Transition Metal Polyhydrides: From Qualitative Ideas to Reliable Computational Studies[†]

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I. Introduction

Why should we, as theoreticians, bother about transition metal hydride complexes?

A. Hydride Is the Smallest Ligand and the Only One To Make a Pure Single Bond to a Metal

Hydride is the ligand with the smallest number of valence electrons and thus an ideal choice for a precise calculation. An H-containing transition metal system (MnH) was among the first species for testing the performance of ab initio computational methods on transition metal systems.[1] Since hydride can only make a single bond to a transition metal center and has minimal steric influence, it is also the ideal ligand for establishing a basic bonding pattern associated with a given metal and coordination sphere. It has thus been a ligand of choice for EHT molecular orbital analysis. It is also an ideal ligand for establishing symmetry arguments and valence bond analysis. Hydride is the least computationally costly model for any σ donor group and has been used in ab initio calculations in particular to represent alkyl groups. Finally, it is a crucial computational benchmark
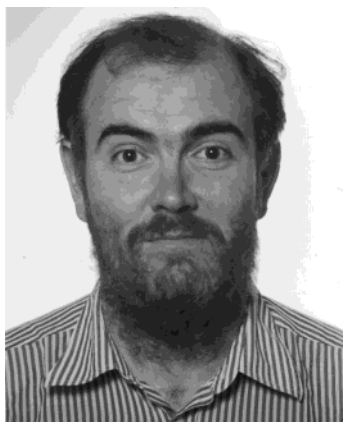
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ligand. The comparison of metal—X- with metal—H-containing complexes has led to a better understanding of the role of X as a σ or π ligand. Such a comparison is not always feasible via experimental studies due to synthetic difficulties. This is thus the extension to transition metal chemistry of the type of modeling done by theoreticians in the early period of organic chemistry when H was used to represent a large number of chemical groups.

B. H Is Easy To Locate through Quantum Calculations but Hard To Locate through Experimental Techniques

Whereas there is, in general, no intrinsic difficulty in calculating an H-containing complex and in ob-taining a good structure through optimization, the experimental location of H has presented some significant challenges and difficulties. The commonly used X-ray diffraction method does not properly locate a hydrogen center. Neutron diffraction is optimal, but the difficulty of growing large mono-crystals associated with the limited availability of the international neutron diffraction facilities has probably discouraged a number of experimentalists. Only a few dozen neutron studies have been carried out on transition metal hydrides[2] in contrast with the many thousands of X-ray structures. NMR spectroscopy has been an invaluable tool for getting struc-

tural information, but it does not give the detailed geometry of the complex. We strongly believe that computational chemistry is presently a low-cost high-quality technique for structural determination in transition metal complexes having the greatest impact for metal hydrides. Calculations have in fact been used to correct a structure determination wrongly assigned by X-ray crystallography[3] and even to find missing hydrides in a binuclear complex.[4]

C. Hydride Complexes Are Full of Surprises

In the wealth of experimental results in transition metal chemistry, the hydride ligand has been the one that has led to the largest number of surprising findings. Even though the first metal hydride was reported as early as 1931,[5] the field continues to surprise the chemical community. While only classical polyhydride complexes were recognized till 1984, the discovery of the first dihydrogen complex by Kubas and co-workers[6,7] has resulted in a continuing burst of activity and a new perspective in the field of polyhydride chemistry. Although metal−hydride bonds are very strong—in fact among the strongest metal−ligand bonds[8]—H ligands seem to be able to trade places in the coordination sphere with amazing facility. Whereas in a vast number of complexes, T_{1min}[9] and J_{HD} NMR coupling constants[10,11] give reliable H−H distances, recent work has shown abnormally large J_{HH} values, which could have been wrongly interpreted in terms of an H−H distance less than in free H_2.[12,13]

While hydrogen bonding has been seen for many years between a lone pair of X and a polar H−Y bond, it has recently been discovered that a H···H bond is also possible between a hydridic M−H center and a polar H−Y bond.[14,15] Although the calculation of the electronic wave function has been sufficient to obtain the position of the nuclei for almost all calculated molecules, some recently discovered hydride complexes seem to defy this approach (the elongated H−H bond).[16] These are only some of the highlights among the reasons that have kept theoretical chemists working in this field.

D. H_2 Is the Ideal Model for a σ Bond Coordinating to a Metal

A number of *unsaturated* carbon-based ligands (olefin, alkyne, benzene, etc.) are known to make stable complexes, whereas the coordination of a *saturated* organic ligand without π-bonding electrons or an active lone pair (e.g., CH_4) is a kind of a holy grail for transition metal chemists. The coordination of alkanes to a transition metal center has been especially sought as giving information on the factors that could cleave especially inert bonds, and evidence for alkane coordination has been shown to occur only very recently.[17−20]

The discovery by Kubas and co-workers that H_2 could coordinate to a transition metal while maintaining its H−H bond shook the community of transition metal chemists. Maybe even more remarkable was the fact that theoreticians first suggested that H_2 could make a stable complex with a transition

metal. The possibility of a stable Pd−H_2 interaction was studied first by CNDO calculations and then by simple ab initio calculations.[21−25] A detailed qualitative extended Hückel analysis of the bonding of H_2 and CH_4 to transition metal centers led Saillard and Hoffmann[26] to suggest the possibility of a stable H_2 complex at the same time the Kubas complex was published. It is clear that, in this field, theory and experiments have run parallel and, more important, hand in hand.

E. H_2 Is the Ideal Model for Activation of a Single Bond

Understanding how a transition metal could cleave a strong single bond is fundamental to the understanding of any catalytic step. H_2 is certainly the ideal system to study because high-quality calculations can be applied with reasonable computational effort to the determination of the transition state for cleaving H_2. This also gives an important benchmark for comparison with activation of other bonds.

F. Scope and Limitations of the Review

There are therefore many reasons for theoreticians to have been (and still to be) interested in the deceptively simple case of transition metal hydrides. With few exceptions, this review is limited to molecular transition metal complexes containing only one metal. The numerous studies of clusters and of solid-state chemistry have been left aside; some of them are part of other reviews in this issue. The theoretical studies of both short-lived and long-lived species, which have been identified either in the gas phase or in solution, have been included. With rare exceptions, we have also excluded monohydride species. In the section on reactivity, we have limited our presentation to that part of the reaction scheme involving H_2 and have thus excluded all studies of reaction between a unique M−H bond and another ligand.

The experimental references are limited to those closely related to the calculated systems. For additional information on the experimental aspects, the interested reader should refer to the following reviews (inter alia): structures of metal hydrides,[2] dihydrogen complexes,[9−11,16,25,27−29] polyhydride complexes,[30] dynamics of polyhydrides complexes,[31] NMR quantum exchange coupling,[32] dihydrogen complexes in catalysis,[33] and the reactivity of metal hydrides with acid.[34] Furthermore, an especially useful description of the theoretical calculations in transition metal polyhydrides can be found in the book edited by Dedieu[35] and in the review by Lin and Hall.[36]

II. Small Gas-Phase Systems

Gas-phase transition metal ion chemistry has experienced a tremendous growth in the last few decades.[37] The study of transition-metal-containing ions in the gas phase offers the opportunity to probe the chemical properties of these species in the absence of complicating factors such as solvation. However, this usually comes at the cost of eliminating ancillary ligands on the metal, which therefore

remains in a highly unsaturated state, and may not necessarily constitute a good model for the more saturated systems usually found in solution. Hydrogen, as the simplest chemical substituent, has been present in a large number of these experimental studies. Consequently, it has also been the subject of a large number of theoretical studies.

Systems described in this section differ from those of the following sections. The high unsaturation of the experimental gas-phase ions usually implies the presence of low-energy excited states. This requires the use of very high level computational methods that can be applied only on small-size systems.

Although this review is focused on polyhydride systems, mention needs to be made of some diatomic M−H systems. These are among the first transition metal molecules studied with ab initio computational methods. One should cite the early efforts in the 1970s by Bagus and Schaefer,[1] and by Scott and Richards,[38] using HF wave functions. The need for electron correlation, both dynamical and nondynamical, became progressively clear in the following years through the studies on VH,[39] ScH,[40] and NiH.[41] By 1983, Walch and Bauschlicher[42] were already able to carry out a systematic study on the properties of TiH, VH, CrH, MnH, FeH, and NiH with a CASSCF/CI method. They found a strong admixture of terms from the $4s^2 3d^n$ and $4s^1 3d^{n+1}$ states of the transition metal atom, whose precise contribution depends on the metal. A later paper by Bauschlicher[43] further analyzed the methodological requirements for an accurate study of unsaturated transition metal monohydrides through a full configuration interaction benchmark calculation for TiH. This system required substantial amounts of both dynamical and nondynamical electron correlation, and the conclusions were that CASSCF/MRCI followed by natural orbital iterations provided optimal results—better than CPF or MCPF approaches.

Research has continued unabated on the subject of hydrogen−metal diatomics,[44−46] but it is not discussed in detail here. However, mention needs to be made of the systematic study by Goddard and co-workers[47−50] on 30 MH$^+$ diatomics of the d block transition metals. The study of these species with the GVB method led the authors to the finding that the metal valence orbital involved in the bond has a mixture of valence s and d character, with little p participation. The relative amounts of s−d hybridization vary considerably among the rows, the lowest d participation corresponding to the first transition metal row. It was shown that the strong variations of M−H bond energies that were found originated from two factors: (i) the change in exchange energy upon binding of hydrogen and (ii) the promotion energy to obtain an atomic configuration suitable for bonding.

Studies of small gas-phase systems, in which more than one hydrogen atom is attached to the metal, are also abundant. They can be classified in three groups: (i) pure hydride systems with no direct H−H interaction, (ii) "molecular hydrogen" systems, with a H−H bond, and (iii) complexes with hydrogen

atoms occupying a bridging position between metal centers.

A large number of calculations on pure hydride systems have been carried out on neutral triatomic MH$_2$ species, probably because of their simplicity. Most of this work focuses on the study of the formation of a dihydride complex from the reaction of H$_2$ with the metal atom. In many cases, the goal of these studies was to model the interaction of H$_2$ with a metal surface. Although the modeling was later improved in calculations with metal clusters, the studies on gas-phase systems have given rise to a better understanding of the nature of bonding in dihydride complexes. Representative studies were carried out in the early 1980s on NiH$_2$, CoH$_2$, FeH$_2$, and CuH$_2$ at the CI level by Siegbahn and co-workers.[51,52] The authors concluded that the most stable electronic state was the linear high-spin state, although they focused the analysis on the bent low-spin state, which they felt would better model the electronic properties of a metal surface. Ni, Co, and Fe showed a similar behavior in their reaction with H$_2$, but Cu behaved quite differently. The M + H$_2$ reaction was thoroughly studied in the late 1980s and early 1990s for a number of second- and third-row transition metal atoms by Balasubramanian and co-workers.[53−61] Their calculations included dynamical and nondynamical correlation, as well as relativistic corrections. For a significant number of metals, the H−M−H angle was calculated to be fairly large although a big variation in this angle was found. The insertion does not require a barrier for all metals. Other authors have also analyzed the insertion of metals (such as Fe),[62,63] and of the series Re, Os, Ir, and Ru into H$_2$.[64]

The electronic structure has been discussed in more detail for some triatomic MH$_2$ systems. Siegbahn[65] analyzed the sequential bonding energies of the two hydride ligands in MH$_2$, in which M is a second-row transition metal, and found that they are much more similar than the bonding energies of difluoride and of dichloride systems. Other authors have studied the properties[66] of a number of early first-row transition metal dihydrides including the fine-structure effects[67] in the vibronic spectrum of FeH$_2$ and FeD$_2$.

Calculations on small transition metal polyhydrides have also been informative as tests for the importance of relativistic effects. Dyall[68] analyzed the ground state of PtH$_2$ and several low-lying states of PtH$^+$ and PtH with an all-electron basis set. He reached the conclusion that any treatment of Pt compounds should treat relativistic effects explicitly. This view was partially corrected later by Hertwig et al.,[69] who have shown through calculations on WH$_6$ that relativistic effects can be introduced in a sufficiently accurate way through the use of relativistic effective core potentials. A methodological discussion has also taken place recently on the ground state of NiH$_2$ that had been assigned[52] in 1984 as a triplet with a linear structure, and was considered as such until this assignment was recently challenged by experiment[70] and high-level calculations,[71,72] which showed that the ground state of NiH$_2$ is actually a singlet with a bent geometry. NiH$_2$ was also used as

a benchmark for the performance of natural population analysis on transition metal compounds.[73]

As the size of the polyhydride systems grows, the studies quickly become concerned with structural models in which hydride is used as a generic ligand, or with models of saturated complexes in solution. These subjects are addressed in the following sections. One borderline case has been treated by several groups,[74−77] most notably Schaefer and co-workers,[78,79] on TiH_4 and related species. TiH_4 has been observed in krypton and argon matrixes.

Molecular hydrogen complexes, where a dihydrogen molecule is coordinated to a metal center without breaking the H−H bond, were originally discovered in 1984 in large saturated complexes.[6,7] For this reason the first dihydrogen complex to be calculated had the metal saturated by spectator ligands. Coordination of H_2 to $M(CO)_5$ (M = Cr, Mo, W) was also observed through matrix isolation[80,81] and gas-phase reaction.[82,83] Some of the first complexes to be calculated by ab initio methods involved Cu.[84,85] In the case of $Cu(H_2)Cl$, the geometry and frequencies were found in good agreement with experimental data obtained in an argon matrix.[85] This neutral system is not representative of the large number of studies of gas-phase transition metal dihydrogen complexes, which are usually cationic. Different authors have analyzed the interaction of dihydrogen with Cr^+ and CrH^+,[86] with FeO^+,[87] with Co^+,[88] with Ni^+,[89] and with V^+.[90] Highly relevant studies have been carried out by Bauschlicher, Maître, and co-workers in collaboration with the experimental group of Bowers.[91−98] These authors have examined the sequential interaction of a naked first-row transition metal with an increasing number of dihydrogen molecules (up to 6). They found that the interaction of dihydrogen with a metal has an important covalent component, in contrast with what happens with alkali metal ions. Important differences in behavior are found for the different metals, with the limiting case of Sc^+ which is able to insert into the H−H bond, producing a dihydride. From the variety of data on different metals, the authors identified the main contributions to the M−(H_2) interaction, which are summarized in a recent paper[98] as follows: (i) donation from the H_2 σ orbital to the metal to stabilize the ion charge; (ii) back-donation to the H_2 σ^* orbital from metal occupied d_π orbitals; (iii) hybridization between the $3d_{z^2}$ and 4s orbitals, in case the $3d_\sigma$ orbital is half-filled; (iv) a minor contribution from hybridization with 4p orbitals, despite the fact that they are significantly higher in energy; (v) a minor contribution from electrostatic noncovalent interactions, such as a charge-induced dipole and a charge quadrupole.

Regarding bridging hydride ligands, the presence of two metal atoms makes these systems hard to access in the gas phase, but the experimental observation of gaseous titanium tris(tetrahydroborate) and the presence of unexplained signals in the IR spectra from Ti/H_2 matrix experiments have prompted the theoretical study of a number of titanium systems of this type by the groups of Gordon[99,100] and Ugalde.[101−103] Studies have been carried out on H_3-TiX systems, with X = BH_3, AlH_3, GaH_3, CH_3, SiH_3,

TiH_3, among others. The hydride ligands take bridging positions in a number of cases. The discussion on Ti_2H_6 has been particularly informative regarding the methodological subtleties involved in this type of system. The original assignment of a singlet C_{3v} structure obtained by using a single-determinant closed-shell reference wave function[101] has been recently proved false by multiconfigurational calculations that yield a C_s triplet as the most stable structure.[100]

The brief summary of results on small gas-phase polyhydride molecules presented in this section shows that most of the situations, which can be found in larger saturated systems, are already represented in small molecules. The introduction of additional ligands, giving rise to complexes usually found in solution, changes the behavior observed for the small ligand-free polyhydrides sometimes in subtle and sometimes in major ways (see the following sections).

III. H as an Ideal Ligand

A. General Approach for Bonding in Transition Metal Complexes

The replacement of a large variety of σ-bonding ligands by a hydride, which can only make a σ bond to a metal, has led to the establishment of fundamental electronic patterns associated with the transition metal center, the coordination sphere, and the number of valence electrons as obtained by the angular overlap model[104] or extended Hückel calculations.[105] This idealization is the basis of the isolobal analogy.[106]

The validity of the replacement of ligands by hydrides was tested for a few systems in an earlier period in the history of ab initio calculations. In a study devoted to understanding hybridization effects on metal−ligand bond lengths in cyclopentadienyl (Cp) complexes, $X_3Ti−CH_3$, $X_2Ti=CH_2$, and $XTi≡CH$ (X = H, Me, F, Cl) were calculated at the HF level.[107] It appears that all of these X ligands properly establish the hybridization of the metal that would have been produced by cyclopentadienyl (Cp), and the variation in Ti−C bond length going from alkyl to carbyne is also properly reproduced. A similar approach was chosen by Streitwieser et al.[108] in a study of hydrogen exchange reactions at group 3 and group 4 metals in comparison to those at alkali metals. High-level calculations on MH_3, on MH_4, and of the reaction of these species with H_2 were carried out. The formation of weak complexes (0.1−3 kcal·mol^{-1}) was established at the CISD+Q level. The barrier for exchange is shown to increase from group 3 to alkali metal and finally to group 4 transition metal hydrides. The electrostatic contribution to bonding in these systems has been discussed.

The factors that control the shape of molecules have been the focus of recent work associating geometry optimization (B3LYP) of a large variety of neutral and charged hydrides MH_n^q with a valence bond analysis.[109−112] It appears that a simple VB analysis can explain the shape of such complexes as well as the shape of main group compounds. It has been shown that Lewis-like structures and rather

simple bond hybridization rules apply to transition metal hydrides. In the cases where covalent bonding dominates, sd^n hybridization determines the structure and there is little valence p orbital participation. In the case of hypervalent metal complexes, it is suggested that the metal center does not expand its valency through the use of valence p orbitals either. Instead three-center four-electron bonding interactions occur, which leads to significant analogies between hypervalent main group and transition metal complexes. These studies led the authors to point out that most of the transition metal complexes are hypervalent since they have more than 12 electrons in the valence space. Ternary metal hydrides were also studied by molecular orbital analysis[113] and valence bond analysis.[112]

A different point of view was recently presented by Bayse and Hall.[114] Using a symmetry-based analysis method (ORSAM or orbital ranked symmetry analysis method), they could account with success for the geometry of 114 simple polyhydrides. In this model, $(n+1)$s and nd orbitals are used before $(n+1)$p orbitals. Nonbonded metal electrons (lone pairs) are accommodated in pure d orbitals. In contrast to the study of Landis and co-workers,[109−112] metal p orbitals are used where the number of ligands exceeds the number of s and d orbitals available for bonding. In this model, there is thus no necessity to invoke hypervalency in transition metal complexes.

B. The d⁰ ML₆ Case

The correspondence between the structure of a pure polyhydride complex and that of a real system is a crucial problem for theoreticians. The hydride is in general found to be a good model both for bulky and for nonbulky alkyl groups.[111] Ligands carrying π orbitals are usually poorly represented by hydrides, as expected from their inability to make d_π/p_π interactions. This comparison has been the focus of a long-standing discussion in the literature about d⁰ ML₆ structures. This topic is very representative of the validity of modeling ligands by hydrides.

The first proposal that d⁰ ML₆ complexes may not always be octahedral derived from an extended Hückel calculation[115] for TiH₅(C₂H₅)²⁻, as a model for Ti(dmpe)Cl₃(C₂H₅). In this study it was suggested that TiH₆²⁻ has a trigonal prismatic structure with nonequivalent triangular faces (see the related case of WH₆ in Chart 1).

