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Molecular Hydrogen Complex vs Dihydride in $ML_4 + H_2$ Systems. Influence of the ML_4 Fragment Geometry

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Received October 17, 1988

The influence of the d^8 ML_4 $[Rh(PH_3)_4]^+$ metallic fragment geometry on the H_2 coordination shape is analyzed with the ab initio MO method. The potential energy surface minima are found to be essentially different when the fragment has a classic C_{2v} form or a rigid pyramidal C_{3v} structure. In C_{2v} symmetry, the stable species turns out to be the dihydride, whereas in C_{3v} symmetry the η^2 molecular complex is the stable structure, in good agreement with experimental data. Through the analysis of a few selected molecular orbitals, the different hybridization of the Rh d orbitals is shown to be the key factor to explain the experimental behavior.

I. Introduction

The synthesis of a new kind of complex between hydrogen and transition metals has recently become the research focus of many different groups.[1] These new compounds are the so-called molecular hydrogen complexes, where the coordination is made in the η^2 shape and the two hydrogens are still bound to each other. These compounds are essentially different from the classical dihydride-type hydrogen complexes, where the H–H bond is completely broken.

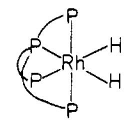
Since Kubas[2] first reported the characterization of the first isolable η^2-H_2 transition-metal complexes, many others have been identified. Even some previously known polyhydrides have been reformulated to contain H_2 ligands.[3] Several reasons justify the interest generated by the new molecular hydrogen complexes. On one hand, there is the originality of their structure, since they turn out to be the first example of stable intermolecular coordination of a σ bond to a metallic center. On the other hand, these compounds are intimately related to oxidative addition reactions, which are the key step of many catalytic processes of industrial interest. Furthermore, their existence has also been postulated in certain biochemical processes.[4]

Different theoretical studies have been made to rationalize the nature of this kind of systems.[5] They show that the main factors that contribute to the stability of the $ML_n(H_2)$ complexes are the electron donation from the filled H_2 σ molecular orbital into an empty σ orbital on the metal and the back-donation from an occupied metal π orbital to the H_2 σ^* orbital. In other words, a scheme analogous to that of typical π-acceptor ligands. The essential difference between systems with π-acceptor ligands and molecular hydrogen complexes is that, since there is no underlying supporting framework (actually σ bonding in the case of olefins), too much back-donation leads to H–H cleavage and production of a dihydride ML_nH_2.[5c] Therefore, the existence of these molecular hydrogen complexes requires a subtle equilibrium between two contributions; the interaction must be strong enough to allow its formation from the separated fragments but also weak enough to prevent evolution to dihydride.

The conditions that make a metallic fragment suitable for the formation of molecular hydrogen complexes are thus a rather low basicity and the presence of strong π-acceptor ligands (generally CO) to help the H_2 σ-orbital donation to the metal and to discourage the back-donation to the H_2 σ^* orbital, which can lead to the dihydride. The electron configuration of the d^6 ML_5 metallic fragment fulfills especially well these conditions. This is the reason why in most molecular hydrogen complexes the metallic fragment exhibits this formal structure.[2,6] Most theoretical studies published to date have been dedicated to this kind of complex,[5a,5b] including the first one carried out through an ab initio method.[5b] Besides these complexes, others have been experimentally reported,[7] although their systematization is difficult. In particular, the d^{10} $ML_3(H_2)$ complexes[7a] have been explained through the extended Hückel method.[5d]

Among the molecular hydrogen complexes that were first synthesized, none were of the d^8 $ML_4(H_2)$ type. This is not surprising, because d^8 ML_4 systems are well-known as efficient catalysts for homogeneous hydrogenation,[8] one of whose steps is precisely the oxidative addition of hydrogen to give a dihydride. The scientific and industrial importance of this catalytic process, one of the most studied reactions from both experimental[9] and theoretical[10] points of view, makes the study of d^8 ML_4 molecular hydrogen complexes to be of special interest. Recently, the synthesis of the $[Rh(P(CH_2CH_2PPh_2)_3)(H_2)]^+$ cation system, the first complex of this kind, has been reported by Bianchini et al.[11]

This system exhibits also the interesting property of presenting two isomeric forms in the metallic fragment, one with C_{2v} symmetry and the other one with C_{3v} symmetry. Each of them is associated to a different H_2 coordination (dihydride **1** or molecular complex **2**). It is worthwhile to stress the absence of strong π-acceptor ligands, which had been claimed in a previous theoretical study[5c] as a stabilizing factor for the d^8 $ML_4(H_2)$ complexes. This compound is also the first molecular complex of rhodium, a metal that is very used in homogeneous catalysis.



