

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

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**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.<sup>1</sup> The success of the method has been attributed to the repulsions of electrons<sup>2</sup> through the Pauli exclusion principle. However, later studies<sup>3</sup> showed that Pauli repulsions between lone pairs of electrons were not sufficient to rationalize the shapes of molecules. Instead, the physics behind VSEPR involves the preference for the main-group central atom to maximize the electron density in its  $ns$  orbital at the expense of its less stable  $np$  orbitals.<sup>4</sup> Nevertheless, VSEPR rules work reasonably well for predicting geometries of main group systems, but they fail for many transition metal complexes. For example, VSEPR rules cannot provide an explanation for the structures of  $WH_6$ , a distorted trigonal prism ( $C_{3v}$ ),<sup>5</sup> or the experimentally known  $W(CH_3)_6$  ( $C_3$ ) molecule.<sup>6</sup>

The complementary spherical electron density model (CSEDM) is based upon the spherical distribution of cluster components or of ligands around a central atom such that the inert-gas or 18-electron rule is fulfilled.<sup>7</sup> Ligands can be distributed in either

a best packing or best covering fashion<sup>8</sup> such that the linear combinations of ligand orbitals match the central atom's spherical harmonics. While this method seems to work well for 18-electron transition metal complexes, it fails to explain the geometries of  $d^0$  12-electron complexes such as  $W(CH_3)_6$  or  $WH_6$ .

The valence bond (VB) method<sup>9</sup> 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  $\pi$ -ligands.<sup>10</sup> In electron-rich systems one must invoke the use of either high-energy  $d$  orbitals or three-center–four-electron ( $3c-4e$ ) bonds<sup>11</sup> formed from the following resonance structures:  $L^- M^+ - L \leftrightarrow L - M^+ L^-$ .

Recently, Landis has applied VB methods to transition metal polyhydride complexes.<sup>12</sup> In this model, the bonding around the metal is considered to occur only through  $ds$ -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!”<sup>12a</sup>

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(12) (a) Landis, C. R.; Cleveland, T.; Firman, T. K. *J. Am. Chem. Soc.* **1995**, *117*, 1859. (b) Landis, C. R.; Firman, T. K.; Root, D. M.; Cleveland, T. *J. Am. Chem. Soc.* **1998**, *120*, 1842. (c) Landis, C. R.; Cleveland, T.; Firman, T. K. *J. Am. Chem. Soc.*, **1998**, *120*, 2641.

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.<sup>13</sup> In fact, while studies<sup>14</sup> 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.<sup>15a</sup>

In this work, we develop a method for predicting the structure of transition metal polyhydride complexes through the use of symmetry analysis coupled with the preferential 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 CSEDM 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<sup>7,8</sup>) 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  $(n + 1)s$  and  $nd$  orbitals, but  $(n + 1)p$  orbitals are incorporated into the bonding scheme such that more systems can be adequately described without invoking hypervalency. A preliminary report of the application of our approach to  $WH_6$  and  $OsH_6$  has appeared.<sup>16</sup> The work reported here is most closely related to the application of symmetry to molecular geometry recently discussed by King.<sup>17</sup> The present work extends the ideas presented in work by the present authors<sup>4,16</sup> and King.<sup>17</sup>

### 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),<sup>18</sup> which are usually separable into radial functions  $R_{nl}(r)$  and spherical harmonics  $Y_{lm}(\theta, \phi)$ . For the central atom of a complex,  $ML_x$ , 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.<sup>19</sup> 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

(13) Excitation energies for main group atoms range from  $62\,751\text{ cm}^{-1}$  for As to  $95\,696\text{ cm}^{-1}$  for Cl; second- and third-row transition metals range from  $10\,529\text{ cm}^{-1}$  for Y to  $37\,645\text{ cm}^{-1}$  for Hg. Most of the first-row metals lie between  $15\,000$  and  $25\,000\text{ cm}^{-1}$ . Moore, C. E. *Atomic Energy Levels*; NSRDS–NBS 35; U.S. National Bureau of Standards: Washington, DC; Vols. I–III. The values for several elements are listed in Table S1 of the Supporting Information.

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**Table 1.** Orbital Counts ( $d^m sp^n$ ) for Each Stoichiometry and d Electron Count

	$d^0$	$d^2$	$d^4$	$d^6$	$d^8$
MH <sub>3</sub>	$d^2s$	$d^2s$	$d^2s$	$d^2s$	$dsp$
MH <sub>4</sub>	$d^3s$	$d^3s$	$d^3s$	$d^2sp$	$dsp^2$
MH <sub>5</sub>	$d^4s$	$d^4s$	$d^3sp$	$d^2sp^2$	$dsp^3$
MH <sub>6</sub>	$d^5s$	$d^4sp$	$d^3sp^2$	$d^2sp^3$	
MH <sub>7</sub>	$d^5sp$	$d^4sp^2$	$d^3sp^3$		
MH <sub>8</sub>	$d^5sp^2$	$d^4sp^3$			
MH <sub>9</sub>	$d^5sp^3$				

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  $MH_x$  with a symmetry of  $C_{2v}$  or higher and determine the irreducible representations for the hydride ligands. It is assumed that lower symmetry ( $<C_{2v}$ ) 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 ( $d^m sp^n$ ) 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,<sup>20,21</sup> 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  $d^4$  system.

(b) Because they have low-lying  $(n + 1)p$  orbitals, anionic complexes of high-oxidation-state, early transition metals should include the possible geometries for the complex with an additional  $(n + 1)p$  orbital (i.e., both  $d^4s$  and  $d^3sp$  for  $MH_5$ ).

(3) Match the hydride irreducible representations to the metal orbitals with the same symmetry type. All components of a degenerate representation must be equally occupied or the system will undergo distortion. The irreducible representations

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

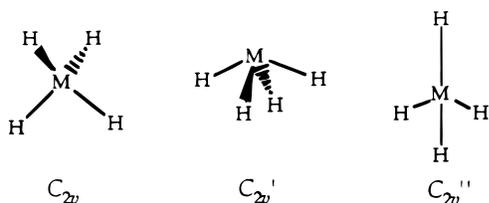
	$\Gamma_{Md}$	$\Gamma_{Ms}$	$\Gamma_{Mp}$
$O_h$	$e_g + t_{2g}$	$a_{1g}$	$t_{1u}$
$T_d$	$e + t_2$	$a_1$	$t_2$
$D_{6h}$	$a_{1g} + e_{1g} + e_{2g}$	$a_{1g}$	$a_{2u} + e_{1u}$
$D_{5h}$	$a_1' + e_2' + e_1''$	$a_1'$	$a_2'' + e_1'$
$D_{4h}$	$a_{1g} + b_{1g} + b_{2g} + e_g$	$a_{1g}$	$a_{2u} + e_u$
$D_{3h}$	$a_1' + e' + e''$	$a_1'$	$a_2'' + e'$
$D_{2h}$	$2a_g + b_{1g} + b_{2g} + b_{3g}$	$a_g$	$b_{1u} + b_{2u} + b_{3u}$
$D_{4d}$	$a_1 + e_2 + e_3$	$a_1$	$b_2 + e_1$
$D_{3d}$	$a_{1g} + 2e_g$	$a_{1g}$	$a_{2u} + e_u$
$D_{2d}$	$a_1 + b_1 + b_2 + e$	$a_1$	$b_2 + e$
$C_{6v}$	$a_1 + e_1 + e_2$	$a_1$	$a_1 + e_1$
$C_{5v}$	$a_1 + e_1 + e_2$	$a_1$	$a_1 + e_1$
$C_{4v}$	$a_1 + b_1 + b_2 + e$	$a_1$	$a_1 + e$
$C_{3v}$	$a_1 + 2e$	$a_1$	$a_1 + e$
$C_{2v}$	$2a_1 + a_2 + b_1 + b_2$	$a_1$	$a_1 + b_1 + b_2$