Chart 1

Calc.   **Exp.**
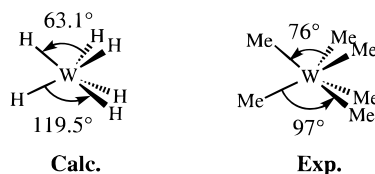
This finding was in disagreement with the VSEPR rules.[116,117] Several quantitative calculations were consequently carried out. The octahedral shape was calculated to be preferred over the trigonal prismatic structure for TiH₆²⁻ although the difference in ener-

gies between the two structures was found to be dependent on the level of calculations.[118,119] In contrast, the neutral CrH₆, MoH₆, and WH₆ complexes were shown to be nonoctahedral at any level of calculations (Chart 1).[109,120−123] Cations such as TcH₆⁺ [109] and monoanionic complexes such as VH₆⁻ [119] were also calculated to prefer trigonal prismatic geometries (although distorted). The importance of including the correlation energy to get a proper estimate of the relative energies of several possible structures was pointed out.[119,122] The most stable geometry of WH₆ is close to the calculated structure of WMe₆.[121,124] According to the calculations of Albright et al.,[121] the potential energy surface for WH₆ presents a large number—up to 20—of secondary minima, which is not the case for WMe₆. Kaupp[124] has shown that all M(Me)₆^q (M = group 4, 5, 6; q = −2, −1, 0) are either distorted trigonal prismatic (C_3) or prismatic (D_3). While the structure of WMe₆ was not known with certitude and the limited spectroscopic data were not in contradiction with an O_h geometry,[125] definitive experimental proof of the nonoctahedral structure of WMe₆ came first from an electron diffraction study in the gas phase[126] and more recently from a crystal structure determination (Chart 1).[127,128]

As expected, hydride is a very poor model for any ligand that has one or more π bonds or lone pairs, and for example, MF₆ has been calculated to be octahedral.[120,121,123,129,130] With other ligands such as acetylide[131] or alkoxide,[132] a structure intermediate between trigonal prismatic and octahedral may be adopted. Although ionic factors play a role in favoring an octahedral geometry, the nonoctahedral geometry of d⁰ MH₆ and MMe₆ has been attributed to a second-order Jahn–Teller distortion, which allows better bonding by the d metal orbitals.[109,110,114,115,120,121] The second-order Jahn–Teller effect has also been discussed by Bayse and Hall[133] for several hydrido complexes including d⁰ MH₆. The presence of a π donor ligand changes the bonding pattern by using the d orbitals of the metal through d_π/p_π bonding. Likewise adding d electrons to make d¹ or d² complexes decreases the preference for a trigonal prismatic structure.[124]

C. The d⁶ ML₅ Case

The structure of this family of unsaturated 16-electron species was properly understood by comparing the hydrido species with the real systems. Whereas saturated d⁸ ML₅ complexes have a trigonal bipyramidal structure, this is not the case for complexes with two electrons less. The highly reactive Cr(CO)₅, which was assigned a square pyramidal structure (rare gas matrix studies), initiated some theoretical arguments in the literature (Chart 2).[134,135] The

Chart 2
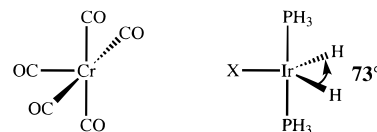
square pyramidal structure was the only known

structure in a larger number of complexes until the publication of the X-ray structure of Ir(H)(Ph)ClL$_2$.[136] This complex is best viewed as a distorted trigonal bipyramid with a strongly acute angle (around 75– 80°) between the equatorial H and Ph ligands. Extended Hückel calculations[137,138] followed by an ab initio HF study[139] of IrH$_3$(PH$_3$)$_2$ and IrH$_2$X(PH$_3$)$_2$ (X = Cl, NH$_2$) show that the replacement of H by X has important consequences for the structures. Whereas the trihydride complex has a preference for a square pyramidal structure with an apical hydride, the presence of a π donor ligand X leads to a preference for a distorted trigonal bipyramidal structure with an H–Ir–H angle around 80°, analogous to the H–Ir–Ph angle found experimentally for Ir(H)(Ph)-ClL$_2$ (Chart 2). The square pyramidal structure was also called the T structure (from the geometry adopted by the three H atoms), whereas the distorted trigonal bipyramid was called the Y structure from the shape made by the two H atoms and the X ligand. Neutron diffraction studies of IrH$_2$Cl(P^{t}Bu$_2$Ph)$_2$ confirmed the calculated Y structure,[140] and further calculations (B3LYP), including the real experimental phosphines, reproduced well the detailed shape of the complex.[141] As will be mentioned in section IV, although PtH$_3$L$_2$$^+$ and IrH$_3$L$_2$ are isoelectronic, they are not isostructural.

D. Other Systems

The most stable minimum for TaH$_5$ was shown to be similar to the optimal structure of TaMe$_5$.[142] In agreement with electron diffraction studies,[143] the structure is square pyramidal and not trigonal bipyramidal.

The enneahydridorhenate dianion ReH$_9$$^{2-}$ is the only mononuclear complex with nine hydrogen atoms. A neutron diffraction study has shown the molecular structure to be a tricapped trigonal prism (D_{3h}, Chart 3).[144] The structure of ReH$_9$$^{2-}$ was optimized within

Chart 3
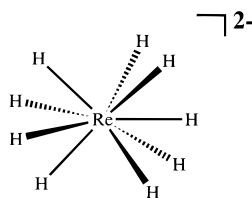
D_{3h} symmetry with all-electron, nonrelativistic SCF calculations with large basis sets.[145] This very large calculation—at this period—led to good agreement with the experimental data for the structure and for the vibrational frequencies. As mentioned, the good agreement at the RHF level might have come from an accidental cancellation of relativistic and of electron correlation contributions. Calculations (MP2) with relativistic pseudopotentials also gave good structural results.[114]

Exploration of potential energy surfaces with hydride as a model for the real ligand has been carried out. Minima, unrealistic with the real ligand, can appear for the all-hydrido systems (20 secondary minima in CrH$_6$, 9 minima in WH$_6$ with no cor-

respondence in WMe$_6$).[121] However, all these species have the same global minimum. Even with this caveat in mind, the unusual fluxional behavior of M(O)Me$_4$ (M = W, Re) was successfully studied through calculations on M(O)H$_4$.[146]

IV. "Computational Crystallography" of Hydride Complexes, a Cost-Effective Method for High-Quality Structural Determination

As mentioned in the Introduction, hydrogen centers are especially hard to locate experimentally, and nonempirical quantum calculations have been the most cost-effective high-quality technique for precise location of the position of this nucleus. An undoubted recognized success of MO and more recently of DFT methods has been to provide highly accurate structures for transition metal complexes of rather large size. The success of "computational crystallography" can only expand in the coming years. It should also be noted that, in the vast majority of calculations, all bulky ligands have been replaced by smaller models for the sake of computational time. Although many excellent results have been published with this drastic simplification, an increasing number of cases have appeared recently that illustrate the limitations of such a model. In the second part of this section, we present some studies in which the real ligands have been fully implemented. A more detailed presentation of the methods used for treating realistic ligands has been the subject of a review.[147]

## A. Good Success with Simplified Models

While the earliest calculations were carried out at a level significantly inferior to the present standard, the successful results of this pioneering period were important in increasing our confidence in the validity of moderate quality calculations (HF calculations, optimization with geometry constraints) on systems much larger than those described in section II. One of the first studies concerned the comparison of *cis*- and *trans*-dihydrides of Pt(PH$_3$)$_2$H$_2$. Keeping several constraints such as planarity of the coordination at Pt, the metal–ligand distances and ligand–metal–ligand angles were optimized in successive steps at the HF level.[148] This led to the trans isomer being more stable, in agreement with experiment. The structure of ReH$_7$(PPh$_3$)$_2$ led to several arguments due to different interpretations of the NMR T_{1min} relaxation time.[29,149–152] A neutron diffraction study on ReH$_7$(dppe) (dppe = 1,2-bis(diphenylphosphino)-ethane) reported a nine-coordinate polyhydride.[153] The model complex ReH$_7$(PH$_3$)$_2$ was optimized[154,155] as a nine-coordinate structure with C_{2v} symmetry, in good agreement with the experimental values for ReH$_7$(dppe). A dihydrogen complex and a bis(dihydrogen) form were investigated and were found to be less stable than the heptahydride.[155] In contrast, a dihydrogen complex was found to be preferred for technetium (structure experimentally unknown).[155] The structure of ReH$_7$L$_2$ (L = trisarylphosphine) was shown however to be very sensitive to the nature of the phosphine ligands, with the internuclear distance between two of the hydrides varying from 1.24 to 1.42

Å.[156] The ease for varying this H−H distance is addressed in section IX.

Full optimization of geometry at a good level of calculation is demanding in computing time and has only recently become a systematic procedure. An efficient way to locate the hydrides was thus to optimize their position by fixing the position of all heavy atoms as given by X-ray diffraction. This method has been used to locate the hydrides in ReH_2-$(SiH_3)(CO)(PH_3)_3$ as a model for $ReH_2(SiPh_3)(CO)$-$(PMe_2Ph)_3$ and in $ReH_6(SiH_3)(PH_3)_2$ as a model for $ReH_6(SiR_3)(PPh_3)_2$.[154] The calculated positions agreed with the structures by Crabtree and co-workers[157,158] on the basis of NMR data. The calculations suggest the presence of some Si···H interactions, a problem that would be the concern of several studies in the following years.[159,160]

The study of $[Os(PR_3)_3"H_5"]^+$ nicely illustrates the method used in the absence of any structural information. The structure of this complex was studied by calculations[161] prior to the publication of the neutron diffraction results. From an NMR study[162] and from the neutron diffraction data[163] on the isoelectronic neutral $Re(PR_3)_3H_5$ system, a pentahydride structure was thought to be likely. The search for the structure of $[Os(PR_3)_3"H_5"]^+$ illustrates the precautions necessary in a search for the absolute minimum. Locating *any* minimum by theoretical methods does not ensure the absence of a lower minimum in a totally different region of the potential energy surface. The gradient minimization procedure is blind to the existence of multiple wells. It is thus necessary to start with different likely geometries (guesses) and optimize each one. Chemical knowledge remains the most reliable guide to avoid missing a reasonable geometry. Complexes having coordination number 8 are a good example where chemical intuition may be lacking and a systematic procedure can thus be implemented. Twenty-two different initial structures were thus considered for $[Os(PR_3)_3"H_5"]^+$. Six-coordinate bis(dihydrogen) and seven-coordinate dihydrogen structures were eliminated by a combination of RHF optimizations and single-point MP2 calculations. It was also recognized that RHF was inappropriate for optimizing the geometry of these transition metal complexes. Full MP2 optimizations were thus carried out on five guesses of eight-coordinate complexes, leading unambiguously to a dodecahedral structure (Chart 4) very similar to that

Chart 4

H_1-Os-H_2 = 58.2°
H_3-Os-H_4 = 62.5°
H_4-Os-H_5 = 69.1°
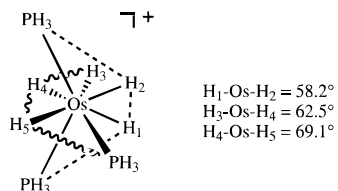
of $Re(PR_3)_3H_5$. One year later the publication of the neutron diffraction study[164] of $[Os(PMe_2Ph)_3H_5]^+$ gave full credit to the theoretical calculations. Optimization (B3LYP) of $[Os(PH_3)_3H_5]^+$ gave essentially the same structure with minor variations in bond angles.[164] The sensitivity of the structure to chemical

changes is illustrated by the fact that neutral $OsCl(PH_3)_2(H)_5$ has been shown (B3LYP) to be a dihydrogen complex in which H_2 takes one basal site of a pentagonal bipyramid whose apical sites are occupied by PH_3.[165] This result is in agreement with ^1H NMR analysis.[166]

Some features of seven-coordination have been investigated for $Os(PH_3)_3H_4$.[167] Neutron diffraction data[168] were available (PMe_2Ph as phosphine) to serve as calibration. The calculations confirm the necessity for using post-HF level methods and unequivocally establish the preference for a pentagonal bipyramid with formally neutral ligands (PH_3) in the axial sites and formally negative ligands (H^-) in the equatorial sites. A preference for an equatorial site was also found for SiH_3, CH_3, BeH, and Li, whereas BH, NH_3, Be, and He all prefer an axial site.

An X-ray structural determination of $OsH_3(CO)$-$(SiHPh_2)(P^iPr_3)_3$ located all heavy atoms arranged in a distorted trigonal pyramid geometry around Os. MP2 full optimization of $OsH_3(CO)(SiH_3)(PH_3)_3$ gave a structure with three chemically inequivalent hydrides in agreement with the ^1H NMR of $OsH_3(CO)$-$(SiHPh_2)(P^iPr_3)_3$. Different starting geometries were tested, and all converged to the same structure, providing good support for the uniqueness of the minimum structure.[169]

The NMR spectrum of $PtH_3(P^tBu_3)_2^+$ at low temperature suggests the presence of a coordinated H_2 trans to a hydride. MP2 calculations[170] on PtH_3-$(PH_3)_2^+$ supported the characterization of this species, which was the first square planar dihydrogen complex (Chart 5). Interestingly the isoelectronic IrH_3-

Chart 5
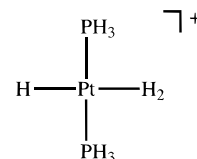
$(PH_3)_2$, not observed experimentally, has been optimized as a trihydride.[139]

The coordination of Si−H bonds to the metal has been the subject of only a few studies. The calculations have supported the experimental finding that Si−H can coordinate to a metal and still maintain some Si−H bonding. One calculation, which can be compared directly to that of a real system, is that of $Ru(H)_2(PH_3)_2(\kappa-\eta^2$-H···$SiH_2$−$C_2H_2$−$SiH_2$···H) shown in Chart 6.[171] In the experimental complex, the X-ray

Chart 6

Exp.   **Calc.**
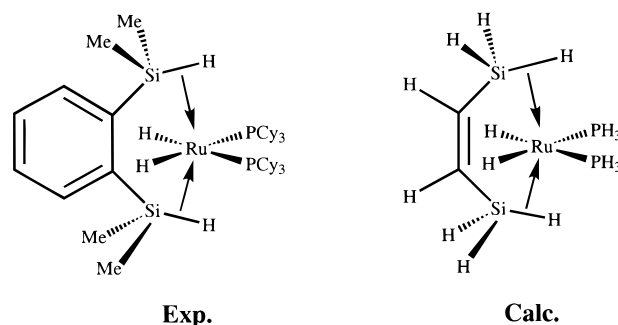
study shows that H···SiMe$_2$−o-(C$_6$H$_4$)−SiMe$_2$···H is coordinated to Ru in a highly distorted octahedral geometry (Chart 6).[172] Optimization (B3LYP) gave a structure very close to that for the experimental data and shows the presence of a Si−H interaction. By carrying out a calculation with two SiH$_4$ molecules in place of the bidentate bis(silyl) complex, it has been shown that the distortion is not entirely determined by the bite angle. In the distorted structure (coplanar but not parallel Si−H bonds), the two Si−H bonds avoid competing with the same d orbital of Ru for back-bonding. Calculations were also used to study the competition between Si−H and H−H bonding in Ru(H$_3$Si−H)$_2$(H)$_2$(PH$_3$)$_2$,[173,174] as well as interconversion between isomers in TpRu(PH$_3$)H(HSiR$_3$).[175]

It was mentioned in section III that d^0 complexes could have an unusual geometry that does not agree with VSEPR analysis. In most of the examples in section III, the hydride was a model ligand to represent a polyatomic pure σ donor. The next case represents a study of a system close to the experimental compounds. From the studies of the intensity of the M−H stretching bands, it has been suggested that two "*trans*"-hydrides in M(X)(OAr)$_2$(PR$_3$)(H)$_2$ (M = Ta; X = Cl, OAr) are displaced toward the phosphine (P−Ta−H = 60°), which is an unprecedented distortion for a hexacoordinate d^0 complex. The calculations (MP2 and B3LYP)[176] of Ta(X)(OH)$_2$(PH$_3$)-(H)$_2$ (X = H, Cl, OH) confirmed this assignment. It was suggested that the distortion permits a better π bond between one lone pair of X and the d^0 metal. In later work,[177] full optimization calculations (MP2) were carried out for Ta(OH)$_2$(L′)(H)$_2$(L) (L′ and L = OH, F, Cl, Br, CO, CN, CS, BF, N$_2$, CH$_3$, NH$_3$, PH$_3$, CH$_3$CN, NH$_2$, and H). The calculations have been used to examine the effect of the σ and π bonding of the ligands L and L′ on the direction of H−Ta−H bending (A vs B in Chart 7). Although the trend in

Chart 7

A   **B**
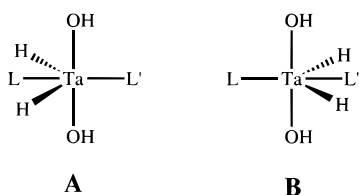
the trans influence, which dominates the Ta−L bond length of the ligand trans to L′, originates primarily from σ bonding, the direction of the distortion of the *trans*-hydrides originates primarily from the relative π-donating ability of L compared to that of L′. Generally, as the ligands are varied, the hydrides will bend away from the stronger donor.

An analogous geometrical distortion was calculated in d^4 OsH$_3$(η^2-BH$_4$)(PH$_3$)$_2$ as a model complex for OsH$_3$(η^2-BH$_4$)(P^{i}Pr$_3$)$_2$, in which T_{1min} measurements[178] suggested a rather close proximity of the three terminal hydrides. MP2 optimizations[178] reveal a pentagonal bipyramidal structure with the five hydrides (three terminal H atoms and two bridging H atoms with B) in the equatorial plane (A in Chart 8). The nonbonded distance (1.6 Å) between adjacent hydrides is consistent with the measured NMR
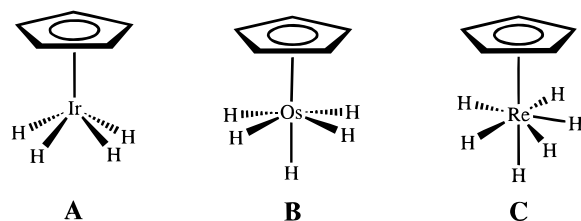
Chart 8

A   **B**
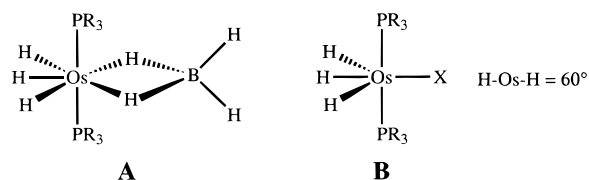
relaxation time T_{1min}. This system shows a complicated exchange process, which has been studied in detail and is discussed in section VII. The replacement of the borohydride by the bidentate ligand NH=C(Ph)C$_6$H$_4$, modeled by NH=C(H)C$_6$H$_4$, led to the same arrangement of the OsH$_3$ unit.[179]

The complexes with halides (X = Cl, I) in place of borohydride have also been synthesized[180,181] (OsH$_3$-(X)L$_2$; L = P^{i}Pr$_3$, P^{t}Bu$_2$Ph). It is remarkable that the structures of both the 18-electron borohydride and the 16-electron halide complexes have a similar arrangement of the OsH$_3$ moiety, on the basis of T_{1min} relaxation time measurements. Full optimization at the RHF[180] and MP2 levels[181] shows that the H···H distance is also around 1.6 Å for X = Cl or I (B in Chart 8). The reason for this geometry being adopted is very similar to that proposed in the tantalum complex.[176,177] The distortion of the *trans*-hydrides away from X permits the establishment of stronger Os−H σ bonds and an increase in the electron donation from one of the lone pairs of X into the empty d orbital of the metal. The calculated (X = OH) and experimental (X = OCH$_2$CF$_3$) preference for the alkoxy single-face donor to eclipse the P−Os−P bond in OsH$_3$(X)(PR$_3$)$_2$ is in full support of the presence of Os−X π bonding.[181]

The structure of [(PP$_3$)M(H)(η^2-H$_2$)]$^+$ (M = Fe, Ru; PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$) was investigated by X-ray and NMR studies.[182] Although the presence of a dihydrogen ligand was clearly established, its position and orientation could not be determined. Optimization of [P(CH$_2$CH$_2$PH$_2$)$_3$M(H)(η^2-H$_2$)]$^+$ (M = Fe, Ru) as model systems was carried out without any constraint with DFT (LDA) methodology.[182] The structure of the complexes was properly reproduced, and the H$_2$ ligand (H−H = 0.95 Å for Fe, and H−H = 0.89 Å for Ru) was located cis to the hydride and eclipsing the M−H bond (see section VI). Calculations, in which H$_2$ was replaced by C$_2$H$_4$, CO, and N$_2$, also gave results in good agreement with the experimental data.[182] In particular the data support the fact that Fe is better suited for π back-donation in this system.

Several polyhydrides in high oxidation states, which contain cyclopentadienyl and related ligands, have been studied by calculations. Cp*IrH$_4$ (Cp* = C$_5$Me$_5$) presents only one hydride peak in the ^{1}H NMR spectrum, suggesting that the compound has a 4-fold orientation of the hydrides about the metal center.[183] An RHF optimization[184] of CpIrH$_4$ gave a four-legged piano stool (A in Chart 9). Cp*ReH$_6$ has highly fluxional hydrides at high temperature, but at lower temperature the hydride motion could be frozen out to reveal a 5-fold umbrella structure.[185] An MP2 optimization[186] of CpReH$_6$ shows the presence of one hydride trans to the cyclopentadienyl ring
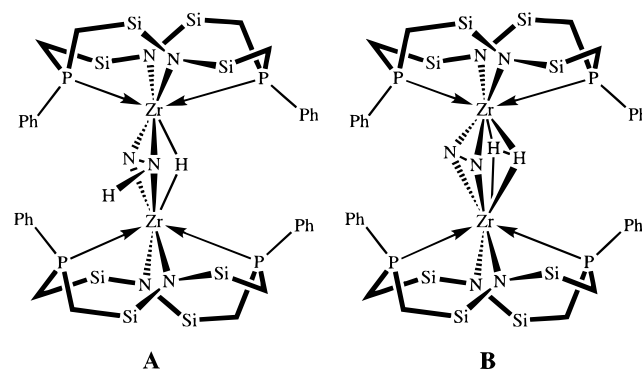
Chart 9

and five equivalent radiating hydrides (C in Chart 9). Cp*OsH$_5$, a species intermediate between the two preceding ones, has been recently synthesized and displays a singlet in the ^{1}H NMR, which persists even at low temperature.[187] Full optimization of CpOsH$_5$ at the MP2 level with additional calculations at the MP3, CISD, CCSD, and CCSD(T) levels indicated that the pseudo-C_{4v} structure with four radiating hydrides and one hydride trans to Cp is preferred (B in Chart 9).[188] The C_{5v} structure (a 5-fold piano stool) is a maximum at higher energy. It should be noticed that only post-HF calculations provide a reliable answer for the greater stability of the pseudo-C_{4v} structure. At the HF level the C_{4v} and C_{5v} structures are essentially of the same energy. The H exchange mechanism is discussed in section VII. The story of these three complexes illustrates the evolution of computational techniques and the possibility of examining problems involving smaller and smaller differences in energies.

