Prediction of the Geometries of Simple Transition Metal Polyhydride Complexes by Symmetry Analysis

Craig A. Bayse and Michael B. Hall*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843
Received June 5, 1998. Revised Manuscript Received November 17, 1998

Abstract: The principle of correspondence between the symmetry decompositions of the valence atomic orbitals (AOs) of the central metal and those of the hydride ligands is used to predict and rationalize the geometries of simple transition metal polyhydride complexes. In this orbitally ranked symmetry analysis method (ORSAM) the minimum energy structures have metal AOs whose irreducible representations match those of the hydrides. In agreement with previous work, the hydrides prefer to bond to the metal (n + 1)s and nd orbitals, but ORSAM also includes (n + 1)p orbitals in a natural way and avoids having to postulate hypervalency for transition metal complexes with electron counts greater than 12. Comparison with ab initio structures of 114 simple transition metal polyhydrides shows that ORSAM correctly predicts and rationalizes the geometries of both classical and nonclassical complexes.

Introduction

Simple methods for the reliable prediction and rationalization of molecular structure are essential to chemistry. The well-known valence shell electron pair repulsion (VSEPR) method developed by Sidgwick and Powell and later Gillespie and Nyholm predicts geometries by placing areas of high density (ligands or lone pairs) as far apart as possible. The success of the method has been attributed to the repulsions of electrons as far as possible.1 The success of Nyholm predicts geometries by placing areas of high density of molecular structure are essential to chemistry. The well-

References


a best packing or best covering fashion such that the linear combinations of ligand orbitals match the central atom’s spherical harmonics. While this model seems to work well for 18-electron transition metal complexes, it fails to explain the geometries of d6 12-electron complexes such as W(CH3)6 or WH6.

The valence bond (VB) method is based upon the concept of two-center–two-electron (2c–2e) ligand bonding to hybridized orbitals on a central atom. The method is simple and chemically intuitive, but it can be difficult to apply to electron deficient systems and transition metal complexes with π-ligands. In electron-rich systems one must invoke the use of either high-energy d orbitals or three-center–four-electron (3c–4e) bonds formed from the following resonance structures: L−M+−L ↔ L−−M+ −L.

Recently, Landis has applied VB methods to transition metal polyhydride complexes. In this model, the bonding around the metal is considered to occur only through dσ-type hybrid orbitals in analogy to main group sp hybrids. Since the (n + 1)s and nd metal atomic orbitals define the valence space, the metal may form a maximum of six 2c–2e bonds. Thus, 12 electrons will fill the transition metal valence shell, rather than the 18 electrons that might be expected if the (n + 1)p orbital were part of the valence shell. Lone pairs on the metal occupy pure d orbitals, and the metal s character of the bond orbitals should be maximized. If the transition metal complex has more than 12 electrons in the valence space it is considered hypervalent and linear H−M−H 3c–4e units are required in the bonding scheme. As Landis points out, this scheme “leads to the conclusion that most transition metal complexes are hypervalent”.12a

10.1021/ja981965+ CCC: $18.00 © 1999 American Chemical Society
Published on Web 01/29/1999
Since many hypervalent complexes in the main group are unstable, it seems odd to classify transition metal complexes with more than 12e\(^-\) (all the very stable complexes) as hypervalent. While hypervalency in main group complexes is due to the inaccessibility of the nd orbitals, this is not the case for transition metals because their \((n + 1)p\) orbitals are more readily available. The excitation energies for main group elements from the ground state to the first excited state containing an nd orbital are roughly 2–9 times larger than those for the corresponding excitation (ground state to the first excited state containing a \((n + 1)p\) orbital) for transition elements.\(^{11}\) In fact, while studies\(^{14}\) have shown that the optimal exponent for a d function is roughly the same for any main group element, recent studies by this group have shown that an accurate representation of transition metal \((n + 1)p\) orbitals is necessary to correctly describe the energetics of transition metal complexes and their reactions.\(^{15a}\)

In this work, we develop a method for predicting the structure of transition metal polyhydride complexes through the use of symmetry analysis combined with the preferred bonding of hydrides to metal \((n + 1)s\) and nd orbitals. The method, an application of MO theory to molecular geometry, is similar in some ways to CSEDW with the exception that electron counts which do not fulfill the 18e\(^-\) rule are incorporated. In addition, our method does not require a spherical distribution of ligands (best covering or best packing\(^7,8\)) such that a greater variety of geometries are allowed. Our method bears some similarity to that of Landis in the sense that bonding is favored through that of Landis in the sense that bonding is favored through \((n + 1)s\) and nd orbitals, but \((n + 1)p\) orbitals are incorporated into the bonding scheme such that more systems can be adequately described without invoking hypervallancy. A preliminary report of the application of our approach to WH\(_6\) and OsH\(_6\) has appeared.\(^{16}\) The work reported here is most closely related to the application of symmetry to molecular geometry recently discussed by King.\(^{17}\) The present work extends the ideas presented in work by the present authors\(^4,16\) and King.\(^{17}\)

**Orbitally Ranked Symmetry Analysis Method (ORSAM)**

An important approximation in MO theory is the construction of the MOs of a complex from a linear combination of atomic orbitals (LCAO),\(^{18}\) which are usually separable into radial functions \(R_m(\rho)\) and spherical harmonics \(Y_m(\theta, \phi)\). For the central atom of a complex, \(M\), the radial portions of the AOs are always spherically symmetric (i.e., unaffected by any symmetry operation), but the spherical harmonics transform as specific irreducible representations depending on the point group of the molecule.\(^{19}\) In the most stable complexes, the ligands must orient themselves such that there is maximum correspondence between their valence orbitals’ irreducible representations and those of the central atom. Thus, a group-theoretical analysis of the central atom’s and ligands’ AO combinations can be used to eliminate conformations with mismatching irreducible representations. Consideration of the ligand type (\(\sigma\)-donor and \(\pi\)-donor or acceptor) and central atom (main group or transition metal) can be used to further reduce the number of possible geometries. Since the spherical harmonics are identical for all atoms, the application of the above criteria provides a set of possible geometries for any isoelectronic complex with the same type of ligands and central atom. However, the global minimum for a given system will be determined by details of the electronic structure including the radial portion of the wave function.

In this work, the principles discussed above are applied to the problem of determining the geometries of simple transition metal polyhydride complexes. The set of possible geometries for a given stoichiometry is reduced by the fact that hydride ligands prefer to bond to transition metals through \((n + 1)s\) and nd metal AOs. The relative importance of the central atom’s AOs in bonding forms the basis for the orbitally ranked symmetry analysis method (ORSAM) presented below.