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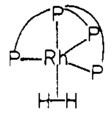

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It seemed thus necessary to perform a theoretical study on this system to clarify the influence of the geometric arrangement of ligands on the relative stabilities of the molecular hydrogen and

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Table I. Values (in Å) of the Rh–H Distances and the Geometric Parameters Depicted in Figure 1 for the Dihydride and the Molecular Hydrogen Complexes

$[Rh(PH_3)_4H_2]^+$ form		R_1	R_2	Rh–H
dihydride	basis set I	1.15	2.05	1.54
	basis set II	1.14	2.02	1.52
molecular hydrogen	basis set I	1.87	0.76	1.90
	basis set II	1.59	0.80	1.64

dihydride complexes. The goal of the present paper is to build a general interpretation scheme that is able to explain experimental data. In particular, we present results of ab initio calculations on the model system $[Rh(PH_3)_4]^+ + H_2$.

II. Methodology

All calculations were carried out through an ab initio method at the RHF–SCF level of theory. The effect of the core electrons of the rhodium and phosphorus atoms was represented by ab initio effective core potentials with relativistic corrections in the former.[12] Two different quality basis sets were used. In a lowest level, which from now on will be referred to as basis set I, a primitive (3s 3p 4d) and (3s 3p) Gaussian basis set contracted to [1s 1p 1d] and [1s 1p] was used to represent the valence orbitals of rhodium[12a] and phosphorus,[12b] respectively, while the STO-3G basis set[13] was used for all hydrogens. In a higher level, which will be called basis set II, a modification of the former one was made by uncontracting the outermost d Gaussian of the rhodium atom (i.e., [1s 1p 2d]) and by using the 3-21G basis set[14] for the two hydrogens of the entering hydrogen molecule, while the STO-3G basis set was kept for phosphine hydrogens.

A first stage in the study consisted in constructing with basis set I a potential energy surface for the two isomeric structures by using as variables R_1 and R_2, namely the Rh–(center of H_2) and H–H distances, respectively. In a second phase, and with a start from the approximate minima found in the first study, the two minima were located exactly by using Schlegel's method.[15] Finally, minima found with basis set I were relocated with basis set II. With regards to geometry constraints, in the C_{3v} fragment, a completely rigid triangular base pyramid structure was considered, while in the C_{2v} system optimization of the bending angle of phosphines in the hydrogen plane was allowed. The Rh–P distance was kept fixed to 2.29 Å, as taken from the X-ray analysis of a similar compound, an octahedral dihydride of Rh(III) with chelating phosphored ligands.[16] For the PH_3 groups, the angles were assumed to be tetrahedral, and the P–H distance was taken to be 1.42 Å.

III. Results and Discussion

The presentation and discussion of the obtained results are divided in three sections, which contain respectively the geometrical parameters and energies, the electron density study, and the orbital analysis.

Geometrical Parameters and Energies. Figure 1 presents the bidimensional potential energy surfaces obtained through basis set I when the H_2 molecule approaches the $[Rh(PH_3)_4]^+$ system with C_{2v} (Figure 1a) and C_{3v} (Figure 1b) symmetry. The two variables chosen are the distance between Rh and H–H midpoint (R_1) and the H–H bond length (R_2). Although the variables chosen in both cases are the same, the difference between the two hypersurfaces is evident. The minimum turns out to be the dihydride in the C_{2v} symmetry and the molecular hydrogen complex in the C_{3v} structure, thereby in agreement with experimental results. This important fact confirms that, despite the introduced approximations (even use of minimal basis sets), the main aspects of the difference between the two cases are preserved.

