition mechanism ($\mathbf{DiH_2} \rightarrow \mathbf{PB2}$) is that the first step involves the breaking of the H−H bond, leading to a **PB1**-like structure. The question remains how to reorganize **PB1** into **PB2**. The interconversion between two PB structures in seven-coordinate complexes can be achieved by various mechanisms, involving either a CO or a CTP structure as an intermediate. According to the mechanisms proposed by Drew,[30b] a CO structure can be formed by the migration of an equatorial ligand of the starting PB. On the other hand, two rearrangements from a PB to a CTP structure are possible, depending on whether an axial or an equatorial ligand becomes the capping ligand in the CTP. All these mechanisms were applied to **PB1**, but in no case was **PB2** found to be the product of the rearrangement. Therefore, single-step mechanisms such as **PB1** → **CO** → **PB2** or **PB1** → **CTP** → **PB2** cannot be proposed for the conversion of **PB1** into **PB2**. The reaction process is thus likely to be a several-step process which might involve several intermediate structures. This result is not too surprising, since the potential energy surfaces associated with seven-coordinate complexes are usually believed to be characterized by several minima and transition-state structures lying in a rather narrow energy range. It is also consistent with the fluxionality of the dihydride complex at room temperature, which means that several structures can be reached without going back to the molecular dihydrogen complex.

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[32] (a) Lyons, D.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 695. (b) Kubas, G. J.; Ryan, R. R.; Unkefer, C. J. *J. Am. Chem. Soc.* **1987,** *109*, 8113.

[33] Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977,** *16*, 511.

[34] An analysis of the coordination polyhedron of seven-coordinate species has indicated that a capped-octahedral structure was seemingly favored for W(II) complexes.[35] However, it must be noted that all the W(II) structures analyzed involve combinations of π-acceptors with donor halides. Following the rules for ligand site preferences in heptacoordinated species,[33] the π-donor ligands can be well-accommodated in the uncapped face of the **CO**. This kind of ligand, also present in the $MoCl_2(CO)_3(PEt_3)_2$ complex, which also adopts a **CO** structure, is lacking in the dihydride studied in this work.

[35] Maseras, F.; Eisenstein, O. *New J. Chem.* **1997**, *21*, 961.