

# Intramolecular Atom Exchange between Molecular Hydrogen and Hydride Ligands in *cis*-[Fe(PR<sub>3</sub>)<sub>4</sub>H(H<sub>2</sub>)]<sup>+</sup> Complexes. An ab Initio Theoretical Study<sup>†</sup>

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**Abstract:** The intramolecular reaction involving exchange of a hydrogen atom between molecular hydrogen and hydride ligands is studied in the model system *cis*-[Fe(PH<sub>3</sub>)<sub>4</sub>H(H<sub>2</sub>)]<sup>+</sup> by means of the molecular orbital ab initio method. Several possible mechanisms are considered for the reaction and compared according to their energetic barriers. The favored mechanism is the so-called open direct transfer, which consists of a single step transfer of the hydrogen atom between the two ligands. In the transition state of this mechanism the central hydrogen atom is bound to the other two hydrogens. Traditional  $\sigma$ -bond activation processes like oxidative addition and  $\sigma$ -bond metathesis are compared to the most favored mechanism arising from our results. This mechanism carries essential differences from the others, thus constituting a model for a new kind of reaction.

## Introduction

The discovery of molecular hydrogen complexes<sup>1</sup> in 1984 opened a new topic of research that since then has attracted the attention of a growing number of scientists. As a result, at present there is a considerable amount of literature on molecular hydrogen complexes from both experimental<sup>2</sup> and theoretical<sup>3-7</sup> points of view. These compounds are represented in distinct areas like binuclear complexes,<sup>8</sup> bioinorganic compounds,<sup>9</sup> and rare-earth species.<sup>10</sup>

In spite of all this extensive work, there are some points in the chemistry of these compounds that are still unclear. Certainly, one of the most challenging open questions on the molecular hydrogen complexes concerns their potential role as intermediates in the activation of the hydrogen molecule, i.e., the breaking of the strong H-H bond to give rise to new bonds between other fragments and the hydrogen atoms. The scarce data available about the reactivity of molecular hydrogen complexes consist essentially of its formation, substitution by other ligands, and oxidative addition to yield the dihydride complex.<sup>2</sup> However, some processes involving  $\eta^2$  H<sub>2</sub> complexes have already been claimed to have a more elaborated chemistry. In particular, for [Os(P(*i*-Pr)<sub>3</sub>)<sub>2</sub>(CO)ClH(H<sub>2</sub>)]<sup>11</sup> and [Os(P(CH<sub>3</sub>)<sub>2</sub>Ph)<sub>3</sub>H<sub>3</sub>(H<sub>2</sub>)]<sup>12</sup> the molecular hydrogen complex seems to act as a precursor of the reacting species after loss of hydrogen. Further, the very molecular hydrogen ligand has been postulated to play an active role in catalytic cycles in at least two cases: the alkene hydrogenation with [Rh(PP<sub>3</sub>)(H<sub>2</sub>)]<sup>13</sup> and the alcohol dehydrogenation through [Ru(PPH<sub>3</sub>)<sub>3</sub>H<sub>2</sub>(H<sub>2</sub>)]<sup>14</sup>.

However, the most commonly identified reactions implying cleavage of the coordinated H-H bond seem to be those of intramolecular exchange between molecular hydrogen and hydride ligands in the complexes where both ligands coexist. In particular, this intramolecular process has been observed for [Ir(bq)(PCy<sub>3</sub>)<sub>2</sub>H(H<sub>2</sub>)]<sup>15</sup>, [Cr(CO)<sub>4</sub>(H<sub>2</sub>)<sub>2</sub>]<sup>16</sup>, [Os(PR<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub>H(H<sub>2</sub>)]<sup>17</sup>, [Re(CO)(PMe<sub>2</sub>Ph)<sub>3</sub>(H<sub>2</sub>)<sub>2</sub>]<sup>18</sup> and, especially, *trans*-[Fe(R<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub>H(H<sub>2</sub>)]<sup>19</sup> complexes.

Experimental problems related to the study of these systems make the mere existence of the intramolecular exchange reaction be the only conclusive experimental information about these processes. Thus, data about their mechanisms are very scarce. From a theoretical point of view, the problem has been extensively analyzed at a qualitative level through the extended Hückel method<sup>4</sup> and partially discussed in the ab initio structural study of [Cr(CO)<sub>4</sub>(H<sub>2</sub>)<sub>2</sub>] complexes.<sup>6</sup>

In this paper we present the first complete ab initio study of the mechanistic possibilities in a model system containing only

one molecular hydrogen and one hydride ligand. The system chosen is the [Fe(PH<sub>3</sub>)<sub>4</sub>H(H<sub>2</sub>)]<sup>+</sup> complex, that is a model for the well-known [Fe(PR<sub>3</sub>)<sub>4</sub>H(H<sub>2</sub>)]<sup>+</sup> systems<sup>20</sup> which we had already

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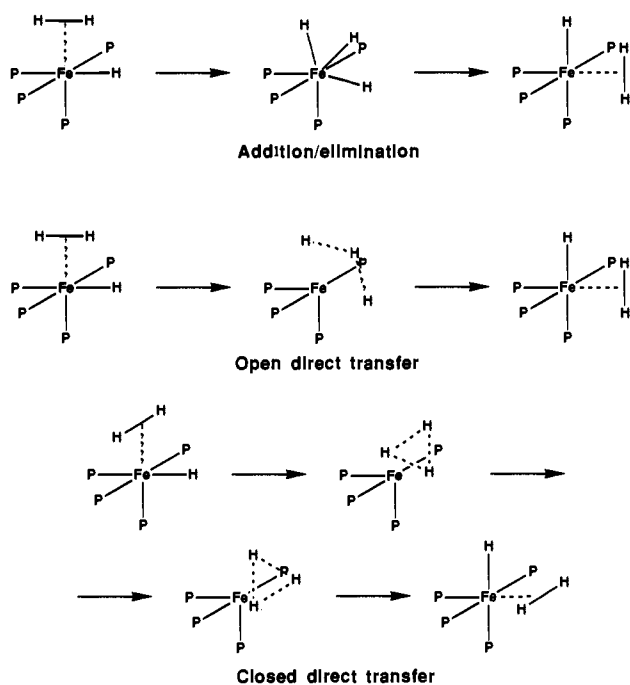
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<sup>†</sup> A contribution from the "Grup de Química Quàntica de l'Institut d'Estudis Catalans".

