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reaction coordinate. In turn, this electronic advance will augment the probability of these fluctuations and guarantee their kinetic success.

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Molecular Hydrogen Complexes with a Hydride Ligand. An ab Initio Study on the $[Fe(PR_3)_4H(H_2)]^+$ System[†]

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Abstract: Specific effects of the hydride ligand in the coordination of the hydrogen molecule to metallic centers are studied by means of ab initio MO calculations in the model system $[Fe(PH_3)_4H(H_2)]^+$. The two different isomers of this complex (cis and trans) are optimized, several orientations of the hydrogen molecule being considered for the cis isomer. In contrast to phosphine, the hydride ligand favors the coordination of hydrogen to the metal both in the cis and trans positions. When the hydride is placed in the cis position and oriented suitably, there is a strong attractive effect between it and the molecular hydrogen. Discussion of the obtained results is carried out in comparison with the available experimental data.

Introduction

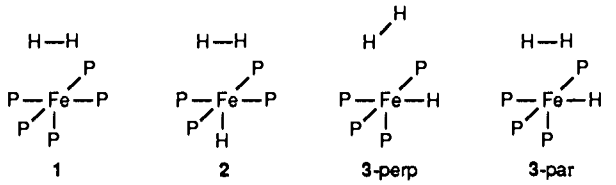
After their discovery in the mid-eighties,[1] molecular hydrogen complexes have come a long way. Nowadays, nonoxidative coordination of molecular hydrogen to metallic centers is quite common, as shown in the growing number of reviews[2] reflecting the large scientific activity[3] developed on this subject. From being initially a scientific oddity, namely, feasible intermediates in certain chemical reactions, molecular hydrogen complexes have become compounds of definite stability whose specific chemical reactivity is the subject of an increasing number of studies.

One of the most interesting subgroups of molecular hydrogen complexes is constituted by those where the H_2 ligand coexists with the hydride ligand. Besides the curiosity arising from any chemical species reported so recently, the possible interchange of a hydrogen atom between hydride and H_2 makes the molecular hydrogen–hydride complexes the simplest model for the very general class of heterolytic activation reactions[4] (also referred to in the literature as σ-bond metathesis[5a] and tetracentric mechanism activations).[5b]

The experimental study of molecular hydrogen–hydride complexes is made more difficult by the problems inherent to the identification of the molecular hydrogen ligand. These problems turn out to be especially important when yet more hydrogens are involved as ligands. The only method allowing for their unequivocal identification is neutron diffraction. However, this method requires the existence of fairly large crystals, so the amount of available data is still scarce.[1,6,7] Although other techniques like X-ray diffraction[1,8] and IR[9] or NMR[10] spectroscopy have been also applied, they have not found universal application.

Among the complexes that could be considered as candidates to contain simultaneously molecular hydrogen and hydride as ligands, mention can be made of the following complexes: $[Ir(bq)(PR_3)_2H(H_2)]^+$,[11a] $[Fe(R_2PCH_2CH_2PR_2)_2H(H_2)]^+$,[6,11b] $[Fe(P(OEt)_3)_4H(H_2)]^+$,[11c] $[Fe(P(CH_2CH_2PR_3)_3)H_3]^+$,[11d,e] $[Fe[PR_3)_3H_2(H_2)]^+$,[7] $[Ru(Cp)(PR_3)H_3]$,[11f] and $[Ir(Cp)(PR_3)H_3]^+$.[11g] All complexes in this list have the formal structure d^6 $ML_5(H_2)$, which otherwise is quite common among molecular hydrogen complexes. It is worth remarking the relative abundance of data for iron complexes having the metal coordinated to four PR_3 groups, one hydrogen molecule, and one hydride; one of them is *trans*-$[Fe(R_2PCH_2CH_2PR_2)_2H(H_2)]^+$, perhaps one of the best known molecular hydrogen complexes. For this species, the

Scheme I



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following data are available: (a) neutron diffraction,[6] (b) thermodynamics on the acidity of the molecular hydrogen coordinated to the metal,[11b] and (c) inelastic neutron scattering on the rotation barrier of the hydrogen molecule.[12] This abundance of data on a complex where the molecular hydrogen and the hydride are found on opposite sides of an octahedron is not found in complexes where the two ligands are adjacent to each other (cis isomer). Nevertheless, the existence of the cis isomer in equilibrium with the trans isomer has been postulated from NMR studies for the $[Fe(P(OEt)_3)_4H(H_2)]^+$ complex.[11c] Likewise, the $[Fe(P(CH_2CH_2PR_3)_3)H_3]^+$ complex, where steric requirements prevent the trans disposition between the two ligands, seems to be a molecular hydrogen–hydride complex.[11d,e] A final remark concerns a subject closely related to molecular hydrogen–hydride complexes, namely, the hypothetical existence of the H_3 ligand,[13] which has been suggested for the $[Fe(P(CH_2CH_2PR_3)_3)H_3)]^+$ complex.[11d] However, lack of neutron diffraction data makes the interpretation of experimental data somewhat puzzling.