The application of ORSAM to transition metal polyhydride complexes consists of the following steps:

1. Choose a set of possible geometries for a given stoichiometry \(MH\), with a symmetry of \(C_2\), or higher and determine the irreducible representations for the hydride ligands. It is assumed that lower symmetry (\(<C_2\)) structures are available, but they are not explicitly analyzed due to the large number of possible geometries.

2. Determine the “orbital count” for a given metal system. The orbital count \(d(\text{sp})^{n}\) is the number of metal AOs of each angular momentum type necessary to construct \(x\) delocalized symmetry-adapted M–H bonding orbitals. Since hydride ligands prefer to bond through \((n + 1)s\) and nd orbitals,\(^{20,21}\) these metal AOs should be used before \((n + 1)p\) orbitals. Nonbonded metal electrons (lone pairs) are accommodated in pure d orbitals. Metal p orbitals are used when the number of ligands exceeds the number of s and d orbitals available for bonding. The orbital counts for all stoichiometries and d electron counts are listed in Table 1.

(a) In this discussion, only the singlet states are considered, but the method can be easily extended to open-shell states by considering the number of partially occupied d orbitals rather than the formal count of d electrons. For example, a triplet d\(^2\) system should have the same orbital count as a singlet d\(^3\) system.

(b) Because they have low-lying \((n + 1)p\) orbitals, anionic complexes of high-oxygenation-state, early transition metals should include the possible geometries for the complex with an additional \((n + 1)p\) orbital (i.e., both d\(^s\) and d\(^sp\) for MH\(_3\)).


Table 2. Symmetry Combinations of Metal nd, (n + 1)s, and (n + 1)p Orbitals in Various Groups

<table>
<thead>
<tr>
<th>(n + 1)s</th>
<th>(n + 1)p</th>
<th>nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>a1g</td>
<td>a1u</td>
<td>(n + 1)p</td>
</tr>
<tr>
<td>T_d</td>
<td>e + t_2</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>D_4h</td>
<td>a1g + e_u + e_u'</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>D_2d</td>
<td>a1 + e + e_1</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>D_4h</td>
<td>a1g + b_1 + b_2 + e_1</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>D_4h</td>
<td>a1 + e' + e_1</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>D_2h</td>
<td>2a_1 + b_1 + b_2 + b_3</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>D_4d</td>
<td>a1 + e + e_1</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>D_4h</td>
<td>a1 + 2e_1</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>C_3v</td>
<td>a1 + b_1 + b_2 + e</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>C_3v</td>
<td>a1 + e + e_1</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>C_3v</td>
<td>a1 + b_1 + b_2 + e</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>C_2v</td>
<td>2a_1 + a_2 + b_1 + b_2</td>
<td>(n + 1) s</td>
</tr>
</tbody>
</table>

Table 3. Symmetry Decompositions of MH₄ Systems.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>a1 + 12</th>
<th>N</th>
<th>Y</th>
<th>N</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_d</td>
<td>a1 + b_2</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>D_4h</td>
<td>a1 + b_2 + b_3</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>D_2d</td>
<td>a1 + 2e_1</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>C_3v</td>
<td>a1 + b_1 + e</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>C_2v</td>
<td>2a_1 + e</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>C_2v'</td>
<td>2a_1 + b_1 + b_2</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>C_2v''</td>
<td>3a_1 + b_1</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
</tbody>
</table>

Table 4. Sets of Possible Geometries for MH₄

<table>
<thead>
<tr>
<th>Geometry</th>
<th>(n + 1)s</th>
<th>(n + 1)p</th>
<th>nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_4h</td>
<td>a1 + b_2</td>
<td>a1 + b_2</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>D_2d</td>
<td>a1 + b_2</td>
<td>a1 + b_2</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>C_3v</td>
<td>a1 + b_2</td>
<td>a1 + b_2</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>C_2v</td>
<td>2a_1 + e</td>
<td>2a_1 + e</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>C_2v'</td>
<td>2a_1 + b_1 + b_2</td>
<td>2a_1 + b_1 + b_2</td>
<td>(n + 1) s</td>
</tr>
<tr>
<td>C_2v''</td>
<td>3a_1 + b_1</td>
<td>3a_1 + b_1</td>
<td>(n + 1) s</td>
</tr>
</tbody>
</table>

The hydride irreducible representations for each of these complexes are listed in the second column of Table 3. The number of d lone pairs has to be accounted for in order to determine the sets of possible geometries for these complexes. For d⁰ through d⁵, the orbital count for MH₄ is d³s, or three nd orbitals and one (n + 1)s orbital. At d⁶ one (n + 1)p orbital must be introduced to make the orbital count d⁵sp, while at d⁷ it would be d⁶sp². The results of matching the irreducible representations of the hydride ligands to the metal AO irreducible representations under the constraint of maximizing the use of s and d orbitals are listed in Table 3. It should be noted the high-symmetry geometries (T_d and D_4h) often expected for ML₄ complexes are only allowed in two d-electron counts for T_d (d⁰ and d⁴) and one d-electron count for D_4h (d⁵). The hydrides in the D_4h conformation require two p orbitals (e_u) in order to bond to the metal so that only d⁴ complexes (orbital count = d⁵sp) can assume this geometry. The highest symmetry structures for d⁵ are the first-order Jahn–Teller (FOJT) distortion from T_d (D_4h) and the pseudo-second-order Jahn–Teller (PsoJT) distortion from D_4h (C_4v). The d⁶ system has the D_4h and distorted tetrahedral C_3v geometries as high-symmetry possibilities.

By applying this reasoning to other MH₄ systems, one arrives at the general results of ORSAM listed in Table 4. The tables of hydride ligand irreducible representations and schemes of all geometries considered are included in Supporting Information (Tables S2–S7 and Schemes S1–S7). Dihydride complexes can also be rationalized as part of this analysis. Since the dihydrogen ligand is a σ-donor ligand, it will act like a hydride ligand. When the dihydrogen is considered a hydride ligand, the dihydrogen complex fits into a symmetry class with fewer H’s and more d electrons. For example, the all-hydride system AgH₄ (d⁰) could reduce to a d¹⁰ dihydrogen complex Ag(η²-H₂)H. If the dihydrogen is considered a hydride ligand, then the complex would follow a set of rules for d¹⁰ ML₂ systems for which ORSAM would predict D_4h.

The method can also be used for ligands other than hydride by applying the same principles listed above. Ligands such as phosphine can replace dihydrogen ligands forming (M(PR₃)₃H₄−ₙ) complexes that would be similar to M(H₃)₃H₄−ₙ Systems. Strong one-electron ligands like CR₃ can replace hydrides. However, these complexes would not necessarily have the same minimum energy structure as the all-hydride complexes due to the steric bulk and different electronic requirements of the phosphine ligands.

