4262 *Inorg. Chem.* **1992,** *31,* 4262–4265

Transition Metal Polyhydride Complexes. 4. Highly Stable Nonclassical Isomers with Octahedral Structures

Zhenyang Lin and Michael B. Hall*

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received February 19, 1992

Ab initio calculations at the MP2 level with effective core potentials have been used to study the relative stabilities of classical and nonclassical isomers of 14 second- and third-row transition-metal polyhydride complexes with the formula $ML_{8-n}H_n$, where $n = 4–7$ and $L = PH_3$. Results show that the model complexes are divided into two groups. One group has as its most stable structure a classical one with the maximum coordination number, while the other has as its most stable structure a nonclassical one with an octahedral geometry. Through the detailed analyses of valence-electron densities, a model is proposed to explain the highly stable six-coordinate octahedral structure for those transition-metal polyhydride complexes which prefer a nonclassical isomer. From the model, we can make a general conclusion about these $ML_{8-n}H_n$ complexes. When twice the ionization enthalpy of an electron in the M–H bond is greater than sum of the ionization enthalpies of an electron in the H–H bond and one in the metal d orbital, a classical isomer is definitely preferred. Otherwise, a nonclassical isomer with an octahedral structure is adopted.

Introduction

The subject of transition-metal polyhydride complexes has been of much theoretical and experimental interest since the characterization of the first isolable η^2-H_2 nonclassical hydride complex.[1-28] Theoretically, a number of quantum-chemical studies have been done on their electronic structures and the relative energies of classical (having terminal hydride ligands) and nonclassical isomers (containing η^2-H_2 ligand(s)).[23-28] In a series of papers,[28] we examined the effect of electron correlation and suggested that second-order Möller–Plesset (MP2)[29] perturbation calculations provide reliable results for determining the relative stability of classical and nonclassical isomers although oscillations were found in the application of the perturbation theory to some first–row transition–metal fluoride complexes.[30] We also examined the factors that contribute to stabilizing one isomer over the other and provided some qualitative rules governing their stabilities. In general, nonclassical isomers are preferred for complexes with strong π-acceptor ligands and contracted central-metal d orbitals.

In systematic quantum-mechanical calculations on $ML_{7-n}H_n$ and $ML_{8-n}H_n$ ($n = 2–7$) polyhydride model complexes,[28] where M ranges from group 6 to group 9 second- and third-row transition-metal atoms and L is the PH_3 ligand, we found 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 neutral complexes without strong π-accepting

---

(1) (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. J.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) Kubas, G. J.; Ryan, R. R.; Wroblewski, D. *J. Am. Chem. Soc.* **1986**, *108*, 1339. (c) Kubas, G. J.; Unkefer, C. J.; Swanson, B. J.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (d) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

(2) (a) Sweany, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374. (b) Upmacis, R. K.; Poliakoff, M.; Turner, J. *J. Am. Chem. Soc.* **1986**, *108*, 3645.

(3) (a) Bautista, M. T.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780. (b) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780. (c) Earl, K. A.; Polito, M. A.; Morris, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 3780.

(4) (a) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (b) Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823. (c) Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027.

(5) Albertin, G.; Antoniatti, S.; Bordignon, E. *J. Am. Chem. Soc.* **1989**, *111*, 2072.

(6) (a) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865.

(7) Hart, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 7557.

(8) Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L. *Inorg. Chem.* **1987**, *26*, 2930.

(9) Lyons, D.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 695.

(10) Gregson, D.; Mason, S. A.; Howard, J. A. K.; Spencer, J. L.; Turner, D. G. *Inorg. Chem.* **1984**, *23*, 4103.

(11) (a) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 2181. (b) Cotton, F. A.; Luck, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5757. (c) Cotton, F. A.; Luck, R. L. *J. Chem. Soc., Chem. Commun.* **1988**, 1277.

