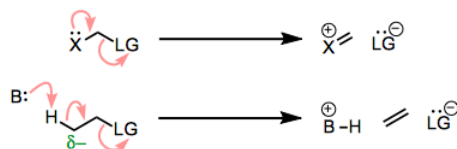


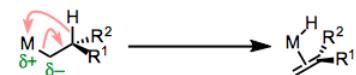
## 4.1: $\beta$ -Elimination Reactions

In organic chemistry class, one learns that elimination reactions involve the cleavage of a  $\sigma$  bond and formation of a  $\pi$  bond. A nucleophilic pair of electrons (either from another bond or a lone pair) heads into a new  $\pi$  bond as a leaving group departs. This process is called  $\beta$ -elimination because the bond  $\beta$  to the nucleophilic pair of electrons breaks. Transition metal complexes can participate in their own version of  $\beta$ -elimination, and [metal alkyl complexes](#) famously do so. Almost by definition, metal alkyls contain a nucleophilic bond—the M–C bond! This bond can be so polarized toward carbon, in fact, that it can promote the elimination of some of the world's worst leaving groups, like  $\text{--H}$  and  $\text{--CH}_3$ . Unlike the organic case, however, the leaving group is not lost completely in organometallic  $\beta$ -eliminations. As the metal donates electrons, it receives electrons from the departing leaving group. When the reaction is complete, the metal has picked up a new  $\pi$ -bound ligand and exchanged one X-type ligand for another.

### organic $\beta$ -eliminations



### organometallic $\beta$ -eliminations



- There is no change in oxidation state at M.
- Total electron count increases by 2.
- A new  $\pi$ -bound ligand appears on M.

*Comparing organic and organometallic  $\beta$ -eliminations. A nucleophilic bond or lone pair promotes loss or migration of a leaving group.*

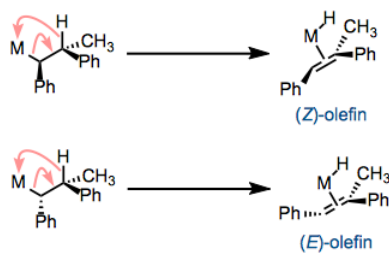
In this post, we'll flesh out the mechanism of  $\beta$ -elimination reactions by looking at the conditions required for their occurrence and their reactivity trends. Many of the trends associated with  $\beta$ -eliminations are the opposite of analogous trends in [1,2-insertion reactions](#). A future post will address other types of elimination reactions.

### $\beta$ -Hydride Elimination

The most famous and ubiquitous type of  $\beta$ -elimination is  **$\beta$ -hydride elimination**, which involves the formation of a  $\pi$  bond and an M–H bond. Metal alkyls that contain  $\beta$ -hydrogens experience rapid elimination of these hydrogens, provided a few other conditions are met.

The complex must have an open coordination site and an accessible, empty orbital on the metal center. The leaving group ( $\text{--H}$ ) needs a place to land. Notice that after  $\beta$ -elimination, the metal has picked up one more ligand—it needs an empty spot for that ligand for elimination to occur. We can envision hydride “attacking” the empty orbital on the metal center as an important orbital interaction in this process.

The M–C $_{\alpha}$  and C $_{\beta}$ –H bonds must have the ability to align in a syn coplanar arrangement. By “syn coplanar” we mean that all four atoms are in a plane and that the M–C $_{\alpha}$  and C $_{\beta}$ –H bonds are on the same side of the C $_{\alpha}$ –C $_{\beta}$  bond (a dihedral angle of 0°). You can see that conformation in the figure above. In the syn coplanar arrangement, the C–H bond departing from the ligand is optimally lined up with the empty orbital on the metal center. Hindered or cyclic complexes that cannot achieve this conformation do not undergo  $\beta$ -hydride elimination. The need for a syn coplanar conformation has important implications for eliminations that may establish diastereomeric olefins:  $\beta$ -elimination is stereospecific. One diastereomer leads to the (E)-olefin, and the other leads to the (Z)-olefin.



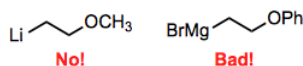
*$\beta$ -elimination is stereospecific. One diastereomer of reactant leads to the (Z)-olefin and the other to the (E)-olefin.*

The complex must possess 16 or fewer total electrons. Examine the first figure one more time—notice that the total electron count of the complex increases by 2 during  $\beta$ -hydride elimination. Complexes with 18 total electrons don't undergo  $\beta$ -elimination because the product would end up with 20 total electrons. Of course, dissociation of a loose ligand can produce a 16-electron complex pretty easily, so watch out for ligand dissociation when considering the possibility of  $\beta$ -elimination in a complex. Ligand dissociation may be reversible, but  $\beta$ -Hydride elimination is almost always irreversible.

The metal must bear at least 2 d electrons. Now this seems a bit strange, as the metal has served as nothing but an empty bin for electrons in our discussion so far. Why would the metal center need electrons for  $\beta$ -hydride elimination to occur? The answer lies in an old friend: backbonding. The  $\sigma_{\text{C-H}} \rightarrow \text{M}$  orbital interaction mentioned above is not enough to promote elimination on its own; an  $\text{M} \rightarrow \sigma^*_{\text{C-H}}$  interaction is also required! I've said it before, and I'll say it again: backbonding is everywhere in organometallic chemistry. If you can understand and articulate it, you'll blow your instructor's mind.