Minima were located for the two symmetries with both basis sets by starting from an approximation obtained by inspection of the reduced potential energy surfaces. Optimized geometrical values are collected in Table I. The hydrogen atoms are closer to the metal and more separated in the C_{2v} complex than in the C_{3v} one, which correlates with the oxidative-addition process associated with the dihydride. The H–H distance (0.80 Å with basis set II) in the molecular complex is significantly longer than

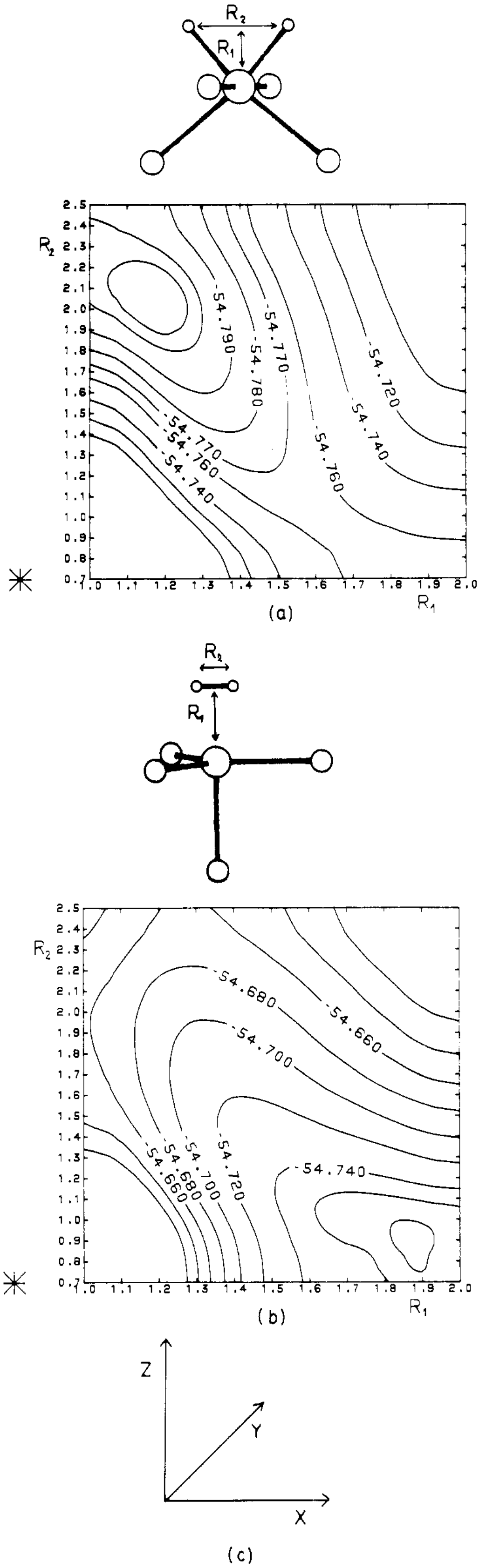

Figure 1. Potential energy surfaces obtained with basis set I for the $[Rh(PH_3)_4]^+ + H_2$ system with C_{2v} (a) and C_{3v} (b) symmetry. The coordinates are the defined in (c).

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Table II. Relative Energies (kcal/mol) of the Considered Systems

	basis set I	basis set II
C_{2v} $[Rh(PH_3)_4]^+ + H_2$	0.00	0.00
C_{3v} $[Rh(PH_3)_4]^+ + H_2$	1.80	10.11
C_{2v} $[Rh(PH_3)_4H_2]^+$	-33.41	-41.45
C_{3v} $[Rh(PH_3)_4(H_2)]^+$	-5.07	-10.53

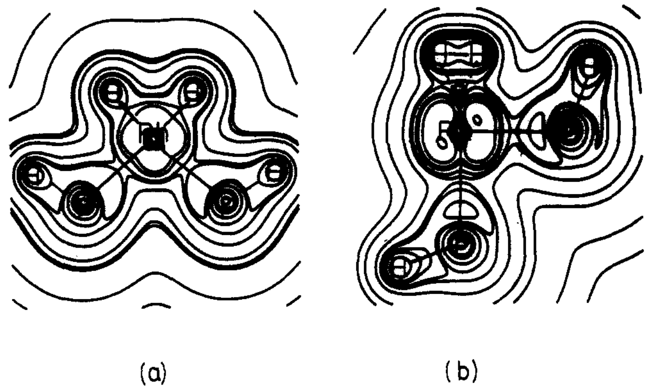
(a) (b)