(12) (a) Howard, J. A. K.; Mason, S. A.; Johnson, O.; Diamond, I. C.; Crennell, S.; Keller, P. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1502. (b) Brammer, L.; Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L.; Stinger, A. M. *J. Chem. Soc., Chem. Commun.* **1991**, 241.

(13) (a) Luo, X. L.; Baudry, D.; Boydell, P.; Charpin, P.; Nierlich, M.; Ephritikhine, M.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 1511. (b) Luo, X. L.; Schutle, G. K.; Demoll, P.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 4268.

(14) (a) Luo, X. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912. (b) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95.

(15) Garlaschelli, L.; Khan, S. I.; Bau, R.; Longoni, G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1985**, *107*, 7212.

(16) (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. (b) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.

(17) Mediati, M.; Tachibana, G. N.; Jensen, C. M. *Inorg. Chem.* **1990**, *29*, 5.

(18) (a) Lundquist, E. G.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165. (b) Lundquist, E. G.; Folting, K.; Streib, W. E.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 855.

(19) Jackson, S. A.; Hodges, P. M.; Poliakoff, M.; Turner, J. J.; Grevels, F. W. *J. Am. Chem. Soc.* **1990**, *112*, 1221.

(20) (a) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909. (b) Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, G. N.; Neshyba, S. P.; Duchamp, J. C.; Szczyrba, J. *J. Am. Chem. Soc.* **1990**, *112*, 920. (c) Albeniz, A. C.; Heinekey, D. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 3632. (d) Heinekey, D. M.; Harper, T. G. *Organometallics* **1991**, *10*, 2891.

(21) Desrosiers, P. J.; Cai, L.; Lin, Z. R.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173.

(22) (a) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548. (b) Bianchini, C.; Mealli, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 8725.

(23) (a) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705. (b) Eckert, J.; Kubas, G. J.; Hall, J. H.; Hay, P. J.; Boyle, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 2324.

(24) (a) Burdett, J. K.; Mohammad, R. P. *Organometallics* **1987**, *6*, 1684. (b) Burdett, J. K.; Phillips, J. R.; Mohammad, R. P. *Inorg. Chem.* **1987**, *26*, 3054.

(25) Maseras, F.; Duran, M.; Lledos, A.; Bertran, J. *Inorg. Chem.* **1989**, *28*, 2984.

(26) Pacchioni, G. *J. Am. Chem. Soc.* **1990**, *112*, 80.

(27) Maseras, F.; Duran, M.; Lledos, A.; Bertran, J. *J. Am. Chem. Soc.* **1991**, *113*, 2879.

(28) (a) Lin, Z.; Hall, M. B. *Inorg. Chem.* **1991**, *30*, 2569. (b) Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 2928. (c) Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 6574.

(29) (a) Möller, C.; Plesset, M. S. *Phys. Rev.* **1936**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *S10*, 1.

(30) (a) Marsden, C. J.; Wolynec, P. P. *Inorg. Chem.* **1991**, *30*, 1681. (b) Hope, E. G.; Levason, W.; Ogden, J. S. *Inorg. Chem.* **1991**, *30*, 4873.

0020-1669/92/1331-4262$03.00/0

ligands. For monocationic hydride complexes, the corresponding diagonal line shifts slightly toward early transition metals and crosses between Tc/Ru and Os/Ir atoms. We also found that a six-coordinate structure is the most stable for those complexes which prefer nonclassical forms. Experimentally, nearly all the known η^2-H_2 complexes have a six-coordinate d^6 configuration.[14] While many of the factors stabilizing the isomer over the other have been known,[28c] the reasons behind the highly stable six-coordinate d^6 configuration have not been studied until now. Here, we will investigate this question through an electron density analysis of the ab initio calculations.

Theoretical Details

Ab initio effective core potentials[30] were employed in all calculations. All geometries were optimized at the restricted Hartree–Fock (HF) level. Energies were recalculated with electron correlation included at the MP2 level for all model complexes. In this study, all aryl and alkyl groups were replaced by H atoms; i.e., PR_3 was replaced by PH_3. The M–P–H (M = transition metal atom) angle was fixed to be 115° and P–H bond distance to be 1.44 Å.

