

Transition Metal Polyhydride Complexes. 6. CpML_{6-n}H_n (n = 4-6) Complexes

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Ab initio calculations with effective core potentials have been used to study the relative stabilities of classical and nonclassical isomers of 18-electron polyhydride transition metal complexes, [CpML_{6-n}H_n]^{x+} (n = 4-6, x = 0-2, and L = PH₃), where M = Nb, Ta, Mo, W, Tc, Re, Ru, Rh, Os, and Ir. These systematic calculations reveal that a diagonal line in the periodic table through Ru and Ir atoms divides the classical forms (left side of the line) and nonclassical forms (right side of the line). Most of these polyhydrides adopt classical isomers with a pseudo-pentagonal-bipyramidal geometry, where the Cp ring occupies one of the two axial positions. In this pseudo-pentagonal-bipyramidal structure, the Cp-M-H_e (H_e: an equatorial hydrogen) angle is found to be about 110.0°, significantly greater than the 90.0° expected for a regular pentagonal bipyramid. This unexpected large deviation results from a pseudo-second-order Jahn-Teller (SOJT) distortion, which allows a stronger interaction between the equatorial hydrogens' e₁ set of orbitals and metal d_{xz} and d_{yz} orbitals.

Introduction

Since the discovery of nonclassical hydrides, dihydrogen complexes containing η²-H₂ ligands, there has been enormous interest in transition metal polyhydride complexes.¹⁻⁴ In a series of papers,⁵ we have studied the relative stabilities of classical and nonclassical isomers for a variety of polyhydride systems. Systematic quantum mechanical calculations of neutral ML_{7-n}H_n and ML_{8-n}H_n (M = transition metal atom; L = phosphine ligand; n = 2-7) polyhydride model complexes show that a diagonal line in the periodic table through Ru and Ir atoms divides the classical (left side of the line) and nonclassical (right side of the line) forms. For monocationic hydride complexes the corresponding diagonal line shifts slightly toward the early transition metals and crosses between Tc/Ru and Os/Ir atoms.^{5c} Studies of MH_nL_{4-n}Cp (n = 1-4, Cp = η⁵-C₅H₅) polyhydride complexes showed that most of these polyhydrides adopt classical isomers due to the strong "σ" and "π" donating ability of the Cp ligand.^{5e}

Recently, a new class of polyhydrides containing a cyclopentadienyl ligand and a high coordination number, i.e., CpM(PR₃)_{6-n}H_n (n = 5 or 6), has been studied both in the solid state and in solution.^{6,7} For example, CpM-

(PR₃)H₅ (M = Mo or W; Cp = η⁵-C₅H₅ or η⁵-C₅Me₅) complexes have been identified as classical, pentagonal-bipyramidal structures with five equivalent hydrogens by ¹H NMR measurements.⁶ Both X-ray and electron diffraction of the CpReH₆ complex also suggested a classical, pentagonal-bipyramidal structure. The X-ray crystal structure gave significantly large angles (>110°) from the center of the Cp ring through the metal to the equatorial hydrogens, while the electron diffraction result predicted much smaller angles (ca. 95°).⁷ However, none of polyhydrides in this class has been unequivocally characterized by neutron diffraction. Therefore, theoretical studies will play a significant role in determining the hydrogen coordination geometry and understanding the role of the hydrogen-metal bonding in their structure and properties.

In this paper, we will focus our studies on this new and different class of polyhydrides, e.g., [CpML_{6-n}H_n]^{x+} (n = 4-6, x = 0-2), where M ranges from group 5 to group 9 of the second and third row of transition metals. In a previous paper, we examined the effect of electron correlation and found it to be critical in determining the relative energies of these isomers. Comparison of the different types of configuration interaction (CI) calculations^{5b} showed that second-order Møller-Plesset (MP2) perturbation calculations reliably determine the relative stabilities of classical and nonclassical isomers, while configuration interaction calculations with single-and-double-excitation (CISD) underestimate the stability of classical hydrides. Because they have not been studied previously, we will give a detailed comparison between HF and MP2 results of these CpMH₆ complexes.