Figure 2. Electron density plots for the $[Rh(PH_3)_4H_2]^+$ dihydride (a) and the $[Rh(PH_3)_4(H_2)]^+$ molecular hydrogen complex (b). Isodensity contours are given for density values of 0.00 01, 0.001, 0.01, 0.02, 0.05, 0.08, 0.09, 0.12, 0.14, 0.20 and 0.50 au.

in the free H_2 molecule, in good agreement with the experimental results for other complexes of this kind (0.82^{2} or 0.89^{6c} Å). In the dihydride, the computed Rh–H distance is in reasonable agreement with that reported for other rhodium hydrides (from 1.42 to 1.64 Å).[11,16,17] The computed bending angles of phosphines in the $[Rh(PH_3)_4H_2]^+$ dihydride are very close to those expected for an octahedral complex, with a small deviation that must be attributed to the different volume between hydrogen and phosphines. In particular, the values obtained for the H–Rh–H and P–Rh–P angles are 83.4 and 97.9° with basis set I and 83.1 and 98.7° with basis set II.

Table II collects the relative energies of the located minima. A general trend shown by both basis sets is that for the $[Rh(PH_3)_4]^+$ fragment, the C_{2v} structure is less than 15 kcal/mol more stable than the C_{3v} one. Likewise, the dihydride complex is much more stable (>25 kcal/mol) than the molecular complex. This is the first indication of a fact that will be proven by a posterior analysis: the molecular hydrogen complex, associated with the C_{3v} symmetry for the ML_4 fragment, will be accessible only when there is some problem in forming the C_{2v} structure. There are no experimental values to be compared with the computed energetics of the molecular hydrogen complex.[18] However, the well depth is close to those of 17^{5b} and 20^{10b} kcal/mol reported in previous theoretical studies for other molecular hydrogen complexes. The situation as far as the dihydride energetics experimental data is concerned is not much better. Anyway, a rough approximation can be made by taking into account that the dissociation energy of a transition-metal–hydride bond is estimated to be ca. 60 kcal/mol.[19] If 103 kcal/mol is taken as the dissociation energy for the hydrogen bond, and a simple algebraic operation is performed, the values for the rhodium–hydride bond in the calculations presented here can be evaluated to be 68 kcal/mol (basis set I) and 72 kcal/mol (basis set II), which are good enough for the introduced approximations.

A final analysis of the results presented in Tables I and II can be made by comparing the two basis sets. The fact is that the geometry and the energy of the molecular hydrogen complex are

Table III. Energies (au) Obtained with Basis Set II for the Selected Molecular Orbitals of the $[Rh(PH_3)_4]^+$ Complexes

	C_{2v} complex	C_{3v} complex
d_{xz}-like	-0.369 19	-0.551 86
$d_{x^2-z^2}$-like	-0.487 67	
d_{y^2}-like	-0.111 85	
$d_{x^2-y^2}$-like		-0.405 44
d_{z^2}-like		-0.059 90

far more sensitive to basis set extension than those of the dihydride.

Electron Density Maps. Figure 2 shows the electron density plots corresponding to the dihydride (Figure 2a) and the molecular hydrogen complexes (Figure 2b) computed with basis set II. The electron density collects the contributions from the molecular orbitals explicitly considered in the SCF calculation. That is, the existence of the core electrons, accounted for by the effective core potentials, is neglected. It must not affect the meaningful points of the map, which depend indeed on valence electrons.

