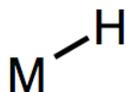


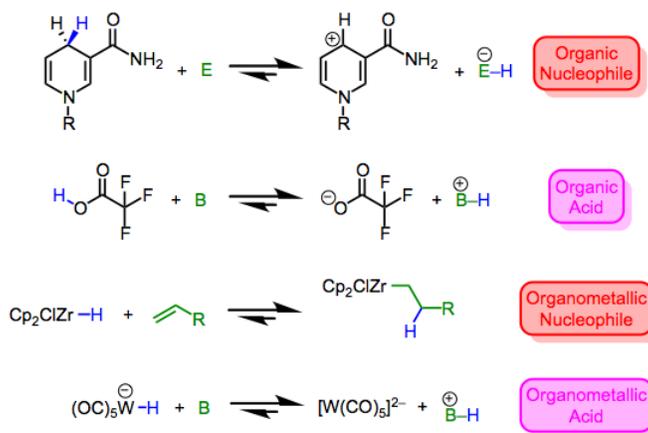
2.6: Metal Hydrides

Metal-hydrogen bonds, also known (misleadingly) as **metal hydrides**, are ubiquitous X-type ligands in organometallic chemistry. There is much more than meets the eye to most M-H bonds: although they're simple to draw, they vary enormously in polarization and pKa. They may be acidic or hydridic or both, depending on the nature of the metal center and the reaction conditions. In this post, we'll develop some heuristics for predicting the behavior of M-H bonds and discuss their major modes of reactivity (acidity, radical reactions, migratory insertion, etc.). We'll also touch on the most widely used synthetic methods to form metal hydrides.



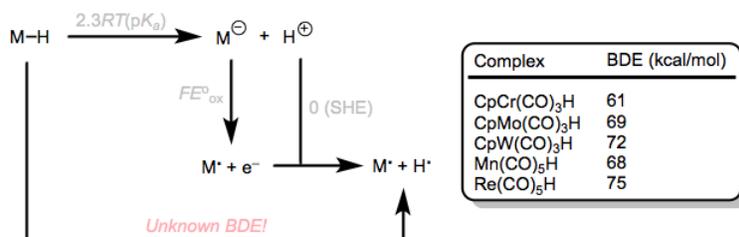
General Properties

Metal hydrides run the gamut from nucleophilic/basic to electrophilic/acidic. Then again, the same can be said of X-H bonds in organic chemistry, which may vary from mildly nucleophilic (consider Hantzsch esters and NADH) to extremely electrophilic (consider triflic acid). As hydrogen is what it is in both cases, it's clear that the nature of the X fragment—more specifically, the stability of the charged fragments X⁺ and X⁻—dictate the character of the X-H bond. Compare the four equilibria outlined below—the stabilities of the ions dictate the position of each equilibrium. By now we shouldn't find it surprising that the highly π-acidic W(CO)₅ fragment is good at stabilizing negative charge; for a similar reason, the ZrCp₂Cl fragment can stabilize positive charge.*



Metal-hydrogen bonds may be either hydridic (nucleophilic) or acidic (electrophilic). The nature of other ligands and the reaction conditions are keys to making predictions.

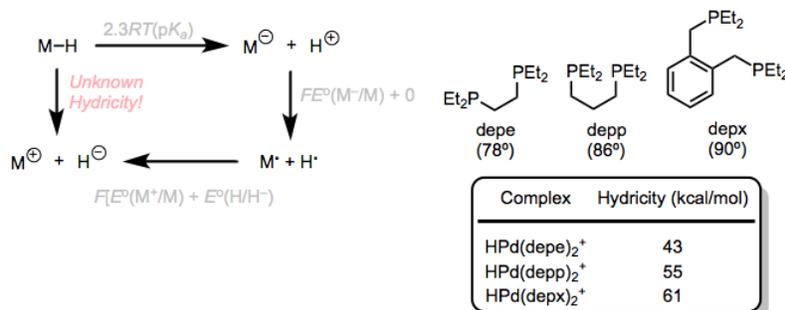
Let's turn our attention now to *homolytic* M-H bond strength. A convenient thermodynamic cycle allows us to use the acidity of M-H and the oxidation potential of its conjugate base in order to determine bond strength. This clever method, employed by Tilset and inspired by the inimitable Bordwell, uses the cycle in the figure below. BDE values for some complexes are provided as well. From the examples provided, we can see that bond strength increases down a group in the periodic table. This trend, and the idea that bridging hydrides have larger BDEs than terminal M-H bonds, are just about the only observable trends in M-H BDE.