Calculations are the only way to access the structure of unstable species, which defy any experimental determination. Thus, [Cp*MoH$_6$(PMe$_3$)]$^+$ is sufficiently stable for NMR characterization only below 220 K ($t_{1/2}$ = 30 s at −60 °C), whereas the W equivalent can be investigated up to 250 K ($t_{1/2}$ = 2 min at −20 °C), and a dihydrogen complex has been suggested in both cases. Full optimization[189] of [CpMoH$_6$(PH$_3$)]$^+$ at the MP2 level reveals the existence of a dihydrogen complex with a typical H−H distance (0.898 Å). MP2 calculations were also used to clarify the nature of the transient dihydrogen complex postulated from the variable-temperature NMR spectra of the formato compound OsH(η^2-O$_2$-CH)(CO)(P^{i}Pr$_3$)$_2$.[190] DFT calculations can successfully reproduce the change in structure associated with a change in oxidation state. Thus, the trigonal prismatic CpWH$_3$(PH$_2$CH$_2$CH$_2$PH$_2$) becomes intermediate between octahedral and trigonal prismatic upon oxidation.[191]

The following two examples are especially illustrative of the power of computation methods to locate hydrides. The crystallographic characterization of Cp$_2$Co$_2$ indicated a very short (2.253 Å) Co−Co distance, which was said to be consistent with an unsaturated Co−Co double bond unsupported by bridging ligands.[192] Fenske−Hall calculations suggested a singlet-state electronic structure, whereas the experimental data were indicative of a paramagnetic state. The calculations also indicated the absence of any σ Co−Co bonding in disagreement with the observed very short Co−Co distance. In part on the basis of this theoretical study, the compound was reformulated as saturated Co−Co with one or more bridging H ligands.[4]

The reaction of [P$_2$N$_2$]Zr(μ-η^2-N$_2$)Zr[P$_2$N$_2$] (P$_2$N$_2$ = PhP(CH$_2$SiMe$_2$NSiMe$_2$CH$_2$)$_2$PPh) with H$_2$ gave a product that contains an N−H bond and a bridging hydride, on the basis of ^{1}H and ^{15}N NMR spectroscopy. However, low-temperature X-ray diffraction studies[193] could be interpreted in terms of a complex having a side-on bridging H$_2$ unit (H−H = 1.21 Å) and an intact N$_2$ moiety. A combination of experimental (inelastic neutron scattering (INS), neutron diffraction) and theoretical methods[3] was used to investigate the problem. B3LYP calculations on model compounds showed a complex containing a N−N−H group bridging the two metal centers through the N−N bond, and a bridging hydride (A in Chart 10) as a unique minimum. Conspicuously absent from

Chart 10

the calculations is any minimum structure with a bridging dihydrogen (B in Chart 10). Regardless of the basis set, any initial geometry guess converged to the same minimum. The neutron diffraction shows the presence of a singly bridging hydride. However, this hydride is associated with atomic displacement parameters large enough, even at 25 K, to account for the incorrect characterization as two hydrogen atoms side-on-bonded with a H−H distance of 1.21 Å. Finally, INS measurements were also in agreement with a bridging hydride. The DFT study of the reactivity of H$_2$ with the dinuclear Zr(N$_2$) complex was shown not to lead to the thermodynamic product A (Chart 10).[194]

B. Improving the Model

Theoreticians have been tempted to simplify the real systems as much as possible. In particular, all large groups bonded to the metal have been replaced by the smallest analogous group: PH$_3$ is the model for any phosphine, SiH$_3$ for any silyl, Cp for any cylopentadienyl derivative, etc. Whereas the primary reason for this choice is to save computational time, the simplified model also brings some interesting information. If the structures for the calculated (small ligands) and experimental (large ligands) systems are in close agreement, it is suggested that the bulk or the precise electronic features of the ligands are not responsible for the observed structure or property. Clearly, such simplification has limitations. In what follows we have selected cases where the full nature of the ligands plays an important role.

Some studies have improved an oversimplified ligand (e.g., PH$_3$) by a model closer to the experi-

mental system (e.g., PMe$_3$). The X-ray structures of FeL$_4$H$_3^+$ show a different coordination sphere for L = PMe$_3$ and L = PEt$_3$. DFT calculations,[195] carried out with L = PH$_3$ and L = PMe$_3$, show that the relative energies of the possible isomers vary with the nature of L. The nature of L also has consequences on the mechanism of H site exchange (see section VII). The X-ray diffraction of M(SiR$_3$)H$_3$-(PPh$_3$)$_3$ (M = Ru, Os; R = *N*-pyrrolyl) does not permit location of the hydrides, and MP2 optimizations were carried out for several models with the purpose of positioning the hydrides. Replacing the silyl by SiH$_3$ and the phosphine group by PH$_3$ gave poor agreement with the experimental data. Replacing SiH$_3$ by Si-(NH$_2$)$_3$ and, finally, by the computationally demanding Si(pyr)$_3$ led to very good agreement between calculated and experimental data and permitted reproducing the Os−Si bond length and locating the three H atoms that bridge the Os−Si bond.[196]

The alternative approach to the representation of the true ligand is to use a hybrid quantum mechanics and molecular mechanics (QM/MM) method such as IMOMM.[197] This approach is discussed in detail elsewhere,[147] and only examples in the case of polyhydride complexes are given here. Frozen geometry approaches to IMOMM had been applied already before the development of the method, with the goal of clarifying the wide differences observed in the experimental NMR data for [Ru(P−P)$_2$"H"$_3$]$^+$ (P−P = 1,4-bis(diphenylphosphino)butane, "dppb"; (*R,R*)-4,5-bis(diphenylphosphino)methyl-2,2-dimethyl-1,3-dioxolane, "diop"; 1,2-bis(diphenylphosphino)methylbenzene, "dpmb"; 1,2-bis(diphenylphosphino)ethane, "dppe").[198] The calculations show that the main isomers in solution are an essentially octahedral six-coordinate isomer with *trans*-H and -H$_2$ ligands (*trans*-M(H)(H$_2$)) and a fairly heavily distorted six-coordinate isomer (*cis*-M(H)(H$_2$)). The bite angle of the various diphosphine ligands is shown to play an important role. Thus, the ligand with the larger tendency to open the P−Ru−P angle, diop, is proposed to be the only one to give rise to the trihydride complex with the phosphines in a tetrahedral disposition.

The complexes [ReH$_5$(L)$_2$(SiHPh$_2$)$_2$] (L = PPh^{i}Pr$_2$, PCy$_3$)[199] were studied with the IMOMM methodology, and the results were compared to the qualitatively good results obtained from MP2 calculations for [ReH$_5$(PH$_3$)$_2$(SiH$_3$)$_2$].[200] With very similar computational cost, the IMOMM calculations provided structures significantly closer to the experimental data than those at the MP2 level of the simplified system. As expected, the main steric relaxation took place between the silyl and phosphine groups. In the case of OsCl$_2$H$_2$(P^{i}Pr$_3$)$_2$,[201] the ab initio calculations[202] of OsCl$_2$H$_2$(PH$_3$)$_2$ gave a bicapped tetrahedron structure (QM in Chart 11). An IMOMM (B3LYP:MM3) calculation[203] on the real system reproduced the uncommon trigonal prismatic X-ray structure of OsCl$_2$H$_2$-(P^{i}Pr$_3$)$_2$ and showed how the actual structure is a compromise between an electronic effect favoring coplanarity of the chlorine and phosphine ligands (QM in Chart 11) and a steric effect favoring motion

Chart 11

QM   QM/MM
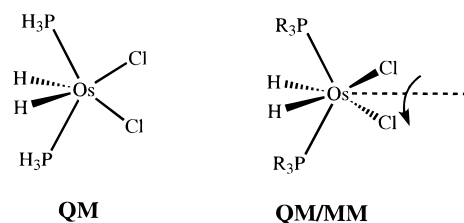
of the chlorine ligands away from the phosphine ligands (QM/MM in Chart 11).

The case of IrH$_2$Cl(P^{t}Bu$_2$Ph)$_2$ is another example where the replacement of the phosphine by PH$_3$ accounted for only part of the experimental results. The optimization at any level (RHF, MP2, DFT) of IrH$_2$Cl(PH$_3$)$_2$ gave the same geometry: a distorted trigonal bipyramid with apical phosphines and an H−Ir−H angle around 80° (see also section III). The H−Ir−H angle is thus very close to that obtained from neutron diffraction (76°), the main difference being that the Ir−Cl axis bisects the H−Ir−H angle in IrH$_2$Cl(PH$_3$)$_2$ (*C$_{2v}$* symmetry) but not in IrH$_2$Cl-(P^{t}Bu$_2$Ph)$_2$. An IMOMM (B3LYP:MM3) calculation[141] of IrH$_2$Cl(P^{t}Bu$_2$Ph)$_2$ shows that the Ir−Cl vector moves away from the bisector plane of H−Ir−H so Cl can avoid close contacts with some of the dangling C−H bonds of the phosphine ligands. Recent measurements[204] of the site exchange between the two inequivalent H atoms support a steric interpretation. The bulky substituents of the phosphine ligands have also been shown to play a leading role in the formation of agostic interactions in the hydride complexes Ir(H)$_2$(P^{t}Bu$_2$Ph)$_2^+$,[205] Ir(H)(η^2-C$_6$H$_4$P^{t}Bu$_2$)(P^{t}Bu$_2$Ph)$^+$, and Ir(H)$_2$(PCy$_2$Ph)$_3^+$.[206]

V. The Dihydrogen Saga

A. Dihydrogen as a Ligand

The saga of dihydrogen complexes has been described in a number of reviews and need not be repeated here (see the Introduction). It could be worth mentioning that coordination of H$_2$ was observed first in group VI metal complexes in matrixes,[80,81] in the gas phase,[82,83] and in the solid state.[6] There are now a very large number of dihydrogen complexes known for a wide variety of metal centers.

The bonding of a dihydrogen ligand to a transition metal can be described using an adaptation of the Dewar−Chatt−Duncanson model of bonding and back-bonding. The σ(HH) occupied orbital gives electrons to an empty orbital of the metal, whereas the σ*(HH) empty orbital receives electrons from an occupied orbital of the metal. The most stable H$_2$ complex (coordination site, conformational preference) corresponds to the stronger M−H$_2$ interaction. The two components of the M−H$_2$ interaction contribute to the lengthening of the H−H bond with respect to free H$_2$ (0.74 Å) through loss of electron density from an occupied orbital and addition of electron density into an empty orbital. In the case where these two interactions are strong, the H−H bond could be cleaved and two metal−hydride bonds could be formed. Understanding the factors that can

stabilize H_2 as a ligand without cleaving the H−H bond has thus attracted the interest of many theoreticians.

Extended Hückel calculations have been used for analyzing the bonding between H_2 and the transition metal center and have provided a proper framework of concepts for further studies. The possibility that a stable H_2 complex could exist was published by Saillard and Hoffmann[26] a few months after the report of the experimental evidence by Kubas and co-workers. This first paper was followed by a continuous flow of publications. From an EHT study[207] on the Kubas complex it appeared that the LUMO (lowest unoccupied molecular orbital) of $W(CO)_3L_2$ has the correct symmetry to interact with $\sigma(HH)$ as shown in Chart 12. An occupied d orbital belonging

Chart 12

LUMO $\sigma(HH)$ HOMO $\sigma^*(HH)$
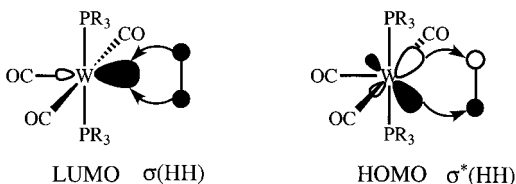
to the approximate t_{2g} set interacts with $\sigma^*(HH)$ (Chart 12). The highest occupied d orbital provides the most efficient back-donation; therefore, H_2 is coplanar with the phosphine ligands, which agrees with experiment.[6] Increased back-donation is a consequence of going down a triad since 5d orbitals are higher in energy and more diffuse than 3d or 4d orbitals. Therefore, a dihydride is more likely to be formed with the heaviest metal. The role of π-accepting ancillary ligands in decreasing the back-donation and thus in preventing the cleavage of the H−H bond has been highlighted. These π-accepting ligands are responsible for the existence of H_2 complexes of d^{10} ML_3 fragments $Ni(CO)_3$, $Co(CO)_2(NO)$, and $Fe(NO)_2$-(CO).[208] These qualitative ideas were pursued and expanded in work by Burdett who analyzed the bonding within the $A(H_2)$ system. Using the isolobal analogy and the method of moments, Burdett and co-workers[209−212] show the intimate analogy between organic systems and dihydrogen complexes. They also discussed the possibility for a transition metal to stabilize clusters of H_n ($n \geq 2$).

These qualitative ideas were quantified by ab initio calculations. However, it quickly appeared that a good level of calculations was required for representing these complexes correctly. The pioneer ab initio (HF) partial optimization of $W(CO)_3(PH_3)_2(H_2)$ showed the existence of a minimum with a side-bonded dihydrogen (η^2-H_2) but gave a much too short H−H distance (0.796 Å) and too low rotational barrier (0.3 kcal·mol^{-1}).[213] In the following study (HF), the use of different effective core potentials led to considerable improvement: the H−H distance was found to be 0.812 Å, close to the experimental 0.82 Å, and the rotational barrier was found to lie between 1.4 and 1.8 kcal·mol^{-1}, close to the experimental value (2.2−2.4 kcal·mol^{-1}).[214] The corresponding Mo complex has a shorter H−H distance and a smaller rotational barrier for H_2. Further studies were carried out with

Table 1. Calculated Bond Lengths (Å) and Theoretically Predicted H_2 Bond Dissociation Energies (kcal·mol^{-1}) for $M(CO)_n(PR_3)_{5-n}(\eta^2$-$H_2)$ Complexes

	H−H				D_e		
	calcd[218]	calcd[215]	calcd[216]	exptl	calcd[218]	calcd[215]	calcd[216]
			$M(CO)_3(PH_3)_2(H_2)$				
Cr	0.808	0.822		0.85[220]	16.9	21.3	
Mo	0.804	0.848		0.87[221]	17.1	19.2	
W	0.832	0.862		0.89[221]	21.3	20.9	
			$M(CO)_5(H_2)$				
Cr	0.794		0.814		17.9		19.8
Mo	0.787	0.824	0.791		15.7	19.6	16.6
W	0.802		0.810		19.1		19.8
			$M(PH_3)_5(H_2)$				
Cr	0.829				18.7		
Mo	0.858				23.5		
W	0.911				29.8		

post-HF calculations (MP2 and CCSD(T)) and DFT calculations.[215−218] They show the trends in H−H bond distances and rotational barrier (see section VII) as a function of the metal and the ligands as summarized in Table 1. Even though the absolute value of the H−H distance depends on the method of calculations, all calculations agree that (i) the H−H bond is shorter for Cr than for W although there may be some discrepancy for Mo with respect to Cr and W (see $Mo(CO)_3(PH_3)_2$) and (ii) the H−H bond distance increases upon replacement of CO by PH_3. Bond dissociation energies (BDEs) also increase on replacement of CO by phosphine ligands. Variation of the BDE within a triad depends on the method of calculation. Direct comparison of the calculated BDE with an experimental value is prevented by the fact that an agostic interaction with a pendant C−H bond of a phosphine ligand occurs in the absence of H_2.[219] Such an interaction is not included in the calculation of the $M(CO)_3(PH_3)_2$ fragment and hence not in the BDE of H_2.

A systematic study of the influence of the L ligand trans to H_2 in $M(CO)_4(L)(H_2)$ (L = CO, SiO, CS, CN, NC, NO, N_2, H, F, Cl, and PH_3) has been carried out with CCSD(T)//MP2 calculations (Table 2).[222] There is a nearly linear correlation between the calculated bond energies and the H−H distance. It follows that the stronger the M−H_2 bond, the longer the calculated distance between the hydrogen atoms. Ligands that are π acceptors weaken the M−(H_2) bond, whereas ligands that are poor π acceptors tend to strengthen the M−(H_2) bond. For any L, the H−H bond is the shortest for Cr and the longest for Mo, although in general very close to that calculated for W.

The previous study shows the influence of the trans ligand on the BDE of H_2. It was shown that the energy of the metal fragment, in the geometry of the complex, also needs to be taken into consideration for a better understanding of the overall stability of the dihydrogen complex. Two isomers are known for $IrHCl_2(H_2)(PR_3)_2$,[140] but only one is known for IrH_2-$Cl(H_2)(PR_3)_2$.[223,224] In general, H_2 prefers to coordinate trans to a ligand of high trans influence (such as hydride) because the metal fragment is either in its best geometry or close to it.[139] The influence of the

Table 2. Calculated (MP2) Bond Lengths (Å) and Theoretically Predicted (CCSD(T)//MP2) H_2 Bond Dissociation Energies (kcal·mol^{-1}) for $ML(CO)_4(\eta^2\text{-}H_2)$ Complexes[222]

M	L	M−H	H−H	D_e
Cr	CO	1.745	0.814	19.8
Mo		1.959	0.791	16.1
W		1.915	0.810	19.8
Cr	SiO	1.675	0.841	19.0
Mo		1.929	0.798	16.2
W		1.893	0.817	20.2
Cr	CS	1.811	0.790	17.8
Mo		2.055	0.775	12.5
W		1.981	0.794	16.0
Cr	CN	1.655	0.910	26.3
Mo		1.876	0.838	21.6
W		1.844	0.870	26.5
Cr	NC	1.625	0.956	24.4
Mo		1.838	0.861	24.7
W		1.817	0.893	30.6
Cr	NO	2.137	0.742	13.1
Mo		2.161	0.757	11.7
W		2.105	0.763	14.4
Cr	N_2	1.687	0.895	21.8
Mo		1.868	0.821	21.8
W		1.847	0.840	26.8
Cr	H	1.668	0.884	30.1
Mo		1.909	0.827	19.0
W		1.868	0.861	27.7
Cr	F	1.618	0.958	26.0
Mo		1.832	0.879	25.5
W		1.741	1.756	35.6
Cr	Cl	1.593	0.980	24.2
Mo		1.804	0.886	26.3
W		1.727	1.693	39.1
Cr	PH_3	1.638	0.886	34.2
Mo		1.881	0.818	22.7
W		1.856	0.840	27.6

substituent effect on an unsaturated fragment $IrXH_2(PR_3)_2$ and on the dihydrogen adduct to this metal fragment has been calculated (B3LYP, MP2) in detail (X = Cl, Br, I; R = H, Me).[225] The calculated BDEs (increasing in the order Cl, Br, and I) are in quantitative agreement with the experimental values for $PR_3 = P^tBu_2Me$.[226]

Even in the absence of observable isomers, the competing coordination sites of H_2 in a given complex have also been studied because they could provide some information on the site exchange process, frequent in most polyhydrides (see section VII). Thus, the isomers *trans*-$M(H)(H_2)$ and *cis*-$M(H)(H_2)$ were suggested to be close in energy in $Fe(PH_3)_4(H)(H_2)^+$.[227] This agrees with the data on $Fe(R_2PCH_2CH_2PR_2)_2H(H_2)^+$, where H and H_2 are preferably trans but where access to a cis isomer or trihydride is necessary to account for the reactivity.[10] The possibility for H to be either trans or cis to H_2 was calculated (MP4//MP2)[228] for $OsHCl(H_2)(CO)(PH_3)_2$ and for $M(H)_2(H_2)(CO)(PH_3)_2$ (M = Os, Ru) with MP2 calculations.[229] In both cases, the coordination of H trans to H_2 is preferable and the other coordination is energetically accessible, in agreement with experimental evidence.

B. Dihydrogen versus Dihydride

The transformation of coordinated dihydrogen into a dihydride is a key problem in the field of transition metal polyhydrides. Originally all H-containing transition metal complexes were considered as polyhy-

drides. After the discovery by Kubas, the structures of many of them were reattributed as dihydrogen complexes.[9] A complex that contains only hydride ligands is called a classical polyhydride, whereas a complex containing one or more dihydrogen ligands is called a nonclassical polyhydride.[230] The experimental methods and techniques that have been used to assign the structure are described in several excellent reviews on this topic.[9−11,16,27−29] The $M(H)_2$/$M(H_2)$ dichotomy has been the subject of almost all theoretical papers and has also been addressed in most of the papers cited in section V.A. Therefore, this section (V.B) is limited to contributions specifically concerned with this dichotomy.

Through the study of $MH_n(PH_3)_m$, $CpMH_nL_{4-n}$ (M = Ru, Os, Rh, Ir), $CpMH_nL_{6-n}$, $MH_n(CO)_mL_p$, and $MH_nCl_mL_p$ (with 4d and 5d metals from group 6 to group 9, and neutral or cationic complexes), Lin and Hall[36,154,184,186,231−234] searched for periodic trends. The factors that favor classical over nonclassical structure are, as expected, identical to those that are responsible for stretching of the H−H bond. Classical hydrides are preferred for transition metals with more diffuse d orbitals, i.e., early transition metals. Likewise, down a triad, classical hydrides are preferred for the heaviest elements. For transition metals from the same row, the nonclassical isomer is preferred for the later metal. Lin and Hall[36] postulated that a diagonal line divides the transition metals into those that prefer classical forms (left side of the line) and those that prefer nonclassical forms (right side of the line). For those complexes along the diagonal line, both classical and nonclassical isomers may exist. For cationic complexes, the corresponding diagonal line shifts toward early transition metals (Chart 13).The structures of a large number of

Chart 13
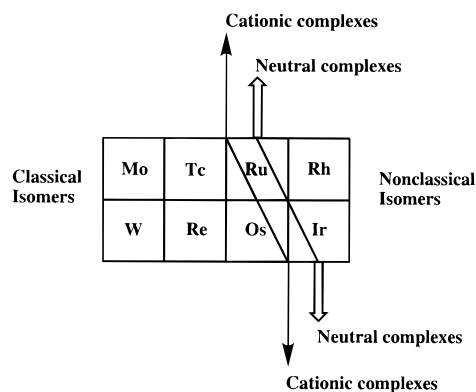
complexes were properly assigned through these studies.

Other studies focused on the existence of two minima, corresponding to either classical or nonclassical structures. The impetus for such studies was initiated by the observed equilibrium between $M(H_2)$ and $M(H)_2$ for the Kubas complex.[235]

In the absence of any d electrons on the metal, only the dihydrogen form can exist as shown in $[CpMoH_6(PH_3)]^+$.[189] In early work, EHT calculations[236,237] had suggested the possibility that an H_2 or H_3^- ligand could be bonded to a d^0 metal. Very recently, a stable

Ti^{IV} dihydrogen complex was located as a secondary minimum in a combined DFT and molecular dynamics study[238] of the reaction mechanism of olefin polymerization by (CpSiH$_2$NH)Ti^{IV}R$^+$.