In the effective core potentials (ECPs) for the transition metals, the outermost core orbitals, which correspond to the ns^2np^6 configuration, were treated explicitly on an equal footing with the nd, $(n + 1)$s, and $(n + 1)$p valence orbitals.[31a] The basis sets of the second and third transition series atoms were described with (541/41/211) and (541/41/111), respectively, which correspond to a double-ζ representation of the $(n + 1)$s/np electrons and a triple-ζ representation of the nd electrons. For ligand atoms, the ECPs and double-ζ basis sets of Stevens, Basch, and Krauss were used.[31b] [He] and [Ne] configurations were taken as cores for the first- and second-row main-group atoms. The Dunning–Huzinaga double-ζ basis set (31) was used for the H atom.[32]

All HF calculations were performed with the GAMESS package,[33] while all MP calculations were made by the use of the Gaussian 88 program.[34] All GAMESS calculations were made at the Cornell National Supercomputer Facility (CNSF) on an IBM 3090-600VF, at the Supercomputer Center of Texas A&M University on a Cray Y-MP2/116, and at the Chemistry Department on a FPS Model 522. The Gaussian 88 program was run at the CNSF. The Laplacian map of valence electron density was plotted with the use of the program MOPLOT.[35]

Results and Discussion

Relative Energies. Geometry optimizations at the HF level have been done on the polyhydride model complexes listed in Figure 1. The energies were recalculated with the MP2 method. All these model complexes conform to the 18-valence-electron rule. For each model complex, three isomers, which correspond to dodecahedral (eight-coordinate), pentagonal-bipyramidal (seven-coordinate), and octahedral (six-coordinate) geometries, are obtained through full or partial geometry optimization. The geometry optimizations are described in detail in a previous paper.[28c] The geometries of these isomers are illustrated in Chart I. The relative energies of different isomers for each model complex are plotted against coordinate numbers in Figure 1. In the figure, zero relative energy is defined as the energy of the eight-coordinate dodecahedral isomer. ΔE_1 and ΔE_2 in the figure are defined as