**Table 3.** Symmetry Decompositions of  $MH_4$  Systems.

symm	$\Gamma_H$	SA? for d occupancy (orb count)				
		$d^0$ ( $sd^3$ )	$d^2$ ( $sd^3$ )	$d^4$ ( $sd^3$ )	$d^6$ ( $spd^2$ )	$d^8$ ( $sp^2d$ )
$T_d$	$a_1 + t_2$	Y	N	Y	N	N
$D_{4h}$	$a_{1g} + b_{1g} + e_u$	N	N	N	N	Y
$D_{2h}$	$2a_g + b_{2u} + b_{3u}$	N	N	N	N	Y
$D_{2d}$	$a_1 + b_2 + e$	Y	Y	Y	Y	Y
$C_{4v}$	$a_1 + b_1 + e$	Y	Y	Y	N	Y
$C_{3v}$	$2a_1 + e$	Y	N	Y	Y	Y
$C_{2v}$	$2a_1 + b_1 + b_2$	Y	Y	Y	Y	Y
$C_{2v}'$	$2a_1 + b_1 + b_2$	Y	Y	Y	Y	Y
$C_{2v}''$	$3a_1 + b_1$	Y	Y	Y	Y	Y

of the metal AOs in various symmetry groups are found in Table 2. Any geometry whose orbitals completely match between the metal and the hydrides is referred to as “symmetry allowed” (SA) and is included in a set of possible geometries for the given stoichiometry and d electron count.

The application of the method to  $MH_4$  systems is presented as an illustration. The total set of possible geometries for  $MH_4$  includes the high-symmetry tetrahedral  $T_d$  and square planar  $D_{4h}$  geometries along with various “distortions” from these geometries: rhomboidal  $D_{2h}$ , distorted tetrahedral  $D_{2d}$ , square pyramidal  $C_{4v}$ , trigonal pyramidal  $C_{3v}$ , and three  $C_{2v}$  geometries



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  $d^0$  through  $d^4$ , the orbital count for  $MH_4$  is  $d^3s$ , or three  $nd$  orbitals and one  $(n + 1)s$  orbital. At  $d^6$  one  $(n + 1)p$  orbital must be introduced to make the orbital count  $d^2sp$ , while at  $d^8$  it would be  $dsp^2$ . 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  $ML_4$  complexes are only allowed in two d-electron counts for  $T_d$  ( $d^0$  and  $d^4$ ) and one d-electron count for  $D_{4h}$  ( $d^8$ ). The hydrides in

**Table 4.** Sets of Possible Geometries for  $MH_x$ 

		$\{MH_x\} + O (<C_{2v})$
$MH_3$	$d^0$	$D_{3h}, C_{3v}, C_{2v}, C_{2v}'$
	$d^2$	$D_{3h}, C_{3v}, C_{2v}, C_{2v}'$
	$d^4$	$D_{3h}, C_{3v}, C_{2v}, C_{2v}'$
	$d^6$	$D_{3h}, C_{3v}, C_{2v}, C_{2v}'$
	$d^8$	$C_{2v}, C_{2v}'$
$MH_4$	$d^0$	$T_d, D_{2d}, C_{4v}, C_{3v}, C_{2v}, C_{2v}', C_{2v}''$
	$d^2$	$D_{2d}, C_{4v}, C_{2v}, C_{2v}', C_{2v}''$
	$d^4$	$T_d, D_{2d}, C_{4v}, C_{3v}, C_{2v}, C_{2v}', C_{2v}''$
	$d^6$	$D_{2d}, C_{3v}, C_{2v}, C_{2v}', C_{2v}''$
	$d^8$	$D_{4h}, D_{2h}, D_{2d}, C_{4v}, C_{3v}, C_{2v}, C_{2v}', C_{2v}''$
$MH_5$	$d^0$	$C_{5v}, C_{4v}, C_{2v}, C_{2v}'$
	$d^2$	$C_{5v}, C_{4v}, C_{2v}, C_{2v}'$
	$d^4$	$D_{3h}, C_{4v}, C_{3v}, C_{2v}, C_{2v}', C_{2v}''$
	$d^6$	$D_{5h}, C_{5v}, C_{4v}, C_{2v}, C_{2v}', C_{2v}''$
	$d^8$	$D_{3h}, C_{4v}, C_{3v}, C_{2v}, C_{2v}'$
$MH_6$	$d^0$	$C_{5v}, C_{3v}, C_{3v}'$
	$d^2$	$D_{3h}, D_{2d}, C_{5v}, C_{4v}, C_{3v}, C_{3v}', C_{2v}, C_{2v}', C_{2v}''$
	$d^4$	$C_{5v}, C_{3v}, C_{3v}', C_{2v}, C_{2v}', C_{2v}''$
	$d^6$	$O_h, D_{4h}, D_{3h}, D_{2h}, D_{3d}, D_{2d}, C_{5v}, C_{4v}, C_{3v}, C_{3v}', C_{2v}, C_{2v}', C_{2v}''$
	$d^8$	$C_{5v}, C_{3v}, C_{3v}'$
$MH_7$	$d^0$	$C_{5v}, C_{3v}, C_{3v}', C_{2v}, C_{2v}''$
	$d^2$	$C_{2v}, C_{2v}', C_{2v}'', C_{2v}'''$
	$d^4$	$D_{5h}, C_{5v}, C_{3v}, C_{3v}', C_{2v}, C_{2v}', C_{2v}''$
	$d^6$	$D_{5h}, C_{5v}, C_{3v}, C_{3v}', C_{2v}, C_{2v}', C_{2v}''$
$MH_8$	$d^0$	$D_{2d}', C_{4v}', C_{2v}', C_{2v}'', C_{2v}'''$
	$d^2$	$D_{4d}, D_{2d}, D_{2d}', C_{4v}', C_{2v}', C_{2v}'', C_{2v}'''$
$MH_9$	$d^0$	$D_{3h}, D_{3h}', C_{4v}', C_{3v}, C_{3v}', C_{2v}'$

the  $D_{4h}$  conformation require two p orbitals ( $e_u$ ) in order to bond to the metal so that only  $d^8$  complexes (orbital count =  $dsp^2$ ) can assume this geometry. The highest symmetry structures for  $d^2$  are the first-order Jahn–Teller (FOJT) distortion from  $T_d$  ( $D_{2d}$ ) and the pseudo-second-order Jahn–Teller (PSOJT) distortion from  $D_{4h}$  ( $C_{4v}$ ). The  $d^6$  system has the  $D_{2d}$  and distorted tetrahedral  $C_{3v}$  geometries as high-symmetry possibilities.

By applying this reasoning to other  $MH_x$  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). Dihydrogen complexes can also be rationalized as part of this analysis. Since the dihydrogen ligand is a  $\sigma$ -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  $AgH_3$  ( $d^8$ ) could reduce to a  $d^{10}$  dihydrogen complex  $Ag(\eta^2-H_2)H$ . If the dihydrogen is considered a hydride ligand, then the complex would follow a set of rules for  $d^{10} ML_2$  systems for which ORSAM would predict  $D_{\infty h}$ .

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  $(M(PR_3)_nH_{x-n})$  complexes that would be similar to  $M(H_2)_nH_{x-n}$  systems. Strong one-electron ligands like  $CR_3$  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<sup>22</sup> have been performed on a variety of simple transition metal polyhydride complexes ( $MH_x$ ) including neutral, anionic, and cationic systems of all second- and third-row metals. The metals were represented by modified Emler–Christiansen RECP basis sets.<sup>23</sup> These bases were of double- $\zeta$  quality

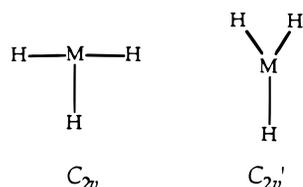
in the s and p space with triple- $\zeta$  quality in the d space. The  $(n + 1)s$  and  $(n + 1)p$  orbitals have been included in these basis sets in accordance with recent studies on transition metal systems.<sup>15</sup> The hydride basis functions were triple- $\zeta$  quality.<sup>24</sup>

Geometry optimizations and frequency calculations have been performed at the restricted Hartree–Fock (RHF) level.<sup>25</sup> Geometry optimizations at the MP2 level<sup>26</sup> were performed for all third-row neutral systems. The relative energies of the neutral systems were recalculated at the MP2, MP3, and CCSD levels.<sup>27</sup> Relative energies at the MP2 level were calculated for systems with dihydrogen ligands due to the overestimation of H<sub>2</sub> 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<sup>28</sup> and relative energies were calculated at the GMO2(PEMCSF) and GMO2(SDTQ) levels.<sup>29</sup>

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

## Results

**MH<sub>3</sub>.** Four geometries have been considered for MH<sub>3</sub> complexes: trigonal planar  $D_{3h}$ , trigonal pyramidal  $C_{3v}$ , T-shaped  $C_{2v}$ , and Y-shaped  $C_{2v}'$ .