Where the metal center has d electrons and where the two forms are in principle possible, the outcome of the calculations is generally that the existence of two minima is rare and the existence of a single stable structure (dihydrogen or dihydride) is common. Furthermore, all studies show that the rules suggested in the very early EHT work and the large series of Lin and Hall[36] are followed. Thus, RuI(H)-(H$_2$)(PR$_3$)$_2$ is an H$_2$ complex,[239] whereas changing Ru to Os makes the complex become a dihydride.[180] Likewise OsH$_3$(η^2-BH$_4$)(PH$_3$)$_2$ has only a classical polyhydride structure.[178,240]

The discovery of quantum exchange coupling (section VIII) in trihydride complexes has prompted many studies on these systems with a special focus on the existence of a dihydrogen complex isomer. Many of these complexes (CpIr(H$_3$)(L)$^+$, L = PH$_3$, CO) have been found to have a trihydride structure as a single minimum.[241,242] In the family of bis(cyclopentadienyl) complexes, some of the first ab initio calculations were carried out by modeling Cp by Cl. The presence of two minima in Cl$_2$MH$_3$ (M = Nb, Ta)[243] was not reproduced with Cp ligands in the calculations. Thus, Cp$_2$MH$_3^{n+}$ (M = Mo, W, n = 1; M = Nb, Ta, n = 0)[244] are only trihydrides (B3LYP). In agreement with the idea that diminishing electron density at the metal should favor the dihydrogen structure, coordination of one wingtip hydride by Lewis acids of increasing strength decreases the internuclear distance between the two other *cis*-hydrogen atoms. A dihydrogen complex can even be preferred. For Cp$_2$NbH$_3$, calculations (B3LYP) give the following distances between the two *cis*-H atoms: no Lewis acid, H$\cdots$H = 1.771 Å; (HO)$_2$BH, a model of catecholborane, H$\cdots$H = 1.768 Å; AlH$_3$, H$\cdots$H = 1.646 Å; BF$_3$, H$\cdots$H = 0.918 Å; BH$_3$, H$\cdots$H 0.913 Å.[245-247] Replacing the wingtip hydrogen by a p-accepting ligand (CO, CNR) also favors the dihydrogen complex as shown by experimental and theoretical approaches.[248,249]

A systematic study of ligand effects on the possibility of having two minima (M(H$_2$) or M(H)$_2$) was carried out (MP2)[222] on M(CO)$_4$(L)(H$_2$) (L = CO, SiO, CS, CN, NC, NO, N$_2$, H, F, Cl, PH$_3$). Most of the complexes were found to be only dihydrogen complexes. The dihydride was found as the minimum only for M = W with X = F and Cl (5d metal with a π donor ligand trans to the "H$_2$" ligand). Only five molecules were found to be more stable as dihydrogen with a dihydride as a secondary minimum (M = W with X = CN, NC; M = Cr with X = H; and M = Mo with X = H). One system is a stable dihydride with dihydrogen as a secondary minimum (M = W with X = H).[222]

The series M(PH$_3$)$_3$H$_4$ (M = Fe, Ru, Os) was studied with DFT calculations.[250] It is found that inclusion of relativistic effects is necessary to represent properly the changes in structure from Fe to Os with all-electron basis sets. Without relativistic effects, all three complexes prefer to be dihydrogen complexes.

Including relativistic effects increases the energy of the 5d orbital of Os and results in a tetrahydride structure being preferred for Os, whereas a dihydrogen form remains the more stable for Fe and Ru.

The search for cases showing the existence of two minima raises a fundamental problem. Even if two minima could coexist, their experimental observation might require that a significant energy barrier prevents an otherwise too easy interchange between them. Location of the transition state between W(CO)$_3$(PH$_3$)$_2$(H$_2$) and *cis*-W(CO)$_3$(PH$_3$)$_2$(H)$_2$ (A in Chart 14)

Chart 14

A   **B**
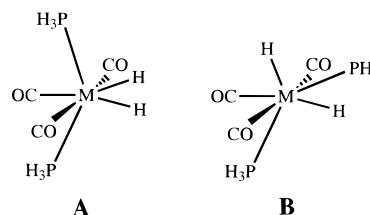
shows the absence of any significant barrier for transforming the more unstable M(H)$_2$ into M(H$_2$).[218] This contradicts the spin saturation measurements[235] that show a nonnegligible activation energy ($\Delta G^\ddagger$ = 16.0 kcal·mol^{-1}, $\Delta H^\ddagger$ = 10.1 kcal·mol^{-1}, $\Delta S^\ddagger$ = −19.9 eu) for the transformation of dihydride into dihydrogen. Another dihydride structure was found as a minimum at an energy very close to that of the *cis*-dihydride. In this seven-coordinate alternative minimum the two hydrides are separated by a W−phosphine bond (B in Chart 14). A stable dihydride structure, in which the two H atoms are not cis, was also located by calculations (B3LYP) in MH$_2$(CO)$_3$(PH$_3$)$_2$ and in MH$_2$(PH$_3$)$_5$ (M = Cr, Mo, W).[217] This structure also agrees with the proposed X-ray structure of MoH$_2$(PR$_3$)$_5$. Although the transition state for the transformation of the dihydride into the H$_2$ complex was not located, it is likely to be associated with a nonnegligible activation energy.[218] This dihydride structure with non-*cis*-hydrides is thus probably the one observed experimentally. In the study (B3LYP) of CpRuH$_2$(PH$_2$CH$_2$PH$_2$)$^+$ a dihydrogen and a *trans*-dihydride are also found as two minima close in energy.[251] Changing the shape of the metal fragment can also lead to a change in the coordination of H$_2$ as shown by a study of [Rh(PH$_3$)$_4$(H$_2$)]$^+$ [252] as a model of [Rh(P(CH$_2$CH$_2$PPh$_2$)$_3$)(H$_2$)]$^+$.[253] The role of the spectator phosphine ligands in determining the structure can be drastic.[254] Thus, it seems that the observation of a dihydrogen and a dihydride in a complex not only may be associated with the simple cleavage of the dihydrogen bond, but may involve a more extensive structural change in the complex.[255]

C. Theoretical Tools for Analysis of the H$\cdots$H Interaction

Several types of analysis have been used to quantify the interaction of H$_2$ with the metal center: the energy decomposition analysis (EDA),[167,256] the extended transition state (ETS) decomposition scheme,[250,257,258] and the charge decomposition analysis (CDA).[222,259] They all point to the importance of back-donation. The H−H and M−H vibrational fre-
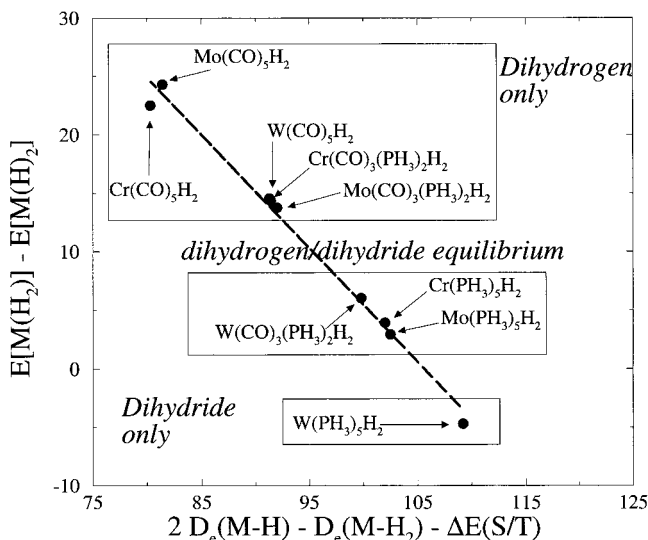
Figure 1. ΔE(S/T) for M(CO)$_n$(PH$_3$)$_{5-n}$(H$_2$) complexes (see the text for definitions).[218]

quencies have also been calculated to quantify the weakening of the H−H bond upon coordination. As expected the H−H stretching frequency is calculated[213,216] to be weaker for coordinated H$_2$ than for free H$_2$. Agreement with experiment, which is fairly good, is however limited by the difficulty of observing some of these frequencies.[214,216,217] The atoms in molecules analysis[260,261] has also been used to assign the chemical bonds in several H$_2$ complexes as a function of H−H separation.[262] This point is especially relevant for stretched H$_2$ complexes discussed in section IX.

An alternative approach for analyzing the M(H$_2$)/ M(H)$_2$ dichotomy was developed from the study of the electronic state of the metal fragment adapted to bond to H$_2$ or to two hydrides. It has been shown by Hay[213] that the bonding for a dihydrogen complex is best described by the singlet state of the metal fragment interacting with H$_2$, whereas the bonding for the dihydride is described by the triplet state of the metal fragment interacting with two hydrides. This idea was developed and enlarged for analyzing the trend in the family of complexes M(CO)$_n$(PH$_3$)$_{5-n}$ (M = Cr, Mo, W; n = 0, 3, 5).[218] It is shown that there is a linear relationship between E[M(H$_2$)] − E[M(H)$_2$] and $2D_e$(M−H) − D_e(M−H$_2$) − ΔE(S/T), where D_e-(M−H) is the metal−hydride bond energy, D_e(M−H$_2$) is the metal−dihydrogen bond energy, and ΔE(S/T) is the singlet/triplet energy gap of the metal fragment (Figure 1). For a given set of ligands with CCSD(T)// B3LYP calculations, the smallest ΔE(S/T) and D_e(M−H) are found for Cr. In the Mo analogue, D_e(M−H) is stronger but ΔE(S/T) is also larger. The similar behaviors of Cr and Mo complexes are therefore coming from factors working in opposite directions. Going from Mo to W increases D_e(M−H) and decreases ΔE(S/T), favoring the dihydride in the later.

VI. Interactions with M–H and with M–H$_2$. Hydrogen Bonds Again!

While the dihydrogen ligand interacts most strongly with the metal center, it was also soon recognized

that coordinated H$_2$ has the unusual capability of interacting with other centers, notably other ligands in the coordination sphere. This interaction was first suggested to explain the unprecedented orientation of H$_2$ in FeH$_2$(H$_2$)(PEtPh$_2$)$_3$. Neutron diffraction has revealed the presence of an H$_2$ ligand bisecting the cis H−Fe−P angle (A in Chart 15).[263] An EHT

**Chart 15**
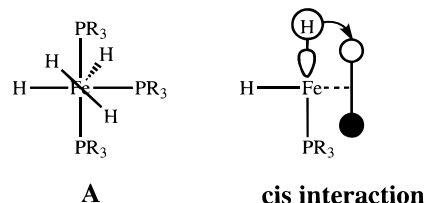
A   **cis interaction**

study[263] of the rotational barrier of H$_2$ showed that the observed conformation was the result of a compromise between back-donation between Fe and H$_2$ (maximum where H$_2$ eclipses P−Fe−P) and a stabilizing interaction between H$_2$ and the cis Fe−H bond (the cis interaction; see Chart 15). The attraction between the hydride and H$_2$ was represented at the molecular orbital level as the Fe−H σ bond, localized on the hydride, acting as an electron donor toward σ*(HH). The best overlap between σ(FeH) and σ*(HH) is obtained when the four atoms are coplanar. An ab initio study of the conformational preference of H$_2$ (all other atoms at fixed positions) confirmed that the experimentally observed orientation of H$_2$ corresponds to a minimum.[264] The cis interaction between H$_2$ and the hydride has been found through other theoretical studies in a number of complexes.[140,182,189,227,239,265−268]

Theoretical studies have not characterized any form of covalent bonding between the hydride and the coordinated H$_2$. An alternative explanation for this attractive interaction is based on purely electrostatic arguments. It is well established that a dihydrogen coordinated to a metal is strongly acidic,[10] and calculations on Ru and Os complexes show the importance of spectator ligands on this property.[269] A hydrogen center of coordinated H$_2$ is thus positively charged. An electrostatic attraction or a dipole/ induced dipole interaction can thus be established between the negatively charged hydride (the hydridic nature of H-containing metal complexes has been discussed[270]) and the positively charged extremity of coordinated H$_2$.

The proposal of an attraction between a negatively charged hydride and a positively charged H atom was not new in the literature. The coplanarity of O−H and Ir−H bonds and the relatively short H⋯H distance (2.4 Å) in [Ir(PMe$_3$)$_4$(H)(OH)]$^+$, whose structure was determined by neutron diffraction, was explained by an attraction between Ir$^{+\delta}$−H$^{-\delta}$ and O$^{-\delta}$−H$^{+\delta}$ (Chart 16).[271] A recent X-ray determination

Chart 16
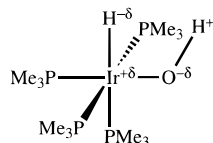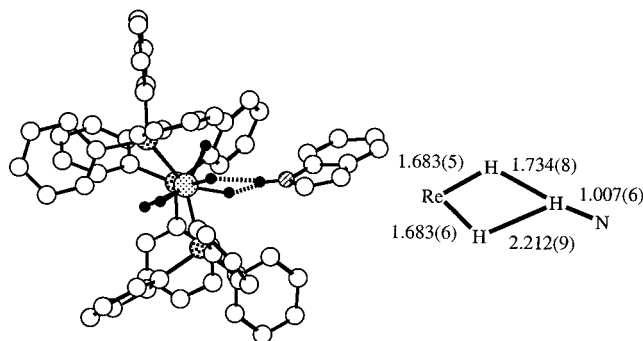
Figure 2. Neutron diffraction structure for Re(H)$_5$(PPh$_3$)$_3$·indole.[280]

of [FeH(H$_2$)(PMe$_3$)$_4$]$^+$ [272] found a structural distortion compatible with an H···H$_2$ interaction calculated in [Fe(H)(H$_2$)(PR$_3$)$_4$]$^+$ (R = H,[195,227] Me[195]). This idea was generalized and expanded independently by Morris[14,273] and Crabtree,[15,274,275] and a number of theoretical studies were carried out to study this new type of hydrogen bonding, which was named an H···H or dihydrogen bond to distinguish it from the traditional hydrogen bond.[275]

Although the focus of this review is on transition-metal-containing systems, it is necessary to mention that the first quantitative calculations on the dihydrogen bond were carried out for main group compounds. Thus, the study of the gas-phase dimer [BH$_3$NH$_3$]$_2$ by PCI-80/B3LYP (a modification of DFT tailored to obtain CCSD(T) quality results) shows the presence of two identical short B−H···H−N interactions.[275,276] The magnitude of each interaction was evaluated to be 6 kcal·mol^{-1}, and point charge analysis indicates an electrostatic origin for the H···H bond.

In the field of transition metal chemistry, the first calculations concerned an intramolecular dihydrogen bond. In IrH$_2$X(PR$_3$)$_2$L′ (L′ = 2-aminopyridine), an interaction between a hydride and an amino proton was detected by NMR and IR studies.[277] The strength of the H···H interaction based on the C=N rotation barrier was calculated (HF) on IrH$_2$X(PH$_3$)$_2$(HN= C(H)NH$_2$) as a model and was found to be around 5.8 kcal·mol^{-1} (X = H). Decreasing the electron density on the hydride by decreasing the trans influence of X (Cl in place of H) diminishes the interaction as found by calculations (4.3 kcal·mol^{-1}) and experiment.[277] The nature of the attractive interaction in a number of related systems was discussed from a molecular orbital point of view.[278] A weak intramolecular interaction was also detected by DFT calculations in [Ir(PH$_3$)$_4$(H)(OH)]$^+$ and in [Ir(PH$_3$)$_4$(H)(SH)]$^+$. However, interestingly, the intermolecular interaction with the neighboring counteranion is also shown to play a role and to affect the geometry of these iridium complexes in a significant way.[279]

Intermolecular interactions of this type have also been observed between neutral systems as, for example, in the cocrystallization of ReH$_5$(PPh$_3$)$_3$ with indole. The X-ray and neutron diffraction studies show the presence of an N−H···H−N hydrogen bond (Figure 2).[280,281] This can be considered as a three-center H bond, with one hydrogen tightly bonded

(d(H···H) = 1.734(8) Å) and one very weakly bound (d(H···H) = 2.212(9) Å). The Re−H···H−N angles are strongly bent (118.9(4)° for the stronger and 97.2(3)° for the weaker interaction), as in the B−H···H−N case. Calculations (B3LYP) were carried out on [(ReH$_5$(PH$_3$)$_3$)(H−NH$_2$)] as a model (i) to prove the presence of an attractive interaction between the metal hydride and the proton donor and (ii) to determine if the interaction was selective toward some of the hydrides. Optimization of the relative positions of structurally frozen partners led to longer distances between the interacting molecules (1.92 and 2.48 Å) than seen in the neutron diffraction data. The stabilization energy (4.3 kcal·mol^{-1}) was found to be equal for all hydrides. Replacement of NH$_3$ by pyrrole led to a slightly larger interaction energy.[281] Only significantly polar H−X bonds can become involved in this H···H interaction as demonstrated by the lack of experimental interaction or significant stabilization when the N−H bond is replaced by a C−H bond in the rhenium case.[282] However, some M−H···H−C interaction has been detected for other systems in the solid state.[283]

The dihydrogen bonding interaction has been found to also have an influence on the reactivity of a polyhydride. The H site exchange should be faster if a stabilizing H···H interaction lowers the energy of the transition state. To test this point, the dynamics of H site exchange was studied in ReH$_5$(PPh$_3$)$_2$(L) (L = 2-(acetylamino)pyridine). A rate increase in the H site exchange of a surprisingly moderate magnitude was observed. Determination of the transition states (B3LYP) for the permutation of the hydrides corresponding to a turnstile rotation (Chart 17) in ReH$_5$-

Chart 17
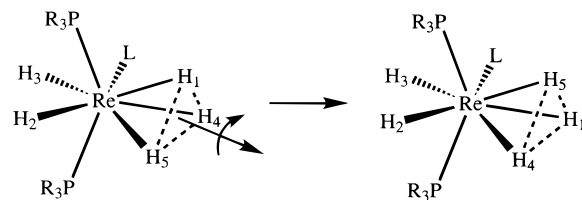
(PH$_3$)$_2$(L) (L = 2-(amino)pyridine) revealed that the two interacting H centers were in too close proximity in the transition state, thus preventing maximum H···H stabilization.[284] Recently, a DFT (B3PW91) study of (Cp-N)RuH(PH$_3$)$_2$ (Cp-N = C$_5$H$_4$CH$_2$CH$_2$-NMe$_2$) has shown the importance of the dihydrogen bonding in the protonation process of this complex.[285]

The discovery of the dihydrogen bonding has resulted in a significant rebirth of interest in hydrogen bonding in the transition metal chemistry field.[286−290] It is certainly going to expand considerably since hydrogen bonding governs so many aspects of chemistry. It is an important contributor to the interactions between molecules in the solid state.[279,291,292] It could also be the initial step for protonation. Thus, considerable effort has been devoted to the understanding of the factors that control selectivity of protonation.[34] From a theoretical point of view, it is an extremely challenging topic owing to the small energies involved. One can illustrate these challenges and partial successes through two recent

Table 3. Calculated Hydrogen Exchange Processes in Polydride Complexes[a]

complex		methodology	ref.
Pairwise Exchange			
$OsH_3\{NH{=}C(H)C_6H_4\}(PH_3)_2$	20.1; 12.3[b]	B3LYP	179
$OsH_3\{\kappa\text{-N},\kappa\text{-S-(2-Spy)}\}(PH_3)_2$	14.9; 16.2[b]	B3LYP	295
$CpIr(PH_3)H_3^+$	14.1	MP2	242
	17.9	MP2	268
$CpIr(CO)H_3^+$	10.7	MP2	242
$Cp_2MoH_3^+$	16.4	B3LYP	244
$Cp_2WH_3^+$	28.5	B3LYP	244
Cp_2NbH_3	25.4	B3LYP	244
Cp_2TaH_3	37.7	B3LYP	244
$OsH_3Cl(PH_3)_2$	12.9	MP2	296
$OsH_3I(PH_3)_2$	14.6	MP2	296
$OsH_3Cl(PH_3)_3$	9.8	MP2	181
$CpRhH_4$	6.8	CCSD(T)//B3LYP	297
Other Mechanisms			
$FeH_3(PMe_3)_4^+$ (tedrahedral jump)	7.4	DFT	195
$CpOsH_5$ (trigonal twist)	5.2	CCSD(T)//MP2	188
$ReH_5(PH_3)_2(Py)$ (turnstile)	9.0	B3LYP	284
$(\eta^2\text{-BH}_4)Mn(CO)_4$ (H-bridging/H-terminal via η^3)	25.9	MP2//RHF	298
$(\eta^3\text{-BH}_4)Cu(PH_3)$ (H-bridging/H-terminal via η^2)	2.5	MP4//MP2	299
$(\eta^2\text{-BH}_4)Cu(PH_3)_2$ (H-bridging/H-terminal via η^3)	7.4	MP2//RHF	298
	11.7	MP4//MP2	299
$(\eta^1\text{-BH}_4)Cu(PH_3)_3$ (H-bridging/H-terminal via η^2)	3.0	MP4//MP2	299
$Ti(\eta^3\text{-BH}_4)_3$ (H-bridging/H-terminal via η^3,η^3,η^2)	5.1	MP2//UHF	300
$OsH_3(\eta^2\text{-BH}_4)(PH_3)_2$ (H-hydride/H-hydride pairwise)	9.5	CCSD(T)//MP2	240
$OsH_3(\eta^2\text{-BH}_4)(PH_3)_2$ (H-hydride/H-bridging polytopal)	19.0	CCSD(T)//MP2	240
$OsH_3(\eta^2\text{-BH}_4)(PH_3)_2$ (H-bridging/H-terminal via η^1)	20.8	CCSD(T)//MP2	240

[a] Energy barrier $\Delta E^{\ddagger}$ in kcal·mol^{-1}. [b] Two different hydride site exchange processes; see the text.

studies. A study of the hydrogen bonding between $OsH(Cl)(CO)(P^tBu_2Me)_2$ and $(CF_3)_2CHOH$ was only successful if the real nature of the two partners was taken into consideration. With the usual simplified model of PH_3 as phosphine and CH_3OH as proton donor, the preferred interaction between the transition metal complex and the alcohol was calculated (B3LYP) to occur between the electron-deficient Os center and the electron-rich oxygen center. The results were changed in a drastic way by using the IMOMM methodology for representing $OsH(Cl)(CO)$-$(P^tBu_2Me)_2$ and $(CF_3)_2CHOH$. The Os center is protected from approach by the steric bulk of the phosphine ligands. The only remaining interaction is between Cl and the proton of $(CF_3)_2CHOH$ as observed experimentally by IR spectroscopy.[293]

Similar difficulties were recently met in modeling the products that result from H_2 addition to IrH-$(H_2O)(bq\text{-}NH_2)(PR_3)_2^+$ (bq-NH_2 = 2-amino-7,8-benzoquinolate ligand).[294] The addition of H_2 to this complex leads, after departure of H_2O, either to an H_2 complex or to proton transfer from the coordinated H_2 to the bq-amino group to give an ammonium ion stabilized through H···H interaction by the nearby Ir−H bond. Calculations (B3PW91) with PH_3 as model phosphine show the dihydrogen complex to be strongly favored, while the successive replacement of H in each PH_3 group by F, to model the more electron-withdrawing phosphines used in the experiment, shows an increasing preference for the ammonium ion stabilized by Ir−H···H−N interaction. The experimental data show that only the least electron-donating PPh_3 group favors the ammonium ion, whereas the more electron-donating trialkylphosphine groups favor the dihydrogen complex. Remarkably, the experimental change of phosphine

ligands leading to the experimental detection of the predicted second isomer was only made as a consequence of the apparent disagreement between the theoretical and experimental results. These two examples illustrate some of the difficulties to be expected in future theoretical works in this field as well as the increasing necessity to take into account the real nature of the chemical compounds.