The experimental work on molecular hydrogen complexes has also given rise to increased interest to theoretical chemists. Several studies have appeared on this subject, some of them carried out with the extended Hückel method,[13,14] and others performed through ab initio methods.[15] These calculations have made it possible to understand more clearly the bonding between the hydrogen molecule and the metallic center. This bonding arises from two different contributions: first, from the donation from the filled σ orbital of the H_2 molecule toward an empty orbital of the metallic fragment; and second, the back-donation from a filled orbital of the metal toward the σ^* orbital of the hydrogen molecule. Anyway, one must note that the size of the considered systems prevented full optimizations in ab initio calculations, so rigid geometries were always used for the metallic fragment.

The interest in polyhydrides and the copious amount of unexplained data on complexes of the type $[Fe(PR_3)_4H(H_2)]$ have led us to carry out theoretical calculations on these compounds, results of which are presented in the present paper. Because of the confusion in the experimental data for the cis complexes, optimization of the geometrical structure of the metallic fragment has been performed. The ultimate purpose of the present work is to clarify the change introduced in the bonding between the metal and the molecular hydrogen by the presence of the hydride ligand. More precisely, our goal is to know the difference introduced by the presence of a particular ligand like hydride with respect to a much more common ligand like phosphine, and to know how this change is reflected in the structure of the complexes.

In order to fulfill these objectives we have carried out calculations on the four types of complexes shown in Scheme I. In all complexes, the PR_3 groups have been modeled by PH_3 ligands. Complex **1**, though not containing any hydride, has also been considered for comparative purposes. As for molecular hydrogen–hydride complexes, we have considered the two topologically possible structures: *trans* (**2**) and *cis* (**3**). Moreover, for the cis isomer we have considered two different initial orientations of the hydrogen molecule: **3**-perp and **3**-par).

Computational Details

All calculations have been performed with an all-electron molecular-orbital ab initio method at the RHF-SCF level. For iron, a valence double-ζ basis set has been used; the valence shell has been considered to include the 3d, 4s, and 4p orbitals; i.e., in a compact notation the basis set for the metal is [33321/3321/21].[16] For the two hydrogens of the molecular hydrogen fragment and for that of the hydride, which are the most important ligands in these complexes, a double-ζ basis set has also been chosen,[17a] supplemented by a p shell with an exponent of 1.10,[17b] which has been found to be required for the adequate description of this kind of systems.[18] For the atoms of phosphines, which are considered as spectator ligands, a minimal basis set has been chosen.[19]

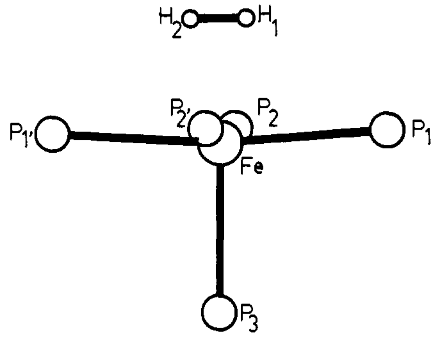

Figure 1. Optimized structure for $[Fe(PH_3)_5(H_2)]^{2+}$ complex **1**. Hydrogen atoms of phosphines have been omitted from the plot for the sake of clarity.

Table I. Selected Geometrical Parameters of the Optimized Structures[a]

	1	**2**	**2**(exp.)	**3**-perp	**3**-par
Fe–H_1 distance	1.701	1.631	1.62	1.696	1.619
Fe–H_2 distance	1.697	1.631	1.62	1.696	1.743
H_1–H_2 distance	0.744	0.770	0.82	0.743	0.786
Fe–H_3 distance		1.709	1.54	1.666	1.657
P_3–Fe–P_1 angle	94.5			100.8	99.7
P_3–Fe–P_2 angle	94.8			92.8	94.1
H_3–Fe–P_1 angle		86.1	83.3		
H_3–Fe–P_2 angle		89.3	94.0		
P_3–Fe–H_3 angle				94.0	91.7
$P_{1'}$–Fe–H_2 angle	73.8	80.3	82.1		83.9
H_3–Fe–H_1 angle					57.9
P_2–Fe–H_1 angle				72.9	

[a] Experimental data for the *trans*-$[Fe(R_2PCH_2CH_2PR_2)_2H(H_2)]^+$ complex[6] are given in column **2**(exp). Distances are given in Å, and angles in degrees.