Scheme I



considered in a previous study.<sup>7</sup> In this complex the ligands happen to be in an essentially octahedral distribution around the metallic atom. The existence of an important *cis* effect when the molecular hydrogen and hydride ligands are adjacent was demonstrated, in agreement with experimental and theoretical results for another complex.<sup>21</sup> In the *cis* isomer, the only isomer to be considered here owing to topological reasons, the orientation of the hydrogen molecule parallel to the P-Fe-H axis happened to be the lowest in energy, so this conformation will be that considered in this paper unless otherwise stated. An additional feature of this system involves the symmetry of the reaction, since the reactant and the product are identical.

This model system preserves the essential complexity of the real systems, and can actually be related with both the oxidative addition and the  $\sigma$ -bond metathesis, which are the two major routes for the activation of the H-H bond and, in general, of any nonpolar  $\sigma$  bond.<sup>22,23</sup> However, the diversity of possible mechanisms dictates their classification.

The first criterion to classify the possible mechanisms consists of pondering the presence of a trihydride complex as an intermediate. The mechanisms including such an intermediate must necessarily imply an oxidative addition of the hydrogen molecule followed by a reductive elimination. That is why they will be referred to as addition/elimination mechanisms. On the other hand, mechanisms without a trihydride intermediate must consist of the direct transfer of a hydrogen atom between the two ligands, with no simultaneous breaking of all hydrogen-hydrogen bonds. Moreover, for this direct transfer process two different possibilities have been considered, referred to as open and closed mechanisms. Scheme I contains a pictorial presentation of these three mechanisms.

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In what follows, and after a section dealing with the computational aspects of this work, the study of these three mechanisms will be presented, followed by a more detailed analysis of the process that appears as being more favored. Through this study, a more detailed knowledge about the mechanistic features of this reaction, about the role of molecular hydrogen complexes in chemistry, and about the very general process of  $\sigma$ -bond activation must be achieved.

### Computational Details

Since in some way this paper continues our earlier work on the structure of the  $[\text{Fe}(\text{PH}_3)_4\text{H}(\text{H}_2)]^+$  systems,<sup>7</sup> the computational method is essentially the same one that revealed itself as sufficient for a semiquantitative description in that case. Thus, we have used an all-electron molecular orbital ab initio method at the RHF-SCF level, with a valence double- $\zeta$  basis set for iron,<sup>24</sup> a double- $\zeta$  plus polarization basis set for molecular hydrogen and hydride,<sup>25</sup> and a minimal basis set for phosphines.<sup>26</sup>

The sort of geometry optimization has been rather dependent of each case, only the common background being commented here. The Schlegel method<sup>27</sup> with analytically calculated gradients has been used everywhere. Further, some geometrical parameters which are not essential for the reaction have been frozen; namely, the P-H distances have been fixed as 1.42 Å, a tetrahedral distribution around the P atoms has been assumed, and the Fe-P distances have been fixed at 2.242 Å.<sup>20a</sup> Symmetry has been considered whenever possible, thus restricting rotation of phosphines around Fe-P axis. More accurate details about optimization details will be given upon presentation of each calculation.

### Survey of the Possible Mechanisms

In this first section regarding results and discussion, a general survey of the three different mechanisms proposed in Scheme I is made with a somehow imprecise method. Another section will deal later more accurately with the favored mechanism of this first approach. Two subsections are considered, one for the addition/elimination process and another for direct transfer processes.

**Addition/Elimination Mechanism.** As its name suggests, this mechanism has two steps. The first one consists of the oxidative addition of the hydrogen molecule, leading to a trihydride complex; the second step involves a reductive elimination of two hydride ligands to yield again a molecular hydrogen ligand. The feature that distinguishes this mechanism is the existence of a point along the reaction path where there is no chemical bond between the hydrogen atoms, which are bound exclusively to the metal. This point of the reaction path is precisely the trihydride complex, a necessary intermediate in this process. The eventual existence of such a trihydride complex is the test that will be applied to evaluate the feasibility of this mechanism.

In the trihydride complex  $[\text{Fe}(\text{PH}_3)_4\text{H}_3]^+$  the iron atom is bound to seven ligands. This coordination number is not associated to an only geometric disposition. Among the different possible geometries, one can consider a pentagonal bipyramid with the equatorial ligands following the orientations of a regular pentagon. Such a structure, with three hydride ligands in contiguous equatorial positions, is likely to be obtained from the *cis*- $[\text{Fe}(\text{PH}_3)_4\text{H}(\text{H}_2)]^+$  complex in its most stable conformation; it will be used to estimate the energy that a hypothetical trihydride complex would have. The attainment of this geometry is assured by means of a partial geometry optimization, where the orientation of the equatorial ligands is restricted to that of a regular pentagon ( $L - \text{M} - L = 72^\circ$ ).

