

# Structure and Dynamics of LRh“H<sub>4</sub>” (L = Cp, Tp) Systems. A Theoretical Study

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A density functional theory study on the LRh“H<sub>4</sub>” (L = Cp, Tp) systems has been carried out. When L = Cp, a piano-stool tetrahydride structure has been found to be the most stable, and a  $\eta^2$ -H<sub>2</sub> structure has been found slightly higher in energy. Conversely, when L = Tp only an octahedral dihydrogen–dihydride structure has been determined. Rotational barriers corresponding to dihydrogen–dihydride structures when L = Cp and L = Tp are obtained and their differences are interpreted in terms of the dependence of  $\pi$ -back-donation along the librational motion of the dihydrogen unit. Finally, a value of 9.2 cm<sup>-1</sup> has been theoretically determined for the rotational tunneling splitting of the librational ground state of TpRh( $\eta^2$ -H<sub>2</sub>)H<sub>2</sub>, in excellent accord with experimental measurements obtained by means of INS experiments.

## I. Introduction

Understanding the nature of the interaction between a metal center and a bound dihydrogen ligand has been a key subject in recent years, mainly due to the fact that this knowledge will probably give insights into the mechanism of catalysis and hydrogen bond activation.<sup>1</sup> The nature of this interaction shows a dependency on the ligands also bound to the metal center. Actually the mode of bonding of dihydrogen is quite sensitive to the nature of the rest of the ligands bound to the metal atom.<sup>1</sup> Often it has been assumed that high electron density at the central atom is necessary in order to strengthen the metal–dihydrogen interaction by means of  $\pi$ -back-donation. To support this assumption, the majority of complexes which contain dihydrogen ligands also contain, in the role of coligands, molecular species of strong electron-donor character such as cyclopentadienyl (Cp) and phosphine ligands. Nevertheless, the stabilization of  $\eta^2$ -H<sub>2</sub> is the result of a delicate equilibrium between donation and back-donation. Thus, excessive back-donation leads to the classical dihydride isomer. Because of this,  $\pi$ -acceptors such as CO can be found as ligands in several stable dihydrogen complexes.

Recently, a ligand which already had ample application in the field of organometallic chemistry has forcibly irrupted in the field of chemistry of metal polyhydride complexes. This ligand is hydridotris(pyrazolyl)borate (Tp) and a series of derivatives made up with different substitutions on the pyrazolyl rings.<sup>2</sup> In spite of having properties similar to those of Cp (concretely, both present similar donating properties), this ligand behaves differently from Cp in polyhydride systems, with a stronger tendency toward the stabilization of nonclassical structures. For instance, the complexes (C<sub>5</sub>R<sub>5</sub>)-Ru(PR'<sub>3</sub>)H<sub>3</sub> (R = H, R' = Me; R = Me, R' = Ph, <sup>i</sup>Pr, Cy)

have been described as classical trihydride complexes,<sup>3</sup> whereas the complex RuTp(PCy<sub>3</sub>)(H<sub>2</sub>)H was formulated as a nonclassical dihydrogen complex.<sup>4</sup> Furthermore, the system [LIr(PMe<sub>3</sub>)(H<sub>3</sub>)<sup>+</sup>, when L = Cp, is a trihydride complex,<sup>5</sup> but when L = Tp the NMR data suggest a dihydrogen–hydride structure with a very low activation barrier for the hydrogen exchange.<sup>6</sup> The stabilization of a bis(dihydrogen) complex has been achieved by using Tp as a ligand, in TpRuH( $\eta^2$ -H<sub>2</sub>)<sub>2</sub>.<sup>7</sup> On the other hand, for the complex TpIrH<sub>4</sub> a very fluxional polyhydride structure has been proposed.<sup>8</sup> None of these complexes have been characterized by diffraction techniques up to now.

Among the complexes which incorporate Tp as a ligand, there is one which has aroused considerable interest: Tp<sup>Me2</sup>RhH<sub>2</sub>( $\eta^2$ -H<sub>2</sub>) (Tp<sup>Me2</sup> = hydridotris(3,5-dimethylpyrazolyl)borate), first reported by Bucher and co-workers<sup>9,10</sup> (Chart 1). This was the first dihydrogen complex stabilized only by nitrogen donors. However, despite the fact that its structure has not yet been determined, it has been extensively studied by means of inelastic neutron scattering (INS) and IR spectroscopies by Eckert *et al.*<sup>10</sup> The dihydrogen and hydride ligands in **1** are highly fluxional on the NMR

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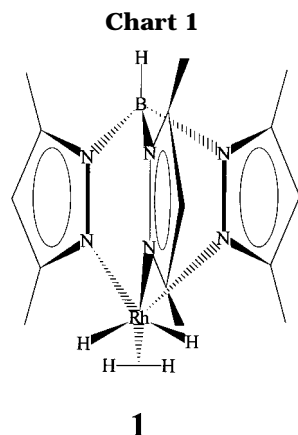
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time scale, and a dynamic exchange between the dihydrogen ligand and the two hydrides takes place. The H–H interaction in the dihydrogen ligand is associated with a stretching frequency of  $2238\text{ cm}^{-1}$ . While it compares satisfactorily to that of several dihydrogen complexes, it is significantly lower than the stretching frequency of free dihydrogen, this being  $4160\text{ cm}^{-1}$ . Eckert *et al.* attribute this fact to the existence of important back-donation from the metal  $d_{\pi}$  orbitals to the  $\sigma^*$  orbital of the dihydrogen ligand.<sup>10</sup> Other interesting data were obtained from the INS spectrum once the low-frequency spectrum and the difference spectrum were obtained. In this way it was discovered that the librational ground state of the coordinated dihydrogen ligand was split due to the rotational tunneling effect, the magnitude of the splitting being  $6.7(5)\text{ cm}^{-1}$ . Apart from this interesting fact, and in order to determine the barrier height, Eckert *et al.* estimated the height of the energy barrier, solving the equation for a hindered rotor. The rotational constant and the potential energy terms were obtained by fitting the theoretical rotational transitions to the experimental ones.<sup>10</sup>

Once the optimum parameters were obtained, a value of  $0.94\text{ \AA}$  was estimated for the equilibrium H–H distance from the value of the rotational constant. This elongated distance together with the small stretching frequency found for the dihydrogen ligand seem to indicate that the M–H<sub>2</sub> interaction is quite strong. As for the rotational barrier, the optimized parameters of the potential yielded a rotational barrier of  $0.56\text{ kcal/mol}$ . This barrier is very low and is somewhat surprising if the signs pointing to a strong interaction metal–dihydrogen are borne in mind. The authors of the previously mentioned study<sup>10</sup> suggest several explanations for this fact, finally concluding that the main interactions between the metal atom and the H<sub>2</sub> fragment are due to  $\sigma$  effects, which do not directly contribute to the rotational energy barrier, and ascribing the low barrier for the rotation to the existence of a *cis*-H effect which should lower the energy barrier. However, as the authors themselves conclude, in the absence of structural data their conclusions are only tentative.

Since the beginning of modern transition-metal chemistry, theory and experiment have advanced together in the development and comprehension of transition-metal polyhydride complexes.<sup>1,11,12</sup> As well as interpreting the nature of the bond, theory has provided numer-

ical values, such as positive identification of structures as dihydride or dihydrogen,<sup>13</sup> elucidation of exchange mechanisms,<sup>14</sup> and energy barrier determination for the motions of the different hydrogen atoms bound to the metal.<sup>14</sup> In spite of this, the theoretical study of a complex of the size of **1** is a challenge to computational methods in such a way that it would have been unthinkable some years ago, unless such a study were carried out by means of extensive modelization. However, modern computational chemistry has developed certain methodologies which have allowed the study of systems of increasing complexity with a surprising degree of success.<sup>15</sup> Concretely, the density functional theory (DFT) has allowed computational chemistry to predict molecular structures which are in excellent accord with experimental ones<sup>16</sup> and which, besides, has demonstrated its ability to reproduce several molecular properties theoretically, thus turning the study of complex inorganic molecules into a fertile working field for theoretical chemistry.