VII. Hydrogen Exchange Processes

Classical and nonclassical transition metal polyhydride complexes present a great diversity of dynamic processes involving hydrogen atoms coordinated to the metal, but their unequivocal assignment from experimental measurements, usually from variable-temperature ^1H NMR, is difficult. Theoretical calculations have greatly contributed to the understanding of the mechanisms of these dynamic processes. Calculations of hydrogen exchange processes in polyhydrides, dihydrogen and $M(H)(H_2)$ complexes are summarized in Tables 3−5, respectively.

A. Pairwise Exchange

Despite the strength of the M−H bonds,[8] hydride ligands show a great mobility, and hydride site exchange is often observed. Pairwise exchange involving a rotation of the H−M−H plane by 180° has been frequently characterized. Calculations have shown a significant shortening of the H−H distance during the exchange process and the possible implication of a thermally accessible η^2-H_2 structure. The kinetics of H/H exchange in $Re(CO)H_2(PR_3)_2(NO)$ was determined by variable-temperature ^1H NMR experiments. From both the kinetic data and extended

Table 4. Calculated Dihydrogen Rotational Barriers ΔE (kcal·mol^{-1})

complex	ΔE	exptl	methodology	ref
W(CO)$_3$(PH$_3$)$_2$(H$_2$)	2.1	2.2−2.4[a]	EHT	207
	1.8		RHF	214
	3.6		DFT	215
	1.0		CCSD(T)//B3LYP	217
Cr(CO)$_3$(PH$_3$)$_2$(H$_2$)	1.2	1.2[b]	DFT	215
Mo(CO)$_3$(PH$_3$)$_2$(H$_2$)	3.3	1.5−1.7[a]	DFT	215
OsHCl(CO)(PH$_3$)$_2$(H$_2$)	3.4		MP4//MP2	228
Os(NH$_3$)$_5$(H$_2$)$^{2+}$	0.6		CCSD(T)//B3LYP	302
cis-Os(NH$_3$)$_4$(H$_2$)(CH$_2$)$^{2+}$	1.0		CCSD(T)//B3LYP	302
trans-Os(NH$_3$)$_4$(H$_2$)(CH$_2$)$^{2+}$	2.1		CCSD(T)//B3LYP	302
Mo(CO)(H$_2$PC$_2$H$_4$PH$_2$)(H$_2$)	1.4	0.7	EHT	303
TpRh(H)$_2$(H$_2$)	0.5	0.6[c]	B3LYP	297
Fe(PH$_3$)$_4$(H)(H$_2$)$^+$	7.0		RHF	227
cis-IrCl$_2$(H)(H$_2$)(PH$_3$)$_2$	6.5		MP2//RHF	140
trans-IrCl$_2$(H)(H$_2$)(PH$_3$)$_2$	2.3		MP2//RHF	140
IrCl(H)$_2$(H$_2$)(PH$_3$)$_2$	2.2	0.5	MP2//RHF	305
{P(CH$_2$CH$_2$PH$_2$)$_3$}Fe(H)(H$_2$)$^+$	1.5	1.8[d]	DFT	182
Os(H$_2$)Cl(H$_2$PCH$_2$CH$_2$PH$_2$)$_2$$^+$	2.0		DFT	306
CpRh(H)$_2$(H$_2$)	4.9		CCSD(T)//B3LYP	297
CpRu(H$_2$)(H$_2$PCH$_2$PH$_2$)$^+$	4.2		B3LYP	251
CpMo(H)$_4$(H$_2$)(PH$_3$)$^+$	4.2		CCSD(T)//MP2	189
CpW(H)$_4$(H$_2$)(PH$_3$)$^+$	5.2		CCSD(T)//MP2	189
Cl$_2$Ta(H$_2$)(CO)$^+$	9.7	9.6	RHF	307
Cp$_2$Nb(H$_2$)(CNCH$_3$)$^+$	10.9	8.4−8.9	B3LYP	248
Os{NH=C(H)C$_6$H$_4$}(H$_2$)(PH$_3$)$_2$	11.0	12	B3LYP	179
Cr(CO)$_4$(H$_2$)$_2$	4.8		RHF	308
Ru(H)$_2$(H$_2$)$_2$(PH$_3$)$_2$	1.4	2.2	CCSD(T)//B3LYP	267

[a] Reference 301. [b] Reference 220. [c] Reference 304. [d] Reference 330.

Table 5. Calculated Activation Energy $\Delta E^{\ddagger}$ (kcal·mol^{-1}) for Hydrogen Exchange Processes in ML$_n$(H)(H$_2$) Complexes

complex	mechanism		methodology	ref
Fe(PH$_3$)$_4$(H)(H$_2$)$^+$	H/H$_2$ exchange, open direct transfer	3.2	RHF	309
Fe(PMe$_3$)$_4$(H)(H$_2$)$^+$	H/H$_2$ exchange, open direct transfer	0.5	DFT	195
trans-Os(H)Cl(H$_2$)(CO)(PH$_3$)$_2$	H/H$_2$ exchange via a cis intermediate	15.6	MP4//MP2	228
Ir(H)$_2$(H$_2$)(PH$_3$)$_2$$^+$	two sites H exchange between inequivalent H atoms	6.9	B3LYP	310
Ru(H)$_2$(H$_2$)(CO)(PH$_3$)$_2$	hydride exchange	7.9	B3LYP	229
Os(H)$_2$(H$_2$)(CO)(PH$_3$)$_2$	hydride exchange	6.1	B3LYP	229
TpRh(H)$_2$(H$_2$)	H/H$_2$ exchange via a tetrahydride	14.1	B3LYP	297
Cr(CO)$_4$(H$_2$)$_2$	H$_2$/D$_2$ exchange via a dihydride−dihydrogen	24.	RHF	308
Ir(H$_2$)$_2$(H$_2$)(PH$_3$)$_2$$^+$	cleavage of one dihydrogen	15.7	B3LYP	310
	HD formation	24.1	B3LYP	310
CpMo(H)$_4$(H$_2$)(PH$_3$)$^+$	open direct transfer	7.4	CCSD(T)//MP2	189
CpW(H)$_4$(H$_2$)(PH$_3$)$^+$	open direct transfer	7.0	CCSD(T)//MP2	189

Hückel calculations, an intramolecular exchange mechanism via a trigonal bipyramidal η^2-H$_2$ complex was proposed.[311] The pentagonal bipyramidal osmium trihydrides OsH$_3${NH=C(Ph)C$_6$H$_4$}(P^{i}Pr$_3$)$_2$[179] and OsH$_3${κ-N,κ-S-(2-Spy)}(P^{i}Pr$_3$)$_2$[295] show two different hydride site exchange processes involving two adjacent H atoms pseudo-trans to either X (H$_2$ and H$_3$ in Chart 18) or Y (H$_1$ and H$_2$ in Chart 18).

Chart 18
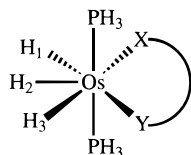
The respective transition states for the exchange have been located by calculations (B3LYP) on OsH$_3$-{NH=C(H)C$_6$H$_4$}(PH$_3$)$_2$ and OsH$_3${κ-N,κ-S-(2-Spy)}-(PH$_3$)$_2$ as model systems. They can be described as octahedral Os(II) species containing a dihydrogen ligand (H−H distances of 0.89 and 0.95 Å). A topological analysis of the electron density for the OsH$_3$-{κ-N,κ-S-(2-Spy)}(PH$_3$)$_2$ supports the presence of an Os(η^2-H$_2$) moiety. In OsH$_3${NH=C(H)C$_6$H$_4$}(PH$_3$)$_2$ the transition state, in which the dihydrogen ligand lies trans to the nitrogen atom, is found 20.1 kcal·mol^{-1} above the trihydride minimum, whereas the transition state, in which the dihydrogen ligand is trans to the ortho-metalated phenyl ring is only 12.3 kcal·mol^{-1} above the minimum.[179] In OsH$_3${κ-N,κ-S-(2-Spy)}(PH$_3$)$_2$ the activation barriers are 14.9 kcal·mol^{-1} for the exchange that involves a transition state with the dihydrogen trans to the nitrogen atom, and 16.2 kcal·mol^{-1} for the one trans to the sulfur atom.[295] It has been shown that the differences in activation barriers parallel the difference in energy needed for the exchanging hydrogen atoms to get in close proximity before undergoing the rotation. The energy barriers are thus directly related to the energetic cost for reaching a dihydrogen species. The exchange mechanism consists of an out-of-plane twist

of two adjacent hydride ligands, which come close enough to make an η^2-H$_2$ in the transition state (Chart 19). This mechanism is reminiscent of the

Chart 19
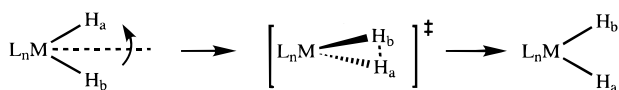
dihydrogen rotation, operative in dihydrogen complexes (vide infra), but it is associated with higher energy barriers because the rotation is coupled with the approach of the two hydrides.

The same pairwise exchange mechanism via an η^2-H$_2$ species has been proved to be operative in the trihydride species [CpIrH$_3$L]$^+$ (L = PH$_3$, CO)[241,242] and [Cp$_2$MH$_3$]$^{n+}$ (M = Mo, W, n = 1; M = Nb, Ta, n = 0).[244] The inter-ring angle in ansa bis(cyclopentadienyl)tungsten trihydride influences the energy barrier for pairwise site exchange. DFT calculations[312] on Cp$_2$WH$_3^+$, (η^5-(C$_5$H$_4$)$_2$SiR$_2$)WH$_3^+$, and (η^5-(C$_5$H$_4$)$_2$-SiR$_2$)WH$_3^+$ (R = H) have shown that the exchange requires a higher energy of activation as the Cp$_{cent}$−W−Cp$_{cent}$ angle decreases, in agreement with experimental NMR data[313,314] for R = Me.

The possibility that η^3-H$_3$ species were involved in the mechanism for hydrogen site exchange was discarded from MP2 calculations on [CpIr(PH$_3$)-H$_3$]$^+$.[268] It must be stressed that the extent to which the two exchanging hydrides approach each other in the transition state can be dependent on the particular system and/or the methodology employed. MP2 calculations of the hydride site exchange in OsH$_3$X-(PH$_3$)$_2$ (X = Cl, I) and OsH$_3$Cl(PH$_3$)$_3$ have found the pairwise exchange mechanism to be operative, but in the located transition states the H···H distances range from 1.34 to 1.38 Å.[181,296] These values fall in the range of the so-called elongated dihydrogen complexes, discussed in section IX. In these systems the H−H distance can vary with a very low energy cost. In some of these complexes, a low barrier for hydride site exchange is associated with the occurrence of quantum exchange coupling described in the following section.

The M(H)(H*)/M(H*)(H) exchange through an η^2-H$_2$ species is not restricted to transition metal di- or trihydride compounds. B3LYP and CCSD(T)//B3LYP calculations have predicted a piano-stool tetrahydride structure for the CpRhH$_4$ complex, a still unknown complex similar to TpRhH$_4$. In this system, a CpRh-(η^2-H$_2$)(H)$_2$ structure energetically slightly above the tetrahydride allows for a fast hydride exchange to take place.[297]

B. Polytopal Rearrangements

Hydride exchange through an η^2-H$_2$ structure often involves a significant motion of the two exchanging hydrides and only minor motions of the other ligands. In this mechanism, the formal oxidation state of the metal may change along the exchange pathway. In high-coordinate polyhydrides, alternative mechanisms are possible that require neither change in the metal oxidation state nor extensive participation of all ligands in the rearrangement process. The ster-

eochemical nonrigidity in seven-, eight-, or nine-coordinate polyhydrides has been well established.[315] This has been interpreted in terms of the various geometries available in seven-, eight-, and nine-coordination. It has been proposed that the permutation of the hydrides is possible via these alternative geometries.[30,316,317] The seven-coordinate [Fe(H)$_3$-(PEt$_3$)$_4$]$^+$ presents fast exchanging hydrides and was characterized as a distorted FeP$_4$ tetrahedron with the hydride ligands capping three of the faces.[272] DFT calculations on [Fe(H)$_3$(PMe$_3$)$_4$]$^+$ as a model have located a pentagonal bipyramid transition state for the hydrogen exchange with an activation barrier in very good agreement with the experimental data. The hydrogen exchange can be described as a tetrahedral jump or, alternatively, as a dodecahedral distortion of a cubic arrangement.[195] CCSD(T)//MP2 calculations[188] have shown that the hydride exchange in CpOsH$_5$ takes place according to a trigonal twist mechanism associated with a fairly small barrier (Chart 20). A turnstile mechanism was proposed to

Chart 20
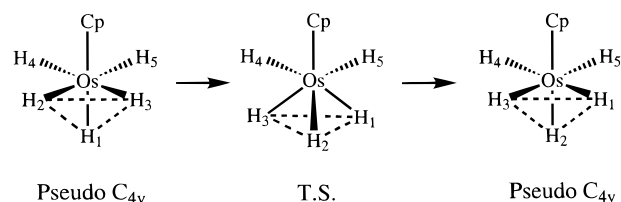
account for the decoalescence at low temperature of the ^{1}H NMR spectrum of [ReH$_5$(PPh$_3$)$_2$(py)] (py = pyridine). B3LYP calculations on ReH$_5$(PH$_3$)$_2$(py) located the transition state as a dodecahedral tautomer of the global minimum. Replacement of pyridine by 2-aminopyridine in the calculations has clarified the effects of H···H hydrogen bonding on the fluxionality process (see section VI).[284]

C. Site Exchange with H Atoms outside the Coordination Sphere

Transition metal tetrahydroborate compounds exhibit fluxionality associated with hydride exchange. In tetrahydroborate complexes, one (η^1), two (η^2), or three (η^3) hydrides of BH$_4^-$ bridge the transition metal and the boron atom (Chart 21).[318] Almost all

Chart 21
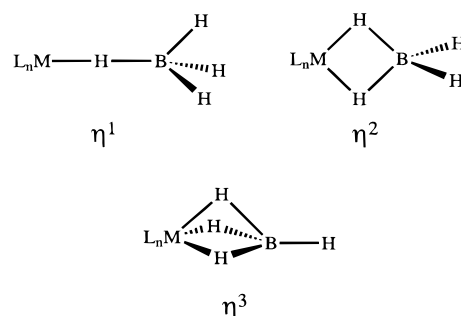
of these complexes display a fast exchange between bridging and terminal hydrogen atoms attached to the boron atom. The mechanisms proposed involve a

change in the coordination mode of the tetrahydroborate ligand.[319,320] For example, it has been suggested that the exchange in bidentate tetrahydroborate complexes can proceed via either a unidentate or a tridentate intermediate. However, it has not been possible to differentiate between the two mechanisms from ^{1}H NMR measurements. HF calculations on $(\eta^2\text{-}BH_4)Mn(CO)_4$ and $(\eta^2\text{-}BH_4)Cu(PH_3)_2$ indicate that, in both systems, the mechanism of bridging−terminal hydride exchange occurs via an associative rather than dissociative pathway. Single-point MP2 calculations have shown that the η^1-structure lies at a decisively higher relative energy than the η^3-structure for both molecules.[298]

The exchange between terminal and bridging hydrogen atoms in $[Cu(BH_4)(PH_3)_n]$ (n = 1, 2, 3) has been studied at the MP4//MP2 level.[299] In $Cu(PH_3)$-$(\eta^3\text{-}BH_4)$ the exchange takes place with a very low barrier via the η^2-structure. The energy barrier for the exchange in $Cu(PH_3)_2(\eta^2\text{-}BH_4)$ is 11.7 kcal·mol^{-1}, and the transition state can be described as a distorted η^3-structure. The $Cu(PH_3)_3(BH_4)$ complex adopts a strongly nonlinear η^1-structure. The exchange between the strongly and the weakly bridged hydrogen atoms goes through a symmetrical η^2-complex with a very low energy barrier. A more complicated exchange pathway has been found for d^1 $Ti(BH_4)_3$. In agreement with the experimental data, UHF calculations followed by single-point MP2 calculations gave the C_{3h} $Ti(\eta^3\text{-}BH_4)_3$ structure as the most stable one. The relative energy of $Ti(\eta^3\text{-}BH_4)_2$-$(\eta^2\text{-}BH_4)$, where the two bridging hydrides are orthogonal to the TiB$_3$ plane, allows for an easy exchange mechanism between bridging and non-bridging hydrogen atoms.[300]

Transition metal hydride complexes may undergo another type of dynamic process: an H/H exchange between the hydride ligand and a hydrogen atom from another ligand. Most of the examples occur with dihydrogen ligands (vide infra), but other ligands can also be involved. Isotopic labeling experiments are useful to detect the exchange, but are not informative to identify the mechanism. An intramolecular H/D exchange between thiol and hydride was reported for $[IrH_2(HS(CH_2)_3SH)(PCy_3)_2]^+$.[321] Intramolecular protonation of a hydride ligand by an acidic ancillary ligand to give a dihydrogen ligand has also been postulated in $[IrH(Cl)(NH_3)_2(PEt_3)_2]^+$ [322] and $[IrH(H_2O)(bq)(PCy_3)_2]^+$ [323] (bq = 7,8-benzoquinolinate). A facile H/D exchange reaction between anionic transition metal carbonyl hydrides $[HM(CO)_4L]^-$ (M = Cr, Mo, W; L = CO, PR$_3$) and CH_3OD, D_2O, and CH_3-CO_2D has been reported.[324] A similar fast H(hydride)/H(acid) exchange has been shown to be operative in $Re(CO)H_2(NO)L_2$ compounds.[325] It has been reported that bridging hydrides exchange with terminal hydrides on osmium in $[OsH_3(\eta^2\text{-}BH_4)(PR_3)_2]$.[240,326] Rapid exchange of hydrogen atoms between hydride and methyl ligands has been shown to occur in $[Cp^*Os$-$(dmpm)(CH_3)H]^+$, presumably through an alkane complex.[327]

Theoretical studies on this subject are still scarce. Extended Hückel calculations have shown that experimental H/D exchange between $(Cp^*_2LnH)_2$ (Ln

= Lu, Y) and deuterated arenes can be explained in terms of σ bond metathesis involving a direct single-step H/H exchange. An orbital analysis indicated that the ease with which an RH molecule may undergo the H/H exchange process is associated with the ability of the α carbon to stabilize an entering nucleophile.[328] The complex $OsH_3(\eta^2\text{-}BH_4)(PH_3)_2$ was studied for unraveling the mechanism of the possible hydride exchange processes (Chart 22). The exchange

Chart 22
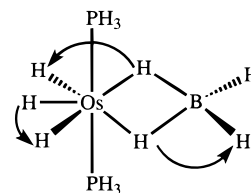
may involve two of the three terminal hydrides on Os, or one bridging hydride and a terminal hydride from either Os or B. A CCSD(T)//MP2 study has allowed for the characterization of three different intramolecular rearrangements.[240] The lowest energy barrier is associated with the exchange of the two hydrides on Os. The pairwise exchange process of two adjacent hydride ligands goes through an $(\eta^2\text{-}H_2)$-like transition state. The second lowest energy barrier corresponds to the H(Os)/H(bridged) exchange.

In this case, the process goes through a seven-coordinate $OsH_4(BH_3)(PH_3)_2$ intermediate containing an η^2-BH$_3$ ligand. Finally, the highest energy barrier is associated with the exchange process between the bridging and terminal hydrides of the BH$_4^-$ ligand. This rearrangement goes, via a transition state with a monodentate BH$_4^-$ ligand, along a dissociative pathway.