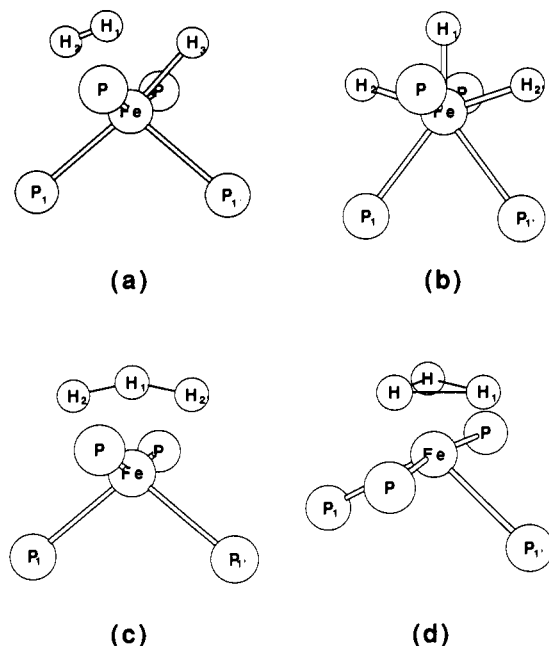
Thus, the only parameters to be optimized in the  $[\text{Fe}(\text{PH}_3)_4\text{H}_3]^+$  complex are the Fe-H distances and the position of the axial

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**Figure 1.** Optimized structures for the absolute minimum of the system  $[\text{Fe}(\text{PH}_3)_4\text{H}(\text{H}_2)]^+$  (a), and for the estimated midpoint geometries of the addition/elimination (b), open direct transfer (c), and closed direct transfer (d) mechanism of the intramolecular hydrogen exchange reaction.

phosphines. The geometry arising from this optimization is presented in Figure 1, together with the other optimized geometries. In particular, the trihydride complex corresponds to Figure 1b, while Figure 1a shows the true energy minimum of the system for comparative purposes. The optimized values of the Fe–H<sub>1</sub> and Fe–H<sub>2</sub> distances in the trihydride complex are 1.42 and 1.48 Å, respectively. The most meaningful result of this calculation is the energy, which is 65.3 kcal/mol larger than that of reactants. This fact alone makes the existence of this intermediate extremely unlikely. Furthermore, mention must be made that this trihydride geometry is imposed externally by restricting the orientation of the equatorial ligands. Inspection of the energy gradients reveals that the partially optimized geometry is actually very far from being a minimum in the full potential hypersurface, since the gradients for the angles H<sub>1</sub>–Fe–H<sub>2</sub> and P<sub>1</sub>–Fe–P<sub>2</sub> are –0.117 and +0.246 au (the meaning of this values can be better assessed if one takes into account that a usual threshold for geometry optimizations is 10<sup>–4</sup> au). When the regular pentagon restriction for the equatorial ligands is relaxed, geometry optimization leads to the molecular hydrogen hydride complex, thus confirming that the proposed trihydride structure does not correspond to a local minimum in the potential hypersurface. In other words, this geometry is not a stable species; it cannot even be an intermediate.

Exploration of other possible trihydride complexes did not lead to better results, neither to lower-energy geometries nor to stable species. The straightforward conclusion turns out to be that the addition/elimination mechanism is not efficient for the intramolecular transfer of a hydrogen atom in the  $[\text{Fe}(\text{PH}_3)_4\text{H}(\text{H}_2)]^+$  complex.

This result is not at all surprising. The hypothetical trihydride would be a heptacoordinated complex of a first-row transition metal, with an oxidation state of IV for iron. Both facts are quite unusual. The behavior in systems containing other second- and third-row transition metals can be different. However, it is clear that there must exist at least another energetically economical mechanism for the intramolecular transfer with no oxidative addition.

**Direct Transfer.** If the intramolecular exchange of a hydrogen atom between the molecular hydrogen and hydride ligands does not include an oxidative addition step, the mechanism must necessarily involve species where a hydrogen atom is simultaneously bound to the other two hydrogen atoms, i.e., the atom being

transferred must begin to bind the hydride while it is still bound to the other atom in the initial hydrogen molecule. In a sense, the reaction takes place directly between the ligands, with no direct intervention of the metal. This is the reason why this process is called direct transfer throughout this paper.

This general mechanism may have many different manifestations, which can be classified, nevertheless, in two big blocks, depending on whether the process implies only bonds of the central atom with the other two (open mechanism) or it implies simultaneous bonds between the three hydrogens (closed mechanism). The reasons for these names are related to the geometry of the trihydrogen fragment: in the first case, the geometry of the three hydrogens is linear-like, while in the second case it is triangular-like. Actually, this nomenclature is somehow based in previous theoretical works in the area.<sup>4</sup> These two mechanisms have already been plotted in Scheme I and will be analyzed in what follows.

**Open Mechanism.** The open direct transfer mechanism is related to the parallel conformation of the *cis*- $[\text{Fe}(\text{PH}_3)_4\text{H}(\text{H}_2)]^+$  complex, which had been previously demonstrated to be the most stable structure.<sup>7</sup> During the reaction, the three hydrogen atoms of the hydride and the hydrogen molecule, the iron atom, and two of the phosphorus atoms are always coplanar, all six atoms lying in the symmetry plane of the molecule. Thus, the reaction consists essentially of a change in the bonding of the central hydrogen atom, which is bound to the hydrogen on his left in the reactant and is bound to that on his right in the product.

Estimation of the energetic barrier for this reaction path is made through the energy of its midpoint. The strategy for the search of such a point is based in the imperative existence of a geometry where the transferring hydrogen is as close to its position in the reactant as it is to its position in the product. This geometry is likely to have a more symmetric structure than that of reactant and product, with the two other hydrogen atoms being equivalent. Thus, the method used to estimate the geometry of the reaction midpoint consists of an optimization within a higher symmetry, namely C<sub>2v</sub>.

