J. Am. Chem. Soc. 1995, 117, 1859−1860

Making Sense of the Shapes of Simple Metal Hydrides[†]

Clark R. Landis,* Thomas Cleveland, and
Timothy K. Firman

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received October 31, 1994

Both computational[1−6] and experimental studies[7−9] from the last few years indicate that the simplest metal complexes, closed-shell complexes with hydride and alkyl ligands, have surprisingly complex geometries. The finding of such unexpected structures challenges our understanding of the forces controlling molecular shapes at metals. In this communication, we demonstrate that (1) the geometries of many simple metal hydrides and alkyls can be understood using the concepts of approximate valence bond theory formulated by Pauling over 60 years ago[10] and (2) these simple theoretical concepts form the basis of an accurate molecular mechanics description of the shapes of simple metal complexes.

We recently have shown[11] that Pauling's formulas for hybrid orbital strength functions[12−15] can be extended to any arbitrary combination of s, p, and d orbitals and form the basis of an angular potential energy term in MM computations.[11,16,17] Energy functions for sd^n hybrids are shown in Figure 1. The following set of rules guide the application of these valence bond concepts to simple transition metal hydrides and alkyls: (1) use only s and d orbitals in forming hybrid orbitals; (2) hybrid bond orbitals have maximal s character (or sd^{n-1} hybridization when making *n* bonds); (3) lone pairs are placed in pure d orbitals; and (4) when the metal valency exceeds 12 electrons, delocalized bonding units are used; e.g., linear H−M−H three-center four-electron bonds[17] are formed by resonance between Lewis structures $H-M^+H^- \leftrightarrow {}^-H^+M-H$. We note that others[1,18−22] previously have rationalized the geometries of simple metal complexes by invoking sd hybridization.

Consider the structure of WH_6. On the basis of *ab initio* computations, Albright *et al.*[2−4] and Schaefer *et al.*[6] have concluded that d^0 WH_6 is not octahedral and exhibits at least four lower symmetry minima that are similar in energy (within *ca.* 16 kcal/mol) and stabilized by *ca.* 130 kcal/mol relative to the octahedron. For WH_6 and $W(CH_3)_6$, the formation of localized, electron pair bonds draws from all s and d orbitals of the metal to form six sd^5 hybrids. A pair of sd^5 hybrid orbitals (Figure 1) have energy minima at angles of 63° and 117°. Four arrangements of WH_6 that satisfy the minimal hybrid overlap criteria are the two C_{3v} and the two C_{5v} structures shown in Figure 2; these structures are essentially identical to the structures of local minima found by *ab initio* methods.

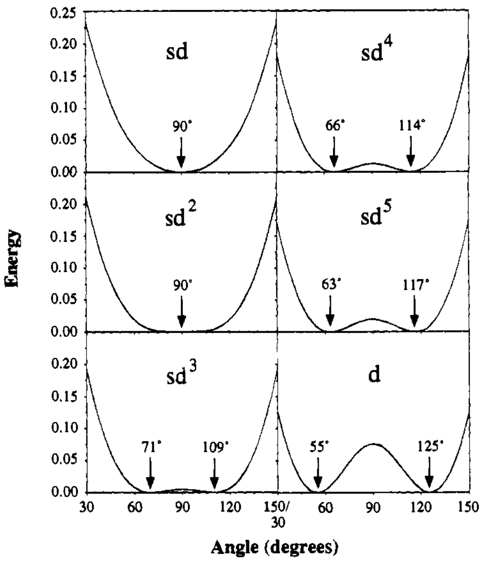

Figure 1. Pair defect functions for two hybrid orbitals of sd^n hybridization as a function of bond angle.