Our purpose has been to carry out an *ab initio* study of the behavior and properties of complex **1** by means of the density functional formalism, in order to obtain reliable data regarding its structure, the dynamics of the rotation of the dihydrogen fragment, and also the spectroscopic data for this complex, mainly with respect to the tunneling splitting. This will enable us to reach conclusions on the nature of the interaction between the metal atom and the H<sub>2</sub> ligand. In addition, we will study the fluxionality of the exchange of a hydride and a hydrogen in the previously mentioned complex. Additionally, the effects of the substitution of Tp by Cp in this kind of system will be studied.

## II. Computational Details

In the following section the methodologies used to carry out the calculations in this paper will be described. In subsection A, the DFT methodology used in order to locate the minima, transition-state structures, and other nonstationary points of the corresponding energy hypersurface are described. In subsection B, details regarding the tunneling study can be found.

**A. DFT Calculations.** As has been stated in the Introduction, a system of the size of **1** would have been very costly

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to study were it not for the existence of the density functional theory, which has allowed the treatment of systems of increasing complexity in recent years, with an encouraging degree of success. However, even using DFT methods, the study of a complex of this size would have been a near-impossible task. Consequently, a certain degree of modelization was needed. Concretely, the six methyl groups present in the Tp<sup>Me2</sup> ligand were turned into simple hydrogen atoms, with the implicit assumption that this change would have negligible effect on the dynamics of the dihydrogen ligand. On the other hand, all cyclopentadienyl complexes theoretically studied in this paper were not modelized at all. In all calculations the geometry of the Cp ligand was restricted to a local C<sub>5v</sub> symmetry. On the Tp complexes no restrictions on symmetry have been enforced.

All calculations were performed with the GAUSSIAN 94<sup>17</sup> series of programs, and DFT<sup>18</sup> was used throughout the calculations with the three-parameter hybrid functional of Becke and the LYP correlation functional, best known as the Becke3LYP functional.<sup>19</sup> This functional has already been used with success to study several dihydrogen/polyhydride systems.<sup>14e,16b,20</sup>

The core electrons of the rhodium atom were replaced by an effective core potential operator. This comprised a total of 28 electrons for the rhodium atom. The basis set used for the rhodium atom was the one associated with the pseudopotential of Hay and Wadt,<sup>21</sup> with a standard valence double- $\zeta$  LANL2DZ contraction.<sup>17</sup> For the rest of the atoms, the valence double- $\zeta$  6-31G basis set<sup>22a</sup> was used, except for the hydrogen atoms directly bound to the metal, in which case the double- $\zeta$  6-31G-(p) basis set was used.<sup>22a,b</sup> This resulted in a total of 97 basis functions for the cyclopentadienyl complexes and of 206 basis functions for the Tp one.

When necessary, several higher level calculations were carried out on the cyclopentadienyl complexes. In these cases, an *f* shell was added to the basis set of the rhodium atom.<sup>22c</sup> Electronic correlation was then included via Møller-Plesset perturbation theory, at second and fourth order (MP2 and MP4(SDTQ)).<sup>23</sup> Additionally, in selected cases coupled cluster calculations involving single, double, and perturbatively triple excitations (CCSD(T)) were also carried out.<sup>24</sup>

**B. Tunneling Calculations.** At least in theory, to study the tunneling dynamics of any system one should diagonalize the matrix representation of the exact Hamiltonian of the system on a given set of basis functions and in this way obtain the energy levels and wave functions associated with eigenstates of the nuclear motion. Obviously, the high number of degrees of freedom in any real system, and in these systems in particular, makes this colossal task impossible to carry out. In order to somehow tackle this task, several approximate methods with varying degrees of success have been devised

to simplify the problem.<sup>25</sup> The most straightforward simplification consists of reducing the dimensionality of the system, this being the strategy adopted here.

The whole dimensionality of the “true” hypersurface is reduced then to just one dimension, and this corresponds to the path followed along the dihydrogen rotation. In this way, obtaining both the eigenvalues and eigenvectors which correspond to nuclear motion is the same as solving Schrödinger’s equation for the motion of the nuclei:

$$[\hat{T} + V(s)]\Psi = E\Psi \quad (1)$$

where  $V(s)$  stands for the potential energy function of the system along the rotation, and  $s$  is just the arc length moved in such a rotation. The key problem is then obtaining this potential energy function. To this end, *ab initio* energies corresponding to structures in different stages of the rotation, for which  $s$  values are known, are fitted by means of cubic splines into a usable function.<sup>26</sup>

Finally, in order to solve eq 1, a basis set methodology has been adopted. A basis set has been used, made up of Gaussian functions of the form<sup>27</sup>

$$\chi_i = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(-\frac{\alpha}{2}(s - s_i)^2\right) \quad (2)$$

where  $\{s_i\}$  values are equally spaced points along the coordinate space and  $\alpha$  a variational parameter. By using  $n$  basis functions one can obtain variationally the lowest  $n$  eigenvalues and eigenfunctions of the system under study. In the present study 95 Gaussian functions were used. It was determined that a further increase in the number of basis functions did not noticeably change the position of the vibrational levels. This methodology has already been used successfully in the study of the quantum exchange in [CpIrLH<sub>3</sub>]<sup>+</sup> (L = PH<sub>3</sub>, CO)<sup>14b,c</sup> and [Cp<sub>2</sub>MH<sub>3</sub>]<sup>n+</sup> (M = Mo, W,  $n = 1$ ; M = Nb, Ta,  $n = 0$ ) trihydride systems.<sup>14e</sup>

### III. Results and Discussion

**A. Structure and Dynamics of the CpRh“H<sub>4</sub>” System.** To begin with, and in order to study the effects of the substitution of Cp by Tp, a preliminary study on a complex similar to TpRhH<sub>2</sub>( $\eta^2$ -H<sub>2</sub>), but in which the Tp ligand has been substituted by a Cp, has been carried out. Although no experimental evidence exists that such a complex is stable, its study will serve the purpose of studying the Cp/Tp substitution effect. Besides, the resulting complex from a computational point of view is sensibly smaller than the Tp one, thus allowing us to test the accuracy of our Becke3LYP results in this smaller system by means of other, higher level calculations, which would be impossible to carry out in a system much greater.