The result of this C<sub>2v</sub> geometrical optimization is presented in Figure 1c. The main feature of this geometry may be that the H<sub>1</sub>–H<sub>2</sub> distance is 1.04 Å, short enough to reveal the existence of a chemical bond between the hydrogen atoms, thus confirming the relation of this structure to the direct transfer process. However, the most meaningful result turns out to be the energy, which is only 3.2 kcal/mol larger than that of the energetic minimum. This fact converts this mechanism into an excellent candidate to be that active in the experimental systems.

The last point from this calculation to remark here concerns the true nature of this geometry as stationary point. That is, it is not a false stationary point arising from the geometrical restrictions, as was the case for the addition/elimination mechanism. On the contrary, it has actually a null first derivative with respect to all considered geometrical parameters. These calculations do not allow, however, to clarify whether this geometry corresponds to an intermediate or to a transition state. This question will be addressed later in this paper.

**Closed Mechanism.** This is the last general mechanism proposed in Scheme I left to be analyzed. In this particular case, the related conformation of the *cis*- $[\text{Fe}(\text{PH}_3)_4\text{H}(\text{H}_2)]^+$  complex does not correspond to a parallel arrangement like in the absolute minimum, but to a perpendicular one, demonstrated previously to have a higher energy.<sup>7</sup> Geometrical considerations in Scheme I disclose that this mechanism is somewhat more complicated than the other two. In a first phase of the reaction, a symmetry plane is conserved, containing only one of the hydrogen atoms (that starting as a hydride), the iron atom, and two phosphorus atoms. Later, a geometry is found where the three hydrogens are coordinated to the metallic atom in a way essentially similar. A further evolution may consist in a rotation of this triangle to regenerate the molecular hydrogen hydride complex, the position of the ligands having been interchanged.

Moreover, this hypothetical mechanism should still be preceded by a rotation of the hydrogen molecule around the Fe–H<sub>2</sub> center, since the most stable conformation involves a parallel arrangement,

**Table I.** Estimated Energy Barriers (in kcal/mol) for Each Mechanism

mechanism	energy
addition/elimination	65.3
open direct transfer	3.2
closed direct transfer	69.0

as mentioned above. This rotation implies an energetic barrier of ca. 7 kcal/mol,<sup>7</sup> which, together with the geometric complexity of the mechanism and the low barrier estimated above for the open process, makes the closed mechanism a bad candidate to be the most efficient mechanism. However, its barrier will be estimated according to the strategy proposed initially in order to evaluate its relative position with respect to the other possible mechanisms. This will serve, at least, to understand to which extent this process can become competitive for other systems that are different from [Fe(PH<sub>3</sub>)<sub>4</sub>H(H<sub>2</sub>)]<sup>+</sup>.

The closed direct transfer process must proceed by definition through geometries where the three hydrogens form roughly an equilateral triangle, their distances to the metal being similar. Its energetic barrier will be estimated through an optimization where these approximate considerations are strictly enforced. That is, the three atoms will be compelled to form an equilateral triangle; the axis defined by the Fe atom and the center of the trihydrogen will be forced to be perpendicular to the triangle plane. In other words, the three hydrogens will occupy the basal vertices of a regular triangular base pyramid where the apical vertex is occupied by the iron atom.

The performance of an optimization under such restrictions does not lead to a true stationary point, the gradients in the final point having nonzero components. In particular, the sum of the gradients of the H-triangle center distances is certainly zero. However, they arise from the addition of a value of +0.052 au with two other values of -0.026 au. This cannot be attributed to a bad geometrical initialization, since different attempts were made starting from different points and including calculated Hessian values instead of estimated values. On the contrary, this result is due to the peculiarities of the optimization algorithm employed, which proves that there is no stationary point accomplishing the imposed geometric restrictions.

In spite of the previous considerations, the "optimized" geometric structure (Figure 1d) seems to be actually the energetic minimum within the applied restrictions, so its analysis can be orientative. In this structure, the H-H distance is 1.47 Å, whereas the Fe-H distance is 1.44 Å; these numeric values are incompatible with a direct transfer process, since there is no H-H bond at all. Really, these values are akin to those presented above for the trihydride complex. A final remark concerns the energy associated to this geometry, which is 69.0 kcal/mol larger than that of the reactant, thus confirming conclusively the inefficiency of the closed direct transfer mechanism.

#### A More Accurate Study on the Open Direct Transfer Mechanism

Table I collects the estimated energy barriers of three different representative mechanisms for the intramolecular hydrogen transfer in the *cis*-[Fe(PH<sub>3</sub>)<sub>4</sub>H(H<sub>2</sub>)]<sup>+</sup> complex. From these values a clear conclusion emerges: the most efficient process turns out to be the open direct transfer, since its barrier is estimated to be ca. 3 kcal/mol vs values over 60 kcal/mol for the other two alternatives. This rules out definitively the addition/elimination and closed direct transfer mechanisms, which will be no longer considered in this paper. This result is not in contradiction with previous suggestions about the possible mechanism of the studied reaction,<sup>4,6,28</sup> and agrees with the mechanism recently proposed for the hydrogen exchange in the [Re(CO)(PMe<sub>2</sub>Ph)<sub>3</sub>(H)<sub>2</sub>(H<sub>2</sub>)]<sup>+</sup> complex.<sup>18</sup>

**Table II.** Selected Geometrical Parameters of the Optimized Structures Corresponding to Stationary Points of the Intramolecular Exchange Reaction of a Hydrogen Atom in the [Fe(PH<sub>3</sub>)<sub>4</sub>H(H<sub>2</sub>)]<sup>+</sup> System via the Open Direct Transfer Mechanism<sup>a</sup>

	reactant	transition state	product
H <sub>1</sub> -H <sub>2</sub> distance	0.79	1.04	1.57
H <sub>1</sub> -H <sub>3</sub> distance	1.57	1.04	0.79
Fe-H <sub>1</sub> distance	1.61	1.56	1.61
Fe-H <sub>2</sub> distance	1.75	1.67	1.65
Fe-H <sub>3</sub> distance	2.65	1.67	1.75
H <sub>1</sub> -Fe-H <sub>2</sub> angle	26.9	37.5	57.5
H <sub>1</sub> -Fe-H <sub>3</sub> angle	57.5	37.5	57.5
P <sub>1</sub> -Fe-P <sub>1</sub> angle	99.6	100.1	99.6
H <sub>2</sub> -H <sub>1</sub> -H <sub>3</sub> angle	140.6	154.8	140.6

<sup>a</sup> All distances are given in Å, while angles are given in degrees.