Theoretical Details

Effective core potentials were employed in all *ab initio* calculations. All geometries were optimized at the restricted

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Table I. CpMH₆ Complexes and Their Relative Energies (kcal/mol) of Classical and Nonclassical Isomers (MP2 and HF Results)^{a,b}

| isomer | CpTcH ₆ | | CpRuH ₆ ⁺ | | CpRhH ₆ ²⁺ | |
|--------|--------------------|--------|---------------------------------|-------|----------------------------------|--------|
| | MP2 | HF | MP2 | HF | MP2 | HF |
| 1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | (0.0) |
| 2 | 14.0 | (13.0) | 12.2 | (8.2) | * | * |
| 3 | (23.9) | -3.8 | 7.8 | -13.2 | -9.6 | -51.0 |
| 4 | (47.5) | -30.7 | 0.3 | -81.6 | -71.0 | -128.8 |

| isomer | CpReH ₆ | | CpOsH ₆ ⁺ | | CpIrH ₆ ²⁺ | |
|--------|--------------------|------|---------------------------------|--------|----------------------------------|--------|
| | MP2 | HF | MP2 | HF | MP2 | HF |
| 1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2 | 15.9 | 15.9 | 15.0 | (15.5) | 12.1 | (10.7) |
| 3 | (23.4) | 9.5 | (18.2) | 2.4 | 2.1 | -15.6 |
| 4 | (58.8) | 20.3 | (38.5) | -15.2 | -13.7 | -59.3 |

^a * denotes that the isomer is not a minimum. ^b Number in parentheses in the MP2 columns indicates that the isomer is not a minimum at the MP2 level, but is a minimum at the HF level. The MP2 energy is calculated on the basis of the corresponding HF geometry. Vice versa for those numbers in the HF column.

Hartree-Fock (HF)^a and second-order Møller-Plesset (MP2)^{b,c} levels. In this study, all aryl and alkyl groups were replaced by hydrogen atoms; i.e. PR₃ was replaced by PH₃. The H-P-H angle was fixed at 103.4°, and the P-H bond distance was fixed at 1.44 Å. The C₅H₅ unit is also fixed as planar with C-C and C-H bond lengths of 1.41 and 1.08 Å, respectively.

In the effective core potentials⁹ (ECPs) for the transition metals, the outermost core orbitals, which correspond to a *ns*²*np*⁶ configuration, were treated explicitly along with the *nd*, (*n* + 1)*s* and (*n* + 1)*p* valence orbitals. The ECP basis sets of the second and third transition series atoms were described with double- ζ representations for the (*n* + 1)*s*/*np*/*nd* electrons, (541/41/31) and (541/41/21), respectively. For ligand atoms, the ECPs and double- ζ basis sets of Stevens, Basch, and Krauss^{9b} were used. [He] and [Ne] configurations were taken as cores for the first and second row main group atoms, respectively. The Dunning-Huzinaga(31) double- ζ basis set was used for the hydrogen atom.^{9c,d}

All *ab initio* calculations were performed with the GAMESS and Gaussian 92 software,¹⁰ at the Cornell National Supercomputer Facility (CNSF) on an IBM ES9000, at the Supercomputer Center of Cray Research, Inc., Minnesota on a Cray Y-mp81/8128-2, and on a Silicon Graphic Iris Indigo workstation. The Laplacian of valence electron density was plotted with the use of the MOPLLOT program.¹¹

Results and Discussion

CpMH₆ Complexes. The model complexes of this type which were studied are listed in Table I. All these complexes conform to a closed-shell configuration of 18