Geometry optimizations for each complex have been carried out with the Schlegel method[20] using gradients calculated analytically. The internal structure of phosphines has been frozen, with a tetrahedral distribution about the phosphorus atom and a value for the P–H distance of 1.42 Å. The Fe–P distance has been fixed at 2.242 Å, which is that found from the neutron diffraction study of the more similar compound available.[6] The remainder of geometrical parameters, including all angles and dihedral angles about the metal atom, have been optimized in the present calculations. Use has been made of symmetry when possible (C_{2v} for complex **2** and C_s for the others).

Results and Discussion

The results arising from this study have been divided into four sections. In the first section we present the results for the $[Fe(PH_3)_5(H_2)]^{2+}$ complex, which does not contain the hydride ligand but is useful for comparison purposes. In the second and third sections, we analyze the influence of the hydride ligand in the bonding between the molecular hydrogen and the metal for the two possible positions, namely, cis and trans. The discussion in these three first sections is especially based on structural aspects. Attention to dissociation energies is considered in the fourth section.

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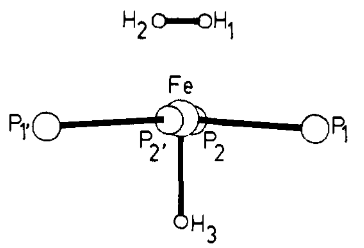

Figure 2. Optimized structure for *trans*-[Fe(PH$_3$)$_4$H(H$_2$)]$^+$ complex **2**. Hydrogen atoms of phosphines have been omitted from the plot for the sake of clarity.

The [Fe(PH$_3$)$_5$(H$_2$)]$^{2+}$ Complex. Although a complex containing five phosphine ligands and one molecular hydrogen ligand has not been synthesized yet, the analysis of the differential effects of hydride and phosphine on the bonding between the molecular hydrogen and the metal can be carried out more efficiently from theoretical data for such a complex.

In Figure 1 we depict the optimized geometry for complex **1**, while in Table I we collect its most significant geometrical parameters, together with those of the other complexes. The first remark on this complex is that it is a minimum in the potential energy hypersurface; i.e., it is a stable species. The distortion from the regular octahedral disposition is very small, thus showing an acceptable agreement with the octahedral model anticipated for d^6 ML$_6$ complexes. It is also worth pointing out that the distance between the atoms of the hydrogen molecule and the metal is practically the same, although it is not required by the symmetry of the system.

As to the particular chemical aspects of this complex, mention must be made that, although the molecular hydrogen complex corresponds to a stable minimum in the potential energy hypersurface, the bonding between the hydrogen molecule and the metal seems to be very weak. The coordination strength of a molecular hydrogen within an organometallic complex is always associated with a lengthening of the H–H bond. Since the optimized H–H distance is 0.744 Å, which is only slightly longer than the same distance in the free H$_2$ molecule optimized with the same basis set, one can conclude that the coordination strength is quite small. Another geometrical aspect worth mentioning concerns the direction of the deformation from the octahedral geometry. The deformation is very small, consisting of a bending of the equatorial phosphines toward the molecular hydrogen. This behavior, which is not repeated for other complexes reported below, will be widely commented on later.

The *trans*-[Fe(PH$_3$)$_4$H(H$_2$)]$^+$ Complex. Since a neutron diffraction study on the *trans*-[Fe(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$H(H$_2$)]BPh$_4$ complex[6] is available, we present the results for the trans isomer before reporting those for isomer **3**. Results for the former isomer will also be useful to test the ability of the present calculations to reproduce experimental data.

Comparison of the optimized geometrical parameters (Table I and Figure 2) with experimental data on complex [Fe(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$H(H$_2$)]BPh$_4$ is quite satisfactory. It is worth mentioning that the optimized Fe–H$_1$ distance (1.631 Å) almost equals the experimental distance (1.62 Å). Likewise, equatorial phosphines are also in similar positions. Phosphines P$_1$ and P$_{1'}$, which are coplanar with the hydrogen molecule, bend toward the same direction in our theoretical calculation and experimentally. However, the experimental distortion is larger, since the calculated value for the P$_1$–Fe–P$_{1'}$ angle is 172.1°, whereas the experimental value is 166.6°. Although other geometrical parameters are not so well-described (e.g., the H$_1$–H$_2$ bond length, which is 0.82 Å experimentally but is computed to be 0.770 Å), it seems that the level at which the system is described is fairly good, especially if one considers the model employed for the ligands.

Comparison of the optimized geometry for **2** with that of **1** shows at first glance the predictable correlation between the lengthening of the H–H bond and the approach of the hydrogen molecule to the metal atom. This is consistent with the common point of view on the correlation between bond strength and distance. A shorter metal–molecular hydrogen distance, i.e., a stronger metal–molecular hydrogen bond, implies a longer hydrogen–hydrogen distance, and hence a weaker bond between the two atoms of the hydrogen molecule.