This section, which will be partitioned in two subsections, is concerned with a more accurate analysis of the open direct transfer mechanism. The first subsection will deal specifically with a deeper study of this mechanism, and the second one will relate results to current ideas on the field of  $\sigma$ -bond activation.

**Mechanistic Characteristics.** The preliminary study presented in the previous section on this mechanism consisted only of locating a likely midpoint along the reaction path and computing its energy. However, no attention was focused on other essential aspects of the mechanism which will be analyzed here in more detail.

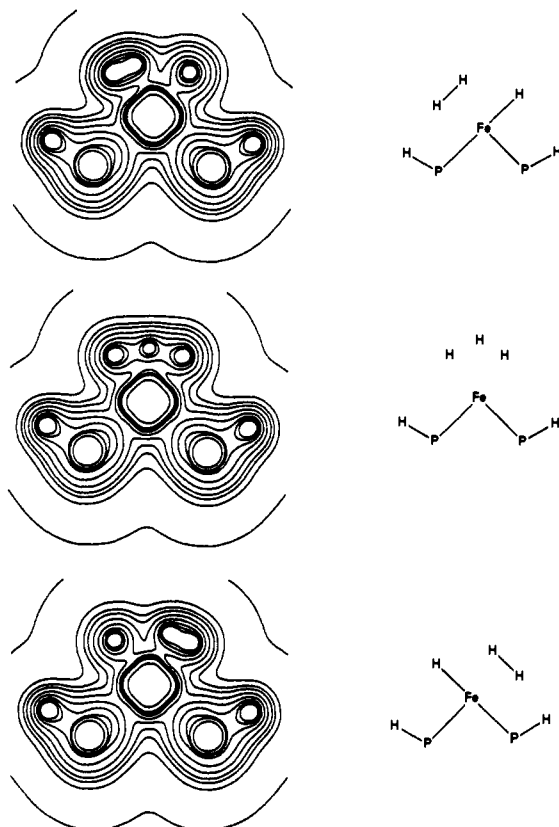
The first issue to be solved concerns the nature of the calculated midpoint, whose geometry is displayed in Figure 1c. Its nature as a stationary point in the potential hypersurface has already been confirmed, with a zero energy gradient with respect to the considered geometric parameters. Nevertheless, no calculation was made about the number of negative eigenvalues of the matrix of the energy second derivatives with respect to the geometrical parameters. This constitutes an essential aspect to determine its chemical nature, since that number defines whether it is an intermediate or a transition state. Actually, diagonalization of the matrix of energy second derivatives leads to an only negative eigenvalue whose value is -0.19 au.

This result means that the structure presented in the previous section corresponds to a true transition state. Moreover, the eigenvector associated to its negative eigenvalue corresponds just to the transfer of a hydrogen atom between the two ligands. Both the geometry of the transition state and the nature of its negative eigenvector rule out ultimately the possibility of a stable intermediate complex in the reaction path. The aftermath is that the intramolecular exchange between the two ligands takes place in a single step.

Table II collects the main geometric parameters of the reactant, transition state, and product of the hydrogen transfer reaction through this mechanism. If attention is paid to the H-H distances in the transition state (1.04 Å), one notices that they are quite short, showing that the central hydrogen atom is chemically bound to the other two hydrogens. This does not happen at all in the reactant or product, where one distance is quite long (1.57 Å). Another interesting feature emerging from Table II is the small change experienced by the [Fe(PH<sub>3</sub>)<sub>4</sub>] fragment along the reaction coordinate with a tiny variation (1°) in the P<sub>1</sub>-Fe-P<sub>1</sub> angle. Finally, the value of the H<sub>2</sub>-H<sub>1</sub>-H<sub>3</sub> angle also deserves some comment. It reaches 154.8° in the transition state, which may be considered as being relatively close to the 180° associated to a linear structure of the H<sub>3</sub> fragment.

Another interpretative tool for the obtained results is the Mulliken population analysis. In the structures corresponding to the energy minima (reactant and product) the hydride has a charge of -0.40 au, while the atoms of the molecular hydrogen ligand support +0.10 and -0.13 au. In the transition state, the central hydrogen bears a charge of +0.11 au, while charge is -0.28 au for each of the other two hydrogens. That is, the total charge of the three hydrogens is -0.43 au in reactant and product, and -0.45 au in the transition state. Although the quantitative validity of the Mulliken populations in systems containing metals is doubtful, they provide a measure of the evolution of charges along

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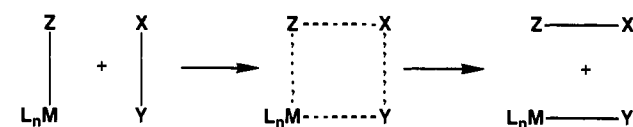
**Figure 2.** Electron isodensity contour maps of the reactant (top), the transition state (middle), and the product (bottom) of the intramolecular hydrogen transfer reaction in the  $[\text{Fe}(\text{PH}_3)_4\text{H}(\text{H}_2)]^+$  system through the open direct transfer mechanism. The isodensity lines plotted correspond to the values of 0.0001, 0.01, 0.02, 0.03, 0.05, 0.08, 0.12, 0.16, 0.20, and 0.50 au.

a process. In this particular case, they show that there is no change in the oxidation state of the iron atom.