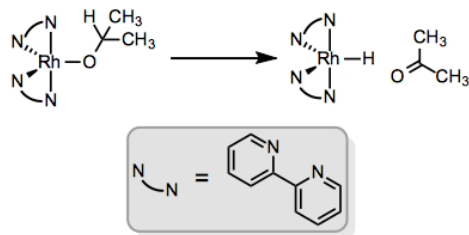
## Other $\beta$ -Elimination Reactions

The leaving group does not need to be hydrogen, of course, and a number of more electronegative groups come to mind as better candidates for leaving groups.  $\beta$ -Alkoxy and  $\beta$ -amino eliminations are usually thermodynamically favored thanks to the formation of strong M–O and M–N bonds, respectively. These reactions are so favored in  $\beta$ -alkoxyalkyl “complexes” of alkali and alkaline earth metals (R–Li, R–MgBr, etc.) that using these as  $\sigma$ -nucleophiles at carbon is untenable. Such compounds eliminate immediately upon their formation. I had an organic synthesis professor in undergrad who was obsessed with this—using a  $\beta$ -alkoxyalkyl lithium or  $\beta$ -alkoxyalkyl Grignard reagent in a synthesis was a recipe for red ink.  $\beta$ -Haloalkyls were naturally off limits too.



*Watch out...these are not stable compounds!*

The atom bound to the metal doesn't have to be carbon.  $\beta$ -Elimination of alkoxy ligands affords ketones or aldehydes bound to oxygen or through the C=O  $\pi$  bond (this step is important in many [transfer hydrogenations](#), and an analogous process occurs in the [Oppenauer](#) oxidation). Amido ligands can undergo  $\beta$ -elimination to afford complexes of imines; however, this process tends to be slower than  $\beta$ -alkoxy elimination.



*$\beta$ -Elimination helps transfer the elements of dihydrogen from one organic compound to another.*

Incidentally, I haven't seen any examples in which the  $\beta$  atom is not carbon, but would be interested if anyone knows of an example!

## Applications of $\beta$ -Eliminations

As with many concepts in organometallic chemistry, there are two ways to think about applications of  $\beta$ -elimination. One can take either the “inorganic” perspective, which focuses on the metal center, or the “organic” perspective, which focuses on the ligands.

With the metal center in focus, we can recognize that  $\beta$ -hydride elimination has the wonderful side effect of establishing an M–H bond—a feat generally difficult to achieve in a selective manner via oxidative addition of X–H. If the ligand from which the hydrogen came displaced something more electronegative, the whole process represents reduction at the metal center. For example, imagine rhodium(III) chloride is mixed with sodium isopropoxide,  $\text{NaOCH}(\text{CH}_3)_2$ . The isopropoxide easily displaces chloride, and subsequent  $\beta$ -hydride elimination affords a rhodium hydride, formally reduced with respect to the chloride starting material. See p. 236 of [this review](#) for more.

With the ligand in focus, we see that the organic ligand is oxidized in the course of  $\beta$ -hydride elimination. Notice that the metal is reduced and the ligand oxidized! A  $\pi$  bond replaces a  $\sigma$  bond in the ligand, and if the conditions are right, this represents a bona fide oxidation (as opposed to a mere elimination). For example, oxidative addition into a C–H bond followed by  $\beta$ -hydride elimination at a C–H bond next door sets up an alkene where two adjacent C–H bonds existed before, an oxidation process. These [dehydrogenation reactions](#) are incredibly appealing in a theoretical sense, but still at an early stage when it comes to scope and practicality.

## Summary

We already encountered  $\beta$ -hydride elimination in an earlier series of posts on [metal alkyl complexes](#), where we noted that it's a very common decomposition pathway for metal alkyls.  $\beta$ -Hydride elimination isn't all bad, however, as it can be an important step in catalytic reactions that result in the oxidation of organic substrates (dehydrogenations and transfer hydrogenations) and in reactions that reduce metal halides to metal hydrides. The general idea of  $\beta$ -elimination involves the transfer of a leaving group from a ligand to the metal center with simultaneous formation of a  $\pi$  bond in the ligand.  $\beta$ -Elimination requires an open coordination site and at least two d electrons on the metal center, and eliminations of chiral complexes are stereospecific. The leaving group is commonly hydrogen, but need not be—the more electronegative the leaving group, the more favorable the elimination. Stronger  $\pi$  bonds in the product also encourage  $\beta$ -elimination, so eliminations that form carbonyl compounds or imines are common.

In the next post, we'll explore other types of organometallic elimination reactions, which establish  $\pi$  bonds at different positions in metal alkyl or other complexes.  $\alpha$ -Eliminations, for example, establish metal-carbon, -oxygen, or -nitrogen multiple bonds, which are generally difficult to forge through other means

## Contributors and Attributions

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