The results of ORSAM for MH<sub>3</sub> 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  $d^8$  systems.

Most of the complexes examined in this study (Table 5) have minima at one of the high symmetry ( $>C_{2v}$ ) 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 LaH<sub>3</sub> complex, the  $d^0$  YH<sub>3</sub> complex is  $D_{3h}$  due to the ligand repulsions around a small metal center and the high contribution of p orbitals to the bonding orbitals. Mulliken population analysis<sup>30</sup> 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

(22) GAMESS-UK is a package of ab initio programs written by M. F. Guest, J. H. van Lenthe, J. Kendrick, K. Schoffel, and P. Sherwood, with contributions from R. D. Amos, R. J. Buenker, M. Dupuis, N. C. Handy, I. H. Hillier, P. J. Knowles, V. Bonacic-Koutecky, W. von Niessen, R. J. Harrison, A. P. Rendell, V. R. Saunders, and A. J. Stone. The package is derived from the original GAMESS code due to Dupuis, M.; Spangler, D.; Wendoloski, J. *NRCC Software Catalog*; NRCC: Warrington, U.K., Vol. 1, Program No. QG01 (GAMESS).

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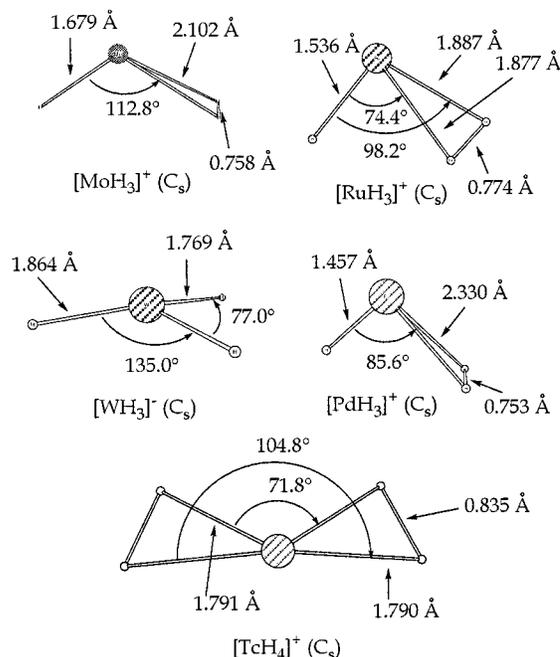
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**Table 5.** Minimum Energy Structures for MH<sub>3</sub>

species	species	species
$d^0$ none	YH <sub>3</sub> $D_{3h}$	[ZrH <sub>3</sub> ] <sup>+</sup> $C_{3v}$
none	LaH <sub>3</sub> $C_{3v}$	[HfH <sub>3</sub> ] <sup>+</sup> $C_{3v}$
$d^2$ [ZrH <sub>3</sub> ] <sup>-</sup> $D_{3h}$	NbH <sub>3</sub> $D_{3h}$	[MoH <sub>3</sub> ] <sup>+</sup> $<C_{2v}$ ( $C_s$ ) <sup>a,b</sup>
[HfH <sub>3</sub> ] <sup>-</sup> $C_{2v}$	TaH <sub>3</sub> $D_{3h}$	[WH <sub>3</sub> ] <sup>+</sup> $C_{3v}$
$d^4$ [MoH <sub>3</sub> ] <sup>-</sup> $D_{3h}$	TcH <sub>3</sub> $C_{3v}$	[RuH <sub>3</sub> ] <sup>+</sup> $<C_{2v}$ ( $C_s$ ) <sup>a,b</sup>
[WH <sub>3</sub> ] <sup>-</sup> $<C_{2v}$ ( $C_s$ ) <sup>a</sup>	ReH <sub>3</sub> $C_{3v}$	[OsH <sub>3</sub> ] <sup>+</sup> $C_{3v}$
$d^6$ [RuH <sub>3</sub> ] <sup>-</sup> $C_{3v}$	RhH <sub>3</sub> $C_{3v}$	[PdH <sub>3</sub> ] <sup>+</sup> $<C_{2v}$ ( $C_s$ )
[OsH <sub>3</sub> ] <sup>-</sup> $C_{3v}$	IrH <sub>3</sub> $C_{3v}$	[PtH <sub>3</sub> ] <sup>+</sup> $C_{3v}$
$d^8$ [PdH <sub>3</sub> ] <sup>-</sup> $C_{2v}$	AgH <sub>3</sub> $C_{2v}'$	[CdH <sub>3</sub> ] <sup>+</sup> $C_{2v}'$
[PtH <sub>3</sub> ] <sup>-</sup> $C_{2v}$	AuH <sub>3</sub> $C_{2v}'$	[HgH <sub>3</sub> ] <sup>+</sup> $C_{2v}'$

<sup>a</sup> Refer to Figure 1. <sup>b</sup> Dihydrogen complex: [MoH<sub>3</sub>]<sup>+</sup>,  $C_{2v}$   $d^4$  ML<sub>2</sub>; [RuH<sub>3</sub>]<sup>+</sup>,  $C_{2v}$   $d^6$  ML<sub>2</sub>; [PdH<sub>3</sub>]<sup>+</sup>,  $C_{2v}$   $d^8$  ML<sub>2</sub>.



**Figure 1.** Structural parameters for MH<sub>3</sub> and MH<sub>4</sub> complexes ([MoH<sub>3</sub>]<sup>+</sup>, [RuH<sub>3</sub>]<sup>+</sup>, [WH<sub>3</sub>]<sup>-</sup>, [PdH<sub>3</sub>]<sup>+</sup>, [TcH<sub>4</sub>]<sup>+</sup>) with symmetry  $<C_{2v}$ .

the metal. A previous study<sup>31</sup> 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  $d_{z^2}$  orbital ( $a_1'$ ). However, the potential energy surface for [HfH<sub>3</sub>]<sup>-</sup> 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 [MoH( $\eta^2$ -H<sub>2</sub>)]<sup>+</sup> complex ( $C_s$ , Figure 1) analogous to a  $\sim C_{2v}$   $d^4$  ML<sub>2</sub> system. The positive charge on  $d^2$  [WH<sub>3</sub>]<sup>+</sup> increases the gap between the d and p orbitals, thus favoring the  $C_{3v}$  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  $e'$  and  $e''$  d combinations.

While most of the  $d^4$  systems are  $C_{3v}$ , the  $D_{3h}$  [MoH<sub>3</sub>]<sup>-</sup> complex is stabilized by the occupancy of the  $d_{xz,yz}$  orbitals ( $e''$ ). The  $d^4$  tungsten anion optimizes to a distorted  $C_{2v}'$  ( $C_s$ , Figure 1) geometry. The ruthenium cation reduces to a mono-(dihydrogen) complex ( $C_s$ , Figure 1) which is analogous to a  $\sim C_{2v}$   $d^6$  ML<sub>2</sub> complex. The  $d^6$  systems prefer the  $C_{3v}$  geometry except for [PdH<sub>3</sub>]<sup>+</sup> which reduces to a dihydrogen complex ( $C_s$ , Figure 1).