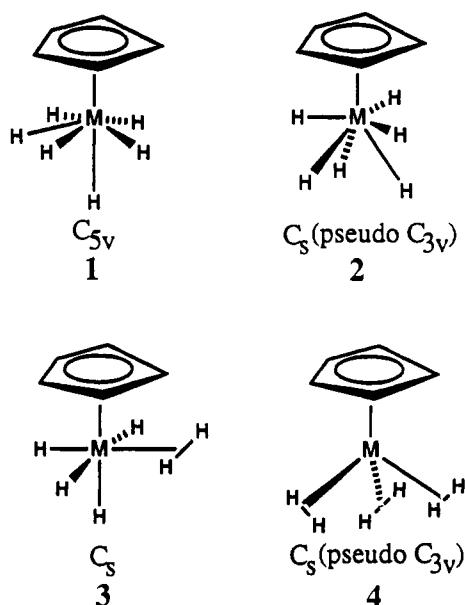
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Chart I
CpMH₆



valence electrons. Geometries for the different isomers of these model complexes are illustrated in Chart I. All isomers in Table I (see Chart I) were optimized at the restricted HF and MP2 levels. The relative energies for different isomers are also given in Table I.

As can be seen from Table I, at the HF level most nonclassical isomers are more stable than classical isomers except for the Re complex. For the Re complex, all four isomers (1-4) are minima at the HF level while only the two classical isomers (1 and 2) are minima at the MP2 level. These results illustrate the overemphasis of the H-H interaction relative to the M-H interaction at the HF level, particularly for late transition metal polyhydride complexes (as discussed in a previous paper^{5b}).

Since we have previously shown that MP2 calculations produce reliable results on the relative stability of classical and nonclassical isomers, we conclude, on the basis of the MP2 results in Table I, that a diagonal line in the periodic table through Ru and Ir atoms divides the classical forms (left side of the line) and nonclassical forms (right side of the line) for this class of polyhydride complexes. For the CpRuH₆⁺ complex, the classical isomer (1) and nonclassical one (4) are of almost equal energy. For both CpRhH₆²⁺ and CpIrH₆²⁺ complexes, the nonclassical isomer (4) is more stable than the classical one (1). As the charge increases on a complex, its metal d orbitals contract and stabilize. Therefore, nonclassical isomers will eventually be favored in any such series of complexes.

When the two classical isomers (1 and 2) are compared, the pentagonal-bipyramidal structure (1) is always more stable than the capped trigonal antiprism (it can also be considered as a pseudo tricapped trigonal prism if we assume that the Cp coordinates as a tridentate ligand). Apparently, few, if any, CpMH₆ complexes adopt a structure of the analog, [ReH₉]²⁻, which is a tricapped trigonal prism. Since the transition metal atom in the classical hydride CpMH₆ has a formal d⁰ configuration, we expect that the ligand-ligand repulsive interaction will play a role in the gross stability of different classical isomers (geometries). Interestingly, the potential surface of ligand-

Table II. Selected Structural Parameters of the Classical (1) Isomer for All CpMH₆ Complexes and Nonclassical Isomers (4) for Ru, Rh, and Ir Complexes (MP2 and HF Results)^a

| structural params | CpTcH ₆ (1) | | CpRuH ₆ ⁺ (1) | | CpRhH ₆ ²⁺ (1) | |
|----------------------|------------------------|-------|-------------------------------------|-------|--------------------------------------|--------|
| | MP2 | HF | MP2 | HF | MP2 | HF |
| M-Cp | 2.08 | 2.05 | 2.06 | 1.98 | 2.07 | not |
| M-H _e | 1.64 | 1.61 | 1.61 | 1.58 | 1.61 | a |
| M-H _a | 1.62 | 1.59 | 1.58 | 1.57 | 1.57 | minima |
| Cp-M-H _e | 112.6 | 113.7 | 111.9 | 114.0 | 111.0 | |

| structural params | CpReH ₆ (1) | | CpOsH ₆ ⁺ (1) | | CpIrH ₆ ²⁺ (1) | |
|----------------------|------------------------|-------|-------------------------------------|-------|--------------------------------------|-------|
| | MP2 | HF | MP2 | HF | MP2 | HF |
| M-Cp | 2.09 | 2.07 | 2.07 | 2.02 | 2.09 | 2.02 |
| M-H _e | 1.64 | 1.62 | 1.62 | 1.59 | 1.61 | 1.59 |
| M-H _a | 1.62 | 1.60 | 1.59 | 1.57 | 1.56 | 1.55 |
| Cp-M-H _e | 111.9 | 112.0 | 111.6 | 112.5 | 110.0 | 111.2 |

