New Orbital Hybridization Schemes for Metal Hydrides

Keeping p Orbitals out of the Picture

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One of the most widely applied concepts in bonding theory is hybridization. The idea was introduced by Linus Pauling 65 years ago as a simple way of explaining shapes of molecules. Pauling considered combinations of atomic orbitals, rather than 'pure' s and p orbitals, to form bonds (and to hold lone pairs of electrons). For example, an s and a p (say p_x) orbital can be combined in two ways: $(s + p_x)$ and $(s - p_x)$. It is easy to see that these sp hybridized orbitals have one large lobe each (*Figure 1*). These are extended along the +x and -x directions. Because of their spatial extension, these orbitals can overlap better than the pure s and p_x orbitals. The bonds formed using hybrid orbitals will therefore be stronger. Further, the bonds will have directional character. The preferred bond angle will be 180°. One can readily understand why acetylene is linear. In order to form two strong σ bonds, each carbon atom is sp hybridized. The remaining p orbitals are used to form the bonds of the molecule.

Using similar arguments, the tetrahedral coordination of saturated carbon and trigonal planar geometry at olefinic centres can be rationalized. The optimum way to form

Figure 1 Shapes of sp hybridized orbitals.
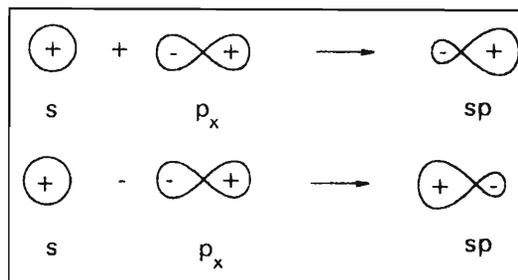
4 σ bonds is to use sp^3 hybridization. The 4 combinations have one large lobe along each corner of a tetrahedron. Similarly, 3σ bonds can be formed best using sp^2 hybrid orbitals, whose extended lobes make an angle of 120° to each other.

The idea is not restricted to organic molecules. More complex shapes encountered in inorganic systems can be explained using suitable hybridization schemes. For example, d^2sp^3 hybrid orbitals have lobes extending towards the corners of an octahedron. Similarly, square planar geometry is compatible with dsp^2 hybridization. The coordination geometries resulting from admixtures of s, p and d orbitals are summarised in *Table 1*.

Table 1 Hybridization schemes and resulting geometries

Orbitals used	Coordination Geometry
sp^3	Tetrahedral
sp^2	Trigonal planar
sp	Linear
d^2sp^3	Octahedral
dsp^2	Square Planar
dsp^3	Trigonal Bipyramidal

Although Pauling suggested hybridization schemes for all types of molecules, the idea is generally used in systems with 2- centre 2-electron bonds. These include the vast majority of molecules of interest to organic chemists. But for inorganic molecules, some extra rules are needed to derive the shapes. In one popular version, the relative magnitude of repulsions involving lone pairs and bond pairs, placed in hybrid orbitals, is considered (Valence Shell Electron Pair Repulsion Theory). In the extreme case of electron–deficient molecules, like boron hydrides, the additional factors to be taken into account become cumbersome. The hybridization idea is not even used as a starting point. Instead, alternative bonding models (Molecular Orbital correlation diagrams) are usually employed. Different horses for different courses!

It was therefore somewhat surprising to find a claim last year that the hybridization model represents the simplest way to 'make sense of the shapes of simple metal hydrides' (C. R. Landis, T. Cleveland and T. K. Firman, *Journal of American Chemical Society*, Vol. 117, 1859-1860, 1995). Geometry optimization using high level computational methods led to unusually complex shapes for transition metal hydrides and alkyls. For example, the minimum energy form of WH_6 was not octahedral. Several low symmetry forms were computed to have lower energy. In order to explain the unusual structures they ob-

tained, the authors proposed a new set of hybridization schemes, using combinations of s and d orbitals, but leaving out p orbitals. Although s, d hybrids had been sporadically used before, Landis et al. were the first to provide systematic rules for using sd^n hybridization.

The procedure for deriving the shape of a metal hydride is as follows. (a) Count the number of valence electrons in the metal and the electrons provided by the ligands. For WH_6, the total is 12. (b) Place the n bonding electron pairs in sd^{n-1} hybrid orbitals. Since there are 6 bonds in WH_6, the appropriate set is sd^5 hybrid orbitals. The shape of the molecule is determined from the angular characteristics of these hybrids. (There are two more rules which are not relevant for WH_6. For the sake of completeness, they are: (c) Additional electrons, if present, are placed in pure d orbitals as lone pairs. (d) If all d orbitals are used up, use multi-centre bonding. Back to the never-say-die approach of Pauling!)

It turns out that sd^n hybrids have peculiar directional character. For example, consider combinations from an s and a d orbital. Instead of getting a single extended lobe as in sp hybrid orbitals, two lobes get enlarged in the sd hybrids (*Figure 2*). Although only one of these lobes can be used for bonding, the hybrid orbital can still overlap better than a pure s or d orbital.

Figure 2 *Shapes of sd hybridized orbitals.*
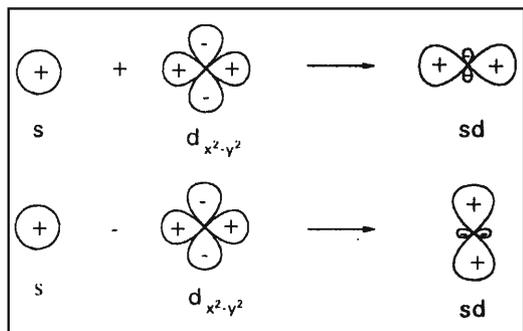
Whichever pair of lobes is used, the resulting bond angle would be 90°

The presence of two extended lobes per sd^n hybrid has an interesting consequence. If θ is one of the preferred bond angles, $(180° - \theta)$

is also equally favoured. Landis et al. have worked out the preferred bond angles (rounded to the nearest degree) to be as follows:

sd^2: 90°; sd^3: 71° and 109°; sd^4: 66° and 114°; sd^5: 63° and 117°.