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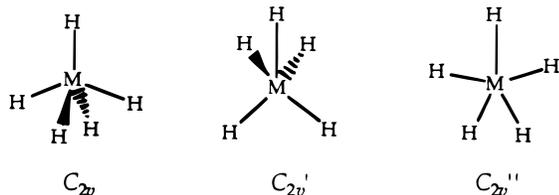
**Table 7.** Minimum Energy Structure for MH<sub>5</sub>

species	species	species
d <sup>0</sup> [ZrH <sub>5</sub> ] <sup>-</sup>	C <sub>4v</sub>	NbH <sub>5</sub> C <sub>4v</sub>
[HfH <sub>5</sub> ] <sup>-</sup>	D <sub>3h</sub> <sup>a</sup>	TaH <sub>5</sub> C <sub>4v</sub>
d <sup>2</sup> [MoH <sub>5</sub> ] <sup>-</sup>	C <sub>2v</sub> <sup>'</sup>	TcH <sub>5</sub> C <sub>5v</sub>
[WH <sub>5</sub> ] <sup>-</sup>	C <sub>5v</sub> <sup>d</sup>	[RuH <sub>5</sub> ] <sup>+</sup> C <sub>5v</sub> <sup>d</sup>
d <sup>4</sup> [RuH <sub>5</sub> ] <sup>-</sup>	C <sub>3v</sub>	RhH <sub>5</sub> <C <sub>2v</sub> <sup>b,c</sup> (C <sub>s</sub> )
[OsH <sub>5</sub> ] <sup>-</sup>	C <sub>3v</sub>	IrH <sub>5</sub> <C <sub>2v</sub> <sup>b,c</sup> (C <sub>s</sub> )
d <sup>6</sup> [PdH <sub>5</sub> ] <sup>-</sup>	C <sub>2v</sub> <sup>''c</sup>	[PtH <sub>5</sub> ] <sup>+</sup> <C <sub>2v</sub> <sup>b,c</sup> (C <sub>s</sub> )
[PtH <sub>5</sub> ] <sup>-</sup>	C <sub>2v</sub> <sup>''c</sup>	

<sup>a</sup> See text. <sup>b</sup> Refer to Figure 2. <sup>c</sup> Dihydrogen complex: RhH<sub>5</sub>, C<sub>2v</sub> d<sup>6</sup> ML<sub>4</sub>; IrH<sub>5</sub>, C<sub>2v</sub> d<sup>6</sup> ML<sub>4</sub>; [PdH<sub>5</sub>]<sup>+</sup>, C<sub>2v</sub> d<sup>6</sup> ML<sub>4</sub>; [PtH<sub>5</sub>]<sup>+</sup>, C<sub>2v</sub> d<sup>6</sup> ML<sub>4</sub>; [PdH<sub>5</sub>]<sup>-</sup>, D<sub>4h</sub> d<sup>8</sup> ML<sub>4</sub>; [PtH<sub>5</sub>]<sup>-</sup>, D<sub>4h</sub> d<sup>8</sup> ML<sub>4</sub>. <sup>d</sup> MP2 optimized geometry.

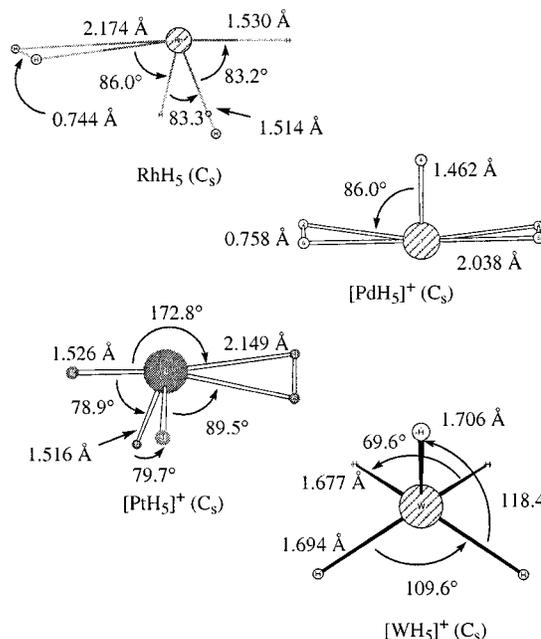
systems would have an orbital count of sp<sup>3</sup> and thus be expected to act like main-group systems; the d<sup>5</sup> [MnH<sub>4</sub>]<sup>-</sup> anion is T<sub>d</sub>.<sup>40</sup>

**MH<sub>5</sub>.** The results of ORSAM for the MH<sub>5</sub> complexes are listed in Table 4. The pentagonal pyramidal structure C<sub>5v</sub> and square pyramidal C<sub>4v</sub> geometries are allowed high-symmetry structures for the d<sup>0</sup> and d<sup>2</sup> systems; for the latter the d<sub>z<sup>2</sup></sub> and d<sub>xy</sub> orbitals are obvious lone pair orbitals for C<sub>5v</sub> and C<sub>4v</sub>, respectively. Occupancies of d<sup>4</sup> and higher require the addition of one or more p orbitals into the bonding scheme. ORSAM shows that trigonal bipyramidal D<sub>3h</sub> structures are only SA for d<sup>4</sup> and d<sup>8</sup> 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 D<sub>5h</sub> is SA for d<sup>6</sup> only and several C<sub>2v</sub> geometries are available for all electron counts.



The results of the ab initio calculations are listed in Table 7. The anionic and neutral d<sup>0</sup> complexes have the C<sub>4v</sub> square pyramidal geometry except for [HfH<sub>5</sub>]<sup>-</sup> which optimizes to a D<sub>3h</sub> trigonal bipyramidal structure. Both of these conformations fit the ORSAM model with the Hf anion using the expanded rules for high-oxidation state early metals (d<sup>3</sup>sp in addition to d<sup>4</sup>s). There are several low-energy conformations for the [WH<sub>5</sub>]<sup>+</sup> system as discussed by Landis.<sup>12</sup> We obtain a distorted C<sub>4v</sub> (C<sub>s</sub>, Figure 2) for the minimum energy structure and two low-lying C<sub>4v</sub> minima at the MP2 level corresponding to "open" and "closed" umbrella geometries. The analogous Mo cation is a "closed" umbrella C<sub>4v</sub> complex at the MP2 level. Landis<sup>12</sup> reports similar results for [WH<sub>5</sub>]<sup>+</sup> but obtains a C<sub>4v</sub> 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 d<sup>2</sup> MH<sub>5</sub> systems form C<sub>5v</sub> complexes with the lone pair of electrons in the d<sub>z<sup>2</sup></sub> orbital. The [MoH<sub>5</sub>]<sup>-</sup> anion forms a C<sub>2v</sub><sup>'</sup> complex that is a "squashed" D<sub>2d</sub> structure capped along one of the long edges. The anionic d<sup>4</sup> systems are C<sub>3v</sub>, but both the neutral and cationic systems form dihydrogen complexes. The RhH<sub>5</sub>, IrH<sub>5</sub>, and [PtH<sub>5</sub>]<sup>+</sup> systems reduce to mono(dihydrogen) M(η<sup>2</sup>-H<sub>2</sub>)H<sub>3</sub> complexes (Figure 2) which follow the ORSAM rules for C<sub>2v</sub> d<sup>6</sup> ML<sub>4</sub> systems. The cationic palladium system forms a bis(dihydrogen) complex (Figure 2) resembling