| structural params | CpRuH ₆ ⁺ (4) | | CpRhH ₆ ²⁺ (4) | | CpIrH ₆ ²⁺ (4) | |
|----------------------------------|-------------------------------------|------|--------------------------------------|------|--------------------------------------|------|
| | MP2 | HF | MP2 | HF | MP2 | HF |
| M-Cp | 1.87 | 1.93 | 1.92 | 1.88 | 1.89 | 1.88 |
| M-η ² -H ₂ | 1.86 | 1.95 | 2.12 | 2.17 | 1.96 | 1.96 |
| H-H | 0.79 | 0.75 | 0.76 | 0.75 | 0.78 | 0.76 |

^a H_e or H_a: equatorial or axial hydrogen in a pseudo-pentagonal-bipyramidal geometry. Bond distances in angstroms and bond angles in degrees.

ligand repulsion calculated by Kepert¹² showed that for MA₅B type molecules with a shorter M-B bond, a pentagonal bipyramid with the short bond in one of the axial sites is the most stable structure. If, due to its large size, Cp effectively acts like a ligand with a short strong metal-ligand bond, i.e. like the B ligand above, a pseudo-pentagonal-bipyramidal structure might be expected for the CpMH₆ complexes.

Table II lists selected, calculated structural parameters of the classical isomer (1) for all CpMH₆ complexes. Selected structural parameters of the nonclassical isomer (4) for Ru, Rh, and Ir complexes are also listed in Table II, since they either are the most stable isomer or are comparable in stability. From Table II, we can see that the calculated structural parameters at both HF and MP2 levels agree quite well with each other. From the available average Re-H and Os-H bond distances (1.67 and 1.66 Å, respectively) derived from single-crystal neutron diffraction data,¹³ we conclude that the MP2 calculations give slightly better results.

Examining the detailed structural parameters in Table II, one can see that for the classical isomer (1) of all CpMH₆ complexes, the angle from the center of the Cp ring through the metal to the equatorial hydrogen in the pseudo-pentagonal bipyramid, Cp-M-H_e, is greater than 110.0°, an angle significantly greater than the expected 90.0°. This significant deviation from 90° could be due to the repulsive Cp-H interaction, to a M-H electronic factor, or to the combination of these two. To determine if the ligand-ligand repulsive interaction dominates, we optimized at the HF level the model complex ClReH₆, in which the Cp is replaced by an axial Cl. Geometry optimizations were done with the C_{5v} point group. Results showed that the calculated structure for ClReH₆¹⁴ has a Cl-M-H_e angle of 115.0° and is vastly lower in energy (115.7 kcal/mol) than the one partially optimized at fixed Cl-Re-H_e = 90.0°. The Cl-Re-H_e angle in ClReH₆ is even greater than the Cp-Re-H_e angle in CpReH₆, although the size of the Cp

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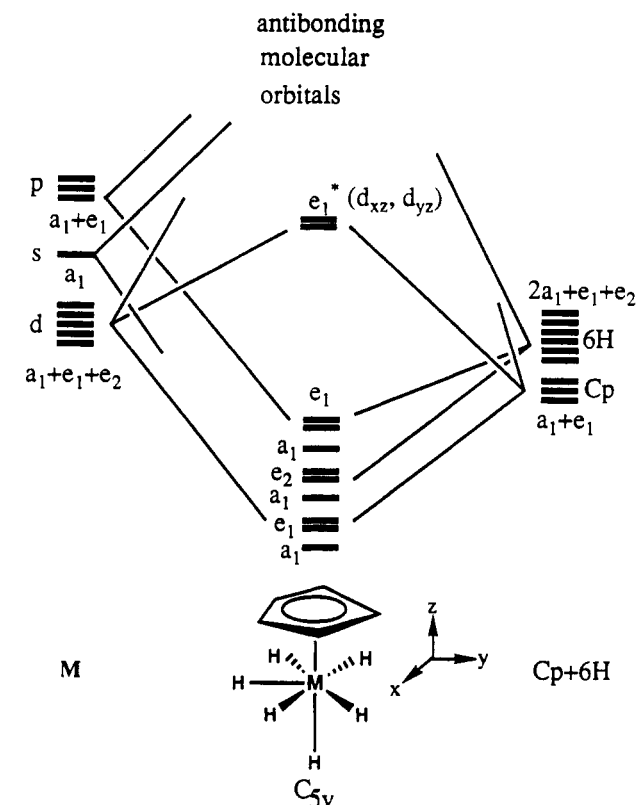