Theoretical Methods

Ab initio calculations with relativistic effective core potentials (RECPs) using the GAMESS-UK package have been performed on a variety of simple transition metal polyhydride complexes (MH₄) including neutral, anionic, and cationic systems of all second- and third-row metals. The metals were represented by modified Ermelr–Christiansen RECP basis sets. These bases were of double-ζ quality.
in the s and p space with triple-$\zeta$ quality in the d space. The $(n + 1)s$ and $(n + 1)p$ orbitals have been included in these basis sets in accordance with recent studies on transition metal systems. The hydride basis functions were triple-$\zeta$ quality.

Geometry optimizations and frequency calculations have been performed at the restricted Hartree–Fock (RHF) level. Geometry optimizations at the MP2 level were performed for all third-row neutral systems. The relative energies of the neutral systems were recalculated at the MP2, MP3, and CCSD levels. Relative energies at the MP2 level were calculated for systems with dihydrogen ligands due to the overestimation of $\mathrm{H}_2$ binding in RHF. If the order of the relative energies was changed, geometry optimizations at the MP2 level were performed. Relative energies are listed in Tables S8–S21 of the Supporting Information. In select cases, geometry optimizations were performed at the CISD level and relative energies were calculated at the G02/(PESMCSF) and G02(DTQ) levels.

All calculations were performed on SGI Indigo R4400 and O2 workstations.

**Results**

$\mathrm{MH}_3$. Four geometries have been considered for $\mathrm{MH}_3$ complexes: trigonal planar $D_{3h}$, trigonal pyramidal $C_{3v}$, T-shaped $C_{2v}$, and Y-shaped $C_{2v}'$.

The results of ORSAM for $\mathrm{MH}_3$ complexes are found in Table 4. While any of the four geometries is possible for the $d^0$–$d^6$ complexes, only the two $C_{2v}$ geometries are SA for the $d^6$ systems.

Most of the complexes examined in this study (Table 5) have minima at one of the high symmetry ($\geq C_{2v}$) geometries predicted by ORSAM. While one might expect the results for the second- and third-row metal complexes to be the same, the results show that this is not always the case. Unlike the La$\mathrm{H}_3$ complex, the $d^0$ $\mathrm{YH}_3$ complex is $D_{3h}$ due to the ligand repulsions around a small metal center and the high contribution of p orbitals to the bond orbitals. Mulliken population analysis shows that 36% of the yttrium valence electrons are located in p orbitals. The lanthanum complex also has a high amount of p character in its bond orbitals, but the relative size of the metal allows the hydride ligands to bend slightly out of planar with the metal. A previous study on these two complexes constrained the geometry to planar ($D_{3h}$) and thus did not observe the $C_{3v}$ lanthanum complex. Most of the $d^2$ systems are $D_{3h}$ where it is favorable for the lone pair of electrons to occupy the $d_2$ orbital ($a_1$). However, the potential energy surface for $[\mathrm{HHF}]^-$ is very flat such that the $D_{3h}$ structure is a maximum $< 1$ kcal/mol above nearly degenerate $C_{2v}$ and $C_{2v}'$ minima. The $d^2$ molybdenum cation reduces to an $[\mathrm{MoH}(\eta^2-\mathrm{H}_2)]^{2+}$ complex ($C_i$, Figure 1) analogous to a $\sim C_{2v}$ $d^8$ ML$_2$ system. The positive charge on $d^2$ $[\mathrm{WH}_3]^+$ increases the gap between the d and p orbitals, thus favoring the $C_{2v}$ conformation where there is less mixing of the p orbitals into the bond orbitals. Thus, the system undergoes a PSOJT distortion that allows the mixing of the e$^0$ and e$^+$ d combinations.

While most of the $d^2$ systems are $C_{3v}$, the $D_{3h}$ $[\mathrm{MoH}_3]^{2+}$ complex is stabilized by the occupancy of the $d_{3z^2}$ orbitals ($e^0$). The $d^2$ tungsten anion optimizes to a distorted $C_{2v}$ ($C_{2v}'$, Figure 1) geometry. The ruthenium cation reduces to a monodihydrogen complex ($C_i$, Figure 1) which is analogous to a $\sim C_{2v}$ $d^8$ ML$_2$ complex. The $d^8$ systems prefer the $C_{3v}$ geometry except for $[\mathrm{PDH}_3]^+$ which reduces to a dihydrogen complex ($C_i$, Figure 1).

---

**Table 5.** Minimum Energy Structures for $\mathrm{MH}_3$

<table>
<thead>
<tr>
<th>Species</th>
<th>$d^0$</th>
<th>$d^2$</th>
<th>$d^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>$\mathrm{YH}_3$</td>
<td>$\mathrm{LaH}_3$</td>
<td>$[\mathrm{HHF}]^+$</td>
</tr>
<tr>
<td>none</td>
<td>$D_{3h}$</td>
<td>$C_{3v}$</td>
<td>$C_{2v}$</td>
</tr>
<tr>
<td>$[\mathrm{ZrH}_3]^{+}$</td>
<td>$D_{3h}$</td>
<td>$[\mathrm{MoH}_3]^{2+}$</td>
<td>$&lt; C_{2v}$, ($C_i$)$<em>{d</em>{h}}$</td>
</tr>
<tr>
<td>$[\mathrm{TaH}_3]^{+}$</td>
<td>$D_{3h}$</td>
<td>$[\mathrm{WH}_3]^{2+}$</td>
<td>$C_{2v}$</td>
</tr>
<tr>
<td>$[\mathrm{ReH}_3]^{+}$</td>
<td>$D_{3h}$</td>
<td>$[\mathrm{OsH}_3]^{2+}$</td>
<td>$&lt; C_{2v}$, ($C_i$)$<em>{d</em>{h}}$</td>
</tr>
<tr>
<td>$[\mathrm{RhH}_3]^{+}$</td>
<td>$D_{3h}$</td>
<td>$[\mathrm{IrH}_3]^{2+}$</td>
<td>$C_{2v}$</td>
</tr>
<tr>
<td>$[\mathrm{PdH}_3]^{+}$</td>
<td>$D_{3h}$</td>
<td>$[\mathrm{CdH}_3]^{2+}$</td>
<td>$C_{2v}'$</td>
</tr>
<tr>
<td>$[\mathrm{PtH}_3]^{+}$</td>
<td>$D_{3h}$</td>
<td>$[\mathrm{HgH}_3]^{2+}$</td>
<td>$C_{2v}'$</td>
</tr>
</tbody>
</table>

* Refer to Figure 1. Dihydrogen complex: $[\mathrm{MoH}_3]^{2+}$, $C_{d_{h}}$, $d^8$ ML$_2$; $[\mathrm{RuH}_3]^{2+}$, $C_{d_{h}}$, $d^8$ ML$_2$; $[\mathrm{PDH}_3]^{+}$, $C_{d_{h}}$, $d^6$ ML$_2$.