**Figure 2.** Structural parameters for MH<sub>5</sub> complexes (RhH<sub>5</sub>, [PdH<sub>5</sub>]<sup>+</sup>, [PtH<sub>5</sub>]<sup>+</sup>, [WH<sub>5</sub>]<sup>+</sup>) with symmetry <C<sub>2v</sub>.**Table 8.** Minimum Energy Structure for MH<sub>6</sub>

species	species	species
d <sup>0</sup> [NbH <sub>6</sub> ] <sup>-</sup>	C <sub>3v</sub>	MoH <sub>6</sub> C <sub>3v</sub>
[TaH <sub>6</sub> ] <sup>-</sup>	D <sub>3h</sub> <sup>a</sup>	WH <sub>6</sub> C <sub>3v</sub>
d <sup>2</sup> [TcH <sub>6</sub> ] <sup>-</sup>	C <sub>2v</sub> <sup>''d</sup>	RuH <sub>6</sub> C <sub>2v</sub> <sup>''d</sup>
[ReH <sub>6</sub> ] <sup>-</sup>	<C <sub>2v</sub> <sup>b</sup> (C <sub>s</sub> )	OsH <sub>6</sub> C <sub>2v</sub> <sup>''c</sup>
d <sup>4</sup> [RhH <sub>6</sub> ] <sup>-</sup>	C <sub>5v</sub> <sup>d</sup>	PdH <sub>6</sub> <C <sub>2v</sub> <sup>e</sup>
[IrH <sub>6</sub> ] <sup>-</sup>	C <sub>5v</sub>	PtH <sub>6</sub> C <sub>2v</sub> <sup>''c</sup>

<sup>a</sup> See text. <sup>b</sup> Refer to Figure 3. <sup>c</sup> Dihydrogen complex: [RhH<sub>6</sub>]<sup>+</sup>, C<sub>2v</sub> d<sup>6</sup> ML<sub>4</sub>; [IrH<sub>6</sub>]<sup>+</sup>, C<sub>s</sub> d<sup>4</sup> ML<sub>5</sub>; PtH<sub>6</sub>, D<sub>4h</sub> d<sup>8</sup> ML<sub>4</sub>. <sup>d</sup> MP2 optimized geometry. <sup>e</sup> Complex dissociates to H<sub>2</sub> + Pd(η<sup>2</sup>-H<sub>2</sub>)<sub>2</sub> (D<sub>2d</sub>).

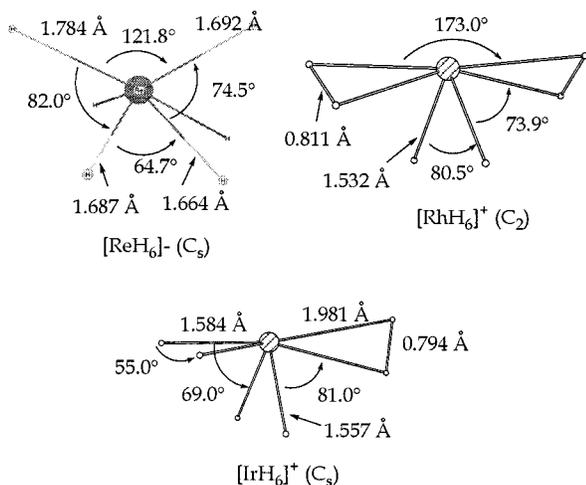
a T-shaped C<sub>2v</sub> d<sup>8</sup> ML<sub>3</sub> complex due to the stability of the +2 oxidation state in Pd. The anionic d<sup>6</sup> palladium and platinum complexes form dihydrogen C<sub>2v</sub><sup>'</sup> M(η<sup>2</sup>-H<sub>2</sub>)H<sub>3</sub> complexes that follow the rules for D<sub>4h</sub> d<sup>8</sup> ML<sub>4</sub> systems. The d<sup>8</sup> MH<sub>5</sub> complexes have not been included in this study, but [IrH<sub>5</sub>]<sup>4-</sup> has been shown to be C<sub>4v</sub><sup>41</sup> in agreement with our symmetry analysis.

**MH<sub>6</sub>.** The sets of SA geometries for MH<sub>6</sub> systems are listed in Table 4. The d<sup>0</sup> hexahydride and hexamethyl complexes have been the subject of a considerable amount of research<sup>5,42,16</sup> with geometries ranging from O<sub>h</sub> to C<sub>3v</sub>. ORSAM shows that only the pentagonal pyramidal C<sub>5v</sub>, distorted trigonal prismatic C<sub>3v</sub>, and distorted trigonal antiprismatic complexes C<sub>3v</sub><sup>'</sup> complexes are possible geometries for d<sup>0</sup> MH<sub>6</sub> complexes. The d<sup>2</sup> complexes incorporate a p orbital into their bonding scheme and allow a variety of high-symmetry geometries including trigonal prismatic D<sub>3h</sub>, bicapped tetrahedral D<sub>2d</sub>, C<sub>5v</sub>, and C<sub>4v</sub>. The d<sup>4</sup> system allows for a high-symmetry C<sub>5v</sub> complex that most likely has 90° H<sub>ax</sub>-M-H<sub>eq</sub> bond angles due to the replacement of the e<sub>2</sub> d orbitals with the e<sub>2</sub> p orbitals in the bonding scheme (i.e., the pseudo-second-order Jahn-Teller effect<sup>16</sup> should be absent). It is only for d<sup>6</sup> systems that O<sub>h</sub> complexes can be expected among other lower symmetry structures. Several C<sub>2v</sub>

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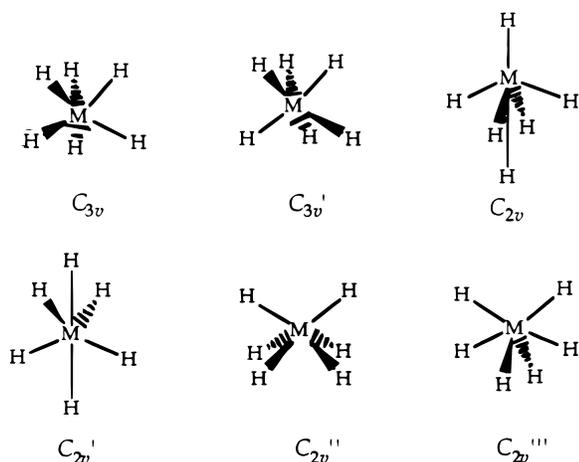
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**Figure 3.** Structural parameters for  $MH_6$  complexes ( $[ReH_6]^-$ ,  $[RhH_6]^+$ ,  $[IrH_6]^+$ ) with symmetry  $<C_{2v}$ .

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.



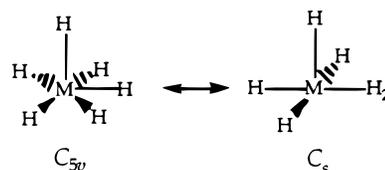
The present study finds that most of the  $d^0$  complexes prefer the distorted trigonal prismatic  $C_{3v}$  geometry except  $[ReH_6]^+$  which prefers the distorted trigonal antiprismatic  $C_{3v}'$  one. In addition to minima at these two  $C_{3v}$ -type geometries, the complexes tend to have low-lying  $C_{5v}$  complexes that are nearly degenerate with the  $C_{3v}$  geometry in some cases.<sup>43</sup> The  $[TaH_6]^-$  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  $d^2$   $OsH_6$  complex was discussed previously,<sup>16</sup> where the distorted trigonal prismatic  $C_{2v}''$  geometry was determined to be the lowest in energy because, compared to structures such

(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.<sup>5a</sup> 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  $C_{3v}$  isomer 0.1–0.9 kcal/mol below the  $C_{5v}$  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  $C_{3v}$  and  $C_{5v}$  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.

as  $D_{3h}$  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.<sup>16</sup> The analogous  $CpOsH_5$  complex is pseudo- $C_{4v}$ <sup>44,45</sup> and represents an example of an  $MH_{x-n}L_n$  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  $[TcH_6]^-$  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  $M(\eta^2-H_2)_2H_2$  that follows the rules for  $C_{2v}$   $d^6$   $ML_4$  complexes.