As starting points for the geometry optimizations in the CpRh“H<sub>4</sub>” system, both the tetrahydride and the dihydrogen–dihydride structures were checked (the “H<sub>4</sub>” in quotation marks is used to refer to both the dihydrogen–dihydride structure and the tetrahydride structure). In this way two different minima were obtained within the C<sub>s</sub> symmetry point group: one, the lower in energy, corresponding to the stable tetrahydride structure CpRhH<sub>4</sub> (**2**), and the other, 1.25 kcal/mol above the former, corresponding to a stable dihy-

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**Table 1. Structural Parameters for Cp Complexes<sup>a</sup>**

	<b>2</b>	<b>4<sup>b</sup></b>	<b>3</b>	<b>5</b>	<b>6</b>
mean Rh–C	2.374	2.283(9)	2.365	2.370	2.371
Rh–H1	1.550	1.581(3)	1.640	1.582	1.706
Rh–H2	1.550		1.553	1.552	1.689
Rh–H3	1.550	1.581(3)	1.553	1.552	1.555
Rh–H4	1.550		1.640	1.582	1.555
H1···H2	1.702		1.969	1.867	2.444
H1···H3	2.407	2.328(9)	2.365	2.356	2.444
H1···H4	1.702		0.943	1.153	0.850
Rh–X(H <sub>2</sub> ) <sup>c</sup>			1.572	1.437	1.643
H2···H3	1.702		1.819	1.792	1.937
H2···H4	2.407		2.365	2.356	1.965
H3···H4	1.702		1.969	1.867	1.965
∠H1RhH2	66.7		76.1	73.1	97.0
∠H1RhH3	101.9	94.84(18)	95.5	97.5	97.0

<sup>a</sup> Distances are given in Å and angles in degrees. For atom numbering see Figures 1 and 2. <sup>b</sup> Neutron diffraction data corresponding to complex CpRhH<sub>2</sub>(SiEt<sub>3</sub>)<sub>2</sub>, from ref 29. <sup>c</sup> Distance from the rhodium atom to the center of the dihydrogen unit, when appropriate.

drogen–dihydride structure, CpRhH<sub>2</sub>(η<sup>2</sup>-H<sub>2</sub>) (**3**). The stationary points were localized with the Schlegel gradient optimization algorithm. If the approximate derivative matrix is forced to contain no negative eigenvalues, the optimization converges to a minimum. Selected geometrical parameters corresponding to **2** and **3** can be found in Table 1, while their optimized structures are featured in Figure 1.

The most stable isomer (**2**) corresponds to a four-legged piano stool structure, which can then be described as a rhodium(V) complex. Such a high formal oxidation state is far from common in rhodium organometallic chemistry.<sup>28</sup> The first complex of this kind characterized by means of neutron diffraction was (C<sub>5</sub>-Me<sub>5</sub>)Rh(H)<sub>2</sub>(SiEt<sub>3</sub>)<sub>2</sub> (**4**),<sup>29</sup> whose structural parameters can also be found in Table 1. As can be seen, the structural parameters of **2** are in good agreement with those of **4**. Besides, Lin and Hall carried out *ab initio* calculations on this same system at the Hartree-Fock level, obtaining data which compare well with ours.<sup>30</sup> The most remarkable feature of the dihydrogen isomer is the long H–H distance (0.943 Å), noticeably longer than in Kubas' complex (0.82 Å).<sup>31</sup> The complex [(C<sub>5</sub>-Me<sub>5</sub>)Ru(η<sup>2</sup>-H<sub>2</sub>)(dppm)]<sup>+</sup>, the only dihydrogen complex with a Cp-type ligand on which neutron diffraction studies have been carried out, also presents a remarkably long H–H distance (1.08 Å).<sup>32</sup> A complex strongly related to **2**, (C<sub>5</sub>Me<sub>5</sub>)Ir(H)<sub>4</sub>, has been characterized by means of spectroscopic techniques and X-ray diffraction as having a tetrahydride structure.<sup>33</sup> It is interesting that this complex extrudes dihydrogen upon radiation and also it allows for the exchange of hydrogen by deuterium when thermally activated. Both experimental behaviors suggest that a η<sup>2</sup>-H<sub>2</sub> situation is energetically accessible.

Given that two different minima have been found, the transition-state structure connecting both was sought. This structure, **5**, was found to be 1.61 kcal/

mol above **2** and its geometrical parameters appear also in Table 1, while it is depicted in Figure 2. This transition-state structure is closer to the dihydrogen structure than to the tetrahydride one, and as can be seen the H–H distance in this transition-state structure (1.153 Å) corresponds to that of an elongated dihydrogen.

Additionally, the rotational dynamics for the less stable dihydride–dihydrogen isomer **3** was studied. To this end, the transition-state structure of the rotation of the H<sub>2</sub> fragment was localized, forcing the H<sub>2</sub> fragment to lie within the plane of symmetry of the molecule. In this way the stationary point **6** was found with an energy 4.88 kcal/mol above that of **3**. This transition-state structure is shown in Figure 2, and its structural parameters can be found in Table 1.

There are no experimental measurements of rotational barriers in dihydrogen complexes with Cp ligands. The height of such rotational barriers has been related to the existence of π-back-donation along the entire rotation.<sup>34</sup> In our present case, the value found for the rotational barrier is higher than that of the rotational barriers determined by means of INS for octahedral d<sup>6</sup> complexes (values between 0.5 and 3.5 kcal/mol).<sup>10,34,35</sup> In those complexes the back-donating powers of the different occupied d orbitals are similar, and due to this fact π-back-donation is partially preserved along the rotation, although in the transition state of the rotation the identity of the orbital responsible for the back-donation changes. Recently, very high barriers (8–10 kcal/mol) have been found for the same rotation in d<sup>2</sup> complexes.<sup>36</sup> In this case, these high barriers can be interpreted by means of a complete loss of π-back-donation in the transition state structure. Our case corresponds to an intermediate situation, which suggests a considerable loss of back-donation in the transition state. This conclusion is consistent with the evolution of the H–H distance, from 0.943 Å in the minimum to 0.850 Å in the transition state, and also with the evolution of the distance between the rhodium atom and the center of the dihydrogen unit, which is 1.572 Å in the minimum and 1.643 Å in the transition state. The arrangement of the occupied d orbitals in a d<sup>6</sup> complex with a Cp ligand is responsible for this behavior. The orbitals of a CpML<sub>2</sub> fragment and the way in which they interact with a π-acceptor ligand have been developed by Hoffmann and co-workers.<sup>37</sup> As can be seen in Chart 2, when the system is in structure **3** back-donation occurs from the a'' orbital of the CpML<sub>2</sub>