---

**Figure 1.** Structural parameters for $\mathrm{MH}_3$ and $\mathrm{MH}_4$ complexes ($[\mathrm{MoH}_3]^{2+}$, $[\mathrm{RuH}_3]^{2+}$, $[\mathrm{WH}_3]^{2+}$, $[\mathrm{PDH}_3]^{+}$, $[\mathrm{TeH}_4]^{+}$) with symmetry $< C_{2v}$.
ORSAM predicts only the \( C_{2v} \) T-shaped and \( C_{2v}' \) Y-shaped geometries for \( d^0 \) complexes due to the incorporation of one p orbital into the orbital count. Both of the anionic complexes ([PdH]\(^-\)) and ([PtH]\(^-\)) form the T-shaped geometry while the neutral and cationic systems reduce to \( C_{2v} \) \( M(q^2-H_2)H \) complexes which follow the rules for \( D_{2d} \) \( d^{10} \) MH\(_4\) complexes. If we consider distortions from an open-shell \( d^1 \) \( D_{2h} \) geometry to the T-shaped (\( C_{2v} \)) or Y-shaped (\( C_{2v}' \)) complex, we see that the doubly occupied \( e' \) (M–H bonds through the metal p\(_{x,y} \) AOs) orbitals transform as \( a_1 \) and \( b_2 \) in \( C_{2v} \) symmetry. As a complex distorts toward the T-shaped (\( b_2 \) becomes stabilized) or Y-shaped geometry (\( a_1 \) becomes stabilized), respectively, it will be stabilized by a FOJT effect (Scheme 1). Metals that prefer to have low oxidation states such as Ag will prefer to distort toward the Y-shaped structure leading to a dihydrogen complex. The gold complex is an interesting case as both the \( +1 \) and \( +3 \) oxidation states are common. Ab initio results at the RHF and MP2 levels show that the nonclassical Y-shaped \( C_{2v}' \) \( Au(q^2-H_2)H \) complex is stabilized by 28.7 kcal/mol (MP2) over the classical T-shaped \( C_{2v} \) configuration (Au(III)). Previously, it was expected that AuH\(_3\) would be T-shaped from hybridization and FOJT arguments;\(^{32} \) however, the Jahn–Teller distortion was only performed toward the T-shaped system, so the dihydrogen global minimum was not observed.

MH\(_4\): The results of ORSAM for MH\(_4\) complexes were discussed above with the results listed in Table 4, and the minimum energy geometries for specific systems are listed in Table 6. The \( d^0 \) complexes form \( T_d \) complexes except for \([\text{NbH}_4]^+\) (\( C_{4v} \) at MP2). This niobium complex also has a low-lying \( C_4 \) dihydrogen complex (+6.5 kcal/mol) resembling a \( C_4 \) complex with a dihydrogen trans to a vacant site. Both the \([\text{YH}_4]^-\) and \([\text{LaH}_4]^-\) complexes have long (>2.0 Å) M–H bonds due to the mixing of low-lying \( t_2 \) \((n + 1)p \) orbitals and the stronger ionic character of the hydride ligands in these early high-oxidation state metal complexes. The \( T_d \) ZrH\(_4\) and HfH\(_4\) have been synthesized by pulsed laser ablation and characterized by IR spectroscopy.\(^{33} \) The experimentalists observe an increase in the asymmetric M–H stretch from Zr to Hf (1623.6 and 1678.4 cm\(^{-1}\), respectively) consistent with the shorter Hf–H bond obtained in this work and others.\(^{31} \) This increase in stretching frequency is also observed theoretically (RHF: Zr, 1679 cm\(^{-1}\); Hf, 1712 cm\(^{-1}\)). The shorter Hf–H bond distance is due, at least in part, to relativistic bond contraction.\(^{34} \)

The \( d^2 \) MH\(_4\) systems generally form the \( D_{2d} \) ([NbH\(_4\)]\(^-\), [TaH\(_4\)]\(^-\), WH\(_4\)) complex. The molybdenum system has a global minimum at the \( C_{2v} \) geometry but also has a low-lying (+4 kcal/mol) \( D_{2d} \) geometry. The cationic rhenium complex forms a dihydrogen complex at the RHF level, but geometry optimizations at the MP2 level give a \( C_{2v} \) geometry. At either level of theory the [TC\(_4\)]\(^+\) system is a dihydrogen complex (Figure 1). The molybdenum system has been synthesized,\(^{35} \) but since it is most likely a triplet the \( d^2 \) rules apply. Geometry optimizations at the unrestricted Hartree–Fock level give a \( T_d \) structure for triplet MoH\(_4\) as expected by ORSAM.

The \( d^3 \) systems are equally divided into \( T_d \) ([TcH\(_4\)]\(^-\), [ReH\(_4\)]\(^-\), OsH\(_4\)), and \( C_{2v} \) (RuH\(_4\), [RhH\(_4\)]\(^+\), [IrH\(_4\)]\(^+\)) systems which are the high symmetry conformations predicted by ORSAM. In all cases both of these geometries are minima on the potential energy surface with \( \sim 15–45 \) kcal/mol separating the isomers except in the case of OsH\(_4\) for which they are nearly degenerate at the MP2 level. The tetrahedral system is favored by systems where the p orbitals are low enough in energy to mix into the \( t_2 \) orbital (anionic and third-row systems).

The neutral Pd and cationic \( d^4 \) systems correspond to \( D_{2d} \) minima that have reduced to linear bis(dihydrogen) complexes (\( D_{2d} \) d\(^{10} \) ML\(_2\)) due to the stability of the d\(^{10} \) metal centers in these late-row transition metals (Pd, Ag, Au). However, the neutral Pt system and the anionic complexes possess the saw horse \( C_{2v} \) geometry:

\[
\begin{align*}
\text{H} & \quad \text{M} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{C}_{2v} & \quad \text{H}
\end{align*}
\]

The \( d^8 \) [AuH\(_4\)]\(^-\) complex studied here has been determined to be a \( D_{2d} \) complex as in a previous study.\(^{35} \) Several other \( d^8 \) complexes have also been structurally determined as \( D_{2d} \) by both experimental and theoretical methods ([RhH\(_4\)]\(^+\),\(^{36} \) [NiH\(_4\)]\(^2-\), [PdH\(_4\)]\(^2-\),\(^{37} \) and [PtH\(_4\)]\(^2-\)). High-spin \( d^5 \) and \( d^{10} \) MH\(_4\) complexes have also been synthesized by pulsed laser ablation and characterized by IR spectroscopy.\(^{33} \) The experimentalists observe an increase in the asymmetric M–H stretch from Zr to Hf (1623.6 and 1678.4 cm\(^{-1}\), respectively) consistent with the shorter Hf–H bond obtained in this work and others.\(^{31} \) This increase in stretching frequency is also observed theoretically (RHF: Zr, 1679 cm\(^{-1}\); Hf, 1712 cm\(^{-1}\)). The shorter Hf–H bond distance is due, at least in part, to relativistic bond contraction.\(^{34} \)