The anionic rhodium and iridium  $d^4$   $MH_6$  systems are pentagonal pyramidal with  $\sim 90^\circ$   $H_{ax}-M-H_{eq}$  bond angles. A complex in which a dihydrogen forms from 2 equatorial hydrides ( $C_s$ , analogous to  $C_{4v}$   $d^6$   $ML_5$ ) 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 ( $d^6$ ). The neutral palladium system dissociates into an  $H_2$  and the  $PdH_4$   $D_{2d}$  complex ( $Pd(\eta^2-H_2)_2$ ). The platinum system is  $C_{2v}''$  where four hydrides come together into two dihydrogen ligands ( $Pt(\eta^2-H_2)_2H_2$ ) 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<sup>46</sup> and theoretical<sup>39</sup> 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  $Pd(IV)$ .<sup>46</sup> Mulliken population analyses<sup>30</sup> 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.<sup>39</sup> The  $[FeH_6]^{4-}$  and  $[RuH_6]^{4-}$  anions have also been characterized as octahedral by X-ray diffraction.<sup>47</sup> A non- $O_h$   $d^6$  system is the  $C_{2v}$  *mer*- $Ir(PPh_3)_3(H)_3$  complex where the trans phosphines bend away from the axial phosphine by  $\sim 15^\circ$ .<sup>48</sup>

**MH<sub>7</sub>.** The results of ORSAM for the  $MH_7$  systems are listed in Table 4. The  $d^0$  and  $d^4$  systems favor the pentagonal bipyramidal structure  $C_{5v}$ , the capped trigonal prism  $C_{3v}$ , or the capped trigonal antiprism  $C_{3v}'$  as high-symmetry structures. The  $d^4$  systems also include the pentagonal bipyramidal  $D_{5h}$  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  $D_{5h}$  structure.<sup>16</sup> The  $d^2$  systems can only possess various  $C_{2v}$  geometries as their

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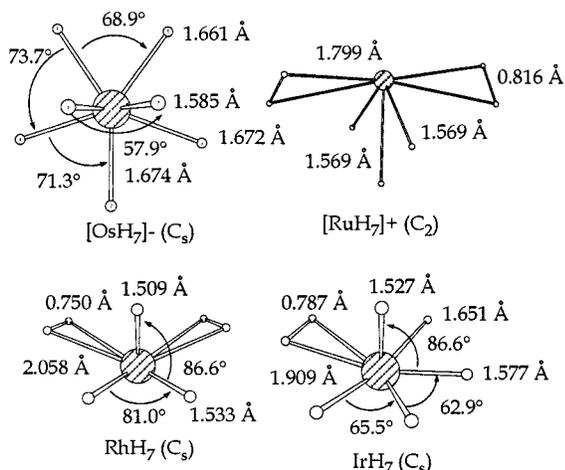
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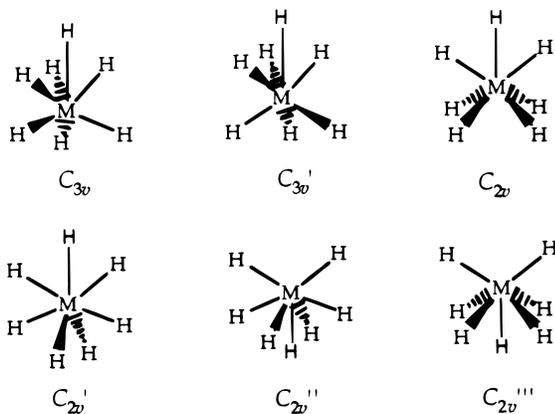
**Table 9.** Minimum Energy Structure for MH<sub>7</sub>

species	species	species
d <sup>0</sup> [MoH <sub>7</sub> ] <sup>-</sup> C <sub>3v</sub> '	TcH <sub>7</sub> C <sub>2v</sub> ''' <sup>c</sup>	[RuH <sub>7</sub> ] <sup>+</sup> <C <sub>2v</sub> <sup>b,c</sup> (C <sub>2</sub> )
[WH <sub>7</sub> ] <sup>-</sup> C <sub>3v</sub> '	ReH <sub>7</sub> <C <sub>2v</sub> (C <sub>s</sub> )	[OsH <sub>7</sub> ] <sup>+</sup> <C <sub>2v</sub> <sup>b,c</sup> (C <sub>2</sub> )
d <sup>2</sup> [RuH <sub>7</sub> ] <sup>-</sup> <C <sub>2v</sub> <sup>c</sup> (C <sub>s</sub> )	RhH <sub>7</sub> <C <sub>2v</sub>	
[OsH <sub>7</sub> ] <sup>-</sup> <C <sub>2v</sub> <sup>c</sup> (C <sub>s</sub> )	IrH <sub>7</sub> <C <sub>2v</sub> <sup>c</sup> (C <sub>s</sub> )	

<sup>a</sup> Refer to Figure 4. <sup>b</sup> Dihydrogen complex. [RuH<sub>7</sub>]<sup>+</sup>, C<sub>2v</sub>' d<sup>4</sup> ML<sub>5</sub>; [OsH<sub>7</sub>]<sup>+</sup>, C<sub>2v</sub>' d<sup>4</sup> ML<sub>5</sub>; RhH<sub>7</sub>, C<sub>4v</sub> d<sup>6</sup> ML<sub>5</sub>; IrH<sub>7</sub>, C<sub>5v</sub> d<sup>4</sup> ML<sub>6</sub>. <sup>c</sup> MP2 optimized geometry.

**Figure 4.** Structural parameters for MH<sub>7</sub> complexes ([OsH<sub>7</sub>]<sup>-</sup>, [RuH<sub>7</sub>]<sup>+</sup>, RhH<sub>7</sub>, IrH<sub>7</sub>) with symmetry <C<sub>2v</sub>.

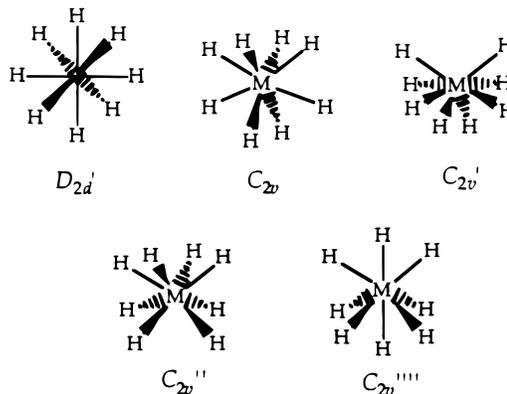
highest symmetry minima. The results of ab initio calculations for specific systems are listed in Table 9.



The d<sup>0</sup> anionic complexes of molybdenum and tungsten both have C<sub>3v</sub>' capped trigonal antiprismatic geometries. The C<sub>3v</sub>' geometry is preferred to C<sub>5v</sub> due to the ability of C<sub>3v</sub>' to delocalize the contribution of the metal p orbital. The d<sup>0</sup> TcH<sub>7</sub> system adopts a C<sub>2v</sub>''' geometry while the classical ReH<sub>7</sub> complex is a slightly distorted C<sub>2v</sub>''' complex. Both of these complexes are analogous to their protonated d<sup>2</sup> MH<sub>6</sub> analogues where the proton adds along the C<sub>2</sub> (~C<sub>2</sub> for ReH<sub>7</sub>) axis between four hydrides. The cationic ruthenium and osmium systems (Figure 4) are bis(dihydrogen) complexes [M(η<sup>2</sup>-H<sub>2</sub>)<sub>2</sub>H<sub>3</sub>]<sup>+</sup> with trans dihydrogen ligands and an additional hydride between the two cis hydrides. This structure can be viewed as a C<sub>2v</sub>' d<sup>6</sup> ML<sub>5</sub> system. Both neutral d<sup>2</sup> systems reduce to dihydrogen complexes (Figure 4) where the Rh system forms a cis bis(dihydrogen) complex (C<sub>4v</sub> d<sup>6</sup> ML<sub>5</sub>) and the Ir system forms a mono(dihydrogen) complex (C<sub>5v</sub> d<sup>4</sup> ML<sub>6</sub>). At the MP2 level, the anionic ruthenium and osmium systems (d<sup>2</sup>) have five hydrides that are nearly planar with the metal and two hydrides both above the MH<sub>5</sub> plane (Figure 4).