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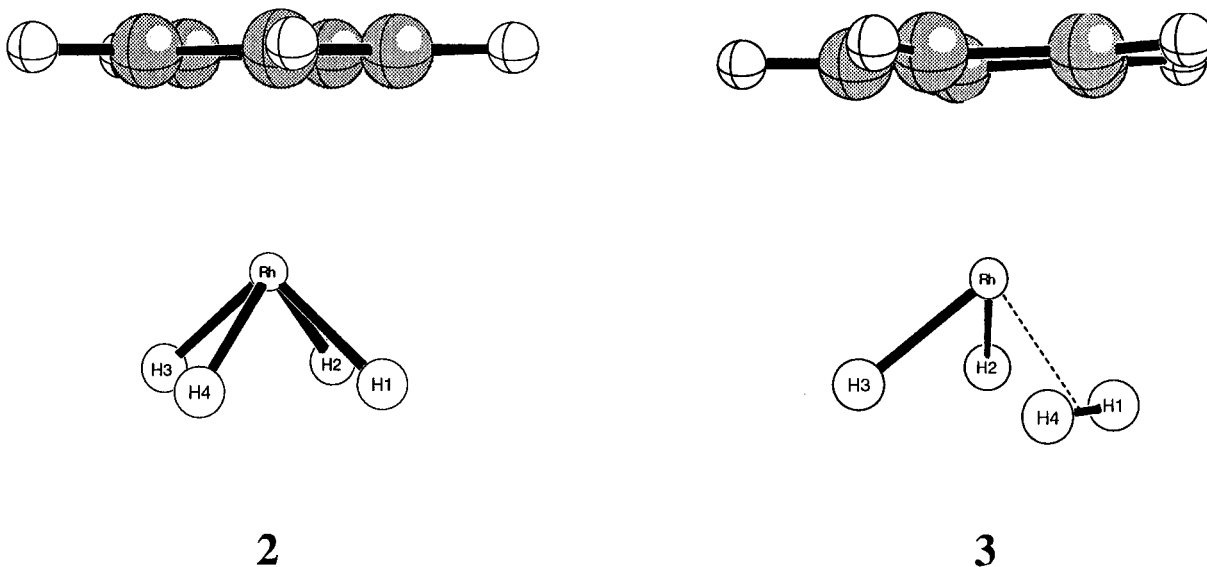
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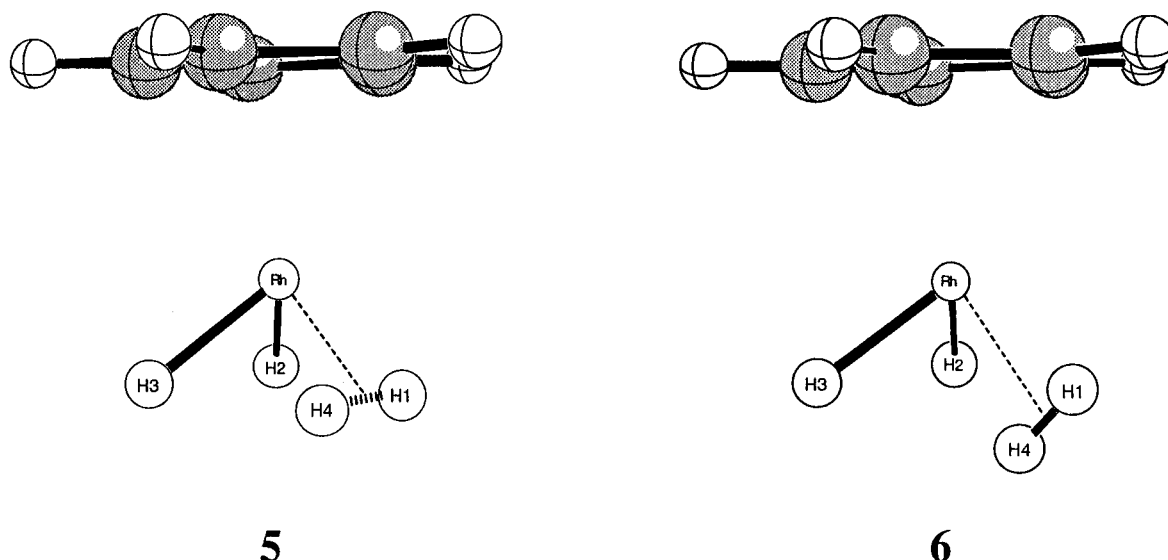
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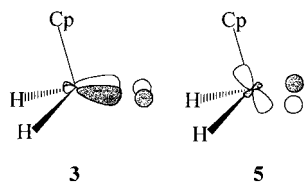


**Figure 1.** Optimized structures for the tetrahydride (**2**) and dihydride–dihydrogen (**3**) isomers of CpRh“H<sub>4</sub>”.



**Figure 2.** Optimized structures for the transition state of the interconversion between tetrahydride and dihydride–dihydrogen isomers (**5**) and the transition state of the rotation of the  $\eta^2$ -H<sub>2</sub> unit (**6**) in CpRh“H<sub>4</sub>”.

### Chart 2



fragment to the  $\sigma^*$  molecular orbital of the dihydrogen ligand. Once in the transition state, **5**, back-donation occurs from the  $a'$  orbital in the metal fragment. This last orbital is lower in energy than the  $a''$  one, and additionally the overlap in this later case would be lower. The change from the first situation to the second is responsible for the rotational barrier. The similarities between the behavior of the dihydrogen ligand in our case and that of strong  $\pi$ -acceptor ligands such as CH<sub>2</sub> and CH<sub>2</sub>=CH<sub>2</sub> indicates the strong  $\pi$ -acceptor properties of the dihydrogen ligand.<sup>12,38</sup> In fact, it is remarkable that for the  $\eta^2$ -H<sub>2</sub> isomer it is easier to form the

tetrahydride isomer (potential energy barrier of 0.36 kcal/mol) than to make the dihydrogen rotate (potential energy barrier of 4.88 kcal/mol).

Upon reaching this point, a series of calculations have been performed in order to test the reliability and accuracy of the Becke3LYP functional to satisfactorily study a system such as this, in order to extrapolate these results to the greater Tp system. Russo *et al.* have demonstrated that for a small but significant set of transition-metal complexes the effective core potentials generated from Hartree-Fock atomic calculations may be used in DFT-based methods as well.<sup>39</sup> However, what has not yet been clearly checked is whether the basis sets derived for use with Hartree-Fock effective core potentials may also be used in DFT studies. To carry out this test, single-point high-level calculations were carried out on the geometries of the stationary points optimized at the Becke3LYP level. Moreover, the basis set for the rhodium atom was enlarged for these calculations with an additional  $f$  shell, for a grand total

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**Table 2. Comparison between Different Computational Methods for the CpRh“H<sub>4</sub>” Systems<sup>a</sup>**

	B3LYP// B3LYP	MP2// B3LYP <sup>b</sup>	MP4(SDTQ)// B3LYP <sup>b</sup>	CCSD(T)// B3LYP <sup>b</sup>
<b>2</b> <sup>c</sup>	0.00	0.00	0.00	0.00
<b>3</b>	1.25	8.43	4.44	1.96
<b>5</b>	1.61	4.95	2.89	1.96
<b>6</b>	6.13	16.06	10.70	6.84

<sup>a</sup> Relative energies are given in kcal/mol. <sup>b</sup> An f shell has been added when calculating MP2, MP4, and CCSD(T) energies. <sup>c</sup> Absolute energies for **2** in the different calculational levels (au): -305.3664 (B3LYP//B3LYP), -303.9923 (MP2//B3LYP), -304.0476 (MP4(SDTQ)//B3LYP), -304.0326 (CCSD(T)//B3LYP).

of 104 basis functions. The results obtained are summarized in Table 2.

Several interesting points arise from Table 2. All methods give the tetrahydride structure as the most stable for the CpRh“H<sub>4</sub>” system, but the difference between the classical and nonclassical isomers varies sensibly with the methodology used: MP2 exaggerates the instability of the  $\eta^2$ -H<sub>2</sub> group, whereas MP4 corrects this but still gives values far from CCSD(T) ones.<sup>40,41</sup> In contrast, the values obtained with the Becke3LYP functional are very close to the CCSD(T) ones. Even though stationary points have not been relocalized, the MP2 energy value for the dihydrogen exchange transition-state structure **5** suggests that the energy will rise monotonously on going from **2** to **3**, hence making it doubtful that an  $\eta^2$ -H<sub>2</sub> minimum could exist. CCSD(T) values are very similar to Becke3LYP ones, which seems to indicate that this secondary minimum could exist. As for the rotational energy barrier, Becke3LYP and CCSD(T) yield very similar values as well, while MP2 and MP4 both exaggerate its value. This whole set of results points in the direction that Becke3LYP calculations are able to correctly describe the whole potential energy hypersurface of this system, without exaggerating the relative stability of either dihydrogen-dihydride or tetrahydride structures. These results are similar to those for other H<sub>2</sub> complexes.<sup>16b,20</sup> As a conclusion it can be said that Becke3LYP combined with the Hartree-Fock-based effective core potential and using the associated basis sets gives the most reasonable approximation to energy barriers and stabilities for this kind of system, comparable to those given by CCSD(T) (allegedly near full-CI in quality)<sup>42</sup> but at a much lower cost. This fact, combined with the proven ability of Becke3LYP to reproduce experimental geometries for organometallic complexes, reveals this functional to be an invaluable tool in organometallic chemistry.