Figure 1. Molecular-orbital interaction scheme for a C_{5v} CpMH₆ transition metal complex.

ligand is sterically larger than the Cl ligand. Consequently, the ligand-ligand repulsion can be excluded as an important factor in this geometry. There must be an electronic "driving force" behind the bending of the five equatorial hydrogens away from the Cp ligand.

Before explaining this result, we present in Figure 1 a schematic molecular-orbital diagram for the interaction between the metal atom and the ligands' σ-donor orbitals for a regular C_{5v} pentagonal-bipyramidal CpMH₆ complex. The energy ordering in Figure 1 is not necessarily correct nor is it important for our discussion. The e₂ (d_{x²-y², d_{xy}) set of the transition metal atom can only interact with the e₂ set derived from the five equatorial hydrogens. Both Cp and the five equatorial hydrogens have a set of e₁ σ-donor orbital combinations which can interact with both (p_x, p_y) and (d_{xz}, d_{yz}) orbitals of the central metal atom. In a regular pentagonal bipyramid (PB) where Cp-M-H_e = 90.0°, the metal (d_{xz}, d_{yz}) orbitals, which are nonbonding orbitals in an ML₇ pentagonal-bipyramidal complex, maximize their overlap with the Cp's e₁ combinations and minimize it (zero overlap) with the equatorial hydrogens' orbitals. Thus, the equatorial hydrogens' e₁ orbitals can only have net overlap with the metal (p_x, p_y) orbitals. Comparing the energy and shape of the transition metal valence d and p orbitals, we expect that a hydrogen's orbital in a metal hydride complex has more effective interaction with metal d orbitals than with metal p orbitals. Therefore, one will expect that for a regular PB CpMH₆ complex the}

(14) The frequency calculation based on the optimized ClReH₆ (C_{5v}) showed that the calculated structure is a local minimum on the potential surface. The frequencies (in cm⁻¹) involving the stretching of bonds are ν(a₁) = 342.1 (Re-Cl), ν(a₁) = 2160.4 (Re-H_a mixed with Re-H_e), ν(e₂) = 2286.2 (Re-H), ν(e₁) = 2344.5 (Re-H), ν(a₁) = 2402.3 (Re-H_e mixed with Re-H_a). The bending frequencies of the H-Re-H bond angles are ν(e₁) = 778.6, ν(e₂) = 813.7, ν(e₂) = 1221.0, ν(a₁) = 1265.7, ν(e₁) = 1397.8. The energy changes of the Re-Cl bending motion are very small.