Table 6. Minimum Energy Structures for MH\(_4\)

<table>
<thead>
<tr>
<th>species</th>
<th>( T_d )</th>
<th>( C_{2v} )</th>
<th>( C_{2v}' )</th>
<th>( D_{2d} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{YH}_4]^-)</td>
<td>( T_d )</td>
<td>( \text{ZrH}_4 )</td>
<td>( \text{Td} )</td>
<td>( \text{[YH}_4]^+ )</td>
</tr>
<tr>
<td>([\text{LaH}_4]^-)</td>
<td>( T_d )</td>
<td>( \text{HfH}_4 )</td>
<td>( \text{Td} )</td>
<td>( \text{[LaH}_4]^+ )</td>
</tr>
<tr>
<td>([\text{NbH}_4]^+)</td>
<td>( D_{2d} )</td>
<td>( \text{MoH}_4 )</td>
<td>( \text{C}_{2v} )</td>
<td>( \text{[TcH}_4]^+ )</td>
</tr>
<tr>
<td>([\text{TaH}_4]^+)</td>
<td>( D_{2d} )</td>
<td>( \text{WdH}_4 )</td>
<td>( \text{D}_{2d} )</td>
<td>( \text{[ReH}_4]^+ )</td>
</tr>
<tr>
<td>([\text{IrH}_4]^+)</td>
<td>( D_{2d} )</td>
<td>( \text{OsH}_4 )</td>
<td>( \text{D}_{2d} )</td>
<td>( \text{[RhH}_4]^+ )</td>
</tr>
<tr>
<td>([\text{AgH}_4]^+)</td>
<td>( D_{2d} )</td>
<td>( \text{RhH}_4 )</td>
<td>( \text{D}_{2d} )</td>
<td>( \text{[IrH}_4]^+ )</td>
</tr>
<tr>
<td>([\text{AuH}_4]^+)</td>
<td>( D_{2d} )</td>
<td>( \text{PdH}_4 )</td>
<td>( \text{D}_{2d} )</td>
<td>( \text{[AuH}_4]^+ )</td>
</tr>
</tbody>
</table>

\(^{a}\) Refer to Figure 1. \(^{b}\) Dihydrogen complex: [Tc\(_4\)]\(^-\), [C\(_2\)]; PdH\(_4\), D\(_{2d}\); [AgH\(_4\)]\(^+\), D\(_{2d}\); [AuH\(_4\)]\(^+\), D\(_{2d}\). \(^{c}\) Minimum Energy Structures for MH\(_4\). \(^{d}\) Closed shell.

systems would have an orbital count of sp³ and thus be expected to act like main-group systems; the d⁰ [M(H₂)]⁻ anion is T₆.⁴⁰

MH₅. The results of ORSAM for the MH₅ complexes are listed in Table 4. The pentagonal pyramidal structure C₅₀ and square pyramidal C₄₀ geometries are allowed high-symmetry structures for the d⁴ and d⁵ systems; for the latter the d₂ and d₅ orbitals are obvious lone pair orbitals for C₅₀ and C₄₀, respectively. Occupancies of d⁴ and higher require the addition of one or more p orbitals into the bonding scheme. ORSAM shows that trigonal bipyramidal D₅₀ structures are only SA for d⁴ and d⁵ complexes where the e' and both the e'' and e'' d orbitals are lone pairs, respectively. In addition to these higher symmetry structures, a pentagonal planar D₅₀ is SA for d⁵ only and several C₂ᵥ geometries are available for all electron counts.

The results of the ab initio calculations are listed in Table 7. The anionic and neutral d⁰ complexes have the C₄₀ square pyramidal geometry except for [WH₄]^+ which optimizes to a D₅₀ trigonal bipyramidal structure. Both of these conformations fit the ORSAM model with the Hf anion using the expanded rules for high-oxygenate state early metals (d⁴sp in addition to d⁸s). There are several low-energy conformations for the [WH₄]^+ system as discussed by Landis.¹² We obtain a distorted C₄₀ (C₁, Figure 2) for the minimum energy structure and two low-lying C₄₀ minima at the MP2 level corresponding to "open" and "closed" umbrella geometries. The analogous Mo cation is a "closed" umbrella C₄₀ complex at the MP2 level. Landis¹² reports similar results for [WH₄]^+ but obtains a C₄₀ minimum energy structure. The potential energy surface is too flat to obtain an accurate geometry at the level and basis set used in either study, but either set of results is consistent with ORSAM.

Most of the d² MH₅ systems form C₅₀ complexes with the lone pair of electrons in the d₂ orbital. The [MoH₃]^+ anion forms a C₅₀ complex that is a "squashed" D₅₀ structure capped along one of the long edges. The anionic d⁴ systems are C₄₀, but both the neutral and cationic systems form dihydrogen complexes. The RhH₅, IrH₅, and [PtH₃]^+ systems reduce to mono(dihydrogen) Moη²-H₂H₃ complexes (Figure 2) which follow the ORSAM rules for C₅₀, d⁴ ML₄ systems. The cationic palladium system forms a bis(dihydrogen) complex (Figure 2) resembling a T-shaped C₂ᵥ d⁸ ML₃ complex due to the stability of the +2 oxidation state in Pd. The anionic d⁶ palladium and platinum complexes form dihydrogen C₂ᵥ, Moη²-H₂H₃ complexes that follow the rules for D₅₀ d⁸ ML₄ systems. The d⁸ MH₅ complexes have not been included in this study, but [IrH₅]^+ has been shown to be C₄₀,⁴¹ in agreement with our symmetry analysis.

MH₆. The sets of SA geometries for MH₆ systems are listed in Table 4. The d⁴ hexahydride and hexamethyl complexes have been the subject of a considerable amount of research⁵,¹²,¹⁶ with geometries ranging from O₅ to C₃ᵥ. ORSAM shows that only the pentagonal pyramidal C₃ᵥ, distorted trigonal prismatic C₃ₐ, and distorted trigonal antiprismeric complexes C₃ₐ complexes are possible geometries for d⁴ MH₆ complexes. The d² complexes incorporate a p orbital into their bonding scheme and allow a variety of high-symmetry geometries including trigonal prismatic D₅₀, bicapped tetrahedral D₅₀, C₃ᵥ, and C₆ₐ. The d⁴ system allows for a high-symmetry C₃ᵥ complex that most likely has 90° Hax—M—Heq bond angles due to the replacement of the e₂ d orbitals with the e₂ p orbitals in the bonding scheme (i.e., the pseudo-second-order Jahn—Teller effect should be absent). It is only for d⁴ systems that O₅ complexes can be expected among other lower symmetry structures. Several C₂ᵥ