Overall, results obtained up to now seem to indicate that a CpRhH<sub>4</sub> complex could exist and that a fast equilibrium could take place between it and the CpRhH<sub>2</sub>( $\eta^2$ -H<sub>2</sub>) isomer, which is close, although somewhat higher, in energy, and connected to the first through a low barrier. From an experimental point of view, this complex would appear to have a classical tetrahydride structure with very fluxional hydride exchanges.

**B. Structure and Dynamics of the TpRhH<sub>2</sub>( $\eta^2$ -H<sub>2</sub>) System.** The experimental data for complex **1** point

in the direction of a dihydrogen-type coordination, even though the geometrical parameters are not known experimentally. Due to this fact the theoretical study of the TpRh“H<sub>4</sub>” system was initiated by seeking a minimum with a dihydrogen-dihydride structure. As will be seen later, in this system a tetrahydride structure could not be located as a minimum. The structure corresponding to the minimum in potential energy for TpRhH<sub>2</sub>( $\eta^2$ -H<sub>2</sub>) (**7**) can be found in Figure 3, while the structural parameters appear in Table 3.

The most striking feature of this system is the near-octahedral arrangement of the ligands around the metal center; in particular, the “bite angles” are very close to 90°:  $\angle$ N1RhN2 = 86.3°,  $\angle$ N2RhN3 = 85.1°, and  $\angle$ N1RhN3 = 87.0°. The angles relating ligands situated *trans* to each other are as follows:  $\angle$ N2RhH1 = 174.8°,  $\angle$ N3RhH2 = 176.6°, and  $\angle$ N1RhX(H<sub>2</sub>) = 175.3°, where X(H<sub>2</sub>) stands for the point halfway between both hydrogens in the dihydrogen fragment. As can be seen, these values are quite close to the values expected for a regular octahedral coordination, which is surprising considering the bulk of this ligand. It is known that in Cu-Tp complexes not all metal-nitrogen bonds are equivalent.<sup>43</sup> The same happens in our Rh-Tp complex. The two Rh-N distances corresponding to nitrogen atoms situated *trans* to hydride ligands are significantly longer (Rh-N2 = 2.224 Å, Rh-N3 = 2.234 Å) than that of the nitrogen atoms situated *trans* to the dihydrogen ligand (Rh-N1 = 2.044 Å). This fact denotes the different *trans* influences exerted by the dihydrogen and hydride ligands.

The H-H dihydrogen distance we have found in **7** (0.836 Å) is very similar to the same distance in other octahedral d<sup>6</sup> complexes which have been characterized by means of neutron diffraction, such as W( $\eta^2$ -H<sub>2</sub>)(CO)<sub>3</sub>(P'Pr<sub>3</sub>)<sub>2</sub> (0.82 Å),<sup>31</sup> Mo( $\eta^2$ -H<sub>2</sub>)(CO)(dppe)<sub>2</sub> (0.80–0.85 Å),<sup>35e</sup> and *trans*-[Fe( $\eta^2$ -H<sub>2</sub>)H(dppe)<sub>2</sub>]<sup>+</sup> (0.82 Å).<sup>44</sup> The value of this distance indicates a back-donation of intensity similar to that of these complexes, in which the lengthening of the H-H bond with respect to isolated dihydrogen does not exceed 0.1 Å. Yet another interesting subject is the orientation of the H<sub>2</sub> molecule in the minimum, which is close to an eclipsed conformation with respect to a N-Rh-H axis. With respect to this fact, this complex resembles those octahedral complexes in which there are four phosphorus atoms in the same plane coordinated to the metal and in which neutron diffraction experiments have shown that the dihydrogen is aligned with a P-metal-P' axis.<sup>35e,44</sup> In these cases it has been observed that the angle formed by the ligands which eclipse the dihydrogen fragment with respect to the metal center closes itself away from the dihydrogen. We have checked this point in our complex, and this is precisely what happens. This fact has been interpreted in the literature by means of a rehybridization of the orbital of the metal responsible for the back-donation in such a way that it increases the overlap of this orbital with the  $\sigma^*$  molecular orbital of the dihydrogen fragment.<sup>12c,35c,e</sup> In the complex *cis*-mer-FeH<sub>2</sub>( $\eta^2$ -H<sub>2</sub>)(PEtPh<sub>2</sub>)<sub>3</sub> it has been discovered, by means of neutron diffraction as well, that the hydrogen molecule adopts an unusual conformation, staggered

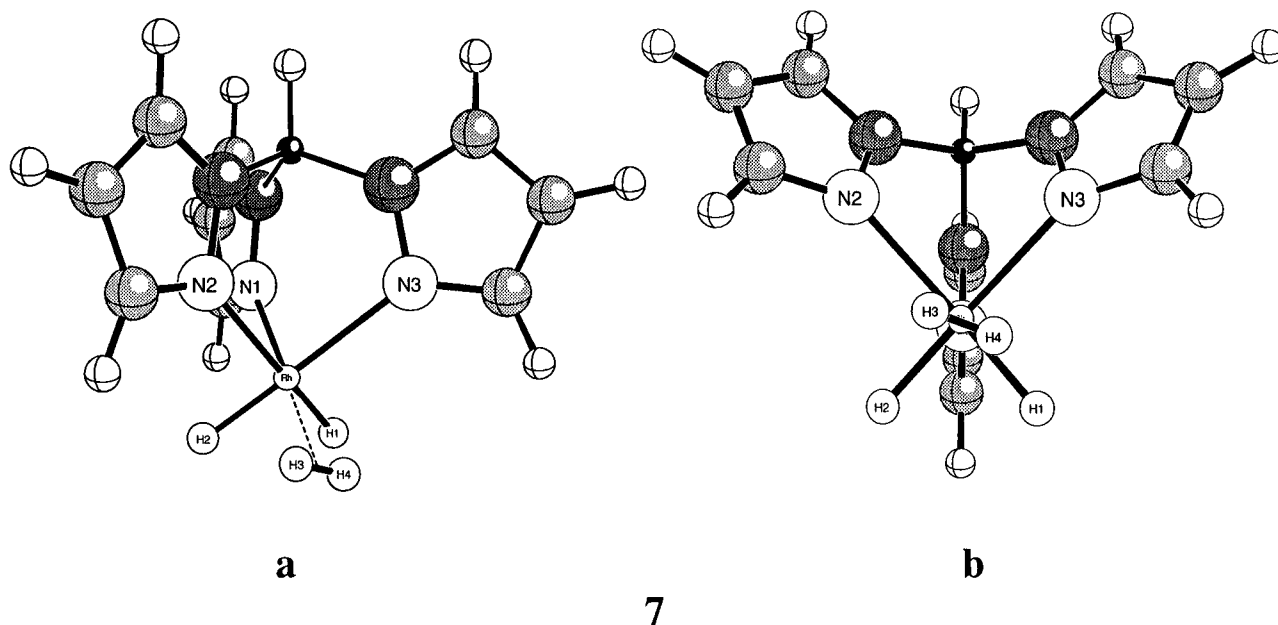
(40) A difference in stability of 11.8 kcal/mol in favor of the tetrahydride, similar to that determined by us (8.4 kcal/mol), was found by Hall for the same system with MP2 calculations carried out on Hartree-Fock geometries.<sup>41</sup>

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7

**Figure 3.** Optimized structure of the minimum of the  $\text{TpRhH}_2(\eta^2\text{-H}_2)$  isomer (**7**): (a) general view of the structure; (b) view in which the point of view is aligned with the N1–Rh axis.