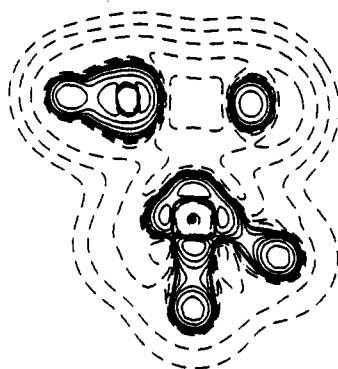


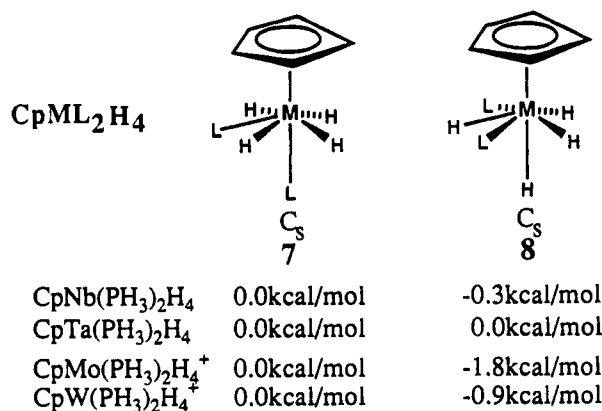
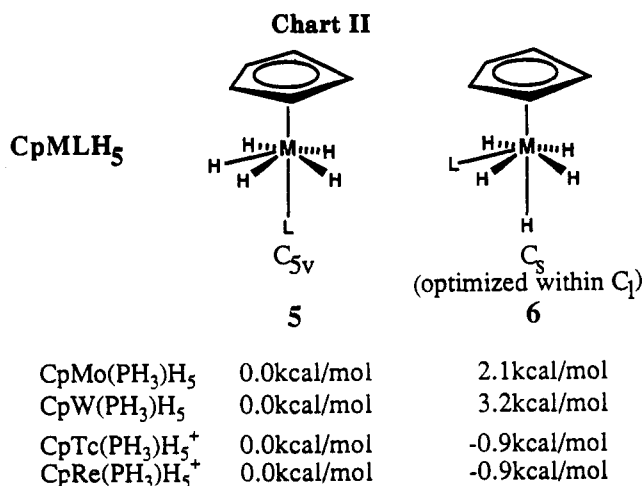
Figure 2. The plots of the Laplacian of the valence electron density, $-\nabla^2\rho$, in a plane defined by the center of the Cp ring, Re, and two (axial and equatorial) hydride ligands in the CpReH_6 complex.

HOMOs are the the metal(*p*)-hydrogen e_1 bonding orbitals while the LUMOs are the metal(*d*)-Cp e_1^* antibonding orbitals (see Figure 1).

As a result, a regular PB structure provides a geometry with minimal metal-hydrogen e_1 bonding interaction because only metal *p* orbitals are available. Thus, a distortion from the regular PB structure is likely to occur through a pseudo-second-order Jahn-Teller effect,¹⁵ which allows a maximum orbital mixing between occupied and unoccupied molecular orbitals, usually the HOMO and LUMO, and increases their energy gap. Bending the equatorial hydrogens away from the Cp ligand allows a stronger interaction between the equatorial hydrogens' e_1 set of orbitals and metal d_{xz} and d_{yz} orbitals and, therefore, stabilizes the HOMO (e_1) bonding orbitals. The hydrogens' nearly exclusive use of the metal d_{xz} and d_{yz} orbitals in ClReH_6 results in a larger X-Re-H_o angle for X = Cl than for X = Cp, where in the latter the Cp ring competes more effectively for these *d* orbitals. This pseudo-second-order Jahn-Teller distortion is particularly noticeable for the hydrides because of their small size and the short covalent metal-hydrogen bond.¹⁶ Calculation on a model CpReF_6 complex (C_{5v}) gave an angle of only about 98°.

To support the argument above, we optimized CpReH_6 (1) at the HF level with fixed Cp-M-H_o angles at 90.0°. The resulting Re-H_o and Re-Cp distances are 1.68 and 2.10 Å, respectively, which are both significantly longer than 1.62 and 2.07 Å obtained without angle restriction. The energy of this structure is also significantly higher (94.0 kcal/mol, a value which is comparable to the result of calculation on the model ClReH_6 complex discussed above). The longer Re-H_o and Re-Cp bonds result from the poor metal-hydrogen and metal-Cp bonding interactions at this regular PB structure, as discussed above.

The preference of metal(*d*)-hydrogen bonding interaction also can be seen from a plot of the Laplacian of the total valence electron density, $-\nabla^2\rho$, of CpReH_6 (1) shown in Figure 2 in a plane defined by the center of the Cp ring, Re, and two hydride ligands. In the contour plots, solid lines denote $-\nabla^2\rho > 0$,¹⁷ where the electron density is locally concentrated, and dashed lines denote $-\nabla^2\rho < 0$, where the electron density is locally depleted. As we can see from Figure 2, the hydride ligands are bonded to the central metal atom through *d*-type concentrations. Laplacian



maps of this form have been interpreted as indicating significant covalent bonding.¹⁷

In summary, for the d^0 CpMH_6 complexes (1), our calculations predict that a pseudo-pentagonal-bipyramidal geometry will be adopted. The structural details for an adopted geometry are electronically controlled. For isomer 1, a mixing between HOMOs and LUMOs, which increases the metal-hydrogen bonding interaction, results in a large Cp-M-H_o angle.