Table II. Geometrical Parameters Obtained in the Octahedral Optimization, Carried Out by Imposing Regular Octahedral Disposition of the Ligands about the Iron Atom[a]

	1	2	3-perp	3-par
Fe–H$_1$ distance	1.661	1.651	1.661	1.632
H$_1$–H$_2$ distance	0.753	0.760	0.751	0.772
Fe–H$_3$ distance		1.707	1.670	1.643

[a] All distances are given in Å.

There are, however, two remarkable aspects of our theoretical results that were not foreseeable, a priori: (a) the bonding between the metal and the hydrogen molecule seems to be stronger in **2** than in **1**. This fact can be observed both in the Fe–H$_1$ distances (1.701 Å in **1** versus 1.631 Å in **2**) and in the H$_1$–H$_2$ distances (0.744 and 0.770 Å, respectively). (b) The bending direction of phosphines is opposite in **1** and **2**. In complex **1**, the P$_3$–Fe–P$_1$ and P$_3$–Fe–P$_2$ angles are 94.5 and 94.8°, respectively, i.e., larger than 90°. On the contrary, the corresponding angles in complex **2**, H$_3$–Fe–P$_1$ and H$_3$–Fe–P$_2$, are smaller than 90° (86.1 and 89.3°, respectively). That is, in **1** the phosphines bend toward the hydrogen molecule, whereas in **2** they bend away from it.

To clarify further the difference between both complexes, supplementary calculations have been made introducing restrictions in the geometries. The restrictions have consisted of imposing a regular octahedral structure of the ligands about the metal atom by fixing the angles at 90 or 180°. These octahedral optimizations, since they do not allow for reorientation of the ligands, allow clarification of their electronic effects. Comparison with unrestricted optimizations allows one to see more clearly the origin and effects of geometrical distorsions.

In Table II we collect the values obtained for geometries optimized under the above restrictions. The two most remarkable effects appearing upon comparison between the *trans*-[Fe(PH$_3$)$_4$H(H$_2$)]$^+$ **2** and [Fe(PH$_3$)$_5$(H$_2$)]$^{2+}$ **1** complexes presented in Tables I and II are the following.

(a) The bending of phosphines away from the hydrogen molecule favors the bonding of the latter molecule to iron. This is the reason why in complex **1** the restriction on octahedral optimization approaches the hydrogen molecule to the metal, whereas in complex **2** the restriction causes the opposite effect.

(b) Despite the disappearance of effects due to phosphine bending, the bond between the hydrogen molecule and the iron atom is still stronger when there is a hydride in the trans position than when a phosphine is there.

The effect of bending of the cis ligands (in this case phosphines) on the strength of the bond between ligands bearing π-acceptor properties has already been discussed by other authors from extended Hückel calculations. Examples involve ethylene[21] and the very molecular hydrogen case.[7] In short, such a deformation produces a hybridation of the orbital of the metal atom responsible for the back-donation to the σ^* orbital of the hydrogen molecule; this fact favors this process from both an energetic and an overlap points of view. This theory is coherent with the fact that the phosphines lying in the plane defined by the metal and the hydrogen molecule are more bent away than those lying outside that plane.

Nevertheless, one may question why phosphines bend toward different directions in complexes **1** and **2**, or, more specifically, why in complex **1** the phosphines bend toward the hydrogen molecule if this leads to a weakening of the bonding between the metallic center and the hydrogen molecule.

We think that the bending direction of the phosphines depends on the strength of the bonding of the hydrogen molecule. It is interesting to remind one here that the geometry predicted for a singlet d^6 ML$_5$ complex, which is the formal structure for the

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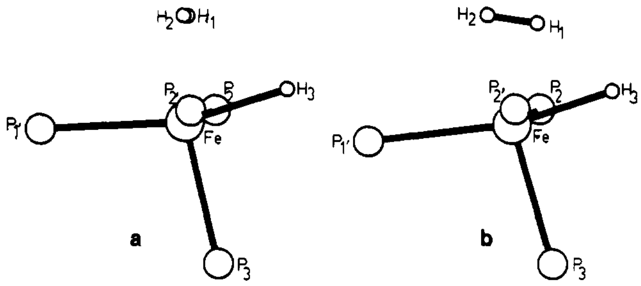

Figure 3. Optimized structure for *cis*-$[Fe(PH_3)_4H(H_2)]^+$ complex **3**. The two structures correspond to the different orientations of hydrogen molecule: (a) perpendicular and (b) parallel. Hydrogen atoms of phosphines have been omitted from the plot for the sake of clarity.

metal fragment, is a square pyramid with the base ligands bent slightly toward the vacant site. For complex **1**, having a weak bond between the hydrogen molecule and the iron atom, the geometrical arrangement preserves the memory of the d^6 ML_5-$[Fe(PH_3)_5]^{2+}$ complex, from which it originates, with a square-pyramidal structure having the phosphines bent toward the vacant site. If the bond is stronger, as in complex **2**, the presence of a hydrogen molecule deforms the geometry of the square pyramid to such an extent that it inverts the deviation of the angles about 90°.