**Table 3. Structural Parameters for Tp Complexes<sup>a</sup>**

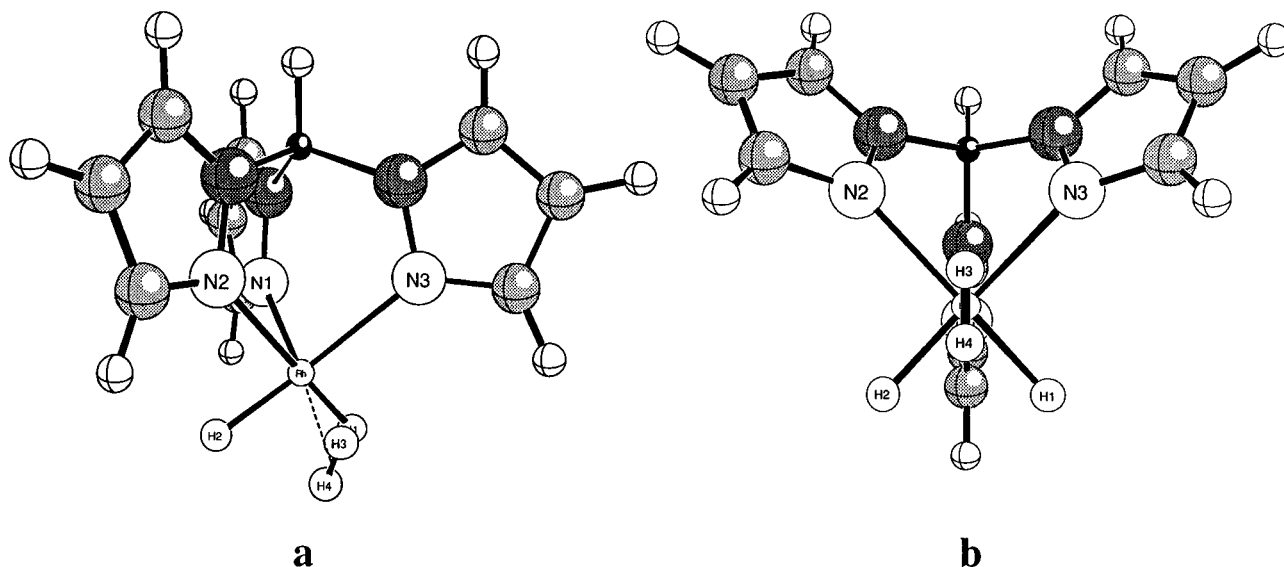
	7	8	9	10
Rh–H1	1.554	1.553	1.542	1.668
Rh–H2	1.550	1.553	1.542	1.670
Rh–H3	1.721	1.736	1.542	1.670
Rh–H4	1.710	1.720	1.542	1.668
Rh–N1	2.044	2.042	2.216	2.195
Rh–N2	2.224	2.225	2.216	2.195
Rh–N3	2.234	2.225	2.216	2.195
H1···H2	2.051	2.100	2.370	2.402
H1···H3	2.500	2.477	1.676	2.245
H1···H4	1.981	2.047	1.676	0.855
H2···H3	2.167	2.477	1.676	0.855
H2···H4	2.363	2.047	1.676	2.245
H3···H4	0.836	0.828	2.370	2.402
Rh–X(H <sub>2</sub> ) <sup>b</sup>	1.664	1.678		1.614 <sup>c</sup>
$\angle\text{NRhN}^c$	86.1	86.4	83.6	84.8
$\angle\text{NRhH}^{c,d}$	175.6	175.6		

<sup>a</sup> Distances are given in Å and angles in degrees. For atom numbering see Figures 3–5. <sup>b</sup> Distance from the rhodium atom to the center of the dihydrogen unit, when appropriate. <sup>c</sup> Averaged quantities. <sup>d</sup> This measurement comprises two NRhH angles and one NRhX(H<sub>2</sub>) angle, where X stands for the point halfway between the two hydrogen atoms of the dihydrogen ligand.

with respect to the *cis* Fe–P and Fe–H axes, even though in this case there are three phosphorus atoms and a hydride in the plane parallel to the one in which the librational motion takes place.<sup>35c</sup> This latter behavior has been explained in terms of an attractive interaction between the H<sub>2</sub> molecule and the hydride, known as the *cis* effect,<sup>12c,35c</sup> in competition with the usual tendency. In our system there are two N–Rh–H axes, and the conformation which favors this *cis* effect appears just when the dihydrogen molecule is aligned with either of these axes. The structural data of the minimum suggest the existence of a *cis* effect. This can be seen both in the orientation of the hydrogen molecule in the complex, which is approximately aligned with a N–Rh–H axis, and in the values of certain distances and bond angles:  $\angle\text{N2RhX(H}_2) = 115.0^\circ$  while  $\angle\text{H1RhX(H}_2) = 87.0^\circ$ , and the distance Rh–H1 is slightly longer than the distance Rh–H2. All this seems to indicate that there is an interaction between the hydrogen molecule and H1.

Finally, to fully complete the characterization of the minimum found, a frequency calculation was carried out numerically, including all H atoms in the immediate vicinity of the dihydrogen ligand and the dihydrogen ligand itself. By doing this, it has been assumed that the motion of the H atoms can be separated from the motion of the rest of atoms of the molecule. It was found that, with respect to the rotation of the bound H<sub>2</sub>, this geometry was a minimum. Moreover, the frequency associated with the H–H stretch was 3114 cm<sup>-1</sup>. It can be seen that, despite the simplification involved, there is a notable agreement between our theoretically obtained value and the experimental one (2238 cm<sup>-1</sup>).

In order to study the rotational dynamics of complex **1**, the transition state has been located (**8**). Its structure is presented in Figure 4, and a list of selected structural parameters appears in Table 3. It is worth mentioning that the global structure does not change with respect to the minimum. The H–H dihydrogen distance (0.828 Å) is almost the same as in **7** (0.836 Å). The same happens with Rh–H<sub>2</sub> distances. The transition-state structure belongs to the C<sub>s</sub> symmetry point group, and the dihydrogen fragment is contained within the plane of symmetry of the molecule, aligned with the *trans* pyrazolyl ring, and bisects the angle formed by both N–Rh–H axes. Additionally, the angle between the ligands situated *trans* to each other in these axes is 175.8°. The energy barrier for the librational motion is 0.45 kcal/mol, in excellent accord with the value determined experimentally by Eckert *et al.* (0.56(2) kcal/mol).<sup>10</sup> This low energy barrier can be compared with other energy barriers determined by means of INS in the complexes IrClH<sub>2</sub>(η<sup>2</sup>-H<sub>2</sub>)(P<sup>t</sup>Pr<sub>3</sub>)<sub>2</sub> (~0.65 kcal/mol)<sup>35f</sup> and Mo(CO)(η<sup>2</sup>-H<sub>2</sub>)(dppe)<sub>2</sub> (~0.7 kcal/mol).<sup>35e</sup> On the other hand, in other d<sup>6</sup>-octahedral complexes in which the presence of π-donating ligands makes one alignment of the dihydrogen ligand more favorable than the other, the energy barriers are higher, as happens for instance in Kubas' complexes W(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>-H<sub>2</sub>), where the energy barriers are around 2.2 kcal/mol.<sup>35a,b</sup> It seems that in complex **1** back-donation does not vary



## 8

**Figure 4.** Optimized structure of the rotational transition state of  $\text{TpRhH}_2(\eta^2\text{-H}_2)$  (**8**): (a) general view of the structure; (b) view in which the point of view is aligned with the N1–Rh axis.

significantly along the rotation of the hydrogen molecule, and the evolution of both Rh–H<sub>2</sub> and H–H dihydrogen distances supports this statement. In addition to that, a subtle effect which could affect the energy barrier height is the diminution of the *cis*-H effect in the transition state. In the minimum there is a distance of 1.981 Å between the nearest hydride (H1) and hydrogen (H4) atoms, whereas in the transition-state structure this distance is 2.047 Å, even though then the interaction is between a hydrogen atom and two hydrides. To summarize, the damped dependence of back-donation with the rotation of the dihydrogen unit, added to small changes in the intensity of the *cis* effect, leads to very low values for the energy barrier.