The work of Gusev and Berke<sup>49</sup> on group 8 polyhydrides [M(PR<sub>3</sub>)<sub>4</sub>H<sub>3</sub>]<sup>+</sup>, M = Fe, Ru, and Os, shows that while several of these systems have nonclassical ~O<sub>h</sub> d<sup>6</sup> ML<sub>6</sub> geometries, the classical polyhydride complexes have been determined by X-ray diffraction to have either the MH<sub>7</sub> C<sub>2v</sub> ([Os(PMe<sub>3</sub>)<sub>4</sub>(H)<sub>3</sub>]<sup>+</sup>) or the MH<sub>7</sub> C<sub>3v</sub>' ([Fe(PET<sub>3</sub>)<sub>4</sub>(H)<sub>3</sub>]<sup>+</sup>, [Os(PET<sub>3</sub>)<sub>4</sub>(H)<sub>3</sub>]<sup>+</sup>) geometry, both predicted as possibilities by symmetry analysis. The D<sub>5h</sub> geometry of the Ir(PiPr<sub>3</sub>)<sub>2</sub>H<sub>5</sub><sup>49</sup> complex is also in agreement with our results for d<sup>4</sup> MH<sub>7</sub>. The "distorted D<sub>5h</sub>" structure of Os(PMe<sub>2</sub>Ph)<sub>3</sub>(H)<sub>4</sub><sup>51</sup> is better explained as a C<sub>2v</sub>' ML<sub>7</sub> geometry. Theoretical<sup>52</sup> and experimental<sup>53</sup> characterization of the Cp\*ReH<sub>6</sub> complex as a C<sub>5v</sub> complex provides further support for the broad applicability of ORSAM.

**MH<sub>8</sub>.** The results of ORSAM for the MH<sub>8</sub> complexes are listed in Table 4. A high-symmetry geometry for a ML<sub>8</sub> complex is the dodecahedral D<sub>2d</sub>, but our symmetry analysis shows that this conformation is only SA for d<sup>2</sup> MH<sub>8</sub> systems. For the d<sup>0</sup> complexes, the highest symmetries allowed are the D<sub>2d</sub>' and distorted square antiprismatic C<sub>4v</sub>' geometries. The d<sup>2</sup> systems can also possess dodecahedral D<sub>2d</sub> and square antiprismatic D<sub>4d</sub> geometries. In addition to the high-symmetry structures, several C<sub>2v</sub> geometries are available. The final results for specific systems are given in Table 10.



The neutral d<sup>0</sup> RuH<sub>8</sub> system is a dihydrogen complex (Figure 5) while the classical osmium complex is a protonated version of [OsH<sub>7</sub>]<sup>-</sup> (C<sub>s</sub> 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 rhenium 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) complexes similar to that shown for [IrH<sub>8</sub>]<sup>+</sup> in Figure 5. These [M(η<sup>2</sup>-H<sub>2</sub>)<sub>3</sub>H<sub>2</sub>]<sup>+</sup> systems behave like C<sub>4v</sub> d<sup>6</sup> ML<sub>5</sub> complexes.

Both of the d<sup>2</sup> complexes are dodecahedral (D<sub>2d</sub>) at the MP2 level. Theoretical and experimental studies of the [Os(PR<sub>3</sub>)<sub>3</sub>(H)<sub>5</sub>]<sup>+</sup> complex<sup>54-56</sup> and a neutron diffraction study of Os-

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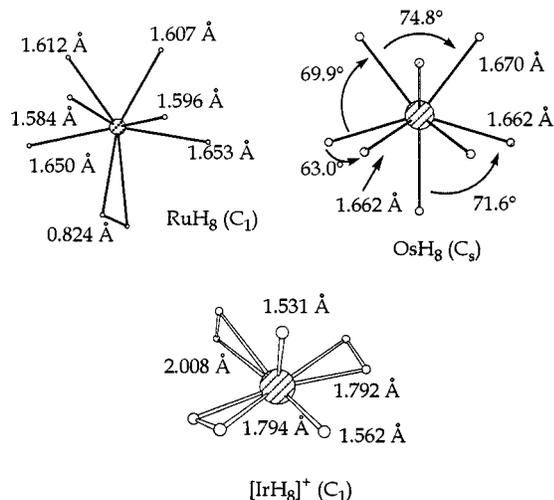
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**Table 10.** Minimum Energy Structure for  $MH_8$  and  $MH_9$ 

		species		species		species	
$MH_8$	$d^0$	$[TcH_8]^-$	$<C_{2v}^c(C_s)$	$RuH_8$	$<C_{2v}^{b,c}$	$[RhH_8]^+$	$<C_{2v}(C_s)^{b,c}$
		$[ReH_8]^-$	$<C_{2v}^c(C_s)$	$OsH_8$	$<C_{2v}^c(C_s)$	$[IrH_8]^+$	$<C_{2v}^b$
	$d^2$	$[RhH_8]^-$	$D_{2d}$				
$MH_9$	$d^0$	$[TcH_9]^{2-}$	$D_{2d}$	$[RuH_9]^-$	$D_{3h}'$	$RhH_9$	$<C_{2v}(C_3)^{b,c}$
		$[ReH_9]^{2-}$	$D_{3h}'$	$[OsH_9]^-$	$D_{3h}'$	$IrH_9$	$D_{3h}'^c$
			$D_{3h}'$				

<sup>a</sup> Refer to Figure 5. <sup>b</sup> Dihydrogen complex. <sup>c</sup> MP2 optimized geometry.



**Figure 5.** Structural parameters for  $MH_8$  complexes ( $RuH_8$ ,  $OsH_8$ ,  $[IrH_8]^+$ ) with symmetry  $<C_{2v}$ .

( $PC_{12}H_{19}$ ) $_2H_6$ <sup>57</sup> reveal that both of these complexes are substituted dodecahedra as expected for  $d^2$  eight-coordinate polyhydride complexes.

**$MH_9$ .** The results of ORSAM for the  $MH_9$  systems are listed in Table 4. In addition to monoanionic systems, we have also calculated structures for the polyhydride complexes  $[TcH_9]^{2-}$  and  $[ReH_9]^{2-}$  which are known experimentally.<sup>58</sup> Theoretical studies of the  $[ReH_9]^{2-}$  species have been performed by several groups.<sup>59</sup> The ORSAM model predicts high-symmetry conformations for these  $d^0$  complexes as either a tricapped trigonal prism (edgewise  $D_{3h}$  or facial  $D_{3h}'$ ) or  $C_{4v}'$  (capped square antiprism). The calculations for the rhenium and technetium dianions are  $D_{3h}'$  in agreement with the experimental results. In addition, our calculations predict that  $[RuH_9]^-$ ,  $[OsH_9]^-$ , and  $IrH_9$  are also  $D_{3h}'$  (Table 10). The rhodium complex is a  $C_3$  complex with *fac* tris(dihydrogen) ligands  $Rh(\eta^2-H_2)_3H_3$ . A *mer*  $Rh(\eta^2-H_2)_3H_3$  complex lies  $\sim 20$  kcal/mol above the  $C_3$  complex. Both of these tris(dihydrogen) species are pseudo- $O_h$  and can be described using the rules for  $O_h$   $d^6$   $ML_6$ . The  $D_{3h}'$  complexes have  $C_{4v}'$  transition states that lie  $<1$  kcal/mol above the global minimum through which the systems rapidly exchange hydrides as observed in NMR studies.<sup>58b</sup> In addition, more recent studies

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show that the counterions can reverse this ordering; for example, in  $Rb_3ReH_{10}$  the  $[ReH_9]^{2-}$  units are  $C_{4v}'$  at low temperatures.<sup>60</sup>

Several substituted  $ML_xH_{9-x}$  complexes have been discussed in the literature. A theoretical study of  $M(PH_3)_2H_7$ ,  $M = Re$  and  $Tc$ ,<sup>61</sup> gave a theoretical minimum for the rhenium system similar to the  $C_{2v}'$  geometry for  $MH_9$  in this study. The technetium system was shown to reorient to a bis(dihydrogen) system corresponding to  $\sim C_{2v}$   $d^4$   $MH_7$  in this study. Neutron diffraction studies of  $W(PPh_3Pr_2)_3H_6$  have shown that the complex is  $C_{2v}'$ .<sup>62</sup>

## 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  $WH_6$  or  $W(CH_3)_6$  could be anything other than  $O_h$  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,  $D_{3h}$  and  $C_{4v}$  are SA high-symmetry possibilities for  $OsH_6$  species. However, the former uses a pure p  $a_2''$  orbital for bonding and the latter requires sp hybrids to accommodate the trans hydrides along the axis. The system prefers the  $C_{2v}'$  geometry where the required p contribution (orbital count =  $d^4sp$ ) of  $b_2$  symmetry can be "diluted" by the  $b_2$  d orbital. One should note that many studies,<sup>5a,20,63</sup> which have been used as evidence for the unimportance of p orbitals, are of small complexes such as  $MH$  diatomics and  $d^0$   $ML_x$  ( $x \leq 6$ ) 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 second-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.