A clever cycle for determining BDEs from other known quantities, with select BDE values. I've left out solvation terms from the thermodynamic cycle. For more details, see the Tilset link above.

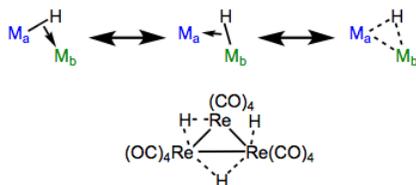
Why is knowing M-H BDEs useful? For one thing, the relative BDEs of M-C and M-H bonds determine the thermodynamics of β -hydride elimination, which results in the replacement of a covalent M-C bond with an M-H bond. Secondly, complexes containing weak M-H bonds are often good hydrogen transfer agents and may react with organic radicals and double bonds, channeling stannane and silane reductants from organic chemistry.

Hydricity refers to the tendency of a hydride ligand to depart as H^- . A similar thermodynamic cycle relates the energetics of losing H^- to the oxidation potentials of the conjugate base and the oxidized conjugate base; however, this method is complicated by the fact that hydride loss establishes an open coordination site. I've provided an abridged version of the cycle below. Hydricities are somewhat predictable from the electronic and steric properties of the metal center: inclusion of electron-donating ligands tends to increase hydricity, while electron-withdrawing or acidic ligands tend to decrease it. For five-coordinate hydrides that form 16-electron, square planar complexes upon loss of hydride, the bite angle of chelating phosphines plays an interesting role. As bite angle increases, hydricity does as well.



A thermodynamic cycle for hydricity, with some examples. Hydricity and bite angle are well correlated in five-coordinate palladium hydrides.

Bridging hydrides are an intriguing class of ligands. A question to ponder: how can a ligand associated with only two electrons possibly bridge two metal centers? How can two electrons hold three atoms together? Enter the magic of three-center, two-electron bonding. We can envision the M-H sigma bond as an electron donor itself! With this in mind, we can imagine that hydrides are able to bind end-on to one metal (like a standard X-type ligand) and side-on to another (like an L-type π system ligand, but using sigma electrons instead). Slick, no? We'll see more side-on bonding of sigma electrons in a future post on sigma complexes.



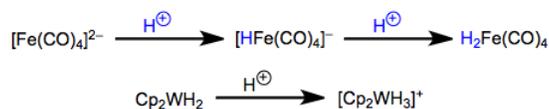
Resonance forms of bridging hydrides, with an example. Sigma complexes like these show up in other contexts, too!

Consistent with the idea that bridging is the result of "end-on + side-on" bonding, bond angles of bridging hydrides are never 180° .

Synthesis

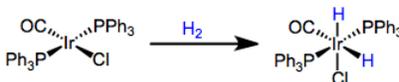
Here we'll discuss four ways to make hydrides: metal protonation, oxidative addition of H_2 , addition of nucleophilic main-group hydrides (borohydrides, aluminum hydrides, and silanes), and β -hydride elimination.

Just as in organic chemistry, the basicity of an organometallic complex is inversely related to the acidity of its conjugate base. Furthermore, charges have a predictable effect on the basicity of organometallic complexes: negatively charged complexes lacking π -acidic ligands are highly basic. Even neutral complexes containing strong donor ligands, like the tungsten complex below, can be protonated effectively. Notice that protonation is actually a kind of oxidative addition—the oxidation state of Fe in the first reaction below goes from -2 to 0 to +2! All coordination events of isolated electrophiles can also be viewed in this light. Reactions of this type are sometimes called **oxidative ligations** to distinguish them from oxidative addition reactions, which involve the addition of two ligands to the metal center with oxidation.



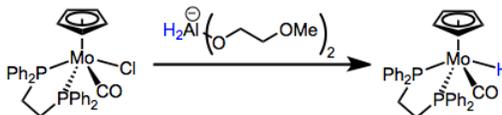
Metal protonation reactions involve the metal center as a base.

Contrast oxidative ligation with the **oxidative addition** of dihydrogen (H_2), a second method for the synthesis of hydride complexes. A key requirement here is that the starting metal center is at least d^2 —two electrons are formally lost from the metal center, and metals can't possess a negative number of d electrons. An open coordination site on the starting material must also be present (or possible through ligand dissociation). The reaction below is a standard example of the addition of H_2 to Vaska's complex, but there are some funky variations on this theme. These riffs include third-order homolytic cleavage of H_2 by two metal radicals, and oxidative addition followed by deprotonation by the starting complex (apparent heterolytic cleavage).