The bonding in $W(CH_3)_6$ should be similar to that in WH_6, although we anticipate some distortion that can be attributed to intermethyl steric effects. Using the VALBOND force field,[23] we predict the lowest energy structure to be midway between the WH_6 C_{3v} structure and a trigonal prism. Motion along the $C_{3v} \rightarrow D_{3h} \rightarrow C'_{3v}$ inversion coordinate is facile. A computed transition state energy of 3.0 kcal/mol occurs at the D_{3h} geometry. Preliminary molecular dynamics simulations yield internuclear radial distributions that are consistent with the electron diffraction data.[7]

As shown in Figure 2, the VALBOND scheme predicts minimum energy structures[24] that are in excellent agreement with those predicted by geometry optimization at the MP2 level for a wide variety of metal hydrides. The examples of ZrH_3^+, TcH_5, and RhH_4^- illustrate the hybridization bonding rules well. For ZrH_3^+, three bonding orbitals of sd^2 hybridization, leading to a trigonal pyramidal structure, are deduced from rules 1 and 2. The 12 valence electrons of TcH_5 are accommodated in a pure d lone pair and five sd^4 hybrid orbitals according to the first three rules. The saw horse geometry of RhH_4^- arises from the arrangement of 14 valence electrons as follows: six electrons are placed in pure d lone pairs, six more electrons are placed in sd^2-hybridized bond orbitals that make 90° angles with one another, and the final electron pair is placed in resonance with one of the sd^2 bond orbitals to make a linear three-center four-

---

[†] This paper is dedicated in memory of Linus Pauling.

(1) Siegbahn, P. E. M.; Blomberg, M. R. A.; Svensson, M. *J. Am. Chem. Soc.* **1993**, *115*, 4191.

(2) Albright, T. A.; Tang, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1462.

(3) Kang, S. K.; Albright, T. A.; Eisenstein, O. *Inorg. Chem.* **1989**, *28*, 1611.

(4) Kang, S. K.; Tang, H.; Albright, T. A. *J. Am. Chem. Soc.* **1993**, *115*, 1971.

(5) Jonas, V.; Frenking, G.; Gauss, J. *Chem. Phys. Lett.* **1992**, *194*, 109.

(6) Shen, M.; Schaefer, H. F.; Partridge, H. *J. Chem. Phys.* **1992**, *98*, 508.

(7) Haaland, A.; Hammel, A.; Rypdal, K.; Volden, H. V. *J. Am. Chem. Soc.* **1990**, *112*, 4547.

(8) Morse, P. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 4114.

(9) Pulham, C.; Haaland, A.; Hammel, A.; Rypdal, K.; Verne, H. P.; Volden, H. V. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1464.

(10) Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367.

(11) Root, D. M.; Landis, C. R.; Cleveland, T. *J. Am. Chem. Soc.* **1993**, *115*, 4201.

(12) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 274.

(13) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 4200.

(14) Hultgren, R. *Phys. Rev.* **1932**, *40*, 891.

(15) Kimball, G. E. *J. Chem. Phys.* **1940**, *8*, 188.

(16) Pauling, L.; Herman, Z. S.; Kamb, B. J. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 1361.

(17) Cleveland, T.; Landis, C. R. Manuscript in preparation.

(18) Blomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. *New J. Chem.* **1991**, *15*, 727.

(19) Villalta, P. W.; Leopold, D. G. *J. Chem. Phys.* **1993**, *98*, 7730.

(20) Low, J. J.; Goddard, W. A. *Organometallics* **1986**, *5*, 609.

(21) Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 6928.

(22) Ohanessian, G.; Brusich, M. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1990**, *112*, 7179.

(23) The following parameters were used with the standard CHARMM potential energy functions augmented with the VALBOND angular terms: $k^{\mathrm{stretch}} = 200$ kcal/(mol·Å^2) for all M−H and M−C bonds, $k^{\mathrm{stretch}} = 300$ kcal/(mol·Å^2) for C−H bonds; VALBOND hybridization of CH_3 groups was sp^3, and the VALBOND parameters were 150 kcal/mol for C−H bonds and 40 kcal /mol for M−H and M−C bonds; no proper or improper torsion terms were used; the CHARMM van der Waals parameters were as follows: *H*, $r_0 = 1.33$ Å, $E_0 = -0.0420$ kcal/mol; C, $r_0 = 1.800$ Å, $E_0 = -0.0903$ kcal/mol; M, $r_0 = 0.650$ Å, $E_0 = -0.001$ kcal/mol.