It is worth pointing out here that a mere inspection of the two maps confirms the radically different nature of the compounds corresponding to each symmetry. The dihydride presents two typical Rh–H bonds, which are clearly localized. That is, the central zone of the straight line connecting the rhodium and hydrogen nuclei exhibits a minimum in a point that is a maximum in the perpendicular direction. In other words, it is a typical saddle point (a bond critical point in Bader's terminology),[20] indicative of simple bonding. The situation is not at all the same for the molecular hydrogen complex. There are bond critical points between the two hydrogens and between each of them and the rhodium nucleus, and there is a density local minimum (a ring point) inside the triangle defined by the three nuclei. That is, a three-atom cycle is formed. The existence of the incipient Rh–H bonds reflects the back-donation from the metallic fragment into the H_2 molecule and shows the subtle equilibrium mentioned above that the molecular hydrogen complex must keep to avoid evolution to dihydride. Finally, the low value of the electron densities in the bond critical points of the molecular complex compared to those in the dihydride demonstrates the weakness of the former system.

Orbital Analysis. The study of molecular orbitals and their evolution along chemical reactions is a fundamental tool for chemical comprehension that has been extensively used.[21] Although an accurate study of any system would demand the analysis of all orbitals, the study of a selected group of them usually allows a consistent and satisfactory explanation of experimental facts.

Before starting the detailed description of which orbitals have been chosen, we must state three considerations. First, to avoid an excess of information, this part will deal only with results obtained with basis set II. Second, only the $[Rh(PH_3)_4]^+$ fragment orbitals will be analyzed, because they are more adequate for comparison between the two isomeric structures; the noticeably different H–H distances could lead to misinterpretation should hydrogenated species be considered. Finally, we want to remind that the orientation is always that indicated by the axis depicted in Figure 1c.

In order to choose the meaningful orbitals to consider, a first selection is made by taking into account only those with a larger contribution of rhodium d orbitals. In both cases they happen to be the four highest energy occupied orbitals and the lowest unoccupied one. It is a perfectly satisfactory result, since the complexes are formally d^8. Two of these five orbitals are eliminated: those having a node in the incoming plane of the hydrogen molecule, i.e., the molecular orbitals that are fundamentally d_{yz} and d_{xy}, which are occupied. Thus, three orbitals are considered for each isomeric form, one unoccupied and two occupied.

The analysis that follows is divided in two subsections. The first one is concerned with π interactions and with back-donation

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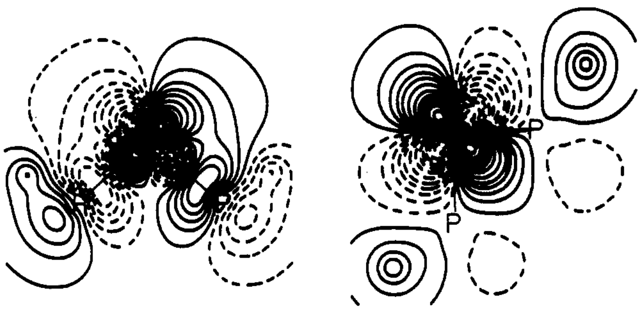

Figure 3. Representation in the *xz* plane of the main molecular orbitals of $[Rh(PH_3)_4]^+$ complexes implied in π interactions with H_2: on the left side, C_{2v} d_{xz}-like; on the right side, C_{3v} d_{xz}-like.

from the metallic fragment to the empty molecular hydrogen σ^* orbital. The second one deals with the σ interactions, related to the H_2 σ orbital.

π Interactions. It has been clearly established[5] that an excess in back-donation from the metallic fragment to the hydrogen molecule does not allow for molecular complex formation and leads to the dihydride. In fact, the back-donation is responsible for the change in rhodium formal oxidation state in the C_{2v} system. $[Rh(PH_3)_4]^+$, originally d^8, becomes d^6 in the dihydride $[Rh(PH_3)_4H_2]^+$ species, because the electrons in the d_{xz} orbital of rhodium are formally transferred to the hydrogen atoms, in such a way that they become hydrides.

The only selected orbital implied in a π interaction is precisely the d_{xz}-like one; Figure 3 shows these orbitals in the C_{2v} and C_{3v} $[Rh(PH_3)_4]^+$ fragments. Inspection of Table III, where the orbital energies are collected, shows a clear difference between them. In the C_{2v} fragment, this orbital, in fact the HOMO, has a far higher energy than that in the C_{3v} fragment. With no doubt, this energetic difference is due to the fact that the C_{2v} orbital is antibonding with the two bent phosphines in the direction of two of its lobes, whereas the C_{3v} orbital is nonbonding with all the phosphines.