CpMLH₅ Complexes. The periodic trend in the relative stability of classical and nonclassical isomers in this and the other systems investigated leads us to believe that most CpMLH_5 complexes with an early or a middle transition metal atom should adopt a classical structure. Since we are interested in determining the structure of the most stable classical isomers, only two classical isomers (5 and 6) are considered here for CpMLH_5 complexes. All geometry optimizations were performed at the MP2 level. For isomer 6, we optimized the structure without any symmetry restriction so that a nonclassical isomer may be found if there is a corresponding minimum. Chart II shows the results of our calculations on $\text{CpMo}(\text{PH}_3)_5$, $\text{CpW}(\text{PH}_3)_5$, $[\text{CpTc}(\text{PH}_3)_5]^+$, and $[\text{CpRe}(\text{PH}_3)_5]^+$. Selected structural parameters are listed in Table III.

Chart II shows that the energy differences between 5 and 6 are not very large for any of the complexes studied here. For both $\text{CpMo}(\text{PH}_3)_5$ and $\text{CpW}(\text{PH}_3)_5$, isomer 5 has a lower energy than isomer 6. However, isomer 6 is slightly lower in energy than isomer 5 for $[\text{CpTc}(\text{PH}_3)_5]^+$

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Table III. Selected Structural Parameters of CpM(PH₃)H₅ and CpM(PH₃)₂H₄ Complexes (MP2 Results)^a

| structural params | CpMo(PH ₃)H ₅ | | CpW(PH ₃)H ₅ | | CpTc(PH ₃)H ₅ ⁺ | | CpRe(PH ₃)H ₅ ⁺ | |
|--------------------------|--------------------------------------|-------|-------------------------------------|-------|---|-------|---|-------|
| | 5 | 6 | 5 | 6 | 5 | 6 | 5 | 6 |
| M-Cp | 2.06 | 2.10 | 2.06 | 2.10 | 2.03 | 2.07 | 2.04 | 2.08 |
| M-H _e (av) | 1.71 | 1.70 | 1.72 | 1.71 | 1.65 | 1.64 | 1.65 | 1.64 |
| M-H _a | | 1.68 | | 1.69 | | 1.62 | | 1.61 |
| M-P | 2.54 | 2.56 | 2.55 | 2.57 | 2.52 | 2.53 | 2.53 | 2.55 |
| Cp-M-H _e (av) | 107.2 | 110.5 | 106.6 | 108.7 | 107.1 | 110.8 | 107.2 | 110.3 |
| Cp-M-P _e | | 110.1 | | 109.6 | | 110.9 | | 110.6 |

| structural params | CpNb(PH ₃) ₂ H ₄ | | CpTa(PH ₃) ₂ H ₄ | | CpMo(PH ₃) ₂ H ₄ ⁺ | | CpW(PH ₃) ₂ H ₄ ⁺ | |
|----------------------------------|--|-------|--|-------|---|-------|--|-------|
| | 7 | 8 | 7 | 8 | 7 | 8 | 7 | 8 |
| M-Cp | 2.14 | 2.18 | 2.13 | 2.18 | 2.06 | 2.10 | 2.06 | 2.10 |
| M-H _e (av) | 1.79 | 1.79 | 1.79 | 1.78 | 1.70 | 1.70 | 1.71 | 1.71 |
| M-H _a | | 1.77 | | 1.77 | | 1.68 | | 1.69 |
| M-P(av) | 2.68 | 2.63 | 2.67 | 2.64 | 2.61 | 2.56 | 2.61 | 2.57 |
| Cp-M-H _e (av) | 104.1 | 107.5 | 104.4 | 105.7 | 103.8 | 108.9 | 103.8 | 108.0 |
| Cp-M-P _e | 109.3 | 108.6 | 108.3 | 107.6 | 110.0 | 110.6 | 110.4 | 109.9 |
| P _a -M-P _e | 84.1 | | 83.5 | | 84.7 | | 83.7 | |

^a H_e or H_a: equatorial or axial hydrogen in a pseudo-pentagonal-bipyramidal geometry. Same definition for P_e or P_a. Bond distances in angstroms and bond angles in degrees.