The last point of the comparison between the two complexes needing clarification concerns the different strengths of the bonding with the hydrogen molecule. The hydride, when situated in the trans position with respect to the hydrogen molecule, causes a stronger bond than does the phosphine. Actually, this is just the opposite to what one would expect from the traditional trans effect,[4] since the hydride is a σ-donor ligand which is obviously stronger than phosphine. No definitive explanation for this behavior has been found. Possible explanations would involve either π-acceptor effects of phosphine or the different charges of complexes. It could also be argued that bond strengths are not always correlated with bond lengths. However, we think that there could be a nontypical trans effect associated with the presence of two ligands as special as hydride and molecular hydrogen. In fact, the trans effect due to the hydride favoring the molecular hydrogen coordination has already been postulated.[2a]

Unfortunately, the scarcity of experimental data on neutron diffraction, which are the only ones that are unquestionable, does not allow one to discard the possibility of this behavior being an artifact of the method of calculation. Anyway, more cases are known involving trans isomers, whereas the existence of cis isomers is not so well established. This could be a favorable clue for a stronger bond between the metal and the hydrogen molecule associated with the presence of the hydride in the trans position.

The *cis*-$[Fe(PH_3)_4H(H_2)]^+$ Complex. The *cis*-$[Fe(PH_3)_4H(H_2)]^+$ complex **3** is likely to be more sensitive to the orientation of the hydrogen molecule with respect to the hydrogen molecule–iron axis than the *trans*-$[Fe(PH_3)_4H(H_2)]^+$ complex **2**. To carry out an insight into this effect, we have performed an optimization of this complex in the two orientations of Scheme I. These two orientations have been chosen because of symmetry reasons and because of simplification in the later analysis. We will refer to the complex where the hydrogen molecule is placed in the P–Fe–H plane as **3**-parallel (**3**-par), whereas we will refer to the other complex as **3**-perpendicular (**3**-perp).

The most meaningful geometrical parameters of these two optimized isomers are collected in Table I, together with those of the other complexes analyzed above. The optimized geometries have been also plotted in Figure 3. Unfortunately, the values obtained cannot be compared with experimental data because no experimental geometries are available on iron complexes having four PR_3 ligands with a hydrogen molecule and a hydride in a cis disposition.

The first appealing point of the geometries of these two cis isomers concerns the observed deformation relative to the octahedral disposition, which is far more important than in the trans isomer. Furthermore, it is worth pointing out that the deformation of the $[Fe(PH_3)_4H]^+$ fragment is very similar in the **3**-perp and the **3**-par complexes. This fact must be interpreted in the sense that the distortion is intrinsic to the metallic fragment and is not induced by electronic effects of the hydrogen molecule, because the latter must interact with hydride in a different way in the perpendicular and parallel conformations. In Table III we present the distortion energies of each optimized complex, calculated as the difference between the energy of the fully optimized systems and that obtained by fixing the ligands in the ideal octahedral positions. This confirms the larger distortion, with respect to the octahedral disposition, of the cis isomers relative to the other systems; for complexes **3** the distortion energies are far larger than for **1** and **2**. Therefore, consideration of a regular octahedral geometry would be a more severe error for the cis isomers.

Table III. Relative Energies (in kcal/mol) of the Geometries Obtained in the Octahedrally Restricted and Unrestricted Optimizations

	complex	optimized	octahedral	distortion energy
1	$[Fe(PH_3)_5(H_2)]^{2+}$			4.0
2	*trans*-$[Fe(PH_3)_4H(H_2)]^+$	0.0	+1.0	1.0
3	perp, *cis*-$[Fe(PH_3)_4H(H_2)]^+$-perp	−4.1	+7.1	11.2
3	par, *cis*-$[Fe(PH_3)_4H(H_2)]^+$-par	−11.0	+2.2	13.2

Let us now carry out a more accurate study of each cis complex. The most remarkable aspect of the bonding in the hydrogen molecule in the **3**-perp isomer is its large similarity to that existing in complex **1**: the distances between the Fe, $\mathbf{H_1}$ and H_2 atoms are coincident to 0.01 Å, their value being 1.70 for the iron–hydrogen bond and 0.74 for the hydrogen–hydrogen bond. An immediate consequence turns out to be that the ligands in an octahedral complex affecting the coordination of a hydrogen molecule are those being in trans with respect to $\mathbf{H_2}$, and those being in cis in such a way they lie parallel to the H–H bond; however, ligands cis oriented perpendicularly to the H–H bond do not affect the coordination of the hydrogen molecule. Since the only difference between **1** and **3**-perp complexes is the substitution of a phosphine by a hydride in the perpendicular plane, the bonding of the hydrogen molecule is not affected.

