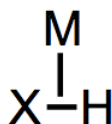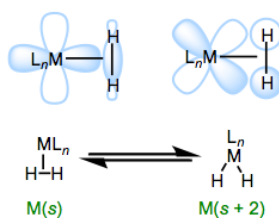## 2.3: σ Complexes

Ligands can, shockingly enough, bind through their σ electrons in an L-type fashion. This binding mode depends as much on the metal center as it does on the ligand itself—to see why, we need only recognize that σ complexes look like intermediates in concerted oxidative additions. With a slight reorganization of electrons and geometry, an L-type σ ligand can become two X-type ligands. Why, then, are σ complexes stable? How can we control the ratio of σ complex to X_2 complex in a given situation? How does complexation of a σ bond change the ligand's properties? We'll address these questions and more in this post.

General Properties

The first thing to realize about σ complexes is that they are highly sensitive to steric bulk. Any old σ bond won't do; hydrogen at one end of the binding bond or the other (or both) is necessary. The best studied σ complexes involve dihydrogen (H_2), so let's start there.

$$
\begin{array}{c}
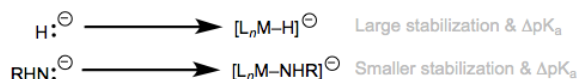M \\
| \\
X{-}H
\end{array}
$$

Mildly backbonding metals may bind dihydrogen "side on." Like side-on binding in π complexes, there are two important orbital interactions at play here: $\sigma H{-}H \rightarrow d\sigma$ and $d\pi \rightarrow \sigma^{*}H{-}H$. Dihydrogen complexes can "tautomerize" to $(H)_2$ isomers through oxidative addition of the H–H bond to the metal.
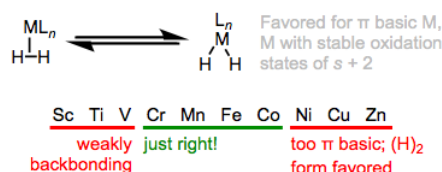

Orbital interactions and L-X_2 equilibrium in σ complexes.

H_2 binding in an L-type fashion massively acidifies the ligand—changes in pKa of over thirty units are known! Analogous acidifications of X–H bonds, which we touched on in a previous post, rarely exhibit ΔpKa > 5. What gives? What's causing the different behavior of X–H and H–H ligands? The key is to consider the conjugate base of the ligand—in particular, how much it's stabilized by a metal center relative to the corresponding free anion. The principle here is analogous to the famous dictum of organic chemistry: consider charged species when making acid/base comparisons. Stabilization of the unhindered anion H– by a metal is much greater than stabilization of larger, more electronegative anions like HO– and NH_2– by a metal. As a result, it's more favorable to remove a proton from metal-complexed H_2 than from larger, more electronegative X–H ligands.
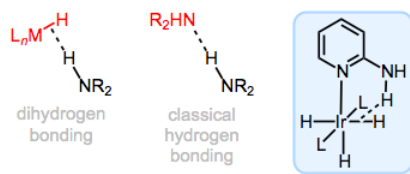

Remarkably large stabilization by an acidic metal fragment, without any counterbalancing from steric factors, explains the extreme acidification of dihydrogen upon metal binding.

The electronic nature of the metal center has two important effects on σ complexes. The first concerns the acidity of H_2 upon metal binding. The principle here is consistent with what we've hammered into the ground so far. In the same way cationic organic acids are stronger than their neutral counterparts, σ complexes of electron-poor metals—including (and especially) cations—are stronger acids than related complexes of electron-rich metals. The second concerns the ratio of L-type to X_2-type binding. We should expect more electron-rich metal centers to favor the X2 isomer, since these should donate more strongly into the $\sigma^{*}H{-}H$ orbital. This idea was masterfully demonstrated in a study by Morris, in which he showed that H2 complexes of π-basic metal centers show all the signs of X2 complexes, rather than L complexes. More generally, metal centers in σ complexes need a good balance of π basicity and σ acidity (I like to call this the "Goldilocks effect"). Because of the need for balance, σ complexes are most common for centrally located metals (groups 6-9).

Oxidative addition of H2 is important for electron-rich, π-basic metal centers. Groups 6-9 hit the "Goldilocks" spot.