**Table 7. Minimum Energy Structure for MH₅**

<table>
<thead>
<tr>
<th>species</th>
<th>species</th>
<th>species</th>
</tr>
</thead>
<tbody>
<tr>
<td>d⁰ [ZrH₅]^+</td>
<td>C₄₀</td>
<td>NbH₅</td>
</tr>
<tr>
<td>[WH₄]^+</td>
<td>D₅₀</td>
<td>TaH₅</td>
</tr>
<tr>
<td>d²</td>
<td>[MoH₃]^+</td>
<td>C₄₀</td>
</tr>
<tr>
<td>[OsH₅]^+</td>
<td>C₄₀</td>
<td>ReH₅</td>
</tr>
<tr>
<td>d⁴</td>
<td>[RuH₅]^+</td>
<td>C₄₀</td>
</tr>
<tr>
<td>[OsH₅]^+</td>
<td>C₄₀</td>
<td>Rh₅</td>
</tr>
<tr>
<td>d⁶</td>
<td>[PdH₅]^+</td>
<td>C₄₀</td>
</tr>
</tbody>
</table>

*See text. Refer to Figure 2. Dihydrogen complex: RhH₅, C₅₀ d⁶ ML₄; IrH₅, C₅₀ d⁶ ML₄; [PdH₅]^+, C₄₀ d⁶ ML₄; [PtH₃]^+ C₄₀ d⁶ ML₄; MP2 optimized geometry.

**Table 8. Minimum Energy Structure for MH₆**

<table>
<thead>
<tr>
<th>species</th>
<th>species</th>
<th>species</th>
</tr>
</thead>
<tbody>
<tr>
<td>d⁰</td>
<td>[NbH₆]^+</td>
<td>C₅₀</td>
</tr>
<tr>
<td>[IrH₅]^+</td>
<td>D₅₀</td>
<td>WH₃</td>
</tr>
<tr>
<td>d²</td>
<td>[IrH₅]^+</td>
<td>C₅₀</td>
</tr>
<tr>
<td>[RhH₅]^+</td>
<td>C₅₀</td>
<td>[IrH₅]^+</td>
</tr>
<tr>
<td>d⁴</td>
<td>[IrH₅]^+</td>
<td>C₅₀</td>
</tr>
</tbody>
</table>

*See text. Refer to Figure 3. Dihydrogen complex: [RhH₅]^+, C₅₀ d⁶ ML₄; [IrH₅]^+, C₅₀ d⁶ ML₄; [PtH₃]^+ C₅₀ d⁶ ML₄; MP2 optimized geometry. Complex dissociates to H₂ + Pd(η²-H₂) (D₅₀).
structures are also possible for most of these d occupancies. The d^2−d^6 complexes are hypervalent according to Landis’ model and would thus be expected to have linear H−M−H interactions. The final results for specific systems are listed in Table 8, but none of the systems have linear H−M−H units.

The present study finds that most of the d^0 complexes prefer the distorted trigonal prismatic C_{2v} geometry except [ReH_6]^+ which prefers the distorted trigonal antiprismatic C_{2v}^− one. In addition to minima at these two C_{3v}-type geometries, the complexes tend to have low-lying C_{5v} complexes that are nearly degenerate with the C_{3v} geometry in some cases. The [TaH_6]^{2−} complex gives a D_3h geometry in accordance with the OSRAM model for high-oxidation-state early transition metal anions that incorporate (n + 1)p orbitals earlier than other species.

The d^0 OsH_6 complex was discussed previously, where the distorted trigonal prismatic C_{2v} geometry was determined to be the lowest in energy because, compared to structures such as D_8h and C_{4v}, C_{2v}'' is able to minimize the contribution of the p orbital to the b_2 bonding orbital by mixing in d character. The analogous CpOsH_4 complex is pseudo-C_{2v} and represents an example of an MH_{n-1}L_n complex described as SA by the ORSAM model but having geometry different from that of the simple hydride because of the steric requirements of the Cp ring. The [TcH_6]^{2−} and RuH_6 complexes also show the C_{2v}'' geometry. The d^2 [ReH_6]^+ anion optimizes to a nonclassical distorted C_{2v}'' geometry (C_s, Figure 3). The cationic Rh system optimizes to sawhorse bis(dihydrogen) complex M(η^2-H_2)H_2 that follows the rules for C_{2v}, d^3 ML_4 complexes.

The anionic rhodium and iridium d^4 MH_6 systems are pentagonal pyramidal with ~90° H−M−H bond angles. A complex in which a dihydrogen forms from 2 equatorial hydrides (C_{3v}, analogous to C_{4v} d^5 ML_5) lies 6−10 kcal/mol above the C_{5v} minimum. This process is low energy because the reduction of the metal allows the pseudo-t_2g orbital to be filled (d^9). The neutral palladium system dissociates into an H_2 and the PdH_4 D_{2d} complex (Pd(η^2-H_2)H_2). The platinum system is C_{2v}'' where four hydrides come together into two dihydrogen ligands (Pt(η^2-H_2)H_2) such that the complex is pseudo-square planar and follows the ORSAM model for D_{4h} d^8 ML_4.

Although the set of possible geometries of d^6 MH_6 is fairly large, the highest SA geometry is the familiar O_h. There have been several experimental and theoretical studies of the [PdH_6]^{2−} and [PtH_6]^{2−} ions by various groups. The platinum complex exists as an octahedron, but the palladium system cannot be isolated due to the instability of Pd(IV). Mulliken population analyses of these complexes show that the valence p orbitals do play a significant part in the bonding of these complexes and that the use of a Madelung potential is essential to obtain the correct theoretical bonding picture for these complexes. The [FeH_6]^{2−} and [RuH_6]^{2−} anions have also been characterized as octahedral by X-ray diffraction. A non-O_h d^6 system is the C_{2v}, mer-Ir(PPh_3)_2(H)_3 complex where the trans phosphines bend away from the axial phosphine by ~15°. The results of ORSAM for the MH_7 systems are listed in Table 4. The d^0 and d^4 systems favor the pentagonal bipyrudal structure C_{5v}, the capped trigonal prism C_{3v}, or the capped trigonal antiprism C_{5v} as high-symmetry structures. The d^6 systems also include the pentagonal bipyrudal D_{3h} structure which is not allowed for d^0 complexes because two p orbitals are necessary for bonding to the equatorial hydrides. The C_{5v} structure can be considered a PSOJT distorted D_{3h} structure.