The near invariance of both the geometry and the charge of the  $[\text{Fe}(\text{PR}_3)_4]$  fragment along the process suggests that for interpretative purposes the system can be viewed as composed by two fragments. These fragments must be  $[\text{Fe}(\text{PR}_3)_4]^{2+}$  and  $\text{H}_3^-$ , from considerations on the recently discussed charges. This partition allows for a straightforward interpretation of the preference of the system for the open vs the closed direct transfer mechanism. Earlier complete theoretical studies on the  $\text{H}_3$  fragments<sup>4,29</sup> showed clearly that a linear structure is preferred when the overall charge is negative ( $\text{H}_3^-$ ), whereas a triangular arrangement is preferred when the overall charge is positive ( $\text{H}_3^+$ ). Furthermore, correlation between the type of geometries and the kind of mechanism is obvious.

Electron density plots (Figure 2) help further in the analysis of the obtained results. The analysis of this kind of plot has been demonstrated to be a powerful method in theoretical chemistry, especially through bond identification by means of the so-called bond critical points.<sup>30</sup> In this particular case, analysis of the plots depicted in Figure 2 refines the previous comments in this subsection to a certain extent. The reaction studied implies indeed a change in the electronic structure of the system formed by the metal and three hydrogens. Moreover, there is a simultaneous interaction between the three hydrogens in the transition state that is not present in the reactant or the product. However, the peculiar electronic structure of the transition state requires further comment. The trihydrogen fragment is connected to the metal only once through bonding of the central hydrogen. Thus, the

**Scheme II**



reaction seems to be a reorganization between the three hydrogen atoms in the coordination sphere of the metal. Further implications of the electronic structure of this transition state will be extensively discussed in the next subsection.

**Comparison with the "Classical"  $\sigma$ -Bond Metathesis.** Mention has been made in the Introduction that one of the main features of molecular hydrogen-hydride complexes is its eventual ability as models for  $\sigma$ -bond activation reactions. One of the main routes of  $\sigma$ -bond activation is clearly the so-called  $\sigma$ -bond metathesis<sup>31</sup> (Scheme II), which looks very similar to the open direct transfer mechanism.

Certainly, the  $\sigma$ -bond metathesis mechanism also quoted as hydrogenolysis or heterolytic activation,<sup>22</sup> exhibits striking resemblances with the above studied mechanism. It actually consists of the interaction of a generic X-Y  $\sigma$  bond with another M-Z  $\sigma$  bond involving a metal atom M. This interaction leads to the cleavage of these two bonds and to the formation of two other new bonds, namely X-Z and M-Y. If one considers the X, Y, and Z atoms to be hydrogens, and an  $\eta^2$  coordination of the  $\sigma$  bond to the metal in reactant and product is taken, then this constitutes exactly the molecular hydrogen-hydride exchange reaction that is being considered in this paper.

However, there is an important difference between the traditional  $\sigma$ -bond metathesis reaction and the intramolecular hydrogen transfer. The process considered in this paper takes place with a complex of the relatively electron-rich metal iron, which has a formal  $d^6$  electronic state. On the contrary, heterolytic activation works only with electron-poor metals, typically early transition metals, lanthanides, and actinides. For instance, efficient reactants for this kind of reaction are  $[\text{MCp}_2^*\text{R}]$  (M = Sc,<sup>31,32a</sup> Lu<sup>32b</sup>) and  $[\text{ThCp}_2^*\text{R}_2]$ .<sup>32c</sup>

The efficiency of this kind of reaction in electron-rich metals is not so well established, though some suggestions are found in this direction.<sup>33</sup> This process has been speculated to exist in relation with molecular hydrogen complexes themselves<sup>2</sup> and other reactions,<sup>34</sup> especially in relation to the important hydroformylation process.<sup>35</sup> Further, ab initio theoretical calculations on an electron-rich cobalt complex intervening in the hydroformylation reaction show that the studied process is competitive with another possible addition/elimination pathway.<sup>36</sup> Nevertheless, available data on this kind of processes are still somehow scarce. Therefore, it is relevant to compare here the process we have just characterized to the usual  $\sigma$ -bond metathesis reactions taking place on electron-deficient transition-metal complexes.

Theoretical studies on  $\sigma$ -bond metathesis have not been at all so extensive as those on oxidative addition.<sup>23,37</sup> Nevertheless, some studies have been made using either semiempirical<sup>34,38</sup> or ab initio methods,<sup>39,40</sup> providing a satisfactory explanation of the mechanism

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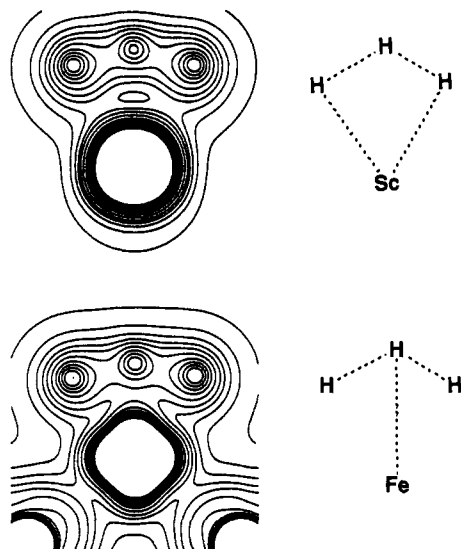
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**Figure 3.** Electron isodensity contour maps for the transition states of the hydrogen transfer reaction in the  $[\text{ScCl}_2\text{H}] + \text{H}_2$  (top) and  $[\text{Fe}(\text{PH}_3)_4\text{H}(\text{H}_2)]^+ + \text{H}_2$  (bottom) systems. The isodensity lines plotted correspond to the values of 0.0001, 0.01, 0.02, 0.03, 0.05, 0.08, 0.12, 0.16, 0.20, and 0.50 au.