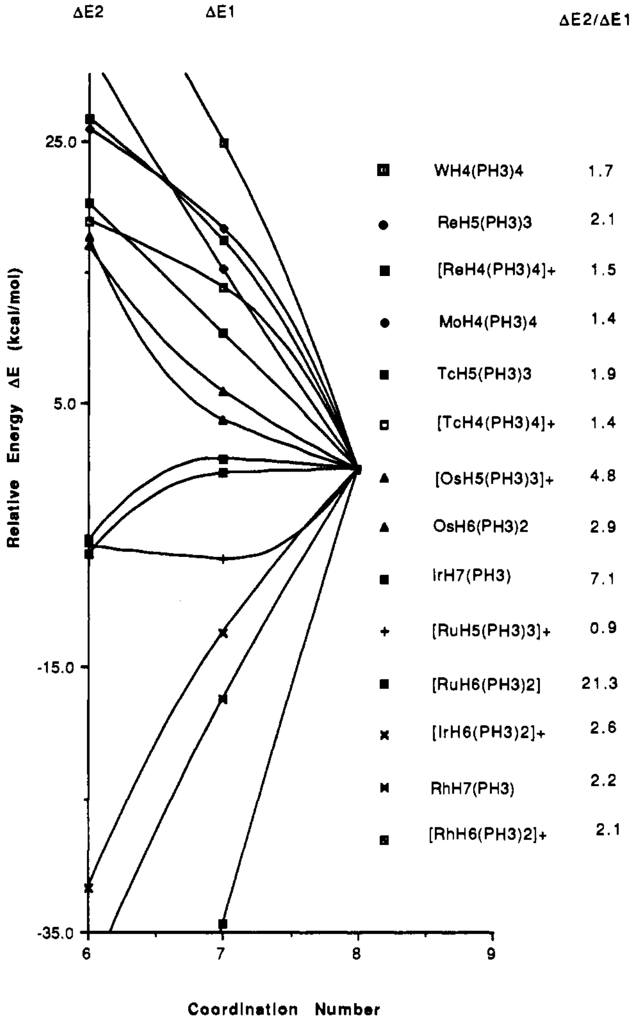


Figure 1. Plots of the relative energies of different isomers for polyhydride complexes against coordinate number. ΔE_1 and ΔE_2 are defined in eqs 1 and 2, respectively. The complexes listed on the right follow the order of decreasing ΔE_2. Each complex in the list has three isomeric structures which can be found in Chart I.

$$\Delta E_1 = E\{M(H)_nL_{8-n}\} - E\{M(H)_{n-2}(\eta^2\text{-}H_2)L_{8-n}\} \quad (1)$$

$$\Delta E_2 = E\{M(H)_nL_{8-n}\} - E\{M(H)_{n-4}(\eta^2\text{-}H_2)_2L_{8-n}\} \quad (2)$$

In the figure the ratio of ΔE_1 and ΔE_2, i.e., $\Delta E_2/\Delta E_1$, for each model complex is also presented.

It can be seen from Figure 1 that the model complexes are divided into two groups. One group has the classical structure with a maximum coordination number of 8 as the most stable, while the other has a six-coordinate nonclassical structure as the most stable geometry. Seven-coordinate nonclassical complexes are intermediate in energy between six- and eight-coordinate complexes. These observations imply that for a polyhydride complex a geometry with maximum coordinate number will be favored when a classical isomer is adopted and a six-coordinate octahedral geometry will be favored when a nonclassical isomer is adopted. Thus, the seven-coordinate nonclassical complexes are unusually difficult to stabilize, a result consistent with the experimental observations.[14]

Electron Density Analysis. Before providing a more detailed discussion, we first examine the gross electronic structural changes from one isomer to the other on a convenient model complex, $[ReH_4(PH_3)_4]^+$, with isomers **1**–**3**. Figure 2 shows Laplacian plots of the valence-electron density, $-\nabla^2\rho$,[36] in various metal–ligand planes from ab initio HF results for $[Re(H)_4(PH_3)_4]^+$ (**1**), $[Re(H)_2(\eta^2\text{-}H_2)(PH_3)_4]^+$ (**2**), and $[Re(\eta^2\text{-}H_2)_2(PH_3)_4]^+$ (**3**)

---

(31) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (b) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026.

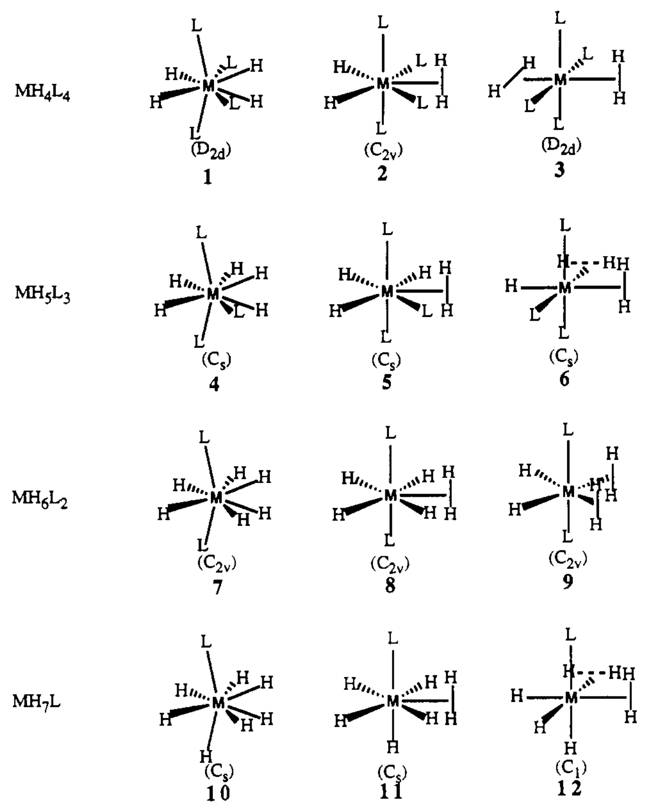
(32) (a) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. (b) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823.