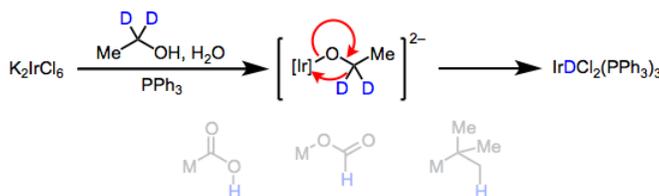
Oxidative addition of dihydrogen for the synthesis of metal hydrides.

Main-group hydrides like borohydrides and aluminum hydrides are great sources of H^- for organometallic complexes. These reactions seem more natural than metal protonations, since we often think of metals as electropositive or electrophilic species. Indeed, the combination of main-group sources of nucleophilic hydride with complexes containing metal-leaving group bonds is a very general method for the synthesis of metal hydride complexes. Check out the reaction below—what's the most likely mechanism? Is associative or dissociative substitution more likely? Hint: count electrons!



Nucleophilic substitution with a hydride source. What's the most likely mechanism?

β -hydride elimination forms metal hydride complexes and double bonds within organic ligands. Alkoxide ligands are commonly used for this purpose—elimination to form the hydride complex and aldehyde is more favorable than the reverse, migratory insertion of $\text{C}=\text{O}$ into the $\text{M}-\text{H}$ bond. Since the unsaturated byproduct is thrown away, it's desirable to make it something small, cheap, and gaseous. Hydroxycarbonyl, formate, and tert-butyl ligands have been applied successfully with this goal in mind...what are the byproducts?



Beta-hydride elimination for the synthesis of metal hydrides.

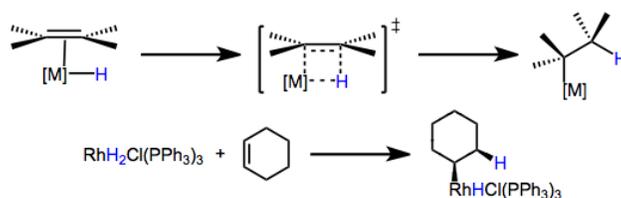
Reactions

Metal hydrides are characterized by nucleophilic, electrophilic, and radical behavior. The exact behavior of a given metal hydride complex depends on its electronic properties, its $\text{M}-\text{H}$ bond dissociation energy, and the nature of the reacting partner. Basic metal hydrides react with acids to free up a coordination site on the metal center (file this reaction alongside photolytic $\text{M}-\text{CO}$ cleavage and $\text{M}-\text{CO}$ cleavage with amine oxides).



"Protonolysis" generates two open coordination sites with loss of hydrogen gas.

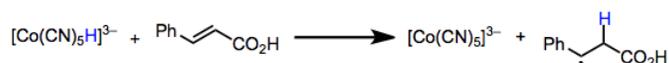
Migratory insertion reactions involving M–H bonds are extremely important in a practical sense (see hydrogenation and hydroformylation), and are conceptually related to nucleophilic hydride transfers from the metal center. We can think of insertions of π bonds into M–H as internal nucleophilic attack by the hydride ligand at one end of the π bond, with coordination of the metal center to the other. The figure below depicts the transition state for migratory insertion of an olefin into M–H and an example reaction. Notice the coplanarity of M, H, and the C=C bond in the transition state for insertion, which determines the cis configuration of the product. The same is required for the microscopic reverse (β -hydride elimination) but this essential geometry is easily overlooked for β -hydride elimination.



Migratory insertion of an olefin into M–H. Note the relative configuration of M–C and C–H!

It is important to note that insertions of CO into M–H bonds are rare, because such insertions are usually unfavorable thermodynamically.

Finally, the radical behavior of certain metal hydrides in the presence of olefins deserves a nod. The behavior of the cobalt hydride complex in the reaction below is typical of these types of reactions.



Hydrogen atom transfer to olefins. Radical reduction of carbon tetrachloride is a related process.

And there you have it: the properties, synthesis, and reactivity of metal hydrides in a nutshell. Like other ligands we've seen so far, the behavior of hydrides is controlled by the nature of the metal center and its accompanying ligands. However, it's interesting to note that the observed behavior of hydrides often depends on the nature of the reaction conditions, as well. Some complexes display "schizophrenic" behavior, so to speak, putting on their nucleophile hat in the presence of an electrophile and their electrophile hat in the presence of a nucleophile.

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