In complex **3**-par, the bonding between the hydrogen molecule and the metal is much stronger than in complex **3**-perp, as demonstrated by the longer H_1–H_2 distance (0.743 Å for the 3-perp complex versus 0.786 Å for 3-par). Another striking aspect in complex **3**-par turns out to be the asymmetry in the bonding between both hydrogens and the metal; whereas the H_1–Fe distance is 1.619 Å, the H_2–Fe distance is 1.743 Å, so the hydrogen molecule is bent toward the hydride ligand, the H_1–H_3 distance being 1.587 Å. This kind of asymmetry, which otherwise is not found in any of the other optimized complexes, is also present to a smaller extent in the experimental structure of the only molecular hydrogen complex known at present[7] with a hydride in a cis position. This behavior demonstrates the existence of an attractive effect between the two ligands which are cis to each other: the hydride and the hydrogen molecule. This attractive effect turns also into a difference of 7.0 kcal/mol between the **3**-par and **3**-perp isomers. This difference can only be attributed to the distinct interaction between the two neighboring ligands.

To get a further insight into the peculiarities of the bonding between iron and the hydrogen molecule, we have calculated the total electron density in the plane containing the metal and the hydrogen molecule for the four optimized structures **1**, **2**, **3**-perp, and **3**-par. As seen from the contour plots depicted in Figure 4, the most interesting stationary points are the so-called bond critical points, which have only a positive eigenvalue of the second derivative of the electron density function, thus indicating the existence of a chemical bond. In turn, the value of the density at a given bond critical point provides an indication of the bond strength.[22] The electron density map of the complex **3**-par (Figure 4d) is quite peculiar and reflects the asymmetry of the bonding

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[22] Bader, R. W. F.; Anderson, S. G.; Duke, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1389–1395.

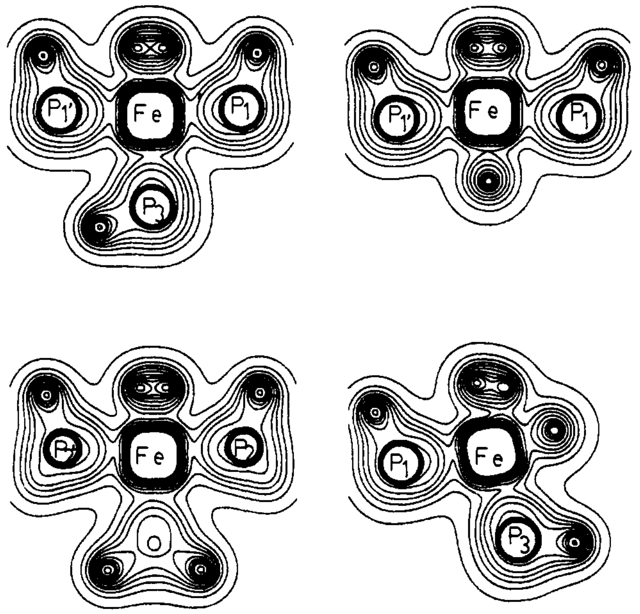

Figure 4. Electron isodensity contour maps of the optimized systems **1**, **2**, **3**-perp, and **3**-par. The lines plotted correspond to the values of 0.01, 0.03, 0.05, 0.07, 0.09, 0.12, 0.16, 0.20, 0.24, 0.28, 0.34, and 0.40 au.

between the metal and the hydrogen molecule. Actually, whereas in all remaining complexes the iron atom is bonded to a similar extent to both atoms of the hydrogen molecule thus forming a three-centered ring, in the complex **3**-par the hydrogen molecule seems to be bonded to the iron atom through only one of its hydrogens. Moreover, no bond critical point is detected between the hydrogen molecule and the hydride ligand. Therefore, the interaction between the hydride and the hydrogen molecule cannot be described in terms of the incipient formation of a covalent bond.

Another reason that could account for the strong interaction between the two cis ligands, the hydride and the molecular hydrogen, is an electrostatic effect. This is feasible if one takes into account the negative charge supported by the hydride. Although Mulliken populations are not the best method to analyze calculations on organometallic complexes, inspection of atomic charges deducted from them is in this case quite clarifying. In complex **3**-par, H_3 (hydride) supports a charge of −0.40 au, H_1 supports +0.10 au, and H_2 supports −0.13 au. To assess the meaning of the values, one must consider that in the other three optimized complexes the charge associated with the hydride is of the same order, whereas those of the atoms belonging to the hydrogen molecule ligand oscillate between −0.04 for complex **1** and 0.00 for complex **3**-perp. Thus, the difference in charge between H_1 and H_2, which is minimal in other cases, increases in complex **3**-par to 0.23 au. This fact can be explained by the close presence of the hydride ligand, which polarizes the hydrogen molecule which in turn is coordinated to the metal. The hydride ligand supports a large negative charge and is situated at a short distance from the hydrogen molecule, whose electronic cloud is polarized, thus altering its initial symmetry. Actually, the hydride ligand bears special characteristics which make it a suitable candidate for this kind of interaction: (a) it is very close to the metal, thus being close to other ligands; and (b) there is no directionality in its spherical 1s orbital.