(33) Guest, M. F. *GAMESS*; Daresbury Laboratory: Warrington WA4 4AD, U.K.

(34) Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. *Gaussian 88*; Gaussian, Inc.: Pittsburgh, PA 1988.

(35) Interactive MOPLOT: a package for the interactive display and analysis of molecular wave functions, incorporating the programs MOPLOT (D. Lichtenburger), PLOTDEN (R. F. W. Bader, D. J. Kenworthy, P. M. Beddal, G. R. Runtz, and S. G. Anderson), SCHUSS (R. F. W. Bader, G. R. Runtz, S. G. Anderson, and F. W. Biegler-Koenig), and EXTREM (R. F. W. Bader and F. W. Biegler-Koenig), by P. Sherwood and P. J. MacDougall, 1989.

Chart I



isomers. In the contour plots, solid lines denote $-\nabla^2\rho > 0$, where the electron charge is locally concentrated, and dashed lines denote $-\nabla^2\rho < 0$, where the electron charge is locally depleted.

From Figure 2 we can see that for the six-coordinate octahedral isomer all six ligands are bonded to the metal through the depletions around the central atom, as is usual for dative bonds, and the three d-type concentrations on the x, y, and z planes correspond to the well-known "t_{2g}" nonbonding orbital set in an octahedral complex. For the seven-coordinate pentagonal-bipyramidal isomer two d-type concentrations on the x and y planes, which correspond to the d_{xz} and d_{yz} nonbonding orbitals in a pentagonal-bipyramidal complex, are retained, and two of the four concentrations on the z plane merge with the concentrations of the two hydride ligands, as is usual for covalent bonds. For the eight-coordinate dodecahedral isomer, only one d-type concentration, which corresponds to the nonbonding d orbital in a dodecahedral complex, is retained, and the other two d-type concentrations form covalent bonds with hydride ligands. All these observations are consistent with simple molecular orbital pictures for octahedral, pentagonal-bipyramidal, and dodecahedral hydride complexes.

As we discussed before,[28] the classical hydrides are preferred for those transition metals with more diffuse d metal orbitals, while the nonclassical isomers are more likely for those metals with more contracted d metal orbitals. Therefore, polyhydride complexes of later transition metals will tend to maximize the number of pure d electrons by adopting an octahedral structure. Further reduction of the complex to a trigonal-bipyramidal transition metal complex, in which the two high-energy orbitals (e′) have significant d–p mixing, leads to destabilization of the d electrons. Since the tendency of intramolecular charge transfer increases with the diffuseness of metal d orbitals, polyhydride complexes of earlier transition metals tend toward complexes which maximize the number of M–H bonds. A model provided below will explain why this dichotomy (maximizing M–H bonds or $M(\eta^2\text{-}H_2)$ units) is so strong.