If an occupied orbital that must interact with an empty one has a higher energy, the interaction will obviously grow. In this particular case, the bigger interaction leads to dihydride, so its correspondence with the C_{2v} symmetry is satisfactory. Therefore, the difference in π interactions correlates with experimentally observed tendencies. However, we think that the mere consideration of this interaction is not enough to explain the experimental behavior. For instance, it does not justify the molecular complex stability. The scheme will be completed with the study of the remaining interactions, performed in the following subsection.

σ Interactions. The σ interaction, that is, the electron donation from the σ H_2 orbital to the metallic fragment $[Rh(PH_3)_4]^+$ empty orbitals, is the main reason for the molecular hydrogen complex formation, i.e., the reason for its stability in front of the isolated species and the dihydride complex.[5]

It is not possible to compare directly each implied orbital of the C_{2v} fragment with those of the C_{3v} symmetry because they correspond to different hybridizations. Let us recall that the two molecular orbitals that remain to be analyzed must be the $d_{x^2-y^2}$- and the d_{z^2}-like. The fact is that in C_{3v} complex both orbitals can be recognized with this shape, but in the C_{2v} system they are recombined to give a couple of orbitals that could be identified as essentially $d_{x^2-z^2}$- and d_{y^2}-like.[22] This different behavior can be clearly observed in Figures 4 and 5, where the orbitals are represented in the *xz* and *xy* planes.

We think that the difference in electronic occupation of each symmetry complex is the key factor to explain their different behavior in front of the hydrogen molecule. Let us inspect thus the resulting situation for each case:

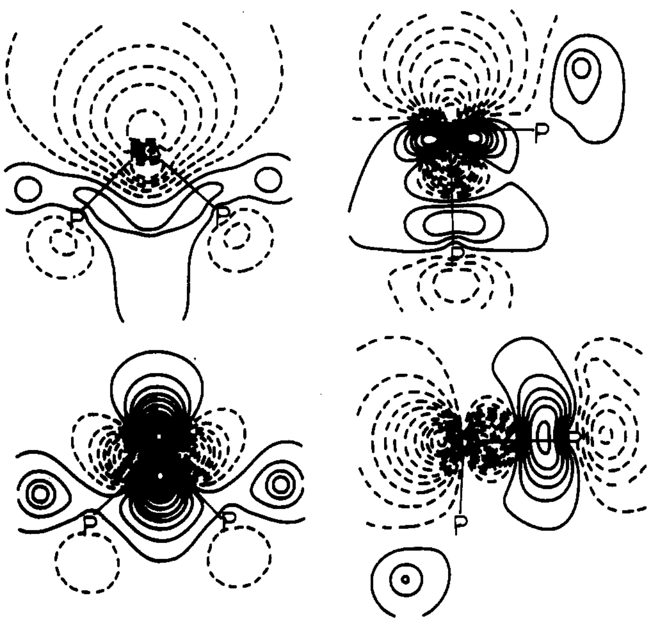

Figure 4. Representation in the *xz* plane of the main molecular orbitals of $[Rh(PH_3)_4]^+$ complexes implied in σ interactions with H_2. From the left to right side: above, C_{2v} d_{y^2}-like and C_{3v} d_{z^2}-like; below, C_{2v} $d_{x^2-z^2}$-like and C_{3v} $d_{x^2-y^2}$-like.