In the experimental study of **1** and of other complexes with Tp ligands and hydride and dihydrogen ligands, the process of exchanging the dihydrogen by a hydride has been observed. Ideally, in order to study the exchange of a hydride and a hydrogen molecule, the transition-state structure for this interchange should be located. However, in a system such as this, bearing in mind the lack of symmetry of the structure of the minimum, this task would certainly be very time-consuming. Instead, the barrier for such an exchange has been estimated rather than precisely located. Two different mechanisms for this exchange process have been studied. One of them involves the breaking of the H–H bond in the hydrogen molecule, leading to a tetrahydride structure, whereas the other implies the association of the two hydrides to form a bis(dihydrogen) structure. In subsection IIIA it has been shown that a tetrahydride structure is precisely the most stable one for the CpRhH<sub>4</sub> system. On the other hand, there are reports of a bis(dihydrogen) complex with Tp,  $\text{TpRuH}(\eta^2\text{-H}_2)_2$ .<sup>7</sup> Hence, structures corresponding to  $\text{TpRhH}_4$  (**9**) and  $\text{TpRh}(\eta^2\text{-H}_2)_2$  (**10**) have been sought. No classical tetrahydride structure could be found unless restrictions on geometry were enforced. Concretely, we imposed the restrictions that all four Rh–H distances were equal and that the TpRh unit remained within local C<sub>3v</sub> symmetry. Likewise, no bis(dihydrogen) structure could be found without imposing geometrical

constraints, which in this case were that both H–H dihydrogen distances were equal to the dihydrogen distance in structure **7** and also that the TpRh block remained within local C<sub>3v</sub> symmetry. Neither of these structures correspond to a stationary point in the complete energy hypersurface, but they do serve as good approximations to the energy barriers of the exchange processes previously mentioned. Both structures are depicted in Figure 5, and their structural parameters are shown in Table 3. The tetrahydride structure **9** lies 14.1 kcal/mol above the minimum, while the bis(dihydrogen) species **10** is 24.5 kcal/mol above **7**. Considering these data, it seems reasonable to conclude that a tetrahydride structure (and not a bis(dihydrogen) one) would be implied in the process of exchange of a hydride and the hydrogen molecule.

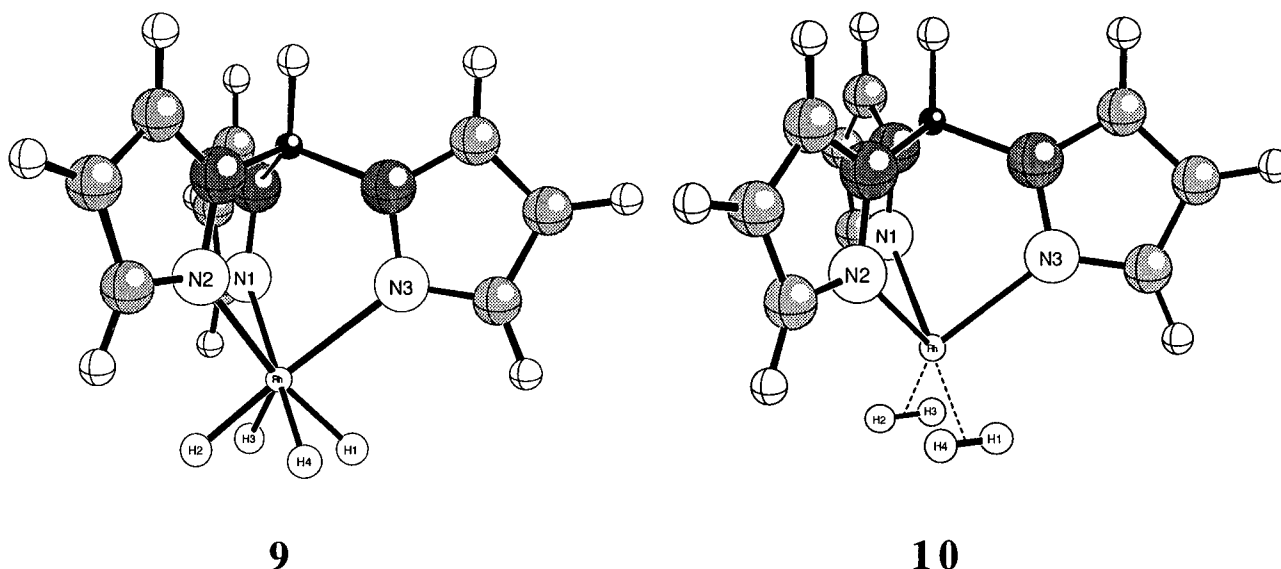
It is worthwhile to compare the results obtained up to now for the Tp and Cp systems. First, we have found the dihydrogen–dihydride structure to be the most stable in the Tp case (in fact, this structure is the only one which corresponds to a minimum), whereas in the Cp complex, even though both structures correspond to minima in the potential energy surface, the most stable one is that of the tetrahydride structure. A similar behavior was found experimentally by Heinekey and Oldham for the system  $[\text{LIr}(\text{PMe}_3)_3\text{H}_3]^+$  (L = Tp, Cp).<sup>6</sup> This seems to indicate that the electron-donor power of Cp is greater than that of Tp. This statement is in agreement with the fact that CO stretching frequencies are systematically lower in iridium Cp complexes than in analogous Tp complexes:  $\text{LIRh}_2(\text{CO})$  (L = Tp, Cp)<sup>45</sup> and  $\text{LIR}(\text{C}_2\text{H}_4)(\text{CO})$ .<sup>46</sup> In fact, Tanke and Crabtree determined that, on the basis of CO stretching frequencies in complexes of the type  $\text{LIR}(\text{CO})_2$  (L = Tp, Cp, among others), Tp has less donating power than Cp.<sup>47</sup> In our case, a measurement of the different electron-

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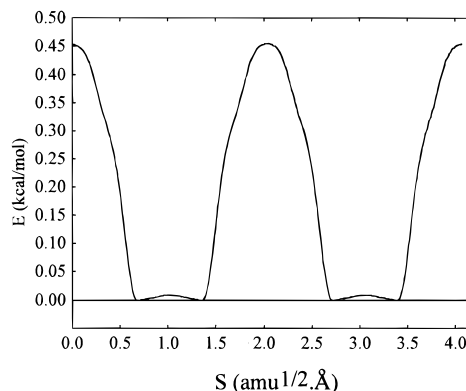
**Figure 5.** Optimized structures corresponding to  $\text{TpRhH}_4$  (**9**) and  $\text{TpRh}(\eta^2\text{-H}_2)_2$  (**10**).

donor characters of both ligands comes from the different elongations displayed by the  $\eta^2\text{-H}_2$  unit. In good accord with the aforementioned experimental tendencies, we find that the Cp complex has a much longer H–H distance (0.943 Å) than the Tp one (0.836 Å). To our knowledge, there has been only a theoretical comparison between Tp and Cp in complexes of the type  $\text{LMo}(\text{CO})_3$  (L = Cp, Tp), carried out at the extended Hückel level.<sup>48</sup>

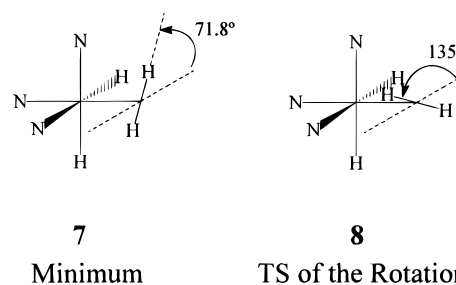
**C. Rotational Tunneling in  $\text{TpRhH}_2$  ( $\eta^2\text{-H}_2$ ).** The next step in this study will be the evaluation from a theoretical point of view, quantitatively, of the value of the energy splitting due to the rotational tunneling effect in this complex. To this aim the method set forth in subsection IIB has been adopted.