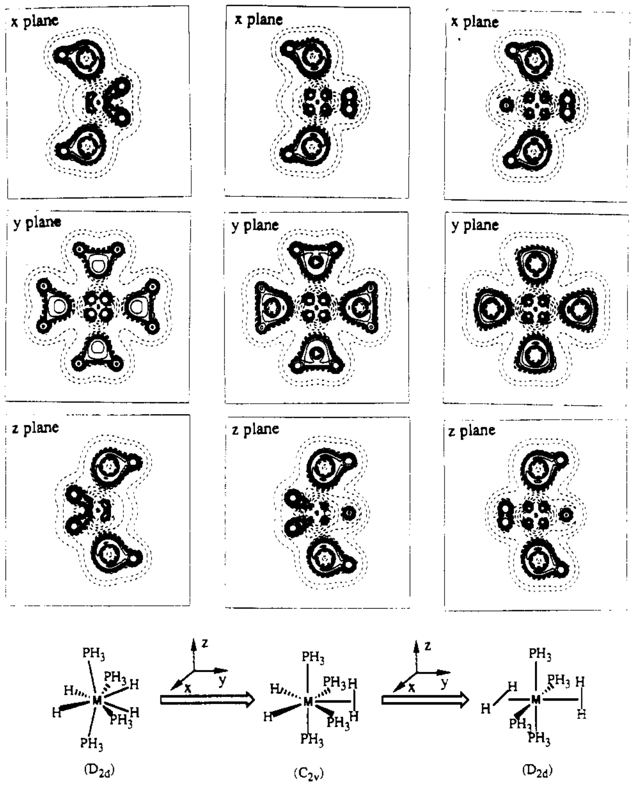


Figure 2. Laplacian plots of the valence-electron density, $-\nabla^2\rho$, on various metal–ligand planes from ab initio results on three isomers of $[ReH_4(PH_3)_4]^+$: left column, plots for classical isomer, $[ReH_4(PH_3)_4]^+$; center column, plots for nonclassical isomer, $[ReH_2(\eta^2\text{-}H_2)(PH_3)_4]^+$; right column, plots for nonclassical isomer, $[Re(\eta^2\text{-}H_2)_2(PH_3)_4]^+$. The x, y, and z planes are planes perpendicular to x, y, and z planes, respectively, which correspond to yz, xz, and xy planes.

Molecular Orbital Model. Combining a molecular-orbital perspective with the analyses of valence-electron density above, we propose a simple model to understand the energy differences between different isomers. Figure 3 illustrates the changes of relevant energy levels from one isomer to another for an 18-e model complex, MH_nL_{8-n} (n = 4–8). The M–L energy levels are omitted from the figure, since they are relatively constant from one isomer to the others. ΔE_1 and ΔE_2 in Figure 3 have the same definitions as in eqs 1 and 2. When the dodecahedral classical isomer, $M(H)_nL_{8-n}$, transforms into the pentagonal-bipyramidal nonclassical isomer, $M(H)_{n-2}(\eta^2\text{-}H_2)L_{8-n}$, two M–H bonds become one pair of d electrons and an $M(\eta^2\text{-}H_2)$ unit. A similar transformation leads from the pentagonal-bipyramidal isomer to the octahedral nonclassical isomer, $M(H)_{n-4}(\eta^2\text{-}H_2)_2L_{8-n}$. This view of the successive reductive formation of $\eta^2\text{-}H_2$ units is strongly supported by the electron density analyses above (see Figure 2). In Figure 3, $|\Delta_1|$ is the energy level difference between M–H and the metal d orbital and $|\Delta_2|$ is the energy level difference between the $M(\eta^2\text{-}H_2)$ unit and the M–H bond. When $|\Delta_1| > |\Delta_2|$, the classical isomer with the maximum coordination number will be the most stable. When $|\Delta_1| < |\Delta_2|$, the octahedral, nonclassical isomer with the maximum number of d electrons will be the most stable. This model clearly explains the trends observed therotetically and experimentally.

Further support of this model is obtained from our calculations of $\Delta E_2/\Delta E_1$ ratios for different complexes (see the right column of Figure 1). The model illustrated in Figure 3 predicts an $\Delta E_2/\Delta E_1$ ratio of 2 (see top of Figure 3). Of the 14 complexes (see Figure 1) investigated in this paper, 10 complexes have $\Delta E_2/\Delta E_1$ ratios in the range 1.4–2.9 and one has a slightly large (4.8) ratio. For the three complexes with abnormal $\Delta E_2/\Delta E_1$ ratios, the

---

(36) (a) Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc.* **1984**, *106*, 1594. (b) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9.