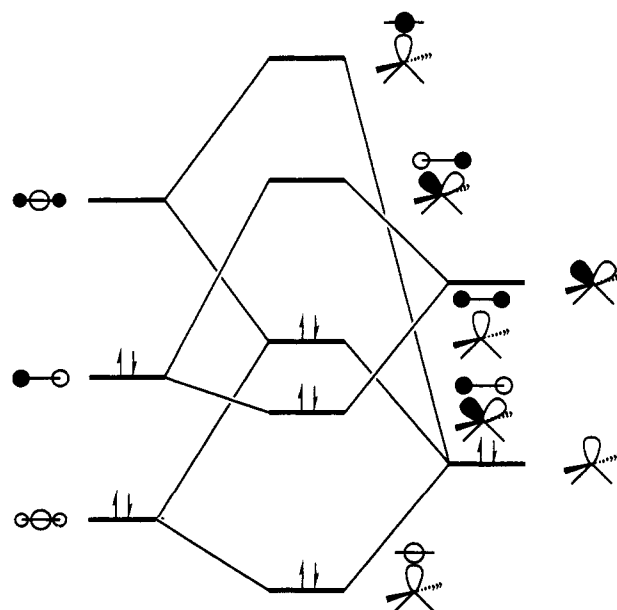
operating in complexes with electron-poor metals. Moreover, these results for transition state geometries are strikingly similar to those for the transition state we have reported above for the intramolecular hydrogen exchange. For instance, an ab initio study by Steigerwald and Goddard<sup>39</sup> on the  $[\text{ScCl}_2\text{H}] + \text{H}_2$  system reports an H-H distance in the transition state whose value is 1.01 Å, which is very close to the value of 1.04 Å we have reported. The values for the angles are also similar; following nomenclature used in Table II, the optimized values for angles  $\text{H}_2 - \hat{\text{H}}_1 - \text{H}_3$  and  $\text{H}_1 - \text{Fe} - \text{H}_2$  are 149° and 31° in the work of Steigerwald and Goddard, quite close to the values of 155° and 37.5° obtained for the present iron complex.

This similarity, however, is surprising if one realizes the different electronic requirements that should be associated to the different electronic population of the scandium and iron complexes. To solve this apparent contradiction, we decided to compare the electron density maps of the two transition states.

To allow for such a comparison, we had to plot the electron density for the  $[\text{ScCl}_2(\text{H}_3)]$  transition state. The electronics wavefunction of this species was determined by means of an energy-only calculation at the RHF level using the geometry reported by Steigerwald and Goddard.<sup>39</sup> We used a basis set similar to that employed for the iron complexes (valence double- $\zeta$  for the metal, double- $\zeta$  plus polarization for the hydrogens, minimal for the spectator ligands) to avoid distortions when comparing the results. From the density plots of the two different transition states (Figure 3), differences in the topology of the bonds formed between the trihydrogen fragment and the metal are obvious. In the  $[\text{ScCl}_2(\text{H}_3)]$  system there is a four-membered ring defined by the three hydrogens and the scandium, because a ring point appears in the center and there are bond critical points<sup>30</sup> between every two contiguous atoms. In contrast, for  $[\text{Fe}(\text{PH}_3)_4(\text{H}_3)]^+$  such a rich does not exist, the iron being bound to the trihydrogen fragment by a single bond critical point<sup>30</sup> through the central hydrogen. Thus, the density plot for the  $[\text{ScCl}_2(\text{H}_3)]$  system agrees with the traditional view of  $\sigma$ -bond metathesis, with a four-membered ring in the transition state involving the two  $\sigma$  bonds that are being broken and the other two  $\sigma$  bonds that are being formed<sup>31</sup> (Scheme II). However, the case is very different for the  $[\text{Fe}(\text{PH}_3)_4(\text{H}_3)]^+$  complex. From an electronic point of view, no four-membered ring exists, but rather a trihydrogen unit appears connected via its center to the metal, in a topology that could be seen as "trefoil".

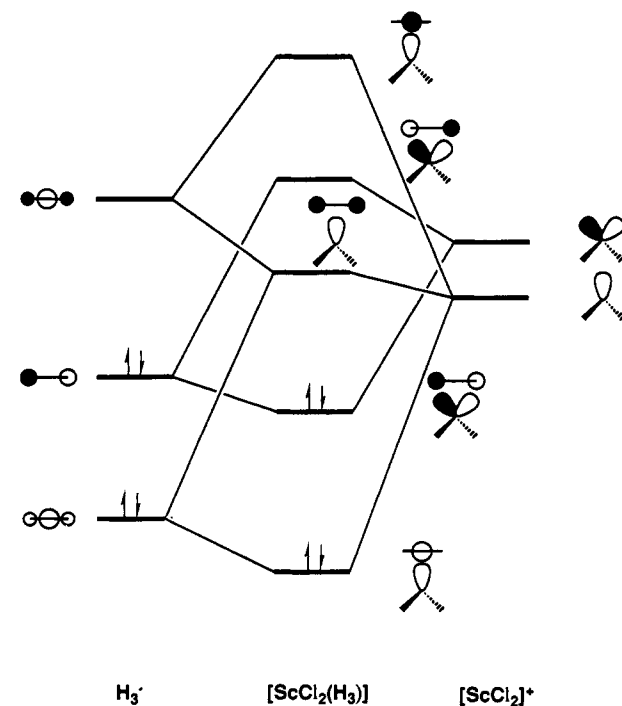
The electron isodensity contours (Figure 3) demonstrate that the formal similarity between the mechanism of the intramolecular

Scheme III



$\text{H}_3^-$        $[\text{Fe}(\text{PH}_3)_4(\text{H}_3)]^+$        $[\text{Fe}(\text{PH}_3)_4]^{2+}$

Scheme IV



$\text{H}_3^-$        $[\text{ScCl}_2(\text{H}_3)]$        $[\text{ScCl}_2]^+$

exchange in the  $[\text{Fe}(\text{PR}_3)_4\text{H}(\text{H}_2)]^+$  and that of the classical heterolytic activation does not correspond to an intimate coincidence of both processes. The absolutely different electron density topology of the transition states requires different electronic factors to govern the reactions. It is thus important to distinguish between these two mechanisms, so it might well be adequate to talk about two different kinds of  $\sigma$ -bond metathesis.