We have mentioned above the existence of an energy difference of 7.0 kcal/mol between the two conformations of the *cis*-$[Fe(PH_3)_4H(H_2)]^+$ complex **3**. It would be interesting to discuss whether, besides being interesting tools for our analyses, they do correspond to real minima of the potential energy hypersurface. To clarify this question, we have studied the rotation of the hydrogen molecule while fixing the geometry of the metal fragment. Starting from the geometry of the $[Fe(PH_3)_4H]^+$ fragment associated with the *cis*-$[Fe(PH_3)_4H(H_2)]^+$–perpendicular complex **3**-perp, we carried out a series of energy-only calculations, the hydrogen molecule being rotated at intervals of 10°. We have obtained a sinusoidal profile whose energy maximum corresponds to the perpendicular orientation, and the energy minimum corresponding to the parallel orientation. Thus, even though we took for the $[Fe(PH_3)_4H]^+$ fragment the geometry optimized for the perpendicular orientation, the parallel orientation is still the most stable. In conclusion, the only stationary point in this system corresponds to the parallel orientation, which is the geometry an experimental structure should exhibit, the barrier to rotation being estimated from this calculation as 7.0 kcal/mol.

Table IV. Dissociation Energies (in kcal/mol) of the Molecular Hydrogen Ligand from the Metallic Fragment

complex	dissociation energy
1, $[Fe(PH_3)_5(H_2)]^{2+}$	4.9
2, *trans*-$[Fe(PH_3)_4H(H_2)]^+$	12.0
3-perp, *cis*-$[Fe(PH_3)_4H(H_2)]^+$-perp	3.9
3-par, *cis*-$[Fe(PH_3)_4H(H_2)]^+$-par	11.0

It is convenient here to compare a critical review of the above results with the recently published neutron diffraction study on the $Fe(PEtPh_2)_3H_2(H_2)$ compound.[7] This system corresponds to a distorted octahedron, and its ligand distribution corresponds to the cis isomer, one hydride ligand being cis and another hydride being trans with respect to the hydrogen molecule. The distance between the hydrogen molecule and the metal is of the same order as that in the *trans*-$[Fe(PPh_2CH_2CH_2PPh_2)_2H(H_2)]BPh_4$ complex,[6] although in the former molecule the hydrogens are disposed in an asymmetric fashion (distances of 1.61 and 1.58 Å). Likewise, an attractive effect between the hydrogen molecule and the cis hydride ligand is observed. Nevertheless, the most appealing aspect of this complex is the staggered orientation observed for the hydrogen molecule, which does not eclipse any axes corresponding to equatorial ligands, but disposes approximately along their bisector. This behavior is attributed[7] to the compensation of two effects, namely, (a) the bending of the phosphines which tends to align the hydrogen molecule along the P–Fe–P axis, and (b) the cis effect due to the hydride ligand, which tends to align the hydrogen molecule in the P–Fe–H direction. The difference between this experimental system and that studied theoretically here (*cis*-$[Fe(PH_3)_4H(H_2)]^+$, **3**) can be found in the fact that there is no effect due to phosphine bending, because this effect is found only when there is a hydride situated trans relative to the hydrogen molecule.

Dissociation Energies. The discussion in the previous sections has been carried out from structural results, assuming they correlate well with the implied energetics. The main reason for this way to proceed is the problem of calculating the dissociation energy of the hydrogen molecule from the metallic fragment. This dissociation energy must obviously be calculated as the difference between the energies of the $ML_5(H_2)$ system and those of the ML_5 and H_2 systems. The problem turns out to be which geometry must be considered for the isolated ML_5 fragment. The simplest option would consist of considering full optimization, but this could lead to a geometry which is very different from that in the related $ML_5(H_2)$ system, and the big distortion energies could mask the value of the interaction energy with the H_2 ligand.

To solve this problem, the model chosen in this paper involves freezing the geometry of the ML_5 fragment to that of the optimized $ML_5(H_2)$ complex, and carrying out an energy-only calculation at this geometry. Use of this approach provides an unbiased estimation of the dissociation energy of the ligand from the metal for all the cases, and eases the comparison between different systems.