D. Dihydrogen Rotation

The hydrogen atoms of a dihydrogen ligand may exchange their positions by a rotation about the M−H$_2$ axis. This process is usually so rapid that, even at very low temperature, only one peak is observed for H$_2$ in the ^{1}H NMR spectrum. INS experiments have been used to determine the height of the rotation barrier.[301] The main contributions to the rotational barrier are the direct electronic interaction between the dihydrogen and the transition metal fragment and, in some cases, the nonbonded interactions between the hydrogen atoms and the ancillary ligands. For this reason, the barrier to rotation of dihydrogen serves as a very sensitive probe of the electronic interactions between the metal and its ligands. Theoretical determination of dihydrogen rotational barriers has also served as a quantitative benchmark for electronic calculations in dihydrogen complexes. The rotational barrier is mainly sensitive to the d$_\pi$−σ^* back-bonding. It must be stressed that the rotational barrier is only related to the change between the minimum and the transition state and not to the absolute magnitude of the M−H$_2$ interaction at the minimum.

INS studies have permitted measurement of the low barrier for octahedral d^6 complexes. Experimen-

tal values have been found to lie between 0.5 and 2.0 kcal·mol^{-1}. Such low barriers are obtained because the d_π–σ^* interaction does not change much upon rotation of H_2. Back-donation is preserved during the rotation, and the d orbitals that are responsible for the back-donation in the different orientations of H_2 have similar energies and shapes. The rotational barrier in $W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ has been calculated by a number of methods. A barrier height of 2.2 kcal·mol^{-1} was determined from INS measurements (R = Cy).[214] Early extended Hückel calculations correctly predicted the orientation of the H_2 ligand and gave a rotation barrier of 2.1 kcal·mol^{-1}.[207] HF calculations[214] showed that the electronic component yields a barrier of 1.8 kcal·mol^{-1} (R = H). Molecular mechanics (MM2) calculations[214] gave a steric component of 0.6 kcal·mol^{-1}. It was clear that neither the bulk of the phosphine ligands nor the other steric factors significantly hinder H_2 rotation in these complexes.[214] Barriers of 3.6 kcal·mol^{-1} (DFT)[215] and 1.0 kcal·mol^{-1} (CCSD(T)//B3LYP)[217] have been obtained.

Theoretical studies have traced the origin of this barrier to the decrease of the back-donation in the $\sigma^*(HH)$ orbital when the H–H ligand becomes coplanar with the adjacent metal–carbonyl bond.[207,213–215,217] The evolution of the W–H_2 geometrical parameters along the rotation pathway supports this analysis: the H–H distance decreases from 0.832 to 0.805 Å, and at the same time, the W–H distances increase from 1.918 to 1.965 Å.[217] Rotational barriers of 1.2 and 3.3 kcal·mol^{-1} have been reported (DFT) for $Cr(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$ and $Mo(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$.[215] Experimental values for $M(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ compounds are 1.2 kcal·mol^{-1} for M = Cr[220] and 1.5–1.7 kcal·mol^{-1} for M = Mo.[301] An energy barrier of 3.4 kcal·mol^{-1} was calculated at the MP4//MP2 level for $OsHCl(\eta^2\text{-}H_2)(CO)(PH_3)_2$ (H and H_2 trans).[228] In d^6 octahedral complexes with a more symmetrical ligand field, even lower barriers can be expected. In these compounds the π back-donation interaction is roughly constant during the rotation. The set of t_{2g}-like metal orbitals being fully occupied, one component or a linear combination of two components is always ideally oriented to interact with $\sigma^*(HH)$. A rotational barrier of 0.6 kcal·mol^{-1} was calculated at the CCSDT(T)//B3LYP level in $[Os(NH_3)_5(H_2)]^{2+}$.[302] For $Mo(CO)(R_2PC_2H_4PR_2)_2(\eta^2\text{-}H_2)$, a barrier to rotation of 0.7 kcal·mol^{-1} was determined from INS measurements. EHT calculations gave a value of 1.4 kcal·mol^{-1}.[303] B3LYP calculations on $TpRhH_2(\eta^2\text{-}H_2)$ have also found a very low rotational barrier (0.5 kcal·mol^{-1}),[297] in excellent accord with the value determined by means of INS in $Tp^{Me_2}RhH_2(\eta^2\text{-}H_2)$ (0.56(2) kcal·mol^{-1}).[304] It seems that in this complex back-donation does not vary significantly during the rotation of the dihydrogen.[329]

The attractive cis effect[263] between dihydrogen and *cis*-hydride ligands has been found to influence the rotational barrier. The implications of the cis effect on the structure of the complexes have been discussed in section VI. The rotational barriers found in $[Fe(PH_3)_4(H)(\eta^2\text{-}H_2)]^+$ (7.0 kcal·mol^{-1}, RHF)[227] and $IrCl_2(H)(H_2)(PH_3)_2$ (6.5 kcal·mol^{-1}, MP2//RHF)[140] have

high values that have been attributed to the loss of the cis effect in the transition state. For the iridium complex the calculated rotational barrier is remarkably lower in the *trans*-M(H)(H$_2$) isomer, where the cis interaction is absent.[140] The MP2//RHF barrier[305] is also lower (2.2 kcal·mol^{-1}) in the related compound $IrCl(H)_2(\eta^2\text{-}H_2)(PH_3)_2$. DFT calculations pointed out that the cis effect could govern the rotational barrier in $[(PP_3)Fe(H)(\eta^2\text{-}H_2)]^+$.[182,330]

Rotational barriers higher than 4 kcal·mol^{-1} have been calculated in dihydrogen complexes with Cp ligands. CCSDT//B3LYP calculations have found an energy barrier of 4.9 kcal·mol^{-1} in $CpRhH_2(\eta^2\text{-}H_2)$.[297] This value suggests a considerable loss of back-donation in the transition state. This conclusion is consistent with the evolution of the H–H distance, from 0.943 Å at the minimum to 0.850 Å at the transition state.[297] The cyclopentadienyl ring significantly distorts the shape and energy of the three nonbonding metal orbitals that are no longer a t_{2g}-like set of orbitals. Back-donation occurs through metal orbitals that are different in energy and shape at the minimum and in the transition state.[244,297,331] An energy barrier of 4.2 kcal·mol^{-1} was obtained (B3LYP) for the elongated dihydrogen complex $[CpRu(H\cdots H)(H_2PCH_2PH_2)]^+$.[251] In this system the H–H distance is also notably shortened in the transition state. Barriers to rotation of 4.2 and 5.2 kcal·mol^{-1} have been calculated at the CCSD(T)//MP2 level for $[CpM(\eta^2\text{-}H_2)H_4(PH_3)]^+$ complexes (M = Mo, W).[189] These d^0 complexes lack any d_π–σ^* donor effect, and the high value of the barriers has been attributed to a strong cis effect.[189]

High rotation barriers (around 10 kcal·mol^{-1}) have been observed in d^2 $Cp_2M(H_2)L^+$ (M = Nb, Ta). This is higher than in most dihydrogen complexes but smaller than the barrier for site exchange in Cp_2MH_3. Rotation of coordinated HD has even been frozen on the NMR time scale.[248,307,332] The rotational barrier (9.7 kcal·mol^{-1}, HF) for $Cl_2Ta(H_2)(CO)^+$ is thus very close to the experimental value (9.6 kcal·mol^{-1}) for $Cp_2Ta(H_2)(CO)^+$.[307] Calculations (B3LYP) for $Cp_2Nb(H_2)(CNCH_3)^+$ gave a rotational barrier of 10.9 kcal·mol^{-1}, which compares well to the experimental $\Delta G^\ddagger$ (8.4–8.9 kcal·mol^{-1}) obtained from NMR data in $(\eta^5\text{-}(C_5H_4SiMe_3)_2Nb(H_2)(CNR)^+$ (R = ^{t}Bu, Cy, xylyl).[248] The high rotation barrier in these complexes has been attributed to the complete loss of back-donation on going from the global minimum to the transition state. In the global minimum, H_2 lies in the plane bisecting the Cp–M–Cp angle, where back-donation from the unique occupied d orbital is maximal. When H_2 is rotated by 90°, the overlap with the d orbital is lost, and no other occupied orbital is available for back-donation. This accounts for a significant shortening of the H–H bond (from 0.871 to 0.765 Å) and lengthening of Nb–H (from 1.870 to 2.09 Å) upon rotation.[248] A combination of calculations (B3LYP) and one-dimensional dynamical studies has shown that the absence of decoalescence of the H signal is due to the presence of a large quantum exchange coupling.[248] This is the unique case of quantum exchange coupling (see section VIII) involving only a dihydrogen ligand.

The observed high energy for rotating H_2 in OsX-$\{NH{=}C(Ph)C_6H_4\}(H_2)(P^iPr_3)_2$ (X = Cl, Br, I) has been properly reproduced in $Os(Cl)\{NH{=}C(H)C_6H_4\}(H_2)$-$(PH_3)_2$ as a model system (11 kcal·mol^{-1}, B3LYP).[179] This high rotation barrier has been related to the presence an elongated dihydrogen. The relationship between the rotational barrier and the H−H distance has been discussed in $Os(H{\cdots}H)Cl(H_2PCH_2CH_2$-$PH_2)_2^+$, where the presence of an elongated H−H bond has been proposed.[306]

In the case of bis(dihydrogen) ligands, HF calculations for $Cr(CO)_4(H_2)_2$ give a barrier height of 4.8 kcal·mol^{-1} for rotating by 90° the two H_2 from their most stable orientation.[308] Geometry optimizations (B3LYP) and energy barrier calculations (CCSD(T)//B3LYP) have been carried out for $RuH_2(H_2)_2(PH_3)_2$, where PH_3 was the model for PCy_3. Although the two *cis*-dihydrogen ligands should be perpendicular to each other to benefit from back-donation from two different occupied d orbitals, the calculations show that the two H_2 ligands lie in the H−Ru−H plane, presumably because of the cis effect. The calculated barrier is very low (1.4 kcal·mol^{-1}), in agreement with the INS measurement.[267]

Since H_2 is a single-face π acceptor, its rotation is expected to be coupled with the rotation of the other single-face π acceptor ligands. This was calculated to be the case in $RuH_2(H_2)_2(PH_3)_2$, where a C_2 conrotatory pathway was shown to be slightly preferred.[267] In $Os(NH_3)_4(H_2)(CH_2)^+$, the coupled rotation of H_2 and CH_2 was studied (CCSD(T)//B3LYP) for the case where the two ligands are cis or trans.[302] The rotational barriers for H_2 and CH_2 remain low because the most unfavorable situation for backbonding is always avoided.

E. Exchange Processes in M(H)(H₂) Complexes

Exchange between hydride and hydrogen of H_2 has been shown to occur in complexes where dihydrogen and hydride ligands coexist. The simplest case is the exchange between dihydrogen and one hydride in $L_nM(\eta^2\text{-}H_2)(H)$. Several possible mechanisms were considered in an HF study of the octahedral model complex $[Fe(PH_3)_4(H)(\eta^2\text{-}H_2)]^+$.[309] The favored mechanism consists of a single-step transfer of the hydrogen atom between the two ligands ("open direct transfer") and is associated with a very low energy barrier. This mechanism requires elongation of the H−H bond with concomitant shortening of the separation between the hydride and the vicinal hydrogen of the H_2 ligand (Chart 23). The two H$\cdots$H distances

Chart 23
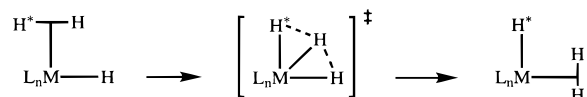
become equal and relatively short in the transition state, which can be viewed as containing an H_3^- ligand. This H exchange does not require a drastic rearrangement of the phosphine ligands, and is mainly determined by the motion of the H atoms. This exchange can be envisaged as a nondissociative

mechanism, and does not require an oxidative addition of the dihydrogen.

An experimental study on $[ReH_2(H_2)(CO)(PMe_2$-$Ph)_3]^+$ has demonstrated the existence of a nondissociative hydrogen exchange pathway, with no oxidative addition of H_2.[333] Further evidence has been found favoring this mechanism with *cis*-H and -H_2 ligands (*cis*-M(H)(H_2) complexes). The ^{1}H NMR spectra of $[Fe(\eta^2\text{-}H_2)(H)(PMe_3)_4]^+$ indicated a very fast H/H_2 scrambling.[272] DFT calculations have located a transition state, which agrees with the proposed mechanism.[195] In the octahedral complex $[Os(H)Cl$-$(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]$ with *trans*-H and -H_2 ligands (*trans*-M(H)(H_2)), hydride exchange also takes place, although at a slow rate. The study of this dynamic behavior has been carried out by means of NMR and ab initio MP2 studies.[228] Two seven-coordinate trihydrides and a *cis*-M(H)(H_2) complex, relevant to the exchange process, were located in the MP2 potential energy surface. The proposed mechanism involves the initial cleavage of the dihydrogen ligand in *trans*-M(H)(H_2) to form a fluxional M(H_3) complex that rearranges into a *cis*-M(H)(H_2) intermediate, where H exchange can occur. The estimated barrier (15.6 kcal·mol^{-1}) agrees with the experimental activation parameters ($\Delta H^{\ddagger} = 17.4 \pm 0.5$ kcal·mol^{-1}). The possible coexistence of *trans*- and *cis*-M(H)(H_2) isomers with M(H_3) has also been proposed from an ab initio MP2 and molecular mechanics study of $[Ru$-$(P{-}P)_2\text{"}H_3\text{"}]^+$ (P−P = dppb, diop, dpmb, dppe) complexes to explain the NMR spectra.[198]

In systems such as $L_nM(\eta^2\text{-}H_2)(H)_2$ several types of exchanges are possible. The variable-temperature ^{1}H NMR spectra of $[Ir(H)_2(\eta^2\text{-}H_2)(P^tBu_2Ph)_2]^+$ indicate a pairwise exchange process between the inequivalent hydrides. B3LYP calculations reveal a mechanism ($\Delta E = 6.9$ kcal·mol^{-1}) involving a sliding of the two hydrides in the plane perpendicular to P−Ir−P with no associated rotation of the H−Ir−H plane with respect to the rest of the complex.[310] Steric factors may be responsible for the energy barrier in $Ir(H_2)$-$(X)(PR_3)_2$ complexes.[204] Calculations (B3LYP) have established that the two hydride ligands are cis in $M(H)_2(\eta^2\text{-}H_2)(CO)(PR_3)_2$ (M = Ru, Os) complexes.[229] The hydrogen site exchange involves a structure in which the two hydrides become trans.

The dihydrogen and hydride ligands in $Tp^{Me_2}Rh$-$(H)_2(\eta^2\text{-}H_2)$ (Tp^{Me_2} = hydridotris(3,5-dimethylpyrazolyl)borate) are highly fluxional on the NMR time scale, and a dynamic exchange between the dihydrogen ligand and the two hydrides takes place.[334] The fluxionality of the exchange between a hydride and H_2 in $TpRh(H)_2(\eta^2\text{-}H_2)$ as a model complex has been studied by means of B3LYP calculations. Two different mechanisms involving either a tetrahydride or a bis(dihydrogen) have been considered. The bis(dihydrogen) structure lies 10 kcal·mol^{-1} above the tetrahydride isomer, suggesting a preference for the exchange to go through the tetrahydride structure.[297] A possible low-energy reaction pathway for the H_2/D_2 exchange in the bis(dihydrogen) complex $Cr(CO)_4$-$(H_2)_2$ involving a $M(H)_2(H_2)$ complex was obtained from RHF calculations.[308,335] Two recent theoretical studies have treated the hydrogen exchange pro-

cesses in six-hydrogen systems containing dihydrogen and hydride ligands (Chart 24). In $[CpM(\eta^2\text{-}H_2)(H)_4$-

Chart 24

TS
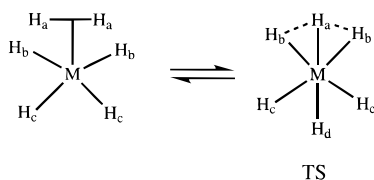
$(PH_3)]^+$ (M = Mo, W) complexes, stretching the dihydrogen toward an adjacent hydride is a low-energy process and leads to a transition state with "H_3^-" character. The energy barriers (CCSD(T)//MP2) for these exchanges (ca. 4 kcal·mol^{-1}) agree with the inability to decoalesce the hydride signals at -140 °C.[189]

In $[Ir(H)_2(\eta^2\text{-}H_2)_2(PH_3)_2]^+$, two transition states corresponding to two different hydrogen exchange processes have been located from B3LYP calculations.[310] The two-step mechanism accounts for the exchange of H and H_2 and for the results of isotope incorporation.

VIII. Quantum Exchange Couplings in Polyhydrides

Within the Born–Oppenheimer approximation, the electronic energy of a molecule is a function of the relative positions (configuration) of its atoms, which are considered to be fixed. A given configuration of the nuclei has a given energy, which corresponds to a given point in the configuration space. If two identical nuclei in the molecule are permuted, a new configuration corresponding to a different point in the configuration space is obtained with the two configurations having the same energy. Thus, a single potential energy well does not properly represent the chemical system because of the presence of identical potential wells in the configuration space.

In quantum mechanics, the system explores the whole configuration space, and in the case of ethylene, for example, there are 12 such different wells each corresponding to the same ground-state geometry.[336] Therefore, a rovibrational state for a configuration corresponding to a particular well is indeed composed of 12 different rovibrational levels each carrying different symmetry labels with respect to the permutation operations. However, the difference in energy among all these levels is very small and is dependent upon the ease of transfer from one well to the other.

Restricting the configuration space to only one well is valid if no experimental method is able to probe the splitting between the aforementioned levels. The dynamics of the system is confined to this particular well, and all the equivalent wells behave independently. On the other hand, if a spectroscopic technique can "see" the splitting, the different wells have to be considered together. We discuss in this section the theoretical description of a phenomenon observed spectroscopically in polyhydride complexes that is related to the easy permutation of two identical hydrides.

A. Physical Origin of Quantum Exchange Couplings

In the mid-1980s, the groups of Chaudret and Heinekey independently observed very unusual low-temperature ^1H NMR spectra in Cp^*RuH_3L (L = PMe_3, P^iPr_3, PCy_3)[12] and $CpIrH_3L^+$ (L = PMe_3, PPh_3, $AsPh_3$).[13] Whereas only one peak was observed in the hydride region of the ^1H NMR spectra at room temperature, lowering the temperature led to a decoalescence of the signals and a second-order AB_2 spectrum with an abnormal coupling constant J_{ab}.

The value of J_{ab} is much higher than expected for a coupling constant between any two hydrides or even mutually bonded ones. In the case of $CpIrH_3$-$(AsPh_3)^+$ $J_{ab} = 570$ Hz at 185 K.[13] In addition, the magnitude of J_{ab} increases with the temperature in a way not expected for magnetic couplings. For $Cp^*RuH_3(P^iPr_3)$ J_{ab} goes from 57 Hz at 168 K to 131 Hz at 203 K.[12] A detailed experimental description of this phenomenon can be found in the very recent review by Sabo-Etienne and Chaudret.[32] We focus here on the theoretical analysis.

The experimental observations were originally tentatively explained by an equilibrium between $M(H)_3$ and cis-$M(H)(H_2)$ geometries[12] or by the participation of a H_3-type ligand.[13] However, both explanations were later ruled out by the experimental evidence.

The presence of a chemical equilibrium between a ground-state classical MH_3 structure with low J_{ab} and an intermediate $M(H)(H_2)$ complex with high J_{ab} should have led to temperature-dependent chemical shifts of the hydrides, and this was not observed. Moreover, the magnitude of the coupling constant could not have been higher than that of free H_2, which is 280 Hz as calculated from measurement on HD. Finally the H_3 ligand hypothesis was discarded because the neutron diffraction for $CpIrH_3(PMe_3)^+$ showed a long H···H distance[337] and because substitution of one H by a deuterium (D) did not quench the phenomenon. The coupling constant is 6% larger for the isotopomer $CpIr(PPh_3)(H_aH_bD_b)^+$.[337]

In papers submitted 3 days apart, Weitekamp et al.[338] and Zilm et al.[339] both simultaneously proposed a similar explanation of the physical origin of the phenomenon in terms of quantum exchange coupling (QEC). The two groups recognized that the observed coupling constant could not come only from a magnetic interaction but was the manifestation of a tunnel effect between two equivalent configurations (Chart 25). The energetically easy permutation of the two hydrides corresponds to a splitting of rovibrational levels detectable by an NMR spectrometer. Although three hydrides are present, the tunnel effect involves only two hydrogen atoms at a time and is thus associated with a pairwise exchange. The QEC has also been observed in a tantalum dihydride complex.[340]

Within the framework of pairwise exchange, Zilm has shown how an NMR AB spectrum can result from a tunnel effect between two equivalent configurations.[339,341] The value of the splitting between vibrational levels is large enough to be detected by NMR

Chart 25
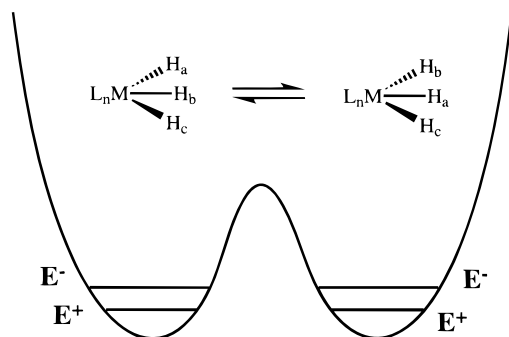
because the exchange between the two configurations is easy. One of the levels, E^+, is symmetric under the permutation of the two H atoms, whereas the other, E^-, is antisymmetric (a similar analysis holds for ammonia inversion). Consequently, due to the fermionic nature of H, the nuclear spin wave function associated with each level is a priori fixed: singlet for E^+ and triplet for E^- (case of two H atoms only). Without including any magnetic coupling term $J \cdot \bar{I}_a \cdot \bar{I}_b$, it can be shown that the NMR spectrum corresponds to an AB spectrum with $J_{ab} = E^- - E^+$.

This phenomenon is in principle present in *any* chemical species having more than one H. However, in organic molecules, the energy for exchange of two hydrogen atoms is often very high. This leads to a nonobservable yet nonzero J_{ab}. Transition metal polyhydrides where the permutation of H atoms can be energetically facile are for the moment the only systems where QEC is seen experimentally. The temperature dependence of J_{ab} is easily explained by considering all the vibrational levels E_n below the barrier to exchange between the two configurations. Each level is in fact a doublet $\{E_n^+, E_n^-\}$ with an associated coupling constant $J_n = E_n^- - E_n^+$. The observed coupling constant is the Boltzmann average of the various contributions J_n.