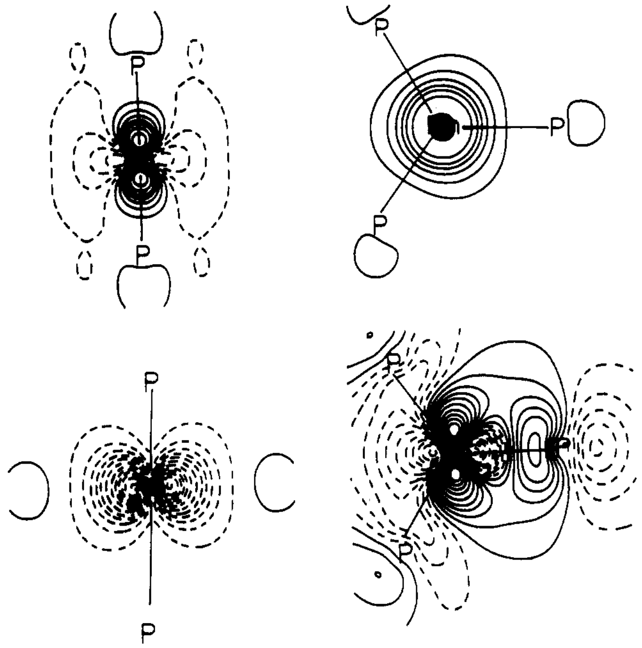

Figure 5. Representation in the *xy* plane of the main molecular orbitals of $[Rh(PH_3)_4]^+$ complexes implied in σ interactions with H_2. From the left to right side: above, C_{2v} d_{y^2}-like and C_{3v} d_{z^2}-like; below, C_{2v} $d_{x^2-z^2}$-like and C_{3v} $d_{x^2-y^2}$-like.

(a) C_{2v} $[Rh(PH_3)_4]^+$. The LUMO, which should receive the electrons from the hydrogen molecule, orients its larger lobes in the perpendicular direction. Furthermore, there is a relatively high-energy occupied orbital, the $d_{x^2-z^2}$-like one, oriented toward the vacant site of the coordination sphere. This last orbital will produce a strong repulsion with the H_2 σ orbital.

(b) C_{3v} $[Rh(PH_3)_4]^+$. The LUMO's most external lobe is oriented toward the vacant site, while the $d_{x^2-y^2}$-like orbital, in fact the HOMO, concentrates the major part of its electron density in another region of the molecule, thus minimizing the repulsions.

Analysis of σ interactions shows that there is always one of the two orbitals implied in σ interactions adequately oriented to interact strongly. When such orbital is occupied (C_{2v} fragment), the interaction with the H_2 σ orbital turns out to be destabilizing. On the contrary, when such orbital (C_{3v} fragment) is empty, it receives the electron donation of the H_2 σ orbital, thus leading

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(22) From a mathematical point of view, this d-orbital rehybridization is not problematic. Elementary calculations[23] show that $\{d_{x^2-y^2},d_{z^2}\}$ constitute the basis set of a vectorial subspace for which other basis sets could be chosen, e.g., $\{d_{y^2-z^2},d_{x^2}\}$ or $\{d_{x^2-z^2},d_{y^2}\}$.

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to stabilization of the molecular complex.

The preceding orbital analysis of σ and π interactions between an ML_4 fragment and a H_2 molecule may be related to the classical view of coordination in an ML_5 d^8 complex.[24] Rossi and Hoffmann have rationalized the preferred site (axial or equatorial) for a determined ligand, according to its electronic properties, in a d^8 ML_5 complex with a trigonal-bipyramid geometry.[24] Two conclusions turn out to be of special relevance to the present study: (a) the best σ donor occupies an axial position; (b) the equatorial π interaction is stronger than the axial. Coordination of the H_2 molecule with a C_{2v} ML_4 system would lead to a trigonal bipyramid with an equatorial H_2 molecule, whereas coordination with a C_{3v} ML_4 system leads to a trigonal bipyramid with an axial H_2 molecule. Since phosphines are better σ donors than a H_2 molecule, they will likely occupy the axial positions, so the H_2 molecule will occupy an equatorial site. The present results do not allow us to compare the different relative stabilities of the complexes with H_2 in either position, because placement of H_2 in equatorial site leads to dihydride. Axial placement of the H_2 molecule in the experimental complex[11] can be justified by the presence of strong steric requirements that make this position of H_2 the only available.