(24) In the VALBOND computations all 1-3 nonbonded interactions were excluded. For any given molecule the energies of the minima were within 1 kcal/mol of each other.

0002-7863/95/1517-1859$09.00/0

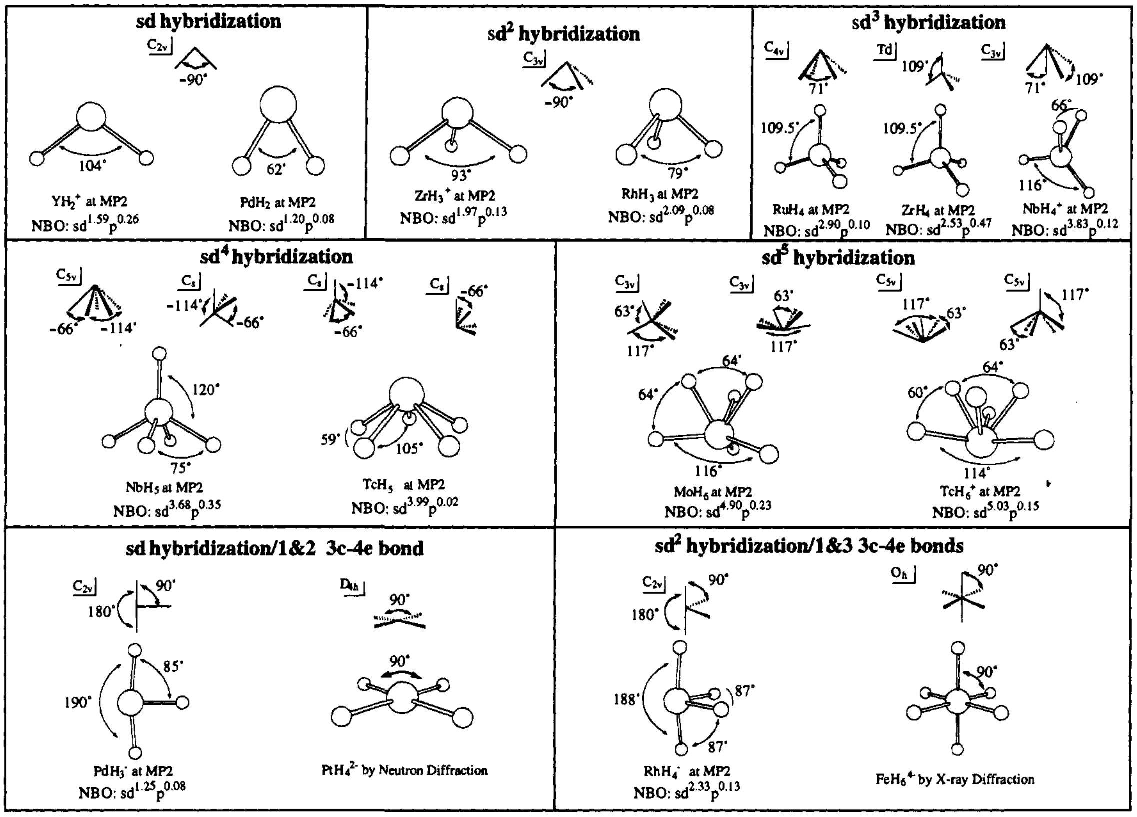

Figure 2. A comparison of VALBOND-predicted minima with *ab initio* and/or experimental structures for various metal hydrides. The simple stick figures represent minima on the VALBOND potential energy surface, and the ball-and-stick representations are either experimental structures or structures computed at the MP2 level. The NBO hybridizations determined for the MP2 calculations also are given; for the hypervalent cases, the NBO hybridizations are for the two-center two-electron bonds. (Gaussian 92, Revision E.2: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 1992. NBO 4.0: Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 1994. Basis sets, metal: Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. Hydrogen: Dunning, T. H; Hay, P. J. *Modern Theoretical Chemistry*; Plenum: New York, 1976; Chapter 1, pp 1–28. PtH_4^{2-} structural data: Bronger, W.; Müller, P.; Schmitz, D.; Spittank, H. *Z. Anorg. Allg. Chem.* **1984**, *516*, 35–41. FeH_6^{4-}: Didisheim, J.-J.; Zolliker, P.; Yvon, K.; Fischer, P.; Schefer, J.; Gubelmann, M.; Williams, A. F. *Inorg. Chem.* **1984**, *23*, 1953–1957.)

electron, or hypervalent, bond. Hence, the C_{2v} geometry is obtained. We have found that the hybridization prescriptions of the VALBOND scheme are in accord with natural bond orbital analyses[25–27] of the MP2 density matrices (Figure 2).

On the basis of a localized bonding scheme, we can draw clear analogies between main group and transition metal geometries. The hydrides $WH_6 \leftrightarrow CH_4$ are akin in that they represent valencies that are filled via formation of electron pair bonds, only. Two and four electron deficiencies (unfilled valencies) occur for the pairs $NbH_5 \leftrightarrow BH_3$ and $ZrH_4 \leftrightarrow BeH_2$, respectively. Similar hypervalencies and structures are found for the pairs $PdH_3^- \leftrightarrow ClF_3$, $RhH_4^- \leftrightarrow SF_4$, $PtH_4^{2-} \leftrightarrow XeF_4$, and $FeH_6^{4-} \leftrightarrow XeF_6$.[28] The structural similarities originate from (1) the presence of linear three-center four-electron delocalizations and (2) the preference of *ca.* 90° bond angles for hybrids with high p-character (i.e., the main group fluorides) and for those with sd and sd^2 (i.e., the metal hydrides) hybridizations. Thus, our scheme leads to the conclusion that most transition metal complexes are hypervalent!