The quantum nature of the QEC also explains why, upon incorporation of tritium, the observed coupling constant dramatically decreases, contrary to what is expected from the relative values of γ_T and γ_H.[337,342] In the case where the two particles are not identical, there are no longer any symmetry properties associated with the permutation operation, and therefore, the observed AB spectrum results only from the usual magnetic coupling. Heinekey et al.[342] estimated the magnetic contribution to the experimental coupling constant from measurements of J_{HT} and, thus, extracted the pure quantum mechanical exchange component.

B. Simulation of Quantum Exchange Couplings

The mechanism for permuting the H centers has been the subject of some controversy. Zilm first proposed a mechanism where the two exchanging hydrides approach within a given distance λ by a bending mode of frequency ν before undergoing the exchange.[339,341] The mechanism was derived from a prior study of exchange phenomena in liquid[3] He by Landesman.[343] The two exchanging hydrides are restricted to the plane corresponding to the ground-state geometry. This leads to the following expression for J_{ab}:

$$J_{ab} = \frac{3\hbar a}{4\pi m \delta^3} \left(\frac{3}{\pi}\right)^{1/2} \exp\left\{-\frac{3}{4}\frac{a^2 + \lambda^2}{\delta^2}\right\}$$

where a is the equilibrium H$\cdots$H separation and δ the amplitude of the bending vibrational motion. The temperature dependence of J_{ab} is taken into account through δ:

$$\delta^2(T) = \frac{3\hbar}{4\pi m \nu} \coth\left\{\frac{h\nu}{kT}\right\}$$

Zilm obtained values for a and ν by adjusting the parameters to the experimental data. QEC is larger if the ground-state distance a between two neighboring hydrides is small and if the bending motion is soft. Typical values for a lie between 1.6 and 1.7 Å, whereas ν values lie between 400 and 600 cm^{-1}.

Zilm's model was used by Daudey et al.[243] to account for the behavior of the trihydrides Cp_2TaH_3 and Cp_2NbH_3; the Nb complex shows QEC while the Ta analogue does not.[344] This study was the first ab initio calculation in this field. The experimental systems were modeled by Cl_2MH_3 (M = Nb and Ta) and optimized at the RHF level. Bending frequencies were calculated to be 603 cm^{-1} for Nb and 1032 cm^{-1} for Ta. The ratio J^{Ta}/J^{Nb} was estimated to be 2.3 × 10^{-9} by using the computed frequencies within Zilm's model for J_{ab}. This accounts for QEC being measurable in the case of Nb but not in the case of Ta.

The difference in behavior between Nb and Ta was traced to the relative energies of an $M(H)(H_2)$ isomer. The latter was 14.6 kcal·mol^{-1} more stable than the trihydride for Nb and 7.3 kcal·mol^{-1} less stable for Ta. Although the calculations did not properly reproduce the trihydride ground state, they correctly mimicked the greater tendency for Nb to form an H_2 complex. This is probably due to the approximate nature of the modeling (Cl for Cp) or to the lack of electron correlation in the HF method used at that time because of computational limitations. A recent study at the B3LYP level on the real systems Cp_2MH_3 proved the trihydride to be the ground state for both metals.[244] The $M(H)(H_2)$ isomer is energetically more accessible for Nb (+11.4 kcal·mol^{-1}) than for Ta (+19.8 kcal·mol^{-1}), which accounts for the observed differences in QEC.

The relation between the ease of reaching a $M-(H_2)$ configuration and the occurrence of QEC has been discussed. Limbach based his model on this relationship.[345] He considered three different mechanisms to accomplish the exchange. Mechanism I is identical to Zilm's model. Mechanism II consists of an out-of-plane rotation of the two hydrides, keeping the H$\cdots$H distance constant. Mechanism III first considers a preequilibrium between the ground-state trihydride and a $M(H)(H_2)$ isomer. The rotation of the H_2 ligand is then responsible for the exchange.

These three mechanisms lead to different behaviors of J_{ab} with temperature. Mechanism II was discarded because it would lead, in contradiction with experiments, to a decrease of J with increasing temperature. Mechanism I (Zilm's model) leads to a nonzero

plateau at very low temperature, whereas for mechanism III the low-temperature limit should be zero. The M(H)(H$_2$) configuration, where the tunnel effect is effective, would not be populated at this temperature, and the resulting J_{ab} should be zero. Mechanism III also predicts first an increase and then a decrease of J with increasing T if highly excited rotational tunneling states are significantly populated. However, at the onset of classical exchange, the quantum exchange coupling is no longer seen, and such temperature-dependent behavior might be impossible to detect.

Following Limbach's model (mechanism III), Lluch, Lledós, and co-workers carried out the first combined ab initio/dynamics study of QEC[241,242] for CpIr(PH$_3$)-H$_3^+$ as a model of CpIr(PMe$_3$)H$_3^+$ [337] at the RHF and MP2 levels. The study was divided into two parts. A potential energy surface was first constructed. The variables were the H−H distance R_{HH}, the distance between the metal and the midpoint of the H···H bond R_{MX}, and the rotation angle ϕ around the M−X axis (Chart 26).

Chart 26
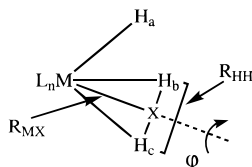
A one-dimensional tunneling path was then derived. It starts from a trihydride ground-state structure and goes through a M−(H$_2$) configuration by an in-plane bending of two H atoms; exchange is then achieved by rotation of H$_2$. Within this monodimensional potential energy surface, the vibrational levels were computed by using a distributed Gaussian basis set along the path. The temperature dependence of J_{ab} could be reproduced with fairly good agreement with the experimental data. The same methodology was used for a study of the influence of a Lewis acid on QEC.[246] It was shown that QEC is increased by coordination of a Lewis acid to the wingtip hydride. QEC in a niobium dihydrogen system with blocked H$_2$ rotation was also calculated.[248]

Another approach was derived by Clot et al.[296] who were the first to use a two-dimensional model (2D). The 16-electron complex OsXH$_3$(PH$_3$)$_2$ (X = Cl, I) as a model system for OsXH$_3$(P^{i}Pr$_3$)$_2$ (X = Cl, I) synthesized by Caulton et al.[180] was considered. In the dynamical model, the two variables were the angle ϕ describing the rotation (Chart 26) of the H···H entity and the distance R_{HH} between the two H atoms. The reaction coordinate is the angle ϕ, whereas R_{HH} adapts itself rapidly to every change in ϕ. A reaction path Hamiltonian[346] was constructed by computing the potential energy surface (PES) along ϕ at the MP2 level and by using a ϕ-dependent harmonic term to describe R_{HH}. The vibrational levels were then computed within a discrete variable representation (DVR).[347]

The calculated J_{ab} values were in fairly good agreement with the experimental data. In a later study, it was shown how QEC could be used as a hypersensitive indicator of weak interactions.[181] By considering the 18-electron complex OsClH$_3$(PH$_3$)$_3$, J_{ab} was calculated to be larger in an 18-electron complex than in a 16-electron complex. Note that the other complexes exhibiting QEC are also saturated 18-electron complexes. However, it was shown that the classical barrier to exchange is lower and wider for the 18-electron complex. As a consequence, although J_{ab} from QEC is larger, the classical exchange is also easier and QEC might not always be observed.

The main conclusion that can be drawn from these combined ab initio/dynamics studies is that the two exchanging hydrides need to get closer in the transition state than they are in the ground-state structure. This is probably why QEC has been observed for trihydrides in which the three H nuclei are already in close proximity in the ground-state geometry (~1.6 Å). However, there is no specific requirement to reach a M(H)(H$_2$) configuration. The low-energy barrier for permuting the two H atoms, and the small displacement of the other nuclei during the exchange, seem to be the important criteria for observing large J_{ab}.

Other theoretical studies have been devoted to the QEC phenomenon. Scheurer et al. used Lledós' PES[242] to simulate QEC for CpIrLH$_3^+$.[348] Their 2D dynamical model was similar in essence to the one developed by Clot et al., although not equivalent. They also included an explicit coupling with the bath and studied the influence of pressure on QEC. Hiller and Harris used a tight binding model with inclusion of coupling with the bath to simulate QEC.[349−351]

The problem of the transition between the low- and high-temperature domains was first addressed by Szymanski.[352] He used a density matrix formalism to study the coherences responsible for QEC and how the activated classical exchange destroys them. Limbach et al. also studied this transition.[353] The similarity between QEC for trihydride complexes and INS for dihydrogen complexes was noticed.[248,354−356] Lluch and co-workers[297] obtained a good agreement with the experimental INS results[304] for TpRh(H$_2$)(H)$_2$ through the combination of B3LYP calculations with nuclear motion calculations. Clot and Eckert[356] applied the same model used for QEC to study INS transitions in several dihydrogen complexes. By using a parametrized dynamical model, structural information from INS spectra of the dihydrogen complexes could be extracted. Notably, this model enables determination of the equilibrium H−H bond distance of the H$_2$ ligand from the calculations of the INS transitions within a parametrized Hamiltonian.

IX. Stretched Dihydrogen Complexes

At the beginning of this decade, polyhydride complexes were classified into two groups: classical polyhydrides with H−H separation longer than 1.6 Å, and nonclassical polyhydrides with H−H distance ranging from 0.8 to 1.0 Å. However, an increasing number of species where the H−H distance falls between these limits is now known. This third class of complexes has been called elongated or stretched dihydrogen complexes.[10,16]

A. The Electronic Point of View

Neutron diffraction data show that these elongated dihydrogen complexes cover a wide range of H−H distances: $Cp*Os(H\cdots H)H_2(PPh_3)^+$, 1.014 Å;[357] $Cp*Ru(H\cdots H)(dppm)^+$, 1.10 Å;[358] $IrH(H\cdots H)Cl_2(P^iPr_3)_2$, 1.11 Å;[140] $Os(H\cdots H)Cl(dppe)_2^+$, 1.22 Å;[359] $Os(H\cdots H)(en)_2(CH_3CO_2)^+$, 1.34 Å;[360] $Re(H\cdots H)H_5(P(p\text{-tolyl})_3)_2$, 1.357 Å[361] (in which a strong dependence of the H−H distance on the phosphine ligands has been seen);[156] $OsH_5(PMe_2Ph)_3^+$, 1.49 Å.[164] These complexes have been considered as arrested states on the oxidative addition pathway of dihydrogen to the transition metal center. The existence of a continuous range of species that spans the oxidative addition pathway was remarkable. The existence of H−H interaction between remote H centers[362] and later of an H−H bond in these elongated dihydrogen complexes was discussed. The "atoms in molecules" analysis[261] applied to the electron density provides information on the existence of a bond between atoms. This analysis was carried out on four different complexes spanning the whole range of possible cases: the dihydrogen complex $W(H_2)(CO)_3(PH_3)_2$, the dihydride complex $OsH_4(PH_3)_3$, and two species that may be described as elongated dihydrogen complexes with quite different H−H distances, $IrH(H\cdots H)Cl_2(PH_3)_2$ and $[Os(H\cdots H)(NH_2(CH_2)_2NH_2)_2(HCO_2)]^+$.[262] The optimized (B3LYP) H−H distances of the four complexes are, respectively, 0.818, 1.861, 0.984, and 1.428 Å. An H−H bond was found in $W(H_2)(CO)_3(PH_3)_2$ and $IrH(H\cdots H)Cl_2(PH_3)_2$. However, no bond critical point connecting the two hydrogen atoms was located in $OsH_4(PH_3)_3$ and $[Os(H\cdots H)(NH_2(CH_2)_2NH_2)_2(HCO_2)]^+$, suggesting the absence of an H−H bond. The calculations show the absence of any density accumulation in the case of two H atoms separated by more than 1 Å. According to this analysis, $cis\text{-}IrH(H\cdots H)Cl_2(PH_3)_2$ should be a true elongated dihydrogen complex, whereas $[Os(H\cdots H)(NH_2(CH_2)_2NH_2)_2(HCO_2)]^+$ should be better described as a dihydride complex with short H⋯H contact.[262]

The metal−H_2 bonding in elongated complexes has also been analyzed through a study of M−H_2 bonding and back-bonding interactions. A decomposition of the components of the interaction energy between $[Os(NH_3)_4Cl]^+$ and H_2 at the equilibrium geometry of $[Os(NH_3)_4Cl(HH)]^+$ ($R_{HH} = 1.40$ Å) has shown that the metal−H_2 charge-transfer energy becomes significantly larger in stretched H_2 systems,[363] close to the limiting case for the formation of two M−H bonds. This leads to a strong bond between M and H_2. The dihydrogen binding energies (B3LYP) in stretched complexes range from 23 to 45 kcal·mol^{-1},[251,306,364] and are markedly larger than in dihydrogen complexes (15−20 kcal·mol^{-1}).[215,216,218,222,250] It has been shown that the calculated binding energies correlate reasonably well with the H−H distances[363] as was the case in dihydrogen complexes.[222]

The shape of the potential energy surface along the R_{HH} coordinate in the elongated dihydrogen complexes was discussed. If elongated dihydrogen complexes are considered as species where the homolytic cleavage of H_2 is arrested at an intermediate stage between the M(H_2) complex and the M(H)$_2$ structure,

the potential energy curve as a function of H−H distance should have one minimum at the equilibrium distance.[10] However, the properties of M(H⋯H)-L_n might also be accounted for by averaging the properties of M(H_2) and M(H)$_2$ complexes in equilibrium through a low-energy bond-splitting/bond-forming process. In such a case, a potential surface with a double well should be found.[10]

An alternative description is based on the rapid motion of two hydrogen atoms on a flat potential energy surface with a shallow minimum.[359] The energy profile for the stretch of the H−H bond is notably flat regardless of the method of calculation.[179,251,306,363,365,366] Calculations show a very flat potential energy surface with a shallow minimum for $[Os(NH_3)_4L(H\cdots H)]^+$ (L = CH_3COO, Cl; MP2),[363,365] $[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$ (B3LYP),[306] $[CpRu(H\cdots H)(H_2PCH_2PH_2)]^+$ (B3LYP),[251] and $OsCl_2(H\cdots H)(NH=CH_2)(PH_3)_2$ (CCSD(T)//B3LYP).[366] Strong anharmonicity with respect to the variation in H−H distance is also often observed. It costs less than 2 kcal·mol^{-1} to stretch an H−H bond in a metal complex from 1.0 to 1.6 Å.[363,366]

It seems that the flatness of the potential energy curve for the H−H stretch is a distinctive characteristic of the elongated dihydrogen complexes. This property was used to suggest that $OsCl\{NH=C(Ph)C_6H_4\}(H_2)(P^iPr_3)_2$, modeled by $OsCl\{NH=C(H)C_6H_4\}(H_2)(PH_3)_2$, may contain a stretched dihydrogen ligand.[179] Theoretical calculations have thus considered a new point of view for this class of compounds. Instead of being species representative of an arrested state along the oxidative addition pathway, stretched H_2 complexes may be better described as complexes containing two hydrogen atoms moving almost freely in a large region within the coordination sphere of the metal.

The very flatness of the surface is surprising, and an interpretation has been proposed. Energy decomposition at several points along the energy profile for the H−H stretch in $OsCl_2(H\cdots H)(NH=CH_2)(PH_3)_2$ was built upon (i) the distortion of the ML$_5$ fragment which does not vary significantly, (ii) the stretching of H_2 which is destabilizing, and (iii) the stabilizing interaction between the distorted ML$_5$ and the elongated H_2 fragments. This indicates that the very flat potential energy curve results from the almost exact compensation of the stabilizing interaction term and the destabilizing H_2 stretching term *all along the reaction path*.[366]

Despite the success of theoretical calculations in accurately locating the H positions in both dihydrogen and polyhydride compounds, structural modeling of elongated dihydrogen complexes has proved to be an elusive target for computational chemistry. MP2[140] and B3LYP[262] optimizations for $IrH(H\cdots H)Cl_2(PH_3)_2$ gave H−H values of 1.40 and 0.984 Å, respectively, and did not reproduce the neutron diffraction value for $IrH(H\cdots H)Cl_2(P^iPr_3)_2$ (1.11 Å).

It is difficult to know if $ReH_7(PH_3)_2$ is a good model for $ReH_7(PR_3)_2$ because a strong dependence of the H−H distance on the nature of the phosphine (L) has been observed.[156] An MP2 geometry optimization on the model complex $ReH_7(PH_3)_2$ failed to reproduce the
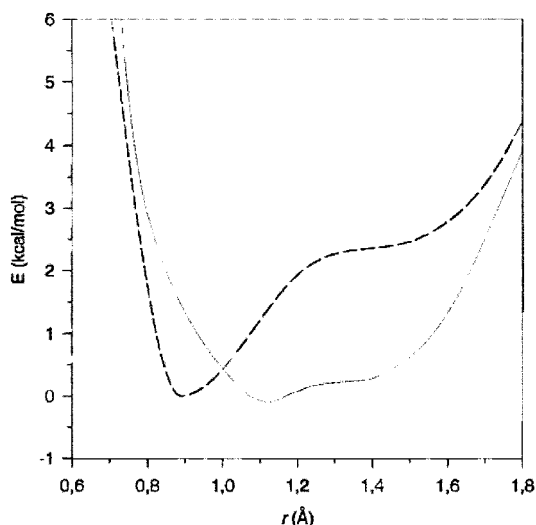
Figure 3. Energy profile for H···H stretching: [CpRu(H···H)(H$_2$PCH$_2$PH$_2$)]$^+$ (dashed line) and [Os(H···H)Cl(H$_2$PCH$_2$CH$_2$PH$_2$)$_2$]$^+$ (solid line).[306]

H−H separation (1.37 Å) found in the neutron structure of the Re(H···H)H$_5$(P(p-tolyl)$_3$)$_2$ complex.[36] Furthermore, the M−H and H−H distances in the optimized structure of elongated dihydrogen complexes are found to be very dependent on the method of calculation. For instance, the calculated H−H distance in [Os(NH$_3$)$_4$H(H···H)]$^+$ is 0.936 Å at the B3LYP level and 1.330 Å at the MP2 level.[364] A comparison of B3LYP and MP2 methods in [Os-(NH$_3$)$_4$(L)(η^2-H$_2$)]$^{2+}$ complexes shows that B3LYP calculations predict stronger H−H but weaker M−H bonding than MP2.[364] This tendency already present in unstretched H$_2$ complexes[225] is considerably enhanced in stretched dihydrogen complexes.

B. The Dynamic Point of View

A fundamentally different approach involves combining DFT calculations and nuclear motion calculations on [CpRu(H···H)(H$_2$PCH$_2$PH$_2$)]$^{+\ 251}$ as a model for [Cp*Ru(H···H)(dppm)]$^+$.[358] The calculations (B3LYP and CCSD(T)//B3LYP) gave a single minimum, in a strongly anharmonic surface, with a H−H distance of 0.89 Å, far from the neutron diffraction value (1.10 Å). Quantum nuclear motion calculations were carried out for this complex to obtain the nuclear vibrational energy levels. Taking into account the zero-point energy, the first vibrational level is placed above the shoulder of the potential energy surface (Figure 3). The shape of the vibrational ground-state wave function suggests a delocalization of the η^2-H$_2$ unit. The expectation values obtained from this analysis for H−H and Ru−H$_2$ distances are in very close agreement with neutron diffraction data. The same treatment has been successfully applied to [Os-(H···H)Cl(H$_2$PCH$_2$CH$_2$PH$_2$)$_2$]$^+$.[306] These dynamic studies suggest that significant variations of the internuclear H−H distances may be found when H is replaced by its isotope D.

Theoretical calculations have been able to reproduce subtle properties of the elongated dihydrogen compounds. The NMR H−D spin−spin coupling constant J_{HD} is indicative of the presence of an elongated dihydrogen ligand. Values of J_{HD} coupling between 5 and 25 Hz denote a stretched dihydrogen complex.[10] An inverse correlation between J_{HD} and the H−H distance for a series of dihydrogen complexes has been experimentally established.[10,11,358,359,367,368] The coupling constant J_{HD} has been calculated for [Os(NH$_3$)$_4$(L)(H···H)]$^{2+}$, where L trans to H−H represents a wide variety of ligands by using B3LYP methodology.[369] The calculated J_{HD} values are in good agreement with the experimental data. Previous MP2 calculations of J_{HD} for these complexes yielded considerably less satisfactory agreement with experiment.[363] A high degree of correlation among the calculated J_{HD}, H−H bond length, and Os−H$_2$ interaction energy has been highlighted.[369] In agreement with experimental data, J_{HD} varies inversely with R_{HH}[370] and hence with the strength of the metal−H$_2$ interaction.[369,371] Some unusual temperature dependence of J_{HD} has been observed in the few cases of elongated dihydrogen complexes where detailed NMR studies have been carried out. The reported temperature dependence of J_{HD} in [Cp*Ru-(H···H)(dppm)]$^{+\ 358}$ and [Os(H···H)Cl(dppe)$_2$]$^{+\ 359}$ has been qualitatively reproduced by considering the expectation value from a Boltzmann distribution among the vibrational levels calculated, respectively, for [CpRu(H···H)(H$_2$PCH$_2$PH$_2$)]$^{+\ 251}$ and [Os(H···H)-Cl(H$_2$PCH$_2$CH$_2$PH$_2$)$_2$]$^+$ as model systems.[306] The B3LYP and nuclear motion quantum calculations have also been able to reproduce and analyze the unusually low ν(H−H) stretching mode detected in the Raman spectrum of the complex [CpRu(H···H)-(dppm)]$^+$.[372] As harmonic behavior is not an acceptable assumption for an elongated dihydrogen complex, the vibrational levels were directly calculated without resorting to the harmonic approximation. Remarkable agreement between the calculated and the experimental vibrational transitions for this complex were found, for both the (η^2-H$_2$) and the (η^2-D$_2$) isotopomers.[373] It was shown that the H−H and the Ru−H$_2$ stretches were thoroughly mixed in this complex, as already shown from a normal-mode analysis in W(CO)$_3$(PCy$_3$)$_2$(η^2-H$_2$).[374]

X. Breaking the H–H Bond by Transition Metal Complexes

Previous sections have shown how the coordination of a hydrogen molecule to a metal center can give rise to dihydrogen complexes, with variable degrees of interaction between the metal and the dihydrogen ligand, associated with variable stretches of the H−H bond. This section is concerned with the simplest interaction between dihydrogen and a metal center, in which the dihydrogen molecule is broken without the intermediacy of a dihydrogen complex. H−H activation is the paradigm of σ bond activation, and as such has been included in previous reviews of theoretical calculations.[375−377] We will collect here only the aspects relevant to the interaction of dihydrogen with transition metals, namely, the location of transition states, as well as aspects concerning the relative stability of isomeric products of the reaction.