(43) An MCPF calculation in an all-electron basis set predicts the WH_6 C_{5v} complex to be lower in energy by 0.4 kcal/mol but only when first-order perturbative relativistic corrections are added. We have examined the relative energies of the WH_6 system at various levels (HF, MP2, MP3, GMO2) in the basis sets with and without polarization functions (Supporting Information Table S22). All our calculations place the C_{5v} isomer 0.1−0.9 kcal/mol below the C_{3v} isomer. A recent study of basis set, electron correlation, and relativistic effects in WH_6 (Hertwig, R. H.; Koch, W.; Yates, B. F. J. Comput. Chem. 1998, 19, 1604) shows that the C_{5v} and C_{3v} geometries are near-degenerate; their MCPF calculations with the Douglas–Kroll relativistic operator place the C_{3v} geometry 1.3 kcal/mol more stable than the C_{5v} geometry.
The neutral d0 RhH5 system is a dihydrogen complex (Figure 5) while the classical osmium complex is a protonated version of [OsH5]+ (C5 at MP2, Figure 5). The system has five equatorial hydrides and three more coordinated on one side of the molecule. At the MP2 level, the anionic ruthenium and technetium systems have the same general structure as the osmium complex. Both of the cationic systems (Rh and Ir at MP2) reduce to tris-dihydrogen(117) complexes similar to that shown for [IrH3]+ in Figure 5. These [M(q2-H3)3]+ systems behave like C4v, d0 ML5 complexes.

Both of the d2 complexes are dodecahedral (D5d) at the MP2 level. Theoretical and experimental studies of the [Os(PR3)3(H)3]+ complex(34–56) and a neutron diffraction study of Os-ML7 geometry. 

The work of Gusev and Berke(49) on group 8 polyhydrides [M(PR3)2H]+, M = Fe, Ru, and Os, shows that while several of these systems have nonclassical ~O8 d6 ML6 geometries, the classical polyhydride complexes have been determined by X-ray diffraction to have either the MH3 C3v ([O5(Me)3(H)]+) or the MH5 C2v (([Fe(PEt3)3(H)]+, [Os(PEt3)3(H)]+) geometry, both predicted as possibilities by symmetry analysis. The D3h geometry of the Ir(PPr3)2H5(50) complex is also in agreement with our results for d6 MH5. The “distorted D5d geometry” of Os(PMe2Ph)(H)5(51) is better explained as a C2v′ ML5 geometry. Theoretical(52) and experimental(53) characterization of the C6RuH6 complex as a C6v′′′ complex provides further support for the broad applicability of ORSAM.

MH8. The results of ORSAM for the MH8 complexes are listed in Table 4. A high-symmetry geometry for a ML5 complex is the dodecahedral D5d, but our symmetry analysis shows that this conformation is only SA for d5 MH8 systems. For the d6 complexes, the highest symmetries allowed are the D6h′ and distorted square antiprismatic C4v geometries. The d5 systems can also possess dodecahedral D5d′ and square antiprismatic D5d geometries. In addition to the high-symmetry structures, several C2v geometries are available. The final results for specific systems are given in Table 10.
show that the counterions can reverse this ordering; for example, in RhReH₁₀ the [ReH₉]²⁻ units are C₄ᵥ at low temperatures.

Several substituted ML₄H₇ complexes have been discussed in the literature. A theoretical study of M(PhH₃)₂H₇, M = Re and Tc,⁶³ gave a theoretical minimum for the rhenium system similar to the C₂ᵥ geometry for MH₉ in this study. The technetium system was shown to reorient to a bis(dihydrogen) system corresponding to ~C₂ᵥ d₄ MH₉ in this study. Neutron diffraction studies of W(PhH₃Pt₃)H₆ have shown that the complex is C₃ᵥ.⁶²

**Discussion**

ORSAM correctly predicts the geometries for all systems studied. While the variety of SA geometries is large, and this may be a criticism of the method, the range of possibilities better reflects the variety of experimentally observed geometries. Adding rules to ORSAM that would reduce the possible geometries would make the method prone to fail because of their inflexibility. There is a pitfall for a user in arbitrarily restricting the number of possible geometries to a very limited set. For example, many chemists were hesitant to accept that WH₄ or W(CH₃)₆ could be anything other than O₈ due to the expectation of this structure by other more restrictive methods.

In general, these polyhydride complexes will not always possess the SA geometry with the highest symmetry. Since hydrides avoid bonding to p orbitals when possible, high-symmetry geometries with pure p or sp combinations will be less favorable than lower symmetry conformations where dp mixing can occur. For example, D₁₇h and C₄v are SA high-symmetry possibilities for OsH₈ species. However, the former uses a pure p a₁'' orbital for bonding and the latter requires sp hybrids to accommodate the trans hydrides along the axis. The system prefers the C₂ᵥ geometry where the required p contribution (orbital count = d₄sp) of b₁ symmetry can be "diluted" by the b₂ d orbital. One should note that many studies,⁵⁶,⁶⁰,⁶³ which have been used as evidence for the unimportance of p orbitals, are of small complexes such as MH diatomics and d⁴ ML₄⁻ (x ≤ 6) where enough nd and (n + 1)s orbitals are present such that p orbitals will not contribute significantly.

It is also worthwhile to note the many diagonal relationships in these systems. Generally, anionic systems and neutral third-row systems will be similar as will cationic systems and neutral third-row systems. This observation results from the greater ability of anionic and third-row systems to mix p contributions with the same symmetry as the d orbitals and for these same species to form strong covalent bonds to H because of their expanded d orbitals.

---


In the valence bond approach\textsuperscript{12} to transition metal polyhydride complexes, analogies are made between hypervalent main group and so-called hypervalent transition metal complexes. An example is [PdH\textsubscript{3}]\textsuperscript{−}, a complex said to have one Pd–H 2e–2e bond and a linear 3c–4e H–Pd–H unit constructed from H–Pd–H'–Pd H' resonance structures. Thus, the system would be similar to ClH\textsubscript{3}, a simple hydride analogue of the known CIF\textsubscript{3} molecule. In the previous study,\textsuperscript{64} NBO analysis\textsuperscript{64} was used in the discussion of these complexes, but Maseras and Morokuma\textsuperscript{65} have shown that NBO cannot give an adequate description of the contribution of ($n+1$)p orbitals since it does not include them in the valence space. Using a modified version of NBO, they showed that for NiH\textsubscript{2} the population of the 4p orbital was 0.05 with a valence space of 3d4s to 0.27 when 4p orbitals were included as part of the valence space (3d4s4p). As a result of this ambiguity in NBO analysis, we have chosen to analyze these complexes using Foster–Boys\textsuperscript{66} and Pipek–Mezey\textsuperscript{67} localized orbitals. The localized orbitals were analyzed by summing the squares of the coefficients of the CGTO’s and determining the percentage of the total belonging to individual contributions.