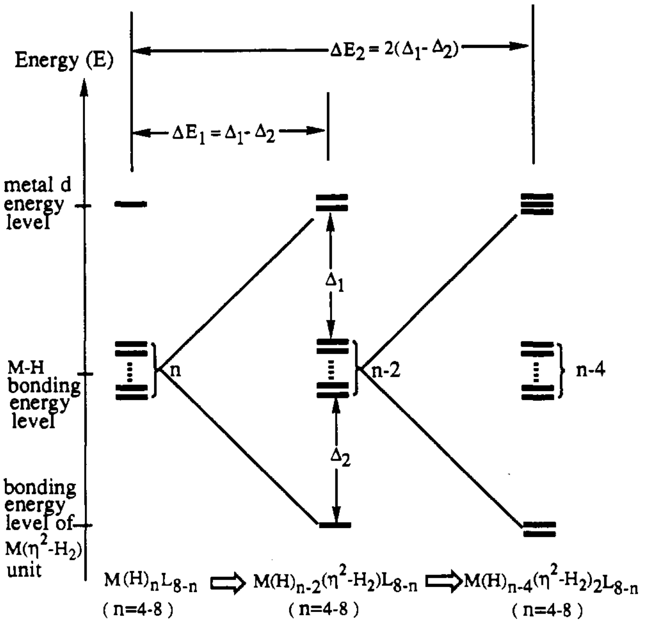


Figure 3. Illustration of the changes of relevant energy levels in the dodecahedral → pentagonal-bipyramidal → octahedral isomerization process for an 18-electron model complex, MH_nL_{8-n} (n = 4–8). ΔE_1 and ΔE_2 are defined in eqs 1 and 2.

transition metals (Ru and Ir) are on (or near) the diagonal lines which divide the classical and nonclassical isomers; here, $|\Delta_1|$ and $|\Delta_2|$ are close in magnitude.

Because cationic complexes have more contracted d orbitals, the line which divides the transition metals into classical and nonclassical complexes occurs earlier in the series. In our model the contraction is intimately related to a lowering of the metal d orbital energy levels (see Figure 3) ($|\Delta_1|$ decreases). In addition, the contraction weakens the metal–hydrogen interaction ($|\Delta_2|$ increases). Therefore, the relative stability of nonclassical isomer increases when the complex is cationic or has electron-withdrawing ligands.

According to Koopmans' theorem, $|\Delta_1|$ is the ionization enthalpy (or potential, IP) difference between an electron in the M–H bond and one in the metal d orbital and $|\Delta_2|$ is the ionization enthalpy difference between an electron in the $M(\eta^2\text{-}H_2)$ interaction and one in the M–H bond. Mathematically

$$|\Delta_1| = \mathrm{IP(M\text{-}H)} - \mathrm{IP(M{:})} \tag{3}$$

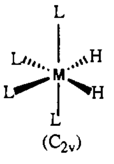
$$|\Delta_2| = \mathrm{IP}(\mathrm{M}(\eta^2\text{-}\mathrm{H}_2)) - \mathrm{IP(M\text{-}H)} \approx \mathrm{IP(H\text{-}H)} - \mathrm{IP(M\text{-}H)} \tag{4}$$

$$|\Delta_1| - |\Delta_2| = 2\mathrm{IP(M\text{-}H)} - [\mathrm{IP(M{:})} + \mathrm{IP(H\text{-}H)}] \tag{5}$$

The approximation made in eq 4 is based on the fact that the interaction between the metal and H_2 in most nonclassical polyhydride complexes is very weak.