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**Table 11.** Structural Parameters and Total Mulliken Populations for  $\text{ClH}_3$  and  $[\text{PdH}_3]^-$  at the RHF Level

	$\text{ClH}_3^a$	$\text{ClH}_3^b$	$[\text{PdH}_3]^-$
X-H <sub>ax</sub> , Å	1.286	1.258	1.518
X-H <sub>eq</sub> , Å	1.737	1.590	1.702
H <sub>ax</sub> -X-H <sub>eq</sub> , deg	86.59	85.28	88.67
tot. Mull. pop., X	6.787 49	6.923	18.619 65
tot. Mull. pop., H <sub>ax</sub>	0.724 44	0.635	0.965 08
tot. Mull. pop., H <sub>eq</sub>	1.244 04	1.22	1.207 64

<sup>a</sup> No polarization functions were used on Cl. <sup>b</sup> Polarization function included on Cl ( $\zeta = 0.6$ ).

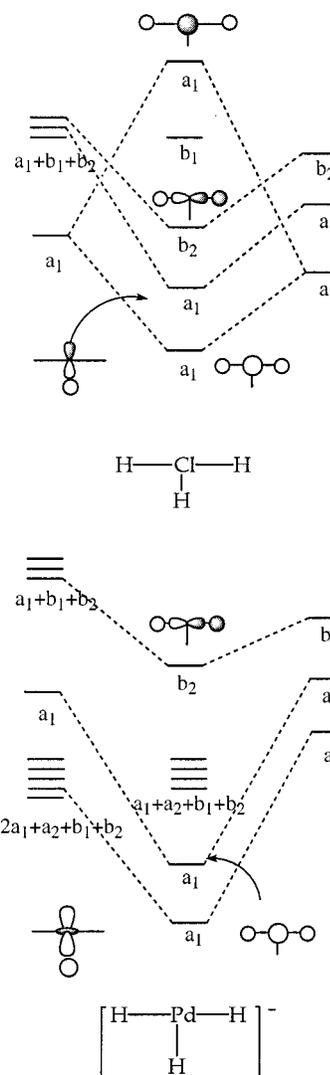
**Table 12.** Percentages of Orbital Types in Foster-Boys Localized Orbitals<sup>a</sup> (See Text)

bond	% s	% p	% d	% H <sub>ax</sub>	% H <sub>eq</sub>	% H <sub>eq</sub> '
Cl-H <sub>ax</sub> <sup>b</sup>	18.9	50.5	3.4	23.2	2.0 <sup>c</sup>	2.0 <sup>c</sup>
Cl-H <sub>eq</sub> <sup>b</sup>	2.7	36.8	3.2	2.1 <sup>c</sup>	43.4	11.8 <sup>c</sup>
Pd-H <sub>ax</sub>	17.9	4.5	45.9	31.3	0.2 <sup>c</sup>	0.2 <sup>c</sup>
Pd-H <sub>eq</sub>	16.8	13.0	18.4	0.4 <sup>c</sup>	50.4	1.0 <sup>c</sup>

<sup>a</sup> See text. <sup>b</sup> Polarization functions (d,  $\zeta = 0.6$ ) were included on Cl. <sup>c</sup> Residual contributions.

In the valence bond approach<sup>12</sup> to transition metal polyhydride complexes, analogies are made between hypervalent main group and so-called hypervalent transition metal complexes. An example is  $[\text{PdH}_3]^-$ , a complex said to have one Pd-H 2c-2e bond and a linear 3c-4e H-Pd-H unit constructed from H<sup>-</sup> Pd-H<sup>+</sup> H<sup>-</sup> Pd H<sup>-</sup> resonance structures. Thus, the system would be similar to  $\text{ClH}_3$ , a simple hydride analogue of the known  $\text{ClF}_3$  molecule. In the previous study,<sup>12</sup> NBO analysis<sup>64</sup> was used in the discussion of these complexes, but Maseras and Morokuma<sup>65</sup> 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  $\text{NiH}_2$  the population of the 4p<sub>z</sub> orbital changed from 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<sup>66</sup> and Pipek-Mezey<sup>67</sup> 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  $\text{ClH}_3$  was optimized at the RHF level (Table 11) using the Wadt-Hay RECP and double- $\zeta$  basis set for chlorine<sup>68</sup> and the Dunning triple- $\zeta$  basis set for hydrogen.<sup>23</sup> Calculations were performed both with and without a d polarization function on the chlorine atom ( $\zeta = 0.6$ ). The structural parameters and total Mulliken populations<sup>29</sup> 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 Cl contribution for a Cl-H<sub>ax</sub> bond and 86.2% for a Cl-H<sub>eq</sub> bond), as expected. The localized orbitals for the Cl-H<sub>eq</sub> bonds are actually delocalized over both hydrogens with 1/5 of the H<sub>eq</sub> contribution arising from the H<sub>eq</sub> 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

**Scheme 2**

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  $[\text{PdH}_3]^-$ . In contrast to the results for  $\text{ClH}_3$ , both the Foster-Boys and Pipek-Mezey localizations provide cleanly localized Pd-H bond orbitals with residual contributions smaller than those in  $\text{ClH}_3$ . The Pd-H<sub>ax</sub> bond is a mixture of s and d contributions and the Pd-H<sub>eq</sub> bonds have almost a 1:1:1 ratio for s, p, and d character (Table 12). Thus, while a hypervalent description may be appropriate for  $\text{ClH}_3$ , it is less appropriate for  $[\text{PdH}_3]^-$ .

In the MO picture (Scheme 2) for  $\text{ClH}_3$ , 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 Cl atom to the first excited state containing a 3d orbital is 95 696  $\text{cm}^{-1}$ .<sup>13</sup> In this electron-rich system, an extra pair of electrons occupies an antibonding a<sub>1</sub> orbital thus canceling one of the a<sub>1</sub> bonding contributions. The net result is a 3c-4e bond between Cl and the H<sub>eq</sub>'s. The addition of d functions to the chlorine does not change the overall nature of the a<sub>1</sub>\* orbital as they act as polarization functions rather than valence 3d orbitals. In the case of  $[\text{PdH}_3]^-$ , there are no 5d orbitals of the proper symmetry to form a T-shaped structure (the hydrides lie in the node of the b<sub>2</sub> d<sub>yz</sub> AO). Since the 5p orbitals are much more accessible for Pd (excitation into a 5p

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orbital is  $34\,068\text{ cm}^{-1}$ ), the  $b_2 p_y$  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.,  $[\text{RhH}_4]^-$  and  $\text{SF}_4$ ,  $[\text{PtH}_4]^{2-}$  and  $\text{XeF}_4$ ,  $[\text{FeH}_6]^{4-}$  and  $\text{XeF}_6$ ). The  $[\text{RhH}_4]^-$  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<sup>12</sup> also has difficulty with the structures of complexes such as  $[\text{WH}_7]^-$  and  $[\text{W}(\text{CH}_3)_7]^-$  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  $[\text{ReH}_9]^{2-}$ ,<sup>56</sup> 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  $\text{MH}_x$  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.

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**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.

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