Two major types of processes have been documented for the breaking of the hydrogen−hydrogen

bond at a metal center: oxidative addition and σ bond metathesis (Chart 27).

Chart 27

Oxidative addition

σ-Bond Metathesis
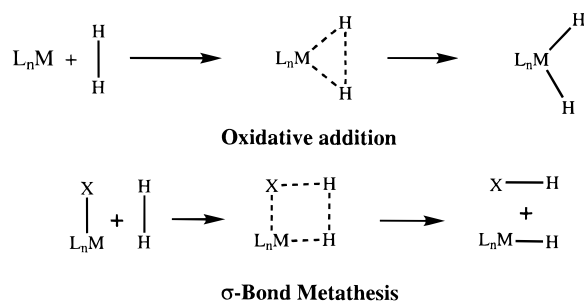
A. Oxidative Addition

Oxidative addition is the process by which the H−H σ bond is broken and two M−H σ bonds are formed. Due to the change in the formal charge of the hydrogen atoms (from 0 in molecular dihydrogen to −1 in hydride), the oxidation state of the metal has to increase by 2 units, thus, the name "oxidative addition".

From a molecular orbital point of view, the analysis is quite similar to that of molecular hydrogen complexes discussed in previous sections.[26] The hydrogen molecule approaches the metal center in an η^2 orientation, and its $\sigma^*(HH)$ orbital receives one electron pair from a metal d orbital of the appropriate symmetry. In the case of oxidative addition, the transfer to the $\sigma^*(HH)$ orbital is more significant than in molecular hydrogen complexes, and this leads to the breaking of the H−H bond. The d orbital appropriate to interact with $\sigma(HH)$ is usually occupied in metal fragments associated with oxidative addition, which destabilizes the possible formation of a dihydrogen complex because of a four-electron interaction between the two occupied orbitals.

Oxidative addition reactions of dihydrogen to transition metal complexes have also been the subject of a variety of ab initio studies. The first work focused on the reaction of hydrogen with d^{10} ML$_2$ fragments to give rise to square planar d^8 ML$_4$ complexes (Chart 28). This is one of the simplest models of an organo-

Chart 28
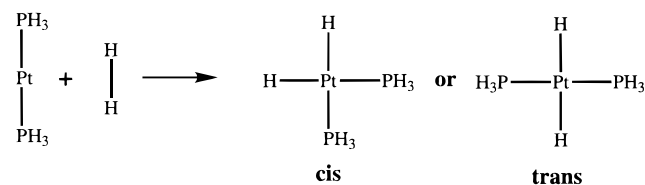
metallic reaction from a theoretical point of view. It is thus little wonder that the first application of analytical gradient techniques to the ab initio determination of the transition state structure was carried out by Kitaura et al.[378] for the reaction Pt-(PH$_3$)$_2$ + H$_2$. This same reaction was studied almost simultaneously in the early 1980s by the groups of Morokuma,[378−380] Hay,[381] and Goddard.[382,383] Its analysis, together with that of the closely related processes of activation of H$_2$ by Pd(H$_2$O)$_2$,[384] and Pt(PH$_3$)$_2$,[383,385] led to the clarification of the key features of the

oxidative addition process. These studies showed that the transition state for the formation of the cis product is located at an early stage of the reaction, and adopts a geometry with the two hydrogen atoms equidistant from the metal and separated from each other by a distance ranging from 0.75 to 0.90 Å. The same Pt(PR$_3$)$_2$ + H$_2$ process has been recently used for the calibration of hybrid QM/MM methods for the introduction of the real substituents in the phosphine ligands.[386,387]

A second group of oxidative addition processes that has been the focus of significant attention from the theoretical community is the addition of dihydrogen to Vaska-type d^8 square planar Ir(PR$_3$)$_2$(CO)X complexes (Chart 29).[388] The oxidative addition of a

Chart 29

Addition in P-Ir-P plane   **Addition in OC-Ir-X plane**
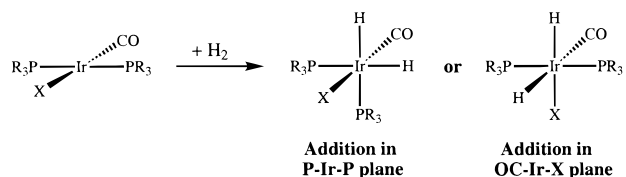
dihydrogen molecule to these complexes produces two different d^6 octahedral complexes depending on the plane of entry of H$_2$. In the case of *trans*-Ir(PR$_3$)$_2$-(CO)X, the dihydrogen molecule can enter either parallel to the P−Ir−P axis or parallel to the C−Ir−X axis.[389−391] An early study at the extended Hückel level[392] showed a leading role of the p effects of the halide X and carbonyl groups, a result that was later confirmed by ab initio calculations.[393] This type of complex has also been the object of intense scrutiny by Krogh-Jespersen and co-workers,[394−397] who have analyzed the effect of the electronic properties of X on the thermodynamic stability of the products of oxidative addition (X = F, Cl, Br, I, CN, H, CH$_3$, SiH$_3$, OH, SH). The π-bonding properties of X are shown to have a larger effect than the σ-bonding abilities, with π acceptors promoting the addition of H$_2$ and π donors disfavoring it.

The oxidative addition of dihydrogen to other d^8 ML$_4$ fragments has also been studied theoretically.[398−401] The activation barriers for the reaction of hydrogen with Fe(CO)$_4$[401] and Fe(PH$_3$)$_4$ and Ru(PH$_3$)$_4$[400] are very small, if not zero, in contrast to what happens for [Rh(PH$_3$)$_4$]$^+$,[400] RhCl(CO)(PH$_3$)$_2$,[399] or the Vaska-type complexes discussed above. The very low barrier for Fe and Ru systems seems to be related to the high energy level of the occupied d orbitals as well as to the proximity between the singlet and triplet electronic states in these metal fragments.

The studies mentioned so far have clarified the oxidative addition process to transition metal complexes from a theoretical point of view. Other studies have been carried out on some specific systems. The oxidative addition process of a number of substrates, including H−H, to CpRh(CO)[402] and Rh(PMe$_3$)$_2$Cl and Ir(PMe$_3$)$_2$Cl[403] was studied. The changes induced by tunneling effects in the oxidative addition of dihydrogen to small palladium clusters have been analyzed.[404,405] The effect of the presence of Lewis acids

on the reductive elimination of hydrogen from [Cp$_2$-NbH$_3$]L (L = HBO$_2$C$_2$H$_2$, BF$_3$, BH$_3$) has also been studied.[245,247]

Another subject that has been little explored so far, obviously because of its complexity, is the computation of catalytic cycles, where oxidative addition of hydrogen is a common step. One must cite the early efforts by Dedieu,[406] and the work by Morokuma and co-workers on olefin hydrogenation,[407] hydroboration,[408] and hydroformylation[409] and alkane dehydrogenation.[410]

B. σ Bond Metathesis

σ bond metathesis is a process by which an H−H σ bond and a M−X σ bond are broken and new M−H and X−H σ bonds are formed. (Chart 27). M can be any metal fragment, and X can be any ligand, including a hydride, in which case the reaction becomes an intermolecular hydrogen atom exchange. In contrast to oxidative addition, the oxidation state and the coordination number of the metal atom remain unchanged in σ bond metathesis.

The σ bond activation is typical of early transition metals, formally d^0 in a number cases. The d^0 fragments could only donate electrons from internal shells, at prohibitive energy cost, and therefore do not undergo oxidative addition. The early recognition that d^0 fragments, such as Cp$_2$ZrH$^+$ and Cp$_2$LuH$^+$, can exchange their hydride ligand with hydrogen atoms from free hydrogen molecules in solution prompted a theoretical search of plausible mechanisms through the extended Hückel formalism.[236,237] This work provided a picture that remains essentially valid, where the reaction goes through a four-center transition state, the presence of low-lying empty orbitals in the metal accounting for the ease of this otherwise symmetry-forbidden [2$_\sigma$ + 2$_\sigma$] process.

Ab initio studies on this type of process were limited for a long time to Cl$_2$MH + H$_2$ models because of the prohibitive size of the real Cp$_2$MH + H$_2$ systems. In 1984, Steigerwald and Goddard[411] studied the reaction of H$_2$ with Cl$_2$TiH$^+$, Cl$_2$TiH, and Cl$_2$ScH and confirmed that the hydrogen exchange reaction takes place through a low-barrier four-center transition state, and that the presence of one d electron in Cl$_2$TiH seriously hampers the reaction. Later on, Rappé and co-workers[412−414] analyzed the reaction of similar fragments with systems involving π electrons, and compared its features with those of isolobal main group derivatives such as Cl$_2$AlH. This type of system was also used as a benchmark for the validity of effective core potentials.[415]

The increase in computer power allowed in the 1990s the introduction of the real cyclopentadienyl ligands into the ab initio calculations. Ziegler's group studied the reaction Cp$_2$ScH + H$_2$,[416] among other processes,[417,418] and found results in close agreement with those previously reported with the simpler models: a very low barrier and a four-center transition state. This proves that valuable results can be obtained even with drastic modelizations if the calculations are carefully done and comparison with experiment is systematic.

The well-established existence of σ bond metathesis as the mechanism of hydrogen breaking by early transition metal complexes raised the question of its feasibility in late transition metal complexes. This topic is closely related to the exchange process in M(H)(H$_2$) already discussed in section VII. An early proposal[309] for the hydrogen exchange mechanism in [Fe(PH$_3$)$_4$(H)(H$_2$)]$^+$ could not be experimentally tested, but success seems to have been reached by Dedieu and co-workers on the mechanism of hydrogen activation by palladium complexes.[419−422] In one of their papers, the specific problem of H$_2$ σ bond metathesis by a series of Pd complexes was examined. The reaction happens to have a low barrier in a number of cases, such as that presented in Chart 30, where

Chart 30
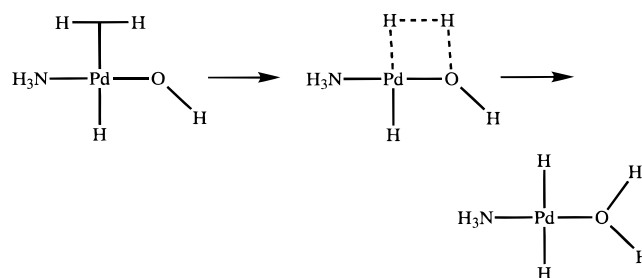
the barrier is below 15 kcal·mol^{-1}. A necessary feature for the accomplishment of a low-barrier σ-bond-type metathesis process in these systems seems to be the presence of a lone pair in the oxygen atom where the hydrogen is to be transferred.

Current research focuses on specific topics. In particular, it must be mentioned that the knowledge acquired on H−H σ bond metathesis processes is being profusely used in the ever-growing field of olefin polymerization catalysis,[423−425] even if the key steps do not necessarily involve hydrogen−hydrogen bonds. Another field where a large number of applications can be foreseen soon is biochemistry, where one can already note recent studies of the reaction mechanism of hydrogen cleavage by nickel−iron hydrogenases.[426−429]

XI. Methodological Peculiarities in the Study of Polyhydride Systems

This review has summarized the computational studies that have been carried out on transition metal polyhydrides from the perspective of the chemical insight that has been obtained from those calculations. This last section analyzes the available data from the point of view of a computational chemist. The following general question is addressed here: What are the most appropriate methods available for the study of transition metal polyhydride systems? This general question can be reformulated by asking whether there is something special about transition metal polyhydride systems that makes their theoretical study different from that of other transition metal complexes. We consider that such a specificity exists, and that it is related to the possibility of interaction between hydride ligands to give rise to dihydrogen units coordinated to the metal.

However, before discussing the meaning of this peculiarity from a methodological point of view, we set apart two types of studies for which general viewpoints still hold. These concern the two extremes of quality and computational cost: the qualitative extended Hückel studies and the most sophisticated ab initio studies on small gas-phase systems. The validity of methods based on the extended Hückel description is well-known to be essentially of a qualitative nature and especially useful for studying trends. Calculations on polyhydride systems bring little novelty in this respect. The performance of this type of method is valid for the study of polyhydride systems with no additional caveat. It may be worth mentioning here that the very first studies on transition metal complexes confirmed that extended Hückel methods are efficient in the calculation of optimal orientations of dihydrogen ligands, but are meaningless as far as the H−H or M−H bond distances are concerned.[207]

The other case where transition metal polyhydrides are not different from other transition metal systems from a computational point of view is small gas-phase systems. This type of system, which has been collected in section II, is usually characterized by the presence of empty low-energy atomic orbitals, with the associated requirement for nondynamical correlation, and an enormous methodological complexity. Because of this, it is no surprise that a number of predictions of high-level calculations have been corrected afterward by even more accurate calculations. As the first example, the assignment of the ground state of NiH_2, for which the early prediction (multireference CI)[51] suggested a triplet state, has been recently corrected by QCISD and CASPT2 calculations.[71,72] A second example is provided by the bonding energies of hydrogen molecules in $V(H_2)_n^+$ clusters, in which it has also been proved that a spin change occurs upon addition of a sixth ligand,[96] contrary to previous predictions based on high-level MP4SDTQ calculations on Hartree−Fock optimized geometries.[90] A third example is constituted by the nature of the ground-state geometry of Ti_2H_6, with substantial changes upon the use of a multireference method.[100,101] Therefore, the advice for researchers interested in the study of small gas-phase transition metal polyhydrides should be to run systematic tests, to compare carefully with experimental data, and to be ready to use the most accurate methods available. This is, in fact, also common for all gas-phase systems,[430] and in this sense the presence of hydride ligands brings no specific problems.

The peculiarities of transition metal polyhydride complexes acquire methodological significance if one considers the case of saturated complexes of the type usually found in solution. The energy cost associated with the elongation of a H−H bond is dramatically reduced when H_2 is in the coordination sphere of a transition metal complex. This was nicely proved by Craw et al.,[365] who computed that the elongation in the H−H distance from 0.8 to 1.4 Å costs no more than 10 kcal·mol^{-1} for H_2 coordinated to $[Os(NH_3)_4(OAc)]^+$, whereas the energy cost of an elongation of free hydrogen from 0.74 to 1.0 Å is already above 15

kcal·mol^{-1}. This low sensitivity of the energy to large geometry changes has important implications for the accuracy of calculations in these systems. Small errors in energy can lead to substantial errors in geometry, even leading to the wrong qualitative assignment of the most stable species.

The first aspect of the required methodological level is concerned with the basis set. Work by Barea et al.[431] on the dihydrogen complex $[Os(PH_3)_2Cl(CO)H(H_2)]$ shows that the addition of diffuse functions on the hydrogen atoms, or the shift from double-ζ to triple-ζ quality, has little effect on the energy or the geometry of the system. On the other hand, addition of polarization functions on hydrogen has a significant effect on the coordination of the dihydrogen molecule (changes in Os−H distances up to 0.05 Å), but little effect on the coordination of the hydride ligand (changes in Os−H below 0.01 Å). This is a general methodological feature of polyhydride systems: the coordination of a dihydrogen is always much more sensitive to the method than that of a hydride ligand. Another observation related to the basis set is the importance of relativistic effects. They have been proved to have a substantial weight in the case of elements of the third transition metal row.[250] Fortunately, they can be introduced into conventional calculations through the use of pseudopotentials involving relativistic effects.

The second aspect to be discussed is the importance of electron correlation. In other words, to what extent are HF calculations valid? One could expect a priori that dynamical correlation associated with the presence of a significant back-donation from the metal to the σ^* orbital of dihydrogen would stabilize dihydride with respect to dihydrogen coordination, but one could not predict its weight a priori. The accumulated experience throughout the years on this topic proves overwhelmingly that electron correlation is essential for the proper description of transition metal polyhydride systems. Maseras et al.[161] found how an energy difference of −13.9 kcal/mol at the RHF level between two different isomers (one bis-(dihydrogen) and one pentahydride) of $[Os(PH_3)_3"H_5"]^+$ became +20.3 kcal/mol (a change of 34.2 kcal/mol), when the calculation was carried out at the MP2 level on the HF geometries. Evidence of the substantial changes associated with the introduction of correlation energy at the MP2 level for the description of dihydrogen complexes has also been provided in a number of studies by the groups of Hall[186,231] and Hush.[363,365] Interestingly enough, in a study on the effect of correlation on the protonation reaction of $[PdH_2Cl(NH_3)]^-$ and $[PdH_2(NH_3)_2]$, Milet and Dedieu[432] proved that the effect is important, but not as spectacularly so as in the other cases. One must realize that in this particular study there is no significant hydrogen−hydrogen interaction, because all hydrides are attached to the metal center. Although the years have proven that electron correlation is essential for the description of transition metal polyhydride systems, all early calculations on dihydrogen systems and H−H activation were carried out at the RHF level. This does not mean that the conclusions from those calculations are wrong. How-

ever, it suggests that the quantitative description could be significantly improved.

The introduction of electron correlation is thus mandatory, with effects on relative energies above 15 kcal·mol^{-1}. Luckily enough, its simple introduction at the MP2 level, or with a DFT nonlocal functional, brings the discrepancies with respect to experiment down to a few kcal·mol^{-1}. This is usually sufficient for practical purposes, especially because this error should be similar to that introduced by the modeling of ligands[225] or the neglect of solvent and packing effects. Nevertheless, from a methodological point of view it is interesting to learn which method is more precise: MP2 or DFT nonlocal functionals? Two studies have been devoted to this particular topic. The first of them,[364] by Bytheway et al., analyzes the complexes $[Os(NH_3)(L)(H_2)]^{2+}$ (L^z = hydride, pyridine, acetonitrile, cyanide, hydroxylamine, ammonia) (A in Chart 31) with the MP2- and the DFT-based BLYP

Chart 31

A   **B**
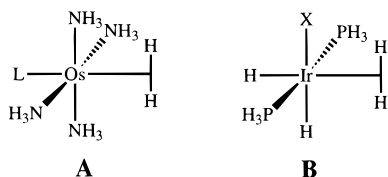
and B3LYP methods. They find that MP2 and DFT geometries are quite similar, although MP2 predicts consistently longer H−H and shorter Os−H bonds than DFT. Consequently, MP2 predicts a stronger binding energy of dihydrogen (by 7 kcal·mol^{-1} at most) than BLYP. Single-point higher level calculations at the MP4(SDQ) level provide results that are approximately halfway between those of MP2 and BLYP, leading the authors to conclude that MP2 overestimates and BLYP underestimates the interaction between the dihydrogen molecule and the metal complex.

The conclusions of Bytheway et al. were mostly confirmed in a study by Clot and Eisenstein[225] on the reaction $H_2 + IrXH_2(PR_3)_2$ (X = Cl, Br, I; R = H, Me) (B in Chart 31) at the MP2 and B3LYP levels. In this case, the work included the study of a dihydrogen complex, a dihydride complex, and the transition state for H_2 addition to the dihydride, and the high-level single-point calculations were brought up to CCSD(T). Again, the high-level result was shown to lie between those of MP2 and B3LYP. In this case, the effect of the substituents on phosphine ligands was analyzed through the explicit use of PMe_3, and results were systematically compared with available experimental data. The conclusion was that MP2 seems to be slightly more precise than B3LYP for this particular system. This result may be related to the previously reported observation that DFT methods seem to have trouble in the accurate reproduction of weakly bound systems,[433] to which dihydrogen complexes are related. In any case, the performance of MP2 and B3LYP for transition metal polyhydrides is similar and in both cases quite satisfactory. The similarity is further stressed by recent claims that B3LYP can be more accurate for some particular polyhydride systems.[297]

In summary, from a methodological point of view the main peculiarity of transition metal polyhydrides is the extreme flatness of the dihydrogen/dihydride surface in a number of cases, which makes small imprecisions in the energy responsible for large errors in computed geometries. In fact, this flatness, coupled with the low nuclear mass of hydrogen, has prompted recent work suggesting that the geometry observed by neutron diffraction does not necessarily correspond to the minimum in the electronic potential energy surface.[251,306] This paves the way for new developments in the field of theoretical chemistry of transition metal complexes, pioneered again by work on transition metal polyhydrides.

XII. Conclusions and Perspectives

The results collected in this review prove that transition metal polyhydride complexes have played a leading role in the application of theoretical methods to transition metal chemistry. Although H-containing transition metal systems may have initially attracted theoreticians because of their apparent simplicity, over time the experimental results have revealed a wealth of chemical properties unmatched in any other system. Most of these properties could be interpreted with very simple bonding models and were discussed at an early period. However, quantitative description of the same properties challenged theoretical methods, and it has appeared that state-of-the art quantum methods need to be used. Dynamic approaches were even found to be necessary in some cases. This explains why a large community of theoretical chemists using various methods have been attracted to this topic. Most remarkably, many of the advances in this chemistry have been achieved through a joint effort of experimentalists and theoreticians. Transition metal hydride complexes may still have big surprises in store for us.

XIII. Acknowledgment

XIV. References

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