In Table IV, dissociation energies calculated in the way described in the preceding paragraph are presented. These energetic results are in perfect agreement with the estimations on bond strengths made in previous sections from geometrical results. This is the obvious interpretation of the similarity between the dissociation energy of the H_2 ligand in complexes **1** and **3**-perp. This emerges also from the fact that the bond is much stronger in complexes **2** and **3**-par.

A final application of Table IV consists of using it as a test for the validity of the method by comparing the results with those of previous experimental and theoretical works reported in the literature for other molecular hydrogen complexes. The comparison is satisfactory. Theoretically calculated binding energies[15] of the molecular hydrogen ligand in several complexes range from 10 to 21 kcal/mol. Experimental data[23] give values between 7 and 10 kcal/mol, probably being underestimated by the interference of agostic effects in the ML_5 fragment. In any case, all these values are of the same order as those presented in this paper, which are 12.0 and 11.0 kcal/mol for the stable compounds **2** and **3**-par, respectively.

Conclusions

The present ab initio study on $[Fe(PH_3)_4H(H_2)]^+$ systems has shown the peculiar effects of the hydride ligand on the bonding between the hydrogen molecule and the metal. The presence of a hydride trans to the hydrogen molecule increases the strength of the bonding of hydrogen to metal relative to the same position being occupied by a phosphine. If the hydride ligand is placed in the cis position, there is an important distortion in the ML_4H fragment, although this distortion is independent of the orientation of the hydrogen molecule. However, the bonding of the hydrogen molecule to the metal depends strongly on this orientation. Actually, the bonding between the hydrogen molecule and the metal is unaffected by ligands oriented perpendicularly to the plane defined by the atoms of the metal and the hydrogen molecule. When suitably oriented, the hydride ligand in the cis position exhibits a strong attractive interaction, the hydrogen molecule being polarized in a process which can be considered to have essentially an electrostatic origin.

The optimized geometries present small distortions relative to a regular octahedron, but the coordination of the hydrogen molecule is very sensitive to such distortions. Bending of phosphines away from the hydrogen molecule increases the strength of its coordination and magnifies the different effects caused by the presence in a trans position of the hydride and phosphine ligands. This fact makes the optimization of the relative position of spectator ligands especially important in these cases.

The quantitative value of the results obtained is indeed relative owing to simplifications, namely, (a) the modeling of the systems, (b) the lack of correlation energy, and (c) the possible decompensations in the employed basis set. However, our results agree qualitatively with available experimental data, so we think that they are quite useful as a tool in interpreting qualitatively these types of complexes.

Understanding the peculiarities of the hydride ligand in molecular hydrogen complexes is a first step in the comprehension of the chemical interaction between these two ligands, i.e., the interchange reaction between hydrogen atoms. Really, the interaction between the hydride and the hydrogen molecule observed for the *cis*-$[Fe(PH_3)_4H(H_2)]^+$ complex is directly related to these processes. The interchange reaction, which has an obvious chemical interest, is presently the subject of theoretical research in our group.

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Properties of Small Group IIIA Hydrides Including the Cyclic and Pentacoordinate Structures of Trialane (Al_3H_9) and Trigallane (Ga_3H_9): Can Dialane Be Isolated?

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Abstract: The structure of small group IIIA hydrides up to the trimers are studied using the self-consistent field (SCF), single and double excitation configuration interaction (CISD), and single and double excitation coupled cluster (CCSD) methods in conjunction with a double-zeta plus polarization basis set (DZP). The dimerization energy for the unknown dialane is found to be significantly greater than that for the recently synthesized digallane. Unlike the analogous boron compound, cyclic trialane(9) and trigallane(9) incorporate planar six-membered rings according to the DZP SCF predictions. Acyclic trimer structures with pentacoordinated heavy atoms are also considered. The pentacoordinate trialane(9) is nearly isoenergetic with the cyclic structure, and the pentacoordinate triborane(9) is only slightly higher in energy than the cyclic triborane. This new pentacoordinated triborane may be involved in the pyrolysis of diborane and may be the key to the resolution of a dispute concerning the kinetics of this process.

1. Introduction

With the recent successful synthesis of digallane,[1] having a diborane-like structure, the absence of dialane poses a challenge to both experimentalists and theorists.[2,3] Two hypotheses can be made. First, dialane may be sufficiently stable to exist,[3] but no suitable synthetic route has yet been discovered. Certainly the key to the synthesis of digallane, and also galloborane,[4] was Downs' use of the monochlorogallane dimer as a precursor. The stability of dialane, as compared to diborane and digallane, has been studied by Lammertsma and Leszczynski[3] who reported the dimerization energies for borane, alane, and gallane obtained from molecular electronic structure theory with inclusion of electron correlation effects by Møller–Plesset perturbation theory. They concluded that dialane should be experimentally observable since its binding

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