The geometry of ClH\textsubscript{3} was optimized at the RHF level (Table 11) using the Wadt–Hay RECP and double-$\zeta$ basis set for chlorine\textsuperscript{68} and the Dunning triple-$\zeta$ basis set for hydrogen.\textsuperscript{23} Calculations were performed with and without a d polarization function on the chlorine atom ($\zeta = 0.6$). The structural parameters and total Mulliken populations\textsuperscript{29} are listed in Table 11. The analysis of the localized orbitals shows that the hydrogens are strongly bound to the chloride through the p orbital (69.4% of the CI contribution for a Cl–H\textsubscript{eq} bond and 86.2% for a Cl–H\textsubscript{ax} bond), as expected. The localized orbitals for the Cl–H\textsubscript{eq} bonds are actually delocalized over both hydrogens with $1/3$ of the H\textsubscript{eq} contribution arising from the H\textsubscript{ax} trans to the primary bond (Table 12). It should be noted that only the Foster–Boys method could provide “localized” orbitals; the Pipek–Mezey method gave a 3c–4e interaction. The d polarization function contributes only 3% to each bonding orbital (though it does stabilize the molecule by 37.8 kcal/mol). Only 1.7% of the chlorine electrons are located in d orbitals. A similar analysis was conducted on the RHF optimized geometry (Table 11) of [PdH\textsubscript{3}]\textsuperscript{−}. In contrast to the results for ClH\textsubscript{3}, both the Foster–Boys and Pipek–Mezey localizations provide cleanly localized Pd–H bond orbitals with residual contributions smaller than those in ClH\textsubscript{3}. The Pd–H\textsubscript{ax} bond is a mixture of s and d contributions and the Pd–H\textsubscript{eq} bonds have almost a 1:1 ratio for s, p, and d character (Table 12). Thus, while a hypervalent description may be appropriate for ClH\textsubscript{3}, it is less appropriate for [PdH\textsubscript{3}]\textsuperscript{−}.

In the MO picture (Scheme 2) for ClH\textsubscript{3}, an antibonding orbital must be incorporated into the bonding scheme due to the inaccessibility of the 3d orbitals; the excitation energy from the ground state of the CI atom to the first excited state containing a 3d orbital is 95 696 cm\textsuperscript{−1}.\textsuperscript{11} In this electron-rich system, an extra pair of electrons occupies an antibonding a\textsubscript{1} orbital thus canceling one of the a\textsubscript{1} bonding contributions. The net result is a 3c–4e bond between Cl and the H\textsubscript{eq}’s. The addition of d functions to the chlorine does not change the overall nature of the a\textsubscript{1} orbital as they act as polarization functions rather than valence 3d orbitals. In the case of [PdH\textsubscript{3}]\textsuperscript{−}, there are no 5d orbitals of the proper symmetry to form a T-shaped structure (the hydrides lie in the node of the b\textsubscript{2} d\textsubscript{z}z AO). Since the 5p orbitals are much more accessible for Pd (excitation into a 5p

<table>
<thead>
<tr>
<th>Table 11. Structural Parameters and Total Mulliken Populations for ClH\textsubscript{3} and [PdH\textsubscript{3}]\textsuperscript{−} at the RHF Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond</td>
</tr>
<tr>
<td>Cl–H\textsubscript{ax}</td>
</tr>
<tr>
<td>Cl–H\textsubscript{eq}</td>
</tr>
<tr>
<td>H\textsubscript{ax}–X–H\textsubscript{eq}, deg</td>
</tr>
<tr>
<td>tot. Mull. pop., H\textsubscript{ax}</td>
</tr>
<tr>
<td>tot. Mull. pop., H\textsubscript{eq}</td>
</tr>
</tbody>
</table>

* No polarization functions were used on Cl. * Polarization function included on Cl ($\zeta = 0.6$).

<table>
<thead>
<tr>
<th>Table 12. Percentages of Orbital Types in Foster–Boys Localized Orbitals* (See Text)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond</td>
</tr>
<tr>
<td>Cl–H\textsubscript{ax}</td>
</tr>
<tr>
<td>Cl–H\textsubscript{eq}</td>
</tr>
<tr>
<td>Pd–H\textsubscript{ax}</td>
</tr>
<tr>
<td>Pd–H\textsubscript{eq}</td>
</tr>
</tbody>
</table>

* See text. a Polarization functions (d, $\zeta = 0.6$) were included on Cl. b Residual contributions.
orbital is 34.068 cm$^{-1}$), the $b_2 p_z$ bonding orbital can be incorporated into the bonding scheme (Scheme 2) and all Pd–H interactions can be transformed into 2c–2e bonds. Similar diagrams can be constructed for other pairs of main group and transition metal complexes which are called analogous in a hypervalent picture (e.g., [RhH$_4$]$^-$ and SF$_4$, [PtH$_4$]$^{2-}$ and XeF$_4$, [FeH$_4$]$^{4-}$ and XeF$_8$). The [RhH$_4$]$^-$ complex possesses the saw horse $C_2v$ geometry. However, rather than forming 3c–4e linear H–M–H interactions analogous to a main group hypervalent complex, this system forms a linear $b_2$ bond orbital through the metal $p_y$ AO.

The hypervalent model also has difficulty with the structures of complexes such as [WH$_7$]$^-$ and [W(CH$_3$)$_7$]$^-$ as neither of these “hypervalent” complexes has a linear L–M–L unit as required for a 3c–4e bond. The $C_{5v}$ structure with a linear L–M–L unit would be expected from hypervalency arguments; however, this complex is a maximum on the potential energy surface lying 12 kcal/mol above the $C_{3v}$ geometry in the hydride complex. Also, hypervalency arguments cannot be used to rationalize the known geometries of numerous eight- and nine-coordinate transition metal polyhydride systems, such as [ReH$_9$]$^{2-}$, none of which contain linear H–M–H units. ORSAM is able to correctly predict all of these complexes.

**Conclusions**

Symmetry and group theoretical analysis is one of the most powerful tools available to the modern chemist. Their application to transition-metal hydride complexes in the orbitally ranked symmetry analysis method (ORSAM) can be used to determine a set of geometries for a given d electron count and MH$_x$ stoichiometry among which the minimum energy structure will be found. Geometry optimizations of a number of these complexes show that all of the minimum energy geometries are predicted by ORSAM. Furthermore, the geometries of nonclassical polyhydrides can also be rationalized as part of this method. When the results of ORSAM are compared with experimental data many unusual geometries can be rationalized. In addition, these transition-metal hydride complexes are not hypervalent in the usual sense of the term but make substantial use of the $(n + 1)p$ orbital after the nd and $(n + 1)s$ orbitals are completely employed.

**Acknowledgment.** This research has been supported by the Robert A. Welch Foundation (Grant No. A-648) and the National Science Foundation (Grant Nos. CHE91-13634 and 94-23271).

**Supporting Information Available:** Tables and figures containing symmetry analysis data (33 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.