With the idealized bond angles, four geometries can be constructed for the supposedly sd^5 hybridized WH_6 molecule. Two have C_{3v} symmetry and two more have C_{5v} symmetry (*Figure 3*). All were calculated to be fairly close to each other in energy.

Figure 3 *The four possible geometries of WH₆ using sd⁵ hybridization on the metal. The first C₃ᵥ structure is related to a distorted trigonal prism; the top half is compressed, while the bottom half is expanded. The second C₃ᵥ form is a distorted octahedron; the two 3-fold units are staggered. The five-fold symmetric structures resemble normal and 'inverted' umbrellas. Note that in two of the four structures, all the bonds point to the same half of a hemisphere around the metal.*
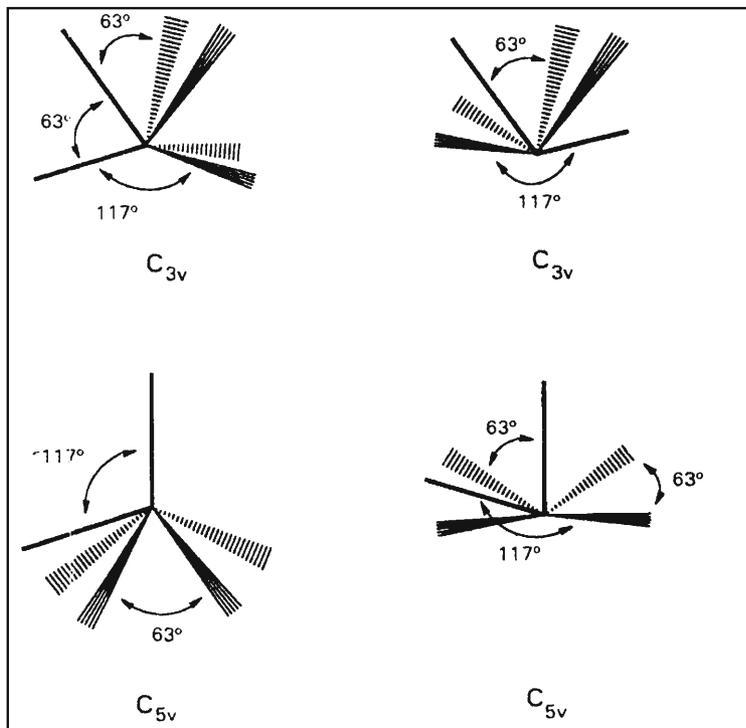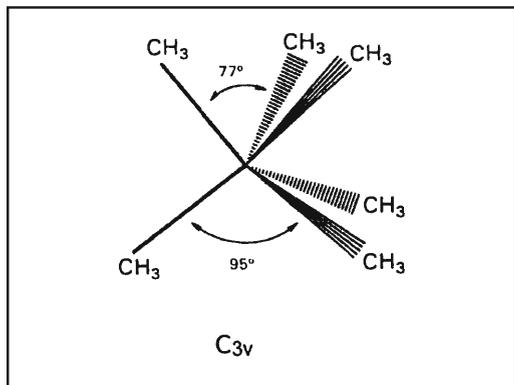
Oblivious of this work, V Pfennig and K Seppelt were carrying out a difficult experiment with hexamethyltungsten, $W(CH_3)_6$. They managed to recrystallize the thermally unstable (explosive!) substance from acetone at $-90°C$ and determined the X-ray structure at $-163°C$ (*Science*, Vol. 271, 626–628, 1996). The molecule was found to have a shape derived from a distorted trigonal prism (*Figure 4*). The authors justified the preference using a molecular orbital correlation diagram connecting an octahedron, trigonal prism and a C_{3v} distorted form. The filled orbitals in this d^0 system were shown to be stabilized in the C_{3v} form to a greater extent.

Landis et al. pointed out (*Science*, vol. 272, 182, 1996) that the observed non-octahedral structure of $W(CH_3)_6$ is the same as the one they had predicted a year earlier. The form with the least steric repulsion between the methyl groups would be the C_{3v} structure derived from the trigonal prism. The

interactions alter the bond angles to 77° and 95°, instead of the idealized values of 63° and 117°. Landis et al. had anticipated these changes too in their original work.

Seppelt was quick to acknowledge the simplicity and accuracy of the sd^n hybridization model for metal hydrides and alkyls. He has also graciously stressed that the prediction of Landis et al. was made before and without prior knowledge of the crystallographic work.

Interested readers may find many more predictions of shapes of species like $NbH5$, TcH_5, PdH_3^-, RhH_4^-, PtH_4^{2-}, FeH_6^{4-}, etc., in the publication of Landis and coworkers.

One may wonder why p orbitals do not seem to be important in bonding in these systems. Hybridization leads to stabilization only if the promotion energy is relatively small. It therefore appears that the np orbitals are considerably higher in energy than the $(n-1)d$ and ns orbitals. This may be generally true in the lower right half of the transition metal series, especially if the effective charge on the metal is very low. There is also no metal-ligand π bonding in the hydrides and alkyls. Under these special circumstances, sd^n hybridization may be the preferred mode of bonding.

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