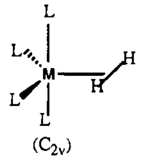
From eq 5, we can see that when twice the ionization enthalpy of an electron in the M–H bond is greater than the sum of the ionization enthalpies of an electron in the H–H bond and one in the metal d orbital, a classical isomer is definitely preferred. Otherwise, a nonclassical isomer with an octahedral structure is adopted. The ionization enthalpy of the M–H bonding electrons depends primarily on two factors: the M–H overlap and the energy of the metal orbital. As one moves across the transition series, both M–H overlap and the energy of the metal orbital decrease. If the former effect dominates, IP(M–H) will decrease across the series, while if the latter factor dominates, IP(M–H) will increase. In either case, the trend of the $|\Delta_1| - |\Delta_2|$ difference will be dominated by IP(M:) because IP(M–H) is changing more slowly. Therefore, nonclassical isomers are preferred for those complexes with transition metals on the right side of the diagonal line, where $|\Delta_1| = |\Delta_2|$.

Five-Coordinate Complexes. For completeness, we also examined $[RhH_2(PH_3)_4]^+$ as a model for the $[Rh(H)_2(PP_3)]^+$ [PP_3 = $P(CH_2CH_2PPh_2)_3$]^{22} complex to study the relative stability of the five-coordinate nonclassical $\eta^2\text{-}H_2$ complex **14** and its classical isomer **13**. The classical isomer (**13**) was obtained through geometry optimization at the HF level. Starting from geometry **14**, we tried to optimize the nonclassical form. However, the geometry optimization led to the dissociation of the $\eta^2\text{-}H_2$ unit and the formation of the square-planar d^8 $[Rh(PH_3)_4]^+$ complex. This result derives from the strong tendency to maximize the number of pure d electrons, as discussed above. For a d^8 square-planar complex, ML_4, the eight metal valence electrons occupy b_{2g} (d_{xy}), e_g (d_{xz}, d_{yz}), and a_{1g} (d_{z^2}, slightly mixed with s character) nonbonding orbitals, while for a d^8 trigonal-bipyramidal transition-metal complex, ML_5, the eight valence electrons occupy e″ (d_{xz}, d_{yz}) and e′ (d–p mixing) orbitals. Therefore, the trigonal-bipyramidal nonclassical isomer is disfavored, since four of the eight valence electrons have to occupy the high-energy e′ orbitals. The instability of the trigonal-bipyramidal (TBP) nonclassical isomer is closely related to why a TBP geometry is found to be a transition state rather than an intermediate in the oxidative addition of dihydrogen to a d^8 square-planar iridium complex.[37] Since very few five-coordinate nonclassical polyhydrides have been reported so far, we leave the discussion of the special requirement for stabilizing a five-coordinate nonclassical complex with different isomers for a future study.



(C_{2v})

13



(C_{2v})

14

Conclusion

From the analyses of valence-electron densities of classical and nonclassical transition-metal polyhydride isomers, we proposed a model to explain why the octahedral structure is highly stable for those transition-metal polyhydride complexes which prefer a nonclassical isomer. In the model, two parameters, $|\Delta_1|$ and $|\Delta_2|$, are defined. $|\Delta_1|$ is the ionization enthalpy difference between an electron in the M–H bond and one in the metal d orbital. $|\Delta_2|$ is the ionization enthalpy difference between an electron in the H–H bond and one in the M–H bond. For the early-transition-metal polyhydrides, $|\Delta_1|$ is greater than $|\Delta_2|$, and therefore, the classical isomers are preferred. For the late-transition-metal polyhydrides, $|\Delta_1|$ is smaller than $|\Delta_2|$, and a nonclassical isomer with an octahedral structure is adopted. For $RuH_6(PH_3)_2$, $IrH_7(PH_3)$, and $[RuH_5(PH_3)]^+$ complexes, $|\Delta_1|$ and $|\Delta_2|$ are likely close to each other. Therefore, they could adopt either or classical or nonclassical isomers or both.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE 91-13634) and Robert A. Welch Foundation (Grant No. A-648) for financial support and M. F. Guest for providing the GAMESS package of programs. This research was conducted in part with use of the Cornell National Supercomputer Facility.

---

[37] (a) Sargent, A. L.; Hall, M. B.; Guest, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 517. (b) Sargent, A. L.; Hall, M. B. *Inorg. Chem.* **1992**, *32*, 317.