The last point left in this analysis concerns clarification of why electron-rich and electron-poor complexes give rise to such a different reaction topology in the transition state of such a formally similar reaction. Explanation is easy from the orbital diagrams of Schemes III and IV, where the interaction between a linear  $\text{H}_3^-$  fragment and the  $[\text{Fe}(\text{PH}_3)_4]^{2+}$  and  $[\text{ScCl}_2]^+$  fragments is qualitatively depicted. The orbitals of the metallic fragment are simplified to only two having different symmetry and accounting

for the  $\sigma$  and  $\pi$  interactions with the ligand. The key difference between the two systems happens to be the electron count. In the  $d^6$  "butterfly"  $[\text{Fe}(\text{PH}_3)_4]^{2+}$  complex, the  $\sigma$  orbital is occupied,<sup>5b</sup> while both  $\sigma$  and  $\pi$  orbitals are unoccupied in the  $[\text{ScCl}_2]^+$  complex. This different occupation is reflected in the occupation or vacancy of one of the molecular orbitals of the transition state, namely an antibonding orbital between the metal and the extreme hydrogens. When this orbital is unoccupied ( $[\text{ScCl}_2(\text{H}_3)]$ ) the metal is bound to these extreme hydrogens, thus leading to a four-membered ring. When this orbital is occupied ( $[\text{Fe}(\text{PH}_3)_4(\text{H}_3)]^+$ ) the metal is bound only to the central hydrogen, thus leading to a "trefoil" topology.

### Conclusions

In this paper three different possible mechanisms for the intramolecular exchange of a hydrogen atom between the hydride and molecular hydrogen ligands in octahedral  $d^6$  *cis*- $[\text{Fe}(\text{PR}_3)_4\text{H}(\text{H}_2)]^+$  complexes have been considered. One of them happens to be by far the most favored, with an energetic barrier of only 3.2 kcal/mol. This mechanism is the so-called open direct transfer mechanism and consists essentially of a single step transfer of the hydrogen atom between the two ligands, while the three hydrogen atoms are in a linear-like arrangement. The low barrier of ca. 3 kcal/mol agrees with the experimental observation of an easy exchange between the molecular hydrogen and hydride ligands. Moreover, the barrier is so small that this mechanism can even be claimed to be operative for the trans octahedral structures, via a small amount of the *cis* isomer in equilibrium with the *trans* isomer. Actually, the efficiency of this mechanism demonstrated here rejoins the few evidences supporting an active role of mo-

lecular hydrogen complexes in the breaking of the strong H-H bond.

Besides the importance of the very molecular hydrogen complexes, it is also interesting to set the results of this paper into the framework of current ideas on  $\sigma$ -bond activation by transition-metal complexes. The two main mechanisms proposed so far are (a) oxidative addition, acting on electron-rich systems, with late transition metals, and (b)  $\sigma$ -bond metathesis (also called heterolytic activation), acting on electron-poor systems, typically early transition metal or rare-earth complexes. The mechanism reported here seems to lie outside this scheme. It takes place with a relatively electron-rich  $d^6$  complex of iron and has formal resemblances to heterolytic activation. Furthermore, the electron topology in the transition state shows it is absolutely different from traditional  $\sigma$ -bond metathesis. Thus, it could be envisioned as the first characterized example of a new kind of activation mechanism for  $\sigma$  bonds. Actually, this mechanism could also be acting in some reactions that have been considered so far to be oxidative additions.

Although generalization of the results presented here might be questioned by the limitations of the applied methodology, we think that the interest of this subject and the important implications suggested by these results make its presentation and prosecution of research in this area definitely worthy.

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## Transition Metal Polyhydride Complexes. 2. Theoretical Methods for the Determination of Stabilities of Classical and Nonclassical Isomers

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**Abstract:** Ab initio calculations with effective core potentials have been used to study the relative stability of classical and nonclassical isomers of the model complexes,  $\text{IrH}_5\text{L}_2$  ( $\text{L} = \text{Be}, \text{PH}_3, \text{and PMe}_3$ ). The examination of different levels and techniques of electron correlation suggests that the second-order Moller-Plesset (MP2) method will provide a reliable prediction of the stability of one isomer over the other. The conventional substitution of a  $\text{PR}_3$  ligand by  $\text{PH}_3$  in quantum chemical calculations has also been examined. The small error (ca. 2 kcal/mol) caused by this replacement suggests that it is a reasonable choice in this class of transition metal polyhydride complexes. Our results on the electronic structural difference between classical and nonclassical isomers suggest that the nonclassical isomer is preferred for complexes with strong  $\pi$  acceptor ligands and contracted central-metal d orbitals.

### Introduction

Since the first discovery of a stable nonclassical dihydrogen complex,  $\text{W}(\text{CO})_3[\text{P}(i\text{-Pr})_3]_2(\eta^2\text{-H}_2)$ , by Kubas et al.,<sup>1</sup> transition metal polyhydride complexes have been the subject of considerable interest.<sup>2-25</sup> The intensive studies in this subject have resulted

in the discovery of many complexes containing nonclassical or classical isomers in solution. However, only a few  $\eta^2\text{-H}_2$  complexes

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