Of course, such simple approaches cannot be expected to work well for all transition metal complexes. We anticipate deviations from these simple rules in the following circumstances: (1) early transition metal complexes which may have significant p-orbital character, (2) metal complexes for which promotion from s^2d^n to s^1d^{n+1} is exceptionally large,[1,29] (3) strong π-bonding interactions (either π-donor or π-acceptor ligands) which offset the shape-controlling forces of the σ-framework, (4) highly ionic structures, and (5) the presence of two or more resonance configurations in close energetic proximity (e.g., molecular H_2 vs metal dihydrides).

In summary, a simple localized bond perspective predicts the unusual geometries of transition metal hydrides and alkyls that are found via quantum mechanical computations and experiment. This perspective not only provides a satisfying conceptual framework for understanding the shapes of these metal complexes but also leads to the derivation of a practical MM algorithm for describing molecular shapes. The VALBOND scheme is a direct descendant of the ideas first formulated by Pauling over 60 years ago and to which he returned in the last two decades of his life. We have identified a number of potential difficulties in applying these ideas to *all* transition metal complexes, but our preliminary work suggests that our approach will work well for many ligand types (e.g., phosphines, halides with late transition metals, etc.).

Acknowledgment. This work was supported by the NSF and by a studentship from Molecular Simulations, Inc. We thank Prof. Frank Weinhold for his patient assistance and Prof. Martin Karplus for suggesting that we consider a valence bond viewpoint in deriving force field potentials.

JA9435302

---

(25) Reed, A. E.; Weinhold, F.; Curtiss, L. A.; Pochatko, D. J. *J. Chem. Phys.* **1986**, *84*, 5687.

(26) Carpenter, J. E.; Weinhold, F. *J. Am. Chem. Soc.* **1988**, *110*, 368.

(27) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211.

(28) A referee has correctly pointed out that these analogies involve dissimilar ligands. However, the NBO-localized electronic structures of analogous pairs decompose into similar 2-center and 3-center interactions.

(29) Bierwagen, E. P.; Bercaw, J. E.; Goddard, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 1481.