The M–H bond in hydride complexes is a good base—anyone who's ever quenched lithium aluminum hydride can attest to this! Intriguingly, because it's a good base, the M–H bond can participate in hydrogen bonding with an acidic X–H bond, where X is a heteroatom. This kind of bonding, called dihydrogen bonding (since two hydrogen atoms are involved), is best described as a sort of $\sigma M–H \rightarrow \sigma^*X–H$ orbital interaction. Think of it as analogous to a traditional hydrogen bond, but using a σ bond instead of a lone pair. Crazy, right?!
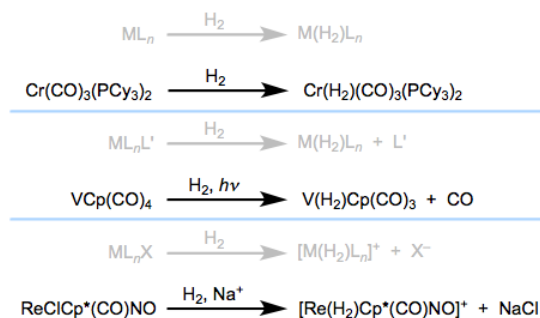

Dihydrogen bonding in metal hydrides: a sort of "interrupted protonation" of M–H.

Other kinds of σ complexes are known, but these are rarer than H–H complexes. One class that we've seen before involve agostic interactions of C–H bonds in alkyl ligands. σ Complexes of inorganic ligands like silanes and stannanes may involve complex bonding patterns, but we won't concern ourselves with those here.
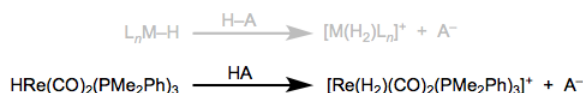
Synthesis

If a metal center with an open coordination site has the "Goldilocks combination" of electronic factors, simply treating it with dihydrogen gas is enough to form the σ complex. Metals that bear labile L- or X-type ligands can also yield σ complexes upon treatment with H2.

Methods for the synthesis of σ complexes from dihydrogen gas. Displacement of a labile ligand or occupation of a vacant site represent the essence of these methods.
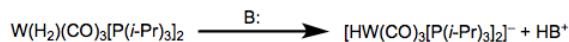
An alternative synthetic method involves the protonation of a basic M–H bond…taking dihydrogen bonding to the extreme! This method is especially nice if a cationic complex is the goal; of course, the metal needs to be π basic to make protonation favorable.

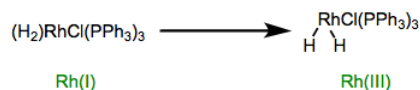*Protonation of an M–H bond for the synthesis of dihydrogen σ complexes.*

Reactions

Deprotonation of an L-type X–H ligand is probably the simplest reaction of this class of ligands. This process is just the reverse of the synthetic method described above. We can refer to it as heterolytic cleavage, since the X atom that stays bound to the metal holds on to the electrons of the X–H bond. The charge of the product complex is one less than that of the starting material. A variation on this theme involves intramolecular proton transfer.

$$W(H_2)(CO)_3[P(i\text{-}Pr)_3]_2 \xrightarrow{\text{B:}} [HW(CO)_3[P(i\text{-}Pr)_3]_2]^- + HB^+$$

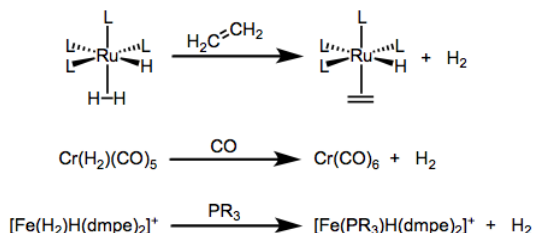*Deprotonation of dihydrogen complexes produces metal hydrides.*

Homolytic cleavage of X–H is also possible, and it can happen in two ways. Intramolecular oxidative addition is the first, and we've seen it already. Since this process is intramolecular and little geometric reorganization is necessary, kinetic barriers tend to be low and the process may be reversible (unless the electronic circumstances of the metal are extreme). This sort of oxidative addition is important for many hydrogenation reactions, such as those employing Wilkinson's catalyst.

$$(H_2)RhCl(PPh_3)_3 \longrightarrow \underset{H \quad H}{RhCl(PPh_3)_3}$$

Rh(I)   Rh(III)

Oxidative addition of dihydrogen via a sigma complex. In some cases, this process is a finely balanced equilibrium.

And the second way? In theory at least, intermolecular homolytic cleavage is possible. This process corresponds to one-electron oxidation of two distinct metal centers. Contrast this pattern of electron exchange with intramolecular oxidative addition, which involves two-electron oxidation of a single metal center. This kind of reactivity is rare in practice.

Ligand substitutions with other L-type ligands— including CO, N2, phosphines, and unsaturated organics—are also known. In fact, this process has been implicated in catalytic cycles for some hydrogenation reactions.

$$Cr(H_2)(CO)_5 \xrightarrow{\text{CO}} Cr(CO)_6 + H_2$$

$$[Fe(H_2)H(dmpe)_2]^+ \xrightarrow{PR_3} [Fe(PR_3)H(dmpe)_2]^+ + H_2$$

Ligand substitution reactions of sigma complexes. Can you justify the favorability of these reactions?