The first task to fulfill in order to quantitatively evaluate the tunneling splitting by means of the methodology described previously is obtaining an energy profile along the rotation of the  $\eta^2\text{-H}_2$  unit. This has been carried out by fixing the progress of such a rotation at different convenient points and then fully optimizing the whole structure subject to the following constraint: that the dihydrogen unit remained perpendicular to the axis of rotation. It has to be noted that none of the points in such a rotation belonged necessarily to the minimum energy path (MEP) of the rotation because they were not obtained by the steepest descent method.

To fully determine the aforementioned energy profile, the abscissa value, i.e. arc length moved along the rotation, should also be determined. Given that all the atoms in the structure experienced motion on going from one point to the next, a simple evaluation of the path as the distance moved by a dihydrogen rotating with a given rotation radius should not be used. Instead, these distances were evaluated in mass-weighted Cartesian coordinates as the linear interpolation between two structures, in such a way that in the displacement between any two consecutive configurations neither linear nor angular momenta were generated.<sup>49</sup> This profile was computed only for the first 90° of the



**Figure 6.** Energy profile for the rotation of the dihydrogen unit in  $\text{TpRhH}_2(\eta^2\text{-H}_2)$ .



**Figure 7.** Scheme of the rotation of the dihydrogen unit in  $\text{TpRhH}_2(\eta^2\text{-H}_2)$ .

rotational motion, starting at the transition state structure of the rotation, and then replicated to encompass the whole 360° of the rotation, making use of the symmetry properties of the molecule. The energy profile obtained is shown in Figure 6, and a scheme of the rotation is shown in Figure 7.

The profile in Figure 6 shows some interesting details worth mentioning. To begin with, the energy barrier is very low, so that it seems unlikely that there would be bound vibrational states below its energy were it not for the fact that the distance between minima is large. However, even though at first sight this distance could seem large it has to be borne in mind that each and every atom has been allowed to move when optimizing each structure and that consequently the value depicted

(48) Curtis, M. D.; Shiu, K.-B.; Butler, W. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3335.

(49) Miller, W. H.; Ruf, B. A.; Chang, Y. *J. Chem. Phys.* **1988**, *89*, 6298.

in the abscissa axis of Figure 6 is made up both of the motion of the dihydrogen part and of several contributions coming from the motion of the rest of the atoms of the molecule. In this way, it can be said that the distance involved is even small, that while the  $\eta^2$ -H<sub>2</sub> unit rotates the rest of the molecule remains quite still, even though it has never been forced to remain this way.

Once the energy profile has been constructed, following the procedure outlined in subsection IIB, the energy splitting can be determined. The first two vibrational states appear at 0.166 and 0.193 kcal/mol. The energy splitting obtained was 9.2 cm<sup>-1</sup>, in excellent accord with the value spectroscopically found by means of INS and reported by Eckert *et al.* (6.7(5) cm<sup>-1</sup>).<sup>10</sup> Finally, the same procedure outlined above was carried out again, this time with the deuterated complex TpRhH<sub>2</sub>( $\eta^2$ -D<sub>2</sub>). This implied recalculating the distances moved along the rotation, given that such distances are dependent upon the mass of the atoms that move, for these distances must be evaluated in mass-weighted Cartesian coordinates. It was found that in this case the first two energy levels were at 0.112 and 0.116 kcal/mol, yielding a predicted energy splitting of 1.5 cm<sup>-1</sup>. As expected, an increase in mass of the rotating unit reduces notably the energy splitting due to rotational tunneling. Experimental measurements of rotational tunneling splitting in TpRhH<sub>2</sub>( $\eta^2$ -D<sub>2</sub>) would serve as a more stringent test for our tunneling model.

#### IV. Conclusions

In this paper LRh“H<sub>4</sub>” (L = Cp, Tp) systems have been theoretically studied. The results obtained indicate that when L = Cp a tetrahydride isomer corresponding to a piano-stool structure is the most stable one. Moreover, a dihydrogen-dihydride structure was found to be very close, although higher, in energy (1.25 kcal/mol). Both structures are connected by a very low barrier. This complex would experimentally appear to have a classical tetrahydride structure with a very fluxional hydride exchange.

Conversely, when L = Tp the only minimum found is that corresponding to a dihydride-dihydrogen structure, which presents a near-octahedral arrangement of the ligands around the metal center. Neither a tetrahydride nor a bis(dihydrogen) structure could be localized as true minima. However, when certain geometrical constraints were enforced, two different structures could be found: a tetrahydride structure was found 14.1 kcal/mol above the minimum and a bis(dihydrogen) one at 24.5 kcal/mol. While it is likely that these structures do not truly exist as stable complexes, their energies indicate that a hydride-hydrogen molecule exchange could take place through a tetrahydride-like transition state.

The difference in behavior between L = Cp and L = Tp arises from the stronger electron-donor character of Cp when compared with Tp, as can be seen from the difference in H-H distances in both complexes (0.943 Å in the Cp complex, considerably greater than 0.836 Å in the Tp complex). In addition to that, the bite angles of Tp are very close to 90°. This fact, together with the chelating character of this ligand, imposes a near-octahedral coordination. The complex is reluctant to depart from this coordination number, as can be seen from the energies of the hypothetical TpRhH<sub>4</sub> and TpRh( $\eta^2$ -H<sub>2</sub>)<sub>2</sub> structures.

Another important point is the different behavior observed on changing Cp and Tp in dihydride-dihydrogen structures. In the case of Tp the barrier for the rotation is very low (0.45 kcal/mol), in very good agreement with the experimental value (0.56(2) kcal/mol), while for the Cp complex the rotational energy barrier is substantially higher (4.88 kcal/mol). This can be understood by taking into account the dependence of  $\pi$ -back-donation along the librational motion. There is less back-donation in the case of the Tp complex, as can be seen from the H-H distances in both dihydrogen complexes, and in addition to that its magnitude does not vary noticeably along the rotation. In contrast, the Cp complex has a stronger back-donation in the minimum which greatly diminishes when reaching the transition state. This is due to the change of identity of the orbital responsible for the back-donation.

Finally, it should be highlighted that theoretical methods have become excellent tools to obtain structural, dynamic, and spectroscopic data for polyhydride complexes, with an accuracy comparable to experimental methods available. Becke3LYP within the DFT formalism has already shown its ability to correctly describe the features for this kind of systems. Concretely, in our system it has been shown that Becke3LYP relative energies are similar to those given by CCSD-(T), but obtained at a much lower cost. Moreover, the rotational tunneling splitting obtained by means of the Becke3LYP energy profile (9.2 cm<sup>-1</sup>) is in outstandingly good agreement with the value found spectroscopically by means of INS experiments (6.7(5) cm<sup>-1</sup>). A value of 1.5 cm<sup>-1</sup> is predicted for the energy splitting due to tunneling in the deuterated complex TpRhH<sub>2</sub>( $\eta^2$ -D<sub>2</sub>).

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