Regarding the π interaction, the present results agree completely with the aforementioned paper[24] in that the π interaction is stronger in the equatorial position than in the axial one. For the H_2 molecule, such interaction consists of a back-donation to the σ^* orbital. An excess of back-donation leads to the dihydride; as happens in this complex for the placement of the H_2 molecule in the equatorial site. Analysis by Rossi and Hoffmann of the stronger π interactions in the equatorial site is thus completely adequate for the present case. The orbital that accounts for such interaction in the C_{2v} fragment is clearly antibonding with both equatorial phosphines. Thus, it has a higher energy than it does in the C_{3v} fragment and can overlap much better with a π-type orbital, since it is hybridized away from the other equatorial ligands (see Table III and Figure 3).

IV. Conclusions

Through a study on the $[Rh(PH_3)_4]^+ + H_2$ system, we have explained the experimental results of Bianchini et al.[11] on the stability of the molecular hydrogen complex $[Rh(PH_3)_4(H_2)]^+$ vs the dihydride $[Rh(PH_3)_4H_2]^+$ when the ligands have a pyramidal C_{3v} structure around the metal and on the opposite stability when they have a C_{2v} structure.

Generalization of these results to other d^8 ML_4 complexes might be partially questioned by an interesting work published recently by Sweany et al.,[25] where synthesis of a C_{2v} symmetry $[Co(CH_3)(CO)_3(H_2)]$ complex is reported, as a first step toward formation of the dihydride. In this case, presence of π-acceptor ligands retards back-donation as we have explained before, thus favoring the existence of the molecular hydrogen complex.

Therefore, we conclude that if the d^8 ML_4 complexes adopt a C_{3v} symmetry structure, their preferred way to coordinate H_2 is the η^2 one; otherwise, the dihydride is more stable. The reason for the so recent synthesis of this kind of molecular complex must be attributed to the intrinsic instability of the C_{3v} geometry with respect to the C_{2v} one. In the case of the complex prepared by Bianchini et al., this instability is compensated by the strong steric requirements of the ligands.

Further work will analyze the influence of analogous effects on the mechanism and transition-state nature of typical oxidative-addition reactions of either H–H bonds or C–H bonds.

Acknowledgment. We are grateful to Prof. Y. Jean (Orsay, France) for helpful discussions. This work has been supported by the Spanish "Direcciôn General de Investigaciôn Cientîfica y Têcnica" under Project No. PB86-0529.

Registry No. $[Rh(PH_3)_4]^+$, 121176-09-8; $[Rh(PH_3)_4H_2]^+$, 121176-10-1; H_2, 1333-74-0.

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Platinum(III) in the REOA Mechanism of $PtCl_4^{2-}$ and $PtCl_6^{2-}$. A Pulse-Radiolysis Study

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Received November 18, 1987

In aqueous solutions $PtCl_4^{2-}$ is oxidized by OH to $PtCl_4OH^{2-}$ and $PtCl_6^{2-}$ reduced by e_{aq}^- or H to $PtCl_6^{3-}$. These Pt(III) species both react subsequently with H_2O to produce $PtCl_4(OH)_2^{3-}$ and H^+. All these processes are fast, whereas decay of $PtCl_4(OH)_2^{3-}$ by disproportionation is relatively slow. Kinetics of reactions and properties of intermediate species are described. The early stage of the reductive elimination/oxidative addition (REOA) mechanism of Pt(II) and Pt(IV) is proposed.

Introduction

About 30 years ago Rich and Taube[1] observed that labile Pt(III) plays an important role in exchange reactions of $PtCl_6^{2-}$. Grinberg and Shagisultanova[2] determined that exchange of bromide in $PtBr_4^{2-}$ and $PtBr_6^{2-}$ is mediated by a redox process. Since then, the problem of the reductive elimination/oxidative addition mechanism (REOA) has been the subject of numerous studies, summarized by Mason,[3] Peloso,[4] and Elding and Gustafson.[5] The participation of Pt(III) as an intermediate was usually not discussed.

In general, within the REOA mechanism the processes involving Pt(II) are described as oxidative addition to the square plane and as the elimination of ligands from the reduced octahedron of Pt(IV). In both cases, the initial fast reaction is followed by subsequent ligand exchange, which may be less rapid.

The technique of pulse radiolysis is very suitable for studying redox reactions in aqueous solutions. Pt(III), a logical intermediate

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