H₅⁺ and [CpRe(PH₃)H₅]⁺ complexes. From the viewpoint of ligand-ligand repulsion, one would expect greater ligand-ligand repulsion in 6 than in 5 since isomer 5 has a Cp-M-P angle of 180.0°, while isomer 6 has an angle of near 110.0°. Electronically, when the phosphine ligand occupies the axial position, it pushes all equatorial hydrogens away from it because of its large donor (to metal) electron pair. This effect decreases the Cp-M-H_e angle, and therefore weakens the M-H_e bonds. The steric factor favors the isomer 5, while the electronic factor disfavors it. The results here indicate the two factors are of nearly equal importance in the determination of the relative stabilities, at least for small phosphines.

For isomer 5 of those complexes studied in Table III, the Cp-M-H_e angles are smaller than the Cp-M-H_a angles found in CpMH₆ (1) complexes (see Table II). This is, again, due to the large donor (to metal) electron pair of the phosphine ligand. As a result of smaller Cp-M-H_e angles in 5, for a specific metal (M), the M-H_e bond length becomes longer than that in 1.

CpML₂H₄ Complexes. For formulas of [CpML₂H₄]^{x+} (x = 0 or 1), the transition metal has to be group 4 or 5. From the periodical trend found above, we expect all complexes studied here must have classical structures as the most stable isomer. Therefore, for complexes of the type CpML₂H₄, only classical isomers 7 and 8 (see Chart II) were studied. Selected structural parameters are listed in Table III.

From Chart II, we can see that isomers 7 and 8 are almost of equal energy for CpNb(PH₃)₂H₄, CpTa(PH₃)₂H₄, [CpMo(PH₃)₂H₄]⁺, and [CpW(PH₃)₂H₄]⁺ complexes. Again, both steric and electronic factors may account for the relative stabilities. Isomer 7 has two Cp-phosphine repulsions while isomer 8 has one Cp-phosphine and one phosphine-phosphine repulsions. An axial occupation of one phosphine ligand disfavors isomer 7 electronically, as discussed above. Therefore, one can see the reason of almost equal energy between isomers 7 and 8.

In 7, the axial occupation of one phosphine leads to smaller Cp-M-H_e angles for all CpM(PH₃)₂H₄ complexes (see Table III). The structural parameters for the Mo and W complexes are very similar to those for CpMLH₅

complexes. When a phosphine ligand or ligands occupy one of the equatorial positions in the distorted PB structure, the M-Cp bond length increases. Isomer 7 has longer M-P bond lengths than 8 has. This is possibly due to greater phosphine-phosphine repulsive interactions.

Conclusion

The systematic studies on the relative stabilities of classical and nonclassical polyhydride cyclopentadienyl transition metal complexes with a formula of [Cp-ML_{6-n}H_n]^{x+} (n = 4-6, x = 0-2) reveal that a diagonal line in the periodic table through Ru and Ir atoms divides the complexes into classical ones (left side of the line) and nonclassical ones (right side of the line). Our calculations also indicate that these classical isomers adopt a pseudo-pentagonal-bipyramidal geometry with the Cp ring in one of the two axial positions. In this geometry, the Cp-M-H_e (H_e = an equatorial hydrogen) angle is found to be significantly deviated from the expected 90.0°. This distortion allows a stronger interaction between the equatorial hydrogens' e₁ set of orbitals and metal d_{zz} and d_{yz} orbitals. Pseudo-second-order Jahn-Teller (SOJT) effects, such as this one, are particularly evident in those systems with strong metal-ligand covalent σ bonds and have been used to predict distortions in the structures of d⁰MH₆ and MH₅ complexes.¹⁸ Here, their geometries are significantly different from the octahedron and trigonal-bipyramid, respectively, as expected by the VSEPR model.¹⁹

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